A Five-co-ordinate Copper Dimer: the Structure and Magnetic Properties of the Di-μ-chlorobis[trichlorocuprate(II)] Anion, $[Cu_2Cl_8]^{4-}$

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Summary The $[Cu_2Cl_8]^{4-}$ ion, consisting of two distorted trigonal bipyramids linked by two chlorine bridges, has been shown to occur in $Co(en)_3CuCl_5(H_2O)$, and the magnetic properties of the dimer are found to be consistent with exchange coupled copper ions.

A COMPLEX of formulation $Co(en)_3CuCl_5(H_2O)$(en = ethylenediamine, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$) has been known for more than seventy years,[1] but it is not possible to interpret its near i.r. spectrum[2] on the basis of either trigonal-bipyramidal geometry, as found[3] in $[Cr(NH_3)_6][CuCl_5]$, or of six-co-ordinate geometry[4] at the copper. Because of this apparent inconsistency between the spectral data and either of the suggested structures, we have determined the structure of this compound by means of single crystal *X*-ray diffraction.

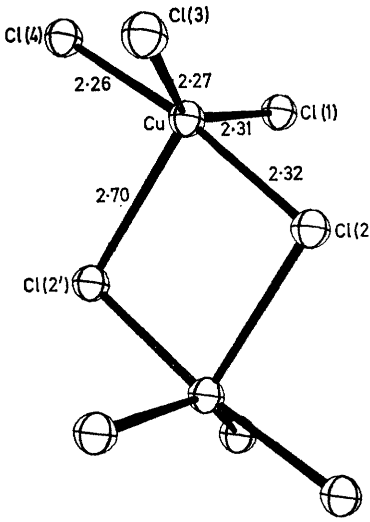

FIGURE. *View of the* $[Cu_2Cl_8]^{4-}$ *ion. Estimated standard deviations on* Cu–Cl *bond lengths are* 0·01Å. *Bond angles are*: Cu–Cl(2)–Cu′ = 95·2(3)°, Cl(2)–Cu–Cl(2′) = 84·8(3)°, Cl(1)–Cu–Cl(3) = 145·3(2)°, Cl(2)–Cu–Cl(4) = 172·6(2)°, Cl(2′)–Cu–Cl(3) = 118·3(2)°, Cl(2)–Cu–Cl(3) = 92·0(2)°. *The angle between the plane* Cu, Cl(3), Cl(1) *and the plane* Cu, Cl(2), Cl(2′) *is* 89·0(2)°.

The material crystallizes in the unique space group *Pbca* (D_{2h}^{15}) of the orthorhombic system, with eight formula units in a cell of dimensions a = 13·560(9), b = 14·569(9), c = 17·885(12) Å; hence, no crystallographic symmetry need be imposed on the molecule. 2078 independent reflections were measured on an automatic diffractometer using Mo-K_α radiation and a niobium filter. At the present stage of refinement, the R factor (on F) is 0·067.

The anion consists of dimeric $[Cu_2Cl_8]^{4-}$ ions and there is one unco-ordinated chloride ion *per* copper in the cell. The geometry of the dimer is shown in the Figure; it is best described as two distorted trigonal bipyramids bridged by one axial and one equatorial chlorine atom. There is a centre of symmetry in the dimer, which causes the Cu–Cl(2)–Cu′–Cl(2′) moiety to be planar, but there is no direct copper–copper bond, since the Cu–Cu distance is 3·714(8) Å. The Cl(2)–Cl(2′) separation is 3·40(1) Å, which is approximately 0·2 Å smaller than twice the sum of the van der Waals' radius of chlorine.[5] The geometry of the ion is considerably different from that found[6] for nickel in $[Ni_2Cl_8]^{4-}$. These structural data explain why the electronic spectrum is unlike that of other known chlorocuprates.[4]

In view of the novel structure of this dimeric anion, it was important to study the magnetic properties of the compound in order to assess the degree of the copper–copper interaction. The magnetic susceptibility of a powdered sample was determined over the range 77—300°K using a Faraday balance.[7] The susceptibility data follow the Curie–Weiss law over the entire temperature range, yielding a Curie constant C of 0·442 e.m.u. deg mol^{-1}; the extrapolated value of the temperature at which χ^{-1} equals zero is +1°K. The magnetic moment calculated from these data is 1·88 B.M. per copper atom, in agreement with the moment of 1·85 B.M. found[4] for the $[CuCl_5]^{3-}$ ion in $[Co(NH_3)_6]$-**$[CuCl_5]$**.

The e.s.r. spectrum obtained at 77°K from a powdered sample in a carefully selected quartz tube, however, shows evidence of spin–spin coupling. There is a broad line at 1500 G (9·185 GHz) arising from the $\Delta M_s = \pm 2$ transition, characteristic of magnetically coupled copper ions.[8] In the $g = 2$ region of the spectrum, there is a broad line centred at 3055G with a distinct band at 2870G and a shoulder at 3200G. The presence of the low-field absorption leads us to assign the latter two bands to the low and high field parallel $\Delta M_s = \pm 1$ transitions of the triplet state, rather than to assign the three lines as the components of an anisotropic g-tensor with $g_1 = 2{\cdot}29$, $g_2 = 2{\cdot}15$, and $g_3 = 2{\cdot}05$. This assignment leads to $g_{\parallel}$ of 2·16 with the zero field splitting parameter, D, approximately equal to 0·02 cm^{-1}. The splitting of the perpendicular band at 3055 was not resolved. Unfortunately, the experimental data do not permit an accurate assessment of the magnitude of the spin–spin coupling interaction but a range of values may be approximated. Using the point-charge model and the experimental internuclear separation, the dipolar contribution to D is estimated to be 0·06 cm^{-1}. Since $D_{\text{exptl}} = D_{\text{dipolar}} + D_{\text{exchange}}$, it follows that $|D_{\text{exchange}}| = 0{\cdot}04$ or 0·08 cm^{-1}. With this range for D_{exchange}, the Bleaney–Bowers[9] relationship gives $|2J| = 5$ or 10 cm^{-1}. Investigation of the magnetic properties at 4·2°K should yield the sign of J and a closer approximation of its magnitude.

We gratefully acknowledge the financial support of the Materials Research Center of the University of North Carolina under contract with the Advanced Research Projects Agency, and of the National Science Foundation.

(*Received, April 20th,* 1970; *Com.* 550.)

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