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The Magnetic Properties of Dinuclear Copper(II) 2-Fluoroalkanoates

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Synopsis. Copper(II) pentafluoropropionate and heptafluorobutyrate adducts with 1,4-dioxane, tetrahydropyran, and tetrahydrofuran have been prepared and characterized by means of magnetic-susceptibility and IR-spectroscopy measurements. The variation in their magnetic moments is discussed in terms of the acidity of the parent acid and the hyperconjugative effect of the fluoroalkyl group.

Numerous studies have been carried out to ascertain the factors which determine the magnetic properties of dinuclear copper(II) carboxylates, because they are necessary to understand the mechanism of the spin-exchange coupling. For several series of copper(II) carboxylates, a correlation between the strength of spin-exchange coupling and the acidity of the parent carboxylic acid has been recognized;[1-4] this correlation is supported by molecular orbital calculations.[5,6] However, there are also some exceptions, such as the unusually strong couplings observed for dinuclear copper(II) formates[7] and fluoroacetates,[3,4] which have led many investigators to be critical of such a correlation.[8] They have presumed alternative factors, such as the group polarizability of the carboxylate substituents[9] and the steric hindrance between the substituents and the axial donor ligands.[1] However, these alternative factors have soon been found unjustifiable.[3] In order to investigate the general trend of the magnetic properties of fluoroalkanoates, we have prepared the 1,4-dioxane (dox), tetrahydropyran (THP), and tetrahydrofuran (THF) adducts of copper(II) pentafluoropropionate and heptafluorobutyrate. For the sake of comparison, the corresponding adducts of copper(II) fluoroacetate and difluoroacetate have also been prepared.

The compounds were obtained by standard procedures.[1,10] Their effective magnetic moments (Table 1) were evaluated from the room-temperature molar magnetic susceptibilities (χ_M) using this equation: $\mu_{eff}=2.83\ [(\chi_M-\chi_{dia}-N\alpha)T]^{1/2}$. The appropriate diamagnetic corrections (χ_{dia}) were estimated from the Pascal constants,[11] while 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 the dioxane adducts of copper(II) difluoroacetate and pentafluoropropionate, the temperature dependence of their magnetic susceptibilities was measured in the temperature range of 80—300 K; it can be represented by the Bleaney-Bowers equation,[12] with parameters of $g=2.17$ and $2J=-314$ cm^{-1} for the difluoroacetate and of $g=2.18$ and $2J=-296$ cm^{-1} for the pentafluoropropionate. The IR spectra of the solid compounds show bands characteristic of bridging carboxylate due to unsymmetric and symmetric carboxyl stretching vibrations.[13] The magnetic and IR spectral data indicate that the present compounds have their "dinuclear tetracarboxylate frameworks."

It has been found that the magnetic moments of dinuclear copper(II) alkanoate adducts with unhindered hard donors, except those of fluoroalkanoate adducts, are determined by these factors: the acidities of the bridging carboxylato and axial donor ligands,[14] the steric strain among the substituents,[14] and the hydrogen bonding between the carboxylato oxygen atoms and the neighboring hydrogen donors.[15] For

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

Compound		Found(Calcd)/%			μ_{eff}/BM
		Cu	C	H	
$Cu(CF_3CF_2COO)_2\cdot 1/2dox$	(**1**)	14.69	22.17	0.95	1.41
		(14.65)	(22.16)	(0.93)	
$Cu(CF_3CF_2COO)_2\cdot THP$	(**2**)	13.05	22.83	2.15	1.44
		(13.36)	(22.77)	(2.12)	
$Cu(CF_3CF_2COO)_2\cdot THF$	(**3**)	13.67	25.95	1.73	1.42
		(13.76)	(26.01)	(1.75)	
$Cu(CF_3CF_2CF_2COO)_2\cdot 1/2dox$	(**4**)	11.78	22.58	0.79	1.38
		(11.91)	(22.51)	(0.76)	
$Cu(CF_3CF_2CF_2COO)_2\cdot THP$	(**5**)	10.95	27.33	1.76	1.43
		(11.04)	(27.12)	(1.75)	
$Cu(CF_3CF_2CF_2COO)_2\cdot THF$	(**6**)	11.28	25.73	1.46	1.46
		(11.31)	(25.66)	(1.44)	
$Cu(F_2CHCOO)_2\cdot 1/2dox$	(**7**)	21.11	24.05	2.14	1.36
		(21.35)	(24.21)	(2.03)	
$Cu(F_2CHCOO)_2\cdot THP$	(**8**)	18.86	31.89	3.61	1.36
		(18.70)	(31.82)	(3.56)	
$Cu(FCH_2COO)_2\cdot 1/2dox$	(**12**)	24.45	27.49	3.27	1.29
		(24.28)	(27.54)	(3.08)	

