Antiferromagnetic Complexes of Copper(II) with 2-Methoxyphenols

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WE have found that 2-methoxyphenols (guaiacols) give polymeric copper(II) complexes which show a variety of stereochemistries and are often antiferromagnetic. 4-Formylguaiacol and 4-nitroguaiacol give both distorted octahedral and square-planar complexes whilst guaiacol yields a distorted tetrahedral one.

TABLE

	Compound	Colour	$\mu_{\text{eff.}}$ (B.M.) 295° K	$\mu_{\text{eff.}}$ (B.M.) 90° K	θ°	$-2J$ (cm.$^{-1}$)	g (calc.)
A	$(C_8H_7O_3)_2(H_2O)_2Cu$	yellow-green	1·92	1·82	12	—	—
B	$(C_7H_6NO_4)_2(H_2O)_2Cu,2H_2O$	yellow	1·89	—	—	—	—
C	$(C_7H_7O_2)_2Cu$	light brown	1·65	0·85	—	124·3	2·51
D	$(C_8H_7O_3)_2Cu$	brown	1·74	1·43	102	39·3	2·22
E	$(C_7H_6NO_4)_2Cu$	brown	1·69	1·39	68	27·2	1·98

The complexes, bis-(4-formylguaiacolato)diaquocopper(II) (A, Table), bis-(4-nitroguaiacolato)-diaquocopper(II) dihydrate (B), and bis(guaiacolato)copper(II) (C) were prepared by the addition of an aqueous solution of a copper(II) salt (1 mol.) to an aqueous solution of the ligand (2 mol.) and base. Dehydration of A and B yields bis-(4-formylguaiacolato)copper(II) (D) and bis-(4-nitroguaiacolato)copper(II) (E), respectively. The complexes were pure and B contained water in two different environments (i.r.).

The diffuse reflectance spectra (Figure 1) of the hydrated complexes A and B were similar and indicated[1] that each copper(II) ion had a distorted octahedral environment. The single, broad absorption band observed for the complexes D and E suggested planar geometry[2] whilst the spectrum of bis(guaiacolato)copper(II) (C) was similar to those of some distorted tetrahedral copper(II) complexes.[3,4] No hydrated guaiacol complex was obtained.

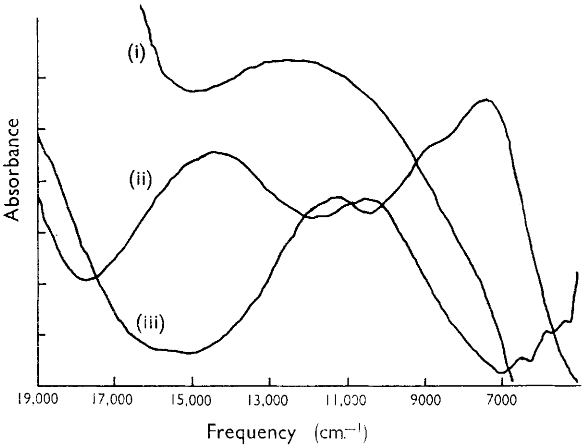

FIGURE 1. *Diffuse reflectance spectra*: (i), *bis-(4-formylguaiacolato)diaquocopper*(II); (ii), *bis-(4-formylguaiacolato)copper*(II); (iii), *bis(guaiacolato)copper*(II). *The absorbance values of* (ii) *are* ca. 3·5 × *greater than those of* (i) *and* (ii).

The room temperature magnetic moments (Table) of the hydrated complexes A and B were normal[5] and the complex A obeyed the Curie–Wiess Law with $\theta \simeq 12°$. The square-planar complexes D and E had subnormal effective magnetic moments but followed the Curie–Wiess Law with high values of θ (Table) whilst the guaiacol complex C displayed a Neel point at 180 ± 15° K (Figure 2). The magnetic data for the complexes C, D, and E was analysed in terms of the one-dimensional Ising[6] model of antiferromagnetism. This model gives the expression:

$$\chi_m = \frac{Ng^2\beta^2}{4kT}\exp\left(\frac{2J}{kT}\right) + N\alpha$$

where J is the interaction energy between nearest neighbouring copper(II) ions. Excellent agreement between theory and experiment was found (Figure 2). The electron density at the phenolic oxygen atom should increase with decreasing electron-withdrawing power of the 4-substituents in the order:

$$\text{C(4-H)} > \text{D(4-CHO)} > \text{E(4-NO}_2\text{)}.$$

The calculated values of $-2J$ support this assertion (Table).

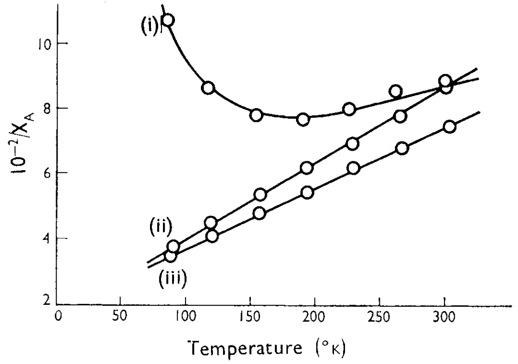

FIGURE 2. *Variation with temperature of reciprocal susceptibility*: (i), *bis(guaiacolato)copper*(II); (ii), *bis-(4-nitroguaiacolato)copper*(II); (iii), *bis-(4-formylguaiacolato)copper*(II). *The lines are calculated and circles represent observations.*

On the basis of the above data we suggest that the complexes A and B have polymeric structures. Each copper(II) ion would have a half share of four bridging oxygen atoms, derived from the phenolic moieties, in the equatorial plane, to give linear chains of metal ions, and water molecules in the axial positions leading to distorted octahedral structures. The complexes D and E, produced by dehydration, are rendered square-planar by the removal of the axial water molecules and have an antiferromagnetic interaction along the chains of copper(II) ions. The complex C, which probably has a distorted tetrahedral structure, is polymeric, with shared phenolic oxygen atoms and has a strong antiferromagnetic interaction along a linear chain of copper(II) ions.

We could not prepare complexes of 3- and 4-hydroxybenzaldehydes but as no evidence was found to suggest that the 2-methoxy-group was co-ordinated to copper(II) in the complexes reported here, we consider that the 2-methoxy-group lends steric rigidity to these systems.

We thank Unilever Limited for a maintenance grant to one of us (S.L.J.).

(*Received, June* 12*th,* 1968; *Com.* 769.)

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