# Copper(II) Complexes of 3-Formyl-5-methylsalicylaldehyde and Its Schiff Bases with Alkyl Amines

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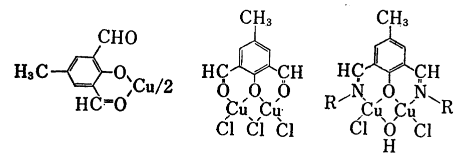
Two new copper(II) complexes of 3-formyl-5-methylsalicylaldehyde,[1] bis(3-formyl-5-methylsalicylaldehydato)copper(II) (**1**) and dichloro-$\mu$-chloro-$\mu$-(2,6-diformyl-4-methylphenolato)dicopper(II) (**2**) (Fig. 1), have been prepared by using copper(II) acetate monohydrate and copper(II) chloride dihydrate respectively as metal sources. Both were easily obtained by adding a solution of the copper(II) salt in ethanol to a solution of 3-formyl-5-methylsalicylaldehyde in ethanol.

In addition to these complexes, new series of oxygen-bridged binuclear copper(II) complexes (**3** type) have been synthesized by using the aldehyde, copper(II) chloride dihydrate, and alkyl amines ($R\text{-}NH_2$), in which R represents methyl, ethyl, isopropyl, *t*-butyl, or chclohexyl groups. The method of synthesizing the complexes was as follows. To a warm solution of the aldehyde and copper(II) chloride dihydrate in ethanol we added a solution of an amine in ethanol to give green or brown needles; these needles were collected and washed with ethanol. The results of the molecular-weight determinations of these complexes support the formula given for the complex **3** in Fig. 1. The analytical data of the complexes obtained are given in Table 1.

In the complexes **2** and **3**, the organic moiety acts as a quadridentate chelating agent with the bridging phenolic oxygen, and the copper atoms are held sufficiently close to each other to cause antiferromagnetic interactions; the magnetic moments determined for the complexes **2** and **3** at room temperature were 1.58 and 0.80—1.29 B. M. respectively. On the other hand, the complex **1** has a normal magnetic moment of 1.81 B. M.



**1** **2** **3**

Fig. 1.

The reflectance spectra of the complexes **2** and **3** each have one d-d transition band, located at 11,100 cm$^{-1}$ for the complex **2** and at 12,000—14,400 cm$^{-1}$ for the complex **3**; these energies are lower than those expected for mononuclear copper(II) complexes of similar ligands, supporting a binuclear structure and in agreement with the findings of Harris *et al.*[2] It is noteworthy that the complexes also have a binuclear structure in a solution, judging from the spectra in a solution, which are very similar to those measured by the diffuse-reflection method, although the complex **2** is decomposed in the presence of water to the complex **1**.

The details of this work will be reported shortly.

TABLE 1. ANALYTICAL DATA OF COMPLEXES

| Complex | | Found (%) | | | | Calcd (%) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | C | H | N | Cu | C | H | N | Cu |
| **1** | | 55.55 | 3.87 | | 15.96 | 55.46 | 3.62 | | 16.30 |
| **2** | | 27.28 | 1.85 | | 31.32 | 27.26 | 1.78 | | 32.04 |
| **3** | R | | | | | | | | |
| | $CH_3$ | 32.46 | 3.24 | 6.71 | | 32.68 | 3.49 | 6.93 | |
| | $C_2H_5$ | 36.39 | 4.01 | 6.33 | | 36.12 | 4.20 | 6.43 | |
| | $i\text{-}C_3H_7$ | 39.60 | 4.67 | 5.73 | | 39.14 | 4.82 | 6.09 | |
| | $t\text{-}C_4H_9$ | 41.65 | 5.19 | 5.54 | | 41.81 | 5.37 | 5.74 | |
| | $C_6H_{11}$* | 45.97 | 5.42 | 4.83 | | 45.90 | 5.69 | 5.10 | |

* It denotes cyclohexyl. With a half molecule of water.

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1) D. A. Denton and H. Suschitzky, *J. Chem. Soc.*, **1963**, 4741.

2) C. M. Harris, J. M. James, P. J. Milham and E. Sinn, *Inorg. Chim. Acta*, **3**, 81 (1969); B. Coles, C. M. Harris and E. Sinn, *Inorg. Chem.*, **8**, 2607 (1969).