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Lanthanide complexes of a cross-bridged cyclam ligand: Isolation and structural characterization of unusual trinuclear μ^3-imido Yb(III) cluster cations and a mixed valence Yb(II/III) salt containing an Yb(II) anion

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Dedicated to Professor Brian James for his lifelong contributions to inorganic chemistry.

Abstract

The reaction of the cross-bridged cyclam ligand H_2CBC with divalent ytterbium precursors, $Yb[N(SiMe_3)_2]_2[L]_2$ (L = THF or Et_2O) or $Yb(C_5Me_5)_2(OEt_2)$ afforded polymeric $[Yb(CBC)]_n$ (**1**), as the primary product. In addition, the $Yb[N(SiMe_3)_2]_2[L]_2$ reactions also afforded a small amount of an unusual mixed valence salt containing a trinuclear Yb(III) cluster cation featuring a triply bridging NH group and a mononuclear Yb(II) anion, $\{[Yb(CBC)]_3[\mu^3\text{-NH}]\}^+ \{Yb[N(SiMe_3)_2]_3\}^-$ (**2**). A related cluster containing an iodide counterion, $\{[Yb(CBC)]_3[\mu^3\text{-NH}]\}^+ I^-$ (**3**), was also isolated in one case. The structures of salts **2** and **3** were determined by X-ray crystallography. Reaction of $[Yb(CBC)]_n$ with *p*-tolyldisulfide, $(C_6H_4MeS)_2$, produced burgundy crystals of $[Yb(CBC)(S\text{-p-}C_6H_4Me)]_n$ (**4**). The ^1H NMR spectra of **2** suggests that the trinuclear cation remains intact in THF-d_8 solution.

Keywords: X-ray crystal structures; Ytterbium complexes; Imide; Mixed valence; Macrocyclic ligands; Cyclam; Amide; Trinuclear cluster

1. Introduction

The development of non-cyclopentadienyl ancillary ligand systems has been one of the major themes in lanthanide research over the past 15 years [1]. Lanthanide complexes containing amido functionality as part of a polydentate ligand framework have played a large role in the development of new organometallic and coordination chemistry of these elements [1,2]. Several years ago, we reported a number of organolanthanide complexes containing the chelating diamides derived from deprotonated aza- and diaza-18-crown-6 ligands (Fig. 1, MAC and DAC) [3]. While ligands of this class did afford some interesting chemistry including the formation of stable dialkyls [3d], moderately stable alkyl cations [3d] and the reversible dimerization of alkynides to butatrienediyls [3c], their flexibility often resulted in polymeric products containing bridging amido groups, especially with the larger, divalent lanthanide ions [3a]. In addition, the six donor N_2O_4 array represented in MAC and DAC was thought to be responsible for the relatively low reactivity that complexes of the type Ln(DAC)R and Ln(MAC)R_2 (Ln = Y or a lanthanide) displayed towards unsaturated substrates such as alkenes and alkynes.

With the limitations of MAC and DAC in mind, a ligand system with fewer donors and greater rigidity seemed attractive. The cross-bridged cyclam ligand (Fig. 1, CBC), containing a N_4 donor array and an ethylene

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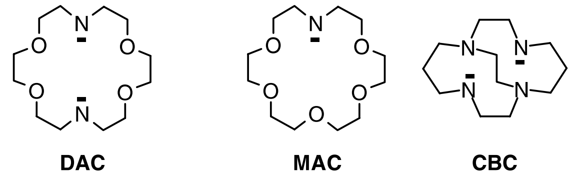


Fig. 1. Select macrocyclic amido ligands.

bridge that restricts macrocycle flexibility, was readily available using literature procedures [4] and a number of transition metal complexes were known [5], although no lanthanide complexes had been reported. Initial attempts to prepare trivalent lanthanide complexes by direct reaction of $LnCl_3$ with the CBC^{2-} dianion alkali metal salts was not successful, presumably due to our inability to remove alkali chloride metathesis products. We experienced similar problems in zirconium chemistry but we were successful in isolating $Zr(CBC)(CH_2Ph)_2$ and $Zr(CBC)Cl_2$ by acid–base reactions between H_2CBC and $Zr(CH_2Ph)_4$ or $Zr[N(SiMe_3)_2]_2Cl_2$, respectively [6]. Our attempts to prepare trivalent Ln(CBC)X complexes by acid–base reactions therefore focused on the direct reaction of $Ln[N(SiMe_3)_2]_3$ with H_2CBC. Unfortunately, although this reaction did proceed slowly, the products obtained were not clean. Similar results were observed during attempts to use $Y[CH(SiMe_3)_2]_3$ or $Y[CH_2SiMe_3]_3[THF]_2$.

Perhaps somewhat surprisingly, direct reaction of H_2CBC with divalent $Yb[N(SiMe_3)_2]_2[L]_2$ ($L = OEt_2$ or THF) proceeds within minutes at room temperature to afford a polymeric product $\{Yb[CBC]\}_n$ and an unusual mixed valence salt containing a trinuclear Yb(III) cation and a monomeric Yb(II) anion. The cation contains a capping μ^3-NH, the first structurally characterized example of such a group in a lanthanide cluster. In this paper, we discuss the solution behaviour and solid state structure of this unique compound as well as a related byproduct. A pathway that explains the formation of this cluster is also presented.

