

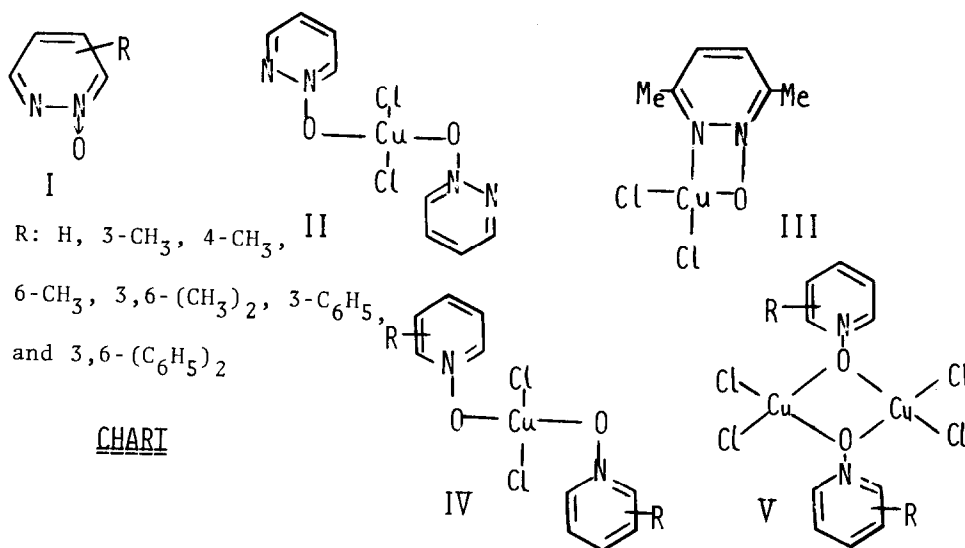
## Copper-complexes of Pyridazine N-Oxides; The Synthesis and X-ray Studies

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Nature of a large number of pyridine N-oxide-metal complexes<sup>1)</sup> has been investigated in details, and pyridazine and its derivatives are also known to afford complexes with a variety of metal ions.<sup>2)</sup> However, no attention has been given to complex formation between pyridazine N-oxides(I) and metal ions.<sup>3)</sup>

It is interesting to examine the structures and properties of the complexes of I because I has two available coordination centers, i.e., nitrogen and oxygen atoms, having unshared electron pairs. We describe herein the formation of pyridazine N-oxides(I) with cupric chloride, and the crystal structures of the two modes of the arrangement(II and III in the Chart).



The complexes were prepared by a reaction of I with CuCl<sub>2</sub>·2H<sub>2</sub>O in MeOH. All examined I provided crystalline complexes in moderate yields. The Table

shows the compositions, yields, and some physical data of the complexes.

TABLE

I	Complex	mp	Yield(%)	ir(N-O)cm <sup>-1</sup> (KBr) <sup>4)</sup>	
				Free I	Complex
C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> O	(I) <sub>2</sub> CuCl <sub>2</sub>	182-183°(dec.)	82	1318	1265
6-CH <sub>3</sub> -C <sub>4</sub> H <sub>3</sub> N <sub>2</sub> O	(I) <sub>2</sub> CuCl <sub>2</sub>	155-156.5°	65	1320	1275
3-CH <sub>3</sub> -C <sub>4</sub> H <sub>3</sub> N <sub>2</sub> O	(I) <sub>2</sub> CuCl <sub>2</sub>	182.5-183.5°	73	1323	1260
4-CH <sub>3</sub> -C <sub>4</sub> H <sub>3</sub> N <sub>2</sub> O	(I)CuCl <sub>2</sub>	185-187°(dec.)	61	1305	1250
3,6-(CH <sub>3</sub> ) <sub>2</sub> -C <sub>4</sub> H <sub>2</sub> N <sub>2</sub> O	(I)CuCl <sub>2</sub>	191-193°(dec.)	75	1325	1230
	(I) <sub>2</sub> CuCl <sub>2</sub>	173-175°			1272
3-C <sub>6</sub> H <sub>5</sub> -C <sub>4</sub> H <sub>3</sub> N <sub>2</sub> O	(I) <sub>2</sub> CuCl <sub>2</sub>	174-176°(dec.)	86	1345	1240
3,6-(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> -C <sub>4</sub> H <sub>2</sub> N <sub>2</sub> O	(I) <sub>2</sub> CuCl <sub>2</sub>	205-207°	91	1365	1330,1305,1260

