2426 © 1990 *The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, *63*, *2426—2427 (1990)* [Vol. 63, No. 8

The Magnetic Properties of Copper(II) 3- and 5-Substituted 2-Pyridinolates

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(Received March 26, 1990)

Synopsis. The *N,N*-dimethylformamide adducts of copper(II) 3- and 5-substituted 2-pyridinolates were prepared, and then characterized by means of magnetic susceptibility and IR-spectroscopy. The variation in their magnetic moments is discussed in terms of the basicities of the parent 2-pyridones.

Most copper(II) carboxylates have dinuclear structures similar to that of copper(II) acetate monohydrate,[1,2] and exhibit strong antiferromagnetic interactions between pairs of copper(II) ions. In conformity with a superexchange mechanism, the strength of spin-exchange coupling has been correlated with the acidity of the parent carboxylic acid ($\mathrm{p}K_{a2}$).[3,4] However, it might be correlated more simply with the basicity of the parent carboxylic acid ($\mathrm{p}K_{a1}$), since the bridging carboxylate acts as a bidentate ligand. A magnetic study of a series of copper(II) 3- and 5-substituted 2-pyridinolates, which have copper(II) acetate-type dinuclear structures,[5,6] may provide answers to such questions, since the ionization constants of pyridones are well characterized[7] and in a series of 3- and 5-substituted 2-pyridones, the $\mathrm{p}K_{a1}$ values increase in a different order from the $\mathrm{p}K_{a2}$ values. We thus prepared some copper(II) 3- and 5-substituted 2-pyridinolate adducts with *N,N*-dimethylformamide, $\mathrm{Cu(XpyO)_2 \cdot DMF}$ and investigated their magnetic properties.

The 3- and 5-substituted 2-pyridones studied here, except for the 3-halo derivatives, were obtained commercially. 3-Chloro- and 3-bromo-2-pyridones were prepared by the thermal rearrangement of the corresponding pyridine *N*-oxides.[8] The DMF adducts of their copper(II) salts were prepared according to procedures very similar to those previously reported for the 2-pyridinolate and 3-methyl-2-pyridinolate compounds.[5] The IR spectra of the solid compounds show bands of coordinated carbonyl stretching vibrations, while the C=O stretching vibrations intermix with the adjacent C=C stretching motions.[6,11] Their effective magnetic moments (Table 1) were evaluated from the room-temperature molar magnetic susceptibilities (χ_M) using the equation $\mu_{\mathrm{eff}}=2.83[(\chi_M-\chi_{\mathrm{dia}}-N\alpha)T]^{1/2}$. The appropriate diamagnetic corrections (χ_{dia}) were estimated from the Pascal constants,[9] and the temperature-independent paramagnetic contribution ($N\alpha$) was taken as 60×10^{-6} emu mol^{-1} (1 emu$=4\pi\times10^{-6}$ m^3). For 3-nitro-2-pyridinolate, the temperature dependence of its magnetic susceptibility was measured in the temperature range 80—300 K, and could be represented by the Bleaney-Bowers equation[10] with parameters $g=2.17$ and $2J=-314$ cm^{-1}. The magnetic and spectral data indicate that the present compounds have pyridinolate-bridged dinuclear structures. The variation in the singlet-triplet separation values (e.g., $-2J=405$,[5] 365,[5] and 314 cm^{-1} for the DMF adducts of copper(II) 3-methyl-2-pyridinolate, 2-pyridinolate, and 3-nitro-2-pyridinolate, respectively) indicates that the smaller magnetic moment is accompanied by a stronger magnetic interaction between copper(II) ions.

Comparisons of the room-temperature magnetic moments for the 3- and 5-chloro-2-pyridinolate compounds or 3- and 5-nitro-2-pyridinolate compounds (Table 1) with that for the 2-pyridinolate compound show that these magnetic moments are affected more strongly by the 3-substituents than by the 5-substituents like the basicities of the parent 2-pyridones. This implies that the strength of the spin-exchange coupling is correlated more closely with the $\mathrm{p}K_{a1}$ value than with the $\mathrm{p}K_{a2}$ value, irrespective of some steric and resonance effects. In order to demonstrate such a correlation, the room-temperature magnetic moments (in BM) of the present compounds, together with the literature data for the DMF adducts of copper(II) 2-pyridinolate, 3-methyl-2-pyridinolate, and 3-ethyl-2-pyridinolate,[5] are plotted against the $\mathrm{p}K_{a1}$ values of the ligands in Fig. 1. The plot consists of a straight line which has the same slope as that for dinuclear copper(II) carboxylates:[4]

Table 1. Analytical Data and Effective Magnetic Moments at 20 °C

Compound		Found(Calcd)/%				μ_{eff}/BM
		Cu	C	H	N	
$\mathrm{Cu(3\text{-}ClpyO)_2 \cdot DMF}$	(1)	16.31 (16.14)	39.30 (39.66)	3.35 (3.33)	10.64 (10.67)	1.36
$\mathrm{Cu(3\text{-}BrpyO)_2 \cdot DMF}$	(2)	13.35 (13.17)	32.08 (32.35)	2.74 (2.71)	8.60 (8.71)	1.33
$\mathrm{Cu(3\text{-}NO_2pyO)_2 \cdot DMF}$	(3)	15.49 (15.32)	37.42 (37.64)	3.21 (3.16)	16.68 (16.88)	1.41
$\mathrm{Cu(5\text{-}ClpyO)_2 \cdot DMF}$	(4)	16.33 (16.14)	39.38 (39.66)	3.36 (3.33)	10.59 (10.67)	1.28
$\mathrm{Cu(5\text{-}NO_2pyO)_2 \cdot DMF}$	(5)	15.47 (15.32)	37.69 (37.64)	3.24 (3.16)	16.90 (16.88)	1.34

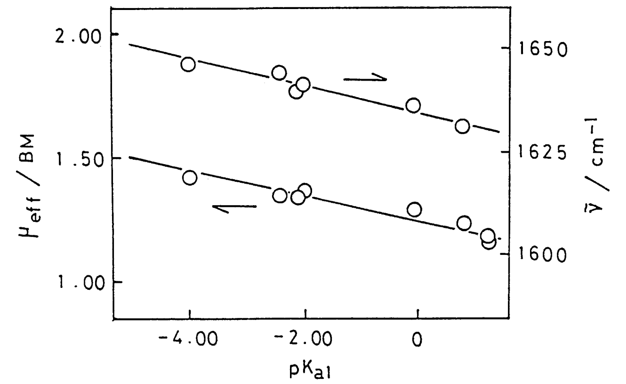

Fig. 1. The magnetic moments at 20 °C and the carbonyl stretching frequencies for the DMF adducts of copper(II) 3- and 5-substituted 2-pyridinolate plotted against the basicities of the parent 2-pyridones.

$$\mu_{\mathrm{eff}} = -0.052(\mathrm{p}K_{\mathrm{a1}} - 0.77) + 1.19_3. \qquad (1)$$

Similarly, the carbonyl frequencies (in cm^{-1}) for the present compounds show systematic shifts against the basicities of the parent 2-pyridones ($\tilde{\nu}=1634-3.2\times \mathrm{p}K_{\mathrm{a1}}$). These linear correlations indicate that (1) the influence exerted by the 3- and 5-substituents is mainly inductive, i.e., their resonance and steric effects are practically negligible, and (2) the strength of spin-exchange coupling is governed by the strength of the Cu–O bond, not the Cu–N bond, i.e., it is determined by the strength of the weakest bond in the coupling pathway.

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