2. Experimental

2.1. General

All reactions were carried out in a M. Braun glove box under an atmosphere of nitrogen. Solvents were dried by distillation from sodium benzophenone ketyl under argon and used immediately or stored in the glove box until use. THF-d_8 for NMR experiments was dried by distillation from potassium metal and stored over 4 Å sieves in the glove box. Samples for NMR spectroscopy were prepared in the glove box and loaded into 5 mm tubes fitted with sealable Teflon valves (Brunfeldt). ^1H NMR spectra were recorded on a Bruker AMX-360 MHz spectrometer at various temperatures. FT-IR spectra were recorded as Nujol mulls on NaCl plates. Melting points were obtained using a Büchi melting point apparatus on samples sealed under nitrogen in a glass capillary; melting points are uncorrected. Elemental analyses were performed by Canadian Microanalytical in Delta, BC, on microcrystalline samples sealed for shipment in a glass ampoule.

H_2CBC was prepared by a modification of the literature procedure [4b,6] starting from cyclam, purchased from Aldrich and used as received. $Ln[N(SiMe_3)_2]_3$ [7], $Yb[N(SiMe_3)_2]_2[OEt_2]_2$ [8], $Yb[N(SiMe_3)_2]_2[THF]_2$ [9] and $Yb(C_5Me_5)_2(OEt_2)$ [10] were prepared as described in the literature. *p*-Tolyldisulfide was purchased from Aldrich and used as received.

2.2. Synthesis of $\{Yb[CBC]\}_n$ (**1**)

A solution of H_2CBC (0.100 g, 0.442 mmol) in 5 mL toluene was added slowly to a solution of $Yb[N(SiMe_3)_2]_2[OEt_2]_2$ (0.286 g, 0.435 mmol) in 3 mL toluene with rapid stirring. An immediate color change was observed from dark red to green–brown and precipitation of a dark red–brown powder commenced within minutes. The solution was allowed to stir overnight followed by collection of the precipitate by vacuum filtration through a fine sintered glass frit. The amber colored filtrate was cooled at −30 °C but no further precipitation was observed. The dark red–brown solid was first washed with THF, then three times with toluene and finally with hexane before being dried under reduced pressure for several hours. Yield: 0.122 g (71%). M.p. >275 °C. *Anal.* Calc. for $C_{12}H_{24}N_4Yb$: C, 36.27; H, 6.09; N, 14.10. Found: C, 34.88; H, 6.15; N, 13.65%.

When the reaction was carried out on the same scale using $Yb(C_5Me_5)_2(OEt_2)$ (0.230 g, 0.444 mmol) as the Yb(II) precursor, a dark rust-red precipitate formed slowly over the course of an hour. Isolation of this solid as described above yielded 0.145 g (84%) of **1**.

2.3. Isolation of $\{[Yb(CBC)]_3[\mu^3\text{-}NH]\}^+$ $\{Yb[N(SiMe_3)_2]_3\}^-$ (**2**)

When the reaction above was carried out with $Yb[N(SiMe_3)_2]_2[THF]_2$ (0.110 g, 0.172 mmol) and H_2CBC (0.050 g, 0.22 mmol) for 2 days in toluene, green crystals were easily discernible in the reaction mixture in addition to the red–brown powder. These crystals dissolved in THF and were separated from the insoluble red–brown powder (**1**) by filtration. Removal of the THF afforded **2** as a green powder. Yield: 0.015 g (5%). M.p. >275 °C. IR (Nujol mull on NaCl): 3280 cm^{-1} (m, NH stretch). ^1H NMR (THF-d_8, 360 MHz, 293 K): δ 98.3 (rel. int. = 3H, $\nu_{1/2} = 220$ Hz), 66.7 (3H, 400 Hz), 65.1 (3H, 260 Hz), 57.5 (3H, 680 Hz), 13.1 (3H, 180 Hz), 3.25 (3H), 3.02 (3H), 2.71 (3H), 2.58 (3H), 2.46 (3H), 0.03 (54H), −7.9 (3H, 220 Hz), −31.4 (3H, 360 Hz), −45.8 (3H, 120 Hz), −85.4 (3H, 290 Hz), −90.9 (3H, 150), −96.1 (3H, 280 Hz), −99.6 (3H, 230 Hz), −131.3 (3H, 240 Hz), −132.0 (6H, 670), −143.4 (3H, 120 Hz), −169.0 (3H, 600 Hz). *Anal.* Calc. for

$C_{54}H_{127}N_{16}Si_6Yb_4$: C, 34.85; H, 6.88; N, 12.03. Found: C, 32.81; H, 6.45; N, 11.12%.

When the reaction was repeated with $Yb[N(SiMe_3)_2]_2[OEt_2]_2$, the yield of **2** obtained by extraction of the initial precipitate with THF was 18% (on a 0.2 mmol scale).

2.4. Isolation of $\{[Yb(CBC)]_3[\mu^3\text{-}NH]\}^+\ I^-$ (**3**)

Complex **3** was isolated as yellow crystals (<2 mg) that slowly deposited from a solution of **2** in THF-d_8 over a period of several days. The crystals were only obtained with one batch of **2**, prepared from $Yb[N(SiMe_3)_2]_2[THF]_2$. Presumably the iodide ion was present as a minor contaminant in the starting silylamide complex since it was prepared by the metathesis reaction between YbI_2 and $NaN(SiMe_3)_2$.

