Acknowledgment. We acknowledge the financial support of the National Research Council of Canada.

Registry No. $PtCl_2(Ph_2PC\equiv CEt)_2$, 42847-15-4; $PtCl_2(Ph_2PC\equiv CPh)_2$, 42847-16-5; $PtCl_2(Ph_2PC\equiv CPr\text{-}i)_2$, 42847-17-6; $PtCl_2(Ph_2PC\equiv CBu\text{-}t)_2$, 42847-18-7; $Pt(NCS)(SCN)(Ph_2PC\equiv CEt)_2$, 42921-68-6; $Pt(NCS)(SCN)(Ph_2PC\equiv CPh)_2$, 42847-19-8; $Pt(NCS)(SCN)(Ph_2PC\equiv CPr\text{-}i)_2$, 42847-20-1; $Pt(NCS)_2(Ph_2PC\equiv CBu\text{-}t)_2$, 42847-21-2; $Pt(NCS)(SCN)(Ph_2PC\equiv CBu\text{-}t)$, 42847-22-3; $Pt(^{15}NCS)(SC^{15}N)(Ph_2PC\equiv CEt)_2$, 42847-23-4; $Pt(^{15}NCS)(SC^{15}N)(Ph_2PC\equiv CBu\text{-}t)_2$, 42847-24-5; $Pt(^{15}NCS)_2(Ph_2PC\equiv CBu\text{-}t)_2$, 42847-25-6.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-284.

(41) Solid $Pt(CNS)_2(Ph_3P)_2$ is N bonded and cis in the solid state although *trans*-$PtCl_2(Ph_3P)_2$ apparently yields the S-bonded species initially on reaction with CNS^- ion.[42]

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Contribution from the Institute of Inorganic and Physical Chemistry, University of Stockholm, S-10405 Stockholm, Sweden, and the Department of Chemistry, Helsinki University of Technology, SF-02150 Otaniemi, Finland

Crystal Structure of Ammonium Samarium Sulfate Tetrahydrate

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The structure of $NH_4Sm(SO_4)_2 \cdot 4H_2O$ has been determined by single-crystal X-ray diffraction techniques. The positions of all nonhydrogen atoms were deduced, from 1145 diffractometer-measured intensities, by means of Patterson and Fourier methods. Refinement by the method of least-squares calculations, with anisotropic thermal motion for each atom, resulted in an R value of 0.046. The monoclinic cell has the dimensions $a = 6.582$ (2), $b = 18.886$ (7), $c = 8.736$ (4) Å, and $\beta = 96.88$ (4)°; it contains four formula units. The space group is $P2_1/c$. The unit cell dimensions for the isostructural ammonium lanthanide sulfates (La–Tb) have also been determined. The samarium atom is coordinated by six oxygen atoms, belonging to sulfate ions, at distances of 2.378–2.559 Å and by three water molecules at distances of 2.442–2.512 Å. The nine oxygen atoms form a polyhedron, which can equally well be described either as a tricapped trigonal prism or as a monocapped square antiprism. Cross-linking of samarium atoms occurs through sharing of sulfate ions; in this way layers are formed which are held together by hydrogen bonds. Ir and thermal data for the compound have also been measured and are discussed.

Introduction

The lanthanides form a variety of double sulfates with the alkali and ammonium ions. The composition and properties of these sulfates have been studied extensively. However, the knowledge of their structure is very scarce and based on thermal and spectroscopic studies; no X-ray structural determination seems to have been done.

The present investigation was undertaken to elucidate the crystal structure of the double sulfate of ammonium and samarium. The existence of such a phase with the formula $NH_4Sm(SO_4)_2 \cdot 4H_2O$ has been confirmed earlier.[2] This compound is isostructural with $NH_4Nd(SO_4)_2 \cdot 4H_2O$[3] and $NH_4Ce(SO_4)_2 \cdot 4H_2O$.[4] The present report also describes the unit cell dimensions of the isostructural double sulfate series from lanthanum to terbium. The heavier lanthanides form double sulfates with ammonium, which have the same composition but different structure as indicated by the published powder pattern of $NH_4Dy(SO_4)_2 \cdot 4H_2O$.[5]

Experimental Section

Preparation of the Compounds. The crystals were prepared as described earlier; aqueous solutions of lanthanide sulfate and ammonium sulfate were mixed in the approximate molar ratio of 1:4 and the solution was left to stand in air.[2] Upon evaporation prismatic crystals were obtained which showed the characteristic color of the lanthanide ion. The crystals were washed with small amounts of water, ethanol, and ether. The lanthanide sulfate solutions were prepared from lanthanide oxides of 99.5–99.9% purity; all other reagents were of analytical reagent grade.

Spectroscopic and Thermal Studies. Infrared spectra in the region 4000–400 cm^{-1} were recorded with a Perkin-Elmer 125 spectrophotometer using the KBr pellet technique. The sample showed no reaction with KBr.

Tg, dtg, and dta curves were recorded simultaneously with a Mettler Thermoanalyzer. The furnace atmosphere was a dynamic air atmosphere with a flow rate of 90 cm^3/min. The heating rate was 2°/min and two kinds of platinum crucibles were employed: (i) long and relatively narrow ones (diameter 7 mm, depth 19 mm, weight 2.0 g) and (ii) small and broad ones (diameter 6 mm, depth 5 mm, weight 0.25 g). Alumina was used as reference material.

