

An unprecedented trinucleating bridging mode ($\mu_3\text{-}\eta^1:\eta^1:\eta^1$) of a tris(pyrazolyl)borate ligand in a trinuclear silver(I) complex

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The crystal structure of $[\text{Ag}_3(\text{Tp}^{\text{An}})_2][\text{ClO}_4]$, where Tp^{An} is tris[3-(2-methoxyphenyl)pyrazol-1-yl]hydroborate, shows a unique trinucleating bridging coordination mode for the tris(pyrazolyl)borate: each of the two ligands coordinates one pyrazolyl donor to each of the three two-coordinate $\text{Ag}(\text{I})$ ions, affording a triangular complex in which each face is capped by a $\mu_3\text{-}\eta^1:\eta^1:\eta^1$ -tris(pyrazolyl)borate.

The tris(pyrazolyl)borates are a very well known class of ligand which almost invariably coordinate as terdentate chelates to a single metal ion, 'capping' one triangular face of the coordination polyhedron.¹ This predictability in their mode of coordination is one of the reasons for their popularity as it has allowed the preparation of complexes with coordination geometries which can be planned in advance. This has found use in diverse areas. In the realm of bioinorganic chemistry, three pyrazoles of a chelating tris(pyrazolyl)borate ligand are a reasonable structural and electronic mimic for the tris(imidazolyl) coordination which occurs at a variety of metalloprotein active sites.^{1,2} Tris(pyrazolyl)borate derivatives with bulky substituents at the pyrazolyl C³ positions form four-coordinate pseudo-tetrahedral complexes in which a protective screen around the fourth coordination site allows the stabilisation of low-coordinate complexes which would otherwise be inaccessible or highly reactive.¹

The only well-characterised exceptions to this rule with simple tris(pyrazolyl)borates are (i) a few 16-electron square-planar complexes in which a tris(pyrazolyl)borate is bidentate with one pyrazolyl arm pendant;³ and (ii) some dinuclear complexes [mostly of $\text{Cu}(\text{I})$] in which a tris(pyrazolyl)borate acts as a bridging ligand, acting as a bidentate donor to one metal ion and a monodentate donor to the second.⁴ Also, we have recently described some complexes of the hexadentate podand tris[3-(2-pyridyl)pyrazol-1-yl]hydroborate (Tp^{Py}) in which the three bidentate chelating arms each coordinate to a different metal ion, however the nature of this ligand makes it a special case as it behaves completely differently from 'conventional' tris(pyrazolyl)borates.⁵

We describe here the crystal structure of a trinuclear $\text{Ag}(\text{I})$ complex of the ligand tris[3-(2-methoxyphenyl)pyrazol-1-yl]hydroborate (Tp^{An} , where the suffix 'An' denotes the anisyl substituent), $[\text{Ag}_3(\text{Tp}^{\text{An}})_2][\text{ClO}_4]$, in which the ligand adopts the previously unknown trinucleating bridging mode with each pyrazolyl donor coordinated to a separate $\text{Ag}(\text{I})$ ion. We prepared Tp^{An} recently to see if it would act as an N_3O_3 -donor hexadentate podand (analogous to Tp^{Py}), but found that the methoxy groups did not coordinate in any of the complexes that we structurally characterised.⁶ This ligand therefore behaves like conventional tris(pyrazolyl)borates bearing a bulky substituent at the pyrazolyl C³ positions.¹ Reaction of $\text{K}[\text{Tp}^{\text{An}}]$ with AgClO_4 in thf afforded a precipitate whose FAB mass spectrum indicated the formation of the $[\text{Ag}_3(\text{Tp}^{\text{An}})_2]^+$ cation.† Recrystallisation from acetone-diethyl ether afforded X-ray quality crystals of $[\text{Ag}_3(\text{Tp}^{\text{An}})_2][\text{ClO}_4] \cdot 1.5\text{OCMe}_2 \cdot 0.5\text{Et}_2\text{O}$; the structure of the complex cation is shown in Figs. 1 and 2.‡

