Crystal Structure of a Binuclear Five-co-ordinate Copper(II) Complex with Tetra-amine Macrocyclic Ligands and Single Chloride Bridge

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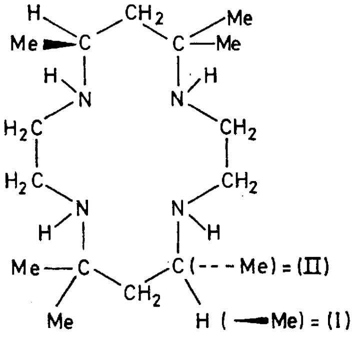
Summary Hydrogen bonding between tet b and perchlorate ions stabilizes $[Cu(tet\ b)]_2Cl^{3+}$ which contains trigonal bipyramidal co-ordinate Cu^{2+} with an almost linear Cu–Cl–Cu bridge and with the tet b ligand in its most stable, folded form.

Copper(II) salts react with tet b [(±)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane] (I) in basic solution to form a blue complex which readily converts to a more stable red complex. The blue-to-red conversion can be prevented by quenching the basic solution with acid a few seconds after mixing the reactants. The resulting copper-tet b(blue) complex is thermodynamically and kinetically stable in regard to acid decomposition and its rate of conversion into the red complex is negligible in acid. In the presence of chloride and perchlorate ions a binuclear, five-co-ordinate compound of the blue tet b complex, $[Cu(tet\ b)]_2Cl(ClO_4)_3$, has been isolated and the crystal structure of this compound has been determined.

The compound crystallizes in the monoclinic space group $C2/c$ with the cell dimensions $a = 28{\cdot}03 \pm 0{\cdot}08$, $b = 9{\cdot}334 \pm 0{\cdot}009$, $c = 20{\cdot}96 \pm 0{\cdot}05$ Å, $\beta = 116{\cdot}9 \pm 0{\cdot}1°$ determined from calibrated precession measurements. An observed density of $1{\cdot}41\ g\ cm^{-3}$ indicates the presence of four formula units per unit cell ($D_c = 1{\cdot}40\ g\ cm^{-3}$). A set of intensity data was collected using a diffractometer of Weissenberg geometry with filtered Cu-K_α radiation. Following Lorentz-polarization and absorption corrections, a set of 1039 reflections with $I > 3\sigma(I)$ was obtained. The structure was solved using Patterson and Fourier methods and refined by full-matrix least-squares techniques (Cu, Cl, anisotropic; C, N, O, isotropic) to a current R of 0·115.

The co-ordination about copper as shown in the Figure is a slightly distorted trigonal bipyramid, atoms N(2), N(4), Cl(1), comprising the trigonal plane and atoms N(1), N(3) the apices. The Cu atom lies only 0·013 Å out of the trigonal plane. The copper–axial nitrogen distances are 1·99(2) and 2·00(2) Å while the equatorial Cu–N distances are 2·04(2) and 2·07(2) Å The Cu–Cl distance is 2·501(4) Å. Deviations of bond angles from 120° in the trigonal plane [Cl–Cu–N(2), 123·7(6)°; Cl–Cu–N(4), 121·1(6)°] are probably due to the constricting influence of the rather inflexible ligand and the repulsive influence of the chlorine atom. The conformation of the ligand, tet b, is its most stable, folded form,[1] with both six-membered chelate rings having a symmetrical chair form.



(I) tet b (±)
(II) tet a (*meso*)

An unusual aspect of this structure is the single chlorine bridge between two metal atoms. Halide bridges hav been observed in other copper complexes, but these have a least two bridges with angular Cu–halogen–Cu bonds.[2–] The Cu–Cl bond distance in the present structure is very close to the average of the bridging Cu–Cl bond distance (2·514 Å) in $[Co(en)_3]_2[Cu_2Cl_8]Cl_2,2H_2O$[4] and in $[(C_5H_5NO)CuCl_2]_2$[2] in which the average of the Cu–Cl bridging distance is 2·526 Å. Normal nonbridging Cu–Cl bond lengths in trigonal bipyramidal structures are shorter,[4,5] for example 2·2964 Å (apical) and 2·3812 Å (planar) in $[CuCl_5]^{3-}$ (ref. 5) and 2·284 Å (average) in $[Cu_2Cl_8]^{4-}$ (ref. 4).

The cation is extensively hydrogen bonded to the oxygen of the perchlorate anions as is indicated in the Figure. Th slight deviation of the Cu–Cl–Cu bond from linearity (174·2° appears to be the result of the disposition of the perchlorat groups situated in special positions along the two-fold axis An oxygen of one perchlorate group, O(21), lies on the two fold axis and is hydrogen bonded to axial nitrogens in th co-ordination polyhedra of both copper ions. Translatio of this perchlorate group directs second and third oxygen atoms, O(23)* and O(24)*, towards the other axial nitrogens of the co-ordination polyhedra giving a wider bite of the cation with the resultant bending of the Cu–Cl–Cu′ bridge. The disorder of the bridging perchlorate group about the two-fold axis generates two orientations of this ion in the crystal. In one orientation (that indicated in the Figure) O(23)* is located 2·91 Å from N(3) while O(24)* is located 3·25 Å from N(3)′. In the second, two-fold related orientation of O(23)* is now located 2·91 Å from N(3)′ while the related O(24)* is located 3·24 Å from N(3). The perchlorate ions in the general positions are hydrogen bonded to the equatorial nitrogen atoms. All N–H · · · O hydrogen bonded distances are in the range of other hydrogen bonds of this type.

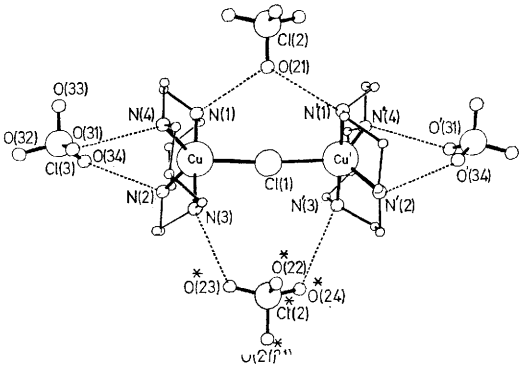


FIGURE. *A view of the cation along the z-axis showing the hydrogen-bonding of the perchlorate groups. Primed atoms are related to the corresponding unprimed atoms by a 2-fold operation. Starred atoms are related to the corresponding unprimed atoms by a unit cell translation along* y. *Methyl groups have been omitted for clarity.*

The corresponding binuclear complexes with bromide and iodide do not form although the monomeric halide adducts $[Cu(tet\ b)Br]ClO_4$ and $[Cu(tet\ b)I]ClO_4$ may be isolated.[6] The binuclear chloro-complex apparently does not exist as a principal species in aqueous solution. Copper-tet b(blue) is monomeric in aqueous solution, forming weak adducts with H_2O, OH^-, and halide ions.[6] The relative insolubility of the chloride bridged complex and its formation in the solid state is probably due to the stabilizing influence of the hydrogen bonding network in the crystal lattice. It would appear that the same type of hydrogen bonding cannot stabilize bromide and iodide bridges, because the increased Cu–X–Cu bond distances with these halides would increase the NH · · · O distances making hydrogen bonding unfavourable. It is interesting to note that $[Cu(tet\ b)]_2Cl(ClO_4)_3$ may be recrystallised from 0·01 M perchloric acid several times with no loss of chloride.

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