Low Co-ordination Numbers in Lanthanide and Actinide Compounds. Part I. The Preparation and Characterization of Tris{bis(trimethylsilyl)-amido}lanthanides

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The new three-co-ordinated lanthanide complexes [Ln{$N(SiMe_3)_2$}$_3$], where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Ho, Yb, and Lu, and [Y{$N(Sime_3)_2$}$_3$], have been prepared and their ^1H n.m.r. and electronic spectra are reported and discussed. The magnetic susceptibility of the Gd complex at 98 and 298 K is reported.

THE chemistry of the lanthanide elements is characterized by a tendency to exhibit high co-ordination numbers (*i.e.* >6) in their compounds, which are predominantly ionic in nature. Typical co-ordination numbers for these large ions are 8, 9, and 10, though 6, 7, and 12 are also known. Even six-co-ordination, so common for *d*-transition metals, is quite rare for lanthanides; an example is provided by the hexahalide complex $[LnX_6]^{3-}$ (X = Cl, Br, or I).[1,2] Co-ordination polyhedra are often of quite low symmetry, which hinders interpretation of electronic spectra, though O_h six-co-ordination, D_{3h} nine-co-ordination, and near-I_h twelve-co-ordination are known.

Recent *X*-ray crystallographic work[3] has shown that the tris{bis(trimethylsilyl)amido}chromium and iron compounds [M{$N(SiMe_3)_2$}$_3$] (I) (M = Cr or Fe), originally prepared by Bürger and Wannagat,[4] are authentic three-co-ordinated complexes with D_3 molecular symmetry. Other transition metal derivatives (I; M = Sc, Ti, or V) have since been isolated[5] and crystal-field calculations using electronic spectral data have shown that considerable splitting of the *d*-orbitals occurs.[6] E.s.r. spectra have shown that the chromium (d^3) and iron (d^5) compounds have large zero-field splittings.[7] It was therefore of interest to synthesize the corresponding lanthanide complexes (I; M = Ln), particularly because they might have low and (for these elements) otherwise unknown co-ordination numbers. Reaction (1) involving the anhydrous lanthanide chloride and the

$$LnCl_3 + 3LiN(SiMe_3)_2 \longrightarrow Ln\{N(SiMe_3)_2\}_3 + 3LiCl \quad (1)$$

theoretical amount of $LiN(SiMe_3)_2$ proved successful[8] and we now present a full account of the preparation and properties of a number of three-co-ordinated lanthanide complexes (I; M = La, Ce, Pr, Nd, Sm, Eu, Gd, Ho, Yb, and Lu) and the corresponding yttrium complex.

The new compounds are readily hydrolysed, soluble in organic solvents, and crystallize as needles from pentane. The cerium compound is exceedingly readily oxidised by even minute traces of air. The m.p.s all lie within the range 149—170° except for the yttrium compound (m.p. 184°). Some physical properties are presented in the Table. The monomeric nature of these compounds, suggested by their volatility at 75—100 °C and 10^{-4} mmHg, was confirmed by molecular weight determinations (ebullioscopically in benzene) of the La, Sm, and Eu derivatives. Preliminary *X*-ray crystallographic work[9] has shown that the Eu and Yb compounds are

Analytical data

M in M[$N(SiMe_3)_2$]$_3$	Colour	M.p. (°C)	Volatility [a]	τ [b]	*M* [c]	M% Found	M% Calc.	$N(SiMe_3)_2$% Found	$N(SiMe_3)_2$% Calc.
La	White	145—149	100—102	9·75	612 ± 6 (620·1) [d]	22·35	22·4	78·3	77·6
Ce	Yellow-brown		95—100	13·10		22·6	22·55	78·5	77·45
Pr	Pale green	155—158	88—90	18·64		22·2	22·65	76·8	77·85
Nd	Pale blue	161—164	85—90	15·60		23·25	23·05	76·4	76·95
Sm	Pale yellow	155—158	83—84	11·58	611 ± 6 (631·7) [e]	23·55	23·8	77·3	76·2
Eu	Orange	159—162	82—84	3·57	637 ± 6 (633·2) [f]	23·8	23·9	77·1	76·1
Gd	White	160—163	80—83			24·3	24·6	76·5	75·5
Ho	Cream	161—164	80—85			25·55	25·5	74·6	74·5
(Y) [g]	White	180—184	100—105	9·72		15·3	15·6	85·1	84·4
Yb	Lemon-yellow	162—165	78—82			26·35	26·45	74·2	73·55
Lu	White	167—170	75—80	9·70		26·4	26·65	74·1	73·35

[a] Sublimation temperature (°C) at 10^{-4} mmHg. [b] ^1H N.m.r. chemical shift (TMS = 10·00) in C_6D_6. [c] Calculated values in parentheses. [d] 0·021—0·083M Solutions. [e] 0·013—0·051M Solutions. [f] 0·012—0·031M Solutions. [g] Yttrium is placed according to its M^{3+} radius in the lanthanide series.

