

Square-prismatic vs. square-antiprismatic coordination in complexes of lead(II) with a simple bidentate chelating ligand; effects of intermolecular hydrogen bonding

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Whereas the eight-coordinate complex cation of $[\text{PbL}_4][(\text{MeO})_2\text{PO}_2]\cdot 2\text{H}_2\text{O}$ [L = 3-(2-pyridyl)pyrazole] has square prismatic geometry stabilised by hydrogen bonding between the pyrazolyl NH groups and the dimethylphosphate anion, the complex cation of $[\text{PbL}_4][\text{PF}_6]_2$, in which there are no significant hydrogen-bonding interactions, has a structure distorted towards square antiprismatic with a 22° twist between the planes.

Eight-coordination in metal complexes is largely confined to two common geometries: square antiprismatic (D_{4d}) and dodecahedral (D_{2h}). Rather rarer, but also well represented, are other geometries such as bicapped trigonal prismatic and hexagonal bipyramidal.^{1–3} In contrast, the simple cubic (or square prismatic, D_{4h}) geometries are very rare in discrete metal complexes, although well known in ionic solids with the CsCl or CaF_2 structures.

Regular cubic coordination requires monodentate ligands, as in $\text{Na}_3[\text{MF}_8]$ (M = Pa, U, Np)⁴ and $[\text{NEt}_4]_4[\text{M}(\text{NCS})_8]$ (M = U,⁵ Th⁶). In the latter examples crystal packing forces are significant in imposing the cubic geometry on the complex anion, as $[\text{U}(\text{NCS})_8]^{4-}$ is square-antiprismatic both in solution⁷ and in crystals with Cs^+ as the cation.⁸ $[\text{NEt}_4]_4[\text{M}(\text{SCN})_7(\text{H}_2\text{O})]$ (M = various lanthanoid ions) are also cubic.⁹ In contrast, the bite-angle limitations of bidentate chelating ligands mean that regular cubic geometry is not possible. Instead, compressed square-prismatic structures arise with the bidentate chelating ligands lying along the four shorter edges, linking the two square planes.^{10–13} Most of these examples have a lanthanide or actinide ion as the central metal, consistent with the requirement for f-orbital participation.³

We describe here two eight-coordinate complexes of lead(II) with the bidentate chelating ligand 3-(2-pyridyl)pyrazole (L), of which one is square prismatic and the other is skewed towards a square-antiprismatic geometry. This pair of structures is of interest for two reasons: firstly, they provide a very rare example of square-prismatic geometry outside of the f-block elements, and secondly, they show how intermolecular hydrogen-bonding interactions can overcome the steric problems associated with a square prismatic structure.

We recently reported the synthesis and crystal structure of $[\text{PbL}_2]\cdot\text{H}_2\text{O}$, containing the potentially tridentate ligand bis[3-(2-pyridyl)pyrazol-1-yl]phosphinate (L^1).¹⁴ On recrystallising a batch of this material from MeOH we found that it had been converted to $[\text{PbL}_4][(\text{MeO})_2\text{PO}_2]\cdot 2\text{H}_2\text{O}$, via solvolysis of the phosphinate group.[†] The crystal structure of the centrosymmetric complex is shown in Fig. 1.[‡] The four bidentate ligands L form a square-prismatic array about the Pb^{II} centre with each ligand spanning one of the short edges of the square prism, as in $[\text{U}(\text{bipy})_4]$.¹⁰ The sides of each 'square' [N(21), N(41), N(11A), N(31A)] are all between 3.30 and 3.50 Å in length, with the distance between the parallel planes [*i.e.* N(11)–N(21) and N(31)–N(41)] being 2.78 Å. The angles within the square prism described by the eight N atoms all lie between 87.5 and 92.3°.