Data Collection and Reduction. The accurate unit cell dimensions were calculated for the eight ammonium lanthanide sulfates from powder photographs. These were obtained at 25° in a Guinier-Hagg focusing camera of 80-mm diameter, with strictly monochromatized Cu $K\alpha_1$ radiation (λ 1.54050 Å). Potassium chloride ($a = 6.29228$ Å)[6] was used as internal standard. The powder photographs were measured and interpreted to $\sin^2 \theta = 0.35$.

Single-crystal intensity data for $NH_4Sm(SO_4)_2 \cdot 4H_2O$, chosen for the complete crystal structure analysis, were obtained on a Philips PW 1100 computer-controlled four-circle diffractometer. Graphite-monochromatized Cu K radiation and a scintillation counter with pulse height discrimination were used. The dimensions of the crystal were 0.09 × 0.08 × 0.07 mm^3. The θ–2θ scan technique was employed, with a scan range of 1.5° and a speed of 0.015°/sec; the background was measured for 50 sec at each end of the scan interval. Three test reflections were measured hourly to check for the possible deterioration of the crystal in the X-ray beam, but the intensity was found to remain constant within ±2%. Therefore no correction for radiation damage was made. The background intensities were calculated as averages of the intensities at each end of the scan interval.

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(1) To whom correspondence should be addressed at Helsinki University of Technology.

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All 1822 reflections with $\theta < 60°$ were recorded, and out of these 1145 independent reflections, with $\sigma(I_{net})/I_{net} < 0.25$, were accepted for further calculations. The net intensity, I_{net}, was calculated as $I_{tot} - I_{back}$ and its standard deviation, $\sigma(I_{net})$, was estimated as $(I_{tot} + I_{back})^{1/2}$, where I_{tot} and I_{back} are the number of counts for the total intensity and background intensity, respectively.

The data were corrected by application of Lorentz and polarization factors. Absorption correction was made by the method of Coppens, *et al.*[7] The crystal was defined by eight faces, and the linear absorption coefficient, $\mu = 414.3$ cm^{-1}, was calculated from the mass absorption coefficients given in ref 8. The transmission factor varied from 0.071 to 0.184. All calculations were performed on IBM 1800 and 360/75 computers in Stockholm and on a UNIVAC 1108 computer in Helsinki.[9]

Structure Determination. The space group of the structure, $P2_1/c$ (No. 14), was uniquely determined from the reflections systematically absent, *viz*; $h0l$ with l odd and $0k0$ with k odd. The calculated density, 2.67 g cm^{-3} ($d_{obsd} = 2.65$ g cm^{-3}), indicates that there are four formula units in the cell.

A three-dimensional Patterson synthesis was calculated and interpreted to place the Sm atom in the general position 4e of the space group. The coordinates of the samarium atom were refined by the method of full-matrix least-squares calculations to an R value of 0.28 ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$). The phases calculated from that atom alone were used in computing a three-dimensional electron density map using all observations. This map revealed the presence of all nonhydrogen atoms (2 S, 12 O, and 1 N) in general positions 4e, thus corroborating the stoichiometry. After a preliminary isotropic refinement ($R = 0.070$), anisotropic vibrational parameters were introduced whereupon the R value dropped to 0.058. The general agreement between observed and calculated structure factors was consistent with the estimated error in the values of F_o, but 24 reflections showed discrepancies greatly exceeding the estimated errors. These reflections were obviously affected by extinction, as they were strong low-angle reflections with observed structure factor amplitudes much smaller than the calculated amplitudes. These low-angle reflections as well as 21 weak reflections having badly defined background values were given zero weight, and all parameters were further refined. A single scale factor was refined, and the weighting scheme of Hughes with $|F_{o,min}| = 10.0$ and $h = 4.0$ was used. The scattering factors for Sm, S, and O were those given by McMaster, *et al.*,[10] and for NH_4^+ the scattering factor was that given by Davis.[11] The refinement was considered complete when the shifts in the parameters were all less than 1% of their standard deviations. The final R value was 0.046. After the refinement was completed, a difference synthesis was calculated in an attempt to locate the hydrogen atoms, but the only significant features were several maxima of 0.5 e Å^{-3} in the vicinity of the Sm atom. These maxima may be due to series termination errors.

Results and Discussion

The unit cell dimensions for the isostructural series from lanthanum to terbium are given in Table I. The unit cell parameters and observed intensity distribution of the powder photographs confirmed the expected isostructurality.

There is a rather linear decrease in $V^{1/3}$ when plotted against the ionic radii of the trivalent lanthanide ions (the correlation coefficient is −0.997; *cf.* Figure 1). The ionic radii used are those given by Shannon and Prewitt[12,13] for the six-coordinated lanthanides. These were considered to be the most reliable values available. In the sulfates studied the coordination number for the lanthanides is 9, but no complete set of values for nine-coordination has been published. However, it can be assumed that the increase of the ionic radii is fairly parallel when the coordination number is increased, as seen from the values of ionic radii for six- and eight-coordination.[12]

