

Bis(1,3-diphenylpropane-1,3-dionato- κ^2O,O'){hydrotris[3-(2-pyridyl)pyrazol-1-yl]borato}praseodymium(III): another member of an unpredictable series

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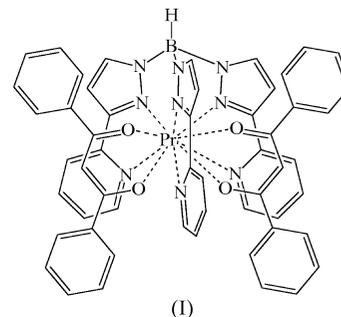
Reaction of praseodymium(III) chloride with stoichiometric quantities of dibenzoylmethane (Hdbm) and hydrotris[3-(2-pyridyl)pyrazol-1-yl]borate ($\text{Tp}^{2\text{py}}$) affords the title complex, $[\text{Pr}(\text{C}_{24}\text{H}_{19}\text{BN}_9)(\text{C}_{15}\text{H}_{11}\text{O}_4)_2]$. The lanthanide ion in this ternary complex exhibits an N_6O_4 ten-coordinate geometry arising from the five bidentate arms found on the anionic ligands. The structure is entirely different from those found in other lanthanide complexes with the same ligand set.

Comment

Since their introduction, poly(pyrazolyl)borate ligands [for a review, see Trofimenko (1993)] have proved extremely popular for the coordination chemistry of lanthanide(III) ions (Marques *et al.*, 2002). This is largely for two reasons: firstly, their multiple denticity, hard donor set and single negative charge are ideally attractive to the hard lanthanide(III) cations; secondly, the ease with which substituents can be added at the 3- and 5-positions of the pyrazolyl rings allows fine-tuning of the size of the ligand cavity. We have been interested in both the structural and photophysical properties of such complexes (Amoroso *et al.*, 1994; Bardwell *et al.*, 1997; Jones *et al.*, 1997; Armaroli *et al.*, 1999; Reeves *et al.*, 1999; Beeby *et al.*, 2002), particularly with the ligand hydrotris[3-(2-pyridyl)pyrazol-1-yl]borate ($\text{Tp}^{2\text{py}}$), in which the pyrazolyl rings are functionalized with 2-pyridyl substituents, creating a hexadentate podand-type ligand.

We have used dbm (Hdbm is dibenzoylmethane) as a co-ligand in order to exclude solvent molecules from the coordination sphere of the metal ion, which is essential for optimization of the photophysical properties of lanthanide(III) complexes (Beeby *et al.*, 1999), and have recently structurally characterized two types of mixed-ligand $\text{Tp}^{2\text{py}}/\text{dbm}$ complex with lanthanide(III) ions. In eight-coordinate $[\text{Ln}(\text{Tp}^{2\text{py}})(\text{dbm})_2]$ (Ln is Eu or Tb), one of the three bidentate arms of

$\text{Tp}^{2\text{py}}$ is pendant, such that this ligand is only tetradentate and the metal centre has an N_4O_4 coordination sphere (Ward *et al.*, 1999; Davies *et al.*, 2004). In contrast, $[\text{Nd}(\text{Tp}^{2\text{py}})_2][\text{Nd}(\text{dbm})_4]$ contains 12-coordinate $[\text{Nd}(\text{Tp}^{2\text{py}})_2]^+$ cations and eight-coordinate $[\text{Nd}(\text{dbm})_4]^-$ anions, the former with an icosahedral N_{12} coordination and the latter with unusual O_8 cubic geometry (Davies *et al.*, 2004). In this paper, we report a new structural type in this series, the title compound, $[\text{Pr}(\text{Tp}^{2\text{py}})(\text{dbm})_2]$, (I), which is ten-coordinate, with the Pr^{III} ion in an N_6O_4 environment with all three chelating arms of $\text{Tp}^{2\text{py}}$ attached to the metal centre.



