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Inorganic Lanthanide Compounds with Complex Anions

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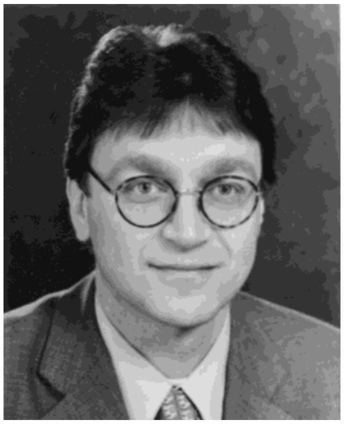

Mathias S. Wickleder was born in Bergen, Germany, in 1965. He received his Dr. rer. nat. degree at the University of Hannover under the direction of Professor G. Meyer in 1994. Thereafter he joined the group of Professor H. U. Güdel, Bern, Switzerland, as a postdoctoral fellow for two years. In 2000 he finished his Habilitation at the Institute for Inorganic Chemistry in Cologne. His research interests include the structural chemistry and thermal behavior of rare-earth and transition-metal compounds with complex anions.

I. Introduction

Complex anions play an important role in the chemistry of rare-earth elements. The most important natural sources of lanthanides are silicates such as *gadolinite*, phosphates such as *xenotime* and *monazite*, and carbonates such as *bastnasite*. In the early days of rare-earth chemistry double nitrates and double sulfates were used to separate the elements by means of fractional crystallization.[1] However, also when more sophisticated separation procedures such as chromatographic methods and solvent

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extraction were developed,[2] there was still considerable interest in these complex compounds. In the 1950s and 1960s both inorganic and organic ligands were used to prepare lanthanide complexes in order to investigate their properties in solution and in the solid state.[3] However, structural investigations were only rarely done at that time. With the improvement of X-ray crystallography the number of crystal structure determinations increased dramatically, and during the last 25 years our knowledge of coordination numbers and geometries of rare-earth ions has improved remarkably. On the other hand, this knowledge is mainly restricted to those compounds which can be gained easily in single-crystalline form. Crystal growth is always easy to achieve from solution or from the melt. Growing from a melt requires a certain thermal stability of the compounds, while solution growth methods lead very often to solvent-containing complexes. Thus, crystal structures of solvent-free nitrates, carbonates, and others are still not known. This review will focus on the recent results of the structural characterization of rare-earth compounds with inorganic complex anions. In some cases the preparative aspects and selected properties will also be mentioned. Excluded are carboxylates which are not inorganic in a strictly sense and, of course, organic complexes which have been subject of various excellent reviews and which will be presented elsewhere. Although they have gained some attraction as catalysts, the triflates of the rare-earth elements are not considered in this review, not only because they might be seen as not typical inorganic, but more importantly because structural information of these compounds is still lacking, except for the nonahydrates. To not go beyond the scope of this review, some other interesting anions have been left out. For example, the rare-earth borates are not considered here but some recent papers on the crystal chemistry and properties of borates might be helpful substitutes.[4,5] Also, octahedral or even larger anions are not regarded being aware that a lot of interesting chemistry has been done in that field.

A comprehensive review of rare-earth compounds with complex anions was presented in 1986 by Niinistö and Leskelä with a coverage of the literature until 1985.[6,7] Also, Gmelin's handbook provides a good overview of the early literature.[8] The present work strongly emphasizes the structural chemistry of the compounds under investigation and covers the results of roughly the last 20 years. However, to be comprehensive and attempting to provide helpful data at least the tables will include (to the best of the author's knowledge) all data of structurally characterized compounds known so far. Only those compounds will be considered for which X-ray single-crystal data have been provided or for which at least high-quality Rietveld refinements have been performed. For many compounds several refinements have been carried out, and sometimes it is obvious that exactly the same data appear in different publications, presumably in a different context. Nevertheless, all of these references are included in the tables, and it is for the reader to decide which might be the appropriate paper for him.

If it seems worthwhile, known structures may be also described in the text, but new developments will be emphasized in more detail. As a guide throughout this review the shape of the respective anions shall serve. Starting with the tetrahedral anions (section II), which will provide the largest part, we will focus on tetra-atomic anions which might be pyramidal (section III) or planar (section IV) and then move to bent and linear anions (section V).

II. Tetrahedral Anions

A. Silicates

Silicates belong to the most important rare-earth minerals being a natural reservoir of the rare-earth elements. As examples, the minerals *thortveitite* ($Sc_2Si_2O_7$) and *gadolinite* ($Be_2FeY_2O_2(SiO_4)_2$) may serve with the former being a mineral nearly pure in scandium. Due to the well-known tendency of the $[SiO_4]$ tetrahedra to condense to disilicates, trisilicates, or even more extended polyanionic arrays, the number of different compositions is very large. Furthermore, due to the thermal stability of the silicates, the growth of single crystals is quite easy. Thus, there is a huge number of structurally characterized compounds (Tables 1−3). Extensive systematic studies were undertaken in the early 1970s by Felsche, who has summarized the results in an excellent review.[9] Nevertheless, there are new developments especially in the crystal chemistry of halide silicates and transition-metal-containing silicates. Mainly these new findings are summarized in the following.

1. Ortho-Silicates

Interestingly, there is no simple *ortho*-silicate with the composition $M_4(SiO_4)_3$ for the trivalent rare-earth elements. On the other hand, with divalent europium, two modifications of Eu_2SiO_4 are known which adopt the monoclinic β-Ca_2SiO_4 and the orthorhombic α-K_2SO_4 type of structure, respectively.[10,11] With the trivalent rare-earth ions, oxide silicates, $M_2O(SiO_4)$, frequently occur. Two structures are known, called A- and B-type. In former times it was believed that the A-type is adopted by the larger lanthanides La−Tb and the B-type by the smaller ones Tb−Lu.[9,12−16] However, recent studies showed that the oxide silicates with M = Dy−Lu,Y may also be obtained in the A-type structure, so that a dimorphism with the A-type as the low-temperature form and the B-type as the high-temperature form can be assumed.[17,18] Both types of structures are similar in the sense that they contain oxide-centered $[OM_4]$ tetrahedra as the characteristic structural feature. In the A-type the tetrahedra are linked to a two-dimensional network according to ${}^{2}_{\infty}[O(M1)_{1/1}(M2)_{3/3}]^{4+}$, while anti-$SiS_2$ type chains ${}^{1}_{\infty}[O(M1)_{2/2}(M2)_{2/2}]^{4+}$ are found in the B-type structure (Figure 1). Charge compensation is achieved by the SiO_4^{4-} anions. The coordination numbers for the crystallographically different M^{3+} ions is seven and nine for the A-type and six and seven in the B-type, respectively.

The substitution of the oxygen atom which is not part of the SiO_4^{4-} tetrahedron for the heavier chal-

Table 1. Crystallographic Data of *Ortho*-Silicates

		lattice parameters						
compound	space group	a/Å	b/Å	c/Å	α/°	β/°	γ/°	ref
Eu_2SiO_4	$Pnma$	7.137(3)	5.665(2)	9.767(3)				10
Eu_2SiO_4	$P2_1/c$	5.661	7.101	11.518		122.01		11
chalcogenide−silicates								
$Gd_2(SiO_4)O$	$P2_1/c$	9.120(10)	7.060(10)	6.730(10)		107.6(2)		12
$Yb_2(SiO_4)O$	$B112/b$	14.28(1)	10.28(1)	6.653(5)			122.2(1)	13
$Y_2(SiO_4)O$	$I2/c$	10.410(3)	6.721(2)	12.490(5)		102.65(2)		14
$Y_2(SiO_4)O$	$B112/b$	14.590	10.520	6.820			122.25	15
$Tm_2(SiO_4)O$	$P2_1/c$	9.0017(7)	6.7874(4)	6.6271(4)		105.44(1)		18
$Lu_2(SiO_4)O$	$P2_1/c$	8.987(1)	6.706(1)	6.5951(7)		104.18(1)		18
$Er_2(SiO_4)O$	$P2_1/c$	8.9964(9)	6.8328(6)	6.6503(7)		105.95(1)		18
$Nd_2(SiO_4)Se$	$Pbcm$	6.182(2)	7.174(2)	11.024(2)				19
$La_2(SiO_4)Se$	$Pbcm$	6.279(4)	7.306(5)	11.177(7)				20
$Er_2(SiO_4)Se$	$Pbcm$	6.002(2)	6.880(2)	10.752(2)				21
$Pr_2(SiO_4)Te$	$Pbcm$	6.3370(3)	7.2442(4)	11.2513(8)				22
$Pr_2(SiO_4)Te$	$P2_1/c$	9.8990(7)	6.4803(4)	8.7068(7)		94.31(1)		22
halide−silicates								
$La_3(SiO_4)_2Cl$	$C2/c$	14.512(2)	6.526(7)	8.844(2)		98.35(1)		23
$Pr_3Cl(SiO_4)_2$	$C2/c$	14.300(2)	6.430(1)	8.754(2)		98.36(2)		24
$Nd_3Cl(SiO_4)_2$	$C2/c$	14.166(1)	6.3879(6)	8.7221(9)		98.40(1)		25
$Nd_3Cl(SiO_4)_2$	$Pnma$	7.0936(7)	18.157(2)	6.3148(6)				25
$Sm_3Cl(SiO_4)_2$	$Pnma$	7.0174(8)	18.008(2)	6.2663(7)				26
$Sm_3Cl(SiO_4)_2$	$Pmna$	7.023(2)	18.022(4)	6.282(3)				27
$Y_3Cl(SiO_4)_2$	$Pnma$	6.8584(4)	17.752(1)	6.1865(4)				28
$Yb_3(SiO_4)_2Cl$	$Pnma$	6.731(2)	17.556(8)	6.129(2)				29
$Gd_3Br(SiO_4)_2$	$Imma$	6.960(3)	18.176(6)	6.284(2)				31
$Ce_3Cl_5(SiO_4)$	$Pnma$	16.197(2)	4.1526(4)	14.236(1)				32
$La_3Cl_5(SiO_4)$	$Pnma$	16.225(2)	4.262(1)	14.238(2)				33
$Eu_5Cl_6(SiO_4)$	$C2/c$	9.004(1)	14.017(2)	11.123(2)		103.51(1)		34
$La_2I_2(SiO_4)$	$P\bar{1}$	8.479(4)	8.574(4)	11.95(2)	99.6(1)	108.3(2)	90.1(1)	35
$La_2I_2(SiO_4)$	$P2_1/c$	8.474(3)	8.578(4)	22.36(3)		92.6(1)		35
$La_7OF_7(SiO_4)_3$	$C2/c$	10.7020(1)	18.7089(2)	9.7906(1)		123.15(1)		36
apatite-derived silicates								
$La_{4.67}(SiO_4)_3O$	$P6_3/m$	9.550		7.140				37
$Ce_{4.67}(SiO_4)_3O$	$P6_3/m$	9.736		7.116				38
$Gd_{4.67}(SiO_4)_3O$	$P6_3/m$	9.45(1)		6.87(1)				39
$Sm_{4.67}(SiO_4)_3O$	$P6_3/m$	9.550		7.140				37
$Sm_{10}(SiO_4)_6N_2$	$P6_3$	9.517(6)		6.981(4)				40
$CaLa_4(SiO_4)_3O$	$P6_3/m$	9.651(1)		7.155(1)				41
$NaPr_9S_2(SiO_4)_6$	$P6_3/m$	9.8105(4)		6.8968(2)				42
$NaSm_9S_2(SiO_4)_6$	$P6_3/m$	9.7532(9)		6.7646(7)				43
$KNd_9(SiO_4)_6O_2$	$P6_3$	9.576(2)		7.009(2)				44
$Ca_2Nd_8(SiO_4)_6O_2$	$P6_3/m$	9.5291(5)		7.0222(1)				46
$Ca_{2.2}Nd_{7.8}(SiO_4)_6O_{1.9}$	$P6_3/m$	9.5303(4)		7.0147(1)				46
$MnSm_4(SiO_4)_3O$	$P6_3/m$	9.444(2)		6.829(2)				47
$Er_6Pb_3(SiO_4)_6$	$P6_3/m$	9.642		6.780				48
$Ca_{2.2}Nd_{7.8}(SiO_4)_6O_{1.9}$	$P6_3/m$	9.5300(4)		7.0147(1)				46
$Nd_4Mn(SiO_4)_3O$	$P6_3/m$	9.4986(9)		6.9436(5)				49
$CdNd_4(SiO_4)_3O$	$P6_3/m$	9.562(2)		7.075(1)				50
$La_{9.31}(Si_{1.04}O_4)_6O_2$	$P6_3$	9.699(1)		7.125(1)				51
$(Li_{0.142}Sm_{0.756})_2Sm_3Si_3O_{12.91}$	$P6_3/m$	9.4601(1)		6.9113(1)				52
$La_{7.58}(Si_{1.048}O_4)_6(H_2O)_2$	$P6_3$	9.629(1)		7.059(2)				51
$La_3Nd_{11}(SiO_4)_9O_3$	$P6_3/m$	9.638(2)		21.350(8)				53
$NaY_9(SiO_4)_6O_2$	$P6_3/m$	9.334(2)		6.759(1)				54
$Eu_5(SiO_4)_3F$	$P6_3/m$	9.5479(9)		7.0416(6)				55
$Yb_5(SiO_4)_3S$	$P6_3/m$	9.7236(9)		6.4849(6)				55
ternary silicates								
$LiTm(SiO_4)$	$Pnma$	10.7896(2)	6.2677(2)	4.898(1)				56
$NaNdSiO_4$	$Pna2_1$	20.000	9.280	5.450				57
$NaSmSiO_4$	$I4/m$	11.800		5.450				58
$NaGd(SiO_4)$	$I4/m$	11.630		5.410				59
$NaYSiO_4$	$Pc2_1n$	5.128(1)	6.393(1)	11.135(3)				60
$NaYSiO_4$	$Pbn2_1$	4.950	11.300	6.300				61
$LiYSiO_4$	$P112_1/b$	5.368(5)	10.806(6)	6.191(5)			113.40(2)	62
$LiScSiO_4$	$Pbnm$	4.8214(7)	10.444(1)	5.973(1)				63
$Y_4Ti(SiO_4)_2OF_6$	$Cmcm$	14.949(4)	10.626(2)	7.043(2)				64
$Na_5Y_4(SiO_4)_4F$	$I\bar{4}$	11.579(3)		5.396(1)				65
Li_2EuSiO_4	$P3_121$	5.0270(5)		12.470(2)				66
$Eu_3(BSiO_6)(SiO_4)$	$Pbca$	9.673(1)	6.992(3)	22.867(3)				67
$Gd_3(BSiO_6)(SiO_4)$	$Pbca$	9.630(1)	6.959(1)	22.792(3)				68
$Ce_3(BSiO_6)(SiO_4)$	$Pbca$	9.9007(6)	7.2036(4)	23.292(2)				69

Table 1. (Continued)

compound	space group	lattice parameters						ref
		a/Å	b/Å	c/Å	α/°	β/°	γ/°	
$Ce_2Ti_2O_5(SiO_4)$	$C2/m$	16.907(3)	5.7078(8)	7.574(2)		111.38(1)		71
$La_2Ti_2O_5(SiO_4)$	$C2/m$	17.029(3)	5.7415(4)	7.631(1)		111.22(1)		72
$La_3Mo_4O_{10}(SiO_4)$	$Pnma$	17.684(4)	5.643(1)	11.037(2)				73
$La_3Ga_5O_{10}(SiO_4)$	$P321$	8.168(3)		5.095(1)				74
$Y_2(SiO_4)(CO_3)$	$P\bar{1}$	6.574(2)	6.649(2)	6.465(3)	116.38(3)	92.58(3)	92.35(2)	a
$(Y_{1.44}Er_{0.56})(SiO_4)(CO_3)$	$P\bar{1}$	6.549(1)	6.629(1)	6.439(1)	116.36(1)	92.56(1)	96.51(2)	b
$Y_3Ca_2(SiO_4)_3(OH)$	$P112_1$	9.504(5)	9.414(4)	6.922(2)			119.71	c
$Ca_3Sc_2(SiO_4)_3$	$Ia\bar{3}d$	12.250(2)						d
$Ba_9Sc_2(SiO_4)_6$	$R\bar{3}$	9.8716(2)		21.9376(7)				e

[a] Pushcharovsky, D. Yu.; Arakcheeva, A. V.; Voloshin, A. V.; Zubkova, N. V.; Lubman, G. U. *Kristallografiya* **1999**, *44*, 458. [b] Hughes, J. M.; Foord, E. E.; Jai-Nhuknan, J.; Bell, J. M. *Can. Miner* **1996**, *34*, 817. [c] Zhang, J.-H.; Fang, Z.; Liao, L.-B. *Kuangwue Xuebao* **1992**, *12*, 131. [d] Mill, B. V.; Belokoneva, E. L.; Simonov, M. A.; Belov, N. V. *Zh. Struk. Khim.* **1977**, *18*, 399. [e] Wang, L.-H.; Schneemeyer, L. F.; Cava, R. J.; Siegrist, T. *J. Solid State Chem.* **1994**, *113*, 211.

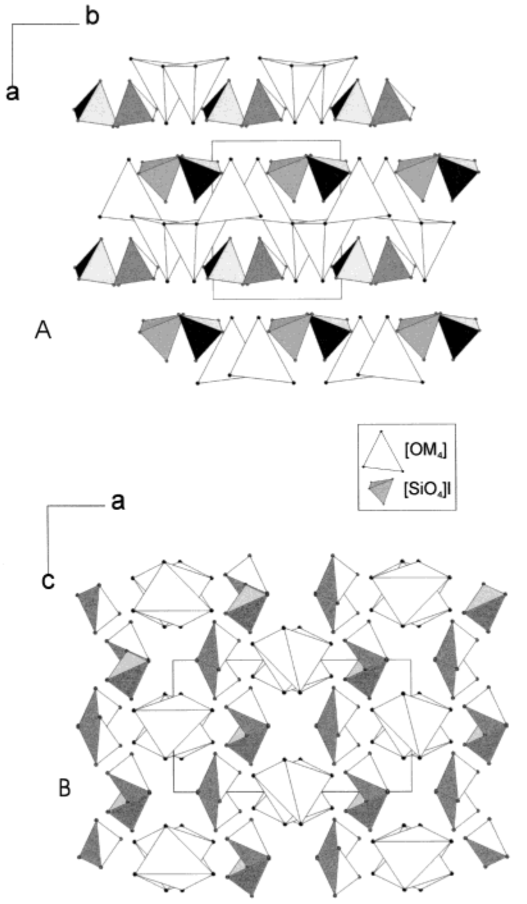

Figure 1. Crystal structures of the two modifications (A-type and B-type) of the oxide silicates $M_2O(SiO_4)$.

cogenides Se and Te is possible and leads to the selenide and telluride *ortho*-silicates $M_2X(SiO_4)$ ($X =$ Se,[19−21] Te[22]), which also adopt two different structure types, again named A- and B-type. The structures shall be described for $Pr_2Te(SiO_4)$ because for this compound both modifications were confirmed by X-ray single-crystal determinations.[22] Single crystals were obtained on reacting Pr, TeO_2, and SiO_2 in silica ampules with CsCl as a flux. The A-type has an orthorhombic crystal structure with alternating layers of the composition $[Pr(2)Te]^+$ and $[Pr(1)(SiO_4)]^-$ parallel to (001) (Figure 2a). $Pr(1)^{3+}$ is surrounded by six oxygen atoms and three Te^{2-} ions, whereas $Pr(2)^{2+}$ is surrounded by six oxygen atoms and four telluride ions. In contrast, the monoclinic crystal structure of the B-type consists of double layers $[(Pr(1)Te)_2]^{2+}$ and $[(Pr(2)(SiO_4))_2]^{2-}$ which are alternating stacked in the [100] direction (Figure 2b). For the cations a coordination number of eight (Pr(2), $4O^{2-}$ and $4Te^{2-}$) and nine (Pr1, $8O^{2-}$ and $1Te^{2-}$) results. Figure 2 compares both structures.

Halide *ortho*-silicates of the rare-earth elements are mainly known with Cl^- as the halide component. Those with the composition $M_3Cl(SiO_4)_2$ crystallize either in a monoclinic (A-type) or an orthorhombic (B-type) modification.[23−29] The A-type occurs with the larger M^{3+} ions and the B-type with the smaller ones (cf. Table 1). Dimorphism has been observed for $Nd_3Cl(SiO_4)_2$, and both structure types were established by X-ray data.[25] Each of them contains anionic double layers $[(Nd1)_2(SiO_4)_2]^{2-}$ and cationic monolayers $[(Nd2)Cl]^{2+}$ which are stacked alternating in the [100] (A-type) and [010] direction (B-type), respectively. As can be judged from Figure 3, the packing of the double layers is more dense in the A-type structure. This leads to higher coordination numbers for the two different Nd^{3+} ions in $A{-}Nd_3Cl(SiO_4)_2$ (Nd(1) $1Cl^-$, $8O^{2-}$; Nd(2) $2Cl^-$, $8O^{2-}$) compared to $B{-}Nd_3Cl(SiO_4)_2$ (Nd(1) $1Cl^-$, $7O^{2-}$; Nd(2) $2Cl^-$, $6O^{2-}$). Due to its higher density, the A-type has been assumed to be adopted even with the smaller M^{3+} ions under high pressure. This was confirmed by high-pressure X-ray powder diffraction recently.[30] The only structurally investigated bromide *ortho*-silicate known so far is $Gd_3Br(SiO_4)_2$.[31] It has, in principle, the B-type structure of the chloride compounds, but the symmetry of the unit cell is slightly higher now (*Imma* instead of *Pnma*, cf. Table 1) due to a slightly different orientation of the SiO_4^{4-} tetrahedra (Figure 3). With $La_3Cl_5(SiO_4)$ and $Ce_3Cl_5(SiO_4)$, two examples of chlorine-rich chloride *ortho*-silicates are known.[32,33] They are isotypic and show a certain similarity to the trichlorides $LaCl_3$ and $CeCl_3$ (UCl_3 type of structure) when four Cl^- ions of the tripled formula are substituted for SiO_4^{4-}. For the discrete silicate anions a statistical distribution on two cyrstallographic positions is found. A chloride *ortho*-silicate is also known for divalent europium with the composition $Eu_5Cl_6(SiO_4)$. It contains three crystallographically different Eu^{2+} ions which are in 8- and 9-fold coordination of oxygen atoms and chloride ligands.[34]

Table 2. Crystallographic Data of Disilicates

compound	space group	lattice parameters						ref
		a/Å	b/Å	c/Å	α/°	β/°	γ/°	
pure disilicates								
$La_2(Si_2O_7)$	$P4_1$	6.846(3)		24.855(5)				80
$La_2(Si_2O_7)$	$P2_1/c$	5.4075(8)	8.792(1)	14.199(3)		111.93(2)		81
$La_2(Si_2O_7)$	$P2_1/c$	5.4109(6)	8.7976(8)	14.287(1)		112.74(2)		82
$Ce_2(Si_2O_7)$	$P2_1/c$	5.401(1)	8.723(1)	14.169(2)		112.61(6)		82
$La_2(Si_2O_7)$	$P2_1/c$	7.2614(4)	23.5320(8)	10.1311(5)		90.16(1)		83
$La_2(Si_2O_7)$	$P4_1$	6.8383(7)		24.736(4)				84
$La_2(Si_2O_7)$	$P\bar{1}$	6.8113(4)	6.8664(4)	12.5023(8)	82.53(1)	88.03(1)	88.96(1)	84
$Ce_2(Si_2O_7)$	$P2_1/n$	13.080	8.727	5.405		90.13		85
$Ce_2(Si_2O_7)$	$P2_1/c$	5.4116(7)	8.742(2)	14.158(3)		112.26(1)		86
$Pr_2(Si_2O_7)$	$P4_1$	6.766		24.608				87
$Pr_2(Si_2O_7)$	$P2_1/c$	5.405	8.674	14.082		112.50		88
$Pr_2(Si_2O_7)$	$P4_1$	6.769(1)		24.607(5)				9
$Pr_2(Si_2O_7)$	$P4_1$	6.769		24.607				89
$Pr_2(Si_2O_7)$	$P2_1/c$	5.407(1)	8.679(1)	14.082(2)		112.53(7)		89
$Nd_2(Si_2O_7)$	$P4_1$	6.738(2)		24.532(3)				90
$Nd_2(Si_2O_7)$	$P2_12_12_1$	5.394(5)	12.95(1)	8.72(1)				91
$Nd_2(Si_2O_7)$	$P2_12_12_1$	5.394(5)	12.95(1)	8.72(1)				92
$Sm_2(Si_2O_7)$	$P\bar{1}$	8.553(5)	12.849(5)	5.392(2)	91.08(2)	88.61(4)	89.68(4)	93
$Sm_2(Si_2O_7)$	$P4_1$	6.695(5)		24.40(2)				94
$Eu_2(Si_2O_7)$	$Pna2_1$	13.914	5.055	8.349				9
$Gd_2(Si_2O_7)$	$Pna2_1$	13.870	5.073	8.330				95
$Gd_2(Si_2O_7)$	$Pna2_1$	13.87(2)	5.073(5)	8.33(1)				92
$Ho_2(Si_2O_7)$	$Pna2_1$	13.681(4)	4.997(3)	8.187(2)				82
$Ho_4(Si_4O_{14})$	$P\bar{1}$	6.612(4)	6.669(4)	12.085(9)	85.81(2)	89.38(3)	88.57(3)	96
$Er_2(Si_2O_7)$	$C2/m$	6.849(1)	8.940(1)	4.7222(5)		101.81(1)		97
$Er_2(Si_2O_7)$	$C2/m$	6.843(2)	8.939(2)	4.720(1)		101.77(2)		98
$Er_2(Si_2O_7)$	$P112_1/b$	4.683(5)	5.556(5)	10.79(1)			96.0(2)	92
$Er_2(Si_2O_7)$	$P112_1/b$	4.683(5)	5.556(5)	10.79(1)			96.0(2)	99
$Yb_2(Si_2O_7)$	$C2$	6.802(5)	8.875(5)	4.703(5)		102.1(2)		100
$Yb_2(Si_2O_7)$	$A2/m$	4.715(1)	8.870(3)	6.805(3)		102.0(1)		101
$Yb_2(Si_2O_7)$	$C2/m$	6.7988(3)	8.8759(4)	4.7101(3)		101.98(1)		97
$Yb_2(Si_2O_7)$	$C2/m$	6.802(5)	8.875(10)	4.703(5)		102.12(3)		92
$Y_2(Si_2O_7)$	$Pnam$	13.665(5)	5.016(3)	8.139(3)				102
$Y_2(Si_2O_7)$	$Pna2_1$	13.6650(1)	5.0166(1)	8.1494(1)				97
$Y_2(Si_2O_7)$	$P2_1/m$	7.50(3)	8.06(3)	5.02(2)		112.0(9)		103
$Y_2(Si_2O_7)$	$P2_1/\mathrm{a}$	5.544	10.780	4.660		96.10		104
$(Y_{1.335}La_{0.665})(Si_2O_7)$	$P2_1/c$	5.375(1)	8.569(1)	13.863(1)		111.79(1)		105
$Sc_2(Si_2O_7)$	$Fd\bar{3}m$	9.287(3)						106
$Sc_2(Si_2O_7)$	$P2/m$	6.503(2)	8.498(3)	4.682(2)		102.77(7)		107
$Sc_2(Si_2O_7)$	$C2/m$	6.542(5)	8.519(5)	4.669(5)		102.6(2)		108
$Sc_2(Si_2O_7)$	$C2/m$	6.560	8.580	4.740		103.13		109
$Sc_2(Si_2O_7)$	$C2/m$	6.5304(4)	8.5208(4)	4.6806(5)		102.63(1)		110
$(Sc_{1.2}Y_{0.8})(Si_{1.95}Al_{0.04}O_7)$	$C2/m$	6.650(1)	8.616(1)	4.686(1)		102.20(1)		111
$(Sc_{1.4}Y_{0.6})(Si_{1.96}Al_{0.05}O_7)$	$C2/m$	6.587(1)	8.547(1)	4.695(1)		103.65(1)		112
$(Sc_{1.7}Y_{0.3})(Si_{1.96}Al_{0.05}O_7)$	$C2/m$	6.582(1)	8.555(1)	4.693(1)		102.59(1)		112
$(Sc_{1.94}Y_{0.06})(Si_{1.97}Al_{0.06}O_7)$	$C2/m$	6.527(1)	8.507(1)	4.691(1)		102.78(1)		112
chalocogenide and halide disilicates								
$La_4Se_3(Si_2O_7)$	$I4_1/amd$	12.285(1)		14.699(1)				118
$La_4S_3(Si_2O_7)$	$I4_1/amd$	12.098(3)		14.379(5)				119
$Ce_4Se_3(Si_2O_7)$	$I4_1/amd$	12.217(1)		14.566(2)				120
$Pr_4Se_3(Si_2O_7)$	$I4_1/amd$	12.154(1)		14.455(3)				121
$Pr_4S_3(Si_2O_7)$	$I4_1/amd$	12.016(1)		14.120(2)				122
$Nd_4Se_3(Si_2O_7)$	$I4_1/amd$	12.099(1)		14.387(3)				120
$Nd_4S_3(Si_2O_7)$	$I4_1/amd$	11.986(1)		14.064(2)				121
$Sm_4S_3(Si_2O_7)$	$I4_1/amd$	11.839(5)		13.928(5)				117
$Sm_4Se_3(Si_2O_7)$	$I4_1/amd$	12.013(1)		14.211(2)				121
$Sm_4S_3(Si_2O_7)$	$I4_1/amd$	11.864(1)		13.870(2)				123
$Gd_4Se_3(Si_2O_7)$	$I4_1/amd$	11.940(1)		14.105(2)				121
$Er_4S_3(Si_2O_7)$	$I4_1/amd$	11.646(1)		13.473(2)				121
$Yb_4S_3(Si_2O_7)$	$I4_1/amd$	11.543(1)		13.322(1)				124
$La_3(Si_2O_7)Cl_3$	$P2_1$	5.364(8)	12.148(9)	7.922(4)		108.87(6)		125
$Pr_3Cl_3(Si_2O_7)$	$P2_1$	5.3096(6)	12.002(1)	7.8311(8)		109.07(1)		126
$Er_4F_2(Si_2O_7)(SiO_4)$	$P1$	6.4849(5)	6.6035(5)	13.244(1)	87.45(1)	85.79(1)	60.82(1)	127
ternary disilicates								
$Na_3Lu(Si_2O_7)$	$P6_3/m$	9.385(1)		13.716(2)				128
$K_3Nd(Si_2O_7)$	$P6_3/mcm$	10.025(1)		14.526(1)				129
$Na_3Tm(Si_2O_7)$	$P6_3$	9.387(2)		13.717(4)				130
$Na_3Y(Si_2O_7)$	$P6_3/m$	9.422(1)		13.790(2)				131
$Na_3Sc(Si_2O_7)$	$Pbnm$	5.354(3)	9.347(4)	13.089(4)				132
$Na_6YSc(Si_2O_7)_2$	$P6_3$	10.726(2)		13.491(3)				133
$Na_6YSc(Si_2O_7)_2$	$P6_3$	10.726		13.491				134

Table 3. Crystallographic Data of Higher Silicates

compound	space group	lattice parameters						ref
		a/Å	*b*/Å	*c*/Å	α/°	*β*/°	*γ*/°	
$Y_3F(Si_3O_{10})$	$P2_1/n$	7.3038(5)	11.1247(8)	10.3714(7)		97.24(1)		142
$(Y_{2.7}Er_{0.3})F(Si_3O_{10})$	$P2_1/n$	7.318(2)	11.134(3)	10.379(3)		97.2(1)		143
$Dy_3F(Si_3O_{10})$	$P2_1/n$	7.3406(6)	11.1655(9)	10.4062(8)		97.28(1)		144
$Ho_3F(Si_3O_{10})$	$P2_1/n$	7.3091(6)	11.1168(9)	10.3783(8)		97.24(1)		144
$Er_3F(Si_3O_{10})$	$P2_1/n$	7.2789(6)	11.0702(9)	10.3521(8)		97.21(1)		144
$Y_3(OH)(Si_3O_{10})$	$P112_1/n$	10.343(5)	7.294(6)	11.093(8)			97.3(1)	145
$La_3F_3(Si_3O_9)$	$P\bar{6}2c$	7.0832(3)		10.8948(6)				146
$Ce_3(Si_3O_6N_3)$	$P\bar{6}2c$	7.256		9.459				147
$La_3(Si_3O_6N_3)$	$P\bar{6}2c$	7.310		9.550				147
$Y_3(Si_3O_6N_3)$	$P11m$	7.021	7.021	9.100			120.0	148
$Y_3(Si_3O_6N_3)$	$Cmcm$	12.161	7.021	9.100				149
$KEu_2(Si_4O_{10})F$	$P2_1/n$	11.499(3)	8.488(2)	11.626(4)		112.10(1)		*x*
$Na_2MgGd_2(Si_4O_{12})F_2$	$P2_1/c$	5.178(3)	7.510(2)	14.381(4)		90.22(2)		*w*
$Y_6Cl_{10}(Si_4O_{12})$	$C2/m$	10.6146(8)	10.3091(6)	11.5615(9)		103.28(1)		151
$Na_2BaNd_2(Si_4O_{12})(CO_3)$	$Pcmn$	6.9522(7)	13.463(3)	14.027(1)				*a*
$Nd_2Ba_2(Si_4O_{13})$	$P\bar{1}$	6.657(1)	8.924(2)	10.084(1)	86.44(1)	73.58(1)	86.24(1)	115
$Na_4Sc_2(Si_4O_{13})$	$Pna2_1$	14.442(3)	5.288(1)	14.219(4)				116
$Eu_2Cl_2(SiO_3)$	$I4/m$	11.187(5)		9.526(1)				152
$Na_6Eu_3(Si_6O_{18})$	$R\bar{3}m$	10.682(1)		13.487(2)				153
$Y_4(Si_2O_7N_2)$	$P2_1/c$	7.5601(2)	10.4411(3)	10.7626(3)		110.04(1)		*b*
$Na_{15}Lu_3(Si_{12}O_{36})$	$R32$	21.926(4)		12.556(2)				154
$Na_{15}Lu_3(Si_{12}O_{36})$	$R32$	21.926(4)		12.556(2)				155
$Na_{15}Dy_3(Si_{12}O_{36})$	$R\bar{3}c$	22.096(5)		12.619(4)				156
$Ag_{15}Ho_3(Si_{12}O_{36})$	$R\bar{3}c$	22.175(5)		12.863(4)				157
$Na_{15}Yb_3(Si_{12}O_{36})$	$R\bar{3}c$	21.960(5)		12.566(9)				158
$Na_{15}Yb_3(Si_{12}O_{36})$	$R\bar{3}c$	22.082(5)		12.716(9)				158
$Ag_{15}Yb_3(Si_{12}O_{36})$	$R\bar{3}c$	22.077(4)		12.814(3)				158
$Na_{15}Y_3(Si_{12}O_{36})$	$R\bar{3}c$	22.062(8)		12.621(4)				159
$Na_{15}Y_3(Si_{12}O_{36})$	$R\bar{3}c$	22.109(9)		12.692(5)				159
$Na_{15}Y_3(Si_{12}O_{36})$	$R\bar{3}c$	22.000		12.610				160
$Na_{15}Y_3(Si_{12}O_{36})$	$R\bar{3}c$	22.035(1)		12.604(1)				161
$Na_{15}Sc_3(Si_{12}O_{36})$	$R\bar{3}c$	21.679(3)		12.441(2)				162
$K_3Ho(Si_3O_9)$	$P2_1mn$	13.949(8)	12.905(7)	5.857(5)				163
$K_6Lu_2(Si_6O_{18})$	$Pm2_1n$	14.011(2)	12.919(2)	5.853(2)				165
$K_3Ho(Si_3O_9)$	$Pm2_1n$	13.949(8)	12.905(7)	5.857(5)				164
$Na_3Y(Si_3O_9)$	$P2_12_12_1$	15.033(1)	15.142(1)	15.213(1)				167
$La(BSiO_5)$	$P3_1$	6.815(1)		6.758(1)				168
$La(B_{0.95}SiO_{4.93})$	$P3_121$	6.839(2)		6.782(1)				169
$La(BSiO_5)$	$P3_121$	6.827(2)		6.779(2)				170
$Ce(BSiO_5)$	$P3_1$	6.85(3)		6.70(3)				171
$Ce(BSiO_5)$	$P3_1$	6.844(3)		6.700(4)				172
$La(BSiO_5)$	$P3_1$	6.874(1)		6.717(3)				173
$Nd(BSiO_5)$	$P3_121$	6.8035(4)		6.6487(3)				174
$La(B_{0.95}SiO_{4.93})$	$P3_1$	6.876(2)		6.747(1)				175
$La(BSiO_5)$	$P3_1$	6.838(2)		6.773(2)				176
$K_3Nd(Si_6O_{15})$	$Pbam$	16.011(9)	14.984(3)	7.276(5)				177
$K_3Nd(Si_6O_{15})$	$Pbam$	15.951(5)	14.909(4)	7.260(2)				178
$Na_3Y(Si_6O_{15})$	$Ibmm$	10.468(2)	15.247(1)	8.3855(6)				179
$Na_2LiY(Si_6O_{15})$	$Cmca$	14.505(1)	17.596(1)	10.375(1)				180
$K_2Ce(Si_6O_{15}$	$B112/b$	17.661(6)	11.854(4)	8.698(2)			132.32(1)	181
$Na_3Y(Si_6O_{15})$	$Cmca$	14.744(8)	17.844(8)	10.610(3)				*c*
$NaPr(Si_6O_{14})$	$Ibam$	7.682(2)	15.445(3)	19.724(6)				*d*
$NaNd(Si_6O_{14})$	$Ibam$	7.662(5)	15.392(5)	19.679(7)				*d*
$Ca_3Y_2(Si_3O_9)_2$	$C2/c$	13.320(3)	7.729(2)	14.785(2)				*e*
$*Ca_3Sc_2(Si_3O_{12})$	$Ia\bar{3}d$	12.220						*f*
$K_3Y(Si_3O_8)(OH)_2$	$Pmnb$	13.536(5)	13.18(1)	5.867(2)				*g*
$LiSc(Si_2O_6)$	$C2/c$	9.8033(7)	8.9581(7)	5.3515(4)		110.28(1)		*h*
$Y_{0.5}(Si_{9.75}Al_{2.25})(N_{15.25}O_{0.75})$	$P3_1c$	7.8295(1)		5.7077(1)				*i*
$Y_{0.5}(Si_{9.3}Al_{2.7})(N_{15.1}O_{0.9})$	$P3_1c$	7.8293(1)		5.7076(1)				*j*
$Na(In_{0.80}Sc_{0.20})(Si_2O_6)$	$C2/c$	9.8907(5)	9.1164(2)	5.3623(3)		107.20(1)		*k*
$Na(In_{0.65}Sc_{0.35})(Si_2O_6)$	$C2/c$	9.8811(5)	9.1043(2)	5.3592(3)		107.19(1)		*k*
$Na(In_{0.60}Sc_{0.40})(Si_2O_6)$	$C2/c$	9.8782(5)	9.1008(3)	5.3582(3)		107.19(1)		*k*
$Na(In_{0.55}Sc_{0.45})(Si_2O_6)$	$C2/c$	9.8734(5)	9.0947(2)	5.3570(3)		107.19(1)		*k*
$Na(In_{0.50}Sc_{0.50})(Si_2O_6)$	$C2/c$	9.8701(4)	9.0901(2)	5.3559(2)		107.18(1)		*k*
$Na(In_{0.40}Sc_{0.60})(Si_2O_6)$	$C2/c$	9.8634(6)	9.0827(3)	5.3542(4)		107.17(1)		*k*
$Na(In_{0.20}Sc_{0.80})(Si_2O_6)$	$C2/c$	9.8659(5)	9.0848(2)	5.3553(3)		107.18(1)		*k*
$CaSc(Si_3O_8)(OH)$	$C\bar{1}$	9.791(8)	10.420(9)	7.076(6)	98.91(8)	102.63(8)	84.17(8)	*l*
$CaSc(AlSiO_6)$	$C2/c$	9.884(2)	8.988(1)	5.446(1)		105.86(1)		*m*
$(Mg_{38.63}Sc_{3.10})(Li_{1.16}Si_{0.07})Si_{40}O_{127}$	$P2/a$	9.429(2)	8.748(2)	27.038(8)		93.25(2)		*n*
$(Mg_{28.40}Sc_{4.62})Li_{1.33}Si_{32}O_{100}$	$P2/a$	9.429(2)	8.741(1)	21.808(6)		91.20(2)		*n*
$(NaSc)(Si_2O_6)$	$C2/c$	9.8438(4)	9.0439(4)	5.3540(2)		107.21(1)		*o*
$NaSc(Si_2O_6)$	$C2/c$	9.837(1)	9.0550(5)	5.3488(6)		107.18(1)		*p*

Table 3. (Continued)

compound	space group	lattice parameters						ref
		a/Å	b/Å	c/Å	α/°	β/°	γ/°	
$Ca_3Y_2(SiO_4)_3$	$Pnma$	6.536(4)	15.626(3)	10.029(2)				q
$(Li_{0.3}Mg_{0.7})(Sc_{0.3}Mg_{0.7})(Si_2O_6)$	$Pbcn$	9.251(2)	8.773(2)	5.377(1)				r
$Ca_2Y_2O_2(Si_2O_7)$	$Pnma$	10.453(3)	3.720(2)	10.290(2)				s
$(Mg_{1.54}Li_{0.23}Sc_{0.23})(Si_2O_6)$	$Pbcn$	9.2554(4)	8.7650(5)	5.3333(2)				t
$(Mg_{1.54}Li_{0.23}Sc_{0.23})(Si_2O_6)$	$Pbcn$	9.2351(6)	8.7310(7)	5.3216(2)				t
$(Mg_{1.54}Li_{0.23}Sc_{0.23})(Si_2O_6)$	$Pbcn$	9.2178(6)	8.7039(6)	5.3119(4)				t
$(Mg_{1.54}Li_{0.23}Sc_{0.23})(Si_2O_6)$	$P2_1cn$	9.1167(4)	8.7857(4)	5.1837(2)				t
$(Mg_{1.54}Li_{0.23}Sc_{0.23})(Si_2O_6)$	$P2_1cn$	9.0877(5)	8.7526(5)	5.1531(3)				t
$(Mg_{1.54}Li_{0.23}Sc_{0.23})(Si_2O_6)$	$P2_1cn$	9.0548(6)	8.7120(6)	5.1209(3)				t
$(Mg_{1.54}Li_{0.23}Sc_{0.23})(Si_2O_6)$	$P2_1cn$	9.0219(7)	8.6711(6)	5.093(4)				t
$(Mg_{1.54}Li_{0.23}Sc_{0.23})(Si_2O_6)$	$P2_1cn$	8.9921(8)	8.6310(7)	5.0659(5)				t
$K_2Sc(Si_2O_6)(OH)$	$Pbam$	12.725(4)	12.741(6)	8.441(3)				u
$(Mg_{39.20}Sc_{2.56})(Mg_{0.08}Si_{0.44})Si_{40}O_{124}$	$P2/a$	9.424(2)	8.738(2)	27.021(8)		93.2(1)		v
$(Mg_{31.24}Sc_{2.76})(Mg_{0.60}Si_{0.04})Si_{32}O_{100}$	$P2/a$	9.434(1)	8.731(1)	21.791(4)		91.30(5)		v
$(Mg_{34.80}Sc_{2.98})(Mg_{0.32}Si_{0.24})Si_{36}O_{112}$	$P2/a$	9.424(1)	8.740(1)	48.808(6)		92.40(8)		v
$Eu_{.92}(Al_{1.76}Si_{2.24}O_8)$	$C2/m$	8.373(2)	12.959(1)	7.124(1)		115.5(1)		192
$La_{1.3}(Al_4Si_{12}O_{32})$	$Fd\bar{3}m$	24.730						193
$La_{25.68}(Al_{76.8}Si_{115.2}O_{384})$	$Fd\bar{3}m$	25.050						194
$La_{1.3}(Al_4Si_{12}O_{32})$	$Fd\bar{3}m$	24.730						195
$Pr_4V(Si_2O_7)_2(V_2O_4)_2$	$C2/m$	13.410(2)	5.5998(9)	11.027(3)		100.57(2)		135
$La_4V(Si_2O_7)_2(V_2O_4)_2$	$C2/m$	13.482(7)	5.604(3)	11.091(3)		100.44(3)		136
$Nd_4V(Si_2O_7)_2(V_2O_4)_2$	$C2/m$	13.377(4)	5.589(4)	10.983(3)		100.61(2)		137
$La_4V(Si_2O_7)_2(V_2O_4)_2$	$C2/m$	13.510(3)	5.605(1)	11.114(2)		100.45(2)		138
$La_4Ti(Si_2O_7)_2(TiO_2)_8$	$C2/m$	13.545(2)	5.751(1)	15.188(1)		110.92(2)		139
$La_4Ti(Si_2O_7)_2(TiO_2)_8$	$C2/m$	13.536(2)	5.750(1)	14.252(1)		95.39(2)		139
$La_4Ti_5(Si_2O_7)_2O_8$	$C2/m$	13.621(4)	5.673(3)	11.143(2)		100.59(2)		140
$La_4Ti(Si_2O_7)_2(Ti_8O_{16})$	$C2/m$	13.542(8)	5.750(3)	15.186(3)		110.94(2)		141
$La_4Mn(Si_2O_7)_2(Mn_2O_4)_2$	$C2/m$	14.024(2)	5.571(2)	11.703(2)		114.34(2)		138
$Nd_2(SiBe_2O_7)$	$P\bar{4}2_1m$	7.470(1)		4.864(1)				186
$Ho_2(SiBe_2O_7)$	$P\bar{4}2_1m$	7.288(2)		4.754(3)				186
$Y_2(SiBe_2O_7)$	$P\bar{4}2_1m$	7.283(2)		4.755(1)				187
$Er_6(Si_{11}N_{20}O)$	$P3_1\mathrm{c}$	9.773(1)		10.597(1)				190
$Er_{6.254}(Si_{11}N_{20.762}O_{0.238})$	$P3_1c$	9.785(1)		10.644(1)				190
$Ce_{16}(Si_{15}O_6N_{32})$	$Pa\bar{3}$	15.4039(9)						191
$Sm_2(Si_3O_3N_4)$	$P\bar{4}2_1m$	7.6889(4)		4.9960(4)				182
$Y_2(Si_3O_3N_4)$	$P\bar{4}2_1m$	7.5974(5)		4.9082(3)				183
$Y_2(Si_3O_3N_4)$	$P\bar{4}2_1m$	7.6083(1)		4.9113(1)				184
$Y_2(Si_3O_3N_4)$	$P\bar{4}2_1m$	7.6137(2)		4.9147(2)				185

[a] Malinovskii, Y. A. *Dokl. Akad. Nauk SSSR* **1983**, *272*, 1375. [b] MacKenzie, K. J. D.; Gainsford, G. J.; Ryan, M. J. *J. Eur. Ceram. Soc.* **1996**, *16*, 553. [c] Bourguiba, N. F.; Dogguy, L. S. *Mater. Res. Bull.* **1994**, *29*, 427. [d] Karpov, O. G.; Pushcharovskii, D. Y.; Pobedimskaya, E. A.; Belov, N. V. *Dokl. Akad. Nauk SSSR* **1976**, *228*, 88. [e] Yamane, H.; Nagasawa, T.; Shimada, M.; Endo, T. *Acta Crystallogr.* **1997**, *53*, 1533. [f] Novak, G. A.; Gibbs, G. V. *Am. Mineral.* **1971**, *56*, 791. [g] Maksimov, B. A.; Ilyukhin, V. V.; Belov, N. V. *Dokl. Akad. Nauk SSSR* **1968**, *181*, 591. [h] Hawthorne, F. C.; Grundy, H. D. *Can. Miner.* **1977**, *15*, 50. [i] Izumi, F.; Mitomo, M.; Suzuki, J. *J. Mater. Sci. Lett.* **1982**, *1*, 533. [j] Izumi, F.; Mitomo, M.; Bando, Y. *J. Mater. Sci.* **1984**, *19*, 3115. [k] Ohashi, H.; Osawa, T.; Sato, A. *Acta Crystallogr.* **1990**, *B46*, 742. [l] Mellini, M.; Merlino, S. *Am. Mineral.* **1982**, *67*, 604. [m] Ohashi, H.; Ii, N. *Assoc. Miner. Petrol. Geol. Sendai* **1978**, *73*, 267. [n] Takeuchi, Y.; Kudoh, Y.; Ito, J. *Acta Crystallogr.* **1984**, *B40*, 115. [o] Hawthorne, F. C.; Grundy, H. D. *Acta Crystallogr.* **1973**, *B29*, 2615. [p] Ohashi, H.; Osawa, T.; Sato, A. *Acta Crystallogr.* **1994**, *50*, 838. [q] Yamane, H.; Nagasawa, T.; Shimada, M.; Endo, T. *Acta Crystallogr.* **1997**, *53*, 1367. [r] Smyth, J. R.; Ito, J. *Am. Mineral.* **1977**, *62*, 1252. [s] Yamane, H.; Nagasawa, T.; Murakami, Y.; Kamata, T.; Shindo, D.; Shimada, M.; Endo, T. *Mater. Res. Bull.* **1998**, *33*, 845. [t] Yang, H.-X.; Finger, L. W.; Conrad, P. G.; Prewitt, C. T.; Hazen, R. M. *Am. Mineral.* **1999**, *84*, 245−256. [u] Pyatenko, Y. A.; Zhdanova, T. A.; Voronkov, A. A. *Dokl. Akad. Nauk SSSR* **1979**, *248*, 868. [v] Takeuchi, Y.; Mori, H.; Kudoh, Y.; Ito, J. *Acta Crytallogr.* **1984**, *B40*, 126. [w] Maisonneuve, V., Leblanc, M. *Can. Miner.* **1998**, *36*, 1039. [x] Jacobsen, H.; Meyer, G. *Z. Kristallogr.* **1994**, *209*, 348.

The two modifications of $La_2I_2(SiO_4)$ are the only iodide *ortho*-silicates which have been described so far.[35] Both of the structures, triclinic (Figure 4a) and monoclinic (Figure 4b), exhibit double layers of I^- ions which are alternating stacked with cationic $[La_2(SiO_4)]^{2+}$ sheets. The coordination numbers of the La^{3+} ions are eight ($5O^{2-}$, $3I^-$) and nine ($7O^{2-}$, $2I^-$) in both structures.

Interestingly, the number of fluoride *ortho*-silicates is very limited. Besides the mixed disilicate−*ortho*-silicate $Er_4F_2(Si_2O_7)(SiO_4)$ and the mixed-valent apatite $Eu_5(SiO_4)_3F$, which will be described below, the recently published oxide fluoride $La_7OF_7(SiO_4)_3$[36] is the only example. The crystal structure consists of cationic chains according to ${}^1_\infty[La_3F_5]^{4+}$ oriented along [001] which are arranged in a hexagonal fashion and linked by $[La_4F_2]^{10+}$ double triangles. The empty voids in this La−F substructure are filled by $SiO_4{}^{4-}$ tetrahedra and lonesome oxide ions (Figure 5). For the La^{3+} ions, coordination numbers of 8, 9 and 10, respectively, are found.

A huge number of rare-earth *ortho*-silicates can be derived from the structure of the mineral *fluoroapatite*, $Ca_5(PO_4)_3F$,[37−55] (Table 1). As can be seen from the scheme in Figure 6, the structure is retained when the $SiO_4{}^{4-}$ ion is placed for $PO_4{}^{3-}$ and F^- is substituted for O^{2-}. However, to maintain the charge balance, the Ca^{2+} ions cannot be replaced completely by M^{3+} ions. In the so-called rare-earth *oxy-apatites* the 4f site is only partly occupied with M^{3+} ions,

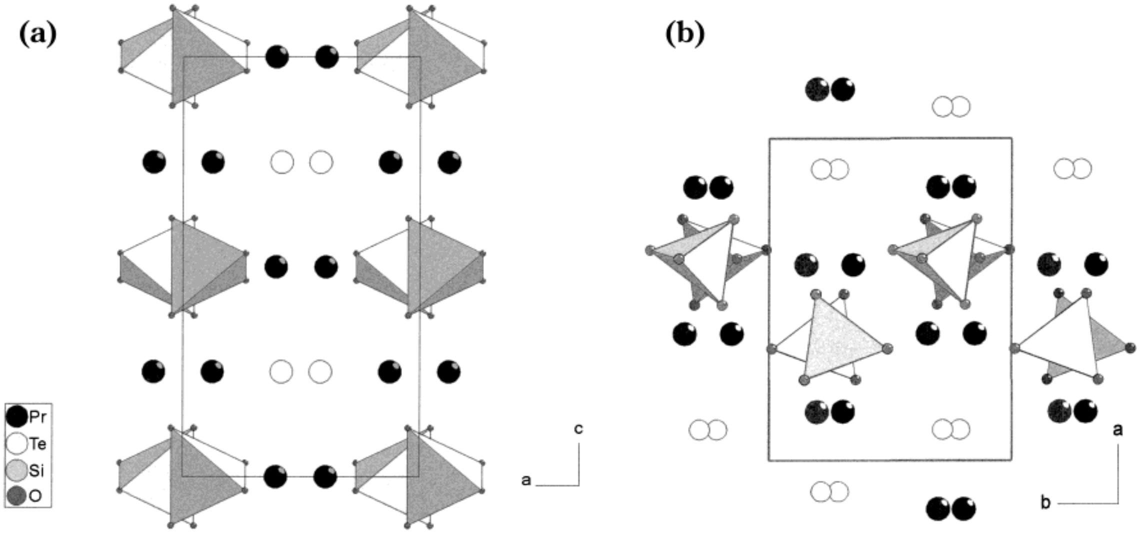

Figure 2. A and B-type structure of chalcogenide *ortho*-silicates $M_2X(SiO_4)$ (X = Se, Te) for the example of A−$Pr_2Te(SiO_4)$ (a) and B−$Pr_2Te(SiO_4)$ (b).

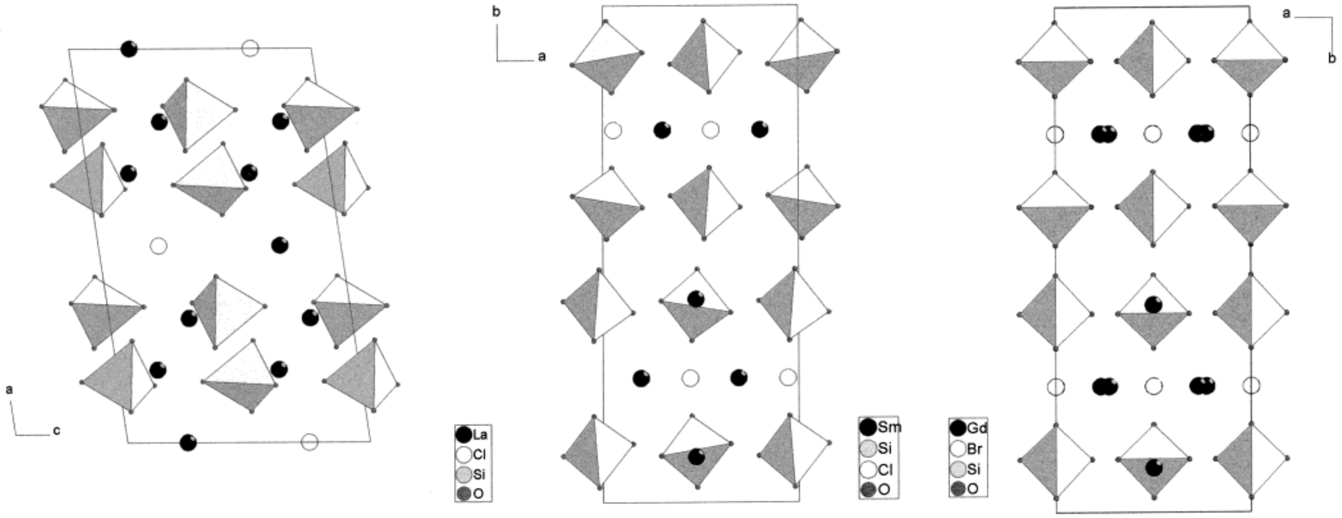

Figure 3. Comparison of the A- and B-type of $Nd_3Cl(SiO_4)_2$ (on the example of the lanthanum samarium compound) with $Gd_3Br(SiO_4)_2$.

leading to cation defect compounds $M_{4.667}(SiO_4)_3O$. Another possibility to achieve electroneutrality is the mixed occupancy of cationic sites with rare-earth ions and lower valent ions such as Ca^{2+}, K^+, or Na^+. This may occur for both of the crystallographically different sites as found, for example, for $CaLa_4(SiO_4)_3O$ or for one specific site as in $NaSm_9(SiO_4)_6S_2$. The latter compound shows another frequently observed variety of the apatite structure: The smaller F^- or O^{2-} may be substituted for the larger Br^- or S^{2-} ions, because the structure offers not only a site with trigonal planar coordination (Wyckoff notation 2a; 0, 0, 1/4) which is preferred by F^- and O^{2-} but also a site (2b; 0, 0, 0) with octahedral coordination, necessary for the large Br^- and S^{2-} ions. With respect to the natural abundant minerals these compounds are called *bromo-apatites*. The flexibility of the apatite type of structure allows a great variability of the composition as may be seen from the various examples given in Table 1. Finally, it should be emphasized that even mixed-valent rare-earth *ortho*-silicates with apatite structure have been prepared.[55] In the ruby red $Eu_5(SiO_4)_3F$, the larger Eu^{2+} ions occupy the 4f site leading to a 9-fold coordination while the Eu^{3+} ions are in 7-fold coordination on the 6h position. Thus, one can formulate the compound as $(Eu^{III})_3(Eu^{II})_2(SiO_4)_3F$. In the black ytterbium apatite $Yb_5(SiO_4)_3S$ (*bromo-apatite* structure) there must be a certain mixture of Yb^{2+} and Yb^{3+} that may be expressed by the formula $(Yb^{III})_3(Yb^{III/II})_2(SiO_4)_3S$.

A further group of rare-earth *ortho*-silicates are the pseudo-ternary compounds $NaM(SiO_4)$ (M = Nd, Sm, Gd, Y) and $LiM(SiO_4)$ (M = La, Y, Sc) which have been known for a long time.[56−63] Recently, the lithium compound $LiTm(SiO_4)$ which crystallizes with the olivine type of structure has been investigated in more detail due to its lithium ionic conductivity.[56] Besides the mineral *yftisite*, $Y_4TiOF_6(SiO_4)_2$,[64] and $Eu_5(SiO_4)_3F$, $Na_5Y_4(SiO_4)_4F$ is one of the few examples of an *ortho*-silicate containing a fluoride ion additionally.[65] The latter is coordinated by four Y^{3+} ions in a square planar manner. The $[FY_4]^{11+}$ units are surrounded by four $SiO_4{}^{4-}$ groups, and charge compensation is achieved by the Na^+ ions (Figure 7). A

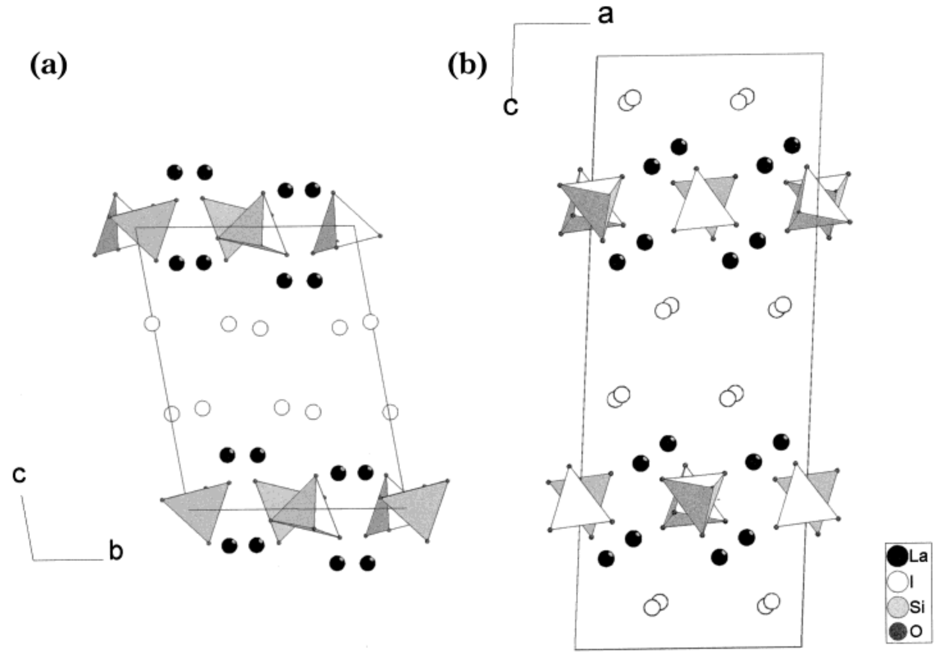

Figure 4. Crystal structures of the two modifications of $La_2I_2(SiO_4)$: (a) triclinic, (b) monoclinic.

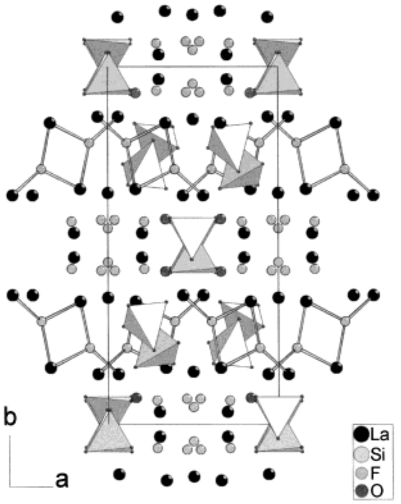

Figure 5. Crystal structure of $La_7OF_7(SiO_4)_3$; the $[F_2La_4]^{10+}$ units built up from edge-sharing $[FLa_3]^{8+}$ triangles are emphasized.

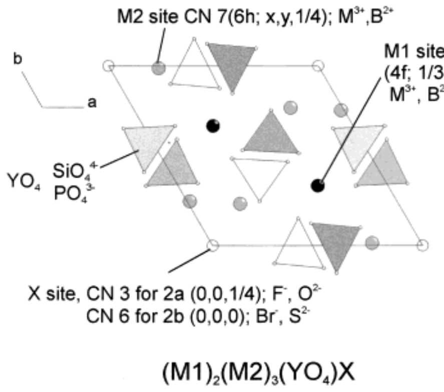

Figure 6. Schematic representation of the apatite type of structure and its derivatization.

