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Magnetic Properties of the Dinuclear Copper(II) Compounds Bridged by Oxalato-Type Ligands

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Synopsis. Various dinuclear copper(II) compounds bridged by the oxalato, oxamato, and oxamidato ligands were prepared and characterized by means of magnetic susceptibility and IR spectroscopy. The strong antiferromagnetic couplings through their carboxylate or carboxamidate groups are interpreted in terms of the ligand basicities and the electron withdrawal due to the resonance of the substituents.

The oxalate anion acts as a bilateral ligand to bridge two adjacent chelates,[1—5] whereas most other α,ω-dicarboxylate anions act as linked carboxylate ligands to bridge two copper(II) acetate-type dinuclear moieties.[6] By referring to these bridging geometries, a variety of magnetic behaviors of dicarboxylatocopper(II) compounds can be seen.[7] However, the reason why the carboxylate group of oxalate is much more effective than that of any alkanoate in transmitting a magnetic exchange has not yet been sufficiently investigated. For this purpose, it is desired to examine how the exchange couplings through the oxalato and related ligands are affected by their donor characters, and to compare the resulting correlation with that in the alkanoato-bridged compounds. Hence, in order to accumulate reliable magnetic data concerning an analogous series of compounds, we prepared compounds involving the $[\mathrm{L'Cu}(\mu\text{-}\mathrm{L})\mathrm{CuL'}]^{2+}$ cations, where L is a bridging oxalato-type ligand (oxalato, oxamato, and oxamidato), and L′ is a endcapping bidentate ligand (bpy=2,2′-bipyridine and $\mathrm{Me_4en}$=*N*,*N*,*N*′,*N*′-tetramethylethylenediamine), and studied their magnetic properties (Table 1).

All of the compounds were obtained in nearly the same way as described below. To an aqueous suspension of 0.01 mol of $\mathrm{CuC_2O_4{\cdot}1/2H_2O}$ were added 0.02 mol of bpy and 0.002 mol of $\mathrm{H_2C_2O_4}$ powder with stirring; to the deep-blue solution thus obtained was added 0.01 mol of $\mathrm{CuBr_2}$. Blue fine crystals which separated were collected by filter suction, and dried over silica gel. The effective magnetic moments (Table 1) were evaluated from the room-temperature magnetic susceptibilities (χ_A in $\mathrm{m^3\,mol^{-1}}$) using the equation $\mu_\mathrm{eff}=798[(\chi_\mathrm{A}-N\alpha)T]^{1/2}$. The temperature-independent paramagnetic contribution ($N\alpha$) was taken as 0.75×10^{-9} $\mathrm{m^3\,mol^{-1}}$. The Pascal constants[8] were used to correct the diamagnetic contributions. For compounds (**4**), (**8**), and (**12**), the variable-temperature magnetic susceptibilities were determined over the temperature range 80—300 K. The IR spectra were recorded using Nujol mulls in the 4000—600 $\mathrm{cm^{-1}}$ range.

The obtained compounds exhibited infrared absorption frequencies assignable to the bilateral bridging modes of the oxalato, oxamato, or oxamidato ligands,[9] and showed magnetic moments of 1.1—1.4 BM at room temperature, similar to those of well-characterized compounds. As reported,[10—12] these magnetic moment values depend little on the nature of the endcapping bidentate ligand or of the counter anion either, and decrease in the order of the oxalato, oxamato, and oxamidato bridges. The temperature dependencies of the magnetic susceptibilities for the oxalate (**4**), oxamate (**8**), and oxamidate (**12**) compounds agree well with the Bleaney–Bowers equation[13] with parameters $g=2.17$ and $2J=-302$ $\mathrm{cm^{-1}}$, $g=2.15$ and $2J=-366$ $\mathrm{cm^{-1}}$, and $g=2.16$ and $2J=-442$ $\mathrm{cm^{-1}}$, respectively, where the smaller magnetic moment is accompanied by a stronger exchange coupling within the dinuclear cation.

Recent structure determinations of the oxalato-bridged[2—5] and oxamidato-bridged[14,15] copper(II) compounds have shown that the copper(II) coordination is square pyramidal or elongated octahedral with the bridging ligand occupying two equatorial coordination sites in each case. Since their Cu-ligand distances are 1.99—2.02 Å for Cu–O (oxalato) and 1.96—1.99 Å for Cu–O (oxamidato), being almost the same as each other, so the variation in the present magnetic moments is attributable to the electronic factors, such as the donor characters, of these bridging ligands. The magnetic moments vs the $\mathrm{p}K_\mathrm{a}$ values of the bridging ligands are plotted in Fig. 1, together with some literature data.[3,5,10—12,15] Here, $\mathrm{p}K_\mathrm{a}$ is the dissociation exponent averaged for the two conjugate cation acids of an oxalato-type ligand, which were estimated to be −9.90, −4.25, and 1.41 for oxalato, oxamato, and oxamidato, respectively, by using an empirical equation.[16] The points give a straight line with a slope of −0.022 BM, which is nearly equal to half the slope for a series of copper(II) acetate-type carboxylates (−0.037 BM),[17—19] in conformity with the number of exchange pathways between the copper(II) ions (n=2 for the dicarboxylato-bridged compounds and 4 for the quadruply carboxylato-bridged compounds).

