

Complexes of main-group elements containing stereochemically active lone pairs: the crystal structures of $[\text{Tl}(\text{Tp}^{\text{An}})]$ $\{\text{Tp}^{\text{An}} = \text{tris}[3-(2\text{-methoxyphenyl})\text{pyrazol-1-yl}]\text{hydroborate}\}$ and $[\text{Pb}(\text{Tp}^{\text{Py}})(\text{NO}_3)] \cdot 0.5\text{Et}_2\text{O}$ $\{\text{Tp}^{\text{Py}} = \text{tris}[3-(2\text{-pyridyl})\text{pyrazol-1-yl}]\text{hydroborate}\}$

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Abstract—The new podand ligand tris[3-(2-methoxyphenyl)pyrazol-1-yl]hydroborate (Tp^{An}) has been prepared and the crystal structure of $[\text{Tl}(\text{Tp}^{\text{An}})]$ determined. The metal ion is in a trigonal pyramidal geometry arising from the three pyrazolyl N-donors, with the lone pair of the Tl^{I} ion in the fourth position of the tetrahedron of electron pairs. There is also a weak but significant interaction with one of the anisyl oxygen atoms ($\text{Tl} \cdots \text{O} = 3.018 \text{ \AA}$), and the displacement of the metal ion towards this oxygen atom results in a noticeable lengthening of the $\text{Tl}-\text{N}(\text{pyrazolyl})$ bond which lies approximately *trans* to it (2.70 \AA , compared with 2.54 \AA for the other two $\text{Tl}-\text{N}$ bonds). The crystal structure of $[\text{Pb}(\text{Tp}^{\text{Py}})(\text{NO}_3)] \cdot 0.5\text{Et}_2\text{O}$ shows that the Pb^{II} ion has four strong interactions (with the pyrazolyl nitrogen atoms and one of the nitrate oxygen atoms; range of bond lengths $2.49\text{--}2.67 \text{ \AA}$) and four weak ones (with the pyridyl nitrogen atoms and the other nitrate oxygen atom; range of bond lengths $2.80\text{--}2.99 \text{ \AA}$). If only the four stronger interactions are considered, the irregular coordination sphere of the Pb^{II} ion has an obvious gap in it which is the site of the stereochemically active lone pair. © 1997 Elsevier Science Ltd

Keywords: tris(pyrazolyl)borate; lead; thallium; crystal structures.

As part of our studies on the coordination behaviour of podand ligands derived from tris(pyrazolyl)borates we have become interested in the structures of complexes with non-transition-metal ions [1–4]. One can see how the coordination behaviour of the ligands is determined by the size and charge alone of the metal ions, without competing stereoelectronic preferences arising from the partially filled *d*-shell of the metal ions. Our recent studies have concentrated on the hexadentate N-donor podand tris[3-(2-pyridyl)pyrazol-1-yl]hydroborate (Tp^{Py}). In $[\text{Tl}(\text{Tp}^{\text{Py}})]$ for example the Tl^{I} ion is coordinated principally by the three pyrazolyl donors, with much weaker interactions with the remote pyridyl donors; in contrast,

using Ag^{I} —which is of a similar size and has the same charge as Tl^{I} —the unusual cluster complex $[\text{Ag}_3(\text{Tp}^{\text{Py}})_2]^+$ forms in which a triangular cluster is encapsulated by two podand ligands [1]. Lanthanide [2,3] and actinide [4] ions are large enough to occupy the cavity fully resulting in donation of all six N-donor atoms to a single metal centre. In this paper we describe the crystal structure of the Pb^{II} complex of this podand, $[\text{Pb}(\text{Tp}^{\text{Py}})(\text{NO}_3)]$.

In an effort to prepare related podand ligands with different donor sets, we have also synthesized tris[3-(2-methoxyphenyl)pyrazol-1-yl]hydroborate (Tp^{An} , where the suffix “An” denotes the 2-anisyl substituents on the pyrazolyl rings). This could act as an N_3O_3 donor if the ether oxygen atoms coordinate or just as a conventional terdentate tris(pyrazolyl)borate with bulky aryl substituents shielding the metal centre

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[5] if they do not. The synthesis of this ligand and the crystal structure of its thallium(I) complex [Tl(Tp^{An})] are described in this paper.

