Binuclear Copper(II) Complexes Derived From 3-Formyl-5-methylsalicylaldehyde and Glycine

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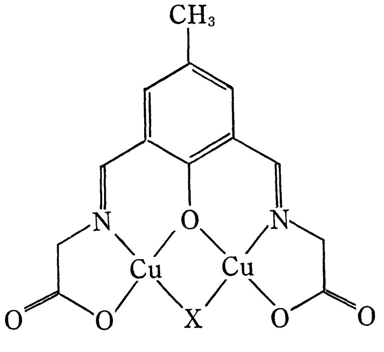
Although many binuclear copper(II) complexes have been synthesized, there are few in which two copper (II) ions are bridged with two different groups.[1,2] We report here the syntheses of three new binuclear copper (II) complexes formed by the reaction of copper(II) ion with 3-formyl-5-methylsalicylaldehyde and glycine. These complexes possess the same surrounding organic moiety except for the second bridging group, which is chloride, bromide, or hydroxide anion (Fig. 1), and seem useful in investigating the role of the bridging group in exchange interaction.

The Cl-bridged complex (green needles) was prepared as follows. To a hot ethanolic solution of copper(II) chloride dihydrate and aldehyde was added an aqueous solution of a stoichiometric amount of glycine. The resulting clear solution was heated on a water-bath for ten min to give green needles. The same procedure was employed in the synthesis of the corresponding Br-bridged complex (green needles) by using anhydrous copper(II) bromide instead of copper(II) chloride dihydrate. The OH-bridged complex was obtained as blue prisms, when copper(II) acetate monohydrate or copper(II) sulfate pentahydrate was used as a metal source. Analytical data of the complexes given in Table 1 agree with the formulas shown in Fig. 1.



X=Cl, Br, OH
Fig. 1.

Table 1. Analytical data of complexes

Complex	Found(%) C	Found(%) H	Found(%) N	Calcd(%) C	Calcd(%) H	Calcd(%) N
X=Cl	35.42	2.67	6.11	35.67	2.53	6.40
Br	32.65	2.41	5.51	32.38	2.30	5.81
OH	35.88	3.25	6.33	35.70	3.23	6.41[a]

a) Calculated for monohydrate.

Infrared spectra of the complexes exhibit no $\nu_{C=O}$ mode of a formyl group and show a strong broad band due to the C=O (carboxylate), C=N, and C=C vibration in the region 1645—1600 cm^{-1}. The reflectance spectra of the Cl-, Br-, and OH-bridged complexes show one broad *d-d* band at 695, 695, and 650 mμ respectively. The Cl- and Br-bridged complexes seem to take a binuclear structure in water as well as in pyridine, judging from the close resemblance of the spectra in solutions to those in solid states. Magnetic moments of the Cl- and Br-bridged complexes measured at room temperature were 1.72 and 1.76 B.M. respectively, which are close to the value 1.73 B.M. calculated from the spin-only formula. The magnetic moment of the OH-bridged complex was 1.09 B.M., suggesting a fairly strong antiferromagnetic interaction between the copper (II) ions.

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[1] H. Okawa, This Bulletin, **43**, 3019 (1970).
[2] R. Robson, *Inorg. Nucl. Chem. Lett.*, **6**, 125 (1970); *Aust. J. Chem.*, **23**, 2217 (1970).