2.5. Synthesis of $[Yb(CBC)(S\text{-}p\text{-}Tol)]_n$ (**4**)

A deep green solution of $Yb(C_5Me_5)_2(OEt_2)$ (0.253 g, 0.489 mmol) was prepared in 10 mL toluene in the glovebox. To this was added 0.110 g H_2CBC (0.486 mmol) in 5 mL toluene with vigorous stirring. An immediate color change to red was observed and precipitation of rust-red **1** took place within 1 h. The suspension was stirred for a further 3 h followed by addition of a solution of *p*-tolyldisulfide, $(p\text{-}C_6H_4MeS)_2$, 0.060 g (0.244 mmol) in 5 mL toluene by pipette. An immediate color change to a deep burgundy and complete dissolution of all solids was observed. The solution was stirred for 2 h, filtered through Celite and layered with hexane. Dark maroon crystals of **4** formed on standing overnight. These were isolated by decanting off the mother liquor and were washed with a small amount of cold toluene followed by hexane and drying under reduced pressure for several hours. The mother liquor afforded a second crop of crystals on cooling to −30 °C. Once isolated, the crystals of **4** dissolve very sparingly in toluene but remain very soluble in THF. Overall yield: 0.18 g (72%). M.p. 165 °C (dec). ^1H NMR (THF-d_8, 333 K): δ 27.9 (1H, $\nu_{1/2} = 17$ Hz), 21.0 (1H, 34 Hz), 20.7 (2H, 42 Hz), 17.7 (2H, 70 Hz), 12.7 (1H, 12 Hz), 10.5 (1H, 20 Hz), 7.05 (2H), 7.00 (1H), 1.99 (2H), 1.60 (4H, overlaps solvent), 1.32 (1H), 0.85 (2H, m-aryl*H*, 10 Hz), −0.24 (3H, *p-Me*, 18 Hz), −6.6 (2H, *o*-aryl*H*, 200 Hz). Not all resonances of the CBC ligand were observed. At room temperature, many more resonances were observed suggesting a more complex structure. In the absence of X-ray crystallographic data, no assignment of the ambient temperature structure is possible but the observed solubility and NMR data are more consistent with a structure involving bridging, either by the thiolate or amide ligands (or by both). *Anal.* Calc. for $C_{19}H_{31}N_4SYb$: C, 43.84; H, 6.00; N, 10.76. Found: C, 43.05; H, 6.05; N, 10.25%.

2.6. X-ray crystallographic studies

X-ray diffraction experiments were carried out at 83(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, $\lambda = 0.71073$ Å) equipped with a Cryocool NeverIce low temperature device. A crystal of **2** was removed from a sealed glass ampoule under nitrogen and immediately covered with a layer of hydrocarbon oil, mounted on a glass fiber and placed in the low temperature nitrogen stream [11]. Data were measured using omega scans of 0.3° per frame for 5 s, and a full sphere of data were collected. A total of 2132 frames were collected with a final resolution of 0.83 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART [12] software and refined using SAINTPlus [13] on all observed reflections. Data reduction and correction for Lorentz polarization and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS [14]. The structure was solved by direct methods and refined by least squares method on F^2 using the SHELXTL program package [15]. The structure was solved in the space group $P2_1/n$ (No. 14) by analysis of systematic absences. There is disorder in two of the cyclam rings (C7, C11, C12, C18, C19). The occupancy

Table 1
Crystallographic data for $[Yb_3(\mu\text{-}CBC)_3(\mu^3\text{-}NH)]^+\ [Yb(N(SiMe_3)_2)_3]^-$ (**2**) and $[Yb_3(\mu\text{-}CBC)_3(\mu^3\text{-}NH)]^+\ I^- \cdot 2\ THF$ (**3**)[a,b]

Compound no.	**2**	**3**
Formula	$C_{54}H_{127}N_{16}Si_6Yb_4$	$C_{44}H_{89}IN_{13}Yb_3$
Fw (g mol^{-1})	1861.4	1478.3
Crystal system[c]	monoclinic	monoclinic
Space group	$P2_1/n$(No. 14)	$P2_1/c$(No. 14)
a (Å)	17.6328(7)	11.8789(6)
b (Å)	19.3118(7)	13.3853(6)
c (Å)	23.4494(9)	31.9485(15)
β (°)	109.930(1)	92.966(1)
Volume (Å^3)	7506.8(5)	5073.1(4)
Z	4	4
Density (calc., g/cm^3)	1.647	1.936
Absorption coefficient μ (mm^{-1})	5.077	6.143
Crystal size (mm)	0.32 × 0.28 × 0.12	0.21 × 0.05 × 0.05
Crystal color and habit	green prism	yellow needle
θ Range (°)	1.40–25.25	1.65–25.25
Reflections collected	98 901	61 429
Independent reflections	13 595	9181
Maximum and minimum transmission	0.546 and 0.223	0.733 and 0.322
Data/restraints/parameters	13 595/25/748	9181/55/540
Goodness-of-fit on F^2	1.037	1.147
Final R indices $[I > 2\sigma(I)]$[d]	$R_1 = 0.026$, $wR_2 = 0.059$	$R_1 = 0.044$, $wR_2 = 0.085$
R (all data)	$R_1 = 0.031$	$R_1 = 0.056$
Largest difference in peak and hole (e Å^{-3})	2.24 and −0.54	2.73 and −1.09

[a] Mo (Kα) 0.71073 Å radiation at 83(2) K on a Bruker/Siemens Smart APEX diffractometer.

[b] Data collection and reduction, direct methods structure solution and refinement were carried out using SMART, SAINTPlus and SHELXTL software, respectively [11–15].

[c] International tables for X-ray crystallography, vol. 1: Symmetry Groups; Henry, N.F.M.; Lonsdale, K., Eds.; Kyntoch Press, England, 1969.

[d] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR = [\sum w(|F_o| - |F_c|^2)/\sum w(|F_o|)^2]^{1/2}$.

was refined and set at 50% for each moiety. The counter ion also shows disorder in one $SiMe_3$ group (Si2, C40-C42) as well as the central Yb position. The occupancies were refined as 57% and 50%, respectively. There are large residuals of ca. $2\,e^-/Å^3$ near Yb1 and Yb2. All non-hydrogen atoms, except disordered carbon atoms, were refined anisotropically. No decomposition was observed during data collection.

Crystal mounting and data collection, reduction and refinement for a yellow crystal of **3** were carried out in the manner described above. The structure was solved in the space group $P2_1/c$ (No. 14) by analysis of systematic absences. The disorder in the cyclam rings was refined as 60% for the major fraction. One of the THF molecules is completely disordered with an occupancy of 60% for the major fraction. Disordered atoms were held isotropic and all other atoms were refined anisotropically. The thermal parameters of each disordered moiety were constrained to be approximately equal. The hydrogen atom of the NH group was located on the difference map and restrained with a riding model. Large residuals of ca. $3\,e^-/Å^3$ are located ca. 1 Å from the Yb centers. These are due to absorption effects and could not be modeled or eliminated. No decomposition was observed during data collection. A summary of the data collection parameters is given in Table 1 for **2** and **3**. All thermal ellipsoid plots were prepared using ORTEP3 [16].

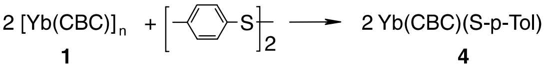
3. Results and discussion

Reaction of H_2CBC with either $Yb(C_5Me_5)_2(OEt_2)$ or $Yb[N(SiMe_3)_2]_2[L]_2$ (L = THF or diethyl ether) resulted in precipitation of a dark rust-red powder (**1**) that was insoluble in hydrocarbons and ethereal solvents, Eqs. (1) and (2). This compound analyzed reasonably well for $[Yb(CBC)]_n$ and the color is consistent with a divalent Yb center; however, the very low solubility of this material prevented ^1H NMR analysis that would allow unambiguous assignment of the metal oxidation state. The low solubility of this compound is presumably due to formation of extensive bridges by the amido nitrogens of the CBC ligand, as might be expected for what would otherwise be a four-coordinate Yb^{2+} center in a monomeric unit. Similar bridging was observed in a linear trinuclear Yb(II) complex containing 4,13-diaza-18-crown-6 (DAC), $[(Me_3Si)_2N]Yb(\mu\text{-DAC})Yb(\mu\text{-DAC})Yb[N(SiMe_3)_2]$ [3a].

$$\underset{L=THF,Et_2O}{YB[N(SiMe_3)_2]_2L_2} + H_2CBC \xrightarrow[-2L]{-2HN(SiMe_3)_2} \underset{\mathbf{1}}{[Yb(CBC)]_n} \quad (1)$$

$$Yb(C_5Me_5)_2(OEt_2) + H_2CBC \xrightarrow[-Et_2O]{-2HC_5Me_5} \underset{\mathbf{1}}{[Yb(CBC)]_n} \quad (2)$$

Oxidation of **1** with *p*-tolyldisulfide, $(p\text{-}C_6H_4MeS)_2$, resulted in a color change to burgundy, consistent with formation of the trivalent *p*-tolylthiolate complex **4**, Eq. (3) [17]. This complex was soluble in toluene and showed a paramagnetic ^1H NMR spectrum. The ^1H NMR spectrum of this compound was extremely complex at 293 K, showing at least 40 resonances between +100 and −150 ppm. However, on heating to 333 K, the NMR spectrum simplifies considerably so that only 18 resonances for the CBC ligand and 3 resonances assignable to the *p*-tolylthiolate group are observed. This is consistent with a dynamic process taking place in THF-d_8 solution over this temperature range. Given the low solubility of **4** in non-coordinating solvents, bridging amido and (or) thiolate groups could be present in this compound. The variable temperature behavior might therefore be explained by reversible bridge cleavage on the NMR timescale. Although the complexity and paramagnetism of this spectrum made a definitive structural assignment impossible, the formation of a trivalent thiolate by reduction of *p*-tolyldisulfide lends further support to the assignment of **1** as a polymeric Yb(II)-CBC complex.



(3)

An interesting observation was made during the preparation of **1** from $Yb[N(SiMe_3)_2]_2[THF]_2$: at longer reaction times, in addition to the rust-red powder of **1**, green crystals were also observed to form. These crystals dissolved readily in THF and it was subsequently discovered that regardless of which starting silylamide complex was used (Eq. (1)), extraction of the rust-red precipitate with THF afforded small, but reproducible, amounts of a green powder after removal of the solvent. Recrystallization of the green powder yielded green crystals of **2** suitable for X-ray crystallography.

