

Crystal Structures of Silver(I) and Thallium(I) Complexes of Tris[3-(2-pyridyl)pyrazol-1-yl]borate; Encapsulation of Either a Single Thallium(I) Ion or a Trinuclear Silver(I) Cluster by a Hexadentate Podand

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The title ligand (L^-) forms a 1:1 complex [TIL] in which the Tl^I ion lies within the hexadentate cavity, coordinated strongly by the pyrazolyl N atoms but only very weakly by the pyridyl N atoms; in contrast the 3:2 complex $[Ag_3L_2][ClO_4]$ contains a triangular $\{Ag_3\}^{3+}$ cluster core within the cavity of each ligand which accommodates the larger guest by increasing the apical N–B–N angles.

We have recently found that the ligand tris[3-(2-pyridyl)pyrazol-1-yl]borate, L^- , has a remarkably varied coordination chemistry.^{1–3} This ligand is the first example of a tris(pyrazol-1-yl)borate derivative in which an additional coordinating group (as opposed to an alkyl or aryl group)⁴ is attached at the pyrazolyl C³ positions to form a podand with three bidentate arms linked at the apical boron atom. The cavity is of an appropriate size to encapsulate lanthanide(III) and actinide(III) ions, giving complexes either with a 1:1 metal to ligand ratio such as nine-coordinate $[EuL(MeOH)_2F]^+$ or icosahedral twelve-coordinate 1:2 complexes such as $[SmL_2]^+$ and $[UL_2]^+$.² These ions are an ideal match for the ligand cavity, both in terms of their size and their tolerance for high coordination numbers. In contrast, with first-row transition metal dications, the mismatch between the large ligand cavity and the small metal ion, together with the preference of the metal ions for octahedral geometry, results in self-assembly of tetrameric complexes $[M_4L_4]^{4+}$ ($M = Mn, Fe, Co, Ni, Zn$).³ In these complexes each ligand donates each bidentate arm to a different metal ion, and therefore no longer acts as an encapsulating podand. We now report the structures of the complexes of L^- with Tl^I and Ag^I . Although the size of these ions is well matched with the cavity of L^- their preference for low coordination numbers is not, so there is now a metal/ligand mismatch based on coordination number rather than size. The results of the mismatch are very different in each case, despite the similar size and charge of Ag^I and Tl^I , and show how the ligand cavity may coordinate both relatively small and very large guests.

Reaction of equimolar amounts of KL with thallium(I) formate in methanol afforded a white solid whose mass spectrum [$m/z = 649$] and elemental analysis indicated the

formulation [TIL]. The crystal structure of [TIL] is shown in Fig. 1.† The Tl^I ion is in a '3 + 3' coordination environment, with three short bonds to the pyrazolyl N atoms [2.636, 2.674 and 2.699 Å] and three long interactions with the pyridyl N atoms [3.087, 3.257 and 3.183 Å, respectively]. At first glance the coordination environment of the Tl^I looks very similar to those in $Tl[HB\{pz-3-(p\text{-tolyl})\}_3]$ and $Tl[HB\{pz-3-Bu^t\}_3]$ ($pz = \text{pyrazol-1-yl}$), where the Tl^I is coordinated solely by the three pyrazolyl N atoms in a pyramidal arrangement.^{5,6} However, two factors suggest that the Tl^I –pyridyl interactions are significant. Firstly, if there were no interaction the pyridyl N atoms would not be directed towards the centre of the cavity, but would point away from each other to minimise lone-pair electrostatic repulsion. Secondly, in $Tl[HB\{pz-3-(p\text{-tolyl})\}_3]$ and $Tl[HB\{pz-3-Bu^t\}_3]$ the Tl –N bond lengths lie in the range 2.57–2.59 Å.^{5,6} In [TIL], therefore, movement of the Tl^I ion towards the pyridyl ligands results in a lengthening of the Tl –N(pyrazolyl) bonds by *ca.* 0.09 Å on average. This in turn decreases the N– Tl –N angles involving the pyrazolyl donors, from 75–79° in $Tl[HB\{pz-3-(p\text{-tolyl})\}_3]$ and $Tl[HB\{pz-3-Bu^t\}_3]$ to 70–72° in [TIL]. The apical N–B–N angles are exactly tetrahedral (109–110°) indicating that the ligand is in a strain-free conformation. The relatively open structure of the complex allows a degree of interpenetration in adjacent units in the crystal, giving rise to aromatic π -stacking interactions between the pyridyl rings of adjacent complex units and three non-bonded Tl^I –H interactions per metal (Fig. 2).

