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Copper Complexes of Binucleating N,N'-Hydroxyalkyldiaminebis(salicylidine) Ligands containing a Cu–O–Cu Bridge and an Exogenous Bridge

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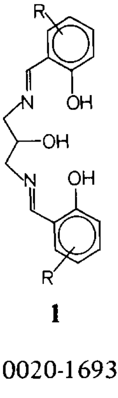
Binuclear and polynuclear metal complexes are potentially very important in catalysis and electron transfer [1–4]. Hemocyanin binds oxygen at the binuclear copper site, and is crucial to the electron transfer process in arthropods and molluscs [5]. The magnetic coupling between the metal atoms is strong [6]. Small molecule complexes can also catalyze such two-electron transfers [7–9], and there is a possible correlation between the redox properties and the strength of magnetic coupling between the metal atoms [9–10].

Binucleating ligands have been the subject of considerable recent interest [11–17] due to their ability, on demand, to hold pairs of metal atoms in close physical proximity. Ligands of LH_3, type (**1**) such as N,N'-2-hydroxy-1,3-propylenebis(salicylaldimine), can fulfil this function. LH_3 can be deprotonated at the phenolic oxygens to form a conventional Schiff base ligand, LH^{2-} (**2**). It can be further deprotonated at the alkanolic oxygen to form a binucleating ligand L^{3-} (**3**). In this mode, with the central alkanolic oxygen acting as a one atom bridge between the metal atoms, the ligand acts as a one atom bridge between the metal atoms, the ligand acts as a pair of tridentates.



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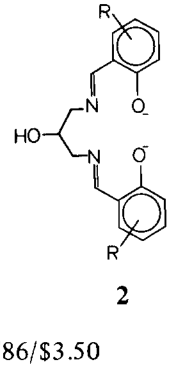

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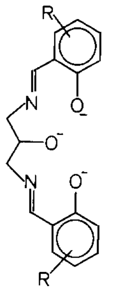
Variations of the reaction conditions produces complexes LH^{2-} and L^{3-}, which were characterized with UV-Vis and IR spectroscopy, variable temperature magnetic susceptibility, electrochemistry and X-ray crystallography.

The copper complexes with LH^{2-}-type ligands are monomeric (**4**) with LH^{2-} acting as a tetradentate, with two Cu–N bonds and two shorter Cu–O bonds to the phenolic oxygens of the ligand. The alkanolic OH group remains protonated, and is not coordinated to the metal atom, but is involved in hydrogen bonding with neighbouring OH groups or solvent molecules of crystallization. The copper atoms are fairly well separated: in [Cu(Sal-2-OH-propylenediamine)] the nearest Cu–Cu distance is 4.454 Å.



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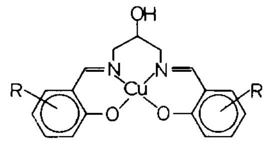

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The copper complexes with L^{3-} are binuclear with a single oxygen bridge from the deprotonated alkanoic OH group, and a second ligand X^-. A systematic study of complexes with deprotonated carboxylic acids acting as a three-atom bridge for ligand X, including benzoic acids and primary, secondary and tertiary alkanolic acids was carried out. An example of a complex with a primary alkanoic acid is **5**. Other ligands X include pyrazole **6**.

Most of these binuclear complexes **5** exhibit antiferromagnetic interactions of moderate strength, but somewhat less strong than those observed in hemocyanin and oxyhemocyanin [6], or in analogous Schiff base binuclears [12, 13].

Complexes **5** contain two superexchange bridges which cannot both be simultaneously oriented in the optimal configuration for maximum coupling. Further studies are being carried out to determine the relationship between the strength of coupling in these complexes and the molecular geometry.

The Cu–Cu distance ranges around 3.5 Å for most complexes, which compares with the 3.5 ± 0.2 Å value suggested from EXAFS data for the oxy and met forms of hemocyanin [18, 19]. In $[Cu_2(3\text{-EtOSal})\text{propylene}(C_2H_5\cdot COO)(H_2O)]\cdot H_2O$ with a coordinated water molecule, Cu–Cu = 3.473 Å, in $[Cu_2(\text{Sal})\text{propylene}(Cl_2CH\cdot COO)]$, with no coordinated

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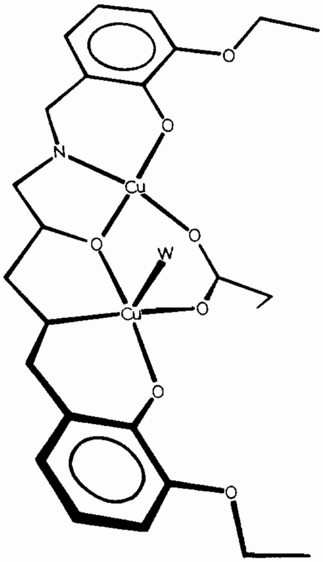

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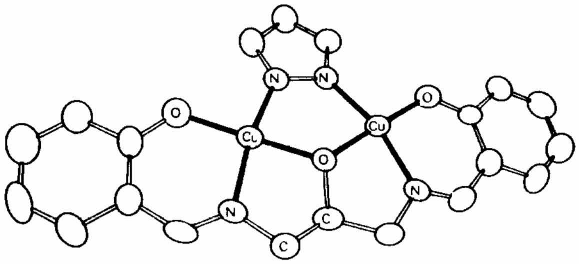

solvent molecules, Cu–Cu = 3.526 Å. In [Cu_2(Sal)-propylene(($(CH_3)_3C \cdot COO$)DMF], there is a solvent of crystallization, weakly bonded (2.384 Å) and Cu–Cu = 3.137 Å, but in this complex there is a severe distortion, which may relate to the t-butyl group on the carboxyl group (pivalate). The distortion takes the form of bending between the copper planes, while keeping the copper environment essentially planar. The copper geometry is evidently little affected by the bulkiness of the carboxylate substituent, though the length of the alkyl chain alters the metal environment.

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