An Example of a New Type of Five-co-ordinate Transition Metal Complex: $[\mathrm{Cr(NH_3)_6}][\mathrm{CuBr_3Cl_2}]$

By KENNETH N. RAYMOND
(*Chemistry Department, University of California, Berkeley, California* 94720)

Summary The first five-co-ordinate mixed-halide metal complex has been prepared and characterised.

ALTHOUGH a great many five-co-ordinate metal complexes have been prepared and characterized,[1,2] few of these are formed entirely from simple, monodentate ligands such as halide ions. Both the hexamminecobalt(III)[3] and hexamminechromium(III)[4] salts of the $[\mathrm{CuCl_5}]^{3-}$ ion are known, and a preliminary *X*-ray diffraction analysis[5] of the chromium salt has been followed by a detailed structure analysis.[6] The corresponding bromide salt, $[\mathrm{Cr(NH_3)_6}][\mathrm{CuBr_5}]$, has also been reported[4] and pentahalide complexes of other metal ions are known, such as $[\mathrm{MnCl_5}]^{2-}$[7], $[\mathrm{SnCl_5}]^{-}$[8], $[\mathrm{InCl_5}]^{2-}$[9] and $[\mathrm{CdCl_5}]^{3-}$[7]. I report the preparation of a mixed halide complex of this type, $[\mathrm{Cr(NH_3)_6}][\mathrm{CuBr_3Cl_2}]$.

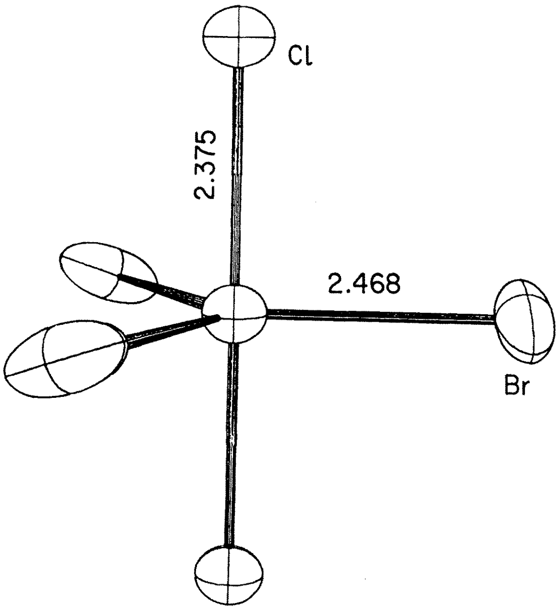

FIGURE. *A perspective drawing of the* $[\mathrm{CuBr_3Cl_2}]^{3-}$ *anion. The ellipsoids represent* 50% *probability contours of thermal motion.*

Red, octahedral, crystals of this compound (analysis correct) suitable for diffraction studies were obtained from aqueous solutions of HBr and HCl containing $[\mathrm{Cr(NH_3)_6}]\mathrm{Br_3}$[10] and $\mathrm{CuSO_4}$. Over-exposed Weissenberg and precession photographs indicated the space-group *Fd*3*c*, isomorphous with the yellow pentachlorocuprate(II) salt: single cell constant 22·644(7) Å† (22°), by least-squares refinement of the setting angles of 20 reflections, carefully centred on a GE XRD-5 diffractometer: $Z = 32$, D_m 2·45, D_c 2·42 g.cm.$^{-3}$.

A complete structure analysis[11] shows that the salt is isostructural with $[\mathrm{Cr(NH_3)_6}][\mathrm{CuCl_5}]$. The chlorine atoms of the $[\mathrm{CuBr_3Cl_2}]^{3-}$ anion occupy the axial positions. The crystallographic point symmetry is 32 (D_3); the $[\mathrm{CuBr_3Cl_2}]^{3-}$ anion is therefore a perfect trigonal bipyramid. Refinement of the atom occupation factors showed no significant change from the theoretical values as determined from the rank of each of the equipoints.‡ The thermal motion observed for this compound is very similar to that of the $[\mathrm{CuCl_5}]^{3-}$ salt. The outstanding feature is the large vibrational or librational motion around the three-fold axis of the $[\mathrm{CuBr_3Cl_2}]^{3-}$ anion (Figure). The $[\mathrm{Cr(NH_3)_6}]^{3+}$ cation has crystallographic $\bar{3}$ (S_6) point symmetry with the same geometry observed in the $[\mathrm{CuCl_5}]^{3-}$ salt, as expected.

The $[\mathrm{CuCl_5}]^{3-}$ ion provided the first unequivocal example of a trigonal-bipyramidal complex with axial bond lengths shorter than the equatorial bond lengths. The bond lengths are 2·2964(12) and 2·3912(13) Å for axial and equatorial, respectively.[6] For most trigonal-bipyramidal complexes, ligand–ligand repulsion acts to make the axial bond length very slightly longer. The shortening of the

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† The numbers enclosed in parentheses give the standard deviation in the least significant digits.

‡ This refinement is effectively the same as allowing the number of electrons to vary for the atoms assigned as chlorine and bromine. No change proves that there is no disorder between the bromine and chlorine atoms.

axial bond lengths observed in the $[CuCl_5]^{3-}$ ion has been attributed to a balance between the opposing forces of ligand–ligand repulsion and stereochemical activity of the metal *d*-electrons.

Since the replacement of chlorine by bromine increases ligand–ligand repulsion, the $[CuBr_3Cl_2]^{3-}$ ion should exhibit an axial bond length significantly greater than that observed for the $[CuCl_5]^{3-}$ ion. The observed values are: Cu–Cl 2·375(2) and Cu–Br 2·468(2) Å. The increase in the axial Cu–Cl bond length of 0·079 Å relative to that in $[CuCl_5]^{3-}$ is as expected and is clearly significant.

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