EXPERIMENTAL

Electron-impact (EI) and fast-atom bombardment (FAB) mass spectra were recorded on a VG-Auto-spec; ¹H NMR spectra were recorded with a Jeol Lambda-300 spectrometer. The ligand [Tp^{Py}]⁻ (as its potassium salt) was prepared according to the published method [2]. Reagents were purchased from Aldrich, Lancaster or Avocado and used as received.

Preparation of 1-(2'-methoxyphenyl)-3-dimethylamino-2-propene-1-one (A)

A solution of 2-methoxyacetophenone (15.02 g, 0.1 mol) in dimethylformamide-dimethylacetal (20 cm³, a large molar excess) was heated to reflux for 10 h under N₂ to yield a red solution. Removal of excess dimethylformamide-dimethylacetal *in vacuo* afforded an oily red liquid. The pure product A (13.1 g, 64%) was obtained from this by vacuum distillation (184–188°C, 1.5 mm Hg). EI-MS: *m/z* = 205 (M⁺). ¹H NMR (300 MHz, *d*₆-acetone): δ 7.46 (2 H, m, phenyl H⁶ and vinylic CH), 7.32 (1 H, ddd, *J* = 8.2, 7.3, 1.8; phenyl H⁵), 6.99 (1 H, d, *J* = 7.7; phenyl H³), 6.94 (1 H, td, *J* = 7.4, 1.1; phenyl H⁴), 5.55 (1 H, d, *J* = 12.8 Hz; vinylic CH), 3.79 (3 H, s; OCH₃), 2.96 (3 H, s; NCH₃), 2.91 (3 H, s; NCH₃). Found: C, 69.8; H, 7.4; N, 6.5. C₁₂H₁₅NO₂ requires: C, 70.2; H, 7.4; N, 6.8%.

Preparation of 3-(2-methoxyphenyl)pyrazole (B)

To a solution of A (12.64 g, 0.062 mol) in EtOH (20 cm³) was added hydrazine hydrate (17 cm³, a large excess). The mixture was heated to reflux in air for 30 min. The yellow solution was cooled and water (150 cm³) added, affording a white precipitate. The mixture was refrigerated overnight to allow precipitation of the product to complete. The solid was filtered off, washed with cold water (50 cm³) and then pentane (50 cm³) and dried *in vacuo*. Subsequent recrystallization from CHCl₃/hexane afforded white microcrystals of B (8.7 g, 81%). EI-MS: *m/z* = 174 (M⁺). ¹H NMR (300 MHz, CD₂Cl₂): δ 11.5 (1 H, broad s; pyrazole NH), 7.71 (1 H, dd, *J* = 8.0, 1.8; phenyl H⁶), 7.58 (1 H, d, coupling unresolved; pyrazole H⁵), 7.32 (1 H, td, *J* = 8.2, 1.8 Hz; phenyl H⁵), 7.04 (2 H, m; phenyl H³/H⁴), 6.68 (1 H, d, coupling unresolved; pyrazole H⁴), 3.98 (3 H, s; OCH₃). Found: C, 69.2; H, 6.0; N, 16.1. C₁₀H₁₀N₂O requires: C, 69.0; H, 5.8; N, 16.1%.

