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Magnetic Moments and d–d Bands of Copper(II) Halide Complexes with Substituted Pyridine *N*-Oxides and Some Related Ligands[*1]

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In order to test the substituent effect or the effect of variations in chemical structures on the demagnetization and d–d band shift in dimeric copper(II) halide complexes with pyridine *N*-oxides and some related ligands, a variety of electron-donating or electron-withdrawing substituents attached in 2-, 3- and 4-positions in the pyridine ring of the ligand were extensively studied. In these dimeric complexes, no correlation was observed between the Hammett's σ constants and the observed d–d band positions or magnetic moments. However, irrespective of the nature of the substituents, a linear relation was observed to exist between the d–d band positions and the magnetic moments, indicative of a magnetochemical support for the interpretation of the spectrochemical series through the idea of symmetry-restricted covalency. For the monomeric complexes with the same ligands, a linear relation exists between Hammett's constants and the d–d band positions for each series of the electron-donating and electron-withdrawing substituents. Experimental results indicate that the most important factor determining the non-applicability of Hammett's Rule in these dimeric complexes is the steric condition of the metal ions which shields them from the influence of other molecules or ions. The larger demagnetization effect of the bromide ion compared to the chloride ion has been interpreted as due to its larger nephelauxetic effect. On the basis of the established structure of the parent compound, two pathways for super-exchange interaction have been proposed. The importance of a σ type orbital overlap compared to the π type is discussed.

Recently a large number of copper(II) complexes have been reported which have subnormal magnetic moments at room temperature. Quagliano and his coworkers[1)] noticed a low magnetic moment, 0.85 B.M., for the 1 : 1 complex of copper(II) chloride with pyridine *N*-oxide. Many studies have been undertaken on this compound and its homologues in order to elucidate the relations between the chemical structures or substituent effects on the demagnetization mechanism. The structure of the parent compound which has recently been determined by X-ray analysis,[2–5)] is an excellent model to examine these correlations for the following reasons:

1) Since pyridine *N*-oxide is a monodentate ligand, its coordinate bond to the metal ion is not involved in any other metal ligand bond. This

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[*1] A part of this study was presented a) by Y. Muto, M. Kato, H. N. Ramaswamy and H. B. Jonassen at the 19th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1966, Proceedings Vol. II, p. 134; b) by Y. Muto, M. Kato and H. B. Jonassen at the 16th Conference on Coordination Chemistry of the Chemical Society of Japan, Tokyo, December, 1966, Proceedings, p. 66; c) by Y. Muto, M. Kato, H. B. Jonassen and F. Itabe at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967, Proceedings Vol. II, p. 76; d) by Y. Muto, M. Kato, H. B. Jonassen, H. N. Ramaswamy and K. Imai at the 10th International Conference on Coordination Chemistry, Nikko, September, 1967, Proceedings, p. 337; e) by Y. Muto, M. Kato, H. B. Jonassen and H. N. Ramaswamy, This Bulletin, **40**, 1535 (1967); f) by M. Kato, Y. Muto and H. B. Jonassen, *ibid.*, **40**, 1738 (1967), and g) by Y. Muto, M. Kato, H. B. Jonassen and K. Kakiuchi at the 21th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968, Proceedings Vol. II, p. 1119.

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TABLE 1. ANALYTICAL DATA

Ligand (L)	Complex	C%		H%		N%		Cu%	
		Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
Pyridine *N*-oxide	$CuL_4(ClO_4)_2$	37.44	37.37	3.18	3.14	8.67	8.72	9.62	9.88
4-Methylpyridine *N*-oxide	$CuL_4(ClO_4)_2$	41.15	41.24	4.02	4.04	8.09	8.02	8.86	9.09
3-Chloropyridine *N*-oxide	$CuLCl_2$	22.81	22.75	1.70	1.53	5.36	5.31	24.12	24.07
	$CuLBr_2$	17.08	17.02	1.25	1.14	4.06	3.97	17.94	18.00
	$CuL_4(ClO_4)_2$	30.69	30.77	2.04	2.07	7.26	7.18	8.13	8.14
3-Bromopyridine *N*-oxide	$CuLBr_2$	15.30	15.11	1.21	1.02	3.56	3.53	15.72	15.99
Nicotinic acid *N*-oxide	$CuLCl_2$	26.63	26.34	1.91	1.84	5.17	5.12	23.18	23.23
Ethylnicotinate *N*-oxide	$CuLCl_2$	31.86	31.86	3.01	3.01	4.62	4.64	21.24	21.07
	$CuLBr_2$	24.71	24.60	2.44	2.32	3.70	3.59	16.21	16.27
	$CuL_4(ClO_4)_2$	41.32	41.28	4.02	3.90	5.97	6.02	6.75	6.82
Ethylisonicotinate *N*-oxide	$CuLCl_2$	31.59	31.86	3.08	3.01	4.65	4.64	21.14	21.07
	$CuLBr_2$	24.68	24.60	2.47	2.32	3.41	3.59	16.30	16.27
	$CuL_4(ClO_4)_2$	41.25	41.28	3.94	3.90	6.08	6.02	6.76	6.82
3-Acetylpyridine *N*-oxide	$CuLCl_2 \cdot \frac{1}{2}C_2H_5OH$	32.44	32.61	3.41	3.42	4.77	4.75	21.34	21.57
	$CuLBr_2 \cdot \frac{1}{2}C_2H_5OH$	25.17	25.05	2.39	2.63	3.77	3.65	16.79	16.57
	$CuL_4(ClO_4)_2$	41.52	41.47	3.43	3.48	7.02	6.91	7.79	7.83
4-Acetylpyridine *N*-oxide	$CuL_4(ClO_4)_2$	41.48	41.47	3.51	3.48	6.94	6.91	7.81	7.83
4-Nitropyridine *N*-oxide	$CuLCl_2$	21.45	21.87	1.60	1.47	10.07	10.20	23.32	23.14
	$CuLBr_2$	16.22	16.52	1.04	1.11	7.63	7.71	17.46	17.48
	$CuL_4(ClO_4)_2$	29.38	29.19	2.08	1.96	13.59	13.62	7.69	7.72
3-Cyanopyridine *N*-oxide	$CuL_4(ClO_4)_2$	38.82	38.80	2.21	2.17	15.05	15.08	8.40	8.55
4-Cyanopyridine *N*-oxide	$CuLCl_2$	28.21	28.31	1.79	1.58	11.01	11.00	24.58	24.96
	$CuLBr_2$	20.83	20.98	1.17	1.17	8.37	8.16	18.44	18.50
	$CuL_4(ClO_4)_2$	38.96	38.80	2.23	2.17	15.21	15.08	8.23	8.55
3-Hydroxypyridine *N*-oxide	$CuLCl_2$	24.52	24.46	2.12	2.05	5.72	5.70	25.73	25.88
	$CuLBr_2$	18.22	17.96	1.54	1.51	4.24	4.19	18.73	19.00
4-Hydroxypyridine *N*-oxide	$CuLCl_2 \cdot H_2O$	23.07	22.79	2.58	2.68	5.56	5.31	24.17	24.11
	$CuLBr_2 \cdot \frac{1}{2}C_2H_5OH$	20.11	20.14	2.57	2.24	3.86	3.92	17.57	17.78
2-Ethylpyridine *N*-oxide	$CuLCl_2$	32.70	32.64	3.63	3.52	5.51	5.44	24.68	24.67
	$CuLBr_2$	24.83	24.26	2.61	2.62	4.06	4.04	18.32	18.34
3-Ethylpyridine *N*-oxide	$CuLCl_2$	32.40	32.64	3.46	3.52	5.48	5.44	24.70	24.67
	$CuLBr_2$	24.13	24.26	2.53	2.62	4.02	4.04	18.47	18.34
4-Ethylpyridine *N*-oxide	$CuLCl_2$	32.61	32.64	3.50	3.52	5.49	5.44	24.72	24.67
	$CuLBr_2$	24.16	24.26	2.54	2.62	3.85	4.04	18.44	18.34
2,4-Lutidine *N*-oxide	$CuLCl_2$	32.47	32.64	3.56	3.52	5.57	5.54	24.67	24.67
	$CuLBr_2$	24.44	24.26	2.64	2.62	4.11	4.04	18.50	18.34
2-Hydroxymethylpyridine *N*-oxide	$CuLCl_2$	27.66	27.76	2.72	2.72	5.30	5.40	24.48	24.48
	$CuLBr_2$	20.15	20.68	2.20	2.02	3.90	4.02	18.02	18.23
3-Hydroxymethylpyridine *N*-oxide	$CuLCl_2$	27.76	27.76	2.57	2.72	5.31	5.40	24.36	24.48
	$CuLBr_2$	20.46	20.68	2.07	2.02	4.05	4.02	18.22	18.23
4-Hydroxymethylpyridine *N*-oxide	$CuLCl_2$	28.01	27.76	2.73	2.72	5.44	5.40	24.42	24.48
	$CuLBr_2$	20.98	20.68	2.01	2.02	4.07	4.02	18.26	18.23
Quinoline *N*-oxide	$CuLCl_2$	38.73	38.66	2.46	2.52	5.15	5.01	22.74	22.72
	$CuLBr_2$	29.41	29.33	1.89	1.91	3.78	3.80	17.27	17.24
4-Methylquinoline *N*-oxide	$CuLCl_2$	41.12	40.90	2.90	3.09	4.59	4.77	21.40	21.64
	$CuLBr_2$	31.77	31.40	2.21	2.37	3.56	3.66	16.33	16.61
Isoquinoline *N*-oxide	$CuLCl_2$	38.57	38.66	2.53	2.52	5.02	5.01	22.52	22.72
	$CuLBr_2$	29.41	29.33	2.02	1.91	3.63	3.80	17.15	17.24

eliminates the possible complexity in the demagnetization mechanism which may occur if a similar coordinate bond were part of a chelate ring.