Complex (I) (Fig. 1) was prepared by the reaction of praseodymium(III) chloride hydrate with $\text{KTp}^{2\text{py}}$ and Hdbm (1:1:2 molar ratio) in aqueous methanol with a few drops of triethylamine added. By comparison with the analogous Eu^{III} and Tb^{III} structures, the original concept of the ligand design is achieved in this case, with all three arms of the $\text{Tp}^{2\text{py}}$ molecule chelating to the Pr^{III} ion. The larger ionic radius of Pr^{III} allows the two dbm units to coordinate without displacing one of the arms of the scorpionate, in contrast with the behaviour shown

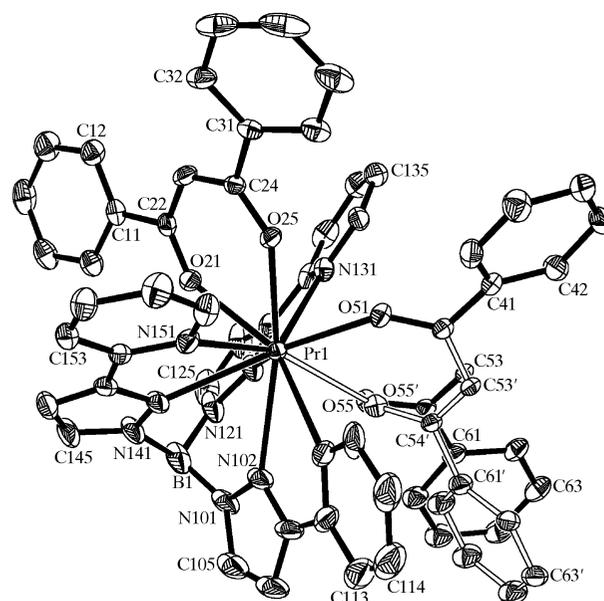


Figure 1

A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms have been omitted for clarity.

by the smaller ions Eu^{III} and Tb^{III} . This places the metal ion in a ten-coordinate N_6O_4 coordination environment, with all five chelating units (three pyrazolyl-pyridine units and two dbm ligands) being approximately parallel to one another.

Many ten-donor coordination spheres exist among Pr^{III} complexes, although only two previous examples of N_6O_4 environments have been reported to date (Jones *et al.*, 1997; Tamboura *et al.*, 2004). The Pr–N and Pr–O bond lengths are unremarkable, with averages of 2.652, 2.738, and 2.469 Å for the Pr–N_{pz}, Pr–N_{py} and Pr–O bonds (pz is pyrazolyl and py is pyridyl), respectively, all of which are understandably longer than those of the Eu^{III} and Tb^{III} analogues.

The coordination geometry of (I) does not obviously match any of the ‘ideal’ arrangements of ten-coordination (Kepert, 1987). The best way of looking at the coordination geometry is down the N122–Pr1 bond (Fig. 2). The other two pyrazole N atoms, N102 and N142, form a pentagon with pyridyl atom N131 and atoms O55 and O21 from the dbm units. The average edge length and angle for this pentagon are 2.818 Å and 107.6°, respectively, using O55; if O55' is used instead, these values become 2.871 Å and 106.9°, respectively. These five atoms display an average deviation from their mean plane of 0.095 (if O55 is used) or 0.180 Å (if O55' is used). The pentagon is capped by atom N122, while on the other side of the pentagon resides a distorted square described by atoms O25, N151, N111 and O51. This ‘square’ has an average edge of 2.983 Å and an average angle of 89.5° at its corners, but is rather irregular, with the corner angles varying from 75.50 to 102.31°. The mean deviation from the plane of these four atoms is 0.135 Å.

In conclusion, the contrast of this structure with those of the Eu^{III} , Tb^{III} and Nd^{III} analogues with the same stoichiometry is remarkable. The difference between this Pr^{III} structure and the eight-coordinate complexes with Tb^{III} and Eu^{III} can be rationalized on the basis of the larger ionic radius of Pr^{III} . The contrast with the structure of $[\text{Nd}(\text{Tp}^{2\text{py}})_2][\text{Nd}(\text{dbm})_4]$ is less easy to explain. It is possible that there is an equilibrium mixture of structural types in solution which is perturbed in one direction or another by crystallization. We examined

