Organoamido- and Aryloxo-lanthanoids, 14[◇]
Organometallic Compounds of the Lanthanoids, 106[◇◇]

# Synthesis and Characterisation of Complexes of Lanthanoid Pyrazolates with 1,2-Dimethoxyethane and the X-Ray Structures of (1,2-Dimethoxyethane-$O^1$:$O^2$)(1,2-dimethoxyethane-$O^1$)tris(3,5-diphenylpyrazolato)erbium(III) and *catena*-Poly[tris(3,5-di-*tert*-butylpyrazolato)-μ-(1,2-dimethoxyethane-$O^1$:$O^2$)-neodymium(III)]

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The complexes $[Ln(Ph_2pz)_3(DME)_2]$ and $[Ln(tBu_2pz)_3(DME)]$ (Ln = La, Nd, Er; $Ph_2pzH$ = 3,5-diphenylpyrazole; $tBu_2pzH$ = 3,5-di-*tert*-butylpyrazole; DME = 1,2-dimethoxyethane) have been prepared by reaction of the lanthanoid metal with bis(pentafluorophenyl)mercury and the pyrazole in DME. The molecular structures of $[Er(Ph_2pz)_3(DME)_2]$ (**3**) and $[Nd(tBu_2pz)_3(DME)]_\infty$ (**5**) have been determined by X-ray diffraction. Complex **3** has nine-coordinate Er with three chelating $Ph_2pz$ ligands and one chelating and one $\eta^1$-bound DME. There is a trigonal prismatic arrangement of the oxygen donors and the centres of the N–N bonds. **5** was found to be a linear polymer with transoid DME ligands bridging $Nd(tBu_2pz)_3$ units in a novel manner. The centres of the N–N bonds (which are essentially coplanar with Nd), and the oxygen donor atoms adopt an arrangement intermediate between trigonal-bipyramidal and square-pyramidal [O–Nd–O 153.5(2)°].

Pyrazolate ($pz^-$) and substituted pyrazolate ions mainly coordinate as bridging ligands, especially with d-block metals[2,3], but unidentate bonding is also known where the metal has lower coordination numbers[4]. Chelating ($\eta^2$) bonding has been observed only with f-block metals[5–11], often in conjunction with cyclopentadienyl ligands[5] or bridging pyrazolate ligands[1,6]. By using the bulky 3,5-diphenylpyrazolate ($Ph_2pz^-$) and 3,5-di-*tert*-butylpyrazolate ($tBu_2pz^-$) ions, we have prepared the first tris($\eta^2$-pyrazolato)lanthanoid(III) complexes, viz. $[Ln(\eta^2\text{-}Ph_2pz)_3(THF)_3] \cdot (THF)$[9] (THF = tetrahydrofuran), $[Ln(\eta^2\text{-}Ph_2pz)_3(Ph_3PO)_2]$[9], and $[Ln(\eta^2\text{-}tBu_2pz)_3(THF)_2]$[10,11]. For the complexes with two neutral ligands, these either have a *trans* ($[Ln(\eta^2\text{-}Ph_2pz)_3(Ph_3PO)_2]$) or transoid [O–Ln–O 140.1(4)–145.2(6)°] ($[Ln(\eta^2\text{-}tBu_2pz)_3(THF)_2]$) arrangement. As an approach to *cis*-$[Ln(\eta^2\text{-}R_2pz)_3L_2]$ complexes, we have investigated 1,2-dimethoxyethane (DME) as a ligand, since it usually chelates to lanthanoid metals (e.g. in organometallics, organoamides, and aryl oxides[12–22]), although there is one example of a polymeric complex with bridging DME[23]. We now report on the syntheses of $[Ln(Ph_2pz)_3(DME)_2]$ and $[Ln(tBu_2pz)_3(DME)]$ complexes and the X-ray crystal structure of a representative of each class, in which DME shows unexpected coordination behaviour.

## Results and Discussion

### Synthesis

The complexes $[Ln(Ph_2pz)_3(DME)_2]$ with Ln = La (**1**), Nd (**2**), and Er (**3**) as well as $[Ln(tBu_2pz)_3(DME)]$ with Ln = La (**4**), Nd (**5**), and Er (**6**) were prepared by reaction of lanthanoid metal with bis(pentafluorophenyl)mercury and the pyrazole in 1,2-dimethoxyethane (eq. 1).

Similar reactions in tetrahydrofuran give $[Ln(Ph_2pz)_3(THF)_3] \cdot (THF)$ (Ln = La, Nd)[9] and $[Ln(tBu_2pz)_3(THF)_2]$ (Ln = Y, La, Pr, Nd, Sm, Gd, Dy, Er,

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[◇] Part 13: Ref.[1]. – [◇◇] Part 105: Ref.[1].

$$2\ Ln + 3\ Hg(C_6F_5)_2 + 6\ R_2pzH \xrightarrow{DME} 2\ [Ln(R_2pz)_3(DME)_n] + 6\ C_6F_5H + 3\ Hg\downarrow \qquad (1)$$

**1 – 6**

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| R | Ph | Ph | Ph | *t*Bu | *t*Bu | *t*Bu |
| Ln | La | Nd | Er | La | Nd | Er |

