Structural Diversity in Solvated Lanthanide Halide Complexes[1]

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Crystallization of lanthanide trichlorides from neat ϵ-caprolactone ($C_6H_{10}O_2$) and caprolactone/THF mixtures has revealed a much more diverse structural chemistry for solvated lanthanide trichloride complexes than had previously been observed. As the metal is varied, different products preferentially crystallize under the same conditions to give a series of complexes which do *not* vary smoothly in composition as a function of radial size. The following compounds, in order of increasing radial size of the metal, have been structurally characterized: $YbCl_3(C_6H_{10}O_2)(THF)_2$, **1**; $YCl_3(C_6H_{10}O_2)_3$, **2**; $[TbCl_4(THF)_2]^-[TbCl_2(THF)_5]^+$, **3**; $[Cl_3Sm(\mu\text{-}Cl)_3SmCl_3]^{3-}[Sm(C_6H_{10}O_2)_8]^{3+}$, **4**; $[Cl_3Nd(\mu\text{-}Cl)_3NdCl_3]^{3-}$ $[Nd(C_6H_{10}O_2)_8]^{3+}$, **5**. In the course of these studies, the polymeric halides $[NdCl(\mu\text{-}Cl)_2(THF)_2]_n$, **6**, and $[CeCl(\mu\text{-}Cl)_2(THF)_2]_n$, **7**, were also identified by X-ray crystallography. Although both **1** and **2** have octahedral geometries, they differ in the amount of caprolactone present and the fact that **1** is facial while **2** is meridional. The ion pair system **3** contains a six-coordinate anion with a *trans* octahedral geometry and a seven-coordinate cation with axial chloride ligands in a pentagonal bipyramidal structure. Complexes **4** and **5** contain bimetallic trianions devoid of caprolactone which adopt a face-sharing bioctahedral geometry. The eight-coordinate cations in **4** and **5** contain no chloride ligands and adopt a square antiprismatic geometry. Isostructural **6** and **7** contain seven-coordinate pentagonal bipyramidal metal centers surrounded by four bridging chloride atoms, one terminal chloride, and two terminal THF ligands. $YbCl_3(C_6H_{10}O_2)(THF)_2$, **1**, crystallized from ϵ-caprolactone/THF in space group $P2_1/n$ [C_{2h}^5; No. 14] with $a = 11.580(2)$ Å, $b = 12.802(3)$ Å, $c = 13.532(3)$ Å, $\beta = 103.462(15)°$, $V = 1951.0(7)$ Å^3, and $D_{calcd} = 1.831$ Mg/m^3 for $Z = 4$. Least-squares refinement of the model based on 3894 reflections ($|F_o| > 3.0\sigma(|F_o|)$) converged to $R_F = 3.5\%$. $YCl_3(C_6H_{10}O_2)_3$, **2**, crystallized from both ϵ-caprolactone/THF and neat ϵ-caprolactone in the space group $P\bar{1}$ with $a = 10.083(1)$ Å, $b = 11.706(1)$ Å, $c = 11.702(1)$ Å, $\alpha = 60.071(7)°$, $\beta = 81.274(9)°$, $\gamma = 75.741(8)°$, $V = 1159.4(2)$ Å^3, and $D_{calcd} = 1.540$ Mg/m^3 for $Z = 2$. Least-squares refinement of the model based on 4846 observed reflections ($|F_o| > 2.0\sigma(|F_o|)$) converged to $R_F = 4.0\%$. $[TbCl_4(THF)_2]^-[TbCl_2(THF)_5]^+$, **3**, crystallized from ϵ-caprolactone/THF in the space group $C2/c$ [C_{2h}^6; No. 15] with $a = 12.401(2)$ Å, $b = 11.420(2)$ Å, $c = 27.413(3)$ Å, $\beta = 91.100(11)°$, $V = 3881.4(9)$ Å^3, and $D_{calcd} = 1.772$ Mg/m^3 for $Z = 8$. Least-squares refinement of the model based on 3936 reflections ($|F_o| > 3.0\sigma(|F_o|)$) converged to $R_F = 3.4\%$. $[Cl_3Sm(\mu\text{-}Cl)_3SmCl_3]^{3-}[Sm(C_6H_{10}O_2)_8]^{3+}$, **4**, was found to be isomorphous with **5** by a unit cell determination. $[Cl_3Nd(\mu\text{-}Cl)_3NdCl_3]^{3-}[Nd(C_6H_{10}O_2)_8]^{3+}$, **5**, crystallized from both ϵ-caprolactone/THF and neat ϵ-caprolactone in the space group $P2_1/c$ [C_{2h}^5; No. 14] with $a = 19.661(4)$ Å, $b = 11.775(4)$ Å, $c = 28.141(5)$ Å, $\beta = 96.615(16)°$, $V = 6471(3)$ Å^3, and $D_{calcd} = 1.709$ Mg/m^3 for $Z = 4$. Least-squares refinement of the model based on 6823 reflections ($|F_o| > 3.0\sigma(|F_o|)$) converged to $R_F = 5.5\%$. $[NdCl(\mu\text{-}Cl)_2(THF)_2]_n$, **6**, crystallized from a solution of benzophenone in THF in the space group $P\bar{1}$ [C_i^1; No. 2] with $a = 8.2327(13)$ Å, $b = 8.6177(14)$ Å, $c = 9.736(2)$ Å, $\alpha = 79.621(13)°$, $\beta = 70.594(12)°$, $\gamma = 82.595(13)°$, $V = 639.0(2)$ Å^3, and $D_{calcd} = 2.052$ Mg/m^3 for $Z = 2$. Least-squares refinement of the model based on 2922 reflections ($|F_o| > 3.0\sigma(|F_o|)$) converged to a final $R_F = 1.9\%$. $[CeCl(\mu\text{-}Cl)_2(THF)_2]_n$, **7**, crystallized from a solution of L,L-lactide in THF in the space group $P\bar{1}$ [C_i^1; No. 2] with $a = 8.2558(12)$ Å, $b = 8.7154(10)$ Å, $c = 9.7892(12)$ Å, $\alpha = 79.568(10)°$, $\beta = 70.580(10)°$, $\gamma = 82.583(10)°$, $V = 651.50(14)$ Å^3, and $D_{calcd} = 1.991$ Mg/m^3 for $Z = 2$. Least-squares refinement of the model based on 1614 reflections ($|F_o| > 3.0\sigma(|F_o|)$) converged to $R_F = 2.1\%$.

Introduction

Yttrium and lanthanide trichlorides, which are common starting materials for syntheses of many types of complexes involving these metals, typically crystallize in the presence of donor ligands, L, as monometallic seven-coordinate pentagonal bipyramidal species of general formula $LnCl_3L_4$. Crystallographically characterized examples include the complexes $YCl_3(DME)_2$ (DME = dimethoxyethane),[2] $GdCl_3(DME)_2$,[3] $LnCl_3(THF)_4$ (Ln = Eu,[4] Nd[5]), $SmCl_3(DME)(THF)_2$,[6] and $EuCl_3(pyridine)_4$.[7] With some donor ligands, polymeric seven- or eight-coordinate species are observed, e.g. $[YCl_3(TEG)(18\text{-}crown\text{-}6)]_n$[8] (TEG = triethylene glycol) and $[La(\mu\text{-}Cl)_3(C_7H_8O_2)_2]_n$[9] ($C_7H_8O_2$ = 2,6-dimethyl-4-pyrone).

Recently, as part of an investigation of the initial steps in the ring opening polymerization of monomers such as ϵ-capro-

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lactone, which are of interest because they form biodegradable polymers,[10] we isolated a *six-coordinate* lanthanide chloride, $YCl_3(C_6H_{10}O_2)_3$, **2** ($C_6H_{10}O_2$ = ε-caprolactone).[11] Prior to this time, the only six-coordinate lanthanide trichlorides in the literature were the complexes $GdCl_3$(2,6-dimethyl-4-pyrone)$_3$[12] and $LnCl_3(HMPA)_3$ (Ln = Pr,[13] Yb;[14] HMPA = hexamethylphosphoramide). Recently, the complexes $[YbCl_2(\mu\text{-Cl})(THF)_2]_2$,[15] $YbCl_3(THF)_3$,[15] and $LuCl_3(THF)_3$,[16] which are also six-coordinate, appeared in the literature. Since $YCl_3(C_6H_{10}O_2)_3$ was unusual in that it crystallized as a six-coordinate structure even in the presence of an adjacent oxygen donor atom in the coordinating ε-caprolactone, we decided to look more broadly at the effects of caprolactone and related species, such as L,L-lactide[10] and benzophenone, in the coordination chemistry of lanthanide trichlorides.

On the basis of previous results with solvated lanthanide trihalides and a variety of other types of lanthanide complexes,[17,18] one would expect that ε-caprolactone trichloride complexes of lanthanides with radii similar to that of yttrium would have a similar structure and that, at some point as the metal size is increased, a higher coordinate structure might form. The solid state structures of the unsolvated lanthanide trihalides also follow this trend; i.e., they are rather uniform in structure across the lanthanide series.[19] We report here that, with caprolactone, a diverse array of products forms which shows no particular pattern in terms of ease of formation, method of crystallization, size of the metal, or nature of the coordinating ligand. These results suggest that the structural chemistry of solvated lanthanide trichlorides is not nearly as simple as previously assumed. The structures of several complexes and their implications in lanthanide reaction chemistry are described here.

