Lewis-base Adducts of Group 1B Metal(I) Compounds. Part 11.* Synthesis and Crystal Structure † of Adducts of Silver(I) Bromide with Monomethyl-substituted Pyridine Bases

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Recrystallization of silver(I) bromide from 2-, 3-, and 4-methylpyridine yields the 1 : 2, 1 : 1, and 1 : 1 adducts respectively; single-crystal *X*-ray structure determinations are reported at 295 K for the three complexes. The silver(I) bromide–bis(2-methylpyridine) adduct consists of a triclinic unit cell of space group $P\bar{1}$, with $a = 9.870(8)$, $b = 9.249(9)$, $c = 9.185(8)$ Å, $\alpha = 109.67(7)$, $\beta = 118.38(5)$, $\gamma = 93.23(7)°$, and $Z = 2$, containing one centrosymmetric di-μ-bromo-bridged binuclear molecular species, $[(C_6H_7N)_2AgBr_2Ag(C_6H_7N)_2]$, in the unit cell. R is 0.067 for 1 082 independent 'observed' reflections. Distances include Ag–Br of 2.735(3) and 2.741(4) Å, and Ag–N of 2.32(2) and 2.35(2) Å. For the silver(I) bromide–3-methylpyridine adduct, the unit cell is orthorhombic, space group *Pccn*, with $a = 14.718(4)$, $b = 14.407(4)$, $c = 7.301(2)$ Å, and $Z = 8$; $R = 0.041$ for 850 independent 'observed' reflections. The structure is unique among those hitherto reported for coinage metal(I) halide–base adducts, being an infinite polymeric array of dimeric $Ag_2Br_2(base)_2$ units linked face-to-face yielding a 'tube' structure, which like all other (MXL) structures may be considered a derivative of the parent metal(I) halide lattice. For the silver(I) bromide–4-methylpyridine adduct, a monoclinic $P2_1/n$ cell is found, with $a = 10.286(5)$, $b = 18.066(9)$, $c = 4.390(3)$ Å, $\beta = 104.31(5)°$, and four AgBr(base) units in the cell; $R = 0.074$ for 616 'observed' reflections. The structure is the familiar 'stair polymer' found in a number of other coinage metal(I) halide–base systems.

Following the synthetic and structural definition of a wide range of stoicheiometric and structural types for the adducts formed by the crystallization of copper(I) iodide with monodentate nitrogen bases,[1,2] we have turned our attention to the silver(I) analogues. For silver(I) halides, crystalline adducts, usually only of 1 : 1 stoicheiometry, are frequently obtained only when the neat base itself is used as solvent. With silver(I) iodide,[3] many crystalline derivatives suitable for single-crystal *X*-ray structure determination are obtained easily with a variety of bases. With morpholine,[4] 2- and 3-methylpyridine,[3] and quinoline,[3] 'stair polymer' structural types have been found, while with piperidine [5] and triethylamine,[3] the pseudo 'cubane' unit is observed. Adducts with pyridine and 4-methylpyridine have also been obtained but of unsatisfactory crystal quality for structure determination. With silver(I) chloride, crystalline adducts appropriate for *X*-ray work are obtained only with difficulty and, although adduct formation appears to occur with piperidine, morpholine, and triethylamine, so far only that obtained with quinoline [6] has been amenable to single-crystal *X*-ray study, being found to be the novel 1 : 1 'saddle' polymer. [With silver(I) chloride and 2- and 4-methylpyridine, well formed crystals of silver(I) chloride itself are obtained.]