Yb, Lu)[10,11]. It has been shown that $Ph_2pzH$ does not react with $Hg(C_6F_5)_2$ in the absence of lanthanoid metal[9], and so it is considered that the reactions occur via oxidation of the lanthanoid metal by $Hg(C_6F_5)_2$ followed by protolytic ligand exchange with $R_2pzH$. It is unclear whether this is a stepwise [e.g. via $Ln(R_2pz)_2C_6F_5$] or concerted reaction [e.g. via $Ln(C_6F_5)_3$]. Attempts to prepare $Ln(C_6F_5)_3$ (Ln = Nd or Er) gave only decomposition products[24], but this does not rule out transitory formation of $Ln(C_6F_5)_3$ and rapid trapping by protolytic ligand exchange to give $Ln(R_2pz)_3$. The high $pK_a$ value of $C_6F_5H$ (25.6 in THF[25]) encourages the ligand exchange with the more acidic pyrazole ($pK_a$ values of $t$$Bu_2pzH$ and $Ph_2pzH$ are 15.13 and 13.03, respectively, in $H_2O$[26]).

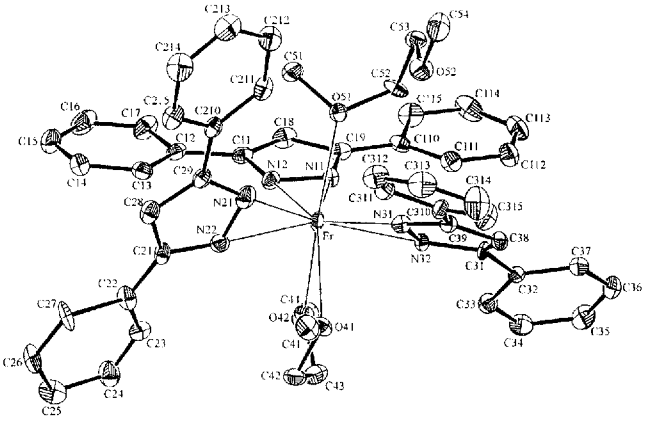
## Characterisation and Properties

The composition of $[Ln(Ph_2pz)_3(DME)_2]$ complexes was established by C, H, Ln analyses. Only Ln analyses were obtained for $[Ln(tBu_2pz)_3(DME)]$ because C, H analyses fail to distinguish satisfactorily between compositions $[Ln(tBu_2pz)_3(DME)_n]$ ($n$ = 0, 1, or 2). The presence of $Ln(tBu_2pz)_3$ units in the 3,5-di-*tert*-butylpyrazolate complexes was supported by observation of $[Ln(tBu_2pz)_3]^+$ (Ln = La or Nd) or $[Er(tBu_2pz)_2(tBu_2pzH)]^+$ ions in their mass spectra. No metal-containing ions are observed in mass spectra of $Ph_2pz$ complexes[27], and this was confirmed in the present study for **2**. No ν(NH) absorption was observed consistent with pyrazolate complexes, though this is more significant for $[Ln(tBu_2pz)_3(DME)]$ than $[Ln(Ph_2pz)_3(DME)_2]$, since ν(NH) is sharp for $t$$Bu_2pzH$ but broad for $Ph_2pzH$. All complexes have strong absorption at 1065–1050 and 900–870 $cm^{-1}$ attributable to ν(C–O) of coordinated DME shifted from free ligand values at 1106 and 858 $cm^{-1}$[28]. There are close similarities between the infrared spectra of all $[Ln(Ph_2pz)_3(DME)_2]$ (Ln = La, Nd, or Er) complexes (see intense bands in Experimental Section; more complete data are available[27]), suggesting all three complexes have similar structures. Isostructural $[Ln(Ph_2pz)_3(OPPh_3)_2]$ (Ln = Er or Nd) also show very similar spectra[9] as do isostructural $[Ln(tBu_2pz)_3(THF)_2]$ (Ln = Nd or Er)[10,11]. With $[Ln(tBu_2pz)_3(DME)]$, the spectra with Ln = La or Nd are similar, but that for Ln = Er differs notably in ν(C–O) frequencies [e.g. 898 vs (La), 900 vs (Nd), 870 s (Er) $cm^{-1}$], implying some structural modification. In the $^1H$-NMR spectra of $[La(Ph_2pz)_3(DME)_2]$ and $[Ln(tBu_2pz)_3(DME)]$ (Ln = La or Nd), integrations for DME protons were lower (75–85%) than expected for the analytical composition. For the neodymium complex, this could be due to difficulties in accurately integrating the paramagnetic broadened DME resonances, but $[Nd(Ph_2pz)_3(DME)_2]$ gave satisfactory integrations. In the case of the La complexes, there was possibly some DME loss between La analyses, which were performed immediately on isolation, and the subsequent NMR examination.