The crystal structure of **2** reveals a unique mixed valence salt consisting of a trinuclear Yb(III) cluster cation and a mononuclear Yb(II) anion (Figs. 2 and 3, Table 2) [16]. The cation is made up of three Yb(III) centers in a triangular arrangement, bridged on each side by an amido N of a CBC ligand and capped on one face by a μ^3-NH group. Each six-coordinate Yb(III) center in the cation is therefore coordinated by two bridging amido N (of two different CBC ligands), one terminal amido and two amino N, as well as by the capping imido N (Fig. 3). The μ-amido groups of the CBC ligand bridge asymmetrically between Yb centers with short and long average Yb–N distances of 2.370 and 2.427 Å ($\Delta = 0.057$ Å), respectively. The closest comparison to this bridging mode in a simple trivalent lanthanide

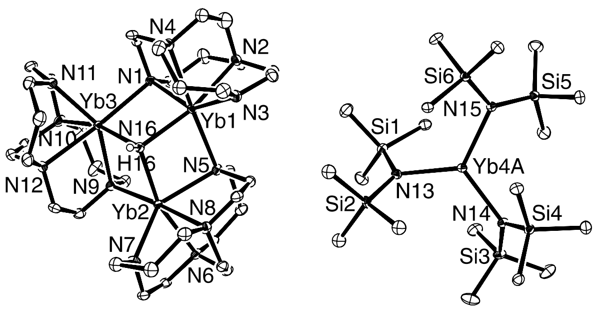


Fig. 2. ORTEP3 [16] plot of $\{[Yb(CBC)]_3[\mu^3\text{-}NH]\}^+\ \{Yb[N(SiMe_3)_2]_3\}^-$ (**2**) (30% probability ellipsoids).

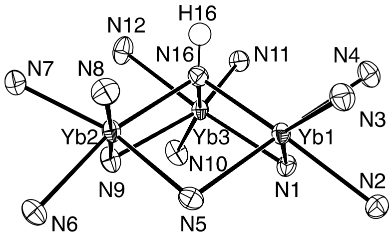


Fig. 3. Metal coordination in the cation of **2** (30% probability ellipsoids).

Table 2
Selected distances and angles for $[Yb_3(\mu\text{-CBC})_3(\mu^3\text{-NH})]^+[Yb(N(SiMe_3)_2)_3]^-$ (**2**) and $[Yb_3(\mu\text{-CBC})_3(\mu^3\text{-NH})]^+ I^- \cdot 2$ THF (**3**)[a]

2		**3**	
Distances			
Yb(1)–N(16)	2.251(3)	Yb(1)–N(13)	2.248(6)
Yb(2)–N(16)	2.253(3)	Yb(2)–N(13)	2.248(6)
Yb(3)–N(16)	2.261(3)	Yb(3)–N(13)	2.278(6)
Yb(1)–N(1)	2.367(3)	Yb(1)–N(4)	2.352(6)
Yb(1)–N(5)	2.442(3)	Yb(1)–N(8)	2.434(6)
Yb(2)–N(5)	2.369(3)	Yb(2)–N(8)	2.386(6)
Yb(2)–N(9)	2.422(3)	Yb(2)–N(12)	2.399(6)
Yb(3)–N(9)	2.374(3)	Yb(3)–N(12)	2.382(6)
Yb(3)–N(1)	2.416(3)	Yb(3)–N(4)	2.412(6)
Yb(1)–N(3)	2.181(3)	Yb(1)–N(2)	2.184(7)
Yb(2)–N(7)	2.191(3)	Yb(2)–N(6)	2.190(7)
Yb(3)–N(11)	2.185(3)	Yb(3)–N(10)	2.181(6)
Yb(1)–N(2)	2.443(3)	Yb(1)–N(1)	2.452(6)
Yb(1)–N(4)	2.477(3)	Yb(1)–N(3)	2.463(6)
Yb(2)–N(6)	2.443(3)	Yb(2)–N(5)	2.464(7)
Yb(2)–N(8)	2.459(3)	Yb(2)–N(7)	2.462(7)
Yb(3)–N(10)	2.454(3)	Yb(3)–N(9)	2.455(7)
Yb(3)–N(12)	2.439(3)	Yb(3)–N(11)	2.433(6)
Yb(4A)–N(13)	2.362(4)		
Yb(4B)–N(13)	2.344(4)		
Yb(4A)–N(14)	2.325(4)		
Yb(4B)–N(14)	2.350(4)		
Yb(4A)–N(15)	2.318(4)		
Yb(4B)–N(15)	2.349(4)		
Angles			
Yb(1)–N(16)–Yb(2)	101.54(12)	Yb(1)–N(13)–Yb(2)	101.4(2)
Yb(1)–N(16)–Yb(3)	100.36(12)	Yb(1)–N(13)–Yb(3)	99.8(2)
Yb(2)–N(16)–Yb(3)	100.15(12)	Yb(2)–N(13)–Yb(3)	100.3(2)
Yb(1)–N(1)–Yb(3)	92.87(10)	Yb(1)–N(4)–Yb(3)	93.2(2)
Yb(1)–N(5)–Yb(2)	92.95(11)	Yb(1)–N(8)–Yb(2)	92.4(2)
Yb(2)–N(9)–Yb(3)	92.43(11)	Yb(2)–N(12)–Yb(3)	93.2(2)
N(1)–Yb(1)–N(3)	144.54(11)	N(2)–Yb(1)–N(4)	145.2(2)
N(5)–Yb(2)–N(7)	143.89(12)	N(6)–Yb(2)–N(8)	144.1(2)
N(9)–Yb(3)–N(11)	142.82(12)	N(10)–Yb(3)–N(12)	142.8(2)

[a] Estimated standard deviations in parentheses.

