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Reduced Halides of the Rare-Earth Elements[†]

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I. Introduction

Early efforts concerning the reduction of lanthanide(III) halides were motivated through the development of the *systematics of the lanthanides*, at a time when there were more problems left with the periodic table than just the development of a new numbering scheme. Inspired by G. von Hevesy, Klemm[1] developed a systematic based on his own synthetic work that explained the more or less easy access to the tetravalent or divalent states through the "desire" of some of the lanthanoids to achieve electronic configurations like those of the elements lanthanum, gadolinium, and lutetium (Figure 1). In fact, standard electrode potentials, $E°(M^{4+}/M^{3+})$ and $E°(M^{3+}/M^{2+})$ (Figure 2), are like reciprocal representations of Klemm's systematic although they are for aqueous solutions and are mainly assessed or calculated by indirect means (see below). Not only are the redox potentials $E°(M^{3+}/M^{2+})$ connected to the relative stabilities of the dipositive states of Eu, Yb, Sm, Tm, Dy, Nd, and Ho, but they can be brought together with metallic, i.e., $M^{3+} + e^-$, and so-called more reduced states where isolated or "condensed" clusters are important, stabilized or not by interstitials.

The first discovery of such a cluster compound, Gd_2Cl_3,[2] in the early 1960s was an outgrowth of the interest in molten-salt chemistry, fashionable in those years. Its structure determination several years later[3] revealed that Gd_2Cl_3 with the then incredibly low "oxidation state" of +1.5 was indeed a landmark. It may be described as being built from $[Gd_6Cl_8]$ metal clusters "condensed" by sharing common trans metal edges. Indeed, this compound is more like a quasi-one-dimensional part of gadolinium metal with Gd^{3+} cations and "free" electrons surrounded by chloride, according to the formulation $(Gd^{3+})_2(e^-)_3(Cl^-)_3$. This discovery shows the close proximity of gadolinium to the early-transition-metal (d) elements. It immediately comes to mind that Gd_2Cl_3 cannot be unique, that there *must* be a cornucopia of unusual, anomalous compounds. On the other hand, except for the dipositive state in the seven elements listed above (europium through holmium), there is no stable (localized) lower valence state other than +2. Instead, there are mixed-valence or metallic cluster or noncluster halides that account only by arithmetic for oxidation states lower than +3 and other than +2.

Since *reduced halides of the rare-earth elements* were reviewed only a sesquidecade ago,[4] why on earth do it again now? The rationale becomes obvious from a comparison of the number of, for example, chloride "phases", 16, known or assumed in 1973 (Table I of ref 4, Figure 3) vs the number of entries that an analogously designed table would have now: ≃90![5] It is the prime desire of the author to make clear what tremendous successes a few research groups may have through the development of proper preparative techniques.

In the following, the term *reduced rare-earth halide* is used for such halides that contain the elements Sc, Y, and La through Lu in formal, overall oxidation states

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[†] In memoriam Professor Wilhelm Klemm.

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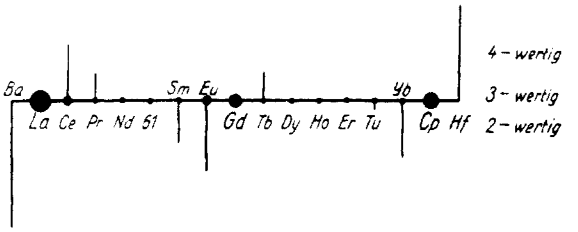


Figure 1. Klemm's systematic of the rare earths. Schematic representation of the "stability" of divalent (down) and tetravalent (up) states. Cf. ref 1.

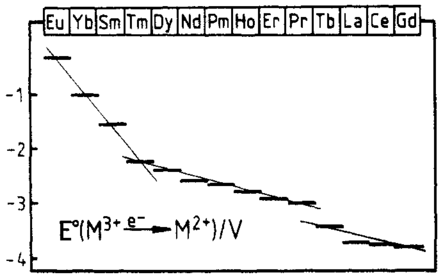
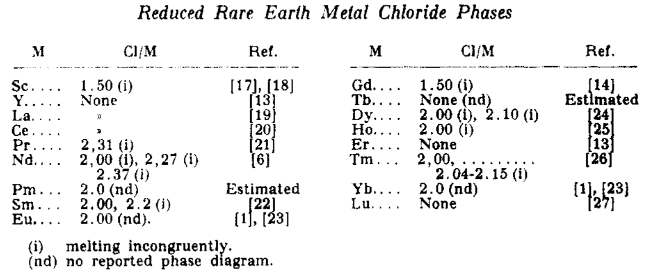


Figure 2. Standard electrode ("reduction") potentials $E°(M^{3+}/M^{2+})$. Values from ref 95b.



Reduced Rare Earth Metal Chloride Phases

M	Cl/M	Ref.	M	Cl/M	Ref.
Sc....	1.50 (i)	[17], [18]	Gd....	1.50 (i)	[14]
Y.....	None	[13]	Tb....	None (nd)	Estimated
La....	»	[19]	Dy....	2.00 (i), 2.10 (i)	[24]
Ce....	»	[20]	Ho....	2.00 (i)	[25]
Pr....	2,31 (i)	[21]	Er....	None	[13]
Nd....	2,00 (i), 2,27 (i) 2.37 (i)	[6]	Tm...	2,00, ... 2.04-2.15 (i)	[26]
Pm...	2.0 (nd)	Estimated	Yb....	2.0 (nd)	[1], [23]
Sm...	2.00, 2.2 (i)	[22]	Lu....	None	[27]
Eu....	2.00 (nd).	[1], [23]			

(i) melting incongruently.
(nd) no reported phase diagram.

Figure 3. The reduced rare-earth metal chloride phases as known in 1973. From ref 4 (Table I).

less than +3 or, better, halide:metal (X:M) ratios of less than 3. Other than binary reduced halides, MX_z, ternary halides containing mostly alkali metal as the third component, $A_xM_yX_z$, are considered, e.g., KNd_2Cl_5, but also $Sc[Sc_6Cl_{12}]$, a pseudobinary chloride of (formal, overall) oxidation state +1.71. "Polynary" halides such as $Cs_2Lu_7Cl_{18}C$ or Li_zErClH_x are also included.

Crystallographic details of the compounds discussed in this review are summarized in a table that may be obtained as supplementary material from the author, who plans to keep it updated.

II. Synthetic Approaches

The trail of reduced rare-earth halide chemistry follows the development of synthetic *and* analytical techniques in this century. In the 1920s, hydrogen reduction was the only feasible preparative technique to reduce the oxidation state of lanthanoids from +3 to +2. Of course, only the most stable divalent states, i.e., those with the smallest reduction potentials, in the dichlorides of europium, ytterbium, and samarium, are safe against further reduction through abstraction of all the halide and formation of the hydrides.[6]

At that time, the metallic elements were either not prepared or not available in sufficient purity. In fact, it was the motif to investigate the magnetic and crystallographic properties of the metals as a whole that revived a historic route for the preparation of the metals that is presently widely used in a similar way as an industrial process, the *metallothermic reduction* of halides with electropositive metals. This route, initiated by Berzelius, was developed by Wöhler[7] and used for the first time to produce yttrium metal in 1828 via

$$YCl_3 + 3K = Y + 3KCl$$

After Klemm[8] had used it to produce all the lanthanide metals in 1939, it again hibernated for about 45 years, at least when focusing on reduced halide "phases" as opposed to metal production.

Rather, the increasing availability of the rare-earth metals in the early 1950s and the aforementioned interest in molten-salt chemistry as an outgrowth of and sponsored through nuclear reactor research stimulated phase diagram determinations in the MX_3/M systems. These revealed in many cases, although mostly incongruently melting, "intermediates", true "reduced" halides. Synproportionation reactions became, therefore, increasingly important and led to most of the now known (pseudo)binary reduced halides. Although the successes were tremendous, the investigations were troubled by often mysteriously low yields, high reaction temperatures, and long reaction periods. This was explained in terms of slow kinetics, with the molten trihalide reacting at the solid metal surface and the possibility of the formation of blocking, passivating reduced "phases" at the halide–metal interface. It was not before it became clear that many, but by no means all, of the phases hitherto believed to be "true" binaries were in fact ternaries interstitially stabilized by minute amounts of ubiquitous "impurities", elements such as hydrogen, carbon, etc., that the mystery of the low yields vanished. The hydrogen- and carbon-stabilized lutetium monochlorides, $LuClH_x$ and $LuClO_{0.5}$ may serve as examples at this stage. This recognition, however, opened a realm of new chemistry extremely important for the understanding of the electronic "structure" of such compounds.

A different approach, the action of alkali metals on lanthanide halides,[10] was originally hoped to serve as a solution to slow kinetics. Although this is obviously not so important anymore, relatively low reaction temperatures and the usual presence of surplus alkali metal halide in the reaction medium prove to be an easy means to single-crystalline products from the melt not only of reduced halides, binary and/or ternary, but also of ternary halides of the trivalent lanthanides, for example, Na_3ErCl_6.[11] Moreover, this route is a *preparative* approach to the investigation of the relative successions of the reduction potentials and their importance for the type of reduced phase formed, be it with dipositive or isolated tripositive states (plus electrons) of with isolated or "condensed" clusters. Such a picture is indeed emerging from the experimental work pursued during the past 5 years or so. That, also, nothing new was invented (never is) is shown by the observation of Klemm that the reduction of $SmCl_3$ with even a large excess of sodium is brought to a halt at least partly at $SmCl_2$,[8] an intermediate stable reduced phase. The systematic investigation of this historic route, the metallothermic reduction, has, however, brought to light a plethora of new reduced and not reduced binary, ternary, and quaternary halides that had otherwise not been observed before, or not in crystalline form. The application of inert container materials, especially tantalum, and techniques for clean welds[12] made the wide use of this route and the synproportionation reactions alike possible.

Aside from experimental techniques, the importance of pure starting materials should be stressed. For chlorides and bromides (often also for iodides) the rare-earth metal trihalides, MX_3, are the most important starting materials, and a wide variety of preparative techniques has been explored.[13] With the recently acquired knowledge taken into account,[14-17] the ammonium halide route[18] is apparently the most inexpensive and easiest to perform provided that the advised procedure is followed precisely. The proper starting ratio of, for example, NH_4Cl to M_2O_3 ($\geqslant$12:1) helps to evade the contamination with oxidic impurities, MOCl in particular.[19] For ultrahigh purities, one or more subsequent sublimations in an all-tantalum apparatus are advisable.[20] If such a purification step is to be put up with anyway, MCl_3/MOCl mixtures obtained by the (primitive) thermal decomposition of hydrated chlorides, e.g., $MCl_3 \cdot 6H_2O$, may also be used as starting materials. If the pure metals are easily available, these may be oxidized to the trichlorides with, e.g., HCl[20] or NH_4Cl.[17]

Reliable syntheses for triiodides start usually with the rare-earth elements, with the iodine component being either the element or mercuric iodide.[21]

Sometimes ternary halides such as $Cs_3Tm_2Cl_9$ may be reduced, to $CsTmCl_3$ in this case. Easy-to-perform syntheses have been worked out for such starting materials.[22]

The electrochemical reduction of rare-earth trihalides is an important industrial route to pure metals or misch metal especially when alkali metal halides are added to depress the melting point. Intermediate products en route trichloride → metal have been explored only very briefly.[23] "GdCl" and Gd_2Cl_3 were obtained by electrochemical reduction of $GdCl_3$ in a tantalum crucible and, additionally, the first chloride–carbide of gadolinium, $Gd_5Cl_9C_2$, when a graphite crucible was used instead as the cathode.

