Simple linear asymmetrical complexes of silver(I): NC–Ag–NH_3 and Br–Ag–NH_3†

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The compounds Ag(CN)(NH_3) and Ag(Br)(NH_3) are remarkable in that they form solids containing the simple molecular units NC–Ag–NH_3 and Br–Ag–NH_3, rather than extended solids, and are the first examples of simple linear asymmetric complexes of silver(I).

Symmetrical linear complexes of silver(I) (d^{10}) *e.g.* $[Ag(NH_3)_2]^+$ and $[AgX_2]^-$ (X = Cl, Br I, CN), are well documented and discussed in every inorganic chemistry textbook.[1] However, asymmetric variants of these simple complexes appear to be unknown. Whilst exploring the chemistry of the group 11 cyanides, we were curious to discover whether Ag(CN)(NH_3) could be prepared. The copper compound, CuCN·NH_3, is known and adopts an interesting extended layer structure,[2] in which copper has a coordination number of four. Although four coordination is not unknown for silver in silver–cyanide compounds,[3] lower coordination numbers of silver are more common. For example, silver cyanide reacts with pyridine and related amines to form structures retaining the –(Ag–CN)– chains, with nitrogen atoms from the amine coordinated to produce three-coordinate silver.[4] Discrete molecular units also containing three-coordinate silver are known with bidentate amines and cyclic amines bound to isolated Ag–CN units.[5] We have prepared Ag(CN)(NH_3) and are surprised to find that it does not form an extended structure, but rather a molecular complex, NC–Ag–NH_3. This is the first example of a simple asymmetrical mononuclear complex of Ag(I).

Crystals of Ag(CN)(NH_3) were formed on partial loss of ammonia from AgCN dissolved in concentrated ammonia solution.‡ Total loss of ammonia resulted in the formation of AgCN and indeed, this method has been used previously to prepare single crystals of AgCN.[6] The crystals of Ag(CN)(NH_3) decomposed rapidly when removed from the supernatant, and this probably explains why they have previously been overlooked. Single-crystal X-ray diffraction studies were carried out at 230 and 150 K.§ Fig. 1 shows the structure of Ag(CN)(NH_3) at 230 K (form I), which crystallises in space group *Cmcm* and contains discrete NC–Ag–NH_3 molecules. The Ag1–C1 and Ag1–N2 distances are close to the values found in the simple symmetrical complex ions, $[Ag(CN)_2]^-$,[7] and $[Ag(NH_3)_2]^+$.[8] The C1–Ag1–N2 bond angle is 180° by symmetry. The NC–Ag–NH_3 units pack in layers in the *ac* plane (Fig. 1(a)) yielding four equal near-neighbour head-to-tail interactions between the CN and NH_3 ends of the molecules (N1···N2, 3.300(4) Å). In addition, there are two equivalent (N1···N2) contacts of 3.312(4) Å between layers, of similar length to the intralayer contacts (Fig. 1(b)). The hydrogen atoms of the ammonia group were located in