Experimental Section

All compounds described below were handled under nitrogen with rigorous exclusion of air and water using standard Schlenk, vacuum line, and glovebox techniques. Solvents were prepared and physical measurements obtained as previously described.[20] ε-Caprolactone was dried over 4-Å molecular sieves and degassed. Benzophenone (Aldrich) and L,L-lactide (Aldrich) were sublimed prior to use. Lanthanide trichlorides were dried as previously described.[21]

General Procedure. In a glovebox, an array of crystallizations was set up using both a 1:1 solution (v/v) of ε-caprolactone/THF and neat ε-caprolactone for trichlorides of the following metals: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, Er, Yb, Lu. For all of the metals used, it was observed that the trichlorides readily dissolve in the presence of caprolactone whereas in pure THF they exhibit only low solubility. It was also observed that some lanthanides were more soluble than others in this solvent mixture, but this behavior did not vary consistently with the radial size of the metal. The effective solubility of each trichloride was evaluated by slowly adding (2−3 mg at a time) anhydrous $LnCl_3$ both to 2.0 mL of a premixed 1:1 solution of ε-caprolactone and THF and to 2.0 mL of THF until no further solid was dissolved. The amount of material which went into solution varied in the following way at 24 °C. $LnCl_3$, mg/mL, in 1:1 ε-caprolactone/THF (color): $LaCl_3$, 20 (colorless); $CeCl_3$, 20 (colorless); $PrCl_3$, 25 (pale green); $NdCl_3$, 50 (pale blue); $SmCl_3$, 110 (peach); $EuCl_3$, 40 (yellow); $GdCl_3$, 40 (peach); $TbCl_3$, 220 (pale orange); $DyCl_3$, 40 (colorless); YCl_3, 255 (pink-brown); $ErCl_3$, 60 (pink); $YbCl_3$, 140 (pink); $LuCl_3$, 60 (pink). $LnCl_3$, mg/mL, in THF, (color): $LaCl_3$, 2 (colorless); $CeCl_3$, 2 (colorless); $PrCl_3$, 5 (colorless); $NdCl_3$, 5 (very pale blue); $SmCl_3$, 10 (colorless); $EuCl_3$, 15 (colorless); $GdCl_3$, 8 (colorless); $TbCl_3$, 12 (colorless); $DyCl_3$, 1 (colorless); YCl_3, 1 (colorless); $ErCl_3$, 6 (very pale pink); $YbCl_3$, 12 (colorless); $LuCl_3$, 14 (colorless).

Solutions for crystallizations were prepared by adding the lanthanide trichlorides to ca. 5 mL solutions of 1:1 ε-caprolactone/THF or of neat caprolactone until no more was dissolved. The solutions were stirred for 12 h and excess solid was removed by centrifugation. Crystals were formed by slow evaporation of the solution at ambient temperature. Only those systems which formed crystals suitable for X-ray crystallography could be fully defined. These are described below. Complexes **6** and **7** were crystallized from a 1:10 mixture of $NdCl_3$ and benzophenone in THF (ca. 5 mL) and a 1:10 mixture of $CeCl_3$ and L,L-lactide in THF (ca. 5 mL), respectively. Handling the crystals was complicated by their tendency to desolvate. IR spectra were obtained for the following samples. $YCl_3(C_6H_{10}O_2)_3$ (KBr): 4359 w, 4276 w, 4029 w, 3348 br, s, 3230 br, s, 2937 s, 2866 m, 2701 w, 1728 s, 1634 m, 1475 m, 1440 m, 1393 m, 1346 m, 1328 m, 1293 s, 1252 s, 1223 m, 1164 s, 1090 s, 1052 s, 1017 s, 987 m, 958 m, 887 w, 864 m, 846 m, 735 w, 693 w, 564 m cm^{-1}. $YbCl_3(THF)_2(C_6H_{10}O_2)$ (KBr): 4347 w, 4041 w, 3348 br, s, 2937 s, 2866 s, 1728 s, 1640 s, 1475 m, 1440 m, 1393 m, 1346 m, 1322 m, 1293 s, 1252 s, 1222 m, 1164 s, 1090 s, 1052 s, 1011 s, 981 m, 964 m, 893 w, 858 w, 840 w, 735 w, 693 w, 570 w cm^{-1}. $[Nd(C_6H_{10}O_2)_8][Nd_2Cl_9]$ (KBr): 4359 w, 3935 w, 3348 br, s, 2948 br, s, 2866 s, 1687 br, s, 1616 br, s, 1475 m, 1440 m, 1399 m, 1352 m, 1328 m, 1293 s, 1252 s, 1228 m, 1175 s, 1090 s, 1046 s, 1011 s, 987 m, 958 w cm^{-1}.

General Aspects of X-ray Data Collection, Structure Determination, and Refinement for 1−3 and 5−7. In each case, a crystal was immersed in Paratone-D oil under nitrogen and then manipulated in air onto a glass fiber and transferred to the nitrogen stream of a Syntex $P2_1$ diffractometer equipped with a modified LT-1 low-temperature system or a Siemens P3 diffractometer (Siemens R3m/V System) equipped with a modified LT-2 low-temperature system. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out using standard techniques similar to those of Churchill.[22] All data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. Any reflection with I(net) < 0 was assigned the value $|F_o| = 0$. All crystallographic calculations were carried out using either our locally modified version of the UCLA Crystallographic Computing Package[23] or the SHELXTL PLUS program set.[24] The analytical scattering factors for neutral atoms were used throughout the analysis,[25] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included. The quantity

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Table 1. Experimental Data for X-ray Diffraction Studies of $YbCl_3(C_6H_{10}O_2)(THF)_2$, **1**, $YCl_3(C_6H_{10}O_2)_3$, **2**, $[TbCl_4(THF)_2]^-[TbCl_2(THF)_5]^+$, **3**, $[Cl_3Nd(\mu\text{-}Cl)_3NdCl_3]^{3-}[Nd(C_6H_{10}O_2)_8]^{3+}$, **5**, $[NdCl(\mu\text{-}Cl)_2(THF)]_n$, **6**, and $[CeCl(\mu\text{-}Cl)_2(THF)]_n$, **7**[a]

	1	**2**	**3**	**5**	**6**	**7**
formula	$C_{14}H_{26}O_4Cl_3Yb$	$C_{18}H_{30}O_6Cl_3Y$	$C_{28}H_{56}O_7Cl_6Tb_2$	$[Cl_9Nd_2][C_{48}H_{80}O_{16}Nd]$	$[C_8H_{16}O_2Cl_3Nd]_n$	$[C_8H_{16}O_2Cl_3Ce]_n$
fw	537.7	537.7	1035.3	1664.9	394.8	390.7
temp (K)	158	168	168	158	158	163
crystal system	monoclinic	triclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$C2/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.580(2)	10.083(1)	12.401(2)	19.661(4)	8.2327(13)	8.2558(12)
b (Å)	12.802(3)	11.706(1)	11.420(2)	11.775(4)	8.6177(14)	8.7154(10)
c (Å)	13.532(3)	11.702(1)	27.413(3)	28.141(5)	9.736(2)	9.7892(12)
α (deg)		60.071(7)			79.621(13)	79.568(10)
β (deg)	103.462(15)	81.274(9)	91.100(11)	96.615(16)	70.594(12)	70.580(10)
γ (deg)		75.741(8)			82.595(13)	82.583(10)
V (Å^3)	1951.0(7)	1159.4(2)	3881.4(9)	6471(3)	639.0(2)	651.50(14)
Z	4	2	8	4	2	2
D_{calcd} (Mg/m^3)	1.831	1.540	1.772	1.709	2.052	1.991
diffractometer	Siemens P3	Siemens P3	Syntex P2$_1$	Siemens P3	Siemens P3	Syntex P2$_1$
data collected	$+h,+k,\pm l$	$+h,\pm k,\pm l$	$+h,+k,+l$	$+h,+k,\pm l$	$+h,\pm k,\pm l$	$+h,\pm k,\pm l$
scan type	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$
2θ range (deg)	4.0−55.0	4.0−55.0	4.0−55.0	4.0−45.0	4.0−55.0	4.0−45.0
μ(Mo Kα), mm^{-1}	5.206	2.907	4.112	2.814	4.689	3.890
no. of reflns collected	4980	5668	4918	9317	3166	1853
no. of reflns with $\lvert F_o\rvert > X\sigma(\lvert F_o\rvert)$	3894 ($X = 3$)	4846 ($X = 2$)	3936 ($X = 3$)	6823 ($X = 3$)	2922 ($X = 3$)	1614 ($X = 3$)
no. of variables	209	253	197	685	192	191
R_F, %	3.5	4.0	3.4	5.5	1.9	2.1
R_{wF}, %	4.5	5.8	4.4	5.8	2.9	2.8
goodness of fit	1.36	0.87	1.56	1.72	1.72	1.07

[a] Radiation: Mo Kα ($\bar{\lambda} = 0.710\,730$ Å). Monochromator: highly oriented graphite. Scan range: 1.20° plus Kα separation. Scan speed: 3.0° min^{-1} (in ω). Absorption correction: semiempirical (φ-scan method).

minimized during least-squares analysis was $\Sigma w(|F_o| - |F_c|)^2$ where w^{-1} is defined below. The structures were refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with d(C−H) = 0.96 Å and U(iso) = 0.08 Å^2 except where noted. Experimental details are given in Table 1 and in the supplementary material.