## X-Ray Crystallography

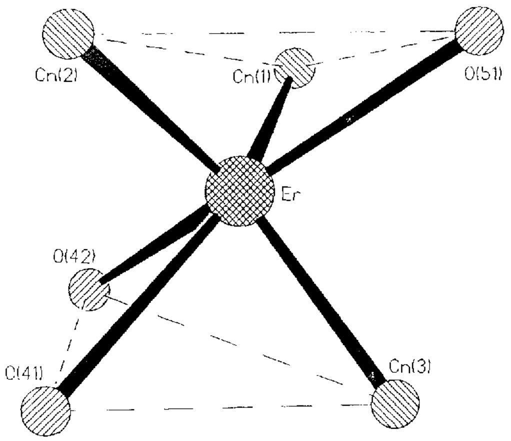
In the solid state **3** crystallises in discrete monomer units (Figure 1). Erbium is formally nine-coordinated with three chelating $Ph_2pz$, one chelating DME and one $\eta^1$-bound DME ligand. To our knowledge this is the first example of $\eta^1$-binding of DME to any metal. Previously, DME was known to have only two coordination modes: chelating (or $\eta^2$) and bridging ($\mu$-$O^1$:$O^2$), which is quite rare and occurs mainly for alkali metals (e.g. Li[29] and K[30]), although it has been observed in two neodymium complexes, $[Nd_2(OCH{-}iPr_2)_6(\mu\text{-}DME)]_\infty$[23] and **5**. Apart from these examples, all of the reported crystal structures of rare earth DME complexes exhibit chelating DME[12–22,31–33]. Very few of them show more than one DME bound to the metal. The exceptions either have very small bite anionic ligands, e.g. $[Ce(NO_3)_3(DME)_2]$[16], $[YCl_3(DME)_2]$[31], $[Yb(\mu\text{-}Cl)(DME)_3]_2[Sn(SnPh_3)_3]_2$[32] or a lower coordination number, e.g. $[Yb(DME)_2(THF)_2][Hg(GeMe_3)_3]_2$[33] and $[Yb(SC_6H_2{-}2,4,6\text{-}tBu_3)_2(DME)_2]$[22].

Figure 1. Molecular structure of $[Er(Ph_2pz)_3(\eta^2\text{-}DME)(\eta^1\text{-}DME)]$ (**3**). – Selected bond lengths [Å] and angles [°]: Er–N(11) 2.421(6), Er–N(12) 2.403(7), Er–N(21) 2.24(2), Er–N(22) 2.319(5), Er–N(31) 2.302(6), Er–N(32) 2.353(9), Er–O(41) 2.504(5), Er–O(42) 2.506(14), Er–O(51), 2.432(7); O(41)–Er–O(42) 64.4(4), O(41)–Er–O(51) 144.4(2), O(42)–Er–O(51) 149.1(5), Cn(1)–Er–Cn(2) 108.0(4), Cn(1)–Er–Cn(3) 119.5(2), Cn(2)–Er–Cn(3) 130.3(4), O(41)–Er–Cn(1) 139.3(2), O(41)–Er–Cn(2) 80.7(3), O(41)–Er–Cn(3) 73.0(2), O(42)–Er–Cn(1) 74.9(4), O(42)–Er–Cn(2) 103.0(6), O(42)–Er–Cn(3) 102.5(4), O(51)–Er–Cn(1) 75.8(2), O(51)–Er–Cn(2) 95.0(4), O(51)–Er–Cn(3) 83.8(2)



If the centres [Cn(1–3)] of the pyrazolate N–N bonds are considered along with the coordinated DME oxygen atoms, their arrangement around erbium can best be described as trigonal-prismatic (Figure 2) (calculation basis[34]). Er is within 0.19(2) Å of being coplanar with Cn(1–3) and Σ(Cn–Er–Cn) is 357.8°. The three coordinated oxygen atoms are also coplanar with Er [metal deviation is 0.18(2) Å] and this plane lies at 87.2(4)° to the Er, Cn(1−3) plane. This arrangement is similar to that in [$Nd(Ph_2pz)_3(THF)_3$] · (THF)[9].

Figure 2. The trigonal prismatic arrangement of centres (Cn) of the N−N bonds of $Ph_2pz$ and oxygen donor atoms in the structure of [$Er(Ph_2pz)_3(\eta^1$-DME)($\eta^2$-DME)] (3)



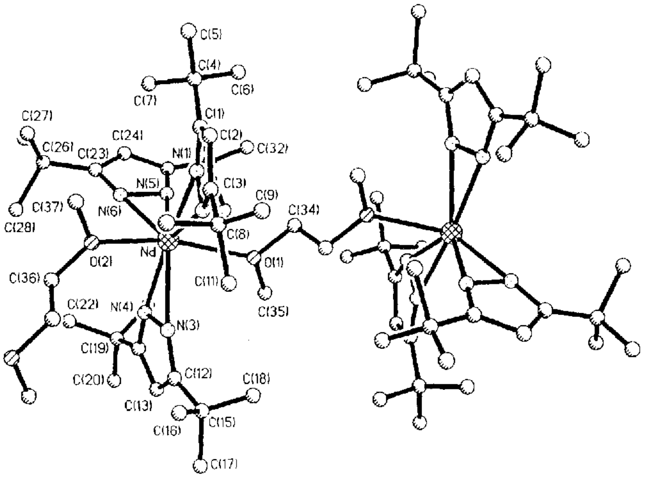
Alternatively, if the midpoint between the two oxygen atoms of the chelating DME [Cn(4)] is considered, then the arrangement is considered to be trigonal-bipyramidal with O(51) and Cn(4) as the apices and Cn(1−3) in the equatorial positions. The Cn(4)−Er−O(51) angle is 171.2(5)°.

