The Substituent Effect on the Magnetic Interaction and d–d Bands in Dimeric Copper(II) Halide Complexes with Pyridine *N*-Oxides

Yoneichiro MUTO,* Michinobu KATO,** Hans B. JONASSEN***
and Koji KAKIUCHI*

* *Department of Chemistry, Saga University, Saga*
** *Aichi Prefectural University, Mizuho-ku, Nagoya*
*** *Department of Chemistry, Tulane University, New Orleans, La., U. S. A.*

(Received April 23, 1968)

In the previous papers,[1] we reported the correlation between the magnetic moments and d–d bands in dimeric copper(II) halide complexes with 3- or 4-substituted pyridine *N*-oxides. In these dimeric complexes, no correlation was observed between Hammett's constants and the magnetic moments or the d–d band positions. In order to elucidate why Hammett's rule is not obeyed in these complexes, we have now prepared copper(II) halide complexes with pyridine *N*-oxides with substituents in 2-, 3- and 4-positions on the pyridine ring and measured the magnetic susceptibilities and the reflectance spectra (*cf.* Table 1).

From the data in Table 1 the following conclusions about the substituent effect can be obtained: 1) For the same substituent group, the closer the site of substitution to the central metal ion is, the greater are the demagnetization and the blue shift of the d–d band. In the case of ethyl group, *e. g.*, these effects increase in the following order of substitution: 2->3->4-. It can also be seen that the difference between the λ_{max} of the d-d bands of 2- and 3-substituted complexes is fairly large, whereas the difference between those of 3- and 4-substituted complexes is small. 2) As for different substitutions at the same site (ethyl *vs.* methyl), the more bulky group has a greater demagnetization effect. This can also be observed in the greater demagnetization in the quinoline *N*-oxide complexes in comparison with pyridine *N*-oxide complexes.

These data seem to indicate that, in these dimeric complexes, the steric factor is more important in determining the extent of magnetic interaction or λ_{max} of d–d bands than the electronic effect.

The molecular framework model built up on the basis of the determined structure of the parent complex, $(CuCl_2{\cdot}PyO)_2$,[2] indicates that, the ethyl groups attached in the 2 position of pyridine rings, which are almost perpendicular to the copper-oxygen plane, come above or below the plane to shield the fifth coordination sites of the copper ions. Such shielding of the coordination sites by chemically inert groups usually increases the tetragonality of complexes and the strength of the four coordinate bonds in the plane, as is seen in the unusual red color or the extremely large values of tetragonality ratio R of bis(*N,N*-dialkylethylenediamine)copper(II) complexes.[3] Therefore, it is very probable that, in the dimeric pyridine *N*-oxide complexes, the covalent bonding between the copper and the bridging oxygen atoms, through which the magnetic interaction occurs, is strengthened by the shielding effect of inert groups on the pyridine rings, and a much greater demagnetization or blue shift of d-d bands than expected from the electronic effect of the group is produced through it.

TABLE 1. MAGNETIC MOMENTS CORRECTED TO THOSE AT 25°C[a] AND d–d BANDS

Ligand	1 : 1 $CuCl_2$ Complex		1 : 1 $CuBr_2$ Complex	
	$\mu_{\mathrm{eff}}^{25°\mathrm{C}}$(B. M.)	λ_{max}(mμ)	$\mu_{\mathrm{eff}}^{25°\mathrm{C}}$(B. M.)	λ_{max}(mμ)
2-C_2H_5PyO[b]	0.32	763	0.31	765
3-C_2H_5PyO	0.46	810	0.37	812
4-C_2H_5PyO	0.59	820	0.41	820
2,4-$(CH_3)_2$PyO	0.37	765	0.35	760
QNO	0.33	733	0.33	735
4-CH_3QNO	0.40	750	0.33	745
i-QNO	0.51	810	0.43	807

a) *cf.* Ref. 1 b) PyO : Pyridine *N*-oxide c) QNO : quinoline *N*-oxide

---

[1] Y. Muto, M. Kato, H. B. Jonassen and H. N. Ramaswamy, This Bulletin, **40**, 1535 (1967); M. Kato, Y. Muto and H. B. Jonassen, *ibid.*, **40**, 1738 (1967).

[2] H. L. Schäfer, J. C. Morrow and H. M. Smith, *J. Chem. Phys.*, **42**, 504 (1965); R. S. Sager, R. J. Williams and W. H. Watson, *Inorg. Chem.*, **6**, 951 (1967).

[3] S. Yamada and S. Miki, This Bulletin, **36**, 680 (1963); C. K. Jørgensen, "Biochemistry of Copper," ed. by J. Peisach, P. Aisen and W. E. Blumberg, Academic Press Inc., New York, N. Y. (1966), p. 1.