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The Synthesis, Structures and Polymorphism of the Dimeric Trivalent Rare-Earth 3,5-Dimethylpyrazolate Complexes [Ln(Me₂pz)₃(thf)]₂

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A variety of rare-earth 3,5-dimethylpyrazolate (Me₂pz) complexes have been synthesised by (i) the direct reaction of Hg-activated metal with Me₂pzH as a pro-ligand at elevated temperatures, (ii) by redox transmetalation/protolysis with the lanthanoid element, Hg(C₆F₅)₂, and Me₂pzH, and (iii) by protolysis of tris[bis(trimethylsilyl)amido]cerium(III) with Me₂pzH. Each product, upon crystallisation from tetra-hydrofuran (thf), formed a dimeric complex, [Ln(Me₂pz)₃-(thf)]₂ (Ln = La, Ce, Pr, Nd, Ho, Yb, or Lu). Despite the common formulation, two completely different structures were observed in two distinct crystallographic "domains of existence", together presumptively spanning the gamut of Ln and Y. For the larger rare-earth ions (La–Pr), there are two

Introduction

In the last fifteen years, the coordination chemistry of pyrazolate ("pyrazolide") ligands has been transformed and enriched by the discovery of many new binding modes^[1] and by the extension of η^2 -coordination from f-block^[2] to transition metal^[3] and main group^[4] elements. Many of the new binding modes were initially observed in the trivalent lanthanoid pyrazolates,^[5] for which the chemistry has been dominated by complexes of the bulky 3,5-di-*tert*-butylpyr-azolate (*t*Bu₂pz) and 3,5-diphenyl-pyrazolate (Ph₂pz) ligands.^[2e-2g,2k,5a-5d] However, there have been recent developments in the synthesis and structures of lanthanoid unsubstituted pyrazolate complexes,^[5e,6] and in complexes

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terminal η^2 -Me₂pz ligands and one thf donor on each Ln atom, with the metal atoms being linked by a pair of bridging pyrazolate ligands of an uncommon type ($\eta^2:\eta^5$), resulting in formal ten-coordination. A Me₂pzH complex [Ce(Me₂pz) ₃(Me₂pzH)], although not isomorphous, has a similar structure. For the smaller rare-earth elements (Nd–Lu), the bridging is entirely different, with two μ - $\kappa^1(N)$: $\kappa^1(N)$ pyrazolate and two unusual bridging thf ligands. Each Ln atom also has two chelating Me₂pz ligands, resulting in formal eightcoordination. Crystallisation of [Nd(Me₂pz)₃(thf)]₂ from pyridine yields monomeric, nine-coordinate [Nd(Me₂pz)₃-(pyridine)₃] with only chelating Me₂pz ligands.

with unsymmetrically 3,5-disubstituted pyrazolate ligands.^[7] The moderately bulky, commercially available (as the pyrazole), 3,5-dimethylpyrazolate ligand (Me₂pz) has had a prominent role in the development of transition metal and main group complexes^[1a,1c,1d] as well as in cyclopentadienyllanthanoid pyrazolates,^[8] and the oxygen-centred Na-Ln bimetallic 3,5-dimethylpyrazolate cages were the first structurally characterised lanthanoid pyrazolates.^[2c] However, tris(3,5-dimethylpyrazolato)lanthanoid complexes $[Ln(Me_2pz)_3(L)_n]$ (L = neutral donor) with crystallographically defined structures are few in number, and are restricted to monomeric $[Er(Me_2pz)_3(tBupy)_2]$ ($tBu_2py = 4$ -tertbutylpyridine)^[2i] (which has been used as an MOCVD dopant source^[9]), dimeric [Ln₂(Me₂pz)₄(µ-Me₂pz)₂(µ-thf)₂] (Ln = $Nd^{[2d]}$ Y^[10]), and the first complex with monodentate pyrazolate-N-Ln coordination $[{Nd(\eta^2-Me_2pz)_2}\kappa^1-(N)-$ Me₂pz}}(Me₂pzH)].^[5b] The structurally uncharacterised $[Ln(Me_2pz)_3(thf)]$ (Ln = La, Er)^[2h] and $[Nd(Me_2pz)_3-$ (py)]^[5b] (py = pyridine) are also known.

We now report the synthesis of a range of lanthanoid(III) tris(3,5-dimethylpyrazolate) complexes by a variety of preparative routes and the structural characterisation of representative complexes, thereby defining structures that span the whole La–Lu (Y) array. These differ markedly from those of the corresponding Ph₂pz and *t*Bu₂pz complexes.^[2e–2g,2k] Of particular interest is the observation of μ - η^2 : η^5 coordination in complexes of the larger lanthanoids.

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This binding mode is quite uncommon, but has been observed for lanthanoid complexes with bulkier pyrazolate substituents, such as $[Eu(tBu_2pz)_2]_{4,}$ ^[5a] $[Ln_3(Ph_2pz)_9]$ (Ln = La, Nd),^[5d] and $[K(PhMe)Ln(tBu_2pz)_4]$ (Ln = La, Sm, Tb, Yb) { $\eta^{5}(K):\eta^{2}(Ln)$ },^[5c] and has also been observed in some alkaline earth pyrazolate complexes.^[4c,4d,11] It should be noted that η^{5} -pz-Nd binding has been observed in $[Nd_3(pz)_9-(pzH)_2]$ as part of a unique μ_3 - $\eta^{5}:\eta^{1}:\eta^{1}$ binding mode,^[5e] and there is η^{5} -binding of pyrazole ligand (pzH) in $[Eu(pz)_2-(pzH)_2]_{\infty}$.^[5c,6c] The mixed sandwich compounds $[Ru(C_5Me_5)(\eta^{5}-Me_2pz)]^{[12]}$ and $[Os(C_5Me_5)(\eta^{5}-tBu_2pz)]^{[13]}$ remain special examples of standalone η^{5} -pyrazolate binding.

