BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 58—64 (1966)

Copper(II) Halide Complexes with Substituted Pyridine *N*-Oxides

By Yoneichiro MUTO* and Hans B. JONASSEN

Department of Chemistry, Tulane University, New Orleans, Luisiana, U. S. A.

(Received April 14, 1965)

Pyridine *N*-oxide copper(II) chloride, the structure of which has recently been elucidated by X-ray analysis [J. C. Morrow and H. L. Schäfer, private communication], has a subnormal magnetic moment (0.85 B. M. [J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley and S. Y. Tyree (*J. Am. Chem. Soc.*, **83**, 3770 (1961)]). It consists of a binuclear molecule $[Cu(C_5H_5NO)Cl_2]_2$ in which copper atoms are bridged in pairs by two oxygen atoms. In this work, copper(II) complexes with the empirical formulae of CuX_2L, CuX_2L_2 and CuX_2LY (X=Cl, Br; L=pyridine *N*-oxide, 3-picoline *N*-oxide, 4-picoline *N*-oxide, 4-chloropyridine *N*-oxide, 2, 4-lutidine *N*-oxide, 2, 4, 6-collidine *N*-oxide, 4-nitroquinoline *N*-oxide; Y=*N, N′*-dimethylformamide, dimethylsulfoxide) have been prepared, and magnetic and spectral studies of these complexes have been made. The room-temperature magnetic susceptibilities of CuX_2L complexes have been found to be correlated with the pK_a (acid-dissociation constant) values of the attached *N*-oxides. The absorption band in the 735—900 mμ region (the so-called copper band) in the solid-state reflectance spectra of CuX_2L complexes has been found to shift towards a lower frequency as the ligand field strength decreases, and a good parallelism between the frequencies and the magnetic moments has been observed. The effect of the attached ligand on the magnetic interaction has been discussed in terms of the electronic effect of the substituent on the pyridine ring. The infrared spectral data on the N–O stretching frequency indicate the absence of Cu–O–Cu linkage in the CuX_2L_2 complexes with normal magnetic moments.

Quagliano et al.[1] prepared pyridine *N*-oxide copper(II) chloride with an abnormally low magnetic moment of 0.85 B. M. Kubo et al.[2] then suggested that this low magnetic moment is caused by the formation of binuclear oxygen-bridged molecules. Very recently this binuclear structure has been determined by a complete X-ray analysis[3] (Fig. 1.). Harris et al.[4] suggested, in a study of the temperature dependence of the magnetic susceptibility for this complex, that electron exchange demagnetization can occur between pairs of adjacent copper(II) ions via the oxygen atoms. In this case, the following two pathways for the migration of an electron may be set up:

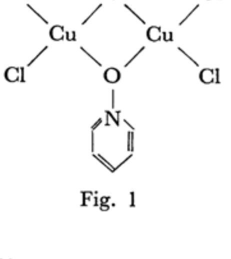


Fig. 1

$$\sigma\text{-path:}\quad 3d_\sigma(Cu)-2sp_\sigma{}^2(O)-3d_\sigma(Cu)$$

$$\pi\text{-path:}\quad 3d_\pi(Cu)-2p_\pi(O)-3d_\pi(Cu)$$

Either way, via the σ-path or via the π-path, the electron exchange interaction between Cu–O–Cu will become larger as the covalent bond between Cu–O becomes stronger.

The present work was undertaken in an attempt to elucidate the magnetic property in the dihalo copper(II) complexes with pyridine *N*-oxides. First, the complex of the empirical formula CuX_2L (1:1 complex) CuX_2L_2 (1:2 complex) and CuX_2L (1:1 complex) CuX_2L_2 (1:2 complex) and CuX_2LY (X=Cl, Br; L=pyridine *N*-oxide, 3-picoline *N*-oxide, 4-picoline *N*-oxide, 4-chloropyridine *N*-oxide, 2, 6-lutidine *N*-oxide, 2, 4, 6-collidine *N*-oxide, 4-nitroquinoline *N*-oxide; Y=*N, N′*-dimethylformamide, dimethylsulfoxide) were prepared. Secondly, the acid-dissociation constants (pK_a) of pyridine *N*-oxides and the magnetic susceptibilities of the copper(II) complexes at room temperature were determined in order to investigate the effect of the nature of the attached ligand on the magnetic interaction. Thirdly, the infrared and visible absorption spectra and the

---

* Presented address: Department of Chemistry, Saga University, Saga.

