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Syntheses and Magnetic Properties of Three Modifications of Dichloro[2-(hydroxymethyl)pyridine *N*-oxide]copper(II)

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Three modifications of dichloro[2-(hydroxymethyl)pyridine *N*-oxide]copper(II), $CuCl_2(2\text{-}CH_2OH\cdot pyo)$, were prepared and characterized by the temperature dependences of their magnetic susceptibilities and their IR spectra. The greenish-yellow modification shows ferromagnetic behavior ($\theta/K=+20$), whereas both the yellow and deep-green modifications exhibit a dimer type of antiferromagnetism ($J/cm^{-1}=-585$ and -565). The hemi adducts with the empirical formula of $CuCl_2(2\text{-}CH_2OH\cdot pyo)\cdot 1/2L$, where $L=C_2H_5OH$ and H_2O, were also isolated. The structural assignments for the three modifications and the two adducts were made on the basis of the similarity of their magnetic and spectral properties to those of dimeric copper(II) pyridine *N*-oxide complexes, and the whole preparative scheme of these complexes was interpreted in terms of their structural features.

In a previous study of copper(II) halide complexes with substituted pyridine *N*-oxides,[1] we found that dichloro[2-(hydroxymethyl)pyridine *N*-oxide]copper(II), $CuCl_2(2\text{-}CH_2OH\cdot pyo)$,[2] formed two magnetically different modifications: a greenish-yellow modification with a normal magnetic moment at room temperature and a yellow one with a subnormal moment. The normal moment is unusual, since many 1:1 complexes of copper(II) chloride with substituted pyridine *N*-oxides, including 3-and 4-(hydroxymethyl)pyridine *N*-oxides, exhibit antiferromagnetic interaction between the copper ions.[1]

This study was initiated in order to investigate the factors which cause such a difference in the magnetic properties. We have now prepared another modification and its hemi adducts with ethanol or water. A complex with the empirical formula of $Cu(2\text{-}CH_2OH\cdot pyo)_2(ClO_4)_2$ has also been prepared to help the investigation of the structural differences among the three modifications. We wish to report here the results of our preparative, IR spectral, and cryomagnetic studies of these complexes.

Results and Discussion

Preparation Scheme. The preparation scheme of the complexes studied in this work is shown diagrammatically in Fig. 1, together with the colors and the room-temperature magnetic moments. Compound **1** was easily converted into **2** either by keeping it over calcium chloride in a vacuum desiccator at room temperature for about one month[1] or by recrystallizing it from 1-butanol. On the other hand, attempts to convert **2** into **1** were unsuccessful. Compound **5** was readily converted into the hydrated form, **4**, on standing in the air at room temperature, whereas **1** and

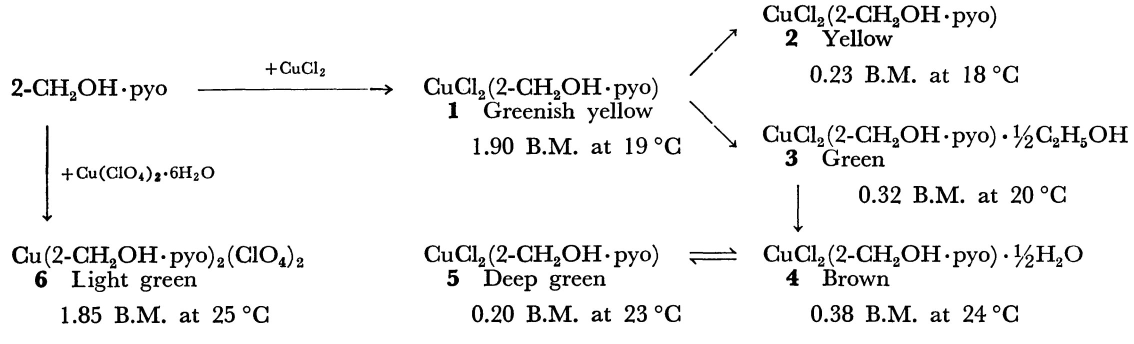


Fig. 1. Preparation scheme of complexes.

