

Synthesis and structure of a co-ordination polymer based on silver(I) triangles linked by isonicotinate anions

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Reaction of AgBF_4 with isonicotinic acid ($\text{NC}_5\text{H}_4\text{CO}_2\text{H}$ -4) led to the formation of an unusual polymeric structure consisting of Ag_3 triangles linked together by two isonicotinate ligands: this co-ordination polymer, containing both bridged and unbridged short $\text{Ag}\cdots\text{Ag}$ contacts has been characterised crystallographically.

There is currently considerable interest in exploiting both co-ordinative bonds¹ and hydrogen bonds^{2,3} to facilitate the crystal engineering of structures based on metal complexes. We are interested in systems that are capable of self-assembly using both types of interaction⁴ and as part of this programme we have been studying isonicotinic acid HL ($\text{NC}_5\text{H}_4\text{CO}_2\text{H}$ -4), which is capable of co-ordinative bonding *via* the nitrogen and oxygen atoms and hydrogen bonding *via* the carboxylic acid functionality.

The reaction of $[\text{Pd}(\text{dppe})\text{Cl}_2]$ [dppe = bis(diphenylphosphino)ethane] with isonicotinic acid and silver(I) tetrafluoroborate in acetone, followed by recrystallisation from acetone-hexane, resulted in the formation of a mixture of two sets of crystals, one yellow and the other colourless. The yellow crystals lost solvent extremely rapidly, whereas the colourless crystals were stable in air. Spectroscopic data suggested that these colourless crystals contained neither palladium nor dppe, and were instead of a silver isonicotinate complex **1**. Further evidence for this conclusion was obtained by the formation of similar crystals from the reaction of silver(I) tetrafluoroborate with isonicotinic acid in the absence of $[\text{Pd}(\text{dppe})\text{Cl}_2]$.[†] The microanalytical data were consistent with a formulation $[\text{Ag}_3(\text{L})_2]\text{BF}_4$, and a single X-ray analysis[‡] was undertaken both to confirm this and to determine the structure. Although the structural analysis for **1** proceeded smoothly, poor spot shape resulting from variable and large mosaicity within the sample led to unusually small thermal displacement parameters for some of the light atoms. However, this does not detract from the unexpected insight gained as a result of the crystal structure determination.

The asymmetric unit (Fig. 1) was found to consist of three

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[†] Silver(I) tetrafluoroborate (316 mg, 1.6 mmol) was added to a stirred suspension of isonicotinic acid (200 mg, 1.6 mmol) in acetone (40 cm³). After stirring for 48 h in darkness, a colourless solution was separated by filtration, the solvent evaporated under reduced pressure and the crude solid obtained recrystallised from acetone-hexane to yield colourless crystals of **1**. IR (Nujol): $\nu(\text{CO}_2)$ 1580, 1545, 1394; $\nu(\text{BF}_4)$ 1156, 1091, 1026, 1010, 984 cm⁻¹. ¹H NMR [(CD₃)₂CO]: δ 9.24 [d, ³J(HH) 7, CH], 8.65 [d, ³J(HH) 7 Hz, CH] (Found: C, 22.0; H, 1.25; N, 4.32. Calc. for C₁₂H₈Ag₃BF₄N₂O₄: C, 22.0; H, 1.23; N, 4.28%).

[‡] Crystal data for compound **1**. C₁₂H₈Ag₃BF₄N₂O₄, *M* = 654.62, triclinic, space group *P* $\bar{1}$, *a* = 8.328(6), *b* = 10.43(2), *c* = 10.618(3) Å, α = 61.49(9), β = 71.48(9), γ = 81.66(10)°, *U* = 769(2) Å³, *Z* = 2, $\mu(\text{Mo-K}\alpha)$ = 3.852 mm⁻¹, *T* = 150(2) K, Pre-DIFABS *R*_{int} = 0.0809, *R*1 = 0.0325 for 1381 unique reflections from 2146 data collected over the whole sphere of reciprocal space. CCDC reference number 186/1007.

silver atoms at the apices of a triangle, two isonicotinate anions and one tetrafluoroborate anion. Each nitrogen atom in the isonicotinate groups is co-ordinated to a silver atom with Ag–N distances similar to those reported for $[\text{Ag}(\text{L})(\text{HL})]\cdot 4\text{H}_2\text{O}$ (2.166 Å).⁵ The silver–silver distances within the triangle in **1** range from 2.969(5) to 3.236(5) Å (see below).