μ-NR_2 amide without additional bridging ligands is found in $\{Na(THF)_6\}^+\{Lu_2[N(SiMe_3)_2]_4[\mu\text{-}NH_2]\ [\mu\text{-}N(SiMe_3)]\}^-$ [18]. The μ-NH_2 bridge in this compound predicts short and long Ln–N bond distances of 2.387 and 2.419 Å (Δ = 0.032 Å), respectively, after correction for the difference in ionic radii [19]. As expected, the average Yb–N bond length for the terminal amido nitrogens of CBC is considerably shorter at 2.186 Å, a value that also compares well with other six-coordinate, Yb(III) terminal amides (range 2.139–2.236 Å, median 2.19 Å) [20]. The terminal amido N atoms are not quite planar (sum of angles at N: N3, 354.5; N7, 358.1; N11, 355.6°) as is usually observed for terminal lanthanide amides (range 358.7–360°, median = 359.9° [20]) but such a small distortion from planarity is most likely due to the constraints imposed by the ethylene cross-bridge of the CBC ligand. Zirconium complexes of the type Zr(CBC) $(X)_2$ also display similar distortions from planarity (X = $OSiH(CMe_3)_2$, sum of angles at N = 354.7° [21]; *o*-$C_6H_3Me_2O$, 353.1° [6]; CH_2SiMe_3, 353.8° [6]; X_2 = C_4Ph_4, 354.4° [6]).

The capping μ^3-NH group found in **2** (and **3**) is the first structurally characterized example of a triply bridging NH in lanthanide chemistry, although at this writing there have been five structures reported that contain μ^3-NR groups: $[Ln(C_5Me_4SiMe_3)]_4(\mu^3\text{-NR})_4$ (Ln = Lu, R = CH_2Ph [22]; Ln = Y, R = Et [23]), $[Y(C_5Me_4SiMe_3)]_4(\mu^3\text{-NEt})_2(\mu\text{-N}=\text{CHPh})_2$ [23], $Yb_4(THF)_2(\mu\text{-}\eta^2\text{-PhNNPh})_4(\mu^3\text{-NPh})_2$ [24] and $Sm_4(THF)_6(\mu\text{-}\eta^2\text{-PhNNPh})_4(\mu^3\text{-NPh})_2$ [25]. The average Ln-μ^3-N distance in these complexes ranges from 2.243 to 2.363 Å. These distances predict a Yb-μ^3-N distance between 2.24 and 2.28 Å after correction for the differences in metal ionic radii [19], in excellent agreement with the observed average value of 2.255 Å. It should be noted that there are two reports of structurally characterized μ^4-NH lanthanide complexes [26] but the geometry at the imide nitrogen in these structures is not comparable to that found here.

The anion in **2** contains a Yb(II) center coordinated to three bis(trimethylsilyl)amido ligands. Anions of this type have been structurally characterized in the divalent lanthanide salts $Na^+\{Ln[N(SiMe_3)_2]_3\}^-$ (Ln = Yb, Eu), although in both structures two of the amido groups bridge between the lanthanide and the sodium cation [27]. The average terminal Ln–N distances in these complexes are 2.384 and 2.446 Å for Ln = Yb and Eu, respectively. After correction for the larger ionic radius of europium(II) [19], the latter predicts a divalent, terminal Yb–N distance of 2.31 Å. The observed average Yb–N distance of 2.341 Å falls within this range and clearly indicates that this is a divalent Yb center, as required for charge balance. There are several close contacts (<3.3 Å) between silyl methyl groups and Yb4 but since there is positional disorder at this Yb site, it is difficult to assess the significance of this observation. However, agostic interactions between silyl methyls and lanthanide centers have been reported in many cases [20a,28], so these interactions could well be meaningful in **2**.

While it is true that the crystal structures of **2** and **3** refine marginally better with the μ^3 capping group as an NH, the distinction from a μ^3-O (oxo) group, which would not alter the charge on the cation, rests on a detailed analysis of the metrical data and on the observation of an N–H stretch at 3280 cm^{-1} [26] in the IR spectrum of **2**. There are also five lanthanide structures reported in the literature that contain μ^3-O groups [20a,20c,29]; a comparison of the angles at the μ^3-E atom and the equivalent Ln–E bond lengths (corrected to compare with Yb(III) [19]) for these five structures, the five μ^3-NH structures and the two

Table 3
Comparison of X-ray data for trivalent lanthanide μ^3-O and μ^3-NH complexes

	Average	Median	Range
Lanthanide μ^3-O structures [20a,20c,29]			
Ln–O (Å)	2.13	2.14	2.08–2.20
Sum of Ln–O–Ln angles (°)	111	111	99–120
Lanthanide μ^3-NH structures [22–25]			
Ln–N (Å)	2.27	2.27	2.24–2.28
Sum of Ln–N–Ln angles (°)	99	98	96–102
$\{[Yb(CBC)]_3[\mu^3\text{-}NH]\}^+ \{Yb[N(SiMe_3)_2]_3\}^-$ (**2**)			
Ln–N (Å)	2.255	2.253	2.251–2.261
Sum of Ln–N–Ln angles (°)	100.7	100.4	100.2–101.5
$[Yb_3(\mu\text{-}CBC)_3(\mu^3\text{-}NH)]^+ I^- \cdot 2\ THF$ (**3**)			
Ln–N (Å)	2.258	2.248	2.248–2.278
Sum of Ln–N–Ln angles (°)	100.5	100.3	99.8–101.4

structures in this work are summarized in Table 3. It is quite clear from the available structural data and from IR (for **2**) that **2** and **3** contain triply bridging NH groups.

