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Reduced Halides of Yttrium with Strong Metal–Metal Bonding: Yttrium Monochloride, Monobromide, Sesquichloride, and Sesquibromide

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Reaction of Y with YCl_3 or YBr_3 in sealed tantalum capsules at 1000–1150 K leads to the new compounds YCl, YBr, Y_2Cl_3, and Y_2Br_3. All products were characterized by modified Guinier techniques, which led to the following lattice parameters: YCl (hexagonal), a = 374.8 (1), c = 2731.8 (9) pm; YBr, a = 380.6 (1), c = 2915.8 (4) pm; Y_2Cl_3 (monoclinic), a = 1514.4 (3) pm, b = 382.5 (1) pm, c = 1007.7 (2) pm, β = 118.24 (2)°; Y_2Br_3, a = 1646.3 (2) pm, b = 389.8 (1) pm, c = 1069.5 (2) pm, β = 120.08 (1)°. YCl and YBr are isotypic with ZrBr and ZrCl, respectively, while Y_2Cl_3 and Y_2Br_3 crystallize in the space group $C2/m$ and are isotypic with Gd_2Cl_3. The structure of Y_2Cl_3 was refined on the basis of single-crystal diffractometer data by least-squares techniques (R = 0.048, R_w = 0.058, Mo Kα). The structure consists of parallel infinite chains of composition $Y_{4/2}Y_2Cl_4Cl_2$ formed by condensing M_6X_8-type clusters via trans edges, the shorter metal–metal distances being 326.6 (2) (shared edge), 363.8 (2), and 369.4 (2) pm. A detailed consideration of distances suggests predominantly ionic bonding between Y and Cl with metal–metal bonding within the chains. A discussion is given of the fact that M–M distances in Y_2Cl_3 are 7–11 pm less than those in Gd_2Cl_3, in contrast to their nearly identical metallic radii.

Introduction

Although the dipositive oxidation state for scandium, yttrium, and many of the lanthanides was once considered unusual, halides with formal oxidation states below 2 are now known for the majority of these elements. Moreover, these halides all exhibit remarkable metal–metal bonding features. Table I summarizes those compounds which have been characterized analytically and structurally to date.

In the case of yttrium, early thermal analysis on the system YCl_3–Y^{13} revealed only a small interaction in the melt, with a eutectic at 2 mol % Y and 989 K. An additional thermal effect observed at 1010 K was attributed to a monotectic transformation, the nature of which was not specified further. Later measurements confirmed the eutectic only[14] and corrected the liquidus composition at higher temperatures.[15] The present study shows that the thermal effect observed earlier at 1010 K indeed reflects something of the existence of metal-rich yttrium chlorides.

The addition of YCl and YBr to the widening collection of monohalides, Table I, is entirely reasonable and further suggests that this type of compound might become quite general for most of the rare-earth elements. On the other hand the discovery of only the sesquihalides Y_2Cl_3, Y_2Br_3, Gd_2Cl_3, Gd_2Br_3, Tb_2Cl_3, Er_2Cl_3, and Lu_2Cl_3 may indicate stability with a more limited range of metals, possibly because of relative size. However, kinetic factors are evidently so extremely significant in these syntheses[16] that the *absence* of any compound probably cannot be concluded with great certainty, especially if it is not the phase in equilibrium with the metal, as in the case of the sesquihalides.

We here report on the experimental details for the synthesis and identification of the compounds YCl, YBr, Y_2Cl_3, and Y_2Br_3 and on single-crystal studies of Y_2Cl_3.

