The first neutral homoleptic lanthanoid pyrazolates, including the mixed oxidation state species [$Yb_2(Bu^t{}_2pz)_5$] ($Bu^t{}_2pz$ = 3,5-di-*tert*-butylpyrazolate), from a simple new synthesis of pyrazolate complexes

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Reaction of 3,5-di-*tert*-butylpyrazole ($Bu^t{}_2pzH$) with lanthanoid metals and mercury at 220 °C in the absence of an added solvent yields [$Ln(Bu^t{}_2pz)_3$] (Ln = Nd, Sm), [$Eu(Bu^t{}_2pz)_2$] and [$Yb_2(Bu^t{}_2pz)_5$], which is a mixed oxidation state complex with the structural arrangement [(η^2-$Bu^t{}_2pz$)Yb^{II}(μ-$\eta^2:\eta^2$-$Bu^t{}_2pz$)$_2$$Yb^{III}$($\eta^2$-$Bu^t{}_2pz$)$_2$].

Pyrazolate coordination chemistry[1] has recently been stimulated by expansion of recognised binding modes from the long standing (i) μ-$\eta^1:\eta^1$, (ii) η^2 and (iii) η^1 (N-bonded)[1] to (iv) μ_3-$\eta^1:\eta^2:\eta^1$, (v) μ-$\eta^2:\eta^2$, (vi) π-η^1 (C-bonded), (vii) η^3 and (viii) η^5.[2–6] In addition, a 14-year restriction of η^2 coordination to f-block elements has been removed by recent examples of η^2-bonding to d-block[7] and main group elements.[8] Although there are now a wide variety of synthetic routes to rare earth pyrazolates,[3,5,9,10] no structurally characterised neutral homoleptic pyrazolatolanthanoid(II or III) complexes, [$Ln(R_mpz)_n$] (n = 2 or 3; R possible substituents, m = 0–3), have been prepared,[11] presumably because the large size of Ln^{n+} leads to attachment of coligands, often derived from the synthesis solvent, giving [$Ln(R_mpz)_3(L)_x$] (*e.g.* L = dme, thf, Ph_3PO, x = 1–3)[9] or [$Ln(R_mpz)_2(L)_x$] (*e.g.* L = dme, x = 2).[3,10] Neutral homoleptic complexes would be of major structural interest, because of the need to attain coordination saturation in the absence of coligands. We now report that both di- and tri-valent neutral homoleptic pyrazolatolanthanoid complexes [$Ln(Bu^t{}_2pz)_n$] ($Bu^t{}_2pz$ = 3,5-di-*tert*-butylpyrazolate, n = 2 or 3), and the novel mixed oxidation state complex [$Yb_2(Bu^t{}_2pz)_5$], can be prepared by a new synthesis of pyrazolate complexes. The method has potential general applicability to pyrazolates of electropositive metals.

Reaction of 3,5-di-*tert*-butylpyrazole with an excess of lanthanoid metal and mercury under vacuum at 220 °C without added solvent, followed by extraction with toluene and crystallisation yielded [$Yb_2(Bu^t{}_2pz)_5$] **1**, [$Eu(Bu^t{}_2pz)_2$] **2**, [$Sm(Bu^t{}_2pz)_3$] **3** and [$Nd_2(Bu^t{}_2pz)_6$] **4** in satisfactory yield.† The oxidation state diversity suggests the method has considerable versatility.

$$Ln + nBu^t{}_2pzH \xrightarrow{Hg} [Ln(Bu^t{}_2pz)_n] + n/2\ H_2\ (n = 2, 2.5 \text{ or } 3)$$

The dried complexes (single crystals of **1** and **4** were toluene solvates) gave satisfactory C, H, N, Ln analyses for the above compositions. For **1**, **3** and **4**, visible/near IR absorptions characteristic[12] of the appropriate Ln^{3+} ions were observed. X-Ray structures of **1**·PhMe‡ and **4**·2PhMe‡[13] revealed a bimetallic mixed oxidation state complex and a dimeric structure [{$Nd(\eta^2$-$Bu^t{}_2pz)_2(\mu$-$\eta^2:\eta^2$-$Bu^t{}_2pz)$}$_2$][13] respectively (below). Neither **2** or **3** have yet been obtained as single crystals, but divalent **2** requires a μ-$\eta^2:\eta^2$ pyrazolate bridged dimeric or associated structure to have reasonable coordination number whilst **3** is expected to have a dimeric structure similar to **4**. However, a monomer parent ion for **3**, in contrast to the absence of metal-containing ions for **4**, does leave open the possibility of a monomeric six-coordinate structure. The ^1H NMR spectrum of **1** in d_8-THF is indicative of dissociation into separate $Yb(Bu^t{}_2pz)_2$ and $Yb(Bu^t{}_2pz)_3$ complexes owing to solvent coordination.