With silver(I) bromide, adduct formation appears to occur with 2,6-dimethylpyridine and triethylamine, but material suitable for single-crystal study has not so far been obtained. With 2-, 3-, and 4-methylpyridine and quinoline, however, dissolution of silver(I) bromide on warming, followed by recrystallization on cooling with the neat base in all cases yields crystalline material more or less suitable for single-crystal *X*-ray study. Determination of the unit-cell dimensions and space group of the quinoline adduct [6] strongly suggests it to be isostructural with the 1 : 1 silver(I) chloride–quinoline adduct. For the adducts obtained on recrystallization of 2-, 3-, and 4-methylpyridine (2Me-py, 3Me-py, and 4Me-py) solutions of silver(I) bromide, single-crystal *X*-ray structure determinations have been carried out and are reported hereunder, establishing the silver(I) bromide–base ratios to be 1 : 2, 1 : 1, and 1 : 1 respectively. As is customary in handling materials of this type (which do not lend themselves to characterization by conventional methods), single crystals wet with mother-liquor were sealed in capillary tubes. The structure of the 1 : 2 silver bromide-2-methylpyridine adduct, $[\{AgBr(2Me\text{-}py)_2\}_2]$ (1), is the only silver(I) halide–pyridine base adduct with that stoicheiometry so far to be structurally characterized. The 1 : 1 adduct with 3-methylpyridine, $[\{AgBr(3Me\text{-}py)\}_n]$ (2), is of the totally new 'tube polymer' structural type, while that with 4-methylpyridine, $[\{AgBr(4Me\text{-}py)\}_n]$ (3), is the first example of a 'stair polymer' type to be reported for a nitrogen base adduct of silver(I) bromide.

Experimental

Crystallography.—For each compound a unique data set was measured within a predetermined $2\theta_{max.}$ limit, set after consideration of the extent of the available data, using a Syntex $P2_1$ four-circle diffractometer in conventional 2θ–θ scan mode. N Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after solution of the structure by vector methods. Analytical absorption corrections were applied to the data. For the non-hydrogen atoms anisotropic thermal parameters were refined; $(x, y, z, U_{iso})_H$ were included as constrained estimates. Conventional residuals R, R' (on $|F|$) at convergence are quoted, reflection weights being $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral complex scattering factors

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* Part 10, L. M. Engelhardt, P. C. Healy, R. I. Papasergio, and A. H. White, *Inorg. Chem.*, in the press.

† *Supplementary data available* (No. SUP 56057, 9 pp.): H-atom coordinates, thermal parameters, ligand non-H geometries, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Non-hydrogen atomic co-ordinates for complex (1)

Ligand	$n = 1$			$n = 2$		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Ag	0.362 7(2)	0.372 7(2)	0.317 0(2)			
Br	0.644 7(2)	0.319 1(2)	0.531 9(2)			
N(*n*1)	0.368(2)	0.307(2)	0.053(2)	0.140(2)	0.236(2)	0.294(2)
C(*n*2)	0.287(2)	0.361(2)	−0.073(2)	0.118(2)	0.083(2)	0.272(2)
C(*n*21)	0.166(3)	0.444(3)	−0.057(3)	0.223(3)	−0.011(2)	0.234(3)
C(*n*3)	0.315(3)	0.337(3)	−0.212(2)	−0.001(3)	0.021(3)	0.293(3)
C(*n*4)	0.425(4)	0.259(4)	−0.220(3)	−0.100(2)	0.111(3)	0.322(3)
C(*n*5)	0.505(3)	0.201(3)	−0.099(3)	−0.079(3)	0.261(3)	0.340(3)
C(*n*6)	0.474(2)	0.231(2)	0.043(3)	0.042(3)	0.319(2)	0.325(2)

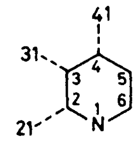
Table 2. Non-hydrogen atomic co-ordinates for complex (2)

Atom	*x*	*y*	*z*
Ag	0.331 30(5)	0.185 89(6)	0.131 67(12)
Br	0.329 02(6)	0.131 73(6)	0.490 70(13)
N(1)	0.476 7(5)	0.141 3(5)	0.054 5(11)
C(2)	0.511 8(6)	0.160 6(6)	−0.109 5(13)
C(3)	0.595 1(6)	0.129 0(7)	−0.170 7(13)
C(31)	0.628 5(9)	0.150 7(9)	−0.358 5(17)
C(4)	0.644 1(6)	0.074 2(7)	−0.052 8(16)
C(5)	0.611 7(6)	0.054 1(7)	0.121 9(16)
C(6)	0.525 6(6)	0.088 2(7)	0.169 6(13)