[1] J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley and S. Y. Tyree, *J. Am. Chem. Soc.*, **83**, 3770 (1961).

[2] M. Kubo, Y. Kuroda, M. Kishita and Y. Muto, *Australian J. Chem.*, **16**, 7 (1963).

[3] J. C. Morrow and H. L. Schäfer, private communication.

[4] C. M. Harris, E. Kokot, S. L. Lenzer and T. N. Lockyer, *Chem. & Ind.*, **1962**, 651.

TABLE I. ANALYTICAL DATE

Compound		Analysis, % C	H	N	Cu
$CuCl_2 \cdot 3\text{-}CH_3C_5H_4ON$	Found	29.65	2.98	5.61	26.11
	Calcd.	29.59	2.90	5.75	26.09
$CuBr_2 \cdot 3\text{-}CH_3C_5H_4ON$	Found	21.68	2.14	3.51	19.24
	Calcd.	21.68	2.12	4.21	19.11
$CuCl_2 \cdot 4\text{-}CH_3C_5H_4ON$	Found	29.73	3.03	5.81	26.06
	Calcd.	29.59	2.90	5.75	26.09
$CuBr_2 \cdot 4\text{-}CH_3C_5H_4ON$	Found	21.79	2.26	4.17	19.19
	Calcd.	21.68	2.12	4.21	19.11
$CuBr_2 \cdot (4\text{-}CH_3C_5H_4ON)_2$	Found	32.10	3.24	6.32	14.64
	Calcd.	32.64	3.20	6.34	14.39
$CuBr_2 \cdot (4\text{-}CH_3C_5H_4ON) \cdot (CH_3)_2SO$	Found	23.10	3.34	3.28	15.43
	Calcd.	23.40	3.19	3.41	15.47
$CuCl_2 \cdot 4\text{-}ClC_5H_4ON$	Found	23.09	1.71	4.79	23.95
	Calcd.	22.75	1.53	5.31	24.07
$CuCl_2 \cdot (4\text{-}ClC_5H_4ON)_2$	Found	30.33	2.19	6.75	16.34
	Calcd.	30.52	2.05	7.12	16.15
$CuBr_2 \cdot 4\text{-}ClC_5H_4ON$	Found	17.71	1.36	4.17	17.81
	Calcd.	17.02	1.14	3.97	18.00
$CuCl_2 \cdot 2,6\text{-}(CH_3)_2C_5H_3ON$	Found	32.82	3.52	5.37	24.79
	Calcd.	32.64	3.52	5.44	24.67
$CuBr_2 \cdot 2,6\text{-}(CH_3)_2C_5H_3ON$	Found	24.57	2.75	3.60	18.27
	Calcd.	24.26	2.62	4.06	18.34
$CuCl_2 \cdot 2,4,6\text{-}(CH_3)_3C_5H_2ON$	Found	35.42	4.13	4.87	23.20
	Calcd.	35.38	4.08	5.16	23.39
$CuCl_2 \cdot [2,4,6\text{-}(CH_3)_3C_5H_2ON]_2$	Found	46.98	5.53	6.91	15.66
	Calcd.	47.00	5.42	6.85	15.44
$CuBr_2 \cdot 2,4,6\text{-}(CH_3)_3C_5H_2ON$	Found	26.63	3.19	3.42	17.48
	Calcd.	26.65	3.06	3.89	17.62
$CuBr_2 \cdot [2,4,6\text{-}(CH_3)_3C_5H_2ON]_2$	Found	38.60	4.50	5.03	12.61
	Calcd.	38.61	4.46	5.63	12.77
$CuCl_2 \cdot 4\text{-}NO_2C_9H_6ON$	Found	33.22	1.80	8.08	19.55
	Calcd.	33.30	1.86	8.63	19.57
$CuCl_2 \cdot (4\text{-}NO_2C_9H_6ON)_2$	Found	42.16	2.26	10.77	12.32
	Calcd.	42.00	2.35	10.88	12.34

reflectance spectra were measured for the complexes in order to study the relation between the structure and the magnetic property.

