References


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

BY JOHN C. BOWLES AND DAVID HALL

Chemistry Department, University of Auckland, New Zealand

(Received 9 December 1974; accepted 17 March 1975)

Abstract. (NH₄)₆(AuCl₄)₃Ag₂Cl₅, 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 AuCl₄⁻ ions stack alternately with the chlorine bridged Ag₂Cl₅⁻ ion to form a double-stranded analogue of the chain structure previously reported for Cs₂(AuCl₄)(AgCl₂).

Introduction. Deep-red crystals were prepared as described by Pollard (1920). Intensities were measured visually from Weissenberg photographs taken with Cu Kα radiation for the layers hkl, when h+k+l≠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 co-ordinates 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 (NH₄)₆Au₃Ag₂Cl₁₇ has long been supposed to be analogous to Cs₂(AuCl₄)(AgCl₂) (Elliott & Pauling, 1938), with a similar chain of alternate AuCl₄⁻ and AgCl₂⁻ ions which would permit inter-valence 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 AgCl₂⁻ ion but the chlorine bridged ion Ag₂Cl₅⁻. 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

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B₁₁</th>
<th>B₂₂</th>
<th>B₃₃</th>
<th>B₁₂</th>
<th>B₁₃</th>
<th>B₂₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.036 (5)</td>
<td>0.13 (2)</td>
<td>1.2 (1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au(2)</td>
<td>0.3384 (1)</td>
<td>0</td>
<td>0</td>
<td>0.032 (3)</td>
<td>0.06 (1)</td>
<td>0.43 (5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>0.3713 (3)</td>
<td>½</td>
<td>0</td>
<td>0.08 (1)</td>
<td>0.07 (3)</td>
<td>3.0 (2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl(1)</td>
<td>0</td>
<td>0.2036 (14)</td>
<td>0</td>
<td>0.08 (3)</td>
<td>0.29 (11)</td>
<td>2.4 (6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl(2)</td>
<td>0.1098 (8)</td>
<td>0</td>
<td>0</td>
<td>0.05 (2)</td>
<td>0.32 (7)</td>
<td>0.6 (2)</td>
<td>-0.01 (1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl(3)</td>
<td>0.3433 (4)</td>
<td>0.2869 (10)</td>
<td>0</td>
<td>0.11 (2)</td>
<td>0.45 (9)</td>
<td>1.1 (3)</td>
<td>0.2 (1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl(4)</td>
<td>0.2613 (6)</td>
<td>0</td>
<td>0.236 (2)</td>
<td>0.11 (2)</td>
<td>0.248 (2)</td>
<td>0.11 (2)</td>
<td>0.34 (8)</td>
<td>1.7 (4)</td>
<td>0.2 (1)</td>
</tr>
<tr>
<td>Cl(5)</td>
<td>0.4135 (6)</td>
<td>0</td>
<td>0.248 (2)</td>
<td>0.11 (2)</td>
<td>0.248 (2)</td>
<td>0.11 (2)</td>
<td>0.34 (8)</td>
<td>1.7 (4)</td>
<td>0.2 (1)</td>
</tr>
<tr>
<td>Cl(6)</td>
<td>0.7778 (9)</td>
<td>0</td>
<td>0.268 (6)</td>
<td>0</td>
<td>0.09 (4)</td>
<td>0.12 (15)</td>
<td>3.8 (11)</td>
<td>3.3 (1-1)</td>
<td>1.4 (9)</td>
</tr>
<tr>
<td>N(1)</td>
<td>0.183 (3)</td>
<td>0.268 (6)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>N(2)</td>
<td>0.3384 (1)</td>
<td>0.209 (6)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

A C 31B – 11*
ions stack with $\text{AuCl}_4^-$ 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 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 $\text{AuCl}_4^-$ ions are so involved. The remaining $\text{AuCl}_4^-$ [centred on Au(1)] is stacked parallel to and interleaving with the $\text{Ag}_2\text{Cl}_3^-$ 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 $\text{AuCl}_4^-$ are significantly longer than in the other.

Within the $\text{Ag}_2\text{Cl}_3^-$ 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 $\text{Ag}_2\text{Cl}_3^-$, 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