Experimental Section

Preparation. The trihalides of yttrium were prepared from Y_2O_3 and NH_4X^{17} or metal plus high-purity HCl^{11} and were purified by repeated sublimation in Ta crucibles at $p \approx 10^{-6}$ torr. The metal used for reduction (Kelpin and Ames Laboratory, 99.8 and 99.9(total)%, respectively) was either (a) melted at $p \approx 10^{-6}$ torr to small lumps of ca. 0.1 cm^3, (b) cold-rolled with intermediate annealing to strips of ca. 0.03 × 1 × 6 cm and electropolished, or (c) prepared as a powder by decomposing the coarsely ground hydrides at 1020 K in high vacuum. The reactions of YX_3 and Y were performed in Ta ampules welded[18] under ca. 100 torr of Ar or 400 torr of He which were in turn sealed under vacuum in a stainless steel or fused silica jacket, respectively. All halide phases are characteristically moisture sensitive[7,11] and were handled only in the drybox. Most synthesis results do not pertain to systems at equilibrium.

YCl. A 180-mg sample of YCl_3 and 240 mg of Y (a) were heated to 1020 K for 11 days. After being quenched to room temperature, the reaction product contained approximately 10% YCl besides unreacted YCl_3, Y, some Y_2Cl_3, and traces of YOCl. In a different technique 255 mg of YCl_3 and 1144 mg of Y (c) were heated in a 8 × 1 cm tube at ~1060 K for 30 days. YCl was found to be the only reaction product, growing as thin, highly reflective, black plates, some aggregated, on the excess metal.

YBr. YBr_3 and Y (a) were heated in a gradient 1090/1220 K for 11 days. The product was ~10% yield of black plates of YBr, a small amount of YOBr, YBr_3, but no Y_2Br_3.

Y_2Cl_3. A 110-mg sample of YCl_3 and 120 mg of Y (a) (molar ratio 1:2.4) were reacted at 1000 K for 30 days. The quenched product contained approximately 90% Y_2Cl_3 plus YCl_3, Y (identified by X-ray investigation), and traces of YOCl (optical identification). In a modified procedure 272 mg of YCl_3 and 1170 mg of metal strips (b) (molar ratio 1:10) were sealed in a Ta tube of approximately 200-mm length, heated in a two-zone furnace (870/1070 K) for 30 days and cooled slowly. (The temperatures pertain to the exterior of the glass jacket and so exaggerate the actual gradient within the Ta tube.) Black, furlike aggregates of Y_2Cl_3 needles in ca. 75% yield were found on the metal strips along the entire length of the ampule with some larger crystals in the middle of the cooler half. No transport reaction

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Table I. Reduced Halides (X/M < 2) of Scandium and the Lanthanides and Their Metal-Metal Bonding Features

av oxidn state	compd	ref	structural features
1.714	Sc_7Cl_{12}	2	discrete M_6X_{12} clusters
	La_7I_{12}, Pr_7I_{12}, Tb_7I_{12}	3	
1.600	Sc_5Cl_8	4	single chains of edge-sharing metal octahedra with M_6X_{12}-type environment (edge capped by halide) with parallel chains of MX_6 octahedra sharing edges
	Gd_5Br_8, Tb_5Br_8	5	
1.500	Gd_2Cl_3	6, 7	single chains of edge-sharing metal octahedra with M_6X_8-type environment (face capped by halide)
	Gd_2Br_3, Tb_2Cl_3	7, 8	
	Y_2Cl_3, Y_2Br_3	this work	
	Er_2Cl_3, Lu_2Cl_3	5	
1.429	Sc_7Cl_{10}	9	double chains of edge-sharing metal octahedra with M_6X_8-type environment with parallel chains of edge-sharing MCl_6 octahedra
1.167	Er_6I_7, Tb_6Br_7	10	double chains of edge-sharing metal octahedra with M_6X_8-type environment
1.000	ScCl	11	double metal layers from edge-sharing metal octahedra, M_6X_8-type environment
	YCl, YBr	this work	
	LaBr, PrBr, GdCl, TbCl	8, 12	
	GdBr, TbBr, HoBr, ErBr		

