A Near-Planar Pentadentate Silver(I) Complex; the Crystal and Molecular Structure of (2,2′ : 6′,2″ : 6″,2‴ : 6‴,2⁗-Quinquepyridine)silver(I) Hexafluorophosphate

Edwin C. Constable,[a]* **Michael G. B. Drew,**[b]* **G. Forsyth,**[b] **and Michael D. Ward**[a]

[a] *University Chemical Laboratory, Lensfield Road., Cambridge CB2 1EW, U.K.*

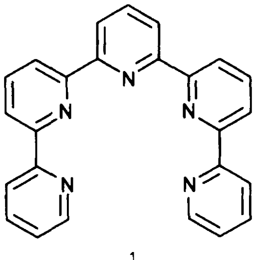
[b] *Department of Chemistry, The University, Whiteknights, Reading RG6 2AD, U.K.*

The complex [AgL^1][PF$_6$] (L^1 = 2,2′ : 6′,2″ : 6″,2‴ : 6‴,2⁗-quinquepyridine) has been prepared and structurally characterised; in contrast to the double helical binuclear complexes formed with first row transition metal ions, the title complex is mononuclear, with a near-planar arrangement of the ligand about the metal, and the cation exhibits weak π-interactions with adjacent cations, but there is no direct Ag–Ag interaction.

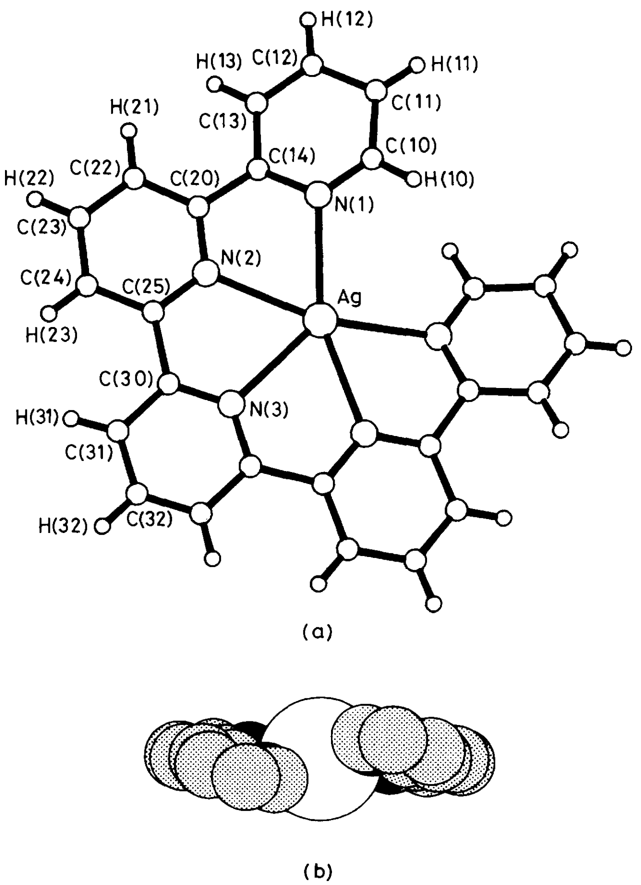
The observed geometry in co-ordination compounds is a balance between the geometric, steric and electronic demands of both the ligands and the metal. In complexes incorporating higher multidentate ligands a plethora of bonding modes and conformations may be expressed. We have been particularly interested in the geometrical and chemical consequences of the interplay of metal and ligand bonding requirements, and have recently described the preparation and structural characterisation of double helical binuclear complexes of copper,[1,2] nickel,[3] and silver[4] with open-chain pentadentate ligands. In an attempt to quantify the factors responsible for the formation of helical complexes, we have investigated a series of pentadentate ligands, and report herein the crystal and molecular structure of [AgL^1][PF$_6$] (L^1 = 2,2′ : 6′,2″: 6″,2‴- : 6‴,2⁗-quinquepyridine).†

The complex [AgL^1][PF$_6$] is readily prepared by the reaction of L^1 in MeOH with silver(I) acetate, followed by the addition of [NH$_4$][PF$_6$]. The ^{1}H n.m.r. spectrum of a solution of [AgL^1][PF$_6$] in CD$_3$CN consisted of nine well-resolved resonances, indicative of a highly symmetric configuration on the ^{1}H n.m.r. time-scale. There was no evidence for dissociation of the complex in solution. The fast atom bombardment (f.a.b.) mass spectrum of the complex exhibited peaks clustered around *m/z* 495 ([AgL^1]$^+$) and 990 ([Ag$_2$L$^1_2$]$^+$). Our previous studies of copper complexes of L^1 had indicated that the [M$_2$L$^1_2$]$^+$ stoicheiometry was associated with the formation of double helical complexes, and we therefore determined the crystal and molecular structure of [AgL^1][PF$_6$].