Reaction of KL with $AgNO_3$ in methanol followed by treatment with $NaClO_4$ afforded a precipitate whose mass spectrum [$m/z = 1209$ based on ^{107}Ag , corresponding to $\{Ag_3L_2\}^+$] and elemental analysis indicated the formulation $[Ag_3L_2][ClO_4]$. This was obtained initially using a 1:1 ratio of KL and $AgNO_3$, but the yield was optimised by using a 2:3 ratio of reactants. The crystal structure (Fig. 3) shows how an

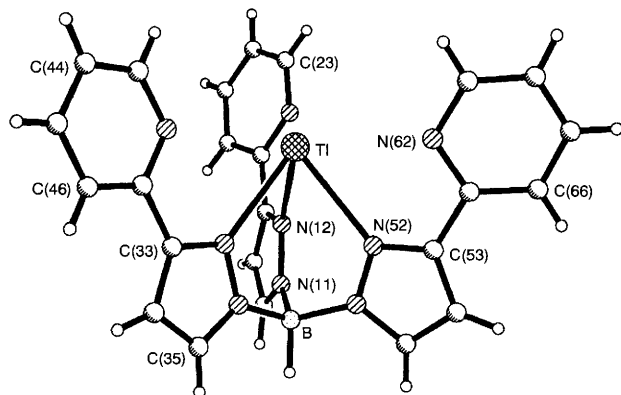


Fig. 1 Crystal structure of [TIL]. Selected bond lengths (Å) and angles (°): Tl –N(12) 2.674(6), Tl –N(32) 2.636(6), Tl –N(52) 2.699(7), Tl –N(22) 3.257(7), Tl –N(42) 3.087(7), Tl –N(62) 3.183(7), N(12)– Tl –N(32) 70.2(2), N(32)– Tl –N(52) 72.1(2), N(12)– Tl –N(52) 71.7(2). Torsion angles (°) between pyridyl and pyrazolyl rings: rings 1/2, 22; rings 3/4, 7; rings 5/6, 16.

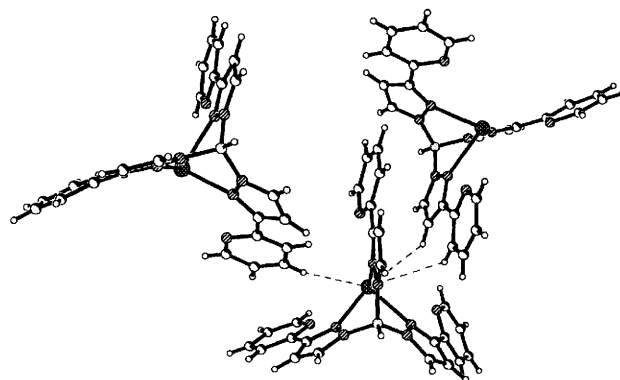


Fig. 2 Part of the packing diagram for [TIL] showing two intermolecular interactions: aromatic stacking between pyridyl rings, and Tl^I –H interactions. The average separation between the overlapping planar segments is 3.56 Å; the Tl^I –H separations are 3.52, 3.35 and 3.36 Å.

entire trinuclear cluster is encapsulated by the ligands. The complex has threefold rotational symmetry along the B–B axis. The core comprises an equilateral triangular cluster of Ag^{I} ions (Ag–Ag separations 2.977 Å); the ligands lie above and below the Ag_3 plane, and each ligand coordinates one bidentate arm to each of the three Ag^{I} ions. To accommodate the large Ag_3 unit, the arms of each ligand are ‘splayed out’ such that the apical N–B–N angles are 114.1° , in contrast to $109\text{--}110^\circ$ in [TiL]. Each Ag^{I} is therefore coordinated by a bidentate arm from each of the two ligands in addition to the two Ag–Ag interactions. The Ag^{I} ions are in highly distorted six-coordinate geometries which may loosely be considered as ‘octahedral’ given the constraints due to the bite angles of the *N,N*-chelating groups (70.5 and 72.0°) and the 60° angles within the Ag_3 cluster. The Ag–N bond lengths are unremarkable. As we have seen in other complexes of L^- , the Ag–N(pyridyl) bonds (average length 2.43 Å) are longer than the Ag–N(pyrazolyl) bonds (average length 2.27 Å).^{1–3}

The question of what constitutes an Ag–Ag bond is a difficult one. Ag^{I} often forms clusters in which the Ag–Ag separations may be longer than that in metallic silver (2.89 Å). The structural significance of these is often masked by presence of additional bridging ligands which could hold the metal ions close together even if there were no direct metal–metal interaction.⁷ However, $[\text{Ag}(\text{imidazole})_2][\text{ClO}_4]$ forms a hexanuclear cluster in which there are Ag–Ag separations of 3.49 Å between atoms where there is no other bridge: the cluster core is held together solely by these interactions.⁸ Other non-bridged Ag–Ag bond lengths typically lie in the range 2.8–3.3 Å,^{9,10} and it has been estimated for a binuclear complex with an Ag–Ag separation of 2.916 Å that a bond of order approximately 1/3 exists between the metals.⁹ We therefore feel justified in regarding $[\text{Ag}_3\text{L}_2]^+$ as containing an $\{\text{Ag}_3\}^{3+}$ cluster encapsulated by two ligands L^- , rather than three separate Ag^{I} cations.