Table I. Unit Cell Dimensions for the Isostructural Ammonium Lanthanide Sulfate Tetrahydrates

	a, Å	b, Å	c, Å	β, deg	V, Å^3
La	6.719 (1)	19.073 (4)	8.843 (2)	97.45 (2)	1123.7 (0.6)
Ce	6.676 (5)	19.005 (8)	8.821 (4)	97.28 (3)	1110.2 (1.7)
Pr	6.644 (2)	18.963 (5)	8.798 (3)	97.18 (3)	1099.8 (0.9)
Nd	6.625 (5)	18.928 (7)	8.789 (2)	97.06 (3)	1093.8 (1.4)
Sm	6.582 (2)	18.886 (7)	8.736 (4)	96.88 (4)	1078.1 (1.1)
Eu	6.568 (5)	18.833 (8)	8.727 (4)	96.98 (6)	1071.4 (1.6)
Gd	6.548 (4)	18.831 (4)	8.701 (4)	96.75 (3)	1065.4 (1.2)
Tb	6.524 (2)	18.832 (4)	8.684 (2)	96.72 (2)	1059.6 (0.8)

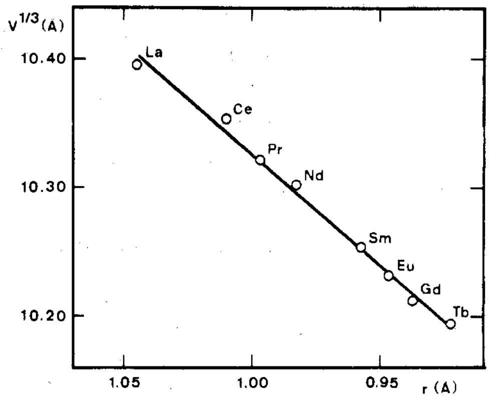

Figure 1. Values of $V^{1/3}$ for the isostructural series $NH_4Ln(SO_4)_2 \cdot 4H_2O$ (Ln = La–Tb) plotted *vs.* r.

The powder data are in agreement with the results obtained by Erametsa and Niinisto[2] ($a = 6.574$, $b = 18.842$, $c = 8.736$ Å, and $\beta = 96.90°$ for the samarium compound), Staritzky and Cromer[3] ($a = 6.63$, $b = 18.94$, $c = 8.80$ Å, and $\beta = 96.2°$ for the neodymium compound), and by Blandin and Rerat[4] ($a = 6.71 \pm 0.02$, $b = 19.01 \pm 0.02$, $c = 8.82 \pm 0.02$ Å, and $\beta = 97.50 \pm 0.50°$ for the cerium compound).

A complete structural analysis was performed for $NH_4Sm(SO_4)_2 \cdot 4H_2O$ and the final values of the atomic parameters, with standard deviations, are presented in Table II. The observed and calculated structure factors are listed in Table III.[14]

The samarium ion is coordinated to nine oxygen atoms; six of these are sulfate oxygen atoms and three are water oxygens. The arrangement of the six sulfate oxygen atoms, belonging to four sulfate groups, and the three water molecules around the samarium atom, as well as the atom-numbering system used in this investigation, is shown in Figure 2. Bond lengths and angles involving Sm and SO_4 groups are given in Tables IV and V, respectively. Additional distances less than 3.0 Å, including polyhedral edges and possible hydrogen bond distances, are given in Table VI.

In the coordination sphere the nine Sm–O distances vary between 2.378 and 2.559 Å, and the average value, 2.467 Å, corresponds to the sum (2.49 Å) of the ionic radii (1.40 Å for O^{2-} and 1.09 Å for $(Sm^{VIII})^{3+}$).[12] The mean samarium–sulfate oxygen distance (2.47 Å) is approximately the same as the mean distance from samarium to the water oxygen (2.46 Å). This can be compared with the corresponding distances in $Ce_2(SO_4)_3 \cdot 9H_2O$, where the second cerium atom is nine-coordinated: there are no significant differences in

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[9] The computer programs used in this study have been identified elsewhere: L. Niinisto and L. O. Larsson, *Acta Crystallogr., Sect. B*, 29, 623 (1973).

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[12] R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, 25, 925 (1969).

[13] R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, 26, 1046 (1970).

[14] See paragraph at end of paper regarding supplementary material.

Table II. Atomic Coordinates and Thermal Parameters[a]

Atom	x	y	z	β_{11}	β_{22}	β_{23}	β_{12}	β_{13}	β_{23}	B, Å^2
Sm	1484 (1)	1231 (1)	7870 (1)	45 (2)	5 (0)	40 (1)	4 (1)	19 (2)	3 (1)	0.8
S(1)	1248 (4)	2769 (2)	9152 (3)	76 (7)	3 (1)	31 (4)	15 (4)	8 (7)	5 (3)	0.7
S(2)	6892 (1)	766 (2)	7659 (4)	21 (6)	6 (1)	101 (5)	−2 (4)	85 (9)	−8 (3)	1.1
O(1)	936 (15)	1597 (5)	3198 (10)	174 (24)	9 (3)	52 (12)	−13 (13)	12 (28)	12 (9)	1.9
O(2)	1419 (18)	295 (5)	803 (10)	356 (35)	8 (3)	29 (12)	48 (15)	68 (33)	−6 (10)	2.5
O(3)	9561 (13)	2752 (5)	3779 (11)	79 (20)	16 (3)	79 (14)	−8 (13)	40 (27)	10 (10)	1.7
O(4)	3129 (12)	2617 (5)	3841 (10)	43 (19)	16 (3)	74 (13)	−31 (12)	−39 (25)	41 (10)	1.8
O(5)	5113 (13)	3812 (5)	2889 (12)	44 (20)	8 (3)	137 (16)	−23 (11)	82 (28)	15 (12)	1.7
O(6)	6323 (17)	58 (6)	7278 (19)	171 (32)	11 (3)	333 (32)	−28 (52)	208 (52)	−55 (18)	3.9
O(7)	8026 (16)	3883 (6)	1476 (11)	157 (26)	23 (4)	46 (12)	16 (14)	52 (29)	8 (14)	2.1
O(8)	8381 (14)	4218 (5)	4090 (11)	102 (22)	17 (3)	81 (14)	24 (13)	14 (29)	−50 (11)	2.4
W(1)	1709 (15)	4442 (5)	415 (11)	160 (25)	13 (3)	84 (14)	54 (13)	45 (30)	−29 (10)	2.1
W(2)	2505 (17)	1107 (5)	670 (11)	195 (28)	16 (3)	65 (13)	42 (14)	39 (31)	−11 (10)	2.3
W(3)	6380 (18)	1066 (6)	3394 (12)	209 (31)	27 (4)	84 (15)	−25 (16)	−14 (34)	33 (13)	3.5
W(4)	8057 (17)	27 (5)	1679 (10)	243 (29)	7 (3)	67 (13)	29 (14)	136 (32)	22 (10)	2.1
NH_4	6622 (18)	2225 (7)	1157 (15)	130 (30)	16 (4)	93 (19)	−25 (17)	−138 (38)	30 (14)	1.9

