Synthesis of the First Lanthanoid(II) Pyrazolate Complex by Redox Transmetallation from Thallium and Mercury Reagents

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Ytterbium metal reacts with thallium(I) 3,5-diphenylpyrazolate, or with diphenylmercury and 3,5-diphenylpyrazole (Ph_2pzH) in tetrahydrofuran or 1,2-dimethoxyethane (DME) giving, after appropriate isolation, the first lanthanoid(II) pyrazolate complex, $[Yb(Ph_2pz)_2(DME)_2]$. The molecular structure reveals eight coordinate ytterbium(II) with two *cisoid* η^2-3,5-diphenylpyrazolate and two chelating 1,2-dimethoxyethane ligands.

Redox transmetallation between lanthanoid metals and metal complexes (eq. 1; $n = 2$ or 3; $m = an/b$) and redox transmetallation/ligand exchange involving mercurials (eq. 2; $n = 2$ or 3) provide simple halide free routes to lanthanoid complexes[1][2][3].

$$a\mathrm{Ln} + b\mathrm{M(L)}_m \rightarrow a\mathrm{Ln(L)}_b + b\mathrm{M}\downarrow \quad (1)$$

$$2\mathrm{Ln} + n\mathrm{HgR}_2 + 2n\mathrm{LH} \rightarrow 2\mathrm{Ln(L)}_n + n\mathrm{Hg}\downarrow + 2n\mathrm{RH} \quad (2)$$

Recent examples of eq. 1 involve mercury[4][5] and tin[6] compounds. Use of thallium(I) reagents is currently restricted to cyclopentadienyls[7][8][9][10] and phenolates[11]. We now report the synthesis of the first lanthanoid(II) pyrazolate, $Yb(Ph_2pz)_2$ (Ph_2pzH = 3,5-diphenylpyrazole), by redox transmetallation between thallium(I) 3,5-diphenylpyrazolate, and ytterbium metal and by redox transmetallation/ligand exchange between Yb, Ph_2pzH and $HgPh_2$, together with the X-ray crystal structure of $[Yb(Ph_2pz)_2(DME)_2]$ (DME = 1,2-dimethoxyethane). This opens the use of thallium-based redox transmetallation as a source of lanthanoid organoamides, and increases the versatility of reaction (2).

Thallium(I) 3,5-diphenylpyrazolate was obtained in high yield by reaction of thallium(I) ethoxide with 3,5-diphenylpyrazole in dichloromethane (eq. 3).

$$\mathrm{TlOEt} + \mathrm{Ph_2pzH} \longrightarrow \mathrm{Tl(Ph_2pz)} + \mathrm{EtOH} \quad (3)$$

Reaction of the thallium complex with ytterbium metal in the presence of mercury metal in tetrahydrofuran (THF) and evaporation and crystallisation from DME or reaction of Yb and $Tl(Ph_2pz)$ in DME gave $[Yb(Ph_2pz)_2(DME)_2]$ in good yield (eq. 4). Satisfactory crystallisation was not achieved from THF.

$$\mathrm{Yb} + 2\mathrm{Tl(Ph_2pz)} \xrightarrow{\mathrm{Hg}} \mathrm{Yb(Ph_2pz)_2} + 2\mathrm{Tl}\downarrow \quad (4)$$

The highly air-sensitive product was characterised by elemental analysis and infrared and ^{1}H-NMR spectra, whilst the visible/near infrared spectrum (no bands at 450−1200 nm) indicated the absence of Yb(III). The structure was established by X-ray crystallography below. Although a range of lanthanoid(III) pyrazolates are known[12], particularly $[Ln(R_2pz)_3(L)_n]$ complexes (R = Me, L = THF, n = 1[12c]; R = Ph or *t*Bu, L = THF, DME, or Ph_3PO, n = 1−3[12d-h]), no lanthanoid(II) pyrazolates have previously been reported. It is of particular interest that redox transmetallation/ligand exchange reactions of an excess of ytterbium metal with $Hg(C_6F_5)_2$ and 3,5-di-*tert*-butylpyrazole gave $[Yb((tBu)_2pz)_3(THF)_2]$ rather than a divalent complex[12d][12f], and analogous reactions with 3,5-diphenylpyrazole in this work gave an unidentifiable black insoluble material. However, with $HgPh_2$ as the reagent instead of the commonly used $Hg(C_6F_5)_2$, a smooth high yield synthesis of $[Yb(Ph_2pz)_2(DME)_2]$ was achieved (eq. 5).

$$\mathrm{Yb} + 2\mathrm{Ph_2pzH} + \mathrm{HgPh_2} \rightarrow \mathrm{Yb(Ph_2pz)_2} + 2\mathrm{PhH} + \mathrm{Hg}\downarrow \quad (5)$$

The successful outcome of eq. 5 compared with the failed preparation with $Hg(C_6F_5)_2$, shows that $HgPh_2$ has excellent prospects in redox transmetallation/ligand exchange (eq. 2), despite lower reactivity towards lanthanoid metals than $Hg(C_6F_5)_2$.