Results and Discussion

Synthesis and Characterisation of Rare-Earth 3,5-Dimethylpyrazolate Complexes

The lanthanoid pyrazolate complexes $[Ln(Me_2pz)_3(thf)]_2$ (1–7) {Ln = La (1), Ce (2a), Pr (3), Nd (4), Ho (5), Yb (6), Lu (7)}, have been synthesised by three methods, namely: (i) direct reaction of activated Ln metal with the pro-ligand Me₂pzH at elevated temperatures followed by extraction with thf (1); (ii) redox transmetalation/protolysis (RTP) with Hg(C₆F₅)₂, Ln metals and Me₂pzH (1–7), and (iii) protolysis of [Ce{N(SiMe_3)₂}] with Me₂pzH (2a) (Scheme 1).



Scheme 1. Synthesis of lanthanoid pyrazolate complexes by (i) the direct method at elevated temperature; (ii) redox transmetalation/ protolysis (RTP); (iii) the protolysis reaction of $[Ce\{N\{Si-(CH_3)_3\}_2\}_3]$, also giving $[Ce(Me_2pz)_3(Me_2pzH)]$ (**2b**) in low yield; (iv) ligand exchange between thf and pyridine (py).

In an attempt to synthesise an unsolvated lanthanoid(III) 3,5-dimethylpyrazolate complex, $[La(Me_2pz)_3]$, lanthanum metal and 3,5-dimethylpyrazole (Me₂pzH) were heated to 300 °C. Although the synthesis was successful, extraction of unsolvated $[La(Me_2pz)_3]$ was difficult due to its insolubility in noncoordinating solvents. Addition of thf allowed separation from the metal residue and isolation of 1 in 58% yield, which is higher than from a previously reported synthesis by metathesis (yield $35\%^{[2h]}$). This elevated temperature synthesis also succeeds with tBu_2pzH ,^[5a] Ph₂pzH^[5d] and pzH^[5e,6b] and thus can now be considered a general method for unsolvated rare-earth pyrazolates. The $[Ln(Me_2pz)_3(thf)]$ species synthesised by the RTP method

were obtained in good yields (1-5 and 7; 50-77%), with the exception of Ln = Yb. Monitoring the synthesis of both the Ln = La (1) and Ln = Lu (7) complexes by 19 F NMR spectroscopy indicated the complete consumption of $Hg(C_6F_5)_2$, with corresponding formation of C_6F_5H , so that reduction in yield from quantitative appears to be solely a result of loss on isolation. The synthesis of [Yb- $(Me_2pz)_3(thf)]_2$ (6) was problematic by the RTP route and required isolation of the complex within minutes of synthesis, otherwise an insoluble grey material formed. Even more unsuccessful was the corresponding reaction with 3,5-diphenylpyrazole, for which decomposition was observed from the outset.^[2j] By contrast, the reaction of ytterbium with Hg(C₆F₅)₂ and 3,5-di-tert-butylpyrazole gave [Yb-(tBu₂pz)₃(thf)₂] in good yield.^[2f] Furthermore, complex 6 soon lost thf on workup, forming a yellow powder that was insoluble in thf, toluene or pyridine. The lutetium analogue (7), once separated from the metal residue, was sparingly soluble in cold thf, but crystallisation from hot thf solution produced crystals of $[Lu(Me_2pz)_3(thf)]_2$ (7). Complex 2a was also synthesised by protolysis of $[Ce{N{Si(CH_3)_3}_2}_3]$ with Me₂pzH. Although the synthesis was rapid, purification required separation of 2a from a small amount of a Me_2pzH substituted complex, $[Ce(Me_2pz)_3(Me_2pzH)]_2$ (2b), resulting from the use of a small excess of Me₂pzH in the synthesis. Crystallisation of complex 4 from pyridine gave the mononuclear complex $[Nd(Me_2pz)_3(py)_3]$ (8) (py = pyridine) in high yield, contrasting with the formation of [Er- $(Me_2pz)_3(tBupy)_2$ ^[2i] with a rather smaller lanthanoid metal.

Bulk samples of 1, 5 and 7 gave microanalyses that were consistent with the compositions of their single crystals (see below), and diamagnetic 7 had a satisfactory ¹H NMR spectrum. When C_6D_6 was added to 1, a white, insoluble precipitate formed and the ¹H NMR spectrum of the supernatant solution showed a ratio of thf to pyrazolate of 2:3. Upon D₂O addition, the spectrum indicated a corresponding ratio of 1:3, consistent with the analytical composition. This observation highlights the labile nature of the coordinating thf in [La(Me₂pz)₃(thf)]₂, and implies that the insoluble precipitate was unsolvated and presumably polymeric $[La(Me_2pz)_3]$. This is consistent with the inability to extract unsolvated $[La(Me_2pz)_3]$ with nonpolar solvents following the synthesis by method (i) (Scheme 1). It is less likely that the product of the reaction shown in Scheme 1 (i) is $[La(Me_2pz)_3(Me_2pzH)]$ because the cerium analogue **2b** is soluble in toluene. Metal analyses for freshly prepared 6 and 8, and the ¹H NMR spectrum of the latter were as expected for a mono-thf and a tris-py complex, respectively, but subsequent microanalyses indicated complete loss of thf from the former and 0.5 py/Nd from the latter. The ready loss of pyridine from 8 indicates that this compound may be the precursor of structurally uncharacterised [Nd(Me₂pz)₃-(py)], the bulk product of an RTP reaction between Nd metal, $Hg(C_6F_5)_2$, and Me_2pzH in pyridine, followed by work up with nonpolar solvents (hexane and toluene).^[5b] Microanalysis of 2a was indicative of the loss of one thf molecule per two cerium atoms, although ¹H NMR analysis

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of a hydrolysed sample was consistent with the single-crystal composition. The infrared spectra of complexes 1, 2a and 3–8 showed no v(N–H) absorptions, indicating that the Me₂pzH was completely deprotonated. Isomorphous 1 and 2a (see below) showed v(C–O) bands ascribable to coordinated thf at ca 880 cm⁻¹, whereas for isomorphous 4, 5 and 7 (see below), the corresponding absorptions were at ca. 840 cm⁻¹. On the other hand, no such band was observed for 6, indicating loss of thf (consistent with the microanalysis).