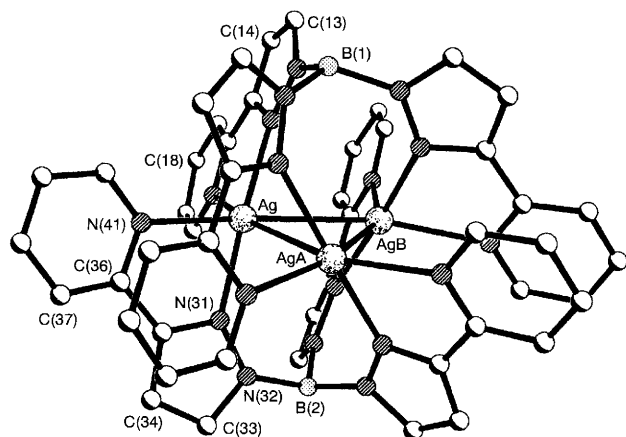


Fig. 3 Crystal structure of $[\text{Ag}_3\text{L}_2][\text{ClO}_4]$; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Ag–N(11) 2.282(9), Ag–N(31) 2.264(9), Ag–N(21) 2.444(10), Ag–N(41) 2.420(10), all Ag–Ag 2.9773(12), N(11)–Ag–N(31) 175.8(3), N(31)–Ag–N(41) 70.5(3), N(11)–Ag–N(41) 111.0(4), N(21)–Ag–N(31) 111.6(4), N(11)–Ag–N(21) 72.0(3), N(41)–Ag–N(21) 104.4(2), N(31)–Ag–Ag(A) 103.4(2), N(11)–Ag–Ag(A) 73.6(3), N(41)–Ag–Ag(A) 156.5(4), N(21)–Ag–Ag(A) 98.9(4), N(31)–Ag–Ag(B) 72.4(3), N(11)–Ag–Ag(B) 103.5(2), N(41)–Ag–Ag(B) 97.0(3), N(21)–Ag–Ag(B) 158.4(4), all Ag–Ag–Ag 60.0 , all apical N–B–N $114.1(8)$.

This work shows how the cavity size of L^- may vary to suit either a single metal or an entire cluster by modifying the apical N–B–N angles.

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† Crystal data for [TiL]: $[\text{Ti}\{\text{HB}(\text{C}_8\text{N}_3\text{H}_6)_3\}]$, colourless blocks, crystal size $0.6 \times 0.7 \times 0.6$ mm, $M = 648.66$, monoclinic, space group $P2_1/n$, $a = 8.732(4)$, $b = 16.178(6)$, $c = 16.871(7)$ Å, $\beta = 95.37(3)^\circ$, $U = 2372(2)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.816$ g cm^{−3}, $\mu(\text{Mo-K}\alpha) = 6.839$ mm^{−1}. 4112 Independent reflections were collected with $2\theta_{\text{max}} = 50^\circ$. Refinement converged at $R_1 = 0.042$, $wR_2 = 0.107$.

For $[\text{Ag}_3\text{L}_2][\text{ClO}_4]$: $[\text{Ag}_3\{\text{HB}(\text{C}_8\text{N}_3\text{H}_6)_3\}_2][\text{ClO}_4]$, colourless blocks, crystal size $0.6 \times 0.6 \times 0.6$ mm, $M = 1310.62$, cubic, space group $F\bar{4}3c$, $a = 34.746(6)$ Å, $U = 41948(13)$ Å³, $Z = 32$, $D_{\text{calc}} = 1.662$ g cm^{−3}, $\mu(\text{Mo-K}\alpha) = 1.223$ mm^{−1}. 1897 Independent reflections were collected with $2\theta_{\text{max}} = 50^\circ$. Refinement converged at $R_1 = 0.041$, $wR_2 = 0.122$. The complex cation and perchlorate anion both lie on a threefold rotation axis, so the asymmetric unit contains one third of each; there are 96 asymmetric units in the unit cell giving 32 complete molecules.

Crystals of [TiL] were grown from $\text{CH}_2\text{Cl}_2\text{--MeOH}$ by slow evaporation, and crystals of $[\text{Ag}_3\text{L}_2][\text{ClO}_4]$ by slow diffusion of diethyl ether vapour into an acetone solution of the complex. Details in common: Crystals were mounted in sealed glass capillary tubes with some of the mother liquor as a precaution against solvent loss. Data were collected on a Siemens R3m/V four-circle diffractometer at 293 K with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Regular check reflections showed no significant decay. Data were corrected for Lorentz and polarisation effects, and for absorption effects using azimuthal scan data. Both structures were solved by conventional heavy-atom methods and refined by full-matrix least-squares methods on all F^2 data using SHELX93. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in calculated positions with fixed isotropic thermal parameters.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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