Preparation of the Bis(trimethylsilyl)amido Lanthanide Chlorides $[\{Ln[N(SiMe_3)_2]_2(\mu\text{-}Cl)(thf)\}_2]$ (thf = tetrahydrofuran), and the Crystal and Molecular Structures† of the Gadolinium and Ytterbium Complexes

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Reaction of $LnCl_3$ with 2 equivalents of LiL [L = $N(SiMe_3)_2$] in tetrahydrofuran (thf) at −5 °C yields $[\{LnL_2Cl(thf)\}_2]$ for Ln = Eu, Gd, or Yb or $[YL_2Cl(thf)_2]$ for Ln = Y. *X*-Ray crystal structure analysis of the compounds of Gd and Yb confirms the formation of halide-bridged dimers. In the M_2Cl_2 bridging unit the M–Cl bond lengths differ slightly and the angle at the metal (*ca.* 74°) is much smaller than at chlorine (*ca.* 106°). The metal co-ordination geometries are irregular but can be best described as distorted trigonal bipyramidal with the bridging chlorines spanning one axial and one equatorial site. The bond lengths M–Cl and M–N indicate a Gd − Yb radius difference of *ca.* 0.07 Å, but the M–O distances differ by 0.093 Å. Variable-temperature n.m.r. studies of $[\{EuL_2Cl(thf)\}_2]$ and $[\{YbL_2Cl(thf)\}_2]$ show that there is free rotation about Ln–N and Ln–O bonds at room temperature. These rotations are frozen out at low temperatures to give a solution structure having higher symmetry (C_{2h}) than that found in the crystal.

The bulky ligand $N(SiMe_3)_2$ (L) was first employed in lanthanide chemistry in the preparation of the novel three-co-ordinate LnL_3 complexes.[1] These complexes appear to have a rather limited co-ordination chemistry; adding 1 equivalent of Ph_3PO gave only the four-co-ordinate complexes $[LnL_3(Ph_3PO)]$, characterised by *X*-ray diffraction for Ln = La,[2] whilst with Me_3PO there was ^1H n.m.r. evidence for the formation of five-co-ordinate $[LnL_3(Me_3PO)_2]$ species in solution, where Ln = Eu or Pr.[3]

The ligand L has many attractive features in lanthanide chemistry; it is bulky enough that bridge formation is unlikely and therefore polymeric compounds will not be formed, it generally gives soluble complexes, and it has a simple n.m.r. signal. Therefore it seemed that the chemistry of LnL_2X compounds would be worth exploring, and as a starting point into this chemistry the monochloride species LnL_2Cl was important.

In this paper we report the preparation of $[\{LnL_2Cl(thf)\}_2]$ (Ln = Eu, Gd, or Yb; thf = tetrahydrofuran) and the *X*-ray crystal structures of the complexes of Gd and Yb. The use of these compounds as starting material for the synthesis of the thiolate complexes $[\{LnL_2(SBu^t)\}_2]$ has already been reported.[4]

Results and Discussion

Andersen and co-workers[5] have reported the synthesis of LnL_2Cl by the reaction of $LnCl_3$ with LnL_3 [equation (1)] but

$$LnCl_3 + 2LnL_3 \longrightarrow 3LnL_2Cl \qquad (1)$$

they were unable to isolate any product.

We found that careful addition of a thf solution of LiL (2 equivalents) to a thf suspension of $LnCl_3$ (Ln = Eu, Gd, or Yb; 1 equivalent) led to complete reaction after *ca.* 30 min at −5 °C to give clear solutions; red for Eu, colourless for Gd, and deep yellow for Yb. After removal of solvent *in vacuo* and extraction of the solid residue with pentane or toluene, the products were isolated in *ca.* 70% yield as well formed prisms. *X*-Ray crystallography of the complexes of Gd and Yb established the identity of the products as $[\{LnL_2(\mu\text{-}Cl)(thf)\}_2]$. The solubilities of $[\{LnL_2Cl(thf)\}_2]$ are considerably higher than those of the corresponding tris(silylamides), and the colours are more intense; the europium complex is very deep red (EuL_3 is orange) and the ytterbium complex is deep yellow (YbL_3 is primrose yellow). The air sensitivity of $[\{LnL_2Cl(thf)\}_2]$ is also considerably higher than for LnL_3, presumably due to less steric crowding around Ln.

