Synthesis and Structural Characterization of Some Potassium Complexes of Some Bis(phenolate) Ligands and Some Novel Heterobimetallic Binuclear Arrays Formed with Trivalent Lanthanoid Ions

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Abstract. The structural characterizations of the potassium complexes of a pair of dianionic bis(phenolate) ligands, $\{L^R = [{}^{-}OC_6H_2(2,4-Bu^t)(6-CH_2)]_2NCH_2CH_2R\}$ R = NMe₂, OMe, crystallized from 1,2,-dimethoxyethane (DME) are recorded, showing them to take the binuclear form $[K_2L^R(DME)_3]$. A pair of neutral binuclear heterobimetallic isotypic complexes are defined with ytterbium(III), with phenol, as sodium salts, of the form $[Yb(L^R)(OPh)_2Na(DME)(HOPh)]$, and a further array with

samarium(III), of the (partially protonated) form $[Sm(L^{OMe})_2-Na(OH_2)]$. A further complex, $[Na(DME)_3][Yb(*L^{py})_2]$, results from an unusual ligand reduction by an ytterbium(II) species to give a new dianionic Schiff base ligand which is coordinated to ytterbium(III) {*L^{py} = $-OC_6H_2(2,4-Bu^t)(6-CH=N-CH-2-C_6H_4N)$ }.

Keywords: Lanthanoids; Alkali metals; Phenolates; Ytterbium; Samarium

Introduction

There has been a recent upsurge of interest in the synthesis of lanthanoid complexes supported by non-Cp ligands. Specifically, non-lanthanocene compounds containing multidentate anionic ligands such as guanidinates [1-4], β diketiminates [5-8], salen [9, 10], diamides [11, 12] and bis-(phenolate)s [13-17] are of interest (Figure 1) since they are considered more 'chemically robust' (i.e. they are less susceptible to hydrolysis and are less likely to undergo ligand redistribution reactions) compared with their Cp counterparts. As a result, such lanthanoid compounds have found great utility in catalysis [14, 18, 19] and luminescence [20, 21] studies. Among these ligand systems, lanthanoid compounds comprising multidentate phenolate and bis(phenolate) ligands have recently exhibited excellent catalytic properties towards ring-opening polymerization (ROP) reactions of cyclic esters such as lactide (LA) and ε caprolactone (ε -CL) [9, 14, 16–18, 22–27]. In many cases these ligands are not easily displaced from the lanthanoid metal center during the polymerization reaction, making them highly valuable as stationary 'spectator ligands'. For these reasons, the authors' attention has focussed on synth-

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Figure 1 Some non-Cp ligands used in lanthanoid synthesis.

eses of lanthanoid phenolate and bis(phenolate) compounds.

To the authors' knowledge, only two studies [13, 28] have investigated the synthesis and complete structural studies of anionic lanthanoid bis(phenolate)s containing alkali metal counter ions. This class of complex (commonly referred to as '*ate*' complexes) has very interesting coordination chemistry, leading to intriguing solid state structures. Reported herein are some recent findings concerning the syntheses and detailed X-ray crystal structure studies of some novel lanthanoid bis(phenolate) 'ate' complexes, containing sodium counter-ions, as well as the corresponding parent potassium bis(phenolate) compounds. In addition, a highly novel and unusual ytterbium(III) phenolate compound is reported where the phenolate ligand has been reduced by the initial Yb^{II} atom *via* a hydrogen abstraction pathway making the initially monoanionic phenolate ligand dianionic.



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Experimental Section

General

The complexes described herein are air- and moisture-sensitive, such that all manipulations were performed under nitrogen atmospheres employing typical Schlenk line and glove box techniques. Solvents were dried and purified by distillation under nitrogen from sodium or potassium metal mixed with benzophenone, while deuterated solvents, purchased from Cambridge Isotope Laboratory, were dried over sodium metal or CaH₂, deoxygenated and purified by vacuum transfer. The reagents $[Ln(N(SiMe_3)_2)_2(THF)_2]$ [29] (Ln = Sm, Yb), $H_2L^R \{L^R = [-OC_6H_2(2, 4-Bu^t)(6-CH_2)]_2NCH_2CH_2R\} (R = NMe_2, CH_2R)$ OMe) [30, 31] (THF = tetrahydrofuran) and HL^{py} [32] {L^{py} = $-OC_6H_2(2,4-Bu^t)(CH=N-CH_2-C_6H_5N)$ were synthesized by the indicated reported procedures. The complexes [YbL^{NMe2}]₂ and [YbL^{OMe}] were synthesized according to the reported literature procedures [13]. All the other reagents were purchased from Acros and used as received. Melting points were obtained from sealed capillaries on a Mel-Temp apparatus and are uncorrected. IR spectra (4000-450 cm⁻¹) were recorded as KBr Nujol mulls on an ATI Mattson Genesis Series FTIR Spectrometer. The ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE-500 NMR spectrometer and referenced to C₆D₅H or C₄D₇HO or CDHCl₂ (¹H) and C_6D_6 or C_4D_8O or CD_2Cl_2 (¹³C). Elemental analyses (sealed ampoules under inert atmosphere) were performed by Midwest Microlab, Indianapolis IN.

Synthesis of Complexes [K₂(L^{NMe2})(DME)₃] (1)

KH (0.31 g, 7.73 mmol) was slowly added to a stirred 1,2-dimethoxyethane (DME) (40 mL) solution of H_2L^{NMe2} (2.0 g, 3.87 mmol) at room temperature. Stirring was then continued 12 h to afford colourless crystals of 1 (3.0 g, 91 %). Mp: 200 °C (dec.). C₄₆H₈₄ K₂N₂O₈ (871.38 g/mol): C 63.80, H 9.41, N 3.52 (calc. C 63.41, H 9.72, N, 3.21) %.

IR (KBr, Nujol) 2360(w), 1600(w), 1538(w), 1326(s), 1303(s), 1257(m), 1230(m), 1199(m), 1157(m), 1122(s), 1079(s), 1022(m), 979(m), 848(w), 806(w), 732(w), 674(w), 640(w), 574(w), 507(w) v cm⁻¹; ¹H NMR, δ : (500.1 MHz, CD₂Cl₂, 298K) 1.21 (s, 18H, Bu'), 1.38 (s, 18H, Bu'), 1.51 (s, 6H, NMe₂), 2.01 (t, 2H, *J* 7.1, NCH₂CH₂NMe₂), 2.60 (t, 2H, *J* 7.1, NCH₂CH₂NMe₂), 2.60 (t, 2H, *J* 7.1, NCH₂CH₂NMe₂), 2.60 (t, 2H, *J* 7.1, NCH₂CH₂NMe₂), 3.56 (s, 12H, OCH₂CH₂O, DME), 4.03 (d, 2H, *J* 11.3, ArCH₂N), 6.98 (s, 2H, Ar), 7.16 (s, 2H, Ar); ¹³C NMR, δ : (125.8 MHz, CD₂Cl₂, 298K) 30.17 (CMe₃), 32.54 (CMe₃), 34.23 (CMe₃), 35.96 (CMe₃), 44.88 (NMe₂), 54.61 (NCH₂CH₂NMe₂), 60.01 (OCH₃, DME) 63.58 (NCH₂CH₂NMe₂), 65.71 (ArCH₂N), 72.46 (OCH₂CH₂O, DME), 123.00 (arom-CH), 127.76 (arom-CBu'), 127.93 (arom-CH), 130.17 (arom-CBu'), 136.93 (arom-CCH₂N), 167.33 (arom-CO).

