

Preliminary communication

The first structurally authenticated divalent lanthanide siloxide derivative, $[\text{Yb}(\text{OSiMe}_2^t\text{Bu})(\eta^2\text{-dme})(\mu\text{-OSiMe}_2^t\text{Bu})]_2$

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Abstract

The reaction between Yb metal and $\text{Si}(\text{OH})\text{Me}_2^t\text{Bu}$ in liquid ammonia affords, in high yield, the diamagnetic ytterbium siloxide derivative $[\text{Yb}(\text{OSiMe}_2^t\text{Bu})(\eta^2\text{-dme})(\mu\text{-OSiMe}_2^t\text{Bu})]_2$, (1), (where $\text{Me} = \text{-CH}_3$, $^t\text{Bu} = \text{-C}(\text{CH}_3)_3$ and $\text{dme} = 1,1,2,2\text{-dimethoxyethane}$) which has been characterised by multinuclear nmr (^{29}Si , ^{171}Yb and ^{13}C) and X-ray crystallography. The X-ray structure of crystalline (1) shows a distorted trigonal bipyramidal environment at each Yb centre with both bridging and terminal $\text{-OSiMe}_2^t\text{Bu}$ groups present. Exchange of these groups, at room temperature, is fast relative to the nmr time scale, with a calculated activation energy of 44 kJ mol^{-1} measured by ^{29}Si NMR and a measurement of the first Yb–Si coupling constant.

Keywords: Silicon; Siloxide; Ytterbium; Lanthanides

The chemistry of the +II oxidation state derivatives of the lanthanides Sm, Eu and Yb has received considerable interest recently due to their unique reactivity, especially as selective reducing agents and in the activation of small molecules [1]. Exploration of the Yb(II) oxidation state has been facilitated considerably by the development, by us, of ^{171}Yb NMR [2]. Furthermore there has also been substantial research employing siloxide, -OSiR_3 , as ligands with alkali metals [3], alkaline earths [4], transition metals [5–10], lanthanides [11,13–15] and actinides [12]. Herein we report the first siloxide derivative of a divalent lanthanide and a similarly unique measurement of Yb–Si coupling constant. Furthermore, we also provide evidence for site exchange in this siloxide derivative.

Few X-ray characterised lanthanide–siloxide derivatives have been reported to date; the Ln(III) complexes $\{[\text{Y}(\text{OSiMe}_2^t\text{Bu})_2(\text{HOSiMe}_2^t\text{Bu})]\{[\text{Y}(\text{OSiMe}_2^t\text{Bu})_2](\mu\text{-OSiMe}_2^t\text{Bu})_2\}$ [13]; $[\text{Ln}(\text{OSiPh}_3)_3(\text{THF})_3]\text{THF}$ (Ln = Y or La) [13]; $[\text{Y}(\text{OSiPh}_3)_3(\text{OP}(\text{n-Bu})_2)_2]$ [13]; $[\text{K}(\eta^2\text{-dme})_3(\eta^1\text{-dme})][\text{Y}(\text{OSiPh}_3)_4(\eta^2\text{-dme})]$ [13]; $[\text{Ln}(\text{OSiPh}_3)_2(\mu\text{-OSiPh}_3)]_2$ [15] (Ln = Ce or La), $[\text{Y}(\mu\text{-OSiPh}_3)(\text{OSiPh}_3)_2]_2$ [13]; together with the Ln(IV) compound $\text{Ce}(\text{OSiPh}_3)_4(\text{dme})$ [11] are well characterised. However, until now no divalent complexes were known.

The reaction of Yb metal and $\text{Si}(\text{OH})\text{Me}_2^t\text{Bu}$ (where $\text{Me} = \text{CH}_3$, $^t\text{Bu} = \text{C}(\text{CH}_3)_3$) in liquid ammonia affords, after evaporation of the ammonia, a purple solid. When dme (where $\text{dme} = 1,2\text{-dimethoxyethane}$) is added to the solid a red solution is obtained from which red, crystalline $[\text{Yb}(\text{OSiMe}_2^t\text{Bu})(\eta^2\text{-dme})(\mu\text{-OSiMe}_2^t\text{Bu})]_2$, (1), is isolated in 70% yield [16].