Preparation of potassium tris[3-(2-methoxyphenyl)pyrazol-1-yl]hydroborate, K[Tp^{An}]

A mixture of B (8.71 g, 0.05 mol) and KBH₄ (0.67 g, 0.013 mol) was ground together finely and then

heated gradually to 200°C (the mixture melted at *ca* 86°C). Evolution of H₂ commenced at *ca* 115°C. After 2 h at 200°C, H₂ evolution had ceased. The mixture was cooled and warm toluene (100 cm³) was added and the mixture stirred overnight. A sticky white solid could then be precipitated by addition of pentane (50 cm³). Vigorous stirring and treatment of the mixture in an ultrasound bath resulted in a tractable white powder which was filtered off, washed with pentane (100 cm³) and dried in air. This crude product was shown by IR to contain some unreacted B as well as the desired product. It was purified by Soxhlet extraction of unreacted B into dry refluxing hexane for 8 days. The solid residue in the Soxhlet thimble was dissolved in CH₂Cl₂ and re-precipitated by addition of hexane. The white solid was filtered off, washed with more hexane and dried *in vacuo* for several hours to afford K[Tp^{An}] (4.45 g, 61%). It is hygroscopic and best stored in a desiccator. EI-MS: *m/z* = 531 (M⁺ - K). IR (KBr disc): ν_{B-H} = 2423 cm⁻¹. ¹H NMR (300 MHz, *d*₆-acetone): δ 7.89 (1 H, dd, *J* = 7.7, 1.8; phenyl H⁶), 7.70 (1 H, d, *J* = 2.2; pyrazole H⁵), 7.17 (2 H, m; phenyl H³/H⁴), 6.89 (1 H, td, *J* = 7.5, 1.1; phenyl H⁵), 6.57 (1 H, d, *J* = 2.2 Hz; pyrazole H⁴), 3.82 (3 H, s; OCH₃). Due to the hygroscopic nature of this compound the elemental analytical data were rather poor and variable; however, the ¹H and ¹³C NMR spectra were clean.

Preparation of [Tl(Tp^{An})]

A solution of K[Tp^{An}] (0.15 g, 0.26 mmol) in MeOH (10 cm³) was added to a solution of thallium(I) formate (0.066 g, 0.26 mmol) in MeOH (10 cm³). A white precipitate appeared and the suspension was stirred for 15 min. The solid was then filtered off, washed with MeOH and dried *in vacuo* to give Tl(Tp^{An}) (0.063 g, 33%). FAB-MS: *m/z* = 737 (M⁺), 563 (M⁺ - one equivalent of B by B-N cleavage). IR (KBr disc): ν_{B-H} = 2432 cm⁻¹. Found: C, 48.7; H, 3.6; N, 11.0. C₃₀H₂₈N₆O₃BTL requires: C, 49.0; H, 3.8; N, 11.4%. X-ray quality crystals were grown by layering hexane onto a CH₂Cl₂ solution of the material and allowing the layers to mix.

Preparation of [Pb(Tp^{Py})(NO₃)]

A solution of K[Tp^{Py}] (0.242 g, 0.5 mmol) in MeOH (10 cm³) was added to a solution of Pb(NO₃)₂ (0.166 g, 0.5 mmol) in MeOH and the mixture was stirred at room temperature. The resulting white precipitate was collected by filtration, washed with MeOH and air-dried to give [Pb(Tp^{Py})(NO₃)] (0.31 g, 87%). FAB-MS: *m/z* = 652 [Pb(Tp^{Py})⁺]. IR (KBr disc): ν_{B-H} = 2479 cm⁻¹. Found: C, 40.7; H, 2.3; N, 19.2. C₂₄H₁₉N₁₀O₃BPb requires: C, 40.4; H, 2.7; N, 19.6%. X-ray quality crystals were grown by diffusion of diethyl ether vapour into a concentrated dmf solution of the material over several days.

Crystal structure determinations

Suitable crystals were coated with paraffin oil, mounted on a brass pin and quickly transferred to the diffractometer under a stream of cold N₂. Data were collected using a Siemens SMART three-circle diffractometer with a CCD area detector (173 K, graphite-monochromatized Mo-K_α X-radiation, $\lambda = 0.71073 \text{ \AA}$). Data were collected for Lorentz and polarization effects, and for absorption effects by an empirical method based on multiple measurements of equivalent data. Details of the crystal parameters, data collection and refinement are in Table 1, and bond lengths and angles are in Tables 2 and 3. The structures were solved by conventional direct or heavy-atom methods, and refined by the full-matrix least-squares method on all F^2 data, using the SHELX suite of programs [6] on a Silicon Graphics Indy computer. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in

calculated positions and refined with isotropic thermal parameters. The structure determination of [Tl(Tp^{An})] was straightforward, with one complex molecule per asymmetric unit.