[K₂(L^{OMe})(DME)₃] (2)

Using a similar procedure for the synthesis of complex **1**, treatment of KH (0.31 g, 7.73 mmol) with H_2L^{OMe} (1.98 g, 3.87 mmol) in 40 mL of DME afforded **2** (3.1 g, 92 %) as pale yellow crystals. Mp: 180 - 182 °C (dec.). $C_{45}H_{81}K_2NO_9$ (858.34 g/mol): C 63.32, H 9.28, N, 1.57 (calc. C 62.97, H 9.51, N 1.63) %.

IR (KBr, Nujol): 1600(w), 1330(s), 1295(s), 1257(m), 1230(m), 1199(m), 1130(s), 1095(s), 1022(s), 983(m), 925(w), 883(m), 856(m), 806(m), 732(m), 640(w), 578(w), 509(w) v cm⁻¹; ¹H NMR, δ : (500.1 MHz, CD₂Cl₂, 298K) 1.27 (s, 18H, Bu'), 1.42 (s, 18H, Bu'), 2.66 (t, 2H, *J* 4.9, NCH₂CH₂O), 2.79 (s, 3H, OMe), 3.17 (d, 2H, *J* 12.1, ArCH₂N), 3.28 (s, 18H, OCH₃, DME) 3.38 (t, 2H, *J* 4.9, NCH₂CH₂O), 3.54 (s, 12H, OCH₂CH₂O, DME), 3.96 (d, 2H, *J* 12.1, ArCH₂N), 6.92 (d, 2H, *J* 2.7 Ar), 7.07 (d, 2H, *J* 2.7 Ar); ¹³C

NMR, δ : (125.8 MHz, CD₂Cl₂, 298K) 30.21 (CMe₃), 32.61 (CMe₃), 34.24 (CMe₃), 35.97 (CMe₃), 54.62 (NCH₂CH₂O), 57.86 (NCH₂CH₂O), 59.35 (OCH₃, DME) 71.28 (OMe), 72.36 (OCH₂CH₂O, DME), 75.51 (ArCH₂N), 122.99 (arom-CH), 127.36 (arom-CBu'), 128.16 (arom-CH), 129.48 (arom-CBu'), 136.88 (arom-CCH₂N), 167.86 (arom-CO).

[Sm(L^{OMe})] (5)

To a dark purple hexanes (15 mL) solution of $[Sm(N(SiMe_3)_2)_2(THF)_2]$ (0.61 g, 1.00 mmol) at room temperature, H_2L^{OMe} ligand (0.51 g, 1.00 mmol) in hexanes (10 mL) was added *via* a cannula to give a black solution with black precipitate, which was stirred overnight. The black precipitate was separated from the black solution and dried to afford **5** (0.55 g, 83 %). Mp: 189–192 °C (dec.). $C_{33}H_{51}NO_3Sm$ (660.13 g/mol): C 60.07, H 7.84, N 2.24, (calc. C 60.04, H 7.79, N 2.12) %.

IR (KBr, Nujol): 1764(w), 1748(w), 1599(s), 1545(w), 1411(w), 1305(m), 1264(s), 1236(w), 1199(m), 1162(m), 1132(m), 1117(m), 1067(s), 1039(s), 1001(m), 954(w), 927(w), 910(w), 877(s), 829(s), 735(s), 642(w), 608(w), 574(w), 517(m), 426(m) v cm^{-1}, ¹H NMR, δ : (500.1 MHz, C₄D₈O, 298K): -8.10 (b, 18H, Bu'), 0.02 (s, 18H, Bu'), 0.79 (s, 4H, ArCH₂N), 1.32 (b, 2H, NCH₂CH₂OMe), 1.43 (b, 2H, NCH₂CH₂OMe), 2.38 (s, 3H, OMe), 3.14 (s, 2H, CH arom.), 4.89 (b, 2H, CH arom.); (500.1 MHz, C₇D₈, 378K): -2.78 (b, 1H, CH arom.), -1.67 (b, 1H, CH arom.), -1.28 (b, 1H, CH arom.), 0.24 (s, 2H, ArCH₂N), 0.87 (s, 2H, ArCH₂N), 1.25 (b, 2H, NCH₂CH₂OMe), 1.48 (b, 18H, 2×Bu'), 1.70 (s, 3H, OMe), 2.00 (s, 9H, Bu'), 2.32 (s, 1H, CH arom.), 3.61 (s, 9H, Bu').

$[Yb(L^{NMe2})(OPh)]$ (6)

A DME (10 mL) solution of phenol (0.26 g, 2.77 mmol) was added to a stirred DME (15 mL) solution of $[YbL^{NMe2}]_2$ (hexane) (1.00 g, 0.67 mmol) and heated at 50 °C for 11 h to give a yellow solution after which time the DME was removed to yield a yellow solid. Light yellow microcrystals of **6** (0.95 g, 81 %) were grown at room temperature from a hexanes solution. From one reaction pale yellow single crystals of $[Yb(L^{NMe2})(OPh)_2Na(DME)(HOPh)]$ (**9**) were grown and subjected to a single crystal X-ray diffraction study. Mp: 173 °C (dec.). C₄₀H₅₉N₂O₃Yb (788.96 g/mol): C 60.19, H 7.63, N 2.93 (calc. for no DME: C 60.90, H 7.54, N 3.55; for one DME: C 60.12, H 7.91, N 3.19) %.

IR (KBr, Nujol): 2854(s), 1592(w), 1335(w), 1203(w), 1161(w), 1076(s), 1022(s), 924(w), 875(w), 802(s), 760(m), 694(w), 579(w), 528(w), 451(w) ν cm^{-1}.