A single crystal X-ray study [17] of (1) (Fig. 1) reveals that the dimer possesses both bridging and terminal siloxide ligands and two coordinated molecules of dme. The geometry about the metal center may be described as either distorted trigonal bipyramidal or distorted square based pyramidal. The Yb–O–Si bond angle associated with the terminal siloxide ligands is essentially linear 173° , while the bridging ligands have associated angles of 141° and 119° for Yb–O–Si and Yb'–O–Si respectively. In addition the O–Si bond lengths, 1.60 and 1.64 Å, for the terminal and bridging siloxides are essentially identical and all the above data are consistent with other previously reported lanthanide siloxide dimers [13,14]. The terminal Yb–O bond lengths are somewhat smaller, 2.16 Å, than the two effectively equivalent bridging Yb–O bond lengths, 2.31 Å and 2.27 Å. Since (1) possesses an inversion centre the -Yb-O-Yb'-O'-ring is planar (' indicating the elements related by the inversion centre). The terminal

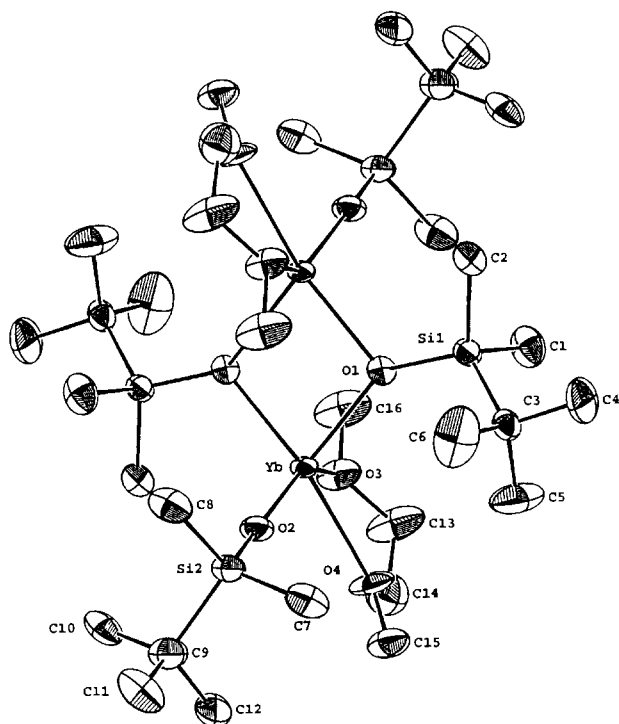


Fig. 1. X-Ray structure of (1) with atom numbering scheme. Selected intramolecular bond lengths (Å) and angles (°). Estimated standard deviations in parenthesis: Yb–O(1) 2.269(9), Yb–O(1') 2.311(8), Yb–O(2) 2.163(11), Yb–O(3) 2.538(13), Yb–O(4) 2.496(11), Si(1)–O(1) 1.635(10), Si(2)–O(2) 1.604(12), O(1)–Yb–O(1') 81.1(3), O(1)–Yb–O(2) 117.2(4), O(1)–Yb–O(3) 96.5(4), O(1)–Yb–O(4) 114.1(3), O(1')–Yb–O(2) 108.3(4), O(1')–Yb–O(3) 88.6(4), O(2)–Yb–O(3) 143.8(4), O(2)–Yb–O(4) 88.4(4), O(3)–Yb–O(4) 64.7(4), O(1')–Yb–O(3) 88.6(4), O(1')–Yb–O(4) 149.8(4), Yb–O(1)–Yb' 98.9(3), Yb–O(1)–Si(1) 141.5(5), Yb'–O(1)–Si(1) 119.1(5), Yb–O(2)–Si(2) 172.9(7).

siloxide ligands are disposed trans to one another with respect to this plane. The thermal ellipsoids associated with the dme ligands may result in a slight positional disorder for these ligands.

The ^{171}Yb NMR spectrum of (1) in dme at 298 K reveals a single sharp resonance at 641 ppm. The ^{29}Si NMR spectrum of (1) in dme at 298 K shows a single resonance at 3.68 ppm that, upon cooling, broadens (reaching a coalescence point at 238 K) which then separates into two sharp signals, -0.73 ppm and -9.46 ppm, at 198 K, the upfield signal being remarkable due to the presence of Si–Yb satellites ($J_{\text{Si}-\text{Yb}} = 66$ Hz) the other signal showing no such coupling. This is the first measurement of an Yb(O)Si coupling.

