

Syntheses, Structures and Vibrational Spectroscopy of Some Adducts of Silver(I) Cyanide with (Oligo-)Pyridine Bases

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

Crystalline materials obtained by the crystallization of silver(I) cyanide from/with a variety of (oligo-)pyridine bases, L, of various bulk, have been characterized by room temperature single crystal X-ray structure determination. From L = quinoline (= 'quin'), AgCN : quin (1:2), is obtained, the structure being a single-stranded polymer, the successive silver atoms located on two-fold axes linked by linearly bridging cyanide groups and four-coordinate, the other two coordination sites being occupied by symmetry related quinoline nitrogen atoms. From L = 2,4,6-trimethylpyridine ('collidine' \equiv 'coll') AgCN : coll (1:1) is obtained; it is similarly a one-dimensional polymer with bridging cyanide linkages, but now with three-coordinate silver(I), the one ligand nitrogen being coordinated. The adduct for L = pyridine (= 'py'), is of novel AgCN : py (10:9) stoichiometry; it also is a one-dimensional polymer, with three-coordinate silver(I) atoms also coordinated by pyridine nitrogen, but with periodic 'errors' in a wave-like array (similar to that recently reported for 'LT-CuCN'), here associated with the incorporation of occasional two-coordinate silver(I) lacking the pyridine – an unusual coordination complex example of a 'modulated' structure?

1:1 adducts are obtained with L = 2,2'-bipyridine, 'bpy', 1,10-phenanthroline, 'phen', and 2,9-dimethylphenanthroline, 'dmp', the latter two adducts being 'solvated' with additional moles of phen and pyridine respectively. AgCN : bpy (1:1) is a single-stranded polymer with four-coordinate silver atoms linearly bridged by cyanides. The complex components of AgCN : phen (1:2) (\equiv AgCN : phen (1:1), phen) and AgCN : dmp (: py) (1:1(:1)) are both mononuclear 1:1 species, [LAgCN], with three-coordinate metal atoms. With 2,2':6',2''-terpyridyl, 'tpy', a pyridine solvated adduct of AgCN : tpy : py (8:2:1) stoichiometry is found, the pyridine being incorporated in the one-dimensional polymer which comprises an ...Ag'(NCAgCN)Ag'(NCAgCN)Ag'... spine, with (tpy)Ag(NCAgCN)Ag' and Ag'(NCAg(py)CN)(tpy) units pendant to either side at alternate three-coordinate Ag'. In all of the oligodentate ligand complexes, the molecular packing is of interest, being dominated by the usual interleaving and perpendicular aromatic planar moieties.

The IR spectra of the one-dimensional polymers show bands that are assigned to vibrations of the extended AgCN chains in these complexes: $\nu(\text{CN})$, $\nu(\text{AgC/N})$ (the AgC/AgN stretching mode, involving vibration of the CN group between its two neighbouring Ag atoms), $\delta(\text{AgCN})$ (the restricted rotation of the CN group), and $\delta(\text{NAgC})$ (the counter-vibration of the Ag substructure against the CN substructure). The $\nu(\text{CN})$ and $\nu(\text{AgC/N})$ bands in AgCN : py (10:9) occur in the ranges 2096 – 2154 and 360 – 460 cm^{-1} respectively, and show splittings that can be attributed to the unusual structure of this complex in the solid state. The Raman spectra of the py complex in the solid state and in solution are also discussed. In the other two unidentate ligand complexes, single bands are observed for the $\nu(\text{CN})$ and $\nu(\text{AgC/N})$ modes at 2140, 392 (AgCN : coll (1:1)) and 2140, 422 cm^{-1} (AgCN : quin (1:2)) respectively. The monomeric AgCN : bidentate ligand complexes AgCN : phen (1:1) and AgCN : dmp (1:1) show lower $\nu(\text{CN})$ and $\nu(\text{AgC/N})$ frequencies than the polymeric AgCN : bpy (1:1), despite the fact that the Ag-C/N distances in the former are shorter than that in the latter, in agreement with previously observed trends in AgCN/ER₃ compounds.

Key words: Silver Cyanide, Pyridine, Structure, Infrared Spectroscopy, Raman Spectroscopy

Introduction

Unidentate nitrogen base adducts of coinage metal(I) pseudo-halides, frequently conveniently obtained by crystallizing the metal pseudohalide from the many conveniently liquid nitrogen bases at room temperature, perhaps in the presence of a coordinating supporting solvent, have been described for a number of adducts of copper(I) cyanide (of 1:1 stoichiometry with EtNH₂ and NEt₃, and 2:3 stoichiometry with 4-methylpyridine (4mp)) [1, 2], copper(I) thiocyanate (of 1:1 stoichiometry with 2mp and 2,6-dimethylpyridine (2,6-lut), and of 1:2 stoichiometry with 2-,3- and 4mp, 2,4-lut and quinoline ('quin')) [3] and of silver(I) thiocyanate (of 1:1 stoichiometry with 2- and 3mp and 2,6-lut, and of 1:2 stoichiometry with py (pyridine) and quin) [4, 5]; mixed metal adducts [Ag_xCu_y(SCN)_(z)] have also recently been recorded [5]. In such adducts, the ambidentate role of the pseudohalide is pronounced, inasmuch as that all of the above adducts are infinite polymers, linked by pseudohalide species coordinating through both ends, whereas in halide analogues, despite the presence of bridging halide species in the lower stoichiometries concomitant with coordinative saturation of the metal, polymeric arrays are rather more rare although by no means unknown. In the above array, complexes of silver(I) cyanide are absent. Indeed, rather surprisingly, the structure of silver(I) cyanide itself has been determined only recently [6, 7]. While there have been a few recent reports of complexes of silver(I) cyanide with S-donor ligands such as thioureas and sulfones [8], there is very little information on such complexes with N-donor ligands. The present work is an initial contribution towards establishing their existence and nature, describing the synthesis, single crystal structural characterization, and vibrational spectra of those adducts obtained by the crystallization of silver(I) cyanide from the pyridine bases: quin, 2,4,6-trimethylpyridine ('collidine'≡'coll'), and py, these being unidentate py base ligands. Adducts are also described with the oligo-dentate extensions 2,2'-bipyridine, ('bpy'), 1,10-phenanthroline, ('phen'), 2,9-dimethylphenanthroline ('dmp') and 2,2':6',2''-terpyridine, ('tpy'). The structural characterisation of decahydropyrazine[2,3-*b*]pyrazine, C₆H₁₄N₄, obtained crystalline from a silver(I) cyanide/ethylenediamine ('en') reaction mixture, is also recorded.

Experimental Section

Synthesis

The unidentate pyridine base complexes were obtained by dissolving silver cyanide (0.15 g, ~ 0.1 mmol) in the relevant liquid base (~ 5 ml) with warming, giving clear solutions which deposited colourless crystals of the product on cooling and standing. The parent py complex loses solvent very readily on exposure to the atmosphere and was accordingly not sent for analysis. Specimens were mounted in capillaries for the X-ray work.

AgCN : quin (1:2). C₁₉H₁₄AgN₃ (392.2): calcd. C 58.19, H 3.60, N 10.71; found C 57.9, H 3.6, N 10.8.

AgCN : coll (1:1). C₉H₁₁AgN₂ (255.1): calcd. C 42.38, H 4.35, N 10.98; found C 42.5, H 4.4, N 11.0.

Crystalline oligodentate base complexes were obtained by dissolution and crystallization of a 1:1 stoichiometry of silver(I) cyanide with the appropriate base from a suitable supporting solvent, acetonitrile being used for the bpy and phen complexes, and py for the dmp and tpy, the scale typically being millimolar in 5 ml solvent, with volume reduction as necessary.

AgCN : bpy (1:1). C₁₁H₈AgN₃ (290.1): calcd. C 45.55, H 2.78, N 14.49; found C 46.0, H 2.8, N 15.1.

AgCN : phen (1:2). C₂₅H₁₆AgN₅ (494.3): calcd. C 60.75, H 3.26, N 14.17; found C 60.7, H 3.2, N 14.2.

AgCN : dmp : py (1:1:1). This complex also is susceptible to ready loss of solvent, the 'best' analysis obtained being: C₂₀H₁₇AgN₄ (421.3): calcd. C 57.03, H 4.07, N 13.30; found C 56.5, H 4.0, N 13.4.

AgCN : tpy : py (8:2:1). This complex also loses solvent readily and satisfactory analyses were not obtained.

An attempt was also made to obtain a complex between silver(I) cyanide and 'ethylenediamine' ('en' = H₂NCH₂CH₂NH₂) by dissolution and crystallization of AgCN from the liquid parent base. AgCN (0.134 g, 1.0 mmol) and en (1.5 g, 25.0 mmol) were combined, whereupon an exothermic reaction occurred. The solution was held at 70 °C for 1 h, and allowed to cool. After removal of excess en there remained a grey solid (0.37 g). Recrystallization from methanol afforded a white powder (sub. > 190 °C), which, even after several recrystallizations, continued to deposit grey powder, presumably Ag metal. Notwithstanding, the analysis ultimately obtained [C₆H₁₄N₄ (142.2): calcd. C 50.68, H 9.92, N 39.40; found C 50.8, H 9.7, N 39.0], in combination with the structure determination establishes the compound as *decahydropyrazine*[2,3-*b*]*pyrazine* [9]. On subsequent occasions, on reacting other silver(I) salt/ligand mixtures with en, this substance has been also obtained, indicating that the presence of cyanide is only incidental.

The samples used in the IR spectroscopic studies were prepared in the above manner, and also *in situ* by adding an excess of the liquid ligand to solid AgCN, removing the excess liquid, and then preparing the sample as a mull in the normal way. In the case of AgCN : 4mp (1:1) and AgCN : en (1:1), samples were also prepared by direct addition of ligand and vapour to solid AgCN. A weighed amount of AgCN in a glass tube was placed in a Schlenk tube containing an excess of the liquid ligand, and the tube was sealed, evacuated, and allowed to stand. The mass of the final products confirmed that uptake of 1 mole of 4mp and 1 mole of en per mole of AgCN had occurred, the IR spectrum for the 4mp adduct confirming that the complex is the same as the compound obtained from the liquid ligand synthesis.

Spectroscopy

Procedural details are given in an accompanying paper [1]. Fresh samples of the complexes obtained from the preparative procedure described above were used. Samples of the complexes involving liquid ligands were also prepared *in situ* for IR spectroscopy by adding a few drops of the appropriate ligand to a small amount of solid AgCN, removing the excess liquid, and then preparing the sample as a mull in the normal way.