Table II. Lattice Parameters for YCl, YBr, Y_2Cl_3, and Y_2Br_3 from Modified Guinier Diagrams (Standard Deviations in Parentheses)

compd	structure type	parameters (pm; deg)
YCl	ZrBr[20] (hexagonal)	374.8 (1), 2731.8 (9)
YBr	ZrCl[21] (hexagonal)	380.6 (1), 2915.8 (4)
Y_2Cl_3	Gd_2Cl_3[6] (monoclinic)	1514.4 (3), 382.5 (1), 1007.7 (2); 118.24 (2)
Y_2Br_3	Gd_2Cl_3	1646.3 (2), 389.8 (1), 1069.5 (2); 120.08 (1)

was evident. Y_2Cl_3 in about 30% yield together with unreacted YCl_3 and Y (b) is readily made from Y:YCl_3 ratios of ~5:1 heated to 1070 K for ~9 days and cooled slowly. The absence of YCl appears related to the use of strips and slow cooling. Experiments, in which samples of Y_2Cl_3 sealed in small Ta containers were equilibrated at temperature for a few hours and quenched, indicate the decomposition point of Y_2Cl_3 is between about 1070 and 1122 K.

Y_2Br_3. YBr_3 was heated with a large excess of Y (a) to 1180 K. After 2 days, the temperature was lowered to 1020 K and kept constant for 40 days. Approximately 5% of the reaction product consisted of fine needles of Y_2Br_3; the remainder consisted of YBr_3 and Y.

Characterization. All products were characterized by the modified Guinier technique[19] using glass capillaries of 0.1- or 0.2-mm diameter. The diagrams were evaluated with a coincidence measuring device (accuracy ±0.02 mm). Least-squares refinement with 15–20 unambiguously indexed reflections led to the lattice parameters given in Table II.

A mixture of YCl_3 and what turned out to be Y_2Cl_3 was examined by microprobe (Applied Research EMX). Relative to an emission standard of YCl_3 a bundle of Y_2Cl_3 crystals gave typical Cl:Y ratios of 1.42 and 1.47, with an estimated uncertainty of ±0.1. No other elements heavier than Ne could be detected.

Single-Crystal Diffraction. Crystals of Y_2Cl_3 occur as black, brass-reflective needles, blades, and plates either on the metal or distributed in the unreacted YCl_3. The crystals are very fibrous in nature and cannot be cut without fraying. Presumably related imperfections were often observed with oscillation or Weissenberg photographs via either multiple spots or streaking, but a relatively good crystal was still fairly easy to locate.

The structure of Y_2Cl_3 was in fact investigated separately in both laboratories by using both Cu and Mo radiation, and the two studies yielded final positional parameters differing by less than 1σ from one another. The data from the better refinement given here were collected from a blade-shaped crystal ca. 0.049 × 0.098 × 0.673 mm in extreme dimensions. This was transferred to and sealed in a thin-walled glass capillary within the drybox so that the long dimension (*b* axis) was approximately parallel to the capillary and to the ϕ axis of the diffractometer during data collection.

Diffraction data were collected at room temperature utilizing Mo $K\alpha$ radiation monochromatized with a graphite single crystal (λ 70.954 pm). The diffractometer and its operating procedures have been described before.[22] All reflections within the octants HKL, $HK\bar{L}$, $H\bar{K}L$, and $H\bar{K}\bar{L}$ with $2\theta < 55°$ were examined in the ω-scan mode. The *C*-centering condition for the indicated monoclinic cell was evident early on. The 2θ values for 13 independent reflections with $2\theta > 33°$ which had been tuned on the diffractometer yielded refined lattice parameters within 1σ of those determined independently with the modified Guinier technique (Table II).

Structure Determination. Programs utilized for the data reduction, structure solution and refinement, and illustration as well as the source of atomic scattering factors for neutral atoms (including corrections for both the real and imaginary parts of anomalous dispersion) were as referenced before.[23] Reduction of the diffractometer data yielded 1283 reflections classed as observed ($I > 3\sigma(I)$), about 65% of the total possible, and averaging of duplicate reflections yielded 589 independent data.