The molecular structure of **1** (Fig. 1),‡ determined for the toluene solvate, shows a six-coordinate Yb^{2+} ion with one terminal η^2-$Bu^t{}_2pz$ ligand linked through two μ-$\eta^2:\eta^2$-$Bu^t{}_2pz$ groups to an eight-coordinate Yb^{3+} which has two terminal η^2-$Bu^t{}_2pz$ ligands. It is only the second complex with μ-$\eta^2:\eta^2$-pyrazolate coordination. The oxidation states of Yb(1) and Yb(2) (Fig. 1) are clearly evident from the bond distances. Thus, terminal (ter) Yb(1)–N(12) [2.334(7) Å] is comparable with $Yb–N_{ter}$ [2.404(6) and 2.378(5) Å] of [{$Yb(\eta^2$-$Bu^t{}_2Pz)(\mu$-$\eta^2:\eta^2$-$Bu^t{}_2pz)(thf)$}$_2$][3] when the difference in ionic radii (0.06 Å)[14] between six- and seven-coordinate Yb^{2+} is considered. In addition Yb(2)–N_{ter} distances [2.287(7) and 2.270(7) Å] are comparable with Er–N of eight-coordinate [$Er(Bu^t{}_2pz)_3(thf)_2$] [2.274(7)–2.386(8) Å, av. 2.34 Å][9c] (ionic radius $Er^{3+} > Yb^{3+}$

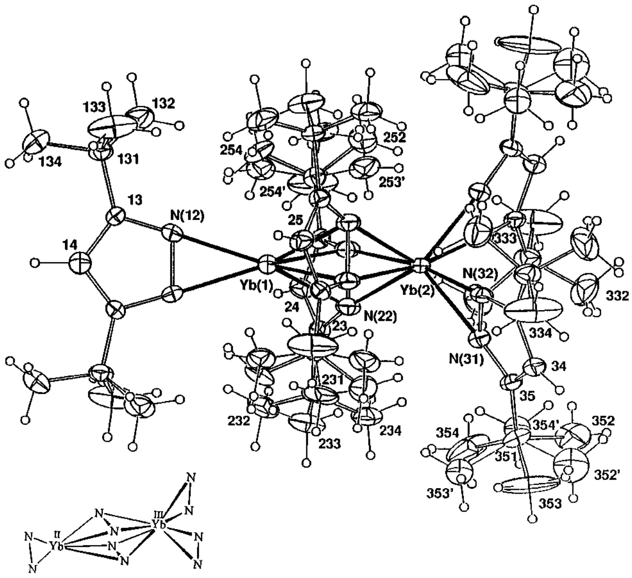

Fig. 1 Molecular projection of **1**; 20% probability ellipsoids are shown for the non-hydrogen atoms, hydrogens having arbitrary radii of 0.1 Å. Key carbon atoms are denoted by number only. [Insert: Yb(1) and Yb(2) coordination spheres]. Selected bond distances (Å) and angles (°): Yb(1)–N(12,21,22) 2.334(7), 2.534(8), 2.587(8); Yb(2)–N(21,22,31,32) 2.402(8), 2.425(8), 2.287(7), 2.270(7), N(12)–N(12*) 1.43(1), N(21)–N(22) 1.37(1), N(31)–N(32) 1.38(1); Yb(1)···C(23,24,25) 3.167(9), 3.468(10), 3.109(10); N(12)–Yb(1)–N(21,22,12*,21*,22*) 131.6(3), 145.0(3), 35.6(3), 138.7(3), 125.7(3); N(21)–Yb(1)–N(22,21*,22*) 31.1(2), 84.0(3), 76.1(3); N(22)–Yb(1)–N(22*) 85.1(3); N(21)–Yb(2)–N(22,31,32,21*,22*,31*,32*) 33.1(3), 138.5(3), 169.3(3), 89.8(3), 81.7(3), 94.0(3), 82.9(3); N(22)–Yb(2)–N(31,32,22*,31*,32*) 106.8(3), 137.2(3), 92.3(3), 120.7(3), 96.0(3), N(31)–Yb(2)–N(32,31*,32*) 35.3(3), 109.4(3), 96.7(3); N(32)–Yb(2)–N(32*) 105.4(3), Yb(1)–N(21,22)–Yb(2) 93.1(3), 91.3(3). The molecule has mirror symmetry, the mirror lying horizontal and almost normal to the page. Symmetry generated atoms are denoted by asterisks.

