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The Magnetic Properties of the Copper(II) Compounds with 3- and 4-Piperidinecarboxylic Acids

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Synopsis. Compounds of formula $[CuX_2(C_5H_{11}NCOO)_2]\cdot 3H_2O$ ($X=NO_3$, Cl, Br), $[Cu(NO_3)_2(C_5H_{11}NCOO)_2]\cdot 2(NH_2)_2CO$, and $Cu[(CH_3)_2CHCOO]_2\cdot(NH_2)_2CO$ have been prepared. The correlation of their magnetic properties with the pK_a values of their parent carboxylic acids is discussed.

A recent X-ray study[1] of a compound formed by the reaction of copper(II) nitrate with *β*-alanine has shown that four 3-ammoniopropionates bridge two copper(II) ions, forming a dimeric structure similar to that of copper(II) acetate monohydrate.[2,3] Previously, we also found that dinuclear copper(II) *ω*-ammonio carboxylates were obtained during a treatment of *ω*-amino carboxylic acids with copper(II) halides.[4] Since there still remain unclear points about the influence of a carboxylato substituent on the magnetic properties of dinuclear copper(II) carboxylates,[5] these ammonio carboxylates seem to be appropriate for studying the substitution effects. Then, as a continuation of our studies, we have prepared several new copper(II) compounds with 3- and 4-piperidinecarboxylic acids (nipecotic and isonipecotic acids) and examined the relation between their magnetic properties and the pK_a values of their parent acids. For the sake of discussion, the urea adduct of copper(II) isobutyrate was also prepared.

Compounds with a stoichiometry of $[CuX_2(C_5H_{11}NCOO)_2]\cdot 3H_2O$ ($X=NO_3$, Cl, Br) were prepared by a previously described method for copper(II) *ω*-amino carboxylates.[4] The urea adducts, $[Cu(NO_3)_2(C_5H_{11}NCOO)_2]\cdot 2(NH_2)_2CO$ and $Cu[(CH_3)_2CHCOO]_2\cdot(NH_2)_2CO$, were prepared according to the reported general procedure.[6]

The IR spectra of the copper(II) piperidinecarboxylate show bands near 1585—1593 cm^{-1} connected with NH_2^+ deformations[7] in addition to the characteristic bands in the ranges of 1430—1450 and 1600—1660 cm^{-1} connected with symmetric and unsymmetric COO stretching vibrations of the carboxyl groups.[8]

The effective magnetic moments (Table 1) were evaluated from the room-temperature magnetic susceptibilities, which were corrected for the diamagnetic contribution of constituent atoms using Pascal constants[9] and $N\alpha=60\times10^{-6}$ emu mol^{-1} (1 emu$=4\pi\times10^{-6}$ m^3). The temperature dependence of the magnetic susceptibilities (80—300 K) of $[Cu(NO_3)_2(3\text{-}C_5H_{11}NCOO)_2]\cdot 3H_2O$, $[Cu(NO_3)_2(4\text{-}C_5H_{11}NCOO)_2]\cdot 3H_2O$, and $Cu[(CH_3)_2CHCOO]_2\cdot(NH_2)_2CO$ were measured. The results agreed well with the Bleaney-Bowers equation,[10] using the following parameters: $g=2.13$ and $2J=-314$ cm^{-1}, $g=2.14$ and $2J=-330$ cm^{-1}, and $g=2.18$ and $2J=-342$ cm^{-1} for the compounds with 3- and 4-piperidinecarboxylic acids and isobutyric acid, respectively, indicating the presence of a dinuclear unit, which contains four zwitterionic (piperidinio)formate ($C_5H_9NH_2^+\text{-}COO^-$) bridges between the copper(II) ions similarly to copper(II) acetate monohydrate.

For dimers with this type of structure, it has been pointed out that the magnitude of a superexchange interaction through carboxylato bridging groups is inversely related to the basicity of the bridging group, as measured by the pK_a value of its parent acid.[11] In a previous study of copper(II) (substituted propionate)s, we found that this trend was maintained for a series of copper(II) *ω*-ammonio carboxylates.[4] In the present study, the bridging groups were substituted isobutyrate ligands and the pK_a values of the parent acids

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

Compound	Found(Calcd)/%					μ_{eff}/BM
	Cu	X	H	C	N	
$[Cu(NO_3)_2(3\text{-}C_5H_{11}NCOO)_2]\cdot 3H_2O$	12.78		5.63	29.06	11.29	1.37
	(12.71)		(5.65)	(28.83)	(11.21)	
$[CuCl_2(3\text{-}C_5H_{11}NCOO)_2]\cdot 3H_2O$	14.15	16.18	5.97	32.47	6.25	1.32
	(14.22)	(15.87)	(6.32)	(32.26)	(6.27)	
$[Cu(NO_3)_2(4\text{-}C_5H_{11}NCOO)_2]\cdot 3H_2O$	12.82		5.59	28.94	11.24	1.34
	(12.71)		(5.65)	(28.83)	(11.21)	
$[Cu(NO_3)_2(4\text{-}C_5H_{11}NCOO)_2]\cdot 2(NH_2)_2CO$	11.31		5.36	29.61	19.66	1.37
	(11.23)		(5.34)	(29.71)	(19.80)	
$[CuBr_2(4\text{-}C_5H_{11}NCOO)_2]\cdot 3H_2O$	11.82	29.51	5.12	26.90	5.19	1.31
	(11.86)	(29.83)	(5.27)	(26.90)	(5.23)	
$Cu[(CH_3)_2CHCOO]_2\cdot(NH_2)_2CO$	21.11		6.08	35.77	10.22	1.33
	(21.34)		(6.09)	(36.30)	(9.41)	

varied from 3.53 and 4.03 (estimated from the Branch–Calvin equation[12]) for 3- and 4-piperidinecarboxylic acids to 4.63 for isobutyric acid. The singlet-triplet separation value ($-2J$) of $[Cu(NO_3)_2(4\text{-}C_5H_{11}NCOO)_2]\cdot 3H_2O$ (330cm^{-1}) is larger than that of $[Cu(NO_3)_2(3\text{-}C_5H_{11}NCOO)_2]\cdot 3H_2O$ (314 cm^{-1}), and also the magnetic moment of $[Cu(NO_3)_2(4\text{-}C_5H_{11}NCOO)_2]\cdot 2(NH_2)_2CO$ (1.37 BM) is larger than that of $Cu[(CH_3)_2CHCOO]_2\cdot (NH_2)_2CO$ (1.33 BM). Therefore, the order for the extent of an antiferromagnetic interaction between the two copper(II) ions is isobutyrate>4-piperidinecarboxylate>3-piperidinecarboxylate, indicating that the magnetic interaction in the series of copper(II) dialkylacetates also tends to decrease as the acid strength of the parent acid becomes stronger.

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