Inorganica Chimica Acta, 34 (1979) L213–L214

Synthesis and Crystal Structure of Methanol and Acetic Acid Adducts of Copper Acetate. Predominance of σ-Interaction between the Two Copper Atoms in the Dimer

V. MOHAN RAO and H. MANOHAR*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India

Received February 12, 1979

The nature of the copper–copper interaction in dinuclear copper(II) carboxylates has been a subject of much discussion ever since the structure of copper (II) acetate monohydrate, the first of its type, was reported [1]. Bleaney and Bowers, from a study of the EPR spectrum of the monohydrate, had earlier suggested [2] "a coupling of isolated pairs of copper atoms by exchange forces" resulting in a singlet ground state and an excited triplet state and explained the anti-ferromagnetic behaviour. The existence of (isolated) pairs of copper atoms was confirmed a year later by an X-ray crystal structure analysis [1]. Figgis and Martin [3] on the basis of Polder's energy level diagram [4] suggested a weak covalent δ-bond between the two copper atoms which are only 2.64 Å apart. However, Forster and Ballhausen [5] favoured a σ-bond between the two copper atoms on consideration of the overlap criteria in molecular orbital calculations. Comparison with the very short Mo–Mo separation (2.11 Å) in $Mo(OAC)_2$ [6] has been used by Cotton [7] as a basis for ruling out significant metal–metal bonding. From the results of their structural and magnetic studies, Goodgame *et al.* [8] have supported the idea of superexchange of spins through the bridging ligands. However, their arguments have been questioned by Gregson *et al.* [9]. Also a drawback of the superexchange concept according to Catterick and Thornton [10] is the qualitative nature of the discussion. Many authors have reviewed the subject [11], perhaps the most exhaustive one being by Kato *et al.* [12]. It is evident that lack of enough experimental data in analogous copper(II) acetate complexes makes any precise conclusion regarding the nature of the interaction difficult and unreliable.

We report here the crystal structures of methanol and acetic acid adducts of copper acetate. Polycrystalline copper(II) acetate monohydrate was dehydrated at 115 °C to a calculated weight loss and dissolved in absolute methanol (+5% 2,2-dimethoxypropane) and in acetic acid–acetic anhydride (3:1) mixture. The flasks were sealed and kept at −10 °C. Blue-green crystals of the adducts appeared after two days. The compounds were highly unstable and 'single crystals' on exposure to moisture give rise to the polycrystalline monohydrate (as observed from X-ray diffraction photographs). The chemical composition could not be determined due to their high instability. Small crystals of dimensions 0.3 × 0.3 × 0.5 mm^3 were sealed in Lindemann glass capillaries and cell dimensions and space-group were determined from Weissenberg photographs. Both the compounds crystallise in the monoclinic space-group $P2_1/n$. The cell-dimensions are $a = 8.129$ Å, $b = 7.447$ Å, $c = 13.332$ Å, $\beta = 92.21°$ for the methanol adduct and $a = 15.153$ Å, $b = 7.772$ Å, $c = 8.229$ Å, $\beta = 103.08°$ for the acetic acid adduct. The molecular weight calculated using the density of monohydrate corresponds to the formula of copper acetate with one molecule of solvent in both cases. Intensity data were collected on a 4-circle CAD-4 diffractometer by the ω–2θ scan technique. The structures were solved by the heavy-atom method and refined by full-matrix least-squares using anisotropic thermal parameters to R values of 0.041 and 0.037 for 1830 and 1957 reflections respectively. The molecular structures shown in Fig. 1 and Fig. 2 are dimeric and are similar to that of monohydrate. The observed copper–copper distances are shorter than in the monohydrate.