$YbCl_3(C_6H_{10}O_2)(THF)_2$, 1. **1** was crystallized from anhydrous $YbCl_3$ in a 1:1 mixture of ϵ-caprolactone and THF. Repeated attempts to obtain crystals from a solution of $YbCl_3$ in neat ϵ-caprolactone were unsuccessful. A total of 4980 data were collected on a colorless crystal of approximate dimensions 0.30 × 0.30 × 0.43 mm^3 at 158 K. The diffraction symmetry was $2/m$ with systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/n$, a nonstandard setting of $P2_1/c$ [C_{2h}^5; No. 14], is therefore uniquely defined. The quantity w^{-1} was defined as $\sigma^2(|F_o|) + 0.0005(|F_o|)^2$. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Carbon C(8) is disordered and was included with two components C(8) and C(8A) with site occupancy factors of 0.55 and 0.45, respectively. Refinement of positional and thermal parameters led to a convergence with $R_F = 3.5\%$, $R_{wF} = 4.5\%$, and GOF = 1.36 for 209 variables refined against those 3894 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier map yielded ϱ(max) = 1.04 e Å^{-3}.

$YCl_3(C_6H_{10}O_2)_3$, 2. For the complete structural determination, **2** was crystallized from anhydrous YCl_3 in ϵ-caprolactone. **2** was also crystallized from a 1:1 mixture of ϵ-caprolactone and THF, and the crystals were identified by a unit-cell determination. A total of 5668 data were collected on a colorless crystal of approximate dimensions 0.33 × 0.40 × 0.50 mm^3 at 168 K. The diffraction symmetry was $P\bar{1}$. The quantity w^{-1} was defined as $\sigma^2(|F_o|) + 0.0031(|F_o|)^2$. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix and least-squares techniques. Refinement of positional and thermal parameters led to a convergence with $R_F = 4.0\%$, $R_{wF} = 5.8\%$, and GOF = 0.87 for 253 variables refined against those 4846 data with $|F_o| > 2.0\sigma(|F_o|)$. A final difference-Fourier map yielded ϱ(max) = 0.48 e Å^{-3}.

$[TbCl_4(THF)_2]^-[TbCl_2(THF)_5]^+$, 3. **3** was crystallized from anhydrous $TbCl_3$ in a 1:1 mixture of ϵ-caprolactone and THF. A total of 4918 data were collected on a colorless crystal of approximate dimensions 0.30 × 0.32 × 0.50 mm^3 at 168 K. The systematic extinctions observed were hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$; the diffraction symmetry was $2/m$. The two possible monoclinic space groups are Cc [C_s^4; No. 9] and $C2/c$ [C_{2h}^6; No. 15]. The centrosymmetric space group $C2/c$ was later determined to be the correct choice. The quantity w^{-1} was defined as $\sigma^2(|F_o|) + 0.0004(|F_o|)^2$. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. There are two independent and different ions in the asymmetric unit cell. Tb(1) is located on a 2-fold rotation axis at (0, y, $^1/_4$), and Tb(2) is located on an inversion center at ($^1/_4$, $^1/_4$, 0). Refinement of positional and anisotropic thermal parameters led to a convergence with $R_F = 3.4\%$, $R_{wF} = 4.4\%$, and GOF = 1.56 for 197 variables refined against those 3936 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier map was devoid of significant features, ϱ(max) = 0.79 e Å^{-3}.

$[Cl_3Sm(\mu\text{-}Cl)_3SmCl_3]^{3-}[Sm(C_6H_{10}O_2)_8]^{3+}$, 4. **4** was crystallized from anhydrous $SmCl_3$ in a 1:1 mixture of ϵ-caprolactone and THF. The crystal was of poor quality; therefore only unit-cell data were obtained. Unit cell: a = 19.69(1) Å, b = 11.78(1) Å, c = 28.2(1) Å, β = 96.54(6)°, V = 6450 Å^3.

$[Cl_3Nd(\mu\text{-}Cl)_3NdCl_3]^{3-}[Nd(C_6H_{10}O_2)_8]^{3+}$, 5. For the complete structural determination, **5** was crystallized from anhydrous $NdCl_3$ in a 1:1 mixture of ϵ-caprolactone and THF. **5** was also crystallized from neat ϵ-caprolactone and identified by a unit-cell determination. A total of 9317 data were collected on a pale blue crystal of approximate dimensions 0.30 × 0.33 × 0.33 mm^3 at 158 K. The diffraction symmetry was $2/m$ with systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14] is therefore uniquely defined. The quantity w^{-1} was defined as $\sigma^2(|F_o|) + 0.0004(|F_o|)^2$. The structure was solved by direct methods (SHELXTL PLUS) and refined by least-squares techniques. There are two different independent molecules in the asymmetric unit. Refinement of positional and anisotropic thermal parameters led to a convergence with $R_F = 5.5\%$, $R_{wF} = 5.8\%$, and GOF = 1.72 for 685 variables refined against those 6823 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier map yielded ϱ(max) = 0.87 e Å^{-3}.

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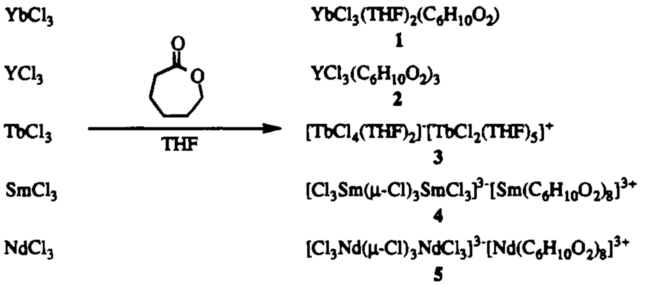
(24) Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990. Sheldrick, G. M. *SHELX: A System of Computer Programs for X-ray Structure Determination;* 1976.

(25) *International Tables for X-ray Crystallography*; Kluwer: Dordrecht, The Netherlands, 1992; Vol. C.

Scheme 1



$[NdCl(\mu\text{-}Cl)_2(THF)_2]_n$, 6. **6** was crystallized from anhydrous $NdCl_3$ in a solution of 10-fold molar excess (based on Nd) of benzophenone in THF. A total of 3166 data were collected on a pale blue crystal of approximate dimensions 0.23 × 0.30 × 0.42 mm^3 at 158 K. There were no systematic extinctions nor any diffraction symmetry other than the Friedel condition. The two possible triclinic space groups are the noncentrosymmetric $P1$ [C_1^1; No. 1] or the centrosymmetric $P\bar{1}$ [C_i^1; No. 2]. Refinement of the model using the centrosymmetric space group proved it to be the correct choice. The quantity w^{-1} was defined as $\sigma^2(|F_o|) + 0.00023(|F_o|)^2$. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. The complex is a chain structure elongated along the b axis with inversion centers at (0, 0, 0; 0, $^1/_2$, 0; 0, 1, 0; etc.) resulting in two different Nd_2Cl_2 units. Hydrogen atoms were located from a difference-Fourier synthesis and refined with isotropic thermal parameters. Refinement of the model led to convergence with $R_F = 1.9\%$, $R_{wF} = 2.9\%$, and GOF = 1.72 for 192 variables refined against those 2922 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier map yielded $\varrho(\max) = 0.89$ e Å^{-3}.

$[CeCl(\mu\text{-}Cl)_2(THF)_2]_n$, 7. **7** was crystallized from anhydrous $CeCl_3$ in a solution of a 10-fold molar excess (based on Ce) of L,L-lactide in THF. A total of 1853 data were collected on a colorless crystal of approximate dimensions 0.20 × 0.20 × 0.26 mm^3 at 163 K. The unit cell suggested that the complex was isostructural with its neodymium analog, **6**, and the coordinates from the neodymium complex were used as a starting model for least-squares refinement. Hydrogen atoms were refined with isotropic thermal parameters. Refinement of the model led to convergence with $R_F = 2.1\%$, $R_{wF} = 2.8\%$, and GOF = 1.07 for 191 variables refined against those 1614 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier map yielded $\varrho(\max) = 1.03$ e Å^{-3}.

Results

Yttrium and lanthanide trichlorides typically exhibit low solubility when placed in THF. However, the trichlorides of yttrium and all of the lanthanides studied here (Pm, Tm, and Ho were not examined) readily dissolve in the presence of caprolactone with Tb, Sm, Y, and Yb dissolving more readily in caprolactone/THF mixtures than La, Ce, Pr, Nd, Er, and Lu. Crystallization of the metal trichlorides from this solvent system gave the results shown in Scheme 1. Each system is described in more detail below.