III. The Dihalides

The dichlorides of samarium and europium, $SmCl_2$ and $EuCl_2$, were the first compounds of divalent lanthanides to be discovered at the beginning of this century.[24,25] When the picture of the electronic structure of the, at that time, still novel f elements emerged, it was Klemm who recognized that divalent ytterbium should be comparably stable as divalent europium, taking into account that empty (La^{3+}, Ce^{4+}), half-filled (Eu^{2+}, Gd^{3+}, Tb^{4+}), and filled (Yb^{2+}, Lu^{3+}, Hf^{4+}) 4f shells were of comparable stability.[1] $YbCl_2$ was then indeed obtained by hydrogen reduction of $YbCl_3$.[26] Immediately he foresaw that divalent thulium, in $TmCl_2$, could be stable because of its position preceding ytterbium, like samarium precedes europium. It took, however, some 30 years before $TmCl_2$ was finally prepared[27] and its crystal structure determined.[28] Considerable synthetic developments (inert reaction containers) and the availability of pure rare-earth elements were necessary to achieve this goal. Systematic investigations into the MX_3/M systems via synproportionation reactions have established, in addition to the classical four, divalent dysprosium, neodymium,[29] and holmium, although the latter only in the mixed-valence Ho_5Cl_{11} ("$4HoCl_2 \cdot HoCl_3$").[30,31] This proves that the electronic structure of the rare-earth elements cannot be all that simple as Klemm had believed although it does not at all diminish his intuition and imagination in this particular area.

TABLE 1. The Dihalides: Structure Types and Coordination Numbers[a]

	SmF_2 CaF_2 [8]	EuF_2 CaF_2 [8]			YbF_2 CaF_2 [8]
$NdCl_2$ $PbCl_2$ [9] X	$SmCl_2$ $PbCl_2$ [9] X	$EuCl_2$ $PbCl_2$ [9] X	$DyCl_2$ $SrBr_2$ [8]	$TmCl_2$ SrI_2 [7] X	$YbCl_2$ SrI_2 [7] X
$NdBr_2$ $PbCl_2$ [9] X	$SmBr_2$ $SrBr_2$ [8]	$EuBr_2$ $SrBr_2$ [8]	$DyBr_2$ SrI_2 [7]	$TmBr_2$ SrI_2 [7]	$YbBr_2$ SrI_2 [7]
NdI_2 $SrBr_2$ [8]	SmI_2 EuI_2 [7]	EuI_2 EuI_2 [7] X	DyI_2 $CdCl_2$ [6]	TmI_2 CdI_2 [6]	YbI_2 CdI_2 [6]

[a] $SmBr_2$: dimorphic; also $PbCl_2$ type. EuI_2: I, monoclinic EuI_2; II, orthorhombic SrI_2 type. X indicates single-crystal structure determination.

Table 1 summarizes the "true" dihalides (i.e., those with metal M^{2+} states with (Xe)$4f^{n+1}5d^06s^0$ configuration) that are now known. Such that were established from single-crystal data are marked with an "X". It was only recently that the structures of $NdCl_2$[32] and $SmCl_2$[33] were refined, both like $EuCl_2$[34] and $NdBr_2$[35] crystallizing with the $PbCl_2$ type structure. Most of the other dihalides were characterized by X-ray *powder* diffraction. Coordination numbers (CN) decrease from 9, passing through 8 and 7 (essentially tri-, bi-, and monocapped trigonal prisms), to, finally, 6 (trigonal antiprism, "octahedron") with decreasing ionic radii of M^{2+} and increasing anion size, most strikingly exhibited for the dysprosium halides with CN of 8 ($DyCl_2$), 7 ($DyBr_2$), and 6 (DyI_2). That, however, the crystal chemistry of the dihalides is not at all completely understood may be seen from the thorough investigations into the *high-temperature* behavior of the heavier dibromides.[36] $YbBr_2$, for example, undergoes three phase transitions at 540, 720, and 750 K upon heating, from $SrI_2 \rightarrow \alpha\text{-}PbO_2 \rightarrow CaCl_2 \rightarrow$ rutile types. $TmBr_2$ behaves analogously.

Furthermore, the *high-pressure* behavior was touched upon only briefly. It was shown that NdI_2 undergoes a phase transition from the $SrBr_2$ ("ionic", localized +2 state) to the $CuTi_2$ ($MoSi_2$) type structure and should as such be formulated as "metallic" $(Nd^{3+})(e^-)(I^-)_2$.[37] Recalling that NdO is only obtained under high pressure[38] and is metallic as well indicates that there is more to come when the high-pressure behavior and high-temperature behavior are investigated systematically. Even new compounds (compositions) seem not to be out of sight.

Four additional diiodides are known, of lanthanum, cerium, praseodymium, and gadolinium.[39] These are salt-like in the usual sense *plus* metallic in a sense that

TABLE 2. Fluoride–Halides and Hydride–Halides of the Lanthanides (PbFCl Type, Tetragonal)

	Chlorides		
EuFCl	YbFCl	SmFCl	TmFCl
EuHCl	YbHCl		
	Bromides		
EuFBr	YbFBr	SmFBr	TmFBr
EuHBr	YbHBr	SmHBr	
	Iodides		
EuFI	YbFI	SmFI	TmFI
EuHI	YbHI		

they exhibit metal-like electronic conductivity[40] and may therefore be formulated as, e.g., $(La^{3+})(e^-)(I^-)_2$. Again, a rich crystal chemistry is expected, as the example of PrI_2 indicates. Five modifications were reported,[41] four of which may be considered quite normal, covering the whole range from metallic ($CuTi_2$ type) to ionic "structures" (MoS_2, $CdCl_2$). PrI_2–V is unique in that it contains cubane-like $[Pr_4I_4]$ clusters. GdI_2 (2H–MoS_2 type) exhibits magnetic ordering below 313 K with strongly coupled ferromagnetic layers of Gd^{3+} moments and (probably) antiferromagnetic interlayer ordering, suggesting that GdI_2 is a two-dimensional Heisenberg system.[42] A cation-deficient CdI_2 type scandium "diiodide", Sc_xI_2, with $x = 0.9$,[43] is also known and awaiting further investigation.

Additionally, there are iodides of M = La, Ce, Pr, Gd, Er, and Lu[44] that are almost diiodides, $MI_2(M_{1/6}Z_{1/6})$, i.e., $M_7I_{12}Z$ with interstitially (Z) stabilized "octahedral" M_6 clusters with the seventh M in a normal octahedral I_6 interstice adding electrons to the cluster.[45] These will be discussed together with the other interstitially stabilized clusters in section VII.

IV. Ternary Halides with Localized Divalent States

A. Hydride–Halides and Mixed Halides

Hydride–halides (MHX) and mixed halides (MX′X) of the divalent lanthanides are structurally closely related. In fact, those with X′ = F and X = Cl, Br, and I[46] crystallize with the same structure as the known halide–hydrides[47] (Table 2), the PbFCl type, which is closely related to the $PbCl_2$ type of structure.

The PbFCl (matlockite) type structure (Figure 4) is also adopted by many oxyhalides with trivalent rare earths, for example, MOCl with M = La–Er, and Y.[48] This is reasonable because O^{2-}, F^-, and H^- are almost of the same size and afford volume increments of about 10 $cm^3\ mol^{-1}$.[49] Indeed, YbHCl and YbFCl, for example, have about the same molar volume, V_m, of 30.4 and 31.9 $cm^3\ mol^{-1}$, respectively. This may be taken as a proof for their predominantly ionic, salt-like character. On the other hand, one should bear in mind that there are, in principle, different ways to allow for an optimal volume. A comparison of the molar volumes of the salt-like YbHCl (30.4 $cm^3\ mol^{-1}$) and the metallic $LuClH_x$[9] (31.2 $cm^3\ mol^{-1}$) shows this profoundly. The latter contains essentially trivalent lutetium bound into a double metal layer of "condensed" $[Lu_6Cl_8]$ clusters whose tetrahedral interstices are occupied by "hydrogen" (Figure 4).

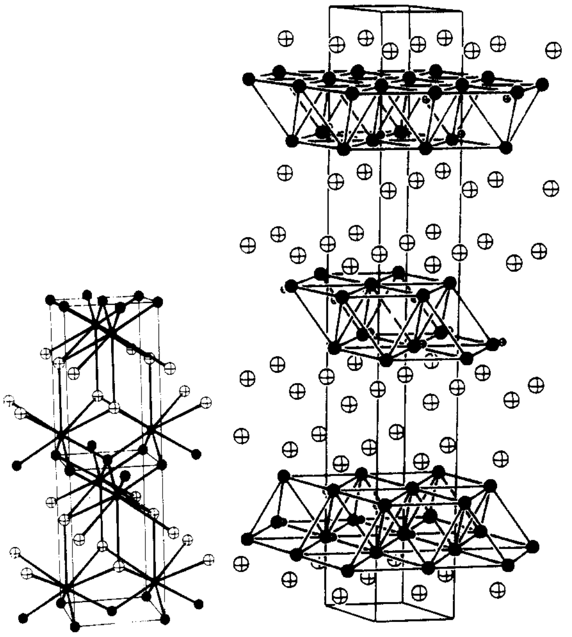


Figure 4. Comparison of the crystal structures of YbHCl (PbFCl type, left; large closed circles represent H^-) and $LuClH_x$ (ZrCl type, right, assuming $x = 1$; closed circles represent Lu^{3+}, and small open circles represent hydrogen in tetrahedral interstices between the metal arrays); in both, large open circles represent Cl^-.

It is important to note in this connection that halide–hydrides seem to exist for all of the rare-earth elements and may be divided into two groups: (i) salt-like PbFCl type MHX hydride–halides with M = Eu, Yb, and Sm with "truly" divalent states and (ii) metallic MXH_x halide–hydrides crystallizing with the ZrCl[50] or ZrBr[51] type parent structures for the remainder of the rare-earth elements that contain trivalent rare earths and additional electrons essentially in metal–interstitial bonding states necessary to hold the condensed metal cluster arrangement of the "monohalides" together.

Generally, the MXH_x type halide–hydrides seem to be capable of taking up additional hydrogen to form, finally, salt-like halide–hydrides of trivalent rare earths, for example, from graphite-like $GdBrH_x$ to green $GdBrH_2$,[52] thereby retaining essentially the double-metal-layer parent structure. Hydrogen positions have been determined for the example of $TbBrD_2$.[53] Space for additional hydrogen seems to be readily available: the molar volume shows almost no change when hydrogen is taken up: for GdBrH, $V_m = 37.9\ cm^3\ mol^{-1}$ and for $GdBrH_2$, $V_m = 39.3\ cm^3\ mol^{-1}$.

