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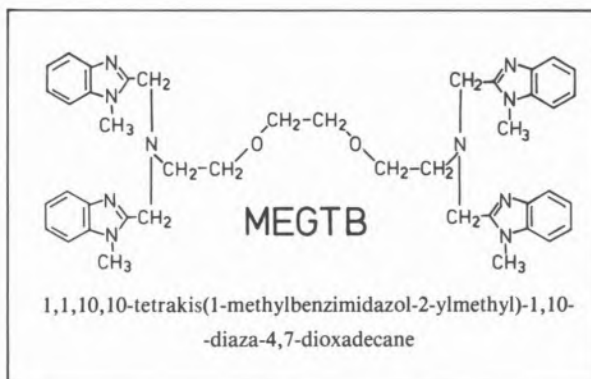
The Netherlands

COPPER CHELATES OF A DINUCLEATING BENZIMIDAZOLE-CONTAINING LIGAND AS MODELS FOR TYPE III COPPER PROTEINS

The active site in Type III copper proteins is generally believed to contain two copper ions close together and each coordinated by at least two imidazole groups of histidine residues [1]. The coordination geometry, imposed by the structure of the protein, is known to influence the specific properties, like O_2 transport or oxidative catalysis. To help elucidating the structures and understanding the reactivities of these proteins, low molecular weight compounds are studied as models. The steric constraints in polydentate ligands, *e.g.* the size of the bite and the presence of bulky substituents, are used as tools in tuning the model system. The incorporation of benzimidazole groups has the advantages of a biomimetic group being easily synthesized and having a bulky substituent.

The ligand megtb (see figure) has the potential to bind two metal ions with several possibilities for the metal-metal distances, both with and without exogeneous bridging ligands. The ligand has been prepared in two steps, *i.e.* a ring closure reaction by condensation of *o*-diaminobenzene with the polyaminocarboxylic acid EGTA (ethylene glycol bis-(β -aminoethyl ether) *N,N,N',N'*-tetraacetic acid), followed by *N*-methylation [2].

The coordination compounds with copper(II) appear to have two general formulae: a) $Cu_2LX_4 \cdot nH_2O$ with different kind of anions and



$Cu_2LX_2Y_2 \cdot nH_2O$ for X =halide and Y =a non-coordinating anion; b) $Cu_2LXY_3 \cdot nH_2O$ for X =1,3-azolate and Y =a non-coordinating anion. The crystal structures of $Cu_2(megtb)F_2(BF_4)_2 \cdot 3H_2O$ and $Cu_2(megtb)Cl_4 \cdot 6H_2O$ show a coordination geometry close to a square pyramid with 3 N atoms and the halide anion in the equatorial plane and an O ether atom on the apical position. The halide anion is also a sixth donor atom for a neighbouring Cu(II) ion at a larger, non-bonding distance. The resulting intermolecular Cu-Cu distance is slightly shorter than the intramolecular one. The magnetic exchange is weak in these compounds.

When bridging ligands are used in a sub-stoichiometric ratio, together with non-coordinating anions, intramolecular dicopper species can be obtained. They have a typical spin-triplet EPR spectrum both in the solid state and in solution, and *J*-values characteristic for copper dimers with bridging 1,3-azolates.

With Cu(I) both stable mononuclear compounds with non-coordinating anions, as well as dinuclear compounds with coordinating (pseudo)halides, are formed. Reaction with carbon monoxide results in a stable 1:1 (Cu:CO) product. The compounds react stepwise with dioxygen and are active in the oxidative coupling of 2,6-dialkylphenols. This reaction is used as a test reaction to investigate the catalytic properties of these and related systems.

REFERENCES

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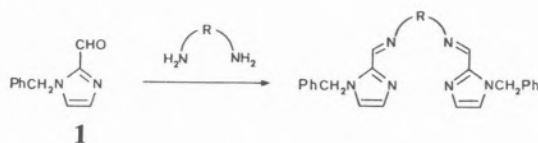
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IMIDAZOLE-CONTAINING SCHIFF BASE LIGANDS AS VERSATILE MODELS FOR COPPER PROTEIN ENVIRONMENTS

The active sites of cuproproteins, for which crystal structures are available, contain copper(II) ion bound by one or more histidine imidazole groups [1]. Consequently it is of interest to prepare complexes of ligands containing imidazole groups as small molecule models for these copper(II) sites.