The disposition of the four asymmetric chelating ligands is 'up–up–down–down', such that each end of the complex has two *cis*-related pyridyl donors and two *cis*-related pyrazolyl donors. This allows the two pyrazolyl NH groups at each side of the complex to form an $\text{NH}\cdots\text{O}$ hydrogen-bonding interaction with O(3) of the dimethylphosphate anion, with the non-bonded O(3)–N(32) and O(3)–N(12) distances being 2.81 and 2.96 Å respectively. This hydrogen-bonding interaction is a significant factor in the adoption of square-prismatic geometry, since the two pyrazolyl NH groups need to be held close enough together to be able to hydrogen bond to the same oxygen atom; the non-bonded N(12)–N(32) separation is 3.73 Å.

To test this theory we prepared the complex cation $[\text{PbL}_4]^{2+}$ as its hexafluorophosphate salt.[†] The crystal structure of $[\text{PbL}_4][\text{PF}_6]_2$ is in Fig. 2.[‡] There are three significant differences between this structure and that of $[\text{PbL}_4][(\text{MeO})_2\text{PO}_2]\cdot 2\text{H}_2\text{O}$. Firstly, the four ligands all have the same 'head-to-tail' orientation such that all four pyridyl groups are at one end

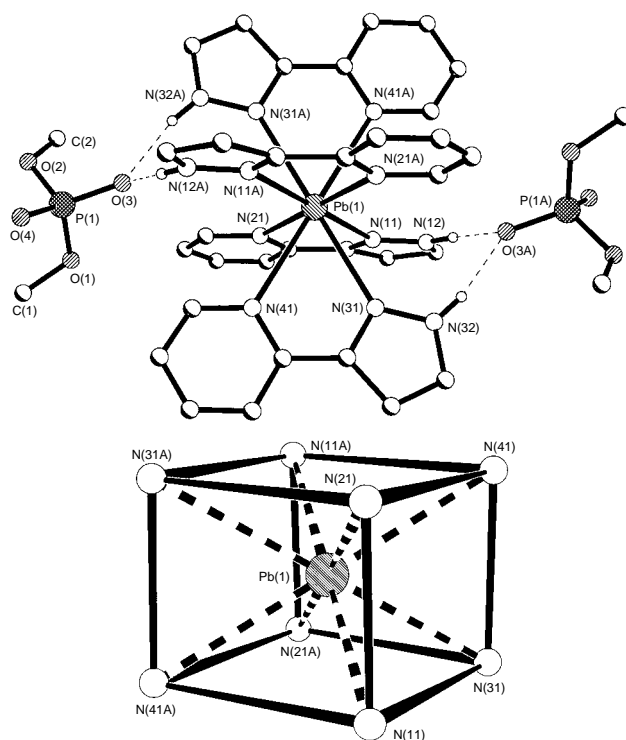


Fig. 1 Crystal structure of $[\text{PbL}_4][(\text{MeO})_2\text{PO}_2]\cdot 2\text{H}_2\text{O}$, showing (top) the complex cation and the hydrogen-bonded anions, and (bottom) the coordination geometry. Selected bond lengths (Å) and angles (°): Pb(1)–N(11) 2.765(6), Pb–N(21) 2.718(6), Pb–N(31) 2.760(6), Pb(1)–N(41) 2.794(6); N(11)–Pb(1)–N(21) 60.3(2), N(31)–Pb(1)–N(41) 59.9(2). Non-bonded N–N separations within the square prism (Å): N(11)–N(31) 3.37, N(31)–N(21A) 3.31, N(21)–N(41) 3.50, N(11)–N(41A) 3.34, N(11)–N(21) 2.78, N(31)–N(41) 2.78.

