Unprecedented μ-η^2:η^2-Pyrazolate Coordination in [{Yb(η^2-tBu$_2$pz)(μ-η^2:η^2-tBu$_2$pz)(thf)}$_2$]**

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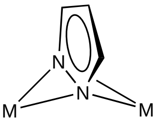
Pyrazolate (pz) ions coordinate[1–5] as bridging (*exo*-bidentate) ligands (commonly for *d*-block elements), chelating (*endo*-bidentate or η^2) ligands (both for *f*-block elements,[6–8] and, recently, for *d*-block[9]), and less commonly as unidentate ligands,[1–5, 9c] whilst η^5-binding has been postulated but never observed.[1, 2, 5] The possibility of the formally electron-deficient μ-η^2:η^2-pyrazolate binding **I** has never been considered. We now report the synthesis and X-ray structure of a ytterbium(II) pyrazolate, [Yb(η^2-tBu$_2$pz)(μ-η^2:η^2-tBu$_2$pz)(thf)]$_2$ (tBu$_2$pz = 3,5-di-*tert*-butylpyrazolate; thf = tetrahydrofuran) **1**, which exhibits this unexpected coordination mode. Only one lanthanoid(II) pyrazolate complex has previously been reported, namely [Yb(η^2-Ph$_2$pz)$_2$(dme)$_2$] (Ph$_2$pz = 3,5-diphenylpyrazolate; dme = 1,2-dimethoxyethane) **2**,[8] which has solely η^2-pyrazolate ligands.

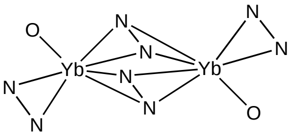


I

3,5-Di-*tert*-butylpyrazolatoytterbium(II) was prepared by redox transmetalation/ligand exchange [Eq. (a)] in tetrahydrofuran, and gave **1** on crystallization from light petroleum.

$$\mathrm{Yb} + \mathrm{HgPh_2} + 2\,t\mathrm{Bu_2pzH} \rightarrow [\mathrm{Yb}(t\mathrm{Bu_2pz})_2] + \mathrm{Hg} + 2\,\mathrm{PhH} \qquad \text{(a)}$$

A similar preparation followed by crystallization from DME gave **2**,[8] but the solubility properties of the initial product precluded the crystallization from light petroleum that is a key factor in obtaining **1** (see below). X-ray crystallography[10] revealed **1** to be a centrosymmetric dimer with the metals *bridged* by two *chelating* pyrazolate groups (Figure 1). Each ytterbium atom is seven-coordinate with one tetrahydrofuran, one terminal η^2-tBu$_2$pz and two bridging η^2:η^2-tBu$_2$pz ligands (see **II**). η^2-Pyrazolate groups have previously been observed only as terminal ligands,[2–9] whilst known bridging pyrazolates are attached to each metal atom by a single nitrogen atom.[1–5] The structure of **1** strikingly contrasts that of **2**, which is monomeric with eight-coordinate ytterbium and only η^2-pyrazolate ligands. The Yb$\cdots$Yb′ axis of **1** intersects the *N,N,N′,N′* plane at 78.3(1)°, whereas N–N bonds of previous bridging pyrazolato ligands are near parallel to the M$\cdots$M axis. Not unexpectedly, the Yb–N$_{\text{terminal}}$ distances (Figure 1) are shorter (by ca. 0.1–0.25 Å) than the Yb–N$_{\text{bridging}}$ distance, whilst the Yb–N$_{\text{terminal}}$ distance is 0.03 Å shorter in **1** than **2**, marginally less than the 0.06 Å expected[11] for the difference in coordination number. There is some asymmetry in the bridging with the nitrogen atoms of each μ-η^2:η^2-tBu$_2$pz ligand 0.07–0.11 Å closer to one ytterbium. The asymmetry in the bridging is also reflected in tilting of the bridging pyrazolate towards the more weakly bound ytterbium center. This is shown by the intersection angle of 116.7° between the Yb–Yb′ axis and the C(24)–cen(2) (cen(2) = center of N(21)–N(22)) axis, instead of 90° for fully symmetrical bridging. It is unlikely that the tilting indicates π-η^5-pz-Yb′ bonding, but weak agostic π-C$\cdots$Yb interactions between Yb′ and C(23) and C(25) are plausible. Subtraction of the ionic radius for seven-coordinate Yb^{2+} ions (1.08 Å)[11] from Yb′$\cdots$C(2n)[12] (n = 3,4,5) gives 2.24, 2.46, and 2.14 Å, respectively. The two smallest values are near the upper limit (2.16 Å) of similarly derived values for complexes with inter- or intramolecular π-arene–Ln coordination (Ln = lanthanoid),[13] though they are significantly longer than values derived from Ln–C bonds of arene–Ln$^{\text{II}}$ complexes.[13]