Crystals of [Pb(Tp^{Py})(NO₃)]·0.5Et₂O lost solvent very rapidly and underwent substantial decomposition during the few seconds that it took to transfer them from the mother liquor to the cold N₂ stream on the diffractometer. Attempts to transfer small crystals resulted in very weak diffraction due to the extent of decomposition; for this reason we had to use a large crystal. This allowed us to collect a data set, but resulted inevitably in substantial absorption and a poor absorption correction, causing significant residual electron-density peaks near the Pb atom and a concomitant rather poor level of the refinement ($R_1 = 9.9\%$). The results described here are the best of several attempts. Each asymmetric unit contains two independent complex molecules and one molecule of ether which is disordered over two sites.

Table 1. Crystallographic data for the new complexes

Complex	[Tl(Tp ^{An})]	[Pb(Tp ^{Py})(NO ₃)]·0.5Et ₂ O
Formula	C ₃₀ H ₂₈ BN ₆ O ₃ Tl	C ₂₆ H ₂₃ BN ₁₀ O _{3.5} Pb
Formula weight	735.76	749.54
System, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
<i>a</i> (Å)	12.617(1)	20.670(3)
<i>b</i> (Å)	8.189(1)	21.649(4)
<i>c</i> (Å)	28.078(4)	13.552(2)
β (°)	90.15(1)	107.43(1)
Volume (Å ³)	2901.1(6)	5786(1)
<i>Z</i>	4	8
ρ_{calc} (g cm ⁻³)	1.685	1.721
μ (mm ⁻¹)	5.61	5.88
<i>F</i> (000)	1440	2912
Crystal size (mm)	0.5 × 0.1 × 0.1	0.5 × 0.6 × 0.7
2 θ range for data collection (°)	5–50	5–50
Temperature for data collection (K)	173	138
Total reflections collected	13,530	26,169
Independent data after merging	5102 ($R_{\text{int}} = 0.058$)	10058 ($R_{\text{int}} = 0.102$)
Data : parameter ratio	13.5	13.5
Final <i>R</i> indices ^{a,b}	$wR_2 = 0.103$ ($R_1 = 0.041$)	$wR_2 = 0.247$ ($R_1 = 0.099$)
Weighting factors ^b	$a = 0.0398$, $b = 23.41$	$a = 0.0385$, $b = 330.106$

^a Structure was refined on F_0^2 using all data; the value of R_1 in parentheses is given for comparison with older refinements based on F_0 with a typical threshold of $F \geq 4\sigma(F)$.

^b $wR_2 = [\sum(w(F_0^2 - F_c^2)^2)/\sum w(F_0^2)^2]^{1/2}$, where $w^{-1} = [\sigma^2(F_0^2) + (aP)^2 + bP]$ and $P = [\max(F_0^2, 0) + 2F_c^2]/3$.

Table 2. Selected internuclear distances (Å) and bond angles (°) for [Tl(Tp^{An})]

Tl—N(32)	2.540(6)	Tl···O(27)	6.007 ^a
Tl—N(52)	2.543(6)	Tl···O(47)	3.382 ^a
Tl—N(12)	2.697(6)	Tl···O(67)	3.018 ^a
N(32)—Tl—N(52)	72.6(2)	N(11)—B—N(51)	111.2(6)
N(32)—Tl—N(12)	73.3(2)	N(11)—B—N(31)	111.2(6)
N(12)—Tl—N(52)	75.3(2)	N(31)—B—N(51)	108.8(6)

^aThese distances are above those recognized as normal bonds by the software; consequently estimated standard deviations are not provided in the output.