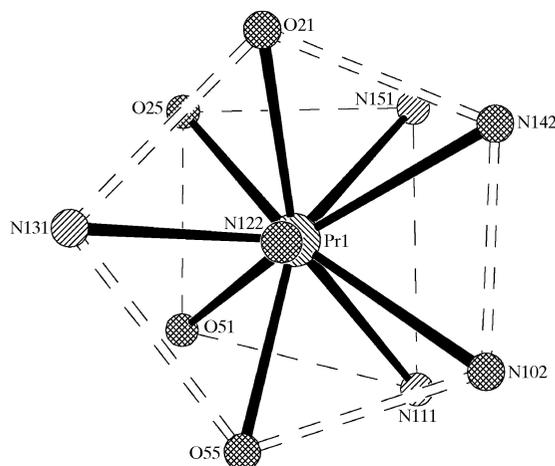


Figure 2
The coordination geometry about the Pr^{III} ion in (I). Only the major component of the disorder is shown.

several crystals of (I) and found them all to have the same unit cell.

Experimental

$\text{KTp}^{2\text{py}}$ was prepared according to the published method of Amoroso *et al.* (1994). $\text{KTp}^{2\text{py}}$ (202 mg, 0.42 mmol) in MeOH (5 ml) was added to a solution of $\text{PrCl}_3 \cdot 6\text{H}_2\text{O}$ (148 mg, 0.42 mmol) in MeOH (5 ml) and allowed to stir for 5 min at room temperature. A solution of Hdbm (188 mg, 0.84 mmol) in MeOH (5 ml) with Et_3N (1 ml) was added and, after a further 5 min, water (20 ml) was added, generating a lime-green precipitate. The product was isolated by filtration and slowly recrystallized by the layering of hexanes onto a concentrated solution of the product in dichloromethane. After 5 d, the green crystals which formed were collected by filtration and washed with hexane and ether to give (I) in 67% yield. IR: $\nu_{(\text{B-H})}$ 2444 cm^{-1} . Analysis found: C 62.2, H 4.0, N 12.0%; calculated for $[\text{Pr}(\text{C}_{24}\text{H}_{19}\text{BN}_9)(\text{C}_{15}\text{H}_{11}\text{O}_4)_2]$: C 61.8, H 4.1, N 12.0%. FAB–MS gave a strong peak at $m/z = 808$, corresponding to the loss of one dbm unit to give the fragment $\{\text{Pr}(\text{Tp}^{2\text{py}})(\text{dbm})\}^+$; a weaker signal at $m/z = 1029$ suggested the presence of the $\{\text{Pr}(\text{Tp}^{2\text{py}})(\text{dbm})_2\}$ unit minus two H atoms. The crystals were suitable for single-crystal X-ray diffraction and were completely air-stable. A suitable crystal was coated in engine oil to clean it of subsidiary grains.

Crystal data

$[\text{Pr}(\text{C}_{24}\text{H}_{19}\text{BN}_9)(\text{C}_{15}\text{H}_{11}\text{O}_4)_2]$	$Z = 2$
$M_r = 1031.68$	$D_x = 1.476 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 11.6308 (15) \text{ \AA}$	Cell parameters from 4832 reflections
$b = 11.9248 (16) \text{ \AA}$	$\theta = 4.7\text{--}54.6^\circ$
$c = 18.569 (2) \text{ \AA}$	$\mu = 1.11 \text{ mm}^{-1}$
$\alpha = 96.558 (2)^\circ$	$T = 150 (2) \text{ K}$
$\beta = 106.782 (2)^\circ$	Block, green
$\gamma = 105.669 (2)^\circ$	$0.34 \times 0.25 \times 0.18 \text{ mm}$
$V = 2321.9 (5) \text{ \AA}^3$	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	8143 independent reflections
ω scans	7003 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.032$
$T_{\text{min}} = 0.705, T_{\text{max}} = 0.826$	$\theta_{\text{max}} = 25.0^\circ$
22 669 measured reflections	$h = -13 \rightarrow 13$
	$k = -14 \rightarrow 14$
	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0285P)^2 + 2.7047P]$
$R[F^2 > 2\sigma(F^2)] = 0.033$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.074$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.73 \text{ e \AA}^{-3}$
8143 reflections	$\Delta\rho_{\text{min}} = -0.72 \text{ e \AA}^{-3}$
680 parameters	
H-atom parameters constrained	

