The Crystal and Molecular Structure of Pollards Salt, $(NH_4)_6(AuCl_4)_3Ag_2Cl_5$

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Summary Crystal structure determination of $(NH_4)_6Au_3Ag_2Cl_{17}$ has shown that it contains the anions $AuCl_4^-$ and the hitherto unreported $Ag_2Cl_5^{3-}$, the ions being so arranged that intervalence exchange occurs between them.

THE mixed gold–silver halide $Cs_2AuAgCl_6$ has been shown[1] to contain the ions $AuCl_4^-$ and $AgCl_2^-$ in a chain structure (Figure 1) similar to that of the mixed valence gold complex

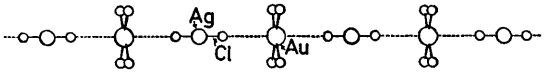

FIGURE 1

$Cs_2(AuCl_2)(AuCl_4)$. Each gold atom is thus surrounded by an axially elongated octahedron of chlorine atoms, whereas the stacking of chains is such that each silver also has an octahedral environment of chlorines, but in this case only the axial bonds are of covalent bond dimension. Crystals of both compounds are black, the absorption of visible light being ascribed to intervalence exchange.[2] A compound which appeared to be analogous is the deep red salt first described by Pollard[3] as $(NH_4)_3Ag_3Au_4Cl_{23}$, and subsequently by Wells[4] as $(NH_4)_6Au_3Ag_2Cl_{17}$, and by Yamada and Tsuchida[5] as $(NH_4)_3AgAuCl_{17}$.

Crystal structure determination confirms the formula suggested by Wells. Crystals are orthorhombic, $a = 11{\cdot}20$, $b = 20{\cdot}86$, $c = 6{\cdot}11$ Å, space group *Immm*, $D_m = 3{\cdot}18$ g cm^{-3}, $D_c = 3{\cdot}18$ g cm^{-3} for 2 molecules per unit cell. Data were collected photographically, using Cu-K_α radiation, and least-squares refinement of the structure gives a current R index of 0·113. An unusual feature of the structure is that the silver exists not as the ion $AgCl_2^-$ but as the chlorine-bridged planar ion $Ag_2Cl_5^{3-}$ in which the silver atoms have approximately trigonal environment. These ions stack with $AuCl_4^-$ ions to form a double-strand analogue of the chain observed in $Cs_2AuAgCl_6$, as in Figure 2.

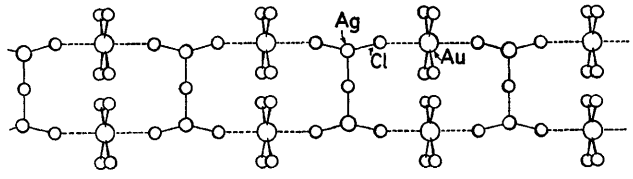

FIGURE 2

The terminal chlorines of the $Ag_2Cl_5^{3-}$ ion again complete an axially elongated octahedron of chlorine atoms about the gold atom, the axial Au–Cl separation being 3·21 Å; the Au–Cl separation within the $AuCl_4^-$ ion is 2·28 Å. The Ag–Cl separations are 2·69 Å to the bridging chlorine and 2·46 Å to the terminal chlorines. The bond angles at the silver between terminal chlorine atoms is 152·5°. A crystallographically distinct $AuCl_4^-$ ion is not obviously involved in an intervalence exchange chain, but lies parallel to and between $Ag_2Cl_5^{3-}$ ions such that bridging chlorines complete a further axially distorted octahedron with respect to this gold atom.

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