Structure determinations

General procedures are given in ref. [1]; specific crystal/refinement details are as follows:

AgCN : quin (1:2). $C_{19}H_{14}AgN_3$, $M = 392.2$. Single counter instrument; T ca. 295 K. Monoclinic, space group $C2/c$ (C_{2h}^6 , No. 15), $a = 13.904(3)$, $b = 11.712(3)$, $c = 9.972(2)$ Å, $\beta = 94.82(2)^\circ$, $V = 1618$ Å³. $Z = 4$; $\rho_{\text{calcd.}} = 1.610$ g cm⁻³. $\mu_{\text{Mo}} = 11.3$ cm⁻¹; specimen: $0.07 \times 0.11 \times 0.32$ mm; $T_{\text{min,max}} = 0.89, 0.94$. $2\theta_{\text{max}} = 65^\circ$; $N = 2917$, $N_o = 1396$; $R = 0.040$, $R_w = 0.040$. $|\Delta\rho_{\text{max}}| = 0.65(4)$ e Å⁻³. (x, y, z, U_{iso})_H were refined.

Variata. As modelled in space group $C2/c$, the silver atoms are located on two-fold axes with inversion centres at the centre of the linearly coordinated cyanide groups, which must necessarily be disordered. Although not possible to fruitfully refine the structure in space group Cc , disordered C,N components of the cyanides were resolvable and refinable, assignment of the fragments being made on the basis of displacement parameter magnitudes and site occupancy considerations.

AgCN : coll (1:1). $C_9H_{11}AgN_2$, $M = 255.1$. Single counter instrument; T ca. 295 K. Monoclinic, space group $P2_1/c$ (C_{2h}^5 , No. 14), $a = 8.6535(5)$, $b = 9.776(1)$, $c = 14.286(4)$ Å, $\beta = 121.97(1)^\circ$, $V = 1052$ Å³. $Z = 4$; $\rho_{\text{calcd.}} = 1.652$ g cm⁻³. $\mu_{\text{Mo}} = 17.5$ cm⁻¹; specimen: $0.10 \times 0.35 \times 0.08$ mm; $T_{\text{min,max}} = 0.80, 0.89$. $2\theta_{\text{max}} = 65^\circ$;

$N = 3697$, $N_o = 1427$; $R = 0.039$, $R_w = 0.039$. $|\Delta\rho_{\text{max}}| = 0.69(5)$ e Å⁻³. (x, y, z, U_{iso})_H were refined.

Variata. As in (1), the nitrogen of the cyanide was assigned by refining both atoms as carbon with variable population, and assigning the greater of the two (where significantly so, as in both cases) as nitrogen.

AgCN : py (10:9). $C_{55}H_{45}Ag_{10}N_{19}$, $M = 2050.7$. Single counter instrument; T ca. 295 K. Monoclinic, space group $P2_1/c$, $a = 8.594(2)$, $b = 49.85(2)$, $c = 7.419(3)$ Å, $\beta = 92.70(3)^\circ$, $V = 3175$ Å³. $Z = 2$; $\rho_{\text{calcd.}} = 2.145$ g cm⁻³. $\mu_{\text{Mo}} = 30.6$ cm⁻¹; specimen: $0.02 \times 0.10 \times 0.28$ mm; $T_{\text{min,max}} = 0.74, 0.94$. $2\theta_{\text{max}} = 65^\circ$; $N = 9804$, $N_o = 3169$; $R = 0.056$, $R_w = 0.054$. $|\Delta\rho_{\text{max}}| = 0.86$ e Å⁻³.

Variata. Except in pyridine py(1), nitrogen atoms were modelled as disordered at the 1,4-positions with carbon throughout (see Discussion). The long axis presented difficulties of the usual kind, and in view of such problems, as well as possible twinning, the problem was treated circumspectly to guard against the unusual result being an artifact of profile overlap in the data or other causes; data were measured using an ω -scan mode. A number of specimens were tried, all behaving similarly, prior to choice of the 'best', the above, which although small, diffracted surprisingly strongly.

AgCN : bpy (1:1). $C_{11}H_8AgN_3$, $M = 290.1$. CCD instrument; T ca. 300 K. Monoclinic, space group $C2/c$ (C_{2h}^6 , No. 15), $a = 12.468(2)$, $b = 8.696(1)$, $c = 10.058(2)$ Å, $\beta = 105.657(2)^\circ$, $V = 1050.0$ Å³. $Z = 4$; $\rho_{\text{calcd.}} = 1.835$ g cm⁻³. $\mu_{\text{Mo}} = 18.9$ cm⁻¹; specimen: $0.21 \times 0.14 \times 0.06$ mm; $T'_{\text{min/max}} = 0.80$. $2\theta_{\text{max}} = 58^\circ$; $N_t = 6043$; $N = 1320$ ($R_{\text{int}} = 0.017$), $N_o = 1158$; $R = 0.027$, $R_w = 0.038$. $|\Delta\rho_{\text{max}}| = 0.84(1)$ e Å⁻³. (x, y, z, U_{iso})_H were refined.

Variata. Cyanide C, N were modelled as C/N composites.

AgCN : phen (1:1). **phen.** $C_{25}H_{16}AgN_5$, $M = 494.3$. CCD instrument; T ca. 300 K. Orthorhombic, space group $Pnna$ (D_{2h}^6 , No. 52), $a = 7.1945(9)$, $b = 18.617(2)$, $c = 15.207(2)$ Å, $V = 2037$ Å³. $Z = 4$; $\rho_{\text{calcd.}} = 1.612$ g cm⁻³. $\mu_{\text{Mo}} = 10.1$ cm⁻¹; specimen: $0.65 \times 0.24 \times 0.21$ mm; $T'_{\text{min/max}} = 0.66$. $2\theta_{\text{max}} = 58^\circ$; $N_t = 20375$; $N = 2625$ ($R_{\text{int}} = 0.023$), $N_o = 1861$; $R = 0.033$, $R_w = 0.046$. $|\Delta\rho_{\text{max}}| = 0.57(1)$ e Å⁻³. (x, y, z, U_{iso})_H were refined.

AgCN : dmp (1:1). **py** $C_{20}H_{17}AgN_4$, $M = 421.3$. CCD instrument; T ca. 300 K. Orthorhombic, space group $Pnna$ (D_{2h}^6 , No. 52), $a = 24.996(3)$, $b = 6.7408(8)$, $c = 10.455(1)$ Å, $V = 1761.6$ Å³. $Z = 4$; $\rho_{\text{calcd.}} = 1.588$ g cm⁻³. $\mu_{\text{Mo}} = 11.5$ cm⁻¹; specimen: $0.13 \times 0.18 \times 0.12$ mm; $T'_{\text{min/max}} = 0.79$. $2\theta_{\text{max}} = 58^\circ$; $N_t = 18828$; $N = 2434$ ($R_{\text{int}} = 0.036$), $N_o = 1768$; $R = 0.040$, $R_w = 0.055$. $|\Delta\rho_{\text{max}}| = 0.72(1)$ e Å⁻³. (x, y, z, U_{iso})_H were refined.

Variata. The pyridine nitrogen, assigned on the basis of refinement behaviour, is disordered about the mirror plane.

AgCN : tpy : py (8:2:1). $C_{43}H_{27}Ag_8N_{15}$, $M = 1616.7$. CCD instrument; T ca. 300 K Monoclinic, space group $P2_1/c$, $a = 15.854(2)$, $b = 17.092(2)$, $c = 17.660(2)$ Å, $\beta = 103.895(2)^\circ$, $V = 4645$ Å³. $Z = 4$; $\rho_{\text{calcd.}} = 2.311$ g cm⁻³. $\mu_{\text{Mo}} = 33.5$ cm⁻¹; specimen: $0.16 \times 0.07 \times 0.04$ mm; $T'_{\text{min/max}} = 0-64$. $2\theta_{\text{max}} = 50^\circ$; $N_t = 54149$; $N = 8152$ ($R_{\text{int}} = 0.041$), $N_o = 2982$; $R = 0.039$, $R_w = 0.035$. $|\Delta\rho_{\text{max}}| = 0.73(2)$ e Å⁻³.

Variata. All cyanide C, N atoms were modelled as C/N composites.

Decahydropyrazine [2,3-b] pyrazine. $C_6H_{14}N_4$, $M = 142.2$. Single counter instrument; T ca. 295 K. Monoclinic, space group $C2/m$ (C_{2h}^3 , No. 12), $a = 5.300(1)$, $b = 16.04(2)$, $c = 4.639(2)$ Å, $\beta = 109.02(3)^\circ$, $V = 372.0$ Å³. $Z = 2$; $\rho_{\text{calcd.}} = 1.269$ g cm⁻³. $\mu_{\text{Mo}} = 0.8$ cm⁻¹ (no correction); specimen: $0.52 \times 0.21 \times 0.30$ mm; $2\theta_{\text{max}} = 60^\circ$; $N = 689$, $N_o = 391$; $R = 0.061$, $R_w = 0.069$. $|\Delta\rho_{\text{max}}| = 0.38(4)$ e Å⁻³. $(x, y, z, U_{\text{iso}})_H$ were refined.

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC 246176–246183. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

Discussion

Structural studies

Structural characterisations of adducts obtained by the crystallization of coinage metal(I) (pseudo-) halides, MX, from/with (liquid) unidentate nitrogen bases have been reported in our earlier systematic studies, most widely for 1:n MX : L stoichiometry for $n = 3, 2, 1$ depending on a variety of factors, most conspicuously including: the metal (lower n predominating for $M = \text{Ag}$ *ceteris paribus*), available ligand stoichiometry, and ligand steric profile, readily tunable through “one”-, “two”- and “three”-dimensional anions/bases as in oxyanions, pyridine and aliphatic amine donors, previous work focussing heavily on those of substituted pyridines. From these arrays MX : L (1:2) takes three forms L_2MX (copper only) [10] and $L_2M(\mu-X)_2ML_2$ [11] (both discrete) and polymeric $\dots(L_2)MX(L_2)MX\dots$ [3], the latter two both rare for silver(I) [4, 12, 13] and running counter to common prejudices about the nature of $\text{AgX} : \text{NH}_3$ complexes. For MX : L (1:1), there is a wide variety of well-exemplified forms structurally authenticated: discrete tetramers (‘cubane’ form) [14], dimers [15] and monomers [15], described for $M = \text{Cu}$, and polymers:

Table 1. Selected polymer geometries: AgCN : quin, coll (1:2,1).

(a) AgCN : quin (1:2) (see text).