Whereas anion ordering in fluoride–halides and hydride–halides crystallizing with the PbFCl type structure appears to be normal, there is only one account of anion ordering in other mixed anion–halide systems. Within the $EuCl_2/EuBr_2$ system,[54] a single-crystal study has been undertaken for a crystal of the composition $EuBr_{1.5}Cl_{0.5}$.[55] Although the $PbCl_2$ type structure is retained from $EuCl_2$, one bromide occupies completely the larger hole (square pyramidal), and the smaller chloride + bromide occupies the "tetrahedral" sites. Other mixed-halide systems have been investigated, extensively with ytterbium, but no indication was found for anion ordering.[56]

B. Oxyhalides M_4OX_6

Except for the appearance of oxygen (oxide) in the previously thought-to-be mixed-valence halides $Nd_{14}Cl_{32}O$[57] and $Eu_{14}Cl_{32}O$[58] ($\equiv MCl_{2.29}$; below) and the insertion of oxygen between metal–metal layers of alkali

TABLE 3. Ternary Alkali Metal-Lanthanide(II) Chlorides

	Nd	Sm	Eu	Dy	Tm	Yb
Li				$LiDy_2Cl_5$	$LiTm_2Cl_5$	$LiYb_2Cl_5$
Na	$NaNd_2Cl_6$					
K	KNd_2Cl_5	KSm_2Cl_5	KEu_2Cl_5		$KTmCl_3$	$KYbCl_3$
Rb		$RbSm_2Cl_5$	$RbEu_2Cl_5$		$RbTmCl_3$	$RbYbCl_3$
Cs		$CsSmCl_3$	$CsEuCl_3$		$CsTmCl_3$	$CsYbCl_3$
					Cs_2TmCl_4	Cs_2YbCl_4

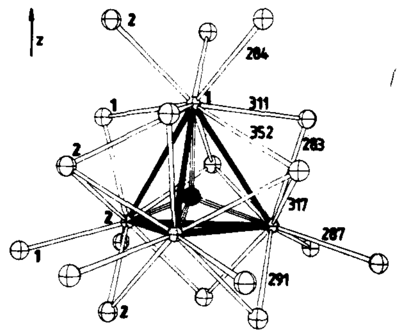


Figure 5. Part of the crystal structure of M_4OCl_6 (M ≡ Sm, Eu, Yb) showing the O^{2-}-centered M_4 tetrahedron surrounded by 18 chloride ions. Distances (in pm) are from Yb_4OCl_6.[60]

metal intercalated "monohalides", for example, Na_xYClO,[59] which are rather to be addressed as alkali metal intercalated oxyhalides of special structure types (YOF or SmSI), oxyhalides of the *divalent* lanthanides seem to be limited to europium, ytterbium, and samarium.

Precise structural data for such oxyhalides uniquely of the composition M_4OX_6 have been obtained for Yb_4OCl_6,[60] Eu_4OX_6 (X = Cl, Br),[61] and Sm_4OCl_6.[62] This was possible because a facile crystal growth technique emerged from the metallothermic reduction of the trihalides MX_3 with lithium in the presence of oxide or oxyhalide, M_2O_3 or MOCl, respectively.

Interestingly, the M_4OX_6 oxyhalides contain isolated oxide-centered and only very slightly compressed M_4 "tetrahedra". These are surrounded by 18 chloride ligands, of which 9 are terminal, 6 edge-capping, and 3 face-capping, interconnecting $[M_4O]$ entities to allow for the $[M_4O]X_6$ stoichiometry (Figure 5). Although the M^{2+}–M^{2+} distances are close to or even shorter than those in the respective metals, no metal–metal bonding occurs. Furthermore, Sm_4OCl_6 is believed to be the first compound that contains divalent samarium *and* oxide anions in close proximity (d = 236.0, 237.6 pm (3×)). It should be noted that samarium monoxide, even under pressures as high as 50 kbar, essentially does not contain divalent samarium,[38] but rather is $(Sm^{3+})(e^-)(O^{2-})$, in particular contrast to EuO and YbO with "true" divalent states.

$[M_4O]$ units, on the other hand, seem to have become increasingly common. Not only can they be depicted in the rare-earth sesquioxides M_2O_3,[63] but they also appear in oxysulfides, e.g., $(NdO)_4Ga_2S_5$.[64] Elements other than the rare earths are also drawn into such groups exhibiting a remarkable diversity throughout the periodic table as in Ba_4OCl_6,[65] $Be_4O(CH_3COO)_6$,[66] and $Cu_4OCl_6(TPPO)_4$.[67] Finally, anti-type structures occur with "normal" oxides and sulfides, for example, Na_6ZnO_4[68] (≡Cl_6OYb_4) and K_6HgS_4.[69]

C. Ternary Halides, $A_xM_yX_z$

High oxidation states in particular can often only be stabilized in ternary compounds, especially in oxides and fluorides. Frequently, an increasing coordination number and therefore the formation of additional bonds add to the marginal stability of the particular oxidation state. For lower oxidation states, especially with 4f elements where the valence electrons are believed to be buried in the Xe core, the picture is not so simple. Frequently, although not exclusively, the coordination number is decreased when a ternary halide in an alkali metal halide–rare-earth metal halide system, AX–MX_2, is formed. Therefore, not very many compounds are found in these systems and they all seem to be of marginal stability. Table 3 gives an overview of examples of the ternary chlorides that are still the best investigated.[70,71]

Some of these chlorides have so far only been obtained by alkali metal reduction of the trichlorides. The reason for this might be that reaction temperatures were considerably lower than for imaginable synproportionation reactions and, additionally, crystal growth is easily achieved in many cases because along with the formation of the ternary chloride, (often) alkali metal chloride forms in the same molar amount, which is then believed to act as a solvent; e.g.[72]

$$2Li + 2DyCl_3 = LiDy_2Cl_5 + LiCl$$

That these compounds have indeed only marginal stability can be seen, first, from the disproportionation reactions that occur upon prolonged heating of, for example, KNd_2Cl_5

$$6KNd_2Cl_5 = 3K_2NdCl_5 + 5NdCl_3 + 4Nd$$

and, second, from the thermochemical data that are now available for the perovskites, $CsMCl_3$ (M = Eu, Yb, Sm, Tm).[73]

The pseudobinary systems $LiCl/MCl_2$ are apparently simple eutectic for M = Nd, Sm, Eu and contain the chlorides LiM_2Cl_5 for M = Dy, Tm, Yb.[74] These three have now all been studied with single crystals. They are isostructural and belong to a growing structural family that includes carbides and borides as well. The M^{2+} ions are in an eight-coordinate (Figure 6), essentially bicapped trigonal prismatic surrounding with $\bar{d}$ = 296.2 pm for $LiDy_2Cl_5$ ($DyCl_2$: 295.2 pm) and 291.9 and 290.3 pm for $LiTm_2Cl_5$ and $LiYb_2Cl_5$, respectively. The latter two are interesting because Tm^{2+} and Yb^{2+} are seven-coordinate in the dichlorides with $\bar{d}$ = 284.7 and 284.3 pm, respectively. These are about the only two cases where in the systems under consideration in this article complex chloride formation leads to an increase in coordination number.

One surprising case is $NaNd_2Cl_6$, which resulted from a Na + $NdCl_3$ reaction and is the first known example for a ternary mixed-valence chloride, $Na^+(Nd^{2+,3+})_2(Cl^-)_6$.[75] In fact, divalent neodymium and trivalent neodymium are indistinguishable crystallographically; the distances $Nd^{2+,3+}$–Cl^- average to 299.0 pm, about

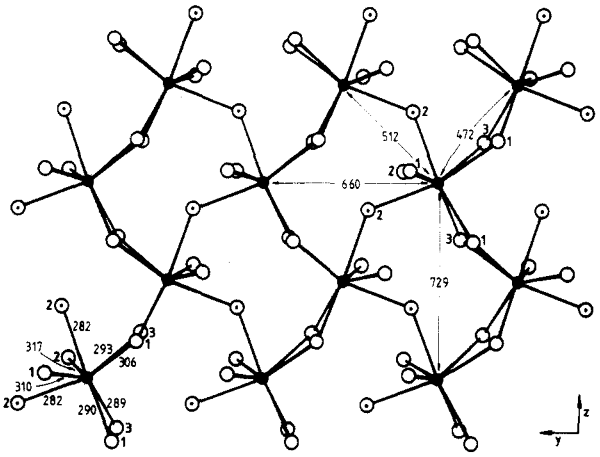


Figure 6. Part of the crystal structure of LiM_2Cl_5 (M ≡ Dy, Tm, Yb) showing edge- and vertex-connected bicapped trigonal prisms, $[MCl_8]$. Distances (in pm) are from $LiDy_2Cl_5$.[72]

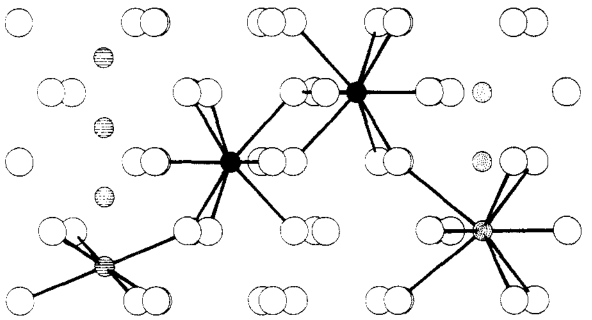


Figure 7. Side view of the crystal structures of $NaPr_2Cl_6$, $Pr_{0.58}Pr_2Cl_6$, and $NaNd_2Cl_6$. Black circles represent nine-coordinate Pr^{3+} and $Nd^{2+,3+}$. Left: Na^+ or 0.58 Pr^{3+} in octahedral holes of the praseodymium compounds; right: nine-coordinate Na^+ in $NaNd_2Cl_6$.

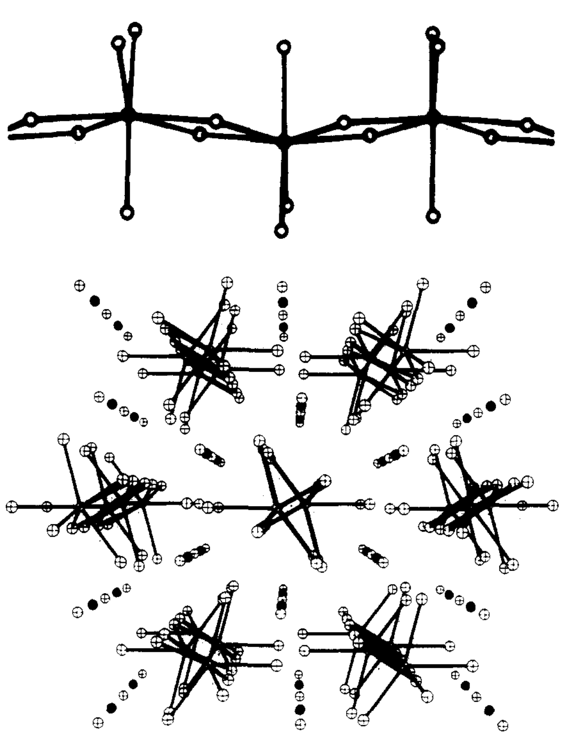


Figure 8. Crystal structure of KNd_2Cl_5. Chains of trans-edge-connected monocapped trigonal prisms, $[NdCl_{3/1}Cl_{4/2}] \equiv [NdCl_5]$, and their "hexagonal" arrangement. Additional closed and open circles represent K^+ and Nd^{2+} according to $KNd[NdCl_5]$.

