

New-Type of Copper(II) Complexes with a Subnormal Magnetic Moment Derived from *N,N'*-Bis(2-carboxyethyl)oxamide

Heijiro OJIMA and Kiyoko YAMADA

Department of Chemistry, Aichi Kyoiku University, Kariya, Aichi

(Received February 12, 1970)

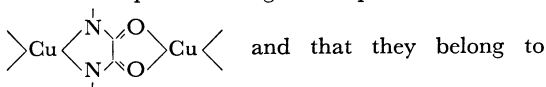
The present authors are continuing their syntheses and characterization of metal complexes coordinating negative amide nitrogen.¹⁾ This paper will report that the *N,N'*-bis-substituted-oxamidato copper(II) acts as a bidentate ligand to afford new-type copper(II) complexes with a subnormal magnetic moment: that is, a new ligand, *N,N'*-bis(2-carboxyethyl)oxamide, has been synthesized, and then three kinds of copper(II) complexes with this ligand (abbreviated, Na₂[Cu-CEoxd], [Cu-CEoxd-Cu-bipy], and [Cu(CEoxdH)(OH)]₂) have been isolated.

The [Cu-CEoxd-Cu-bipy] was obtained as yellowish-green fine crystals by mixing one mole of the Na₂[Cu-CEoxd] and one mole of mono-

(2,2'-bipyridyl)-copper(II) nitrate in a water solution in which the pH value had been adjusted at 9. Found for the tetra-hydrate, Cu, 21.50%; N, 9.99%; H₂O, 12.66%. Calcd for C₁₈H₁₆O₆N₄Cu₂·4H₂O, Cu, 21.78%; N, 9.60%; H₂O, 12.35%. Found for the anhydrous salt, Cu, 24.85%. Calcd for anhydrous salt, Cu, 24.85%.

The [Cu(CEoxdH)(OH)]₂ was obtained as green fine crystals by the reaction of one mole of Na₂[Cu-CEoxd] with one mole of copper(II) salt in a water solution at room temperature. Found for deca-hydrate, Cu, 27.38%; N, 6.18%; H₂O, 19.59%. Calcd for C₁₆H₂₀O₁₄N₄Cu₄·10H₂O, Cu, 27.43%; N, 6.05%; H₂O, 19.44%. Found for anhydrous salt, Cu, 34.12%; N, 7.59%. Calcd for anhydrous salt, Cu, 34.05%; N, 7.51%.

The values of the magnetic moment for the [Cu-CEoxd-Cu-bipy] and [Cu(CEoxdH)(OH)]₂ are obviously subnormal. This suggests that the mutual interaction between the two copper(II) ions must take place through the partial structure:



and that they belong to the category of "super exchange interaction."²⁾ Putting it concretely, the interaction may take place through a π -path way (Cu=N=C=C=O=Cu) set up by using $3d_{yz}$ (or $3d_{xz}$) orbitals of the cupric ions and $2p_{\pi}$ orbitals of the bridging oxamide group. These two complexes are new-type complexes with a subnormal magnetic moment.

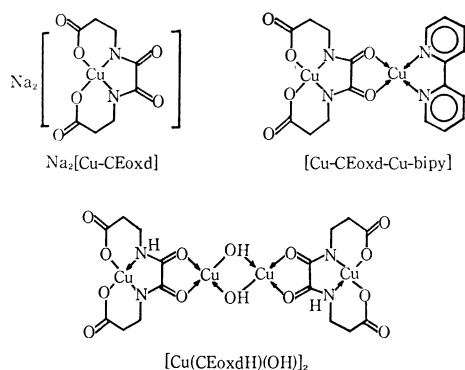


Fig. 1. Copper (II) complexes isolated.

TABLE 1. SOME PROPERTIES OF COPPER (II) COMPLEXES ISOLATED.

Ligand and its complex	Magnetic data				IR-spectra ^{c)}			
	$10^6 \chi_g$	$10^6 \chi_M$	μ_{eff} (BM)	T°K	ν_{N-H}	COOH	COO-Cu	amide I
Ligand CEoxdH ₄	—	—	—	—	3310	1700	d)	1645
Na ₂ [Cu-CEoxd]·4H ₂ O	2.86	1173.5	1.78	287				
anhydrous salt	3.44	1160.6	1.79	300	d)	d)	1630	1585 ^{b)}
[Cu-CEoxd-Cu-bipy]·4H ₂ O	1.32	385.4	1.10	287				
anhydrous salt	1.73	442.4	1.13	287	d)	d)	1654	1619
[Cu(CEoxdH)(OH)] ₂ ·10H ₂ O	2.61	605.3	1.27	286				
anhydrous salt ^{a)}	3.28	612.7	1.25	287	3350 ^{b)}	d)	1650	1635

a) The band which is due to the ν_{O-H} (bridged OH group) was observed at 3230 cm⁻¹.

b) Broad band. c) Anhydrous salts were used for the determinations. d) Disappeared.

1) H. Ojima, and K. Yamada, *Nippon Kagaku Zasshi*, **88**, 329, 333, 952, 1056 (1967); *ibid.*, **89**, 490 (1968); *ibid.*, **91**, 49 (1970).

2) M. Kato, H. B. Jonassen and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).