Synthesis, solid state structure, and solution behaviour of the lighter lanthanide bis(trimethylsilyl)amido chlorides, [Ln{N(SiMe₃)₂}₂(THF)(μ-Cl)]₂ (Ln = Ce, Nd)

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Abstract: The synthesis of $[Ln{N(SiMe_3)_2}_2(THF)(\mu-Cl)]_2$ (Ln = Ce, **1**; Nd, **2**) by reaction of sodium bis(trimethylsilyl)amide (2 equiv.) with LnCl₃ is reported. The same complexes were also isolated from the ligand redistribution reactions of Ln[N(SiMe_3)_2]_3 and LnCl₃ (2:1 ratio) in THF at 80°C. The crystal structure of **2**, determined by X-ray diffraction, revealed a centrosymmetric dimer with bridging chlorides and pentacoordinate metal centres. ¹H NMR studies show that the solid state structure is not maintained in solution. NMR evidence for the presence of Ln[N(SiMe_3)_2]_3 and two other bis(trimethylsilyl)amide containing species, presumably Ln[N(SiMe_3)_2]Cl₂(THF)_x and Ln[N(SiMe_3)_2]₂Cl(THF)_y, is presented.

Key words: lanthanide, amide, neodymium, cerium, crystal structure, X-ray, nuclear magnetic resonance, redistribution.

Résumé : On a effectué la synthèse du $[Ln{N(SiMe_3)_2}(THF)(\mu-Cl)]_2$ (Ln = Ce, 1; Nd, 2) par réaction du bis(triméthylsilyl)amide (2 équiv.alents) avec du LnCl₃. On a aussi isolé les mêmes complexes à partir de réactions de ligands de Ln[N(SiMe_3)_2]_3 et LiCl₃ (rapport 2:1) dans le THF à 80°C. La structure cristalline du produit 2, déterminée par diffraction des rayons X, met en évidence la présence d'un dimère centrosymétrique comportant des atomes de chlore agissant comme pont et des centres métalliques pentacoordinés. Les études de RMN du ¹H montrent que la structure solide n'est pas maintenue en solution. On rapporte des données de RMN qui mettent en évidence la présence de Ln(N(SiMe_3)_3]_3 et de deux autres espèces contenant du bis(triméthylsilyl)amide, probablement du Ln[N(SiMe_3)_2]Cl₂(THF)_x et Ln[N(SiMe_3)_2]Cl(THF)_y.

Mots clés : lanthanide, amide, néodyme, cérium, structure cristalline, rayons X, résonance magnétique nucléaire, redistribution.

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Introduction

The incorporation of anionic ligands into lanthanide complexes is usually achieved by metathetical reactions between a lanthanide halide or alkoxide and a salt of the ligand (eqs. [1], [2]). While often useful, there are many instances when pure products can not be obtained by this method due to incomplete substitution of the leaving group or formation of an anionic "ate" complexes (an addition reaction, eq. [3]) (for some representative examples see ref. (1)). A protonolysis reaction between an acidic, protonated form of the incoming ligand and strongly basic anionic leaving groups is an attractive alternative in many cases, particularly when the leaving group has little propensity to coordinate to the product complex (eq. [4]). Bis(trimethylsilyl)amido complexes

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¹Author to whom correspondence may be addressed. Telephone: (250) 721-7161. Fax: (250) 721-7147. e-mail: DJBERG@UVIC.CA are attractive alternative precursors because the amido group is quite basic and the bis(trimethylsilyl)amine that is formed is noncoordinating and volatile, making its removal straightforward.

[1] 3 M⁺L⁻ + LnCl₃ \rightarrow LnL₃ + 3 M⁺Cl⁻ \downarrow (M = Li, Na, K)

$$[2] \quad 3 \text{ M}^+\text{L}^- + \text{Ln}(\text{OAr})_3 \rightarrow \text{LnL}_3 + 3 \text{ MOAr} \downarrow$$
$$(\text{Ar} = 2,6\text{-}t\text{-Bu}_2\text{C}_6\text{H}_3)$$

$$[3] \qquad 3 M^+L^- + LnCl_3 \rightarrow [LnL_3Cl]^- M^+ + 2 M^+Cl^- \downarrow$$

$$(M = Li, Na, K)$$

$$[4] \quad 3 \text{ HL}' + \text{LnL}_3 \quad \rightarrow \text{LnL}'_3 + 3 \text{ HL}$$

 $(L = N(SiMe_3)_2)$

The synthesis of mixed ligand complexes of the lanthanides by methathetical reactions is even more challenging because controlled substitution of the leaving groups is difficult and ligand redistribution often occurs under these conditions. (2) The successful isolation of mixed bis(trimethlsilyl)amido chloride complexes $[Ln{N(SiMe_3)_2}_2(THF)(\mu-Cl)]_2$ (Ln = Eu, Gd, Yb) by Aspinall et al. (3) using metathesis is noteworthy

Table 1. Crystallographic data for 2.