Considering a σ-bond between the two copper atoms in the dimer, the principal contributor will be the d_{z^2} orbital. The metal-axial ligand bonding also uses the same d_{z^2} orbital to some extent. As a result, in presence of an axial ligand, there will be a competition between the two. From a structural point of view as the axial ligand approaches closer to the metal atom, the metal–metal distance tends to be larger. This point could be verified by correlating the

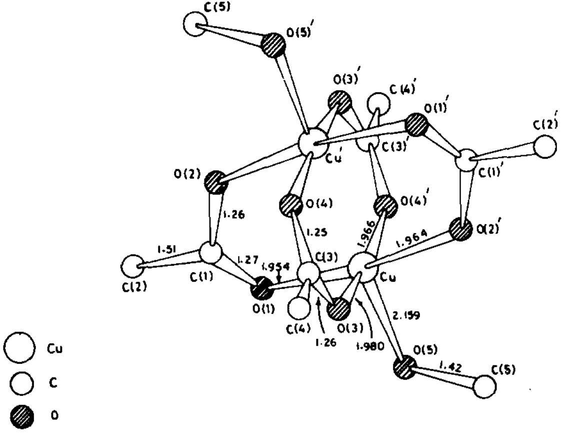

Fig. 1. Molecular structure of copper acetate methanol adduct.

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*Author to whom correspondence should be addressed.

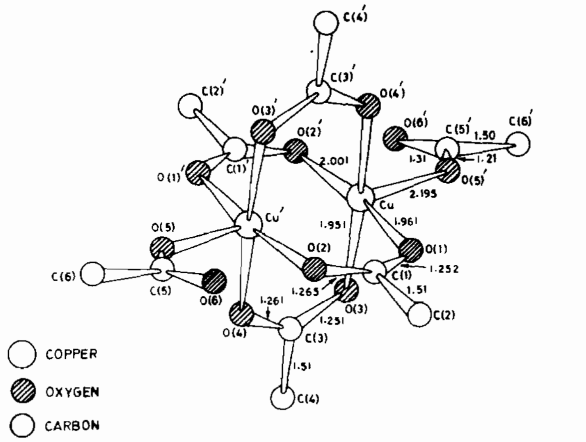

Fig. 2. Molecular structure of copper acetate acetic acid adduct.

TABLE. Cu–Cu and Cu–L Distances (Å) in the Dimeric Structures of Copper Acetate Adducts.

Axial Ligand	Cu–Cu (Å)	Cu–L (Å)	Reference
Pyridine[a]	2.645(3)	2.186(8)	13
Pyridine[b]	2.630(3)	2.126(10)	14
Quinoline	2.642	2.17	15
Thiocyanate	2.643(4)	2.08	8
Pyrazine (300 K)	2.584(1)	2.171(4)	16
Pyrazine (100 K)	2.576(1)	2.162(6)	16
Water	2.616(1)	2.156(3)	17
Methanol	2.597(1)	2.159(7)	Present
Acetic Acid	2.582(1)	2.195(6)	work

[a]Monoclinic. [b]Orthorhombic.

two distances in the nine structures reported so far. The distances are presented in the Table.

The plot in Fig. 3 shows a reasonably good linear relationship but for the two points corresponding to the quinoline adduct and the orthorhombic form of pyridine adduct. The approach of the bulky quinoline molecule could be hindered due to steric reasons but the reason for the deviation of the orthorhombic form of pyridine adduct is not clear. The observation of a definite negative slope indicates that the two parameters bear an inverse relation. This suggests that the σ-bond type of interaction between the two copper atoms is more predominant in these structures.

Acknowledgements

We thank Dr. D. N. S. Narayana and Dr. H. S. G. K. Murthy for valuable discussions and comments.

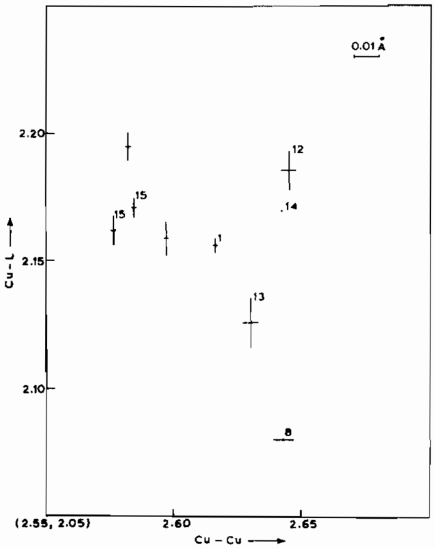

Fig. 3. Plot of Cu–Cu *vs.* Cu–L distances (Å) in dimeric copper acetate adducts.

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