2) The electronic effect of the substituents on the pyridine ring should transmit directly to the *N*-oxide oxygen atom which is an atom in the superexchange pathway, Cu–O–Cu.

3) Pyridine *N*-oxide is presently the only ligand which is monodentate and gives dimeric copper(II) complexes with a variety of substituents on the pyridine ring. As the experimental data for these pyridine *N*-oxide complexes have accumulated, it has become obvious that the relation between the magnetic properties of the complexes and the electronic nature of the substituents is much more complex than was anticipated earlier.

In order to clarify some of the causes which bring about a lack of correlation between the demagnetization or the d–d band positions and the electronic effects of the substituents, we have extended our previous studies.[*1,6] We have recently prepared a number of copper(II) halide complexes of pyridine *N*-oxides with a variety of electron-donating and electron-withdrawing substituents attached in 2-, 3- and 4-positions of pyridine ring. For purposes of comparison, some monomeric complexes of the type, [Cu(X-PyO)$_4$](ClO$_4$)$_2$, were also prepared and their spectral properties were characterized in connection with the Hammett's constants.

Experimental

Materials. Pyridine *N*-oxide, and 2-hydroxymethyl-, 3-hydroxymethyl-, 4-hydroxymethyl-, 4-methyl- and 4-nitro-pyridine *N*-oxides were obtained commercially. 3-Chloro-, 3-bromo-, 3-acetyl-, 4-acetyl-, 3-cyano-, 4-cyano-, 3-hydroxy-, 2-ethyl-, 3-ethyl- and 4-ethylpyridine *N*-oxides, and nicotinic acid-, ethylnicotinate-, ethylisonicotinate-, 2,4-lutidine-, quinoline-, 4-methylquinoline- and isoquinoline-*N*-oxides were prepared by oxidation of the corresponding pyridines by the method of Ochiai.[7] 4-Hydroxypyridine *N*-oxide was prepared by reaction of 4-nitropyridine *N*-oxide with dimethylaniline according to Ochiai's direction.[7] All these ligand materials were recrystallized from chloroform or benzene for use of the preparation of the copper(II) complexes.

The Preparation of the Copper(II) Complexes. *1 : 1 Complexes.* These complexes were prepared by heating the mixture of anhydrous copper(II) halide and the stoichiometric amount of ligand in ethanol on a hot plate for a short time. Purification was obtained by recrystallizing them from ethanol or *N,N*-dimethylformamide. Copper(II) chloride complexes with 2-hydroxymethylpyridine *N*-oxide, which crystallized as a yellowish green material from ethanol, exhibited a

TABLE 2. MAGNETIC DATA OF 1 : 1 COMPLEXES

Ligand	CuCl$_2$ complex				CuBr$_2$ complex			
	$10^6\cdot\chi_g$[a] (c.g.s., e.m.u.)	Temp. (°K)	μ_{eff} (B.M.)	$\mu_{eff}^{25°C}$ (B.M.)	$10^6\cdot\chi_g$[a] (c.g.s., e.m.u.)	Temp. (°K)	μ_{eff} (B.M.)	$\mu_{eff}^{25°C}$ (B.M.)
3-Cl·PyO[b]	−0.12	297	0.46	0.46	−0.31	291	0.25	0.27
3-Br·PyO					−0.19	287	0.42	0.45
3-COOH·PyO	0.00	294	0.53	0.54				
3-COOC$_2$H$_5$·PyO	−0.14	297	0.48	0.48	−0.24	297	0.39	0.39
4-COOC$_2$H$_5$·PyO	−0.12	297	0.50	0.50	−0.32	296	0.28	0.29
3-CH$_3$CO·PyO	0.02	303	0.58	0.57	−0.11	304	0.52	0.50
4-NO$_2$·PyO	1.72	303	1.21	1.20	−0.12	298	0.45	0.45
4-CN·PyO	1.05	296	0.95	0.96	0.38	297	0.79	0.79
3-OH·PyO	−0.24	286	0.33	0.37	−0.22	287	0.34	0.37
4-OH·PyO	−0.29	291	0.31	0.33	−0.34	294	0.22	0.23
2-C$_2$H$_5$·PyO	−0.35	286	0.29	0.32	−0.32	286	0.28	0.31
3-C$_2$H$_5$·PyO	−0.19	286	0.42	0.46	−0.27	288	0.34	0.37
4-C$_2$H$_5$·PyO	0.03	285	0.55	0.59	−0.24	286	0.38	0.41
2,4-(CH$_3$)$_2$·PyO	−0.29	289	0.34	0.37	−0.29	289	0.32	0.35
2-CH$_2$OH·PyO	−0.24	292	0.37	0.39	−0.24	286	0.36	0.40
3-CH$_2$OH·PyO	−0.08	292	0.48	0.50	−0.22	283	0.38	0.42
4-CH$_2$OH·PyO	−0.09	281	0.47	0.53	−0.20	285	0.40	0.44
QNO[c]	−0.35	286	0.30	0.33	−0.33	284	0.29	0.33
4-CH$_3$·QNO	−0.32	283	0.36	0.40	−0.34	285	0.30	0.33
iso-QNO	−0.18	280	0.45	0.51	−0.25	284	0.39	0.43

a) magnetic susceptibility per gram b) PyO: pyridine *N*-oxide c) QNO: quinoline *N*-oxide

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normal magnetic moment, 1.88 B.M. at 11°C. The color of this compound gradually changed to yellow on standing in air for a week. The yellow compound was then transferred to a desiccator over silica gel for one month. After this period a very low magnetic moment, 0.37 B.M. at 19°C, was observed.*2

1 : 4 Complexes. These complexes were precipitated immediately from the ethanol solution of stoichiometric mixtures of copper(II) perchlorate hexahydrate and the ligands. They were purified by repeated washing with ethanol.

The preparation was repeated at least twice for each of the 1 : 1 and 1 : 4 complexes. The results of elementary analysis of the complexes are listed in Table 1.

Magnetic Susceptibility Determinations. These data were obtained by the Gouy method at room temperature. The effective magnetic moment, $\mu_{\rm eff}$, per copper atom was calculated from the expression $\mu_{\rm eff} = 2.83\sqrt{\chi_{\rm M}\cdot T}$ B.M. where $\chi_{\rm M}$ is the molar susceptibility corrected using Pascal's constants[8] for the diamagnetism of the other atoms in the compounds. The magnetic moments observed at room temperature were corrected for minor room temperature variations to those at 25°C, $\mu_{\rm eff}^{25°C}$, by using Bleaney and Bowers' equation[9] assuming $g=2.2$.[10] These results are presented in detail in Table 2.

TABLE 3. d–d BAND MAXIMA OF 1 : 1 COMPLEXES

Ligand	$CuCl_2$ complex $\lambda_{\rm max}$ (mμ)	$CuBr_2$ complex $\lambda_{\rm max}$ (mμ)
3-Cl·PyO	820	775
3-Br·PyO		825
3-COOH·PyO	885	
3-$COOC_2H_5$·PyO	825	820*
4-$COOC_2H_5$·PyO	830*	790*
3-CH_3CO·PyO	900*	840
4-NO_2·PyO	1100*	830
4-CN·PyO	805	800
3-OH·PyO	795	780
2-C_2H_5·PyO	763	765*
3-C_2H_5·PyO	810*	812
4-C_2H_5·PyO	820*	820
2,4-$(CH_3)_2$·PyO	765	760
2-CH_2OH·PyO	800*	812
3-CH_2OH·PyO	813	817
4-CH_2OH·PyO	818*	823
QNO	733	735
4-CH_3·QNO	750	745
iso-QNO	810	807

* broad

TABLE 4. d–d BAND MAXIMA OF 1 : 4 COMPLEXES

Complex	$\lambda_{\rm max}$ (mμ)
$(PyO)_4Cu(ClO_4)_2$	675
$(4\text{-}CH_3\cdot PyO)_4Cu(ClO_4)_2$	670
$(3\text{-}Cl\cdot PyO)_4Cu(ClO_4)_2$	695
$(3\text{-}COOC_2H_5\cdot PyO)_4Cu(ClO_4)_2$	685
$(4\text{-}COOC_2H_5\cdot PyO)_4Cu(ClO_4)_2$	770
$(3\text{-}CH_3CO\cdot PyO)_4Cu(ClO_4)_2$	685
$(4\text{-}CH_3CO\cdot PyO)_4Cu(ClO_4)_2$	760
$(4\text{-}NO_2\cdot PyO)_4Cu(ClO_4)_2$	710
$(3\text{-}CN\cdot PyO)_4Cu(ClO_4)_2$	700
$(4\text{-}CN\cdot PyO)_4Cu(ClO_4)_2$	735

Diffuse Reflectance Spectra. The diffuse reflectance spectra of some compounds were measured in 400—1200 mμ region on a Hitachi spectrophotometer of Model EPU-2A. Magnesium oxide was used as the standard of light reflectance and as the base material to dilute the compounds to obtain appropriate intensities in the reflected light. The spectra of other compounds were recorded in 340—1000 mμ region on a Hitachi spectrophotometer of Model EPS-3T without diluting the compounds with the base. The band maxima are recorded in Tables 3 and 4.