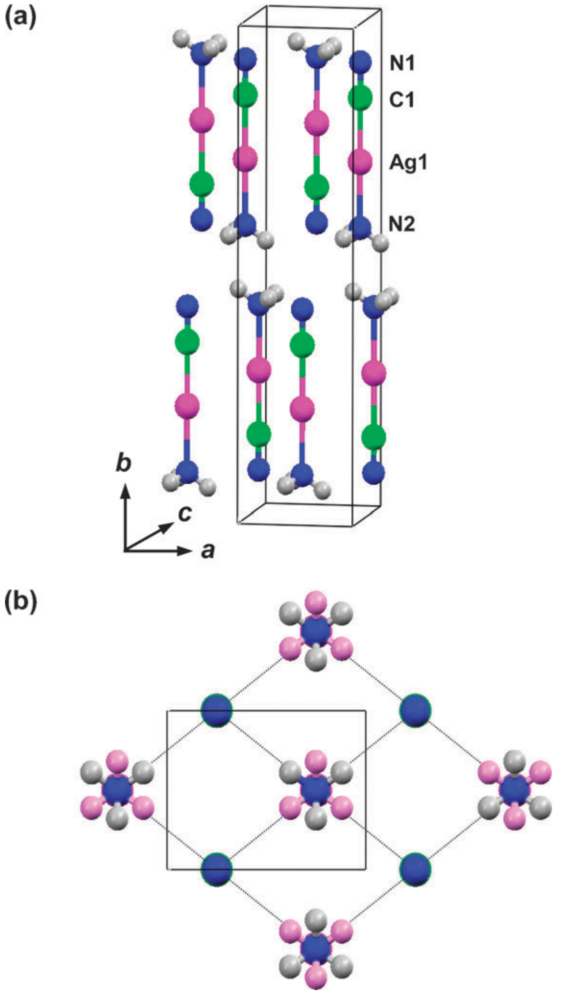

Fig. 1 Ag(CN)(NH_3) (form I) at 230 K showing (a) NC–Ag–NH_3 molecules packed into layers in the *ac* plane (note only one of the two symmetry equivalent orientations of the NH_3 molecule is shown) and (b) the view down *b* showing the two possible orientations of the NH_3 molecule (grey and pink hydrogen atoms) and the resulting *intra*layer hydrogen bonds. Selected bond lengths (Å) and angles (°): Ag1–C1 2.051(5), Ag1–N2 2.114(4), C1≡N1 1.136(6); C1–Ag–N2 180, Ag1–C1–N1 180. [Note: The labelled molecule is not the original molecule of the CIF].

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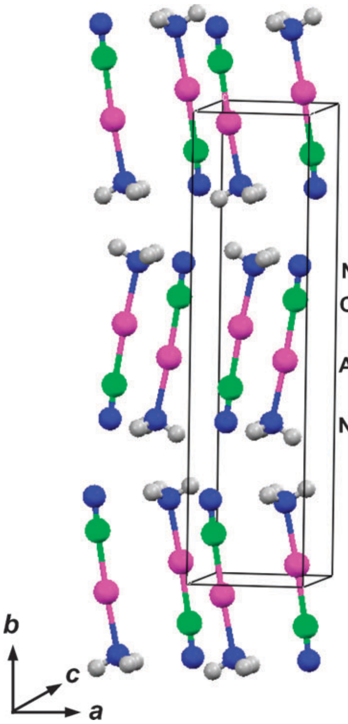

Fig. 2 Ag(CN)(NH$_3$) (form II) at 150 K showing canted NC–Ag–NH$_3$ molecules lying in layers in the *ac* plane. Selected bond lengths (Å) and angles (°): Ag1–C1 2.057(3), Ag1–N2 2.123(2), C1$\equiv$N1 1.142(4); C1–Ag1–N2 177.35(8), Ag1–C1–N1 177.5(3). [Note: The labelled molecule is not the original molecule of the CIF].

difference Fourier maps. The NH$_3$ group is rotationally disordered over two symmetry equivalent positions, which yield for each orientation, two *intra*- and one *inter*-layer hydrogen bond. The layers stack in *ABAB* manner along *b*.

On cooling to 150 K, another polymorph (form II), space group *Pbcm*, is found (Fig. 2). This also contains NC–Ag–NH$_3$ molecules with Ag1–C1 and Ag1–N2 bond lengths similar to those found in form I. However, the C1–Ag1–N2 bond angle is no longer symmetry constrained and is slightly distorted from linearity at 177.35(8)°. The molecules are now tilted by ~9° about the *c* axis and are no longer parallel to the *b* axis, as found in form I. Instead of four equivalent near-neighbour head-to tail *intra*layer interactions, as found in form I, there are two slightly shorter (N1···N2, 3.267(2) Å) and two slightly longer interactions (N1···N2, 3.351(2) Å). In addition, there are now two non-equivalent *inter*layer N1···N2 distances of 3.222(3) and 3.307(3) Å. In contrast to form I, the hydrogen atoms of the ammonia group are ordered. The ammonia orientation appears to be controlled by forming the shorter hydrogen bond between the layers as the *intra*layer hydrogen bonds form between the slightly longer N1···N2 contacts. On heating the crystal *in situ* under nitrogen, the structure of form I was retained until decomposition occurred at 370 K with the formation of polycrystalline AgCN.