We have not attempted the preparation of $[\{LnL_2Cl(thf)\}_2]$ for Ln lighter than Eu. Although it may be possible to isolate a stable complex for Sm, it is most unlikely that such complexes could be prepared for La–Nd, where the larger size of Ln would lead to considerable steric unsaturation and thus instability in solution. Indeed, we have found that $[\{EuL_2Cl(thf)\}_2]$ is unstable in solution with respect to disproportionation to EuL_3 and $EuCl_3$: ^1H n.m.r. spectra of solutions of pure $[\{EuL_2Cl(thf)\}_2]$ invariably show a resonance due to EuL_3.

Surprisingly, we found that reaction of YCl_3 with 2 equivalents of LiL in thf gave colourless crystals which appear from ^1H n.m.r. integration to be $YL_2Cl(thf)_2$. These crystals rapidly decompose in the absence of solvent to give YL_3 and YCl_3, and we have therefore been unable to obtain satisfactory microanalytical data. The complex $YL_2Cl(thf)_2$ is presumably a five-co-ordinate monomer which is surprising considering that Gd and Yb, with larger and smaller ionic radii respectively, both give a dimeric complex.

The structures of the complexes $[\{M[N(SiMe_3)_2]_2Cl(thf)\}_2]$ (M = Gd or Yb) have been determined by *X*-ray crystallography; the crystals are isostructural. A diagram of the dimeric molecule found in both structures is given in Figure 1; selected bond lengths and angles are given in Table 1.

The geometry at the metal atom is irregular, due almost certainly to the widely differing steric size of the ligands, but can be conveniently described as trigonal bipyramidal. In this definition the atoms Cl, N(1), and N(2) form the equator, with the relevant interbond angles summing to 360°, within error. The individual values, however, differ considerably.

Although this latter feature may be indicative of steric crowding, the silylamide ligands bond to the metal quite symmetrically, with M–N–Si angles falling in the narrow range 117—123°. The Si–N–Si angles of *ca.* 120° and the N–Si

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Selected bond lengths (Å) and angles (°) in [{M[N(SiMe$_3$)$_2$]$_2$Cl(thf)}$_2$] (M = Gd or Yb)

	Gd	Yb
M–Cl	2.765(4)	2.690(4)
M–Cl′	2.740(4)	2.667(4)
M–N(1)	2.239(5)	2.174(5)
M–N(2)	2.264(5)	2.198(5)
M–O(1)	2.444(5)	2.351(5)
N(1)–Si(1)	1.724(5)	1.731(5)
N(1)–Si(2)	1.723(5)	1.730(5)
N(2)–Si(3)	1.718(5)	1.713(6)
N(2)–Si(4)	1.717(5)	1.726(6)
M–Cl–M′	105.7(2)	105.5(1)
Cl–M–Cl′	74.3(2)	74.5(1)
N(1)–M–N(2)	116.2(2)	115.6(2)
Cl–M–N(1)	112.4(2)	110.9(2)
Cl′–M–N(1)	94.1(2)	94.9(2)
Cl–M–N(2)	131.4(1)	133.4(1)
Cl′–M–N(2)	100.6(2)	100.7(1)
O(1)–M–Cl	78.4(2)	78.5(2)
O(1)–M–N(1)	110.8(2)	109.1(2)
O(1)–M–N(2)	85.8(2)	86.7(2)
Si(1)–N(1)–Si(2)	120.8(3)	119.2(3)
M–N(1)–Si(1)	121.1(3)	122.7(3)
M–N(1)–Si(2)	118.1(3)	118.1(2)
Si(3)–N(2)–Si(4)	120.5(3)	119.1(3)
M–N(2)–Si(3)	121.6(3)	123.5(3)
M–N(2)–Si(4)	117.9(3)	117.4(3)