Experimental

Materials.—Pyridine *N*-oxides were obtained commercially. The HCl salts of pyridine *N*-oxides for the pK_a determination were purified by recrystallization from ethanol.

The Preparation of the Copper(II) Complexes.—*1:1 Complexes.*—The complexes were prepared by mixing ethanol solutions of copper(II) halide and pyridine *N*-oxides in a 1:1 molar ratio. In the case of 2,4,6-collidine *N*-oxide, even though ethanol solutions of copper(II) halide and the *N*-oxide in a 1:1 molar ratio were mixed, the 1:2 complexes precipitated immediately. The 1:1 complexes were prepared by refluxing the 1:2 complexes and anhydrous copper(II) halide in a 1:1.5 molar ratio in ethanol for 1 to 2 hr. on a heater plate. However, the 1:1 complexes were rapidly converted to the 1:2 complexes in water, moist air, acetonitril, dioxane, dimethylformamide or dimethylsulfoxide.

1:2 Complexes.—The complexes were prepared by mixing ethanol solutions of copper(II) halide and

TABLE II. MAGNETIC SUSCEPTIBILITY DATA (c. g. s., e. m. u.)

Ligand (L)	Complex	$10^6\chi_g$[b]	T °K	μ B. M.
4-Nitroquinoline *N*-oxide	$CuCl_2L$	4.72	297	1.99
	$CuCl_2L_2$	2.57	299	1.93
4-Chloropyridine *N*-oxide	$CuCl_2L$	−0.06	296	0.49
	$CuCl_2L_2$	2.79	284	1.71
	$CuBr_2L$	−0.14	294	0.45
3-Picoline *N*-oxide	$CuCl_2L$	0.05	297	0.55
	$CuBr_2L$	−0.10	291	0.48
4-Picoline *N*-oxide	$CuCl_2L$	0.00	298	0.52
	$CuBr_2L$	−0.12	291	0.47
	$CuBr_2L_2$	1.30	291	1.34
	$CuBr_2L \cdot$ DMS[a]	0.77	291	1.07
2,6-Lutidine *N*-oxide	$CuCl_2L$	−0.39	297	0.22
	$CuCl_2L_2$	2.86	292	1.74
	$CuBr_2L$	−0.34	298	0.30
	$CuBr_2L_2$	2.48	289	1.80
2,4,6-Collidine *N*-oxide	$CuCl_2L$	−0.38	294	0.27
	$CuCl_2L_2$	4.44	298	2.20
	$CuBr_2L$	−0.22	289	0.42
	$CuBr_2L_2$	2.45	292	1.85

a) DMS is an abbreviation for dimethylsulfoxide.

b) χ_g is the gram susceptibility of the copper(II) complex.

TABLE III. CORRELATION BETWEEN pK_a VALUES OF THE LIGAND AND MAGNETIC MOMENTS OF THE COMPLEXES

Ligand (L)	pK_a (at 20±1°C)	Magnetic moment of complex, B. M.			
		$CuCl_2L$	$CuBr_2L$	$CuCl_2L_2$	$CuBr_2L_2$
4-Nitroquinoline *N*-oxide	−0.8	1.99		1.93	
4-Chloropyridine *N*-oxide	0.60	0.49	0.45	1.71	g)
		0.58b)	0.23b)	1.75b)	
Pyridine *N*-oxide	0.79a)	0.73c)	0.53c)	0.59c)	1.46c)
		0.77d)	0.65d)	0.63e)	
		0.85e)			
3-Picoline *N*-oxide	1.08a)	0.55	0.48	g)	g)
4-Picoline *N*-oxide	1.29a)	0.52	0.47	g)	1.34
		0.51b)	0.26b)		1.33b)
2,6-Lutidine *N*-oxide	1.60	0.22	0.30	1.74	1.80
2,4,6-Collidine *N*-oxide	2.07	0.27	0.42f)	2.20	1.85

a) These values were quoted from H. H. Jaffé and G. O. Dork, *J. Am. Chem. Soc.*, **77**, 4441 (1955).
b) Ref. 6.
c) M. Kishita, Y. Muto, M. Inoue and M. Kubo, presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, March—April, 1963.
d) Ref. 4.
e) Ref. 1.
f) The reason for the relatively high value seems to be that this sample is contaminated with a very small amount of the 1 : 2 complex; see the Experimental section.
g) These complexes have not been obtained.

pyridine *N*-oxides in a 1:2 molar ratio. Bis-2,4,6-collidine *N*-oxide copper(II) halide was purified by recrystallization from dimethylformamide, while the other complexes were purified by repeatedly washing them with cold ethanol. Except for the collidine *N*-oxide complexes, they all easily lost one mole of the ligand when heated in ethanol. Bis-4-picoline *N*-oxide copper(II) bromide, for instance, gradually lost one mole of 4-picoline *N*-oxide, even in cold ethanol.