Atoms	Distance [Å]	Atoms	Angles [°]
Ag-N(1)	2.497(3)	N(1)-Ag-C	98(1)
Ag-C	2.28(3)	N(1)-Ag-N ⁱ	111(1)
Ag-N ⁱ	2.04(3)	N(1)-Ag-N(1 ⁱⁱ)	98.5(1)
C-N	1.12(4)	C-Ag-N(1 ⁱⁱ)	108(1)
(C-N ⁱ)	0.33(4)	C-Ag-N ⁱ	134(2)
		N ⁱ -Ag-N(1 ⁱⁱ)	102(1)
		Ag-N(1)-C(2)	119.3(3)
		Ag-N(1)-C(8a)	122.0(2)
		Ag-C-N	172(4)
		Ag-N ⁱ -C ⁱ	175(5)

Transformations of the asymmetric unit: ⁱ $x, 1-y, \frac{1}{2}+z$; ⁱⁱ $1-x, y, \frac{1}{2}-z$.

(b) AgCN : coll (1:1)

Atoms	Distance [Å]	Atoms	Angles [°]
Ag-C	2.056(6)	C-Ag-N ⁱ	127.7(2)
Ag-N ⁱ	2.261(5)	C-Ag-N(1)	140.8(2)
Ag-N(1)	2.266(4)	N ⁱ -Ag-N(1)	91.4(2)
C-N	1.128(6)	Ag-C-N	177.7(5)
		Ag-C ⁱ -N ⁱ	169.9(4)

Transformation: ⁱ $2-x, \frac{1}{2}+y, \frac{3}{2}-z$.

‘stair/ribbon’ polymers (both Cu [16], Ag [17]), ‘split stair’ (Cu) [18], ‘saddle’ [19] and ‘tube’ (Ag only) [12, 17]. For silver, a diversity of results has been reported for derivatives of the pseudo-halide thiocyanate [4, 5], but with nothing as yet for cyanides in such systems.

In the present study, colourless, crystalline materials have been obtained by the crystallization of silver(I) cyanide from neat liquid py bases and subjected to room temperature single crystal X-ray studies. The results of the latter are consistent with their description as silver(I) cyanide : nitrogen base adducts of 1 : x stoichiometry (x various). All incorporate cyanide species as end-bound ambidentate entities bridging the silver atoms into single stranded infinite polymers without crosslinking, the additional coordination sites on the silver being occupied by unidentate nitrogen base entities. In many such polymeric cyanide complexes, the coordination mode of the cyanide is ambiguous, end-for-end interchange being feasible, and not infrequently in a context where even if the two atoms do/can exist in putatively different environments, their distinction by refinement techniques in the X-ray study has been, for a variety of reasons, not practicable. Such is the case here in the quin and py adducts; in the former, the space group is $C2/c$ or very nearly so, with, in that

Table 2. Selected structural parameters: AgCN : py (10:9). C/N composites are denoted by X.

Atoms	Params	Atoms	Params
<i>Distances [Å]:</i>			
Ag(1)-X(1)	2.117(8)	X(1)-X(2)	1.11(1)
X(2)-Ag(2a,b)	2.086(9), 2.094(9)	Ag(2a)...Ag(2b)	0.809(4)
Ag(2a,b)-X(3)	2.035(9), 2.165(9)	X(3)-X(4)	1.11(1)
X(4)-Ag(3a,b)	2.144(9)	Ag(3a)...Ag(3b)	1.799(2)
Ag(3a,b)-X(5)	2.239(8), 2.170(9)	X(5)-X(6)	1.07(1)
X(6)-Ag(4a,b)	2.208(9), 2.110(9)	Ag(4a)...Ag(4b)	1.806(2)
Ag(4a,b)-X(7)	2.205(8), 2.298(9)	X(7)-X(8)	1.06(1)
X(8)-Ag(5a,b)	2.094(9), 2.184(9)	Ag(5a)...Ag(5b)	1.623(2)
Ag(5a,b)-X(9)	2.222(8), 2.255(9)	X(9)-X(10)	1.10(1)
X(10)-Ag(1 ⁱ)	2.078(9)		
N(11)-Ag(1)	2.473(8)		
X(21)-Ag(2b)	2.52(1)	X(24)-Ag(5b ⁱⁱ)	2.52(1)
X(41)-Ag(3b)	2.320(8)	X(44)-Ag(4b ⁱⁱⁱ)	2.331(9)
X(31)-Ag(3a)	2.403(9)	X(34)-Ag(5a ⁱⁱⁱ)	2.424(8)
X(51)-Ag(4a)	2.314(9)		
<i>Angles [°]:</i>			
X(1)-Ag(1)-X(10 ^{iv})	153.5(3)		
Ag(1)-X(1)-X(2)	178.7(9)		
X(1)-X(2)-Ag(2a)	171.2(9)	X(1)-X(2)-Ag(2b)	166.5(9)
X(2)-Ag(2a)-X(3)	166.7(4)	X(2)-Ag(2b)-X(3)	148.0(4)
Ag(2a)-X(3)-X(4)	167.3(9)	Ag(2b)-X(3)-X(4)	170.5(9)
X(3)-X(4)-Ag(3a)	156.4(9)	X(3)-X(4)-Ag(3b)	154.8(9)
X(4)-Ag(3a)-X(5)	131.4(4)	X(4)-Ag(3b)-X(5)	131.6(4)
Ag(3a)-X(5)-X(6)	158.6(9)	Ag(3b)-X(5)-X(6)	153.2(9)
X(5)-X(6)-Ag(4a)	154.9(9)	X(5)-X(6)-Ag(4b)	155.7(9)
X(6)-Ag(4a)-X(7)	131.5(4)	X(6)-Ag(4b)-X(7)	131.8(4)
Ag(4a)-X(7)-X(8)	154.3(10)	Ag(4b)-X(7)-X(8)	158.3(9)
X(7)-X(8)-Ag(5a)	160.7(9)	X(7)-X(8)-Ag(5b)	154.8(9)
X(8)-Ag(5a)-X(9)	140.5(4)	X(8)-Ag(5b)-X(9)	132.5(4)
Ag(5a)-X(9)-X(10)	155.1(9)	Ag(5b)-X(9)-X(10)	162.2(9)
X(9)-X(10)-Ag(1 ⁱ)	178.4(9)		

model, the cyanide located with its midpoint (or thereabouts) at an inversion centre, and with the small perturbation offered by an ordered model of lower symmetry offering little hope of stable refinement in that symmetry (Fig. 1(a)). Nevertheless, individual C, N components were discernible in difference maps and sufficiently separated to refine in a stable manner; silver/cyanide geometries offered in Table 1, are presented on the premise that, given the absence of any apparent abnormal displacement parameter or difference map behaviour about the silver atoms, the silver environment is four-coordinate [(quin-N)₂Ag(CN)]_(∞∞), *i.e.* there is local order in the polymer of a concerted

Table 2 (continued).

Atoms	Params	Atoms	Params
X(1)-Ag(1)-N(11)	96.0(3)	X(10 ⁱ)-Ag(1)-N(11)	110.1(3)
X(2)-Ag(2b)-X(21)	103.4(4)	X(3)-Ag(2b)-X(21)	107.7(4)
X(4)-Ag(3a)-X(31)	104.9(3)	X(5)-Ag(3a)-X(31)	113.2(3)
X(4)-Ag(3b)-X(41)	107.7(3)	X(5)-Ag(3b)-X(41)	112.2(3)
X(6)-Ag(4a)-X(51)	112.8(1)	X(7)-Ag(4a)-X(51)	105.9(3)
X(6)-Ag(4b)-X(44)	122.6(3)	X(7)-Ag(4b)-X(44)	98.5(3)
X(8)-Ag(5a)-X(34 ⁱⁱⁱ)	120.9(3)	X(9)-Ag(5a)-X(34 ⁱⁱⁱ)	94.9(3)
X(8)-Ag(5b)-X(24 ⁱⁱ)	132.0(4)	X(9)-Ag(5b)-X(24 ⁱⁱ)	91.5(4)
Ag(1)-N(11)-C(12)	122.3(7)	Ag(1)-N(11)-C(16)	123.2(7)
Ag(2b)-X(21)-C(22)	129.9(10)	Ag(2b)-N(21)-C(26)	113.7(9)
Ag(5b ⁱⁱ)-X(24)-C(23)	133(1)	Ag(5b ⁱ)-X(24)-C(25)	111.1(9)
Ag(3a)-X(31)-C(32)	113.2(7)	Ag(3a)-C(31)-C(36)	127.7(7)
Ag(5a ⁱⁱⁱ)-X(34)-C(33)	113.9(7)	Ag(5a ⁱⁱⁱ)-X(34)-C(35)	128.1(7)
Ag(3b)-X(41)-C(42)	124.1(6)	Ag(3b)-X(41)-C(46)	117.2(7)
Ag(4b ⁱⁱ)-X(44)-C(43)	127.1(7)	Ag(4b ⁱ)-X(44)-C(45)	114.3(6)
Ag(4a)-X(51)-C(52)	121.0(6)	Ag(4a)-C(51)-C(53 ⁱⁱⁱ)	121.3(6)

Transformations of the asymmetric unit: ⁱ \bar{x} , $\frac{1}{2} + y$, $\frac{1}{2} - z$; ⁱⁱ $1 - x$, \bar{y} , \bar{z} ; ⁱⁱⁱ $\bar{x} - 1$, \bar{y} , $\bar{z} - 1$; ^{iv} \bar{x} , $y - \frac{1}{2}$, $\bar{z} - \frac{1}{2}$; ^v \bar{x} , \bar{y} , \bar{z} . For py planes 1–5, χ^2 are 1.1, 4.4, 5.1, 0.4, 0.9 respectively; deviations of associated Ag components are: plane 1: Ag(1), 0.24(2); plane 2: Ag(2b), 0.38(2); Ag(5bⁱⁱ), 0.11(2); plane 3: Ag(3a), 0.45(2), Ag(5aⁱⁱⁱ), 0.09(2); plane 4: 0.02(2), Ag(3b), 0.22(1); plane 5: Ag(4c), 0.16(1) Å.