[Yb(L^{OMe})(OPh)] (7)

Using similar procedure to that described for the synthesis of **6**, treatment of [YbL^{OMe}] (0.50 g, 0.73 mmol) with phenol (0.10 g, 1.10 mmol) in DME (25 mL) with heating at 50 °C for 11 h afforded a green yellow solution. Solvent removal and recrystallization from hexanes gave crystals of **7** (0.48 g, 85 %). From one reaction pale green yellow single crystals of [Yb(L^{OMe})(OPh)₂Na-(DME)(HOPh)] (**10**) were grown and subjected to a single crystal X-ray diffraction study. Mp: 171-173 °C (dec.) $C_{39}H_{56}NO_4Yb$ (775.91 g/mol): C 59.70, H 7.55, N 1.59 (calc. for no DME: C 60.37, H 7.27, N 1.81; for one DME C 59.64, H 7.68, N, 1.62) %. **IR** KBr, nujol) 2858(s), 1770(w), 1592(m), 1296(s), 1265(s), 1203(m), 1165(m), 1076(s), 1022(s), 910(w), 833(m), 802(m), 759(m), 694(m), 602(w), 579(w), 528(w), 455(w) v cm⁻¹.

[Sm(L^{OMe})(OPrⁱ)] (8)

Isopropanol (1.0 mL, 13.1 mmol) was added to a black DME (15 mL) solution of complex 5 (0.30 g, 0.45 mmol) at room tem-

perature *via* a syringe and stirred overnight. The solution gradually turned into a pale yellow solution after which time all volatiles were removed *in vacuo*, to yield a yellow powder of **8** (0.21 g, 61 %). From one reaction pale yellow single crystals of $[Sm(L^{OMe})_2Na(OH_2)]$ (11) were grown and subjected to a single crystal X-ray diffraction study. Mp: 190–194 °C (dec.). C₃₆H₅₈NO₄Sm (719.22 g/mol): C 59.67, H 8.11, N 2.02 (calc. C 60.12, H 8.13, N 1.95) %.

IR (KBr, Nujol): 1772(w), 1603(m), 1412(w), 1379(m), 1360(w), 1323(w), 1260(s), 1202(m), 1163(w), 1093(s), 1023(s), 931(w), 911(w), 876(s), 803(s), 740(s), 645(w), 521(s), 424(m) v cm⁻¹; ¹H NMR, δ : (500.1 MHz, C₆D₆, 298K): 1.34 (s, 3H, OMe), 1.45 (b, 18H, Bu¹), 1.60 (b, 18H, Bu¹), 1.69 (s, 4H, 2×ArCH₂N), 1.83 (b, 1H, NCH₂CH₂OMe), 2.13 (b, 6H, CH₃CHCH₃), 2.32 (m, 1H, CH₃CHCH₃), 3.03 (s, 1H, NCH₂CH₂OMe), 3.30 (s, 1H, NCH₂CH₂OMe), 3.50 (s, 1H, NCH₂CH₂OMe), 7.52 (s, 2H, CH arom.), 8.01 (s, 2H, CH arom).

$[Yb^{III}(L^{py})_2]^+[Yb^{III}(*L^{py})_2]^-$ (12)

A deep orange hexanes solution (10 mL) of $[Yb(N(SiMe_3)_2)_{c}(THF)_2]$ (0.64 g, 1.00 mmol) was treated with a yellow hexanes solution (9 mL) of $HL^{py} \{L^{py} = {}^{-}OC_6H_2(2,4\text{-Bu}^{+})(6\text{-}CH=\text{N-}CH_2\text{-}2\text{-}C_6H_4\text{N})\}$ (0.65 g, 2.00 mmol) at room temperature to form an instant dark blue solution. The solution was stirred for 4 h and dark blue crystals of **12** (0.93 g, 57 %) were obtained from hexanes and appropriate amount of DME. From one reaction dark blue single crystals of $[Na(DME)_3][Yb(*L^{py})_2]$ (**13**) $\{*L^{py} = {}^{-}OC_6H_2(2,4\text{-}Bu^{+})(CH=\text{N-}CH\text{-}C_6H_5\text{N})\}$ were grown and subjected to a single crystal X-ray diffraction study. Mp: 239 °C. $C_{84}H_{106}N_8O_4Yb_2$ (1637.90 g/mol): C 60.03, H 7.20, N 6.18, Yb 21.61 (calc. C 61.60, H 6.52, N 6.84, Yb 21.13) %.

IR (KBr, Nujol) 1542(w), 1508(w), 1199(w), 1169(m), 1088(s), 1018(s), 933(m), 802(s), 752(w), 686(w) v cm^{-1}.

Structure determinations

Full spheres of CCD area-detector diffractometer data were measured (Bruker AXS instrument, ω -scans; monochromatic Mo K α radiation; $\lambda = 0.7107_3$ Å), yielding $N_{t(otal)}$ reflections, these merging to N unique (R_{int} cited) after 'empirical'/multiscan absorption correction (proprietary software), N_{o} with $F > 4\sigma(F)$ being considered 'observed'. Full matrix least squares refinement on F^2 (all data, Xtal 3.7 program system [33], neutral atom complex scattering factors) refined anisotropic displacement parameter forms for the non-hydrogen atoms, hydrogen atom inclusion following a riding model. Conventional residuals R, Rw are cited (reflection weights: $(\sigma^2(F^2) + n_w F^2)^{-1}$. Pertinent results are given below and in the Tables and Figures. Individual variations in procedure are noted as 'variata'. Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC 657332-657337. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+ (1223) 336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

Crystallrefinement data

[K₂(L^{NMe2})(DME)₃] (1). C₄₆H₈₄K₂N₂O₈, M = 871.4. Monoclinic, space group $P_{2_1/c}$ (C_{2h}^5 No. 14), a = 21.651(10), b = 16.462(10), c = 17.329(10) Å, $\beta = 95.279(10)^\circ$, V = 6150 Å³. D_c (Z = 4) = 0.94₁ g cm⁻³. μ_{Mo} = 0.19 mm⁻¹; specimen: 0.22 x 0.16 x 0.12 mm;

 ${}^{\circ}T_{\text{min/max}} = 0.79. \ 2\theta_{\text{max}} = 50^{\circ}; \ N_{\text{t}} = 44216, \ N = 10924 \ (R_{\text{int}} = 0.073), \ N_{\text{o}} = 4096; \ R1 = 0.081, \ wR2 = 0.30, \ S = 0.96. \ |\Delta\rho_{\text{max}}| = 0.27 \ \text{e} \ \text{\AA}^{-3}. \ T \ ca. \ 298 \ \text{K}.$

Variata. DME group (2) was modelled as disordered over two sets of sites, as also was t-butyl group (15) (the latter rotationally disordered about its pendant bond), the components of each being modelled with site occupancies 0.5, constrained with idealized geometries. The CH₂CH₂NMe₂ pendant was also modelled as disordered, component occupancies refining to 0.701(2) and complement (constrained geometries). Refinement used the SHELXL 97 program [34]; reflection weights being $(\sigma^2(F^2) + (0.170P)^2)^{-1}$ ($P = F_o^2 + 2F_c^2$)/3).