The addition compounds of dimethylformamide or dimethylsulfoxide with 1:1 complexes were prepared by the recrystallization of the 1:1 complexes from the respective solvents.

The results of elementary analysis of the complexes are listed in Table I.

Magnetic Susceptibility Determinations.—These were made by the Gouy method at room temperature. The effective magnetic moment, μ, per copper atom was calculated from the expression $\mu=2.83\sqrt{\chi_M\cdot T}$ B. M. where χ_M is the molar susceptibility corrected using Pascal's constants5) for the diamagnetism of the other atoms in the compounds. The experimental results are presented in detail in Table II, while the correlation between the pK_a values of the ligands and the magnetic moments of the complexes are listed in Table III.

pK_a Determination.—The pK_a values of the various bases were determined by ultraviolet absorption spectroscopy, which was used to measure the concentration of the free and protonated *N*-oxide bases in solutions with measured pH values. The pH measurements were made with a Beckman Zeromatic pH meter which had been calibrated with buffers; the pH values were determined at 20°C 1.07, 2.27, 3.33 and 7.00. The ultraviolet absorption spectra were obtained with a Beckman DB spectrophotometer.

Infrared Spectra.—These were recorded on a Beckman IR-8 recording spectrophotometer. The

TABLE IV. ENERGIES OF THE N–O STRETCHING VIBRATION FOR THE PYRIDINE *N*-OXIDES AND COMPLEXES*

N-Oxide (L)	ν, cm^{-1}	Complex	ν, cm^{-1}
Pyridine *N*-oxide	1265a)	$CuCl_2L$	1203b)
		$CuCl_2L_2$	1223, 1206b)
		$CuCl_2L\cdot$DMF**	1203
		$CuCl_2L\cdot$DMS	1203
		$CuBr_2L$	1200
		$CuBr_2L_2$	1211, 1201
		$CuBr_2L\cdot$DMF	1202
3-Picoline *N*-oxide	1285a)	$CuCl_2L$	1248
		$CuBr_2L$	1244
4-Chloropyridine *N*-oxide	1269a)	$CuCl_2L$	1195
		$CuCl_2L_2$	1209, 1195
		$CuBr_2L$	1199
4-Picoline *N*-oxide	1260a)	$CuCl_2L$	1200
		$CuBr_2L$	1203
		$CuBr_2L_2$	1240, 1209
		$CuBr_2L\cdot$DMS	1211
2,6-Lutidine *N*-oxide	1255a)	$CuCl_2L$	1199
		$CuCl_2L_2$	1208
		$CuBr_2L$	1195
		$CuBr_2L_2$	1203
2,4,6-Collidine *N*-oxide	1247a)	$CuCl_2L$	1199
		$CuCl_2L_2$	1208
		$CuBr_2L$	1202
		$CuBr_2L_2$	1205

* The values with superscript a and b were quoted from Ref. 7 and Ref. 1, respectively.
** DMF is an abbreviation for *N*, *N'*-Dimethylformamide.

---

5) G. Foëx, "Constantes Sélectionées Diamagnétisme et Paramagnétisme," Masson & Cie, Paris (1957), p. 222.

TABLE V. REFLECTANCE SPECTRA DATA: λ_{max} (mμ)

Ligand (L)	CuCl$_2$L		CuBr$_2$L		
	λ_1	λ_2	λ_1	λ_2	λ_{Br}
1. 2,4,6-Collidine *N*-oxide	750	410	735	425	530
2. 2,6-Lutidine *N*-oxide	760	425	745	440	530
3. 4-Chloropyridine *N*-oxide	800	430	800	*	525
4. 4-Picoline *N*-oxide	835	425	830	*	505
5. 3-Picoline *N*-oxide	850	420	840	455	520
6. Pyridine *N*-oxide	940	418	900	*	510
7. 4-Nitroquinoline *N*-oxide		400			

* The band with this mark is so broad that the exact band peak can not be determined.

