Magnetic Susceptibilities of Aqueous Solutions of the Copper(II) Compounds with ω-Pyridiniocarboxylate

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Synopsis. Copper(II) compounds: $CuCl_2[C_5H_5NCH_2COO]\cdot3H_2O$, $CuCl_2[C_5H_5N(CH_2)_nCOO]\cdot2H_2O$ (n=2, 3), and $CuCl_2[C_5H_5N(CH_2)_nCOO]_2$ (n=1—3) were prepared. Then they were characterized by means of magnetic susceptibility and IR spectroscopy. The equilibria between mono- and dinuclear species in their aqueous solutions were studied using magnetic susceptibility measurements. The tendency for adopting dinuclear species in water increased in the order: pyridinioacetate<3-pyridiniopropionate<4-pyridiniobutyrate.

Most copper(II) carboxylates have copper(II) acetate-type dinuclear structures[1,2] not only in the solid state but also in such organic solvents as ethanol, chloroform, cyclohexane, and benzene.[3—11] In water, on the other hand, they dissociate to a considerable extent into mononuclear species.[4,8,9] So their aqueous solutions have been presumed to contain mono- and dinuclear species in equilibria. We attempt here to elucidate the factors affecting such equilibria, particularly those which involve the electronic properties of the ligands. For this purpose, amphoteric carboxylate ligands[12,13] seem to be suited because of their high solubilities in water and because we can easily control the electron density on the carboxylate group. We thus prepared and characterized the copper(II) compounds with ω-pyridiniocarboxylate and measured the magnetic susceptibilities of their aqueous solutions.

The pyridinioacetate, 3-pyridiniopropionate, and 4-pyridiniobutyrate ligands were prepared according to the general procedure for the reaction between pyridine and haloalkanoic acid.[14,15] Their compounds with copper(II) chloride were prepared by methods similar to those for the analogous ammoniocarboxylate derivatives.[12,13] An aqueous solution containing copper(II) chloride and appropriate pyridiniocarboxylate in a 1:1 or 1:2 molar ratio was allowed to stand in a refrigerator for a few days. Resulting precipitates were recrystallized from water or ethanol/water (1:9 by volume) to yield pale green crystals $CuCl_2[C_5H_5NCH_2COO]\cdot3H_2O$,[16] brown crystals $CuCl_2[C_5H_5N(CH_2)_nCOO]\cdot2H_2O$ (n=2, 3), or green crystals $CuCl_2[C_5H_5N(CH_2)_nCOO]_2$ (n=1—3). These products cannot be the pyridine adducts of the reactants, $Cu[Cl(CH_2)_nCOO]_2\cdot2C_5H_5N$,[17] since both compounds differ entirely in colors and magnetic properties (vide infra). The magnetic susceptibilities of the solid compounds and their aqueous solutions were measured with a Gouy balance at 20 °C. For calculations of their effective magnetic moments per one copper(II) ion, the susceptibility data were corrected for diamagnetic contributions using Pascal constants[18] and for temperature-independent paramagnetism using a value of 0.75×10^{-9} m^3 mol^{-1}. For compounds (**2**), (**4**), and (**6**), their variable-temperature susceptibilities were determined over 80—300 K. The IR spectra of the solid compounds were recorded using nujol mulls in the 4000—600 cm^{-1} range.

The 1:1 compounds of copper(II) with pyridiniocarboxylate, (**1**), (**3**), and (**5**), showed magnetic moments of 1.73—1.84 BM at room temperature (Table 1) slightly larger than the spin-only value 1.73 BM for a single electron, indicating that they have weak spin-exchange couplings between the copper(II) ions. On the other hand, the 1:2 compounds, (**2**), (**4**), and (**6**), showed magnetic moments of 1.34—1.39 BM, similar to those of well-characterized dinuclear copper(II) carboxylates, and showed COO stretching bands at 1665—1605 and 1455—1435 cm^{-1}, characteristic of bridging carboxylate groups. Furthermore, their susceptibility variations with temperature were able to be simulated by the singlet–triplet equation[19] when the following parameters were used: $2J=-294$ cm^{-1} and $g=2.16$ for (**2**), $2J=-310$ cm^{-1} and $g=2.17$ for (**4**), and $2J=-320$ cm^{-1} and $g=2.16$ for (**6**). These magnetic and IR spectral data indicate that compounds (**2**), (**4**), and (**6**) have copper(II) acetate-type dinuclear structures. The evaluated singlet–triplet separations ($-2J$) are consistent with the well-known correlation between the $-2J$ values of dinuclear copper(II) carboxylates and pK_a values of their parent carboxylic acids,[12,13,20,21] suggesting that the exchange couplings in the present dinuclear compounds are operating in mechanisms similar to those in other copper(II) carboxylates.