Results and Discussion

I. Nonapplicability of Hammett's Rule to Dimeric Complexes. The early studies of the effect of the ring substituent on the spin-spin coupling mechanism in the dimeric copper(II) halide complexes with pyridine *N*-oxides, the electronic natures of the substituents seemed to correlate well with the demagnetization.[6,11,12] However, the magnetic data of recently prepared complexes with a variety of substituents on the 3- and 4-positions in the pyridine ring revealed that no definite correlation exists between the electronic nature of the substituents in terms of Hammett's σ constants and the extent of the demagnetization or the d–d band positions.

Although some doubt had been thrown on the validity of the commonly used Hammett substituent constant,[13,14] Jaffé and coworkers[15] reported a linear relationship between the basicity

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*2 The details of the two modifications with normal and subnormal magnetic moments will be reported shortly.

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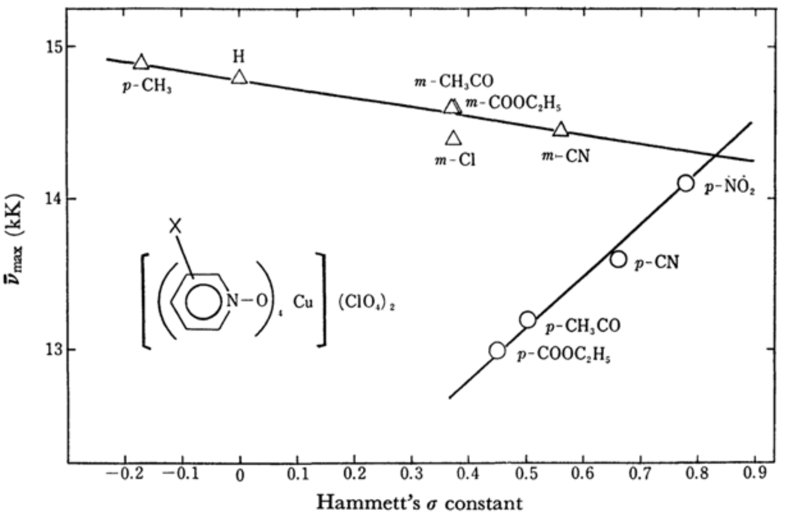

Fig. 1. The plot of the wave numbers ($\bar{\nu}_{max}$ in kK) of d–d band positions of copper(II) perchlorates with substituted pyridine *N*-oxides against Hammett's σ constant.

of a series of substituted pyridine *N*-oxides and the σ values.

Among the infrared active modes of substituted pyridine *N*-oxides,[16–18] Shindo[18] found that the N–O stretching frequencies of a variety of pyridine *N*-oxides derivatives correlate well with the Hammett's constant. Recently Kubota and Miyazaki[19] reported that a plot of the half-wave reduction potentials of substituted pyridine *N*-oxides against Hammett's σ constant gave a good linear relation.

II. Validity of Hammett's Rule in Monomeric Complexes. Recently, metal complexes with pyridine *N*-oxides were reported to confirm the correlation of physicochemical properties of the complexes with the electronic nature of the substituents.[6,11–12,20–27] The correlations were studied for complexes with substituents at the 4-position of the *N*-oxide molecules, where the electronic effect is transmitted to the *N*-oxide oxygen atom by a mesomeric mechanism. However, no test of correlations has been made for the copper(II) complexes with substituents attached in 3-position of the pyridine ring. In these studies furthermore the substituent constants used were σ in some cases and σ^+ or σ^- in others.[28] Hatfield and his coworkers[27] prepared the complexes of the type, $[Cu(X\text{-}PyO)_4](ClO_4)_2$, with X at 4-position in pyridine ring. They found that the d–d bands correlated with the σ^+ value of X.

We prepared the same type of complexes with X of electron-donating and electron-withdrawing nature at the 4- and 3-positions in pyridine ring. For these complexes, two linear relations between the d–d band positions, $\tilde{\nu}_{max}$(kK), and Hammett's σ constant, were observed. One has a negative and the other a positive slope (*cf.* Fig. 1).[29] The line with the negative slope is for the compounds with substituents in the 3-position. This line further includes two more compounds, one with *p*-CH_3 and the other with H (standard). This linear relation in this case can be explained if it is assumed that the ligand field band positions are determined mainly by the electron density of the coordinating

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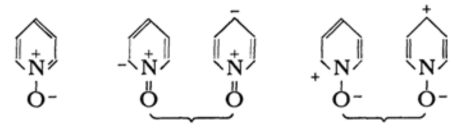
[27] R. Whyman, W. E. Hatfield and J. S. Paschal, *Inorg. Chim. Acta*, **1**, 113 (1967).

[28] J. Hine, "Physical Organic Chemistry," 2nd ed., McGraw-Hill Book Co., INC., New York, N. Y. (1962), p. 81.

[29] J. R. Joy and M. Orchin, *J. Am. Chem. Soc.*, **81**, 305 (1959).

oxygen atoms. Therefore as Hammett's σ constant decreases, these substituents produce larger electron densities on the oxygen atoms. This in turn leads to stronger ligand fields accompanied by higher wave numbers for the ligand field bands.

The line with the positive slope is for the compounds with 4-substituents of great electron-withdrawing power. This linear relation can be explained if it is assumed that back-bonding from the metal to the π-electron systems of ligand molecules[23,30-33] determines the band positions. The back-bonding is considered to take place through resonance structure B,[6] the weight of which should increase with the increase in the electron-withdrawing nature of the substituents.