The presence of satellites on the upfield signal unambiguously identify this resonance as that resulting from the terminal siloxides, where the almost linear Yb–O–Si angle results in a much greater Yb–Si coupling constant, the bridging siloxides having smaller Yb–O–Si angles (141.5° and 119.1°) and hence a smaller Yb–Si coupling. From the coalescence point and data from low temperature ^{29}Si NMR experiments the rate of ligand

site exchange and the activation energy barrier to ligand site exchange was calculated [18].

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- [16] To a Schlenk tube containing 100 ml of dry liquid ammonia fitted with a dry-ice condenser was added in small pieces solid ytterbium metal (1.0 g, 5.78 mmol). When all the ytterbium metal had been consumed a deep blue solution was obtained to which liquid $\text{Si}(\text{OH})\text{Me}_2\text{Bu}$ (1.52 g, 11.51 mmol), was added with stirring. The resultant deep brown solution was stirred at -78°C for 3 h and the ammonia subsequently removed by warming to room temperature. Extraction of the residue with dme, filtration, and slow cooling of the filtrate to -30°C afforded dark red crystals of (1) (2.1 g, 70%). ^{171}Yb NMR (C_6D_6 (20%): dme (80%), 298 K); δ 641 (relative to $\{\text{Yb}(\eta\text{-C}_5\text{Me}_5)_2(\text{THF})_2\}$ in THF). ^{29}Si NMR $\{^1\text{H}\}$ (C_6D_6 (20%): dme (80%), 298 K); δ 3.68. ^{29}Si NMR $\{^1\text{H}\}$ (C_6D_6 (20%): dme (80%), 198 K); δ -0.73 and δ -9.46 . ^{13}C NMR $\{^1\text{H}\}$ (C_6D_6 (20%): dme (80%), 298 K); δ 26.08 [$\text{OSi}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$], δ 18.53 [$\text{OSi}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$], δ -2.05 [$\text{OSi}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$]. Found: C, 39.04; H, 8.17. $\text{C}_{32}\text{H}_{80}\text{O}_8\text{Si}_4\text{Yb}_2$ Calc.: C, 39.54; H, 8.30.

7] Crystal data: $C_{32}H_{80}O_8Si_4Yb_2$, $M = 1051.4$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.231(4)$, $b = 10.971(10)$, $c = 11.282(6)$ Å, $\alpha = 75.26(6)^\circ$, $\beta = 80.46(4)^\circ$, $\gamma = 79.05(5)^\circ$, $U = 1193$ Å³, $Z = 1$, $D_c = 1.46$ g cm⁻³, $F(000) = 532$ Monochromated Mo K_α radiation, $\lambda = 0.71069$ Å, $\mu = 40.2$ cm⁻¹, $T = 173$ K. Data were collected using a crystal ca. $0.3 \times 0.3 \times 0.1$ mm, on an Enraf-Nonius CAD4 diffractometer in the θ - 2θ mode. A total of 3308 unique reflections were measured for $2 < \theta < 23^\circ$ and $+h \pm k \pm l$, and 2711 reflections with $|F_2| > 2\sigma(F_2)$, where $\sigma(F_2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/Lp$, were used in refinement. An empirical correction based on Psi scans (Tmax. 1.00, Tmin. 0.78) was applied for absorption. The structure was solved by heavy atom methods using SHELXS-86 and refined by full matrix least squares. All non hydrogen atoms except C(14) were anisotropic. Hydrogen atoms were held fixed at calculated positions with $U_{iso} = 1.3 U_{eq}$ for the parent carbon

atom. With a weighting scheme of $\omega = 1/\sigma^2(F)$, the final residuals were $R = 0.066$, $R' = 0.074$, with a ratio of observations to variables of 13:1, and $S = 1.8$. Programs from the Enraf-Nonius SDP-Plus package were run on a microVax II computer. Thermal ellipsoid probability level was set at 50%. Hydrogen atom coordinates, thermal parameters, and a complete list of bond lengths, and angles, have been deposited at the Cambridge Crystallographic Data Centre.

$$[18] \Delta G^\ddagger = RTc[23 + \ln(Tc/\Delta\nu)]$$

Where $\Delta\nu = 434$ Hz (peak to peak separation at 198 K)

Tc = Coalescence temperature in K

for (1) $\Delta G^\ddagger = 44$ kJ mol⁻¹

$$k = \pi\Delta\nu/2$$

Gives $k = 964$ s⁻¹ (i.e. rate of ligand exchange at coalescence temperature).