nature. The problem is further compounded in the py adduct by further practical difficulties of a higher order, (see below), and accordingly in both determinations, a disordered model is adopted with 50:50 composite C/N components. By contrast, the coll adduct may well be ordered and is modelled as such after consideration of refinement behaviour. Quin as a unidentate ligand in contexts such as the present not infrequently displays unusual behaviour, presumably because of its rather unusual and extended steric characteristics, *e.g.* copper(I) and silver(I) halides crystallized from the neat base fail to achieve the 1:3 stoichiometry displayed by many related systems. (Although the copper(I) chloride and bromide: ligand stoichiometries are ostensibly 1:2.5, this is achieved by solvation, the complexes being hemisolvated binuclear 1:2 adducts : [(quin)₂Cu(μ-X)₂Cu(quin)₂] [11]). The silver halide adducts (chloride and bromide) obtained similarly are of 1:1 stoichiometry, the isomeric form unique to this array being the ‘saddle polymer’ [19], which, nevertheless, contains silver atoms at the periphery coordinated by pairs of ligands. In the above examples of the 1:2 complexes, interligand N-M-N are elevated well above the tetrahedral norm; most notably in the 1:1 silver(I) chloride adduct, it is 125.0(5)° [19], while in the 1:2 copper halide adducts cited, it is 131.2(7), 122.3(7) (Cl), 129.8(6), 121.8(6) (Br), 114.8(2)° (I) [11]. While these exaltations may be at-

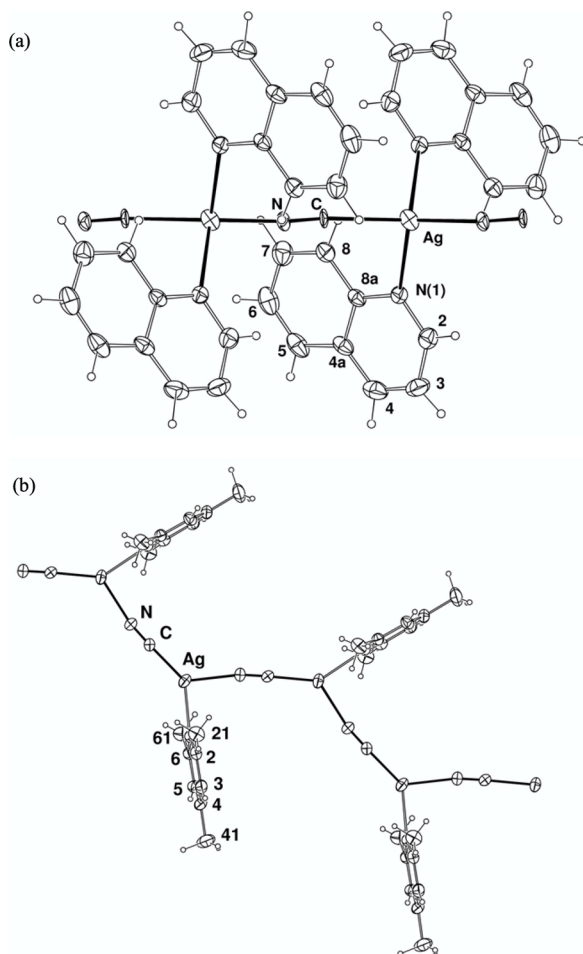


Fig. 1. Projection of single strands of the polymers of (a) the AgCN : quin (1:2) adduct down *b*, coincident with the two-fold axis which passes through the silver atom, the independent components of one deconvoluted cyanide grouping being shown, (b) the AgCN : coll (1:1) adduct, the polymer being generated by the 2_1 -screw axis parallel to the *b* axis.

tributed to the enclosure of the two halide atoms into a cyclic array by way of bridging, with consequent and parallel reduction in $(\mu-X)M(\mu-X)$, nevertheless, it is of interest to note that in the present AgCN complex the N(L)-Ag-N(L) angle is perturbed in the opposite direction from the tetrahedral, presumably because of a tendency on the part of the pair of cyanide donors to approach, albeit rather imperfectly, linearly. The location of the cyanide at a centre of symmetry in space group $C2/c$ has already been noted; we likewise note the location of the silver atom on a two-fold axis. As noted above, the local symmetry has been treated as ordered with C, N' cyanide coordination; in the re-

finement process, displacement parameter refinement behaviour suggests ascription of the two fragments as given, but it should be noted that, modelled as such, the silver-carbon bond is longer than its silver-nitrogen counterpart. The silver atom lies 0.593(6) Å out of the quin skeletal plane.

In the above context, the present complex is remarkable, being one of the very few structurally characterized AgX : N-base adducts of 1:2 stoichiometry, the base in a disproportionate number of these being quin. (Note also the 1:1 saddle polymer forms; see below). The forms available are the $[L_2Ag(\mu-X)_2AgL_2]$ dimer, ($L = 3mp$ (3-methylpyridine), $X = Br$) [12], and the single-stranded (castellated) split-stair polymer $\dots(pip)_2AgX(pip)_2AgX\dots$ [13], ('pip' = piperidine) with one bridging atom $X = Cl$, noted also for the system $X = SCN$ [20], (with a somewhat similar array for $L = py$ [5]) and, in extended form, $X = SCN$ with $L = quin$ [4], the latter form being paralleled by the present. The two compounds are not isomorphous, the thiocyanate crystallizing in orthorhombic space group $P2_12_12_1$, with that polymer a helix propagated by a 2_1 screw, rather than the quasi-*m* symmetry of the AgCl : pip (1:2) 'castellated' polymer. In the present structure, also although the $(AgCN)_{(\infty|\infty)}$ array is essentially planar, the two quin ligands, rather than being related by a mirror in that plane, are related by the 2-axis through the silver atom; the saddle polymer also, may be treated as a polymeric substrate containing peripheral silver which forms a 1:2 complex with quin.

In contrast to the quin complex, one finds in the coll adduct (Fig. 1(b)) that refinement behaviour, in the context of a model unperturbed by evident disorder, suggests ascription of carbon and nitrogen (ordered) identities as given to result in Ag-C being shorter than Ag-N (cyanide), an intuitively more expected outcome. Here the silver atom is three-coordinate, presumably because of ligand steric dictates; the AgN_2C array is agreeably planar ($\chi^2 = 0.9$) with an angle sum at the silver of 360.0° , with the C_5N plane of the ligand approximately normal ($81.9(3)^\circ$) to it and with the methyl groups lying to either side; the silver atom is 0.16(1) Å out of plane. The angular geometries about the metal are considerably perturbed from the 120° norm, the largest angles lying to either side of the shortest (Ag-C) bond, as might be expected from electron pair repulsion theory. Ag-N(1) is appreciably shorter than its counterpart in the quin adduct, in keep-

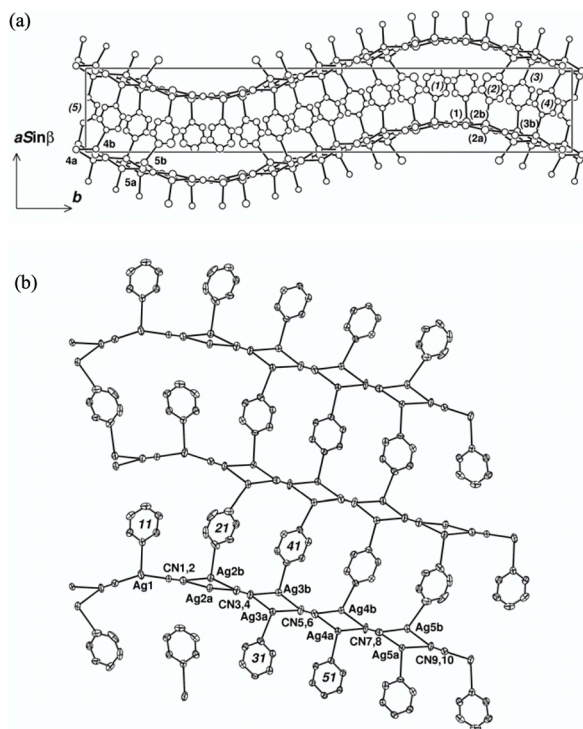


Fig. 2. (a) The unit cell of the AgCN : py (10:9) structure projected down *c*, showing the undulating nature of the array. Silver atoms are labelled by number. Symmetry transformed entities are shown in parentheses. (b) The asymmetric unit strand of the structure projected onto the plane, with associated strands to either side showing possible pyridine affiliations.

ing with the diminished coordination number of the metal atom. Again, with a bulkier ligand presumably driving the stoichiometry here towards 1:1, we have a novel polymer form, being essentially an extended 1:1 split-stair polymer [18], recorded previously for a thiocyanate adduct with the bulky bases *L* = 2,6-lut, AgSCN : *L* (1:1) [4].

The structure of the py adduct (Fig. 2) is remarkable, and, in keeping with a stoichiometry of AgCN : py (10:9), begging comment in company with CuCN : py (10:8), a complex of a smaller metal, postulated on the basis of thermogravimetric evidence in the preceding paper [1]; one half comprises the asymmetric unit as modelled in space group $P2_1/c$. The structure in total is a sheet built up around a parallel series of silver cyanide backbones, each a linear polymer along the long *b* axis of the cell, all silver, cyanide and pyridine moieties being constrained within an array disposed as the sheet about the crystallographic $10\bar{2}$ plane

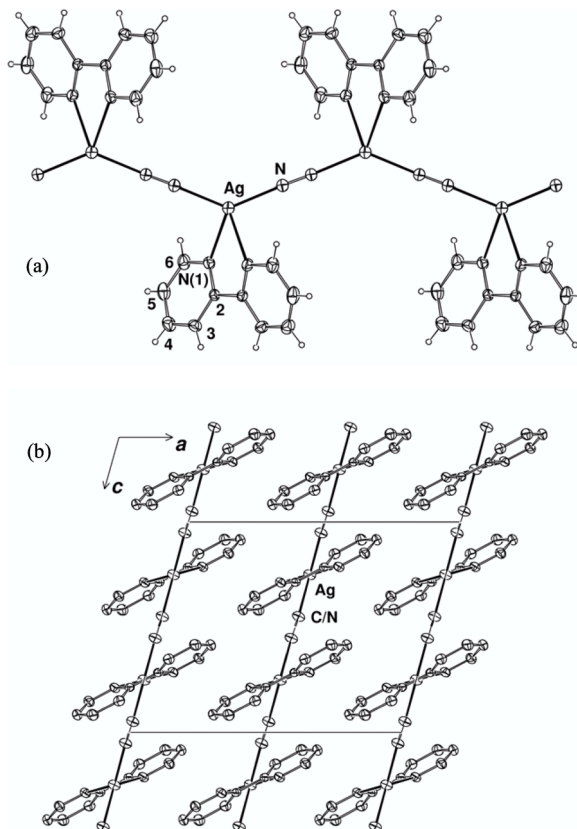


Fig. 3. Projections of AgCN : 2,2'-bpy (1:1) showing (a) a section of a single strand normal to its axis *c*, and (b) the unit cell, down (monoclinic) *b*.