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[1] J. L. Ryan and C. K. Jørgensen, *J. Phys. Chem.*, 1966, **70**, 2845.

[2] J. L. Ryan, *Inorg. Chem.*, 1969, **8**, 2053.

[3] D. C. Bradley, M. B. Hursthouse, and P. F. Rodesiler, *Chem. Comm.*, 1969, 14.

[4] H. Bürger and U. Wannagat, *Monatsh.*, 1963, **94**, 1007; 1964, **95**, 1099.

[5] D. C. Bradley and R. G. Copperthwaite, *Chem. Comm.*, 1971, 764; E. C. Alyea, D. C. Bradley, and R. G. Copperthwaite, *J.C.S. Dalton*, 1972, 1580.

[6] E. C. Alyea, D. C. Bradley, R. G. Copperthwaite, and K. D. Sales, *J.C.S. Dalton*, 1973, 185.

[7] D. C. Bradley, R. G. Copperthwaite, S. Cotton, J. Gibson, and K. D. Sales, *J.C.S. Dalton*, 1973, 191.

[8] D. C. Bradley, J. S. Ghotra, and F. A. Hart, *J.C.S. Chem. Comm.*, 1972, 349.

[9] M. B. Hursthouse and A. J. Welch, personal communication.

isomorphous with space group $P\bar{3}1c$. It thus appears that the whole series of lanthanide complexes are three-co-ordinated and, bearing in mind the large size of the lanthanide ions, it is clear that the *bis*-trimethylsilylamido-ligands (btsa) exert enormous steric screening of the metal atom and the possibility of isolating some analogous actinide complexes is evident.

All the compounds listed in the Table have given mass spectra and, in most cases, significant intensities were found for the parent molecular ions. The existence of parent molecular ions $M(btsa)_3^+$ demonstrates the considerable thermodynamic stability of these compounds and supports the view that they contain appreciably strong metal–nitrogen bonds.

N.m.r. Spectra.—The diamagnetic species (I; M = Y, La, or Lu) gave ^1H chemical shifts near to tetramethylsilane and similar to that of the scandium derivative (τ 9·67),[5] while some of the paramagnetic compounds gave shifted signals characteristic of the presence of pseudo-contact effects. Relative to the diamagnetic lanthanum compound, the paramagnetic shifts are as follows (+ means a high-field shift): +3·35 (Ce); +8·89 (Pr); +5·85 (Nd); +1·83 (Sm); and −6·18 p.p.m. (Eu). Predicted[10] relative values based on a pseudo-contact model (arbitrarily setting the observed and theoretical Pr values equal) are +5·09 (Ce); +8·89 (Pr); +3·39 (Nd); +0·57 (Sm); and −3·2 p.p.m. (Eu). Agreement, while fair and demonstrating the predominance of the pseudo-contact mechanism, is not so close as in some other series and the discrepancy is possibly caused by a contact contribution, for which there is considerable evidence in some amine complexes of lanthanides.[11] Alternatively, a gradually increasing hindrance to free rotation of the $N(SiMe_3)_2$ groups as the ionic size becomes smaller along the series Ce $\longrightarrow$ Eu could progressively affect the value of the averaged geometric factor $(3\cos^2\theta - 1)r^{-3}$ (the progressive decrease of the Ln–N bond distance along the series Ce $\longrightarrow$ Eu will also slightly affect r). A more quantitative discussion must await *X*-ray structural and single-crystal magnetic data.

The τ-values of the diamagnetic complexes $M(btsa)_3$ (M = La, Y, or Lu) show a small (0·05 p.p.m.) shift to low field with decreasing ionic radius as expected from simple inductive deshielding. An interesting feature of the n.m.r. spectra was the detection of the small amount of free ligand base, produced by hydrolysis, as a separate non-shifted signal. This shows that the rate of exchange of the free ligand base with bound ligand (transamination) is slow on the n.m.r. time scale probably due to steric hindrance which could inhibit transamination by preventing the co-ordination of the free ligand nitrogen atom. This is consistent with ebullioscopic molecular weight experiments, which showed the experimental value of the molecular weight of the free ligand $HN(SiMe_3)_2$ to be unaffected by the presence of the complex $Ln(btsa)_3$, demonstrating that there is little, if any, association. Experiments are in progress with less sterically hindered ligands to explore the possible use of this class of compounds as shift reagents.