Table 1. Analytical data

	Complex	Found (%)				Calcd (%)			
		C	H	N	Cu	C	H	N	Cu
1	$CuCl_2(2\text{-}CH_2OH\cdot pyo)$	27.73	2.81	5.42	24.54	27.76	2.72	5.40	24.48
2	$CuCl_2(2\text{-}CH_2OH\cdot pyo)$	27.66	2.72	5.30	24.48	27.76	2.72	5.40	24.48
3	$CuCl_2(2\text{-}CH_2OH\cdot pyo)\cdot \frac{1}{2}C_2H_5OH$	27.72	2.66	5.45	22.46	29.75	3.57	4.96	22.48
4	$CuCl_2(2\text{-}CH_2OH\cdot pyo)\cdot \frac{1}{2}H_2O$	26.84	2.96	5.15	23.65	26.83	3.00	5.22	23.66
5	$CuCl_2(2\text{-}CH_2OH\cdot pyo)$	27.58	2.66	5.33	24.64	27.76	2.72	5.40	24.48
6	$Cu(2\text{-}CH_2OH\cdot pyo)_2(ClO_4)_2$	27.83	2.69	5.29	12.46	28.11	2.75	5.46	12.39

2 do not form such a hydrate under the same conditions.

In contrast with 2-(hydroxymethyl)pyridine *N*-oxide, 3- and 4-(hydroxymethyl)pyridine *N*-oxides form only one kind of 1:1 complex with copper(II) chloride; these complexes show subnormal magnetic moments.[1] This difference in the formation of 1:1 complexes may be due to the different ligand natures of the oxides: 2-(hydroxymethyl)pyridine *N*-oxide may coordinate to a metal ion by both the *N*-oxide and alcohol oxygens to form a six-membered chelate ring, whereas 3- and 4-(hydroxymethyl)pyridine *N*-oxides are not able to form such a chelate. This was confirmed by the observation that 2-(hydroxymethyl)pyridine *N*-oxide forms a 2:1 complex with copper(II) perchlorate (Compound **6**), unlike other aromatic amine *N*-oxides, which generally form 4:1 or 6:1 complexes with copper(II) perchlorate.[1,3-5]

The ethanol adduct, **3**, readily loses its ethanol and absorbs water in the air to give Compound **4**. As a consequence, the analytical data of carbon, nitrogen, and hydrogen for this compound were unsatisfactory. However, the copper analysis carried out immediately after the preparation indicated the formulation of **3**; the weight loss after the sample had stood in the air for 24 h at room temperature also agreed with that calculated on the basis of the structural change from **3** to **4** (*cf.* Table 1).

IR Spectra. The IR spectra of Compounds **1**, **2**, **4**, **5**, and **6** were measured in order to obtain information about the coordination mode of $2\text{-}CH_2OH\cdot pyo$ in these complexes. The IR frequencies pertaining to the alcohol- and *N*-oxide-oxygen atoms may be correlated with the geometric structures of the complexes and with the strength in the oxygen–metal coordination bond. The results for the O–H stretching vibration (νO–H), the N–O stretching vibration (νN–O), and the N–O bending vibration (δN–O) are shown in Fig. 2. For comparison, Fig. 2 also includes the IR spectrum of the copper(II) chloride complex with 2-ethylpyridine *N*-oxide, $CuCl_2(2\text{-}C_2H_5\cdot pyo)$, to which an oxygen-bridged binuclear structure has been assigned.[1]

These complexes can be classified into two groups based on the observed IR spectra and their magnetic moments: A) Compounds **2**, **4**, and **5**, which show subnormal magnetic moments, and B) Compounds **1** and **6**, which exhibit normal moments.

νO–H: In each of the complexes the strong band observed in the 3100—3500 cm^{-1} region may be assigned to the O–H stretching vibration of the CH_2OH group.[6,7] In support of this assignment, no band is observed in this region for the $CuCl_2(2\text{-}C_2H_5\cdot pyo)$ complex(*cf.* Fig. 2). There is a significant difference in the band position between the A and B groups; *i.e.*, the B compounds show the band at a frequency of less than 3300 cm^{-1}, whereas the A compounds exhibit it at *ca.* 3400 cm^{-1}(*cf.* Fig. 2). This fact suggests that the coordination mode of the OH group in the Group A complexes differs from that in the Group B complexes. The other band, at 3500 cm^{-1} in Compound **4**, may be due to the O–H stretching vibration of the water in this compound, because this band is absent in the spectrum of the anhydrous compound, **5**.