TABLE VI. VISIBLE SPECTRA DATA IN A VARIETY OF SOLVENTS: λ_{max} (mμ)

Solvents: A, Methanol; B, Nitromethane;
C, Dioxane; D, Acetone; E, Acetonitril;
F, *N*,*N*′-Dimethylformamide;
G, Dimethylsulfoxide.

1. 2,4,6-Collidine *N*-oxide CuCl$_2$*

	λ_1	λ_2
B	783	

2. 2,4,6-Collidine *N*-oxide CuBr$_2$*

	λ_1	λ_2	λ_{Br}
B	775		630

3. 2,6-Lutidine *N*-oxide CuCl$_2$

	λ_1	λ_2
A	802	
B	789	
C	795	
D	793	
E	790	445
F	794	436
G	802	—**

3. 2,6-Lutidine *N*-oxide CuBr$_2$

	λ_1	λ_2	λ_{Br}
A	800		
B	773		658
C	795		
D	795		
E		429	637
F		—	593
G	799	—	

5. 4-Chloropyridine *N*-oxide CuCl$_2$

	λ_1	λ_2
A	785	
B	786	
C	795	
D	780	480
E	781	458
F	786	435
G	781	—

6. 4-Chloropyridine *N*-oxide CuBr$_2$

	λ_1	λ_2	λ_{Br}
A	790		
B	772		623
C	795		
D			651
E		429	636
F		—	593
G	778	—	

7. 3-Picoline *N*-oxide CuCl$_2$

	λ_1	λ_2
A	778	
B	780	
C	785	
D	777	472
E	780	468
F	780	435
G	778	—

8. 3-Picoline *N*-oxide CuBr$_2$

	λ_1	λ_2	λ_{Br}
A	787		
B	775		618
C	800		
D		428	653
E		425	637
F		—	597
G	778	—	

9. 4-Picoline *N*-oxide CuCl$_2$

	λ_1	λ_2
A	785	
B	785	
C	793	
D	785	470
E	782	457
F	785	435
G	778	—

10. 4-Picoline *N*-oxide CuBr$_2$

	λ_1	λ_2	λ_{Br}
A	788		
B	780		622
C	780		
D		436	652
E		425	638
F		—	592
G	780	—	

11. Pyridine *N*-oxide CuCl$_2$

	λ_1	λ_2
A	791	
B	784	
C	790	
D	782	477
E	784	453
F	782	434
G	795	430

12. Pyridine *N*-oxide CuBr$_2$

	λ_1	λ_2	λ_{Br}
A	783		
B	784		632
C	787		
D		472	653
E		435	632
F		—	590
G	780	—	

13. 4-Nitroquinoline *N*-oxide CuCl$_2$

	λ_1	λ_2
A	778	
B	778	
C	778	
D	788	465
E	778	455
F	788	438
G	790	—

* Compound 1 and 2 converted to the 1 : 2 complex in each solvents employed except nitromethane.

** The band with this mark should be hidden in the absorption band of the ligand.

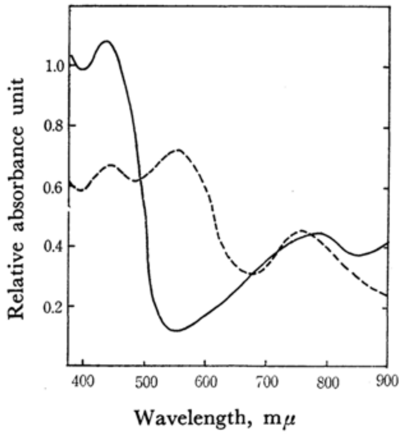


Fig. 2a. Reflectance spectra of 2,6-lutidine *N*-oxide Cu(II) halide.
—— Chloride complex ---- Bromide complex

spectra were taken in both Nujol mulls and KBr disks. The energy of the intense band near 1200 cm^{-1} for each of the complexes and the free ligand are given in Table IV.