[a] All values except B are multiplied by 10^4 and include estimated standard deviations in parentheses. The anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table IV. Bond Lengths (Å) and Angles (deg) Involving Sm

Sm-O(2)	2.378 (9)	Sm-O(5)	2.388 (9)	Sm-W(1)	2.512 (10)
Sm-O(3)	2.483 (9)	Sm-O(7)	2.459 (9)	Sm-W(2)	2.469 (10)
Sm-O(4)	2.531 (9)	Sm-O(8)	2.559 (9)	Sm-W(4)	2.422 (9)

O(2)-Sm-W(1)	71.4 (3)	O(5)-Sm-W(4)	82.0 (3)
O(2)-Sm-O(3)	76.9 (3)	O(5)-Sm-O(7)	150.0 (3)
O(2)-Sm-W(2)	142.4 (3)	O(5)-Sm-O(8)	146.4 (3)
O(2)-Sm-O(4)	70.2 (3)	O(7)-Sm-O(8)	55.9 (3)
O(2)-Sm-O(5)	87.4 (4)	W(1)-Sm-O(3)	139.0 (3)
O(2)-Sm-W(4)	139.0 (3)	W(1)-Sm-W(2)	139.5 (3)
O(2)-Sm-O(7)	75.5 (4)	W(1)-Sm-O(4)	130.9 (3)
O(2)-Sm-O(8)	126.2 (4)	W(1)-Sm-O(5)	80.1 (3)
O(3)-Sm-W(2)	81.1 (3)	W(1)-Sm-W(4)	67.9 (3)
O(3)-Sm-O(4)	56.0 (3)	W(1)-Sm-O(7)	71.3 (3)
O(3)-Sm-O(5)	124.9 (3)	W(1)-Sm-O(8)	108.7 (3)
O(3)-Sm-W(4)	140.0 (3)	W(2)-Sm-O(4)	72.2 (3)
O(3)-Sm-O(7)	75.5 (3)	W(2)-Sm-O(5)	80.6 (4)
O(3)-Sm-O(8)	70.2 (3)	W(2)-Sm-W(4)	74.4 (3)
O(4)-Sm-O(5)	68.9 (3)	W(2)-Sm-O(7)	127.5 (3)
O(4)-Sm-W(4)	138.5 (3)	W(2)-Sm-O(8)	72.0 (3)
O(4)-Sm-O(7)	125.1 (3)	W(4)-Sm-O(7)	94.9 (4)
O(4)-Sm-O(8)	118.4 (3)	W(4)-Sm-O(8)	72.4 (3)

Table V. Bond Lengths (Å) and Angles (deg) in the SO_4 Groups

S(1)-O(1)	1.460 (10)	S(2)-O(5)	1.499 (9)
S(1)-O(2)	1.472 (9)	S(2)-O(6)	1.418 (12)
S(1)-O(3)	1.488 (9)	S(2)-O(7)	1.500 (11)
S(1)-O(4)	1.489 (9)	S(2)-O(8)	1.494 (10)

O(1)-S(1)-O(2)	111.2 (6)	O(5)-S(2)-O(6)	110.8 (6)
O(1)-S(1)-O(3)	111.4 (6)	O(5)-S(2)-O(7)	109.3 (6)
O(1)-S(1)-O(4)	111.13 (6)	O(5)-S(2)-O(8)	109.5 (6)
O(2)-S(1)-O(3)	109.4 (6)	O(6)-S(2)-O(7)	113.2 (8)
O(2)-S(1)-O(4)	108.8 (6)	O(6)-S(2)-O(8)	110.1 (7)
O(3)-S(1)-O(4)	104.7 (5)	O(7)-S(2)-O(8)	103.7 (6)

Table VI. Additional Distances Less Than 3.0 Å

O(1)-O(2)	2.420 (13)	O(5)-O(8)	2.403 (13)
-O(4)	2.432 (13)	-O(7)	2.405 (14)
-O(3)	2.436 (13)	O(6)-O(8)	2.387 (17)
-W(2)	2.710 (14)	-O(7)	2.436 (16)
-W(1)	2.761 (14)	-W(3)	2.787 (16)
O(2)-O(4)	2.408 (13)	-W(2)	2.884 (16)
-O(3)	2.416 (13)	O(7)-O(8)	2.354 (13)
-O(4)	2.825 (13)	-W(3)	2.781 (15)
-W(1)	2.854 (14)	O(8)-W(4)	2.704 (13)
-O(7)	2.963 (15)	-W(4)	2.943 (14)
O(3)-O(4)	2.356 (12)	-W(2)	2.958 (14)
-O(8)	2.899 (14)	W(1)-W(4)	2.756 (14)
$-NH_4$	2.985 (16)	W(2)-W(4)	2.958 (13)
O(4)-O(5)	2.784 (13)	W(3)-W(4)	2.776 (15)
$-NH_4$	2.890 (15)	$-NH_4$	2.952 (17)
-W(2)	2.948 (13)		