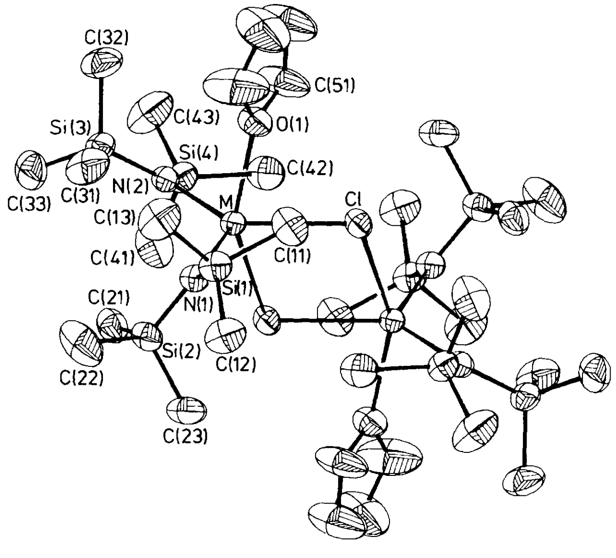

Figure 1.

distances of 1.71—1.73 Å are similar to those found in 'covalently' bound silylamides (*e.g.* with first-row transition metals and main-group elements[6]), in contrast to results obtained for some tris(silylamides) of the lanthanides, where the Si–N–Si angle is enlarged and the N–Si distance is decreased to less than 1.70 Å.[7]

The metal–ligand bond lengths show an interesting trend. Although in both structures the M–Cl–M bridge is slightly asymmetric, with M–Cl bond lengths differing by 0.025 (Gd) and 0.013 Å (Yb), possibly due to steric interactions between the two halves of the molecule, the M–Cl and M–N bond lengths show a similar difference between the two complexes of 0.065—0.075 Å. In contrast, the difference for the M–O bond lengths is 0.093 Å, suggesting some extra shortening due to the increase in polarising power of the smaller Yb ion.

Table 2. Proton n.m.r. data for [{EuL$_2$Cl(thf)}$_2$]

		thf	
T/K	L	α	β
303	1.97		3.32
283	−0.87	11.52 (br)	5.17 (vbr)
263	−4.53	13 (vbr)	−1.18
243	−5.73	vvbr	−1.6 (vbr)
223	−6.1 (vbr)	15.7	
203	−25.8; 11	12*; 21.2*	27*; 31.2*

[a] Assignment uncertain.

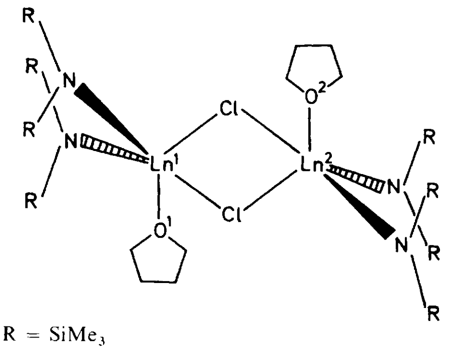

Figure 2. R = SiMe$_3$

Proton N.M.R. Studies.—The ^{1}H n.m.r. resonances for [{EuL$_2$Cl(thf)}$_2$] and [{YbL$_2$Cl(thf)}$_2$] are greatly shifted from the expected values for a diamagnetic compound due to the paramagnetism of the metal ions (Eu^{3+}, $4f^6$; Yb^{3+}, $4f^{13}$). In the case of the europium complex, reasonably sharp resonances were found at room temperature, and on lowering the temperature dramatic changes in the spectrum were seen.