A recent improved determination of the structural parameters of Gd_2Cl_3[7] has established that the acentric space group *Cm* first assigned[6] is incorrect, a circumstance which can also be discerned with some probability by inspection of the published parameters and [010] projection. The solution of the Y_2Cl_3 structure in space group $C2/m$ followed directly from the recognition that it was isostructural with Gd_2Cl_3. Refinement proceeded uneventfully to $R = 0.064$ and $R_w = 0.082$ (conventional definitions). The shape of the crystal and the calculated value of $\mu = 245.8$ indicated an absorption correction was in order after which refinement yielded $R = 0.049$ and $R_w = 0.072$ for 604 reflections. At this point the weaker reflections were observed to have larger weighted errors $[w(|F_o| - |F_c|)^2, w = \sigma_F^{-2}]$, so the data were reweighted in 30 overlapped groups sorted by F_0 so as to equalize these errors. This gave smaller standard deviations for the parameters and, at convergence, $R = 0.048$ and $R_w = 0.058$. A final difference Fourier synthesis was flat to ±1 e/Å^3.

Results and Discussion

Equilibration and quenching experiments indicate Y_2Cl_3 and YCl decompose peritectically to Y_2Cl_3-rich liquid plus YCl and Y, respectively. The reverse reactions are slow, befitting the complexities of the structural transformations involved, and quantitative synthesis reactions are difficult to achieve. The monohalide structure types and some of their properties have been discussed before,[20,21] as has Gd_2Cl_3,[6,7] the only prior example of the sesquihalide structure.

Final positional and thermal parameters for Y_2Cl_3 are listed in Table III, and important distances are listed in Table IV. Observed and calculated structure factor data are available as supplementary material.

Figure 1 provides a perspective projection of a section of the Y_2Cl_3 structure parallel to both the *b* axis and the infinite metal chains, with yttrium atoms in the central chain darkened. The area shown comprises that of two unit cells plus adjoining

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Table III. Atom Parameters for Y_2Cl_3[a]

atom[b]	x	z	B_{11}[c]	B_{22}	B_{33}	B_{13}
Y1	0.41187 (6)	0.04979 (9)	1.18 (4)	1.37 (4)	1.81 (4)	0.62 (2)
Y2	0.13532 (6)	0.2910 (1)	1.22 (3)	1.35 (4)	1.75 (3)	0.66 (3)
Cl1	0.6603 (2)	0.5117 (3)	1.23 (8)	1.73 (11)	1.84 (8)	0.57 (7)
Cl2	0.7699 (2)	0.8831 (3)	1.09 (7)	1.74 (10)	1.89 (8)	0.71 (6)
Cl3	0.9502 (2)	0.2673 (3)	1.16 (8)	1.66 (9)	1.96 (8)	0.78 (6)

[a] Space group: $C2/m$ (No. 12). Refinement: $R = 0.048$, $R_w = 0.058$ (604 reflections). [b] All atoms in positions 4i: $x, 0, z; \bar{x}, 0, \bar{z}; {}^1/_2 + x, {}^1/_2, z; {}^1/_2 - x, {}^1/_2, \bar{z}$. [c] $T = \exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{13}hla^*c^*)]$; $B_{12} = B_{23} = 0$.

Table IV. Important Distances in Y_2Cl_3

atom 1–atom 2[a,b]	dist, pm	atom 1–atom 2[a,b]	dist, pm
Y1–Y1a	326.6 (2)	Y1a–Cl2	313.0 (3)[c]
Y1–Y2b	363.8 (2)	Cl1–Cl2	330.0 (3)
Y1b–Y2a	369.4 (2)	Cl2–Cl2c	330.5 (4)[c]
Y2a–Y2b	443.1 (3)[c]	Cl1–Cl1c	342.1 (4)
Y1a–Y1b	490.3 (2)[c]	Cl2–Cl3c	350.5 (3)
Y1b–Cl2	277.3 (2)	Cl1a–Cl3c	352.6 (3)
Y2a–Cl2	274.2 (3)	Cl2c–Cl3c	352.9 (4)
Y2–Cl3	269.9 (3)	Cl1–Cl3c	386.5 (3)[c]
Y1a–Cl3c	275.7 (2)	Cl1–Cl1a	474.6 (5)[c]
Y2–Cl1a	282.1 (2)	Cl3a–Cl3	419.2 (5)[c]
Y2c–Cl1a	277.7 (3)		

[a] Symmetry operations: (a) $\bar{x}, \bar{y}, \bar{z}$; (b) $x + {}^1/_2, y + {}^1/_2, z$; (c) ${}^1/_2 - x, {}^1/_2 - y, z$. Necessary unit cell translations are not designated. [b] All atoms also have others of like kind at ±b, 382.5 (1) pm. [c] Distances to adjoining chains.