$YCl_3(C_6H_{10}O_2)_3$, 2. This study was initiated because we found that YCl_3 crystallizes from ϵ-caprolactone as the six-coordinate species $YCl_3(C_6H_{10}O_2)_3$ (Figure 1)[11] rather than as a seven- or eight-coordinate structure previously found.[2-9] Crystals of **2** can be isolated from either ϵ-caprolactone or a 1:1 mixture of ϵ-caprolactone and THF. The structure of **2** is only slightly distorted from a regular octahedral geometry with (ligand)−Y−(*trans* ligand) angles of 166.8(1), 177.9(1), and 178.7(1)° (Table 2). Eight of the twelve (ligand)−Y−(*cis* ligand) angles are within 2° of 90°. The three chloride ligands adopt a meridional geometry which is like the T-shaped arrangement of halides in seven-coordinate pentagonal bipyramidal $LnCl_3(L)_4$ complexes.[5-12] The recently reported structures of $YbCl_3(THF)_3$[15] and $LuCl_3(THF)_3$[16] also have meridional geometries as does $PrCl_3(HMPA)_3$.[13] In contrast, $GdCl_3$(2,6-dimethyl-4-pyrone)$_3$[12] has a facial arrangement of halide ligands.

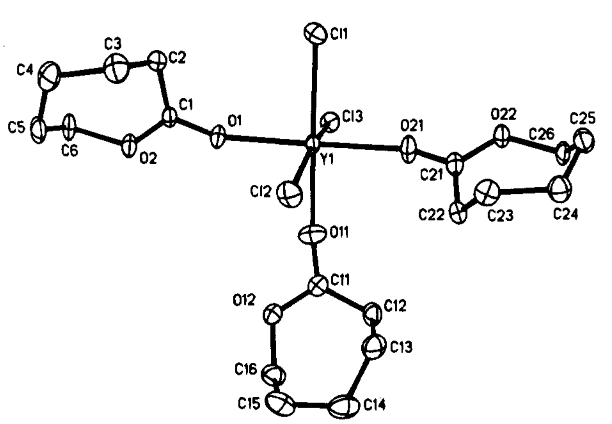


Figure 1. Thermal ellipsoid plot of $YCl_3(C_6H_{10}O_2)_3$, **2**, drawn at the 50% probability level.

As shown in Tables 2 and 4, the 2.574(1)−2.604(1) Å Y−Cl distances in **2** are comparable to the analogous terminal Y−Cl distances in seven-coordinate $[YCl_3(TEG)(18\text{-crown-}6)]_n$ (2.595(3)−2.622(2) Å)[8] and $YCl_3(DME)_2$ (2.597(2)−2.603(2) Å),[2] despite the difference in coordination number.[26] As seen in the summary Table 4, the M−(terminal Cl) distances for all of the reported lanthanide trichlorides when normalized to a single metal radius are all rather similar regardless of the coordination number or the charge on the complex.

The 2.269(2)−2.296(3) Å Y−O(caprolactone) distances in **2** are shorter than the 2.379(3)−2.457(3) Å Y−O(DME) distances in seven-coordinate $YCl_3(DME)_2$.[2] As shown in summary Table 5, these Ln−O distances are more sensitive to coordination number. This differs from the situation found in the series $(C_5Me_5)_2LnX(THF)$ (Ln = Y,[27] Sm,[27] Lu,[28] X = Cl, I), in which the normalized metal−oxygen and metal−carbon distances are quite regular and the normalized halide distances vary.

$YbCl_3(C_6H_{10}O_2)(THF)_2$, 1. Crystals of ytterbium trichloride obtained from ϵ-caprolactone/THF were expected to be six-coordinate, given that $YCl_3(C_6H_{10}O_2)_3$, $[YbCl_2(\mu\text{-}Cl)(THF)_2]_2$,[15] and $YbCl_3(THF)_3$[15] had all been found to be six-coordinate and the radial size of ytterbium is 0.032 Å less than that of yttrium. Indeed, a monometallic six-coordinate complex was observed as shown in Figure 2. The formation of $YCl_3(C_6H_{10}O_2)_3$, even in the presence of THF, suggested that caprolactone was preferred to THF as a donor solvent in these systems. Therefore, it was surprising to find that ytterbium formed a complex containing just *one* caprolactone ligand. **1** also differs from **2** and from $LuCl_3(THF)_3$,[16] $YbCl_3(THF)_3$,[15] and $PrCl_3(HMPA)_3$[13] in that it has a facial, rather than meridional, arrangement of chloride ligands. The ytterbium system is further distinct from the yttrium system in that repeated attempts to grow X-ray quality crystals from neat caprolactone were unsuccessful.

As shown in Figure 2 and Table 2, the octahedral coordination geometry around ytterbium is more distorted than that of **1**. The (ligand)−Yb−(*trans* ligand) angles are 165.6(1), 168.0(1), and 170.4(1)°, and the (ligand)−Yb−(*cis* ligand) angles range from 82.5(1) to 101.0(1)°. The 2.527(5) Å average Yb−Cl bond length is similar to the 2.490(3) Å Yb−Cl(terminal) bond distance in $[YbCl_2(\mu\text{-}Cl)(THF)_2]_2$[15] and the 2.52(5) Å distance in $YbCl_3(THF)_3$[15] (Table 3). The 2.304(6) Å average Yb−O(THF) bond length is similar to the 2.265(7) Å Yb−O(THF)

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[27] Evans, W. J.; Grate, J. W.; Levan, K. R.; Bloom, I.; Peterson, T. T.; Doedens, R. J.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1986**, *25*, 3614−2619.

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Table 2. Selected Bond Distances (Å) and Angles (deg) for $YbCl_3(C_6H_{10}O_2)(THF)_2$, **1**, $YCl_3(C_6H_{10}O_2)_3$, **2**, $[TbCl_4(THF)_2]^-[TbCl_2(THF)_5]^+$, **3**, and $[Cl_3Nd(\mu\text{-}Cl)_3NdCl_3]^{3-}[Nd(C_6H_{10}O_2)_8]^{3+}$, **5**