Formula	C ₁₆ H ₄₄ N ₂ OSi ₄ ClNd
Fw (dimer)	1145.14
Cryst syst	monoclinic
Space group	$P 2_1/n$ (no. 14)
<i>a</i> (Å)	15.210(2)
b (Å)	12.074(1)
<i>c</i> (Å)	16.621(3)
β (deg)	112.62(1)
V (Å ³)	2817.6(4)
Ζ	2 (dimers)
ρ (calcd) (g cm ⁻³)	1.35
μ (cm ⁻¹)	21.1
Radiation, λ (Å)	Μο Κα, 0.7107
Т	ambient
$2\theta_{\text{max}}$ (deg)	45.0
No. obsd reflcns	3667
No. of unique reflcns	2880
R^{a}, R_{w}^{b}	0.047, 0.049

 ${}^{a}R = \Sigma(|F_{o}| - |F_{c}|)/\Sigma|F_{o}|.$

 ${}^{b}R_{w} = [\Sigma w(|F_{o}| - |F_{c}|^{2})/\Sigma w(|F_{o}|)^{2}]^{1/2}.$

because the products are suitable precursors to other mixed ligand complexes by protonolysis of the two silylamido groups. However, these authors did not attempt to isolate the analogous complexes for the lighter lanthanides because they assumed that these complexes would be too coordinatively unsaturated to exist as simple dimers. In this contribution we demonstrate that bis(amido) complexes of these metals are accessible both by metathesis or redistribution reactions.

Results and discussion

Synthesis

The bis(trimethylsilyl)amido chloride complexes $[Ln{N(SiMe_3)_2}_2(THF)(\mu-Cl)]_2$ (Ln = Ce, 1; Ln = Nd, 2) were initially prepared by stirring two equiv. of sodium bis(trimethylsilyl)amide with the appropriate trichloride in THF for 48 h, followed by filtration to remove NaCl, removal of the solvent and recrystallization of the residue from hexane at -30°C (eq. [5]). In agreement with earlier observations (2, 3), complexes 1 and 2 were more intensely coloured (1, canary yellow; 2, lilac) and more soluble than their tris(amido) analogues, Ln[N(SiMe₃)₂]₃. The crystals are also easily distinguishable from the tris(amido) complexes by their form: both 1 and 2 are isolated as wellformed prisms, while the tris(amido) complexes of all the lanthanides form feathery needles.

[5] 2 Na⁺[N(SiMe₃)₂]⁻ + LnCl₃
$$\xrightarrow{\text{THF}}$$

[Ln{N(SiMe₃)₂}₂(THF)(µ-Cl)]₂ + 2 Na⁺Cl⁻
Ln = Ce (1), Nd (2)

Small amounts of the tris(amido) complexes were always isolated along with **1** and **2** during recrystallization but these

Table 2. Selected bond distances and angles for 2^a .

Distances (Å)	
Nd(1)—Cl(1)	2.791(3)
Nd(1)—Cl(1)'	2.854(3)
Nd(1)—O(1)	2.496(7)
Nd(1)—N(1)	2.300(8)
Nd(1)—N(2)	2.335(8)
N(1)—Si(1)	1.702(9)
N(1)—Si(2)	1.732(9)
N(2)—Si(3)	1.705(9)
N(2)—Si(4)	1.707(9)
Angles (deg)	
Cl(1)-Nd(1)-Cl(1)'	73.66(10)
Cl(1)-Nd(1)-O(1)	144.1(2)
Cl(1)-Nd(1)-N(1)	99.0(2)
Cl(1)-Nd(1)-N(2)	108.2(2)
Cl(1)'-Nd(1)-O(1)	76.2(2)
Cl(1)'-Nd(1)-N(1)	107.0(2)
Cl(1)' - Nd(1) - N(2)	136.7(2)
O(1) - Nd(1) - N(1)	108.2(3)
O(1) - Nd(1) - N(2)	81.3(3)
N(1)-Nd(1)-N(2)	115.1(3)
Nd(1)-Cl(1)-Nd(1)'	106.3(1)
Nd(1)-N(1)-Si(1)	122.4(5)
Nd(1)-N(1)-Si(2)	115.9(4)
Nd(1)–N(2)–Si(3)	129.2(5)
Nd(1)–N(2)–Si(4)	110.2(4)
Si(1)–N(1)–Si(2)	121.5(5)
Si(3)–N(2)–Si(4)	120.6(5)

