The Magnetic Properties of the Copper(II) Alkanoate Adducts with Cyclic Ethers and Tertiary Amines

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Synopsis. Various copper(II) alkanoate adducts with cyclic ethers and tertiary amines have been prepared and characterized by means of magnetic susceptibility and IR spectroscopy measurements. The effect on the magnetic moments of the dinuclear copper(II) alkanoates of varying the base strength of the axial ligands is also discussed.

It has often been pointed out that the antiferromagnetic interaction in dinuclear copper(II) carboxylate adducts, $[Cu(RCOO)_2 \cdot L]_2$, is influenced both by the carboxylato substituent R and the axial ligand L.[1,2] As for the latter, Jotham et al. have examined the magnetic properties of the compounds with a series of axial ligands including pyridine and water and have noted that the spin-exchange coupling between the two copper(II) ions tends to increase as the axial ligands become stronger electron donors.[1] However, these magnetic properties may be obscured by other factors, such as the steric hindrance of axial coordination[3] and the intermolecular hydrogen bond between the water molecule and the carboxylato group.[4,5] Actually, the magnetic data of the copper(II) chloroacetate adducts with pyridine analogues[6] rather contradict the remark of Jotham et al.

Thus, we have now prepared various copper(II) alkanoate adducts with 1-azabicyclo[2.2.2]octane (abco), 1,4-diazabicyclo[2.2.2]octane (dabco), 1,3,5,7-tetraazatricyclo[3.3.1.1]decane (tatcd), tetrahydropyran (THP), and tetrahydrofuran (THF), and examined their magnetic moments, together with those of the adducts with 1,4-dioxane (dox). The axial ligands here considered are practically pure sigma donors, containing both oxygen and nitrogen donors. X-Ray analyses[7-9] have shown that the copper(II) propionate adduct with dox and the copper(II) acetate adducts with dabco and tatcd have polymeric structures, in which the carboxylato-bridged dinuclear units are connected by the axial ligands. In spite of this fact, these compounds are appropriate compounds in which to examine the axial-ligand effects on the magnetic properties of dinuclear copper(II) alkanoates, because the interdinuclear interactions are much weaker than the intradinuclear interactions.[10,11]

Various copper(II) alkanoate-abco (1/1), -dabco (2/1), and -tatcd (3/1) compounds were obtained, except for the cyclohexanecarboxylates, in accordance with a method employed by Tennenhouse.[12] The cyclohexanecarboxylates were prepared in a similar way, using dioxane solutions. The 2:1 species of tatcd adducts were obtained according to the procedure of Pickardt.[8] The adducts with the THP and THF were prepared by the use of the procedures reported for the corresponding dox adducts,[13] and their chemical analyses were done and their magnetic susceptibilities were measured within a few hours after preparation to avoid any fluctuations caused by their instabilities.

The effective magnetic moments of these compounds (Table 1) were evaluated from the room-temperature magnetic susceptibilities, which were corrected for the diamagnetic contribution using Pascal constants[14] and for the temperature-independent paramagnetism using the value of 60×10^{-6} emu mol^{-1} (1 emu$=4\pi \times 10^{-6}$ m^3). The values determined for the copper(II) acetate adducts with abco and dabco agreed well with those reported previously.[11,15] For the copper(II) propionate-abco (1/1), -dabco (2/1), and -tatcd (3/1) compounds, 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[16] when the following parameters were used: $g=2.18$ and $2J=-323$ cm^{-1} for the abco adduct, $g=2.17$ and $2J=-329$ cm^{-1} for the dabco adduct, and $g=2.18$ and $2J=-334$ cm^{-1} for the tatcd adduct. The IR spectra of the solid compounds show characteristic bands in the ranges of 1660—1610 and 1425—1405 cm^{-1} connected with the symmetric and unsymmetric COO stretching vibrations of the carboxyl groups.[17] The magnetic and IR

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

R\L	abco	1/2dabco	1/2tatcd	1/3tatcd	THP	THF
CH_3	1.42	1.40	1.38	1.35		
C_2H_5	1.35	1.32		1.30		
C_3H_7	1.37	1.34		1.30		
$ClCH_2CH_2$	1.40	1.35		1.31		1.37
$ClCH_2$		1.42	1.42		1.42	1.40
$(CH_3)_2CH$	1.33	1.31		1.30		
C_6H_{11}	1.35	1.32		1.27		
CH_3CHCl		1.43		1.38	1.42	1.38
CH_3CHBr		1.40		1.39		
Cl_2CH			1.49		1.48	1.48
CH_3CCl_2		1.49			1.46	1.47

spectral data indicate that the present compounds have bridged dinuclear structures similar to that of copper(II) acetate monohydrate.[4,5]

Previously, we have shown that, for the copper(II) (monosubstituted acetate)s and copper(II) (disubstituted acetate)s with coordinated chloride ions in the axial positions, their magnetic moments decrease linearly with the pK_a values of the parent carboxylic acids,[18–20] which may be summarized as follows:

$$\mu_{\mathrm{eff}} = -0.052(\mathrm{p}K_a - 4.56) + \Delta\mu_\alpha + 1.37_9, \qquad (1)$$

where $\Delta\mu_\alpha$ is the correction term for the substitution in the methyl group of acetic acid (−0.06 and −0.07 for the series of mono- and disubstituted acetates respectively), including the corrections for steric strain, field effect, and hyperconjugation. Similarly, the magnetic moments of a series of copper(II) alkanoates with other axial ligands may be expressed as follows.

$$\mu_{\mathrm{eff}} = -0.052(\mathrm{p}K_a - 4.56) + \Delta\mu_\alpha + A_{\mathrm{ax}}, \qquad (2)$$

where A_{ax} is a correction term for axial coordination; its value can be evaluated by graphic interpolation (Fig. 1). To plot the points for the 2,2-dichloropropionates, $\Delta\mu_\alpha=-0.08$ BM[21] is used tentatively, since insufficient data are available to evaluate it precisely. The obtained A_{ax} values are 1.42_2, 1.39_3, 1.38_1, and 1.35_9 BM for the abco, 1/2dabco, 1/2tatcd, and 1/3tatcd adducts respectively, and 1.37_2, 1.37_0, and 1.36_3 BM for the THP, THF, and 1/2dox adducts respectively.