1		2		3		5					
						Nd(1)−Nd(2)	3.956(2)				
Yb(1)−Cl(1)	2.532(2)	Y(1)−Cl(1)	2.590(1)	Tb(1)−Cl(1)	2.598(1)	Nd(1)−Cl(1)	2.851(3)	Nd(1)−Cl(5)	2.653(3)	Nd(2)−Cl(3)	2.857(3)
Yb(1)−Cl(2)	2.521(1)	Y(1)−Cl(2)	2.574(1)	Tb(2)−Cl(2)	2.637(1)	Nd(1)−Cl(2)	2.803(3)	Nd(1)−Cl(6)	2.653(3)	Nd(2)−Cl(7)	2.672(3)
Yb(1)−Cl(3)	2.527(4)	Y(1)−Cl(3)	2.604(1)	Tb(2)−Cl(3)	2.621(1)	Nd(1)−Cl(3)	2.807(3)	Nd(2)−Cl(1)	2.813(3)	Nd(2)−Cl(8)	2.660(3)
						Nd(1)−Cl(4)	2.654(3)	Nd(2)−Cl(2)	2.807(3)	Nd(2)−Cl(9)	2.630(3)
Yb(1)−O(1)	2.271(4)	Y(1)−O(1)	2.274(2)	Tb(1)−O(1)	2.385(3)	Nd(3)−O(1)	2.480(7)	Nd(3)−O(7)	2.501(8)	Nd(3)−O(13)	2.366(8)
Yb(1)−O(3)	2.298(4)	Y(1)−O(11)	2.296(3)	Tb(1)−O(2)	2.406(3)	Nd(3)−O(3)	2.482(7)	Nd(3)−O(9)	2.523(7)	Nd(3)−O(15)	2.418(7)
Yb(1)−O(4)	2.310(4)	Y(1)−O(21)	2.269(2)	Tb(1)−O(3)	2.430(5)	Nd(3)−O(5)	2.453(7)	Nd(3)−O(11)	2.450(7)		
				Tb(2)−O(4)	2.344(3)						
Cl(1)−Yb(1)−Cl(2)	97.1(1)	Cl(1)−Y(1)−Cl(2)	98.1(1)	Cl(1)−Tb(1)−O(1)	94.6(1)	Cl(1)−Nd(1)−Cl(2)	76.3(1)	Cl(1)−Nd(2)−Cl(8)	97.5(1)	O(5)−Nd(3)−O(9)	81.4(2)
Cl(1)−Yb(1)−Cl(3)	101.0(1)	Cl(1)−Y(1)−Cl(3)	95.0(1)	Cl(1)−Tb(1)−O(2)	85.4(1)	Cl(1)−Nd(1)−Cl(3)	75.5(1)	Cl(2)−Nd(2)−Cl(8)	171.3(1)	O(7)−Nd(3)−O(9)	72.0(3)
Cl(2)−Yb(1)−Cl(3)	96.9(1)	Cl(2)−Y(1)−Cl(3)	166.8(1)	O(1)−Tb(1)−O(2)	72.4(1)	Cl(2)−Nd(1)−Cl(3)	77.4(1)	Cl(3)−Nd(2)−Cl(8)	95.7(1)	O(1)−Nd(3)−O(11)	71.5(2)
Cl(1)−Yb(1)−O(1)	86.8(1)	Cl(1)−Y(1)−O(1)	90.1(1)	Cl(1)−Tb(1)−O(3)	89.9(1)	Cl(1)−Nd(1)−Cl(4)	93.2(1)	Cl(7)−Nd(2)−Cl(8)	95.3(1)	O(1)−Nd(3)−O(11)	73.9(2)
Cl(2)−Yb(1)−O(1)	91.1(1)	Cl(2)−Y(1)−O(1)	89.2(1)	O(1)−Tb(1)−O(3)	72.0(1)	Cl(2)−Nd(1)−Cl(4)	168.2(1)	Cl(1)−Nd(2)−Cl(9)	162.6(1)	O(5)−Nd(3)−O(11)	77.3(2)
Cl(3)−Yb(1)−O(1)	168.0(1)	Cl(3)−Y(1)−O(1)	89.8(1)	O(2)−Tb(1)−O(3)	143.6(1)	Cl(3)−Nd(1)−Cl(4)	94.8(1)	Cl(2)−Nd(2)−Cl(9)	89.4(1)	O(7)−Nd(3)−O(11)	147.7(3)
Cl(1)−Yb(1)−O(3)	165.6(1)	Cl(1)−Y(1)−O(11)	177.9(1)	Cl(1)−Tb(1)−Cl(1′)	180.0(2)	Cl(1)−Nd(1)−Cl(5)	163.9(1)	Cl(3)−Nd(2)−Cl(9)	91.2(1)	O(9)−Nd(3)−O(11)	116.9(3)
Cl(2)−Tb(1)−O(3)	88.1(1)	Cl(2)−Y(1)−O(11)	83.3(1)	O(1)−Tb(1)−Cl(1′)	85.3(1)	Cl(2)−Nd(1)−Cl(5)	92.2(1)	Cl(7)−Nd(2)−Cl(9)	96.7(1)	O(1)−Nd(3)−O(13)	137.7(2)
Cl(3)−Yb(1)−O(3)	91.6(1)	Cl(3)−Y(1)−O(11)	83.5(1)	O(1)−Tb(1)−O(1′)	144.0(2)	Cl(3)−Nd(1)−Cl(5)	91.2(1)	Cl(8)−Nd(2)−Cl(9)	94.8(1)	O(3)−Nd(3)−O(13)	72.1(3)
O(1)−Yb(1)−O(3)	79.6(1)	O(1)−Y(1)−O(11)	91.4(1)	O(2)−Tb(1)−O(1′)	143.1(1)	Cl(4)−Nd(1)−Cl(5)	96.8(1)	Nd(1)−Cl(1)−Nd(2)	88.6(1)	O(5)−Nd(3)−O(13)	75.2(3)
Cl(1)−Yb(1)−O(4)	89.7(1)	Cl(1)−Y(1)−O(21)	88.6(1)	O(2)−Tb(1)−O(2′)	72.8(2)	Cl(1)−Nd(1)−Cl(6)	96.1(1)	Nd(1)−Cl(2)−Nd(2)	89.7(1)	O(7)−Nd(3)−O(13)	80.6(3)
Cl(2)−Yb(1)−O(4)	170.4(1)	Cl(2)−Y(1)−O(21)	90.4(1)	Cl(2)−Tb(2)−Cl(3)	91.9(1)	Cl(2)−Nd(1)−Cl(6)	88.6(1)	Nd(1)−Cl(3)−Nd(2)	88.6(1)	O(9)−Nd(3)−O(13)	148.0(3)
Cl(3)−Yb(1)−O(4)	88.5(1)	Cl(3)−Y(1)−O(21)	90.8(1)	Cl(2)−Tb(2)−O(4)	90.9(1)	Cl(3)−Nd(1)−Cl(6)	165.0(1)	O(1)−Nd(3)−O(3)	71.0(2)	O(11)−Nd(3)−O(13)	79.0(3)
O(1)−Yb(1)−O(4)	82.5(1)	O(1)−Y(1)−O(21)	178.7(1)	Cl(3)−Tb(2)−O(4)	89.8(1)	Cl(4)−Nd(1)−Cl(6)	98.1(1)	O(1)−Nd(3)−O(5)	124.6(2)	O(1)−Nd(3)−O(15)	78.2(2)
O(3)−Yb(1)−O(4)	83.8(1)	O(11)−Y(1)−O(21)	89.8(1)	Cl(2)−Tb(2)−Cl(2′)	180.0(1)	Cl(5)−Nd(1)−Cl(6)	94.8(1)	O(3)−Nd(3)−O(5)	139.6(2)	O(3)−Nd(3)−O(15)	75.3(2)
				Cl(3)−Tb(2)−Cl(2′)	88.1(1)	Cl(1)−Nd(2)−Cl(2)	76.9(1)	O(1)−Nd(3)−O(7)	137.9(3)	O(5)−Nd(3)−O(15)	140.0(2)
				Cl(3)−Tb(2)−Cl(3′)	180.0(1)	Cl(1)−Nd(2)−Cl(3)	75.3(1)	O(3)−Nd(3)−O(7)	122.4(3)	O(7)−Nd(3)−O(15)	69.2(3)
				O(4)−Tb(2)−Cl(2′)	89.1(1)	Cl(2)−Nd(2)−Cl(3)	76.5(1)	O(5)−Nd(3)−O(7)	73.5(2)	O(9)−Nd(3)−O(15)	74.0(2)
				O(4)−Tb(2)−Cl(3′)	90.2(1)	Cl(1)−Nd(2)−Cl(7)	94.5(1)	O(1)−Nd(3)−O(9)	74.0(2)	O(11)−Nd(3)−O(15)	142.2(2)
				O(4)−Tb(2)−O(4′)	180.0(1)	Cl(2)−Nd(2)−Cl(7)	91.8(1)	O(3)−Nd(3)−O(9)	137.2(2)	O(13)−Nd(3)−O(15)	111.5(3)
						Cl(3)−Nd(2)−Cl(7)	165.8(1)				

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[NdCl(\mu\text{-}Cl)_2(THF)]_n$, **6**, and $[CeCl(\mu\text{-}Cl)_2(THF)]_n$, **7**

6		7	
Nd(1)–Cl(1)	2.796(1)	Ce(1)–Cl(1)	2.828(1)
Nd(1)–Cl(2)	2.630(1)	Ce(1)–Cl(2)	2.661(1)
Nd(1)–Cl(3)	2.847(1)	Ce(1)–Cl(3)	2.880(1)
Nd(1)–Cl(1B)	2.823(1)	Ce(1)–Cl(1B)	2.856(1)
Nd(1)–Cl(3A)	2.793(1)	Ce(1)–Cl(3A)	2.825(1)
Nd(1)–O(1)	2.461(2)	Ce(1)–O(1)	2.492(3)
Nd(1)–O(2)	2.476(2)	Ce(1)–O(2)	2.508(3)
Cl(1)–Nd(1)–Cl(2)	95.7(1)	Cl(1)–Ce(1)–Cl(2)	95.9(1)
Cl(1)–Nd(1)–Cl(3)	74.1(1)	Cl(1)–Ce(1)–Cl(3)	74.0(1)
Cl(2)–Nd(1)–Cl(3)	86.7(1)	Cl(2)–Ce(1)–Cl(3)	87.0(1)
Cl(1)–Nd(1)–O(1)	84.4(1)	Cl(1)–Ce(1)–O(1)	84.6(1)
Cl(2)–Nd(1)–O(1)	174.1(1)	Cl(2)–Ce(1)–O(1)	174.2(1)
Cl(3)–Nd(1)–O(1)	99.0(1)	Cl(3)–Ce(1)–O(1)	98.7(1)
Cl(1)–Nd(1)–O(2)	144.4(1)	Cl(1)–Ce(1)–O(2)	144.2(1)
Cl(2)–Nd(1)–O(2)	82.1(1)	Cl(2)–Ce(1)–O(2)	82.0(1)
Cl(3)–Nd(1)–O(2)	140.7(1)	Cl(3)–Ce(1)–O(2)	140.9(1)
O(1)–Nd(1)–O(2)	94.3(1)	O(1)–Ce(1)–O(2)	94.2(1)
Cl(1)–Nd(1)–Cl(1B)	72.8(1)	Cl(1)–Ce(1)–Cl(1B)	72.9(1)
Cl(2)–Nd(1)–Cl(1B)	94.0(1)	Cl(2)–Ce(1)–Cl(1B)	94.3(1)
Cl(3)–Nd(1)–Cl(1B)	146.8(1)	Cl(3)–Ce(1)–Cl(1B)	146.9(1)
O(1)–Nd(1)–Cl(1B)	80.4(1)	O(1)–Ce(1)–Cl(1B)	80.3(1)
O(2)–Nd(1)–Cl(1B)	71.8(1)	O(2)–Ce(1)–Cl(1B)	71.7(1)
Cl(1)–Nd(1)–Cl(3A)	139.7(1)	Cl(1)–Ce(1)–Cl(3A)	140.0(1)
Cl(2)–Nd(1)–Cl(3A)	103.0(1)	Cl(2)–Ce(1)–Cl(3A)	102.7(1)
Cl(3)–Nd(1)–Cl(3A)	71.8(1)	Cl(3)–Ce(1)–Cl(3A)	71.9(1)
O(1)–Nd(1)–Cl(3A)	80.4(1)	O(1)–Ce(1)–Cl(3A)	80.4(1)
O(2)–Nd(1)–Cl(3A)	74.3(1)	O(2)–Ce(1)–Cl(3A)	74.2(1)
Cl(1B)–Nd(1)–Cl(3A)	139.3(1)	Cl(1B)–Ce(1)–Cl(3A)	139.1(1)
Nd(1)–Cl(1)–Nd(1B)	107.2(1)	Ce(1)–Cl(1)–Ce(1B)	107.1(1)
Nd(1)–Cl(3)–Nd(1A)	108.2(1)	Ce(1)–Cl(3)–Ce(1A)	108.1(1)

distance in $[YbCl_2(\mu\text{-}Cl)(THF)_2]_2$ and the 2.272 Å analog in $YbCl_3(THF)_3$. The latter averages involve THF ligands which are *trans* to each other, whereas in **1** the THF ligands are *trans* to chloride ligands. The 2.271(4) Å Yb–O(caprolactone) distance in **1** is comparable to the 2.269(2)–2.296(3) Å Y–O(caprolactone) distances in **2**.