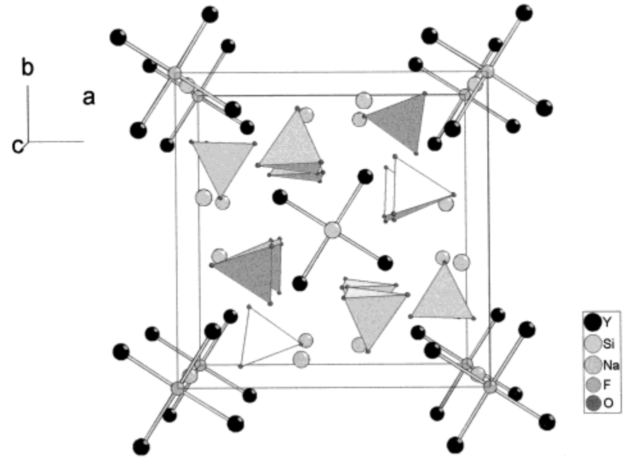

Figure 7. Crystal structure of the fluoride *ortho*-silicate $Na_5Y_4(SiO_4)_4F$.

ternary *ortho*-silicate of divalent europium is $Li_2Eu(SiO_4)$.[66] In the trigonal acentric crystal structure the Li^+ ions are tetrahedrally surrounded. The $[LiO_4]$ and $[SiO_4]$ tetrahedra join common vertexes to build a three-dimensional network which incorporates 8-fold coordinated Eu^{2+} ions. Thus, the compound can be seen as a *litho*-silicate.

The *ortho*-silicates $M_3(BSiO_6)(SiO_4)$ (M = Ce, Nd, Sm, Eu, Gd) contain not only isolated $[SiO_4]$ tetrahedra but also the dianions $[BSiO_6]$ which are built by the vertex linkage of an *ortho*-silicate group and a $[BO_3]$ triangle.[67−70] The *ortho*-silicate and *boro*-silicate anions are arranged in layers which alternate in the [001] direction of the orthorhombic unit cell (Figure 8). The three crystallographically different M^{3+} ions connect the anions and are in 8-fold ($M(1)^{3+}$, $M(2)^{3+}$) and 9-fold coordination ($M(3)^{3+}$) of oxygen atoms.

Ternary *ortho*-silicates containing transition-metal ions were described recently with the compounds $M_2Ti_2O_5(SiO_4)$ (M = La, Ce)[71,72] and $La_3Mo_4O_{10}(SiO_4)$.[73] In both types of compounds the transition-metal ions are in octahedral coordination of oxygen atoms. The octahedra are linked in the same way as that found in the rutile structure. The rutile-type parts of the

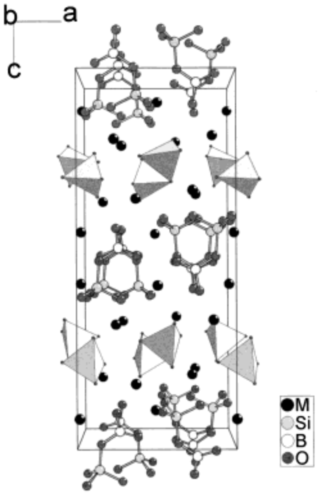

Figure 8. Stacking of $[BSiO_6]^{5-}$ dianions and *ortho*-silicate groups in the crystal structure of $M_3(BSiO_6)(SiO_4)$.

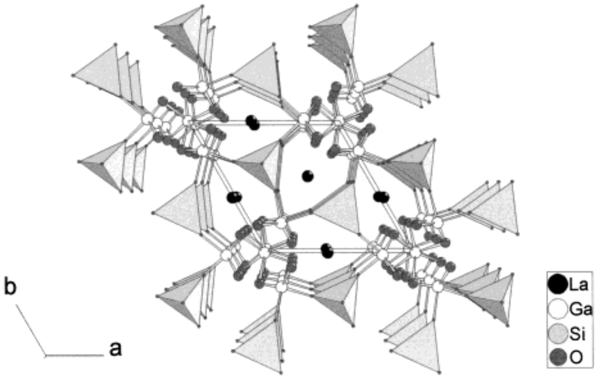

Figure 9. Crystal structure of the so-called *Langasite*, $La_3Ga_5O_{10}(SiO_4)$, with Ga^{3+} in the tetrahedral *and* octahedral environment of oxygen atoms.

structure are linked by the $[SiO_4]$ tetrahedra. The three-dimensional network provides the empty space for the M^{3+} ions, which gain coordination numbers of 10 in the titanium compounds and 8−11 for the molybdenum silicate. A very similar structural feature is also found among the disilicates with even more extended rutile-type arrays (see below). The gallium compound $La_3Ga_5O_{10}(SiO_4)$,[74] the so-called *langasite*, is not isotypic with the respective molybdenum compound but contains the Ga^{3+} ions in both octahedral and tetrahedral coordination of oxygen atoms. The $[GaO_4]$ tetrahedra connect the $[GaO_6]$ octahedra to columns along the [001] direction of the trigonal unit cell. The columns are linked with each other by the silicate groups. In this way, channels are formed along the *c*-axis in which the La^{3+} ions reside (Figure 9). *Langasite* crystallizes with the acentric space group *P*321 and shows an interesting piezoelectric effect. Therefore, the crystal growth of the compound and the investigations of its physical properties has attracted considerable interest.[75−79]

2. Disilicates

Until recently, seven types of rare-earth disilicates, $M_2(Si_2O_7)$, were known.[80−112] According to Felsche they are labeled with the capital letters A−G.[9] The largest number of structure types arises from the variable packing patterns of the $Si_2O_7^{6-}$ ions (Figure 10) and can be attributed to the different coordination requirements of the M^{3+} ions within the lanthanide series. Furthermore, there is a great flexibility of the shape of the disilicate anion. The bridging angle Si−O−Si varies from 128° to 180°. The latter is observed in the C- and D-type and shows the linearity of the bridge. As can be seen from Table 2, different structures occur even for the same rare-earth element, e.g., polymorphism of the disilicates is frequently observed. Attempts to describe the relation between the different polymorphs by T/M^{3+} and p/T diagrams, respectively, were done by Felsche and Bocquillon and are depicted in Figure 11.[113,114] A new polymorph of $La_2Si_2O_7$ has been found recently and, consequently, is named H-type.[84] It is closely related to the well-known A-type, but the stacking sequence of the disilicate anions in the [001] direction is ABA′B′ for the H-type instead of the simple AB stacking in the A-type.

Special emphasis shall be put on the B-type of the disilicates and the recently discovered ninth modification, called the I-type.[83] While the B-type has been confirmed by powder diffraction for the lanthanides Eu−Er,[9] the I-type is exclusively known for lanthanum. Both types are interesting in the sense that they are not real disilicates but mixed *catena*-trisilicate−*ortho*-silicates according to $M_4[Si_3O_{10}][SiO_4]$ (M = Eu−Er) in the case of the B-type and a mixed *catena*-tetrasilicate−*ortho*-silicate according to $La_6[Si_4O_{13}][SiO_4]_2$ for I−$La_2Si_2O_7$. In the trisilicates $M_4[Si_3O_{10}][SiO_4]$, all of the M^{3+} ions are in 8-fold coordination of oxygen atoms. The $[Si_3O_{10}]^{8-}$ ions are linear with angles Si−O−Si of 118° and 132°, respectively. In $La_6[Si_4O_{13}][SiO_4]_2$ the tetrasilicate anion has a unique shape in the form of a horseshoe. Both of the terminating tetrahedra are attached to the same La^{3+} ions. This is the first example for such a coordination feature of a tetrasilicate anion, although other tetrasilicates are found in rare-earth chemistry, namely, $Ba_2Nd_2(Si_4O_{13})$[115] and $Na_4Sc_2(Si_4O_{13})$.[116] The complete crystal structure of I−$La_2Si_2O_7$ can be seen as built up from alternating layers of $[Si_4O_{13}]^{10-}$ and $[SiO_4]^{4-}$ anions in the [010] direction with the La^{3+} ions (CN = 9−11) within and between the layers (Figure 12).

While the disilicates of rare-earth elements have been known for more than 30 years, it was only in 1982 when the first structurally characterized derivative of a disilicate, $Sm_4S_3(Si_2O_7)$, occurred in the literature.[117] It was obtained as a side product during the chemical transport of SmS_2 with I_2 in silica ampules. To date a number of isotypic compounds were obtained, either with larger or smaller M^{3+} ions and with S^{2-} or Se^{2-} as chalcogenide anion[117−124] (Table 2). They all contain two crystallographically different M^{3+} ions which are in 8-fold and 9-fold coordination, respectively. The ligands are five X^{2-} ions (S^{2-} or Se^{2-}) and three oxygen atoms for $M(1)^{3+}$ and three X^{2-} ions and six oxygen atoms for $M(2)^{3+}$. The disilicate anions are arranged in two orientations along the [001] direction of the tetragonal unit cell as can be seen from Figure 13. For all of these compounds the angle Si−O−Si within the $(Si_2O_7)^{6-}$ ion is ca. 130°.

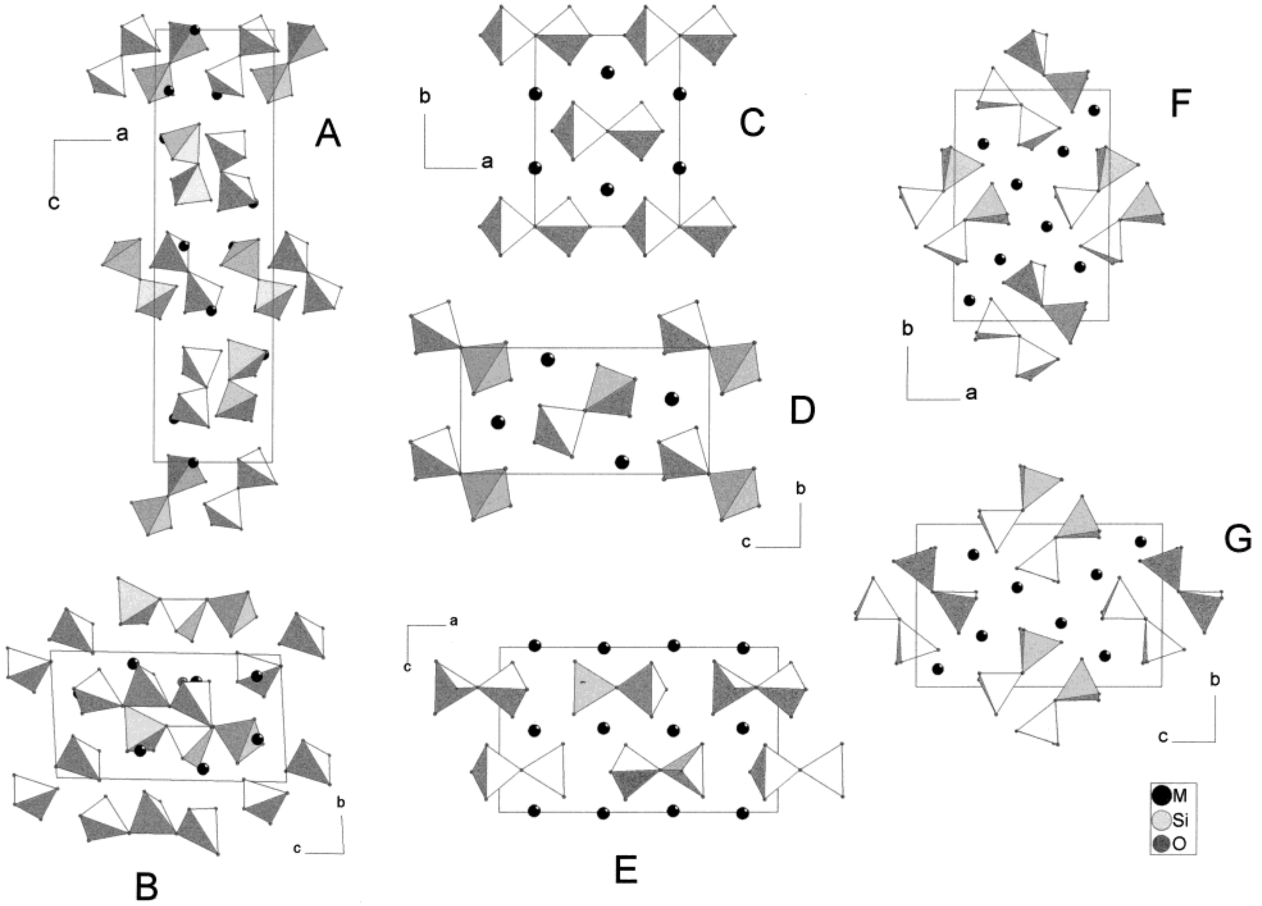

Figure 10. Polymorphs of rare-earth disilicates, after *Felsche* labeled with capital letters A−G. Note that the B-type is not a disilicate but a mixed *tri*- and *ortho*-silicate.

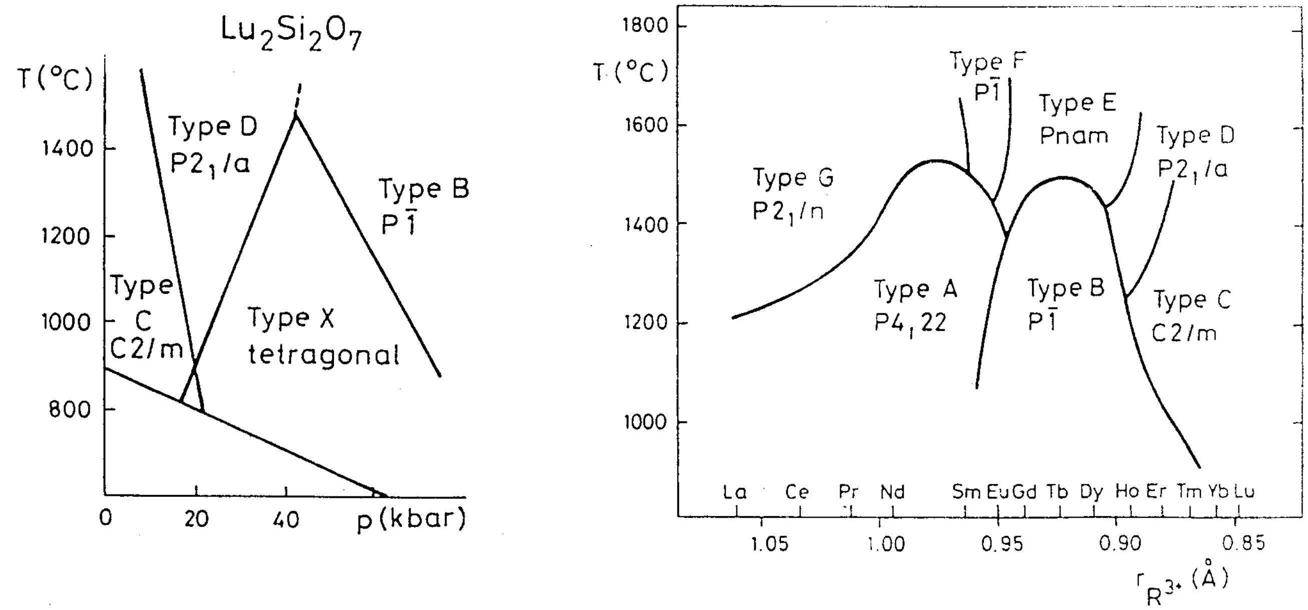

Figure 11. T/M^{3+} and p/T diagrams for the occurrence of rare-earth disilicate modifications.

Derivatization of rare-earth disilicates is also possible by introducing chloride ions in the crystal structure. Two examples are the isotypic compounds $La_3Cl_3(Si_2O_7)$ and $Pr_3Cl_3(Si_2O_7)$.[125,126] The acentric crystal structure (space group $P2_1$) contains three crystallographically different M^{3+} ions, which are coordinated by five Cl^- and five O^{2-} ($M(1)^{3+}$), four Cl^- and five O^{2-} ($M(2)^{3+}$), and three Cl^- and six O^{2-} ($M(3)^{3+}$) ligands, respectively. The angle Si−O−Si in the isolated disilicate ions is 148°. Figure 14 shows the crystal structure of the compounds in the [100] direction. Pure disilicates containing additional F^- ions are not known, but with $Er_4F_2(Si_2O_7)(SiO_4)$ an interesting crystal structure was described contain-

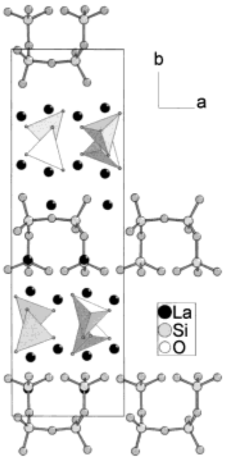

Figure 12. Crystal structure of the I-type of $La_2Si_2O_7$ containing the horseshoe-shaped tetrasilicate anions $[Si_4O_{13}]^{10-}$ and *ortho*-silicate groups according to $La_6[Si_4O_{13}][SiO_4]_2$.

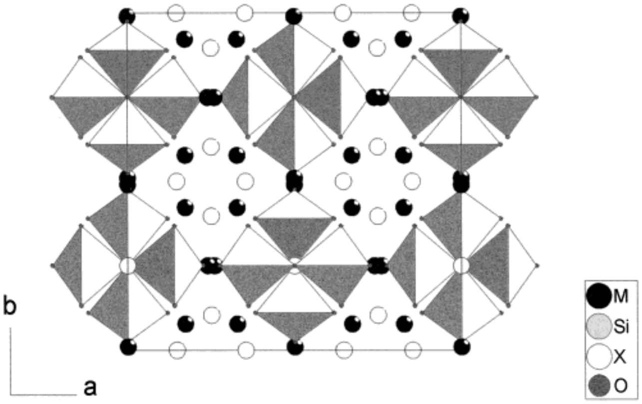

Figure 13. Crystal structure of the chalcogenide disilicates $M_4X_3(Si_2O_7)$ ($X = S, Se$).

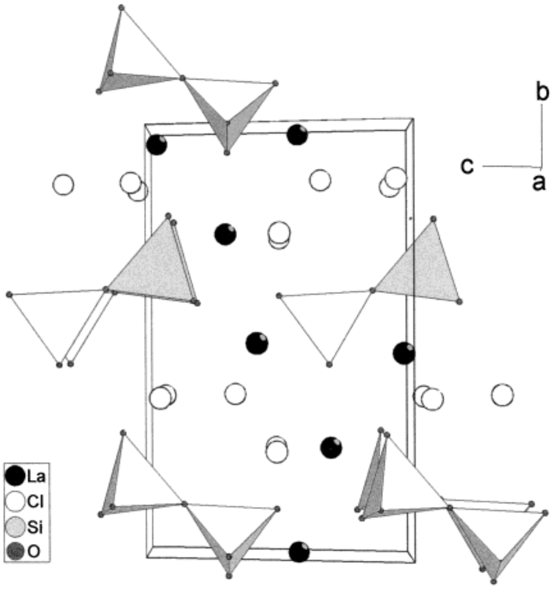

Figure 14. Crystal structure of the chloride disilicates $M_3Cl_3(Si_2O_7)$.

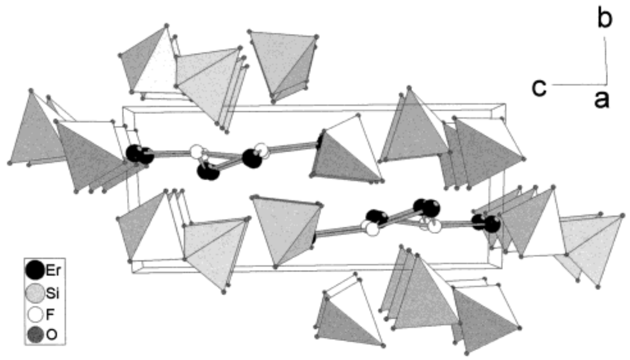

Figure 15. Crystal structure of $Er_4F_2(Si_2O_7)(SiO_4)$ with $[Er_4F_2]^{10+}$ double triangles located in channels formed by $Si_2O_7^{6-}$ and SiO_4^{4-} anions.

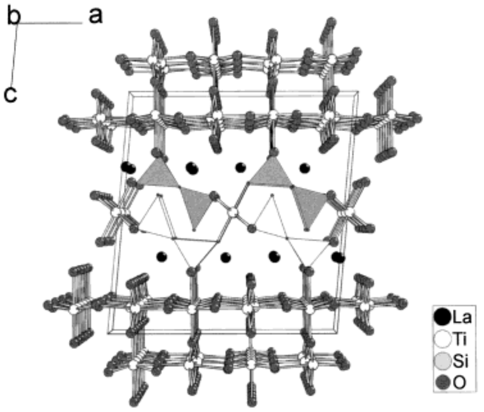

Figure 16. Crystal structure of the disilicates $M_4M'(Si_2O_7)_2(M'O_2)_{4m}$ ($M = La, Pr, Nd$; $M' = Ti, V, Mn$; $m = 1, 2$) containing rutile-type layers (the shown example is $La_4Ti(Si_2O_7)(TiO_2)_8$).

ing disilicate and *ortho*-silicate ions.[127] The F^- ions are surrounded by three Er^{3+} ions in a nearly trigonal planar manner, and two of these triangles are sharing a common edge leading to cationic $[Er_2F_4]^{10+}$ units. The anions form channels in the crystal structure which incorporate these complex cations (Figure 15).

The disilicates $A_3M(Si_2O_7)$ ($A = Na, K$; $M = Nd, Tm, Lu, Y, Sc$) are pseudo-ternary derivatives of rare-earth disilicates containing alkali-metal ions.[128−132] The hexagonal crystal structures show the two crystallographically different M^{3+} ions in 6-fold coordination of oxygen atoms. For $M(1)^{3+}$ a trigonal prism and for $M(2)^{3+}$ an octahedron results as coordination polyhedra. These are arranged along the [001] direction and linked via the disilicate groups which show the same orientation. The empty voids of this three-dimensional network are filled by A^+ ions which are coordinated by six, nine, and eight oxygen atoms, respectively. Mixed crystals with Y and Sc have been also obtained.[133,134]

Another group of disilicates can be seen as composed of rutile slabs ($M'O_2$) and disilicate layers according $M_4M'(Si_2O_7)_2(M'O_2)_{4m}$ ($M = La, Pr, Nd$; $M' = Ti, V, Mn$; $m = 1, 2$).[135−141] If $m = 1$, rutile and silicate slabs are stacked alternating; for $m = 2$, rutile double layers are inserted (Figure 16). Some of the transition-metal ions are located within the silicate layers, being in octahedral coordination of oxygen atoms which belong exclusively to disilicate ions. The rare-earth ions are placed on the borderline between the different layers and show a coordination number of 10. These type of compounds have attracted considerable interest because they are mixed valent with respect to the transition-metal ions. Indeed, the

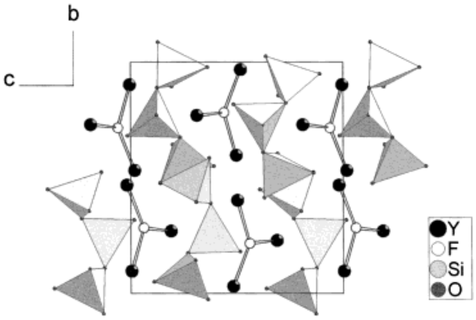

Figure 17. *Thalenite* type of structure for $Y_3F(Si_3O_{10})$.

compounds are shown to be semiconductors with band gaps of 0.25 and 0.12 eV for $La_4Ti(Si_2O_7)(TiO_2)_8$ and $La_4Ti(Si_2O_7)(TiO_2)_8$, respectively.[139]

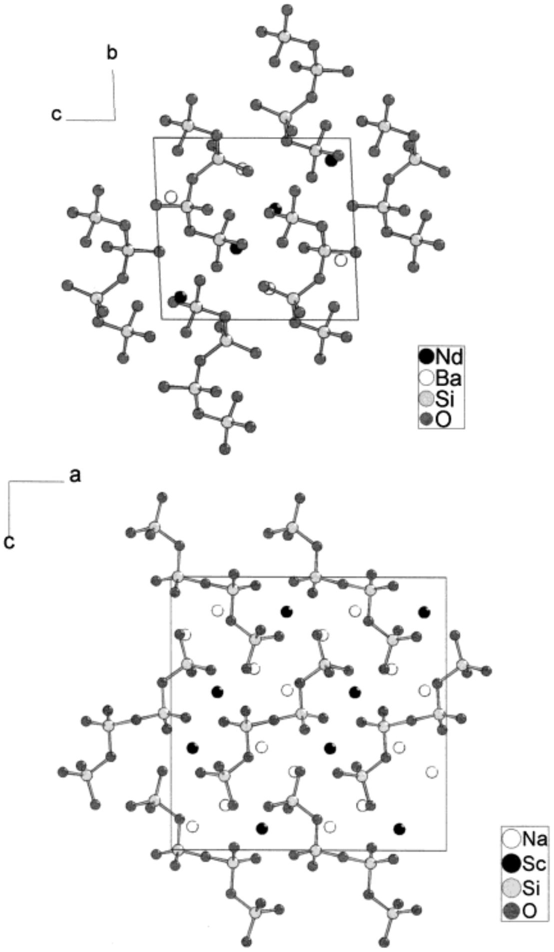

Figure 18. Crystal structures of the *catena*-tetrasilicates $Ba_2Nd_2(Si_4O_{13})$ and $Na_4Sc_2(Si_4O_{13})$. Note, in contrast to the findings for $La_2Si_2O_7 = La_6[Si_4O_{13}][SiO_4]_2$, the tetrasilicate anions $[Si_4O_{13}]^{10-}$ are zigzag shaped in both compounds.

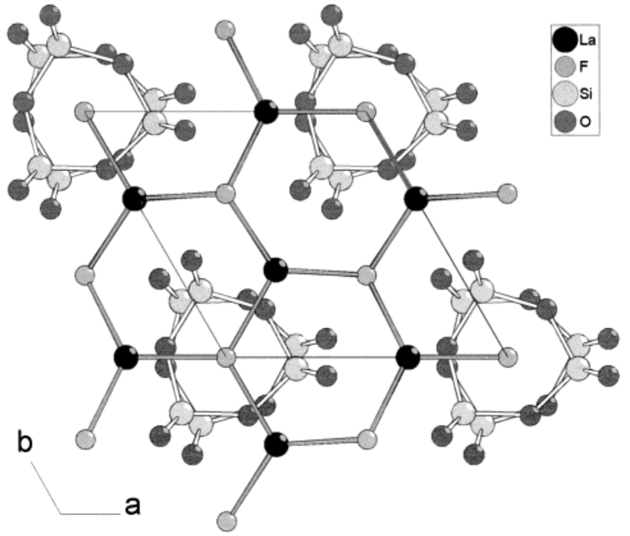

Figure 19. Crystal structure of $La_3F_3(Si_3O_9)$ with honeycomb-shaped ${}^{2}_{\infty}[LaF_{3/3}]^{2+}$ layers and silicate anions alternating stacked along [001].

3. Higher Silicates

With the B-type disilicates $M_2Si_2O_7$ ($= M_4(Si_3O_{10})[SiO_4]$) and I$-La_2Si_2O_7$ ($= La_6[Si_4O_{13}][SiO_4]_2$), rare-earth compounds containing silicate groups of higher condensation were mentioned in the previous section. Further lanthanide compounds with the *catena*-trisilicate anion $[Si_3O_{10}]^{8-}$ are the fluoride silicates $M_3F(Si_3O_{10})$ (M = Dy, Ho, Er, Y).[142−144] They adopt the *thalenite* type of structure, named after a mineral which has nearly the composition $Y_3F(Si_3O_{10})$ but which usually contains various amounts of other rare-earth ions and OH^- instead of F^-.[145] Characteristic features of the crystal structure are trigonal $[FM_3]^{8+}$ units and U-shaped $[Si_3O_{10}]^{8-}$ anions. The ions are arranged as depicted in Figure 17, leading to coordination numbers of 7 (2×) and "7+1", respectively, for the three M^{3+} ions. The *catena*-tetrasilicate anion $[Si_4O_{13}]^{10-}$ is known from two other lanthanide compounds, $Ba_2Nd_2(Si_4O_{13})$ and $Na_4Sc_2(Si_4O_{13})$.[115,116] In contrast to the horseshoe shape found in I$-La_2Si_2O_7$, the anion has a zigzag form in the barium compound and is nearly linear in $Na_4Sc_2(Si_4O_{13})$ (Figure 18). Tri- and tetrasilicates are also known as *cyclo*-silicates, and for the rare-earth elements a limited number of crystal structures were determined. $La_3F_3(Si_3O_9)$ is a fluoride *cyclo*-trisilicate that is built up of honeycomb-shaped ${}^{2}_{\infty}[LaF_{3/3}]^{2+}$ layers which are alternating stacked with the silicate anions along the [001] direction of the hexagonal unit cell (Figure 19).[146] For the La^{3+} ions, a tricapped trigonal prism ($3F^-$, $6O^{2-}$) arises as coordination polyhedron with the distances ranging from 243 to 252 pm. *Cyclo*-trisilicates are additionally found among the *nitrido*-silicates of rare-earth elements. The hexagonal compounds $M_3(Si_3O_6N_3)$ (M = La, Ce,)[147] and the monoclinic or orthorhombic $Y_3(Si_3O_6N_3)$[148,149] contain the anions $[Si_3O_6N_3]^{9-}$ which are stacked in different ways in the two structure types, leading to coordination numbers of 12 (La, Ce) and 8 (Y), respectively. Structural data of *cyclo*-tetrasilicates have been provided for $M_6Cl_{10}(Si_4O_{12})$ (M = Sm, Y)[150,151] and the divalent europium compound $Eu_8Cl_8(Si_4O_{12})$.[152] The former two compounds are isotypic and contain cationic double layers ${}^{2}_{\infty}[M(2)_5Cl_9]^{6+}$ and anionic monolayers ${}^{2}_{\infty}[M(1)Cl(1)(Si_4O_{12})]^{6-}$ which are arranged parallel (001). The two crystallographically different M^{3+} ions are surrounded by six oxygen and two chloride ligands ($M(1)^{3+}$) or by five Cl^- ions and two oxygen atoms ($M(2)^{3+}$). The europium silicate may also be seen as built up from layers; in this case the anionic sheets have the composition ${}^{2}_{\infty}[(Si_4O_{12})Cl_4]^{12-}$ and the cationic ones are composed

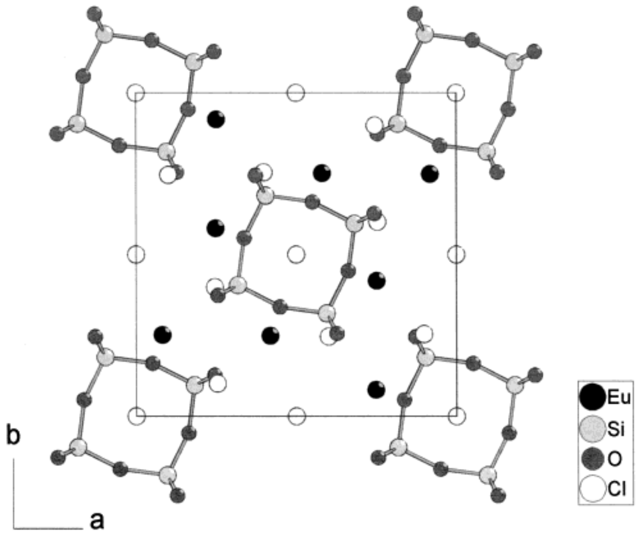

Figure 20. Crystal structure of the *cyclo*-tetrasilicate $Eu_2Cl_2(SiO_3) = Eu_8Cl_8(Si_4O_{12})$. The projection of the tetragonal structure on (001) shows the high symmetry of the anion.

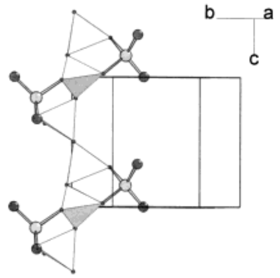

Figure 21. Linkage of $[BO_4]$ and $[SiO_4]$ tetrahedra to chains in the *stillwellite*-type *boro*-silicates $M(BSiO_5)$ (M = La, Ce, Nd, Gd).

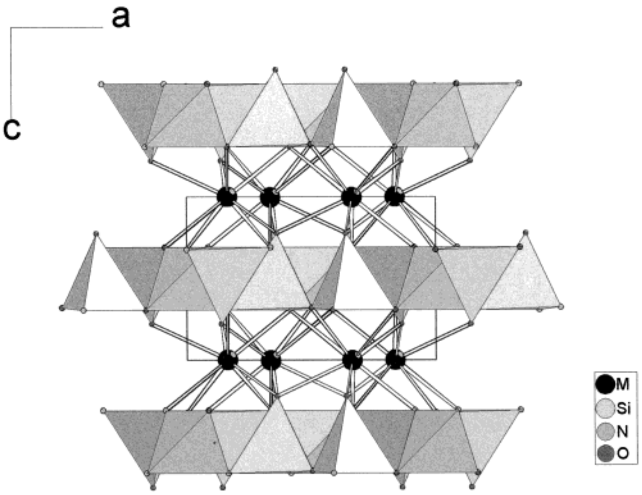

Figure 22. Layer structure of the *melilith*-type *nitrido*-silicates $M_2(Si_3O_3N_4)$ (M = Ce, Nd, Sm, Gd, Y).

according to $^{2}_{\infty}[Eu_2Cl]^{3+}$. They are stacked along [001] in a way that a coordination number of seven ($4O^{2-}$, $3Cl^-$) is gained for Eu^{2+}. A projection of the tetragonal structure on (001) reveals the highly symmetric *cyclo*-tetrasilicate ion which is located on the 4-fold axis of the unit cell (Figure 20).

Even higher condensed *cyclo*-silicates have been prepared. The divalent europium silicate $Na_6Eu_3(Si_6O_{18})$[153] contains the *cyclo*-hexasilicate anion which shows a chair conformation with respect to the Si atom arrangement. The anions are stacked in the [001] direction of the rhombohedral cell and coordinated by the cations. The Eu^{2+} ions have coordination numbers of 6 and 8, respectively. A couple of cyclo-dodecasilicates, $A_{15}M_3(Si_{12}O_{36})$ (A = Na, Ag; M = Dy, Ho, Yb, Lu), are known.[154−162] They have attracted attention because part of the A^+ cations are located in large channels provided by the special arrangement of the ring-shaped anions. These cations are highly disordered, causing the ionic conductivity of these compounds.

More extended arrays of linked $[SiO_4]$ tetrahedra, like chains (*ino*-silicates), sheets (*phyllo*-silicates), and three-dimensional networks (*tecto*-silicates) are known for various rare-earth silicates. The compounds $K_3M(Si_3O_9)$ (M = Ho, Lu)[163−165] contain infinite chains of vertex-sharing $[SiO_4]$ tetrahedra running down the [100] direction. With respect to the crystallographic period of identity, the chain can be named a Sechser−Einfach-chain according to Liebau's nomenclature.[166] The chains are connected by M^{3+} ions in distorted octahedral coordination and in the empty voids of the network formed, thereby the K^+ are located. Another *ino*-silicate is $Na_3Y(Si_3O_9)$,[167] which has a complicated structure with 4 crystallographically different Y^{3+} ions and 12 different $[SiO_4]$ tetrahedra. The latter are linked to infinitely winding Zwölfer−Einfach chains which are joined together by the cations. The *boro*-silicates $M(BSiO_5)$ (M = La, Ce, Nd, Gd),[168−176] which crystallize with the structure of the mineral *stillwellite,* contain Dreier−Einfach chains with respect to the linked $[BO_4]$ tetrahedra. These chains are attached by *ortho*-silicate ions as depicted in Figure 21. By linking the chains, the M^{3+} ions achieve a coordination number of nine in the structure.

$K_3Nd(Si_6O_{15})$ may serve as an example for a *phyllo*-silicate, which has been obtained under high pressure.[177,178] It contains puckered sheets of the composition $^{2}_{\infty}[Si_2O_5]^{2-}$ which are extended in the (010) plane. The K^+ ions are incorporated within these layers, while the Nd^{3+} ions reside between the layers. In contrast, the compounds $Na_3Y(Si_6O_{15})$ and $Na_2LiY(Si_6O_{15})$ contain no layers.[179−181] For the neat sodium silicate two structures are known, one with silicate double chains and the other with discrete $[Si_6O_{15}]$ units. The lithium compound also shows the double-chain structure.

The *nitrido*-silicates $M_2(Si_3O_3N_4)$ (M = Ce, Nd, Sm, Gd, Y)[182−185] are also *phyllo*-silicates with the silicate layers stacked in the [001] direction of the tetragonal unit cell (Figure 22). These *nitrido*-silicates with the M^{3+} in 8-fold coordination are referred to as *melilith*-type phases with respect to their structural similarities with the respective mineral. The same structure has been found for the *beryllo*-silicates $M_2(Be_2SiO_7)$ (M = Nd, Ho, Y)[186,187] with layers of vertex-connected $[BeO_4]$ and $[SiO_4]$ tetrahedra.

In $NaM(Si_6O_{14})$ (M = Pr, Nd) the $[SiO_4]$ tetrahedra are condensed to triple layers containing Na^+ ions in their cavities.[188] Further Na^+ and the M^{3+} ions connect the layers in the [001] direction. Finally, further connection of the silicate tetrahedra lead to the *tecto*-silicates, for which $K_2Ce(Si_6O_{15})$ is an example.[189] The three-dimensional silicate network provides the space for the incorporation of K^+ and Ce^{4+} ions, the latter being in octahedral coordination of oxygen atoms. A three-dimensional network of tetrahedra is also possible with nitrogen-containing silicates, and thus, a few *nitrido-tecto*-silicates are known. Besides $Er_6(Si_{11}N_{20}O)$ and $Er_{6.254}(Si_{11}N_{20.762}O_{0.238})$,[190] the cerium compound $Ce_{16}(Si_{15}O_6N_{32})$ is remarkable because it contains the silicon atoms not only tetrahedrally coordinated but also in an octahedral environment of nitrogen atoms.[191]

Aluminum-containing *tecto*-silicates exist in a great number and with a lot of different compositions. Among the rare-earth compounds, the structure of the *anorthite*-type europium silicate $Eu_{0.92}(Al_{1.76}Si_{2.24}O_8)$[192] and of the *zeolite*-type compounds $La_{1.3}Al_4Si_{12}O_{32}$ and $La_{25.68}Al_{76.8}Si_{115.2}O_{384}$ were determined.[193−195] The europium silicate shows an 8-fold coordination for Eu^{2+}, whereas the La^{3+} ions are distributed over three crystallographically different sites with coordination numbers of “6+4”.

B. Phosphates

Two of the naturally abundant rare-earth phosphates, *monazite* and *xenotime*, are important sources for the production of rare-earth metals. Both are *ortho*-phosphates, MPO_4, with *monazite* containing the larger lanthanide ions La−Nd (and Th) and *xenotime* mainly yttrium and various amounts of the smaller rare-earth ions. These minerals and their artificial analogues have been extensively investigated. Similar to the silicates, the phosphates also show the tendency to condense to larger aggregates, thereby forming either ring-shaped (*cyclo*-phosphates) or chain-like (*catena*-phosphates) polyanions. Thus, the number of different rare-earth phosphates is large. For example, the phase diagram La_2O_3/P_2O_5 shows six compositions with the molar ratios 3:1, 7:3, 1:1, 1:2, 1:3, and 1:5.[196] Additionally, the number of known phosphates increases if one takes the ternary compounds into account. Structural investigations of the phosphates started in the 1940s, and until 1985 roughly 100 structure determinations were performed. Most of them have been reviewed by Palkina in 1982[197] and Niinistö in 1986/1987,[6,7] so emphasis will be put here on more recent investigations.

1. Ortho-Phosphates

The *ortho*-phosphates can be prepared by fusing the binary oxides M_2O_3 and P_2O_5 or by precipitation from aqueous solutions containing M^{3+} ions with alkali phosphates or phosphoric acid. Single crystals are gained hydrothermally or by flux methods.

The *ortho*-phosphates of the larger lanthanides La−Gd crystallize with the monoclinic structure of Monazite and contain the M^{3+} ions in 9-fold coordination of oxygen atoms which belong to seven PO_4^{3-} ions.[198−211] Two of the latter are chelating ligands. With the lighter rare-earth elements Tb−Lu, Y, and Sc, the tetragonal structure of $ZrSiO_4$ is adopted.[212−229] The M^{3+} ions are 8-fold coordinated by oxygen atoms from two chelating and four monodentate phosphate ions. For La, Ce, and Nd, also a hexagonal structure has been found.[230,231] Formerly it was thought that they might contain small amounts of water,[230] but further investigations showed that this it not necessarily the case. Another hydrate that was found for rare-earth *ortho*-phosphates is $DyPO_4{\cdot}1.5H_2O$, which is said to crystallize with an orthorhombic structure.[232] However, besides the monoclinic mineral Weinschenkit,[233] $(Y,Er)PO_4{\cdot}2H_2O$, none of the few *ortho*-phosphate hydrates has been characterized unambiguously by single-crystal data.

Several structure determinations have been performed on *ortho*-phosphates containing mixtures of rare-earth elements. The considerable interest in these types of compounds arose from the possibility of using them as materials for the long-term disposal of nuclear waste[234−236] or as host lattices for spectroscopic investigations.

A large number of *ortho*-phosphates of the composition $A_3M(PO_4)_3$ with M being the rare-earth and A an alkali metal is known. Some of them have been investigated by X-ray single-crystal diffraction (Table 4).[237−243] In general, they all consist of isolated PO_4^{3-} tetrahedra separated by the cations. The great variety of structures arises from the different coordination requirements of the cations. In principle, for all of the different structures the mineral *Glaserite*,[244] $K_3Na(SO_4)_2$, is the aristotype. It has a trigonal crystal structure and contains the Na^+ ions in octahedral and the K^+ ions in 10- and 12-fold coordination, respectively. In the ternary rare-earth phosphates the octahedral position is occupied by the M^{3+} ions. For the small ions such as Lu^{3+} it is possible to retain the Glaserite structure, but an increasing M^{3+} radius may cause severe distortions leading to lower symmetry structures (cf. Table 4). A change of the coordination number is easily achieved by reorientation of the PO_4^{3-} groups (Figure 23). Thus, a temperature dependent polymorphism is frequently observed for a given compound. The distortion from trigonal symmetry can also be confirmed by IR spectroscopy, as has been recently shown for orthorhombic $K_3Sm(PO_4)_2$.[242] During the last 20 years the double phosphates have attracted some interest as host materials for luminescent lanthanide ions, and for that purpose several mixed lanthanide compounds have been prepared.[245−247]

Another group of rare-earth double phosphates is mainly based on the element scandium. The compounds have the composition $A_3Sc_2(PO_4)_3$ and contain the small alkali ions Li^+ and Na^+ or in some cases even Ag^+.[248−266] The Sc^{3+} ions are in an octahedral coordination of oxygen atoms, while for the A^+ ions several crystallographic positions are, in principle, available which are only partly occupied. These partly occupied sites and the low energetic barriers for ion movements make this type of phosphates an excellent ionic conductor.[267] Due to the different ordering schemes of the A^+ ions, the symmetry of the compounds may vary. The structure of the $A_3Sc(PO_4)_3$-type compounds is very similar to that of $NaZr_2(PO_4)_3$ and $Na_4Zr(SiO_4)_3$ (Figure 24). A mixture of the latter two is known as NASICON (*N*a *s*uper *i*onic *con*ductor). Methods to evaluate the conductivity of the alkali scandium double phosphates included impedance and NMR spectroscopy.[268]

Table 4. Data of *Ortho*-Phosphates

		lattice parameters						
compound	space group	a/Å	b/Å	c/Å	α/°	β/°	γ/°	ref
$La(PO_4)$	$P2_1/a$	8.25(2)	7.09(1)	6.47(1)		126.16(9)		211
$La(PO_4)$	$P6_222$	7.081(5)		6.468(8)				230
$Nd(PO_4)$	$P6_222$	6.98(1)		6.34(2)				230
$La(PO_4)$	$P2_1/n$	6.825(4)	7.057(2)	6.482(2)		103.21(4)		198
$Sm(PO_4)$	$P2_1/n$	6.669(1)	6.868(2)	6.351(1)		103.92(2)		199
$Eu(PO_4)$	$P2_1/n$	6.639(3)	6.823(3)	6.318(3)		104.00(4)		199
$Gd(PO_4)$	$P2_1/n$	6.621(2)	6.823(2)	6.310(2)		104.16(2)		199
$Pr(PO_4)$	$P2_1/n$	6.741(3)	6.961(4)	6.416(3)		103.63(3)		200
$Nd(PO_4)$	$P2_1/n$	6.722(1)	6.933(1)	6.390(2)		103.72(2)		200
$Nd(PO_4)$	$P2_1/n$	6.732(2)	6.930(2)	6.383(2)		103.61(2)		201
$Ce(PO_4)$	$P2_1/n$	6.770	7.040	6.460		104.00		202
$Ce(PO_4)$	$P2_1/n$	6.790	7.000	6.460		104.00		203
$Ce(PO_4)$	$P2_1/n$	6.77(1)	6.99(1)	6.45(1)		103.6(2)		204
$Ce(PO_4)$	$P2_1/n$	6.790(1)	7.0203(6)	6.4674(7)		103.38(1)		205
$La(PO_4)$	$P2_1/n$	6.831(1)	7.0705(9)	6.5034(9)		103.27(1)		205
$Ce(PO_4)$	$P2_1/n$	6.788(1)	7.0163(8)	6.4650(7)		103.40(1)		205
$Pr(PO_4)$	$P2_1/n$	6.7596(8)	6.981(1)	6.4344(9)		103.50(1)		205
$Nd(PO_4)$	$P2_1/n$	6.735(1)	6.9500(9)	6.4049(8)		103.68(1)		205
$Sm(PO_4)$	$P2_1/n$	6.682(1)	6.8877(9)	6.3653(9)		103.86(1)		205
$Eu(PO_4)$	$P2_1/n$	6.681(1)	6.8618(9)	6.3491(8)		103.96(1)		205
$Gd(PO_4)$	$P2_1/n$	6.6435(9)	6.841(1)	6.3281(6)		103.98(1)		205
$Lu(PO_4)$	$I4_1/amd$	6.792(2)		5.955(2)				212
$Er(PO_4)$	$I4_1/amd$	6.863(3)		6.007(3)				213
$Dy(PO_4)$	$I4_1/amd$	6.91(1)		6.04(1)				214
$Tb(PO_4)$	$I4_1/amd$	6.940(1)		6.068(1)				215
$Dy(PO_4)$	$I4_1/amd$	6.907(2)		6.046(2)				215
$Ho(PO_4)$	$I4_1/amd$	6.882(2)		6.025(2)				215
$Er(PO_4)$	$I4_1/amd$	6.860(1)		6.003(1)				216
$Tm(PO_4)$	$I4_1/amd$	6.839(1)		5.986(1)				216
$Yb(PO_4)$	$I4_1/amd$	6.816(2)		5.966(2)				216
$Ce(PO_4)$	$P12_1/n1$	6.777(3)	6.993(3)	6.445(3)		103.54(4)		206
$Lu(PO_4)$	$I4_1/amd$	6.792(2)		5.954(2)				217
$Dy(PO_4)$	$I4_1/amd$	6.91(1)		6.04(1)				218
$Tb(PO_4)$	$I4_1/amd$	6.931(1)		6.061(1)				219
$Dy(PO_4)$	$I4_1/amd$	6.905(1)		6.0384(6)				219
$Ho(PO_4)$	$I4_1/amd$	6.877(1)		6.0176(8)				219
$Er(PO_4)$	$I4_1/amd$	6.851(1)		5.997(1)				219
$Tm(PO_4)$	$I4_1/amd$	6.8293(9)		5.980(1)				219
$Yb(PO_4)$	$I4_1/amd$	6.8093(8)		5.9639(5)				219
$Lu(PO_4)$	$I4_1/amd$	6.783(1)		5.9467(6)				219
$Ce(PO_4)$	$P6_222$	7.055(3)		6.439(5)				230
$La_{0.95}(PO_4)$	$P2_1/n$	6.852(4)	7.091(4)	6.510(4)		103.62(4)		207
$Ce_{0.9}U_{0.1}(PO_4)$	$P2_1/n$	6.794(1)	7.020(1)	6.478(1)		103.51(1)		208
$Tb(PO_4)$	$I4_1/amd$	6.9423(1)		6.0640(3)				220
$Tb(PO_4)$	$I4_1/amd$	6.9414(2)		6.0704(4)				220
$Ce(PO_4)$	$P2_1/n$	6.77(1)	6.99(1)	6.45(1)		103.6(2)		209
$Ce(PO_4)$	$P3_121$	7.069(3)		6.443(5)				231
$Ce(PO_4)$	$P2_1/n$	6.770	7.010	6.450		103.63		210
$Sc(PO_4)$	$I4_1/amd$	6.578(2)		5.796(2)				221
$Sc(PO_4)$	$I4_1/amd$	6.574(1)		5.791(1)				217
$Y(PO_4)$	$I4_1/amd$	6.862		6.174				222
$Y(PO_4)$	$I4_1/amd$	6.878(3)		6.036(3)				223
$Y(PO_4)$	$I4_1/amd$	6.8817(5)		6.0177(6)				217
$Y(PO_4)$	$I4_1/amd$	6.8947(6)		6.0276(6)				224
$Sc(PO_4)$	$I4_1/amd$	6.579		5.796				225
$(Sc_{0.96}Y_{0.04})(PO_4)$	$I4_1/amd$	6.589(1)		5.806(1)				226
$(Gd_{0.5}Tb_{0.5})(PO_4)$	$I4_1/amd$	6.9449(9)		6.068(1)				227
$(Gd_{0.75}Tb_{0.25})(PO_4)$	$I4_1/amd$	6.9647(7)		6.090(6)				227
$(Lu_{0.9}Tb_{0.1})(PO_4)$	$I4_1/amd$	6.8003(8)		5.9638(6)				227
$Gd_{0.5}Er_{0.5}(PO_4)$	$I4_1/amd$	6.880(2)		6.017(2)				228
$Gd_{0.5}Y_{0.5}(PO_4)$	$I4_1/amd$	6.914(3)		6.042(4)				228
$Gd_{0.5}Yb_{0.5}(PO_4)$	$I4_1/amd$	6.865(2)		6.004(2)				228
$Gd_{0.75}Yb_{0.25}(PO_4)$	$I4_1/amd$	6.903(2)		6.034(2)				228
$Gd_{0.5}Yb_{0.5}(PO_4)$	$I4_1/amd$	6.865(2)		6.004(2)				229
$Gd_{0.5}Y_{0.5}(PO_4)$	$I4_1/amd$	6.914(3)		6.042(4)				228
$Sc(H_2PO_4)_3$	$R3c$	8.274(5)		25.98(1)				*a*
$Na_3Nd(PO_4)_2$	$Pbc2_1$	15.874(8)	13.952(8)	18.470(9)				237
$K_3Ce(PO_4)_2$	$P2_1/m$	9.621(1)	5.756(3)	7.496(1)		90.6(1)		238
$K_3Lu(PO_4)_2$	$P\bar{3}$	9.601(2)		7.725(4)				239
$K_3Sc(PO_4)_2$	$P\bar{3}$	9.430(2)		7.629(2)				243
$Na_3Ce(PO_4)_2$	$Pca2_1$	14.091(4)	5.357(1)	18.740(3)				240
$K_3Nd(PO_4)_2$	$P2_1/m$	9.532(2)	5.631(3)	7.444(3)		90.95(2)		241

Table 4. (Continued)

		lattice parameters						
compound	space group	a/Å	b/Å	c/Å	α/°	β/°	γ/°	ref
$K_3Sm(PO_4)_2$	$P2_1/m$	7.4347(5)	5.6270(5)	9.4919(5)		90.87(1)		242
$K_2CsSc(PO_4)_2$	$P\bar{3}$	5.4836(6)		7.9157(9)				243
$Na_{4.50}Yb_{1.50}(PO_4)_3$	$R\bar{3}c$	9.12(1)		21.81(6)				248
$Na_{2.28}Sc_2(PO_4)_3$	$C2/c$	15.641	8.913	9.016		124.80		250
$Na_3Sc_2(PO_4)_3$	$B11b$	16.10(1)	9.109(4)	8.928(4)			127.15(4)	251
$Na_3Sc_2(PO_4)_3$	$R\bar{3}c$	8.927(3)		22.34(4)				252
$Li_3Sc_2(PO_4)_3$	$Pcan$	8.828(1)	12.399(2)	8.823(1)				253
$Li_3Sc_2(PO_4)_3$	$P112_1/n$	8.853(2)	12.273(2)	8.802(1)			90.01(2)	253
$Na_{2.63}Sc_2(PO_4)_3$	$C2/c$	15.709(7)	8.936(1)	9.024(1)		126.01(5)		254
$Na_4Sc_2(PO_4)_3$	$C2/c$	15.464(7)	8.936(1)	9.024(1)		124.74(5)		254
$Na_{1.2}Sc_2(PO_4)_3$	$R\bar{3}c$	8.930(2)		22.245(4)				254
$K_2(YZr)(PO_4)_3$	$P2_13$	10.3346(1)						266
$Li_3Sc_2(PO_4)_3$	$Pcan$	8.853	12.273	8.802				255
$Ag_3Sc_2(PO_4)_3$	$R\bar{3}c$	8.986(4)		22.605(7)				56
$Na_3Sc_2P_3O_{12}$	$R\bar{3}c$	8.927		22.367				257
$Na_3Sc_2(PO_4)_3$	$B11b$	15.404(4)	9.103(3)	8.919(2)			123.53(2)	259
$Na_3Sc_2(PO_4)_3$	$R\bar{3}c$	8.950(2)		22.230(4)				259
$Na_3Sc_2(PO_4)_3$	$R\bar{3}c$	8.9273(2)		22.3668(6)				60
$Na_3Sc_2(PO_4)_3$	$R\bar{3}c$	8.9274(1)		22.5493(6)				260
$Na_3Sc_2(PO_4)_3$	$R\bar{3}c$	8.92(1)		22.276(3)				261
$Li_3Sc_2(PO_4)_3$	$P112_1/n$	8.8483(4)	12.2737(5)	8.7959(4)				262
$Li_{3.2}Sc_2(PO_4)_3$	$Pbcn$	12.3998(6)	8.8352(4)	8.8270(4)				262
$Li_3Sc_2(PO_4)_3$	$P2_1/n$	8.847	12.270	8.801		90.02		263
$Li_3Sc_2(PO_4)_3$	$Pcan$	8.829	12.397	8.821				263
$Na_3Sc_2(PO_4)_3$	$R\bar{3}c$	8.931(4)		22.326(7)				264
$Li_{2.96}(Sc_{1.96}Zr_{0.04})(PO_4)_3$	$P112_1/n$	8.8572(3)	12.2998(4)	8.8183(3)				265
$Li_{2.8}(Sc_{1.8}Zr_{0.2})(PO_4)_3$	$Pbcn$	12.3708(4)	8.8086(3)	8.8356(2)				265
$Li_{2.64}(Sc_{0.9}Ti_{0.1})_2(PO_4)_3$	$Pbcn$	12.3332(4)	8.7829(3)	8.8067(3)				262
$Li_{2.96}(Sc_{0.9}Zr_{0.1})_2(PO_4)_3$	$Pbcn$	12.3542(5)	8.7947(4)	8.8202(4)				262
$Sr_3La(PO_4)_3$	$I\bar{4}3d$	10.185(2)						269
$Sr_3La(PO_4)_3$	$I\bar{4}3d$	10.163(1)						269
$Ba_3La(PO_4)_3$	$I\bar{4}3d$	10.5241(5)						270
$Ca_{19}Ce(PO_4)_{14}$	$R3c$	10.4619(1)		37.4713(2)				*b*
$Pr_3(GeO_4)(PO_4)O$	$P2_1/n$	7.021(1)	12.490(2)	9.219(1)		107.58(2)		278
$KEu(PO_4)$	$Pnma$	7.359(3)	9.630(4)	5.569(2)				274
$RbEu(PO_4)$	$Pnma$	7.462(3)	9.797(3)	5.649(2)				274
$Nd_3(PO_4)O_3$	Cm	12.966(3)	13.233(5)	12.266(3)		108.66(2)		275
$Na_2Y(MoO_4)(PO_4)$	$Ibca$	18.02(1)	12.11(1)	6.847(6)				279
$Na_2Y(MoO_4)(PO_4)$	$C2/c$	13.93(1)	18.02(1)	6.847(6)		119.62(6)		279
$Ce_3Cl_5(PO_4)$	$P6_3/m$	12.4636(9)		4.0693(4)				280

[a] Sholin, Y. I.; Shepelev, Y. F.; Domanskii, A. I. *Kristallografiya* **1982**, *27*, 239. [b] Lazoryak, B. I.; Kotov, R. N.; Khasanov, S. S. *Zh. Neorg. Khim.* **1996**, *41*, 1281.

Ternary *ortho*-phosphates with alkaline-earth metal ions are known as $Sr_3La(PO_4)_3$ and $Ba_3La(PO_4)_3$ and crystallize with the *Eulytite* type of structure.[269,270] This highly symmetric structure contains disordered PO_4^{3-} ions, and attempts have been undertaken recently to study the disorder by neutron diffraction.[269] From powder diffraction it is known that the respective europium phosphate $Eu_3La(PO_4)_3$ adopts the same structure.[271] There were a few other Eu(II) phosphates, namely, $Eu_3(PO_4)_2$,[272] $Eu_5(PO_4)_3OH$,[273] and $AEu(PO_4)$ (A = K, Rb),[274] but they have all been investigated only by powder diffraction. Indexing is usually easy because the compounds are isotypic with the respective alkaline-earth phosphates.

A few mixed anionic rare-earth phosphates entered the literature, among them the only structurally characterized oxide *ortho*-phosphate $Nd_3(PO_4)O_3$.[275] The crystal structure consists of oxygen-centered $[OM_4]$ tetrahedra which are linked via four edges to form infinite layers according to ${}^2_\infty[OM_{4/4}]^+$ which are stacked in the [010] direction alternating with layers of PO_4^{3-} ions (Figure 25). The nine crystallographically different Nd^{3+} ions have coordination numbers ranging from 7 to 9. It is surprising that besides $Nd_3(PO_4)O_3$, no crystal structures of further oxide phosphates are known, although the compositions $M_7P_3O_{18} = M_7O_6(PO_4)_3$, $M_8P_2O_{17} = M_8O_9(PO_4)_2$, and $M_{12}P_2O_{23} = M_{12}O_{15}(PO_4)_2$ were additionally found.[276,277] With $Pr_3(GeO_4)(PO_4)O$, another oxide phosphate has been described additionally containing GeO_4^{4-} ions.[278] Again, the oxide ion centers a $[OPr_4]$ tetrahedron. The tetrahedra are linked via a common edge to dimers $[OPr(1)_{2/2}Pr(2)_{2/1}]_2^{14+}$, which are surrounded in the structure by the anionic tetrahedra (Figure 26). The Pr^{3+} ions are in 7- and 9-fold oxygen coordination, respectively. Another compound with mixed tetrahedral anions is known in the form of $Na_2Y(MoO_4)(PO_4)$. Two modifications were investigated, both of which can be grasped as built up from alternating layers of the composition ${}^2_\infty[Y(PO_4)]$ and ${}^2_\infty[Na_2(MoO_4)]$.[279] The dimorphism arises from slightly different orientations of the tetrahedra. In both structures the Y^{3+} ions are 8-fold coordinated.

The chloride phosphate $Ce_3Cl_6(PO_4)$, which has been obtained by reacting $CeCl_3$, Ce, CeO_2, and P_2O_5 in silica tubes, is isotypic with the respective vanadates and shows the Ce^{3+} ions in coordination of

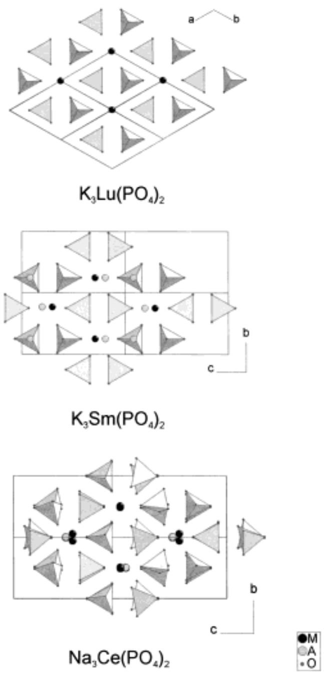

Figure 23. Comparison of $A_3M(PO_4)_3$-type compounds. The structural differences are small and can be attributed to reorientations of the phosphate groups according to the coordination requirements of the A^+ ions.

seven Cl^- ions and three oxygen ligands.[280] The structure can be seen as built up from $[Ce_3Cl_6]$ units in the form of three vertex-connected $[CeCl_3]$ triangles. These units are arranged in a way that pseudo-hexagonal channels occur along [001] which incorporate the PO_4^{3-} ions.