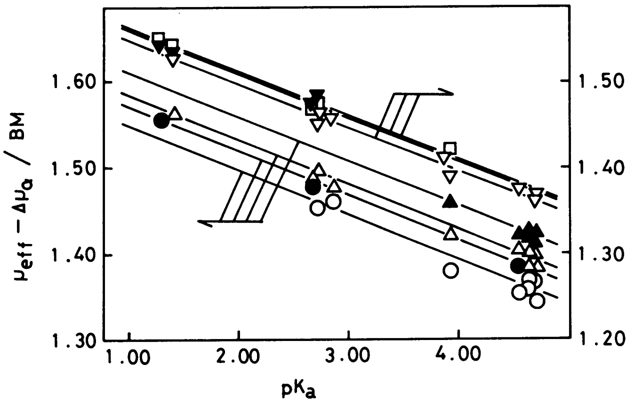

Fig. 1. The corrected magnetic moments at 20 °C plotted against the pK_a values of the parent carboxylic acids for the copper(II) alkanoate adducts with abco (▲), 1/2dabco (△), 1/2tatcd (●), 1/3tatcd (○), THP (▼), THF (□), and 1/2dox (▽). The solid lines are the best fit of the data to the Eq. 2.

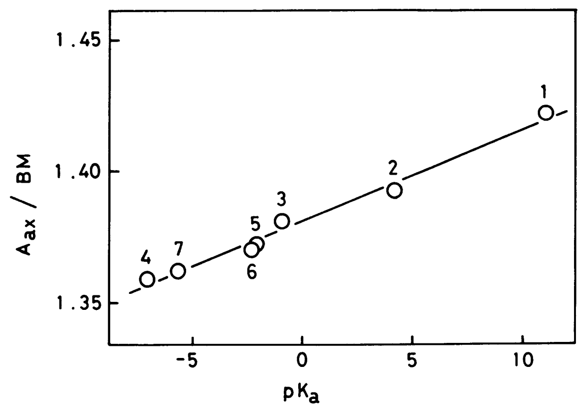

Fig. 2. The axial-coordination correction term plotted against the pK_a value of the conjugate acid of the axial ligand: abco (1), 1/2dabco (2), 1/2tatcd (3), 1/3tatcd (4), THP (5), THF (6), and 1/2dox (7).

Since typical hard bases are involved in this study, it seems likely that the axial-ligation effect of such bases correlates primarily to their donor characters. In order to examine this, the obtained A_{ax}'s are plotted against the pK_a values of the conjugate acids of axial ligands (Fig. 2). To plot the points for dabco and dox ligands, their first dissociation constants are selected, because their second coordination abilities are reduced similarly by H^+- and Cu^{2+}-coordination on the other sites. By similar reasoning, the pK_{a2} and pK_{a3} values (these values are estimated from pK_{a4}[22] by using the Branch–Calvin equation[23]) are selected for the 1/2tatcd and 1/3tatcd adducts respectively. In this series of axial ligands, the pK_a value varies from −7.1 for 1/3tatcd to −5.7, −2.26, −2.10, −1.0, 4.14, and 11.0 for 1/2dox, THP, THF, 1/2tatcd, 1/2dabco, and abco respectively. As can be seen from Fig. 2, there is a linear relation between these quantities. The best line has a slope of +0.0035 BM and the intercept of 1.38_2 BM at pK_a=0. The line in Fig. 2 goes upward to the right, and the variation in singlet-triplet separation values determined for the abco, 1/2dabco, and 1/3tatcd adducts of copper(II) propionate ($-2J$=323, 329, and 334 cm^{-1} respectively) indicates that the antiferromagnetic interactions decrease as the axial ligands become stronger sigma donors. This fact may be explained on the basis of weak Cu–O covalent bonds on the CuO_4 basal plane resulting from a strong sigma donation of the axial ligand.[24] The observation of the shift in the unsymmetric COO stretching bands (1623, 1620, and 1610 cm^{-1} for the abco, 1/2dabco, and 1/3tatcd adducts of copper(II) propionate) supports this explanation. The magnetic moments of copper(II) tetrahydro-2*H*-pyran-2-acetate[25] and the copper(II) chloroacetate adducts with 1,3-dioxolane and 2-(diethylamino)ethanol[26] were also found to vary in accord with this trend. In addition, a numerical comparison of the slopes in Figs. 1 and 2 indicates that, in the series of the present compounds, the axial ligand affects the magnetic moment about 15 times less than the bridging carboxylato does. This ratio suggests that the carboxylato substituent R in dinuclear copper(II) carboxylate adducts, $[Cu(RCOO)_2 \cdot L]_2$, affects the covalent Cu–O bonds more strongly than does the apical ligand L, for the spin-exchange coupling between the two copper(II) ions operates predominantly by superexchange interaction through the bridging carboxylato rather than by direct interaction.[27]

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