example, the room-temperature magnetic moments (BM) for the copper(II) salts of a series of monosubstituted acetic acids can be formulated by the following equation:

$$\mu_{\rm eff}=-0.052(\text{p}K_a-0.068\text{p}K_a'-4.56+C_{\rm HB})+1.32_7, \qquad (1)$$

where pK_a and pK_a' are the acidities of the parent acid and of the conjugate acid of the axial donor ligand respectively, and where $C_{\rm HB}$ is a correction term for the hydrogen bonding in the hydrates and ammonium chloride adducts (the value of $C_{\rm HB}=-0.29$ has been estimated).[15] In order to examine a similar correlation for fluoroalkanoates, the room-temperature magnetic moments of the present compounds, together with the literature data for the hydrates and ammonium choride adducts of copper(II) fluoroalkanoates,[3,4,16] are plotted against the p$K_a-0.068$ p$K_a'+C_{\rm HB}$ values in Fig. 1. These points consist of a straight line, with the best least-squares fit yielding:

$$\mu_{\rm eff}=-0.052(\text{p}K_a-0.068\text{p}K_a'-4.56+C_{\rm HB})+1.18_2. \qquad (2)$$

Although the magnetic moments of the corresponding quinoline adducts (1.32 and 1.40 BM at 20 °C for the fluoroacetate[17] and trifluoroacetate[18] respectively) show a similar trend, they are excluded from the plots because the axial coordination of quinoline is affected by the steric hindrance.[19] The variation in the singlet-triplet separation values (e.g., $-2J=384$,[10] 314, and 296 cm^{-1} for the dioxane adducts of copper(II) 2-fluoropropionate, difluoroacetate, and pentafluoropropionate respectively) indicates that the smaller magnetic moment is accompanied by the stronger magnetic interaction between copper(II) ions. Similarly, the carboxyl frequencies (cm^{-1}) for the present compounds, in conformity with Eq. 3, show systematic shifts against the acidities of the carboxylato and axial ligands:

$$\tilde{\nu}_{\rm unsym}=1692-14.9(\text{p}K_a-0.068\ \text{p}K_a'+C_{\rm HB}). \qquad (3)$$

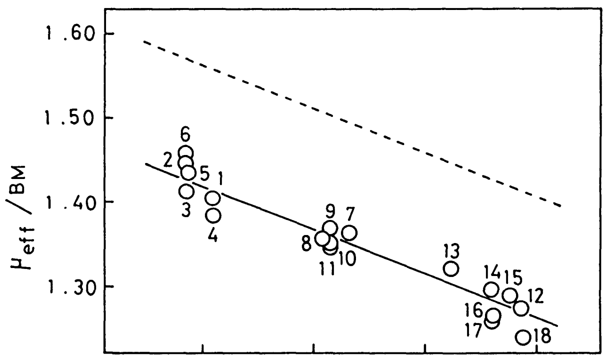

Fig. 1. The magnetic moments at 20 °C plotted against the acidities of the ligands for the copper(II) pentafluoropropionate (**1**—**3**), hexafluorobutyrate (**4**—**6**), difluoroacetate (**7**—**11**), fluoroacetate (**12**—**17**), and 2-fluoropropionate (**18**) adducts with σ-donor ligands. The broken line represents the linear correlation for copper(II) alkanoates except fluoroalkanoates.