An obvious extension to this work is to synthesise Ag(X)NH$_3$ compounds where X is another pseudohalide, such as SCN, or a halide. We have prepared a number of such new compounds and the work on AgSCN will be reported elsewhere. Most pertinent to this communication is the successful preparation of Ag(Br)(NH$_3$). This material also contains an asymmetric molecule, Br–Ag–NH$_3$ (Fig. 3). Both the Ag–Br1 and Ag–N1 distances of 2.5358(5) and 2.192(5) Å, respectively, are longer than those found in the corresponding complex ions, [Ag(Br)$_2$]$^-$ (Ag–Br, 2.43–2.46 Å)[9] and [Ag(NH$_3$)$_2$]$^+$ (Ag–N, 2.11 Å).[8] In Ag(Br)(NH$_3$), the molecule shows a slight distortion from linearity, with a Br1–Ag1–N1 bond angle of 165.01(12)°. This can be ascribed to a weak interaction between silver and the bromine atom of a neighbouring molecule (Ag1···Br1$^{\mathrm{i}}$, 2.9714(5) Å). As in the polymorphs of Ag(CN)(NH$_3$), the molecules stack in layers. The layers contain chains of head-to-tail aligned Br–Ag–NH$_3$ molecules in which the Ag1···Ag1$^{\mathrm{ii}}$ separation is relatively short at 3.260(1) Å, less than twice the van der Waals' radius of silver (3.40 Å), suggesting some degree of *argentophilic* interaction.[3c,7a,10] The Ag···Ag distances between the chains are longer at 4.115(1) and 4.193(1) Å. The weak Ag1···Br1$^{\mathrm{i}}$ interactions mentioned above are between atoms in adjacent chains. In this material, the ammonia molecules are ordered with two hydrogen atoms directed towards bromine atoms within the chains (N1···Br1, 3.619(3) Å). There is a third hydrogen bond to a bromine atom in a neighbouring layer (N1···Br1, 3.656(4) Å). This material is less thermally stable than Ag(CN)(NH$_3$) and on heating the crystals in N$_2$ at 300 K, polycrystalline AgBr is formed.

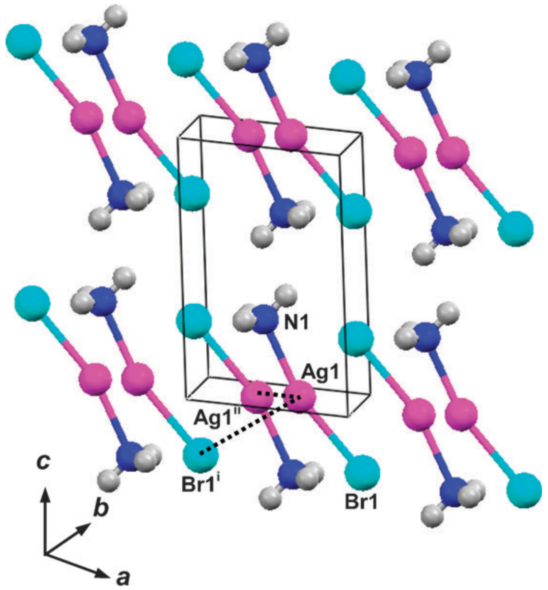

Fig. 3 Ag(Br)(NH$_3$) showing layers of slightly bent Br–Ag–NH$_3$ molecules. The dotted lines indicate weak *inter*molecular *argentophilic* and silver–bromine interactions. Selected bond lengths (Å) amd angles (°): Ag1–Br1 2.5358(6), Ag1–N1 2.192(5), Ag1···Br1^{i} 2.9714(6), Ag1···Ag1$^{\mathrm{ii}}$ 3.2604(3); Br1–Ag1–N1 165.01(12). [Symmetry codes: (i) $x - 1, y, z$; (ii) $1 - x, -y, -z$].

It is remarkable that Ag(CN)(NH$_3$) and Ag(Br)(NH$_3$) exist as such simple compounds and have not been characterised previously either in solution or the solid state. The most closely related complexes in the literature of the form X–Ag–Y have at least one bulky ligand attached to silver.[11] We are curious to find if we can prepare other isomers or polymorphs of these materials, such as a silver analogue of CuCN·NH$_3$, with an extended layer structure, and in particular, an ionic isomer of the form $[Ag(NH_3)_2]^+[Ag(CN)_2]^-$. To date, our efforts using diffusion between solutions containing these ions have yielded the molecular species NC–Ag–NH_3,‡ but we are continuing in our endeavours.