Structures of the Complexes

The structural characterization of $[Ln(Me_2pz)_3(thf)]$ for Ln = Pr, Lu, together with the unit cell determination of the Ln = La adduct (regrettably unavailable in suitable form for a single-crystal structural determination) and data available in the literature for Ln = Nd defines these complexes in two forms " α " and " β ", which putatively span the entire gamut of the lanthanoid series, inclusive also of the Ln = Y complex.^[10] Interestingly, for Ln = Ce, replacement of the thf ligand of 2a by Me₂pzH is possible (compound 2b) without profoundly disturbing the coordination sphere of the complex. Both forms (α and β) are binuclear $[Ln(Me_2pz)_3(thf)]_2$, with form α crystallising in monoclinic $P2_1/n$, and form β in triclinic P1, the dimer in each being disposed about a crystallographic inversion centre so that, in each case, one half of the binuclear formula unit comprises the asymmetric unit. Figure 1 and Table S1 present data for the domain of the α -form, which encompasses Ln = La (1) (regrettably no single crystal data), Ln = Ce (2a)(the largest atom extremal of the detailed geometrical data available at present) to Ln = Pr(3); also included are the counterpart data for [Ce(Me₂pz)₃(Me₂pzH)]₂ (2b) - the pyrazole analogue. Table S2 presents data for the Ln = Nd(4),^[2d] Lu (7) extrema of the β domain, together with values



Figure 1. Molecular projections of (a) $[Ce(Me_2pz)_3(thf)]_2$ (2a) and (b) $[Ce(Me_2pz)_3(Me_2pzH)]_2$ (2b), together with simplified schematics (c,d) of the bridging coordination, as representative structures for 1–3. In 2b, the Me₂pzH H(12) is included to show the intramolecular hydrogen-bond. Selected bond lengths [Å] for 2a: Ce(1)-N(21) 2.580(3), $Ce(1)-N(21)^*$ 2.753(3), Ce(1)-N(22) 2.561(3), $Ce(1)-N(22)^*$ 2.739(3), Ce(1)-N(31) 2.473(3), Ce(1)-N(32) 2.485(3), Ce(1)-N(41) 2.463(3), Ce(1)-N(42) 2.489(3). $Ce(1)-C(23)^*$ 2.953(3), $Ce(1)-C(24)^*$ 3.080(3), $Ce(1)-C(25)^*$ 2.969(3), Ce(1)-O(1) 2.514(2). Selected bond lengths [Å] for 2b: Ce(1)-N(11) 2.6039(15), Ce(1)-N(21) 2.5950(15), $Ce(1)-N(21)^*$ 2.7367(15), Ce(1)-N(22) 2.5813(15), $Ce(1)-N(22)^*$ 2.7451(15), Ce(1)-N(31) 2.5074(16), Ce(1)-N(32) 2.4701(15), Ce(1)-N(41) 2.4621(15), Ce(1)-N(42) 2.4591(16), $Ce(1)-C(23)^*$ 2.990(2), $Ce(1)-C(24)^*$ 3.113(2), $Ce(1)-C(25)^*$ 2.973(18).

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for $Ln = Y^{[10]}$ and Ho (5). As expected for isogeometric ions, the bond lengths and angles are similar for 5 and the Y species.

Complexes of the Larger Lanthanoids with μ - η^2 : η^5 -Pyrazolate Bonding {[Ln(Me₂pz)₃(thf)]₂} {' α' -form; Ln = Ce (2a), Pr (3)}

Because 1, 2a and 3 have very similar unit cells and IR spectra (see Exp. Section), it can be inferred that they have similar structures, but only 2a and 3 allowed full structure determinations. The dimer of 2a, together with its pyrazole analogue 2b, and a schematic of the bonding are presented in Figure 1 together with key bond lengths. The lanthanoid atoms are each ligated by a pair of terminal η^2 -Me₂pz anions and one thf molecule in a trans disposition across the dimer; two further μ - η^2 : η^5 ligands associated with each lanthanoid are also present, so that the lanthanoid atom is ten-coordinate. For ligand N(21,22), the C(24)–N(2n)(centroid)–Ln(1) angle (ca. 177°) is indicative of $\eta^2(\sigma)$ -bonding to the lanthanoid, whereas the C(24)-(ring centroid)–Ln(1')angle (ca. 99°) is consistent with $\eta^5(\pi)$ -bonding (the Ln–C bond lengths of the η^5 -bound ligand are discussed below). Such a symmetrical η^2 : η^5 -pyrazolate-bridged dimeric structure has not previously been observed in lanthanoid chemistry,^[1,14] having only previously been observed among Group 2 complexes.^[4b,4c] Indeed, it is surprising that a complex with this bridging array can be crystallised from thf without cleavage of the bridge. Previous examples of this coordination found in rare-earth chemistry^[5c,5d] come from solventless syntheses or from the use of nonpolar solvents.