All three $Ph_2pz$ ligands are symmetrically chelating and Er−N distances lie in the range 2.24(2)−2.421(6) Å with an average of 2.34 Å. Subtracting the ionic radius of nine-coordinate $Er^{3+}$[35] from the average Er−N distance gives a value of 1.28 Å, which is similar to that (1.30 Å) for [$Nd(Ph_2pz)_3(THF)_3$]·(THF)[9]. The average N−Er−N angle between the pair of N atoms in a $Ph_2pz$ ligand is 34.1°, which is typical for chelated pyrazolates[9−11,27].

The $\eta^2$-DME ligand is chelated symmetrically. The distance between Er and the coordinated oxygen atom of the novel $\eta^1$-DME ligand [Er−O(51)] is 2.432(7) Å, which is shorter than the Er−O distances (average 2.48 Å) for the chelating DME. Subtraction of the ionic radius of nine-coordinated $Er^{3+}$[35] from ⟨Er−O($\eta^2$-DME)⟩ gives a value of 1.42 Å. This lies between the subtraction value (1.34 ± 0.05 Å)[12a] derived from Ln−O(THF) in organolanthanoid−THF complexes and the corresponding range (1.49−1.59 Å) for rare earth complexes with bulky aryloxide ligands[36]. The chelation angle for the $\eta^2$-DME is 64.4(4)° which is similar to values reported for [$Cp_2Yb(DME)$] [67.2(9)°[12a], 69.3(4)°[12b]], [$Ce(NO_3)_3(DME)_2$] [63.1(1)°, 62.1(6)°[16]], [$YCl_3(DME)_2$] [66.8(1)°, 67.5(1)°[31]], and [$Yb(SC_6H_2$−2,4,6-$t$$Bu_3)_2(DME)_2$] [65.8(8)°[22]].

The X-ray structure of [$Nd(tBu_2pz)_3(\mu$-DME)$]_\infty$ (5) has been determined and was found to be an infinite polymer in which successive $Nd(tBu_2pz)_3$ units are bridged by DME in an *anti* configuration (Figures 3 and 4). Each neodymium atom is eight-coordinate. Although the arrangement of oxygen atoms and centroids (Cn) of the pyrazolate N−N bonds around each neodymium atom is closest to a square-based pyramid (see ref.[34]), the arrangement is best described as intermediate between a square-based pyramid and trigonal bipyramid. Cn(1−3) and Nd are coplanar [Nd deviates from the Cn(1−3) plane by 0.0004 Å] and [ΣCn−Nd−Cn = 360°]. The Cn−Ln−Cn angles show a similar variation to those in [$Ln(tBu_2pz)_3(THF)_2$] (Ln = Nd or Er)[10,11] (Table 1). Thus it appears that the structure of the $Ln(tBu_2pz)_3$ unit remains the same independent of the neutral ligand (THF or DME), suggesting that the overall stereochemistry is forced by the steric effects of the $t$$Bu_2pz$ ligands. The preference for *anti*-bridging DME rather than chelation results from the preferred geometry of $Nd(tBu_2pz)_3$. The arrangement of the two smaller Cn−Ln−Cn angles and one larger angle can be explained by the fact that the DME oxygens are located within the larger angle. In the [$Ln(tBu_2pz)_3(THF)_2$] structures, the THF ligands are located between the pyrazolates separated by the largest Cn−Ln−Cn angle. The O(1)−Nd−O(2) angle is 153.5° compared with 145.2 and 140.1° for [$Ln(tBu_2pz)_3(THF)_2$] (Ln = Nd and Er, respectively)[10,11]. In the present structure *monomeric* $Nd(tBu_2pz)_3$ units are bridged by DME whereas in the only other reported, structurally characterized lanthanoid complex with bridging DME ([$Nd_2(OCH-iPr_2)_6(\mu$-DME)$]_\infty$[23]), dimeric $Nd_2(OCH-iPr_2)_6$ units are bridged by DME in an infinite linear polymer (Figure 5). The Nd−O(DME) bonds in this structure appear to be parallel and so also differ from the present structure, lending support to the idea that the coordination of the solvent is dictated by the geometry of $Nd(tBu_2pz)_3$.

