of these reagents in solution[10] and the as of yet uncertain role that copper(I) itself plays in the reaction.[11]

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(11) For a related study, see the accompanying communication: J. Staroscik and B. Rickborn, *J. Amer. Chem. Soc.*, **93**, 3046 (1971). We thank Professor Rickborn for discussions prior to publication.

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## Electron Spin Resonance Evidence for the Existence of a Dimeric Form of the Copper(II) Chelate of Kojic Acid

*Sir:*

On the basis of magnetic susceptibility measurements on the manganese(II), iron(II), cobalt(II), nickel(II), and copper(II) chelates of 2-hydroxymethyl-5-hydroxy-γ-pyrone (kojic acid), Wiley, *et al.*, deduced that the most probable coordination configuration was a tetrahedral one for the chelates of nickel(II), cobalt(II), iron(II), and manganese(II).[1] In the case of the copper(II) chelate, it was not possible on the information provided by magnetic susceptibility measurements alone to draw a distinction between tetrahedral or essentially planar configurations. A more recent investigation confirmed the fact that the copper(II) chelate of kojic acid possessed a magnetic moment corresponding to one unpaired electron per copper(II) ion and that there is no evidence of the presence of exchange coupling. Furthermore, the data drawn from the electronic spectrum provided evidence for a pseudotetrahedral symmetry of the copper(II) ion.[2]

The copper(II) chelate of kojic acid has a very limited solubility in water, a property which commended its study in connection with analytical procedures. A search among organic solvents has, so far, not produced one in which the chelate is soluble to any useful extent and so investigations are confined to the powder form which emerges from the preparative procedure. Electron spin resonance (esr) measurements which have been carried out on frozen solutions of copper(II) chelates have provided a wealth of information which has proved useful in determining the electronic structure and bonding of the chelates, and in recent times the state of aggregation of the chelate species.[3,4] The measurements associated with providing evidence for dimer formations are equally valid for powder samples, though the information may not be as precise as that obtained in frozen solution where magnetic dilution can be more easily controlled. Accordingly, the esr spectra of the copper(II) kojate was recorded at room temperature and 77°K. The spectrum obtained at room temperature is shown by Figure 1. The low-field line is attributed to $\Delta M = 2$ transitions arising from magnetic dipolar coupling between the copper(II) ions in a dimeric form of the copper(II) chelate. As would be anticipated from this situation, the intensity of the low-field line varied very little when the signal was recorded at room temperature.

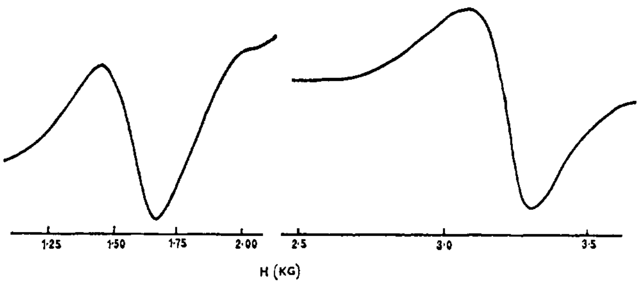

Figure 1. X-Band esr spectra at room temperature and microwave frequency 9499 mHz of copper(II) kojate.

The theory relevant to the interpretation of the results presented here has been described in detail previously, the coupling process being represented by the spin Hamiltonian[4]

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{\mathrm{ex}} + \mathcal{H}_{\mathrm{d}}$$

where $\mathcal{H}_1 = g_{\parallel}\beta H_z S_{iz} + g_{\perp}\beta(H_x S_{ix} + H_y S_{iy}) + A S_{iz} I_{iz} + B(S_{ix} I_{ix} + S_{iy} I_{iy})$. The parameters $g_{\parallel}$, $g_{\perp}$, $A$, and $B$ have their customary significance. Since we assume that the two ions are in identical sites of axial symmetry and that the $z$ direction is along the internuclear axis, we may write

$$\mathcal{H}_{\mathrm{d}} = \beta^2(g_x{}^2 S_{ix} S_{2x} + g_y{}^2 S_{iy} S_{2y} - 2g_z{}^2 S_{iz} S_{2z})/r^3$$

where $i = 1$ or 2 and $r$ is the distance between the magnetic point dipoles and is taken to be equivalent to the internuclear distance. In the systems described here, the major contribution to the zero-field splitting is due to $\mathcal{H}_{\mathrm{d}}$ and it is assumed that high-order effects due to $\mathcal{H}_{\mathrm{ex}}$ may be ignored. Computer simulation of the esr spectra was achieved using methods previously outlined.[4] The parameters obtained from the $\Delta M = 2$ transition of the copper(II) chelate of kojic acid are as follows: $r_{\mathrm{Cu-Cu}} = 4.0 \pm 0.2$ Å, $g_{\parallel} = 2.37 + 0.02$, $g_{\perp} = 2.03 \pm 0.01$, $A = 180 \pm 20 \times 10^{-4}$ cm$^{-1}$, $B = 10 \pm 5 \times 10^{-4}$ cm$^{-1}$, and $\sigma = 35$ G. We do not assume that these results must necessarily mean that the symmetry of the pair of copper(II) ions is axial, but, insofar as the results can be analyzed as described, it can be inferred that the symmetry of the dimer is close to the simple axial model assumed in the theoretical approach.

It is proposed, therefore, that the structure of the copper(II) kojate dimer is similar to that of the β form of 8-hydroxyquinolinate. Palenik[5] has shown that this particular crystal form is composed of dimer-like units in which copper(II) is five-coordinate, with the out-of-plane coordinate position being occupied by the oxygen atom from a second molecule.

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