Notes and references

‡ **Ag(CN)(NH_3):** Single crystals of Ag(CN)(NH_3) were prepared using two methods:

a. Ag(CN)(NH_3) from AgCN and aqueous ammonia: This method is modified from that used by Cromer *et al.*[2] to prepare CuCN·NH_3. AgCN (0.2000 g, 1.5 mmol) was shaken with aqueous NH_3 (35%, 10 ml, 180 mmol) for 3 min and left to settle for 10 min. The supernatant was decanted into a vial. After a few minutes, small colourless crystals in the form of thin diamond-shaped plates started to precipitate. The vial was put into a bell jar, which was then evacuated and left for three days to allow further crystallisation.

b. Ag(CN)(NH_3) from $Ag(CN)_2^-$ and $Ag(NH_3)_2^+$: A solution containing $Ag(NH_3)_2^+$ was prepared by decanting the supernatant formed after stirring Ag_2O (0.2317 g, 1 mmol) with aqueous NH_3 (35%, 8 ml, 144 mmol) for three days. This was layered on top of the supernatant containing $Ag(CN)_2^-$ prepared by reaction between NaCN (0.049 g, 1 mmol) in water (5 ml) and AgCN (0.1333 g, 1 mmol). Colourless crystals immediately formed between the two layers. After three days, the whole of the lower $Ag(CN)_2^-$ layer filled with crystals. The crystals are stable when left in the ammoniacal solution in sealed vials, but decompose rapidly in air. In open vials, ammonia is slowly lost from the supernatants (methods 1 and 2), and Ag(CN)(NH_3) decomposes to form crystals of AgCN.

Ag(Br)(NH_3) from AgBr and aqueous ammonia: Single crystals of Ag(Br)(NH_3) were prepared by shaking AgBr (0.4721 g, 2.5 mmol) with aqueous NH_3 (35%, 10 ml, 180 mmol) for 3 min. It was noted that the remaining solid was white rather than the cream colour of silver bromide. The supernatant was decanted and stored in an evacuated bell jar. After seven days, crystals of Ag(Br)(NH_3) formed as very thin, colourless rectangular plates. These crystals were also difficult to isolate and again decomposed rapidly when removed from the ammoniacal solution. Decomposition appeared facile: in some cases, the act of removing crystals from the supernatant leads to the disappearance of crystals of Ag(Br)(NH_3) and the formation of crystals of AgBr.

§ Crystals of both compounds decomposed readily in air on the microscope slide and so were transferred directly from their ammoniacal solutions into perfluorinated polyether, in which they were moderately stable. Crystals suitable for diffraction studies were picked up with a nylon loop attached to the goniometer head and mounted on the diffractometer under a cold nitrogen stream. Diffraction data were collected using a Oxford Gemini S Ultra diffractometer (graphite-monochromated Mo-Kα radiation). Structures were solved by Direct Methods (SIR-92) and refined by full matrix least-squares on *F* (CRYSTALS). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the ammonia molecules were located in difference Fourier maps and included in the refinements. Drawing package: Mercury.1.4.2.

Crystal data: **Ag(CN)(NH_3) – form I:** CH_3N_2Ag, M = 150.92, orthorhombic, space group *Cmcm*, a = 3.9543(3), b = 15.9183(6), c = 5.2689(2) Å, V = 331.65(3) Å^3, T = 230(1) K, Z = 4, D_c = 3.022 Mg m^{-3}, 2307 reflections measured, 330 unique (R_{int} = 0.017). $R(F)$ = 0.0166, $wR(F)$ = 0.0156, using 264 observed reflections with $I > 3\sigma(I)$. CCDC 679751.

Ag(CN)(NH_3) – form II: CH_3N_2Ag, M = 150.92, orthorhombic, space group *Pbcm*, a = 3.9034(3), b = 15.7268(13), c = 5.3245(5) Å, V = 326.86(5) Å^3, T = 150(1) K, Z = 4, D_c = 3.067 Mg m^{-3}, 1761 reflections measured, 564 unique (R_{int} = 0.014). $R(F)$ = 0.0154, $wR(F)$ = 0.0170, using 391 observed reflections with $I > 3\sigma(I)$. CCDC 679750.

Ag(Br)(NH_3): H_3NBrAg, M = 150.92, monoclinic, space group $P2_1/m$, a = 4.1931(3), b = 5.8730(3), c = 6.7570(4) Å, β = 97.553(5)°, V = 164.955(2) Å^3, T = 100(1) K, Z = 2, D_c = 4.123 Mg m^{-3}, 1409 reflections measured, 575 unique (R_{int} = 0.022). $R(F)$ = 0.0264, $wR(F)$ = 0.0295, using 464 observed reflections with $I > 3\sigma(I)$. CCDC 679752.

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