In 2a and 3, the terminal (ter) and bridging (br) η^2 -Me₂pz (of the μ - η^2 : η^5 donor) chelate symmetrically to the lanthanoid atom and the two Ln–N distances of the η^5 -Me₂pz–Ln interaction are similar. The Ln–N bond lengths decrease in the series η^5 -Me₂pz > $\eta^2_{(br)}$ -Me₂pz > $\eta^2_{(ter)}$ -Me₂pz (Figure 1). A search of the Cambridge Structural Database suggests that 2a (and 2b) are the first structurally characterised monometallic pyrazolatocerium complexes.^[15] In the absence of precedents, the observed Ce-N(pz) bond lengths (Table S1) can be compared with those of appropriate lanthanum pyrazolates, because the ionic radii of tencoordinate La^{3+} and Ce^{3+} (or nine-coordinate Pr^{3+} and nine-coordinate Ce³⁺) differ by less than 0.02 Å.^[16] Thus, for example, the terminal Ce-N bond lengths are similar to the terminal La-N bond length of the ten-coordinate central lanthanum atom of [La₃(Ph₂pz)₉]^[5d] as well as to the corresponding values for the nine-coordinate outer La atoms.^[5d] Likewise, the Ce-N bonds of the η⁵-Me₂pz-Ce interactions are similar to the corresponding data for $[La_3(Ph_2pz)_9]$.^[5d] However, because the η^2 -binding of the μ - η^2 : η^5 -Ph₂pz ligands of this trinuclear complex is highly unsymmetrical, a comparison with the symmetrical μ - η^2 - $Me_{2}pz$ -Ce interactions of 2a is less appropriate, although the bonding appears stronger in **2a**. For the η^5 -Me₂pz-Ce ligation, the observed Ce-C bond lengths [2.953(3)-3.080(3) Å] correspond well with the Ln–C distances in sixcoordinate $[Ln{OC_6H_3(iPr)-2,6-\mu-(O,\eta^6-Ar)-O-C_6H_3(iPr)-2,6}]_2 {Ln = La 2.978(10)-3.164(9) Å; Ln = Nd 2.898(12)-3.183(1) Å^[17]} (Nd³⁺ 0.04 Å smaller than Ce³⁺),^[16] and the La–C distances in nine-coordinate <math>[La(\eta^6-ArH)(AlCl_4)_3]$ (Ar-H = C₆Me₆ or PhMe) [2.927(7)-3.035(7) Å].^[18] In addition, they are similar to the Nd–C distances of the η^5 (pz)-Nd interaction of $[Nd_3(pz)_9(pzH)_2]$ [2.882(3)–3.030(3) Å],^[5e] and to the Ce–C bond lengths of the η^6 -Ar–Ce coordination in seven-coordinate $[Ce(OC_6H_3Ph_2-2,6)_3]$ [2.975(3)–3.167(3) Å].^[19]

In $[Ce(Me_2pz)_3(Me_2pzH)]_2$ {2b; Figure 1 (b)}, the thf solvent donor of 2a is replaced by a molecule of Me₂pzH, retaining the binuclear α -form and the novel bridging pair of μ - η^2 : η^5 -Me₂pz ligands, both cerium atoms of **2b** remaining ten-coordinate with a coordinating pyrazole in place of the thf of 2a. Such replacement of thf by Me₂pzH is known for oxygen-centred Na/Ln 3,5-dimethylpyrazolate cages.^[2c] In the pyrazole-coordinated analogue of 2a, the pairs of nitrogen donor atoms are slightly more symmetrically coordinated than in 2a, but the Me₂pz, Ce–N and Ce–C bond lengths are very similar in both compounds (Figure 1 and Table S1). However, the Ce-N(11) bond of the monodentate Me₂pzH ligand in **2b** is ca. 0.1 Å longer than the Ce-O (thf) bond that it replaces (in 2a), with some quite significant changes in the associated angular geometries being evident (Table S1). The nitrogen-bound hydrogen atom [H(12)] interacts with the nitrogen-atom of an adjacent terminal pyrazolate ligand at a distance of 2.33(Å), with a N(12)-N(31) distance of 3.042(2) Å. Such a distance is longer than the reported hydrogen-bonding distances in $[Nd(\eta^2-Me_2pz)_2{\kappa^1(N)-Me_2pz}(Me_2pzH)_2(py)],$ which shows two, much closer N····H interactions at 1.96(3) and 1.97(2) Å.^[5b] This is ascribed to the presence of the uncoordinated nitrogen of the η^1 -Me₂pz ligand, permitting less hindered access for hydrogen-bonding. However, the Ce-N(11)–N(12)/C(15) angles are very unsymmetrical [117.41(11), 135.82(12)°]. The $\eta^2:\eta^5$ bridging coordination motif displayed in both complexes 2a and 2b contrasts with that of the tetranuclear europium(II) 3,5-di-tert-butylpyrazolate complex $[Eu_2(\mu-\eta^2:\eta^5-tBu_2pz)_2(tBu_2pz)_2]_2$, in which pairs of bridging $\eta^2:\eta^5$ pyrazolate ligands bind η^5 to the same europium atom, with Eu-C(tBu2pz) distances of 3.019(4)-3.178(5) Å.^[5a] In the bimetallic systems, [K(toluene) $Ln(tBu_2pz)_4$] (Ln = La, Sm, Tb, Yb, Lu), the pyrazolate ligands bridge η^2 to the rare-earth and η^5 to potassium.^[5c]

Complexes of the Smaller Lanthanoids with μ - $\kappa^1(N)$: $\kappa^1(N)$ -Pyrazolate Bonding and Bridging O(thf) {[Ln(Me_2pz)_3-(thf)]_2} {'\beta'-form, Ln = Nd (4) [Ho (5)]-Lu (7), Y}

Dimeric complexes **4**, **5** and **7** have two terminal η^2 -pyrazolate ligands (the only common feature with the α -form), two μ - $\kappa^1(N)$: $\kappa^1(N)$ -Me₂pz ligands (the most common pyrazolate ligation,^[1,14] although not for rare-earths), and two bridging thf donors (a very uncommon thf binding mode in non-alkali metal chemistry^[2d,10,15,20]) (Figure 2). The X-



Figure 2. (Left) Molecular projection of $[Lu(Me_2pz)_3(thf)]_2$ (7), a representative structure for the Ln = Nd–Lu domain of the β -form; (Right) A schematic of the bridging mode. Selected bond lengths [Å] for 7: Lu(1)–N(21) 2.3508(15), Lu(1)–N(22)* 2.351(2), Lu(1)–N(31) 2.290(2), Lu(1)–N(32) 2.281(2), Lu(1)–N(41) 2.279(2), Lu(1)–N(42) 2.269(2), Lu(1)–O(11) 2.6076(13), Lu(1)–O(11') 2.6644(14).

ray crystal structures of $[Ho(Me_2pz)_3(thf)]_2$ (5) and $[Lu-(Me_2pz)_3(thf)]_2$ (7) are isomorphous with those of the previously reported $[Nd(Me_2pz)_3(thf)]_2$ (4)^[2d] and $[Y(Me_2pz)_3-(thf)]_2^{[10]}$ analogues. Examination of average bond lengths shows that the decrease in Ln–N/O bond lengths from 4 to 7 is ≥ 0.13 Å (Table S2), and is consistent with the decrease in ionic radii from Nd³⁺ to Lu³⁺,^[16] indicating that there is no steric stress associated with the small Lu³⁺ ion. Given that complexes 4, 5 and 7 (together with the Ln = Y analogue) all crystallise with the same coordination environment, it is likely that the other rare-earth elements included in the progression from Nd to Lu crystallise in the same manner, including 6, for which single crystals could not be obtained.