2. Polyphosphates

The diphosphates as the simplest polyphosphates are known in the form of the alkali-metal-containing species $AY(P_2O_7)$ (A = Na−Cs) and $CsYb(P_2O_7)$.[281−285] They all contain the $P_2O_7^{4-}$ ion in a staggered conformation with typical angles within the P−O−P bridge around 125°. The different crystal structures (Table 4) arise from the different coordination requirements of the A^+ ions. While Na^+ has a coordination number of "6+2", the larger ions have 9 (K^+, Rb^+) and 10 (Cs^+) oxygen ligands. The M^{3+} ions are surrounded by six oxygen atoms in all of the diphosphates. The oxygen atoms belong to five $P_2O_7^{4-}$ ions, i.e., one of the latter acts as a chelating ligand. A unique diphosphate is the sodium compound $Na_7Y_2(P_2O_7)_2(P_3O_{10})$[286] because it contains additionally the *catena*-triphosphate anion $P_3O_{10}^{5-}$. In the crystal structure the Y^{3+} ions are connected by the diphosphate ions which act as chelating ligands to layers in the [001] direction. These are connected further by the triphosphate groups to double layers according to ${}^2_\infty[Y_2(P_2O_7)_2(P_3O_{10})]^{-7}$ (Figure 27). Charge compensation is achieved by the Na^+ ions which are located within and between the layers. To date no other *catena*-triphosphate has been characterized for a rare-earth element, but the analogous *cyclo*-triphosphate anion, $P_3O_9^{3-}$, is found in the crystal structure of $Ce(P_3O_9)\cdot 3H_2O$.[287] It has D_{3h} symmetry, and the angle P−O−P is 131°. Six monodentate $P_3O_9^{3-}$ ions are attached to the Ce^{3+} ions leading to a trigonal prismatic coordination polyhedron with each of its three rectangular faces capped by a water molecule. There are a number of compounds with the composition $M(P_3O_9)$, suggesting them also to be *cyclo*-triphosphates. In fact, two completely different structures are known for that composition, but none of them is a *cyclo*-triphosphate. Most of the compounds are *catena*-polyphosphates (see below) with infinite chains of vertex sharing tetrahedra which should be formulated as $M(PO_3)_3$, and the other are *cyclo*-tetraphosphates according to $M_4(P_4O_{12})_3$. They contain the $P_4O_{12}^{4-}$ anion, which has been confirmed for the scandium compound by single-crystal investigations.[288,289] Additionally this anion occurs in several ternary compounds of the composition $AM(P_4O_{12})$. Again, this notation should be preferred over $AM(PO_3)_4$, which is the formula for the also known ternary *catena*-polyphosphates. Single-crystal investigations were performed for the neodymium compounds $RbNd(P_4O_{12})$ and $CsNd(P_4O_{12})$,[290−297] but

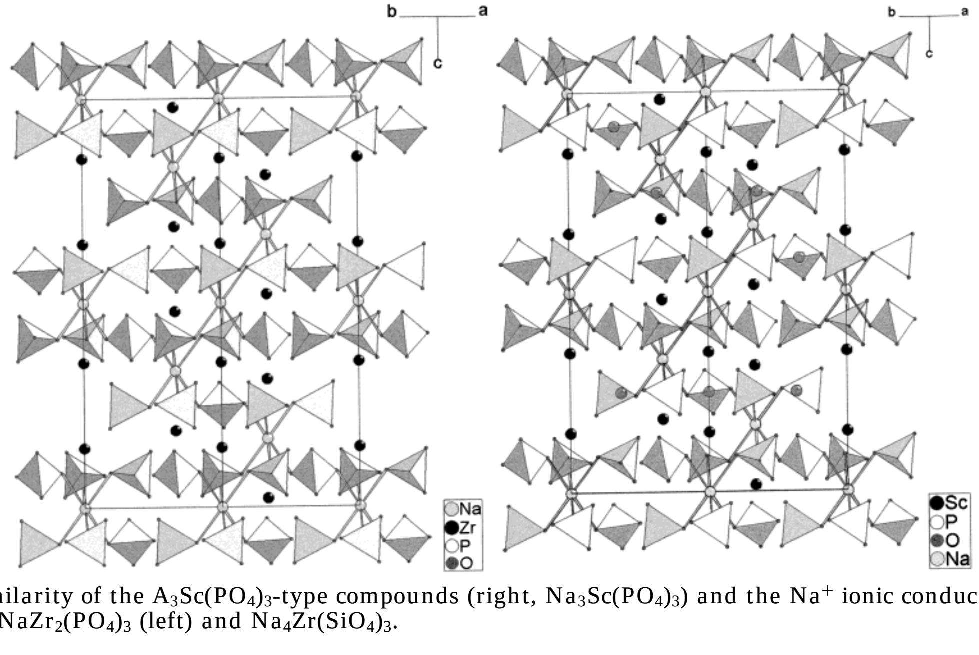

Figure 24. Similarity of the $A_3Sc(PO_4)_3$-type compounds (right, $Na_3Sc(PO_4)_3$) and the Na^+ ionic conductor NASICON, a mixed phase of $NaZr_2(PO_4)_3$ (left) and $Na_4Zr(SiO_4)_3$.

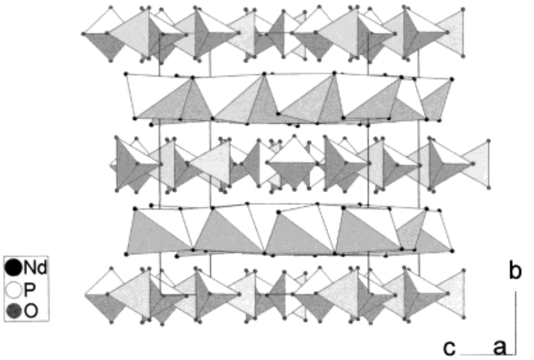

Figure 25. Alternating stacked $^{2}_{\infty}[OM_{4/4}]^{+}$ sheets of edge-connected tetrahedra and PO_4^{3-} ions in the crystal structure of $Nd_3(PO_4)O_3$.

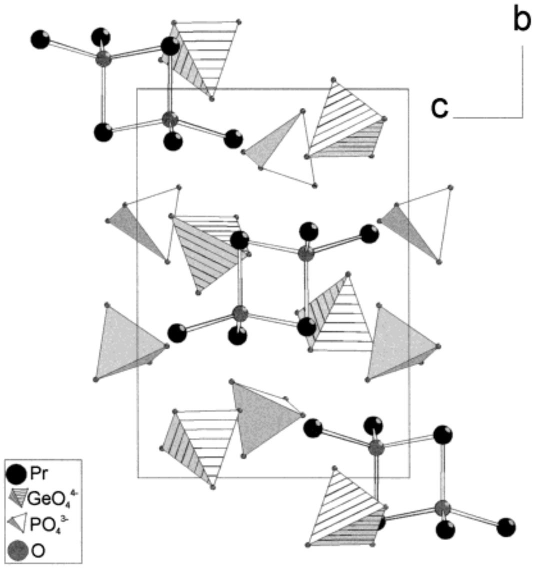

Figure 26. Dimers of edge-connected $[OPr_4]$ tetrahedra according to $[OPr(1)_{2/2}Pr(2)_{2/1}]_2$ in the crystal structure of $Pr_3(GeO_4)(PO_4)O$.

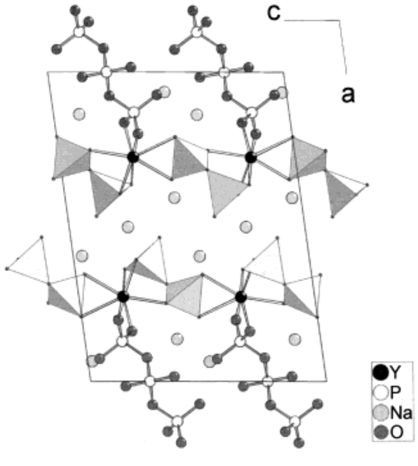

Figure 27. Crystal structure of $Na_7Y_2(P_2O_7)_2(P_3O_{10})$ with $P_2O_7^{4-}$ (shown as polyhedra) and $P_3O_{10}^{5-}$ anions.

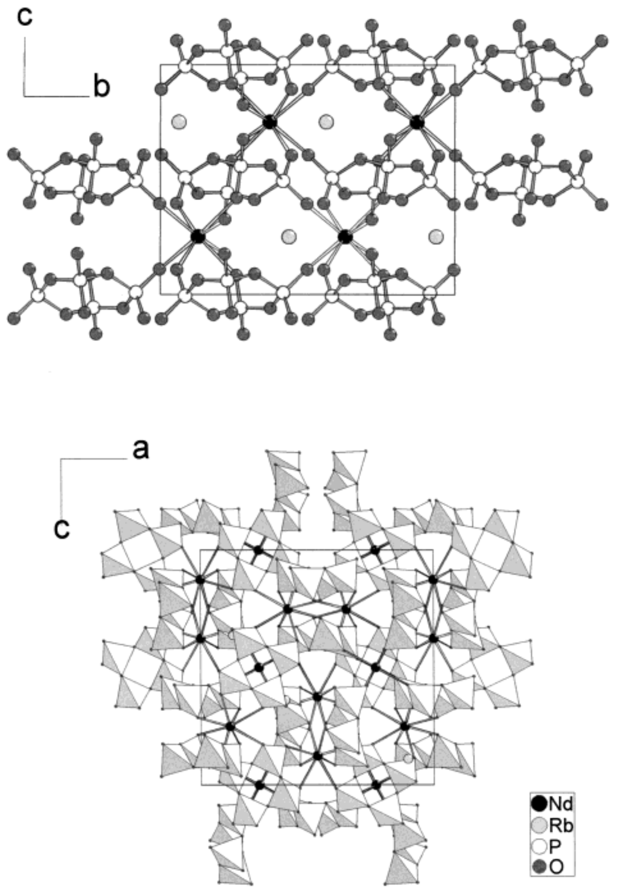

Figure 28. Two modifications of the *cyclo*-tetraphosphate $RbNd(P_4O_{12})$. In the monoclinic form (on top) the anions are arranged to layers; in the cubic form they are in a three-dimensional way.

powder diffraction results proved the structures also to be adopted with other lighter lanthanides.[298−301] The rubidium compound is dimorphic. The monoclinic modification consists of alternating layers of $[NdO_8]$ dodecahedra and $P_4O_{12}^{4-}$ anions, whereas the packing in the cubic modification which is isotypic to the cesium compound occurs in a three-dimensional way (Figure 28). More recent studies showed that even *cyclo*-hexaphosphates can be prepared. They have the compositions $M_2(P_6O_{18})\cdot xH_2O$, and the content of crystal water x may be 6, 10, 12, or 16 (cf. Table 5).[302−306] The $P_6O_{18}^{6-}$ anion can be either "boat"-shaped like in $Nd_2(P_6O_{18})\cdot 6H_2O$[303] or "chair"-shaped as in $Nd_2(P_6O_{18})\cdot 12H_2O$,[304] but it has never been found to exhibit the high symmetries known for the respective *cyclo*-hexasilicates (cf. section II).

By far the largest number of rare-earth phosphates with the compositions $M(PO_3)_3$[307−311] and $AM(PO_3)_4$[312−334] are *catena*-polyphosphates (Table 5). They contain infinite chains of vertex-sharing $[PO_4]$ tetrahedra according to $^{1}_{\infty}[PO_2O_{2/2}]^{1-}$. The huge variety of crystal structures arises from the flexibility of the chain. According to the coordination spheres required by the surrounding cations, it may be folded in several different ways as illustrated for the examples of $La(PO_3)_3$, $Er(PO_3)_3$, $Yb(PO_3)_3$, and $LiNd(PO_3)_4$ in Figure 29. Thus, four structure types are known for the binary and nine for the ternary phosphates of the 1:1:4 composition. The coordination numbers of the rare-earth ions in these structures are usually 6−8 for the smaller lanthanides and 8−10 for the larger ones. A few examples are known with compositions $A_2M(PO_3)_5$, namely, $(NH_4)_2Ce(PO_3)_5$ and $K_2Nd(PO_3)_5$,[335−338] which have been characterized by X-ray data and the isotypic compounds with Tl^{+} and Rb^{+}.[339,340]

Table 5. Crystallographic Data of Polyphosphates

		lattice parameters						
compound	space group	*a*/Å	*b*/Å	*c*/Å	α/°	*β*/°	*γ*/°	ref
diphosphates								
$CsY(P_2O_7)$	$P2_1/c$	7.898(3)	10.891(1)	8.753(3)		104.24(5)		281
$NaY(P_2O_7)$	$P2_1$	7.004(1)	5.3740(8)	8.691(1)		110.18(1)		282
$RbY(P_2O_7)$	$P2_1/c$	7.706(4)	10.927(1)	8.649(5)		105.31(6)		283
$KY(P_2O_7)$	$Cmcm$	5.716(1)	9.216(1)	12.244(1)				284
$CsYbP_2O_7$	$P2_1/c$	7.853(1)	10.771(2)	8.697(2)		104.35(1)		285
$Na_7Y_2(P_2O_7)_2(P_3O_{10})$	$P2/c$	16.205(4)	5.3746(9)	12.309(4)		97.96(2)		286
cyclo-triphosphates								
$Ce(P_3O_9)(H_2O)_3$	$P\bar{6}$	6.770(3)		6.073(3)				287
cyclo-tetraphosphates								
$Sc_4(P_4O_{12})_3$	$I\bar{4}3d$	14.360(5)						288
$Sc_4(P_4O_{12})_3$	$I\bar{4}3d$	14.390(8)						289
$KNd(P_4O_{12})$	$B112/b$	7.888	10.770	12.447			112.70	293
$KHo(P_4O_{12})$	$B112/b$	7.798(1)	10.511(1)	12.310(1)			112.63(1)	294
$RbSm(P_4O_{12})$	$C2/c$	7.868(2)	12.735(3)	10.589(2)		111.25(2)		295
$KPr(P_4O_{12})$	$C2/c$	7.913(2)	12.489(3)	10.659(3)		110.48(2)		296
$KY(P_4O_{12})$	$C2/c$	7.8067(6)	12.322(1)	10.408(1)		111.17(1)		297
$RbNd(P_4O_{12})$	$C2/c$	7.845(2)	12.691(3)	10.688(3)		112.34(1)		291
$RbNd(P_4O_{12})$	$I\bar{4}3d$	15.241(7)						292
$CsNd(P_4O_{12})$	$I\bar{4}3d$	15.233(9)						290
cyclo-hexaphosphates								
$Er_2(P_6O_{18})(H_2O)_{10}$	$P2_1/a$	18.315(8)	13.343(4)	11.211(4)		94.46(3)		302
$Nd_2(P_6O_{18})(H_2O)_6$	$C2$	24.58(1)	9.20(1)	12.14(1)		93.97(8)		303
$Nd_2P_6O_{18}(H_2O)_{12}$	$P2_1/c$	9.149(2)	11.693(3)	11.959(3)		96.92(1)		304
$Ce_2(P_6O_{18})(H_2O)_{10}$	$P2_12_12_1$	13.522(5)	13.105(9)	6.938(3)				305
$Yb_2(P_6O_{18})(H_2O)_{16}$	$P2_12_12_1$	16.019(8)	19.99(1)	9.699(5)				306
catena-polyphosphates								
$Nd(PO_3)_3$	$C222_1$	11.172(2)	8.533(2)	7.284(2)				307
$Yb(PO_3)_3$	$P2_1/c$	11.219(2)	19.983(3)	9.999(3)		97.30(2)		308
$Er(PO_3)_3$	$P11m$	10.943(3)	6.971(2)	9.670(2)			91.82(2)	309
$Yb(PO_3)_3$	$R\bar{3}$	20.974(4)		12.134(3)				*a*
$La(PO_3)_3$	$C222_1$	11.303(4)	8.648(5)	7.397(3)				310
$Sc(PO_3)_3$	Cc	13.558(4)	19.588(6)	9.690(3)		127.11(5)		311
$ErH(PO_3)_4$	$P2_1/a$	9.574(2)	7.096(1)	13.637(3)		100.95(2)		*b*
$YbH_2P_3O_{10}$	$A2$	5.617(2)	6.666(2)	10.011(3)		97.32(2)		*c*
$LiNd(PO_3)_4$	$I2/c$	9.844(2)	7.008(3)	13.25(2)		90.1(2)		312
$NdLi(PO_3)_4$	$C2/c$	16.408(3)	7.035(4)	9.729(4)		126.38(5)		313
$LiEr(PO_3)_4$	$C2/c$	16.229	7.009	9.524		125.92		314
$CsNd(PO_3)_4$	$P2_1$	7.123(2)	9.152(3)	8.782(2)		99.72(3)		315
$CsPr(PO_3)_4$	$P2_1$	7.159(1)(	9.190(2)	8.8091(8)		99.66(2)		316
$CsTb(PO_3)_4$	$P112_1$	7.032(1)	8.705(1)	9.051(1)			100.00(1)	317
$KNd(PO_3)_4$	$P2_1$	7.266(1)	8.436(1)	8.007(1)		91.97(3)		318
$KEr(PO_3)_4$	$P112_1$	7.285(1)	8.012(2)	8.444(1)			91.96(2)	319
$KTb(PO_3)_4$	$P2_1$	7.239(1)	8.325(2)	7.896(1)		91.82(1)		320
$KLa(PO_3)_4$	$P2_1$	8.106(3)	8.551(2)	7.326(3)		92.18(2)		321
$RbHo(PO_3)_4$	$P2_1/n$	10.266(4)	8.853(3)	10.953(3)		106.28(3)		322
$RbTm(PO_3)_4$	$P2_1/n$	10.217(2)	8.803(2)	10.928(2)		106.28(2)		322
$CsEr(PO_3)_4$	$P2_1/n$	10.215(2)	8.833(2)	11.136(2)		106.32(2)		322
$TlNd(PO_3)_4$	$P2_1/n$	10.440(3)	8.050(2)	11.007(2)		105.86(2)		323
$RbNd(PO_3)_4$	$P2_1/n$	10.461(3)	9.041(2)	10.983(4)		106.16(2)		324
$CsNd(PO_3)_4$	$P2_1/n$	10.448(3)	9.039(3)	11.233(2)		106.43(2)		325
$KEr(PO_3)_4$	$P2_1/c$	10.80(1)	8.959(7)	12.70(1)		128.89(6)		326
$KEr(PO_3)_4$	$C222_1$	11.75(1)	10.325(2)	17.31(1)				327
$(NH_4)Y(PO_3)_4$	$C222_1$	11.955(9)	10.374(8)	17.36(1)				328
$NaEr(PO_3)_4$	$P2_1/n$	7.16(2)	12.987(7)	9.66(3)		89.32(2)		329
$KCe(PO_3)_4$	$P2_1/n$	7.236(1)	13.168(4)	9.999(3)		90.46(2)		330
$NaNd(PO_3)_4$	$P2_1/n$	9.907(4)	13.10(1)	7.201(3)		90.51(3)		331
$AgNd(PO_3)_4$	$P2_1/n$	9.947	13.170	7.291		90.48		332
$KYb(PO_3)_4$	$P2_1/n$	7.766(1)	8.853(1)	14.831(2)		96.36(1)		333
$NH_4Yb(PO_3)_4$	$I\bar{4}3d$	15.233						334
$(NH_4)_2Nd(PO_3)_5$	Cc	8.598	11.733	13.375		90.50		335
$K_2Nd(PO_3)_5$	Cc	8.430(1)	11.752(2)	13.272(2)		90.68(1)		338
$(NH_4)_2Nd(PO_3)_5$	$P1$	7.241	13.314	7.241	90.30	107.50	90.30	336
ultra-phosphates								
ErP_5O_{14}	$C2/c$	12.837(8)	12.723(7)	12.381(7)		91.25(5)		341
TmP_5O_{14}	$C2/c$	12.822(2)	12.709(5)	12.358(2)		91.25(1)		342
YbP_5O_{14}	$C2/c$	12.830(3)	12.676(3)	12.337(3)		91.25(2)		343
HoP_5O_{14}	$C2/c$	12.881(5)	12.771(5)	12.424(5)		91.34(5)		344
PrP_5O_{14}	$P2_1/c$	8.777(1)	9.029(2)	13.068(2)		90.35(2)		345
GdP_5O_{14}	$P2_1/a$	12.910(9)	8.890(1)	8.721(6)		90.53(2)		346

Table 5. (Continued)

		lattice parameters						
compound	space group	a/Å	b/Å	c/Å	α/°	β/°	γ/°	ref
TbP_5O_{14}	$P2_1/c$	8.721(3)	8.877(2)	12.91(1)		90.52(2)		347
NdP_5O_{14}	$P2_1/c$	8.7672(2)	8.9948(3)	13.0326(3)		90.48(1)		348
NdP_5O_{14}	$P2_1/c$	8.771(3)	9.012(2)	13.057(3)		89.58(2)		349
SmP_5O_{14}	$P112_1/b$	8.750(4)	12.990(6)	8.944(4)			90.45(1)	350
ErP_5O_{14}	$Pnma$	8.638(2)	12.674(1)	8.8946(8)				351
NdP_5O_{14}	$Pncm$	8.794(2)	9.025(2)	13.066(3)				352
HoP_5O_{14}	$Pnma$	8.726(4)	12.710(6)	8.926(4)				353
HoP_5O_{14}	$Pnma$	8.720	12.710	8.926				354
ErP_5O_{14}	$C2/c$	12.835	12.705	12.363		88.40		355
CeP_5O_{14}	$P1$	9.227(5)	8.890(5)	7.219(4)	110.12(5)	102.68(5)	82.13(5)	356
$CaYP_7O_{20}$	$C2/c$	24.66(1)	6.850(3)	10.698(6)		107.40(4)		357

[a] Anisimova, N. Yu.; Trunov, V. K.; Karmanovskaya, N. B.; Chudinova, N. N. *Izv. Akad. Nauk SSSR* **1992**, *28*, 441. [b] Palkina, K. K.; Chudinova, N. N.; Balagina, G. M.; Maksimova, S. I.; Chibiskova, N. T. *Izv. Akad. Nauk SSSR* **1982**, *18*, 156. [c] Palkina, K. K.; Maksimova, S. I.; Kuznetsov, V. G. *Izv. Akad. Nauk SSSR* **1979**, *15*, 2168.

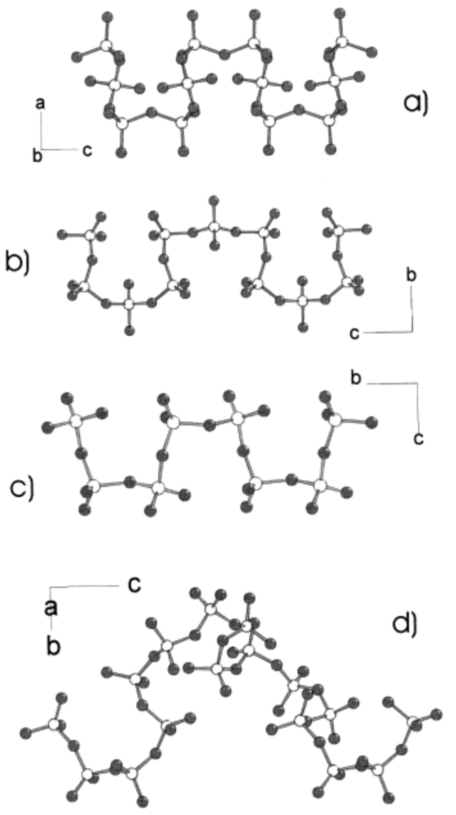

Figure 29. Different foldings of the polyphosphate chain in the *catena*-polyphosphates $La(PO_3)_3$ (a), $Er(PO_3)_3$ (b), $Yb(PO_3)_3$ (c), and $LiNd(PO_3)_4$ (d).

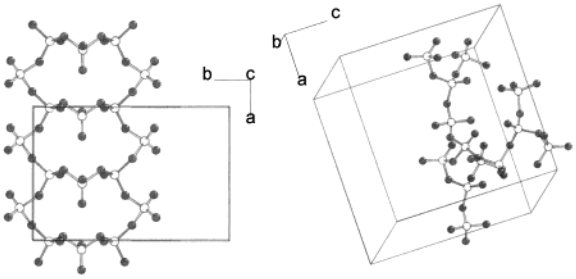

Figure 30. Examples for the branching modes within the anionic $[P_5O_{14}]^{3-}$ network in rare-earth ultra-phosphates $M_3(P_5O_{14})$.

The highest condensation of phosphate groups is found in the so-called ultra-phosphates. They can be prepared from the lanthanide oxides either with phosphoric acid or with $(NH_4)_2HPO_4$ at 600 °C if a great excess of the phosphorus component is used. As in the *catena*-phosphates, part of the $[PO_4]$ tetrahedra share two common vertexes according to $[PO_2O_{2/2}]$ but there are also tetrahedra linked via three corners as expressed by $[PO_1O_{3/2}]$. These building units are composed in a ratio of 3:2, yielding an anionic network $[P_5O_{14}]^{3-}$ as found in the compounds MP_5O_{14} (Table 5). Depending on the linkage one finds cross-linked double chains or a strongly branched network (Figure 30). To date four different structure types are known, as can be seen from Table 5.[341−356] There is one unique example for an ultra-phosphate with another composition. In $CaYP_7O_{20}$, the double-connected and the triple-linked $[PO_4]$ tetrahedra are found in a ratio of 5:2, leading to the anionic network $P_7O_{20}{}^{5-}$.[357] The ultra-phosphates were of certain interest for a period of time because they were thought to be promising laser materials. Unfortunately, large single crystals are hard to grow due to the decomposition of the compounds at higher temperatures.

3. Phosphonates and Phosphinates

Phosphonates (formerly called phosphites) and phosphinates (formerly hypophosphites) are salts of the acids H_3PO_3 and H_3PO_2, respectively. Because part of the hydrogen atoms are attached to the phosphorus atom according to the formulation $HPO(OH)_2$ and $H_2PO(OH)$ the anions have a tetrahedral geometry. However, they are special in the sense that coordination to a metal ion does not occur via one of the hydrogen atoms but only via the oxygen atoms. Thus, they behave more like pyramidal and bent anions, respectively. The only structurally characterized anhydrous phosphonate is $Eu_2(HPO_3)_3$[358] (Table 6). It contains the Eu^{3+} ions in 7-fold coordination of oxygen atoms which belong to six $HPO_3{}^{2-}$ ions. Each of the latter is attached to four Eu^{3+} ions, leading to a three-dimensional structure as may be expressed by ${}^{3}_{\infty}[Eu(HPO_3)_{6/4}]^{3-}$ (Figure 31). The same 3D connectivity of polyhedra is found in the structures of the isotypic monohydrates $M_2(HPO_3)_3{\cdot}H_2O$ (M = Pr, Nd),[359] but additionally one H_2O molecule is coordinated to the M^{3+} ions so that the coordination number increases to eight. An even higher hydrate has been investigated with $Eu_2(HPO_3)_3{\cdot}2.5H_2O$.[360]

Table 6. Crystallographic Data of Phosphonates and Phosphinates

compound	space group	lattice parameters a/Å	b/Å	c/Å	α/°	β/°	γ/°	ref
				phosphonates				
$Eu_2(HPO_3)_3$	$C2/m$	14.822(3)	7.055(1)	10.205(2)		123.79(1)		358
$Pr_2(HPO_3)_3 \cdot H_2O$	$P2_1/n$	9.620(2)	8.005(1)	13.119(2)		108.98(1)		359
$Nd_2(HPO_3)_3 \cdot H_2O$	$P2_1/n$	9.581(2)	7.980(2)	13.056(3)		108.95(1)		359
$La(HPO_3H)_2 \cdot 3H_2O$	$P2_1/c$	9.687(3)	7.138(2)	13.518(5)		104.48(3)		362
$La(HPO_3H)_2 \cdot 3H_2O$	$P2_1/c$	9.687(3)	7.138(2)	13.518(5)		104.48(3)		363
$Eu_2(HPO_3)_3 \cdot 2.5H_2O$	$P\bar{1}$	6.608(1)	6.899(1)	12.977(2)	82.66(1)	80.64(1)	73.97(1)	360
$Nd(H_2PO_3)(HPO_3) \cdot 2H_2O$	$P2_12_12_1$	6.6840(9)	16.503(4)	7.053(3)				365
$Ce(H_2PO_3)(HPO_3) \cdot 2H_2O$	$P2_12_12_1$	7.126(4)	16.539(4)	6.762(1)				364
$La(H_2PO_3)(HPO_3) \cdot 3H_2O$	$P2_1/c$	9.680(2)	7.135(1)	13.479(2)		104.54(2)		364
$La(HPO_3H)_3 \cdot H_2O$	$P\bar{1}$	8.054(2)	9.672(3)	7.225(2)	111.35(2)	75.77(2)	118.66(2)	361
				phosphinates				
$Eu(H_2PO_2)_3 \cdot H_2O$	$P\bar{1}$	9.07(3)	8.30(3)	7.34(3)	115.50(3)	94.20(3)	111.80(3)	369
$La(H_2PO_2)_3$	$P\bar{1}$	6.7912(6)	7.0801(8)	8.863(1)	82.64(1)	74.43(1)	71.91(1)	366
$La(H_2PO_2)_3 \cdot H_2O$	$P\bar{1}$	7.2291(4)	7.983(1)	8.934(1)	110.57(1)	98.26(1)	104.35(1)	366
$La(H_2PO_2)_3 \cdot H_2O$	$P\bar{1}$	8.980	8.080	7.290	104.80	99.00	109.70	367
$Ce(H_2PO_2)_3 \cdot H_2O$	$P\bar{1}$	7.173(1)	7.9827(9)	8.8710(6)	110.64(1)	98.10(1)	104.97(1)	368
$Dy(H_2PO_2)_3$	$C2/m$	14.368(3)	5.734(1)	12.123(1)		122.33(2)		368
$Ho(H_2PO_2)_3$	$C2/m$	14.354(2)	5.7161(9)	12.104(1)		122.4(5)		370
$Er(H_2PO_2)_3$	$B112/m$	14.40(4)	12.14(4)	5.64(2)			111.3(4)	*a*
$Pr(H_2PO_2)(HPO_3) \cdot 2H_2O$	$P2_12_12_1$	6.6558(5)	7.1539(5)	16.551(2)				368
				hypodiphosphonates				
$Er(HP_2O_6) \cdot 4H_2O$	$Pbnn$	7.187(1)	9.816(3)	11.517(3)				371
$Yb(HP_2O_6) \cdot 3H_2O$	$P2nn$	7.325(3)	9.360(5)	11.575(6)				371
$Gd(HP_2O_6) \cdot 4H_2O$	$Pbnn$	7.220(1)	9.927(2)	11.588(9)				373
$Dy(HP_2O_6) \cdot 4H_2O$	$Pbnn$	7.202(2)	9.859(4)	11.530(9)				373
$HoH(P_2O_6) \cdot 4H_2O$	$Pbnn$	7.187(2)	9.840(2)	11.514(3)				373
$Eu(HP_2O_6) \cdot 4H_2O$	$Pbnn$	7.231(2)	9.948(3)	11.604(4)				374
$Nd(HP_2O_6) \cdot 4H_2O$	$Pbnn$	7.281(2)	10.946(2)	11.698(2)				375

[a] Aslanov, L. A.; Ionov, V. M.; Porai-Koshits, M. A.; Lebedev, V. G.; Kulikovskii, B. N.; Novoderedzhkina, T. L. *Izv. Akad. Nauk SSSR* **1975**, *11*, 117. (This structure determination seems to contain an error, cf. ref 370).

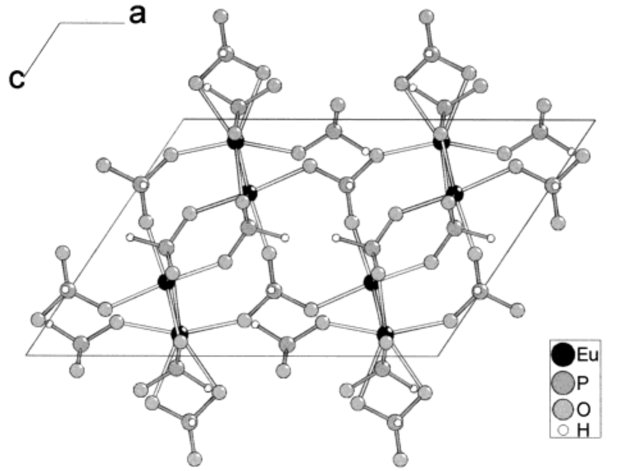

Figure 31. Projection of the crystal structure of $Eu_2(HPO_3)_3$ on (010).

The triclinic structure contains two crystallographically different Eu^{3+} ions. $Eu(1)^{3+}$ is surrounded by six phosphonate groups and one H_2O molecule, while $Eu(2)^{3+}$ has five HPO_3^{2-} ions and two H_2O ligands as neighbors. The anions are attached to four or three Eu^{3+} ions, respectively. An acidic phosphonate is known for the example of $La(H_2PO_3)_3 \cdot H_2O$.[361] Seven monodentate anions and one H_2O molecule coordinate the La^{3+} ions in the form of a distorted square antiprism. Three of the anions are bonded to three La^{3+} ions and the remaining four to two La^{3+} ions to give the three-dimensional structure according to ${}^{3}_{\infty}[La(H_2O)(H_2PO_3)_{3/3}(H_2PO_3)_{4/2}]$ (Figure 32).

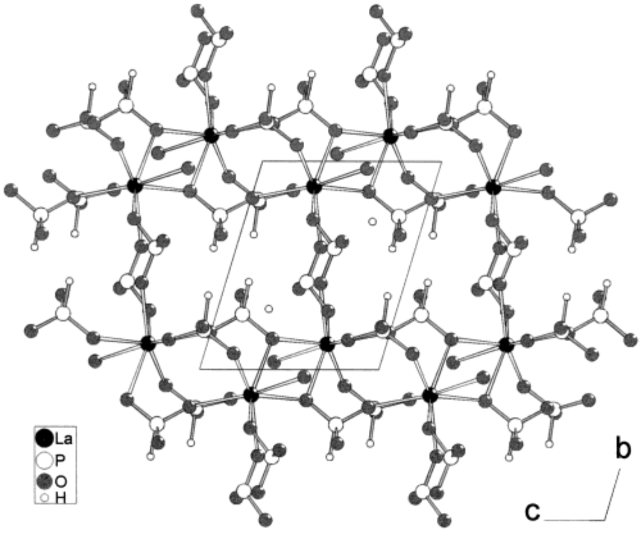

Figure 32. Crystal structure of the acidic phosphonate $La(H_2PO_3)_3 \cdot H_2O$.

For M = La, Ce, and Nd, compounds have been found containing both $H_2PO_3^-$ and HPO_3^{2-} ions. The lanthanum phosphonate is a trihydrate, $La(H_2PO_3)(HPO_3) \cdot 3H_2O$, and has a layer structure.[362−364] The layers are built by the linkage of the HPO_3^{2-} ions, while the $H_2PO_3^-$ groups take care of the connection of the layers by hydrogen bonds (Figure 33). In the latter, also two of the three H_2O molecules are involved whereas the third is coordinated to La^{3+}. The neodymium and cerium compounds are isotypic with each other and crystallize as dihydrates.[364,365]

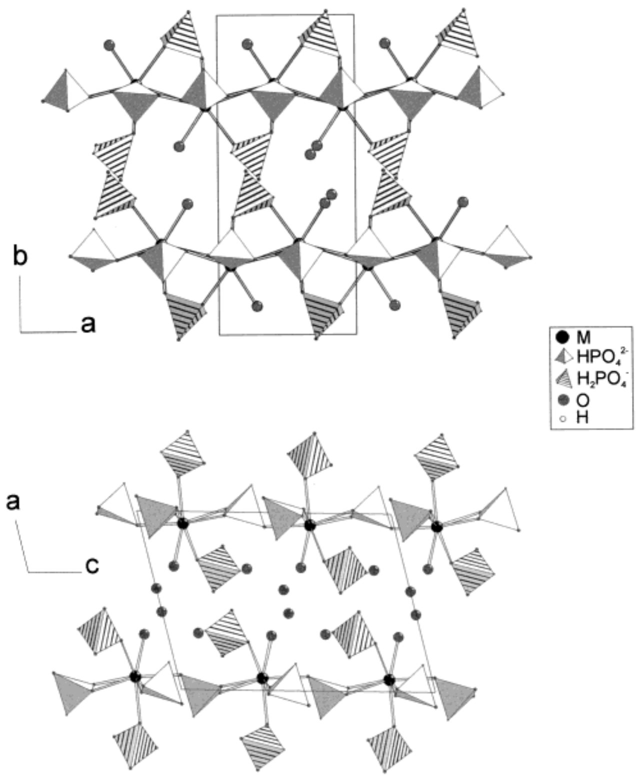

Figure 33. Comparison of the crystal structures of La(H_2PO_3)(HPO_3)·3H_2O and Nd(H_2PO_3)(HPO_3)·2H_2O.

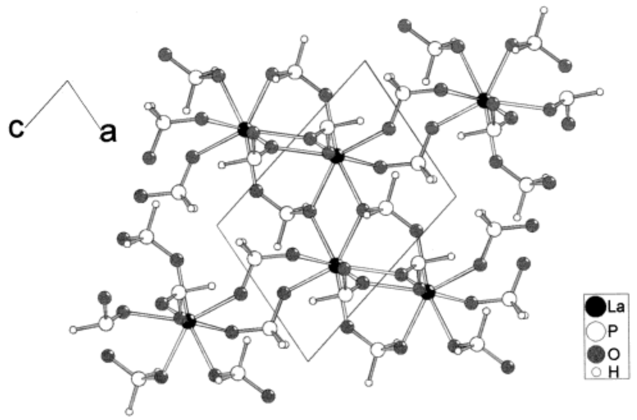

Figure 34. Crystal structure of La(H_2PO_2)$_3$ projected on (010).

The structure is essentially the same as that described for La(H_2PO_3)(HPO_3)·3H_2O, but there is only one water molecule between the layers, which are shifted slightly against each other (Figure 33). For the phosphinates the monohydrates M(H_2PO_2)$_3$·H_2O with M = La, Ce, Eu[366−369] and the anhydrous species with M = La, Dy, Ho, Er[366,368,370] are structurally characterized. The monohydrates are isotypic and contain 8-fold oxygen-coordinated M^{3+} ions. Besides the H_2O molecule, the oxygen atoms belong to seven monodentate $H_2PO_2^-$ ions. These are bonded to three and two M^{3+} ions, leading to layers ${}^{2}_{\infty}[M(H_2O)(H_2PO_2)_{3/3}(H_2PO_2)_{4/2}]$ which are connected by hydrogen bonds. Eight monodentate $H_2PO_2^-$ ions are bonded to La^{3+} in the anhydrous lanthanum phosphinate. Two of them are surrounded by two La^{3+} ions, while six of them have three La^{3+} neighbors leading to the three-dimensional structure ${}^{3}_{\infty}[La(H_2PO_2)_{6/3}(H_2PO_2)_{2/2}]$ shown in Figure 34. With the smaller ions Dy^{3+} and Er^{3+} a layered structure is formed according to ${}^{2}_{\infty}[M(H_2PO_2)_{6/2}]$ with octahedral coordination of the cations. The only structurally investigated compound with $H_2PO_2^-$ and HPO_3^{2-} ions is Pr(H_2PO_2)(HPO_3)·2H_2O.[368] In principle, the same structure as for La(HPO_3)(H_2PO_3)·2H_2O described is found and even the space group is the same. Compared to the lanthanum compound the tetrahedron linking the layers via hydrogen bonds, $H_2PO_3^-$, has been exchanged for $H_2PO_2^-$.

Finally, it should be mentioned that there exist also a series of monohydrogenhypodiphosphonates containing the dianion $HP_2O_6^{3-}$ (cf. Table 6). These compounds are known as tetrahydrates M(HP_2O_6)·4H_2O with M = Nd, Gd, Eu, Dy, Er, Yb.[371−375] The ytterbium compound is originally described as a trihydrate, but with respect to the nearly identical lattice constants compared to the other known compounds, it can be assumed that there is a mistake in the structure analysis, probably due to the poor X-ray data. In the crystal structure of the isotypic compounds, each M^{3+} ion is coordinated by four H_2O ligands and four $HP_2O_6^{3-}$ ions. The latter are themselves attached to four M^{3+} ions. Thus, two of the oxygen atoms remain uncoordinated and the proton needed for charge compensation is obviously distributed over these two oxygen atoms.

C. Sulfates

Due to their former use in the separation of rare-earth elements, the lanthanide sulfates have been intensively studied. Thus, a great number of complexes and salts have been described in the literature, as might be seen from the overviews of several authors.[376,377] Nevertheless, with respect to the plethora of sulfates, structural information is still limited. This is especially true for the anhydrous sulfates, and it was only recently when the first structure determinations were performed. The lacking information for the anhydrous species is due to the difficulties in growing single crystals for the structure determination. Compared to silicates and phosphates, which can be prepared even by high-temperature methods, the sulfates decompose at elevated temperatures so that they cannot be obtained from their melt. On the other hand, the use of a solvent, usually water, does not lead to solvent-free compounds, and also flux grow methods often fail because the flux takes part in the reaction. Thus, most of the known structures are still those of hydrates and ternary sulfates.

Another group of sulfates which should be included in this section are derivatives formally obtained by the substitution of one oxygen atom of the [SO_4] tetrahedron for NH_2 or CH_3 (Figure 35). In the former case, amidosulfates (sulfamates) are obtained; in the latter case, methanesulfonates are obtained. Both of these anions show a certain similarity to the hydrogensulfate ion, HSO_4^-, which might be also seen as a derivative of SO_4^{2-}.

1. Sulfate Hydrates

Investigations of the sulfate hydrates of rare-earth elements are quite numerous although in most cases

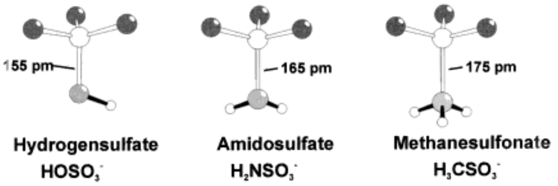

Figure 35. Derivatization of the sulfate group: The substitution of one oxygen atom of the [SO_4] tetrahedron for OH, NH_2, or CH_3 leads to a hydrogensulfate, amidosulfate, or methanesulfonate anion.

not very systematic. The most common hydrated species are the octahydrates $M_2(SO_4)_3\cdot 8H_2O$, which have been characterized by means of single-crystal determinations throughout the whole lanthanide series including yttrium (Table 7).[378−386] It turned out that the compounds are isotypic with each other and contain the M^{3+} in 8-fold coordination of oxygen atoms. The linkage of sulfate groups and M^{3+} ions can be formulated according to $[M(H_2O)_{4/1}(SO_4(1))_{3/3}(SO_4(2))_{1/2}]_2$, indicating that two crystallographically different SO_4^{2-} ions with different functionalities are present in the structure. The water molecules are all coordinated to M^{3+} ions and act as donors in hydrogen bonds with the noncoordinating oxygen atoms of the sulfate groups as acceptors. Very accurate hydrogen positions have been extracted from neutron diffraction measurements on a single crystal of $Nd_2(SO_4)_3\cdot 8H_2O$.[384]

Sulfates with other water contents have been mainly found for the larger M^{3+} ions La−Nd. Enneahydrates, $M_2(SO_4)_3\cdot 9H_2O$, are known for M = La, Ce and contain the M^{3+} ions in 12-fold and 9-fold coordination of oxygen atoms.[383,385,387,388] The high coordination number of 12 arises from six chelating SO_4^{2-} ions (Figure 36), while the second M^{3+} ion is surrounded by three SO_4^{2-} and six H_2O ligands. Three further water molecules are bound via hydrogen bridges in the structure.

The crystal structure of lower hydrates was determined for $M_2(SO_4)_3\cdot 5H_2O$ (M = Ce, Nd)[385,389] and M₂-

Table 7. Crystallographic Data of Sulfate-Hydrates and Anhydrous Sulfates

compound	space group	lattice parameters						ref
		a/Å	*b*/Å	*c*/Å	α/°	*β*/°	*γ*/°	
			sulfate−hydrates					
$Ce_2(SO_4)_3\cdot 8H_2O$	*C*2/*c*	13.743(4)	6.891(4)	18.468(4)		103.13(2)		385
$Pr_2(SO_4)_3\cdot 8H_2O$	*C*2/*c*	13.742(2)	6.883(1)	18.529(2)		102.85(1)		386
$Pr_2(SO_4)_3\cdot 8H_2O$	*C*2/*c*	13.694(8)	6.803(3)	18.061(9)		102.0(1)		380
$Pr_2(SO_4)_3\cdot 8H_2O$	*C*2/*c*	13.675(3)	6.832(3)	18.426(3)		102.8(3)		383
$Nd_2(SO_4)_3\cdot 8H_2O$	*C*2/*c*	13.640(5)	6.825(2)	18.388(9)		102.70(5)		384
$Nd_2(SO_4)_3\cdot 8H_2O$	*C*2/*c*	13.680(2)	6.8405(9)	18.458(3)		102.61(2)		386
$Sm_2(SO_4)_3\cdot 8H_2O$	*C*2/*c*	13.651(2)	6.812(1)	18.402(2)		102.38(1)		386
$Sm_2(SO_4)_3\cdot 8H_2O$	*C*2/*c*	13.43(3)	6.72(2)	18.13(5)		102.8(5)		378
$Eu_2(SO_4)_3\cdot 8H_2O$	*C*2/*c*	13.636(2)	6.7828(7)	18.394(3)		102.34(2)		386
$Gd_2(SO_4)_3\cdot 8H_2O$	*C*2/*c*	13.531(7)	6.739(2)	18.294(7)		102.20(8)		381
$Gd_2(SO_4)_3\cdot 8H_2O$	*C*2/*c*	13.606(2)	6.7677(7)	18.335(3)		102.15(2)		386
$Tb_2(SO_4)_3\cdot 8H_2O$	*C*2/*c*	13.572(2)	6.7465(9)	18.307(3)		102.19(2)		386
$Dy_2(SO_4)_3\cdot 8H_2O$	*C*2/*c*	13.528(2)	6.735(1)	18.320(2)		102.23(1)		386
$Ho_2(SO_4)_3\cdot 8H_2O$	*C*2/*c*	13.524(2)	6.7083(8)	18.268(3)		102.10(2)		386
$Er_2(SO_4)_3\cdot 8H_2O$	*C*2/*c*	13.461(1)	6.6721(9)	18.1621(6)		101.91(1)		382
$Tm_2(SO_4)_3\cdot 8H_2O$	*C*2/*c*	13.490(2)	6.6763(8)	18.193(3)		102.05(2)		386
$Yb_2(SO_4)_3\cdot 8H_2O$	*C*2/*c*	13.417(2)	6.642(1)	18.110(3)		102.0(1)		379
$Yb_2(SO_4)_3\cdot 8H_2O$	*C*2/*c*	13.459(2)	6.6589(8)	18.181(3)		101.98(2)		386
$Lu_2(SO_4)_3\cdot 8H_2O$	*C*2/*c*	13.442(2)	6.6336(6)	18.153(3)		101.89(2)		386
$Lu_2(SO_4)_3\cdot 8H_2O$	*C*2/*c*	13.398(4)	6.621(1)	18.08(1)		101.86(4)		385
$Y_2(SO_4)_3\cdot 8H_2O$	*C*2/*c*	13.475(2)	6.6845(5)	18.219(2)		101.92(1)		386
$La_2(SO_4)_3\cdot 9H_2O$	*P*6₃/*m*	11.015(3)		8.091(5)				385
$La_2(SO_4)_3\cdot 9H_2O$	*P*6₃/*m*	10.980		8.130				388
$La_2(SO_4)_3\cdot 9H_2O$	*P*6₃/*m*	11.01(2)		8.08(2)				383
$Ce_2(SO_4)_3\cdot 9H_2O$	*P*6₃/*m*	10.997(4)		8.018(3)				387
$Nd_2(SO_4)_3\cdot 5H_2O$	*C*2/*c*	15.702(3)	9.586(1)	10.262(2)		120.05(1)		389
$Ce_2(SO_4)_3\cdot 5H_2O$	*C*2/*c*	15.741(3)	9.632(3)	10.358(3)		119.72(2)		385
$La_2(SO_4)_3\cdot 4H_2O$	*P*2₁/*n*	12.388(1)	7.140(1)	14.302(1)		90.65(1)		391
$Ce_2(SO_4)_3\cdot 4H_2O$	*P*2₁/*c*	13.390(2)	7.247(1)	18.328(2)		134.2(1)		390
$Nd_2(SO_4)_3\cdot 4H_2O$	*P*2₁/*n*	12.987(2)	7.190(1)	13.284(2)		92.40(1)		391
$Er_2(SO_4)_3\cdot 4H_2O$	*P*1̄	6.635(1)	9.056(3)	10.465(2)	93.60(3)	107.18(2)	99.12(3)	382
$Tb_2(SO_4)_3\cdot 4H_2O$	*P*1̄	6.701(1)	9.068(2)	10.527(2)	94.15(2)	107.17(2)	99.09(2)	386
$Lu_2(SO_4)_3\cdot 3H_2O$	*Cmc*2₁	13.527(5)	18.415(5)	9.242(7)				385
$Ce(SO_4)_2\cdot 4H_2O$	*Pnma*	14.599(2)	11.0064(4)	5.6601(5)				*a*
$Ce(SO_4)_2\cdot 4H_2O$	*C*2/*c*	35.813(7)	5.633(1)	14.597(3)		113.73(3)		*b*
			anhydrous sulfates					
$Nd_2(SO_4)_3$	*B*112/*b*	21.72(3)	6.904(7)	6.673(6)			109.78(4)	401
$Er_2(SO_4)_3$	*Pbcn*	12.709(1)	9.1301(7)	9.2169(7)				382
$Y_2(SO_4)_3$	*Pbcn*	12.740(1)	9.1676(9)	9.2608(7)				403
$Yb_2(SO_4)_3$	*Pbcn*	12.621(1)	9.0636(8)	9.151(1)				404
$Lu_2(SO_4)_3$	*Pbcn*	12.603(2)	9.075(1)	9.153(1)				404
$Sc_2(SO_4)_3$	*R*3̄	8.707(1)		22.470(4)				403

[a] Filipenko, O. S.; Leonova, L. S.; Atovmyan, L. O.; Shilov, G. V. *Dokl. Akad. Nauk* **1998**, *360*, 73. [b] Lindgren, O. *Acta Chem. Scand. A* **1977**, *31*, 453.

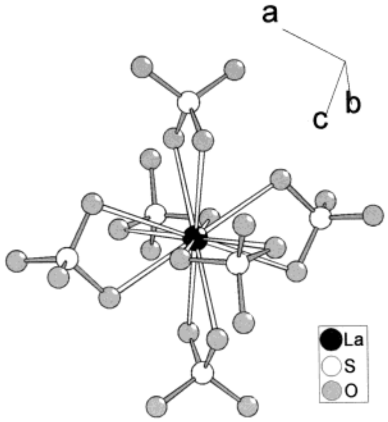

Figure 36. 12-fold coordinated La^{3+} ion in the crystal structure of $M_2(SO_4)_3 \cdot 9H_2O$. The high coordination number is gained by the chelating attachment of all sulfate ions.

$(SO_4)_3 \cdot 4H_2O$ (M = La, Ce, Nd, Tb, Er).[390,391,386,382] The pentahydrates were found to crystallize with the monoclinic space group *C*2/*c*. The M^{3+} ions are surrounded by six sulfate groups and two H_2O molecules. One of the SO_4^{2-} ions is attached in a chelating way, leading to a coordination number of 9 for the cation. According to the formulation $[M(H_2O)_{2/1}(SO_4)_{6/4}]$, each sulfate group is bonded to four M^{3+} ions. One of the H_2O molecules is not bonded to a M^{3+} ion, and the description of the structure in space group *C*2/*c* requires one-half occupation of this oxygen site. However, with respect to piezoelectric measurements on $Ce_2(SO_4)_3 \cdot 5H_2O$, there is clear evidence that the pentahydrates are in fact acentric with the space group *Cc*.[392] With $Sc_2(SO_4)_3 \cdot 5H_2O$ another pentahydrate is known. It is triclinic and shows the Sc^{3+} ions in octahedral coordination of oxygen atoms.[393] With respect to the lattice parameters, $Sc_2(SO_4)_3 \cdot 5H_2O$ seems to be isotypic to the respective selenate (cf. section II.D). However, the latter has been described with the acentric space group *P*1, while the sulfate shows inversion symmetry ($P\bar{1}$).

In the crystal structure of the tetrahydrates $M_2(SO_4)_3 \cdot 4H_2O$ with M = La, Ce, Nd, the CN 8 for the M^{3+} ions is achieved by coordination of two H_2O molecules and five SO_4^{2-} ions. One of the latter is again a chelating ligand. The sulfate groups are surrounded by four and three M^{3+} ions, respectively, as it may be described by $[M(H_2O)_{4/1}(SO_4(1))_{3/3}(SO_4(2))_{2/4}]_2$ in Niggli's formalism.

Recently, lower hydrates of the lanthanide sulfates could be also prepared for the smaller lanthanides Tb, Er, and Lu. The isotypic tetrahydrates $Tb_2(SO_4)_3 \cdot 4H_2O$ and $Er_2(SO_4)_3 \cdot 4H_2O$[382,386] could be obtained from acidic solutions at elevated temperatures in single-crystalline form. In the triclinic crystal structure two crystallographically different M^{3+} ions are present. $M(1)^{3+}$ is coordinated by eight oxygen atoms leading to a square antiprismatic $[MO_8]$ polyhedron. The oxygen atoms belong to five monodentate sulfate ions and three H_2O molecules. $M(2)^{3+}$ has seven oxygen ligands which are provided by six SO_4^{2-} groups and one water molecule. The coordination polyhedron is a monocapped trigonal prism. Two of the three crystallographically different SO_4^{2-} ions link four M^{3+} ions with each other, and the third is attached to three M^{3+} ions (Figure 37). Furthermore, significant hydrogen bonding is observed in the crystal structure.

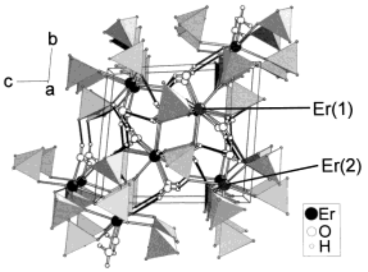

Figure 37. Perspective view of the crystal structure of $Er_2(SO_4)_3 \cdot 4H_2O$ along [100]; hydrogen bonds are emphasized as black lines.

$Lu_2(SO_4)_3 \cdot 3H_2O$ has also been obtained from an acidic solution.[385] The crystal structure is very complex and contains three crystallographic Lu^{3+} ions and fully five different sulfate groups. $Lu(1)^{3+}$ is octahedrally coordinated by the oxygen atoms of six monodentate SO_4^{2-}. The 8-fold coordination of the remaining two Lu^{3+} ions results from six monodentate and two chelating sulfate ligands ($Lu(2)^{3+}$) and five monodentate SO_4^{2-} ions and three water molecules ($Lu(3)^{3+}$), respectively. Thus, all of the three H_2O molecules per formula unit are located at one Lu^{3+} ion. The low content of water in the compound leads to a strong linkage of the polyhedra with four of the sulfate groups being in 4-fold coordination of Lu^{3+} and one SO_4^{2-} ion being attached to two Lu^{3+} ions in a chelating way.

The thermal behavior of the sulfate hydrates has been studied several times by means of DTA/TG measurements, mainly for the octahydrates.[394-398] According to these investigations, the following reaction scheme has been established

$$M_2(SO_4)_3 \cdot 8H_2O \rightarrow M_2(SO_4)_3 + 8H_2O\uparrow$$

$$M_2(SO_4)_3 \rightarrow M_2O_2(SO_4) + 2SO_2\uparrow + O_2\uparrow$$

$$M_2O_2(SO_4) \rightarrow M_2O_3 + SO_2\uparrow + {}^1/_2O_2\uparrow$$

As pointed out by Niinistö et al., the onset temperatures of the last two steps depend on the ionic radii of the M^{3+} ions.[399] Recent investigations on $Gd_2(SO_4)_3 \cdot 8H_2O$ proved the reaction sequence by additional powder diffraction investigations of the intermediates.[381] The dehydration process of $Er_2(SO_4)_3 \cdot 8H_2O$ has been also investigated by temperature-dependent powder diffraction and DTA/TG measurements.[382] It turned out that the trihydrate $Er_2(SO_4)_3 \cdot 3H_2O$, isotypic with the lutetium compound, forms as an intermediate during the process (Figure 38). The dehydration processes of lower hydrates have been investigated occasionally. For example, for $Pr_2(SO_4)_3 \cdot 5H_2O$, a di- and monohydrate have been assumed as dehydration intermediates by means of DTA measurements and kinetic calculations.[400] $Er_2(SO_4)_3 \cdot 4H_2O$ dehydrates in two steps which are, however, not very well resolved.[382]

2. Anhydrous Sulfates

Compared to the respective hydrates, the knowledge of the crystal structures of binary anhydrous

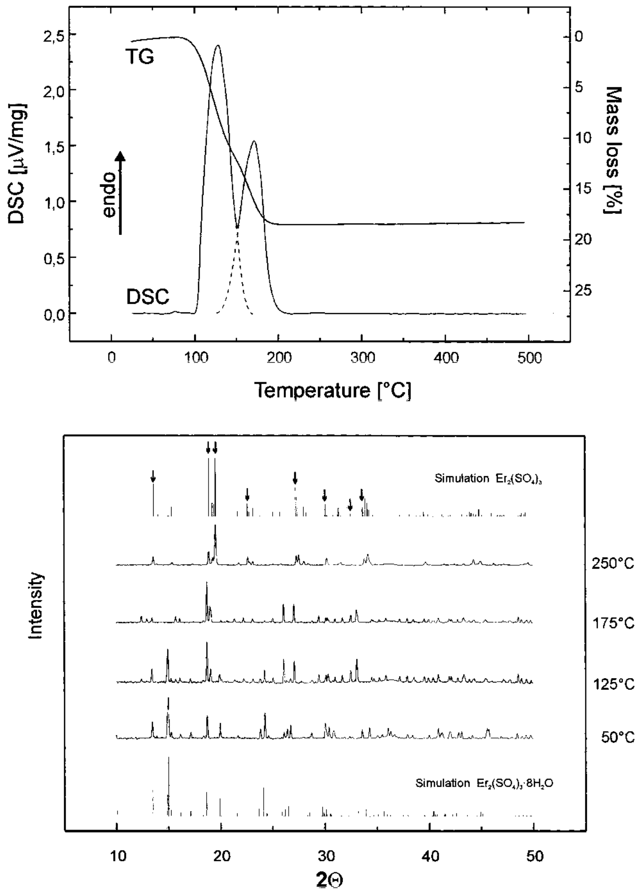

Figure 38. Thermal behavior of $Er_2(SO_4)_3 \cdot 8H_2O$. The temperature-dependent powder diffraction shows that $Er_2(SO_4)_3$ is formed as a mixture of its orthorhombic and trigonal modification (black arrows in the simulated pattern).

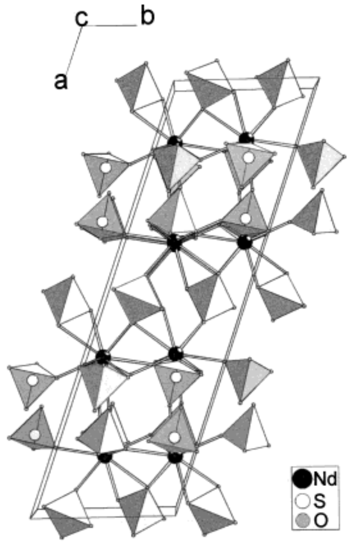

Figure 39. Crystal structure of $Nd_2(SO_4)_3$ viewed along the [010] direction. Note that the crystal structure is closely related to the one of $GdClSO_4$ (cf. Figure 57).

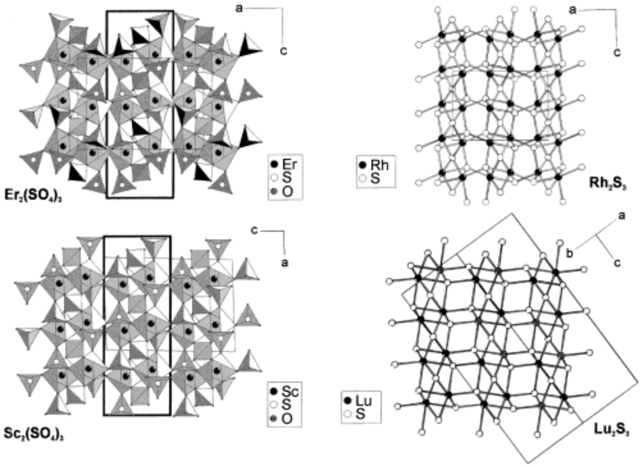

Figure 40. Crystal structure $Er_2(SO_4)_3$ and $Sc_2(SO_4)_3$ and their relation to the binary sulfides Rh_2S_3 and Lu_2S_3 (α-Al_2O_3 type of structure), respectively.

sulfates is rather limited (Table 7). More than 20 years ago Sirotinkin et al. reported the synthesis of $Nd_2(SO_4)_3$ and $Er_2(SO_4)_3$ in single-crystalline form by peritectic decomposition of $LiNd(SO_4)_2$ and $LiEr(SO_4)_2$, respectively.[401,402] The crystals obtained, however, were of poor quality, especially for the erbium compound. On the other hand, it has been shown that single crystals of anhydrous sulfates can be grown from alkaline halide melts, favorably LiF and NaCl, respectively. Unfortunately, the method works only for the smaller rare-earth elements Ho−Lu, Y, and Sc.[382,403,404] The larger lanthanides form sulfate halides under these conditions.

In the crystal structure of $Nd_2(SO_4)_3$, Nd^{3+} is surrounded by seven sulfate groups. Two of the latter are chelating ligands yielding a coordination number of nine for Nd^{3+}. According to the formulation $[Nd(SO_4)_{5/5}(SO_4)_{2/4}]_2$, the SO_4^{2-} ions are coordinated by five or four neodymium ions. The linkage leads to the crystal structure depicted in Figure 39 with the stacking of the crystallographically different sulfate groups to layers parallel (001). Note that the crystal structure is closely related to the one of $GdClSO_4$, which is described below. For the crystal structures of the sulfates $M_2(SO_4)_3$ with M = Ho−Lu,Y, a CN of six with octahedral coordination of the M^{3+} ions is found. The sulfate groups are attached to four M^{3+} ions. Thus, the $[MO_6]$ octahedra and the SO_4^{2-} tetrahedra are linked via all vertexes. If the complex anions are regarded as spheres, the analogy of the crystal structure to the binary sulfide Rh_2S_3 is obvious as can be seen from Figure 40. The same figure compares the crystal structures of $Sc_2(SO_4)_3$ and Lu_2S_3 (α-Al_2O_3 type of structure). The connectivity of the $[ScO_6]$ octahedra and the sulfate tetrahedra in $Sc_2(SO_4)_3$ is the same as just described. However, the arrangement of the SO_4^{2-} ions is different. The close relationship of the structures makes it likely that phase transitions between them may occur. Although this has not been proven to date, it has been shown that the dehydration of $Er_2(SO_4)_3 \cdot 8H_2O$ yields $Er_2(SO_4)_3$ with the rhombohedral structure of $Sc_2(SO_4)_3$.[382] With respect to X-ray powder diffraction investigations, there is strong evidence that the anhydrous rare-earth sulfates of Gd and La have a different crystal structure than those known so far. For $Gd_2(SO_4)_3$, a monoclinic cell with space group $C2/c$ and the lattice parameters $a = 9.097$ Å, $b = 14.345$ Å, $c = 6.234$ Å, and $\beta = 97.75°$ was given.[381] For $La_2(SO_4)_3$, also a monoclinic cell was determined but with different parameters: $a = 18.897$ Å, $b =$

8.948 Å, $c = 12.399$ Å, and $\beta = 115.43°$.[405] Another crystal structure of an anhydrous rare-earth sulfate is the one of tetravalent cerium, $Ce(SO_4)_2$. It contains the Ce^{4+} ions in 8-fold coordination of eight monodentate SO_4^{2-} groups, each of them being attached to four Ce^{4+} ions.[406,407]

3. Ternary Sulfates

There is a large number of ternary rare-earth sulfates with alkaline metal ions or NH_4^+ as the third component. They have been studied in the early days of lanthanide chemistry because of their application in the separation of rare-earth elements. With the beginning of the 1970s, the crystal structures of these compounds were determined, and to date roughly 70 crystal structures are known. Most of the structures have been discussed earlier in the review of Niinistö and Leskälä,[6,7] so that only selected examples will be presented here. However, to be comprehensive, Table 8 includes all compounds of which the crystal structure has been determined to date.