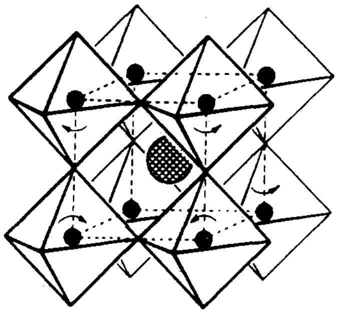


Figure 9. The (ideal) perovskite type structure of ternary lanthanide(II) halides, AMX_3 (A ≡ K, Rb, Cs; M ≡ Sm, Eu, Tm, Yb), that may undergo second-order phase transition(s) through octahedral tilting (indicated by arrows) depending upon composition and temperature.

halfway between $\bar{d}(Nd^{2+}-Cl^-)$ = 312.9 pm in $NdCl_2$ and $\bar{d}(Nd^{3+}-Cl^-)$ = 290.0 pm in $NdCl_3$, all nine-coordinate. The crystal structure of $NaNd_2Cl_6$ is essentially that of $NdCl_3$ (UCl_3 type) with additional interstices filled with Na^+ (Figure 7). There is a close structural relationship between $NaNd_2Cl_6$, $NaPr_2Cl_6$, and $PrCl_{2.33}$ ($\equiv Pr_{0.58}Pr_2Cl_6$) although their behavior is otherwise quite different (vide infra).

With potassium and rubidium, AM_2Cl_5 type ternary chlorides form with M^{2+} (M ≡ Nd, Sm, Eu) both eight- and seven-coordinate. These are closely related to the fully oxidized A_2MCl_5 type chlorides[76] according to $A_2[MCl_5] \equiv AM[MCl_5]$ not only structurally but also chemically in that they form solid solutions. The substitution of, partly or totally, one monovalent A^+ (K^+, Rb^+) in A_2MCl_5 by a divalent M^{2+} has minor effects on the crystal symmetry (orthorhombic *Pbnm* → monoclinic *P*2_1/*c*) and the nearest-neighbor distances, of course. The structural features, however, remain unchanged and these may be described, for example, in terms of a hexagonal packing of $[MCl_5]^{2-}$ chains built from edge-sharing monocapped trigonal prisms according to $^2_\infty[MCl_{3/1}Cl_{4/2}]^{2-}$ held together by either 2 A^+ or $A^+ + M^{2+}$ cations (Figure 8).

Finally, perovskite-type chlorides $AMCl_3$ are observed, but only with M = Eu, Yb, Sm, Tm,[77] in order of increasing reduction potentials. Although frequently attempted via different routes, [$3CsCl + 2MCl_3 + M$], [$CsCl + MCl_2$], [$CsCl + (LiCl + MCl_2)$], and [$Cs + MCl_3$], no indication was found for either $CsNdCl_3$ or $CsDyCl_3$. Obviously, $NdCl_2$ and $DyCl_2$, although well-known as binaries, may disproportionate in the presence of alkali metal chlorides, even at the lowest possible reaction temperatures, ≃500 °C. We return to this subject in the next section.

The perovskites are "ideally" cubic (Figure 9) only for $CsTmCl_3$ and $CsYbCl_3$ (*a* = 545.77 (2) and 543.43 (2) pm, respectively), and at sufficiently high temperatures also for $CsSmCl_3$ and $CsEuCl_3$ and, for example, for $RbTmCl_3$ and $KTmCl_3$ as well. They may undergo several second-order phase transitions with decreasing temperature that are quite well understood as for perovskites in general in terms of two- and three-dimensional octahedral ($[TmCl_6]$) tilting in order to accommodate smaller cations, A^+. Increased tilting is necessary when proceeding in the sequence $Cs^+ \rightarrow Rb^+ \rightarrow K^+$ or, for example, for Rb^+ with decreasing temperature and therefore decreasing effective cation size. All perovskites with M = Sm, Eu, Tm, Yb, no matter how crystallographically "distorted" they might be, have

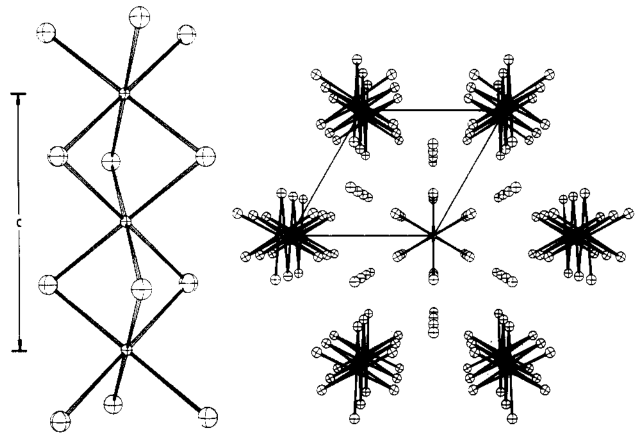


Figure 10. The one-dimensional $[ScCl_{6/2}]$ chain in (ideally) $CsScCl_3$ and their arrangement parallel to [001].

in common that they may be described in terms of cubic closest packing of $[CsCl_3]^{2-}$ layers stacked in the [111] direction of the cubic unit cell. All electrostatically possible octahedral holes, that is, such that are built from Cl^- only, are occupied by M^{2+}. Necessarily, the $[MCl_6]$ octahedra are all vertex-connected according to $Cs^{3}_{\infty}[MCl_{6/2}]$ so that the characteristic three-dimensional network emerges.

Cubic perovskite type fluorides $CsMF_3$, M = Eu, Yb, and $RbYbF_3$ are the only ternary fluorides of divalent lanthanides that have been obtained so far.[78] Some samarium may substitute for europium or ytterbium. Attempts to reduce, for example, $CsTmF_4$ with cesium yield partial reduction to thulium metal and the apparently more stable Cs_3TmF_6 rather than $CsTmF_3$.[79]

The remarkable scandium chlorides, e.g., $CsSc_{1-x}Cl_3$, $0.33 \geqslant x \geqslant 0.00$,[80,81] have the alternative structure with all $[CsCl_3]$ layers stacked in the hexagonal closest packed fashion and all octahedral interstices occupied for $x = 0.0$. The $[ScCl_6]$ octahedra share common faces, and according to $Cs^{1}_{\infty}[ScCl_{6/2}]$, a one-dimensional chain with $d(Sc–Sc) = 302$ pm would occur for $x = 0.0$ ($\equiv CsScCl_3$) with formally divalent scandium (Figure 10). Although $CsScCl_3$ with localized Sc^{2+} could be well accepted geometrically as, for example, the neighboring $CsTiCl_3$[82] crystallizes with the same structure, some stabilization through metal–metal bonding, overlap of d_{z^2} orbitals, is believed to be important for these particular compounds. Evidence comes from their magnetic behavior, which can be described as essentially diamagnetic, and from the apparent nonexistence of $KScCl_3$. This would, from a purely geometric viewpoint, have to have a structure with at least part of the $[ScCl_6]$ octahedra sharing vertices. Sc^{2+}–Sc^{2+} distances would be far too long for direct interactions. Still, the structural behavior of $CsSc_{1-x}Cl_3$ needs some attention. The fully oxidized $CsSc_{0.67}Cl_3$ ($\equiv Cs_3Sc_2Cl_9$)[83] crystallizes with a rhombohedral superstructure with $a' = 3^{1/2}a$ and $c' = 3c$. Confacial bioctahedra $[Sc_2Cl_9]^{3-}$ are ordered rhombohedrally and share common faces with empty $[\square Cl_6]$ octahedra. The dependence of the lattice constants (a, c) upon x suggests that octahedral holes between the confacial bioctahedra are filled either statistically or in a complicated ordered way (recent investigations of single crystals of the composition $CsSc_{0.71}Cl_3$ indicate a complicated superstructure)[84] up to a certain point ($x \simeq 0.86$) where apparently a phase transition occurs that is not understood at all.

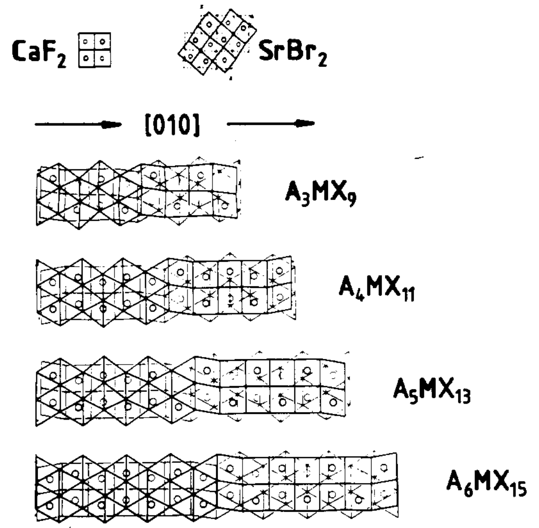


Figure 11. Vernier type structures with A representing divalent cations and M trivalent cations; for example, $Yb_6Cl_{13} \equiv (Yb^{2+})_5(Yb^{3+})Cl_{13}$. Yb^{3+} may be substituted by Er^{3+}. The parent CaF_2 and $SrBr_2$ type structures are shown on top in the same schematic way. After ref 57.

D. Mixed-Valence Ternary Halides

It appears that the same seven elements (Nd, Sm, Eu, Dy, Ho, Tm, Yb) that have stable (localized) divalent states and for which (except for holmium) examples of ternary halides with alkali metals are now known also form reduced pseudobinary halides with $2 \leqslant X/M \leqslant 3$. These are mixed-valent according to $M^{2+}{}_{x}M^{3+}{}_{y}X_{z}$. As the differences in ionic radii are not all that great, M^{2+} and M^{3+} may occupy almost the same polyhedra. This is evident, for example, for $NdCl_2$ and $NdCl_3$ where nine-coordinate neodymium is predominant in both. It is therefore not surprising that structurally and chemically defined intermediate halides occur in the systems MX_2/MX_3. The divalent lanthanide may be substituted by divalent alkaline earths, for example, Ca^{2+} for Yb^{2+} or Sr^{2+} for Sm^{2+}, and the trivalent rare earths may be substituted by other neighboring rare earths, for example, Er^{3+} for Yb^{3+} in $Yb_6Cl_{13} \equiv (Yb^{2+})_5(Yb^{3+})Cl_{13} \rightarrow (Yb^{2+})_5(Er^{3+})Cl_{13}$[85] (Figure 11). For some generalities, see ref 70. Very little has, unfortunately, entered the literature in the meantime.

Difficulties with these phases arise from both synthesis and crystal growth and, especially, crystallographically. Synthesis is possible either by direct means, that is, equilibrating a stoichiometric mixture of MX_2 and MX_3 for the desired "phase", or sometimes through thermal decomposition of the trihalide utilizing chemical vapor phase transport and thereby solving elegantly the problem of crystal growth. The trouble with equilibration becomes clear when one recalls that, for example, for the $TmCl_2/TmCl_3$ system seven distinct phases were reported.[27]

Most of these intermediate mixed-valence halides seem to belong to the class of vernier type structures. These may be understood in terms of intergrowth of the CaF_2 (eight-coordinate) and $SrBr_2$ type (seven-coordinate) parent structures (Figure 11). For chlorides, the basal plane has a dimension of about (710×670) pm^2 and the repeat unit, usually parallel to [010] of the orthorhombic or monoclinic (with angles near 90°) unit cells, is around 700 pm. The number of repeat units equals the number of cations; for example, for Eu_5Cl_{11}

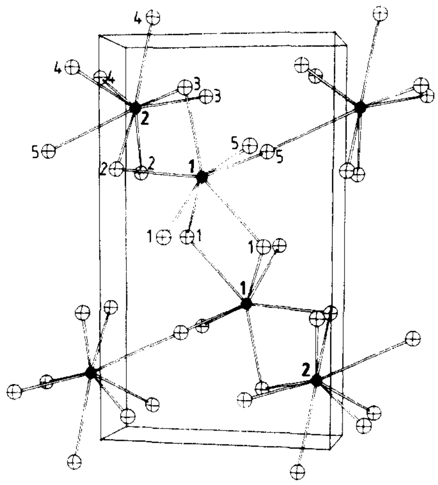


Figure 12. Crystal structure of Pr_2Br_5 built from mono- and bicapped trigonal prisms $[Pr(1)Br_7]$ and $[Pr(2)Br_8]$; respectively. From ref 93.