(note that this produces the most intense reflection in the data, not surprisingly) (Fig. 2(a) (ii)). Five independent silver atoms are found in the asymmetric unit of the one-dimensional polymer in which successive silver atoms are linked by end-coordinated cyanides; the complexity of the structure and associated difficulties do not permit confident assignment of respective ends of the cyanide entities if the structure were to be regarded as ordered, but it is possible that the respective components of local disorder in the model correlate with disorder in the successive silver atoms of the string. Focussing on the only ordered silver atom of the array, Ag(1) we proceed along the string to Ag(2,3,4,5) in succession, each consisting of a disordered pair of components *a*, *b* of site occupancy set at 0.5 after trial refinement, separations between the *a*, *b* components being, respectively, 0.809(4), 1.799(2), 1.806(2), 1.623(2) Å for successive silver atoms (Fig. 2(b)). Ag(1) is three-coordinate: the distance to the py nitro-

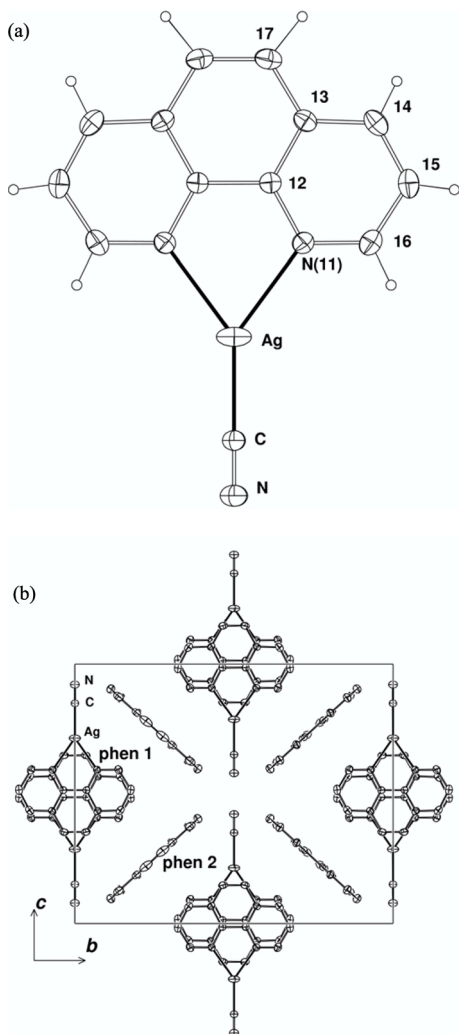


Fig. 4. Projections of AgCN : 1,10-phen (1:2) showing (a) a single molecule of the 1:1 single complex, normal to the molecular plane, and (b) the unit cell contents projected down (orthorhombic) displaying the stacks of complex molecules interleaved by intersecting sheets of free ligand.

gen atom is $2.473(8) \text{ \AA}$, more nearly comparable with the value found in the quin adduct above (in which the silver is four-coordinate) rather than its counterpart in the coll adduct, in which the silver is three-coordinate and which might be thought at least initially to be more nearly comparable. It is evident, however, that the interaction of Ag(1) with its two associated cyanide species is much more nearly linear in the present complex, (N/C(1))-Ag-(N/C(10')) being $153.5(3)^\circ$, so that a long Ag(1)-N(11) (py) contact is not unreasonable. Ag(2,3,4,5) are all disordered over pairs of sites, as de-

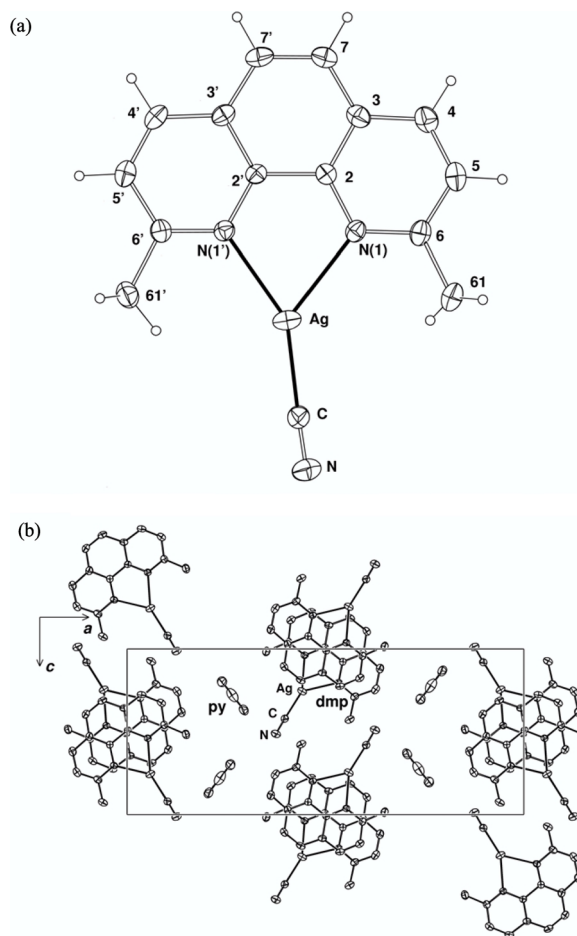


Fig. 5. Projections of AgCN : dmp (1:1). py showing (a) a single molecule of the 1:1 complex, normal to the molecular plane, and (b) the unit cell contents, projected down (orthorhombic) *b*, showing the stacks of complex molecules, interleaved by columns of pyridine solvate.

scribed above; the intermediate cyanides presumably also have disorder within the envelopes modelled as composite C/N, but the latter are not resolvable and the envelopes in fact are of amplitudes of a magnitude not seriously different from those in, *e.g.* the coll structure above, and with reasonably sensible associated interenvelope distances, *i.e.* compatible with a normal C-N length. The C-N (*i.e.* C/N-C/N) fragments, together with Ag(1) therefore form a useful reference point for extending the description of the structure. These components followed through the polymer string are observed to form a 'wave' ten cyanide units long (with, of course, ten intermediate silver atoms) the length corresponding to the length of the cell ($\sim 50 \text{ \AA}$) (\equiv ten

Ag-(C/N) \equiv (C/N)-Ag units), a remarkable similarity to that found unsolvated in LT-CuCN [21]. Each 'wave' lies parallel to others related by inversion centres, one such providing a further convenient reference point for the description of the structure in that it lies at the centre of py 5 which is thus disordered about it, again without grossly excessive elevation of associated displacement parameters. 'N(51)' may thus lie at either end of the ring, in proximity to Ag(4) and with disposition presumably concerted with the two components of the latter: if 'N(51)' is nitrogen, it lies at a bonding distance from Ag(4a), whereas if it is a carbon, then the associated silver atom may be presumed to lie at Ag(4b), the two dispositions perhaps in turn being correlated with particular C or N occupancies of sites 6 and 7. Moving to either side of the py 5/Ag(4a,b)($\times 2$) combination, we find py 3 and Ag(3a), Ag(5a) from the two chains similarly disposed but with a displacement consequent upon the curvature of the 'wave' so that the 'fit' is less tidy, becoming further exacerbated at py 1, so that it becomes fully ordered, coordinating only to Ag(1), while the 'a' component of Ag(2), being devoid of coordinating py constitutes a quasi-linear, familiar Ag(CN)₂ fragment of the chain, generating the mismatch in AgCN stoichiometry. Whereas pairs of Ag(4a) are 'linked' by py 5, Ag(4b) does not immediately confront a like Ag(4b) component in the next adjacent chain on the other side; the inversion centre next in proximity to Ag(4b) lies between a pair of py 4 units and relates pairs of Ag(3b) as intimately as it does Ag(4b) pairs. Accordingly, the function of py 4 is to pair with Ag(3b) and Ag(4b) components, so that pairs of Ag(3b) (py 4) Ag(4b) lie parallel to each other on either side of the inversion centre. Moving outwards from these between the two chains we encounter py 2, disposed between Ag(2) and Ag(5), again an uncomfortable fit, culminating in an Ag(1) (py 1) Ag(1) mismatch. The nature of the structure of the 'wave' also gives room for conjecture; although ostensibly quasi-sinusoidal, the -Ag-CN-Ag- string is approximately linear between successive Ag(1) atoms with C/N and Ag components exhibiting relatively minor deviations from it, while for a line between the corresponding py centroids to one side of the chain, the deviations of the other py centroids are appreciably greater. A plausible sectional view of the chain consists of alternating a and b components of the silver atom with associated ligands with quasi-linear Ag-C/N-C/N-Ag sections creating a zig-zag array; two alternate modes

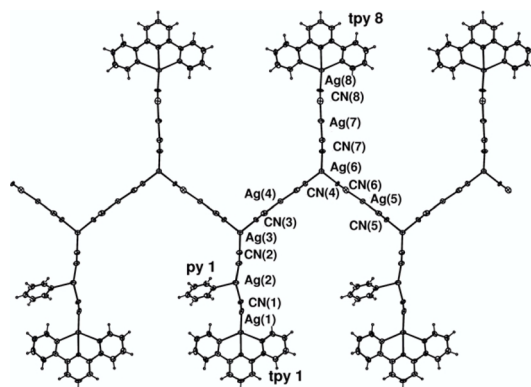


Fig. 6. Projections of AgCN : tpy : py (8:2:1) showing a single strand of the polymer normal to the sheet containing it.

are possible, starting with Ag(1) and its environment as obligatory and followed by either Ag(2a) devoid of py, or Ag(2b) with associated py, with further elements in the sequence concerted, the disjunction at Ag(1) providing the opportunity within the chain to alternative sequencing, although this presumably cannot occur without consequences for interactions with parallel chains. A further constraint may arise by virtue of some rather close distances between silver atoms in adjacent sheets (Fig. 2(b)): Ag(3a)...Ag(5a) ($\bar{x}, \bar{y}, \bar{z} - 1$) 3.188(2); Ag(4a)...Ag(4a) ($\bar{x}, \bar{y}, \bar{z} - 1$), 3.190(2); Ag(4b)...Ag(4b) ($\bar{x}, \bar{y}, \bar{z}$) 3.232(2) Å which may preclude simultaneous occupancy of such pairs of sites. Successive py skeletal planes are approximately parallel, interplanar angles being 1/2, 5.8(5); 1/4, 7.4(4); 2/4, 1.7(4)°, and 3/5, 1.3(3)° with rings 3 and 5 making dihedral angles with 1 of 49.5(5) and 49.9(5)°; planes 1–5 have dihedral angles of 27.3(4), 22.4(4), 24.8(3), 33.4(3) and 24.8(3)° to the overall 10 $\bar{2}$ plane, the associated silver atom deviations being 0.24(1) (Ag(1)); 0.38(2), 0.11(2) (Ag(2b,5b')); 0.45(2), -0.09(2) (Ag(3a,5b')); 0.22(1), -0.02(2) (Ag(3b,4b')); 0.16(1) Å (Ag(4a)) from the py planes. As noted above, the wave structure exhibited by the AgCN chains in this complex is very similar to that reported recently in the remarkable structure of the 'low temperature' phase of CuCN, with a repeat corresponding to nine CuCN units [21].