The variation with temperature of the ^{1}H n.m.r. spectrum of [{EuL$_2$Cl(thf)}$_2$] is shown in Table 2. At room temperature all the Me$_3$Si groups are equivalent, presumably due to free rotation about the Eu–N bond. Similarly the α-CH$_2$ protons in the thf ligand are all equivalent, as are the β-CH$_2$ protons indicating free rotation about the Eu–O bond. However, at 203 K two resonances are seen for Me$_3$Si and four for CH$_2$. This is consistent with a static solution structure as shown in Figure 2 which has a higher symmetry (C_{2h}) than that found in the crystal (C_i). The atoms O(1), Eu(1), Eu(2), O(2) lie in a mirror plane which bisects the N–Eu–N angle. This would lead to two types of Me$_3$Si group, up or down with respect to the nearest thf, and four types of CH$_2$ group, α or β, and proximal or distal with respect to Cl.

The ^{1}H n.m.r. spectrum of the ytterbium complex is far more difficult to interpret. At room temperature there is only one signal which is very broad (*ca.* 400 Hz wide), centred around 22 p.p.m. At 235 K, two broad but well resolved peaks appear at −36.25 and 54.13 p.p.m., and we have assigned these to Me$_3$Si resonances. At 215 K, these peaks have moved to −41.1 and 40.9 p.p.m., and additional lower-intensity peaks have appeared at −24, 60.3, and 86.3 p.p.m. These have been assigned to CH$_2$ resonances, the fourth of which has not been found.

Although the ^{1}H n.m.r. of the ytterbium complex is far less clear than that of Eu, it is obvious that rotation about the Yb–N

Table 3. Crystal data, details of intensity measurements, and structure refinements for [{M[N(SiMe$_3$)$_2$]$_2$Cl(thf)}$_2$] (M = Gd or Yb)[a]

Compound	M = Gd	M = Yb
Formula	$C_{32}H_{88}Cl_2Gd_2N_4O_2Si_8$	$C_{32}H_{88}Cl_2N_4O_2Si_8Yb_2$
M	1 171.3	1 202.7
a/Å	14.349(4)	14.249(3)
b/Å	12.986(2)	12.936(2)
c/Å	16.615(5)	16.446(9)
β/°	113.75(2)	113.44(2)
U/Å^3	2 833.75	2 781.14
Z	2	2
D_c/g cm^{-3}	1.372	1.436
F(000)	1 196	1 220
μ/cm^{-1}	26.20	36.25
h, *k*, *l* range	$-17 \leqslant h \leqslant 17$ $0 \leqslant k \leqslant 15$ $0 \leqslant l \leqslant 19$	$-16 \leqslant h \leqslant 16$ $0 \leqslant k \leqslant 15$ $0 \leqslant l \leqslant 19$
Total no. of reflections	5 594	5 303
No. of unique reflections	4 982	4 886
No. of reflections used in the refinement	4 112	3 702
No. of refined parameters	402[b]	378[c]
Min. and max. height in final Fourier difference map/e Å^{-3}	−0.49, 0.48	−0.31, 0.52
Weighting scheme parameter *g* in $w = 1/[\sigma^2(F) + gF_o^2]$	Unit weights	0.000 155
Final *R*	0.0227	0.0207
Final *R*′	0.0243	0.0254

[a] Details common to both: monoclinic; space group $P2_1/n$; θ range 1.50—25.0; significance test $F > 3\sigma(F_o)$. [b] All H atoms refined freely. [c] Hydrogen atoms in thf carbons idealised with group U_{iso} values, but with constrained C–H distances (0.96 Å).

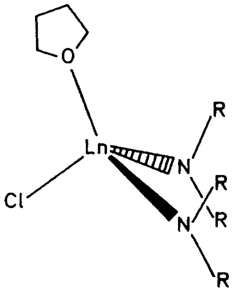

Figure 3. R = SiMe$_3$

bond is frozen out at a considerably higher temperature (235 K) than rotation about the Eu–N bond. Similarly, rotation about the Yb–O bond is frozen out at 215 K compared with 203 K for the Eu–O bond. This is presumably a consequence of the smaller ionic radius for Yb^{3+} (0.858 Å) compared with Eu^{3+} (0.905 Å), and thus a greater degree of steric crowding in the ytterbium complex.