$\equiv Eu^{2+}{}_4Eu^{3+}Cl_{11}$, a = 721.4 (2) pm, b = 3517.0 (10) pm [5 × 703], c = 677.5 (2) pm, and β = 90.34 (1)°.[58]

In a recent beautiful piece of work,[58] it was shown that in the $EuCl_2/EuCl_3$ system, which had been investigated before,[86,87] three intermediates do indeed exist whose empirical formulas are (about) Eu_3Cl_7, Eu_4Cl_9, and Eu_5Cl_{11}. These may be obtained as single crystals by decomposition of $EuCl_3$ *and* vapor phase transport of the products and they are distinguishable by their colors. Eu_4Cl_9 and Eu_5Cl_{11} belong to the class of vernier type structures, with Eu_5Cl_{11} being isotypic with Dy_5Cl_{11}. The formula Eu_3Cl_7 (Cl/Eu = 2.333) is only an approximation of the true composition, which is in fact $Eu_{14}Cl_{32}O$ (Cl/Eu = 2.285) and was also sometimes addressed as $Eu_{14}Cl_{33}$ (Cl/Eu = 2.357). The crystal structure of the fluorite-related $Eu_{14}Cl_{32}O$ contains a building principle that has also been found in some other fluorite-related compounds, for example, in tveitite, approximately $Ca_{14}Y_5F_{43}$,[88] or in β-U_4O_{9-y}.[89]

V. Divalent Praseodymium?

A few accounts of halides that could well contain divalent praseodymium have been made: $PrCl_{2.31}$,[90] *and* $PrBr_{2.4}$,[91] and, with iodine, PrI_2[39] and Pr_2I_5.[92] If these intermediate compositions were analogous to the vernier type phases as known from the neighboring elements neodymium and samarium, they could be mixed-valence compounds. On the other hand, the so-called diiodides MI_2, M = La, Ce, Pr, Gd, are known to be metallic[40] and may be formulated as, e.g., $(Pr^{3+})(e^-)(I^-)_2$ (vide supra), and for Pr_2I_5 an analogous situation is assumed.[92]

A decision whether *divalent* praseodymium could be stabilized in bulk mixed-valence halides (chlorides and bromides) or is rather trivalent throughout and the materials therefore metallic (or semimetallic) can be made from the results of single-crystal structure determinations. Crystals of Pr_2Br_5[93] and $NaPr_2Cl_6$[75] were obtained by lithium reduction of $PrBr_3$ and sodium reduction of $PrCl_3$, respectively. It is clear from a comparison of previous[91] and new X-ray data that Pr_2Br_5 ($\equiv PrBr_{2.5}$) is indeed identical with the above-mentioned $PrBr_{2.4}$ previously known only from a phase diagram determination. The structure (Figure 12) clearly reveals that only trivalent praseodymium is present in Pr_2Br_5 with $\bar{d}$(Pr(1)–Br) = 298.5 pm (CN = 7) and $\bar{d}$(Pr(2)–Br) = 306.8 pm (CN = 8). It turns out that Pr_2I_5,[92] the second compound known in the Pr/PrI_3 system, is isostructural with Pr_2Br_5. Additionally, the analogous bromides and iodides of lanthanum and cerium are believed to have that structure.

TABLE 4. Lattice Parameters of UCl_3 Type Chlorides and Their "Intercalates"

	a/pm	c/pm	c/a	V_m/ (cm^3 mol^{-1})
$Pr_{0.58}Pr_2Cl_6$	741.16 (4)	426.88 (4)	0.5760	122.30 (2)
$PrCl_3$	743.02 (4)	428.89 (4)	0.5772	123.50 (2)^a
$NaPr_2Cl_6$	756.77 (5)	429.34 (4)	0.5673	128.24 (2)
$NdCl_3$	740.39 (4)	424.15 (3)	0.5729	121.28 (2)^a
$NaNd_2Cl_6$	762.60 (5)	438.66 (4)	0.5752	133.05 (2)

$^a Z = 2$.

After the crystal structure of $NaNd_2Cl_6$ had been solved, a reexamination of previous reactions of Na + $PrCl_3$ and Li + $PrCl_3$ and $PrCl_3$ + Pr revealed that these contained black shiny single crystals with lattice constants *very* similar to those of $PrCl_3$, and $NaNd_2Cl_6$ and $NdCl_3$ alike (Table 4). In fact, the crystal structure of $NaPr_2Cl_6$ and $Pr_{0.58}Pr_2Cl_6$[94] ($\equiv PrCl_{2.33}$; cf. ref 90) is that of $PrCl_3$ (UCl_3 type) with octahedral interstices occupied by Na^+ and Pr^{3+}, respectively (Figure 7). A comparison of the distances Pr^{3+}–Cl^- in $PrCl_3$ ($\bar{d}$ = 291.7 pm) and those found in $NaPr_2Cl_6$ ($\bar{d}$ = 295.2 pm) and $PrCl_{2.33}$ ($\bar{d}$ = 290.5 pm) shows that praseodymium behaves structurally trivalent, and $NaPr_2Cl_6$, for example, may therefore be formulated as $(Na^+)(Pr^{3+})_2(e^-)(Cl^-)_6$. Hence, at present there is no evidence left for praseodymium with a localized divalent state, Pr^{2+}, in a bulk halide material. This is important because it seems now clear that a localized divalent state can only be realized for the elements europium, ytterbium, samarium, thulium, neodymium, dysprosium, and holmium. In this series, the reduction potentials, $E°(M^{3+}/M^{2+})$, steadily increase. For thermodynamic reasons, it appears that beyond holmium (assessed $E°$ = −2.80 V) where only one mixed-valence chloride, Ho_5Cl_{11}, has been reported, a stable divalent state cannot be realized.

A somewhat alternative description takes the electronic configuration of praseodymium into account. It appears that a "true" divalent state of praseodymium with the configuration $(Xe)4f^35d^06s^0$ is unstable in such halides. Rather, "Pr^{2+}" adopts the configuration $(Xe)4f^25d^16s^0$ and therefore exhibits a Pr^{3+}-like behavior (see the distances; Pr^{3+}; $(Xe)4f^25d^06s^0$) with a $5d^1$ electron now being capable of entering the conduction band. The formulation $(Pr^{3+})(e^-)$ (above) instead of Pr^{2+} should be understood in this sense. A "true" divalent state, as was often referred to, would be one with a $5d^0$ configuration *and* the Pr^{2+}–Cl^- distances, for example, would then be somewhat larger than those observed in divalent samarium chlorides, perhaps around d = 310–315 pm, depending upon the coordination number.

VI. Stability of the Divalent State

The question arises regarding which factors are important for the stability of the divalent state of the lanthanides, i.e., with the electronic configuration $(Xe)4f^{n+1}5d^06s^0$, and whether these might be influenced by any experimental circumstances or not. Or, to put

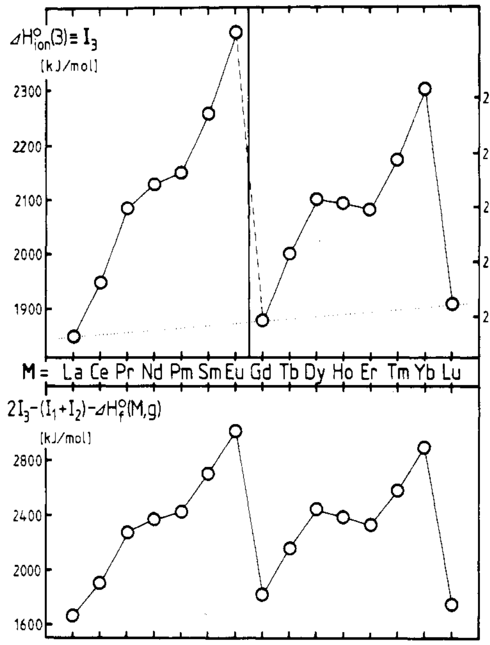


Figure 13. Third ionization potentials I_3 of the rare earth elements (above) and the expression $[2I_3 - (I_1 + \mathrm{I}_2) - \Delta H°_f(\mathrm{M,g})]$ (below) indicating the stability of the divalent state for some of the rare earth elements. Cf. ref 95.

it in other words, in what kind of surroundings, what media do the dipositive ions have to have to be safe from oxidation or disproportionation? Let us consider the historical route of hydrogen reduction first:

$$\mathrm{MX_3} + {}^1/_2\mathrm{H_2} = \mathrm{MX_2} + \mathrm{HX} \tag{1}$$

which might be rewritten, inversely, as

$$\mathrm{MX_2} + {}^1/_2\mathrm{X_2} = \mathrm{MX_3} \tag{2}$$

$$\mathrm{HX} = {}^1/_2\mathrm{X_2} + {}^1/_2\mathrm{H_2} \tag{3}$$

so that this reaction might also be thought of as the oxidation of dihalide by halogen. A Born–Haber cycle for reaction 2 gives[95]

$$\Delta H° = I_3 - L(\mathrm{MX_3}) + L(\mathrm{MX_2}) + C \tag{4}$$

where I_3 is the third ionization potential, L is the lattice energy, and C is a constant. Experience tells us that only the trichlorides of europium, ytterbium, and samarium are susceptible to reduction by hydrogen, with pronounced difficulties for the latter. This trend parallels the stability of the divalent ions $\mathrm{M^{2+}}$ in aqueous solutions against oxidation by $\mathrm{H^+}$. Put in equations, one gets

$$\mathrm{M^{2+}(aq)} + \mathrm{H^+(aq)} = \mathrm{M^{3+}(aq)} + {}^1/_2\mathrm{H_2(g)} \tag{5}$$

$$\Delta G^0 \simeq I_3 + \Delta H^0(\mathrm{M^{3+},g}) - \Delta H^0(\mathrm{M^{2+},g}) + C \tag{6}$$

As it is commonly accepted that the 4f electrons are mainly buried in the Xe core, one is apt to believe that the variations in lattice energies, $L(\mathrm{MCl_3})$ and $L(\mathrm{MCl_2})$, and the hydration enthalpies, $\Delta H°(\mathrm{M^{3+}})$ and $\Delta H°(\mathrm{M^{2+}})$, alike vary only rather smoothly throughout the lanthanide series. This would then mean that the important changes of $\Delta H°$ and $\Delta G°$, according to eq 4 and 6, and therefore the stability of a particular dichloride or a $\mathrm{M^{2+}}$ cation in solution should resemble the variation of I_3. As these are of the $4f^{n+1} \rightarrow 4f^n$ type for the lanthanides, they vary indeed pronouncedly with atomic number. With the deliberate "adjustments" made in Figure 13 accounting for the first and second half of the lanthanide series, these help us to accept that in aqueous solutions only $\mathrm{Eu^{2+}}$, $\mathrm{Yb^{2+}}$, and $\mathrm{Sm^{2+}}$ might be observed with decreasing half-lives in that order. By the same reasoning, only these three elements may be secured by hydrogen reduction as dichlorides.