Table 3. Non-hydrogen atomic co-ordinates for complex (3)

Atom	*x*	*y*	*z*
Ag	0.612 5(4)	0.511 1(2)	0.315 7(8)
Br	0.400 9(4)	0.404 2(2)	0.204 2(9)
N(1)	0.789(3)	0.431(2)	0.362(8)
C(2)	0.786(5)	0.363(3)	0.459(12)
C(3)	0.885(5)	0.315(2)	0.469(20)
C(4)	0.986(4)	0.328(2)	0.341(8)
C(41)	1.096(4)	0.269(3)	0.318(9)
C(5)	0.997(5)	0.396(2)	0.237(15)
C(6)	0.895(7)	0.447(2)	0.250(20)

were used;[7] computation used the *X*-RAY 76 program system[8] implemented on a Perkin-Elmer 3240 computer by S. R. Hall. Non-hydrogen atom labelling in the ligands is as shown below.



Atomic co-ordinates for complexes (1)—(3) are given in Tables 1—3 respectively.

Crystal data. [{AgBr(2Me-py)$_2$}$_2$] (1). (C$_6$H$_7$N)$_2$AgBr ≡ C$_{12}$H$_{14}$AgBrN$_2$, M = 373.8, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), a = 9.870(8), b = 9.249(9), c = 9.185(8) Å, α = 109.67(7), β = 118.38(5), γ = 93.23(7)°, U = 670(1) Å^3, D_c (Z = 2 monomers) = 1.85 g cm^{-3}, $F(000)$ = 364, μ_{Mo} = 47.2 cm^{-1}. Specimen: irregular polyhedron ~0.2 mm (no absorption correction); N, N_o = 1 491, 1 082; $2\theta_{max.}$ = 45°; R, R' = 0.067, 0.082.

[{AgBr(3Me-py)}$_n$] (2). (C$_6$H$_7$N)AgBr ≡ C$_6$H$_7$AgBrN, M = 280.8, orthorhombic, space group $Pccn$ (D_{2h}^{10}, no. 56), a = 14.718(4), b = 14.407(4), c = 7.301(2) Å, U = 1 548.1(7) Å^3, D_c(Z = 8) = 2.41 g cm^{-3}, $F(000)$ = 1 056, μ_{Mo} = 80 cm^{-1}. Specimen: 0.35 × 0.12 × 0.10 mm; N, N_o = 1 395, 850; $2\theta_{max.}$ = 50°; R, R' = 0.041, 0.049.

[{AgBr(4Me-py)}$_n$] (3). (C$_6$H$_7$N)AgBr ≡ C$_6$H$_7$AgBrN, M = 280.8, monoclinic, space group $P2_1/n$ [C_{2h}^5, no. 14 (variant)], a = 10.286(5), b = 18.066(9), c = 4.390(3) Å, β = 104.31(5)°, U = 790.4(8) Å^3, D_c (Z = 4) = 2.36 g cm^{-3}, $F(000)$ = 528, μ_{Mo} = 79 cm^{-1}. Specimen: 0.40 × 0.20 × 0.15 mm; N, N_o = 1 004, 616; $2\theta_{max.}$ = 45°; R, R' = 0.074, 0.138.

Abnormal features. Severe disorder is found in the base of (3) which appears to oscillate about its axis through the nitrogen atom; although modelled conventionally, the anisotropic thermal parameters of the peripheral atoms are very high.

The irregular nature of the crystal of (1) precluded absorption correction.

Discussion

[{AgBr(2Me-py)$_2$}$_2$] (1).—The structure determination establishes the stoicheiometry of the complex obtained by the recrystallization of silver(I) bromide from 2-methylpyridine to be that of the 1 : 2 adduct. The asymmetric unit of the structure is one formula unit, but the molecular complexity is that of the dimer di-μ-bromo-bis[bis(2-methylpyridine)-silver(I)], the centroid of the Ag$_2$Br$_2$ unit being a crystallographic inversion centre (Figure 1). This structural type is well known for copper(I) complexes, particularly of the iodide;[2] however, for silver(I), in spite of the frequent occurrence of such stoicheiometries for complexes in solution this remains the first example of this stoicheiometry to be characterized structurally. We note, however, that for the silver thiocyanate pseudohalide, an example of this stoicheiometry has been structurally characterized with quinoline as the base;[9] the complex, however, is a one-dimensional polymer rather than a dimer.

The parameters of the Ag$_2$Br$_2$ molecular core of complex (1) (Table 4) are remarkably similar to those reported for the copper(I) iodide analogue[2] for which Cu ··· Cu = 3.083(3), I ··· I = 4.407(3), Cu–I = 2.667(3) and 2.714(3) Å, I–Cu–I = 110.05(6), and Cu–I–Cu = 69.95(6)°. Although the unit cells of both complexes are triclinic and, in fact, rather similar, the two compounds are not isomorphous [for the copper(I) iodide adduct: space group $P\bar{1}$, with a = 10.662(5), b = 9.552(6), c = 7.936(6) Å, α = 112.35(4), β = 96.20(4), γ = 104.66(4)°, and U = 704.1(7) Å^3]. However, complex (1) *is* isomorphous with the (as yet unpublished) copper(I) bromide and chloride analogues[10] [for the bromide: triclinic, space group $P\bar{1}$, with a = 9.591(3), b = 9.185(4), c = 9.041(5) Å, α = 108.57(4), β = 117.76(3), γ = 94.38(3)°, and U = 643.7(5) Å^3]. The Cu$_2$Br$_2$ core dimensions are anomalous [Cu ··· Cu, 3.351(3); Br ··· Br, 3.962(2); Cu–Br, 2.581(2) and 2.607(2); Cu–N, 2.027(2) and 2.030(6) Å], with a metal–

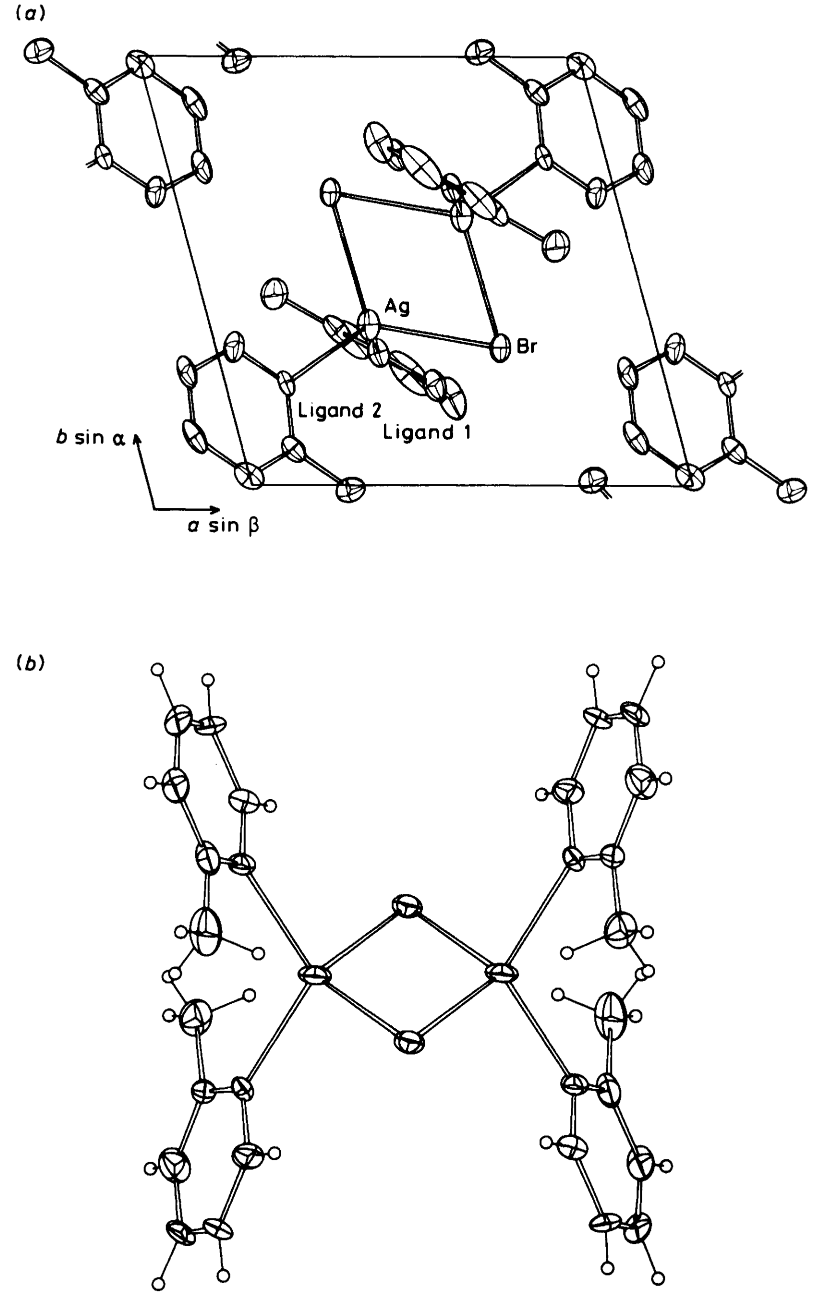


Figure 1. (*a*) Unit-cell contents of (1) projected down *c*; 20% thermal ellipsoids are shown for the non-hydrogen atoms. (*b*) The dimer of (1) projected normal to the Ag ··· Ag line; hydrogen atoms have a arbitrary radius of 0.1 Å

metal distance much longer than in the iodide analogue, and a halide–halide distance much shorter than in compound (1). In the bis(3,5-dimethylpyridine) adduct of copper(I) iodide,[2] Cu ··· Cu is only 2.683(1) Å; there is no 2-substituent on the pyridine. Seemingly, in the anomalous CuBr–bis(2-methylpyridine) adduct Cu ··· Cu is anomalously long because of steric interaction between the ligand substituent and the halide species, an interaction which is diminished in the silver analogue because of the greater silver atom radius, so that in (1) *vis-a-vis* its copper analogue, we find an increased Br ··· Br distance, while the metal–metal separation remains substantially constant. [This theme will be examined in greater detail elsewhere in a full report of the copper(I) complexes.[10]] A further comparison may be made in similar vein in relation to the available data for the bis(triphenylphosphine) adduct of silver(I) bromide;[11] this complex is similarly dimeric, with Ag ··· Ag = 3.720(4), Br ··· Br = 4.030(6), and Ag–Br = 2.742(3) Å. The Ag–Br distances are very similar to those of complex (1), but the metal–metal distance is greatly increased, presumably in consequence of halide–ligand interactions, while Br ··· Br is close to the value found in the CuBr–bis(2-methylpyridine) complex, close to the van der Waals limit.

[{AgBr(3Me-py)}$_n$] (2).—The structure determination establishes the stoicheiometry of the complex obtained by the recrystallization of silver(I) bromide from 3-methylpyridine to be that of the 1 : 1 adduct; the asymmetric unit of the structure is one formula unit and the overall aggregate a polymer (Figure 2). The polymer is of a totally new structural type among the coinage metal(I) halide–Lewis base adducts.

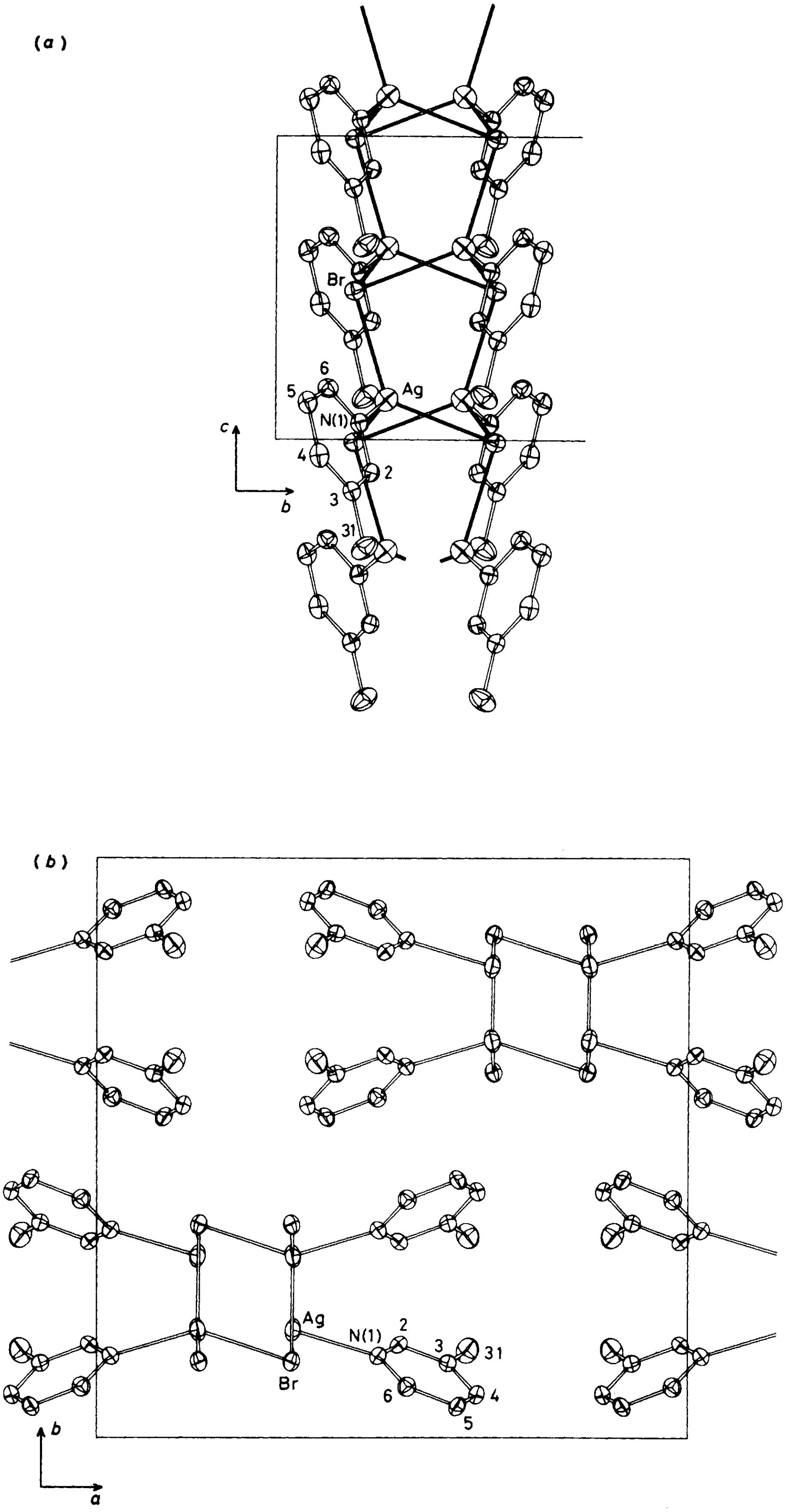


Figure 2. (*a*) Projection of the structure of (2) down *a*. One half of the cell only in *b* is given, but the extension of the polymer along *c* is depicted. 20% Thermal ellipsoids are shown for the non-hydrogen atoms. Ag–Br bonds are shown as full lines. (*b*) Projection of the structure of (2) down *c*, showing the 'tube' configuration

Table 4. Ag/Br core geometries for complex (1); distances (Å) and angles (°) *

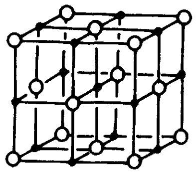
Ag–Br	2.735(3)
Ag–Br′	2.741(4)
Ag–N(11)	2.32(2)
Ag–N(21)	2.35(2)
Ag ··· Ag′	3.080(5)
Br ··· Br′	4.527(5)
Br–Ag–Br′	111.55(8)
Ag–Br–Ag′	68.45(8)
N(11)–Ag–Br	99.8(4)
N(11)–Ag–Br′	114.3(4)
N(21)–Ag–Br	114.0(4)
N(21)–Ag–Br′	100.4(4)
N(11)–Ag–N(21)	117.4(5)

* Primed atoms are generated by the intradimer inversion centre.

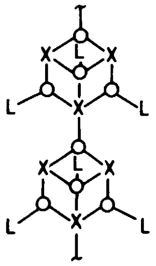
Table 5. Ag/Br core geometries for complex (2); distances (Å) and angles (°) *

Ag–Br	2.735(2)
Ag–N(1)	2.305(8)
Ag–Br^{I}	2.690(1)
Ag–Br^{II}	2.822(1)
Ag ··· Ag^{I,III}	4.365(2)
Ag ··· Ag^{II,IV}	4.091(2)
Br ··· Br^{I,III}	4.329(2)
Br ··· Br^{II,IV}	4.994(2)
N(1)–Ag–Br	99.6(2)
N(1)–Ag–Br^{I}	129.8(2)
N(1)–Ag–Br^{II}	100.5(2)
Br–Ag–Br^{I}	105.85(4)
Br–Ag–Br^{II}	127.95(5)
Br^{I}–Ag–Br^{II}	96.90(4)
Ag–Br–Ag^{III}	107.14(4)
Ag–Br–Ag^{IV}	94.80(4)
Ag^{III}–Br–Ag^{IV}	66.47(3)

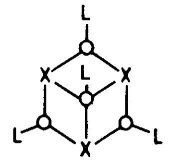
* Transformations of the asymmetric unit: I $\frac{1}{2} - x, y, z - \frac{1}{2}$; II $x, \frac{1}{2} - y, z - \frac{1}{2}$; III $\frac{1}{2} - x, y, z + \frac{1}{2}$; IV $z, \frac{1}{2} - y, z + \frac{1}{2}$.



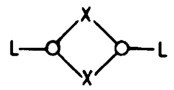
f.c.c. lattice



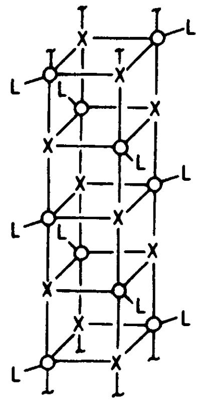
'Linked cubes'



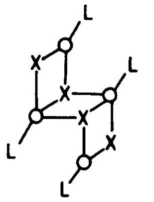
pseudo 'cubane'



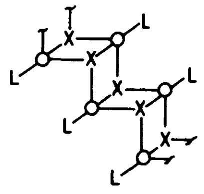
dimer



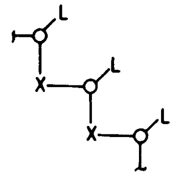
'tube'



'step'



'stair'



'split-stair'

Previous polymers and oligomers in these adducts may be understood in terms of subunits of the parent metal-halide (M–X) face-centred cubic (f.c.c.) lattice, appropriate subdivision yielding the pseudo 'cubane' unit, the 'step', the 'stair' and 'split stair' polymers, the 'linked cube', and 'saddle' polymers, with the dimer and monomer as the smallest states of subdivision.[1,2,6]

In complex (2), the polymer observed may be generated by face-to-face confrontation of an infinite succession of $M_2X_2L_2$ dimers. Equally, however, it may be considered as an infinite stack of cubes, a 'tube', with alternative longitudinal M–X bonds severed by a puckering of the M_2X_2 dimeric units. The structure of (2) is depicted in detail in Figure 2. The basic dimeric unit is generated from the asymmetric unit by the crystallographic two-fold axis which runs down the centre of the tube; within the dimer, the Ag_2Br_2 geometry is not dissimilar to that observed in (1), although the Ag_2Br_2 unit in the present case is a puckered, rather than a rigorous plane. Successive dimers are then generated by alternate glide and unit *c*-translations to give the polymer. The parameters of the 'tube', given in Table 5, may be compared with those of the parent AgBr lattice (a = 5.78 Å),[12] with Ag–Br = 2.89 and $Ag \cdots Ag \equiv Br \cdots Br \equiv a/\sqrt{2} = 4.08$ Å.