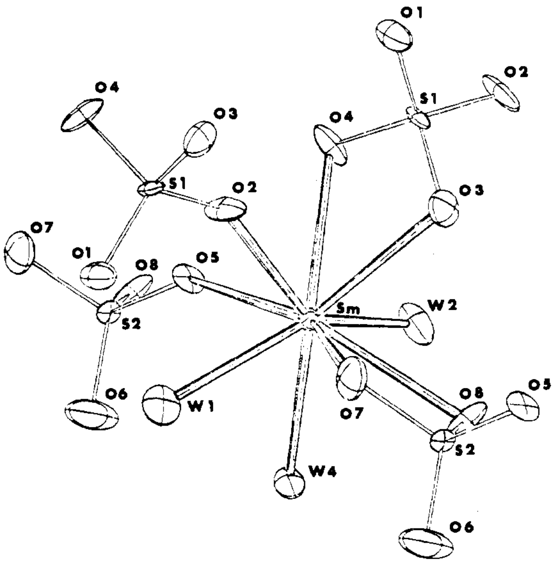

Figure 2. A perspective drawing showing coordination about the samarium atom. The atoms are represented by 50% probability thermal ellipsoids.

the metal-oxygen distances, which are 2.524 and 2.507 Å for Ce-O(sulfate) and Ce-O(water) bonds, respectively.[15] In eight-coordinated $Am_2(SO_4)_3 \cdot 8H_2O$, which is isostructural with $Nd_2(SO_4)_3 \cdot 8H_2O$, the Am-O(sulfate) distance (2.43 Å) is significantly shorter than the Am-O(water) distance (2.47 Å), however.[16]

The coordination of oxygen atoms to the samarium atom can be described equally well in either one of the following two ways: (i) as a distorted monocapped square antiprism or (ii) as a distorted tricapped trigonal prism.

The latter coordination geometry has been encountered more frequently with the lanthanides.[17] There are only three structures which have been described in the literature to have distorted monocapped square-antiprismatic geometry.[18-20] In addition, $Pr(NTA) \cdot 3H_2O$ has recently been

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determined to have a distorted structure intermediate between the two idealized geometries.[21]

In the idealized monocapped square-antiprism atoms O(7), O(8), W(4), and W(1) (*cf.* Figure 3a) would form a square (plane II, Table VII) as would also the atoms O(2), O(3), W(2), and O(5) (plane I, Table VII). The calculations regarding the least-squares planes are shown in Table VII.

Mean planes I and II are almost parallel; they form a dihedral angle of 1.5°. The two four-sided figures have their diagonals inclined 45° to another when projected down Sm-O(4). The Sm atom is 1.56 Å above the mean plane II and 0.95 Å below the mean plane I; the O(4) atom is 1.56 Å above mean plane I, thus forming the cap.

Referring to Figure 3b, the three rectangular faces of the trigonal prism are O(3)-W(2)-O(5)-O(2) (plane III which is equal to plane I in the monocapped square antiprism), O(3)-O(8)-W(1)-O(2) (plane IV), and W(2)-O(8)-W(1)-O(5) (plane V). The two triangular faces of the prism are defined by atoms O(3)-O(8)-W(2) and O(2)-W(1)-O(5), respectively. The three atoms O(4), O(7), and W(4) occupy the capping positions or the central triangular face (plane VI). The angles of the planes III-IV, III-V, and IV-V are 50, 54, and 67°, respectively, and the angles involving the planes III and V and the central plane VI are around 90° (90, 87, 86°). The Sm atom is somewhat out of the central plane (0.17 Å).

The deviation from the idealized geometry for nine-coordination, *i.e.*, a monocapped square antiprism with symmetry C_{4v} or a tricapped trigonal prism with symmetry D_{3h}, may depend on the fact that atoms O(2)-O(3) and O(7)-O(8) also form edges in the sulfate group. The corresponding oxygen-oxygen distances are significantly shorter (2.38 and 2.40 Å) than the other oxygen-oxygen distances within the coordination polyhedron (*cf.* Table V).

The dimensions of the sulfate group are consistent with the values observed in other sulfate structures.[22] The average S-O distances for the two crystallographically nonequivalent SO_4 groups are 1.465 and 1.477 Å; the average O-S-O angle is 109.5° for both groups. However, the variations in the S-O bond lengths are significantly larger in the S(2) sulfate group than in the S(1) group. The S(2)-O(6) distance is only 1.418 ± 0.012 Å, *i.e.*, a difference of 5σ from the average value. The oxygen atom O(6) is not involved in the coordination polyhedron around samarium, and this partly explains the shorter distance. However, the corresponding oxygen atom, O(1), in the other sulfate group has a rather average bond length to S(1) (1.460 ± 0.010 Å). This may depend on interaction by hydrogen bonds (*cf.* Table V).