Thus, there is a size-based structural break for these binuclear rare-earth 3,5-dimethylpyrazolate complexes, suggesting domains of existence are bounded by Ln = La, Pr for the former and Ln = Nd, Lu (Y) for the latter metals. What is noteworthy is the considerable difference in the bridging binding between the two structural classes, and the crystallisation of both from thf without cleavage of the bridging bonding, not even of the μ -(*O*)thf mode of **4**, **5** and **7**.

The Structure of Monomeric [Nd(Me₂pz)₃(py)₃]

Contrasting with the stability of the dimeric complexes 1, 2a, 3, 4, 5 and 7 towards thf, crystallisation of $[Nd(Me_2pz)_3(thf)]_2$ from pyridine gives the mononuclear complex $[Nd(Me_2pz)_3(py)_3]$ (8). Complex 8 crystallises with two similar discrete $[Nd(Me_2pz)_3(py)_3]$ neutral molecules within the asymmetric unit (Figure 3). The neodymium atoms are nine-coordinate with three η^2 -pyrazolate ligands and three pyridine molecules (Figure 3, Table S3), with the pyridine donors adopting a meridional quasioctahedral disposition.



Figure 3. Asymmetric unit of **8** showing the two molecules of $[Nd(Me_2pz)_3(py)_3]$ (**8**) (presented as disposed in the unit cell). Selected bond lengths for molecule 1: Nd(1)–N(11) 2.451(4), Nd(1)–N(12) 2.473(4), Nd(1)–N(21) 2.508(4), Nd(1)–N(22) 2.464(4), Nd(1)–N(31) 2.475(4), Nd(1)–N(32) 2.469(4), Nd(1)–N(41) 2.704(4), Nd(1)–N(51) 2.656(4), Nd(1)–N(61) 2.693(4).

The Nd–N(Me₂pz) distances (av. 2.47 Å) exceed Nd–N_{ter} of **4** (av. 2.41 Å, see Figure 3), concomitant with an increase in coordination number of one,^[16] and are similar to those found in the nine-coordinate neodymium pyrazolate complex [Nd(Ph₂pz)₃(thf)₃]·thf (av. 2.46 Å),^[2g] which has *mer* thf ligands. Similarly, the Nd–N(py) bond lengths (av. 2.63 Å) are longer than that of eight-coordinate [Nd(η^2 -Me₂pz)₂{ κ^1 -(*N*)-Me₂pz}(Me₂pzH)₂(py)], by the expected amount.^[16] The *trans*-influences for some ligands have been noted in rare-earth chemistry^[21] and have been proposed for the Ph₂pz ligand in [Nd(Ph₂pz)₃(thf)₃],^[2g] but there is little evidence for any such effect in the present complex. However, the longer Nd–N(py) bonds could account for the relatively facile loss of py from complex **8** (see above).

Conclusions

Solvated lanthanoid pyrazolate complexes of the composition $[Ln(Me_2pz)_3(thf)]_2$ (Ln = La, Ce, Pr, Nd, Ho, Yb,

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and Lu) have been prepared by three different synthetic routes, with redox transmetalation protolysis (RTP) using $Hg(C_6F_5)_2$ being an effective and high-yielding general method. Despite the common formula, there is a substantial structural break between the domains of the larger rareearth ions (La³⁺, Ce³⁺, Pr³⁺) and the smaller ions (Nd³⁺-Lu³⁺), with a striking change in the bridging bonding from the unusual η^2 : η^5 -pyrazolate coordination for La and Ce to the completely different μ - $\kappa^1(N)$: $\kappa^1(N)$ -Me₂pz and μ -(O)thf bridging for Nd-Lu. Although the bridging bonding resists cleavage by thf, cleavage by pyridine gave nine-coordinate, monomeric [Nd(Me₂pz)₃(py)₃]. Overall, reduction of the bulk of the 3,5-disubstituted pyrazolate ligand substituents from tBu₂pz and Ph₂pz to Me₂pz transforms the structures of thf-solvated tris(pyrazolato)lanthanoid(III) complexes from eight- or nine-coordinate $[Ln(tBu_2pz \text{ or } Ph_2pz)_3(thf)_n]$ (n = 2,3) monomers to $[Ln(Me_2pz)_3(thf)]_2$ dimers with unusual bridging features.

Experimental Section

General Considerations: All products were air-sensitive and required manipulation in an inert atmosphere and hence the use of a glovebox, Schlenk flask and vacuum-line techniques. All solvents were predried with sodium metal and then further dried by distillation over sodium or sodium/benzophenone. The lanthanoid metals used were purchased from either Rhône–Poulenc or Santoku either as fine powders or as metal ingots, which were manually filed into metal filings in an inert atmosphere for use in the reactions. 3,5-Dimethylpyrazole (Me₂pzH) (Aldrich) was purified by sublimation before use. [Ce{N{Si(CH₃)₂}₂] was synthesised by a modified literature procedure,^[22] entailing treatment of [CeCl₃(thf)₂] with three equivalents of [K{N{Si(CH₃)₂}₂] in hexane, and was purified by filtration, evaporation to dryness and crystallisation from fresh hexane.