Figure 3. Molecular structure of [$Nd(tBu_2pz)_3(\mu$-DME)$]_\infty$ (5). − Selected bond lengths [Å] and angles [°]: Nd−N(1) 2.401(7), Nd−N(2) 2.499(7), Nd−N(3) 2.476(6), Nd−N(4) 2.414(7), Nd−N(5) 2.390(5), Nd−N(6) 2.419(5), Nd−O(1) 2.552(5), Nd−O(2) 2.528(6), Nd···Nd 7.82, 7.89; O(1)−Nd−O(2) 153.5(2), Cn(1)−Nd−Cn(2) 139.3(2), Cn(1)−Nd−Cn(3) 110.9(2), Cn(2)−Nd−Cn(3) 109.9(2), O(1)−Nd−Cn(1) 86.5(2), O(1)−Nd−Cn(2) 83.9(2), O(1)−Nd−Cn(3) 103.7(2), O(2)−Nd−Cn(1) 81.4(2), O(2)−Nd−Cn(2) 90.0(2), O(2)−Nd−Cn(3) 102.6(2)



Subtraction of the ionic radius[35] of eight-coordinate $Nd^{3+}$ from the average Nd−N distance gives a value of 1.32 Å which is similar to those found for eight-coordinate [$Er(\eta^2$-$Ph_2pz)_3(OPPh_3)_2$] · DME (1.34)[9] and [$Ln(tBu_2pz)_3(THF)_2$] (1.33 for Ln = Nd or Er)[10,11] and is close to that (1.30) for nine-coordinate [$Nd(\eta^2$-$Ph_2pz)_3(THF)_3$] ·

Figure 4. A simplified representation of the linear polymeric structure of **5**

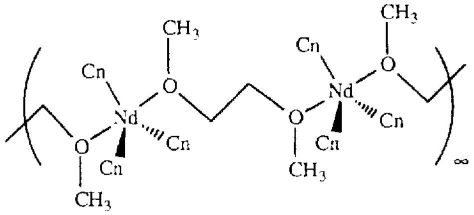
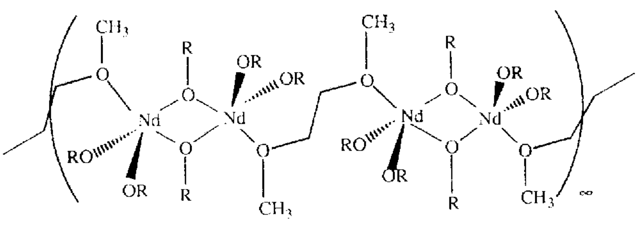


Table 1. Comparison of the arrangement of the $Ln(tBu_2pz)_3$ unit in three complexes

| | $Nd(tBu_2pz)_3(THF)_2$ | $Er(tBu_2pz)_3(THF)_2$ | $Nd(tBu_2pz)_3(DME)$ |
|---|---|---|---|
| Cn-Ln-Cn [°] | 140.1 | 140.3 | 139.3 |
| | 110.3 | 110.6 | 110.9 |
| | 109.6 | 109.2 | 109.9 |

Figure 5. A simplified representation of the linear polymeric structure of $[Nd_2(OCH{-}iPr_2)_6(\mu\text{-}DME)]_\infty$



(THF)[9]. The N−N bond lengths and N−Nd−N angles are in the same range as found previously[9] for $\eta^2$-pyrazolate ligands. Subtraction of the ionic radius[35] of eight-coordinate $Nd^{3+}$ from the average Nd−O distance gives 1.43 Å. This value is greater than those found for $[Ln(tBu_2pz)_3(THF)_2]$ (1.35 Å for Ln = Nd or Er)[10,11] and $[Cp_2Yb(DME)]$ (1.33 Å where DME is chelating)[12b] and reflects the difference between a bridging and a chelating ligand, rather than greater steric hindrance in **5** than in $[Ln(tBu_2pz)_3(THF)_2]$, since Ln−N distances are comparable. Approximate ionic radii subtractions from bridging Nd−O(DME) of $[Nd_2(OCH{-}iPr_2)_6(\mu\text{-}DME)]_\infty$ and from Nd−O(THF) of THF complexes of bulky lanthanoid aryloxides[36,37] show the value for the former to be significantly larger (ca. 0.12 Å).

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## Experimental

Microanalyses: Campbell Microanalytical Laboratory, the University of Otago, New Zealand. Metal analyses were performed by an adapted method described recently[9]. Spectroscopic methods, nitrogen, argon and solvent purification, and handling methods for highly air- and moisture-sensitive lanthanoid complexes were as described previously[37–42]. Petroleum spirit used was b.p. 60−70 °C. Lanthanoid metal powders were from Research Chemicals or Rhône-Poulenc and bis(pentafluorophenyl)mercury was prepared by the reported method[43]. 3,5-Diphenylpyrazole (Lancaster) was used without further purification and 3,5-di-*tert*-butylpyrazole was prepared by reaction of 2,2,6,6-tetramethyl-3,5-heptanedione (Aldrich or Lancaster) with hydrazine hydrate[44] and either sublimed or recrystallised from petroleum spirit before use. − IR: Nujol and Fluorolube mulls for the region 4000−650 $cm^{-1}$ with only medium or greater intensity bands given. − $^1H$ NMR: 200 MHz, 25 °C, referenced either to the solvent or to external chloroform. − Visible-near IR: 1200−300 nm. − Molar absorption coefficients ($\varepsilon_{max}$) are quoted in $dm^3\ mol^{-1}\ cm^{-1}$. − MS: Only metal-containing structurally significant ions are listed. The base peak for all spectra was *m/z* 165 $[tBu_2pzH^+ - CH_3]$. In cases where the metal has more than one isotope, the *m/z* is the most intense peak of a cluster with the appropriate pattern.