The N-oxides of unsubstituted pyridazine, and of 6-methyl-, 3-methyl-, 3-phenyl-, and 3,6-diphenylpyridazines afforded 2:1 complexes of empirical formula (I)<sub>2</sub>CuCl<sub>2</sub>, while those of 4-methyl- and 3,6-dimethylpyridazines afforded 1:1 complexes of (I)CuCl<sub>2</sub>. The compositions of the complexes were constant in regard to each N-oxide although molar ratio of I to CuCl<sub>2</sub>·2H<sub>2</sub>O in the reaction mixture was changed from 1:2 to 2:1. So far as we have checked, (C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>O)<sub>2</sub>CuCl<sub>2</sub> and (6-CH<sub>3</sub>-C<sub>4</sub>H<sub>3</sub>N<sub>2</sub>O)<sub>2</sub>CuCl<sub>2</sub> did not change their compositions even when they were treated with an excess of CuCl<sub>2</sub>·2H<sub>2</sub>O, and also, (4-CH<sub>3</sub>-C<sub>4</sub>H<sub>3</sub>N<sub>2</sub>O)CuCl<sub>2</sub> did not change its composition by the action of excess 4-CH<sub>3</sub>-C<sub>4</sub>H<sub>3</sub>N<sub>2</sub>O, the starting material: being recovered after work-up.

Meanwhile, of those, only [3,6-(CH<sub>3</sub>)<sub>2</sub>-C<sub>4</sub>H<sub>2</sub>N<sub>2</sub>O]CuCl<sub>2</sub> was an exception which afforded [3,6-(CH<sub>3</sub>)<sub>2</sub>-C<sub>4</sub>H<sub>2</sub>N<sub>2</sub>O]<sub>2</sub>CuCl<sub>2</sub> by treatment with excess 3,6-(CH<sub>3</sub>)<sub>2</sub>-C<sub>4</sub>H<sub>2</sub>N<sub>2</sub>O.

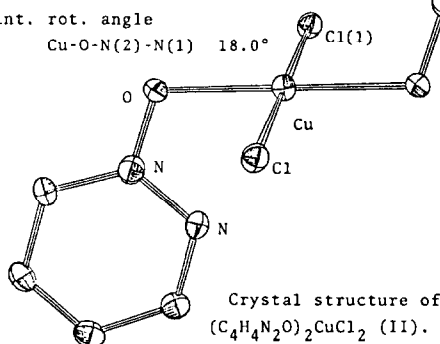
While the ir spectra of free I showed strong absorptions in the region 1300-1365cm<sup>-1</sup> due to the N-O stretching, those complexes exhibited intense absorptions at 1230-1275cm<sup>-1</sup>. This suggests that the energy of N-O stretching is lowered in a complex and this lowering arises from a decrease of the N-O double bond character by the coordination, although detailed assignment of the absorptions: have not been achieved.

In order to obtain confirmation of the structures directly, X-ray studies were carried out on (C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>O)<sub>2</sub>CuCl<sub>2</sub>(II) and [3,6-(CH<sub>3</sub>)<sub>2</sub>-C<sub>4</sub>H<sub>2</sub>N<sub>2</sub>O]CuCl<sub>2</sub>(III). The molecular geometries obtained from the analysis of the data of II and III are shown in the Figures (the crystal data and the conditions of analysis are shown in Footnote 5).