A B C

III. Linear Relation between d–d Band Positions and Corrected Magnetic Moments.

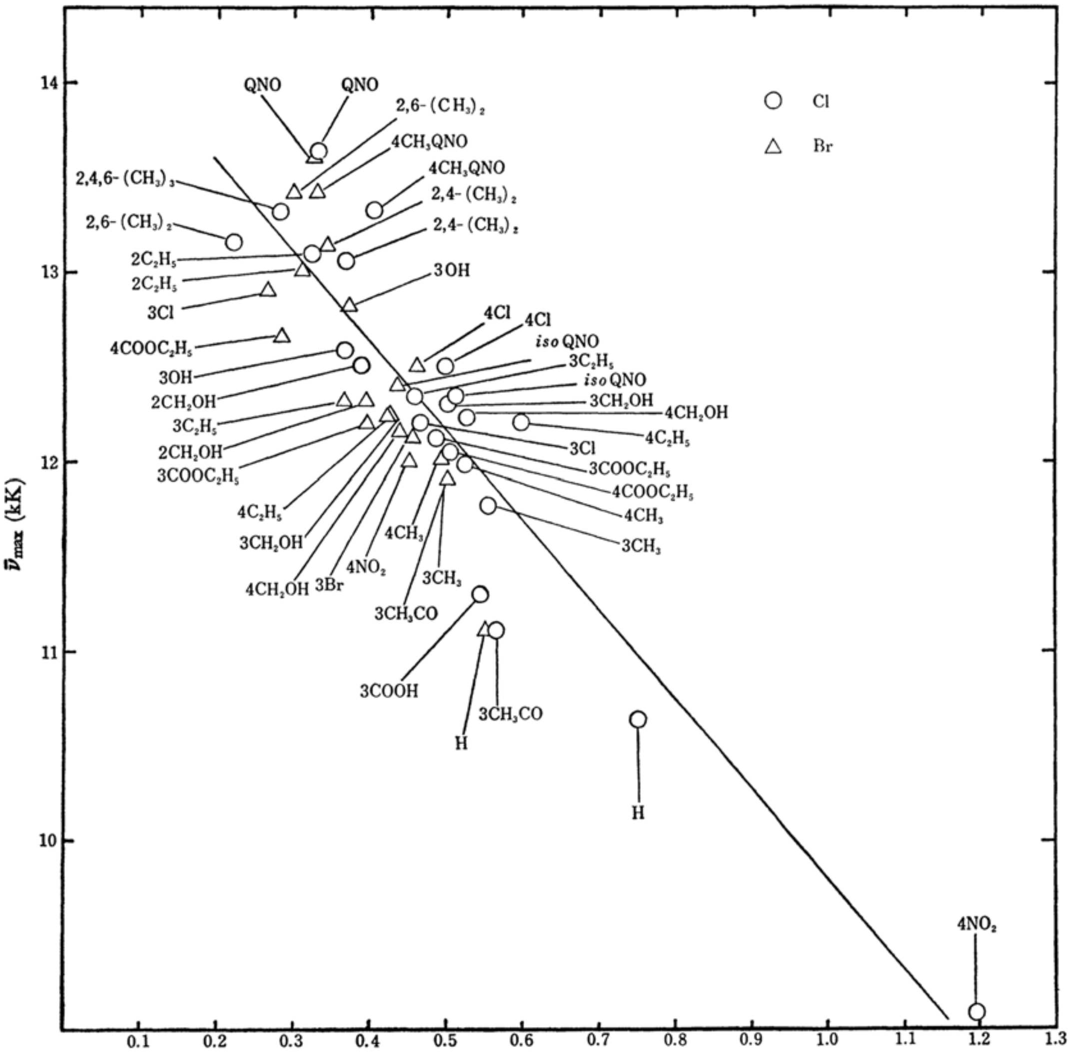


Fig. 2. The plot of the wave numbers ($\bar{\nu}_{max}$ in kK) of d–d bands of copper(II) halide complexes with substituted pyridine *N*-oxides against the corrected magnetic moments ($\mu_{eff}^{25°C}$ in B.M.).
○ and △ indicate the chloro and bromo complexes respectively.

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30) N. S. Gill, R. H. Nuttall, D. E. Scaife and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).

31) W. R. May and M. M. Jones, *ibid.*, **24**, 511 (1962).

32) M. Goldstein, E. F. Mooney, A. Anderson and H. A. Gebbie, *Spectrochim. Acta*, **21**, 105 (1965).

33) L. Morpurgo and R. J. P. Williams, *J. Chem. Soc.*, (*A*), **1966**, 73.

The nonapplicability of Hammett's rule in the dimeric copper(II) halide complexes with pyridine *N*-oxides, could possibly indicate that no correlation between any physicochemical quantities exist. However, it was found that both for bromo and chloro complexes, a linear relation exists between the d–d band positions, $\tilde{\nu}_{\max}$(kK), and the corrected magnetic moments, $\mu_{\mathrm{eff}}^{25°\mathrm{C}}$ (*cf.* Fig. 2). It would be more favorable to use *J* values, the separation energy between singlet and triplet state than $\mu_{\mathrm{eff}}^{25°\mathrm{C}}$. *J* values calculated from the observed magnetic moments assuming $g=2.2$, fitted a good linear relation with the d–d band positions ($\tilde{\nu}_{\max}$ in kK). However, *J* values were not used in this paper because the *J* values calculated as above may be somewhat different from those determined from χ *versus* T curves. On the other hand, the values of $\mu_{\mathrm{eff}}^{25°\mathrm{C}}$ which were calculated from the χ values observed for the same compound at different temperatures, coincided well with each other within experimental errors.

This relation shows that greater demagnetization is accompanied with greater shift of d–d bands toward shorter wavelengths. This linear relationship between the ligand field bands and the magnetic moments can be cited as a magnetochemical support for the recent correlation of the spectrochemical series to the idea of symmetry-restricted covalency.34–37) The spin-spin coupling mechanism should occur through the overlap of metal and ligand orbitals, giving a very symmetrically restricted covalency.

IV. Reasons for the Nonapplicability of Hammett's Rule in Dimeric Complexes. (*A*) *Steric Effects Previously Observed.* It was observed that, in many cases, irrespective of the polar effect of the substituents, the magnetic moments of complexes with 3-substituted ligands are smaller than those of the corresponding compounds with 4-substituted ligands. This observation seems to suggest a mechanism by which a greater magnetic interaction is produced between the copper(II) ions in a pair when a substituent is attached at a position closer to the central metal ion.

A similar trend was obtained in the study of the dimeric copper(II) complexes of the formula, $[\mathrm{Cu}(\overset{2}{\mathrm{O}}\cdot\mathrm{C_6H_4}\cdot\overset{1}{\mathrm{C}}\mathrm{H{=}N{-}R})\mathrm{Cl}]_2$, where R is a mono- or di-substituted aryl group (*cf.* Fig. 3).38,39)

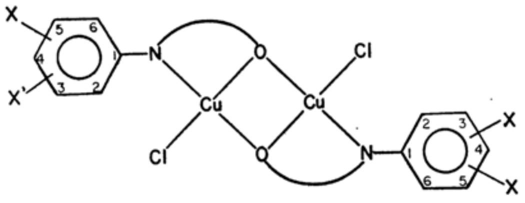

Fig. 3. X=H, Cl, CH_3 and NO_2

Chatt and Shaw40,41) described the metal complexes of the types, $[(\mathrm{PR'_3})_2\mathrm{NiRX}]$ and $[(\mathrm{PR'_3})_2\mathrm{MR_2}]$, where M=Ni, Co, Fe, and R=substituted aryl or some other aromatic groups. They observed that the stability of these complexes has much increased when substituents were attached in the *ortho*-position of R. One of the causes for such additional stabilization of the *ortho*-substituted aryl complexes compared to the meta- or para-substituted aryl compounds, was attributed to the shielding effect of the metal atoms by the *ortho*-substituents.

Such shielding becomes most effective when the aryl group is rotated about the M–C bond such that its plane is perpendicular to that of the complex. Such perpendicular orientations of the aromatic ring with respect to the plane of the complex were observed in molecular models constructed for Chatt's complexes and those reported in this study. Such a stereochemical arrangement is postulated to play an important part in the stabilization of these complexes.

A stabilization of metal complexes by *ortho*-substituents was also observed by Yamada and Miki42) in their mixed complexes of copper(II) with succinimide and picolines or lutidines.

(*B*) *Recent Results Indicative of Steric Effects.* In order to examine the contribution of the steric effect of substituents on the demagnetization or the d–d band shifts the effect of substituting methyl and ethyl groups in the 2-, 3- and 4-positions was first compared. The methyl group has a greater electron donating power than ethyl group at the 4-position. The Hammett's σ constants of these groups at this position are -0.170 and -0.151 respectively. In the 3-position, two σ values are proposed for ethyl group, -0.043 and -0.07.43,44) The smaller value, -0.07, is nearly the same as that for the 3-methyl group, -0.069. The methyl group should therefore have almost the same or

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34) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, New York, N. Y. (1962).

35) C. K. Jørgensen, "Progress in Inorganic Chemistry," Vol. IV, ed. by F. A. Cotton, Interscience Publishers, New York, N. Y. (1962), p. 73.

36) S. Kida, *Kagaku,* **20**, 510 (1965).

37) S. Yamada and S. Komorita, *Kagaku no Ryoiki,* **20**, 645 (1966).

38) M. Kato, Y. Muto, H. N. Ramaswamy, H. B. Jonassen and K. Imai, paper presented at the 16th Conference on Coordination Chemistry of the Chemical Society of Japan, Tokyo, December, 1966, Proceedings, p. 68.

39) Y. Muto, M. Kato, H. B. Jonassen and K. Imai, unpublished data.

40) J. Chatt and B. L. Shaw, *J. Chem. Soc.,* **1960**, 1718.

41) J. Chatt and B. L. Shaw, *ibid.,* **1961**, 285.

42) S. Miki and S. Yamada, This Bulletin, **37**, 1044 (1964).

43) H. H. Jaffé, *Chem. Revs.,* **53**, 191 (1953).

44) D. H. McDaniel and H. C. Brown, *J. Org. Chem.,* **23**, 420 (1958).

a greater electron-donating power than ethyl group in the 3-position. Shindo and Kubota successfully correlated the Hammett's σ values with the N–O stretching frequencies[18] and the half-wave reduction potentials[19] of substituted pyridine *N*-oxides. They used the larger σ value, -0.043, for the 3-substituted ethyl group. The ethyl group which has less electron-donating power but a bulkier size produces a larger effect on the demagnetization or d–d band blue shift than the methyl group which has greater electron-donating power but smaller size. This indicates that the substituent effect in the dimeric copper(II) complexes is at least partly due to a steric factor. Furthermore, since the nature of the polar effect of alkyl groups is mainly inductive, the interpretation of the experimental results observed for the compounds with these substituents is less ambiguous than for those compounds where the substituents have both inductive and mesomeric properties.