Adducts of silver(I) cyanide with oligodentate py donors of 1:1 stoichiometry have been isolated from py solution with bpy, phen, dmp and tpy (Figs. 3–6), some solvated with solvent or excess ligand, with various degrees of invasiveness. The bpy and tpy adducts are polymeric, while the phen and dmp adducts are

discrete mononuclear species, both solvated with potentially coordinating py ligands, all exhibiting diverse packings of interest, as shown in the cell projections, driven by the usual inter/supramolecular considerations [22]; we deal with the simpler mononuclear species first.

The phen adduct, **AgCN : phen (1:2)**, takes the form AgCN : phen (: phen) (1:1(:1)) *i.e.* [(phen)AgCN]. phen, the three-coordinate silver atom lying on a two-fold axis, as does the cyanide grouping (C, N-resolved and refined as such), which passes through the phen ligand, relating its two halves (Fig. 4(a)). The plane of the phen ligand lies approximately normal to *a*, with successive ligands stacking in alternating directions up that axis at a spacing of *a*/2 (2.9 ~ 3.6 Å), the typical 'charge-transfer' spacing. The uncoordinated phen ligand, again only a half being crystallographically independent, also lies disposed about a two-fold axis, but disposed so as to lie approximately in the plane defined by *a* and the *bc* diagonal and thus *quasi*-normal to the plane of the coordinated phen; one half of the formula unit is the asymmetric unit of the structure. The uncoordinated ligand planes partition the columns/stacks of the complex molecules, as shown in the entertaining packing diagram (Fig. 4(b)).

AgCN : dmp (: py) (1:1(:1)) takes a rather similar form (Fig. 5(a)), except that the uncoordinated solvent molecule is the actual solvent pyridine, rather than supernumerary ligand, one half of the formula unit again making up the formula unit, again in an orthorhombic cell of similar symmetry (*Pnma* vs *Pnna*), with stacks of alternating discrete molecules along a crystallographic axis (the molecules lying in mirror planes spaced this time at *b*/2 (3.37 Å)) (Fig. 5(b)). The columns are partitioned by vertical *quasi*-diagonal planes of pyridine molecules, in an overall structural array reminiscent of a distorted version of the parent, perhaps driven by the need to accommodate the methyl substituents of the ligand.

For the AgCN : phen, dmp molecules Ag-N are 2.304(2); 2.344(4), 2.274(4) Å, the distances in the phen adduct conforming to equivalence by symmetry, with Ag-C-N (co-) linear (with the 2-axis), whereas in the dmp adduct they differ appreciably. Here, also, Ag-C-N has no constraint to linearity although it is close to it (178.1(5)°) but C-Ag-N also differ, being 135.6(2), 151.8(2)°, *cf.* 143.54(4)° in the phen adduct. The N-Ag-N bite angles of the two ligands at the silver are very similar (72.92(6);

72.7(1)°). Formally these species may be regarded as analogues of anhydrous AgNO₃ : 6,6'-Me₂-bpy (1:1) [23], with the cyanide being supplanted by the small bite O₂NO chelate, the whole molecule being essentially planar. In the latter, Ag-N are 2.33(2), 2.28(2) Å, very similar to the present, Ag-O being 2.33(2), 2.63(2) Å, somewhat unsymmetrical. In this latter complex, the molecular planes stack parallel, similar to the present, but remarkably, with the silver atoms more nearly pairwise overlapping, with Ag...Ag 3.067(6) Å. The discretely molecular nature of the present adducts, as prepared here, differs from that of their counterpart CuCN : phen, dmp (1:1) homologues, the latter being recorded as linear polymers with ...Cu(cyanide)Cu(cyanide)Cu... chains, the copper chelated by the phen or dmp, being four-coordinate [1, 2, 24].

Although phen and bpy in many situations behave similarly as bidentate ligands, notwithstanding the capacity for free rotation about the central bond in bpy, in some situations they behave differently for no obvious reason, still as bidentates, and with the size of the ligand seemingly the only significant factor. Here the phen, dmp adducts are mononuclear and discrete, the bpy and tpy adducts polymeric; the correlation may or may not be significant – while both ligands have the common factor of rotational flexibility about the inter-ring bonds, this does not appear to be exploited as a pertinent factor in the present complexes. **AgCN : bpy (1:1)**_(∞|∞) is a single-stranded polymer (Fig. 3(a)), the model adopted, with one half of the formula unit comprising the asymmetric unit of the structure in space group *C2/c*, entailing the cyanide group disordered about an inversion centre, the silver atom lying on a two-fold axis which passes through the mid-point of the central C-C bond of the bpy also, relating the two halves of the ligand; in form the structure resembles that of CuCN : phen, dmp as noted above. Again the molecular packing is interesting with interleaving bpy ligands from successive polymer strands propagating along *a*, stacked up *b* (Fig. 3(b)). Here a parallel may be drawn with the structure of AgSCN : bpy (1:1) [25]; in the latter, however, successive silver atoms are linked by single atom (*S*) bridges, with successive bpy planes essentially stacked overlapping and parallel normal to the (AgS)_(∞|∞) spine of the polymer. Many similarities are found between the present polymeric species and recently reported related arrays described for copper(I) [26].

Table 3. Selected geometries: AgCN : tpy : py (8:2:1). C/N composites are denoted by X; atoms i are drawn from the next unit in the polymer. N(n1'') lie to either side of N(n1).

Atoms	Params	Atoms	Params
<i>Distances [Å]:</i>			
Ag(4)-X(3)	2.11(2)	Ag(5)-X(5)	2.10(1)
Ag(4)-X(4)	2.08(1)	Ag(5)-X(6)	2.13(1)
Ag(3)-X(2)	2.11(1)	Ag(6)-X(7)	2.11(1)
Ag(3)-X(3)	2.16(1)	Ag(6)-X(4)	2.17(1)
Ag(3)-X(5')	2.20(1)	Ag(6)-X(6)	2.15(1)
Ag(2)-X(1)	2.13(1)	Ag(7)-X(8)	2.10(1)
Ag(2)-X(2)	2.07(1)	Ag(7)-X(7)	2.03(1)
Ag(2)-N(21)	2.45(1)		
Ag(1)-N(11)	2.357(8)	Ag(8)-N(81)	2.431(9)
Ag(1)-N(11')	2.45(1)	Ag(8)-N(81')	2.41(1)
Ag(1)-N(11'')	2.44(1)	Ag(8)-N(81'')	2.44(1)
Ag(1)-X(1)	2.20(1)	Ag(8)-X(8)	2.15(1)
<i>Angles [°]</i>			
X(3)-Ag(4)-X(4)	178.2(5)	X(5)-Ag(5)-X(6)	173.1(6)
X(2)-Ag(3)-X(3)	130.6(5)	X(7)-Ag(6)-X(4)	129.8(5)
X(2)-Ag(3)-X(5)	126.6(5)	X(7)-Ag(6)-X(6')	125.6(5)
X(3)-Ag(3)-X(5)	101.2(5)	X(4)-Ag(6)-X(6')	104.4(5)
X(1)-Ag(2)-X(2)	153.3(5)	X(7)-Ag(7)-X(8)	178.9(6)
N(21)-Ag(2)-X(1,2)	92.5(5), 113.0(5)		
X(1)-Ag(1)-N(11)	177.1(5)	X(8)-Ag(8)-N(81)	167.5(5)
X(1)-Ag(1)-N(11',11'')	115.1(4), 109.6(4)	X(8)-Ag(8)-N(81',81'')	115.4(5), 107.9(5)
N(11')-Ag(1)-N(11'')	135.3(4)	N(81')-Ag(8)-N(81'')	133.4(4)
tpy C ₅ N interplanar dihedrals (degrees) : n1/n11',n11''; n11'/n11'' : n = 1 : 1.2(5), 12.8(6), 12.9(6); n = 8 : 9.2(5), 8.9(6); 3.0(5). Silver atom deviations from n11, n11', n11'' are (Å): n = 1, 0.24(2), 0.19(3), 0.48(2); n = 8: 0.08(2), 0.45(2), 0.15(2) and for n = 2: 0.00(3).			

With tpy, a complex and interesting one-dimensional polymer has been defined, of stoichiometry **AgCN : tpy : py (8:2:1)**, one formula unit comprising the asymmetric unit of the structure (Fig. 6; Table 3). The structure may be viewed in a number of different ways, in terms of a variety of motifs, although the structure overall is a close parallel to that of CuCN : biquinoly ('bq') (8:2) [27] which crystallizes in a rather similar $P2_1/c$ cell, but with a halved and an asymmetric unit of half the size ($a = 7.3947(7)$, $b = 18.041(2)$, $c = 16.002(1)$ Å, $\beta = 98.550(2)^\circ$, $V = 2111.1(3)$ Å³, $Z = 4$, at 293 K). (Note that in that structure bq is a bidentate ligand.) On the one hand, we note the occurrence of a motif found in the mononuclear AgCN : phen, dmp (1:1) adducts, namely that of planar coordination environments about Ag(1) and Ag(8) at the periphery of the polymer, comprising an oligodentate ligand coordinated symmetrically to the silver atom opposed to a cyanide

moiety (which may be viewed alternatively as the NCAgCN complex ion); the tpy ligand found here of course, is tridentate rather than bidentate as with phen and dmp. The NCAgCN moieties are coordinated to Ag(1) and Ag(8), centred around Ag(2) and Ag(7) respectively. Mysteriously, we find Ag(2) coordinated by a py ligand and Ag(7) not, perturbing the Ag(2) environment from linearity, the angle subtended at Ag(2) being reduced to $153.3(5)^\circ$. Significant differences are found in the geometries at Ag(1) and Ag(8), most noticeably in the bond to the central nitrogen of the tpy $2.357(8)$ vs $2.431(9)$ Å. On the other hand the core of the polymer is the spine of silver atoms bridged by end-coordinated cyanide groups, linearly at Ag(4) and Ag(5), which may be viewed as [(NC)Ag(CN)] groups linking Ag(3) and Ag(6), where, because of their trigonality, the polymer kinks. This provokes an alternative view, of the basis of the polymer as trigonal [Ag(CN)₃] groups linking Ag(4) and Ag(5) (and Ag(2) and Ag(7)). The geometries at the spinal silver atoms Ag(3) and Ag(6) are distorted from truly trigonal planarity to a surprising extent, the angle opposing the pendant group being closed down to $101.2(5)$, $104.4(5)^\circ$, while the 'exo' angles are expanded above 120° . The spine with pendant [Ag(CN)₂] aggregates to [Ag₆(CN)₈]²⁻ (solvated by one pyridine) counterbalanced by a pair of [Ag(tpy)]⁺ cations. Data, although limited, was of tolerable quality, probably with the capability to discriminate between cyanide C and N atoms if ordered; attempts to deconvolute such a distinction were fruitless in both spinal and pendant cyanides, and in the end all were modelled as C/N composites. Packing of the polymer strands, despite the length and complexity of the repeat unit, nevertheless displays the usual interleaved stacking of the aromatic ligands.