A more detailed analysis of these n.m.r. data is not possible at present as we have no analogous diamagnetic compounds with which to compare chemical shifts, and the complexes do not have axial symmetry, leading to more difficult theory. Although the ^{1}H n.m.r. data are consistent with a dimeric structure in solution, they would also be consistent with a four-co-ordinate monomeric structure as shown in Figure 3. However, we feel that a completely dissociated structure in solution is most unlikely due to the high degree of steric unsaturation in such a species. There must, however, be a small concentration of monomer in solution as single crystals grown from a solution of [{EuL$_2$Cl(thf)}$_2$] containing 0.5% of the gadolinium complex gave a small number of sharp lines in the e.s.r. spectrum. This indicates that the species giving rise to the spectrum is [GdEuL$_4$Cl$_2$(thf)$_2$] as magnetic interactions between adjacent Gd^{3+} ions in [{GdL$_2$Cl(thf)}$_2$] would lead to a far more complex spectrum.

Table 4. Fractional atomic co-ordinates (× 10^4) for [{Gd[N(SiMe$_3$)$_2$]$_2$Cl(thf)}$_2$]

Atom	*x*	*y*	*z*
Gd	4 555(0.5)	4 778(0.5)	6 106(0.5)
Cl	4 373(1)	3 940(1)	4 520(1)
N(1)	3 343(2)	5 994(3)	5 944(2)
Si(1)	2 071(1)	5 644(1)	5 296(1)
C(11)	1 909(5)	4 517(5)	4 648(5)
C(12)	1 275(5)	6 694(6)	4 685(5)
C(13)	1 450(5)	5 296(7)	6 155(5)
Si(2)	3 718(1)	7 174(1)	6 328(1)
C(21)	5 048(4)	7 203(5)	7 186(4)
C(22)	2 921(6)	7 748(7)	6 872(7)
C(23)	3 696(5)	8 078(5)	5 446(4)
N(2)	5 715(2)	4 514(3)	7 496(2)
Si(3)	5 365(1)	4 450(1)	8 369(1)
C(31)	4 022(5)	4 882(7)	8 040(5)
C(32)	5 395(6)	3 110(5)	8 801(5)
C(33)	6 170(6)	5 272(6)	9 318(4)
Si(4)	6 963(1)	4 342(1)	7 652(1)
C(41)	7 672(5)	5 580(6)	7 832(6)
C(42)	7 023(5)	3 707(5)	6 665(4)
C(43)	7 731(7)	3 510(9)	8 603(5)
O(1)	3 955(2)	3 041(2)	6 203(2)
C(51)	4 629(7)	2 195(5)	6 259(7)
C(52)	4 145(8)	1 249(6)	6 383(9)
C(53)	3 181(10)	1 550(7)	6 378(8)
C(54)	3 136(6)	2 636(7)	6 392(8)

Experimental

All reactions were carried out under dry, oxygen-free N$_2$, using standard Schlenk techniques. Solvents were distilled from sodium diphenylketyl and stored over 4A molecular sieves prior to use. Elemental analyses were carried out by Butterworth Laboratories Ltd. N.m.r. samples were dissolved in [^{2}H$_8$]-toluene and sealed under vacuum in 5-mm n.m.r. tubes, and spectra were recorded on either a Bruker WP80 or a WM250 spectrometer. Anhydrous lanthanide chlorides were prepared by refluxing the hydrated chlorides with freshly distilled SOCl$_2$.