II

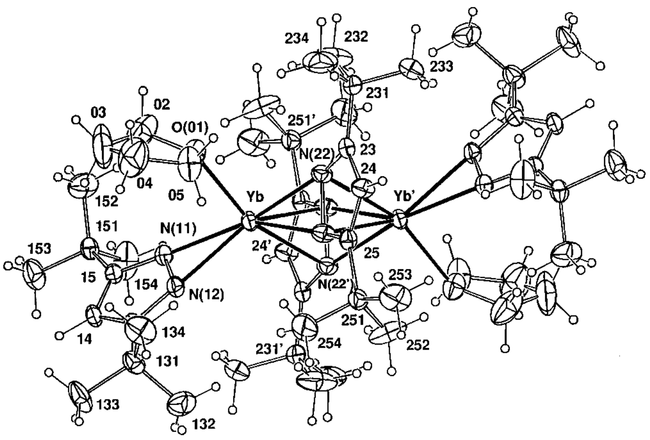


Figure 1. ORTEP plot of [{Yb(tBu$_2$pz)$_2$(thf)}$_2$] showing 20% thermal ellipsoids for the non-hydrogen atoms; the hydrogen atoms were given an arbitrary radius of 0.1 Å. Selected bond lengths [Å] and angles [°]: Yb–N(11) 2.404(6), Yb–N(12) 2.378(5), Yb–N(21) 2.494(8), Yb–N(22) 2.529(7), Yb–O(01) 2.437(9), Yb–N(21′) 2.563(8), Yb–N(22′) 2.641(9), N(11)–N(12) 1.39(1), N(21)–N(22) 1.421(9); N(11)-Yb-N(12) 33.8(3), N(11)-Yb(21) 147.0(2), N(11)-Yb-N(22) 163.4(3), N(11)-Yb-O(01) 85.7(3), N(11)-Yb-N(21′) 113.6(3), N(11)-Yb-N(22′) 105.2(3), N(12)-Yb-N(21) 113.2(2), N(12)-Yb-N(22) 138.2(3), N(12)-Yb-O(01) 87.9(3), N(12)-Yb-N(21′) 133.2(3), N(12)-Yb-N(22′) 108.9(2), N(21)-Yb-N(22) 32.9(2), N(21)-Yb-O(01) 97.7(3), N(21)-Yb-N(21′) 88.7(3), N(21)-Yb-N(22′) 80.7(3), N(22)-Yb-O(01) 78.8(3), N(22)-Yb-N(21′) 81.6(2), N(22)-Yb-N(22′) 91.3(2), O(01)-Yb-N(21′) 131.3(2), O(01)-Yb-N(22′) 162.5(2), N(21′)-Yb-N(22′) 31.6(2).

The ^{1}H NMR spectrum of **1** in C$_7$D$_8$ showed two tBu and two H4 resonances at room temperature, and the ^{13}C{^{1}H} NMR spectrum revealed two resonances for each carbon atom in tBu$_2$pz, consistent with the presence of both η^2- and μ-η^2:η^2-tBu$_2$pz ligands. However, neither the tBu nor the H4

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[**] This work was supported by the Australian Research Council and an Australian Postgraduate Award to E.E.D.

proton resonances were of equal intensity (cf. [{Yb(OR)(μ-OR)}$_2$], R = 2,6-tBu$_2$-4-MeC$_6$H$_2$[14]), and very complex changes occurred on cooling (reversed on warming). Accordingly, some structural modification, possibly involving partial dissociation of THF, occurs on dissolution in C$_7$D$_8$. Nevertheless, the spectra at the two lowest temperatures investigated (213 and 193 K) showed two equal intensity H4 resonances, consistent with a symmetrical dimer. The ^{171}Yb chemical shift at room temperature is within the range[15] for dimeric Yb$^{\text{II}}$ complexes and close to the value of $\delta = 536$[15] for [{Yb(NR$'_2$)(μ-OR)}$_2$](R$'$ = SiMe$_3$).

Crystallization from light petroleum appears to be a vital factor in isolation of **1**, and probably causes loss of THF from a monomeric [Yb(tBu$_2$pz)$_2$(thf)$_n$] species. (Compound **1** in C$_4$D$_8$O shows only single tBu and H4 resonances in the ^{1}H NMR spectrum.) Adoption of μ-η^2:η^2 bonding enables the Yb$^{\text{II}}$ center to attain a higher degree of coordination saturation than is possible with the alternative arrangements of a five-coordinate monomer, [Yb(η^2-tBu$_2$pz)$_2$(thf)], or a five-coordinate μ-η^1:η^1- bridged dimer. Moreover the latter structure would lead to severe steric repulsion between the 3- and 5-tBu substituents of the bridging ligands and the terminal ligands, whereas adverse steric interactions are reduced with the μ-η^2:η^2-tBu$_2$pz ligands. 3,5-Disubstituted (tBu, Ph) pyrazolates are insufficiently bulky to stabilize low-coordinate (≤ 6) Ln$^{\text{III}}$ complexes,[7] and ytterbium is eight-coordinate in **2**.[8]