$[TbCl_4(THF)_2]^-[TbCl_2(THF)_5]^+$, 3. Terbium trichloride crystallizes from a mixture of ϵ-caprolactone and THF quite differently from complexes **1** and **2**. In the Tb case (Figure 3), an ion pair crystallizes which contains an octahedral anion, a pentagonal bipyramidal cation, and *no* caprolactone!

The cation is similar in structure to other seven-coordinate cationic lanthanide complexes with the general formula $[LnZ_2(THF)_5]^+$ (Z = monoanionic ligand) such as $[SmI_2(THF)_5]^+$,[29] $[YCl(OCMe_3)(THF)_5]^+$,[30] and $[CeCl_2(THF)_5]^+$.[31] All of these structures have the anionic ligands at the axial positions with THF molecules at the equatorial sites. The 2-fold rotation axis present in the cation in **3** generates a rather regular pentagonal bipyramidal geometry. The ten Cl–Tb(1)–O(THF) angles cluster around the idealized 90° angle with a range of 85.3(1)°–94.6(1)°. The 72.3(3)° average of the O–Tb–O angles for adjacent THF ligands matches the 72° idealized angle, and the 72.0(1)°–72.8(2)° range of values is narrow. As in the other $[LnZ_2(THF)_5]^+$ complexes, the five THF molecules in **3** are canted in a propeller-like fashion around the metal center.

The octahedral anion has an inversion center and hence very regular bond angles and *trans* THF ligands. The 2.637(1) and 2.621(1) Å Tb(2)–Cl bond lengths in the six-coordinate anion are slightly longer than the 2.598(1) Å Tb(1)–Cl distance in the seven-coordinate cation. In contrast, the 2.344(3) Å Tb(2)–O(THF) bond length in the anion is significantly shorter than the 2.402(16) Å Tb(1)–O(THF) distance in the cation. The latter distance is close to that expected when compared to the 2.41(1) Å average in $[YCl(OCMe_3)(THF)_5]^+$,[30] the 2.46(1) Å average in $[SmI_2(THF)_5]^+$,[29] and the 2.493(13) average in $[CeCl_2(THF)_5]^+$,[31] given the differences in metallic radii.[26]

$[Cl_3Ln(\mu\text{-}Cl)_3LnCl_3]^{3-}[Ln(C_6H_{10}O_2)_8]^{3+}$ (Ln:Sm, 4; Nd, 5). Crystallization of samarium and neodymium trichloride yields isomorphous complexes which have structures that are further different from those described above. Like the terbium complex, **4** and **5** also contain ion pairs (Figure 4), but in this case there is *no* solvated THF and *only* coordinated caprolactone. Moreover, both ions are structurally very different from the terbium ions: the anions contain no solvate ligands, only chlorides, and the cation contains no chloride ligands, only caprolactone! Since the crystal quality of **4** was poor, the discussion of this structural type will focus on **5**.

The cation in **5** contains a Nd^{3+} ion surrounded by *eight* ϵ-caprolactone molecules which are coordinated only through their carbonyl oxygens. The eight oxygen donor atoms best describe a square antiprism. The regularity of this geometry can be evaluated by examining the eight angles α, between the eight metal donor atom vectors and the 8-fold inversion axis which passes through the metal in a regular square antiprism.[32] In the ideal case, α is 59.26°. In **5**, these angles range from 52.9 to 66.3°, with an average value of 59(4)°. The Nd(3)–O bond distances in the cation range from 2.366(8) to 2.523(7) Å. The closest related structure to this cation is the *N*-methylimidazole (*N*-MeIm) substituted cation in $[Sm(N\text{-}MeIm)_8]I_3$,[33] which has 2.563(6) and 2.596(6) Å Sm–N distances.

The anion in **5**, $[Cl_3Nd(\mu\text{-}Cl)_3NdCl_3]^{3-}$, differs from all of the complexes discussed so far in that it is bimetallic and contains no oxygen donor ligands. Although the cofacial bioctahedral M_2X_9 structure found in **5** is well-known for both transition metals[34,35] and main group elements,[36] for yttrium and the lanthanides this has only been observed, to our knowledge, in products obtained from solid state syntheses.[35] The bond angles between the donor atoms of the *cis* ligands range from 75.5(1) to 98.1(1)° in **5**. The Ln–Cl(terminal) bond distances are fairly uniform and range from 2.630(3) to 2.670(3) Å with an average value of 2.65(1) Å. The bridging chlorides are not completely symmetrical. Cl(2) is located midway between the two neodymium ions with Nd(1)–Cl(2) and Nd(2)–Cl(2) bond

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Table 4. Comparison of Average Ln−Cl Bond Lengths in Selected Solvated Trivalent Lanthanide and Yttrium Trichlorides

				dist (Å) normalized to yttrium[a]	
bond	complex	av bond length (Å)	coordn no.	terminal	bridging
Lu−Cl	$LuCl_3(THF)_3$[16]	2.52(1)	6	2.56	
Yb−Cl	$YbCl_3(C_6H_{10}O_2)(THF)_2$, **1**	2.527(5)	6	2.559	
	$[YbCl_2(\mu\text{-}Cl)(THF)_2]_2$[15]	2.490(3), terminal	6	2.522	
		2.683(2), bridging			2.715
	$YbCl_3(THF)_3$[15]	2.52(5)	6	2.55	
	$YbCl_3(HMPA)_3$[14]	2.588(4)	6	2.620	
Y−Cl	$YCl_3(C_6H_{10}O_2)_3$, **2**[11]	2.589(12)	6	2.589	
	$YCl_3(DME)_2$[2]	2.600(3)	7	2.600	
	YCl_3(TEG)(18-crown-6)[8]	2.603(11)	7	2.603	
Tb−Cl	$[TbCl_4(THF)_2]^-$, **3**	2.629(8)	6 (anion)	2.606	
	$[TbCl_2(THF)_5]^+$, **3**	2.598(1)	7 (cation)	2.578	
Eu−Cl	$EuCl_3(THF)_4$[4]	2.628(3)	7	2.578	
Nd−Cl	$NdCl_3(THF)_4$[5]	2.673(11)	7	2.587	
	$[NdCl(\mu\text{-}Cl)_2(THF)_2]_n$, **6**	2.630(1), terminal	7	2.544	
		2.81(1), bridging			2.72
	$[Cl_3Nd(\mu\text{-}Cl)_3NdCl_3]^{3-}$, **5**	2.65(1), terminal	6 (anion)	2.57	
		2.82(2), bridging			2.74
Ce−Cl	$[CeCl(\mu\text{-}Cl)_2(THF)_2]_n$, **7**	2.661(1), terminal	7	2.551	2.73
		2.84(2), bridging			
	$[CeCl_2(THF)_5]^+$[31]	2.688	7	2.578	
La−Cl	$[LaCl_3(C_7H_8O_2)(H_2O)]_n$[37]	2.72(1), terminal	7	2.58	
		2.91(1), bridging			2.77

[a] Using Shannon radii.[26]

Table 5. Comparison of Average Ln−O Bond Lengths in Selected THF and Caprolactone Solvated Trivalent Lanthanide and Yttrium Trichlorides

				dist (Å) normalized to yttrium[a]	
bond	complex	av bond length (Å)	coordn no.	THF	caprolactone
Lu−O	$LuCl_3(THF)_3$[16]	2.29(3)	6	2.33	
Yb−O	$YbCl_3(C_6H_{10}O_2)(THF)_2$, **1**	2.271(4), $C_6H_{10}O_2$ 2.304(6), THF	6	2.336	2.303
	$[YbCl_2(\mu\text{-}Cl)(THF)_2]_2$[15]	2.265(4)	6	2.297	
	$YbCl_3(THF)_3$[15]	2.272	6	2.304	
Y−O	$YCl_3(C_6H_{10}O_2)_3$, **2**[11]	2.280(11)	6		2.280
Tb−O	$[TbCl_4(THF)_2]^-$, **3**	2.344(3)	6 (anion)	2.321	
	$[TbCl_2(THF)_5]^+$, **3**	2.402(16)	7 (cation)	2.382	
Eu−O	$EuCl_3(THF)_4$[4]	2.435(7)	7	2.385	
Nd−O	$NdCl_3(THF)_4$[5]	2.504(17)	7	2.418	
	$[NdCl(\mu\text{-}Cl)_2(THF)_2]_n$, **6**	2.469(8)	7	2.383	
	$[Nd(C_6H_{10}O_2)_8]^{3+}$, **5**	2.46(5)	8 (cation)		2.37
Ce−O	$[CeCl(\mu\text{-}Cl)_2(THF)_2]_n$, **7**	2.500(8)	7	2.390	
	$[CeCl_2(THF)_5]^+$[31]	2.493(13)	7	2.383	

[a] Using Shannon radii.[26]

distances of 2.803(3) and 2.807(3) Å, respectively, but Cl(1) is closer to Nd(2) and Cl(3) is closer to Nd(1): Cl(1)−Nd(1) [Nd(2)], 2.851(3) [2.813(3)]; Cl(3)−Nd(1) [Nd(2)], 2.807(3) Å [2.857(3) Å].

