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Two Modifications of Bi-Nuclear Copper(II) Chloride Complexes with *N*-Methylsalicylideneimine

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We reported previously[1,2] that two modifications of a compound of composition Cu($\overset{2}{O}\cdot C_6H_4\cdot\overset{1}{C}H{=}N{-}CH_3$)Cl (1) were obtained in the reaction of bis-*N*-methylsalicylideneiminatocopper(II) and cupric chloride in ethanol. The brown form (1.5 Bohr magnetons) was prepared by refluxing the alcoholic mixture, whereas the orange one (0.9 B.M.) was obtained at lower temperatures. In order to obtain further information about the polymeric nature of these complexes, we have determined their temperature dependence of magnetic susceptibilities. The observed χ-T data fitted the Bleaney-Bowers equation well,[3] confirming an essentially dimeric structure for both forms (*cf.* Fig. 1) with $J=242$ cm^{-1} and $g=2.10$ for the brown form, and $J=580$ cm^{-1} and $g=2.20$ for the orange form. The d-d bands of these two modifications are markedly different; the brown form showed three bands at 815, 667 and 457 mμ suggesting tetrahedral nature of the stereochemistry around the copper(II) ion,[2] whereas the orange form gave rise to a broad band at 1055 mμ with a shoulder at 855 mμ. In order to investigate some factors which lead to the formation of these two modifications, complexes with a substituent (R) at the 5-position of the benzene ring in (1) have been prepared. The complex

1) Y. Muto, M. Kato, H. B. Jonassen, H. N. Ramaswamy and K. Imai, the paper presented at the 10th International Conference on Coordination Chemistry, Nikko, September, 1967, Proceedings, p. 337.

2) M. Kato, Y. Muto, H. B. Jonassen, K. Iami, K. Katsuki and S. Ikegami, This Bulletin, **42**, 2555 (1969).

3) B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.*, **A 214**, 451 (1952).

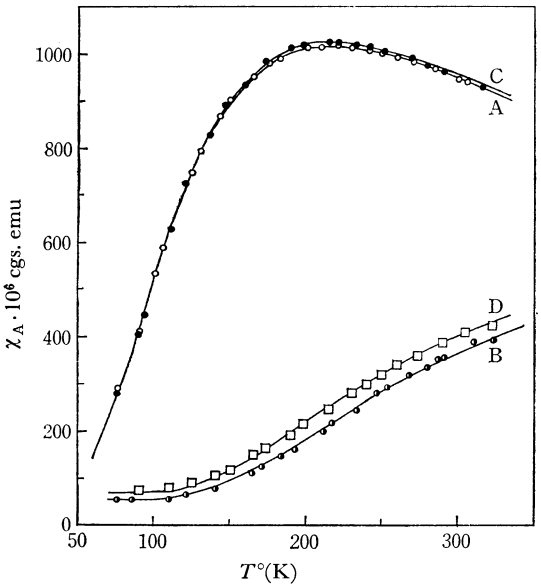

Fig. 1. Variation of magnetic susceptibilities with temperature.
A: R=H* brown form ○, B: R=H* orange form ◑, C: R=CH_3* ●, D: R=Cl* □.
The temperature independent paramagnetism (N_α)[3] is 60(A), 50(B), 60(C) and 60(D) in 10^{-6} cgs, emu respectively.
* *cf.* the text

with R=CH_3 was obtained only in a brown form at lower or higher temperatures (J=243 cm^{-1} and g=2.11), whereas the complex with R=Cl was obtained in an orange form (J=553 cm^{-1} and g=2.17). The complex with R=NO_2 was obtained only as an orange form; the shape of its χ-T curve at low temperatures indicated that it contained a small amount of a paramagnetic impurity. The appropriate values of J (574 cm^{-1}) and g (2.17) for this compound were derived from the χ-T data corrected for the impurity contribution. The details of such variations will be reported shortly. This seems to indicate that electron attracting groups (Cl, NO_2) lead preferably to the formation of the orange form, whereas electron donating group (CH_3) forms the brown complex preferably. The medium polarity of H might explain why the unsubstituted (R=H) complex forms both forms depending upon reaction conditions.

The complexes in the present study all exhibit a bridging phenolic C–O band at *ca.* 1550 cm^{-1}.[4] This indicates that the two copper(II) ions in a dimeric molecule are bridged by phenolic oxygen atoms.

4) C. M. Harris and E. Sinn, *J. Inorg. Nucl. Chem.*, **30**, 2723 (1968).