Pseudo-tetrahedral Geometry in the Copper(II) Complex of a Novel 18-Membered Tetra-aza-macrocyclic Ligand; *X*-Ray Crystal and Molecular Structure†

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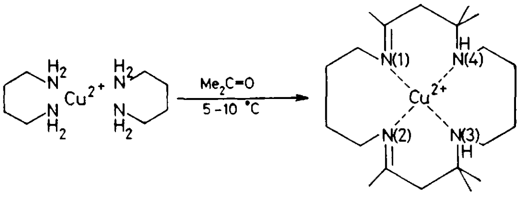
Summary Condensation of acetone with bis-(1,4-diaminobutane)copper(II) perchlorate yields a purple product, [(5*SR*,10*RS*)-2,4,4,11,11,13-hexamethyl-1,5,10,14-tetra-azacyclo-octadeca-1,13-diene]copper(II) perchlorate, which has an unusual pseudo-tetrahedral geometry about Cu^{II}, as indicated by *X*-ray analysis.

TEMPLATE condensation of acetone or other ketones with transition metal complexes of di-, tri-, or tetra-amines yields a variety of macrocyclic complexes. These complexes have received much attention in recent years[1] because of their unusual features and because of their value as models for compounds of biological interest. Similar macrocycles ranging in ring size from 12 to 16 have been reported.[2,3]

We now report the template synthesis of an 18-membered macrocyclic complex, [(5*SR*,10*RS*)-2,4,4,11,11,13-hexamethyl-1,5,10,14-tetra-azacyclo-octadeca-1,13-diene]copper(II) perchlorate, $[CuL][ClO_4]_2$. The complex (Scheme) is of intrinsic interest because the C–N double bonds have the *cis* arrangement[4,5] rather than the *trans* arrangement more commonly observed in tetra-aza macrocyclic complexes.[1,6] Of greater interest however, is the effect which the increased carbon chain length has on the co-ordination geometry about the Cu^{II} ion. The complex adopts a pseudo-tetrahedral geometry, apparently owing to the inability of the 7-membered chelate rings to adopt geometries normally associated with Cu^{II}. Although pseudo-tetrahedral geometry about copper(II) has been observed in complexes of a number of non-cyclic ligands[7] (most recently in a tetradentate Schiff base containing a central 7-membered ring[8]), this is the first report of this geometry in a macrocyclic complex. It is likely that a number of geometries intermediate between square planar and tetrahedral can be obtained for Cu^{II} simply by altering the chain lengths in macrocyclic ligands. These compounds of intermediate geometry should be exceptionally useful as models for copper redox proteins, which often contain intermediate geometries which ease the reduction of Cu^{II} to Cu^{I}.[9]



SCHEME. The *cis* macrocyclic complex, showing the method of preparation and the positions of the double bonds.

Bis-(1,4-diaminobutane)copper(II) perchlorate reacts with acetone at 298 K to yield a mixture of orange-red and purple crystalline products, both of which contain an 18-membered macrocyclic ligand.‡ Monoclinic crystals of the purple compound, $[CuL][ClO_4]_2$, were recrystallized from acetone–methanol. *Crystal data*, space group; *C*2/*c*; $a = 29{\cdot}132(16)$, $b = 14{\cdot}021(8)$, $c = 14{\cdot}838(9)$ Å; $\beta = 113{\cdot}89(6)°$; $Z = 8$.

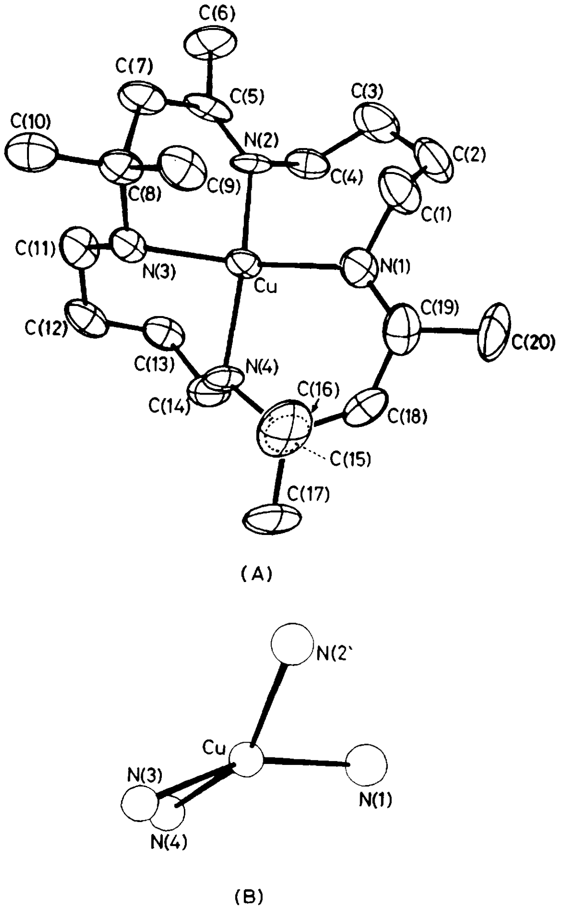


FIGURE. (A) Structure of the macrocyclic complex showing the crystallographic numbering scheme; (B) pseudo-tetrahedral distortion about Cu^{II}.

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‡ The orange-red crystalline form can be prepared as solvates from various solvents and is presently under investigation.

Refinement using 2469 observed reflections $[I > 3\sigma(I)]$ has resulted in an unweighted R factor of 0·084. The structure of the cation (with the crystallographic labelling system) is shown in the Figure.

The cation structure can be considered to arise from the twisting of a square planar configuration, or from extreme Jahn–Teller distortion of a tetrahedral configuration. The dihedral angle between the N(1)–Cu–N(2) and N(3)–Cu–N(4) planes is 36·6°. The macrocyclic ligand is co-ordinated in a pseudo-*meso* arrangement, with both *gem* methyl groups on the same side of the macrocycle. The angles of the co-ordination sphere, X–Cu–X′, in the cyclic sequence N(1), N(2), N(3), N(4) are 93·3(2), 90·7(2), 90·1(2), and 97·5(2)°; the N(1)–Cu–N(3) and N(2)–Cu–N(4) angles are 154·6(2) and 152·7(2)°, respectively. The Cu–N distances are shorter for the imine nitrogens, 1·986(5) Å for N(1) and 1·988(4) Å for N(2), than for the secondary amine nitrogens, 2·010(5) Å for N(3) and 2·024(5) Å for N(4), whereas other bonds are of the expected lengths. The perchlorate anions are not co-ordinated to the Cu^{II} ion (all Cu–O distances >3·5 Å) and therefore exhibit high thermal motion.

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§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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