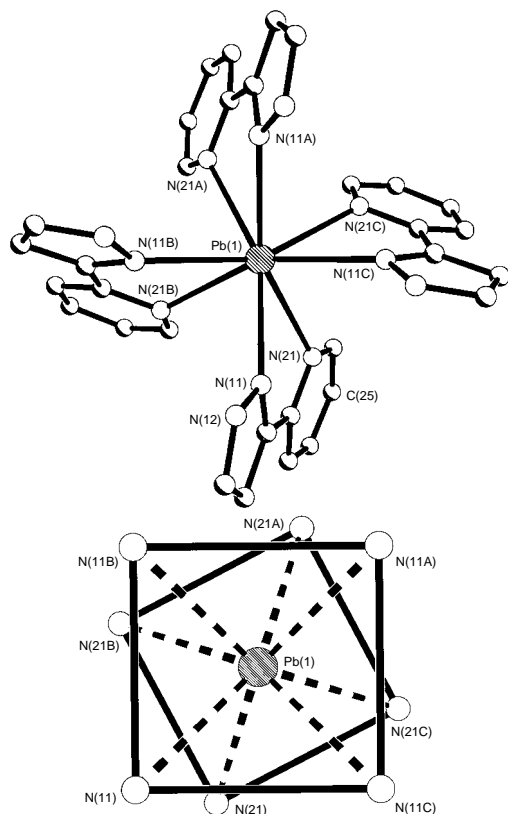


Fig. 2 Crystal structure of $[\text{PbL}_4][\text{PF}_6]_2$, showing (top) the complex cation, and (bottom) the coordination geometry. Selected bond lengths (\AA) and angles ($^\circ$): $\text{Pb}(1)\text{--N}(11)$ 2.702(4), $\text{Pb--N}(21)$ 2.775(4); $\text{N}(11)\text{--Pb}(1)\text{--N}(21)$ 60.80(13), $\text{N}(11)\text{--Pb}(1)\text{--N}(11B)$ 80.23(7), $\text{N}(21)\text{--Pb}(1)\text{--N}(21B)$ 75.07(7). Non-bonded $\text{N}\cdots\text{N}$ separations within the coordination polyhedron (\AA): $\text{N}(11)\cdots\text{N}(11C)$ 3.48 \AA , $\text{N}(21)\cdots\text{N}(21B)$ 3.38 \AA , $\text{N}(11)\cdots\text{N}(21)$ 2.77 \AA .

of the complex and the four pyrazolyl groups are at the other end. The complex has crystallographic C_4 symmetry with all four ligands equivalent. Secondly, the geometry is no longer square prismatic: the two mean planes are skewed with respect to one another by 22° , and the complex is therefore about half way between square prismatic and square antiprismatic. This twist brings the parallel planes closer together (2.52 \AA , compared to 2.78 \AA in the previous structure). This illustrates an important steric factor that does not occur in complexes with eight monodentate ligands, where the adoption of square-antiprismatic geometry to relieve the steric strain of an eclipsed prismatic structure does not have the unfavourable side-effect of also bringing the planes together. With four bidentate ligands of fixed length spanning the two planes this effect is inevitable and may explain why the offset of the two planes is only 22° rather than 45° . Thirdly, there are no significant hydrogen-bonding interactions between the complex cation and the hexafluorophosphate anions. An additional consequence of the 'skew' is that the adjacent pyrazolyl NH groups can move further apart; the separations between them [e.g. $\text{N}(12)\cdots\text{N}(12B)$] have increased to 4.20 \AA , as these groups are no longer held in proximity by forming hydrogen bonds to a common atom. The N_4 planes are perfect squares, with the square described by the four pyridyl groups (edge length 3.38 \AA) being slightly smaller than that described by the four pyrazolyl groups (edge length 3.48 \AA).

Crystal packing effects are known to be able to overcome the steric barrier to adoption of cubic geometries, as shown by comparison of $[\text{NEt}_4]_4[\text{U}(\text{NCS})_8]$ and $\text{Cs}_4[\text{U}(\text{NCS})_8]$.^{5,8} We should be cautious in making comparisons between these two

new structures. It does look however as if the hydrogen bonding in $[\text{PbL}_4][(\text{MeO})_2\text{PO}_2]\cdot 2\text{H}_2\text{O}$ is partly responsible for the adoption of the very rare square-prismatic geometry, the first example of which we are aware for a main-group molecular species.

Footnotes and References

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† *Preparations.* $[\text{PbL}_4][(\text{MeO})_2\text{PO}_2]\cdot 2\text{H}_2\text{O}$: A sample of $[\text{Pb}(\text{L}^1)_2]$ (ref. 14) was dissolved in MeOH and allowed to crystallise by slow evaporation over several days, to give X-ray quality crystals of $[\text{PbL}_4][(\text{MeO})_2\text{PO}_2]\cdot 2\text{H}_2\text{O}$ in 67% yield. $[\text{PbL}_4][\text{PF}_6]_2$: A mixture of L (ref. 15) (0.290 g, 2 mmol) and $\text{Pb}(\text{ClO}_4)_2\cdot 3\text{H}_2\text{O}$ (0.203 g, 0.5 mmol) in MeCN (15 cm^3) was vigorously agitated in an ultrasound cleaning bath for 30 min. To the resulting solution was added aqueous NH_4PF_6 , resulting in precipitation of the product as a white powder in 43% yield. X-Ray quality crystals were grown by slow evaporation of a methanol solution. Both complexes gave satisfactory elemental analyses and FAB mass spectra.

‡ *Crystallographic data.* $[\text{PbL}_4][(\text{MeO})_2\text{PO}_2]\cdot 2\text{H}_2\text{O}$: $\text{C}_{36}\text{H}_{48}\text{N}_{12}\text{O}_{10}\text{P}_2\text{Pb}$, $M = 1073.96$, colourless blocks, crystal size $0.25 \times 0.15 \times 0.10 \text{ mm}^3$, triclinic, space group $P\bar{1}$, $a = 8.9120(13)$, $b = 9.462(2)$, $c = 13.394(2)$ \AA , $\alpha = 102.17(2)$, $\beta = 101.508(14)$, $\gamma = 92.83(2)^\circ$, $U = 1076.9(3)$ \AA^3 , $Z = 1$, $D_c = 1.656 \text{ g cm}^{-3}$, $F(000) = 536$, $\mu(\text{Mo-K}\alpha) = 4.060 \text{ mm}^{-1}$. 4995 data were collected with $2\theta_{\text{max}} = 46.5^\circ$ at -100°C , and merged to give 3079 unique data ($R_{\text{int}} = 0.0485$). Refinement of 284 parameters converged at R_1 [selected data with $I \geq 2\sigma(I)$] = 0.041, wR_2 (all data) = 0.103. The Pb atom lies on an inversion centre.

$[\text{PbL}_4][\text{PF}_6]_2$: $\text{C}_{32}\text{H}_{28}\text{N}_{12}\text{F}_{12}\text{P}_2\text{Pb}$, $M = 1077.79$, colourless blocks, crystal size $0.30 \times 0.20 \times 0.05 \text{ mm}^3$, tetragonal, space group $P4/ncc$, $a = 13.136(2)$, $c = 21.667(3)$ \AA , $U = 3738.8(9)$ \AA^3 , $Z = 4$, $D_c = 1.915 \text{ g cm}^{-3}$, $F(000) = 2096$, $\mu(\text{Mo-K}\alpha) = 4.703 \text{ mm}^{-1}$. 21236 data were collected with $2\theta_{\text{max}} = 55^\circ$ at -100°C , and merged to give 2145 unique data ($R_{\text{int}} = 0.0532$). Refinement of 123 parameters converged at R_1 [selected data with $I \geq 2\sigma(I)$] = 0.032, wR_2 (all data) = 0.080. The Pb atom lies on a C_4 axis.

Both data sets were collected on a Siemens SMART diffractometer with an area detector. See refs. 15 and 16 for experimental details and software used. CCDC 182/586.

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