Magnetic Moments of Some Copper(II) Halide Complexes with Substituted Pyridine *N*-Oxides

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Pyridine *N*-oxide copper(II) chloride has a subnormal magnetic moment (0.85 B.M.)[1] at room temperature. Its structure has recently been determined by X-ray analysis;[2] it consists of a binuclear molecule $[Cu(C_5H_5NO)Cl_2]_2$ in which copper(II) ions in a pair are bridged by the oxygen atoms of the ligand molecules. The magnetic data of this compound and of a number of the same type of complexes with substituted pyridine *N*-oxides suggest that the demagnetization primarily occurs by means of a superexchange interaction between the copper(II) ions in the pair through the bridging oxygen atoms.[3,4]

In order to elucidate the correlation between the demagnetization and the physicochemical properties of these complexes, we have been studying the complexes with a variety of substituents on the pyridine ring.[5] In this paper, we will report on the newly-prepared copper(II) halide complexes of pyridine *N*-oxides with electron-withdrawing substituents. As is shown in Table 1, the complexes prepared all exhibit low magnetic moments and probably all have a binuclear structure similar to that observed in pyridine *N*-oxide copper(II) chloride.

Table 1. Magnetic susceptibilities (c.g.s., e.m.u.) per gram and magnetic moments (B.M.)

Compound	$10^6\chi_g$	T°K	μ
$3\text{-Cl}\cdot C_5H_4NO\cdot CuCl_2$	−0.12	297	0.46
$3\text{-Cl}\cdot C_5H_4NO\cdot CuBr_2$	−0.31	291	0.25
$3\text{-COOH}\cdot C_5H_4NO\cdot CuCl_2$	0.00	294	0.53
$3\text{-COOC}_2H_5\cdot C_5H_4NO\cdot CuCl_2$	−0.14	297	0.48
$3\text{-COOC}_2H_5\cdot C_5H_4NO\cdot CuBr_2$	−0.24	297	0.39
$4\text{-COOC}_2H_5\cdot C_5H_4NO\cdot CuCl_2$	−0.12	297	0.50
$4\text{-COOC}_2H_5\cdot C_5H_4NO\cdot CuBr_2$	−0.32	296	0.28
$3\text{-CH}_3CO\cdot C_5H_4NO\cdot CuCl_2\cdot \frac{1}{2}C_2H_5OH$	0.02	303	0.58
$3\text{-CH}_3CO\cdot C_5H_4NO\cdot CuBr_2\cdot \frac{1}{2}C_2H_5OH$	−0.11	304	0.52
$4\text{-CN}\cdot C_5H_4NO\cdot CuCl_2$	1.05	296	0.95
$4\text{-CN}\cdot C_5H_4NO\cdot CuBr_2$	0.38	297	0.79
$4\text{-NO}_2\cdot C_5H_4NO\cdot CuCl_2$	1.72	303	1.21
$4\text{-NO}_2\cdot C_5H_4NO\cdot CuBr_2$	−0.12	298	0.45

At first, we expected that the electron-withdrawing substituents would produce a comparatively small magnetic interaction by decreasing the electron density of the oxygen atoms, thus weakening the metal-oxygen covalent bonds through which the demagnetization mechanism operates. It is surprising that, contrary to this expectation, the electron-withdrawing substituents in both inductive and resonance effects, such as COOH, $COOC_2H_5$, CH_3CO and NO_2, produce a larger demagnetization than with the parent complex with pyridine *N*-oxide. This indicates that substituent effects in Hammett's sense are broken down in these complexes. Very recently, Hatfield *et al.*[4] have reported that the magnetic interaction in the copper(II) complexes with pyridine *N*-oxides correlates well with the resonance effects of the substituents in terms of σ_R values. Their conclusions differ from ours because: (1) we studied many more complexes; (2) they observed a negligible interaction for the complex with 4-nitropyridine *N*-oxide, which was not the case in our study, and (3) they did not study the complexes with 3-substituents.

Recently, Sacconi *et al.*[6] observed, in their

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study of substituted *N*-isopropylsalicylideneaminato copper(II) complexes, that the steric arrangements of the complexes are influenced by the nature of the substituents on the benzene ring. For instance, the arrangement steadily changes from pseudo-tetrahedral to planar in the order of the substituents, H, CH_3, Cl and NO_2. The degree of overlap of the orbitals of the metal and the coordinating atoms should be determined by the relative orientation of the orbitals in space. A larger orbital overlapping, which should result in stronger magnetic interactions in the dimeric copper(II) complexes, is expected to be produced by the spatial orbital orientations of the planar type rather than by those of the tetrahedral type. In reference to these facts, the observed larger demagnetization of the complexes of pyridine *N*-oxides with CH_3, Cl and NO_2 than with H can be explained if it is assumed that a very similar type of substituent effect exists in both the Sacconi complexes and ours. A reflectance spectral study of these complexes, which is now in progress, seems to support this conclusion.