The Crystal Structure of $[Co(NH_3)_6]_4[Cu_5Cl_{17}]$

By P. MURRAY-RUST, P. DAY,* and C. K. PROUT

(*The Chemical Crystallography and Inorganic Chemistry* Laboratories, South Parks Road, Oxford)

CHLORO- AND BROMO-CUPRATES(I, II) of cobalt and chromium hexammines have been prepared with copper(I) and copper(II) present in various ratios.[1] The pure chromium chlorocuprate(II), $Cr(NH_3)_6$-$CuCl_5$, was shown, by Mori and Watanabe[2], to be cubic, space group $Fd3c$, $a = 22\cdot265$ Å, and to contain discrete, trigonal bipyramidal $CuCl_5^{3-}$ ions. Single-crystal oscillation and rotation photographs of crystals with varying copper(I) content indicate that $Co(NH_3)_6CuCl_5$ is an isotype of this, $a = 21\cdot85 \pm 0\cdot01$ Å, and that the $Co(NH_3)_6CuCl_5$ type phase persists in the mixed compounds until the copper(I): total copper ratio is at least 0·50. Samples with the copper(I): total copper ratio between 0·50 and 0·80 appear to be inhomogeneous and the crystals give diffraction patterns characteristic of disorder in internal structure. From 0·80 to 1·00 copper(I) the crystals are isotypic with the copper(I) phase $[Co(NH_3)_6]_4Cu_5Cl_{17}$. The structure of this phase has been determined.

Crystal Data: $[Co(NH_3)_6]_4Cu_5Cl_{17}$.

$M = 1550\cdot8$. Cubic, $a = 21\cdot80 \pm 0\cdot01$ Å, $D_m = 1\cdot99$, $D_c = 2\cdot00$, $Z = 8$. Space group $Fd3$ (T_h^4, No. 203, origin at 23), Mo-$K\alpha$ radiation, $\mu = 45$ cm.$^{-1}$; single-crystal Hilger and Watts linear diffractometer measurements with balanced filters and scintillation counter.

The structure was determined by Patterson function and Fourier methods and refined by a least-squares full-matrix method with individual isotropic temperature factors. With all atoms except hydrogen the R-factor is now 0·146.

The structure is made up of hexamminecobalt-(III) ions, $Cu_5Cl_{16}^{11-}$ ions, and free chloride ions in the ratio 4 : 1 : 1. The Figure shows one $Cu_5Cl_{16}^{11-}$ ion projected perpendicular to the c-axis. The hexamminecobalt(III) ions, which have normal bond distances, $d(Co–N) = 1·99 \pm 0·01\text{Å}$, and angles, form a rock-salt lattice with the terminal copper atoms $Cu(2)$, $d(Cu–Co) = 5·45\text{Å}$. The point group symmetry of the $Cu_5Cl_{16}^{11-}$ ion is 23, (T), but the copper and bridging chlorine atoms alone are in a regular tetrahedral arrangement $\overline{4}3m(T_d)$ with linear asymmetric chlorine bridges. The terminal copper atoms have a distorted tetrahedral co-ordination sphere with the copper atom only 0·35Å above the plane of the non-bridging chlorine atoms. The free chloride ion is in a large hole in the structure at the 8-fold position $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ etc., and has a high temperature factor.

The structure is very closely related to that of $Cr(NH_3)_6CuCl_5$. The hexamminemetal(III) ions are in the same position and the $Cu(2)$ atoms are only moved by 0·03Å. The bridging chlorine atom corresponds to an "axial" chlorine of the $CuCl_5^{3-}$ bipyramid and is only 0·18Å from this position. The $CuCl_3$ group corresponds to the "equatorial" atoms of the bipyramid and are about 0·6Å distant. The bond lengths in the two ions are also very similar. There are no space-group restrictions on the $Cl(2)$ position and a gradual transition from $Fd3$ to $Fd3c$ is possible.

Light absorption and conductivity of solid chlorocuprates(I, II) have been studied. The maximum light absorption and conductivity were found with equal mole fractions of copper(I) and copper(II).[3] The structural relationship between the copper(I) and copper(II) phases indicates that polymeric units may be expected in the mixed valence compounds. Therefore the observed conductivity and light absorption might result from either "inner sphere" electron transfer within a mixed valence aggregate or an "outer sphere" electron transfer between $CuCl_5^{3-}$ and $Cu_5Cl_{16}^{11-}$ ions. The structures of the mixed valence compounds are under investigation.
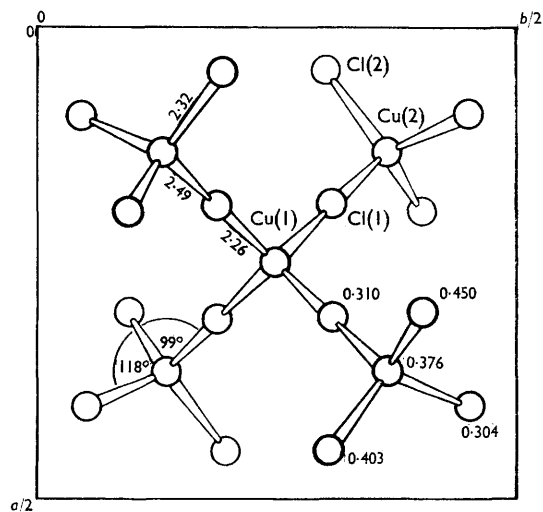

FIGURE. A $Cu_5Cl_{16}^{11-}$ ion projected perpendicular to the c-axis. The average estimated standard deviation in the positional parameters is 0·0004 as a fraction of a unit cell edge, in the interatomic distances is 0·01Å and in the interbond angles is 1·0°. The central copper is at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ from space group requirements.

[1] M. Mori, *Bull. Chem. Soc. Japan*, 1960, **33**, 985; 1961, **34**, 1249.
[2] M. Mori, Y. Saito, and T. Watanabe, *Bull. Chem. Soc. Japan*, 1961, **34**, 295.
[3] D. Culpin, P. Day, P. R. Edwards, and R. J. P. Williams, *Chem. Comm.*, 1965, 450.