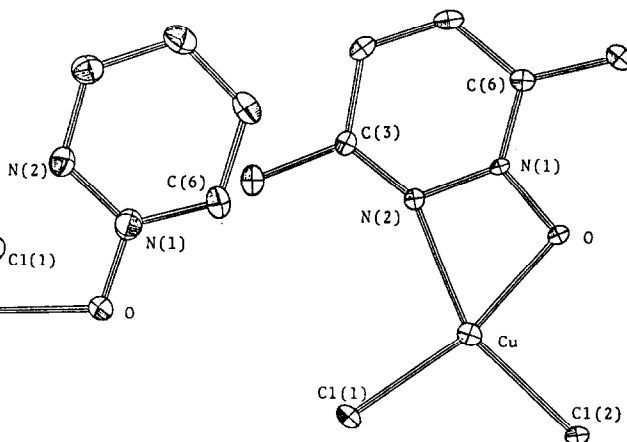
bond lengths(Å) and angles(deg.)			
Cl(1)-Cu	2.245	Cl(1)-Cu-O	90.9
Cu-O	1.984	Cu-O-N(1)	110.6
O-N(1)	1.293	O-N(1)-N(2)	115.7
N(1)-C(6)	1.352	C(6)-N(1)-N(2)	124.2
N(1)-N(2)	1.317	[N(2)-Cu-O	83.4]
[Cu-N(2)	2.693]		

int. rot. angle

Cu-O-N(2)-N(1) 18.0°



bond lengths(Å) and angles(deg.)			
Cl(1)-Cu	2.184	Cl(1)-Cu-Cl(2)	101.8
Cl(2)-Cu	2.181	Cl(1)-Cu-N(2)	102.2
Cu-N(2)	2.142	Cl(2)-Cu-O	91.8
Cu-O	1.998	N(2)-Cu-O	64.2
O-N(1)	1.317	Cu-O-N(1)	96.3
N(1)-N(2)	1.358	O-N(1)-N(2)	110.9
N(2)-C(3)	1.292	N(1)-N(2)-Cu	88.7
N(1)-C(6)	1.324		



Crystal structure of  $[3,6-(CH_3)_2-C_4H_2N_2O]CuCl_2$  (III).

## FIGURES

### Molecular Structure of II.

The structure of II is similar to the assumed structure which have been drawn for complexes of some pyridine N-oxides, *i.e.*,  $(RC_5H_4NO)_2CuCl_2$ .<sup>1a)</sup> The geometry of the coordination in II is almost square planar and two pyridazine N-oxide molecules are located oppositely being linked by Cu-O bonds(trans).

And the interactions are scarcely recognizable between the copper atom and the nitrogen atoms at the 2-positions of the N-oxide molecules (Cu-N(2)=2.69Å).

### Molecular Structure of III.

III has a monomeric structure in which the configuration of the coordination around the copper atom is planar but very deformed from a square. N(2)-Cu-O has an angle of 64.2°, N(2)-Cu-Cl(1) has an angle of 102.2°, and the Cl(1)-Cu-Cl(2) angle is 101.8°, the Cl(2)-Cu-O angle being 91.8 degree.

Bonds Cu-O, O-N(1), N(1)-N(2) and N(2)-Cu form a strained quadrangle. Thus, it is shown that both the oxygen and the nitrogen atoms at the 2-position of N-oxide molecule can coordinate simultaneously, and the molecule forms a chelate type complex in certain case(s) of I.