For anhydrous ternary rare-earth sulfates, the composition $AM(SO_4)_2$ has been found for nearly the whole lanthanide series and for all of the alkaline ions A^+.[408−426] The synthesis may occur by fusing the binary components at elevated temperature or, in a few cases, by crystallization from aqueous solution at 70 °C. The coordination numbers of the M^{3+} ions in these compounds vary from 10, for example, in $NaLa(SO_4)_2$,[411] via 9 and 8 as found for $NaNd(SO_4)_2$[419] and $NaEr(SO_4)_2$,[414] respectively, to 6 in $LiLu(SO_4)_2$.[410] Structural changes are not only observed with decreasing radii of the M^{3+} ions. Different crystal structures are found also for a given composition. Besides $KNd(SO_4)_2$, which can be either triclinic or monoclinic,[418,425] $NaTb(SO_4)_2$ may serve as a striking example for the polymorphism of the double sulfates.[415] $NaTb(SO_4)_2$ adopt three different crystal structures, two of them with CN 8 and one with CN 9 for Tb^{3+}. As it may be seen from Figure 41 these polymorphs are not only very similar to each other but also to the structure of $CaSO_4$. In particular, this is obvious if one compares $CaSO_4$ with the orthorhombic modification of $NaTb(SO_4)_2$. Thus, the latter may be seen as an ordered variant of *anhydride* with Na^+ and Tb^{3+}, respectively, substituting for Ca^{2+}.

In accordance with their size, the A^+ ions show coordination numbers from 4 (Li^+) up to 14 (Rb, Cs). The respective coordination polyhedra are mostly quite irregular. For Li^+, for example, strongly distorted $[LiO_4]$ tetrahedra are found in the crystal structures of $LiPr(SO_4)_2$ and $LiTb(SO_4)_2$.[420,415] Note, the latter compound is isotypic with $LiEu(SO_4)_2$,[417] although an orthorhombic space group has been given for the europium compound. It seems very likely that it has to be corrected to the tetragonal one. The high coordination numbers of Rb^+ and Cs^+ are mainly achieved by chelating sulfate ligands, as may be seen from the surrounding of Cs^+ in the crystal structure of $CsPr(SO_4)_2$: six chelating and two monodentate SO_4^{2-} groups are attached to the ion yielding a coordination number of 14. Another interesting SO_4^{2-} coordination feature is exhibited in the crystal structure of $NH_4La(SO_4)_2$:[426] two of the six sulfate groups around NH_4^+ act as tridentate chelating ligands. Ternary sulfates containing the ammonium ion are of special interest with respect to their application in rare-earth separation techniques and due to their thermal decomposition to anhydrous lanthanide sulfates. Unfortunately, single crystals of NH_4^+ containing anhydrous sulfates are not easy to obtain. Thus, structure determinations for these compounds are rather limited. Because NH_4^+ has a radius comparable to those of K^+ and Rb^+, the crystal structures are often isotypic with each other and can be deduced from powder diffraction patterns.

As shown in Table 8, three ternary sulfates of the type $AgM(SO_4)_2$ are known. As might be expected from the similar ionic radii of Na^+ and Ag^+, two of them, $AgPr(SO_4)_2$[415] and $AgEr(SO_4)_2$,[413] are isotypic with the respective sodium compounds. On the other hand, for $AgTb(SO_4)_2$[415] a new structure type occurs which contains two crystallographically different Tb^{3+} and Ag^+ ions, respectively. The Tb^{3+} ions have CN of “7+2” and 9, while the Ag^+ ions are irregularly surrounded by 8 and 9 oxygen atoms with a wide distance range from 2.26 to 3.30 Å. The crystal structure is depicted in Figure 42.

Compared to the 1:1 compounds, double sulfate compounds of other compositions are not very well characterized, although a great number of phases are supposed to exist. With K^+ and Rb^+ (and NH_4^+), sulfates of the composition $A_3M(SO_4)_3$,[427−433] $A_6M_4(SO_4)_9$,[427,434,435] $A_7M_3(SO_4)_8$,[436,437] and $A_5M(SO_4)_4$[429,438] and the nonstoichiometric compounds $A_{6+3n}M_{4-n}(SO_4)_9$ have been reported.[436,439,440] Single-crystal data are only available for some of the $A_3M(SO_4)_3$ compounds[441,442] (also with A = Cs[443,444]) and the ammonium compounds $(NH_4)_5M(SO_4)_4$ (M = La, Pr).[445,446] The crystal structures of the latter show the same structural characteristic, although they crystallize with different symmetry. Both contain zigzag chains according to $^1_\infty[M(SO_4)_{4/2}(SO_4)_{2/1}]^{5-}$ which are held together by the NH_4^+ ions (Figure 43). Two other crystal structures which might be of interest are those containing Ce^{4+}. $Cs_2Ce(SO_4)_3$[447] consists of sheets formed by the linkage of $[CeO_8]$ polyhedra and SO_4^{2-} tetrahedra in accordance with the formulation $^2_\infty[Ce(SO_4)_{6/2}]^{2-}$. The sheets are connected via the Cs^+ ions. Besides Ce^{4+}, the sulfate $KCe_2(SO_4)_4$ also contains Ce^{3+} ions and, hence, is the only mixed-valent rare-earth sulfate known so far.[448] Both cerium ions are in 8-fold coordination of oxygen atoms, but the oxidation state can be assigned with respect to the distances Ce−O. They range from 2.26 to 2.38 Å for Ce^{4+} and from 2.37 to 2.57 for Ce^{3+}, respectively. The oxygen ligands of the cerium ions belong to eight monodentate sulfate groups which are themselves attached to four cerium ions. Thus, the connectivity may be written as $[Ce^{III/IV}(SO_4)_{8/4}]^{0.5-}$. Charge compensation is achieved by 9-fold coordinated K^+ ions which are incorporated in the three-dimensional network of $[CeO_8]$ and $[SO_4]$ polyhedra. It is remarkable that nearly all of the sulfates with other compositions than $AM(SO_4)_2$ seem to have acentric crystal structures with respect to the given space groups. However, in no case has the acentricity been proven by means of physical measurements, and in

Table 8. Crystallographic Data of Anhydrous and Hydrous Ternary Sulfates

compound	space group	lattice parameters						ref
		a/Å	b/Å	c/Å	α/°	β/°	γ/°	
anhydrous ternary sulfates								
$CsLa(SO_4)_2$	$P2_1/n$	7.929(1)	5.483(1)	17.153(1)		91.46(1)		408
$CsPr(SO_4)_2$	$Pnna$	9.497(3)	14.106(5)	5.457(1)				409
$LiLu(SO_4)_2$	$Pbcn$	12.575(2)	9.051(4)	9.138(4)				410
$NaLa(SO_4)_2$	$P\bar{1}$	7.081(7)	6.765(7)	6.465(5)	102.25(3)	91.20(3)	76.71(3)	411
$NaTm(SO_4)_2$	$P112_1/m$	4.662(3)	10.143(7)	6.837(4)			110.40(4)	412
$NaEr(SO_4)_2$	$P2_1/c$	4.673(2)	6.861(2)	9.575(3)		96.80(3)		414
$AgEr(SO_4)_2$	$P2_1/m$	4.697(1)	6.806(1)	9.886(1)		95.18(2)		413
$AgEr(SO_4)_2$	$P\bar{1}$	6.737(1)	9.363(2)	10.151(2)	86.54(2)	87.54(2)	81.21(2)	415
$NaTb(SO_4)_2$	$P2_1/m$	4.704(1)	6.927(1)	9.589(2)		96.73(2)		415
$NaTb(SO_4)_2$	$Pnma$	7.033(2)	6.960(1)	6.157(1)				415
$NaTb(SO_4)_2$	$P\bar{1}$	6.275(1)	6.833(1)	7.022(1)	99.43(2)	95.70(2)	90.89(3)	415
$RbEu(SO_4)_2$	$C2/c$	13.483(4)	5.372(2)	9.444(2)		102.40(2)		416
$LiEu(SO_4)_2$	$Pnn2$	7.632(4)	7.632(4)	5.566(3)				417
$LiTb(SO_4)_2$	$P\bar{4}n2$	7.622(1)		5.5353(8)				415
$KNd(SO_4)_2$	$P\bar{1}$	6.91(3)	5.30(2)	9.05(3)	92.03(5)	96.87(5)	90.80(5)	418
$NaNd(SO_4)_2$	$P\bar{1}$	6.950(3)	6.343(3)	7.215(4)	96.30(2)	98.95(2)	90.93(2)	419
$NaGd(SO_4)_2$	$P\bar{1}$	6.846(1)	6.270(1)	7.026(1)	95.82(2)	99.26(2)	90.93(2)	415
$NaEu(SO_4)_2$	$P\bar{1}$	6.860(1)	6.2687(9)	7.037(1)	95.97(2)	99.17(2)	90.92(2)	415
$AgPr(SO_4)_2$	$P\bar{1}$	6.4005(9)	6.9944(9)	7.134(1)	98.60(1)	96.12(1)	91.09(1)	415
$LiPr(SO_4)_2$	$P112_1/b$	13.69(2)	7.005(6)	6.692(6)			105.25(4)	420
$KPr(SO_4)_2$	$P\bar{1}$	6.94(2)	5.39(2)	8.47(1)	91.27(3)	94.51(3)	88.33(3)	421
$RbDy(SO_4)_2$	$Pnna$	9.427(4)	13.101(4)	5.316(4)				422
$RbLu(SO_4)_2$	$P2/c$	8.772(1)	8.772(1)	7.590(1)		95.7(4)		423
$KEr(SO_4)_2$	$P2_1/n$	5.435(1)	13.342(1)	8.738(1)		92.80(1)		424
$KNd(SO_4)_2$	$P2_1/c$	8.551(1)	7.159(1)	10.679(1)		92.42(1)		425
$NH_4La(SO_4)_2$	$P2_1/m$	7.138(1)	5.425(1)	9.317(1)		98.85(1)		426
$K_3Yb(SO_4)_3$	$B11b$	10.39(2)	8.99(1)	14.65(3)			124.15(4)	441
$K_3Er(SO_4)_3$	Pc	9.222(2)	14.688(1)	9.008(1)		110.72(2)		442
$Rb_3Tm(SO_4)_3$	Cc	10.649(2)	15.149(3)	9.320(2)		124.49(1)		442
$Cs_3Yb(SO_4)_3$	$R3c$	16.040		9.479				443
$Cs_3Gd(SO_4)_3$	Cc	27.333(1)	10.139(1)	10.099(1)		106.83(2)		444
$(NH_4)_5(La(SO_4)_4)$	$P\bar{1}$	8.109(8)	9.491(7)	12.28(1)	83.22(6)	70.71(7)	69.65(7)	445
$(NH_4)_5Pr(SO_4)_4$	$C1c1$	8.051(1)	22.976(2)	9.431(1)		109.71(1)		446
$Cs_2Ce(SO_4)_3$	$P2_1$	9.772(2)	16.797(2)	14.812(1)		96.40(1)		447
$KCe_2(SO_4)_4$	Cc	11.734(2)	15.695(2)	9.268(1)		132.00(1)		448
$(Na_{1.788}La_{0.062})SO_4$	$P6_3/mmc$	5.331(1)		7.188(1)				[a]
$(Na_{1.748}La_{0.102})SO_4$	$P6_3/mmc$	5.331(1)		7.188(1)				[a]
hydrous ternary sulfates								
$KTb(SO_4)_2\cdot H_2O$	$P112_1/b$	10.180	10.350	8.380			120.0	449
$RbCe(SO_4)_2\cdot H_2O$	$P2_1/c$	10.235(4)	8.645(1)	10.495(2)		118.59(2)		450
$RbGd(SO_4)_2\cdot H_2O$	$P2_1/c$	10.265(1)	8.370(2)	10.443(2)		119.49(1)		451
$RbHo(SO_4)_2\cdot H_2O$	$P2_1/c$	10.210(3)	8.298(2)	10.404(3)		119.63(2)		451
$RbYb(SO_4)_2\cdot H_2O$	$P2_1/c$	10.124(3)	8.255(2)	10.333(3)		119.82(3)		451
$RbHo(SO_4)_2\cdot H_2O$	$P112_1/b$	10.361(4)	17.775(9)	8.320(4)			149.9(3)	452
$KPr(SO_4)_2\cdot H_2O$	$P2_1/c$	10.866(2)	15.361(4)	10.031(3)		112.36(2)		453
$LiCe(SO_4)_2\cdot H_2O$	$P2_1/c$	8.114(2)	4.612(2)	18.202(8)		96.89(4)		454
$NaLa(SO_4)_2\cdot H_2O$	$P3_121$	7.0557(7)		12.9669(9)				456
$NaCe(SO_4)_2\cdot H_2O$	$P3_221$	7.019(1)		12.925(2)				457
$NaCe(SO_4)_2\cdot H_2O$	$P3_121$	7.013(1)		12.920(3)				458
$AgCe(SO_4)_2\cdot H_2O$	$P3_121$	7.013(3)		13.110(9)				459
$NH_4Sm(SO_4)_2\cdot 4H_2O$	$P2_1/c$	6.582(2)	18.886(7)	8.736(4)		96.88(4)		460
$NH_4Nd(SO_4)_2\cdot 4H_2O$	$P2_1/c$	6.6294(8)	18.929(2)	8.782(1)		97.11(1)		461
$CsLu(SO_4)_2\cdot 4H_2O$	$P2_1/c$	6.670(1)	18.497(2)	8.637(1)		94.23(1)		462
$CsPr(SO_4)_2\cdot 4H_2O$	$P2_1/c$	6.671(2)	19.054(3)	8.839(2)		94.55(4)		463
$RbPr(SO_4)_2\cdot 4H_2O$	$P2_1/c$	6.622(2)	18.997(2)	8.749(2)		96.17(2)		464
$RbNd(SO_4)_2\cdot 4H_2O$	$P2_1/c$	6.6047(7)	18.929(2)	8.7448(9)		96.21(1)		461
$CsLa(SO_4)_2\cdot 4H_2O$	$P112_1/b$	6.734(4)	9.975(5)	19.16(1)			94.13(4)	465
$RbSm(SO_4)_2\cdot 4H_2O$	$P2_1/c$	6.565(2)	18.913(6)	8.728(1)		96.26(2)		466
$(NH_4)La(SO_4)_2\cdot 4H_2O$	$P2_1/c$	6.720(1)	19.068(2)	8.841(1)		97.50(1)		467
$(NH_4)Tb(SO_4)_2\cdot 4H_2O$	$P2_1/c$	6.522(4)	18.820(4)	8.681(1)		96.69(3)		467
$KLu(SO_4)_2\cdot 2H_2O$	$P2_1/c$	10.583(1)	7.748(1)	10.014(2)		97.36(1)		468
$TlLa(SO_4)_2\cdot 2H_2O$	$P2_1/n$	7.216(1)	11.853(1)	10.486(1)		92.05(1)		469
$TlPr(SO_4)_2\cdot 2H_2O$	$P2_1/n$	7.153(2)	11.725(2)	10.416(2)		92.52(2)		470
$Na_3(Sc(SO_4)_3)\cdot 5H_2O$	$P6_3$	9.56(4)		9.55(4)				461
$(NH_4)_6Tb_4(SO_4)_9\cdot 2H_2O$	$C2/c$	9.008(5)	18.323(8)	21.39(1)		95.33(5)		[b]
$N_2H_5Nd(SO_4)_2\cdot H_2O$	$Pca2_1$	10.951(3)	9.554(2)	15.762(3)				479
$Sc(NH_3(OH))(SO_4)_2\cdot 1.5H_2O$	$P\bar{1}$	5.123(1)	8.955(1)	10.147(1)	80.93(1)	75.36(1)	89.17(1)	480
$K_2Ce(SO_4)_3\cdot H_2O$	$C2$	20.600(3)	7.0744(6)	18.583(3)		126.08(1)		448
$K_2Ce(SO_4)_3\cdot H_2O$	$C2$	20.594(6)	7.068(2)	17.851(5)		122.72(2)		[c]
$(NH_4)_8(Ce_2(SO_4)_8)\cdot 4H_2O$	$P2_1/c$	12.6472(7)	11.3613(6)	13.6908(7)		110.36(1)		481

[a] Armbruster, R.; Mikhail, P.; Hulliger, J. *J. Solid State Chem.* **1999**, *145*, 309. [b] Iskhakova, L. D.; Gasanov, Y. M.; Bondar, S. A.; Klejnman, I. A.; Novik, V. K.; Trunov, V. K. *Izv. Akad. Nauk SSR* **1988**, *24*, 998. [c] Sizova, R. G.; Voronkov, A. A.; Belov, N. V. *Dokl. Akad. Nauk SSR* **1974**, *217*, 1073.

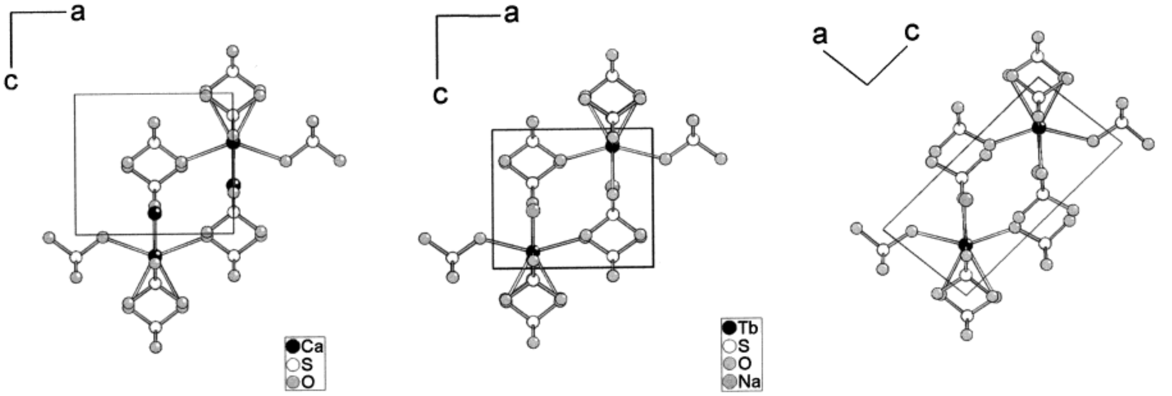

Figure 41. Comparison of the monoclinic and the orthorhombic modification of $NaTb(SO_4)_2$ with the crystal structure of $CaSO_4$.

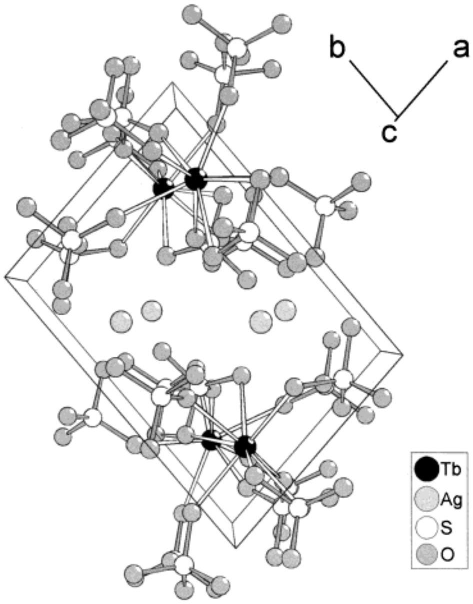

Figure 42. Crystal structure of $AgTb(SO_4)_2$ viewed along [001].

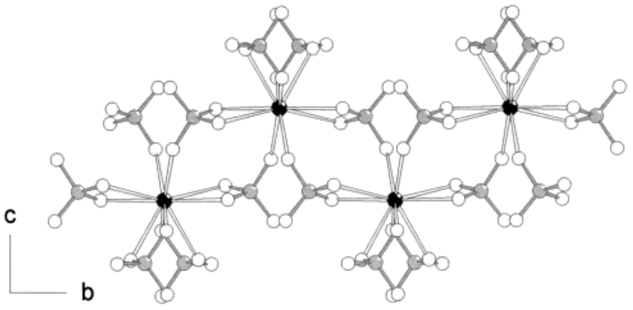

Figure 43. Zigzag chains ${}^{1}_{\infty}[M(SO_4)_{4/2}(SO_4)_{2/1}]^{5-}$ in the crystal structure of $(NH_4)_5M(SO_4)_4$ (M = La, Pr).

some cases the structure determinations are of poor quality, so therefore there remains at least some doubt.

Compounds with a A^+:M^{3+} ratio of 1:1 are also the best investigated group among the hydrous ternary sulfates. They are either monohydrates[449−459] or tetrahydrates[460−467] and in few cases also dihydrates.[468−470] The tetrahydrates are mainly found for the bigger monovalent ions Cs^+, NH_4^+, and Rb^+. They are isotypic with each other and contain the M^{3+} ions in 9-fold coordination of oxygen atoms resulting from the attachment of two chelating and two monodentate sulfate groups and three water ligands. One of the H_2O molecules remains uncoordinated. Each of the SO_4^{2-} tetrahedra has two M^{3+} neighbors leading to two strongly puckered layers according to ${}^{2}_{\infty}[M(SO_4)_{4/2}(H_2O)_3]^-$ which are linked by the A^+ ions. The ammonium compounds have been shown to decompose upon heating according to the reaction sequence

$$NH_4M(SO_4)_2{\cdot}4H_2O \rightarrow NH_4M(SO_4)_2{\cdot}H_2O + 3H_2O\uparrow$$

$$NH_4M(SO_4)_2{\cdot}H_2O \rightarrow NH_4M(SO_4)_2 + H_2O\uparrow$$

$$2NH_4M(SO_4)_2 \rightarrow M_2(SO_4)_3 + (NH_4)_2SO_4\uparrow$$

yielding the anhydrous sulfates.[429,471−473] Furthermore, $RbSm(SO_4)_2{\cdot}4H_2O$ and $NH_4Sm(SO_4)_2{\cdot}4H_2O$ are found to exhibit a phase transition at lower temperature.[474]

For the smaller A^+ ions such as Na^+ the monohydrates became dominating. The crystal structures of the sodium compounds have only be determined for M = La and Ce,[456−458] but powder diffraction results suggest isotypy of the respective sulfates with the smaller M^{3+} ions down to Er.[475−477] The crystal structure has been described with the enantiomorphic space group $P3_121$. Additionally, for $NaCe(SO_4)_2{\cdot}H_2O$ the second enantiomorph with the space group $P3_221$ has been reported.[457] In the structure 9-fold coordinated M^{3+} and 8-fold coordinated Na^+ ions are present. The sulfate groups act as chelating and monodentate ligands and are surrounded by three M^{3+} and three Na^+ ions. The thermal behavior of the monohydrates $NaM(SO_4)_2{\cdot}H_2O$ (M = La, Ce, Nd, Sm) has been studied in great detail in order to determine the decomposition kinetics.[478]

As reported in a more recent work, replacement of Na^+ for Ag^+ is possible in $NaCe(SO_4)_2{\cdot}H_2O$ without structural changes[459] while the incorporation of the small Li^+ ions leads to a new layer structure with 9-fold coordinated Ce^{3+} ions and Li^+ in distorted tetrahedral surrounding (Figure 44).[454,464] Structures with more uncommon monovalent cations have been known for a long time in the form of the dihydrates $TlM(SO_4)_2{\cdot}2H_2O$ (M = La, Pr), which show an interesting lone pair effect of the Tl^+ ions.[469,470] Two more recent works reported ternary sulfates with $N_2H_5^+$

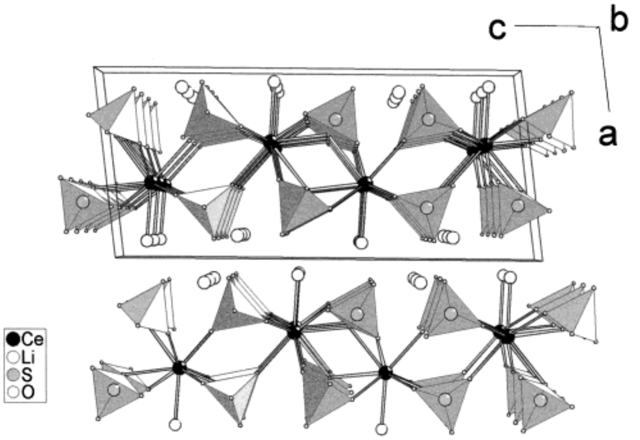

Figure 44. Crystal structure of $LiCe(SO_4)_2 \cdot H_2O$ viewed along [010].

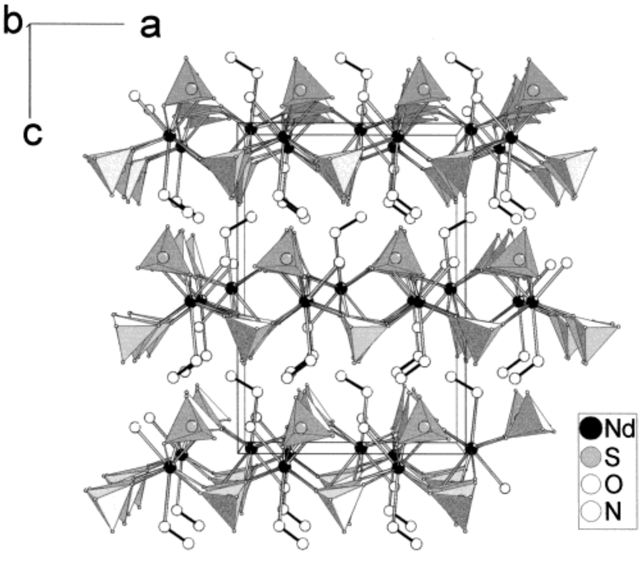

Figure 45. ${}^{2}_{\infty}[Nd(SO_4)_{6/3}]^-$ layers connected by hydrazinium ions in the structure of $N_2H_5Nd(SO_4)_2 \cdot H_2O$. Note that one nitrogen atom of the $N_2H_5^+$ ions belongs to the coordination sphere of Nd^{3+}.

and NH_3OH^+ as complex monovalent ions. $N_2H_5Nd(SO_4)_2 \cdot H_2O$ consists of layers built from $[NdO_8]$ polyhedra and SO_4^{2-} tetrahedra according to ${}^{2}_{\infty}[Nd(SO_4)_{6/3}]^-$ which are connected via the hydrazinium ions.[479] As it is known from various transition-metal compounds, one end of the N_2H_5 ions act also as a ligand with a distance Nd−N of approximately 2.8 Å (Figure 45). In the crystal structure of the sesquihydrate $NH_3OHSc(SO_4)_2 \cdot 1.5H_2O$[480] the NH_3OH^+ ions link double chains of octahedrally coordinated Sc^{3+} ions which are running along [100].

A last structure which might be emphasized here is the one of $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$.[481] Although this Ce^{4+} sulfate is widely used as an oxidant, it was only in 1998 that its crystal structure was determined. It consists of dimeric anions $[Ce_2(SO_4)_8]^{8-}$ which are connected by the NH_4^+ ions. All of the sulfate groups in the structure are chelating ligands as can be seen from Figure 46.

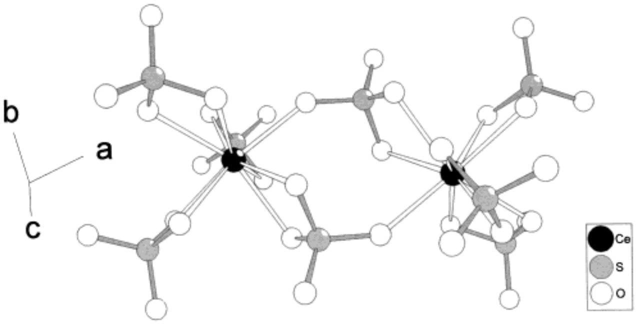

Figure 46. Dimeric anion $[Ce_2(SO_4)_8]^{8-}$ in the crystal structure of $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$.

4. Basic and Acidic Sulfates

Small and highly charged cations are known to undergo hydrolysis very easily, even in acidic solutions. Among the rare-earth elements this is true for Ce^{4+} and Sc^{3+}. Various basic sulfates of Sc^{3+} like $ScOHSO_4 \cdot 2H_2O$, $Sc_3O_2(OH)_3SO_4 \cdot 4.5H_2O$, $Sc_4(OH)_{10}SO_4 \cdot 2H_2O$, and $Sc_8(OH)_{22}SO_4 \cdot 2H_2O$ have been prepared, but in no case are structural data known.[482−484] For Ce^{4+} the crystal structures of three compounds have been investigated (Table 9). In $Ce_2(OH)_2(SO_4)_3 \cdot 4H_2O$,[485] two 8-fold coordinated Ce^{4+} ions are linked via two common hydroxo ligands to the dimeric building unit shown in Figure 47. These are connected further by SO_4^{2-} groups. An even stronger condensation is found in the structure of $CeOSO_4 \cdot H_2O$ (Figure 47), where the oxide ion is attached to three Ce^{4+} ions.[486,487] Finally, in the remarkable crystal structure of $Ce_6O_4(OH)_4(SO_4)_6$, six Ce^{4+} ions are connected via oxide and hydroxide ions, respectively.[488] The cerium ions form an octahedron with metal−metal distances of around 3.7 Å. The eight faces of the octahedron are centered by the oxide and hydroxide ions. Furthermore, the octahedron has four chelating and 16 monodentate sulfate ligands. The connection of these units leads to the tetragonal three-dimensional crystal structure. Structural data of basic sulfates with other rare-earth elements are scarce because they are usually obtained only as powders when precipitated from aqueous solution with NaOH. However, it has been shown in the case of $PrOHSO_4$ that hydrothermal techniques provide a route to single crystals of these compounds.[489] In the crystal structure of $PrOHSO_4$, cationic zigzag chains ${}^{1}_{\infty}[Pr(OH)_{2/2}]^{2+}$ are oriented along [100] and surrounded by SO_4^{2-} ions. The Pr^{3+} ions are 9-fold coordinated by oxygen atoms. In the crystal structure of $Eu_2O_2(SO_4)$, which is the only anhydrous oxide sulfate of an rare-earth element which has been obtained in single-crystalline form, layers from edge-connected $[OM_4]$ tetrahedra are built which are separated by sulfate layers.[490]

The group of acidic sulfate includes hydrogensulfates as well as oxonium compounds where the proton is attached to a H_2O molecule to form H_3O^+ ions or their hydrated species $H_5O_2^+$. It was only in 1994 when the crystal structure of a lanthanide hydrogensulfate, namely, $Gd(HSO_4)_3$, was determined for the first time.[491] The orthorhombic structure has subsequently been shown to be adopted with the rare-earth elements Eu−Lu and Y.[492−494] It is a typical layer structure with the M^{3+} ions being in 8-fold coordination of oxygen atoms (Figure 48). The oxygen atoms belong to eight monodentate HSO_4^- groups which are themselves surrounded by three and two

Table 9. Crystallographic Data of Basic and Acidic Sulfates

compound	space group	lattice parameters a/Å	b/Å	c/Å	α/°	β/°	γ/°	ref
basic sulfates								
$Ce_2(OH)_2(SO_4)_3 \cdot 4H_2O$	$A112/a$	15.58(1)	13.45(1)	6.748(4)			95.39(6)	485
$CeOSO_4 \cdot H_2O$	$P2_12_12_1$	11.987(2)	8.272(2)	4.331(1)				486
$CeOSO_4 \cdot H_2O$	$P2_12_12_1$	11.98(1)	8.27(1)	4.33(1)				487
$Ce_6(SO_4)_6(OH)_4O_4$	$I4/m$	10.661(5)		10.288(5)				488
$PrOHSO_4$	$P2_1/c$	4.488	12.495	7.091		111.08		489
$Eu_2O_2SO_4$	$I2/a$	8.1333(8)	4.1830(4)	13.643(1)		107.28(1)		490
acidic sulfates								
$Ce(HSO_4)_3$	$P6_3/m$	9.433(1)		5.8788(5)				495
$La(HSO_4)_3$	$P6_3/m$	9.4564(9)		5.9087(5)				495
$Nd(HSO_4)_3$	$P6_3/m$	9.3567(8)		5.8236(4)				495
$Pr(HSO_4)_3$	$P6_3/m$	9.399(2)		5.8482(9)				495
$Sm(HSO_4)_3$	$P6_3/m$	9.340(1)		5.7914(8)				494
$Eu(HSO_4)_3$	$P6_3/m$	9.3218(9)		5.7737(5)				494
$Eu(HSO_4)_3$	$Pbca$	12.158(2)	9.673(1)	16.567(2)				494
$Gd(HSO_4)_3$	$Pbca$	12.105(2)	9.6325(8)	16.549(1)				494
$Tb(HSO_4)_3$	$Pbca$	12.087(2)	9.610(1)	16.538(3)				494
$Dy(HSO_4)_3$	$Pbca$	12.053(2)	9.580(1)	16.536(3)				494
$Ho(HSO_4)_3$	$Pbca$	12.019(2)	9.558(1)	16.527(2)				494
$Y(HSO_4)_3$	$Pbca$	12.015(1)	9.5376(8)	16.504(1)				494
$Er(HSO_4)_3$	$Pbca$	11.951(1)	9.4930(7)	16.443(2)				492
$Gd(HSO_4)_3$	$Pbca$	12.080(8)	9.574(8)	16.515(8)				491
$Er(HSO_4)_3$	$P2_1/n$	5.2000(5)	13.578(2)	12.335(1)		92.13(1)		492
$Tm(HSO_4)_3$	$Pbca$	11.961(1)	9.4814(8)	16.443(2)				494
$Yb(HSO_4)_3$	$Pbca$	11.924(1)	9.4501(8)	16.440(2)				494
$Lu(HSO_4)_3$	$Pbca$	11.947(2)	9.445(1)	16.436(3)				494
$Er(HSO_4)(SO_4)$	$P2_1/n$	5.4561(6)	10.757(1)	10.532(1)		104.59(1)		492
$(H_5O_2)Gd(SO_4)_2$	$I4_1/amd$	6.9901(6)		17.423(2)				494
$(H_5O_2)Ho(SO_4)_2$	$I4_1/amd$	6.9140(5)		17.246(2)				496
$(H_5O_2)Er(SO_4)_2$	$I4_1/amd$	6.8967(7)		17.166(2)				496
$(H_5O_2)Y(SO_4)_2$	$I4_1/amd$	6.8875(7)		17.159(2)				496
$Y(HSO_4)_3$	$Pbca$	12.0153(8)	9.5376(4)	16.504(1)				493
$Y(HSO_4)_3 \cdot H_2O$	$P\bar{1}$	6.799(1)	8.028(2)	9.659(2)	79.99(2)	77.32(2)	77.50(2)	493
$Gd(HSO_4)_3 \cdot H_2O$	$P\bar{1}$	6.863(2)	8.056(2)	9.743(3)	80.28(3)	77.27(3)	77.21(3)	494
$(H_3O)Ce(SO_4)_2 \cdot H_2O$	$P2_1/n$	9.359(4)	9.926(4)	8.444(3)		96.53(9)		497
$(H_3O)La(SO_4)_2 \cdot 3H_2O$	$P2_1/c$	11.195(5)	6.933(2)	13.574(4)		110.94(4)		498
$(H_5O_2)(H_3O)_2Pr(SO_4)_3$	$P2_1/n$	11.620(2)	7.127(1)	15.871(2)		96.54(2)		494
$(H_5O_2)(H_3O)_2Nd(SO_4)_3$	$P2_1/n$	11.600(4)	7.109(3)	15.948(6)		96.76(4)		499
$(H_3O)_2Nd(HSO_4)_3(SO_4)$	$P\bar{1}$	9.101(1)	9.404(1)	9.527(1)	100.15(1)	112.36(1)	105.02(1)	499
$Nd(HSO_4)(S_2O_7)$	$P2_1/n$	8.578(1)	10.610(2)	9.724(1)		99.33(2)		500
$H_9Ce_6Nd_7(SO_4)_{27} \cdot 72.33H_2O$	$P6_3/m$	19.165(3)		25.060(4)				*a*
$H_9Tb_7Ce_6(SO_4)_{27} \cdot 79H_2O$	$P6_3/m$	19.341(2)		25.688(3)				*b*

[a] Barnes, J. C.; Paton, J. D.; Seaward, K. F. *Acta Crystallogr. C* **1993**, *49*, 2057. [b] Audebrand, N.; Auffredic, J.-P.; Louër, D. *Z. Kristallogr.-New Cryst. Struct.* **1998**, *213*, 453.

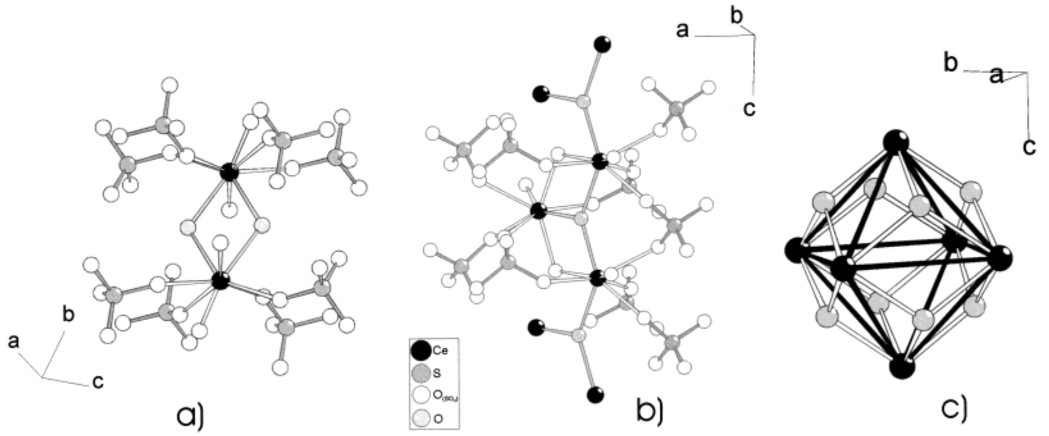

Figure 47. Coordination of O^{2-} and OH^- ions in the crystal structures of the basic sulfates $Ce_2(OH)_2(SO_4)_3 \cdot 4H_2O$ (a), $CeOSO_4 \cdot H_2O$ (b), and $Ce_6O_4(OH)_4(SO_4)_6$ (c).

M^{3+} ions, respectively. The layers ${}^{2}_{\infty}[M(SO_4)_{6/3}(SO_4)_{2/2}]$ are held together by strong hydrogen bonds with donor−acceptor distances of about 2.7 Å. For $Er(HSO_4)_3$ a second modification has been characterized by single-crystal investigations.[492] The structure shows the same coordination of the Er^{3+} ions, but the linkage of the polyhedra now leads to a three-dimensional structure according to ${}^{3}_{\infty}[M(SO_4)_{6/3}$-

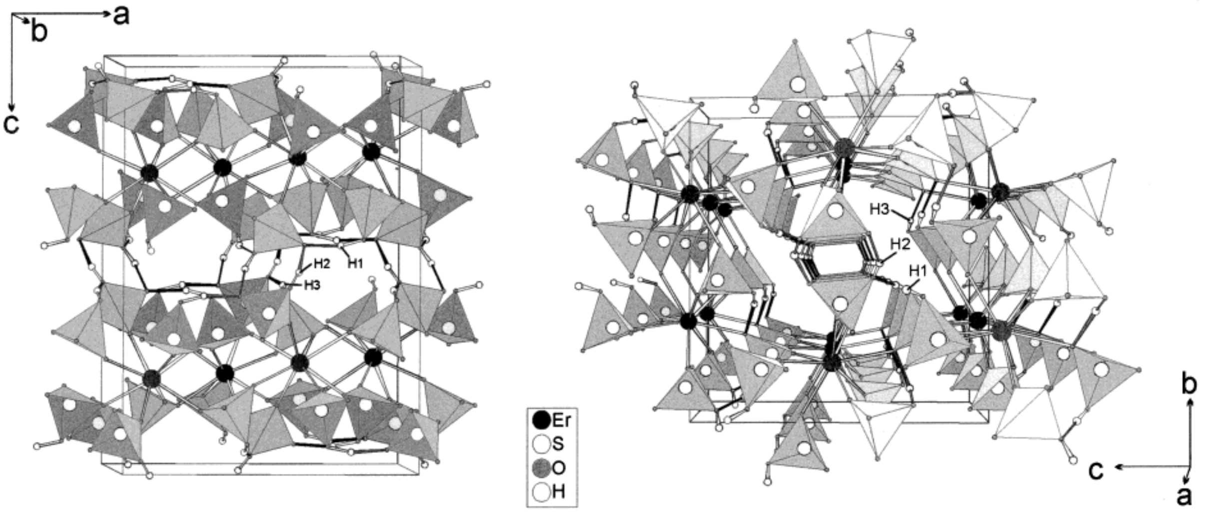

Figure 48. Crystal structures of the two modifications of $Er(HSO_4)_3$; hydrogen bonds are emphasized as black lines.

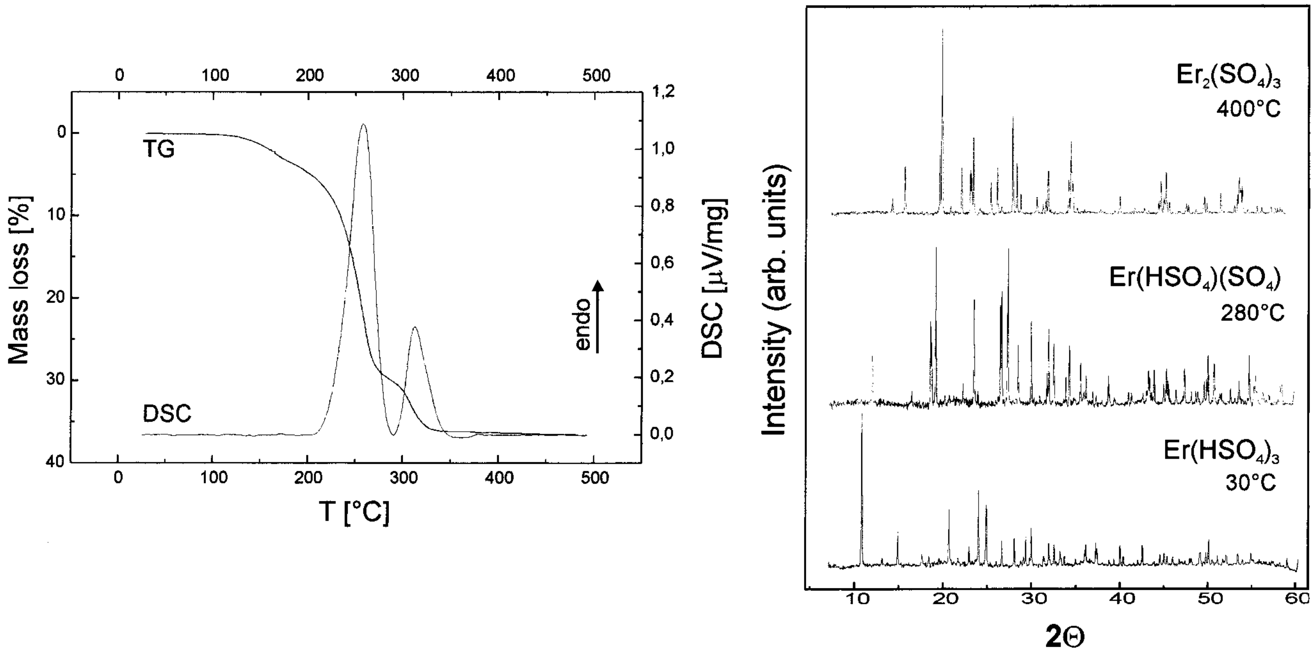

Figure 49. Thermal behavior of $Er(HSO_4)_3$; DSC/TG measurements and temperature-dependent powder diffraction show that $Er(HSO_4)(SO_4)$ is formed as an intermediate.

$(SO_4)_{2/2}]$ (Figure 48). The hydrogensulfates of the larger lanthanides La−Sm crystallize with another crystal structure[494,495] that has also been found for anhydrous lanthanide perchlorates, amidosulfates and methanesulfonates (cf. section II.C.4/5). The M^{3+} ions are 9-fold coordinated by oxygen atoms in the form of a tricapped trigonal prism. The oxygen atoms belong to nine monodentate HSO_4^- ions which are attached to three M^{3+} ions. The OH groups of the ions remain uncoordinated and point toward channels which are formed in the hexagonal structure along [001]. If the hydrogensulfate tetrahedra are reduced to their centers, the structure corresponds to the one of UCl_3, which is well-known for the trichlorides of the larger lanthanides. Note, for $Eu(HSO_4)_3$ both modifications, the hexagonal and the orthorhombic one, are found (Table 9).

The thermal decomposition of the rare-earth hydrogensulfate leads in two steps to the anhydrous sulfates.[494] With respect to DTA/TG and temperature-dependent powder diffraction investigations, the mixed sulfates−hydrogensulfates are formed as intermediates during the reaction (Figure 49).

$$M(HSO_4)_3 \rightarrow M(HSO_4)(SO_4)_2 + H_2SO_4\uparrow$$

$$M(HSO_4)(SO_4) \rightarrow {}^1/_2M_2(SO_4)_3 + {}^1/_2H_2SO_4\uparrow$$

For $Er(HSO_4)(SO_4)$, single crystals of this intermediate could be gained.[492] The crystal structure contains Er^{3+} ions surrounded by four monodentate SO_4^{2-} and three monodentate HSO_4^- ions. The linkage of the tetrahedra and the $[ErO_7]$ polyhedra leads to the three-dimensional structure depicted in Figure 50.

The hydrogensulfates of the rare-earth elements are very moisture sensitive. As can be seen with the help of time-resolved X-ray powder diffraction, Er-

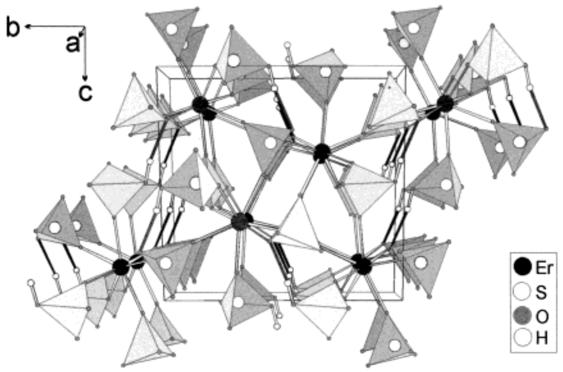

Figure 50. Perspective view of the crystal structure of Er$(HSO_4)(SO_4)$ along [100]; hydrogen bonds are emphasized as black lines.

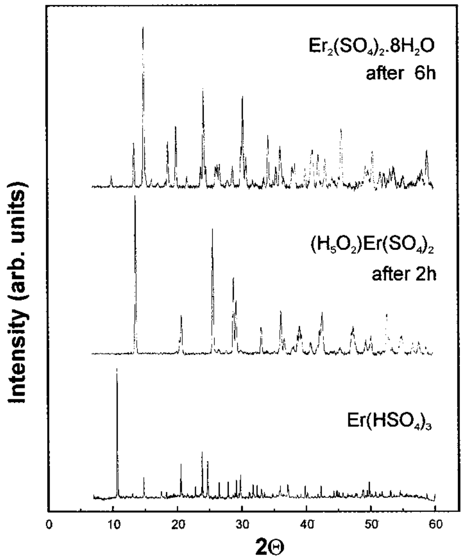

Figure 51. Hydratization of $Er(HSO_4)_3$ followed by powder diffraction. As an intermediate, the acidic sulfate (H_5O_2)-$Er(SO_4)_2$ is formed.

$(HSO_4)_3$ reacts with H_2O in the first step to form $H_5O_2Er(SO_4)_2$ and finally $Er_2(SO_4)_3 \cdot 8H_2O$ (Figure 51).[496] Single crystals of $H_5O_2Er(SO_4)_2$ and the isotypic compounds with Gd, Ho, and Y grow from sulfuric acid (80% H_2SO_4) so that the structure is known.[496] Opposite to $H_3OCe(SO_4)_2 \cdot H_2O$,[497] which has the same composition, in $H_5O_2Er(SO_4)_2$ the H_3O^+ ion and the water molecule are joined to a $H_5O_2^+$ ion with a very short hydrogen bond (Figure 52b). The Er^{3+} ions are in a dodecahedral surrounding of oxygen atoms (Figure 52a). Upon heating, $H_5O_2Er(SO_4)_2$ loses two molecules of water in the first step yielding $Er(HSO_4)(SO_4)$, which finally decomposes to $Er_2(SO_4)_3$.[496] In the hydrogensulfates $Y(HSO_4)_3 \cdot H_2O$[493] and $Gd(HSO_4)_3 \cdot H_2O$[494] the hydrogen atom is not part of an oxonium ion but located on the sulfate group. The compounds are isotypic with the perchlorate Yb$(ClO_4)_3 \cdot H_2O$, which will be discussed later (section II.E.). With $H_3OLa(SO_4)_2 \cdot 3H_2O$[498] a more water-rich compound is known showing a unique structure with strongly hydrogen-bonded H_3O^+ ions and 9-fold coordinated La^{3+} ions (Figure 53). Furthermore, two complicated acidic sulfates of neodymium have been described recently. They contain H_3O^+ and HSO_4^- ions as in $(H_3O)_2Nd(HSO_4)_3SO_4$ or H_3O^+ and $H_5O_2^+$ ions as in $(H_5O_2)(H_3O)_2Nd(SO_4)_3$.[499] Both compounds contain the Nd^{3+} ions in 9-fold coordination of oxygen atoms and show the SO_4^{2-} groups partly as chelating ligands. Furthermore, both sulfates exhibit strong hydrogen bonding as emphasized in Figure 54. The big variations in the composition and the crystal structures of acidic sulfates suggest that there might be further compounds to be discovered. A little more clarity is achieved if the compounds known so far are written as combinations of $Er_2(SO_4)_3$, H_2SO_4, and H_2O, respectively, as done in Figure 55. In this way the acidic compounds can be arranged in a triangle with these three compounds as the vertexes.

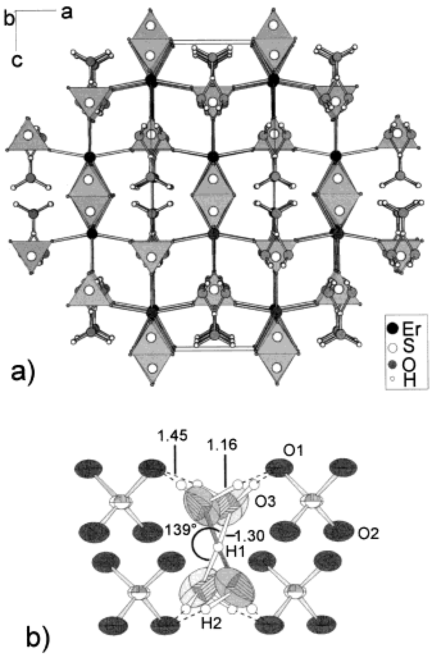

Figure 52. Crystal structure of $H_5O_2Er(SO_4)_2$ viewed along [010] (a). The $H_5O_2^+$ ion is disordered as depicted in the lower part of the figure (b).

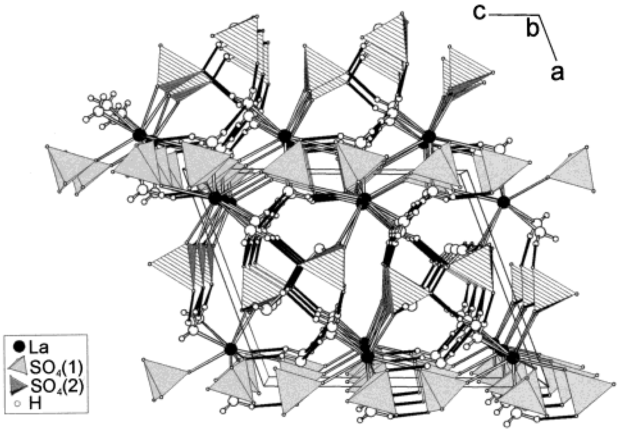

Figure 53. Crystal structure of $H_3OLa(SO_4)_2 \cdot 3H_2O$; hydrogen bonds are emphasized as black lines.

A further hydrogensulfate of neodymium is Nd$(HSO_4)(S_2O_7)$, which has been obtained by treating Nd_2O_3 with fuming sulfuric acid.[500] This compound is interesting because it is the first disulfate of a rare-earth element. In the crystal structure the $S_2O_7^{2-}$ ion acts as a chelating ligand to a Nd^{3+} ion and as a monodentate ligand to three further Nd^{3+} ions. One oxygen atom of the disulfate group remains uncoor-

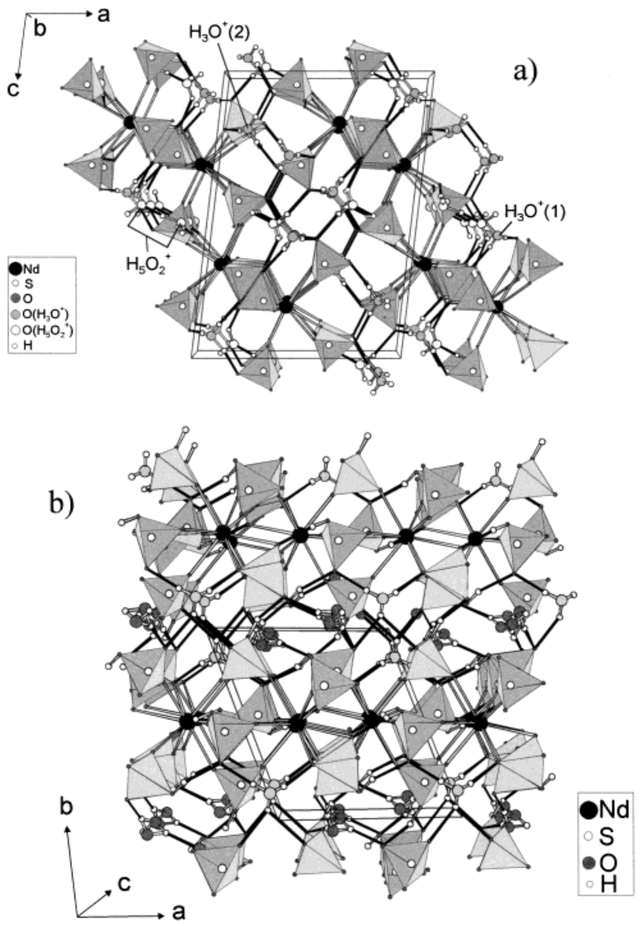

Figure 54. Crystal structures of the acidic neodymium sulfates $(H_5O_2)(H_3O)_2Nd(SO_4)_3$ (a) and $(H_3O)_2Nd(HSO_4)_3$-SO_4 (b).

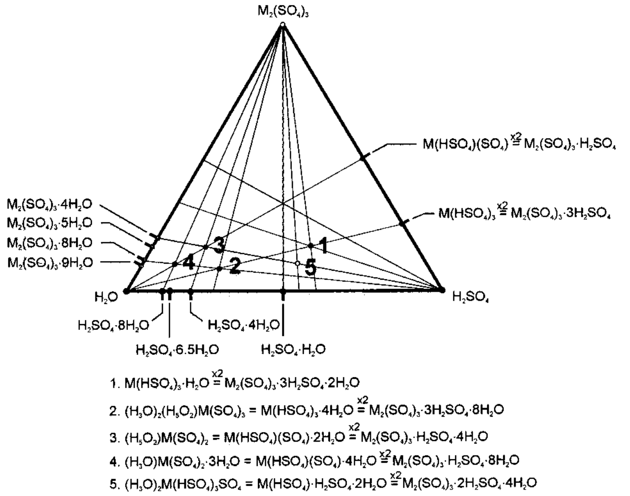

Figure 55. Phase diagram for the acidic rare-earth sulfates known so far.

dinated and acts as the acceptor in a hydrogen bridge (Figure 56). According to $^3_\infty[Nd(S_2O_7)_{4/4}(HSO_4)_{3/3}]$, the Nd^{3+} ions are 8-fold coordinated.

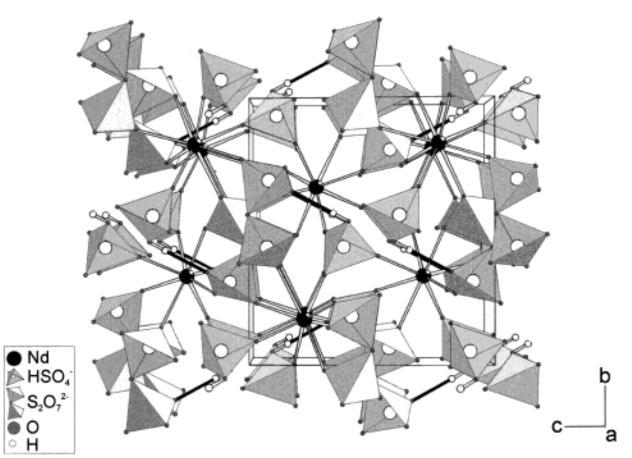

Figure 56. Crystal structure of the mixed disulfate−hydrogensulfate $Nd(HSO_4)(S_2O_7)$.

5. Halide Sulfates

In 1970 Kilian and Matthes investigated the reaction of rare-earth oxidesulfates, $M_2O_2SO_4$, with gaseous HCl. They found that chloride sulfates, $MClSO_4$, were the reaction products, but they were not able to determine the crystal structure of these compounds because no single crystals had been obtained.[501−504] Recently, a structure determination was possible on single crystals which were prepared by the reaction of the trichlorides MCl_3 with the respective sulfate, $M_2(SO_4)_3$, at higher temperatures.[505−507] Two structure types are known to date. With the larger lanthanides La and Pr, a structure is formed which contains M^{3+} ions coordinated by three Cl^- and five SO_4^{2-} ions.[505] Two of the latter act as a chelating ligand, leading to a CN of 10 for the M^{3+} ions. The anions are arranged in layers which extend in the (199) plane (Figure 57a) and are surrounded by three and five M^{3+} ions, respectively, so that one may formulate the linkage according to $^3_\infty[MCl_{3/3}$-$(SO_4)_{5/5}]$. For the smaller lanthanides Sm−Tb, another type of structure has been found which shows the lanthanide ions in 9-fold coordination of three Cl^- ions and six oxygen atoms.[506,507] The latter belong to five sulfate groups with one of them as a chelating ligand. The main difference between the two structures is the arrangement of the anions. As can be seen from Figure 57b for the example of $GdClSO_4$, layers of sulfate groups and layers of chloride ions are now stacked alternating. The structure is closely related to the one of $Nd_2(SO_4)_3$ in a way that layers of sulfate groups in the latter are substituted for Cl^- ions (cf Figure 39).

Fluoride sulfates of the rare-earth elements can be obtained from the reaction of the anhydrous sulfates with LiF in sealed gold ampules. For M = Gd, Tb, Lu, and Y, the crystal structures of $MFSO_4$-type compounds have been solved based on single-crystal data.[506,507] They are isotypic with each other and can be seen as a rod packing from cationic $^1_\infty[M(F)_{2/2}]^{2+}$ and anionic $^1_\infty[SO_4]^{2-}$ columns (Figure 58). The coordination number of the M^{3+} ions is eight. Besides the two F^- ions, six oxygen atoms from five SO_4^{2-} groups contribute to the dodecahedral $[MF_2O_6]$ coordination polyhedron. If the analogous reaction is performed with the sulfates of the larger lanthanides, the simple fluoride sulfates are not obtained but the lithium-containing species $LiM_2F_3(SO_4)_2$ (M = La−Eu).[508,509] A characteristic feature of the monoclinic crystal structure is the dimeric building unit $[M_2F_5(SO_4)_{10}]^{19-}$ which arises from the connection of two $[LaF_4(SO_4)_5]$

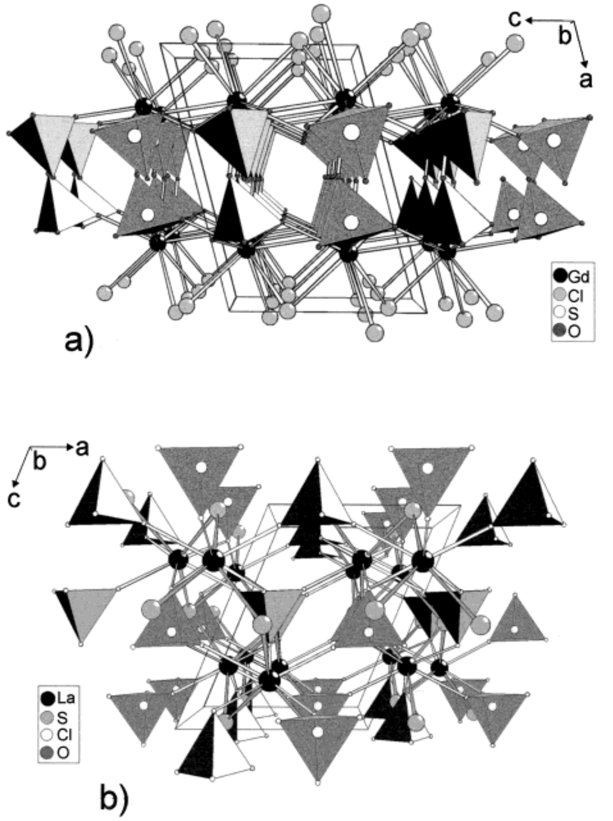

Figure 57. Two modifications of the chloride sulfates $MClSO_4$ on the examples of $GdClSO_4$ (a) and $LaClSO_4$ (b). The layer structure of $GdClSO_4$ is similar to that of $Nd_2(SO_4)_3$ (cf. Figure 39).

polyhedra via three common F^- ions. The dimeric units are linked with each other to chains by fluoride and sulfate anions (Figure 59a). The Li^+ ion is surrounded by four oxygen atoms and one F^- ion. The space for the lithium ion is quite large, as indicated by the distances Li−O of around 2.4 Å. Thus, it is possible to replace Li^+ by Na^+, and the respective fluoride sulfates $NaPr_2F_3(SO_4)_2$ and $NaEu_2F_3(SO_4)_2$ have been prepared (Table 10).[509,510] Compounds of the same composition could be also obtained for the smaller lanthanides Er and Yb under similar synthesis conditions. They show in principle the same crystal structure, but the lower coordination number of the M^{3+} ions (CN 8) leads to an orthorhombic symmetry (Figure 59b). Furthermore, the $M^{3+}-M^{3+}$ distances within the dimeric building units are significantly shorter (3.55 Å) and may cause interest for magnetic measurements on these compounds.