νN–O and δN–O: In the spectra of dimeric copper(II) halide complexes with aromatic amine *N*-oxides, a strong and sharp band at *ca.* 1200 cm^{-1} was assigned to the stretching vibration of the N–O group bridging two copper ions by the oxygen atom.[8,9] The present complexes exhibit the N–O band at 1190—1200 cm^{-1}. Figure 2 shows that the band frequencies in the Group A compounds (1190—1196 cm^{-1}) are lower than those in the Group B componds (1200 cm^{-1}). The lowering of νN–O is possibly due to a decrease in the N–O double-bond character,[9,10] resulting from stronger Cu–O–Cu bridging bonds formation for the A complexes than for the B complexes. The same trend was observed in the frequencies of the δN–O band of these complexes in the region of 840—860 cm^{-1}(*cf.* Fig. 2):[8] the band appeared at *ca.* 843 cm^{-1} for the A complexes and at *ca.* 860 cm^{-1} for the B complexes.

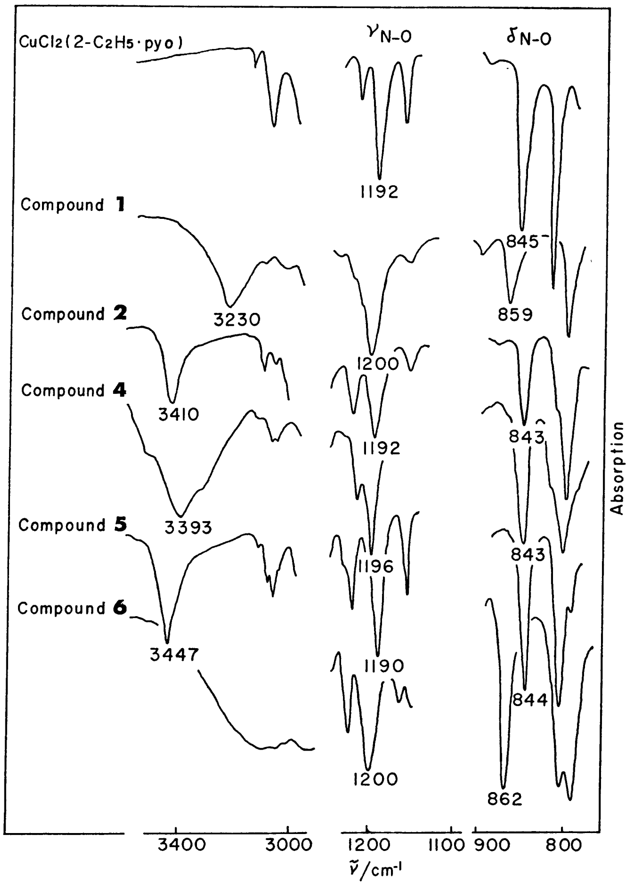


Fig. 2. IR spectra of complexes.

The IR spectrum of Compound **6** shows a broad and strong band around 1100 cm^{-1}, indicating the presence of an uncoordinated perchlorate ion.

For Compound **3**, accurate IR measurements could not be carried out because of its instability in the air.

Magnetic Susceptibility. The magnetic susceptibilities of Compounds **1**—**6** were measured in the temperature range of 80—300 K; the results are shown in Figs. 3 and 4. Their room-temperature magnetic moments, given in Fig. 1, were calculated from this expression:

$$\mu_{\text{eff}} = 2.83\sqrt{(\chi_A - N\alpha)\cdot T} \tag{1}$$

where χ_A is the molar magnetic susceptibility corrected for the diamagnetism of the constituted atoms using Pascal's constants (2-CH_2OH·pyo, −70; C_2H_5OH, −34; H_2O, −13; Cu^{2+}, −11; Cl^-, −26; ClO^-_4, −34 in 10^{-6} cgs emu mol^{-1})11) and, where $N\alpha$ is the temperature-independent paramagnetism per gram-ion of copper(II).** The $N\alpha$ values for Compounds **2**, **3**, **4**, and **5** were obtained from the analyses of their χ_A *vs.* T data (see below). For the other compounds, $N\alpha$ was assumed to be 60×10^{-6} cgs emu.12)

The susceptibility data of Compound **1** follow the Curie-Weiss law in the temperature range studied(*cf.* Fig. 3). The positive Weiss constant, $\theta/\mathrm{K}=+20$, estimated from the slope of the $(\chi_A-N\alpha)^{-1}$ *vs.* T plots, indicates the existence of a ferromagnetic interaction between the copper ions in this complex.

