

References

- COOPER, J. & MARSH, R. E. (1961). *Acta Cryst.* **14**, 202–203.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
 CUNNINGHAM, G. & OEY, T. S. (1955). *J. Amer. Chem. Soc.* **77**, 799–801.
 CURL, R. F. JR (1962). *J. Chem. Phys.* **37**, 779–784.
 CURTI, R., RIGANTI, V. & LOCCHI, S. (1960). *Rend. Ist. Lombardo Sci.* **A94**, 363–371.
 GILLESPIE, R. B., SPARKS, R. A. & TRUEBLOOD, K. N. (1959). *Acta Cryst.* **12**, 867–872.
 LEVI, G. R. & SCHERILLO, A. (1930). *Z. Kristallogr.* **76**, 431–452.
 MORIMOTO, N. (1956). *Mineral. J. (Sapporo)*, **2**, 1–3.
 RAGLE, J. L. (1960). *J. Chem. Phys.* **32**, 403–405.
 RUBEN, H. W., TEMPLETON, D. H., ROSENSTEIN, R. D. & OLOVSSON, I. (1961). *J. Amer. Chem. Soc.* **83**, 820–824.
 SANTORO, A. & MIGHELL, A. D. (1970). *Acta Cryst.* **A26**, 124–127.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 TARIMCI, Ç. & SCHEMPP, E. (1975). To be published.
 TAZZOLI, V., RIGANTI, V., GIUSEPPETTI, G. & CODA, A. (1975). *Acta Cryst.* **B31**, 1032–1037.

Acta Cryst. (1975). **B31**, 2149

Ammonium Tristetrahydroaurate(III) μ -Chloro-bisdichloroargentate(I)

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Abstract. $(\text{NH}_4)_6(\text{AuCl}_4)_3\text{Ag}_2\text{Cl}_5$, orthorhombic, *Immm*, $a=20.86$ (4), $b=11.20$ (2), $c=6.61$ (3) Å, $Z=2$, $D_m=3.18$ g cm⁻³. Two of the three AuCl_4^- ions stack alternately with the chlorine bridged Ag_2Cl_3^- ion to form a double-stranded analogue of the chain structure previously reported for $\text{Cs}_2(\text{AuCl}_4)(\text{AgCl}_2)$.

Introduction. Deep-red crystals were prepared as described by Pollard (1920). Intensities were measured visually from Weissenberg photographs taken with Cu $K\alpha$ radiation for the layers $hk0$ – $hk5$ and $h0l$ – $h5l$, and were corrected for absorption. A set of 677 unique data were obtained, of which 52 were subsequently abandoned as being affected by extinction or as too weak to be reliable. Systematic absences were: hkl , when $h+k+l \neq 2n$. Of the possible space groups the centrosymmetric *Immm* was assumed, and no feature of the structure analysis disagreed with this choice. The structure was solved by Patterson and heavy-atom techniques, and refined by block-diagonal least-squares

calculations to an R of 0.11 (for 625 data).* Atom coordinates and temperature factors are listed in Table 1, and interatomic distances and angles shown in Fig. 2.

Discussion. Although from its manner of preparation and from its dark colour $(\text{NH}_4)_6\text{Au}_3\text{Ag}_2\text{Cl}_{17}$ has long been supposed to be analogous to $\text{Cs}_2(\text{AuCl}_4)(\text{AgCl}_2)$ (Elliott & Pauling, 1938), with a similar chain of alternate AuCl_4^- and AgCl_2^- ions which would permit intervalence exchange (Hush, 1967), the differing stoichiometry has made the detail of the structure far from obvious. The observed structure is shown in Fig. 1, with particular features amplified in Fig. 2. The main difference lies in the fact that it contains not the AgCl_2^- ion but the chlorine bridged ion Ag_2Cl_3^- . These planar

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31000 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atom coordinates and temperature factors*

Anisotropic temperature factors are dimensionless, isotropic factors are in Å²

	<i>x</i>	<i>y</i>	<i>z</i>	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{150}
Au(1)	0	0	0	0.036 (5)	0.13 (2)	1.2 (1)			
Au(2)	0.3384 (1)	0	0	0.032 (3)	0.06 (1)	0.43 (5)			
Ag	0.3713 (3)	$\frac{1}{2}$	0	0.18 (1)	0.07 (3)	3.0 (2)			
Cl(1)	0	0.2036 (14)	0	0.16 (3)	0.11 (9)	0.8 (3)			
Cl(2)	0.1098 (8)	0	0	0.08 (3)	0.29 (11)	2.4 (6)			
Cl(3)	0.3433 (4)	0.2869 (10)	0	0.05 (2)	0.32 (7)	0.6 (2)	–0.01 (1)		
Cl(4)	0.2613 (6)	0	0.236 (2)	0.11 (2)	0.45 (9)	1.4 (3)		0.2 (1)	
Cl(5)	0.4135 (6)	0	0.248 (2)	0.11 (2)	0.34 (8)	1.7 (4)		–0.06 (9)	
Cl(6)	$\frac{1}{2}$	$\frac{1}{2}$	0	0.09 (4)	0.12 (15)	3.8 (11)			
N(1)	0.183 (3)	0.268 (6)	0						3.3 (1.1)
N(2)	$\frac{1}{2}$	0.209 (6)	0						1.4 (9)