[K₂(L^{OMe})(DME)₃] (2). C₄₅H₈₁K₂NO₉, M = 858.5. Monoclinic, space group $P2_1/n$, a = 10.747(2), b = 31.129(6), c = 15.701(3) Å, $\beta = 95.990(2)^\circ$, V = 5224 Å³. D_c (Z = 4 dimers) = 1.09₁ g cm⁻³. $\mu_{Mo} = 0.23$ mm⁻¹; specimen: 0.42 x 0.30 x 0.23 mm; ' $T'_{min/max} = 0.77$. $2\theta_{max} = 50^\circ$; $N_t = 33395$, N = 9261 ($R_{int} = 0.052$), $N_o = 7480$; R = 0.052, $R_w = 0.12$ ($n_w = 1.2$); S = 1.06. $|\Delta \rho_{max}| = 0.84$ e Å⁻³. T ca. 153 K.

Variata. DME group (3) was modelled as disordered over two sets of sites, occupancies refining to 0.839(4) and complement (isotropic displacement parameter refinement for C, O of the latter).

 $[Yb(L^R)(OPh)_2Na(DME)(HOPh)] R = NMe_2$ (9), OMe (10); are isotypic (the structure of the 9 being determined on a capillary mounted specimen at 298 K (the crystals breaking up at 170 K, the temperature at which 10 was studied)), monoclinic, space group $P2_1/n$, Z = 4.

(a) Complex 9: $C_{56}H_{80}N_2NaO_7Yb$, M = 1089.3. a = 10.6226(9), b = 32.144(3), c = 17.075(2) Å, $\beta = 104.839(1)^\circ$, V = 5636 Å³. $D_c = 1.28_4$ g cm⁻³. $\mu_{Mo} = 1.72$ gm⁻³; specimen: 0.45 x 0.30 x 0.20 mm; 'T'_{min/max} = 0.81. $2\theta_{max} = 57^\circ$; $N_t = 51272$, N = 13933($R_{int} = 0.023$), $N_o = 12606$; R = 0.034, $R_w = 0.066$ ($n_w = 35$); S = 0.98. $|\Delta \rho_{max}| = 1.7$ e Å⁻³.

Variata. The pendant methyl groups of the NMe_2 group, as well as the associated methylene group, were modelled as disordered over pairs of sites occupancies refining to 0.793(8) and complement.

(b) Complex 10: $C_{55}H_{77}NNaO_8Yb$, M = 1076.3. a = 10.727(1), b = 32.388(4), c = 17.325(2) Å, $\beta = 106.598(2)^\circ$, V = 5768 Å³. $D_c = 1.23_9$ g cm⁻³. $\mu_{Mo} = 1.68$ gm⁻³; specimen: 0.52 x 0.44 x 0.32 mm; 'T'_{min/max} = 0.79. $2\theta_{max} = 57^\circ$; $N_t = 51664$, N = 14071 ($R_{int} = 0.028$), $N_o = 11994$; R = 0.047, $R_w = 0.084$ ($n_w = 25$); S = 0.95. $|\Delta \rho_{max}| = 2.4$ e Å⁻³.

Variata. C(2) of the $(CH_2)_2OMe$ pendant of the L^{OMe} ligand was modelled as disordered over a pair of sites, occupancies set at 0.5 after trial refinement. The hydroxyl hydrogen atom of the phenol ligand was located in difference maps.

[(L^{OMe}H)(L^{OMe})₃Sm₂Na(OH₂)]_{0.5} (11). C₆₆H_{103.5}N₂Na_{0.5}O_{6.5}Sm, M = 1190.9. Monoclinic, space group $P2_1/n$, a = 14.5300(9), b = 31.929(3), c = 15.589(2) Å, $\beta = 112.573(1)^\circ$, V = 6678 Å³. D_c (Z = 4) = 1.18_4 g cm⁻³. $\mu_{Mo} = 0.93$ mm⁻¹; specimen: 0.25 x 0.17 x 0.10 mm; 'T'_{min/max} = 0.77. $2\theta_{max} = 50^\circ$; $N_t = 58906$, N = 11766 ($R_{int} = 0.062$), $N_o = 9586$; R = 0.073, $R_w = 0.13$ ($n_w = 55$); S = 1.11. $|\Delta \rho_{max}| = 2.7$ e Å⁻³. T ca. 170 K.

Variata. The complex is essentially $[Sm(L^{OMe})_2Na(OH_2)]$. The $(CH_2)_2OMe$ pendant on ligand 2 is modelled as disordered over a

pair of sites (occupancy 0.5), the first component coordinated to the sodium atom, the second component (primed) directed otherwise, (corresponding to a vacant Na site and contacting N(21), considered, *ad hoc*, to be protonated). A further residue was modelled as a water molecule oxygen atom (occupancy 0.5) associated with the sodium atom (no associated hydrogen atoms located). The model thus approximates to $[Sm(L^{OMe})_2Na(OH_2)][Sm(L^{OMe})-(L^{OMe}H)]$. Disordered components were refined with isotropic displacement parameters.

[Na(DME)3][Yb(*L^{py})2] (13). $C_{54}H_{82}N_4NaO_8Yb$, M = 1111.3. Orthorhombic, space group *Pbcn* $(D_{2h}^{14}, No. 60)$, a = 15.683(2), b = 21.369(2), c = 17.168(2) Å, V = 5754 Å³. $D_c = 1.28_3$ g cm⁻³. $\mu_{Mo} = 1.68$ gm⁻³; specimen: 0.25 x 0.15 x 0.11 mm; ' $T'_{min/max} = 0.77$. $2\theta_{max} = 60^\circ$; $N_t = 53093$, N = 7351 ($R_{int} = 0.052$), $N_o = 4698$; R = 0.047, $R_w = 0.092$ ($n_w = 75$); S = 0.96. $|\Delta \rho_{max}| = 2.1$ e Å⁻³. T ca. 170 K.

Variata. The sodium and ytterbium atoms are disposed on crystallographic 2-axes; DME ligand(1) was modelled as disordered over pairs of sites, occupancies 0.5, associated C, O displacement parameter forms isotropic.

Results and Discussion

Synthesis – Lanthanoid and Potassium bis(phenolate) Complexes

The readily prepared H_2L^R ligands [35, 36] (R = NMe₂, OMe) were deprotonated with two equivalents of potassium hydride in DME to yield $[K_2L^R(DME)_3]$ where R = NMe₂ (1); OMe (2) (DME = 1,2-dimethoxyethane). Both of these compounds have been characterized fully and ¹H NMR spectroscopic and elemental analyses are consistent with the formulations elucidated by X-ray crystallographic studies (See Experimental Section for details). These two compounds represent convenient starting materials for the synthesis of lanthanoid bis(phenolate) 'ate' complexes such as $[K(DME)_2][Yb^{III}(L^{OMe})_2]$ [13].

Alternatively, H_2L^R ligands can be treated with one equivalent of $[Ln(N(SiMe_3)_2)_2(THF)_2]$ to give $[LnL^R] Ln =$ Yb, R = NMe₂ (3) or OMe (4); Ln = Sm, R = OMe (5) (Scheme 1). Compounds 1-5 represent excellent starting materials for a variety of heteroleptic and homoleptic lanthanoid compounds with compounds 1 and 2 being employed in metathesis reactions involving lanthanoid halides such as $YbI_2(THF)_2$ [13]. Compounds 3–5 (for which detailed syntheses and reactivity were recently reported [13] for 3 and 4), can be readily treated with easily reduced alcohols to form a variety of heteroleptic compounds [13], to yield [Ln(L^R)(OR')] Ln = Yb, R' = Ph, R = NMe₂ (6) or OMe (7); Ln = Sm, R' = Prⁱ, R = OMe (8).

Compound 5, the samarium analogue of 3 and 4, exhibits similar solution properties to these ytterbium compounds where, in donor solvents, such as tetrahydrofuran (THF), it exists as a monomer and in non-donor solvents (*e.g.* toluene) a dimeric structure is prevalent. This is consistent with the previously reported X-ray crystal structure of 3 [13] which has a dimeric structure (crystallized from hexanes) $[LnL^{R}]_{2}$ where the C_{2} symmetry of the bis(phenolate) ligand is lost upon bridge formation.

While the experimental procedures for 6 and 7 have been reported previously by the authors, their details are reiterated here since two novel and highly unusual compounds (9, 10) were derived from these reactions. Compounds 3-8were routinely synthesized as part of a catalytic study investigating the ROP capabilities of these catalyst precursors towards ε -caprolactone [13]. During particular syntheses of compounds 6-8, single crystals were grown from each reaction mixture, which was believed to be that of the respective target complex. However, X-ray crystallographic studies demonstrated the formation of three remarkable new compounds, $[Yb(L^R)(OPh)_2Na(DME)(HOPh)] R = NMe_2$ (9); OMe (10) derived from compounds 6 and 7 respectively. and $[Sm(L^{OMe})_2Na(OH_2)]$ (11) which is derived from compound 8 (See below for detailed single crystal X-ray structure discussions). Compounds 9 and 10, which have the same formulation and ligand ratio, are ytterbium(III) bis(phenolate) 'ate' complexes where essentially a routine NaOPh component has been combined with a neutral $[Yb(L^R)OPh]$ complex. It is believed that the origin of the sodium component was from contamination of the $[Ln(N(SiMe_3)_2)_2(THF)_2]$ starting material. It has been



 $[Yb(L^{R})(OPh)_{2}Na(DME)(HOPh)] R = NMe_{2}$ (9); OMe (10)

Scheme 1 Synthesis of lanthanoid and potassium phenolate complexes

reported [37] that inadequate and non-rigorous extraction of $[Ln(N(SiMe_3)_2)_2(THF)_2]$ from NaI can lead to its inclusion to give Na[Ln(N(SiMe_3)_2)_3]. Compound 11 $[Sm(L^{OMe})_2Na(OH_2)]$, also containing sodium, presumably from the same source, *i.e.* $[Ln(N(SiMe_3)_2)_2(THF)_2]$, has a residue modelled as a coordinated water molecule which presumably could arise from the presence of adventitious water. As with 9 and 10, compound 11 is a samarium bis(phenolate) 'ate' complex with a sodium counter-ion.

Synthesis of Ytterbium Reduced Phenolate Complex

Treatment of two equivalents of the Schiff base phenol HL^{py} [32]¹) with divalent [Yb(N(SiMe_3)_2)_2(THF)_2] did not produce the expected product as a result of a typical proteolytic ligand exchange reaction (Scheme 2). Rather, the ytterbium(II) atom was able to reduce the Schiff base ligand in a unique fashion, resulting in methylene deprotonation and formation of a dianionic ligand. Ligand redistribution leads to formation of a unique ytterbium(III) phenolate complex (Scheme 2, 12) containing the mono- and di-anionic ligands. From one reaction, crystallization led to the isolation of 13 as indentified by an X-ray study (see below). While there is some precedent for divalent lanthanoid compounds reducing Schiff bases [38], typically involving C=Nreduction followed by ligand coupling through the imine carbon atom, this current type of reduction is unprecedented. Furthermore, imine reductions are usually only



Scheme 2 Syntheses of ytterbium complexes possessing reduced phenolate ligands.

observed for the samarium(II) compounds – the more powerful of the divalent reducing agents. In the present system, however, deprotonation of the the methylene carbon occurs, resulting in the formation of sp^2 hybridized carbon (C(20) in Figure 5 - see below). Due to the highly paramagnetic nature of ytterbium(III), NMR studies were not feasible. Indeed the absence of any intelligible ¹H NMR spectroscopic data provided evidence, albeit indirect, for the oxidation of ytterbium(II). Further evidence to support this claim was provided by the X-ray crystal structure of the related compound [Na(DME)₃][Yb(*L^{py})₂] 13, which crystallized from one reaction mixture of 12. As with many of the bis(phenolate) structures discussed above, the presence of sodium can be readily accounted for by insufficient purification of the [Yb(N(SiMe₃)₂)₂(THF)₂] starting material, where sodium becomes entrained as $Na[Ln(N(SiMe_3)_2)_3]$ [37].

Crystal Structures

The results of single crystal X-ray structure determinations on specimens of the potassium salts of H_2L^R (R = NMe₂, OMe) from DME solution are consistent with their formulation as DME tri-solvates of the salts of the doubly charged ligand/dianion (i.e. the pro-ligand deprotonated at the two phenolic residues), both taking the form of neutral binuclear molecules $[K_2L^R(DME)_3]$ (1) and (2), one such entity, devoid of crystallographic symmetry, comprising the asymmetric unit of the structure in each case; the molecules are similar in aspect, albeit the structures are not isotypic. In each case, the precision of the determination is somewhat degraded by disorder; nevertheless, this is essentially restricted to substituent or pendant saturated chain conformations with little impact on the form of the molecular cores. The two potassium atom environments differ within each complex, but display many similarities between the two complexes. They are presented in Table 1 with two complexes displayed in Figure. 2, showing, despite their considerable formal similarity, considerable differences in the conformations and dispositions of the DME solvent chelate, and the pendant groupings.