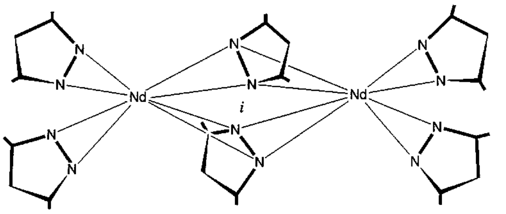

Fig. 2 Simplified representation of the structure of **4**, displaying the Nd/$Bu^t{}_2pz$ connectivity.[13]

by *ca.* 0.02 Å for the same CN)[14] and with $\langle Yb–N \rangle$ (2.30_5 Å) of eight-coordinate $[Yb(\eta^2\text{-}Ph_2pz)_3(dme)]$[13] ($Ph_2pz$ = 3,5-diphenylpyrazolate). Furthermore, it can be calculated from existing lanthanoid pyrazolate structural data (*e.g.* refs. 3, 5, 9, 10) and lanthanoid ionic radii[14] that if Yb(1) were in oxidation state (III) a much shorter $Yb–N_{ter}$ of 2.17 Å would be expected and if Yb(2) were Yb(II), a much longer $\langle Yb–N_{ter} \rangle$ of 2.44 Å would be expected. Both bridging pyrazolate groups of **1** are tilted towards divalent Yb(1) with the pyrazolate ring planes angled at 59.0(3)° to the Yb(1)···Yb(2) axis, *cf.* 90° for symmetrical bridging. Consequently, C(23) and C(25), but not the more distant (by ≥0.3 Å) C(24), of each $\mu\text{-}\eta^2\text{:}\eta^2\text{-}Bu^t{}_2pz$ ligand, may interact marginally with Yb(1). Subtraction of the ionic radius[14] for six-coordinate Yb^{2+} from Yb···C(23) and Yb···C(25) (Fig. 1 legend) gives 2.14 and 2.09 Å, respectively, which are near the upper limit (2.16 Å) of similarly derived values for complexes with inter- and intra-molecular π-arene···Ln coordination.[15] Such interactions would enhance the coordination number of Yb(1) from the low value of six.

The connectivity of **4**[13] is shown in Fig. 2. There is no interaction of the Ln metals with toluene of crystallization in either **1** or **4**, since Ln···C(PhMe) and Ln···H(PhMe) separations lie outside the generous limits of 3.6 and 3.3 Å, respectively, for **1** and 3.7 and 3.4 Å for **4**.

1 is a rare example of a molecular compound combining lanthanoids in both II and III oxidation states and the first with pyrazolate ligands. Other examples of molecular lanthanoid(II, III) complexes include $[\{Yb^{III}(C_5Me_5)_2\}_2Yb^{II}(\mu\text{-}CCPh)_4]$,[16a] $[Yb^{III}(C_5Me_5)_2(\mu\text{-}F)_2Yb^{II}(C_5Me_5)]_2$,[16b] $[Yb^{III}(C_5Me_5)_2(\mu\text{-}F)\text{-}Yb^{II}(C_5Me_5)_2]$,[16c] $[Yb^{III}Ph_2(thf)(\mu\text{-}Ph)_3Yb^{II}(thf)_3]$,[16d] $[\{(C_5Me_4{}^iPr)_2Sm\}_2(\mu\text{-}Cl)]$,[16e] and $[Sm^{III}(C_5Me_5)_2(\mu\text{-}C_5H_5)Sm^{II}(C_5Me_5)_2]$.[16f]

Structures of **1**·PhMe and **4**·2PhMe, suggest that the lanthanoid elements may prefer the newly recognised[3] $\mu\text{-}\eta^2\text{:}\eta^2$ pyrazolate coordination mode as a means of attaining coordination saturation in $[Ln(R_mpz)_n]$ (n = 2 or 3) complexes. The range of different oxidation state products obtained from reaction (1) to this stage indicates that the method should be generally applicable for the homoleptic lanthanoid pyrazolates, and may also extend to pyrazolates of other electropositive metals, with the alkaline earths, uranium and aluminium being of particular interest. Indeed there is a near precedent for barium, where reaction of 3,5-dimethylpyrazole with Ba metal in *refluxing thf* yields the structurally uncharacterized $Ba(Me_2pz)_2$.[17]

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Notes and references

† All operations were carried out under an atmosphere of purified N_2 or Ar or under vacuum because of the extreme sensitivity of the compounds to air and moisture.