*Bis(1,2-dimethoxyethane)tris(3,5-diphenylpyrazolato)lanthanum(III)* (**1**): Lanthanum powder (1.00 g, 7.2 mmol), bis(pentafluorophenyl)mercury (0.70 g, 1.3 mmol), and 3,5-diphenylpyrazole (0.57 g, 2.6 mmol) were stirred in DME (35 ml) for 4 d at room temp. After filtration through a diatomaceous earth pad, the filtrate was concentrated (to 2 ml) and petroleum spirit (10 ml) was added, causing precipitation of a white solid. This was collected on a sinter and dried under vacuum for 5 h to give 0.65 g (77%) of a white powder. − $^1H$ NMR ($[D_8]THF$): δ = 7.96 (d, *J* = 6.8 Hz, 12 H; *o*-H), 7.34 (s, 3 H; CH), 7.03−7.20 (m, 18 H; *m,p*-H), 3.43 (s, 7 H; $CH_2$), 3.27 (s, 10 H, $CH_3$). − IR: $\tilde{\nu}$ = 1603 $cm^{-1}$ m, 1465 m, 1400 m, 1124 m, 1072 m, 1056 vs, 1026 m, 970 s, 861 ms, 760 vs, 696 s, 685 s. − $C_{53}H_{53}LaN_6O_4$ (977.0): calcd. C 65.16, H 5.47, La 14.22; found C 64.35, H 5.12, La 14.71.

*Bis(1,2-dimethoxyethane)tris(3,5-diphenylpyrazolato)neodymium(III)* (**2**): Analogously to **1**, Nd (1.00 g, 6.9 mmol), $Hg(C_6F_5)_2$ (1.23 g, 2.3 mmol), and $Ph_2pzH$ (1.00 g, 4.5 mmol) yielded within 3 d 0.25 g (17%) of a pale lavender powder. − $^1H$ NMR ($[D_8]THF$): δ = 21.78 (br s, 3 H; CH), 15.37 (br s, 12 H; *o*-H), 9.85 (br s, 12 H; *m*-H), 9.59 (br s, 6 H; *p*-H), 4.42 (br s, 20 H; DME); ($[D_8]$Toluene): δ = 20.43 (br s, 3 H; CH), 14.17 (br s, 12 H; *o*-H), 8.3−8.6 (m, 18 H; *m-,p*-H), −7.29 (br s, 12 H; $CH_3$), −16.66 (br s, 8 H; $CH_2$). − IR: $\tilde{\nu}$ = 1604 $cm^{-1}$ m, 1466 s, 1058 s, 970 m, 866 m, 756 s, 703 m, 694 m, 683 m. − Vis/near IR (DME): $\lambda_{max}$ (ε) = 796 nm br (0.62), 727 br (4.5), 581 (33), 450−550 v v br (10), 320−450 v v br (15). − MS (70 eV, EI): showed $Ph_2pzH$ and DME only. − $C_{53}H_{53}N_6NdO_4$ (982.3): calcd. C 64.81, H 5.44, Nd 14.68; found C 63.37, H 5.99, Nd 14.41.

*(1,2-Dimethoxyethane-$O^1$:$O^2$)(1,2-dimethoxyethane-$O^1$)tris(3,5-diphenylpyrazolato)erbium(III)* (**3**): Analogously to **1**, Er (0.81 g, 4.8 mmol), $Hg(C_6F_5)_2$ (0.70 g, 1.3 mmol), and $Ph_2pzH$ (0.57 g, 2.6 mmol) yielded within 3 d 0.25 g (28%) of a pink powder. − IR: $\tilde{\nu}$ = 1602 $cm^{-1}$ m, 1466 vs, 1057 s, 1026 m, 972 s, 872 m, 757 vs, 695 s, 679 m. − Vis/near IR (THF): $\lambda_{max}$ (ε) = 964 nm br (1.6), 740−860 v v br (1.9), 653 (2.0), 520 (32), 488 (9.3), 405 br sh (17), 378 (59), 365 sh (27), 360 sh (25), 357 sh (26); (DME): 973 br (3.4), 745−900 v v br (5.3), 506 (34), 504 (35), 488 br sh (24), 377 (99), 365 sh (69). − $C_{53}H_{53}ErN_6O_4$ (1005.3): calcd. C 63.32, H 5.31, Er 16.64; found C 62.66, H 5.23, Er 16.72.