Examination of the extended structure revealed that all four oxygen atoms within the two isonicotinate anions are co-ordinated, with O(1) and O(2) bonded to Ag(1) and Ag(3) in the asymmetric unit generated *via* the symmetry operator $-x, -y, 1-z$ and similarly, O(3) and O(4) bonded to Ag(1) and Ag(2) generated *via* the symmetry operator $1-x, 1-y, -1-z$. The combined effect of these contacts is to render a series of one-dimensional columnar polymers in the crystal lattice (Fig. 2). When these polymers are considered in isolation, all silver atoms are four-co-ordinate, assuming silver–silver bonds to be present. Of the three silver–silver contacts within each triangle two are bridged by a carboxylate while one is unbridged, and it is this unbridged edge, between Ag(2) and Ag(3), that is the longest. A centre of inversion proximate to Ag(1) (at 0.5, 0, 0) has the effect of interlinking the polymers into sheets by the formation of a short Ag(1)⋯Ag(1) contact, concomitantly raising the co-ordination of Ag(1) to five. This

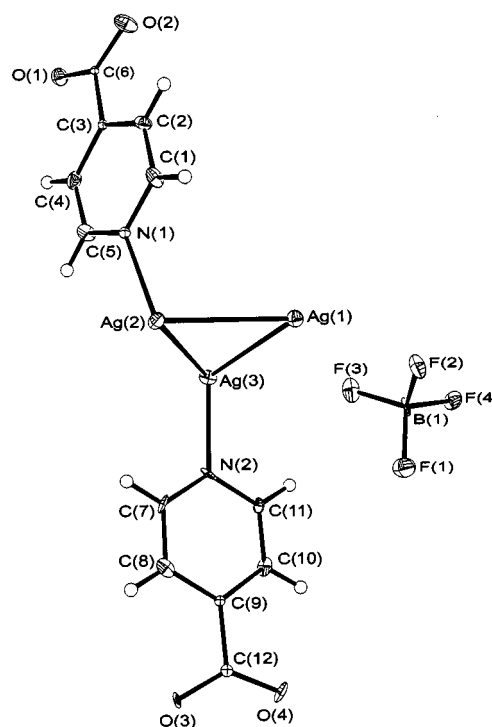


Fig. 1 The asymmetric unit in compound **1** with thermal ellipsoids represented at the 30% probability level. Isotropically refined atoms are represented by non-hatched ellipsoids. Selected bond lengths (Å) and angles (°): Ag(1)–Ag(2) 3.011(2), Ag(1)–Ag(3) 2.969(5), Ag(2)–Ag(3) 3.236(5), Ag(2)–N(1) 2.172(7), Ag(3)–N(2) 2.160(6); Ag(3)–Ag(1)–Ag(2) 65.51(10), Ag(1)–Ag(2)–Ag(3) 56.61(9), Ag(1)–Ag(3)–Ag(2) 57.88(10)

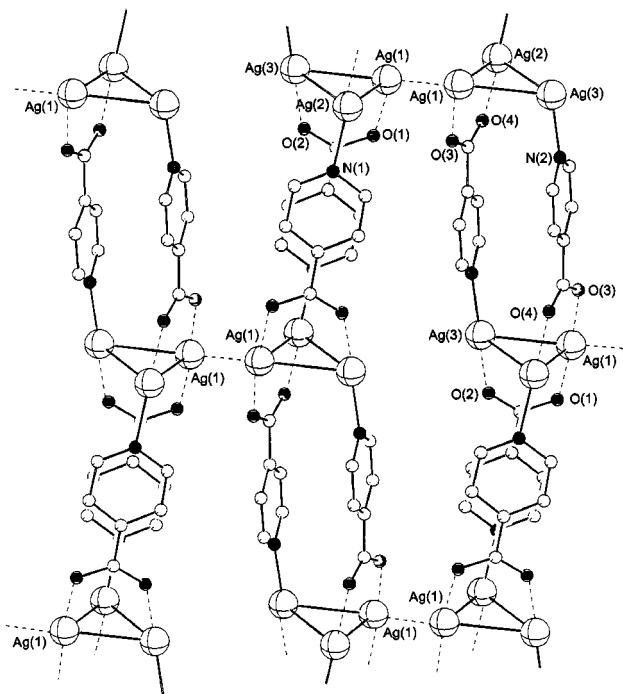


Fig. 2 Part of the linked polymeric columns present in the structure of **1**, with the tetrafluoroborate anions omitted for clarity. Selected bond lengths (Å) and angles (°): Ag(1)–O(1^h) 2.146(6), Ag(1)–O(3^h) 2.134(5), Ag(2)–O(4^h) 2.134(6), Ag(3)–O(2^h) 2.129(5), Ag(1)–Ag(1ⁱⁱⁱ) 3.062(5); Ag(3)–Ag(1)–Ag(1ⁱⁱⁱ) 136.23(8), Ag(2)–Ag(1)–Ag(1ⁱⁱⁱ) 74.07(9), O(1^h)–Ag(1)–O(3^h) 173.9(2), O(4^h)–Ag(2)–N(1) 179.5(3), O(2^h)–Ag(3)–N(2) 175.2(3). Symmetry operations i $-x + 1, -y + 1, -z + 1$, ii $-x, -y, -z$ and iii $-x, -y, -z + 1$, respectively