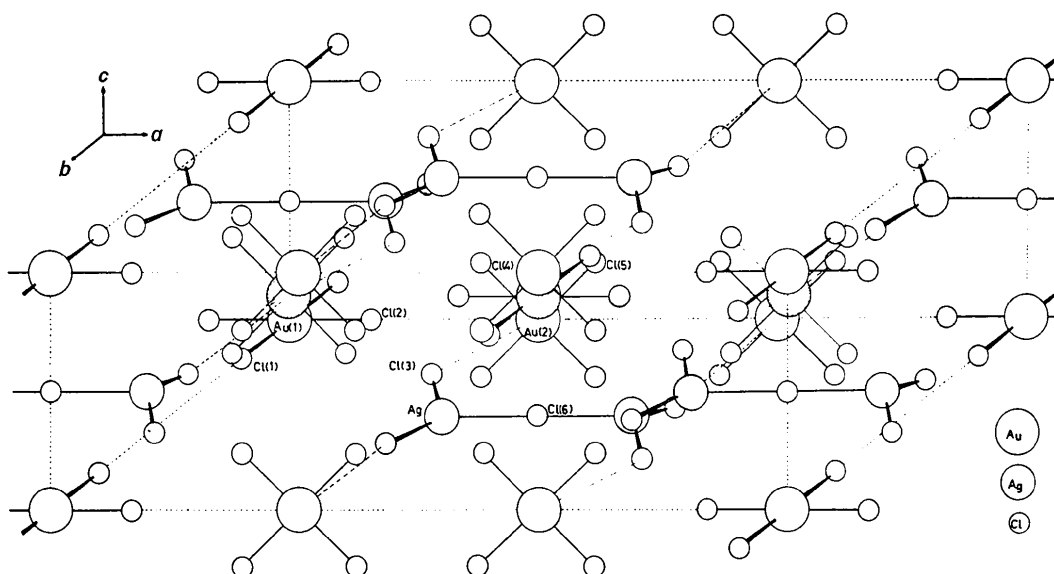


Fig. 1. The unit cell. Ammonium ions are omitted, for clarity.

ions stack with AuCl_4^- ions [as shown in Fig. 2(a)] to form a double-stranded analogue, parallel to **b**, of the chains which exist in $\text{Cs}_2(\text{AuCl}_4)(\text{AgCl}_2)$. The $\text{Au} \cdots \text{Cl}$ approach within the chain (3.21 Å) is similar to that observed in $\text{Cs}_2(\text{AuCl}_4)(\text{AgCl}_2)$, and it may be

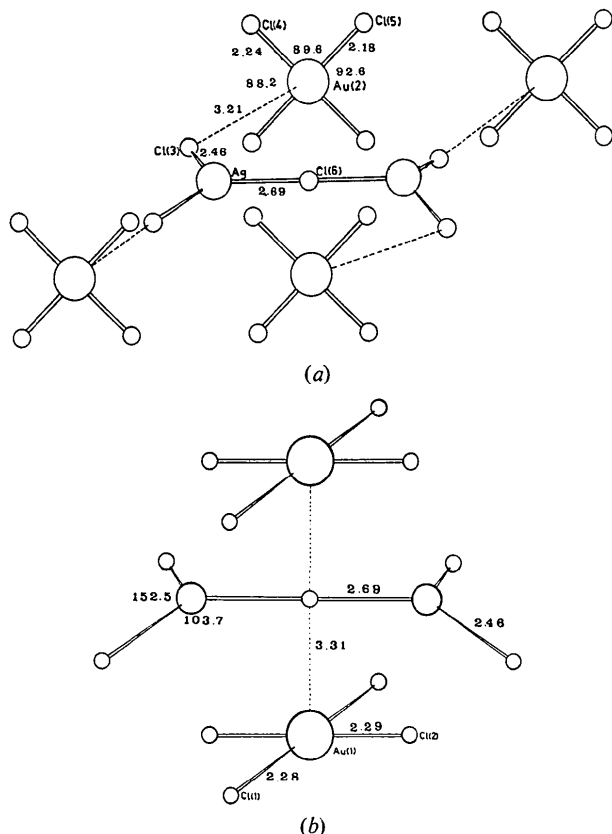


Fig. 2. Details of Fig. 1. (a) The chains parallel to **b**. (b) The chains parallel to **c**.

supposed that similar exchange processes cause the dark colour. It is of interest that crystals of the present compound are not completely opaque and are deep red rather than black, in contrast with the other, and it is possible that this is a consequence of less effective exchange deriving from the non-linearity of the chain, following from the pseudo-trigonal coordination of the silver atom.

Only two of three AuCl_4^- ions are so involved. The remaining AuCl_4^- [centred on Au(1)] is stacked parallel to and interleaving with the Ag_2Cl_3^- ions [Fig. 2(b)], forming chains of a different type parallel to **c**. The gold atoms thus attain octahedral coordination, and the silver atoms slightly distorted trigonal bipyramidal. These axial contacts are only 0.1 Å longer than those in the chain along **b**, but exchange processes are not normally associated with such a geometry. It is notable that the equatorial bonds in this AuCl_4^- are significantly longer than in the other.

Within the Ag_2Cl_3^- ion the terminal Ag-Cl bonds (2.46 Å) are much shorter than the bond to the bridging atom (2.69 Å), whereas the bond angle at silver between terminal chlorines is 152.5°, as opposed to 103.7° between terminal and axial chlorine. This distortion from trigonal geometry, and the absence of any previous report of the existence of Ag_2Cl_3^- , suggest that a description such as 'chlorine bridged AgCl_2^- ions' may be appropriate.

The nitrogen atoms make contacts with neighbour chlorine atoms ranging from 3.26 Å upwards. Some weak hydrogen bonding could be involved.

References

- ELLIOTT, N. & PAULING, L. (1938). *J. Amer. Chem. Soc.* **60**, 1846-1851.
 HUSH, N. S. (1967). *Progr. Inorg. Chem.* **8**, 391-444.
 POLLARD, W. B. (1920). *J. Chem. Soc.* **117**, 99-103.