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Preparation and Magnetic Properties of the Copper(II) Mixed Carboxylates with Haloacetate and Ammonioacetate

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Synopsis. Copper(II) mixed carboxylate compounds, $CuX(X'CH_2COO)(R_3NCH_2COO)\cdot mH_2O$ (X=Cl, Br; X′=F, Cl; R=H, CH_3), were prepared, and then characterized by means of magnetic susceptibility and IR-spectroscopy. The mixed carboxylates with betaine have the copper(II) acetate-type dinuclear structures. The amount of spin-exchange coupling through betaine bridges was estimated.

A study of the ligand displacement reactions of copper(II) acetate with some carboxylate dinucleating ligands, such as the chloroacetate,[1,2] myristate,[3] and 2,6-dimethoxybenzoate anions[4] has shown that these reactions yield mixed carboxylates; an X-ray structure determination[2,4] has shown that these mixed carboxylates retain the copper(II) acetate-type[5,6] dinuclear structures with the bridging ligands of both the acetate and substituent anions. Although some carboxylic acids tend to separate the copper(II) salts characterized by weak spin-exchange couplings, their mixed carboxylates may adopt the copper(II) acetate-type dinuclear structures. We can then estimate the amounts of spin-exchange coupling through such carboxylates acting as bidentate bridging ligands. We, thus, investigated the reactions between copper(II) ammonioacetate compounds and copper(II) haloacetates, and measured the room-temperature magnetic susceptibilities and IR spectra of the obtained compounds. The effective magnetic moments were evaluated from the magnetic susceptibilities, which were corrected for the diamagnetic contribution using the Pascal constants[7] and for temperature-independent paramagnetism using the value of 60×10^{-6} emu mol^{-1} (1 emu=$4\pi\times10^{-6}$ m^3). The IR spectra of the solid compounds were recorded using nujol mulls in the 4000—600 cm^{-1} range.

The ammonioacetate compounds with copper(II) halide, $CuX_2(R_3NCH_2COO)_2\cdot nH_2O$ (X=Cl, Br; R=H, CH_3), were prepared in a way similar to that for the corresponding ω-ammoniocarboxylate compounds.[8] From the reaction mixtures of the bromides, copper(I) species were removed upon recrystallization from 0.1 mol dm^{-3} hydrobromic acid solutions. Their magnetic moments (μ_{eff}=1.75 and 1.81 BM for the betaine and glycine compounds, respectively)[9] are similar to those for the mononuclear copper(II) compounds (μ_{eff}=1.8—2.0 BM), indicating weak spin-exchange couplings between copper(II) ions. These copper(II) ammonioacetate compounds were dissolved in aqueous solutions of copper(II) haloacetates, $Cu(X'CH_2COO)_2\cdot H_2O$ (X′=F, Cl), which are well known to have the copper(II) acetate-type dinuclear structures (μ_{eff}=1.32[10,11] and 1.43[12] BM at room temperature for X′=F and Cl, respectively), in a 1:1.2 molar ratio. The resulting solutions were allowed to stand in a refrigerator until fine green crystals separated. A chemical analysis indicates that the products are mixed carboxylates, $CuX(X'CH_2COO)(R_3NCH_2COO)\cdot mH_2O$ (X=Cl, Br; R=H, CH_3; X′=F, Cl). The products are not equimolar mixtures of the reactants, since their magnetic moments differ entirely from the average of those for the reactants (Table 1).

There is a remarkable difference in the magnetic moments between the mixed carboxylates with glycine and with betaine. The former are characterized by weak spin-exchange couplings (μ_{eff}=1.73 and 1.85 BM), while the latter are characterized by strong antiferromagnetic couplings between copper(II) ions (μ_{eff}= 1.34—1.42 BM). Furthermore, the IR spectra of the latter show bands as 1605—1630 and 1410—1420 cm^{-1} characteristic of bridging carboxylate due to unsymmetric and symmetric carboxyl stretching vibrations,[13] while the bands arising from two kinds of carboxylate groups lie too close together to enable the groupings to be readily differentiated. The temperature dependence

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

Compound	Found (Calcd)/%					μ_{eff}/BM
	Cu	C	H	N	Cl$^-$Br$^-$	
$CuCl(FCH_2COO)[(CH_3)_3NCH_2COO]$	21.65	28.65	4.43	4.79	12.15	1.35
	(21.67)	(28.68)	(4.47)	(4.78)	(12.09)	
$CuBr(FCH_2COO)[(CH_3)_3NCH_2COO]$	18.77	24.78	3.78	4.17	23.53	1.34
	(18.82)	(24.90)	(3.88)	(4.15)	(23.67)	
$CuCl(ClCH_2COO)[(CH_3)_3NCH_2COO]$	20.32	27.03	4.16	4.56	11.65	1.42
	(20.52)	(27.15)	(4.23)	(4.52)	(11.45)	
$CuBr(ClCH_2COO)[(CH_3)_3NCH_2COO]\cdot H_2O$	16.97	22.54	3.97	3.86	21.59	1.41
	(17.08)	(22.60)	(4.06)	(3.76)	(21.47)	
$CuCl(ClCH_2COO)(H_3NCH_2COO)\cdot H_2O$	22.42	16.76	3.04	4.74	12.67	1.85
	(22.25)	(16.82)	(3.18)	(4.90)	(12.42)	
$CuBr(ClCH_2COO)(H_3NCH_2COO)\cdot 3H_2O$	17.56	13.03	3.45	3.84	21.79	1.73
	(17.36)	(13.12)	(3.58)	(3.83)	(21.83)	

of the susceptibilities for $CuCl(X'CH_2COO)[(CH_3)_3NCH_2COO]$ (X'=F, Cl) shows the Bleaney–Bowers behavior[14] with parameters $2J=-311$ cm^{-1} and $g=2.18$ for X'=F and $2J=-270$ cm^{-1} and $g=2.19$ for X'=Cl. The magnetic and IR spectral data indicate that the mixed carboxylates with betaine have bridged dinuclear structures, similar to that of copper(II) acetate monohydrate.[5,6] The crystals may consist of a repetition of the identical dinuclear units with 2:2 mixed bridges, which are seen in copper(II) acetate 2,6-dimethoxybenzoate monohydrate,[4] or may comprise a composite of the dinuclear units with variously mixed bridges, which are seen in the copper(II) acetate chloroacetate adduct with urea.[2]

In either case, because of the additive property of spin-exchange couplings, the magnetic moment for dinuclear mixed carboxylate can be adequately approximated by the average of those for the dinuclear salts of its constituent carboxylic acids. We can thereby estimate the magnetic property of the hypothetical dinuclear betaine compound, $CuCl_2[(CH_3)_3NCH_2COO]_2$, from those for the present mixed carboxylate, chloroacetate (μ_{eff}=1.38—1.40 BM and $2J=-278$ cm^{-1}),[15] and fluoroacetate (μ_{eff}=1.26—1.28 BM and $2J=-359$ cm^{-1})[16] compounds. The estimated values, μ_{eff}=1.44 BM and $2J=-262$ cm^{-1} are a little larger than those of the copper(II) chloroacetate compounds. This fact is consistent with the well known correlation between the magnetic properties of a series of dinuclear copper(II) (substituted acetate)s and the acidities of their parent acids,[19] since betaine is a stronger acid than chloroacetic acid (pK_a=1.8 and 2.68 for betaine and chloroacetic acid, respectively).

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