The potassium atoms K(2) are six-coordinate in both complexes, well-removed from octahedral geometry, the N^O chelate angles being ca. 70°, with the O-K-O angle about 90°, the O^N^O ligand string comprising a quasifac tridentate ligand. The oxygen atoms of DME ligand 2 comprise a chelate donor, occupying a further pair of cissites in the K(2) coordination sphere. The associated K-O distances are rather similar (ca. 2.9 Å), although the two values are greater in the L^{NMe2} complex, 1, cf. their L^{OMe} counterparts (the opposite of what might be expected to result from the different temperatures of the two determinations), with K-O(201) greater than K-O(202) in each case (the former distance being quasi-trans to the central N-donor of the oligodentate ligand). The last coordination site is occupied by the OMe or NMe₂ pendant of the oligodentate ligand, the OMe group being strongly bound with the K-O distance comparable to the K-phenolic-O distances,

¹⁾ The L^{py} ligand is defined as $\{L^{py} = {}^{-}OC_6H_2(2,4-Bu^t)(6-CH=N-CH_2-2-C_6H_4N)\}$ containing a methylene carbon (bolded) whereas the *L^{py} ligand is defined as $\{*L^{py} = {}^{-}OC_6H_2(2,4-Bu^t)(6-CH=N-CH-2-C_6H_4N)\}$ where the methylene carbon atom has been deprotonated.



Figure 2 (a,b) Projections of $[K_2(L^R)(DME)_3]$ (1) and (2) with a common setting of chirality, normal to their central $K(\mu-O)_2K$ core planes. *t*-Butyl methyl groups omitted for clarity.

whereas the K-NMe₂ distance is much longer. In the L^{OMe} complex, O(302) also has a distant approach not evident in the L^{NMe2} complex, more likely a consequence of the proximity of K(1) (to which it is bound) rather than any approach to bond formation. With the angles O(12)-K(2)-O(22) *ca.* 90°, the pairs of phenolic oxygen atoms may then act as further chelate donors, to K(1), forming four-membered KO₂K rings which are the cores of the two molecules. The K(1) atom environments are also six-coordinate, well-removed from the octahedral norm, their coordination spheres being *tris*-bidentate, by virtue of the chelation of the remaining pair of DME ligands, these being of very small 'bite' (*ca.* 60°). Although K(1)-O(12),O(22) are closely similar throughout both complexes (2.622(2)-

Table 1 Potassium atom environments in $[K_2(L^R)(DME)_3] R = NMe_2$ (1), OMe (2). Values for complex 1 lie below those for complex 2; r/Å is the potassium-ligand atom distance; other entries in the matrix are the angles (degrees) subtended at the potassium atom by the relevant atoms at the head of the row and column.

K(1)	r	O(22)	O(101)	O(102)	O(301/301')	O(302/302')
O(12)	2.623(2)	99.16(6)	95.16(6)	123.08(6)	93.62(6), 116.1(2)	84.0(1), 75.5(5)
	2.628(2)	89.60(7)	103.6(1)	161.2(1)	103.1(1)	102.2(1)
O(22)	2.622(2)		147.46(8)	88.16(6)	133.21(6), 115.1(3)	76.8(1), 79.2(5)
	2.662(3)		101.0(1)	95.8(1)	158.4(1)	102.8(1)
O(101)	2.810(2)			59.60(6)	73.97(6), 83.2(3)	133.8(1), 132.8(5)
	2.927(5)			57.7(2)	92.9(2)	144.7(1)
O(102)	2.747(2)				121.20(7), 110.8(2)	151.1(1), 159.4(5)
	2.842(4)				77.8(2)	94.2(6)
O(301)	2.809(2)				-, 24.8(3)	60.0(1), 60.9(5)
O(301')	2.73(1)					, 61.7(6)
	2.913(4)				-	57.9(2)
O(302)	2.780(5)				-, 56.8(3)	-, 8.6(5)
O(302')	2.86(3)					
	2.977(4)					_

K(1)···K(2) are 3.441(1), 3.816(3) Å.

K(2)	r	O(12)	O(22)	N,O(3)	O(201)	O(202)	O(302/302')
N(1)	2.911(2)	68.86(9)	71.83(5)	63.02(6)	152.35(6)	108.03(6)	121.68(9), 124.4(5)
	2.897(3)	73.12(7)	74.06(7)	64.32(1)	160.8(1)	114.8(1)	
O(12)	2.718(2)		94.94(5)	90.48(6)	115.09(6)	165.34(6)	74.2(1), 71.2(5)
	2.778(2)		85.34(6)	109.5(1)	112.7(1)	171.3(1)	
O(22)	2.701(2)			128.80(6)	132.02(6)	97.60(6)	68.15(9), 74.9(5)
	2.722(3)			127.9(1)	123.7(1)	100.0(1)	
O(3)	2.714(2)				89.34(6)	75.74(6)	159.0(1), 152.3(5)
N(3)	3.127(6)				96.9(2)	72.6(1)	
O(201)	2.865(2)					60.68(6)	84.4(1), 80.5(5)
	2.983(5)					58.6(1)	
O(202)	2.819(2)						117.6(1), 119.6(5)
	2.906(4)						
O(302)	3.240(5)						-, 6.9(5)
O(302')	3.04(3)						
	_						

2.662(3) Å), the angles between them differ by nearly ten degrees (being larger in the L^{OMe} complex), reflecting the similar difference found in O(12)-K(2)-O(22), the latter contrary to the difference that might be anticipated to be consequent on any *quasi-trans*-influence contingent on the difference in the strengths of the K(2)-O,N(3) interactions. All K(1)-O(n02)(DME) distances in the L^{NMe2} complex are appreciably longer than their counterparts in the L^{OMe} complex, despite the smaller O(12)-K(1)-O(22) angle in the latter.

With the two dianionic ligands L^{OMe} and L^{NMe2} , the results of the single crystal X-ray studies define the pair of heterobimetallic (Na/Yb) agglomerates 9, 10, complex but well-defined and isotypic, with disorder found only in the peripheral methylene groups of the pendant strings of the L^{R} ligands. The complexes are of the form $[Yb(L^{R})(OPh)_{2}Na(DME)(HOPh)] R = NMe_{2}$ (9), OMe (10); the residual phenolic proton is well-defined in each case, being hydrogen-bonded to an adjacent phenoxide-oxygen atom, O,H(301)...O(201) 2.675(5), 1.9 Å (est.) (L^{OMe} complex); 2.664(4), 1.8 Å (est.) (L^{NMe2} complex). A projection of the L^{OMe} aggregate is given in Figure 3 with metal

atom environment parameters presented in Table 2. The interactions of the vtterbium atoms with the L^R ligands are similar, and similar to those found in the solvated K₂L arrays about the K(2) atoms. The atomic radius of the ytterbium atoms is greatly diminished relative to that of the potassium atoms. The coordination environments are still sixcoordinate, but more nearly octahedral, with M-N more conspicuously longer than M-O, and the angle between the phenolic oxygen donor atoms now splayed more towards linearity, so that the aspect of the O^NO string formed with the central nitrogen atom N(1) is more nearly 'fac', rather than 'mer' as previously, with the phenoxide-oxygen atoms now incapable of coordinating the (now smaller) alkali metal atom. This is accomplished by completion of the six-coordinate array by the coordination, not of a DME chelating ligand, but by a pair of unidentate phenoxide ligands (compensating the additional charge of the ytterbium(III) cf. the potassium(I) atom), the 'equatorial' phenoxide oxygen then, with O(22) of the L ligand, chelating the group I (sodium) counter-ion, again forming a fourmembered MO_2M' ring, this time heterobimetallic. Despite only trivial differences in the associated Yb-O and O-Yb-O parameters of this ring in the ytterbium atom environments, and also in their sodium counterparts, the Na…Yb distances in the two complexes differ by nearly 0.2 A (Table 2). The coordination environments of the sodium atoms are sparse, the five-coordinate arrays being made up of the DME solvent (chelating, and, like the MO_2M' ring chelate, of small 'bite') and a ('solvent') non-deprotonated phenol ligand, the Na-O distance associated with the latter being long.



Figure 3 Projection of $[Yb(L^{OMe})(OPh)_2Na(DME)(HOPh)]$ (10), normal to the $Yb(\mu-O)_2Na$ core plane.

The last complex of this form (11), defined for the MM' = Na/Sm combination, is more tentative in its formulation, but nevertheless of considerable interest. Here, the lanthanoid atom is again six-coordinate, interacting with $L^{OMe}(1)$ in the manner previously described for the ytter-

Table 2 The metal atom environments in $[Yb(L^R)(OPh)_2Na-(DME)(HOPh)] R = NMe_2$ (9), OMe (10). Values for complex 9 lie below those for complex 10, (presentation as in Table 1).

(a) The sodium atoms

Atom	r	O(101)	O(301)	O(401)	O(402)
O(22)	2.390(3)	74.7(1)	87.9(1)	170.2(2)	104.0(2)
	2.416(3)	75.2(1)	85.5(1)	166.4(1)	108.4(1)
O(101)	2.318(3)		88.5(1)	102.8(2)	131.(2)
	2.295(3)		88.6(1)	96.4(1)	136.0(1)
O(301)	2.629(5)			101.6(2)	140.3(2)
	2.546(4)			105.2(1)	135.0(1)
O(401)	2.327(5)				70.3(2)
· /	2.338(4)				70.1(1)
O(402)	2.361(7)				
. ,	2.380(4)				

(b) The ytterbium atoms

Atom	r	O(12)	O(22)	O/N(3)	O(101)	O(201)
N(1)	2.456(3)	79.61(1)	81.4(1)	69.6(1)	95.6(1)	164.5(1)
	2.452(3)	81.0(Ì)	82.8(1)	71.3(1)	92.2(1)	166.9(1)
O(12)	2.107(3)		160.9(1)	86.2(1)	96.8(1)	103.4(1)
	2.099(2)		162.7(1)	88.0(1)	91.8(1)	103.8(1)
O(22)	2.175(3)			89.1(1)	83.0(1)	95.4(1)
· /	2.187(3)			92.4(1)	83.0(1)	93.3(1)
O(3)	2.418(3)				164.2(1)	95.3(1)
N(3)	2.575(3)				163.4(1)	96.4(1)
O(101)	2.137(3)				. ,	99.1(1)
. ,	2.155(3)					99.8(1)
O(201)	2.144(3)					
. /	2.157(3)					

Na…Yb are 3.402(2), 3.419(2) Å.

bium complexes. The fifth and sixth coordination sites are occupied by the phenolic oxygen atoms of a second $L^{OMe}(2)$ ligand, these providing the bridging atoms for the formation of a further four-membered MO₂M' ring, M, M' = Na, Sm by chelating the associated sodium atom, the orientation of that ring now being 'axial' rather than 'equatorial' *cf.* the lanthanoid/ $L^{OMe}(1)$ environment (Figure 4, Table 3). The sodium atom is again five-coordinate, the additional donor atoms being the central nitrogen atom of $L^{OMe}(2)$, and the pendant methoxy oxygen atom, together with a residue modelled as a water molecule oxygen atom. One formula unit, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure.

Formulation as $[Sm(L^{OMe})_2Na(OH_2)]$, although satisfying charge balance requirements in terms of the usual mono- and triply-charged metal atoms and doubly deprotonated ligands, sits uncomfortably with refinement behaviour. The pendant group of the oligodentate ligand is disordered, with components of the disorder lying unrealistically close to the sodium atom; the latter, moreover, together with the residue modelled as the water molecule oxygen atom, have high displacement parameters, becoming reasonable by allowing the site occupancies to refine, these becoming close to 0.5 at which value they were fixed. We thus postulate, that in the absence of the sodium atom and the water molecule, either the central nitrogen atom N(21) of $L^{OMe}(2)$ or the phenolic oxygen atom O(23) becomes



Figure 4 Projection of $[Sm(L^{OMe})(L^{OMe})(HL^{OMe})\{Na(OH_2)\}_{0.5}]$, normal to the $Sm(\mu$ -O)₂Na core plane. *t*-Butyl methyl groups omitted for clarity.

Table 3 The metal atom environments in $Sm_2(L^{OMe})_4H-Na(OH_2)'$ (11).

(a) The sodium atom

Atom	r	O(212)	O(222)	O(23)	O(1)	
N(21) O(212) O(222) O(23) O(1)	2.316(9) 2.373(7) 2.320(7) 2.25(2) 2.30(3)	81.2(3)	81.2(3) 85.9(2)	74.3(5) 121.1(6) 139.2(5)	147.7(7) 128.9(7) 109.0(7) 78.9(8)	
(b) The	samarium a	tom				
Atom	r	O(112)	O(122)	O(13)	O(212)	O(222)
N(11) O(112) O(122) O(13) O(212) O(222)	2.647(5) 2.207(5) 2.250(5) 2.250(5) 2.240(4) 2.246(5)	74.6(2)	76.2(2) 150.7(2)	66.02(2) 81.9(2) 84.9(2)	155.3(2) 105.7(2) 100.1(2) 89.4(2)	113.8(2) 94.2(2) 99.0(2) 176.0(2) 90.9(2)

Na…Sm is 3.249(5); in the absence of Na, H(21'N)…O(23') is 2.6 Å (see text).

protonated, the associated hydrogen component (e.g. H(21'N)) contacting the oxygen atom of the second (reoriented) component of the disordered pendant (N(21), $H(21'N)\cdots O(23')$ 2.96(1), 2.6 Å (est.)).