The ^{1}H NMR spectrum of **2** in THF-d_8 shows the expected wide chemical shift range (+90 to −170 ppm) and Curie–Weiss behavior (Fig. 4) expected of a compound containing paramagnetic Yb(III) centers. There are 24 resonances observed in solution. The largest resonance, with a relative integration of 54 protons, corresponds to the $N(SiMe_3)_2$ groups and shows a typical diamagnetic shift (0.03 ppm) consistent with coordination to the diamagnetic Yb(II) center of the anion. The other 23 resonances integrate to 3 protons each and most of these show significant paramagnetic shifts. This is consistent with an intact C_3 symmetric cation in solution since the 24 protons on a given CBC ligand are all inequivalent in this structure but all CBC ligands are related by symmetry. Not surprisingly given its proximity to three Yb(III) centers, the NH proton is not observed. The observation of Curie–Weiss behavior implies that the species observed are stable towards any redistribution processes over the temperature range studied. In short, it appears that the anion and cation structures are maintained in THF-d_8 solution and reorganization does not occur rapidly.

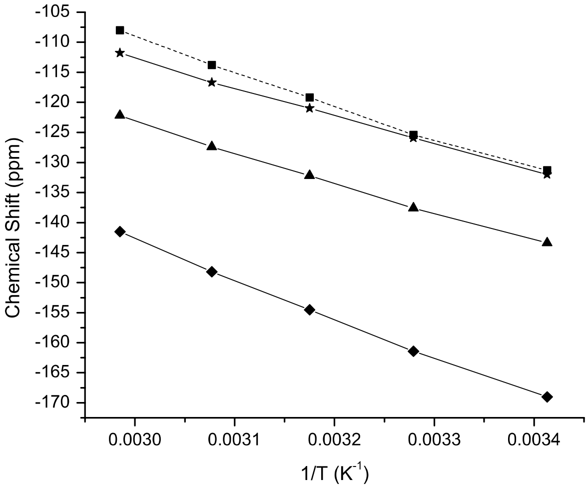
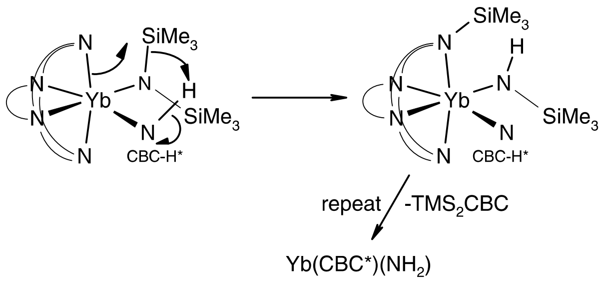


Fig. 4. Variable temperature ^{1}H NMR data for the furthest upfield resonances of **2** in THF-d_8.

In order to explain the formation of **2**, we are faced with two separate issues. The first is the fact that **2** contains three oxidized Yb(III) centers and the second is the source of the μ^3-NH group. The formation of Yb(III) may be explained by competitive reduction of an N–H bond in H_2CBC (Eq. (4)), rather than *exclusive* protonolysis to form **1** (Eq. (1)). There is good precedent for this reaction in divalent lanthanide chemistry in the formation of $Sm[DAC][N(SiMe_3)_2]$ during the reaction of H_2DAC with $Sm[N(SiMe_3)_2]_2[THF]_2$ [3a] and in the reduction of water O–H bonds by $Sm(C_5Me_5)_2(THF)_2$ to form the Sm(III) cluster $[(C_5Me_5)Sm]_6O_9H_6$ [30]. Other examples of reduction competing with hydrolysis or alcoholysis in organometallic Sm(II) chemistry have also been reported [31]. The lower reducing power of Yb(II) would explain why the samarium reaction gives trivalent product exclusively while II/III mixed valence compounds form in the case of ytterbium. We have also observed N–H bond reduction during reaction of $Yb[N(SiMe_3)_2]_2[OEt_2]_2$ with 2-(2′-aminophenyl)oxazolines to form tris[2-(2′-amidophenyl)oxazoline] complexes of Yb(III) [32]. Similarly, reduction of the C–H bond of phenylacetylene has been shown to produce a mixed valence acetylide product, $[(C_5Me_5)_2Yb]_2(\mu\text{-}CCPh)_4Yb$ [33]. There are several other examples of mixed valence Yb complexes [34] but, as far as we are aware, the cases listed above are the only ones where direct E–H (E = O, N) bond reduction is involved in their formation.

$$Yb[N(SiMe_3)_2]_2L_2 + H_2CBC \xrightarrow[-2L]{-1/2\ H_2} Yb(CBC)[N(SiMe_3)_2] \tag{4}$$