*Tris(3,5-di-tert-butylpyrazolato)(1,2-dimethoxyethane)lanthanum(III)* (**4**): Lanthanum powder (0.80 g, 5.8 mmol), bis(pentafluorophenyl)mercury (1.48 g, 2.8 mmol), and 3,5-di-*tert*-butylpyrazole (1.00 g, 5.6 mmol) were stirred in DME (30 ml) for 4 d at room temp. After filtration through a diatomaceous earth pad, the filtrate was concentrated to an oily solution (2 ml), and petroleum spirit (10 ml) was added, causing the solution to cloud slightly. Standing in an iced water bath caused precipitation of only a small amount of solid, so the solution was taken to dryness and the residue stirred with petroleum spirit (8 ml), filtered and dried in vacuo for 5 h. 0.77 g (54%) of a white powder was obtained. – $^1$H NMR ([D$_8$]THF): δ = 6.11 (s, 3H; CH), 3.44 (s, 3H; $CH_2$), 3.28 (s, 4.5H; $CH_3O$), 1.23 (s, 54H; $CH_3C$). – IR: $\tilde{\nu}$ = 2961 cm$^{-1}$ vs, 2926 s, 2899 s, 2863 s, 1519 m, 1501 s, 1458 s, 1428 m, 1409 m, 1359 s, 1307 m, 1286 m, 1250 vs, 1225 vs, 1207 m, 1189 m, 1055 vs, 1016 s, 991 vs, 898 vs, 790 vs, 725 m. – MS (70 eV, EI), *m*/*z* (%): 676 (0.5) [La(*t*Bu$_2$pz)$_3^+$], 661 (0.5) [La(*t*Bu$_2$pz)$_3^+$ – Me], 497 (1.4) [La(*t*Bu$_2$pz)$_2^+$], 481 (1.2) [La(*t*Bu$_2$pz)$_2^+$ – MeH]. – $C_{37}H_{67}LaN_6O_2$ (766.9): calcd. La 18.11; found La 18.01.

*catena-Poly[tris(3,5-di-tert-butylpyrazolato)-μ-(1,2-dimethoxyethane-O$^1$:O$^2$)neodymium(III)]* (**5**): Analogously to **4**, Nd (0.92 g, 6.4 mmol), Hg($C_6F_5$)$_2$ (1.40 g, 2.6 mmol), and *t*Bu$_2$pzH (0.94 g, 5.2 mmol) yielded within 4 d 0.50 g (38%) of a lavender-blue crystalline solid. – $^1$H NMR ($C_6D_6$): δ = 19.69 (br s, 3H; CH), 2.50 (br s, 54H; $CH_3C$), –8.41 (br s, 5.5H; $CH_3O$), –10.78 (br s, 3H; $CH_2$). – IR: $\tilde{\nu}$ = 2960 cm$^{-1}$ vs, 2925 s, 2900 s, 2865 s, 1520 m, 1502 s, 1458 s, 1428 s, 1410 ms, 1359 vs, 1307 m, 1251 s, 1225 s, 1207 m, 1189 m, 1111 m, 1052 vs, 1017 s, 991 s, 936 m, 900 vs, 790 vs, 724 m. – Vis/near IR (DME): $\lambda_{max}$ (ε) = 879 nm (0.44), 863 (0.68), 807 (5.0), 801 sh (5.0), 751 sh (3.5), 744 (3.8), 737 sh (3.2), 588 (38), 578 sh (16), 543 sh (1.5), 529 (5.9), 514 sh (2.1), 371 sh (6.5), 353 (6.5). – MS (70 eV, EI), *m*/*z* (%): 679 (1.3) [Nd(*t*Bu$_2$pz)$_3^+$], 666 (1.5) [Nd(*t*Bu$_2$pzH)$_2$(*t*Bu$_2$pz)$^+$ – Me], 502 (0.5) [Nd(*t*Bu$_2$pzH)$_2^+$], 484 (0.6) [Nd(*t*Bu*t*$_2$pz)$_2^+$ – MeH]. – $C_{37}H_{67}N_6NdO_2$ (772.2): calcd. Nd 18.68; found Nd 18.11.

*Tris(3,5-di-tert-butylpyrazolato)(1,2-dimethoxyethane)-erbium(III)* (**6**): Analogously to **4**, Er (0.94 g, 5.6 mmol), Hg($C_6F_5$)$_2$ (1.48 g, 2.8 mmol), and *t*Bu$_2$pzH (1.00 g, 5.6 mmol), within 5 d yielded 0.55 g (37%) of a pink crystalline solid. – IR: $\tilde{\nu}$ = 2958 cm$^{-1}$ vs, 2925 s, 2897 s, 2857 s, 1518 s, 1501 s, 1456 vs, 1435 s, 1414 m, 1386 m, 1359 vs, 1314 m, 1251 vs, 1226 s, 1205 ms, 1194 m, 1108 s, 1063 vs, 1018 vs, 997 vs, 870 s, 786 vs, 723 s. – Vis/near IR (DME): $\lambda_{max}$ (ε) = 973 nm br (0.93), 750–880 vv br (1.8), 656 (1.7), 652 sh (1.7), 540 sh (4.1), 522 (28), 488 (6.9), 408 sh (9.7), 381 (30), 378 sh (31), 366 sh (12), 358 sh (9.7). – MS (70 eV, EI), *m*/*z* (%): 704 (13) [Er(*t*Bu$_2$pz)$_2$(*t*Bu$_2$pzH)$^+$], 690 (27) [Er(*t*Bu$_2$pzH)$_2$(*t*Bu$_2$pz)$^+$ – Me], 526 (10) [Er(*t*Bu$_2$pzH)$_2^+$], 510 (10) [Er(*t*Bu$_2$pz)(*t*But$_2$pzH)$^+$ – Me], 494 (5) [Er(*t*Bu$_2$pzH)$_2^+$ – 2 Me]. – $C_{37}H_{67}ErN_6O_2$ (795.2): calcd. Er 21.03; found Er 20.26.