^aEstimated standard deviations are given in parentheses.

products were very easy to separate. It is noteworthy that pure crystalline **1** and **2** inevitably produced some of the tris(amido) product during recrystallization supporting facile redistribution in solution. This fact was confirmed by ¹H NMR (vide infra) and by the successful synthesis of **1** and **2** from LnCl₃ and Ln[N(SiMe₃)₂]₃ by redistribution (eq. [6]). The yields obtained by redistribution were comparable to those obtained by metathesis.

[6] 2 Ln[N(SiMe₃)₂]₃ + LnCl₃ $\xrightarrow{\text{THF}}$ 3/2 [Ln{N(SiMe₃)₂}₂(THF)(μ -Cl)]₂ Ln = Ce (1), Nd (2)

Solid-state structure of [Nd{N(SiMe₃)₂}₂(THF)(µ-Cl)]₂ (2)

The solid state structure of the neodymium complex 2 was determined by X-ray crystallography. Crystallographic data for 2 is summarized in Table 1, selected bond distances and angles are given in Table 2, and the structure is shown in Fig. 1. The complex is dimeric in the solid state and consists of two five-coordinate metal centres bridged by chloride ions. The geometry at the metal is approximately trigonal bipyramidal with one chloride and two amido ligands defining the equatorial plane. The observed structure is isostructural with those previously reported for the Gd and Yb analogues (3). The metal–ligand bond distances in 2 are,

Fig. 1. ZORTEP plot (30% probability) of 2.



on average, 0.06 and 0.14 Å larger than those found in the Gd and Yb complexes, respectively in keeping with the difference in ionic radii for these metals (0.04 and 0.11 Å. respectively) (4). The only significant differences between this structure and those for Gd and Yb is that the Ln-N-Si angles span a much wider range (110.2(4)-129.2(5)° vs. $117.4(3)-123.5(3)^{\circ}$) and the bridging chlorides display greater asymmetry ($\Delta = r(Ln-Cl) - r(Ln-Cl') = 0.063(4)$ (Nd), 0.025(6) (Gd), 0.023(6) (Yb) Å) in complex 2. The greater asymmetry in the chloride bridges is surprising because 2 is clearly the least sterically crowded of the three structures. A comparison of the Ln-Cl distances reveals that the shorter Nd—Cl distance in 2 is consistent with that predicted from the earlier Gd and Yb structures (predicted: 2.78(1) Å from both the Yb and Gd structures; observed: 2.791(3) Å). (4) In contrast, the longer Nd—Cl distance in 2 is significantly greater than expected based on the Gd and Yb structures (predicted: 2.80(1) Å; observed: 2.854(3) Å).

Solution behaviour

The solution behaviour of 1 and 2, monitored in d_{5} bromobenzene by variable temperature ¹H NMR spectroscopy (Figs. 2 and 3), clearly indicates that the solid state structure is not maintained in solution. For both complexes, five resonances were observed throughout the temperature range studied (20-125°C). The two smaller resonances (D and E) were established as THF signals by exchange with d_8 -THF. One of the larger resonances (**B**) was established as due to Ln[N(SiMe₃)₂]₃ by addition of a large excess of the authentic tris(amido) complex. The remaining two resonances are tentatively assigned as the mono (A) and bis(amido) (C) complexes, Ln[N(SiMe₃)₂]Cl₂(THF)_x and Ln[N(SiMe₃)₂]₂Cl(THF)_v, respectively on the basis of integration. It is not possible to know the state of aggregation of these two complexes in solution or the extent to which they are solvated by THF, although it is extremely unlikely that either exists as a base-free monomer. If it is assumed that **Fig. 2.** Plot of chemical shift (ppm) vs. $1/T (\times 1000 \text{ K}^{-1})$ for **1**. Assignments: Ce[N(SiMe₃)₂]Cl₂(THF)_x (**A**), Ce[N(SiMe₃)₂]₃ (**B**), Ce[N(SiMe₃)₂]₂Cl(THF)_y (**C**), α -CH₂THF (**D**), and β -CH₂THF (**E**).