To address the second point, we note that **2** appears to form reproducibly in reactions between H_2CBC and $Yb[N(SiMe_3)_2]_2[L]_2$ (L = THF or Et_2O) but not when $Yb(C_5Me_5)_2(OEt_2)$ is used as the Yb(II) precursor – a fact that suggests to us that the μ^3-NH might arise from cleavage of an $N(SiMe_3)_2$ group. This could occur by a protonolysis reaction with trace water since the N–Si bond is well known to be susceptible to hydrolysis, Eq. (5) [35]. Of course, hydrolysis of the Yb–N bond to produce 'Yb–OH' and $HN(SiMe_3)_2$ would normally be expected to occur more rapidly unless the water molecule is unable to access this bond due to steric effects which seems unlikely in the present case. Another option might be exchange of a trimethylsilyl group between an NH group of H_2CBC and $N(SiMe_3)_2$, Scheme 1. The only similar silyl transfer reaction between nitrogens in a metal complex [36] was reported earlier this year involving migration of a silyl from an $N(SiMe_3)_2$ group to an anionic Zr–NH$^-$ group. There are also examples of trimethylsilyl transfer from a M-$N(SiMe_3)_2$ to a thiol with formation of M-NH_2 and 2 equivalents of $RSSiMe_3$ [37].



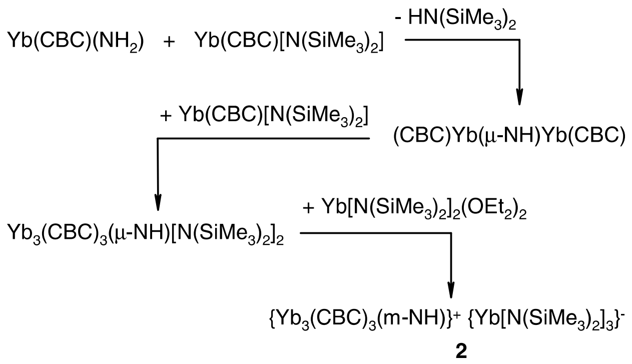
Scheme 1.

$$\mathrm{Yb(CBC)[N(SiMe_3)_2] + H_2O \xrightarrow{-Me_3SiOSiMe_3} Yb(CBC)(NH_2)} \quad (5)$$

Regardless of the pathway by which it forms, Yb[CBC][NH_2] could react with Yb[CBC][N($SiMe_3$)$_2$] by loss of HN($SiMe_3$)$_2$ and formation of a bridging NH unit, Scheme 2. Addition of another equivalent of Yb[CBC][N($SiMe_3$)$_2$] could form a crowded, neutral trimer Yb_3[CBC]$_3$[μ^3-NH][N($SiMe_3$)$_2$]. Abstraction of a N($SiMe_3$)$_2^-$ group by Yb[N($SiMe_3$)$_2$]$_2$ to form the mixed valence salt **2** would then complete the sequence. The exact pathway by which **2** forms is obviously difficult to establish with certainly but its formation seems to indicate that reduction of N–H bonds by Yb(II) may be significant in some cases and that the N–Si bond of N($SiMe_3$)$_2$ ligands may be more reactive in the presence of amines than generally supposed.

In one case, a green solution of **2** in THF-d_8 left to stand for several days slowly deposited a small number of yellow needles of **3** on the walls of the NMR tube. The X-ray structure of these crystals revealed that **3** contained the same trinuclear Yb(III) cluster cation as in **2** but with a simple iodide counterion rather than a divalent {Yb[N($SiMe_3$)$_2$]$_3$}$^-$ anion (Fig. 5 and Table 2).

The iodide counterion most likely arises from trace contamination of the starting Yb[N($SiMe_3$)$_2$]$_2$[THF]$_2$ since this compound is prepared from YbI_2 and NaN($SiMe_3$)$_2$ in THF. Anionic '*ate*' complexes such as Na^+{Yb[N($SiMe_3$)$_2$]$_2$X}$^-$ (X = halide) are very common side products in metathesis reactions of the lanthanides [38]. Compound **3** was produced in very small quantity from only one batch of Yb[N($SiMe_3$)$_2$]$_2$[THF]$_2$ making it impossible to carry out a full characterization. The metrical parameters associated with the cation in the structure of **3** are very similar to those observed for **2** and do not warrant any additional discussion.



Scheme 2.

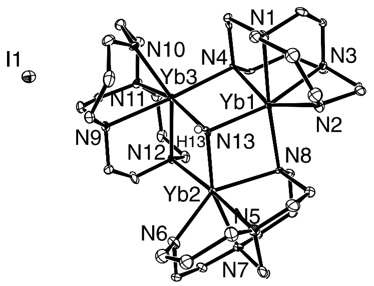


Fig. 5. ORTEP3 [16] plot of {[Yb(CBC)]$_3$[μ^3-NH]}$^+$ I^- (**3**) (30% probability ellipsoids).

4. Conclusions

The primary product of the acid–base reaction between H_2CBC and Yb[N($SiMe_3$)$_2$]$_2$[L]$_2$ or Yb(C_5Me_5)$_2$(OEt_2) is the polymeric amide-bridged [Yb(CBC)$_2$]$_n$ (**1**). However, the consistent observation of small amounts of the mixed valence salt **2** that contains a μ^3-NH group in reactions involving Yb[N($SiMe_3$)$_2$]$_2$[L]$_2$ suggests that silyl transfer between H_2CBC and a Yb-N($SiMe_3$)$_2$ unit may be a competitive process. This is noteworthy in view of the widespread use of N($SiMe_3$)$_2$ as an ancillary ligand in lanthanide chemistry in that it suggests this ligand may not be as inert as previously supposed.

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Appendix A. Supplementary material

Crystallographic data in CIF format are available from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk) under CCDC numbers 286754 and 286753 for **2** and **3**, respectively. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005.11.015.

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