Table 3. Selected internuclear distances (Å) and bond angles (°) for [Pb(Tp^{Py})(NO₃)] · 0.5Et₂O

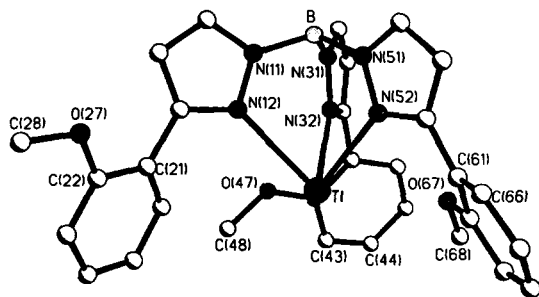
Pb(1)—N(112)	2.51(2)	Pb(2)—N(212)	2.49(2)
Pb(1)—N(152)	2.53(2)	Pb(2)—N(252)	2.50(2)
Pb(1)—N(132)	2.59(2)	Pb(2)—N(232)	2.60(2)
Pb(1)—O(11)	2.649(14)	Pb(2)—O(21)	2.666(14)
Pb(1)—N(162)	2.800(14)	Pb(2)—N(262)	2.87(2)
Pb(1)—N(122)	2.91(2)	Pb(2)—N(222)	2.83(2)
Pb(1)—N(142)	2.99(2)	Pb(2)—N(242)	2.91(2)
Pb(1)—O(12)	2.969(14)	Pb(2)—O(22)	2.976(13)
N(112)—Pb(1)—N(152)	75.1(5)	N(212)—Pb(2)—N(252)	75.1(6)
N(112)—Pb(1)—N(132)	71.3(5)	N(212)—Pb(2)—N(232)	71.0(6)
N(152)—Pb(1)—N(132)	71.9(5)	N(252)—Pb(2)—N(232)	72.1(6)
N(112)—Pb(1)—O(11)	78.3(4)	N(212)—Pb(2)—O(21)	78.1(5)
N(132)—Pb(1)—O(11)	145.0(4)	N(232)—Pb(2)—O(21)	142.7(5)
N(152)—Pb(1)—O(11)	84.1(5)	N(252)—Pb(2)—O(21)	80.2(5)

RESULTS AND DISCUSSION

The synthesis of the new ligand potassium tris[3-(2-methoxyphenyl)pyrazol-1-yl]hydroborate K[Tp^{An}] follows the method used for the related ligand potassium tris[3-(4-methoxyphenyl)pyrazol-1-yl]hydroborate [7,8], in which the methoxy substituent cannot coordinate. Moving this substituent to the 2-position of the phenyl ring means that each arm of the ligand now has the potential to act as an N,O-bidentate donor if the ether oxygen atom coordinates.

The crystal structure of the thallium(I) complex [Tl(Tp^{An})] is in Fig. 1; selected bond lengths and angles are in Table 2. The metal ion is basically in a three-coordinate pyramidal environment, attached to the pyrazolyl nitrogen donor atoms but not to the ether oxygen atoms. However, closer inspection reveals the involvement of at least one of the oxygen atoms in a weak but definite long-range interaction with the metal centre.

The related Tl^I complexes [Tl(Tp^{Tol})] and [Tl(Tp^{Bu})] (where the superscripts Tol and Bu¹ denote *p*-tolyl and tertiary-butyl substituents respectively attached at the pyrazolyl C³ positions, based on sterically hindering tris(pyrazolyl)borate derivatives, are genuinely three-coordinate as there are no other N-donor atoms present in the ligands. In these complexes the Tl—N bond distances all lie in the range 2.57–2.59

Fig. 1. Crystal structure of [Tl(Tp^{An})].