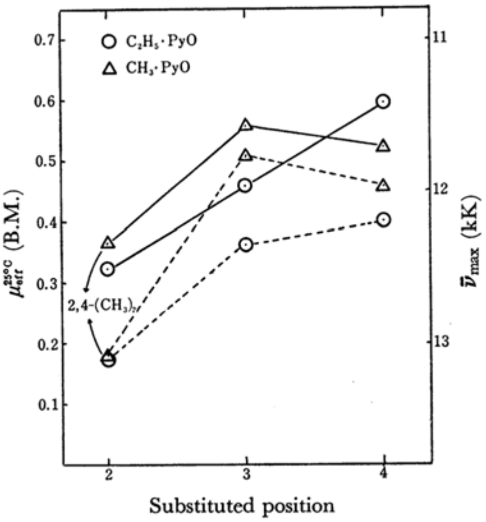

Fig. 4. Variations of magnetic moments ($\mu_{eff}^{25°C}$ in B.M.) and d–d band positions ($\bar{\nu}_{max}$ in kK) of copper(II) chloride complexes with methyl- and ethyl-pyridine *N*-oxides with substituted positions. Solid line is for magnetic moments and dashed line for d–d band positions. △ and ○ indicate complexes with methyl- and ethyl-pyridine *N*-oxides respectively.

The experimental results for chloro complexes are graphically given in Fig. 4. In the 4-position, the methyl group has a greater effect on the demagnetization and the d–d band blue shift than the ethyl group. This is as expected on the basis of the polar effect of substituents in terms of Hammett's constant. The steric effect of the ethyl group which should be larger because of its larger size still however seems not to be operative.

At the 3-position, the magnetic moment of the methyl compound increases to 0.55 B.M. from 0.52 B.M. of the 4-methyl compound as expected from the Hammett's σ values of this substituent. This indicates that, at this position, the steric effect of methyl group can not be observed.

However, at the same position, the magnetic moment value of the 3-ethyl compound decreases from that of the 4-ethyl compound, indicating a larger demagnetization in the 3-substituted compound. The demagnetization of 3-ethyl compound is larger compared to those of 4-methyl and 3-methyl compounds. These observations definitely indicate that the ethyl group in these complexes exerts a steric effect at 3-position. It is remarkable that of substituents with large size, they produce a larger demagnetization, even in the 4-position, than in the parent complex with pyridine *N*-oxide even when their electronic nature is electron-withdrawing in both inductive and mesomeric effects as is the case for $COOC_2H_5$, CH_3CO, *etc.* This seems to indicate stronger metal-ligand bonds in these complexes. Such strengthening of the metal-ligand bonds may occur through back-bonding, metal to ligand, which was observed in the monomeric compounds with pyridine *N*-oxides having the same electron-withdrawing substituents (*cf.* sect. II). However, the established structure of the parent complex is hardly suitable for such back-bonding mechanism (*cf.* sect. VII).

For substitution at 2-position, 2,4-dimethyl compounds were studied instead of the 2-methyl compounds because of the synthetic difficulty of preparing the pure 2-methyl compounds.[45-47]

The magnetic moment of this compound is much smaller than that of the 3-compound as well as that of the 4-compound. It is obvious that the methyl group in the 2-position has a large steric effect on the demagnetization phenomenon.

The magnetic moment of the 2-ethyl compound, 0.32 B.M., is even smaller than that of 2,4-dimethyl-compound, 0.37 B.M. The demagnetization effect of the 4-methyl group in the chloride complexes is estimated to be about 0.2 B.M. in a range from 0.5 to 0.7 B.M., the difference between the values of the 4-methyl and that of the parent complexes. These data indicate that in these dimeric complexes the 2-ethyl group because of its greater steric effect exerts a much greater demagnetization effect than the 2-methyl group.

Molecular framework models were built according to the established structures of the parent complex.[4,5] They indicate that when ethyl groups are attached in the 2-position of the pyridine rings which are almost perpendicular to the copper oxygen plane

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45) M. R. Kidd, R. S. Sager and W. H. Watson, *Inorg. Chem.*, **6**, 946 (1967).

46) R. Whyman and W. E. Hatfield, *ibid.*, **6**, 1859 (1967).

47) Y. Muto, unpublished data.

they are located above or below the plane shielding the fifth and the sixth coordination site (*cf.* Fig. 9).

In accordance with the linear relation between the d–d bands and the magnetic moments, the d–d band positions of the methyl and ethyl compounds vary in the same way as the magnetic moments, as the substitution positions are changed. In contrast to the smooth variation in magnetic moments with substituted positions, the blue shift of d–d bands is much greater between 2- and 3-positions than between 3- and 4-positions, indicating that the ligand fields of 2-alkyl compounds are much greater than those of 3- and 4-alkyl compounds. This becomes apparent in the reflectance spectra of copper(II) chlorides with ethylpyridine *N*-oxides (*cf.* Fig. 5). Such discrepancy between the extents of the variations in magnetic moments and d–d band positions should be improved if the energy differences between singlet and triplet states were used instead of the magnetic moments.

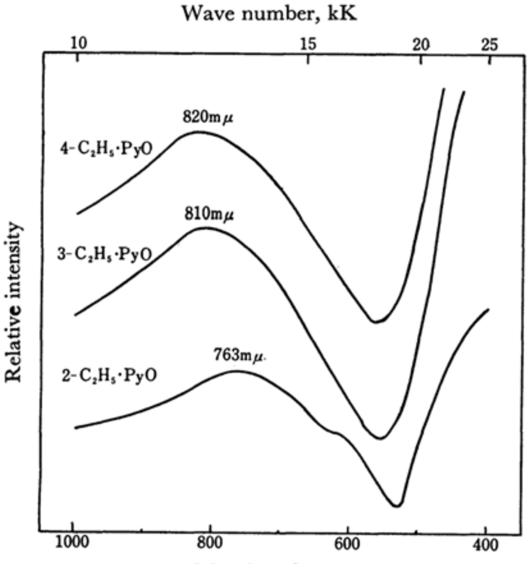

Fig. 5. Reflectance spectra of (ethylpyridine *N*-oxide)-copper(II) chloride.

The variations in spectral and magnetic properties of bromo complexes with changes in substitution positions are essentially the same as those observed for the chloro complexes. However, some interesting differences exist between bromo and chloro complexes in the relative magnitudes of the magnetic moments and the d–d band positions: 1. The magnetic moments of the 4-ethyl bromo complex is smaller than that of the 4-methyl bromo complex. 2. The slope of the line for the variations of magnetic moments with substitution positions is smaller for bromo complexes than for chloro complexes.

(*C*) *Interpretation of Steric Effect.* Yamada and Miki[48] reported that the d–d band of bis(*N*,*N*-diethylethylenediamine)copper(II) perchlorate appears at a much shorter wavelength than expected from its position in the spectrochemical series. They attributed this to the special steric condition of the ligand, which will make it more difficult for other ligands or molecules to approach the fifth and sixth coordination sites of copper(II) ion. It is well known that the quadri-coordinate, planar type of copper(II) complexes display the ligand field bands at much shorter wavelengths than those of sexa-coordinate or pseudo-sexa-coordinate copper(II) complexes. The very large value of the tetragonality ratio $R(\gamma_{Cu}/\gamma_{Ni})$ for this compound was pointed out by Jϕrgensen.[49,50] It is very probable that on the basis of Pauling's electroneutrality principle[51] the increase in the tetragonality of the complex with *N*-alkylethylenediamine compared to that of the parent ethylenediamine complex produces an increase in the strength of the coordinate bonds in the CuN_4 plane. If bonds to the fifth and sixth coordination position perpendicular to the CuN_4 plane which are present to some extent in the parent ethylenediamine complex, are broken or much weakened, extra electron migration from the ligands to the metal should occur through the bonds in the CuN_4 plane. According to the electroneutrality principle, any rearrangement of electron migration must keep the total electron flow-in as constant as possible.

This can also be described in terms of electron affinity. When the longer bonds perpendicular to the CuN_4 plane present in the parent compound are broken or weakened for some reason, the electron affinity of the metal should be increased. Such an increase in electron affinity of the metal, in turn, increases the strength of the four bonds in the plane.

In dimeric copper(II) halide complexes with pyridine *N*-oxides, the increased tetragonality of the complex due to the steric effect of the substituent, will produce stronger metal-ligand bonds, through which the super-exchange mechanism operates. This steric effect may provide a direct way for the determination of the variation of coordinate bond strength caused by changes in the stereochemistry of complexes. This steric factor which weakens the influence of other ions or mole-

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48) S. Yamada and S. Miki, This Bulletin, **36**, 680 (1963).

49) W. E. Hatfield, T. S. Piper and U. Klabunde, *Inorg. Chem.*, **2**, 629 (1963).

50) C. K. Jϕrgensen, "Biochemistry of Copper," ed. by J. Peisach, P. Aisen and W. E. Blumberg, Academic Press Inc., New York, N. Y. (1966), p. 1.

51) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell Univ. Press, Ithaca, New York (1960), p. 172.

cules on the fifth or sixth coordination position does not seem to be the only cause bringing about an increase in metal-ligand bond strength or the d–d band blue shift in copper(II) halide pyridine *N*-oxide complexes. The other factor seems to be due to the partial tetrahedral stereochemistry of these complexes which may call for less orbital overlap between metal and ligand. However, as the tetragonality increases with various substitutions on the pyridine ring, the tetrahedral nature decreases.