Cofacial bioctahedral structures have been thoroughly analyzed as a probe of metal−metal interations by the method of Cotton and Ucko,[37] which examines the elongation or contraction of the complex relative to an ideal bioctahedron. An ideal structure has a 70.5° M(μ-X)M angle (β) and the metal equidistant between the planes defined by the bridging and terminal ligands ($d' = d''$, where d' is the distance between the bridging ligand plane and the metal and d'' is the distance between the terminal ligand plane and the metal). Metal−metal bonded complexes would be expected to distort so that $d'/d'' < 1$, whereas no metal metal bonding is expected when $d'/d'' > 1$ and the structures elongate. In **5**, β ranges from 88.6(1) to 89.7(1)° and $d'/d'' = 1.4$. This plus the 3.956(2) Å Nd(1)−Nd(2) distance is consistent with no metal−metal bonding in this complex.

$[NdCl(\mu\text{-}Cl)_2(THF)_2]_n$, 6, and $[CeCl(\mu\text{-}Cl)_2(THF)_2]_n$, 7. Crystallization of lanthanide trichlorides in the presence of benzophenone and L,L-lactide was examined for comparison with the caprolactone studies. Crystallizations were attempted for Nd, Ce, Tb, Y, and Yb with both donors. However, only two of these systems gave X-ray quality crystals, the two systems turned out to be isostructural, and the complexes incorporated neither benzophenone nor L,L-lactide. For both **6** and **7**, a polymeric structure previously unknown for THF-solvated lanthanide halides was observed as shown in Figure 5. Each metal in **6** and **7** is surrounded by seven ligands (one terminal chloride, two terminal THF ligands, and four bridging

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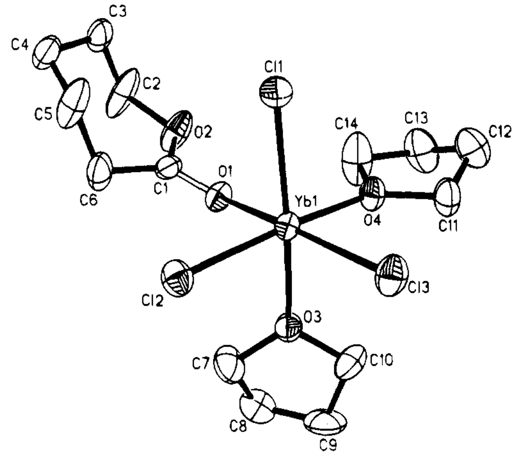

Figure 2. Thermal ellipsoid plot of $YbCl_3(C_6H_{10}O_2)(THF)_2$, **1**, drawn at the 50% probability level.

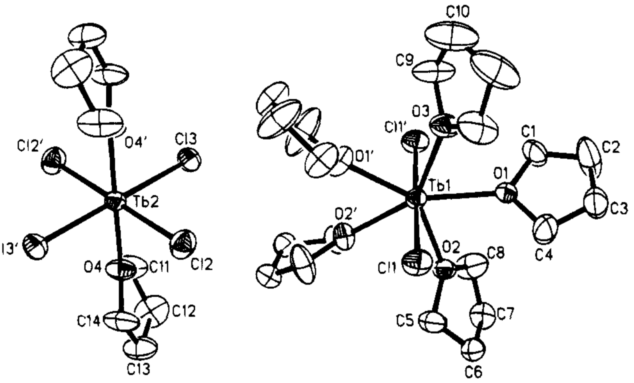

Figure 3. Thermal ellipsoid plot of $[TbCl_4(THF)_2]^-[TbCl_2(THF)_5]^+$, **3**, drawn at the 50% probability level.

chlorides) in a distorted pentagonal bipyramidal geometry with the terminal chloride and one THF in the axial positions. The overall structure is similar to that of $[LaCl_3(C_7H_8O_2)(H_2O)]_n$,[38] and the local coordination environment is similar to that of the cation in the terbium system **3**. For the axial ligands, the Cl(2)−M−O(1) angles are 174.1(1)° for **6** and 174.2(1)° for **7**. The equatorial angles range from 71.1(1) to 74.2(1)° in **6** and from 71.8(1) to 74.3(1)° in **7**.

The 2.630(1) Å Nd−Cl(terminal) bond distance in **6** is consistent with the 2.630(3) −2.670(3) Å range of Nd−Cl(terminal) distances in **5** and matches those in other halide complexes (Table 3). As expected, the bridging Ln−Cl bond lengths are longer than the terminal Ln−Cl distances (Table 4). The bridging chlorides are located asymmetrically with a difference in distance of approximately 0.05 Å on each side: Nd(1)−Cl(1) [Cl(3)], 2.796(1) [2.847(1)]; Ce(1)−Cl(1) [Cl(3)], 2.828(1) [2.880(1) Å].

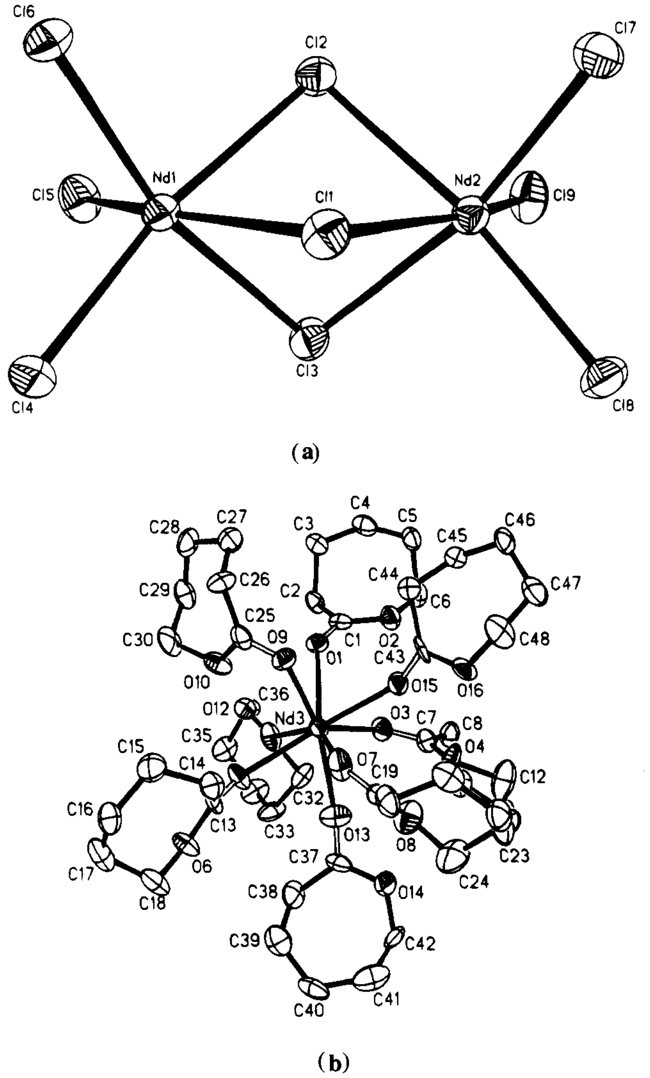

Figure 4. $[Cl_3Nd(\mu\text{-}Cl)_3NdCl_3]^{3-}[Nd(C_6H_{10}O_2)_8]^{3+}$, **5**: thermal ellipsoid plots of (a) $[Cl_3Nd(\mu\text{-}Cl)_3NdCl_3]^{3-}$ and (b) $[Nd(C_6H_{10}O_2)_8]^{3+}$ with probability ellipsoids drawn at the 50% level. The Sm analog, $[Cl_3Sm(\mu\text{-}Cl)_3SmCl_3]^{3-}[Sm(C_6H_{10}O_2)_8]^{3+}$, **4**, is isostructural.