Finally, we record in consequence of our attempts to obtain suitably crystalline the adduct of ethylenediamine with silver(I) cyanide, the formation and isolation of crystalline **decahydropyrazine [2,3-*b*] pyrazine**, in quantity sufficient to suggest its possible use as a synthetic procedure for the latter. Although tempting to postulate reaction schemes involving incorporation of the cyanide with the en, black material presumed to be silver being deposited in quantity, we note the previous record of the formation of the heterocycle from the reflux of en with lanthanum chloride [28], and our own subsequent recognition of it in other circumstances where cyanide was absent. The geome-

Table 4. Molecular non-hydrogen geometry: $C_6H_{14}N_4$.

Atoms ^a	Params	Atoms	Params
Distances [Å]:			
C(1)-N(2)	1.450(3)	C(1)-C(1')	1.526(4)
N(2)-C(3)	1.459(3)	C(3)-C(3')	1.518(3)
Angles [°]:			
N(2)-C(1)-C(1')	110.5(2)	N(2)-C(1)-N(2 ⁱⁱ)	109.3(2)
C(1)-N(2 ⁱⁱ)-C(3 ⁱⁱ)	110.3(2)	N(2)-C(3)-C(3')	111.4(2)
Torsion angles [°] (atoms denoted by number only, <i>N italicized</i>):			
1 ⁱ -1-2-3	-57.5(3)	2 ⁱⁱ -1-2-3	-179.2(2)
2-1-1 ⁱ -2	59.0(3)	1-2-3-3 ⁱ	55.7(3)
2-3-3 ⁱ -2	-54.9(3)		

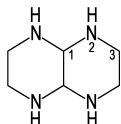
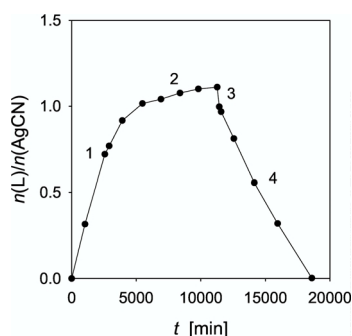
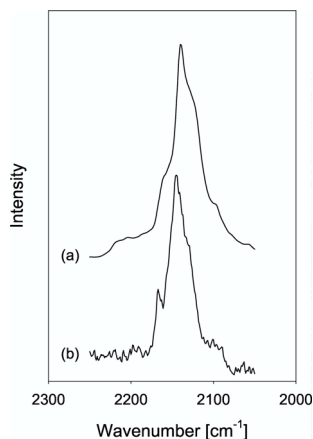
^a Atom numbering:Transformations of the asymmetric unit: ⁱ 1 - x, y, z; ⁱⁱ x, 1 - y, z.

Fig. 7. The time dependence of the composition (ligand (L) : AgCN mole ratio) of the solid formed during the addition of 4mp from the vapour phase to a fixed amount of solid AgCN at ambient temperature (regions 1 and 2), and during ligand loss upon exposure of the resulting solid to the air (regions 3 and 4).

try of the molecule (Table 4) presents no unusual features, having $2/m$ symmetry in space group $C2/m$, one quarter of the molecule comprising the asymmetric unit of the structure, with the two fused rings both of chair conformation.

Vibrational spectra

Since the complexes involving the unidentate ligands readily lose ligand upon exposure to air, it has not been possible to check the identity and homogeneity of the bulk samples prepared for IR spectra by melting point determinations or elemental analysis. However, the composition of the bulk sample was established in one case by gravimetric monitoring of the addition of

Fig. 8. The $\nu(\text{CN})$ stretching region in (a) the IR, and (b) the Raman spectra of AgCN : py (10:9).

ligand from the vapour phase to a known amount of AgCN (see Experimental Section). The progress of the addition of 4mp to AgCN with time is shown in Fig. 7. The rate of addition of the ligand to the solid is fairly constant up to the addition of 1 mol of 4mp per mol of AgCN (region 1 in Fig. 7). After this point there is a much slower process that appears to be physical adsorption or condensation of ligand onto the surface of the 1:1 complex (region 2). If the solid is removed from the ligand vapour at this point, the composition of the solid rapidly reverts to 1:1 (region 3). This is followed by slower loss of ligand, at a nearly constant rate, ultimately yielding uncomplexed AgCN (region 4). This latter behaviour is in contrast with that observed for analogous CuCN/py base complexes; in these complexes ligand loss occurs in several stages *via* a series of well defined adducts, some of which have unusual stoichiometries and structures [1]. A similar study of the AgCN/en reaction established the stoichiometry of the final product as 1:1. In contrast to the situation for the unidentate py bases, this product was stable with respect to ligand loss.

The vibrational spectra of the complexes reported in the present study were recorded in order to establish correlations between the vibrational frequencies of the AgCN chains and the structures of these chains as modelled in the X-ray study. Selected regions of the IR spectra are shown in Figs. 8 to 10, and assignments of the bands due to the AgCN chains are given in Table 5. These assignments are based on those made in a recent study of AgCN itself, which has been shown to consist of infinite, linear -Ag-CN-Ag-CN- chains [6, 29]. The vibrational spectra contain bands due to the CN stretching vibration, $\nu(\text{CN})$, the AgC/AgN stretching

Compound	$\nu(\text{CN})$	$\nu(\text{AgC/N})$	$\delta(\text{AgCN})$	$\delta(\text{NAgC})$
AgCN ^a	2168	480	272	112
AgCN/py (10:9)	2154, 2140, 2122, 2096	460, 435, 380, 360	255, 229	146, 106, 89
AgCN/4mp (1:1)	2140	418	257	130, 94
AgCN/coll (1:1)	2140	392	^b	120, 88
AgCN/quin (1:2)	2140	422	^b	132, 104
AgCN/bpy (1:1)	2133, 2141	383	276, 248	122, 104
AgCN/phen (1:1) ^c	2131	373	^b	^b
AgCN/dmp (1:1)	2125	361	^b	^b
AgCN/terp/py (8:2:1)	2155–2120	^b	^b	132, 111

Table 5. IR band assignments [wavenumbers/cm⁻¹].

^a Ref. [29]; ^b region obscured by ligand bands; ^c in [(phen)AgCN] · phen.

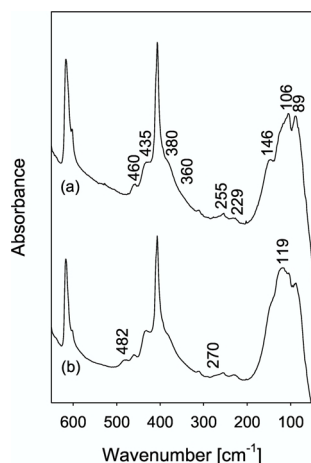


Fig. 9. The far-IR spectrum of AgCN : py (10:9) (a) containing a slight excess, and (b) a slight deficit, of pyridine. Bands assigned to vibrations of the AgCN chains are labelled with their wavenumbers. The bands labelled in (a) are due to the complex, while those labelled in (b) are assigned to uncomplexed AgCN.

mode, $\nu(\text{AgC/N})$, involving vibration of the CN group between its two neighbouring Ag atoms, the AgCN bending mode, $\delta(\text{AgCN})$, which can also be described as a restricted rotation of the CN group, and the NAgC bending mode, $\delta(\text{NAgC})$, which can also be described as a counter-vibration of the Ag substructure against the CN substructure, in a direction perpendicular to the AgCN chains [29].

The IR spectrum of AgCN : py (10:9) (Table 5) shows features that can be readily related to the unusual structure of this compound. The $\nu(\text{CN})$ band (Fig. 8) consists of a number of incompletely resolved sub-bands, which arise from the range of different CN environments in this complex (Table 2). The highest frequency band in the complex (2164 cm⁻¹) is close to that of solid AgCN itself. This band increases in intensity as py is lost from the sample, and so is assigned to uncomplexed AgCN. As noted above, the py complex readily loses py upon exposure to air, and it is diffi-

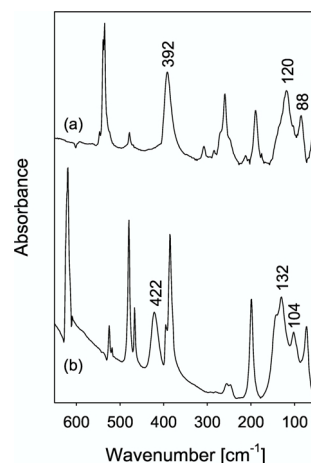


Fig. 10. The far-IR spectra of (a) AgCN : coll (1:1), and (b) AgCN : quin (1:2). Bands assigned to vibrations of the AgCN chains are labelled with their wavenumbers.

cult to obtain a spectrum of the exactly stoichiometric complex; this matter is examined further in the discussion of the far-IR spectrum (see below). The assignment of the remaining $\nu(\text{CN})$ bands is based on a correlation that we have recently demonstrated between the $\nu(\text{CN})$ frequencies in some AgCN : ER₃ complexes that contain infinite AgCN chains and the Ag-C/N bond lengths. The correlation is such that $\nu(\text{CN})$ increases as the Ag-C/N bond lengths decrease [30]. Thus, the highest frequency $\nu(\text{CN})$ band in the pyridine complex occurs at 2154 cm⁻¹, and this is assigned to the CN groups that are associated with the two-coordinate silver atom Ag(2a) (the one without a py molecule attached) since this atom has the shortest Ag-C/N distances (Table 2). The other lower frequency $\nu(\text{CN})$ bands in the range 2140–2096 cm⁻¹ are assigned to the CN groups attached to silver atoms that also bear py, since these have longer Ag-C/N distances. The full range of Ag-C/N distances in the complex is 2.04–2.30 Å; according to the correlation previously established for the AgCN : ER₃ complexes,

this corresponds to $\nu(\text{CN})$ values in the range 2150–2100 cm^{-1} , which agrees very well with the observed range 2154–2096 cm^{-1} . Due to the incomplete resolution of the bands concerned and also to disorder in the structure of the complex, more detailed assignments are not possible.