Magnetic Susceptibility and E.s.r. Spectra.—The gadolinium compound (Gd^{3+}, $^8S_{7/2}$) gave in powder form an e.s.r. signal at room temperature corresponding to the effective *g*-values $g_\perp \sim 8$ and $g_\parallel \sim 2$. This result suggests that the ion in the field of axial symmetry has a substantial zero-field splitting and is of interest in comparison with the large zero-field splittings exhibited by the chromium and iron complexes.[7] The magnetic susceptibility of this compound followed the Curie law over the temperature range 98—298 K (μ^{98}, 7·75; μ^{298}, 7·89 B.M.) in agreement with theory ($\mu_{eff} = 7{\cdot}94$ B.M.).

Electronic Spectra.—Owing to the strongly nucleophilic nature of the $(Me_3Si)_2N^-$ anion, the nitrogen–lanthanide bond might be expected to have a rather greater degree of covalent character than most other ligand–lanthanide bonds, which are usually considered to be of a rather ionic nature. Consequently, the effect of the ligand field on the *f*-orbital levels should be unusually great. The compounds $[Ln(btsa)_3]$ have a trigonal array of ligands and the axial ligand field will be very small while the field in the *xy* plane (taking the three-fold axis as *z*) will be large. This should lead to a comparatively large energy difference between the various single-electron 4*f* orbitals, with correspondingly large ligand field splitting of many individual $^{2S+1}L_J$ levels. Further, the comparatively high symmetry should mean that each $^{2S+1}L_J$ level will be Stark-split into considerably less than $2J + 1$ sub-levels. The overall result should be that the electronic spectra of these compounds would show a few, well-separated, maxima corresponding with a particular $^{2S+1}L_J$ excited state in their absorption spectra instead of the broad envelope which is often observed (particularly in aqueous solution spectra where labile equilibria involving hydration are often involved).

The spectrum of $[Nd(btsa)_3]$ in n-pentane solution illustrates this effect. The Figure shows the general comparison with a corresponding spectrum of the aqueous ion. Also shown are the transitions $^3H_4 \longrightarrow {}^3P_{2,1,0}$ for $[Pr(btsa)_3]$ and for the aqueous Pr^{3+} ion; in this case the reasonable assignment shown means that the overall splitting of $^2P_2$ is as much as 1200 cm^{-1}. In trigonal symmetry, $^3P_2$, $^3P_1$, and $^3P_0$ are split into 3, 2, and 1 levels respectively.

The nephelauxetic effect can in lanthanide chemistry be approximately evaluated from the parameter β, where $\beta = (\sigma_{complex}/\sigma_{aquo\text{-}ion})$ and σ = energy of a specific transition.[1] In many lanthanide complexes, the band positions are moved to lower wavenumber relative to the aquo-ion (taken as a convenient standard having relatively low-field ligands); this effect arises from reduced inter-*f*-orbital repulsions consequent upon increased

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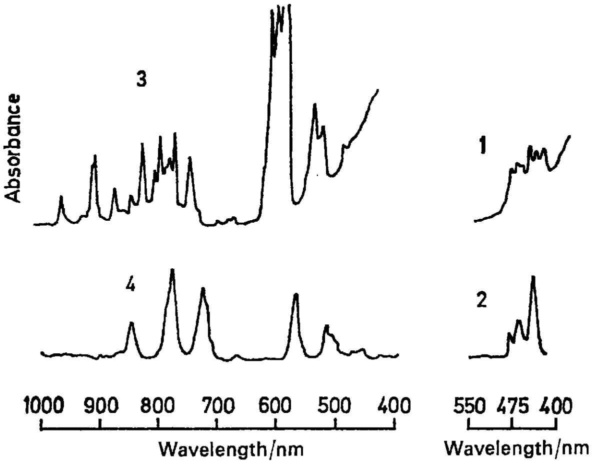
[10] B. Bleaney, C. M. Dobson, B. A. Levine, R. B. Martin, R. J. P. Williams, and A. V. Xavier, *J.C.S. Chem. Comm.*, 1972, 791.

[11] E. R. Birnbaum and T. Moeller, *J. Amer. Chem. Soc.*, 1969, **91**, 7274.

shielding arising from increased σ-donation. Based on the Pr $^3H_4 \longrightarrow {}^3P_{2,1,0}$ and Nd $^4I_{9/2} \longrightarrow {}^4G_{5/2}$ transitions (other assignments are unreliable owing to considerable overlap of the Stark-split levels), β = 0·993 (Pr) and 0·978 (Nd). These values are comparable to those for $[PrCl_6]^{3-}$ and $[NdCl_6]^{3-}$.[1] If β is roughly inversely proportional to the total σ-donation, the $(Me_3Si)_2N^-$ ligand is thus about twice as effective a σ-donor as Cl^-.

The spectra also show strong absorption, probably a ligand ⟶ lanthanide charge transfer band, at energies greater than 25 000 cm^{-1}. This band should be shifted to lower energy in the case of Eu, Yb, and Sm whose dipositive states are particularly stable. In accord with this, a pentane solution of the orange $[Eu(btsa)_3]$ shows strong absorption commencing at *ca.* 16 000 cm^{-1}, while the solid Yb and Sm compounds are yellow.