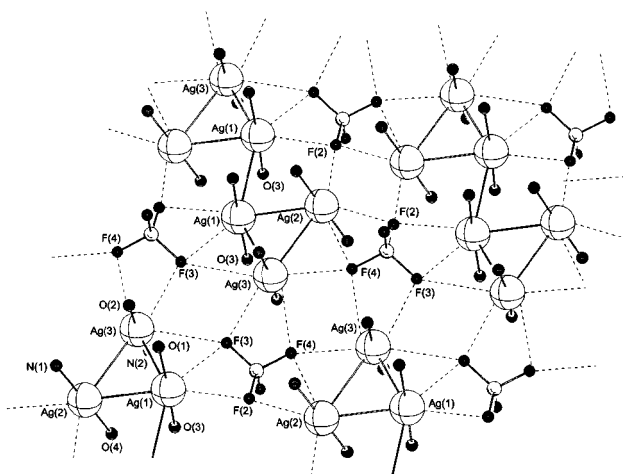


Fig. 3 A section of the structure of polymer **1** showing the interactions between the silver atoms and the tetrafluoroborate anions. The Ag...F contacts (Å) are Ag(1)···F(2) 2.808(6), Ag(1)···F(3) 2.889(7), Ag(2)···F(2^v) 2.870(6), Ag(2)···F(4^v) 3.130(7), Ag(3)···F(4^v) 2.948(6), Ag(2)···F(2^{vi}) 2.898(8), Ag(3)···F(3^{vii}) 2.857(7), Ag(3)···F(4^{vii}) 2.922(7). Symmetry operations v $-1 + x, y, z$, vi $1 - x, -y, -z$ and vii $1 - x, 1 - y, -z$, respectively

Ag...Ag contact is unbridged but significantly shorter [3.062(5) Å] than the unbridged edge of the triangle.

The angles between the plane of the silver atoms and the planes of the isonicotinates are somewhat distorted from the perpendicular, being 88.3(2) [for the isonicotinate containing N(1)] and 77.2(2)° [for the isonicotinate containing N(2)]. Examination of the torsion angles involving the carboxylates

revealed that this functionality in the isonicotinate containing N(2) is considerably more twisted from the pyridyl plane [13(1)°] than that in the isonicotinate containing N(1) [2(1)°].

While most prevalent amongst the coinage metals for gold(I),⁶ d¹⁰–d¹⁰ interactions have also been observed for copper(I) and silver(I).⁷ In many examples containing short silver–silver distances, the metals are linked by bridging ligands and it is therefore difficult to assess whether the d¹⁰–d¹⁰ interaction contributes significantly to the stability of the structure or whether the metal atoms are just held in proximity by the ligand system. Since compound **1** contains both bridged and unbridged silver–silver contacts it is able to offer some insight into the role of the carboxylates. The fact that the two unsupported contacts are longer than those supported by a bridging carboxylate suggests that these ligands do have a significant effect on the silver–silver separation. However, it is noteworthy that the unsupported distances are both considerably shorter than twice the van der Waals' radius of silver suggesting that significant Ag...Ag interactions must be present. Indeed, in the structure of [Ag(Him)₂]₆[ClO₄]₆ (Him = imidazole) where Ag(Him)₂ units are linked together into a triangle solely by silver–silver interactions⁸ the Ag...Ag contact is considerably longer (3.493 Å) than either of the two unsupported contacts in **1**.

Within the plane containing the silver triangles there are, in addition to the Ag...Ag interactions, significant interactions between the silver atoms and the tetrafluoroborate anions (Fig. 3). These anions are oriented such that one fluorine atom [F(1)] is pointing in the direction of the polymeric chains, whereas each of the other three fluorine atoms interact with three silver atoms. The Ag...F distances range from 2.808(6) to 3.130(7) Å, all within the combined van der Waals' radii for both atoms (3.19 Å). Interactions between silver(I) and BF₄⁻ anions have been observed before, most notably in the structure⁹ of [Ag(L')₂]BF₄ (L' = 2,6-dimethylpyridine) in which Ag...F interactions [3.011(8)] serve to link the cations into chains. The reduction of symmetry of the BF₄⁻ anion in the solid state is further evidenced by the infrared spectrum which shows several distinct ν(B–F) resonances as opposed to a single broad peak.

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