Representative syntheses: **1**: a mixture of Yb powder (2.00 g, 11.6 mmol), $Bu^t{}_2pzH$ (0.52 g, 2.9 mmol) and mercury metal (two drops) was heated in a sealed tube under vacuum at 220 °C for 5 h. The dark red product was extracted with hot toluene (50 ml) yielding a dark red solution which was concentrated to 3 ml. The solution was then cooled at −20 °C for two days giving dark-red crystals of **1**·PhMe. The crystalline product was then dried at 80 °C under vacuum affording **1** (0.48 g, 67%) (Found: C, 53.00; H, 7.60; N, 11.35; Yb, 27.53. $C_{55}H_{95}N_{10}Yb_2$ requires C, 53.16; H, 7.71; N, 11.28; Yb, 27.85). IR (Nujol): ν/cm^{-1} 1560w, 1504s, 1314m, 1251s, 1227s, 1206s, 1019s, 993s, 794s. ^1H NMR (d_8-THF): δ 5.84 [s, 2H, H4 pz (Yb^{II})], 1.27 [s, 36H, Bu^t (Yb^{II})], −15.76 [vbr s, Bu^t (Yb^{III}) (satisfactory integration could not be obtained because of broadening)], −41.94 [s, 3H, H4, pz (Yb^{III})]. EIMS (70 eV) *m/z* 532 ($[Yb(Bu^t{}_2pz)_2{}^+$, 9%), 180 ($Bu^t{}_2pzH^+$, 21). λ_{max} (PhMe)/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$): 402 (351), 484sh (186), 925 (8), 945 (7), 976 (18), 981 (15).

4: a mixture of Nd powder (1.15 g, 8.0 mmol), $Bu^t{}_2pzH$ (0.72 g, 4.0 mmol) and mercury metal (two drops) was heated in a sealed tube at 220 °C for 24 h. The reaction product was extracted with hot toluene (50 ml) giving a pale blue solution which was reduced in volume. Pale blue crystals of **4**·2PhMe appeared in a few hours. The product was dried at 80 °C under vacuum affording **4** (0.44 g, 48%) (Found: C, 58.07; H, 8.61; N, 12.57; Nd, 21.29. $C_{66}H_{114}N_{12}Nd_2$ requires C, 58.11; H, 8.42; N, 12.32; Nd, 21.15%). IR (Nujol): ν/cm^{-1} 1558w, 1523m, 1505s, 1414s, 1362s, 1303m, 1278w, 1253s, 1224s, 1206m, 1018s, 1006m, 980s, 808m, 796s, ^1H NMR (d_8-THF): δ 4.93 (s, 108H, Bu^t), 21.53 (s, 6H, H4 pz). λ_{max} (PhMe)/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$): 532 (2), 578 (30), 591 (57), 744 (5). Analogous preparations gave **2** (95%) and **3** (57%).

‡ *Crystallographic data*: **1**·PhMe, $[Yb_2(Bu^t{}_2pz)_5]\cdot PhMe \equiv C_{62}H_{103}N_{10}Yb_2$, M = 1334.7 orthorhombic, *Pnna* (no. 52), a = 20.92(1), b = 20.371(5), c = 15.990(9) Å, V = 6814 Å^3. D_c (Z = 4) = 1.30_1 g cm^{-3}. 12698 absorption corrected four circle diffractometer data ($2\theta–\theta$ scan mode, $2\theta_{max}$ = 50°; monochromatic Mo-Kα radiation, λ = 0.7107_3 Å; T = 295 K) merged to 5998 unique (R_{int} = 0.030), 3248 [$I > 2\sigma(I)$] refining to R = 0.053, R_w (statistical weights) = 0.064, anisotropic thermal parameter forms for Yb, N, C, $(x, y, z, U_{iso})_H$ constrained at estimates. Two Bu^t groups are modelled as rotationally disordered, site occupancies 0.56(1), 0.72(1) and complements, the toluene also being disordered and modelled with constrained geometry. **4**·2PhMe.[13] Unit cell data (153 K), triclinic, $P\bar{1}$, a = 12.4301(9), b = 13.807(1)°, c = 14.015(1) Å, α = 119.480(1), β = 96.436(1), γ = 95.262(1)°, V = 2050 Å^3. CCDC 182/1268.

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