The Magnetic Properties of the Copper(II) (Disubstituted Acetate) Adducts with Ammonium Chloride

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Synopsis. Various copper(II) (disubstituted acetate) adducts with ammonium chloride have been prepared and characterized by magnetic susceptibility and IR spectroscopy measurements. Factors affecting the magnetic moments of the dinuclear copper(II) alkanoates are discussed.

Previously, we have shown that in a series of dinuclear copper(II) (monosubstituted acetate)s with coordinated chloride ions in the axial positions their room-temperature magnetic moments tend to increase as the pK_a values of their parent carboxylic acids decrease,[1] being approximated well by a linear equation:

$$\mu_{\mathrm{eff}} = -0.052\,(\mathrm{p}K_a - 4.56) + 1.31_8. \qquad (1)$$

This empirical relationship has been explained in terms of the inductive effect of the carboxylato substituents, and is supported by molecular orbital analyses,[2,3] However, it seems likely that other factors also contribute to the magnetic properties of copper(II) carboxylates, since several modes of interaction concern the spin-exchange coupling in these dinuclear compounds.[3] Actually, the magnetic moments of the copper(II) salts of acetic acid and fluoroacetic acid deviate from the above trend,[1,4] Thus, in order to obtain more information concerning α-substitution effects in dinuclear copper(II) alkanoates, we have studied copper(II) difluoroacetate, dichloroacetate, *dl*-2-chloropropionate, *dl*-2-bromopropionate, and isobutyrate adducts with the following ammonium chlorides: methylammonium, dimethylammonium, trimethylammonium, tetramethylammonium, *N*-ethylpiperidinium, and quinuclidinium chlorides.

All compounds, apart from the isobutyrates, were prepared by leaving the aqueous solution containing appropriate ammonium chloride and copper(II) carboxylate for a few days in a refrigerator at ca. 5 °C.[4] The isobutyrates were prepared by evaporating the ethanolic solutions under reduced pressure at room temperature.

The effective magnetic moments of these compounds (Table 1) were evaluated from the room-temperature magnetic susceptibilities, which were corrected for the diamagnetic contribution of the constituent atoms using Pascal constants,[6] and a value of $N\alpha = 60 \times 10^{-6}$ emu mol^{-1} (1 emu=$4\pi \times 10^{-6}$ m^3) was used throughout the present study. For the dimethylammonium chloride adducts of copper(II) 2-chloropropionate and copper(II) isobutyrate, the temperature dependence of their magnetic susceptibilities was measured in the temperature range of 80—300 K in order to confirm their dinuclear structures. The results agreed well with the Bleaney-Bowers equation,[7] using the following parameters: g=2.18 and $2J$=−309 cm^{-1} for the 2-chloropropionate and g=2.17 and $2J$=−331 cm^{-1} for the isobutyrate, respectively. The IR spectra of the solid compounds show characteristic bands in the ranges of 1680—1595 and 1465—1460 cm^{-1} connected with symmetric and unsymmetric COO stretching vibrations of the carboxyl groups.[8] The magnetic and IR spectral data indicate that the

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

Compound		Found (Calcd)/%					μ_{eff}/BM
		Cu	Cl$^-$	C	H	N	
$Cu(F_2CHCOO)_2 \cdot CH_3NH_3Cl$	**(1)**	19.74	11.68	18.50	2.56	4.41	1.35
		(19.79)	(11.04)	(18.70)	(2.51)	(4.36)	
$Cu(F_2CHCOO)_2 \cdot (CH_3)_2NH_2Cl$	**(2)**	19.09	10.73	21.40	3.01	4.13	1.35
		(18.96)	(10.58)	(21.50)	(3.01)	(4.18)	
$Cu(F_2CHCOO)_2 \cdot (CH_3)_3NHCl$	**(3)**	18.18	10.19	23.88	3.44	3.91	1.37
		(18.20)	(10.15)	(24.08)	(3.46)	(4.01)	
$Cu(F_2CHCOO)_2 \cdot (CH_3)_4NCl$	**(4)**	17.62	9.72	26.41	3.89	3.83	1.39
		(17.50)	(9.76)	(26.46)	(3.89)	(3.86)	
$Cu(Cl_2CHCOO)_2 \cdot C_7H_{13}NHCl$	**(6)**	13.67	7.45	27.83	3.55	2.79	1.49
		(13.61)	(7.59)	(28.29)	(3.45)	(3.00)	
$Cu(Cl_2CHCOO)_2 \cdot C_7H_{15}NHCl$	**(7)**	13.46	7.40	28.16	3.86	2.93	1.50
		(13.55)	(7.56)	(28.17)	(3.87)	(2.99)	
$Cu(CH_3CHClCOO)_2 \cdot (CH_3)_2NH_2Cl$	**(8)**	17.25	9.88	26.86	4.39	3.70	1.39
		(17.64)	(9.86)	(26.68)	(4.48)	(3.89)	
$Cu(CH_3CHBrCOO)_2 \cdot (CH_3)_2NH_2Cl$	**(9)**	14.02	7.92	21.26	3.77	3.56	1.39
		(14.13)	(7.89)	(21.40)	(3.59)	(3.12)	
$Cu[(CH_3)_2CHCOO]_2 \cdot (CH_3)_2NH_2Cl$	**(11)**	20.22	11.08	37.47	6.96	4.31	1.31
		(19.90)	(11.10)	(37.62)	(6.94)	(4.39)	
$Cu[(CH_3)_2CHCOO]_2 \cdot CH_3NH_3Cl$	**(12)**	20.94	11.60	35.38	6.62	4.53	1.32
		(20.81)	(11.61)	(35.41)	(6.60)	(4.59)	