Fig. 3. Plot of chemical shift (ppm) vs. 1/T (× 1000 K⁻¹) for 2. Assignments: Nd[N(SiMe₃)₂]Cl₂(THF)_x (A), Nd[N(SiMe₃)₂]₃ (B), Nd[N(SiMe₃)₂]₂Cl(THF)_y (C), α -CH₂THF (D) and β -CH₂THF (E).



these are the only species present then a plausible solution equilibrium is given in eq. [7].²

The silylamide integration ratio of $Ln[N(SiMe_3)_2]_3$ (**B**) relative to $Ln[N(SiMe_3)_2]Cl_2(THF)_x$ (**A**) remains approximately

 2 LnCl₃ may also form but this product cannot be observed by NMR and there was no visual evidence for its formation.

Fig. 4. Plot of chemical shift (ppm) vs. 1/T (× 1000 K⁻¹) for the Ln[N(SiMe₃)₂]₃ resonances of **1**(**A**) and **2** (**B**) and pure Ln[N(SiMe₃)₂]₃ (Ln = Ce (×), Nd (+)).



3:1 at all temperatures which is what would be expected based on eq. [7].

[7] 2
$$Ln[N(SiMe_3)_2]_2Cl(THF)_y$$

$$Ln[N(SiMe_3)_2]_3 + Ln[N(SiMe_3)_2]Cl_2(THF)_x$$

Resonances A–C for 1 follow nearly linear behaviour throughout the temperature range sampled. This is consistent with each resonance being due to a single well-defined species. The resonances due to the THF (D-E) do show curvature over this temperature range. The temperature dependence of the amido resonances for 2 show greater curvature although the resonance due to $Nd[N(SiMe_3)_2]_3$ (Fig. 3, **B**) is close to linear. The temperature dependence of the $Ln[N(SiMe_3)_2]_3$ resonances for 1 and 2 are compared with those for separate samples of pure $Ln[N(SiMe_3)_2]_3$ in Fig. 4. The close similarity between these plots confirms the assignments made in Fig. 2 and 3.3 In addition, since the resonances in Fig. 4 are essentially unperturbed from those of pure $Ln[N(SiMe_3)_2]_3$, the forward and reverse reaction rates in eq. [7] must be slow on the NMR timescale over the entire temperature range studied.

The results presented here indicate that it is possible to isolate pure solid bis(amido) chloride complexes such as 1 and 2 for the lighter lanthanides. However, in solution ligand redistribution occurs readily so that mono and tris(amido) species are also present. This does not necessarily preclude the use of these complexes as precursors to other mixed

ligand systems by protonolysis reactions. However, in cases where the reaction proceeds rapidly and irreversibly (for example, giving an insoluble product), it is useful to remember that this kinetic product may be derived from any of the three amido species present in solution.

Experimental

General procedures

All manipulations were carried out under an argon atmosphere, with the rigorous exclusion of oxygen and water, using standard glovebox (Braun MB150-GII) or Schlenk techniques. Tetrahydrofuran (THF) and hexane were dried by distillation from sodium benzophenone ketyl under argon immediately prior to use. $Ln[N(SiMe_3)_2]_3$ (Ln = Ce, Nd) were prepared according to the literature (5).

Variable temperature ¹H NMR spectra were recorded on a Bruker WM-250 MHz spectrometer. Spectra were recorded in C_6D_5Br dried over 4 Å molecular sieves for one week, using 5 mm tubes fitted with a teflon valve (Brunfeldt). The sample was allowed to equilibrate for 15 min at each temperature prior to recording the spectrum. Melting points were recorded using a Reichert hot stage and are not corrected. Elemental analyses were performed by Canadian Microanalytical, Delta, B.C. Mass spectra were recorded on a Kratos Concept H spectrometer using an electron impact (70 eV) source.

