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The Magnetic Properties of Copper(II) Alkanoate Adducts with Pyridine and Quinoline Analogues

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Synopsis. Various copper(II) alkanoate adducts with pyridine and quinoline analogues have been prepared, and characterized by means of magnetic susceptibility and IR measurements. The effects of axial ligands on the magnetic moments are discussed on the basis of their basicities and steric requirements.

In most dinuclear copper(II) carboxylate adducts, the coordination geometry is essentially five-coordinate tetragonal pyramidal.[1-5] The addend donor occupies the apical site (axial position) and affects the strength of the spin-exchange coupling within the dinuclear complex.[2] For adducts with σ-donor ligands, which exhibit no steric hindrance to an axial coordination, the room-temperature magnetic moments (BM) can be expressed according to Eq. 1:

$$\mu_{\mathrm{eff}}=-0.052(\mathrm{p}K_{\mathrm{a}}-0.068\mathrm{p}K_{\mathrm{a}}'-4.56)+\Delta\mu_{\alpha}+1.38_5, \qquad (1)$$

where $\mathrm{p}K_\mathrm{a}$ and $\mathrm{p}K_\mathrm{a}'$ are the acidities of the conjugate acids of alkanoate and axial ligands, respectively.[6] $\Delta\mu_\alpha$ is the correction term for the substitution in the methyl group of acetic acid (-0.05_8 and -0.07_0 for the series of mono- and disubstituted acetates, respectively), including corrections for the steric strain, field effect, and hyperconjugation.[6] On the other hand, for adducts with *N*-heteroaromatic (pyridine-type) donors, the magnetic moments are, more or less, lower than those of the adducts with alkyl-[6,7] and arylamines,[8] owing to a steric hindrance to their axial coordination.[9-11] In order to investigate these steric effects quantitatively, we prepared several copper(II) alkanoate adducts with pyridine (py), 3-chloropyridine (3-Clpy), 3-bromopyridine (3-Brpy), 3,5-dichloropyridine (3,5-$\mathrm{Cl_2}$py), 3-ethylpyridine (3-Etpy), 4-methylpyridine (4-Mepy), pyrazine (pyz), quinoline (quin), 4-methylquinoline (4-Mequin), and quinoxaline (quix), and measured their magnetic susceptibilities at room temperature.

The adducts were obtained, except for the cyclohexanecarboxylates, by standard procedures,[12] and recrystallized from chloroform whenever possible. The cyclohexanecarboxylates were prepared in a similar way, using dioxane as a solvent.[13] The effective magnetic moments of these compounds (Table 1) were evaluated from the room-temperature magnetic susceptibilities, which were corrected for the diamagnetic contribution (χ_{dia}) using Pascal constants[14] and for temperature-independent paramagnetism ($N\alpha$) using the value of 60×10^{-6} emu mol^{-1} (1 emu$=4\pi\times10^{-6}$ m^3). Although a number of copper(II) alkanoate adducts with various pyridine-type donors have been already studied magnetically,[2,15-17] their magnetic moments were reevaluated in order to avoid any errors derived from differences in the standard samples used for susceptibility measurement and in the correction values for χ_{dia} and $N\alpha$. The IR spectra of the solid compounds show characteristic bands connected with unsymmetric and symmetric carboxyl stretching vibrations, the latter with a variable intensity.[18] The magnetic and IR spectral data indicate that the present compounds have a bridged dinuclear structure similar to that of copper(II) acetate monohydrate.[2]

Although a pyridine-type donor can function as a π-acceptor in some circumstances, it functions here almost entirely as a σ-donor base,[5] because X-ray crystallographic analyses indicate that a pyridine or quinoline analogues adopts a staggered orientation with respect to the planes of carboxylato groups.[1-5] By analogy with Eq. 1, the magnetic moments of the present adducts may be expressed as

$$\mu_{\mathrm{eff}}=-0.052(\mathrm{p}K_{\mathrm{a}}-0.068\mathrm{p}K_{\mathrm{a}}'-4.56)+\Delta\mu_{\alpha}+\Delta\mu_{\mathrm{ST}}+1.38_5, \qquad (2)$$

where the correction term $\Delta\mu_{\mathrm{ST}}$ depends on the steric hindrance to an axial coordination; its value can be evaluated from the graphic interpolation shown in Fig. 1. In this series of axial ligands, the $\mathrm{p}K_\mathrm{a}'$ value varies from -2.60 for 1/2quix to -2.10, 0.67, 0.72, 2.89, 3.16, 4.94, 5.23, 5.73, 5.89, and 6.04 for 1/2pyz, 3,5-$\mathrm{Cl_2}$py, quix, 3-Brpy, 3-Clpy, quin, py, 4-Mequin, 3-Etpy, and 4-Mepy, respectively. To plot the points for the 1/2pyz and 1/2quix adducts, the first dissociation constants of pyrazine and quinoxaline are selected, since their

Table 1. Effective Magnetic Moments (BM) at 20 °C for $[\mathrm{Cu(RCOO)_2\cdot L}]_2$ Compounds