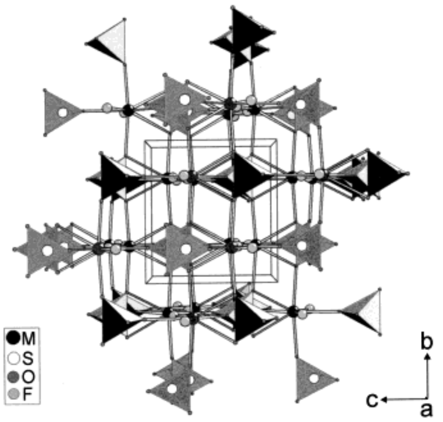

Figure 58. Crystal structure of the fluoride sulfates $MFSO_4$ (M = Gd, Tb, Lu, Y); cationic chains $^1_\infty[M(F)_{2/2}]^+$ and anionic $^1_\infty[SO_4]^{2-}$ columns are arranged along the [100] direction.

6. Amidosulfates

Although amidosulfates (sulfamates) have been investigated intensively for main-group and transition metals,[511] the knowledge of the respective compounds of the f-elements is very limited. In 1960 Capestan pointed out that lanthanide oxides dissolve in aqueous amidosulfuric acid and amidosulfates with various water content can be obtained by evaporation of these solutions.[512] However, in the following years no attempts have been undertaken to characterize the compounds, and only recently the crystal structures of $La(NH_2SO_3)_3 \cdot 2.5H_2O$ and $M(NH_2SO_3)_3 \cdot 2H_2O$ (M = Pr−Lu, Y) (Table 11) and their thermal behavior have been investigated.[513−515] According to these studies in $La(NH_2SO_3)_3 \cdot 2.5H_2O$, La^{3+} is coordinated by nine oxygen atoms in the form of a monocapped square antiprism. The oxygen atoms belong to seven $NH_2SO_3^-$ groups and two H_2O

Table 10. Crystallographic Data of Halide Sulfates

		lattice parameters						
compound	space group	*a*/Å	*b*/Å	*c*/Å	α/°	β/°	γ/°	ref
$LaCl(SO_4)$	$P2_1/n$	6.7588(7)	8.1506(9)	8.5141(9)		112.58(3)		505
$PrCl(SO_4)$	$P2_1/n$	6.6927(9)	8.0167(7)	8.436(1)		112.37(1)		505
$SmCl(SO_4)$	$P2_1/c$	9.480(1)	6.6101(8)	6.854(1)		104.65(1)		509
$GdCl(SO_4)$	$P2_1/c$	9.4371(9)	6.5759(8)	6.801(1)		104.87(2)		506
$GdF(SO_4)$	*Pnma*	8.436(1)	7.0176(8)	6.4338(7)				506
$TbF(SO_4)$	*Pnma*	8.390(1)	7.004(1)	6.4248(9)				509
$LuF(SO_4)$	*Pnma*	8.287(2)	6.905(1)	6.377(1)				509
$YF(SO_4)$	*Pnma*	8.309(1)	6.933(1)	6.411(1)				509
$LiLa_2F_3(SO_4)_2$	*I*2/*a*	8.283(2)	6.947(1)	14.209(3)		95.31(2)		508
$LiCe_2F_3(SO_4)_2$	*I*2/*a*	8.220(1)	6.914(1)	14.031(2)		95.11(2)		509
$LiPr_2F_3(SO_4)_2$	*I*2/*a*	8.1897(8)	6.8805(9)	14.017(1)		95.25(1)		509
$LiSm_2F_3(SO_4)_2$	*I*2/*a*	8.071(1)	6.7766(7)	13.857(2)		95.62(1)		509
$LiEr_2F_3(SO_4)_2$	*Pbcn*	14.791(3)	6.336(1)	8.137(1)				508
$LiYb_2F_3(SO_4)_2$	*Pbcn*	14.658(1)	6.3290(7)	8.0737(8)				509
$NaPr_2F_3(SO_4)_2$	*I*2/*a*	8.223(1)	6.9212(7)	14.199(2)		95.88(2)		510
$NaNd_2F_3(SO_4)_2$	*I*2/*a*	8.190(2)	6.895(1)	14.142(3)		96.03(2)		509
$NaEu_2F_3(SO_4)_2$	*I*2/*a*	8.070(1)	6.781(1)	13.959(2)		95.84(1)		509

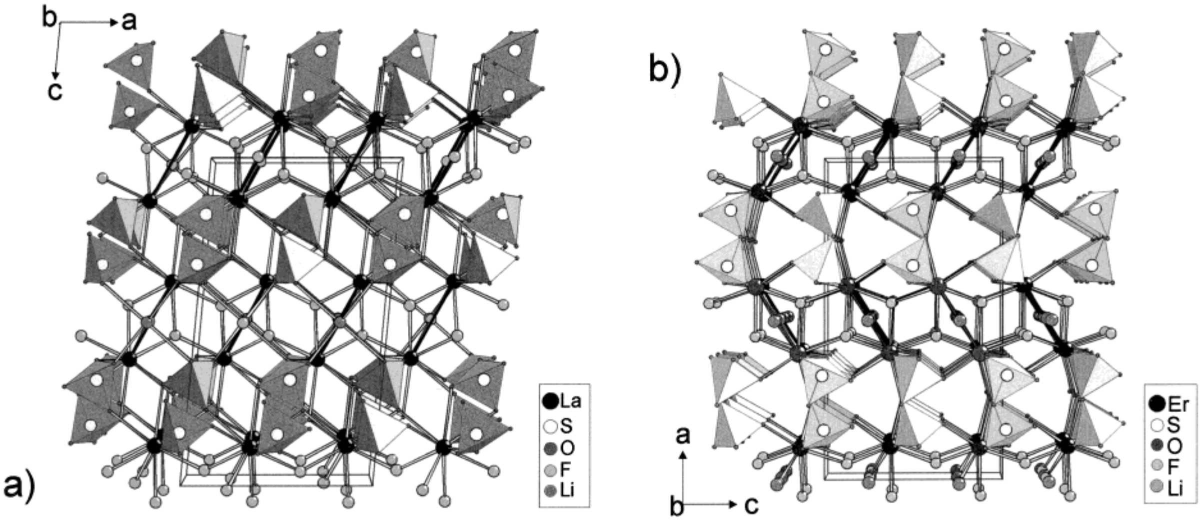

Figure 59. Crystal structures of the fluoride sulfates $LiLa_2F_3(SO_4)_2$ (a) and $LiEr_2F_3(SO_4)_2$ (b).

Table 11. Crystallographic Data of Amidosulfates and Methanesulfonates

compound	space group	lattice parameters a/Å	b/Å	c/Å	α/°	β/°	γ/°	ref
				amidosulfates				
$La(NH_2SO_3)_3{\cdot}2.5H_2O$	$I2/a$	14.139(3)	9.297(2)	19.106(6)		105.60(3)		513
$Pr(NH_2SO_3)_3{\cdot}2H_2O$	$P\bar{1}$	7.921(1)	9.144(1)	9.254(1)	117.69(1)	95.18(1)	92.25(1)	514
$Nd(NH_2SO_3)_3{\cdot}2H_2O$	$P\bar{1}$	7.898(1)	9.114(2)	9.218(2)	117.59(2)	95.24(2)	92.24(2)	514
$Sm(NH_2SO_3)_3{\cdot}2H_2O$	$P\bar{1}$	7.824(1)	9.068(2)	9.164(2)	117.61(2)	95.11(2)	92.10(2)	514
$Gd(NH_2SO_3)_3{\cdot}2H_2O$	$P\bar{1}$	7.831(1)	9.051(1)	9.111(1)	117.20(2)	95.27(2)	92.42(2)	515
$Tb(NH_2SO_3)_3{\cdot}2H_2O$	$P\bar{1}$	7.845(1)	9.077(1)	9.131(1)	117.19(2)	95.26(2)	92.55(2)	515
$Dy(NH_2SO_3)_3{\cdot}2H_2O$	$P\bar{1}$	7.843(1)	9.044(2)	9.106(2)	117.05(2)	95.25(2)	92.50(2)	515
$Ho(NH_2SO_3)_3{\cdot}2H_2O$	$P\bar{1}$	7.814(3)	9.033(3)	9.094(5)	117.00(5)	95.18(6)	92.60(5)	515
$Y(NH_2SO_3)_3{\cdot}2H_2O$	$P\bar{1}$	7.808(1)	9.033(2)	9.067(2)	116.98(2)	95.26(2)	92.68(2)	515
$Er(NH_2SO_3)_3{\cdot}2H_2O$	$P\bar{1}$	7.780(1)	8.995(1)	9.022(1)	116.81(1)	95.28(1)	92.65(1)	515
$Tm(NH_2SO_3)_3{\cdot}2H_2O$	$P\bar{1}$	7.749(1)	8.971(1)	9.007(2)	116.99(2)	95.12(2)	92.29(2)	515
$Yb(NH_2SO_3)_3{\cdot}2H_2O$	$P\bar{1}$	7.785(1)	8.991(2)	9.028(1)	116.80(2)	95.28(2)	92.71(2)	515
$Lu(NH_2SO_3)_3{\cdot}2H_2O$	$P\bar{1}$	7.747(1)	8.956(1)	8.988(1)	116.71(1)	95.28(1)	92.81(1)	515
$Sm(NH_2SO_3)_3{\cdot}H_2O$	$P\bar{1}$	6.815(1)	9.397(2)	9.431(2)	68.06(2)	75.30(2)	83.34(2)	514
$Tb(NH_2SO_3)_3{\cdot}H_2O$	$P\bar{1}$	6.755(1)	9.359(2)	9.377(2)	68.26(2)	75.80(2)	83.58(2)	515
$Nd(NH_2SO_3)(SO_4){\cdot}1.5H_2O$	$P1$	6.892(1)	6.914(1)	9.620(2)	109.64(2)	97.00(2)	109.62(2)	515
	$I1^a$	9.779(2)	7.596(1)	11.130(2)	90.69(2)	115.06(2)	88.98(2)	515
$La(NH_2SO_3)_3$	$P6_3/m$	9.835 (1)		5.8803(7)				513
				methanesulfonates				
$La(CH_3SO_3)_3{\cdot}2H_2O$	$P\bar{1}$	5.2499(8)	10.153(2)	12.980(2)	98.63(2)	91.12(2)	104.61(2)	522
$Ce(CH_3SO_3)_3{\cdot}2H_2O$	$P2_1/c$	9.489(1)	14.319(2)	9.837(1)		91.22(2)		524
$Nd(CH_3SO_3)_3{\cdot}2H_2O$	$P\bar{1}$	5.2218(9)	10.109(2)	12.880(2)	98.27(2)	91.79(2)	104.91(2)	523
$Nd(CH_3SO_3)_3{\cdot}2H_2O$	$P2_1/c$	9.446(1)	14.278(2)	9.792(1)		91.16(1)		524
$Sm(CH_3SO_3)_3{\cdot}2H_2O$	$P2_1/c$	9.381(1)	14.179(2)	9.743(3)		91.19(2)		524
$Sm(CH_3SO_3)_3{\cdot}2H_2O$	$P2_1/c$	9.392(2)	14.195(2)	9.740(2)		91.18(2)		525
$Sm(CH_3SO_3)_3{\cdot}3H_2O$	$P\bar{1}$	6.103(1)	10.316(2)	11.746(2)	85.15(2)	78.24(2)	81.69(2)	525
$Gd(CH_3SO_3)_3{\cdot}3H_2O$	$P\bar{1}$	6.093(1)	10.315(3)	11.664(3)	85.23(3)	78.39(3)	81.76(3)	525
$Tb(CH_3SO_3)_3{\cdot}2H_2O$	$P2_1/c$	9.313(3)	14.072(3)	9.664(3)		91.09(3)		524
$Dy(CH_3SO_3)_3{\cdot}3H_2O$	$P\bar{1}$	6.068(1)	10.296(2)	11.591(2)	85.30(2)	78.36(2)	81.58(2)	525
$La(CH_3SO_3)_3$	$P6_3/m$	9.9826(6)		5.9797(6)				522
$Nd(CH_3SO_3)_3$	$P2_1$	5.0233(7)	11.231(2)	9.987(1)		104.46(2)		523
$Er(CH_3SO_3)_3$	$P2_1$	9.847(2)	5.1334(7)	11.874(2)		107.16(2)		525
$Yb(CH_3SO_3)_3$	$P2_1$	9.798(5)	5.094(2)	11.837(5)		107.16(4)		524
$Lu(CH_3SO_3)_3$	$P2_1$	9.789(2)	5.0854(7)	11.864(2)		107.22(2)		525
$ScOH(CH_3SO_3)$	$Pmc2_1$	7.4392(8)	14.977(3)	15.401(2)				526

[a] Alternative setting of $P1$.

molecules (Figure 60a). Three of the amidosulfate groups connect to two additional La^{3+} ions; the remaining four are attached to another La^{3+} ion. Thus, the connection can be written as $La(H_2O)_2(NH_2SO_3)_{3/3}(NH_2SO_3)_{4/2}$. The linkage occurs exclusively in the *a*−*b* plane, yielding infinite sheets which are held together by hydrogen bonds which also involve the water molecules located between the sheets. The dihydrates $M(NH_2SO_3)_3{\cdot}2H_2O$ are isotypic throughout the series Ce−Lu including Y and crystallize with triclinic symmetry. The coordination polyhedron of the M^{3+} ion is a distorted square antiprism of oxygen atoms which belong to six $NH_2SO_3^-$ groups and two H_2O molecules (Figure 60b). All of the three crystallographically different amidosulfate groups are bound via oxygen atoms to

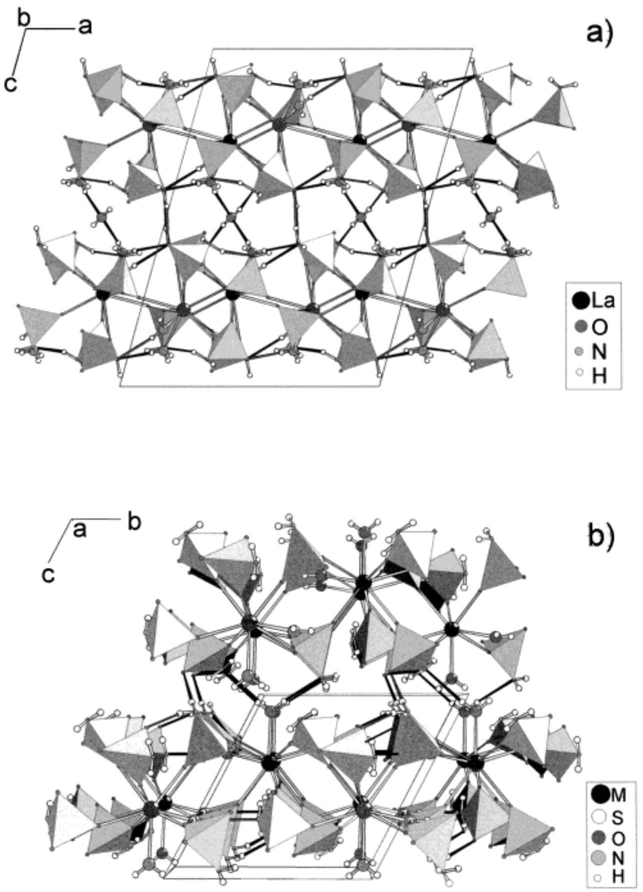

Figure 60. Crystal structures of the hydrated amidosulfates $La(NH_2SO_3)_3{\cdot}2.5H_2O$ and $M(NH_2SO_3)_3{\cdot}2H_2O$ (M = Ce−Lu,Y).

two Pr^{3+} ions according to $[Pr(H_2O)_{2/1}(NH_2SO_3)_{6/2}]$. Just as in $La(NH_2SO_3)_3{\cdot}2.5H_2O$, the linkage occurs only in two dimensions, leading to sheets which are again only connected via hydrogen bonding. In contrast to the lanthanum compound, there are no additional water molecules between the sheets (Figure 60). The thermal decomposition of $La(NH_2SO_3)_3{\cdot}2.5H_2O$ and the dihydrates of Pr and Sm have been studied by means of DTA/TG measurements and temperature-dependent X-ray powder diffraction. The first step of the decomposition is the loss of water. In the case of $Pr(NH_2SO_3)_3{\cdot}2H_2O$ (Figure 61a) and $Sm(NH_2SO_3)_3{\cdot}2H_2O$ (Figure 61b), a monohydrate can be observed as an intermediate. The crystal structure of the monohydrates could be solved for $Sm(NH_2SO_3)_3{\cdot}H_2O$ and $Tb(NH_2SO_3)_3{\cdot}H_2O$.[514,515] They also crystallize with a triclinic symmetry, and the CN of eight for the M^{3+} ions is retained compared to the dihydrates. This is achieved by a higher connectivity of one of the three crystallographically different amidosulfate groups which is linking three Sm^{3+} ions with each other according to $Sm(H_2O)(NH_2SO_3)_{3/3}(NH_2SO_3)_{4/2}$. The linkage of the Sm^{3+} polyhedra and the $NH_2SO_3^-$ tetrahedra again leads to infinite sheets only connected via hydrogen bridges.

The anhydrous amidosulfates which were obtained after complete dehydration were shown to be isotypic for M = La, Ce−Sm and adopt the structure which was previously described for the respective hydrogensulfates. For $La(NH_2SO_3)_3$, a single-crystal structure determination has been performed.[513] It shows that the OH group of the hydrogensulfates is now replaced by a NH_2 group without structural changes (Figure 62). The anhydrous amidosulfates of the rare-earth elements decompose in two steps yielding the respective sulfates. With respect to the mass loss and the DTA signals, a different mechanism can be assumed for the larger lanthanides M = La, Pr and the smaller ones with M = Sm, Er, but clarity can only be achieved by identification of the intermediates. Interestingly, the decomposition of the amidosulfate dihydrates follow a different route when it is carried out in a closed system. For $Nd(NH_2SO_3)_3{\cdot}2H_2O$ it has been found that heating in an argon atmosphere leads to the mixed sulfate−amidosulfate $Nd(NH_2SO_3)(SO_4){\cdot}1.5H_2O$ which crystallizes triclinic with the acentric space group *P*1.[515] By choosing the alternative setting *I*1 of this space group one can see that the structure is nearly monoclinic (Figure 63). The crystal structure contains two crystallographically different Nd^{3+} ions. $Nd(1)^{3+}$ is surrounded by four $NH_2SO_3^-$ groups, two SO_4^{2-} groups, and one H_2O molecule. Both sulfate groups act as bidentate ligands, so that the coordination number of $Nd(1)^{3+}$ is nine. The coordination polyhedron is a distorted tricapped trigonal prism. $Nd(2)^{3+}$ is 8-fold coordinated by oxygen atoms in the form of a square antiprism. The oxygen atoms belong to four sulfate groups, two $NH_2SO_3^-$ groups, and two water molecules. Each SO_4^{2-} group is connected to three Nd^{3+} ions; each $NH_2SO_3^-$ group is attached to two Nd^{3+} ions, so the connectivity can be written as $[Nd(1)(SO_4)_{2/3}(NH_2SO_3)_{4/3}(H_2O)_{1/1}]$ and $[Nd(2)(SO_4)_{4/3}(NH_2SO_3)_{2/3}(H_2O)_{2/1}]$, respectively. In contrast to the hydrates discussed so far, $Nd(NH_2SO_3)(SO_4){\cdot}1.5H_2O$ has no layer structure. The polyhedra are connected to a three-dimensional network as can be seen from Figure 63.

7. Methanesulfonates

The methanesulfonates of the rare-earth elements are known as hydrates (Table 11) and adducts with organic molecules such as TMSO (tetramethylenesulfoxide) and others.[516−519] In a few cases also crystal structures of the anhydrous compounds are known.

Hydrates were obtained from solutions of the rare-earth sesquioxides in aqueous solutions of methane sulfonic acid and crystallize with two or three molecules of water.[520−525] For the dihydrates two different crystal structures occur. Modification I, which has been found for La and Nd,[522,523] contains the M^{3+} ions in 9-fold coordination of oxygen atoms with slightly distorted tricapped trigonal prisms as coordination polyhedra. The oxygen atoms belong to six $CH_3SO_3^-$ ions and three water molecules. Four of the methane sulfonate groups and two of the water molecules connect the polyhedra to infinite chains along [100]. The remaining two $CH_3SO_3^-$ ions link two of these chains to double chains (Figure 64a). The connectivity may be written as ${}^{1}_{\infty}[M(H_2O)(H_2O)_{2/2}(CH_3SO_3)_{6/2}]$. The double chains are connected with each other only by hydrogen bonds with the terminal water molecules and the CH_3 groups as donors and noncoordinating oxygen atoms of the $CH_3SO_3^-$ ions as acceptors. The

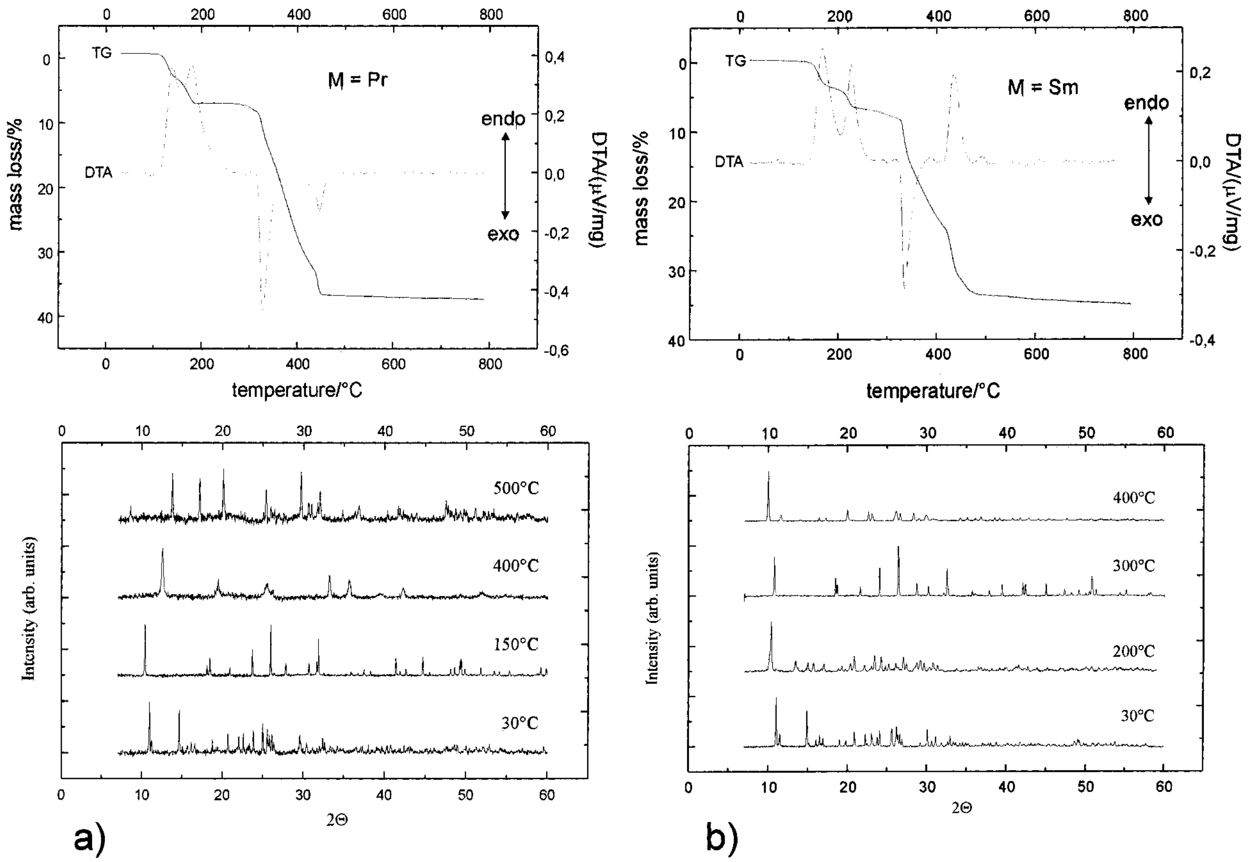

Figure 61. Thermal decomposition of $Pr(NH_2SO_3)_3 \cdot 2H_2O$ (a) and $Sm(NH_2SO_3)_3 \cdot 2H_2O$ (b) followed by DTA/TG measurements and temperature-dependent X-ray powder diffraction.

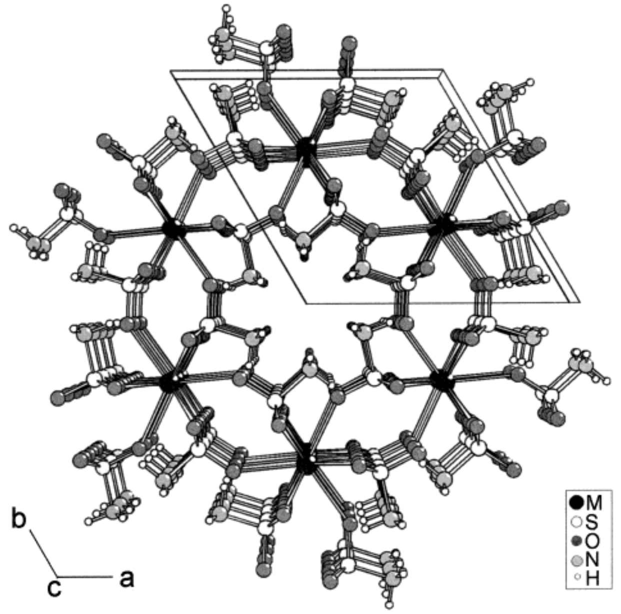

Figure 62. Crystal structure of $La(NH_2SO_3)_3$ viewed along the [001] direction. Note, the same structure is also found for $La(ClO_4)_3$, $La(HSO_4)_3$, and $La(CH_3SO_3)_3$.

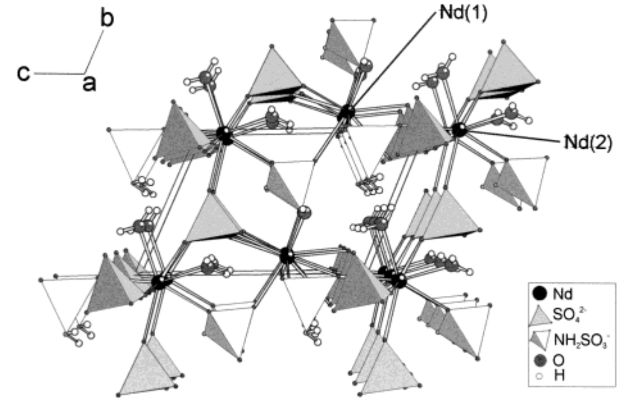

Figure 63. Crystal structure of $Nd(NH_2SO_3)(SO_4) \cdot 1.5H_2O$. The compound is triclinic (space group *P*1), but if the unit cell is transformed to the setting *I*1, the pseudo-monoclinic symmetry is obvious.

second modification for the dihydrates which has been found with M = Ce–Tb[523–525] and also for neodymium shows a layer structure. The crystal structure contains the M^{3+} ions in 8-fold coordination of oxygen. The oxygen atoms belong to six $CH_3SO_3^-$ groups and two H_2O molecules. Each methanesulfonate ions is connected to a further M^{3+} ion according to $^{2}_{\infty}[M(H_2O)_{2/1}(CH_3SO_3)_{6/2}]$. The linkage of the $[MO_8]$ polyhedra via the $CH_3SO_3^-$ groups occurs only in the (100) plane and leads to puckered layers (Figure 64b). These are held together by hydrogen bonds involving the water molecules and CH_3 groups as donors and noncoordinating oxygen atoms of the methanesulfonate ions as acceptors.

In the crystal structure of the trihydrates $M(CH_3SO_3)_3 \cdot 3H_2O$ (M = Sm, Gd, Dy), three H_2O molecules and five $CH_3SO_3^-$ ions are attached to M^{3+} ions. According to $^{1}_{\infty}[M(H_2O)_{3/1}(CH_3SO_4)_{4/2}(SO_4)_{1/1}]$, four of the latter act as bidentate bridging ligands while one of them is monodentate. The chains are held together by hydrogen bonds. The thermal decomposition of the

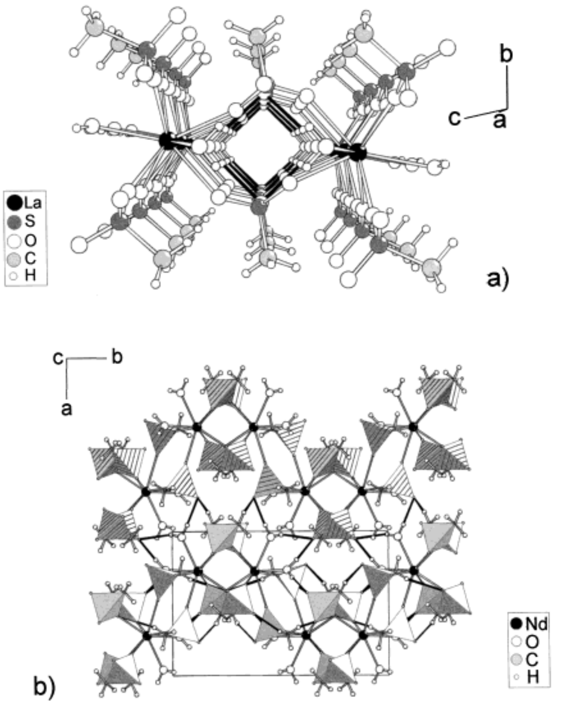

Figure 64. Two modifications of the dihydrates $M(CH_3SO_3)_3{\cdot}2H_2O$ contain double chains $^{1}_{\infty}[M(H_2O)(H_2O)_{2/2}(CH_3SO_3)_{6/2}]$ as shown for the lanthanum compound (a) or puckered sheets $^{2}_{\infty}[M(H_2O)_{2/1}(CH_3SO_3)_{6/2}]$ as depicted for the neodymium compound (b).

hydrates has been followed by temperature-dependent powder diffraction and DSC/TG measurements including the mass spectroscopic detection of released particles.[522,523] The first step can be attributed to dehydration, which leads to the anhydrous compounds. For $La(CH_3SO_3)_3$ the structure could be derived from its powder pattern which could be indexed based on the single-crystal data of $La(NH_2SO_3)_3$.[522] Thus, the methanesulfonate crystallizes also with the hexagonal structure that can be seen as a derivative of the UCl_3 type of structure and which has still been discussed for the hydrogensulfates of the larger lanthanides. This structure occurs obviously only for lanthanum. With the slightly smaller Nd^{3+} ion, another structure has been determined which consists of layers built up from $[NdO_8]$-polyhedra and $CH_3SO_3^-$ ions.[523] Nd^{3+} is surrounded by eight methanesulfonate groups. Six of the latter are attached to three Nd^{3+} ions, while the remaining two are coordinated to only two Nd^{3+} ions. The noncoordinating oxygen atoms of these $CH_3SO_3^-$ ions act as acceptors in hydrogen bonds with the CH_3 groups of adjacent layers as donors. These hydrogen bonds are known to be much weaker than those with oxygen atoms of water molecules as donors for instance. This modification of $Nd(CH_3SO_3)_3$ undergoes a phase transition at higher temperature leading to a crystal structure that is known for $Er(CH_3SO_3)_3$[525] and $Yb(CH_3SO_3)_3$.[524] Thus, the structure changes in a way that the layers found in $Nd(CH_3SO_3)_3$−I are cut into double chains running along [010] which are again connected via hydrogen bonds. If the two structures are viewed in the [100] direction (I) and [010] direction (II), respectively, they turned out to be quite similar (Figure 65). As a result of the decreasing connection of polyhedra, the coordination number of Nd^{3+} decreases to seven and, furthermore, the molar volume expands remarkably. Upon further heating the anhydrous methane sulfonates decompose in a complicated way to give the oxide disulfides $M_2O_2S_2$ and, finally, M_2O_2S. The mass numbers detected during this process indicate the formation of CO, CO_2, SO_2, SO_3, H_2O, and possibly CH_2O and CH_4 during the reaction.[523]

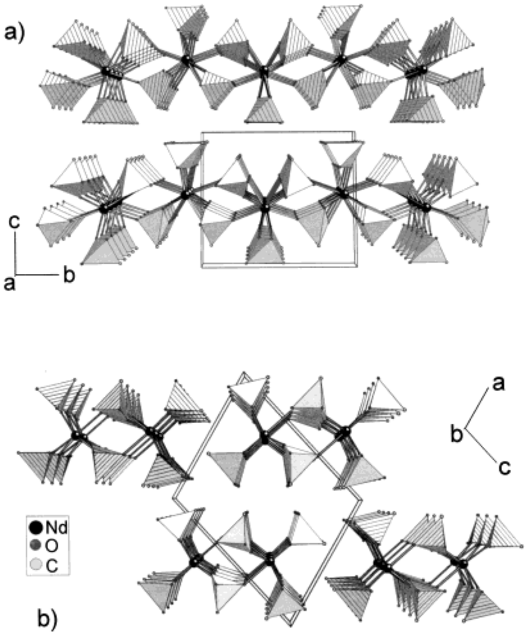

Figure 65. Crystal structure of $Nd(CH_3SO_3)_3$−I (a) and $Nd(CH_3SO_3)_3$−I (b).

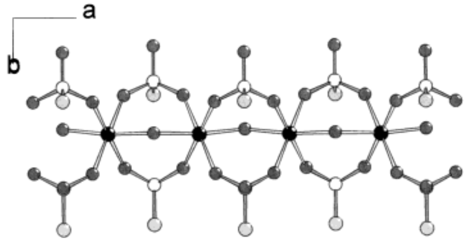

Figure 66. Chain $^{1}_{\infty}[Sc_2(OH)_{2/2}(CH_3SO_3)_{4/2}]$ in the crystal structure of $ScOH(CH_3SO_3)_2$.

Single crystals of the basic scandium methanesulfonate $ScOH(CH_3SO_3)_2$ were obtained from a solution of Sc_2O_3 in methanesulfonic acid at pH 7.[526] According to the X-ray single-crystal determination, the orthorhombic compound contains the Sc^{3+} ions in an octahedral coordination of oxygen atoms belonging to two OH^- and four $CH_3SO_3^-$ ions. The linkage of the Sc^{3+} ions leads to chains according to the formulation $^{1}_{\infty}[Sc_2(OH)_{2/2}(CH_3SO_3)_{4/2}]$ which are oriented along [100] and held together by hydrogen bonds (Figure 66).

D. Selenates

Similarly to the sulfates, the known crystal structures of the rare-earth selenates are mainly restricted to binary and ternary hydrates. They are closely related to the respective sulfates as one would expect from the identical structure and the comparable volume of the anions. On the other hand, the thermal

Table 12. Crystallographic Data of Selenates

compound	space group	lattice parameters						ref
		a/Å	b/Å	c/Å	α/°	β/°	γ/°	
selenate−hydrates								
$La_2(SeO_4)_3 \cdot 12H_2O$	$C2/c$	10.670(2)	20.390(6)	10.740(2)		110.12(2)		531
$Nd_2(SeO_4)_3 \cdot 8H_2O$	$C2/c$	7.102(1)	13.992(2)	18.253(3)		99.84(2)		530
$Sm_2(SeO_4)_3 \cdot 8H_2O$	$C2/c$	7.014(1)	13.878(1)	18.121(2)		99.40(1)		527
$Eu_2(SeO_4)_3 \cdot 8H_2O$	$C2/c$	7.004(1)				99.37		530
$Er_2(SeO_4)_3 \cdot 8H_2O$	$C2/c$	13.728(2)	6.8751(7)	18.602(3)		101.85(2)		530
$Yb_2(SeO_4)_3 \cdot 8H_2O$	$C2/c$	13.704(6)	6.831(3)	18.507(7)		101.90(3)		528
$Yb_2(SeO_4)_3 \cdot 8H_2O$	$C2/c$	13.751(2)	6.8544(9)	18.549(2)		101.80(2)		530
$Y_2(SeO_4)_3 \cdot 8H_2O$	$C2/c$	13.772(2)	6.883(1)	18.650(2)		101.84(2)		530
$Pr_2(SeO_4)_3 \cdot 4H_2O$	$P2_1/n$	13.367(2)	7.404(1)	13.670(2)		92.11(2)		529
$Sc_2(SeO_4)_3 \cdot 5H_2O$	$P\bar{1}$	11.225(4)	11.804(3)	5.766(2)	91.30(4)	100.10(2)	89.03(7)	533
$Sc_2(SeO_4)_3 \cdot 5H_2O$	$P\bar{1}$	5.789(1)	11.239(1)	11.851(1)	89.12(1)	88.81(1)	79.84(1)	530
$Sc_2(SeO_4)_3 \cdot 5H_2O$	$P\bar{1}$	9.109(1)	10.631(1)	17.286(2)	72.21(1)	79.84(1)	89.87(1)	530
$La_2(SeO_4)_3 \cdot 5H_2O$	$P2_1/a$	9.879(1)	14.199(2)	10.761(1)		92.78(2)		530
$Ce_2(SeO_4)_3 \cdot 5H_2O$	$P21/a$	9.820(3)	14.050(5)	10.690(5)		92.00(4)		532
$Ce_2(SeO_4)_3 \cdot 5H_2O$	$P2_1/c$	10.722(2)	14.101(2)	9.876(1)		93.18(2)		530
$Gd_2(SeO_4)_3 \cdot 4H_2O$	$P\bar{1}$	6.947(1)	9.317(2)	10.882(2)	94.81(2)	106.88(2)	99.33(2)	530
anhydrous selenates								
$Sc_2(SeO_4)_3$	$P2_1/c$	8.899(2)	9.212(2)	15.179(3)		124.83(2)		539
$Yb_2(SeO_4)_3$	$P2_1/n$	9.220(2)	9.521(2)	12.886(3)		91.04(1)		540
$Ce(SeO_4)_2$	$Pbca$	9.748(2)	9.174(1)	13.740(3)				541
ternary selenates								
$CsNd(SeO_4)_2 \cdot 4H_2O$	$P2_1/c$	6.850(3)	19.479(5)	8.974(4)		94.80(3)		542
$RbCe(SeO_4)_2 \cdot 5H_2O$	$P2_1/c$	7.200(2)	8.723(1)	19.258(6)		90.88(2)		543
$(NH_4)Pr(SeO_4)_2 \cdot 5H_2O$	$Pccn$	7.019(1)	9.865(2)	17.497(2)				544
$NaLa(SeO_4)_2 \cdot 2H_2O$	$P2_1/c$	11.421(2)	7.135(2)	11.178(2)		107.5(1)		*a*
$RbNd(SeO_4)_2 \cdot 3H_2O$	$P\bar{1}$	5.843(1)	7.021(3)	13.261(1)	91.50(4)	95.33(2)	106.76(2)	545
$KEr(SeO_4)_2 \cdot H_2O$	$P\bar{1}$	5.676(8)	8.611(9)	9.298(8)	108.7(1)	84.1(1)	106.2(1)	*b*
$KPr(SeO_4)_2$	$P2_1/c$	8.823(1)	7.371(1)	11.139(1)		91.33(1)		546
$KDy(SeO_4)_2$	$Pna2_1$	27.470(2)	5.657(1)	8.989(1)				547
$NaPr(SeO_4)_2$	$P\bar{1}$	6.639(1)	7.118(1)	7.361(1)	99.16(2)	96.93(2)	89.77(3)	548
$(NH_4)_3Sc(SeO_4)_3$	$R3$	15.567(5)		9.871(3)				549
$Na_{3.68}Dy_{1.44}(SeO_4)_4$	$I4_1/a$	10.655(1)		12.290(1)				550
acidic selenates								
$La(HSeO_4)_3$	$P6_3/m$	9.717(1)		6.1698(8)				551
$GdH(SeO_4)_2$	$Pbca$	9.204(1)	13.516(2)	10.040(1)				551
$EuH(SeO_4)_2$	$Pbca$	9.232(5)	13.514(6)	10.061(4)				552
$Nd(HSeO_4)(Se_2O_7)$	$Pna2_1$	11.275(2)	6.1836(7)	12.281(2)				553
$ScH(SeO_4)_2 \cdot 2H_2O$	$C2/m$	8.708(5)	5.632(4)	9.105(9)		101.64(7)		554
$(H_5O_2)Sc(SeO_4)_2$	$C2/m$	8.6835(8)	5.6139(6)	9.080(1)		101.75(2)		555
$NaEr(HSeO_4)_2(SeO_4) \cdot 5H_2O$	Pn	11.158(2)	5.7615(7)	11.3893(9)		98.47(2)		556
$H_3OCe^{3+}Ce^{4+}(SeO_4)_4$	Cc	12.297(2)	16.267(2)	9.295(1)		129.51(1)		557

[a] Ovanisyan, S. M.; Iskhakova, L. D.; Trunov, V. K. *Kristallografiya* **1986**, *31*, 1081. [b] Ovanisyan, S. M.; Iskhakova, L. D. *Kristallografiya* **1988**, *33*, 1375.

behavior of sulfates and selenates is completely different. The selenates decompose at lower temperature compared to the sulfates, e.g., single crystals of the anhydrous species are even harder to get than for the sulfates. The lower decomposition temperature can be attributed to the higher stability of the oxidation state IV for selenium. Thus, the product of the first decomposition step of the anhydrous selenates is not an oxide selenate as found for the sulfates but the anhydrous selenite. The higher stability of SeO_3^{2-} compared to SO_3^{2-} makes it much easier to prepare single-crystalline selenites than anhydrous sulfites as will be pointed out later in section III.

1. Selenate Hydrates

Single crystals of rare-earth selenates have been studied to a lesser extent than the respective sulfates. As far as one knows there is a close relationship to the lanthanide sulfates. Thus, from aqueous solutions one obtains mainly the octahydrates $M_2(SeO_4)_3 \cdot 8H_2O$.[527−530] Besides the crystal structure that has already been described for the sulfate octahydrates (Table 7), a second modification has been found for M = Pr, Nd, and Sm (cf. Table 12). Compared to modification I it shows the same connection of $[MO_8]$ polyhedra and SeO_4^{2-} tetrahedra to layers according to $[M(H_2O)_{4/1}(SO_4(1))_{3/3}(SO_4(2))_{1/2}]_2$ which are linked via hydrogen bonds only. However, the arrangement of the polyhedra with respect to each other is different in the two structure types. With $La_2(SeO_4)_3 \cdot 12H_2O$ there is one example for a highly hydrated rare-earth selenate which has no analogue among the respective sulfates.[531] The compound has a layered crystal structure with the La^{3+} ions in 9-fold coordination of oxygen atoms. One-half of the H_2O molecules are coordinated to La^{3+} ions while the remaining are fixed between the layers via hydrogen bonds. Three pentahydrates are known, namely, $La_2(SeO_4)_3 \cdot 5H_2O$,[530] $Ce_2(SeO_4)_3 \cdot 5H_2O$,[532] and $Sc_2(SeO_4)_3 \cdot 5H_2O$.[530,533] The lanthanum and the cerium compound are isotypic and show similar structural characteristics with the respective sulfates although the space

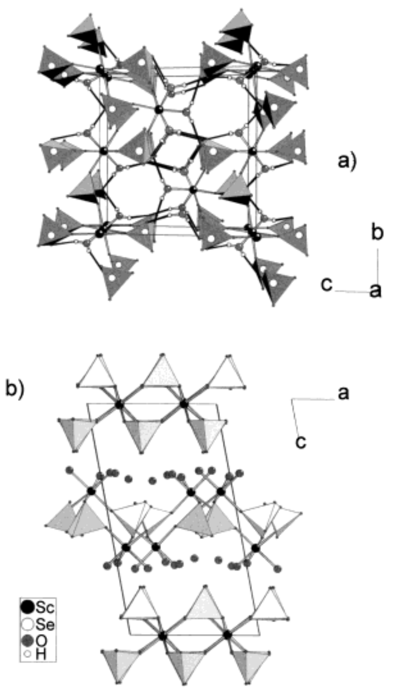

Figure 67. Crystal structures of the two modifications of $Sc_2(SeO_4)_3{\cdot}5H_2O$. While all of the H_2O are coordinated to Sc^{3+} ions in $Sc_2(SeO_4)_3{\cdot}5H_2O{-}I$ (a), modification II contains nonbonded crystal water molecules (b).

group is $P2_1/c$ in contrast to the sulfates. There are two crystallographically different M^{3+} ions in the structure which are coordinated by nine and eight oxygen atoms. In analogy to the sulfates, one of the H_2O molecules is not bonded to a cation but fixed by hydrogen bonds in the structure. For $Sc_2(SeO_4)_3{\cdot}5H_2O$, two modifications are known. Both of them contain the Sc^{3+} ions in octahedral coordination of oxygen atoms. $Sc_2(SeO_4)_3{\cdot}5H_2O{-}I$ has the same structure as $Sc_2(SO_4)_3{\cdot}5H_2O$, and thus, all water molecules are coordinated to scandium ions.[533] Formerly the space group $P1$ was given for the compound, but because of the obvious isotypy with the sulfate it is likely that the space group is $P\bar{1}$. In the triclinic crystal structure of $Sc_2(SeO_4)_3{\cdot}5H_2O{-}II$ the two crystallographically different Sc^{3+} ions are octahedrally coordinated by oxygen atoms.[530] For $Sc(1)^{3+}$ the oxygen atoms belong to six selenate groups which are themselves surrounded by three Sc^{3+} ions. In that way anionic sheets according to $^2_\infty[Sc(1)(SeO_4)_{6/3}]^-$ are formed. $Sc(2)^{3+}$ is attached by three SeO_4^{2-} ions and three H_2O molecules. Again, the SeO_4^{2-} groups are linked to three Sc^{3+} ions leading to cationic layers according to $^2_\infty[Sc(2)(H_2O)_{3/1}(SeO_4)_{3/3}]^+$. Cationic and anionic layers are stacked alternating parallel to (001) (Figure 67). The remaining two H_2O molecules are located between these layers. The selenate hydrates with the lowest water content which were structurally characterized are $Pr_2(SeO_4)_3{\cdot}4H_2O$[532] and $Gd_2(SeO_4)_3{\cdot}4H_2O$.[530] The praseodymium compound is isotypic with the respective sulfate and the gadolinium selenate with $Er_2(SO_4)_3{\cdot}4H_2O$.

Investigations of the thermal behavior of the selenate hydrates were carried out for various compositions mainly by DTA/TG measurements.[534−537] Similarly to the findings for the sulfate hydrates, the decomposition starts with the loss of water yielding the anhydrous species. The dehydration often occurs not in one step but with lower hydrates as intermediates. Thus, upon heating, $La_2(SeO_4)_3{\cdot}12H_2O$ leads to the octahydrate in the first step,[538] and for $Er_2(SeO_4)_3{\cdot}8H_2O$ a trihydrate has been assumed as an intermediate,[530] in analogy to the decomposition of $Er_2(SO_4)_3{\cdot}8H_2O$. On the other hand, the decomposition of the anhydrous selenates is different compared to the sulfates. While the latter form oxide sulfates at higher temperature, the selenates decompose to the respective selenites, $M_2(SeO_3)_3$, in the first step. The different behavior can be attributed to the higher stability of the oxidation state IV for selenium compared to sulfur. Upon further heating the selenites lose successively SeO_2 under formation of $MO(SeO_3)_2$, $MO_2(SeO_3)$, and finally M_2O_3.[530,534−538] The following general decomposition scheme may be formulated

$$M_2(SeO_4)_3{\cdot}xH_2O \rightarrow M_2(SeO_4)_3 + xH_2O\uparrow$$

$$M_2(SeO_4)_3 \rightarrow M_2(SeO_3)_3 + {}^3/_2O_2\uparrow$$

$$M_2(SeO_3)_3 \rightarrow M_2O(SeO_3)_2 + SeO_2$$

$$M_2O(SeO_3)_2 \rightarrow M_2O_2(SeO_3) + SeO_2$$

$$M_2O_2(SeO_3) \rightarrow M_2O_3 + SeO_2$$

One should be aware that not all of the above-mentioned intermediates have necessarily been seen. Besides the nature of the specific rare-earth element, the decomposition scheme depends strongly on the experimental conditions such as heating rates, gas atmosphere, and sensitivity of the measuring device.

2. Anhydrous Selenates

Although the anhydrous selenates are known as intermediates in the thermal decomposition of the selenate hydrates, structural data are still scarce. Single-crystal investigations have only been undertaken for $Sc_2(SeO_4)_3$,[539] $Yb_2(SeO_4)_3$,[540] and $Ce(SeO_4)_2$.[541] The latter is isotypic with $Ce(SO_4)_2$ and thus shows a three-dimensional network according to $^3_\infty[Ce(SeO_4)_{8/4}]$ (cf. section II.C.2). The structural features of $Sc_2(SeO_4)_3$ and $Yb_2(SeO_4)_3$ are identical with each other and with those of the lighter rare-earth sulfates: the M^{3+} ions are coordinated by six monodentate SeO_4^{2-} groups which are attached to four M^{3+} ions. Nevertheless, the symmetry is not rhombohedral or orthorhombic as in the case of the sulfates but monoclinic. However, from temperature-dependent powder diffraction measurements of the decomposition of $Er_2(SeO_4)_3{\cdot}8H_2O$ and $Yb_2(SeO_4)_3{\cdot}8H_2O$ there is some evidence that the anhydrous selenates are polymorphic and can adopt the symmetries of the respective sulfates.[530]

3. Ternary Selenates

As it can be seen from Table 12, the number of structurally characterized ternary selenates is quite limited. $CsNd(SeO_4)_2{\cdot}4H_2O$[542] is isotypic with the sulfate $CsPr(SO_4)_2{\cdot}4H_2O$, and thus, the structure has

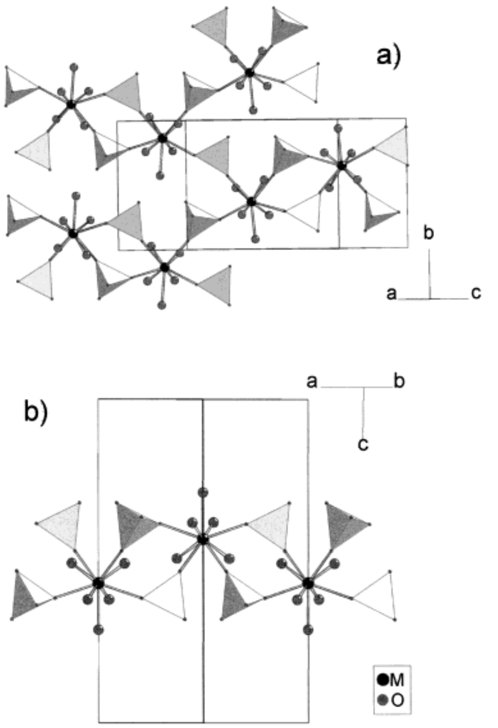

Figure 68. Layers ${}^{2}_{\infty}[M(SeO_4)_{4/2}(H_2O)_5]^-$ (a) and chains ${}^{1}_{\infty}[M(SeO_4)_{4/2}(H_2O)_5]^-$ (b) in the crystal structures of $RbCe(SeO_4)_2{\cdot}5H_2O$ and $(NH_4)Pr(SeO_4)_2{\cdot}5H_2O$, respectively.

to be formulated according to ${}^{2}_{\infty}[M(SeO_4)_{4/2}(H_2O)_3]^-$ as described for the respective sulfates. The pentahydrates $RbCe(SeO_4)_2{\cdot}5H_2O$[543] and $(NH_4)Pr(SeO_4)_2{\cdot}5H_2O$[544] which have no sulfate analogues contain 9-fold oxygen-coordinated M^{3+} ions. The oxygen atoms originate from five H_2O molecules and four selenate groups. In the rubidium compound the linkage of the polyhedra leads to layers ${}^{2}_{\infty}[M(SeO_4)_{4/2}(H_2O)_5]^-$ (Figure 68a), while in the ammonium compound infinite chains according to ${}^{1}_{\infty}[M(SeO_4)_{4/2}(H_2O)_5]^-$ occur (Figure 68b). In the triclinic crystal structure of $RbNd(SeO_4)_2{\cdot}3H_2O$, the Nd^{3+} ions are 8-fold coordinated.[545] The lower H_2O content leads to a higher connectivity of the polyhedra to double sheets ${}^{2}_{\infty}[M(SeO_4)_{3/3}(SeO_4)_{2/2}(H_2O)_5]^-$ which are held together by the A^+ ions.

Among the anhydrous ternary selenates, $KPr(SeO_4)_2$[546] also has a layer structure while the other two compounds, $KDy(SeO_4)_2$[547] and $NaPr(SeO_4)_2$,[548] have three-dimensional structures with the A^+ ions incorporated in the voids formed. In accordance with the ionic radii, Pr^{3+} is 9-fold coordinated in both compounds and Dy^{3+} has a CN of 8 in $KDy(SeO_4)_2$. Anhydrous ternary selenates with a different M^{3+}/A^+ ratio are $(NH_4)_3Sc(SeO_4)_3$[549] with anionic chains of $[ScO_6]$ octahedra and selenate tetrahedra, as may be formulated by ${}^{1}_{\infty}[Sc(SeO_4)_{6/2}]^{3-}$ and the complicated nonstoichiometric selenate $Na_{3.68}Dy_{1.44}(SeO_4)_4$[550] with a mixed occupation of the cationic sites by Dy^{3+} and Na^+.

4. Acidic Selenates

The only homoleptic hydrogenselenate known so far is $La(HSeO_4)_3$,[51] which can be prepared from La_2O_3 and concentrated selenic acid. It crystallizes isotypically with the respective hydrogensulfate and adopts a structure which can be seen as a derivative of the UCl_3 type of structure with complex anions. The mixed selenate hydrogenselenates $Gd(HSeO_4)(SeO_4)$[551] and $Eu(HSeO_4)(SeO_4)$[552] are isotypic with each other and contain the M^{3+} ions in 8-fold coordination of oxygen atoms which belong to four selenate and four hydrogenselenate groups. Each of the anions is attached to four M^{3+} ions, leading to a three-dimensional structure. The hydrogen atom of the $HSeO_4^-$ group is involved in a asymmetric bifurcated hydrogen bond (Figure 69). The diselenate hydrogenselenate $Nd(HSeO_4)(Se_2O_7)$ is not isotypic with the analogous sulfate.[553] In the crystal structure Nd^{3+} is surrounded by six $Se_2O_7^{2-}$ and three $HSeO_4^-$ ions. The anions are monodentate, and tricapped trigonal prisms $[NdO_9]$ are formed. These are linked to chains in the [010] direction which are connected further by $HSeO_4^-$ groups in the [001] and $Se_2O_7^{2-}$ in the [100] direction (Figure 70). $Nd(HSeO_4)(Se_2O_7)$ is the first example for the investigation of crystals containing

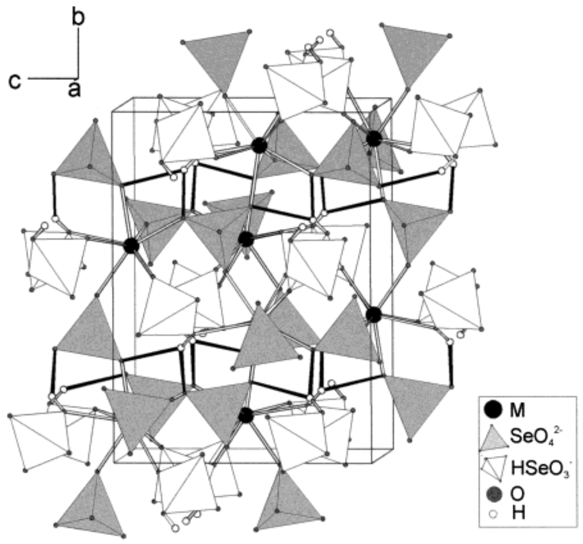

Figure 69. Crystal structure of the mixed hydrogenselenate−selenates $M(HSeO_4)(SeO_4)$ (M = Eu, Gd); $HSeO_4^-$ ions are drawn as light gray tetrahedra.

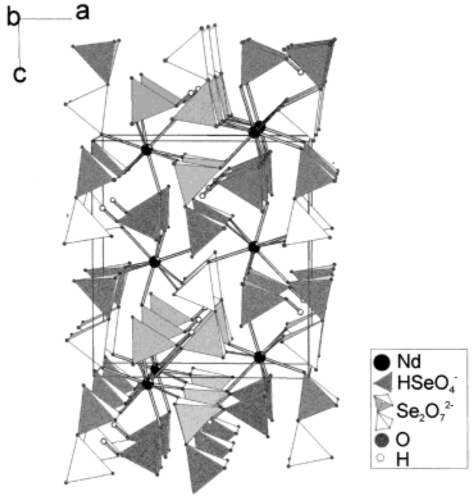

Figure 70. Crystal structure of the diselenate $Nd(HSeO_4)(Se_2O_7)$.

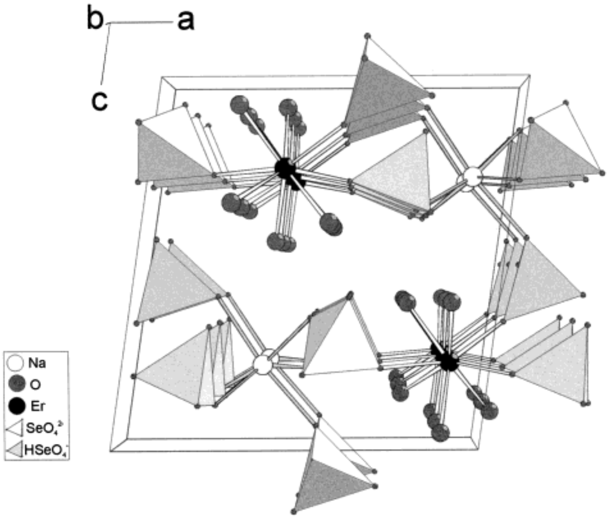

Figure 71. Crystal of the ternary acidic selenate $NaEr(HSeO_4)_2(SeO_4)\cdot 5H_2O$. Note, the H_2O molecules are exclusively bonded to the Er^{3+} ions.

$Se_2O_7^{2-}$ ions by X-ray methods. The angle Se−O−Se within the ion is 124° and comparable to the one of the disulfate ion $S_2O_7^{2-}$. A reinvestigation of the crystal structure of $ScH(SeO_4)_2\cdot 2H_2O$[554] showed that the compound contains $H_5O_2^+$ ions and should preferably be formulated as $(H_5O_2)Sc(SeO_4)_2$.[555] The $H_5O_2^+$ ions are located between sheets built from $[ScO_6]$ octahedra and selenate tetrahedra. The bond length O−O of 2.47 Å within the oxonium ion hints at a strong hydrogen bond.

Besides these binary acidic selenates there is one example for a ternary selenate. $NaEr(HSeO_4)_2(SeO_4)\cdot 5H_2O$[556] contains both hydrogenselenate and selenate groups. The H_2O molecules are exclusively coordinated to Er^{3+} ions which have additionally two SeO_4^{2-} ions and one $HSeO_4^-$ group as ligands (CN 8). Na^+ is surrounded by four selenate and two hydrogenselenate ions which act as monodentate ligands. The linkage of the coordination polyhedra leads to the three-dimensional structure shown in Figure 71. A three-dimensional structure is also found for the structure of the unique mixed-valent cerium compound $(H_3O)Ce_2(SeO_4)_4$.[557] The selenate groups are connected with the $[CeO_8]$ polyhedra via vertexes. The different oxidation state of the cations is significantly reflected by the Ce−O distances.

E. Perchlorates

1. Perchlorate Hydrates

The perchlorate ion, ClO_4^-, is known to be a very weak ligand. Thus, it shows very little tendency to enter the inner coordination sphere of a cation. This is especially true for the lanthanide ions. From aqueous solutions containing M^{3+} and ClO_4^- ions one obtains under ambient conditions exclusively complexes with only water molecules coordinated to the M^{3+} ions. The number of water molecules in the crystal structures has been reported to be 9, 8, or 7,[558,559] but to date structure determinations have been undertaken only for the hexahydrates (Table 13) which exist for the whole series La−Lu and should be formulated as $[M(H_2O)_6](ClO_4)_3$.[560] In the cubic crystal structure the M^{3+} ions are octahedrally coordinated and the perchlorate groups are highly disordered (Figure 72).

Upon heating the hexahydrates melt around 100 °C and the melt loses water molecules over a wide temperature range from 160 to 300 °C followed by complete decomposition of the perchlorate yielding MOCl. Although no significant plateaus can be seen in the thermogravimetry curve, it is possible to obtain lower hydrates by heating the hexahydrates to a certain temperature (Figure 73). For example, the heating of $Yb(ClO_4)_3\cdot 6H_2O$ to 140 °C under an argon

Table 13. Crystallographic Data of Perchlorates

		lattice parameters						
compound	space group	a/Å	b/Å	c/Å	α/°	β/°	γ/°	ref
		perchlorate−hydrates						
$La(ClO_4)_3\cdot 6H_2O$	$Fm\bar{3}m$	12.173(5)						560
$Tb(ClO_4)_3\cdot 6H_2O$	$Fm\bar{3}m$	11.926(5)						560
$Er(ClO_4)_3\cdot 6H_2O$	$Fm\bar{3}m$	11.900(7)						560
$Tb(ClO_4)_3\cdot 3H_2O$	$P\bar{1}$	7.521(1)	11.441(2)	14.879(4)	105.60(3)	100.66(3)	103.51(2)	565
$Lu(ClO_4)_3\cdot 3H_2O$	$P\bar{1}$	7.503(1)	8.384(1)	10.546(2)	79.77(2)	79.18(2)	63.83(2)	563
$Yb(ClO_4)_3\cdot 2H_2O$	$I2/a$	10.575(3)	10.309(3)	11.138(3)		116.66(3)		561
$Yb(ClO_4)_3\cdot H_2O$	$P\bar{1}$	7.802(3)	9.473(4)	6.755(2)	78.14(2)	75.58(2)	77.21(2)	561
$Yb(ClO_4)_3\cdot H_2O$	$P\bar{1}$	7.855(1)	9.549(1)	6.810(1)	78.05(2)	75.63(2)	77.15(2)	562
$Er(ClO_4)_3\cdot H_2O$	$P\bar{1}$	7.834(1)	9.559(1)	6.7831(9)	78.31(1)	75.71(1)	77.29(1)	563
$Pr(ClO_4)_3\cdot H_2O$	$Pnma$	5.8001(7)	7.6235(9)	10.899(2)				564
		anhydrous perchlorates						
$Pr(ClO_4)_3$	$P6_3/m$	9.3361(3)		5.8488(2)				567
$Eu(ClO_4)_3$	$P6_3/m$	9.2496(9)		5.7486(8)				568
$Dy(ClO_4)_3$	$P6_3/m$	9.238(1)		5.6656(6)				565
$Er(ClO_4)_3$	$P6_3/m$	9.197(1)		5.598(1)				567
$Yb(ClO_4)_3$	$P6_3/m$	9.2197(1)		5.5352(1)				566
$Yb(ClO_4)_3$	$R3c$	8.1241(1)		24.0818(1)				566
$Yb(ClO_4)_3$	$R3c$	8.167(2)		24.336(7)				561
		basic perchlorates						
$[\{Nd_6O\}(OH)_8(H_2O)_{24}](ClO_4)_8\cdot 8H_2O$	$P4/mnc$	14.4999(8)		15.249(1)				572
$[\{Sm_6O\}(OH)_8(ClO_4)2H_2O)_{20}](ClO_4)_6\cdot 4H_2O$	$C2/c$	23.583(2)	12.032(1)	21.112(2)		109.99(8)		573
$[\{Gd_6O\}(OH)_8(ClO4)2H_2O)_{20}](ClO_4)_6\cdot 4H_2O$	$C2/c$	23.149(2)	11.9086(6)	21.010(2)		110.220(4)		572
$ScOH(ClO_4)_2\cdot H_2O$	$P2_1/n$	9.428(1)	7.352(8)	11.579(2)		93.76		563

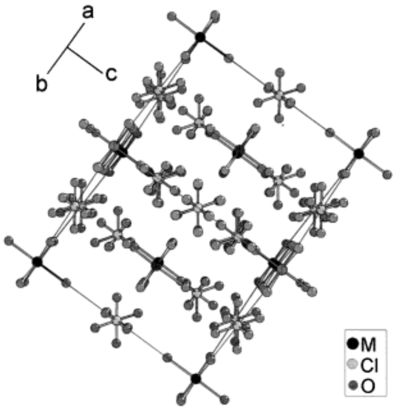

Figure 72. In the crystal structure of the perchlorate hexahydrates $[M(H_2O)_6](ClO_4)_3$, the M^{3+} ions are surrounded only by water molecules and the perchlorate ions are highly disordered.

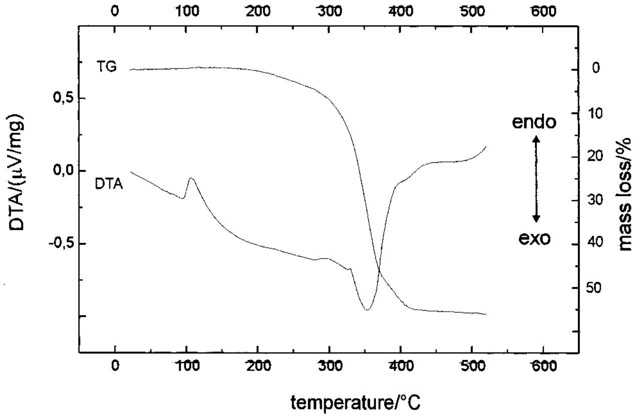

Figure 73. DTA/TG diagram for the thermal decomposition of $Yb(ClO_4)_3{\cdot}6H_2O$. The DTA signal around 100 °C is not accompanied by a mass loss and indicates that the compound melts in its crystal water.

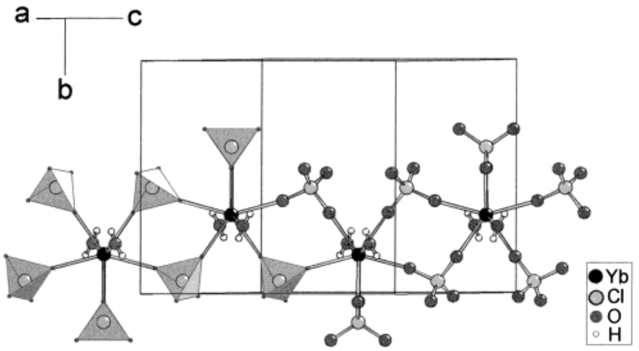

Figure 74. Chains ${}^{1}_{\infty}[Yb(H_2O)_2(Cl(1)O_4)_{1/1}(Cl(2)O_4)_{4/2}]$ in the crystal structure of $Yb(ClO_4)_3{\cdot}2H_2O$.

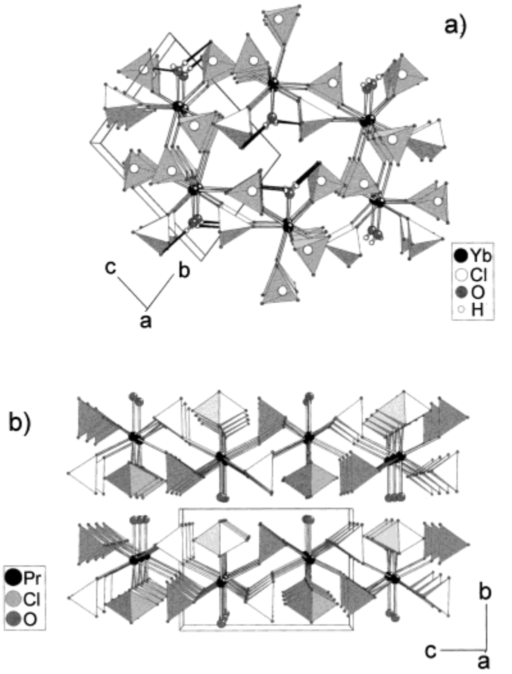

Figure 75. Three-dimensional structure of $Yb(ClO_4)_3{\cdot}H_2O$ (a) and two-dimensional layer structure of $Pr(ClO_4)_3{\cdot}H_2O$ (b).

stream led to the ytterbium perchlorates $Yb(ClO_4)_3{\cdot}2H_2O$[561] and $Yb(ClO_4)_3{\cdot}H_2O$.[561,562] Variation of the procedure like the use of higher temperatures or vacuum conditions led furthermore to the hydrates $Er(ClO_4)_3{\cdot}H_2O$,[563] $Pr(ClO_4)_3{\cdot}H_2O$,[564] $Tb(ClO_4)_3{\cdot}3H_2O$,[565] and $Lu(ClO_4)_3{\cdot}3H_2O$.[563]

The crystal structure of $Yb(ClO_4)_3{\cdot}2H_2O$ contains Yb^{3+} in 8-fold coordination of oxygen atoms. The latter belong to two water molecules and five ClO_4^- groups, which can be divided into two crystallographically different species, $Cl(1)O_4^-$ and $Cl(2)O_4^-$. $Cl(1)O_4^-$ is attached to only one Yb^{3+} ion as a chelating ligand. Each of the four $Cl(2)O_4^-$ perchlorate ligands is coordinated to a second Yb^{3+} ion, leading to chains ${}^{1}_{\infty}[Yb(H_2O)_2(Cl(1)O_4)_{1/1}(Cl(2)O_4)_{4/2}]$ running along [001] (Figure 74). The chains are connected with each other via hydrogen bonds involving the H_2O molecules as donors and noncoordinating oxygen atoms of the ClO_4^- ions as acceptors. In the crystal structure of $Yb(ClO_4)_3{\cdot}H_2O$ and the isotypic erbium compound, besides the water molecule, seven monodentate ClO_4^- groups are connected to the M^{3+} ions leading to a coordination number of eight. Four of these groups are attached to a further M^{3+} ion; the remaining three are coordinated to two additional M^{3+} ions creating a three-dimensional network according to ${}^{3}_{\infty}[M(H_2O)_{1/1}(ClO_4)_{3/3}(ClO_4)_{4/2}]$ (Figure 75a). Hydrogen bonding is observed with the H_2O molecules as donors and noncoordinating O atoms of the ClO_4^- ions as acceptors within the bridge. For $Pr(ClO_4)_3{\cdot}H_2O$ a coordination number of nine is observed for Pr^{3+} with a tricapped trigonal prism as coordination polyhedron. The $[PrO_9]$ and ClO_4^- polyhedra are linked to layers which are held together by hydrogen bonds (Figure 75b). One of the perchlorate groups seems to be disordered, but there is some evidence that this is the effect of a complicated superstructure.[564]

In the crystal structure of $Lu(ClO_4)_3{\cdot}3H_2O$[563] Lu^{3+} is surrounded by eight O atoms in the form of a distorted square antiprism. Five of the O atoms belong to just as many ClO_4^- groups, the remaining three to water molecules. Four of the ClO_4^- ions (2 × $ClO_4(2)^-$, 2 × $ClO_4(3)^-$) connect to further Lu^{3+} ions; the fifth one ($ClO_4(1)^-$) has no additional contact so that the connectivity may be written as $[Lu(H_2O)_{3/1}(ClO_4)_{1/1}(ClO_4)_{4/2}]$. The linkage of the $[LuO_8]$ polyhedra occurs only in one direction so that an infinite chain running along [10−1] is formed (Figure 76). The chain is connected with other ones only via

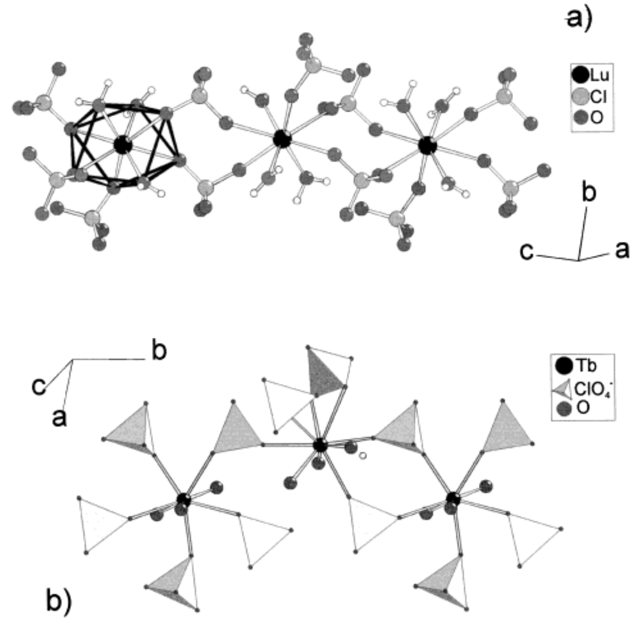

Figure 76. Similar chains $^1_\infty[M(H_2O)_{3/1}(ClO_4)_{1/1}(ClO_4)_{4/2}]$ in the crystal structures of the trihydrates $Lu(ClO_4)_3{\cdot}3H_2O$ (a) and $Tb(ClO_4)_3{\cdot}3H_2O$ (b).

hydrogen bridges. Oxygen atoms of the ClO_4^- groups which are not coordinated to the Lu^{3+} ions show significantly shorter Cl−O bonds (1.40−1.43 Å) than the coordinating ones (1.45−1.46 Å) and act as acceptors in the hydrogen bridges. $Tb(ClO_4)_3{\cdot}3H_2O$[565] also has a chain structure, but it is different in the sense that it contains two crystallographically different Tb^{3+} ions with one of them being in 9-fold coordination of oxygen atoms (Figure 76). Compared to the lutetium compound the increasing coordination number is achieved via the chelating attack of one of the six crystallographic different ClO_4^- ions.

2. Anhydrous Perchlorates

The anhydrous perchlorates can be obtained by complete dehydration of the respective hydrates. Usually this procedure leads only to powder samples so that no single-crystal structure determination can be performed. Nevertheless, a successful elucidation of the crystal structures of anhydrous rare-earth perchlorates was possible using synchrotron or neutron powder data.[566,567] Furthermore, it has been shown that the dehydration can be carried out in a way that even single crystals can be grown so that single-crystal data have become available.[561,568]

Two structure types for anhydrous rare-earth perchlorates are known (Table 13). Most of the lanthanides, namely, La−Tm and Y, crystallize with a hexagonal structure which has already been found for the hydrogensulfates and amidosulfates of the lighter rare-earth elements (cf. section II.C.3/4). Thus, the M^{3+} ions are coordinated by nine perchlorate groups which are attached to three M^{3+} ions leading to a three-dimensional structure according to $^3_\infty[M(ClO_4)_{9/3}]$. If the tetrahedra are regarded as spheres, the well-known UCl_3 type of structure arises (Figure 62). The anhydrous perchlorates of the smallest lanthanides Yb and Lu crystallizes with trigonal symmetry and the acentric space group $R3c$. The M^{3+} ions are surrounded by six perchlorate groups with the chlorine atoms forming an octahedron around the cations. Three of the ClO_4^- groups act as chelating ligands (Figure 77), so that a coordination number of nine results for M^{3+} with a coordination polyhedron which may be viewed as a distorted tricapped trigonal prism. Because there is crystallographically only one ClO_4^- group present, each chelating perchlorate ion to one Yb^{3+} is a monodentate ligand to a second one and vice versa. Thus, the connectivity may be written as $[Yb(ClO_4)_{6/2}]$. The arrangement of anions in $Yb(ClO_4)_3$ is very similar to that found for $Sc(H_2PO_4)_3$;[569] it can be understood as a hexagonal closest packing of tetrahedra with the cations in octahedral voids. Compared to the scandium compound in which the cation is only six-coordinated by oxygen, the ClO_4^- groups in $Yb(ClO_4)_3$ are tilted a little bit in order to increase the coordination number of Yb^{3+}. Both compounds are, however, in principle derivatives of the RhF_3 type of structure with complex anions. $Yb(ClO_4)_3$ has additionally be shown to be dimorphic and to adopt the UCl_3 type of structure at lower temperatures.[566]

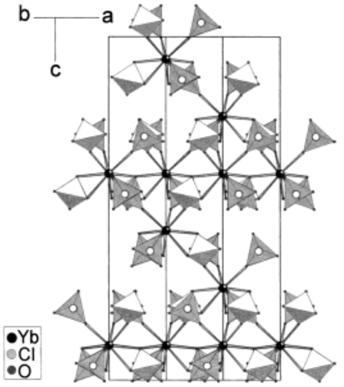

Figure 77. Crystal structure of $Yb(ClO_4)_3$. Three of the six ClO_4^- ions around Yb^{3+} are chelating ligands leading to a coordination number of nine for Yb^{3+}.

The thermal decomposition of the perchlorates occurs around 300 °C and leads usually to the oxide chlorides, MOCl. For $Yb(ClO_4)_3$ the oxide chloride Yb_3O_4Cl was observed also as a decomposition product[566] and $Ce(ClO_4)_3$ yielded exclusively CeO_2.[570] Mass spectrometric investigations of the products released during the decomposition of $Pr(ClO_4)_3$ showed that no Cl_2O is produced, as stated previously, but only O_2 and Cl_2 (Figure 78).[571]

3. Basic Perchlorates

The anhydrous scandium perchlorate cannot be prepared by dehydration of the respective hydrate. Instead, decomposition to the basic compound $ScOH(ClO_4)_2{\cdot}H_2O$ is always observed. Recently it was possible to obtain single crystals of the compound and to determine the crystal structure.[563] According to this investigation the crystal structure contains the Sc^{3+} ion octahedrally coordinated by three ClO_4^- groups, two OH^- ions, and one H_2O molecule. Two of these octahedra share one common edge, which is built from OH^- groups, to form pairs according to $[Sc_2(OH)_2(H_2O)_2(ClO_4)_6]^{2-}$ with a Sc^{3+}−Sc^{3+} distance of 3.20 Å (Figure 79). The $[Sc_2(OH)_2(H_2O)_2(ClO_4)_6]^{2-}$

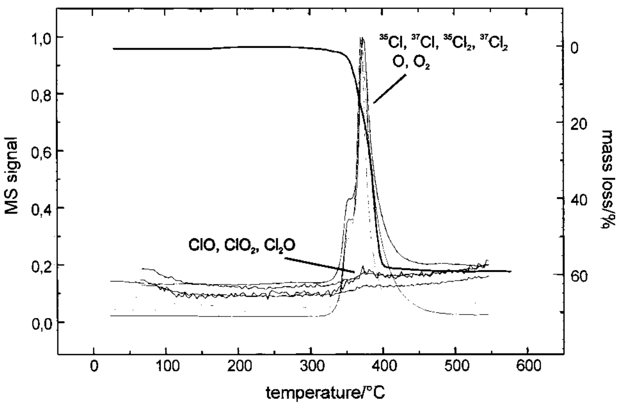

Figure 78. TG/MS diagram for the thermal decomposition of $Pr(ClO_4)_3$. The signals of the mass spectrometer indicate that only chlorine and oxygen are released during the decomposition.

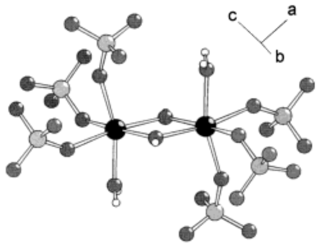

Figure 79. Anionic $[Sc_2(OH)_2(H_2O)_2(ClO_4)_6]^{2-}$ complex in the crystal structure of the basic perchlorate $ScOH(ClO_4)_2 \cdot H_2O$.

complex contains two crystallographically different perchlorate ions, $Cl(1)O_4^-$ (4×) and $Cl(2)O_4^-$ (2×). Each $Cl(1)O_4^-$ ion connects to a further Sc^{3+} ion yielding infinite layers, while $Cl(2)O_4^-$ is not connected to other Sc^{3+} ions. Hence, the connectivity must be formulated as $^{2}_{\infty}[Sc_2(OH)_2(H_2O)_2(ClO_4)_{4/2}(ClO_4)_{2/1}]$. The layers are connected via hydrogen bridges with the water molecules as donors and noncoordinating oxygen atoms O of the ClO_4^- ions as acceptors.

Another kind of basic perchlorate is obtained when an aqueous solution of lanthanide perchlorate is treated with an alkali hydroxide. The compounds known so far have the compositions $[Nd_6(\mu\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{24}](ClO_4)_8 \cdot 8H_2O$[572] and $[M_6(\mu\text{-}O)(\mu_3\text{-}OH)_8(\eta^2\text{-}ClO_4)_2(H_2O)_{20}](ClO_4)_6 \cdot 4H_2O$ (M = Sm,[573] Gd[572]) (Table 13). The common features of all compounds are oxygen-centered M_6 clusters which are capped with OH^- ions over each triangular face. Additionally, the cluster cores are surrounded by water molecules and for the isotypic Sm and Gd compounds by two chelating ClO_4^- ligands (Figure 80). The crystal structures contain further perchlorate groups for charge compensation and nonbonded H_2O molecules. The special arrangement of the metal ions leads to short distances $M^{3+}-M^{3+}$ of about 3.7−3.8 Å, but magnetic measurements show that there are no magnetic interactions, at least under ambient conditions.[572]

Note, the compounds described are the only basic perchlorates known so far. A number of others which were assumed to be basic perchlorates[574,575] turned out to be sulfates in fact.

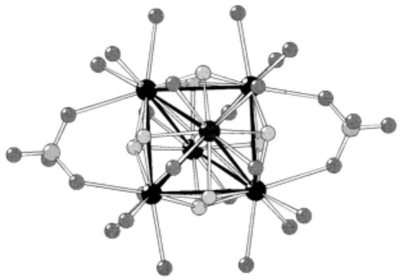

Figure 80. Complex cation $[M_6(\mu\text{-}O)(\mu_3\text{-}OH)_8(\eta^2\text{-}ClO_4)_2(H_2O)_{20}]^{6+}$ in the crystal structure of $[M_6(\mu\text{-}O)(\mu_3\text{-}OH)_8(\eta^2\text{-}ClO_4)_2(H_2O)_{20}](ClO_4)_6 \cdot 4H_2O$ (M = Sm, Gd).

III. Pyramidal Anions

A. Chalcogenites

This section deals with the rare-earth compounds containing SO_3^{2-} and SeO_3^{2-} ions as pyramidal complex anions. Because of the higher stability of Se^{+IV} compared to S^{+IV}, the crystal chemistry of the selenites is much better known and the reported crystal structures are quite numerous. Lanthanide compounds containing Te^{+IV} are not mentioned herein because hardly any of them can be seen as containing distinct $[TeO_3]^{2-}$ anions. The larger ionic radius of Te^{+IV} compared to Se^{+IV} leads to an increasing coordination number and in the structures known so far the Te^{+IV} ions have one or even more additional ligands.[576] Thus, there is only one example for an isotypic crystal structure of a rare-earth tellurite and selenite, namely $Ce(TeO_3)_2$ and $Ce(SeO_3)_2$.[577]

1. Sulfites

As far as one knows the rare-earth sulfites are precipitated as trihydrates or hexahydrates when SO_2 is passed into a slurry of the lanthanide oxides in water. Due to the low solubility of the sulfites, fine amorphous powders are obtained so that structural information is still scarce. To date, a structure determination has been performed only for $Gd_2(SO_3)_3 \cdot 3H_2O$.[578] The triclinic structure contains two crystallographically different Gd^{3+} ions which are in 8-fold coordination of oxygen atoms. For $Gd(1)^{3+}$ the oxygen atoms belong to six SO_3^{2-} groups and one H_2O molecule; $Gd(2)^{3+}$ is surrounded by two water ligands and five sulfite ions. In both cases one of the SO_3^{2-} ions is attached in a chelating way. Two of the three sulfite ions are attached to four Gd^{3+} ions; the third has three Gd^{3+} neighbors. The linkage leads to a three-dimensional network providing empty space for the lone pairs of the sulfite ions (Figure 81).

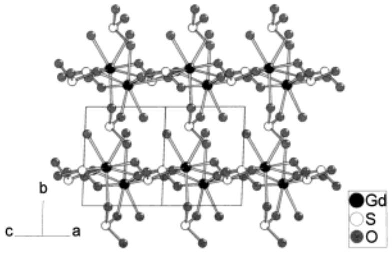

Figure 81. Crystal structure of $Gd_2(SO_3)_3 \cdot 3H_2O$ along [101].

Table 14. Crystallographic Data of Sulfites and Selenites

compound	space group	lattice parameters a/Å	b/Å	c/Å	α/°	β/°	γ/°	ref
				sulfites				
$Gd_2(SO_3)_3 \cdot 3H_2O$	$P1$	6.499(6)	6.621(3)	6.954(3)	110.71(5)	90.54(3)	106.05(1)	578
$(NH_4)_3Dy(SO_3)_3 \cdot H_2O$	$P2/m$	8.880	3.980	9.480		117.40		588
				selenites				
$Sm(HSeO_3)(SeO_3) \cdot 2H_2O$	$P2_12_12_1$	6.667(1)	7.031(1)	16.426(3)				596
$Nd(HSeO_3)(SeO_3) \cdot 2H_2O$	$P2_12_12_1$	6.699(4)	7.101(1)	16.39(2)				597
$Pr_2(HSeO_3)_2(SeO_3)_2$	$Pbc2_1$	7.0471(8)	8.3480(8)	18.987(3)				598
$La(HSe_2O_6)$	$Pc2_1b$	7.139(6)	19.008(9)	8.469(9)				599
$Sc(HSeO_3)_3$	Cc	11.130(2)	9.506(4)	7.598(2)		97.59(2)		604
$Nd_2(Se_2O_5)_3(H_2SeO_3) \cdot 2H_2O$	$Pna2_1$	10.665(5)	7.219(2)	23.662(3)				605
$PrH_3(SeO_3)_2(Se_2O_5)$	$P2_1/c$	12.933(3)	7.334(2)	10.811(2)		91.68(1)		606
$Y(Se_2O_5)NO_3 \cdot 3H_2O$	$P2_12_12_1$	6.216(1)	7.100(2)	20.689(6)				607
$Yb_2(SeO_3)_3$	$P\bar{1}$	6.933(1)	7.974(2)	8.948(2)	71.39(2)	70.24(2)	65.94(2)	608
$Y_2(SeO_3)_3$	$P\bar{1}$	7.017(3)	8.069(3)	9.043(5)	71.20(6)	70.13(6)	65.67(5)	608
$Gd_2(SeO_3)_3$	$P\bar{1}$	7.145(2)	8.157(2)	9.115(2)	71.26(3)	69.84(3)	65.66(3)	608
$Er_2(SeO_3)_3$	$P\bar{1}$	6.982(1)	8.006(1)	8.950(1)	71.38(1)	70.13(1)	65.87(1)	609
$La_2(SeO_3)_3$	$Pnma$	8.467(3)	14.286(1)	7.1003(2)				610
$LaF(SeO_3)$	$P2_1/c$	18.198(3)	7.1575(8)	8.464(1)		96.89		610
$Ce(IV)(Se_2O_6)$	$P2_1/n$	7.008(1)	10.587(2)	7.262(1)		107.00(1)		612
$NaY(SeO_3)_2$	$P2_1cn$	5.397(2)	8.525(2)	12.765(2)				614
$NaLa(SeO_3)_2$	$P2_1/n$	6.696(4)	6.761(4)	13.199(5)		101.51(3)		614
$La_2Cu(SeO_3)_4$	$P2_1/c$	10.512(1)	7.136(1)	8.431(1)		110.61(1)		615
$Tb_2O(SeO_3)_2$	$P4_2/ncm$	10.6457(4)		5.2156(3)				617
$Tb_5O_4Cl_3(SeO_3)_2$	$C2/m$	12.291	5.462	9.788		90.49		619
$Gd_5O_4Br_3(SeO_3)_2$	$C2/m$	12.437	5.499	10.053		91.87		619
$Sm_9O_8Cl_3(SeO_3)_4$	$P\bar{1}$	6.887(1)	8.888(1)	9.591(2)	98.65(1)	95.42(1)	96.031(1)	619
$Cu_3Er(SeO_3)_2O_2Cl$	$Pmmn$	6.299(1)	9.430(3)	6.967(2)				618
$Gd_3(SeO_3)_4F$	$P6_3mc$	10.443(1)		6.9432(2)				620
$Dy_3(SeO_3)_4F$	$P6_3mc$	10.360(1)		6.8647(7)				609
$Nd_3(SeO_3)_4F$	$P6_3mc$	10.5149(7)		712.11(4)				611
$Sm_3(SeO_3)_4F$	$P6_3mc$	10.474(1)		7.0224(7)				611
				mixed selenates−selenites				
$Er(SeO_3)(SeO_4)_{0,5} \cdot H_2O$	$C2$	11.935(2)	6.881(1)	6.473(1)		103.79(4)		621
$NaSm(SeO_4)(SeO_3)$	$P2_1/c$	10.669(2)	6.9166(8)	8.2588(9)		91.00(2)		623
$NaLa(SeO_4)(SeO_3)$	$P2_1/c$	10.751(2)	7.098(1)	8.437(1)		90.90(2)		611
$Pr_4(SeO_3)_2(SeO_4)F_6$	$C2/c$	22.305(3)	7.1054(9)	8.356(1)		98.05(2)		623
$La(HSeO_3)(SeO_4) \cdot 2H_2O$	$P2_1/n$	7.272(1)	9.409(2)	11.940(2)		93.32(1)		622

The trihydrates are known for the whole lanthanide series.[579] Furthermore, for Sm, Eu, and Gd hexahydrates have been prepared.[579] Their structure is not known, but the samarium compound is probably monoclinic with the lattice constants $a = 20.74(1)$ Å, $b = 7.104(5)$ Å, $c = 16.50(1)$ Å, and $\beta = 110.84(6)$. The thermal behavior of the sulfite hydrates was intensively studied under various atmospheres.[580−582] According to these investigations the first step is the dehydration to the anhydrous compounds followed by the decomposition of the sulfite yielding oxide sulfates $M_2O_2SO_4$ and finally the oxides M_2O_3. If the decomposition is carried out under a reducing atmosphere like CO, one arrives at the oxide sulfides M_2O_2S.[583] The latter procedure has been shown to be an appropriate method to prepare Eu^{3+}-doped Y_2O_2S which is an important phosphor material.

Besides the binary sulfites several ternary sulfites are mentioned in the literature,[584−587] but again no structural data are available due to the low solubility of the compounds. The only exception is $(NH_4)_3Dy(SO_3)_3 \cdot H_2O$ for which at least the positions of the Dy and S atoms were determined by X-ray investigations.[588]

2. Selenites

Compared to the sulfites, our knowledge on selenites of the rare-earth elements is much deeper. The main reason might be the higher stability of the oxidation state +IV for selenium compared to sulfur. The resistance of SeO_3^{2-} against oxidation makes it possible to work in aqueous solutions without special precautions. Because in such solutions there exist many different species, such as H_2SeO_3, $HSeO_3^-$, SeO_3^{2-}, and $Se_2O_5^{2-}$, depending on the conditions such as pH value, concentration, and temperatures, the selenite chemistry is rich with different compounds. Furthermore, because SeO_2 is a solid, typical solid-state synthesis techniques can be applied leading additionally to a large number of rare-earth selenites (Table 14). Thermoanalytical investigations showed that in the systems M_2O_3/SeO_2 compounds with the compositions $M_2Se_4O_{11}$, $M_4Se_7O_{20}$, $M_2Se_3O_9$, $M_2Se_2O_7$, and M_2SeO_5 exist.[589,590]

The hydrous rare-earth selenites $M_2(SeO_3)_3 \cdot xH_2O$ were prepared nearly 30 years ago and were shown to contain seven, four, or three molecules of water.[591−593] According to recent investigations of the phase diagram $Tm_2O_3-SeO_2-H_2O$, the stable selenite hydrate is $Tm_2(SeO_3)_3 \cdot 4H_2O$.[594] Unfortunately,

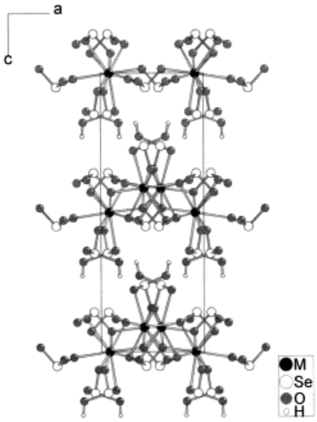

Figure 82. Crystal structure of the acidic selenites $M(HSeO_3)(SeO_3)$ (M = La, Pr). The layers are only connected via hydrogen bonds.

only X-ray powder diffraction and IR measurements have been performed, so that details of the crystal structures are not known.[595] Structure determinations were carried out for the acidic selenites $M(HSeO_3)(SeO_3)\cdot 2H_2O$ (M = Nd, Sm)[596,597] and $M(HSeO_3)(SeO_3)$ (M = La, Pr).[598,599] The first two compounds consist of layers according to ${}^2_\infty[M(SeO_3)_{4/4}(HSeO_3)_{2/2}(H_2O)_{1/1}]$ with the M^{3+} ions in 8-fold coordination of oxygen atoms. The layers are stacked in the [001] direction and held together by hydrogen bonds involving the noncoordinated H_2O molecules. The anhydrous species also have a layer structure, except more strongly puckered (Figure 82). Again, they are held together via hydrogen bonds. For the M^{3+} ions the CN is 10. The oxygen atoms belong to five SeO_3^{2-} and two $HSeO_3^-$ ions. Three of the former act as chelating ligands.

The thermal decomposition of $M(HSeO_3)(SeO_3)\cdot 2H_2O$ (M = Pr−Lu, Y)[597,600,601] and $Pr(HSeO_3)(SeO_3)$[598] was investigated by DTA/TG methods. According to the investigations of the neodymium selenite, the compound decomposes with $Nd_2Se_4O_{11}\cdot 4H_2O$, $Nd_2Se_4O_{11}$, $Nd_4Se_7O_{20}$, $Nd_2Se_3O_9$, and Nd_2SeO_5 as intermediates leading to Nd_2O_3 finally. Similarly, the decomposition of the praseodymium selenite occurs via $Pr_2Se_4O_{11}$, $Pr_2Se_3O_9$, and Pr_2SeO_5 and yields Pr_6O_{11}. The intermediate phases have been investigated by X-ray powder diffraction and IR spectroscopy, but no crystal structures are known.[590,602,603]

$Sc(HSeO_3)_3$ is the only neat hydrogenselenite of which the structure is known.[604] According to ${}^3_\infty[Sc(HSeO_3)_{6/2}]$, a three-dimensional network of $[ScO_6]$ octahedra and selenite groups is formed. Another interesting acidic selenite which can be obtained from selenious acid (57% H_2SeO_3) is $Nd_2(Se_2O_5)_3(H_2SeO_3)\cdot 2H_2O$.[605] It contains two crystallographically different Nd^{3+} ions, both in 9-fold coordination of oxygen atoms. $Nd(1)^{3+}$ is surrounded by seven $Se_2O_5^{2-}$ groups of which two are attached in a chelating way. $Nd(2)^{3+}$ has two chelating and two monodentate $Se_2O_5^{2-}$ neighbors and, furthermore, two H_2O and one H_2SeO_3 ligands. The coordination polyhedra are linked to sheets which are stacked in the [001] direction and held together by hydrogen bonds with the acid and the water molecules as donors (Figure 83). A diselenite group is also observed in $PrH_3(Se_2O_5)(SeO_3)_2$[606] and $Y(Se_2O_5)(NO_3)\cdot 3H_2O$.[607] With respect to the distances Se−O, the former selenite should be formulated according to $Pr(Se_2O_5)(HSeO_3)(H_2SeO_3)$. The distinct anions have different functionalities in the structure. The diselenite and hydrogenselenite groups link the Pr^{3+} ions to double chains which are connected via hydrogen bonds of the H_2SeO_3 molecules. These are only monodentate to the Pr^{3+} ions which are in 9-fold coordination of oxygen atoms. A structure with double layers has also been determined for $Y(Se_2O_5)(NO_3)\cdot 3H_2O$. In this case the layers are connected by hydrogen bonds involving the nitrate ions and the water molecules. The Y^{3+} ions are surrounded by two monodentate and one chelating $Se_2O_5^{2-}$ groups, three H_2O molecules, and one nitrate ion.

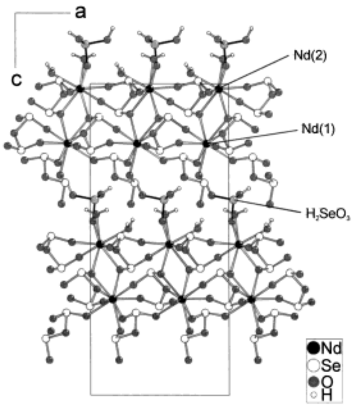

Figure 83. Crystal structure of the diselenite $Nd_2(Se_2O_5)_3(H_2SeO_3)\cdot 2H_2O$.

The anhydrous selenites, $M_2(SeO_3)_3$, were prepared in single-crystalline form either by fusion of the binary oxides in the presence of a alkali halide flux[608] or by decomposition of the respective selenates in a LiF melt.[609] According to the single-crystal determinations carried out so far, the lighter selenites M = Tb−Lu[608,609] crystallize, in contradiction with the findings based on powder diffraction, with a triclinic crystal structure. The compounds contain two crystallographically different M^{3+} ions and three crystallographically different SeO_3^{2-} groups. $M(1)^{3+}$ is coordinated by three $Se(2)O_3^{2-}$ and two $Se(3)O_3^{2-}$ groups and one $Se(1)O_3^{2-}$ ion. Because the latter acts as a chelating ligand, a coordination number of seven results (Figure 84). The coordination polyhedron can be seen as a pentagonal bipyramide. $M(2)^{3+}$ is surrounded by oxygen atoms of three $Se(1)O_3^{2-}$, two $Se(3)O_3^{2-}$, and one $Se(2)O_3^{2-}$ groups, respectively. Two selenite ions (1 × $Se(2)O_3^{2-}$, 1 × $Se(3)O_3^{2-}$) are attached in a chelating way leading to a coordination number of eight. Each of the three crystallographically different selenite groups is attached to four M^{3+} ions in a way that all oxygen atoms of a selenite ion are monodentate and two of them are additionally chelating. Another characteristic of the crystal structure is the stereochemical activity of the lone pairs of the selenium atoms. The linkage of the M^{3+} polyhedra and the selenite ions leads to rectangular channels along [01−1], providing enough space to incorporate the lone pairs. The three-dimensional crystal structure is shown for the example of Er_2-

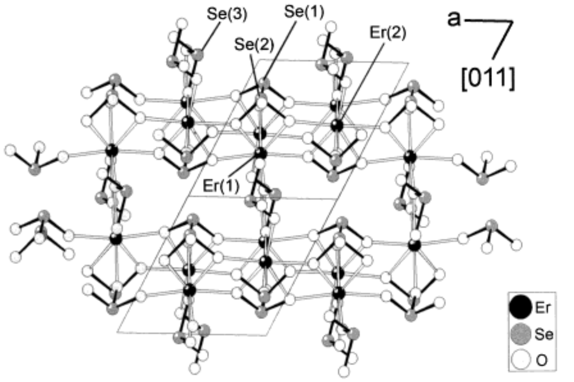

Figure 84. Crystal structure of $Er_2(SeO_3)_3$ viewed along [01−1]. The voids in the structure incorporate the lone pairs of the SeO_3^{2-} groups.

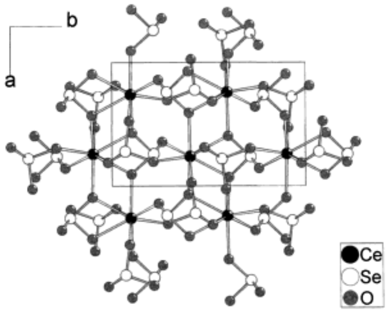

Figure 85. Three-dimensional network ${}^3_\infty[Ce(Se(1)O_3)_{3/3}(Se(2)O_3)_{4/4}]$ in $Ce(SeO_3)_2$.

$(SeO_3)_3$ (Figure 84). A very similar influence of the lone pairs on the crystal structure has been observed for $La_2(SeO_3)_3$.[610] The compound crystallizes in the orthorhombic system and contains 10-fold coordinated La^{3+} ions and two crystallographically different selenite groups. The oxygen atoms belong to seven SeO_3^{2-} ions with three of them being chelating ligands. According to ${}^3_\infty[La(Se(1)O_3)_{2/4}(Se(2)O_3)_{5/5}]$ the selenite ions are 4- and 5-fold coordinated by La^{3+}. The $Se(1)O_3^{2-}$ groups connect the La^{3+} ions to sheets parallel (010) which are linked in the [010] direction via $Se(2)O_3^{2-}$ ions. The three-dimensional network provides empty space for the lone pairs of the selenium atoms (Figure 88a). The anhydrous selenites of the other larger lanthanides M = Ce−Sm seem to adopt in principle the same crystal structure but with a small monoclinic distortion.[611] This leads obviously to a twinning problem of the crystals so that a high-quality structure determination has not been possible to date.

For cerium, the structure of the tetravalent compound, $Ce(SeO_3)_2$, is known also. Single crystals were obtained by the reaction of CeO_2 with excess SeO_2 in a silica tube.[612] In the crystal structure the Ce^{4+} ions are coordinated by eight oxygen atoms which belong to seven SeO_3^{2-} groups with one of them being a chelating ligand. The two crystallographically different selenite ions are attached to four and three Ce^{4+} ions, respectively, and a three-dimensional network ${}^3_\infty[Ce(Se(1)O_3)_{3/3}(Se(2)O_3)_{4/4}]$ is formed which is shown in Figure 85. Although the lone pair activity is not so prominent in the structure compared to the findings for the trivalent lanthanides, the need of space for the lone pairs is still obvious. The reaction of lanthanide oxides with SeO_2 may also lead to oxide selenites. With M_2SeO_5 (=$M_2(SeO_3)O_2$), one possible composition has been observed as an intermediate during the decomposition of the selenites (see above). Another composition, $M_2O(SeO_3)_2$, was obtained in single-crystalline form for M = Tb.[613] The tetragonal structure consists of oxide-centered tetrahedra which are linked to chains according to ${}^1_\infty[OM_{4/2}]^{4+}$. These are oriented along [001] and connected by the SeO_3^{2-} ions. Again, prominent channels are formed incorporating the lone pairs of the selenium atoms (Figure 86).

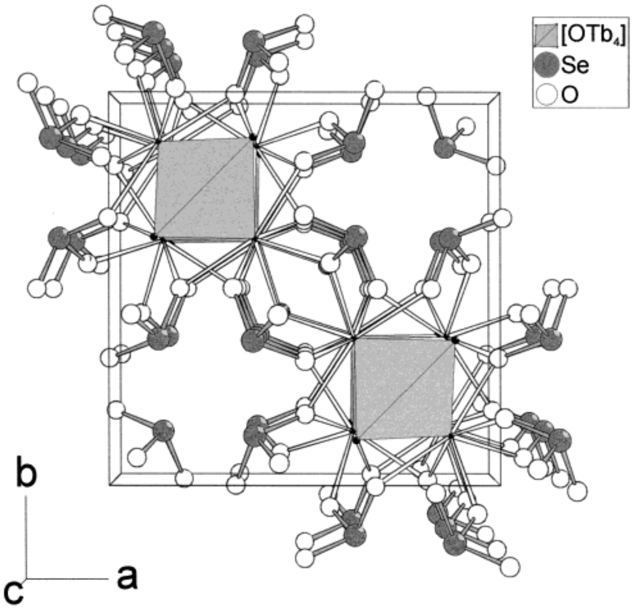

Figure 86. Crystal structure of $Tb_2O(SeO_3)_2$. The chains ${}^1_\infty[OM_{4/2}]^{4+}$ of oxygen-centered $[OM_4]$ tetrahedra are oriented along [001] and shown as polyhedra.

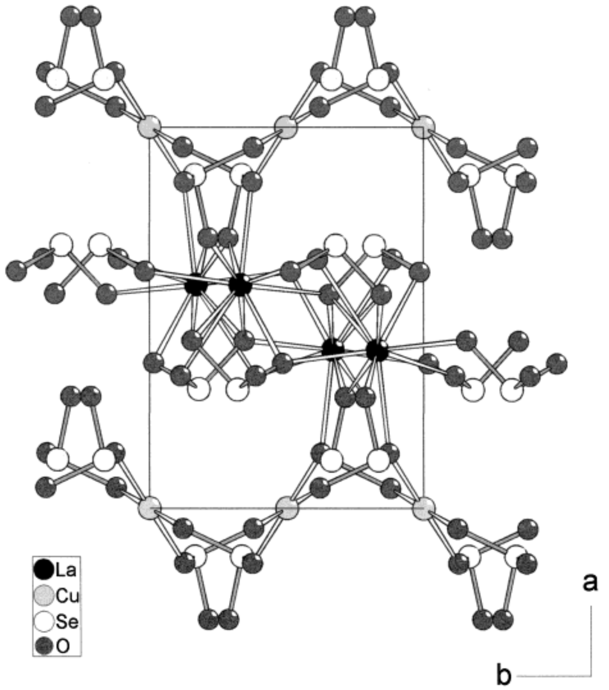

Figure 87. Crystal structure of $La_2Cu(SeO_3)_4$ with the square planar $[CuO_4]$ units.

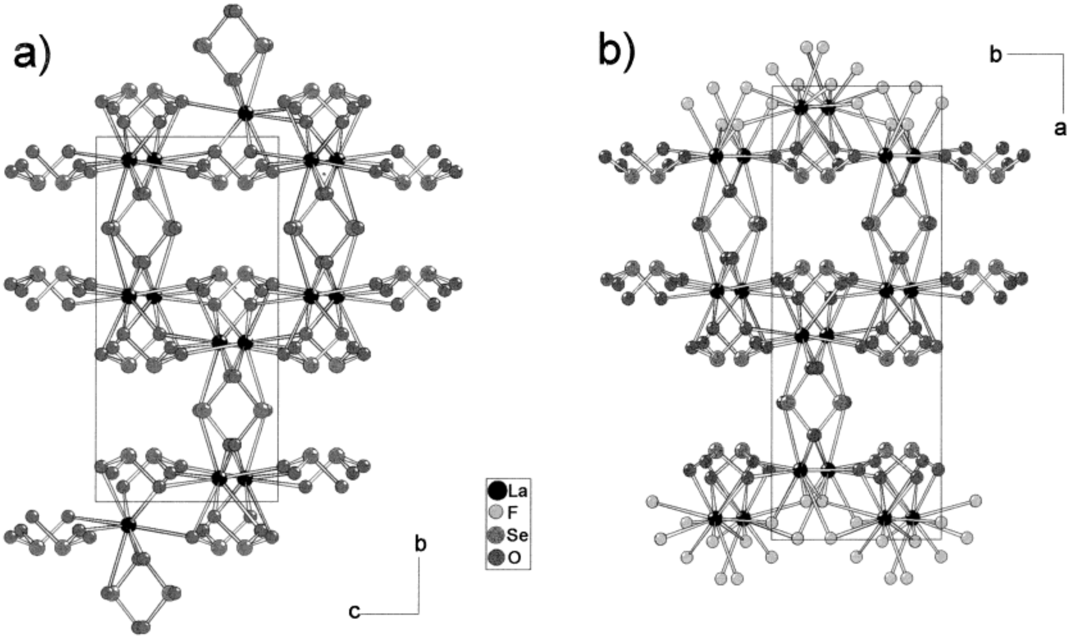

Figure 88. Comparison of the crystal structures of $La_2(SeO_3)_3$ (a) and $LaFSeO_3$ (b). Both structures contain identical building units, and in both structures the need for space for the lone pairs is obvious.

The crystal structures of four ternary anhydrous selenites are known. Two of them, $NaLa(SeO_3)_2$ and $NaY(SeO_3)_2$,[614] contain additional Na^+ ions, the third one, $La_2Cu(SeO_3)_4$, is a copper compound,[615] and another one has the composition $Li_3Lu_5(SeO_3)_9$.[616] The preparation of these selenites was carried out hydrothermally in Teflon-lined steel autoclaves or, in the latter case, by fusing Lu_2O_3 and SeO_2 in a LiCl flux. The lanthanum compound shows the La^{3+} ions in 10-fold coordination of oxygen atoms which are part of three $Se(1)O_3{}^{2-}$ and four $Se(2)O_3{}^{2-}$ ions, respectively. Thus, three of the selenite groups are chelating ligands. In accordance with the formulation ${}^{3}_{\infty}[La(Se(1)O_3)_{3/3}(Se(2)O_3)_{4/4}]^-$, a three-dimensional anionic network is built incorporating the Na^+ ions for charge balance. On the basis of the distances Na–O for the latter, a CN number of "5+2" can be deduced. A three-dimensional anionic substructure is also found for the yttrium compound, but due to the smaller ionic radius of Y^{3+} compared to La^{3+}, the CN is lowered to 7. Five monodentate and one chelating $SeO_3{}^{2-}$ ions are attached to an Y^{3+} ion, and the linkage of the polyhedra according to ${}^{3}_{\infty}[Y(Se(1)O_3)_{3/3}(Se(2)O_3)_{3/3}]^-$ provides channels occupied by the Na^+ ions in "5+3" fold coordination. The CN of 10 for the La^{3+} in $La_2Cu(SeO_3)_4$ is achieved by the attachment of five $Se(1)O_3{}^{2-}$ and two $Se(2)O_3{}^{2-}$ ions, part of them being chelating ligands. In this case the three-dimensional network has to be described as ${}^{3}_{\infty}[La(Se(1)O_3)_{5/5}(Se(2)O_3)_{2/2}]^-$. The Cu^{2+} are located on a special site of the monoclinic space group $P2_1/c$ and occurs one-half as much as La^{3+} in the unit cell. It shows the typical square planar coordination of oxygen atoms (Figure 87).

The usage of a flux for the crystal growth of rare-earth selenites sometimes leads to unexpected compounds. For example, $Tb_3O_2Cl(SeO_3)_2$ was obtained when the reaction of SeO_2, Tb_4O_7, and Tb was carried out using $TbCl_3$ as a flux.[617] Characteristic features of the crystal structure are double chains of oxide-centered Tb tetrahedra and pseudohexagonal channels which incorporate the lone pairs of the selenite ions. Both of the crystallographically different Tb^{3+} ions are in 8-fold coordination. $Tb(1)^{3+}$ has two Cl^- ions and six oxygen as ligands, while $Tb(2)^{3+}$ is surrounded by one Cl^- ion and seven oxygen atoms. The compound is similar to that of $Cu_3Er(SeO_3)_2O_2Cl$,[618] which is isotypic with the mineral francisite, $Cu_3Bi(SeO_3)_2O_2Cl$. In these compounds open channels are formed also which incorporate the lone pairs. In contrast to the terbium compound, the chloride ions are also located in these channels and not attached to the cations. Thus, the 8-fold coordination of Er^{3+} arises only from oxygen ligands. Further examples of the flux participation in the reaction are $Tb_5O_4Cl_3(SeO_3)_2$, $Gd_5O_4Br_3(SeO_3)_3$, and $Sm_9O_8Cl_3(SeO_3)_4$.[619] In these crystal structures double chains of vertex-connected double chains of $[OM_4]$ tetrahedra occur.

If LiF is used as a flux for crystal growth, F^- incorporation is frequently observed. Attempts to grow a single crystal of $La_2(SeO_3)_3$ from a LiF melt led to the fluoride selenite $LaFSeO_3$.[610] The crystal structure contains three crystallographically different La^{3+} and $SeO_3{}^{2-}$ ions. $La(1)^{3+}$ is surrounded by four F^- ions and six oxygen ligands. The latter belong to four monodentate and one chelating selenite groups. $La(2)^{3+}$ has a coordination number of 11 too. Besides seven fluoride ions, two chelating $SeO_3{}^{2-}$ groups are attached. In contrast, $La(3)^{3+}$ is exclusively surrounded by oxygen atoms (Figure 88b). The coordination geometry is the same as that described for $La_2(SeO_3)_3$. Furthermore, in accordance with the findings for $La_2(SeO_3)_3$, in $LaFSeO_3$ the La^{3+} ions are linked to layers, which are linked further in the [100] direction by $SeO_3{}^{2-}$ groups. The main difference between the two compounds is that the connection within the sheet occurs also via fluoride ions in $LaFSeO_3$. The similarity of $La_2(SeO_3)_3$ and $LaFSeO_3$

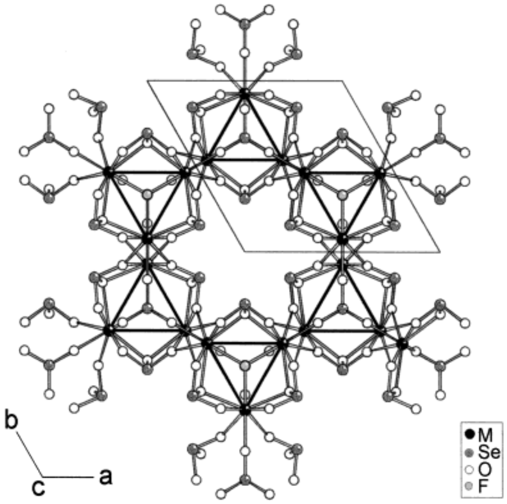

Figure 89. Crystal structure of the fluoride selenites $M_3(SeO_3)_4F$ (M = Nd, Sm, Gd, and Dy). The $[M_3]$ triangles are emphasized by black lines.

can be seen easily from Figure 88 and is also reflected by the lattice parameters in the layer planes (Table 14).

Fluoride selenites with a lower F^- content were obtained for M = Nd, Sm, Gd, and Dy and have the composition $M_3(SeO_3)_4F$.[609,620] The crystal structure of the isotypic compounds contains M^{3+} ions in triangular formation caused by the selenite group $Se(1)O_3^{2-}$ which acts as a μ_3-ligand as well as by a μ_3-F^- ion capping the triangle on the opposite side (Figure 89). Each edge of the ring is bridged by one oxygen atom of the crystallographically second selenite group, $Se(2)O_3^{2-}$. The remaining oxygen atoms of this selenite ion also belong to the coordination sphere of the M^{3+} ions of the ring. The coordination sphere of the three M^{3+} ions is completed by three $Se(1)O_3^{2-}$ and six $Se(2)O_3^{2-}$ ligands, so that the building unit $[M_3F(Se(1)O_3)_4(Se(2)O_3)_9]^{18-}$ results. These fragments are stacked with the same orientation along [001], leading to the acentricity of the crystal structure (space group $P6_3mc$, Table 14). The linkage of the fragments is performed by both selenite groups. The capping $Se(1)O_3^{2-}$ group connects one ring to three others, so that each oxygen atom of the anion is bidentate bridging while $Se(2)O_3^{2-}$ links two other triangles in a way that all oxygen atoms of the group are monodentate and two of them additionally chelating ligands. Thus, the connectivity can be written as $[M_3F(Se(1)O_3)_{4/4}(Se(2)O_3)_{9/3}]$ according to Niggli's formalism. The influence of the lone pairs of the ψ^1-tetrahedral anion is even more prominent than that found for the other selenites. The lone pair of the $Se(1)O_3^{2-}$ ion is oriented along [001] in the direction of the fluoride ion, so that a very long distance Se−F of 3.69 Å results. The lone pairs of the $Se(2)O_3^{2-}$ ions are incorporated in channels which are running parallel to the [001] direction. The diameter of these channels is 6.63 Å with respect to opposite selenium atoms.

3. Selenate Selenites

A handful of compounds are known that contain selenate *and* selenite ions and thus are mixed valent with respect to the oxidation state of the selenium ions. $Er_2(SeO_3)_2(SeO_4)\cdot 2H_2O$ was obtained via the reaction of $Er(NO_3)_3\cdot 5H_2O$ and SeO_2 under hydrothermal conditions.[621] Unfortunately, the crystal structure determination suffers from the disorder of the selenate group. Therefore, the presence of both oxidation states for Se has been proved by means of XANES measurements[621] (Figure 90). The structure consists of layers of 8-fold coordinated Er^{3+} and SeO_3^{2-} ions which are linked via the SeO_4^{2-} tetrahedra. $La(HSeO_3)(SeO_4)\cdot 2H_2O$ was also obtained hydrothermally.[622] The structure shows the La^{3+} ions in 9-fold coordination of oxygen atoms of three SeO_4^{2-}, three $HSeO_3^-$, and two H_2O ligands. One of the hydrogenselenite ions is attached chelating. The $HSeO_3^-$ groups connect the metal ions to double chains which are oriented in the [100] direction and linked to further double chains by the SeO_4^{2-} tetrahedra (Figure 91). Although the hydrogen atoms were not located, hydrogen bonding can be assumed with the H_2O molecules and the $HSeO_3^-$ ions as donors when judged from the donor−acceptor distances which are around 3 Å.

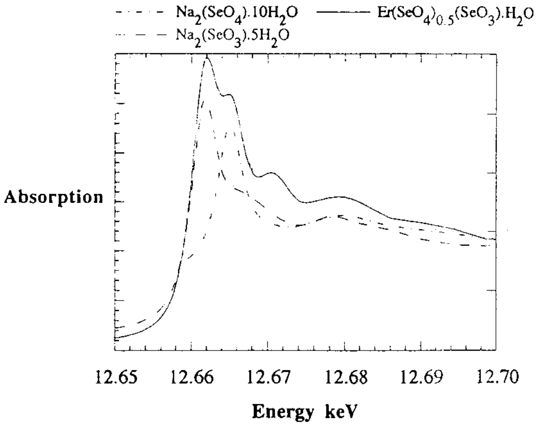

Figure 90. X-ray absorption investigation on $Er_2(SeO_3)_2(SeO_4)\cdot 2H_2O$. The observed signals prove the presence of Se^{4+} and Se^{6+} in the compound.

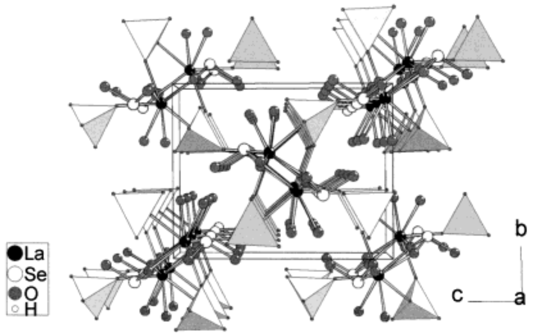

Figure 91. Crystal structure of the hydrogenselenite−selenate $La(HSeO_3)(SeO_4)\cdot 2H_2O$.

Light green single crystals of $Pr_4(SeO_3)_2(SeO_4)F_6$[623] were obtained from the decomposition of $Pr_2(SeO_4)_3$ in the presence of LiF in a gold ampule. The monoclinic compound contains two crystallographically different Pr^{3+} ions. $Pr(1)^{3+}$ is attached by six fluoride ions and two chelating SeO_3^{2-} groups (CN = 10); $Pr(2)^{3+}$ is surrounded by four fluoride ions, three monodentate SeO_3^{2-}, and two SeO_4^{2-} groups. One of the latter acts as a chelating ligand, so the CN of Pr-

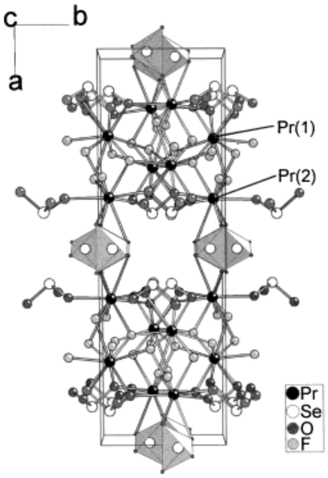

Figure 92. Crystal structure of $Pr_4(SeO_3)_2(SeO_4)F_6$. As can be seen from Figure 88, the structure is very similar to those of $La_2(SeO_3)_3$ and $LaFSeO_3$.

$(2)^{3+}$ is 10. The selenite ions are themselves coordinated by five and the selenate ions by four Pr^{3+} ions. The coordination numbers of the F^- ions are three and four, respectively. The anions F^- and SeO_3^{2-} are arranged in layers parallel (100) together with the Pr^{3+} ions. The layers are connected along [100] via SeO_4^{2-} groups. The linkage of the coordination polyhedra leads to cavities in the crystal structure which incorporate the lone pairs of the selenite ions. The structure of $Pr_4(SeO_3)_2(SeO_4)F_6$ is very similar to those of $La_2(SeO_3)_3$ and $LaFSeO_3$, as may be seen by comparing Figures 92 and 88. The reaction of $Sm_2(SeO_4)_3$ and NaCl in gold ampules yielded light yellow single crystals of $NaSm(SeO_3)(SeO_4)$.[623] The crystal structure contains 10-fold oxygen-coordinated Sm^{3+} ions. The oxygen atoms belong to five SeO_3^{2-} and two SeO_4^{2-} ions. Two of the SeO_3^{2-} groups as well as one of the SeO_4^{2-} groups act as a chelating ligand. The sodium ions are surrounded by five SeO_4^{2-} ions and one SeO_3^{2-} group. One of the selenate ions is attached chelating leading to a coordination number of seven. Each selenite group is coordinated by six ($5 \times Sm^{3+}$ and $1 \times Na^+$) and each selenate ion by seven cations ($5 \times Na^+$ and $2 \times Sm^{3+}$). Again, the structure provides empty voids for the incorporation of the lone pairs.

B. Halogenates

1. Chlorates

Chlorates of the rare-earth elements can be prepared by the reaction of the respective sulfate with $Ba(ClO_3)_2$ in aqueous solutions. A second method is the reaction of rare-earth carbonates with aqueous $HClO_3$. In both cases crystals are obtained by evaporation of the solution. Depending on the exact conditions, hydrates containing from 10 to 2 molecules of crystal water are formed.[624,625] Although the preparation was described more than 30 years ago, it was only recently that the first structure determination has been reported, namely, for $Pr(ClO_3)_3 \cdot 2H_2O$.[626] In the crystal structure Pr^{3+} is 9-fold coordinated by oxygen atoms. The coordination polyhedron can be understood as tricapped trigonal prism. The oxygen atoms belong to two H_2O molecules and seven chlorate groups which can be divided into three crystallographically different species. Three of the seven ClO_3^- ions are attached to two additional Pr^{3+} ions, while the remaining four chlorate groups are connected to only one additional Pr^{3+} ion. The connectivity may therefore be written as $^3_\infty[Pr(H_2O)_2(ClO_3)_{3/3}(ClO_3)_{4/2}]$. The linkage of the polyhedra leads to sheets parallel (001) which are connected with each other by hydrogen bonding with the H_2O molecules as donors and nonbonding oxygen atoms of the chlorate groups as acceptors (Figure 93). DTA/TG measurements show that $Pr(ClO_3)_3 \cdot 2H_2O$ dehydrates in the first step to form $Pr(ClO_3)_3$, which finally decomposes by releasing oxygen and chlorine to give PrOCl.[626] The dehydration is endothermic with an onset temperature of 130 °C and an end temperature of approximately 230 °C. The decomposition of the chlorate is exothermic and occurs between 245 °C (onset) and 384 °C (end). The second structurally characterized rare-earth chlorate is $Er(ClO_3)_3 \cdot 8H_2O$.[627] The Er^{3+} ions are exclusively coordinated by H_2O molecules in the form of square antiprisms, while the ClO_3^- ions remain uncoordinated.

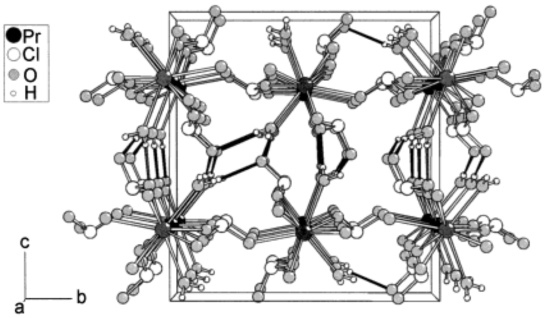

Figure 93. Crystal structure of $Pr(ClO_3)_3 \cdot 2H_2O$ viewed along the [100] direction; hydrogen bonds are emphasized as black lines.

2. Bromates

The same situation as that described for $Er(ClO_3)_3 \cdot 8H_2O$ is found for the bromates $M(BrO_3)_3 \cdot 9H_2O$.[628-632] These can be prepared also from aqueous solution by treating rare-earth sulfates with $Ba(BrO_3)_2$ and are known for the whole lanthanide series. According to X-ray structure determinations for several rare-earth elements (cf. Table 15), they contain the M^{3+} ions in tricapped trigonal prismatic coordination of H_2O molecules. The $[M(H_2O)_9]^{3+}$ complexes are stacked in the [001] direction and separated by the BrO_3^- ions. From thermogravimetric measurements it can be assumed that various bromates of lower water content exist.[633,634] Even the anhydrous compounds were observed as intermediates during the decomposition, especially for the larger lanthanides. The final decomposition product is MOBr in all cases. Unfortunately, none of the intermediate phases have been characterized to date.