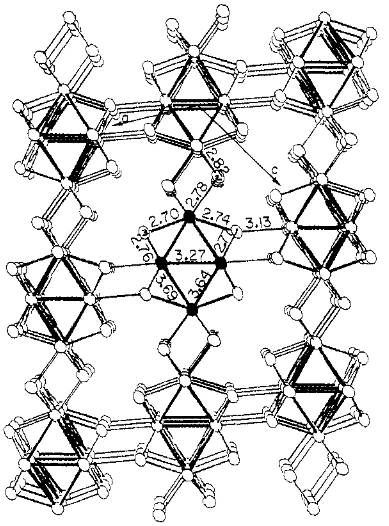

Figure 1. Projection of the Y_2Cl_3 structure along the chains (b direction) showing the packing and bond distances (Å). The metal atoms in the central chain are darkened. Centers of symmetry occur on the shared Y–Y edge, at the midpoint of the metal octahedra, and at $b = {}^1/_4$ and ${}^3/_4$ at three sites between the metal chains. Thermal ellipsoids are at the 90% probability level.

atoms which complete the chains. Figure 2 gives a view of one chain normal to the b axis, including a duplicate set of the bridging chlorine atoms at the top and bottom.

A very simplified description of the structure is that of a hexagonal (honeycomb) packing of Y_2Cl_3 rods.[24] The structure of the individual rods corresponds to a series of metal octahedra sharing trans edges to form infinite chains. All exposed faces of each chain are capped, and exo positions of the chain are filled by chlorine atoms in a regular and sensible way, one which in fact appears[16] to be a typical feature of all of the highly reduced halides listed in Table I. Another description which takes into account the different functionality of chlorine atoms in endo and exo positions seems apt and useful as well, that of chains $Y_{4/2}Y_2Cl_4$ close packed into layers (Figure 1) which are in turn separated by a rather open intermediate layer of the bridging Cl1 atoms. Indeed, voids of approximate octahedral symmetry (edges of 382, 386, and 419 pm) are left in this chlorine layer around centers of symmetry. Independent experiments in both laboratories to occupy these voids in Gd_2Cl_3 with Li^+ (or Mg^{2+}), thereby adding the corresponding number of electrons to the chain, have to date been unsuccessful.

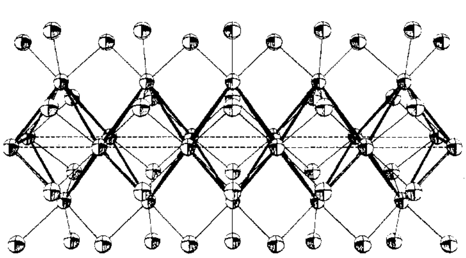

Figure 2. An approximately [20$\bar{1}$] view of a section of one infinite metal chain in Y_2Cl_3 with surrounding chlorine atoms, the row of Cl1 at the top duplicating that at the bottom. The shorter metal–metal distances are marked with heavier lines. The repeat distance in the chain is the β axis, 382.5 pm. Thermal ellipsoids are at the 90% probability level.

The phase Y_2Cl_3 is isotypic with the other compounds of stoichiometry M_2X_3 mentioned in Table I. As has been pointed out repeatedly[7,8,16,25] this structure is closely related to those of transition-metal compounds which contain characteristic M_6X_8 clusters, these being condensed into chains (Figure 2) by sharing trans edges of the octahedra. This condensation does not involve the atoms Cl2 and Cl3, but obviously space is too limited for Cl1 to occupy faces between neighboring octahedra in the chain. Thus Cl1 atoms occupy positions between adjacent chains which are both exo as well as (very much distorted) endo positions with respect to a single octahedral cluster.