Since both of the mono- and dinuclear compounds and their related compound $CuCl_2[C_5H_5NCH_2COO]_{3/2}$[22] were isolated from aqueous solutions, such solutions may contain mono- and dinuclear species in equilibria. In order to study solution equilibria involving the copper(II) compounds with pyridiniocarboxylate, we determined the magnetic susceptibilities of aqueous solutions of compounds (**2**), (**4**), and (**6**) at 20 °C. The range of copper(II) concentrations studied is 0.2—1.3 mol dm^{-3} (Fig. 1). The marked dependence of magnetic moments (μ_{eff}) on copper(II) concentrations (c_{Cu}) provides direct evidence for equilibria between species differing in the number of copper(II) ions; we assumed that the equilibria involved only mono- and dinuclear species with pyridiniocarboxylate (L),

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

Compound		Found (Calcd)/%					μ_{eff}/BM
		Cu	C	H	N	Cl	
$CuCl_2(C_5H_5NCH_2COO)(H_2O)_3$	**(1)**	19.48 (19.51)	26.1 (25.8)	4.00 (4.02)	4.32 (4.30)	21.9 (21.8)	1.84
$CuCl_2(C_5H_5NCH_2COO)_2$	**(2)**	15.32 (15.55)	41.5 (41.1)	3.48 (3.45)	6.91 (6.85)	17.5 (17.4)	1.39
$CuCl_2(C_5H_5NC_2H_4COO)(H_2O)_2$	**(3)**	19.71 (19.76)	30.1 (29.9)	4.05 (4.07)	4.37 (4.35)	22.1 (22.0)	1.76
$CuCl_2(C_5H_5NC_2H_4COO)_2$	**(4)**	14.52 (14.55)	43.8 (44.0)	4.11 (4.15)	6.38 (6.41)	16.5 (16.2)	1.36
$CuCl_2(C_5H_5NC_3H_6COO)(H_2O)_2$	**(5)**	18.96 (18.93)	32.4 (32.2)	4.47 (4.50)	4.14 (4.17)	20.8 (21.1)	1.73
$CuCl_2(C_5H_5NC_3H_6COO)_2$	**(6)**	13.63 (13.67)	46.8 (46.5)	4.80 (4.77)	5.99 (6.03)	15.6 (15.3)	1.34

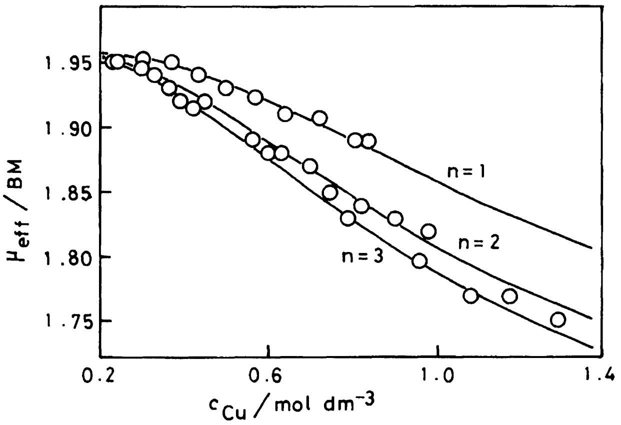

Fig. 1. Magnetic moments of aqueous solutions of the copper(II) compounds with pyridinioacetate, 3-pyridiniopropionate, and 4-pyridiniobutyrate are plotted against copper(II) concentrations.

$$2[\mathrm{CuL}] + 2\mathrm{L} \rightleftharpoons [\mathrm{Cu_2L_4}], \qquad (1)$$

and disregarded their dissociation to free copper(II) ions ($[\mathrm{CuL}]/[\mathrm{Cu}][\mathrm{L}] \cong 10^2\ \mathrm{mol^{-1}\,dm^3}$).[23,24] To simulate the experimental μ_{eff} and c_{Cu} data, we furthermore assumed that the values of magnetic moments in water were practically identical to those in the solid state.

The equilibrium constants, $K' = [\mathrm{Cu_2L_4}]/[\mathrm{CuL}]^2[\mathrm{L}]^2$, were evaluated to be 0.25, 0.55, and 0.70 $\mathrm{mol^{-3}\,dm^9}$ for the pyridinioacetate, 3-pyridiniopropionate, and 4-pyridiniobutyrate systems, respectively. Naturally, these values are much smaller than that for the copper(II)–acetate system in alkanol (e.g., $K' = 2\times10^9\ \mathrm{mol^{-3}\,dm^9}$ in methanol solution[9] and $1\times10^{12}\ \mathrm{mol^{-3}\,dm^9}$ in ethanol solution[8]), where copper(II) acetate almost completely retains the dinuclear structure of the solid compounds. The variation in these equilibrium constants indicates that the tendency for adopting dinuclear species increases in the order: pyridinioacetate < 3-pyridiniopropionate < 4-pyridiniobutyrate. This order may be rationalized on the basis of the increasing basicity and hydrophobicity associated with the carbon-chain elongation. The increase in basicity strengthens the Cu–O bonds to stabilize the dinuclear species more than the mononuclear species. In addition, the increase in hydrophobicity enhances the relative stability of the dinuclear species, for it destabilizes the dinuclear species less than the mononuclear species.

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