TABLE 5. Madelung Parts of the Lattice Energy (MAPLE) (kJ/mol) of Rare-Earth Di- and Trichlorides

element	MAPLE($\mathrm{MCl_2}$)	MAPLE($\mathrm{MCl_3}$)
neodymium	2280	4435
samarium	2301	4473
europium	2312	4487
dysprosium	2354	4484
thulium	2397	4528
ytterbium	2404	4543

For the synthesis of other dihalides one has to resort to different synthetic techniques. The major breakthrough in reduced lanthanide chemistry came with the availability of sufficiently pure metals and inert container materials (vide supra), which made synproportionation reactions in the solid state possible:

$$2\mathrm{MX_3} + \mathrm{M} = 3\mathrm{MX_2} \tag{7}$$

The alternative route, the reduction with other electropositive metals, like alkali metals, may be treated likewise assuming that the rare-earth metal is produced in a finely divided and, hence, a highly reactive form in a preceding step, viz.

$$\mathrm{MX_3} + 3\mathrm{A} = 3\mathrm{AX} + \mathrm{M} \tag{8}$$

Rewriting eq 7 as a disproportionation reaction

$$3\mathrm{MX_2} = 2\mathrm{MX_3} + \mathrm{M} \tag{9}$$

and applying a Born–Haber cycle now yield a somewhat different situation:[95]

$$\Delta H° = 3L(\mathrm{MX_2}) - 2L(\mathrm{MX_3}) + 2I_3 - (I_1 + I_2) - \Delta H°(\mathrm{M,s}) \tag{10}$$

Assuming that, as above, the lattice energies, $L(\mathrm{MX_2})$ and $L(\mathrm{MX_3})$, vary only smoothly, it is now, except for the sums of the first and second ionization potentials, essentially the third ionization potential *and* the enthalpy of atomization that vary the most, but in a like manner, throughout the lanthanide series. In Figure 13 the expression $[(2I_3 - (I_1 + I_2) - \Delta H°(\mathrm{M,s})]$ is plotted against (the atomic number of) the lanthanides. The decreasing stability of a true divalent state may, from this diagram, be put in the order Eu, Yb, Sm, Tm, Dy, Pm, Ho, Nd, Er, Pr, Tb, Ce, Gd, Lu, La. The positions of Ho and Nd have, by all means, to be reversed since there is no dichloride of holmium, only divalent holmium in the mixed-valent $\mathrm{Ho_5Cl_{11}}$ (vide supra). However, in general, this sequence models the synthetic chemist's experience quite well.

Now that the crystal structures for quite a number of di- and trichlorides of the same element have been determined/refined, some attention may be given to the question of whether the lattice energies vary only a little and rather smoothly. Unfortunately, the total lattice energies are not known, but the calculation of the electrostatic (Madelung) parts of the lattice energies, MAPLE,[96] is straightforward. As Table 5 indicates, variations in MAPLE are indeed rather small.

It should be noted in this connection that according to

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

$$\Delta G^\circ = -FE^\circ(M^{3+}/M^{2+}) \quad (12)$$

ΔH° and $E^\circ(M^{3+}/M^{2+})$, the standard electrode potential, are proportional and are used to describe the sequence of the stability of the divalent state. However, $E^\circ(M^{3+}/M^{2+})$ can, in aqueous solution, only be measured for M = Eu, Yb, and Sm (E° = −0.35, −1.15, and −1.55 V, respectively), and little is known for melts.[97] On the other hand, serious assessments have been made from both thermodynamic (above) and spectroscopic data[95b] that exhibit essentially the same picture (Figure 2).

Stabilization of the divalent state for the elements Eu, Yb, Sm, Tm, Nd, Dy, and (Ho) in solid chlorides (MCl_2) appears to be a reasonable compromise between increasing size (necessary for stabilization) and increasing polarizability. The latter leads to the destabilization of the divalent state because electron transfer becomes predominant either via disproportionation

$$3MI_2 = 2MI_3 + M \quad (13)$$

or via the above-discussed "delocalization" of one electron so that the compound may become metallic, e.g.

$$(M^{2+})(I^-)_2 \rightarrow (M^{3+})(e^-)(I^-)_2 \quad (14)$$

Another possibility for the stabilization of the +2 state was thought to be the formation of complex chlorides, for example via

$$CsCl + TmCl_2 = CsTmCl_3 \quad (15)$$

Although a marginal increase in stability seems to arise from favorable lattices,[73,98] it has so far not been possible to obtain any compounds with divalent rare-earth elements other than the six (Eu, Yb, Sm, Tm, Nd, Dy) for which dichlorides are well-known. For neodymium and dysprosium only one ternary chloride, KNd_2Cl_5 and $LiDy_2Cl_5$, has been obtained so far. Surprisingly, it has not been possible to synthesize perovskites like $CsNdCl_3$ or $CsDyCl_3$. As such chlorides are known from neighboring elements, e.g., $CsSmCl_3$ and $CsTmCl_3$, this cannot be a size or matrix effect. It rather has to have thermodynamic reasons. Apparently, the alkali metal chloride favors disproportionation, for example via

$$CsCl + NdCl_2 = {}^1/_3\text{"}Cs_3Nd_2Cl_9\text{"} + Nd \quad (16)$$

("$Cs_3Nd_2Cl_9$", while not stable, yields Cs_3NdCl_6 and $CsNd_2Cl_7$.) Such a disproportionation becomes even more predominant when additional alkali metal chloride is present, for example as the products of a lithium reduction of $NdCl_3$

$$NdCl_3 + Li = NdCl_2 + LiCl \quad (17)$$

are reacted in a subsequent step with CsCl. Instead of complex formation via

$$(NdCl_2 + LiCl) + CsCl = CsNdCl_3 + LiCl \quad (18)$$

the apparently very stable elpasolite type quaternaries are formed essentially via

$$6CsCl + 2LiCl + 3NdCl_2 = 2Cs_2LiNdCl_6 + Nd \quad (19)$$

This clearly shows that complex formation via eq 18 and disproportionation via eq 19 are competing reactions. Table 6 gives an overview of the products that form when such reactions are attempted. Additionally, enthalpies of reaction, ΔH°_R, are given for the examples of M = Nd and Yb calculated with relevant enthalpies of formation, ΔH°_f. Therefore, it is not the enthalpy of formation, which is −1287 kJ/mol for $CsYbCl_3$ and (estimated) −1124 kJ/mol for $CsNdCl_3$, that rules out the "existence" of $CsNdCl_3$ but a competing disproportionation reaction following eq 16 or 19.

TABLE 6. Complex Formation versus Disproportionation: Lanthanide(II) Chlorides in the Presence of Alkali Metal Chlorides (Results and Examples for Enthalpies of Reaction (ΔH°_R, kJ/mol))

M	complexation CsCl + MCl_2	disproportionation CsCl+ (NaCl + MCl_2)
Eu	$CsEuCl_3$	$CsEuCl_3$
Yb	$CsYbCl_3$	$CsYbCl_3$
Sm	$CsSmCl_3$	$CsSmCl_3$
Tm	$CsTmCl_3$	$Cs_2NaTmCl_6$, Tm
Dy	?,[a] Dy	$Cs_2NaDyCl_6$, Dy
Nd	?, Nd	$Cs_2NaNdCl_6$, Nd
	M = Yb	M = Nd
ΔH°_R (1)[b]	−45	+25
ΔH°_R (2)[c]	+89	−19

[a] Essentially unidentified ternary halides belonging to the $CsCl/DyCl_3$ system. [b] $(MCl_2 + NaCl) + CsCl = CsMCl_3 + NaCl$. [c] $(MCl_2 + NaCl) + {}^4/_3CsCl = {}^2/_3Cs_2NaMCl_6 + {}^1/_3M + {}^1/_3NaCl$.

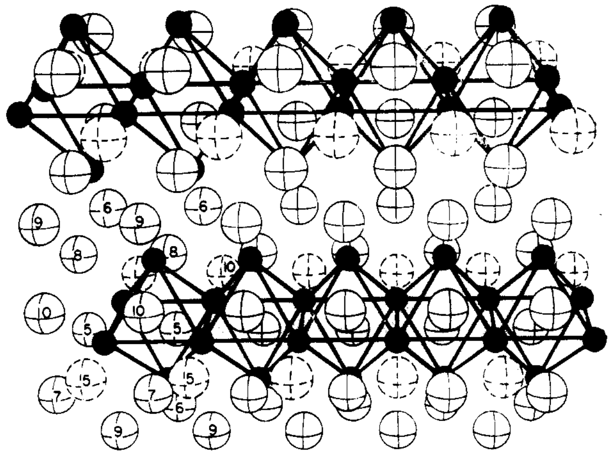


Figure 14. Part of the crystal structure of Gd_2Cl_3 with trans-edge-connected $[Gd_6Cl_8]$ octahedra. From ref 4.

VII. Reduced Halides with Clusters

It has to be considered a major addition to our knowledge of the variety and complexity of reduced rare-earth metal halide chemistry when it was finally recognized in 1970/1973 that a chloride already observed in 1963 with the empirical formula $GdCl_{1.5}$ does contain chains of trans-edge-connected $[Gd_6]$ octahedral clusters[3] (Figure 14). This recognition gave a hint of how the dissolution of rare-earth metals in their molten trihalides and the persistence of the "solution" in a solid compound crystallizing therefrom might be explained. Moreover, this observation linked the rare-earth elements chemically to the early transition elements where octahedral metal clusters were known for a quite a while in both solutions and solids.

In this section a number of compounds will be discussed that could qualify as cluster compounds in a strict sense because relatively small metal arrays (octahedra) occur that might be bound together by a metal–metal bonding system. This is apparently true for a chloride like Gd_2Cl_3 where there is strong evidence from both direct measurements (photoelectron spectra,[99] conductivity[100]) and theoretical calculations (EHMO, LMTO[101]) that aside from each Gd^{3+} core 1.5 electrons are involved in metal–metal interactions and 1.5 electrons are localized as the negative charges of chloride anions. One may put this in the strikingly simple formula $(Gd^{3+})_2(e^-)_3(Cl^-)_3$. When a nitrogen atom is (formally) added to such a system, the three "free" electrons are totally consumed, yielding the salt-like $(Gd^{3+})_2(N^{3-})(Cl^-)_3$.[102]

Gd_2NCl_3 may be described structurally as being built from a Gd_6 octahedral chain degenerated to Gd_4 tetrahedra sharing common opposite edges, thereby forming a $Gd_{4/2}$ chain. Each tetrahedron is centered by N^{3-} and the remaining edges are capped by Cl^-, two of which interconnect neighboring chains according to the formulation $[(Gd_{4/2}N)Cl_{2/2}Cl_2]$. In an additional nitride–chloride of gadolinium, Gd_3NCl_6,[103] such chains are simply cut into pieces of two tetrahedra sharing a common edge.

Although Gd_2NCl_3 and Gd_3NCl_6 ($\equiv Gd_2NCl_3 \cdot GdCl_3$) do not qualify as reduced rare-earth halides and, in a strict sense, not as cluster compounds, it is certainly useful that they be considered together with the "truly" reduced halides because their structural features are so closely related to, e.g., Gd_2Cl_3. One should bear in mind that the shortest Gd^{3+}–Gd^{3+} distances in Gd_2Cl_3, Gd_2NCl_3, and Gd_3NCl_6 are close, 337.1, 335.0, and 344.8 pm, respectively, suggesting that the "metal–metal" distances are not indicative of metal–metal bonding. In other words, crystal chemistry is descriptive and, in principle, insensitive to chemical bonding. The lines drawn are (somewhat) subject to the personal feelings and background of the researcher and are open to interpretation and discussion. The growing chemistry of the reduced and not-so-reduced halides containing isolated or "condensed" clusters with and without interstitials once again teaches us a lesson about where to draw the lines.