Experimental Section

The compound described here is extremely air- and moisture-sensitive and consequently all operations were carried out in an inert atmosphere (purified Ar or N$_2$). Yb metal powder (3.46 g, 20.0 mmol), HgPh$_2$ (1.96 g, 5.56 mmol), and tBu$_2$pzH (2.0 g, 11.1 mmol) in THF (30 mL) were heated at 60 °C for 30 h. Filtration of the red solution to remove excess Yb and precipitated Hg followed by evaporation of THF yielded a red solid which on crystallization from light petroleum at -20 °C afforded large red crystals of **1** (2.58 g 77 %). IR (Nujol): $\tilde{\nu} = 3122$ w, 1601 w, 1562 w, 1500 s, 1432 s, 1404 ms, 1358 s, 1315 m, 1296 m, 1248 vs, 1231 s, 1206 s, 1104 vw, 1037 s, 1006 s, 991 s, 917 m, 882 m, 802 s, 782 s, 732 m, 724 s, 664 w, 626 m cm^{-1}; ^{1}H NMR (300 MHz, [C$_7$D$_8$], 0.02 M, 297 K): $\delta = 6.25$ (s) and 6.13 (s) (total integration 4 H, H4 pz), 3.40 (vbr, 8 H; α-THF), 1.44 (s) and 1.33 (s) (total integration 80 H,tBu; β-THF); ^{1}H NMR (300 MHz, [C$_4$D$_8$O], 0.05 M, 297 K): $\delta = 5.89$ (s, 4 H, H4 pz), 1.29 (s, 72 H; tBu); ^{13}C {^{1}H} NMR (50 MHz, [C$_6$D$_6$], 0.02 M, 297 K): $\delta = 30.6$, 31.4 (CH$_3$), 32.1, 32.2 (C(CH$_3$)$_3$), 96.9, 100.2 (C3,C5), 162.5, 164.0 (C4); ^{171}Yb NMR (52.5 MHz, 0.05 M in PhMe): $\delta = 557$ ($\Delta\nu_{1/2} = 44$ Hz) (relative to [(C$_5$Me$_5$)$_2$Yb(thf)$_2$]); Vis/near IR (4.14 × 10^{-3} M in THF; λ_{max} (ε)) = 386 (383), 429sh (283) nm; elemental analysis calcd for C$_{52}$H$_{92}$N$_8$O$_2$Yb$_2$: C 51.73, H 7.68, N 9.28, Yb 28.66; found: C 51.30, H 7.54, N 9.21, Yb 28.28.

Received: March 12, 1998 [Z 11577 IE]
German version: *Angew. Chem.* **1998**, *110*, 2372–2373

Keywords: lanthanides · N ligands · ytterbium

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[10] Crystal structure analysis of **1:** Air-sensitive red crystals, C$_{52}$H$_{92}$N$_8$O$_2$Yb$_2$, $M_r = 1207.44$, triclinic, space group $P\bar{1}$ with $a = 13.588(3)$, $b = 12.169(6)$, $c = 10.034(7)$ Å, $\alpha = 108.43(5)$, $\beta = 100.76(3)$, $\gamma = 104.68(3)°$, $V = 1457(1)$ Å^3, $Z = 1$, $\rho_{\text{calcd}} = 1.376$ g cm^{-3}, $F(000) = 616$, $\mu_{\text{Mo}} = 32.3$ cm^{-1}, A$^*_{\text{min,max}}$1.45, 2.10. A single crystal 0.12 × 0.22 × 0.25 mm was covered in a heavy oil and sealed into a glass capillary under purified argon. From 5121 diffractometer reflections ($2\theta_{\text{max}} = 50°$, $2\theta/\theta$ scan mode; monochromatic Mo$_{\text{K}\alpha}$ radiation; $\lambda = 0.71073$ Å; $T \approx 295$ K; 10233 total reflections merged ($R_{\text{int}} = 0.038$), 3436 "observed" ($I > 3\sigma(I)$)) used after Gaussian absorption correction in the final least squares refinement (anisotropic thermal parameters for non-hydrogen atoms, x, y, z, and U_{iso} constrained for H atoms). R, R_w on $|F|$ were 0.048, 0.049 (statistical weights). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101 244. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[12] C(23) ··· Yb$'$ 3.32(1), C(24) ··· Yb$'$ 3.64 (1), C(25) ··· Yb$'$ 3.22(1), cf. C(23$'$) ··· Yb 3.83(1), C(24$'$) ··· Yb 4.43(1), C(25$'$) ··· Yb 3.77(1) Å

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Lithium Ephedrinate Mediated Aldol Reaction of Arylacetonitriles: Thermodynamic Control of Enantioselectivity**

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A reaction in which enantioselectivity is thermodynamically controlled is termed an "asymmetric transformation".[1] Both homogeneous ("first kind") and crystallization-induced ("second kind") asymmetric transformations are synthetically attractive, since they offer the possibility of converting a racemic mixture into its enantiomers in quantitative yield. The aldol reaction would appear to be a logical choice for the

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[**] This work was supported by the Research Grants Council of Hong Kong (HKUST 588/95P).