The Correlation between Reflectance Spectra and Magnetic Moments of Copper(II) Halide Complexes with Pyridine *N*-Oxides

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In the preceding communication,[1] we reported that the magnetic moments of dimeric copper(II) halide complexes with substituted pyridine *N*-oxides did not follow the Hammett's σ constants. In order to confirm this, and in order to obtain other experimental facts supporting this finding, we studied the reflectance spectra of these copper(II) complexes. It was observed that the ligand field bands at 700—900 mμ behave in the same way as the magnetic moments, showing the same breakdown in the relation of the Hammett's σ constants to the spectra of these compounds. However, a good linear relation was found to exist between the band positions and the magnetic moments, which were corrected for minor room temperature variations to those at 25°C by using Bleaney and Bowers' equation[2] assuming $g=2.2$ (*cf.* Fig. 1).

In this study, the following results were reconfirmed:[3] 1) The band positions of bromo complexes appear at shorter wavelengths than those of the corresponding chloro complexes. 2) In most cases, the band positions of the complexes with 3-substituted ligands appear at shorter wavelengths than those of the corresponding compounds with 4-substituted ligands. In line with (1) and (2), the magnetic moments of bromo complexes are smaller than those of the corresponding chloro compounds (1′), and the moments of the complexes with 3-substituted ligands are smaller than those with 4-substituted ligands (2′).

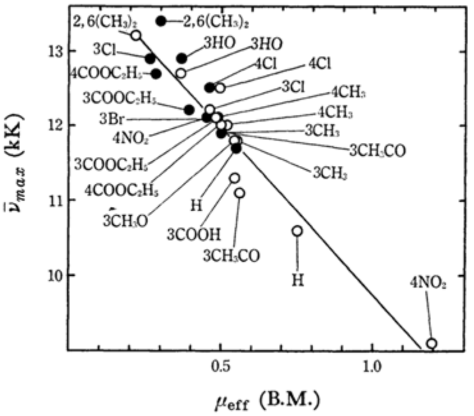

Fig. 1. The plot of the wave numbers of ligand field bands of $R\cdot C_5H_4NO\cdot CuX_2$ (X=Cl, Br), ν_{max} (kK), against the magnetic moments, $\mu_{\rm eff}$ (B. M.), corrected to 25°C.
○ and ● indicate the chloro and bromo complexes respectively.

Hatfield *et al.*[4] suggested that the phenomenon listed in (1′) may be interpreted by the differences of spin-orbit coupling and temperature independent paramagnetism between the chloro and bromo complexes. However, these data seem to indicate that the difference in nephelauxetic effects of chloride and bromide ions produces such differences in magnetic moments. The greater cloud expanding effect of the bromide ions should more effectively lower the effective charges on the metal ions. This will produce a greater covalency of the bonding of the copper ion and the organic ligand molecules, leading to the observed smaller magnetic moment compared to the chloro complexes.[5-7]

The observation of a linear relationship between ligand field bands and the magnetic moments may be taken as a magnetochemical support of the recent interpretation of the spectrochemical series through the idea of symmetry-restricted covalency. The spin-spin coupling mechanism should occur through the overlapping of metal and ligand orbitals, giving a very symmetrically restricted covalency.[5-7]

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

2) B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.* (*London*), **A214**, 451 (1952).

3) Y. Muto and H. B. Jonassen, This Bulletin, **39**, 58 (1966).

4) W. E. Hatfield and J. C. Morrison, *Inorg. Chem.*, **5**, 1390 (1966).

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

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

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