The susceptibilities of Compounds **2**—**5** over the temperature range are very low(*cf.* Fig. 4), indicating the existence of a very strong antiferromagnetic interaction in these complexes. Their cryomagnetic data are represented by the Bleaney-Bowers equation 213) for isotropic exchange in a copper(II) dimer (*cf.* Fig. 4):

$$\chi_A=\frac{N\beta^2g^2}{3kT}\left[1+\frac{1}{3}\exp\frac{-2J}{kT}\right]^{-1}(1-P)+\frac{N\beta^2g_i^2}{4kT}\cdot P+N\alpha \qquad (2)$$

where N is Avogadro's number, g is the average g factor of the binuclear complex, β is the Bohr magneton, k is the Boltzmann constant, J is the exchange integral, P is the mole fraction of the noncoupled Cu(II) impurity, and g_i is the average g factor for the impurity. The second term in Eq. 2 was added to account for the presence of the small amount of a paramagnetic impurity, which was assumed to obey the Curie law.

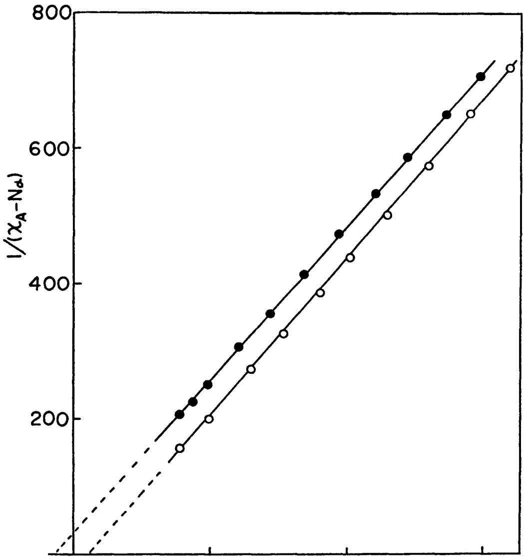


Fig. 3. Variation of reciprocal magnetic susceptibilities with temperature. ○=Compound **1**, ●=Compound **6**.

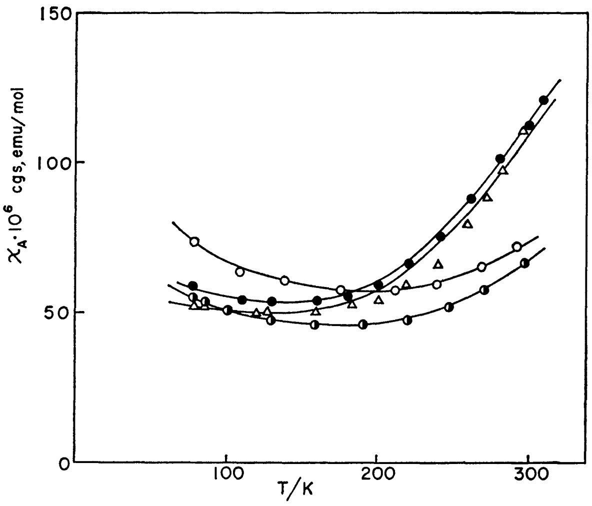
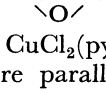


Fig. 4. Temperature dependence of magnetic susceptibilities of (○) Compound **2**, (●) Compound **3**, (△) Compound **4**, and (◑) Compound **5**.
The solid curves were calculated from Eq. 2 using the parameters listed in Table 2.

