Crystal Retro-Engineering: Structural Impact on Silver(I) Complexes with Changing Complexity of Tris(pyrazolyl)methane Ligands

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Details of crystal structure determination:

Compound 1 crystallizes in the triclinic crystal system. The space group P-1 was assumed and confirmed by the successful solution and refinement of the structure. The asymmetric unit consists of five crystallographically independent Ag atoms, two of which (Ag1 and Ag5) are located on inversion centers, four ligands and four BF4 counterions. One of the BF4 anions is disordered over two orientations in a 0.74 / 0.26 ratio, and was refined with the aid of ten geometric restraints (SHELX SAME command). All non-
hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were placed in idealized positions and refined using a riding model.

For compound 2 systematic absences in the intensity data were uniquely consistent with the space group P2_1/c. All atoms are on positions of general crystallographic symmetry: the asymmetric unit contains three chemically and crystallographically inequivalent Ag atoms, two ligands, three triflate ions and half an acetone molecule disordered about an inversion center. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were placed in idealized positions and refined using a riding model.

For compound 3 systematic absences in the intensity data were uniquely consistent with the space group P2_1/n. The asymmetric unit contains two independent Ag atoms, two ligands, two BF_4^- counterions and an acetone molecule of crystallization. All atoms reside on positions of general crystallographic symmetry. Though the Ag atoms and ligands are crystallographically independent, they are chemically similar. The –CH_2OH groups of each ligand were both found to be disordered over two orientations. The refined fractions of each orientation are as follows: C(2)-O(2), 0.68 / 0.32 (A / B); C(4)-O(4), 0.82 / 0.18 (A / B). The oxygen atom of the minor disorder component C(4B)-O(4B) was refined isotropically due to its small occupancy. All other non-hydrogen atoms were refined with anisotropic displacement parameters. Due to the disorder of the –CH_2OH groups, unequivocal hydroxyl H atom positions could not be located. They were therefore placed in positions calculated based on –CH_2O– and likely hydrogen bonding geometries (SHELX AFIX 83) and refined as riding atoms with O-H = 0.84 Å. These H atom positions are best regarded as approximate. H atoms bound to carbon were
placed in calculated positions and refined using a riding model. The two largest residual electron density peaks (ca. 1.95 e\text{-}Å\textsuperscript{3}) are located in the vicinity of a BF\textsubscript{4}\textsuperscript{-} anion and probably represent a very minor disorder component of this anion. No attempt was made to model the disorder.

For compound 4 systematic absences in the intensity data were uniquely consistent with the space group Pnna. The asymmetric unit contains two crystallographically inequivalent Ag cations, the SO\textsubscript{3}CF\textsubscript{3}\textsuperscript{-} counterion and the HOCH\textsubscript{2}C(pz)\textsubscript{3} ligand. The Ag centers are located on two-fold axes of rotation. Ag1 is on the twofold parallel to the c axis, and Ag(2) is on the twofold axis parallel to the a axis. All other atoms are on positions of general crystallographic symmetry. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms except H1 were placed in geometrically idealized positions and refined using a riding model. H1 was located in the difference map and refined subject to an O-H distance restraint of 0.84(2) Å, with an isotropic displacement parameter 1.5 times that of the parent oxygen.

Compound 5 crystallizes in the space group P2\textsubscript{1}/c. All atoms are on positions of general crystallographic symmetry. The asymmetric unit contains two crystallographically inequivalent HC(pz)\textsubscript{3} ligands, two Ag centers, one coordinated CH\textsubscript{3}CN molecule and two BF\textsubscript{4}\textsuperscript{-} counterions. One of the BF\textsubscript{4}\textsuperscript{-} groups (B2) is disordered over two orientations in the refined proportions 0.767(4) / 0.233(4), using 30 geometric restraints. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were placed in geometrically idealized positions and refined using a riding model with isotropic displacement parameters.
For compound 6 systematic absences in the intensity data were uniquely consistent with the space group P2$_1$/c. The asymmetric unit contains one Ag atom, one HC(pz)$_3$ ligand, the PF$_6^-$ counterion and half an acetone molecule disordered about an inversion center. All non-solvent atoms reside on positions of general crystallographic symmetry. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms except H1 were placed in idealized positions and refined using a riding model. H1 was located and refined isotropically.

Compound 7 crystallizes in the triclinic system. The space group P-1 was confirmed by the successful solution and refinement of the data. The asymmetric unit consists of half of a centrosymmetric [µ-(HC(pz)$_3$)$_2$Ag$_2$]$^{2+}$ cation and one triflate anion. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms.