Lewis-base Adducts of Group 1B Metal(I) Compounds. Part 4.[1] Synthesis and Crystal Structure * of the 1 :1 Adduct of Silver(I) Chloride with Quinoline

Nancy K. Mills and Allan H. White
Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands W.A. 6009

The crystal structure of the title compound, $[\{[AgCl(C_9H_7N)]\cdot 0.25C_9H_7N\}_n]$, has been determined by single-crystal *X*-ray diffraction methods at 295(1) K. Crystals are monoclinic, space-group *C*2/*c*, with a = 30.508(5), b = 7.216(1), c = 22.698(5) Å, and β = 122.11(7)°; the structure was refined by least-squares methods to a residual *R* of 0.042 for 1 258 independent ' observed ' reflections. The structure is novel in the context of Group 1B metal(I)–halide–base adducts, and is a polymer, comprising Ag_5X_4 face-centred motifs linked in a linear polymeric array through the silver atoms at opposite corners of the face; the two vacant co-ordination sites at the other corners each accommodate a pair of quinoline ligands. The silver atom at the centre of the motif is pseudo-tetrahedrally co-ordinated by the four halogen atoms, so that the Ag_5X_4 unit adopts a ' saddle ' conformation. The bromide derivative is isomorphous, with a = 30.57(2), b = 7.319(4), c = 23.17(2) Å, and β = 122.19(5)°.

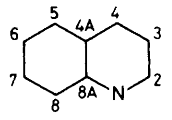
In a previous paper,[1] we extended the available structural data on the adducts (all so far of 1 : 1 stoicheiometry) readily obtained on crystallization of silver(I) iodide from nitrogen bases of various stereochemical aspects; all structurally characterized derivatives of this type are found to have either the pseudo-cubane or ' stair-polymer ' stereochemistry. 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, a derivative suitably crystalline for a single-crystal study has only so far been obtained with quinoline (C_9H_7N). [With silver(I) chloride and 2- and 4-methylpyridine well formed crystals of silver(I) chloride itself may be obtained.] A structure determination of the 1 : 1 silver(I) chloride–quinoline complex, reported herein, shows the adduct to be a novel polymeric type previously unknown in Group 1B metal(I)–halide–base adduct systems. For the crystallographic work, a small single crystal was enclosed in a capillary. [The silver(I) bromide–quinoline adduct, obtained similarly, has a similar unit cell and space group; these data are also recorded.]

Experimental

Crystallography.—Crystal data. $[\{[AgCl(C_9H_7N)]\cdot 0.25C_9H_7N\}_4] = C_{45}H_{35}Ag_4Cl_4N_5$, M = 1 219, monoclinic, space group *C*2/*c* (C^6_{2h}, no. 15), a = 30.508(5), b = 7.216(1), c = 22.698(5) Å, β = 122.11(7)°, U = 4 232(1) Å^3, Z = 4, D_c = 1.91 g cm^{-3}, $F(000)$ = 2 384, μ_{Mo} = 20.7 cm^{-1}. Specimen: 0.10 × 0.20 × 0.10 mm. [$C_{45}H_{35}Ag_4Br_4N_5$, M = 1 397, monoclinic, space group *C*2/*c*, a = 30.57(2), b = 7.319(4), c = 23.17(2) Å, β = 122.19(5)°, U = 4 387(5) Å^3, D_c = 2.11 g cm^{-3}.]

A unique data set was measured to the limit $2\theta_{max.}$ = 40° using a Syntex $P2_1$ four-circle diffractometer in conventional 2θ/θ scan mode at 295 K; the diffractometer was fitted with a monochromatic Mo-K_α radiation source (λ = 0.710 69 Å) and 1 907 independent reflections were obtained. 1 258 of these with $I > 3\sigma(I)$ were considered ' observed ' and used in the 9 × 9 block-diagonal least-squares refinement after analytical absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U)_H$ were estimated and constrained. Residuals R,R' at convergence were 0.042, 0.044, reflection weights being $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral complex scattering factors were used.[2] Computation used the *X*-RAY 76 program system [3] implemented on a Perkin-Elmer 3240 computer.

Ligand atom labelling is as shown below.



Atomic co-ordinates are given in Table 1. Figure 1 shows the unit-cell contents projected down *b* and Figure 2 a view of a single polymer strand.

Discussion

The chloride and bromide derivatives are isomorphous and, it may be reasonably presumed, basically isostructural.

The structure determination establishes the stoicheiometry of the complexes to be 1 : 1 : 1 Ag–X–quinoline (X = Cl or Br) with an additional quarter molecule of quinoline present in the lattice as solvate, giving an overall stoicheiometry of 1 : 1 : 1.25. The solvent molecules, four per unit cell, are located so that the centres of the C(4A)–C(8A) bonds lie at $\frac{1}{4}$, $\frac{3}{4}$, $\frac{1}{2}$ *etc.*, and the molecules are centrosymmetric. Given the nature of the quinoline molecule, this implies either that the symmetry of the space group in reality is less than that of *C*2/*c* or that the molecule is disordered. Given the unlikelihood of refining the structure satisfactorily with the ordered perturbation in the space group *Cc* (photography of the crystal indicates the absence of any superlattice reflections), the solvent has been modelled in terms of disorder. In such a model, it is still possible for the solvent to adopt two dispositions which we have been unable to distinguish between on the basis of the relatively imprecise molecular geometries and thermal parameters, and accordingly, the nitrogen atom has been distributed equally over both of these; *i.e.* over the four possible sites in the molecule.

The structure of the $[\{[AgX(C_9H_7N)]\cdot 0.25C_9H_7N\}_n]$ complex itself is unique and interesting. It comprises an infinite one-dimensional polymer disposed about the crystallographic

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* *Supplementary data available* (No. SUP 23770, 13 pp.): structure factors, thermal parameters, hydrogen parameters, least-squares planes, ligand geometries. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Non-hydrogen atom co-ordinates

Atom	*x*	*y*	*z*
Ag(1)	1	1.189 2(2)	$\frac{1}{4}$
Ag(2)	0.919 10(4)	0.695 8(2)	0.294 80(5)
Ag(3)	1	0.691 7(2)	$\frac{1}{4}$
Cl(1)	0.928 2(1)	0.443 2(5)	0.212 7(2)
Cl(2)	0.998 9(1)	0.937 7(5)	0.333 0(2)
Quinoline ligand 1			
N(1)	0.931 3(4)	0.503 8(15)	0.381 3(5)
C(2)	0.947 9(5)	0.332 1(22)	0.384 1(7)
C(3)	0.959 7(5)	0.208 7(20)	0.436 6(7)
C(4)	0.952 9(5)	0.257 2(17)	0.488 9(7)
C(4A)	0.934 6(4)	0.436 0(20)	0.488 5(7)
C(5)	0.927 7(5)	0.501 3(20)	0.542 4(7)
C(6)	0.908 7(5)	0.675 9(23)	0.538 5(7)
C(7)	0.897 5(5)	0.793 8(20)	0.482 9(7)
C(8)	0.904 3(5)	0.736 8(16)	0.431 2(7)
C(8A)	0.923 4(5)	0.557 9(18)	0.433 2(7)
Quinoline ligand 2			
N(1)	0.848 9(4)	0.882 3(15)	0.231 5(5)
C(2)	0.855 4(6)	1.055 5(21)	0.216 8(8)
C(3)	0.814 6(7)	1.169 8(20)	0.172 4(9)
C(4)	0.765 9(6)	1.106 9(25)	0.143 5(8)
C(4A)	0.756 2(6)	0.931 9(22)	0.157 3(8)
C(5)	0.705 9(6)	0.855 9(26)	0.128 8(9)
C(6)	0.698 4(6)	0.686 0(32)	0.145 8(10)
C(7)	0.741 2(7)	0.575 5(24)	0.190 7(10)
C(8)	0.790 9(5)	0.635 5(19)	0.219 9(7)
C(8A)	0.799 1(4)	0.819 0(18)	0.203 3(6)
Quinoline solvent			
C(1)	1.321 8(8)	0.783 2(36)	0.563 1(9)
C(2)	1.335 0(7)	0.598 0(43)	0.558 3(11)
C(3)	1.297 4(11)	0.473 7(27)	0.514 5(13)
C(4)	1.249 8(8)	0.503 6(27)	0.476 2(10)
C(4A)	1.233 0(7)	0.680 8(27)	0.478 6(7)

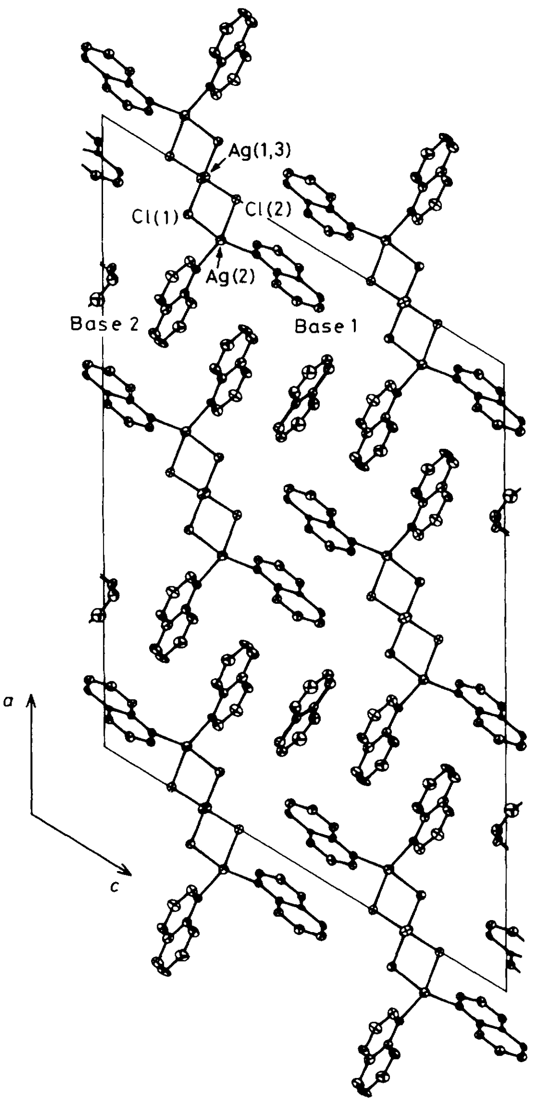

Figure 1. Unit-cell contents of [{[AgCl(C_9H_7N)]·0.25C_9H_7N}$_n$] projected down *b*, showing non-hydrogen atoms with 20% probability thermal ellipsoids

two-fold axes 0, *y*, $\frac{1}{4}$ *etc.*, so that only one half of the repeating unit along the unit *b* translation is independent. The repeat unit along *b* consists of what is essentially one face of the face-centred silver halide unit cell, with the silver atoms at the corners and face centres, and with two of the opposite corner atoms of the face [Ag(1) and its unit translation] defining *b*, with Ag(3) almost exactly midway between them on the face centre. The atoms Ag(1) and Ag(3) are both consequently co-ordinated by four halide atoms, each bridging the two types of silver atom and generating the polymeric array along *b*. In addition, the halide species are three co-ordinate, chelating the pair of silver atoms at the other pair of opposed corners of the face-centred unit; these silver atoms, both Ag(2), with a very similar γ co-ordinate to Ag(3), lie in a dimension normal to that of polymerization and, in consequence, retain two co-ordination sites not occupied by halides, but rather by the quinolines. Symmetry about the Ag(2) · · · Ag(3) · · · Ag(2) line is very nearly two-fold, as it is about a further line normal to this and to *b*; the $Ag_3Ag_{\frac{1}{2}}Cl_4N_4$ polymer ($Ag_{\frac{1}{2}}$ indicates two independent silver atoms) in consequence is a very good approximation to 222 in its overall symmetry. That the pseudo-symmetry of the species is not higher, approaching *mmm*, is a consequence of the non-coplanarity of the face-centred unit by virtue of a tendency in the silver atom co-ordination to tetrahedral rather than square-planar co-ordination. [' In-plane ' angle sums about Ag(1—3) and X(1,2) are shown, together with the mean polymer geometry in Figure 3.] The resulting $Ag_3Ag_{\frac{1}{2}}Cl_4$ unit has a saddle distortion in consequence and we refer to it as a ' saddle polymer ' in further discussion. In considering the geometry of the face-centred unit (Table 2, Figure 3), we note that in the parent silver chloride and bromide face-centred cubic structures, a = 5.56 and 5.78 Å respectively,[4] Ag · · · Ag and X · · · X distances are necessarily equal, being $a/\sqrt{2}$ (3.93 and 4.08 Å, respectively) while Ag–X are $a/2$ (= 2.78 and 2.89 Å).

The present structural type is novel in the context of the Group IB metal(I)/halide/nitrogen–phosphine–arsine 1 : 1 : 1 base adducts, not simply on the grounds of its uniqueness but also in the relationship between them. Previous examples may be derived from the tetrameric ' step ' structure as the basic unit, which may fold into a cube or sever to give dimers and then monomers, or polymerize giving the stair polymer as discussed elsewhere;[5] for these cases, the cube in question relates to a face-centred cubic lattice as one-eighth of its cell,

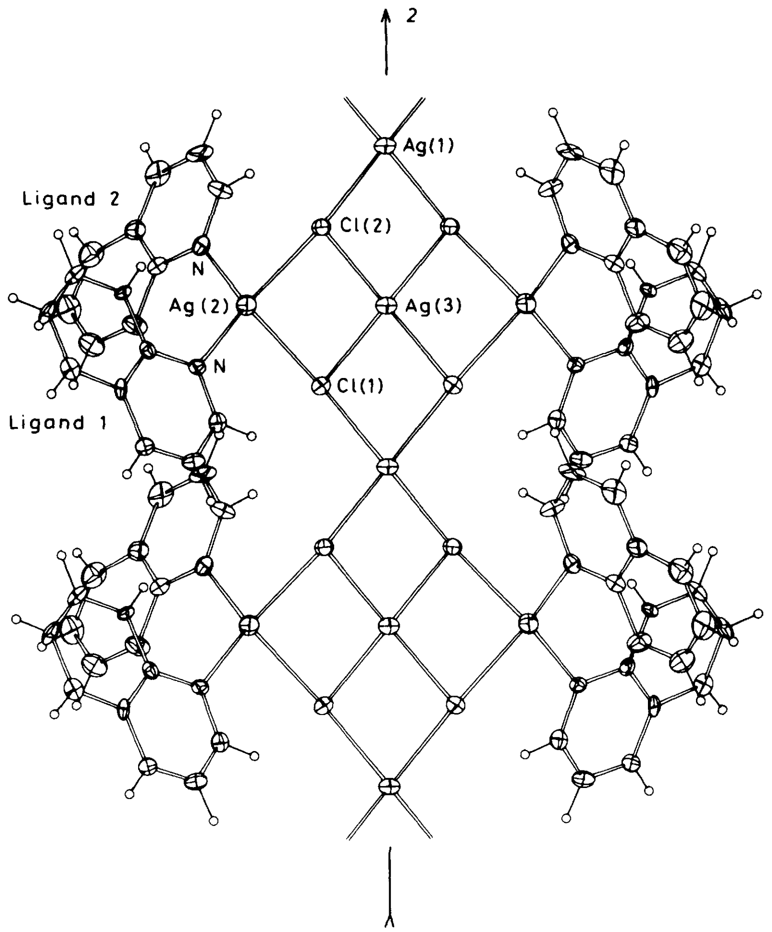

Figure 2. A single polymer strand of [{[AgCl(C_9H_7N)]·0.25C_9H_7N}$_n$] viewed down one of its pseudo-two-fold axes and normal to the face-centred $Ag_3Ag_{\frac{2}{2}}Cl_4$ ' plane.' Hydrogen atoms have an arbitrary radius of 0.1 Å

Table 2. Selected geometrical parameters for [{[AgCl(C_9H_7N)]·0.25C_9H_7N}$_n$]

(*a*) Distances (Å)			
Ag(2) · · · Ag(3)	3.130(2)		
Ag(1) · · · Ag(3)	3.590(3)	Ag(1^{i}) · · · Ag(3)	3.626(3)
Ag(2)–Cl(1)	2.725(4)	Ag(2)–Cl(2)	2.734(4)
Cl(1) · · · Cl(2)	4.311(5)	Cl(1^{i}) · · · Cl(2)	4.376(5)
Ag(3)–Cl(2)	2.603(4)	Ag(3)–Cl(1)	2.600(4)
Ag(1)–Cl(2)	2.630(4)	Ag(1)–Cl(1^{i})	2.627(4)
Ag(2)–N(11)	2.27(1)	Ag(2)–N(21)	2.28(1)
(*b*) Angles (°)			
Cl(1^{i})–Ag(1)–Cl(2)	112.7(1)		
Cl(1)–Ag(1)–Cl(1^{ii})	91.5(1)	Cl(2)–Ag(1)–Cl(2^{iii})	92.7(1)
Cl(1^{ii})–Ag(1)–Cl(2)	125.2(1)		
Cl(1)–Ag(2)–Cl(2)	104.3(1)		
N(11)–Ag(2)–N(22)	125.0(5)		
Cl(1)–Ag(2)–N(11)	98.9(3)	Cl(2)–Ag(2)–N(21)	101.7(3)
Cl(1)–Ag(2)–N(21)	111.6(3)	Cl(2)–Ag(2)–N(11)	114.0(2)
Cl(1)–Ag(3)–Cl(1^{iii})	92.8(1)	Cl(2)–Ag(3)–Cl(2^{iii})	94.0(1)
Cl(1)–Ag(3)–Cl(2)	111.9(1)		
Cl(1)–Ag(3)–Cl(2^{iii})	124.6(1)		
Ag(1^{iv})–Cl(1)–Ag(2)	128.1(1)	Ag(1)–Cl(2)–Ag(2)	124.2(1)
Ag(1^{iv})–Cl(1)–Ag(3)	87.9(1)	Ag(1)–Cl(2)–Ag(3)	86.6(1)
Ag(2)–Cl(1)–Ag(3)	72.0(1)	Ag(2)–Cl(2)–Ag(3)	71.8(1)

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

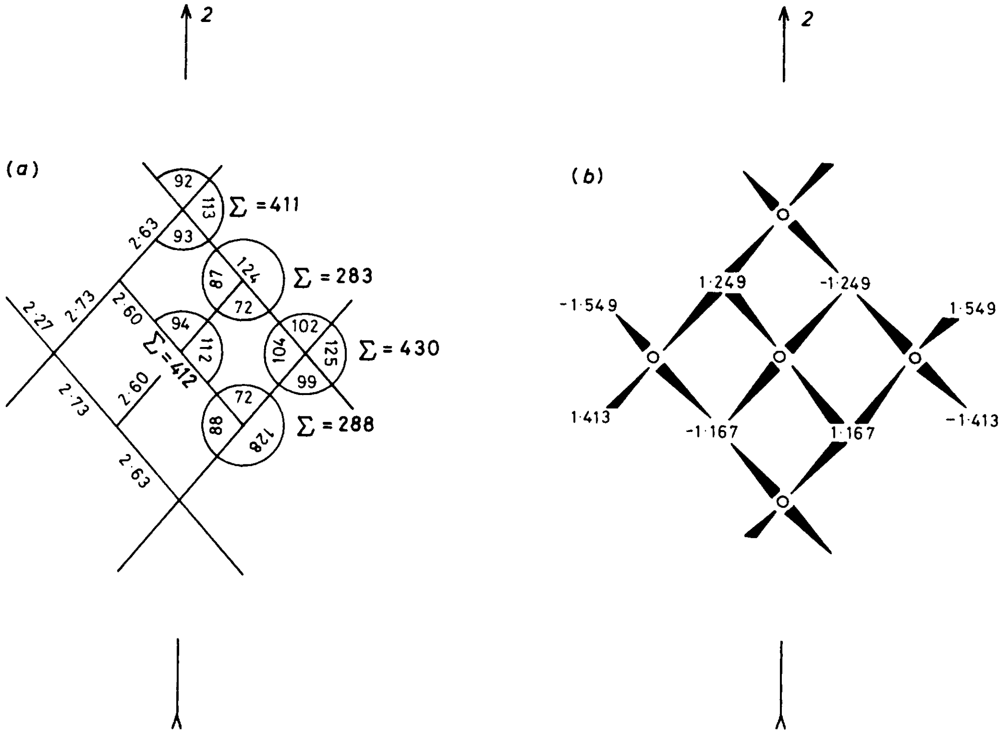

Figure 3. (*a*) Important geometrical parameters (Å) of the polymeric strands of [{[AgCl(C_9H_7N)]·0.25C_9H_7N}$_n$]. Also given are the 'in-plane' angle sums, Σ (°), about each of the silver and halogen atoms. (*b*) Deviations (Å) of the halide and nitrogen atoms from the Ag_5 plane of the face-centred unit

comprising a pair of interpenetrating metal and halide tetrahedra. In the present case, the structure may again be regarded as deriving from a face-centred cubic lattice but utilizing a two-dimensional rather than a three-dimensional unit as the generating motif. In this context also, it is interesting to note that, although (temperature dependent) polymorphism is found among the Group 1B metal halides (notably for silver iodide [6]), the predominant structure (excluding fluoride) is the zinc-blende structure, while, for silver chloride and bromide, it is the rock-salt structure.

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