Preparation of [{EuL$_2$Cl(thf)}$_2$].—Europium(III) chloride (3.36 g, 13.05 mmol) was suspended in thf (80 cm^3) and cooled to −5 °C. A solution of Li[N(SiMe$_3$)$_2$] [prepared from LiBu^n and NH(SiMe$_3$)$_2$, 26.1 mmol] in thf (50 cm^3) was added dropwise to the stirred suspension over a period of 30 min. Solvent was removed *in vacuo* from the resulting clear deep red solution to give a deep red oil. This was warmed to *ca.* 50 °C and pumped at 10^{-4} mmHg (1.33 × 10^{-2} Pa) for 1 h to give a dark red solid, which was extracted with toluene (150 cm^3) to give a deep red solution. Solvent was removed *in vacuo* and the resulting solid crystallised from pentane to give dark red prisms (yield = 5.52 g, 73%) (Found: C, 32.9; H, 7.6; N, 4.7. $C_{32}H_{88}Cl_2Eu_2N_4O_2Si_8$ requires C, 33.1; H, 7.65; N, 4.85%).

Similar reactions using GdCl$_3$, YbCl$_3$, or YCl$_3$ yielded respectively [{GdL$_2$Cl(thf)}$_2$], [{YbL$_2$Cl(thf)}$_2$], and [YL$_2$Cl(thf)$_2$] (Found for [{YbL$_2$Cl(thf)}$_2$]: C, 28.9; H, 7.0; N, 4.1. $C_{32}H_{88}Cl_2N_4O_2Si_8Yb_2$ requires C, 31.95; H, 7.35; N, 4.65%).

X-*Ray Crystallography*.—The crystallographic measurements were made at room temperature (293 K) on crystals

Table 5. Fractional atomic co-ordinates (× 10^4) for [{Yb[N(SiMe$_3$)$_2$]$_2$-Cl(thf)}$_2$]

Atom	*x*	*y*	*z*
Yb	4 570(0.5)	4 773(0.5)	6 092(0.5)
Cl	4 360(1)	3 976(1)	4 518(1)
N(1)	3 374(2)	5 896(2)	5 931(2)
Si(1)	2 086(1)	5 611(1)	5 391(1)
C(11)	1 886(4)	4 502(5)	4 617(4)
C(12)	1 285(4)	6 691(5)	4 697(4)
C(13)	1 470(4)	5 269(6)	6 170(4)
Si(2)	3 737(1)	7 139(1)	6 317(1)
C(21)	5 066(4)	7 199(4)	7 187(4)
C(22)	2 923(5)	7 704(6)	6 863(5)
C(23)	3 708(4)	8 049(4)	5 424(4)
N(2)	5 682(2)	4 526(2)	7 459(2)
Si(3)	5 353(1)	4 472(1)	8 353(1)
C(31)	4 019(5)	4 944(5)	8 076(4)
C(32)	5 382(5)	3 130(5)	8 787(5)
C(33)	6 188(5)	5 286(5)	9 303(4)
Si(4)	6 944(1)	4 347(1)	7 621(1)
C(41)	7 664(4)	5 589(6)	7 799(5)
C(42)	7 027(4)	3 687(5)	6 647(4)
C(43)	7 689(5)	3 491(7)	8 574(4)
O(1)	3 954(2)	3 106(2)	6 171(2)
C(51)	4 594(4)	2 239(4)	6 199(4)
C(52)	4 110(5)	1 291(5)	6 375(5)
C(53)	3 117(6)	1 621(5)	6 332(5)
C(54)	3 137(4)	2 737(5)	6 390(5)

sealed under argon in glass capillaries using a CAD4 diffractometer operating in the ω–2θ scan mode with graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) as previously described.[8] The structure of the gadolinium complex was solved *via* standard heavy-atom procedures and refined using full-matrix least squares. For the ytterbium complex, the co-ordinates of the former structure were used for refinement in the same way. Non-hydrogen atoms were refined anisotropically, hydrogens isotropically. Details of the crystal data, intensity measurements, and refinements are given in Table 3. Final atomic positional parameters are given in Tables 4 and 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Acknowledgements

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