Microanalyses were performed at the Campbell Microanalytical Laboratory of the University of Otago (New Zealand) (an exception was **2a**, which was analysed with an "elementar vario MICRO cube" by Mr. Stephen Boch of Tübingen University). Metal analyses were performed by a literature method.^[2j] IR data were obtained from Nujol mulls for the region 4000–650 cm⁻¹ with a Perkin–Elmer 1600 FTIR spectrometer. ¹H NMR spectra were recorded with a Bruker DRX400 (400 MHz) spectrometer, and with a Bruker DRX300 for the hydrolysed sample of complex **2a**. No interpretable NMR spectra were obtained for paramagnetic complexes **2a**, **2b**, **3**, **4**, **5** and **6**.

[La(Me₂pz)₃(thf)]₂ (1): Method a: Lanthanum filings (0.97 g, 6.98 mmol), 3,5-dimethylpyrazole (1.00 g, 10.4 mmol) and two drops of mercury were sealed under vacuum (ca. 10^{-3} Torr) in a Carius tube and heated to 300 °C for 4 d. The white product was extracted with thf to give colourless microcrystals of the title complex. The ¹H NMR spectrum displayed chemical shifts concordant with those reported.^[2h] Yield: 1.02 g (59%). IR (Nujol): $\tilde{v} = 3311$ (w), 3200 (w), 3100 (w), 1574 (w), 1513 (vs), 1413 (s), 1366 m (sh), 1306 (w), 1260 (w), 1152 (w), 1099 (w), 1047 (m), 1029 (m), 1008 (vs), 962 (m), 877 (m), 806 (m), 775 (m), 740 cm⁻¹.

Method b: Lanthanum filings (0.32 g, 2.3 mmol), $\text{Hg}(C_6F_5)_2$ (1.06 g, 2.0 mmol) and Me₂PzH (0.39 g, 4.0 mmol) were added to a Schlenk flask and dissolved in thf (5 mL) with stirring at room temperature. After 16 h, a small amount of solution was analysed

by ¹⁹F NMR spectroscopy, which indicated complete consumption of Hg(C₆F₅)₂ and formation of C₆F₅H. The solution was separated from the metal residue by filtration and dried under vacuum to give [La(Me₂pz)₃(thf)]₂ (1) as a white powder, yield 0.51 g (76%). ¹H NMR (300 MHz, C₆D₆, 303.2 K): $\delta = 1.38$ [m, 16 H, β-CH₂(thf)], 2.11 (br. s, 36 H, Me), 3.53 [m, 16 H, α -CH₂(thf)], 5.96 (br. s, 6 H, H4-pz) ppm; a precipitate formed on attempted dissolution in C₆D₆. ¹H NMR (300 MHz, C₆D₆ + D₂O, 303.2 K): $\delta =$ 1.42 [m, 8 H, β -CH₂ (thf)], 1.82 (br. s, 18 H, Me), 2.25 (br. s, 18 H, Me), 3.56 [m, 8 H, α -CH₂(thf)], 5.68 (s, 6 H, H4) ppm. C₃₈H₅₈La₂N₁₂O₂ (992.77): calcd. C 45.97, H 5.89, N 16.93; found C 45.84, H 5.71, N 16.82. Complex 1 was crystallised from a thf/ hexane mixture at room temperature and found to be monoclinic P, a = 11.87(2), b = 14.04(3), c = 12.77(2) Å, $\beta = 96.49(3)^{\circ}$; V =2114 Å³; T = 123 K, on a small single specimen.

[Ce(Me₂pz)₃(thf)]₂ (2a) and [Ce(Me₂pz)₃(Me₂pzH)]₂ (2b): Method a: Cerium filings (0.18 g, 1.3 mmol), 3,5-dimethylpyrazole (0.37 g, 3.9 mmol) and Hg(C₆F₅)₂ (1.02 g, 1.9 mmol) were added to a Schlenk flask and dissolved in thf (10 mL). After stirring (1 d) the solution was separated from the metal residue and the solvents were evaporated to dryness, to give [Ce(Me₂pz)₃(thf)]₂ (2) as a white powder (0.37 g, 58%). The ligand to solvent ratio was determined by NMR analysis of a hydrolysed sample. ¹H NMR (300 MHz, C₆D₆ + D₂O, 303.2 K): $\delta = 1.42$ [m, 8 H, β-CH₂(thf)], 2.03 (br. s, 36 H, Me-pzH), 3.58 [m, 8 H, α-CH₂(thf)], 5.69 [s, 6 H, H4 (pzH)] ppm. IR (Nujol): $\tilde{v} = 3327$ (w), 3089 (vw), 1573 (m), 1514 (vs), 1422 (s), 1314 (m), 1261 (m), 1095 (m), 1075 (m), 1034 (m), 1008 (vs), 962 (m), 917 (vw), 881 (m), 813 (m), 789 (m), 772 (m), 730 (m) cm⁻¹.

Method b: In a glove box, $[Ce{N{Si(CH_3)_2}_2}_3] (0.16 g, 0.25 mmol)$ was added to a sample vial charged with Me₂PzH (0.070 g, 0.73 mmol) in thf (3 mL). The reaction mixture was stirred for 18 h then dried under vacuum. After washing with hexane, a thf/hexane mixture (2 mL/5 mL) was added to dissolve the products and the sample was allowed to evaporate slowly, forming large clear needles of $[Ce(Me_2Pz)_3(thf)]_2$ (**2a**; 0.06 g, 48%), and small clear blocks of $[Ce(Me_2pz)_3(Me_2pzH)]_2$ (**2b**; 0.02 g, 15%). Small needles of **2a** were handpicked and dried under vacuum. C₃₄H₅₀Ce₂N₁₂O (loss of one thf, 923.07) calcd. C 44.23, H 5.45, N 18.20; found. C 44.57, H 5.45, N 17.51. Insufficient **2b** for additional characterisation remained after the X-ray study.