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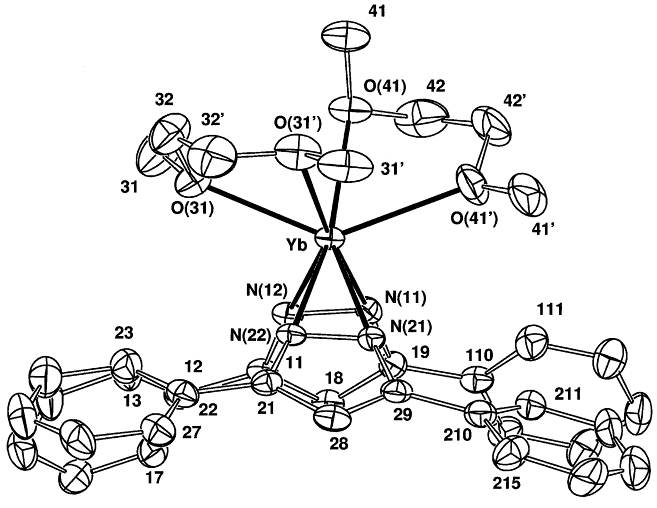
By contrast with eq. 4, treatment of thallium(I) 3,5-diphenylpyrazolate with a large excess of samarium metal gave impure (indicated by the Sm analysis) [Sm(Ph$_2$pz)$_3$(DME)$_2$]. The DME/Ph$_2$pz ratio was established by ^{1}H-NMR spectroscopy and corresponds to that in previously prepared [Ln(Ph$_2$pz)$_3$(DME)$_2$] (Ln = La, Nd, or Er)[12h]. A significant high frequency shift of the Ph$_2$pz resonances from those for [La(Ph$_2$pz)$_3$(DME)$_2$] is consistent with coordination to the paramagnetic ion. The oxidation state was established by the near infrared absorption, which was characteristic of Sm(III)[13], as well as by the typical pale yellow colour of the product solution, whilst the visible region lacked typical Sm(II) absorption near 600cm^{-1}[14]. Thus, even for lanthanoid metals giving accessible divalent compounds, reaction (1) [M(L)$_m$ = Tl(R$_2$pz)] does not necessarily give a lanthanoid(II) complex.

The molecular structure of [Yb(Ph$_2$pz)$_2$(DME)$_2$] is displayed in Figure 1, together with selected bond distances and angles. Two η^2-Ph$_2$pz and two chelating DME ligands are bound to ytterbium, giving approximately dodecahedral YbN$_4$O$_4$ eight coordination. The common ligands are in a *cisoid* relationship to each other, as indicated by a N-N-centroid−Yb−N′-N′-centroid angle of $101._4$° and a O···O-centroid−Yb−O′···O′-centroid angle of $97._9$°. The dihedral angle between the two YbN$_2$ planes is 101.0(2)°. Observation of η^2-pyrazolate coordination for the first lanthanoid(II) pyrazolate is consistent with the predominance of this bonding mode in pyrazolatolanthanoid(III) complexes[12], but where μ-pyrazolate binding, the dominant mode for d-block metals[15], is also known[12a][12b][12c]. The first examples of η^2 coordination for d-block transition metals have recently been reported[15c][16]. With allowance for differences in oxidation state and coordination number[17], the Yb−N distances are comparable with those of lanthanoid(III) pyrazolates[12] and the Yb−O distances are consistent with those of the chelating DME of [Er(Ph$_2$pz)$_3$(η^2-DME)(η^1-DME)][12h]. Thus, subtraction of the ionic radius for eight coordinate Yb^{2+} (1.14 Å)[17] from <Yb-N> gives 1.28 Å comparable (but at the low end) with values, 1.27−1.38 Å[12c-h], for a range of [Ln(η^2-R$_2$pz)$_3$(L)$_n$] (R = Ph or *t*Bu) complexes, whilst a similar subtraction from <Yb-O> gives 1.39 Å, comparable with the 1.42 Å derived from the chelating DME of [Er(Ph$_2$pz)$_3$(η^2-DME)(η^1-DME)][12h] and within the range derived from Ln−O of [Ln(R$_2$pz)$_3$(THF)$_n$] (*n* = 2 or 3) (R = *t*Bu or Ph) complexes[12e][12f].

A wide ranging study of the syntheses and structures of pyrazolatolanthanoid(II) complexes, especially preparation by redox transmetallation reactions from free metals and thallium(I) pyrazolates, is in progress.

