The Crystal Structure of $[Cr(NH_3)_6]\,[CuCl_5]$*

By Masayasu MORI, Yoshihiko SAITO** and Tokunosuké WATANABE

(Received December 9, 1960)

Unstable halogen complexes of heavy metals sometimes exist in more than two forms having considerably different chemical constitutions and structures. Thus bromothallates(III) are found with compositions, $KTlBr_4 \cdot 2H_2O$, $Rb \cdot TlBr_4 \cdot H_2O$ and $CsTlBr_4$. These complexes have the octahedral, pyramidal and square configurations[1]. The interatomic distances Tl-Br in these complexes are considerably different from that found in a more stable complex, $[Co(NH_3)_6]\,[TlBr_6]$[2].

Such variety in ionic species is also found in the case of chlorocuprates, but the information seems much less satisfactory. A pentachlorocuprate(II) of hexamminechromium(III), $[Cr(NH_3)_6]\,[CuCl_5]$ has recently been prepared[3]. It occurred to the present authors that the crystal analysis of this compound would give a useful guide to the structural chemistry of chlorocuprates(II).

Weissenberg photographs for the equatorial, the first and fourth layer lines, and oscillation photographs were prepared using Cu$K\alpha$ (λ= 1.5418 Å) radiation. From these data, it was concluded that the crystals belong to the cubic system, and the systematic reflections were characteristic only for O_h^8-Fd3c. The exact reflection angles of several (*hk*0) reflections for Cu$K\alpha_1$ radiation (λ=1.5405 Å) were determined by means of a GM counter X-ray defractometer which was calibrated with a standard microcrystalline plate of metallic silicon (a=5.4301 Å). From these values the unit cube edge was determined to be a=22.265 ±0.01 Å. There are 32 formula units in each unit cell, the calculated density being 1.901 g. cm^{-3}, in good agreement with the observed value, 1.892 g. cm^{-3}. The relative intensities of reflections were visually estimated with a calibrated standard, and the Lorentz and polarization corrections were made using Cochran's chart[4].

There are 32 Cu, 32 Cr, 160 Cl and 192 N atoms in the unit cell. The observed intensities were best accounted for when these atoms are placed in the following equivalent positions:

32 Cu: (b) 1/4, 1/4, 1/4, etc.,
32 Cr: (c) 0, 0, 0, etc.,
64 Cl: (e) u, u, u, (u=0.190), etc.,
96 Cl: (g) 1/4, v, $-v$, (v=0.075), etc.,
192 N: (h) x, y, z, (x=0.070, y=0.050, z=−0.030), etc.

The parameters were obtained by the trial and error method, by comparing the calculated and observed structure factors, F_c and F_o at the each stage. At the final stage, corrections were made for extinction and the anomalous dispersion of copper and chromium atoms. The atomic coordinates given above, combined with the overall temperature factor, B=2.5, gave for the equatorial (*hk*0) Weissenberg data a reliability factor, R=0.136. The intensities of the unobserved reflections were taken equal to zero in this comparison. For 333 (*hkl*) reflections up to l=8 the R value was 0.190 (in this case the unobserved reflections were excluded).

According to the above atomic coordinates, the crystal is composed of octahedral complex ion, $[Cr(NH_3)_6]^{3+}$ and trigonal bipyramidal complex ion, $[CuCl_5]^{3-}$ arranged the sodium chloride type. Because of the symmetry requirement, however, the unit cube edges are twice as much of a simple sodium chloride

* Presented at the Symposium on Coordination Chemistry, Sendai, September 1960.

** Present Address: Institute for Solid State Physics, the University of Tokyo, Shinryudo-cho, Azabu, Minato-ku, Tokyo.

1) T. Watanabe, Y. Saito, R. Shiono and M. Atoji, *Structure Repts.* **11**, 393 (1947—8).

2) T. Watanabe, M. Atoji and C. Okazaki, *Acta Cryst*, 3, 405 (1950).

3) M. Mori, This Bulletin, 33, 985 (1960).

4) J. Cochran, *J. Sci. Instr.*, 25, 253 (1948).

arrangement. The threefold axis of the $[CuCl_5]^{3-}$ ion lies on the body diagonal of the cube cell, in accordance with the point symmetry of the Cu position, D_3–32. This structure of the $[CuCl_5]^{3-}$ ion is quite a new one, most chlorocomplexes of copper(II) being distorted octahedra. The only exception is the structure of $[CuCl_4]^{2-}$ ion in Cs_2CuCl_4 or its bromine analogue, in which case $[CuCl_4]^{2-}$ ion can be taken to be a flattened tetrahedron or a twisted square[5,6].

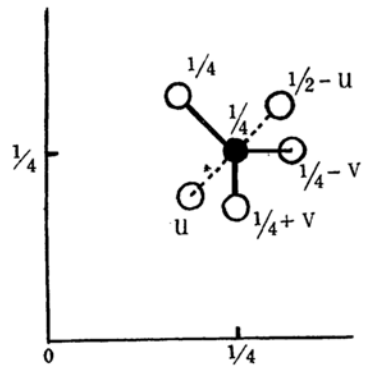

Fig. 1. The structure of $[CuCl_5]^{3-}$ with Cu at 1/4, 1/4, 1/4 (the figure refers to the z coordinate).

The important characteristic of the trigonal bipyramidal structure of $[CuCl_5]^{3-}$ found in the present research is that the distance between the copper atom and the two chlorine atoms on the threefold axis (2.32 Å) is of the same order of magnitude as the distance between the copper atom and the three chlorine atoms at the corner of the triangle (2.35 Å) (Fig. 1). This is in a clear contrast to much greater distances (2.8~3.0 Å) between copper and chlorine atoms on the fourfold or nearly four fold axis found in many distorted octahedral chlorocomplexes.

The authors wish to express their sincere thanks to Dr. Yozo Chatani of Osaka University for the cooperation in preparing Weissenberg photographs.

Institute of Polytechnics
Osaka City University
Kita-ku, Osaka
(M. M.)

Faculty of Science, Osaka University
Kita-ku, Osaka
(T. W.)

5) L. Helmholz and R. F. Kruh, *J. Am. Chem. Soc.*, **74**, 1176 (1952).
6) B. Morosin and E. C. Lingafelter, *Acta Cryst.*, **13**, 80 (1960).