The combination of these two effects – the steric effect and the electronic effects of the substituents on the pyridine ring – are the prime factor which determines the nonapplicability of Hammett's rule to the magnetic and spectral properties of these dimeric copper(II) halide pyridine *N*-oxide complexes. The enhancement of stability of planar nickel(II) complexes by steric conditions compared to the octahedral ones have also been discussed recently.[52]

V. Further Experiments Indicative of the Steric Effect. (*A*) *Complexes with Quinoline N-Oxide.* In order to examine the steric effect in complexes with ligands other than pyridine *N*-oxides, copper(II) halide complexes with quinoline *N*-oxide, 4-methylquinoline *N*-oxide and isoquinoline *N*-oxide were prepared. The magnetic moments of the complexes with quinoline *N*-oxide, a ligand corresponding 2,3-disubstituted pyridine *N*-oxide, are smaller than those of the complexes with isoquinoline *N*-oxide, a ligand corresponding 3,4-disubstituted pyridine *N*-oxide. The behavior of the d–d band shift of these complexes followed the changes in the magnetic moments, as is demonstrated for bromo complexes in Fig. 6. On the other hand, however, the magnetic and spectral properties of 4-methylquinoline *N*-oxide complexes are not those expected from both steric and electronic considerations. Even though 4-methylquinoline *N*-oxide has a greater steric factor and greater electron-donating power than quinoline *N*-oxide, its complexes show smaller demagnetization and d–d band positions at larger wavelengths than those of quinoline *N*-oxide. Hatfield and coworkers[53,54] encountered the same situation in their study of methyl quinoline complexes.

One possible explanation for this may be that steric factors other than those mentioned above are encountered. A methyl group attached to a ligand of large size probably interferes with the smooth packing in the crystal compared to that of the complex of the parent ligand molecule. Such strains would also produce strains in the chemical bonding of the complex.

(*B*) *Complexes with Hydroxymethylpyridine N-Oxides.* If the group substituted on the pyridine ring also has some coordinating ability, the substituent effect might be opposed by the coordination effect. Under such conditions very little change in physical properties might be observed as the substitution positions on the ring are changed.

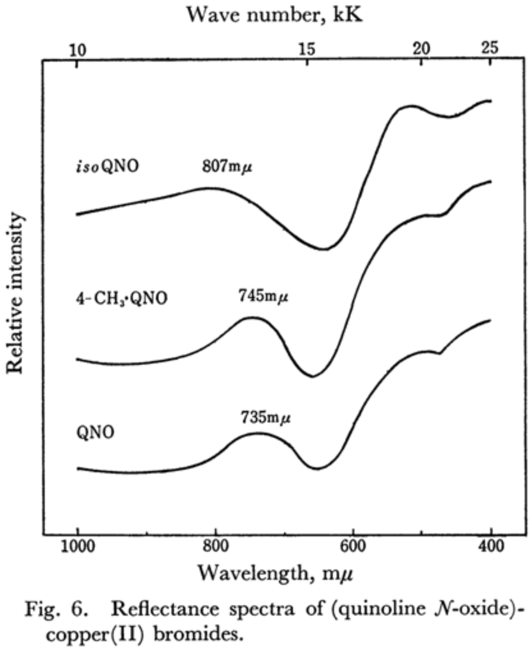

Fig. 6. Reflectance spectra of (quinoline *N*-oxide)-copper(II) bromides.

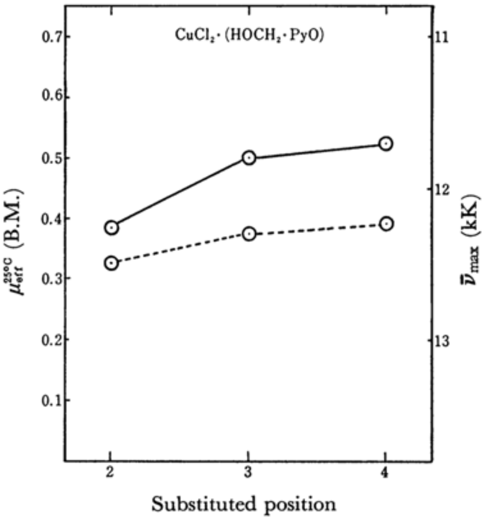

Fig. 7. Variations of magnetic moments ($\mu_{eff}^{25°C}$ in B.M.) and d–d band positions ($\bar{\nu}_{max}$ in kK) of (hydroxymethylpyridine *N*-oxide)-copper(II) chlorides with substituted positions. Solid line is for magnetic moments and dashed line for d–d band positions.

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[52] C. K. Jφrgensen, "Inorganic Complexes," Academic Press Inc., New York, N. Y. (1963), p. 69.

[53] W. E. Hatfield, D. B. Copley and R. Whyman, *Inorg. Nucl. Chem. Letters,* **2**, 373 (1966).

[54] R. Whyman, D. B. Copley and W. E. Hatfield, *J. Am. Chem. Soc.,* **89**, 3135 (1967).

This was indeed observed for the complexes with hydroxymethylpyridine *N*-oxide. Figure 7 shows a plot of the data for the chloro complexes. The slopes of the two lines are not as steep as those for the corresponding methyl and ethyl compounds in Fig. 4 indicating that the two effects have at least partially cancelled each other. In Fig. 8 the spectral curves for these complexes are given.

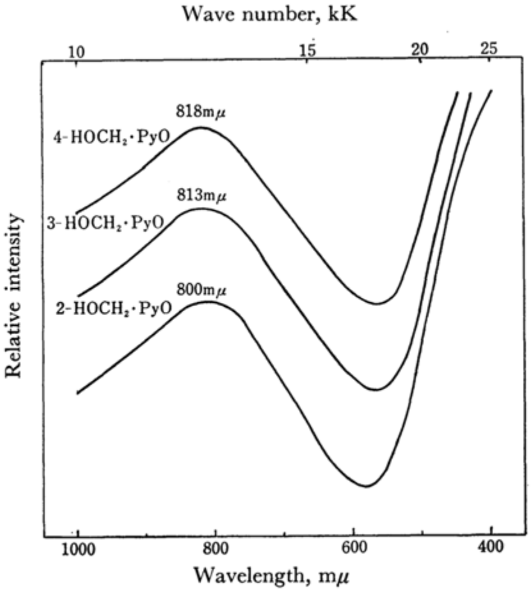

Fig. 8. Reflectance spectra of (hydroxymethylpyridine *N*-oxide)-copper(II) chlorides.

VI. Influence of Halogen Ions on d–d Band and Magnetic Moment. The influence of halide ions on the d–d band positions and the demagnetization in the chloro and bromo complexes is not what would be expected from the positions of these ions in spectrochemical series.

In almost all cases, the magnetic moments of bromo complexes are smaller than those of the corresponding chloro complexes.*[1f,12] Hatfield and coworkers[12] suggested that this phenomenon may be due to the difference in spin-orbit coupling and temperature independent paramagnetism between the chloro and bromo complexes. In a previous paper,*[1f] we suggested that the difference in nephelauxetic effects[34-37] of the chloride and bromide ions produces such differences in magnetic moments. The greater cloud expanding effect of the bromide ions will produce a greater overlapping of the relevant orbitals of the metal ions and the ligand molecules. This would give a greater covalency in their bonds and should give smaller magnetic moments for the bromo complexes.

Recently, Figgis and Nyholm summarized the contributions of the temperature independent paramagnetism and the spin-orbit coupling in metal complexes.[55,56] With a few exceptions, the d–d bands of bromo complexes with pyridine *N*-oxides appear at shorter wavelengths than those of the corresponding chloro complexes. The ligand fields of these bromo complexes are larger than those of the corresponding chloro complexes, suggesting smaller contribution, to spin-orbit coupling. The X-ray determinations of crystal structures of Cs_2CuCl_4 and Cs_2CuBr_4[57,58] revealed that these complexes contain flattened tetrahedral configurations with greater flattening for the bromocuprate ion in spite of its larger ionic size and its earlier position in the spectrochemical series.

Recent studies of copper(II) chloride and bromide complexes with aromatic amines revealed that, in some cases, their d–d bands appear where expected from the positions of these ions in the spectrochemical series whereas in others, the band positions appear in the reverse order.[59-63] Uhlig and Staiger[64] reported copper(II) chloride and bromide complexes of aminoalcohols with dimeric structures whose d–d band positions appear from compound to compound in the two different orders in the spectrochemical series as above. An explanation for such anomalous behavior of bromide and chloride ions in the order of spectrochemical series may be found in the recent concept of softness and hardness of metal ions and ligands.[65,66] However, at present, the physical basis of this concept is still somewhat ambiguous which makes a thorough discussion of this phenomenon difficult.[67,68]

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55) B. N. Figgis, "Introduction to Ligand Fields," Interscience Publishers, New York, N. Y. (1966), p. 253.

56) R. S. Nyholm, "The Plenary Lecture at Xth International Conference on Coordination Chemistry," Tokyo, September 12, 1967; The Japanese Translation by Y. Saito, *Kagaku to Kogyo* (*Chem. & Chem. Ind., Tokyo*), **21**, 338 (1968).