[Nd(Me₂pz)₃(thf)]₂ (4) and [Nd(Me₂pz)₃(py)₃] (8): Neodymium filings (0.91 g, 6.31 mmol), 3,5-dimethylpyrazole (1.01 g, 10.5 mmol) and bis(pentafluorophenyl)mercury (2.78 g, 5.20 mmol) were stirred for 6 d in thf (40 mL). The mixture was then heated for 5 h at 60 °C. The blue solution obtained on filtration of the solids was evaporated, hexane was added, and the solution was left to crystallise at room temperature. Blue single crystals of [Nd(Me₂pz)₃-(thf)]₂ (4) were obtained and characterized by a unit cell determination: $C_{38}H_{58}N_{12}Nd_2O_2$; M = 1003.45; a = 10.720(2), b = 10.780(2), c = 11.200(2) Å, a = 77.65(3), $\beta = 68.72(3)$, $\gamma = 61.17(3)^\circ$; V = 1055.4(4) Å³; Temp = 123 K. The blue crystals of [Nd(Me₂pz)₃-(thf)]₂ (4) were then crystallised from pyridine to give blue crystals of **8**.

 $[Nd(Me_2pz)_3(thf)]_2$ (4): Yield: 1.35 g (77%). IR(Nujol): $\tilde{v} = 1574(m), 1518$ (s), 1414 (s), 1314 (m), 1171 (w), 1090 (w), 1062 (w), 1029 (m), 1008 (m), 956 (m), 931 (w), 842 (w), 814 (m), 794 (m), 768 (m), 742 (w), 726 (m), 654 (w) cm⁻¹ (in agreement with reported data).^[2d]

[Nd(Me₂pz)₃(py)₃] (8): Yield: 0.33 g (61%). ¹H NMR (C₆D₆): $\delta = -0.15$ [s, 6 H, H 2,6 (py)], 3.77 [s, 6 H, H 3,5 (py)], 4.45 [s, 3 H, H4 (py)], 6.60 (s, 18 H, Me), 15.38 [s (br), 3 H, H4 (pz)] ppm. IR

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(Nujol): $\tilde{v} = 1589$ (s), 1577 (s), 1517 (vs), 1412 (vs), 1312 (vs), 1242 (s), 1152 (s), 1008 (s), 770 (s), 721 (s), 701 (s), 668 (s) cm⁻¹. Metal analysis (fresh sample) $C_{30}H_{36}N_9Nd$ (666.92): calcd. 21.63%; found 21.55%. Elemental analysis (after transport to New Zealand) $C_{27.5}H_{33.5}N_{8.5}Nd$ (627.36 – loss of 0.5 pyridine): calcd. C 52.65, H 5.38, N 18.98; found C 52.36, H 5.56, N 18.41.

[Ho(Me₂pz)₃(thf)]₂ (5): Holmium filings (1.04 g, 6.31 mmol), 3,5dimethylpyrazole (1.04 g, 10.8 mmol) and bis(pentafluorophenyl)mercury (2.78 g, 5.20 mmol) in thf (40 mL) were heated to 60 °C with stirring for 2 h and then the reaction mixture was stirred for 10 d at room temperature. The mixture was then filtered, and the orange filtrate was concentrated under vacuum and crystallised from thf/hexane to give 5, yield 1.17 g (63%). IR (Nujol): $\tilde{v} = 1577$ (m), 1520 (vs), 1417 (vs), 1324 (s), 1301 (sh), 1175 (m), 1089 (w), 1068 (m), 1056 (w), 1034 (m), 1010 (m), 997 (m), 959 (m), 933 (w), 839 (w), 812 (m), 793 (m), 769 (m), 743 (w), 726 (m), 652 (m) cm⁻¹. C₃₈H₅₈Ho₂N₁₂O₂ (1044.82): calcd. C 44.02, H 4.86, N 16.21, Ho 31.82; found C 43.20, H 5.99, N 16.59, Ho 31.38.

[Yb(Me₂pz)₃(thf)]₂ (6): Ytterbium filings (1.09 g, 6.30 mmol), 3,5dimethylpyrazole (1.04 g, 10.8 mmol) and bis(pentafluorophenyl)mercury (2.78 g, 5.20 mmol) in thf (40 mL), were stirred for 15 min at room temperature and then filtered, resulting in a bright-orange solution. A peach-coloured, powdery solid precipitated from the filtrate on cooling that was not soluble in thf, thf/hexane, toluene, or pyridine, yield 0.70 g (33%). Metal analysis calculated for **6** (immediately on isolation) $C_{38}H_{58}N_{12}O_2Yb_2$ (1061.02) calcd. Yb 32.62; found Yb 32.46. After extended drying of the sample: IR: \tilde{v} = 1575 (w), 1526 (vs), 1406 (vs), 1342 (w), 1303 (vs), 1147 (w), 1066 (s), 1026 (vs), 981 (m), 778 (s), 736 (s), 721 (m) cm⁻¹. Microanalysis calculated for [Yb(Me₂pz)₃], $C_{15}H_{21}N_6Yb$ (458.41, loss of thf): C 39.30, H 4.62, N 18.33; found C 39.51, H 4.55, N 17.91. Note: When the reaction mixture was stirred for > 15 min, the mixture darkened and a dark-grey solution was obtained on filtration.