The J, $N\alpha$, and P values listed in Table 2 were estimated from the best fit of their cryomagnetic data to Eq. 2, assuming $g=g_i=2.20$. It is noteworthy that the values of $N\alpha(37\times10^{-6}$—46×10^{-6} cgs emu) are much smaller than that generally accepted in published works (60×10^{-6} cgs emu). However, it should also be pointed out that the magnitude of $N\alpha$ is dependent on the ligand-field strength, the stereochemistry around the metal ion, and the covalency of the bond between the metal ion and the ligand. The similarity of the magnetic properties of these complexes to those of a number of 1:1 aromatic amine *N*-oxide copper(II) halide complexes indicates that they are composed of binuclear structural units in crystals similar to that of dichloro(pyridine *N*-oxide)copper(II), $CuCl_2$(pyo).14,15)

The χ_A *vs.* T data of Compound **6** follow the Curie-Weiss law with a small value of the Weiss constant, $\theta/\mathrm{K}=-5$(*cf.* Fig. 3), indicating the absence of any appreciable antiferromagnetic interaction in this compound. It is thus probable that Compound **6** is composed of the monomeric structural units shown in (6). The IR spectral data are also consistent with this assignment.

Structure and Magnetism. On the basis of the experimental results and discussions described in the preceding sections, structural assignments for the three modifications(Compounds **1**, **2**, and **5**) may be made as follows. The most probable structure for Compound **1** is either (1) in which the monomeric $CuCl_2$(2-CH_2-OH·pyo) units are bridged by the Cu–O out-of-plane bonds or (2) in which the copper ions are bridged with chloride ions from the adjacent monomer moieties. The possible structures for both Compounds **2** and **5** are either (3) in which the pyridine rings are nearly perpendicular to the  $\mathrm{Cu}\begin{smallmatrix}\diagup\mathrm{O}\diagdown\\ \diagdown\mathrm{O}\diagup\end{smallmatrix}\mathrm{Cu}$ plane, in a manner similar to that in the $CuCl_2$(pyo) complex14,15) or (4) in which the rings are parallel to the coordination

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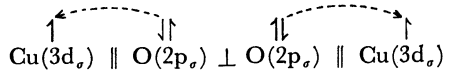
** The value of the molar magnetic susceptibility in m^3 mol^{-1} (SI) can be obtained by multiplying the value in cm^3 mol^{-1} (cgs) by $4\pi\times10^{-6}$.

Table 2. Magnetic parameters

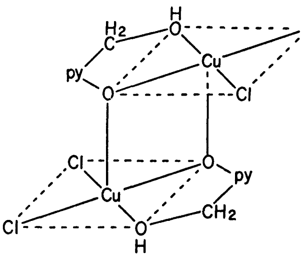
		J/cm^{-1}	$N\alpha$/cgs emu	P/mol
2	$CuCl_2(2\text{-}CH_2OH\cdot pyo)$	−585	44×10^{-6}	5×10^{-3}
3	$CuCl_2(2\text{-}CH_2OH\cdot pyo)\cdot\frac{1}{2}C_2H_5OH$	−470	46×10^{-6}	2×10^{-3}
4	$CuCl_2(2\text{-}CH_2OH\cdot pyo)\cdot\frac{1}{2}H_2O$	−475	46×10^{-6}	1×10^{-3}
5	$CuCl_2(2\text{-}CH_2OH\cdot pyo)$	−565	37×10^{-6}	3×10^{-3}

plane. However, a binuclear structure bridging copper ions with chloride ions is very unlikely for both Compounds **2** and **5**, since dimeric or polymeric copper(II) complexes containing a chloride bridge do not show any strong antiferromagnetism.[16,17] For Compound **1**, consequently, Structure (1) is considered to be more probable than (2), based on the ready conversion of **1** into **2**: the structural change from (1) to (3) or (4) is accompanied by no breaking of chemical bonds, while the change from (2) to (3) or (4) require a breaking and recombination of the coordinate bonds; thus, the former process may take place more easily than the latter. The ferromagnetism observed in Compound **1** may, therefore, be explained, as in the case of $[Cu(NO_3)_2(pyo)_2]_2$,[18] in terms of the 90° cation-anion-cation type of superexchange interaction discussed by Goodenough[19] and Kanamori.[20] The pathway is given by Ginsbergs' notation[21] as follows:

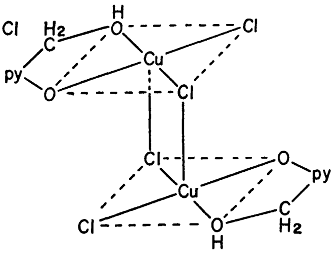


$$Cu(3d_\sigma)\parallel O(2p_\sigma)\perp O(2p_\sigma)\parallel Cu(3d_\sigma)$$

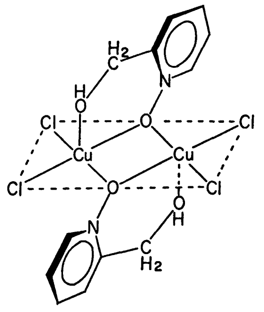
where ‖ and ⊥ indicate spin parallel and antiparallel interactions through orbitals in non-orthogonality and orthogonality respectively and, where the dashed arrows indicate partial electron transfer through the overlapping orbitals. The scheme represents the simultaneous partial electron transfer from a bridging oxygen atom to the pair of copper ions and the successive intra-atomic spin coupling on the oxygen atom. On the other hand, unambiguous structural assignments for Compounds **2** and **5** to either (3) or (4) are not possible on the basis of the present IR and magnetic data. However, the strong antiferromagnetism observed in these complexes may be interpreted on the basis of structure (3) or (4) in essentially the same manner as in the case of $CuCl_2(pyo)$, where we have previously emphasized the σ-type exchange pathway of $Cu(3d_\sigma)$-$O(2p_\sigma)$-$Cu(3d_\sigma)$.[1]



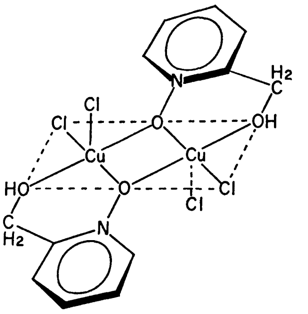
(1)



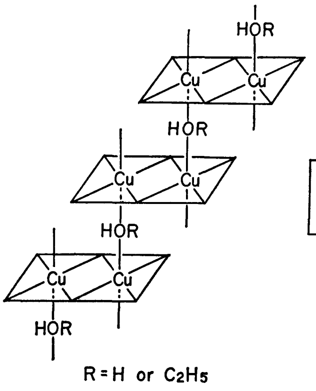
(2)



(3)

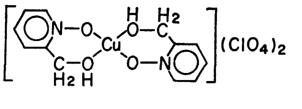


(4)



R = H or C_2H_5

(5)



(6)

The bridging structure of the adducts, **3** and **4**, is considered to be essentially the same as that of the non-adducts with low magnetic moments, judging from their very similar magnetic behavior and the easy interconversion between Compounds **4** and **5**(*cf.* Fig. 1). The easy conversion of the ethanol adduct to the water adduct in the air suggests that the frameworks of the structures of the two compounds are the same; the adding molecules occupy the same position in each structure. The polymeric structure of type (5) can explain all these facts consistently since (a) this structure requires the one-adding-molecule—one-dimer relation, *i.e.*, the formation of hemi adducts, and (b) a water molecule of a higher coordinating ability replaces an ethanol molecule of a lower coordinating ability at the same coordination site of a dimer without destroying the framework of the whole polymeric structure. The **3** and **4** adducts exhibit a definitely weaker antiferromagnetic interaction than the two non-adducts, **2** and **5**, perhaps because the formation of an additional coordinate bond by a ligand at the fifth or sixth coordination site of Cu(II) weakens the in-plane coordinate bonds through which the spin coupling takes place, leading to a weaker antiferromagnetic interaction.

Experimental

Syntheses. *Compound **1***: A solution of $CuCl_2$ (1.57 g, 11 mmol) in ethanol (50 ml) was added to a solution of 2-

CH_2OH·pyo (1.25 g, 10 mmol) in ethanol (50 ml). The mixed solution was stirred at *ca.* 70 °C for 1/2 h. The greenish-yellow microcrystals thus produced were filtered off, washed with ethanol, and dried at 70—80 °C.

Compound ***2***: This was obtained by recrystallizing compound **1** from 1-butanol.