Taking into account the small differences in the coordination-bond lengths (R in Å) of the bridging ligands, the linear correlations for both series of dinuclear copper(II) compounds can be adequately summarized as follows:[17—19]

$$\mu_\mathrm{eff}=1.95\left[1-16.2\times n\times R^{-12}\left(\mathrm{p}K_\mathrm{a}+\mathrm{p}K_\pi+30.0\right)\right], \quad (1)$$

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

Compound		Found (Calcd)/%				μ_{eff}/BM
		Cu	C	H	N	
$Cu_2(C_2O_4)(Me_4en)_2(ClO_4)_2\cdot13/4H_2O$	**(1)**	17.98 (18.03)	23.7 (23.9)	5.60 (5.50)	7.9 (8.0)	1.32
$Cu_2(C_2O_4)(Me_4en)_2Br_2\cdot H_2O$	**(2)**	20.25 (20.32)	26.6 (26.9)	5.36 (5.48)	9.2 (9.0)	1.39
$Cu_2(C_2O_4)(bpy)_2(ClO_4)_2$	**(3)**	17.47 (17.50)	36.5 (36.4)	2.23 (2.22)	7.8 (7.7)	1.36
$Cu_2(C_2O_4)(bpy)_2Br_2\cdot H_2O$	**(4)**	17.96 (18.02)	37.9 (37.5)	2.56 (2.57)	7.9 (7.9)	1.38
$Cu_2(C_2O_3NH)(Me_4en)_2(ClO_4)_2$	**(5)**	19.69 (19.69)	26.1 (26.1)	5.15 (5.15)	10.8 (10.9)	1.19
$Cu_2(C_2O_3NH)(Me_4en)_2Br_2\cdot2H_2O$	**(6)**	19.73 (19.78)	26.1 (26.2)	5.62 (5.81)	10.6 (10.9)	1.26
$Cu_2(C_2O_3NH)(bpy)_2(ClO_4)_2\cdot H_2O$	**(7)**	17.05 (17.10)	35.6 (35.5)	2.59 (2.58)	9.5 (9.4)	1.27
$Cu_2(C_2O_3NH)(bpy)_2Br_2$	**(8)**	18.51 (18.52)	38.4 (38.5)	2.63 (2.50)	10.1 (10.2)	1.24
$Cu_2(C_2O_2N_2H_2)(Me_4en)_2(ClO_4)_2\cdot H_2O$	**(9)**	19.08 (19.18)	34.5 (25.4)	5.17 (5.48)	11.8 (12.7)	1.08
$Cu_2(C_2O_2N_2H_2)(Me_4en)_2Br_2\cdot2H_2O$	**(10)**	19.77 (19.82)	26.0 (26.2)	6.00 (5.97)	12.9 (13.1)	1.11
$Cu_2(C_2O_2N_2H_2)(bpy)_2(ClO_4)_2\cdot H_2O$	**(11)**	17.49 (17.54)	36.8 (36.5)	2.51 (2.50)	11.4 (11.6)	1.10
$Cu_2(C_2O_2N_2H_2)(bpy)_2Br_2\cdot3H_2O$	**(12)**	17.16 (17.19)	35.9 (35.7)	3.22 (3.27)	11.2 (11.4)	1.09

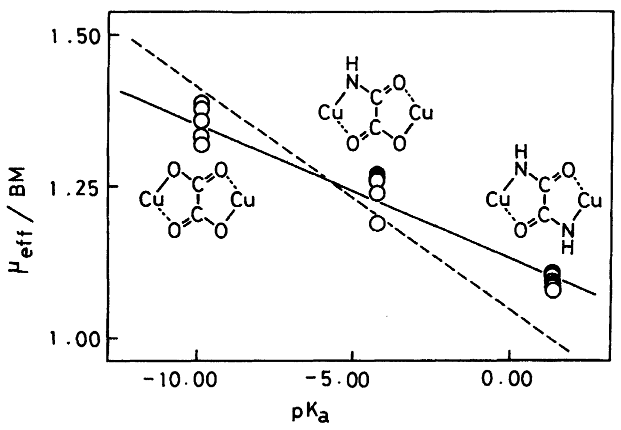

Fig. 1. Magnetic moments at 20 °C of the copper(II) compounds bridged by oxalato-type ligands plotted against the acidities of the ligands. The broken line represents the linear correlation for dinuclear copper(II) alkanoates.

where pK_π is the correction term for the resonance effect by a substituent on the bridging group. This fact suggests that the exchange couplings through the oxalato-type bridge operate by a similar mechanism as that proposed for copper(II) acetate-type carboxylates; unpaired electrons delocalize from the copper(II) ion not only into the σ-bonding system, but also into the π system of the bridging groups.[20] From the graphic interpolation shown in Fig. 1, the pK_π value can be evaluated for the present compounds. The obtained $pK_\pi=7.0$ is consistent with the linear correlation between the pK_π and $R-0.38F$ values found in various substituted-formate compounds,[17] where R and F are the resonance and field constants of Swain and Lupton.[21] This large pK_π value (cf. −6.7 for the alkyl and substituted alkyl substituents[17]) and the long C–C bonds of 1.53—1.56 Å in oxalato and oxamidato[14] are rationalized by the strong electron withdrawal due to the resonance of the carboxylate anion or carboxamidate anion substituents.[21] Conclusively, the strong antiferromagnetic couplings in the present compounds are associated with the strong basicities of the bridging ligands and the electron withdrawals due to the resonance of the substituents.

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