The condensation of 1-benzylimidazole-2-carboxaldehyde, **1**, with primary diamines leads to ligands able to complex a central metal ion in an N_4 donor set:



Visible spectroscopy of the copper(II) complexes of these ligands has been used to examine the effect of the length and nature of the ligand backbone (R) on the geometry of the central metal ion. The crystal structure of the copper(II) complex where $R = (CH_2)_4$, $Cu(Bzic_2tmd)(ClO_4)_2$, has been solved, (Figure).

4-Methyl-5-[(2-aminoethyl)thiomethyl]imidazole, **2**, (an intermediate in the production of the antiulcer drug cimetidine [2]), and related amino-thioetherimidazoles, have been employed in the design and synthesis of Schiff Base chelates capable of providing N_3S , N_2S_2 , or N_2SO donor sets around a central metal ion.

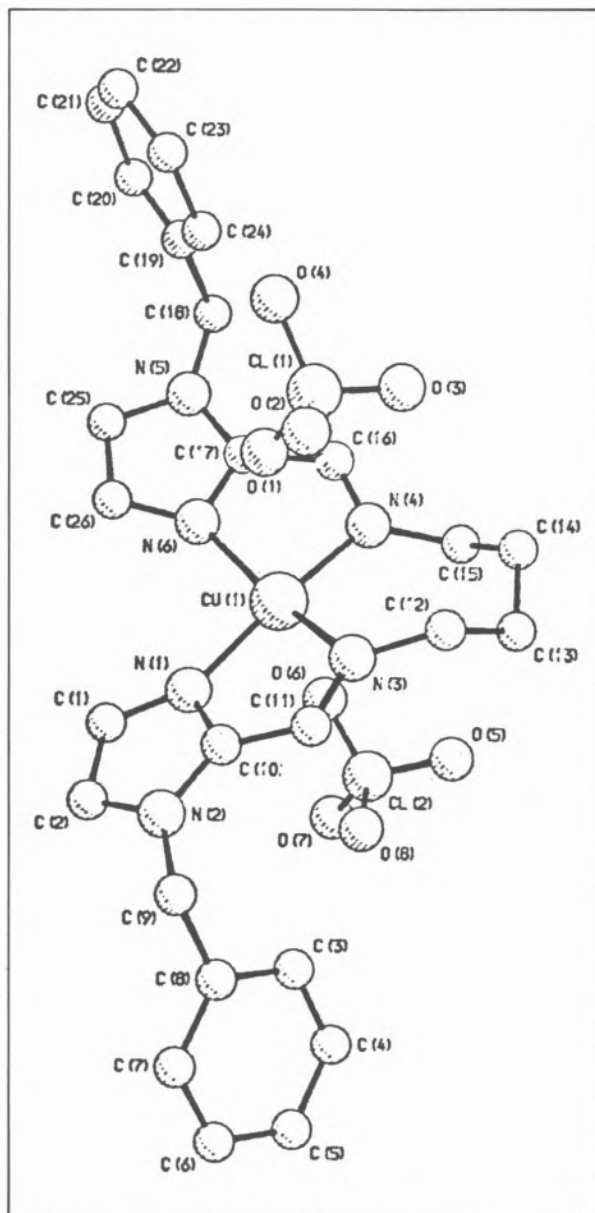
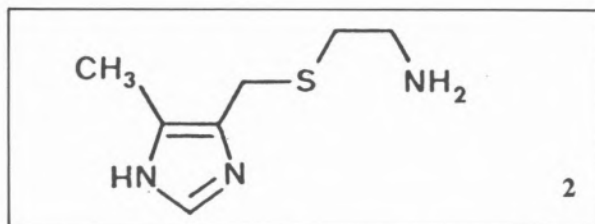


Figure
The crystal structure of $Cu(Bzic_2tmd)(ClO_4)_2$



Mononuclear copper(II) complexes of these ligands can be related to Type I copper protein environments, while homo- and hetero-binuclear