The far-IR spectrum of the py complex (Fig. 9) shows further evidence of the unusual structure of this compound. Despite the overlap with a ligand band at 407 cm^{-1} , it is clear that several bands are present in the range 360–460 cm^{-1} , and these are assigned to $\nu(\text{AgC/N})$ vibrations. This mode occurs at 480 cm^{-1} in AgCN itself, and is expected to move to lower frequency as additional ligands are bound to the silver atom. We have recently shown that a correlation exists between the $\nu(\text{AgC/N})$ frequencies and the Ag-C/N bond length in some AgCN : ER₃ complexes that contain infinite AgCN chains. The correlation is such that $\nu(\text{AgC/N})$ increase as the Ag-C/N bond lengths decrease [30]. As in the case of the $\nu(\text{CN})$ bands discussed above, the highest frequency $\nu(\text{AgC/N})$ mode, at 460 cm^{-1} , is associated with the two-coordinate silver atom Ag(2a) (the one without a py molecule attached) since this atom has the shortest Ag-C/N distances (Table 2), while the lower wavenumber bands are associated with the CN groups attached to silver atoms that also bear a py molecule, since these have longer Ag-C/N distances. The far-IR spectra also contain bands in the range 220–270 cm^{-1} due to $\delta(\text{AgC/N})$, and in the range 80–150 cm^{-1} due to $\delta(\text{NAgC})$. These doubly degenerate (perpendicular) vibrations give rise to single bands in the linear chains of AgCN itself due to the fact that the chains lie on threefold symmetry axes [29], but this symmetry is lost in the py adduct. The observed multiplicity of these bands (Fig. 9) could therefore be due to this loss of symmetry, as well as (or instead of) the range of different Ag and CN environments that give rise to multiplicity in the $\nu(\text{CN})$ and $\nu(\text{AgC/N})$ bands, as discussed above. The far-IR spectrum of a sample that has lost a small amount of py ligand (Fig. 9(b)) shows additional bands at 482, 270 and 119 cm^{-1} , which correspond closely with those in solid AgCN [29]. The positions and relative intensities of the other bands remain the same, indicating that the py loss involves a direct transition from the 10:9 adduct directly to AgCN, rather than the formation of intermediate complexes with a higher AgCN/py ratio. Similarly, the spectrum of the complex in the presence of excess py (Fig. 9(a))

indicates that the presence of additional ligand does not result in the formation of any complex of a lower AgCN/py stoichiometry (*e. g.* 1:1).

The Raman spectrum of the py compound displayed features similar to those discussed above for the IR spectrum. In particular, the $\nu(\text{CN})$ region (Fig. 8(b)) showed broadening and splitting consistent with the range of CN environments found in the crystal structure. As in the case of AgCN itself [29], the $\nu(\text{AgC/N})$ bands were not visible in the Raman spectrum of the complex, but there was a broad $\delta(\text{AgCN})$ band at 255 cm^{-1} . The Raman spectrum of a saturated solution of AgCN in py was also recorded. This showed a $\nu(\text{CN})$ band at 2144 cm^{-1} , with a partially resolved shoulder at 2099 cm^{-1} , and a $\delta(\text{AgCN})$ band at 245 cm^{-1} . The bands are not sufficiently well resolved to allow a detailed analysis, but comparison can be made with the results of a previous study of AgCN in liquid ammonia [31]. In this case the maximum in the $\nu(\text{CN})$ band occurs at 2119 cm^{-1} , significantly lower than the value 2144 cm^{-1} observed for the py solution. The band in the liquid ammonia solution is assigned to “solvated” AgCN. The different $\nu(\text{CN})$ frequency observed for the py solution would support this assignment, as the solvate should show a solvent-dependent frequency. However, it was also noted in the liquid ammonia study that the concentration of linear CN-bridged oligomers increased with increasing AgCN concentration. Such oligomers could be present in py solution as well, as the solubility of AgCN in py is quite high, and this would be consistent with the fact that the $\nu(\text{CN})$ band maximum in solution is almost identical to that in the solid py complex.

In contrast to the case of the py complex, the IR spectra of AgCN : coll (1:1) and AgCN : quin (1:2) show single $\nu(\text{CN})$ and $\nu(\text{AgC/N})$ bands (Fig. 10, Table 5), consistent with the much simpler structures of these complexes. The $\nu(\text{AgC/N})$ bands were assigned by comparison of the spectra of the complexes with those of the corresponding free ligands. Somewhat surprisingly, the value for the four-coordinate quin complex (422 cm^{-1}) is higher than that for the three-coordinate coll complex (392 cm^{-1}). This may be due to the unusually short Ag-NC bond that is present in the former compound (Table 1).

Samples of the above complexes prepared *in situ* (see Experimental Section) showed essentially the same IR spectra as those of the bulk-synthesised complexes. The *in situ* method provides a rapid means

to examine the interaction of other amine base ligands with AgCN, although it does not provide information about the stoichiometry of the resulting complex. This method was applied to the ligands 2- and 4-mp in order to see whether ligands more closely related to py would give similar unusual structures. In both cases only a single, sharp $\nu(\text{CN})$ band was observed at 2140 cm^{-1} , showing that these compounds have simple chain structures with correspondingly simple stoichiometries, like the coll case. Solid AgCN was found to be very soluble in 2mp, so that it was difficult to obtain the spectrum of a solid complex in this case. Also, the ligand bands interfered in the assignment of the low frequency bands in this complex. These problems did not occur for the 4mp case, allowing the assignments $\nu(\text{AgC/N}) = 418$, $\delta(\text{AgCN}) = 257$, $\delta(\text{NAgC}) = 130$, 94 cm^{-1} . A gravimetric study of the addition of 4mp vapour to AgCN confirmed that the complex formed in this system is of 1:1 stoichiometry (see above).

The X-ray structural studies of the (1:1) AgCN complexes with the bidentate ligands bpy, phen and dmp show the existence of both infinite chain polymer and monomeric complexes, and these differences are readily apparent in the IR spectra. Thus, the monomeric AgCN : phen (1:1) and AgCN : dmp (1:1) both have lower $\nu(\text{CN})$ and $\nu(\text{AgC/N})$ frequencies than the polymeric AgCN : bpy (1:1), despite the fact that the Ag-C/N distances in the former (2.057(3) and 2.043(5) Å respectively) are shorter than that in the latter (2.154(3) Å). This is consistent with the trends previously observed in a range of AgCN : ER_3 complexes (E = P, As, Sb) where, for a given Ag-C/N bond length, compounds containing terminal CN groups showed lower $\nu(\text{CN})$ and $\nu(\text{AgC/N})$ frequencies than those with bridging CN groups [30]. In the case of the $\nu(\text{CN})$ mode, this is because co-ordination of the CN group by σ donation to a silver atom results in a frequency increase, and this increase is greater in the bridge bonding mode, since two silver atoms are acting as electron acceptors. In the case of the $\nu(\text{AgC/N})$ mode, the bridge bonding results in a higher frequency because the vibration involves the stretching of both the Ag-C and Ag-N bonds of the $\text{Ag-C}\equiv\text{N-Ag}$ unit [30].

The complex structure of AgCN : tpy : py (8:2:1) is reflected in the IR spectrum, which shows a complex pattern $\nu(\text{CN})$ bands in the range $2155\text{--}2120\text{ cm}^{-1}$. The range of $\nu(\text{CN})$ values corresponds well with the range of Ag-C/N distances $2.03\text{--}2.24\text{ Å}$, according to a recently established correlation between these

quantities for bridging CN groups in silver(I) complexes [30].

The existence of an AgCN : en (1:0.5) complex with $\nu(\text{CN}) = 2144\text{ cm}^{-1}$ has been reported previously [32]. An attempt in the present study to obtain crystals of a complex with a higher en : AgCN ratio, by dissolution of AgCN in neat en, led to conversion of the ligand to decahydropyrazine [2,3-*b*] pyrazine (see above). However, a gravimetric study of the addition of en vapour to solid AgCN (see Experimental Section) showed the formation of AgCN : en (1:1) with $\nu(\text{CN}) = 2114\text{ cm}^{-1}$. Bands due to the coordinated ligand dominate the far-IR spectrum of this compound, and this precludes the observation of the other expected AgCN modes. No definitive conclusions about the structures of these two compounds can be reached on the basis of the $\nu(\text{CN})$ frequencies alone, although the conclusion in the original study [32] of the 1:0.5 complex, that this consists of isolated $[\text{en}(\text{AgCN})_2]$ molecules with terminally bound CN groups, now seems rather unlikely. Inspection of the results in Table 6 shows that $\nu(\text{CN}) = 2144\text{ cm}^{-1}$ for this complex is more consistent with an infinite polymeric structure with bridging CN groups. A possible structure is therefore a single stranded polymer in which adjacent Ag atoms in the string are bridged by bidentate en molecules. In contrast to this, the very low $\nu(\text{CN}) = 2114\text{ cm}^{-1}$ for the 1:1 complex (*cf.* Table 5) seems to preclude a polymeric structure, and would be more consistent with a mononuclear $[\text{enAgCN}]$ structure in which a three-coordinate Ag atom is bound to a bidentate en molecule and a terminal CN group.

Conclusions

The relatively weak inter-chain bonding in solid AgCN can be broken by amine bases, which coordinate to the metal atoms while retaining the extended -Ag-CN-Ag-CN- chain structure in many cases. In contrast to the analogous CuCN complexes [1], however, the breakdown of the solid AgCN structure proceeds further in the presence of bidentate amine ligands, with the breaking of Ag-C/N bonds to yield mononuclear complexes. The dependence of the stoichiometries and structures of the polymeric adducts on the steric profile and the base strength of the unidentate amine ligand concerned appears to be less pronounced (*e.g.* there is little difference between py and 4mp), and is in the reverse direction (*cf.* AgCN : 4mp (1:1) and AgCN :

quin (1:2)) to that of the analogous CuCN complexes, where the maximum ligand to metal ratio for a particular ligand decreases as the size of the ligand increases [1]. Removal of the base molecules from the infinite polymers occurs in a single step. This contrasts with the situation for the analogous CuCN complexes,

where removal of the base occurs in several stages *via* a series of well defined adducts [1]. The differences noted above between the properties of corresponding copper and silver compounds are probably due to differences in the relative strengths of the M-N(amine) and M-C/N(cyanide) bonds for these two metals.

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