57) L. Helmholz and R. F. Kruh, *J. Am. Chem. Soc.*, **74**, 1176 (1952).

58) B. Morosin and E. C. Lingafelter, *Acta Cryst.*, **13**, 807 (1960).

59) I. S. Ahuja, D. H. Brown, R. H. Nuttall and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **27**, 1105 (1965).

60) I. S. Ahuja, D. H. Brown, R. H. Nuttall and D. W. A. Sharp, *ibid.*, **27**, 1625 (1965).

61) W. R. McWhinnie, *ibid.*, **27**. 2573 (1965).

62) A. E. Underhill, *J. Chem. Soc.*, **1965**, 4336.

63) D. E. Billing, A. E. Underhill, D. M. Adams and D. M. Morris, *J. Chem. Soc.*, (*A*), **1966**, 902.

64) E. Uhlig and K. Staiger, *Z. Anorg. Allgem. Chem.*, **346**, 21 (1966).

65) St. Ahrland, "Structure and Bonding," Vol. I, ed. by C. K. Jϕrgensen, J. B. Neilands, R. S. Nyholm, D. Reinen and R. J. P. Williams, Springer-Verlag, Berlin (1966), p. 207.

66) C. K. Jϕrgensen, *ibid.*, p. 234.

67) C.K. Jϕrgensen, The Symposium on Soft and Hard Acids and Bases organized by Professor M. J. Frazer, Northern Polytechnic, Holloway, London N7, March 29—31, 1967; Reports of Cyanamid European Research Institute, Cologny, Switzerland, CERI-TIC-P 130.

68) G. Klopman, the same symposium and the same reports as in Ref. 67; CERI-TIC-P 141.

Ito[69] investigated the anomalous phenomenon that ligands in copper(II) complexes are often out of order in the spectrochemical series. He[70] successfully classified, in conformity with the sense of the series, these ligands into three groups according to the stereochemistry of the complexes; planar-, octahedral- and the intermediate-type. Unfortunately, halide ions were not included in his classification. His classification also does not include the steric shielding effect discussed in this paper.

Since the copper(II) ion has one unpaired electron in any of these stereochemistries, a continuous variation from one stereochemistry to another seems to be possible.[71] Under such conditions, the large size of the bromide ion could display a steric shielding effect different from that of the smaller chloride ion. The cooperation of both factors, large size and cloud expanding, could produce the observed large effect of the bromide ion on the demagnetization and the d–d band blue shift.

It is interesting to note that a plot of the differences of the d–d band positions of the bromide and the chloride complexes with the same ligands, $\bar{\nu}_{\max}$ (bromide) $-\bar{\nu}_{\max}$ (chloride), against $\bar{\nu}_{\max}$ (chloride) decreases from a large value for the 4-nitro compounds to a small value(approximately zero) for the complexes with the largest $\bar{\nu}_{\max}$ values. The same type of convergency was observed for the differences in the magnetic moments of chloride and bromide complexes.

VII. Superexchange Pathways. The extent of the spin-spin coupling in dimeric copper(II) complexes varies significantly with the type of structure. Complexes of one structural type may reveal a considerable amount of demagnetization while others of a different structural type display little demagnetization. A part of this demagnetization is attributed to direct metal-metal exchange interaction. The magnetic moments of cupric acetate monohydrate, acetylacetone-mono-(*o*-hydroxyanil)copper(II), and (pyridine *N*-oxide)copper(II) chloride are 1.43 B.M., 1.37 B.M. and 0.77 B.M. at room temperature respectively[72] whereas the metal-metal distances in the established structures are 2.64 Å, 2.99 Å and 3.25 Å respectively. This fact seems to indicate that the observed demagnetization for copper(II) halide complexes with pyridine *N*-oxides is mainly produced by a superexchange mechanism involving bridging oxygen atoms. It is rather surprising that these pyridine *N*-oxide complexes reveal very low magnetic moments despite the fact that they contain rather weak metal-ligand bondings through which a superexchange mechansim must operate. One of the factors which enhances the electron exchange must be the magnitude of orbital-overlap between the related atoms or ions existing in the superexchange pathway.

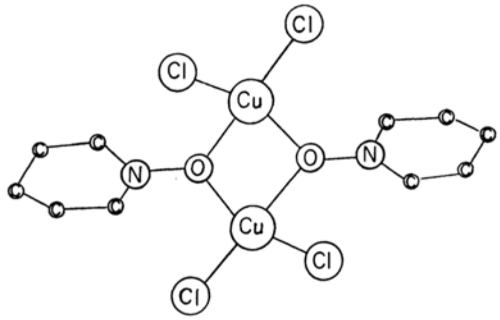

Fig. 9. Structure of (pyridine *N*-oxide)-copper(II) chloride.

On the basis of the known structure of the parent compound (*cf.* Fig. 9),[4,5] we suggest the following two pathways as the most likely ones in dimeric copper(II) halide complexes with pyridine *N*-oxides; one is a σ type- and the other a π type pathway (*cf.* Figs. 10a, 10b and 10c). Figure 10a

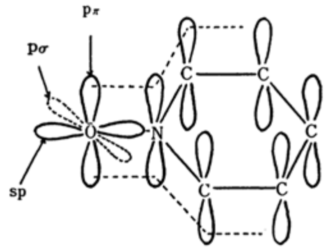

Fig. 10a. Ligand orbital representation in complex.

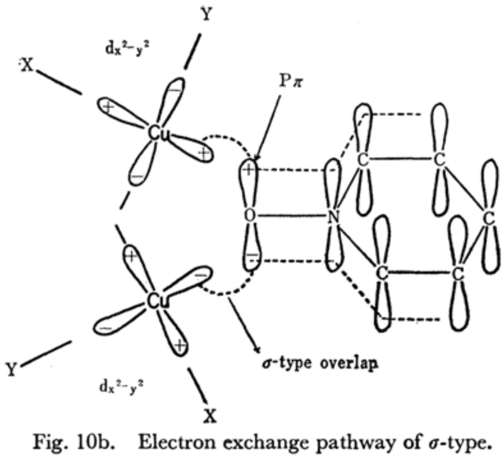

Fig. 10b. Electron exchange pathway of σ-type.

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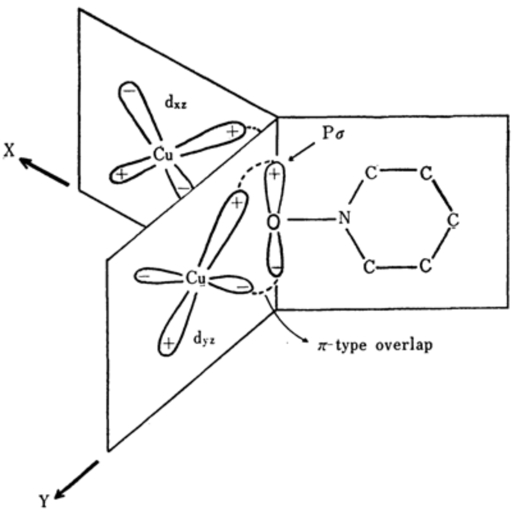

Fig. 10c. Electron exchange pathway of π-type.

provides a representation of the ligand orbitals necessary for describing electron exchange. Orbital-overlap schemes for electron exchange pathways of a σ-type and a π-type are given in Fig. 10b and 10c, respectively. For simplicity, the orbital-overlap schemes in these figures are drawn in idealized form. The actual mode of the orbital-overlapping may differ, in details, from this. The bond angles and other structural parameters should vary somewhat with the nature of the attached substituents or with the packing conditions of the individual molecules. In the structure of the parent complex,[4,5] determined by X-ray analysis, the plane of pyridine ring becomes nearly perpendicular to the $\mathrm{Cu}\begin{smallmatrix}\diagup\mathrm{O}\diagdown\\ \diagdown\mathrm{O}\diagup\end{smallmatrix}\mathrm{Cu}$ plane by rotation about the N–O bond, giving an angle of 70 degrees between these two planes. However, the figures were drawn for the two planes falling at essentially 90 degrees. This angle should vary somewhat from complex to complex.

Another orbital overlap of the σ type should also be examined for electron migration (second type). This is set up with the $3d_{x^2-y^2}$ or $3d_{z^2}$ orbitals of copper and an s orbital of oxygen. This orbital overlap has the characteristic of being rather insensitive to the bond angles.[73–75]

The sigma framework of complex molecules is often discussed in terms of localized bonds among hybrid atomic orbitals. This basis is intentionally avoided in Fig. 10 because it obscures the overlap patterns determining the geometric criteria for superexchange.