Several other aspects of the remarkable sesquihalide structure have not been noted or considered before. With respect to the chlorine bonding to and between the chains, the relatively tighter binding of the nonmetal to the four faces of each metal octahedron (endo position) also supports the above description $(Y_{4/2}Y_2Cl_4)Cl_2$, the Cl1 outside the parentheses linking chains at the top and bottom (average distance 281 pm) while Cl2 and Cl3 cap the octahedral faces at 270–277 pm. Indeed all chlorine atoms are in capping positions to triangles of metal atoms which belong to one M_2Cl_3 chain (Cl2, Cl3) or to adjacent chains (Cl1). The average M–Cl distances for these are 280.6 (Cl1), 276.2 (Cl2), and 273.9 pm (Cl3). These differences of distances are easily understood from inspection of the environments shown in Figure 1. The repulsion between Cl1 atoms arranged along b on both sides of the triangles formed by Y2 atoms accounts for the comparatively large distances Y2–Cl1, whereas the shortest dis-

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tances occur with Cl3 which is only attached to one side of a Y1, Y2 triangle. The Y–Cl2 distances are influenced by the dual functionality of Cl2 which also occupies an exo position on Y1 in a neighboring chain at 313 pm, and vice versa. This additional bonding appears to systematically lengthen the Y–Cl2 distances relative to Y–Cl3. The effect of both bridging steps is to cause the metal chains to alternate in $b/2$ displacements, Figure 1.

Such effective means of occupying exo positions of the metal chain also result in some short nonbonded interactions between chlorine atoms, namely, 330 pm both for Cl2–Cl2 across the bridge (×2) and between Cl2 and the apex-bridging Cl1. The bridging Cl1's each have two Cl1 neighbors at 342 pm, the only contact which would appear to limit contraction of the chain along *b*. Approximate van der Waals contacts (353 pm) are also found between both the bridging Cl1 and Cl3 (×2) and Cl2–Cl3 on the same chain. The structure appears to be quite tightly packed indeed, so that all chlorine atoms achieve 12-coordination when distances to 382 pm are included, Cl2 having one more metal and thence one fewer chlorine neighbor. The whole collection of close nonmetal contacts in fact suggests that these may be responsible for (a) the long period of the chain octahedra along *b*, (b) a lower limit on the size of metal which may be incorporated, excluding scandium for instance, and (c) possibly the large difference in metal–metal distances to the apex metal atoms relative to those in the shared edge.

Metal–chlorine distances in Y_2Cl_3 and related compounds are close to those predicted when one employs standard crystal radii of the *trivalent* metals and halogen. The proper coordination number to use for the yttrium atoms is not very obvious, as these have five halogen and four or five metal neighbors. Taking the values for CN = 8, the sum of crystal radii[26] is 283 pm for yttrium–chlorine and 286 pm for gadolinium–chlorine. These values compare rather well with 270–282 and 273–286 pm for the shorter equivalent M–Cl distances in Y_2Cl_3 and Gd_2Cl_3, respectively.

Of course, the very unbalanced electrostatic environment of the atoms holds against a description in terms of a conventional coordination numbers and radii, as pointed out earlier for the distribution of Y–Cl distances. Yet all compounds of the sort listed in Table I for which accurate distances are available have shorter M–X distances which lie between the sum of crystal radii and 15 pm less (except around the relatively open apicies in Sc_7Cl_{10}[11] where some covalent shortening[26] is implied). The absolute bond lengths as well as the agreement between observed and calculated differences [d(Gd–Cl) – d(Y–Cl) ≈ 3 pm] suggest a description of the bonds as "ionic". More important is the fact that the residual valence electrons at the metal atoms do not screen halides and therefore must be delocalized *within* the chains of polyhedra. Otherwise a lengthening of the M–Cl bonds of about 20 pm might be expected for dipositive states on the basis of observed distances for localized states of titanium(III) and europium(II) for example.[26]