Before the octahedral clusters that dominate reduced rare-earth metal halide chemistry are discussed, we shall draw attention to the fact that there are, additionally, other tetrahedral "clusters". First, the aforementioned Yb_4OCl_6,[60] almost a sesquichloride ($\equiv Yb_2Cl_3O_{1/2}$) contains O^{2-}-centered $(Yb^{2+})_4$ tetrahedra with Yb^{2+}–Yb^{2+} distances of 368.5 and 374.7 pm (3× each), shorther than in ytterbium metal (387.9 pm) but certainly with no bonds between the metal cations but with O^{2-}–Yb^{2+}–Cl^- interactions.

Secondly, PrI_2-V[41] would indeed qualify as a cluster iodide with face-capped Pr_4 tetrahedra to be formulated as ${}^3_\infty[Pr_4I_4]I_{12/3}$, thereby allowing four electrons to be involved in cluster metal–metal bonding.

Other cluster types, except for the tetrahedra discussed above, are hardly known. Nevertheless, in $Sc_4I_6C_2$[104] a (distorted) trigonal prism has now been discovered although edge-connected to metal octahedra with $Sc_8I_{12}(C_2)_2$ as the repeat unit of the infinite $Sc_4I_6C_2$ chain (Figure 15). Additionally, the ternary "divalent" scandium halides, e.g., $CsScCl_3$ (above), may be discussed as $Cs{}^1_\infty[(Sc^{3+})(e^-)(Cl^-)_{6/2}]$ with an, ideally, one-dimensional chain of metal–metal-bonded Sc^{3+} cores, a very simple example of a "true" cluster. That this compound can form an apparently complete "solid solution" with the fully oxidized $Cs_3Sc_2Cl_9$ ($\equiv CsSc_{0.67}Cl_3$) with essentially the same structure suggests that all kinds of smaller units, dimers, trimers, etc., could exist. This view is supported but by no means understood by the nicely structured EPR spectra that are observed.

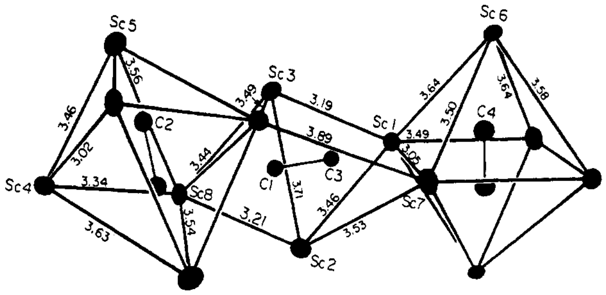


Figure 15. Dicarbon-"centered" scandium clusters sharing common edges in $Sc_4I_6C_2$ as part of an infinite chain. From ref 104. Note that the distances are given in angstroms.

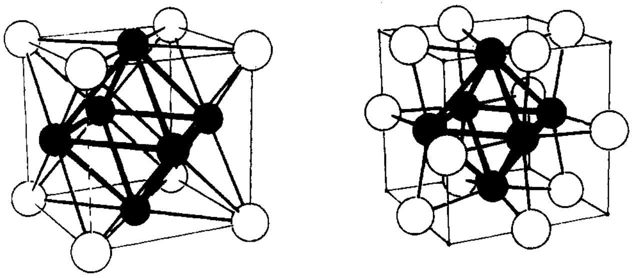


Figure 16. M_6X_8 [6–8] and M_6X_{12} [6–12] type clusters. From ref 110b.

Most of the crystal chemistry of the reduced rare-earth metal halides may, however, be derived from two cluster species, $[M_6X_8]$ and $[M_6X_{12}]$ (Figure 16), abbreviated as [6–8] and [6–12], respectively.

In analogy to the silicates that have been systematized in terms of isolated (*neso*) or vertex-sharing $[SiO_4]$ tetrahedra thereby forming small groups (*soro*-silicates), chains and double chains (*ino*), layers and double layers (*phyllo*), and, finally, three-dimensional networks (*tecto*), the [6–8] and [6–12] clusters can be treated in a similar way (concept of condensed metal clusters).[105] There are, however, pronounced differences. Focusing on the metal octahedra, [6], alone, these are found to be "isolated" (0[6–...]) or trans-metal-*edge*-sharing in groups of two (2×0[6–...]), in chains (1[6–...]), and double chains (2×1[6–...]) and as double-metal layers (2×2[6–...]) in the so-called monohalides (or hemihalides) (Table 7). Only a limited number of such clusters appear to be empty, namely, the sesquihalides, M_2X_3, which are derived from trans-edge-sharing [6–8] clusters, 1[6–8], for example, Gd_2Cl_3, and Sc_7Cl_{10}, which exhibits a double-chain of [6–8] clusters, 2×1[6–8]. The double-metal-layer "monohalides" that are in fact hydrides, MXH_x, may also be derived from [6–8] clusters, 2×2[6–8](H).

None of the [6–12] cluster derivatives seem to be empty. They commonly encapsulate carbon as mono- or dicarbon units, boron, nitrogen, and also transition metals, presently known for manganese up to nickel in the periodic table, for example, $Y_7I_{12}Fe$.[45]

Table 7 contains an overview of most of the formulas and structure types that are now known including examples.

TABLE 7. Reduced Rare-Earth Metal Halides with Octahedral Metal Clusters: An Overview

X/M	formula	structure	example(s)
0.50	M_2XZ	2×2[6–...]	Gd_2IC
1.00	M_3X_3Z	3[6–12] (C)	Gd_3Cl_3C
	MXZ_x	2×2[6–12] (C, N)	$LuClC_{0.5}$
		2×2[6–8] (H)	$LuClH_x$ (ZrCl) $GdClH_x$ (ZrBr)
1.17	M_6X_7Z	2×1[6–12] (C_2)	$Gd_6Br_7C_2$
1.25	M_4X_5Z	1[6–12] (C)	Gd_4I_5C
1.42	$M_{12}X_{17}Z_3$	1[6–12] (C_2)	$Gd_{12}I_{17}C_6$
1.43	M_7X_{10}	2×1[6–8]	Sc_7Cl_{10}
	$M_7X_{10}Z$	2×1[6–12] (C_2)	$Sc_7Cl_{10}C_2$
1.50	M_2X_3	1[6–8]	Gd_2Cl_3
	M_4X_6Z	1[6–12] (B, N, C_2)	Sc_4Cl_6B $Sc_4I_6C_2$
1.60	M_5X_8Z	1[6–12] (C, N)	Sc_5Cl_8C
		2×0[6–12] (C_2)	$Gd_{10}I_{16}(C_2)_2$
1.70	$M_{10}X_{17}Z_2$	2×0[6–12] (C_2)	$Gd_{10}Cl_{17}C_4$
1.71	$M_7X_{12}Z$	0[6–12] (B, C, Mn, Fe)	$Sc_7Cl_{12}C$ $Pr_7I_{12}Mn$
1.80	M_5X_9Z	2×0[6–12] (C_2)	$Gd_{10}Cl_{18}(C_2)_2$
1.83	$M_6X_{11}Z$	0[6–12] (C_2)	$Sc_6I_{11}C_2$
2.57	$A_2M_7X_{18}Z$	0[6–12] (C)	$Cs_2Lu_7Cl_{18}C$

A. Isolated [6–12] Clusters

Only [6–12] type clusters have so far been observed as isolated structural features, and the corresponding halides have, of course, high halide/metal ratios. This then leaves only few electrons for metal–metal bonding in the octahedral cluster. $ScCl_2$, for example, as $[Sc_6Cl_{12}]$ would only have six electrons for metal–metal bonding, a valence electron concentration (VEC) per cluster atom of only one. The additional scandium atom in Sc_7Cl_{12} that enters as Sc^{3+} a "normal" octahedral hole is therefore thought to add three electrons to the cluster, which is then a nine-electron species with the VEC being enhanced to 1.5. The VEC in Gd_2Cl_3 is also 1.5 per Gd so that (by analogy) Sc_7Cl_{12} could exist. Still, for [6–12] clusters VEC's of 1.5 are believed to be too low (Gd_2Cl_3 contains [6–8] clusters) and, indeed, it has recently been found that Sc_7Cl_{12} is in fact $Sc[Sc_6(Z)Cl_{12}]$, with Z being an interstitial atom, boron or nitrogen in particular, occupying the cluster center.[106] These add three or five electrons to the cluster and thereby enhance the total number of electrons to 12 or 14, respectively.

A number of rare-earth iodides $M_7I_{12}Z$ with the same structure have also been obtained. These are novel in a sense that they may contain transition-metal atoms as interstitials, for example, $Pr_7I_{12}Z$ with Z = Mn, Fe, Co, and Ni, giving rise to 16–19 electrons per $[Pr_6Z]$ unit.[45]

Without doubt, the interstitial atom affects the metal–metal bonding in these "clusters" considerably. In other words, most of the so-called clusters could well do without metal–metal bonding but not without interstitial–metal bonding. Results from extended-Hückel molecular orbital (EHMO) calculations for the $[(Sc_6B)Cl_{12}]Cl_6$ cluster[106] predict a dramatic decrease of (metal) d-orbital energies once they mix with s and p (interstitial) orbitals (Figure 17). Still, there is some metal–metal bonding involved as the Sc–Sc orbital population of 0.07 in the cluster suggests (vs 0.19 for the empty cluster).

Analogous EHMO calculations have been undertaken for the iodide $Sc_6I_{11}C_2$, which contains an "isolated" $[Sc_6I_{12}]$ cluster accommodating a C_2 unit located on the pseudo-C_4 axis of the metal cluster. Again, without the contribution of electrons by the interstitial C_2 the cluster just would not exist. Nature obviously has found a way to tune in a very peculiar manner through the nature (size, number of electrons, electronegativity) of the interstitial not only the actual size and the electronic structure but also the composition of the cluster. A C_2 unit, for example, can be viewed as single, double, or triple bonded. The single-bonded dicarbon provides six electrons and $Sc_6I_{11}C_2$ therefore contains a 13-electron cluster.

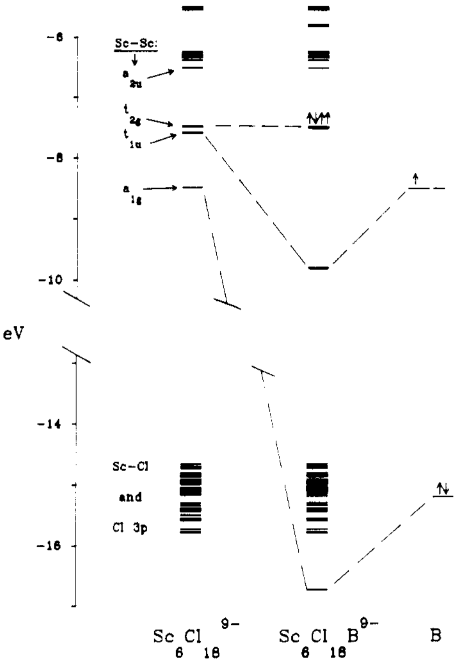


Figure 17. Molecular orbital diagrams from extended-Hückel (EHMO) calculations of the empty vs the boron-centered $(Sc_6Cl_{12})Cl_6^{9-}$ cluster. From ref 106.

