Molecular Structure of the Ground State Triplet $Cu_2Cl_6^{2-}$ Dimer in $(Ph_4As)CuCl_3$

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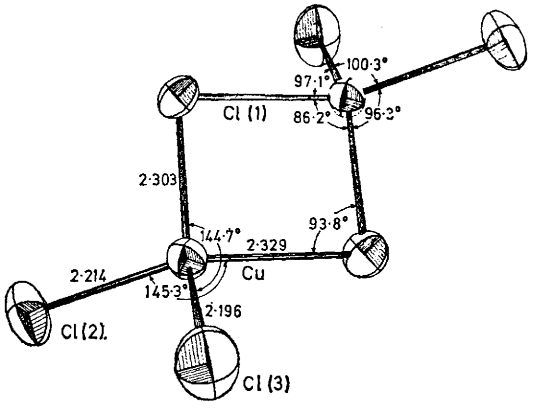
Summary The existence of a symmetrically bridged, ferromagnetically coupled $Cu_2Cl_6^{2-}$ dimer in $(Ph_4As)CuCl_3$, with bridging Cu–Cl–Cu angles of 93·6°, *ca.* 2° smaller than for antiferromagnetically coupled dimers, has been confirmed by an *X*-ray crystal structure determination.

A RECENT magnetic susceptibility study of $(Ph_4As)CuCl_3$ indicated the existence of magnetically isolated $Cu_2Cl_6^{2-}$ dimers with triplet ground states.[1] This behaviour is in contrast to that of $KCuCl_3$, in which the dimers appear to be antiferromagnetically coupled with negligible interdimer interactions,[2] of $Me_2NH_2CuCl_3$, where the singlet and triplet states of the dimer are nearly degenerate and interdimer interactions play a dominant role in the determination of the magnetic properties,[3] and of $LiCuCl{\cdot}2H_2O$, which exhibits three-dimensional antiferromagnetic ordering.[4] The structure of $(Ph_4As)CuCl_3$ was thus undertaken to determine the geometry of the dimeric unit and its crystallographic environment.

The garnet-red monoclinic crystals belong to the space group $P2_1/a$ with $a = 13{\cdot}60(1)$, $b = 19{\cdot}62(2)$, $c = 9{\cdot}32(1)$Å, and $\beta = 111{\cdot}54(2)°$, and the unit cell contains four formula units. Intensity data were collected from a small ($r = 0{\cdot}14$ mm) spherical crystal on an automated G.E. diffractometer equipped with a G.E. SCO, using a θ—2θ scan at an 8° take-off angle. A total of 3245 reflections were obtained out to $2\theta = 45°$ with Mo-K_α radiation. The structure was solved from examination of the Patterson function and subsequent Fourier analyses. Anisotropic refinement of all non-hydrogen atoms proceeded to an R value (based on F) of 0·054 for all reflections with intensity greater than 2σ.

The structure consists of discrete $Cu_2Cl_6^{2-}$ units ionically bound to the tetraphenylarsonium ions. The centrosymmetric anion is illustrated in the Figure. The four-coordinate copper ions have a geometry intermediate between tetrahedral and planar with *trans* Cl–Cu–Cl angles of 145°. The closest interdimer contacts are Cl–Cl contacts of 6·76Å. The geometry of the tetraphenylarsonium ion is normal, with As–C 1·91 Å and C–C 1·41 Å.



FIGURE

Geometry of the $Cu_2Cl_6^{2-}$ ion in $(Ph_4As)CuCl_3$.