Figure 1. ORTEP plot of [Yb(Ph$_2$pz)$_2$(DME)$_2$][a] showing 20% thermal ellipsoids for the non-hydrogen atoms



[a] Selected bond lengths [Å] and angles [°] data with estimated deviations in parentheses: Yb−N(11) 2.426(7), Yb−N(12) 2.414(7), Yb−N(21) 2.424(7), Yb−N(22) 2.430(7), Yb−O(31) 2.502(6), Yb−O(31′) 2.558(7), Yb−O(41) 2.484(6), Yb−O(41′) 2.576(7), N(11)−N(12) 1.362(9), N(21)−N(22) 1.357(9), N(11)−Yb−N(12) 32.7(2), N(11)−Yb−N(21) 95.5(2), N(11)−Yb−N(22) 107.3(2), N(11)−Yb−O(31) 116.7(2), N(11)−Yb−O(31′) 174.7(2), N(11)−Yb−O(41) 91.2(2), N(11)−Yb−O(41′) 87.7(2), N(12)−Yb−N(21) 102.8(2), N(12)−Yb−N(22) 96.4(2), N(12)−Yb−O(31) 86.8(2), N(12)−Yb−O(31′) 150.9(2), N(12)−Yb−O(41) 97.9(2), N(12)−Yb−O(41′) 119.7(2), N(21)−Yb−N(22) 32.5(2), N(21)−Yb−O(31) 122.8(2), N(21)−Yb−O(31′) 87.1(2), N(21)−Yb−O(41) 151.2(2), N(21)−Yb−O(41′) 86.7(2), N(22)−Yb−O(31) 91.0(2), N(22)−Yb−O(31′) 77.3(2), N(22)−Yb−O(41) 161.2(2), N(22)−Yb−O(41′) 116.8(2), O(31)−Yb−O(31′) 65.2(2), O(31)−Yb−O(41) 77.8(2), O(31)−Yb−O(41′) 136.6(2), O(31′)−Yb−O(41′) 84.4(2), O(31′)−Yb−O(41′) 87.9(2), O(41)−Yb−O(41′) 65.6(2).

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Experimental Section

The compounds described here are extremely air- and moisture-sensitive and consequently all operations were carried out in an inert atmosphere (purified argon or nitrogen).

(3,5-Diphenylpyrazolato)thallium(I): Thallium(I) ethoxide (3.55 ml, 12.5g, 50.0 mmol) was added to a CH$_2$Cl$_2$ (200 ml) solution of 3,5-diphenylpyrazole (11.1g, 50.0 mmol). Addition of thallium(I) ethoxide caused undissolved 3,5-diphenylpyrazole to dissolve. Removal of the CH$_2$Cl$_2$ under vacuum yielded 19.4g (92%) of a white crystalline solid, m.p. 195°C (sealed capillary/argon). − IR: $\tilde{\nu}$ = 1600 cm^{-1} m, 1259 m, 1070 m, 1058 s, 1025 m, 972 m, 914 w, 799 m, 758 vs, 693 vs. − ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 7.96 (s, 1 H, 4-H pz),7.12−7.21 (m, 2 H, *p*-H), 7.21−7.27 (m, 4 H, *m*-H), 7.68 (t, 4 H, *o*-H), − MS (70 eV, EI); *m/z* (%): 424 (50) [(^{205}Tl)M$^+$], 220 (80) [C$_{15}$H$_{11}$N$_2$$^+$], 205 (100) [^{205}Tl$^+$]. − C$_{15}H_{11}N_2$Tl (423.6): calcd. C 42.53, H 2.62, N 6.61; found C 42.35, H 2.53, N 6.49.

Bis(1,2-dimethoxyethane)bis(η^2-3,5-diphenylpyrazolato)ytterbium(II) − Method A: A mixture of ytterbium powder (1.73g, 10.0 mmol), mercury metal (ca. 0.10 ml) and (3,5-diphenylpyrazolato)thallium(I) (2.12g, 5.0 mmol) in THF (30 ml) or DME (50 ml) was subjected to ultrasonication for 24 h. The resulting deep red solution with grey suspended solids was allowed to stand for several hours until the suspension settled out. The reaction mixture was then filtered using a filter cannula. In the case where THF was used, the filtrate was evaporated to dryness under vacuum yielding a red solid which was dissolved in DME (40 ml) and allowed to stand for several days at room temp. during which time 1.3 g (66%) of large red crystals formed. In the case where DME was used, evaporation of some DME (ca. 5 ml) and standing for several days afforded large red crystals of similar appearance in similar yield, m.p. >350°C (sealed capillary/argon). − IR: $\tilde{\nu}$ = 1602 cm^{-1} m, 1156 w, 1121 w, 1099 m, 1071 s, 1025 m, 968 s, 914 w, 863 m, 859 m, 801 w, 757 vs, 722 m, 698 s, 685 s. − Visible/near IR (THF): λ_{max} (ε) = 410 nm (774). − ^1H NMR (300 MHz, $[D_8]THF$): δ = 3.24 (s, 12 H, CH_3O DME), 3.41 (s, 8 H, CH_2 DME), 7.07 (t, 4 H, *p*-H), 7.10 (s, 2 H, 4-H), 7.24 (t, 8 H, *m*-H), 7.92 (d, 8 H, *o*-H). − ^{171}Yb NMR (52.5 MHz, 0.04 M in DME): δ = 480 ($\Delta\nu_{1/2}$ 20 Hz) [relative to $Yb(C_5Me_5)_2(THF)_2$] − $C_{38}H_{42}N_4O_4Yb$ (791.8): calcd.: C 57.64, H 5.35, N 7.08, Yb 21.85; found C 56.88, H 5.24, N 7.59, Yb 22.43.

