CHEMISTRY LETTERS, pp. 1401-1402, 1974. Published by the Chemical Society of Japan

BINUCLEAR COPPER(II) COMPLEX BRIDGED WITH ALKYLAMINE OXIDE, BIS[BIS(2-AMINOETHYL)METHYLAMINE OXIDE]DICOPPER(II) PERCHLORATE[1)]

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A copper(II) complex of bis(2-aminoethyl)methylamine oxide was synthesized and characterized by elemental analyses, magnetic susceptibility measurements, and IR and electronic spectroscopies. The compound has the binuclear structure bridged with alkylamine oxide. It has a distinct absorption in the near-ultraviolet region(31×10^3 cm^{-1}) which was assigned to the characteristic CT band of oxygen-bridged copper(II) complexes.

Although there have been reported a mumber of binuclear copper(II) complexes bridged with the oxygen of pyridine-N-oxide,[2)] copper(II) complexes bridged with alkylamine oxide have not yet been known. In this paper we report the synthesis and characterization of a binuclear copper(II) complexes with bis(2-aminoethyl)-methylamine oxide (abbreviated to aema-O), in which two copper(II) ions are bridged with oxygen of the alkylamine oxide(cf., Fig. 1).

Bis(2-aminoethyl)methylamine was prepared according to Mann's procedure.[3)] The amine oxide(aema-O) was obtained as colorless oil when a 3 % H_2O_2 solution of the amine was allowed to stand over night at room temperature, and concentrated under reduced predure. The copper complex was obtained as blue-violet prisms when aema-O and $Cu(ClO_4)_2 \cdot 6H_2O$ were mixed in ethanol with the 1 : 1 mole ratio. The product was recrystallized from 80 % ethanol.

Found: C, 14.50; H, 4.07; N, 10.12; Cu, 15.71 %. Calcd. as $[Cu\ aema\text{-}O](ClO_4)_2\text{-}H_2O$: C, 14.52; H, 4.14; N, 10.16; Cu, 15.36 %.

On the basis of the elemental analyses and the steric consideration of the ligand, the structural formula is most probably the one shown in Fig. 1.

The IR spectrum(in KBr) showed a broad absorption in the region of 1080~1150 cm^{-1}, indicating the presence of uncoordinated perchlorate ion. The band observed at 942 cm^{-1} with a medium intensity is certainly due to the N-O stretching vibration.[4), 5)] This value is a little lower than the ν(N-O) (950 cm^{-1}) of copper complexes of N,N-dialkyl-2-aminoethanol-N-oxide. Such a low-frequency shift may be due to the bridging of N-O group, as often observed for pyridine-N-oxide complexes.

The magnetic moment of this compound was 0.36 B.M. at room temperature(being calculated as $\mu_{eff} = 2.828\sqrt{\chi_A \times T}$). The magnetic susceptibilities gradually decrease from 56×10^6 to 40×10^{-6} c.g.s,e.m.u. with lowering of temperature (298~77 K).

The reflectance and the absorption spectra were shown in Fig. 2. It should be noted that in addition to the d-d band (16.8×10^3 cm^{-1} for reflectance and 15.3×10^3 cm^{-1} for absorption) strong absorption was observed at about 31×10^3 cm^{-1}. Since the free ligand has no absorption around 30×10^3 cm^{-1}, this band should be similar in its origin to the bands which were always observed for alkoxo- or hydroxo-bridged copper(II) complexes in the near-ultraviolet region ($25 \sim 30 \times 10^3$ cm^{-1}) provided with the intramolecular antiferromagnetic interaction.6), 7) These bands were attributed to the charge transfer transition from bridging oxygen to the vacant d-orbitals of copper(II) ions.8) The relatively high frequency (31×10^3) of the present complex can be well explained in terms of the relatively low electron density of the N-oxide oxygen compared to the alkoxide or hydroxide oxygen.

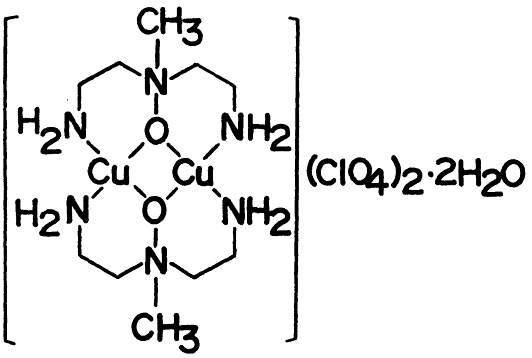

Fig. 1.

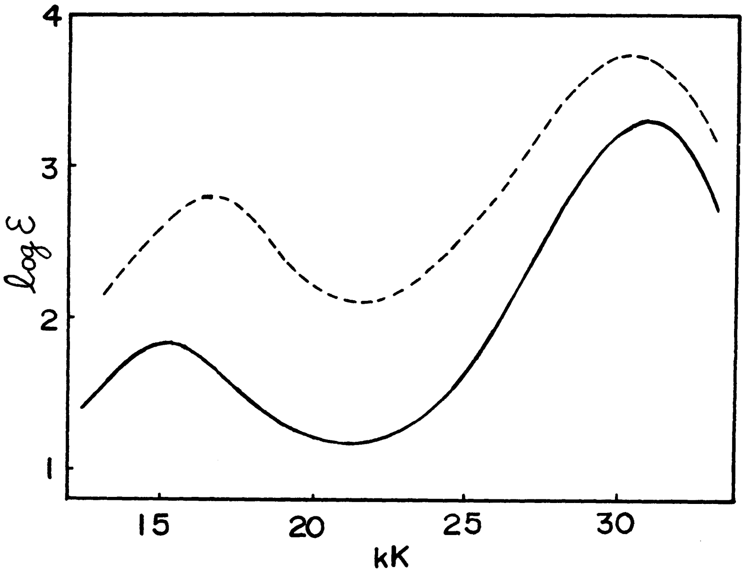

Fig. 2. Electronic spectra of $[Cu_2(aema\text{-}O)_2](ClO_4)_4$.
----- powder reflectance
—— ethanol(80 %) solution

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(Received September 28, 1974)