TABLE

Compound	Cu–Cl Distance, bridging	Cu–Cl–Cu Angle	*trans*-Cl–Cu–Cl Angle, ave.	Cu–Cl Distances	$2J/k$[a]	Other interactions
$LiCuCl_3 \cdot 2H_2O$[b]	2·30Å	95·1°	180°	2·92Å	<0 K	Cu–OH_2, 2·60Å 2Cl ··· H-O, <3·2Å 2Cl ··· Li, <2·5Å
$KCuCl_3$[c]	2·31	95·9	174·5[d]	2·94, 3·11	−55	6 Cl ··· K, <3·3Å
$Me_2NH_2CuCl_3$[e]	2·32	95·6	166	2·73	*ca.* −5	1 Cl ··· N-H, 3·23 Å
$Ph_4AsCuCl_3$	2·32	93·6	145		+33	8 Cl ··· C, <3·6 Å

[a] A positive value of $2J$ corresponds to a triplet ground state. [b] Ref. 5 and 9. [c] Ref. 10. [d] The distortion in this species is towards square-pyramidal, rather than tetrahedral. [e] Ref. 11.

The bridging geometries, environments, and singlet triplet energy separations of the known $Cu_2Cl_6^{2-}$ dimers are summarized in the Table. The values of the singlet–triplet energy separation, $2J$, reported for $KCuCl_3$, $Me_2NH_2CuCl_3$, and $(Ph_4As)CuCl_3$ were obtained from magnetic susceptibility studies.[1–3] The value of $2J$ for $LiCuCl_3 \cdot 2H_2O$ has not been determined, but a combination of neutron diffraction[5] and n.m.r. studies[6] show the intra-dimer coupling must be antiferromagnetic. Two factors are immediately apparent. First, the dimers in $(Ph_4As)CuCl_3$ are well isolated from each other, precluding any magnetic coupling between the dimers and substantiates the interpretation of the magnetic properties in terms of isolated dimer units. Second, the bridging Cu–Cl–Cu angle is 2° smaller in the tetraphenylarsonium salt than the other salts. This is in accord with the expectation of superexchange arguments about the sign of the exchange coupling.[7] The correlation between the bridging angle and $2J$ is not very regular, but this is not surprising since each type of dimer is in a unique environment. Nevertheless, it seems safe to assume the crossover point between ferro- and anti-ferro-magnetic coupling lies somewhere between a 94° and a 95° angle. A similar and apparently more regular trend has been observed in hydroxy-bridged copper complexes.[8]

The Table shows that the distortion of the dimer from planarity increases as the extent of interaction with the environment decreases. This distortion is responsible for the change in the bridging bond-angle. As the geometry becomes more tetrahedral, the *cis* Cl–Cu–Cl angles increase and thus force the bridging angle to become smaller. Since all interactions will remove charge from the chlorines and allow the dimer to become more planar, and interactions in this salt are minimal, the bridging angle of 93·6° reported here should be the smallest obtainable. Thus, it is likely that the span of angles given in the Table represents the maximum range to be observed for this type of dimer.

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[1] C. Chow, R. Caputo, R. D. Willett, and B. C. Gerstein, *J. Chem. Phys.*, in the press.
[2] G. J. Maass, B. C. Gerstein, and R. D. Willett, *J. Chem. Phys.*, 1967, **46**, 401.
[3] B. C. Gerstein, F. D. Gehring, and R. D. Willett, *J. Appl. Phys.*, 1972, **43**, 1932.
[4] P. H. Vossos, L. D. Jennings, and R. E. Rundle, *J. Chem. Phys.*, 1960, **32**, 1590.
[5] S. C. Abrahams and H. J. Williams, *J. Chem. Phys.*, 1963, **39**, 2923.
[6] R. D. Spence and C. R. K. Murty, *Physica*, 1961, **27**, 850.
[7] See, for example, A. P. Ginsberg, *Inorg. Chim. Acta Rev.*, 1971, **5**, 45.
[8] D. L. Lewis, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 1972, **11**, 2216.
[9] P. H. Vossos, D. R. Fitzwater, and R. E. Rundle, *J. Chem. Phys.*, 1963, **38**, 2429.
[10] R. D. Willett, C. Dwiggens, jun., R. F. Kruh, and R. E. Rundle, *J. Chem. Phys.*, 1963, **38**, 2429.
[11] R. D. Willett, *J. Chem. Phys.*, 1966, **44**, 39.