Method B: A mixture of ytterbium powder (1.73 g, 10.0 mmol), $HgPh_2$ (0.80 g, 2.3 mmol) and 3,5-diphenylpyrazole (1.00 g, 4.5 mmol) in THF (40 ml) was stirred and heated at 60°C for 2 d. The resulting red solution with grey suspended solids was filtered and the filtrate was evaporated to dryness. Recrystallisation of the resulting red solid from DME (20 ml) at −20°C gave 1.37 g (76%) of $[Yb(Ph_2pz)_2(DME)_2]$ as deep red crystals. − IR: Identical with that of the product from A. − $C_{38}H_{42}N_4O_4Yb$ (791.8): calcd. Yb 21.85; found Yb 21.48.

Reaction Between (3,5-Diphenylpyrazolato)thallium(I) and Samarium Metal: A mixture of samarium metal (1.50 g, 10.0 mmol), mercury metal (ca. 0.40 ml) and (3,5-diphenylpyrazolato)thallium(I) (0.85 g, 2.0 mmol) in THF (30 ml) was subjected to ultrasonication for 3 d. The resulting pale yellow solution with grey suspended solids was allowed to stand for several hours. Filtration and evaporation as above yielded a white solid which was recrystallised from a DME/light petroleum mixture giving $[Sm(Ph_2pz)_3(DME)_2]$ 0.42 g, (40%) as a white powder. − IR: $\tilde{\nu}$ = 1604 cm^{-1} m, 1513 w, 1422 w, 1282 w, 970 s, 906 w, 864 s, 800 w, 759 vs, 696 s, 684 s. − Visible/near IR (THF): λ_{max} (ε) = 369 nm (1.5), 402 (2.0), 977 (1.0), 1074 (2.0), 1328 (3.5), 1368 (1.0) . − ^1H NMR (300 MHz, $[D_8]THF$): δ = 3.27 (s, 12 H, CH_3O), 3.39 (s, 8 H, CH_2), 7.30 (t, 6 H, *p*-H), 7.54 (t, 12 H, *m*-H), 7.94 (s, 3 H, 4-H), 9.28 (d, 12 H, *o*-H). − $C_{53}H_{53}N_6O_4Sm$ (988.5): calcd. Sm 15.22; found Sm 16.64.

X-ray Crystallography of $[Yb(Ph_2pz)_2(DME)_2]$: Single crystals were grown from a saturated DME solution at room temperature over several days. $C_{38}H_{42}N_4O_4Yb$ (791.82), monoclinic, space group $P2_1/a$ (no. 14). a = 7.882(4), b = 18.959(3), c = 24.080(14) Å, β = 91.03(2)°, V = 3598(3) $Å^3$, Z = 4, D_c = 1.462 g cm^{-3}, μ_{Mo} = 26.4 cm^{-1}, $F(000)$ = 1600, $A^*_{min,max}$ 1.64, 2.17. For X-ray crystallography single crystals 0.20 × 0.38 × 0.33 mm were covered in a heavy oil and sealed into glass capillaries under purified argon. From 6331 diffractometer reflections ($2\theta_{max}$ 50°, 2θ/θ scan mode; monochromatic Mo K_α radiation; λ = 0.7107_3 Å; $T \approx 295$ K; 18381 total reflections merged (R_{int} = 0.048), 50% crystal decomposition compensated by scaling), 3670 "observed" [$I > 3\sigma(I)$] used after absorption correction in the final least squares refinement [anisotropic thermal parameters for non-hydrogen atoms, $(x, y, z, U_{iso})_H$ constrained]. R, Rw on $|F|$ were 0.044, 0.044 (statistical weights). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101118. Copies of the data can be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (int. Code) +44(1223)336-033, E-mail: deposit@chemcrys.cam.ac.uk, World Wide Web: http://www.ccdc.cam.ac.uk].

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