Of these two pathways the σ type is considered more effective for electron migration for the following reasons: 1. The orbital overlap in a σ type pathway is expected to be greater than those of a π type pathway. 2. Dubicki and Martin[76] suggested that, in copper(II) acetate or in the related compounds, the exchange between metal atoms in a molecule becomes operative *via* the bridging π system by mixing of metal d_{xy} and $d_{x^2-y^2}$ orbitals through spin-orbit coupling.[77] This can be applied to the electronic system of the complexes discussed here. Spin-orbit coupling may be decreased with an increase of the ligand field strength. However, the experimental evidence shows that greater ligand fields produce greater demagnetizations, suggesting that in these complexes the π pathway is less important. 3. The linear relation between the magnetic moments and d–d band positions is taken as evidence of greater importance of a σ pathway compared to a π pathway. Since in these complexes the strength of a σ type bond is believed to be the main factor determining the d–d band positions, it is very probable that the apparent parallelism between magnetic moments and d–d band positions, indicates that spin-spin coupling takes place primarily through the σ bonds. 4. The comparison of (pyridine *N*-oxide)-copper(II) chloride and acetylacetone-mono-(*o*-hydroxyanil)copper(II) whose structures have been determined by X-ray analysis is very useful in the examination of the relative importance of the factors controlling the exchange phenomenon for the following reasons: On the basis of its pK values, a phenolic oxygen produces a much stronger σ type bond than pyridine *N*-oxide's oxygen atom.[6,78] Nevertheless, the *N*-oxide complex and its related compounds display much larger demagnetization than the anil copper(II) complex and its related compounds.[72] This indicates that the most important factor in determining the electron exchange is the bond angles rather than the bond strengths in a pathway, though the latter should be the main factor when complexes with the same bond angles are compared. The importance of bond angles implies that the exchange mechanism operates *via* a σ type of orbital overlap rather than a π type. If electron migration takes place through a π type of orbital overlap, the demagnetization should not be sensitive to variations in bond angles. For a σ type of orbital overlap to be most effective, the bond angles, C–O–Cu_1 and C–O–Cu_2 in Fig. 11a or N–O–Cu_1 and N–O–Cu_2 in Fig. 11b, should be the same. The observed bond

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73) L. C. Cusachs, M. Kato and H. B. Jonassen, *Chem. Revs.*, **64**, 122 (1964).

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

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76) L. Dubicki and R. L. Martin, *Inorg. Chem.*, **5**, 2203 (1966).

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78) Ref. 52, p. 108.

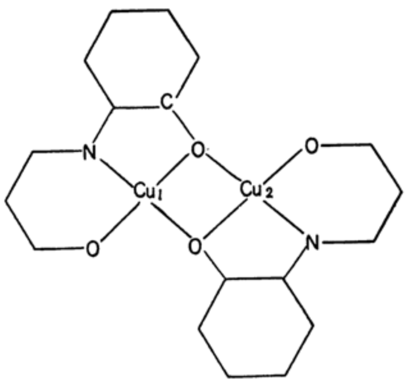

Fig. 11a. Schematic representation of bond angles of acetylacetone-mono-(*o*-hydroxyanil)copper(II).

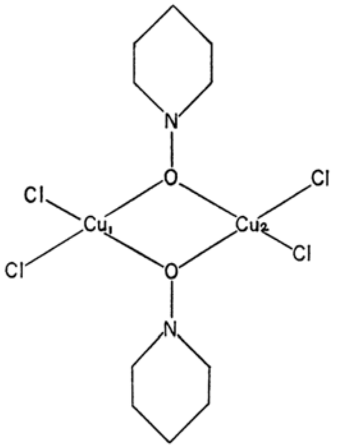

Fig. 11b. Schematic representation of bond angles of (pyridine *N*-oxide)-copper(II) chloride.

angles of the *N*-oxide complex, 127° and 123°,[4,5] are nearly equal. On the other hand, the bond angles of the anil copper(II) differ quite a bit (130° and 111°).[79,80] However, the difference in bond angles in the latter is still not great enough to prevent completely the utilization of a σ type of orbital overlap for electron migration.

The effectiveness of a π pathway and the aforementioned second type of σ pathway for electron migration may be approximately equal in both complexes. It is of interest that among the anil copper(II) and its related complexes, salicylal-*o*-hydroxybenzylamine copper(II) has an extraordinary small magnetic moment, 0.87 B.M.[3,79,81-85] Nearly all tri-coordinated units of these complexes are composed of one *five* and one *six* membered rings. Only the hydroxybenzylamine copper(II) contains two six membered rings in the unit. Molecular framework models indicate that the condition of the equality of the C–O–Cu_1 and C–O–Cu_2 bond angles necessary for an effective σ pathway is best satisfied in this complex (*cf.* Fig. 12). Recent studies of *N*-*n*-propanolsalicylaldiminato-copper(II) and its related complexes[10,86,87] have shown that these complexes all have very low magnetic moments, *ca.* 0.5 B.M. They have tricoordinate units of six-membered rings. Molecular models again indicate only that the condition of similar size bond angle in these complexes is satisfied.

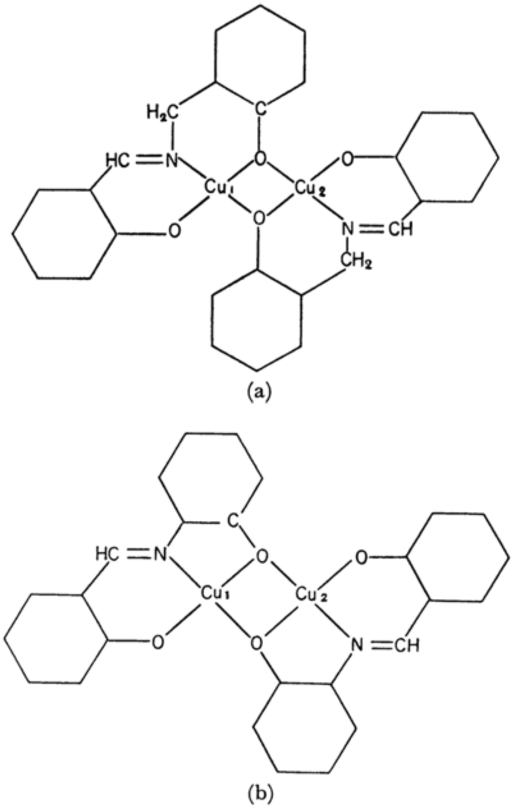

Fig. 12. Schematic representations of the structures fitted (a) and unfitted (b) for the equality condition of bond angles, C–O–Cu_1 and C–O–Cu_2.

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From this, it may be concluded that the large demagnetization observed in copper(II) halide complexes with pyridine *N*-oxides is caused by the availability of the σ type of pathway for electron migration, and the comparatively small amount of demagnetization in acetylacetone-mono-(*o*-hydroxyanil)copper(II) and its related compounds is attributable to the decreased efficiency for utilization of the σ pathway.

Two interesting features can be deduced from the orbital overlap schemes in Fig. 10: 1. The mesomeric effect of substituents attached to pyridine ring is transmitted to a p_π orbital through the π electron system of ligand molecule. In this way, the mesomeric effect of substituents becomes associated with the demagnetization mechanism. The inductive effect of substituents will be transmitted to s or p orbitals of oxygen atom by field effect, π inductive effect, or other effects.[88] 2. In this idealized picture, back-bonding through d_{xz} or d_{yz} orbitals of metal atom is not necessary since the p_σ orbital on the oxygen atom which overlaps these d orbitals is not in conjugation with the π electron system of the pyridine ring. This may be different from the situation to be found in the monomeric copper(II) perchlorate complexes with pyridine *N*-oxides in section II.

The relative effectiveness of direct metal-metal interaction and superexchange interaction in demagnetization should vary with the type of compounds.[2,5,6,12,54,72,79,80,85,89,90] For the latter interaction, the relative importance of the σ and π pathways is a problem for research and, it is expected to vary depending upon the structure of the compounds. It is a surprising fact that the magnetic moments of a great number of copper(II) alkanoates and benzoate fall at about 1.4 B.M.[72,76,91,92]

Molecular orbital calculations suggested by Cusachs, Kato and Jonassen[73] have been carried out for a model complex:[93] Copper(II) formate in the copper acetate cage structure. Although the direct Cu–Cu orbital overlap integrals are entirely insignificant, the two highest, singly occupied, molecular orbitals are of the sigma type with respect to the planes containing the copper and neighboring oxygen atoms, and dominate the computed orbital-orbital coupling terms. The orbital energies of these two molecular orbitals differ by only about 0.3 eV, so it is to be expected that there would be extensive configuration interaction, much as in the case of the ground state of H_2 at large internuclear distances. Coupling was calculated for the asymptotic limit of complete configuration interaction, or localization of a single electron in each half of the molecule, and found to vanish. It may be argued that these one-electron model calculations oversimplify the electron interaction terms quite severely, but no other method is currently available for such large molecules that does not do violence to some of the more important one- and two-electron contributions. These calculations do clearly support the present interpretation of the demagnetization mechanism as proceeding by coupling through the extended *sigma* framework of the molecule.

Progress in the study of spin-spin coupling mechanism in dimeric copper(II) complexes will require more examples of X-ray structural determination along with ESR and NMR experiments.[76]

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