There are other indications that these compounds are indeed highly polar and relatively ionic. Band structure calculations on ScCl and ZrCl[27] indicate only small mixing between the energetically relatively well-separated metal valence (3d or 4d) and chlorine 3p orbitals, and UPS/XPS spectra of a number of the highly reduced zirconium,[20,28] scandium,[28] and gadolinium[29] chlorides show that the energy separation of metal and halogen valence orbitals is sizable and general. This has led to the view[16] that these unusual structures arise from a domination of the metal–metal bonding with only a relatively small nonmetal contribution to the valence band, the halide serving more to compensate charge, to cap exposed faces and to fill otherwise empty exo positions of the metal structures. In the extreme the present structure might be formulated as $[(M^{3+})_2(e^-)_3](Cl^-)_3$ to represent metallic bonding within the chains and ionic bonding between them. This is noteworthy in that it represents just the inverse of the situation found with the alkali-metal suboxides, where ionic metal–oxygen clusters appear surrounded and linked by metallic regions.[30]

The metal–metal bonding in the Y_2Cl_3 chains is the hardest to describe in a qualitative sense. The atom on the shared edge, Y1, is significantly more bonded than that at the apex, Y2, with an additional metal neighbor to the former at 327 pm, and this appears to be reflected in a systematically closer approach (3–6 pm) of chlorine to the presumably more positive or less shielded apex atom Y2 (or Gd2[7]). On the other hand such conclusions on chemical bonding are not too well secured by structural arguments. Thus the different lengths of Y2–Cl3 and Y1–Cl3 could as well be a consequence of keeping the chlorine atoms near the Coulomb minimum of the distorted triangular face of metal atoms.

Comparison of metal–metal distances in Y_2Cl_3 and Gd_2Cl_3 leads at first sight to a rather unusual result. In the elements the interatomic distances are almost identical, leading to definitions of "metallic radii"[31] and "single-bond radii"[32] for both elements which differ by no more than 1 pm. Since their sesquihalide structures are very similar, nearly equal metal–metal distances would be expected, yet the yttrium chain is smaller by 10.5 pm in the short shared waist, 9.1 and 8.9 in the apex–waist dimensions, and 7.1 pm in the long *b* repeat. The distances observed all lie between the separations in the respective metals and twice their "single-bond radii" except for the long *b* repeat.

The separation of the apex and waist metal atoms in the octahedra may well be fixed by the chlorine atoms which cap the faces of the octahedra at fairly acute M–Cl–M angles (85–86°). Thus the 9.0–9.1 pm differences between Y_2Cl_3 and Gd_2Cl_3 reflect something of, but still well exceed, twice the difference of the core radii for M^{3+}. However it is hard to see how the greater difference in short dimer separations, 326.6 vs. 337.1 pm, could be determined by anion contacts. It is evident that the closer the approach of the metal atoms, the larger is the difference between Y–Y and Gd–Gd distances.

This behavior appears to correlate with differences of atomic properties which show up in the macroscopic property of a smaller compressibility for gadolinium.[33] Thus the yttrium–gadolinium comparison which is usually cited is based mostly on a chemical similarity arising principally from effects of core size, but it disregards the fact that the valence bands in the metals involve different orbitals, 4d vs. 5d with $4f^7$ shielding. Accordingly the metals have substantially different Fermi surfaces[34] and their cohesive energies differ by 5%[33] although the densities of occupied states are quite similar. In this view the very similar molar volumes[33] are only an accident in the presence of substantially different bonding of the two metals. Furthermore it should be remarked that gadolinium metal itself is somewhat of an anomaly volumewise, exhibiting a positive deviation in volume of 2–3% from what would produce a smooth trend with its neighboring elements,[33,35] a deviation

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which is however not always reflected in lattice constants of alloys.[31] The present data imply perhaps an even larger effective metallic radius. In any case the metallic radius of gadolinium appears to be a totally unreliable benchmark.