Sulfate groups join the samarium atoms into a layer-like structure. The structure contains continuous chains, composed of alternate Sm atoms and S(2) sulfate groups, running parallel to the *a* axis. A segment of such a chain, with interatomic bond angles indicated is shown in Figure 4. Parallel chains are linked together by S(1) sulfate groups acting as bridges between Sm atoms in adjacent chains, which are thus joined into layers in the structure, parallel to the (010) plane. Short contacts between water molecules W(3) and sulfate oxygen atoms or other water molecules indicate that the layers may be held together by hydrogen bonds. A stereoscopic view of the structure is shown in Figure 5.

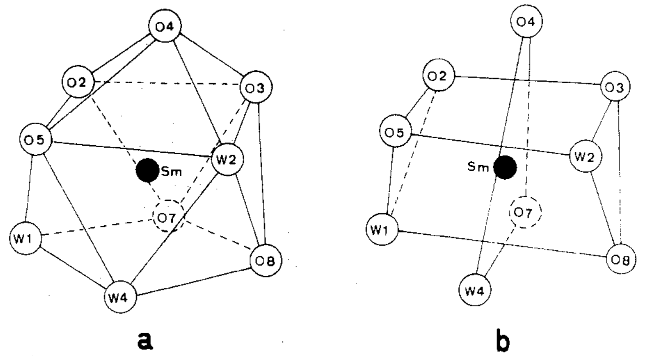

Figure 3. The coordination polyhedron about the Sm atom: (a) monocapped square antiprism; (b) tricapped trigonal prism.

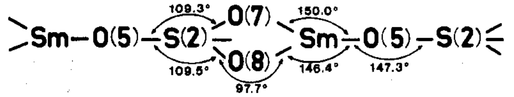

Figure 4. A segment of the chain formed by Sm atoms and S(2) sulfate groups.

Table VII. Deviations (Å) of Atoms from the Least-Squares Planes[a]

	Plane I[b]				Plane II		
A	0.5296	O(2)	−0.179	*A*	0.5511	O(7)	−0.097
B	0.8082	O(3)	0.183	*B*	0.7957	O(8)	0.094
C	0.2575	W(2)	−0.176	*C*	0.2512	W(1)	0.083
D	5.082	O(5)	0.171	*D*	2.526	W(4)	−0.079

	Plane IV				Plane V		
A	0.8644	O(2)	−0.140	*A*	0.2324	W(1)	0.101
B	−0.0912	O(3)	0.135	*B*	−0.9517	O(8)	−0.110
C	0.4944	O(8)	−0.098	*C*	0.2006	O(5)	−0.135
D	3.039	W(1)	0.103	*D*	0.0767	W(2)	0.143

	Plane VI		
A	−0.4499	O(7)	0.0
B	0.0058	O(4)	0.0
C	0.8931	W(4)	0.0
D	5.784	Sm	0.171[c]

[a] The planes are of the form $Ax + By + Cz = D$ where *x*, *y*, and *z* are in angstrom units relative to the axes *a*, *b*, and *c*, respectively. [b] Plane III equals this plane. [c] This atom was omitted from the calculations of the least-squares plane.

Table VIII. Infrared Absorption Frequencies in the Region 4000–400 cm^{-1}

Obsd freq, cm^{-1}	Assignment	Obsd freq, cm^{-1}	Assignment
3400 s, b	$\nu(H_2O)$	975 m	$\nu_1(SO_4)$
3130 vs	$\nu_3(NH_4)$	660 sh	$\nu_4(SO_4)$
1670 sh	$\delta(H_2O)$	645 s	
1625 m		605 sh	
1390 vs	$\nu_4(NH_4)$	585 s	
1190 s	$\nu_3(SO_4)$	475 w	$\nu_2(SO_4)$, Sm–OH_2 wag
1120 vs, b		410 vw	Sm–OH_2 str

The ammonium ion has four close contacts (less than 3.2 Å) in the structure. The average value for these contacts is 2.96 Å, which comes very close to the mean value of 2.97 Å found for N-H· · ·O bond lengths in sulfates.[23]

The infrared absorption spectrum of $NH_4Sm(SO_4)_2 \cdot 4H_2O$ is shown in Table VIII. The assignments of sulfate group frequencies are largely based on the investigation of Postmus and Ferraro[24] on rare earth sulfates.

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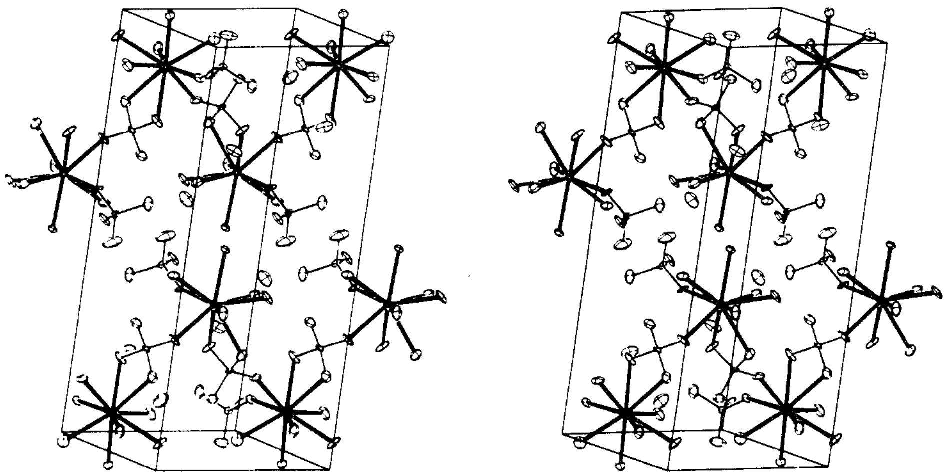

Figure 5. A stereoscopic view of the structure of $NH_4Sm(SO_4)_2 \cdot 4H_2O$ showing the unit cell packing. The *c* axis is horizontal, the *b* axis is vertical, and the *a* axis points into the paper. The atoms are represented by 50% probability thermal ellipsoids.