Å [9,10]. In contrast, in [Tl(Tp^{Py})] we observed that weak interactions with the pyridyl nitrogen atoms [Tl...N(pyridyl) = 3.09–3.26 Å] resulted in a slight lengthening of the Tl—N(pyrazolyl) bonds which had lengths in the region 2.64–2.70 Å. Thus, the Tl—N(pyrazolyl) distances are diagnostic of the presence of other weak bonding interactions to the metal centre. In [Tl(Tp^{An})] two of the Tl—N distances are quite short (2.540 and 2.543 Å), but the Tl—N(12) bond is much longer (2.697 Å). The oxygen atom [O(67)] which is approximately *trans* to N(12) is quite close to the metal, with the Tl...O(67) distance being 3.018 Å. This Tl...O separation is indicative of a weak bonding interaction [cf. the Tl—N(pyridyl) distances in [Tl(Tp^{Py})] and the resulting displacement of the metal atom towards this oxygen atom has resulted in a lengthening of the Tl—N(12) bond. The remaining two Tl...O separations are 3.382 [to O(47)] and 6.007 Å [to O(27)]. The former of these may correspond to a very weak interaction but the latter clearly does not. The Tl^I centre is therefore in an approximate “3+1” coordination, with three strong bonds to nitrogen and one much weaker one to O(67). If only the strong bonds are considered as significant, then the geometry about the Tl^I is trigonal pyramidal, with the stereochemically active lone pair of the Tl^I being considered to occupy the fourth (vacant) coordination site of a tetrahedron, as was observed also in [Tl(Tp^{Py})] [1], [Tl(Tp^{Tol})] [9] and [Tl(Tp^{Bu})] [10]. Recently a similar three-coordinate pyramidal structure has also been observed for [In(Tp^{Ph})] [11].

The separations between the Tl atom and the ether oxygen atoms are related to the torsion angle between the linked pyrazolyl and phenyl rings. If we take a coplanar conformation with the oxygen atom directed towards the metal as constituting a torsion angle of 0°, and number the six ring systems according to the first numeral of the crystallographic labelling scheme [i.e. atoms N(11)–C(15) constitute ring 1, and so on], then the three torsion angles are: rings 1 and 2, 143°; rings 3 and 4, 56°; rings 5 and 6, 42°. Thus ring 2 is twisted away from the metal, resulting in the

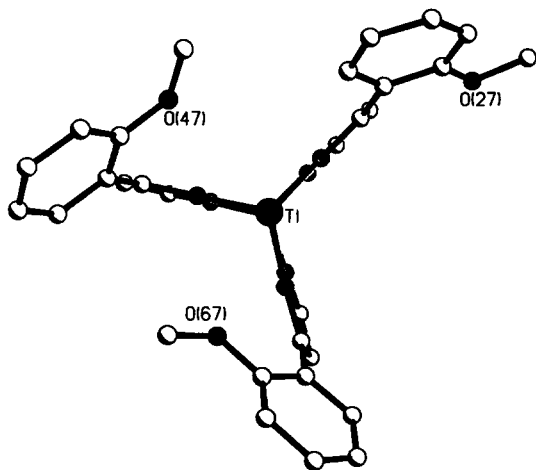


Fig. 2. Alternative view of the crystal structure of $[\text{Tl}(\text{Tp}^{\text{An}})]$ emphasizing the disposition of the phenyl rings.

$\text{Tl} \cdots \text{O}(27)$ separation of 6.007 Å; likewise the close approach of O(67) to the metal is related to the relatively small degree of twist of the phenyl ring away from the plane of the pyrazolyl ring. This aspect of the structure is emphasized in Fig. 2.

Given the penchant of Tl^{I} for low coordination numbers, and the presence of a stereochemically active lone pair, it is not surprising that coordination of all three oxygen atoms does not occur. However, it is clear from this structure that with a suitable metal ion—possibly an oxophilic lanthanide(III) cation—the ligand could act as a hexadentate N_3O_3 donor, as has been seen in other podand ligands with ether oxygen atoms at the periphery of the cavity [12, 13].