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Registry No. YCl, 14530-75-7; YBr, 17655-40-2; Y_2Cl_3, 73728-21-9; Y_2Br_3, 73728-20-8; YCl_3, 10361-92-9; YBr_3, 13469-98-2; Y, 7440-65-5.

Supplementary Material Available: Tables of structure factor amplitudes (2 pages). Ordering information is given on any current masthead page.

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Spectroscopic Study on the Interaction of Tricyclopentadienides of Lanthanoid Elements with Metal Carbonyl Derivatives. 2.[1] Lewis Basicity of Nitric Oxide in Organometallic Nitrosyl Derivatives and Structures of Their Adducts with Tricyclopentadienylsamarium

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The Lewis basicity of nitric oxide, NO, in metal nitrosyl derivatives, $(\eta^5\text{-}C_5H_5)Cr(CO)_2NO$, $[(\eta^5\text{-}C_5H_5)FeNO]_2$, $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$, $(\eta^5\text{-}CH_3C_5H_4)_3Mn_3(NO)_4$, and $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)NO]_2$, has been studied by interaction of these complexes with the Lewis acid tricyclopentadienylsamarium, Cp_3Sm. IR spectra of the reaction mixtures displayed bands diagnostic of Cp_3Sm coordinated to terminal, two-metal bridging, and three-metal bridging NO. The order of the Lewis basicity of nitric oxide toward Cp_3Sm was terminal NO $\gtrsim$ two-metal bridging NO $\sim$ three-metal bridging NO. The proportion of cis-bridged isomers was increased by adding Cp_3Sm to $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$. $(\eta^5\text{-}CH_3C_5H_4)_3Mn_3(NO)_4$ was synthesized by refluxing a benzene solution of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)NO]_2$.

Nitric oxide, NO, forms a variety of complexes which are structurally and electronically similar to metal carbonyl derivatives.[2] However, only a few compounds with bridging nitrosyls have been subjected to structural elucidation.[3,4] Of particular interest in the study of organometallic compounds with bridging nitrosyls is the possibility of NO scrambling similar to the widely recognized phenomenon of CO scrambling.[5] For instance, it has been claimed that $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ shows a cis–trans equilibrium in solutions similar to the case of isoelectronic $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$.[6] So far, infrared spectroscopy has played a major role in the study of this kind of bridged–nonbridged and/or cis–trans equilibrium of metal carbonyl and nitrosyl derivatives in solutions. Of particular importance is the work of Shriver and his group who have employed IR spectra to study the influence of group 3 Lewis acids on bridge–terminal equilibria of metal carbonyl derivatives in solution.[7,8] Because of the isoelectronic nature of NO^+ to CO, the ligand NO in organometallic nitrosyl compounds is expected to display similar Lewis basicity, and therefore Lewis acids might provide valuable insight into the structures and equilibria of organometallic nitrosyl derivatives in solutions. However, only a few studies have so far been made on the Lewis basicity of ligand NO in nitrosyl metal derivatives.[9] The present study was undertaken to investigate the Lewis basicity of NO for three kinds of ligation modes, that is, terminal, two-metal bridged, and three-metal bridged ligation, and to elucidate structures and equilibria between organometallic nitrosyls and the hard Lewis acid tricyclopentadienylsamarium, $(\eta^5\text{-}C_5H_5)_3Sm$.[10]

Experimental Section

All reactions were carried out under a purified nitrogen atmosphere.[11] All solvents were distilled under a nitrogen atmosphere from calcium chloride or sodium benzophenone ketyl. Sampling techniques and IR spectral measurements have been described elsewhere.[1]

The nitrosyl derivatives $(\eta^5\text{-}C_5H_5)Cr(CO)_2NO$, $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$, and $[(\eta^5\text{-}C_5H_5)FeNO]_2$ were synthesized according to literature methods.[9,12,13] Manganese nitrosyl derivatives were synthesized

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