The complex contains a triangular array of $\text{Ag}(\text{I})$ ions, with

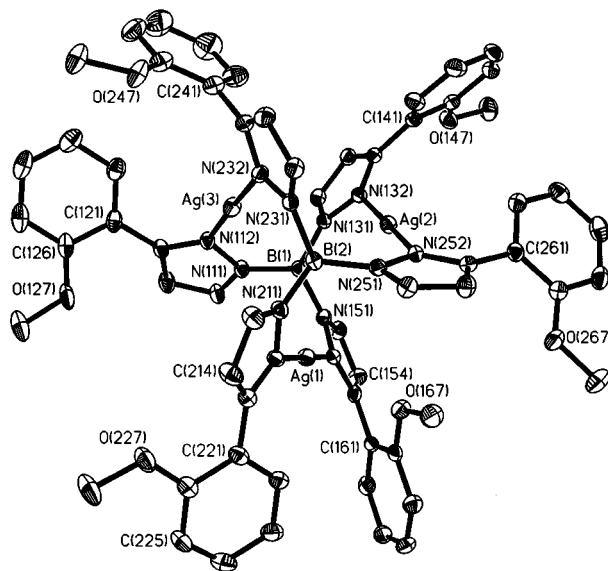
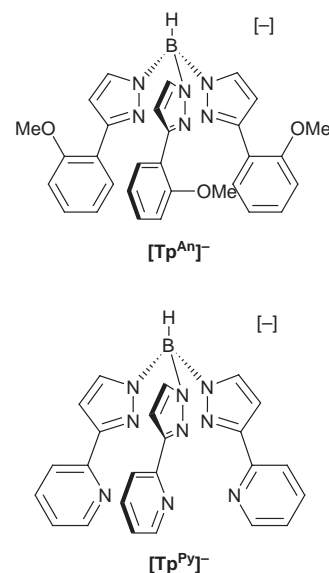


Fig. 1 Crystal structure of the cation of $[\text{Ag}_3(\text{Tp}^{\text{An}})_2][\text{ClO}_4] \cdot 1.5\text{OCMe}_2 \cdot 0.5\text{Et}_2\text{O}$; thermal ellipsoids are at the 40% probability level. Significant bond lengths (Å) and angles (°): $\text{Ag}(\text{I})\text{-N}(\text{I}21)$ 2.131(3), $\text{Ag}(\text{I})\text{-N}(\text{I}52)$ 2.134(3), $\text{Ag}(\text{II})\text{-N}(\text{I}32)$ 2.106(3), $\text{Ag}(\text{II})\text{-N}(\text{I}252)$ 2.104(3), $\text{Ag}(\text{III})\text{-N}(\text{I}232)$ 2.101(3), $\text{Ag}(\text{III})\text{-N}(\text{I}112)$ 2.104(3); $\text{N}(\text{I}21)\text{-Ag}(\text{I})\text{-N}(\text{I}52)$ 179.10(11), $\text{N}(\text{I}32)\text{-Ag}(\text{II})\text{-N}(\text{I}252)$ 176.39(11), $\text{N}(\text{I}232)\text{-Ag}(\text{III})\text{-N}(\text{I}112)$ 177.77(11).



$\text{Ag} \cdots \text{Ag}$ separations of 3.927(2) Å [$\text{Ag}(\text{I}) \cdots \text{Ag}(\text{II})$], 3.936(2) Å [$\text{Ag}(\text{II}) \cdots \text{Ag}(\text{III})$] and 4.189 Å [$\text{Ag}(\text{I}) \cdots \text{Ag}(\text{III})$], each face of the triangle being capped by a single Tp^{An} ligand which donates

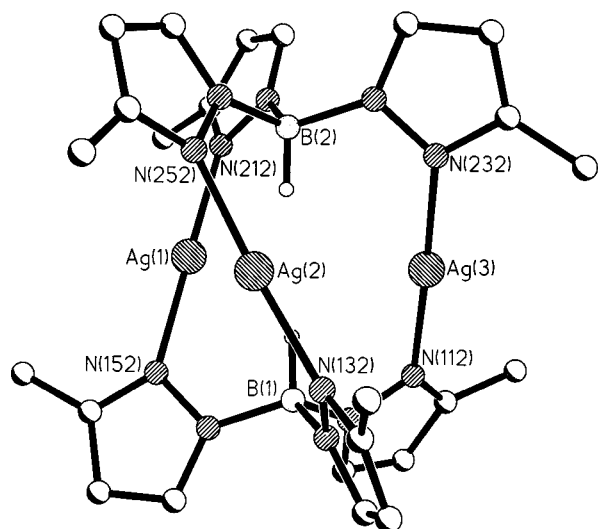


Fig. 2 Alternative view of the $[\text{Ag}_3(\text{Tp}^{\text{An}})_2]^+$ core with the methoxyphenyl groups removed for clarity (only the *ipso* carbon atoms are shown).

one pyrazolyl N atom to each Ag(i) ion. Each Ag(i) ion is therefore in an approximately linear two-coordinate environment, arising from one pyrazolyl donor from each of the two Tp^{An} ligands;⁷ this is a well-known mode of coordination for Ag(i) ions.⁷ All of the Ag–N bond lengths lie within the range 2.10–2.14 Å, and the methoxy groups do not coordinate [the only remotely significant $\text{Ag}\cdots\text{O}$ contact is 2.687(3) Å between Ag(1) and O(167), which is just a weak cation–dipole interaction and much too long to constitute a coordinate bond]. Each ligand has an ‘inverted’ conformation which allows the three pyrazolyl donors to coordinate to separate metal ions rather than converge on the same one, and in consequence the B–H bonds are directed inwards towards each other. The six $\text{Ag}\cdots\text{H}$ separations are in the range 2.5–2.8 Å, too long to be considered as agostic interactions.