*X-Ray Crystallogrpahy* (Table 2): A representative light mauve prismatic crystal of **5** was sealed under argon into a Lindemann glass capillary. The crystal was affixed to the wall of the capillary with a little vacuum grease. The crystal of **3** was selected at low temperature (temperature maintained by a special device[45]), and glued to a glass fibre and placed into the nitrogen stream of the diffractometer. Intensity measurements were made with a Nicolet (Siemens) R3m/V four-circle diffractometer at 294 K for **5** and with an Enraf-Nonius CAD-4 automatic diffractometer at 240 K for **3**. In both cases graphite monochromated Mo-$K_\alpha$ radiation (λ = 0.7107 Å) was used. – A total of 9875 unique data were collected within the limits 3.5 ≤ 2Θ ≤ 55.0° by using the ω-scan technique, with a symmetric scan range of ±0.75° in ω from the calculated Bragg scattering angle, by using a variable scan rate for **5**. – The 6338 unique reflections for a triclinic unit cell of **3** were scanned with variable scan time and ω – 2Θ technique in a range of 1 ≤ 2Θ ≤ 45°. Of these, 6209 were considered to be significantly above background [$F_o > 6\sigma(F_o)$] for **5** and 3046 [$F_o > 4\sigma(F_o)$] for **3**, respectively. Three standard reflections measured every 197 reflections (**5**) and after 2 hours for **3** showed no significant variation; Lorentz and polaristion corrections were applied to the intensity data, and an absorption correction based on indexed crystal faces was applied for **5** with minimum and maximum transmission factors of $A^*_{min,max}$ = 0.7611, 0.8629. Atomic scattering factors used for the neutral atoms were corrected for anomalous dispersion. All calculations were performed on a Microvax 2000 computer (**5**) and an IBM Risk 6000 computer (**3**). The programs used were SHELXLTL PLUS[46] for **5** and SHELX 93[47] for **3**. – The structures were solved by interpreting the three-dimensional Patterson syntheses, which readily gave the positions of the heavy atoms. Subsequent difference-Fourier syntheses then revealed the positions of all the remaining non-hydrogen atoms. Full-matrix least-squares refinement of the model structure, with anisotropic thermal parameters for the neodymium atom (only neodymium was refined anisotropically as there was no evidence for anisotropy of the other atoms) for **5** and all non-hydrogen atoms for **3**, with hydrogen atoms in their geometrically calculated positions (C–H 0.96 Å) (riding model, one fixed thermal parameter), converged at $R$ 0.0574 and $R_w$ 0.0677 [$R_w = \Sigma_w^{1/2}(||F_o|-|F_c||)/\Sigma_w^{1/2}|F_o|$, $w = [\sigma^2(F_o) + 0.0010(F_o)^2]^{-1}$] for **5** and $R$ 0.0166, $R_w$ 0.0495 [$R_w = [\Sigma_w(||F_o|-|F_c||)^2/\Sigma_w|F_o|^2]^{1/2}$] for **3**.

Table 2. Crystallograpic details for **3** and **5**

| | **3** | **5** |
|---|---|---|
| Formula | $C_{53}H_{53}ErN_6O_4$ | $C_{37}H_{67}N_6NdO_2$ |
| Mol. mass | 1005.3 | 772.2 |
| Crystal size [mm] | 0.18 × 0.23 × 0.42 | 0.25 × 0.15 × 0.15 |
| Crystallised from | DME/light petroleum | DME |
| Colour | pink | light mauve |
| Space group | $P2_1/c$ | $P\bar{1}$ |
| $Z$ | 4 | 2 |
| $a$ [Å] | 8.600(2) | 11.866(2) |
| $b$ [Å] | 41.860(8) | 13.445(3) |
| $c$ [Å] | 13.132(3) | 14.652(3) |
| α [°] | ----- | 94.03(2) |
| β [°] | 97.84(2) | 98.26(2) |
| γ [°] | ----- | 111.01(1) |
| $V$ [Å$^3$] | 4683(2) | 2140.6(8) |
| $d_{calc.}$ [gcm$^{-3}$] | 1.426 | 1.198 |
| $F$(000) | 2040 | 814 |
| μ(Mo-$K_a$) [mm$^{-1}$] | 1.770 | 1.250 |
| *hkl* range | ±*h*, ±*k*, +*l* | ±*h*, ±*k*, –*l* |
| Ind. refln. measd. | 6338 | 9875 |
| Refln. used | 3046 [$F_o > 4\sigma(F_o)$] | 6209 [$F > 6\sigma(F)$] |
| Parameters | 577 | 298 |
| $R$ value | 0.0166 | 0.0574 |
| $R_W$ value | 0.0495 | 0.0677 |
| residual e. density, [eA$^3$] | +0.285<br>-0.424 | +1.48<br>-1.17 |

Further details of the crystal structure investigations are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ (UK), on quoting the full journal citation.

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