The structure shows discrete [AgL^1]$^+$ cations and [PF$_6$]$^-$ anions, both with crystallographically imposed C_2 symmetry and the molecular structure of the cation in [AgL^1][PF$_6$] is shown in Figure 1. The cation is mononuclear and relatively flat, in direct contrast to the non-planar configurations observed in the double helical [M$_2$L$^1_2$]$^{n+}$ complexes.[1–5] The double helical geometry arises from a mis-match in the bonding cavity of the electronically favoured (highly-conjugated) planar configuration of L^1 and the first row transition metal ions,[1–5] and interaction with larger metal ions is expected to lead to mononuclear, near planar compounds. The ionic radius of silver(I) (1.09 Å) is larger than that of copper(II) (0.57—0.75 Å),[6] and allows the formation of five



L^1



(a)

(b)

Figure 1. (a) The crystal and molecular structure of the [AgL^1]$^+$ cation in [AgL^1][PF$_6$] showing the numbering scheme adopted. Selected bond lengths (Å): Ag–N(1) 2.475(17), Ag–N(2) 2.439(13), Ag–N(3) 2.479(23). Selected bond angles (°): N(1)–Ag–N(2) 66.6(6), N(1)–Ag–N(3) 130.8(4), N(2)–Ag–N(3) 66.4(4), N(1)–Ag–N(1*) 98.4(6), N(1)–Ag–N(2*) 157.1(6), N(2)–Ag–N(2*) 132.9(7). (b) A second projection of the [AgL^1]$^+$ cation in [AgL^1][PF$_6$] showing the helical twist around the metal.

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† *Crystal Data*: C$_{25}$H$_{17}$F$_6$AgN$_5$P, colourless blocks, M = 640.0, monoclinic, space group *A*2/*a*, a = 7.497(8), b = 26.467(17), c = 12.151(11) Å, β = 104.5(1)°, U = 2334.2 Å^3, D_c = 1.82, D_m = 1.8 g cm^{-3}, Mo-K_α radiation (λ = 0.7107 Å), μ(Mo-K_α) = 9.9 cm^{-1}. 2225 Reflections collected on a four-circle diffractometer with 2θ (max) 50°. The data were averaged and 967 unique reflections with $I > 2\sigma(I)$ were used in structure solution and refinement. The structure was solved by heavy atom methods, and refined (Ag, P, F, N, C anisotropic; H isotropic in calculated positions) to R = 0.095, R_W = 0.098. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

similar Ag–N bonds [2.439(13)—2.479(23) Å]. The ligand is thus closely planar, with the maximum deviation of a nitrogen atom from the AgN_5 being 0.36 Å, and a helical twist may be discerned (Figure 1b).

The cations pack in a parallel stack along the *a* axis, with each silver atom above and below a C(30)–C(31) bond, with Ag–C(30) Å and Ag–C(31) 3.41 Å, presumably representing a weak π-interaction.[7] There is no direct Ag–Ag interaction (Ag–Ag, 5.31 Å). The stacking interactions Ag–C(30) and Ag–C(31) presumably explain the observation of $[Ag_2L^1_2]^+$ peaks in the f.a.b. mass spectrum. Although five-co-ordinate silver(I) complexes have been reported before, the planar pentadentate geometry has not been hitherto observed. Attempts to impose such a geometry on the metal ion have led to non-planar or Ag–Ag bonded species. The closest to a planar AgN_5 environment would appear to be in a macrocyclic complex with a ligand derived from 2,6-diacetylpyridine, but here the greatest deviation of a nitrogen atom from the mean AgN_5 plane is 0.65 Å.[8]

The planar geometry is a result of a 'good' match between the metal ion radius and the ligand bonding cavity. Attempts to form binuclear complexes by electrochemical or persulphate oxidation of the metal to the smaller silver(II) ion were unsuccessful. The planar donor set results in a relatively naked metal ion. Attempts to form binuclear or polynuclear complexes by the reaction of $[AgL^1][PF_6]$ with bridging ligands (pyrazine, 4,4′-bipyridine or *Z*-benzylthioethene) led to decomposition of the complex, as did reaction with potential axial ligands such as thiourea.

The structure of $[AgL^1][PF_6]$ provides confirmatory evidence for our views that the double helical geometry is the result of a small metal ion co-ordinating to a flexible highly-conjugated polydentate ligand. The copper complexes of L^1 are binuclear and double helical, whereas those of the larger silver(I) ion are mononuclear and near planar.

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