Il'yashenko, *et al.*,[25] have studied the ir spectra of the ammonium sulfates of europium, gadolinium, and terbium and obtained results very similar to ours. On the basis of the ir data they concluded that all water molecules are held in the structure by strong hydrogen bonds and that they are not coordinated to the lanthanide ion. In the OH bending region there are, however, two bands indicating two different types of water in the structure. The structure determination is consistent with the latter observation: water molecules W(1), W(2), and W(4) are indeed coordinated to the samarium ion while W(3) is held between the layers by hydrogen bonds. The formation of Sm-O(water) bonds is indicated in the ir spectrum by the presence of a metal-OH_2 wagging mode and a metal-OH_2 stretching band although the former is mixed with the sulfate ν_2 vibration (*cf.* Table VIII).

In ammonium halides it has been observed that the combination band between ν_2 and ν_6 (rotatory lattice vibration) is present if the ammonium ion does not rotate freely in the crystal lattice.[26] This band could not be observed in the ir spectrum of $NH_4Sm(SO_4)_2 \cdot 4H_2O$ and thus it is probable that the ammonium ion does rotate in the structure.

The thermal properties of $NH_4Sm(SO_4)_2 \cdot 4H_2O$ have been described in a previous article.[2] The first stage in the decomposition is the dehydration, which proceeds as follows: $NH_4Sm(SO_4)_2 \cdot 4H_2O \rightarrow NH_4Sm(SO_4)_2 \cdot H_2O \rightarrow NH_4Sm(SO_4)_2$.

A somewhat different decomposition scheme has been reported for the isostructural ammonium sulfates of europium, gadolinium, and terbium: $NH_4Ln(SO_4)_2 \cdot 4H_2O \rightarrow NH_4Ln(SO_4)_2 \cdot 3.5H_2O \rightarrow NH_4Ln(SO_4)_2 \cdot H_2O \rightarrow NH_4Ln(SO_4)_2 \cdot 0.5H_2O \rightarrow NH_4Ln(SO_4)_2$.[23]

Therefore, the thermal measurements from 25 to 300° were repeated using platinum crucibles for greater sensitivity in dta measurements, and a plausible explanation for the discrepancy was found. The decomposition scheme and temperature are greatly influenced by the crucibles used. In long and narrow sample holders with relatively large sample volumes (70-80 mg) the decomposition proceeds as reported earlier.[2] However, with broader crucibles and smaller samples (10-20 mg) the decomposition scheme becomes $NH_4Sm(SO_4)_2 \cdot 4H_2O \rightarrow NH_4Sm(SO_4)_2 \cdot 0.5H_2O \rightarrow NH_4Sm(SO_4)_2$.

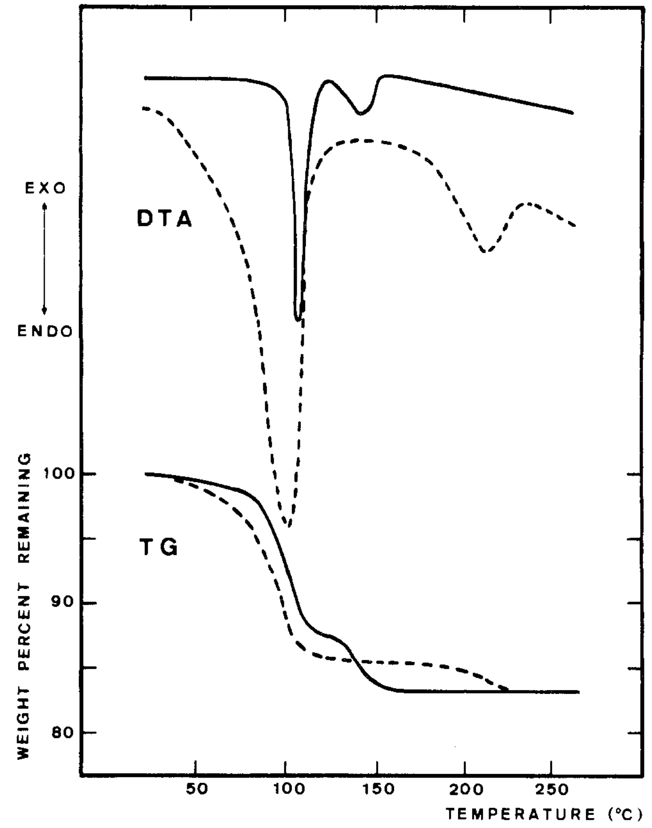

Figure 6. A comparison of tg and dta curves obtained with (i) long and relatively narrow crucibles with a 73.4-mg sample (solid line) and (ii) broader and smaller crucibles with a 18.9-mg sample (dashed line). In the latter case the dta scale has been expanded five times.