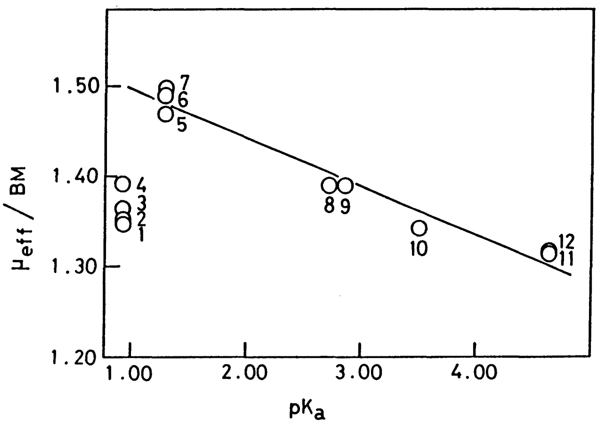

Fig. 1. The magnetic moment at 20 °C plotted against the pK_a value of the parent carboxylic acid for the copper(II) salts of disubstituted acetic acids containing coordinated chloride ions in the axial positions; the difluoroacetates (**1**—**4**), the dichloroacetates (**5**—**7**), the 2-chloropropionate (**8**), the 2-bromopropionate (**9**), the (3-piperidinio)-formate (**10**),[11] and the isobutyrates (**11**, **12**).

present compounds have a bridged dinuclear structure similar to copper(II) acetate monohydrate,[9,10] The ammonium cations in these compounds may affect the dinuclear structure due to packing effects and the hydrogen bonds; however, no marked difference was observed in the magnetic moments for the respective copper(II) carboxylates.

A plot (Fig. 1) of the room-temperature magnetic moment vs. the pK_a value of the parent alkanoic acid for the present compounds, except difluoroacetates, confirms the correlation between these quantities,[1] with the best least-squares fit yielding

$$\mu_{eff} = -0.052\,(\text{p}K_a - 4.56) + 1.30_5. \tag{2}$$

The obtained slope agrees satisfactorily with that for the corresponding series of monosubstituted acetates. The variation of singlet-triplet separation values (e.g. $-2J=271$,[5] 309, and 331 cm^{-1} for the dimethylammonium chloride adducts of copper(II) dichloroacetate, 2-chloropropionate, and isobutyrate compounds, respectively) indicates that the smaller magnetic moment is accompanied by the strong magnetic interaction between copper(II) ions. On the other hand, the slight difference observed between the intercepts for the series of mono- and disubstituted acetates, indicates that some decrease in the magnetic moment (ca. −0.01 BM) is accompanied, probably due to an increase in the steric strain and a decrease of hyperconjugation by the substitution of the methyl group of acetic acid. However, the substantially small magnetic moments of the fluoro- and difluoroacetates can not be explained in terms of the inductive effect of the fluoro substituent. From a study of the ^{19}F NMR in the series of fluoromethanes, Gutowsky and Hoffman have suggested the use of higher energy orbitals in the hybridized orbitals of atoms attached to fluorine atoms.[12] On the other hand, Roberts and Carboni have pointed out that, in the transmission of the electrical influence of the dipolar substituents, the inductive and field effects are of comparable importance.[13] For an explanation of the magnetic moments for the fluoro- and difluoroacetates, it is necessary to consider these effects. The higher magnetic moments of the copper(II) salts of acetic acid[4] may also be explained by the mechanism described above.

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