The results of the study of the final complex **13** are consistent with its formulation as the ionic array $[Na(DME)_3][Yb(*L^{py})_2]$ (Figure 5, Table 4 with L^{py} and $*L^{py}$ as defined above; also see Scheme 2). One half of the formula unit comprises the asymmetric unit of the structure, each metal atom lying on a crystallographic two-fold axis, relating the two ligands of the anion, the cation environment being an aggregate of a pair of ordered DME chelating groups, related by the two-fold axis (ligands 2); ligand 1 (and its image) are disordered, in total making up a complex disordered composite in which Na-O (DME) distances, range closely between 2.38(2)-2.44(1) Å, compare well with the usual norm.



Figure 5 Projection of the anion of [Na(DME)₃][Yb(*L^{py})₂] **13**, normal to the crystallographic 2-axis, which lies horizontal in the page.

Table 4	The ytterbium atom environment	in [Na(DME) ₃][Y	$b(*L^{py})_2](13)$ (s	ee text). Primed a	toms are related	by the crystallo	graphic 2-axis
which pa	asses through the ytterbium atom.	Counterpart value	es are given for	[K(DME)2][Yb(I	$L^{OMe})_{2}$ [13] and	[K(THF) ₃][Yb($[L^{NMe2})_2]$ [39].

Atoms	$[Na(DME)_3][Yb(*L^{py})_2]$	$[K(DME)_2][Yb(L^{OMe})_2]$	$[K(THF)_3][Yb(L^{NMe2})_2]$
Distances/Å			
Yb-N(1)	2.409(5)	2.528(4), 2.508(4)	2.538(3), 2.499(3)
Yb-O(12)	2.083(5)	2.174(4), 2.171(2)	2.160(2), 2.189(2)
Yb-N/O(22)	2.334(5)	2.116(3, 2.132(3)	2.112(2), 2.128(2)
Angles/°			
N(1)-Yb-O(12)	76.7(2)	78.7(1), 79.2(1)	77.18(8), 78.90(9)
N(1)-Yb-N/O(22)	69.4(2)	77.6(1), 77.7(1)	77.97(9), 78.22(9)
N(1)-Yb-N(1')	170.8(2)	177.2(1)	176.98(8)
N(1)-Yb-O(12')	98.0(2)	99.3(1), 98.9(1)	99.53(9), 100.60(8)
N(1)-Yb-N/O(22')	118.2(2)	103.7(1), 104.7(1)	103.19(9), 104.62(9)
O(12)-Yb-N/O(22)	139.7(2)	155.9(2), 156.9(1)	154.74(8), 156.95(9)
O(12)-Yb-O(12')	109.5(2)	88.0(1)	87.01(8)
O(12)-Yb-N/O(22')	96.5(2)	94.1(1), 91.5(5)	94.26(8), 92.68(9)
N/O(22)-Yb-N/O(22')	81.4(2)	95.7(1)	95.73(9)

In the present $[Na(DME)_3]^+$ cation, Na-O range between 2.38(2)-2.44(1) Å.

The charge-balancing component required is arguably a singly charged counter-ion containing ytterbium(III) with a pair of crystallographically equivalent dianionic N^N^O ligand donors. Excluding the *t*-butyl groups, the overall skeleton of the ligand is quite closely planar (χ^2 4307; maximum atom deviation C(14) 0.252(8) Å; maximum deviation within the tridentate OCCCNCCN string $N(1) 0.144(6) \dot{A}$, although the dihedral angle between the peripheral C_6/C_5N aromatic ring planes is 12.8(2)°; the deviation of the ytterbium atom from the overall component chelate ring planes is considerable (overall plane, 0.620(3) Å). Bond lengths in the string C(11)-C(10)-N(1)-C(20)-C(21) are 1.459(9), 1.300(8), 1.368(9), 1.368(10) Å with angles at C(10), N(1), C(20), 128.0(5), 119.8(6), 119.8(6)°, suggesting the assignment of a hydrogen atom apiece (not located by refinement) to each of C(10,20) to be appropriate, as well as the second negative charge of the ligand to the region. Thus C(20), which was formally sp^3 hybridized in the free HL^{py} ligand is now considered as sp^2 hybridized in accordance with the proposed mechanism above (Scheme 2) where C(20) is deprotonated, (the ligand now being designated $(*L^{py})^{2-}$). This is highly unusual and imine reduction may have been anticipated as it would surely have been the preferred site for attack. It is clear, however, that the imine portion of the ligand remains intact, since the C(10)-N(1) distance of 1.300(8) Å observed is typical for an imine C=N [see the related compound, [Me₂AlL^{py}], which reports C=N 1.295(3) Å [32]]. Furthermore, the N(1)-C(20) distance of 1.368(9) A is considerably shorter than that found in $[Me_2]$ AlL^{py}] (*i.e.* C-N is 2.014 Å) implying an increase in bond order of N(1)-C(20), consistent with ligand reduction.

The structure begs comparison with that of the recently reported counterpart DME [13] and THF [39] solvated potassium analogues formed with LOMe, and LNMe2 respecof composition $K[Yb(L^{OMe})_2] \cdot 2DME$ tivelv. and K[Yb(L^{NMe2})₂]·3THF. In both cases, a neutral aggregate with quasi-2 symmetry is formed, the potassium atom being chelated by a pair of phenoxide groups cis in the coordination sphere, diminishing the available coordination sites about the potassium atom so that only two DME chelate or three THF groups are found to be accommodated, thus forming [K(DME)₂][Yb(L^{OMe})₂] or [K(THF)₃][Yb(L^{NMe2})₂] neutral aggregates. In the present 13, with one of the phenoxy groupings of each ligand removed, so that the aggregate has diminished propensity to coordinate the (this time) sodium atom, and to bridge, the sodium atom coordination sphere is fully solvated by the three DME ligands and does not interact with the anion, although the angle O(12)-Yb-O(12') continues to offer a chelating possibility, albeit with a considerably, and perhaps inappropriately, enlarged 'bite'. It is of interest that replacement of the pair of phenoxide groups and their associated potassium atoms by the pair of pyridine groups (Figure 5, Table 4), without any associated chelated alkali metal atom, despite the increase in Yb-N, cf. Yb-O, is accompanied by closure of the N-Yb-N, cf. counterpart O-Yb-O angles. Also of interest are the changes in Yb-central-N and Yb-common-phenoxide-O distances, both of these contracting in the present, with some very substantial changes in associated angles. The structure forms layers, normal to *c*, lying between $z = 0^{-1/2}$ (*etc.*).

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