Preparation of [Ln{N(SiMe₃)₂}₂(THF)(µ-Cl)]₂

In a typical preparation, a solution of sodium bis(trimethylsilyl)amide (2 equiv.) was added to a stirred suspension of $LnCl_3$ under argon at room temperature. The solution was stirred for 48 h and the solvent was removed under reduced pressure. The solid residue was extracted into hexane, filtered through a Celite pad to remove NaCl, and crystallized in the glovebox at -30° C. Generally this resulted in a large mass of block-like crystals of the bis(amide) surrounded by fine needles of $Ln[N(SiMe_3)_2]_3$. The smaller tris(amide) crystals can usually be removed with the mother liquor by a Pasteur pipette. Although the larger bis(amide) crystals are more soluble, they are slow to redissolve so washing with cold hexane is an ideal way to wash off the smaller tris(amide) needles.

Alternatively, the complexes were prepared in comparable yield by heating a THF solution of two equiv. $Ln[N(SiMe_3)_2]_3$ with one equiv. of $LnCl_3$ in a sealed Kontes flask at 80°C overnight. All solids dissolved on heating and remained in solution after the reaction mixture was cooled back to room temperature. The THF solvent was removed under reduced pressure and the residue was recrystallized from hexane in the glove box as described above. Complexes **1** and **2** are readily accessible on a 10 g scale by either preparative route.

$[Ce\{N(SiMe_3)_2\}_2(THF)(\mu-Cl)]_2$ (1)

Canary yellow prisms. Yield: 65%, mp. 151–153°C. Anal. calcd. for $C_{32}H_{88}N_4O_2Si_8Cl_2Ce_2$: C 33.81, H 7.80, N 4.93%; found: C 33.39, H 7.94, N 4.78%.

³The small difference in chemical shift between pure Ln[N(SiMe₃)₂]₃ and that formed in the equilibrium of eq. [7] is likely a result of differences in the concentrations of the paramagnetic ions, which will exhibit differences in bulk susceptibility.

$[Nd{N(SiMe_3)_2}_2(THF)(\mu-Cl)]_2$ (2)

Deep lilac prisms. Yield: 81%, mp. 147–149°C. MS(EI): m/z 499 (10%, Nd{N(SiMe_3)_2}_2Cl⁺), 464 (100%, Nd{N(SiMe_3)_2}_2⁺), 449 (10%, [Nd{N(SiMe_3)_2}_2 - CH_3]⁺), 434 (10%, [Nd{N(SiMe_3)_2}_2 - 2 CH_3]⁺), 419 (10%, [Nd{N(SiMe_3)_2}_2 - 3 CH_3]⁺), 302 (10%, Nd{N(SiMe_3)_2}⁺) amu. Anal. calcd. for C₃₂H₈₈N₄O₂Si₈Cl₂Nd₂: C 33.56, H 7.75, N 4.89%; found: C 33.21, H 7.59, N 4.71%.

X-ray crystallographic studies

Crystallographic data for 2 is summarized in Table 1. Crystals of 2 ($0.5 \times 0.5 \times 0.5$ mm) were loaded into glass capillaries in the glove box and subsequently flame sealed. The crystals were transferred to a Nonius CAD4F diffractometer equipped with MoK α radiation. The unit cell of 2 was refined using 24 reflections in the 2 θ range of 38– 42. An experimental density was not obtained because of the air sensitivity of the compound. Six standard reflections, measured periodically during data collection (9, 0, 7; 7, 0, 1; 8, 9, 0; 0, 7, 1; 0, 0, 8; 3, 5, 7) showed a 10% decline in intensity during data collection. Intensity measurements were collected over one quarter of the sphere. After the usual data reduction procedures, including an absorption correction (max/min transmission: 0.9939, 0.8507) according to a measured PSI scan, the structure was solved by Patterson methods.⁴ The refinements minimized $w((F_o - F_c)^2)$ and proceeded normally using teXsan98.5 Criteria for inclusion of reflections were $I > 3.5 \sigma(I)$. The weighting scheme was determined by counting statistics using $w = 1/(\sigma^2(F) + 0.001F^2)$.

Convergence was satisfactory: max shift/esd < 0.01; the largest positive and negative peaks in the final difference map were 1.64 and -0.97 e/Å^3 , respectively. A total of 227 parameters were refined. Hydrogen atoms were placed in calculated positions. No non-hydrogen intermolecular con-

tacts shorter than 3.5 Å were observed. The structural perspective plots were drawn using ZORTEP.⁶ Complete tables of bond distances, angles, and anisotropic temperature parameters have been deposited as supplementary material.⁷

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