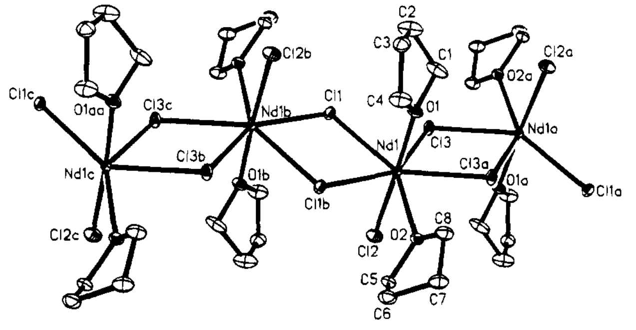

Figure 5. Thermal ellipsoid plot of $[NdCl(\mu\text{-}Cl)_2(THF)_2]_n$, **6**, with probability ellipsoids drawn at the 50% level. The cerium complex, $[CeCl(\mu\text{-}Cl)_2(THF)_2]_n$, **7**, is isostructural.

Discussion

Traditionally, LnZ_3L_x complexes in which Z is a monoanion and L is neutral are expected to vary in structure in a smooth way as the size of the metal is varied from La^{3+} (1.032 Å) to Lu^{3+} (0.861 Å), with yttrium being similar to the lanthanides of similar size, Ho and Er. Extensive crystallographic data on lanthanide complexes support this trend.[17−19,39−42] Since chlorides are rather simple ligands, one would expect lanthanide trichlorides to follow a similar pattern except that since chlorides can bridge, some variation in bridging versus terminal structures might be found. Indeed, for many years, crystallographic data on solvated lanthanide trichlorides showed that seven-coordinate $LnCl_3L_4$ complexes were almost always formed with some

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variation between bridging and terminal structures. The identification of six-coordinate $GdCl_3$(2,6-dimethyl-4-pyrone)$_3$[12] and $PrCl_3$(hexamethylphosphoramide)$_3$[13] could be attributed to unusual donor ligands in these systems.

The isolation of $YCl_3(C_6H_{10}O_2)_3$, **2**, provided an exception to these expectations, since **2** was a six-coordinate structure which did not form a higher coordination number complex using the adjacent oxygen on each ligand. Isolation of the six-coordinate structures $[YbCl_2(\mu\text{-}Cl)(THF)_2]_2$,[15] $YbCl_3(THF)_3$,[15] and $LuCl_3(THF)_3$[16] suggested that, under specific crystallization conditions, six-coordinate structures could form with the small metals late in the series. A change to a lower coordination number with a smaller metal was still consistent with the earlier trends in lanthanide halide coordination chemistry.

However, crystallization of a variety of lanthanide chlorides in the presence of caprolactone shows that many structural variations are possible, including differences from 0 to 8 in the number of caprolactone molecules coordinating to the metal, differences in coordination number from 6 to 8, and differences in formation of neutral versus ion pair complexes. The differences do not appear to be too predictable, even retrospectively. Hence, the differences between $YbCl_3(C_6H_{10}O_2)(THF)_2$, **1**, and $YCl_3(C_6H_{10}O_2)_3$, **2**, the trichloride complexes of yttrium and ytterbium, which differ in radius by 0.032 Å,[26] are found in solubility, crystallization behavior, the amount of caprolactone incorporated, and the particular isomer formed (*fac* versus *mer*). In comparison, the differences between the trichloride complexes of yttrium and terbium, which differ by 0.023 Å,[26] are dramatic in that terbium forms the ion pair complex $[TbCl_4(THF)_2]^-[TbCl_2(THF)_5]^+$, **3**, which is devoid of caprolactone. Since Sm and Nd are larger than Tb, structural differences between their trichloride complexes might be expected, but the observed difference between **3** and $[Cl_3Nd(\mu\text{-}Cl)_3NdCl_3]^{3-}[Nd(C_6H_{10}O_2)_8]^{3+}$, **5**, is not just the addition of one more solvent molecule. Furthermore, the fact that $NdCl_3$ can crystallize in either the more traditional (although not previously observed) neutral seven-coordinate form, $[NdCl(\mu\text{-}Cl)_2(THF)_2]_n$, **6**, or the unusual six- and eight-coordinate ion pair form, **5**, shows how important ancillary coordinating species in solution can be. Since the structures of **6** and **7** are similar to that of $[LaCl(\mu\text{-}Cl)_2(C_7H_8O_2)(H_2O)]_n$,[37] it appears that similar structures can be obtained with very different solvating species and, as shown by **1**–**5**, very differenct structures can be obtained in the presence of the same coordinating species. Clearly, lanthanide halide coordination chemistry can be most diverse and can be strongly affected by the presence of other donor atom species, whether or not they are incorporated into the final complex.

Traditionally, structural differences between f element complexes with different ligands can be explained by differences in ligand size. Comparison of the six-coordinate caprolactone complex, $YCl_3(C_6H_{10}O_2)_3$, **2**, with the more commonly observed seven-coordinate $LnCl_3(THF)_4$ suggested that caprolactone might occupy more room around the metal than THF. This could also be an explanation of why **2** contains three caprolactone groups and $YbCl_3(C_6H_{10}O_2)(THF)_2$, **1**, which contains a smaller metal, contains only one caprolactone. However, examination of the angles between the coordinating atom and the widest part of each molecule in the caprolactone and THF ligands in **1** suggests that caprolactone is less sterically demanding than THF: the O–O–C angle for caprolactone is 64.5° and the C–O–C angle for THF is 108.7°. The fact that eight caprolactone ligands can be placed around Nd^{3+} in **5** is consistent with the fact that caprolactone is not very sterically demanding. Hence, ligand size differences do not rationalize why **2** crystallizes with three caprolactone ligands and **1** with only one caprolactone under the same conditions.

In addition to the surprising differences between $[Cl_3Ln(\mu\text{-}Cl)_3LnCl_3]^{3-}[Ln(C_6H_{10}O_2)_8]^{3+}$ (Ln:Sm, **4**; Nd, **5**) and the other trichlorides, **4** and **5** display some independently uncommon features. First, there are relatively few eight-coordinate complexes of any kind which contain all unidentate ligands.[43–47] Second, crystallographic studies of lanthanide halide complexes containing lanthanide ions surrounded only by solvent have been limited almost exclusively to aqueous systems. For example, $[Ln(H_2O)_x]^{3+}$ ions have been identified in systems such as $[Sm(H_2O)_9]Br_3(dioxane)_2$,[48] $[Ln(H_2O)_8]Cl_3$(crown ether)[49] (Ln = Nd, Gd, Dy, Y, Lu), and $[Ln(H_2O)_8]Cl_3$(4,4′-bipyridine) (Ln = Gd, Y).[50] One exception is the recently reported *N*-methylimidazole (*N*-MeIm) complex $[Sm(N\text{-}MeIm)_8]I_3$.[33]

These results can have significant implications in reaction chemistry. It is well established that bridging ligands are less reactive than terminal ligands in lanthanide chemistry[51,52] and cationic species can have significantly different chemistry compared to neutral analogs.[52,53] If, in a reaction system, there is some coordinating moiety which can exert the same types of effects shown here by caprolactone, then reactivity and reaction rates could be profoundly influenced by the formation of ion pairs and bridging. If a mixture of species is present in solution, the reaction could channel through one of these special unanticipated forms. Moreover, such a coordinating moiety could accomplish these results in an invisible manner just as the ion pair found in the terbium complex **3** is isolated without any caprolactone present. Considering the extensive chemistry being developed with organic carbonyl compounds and mixtures such as "$CeCl_3$"/RLi,[54] the coordination chemistry observed here could explain some of the substrate and reaction condition sensitivity of these lanthanide trichloride based reactions.

Conclusion

Several general conclusions can be drawn from this study. First, solvated lanthanide trichlorides can exhibit a much wider range of structures than was previously known. Second, even with simple ligands like halide, one cannot necessarily expect a smooth progression in structure as one traverses the lanthanide series, gradually changing the radial size of the metal. Third, the presence of an oxygen donor ligand in solution can have profound effects on the arrangement of ligands. The marked differences observed in structures **1**–**7** indicates that under the

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proper conditions of crystallization or in the presence of certain coordinating moieties, the coordination chemistry of the $LnCl_3$ unit can be extremely varied. Variations in formation of neutral complexes versus ion pairs, six-versus seven- and eight-coordinate complexes, and homoleptic oxygen donor environments versus homoleptic halide environments versus heteroleptic coordination can occur. Given the large variation observed with this very simple metal trihalide unit, it is likely that extensive structural variation is also possible with compounds containing ligands more complicated than unidentate monoatomic halides. Understanding and controlling the variations caused by coordinating species such as caprolactone will add a new dimension to our ability to manipulate the reaction chemistry of the lanthanides since coordination environment, charge, and the presence of terminal or bridging ligands are crucial to reactivity. These results may also provide a basis to explain variations in reactivity which were not previously understood.[55]

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Supplementary Material Available: Descriptions of the X-ray experimental details and tables of crystal data, positional parameters, bond distances and angles, and thermal parameters (72 pages). Ordering information is given on any current masthead page.

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(55) We recently learned that $[YCl_4(THF)_2]^-[YCl_2(THF)_5]^+$, which is isostructural with **3**, has been obtained from reacting anhydrous YCl_3 with THF under reflux conditions: Sobota, P.; Utko, J.; Szafert, S. Personal communication. See: *Inorg. Chem.* **1994**, *33*, 5203–5206.