The third isolated cluster that has to be discussed in this connection appears with $Cs_2Lu_7Cl_{18}Z$.[10] Assuming Z = C, for which there is some evidence from an X-ray structure determination, $Cs_2Lu_7Cl_{18}C$ contains a 9-electron 0[6–12] cluster. This is interconnected by six $[LuCl_6]^{3-}$ octahedra that "contribute" six Cl^- to the cluster. This unusually oxidized $[Lu_6]$ cluster has a VEC of only 1.5 and exhibits quite long Lu–Lu distances of 357.7 and 361.5 pm. Compared with $Cs_3[Lu_2Cl_9]$ with a confacial bioctahedron and $d(Lu^{3+}–Lu^{3+})$ = 365.9 pm (through the common face) these are not so unusual. If, on the other hand, one were to assume that this compound is an ionic carbide to be formulated as $(Cs^+)_2(Lu^{3+})_7(Cl^-)_{18}(C^{4-})(e^-)$, there would be only one electron left over. The red color and the transparency of the crystals would be explained a little easier in this way. The truth will, however, as usual be somewhere in between the primitive pictures outlined.

B. Cluster Condensation

The first step of (formal) cluster condensation that has been observed is the connection of two [6–12] clusters through a common metal edge. This is achieved in $Gd_5Cl_9C_2$[107] ≡ $Gd_{10}Cl_{18}(C_2)_2$ ≡ $(Gd_{4/1}Gd_{2/2}Cl_{7/1}Cl_{4/2})_2(C_2)_2$ with the dicarbon units residing on the C_4 axes of the gadolinium clusters (Figure 18). Electronic structure calculations show that metal–metal bonding orbitals are not occupied and it could

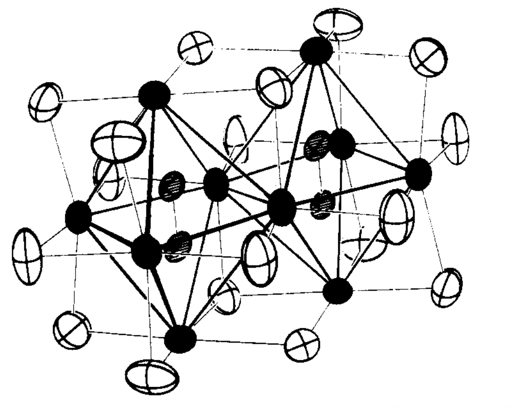


Figure 18. The metal edge-connected $Gd_{10}Cl_{18}(C_2)_2$ dimer. From ref 107.

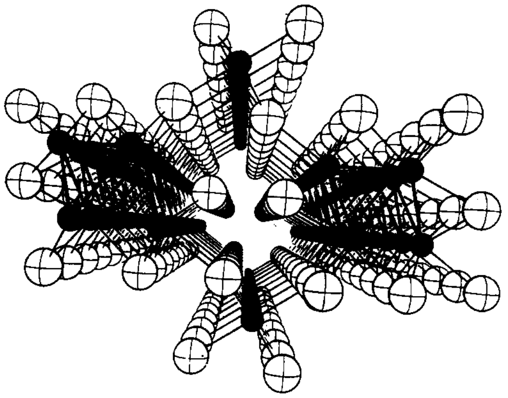


Figure 19. A perspective view parallel to [010] of the crystal structure of Gd_5Br_8[111] and of Sc_5Cl_8C.

therefore be formulated as $(Gd^{3+})_{10}(Cl^-)_{18}(C_2{}^{6-})_2$. The "actual" charge distributions obtained by summing the Mulliken orbital populations over all occupied states are +1.6 for Gd, −0.7 for Cl, and −2.0 for C_2.[108] Similar calculations applying the linear muffin-tin orbital method in its atomic sphere approximation (LMTO–ASA) come, generally, to the same conclusions.[101]

The connection of such $Gd_{10}Cl_{18}(C_2)_2$ "molecules" via common chloride vertices leads to chains of the composition $Gd_{10}Cl_{17}(C_2)_2$, and halide–edge connection yields $Gd_{10}I_{16}(C_2)_2$.[52] In these latter two halides, one and two electrons per formula unit are provided for metal–metal bonding in the gadolinium clusters.

"Isolated" edge-connected triple octahedra that would be the next step of cluster condensation have so far not been identified as such. They are, however, edge-connected to a zigzag chain contained in $Gd_{12}I_{17}(C_2)_3$.[109] Infinite linear trans-metal-edge-connected single chains of [6–12] clusters have been observed in Sc_5Cl_8C[110] and the isostructural Gd_5Br_8[111] (containing an unknown interstitial). In these the fifth metal atom resides in a "normal" octahedral hole, thereby connecting through common chloride two single chains (Figure 19) so that an ionic description like $[(Sc^{3+}(Cl^-)_2][(Sc^{3+})_4(Cl^-)_6(C^{4-})(e^-)_3)]$ appears appropriate and provides three electrons per formula unit for cluster metal–metal bonding. Other alternatives of 1[6–12](Z) single chains are realized in M_4I_5C with M = Gd, Er, and Y,[112–114] also with three electrons for cluster bonding, and in Sc_4Cl_6Z with Z = B and N[106] with three and five (odd number!) electrons "left over". The new $Sc_4I_6C_2$[104] is structurally remarkable because it contains infinite single chains of edge-connected octahedra (trigonal *anti*prisms) and trigonal prisms stabilized by dicarbon units (Figure 15).

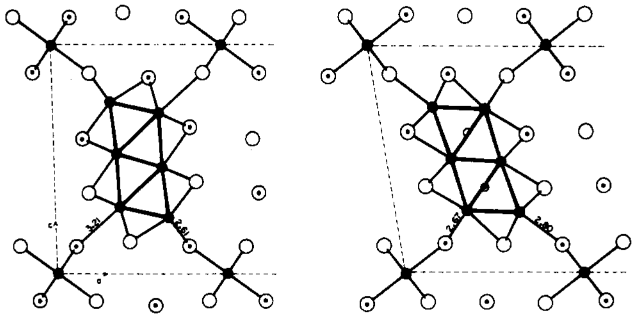


Figure 20. Comparison of the crystal structures of Sc_7Cl_{10} (left, edge-connected [6–8] clusters) and $Sc_7Cl_{10}C_2$ (right, edge-connected [6–12] clusters). From ref 118.

Another alternative way to realize a halide/metal ratio of 1.5 is exhibited by the sesquihalides that contain trans-edge-connected single chains of [6–8] clusters. Gd_2Cl_3[2,3,115] (Figure 14) is the most prominent example for that class of compounds. It may be obtained fairly pure and is therefore already quite well investigated by physical methods.[99,100] The octahedral chain may be treated as a classical Heisenberg chain composed of tetranuclear spin clusters.[116] Metal–metal bonding in Gd_2Cl_3 appears to be strong.[101] The three low-energy d bands per unit cell may be interpreted as the σ- and two π-bonding states along the shared trans edges of adjacent Gd_6 octahedra. Gd_2Cl_3 is a semiconductor with a band gap around 1 eV.

The double chains, 2×1[6–8], in Sc_7Cl_{10},[117] and 2×1-[6–12]Z, in $Sc_7Cl_{10}C_2$,[118] $Gd_6Br_7C_2$,[52,119] and Gd_3I_3C,[113] represent the next step(s) of cluster condensation and, in that order, of halide/metal ratio. Figure 20 shows the close relationship of [6–8] type interstitial-free Sc_7Cl_{10} and [6–12] type $Sc_7Cl_{10}C_2$ where (from left to right) mainly the face-capping chloride has to be changed to edge-bridging.

The next step of cluster condensation is the formation of double-metal layers, 2×2[6–...](Z), where Z is hydrogen for [6–8] type and a second-row nonmetal (B, C, C_2, N) for [6–12] type clusters. These may be understood as four-layer slab structures ...XMMX... (Figure 4) with interstitials occupying tetrahedral ([6–8]) or octahedral ([6–12]) interstices between the double-metal layers, thereby making possible through their electron contributions mainly interstitial–metal and little or no metal–metal bonding. Further electron contribution to such a compound is possible through intercalation of alkali metal (Li in particular) between the (double) halide layers of adjacent slabs.[120] Li^+ resides in octahedral holes, which appears to be possible only in the ZrBr type structure of the [6–8] type "monohalides", whereas the nonintercalated halide-hydride, e.g., $ErClH_x$ and $GdBrH_x$, adopts the ZrCl "heavy-atom" structure, and intercalation to, for example, Li_zErClH_x is accompanied with a structural transformation from ZrCl to ZrBr type.

For quite a while, the double-metal-layered and so-called monohalides with their halide/metal ratio of 1.0 seemed to be the final step of cluster condensation. With $Gd_6Cl_5C_3$ and the most remarkable Gd_2IC, this is no longer true.[113] The latter is, like Ag_2F,[121] closely related to the (anti type) cadmium halides.

The final step of cluster condensation would be a three-dimensional network. Indeed, Gd_3Cl_3C[122] might

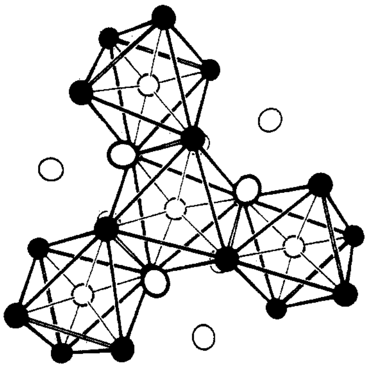


Figure 21. Part of the crystal structure of Gd_3Cl_3C showing the carbon-centered metal octahedra sharing three common edges. From ref 122.

be understood as a deficient superstructure of the NaCl type where $[(Cl^-)_3(C^{4-})]$ arrange in a cubic closest packed fashion. Gd^{3+} occupies three of the four octahedral holes per formula unit in a way that they arrange around the highly charged C^{4-} "anions"; the $[Gd_{6/3}C]$ units so produced (Figure 21) may also be derived from [6–12] type clusters connected via three common edges. The above-mentioned carbide–halides $Gd_{10}Cl_{18}(C_2)_2$ etc. may be understood similarly. Gd_3Cl_3C is isostructural with Ca_3I_3P, a salt, whereas the former is metallic with two electrons per formula unit.

VIII. Epilogue

"First Comes the Synthesis."[123] This insight is, in the author's belief, equally important to solid-state chemistry and materials science as a whole as the Word at creation. In this sense Synthesis has the quality of the Word ("When all Things began, the Word already was."[124]), and Things (i.e., physics, materials development, ...) can only begin when synthesis has been successful. Synthesis is only trivial for old (≡known) materials. New materials, without which future technology and a future are impossible, are a continuous challenge to the synthetic chemist.

It is the author's hope to have shown what tremendous successes can be achieved in a few years when new and novel or even grandfather's routes are applied and further developed in an area that previously seemed to be a laboratory curiosity. Still, it is mainly academic. But we are just at the beginning, at creation. Some of the possible compounds and their structures (≡basic analysis), maybe even of the generalities, are now known, and a few physical measurements have been undertaken which have led to important, but still only first thoughts about "chemical" bonding. At the end of the century we shall look back and see what has then been accomplished.

Acknowledgments. Our work, as described and referenced in this article, was only possible thanks to the excellent infrastructure provided through Professor Rudolf Hoppe at the University of Giessen, the continuous support of the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie, and, most importantly, the enthusiasm of several graduate students, especially Thomas Schleid. The initial writing of this article took place during a leave with Professor John D. Corbett at Iowa State University, without which it would have never been finished.

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