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## **COMMUNICATION**

## Synthesis and X-ray crystal structure of [Li(C<sub>4</sub>H<sub>8</sub>O)<sub>4</sub>][Yb(NPh<sub>2</sub>)<sub>4</sub>]

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**Abstract**—The interaction of Yb(NPh<sub>2</sub>)<sub>2</sub>Cl with one equivalent of Li[(CH<sub>2</sub>)(CH<sub>2</sub>)PPh<sub>2</sub>] in tetrahydrofuran gave the unexpected dark red complex [Li(C<sub>4</sub>H<sub>8</sub>O)<sub>4</sub>][Yb(NPh<sub>2</sub>)<sub>4</sub>] (1) in 30% yield. An X-ray diffraction study reveals that the lanthanide–amide *ate* complex is composed of a discrete cation [Li(C<sub>4</sub>H<sub>8</sub>O)<sub>4</sub>]<sup>+</sup> and a discrete homoleptic tetrahedral Yb-amide anion [Yb(NPh<sub>2</sub>)<sub>4</sub>]<sup>-</sup>. Copyright © 1996 Elsevier Science Ltd

*Keywords*: ytterbium(III); structure; discrete homoleptic amide anion; diphenylamide; homoleptic amide complex; lanthanide-amide *ate* complex.

Lanthanide amide complexes are excellent synthetic precursors for lanthanide-alkoxides [1], phosphides [2] and thiolates [3] which can be prepared *via* protonolysis of the lanthanide-amide bond with alcohols, phosphines and thiols, respectively. Homoleptic three-

coordinate lanthanide amide complexes had been known for some time [4], however, it was not until recently that homoleptic tetra-coordinate lanthanide amide *ate* complexes had been reported [5,6]. There are relatively few structural characterization studies on lanthanide–amide *ate* complexes [6,7], particularly those containing a discrete homoleptic tetra-coordinate lanthanide–amide *ate* anion. In this communication, we report the X-ray crystal structure of a Ybamide complex with a discrete homoleptic tetracoordinate Yb-amide *ate* moiety.

The interaction of  $Yb(NPh_2)_2Cl$  with one equivalent of  $Li[(CH_2)(CH_2)PPh_2]$  in tetrahydrofuran for 16 h, work up gave the unexpected dark red crystals of stoichiometry  $[Li(C_4H_8O)_4][Yb(NPh_2)_4]^{\dagger}$  (1) in 30% yield after recrystallization from a toluene solution. The structure of 1 was established by an X-ray diffraction study.<sup>‡</sup> A perspective drawing of 1 is shown in Fig. 1; and selected bond lengths and bond angles are given in the caption.

The crystal structure analysis revealed that 1 is composed of a discrete cation and a discrete anion. In

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 $<sup>\</sup>dagger$  [Li(C<sub>4</sub>H<sub>8</sub>O)<sub>4</sub>][Yb(NPh<sub>2</sub>)<sub>4</sub>]: Dark red crystals. m.p. 188–190°C dec. Found: C, 66.8; H, 6.0; N, 4.9. Calc. for C<sub>64</sub>H<sub>72</sub>LiN<sub>4</sub>O<sub>4</sub>Yb: C, 67.3; H, 6.3; N, 4.9%. IR (cm<sup>-1</sup>, in KBr): 3038 w, 1596 vs, 1520 vs, 1495 vs, 1458 s, 1418 s, 1320 vs, 1240 w, 1173 m, 1080 w, 1031 w, 991 w, 877 m, 745 vs, 701 m, 690 vs, 504 w, 431 w. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.23 (16 H, br, s). 6.92 (8H. br, s), 4.90 (8H, br, s), 4.43 (16 H, br, s), 2.21 (8H, br, s), 1.36 (8H, br, m), 1.02 (8H, br, s) ppm.