One of the dbm units was shown to contain disorder about atom C52. The disordered phenyl ring was constrained to ideal geometry and the disorder was modelled over two sites, with refined site occupancies of 0.514 (3) and 0.486 (3). All H atoms were positioned geometrically and refined with a riding model, with C–H = 0.93 Å for aromatic rings and 0.96 Å for disordered rings, and with B–H = 1.07 Å. In all cases, $U_{\text{iso}}(\text{H})$ values were constrained to be $1.2U_{\text{eq}}$ of the carrier atom.

Data collection: XSCANS (Siemens, 1996); cell refinement: XSCANS; data reduction: SHELXTL (Bruker, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s)

used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Table 1

Selected geometric parameters (Å, °).

Pr1—O55	2.448 (17)	Pr1—N142	2.656 (3)
Pr1—O25	2.454 (2)	Pr1—N131	2.656 (3)
Pr1—O51	2.464 (2)	Pr1—N102	2.704 (3)
Pr1—O55'	2.492 (17)	Pr1—N151	2.754 (3)
Pr1—O21	2.496 (2)	Pr1—N111	2.804 (3)
Pr1—N122	2.595 (3)		
O55—Pr1—O25	128.4 (6)	O55—Pr1—N102	65.5 (6)
O55—Pr1—O51	71.7 (5)	O25—Pr1—N102	163.61 (8)
O25—Pr1—O51	65.89 (7)	O51—Pr1—N102	117.95 (9)
O55—Pr1—O55'	9.0 (6)	O55'—Pr1—N102	66.0 (7)
O25—Pr1—O55'	126.1 (6)	O21—Pr1—N102	113.69 (9)
O51—Pr1—O55'	65.2 (5)	N122—Pr1—N102	68.87 (11)
O55—Pr1—O21	129.8 (4)	N142—Pr1—N102	59.51 (9)
O25—Pr1—O21	65.98 (7)	N131—Pr1—N102	122.86 (9)
O51—Pr1—O21	128.16 (7)	O55—Pr1—N151	150.3 (5)
O55'—Pr1—O21	138.5 (4)	O25—Pr1—N151	65.76 (8)
O55—Pr1—N122	69.4 (3)	O51—Pr1—N151	98.08 (8)
O25—Pr1—N122	121.82 (9)	O55'—Pr1—N151	142.4 (4)
O51—Pr1—N122	131.58 (8)	O21—Pr1—N151	78.77 (8)
O55'—Pr1—N122	78.1 (4)	N122—Pr1—N151	129.64 (9)
O21—Pr1—N122	65.02 (9)	N142—Pr1—N151	58.98 (9)
O55—Pr1—N142	121.4 (6)	N131—Pr1—N151	135.59 (9)
O25—Pr1—N142	109.44 (8)	N102—Pr1—N151	97.90 (9)
O51—Pr1—N142	154.01 (9)	O55—Pr1—N111	74.0 (5)
O55'—Pr1—N142	124.5 (7)	O25—Pr1—N111	113.86 (9)
O21—Pr1—N142	63.44 (9)	O51—Pr1—N111	68.63 (9)
N122—Pr1—N142	73.55 (9)	O55'—Pr1—N111	66.3 (5)
O55—Pr1—N131	71.2 (6)	O21—Pr1—N111	151.93 (8)
O25—Pr1—N131	73.08 (8)	N122—Pr1—N111	124.18 (10)
O51—Pr1—N131	79.07 (8)	N142—Pr1—N111	92.39 (10)
O55'—Pr1—N131	76.8 (6)	N131—Pr1—N111	138.32 (9)
O21—Pr1—N131	69.66 (8)	N102—Pr1—N111	58.02 (11)
N122—Pr1—N131	61.99 (9)	N151—Pr1—N111	76.31 (9)
N142—Pr1—N131	125.31 (9)		

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1380). Services for accessing these data are described at the back of the journal.

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