These linear correlations suggest that the influence exerted by the fluoro-substituents is mainly inductive. Nevertheless, the value of the constant term in Eq. 2 (1.18_2 BM) is much smaller than the corresponding values for any other series of alkanoates (e.g., 1.32_7 BM in Eq. 1), indicating the existence of an additional factor affecting their magnetic properties. For the 2-fluoroalkanoates, this effect seems to be independent of the number of fluoro-substituents, for the lines in Fig. 1 are parallel to each other. An inspection of the crystal structures of the copper(II) fluoroacetate[20—22] and trifluoroacetate[8] adducts reveals that they have a fluoro-substituent located closely in the plane of the carboxylato group. This fact seems to indicate that the fluoro-substituent in the plane of the carboxylato group is responsible for this effect.

Previously, we have pointed out that the difference in magnetic moments between copper(II) acetate and copper(II) (substituted acetate)s is attributable to the hyperconjugation of the methyl group of the acetato ligand in addition to the difference in acidities between their parent acids.[14] Similarly, the magnetic moments of fluoroalkanoates must be affected by the hyperconjugation of the fluoroalkyl group.[23] Generally, carboxylic acid may be regarded as a substituted formic acid RCOOH, and the perturbation by a substituent R on the carboxyl group is comprised of changes in both the σ- and π-electron distributions. Since the effect of the change in the σ-electron distribution appears in the acidity change, the residual change in the magnetic moment of dinuclear copper(II) carboxylate may be related to the change in the π-electron distribution:

$$\mu_{\rm eff}=-0.052(\text{p}K_a-0.068\text{p}K_a'+C_{\rm HB}-3.55)+\Delta\mu_\pi+1.06_9, \qquad (4)$$

where $\Delta\mu_\pi$ is a correction term for the perturbation of the π-electron density of the carboxyl group, being obtained as 0.16_8, 0.28_5,[14] 0.30_5,[14] 0.36_3,[14] and 0.35_2[24] BM for the R=CF_3, $(CH_3)_3C$, C_2H_5, CH_3, and C_6H_5 substituents respectively. Swain and Lupton have proposed that substituent constants predicting the substituent effects on any kinds of physical properties may be expressed as $fF+rR$,[25] where F and R are field and resonance constants, and where f and r are weight-

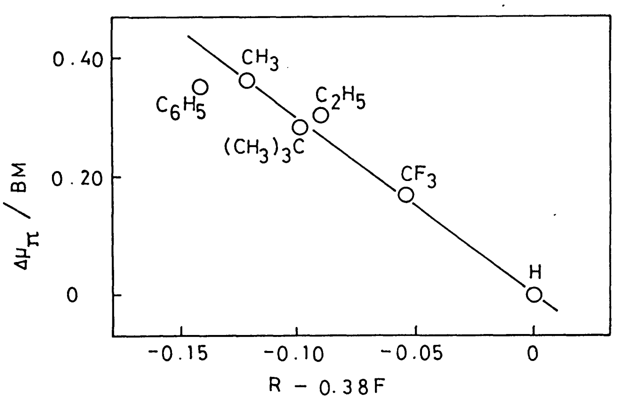

Fig. 2. The correction term for the perturbation on π-electrons in the carboxyl group plotted against the substituent constants $R-0.38F$.

ing factors independent of the particular substituent. The ratio of f to r being chosen as -0.38, the $\Delta\mu_\pi$ values for these substituents are plotted against $R-0.38F$ in Fig. 2. Most data have a linear relation with the slope of -3.0_0 BM, although the plot for the phenyl substituent is a little scattered, perhaps because of the torsion about the C–C bond between the phenyl and carboxyl groups (the dihedral angles are 0.2—27.2°).[26,27] This correlation substantiates the participation of the π-orbitals of the bridging carboxylato in the superexchange pathway. This electron-delocalization mechanism is consistent with the quite large contact shifts observed for the H resonances of copper(II) benzoates[28] and for the ^{13}C resonances of copper(II) butyrate.[29]

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