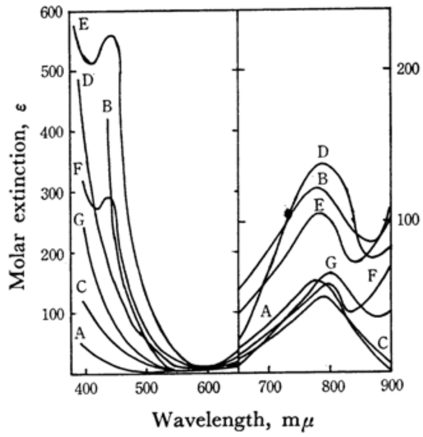


Fig. 2b. Absorption spectra of 2,6-lutidine N-oxide $CuCl_2$ in seven different solvents. The letters indicate the solvents noted in Table VI.

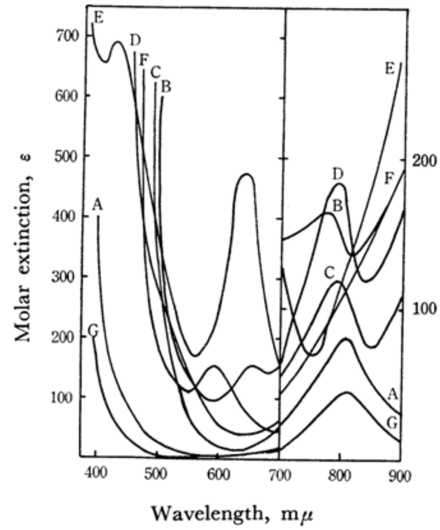


Fig. 2c. Absorption spectra of 2,6-lutidine N-oxide $CuBr_2$ in seven different solvents. The letters indicate the solvents noted in Table VI.

Diffuse Reflectance Spectra.—The diffuse reflectance spectra of the 1:1 complexes were measured in the 375—900 mμ region on a Beckman DU spectrophotometer with a reflectance attachment. The band maxima are recorded in Table V. Fig. 2a gives the reflectance spectra for 2,6-lutidine N-oxide complexes.

Visible Absorption Spectra.—The visible absorption spectra of the 1:1 complexes in a variety of solvents were determined on a Cary model 14 recording spectrophotometer in the 400—900 mμ region. The absorption maxima are recorded in Table VI, while the absorption curves for 2,6-lutidine N-oxide complexes are shown in Figs. 2b and 2c.

Results and Discussion

The pK_a Values of Ligands and Magnetic Moments of Complexes.—The 1:1 Complex (CuX_2L).—As is sown in Table II, there is a good correlation between the pK_a values of the N-oxides and the magnetic moments of the 1:1 complexes with the oxides, except with 4-chloropyridine N-oxide. These data demonstrate that the larger tendency of the N-oxide to coordinate with the copper(II) ion results in a larger magnetic interaction.

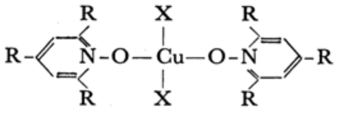
The introduction of the methyl group on the pyridine ring results in an increase in the pK_a value. Since the pK_a value of the N-oxides reflects the σ-electron density on the oxygen atom, such an increase in the value is considered to be caused by the inductive effect of the methyl group. The increase in the electron density on the oxygen atom results in an increase in the Cu-O σ-bond strength, leading to a greater magnetic interaction through the σ-path of the Cu–O–Cu bridge.

The introduction of a chlorine atom on the pyridine ring results in a decrease in the pK_a value as a result of the σ-electron-attracting effect of the chlorine atom. Although the magnetic moment of 4-chloropyridine N-oxide copper(II) halide is to be expected in view of the pK_a value of the ligand being smaller than that of the pyridine N-oxide complex, just the opposite was observed. However, it is a well-known fact that the chlorine atom conjugated to an aromatic ring has both σ-attracting and π-releasing effects. It seems reasonable, therefore, to conclude that the π-electron on the chlorine atom in the 4-position is conjugated with the π-electron system of pyridine N-oxide to increase the π-electron density on the oxygen atom. Consequently, the lowering of the magnetic moment may be interpreted as resulting from the superexchange interaction through the π-path, provided the π-path is more effective for the interaction than the σ-path. The magnetic data for 4-hydroxypyridine N-oxide copper(II) chloride (molar magnetic susceptibility: $\chi_M=0$ at 24.8°C)[6] also suggest the superexchange interaction through the π-path. It is, however, difficult to evaluate the effects of the σ- and π-paths separately at present. Further studies along this line are in progress.