3. Iodates

In the 1970s there was considerable interest in rare-earth iodates because one expected useful optical, magnetic, and dielectric properties. A huge

Table 15. Crystallographic Data of Halogenates

compound	space group	lattice parameters *a*/Å	*b*/Å	*c*/Å	α/°	*β*/°	*γ*/°	ref
				chlorates				
$Pr(ClO_3)_3·2H_2O$	$P2_12_12_1$	5.7603(7)	12.367(2)	13.140(2)				626
$Eu(ClO_3)_3·2H_2O$	$P2_12_12_1$	5.7017(6)	12.312(2)	13.153(2)				627
$Er(ClO_3)_3·8H_2O$	$P\bar{1}$	8.362(1)	8.425(1)	11.124(2)	87.79(2)	86.37(2)	89.16(2)	627
				bromates				
$Sm(BrO_3)_3·9H_2O$	$P6_3/mmc$	11.86(3)		6.76(2)				628
$Nd(BrO_3)3·9H_2O$	$P6_3mc$	11.73(2)		6.76(2)				629
$Pr(BrO_3)_3·9H_2O$	$P6_3/mmc$	11.840(1)		6.8012(9)				630
$Yb(BrO_3)_3·9H_2O$	$P6_3/mmc$	11.706(1)		6.6474(9)				630
$Tb(BrO_3)_3·9H_2O$	$P6_3/mmc$	11.755(2)		6.712(1)				631
$Ho(BrO_3)_3·9H_2O$	$Cmcm$	11.699(1)	20.263(2)	6.671(1)				632
$Ho(BrO_3)_3·9H_2O$	$Cmcm$	11.670(1)	20.213(2)	6.611(1)				632
				iodates				
$Y(IO_3)_3·2H_2O$	$P\bar{1}$	7.3529(2)	10.5112(4)	7.0282(2)	105.177(1)	109.814(1)	95.179(1)	*a*
$Lu(IO_3)_3·2H_2O$	$P\bar{1}$	7.2652(9)	7.4458(2)	9.3030(3)	79.504(1)	84.755(1)	71.676(2)	*a*
$Nd(IO_3)_3·H_2O$	$P2_1$	10.201(1)	6.7053(9)	7.3538(9)		113.11(2)		640
$Sm(IO_3)_3·H_2O$	$P2_1$	10.133(1)	6.6571(6)	7.3110(7)		113.11(1)		641
$La(IO_3)_3·0.5H_2O$	Pn	7.219(2)	11.139(4)	10.708(3)		91.86(1)		*a*
$Sc(IO_3)_3$	$R\bar{3}$	9.738(1)		13.938(1)				*a*
$La_3(IO_3)_9·HIO_3·7H_2O$	$Aba2$	13.1801(1)	21.7208(1)	12.1551(2)				642
$Ce(IO_3)_4·H_2O$	$P2_1/n$	9.57(1)	14.92(2)	8.00(2)		98.0(2)		643
$Ce(IO_3)_4·H_2O$	$P2_1/n$	9.57(1)	14.92(2)	8.00(2)		98.0(2)		644
$Ce(IO_3)_4$	$P4_2/n$	9.90(2)		5.32(1)				645
$Ce(IO_3)_4$	$P4_2/n$	9.900		5.320				646
$Gd(IO_3)_3$	$P2_1/a$	13.4365(9)	8.5226(5)	7.1356(5)		99.72(1)		647

[a] Hector, A. L.; Henderson, S. J.; Levason, W.; Webster, M. *Z. Anorg. Allg. Chem.* **2002**, *628*, 198.

number of iodates $M(IO_3)_3·xH_2O$ were prepared and characterized mainly by X-ray powder diffraction, IR spectroscopy, and thermal analysis.[635−637] According to these investigations, the H_2O content varies between 0.5 and 6 and even the anhydrous compounds are known. Several reviews have summarized the findings,[638,639] and thus, only the single-crystal investigations will be emphasized here. Surprisingly, despite the large number of known iodates, crystal structure determinations are still very limited (cf. Table 15). In the crystal structure of the isotypic monohydrates $Nd(IO_3)_3·H_2O$[640] and $Sm(IO_3)_3·H_2O$,[641] eight monodentate IO_3^- ions are attached to the M^{3+} ions. Two of them have two M^{3+} neighbors; the remaining six are coordinated to three M^{3+} centers, so that according to ${}^3_\infty[M(IO_3)_{6/3}(IO_3)_{2/2}]$ a three-dimensional network is formed in which the crystal water molecules are incorporated (Figure 94). In the complicated structure of the pyroelectric acidic iodate $La_3(IO_3)_9(HIO_3)·7H_2O$[642] the two crystallographically distinct La^{3+} ions are in 8-fold and 10-fold coordination of oxygen atoms, respectively. The iodate $Ce(IO_3)_4·H_2O$[643,644] has a layer structure in which sheets according to ${}^2_\infty[Ce(IO_3)_{8/2}]$ are stacked in the [010] direction and the H_2O molecules are located in empty voids within the layers. The anhydrous iodate $Ce(IO_3)_4$ has a chain structure with the chains ${}^1_\infty[Ce(IO_3)_{8/2}]$ running along [001] of the tetragonal unit cell.[645,646] The only structurally characterized anhydrous iodate of a trivalent rare-earth element, $Gd(IO_3)_3$,[647] has a three-dimensional structure with three and two coordinated IO_3^- ions according to the formulation ${}^3_\infty[Gd(IO_3)_{6/3}(IO_3)_{2/2}]$. All of the anions are monodentate, and thus, Gd^{3+} has a coordination number of 8.

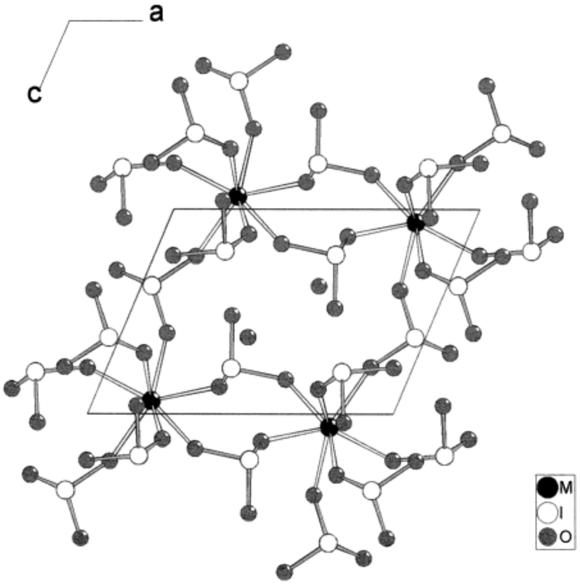

Figure 94. Projection of the crystal structure of $M(IO_3)_3·H_2O$ (M = Nd, Sm) on (010).

IV. Triangular Anions

A. Carbonates

Carbonates of rare-earth elements play an important role in the geochemistry of these elements. The best known carbonate minerals are *lanthanite*, $(La,Ce)_2(CO_3)_3·8H_2O$, *tengerite*, $Y_2(CO_3)_3·2H_2O$, and the fluoride carbonate *bastnaesite*, $(La,Ce)(F,OH)CO_3$. Despite the importance of rare-earth carbonates the knowledge of their crystal chemistry is very limited. This may be due to the difficulties in obtaining suitable single crystals for the structure determination. Thus, most of the work performed so far deals with the behavior of rare-earth carbonato complexes in solution.[648,649] In the following, the structure of the rare-earth carbonates known so far shall be discussed.

1. Carbonate Hydrates

The carbonates of rare-earth elements have low solubilities in water and can therefore be precipitated from aqueous solutions containing the rare-earth ions by adding ammonium carbonate or by passing CO_2 in a suspension of rare-earth hydroxides in water. Unfortunately only powder samples are obtained in that way. A suitable method of growing single crystals is the hydrolysis of rare-earth trichloroacetates under elevated CO_2 pressure.[650] Attempts to obtain single-crystalline carbonates via hydrothermal syntheses or by applying high carbon dioxide pressure were not successful but yielded hydroxocarbonates or oxidecarbonates. Thus, to date no structural data of anhydrous rare-earth carbonates are available. $La_2(CO_3)_3{\cdot}8H_2O$ is the only structurally characterized binary synthetic carbonate hydrate.[651] It contains the two crystallographically different La^{3+} ions in 10-fold coordination of oxygen atoms. The $CO(1)_3{}^{2-}$ and La^{3+} ions are arranged in layers in the (001) plane of the orthorhombic unit cell. The $La(1)^{3+}$ ions are additionally attached by four water molecules and the $La(2)^{3+}$ by two H_2O ligands and one chelating $CO_3{}^{2-}$ group. The layers are connected by hydrogen bonds involving nonbonded water molecules between the layers. According to DTA/TG measurements the octahydrate decomposes in a three-step process yielding La_2O_3. Between 150 and 250 °C the water is driven off, and slightly above 400 °C the carbonate starts to decompose leading to the oxide carbonate $La_2O_2CO_3$. Above 550 °C the latter is transformed to La_2O_3.[652]

In the structure of *tengerite* the Y^{3+} ions are 8-fold coordinated by oxygen atoms.[653] These belong to three chelating and one monodentate $CO_3{}^{2-}$ ions and one H_2O molecule. Crystallographically one can distinguish between two carbonate groups, $C(1)O_3{}^{2-}$ and $C(2)O_3{}^{2-}$. The former are surrounded by four Y^{3+} ions, while the latter are connected to two ions so that the linkage can be written as $[Y(C(1)O_3)_{4/4}(CO_3)_{1/2}(H_2O)]$. The different functionalities of the carbonate groups are easy to recognize in Figure 95. $C(1)O_3{}^{2-}$ is responsible for the linkage in the (001) plane, while $C(2)O_3{}^{2-}$ connects the resulting layers in the [001] direction.

Remarkable carbonate hydrates are the ternary compounds $K_4Ce(CO_3)_3(O_2){\cdot}6H_2O$,[654] $K_3NaCe(CO_3)_3(O_2){\cdot}4H_2O$,[655] and $K_4Ce(CO_3)_3O{\cdot}2H_2O$.[656] While in the latter $[Ce(CO_3)_3]$ units are linked by two oxygen atoms to chains according to ${}^{1}_{\infty}[Ce(CO_3)_3O_{2/2}]$, in the peroxides dimers $[Ce_2(CO_3)_6(O_2)_2]$ are formed. In these dimeric units the $O_2{}^{2-}$ ions are attached *side on* to two Ce^{4+} ions (Figure 96).

2. Basic Carbonates

Attempts to prepare single crystals of anhydrous rare-earth carbonates under hydrothermal conditions never were successful but led to the basic carbonates $M(OH)CO_3$,[657−660] $M_2(OH)_4CO_3$,[661] and $M_2O_2CO_3$.[662,663]

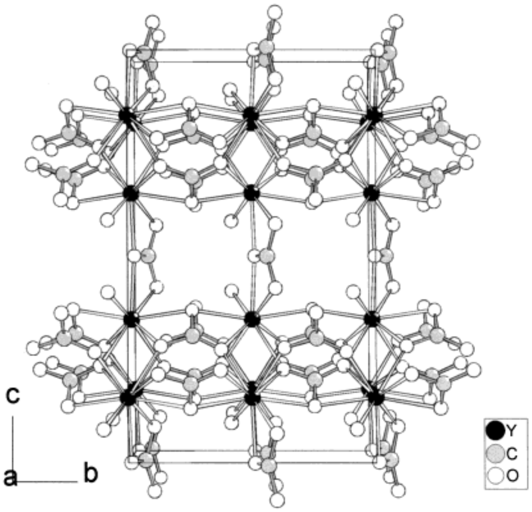

Figure 95. Crystal structure of the mineral *Tengerite,* $Y_2(CO_3)_3{\cdot}2H_2O$. The different functionalities of the carbonate groups are easy to recognize.

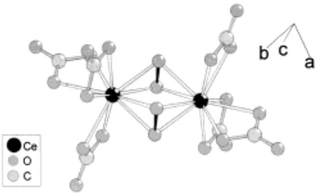

Figure 96. $[Ce_2(CO_3)_6(O_2)_2]^{8-}$ dimer in the crystal structure of $K_4Ce(CO_3)_3(O_2){\cdot}6H_2O$. Note that the bridging $O_2{}^{2-}$ ions are attached side on to the Ce^{4+} ions.

The hydroxides are obtained at lower temperatures (300 °C), while the oxides require temperatures around 600 °C. For the hydroxide carbonates $M(OH)CO_3$ ($M = La{-}Er, Y$) two structure types are known. The hexagonal one was described for $Nd(OH)CO_3$[657] and contains layers of the composition ${}_{\infty}^{2}[(OH)Nd_{3/3}]^{2+}$ with each hydroxide ion connecting three Nd^{3+}. The layers are stacked in the [001] direction and are linked by the carbonate groups which act as chelating and monodentate ligands. For the three crystallographically different Nd^{3+} ions, coordination numbers of 11 and 10 result. The orthorhombic modification has previously been described with the space group *Pmcn*, but a recent investigation on $Dy(OH)CO_3$[659] shows the correct symmetry to be $P2_12_12_1$. In the crystal structure the OH^- ions connect the cation to zigzag chains according to ${}^{1}_{\infty}[(OH)M_{2/2}]^{2+}$ which are oriented along [010] and linked via the $CO_3{}^{2-}$ ions (Figure 97). The coordination number for Dy^{3+} is 10. For the hydroxide-rich carbonates $M_2(OH)_4CO_3$ which are known for M = Ho, Er, Yb, and Y,[661] a formal condensation of these chains to layers of the composition ${}^{2}_{\infty}[M(1)(OH)_{5/3}M(2)(OH)_{4/3}(OH)_{2/2}]^{2+}$ can be observed which extend in the (100) plane. The sheets are connected by the carbonate groups (Figure 98). Further hydroxide carbonates have been mentioned in the literature, for example, the scandium compound $Sc(OH)CO_3{\cdot}xH_2O$ ($x = 1, 3$),[664] but structural data are not available.

The oxides $M_2O_2CO_3$ are described for several lanthanides (cf. Table 16). Three different crystal structures were assumed, a monoclinic, *pseudo*-tetragonal one, a tetragonal one, and a hexagonal

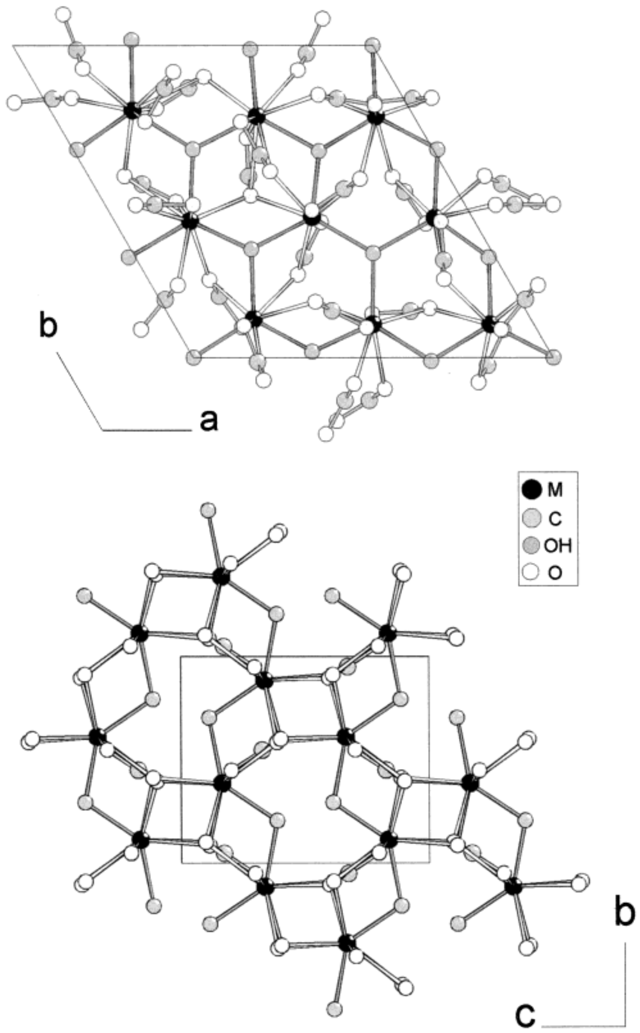

Figure 97. Crystal structures of the hexagonal and the orthorhombic modifications of the basic carbonates $M(OH)CO_3$.

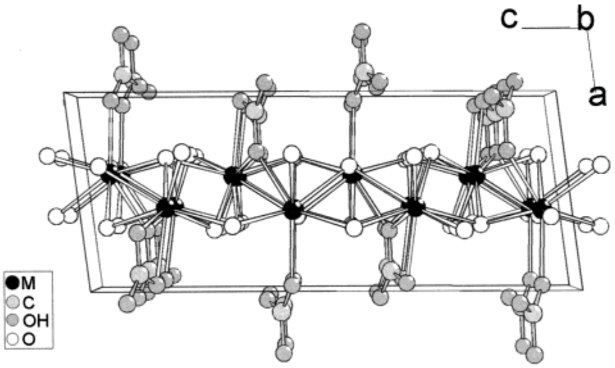

Figure 98. Layers of the composition ${}^{2}_{\infty}[M(1)(OH)_{5/3}M(2)(OH)_{4/3}(OH)_{2/2}]^{2+}$ in the (100) plane of the crystal structure of $M_2(OH)_4CO_3$ (M = Ho, Er, Yb, Y).

one. Only for the latter are structural known. According to these data the carbonates $M_2O_2CO_3$ (M = La−Yb)[662,663,665] contain oxide-centered $[OM_4]$ tetrahedra which share three common *cis*-edges leading to a double layer of composition ${}^{2}_{\infty}\{[OM_{4/4}]\}_2^{2+}$. They are stacked in the [001] direction and connected by CO_3^{2-} groups (Figure 99). The carbonate ions are disordered in a way that the sites of the carbon atom and one of the oxygen atoms are occupied to only one-third.

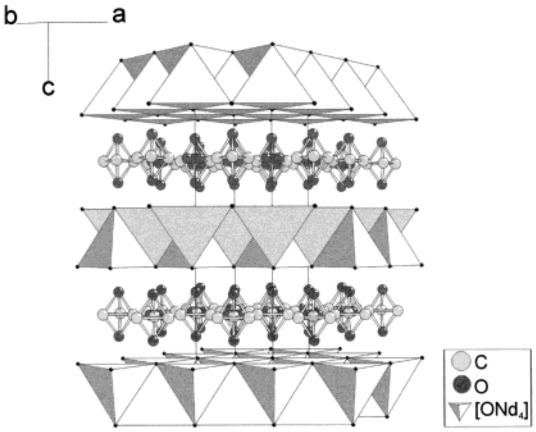

Figure 99. Crystal structure of the oxide carbonates $M_2O_2CO_3$ (M = La−Yb). Double layers of composition ${}^{2}_{\infty}\{[OM_{4/4}]\}_2^{2+}$ are alternating stacked with disordered carbonate ions.

3. Acidic Carbonates

Two binary hydrogencarbonates are described in the literature, $Ho(HCO_3)_3 \cdot 6H_2O$ and $Gd(HCO_3)_3 \cdot 5H_2O$.[666,667] They were obtained by acidifying freshly precipitated carbonates. Both compounds are built up from the molecular complexes $[M(H_2O)_4(HCO_3)_3]$ which contain the M^{3+} ions in 10-fold oxygen coordination due to the chelating attachment of the HCO_3^- ions. Two additional H_2O molecules are present in the holmium compound, whereas in the gadolinium hydrogencarbonate only one of them is found. The neutral complexes are linked in the structures only by hydrogen bonds. Structurally both of the compounds are closely related to the respective rare-earth nitrates, and $Ho(HCO_3)_3 \cdot 6H_2O$ is even isotypic with $M(NO_3)_3 \cdot 6H_2O$ (M = La−Tb, cf. below). Recently, a new rare-earth mineral has been described containing hydrogencarbonate anions. It is named *thomasclarkite* and has the approximate composition $NaY(HCO_3)(OH)_3(H_2O)_4$, but in fact other rare-earth and/or alkaline-earth ions may be incorporated on the cation sites and part of the OH^- groups may be substituted by F^-.[668]

4. Ternary Carbonates

Most of the ternary carbonates have been prepared with alkali metals as the third component and are known either as hydrates or anhydrous species. Unfortunately, structural data are not available for all of these compounds. Furthermore, the data provided are often not of high quality, so that details of the structures remain unknown. Accurate structure determinations of ternary hydrates have been performed mainly for scandium-containing compounds. They have the compositions $Na_5[Sc(CO_3)_4] \cdot 2H_2O$,[669,670] $Na_2[Co(NH_3)_6][Sc(CO_3)_4] \cdot 14H_2O$, $K_5[Sc(CO_3)_4] \cdot 5H_2O$, and $K_7[Sc(CO_3)_4](CO_3) \cdot 9H_2O$[670] and contain the $[Sc(CO_3)_4]^{5-}$ anion. It shows the Sc^{3+} ions in 8-fold coordination of oxygen atoms which belong to the four chelating carbonate groups. In $Na_5[Sc(CO_3)_4] \cdot 2H_2O$ the complex anions and the $[NaO_4]$ tetrahedra are

Table 16. Crystallographic Data of Carbonates

compound	space group	lattice parameters						ref
		a/Å	b/Å	c/Å	α/°	β/°	γ/°	
		carbonate−hydrates						
$La_2(CO_3)_3 \cdot 8H_2O$	$Pccn$	8.984(4)	9.580(4)	17.00(1)				651
$Y_2(CO_3)_3 \cdot 2H_2O$	$Bb2_1m$	6.078(4)	9.157(2)	15.114(6)				653
$K_4Ce(CO_3)_3(O_2) \cdot 6H_2O$	$P\bar{1}$	8.887(1)	10.392(1)	10.958(1)	66.8(1)	68.4(1)	74.4(1)	654
$K_3NaCe(CO_3)_3(O_2) \cdot 4H_2O$	$P\bar{1}$	8.412(1)	9.789(2)	10.186(2)	96.2(1)	102.9(1)	112.2(1)	655
$K_4Ce(CO_3)_3O \cdot 2H_2O$	$Amm2$	4.1741(6)	16.305(2)	9.395(1)				656
		basic carbonates						
$NdOH(CO_3)$	$P\bar{6}$	12.320		9.880				657
$NdOH(CO_3)$	$Pmcn$	4.953(3)	8.477(3)	7.210(3)				658
$Dy(OH)(CO_3)$	$P2_12_12_1$	4.835(1)	6.984(1)	8.449(1)				659
$Y(OH)(CO_3)$	$P2_12_12_1$	4.809(1)	6.957(1)	8.466(1)				660
$Ho_2(OH)_4(CO_3)$	$P2_1/c$	6.274(2)	6.041(1)	15.416(4)		97.38(2)		661
$Y(B(OH)_4)(CO_3)$	$Pbca$	9.089(1)	12.244(1)	8.926(1)				*a*
$Nd_2O_2(CO_3)$	$P6_3/mmc$	3.974		15.703				662
$La_2O_2(CO_3)$	$P6_3/mmc$	4.0755(6)		15.957(1)				663
$La_2O_{2.3}(CO_3)_{0.85}$	$P6_3/mmc$	4.0852(4)		16.2211(6)				664
$Li_{0.52}La_2O_{2.52}(CO_3)_{0.74}$	$P6_3/mmc$	4.0580(1)		16.2219(1)				665
		acidic carbonates						
$Ho(HCO_3)_3 \cdot 6H_2O$	$P\bar{1}$	9.18(2)	11.59(1)	6.73(1)	88.87(6)	112.45(8)	71.54(6)	666
$Gd(HCO_3)_3 \cdot 5H_2O$	$P112_1/a$	6.877(1)	9.575(2)	18.871(2)			102.61(2)	667
$NaY(HCO_3)(OH)_3 \cdot 4H_2O$	$P12_1$	4.556(1)	13.018(6)	4.556(2)		90.15(3)		668
		fluoride carbonates						
$Ce(CO_3)$ F	$P\bar{6}2c$	7.162		9.787				685
$Ce(CO_3)F$	$P\bar{6}2c$	7.117(1)		9.762(1)				686
$Ce(CO_3)F$	$P\bar{6}2c$	7.1438(9)		9.808(2)				687
$Ce(CO_3)F$	$P\bar{6}2c$	7.1561(9)		9.816(1)				*b*
$La(CO_3)F$	$P\bar{6}2c$	7.094(4)		4.859(4)				688
$NaY(CO_3)F_2$	$Pmcn$	6.959(2)	9.170(2)	6.301(1)				689
$Ba_2Y(CO_3)_2F_3$	$Pbcn$	9.458(3)	6.966(2)	11.787(4)				694
$Ba_3Ce_2(CO_3)_5F_2$	$C2/m$	21.42(5)	5.078(5)	13.30(5)		94.8(5)		*c*
$Ba_2Ce(CO_3)_3F$	$P2_1/m$	13.365(3)	5.097(1)	6.638(1)		106.45(1)		690
BaCe(CO3)2F	$R\bar{3}m$	5.072(1)		38.46(1)				691
$Ba_2Gd(CO_3)_2F_3$	$Pbcn$	9.513(1)	6.978(1)	11.864(4)				*d*
$Ba_3La_2(CO_3)_5F_2$	$C2/m$	21.472(6)	5.098(2)	13.325(3)		94.96(1)		*e*
$Ca_{0.5}BaCe_2(CO_3)_4F$	$P\bar{6}2c$	5.093(6)		23.017(6)				*f*
$CaCe(CO_3)_2F$	$P3_1$	7.126(6)		55.08(1)				*g*
$Ca_2Ce_3(CO_3)_5F_3$	$R3$	7.130		69.400				685
$BaSm(CO_3)_2F$	$R\bar{3}m$	5.016(1)		37.944(6)				692
$CaCe(CO_3)_2F$	$C2/c$	12.329(2)	7.110(1)	18.741(2)		102.68(1)		*h*
$KGd(CO_3)F_2$	$Fddd$	7.006(2)	11.181(3)	21.865(6)				693
$NaBaCe_2(CO_3)_4F$	$P6_3/mmc$	5.088(2)		23.168(1)				689
$Na_3Ce_2(CO_3)_4F$	$P6_3/mmc$	5.0612(1)		22.820(9)				*i*
$Na_2Eu(CO_3)F_3$	$Pbca$	6.596(4)	10.774(4)	14.09(1)				*j*
$Na_3La_2(CO_3)_4F$	$P6_3/mmc$	5.083(1)		23.034(5)				*k*
$Na_{15}Y_2(CO_3)_9(SO_3F)Cl$	$P\bar{6}$	8.763(1)		10.736(2)				*l*
$K_4Gd_2(CO_3)_3F_4$	$R32$	9.027(1)		13.684(3)				*m*
$Ba_3Sc(CO_3)F_7$	$Cmcm$	11.519(3)	13.456(3)	5.974(1)				695
		ternary carbonates						
$Na_3Y(CO_3)_3 \cdot 3H_2O$	$Pna2_1$	17.358(8)	10.034(4)	5.946(2)				*c*
$Na_5Sc(CO_3)_4 \cdot 2H_2O$	$P\bar{4}2_1c$	7.46(1)		11.60(2)				669
$Na_5Sc(CO_3)_4 \cdot 2H_2O$	$P\bar{4}2_1c$	7.4637(4)		11.570(2)				670
$K_5Sc(CO_3)_4 \cdot 5H_2O$	$P2_1/n$	8.831(1)	18.262(2)	11.132(2)		93.28(2)		670
$K_7[Sc(CO_3)_4](CO_3) \cdot 9H_2O$	$C2$	13.960(1)	10.8135(7)	33.781(4)		93.76(1)		670
$Na_2[Co(NH_3)_6][Sc(CO_3)_4] \cdot 14H_2O$	$P2/n$	8.7185(9)	10.848(1)	15.632(2)		93.38(1)		670
$Na_2[Co(NH_3)_6][Ho(CO_3)_4] \cdot 14H_2O$	$P2/n$	8.7091(5)	10.8744(6)	15.7971(9)		93.117(1)		671
$[Co(NH_3)_6][Sm(CO_3)_3] \cdot 5H_2O$	$C2/m$	21.895(2)	6.7568(6)	14.578(1)		125.67(1)		672
$K[Co(NH_3)_6]_3[Nd_2(CO_3)_8] \cdot 15H_2O$	$P2_1/c$	13.2320(5)	15.5731(7)	26.015(1)		90.952(1)		673
$[C(NH_2)_3]_6(Nd(CO_3)_5] \cdot 3H_2O$	$Pna2_1$	21.472(1)	6.8615(3)	18.8797(9)				674
$[C(NH_2)_3]_6[Ce(CO_3)_5] \cdot 4H_2O$	$C2/c$	16.0500(1)	13.14(3)	6.6300(1)		108.1(2)		675
$NaLa(CO_3)_2$	$Pb2_1m$	6.41(3)	7.30(3)	5.23(2)				678
$Na_3Eu(CO_3)_3$	$Ama2$	9.942(2)	11.024(3)	7.147(2)				679
$Na_4Ce_2(CO_3)_5$	$P2_1$	20.872(4)	6.367(1)	10.601(2)		120.50(1)		680
$KHo(CO_3)_2$	$C2/c$	8.510(1)	9.455(1)	6.923(1)		111.0(1)		681
$KYb(CO_3)_2$	$C2/c$	8.468(1)	9.381(2)	6.881(1)		110.76(1)		681
$KNd(CO_3)_2$	$Pmn2_1$	9.731(2)	6.4569(8)	8.556(1)				681
$KGd(CO_3)_2$	$C2/c$	8.575(2)	9.573(2)	6.990(1)		111.19(2)		681
$KDy(CO_3)_2$	$C2/c$	8.538(2)	9.491(1)	6.945(1)		111.06(1)		681
$RbSm(CO_3)_2$	$C2/c$	8.819(1)	9.336(1)	7.0991(1)		111.51(1)		682
$CsPr(CO_3)_2$	$P\bar{1}$	8.602(3)	8.874(3)	8.926(3)	98.6(2)	96.2(1)	115.3(2)	683
$CsGd(CO_3)_2$	$P\bar{1}$	8.453(2)	8.778(2)	8.779(2)	98.62(2)	96.58(2)	115.30(2)	684

[a] Grice, J. D.; Ercit, T. S. *Can. Miner.* **1986**, *24*, 675. [b] Terada, Y.; Nakai, I.; Kawashima, T. *Anal. Sci.* **1993**, *9*, 561. [c] Rastsvetaeva, R. K.; Pushcharovskii, D. Yu.; Pekov, I. V. *Eur. J. Miner.* **1996**, *8*, 1249. Yang, Z. M. *Sci. Geol. Sin.* **1996**, *31*, 140. [d] Mercier, N.; Leblanc, M. *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 727. [e] Mercier, N.; Leblanc, M. *Eur. J. Solid State Inorg. Chem.* **1997**, *30*, 195. [f] Shen, J.-C.; Mi, J.-X. *J. China Univ. Geosci.* **1992**, *3*, 17. [g] Gandolfi, E. *Mineral. Petrogr. Acta* **1965**, *11*, 123. [h] Wang, L.-B.; Ni, Y.-X.; Hughes, J. M.; Bayliss, P.; Drexler, J. W. *Can. Mineral.* **1994**, *32*, 865. [i] Grice, J. D.; Chao, G. Y. *Am. Mineral.* **1997**, *82*, 1255. [j] Mercier, N.; Leblanc, M. *Acta Crystallogr.* **1994**, *C50*, 1854. [k] Mercier, N.; Taulelle, F.; Leblanc, M. *Eur. J. Solid State Inorg. Chem.* **1993**, *30*, 609. [l] Grice, J. D.; Gault, R. A.; Chao, G. Y. *Am. Mineral.* **1995**, *80*, 1059. [m] Mercier, N.; Leblanc, M.; Durand, J. *Eur. J. Solid State Inorg. Chem.* **1997**, *34*, 241.

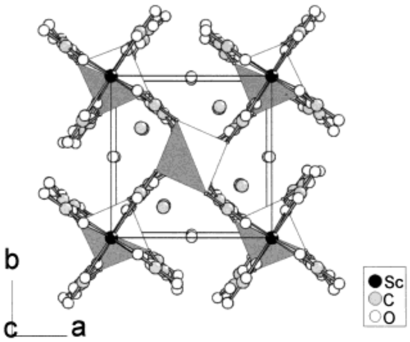

Figure 100. Complex $[Sc(CO_3)_4]^{5-}$ ions and $[NaO_4]$ tetrahedra (drawn as polyhedra) are stacked in the crystal structure of $Na_5[Sc(CO_3)_4]\cdot 2H_2O$.

arranged in layers which are stacked in the [001] direction and held together by further Na^+ ions (Figure 100). The thermal decomposition of the compound proceeds in two steps with the anhydrous carbonate as an intermediate around 300 °C. Final products are Sc_2O_3 and Na_2CO_3. The packing of the complex anions in $K_5[Sc(CO_3)_4]\cdot 5H_2O$ is nearly in a hcp fashion with the K^+ ions and the H_2O molecules in the empty voids. In $K_7[Sc(CO_3)_4](CO_3)\cdot 9H_2O$ formally one formula unit K_2CO_3 and four water molecules are added. The structure is built up from double layers of the anions which are stacked alternating with a double layer of free carbonate groups. The connection within and between the layers is achieved by the K^+ ions. The precipitation of $[Sc(CO_3)_4]^{5-}$ has been achieved using the complex cation $[Co(NH_3)_6]^{3+}$. The resulting compound has the composition $Na_2[Co(NH_3)_6][Sc(CO_3)_4]\cdot 14H_2O$[670] and contains dimeric $[Na(H_2O)_{4/1}(H_2O)_{2/2}]_2{}^{2+}$ units, octahedral $Co(NH_3)_6{}^{3+}$ ions, and free water molecules. The octahedra and the complex anions are arranged in puckered layers in the (010) plane which are held together by the $[Na(H_2O)_{4/1}(H_2O)_{2/2}]_2{}^{2+}$ ions. According to thermoanalytical investigations, the compound decomposes in the first step between 50 and 110 °C to $Na_2[Co(NH_3)_6][Sc(CO_3)_4]\cdot 5H_2O$, which releases H_2O and NH_3 at 165 °C to give $Na_2Co[Sc(CO_3)_4]\cdot H_2O$. In the final step above 350 °C Sc_2O_3, Co_2O_3, and Na_2CO_3 are formed.[670] The tetracarbonatoscandates have been intensively investigated by IR spectroscopy including a detailed theoretical discussion.[670]

A few carbonato complexes with other rare-earth ions are known. $Na_2[Co(NH_3)_6][Ho(CO_3)_4]\cdot 14H_2O$[671] is isotypic with the respective scandium compound, while $[Co(NH_3)_6][Sm(CO_3)_3(H_2O)]\cdot 4H_2O$[672] contains no monomeric complex anions but zigzag chains according to ${}^{1}_{\infty}[Sm(CO_3)_{3/3}(CO_3)_{2/1}(H_2O)]^{3-}$ which are held together by the $[Co(NH_3)_6]^{3+}$ octahedra (Figure 101). In this way a coordination number of nine is achieved for the Sm^{3+} ions. Similarly, a chain structure is found for $K[Co(NH_3)_6]_3[Nd_2(CO_3)_8]\cdot 15H_2O$.[673] In the structure Nd^{3+} is coordinated by four chelating and one monodentate carbonate groups leading to a CN of nine. The chains ${}^{1}_{\infty}[Nd(CO_3)_{2/2}(CO_3)_{3/1}]^{5-}$ are connected by cobalt hexaammine and dimeric $[K_2(H_2O)_{10}]^{2+}$ cations. Monomeric carbonato complexes with larger lanthanide ions are obtained if guanidinium, $[C(NH_2)_3]^+$, is used as the counterion. Structural data are known for $[C(NH_2)_3]_5[Nd(CO_3)_4(H_2O)]\cdot 2H_2O$[674] and the tetravalent cerium compound $[C(NH_2)_3]_6[Ce(CO_3)_5]\cdot 4H_2O$.[675] In the former Nd^{3+} is surrounded by four chelating $CO_3{}^{2-}$ ions and one water molecule, while in the latter Ce^{4+} is exclusively attached by carbonate groups leading to a coordination number of 10.

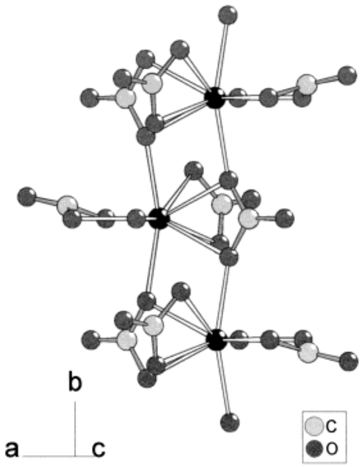

Figure 101. Zigzag chains ${}^{2}_{\infty}[Sm(CO_3)_{3/3}(CO_3)_{2/1}(H_2O)]^{3-}$ in the crystal structure of $[Co(NH_3)_6][Sm(CO_3)_3(H_2O)]\cdot 4H_2O$.

Anhydrous ternary carbonates were synthesized under elevated CO_2 pressure in steel autoclaves from alkali carbonates and rare-earth chlorides or oxalates at 450 °C. Often the products were obtained as powders, so that only powder diffraction data are available. This is especially true for the lithium compounds for which no single-crystal data have been available.[676,677] With Na^+ the structure of $NaLa(CO_3)_2$ is known[678] which contains the La^{3+} ions in 10-fold coordination of oxygen atoms which belong to three chelating and four monodentate $CO_3{}^{2-}$ groups. These are attached to three and four La^{3+} ions, respectively, so that according to ${}^{3}_{\infty}[La(CO_3)_{3/3}(CO_3)_{4/4}]^-$ a three-dimensional network is formed which incorporates the 7-fold coordinate Na^+ ions. With $Na_3Eu(CO_3)_3$ the structure of a sodium-rich carbonate has been determined recently.[679] It crystallizes acentrically with the space group *Ama*2, and two crystallographically different $CO_3{}^{2-}$ ions are found. $C(2)O_3{}^{2-}$ connects the Eu^{3+} ions to chains running along [011], and the linkage of the chains is performed by $C(1)O_3{}^{2-}$ (Figure 102). Due to the chelating attachment of three carbonate ions and the monodentate behavior of three additional $CO_3{}^{2-}$ groups, Eu^{3+} gains a coordination number of nine. A third composition for sodium-containing carbonates has been described for the new mineral Petersenite, $Na_4Ce_2(CO_3)_5$,[680] which has a complicated structure containing four crystallographically different Ce^{3+} and 10 crystallographically different $CO_3{}^{2-}$ ions. For all of the Ce^{3+} ions the CN is 10. The largest number of anhydrous ternary rare-earth carbonates is described for potassium compounds $KM(CO_3)_2$.[681] They are known with Nd, Gd, Dy, Ho, and Yb and adopt two different structure types. The orthorhombic modification was described for $KNd(CO_3)_2$, and its structure can be divided in layers of the composition ${}^{2}_{\infty}[Nd(CO_3)]^+$ and ${}^{2}_{\infty}[K(CO_3)]^-$ which are connected along [010] (Figure

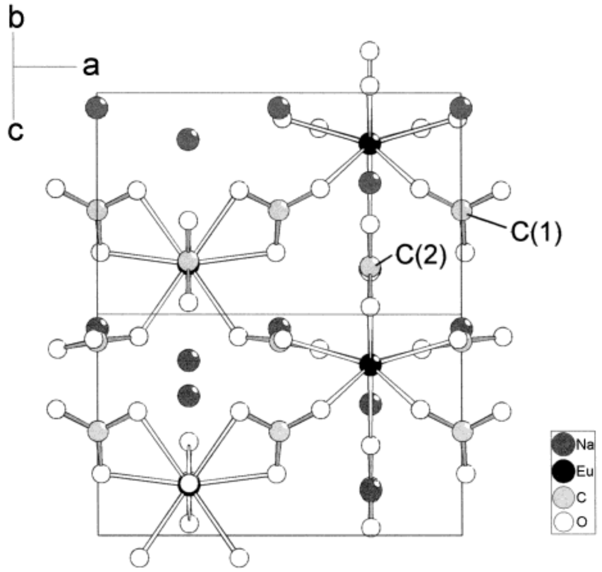

Figure 102. Crystal structure of $Na_3Eu(CO_3)_3$ viewed along [011].

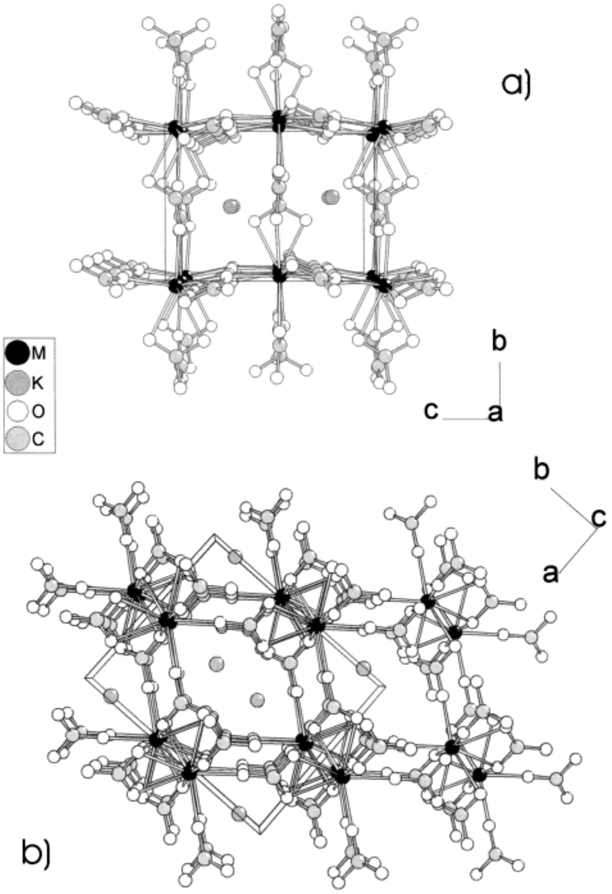

Figure 103. Comparison of the crystal structures of $KNd(CO_3)_2$ (a) and $KDyCO_3)_2$ (b).

103a). Thereby the Nd^{3+} ions are surrounded by three chelating and three monodentate CO_3^{2-}, so that a CN of nine is obtained. The monoclinic modification is observed for the smaller lanthanides and has essentially the same structural features as the orthorhombic one but the carbonate groups are rearranged a little bit in order to decrease the coordination number of M^{3+} to eight (Figure 103b). The same structure has been found for $RbSm(CO_3)_2$,[682] while $CsPr(CO_3)_2$ and $CsGd(CO_3)_2$ adopt a triclinic structure.[683,684] The coordination number for the M^{3+} ions is still eight, but the larger Cs^+ ions lead to a severe distortion of the monoclinic structure.

5. Fluoride Carbonates

The most important fluoride carbonate is the mineral *bastnasite* which has essentially the composition $CeFCO_3$ but may contain other large rare-earth ions on the cerium position. The mineral serves as a natural source for the rare earths. Therefore, its structure has been determined several times.[685−688] It can be described as a stacking of hexagonal layers $^{2}_{\infty}[CeF_{3/3}]^{2+}$ which are stacked alternating with layers of carbonate ions. Thus, it shows a close similarity to the hexagonal modification of $M_2O_2CO_3$-type compounds. Further fluoride carbonates containing additional cations are frequently observed as minerals. They contain very often alkaline-earth metals, mainly barium and calcium, and show a large number of different compositions, for example, $NaBaCe_2(CO_3)_4F$[689] (*baiyuneboite*), $Ba_2Ce(CO_3)_3F$[690] (*zhonghuacerite*), $BaCe(CO_3)_2F$[691] (*huangoite*), and $Ca_2Ce_3(CO_3)_5F_3$[685] (*rontgenite*). Most of these compounds can be also prepared artificially bearing the opportunity to produce similar compound with all of the rare-earth elements. $BaSm(CO_3)_2F$[692] and $KGd(CO_3)F_2$[693] may serve as examples. Two further synthetic fluoride carbonates are $Ba_2Y(CO_3)_2F_3$[694] and $Ba_3Sc(CO_3)F_7$.[695] In the yttrium compound Y^{3+} is surrounded by two chelating and two monodentate CO_3^{2-} and by three F^- ligands. The carbonate groups link the polyhedra to layers $^{2}_{\infty}[Y(CO_3)_{4/2}F_3]^{4-}$ which are connected by 9-fold coordinate Ba^{2+} ions. The fluoride-rich scandium carbonate is built up from complex $[Sc(CO_3)F_5]^{4-}$ anions with a chelating carbonate group. The ions are separated by Ba^{2+} in 11-fold coordination and lonesome fluoride ions. A new sodium-containing fluoride carbonate is the mineral *horvatite*, $NaYCO_3F_2$.[696] The structure contains 8-fold coordinated Y^{3+} ($4 \times O^{2-}$, $4 \times F^-$) and 7-fold coordinated Na^+ ions ($4 \times F^-$, $3 \times O^{2-}$) and consists of layers $^{2}_{\infty}[NaY(CO_3)]^{2+}$ which are connected in the [100] direction by F^- double sheets (Figure 104).

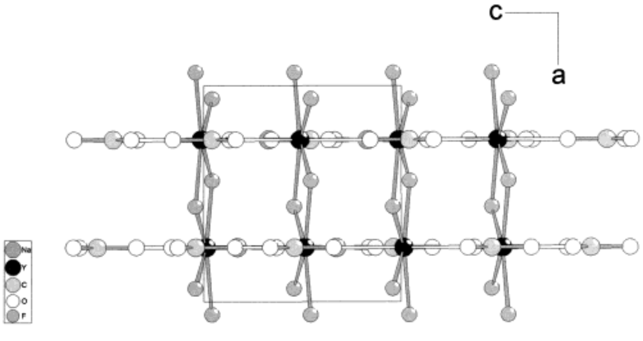

Figure 104. Crystal structure of the mineral *horvatite*, $NaYCO_3F_2$. The structure is composed from $^{2}_{\infty}[NaY(CO_3)]^{2+}$ layers which are connected by F^- double sheets.

B. Nitrates

Nitrates of the rare-earth elements are a strongly investigated group of compounds. On one hand, the

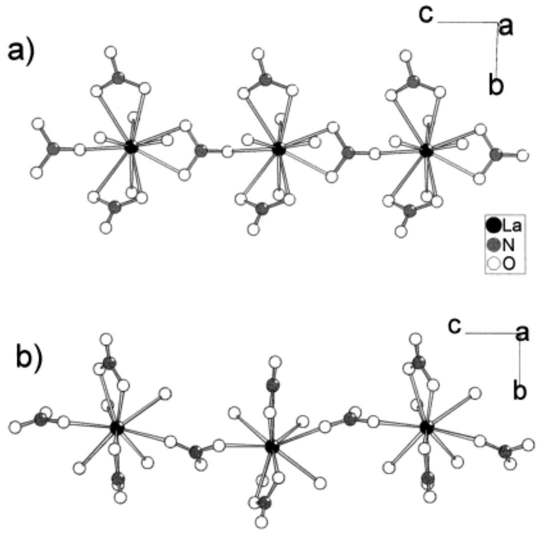

Figure 105. $^{1}_{\infty}[La(H_2O)_{4/1}(NO_3)_{2/1}(NO_3)_{2/2}]$ chains in $La(NO_3)_3{\cdot}4H_2O$–I (a) and $La(NO_3)_3{\cdot}4H_2O$–II (b).

ternary complexes $Mg_3M_2(NO_3)_{12}{\cdot}24H_2O$ and $(NH_4)_2M(NO_3)_5{\cdot}4H_2O$ were formerly used in the separation and purification process of rare-earth elements;[697] on the other hand, nitrates are frequent reagents during various syntheses due to their high solubilities, even in organic solvents. Thus, a large number of structure determinations have been performed for a large variety of compounds (Table 17). However, most of these compounds are hydrates or ternary complexes and, analogously to the carbonates, there is no structure of an anhydrous binary rare-earth nitrate known to date. Two short reviews on the systematics of hydrous and anhydrous ternary rare-earth nitrates were published a few years ago.[698,699]

1. Nitrate Hydrates

The series of the hexahydrates includes the lanthanides from La to Tb and additionally Y.[700−712] The compounds are isotypic and contain neutral $[M(H_2O)_4(NO_3)_3]$ complexes and two molecules of crystal water. The same complexes are known for the pentahydrates, which have been structurally characterized for M = Eu, Gd, Yb, and Y, but in this case only one additional water H_2O molecule is found.[713−716] Dehydration of the hydrates is possible and leads to powder samples of the anhydrous species, also the formation of basic nitrates may readily occur especially for the smaller lanthanides.[717,718] Tetrahydrates are known with La, Ce, and Lu, and for $La(NO_3)_3{\cdot}4H_2O$ two modifications were found.[716,719,720] Both show the La^{3+} ions surrounded by four nitrate groups and four H_2O molecules. According to $^{1}_{\infty}[La(H_2O)_{4/1}(NO_3)_{2/1}(NO_3)_{2/2}]$ the polyhedra are linked to chains which are held together by hydrogen bonds. The difference between the two structures is that in the monoclinic one (Figure 105a) three NO_3^- ions are attached chelating to La^{3+} while the orthorhombic one shows only two chelating ions, e.g., the coordination number decreases from 11 to 10 (Figure 105b). In the structure of $Lu(NO_3)_3{\cdot}4H_2O$,[716] again neutral complexes $[Lu(H_2O)_3(NO_3)_3]$ containing three chelating nitrate groups occur besides a free molecule of crystal water. The different structure compared to the lanthanum nitrates results from the smaller Lu^{3+} radius yielding a lower coordination number of nine. The unique hydrate $Y(NO_3)_3{\cdot}3.5H_2O$[721] is built up from cationic $[Y(H_2O)_5(NO_3)_2]^+$ and anionic $[Y(H_2O)_2(NO_3)_4]^-$ complexes which are arranged in layers alternating stacked in the [001] direction (Figure 106).

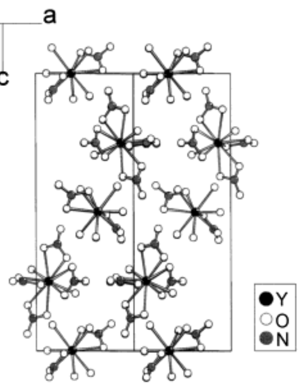

Figure 106. Crystal structure of $Y(NO_3)_3{\cdot}3.5H_2O$ containing cationic $[Y(H_2O)_5(NO_3)_2]^+$ and anionic $[Y(H_2O)_2(NO_3)_4]^-$ complexes.

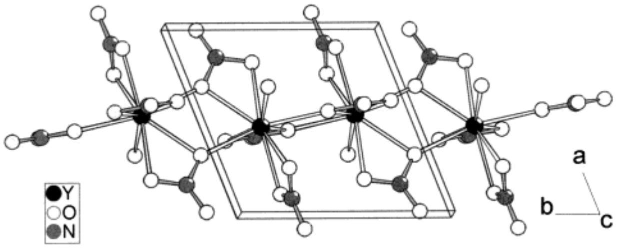

Figure 107. Crystal structure of $Y(NO_3)_3{\cdot}H_2O$ with chains according to $^{1}_{\infty}[Y(H_2O)_{1/1}(NO_3)_{4/2}(NO_3)_{1/1}]$.

Interestingly, the trihydrates of Y,[722] Lu,[716] and Yb[723] are not isotypic with each other, although the ions are of comparable size. All of the three nitrates contain $[M(H_2O)_3(NO_3)_3]$ complexes which can be seen as distorted octahedra, if the NO_3^- ligand is reduced to its nitrogen atom. The difference between the structures arises from the *mer*-configuration of the nitrate ligands in the Y and Lu compounds, respectively, compared to the *fac*-configuration in $Yb(NO_3)_3{\cdot}3H_2O$. Furthermore, the arrangement of the complexes differs slightly in the former two. In the lowest hydrate known so far, $Y(NO_3)_3{\cdot}H_2O$,[724] the Y^{3+} ions are 9-fold coordinated by oxygen atoms which belong to three chelating and two monodentate NO_3^- ligands as well as to one H_2O molecule. Four of the NO_3^- ions connect to further Y^{3+} ions leading to infinite chains $^{1}_{\infty}[Y(H_2O)_{1/1}(NO_3)_{4/2}(NO_3)_{1/1}]$ extending in the [010] direction (Figure 107).

2. Basic Nitrates

A number of basic rare-earth nitrates are known having the composition $M(OH)_2NO_3$.[725−728] They crystallize with the same structure which can be understood as a two-dimensional network $^{2}_{\infty}[M(OH)_{6/3}]^+$ which is slightly puckered and oriented parallel to (001). The OH^- ions are in trigonal pyramidal environment of M^{3+} ions. The coordination sphere of the M^{3+} ion is completed by one chelating attached

Table 17. Crystallographic Data of Nitrates

compound	space group	lattice parameters						ref
		a/Å	b/Å	c/Å	α/°	β/°	γ/°	
nitrate−hydrates								
$La(NO_3)_3\cdot 6H_2O$	$P\bar{1}$	8.896	10.677	6.633	78.90	102.10	92.50	700
$La(NO_3)_3\cdot 6H_2O$	$P\bar{1}$	8.933(5)	10.723(4)	6.664(2)	78.86(3)	77.92(4)	87.91(4)	701
$Ce(NO_3)_3\cdot 6H_2O$	$P\bar{1}$	8.886(6)	10.671(9)	6.612(3)	78.76(6)	102.19(5)	92.08(6)	702
$Pr(NO_3)_3\cdot 6H_2O$	$P\bar{1}$	9.19(3)	11.70(4)	6.78(3)	89.0(5)	110.7(5)	110.2(5)	703
$Pr(NO_3)_3\cdot 6H_2O$	$P\bar{1}$	9.23(3)	11.77(4)	6.78(2)	91.17(8)	111.77(5)	69.5(1)	704
$Pr(NO_3)_3\cdot 6H_2O$	$P\bar{1}$	9.19(3)	11.70(4)	6.78(3)	89.0(5)	110.7(5)	110.2(5)	705
$Nd(NO_3)_3\cdot 6H_2O$	$P\bar{1}$	9.307(1)	11.747(1)	6.776(1)	91.11(1)	112.24(1)	109.15(1)	706
$Nd(NO_3)_3\cdot 6H_2O$	$P\bar{1}$	6.768(5)	9.195(6)	11.726(7)	69.79(5)	88.93(5)	69.33(5)	707
$Sm(NO_3)_3\cdot 6H_2O$	$P\bar{1}$	6.747(1)	9.156(1)	11.673(1)	69.90(1)	88.88(1)	69.29(1)	708
$Eu(NO_3)_3\cdot 6H_2O$	$P\bar{1}$	6.705(1)	9.140(1)	11.647(1)	69.71(1)	88.94(1)	69.29(1)	709
$Gd(NO_3)_3\cdot 6H_2O$	$P\bar{1}$	6.712(3)	9.110(6)	11.607(8)	70.17(5)	88.80(5)	69.04(5)	710
$Tb(NO_3)_3\cdot 6H_2O$	$P\bar{1}$	9.095(7)	11.600(6)	6.705(4)	91.14(4)	110.79(5)	70.14(5)	711
$Y(NO_3)_3\cdot 6H_2O$	$P\bar{1}$	9.151(5)	12.097(8)	6.723(2)	104.50(4)	112.40(3)	104.10(5)	712
$Eu(NO_3)_3\cdot 5H_2O$	$P\bar{1}$	10.638(3)	9.568(3)	6.704(2)	76.12(3)	84.68(2)	63.72(2)	713
$Gd(NO_3)_3\cdot 5H_2O$	$P\bar{1}$	6.692(1)	9.588(2)	10.622(2)	63.70(1)	84.68(1)	76.19(1)	714
$Y(NO_3)_3\cdot 5H_2O$	$P\bar{1}$	6.652(4)	9.558(5)	10.563(5)	63.60(3)	84.60(4)	76.10(4)	715
$Yb(NO_3)_3\cdot 5H_2O$	$P\bar{1}$	6.578(3)	9.514(4)	10.496(4)	63.55(3)	84.61(3)	76.03(3)	716
$La(NO_3)_3\cdot 4H_2O$	$P2_1/m$	6.7778(9)	11.3673(1)	6.5843(1)		90.64(1)		719
$La(NO_3)_3\cdot 4H_2O$	$Pbca$	11.834(1)	12.973(1)	13.531(1)				719
$Ce(NO_3)_3\cdot 4H_2O$	$Pbca$	11.756(6)	12.901(9)	13.522(3)				720
$Lu(NO_3)_3\cdot 4H_2O$	$P2_1/n$	7.379(7)	10.364(5)	14.26(1)		96.09(7)		716
$Y(NO_3)_3\cdot 3.5H_2O$	$C222_1$	9.274(6)	11.001(4)	20.055(9)				721
$Yb(NO_3)_3\cdot 3H_2O$	$R\bar{3}$	11.755(1)		11.177(1)				723
$Lu(NO_3)_3\cdot 3H_2O$	$P\bar{1}$	12.591(4)	12.144(3)	7.355(2)	80.22(2)	77.68(2)	62.30(2)	716
$Y(NO_3)_3\cdot 3H_2O$	$P\bar{1}$	6.946(2)	7.323(1)	10.948(1)	71.50(1)	78.40(1)	67.60(1)	722
$Y(NO_3)_3\cdot H_2O$	$P\bar{1}$	7.388(1)	7.889(1)	8.204(2)	64.40(2)	70.90(1)	62.74(1)	724
$PrCl_2(NO_3)\cdot 5H_2O$	$P2/c$	12.288(2)	6.484(1)	12.66(2)0		91.91(1)		*k*
basic nitrates								
$La(OH)_2(NO_3)\cdot H_2O$	$C2/m$	21.192(2)	3.9899(6)	6.4048(8)		114.15(1)		725
$Nd(OH)_2(NO_3)\cdot H_2O$	$C2/m$	20.996(4)	3.875(2)	6.282(2)		113.73(1)		729
$Ce_2O(NO_3)_6\cdot 8H_2O$	$P2_1/c$	8.7233(8)	8.9397(8)	13.981(1)		94.91(1)		731
$La(OH)_2(NO_3)$	$P2_1/m$	6.488(2)	3.962(2)	7.770(4)		99.96(1)		725
$Pr(OH)_2NO_3$	$P2_1$	6.449(5)	3.881(5)	7.747(8)		98.73(6)		726
$Nd(OH)_2NO_3$	$P2_1$	6.420(1)	3.838(1)	7.746(2)		98.18(2)		727
$Gd(OH)_2NO_3$	$P2_1$	6.340(2)	3.715(1)	7.728(2)		96.95(2)		727
$Sm(OH)_2(NO_3)$	$P2_1$	6.3852(3)	3.7784(2)	7.7402(3)		97.57(1)		728
$YO(NO_3)$	$P4/nmm$	3.859(1)		9.716(6)				730
$Y_4O(OH)_9(NO_3)$	$P2_1$	9.376(2)	16.376(3)	3.623(1)		101.2(2)		724
$Mg_2Nd(NO_3)_6(OH)\cdot 12H_2O$	$R\bar{3}$	10.998(1)		17.314(2)				765
$YBi_2O_4(NO_3)$	$P\bar{4}mm$	3.8671(1)		10.1930(3)				736
$(Sm_6(H_2O)_{12}(OH)_8(NO_3)_6O)(NO_3)_2\cdot 6H_2O$	$P\bar{1}$	11.595(2)	11.697(2)	16.720(3)	91.05(2)	90.00(1)	112.97(2)	733
$(Gd_6O(OH)_8(H_2O)_{12}(NO_3)_6)(NO_3)_2\cdot 5H_2O$	$C2/c$	12.828(3)	19.175(5)	17.554(6)		106.73(1)		734
$(Dy_6(H_2O)_{12}(OH)_8(NO_3)_6O)(NO_3)_2\cdot 5H_2O$	$C2/c$	12.623(3)	18.798(4)	17.465(4)		106.70(2)		733
$(Er_6(H_2O)_{12}(OH)_8(NO_3)_6O)(NO_3)_2\cdot 4H_2O$	$P\bar{1}$	10.056(2)	10.064(2)	11.397(2)	96.49(1)	108.81(2)	110.90(2)	733
$(Yb_6O(OH)_8(H_2O)_{12}(NO_3)_6)(NO_3)_2\cdot 4H_2O$	$P\bar{1}$	10.006(2)	10.040(1)	11.318(5)	96.52(2)	108.68(3)	110.79(2)	734
$(Y_6O(OH)_8(H_2O)_{12}(NO_3)_6)(NO_3)_2\cdot 4H_2O$	$P\bar{1}$	10.09(2)	10.13(2)	11.47(2)	96.7(1)	108.8(1)	110.8(1)	734
$Er_4O_2(OH)_8(HNO_3)$	$P2_1$	9.338(3)	16.369(3)	3.608(1)		101.16(2)		*a*
hydrous ternary nitrates								
$Cs_4La(NO_3)_7\cdot HNO_3$	$P2_1/c$	7.873(2)	13.530(3)	11.418(7)		94.37(3)		*b*
$(H_3O)_2Ce(NO_3)_5\cdot H_2O$	$P2/c$	21.364(7)	7.8990(7)	15.133(2)		91.02(2)		*c*
$(NH_4)_2(La(NO_3)_5\cdot 4H_2O$	$C2/c$	11.152(5)	8.966(4)	17.881(6)		101.6(4)		729
$(NH_4)_2(La(NO_3)_5\cdot 4H_2O$	$C2/c$	10.97(1)	9.012(5)	17.44(1)		100.1(1)		737
$(NH_4)_2(Pr(NO_3)_5\cdot 4H_2O$	$C2/c$	11.047(5)	8.928(3)	17.875(8)		101.78(7)		730
$Rb_{1.69}La(NO_3)_5\cdot 4H_2O$	Cc	11.092(2)	8.984(2)	17.863(6)		100.85(1)		739
$Rb_2La(NO_3)_5\cdot 4H_2O$	Cc	11.073(3)	8.945(3)	17.790(9)		101.15(3)		739
$Rb_{1.82}Ce(NO_3)_5\cdot 4H_2O$	Cc	11.027(4)	8.937(2)	17.817(9)		101.06(3)		739
$Rb_2Ce(NO_3)_5\cdot 4H_2O$	Cc	11.003(9)	8.887(9)	17.737(9)		101.65(7)		739
$Rb_2Ce(NO_3)_5\cdot 4H_2O$	Cc	11.050(1)	8.977(1)	17.859(2)		100.88(1)		740
$Cs_2La(NO_3)_5\cdot 2H_2O$	$I2/a$	10.868(3)	9.063(4)	17.557(4)		103.20(3)		741
$Cs_2Ce(NO_3)_5\cdot 2H_2O$	$C2/c$	11.125(2)	8.798(1)	16.503(2)		103.77(2)		742
$Cs_2Nd(NO_3)_5\cdot 2H_2O$	$C2/c$	11.136(7)	8.750(4)	16.399(9)		103.43(5)		743
$K_2La(NO_3)_5\cdot 2H_2O$	$Fdd2$	11.336(5)	21.62(1)	12.355(9)				744
$K_2La(NO_3)_5\cdot 2H_2O$	$Fdd2$	11.2814(6)	21.480(1)	12.2589(4)				745
$K_2Ce(NO_3)_5\cdot 2H_2O$	$Fdd2$	11.263(3)	21.404(3)	12.230(4)				745
$K_2Pr(NO_3)_5\cdot 2H_2O$	$Fdd2$	11.213(2)	21.392(4)	12.204(2)				745
$K_2Pr(NO_3)_5\cdot 2H_2O$	$Fdd2$	21.411(3)	11.221(1)	12.208(2)				746
$K_2Pr(NO_3)_5\cdot 2H_2O$	$Fdd2$	21.411(3)	11.221(1)	12.208(2)				747
$K_2Nd(NO_3)_5\cdot 2H_2O$	$Fdd2$	11.197(1)	21.378(1)	12.195(1)				745
$K_2Nd(NO_3)_5\cdot 2H_2O$	$Fdd2$	11.137(1)	21.272(3)	12.151(2)				748
$Na_2Nd(NO_3)_5\cdot H_2O$	$P112/a$	15.147(5)	21.216(9)	7.903(4)			90.74(3)	750