Compound ***3***: A solution of Compound **1** (1 g) in ethanol (500 ml) was allowed to stand for several days at *ca.* 5 °C in a freezer. After this period, green crystals were produced. The crystals separated were washed with ethanol and dried in a vacuum desiccator over calcium chloride at room temperature.

Compound ***4***: This was obtained when Compound **3** was allowed to stand overnight in the air.

Compound ***5***: This was obtained when the hydrate complex **4** was dehydrated in a vacuum desiccator at 70 °C over phosphorus pentaoxide.

Compound ***6***: A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (1.08 g, 3 mmol) in ethanol (30 ml) was added to a solution of 2-CH_2OH·pyo (0.75 g, 6 mmol) in ethanol (30 ml). After the mixed solution has been concentrated to a third of its volume, it was allowed to stand for few days at *ca.* 5 °C in a freezer. The green crystals thus precipitated were collected, washed twice with a small quantity of ethanol and once with ether, and dried at *ca.* 70 °C.

The results of the elemental analyses are given in Table 1.

Physical Measurements. The IR spectral measurements were made with a Hitachi EPI-G2 spectrophotometer in 400—4000 cm^{-1} region on Nujol mulls. The magnetic susceptibilities in the temperature range of 80—300 K were determined by the Gouy method for Compounds **1**, **2**, **4**, **5**, and **6** and by the Faraday method for Compound **3**.

References

1) Y. Muto, M. Kato, H. B. Jonassen, and L. C. Cusachs, *Bull. Chem. Soc. Jpn.*, **42**, 417 (1969).

2) ·pyo is used as abbreviation for the C_5H_4NO group, and pyo, for unsubstituted pyridine *N*-oxide.

3) R. L. Carlin, *J. Am. Chem. Soc.*, **83**, 3773 (1967).

4) R. Whyman, W. E. Hatfield, and J. S. Paschal, *Inorg. Chim. Acta*, **1**, 113 (1967).

5) Recently, Okawa *et al.* reported the preparation of $Cu(2\text{-}CH_2OH \cdot pyo)_n(ClO_4)_2$ (n=2 and 4): H. Okawa, H. Matsubara, T. Higuchi, and S. Kida, *Memoirs of the Faculty of Science, Kyushu University, Series C, Chemistry*, **9**, 223 (1975).

6) D. Knetsch and W. L. Croeneveld, *Inorg. Chim. Acta*, **7**, 81 (1973).

7) J. O. Miners and E. Sinn, *Bull. Chem. Soc. Jpn.*, **46**, 1457 (1973).

8) S. Kida, J. V. Quagliano, J. A. Walmsley, and S. Y. Tyree, *Spectrochim. Acta*, **19**, 189 (1963).

9) Y. Muto and H. B. Jonassen, *Bull. Chem. Soc. Jpn.*, **39**, 58 (1966).

10) W. E. Hatfield, Y. Muto, H. B. Jonassen, and J. S. Paschal, *Inorg. Chem.*, **4**, 97 (1965).

11) P. W. Selwood, "Magnetochemistry," Interscience Publishers, New York (1956), pp. 78, 91.

12) B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, **1959**, 1359.

13) B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, **214**, 451 (1952).

14) H. L. Schafer, J. C. Morrow, and H. M. Smith, *J. Chem. Phys.*, **42**, 504 (1965).

15) R. S. Sager, R. J. Williams, and W. H. Watson, *Inorg. Chem.*, **6**, 951 (1967).

16) R. D. Willet, C. Dwiggins, Jr., R. F. Kruh, and R. E. Rundle, *J. Chem. Phys.*, **38**, 2429 (1963).

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

18) W. E. Hatfield, J. A. Barnes, D. Y. Jeter, R. Whyman, and E. R. Jones, Jr., *J. Am. Chem. Soc.*, **92**, 4982 (1970).

19) J. B. Goodenough, "Magnetism and the Chemical Bond," Interscience Publishers, New York (1963), p. 180.

20) J. Kanamori, *J. Phys. Chem. Solids*, **10**, 87 (1959).

21) A. P. Ginsberg, *Inorg. Chem. Acta Rev.*, **5**, 45 (1971).