The 1:2 Complex (CuX_2L_2).—No regular correlation between the pK_a value of the ligand and the magnetic interaction in the 1:2 complexes is observed. The observed magnetic moments seem to indicate that the further addition of a ligand to a 1:1 complex produces either a slight or a complete structural change, because the magnetic interaction must be affected by even a slight change in the bond angle in the Cu–O–Cu bridge. The structure shown in Fig. 3 is reasonable for 1:2 complexes with a normal magnetic moment. In the case of complexes with a subnormal magnetic moment, the easy removal of one ligand molecule

---

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



(R: H, CH_3; X: Cl, Br)

Fig. 3

seems to indicate that one molecule of ligand is weakly bonded to the copper(II) atom, whereas the other forms the Cu–O–Cu linkage with copper atoms. The infrared spectra studies of the N–O stretching frequency support the above conclusion for the 1:2 complexes also, as will be seen in the next section.

Infrared Spectra.—The strong absorption in the 1200—1300 cm^{-1} region in the infrared spectrum of pyridine *N*-oxide and its derivatives has been assigned to their characteristic N–O stretching vibration.[7,8] Kida et al.[9] reported that the coordination of pyridine *N*-oxide with metal ions results in a decrease in the contribution of the mesomeric structure B shown in Fig. 4 and, consequently, in a decrease of the NO double-bond character and in a lowering of the N–O stretching frequency.

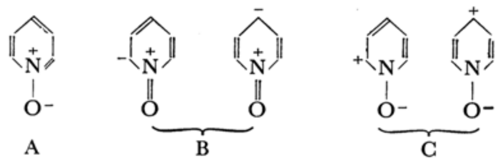


Fig. 4

The NO double-bond character in the 1:1 complexes is expected to be smaller than that in the 1:2 complexes with a normal magnetic moment. This is because a larger electron donation from NO groups is necessary to form the Cu–O–Cu linkage than to form the single coordination shown in Fig. 3 (see also Table IV). The absorption energies of the N–O stretching vibration of the 1:1 complexes were lower than the values for the 1:2 complexes with a normal magnetic moment. This observation is in agreement with our expectation. On the other hand, 1:2 complexes with a subnormal magnetic moment show two N–O stretching frequencies, suggestive of two kinds of NO bonds, for instance, 1223 and 1206 cm^{-1} in bis-pyridine *N*-oxide copper(II) chloride. The assignment of 1223 cm^{-1} to the NO frequency of weakly-bonded pyridine *N*-oxide and 1206 cm^{-1} to the NO frequency of bridged pyridine *N*-oxide are reasonable in view of the chemical property, the magnetic moment and the double-bond character.

Reflectance Spectra.—The spectra which are observed may be conveniently classified into three groups by region: λ_1, 735—940 mμ; λ_2, 400—435 mμ; λ_{Br}505—530 mμ.

λ_1: A band of a relatively low intensity is observed in this region for all the 1:1 complexes studied. From the frequency and the intensity, the band in this region can undoubtedly be attributed to the so-called copper band, a transition within the d shell. This shifts towards lower frequencies as the ligand field strength decreases (cf. Table V). A good parallelism is seen between the frequencies and the magnetic moments. In all the 1:1 complexes the copper atom is combined with two halogen atoms; hence, it may be presumed that the ligand field strength provided by the halogen atoms for the copper atom is almost the same in all the 1:1 complexes.

According to the molecular orbital theory, the splitting of metal d orbitals is essentially attributed to covalent bonding. The greater the overlap of metal d orbitals with the ligand orbitals, the higher in energy will be the antibonding orbital (σd^*).[10] Therefore, the frequency of this band may be taken as a measure of the degree of covalency in the Cu–O linkage. The magnetic interaction will become greater as the orbital overlap between the copper and oxygen atoms becomes larger. It may thus be concluded, provided that the ligand-field strength reflects the σ-bond strength of Cu–O linkage, that the superexchange interaction occurs through the σ-path of the Cu–O–Cu bridge.