<sup>‡</sup> Crystal data for [Li(C<sub>4</sub>H<sub>8</sub>O)<sub>4</sub>][Yb(NPh<sub>2</sub>)<sub>4</sub>]:  $F_w = 1141.24$ , monoclinic,  $P2_1$  (No. 4), a = 10.914 (2), b = 14.094 (3), c = 19.330 (4) Å,  $\beta = 96.66$  (3)°, V = 2953(1) Å<sup>3</sup>, Z = 2, F(000) = 1178,  $D_c = 1.283$  g cm<sup>-3</sup>,  $\mu = 16.31$ cm<sup>-1</sup>. Crystal dimensions:  $0.60 \times 0.20 \times 0.20$  mm. Intensity data were collected on a Rigaku AFC7R diffractometer, using Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å) at 293 K. Unit cell parameters were calculated from least-squares fitting of the



Fig. 1. A perspective view of the molecular structure of  $[Li(C_4H_8O)_4][Yb(NPh_2)_4]$ . Selected bond lengths (Å) and bond angles (°): Yb(1)—N(1), 2.201(9); Yb(1)—N(2), 2.216(9); Yb(1)—N(3), 2.188(9); Yb(1)—N(4), 2.241(9); N(1)—C(1), 1.398(12); N(1)—C(7), 1.391(12); N(2)—C(13), 1.388(12); N(2)—C(19), 1.417(12); N(3)—C(25), 1.395(12); N(3)—C(31), 1.388(12); N(4)—C(37), 1.382(13); N(4)—C(43), 1.412(13); Li(1)—O(1), 1.90(2); Li(1)—O(2), 1.88(2); Li(1)—O(3), 1.90(2); Li(1)—O(4), 1.91(2); N(1)—Yb(1)—N(2), 112.8(3); N(1)—Yb(1)—N(3), 106.7(4); N(1)—Yb(1)—N(4), 110.9(4); N(2)—Yb(1)—N(3), 111.7(3); N(2)—Yb(1)—N(4), 104.0(4); N(3)—Yb(1)—N(4), 110.8(3); C(1)—N(1)—C(7), 116.0(9); C(13)—N(2)—C(19), 115.0(9); C(25)—N(3)—C(31), 118.2(9); C(37)—N(4)—C(43), 119.9(9).

[Li(C<sub>4</sub>H<sub>8</sub>O)<sub>4</sub>]<sup>+</sup>, the Li atom adopts a tetrahedral geometry with four molecules of tetrahydrofuran coordinated to the Li atom *via* the oxygen atoms. The Li—O distances and the O—Li—O angles are normal and lie in the range 1.88 (2)–1.91 (2) Å and 108.1 (10)–111.3 (11)°, respectively. The anion [Yb(NPh<sub>2</sub>)<sub>4</sub>]<sup>-</sup> can be described as a distorted tetrahedron with the Yb atom coordinated by four terminal NPh<sub>2</sub> groups. The Yb—N distances ranging from 2.188 (9)–2.241 (9) Å are longer than the terminal Yb—N(silylamide) bonds of the three-coordinate Yb[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> complex [2.158(13) Å] [8] and shorter than the terminal

Yb-N(silylamide) bond of the five-coordinate  $Yb[OC(CMe_3)(2-CH_2NC_5H_3Me-6)_2]_2[N(SiMe_3)_2] com$ plex [2.260 (5) Å] [9]. The N-Yb-N angles ranging from 104.0(4)-112.8 (3)° are typical of a slightly distorted tetrahedron. The N atoms of the amide groups adopt a planar geometry with C-N-C angles ranging from  $115.0(9)-119.9(9)^{\circ}$  and can be considered as  $sp^2$  hybridized. Lanthanide *ate* complexes with homoleptic NR<sub>2</sub> groups have been structurally characterized recently [6,7]. However, in all of them the cation and the anion moieties of the complexes are linked together via two bridging amide groups. Notably 1 is the first structurally characterized lanthanide amide ate complex to comprise a discrete cation and a discrete homoleptic tetra-coordinate lanthanide-amide anion.

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 $<sup>2\</sup>theta$  angles for 25 selected strong reflections. Crystal stability was monitored by recording three check reflections at intervals of 150 data measurements, and no significant variation was detected. An empirical absorption correction based on Ψ-scans was applied, resulting in relative transmission factors ranging from 0.880 to 1.035 [10]. A total of 5416 unique reflections ( $4^{\circ} \leq 2\theta \leq 50^{\circ}$ ) were measured and 3224 reflections have  $I \ge 2\sigma(I)$ . The structure was solved by the direct method using SHELXTL-PLUS [11] and refined against  $F^2$ using SHELXL-93 [12]. Non-hydrogen atoms were refined anistropically by full-matrix least-squares. Hydrogen atoms were placed in their calculated positions (C-H bond fixed at 0.96 Å) and allowed to ride on their respective parent carbon atoms. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [13]. The final R, Rw values were 0.048, 0.112.

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