The structure of this complex is in interesting contrast to all other structurally characterised Ag(i) complexes of tris(pyrazolyl)borates, in which the tris(pyrazolyl)borate ligands are coordinated in the conventional tridentate manner.⁸ The reason for adoption of this new coordination mode is not obvious. The substituents impose no steric barrier on formation of a conventional 1:1 complex [a 1:1 complex has already been prepared and structurally characterised with Tl(i)];⁶ the methoxyphenyl substituents play no significant role in coordinating to the metal ions; there are no obvious co-operative interactions (such as aromatic π -stacking) between the two ligands; and the $\text{Ag}\cdots\text{Ag}$ separations are too great for the structure to be stabilised by $\text{Ag}\cdots\text{Ag}$ bonding interactions.⁹ It was suggested a while ago on the basis of mass spectroscopic and osmometric results that some binary Ag(i) complexes with simple poly(pyrazolyl)borate ligands were oligomeric *via* a bridging coordination mode of the ligand,¹⁰ but no structural evidence has been available to support this possibility until now. The structure of $[\text{Ag}_3(\text{Tp}^{\text{An}})_2][\text{ClO}_4]$ suggests that a more thorough investigation of the coordination behaviour of appropriately-substituted tris(pyrazolyl)borates with Cu(i) and Au(i) (which also support linear two-coordinate geometries),^{9,11} as well as Ag(i), would be fruitful.

Acknowledgements

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Notes and references

† A mixture of $\text{K}(\text{Tp}^{\text{An}})$ (114 mg, 0.2 mmol) and AgClO_4 (62 mg, 0.3 mmol) in dry thf (20 cm^3) at -15°C under N_2 was stirred for 0.5 h to give a precipitate of crude $[\text{Ag}_3(\text{Tp}^{\text{An}})_2][\text{ClO}_4]$ (brown due to the pres-

ence of colloidal silver). Repeated recrystallisation from acetone–diethyl ether in the dark afforded a small number of X-ray quality colourless crystals. The yield of crystalline material was low (*ca.* 10%) due to the instability of the product in solution: silver(i) complexes of poly(pyrazolyl)borates are known to decompose easily and be light- and oxygen-sensitive.^{8,10} FAB-MS: m/z 1386 [100%, $\{\text{Ag}_3(\text{Tp}^{\text{An}})_2\}^+$], 637 [40%, $\{\text{Ag}(\text{Tp}^{\text{An}})\}^+$] (Found: C, 48.0; H, 3.4; N, 10.9. Required for $[\text{Ag}_3(\text{Tp}^{\text{An}})_2][\text{ClO}_4]$: C, 48.5; H, 3.8; N, 11.3%).

‡ A suitable crystal of $[\text{Ag}_3(\text{Tp}^{\text{An}})_2][\text{ClO}_4]\cdot 1.5\text{OCMe}_2\cdot 0.5\text{Et}_2\text{O}$ (dimensions $0.4 \times 0.4 \times 0.2$ mm) was quickly removed from the mother-liquor and mounted on a Siemens SMART diffractometer at -100°C . Crystal data: $\text{C}_{66.5}\text{H}_{70}\text{Ag}_3\text{B}_2\text{ClN}_{12}\text{O}_{12}$, $M = 1610.0$, monoclinic, space group $P2_1/c$, $a = 15.264(4)$, $b = 15.785(4)$, $c = 29.433(11)$ Å, $\beta = 103.85(2)^\circ$, $U = 6885(4)$ Å³, $Z = 4$, $\rho_{\text{calc}} = 1.553$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 0.953$ mm^{-1} . 42588 reflections were collected to $2\theta_{\text{max}} = 55^\circ$, which after merging gave 15707 unique reflections ($R_{\text{int}} = 0.0526$). Refinement (SHELXTL)¹² of 911 parameters on all F^2 data converged at $R1 = 0.0426$ [data with $F > 4\sigma(F)$], $wR2 = 0.0986$ (all data). Apart from the trinuclear cation and the perchlorate anion, there is one well-behaved acetone molecule in the asymmetric unit and disordered overlapping molecules of acetone (50% site occupancy) and ether (50% site occupancy). Largest residual peak, hole: $+0.899$, -0.728 e Å⁻³. CCDC reference number 186/1138. See <http://www.rsc.org/suppdata/dt/1998/3353/> for crystallographic data in .cif format.

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