L\R	$\mathrm{CH_3}$	$\mathrm{C_2H_5}$	$\mathrm{C_3H_7}$	$\mathrm{ClCH_2CH_2}$	$\mathrm{ClCH_2}$	$\mathrm{(CH_3)_2CH}$	$\mathrm{C_6H_{11}}$	$\mathrm{CH_3CHCl}$	$\mathrm{Cl_2CH}$
1/2pyz	1.32	1.30	1.27	1.30	1.37	1.28			
3,5-$\mathrm{Cl_2}$py	1.35	1.29	1.30	1.33	1.38	1.28	1.24	1.38	1.44
3-Brpy	1.34	1.31	1.29	1.36	1.39	1.29	1.28	1.37	
3-Clpy	1.35	1.30	1.29	1.32	1.39	1.29	1.29	1.37	
py	1.35	1.32	1.32	1.36	1.38	1.28	1.29	1.42	1.47
3-Etpy	1.37	1.32	1.31	1.36	1.40	1.30	1.30	1.41	
4-Mepy	1.36	1.32	1.33	1.36	1.43	1.32	1.29	1.43	
1/2quix					1.38			1.34	
quix	1.37	1.29		1.31		1.28	1.26	1.37	1.45
quin	1.39	1.33	1.33	1.36	1.41	1.32	1.28	1.41	1.48
4-Mequin	1.37	1.33	1.32	1.36	1.41	1.29	1.28	1.39	

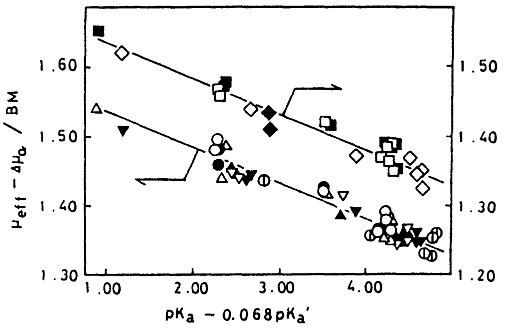

Fig. 1. The corrected magnetic moments at 20 °C plotted against the acidities of the ligands for the copper(II) alkanoate adducts with 1/2quix (◆), 1/2pyz (⦶), 3,5-Cl$_2$py (▼), quix (◇), 3-Brpy (▽), 3-Clpy (▲), quin (■), py (△), 4-Mequin (□), 3-Etpy (●), and 4-Mepy (○).

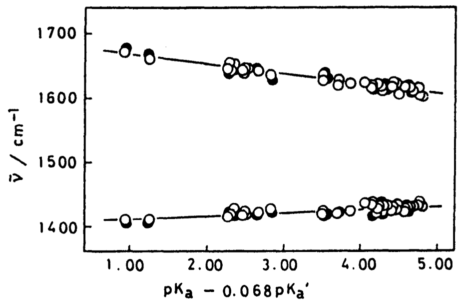

Fig. 2. The carboxyl stretching frequencies plotted against the acidities of the ligands for the copper(II) alkanoate adducts with pyridine analogues (○) and quinoline analogues (●).

second coordination abilities must be reduced by the first coordination on the other sites. The obtained slope of −0.052 BM is exactly the same as that shown in Eq. 2, indicating the validity of the equation, although we disregard interactions between different dinuclear complexes,[19] the presence of modifications,[2] and crystallographically independent dinuclear complexes,[1,4] and packing effects. The obtained values of $\Delta\mu_{ST}$ are -0.03_3 BM for the adducts with pyridine analogues (py, 3-Clpy, 3-Brpy, 3,5-Cl$_2$py, 3-Etpy, 4-Mepy, and pyz) and -0.03_4BM for those with quinoline analogues (quin, 4-Mequin, and quix), being almost the same with each other. This fact is consistent with the coincidence of the singlet-triplet separation values for the copper(II) acetate adducts with pyridine and quinoline,[20] and should be attributed to a similarity of the steric interferences hindering their axial coordination; a mutual repulsion between the adjacent Cu-O and N-C bonding electron pairs may be taken as such a steric hindrance.[21]

The correlation between the magnetic moments and the acidities of the parent carboxlic acids (Eq. 2) suggests that the magnitude of spin-exchange coupling is closely related to the nature of Cu-O bonds. It has been pointed out that, for carboxylate compounds with the same structure, the frequency shift of the carboxyl stretching vibrations can be used as a measure of the relative strengths of the metal-oxygen bonds.[22] Systematic shifts of the carboxyl frequencies against the acidities of the parent carboxylic acids (Fig. 2), which can also be demonstrated for the dimeric aliphatic[23] and arenecarboxylic asids,[24] indicate that an increase in the acidity of the parent carboxylic acid leads to a more asymmetric structure of the carboxyl group, thereby resulting in an increase in the frequency separation of the two carboxyl bands. The slopes and intercepts found here −15.0 and 1682 cm^{-1} for unsymmetric and +4.9 and 1407 cm^{-1} for symmetric vibrations. These slopes are almost the same with those found for the adducts with unhindered σ-donors ($\tilde{\nu}_{unsym}$=1692−15.1(pK_a−0.068pK_a'))[6] and for the dimeric arenecarboxylic acids ($\tilde{\nu}_{unsym}$=1760−14.7pK_a).[24] On the other hand, the difference in the values of the intercept between the adducts with unhindered σ-donors and the present adducts indicates the existence of a steric hindrance to the axial coordination of pyridine-type donors.

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