Absorption spectra of praseodymium and neodymium compounds (1), 0·05M $Pr[N(SiMe_3)_2]_3$ in n-pentane; (2), 0·05M $Pr(ClO_4)_3,9H_2O$ in water; (3), 0·05M $Nd[N(SiMe_3)_2]_3$ in n-pentane; (4), 0·05M $Nd(ClO_4)_3,9H_2O$ in water

EXPERIMENTAL

Since all these compounds are decomposed by traces of moisture, special precautions were taken to exclude air and moisture from the solvents and apparatus. Preparation of these compounds was carried out in an atmosphere of dry nitrogen and most of the manipulations were done in a glove-box as described elsewhere.[12]

Benzene, tetrahydrofuran, and n-pentane were distilled over calcium hydride and redistilled from a blue solution of sodium benzophenone as required for use.

Anhydrous Metal Chlorides.—Oxides of yttrium and lanthanides (Rare Earth Products Ltd.) were converted into their hydrated chlorides by dissolution in hydrochloric acid and subsequent evaporation. The powdered hydrated chlorides were treated under reflux and magnetic stirring with boiling thionyl chloride (purified by distilling over linseed oil) for about 48 h. The resulting materials when dried *in vacuo* gave satisfactory analytical results for metal and chlorine.

Analyses.—Yttrium and lanthanides were determined gravimetrically by alkaline precipitation followed by washing and ignition to the oxides. The bis(trimethylsilyl)-amino-group was estimated by hydrolysing a known weight of the sample with 10% KOH, the liberated hexamethyldisilazane being distilled directly in a known excess of H_2SO_4 (0·1N) and the product titrated with alkali. The analytical data are presented in the Table.

Physical Measurements.—M.p.s were obtained using sealed capillaries in an Electrothermal apparatus.

Molecular weight studies on these air sensitive compounds in benzene were performed using a semi-micro ebulliometer (Gallenkamp MW-120) with a special attachment to provide a dry nitrogen atmosphere and to permit addition of the sample and fluorene calibrant in pellet form. The results are given in the Table.

The electronic spectra of $[Pr(btsa)_3]$ and $[Nd(btsa)_3]$ (0·05M in n-pentane, using sealed 1 cm silica cells) were recorded using a Beckmann DK-2A instrument.

An AEI-MS902 instrument operating at 70 eV and *ca.* 10^{-7} mmHg pressure, with a device designed by Mr. P. Cook for direct insertion of the air-sensitive compounds, was used to obtain mass spectra.

^1H N.m.r. spectra of deuteriobenzene solutions of the samples (10—15% solution prepared in a specially designed apparatus) in tubes sealed under vacuum were recorded on a Varian A-60 spectrometer, using TMS as the internal signal.

A Decca X3 spectrometer was used to measure the e.s.r. spectra of solid $Gd(btsa)_3$ at room temperature. The sample was sealed under vacuum in constant bore (0·4 cm) Pyrex tubing.

Magnetic susceptibility measurements were taken on a commercial (Newport Instruments) variable temperature Gouy balance at 298 and 98 K. At each temperature measurements were made with magnetic fields of 0, 3785, 5750, and 6675 G to detect any field dependence. The apparatus was calibrated over the whole temperature range (98—323 K) by use of tris(ethylenediamine)nickel(II) sulphate and mercury tetrathiocyanatocobaltate. Samples were introduced into a specially fitted Gouy tube *in vacuo* and stoppered under nitrogen.

Preparation of Tris{bis(trimethylsilyl)amido}compounds of Yttrium and Lanthanides.—Since the techniques used and the steps involved in the preparation of these compounds are similar, details of only one representative experiment are given below.

Preparation of $[La\{N(SiMe_3)_2\}_3]$.—Bis(trimethylsilyl)-amidolithium (0·105 mol) was prepared from n-butyllithium (66·5 ml; 1·56N) and hexamethyldisilazane (24 ml; 0·12 mol) in tetrahydrofuran (100 ml). The mixture was cooled (0 °C) and treated with small portions of $LaCl_3$ (0·0346 mol; 8·5 g). The reaction mixture was allowed to attain room temperature and was kept stirring for 24 h before all the solvent was removed at 10^{-4} mmHg. Lithium chloride was separated by extracting the compound into n-pentane (80 ml). Colourless needles of the compound obtained from the n-pentane extract were recrystallised three times from pentane and gave, after drying under vacuum 13·6 g (63% yield) of product. The compound was sublimed at 100—102 °C under 10^{-4} mmHg.

Employing the above procedure the tris[bis(trimethylsilyl)amido]compounds of other lanthanides and yttrium were prepared in a similar fashion in comparable yields (50—70%).

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