Syntheses of {Sulfato, *N*,*N*′-(2-pyridylalkyl)-oxamidatocopper(II)} copper(II)*[1]

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The present paper reports that the *N*,*N*′-bis-(2-pyridylalkyl)oxamidatocopper(II) acts as a bidentate ligand coordinating to cupric sulfate to form binuclear complexes with a subnormal magnetic moment: [Cu(PMoxd)-CuSO$_4$] and [Cu(PEoxd)-CuSO$_4$] (*cf.* Fig. 1). The PMoxdH$_2$ ligand was obtained in a 90% yield by the reaction 2 mol of 2-(aminomethyl)pyridine with 1 mol of diethyl oxalate at 150°C for 1 hr. Recrystallized from ethanol, mp 155—156°C. The PEoxdH$_2$ ligand was obtained similarly in a 95% yield using 2-(2-aminoethyl)pyridine and diethyl oxalate. Recrystallized from ethanol, mp 175—176°C. [Cu(PMoxd)-Cu(OH$_2$)$_2$]SO$_4$·5H$_2$O (A) was obtained as blue crystals by mixing 1 mol of the ligand and 2 mol of cupric sulfate in an aqueous solution at pH 5—6. Recrystallized from water. This complex was converted into [Cu(PMoxd)-CuSO$_4$] (B) concurrently with the elimination of 7 mol of water, by heating it at more than 80°C under vacuum conditions (*cf.* the change in the IR spectra, Fig. 2). The [Cu(PEoxd)-CuSO$_4$]·2.5H$_2$O (C) was isolated as greenish-blue crystals from an aqueous mixture of 1 mol of the PEoxdH$_2$ ligand and 2 mol of cupric sulfate, in which mixture the pH value had been adjusted to 6. Recrystallized from water. It can be understood, considering the analytical data, that the conspicuous spectral change in the SO$_4^{2-}$ region may be due to the change from ionic sulfate to chelated sulfate. The magnetic moment values of the complexes here isolated obviously reflect Cu-Cu interaction. It seems that the Cu-Cu interaction must take place through the π-pathway set up by using $3d_{yz}$(or $3d_{xz}$) orbitals of the cupric ions and $2p_\pi$ orbitals of the bridging oxamide group (*cf.* Fig. 3). When each sulfato complex was dissolved into an aqueous solution, the value of molar conductance fell into the range of 129—133 ℧/cm^2. This value reflects that a part of each sulfato complex changes into a divalent complex cation, [Cu(PMoxd)-Cu(OH$_2$)$_2$]$^{2+}$ or [Cu(PEoxd)-Cu(OH$_2$)$_2$]$^{2+}$.

Table 1. Properties of complex

Complex	Color	Analysis ( ): Calcd			Magnetic Moment		IR-Spectra amide-I[a)]
		Cu %	Nitrogen %	H$_2$O	μ_{eff} (BM)	T°K	
(A)	blue	22.57 (20.58)	9.14 (9.07)	20.47 (20.42)	0.97	292	1655
(B)	green	25.85 (25.85)			0.88	292	1645
(C)	greenish-blue	22.57 (22.51)	9.76 (9.92)	7.75 (7.98)	1.25	287	1635
(D)	green	24.20 (24.47)			1.15	288	1639

a) Ligand PMoxdH$_2$, amide-I 1645 cm^{-1}; ligand PEoxdH$_2$, amide-I 1659 cm^{-1}. (D): anhydride of (C)

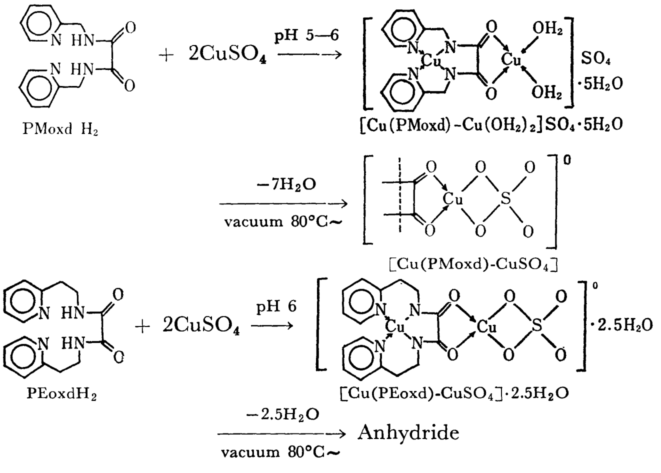

Fig. 1. Formation of copper(II) complexes with a subnormal magnetic moment.

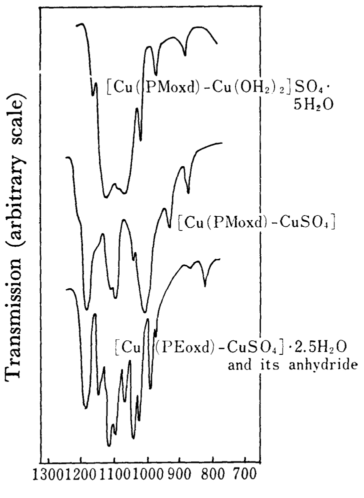

Fig. 2. IR-spectra of SO$_4^{2-}$ region.

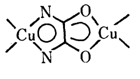

Fig. 3

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*[1] Syntheses and Characterization of Metallic Complexes in which the Negative Amide Nitrogen Coordinates. X. Recent note: H. Ojima, K. Yamada, This Bulletin, **43**, 1601 (1970).