This phenomenon presents a striking contrast to the case of 1:1 adduct of pyridine N-oxide series, in which  $(RC_5H_4NO)CuCl_2$  have dimeric structures, i.e.,  $(L)_2(CuCl_2)_2$  (V).<sup>1c,d)</sup>

As long as we have tried, the pyridazine molecules in  $(C_4H_4N_2O)_2CuCl_2$ ,  $(6-CH_3-C_4H_3N_2O)_2CuCl_2$ , and  $[3,6-(CH_3)_2-C_4H_2N_2O]CuCl_2$  were entirely replaced by the  $(CH_3)_2SO$  molecules when these complexes were treated with excess DMSO resulting in precipitation of almost quantitative  $(DMSO)_2CuCl_2$  and liberation of the quantitative amounts of I. These facts contrast with the case of the complexes of pyridine N-oxide series, in which  $(L)_2CuCl_2$  give  $(L)(DMSO)CuCl_2$ ,<sup>1a,d)</sup> and indicate that the coordination ability of I towards  $CuCl_2$  is weaker than pyridine N-oxides. Further studies on these complexes are presently undertaken (reactivity and synthetic applications etc.).

#### FOOTNOTES

- 1) A.R. Katritzky and J.M. Lagowski, Chemistry of the Heterocyclic N-oxides, pp.160, Academic Press, London & N.Y. (1971) and references cited therein c.g.,  
 a) Y. Muto and H.B. Jonassen, Bull. Chem. Soc. Jap., 39, 58 (1966), b) M. Kubo, Y. Kuroda, M. Kishita, and Y. Muto, Australian J. Chem., 16, 7 (1963), c) H.L. Schäfer, J.C. Morrow, and H.M. Smith, J. Chem. Phys., 42, 504 (1965), d) W.E. Hatfield, Y. Muto, H.B. Jonassen, and J.S. Paschal, Inorg. Chem., 4, 97 (1965), e) J.V. Quagliano, J. Fujita, G. Franz, D.J. Phillips, J.A. Walmsley, and S.Y. Tyree, J. Amer. Chem. Soc., 83, 3770 (1961).  
 2) Many references, e.g., a) J.R. Allan, G.A. Barnes, and D.H. Brown, J. Inorg. Nucl. Chem., 33, 3765 (1971), b) J.J. Porter, J.L. Murray, and K.B. Takvorian, J. Heterocycl. Chem., 10, 43 (1973), c) S. Emori, M. Inoue, and M. Kubo, Bull. Chem. Soc. Jap., 45, 2259 (1972), d) K.E. Hyde, G.F. Kokoszka, and G. Gordon, J. Inorg. Nucl. Chem., 31, 1993 (1969), e) G. Spacu, P. Spacu, and E. Radulescu, Chem. Abstr., 53, 8909e, f) M. Herberhold, W. Golla and K. Leonhard, Chem. Ber., 107, 3209 (1974), g) M. Maeda, A. Tsuji, H. Igeta, and T. Tsuchiya, Chem. Pharm. Bull. (Japan), 18, 1548 (1970) etc.  
 3) Recently, S. Sueyoshi et al. found that some pyridazine N,N'-dioxides form 1:1 complexes with  $CuCl_2$  although their structures have not been clarified; S. Sueyoshi Ph.D. Dissertation pp.14 (1976).  
 4) Differences were very small between the ir spectra, in KBr and in paraffin.  
 5) Crystal data and analysis of III and IIII.  
III: Crystal data; monoclinic, space group  $P2_1/n$  with  $a=7.212$ ,  $b=12.500$ ,  $c=7.133$  Å,  $\beta=114.22^\circ$ ,  $Z=2$ . Reflections' measurement; number of reflections 956 [ $CuK\alpha$ -radiation,  $I>3\sigma(I)$ ,  $\theta<60^\circ$ ]. Analyses; heavy atom method,  $R=0.070$  (by block diagonal least squares method).  
IIII: Crystal data; monoclinic, space group  $P2_1/m$  with  $a=9.340$ ,  $b=6.470$ ,  $c=7.847$  Å,  $\beta=104.76^\circ$ ,  $Z=2$ . Reflections' measurement; number of reflections 808 [ $CuK\alpha$ -radiation,  $I>3\sigma(I)$ ,  $\theta<60^\circ$ ]. Analyses; heavy atom method,  $R=0.068$  (by block diagonal least squares method).