Table 17. (Continued)

compound	space group	lattice parameters						ref
		a/Å	b/Å	c/Å	α/°	β/°	γ/°	
$Na_2Pr(NO_3)_5 \cdot H_2O$	$P2/c$	21.309(6)	7.910(3)	15.16(1)		90.72(3)		751
$Ag_2Ce(NO_3)_5 \cdot H_2O$	$P2/c$	21.472(5)	8.027(1)	15.413(3)		90.45(2)		752
$RbTm(NO_3)_4 \cdot 4H_2O$	$P2_1/n$	10.578(4)	11.641(3)	11.466(2)		111.31(3)		755
$CsDy(NO_3)_4 \cdot 3H_2O$	$P112_1/n$	10.859(3)	11.217(3)	11.887(3)			108.55(2)	753
$CsNd(NO_3)_4 \cdot 3H_2O$	$P\bar{1}$	6.986(5)	7.089(3)	13.908(6)	80.58(4)	104.68(4)	105.33(5)	754
$KTb(NO_3)_4 \cdot 2H_2O$	$P2_1cn$	7.966(2)	11.571(9)	12.694(5)				756
$KSm(NO_3)_4 \cdot 2H_2O$	$Pna2_1$	12.7904(6)	11.6050(4)	7.9968(4)				757
$Rb_5Nd_2(NO_3)_{11} \cdot H_2O$	$C2/c$	15.767(4)	14.593(4)	14.336(4)		108.28(2)		758
$Li_3La_2(NO_3)_9 \cdot 3H_2O$	$P2_13$	13.354(2)						759
$Li_3Nd_2(NO_3)_9 \cdot 3H_2O$	$P2_13$	13.22(1)						759
$Ce_2Mg_3(NO_3)_{12} \cdot 24H_2O$	$R\bar{3}$	11.004(6)		34.59(1)				760
$La_2Mg_3(NO_3)_{12} \cdot 24D_2O$	$R\bar{3}$	11.041(5)		34.59(1)				761
$La_2Mg_3(NO_3)_{12} \cdot 24H_2O$	$R\bar{3}$	10.989(2)		34.63(1)				762
$Mg_3Eu_2(NO_3)_{12} \cdot 24H_2O$	$R\bar{3}$	13.117(3)			49.34(1)			*d*
$MgCe(NO_3)_6 \cdot 8H_2O$	$P2_1/c$	9.003(1)	8.6840(8)	13.533(1)		96.80(1)		763
$MgCe(NO_3)_6 \cdot 8H_2O$	$Pa\bar{3}$	12.5702(7)						763
$LaAl(NO_3)_6 \cdot 12H_2O$	$R\bar{3}$	10.948(1)		16.802(2)				764
$LaAl(NO_3)_6 \cdot 12H_2O$	$P2_13$	12.301(1)						764
		ternary anhydrous nitrates						
$(NH_4)_2Tm(NO_3)_5$	$P3_1$	11.2496(7)		9.316(1)				766
$Rb_2Y(NO_3)_5$	$P3_1$	11.239(2)		9.419(3)				767
$Rb_2Sc(NO_3)_5$	$P3_1$	11.034		9.474				768
$Tl_2Er(NO_3)_5$	$P2_1/c$	8.113(1)	12.079(2)	14.599(2)		103.73(2)		769
$Ag_2Er(NO_3)_5$	$P2_1/c$	7.8821(9)	11.567(1)	13.235(1)		97.32(1)		769
$K_2Er(NO_3)_5$	$P2_1/c$	7.954(4)	11.943(4)	14.269(7)		102.85(4)		770
$Li_2Pr(NO_3)_5$	$Pnnm$	9.020(2)	10.532(2)	11.779(2)				771
$Li_3Er(NO_3)_6$	$P2_1/n$	7.760(1)	7.4886(8)	23.96(1)				780
$(NH_4)_3Pr_2(NO_3)_9$	$P4_332$	13.770(1)						772
$(NH_4)_6Nd(NO_3)_9$	$C2/c$	17.751(4)	9.127(3)	20.723(5)		126.56(1)		781
$Rb_3Pr_2(NO_3)_9$	$P4_332$	13.8091(4)						773
$Rb_3Ce_2(NO_3)_9$	$P4_132$	13.8411(4)						774
$Rb_3Nd_2(NO_3)_9$	$P4_332$	13.759(2)						775
$K_3Pr_2(NO_3)_9$	$P4_332$	13.52(1)						776
$K_3Nd_2(NO_3)_9$	$P4_332$	13.474(3)						777
$K_3Ce_2(NO_3)_9$	$P4_132$	13.5975(8)						778
$K_3La_2(NO_3)_9$	$P4_132$	13.6607(5)						779
$Na_3Nd_2(NO_3)_9$	$P4_132$	13.1279(8)						*e*
$Ag_6Pr(NO_3)_9$	$R\bar{3}c$	16.410(1)		14.631(1)				769
$Ag_6Ce(NO_3)_9$	$R\bar{3}c$	16.402(2)		14.573(2)				*f*
$Ag_5Er_2(NO_3)_{11}$	$C2/c$	26.638(1)	8.2270(7)	25.378(2)		103.86(1)		769
$K_2Ce(NO_3)_6$	$P2_1/n$	12.707(4)	6.6858(6)	8.2535(7)		91.55(1)		*g*
$K_2Ce(NO_3)_6$	$P\bar{3}$	13.5737(4)		6.6624(3)				*h*
$Rb_2Ce(NO_3)_6$	$P2_1/n$	13.0567(5)	6.8684(2)	8.1786(3)		91.44(1)		*i*
$(NH_4)_2Ce(NO_3)_6$	$P2_1/n$	13.061(7)	6.842(4)	8.183(4)		91.34(2)		*j*

[a] Wolcott, H. A.; Milligan, W. O.; Beall, G. W. *J. Inorg. Nucl. Chem.* **1977**, *39*, 59. [b] Manek, E.; Meyer, G. *Z. Anorg. Allg. Chem.* **1992**, *610*, 20. [c] Guillou, N.; Auffredic, J. P.; Louer, M.; Louer, D. *J. Solid State Chem.* **1993**, *106*, 295. [d] Akimov, V. M.; Yanovskii, A. I.; Struchkov, Y. T.; Molodkin, A. K.; Grigorev, Y. A.; Novikov, N. K. *Zh. Neorg. Khim.* **1987**, *32*, 1547. [e] Stockhause, S.; Meyer, G. *Z. Kristallogr.-New Cryst. Struct.* **1997**, *212*, 316. [f] Audebrand, N.; Auffredic, J.-P.; Benard-Rocherulle, P.; Louer, D. *Acta Crystallogr. C* **1997**, *53*, 1748. [g] Guillou, N.; Auffredic, J. P.; Louer, D. *Acta Crystallogr. C* **1995**, *51*, 1032. [h] Guillou, N.; Louer, M.; Auffredic, J. P.; Louer, D. *Acta Crystallogr. C* **1995**, *51*, 1029. [i] Guillou, N.; Auffredic, J. P.; Louer, D. *J. Solid State Chem.* **1996**, *122*, 59. [j] Beineke, T. A.; Delgaudio, J. *Inorg. Chem.* **1968**, *7*, 715. [k] Wickleder, M. S.; Müller, I.; Meyer, G. *Z. Anorg. Allg. Chem.* **2001**, *627*, 4.

nitrate group. The structure may incorporate an additional water molecule as has been shown for $La(OH)_2(NO_3) \cdot H_2O$ and $Nd(OH)_2(NO_3) \cdot H_2O$.[725,729] The structure of these two is essentially the same as that described for the respective anhydrous structure, but the NO_3^- ligand is only monodentate now because the water molecule enters the M^{3+} coordination sphere (Figure 108). The oxide nitrate $YO(NO_3)$[730] is structurally closely related to other rare-earth oxides containing additional anions. It contains O^{2-}-centered $[OM_4]$ tetrahedra, and if the ratio M^{3+}/O^{2-} equals one, these tetrahedra condense to layers ${}^2_\infty[OM_{4/4}]^+$ which are stacked alternating with the anions. This has, for example, been observed for $Nd_3O_3(PO_4)$, the oxide carbonates $M_2O_2(CO_3)$, and the oxide sulfates $M_2O_2(SO_4)$, and it is also a common feature in the structural chemistry of lanthanide halides (MOCl) and sulfides (M_2O_2S). An oxide nitrate of tetravalent cerium is $Ce_2O(NO_3)_6 \cdot 8H_2O$.[731] The structure is built up from dimers $[Ce_2O(H_2O)_6(NO_3)_6]$ with a linear Ce−O−Ce bridge and three chelating NO_3^- groups at each Ce^{4+} ion (Figure 109). The $Ce^{4+}-O^{2-}$ distances to the bridging oxide ions are remarkably short (2.05 Å). The neutral complexes are packed in the unit cell together with two additional water molecules.

In the structure of $Y_4O(OH)_9(NO_3)$,[732] the oxide ion is again found in tetrahedral coordination of Y^{3+} but the structure is more complicated due to the presence of additional OH^- ions. These are attached to three Y^{3+} ions, and a three-dimensional network is built

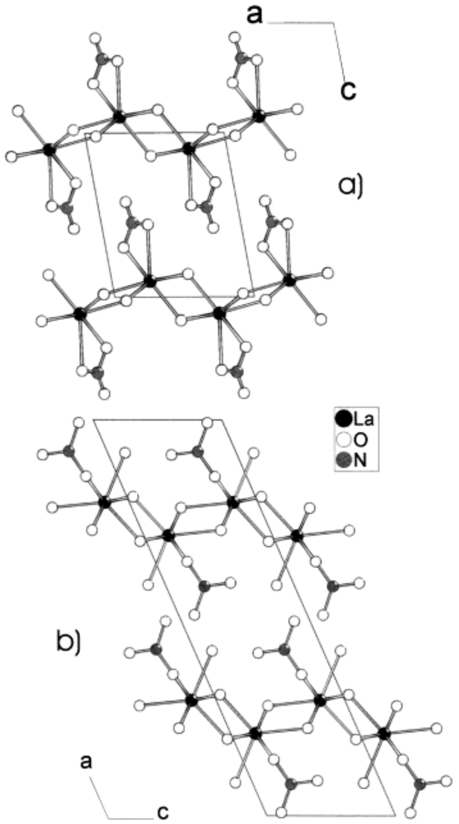

Figure 108. Comparison of the crystal structures of $La(OH)_2(NO_3)$ (a) and $La(OH)_2(NO_3)\cdot H_2O$ (b).

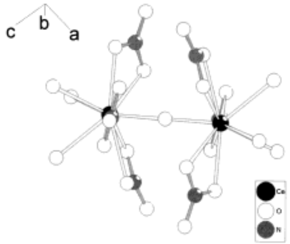

Figure 109. $[Ce_2O(H_2O)_6(NO_3)_6]$ dimers with a linear Ce−O−Ce bridge in the crystal structure of $Ce_2O(NO_3)_6\cdot 8H_2O$.

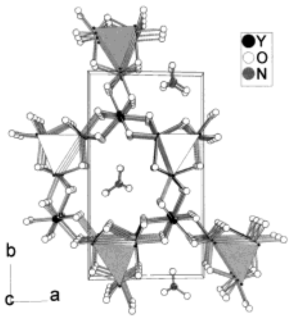

Figure 110. Crystal structure of $Y_4O(OH)_9(NO_3)$; the oxygen-centered $[OY_4]$ tetrahedra are shown as polyhedra.

providing large channels which are occupied by free nitrate ions (Figure 110). Other hydroxide-rich oxide-containing rare-earth nitrates are the compounds $\{[M_6O](OH)_8(H_2O)_{12}(NO_3)_6\}(NO_3)_2\cdot xH_2O$.[733−735] Analogously to the related basic perchlorates, they contain as the characteristic structural feature an oxide-centered $[OM_6]$ octahedron with each of its triangular faces capped by an OH^- ion. Furthermore, 12 H_2O molecules are bridging the 12 edges of the octahedron. Finally, a monodentate nitrate group acts as a terminal ligand for the six vertexes of the octahedron. Because the unit $\{[M_6O](OH)_8(H_2O)_{12}(NO_3)_6\}^{2+}$ is positive, additional nitrate groups are needed for charge compensation. Depending on the rare-earth ion, the crystal structures contain from four to six molecules of crystal water. Finally, the basic yttrium nitrate $YBi_2O_4(NO_3)$ should be mentioned.[736] It consists of layers $^{2}_{\infty}[YO_{8/2}]^{5-}$ which are separated by Bi^{3+} and NO^{3-} sheets, respectively, with severe disorder of the nitrate ions.

3. Hydrous Ternary Nitrates

As previously mentioned, the nitrates $(NH_4)_2M(NO_3)_5\cdot 4H_2O$ were used in previously for the separation of rare-earth elements by fractional crystallization. This type of compound, which can be also obtained with Rb^+, contains the complexes $[M(H_2O)_2(NO_3)_5]^{2-}$ with 12-fold coordinate M^{3+} ions due to the chelating nitrate groups.[737−740] These complexes are packed in the unit cell together with the A^+ ions and two molecules of crystal water. One-half of the free water molecules can evidently be removed from the lattice without structural changes as shown for $(NH_4)_2La(NO_3)_5\cdot 3H_2O$.[737] Furthermore, a disorder in the A^+ sublattice has been observed for the rubidium nitrates $Rb_2M(NO_3)_5\cdot 4H_2O$.[739]

The structure of the dihydrates $Cs_2M(NO_3)_5\cdot 2H_2O$ (M = La, Ce, Nd)[741−743] is also closely related to one of the tetrahydrates, which might also be seen by comparing the lattice constants (Table 17). The same complexes $[M(H_2O)_2(NO_3)_5]^{2-}$ are found in the structure but they are tilted slightly compared to the tetrahydrates. Of much greater interest are the potassium nitrates $K_2M(NO_3)_5\cdot 2H_2O$ (M = La, Pr, Nd).[744−748] Again, the anions $[M(H_2O)_2(NO_3)_5]^{2-}$ are found but they are now packed in a way that a highly symmetric structure with the space group *Fdd*2 is formed (Figure 111). The polar acentric space group of the structure leads to interesting physical properties which have been investigated in detail even on large single crystals of the compounds, revealing that these nitrates are promising materials for frequency doubling.[745,749] Monohydrates $A_2M(NO_3)_5\cdot H_2O$ (M = Ce, Pr, Nd) are known only with the small A^+ ions

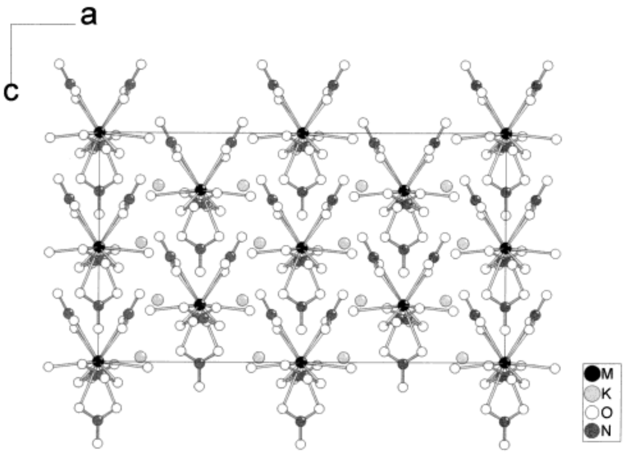

Figure 111. Crystal structure of the acentric nitrates $K_2M(NO_3)_5\cdot 2H_2O$ (M = La, Pr, Nd) containing $[M(H_2O)_2(NO_3)_5]^{2-}$ anions.

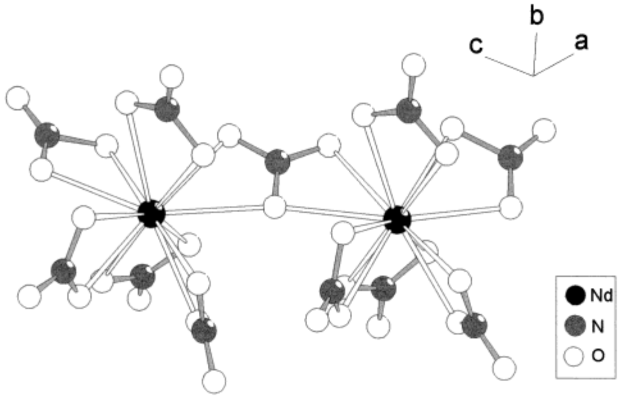

Figure 112. $[Nd_2(NO_3)_{11}]^{5-}$ dimer in the crystal structure of $Rb_5Nd_2(NO_3)_{11}\cdot H_2O$.

Na^+ and Ag^+.[750−752] The M^{3+} ions are surrounded by six chelating nitrate groups. According to $^{1}_{\infty}[M(NO_3)_{4/1}(NO_3)_{2/2}]^{2-}$ the $[M(NO_3)_6]$ complexes are linked by two of the nitrate groups to infinite chains running along [100]. The chains are connected by four crystallographically different A^+ ions being in 8- and 9-fold coordination.

Ternary nitrate hydrates containing A^+ and M^{3+} in a ratio of 1:1 are known as the trihydrates $CsM(NO_3)_4\cdot 3H_2O$ (M = Dy, Nd)[753,754] and $RbTm(NO_3)_4\cdot 3H_2O$[755] and as the dihydrates $KM(NO_3)_4\cdot 2H_2O$ (M = Sm, Tb).[756,757] Two different structures occur for the trihydrates (Table 17). In both modifications the M^{3+} ions are 10-fold coordinated. The coordination number is achieved by four chelating nitrate groups and two water molecules in the monoclinic form and three chelating and one monodentate NO_3^- ions and three water ligands in the triclinic modification. The dihydrates are isotypic with each other and contain the M^{3+} ions coordinated with four chelating NO_3^- ions and two H_2O molecules. The highest A^+/M^{3+} ratio is found in $Rb_5Nd_2(NO_3)_{11}\cdot H_2O$.[758] In the crystal structure dimers $[Nd_2(NO_3)_{11}]^{5-}$ are formed (Figure 112) by the connection of two $[Nd(NO_3)_6]$ units via a common nitrate group. The dimers are separated by the Rb^+ ions and free H_2O molecules. An even higher condensed network of $[M(NO_3)_6]$ complexes has been described for the lithium compounds $Li_3M_2(NO_3)_9\cdot 3H_2O$ (M = La, Nd).[759] In this case the linkage occurs via three NO_3^- groups leading to a three-dimensional arrangement according to $^{3}_{\infty}\{[M(NO_3)_{3/1}(NO_3)_{3/2}]_2\}^{3-}$ which incorporates the Li^+ ions and the H_2O molecules.

A limited number of nitrate hydrates has also been prepared with alkaline-earth metals. Twelve oxygen atoms from six chelating nitrate groups surround the M^{3+} ions icosahedrally in the structures of $Mg_3M_2(NO_3)_{12}\cdot 24H_2O$ (M = La, Ce).[760−762] The icosahedra are stacked in a ccp fashion with octahedral $[Mg(H_2O)_6]^{2+}$ ions in the empty voids. The two modifications of $MgCe(NO_3)_6\cdot 8H_2O$[763] contain tetravalent cerium also surrounded by six chelating nitrate ions, and again, the Mg^{2+} ions are exclusively coordinated by water molecules. With the examples of $AlLa(NO_3)_6\cdot 6H_2O$ and $AlLa(NO_3)_6\cdot 12H_2O$ it has recently been shown that the complex $[La(NO_3)_6]^{3-}$ may also be crystallized with $[Al(H_2O)_6]^{3+}$ countercations.[764] To the group of compounds containing $[M(NO_3)_6]^{3-}$ complexes and hexaaquametal ions also belongs the unusual nitrate $Mg_2Nd(NO_3)_6(OH)\cdot 12H_2O$.[765] If the formula is rewritten as $[Mg(H_2O)_6]_2[Nd(NO_3)_6](OH)$, the close relationship to the compounds described is obvious.

4. Anhydrous Ternary Nitrates

Single crystals of anhydrous ternary nitrates were obtained from melts of alkali, ammonium, thallium, or silver nitrate. The compounds which have been structurally characterized contain the A^+ and M^{3+} ions in a ratio of 2:1, 3:2, 3:1, 5:2, and 6:1, respectively. The 2:1-type compounds are known with A = NH_4^+, Rb^+, K^+ Tl^+, Ag^+, and Li^+. The series $(NH_4)_2M(NO_3)_5$ has been shown to exist with M = Tb−Lu, Y, and a single-crystal investigation has been carried out for the thulium compound.[766] The isotypic rubidium nitrates occur with M = Eu, Lu, Y, Sc,[767,768] and the structure has been elucidated for yttrium and scandium by single-crystal data. For A = K, Ag, and Tl, the respective erbium nitrates have been investigated.[769,770] All of these compounds contain as the characteristic building unit $[M(NO_3)_5]^{2-}$ anions with the five NO_3^- groups as chelating ligands (Figure 113). The differences in the structure arise from the radii of the countercations. In the trigonal acentric (space group $P3_1$) structures of $(NH_4)_2M(NO_3)_5$ and $Rb_2M(NO_3)_5$ the A^+ ions are in 9- and 10-fold coordination, whereas coordination numbers of nine and eight are found for the K^+ and Tl^+ ions in the respective nitrates. Furthermore, for Tl^+ the influence of the lone pair can be seen, although $Tl_2Er(NO_3)_5$ is otherwise isotypic with the potassium compound. The Ag^+ ion in $Ag_2Er(NO_3)_5$ is coordinated by four oxygen ligands with short distances (∼2.4 Å) and five additional oxygen atoms with distances up to 3.2 Å. In contrast, the lithium nitrates $Li_2M(NO_3)_5$ (M = La, Pr−Eu)[771] exhibit the hexanitrate complexes $[M(NO_3)_6]$ which are connected by two of the nitrate ions to chains $^{1}_{\infty}[M(NO_3)_{4/1}(NO_3)_{2/2}]^{2-}$ in the [010] direction. The chains are linked by Li^+ ions in "4+4" coordination.

The $A_3M_2(NO_3)_9$-type nitrates are frequent for the larger lanthanides M = La−Gd and are found with A = NH_4^+, Rb^+, and K^+.[772−779] The isotypic compounds crystallize with the acentric space group $P4_332$. Similarly to the respective hydrates with lithium, they are built up from $[M(NO_3)_6]$ polyhedra ($CN_M{}^{3+}$ = 12) which are linked according to $^{3}_{\infty}\{[M(NO_3)_{3/1}(NO_3)_{3/2}]_2\}^{3-}$ yielding a three-dimensional network which incorporates the A^+ ions. The nitrates of the composition $A_3M(NO_3)_6$ are only known for A = Li[780] and are unique in the sense that they do *not* contain

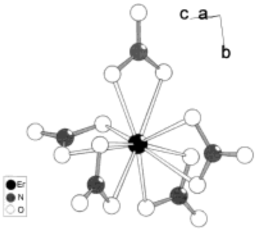

Figure 113. $[M(NO_3)_5]^{2-}$ anion in the crystal structure of $A_2M(NO_3)_5$-type nitrates (A = NH_4^+, Rb^+, K^+ Tl^+, Ag^+, Li^+).

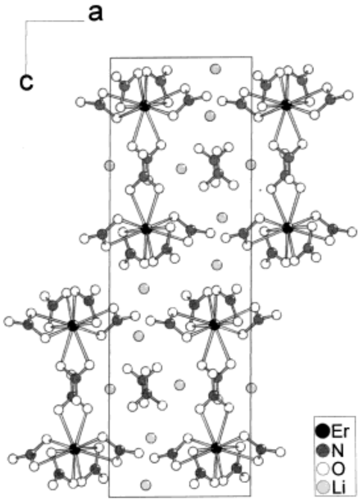

Figure 114. Crystal structure of $Li_3M(NO_3)_6$ (M = Gd–Lu, Y) with $[M(NO_3)_5]^{2-}$ ions *and* “lonesome” nitrate ions.

$[M(NO_3)_6]^{3-}$ complexes but $[M(NO_3)_5]^{2-}$ ions *and* “lonesome” nitrate ions (Figure 114). This might be due to the fact that these compounds are only known with the smaller rare-earth elements M = Gd–Lu, Y, which prefer a lower coordination number. The Li^+ ions are in tetrahedral and octahedral coordination of oxygen atoms, respectively. With $Ag_5Er_2(NO_3)_{11}$ only one example has been reported for $A_5M_2(NO_3)_{11}$-type nitrates.[769] This compound consists of $[Er(NO_3)_5]^{2-}$ ions and additional nitrate groups so that the formula should be rewritten as $Ag_5[Er(NO_3)_5]_2(NO_3)$. The five crystallographically different Ag^+ ions are coordinated by eight and nine oxygen atoms. For the nitrates with the highest A^+ content, $A_6M(NO_3)_9$, two structure types are known. According to the formulation $A_6[M(NO_3)_6](NO_3)_3$ both the monoclinic $(NH_4)_6Nd(NO_3)_9$[781] (Figure 115b) and the trigonal-rhombohedral silver nitrates $Ag_6M(NO_3)_9$ (M = Ce, Pr)[782,769] (Figure 115a) contain the hexanitrate complexes $[M(NO_3)_6]^{3-}$ and additional free nitrate ions. Again, the different structures arise from the different A^+ sizes.

V. Bent and Linear Anions

A. Chlorites

Chlorites of composition $M(ClO_2)_3 \cdot xH_2O$ with x varying between 0.5 and 4 were prepared roughly 40 years ago in a metathesis reaction of the nitrates $M(NO_3)_3$ and sodium chlorite $NaClO_2$.[783] Unfortunately, only one of these chlorites, $La(ClO_2)_3 \cdot 3H_2O$, has been structurally investigated.[784] It has a hexagonal structure, and the La^{3+} ions are coordinated by six monodentate ClO_2^- ions yielding a trigonal prismatic coordination polyhedron. The three H_2O ligands are capping the rectangular faces of the prism. According to the formulation $^{3}_{\infty}[La(H_2O)_{3/1}(ClO_2)_{6/2}]$ each chlorite group links two La^{3+} ions with each other so that a three-dimensional network is gained. Thereby channels are formed along the [001] direction which provide space for the lone pairs of the ClO_2^- groups (Figure 116).

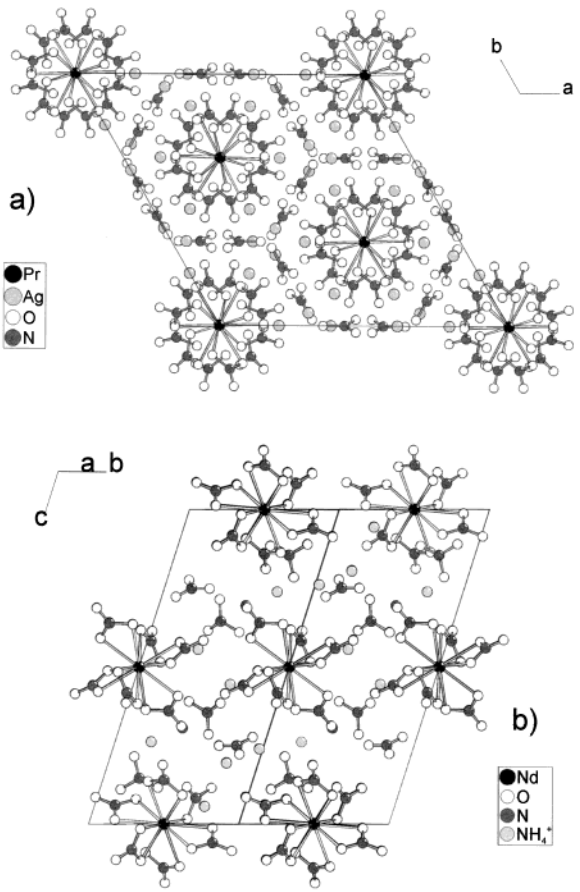

Figure 115. Crystal structures of $(NH_4)_6Nd(NO_3)_9$ (b) and $Ag_6M(NO_3)_9$ (M = Ce, Pr) (a); both compounds contain “lonesome” NO_3^- ions and should be formulated according to $A_6[M(NO_3)_6](NO_3)_3$.

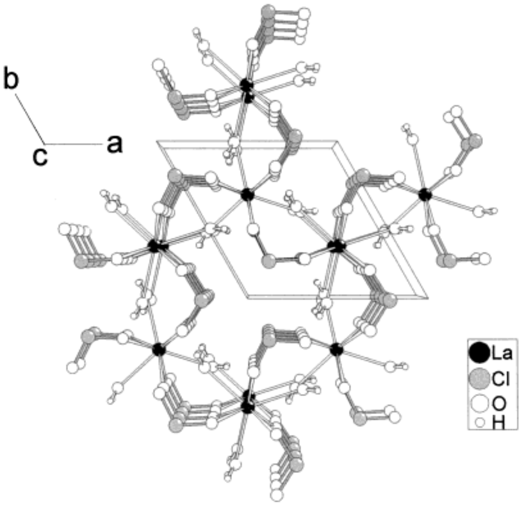

Figure 116. Perspective view of the crystal structure of $La(ClO_2)_3 \cdot 3H_2O$ along [001].

B. Nitrites

Nitrites have been prepared by the reaction of $Ba(NO_2)_2$ and rare-earth sulfates in aqueous solution with precipitation of $BaSO_4$. For M = La–Sm pentahydrates crystallize from the solution.[785,786] Furthermore, rare-earth oxide nitrates $MO(NO_2)$ are said to form in an eutectic melt of $LiNO_2/KNO_2$ or $NaNO_2/KNO_2$.[787] For $Pr(NO_2)_3 \cdot 5H_2O$, IR and thermoanalytical investigations were performed. According to these

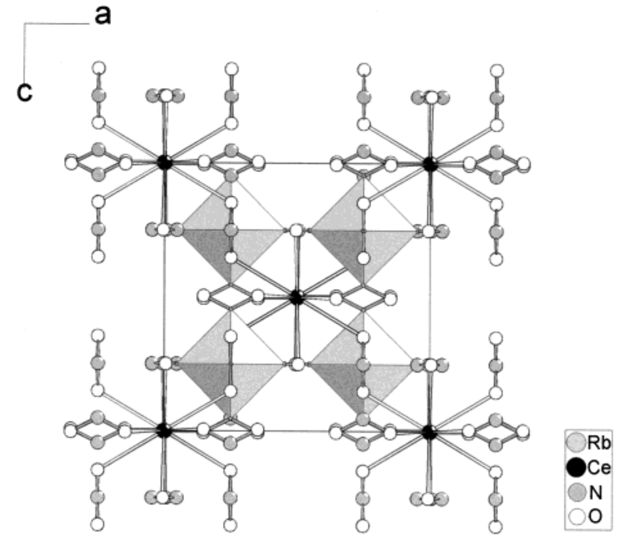

Figure 117. Crystal structure of the nitrites $A_5M[B(NO_2)_6]_2$ (M = Ce, Y, B = Fe, Co, Ni, Cu; A = Tl, K, Rb, NH_4).

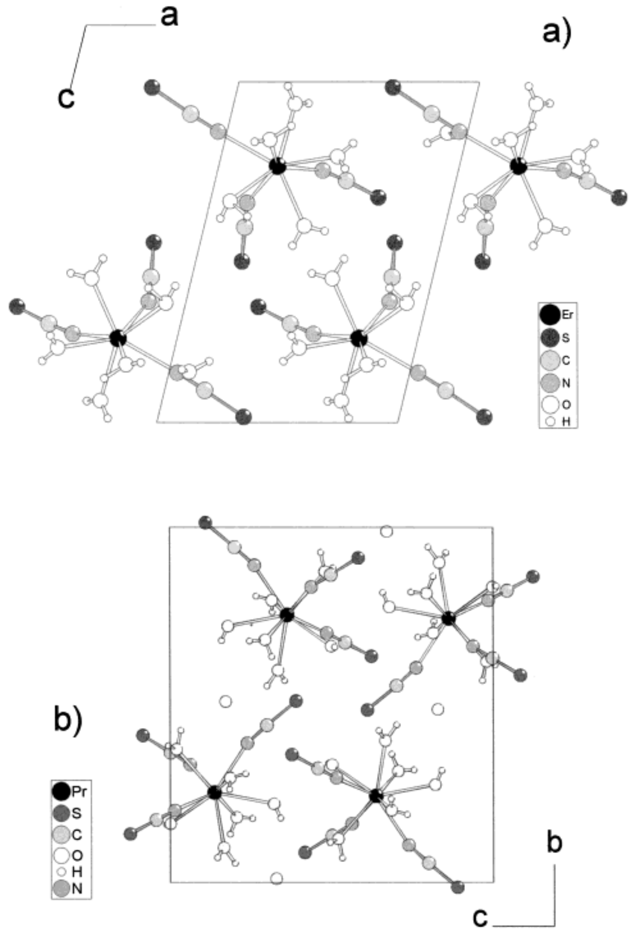

Figure 118. Crystal structures of the thiocyanides $Pr(SCN)_3{\cdot}7H_2O$ (b) and $M(SCN)_3{\cdot}6H_2O$ (M = Ho, Er, Lu) (a) containing the neutral complexes $[Pr(H_2O)_6(SCN)_3]$ and $[M(H_2O)_5(SCN)_3]$, respectively.

data, part of the H_2O molecules are attached to the Pr^{3+} ions and the nitrate ions act as chelating ligands.[785] Upon heating the compound, $PrO(NO_2)$ forns in the first step and decomposes to Pr_6O_{11} finally.[785] Although the preparation of the nitrite–hydrates seems to be quite simple, a structure

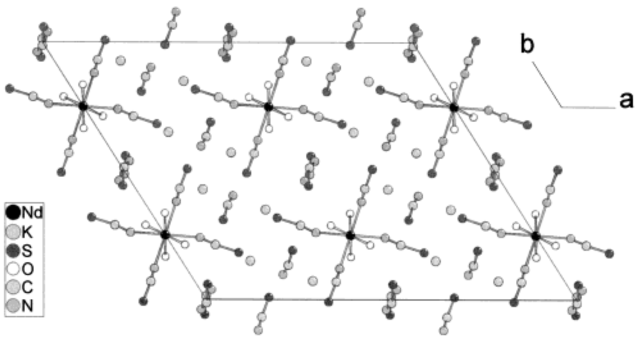

Figure 119. Projection of the crystal structure of $K_4Nd(SCN)_7{\cdot}4H_2O$ on (001).

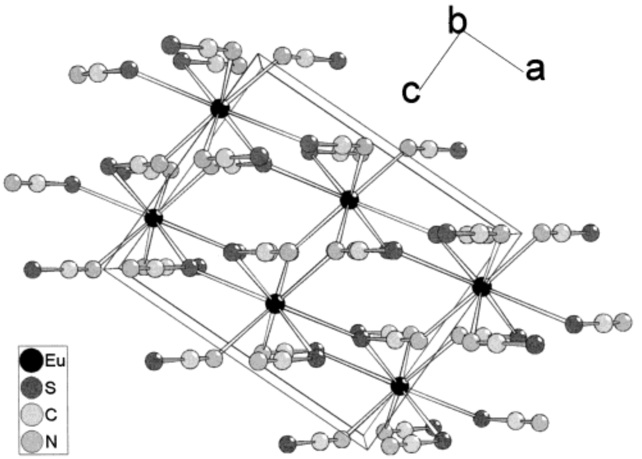

Figure 120. Crystal structure of $Eu(SCN)_2$; according to the different attachment of the anions, the compound should be formulated as Eu(NCS)(SCN).

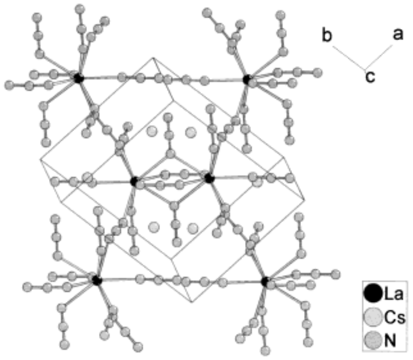

Figure 121. Three-dimensional network $^{3}_{\infty}[Nd(N_3)_{3/1}(N_3)_{6/2}]^{3-}$ in the crystal structure of $Cs_3Nd(N_3)_6$.

determination has never been carried out for any of them. Structural data are provided for the polynary nitrites $A_5M[B(NO_2)_6]_2$ with M = Ce, Y, B = Fe, Co, Ni, Cu, and A = Tl, K, Rb, NH_4.[788] The cubic structure of these compounds consists of $[B(NO_2)_6]$ octahedra, and the M^{3+} as well as the A^+ ions are in icosahedral oxygen coordination (Figure 117). The nitrate $Cs_2NaLa(NO_2)_6$ has been investigated by powder diffraction and conductivity measurements.[789] It has in principle the cubic elpasolite structure if NO_2^- is regarded as a spherical ligand. Surprisingly, the compound turned out to be semiconducting.

C. Thiocyanates

While there are a large number of rare-earth thiocyanato complexes with organic ligands, report

Table 18. Crystallographic Data of Compounds with Bent and Linear Anions

compound	space group	lattice parameters						ref
		a/Å	b/Å	c/Å	α/°	β/°	γ/°	
				chlorites				
$La(ClO_2)_3\cdot 3H_2O$	$P\bar{6}2c$	8.077(1)		8.296(1)				784
$Nd(ClO_2)_3\cdot 3H_2O$		8.037(1)		8.199(1)				793
				nitrites				
$K_5Ce[Fe(NO_2)_6]_2$	$Pn\bar{3}$	10.380						788
$Tl_5Ce[Fe(NO_2)_6]_2$	$Pn\bar{3}$	10.570						788
$K_5Ce[Co(NO_2)_6]_2$	$Pn\bar{3}$	10.490						788
$Rb_5Ce[Co(NO_2)_6]_2$	$Pn\bar{3}$	10.640						788
$Tl_5Ce[Co(NO_2)_6]_2$	$Pn\bar{3}$	10.590						788
$K_5Ce[Ni(NO_2)_6]_2$	$Pn\bar{3}$	10.560						788
$Rb_5Ce[Ni(NO_2)_6]_2$	$Pn\bar{3}$	10.740						788
$Cs_5Ce[Ni(NO_2)_6]_2$	$Pn\bar{3}$	10.830						788
$(NH_4)_5Ce[Ni(NO_2)_6]_2$	$Pn\bar{3}$	10.580						788
$Tl_5Ce[Ni(NO_2)_6]_2$	$Pn\bar{3}$	10.550						788
$K_5Ce[Cu(NO_2)_6]_2$	$Pn\bar{3}$	10.640						788
$Rb_5Ce[Cu(NO_2)_6]_2$	$Pn\bar{3}$	10.680						788
$Cs_5Ce[Cu(NO_2)_6]_2$	$Pn\bar{3}$	11.000						788
$Tl_5Ce[Cu(NO_2)_6]_2$	$Pn\bar{3}$	10.790						788
$K_5Y[Co(NO_2)_6]_2$	$Pn\bar{3}$	10.340						788
$Tl_5Y[Co(NO_2)_6]_2$	$Pn\bar{3}$	10.600						788
$K_5Y[Ni(NO_2)_6]_2$	$Pn\bar{3}$	10.360						788
$Tl_5Y[Cu(NO_2)_6]_2$	$Pn\bar{3}$	10.700						788
				thiocyanates				
$Pr(SCN)_3\cdot 7H_2O$	$P2_1/c$	7.1565(8)	15.200(2)	13.910(3)		92.43(1)		793
$Er(SCN)_3\cdot 6H_2O$	$P2_1$	8.470(1)	7.190(1)	12.228(2)		103.79(1)		793
$Ho(SCN)_3\cdot 6H_2O$	$P2_1$	8.515(1)	7.2317(8)	12.291(3)		103.72(2)		793
$Lu(SCN)_3\cdot 6H_2O$	$P2_1$	8.466(1)	7.216(1)	12.201(1)		103.87(1)		793
$K_4Nd(SCN)_7\cdot 4H_2O$	$B112/b$	25.25(2)	20.62(2)	6.86(1)			122.8(3)	795
$K_4Eu(SCN)_7\cdot 6H_2O$	$B112/b$	25.41(2)	20.32(2)	6.52(1)			122.0(3)	795
$K_4Er(SCN)_7\cdot 6H_2O$	$I2/a$	20.260(8)	6.475(2)	22.401(9)		107.78(4)		795
$[(^nBu)_4N][Er(SCN)_6]$	$A\bar{1}$	22.63(3)	16.73(2)	18.82(2)	87.97(2)	89.08(3)	92.47(3)	790
$BiLa(SCN)_6\cdot 5H_2O$	$P6_3/m$	8.251(6)		18.745(2)				796
$BiNd(SCN)_6\cdot 5H_2O$	$P6_3/m$	8.200(2)		18.606(3)				796
$Eu(SCN)_2$	$C2/c$	9.793(2)	6.609(1)	8.157(2)		91.58(3)		797
				azides				
$Cs_2Nd(N_3)_5$	$C2/c$	24.601(7)	12.568(3)	18.185(5)		113.98(2)		801
$Cs_3Nd(N_3)_6$	$P\bar{1}$	9.445(3)	9.848(2)	10.105(3)	98.58(2)	110.13(2)	102.12(2)	802
				cyanamides				
$La_2O_2(CN_2)$	$I4/mmm$	4.0964(2)		12.333(1)				803
$Pr_2O_2(CN_2)$	$P\bar{3}m$	3.914(1)		8.332(2)				804
$Nd_2O_2(CN_2)$	$P\bar{3}m$	3.8140(7)		8.311(1)				804
$Sm_2O_2(CN_2)$	$P\bar{3}m$	3.8276(9)		8.267(2)				804
$Eu_2O_2(CN_2)$	$P\bar{3}m$	3.8049(6)		8.2515(9)				804
				cyanides				
$Eu(Ag(CN)_2)_3\cdot 3H_2O$	$P6_3/mmc$	6.688(1)		18.479(7)				807
$Sm(Au(CN)_2)_3\cdot 2.6H_2O$	$P\bar{6}2m$	6.589(1)		9.236(1)				808
$Gd(Au(CN)_2)_3\cdot 2.3H_2O$	$P\bar{6}2m$	6.6319(6)		9.108(2)				809
$Nd_2(Pd(CN)_4)_3\cdot 12H_2O$	$C2/c$	11.516(5)	17.569(4)	17.371(5)		92.57(3)		810
$Eu_2(Pd(CN)_4)_3\cdot 12H_2O$	$C2/c$	11.504(2)	17.556(2)	17.298(2)		92.83(1)		811
$LaFe(CN)_6\cdot 5H_2O$	$P6_3/m$	7.554(1)		14.452(1)				812
$LaFe(CN)_6)\cdot 4H_2O$	$P6_3/mmc$	7.541(3)		13.955(9)				813
$LaFe(CN)_6)\cdot 5H_2O$	$P6_3/m$	7.554(1)		14.452(1)				813
$LaCo(CN)_6\cdot 5H_2O$	$P6_3/m$	7.507(2)		14.343(4)				814
$ErFe(CN)_6)\cdot 4H_2O$	$Cmcm$	7.435	12.868	13.729				815
$SmCo(CN)_6)\cdot 4H_2O$	$Cmcm$	7.366(1)	12.780(2)	13.653(2)				816
$SmFe(CN)_6)\cdot 4H_2O$	$Cmcm$	7.435(1)	12.866(3)	13.724(3)				816
$ErFe(CN)_6\cdot 4H_2O$	$Cmcm$	7.435(2)	12.868(3)	13.729(2)				817
$SmFe(CN)_6\cdot 4H_2O$	$Cmcm$	7.436(2)	12.866(3)	13.724(3)				818
$LaCr(CN)_6\cdot 5H_2O$	$P6_3/m$	7.7053(4)		14.8155(9)				819
$ErFe(CN)_6\cdot 4H_2O$	$Cmcm$	7.3212(6)	12.7576(8)	13.5636(9)				820
$GdFe(CN)_6)\cdot 4H_2O$	$Cmcm$	7.3964(3)	12.8372(5)	13.6726(4)				821
$PrCo(CN)_6\cdot 5H_2O$	$P6_3/m$	7.472(2)		14.223(3)				822
$Nd(Co(CN)_6)\cdot 4H_2O$	$Cmcm$	7.4251(8)	12.790(3)	13.723(2)				823
$GdFe(CN)_6\cdot 4H_2O$	$C2$	12.759(6)	7.404(1)	13.654(5)		90.22(3)		824
$SmFe(CN)_6\cdot 4H_2O$	$P2_1/m$	7.431(1)	13.724(3)	7.429(2)		119.95(1)		825
$SmCo(CN)_6\cdot 4H_2O$	$P2_1/m$	7.365(1)	13.653(2)	7.385(2)		120.08(2)		826
$SmFe(CN)_6\cdot 4H_2O$	$Cmcm$	7.433(3)	12.875(4)	13.730(5)				827
$PrFe(CN)_6\cdot 5H_2O$	$P6_3/m$	7.523(2)		14.344(2)				828
$NdFe(CN)_6\cdot 5H_2O$	$P6_3/m$	7.467(2)		13.793(3)				828

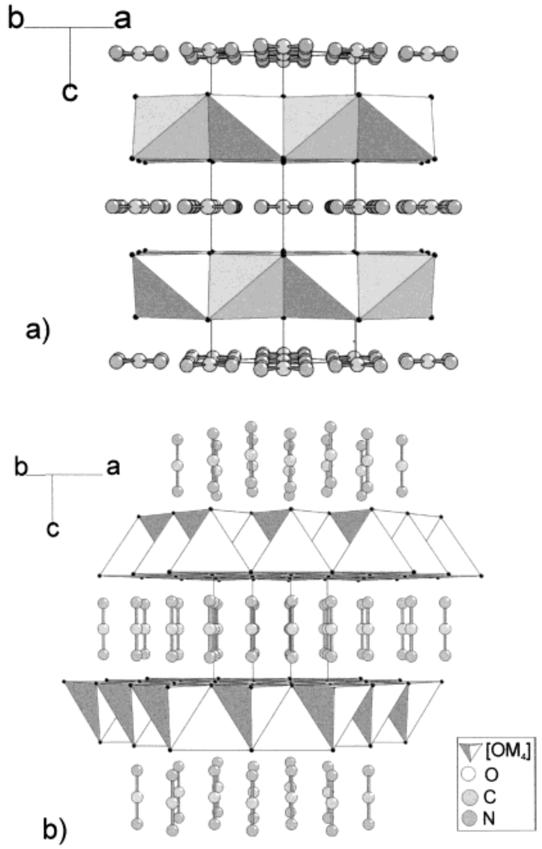

Figure 122. $^{2}_{\infty}[OLa_{4/4}]^{+}$ layers (a) and $^{2}_{\infty}\{[OM_{4/4}]_2\}^{2+}$ double layers (b) in the crystal structures of $La_2O_2(CN_2)$ and $M_2O_2(CN_2)$ (M = Pr, Nd, Sm, Er), respectively.

of the structural knowledge of inorganic rare-earth compounds with SCN^- anions is very limited. The first report on a crystal structure containing an $[M(SCN)_6]^{3-}$ complex occurred in 1968 with the example of $[N(n\text{-}Bu)_4]_3[Er(NCS)_6]$.[790] The complex anion shows the Er^{3+} ion in an octahedral coordination of nitrogen atoms. Further, thiocyanides of that type have been prepared subsequently.[791]

The metathesis reaction of $Ba(SCN)_2$ and rare-earth sulfates in water leads to solutions from which thiocyanate hydrates with 6 or 11 molecules of water crystallize.[792,793] The crystal structure of the heptahydrates $M(SCN)_3{\cdot}7H_2O$, which are found with the larger lanthanides, has been determined for M = Pr and contains neutral complexes $[Pr(H_2O)_6(SCN)_3]$ which are held together by hydrogen bonds involving the free crystal water molecule[793] (Figure 118b). For the smaller lanthanides the hexahydrate occurs. The structure was reported for $M(SCN)_3{\cdot}6H_2O$ (M = Ho, Er, Lu) (Table 18) and shows that again neutral complexes are formed, now with the M^{3+} ion in 8-fold coordination according to $[M(H_2O)_5(SCN)_3]$. In this structure one of the water molecules is also not in the inner Er^{3+} coordination sphere (Figure 118a). The thermal decomposition of the erbium compound shows that first the water is driven off and finally the sulfide forms.[793] Between dehydration and decomposition no significant plateau is observed.

The ternary thiocyanates $K_4Nd(SCN)_7{\cdot}4H_2O$[794,795] and $K_4M(SCN)_7{\cdot}6H_2O$ (M = Eu, Er)[793−795] are composed of the complex anions $[M(H_2O)_4(SCN)_4]^-$ and free SCN^- ions. In the structure, disordered SCN^- ions and the complex anions are arranged in layers which are alternating stacked with further SCN^- groups and the K^+ ions along [001] (Figure 119). Two bismuth-containing rare-earth thiocyanates are known. The isotypic compounds $MBi(SCN)_6{\cdot}5H_2O$ (M = La, Nd)[796] show the Bi^{3+} ions in an octahedral environment of sulfur atoms while the M^{3+} ions are coordinated by six nitrogen atoms in the form of a trigonal prism. The prism is additionally capped by three H_2O molecules. The Bi and M polyhedra are alternating stacked in the [001] direction. Two molecules of free water are incorporated in the structure. The linkage of the polyhedra occurs in a way that each M^{3+} ion is surrounded by six $[Bi(SCN)_6]^{3-}$ groups which are themselves connected to six La^{3+} ions according to $^{3}_{\infty}\{La(H_2O)_3[Bi(SCN)_6]_{6/6}\}$.

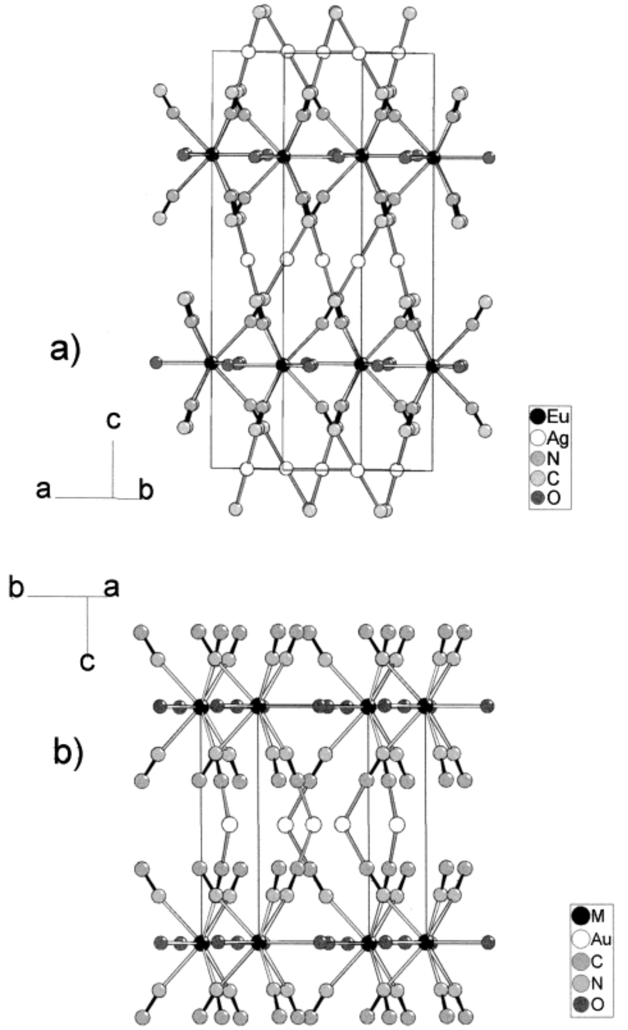

Figure 123. Crystal structures of $Eu[Ag(CN)_2]_3{\cdot}3H_2O$ (a) and $M[Au(CN)_2]_3{\cdot}3H_2O$ (M = Sm, Gd) (b). Note, the $[Au(CN)_2]^-$ anion is bent while $[Ag(CN)_2]^-$ is linear.

For the trivalent lanthanides no simple binary anhydrous thiocyanate is structurally known to date. On the other hand, the preparation of yellow single crystals of $Eu(SCN)_2$ was successful by reacting $EuCl_2$ with NaSCN in glass ampules at 320 °C.[797] The structure is isotypic with the ones of $Sr(SCN)_2$, $Ba(SCN)_2$, and $Pb(SCN)_2$ and contains the Eu^{2+} ions in square antiprismatic coordination of four nitrogen

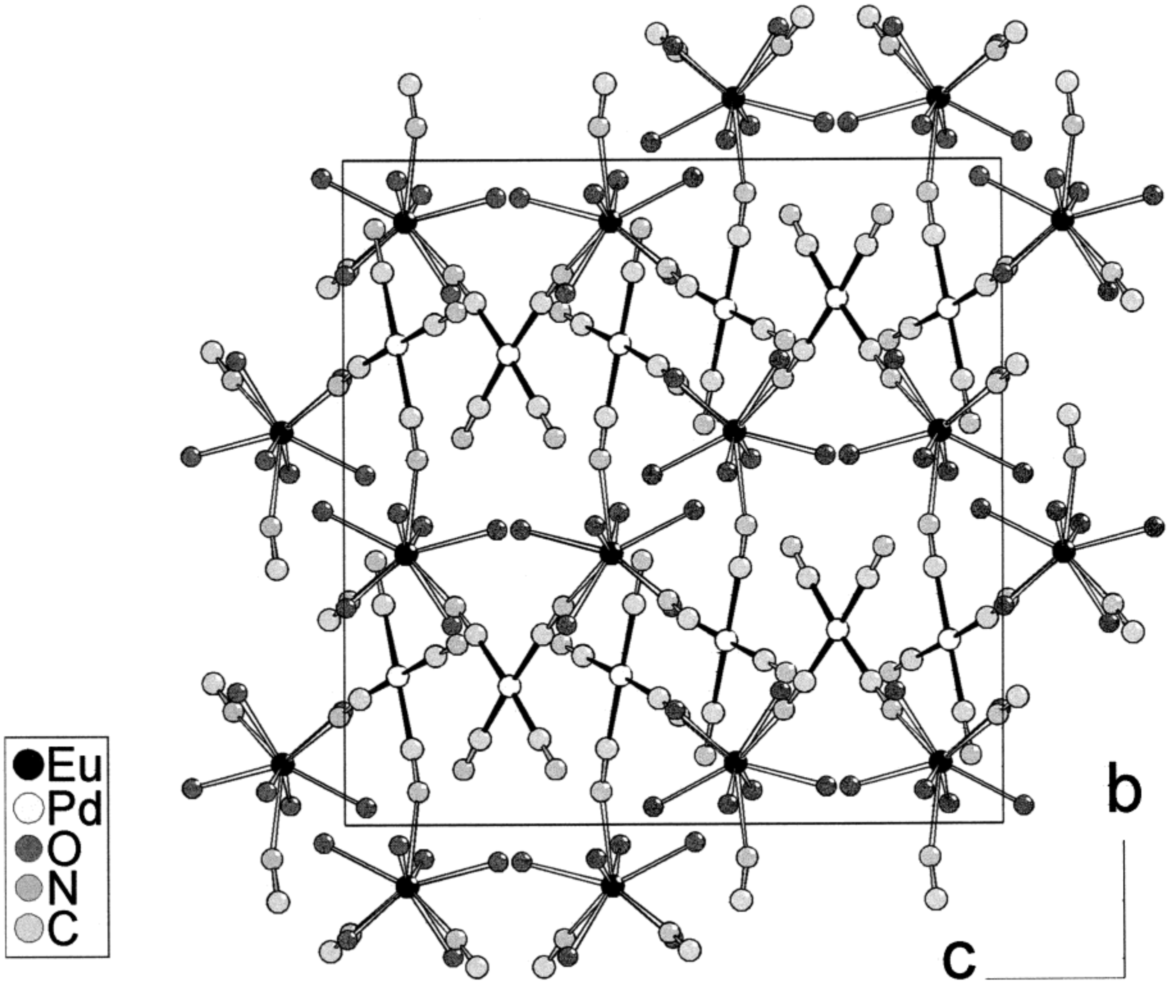

Figure 124. Crystal structure of $M_2[Pd(CN)_4]_3{\cdot}12H_2O$ (M = Eu, Nd) with square planar $[Pd(CN)_4]^{2-}$ groups.

and four sulfur ligands (Figure 120). Thus, the formula is better written as $Eu(NCS)_{4/4}(SCN)_{4/4}$, emphasizing the different attachment of the ligands and indicating that each ligand connects four Eu^{2+} ions with each other. The unusual coordination of Eu^{2+} makes the compound interesting for spectroscopic investigations, and indeed, a bright green luminescence is observed at low temperature. Upon heating, $Eu(SCN)_2$ decomposes at 400 °C by yielding EuS as the final product. Mass spectroscopy showed that mainly $(CN)_2$ is evolved during the reaction.[797]

D. Azides

The formation of azide complexes with rare-earth elements has been known for more than 30 years. In dimethyl sulfoxide as a solvent the species $M(N_3)_3$ and $M(N_3)_4^-$ were found,[798] and from aqueous solution the basic compounds $M(N_3)(OH)_2{\cdot}H_2O$ were precipitated.[799] However, no single-crystal data have been provided to date for neither $M(N_3)_3$ nor $M(N_3)(OH)_2{\cdot}H_2O$. On the other hand, the ternary compounds $Cs_2Nd(N_3)_5$, $Cs_3Nd(N_3)_6$, and $Cs_4Nd(N_3)_7$ have been prepared in single-crystalline form from a solution of Nd_2O_3 and CsN_3 in HN_3.[800] For the first two compounds the structure has been determined. In $Cs_2Nd(N_3)_5$[801] the Nd^{3+} ions are coordinated by eight N_3^- groups. Six of the latter are connected to another Nd^{3+} ion so one can formulate according to $^3_\infty[Nd(N_3)_{2/1}(N_3)_{6/2}]^{2-}$. In the three-dimensional network the four crystallographically different Cs^+ ions are incorporated, being irregularly coordinated by 10 and 12 nitrogen atoms. A coordination number of nine is found for the Nd^{3+} ions in $Cs_3Nd(N_3)_6$.[802] Four of the bridging N_3^- ions connect the $[Nd(N_3)_9]$ polyhedra to dimers which are further linked by N_3^- groups to a three-dimensional network $^3_\infty[Nd(N_3)_{3/1}(N_3)_{6/2}]^{3-}$ (Figure 121). The Cs^+ ions show coordination numbers between 9 and 13.

E. Cyanamides

No simple cyanamides $M_2(CN_2)_3$ of the rare-earth elements are known, but recently the crystal structures of the oxide cyanamides $M_2O_2(CN_2)$ (M = La, Pr, Nd, Sm, Er) have been reported.[803,804] The lanthanum compound crystallizes tetragonally, while those of the others have a trigonal structure. Both structures of both modifications are similar in the sense that they contain oxygen-centered $[OM_4]$ tetrahedra which are connected to infinite layers. In $La_2O_2(CN_2)$ the linkage occurs via four of the six edges of the tetrahedron, leading to tetragonal sheets $^2_\infty[OLa_{4/4}]^+$ (Figure 122a), while the connection via three *cis*-edges leads to trigonal double layers $^2_\infty\{[OLa_{4/4}]_2\}^{2+}$ in the cyanamides of the smaller lanthanides (Figure 122b). The layers are stacked in both cases alternating with CN_2^{2-} ions in the [001] direction. In the trigonal compound the anions are aligned exactly along the *c*-axis and are attached with both of the nitrogen atoms to three M^{3+} ions. In the tetragonal lanthanum compound the CN^{2-} ions are oriented perpendicular to [001] and disordered over two possible positions in the crystal.

F. Cyanides

Cyanides of rare-earth elements were prepared for the first time in 1966 by metathesis reactions of the lanthanide tribromides with LiCN in THF.[805] Subsequently, a method has been elaborated to prepare anhydrous rare-earth cyanides from liquid ammonia.[806] However, no single crystals have been obtained so far. To date, structure determinations were carried out for the dicyanoargentate $Eu[Ag(CN)_2]_3 \cdot 3H_2O$,[807] the dicyanoaurates $M[Au(CN)_2]_3 \cdot 3H_2O$ (M = Sm, Gd),[808,809] the tetracyanopalladates $M_2[Pd(CN)_4]_3 \cdot 12H_2O$ (M = Eu, Nd),[810,811] and the hexacyanometalates of Fe, Co, and Cr with various rare-earth elements (Table 18).[812−828] The dicyanoargentates and aurates contain either the $Ag(CN)_2^-$ or the $Au(CN)_2^-$ anion, respectively. Six of the anions and the three water molecules are attached to the M^{3+} ion, giving a tricapped trigonal prism as a coordination polyhedron. The structure of the argentate (Figure 123a) and the aurates (Figure 123b) are both hexagonal, but while the argentate anion is strictly linear, the aurate shows an angle C−Au−C of 121°. Presumably this effect may be attributed to $d^{10}-d^{10}$ interactions of the Au^+ ions. In the tetracyanopalladates the M^{3+} ions are surrounded by three square planar $[Pd(CN)_4]^{2-}$ groups which are themselves attached to two M^{3+} ions, leading to a two-dimensional network according to ${}^{2}_{\infty}\{M[Pd(CN)_4]_{3/2}\}$. The H_2O molecules complete the coordination sphere of the M^{3+} ions to a tricapped trigonal prism (Figure 124). In the hexacyanometalates the transition metals are octahedrally coordinated by the carbon atoms of six CN^- ions. Each nitrogen atom of the cyanide group is attached to a M^{3+} ion, which has two or three additional H_2O ligands, depending on the ionic radius.

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