The crystal structure of one of the two independent complex units of $[\text{Pb}(\text{Tp}^{\text{Py}})(\text{NO}_3)] \cdot 0.5\text{Et}_2\text{O}$ is shown in Fig. 3; selected bond lengths and angles are in Table 3. The metal ion is in a “4+4” coordination

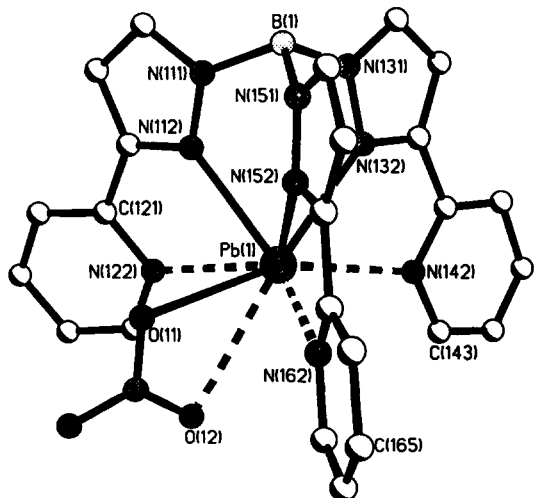


Fig. 3. Crystal structure of one of the independent complex units of $[\text{Pb}(\text{Tp}^{\text{Py}})(\text{NO}_3)] \cdot 0.5\text{Et}_2\text{O}$.

environment, with four short metal–ligand bonds and four long ones. The four short bonds in each independent complex cation are those involving the pyrazolyl nitrogen atoms (2.49–2.60 Å) and one of the nitrate oxygen atoms (2.65–2.67 Å); the four long bonds are those involving the pyridyl nitrogen atoms (2.80–2.99 Å) and the other nitrate oxygen atom (*ca* 2.97 Å). The coordination environment about the metal ion cannot therefore be conveniently described in terms of a simple geometry. It is noticeable that the nitrate is coordinated “off-centre”; it might be expected for steric reasons that it would coordinate centrally, approximately on the B—Pb axis. However, this may be explained if we assume that, as for the Tl^{I} complexes described above, the lone pair of the Pb^{II} centre is stereochemically active. Figure 4 depicts the two independent complex units together and only the four “normal” coordinate bonds are shown. It is clear from this that there is large gap in the coordination sphere approximately along the B—Pb vector, which will be where the lone pair is directed and which therefore explains the “off-centre” coordination of the nitrate ion which has moved out of its way. The partial interleaving of the two complex cations (Fig. 4), driven by the formation of a π -stacking interaction between the pyridyl rings containing N(142) and N(242), will also play a role in determining the distorted coordination geometry about the metal centres: the nitrate ion coordinated to Pb(1) is directed away from the intruding pyridyl ring from the other complex cation, and *vice versa*.

Geometries of this sort in other Pb^{II} complexes of poly(pyrazolyl)borates are known. In $[\text{Pb}\{\text{B}(\text{pz})_4\}_2]$ (pz = pyrazol-1-yl) each tetrakis(pyrazolyl)borate coordinates in a bidentate manner and the disposition of electron pairs about the metal ion is that of a distorted trigonal bipyramid with the lone pair occupying one of the equatorial sites [14]. $[\text{Pb}(\text{Tp}^{\text{Py}})(\text{NO}_3)]$ may be considered to be a highly distorted version of this. In $[\text{Pb}\{\text{HB}(\text{pz})_3\}_2]$ again the lone pair is evident; rather than being a regular octahedron, one of the faces of the octahedron is “opened out” with length-

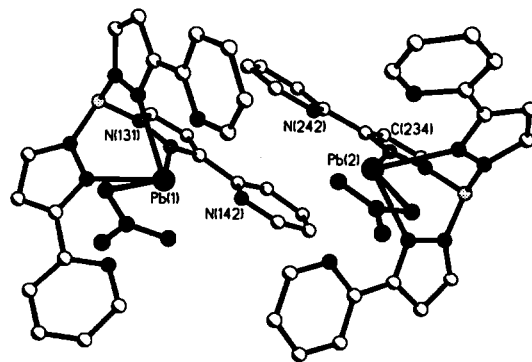


Fig. 4. Alternative view of the crystal structure of $[\text{Pb}(\text{Tp}^{\text{Py}})(\text{NO}_3)] \cdot 0.5\text{Et}_2\text{O}$, showing the interpenetration of the two independent complex units.

ening of the three Pb—N bonds on that face to accommodate the lone pair, giving a capped octahedral disposition of the seven lone pairs about the metal centre [14].

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