λ_2: A band of a relatively high intensity is observed in this region for all the 1:1 complexes studied. This corresponds to the band at 350—400 mμ for bivalent metal complexes with picolinic acid *N*-oxide which has been observed and tentatively assigned to a charge transfer, $d_\varepsilon \rightarrow \pi^*$, by Lever et al.[11] A similar band has been observed in solutions, as will be seen in the next section, though this appears at lower frequencies than the band in crystals.

λ_{Br}: In addition to λ_1 and λ_2, a band of a relatively high intensity is observed in this region for all the bromide complexes studied. It is missing, however from the spectra of all the chloride complexes studied. This band has been observed also in solutions of bromide complexes. This band seems to appear by cooperation of copper(II) ion, bromide ion and π-acceptor in a certain environment. However, more work is necessary before we can give it a definite assignment.[12]

---

[7] H. Shindo, *Chem. Pharm. Bull. (Tokyo)*, **4**, 460 (1956); **6**, 117 (1958); **7**, 191 (1959).

[8] G. Costa and P. Blasina, *Z. Phys. Chem. (Frankfurt)*, **4**, 24 (1955).

[9] S. Kida, J. V. Quagliano, J. A. Walmsley and S. Y. Tyree, *Spectrochemica Acta*, **19**, 189 (1963).

[10] See, for example, K. Ito and Y. Kuroda, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zassi)*, **76**, 766, 934 (1955); B. Basolo and R. Johnson, "Coordination Chemistry," W. A. Benjamin, New York, N. Y. (1964), p. 56.

[11] A. B. P. Lever, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, **1962**, 5262.

[12] M. Kato, Y. Muto and H. B. Jonassen, unpublished.

Visible Absorption Spectra in a Variety of Solvents.—All the 1:1 complexes are very insoluble in solvents with practically no coordination tendency, such as benzene or chloroform, but they are soluble in organic solvents capable of coordination. The spectra in solutions are somewhat different from the reflectance spectra, as is shown in Table VI and in Figs. 2a, b, and c. This shows that solvation occurs even when the coordination power of the solvent is not high, such as in methanol or nitromethane.

Although the absorption bands for various 1:1 complexes in different solvents differ from one another, they may be classified into three groups just as those of crystals: λ_1, 770—800 mμ; λ_2, 420—460 mμ; λ_{Br}, 590—660 mμ.

λ_1: An absorption band of a low intensity ($\varepsilon\sim$ 100) is observed in this region for all the chloride complexes in each solvent. In the case of bromide complexes, an absorption band in this region is observed in weak coordinating solvents, but not in relatively strong coordinating solvents. However, it seems from the shape of the absorption curves that the band peaks in strong coordinating solvents exist at lower frequencies, perhaps near 900 mμ, outside the range of the present measurements.

λ_2: An absorption band is observed in this region for all the complexes in relatively strong coordinating solvents, such as dimethylsulfoxide, *N, N'*-dimethylformamide, acetonitrile and acetone. It is absent, however, from the spectra of the complexes in weak coordinating solvents, such as methanol, nitromethane and dioxane. It has a considerable intensity (ε 300—700) and shifts towards higher frequencies with an increase in the coordination power of the solvents. Recently, a similar band in the near ultraviolet region has been observed for a number of copper(II) complexes; it has been variously ascribed to a d-d transition,(13) a ligand transition,(14) or a charge transfer.(11,15) However, more experimental and theoretical studies are necessary before this band can be assigned definitely.

λ_{Br}: A band in this region is observed for the bromide complexes but not for the chloride complexes, as in crystals. Furthermore, this band is observed in solvents which have a π-electron accepting ability, but not in solvents which do not have an appreciable π-character.

The financial support of the Office of Naval Reseach under Contract No. 47509 is gratefully acknowledged. Fruitful discussions with Dr. M. Kato of Aichi Women's College are also gratefully acknowledged.

---

13) D. P. Graddon, *J. Inorg. Nuclear Chem.*, **14**, 161 (1960).

14) T. S. Piper and R. L. Belford, *Mol. Phys.*, **5**, 169 (1962); R. L. Belford and T. S. Piper, ibid., **5**, 251 (1962); G. Basu, R. L. Belford and R. E. Dickerson, *Inorg. Chem.*, **1**, 438 (1962).

15) D. W. Barnum, *J. Inorg. Nuclear Chem.*, **21**, 221 (1961); R. L. Carlin, *J. Am. Chem. Soc.*, **83**, 3773 (1961).