Both cases are shown in Figure 6. An exact comparison of our results with those obtained by Il'yashenko, *et al.*, [25] is not possible because experimental details of their study are lacking. It is obvious, however, that the self-generated atmosphere of the sample causes the different decomposition modes. This effect has been quite frequently encountered in dehydration reactions.[27]

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appreciate the help of Dr. Sven Westman in correcting the English of this paper. The investigation has been performed with financial support from the Tri-Centennial Fund of the Bank of Sweden and from the Swedish Natural Science Research Council. L. N. gratefully acknowledges financial aid from the Neste Oy Foundation.

Registry No. $\{(NH_4)[Sm(H_2O)_3(SO_4)_2]\cdot H_2O\}_x$, 42949-48-4; $NH_4La(SO_4)_2\cdot 4H_2O$, 42886-02-2; $NH_4Ce(SO_4)_2\cdot 4H_2O$, 10049-02-2; $NH_4Pr(SO_4)_2\cdot 4H_2O$, 13494-85-4; $NH_4Nd(SO_4)_2\cdot 4H_2O$, 42886-04-4; $NH_4Sm(SO_4)_2\cdot 4H_2O$, 34370-41-7; $NH_4Eu(SO_4)_2\cdot 4H_2O$, 14175-66-7; $NH_4Gd(SO_4)_2\cdot 4H_2O$, 25321-74-8; $NH_4Tb(SO_4)_2\cdot 4H_2O$, 15681-94-4.

Supplementary Material Available. Table III, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-290.

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Chemistry of Polynuclear Metal Halides. XI. Crystal and Molecular Structure of Tris(tetramethylammonium) Hexachloro(dodeca-μ-chloro-hexaniobate), $[(CH_3)_4N]_3[(Nb_6Cl_{12})Cl_6]$[1]

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The structure of the new compound $[(CH_3)_4N]_3[(Nb_6Cl_{12})Cl_6]$ was determined by single-crystal X-ray methods and refined to a conventional R factor $R_1 = 0.069$. The compound crystallizes in the trigonal-rhombohedral space group $R3$ with $a_{trig} = 11.408 \pm 0.005$ and $c_{trig} = 30.31 \pm 0.01$ Å, and three formula units in the trigonal unit cell. It contains a close-packed cubic arrangement of $[(Nb_6Cl_{12})Cl_6]^{3-}$ complex cluster anions which are based on $(Nb_6Cl_{12})^{3+}$ central cations. The tetramethylammonium cations occupy all tetrahedral and octahedral holes of this arrangement. Slight deviations of the $(Nb_6Cl_{18})^{3-}$ anion from strict octahedral symmetry are apparently caused by the packing of the $(Nb_6Cl_{18})^{3-}$ and $(CH_3)_4N^+$ units. Important average bond distances are 2.97 Å for Nb-Nb, 2.43 Å for Nb-$Cl_{bridging}$, and 2.52 Å for Nb-$Cl_{terminal}$. Comparison of these data with values reported for $K_4Nb_6Cl_{18}$ and $[(CH_3)_4N]_2[(Nb_6Cl_{12})Cl_6]$ shows that Nb-Nb distances increase gradually and that Nb-$Cl_{terminal}$ distances decrease gradually upon stepwise removal of two electrons from an $(Nb_6Cl_{18})^{4-}$ anion. The results tend to confirm that the two electrons are taken from a bonding MO centered primarily on the metal atoms.

Introduction

Niobium and tantalum are known to form a number of lower valent halides that contain hexanuclear $(M_6X_{12})^{n+}$ cluster cations. Previous work[3] has shown that such cluster cations may occur in three different oxidation states with $n = 2$, 3, and 4. Experimental evidence for metal-metal bonding in $(M_6X_{12})^{n+}$ cations has been established by magnetic[4,5] and spectral[6-8] measurements of compounds containing M_6X_{12} units and by the short metal-metal distances found in the structures of Nb_6F_{15},[9] Nb_6Cl_{14},[10] $K_4Nb_6Cl_{18}$,[11] Ta_6Cl_{15},[12] Ta_6I_{14},[13] and $H_2[Ta_6Cl_{18}]\cdot 6H_2O$.[14]

To describe metal-metal bonding in electron-deficient $(M_6X_{12})^{n+}$ cluster cations, a molecular orbital approach is most advantageous. In a simplified MO treatment by Cotton and Haas,[15] d_{xy}, d_{xz}, d_{yz}, and d_{z^2} orbitals of all six metal atoms are combined to form 8 bonding and 16 antibonding molecular orbitals. With 16 electrons available for metal-metal bonding as in the doubly charged $(M_6X_{12})^{2+}$ cluster cation, all 8 bonding orbitals should be filled and all 16 antibonding orbitals should be vacant. Since oxidation to form clusters with $n = 3$ or 4 removes bonding electrons, an increase in the M-M bond distances under retention of the octahedral symmetry of the cluster would be anticipated.

This present work is part of a study on the influence of oxidation on the structure of the $(Nb_6Cl_{12})^{n+}$ cluster cation. The qualitative correctness of the above MO treatment may be checked by establishing if, upon oxidation of the cluster, niobium-niobium distances increase under retention of octahedral symmetry. A determination of the crystal structure of $[(CH_3)_4N]_2[(Nb_6Cl_{12})Cl_6]$,[16] which contains complex $(Nb_6Cl_{18})^{2-}$ anions based on $(Nb_6Cl_{12})^{4+}$ central cations, and a comparison of the obtained bond distances and angles with data reported for $K_4Nb_6Cl_{18}$[11] has shown that two-electron oxidation of the $(Nb_6Cl_{12})^{2+}$ unit causes a significant increase in Nb-Nb bond distances under retention of octa-

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