 $[Lu(Me_2pz)_3(thf)]_2$ (7): Lutetium metal fillings (0.32 g, 1.8 mmol), $Hg(C_6F_5)_2$ (0.86 g, 1.6 mmol) and Me_2pzH (0.31 g, 3.2 mmol) were

dissolved in thf (5 mL) with stirring at room temperature. After 14 h, a small amount of solution was analysed by ¹⁹F NMR spectroscopy, which indicating complete consumption of Hg(C₆F₅)₂ and formation of C₆F₅H. The reaction mixture was filtered and the filtrate was evaporated under vacuum to give a white powder. The powder was dissolved in hot thf (5 mL) and slowly cooled to produce small clear hexagonal crystals of **7**, yield 0.30 g (53%). ¹H NMR (300 MHz, C₆D₆, 333.2 K): δ = 1.45 [m, 8 H, β -CH₂(thf)], 1.95 (s, 36 H, Me), 3.57 [m, 8 H, α -CH₂(thf)], 5.77 (s, 6 H, H4) ppm. IR (Nujol): $\tilde{\nu}$ = 3108 (w), 1655 (vw), 1578 (m), 1522 (m), 1417 (vs), 1377 (s), 1326 (vs), 1261 (w), 1173 (vw), 1093 (m), 1073 (m), 1037 (s), 1011 (s), 980 (s), 934 (w), 915 (vw), 840 (w), 813 (s), 792 (s), 772 (s), 725 (m) cm⁻¹. C₃₈H₅₈Lu₂N₁₂O₂ (1064.90): calcd. C 42.86, H 5.49, N 15.78; found C 42.84, H 5.54, N 15.68.

Structure Determination: Full spheres of CCD area-detector diffractometer data were measured (ω -scans, monochromatic Mo- K_a radiation, $\lambda = 0.7107_3$ Å), yielding $N_{t(otal)}$ reflections, merging to Nunique reflections after empirical/multiscan absorption correction (R_{int} cited) using either the Apex II program suite,^[23] or SOR-TAV,^[24] with these data being used in the full-matrix least square refinements on F^2 , refining anisotropic displacement parameter forms for the non-hydrogen atoms, hydrogen atom treatment following a riding model. N_o reflections with $I > 2\sigma(I)$ may be considered "observed"; reflection weights were $[\sigma^2(F_o^2) + (aP)^2 (+bP)]^{-1}$ $[P = (F_o^2 + 2F_c^2)/3]$, computation using SHELX software^[25] with the Olex 2 graphical interface.^[26] Pertinent results are presented in the Tables and Figures, with the latter showing the non-hydrogen atoms with 50% probability amplitude displacement envelopes.

CCDC-981984 (for **2a**), -981985 (for **2b**), -981986 (for **3**), -959093 (for **5**), -981988 (for **7**), and -981989 (for **8**) (Table 1) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Further crystallographic data..

Table 1. Crystal/refinement data.[a]

	2b (Ce) ^[b]	2a (Ce) ^[c]	3 (Pr) ^[c]	5 (Ho) ^[c]	7 (Lu) ^[c]	8 (Nd) ^[d]
M _r [Da]	1043.3	995.2	996.8	1044.8	1064.9	666.9
Crystal system	triclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic
Space group	P1 (#2)	$P2_1/n$ (#14)	$P2_1/n$ (#14)	P1 (#2)	P1 (#2)	P1 (#2)
a [Å]	9.1695(2)	11.9695(2)	11.9284(5)	10.6592(6)	10.6049(2)	10.789(2)
b [Å]	12.1187(3)	14.1574(3)	14.2014(7)	10.7415(6)	10.6509(2)	17.481(4)
c [Å]	12.5199(3)	12.8426(2)	12.7677(6)	11.1470(6)	11.0844(2)	19.773(4)
	113.863(1)			77.732(1)	81.831(1)	70.81(3)
β ^[°]	93.963(1)	97.184(1)	97.095(4)	69.029(1)	69.233(1)	64.29(3)
γ [°]	111.751(1)			60.267(1)	60.403(1)	89.07(3)
V [Å ³]	1141.76(5)	2159.18(7)	2146.3(2)	1033.9(2)	1017.07(3)	3138(2)
$D_{c} [g cm^{-3}] (Z)$	$1.51_7(2)$	$1.53_{1}(2)$	$1.54_{2}(2)$	$1.67_{8}(1)$	$1.73_{9}(1)$	$1.41_{2}(4)$
$\mu_{M_0} [mm^{-1}]$	2.0	2.1	2.3	3.9	4.9	1.69
Specimen [mm ³]	0.3, 0.3, 0.2	0.4, 0.1, 0.1	0.1, 0.05, 0.01	0.25, 0.22, 0.18	0.2, 0.1, 0.1	0.25, 0.18, 0.13
$T'_{\rm min/max}$	0.94	0.71	0.74	0.77	0.88	0.74
$2\theta_{\rm max}$ (deg.)	58	59	50	72	61	50
N _t	49552	19508	16421	20979	16671	38934
$N(R_{int})$	6115 (0.025)	5803 (0.029)	3766 (0.062)	9640 (0.018)	5962 (0.015)	11011 (0.067)
$N_{0}[I > 2\sigma(I)]$	5706	5075	3136	9201	5719	9003
RI $[I > 2\sigma(I)]$	0.019	0.032	0.057	0.015	0.013	0.043
wR2 (all data)	0.052	0.072	0.14	0.040	0.047	0.12
a(, b)	0.030, 0.78	0.007, 7.6	0.042, 22	0.022, 0.45	0.026, 0.03	0.071, 4.7
S	1.09	1.18	1.20	1.06	1.24	1.03
$ \Delta \rho_{\rm max} $ [e Å ⁻³]	1.4	1.3	3.3	1.3	0.65	3.7
<i>T</i> [K]	100	100	100	153	123	123

[a] For the Ln = Y analogue,^[10] triclinic $P\overline{I}$ (#2) the recorded dimensions are 10.798(1), 10.808(1), 11.313(1) Å, 76.914(2), 68.940(2), 60.510(2)°, V = 1071.5(2) Å³ (T not specified). [b] C₄₀H₅₈Ce₂N₁₆. [c] C₃₈H₅₈Ln₂N₁₂O₂. [d] C₃₀H₃₆N₉Nd.

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Rare-Earth Complexes

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The Synthesis, Structures and Polymorphism of the Dimeric Trivalent Rare-Earth 3,5-Dimethylpyrazolate Complexes $[Ln(Me_2pz)_3(thf)]_2$

Keywords: Lanthanides / Rare earths / N ligands / Bridging ligands / Structure elucidation / Chelates



Contrasting structures and bridging Me_2pz groups for Ln = La-Pr and Ln = Nd-Lu are described.