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INFLUENCE OF THE WEAK INTERACTION ON THE STRUCTURE OF METALLOCYCLE IN BINUCLEAR COPPER(II) COMPLEX

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ABSTRACT

The structure of binuclear Cu(II) complex containing double oximate bridges was determined by the single-crystal X-ray diffraction analysis. Copper is five-coordinated with perchlorate anion present at the borderline of semi-coordination. Comparison with the structurally related diimine-dioxime Cu(II) complexes revealed the influence of the weak Cu...O(perchlorate) interaction on the geometry of the metallocycle.

INTRODUCTION

Schiff base ligands have been the subject of much research interest owing to their interesting coordination chemistry and a number of established and potential application areas [1,2]. The Schiff base ligands, especially tetradentate, readily form complexes with the transition metals [3]. These studies include development of new Schiff bases containing the diimine-dioxime functionality. Of particular interest is the capability of the deprotonated diimine-dioximes to form bridges between metal ions giving rise to complexes of different nuclearity [4]. Additional interest for complexes with this ligand is connected with the ability of oximate bridges to mediate strong antiferromagnetic interaction between metal centers [5]. Use of copper in the complex synthesis presents a particular problem. Copper is known for its flexible coordination behavior associated with the capability to form weak bonds, a property termed 'plasticity' [6]. This problem becomes more pronounced in the studies of weaker non-bonding interactions [7]. Detailed analysis of the copper environment followed by computational or database studies [8] may provide additional insight into the non-bonding contacts relevant for the properties of copper complexes.

One of the ligands frequently used in the synthesis of copper complexes is perchlorato group. As a ligand the ClO_4^- group may appear in a various bonding arrangements, however its steric properties limit its coordinating ability in the presence of smaller potential ligands [9]. Recently the coordinating properties of the ClO_4^- bonded to Cu were studied [10,11]. However, in most of the crystal structures the ClO_4^- is present as a non-coordinated ion. In the present study the binuclear copper(II) complex of the 4,9-diaza-3,10-diethyl-3,9-dodecadiene-2,11-dione bisoxime ligand (LH) [12] was chosen for study to enable comparison with the previously studied binuclear copper(II) complexes[13-15] of the closely related ligands with a dimethyl group in place of the present diethyl group.

RESULTS AND DISCUSSION

The crystal structure consists of centrosymmetric $[\text{Cu}_2(\text{LH})_2]^{2+}$ cations and perchlorato anions. The copper(II) atom is in a distorted square-pyramidal coordination (Fig. 1). According to the trigonality index $\tau=0.34$, coordination polyhedron can be described as a severely distorted square pyramid. The basal plane is formed by N1, N2, N3 and N4 atoms, and the metal ion deviates by 0.24\AA from this plane, towards the apical positions occupied by oxime oxygen O1 (Fig. 1). Intra-molecular $\text{Cu}\cdots\text{Cu}$ separation is $3.9424(4)\text{\AA}$.

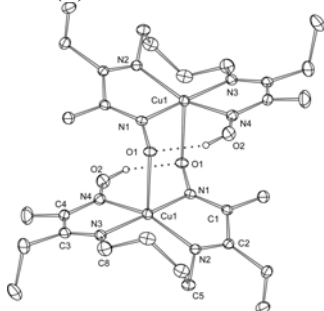


Figure 1. Molecular diagram and atom numbering scheme of $[\text{Cu}_2(\text{LH})_2]^{2+}$. Intramolecular O-H...O hydrogen bonds are depicted by dotted lines.

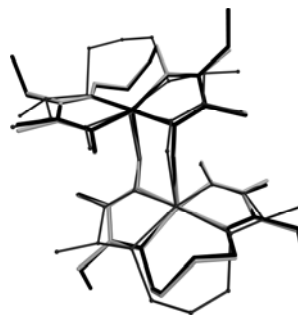


Figure 3. Overlay of the solid state structures of **I** (black), **II** (light grey) and **III** (dark grey, thin line).

This complex exhibits an intramolecular hydrogen bond (Fig. 1) between *cis* oxime groups with an O...O distance of 2.593(3) Å, H...O = 1.83 Å and O-H...O angle of 154°. Different role of O1 and O2 in the nonbonding interactions is associated with different geometry of two N-O bonds. Both, N1-O1 and N1-Cu1 bonds are shorter than N4-O2, and N4-Cu1 bonds, respectively. This finding implies higher multiple bond character in the fragment O1-N1-Cu1, relative to O2-N4-Cu1. Regarding the association of molecules in the solid state, it is interesting to note the lack of strong hydrogen bonding donors. Hence, it was anticipated that intermolecular contacts between the C-H donors and perchlorato oxygen atoms would govern the association of molecules into crystal. Inspection of intermolecular geometry confirms that ClO₄⁻ anion participates in the weak hydrogen bonds to cationic complex through the C-H...O interaction. In order to obtain more insight into the structural features of the title compound **I** we compare obtained results to the crystal structures of similar Cu complexes. Structural formulas of the complexes used for comparison is given in Fig. 2. Three complexes differ in the presence of ethyl instead of methyl substituent at the five-membered chelate ring in **I**, and the presence of six-membered chelate ring, and sulphur instead of nitrogen, in the diimine-dioxime ligand in **III**. Overlay of three solid state structures in Fig. 3 illustrates their overall similarity, confirmed by the examination of geometrical parameters.

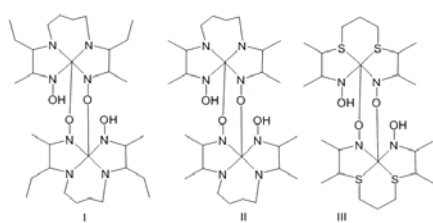


Figure 2. Structural formulas of the cationic complexes used for comparison

Although the overall structures of **I-III** are similar the subtle differences in the geometry of the metallocycle were observed. In **I** and **III** Cu-O bonds are 2.318(2) and 2.293 Å respectively, which is longer than 2.266/2.262 Å found in two polymorphs of **II**. While these differences in the axial Cu-O bonds could be attributed to the 'plasticity' [6] of the copper coordination sphere, it is interesting to examine the possible influence of the closest perchlorato fragment on these bonds. In the crystal structures of **I** and **III** the closest perchlorato oxygen is at the Cu-O distances of 2.947(3) and 2.907 Å, respectively. It is on the borderline of the values which have been reported for the semicoordinated perchlorato group. In the crystal structure

of **II** however, the closest perchlorato oxygen is at a rather larger distance of 3.767/3.766 Å and cannot be considered as semicoordinated to Cu. If the presence of the semicoordinative bond Cu-O(ClO₃) *trans* to Cu-O(oximate) bond is taken into account, the elongation of the Cu-O bonds in **I** and **III**, relative to **II**, could be attributed to the *trans* influence of the weakly coordinated perchlorato oxygen.

CONCLUSION

The crystal structure of complex consist of centrosymmetric [Cu₂(LH)₂]²⁺ cations and perchlorato anions. The copper(II) atom is in a distorted square-pyramidal coordination. During complex formation one oxime proton is lost, and the hydrogen bond between the two oxime groups of the same ligand is formed. Comparison of structurally related dimine-dioxime complexes indicates that geometry of metalocycle is influenced by the presence of weakly coordinated perchlorato anion.

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