[{AgBr(4Me-py)}$_n$] (3).—The structure determination establishes the stoicheiometry of the complex obtained by the recrystallization of silver(I) bromide from 4-methylpyridine to be that of the 1 : 1 adduct; the asymmetric unit of the structure is one formula unit, and the overall aggregate an infinite polymer of the 'stair' variety, a type well known for 1 : 1 silver(I) iodide-nitrogen base adducts.[3] For the latter, those that are found in the $P2_1/c,n$ space groups have short *b* ([{AgI(3Me-py)}$_n$]; *cf.* also [{CuX(py)}$_n$] (X = Cl, Br, or I)) rather than short *c* as in (3); the only hitherto established example of the short *c* type is the silver iodide-quinoline adduct. As a result, the generator of the 'stair' is a sequence of alternate inversion centres and unit translations, in consequence of which successive Ag_2I_2 units are inequivalent, although centrosymmetric, in contrast to the short *b* type where the generator is the 2_1 screw and successive Ag_2I_2 units are

Table 6. Ag/Br core geometries for complex (3); distances (Å) and angles (°) *

Ag–Br	2.861(5)
Ag–Br$^{\mathrm{i}}$	2.637(6)
Ag ··· Ag$^{\mathrm{i}}$	3.162(6)
Ag–N(1)	2.28(3)
Ag ··· Ag$^{\mathrm{ii}}$	3.167(5)
Ag–Br$^{\mathrm{ii}}$	2.724(6)
Br ··· Br$^{\mathrm{i}}$	4.503(5)
Br ··· Br$^{\mathrm{ii}}$	4.602(6)
N(1)–Ag–Br	98.2(8)
N(1)–Ag–Br$^{\mathrm{i}}$	119.4(8)
N(1)–Ag–Br$^{\mathrm{ii}}$	107.7(9)
Br–Ag–Br$^{\mathrm{i}}$	109.9(2)
Br–Ag–Br$^{\mathrm{ii}}$	111.0(2)
Br$^{\mathrm{i}}$–Ag–Br$^{\mathrm{ii}}$	110.0(2)
Ag–Br–Ag$^{\mathrm{i}}$	70.1(1)
Ag–Br–Ag$^{\mathrm{ii}}$	69.0(1)
Ag$^{\mathrm{i}}$–Br–Ag$^{\mathrm{ii}}$	110.0(2)

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

identical. The parameters (Table 6) of the 'stair' configuration of the present example have been comprehensively compared with those of other 'stair' polymers in these complexes elsewhere.[3]

The Co-ordination Number in Copper(I) *and Silver*(I) *Complexes.*—It has become common in recent years for standard textbooks to suggest that both copper(I) and silver(I) compounds show a pronounced tendency to exhibit linear two-fold co-ordination. *ds* Hybridization effects [13] are widely invoked as a rationalization of this presumed predisposition. In this series of studies on compounds of copper(I) and silver(I) halides and pseudohalides we note that the overwhelming majority of structures adopt a four-co-ordinate environment for the metal atom and that, for those systems containing polarizable ligands lower co-ordination numbers are achieved usually only in sterically crowded situations. Early electrochemical studies on copper compounds in solution [14] have suggested that two-co-ordinate species are restricted to non-polarizable σ-donating ligands. While structural data supporting this suggestion are not available for simple mononuclear, neutral copper systems, in the more stable silver(I) system structures of several such σ-bonded two-co-ordinate complexes are available.[15] Examples of two-co-ordination with polarizable ligands however are restricted to the single sterically crowded complex, bis(trimesitylphosphine)silver(I) hexafluorophosphate.[16]

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