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The Magnetic Properties of the Copper(II) Complexes with ω-Amino Carboxylic Acids

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Synopsis. Compounds of formula $CuX_2(OOC(CH_2)_mNH_3)_2\cdot nH_2O$ (m=2—5 and X=Cl or Br) and $CuX_{3/2}(OOCCH_2NH_3)$ (X=Cl or Br) have been prepared and characterized by means of magnetic susceptibility and IR spectroscopy measurements. The correlation of their magnetic moments with the pK_a values of their parent carboxylic acids is discussed.

In general, α- and β-amino carboxylic acids form metal chelates in which the amino nitrogen and carboxylate oxygen atoms act as donors. However, a recent X-ray study[1] of the complex formed by the reaction between copper(II) chloride and glycine, has shown that ammonio acetate coordinates to the metal ion *via* a carboxyl group and that copper(II) acetate-type dimer units are created. This suggests that not only *N*-protected amino carboxylic acids, such as *N*-acetylglycine,[2] *N*-tosylglycine[3] and hippuric acid,[4] but amino carboxylic acids can act generally as simple carboxylic acids. The resultant copper(II) compounds seem to be appropriate to investigate the effect of the NH_3^+ group on their magnetic properties. Thus, we tried to isolate the copper(II) compounds from the acidic solutions with various ω-amino carboxylic acids.

A compound with a stoichiometry of $CuCl_2(OOC(CH_2)_mNH_3)_2\cdot nH_2O$, where m=2—5, was precipitated in green crystals when a slight excess of amino carboxylic acid and a small amount of a 2 mol dm^{-3} HCl solution were added to a warm solution (*ca.* 40 °C) of copper(II) chloride. Then, the mixture was allowed to stand in a refrigerator overnight. The corresponding bromide salt was also obtained in a similar way. Fresh samples of the obtained compounds mostly contain water molecules (IR band at *ca.* 3450 cm^{-1}). The water was gradually lost when stored under anhydrous conditions. The corresponding glycine compound, $CuCl_2(OOCCH_2NH_3)_2\cdot 2H_2O$, was also isolated by Castillo and Ramirez,[5] but its magnetic moment (μ_{eff}=1.81 BM at 22 °C) and IR data indicate that the compound has a monomeric structure. Since two isomers of the analogous chromium(II) bromide compound, $CrBr_2(OOCCH_2NH_3)_2\cdot 2H_2O$, were isolated by Herzog *et al.*,[6,7] we attempted to isolate the isomeric form of $CuCl_2(OOCCH_2NH_3)_2\cdot 2H_2O$. The mixed valence compound $CuCl_{3/2}(OOCCH_2NH_3)$, however, was isolated[1] as dark-green crystals instead of the expected isomer. This compound can be obtained more efficiently by reacting glycine with an acidic aqueous solution including equimolar amounts of copper(I) and copper(II) chlorides and allowing the solution to stand in a refrigerator overnight. The corresponding bromide salt is also obtained in a similar way.

The magnetic moments of the present compounds (Table 1) were evaluated per copper(II) ion from their susceptibilities observed at room temperature and the relevant Pascal constants.[8] The magnetic susceptibilities of the chloride salts were measured from liquid nitrogen up to room temperature (Fig. 1) and agreed well with the theoretical equation for the

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

Compounds	Found (Calcd) (%)					μ_{eff}/BM
	Cu	X	C	H	N	
$CuCl_{3/2}(OOCCH_2NH_3)$	33.02	27.70	12.41	2.66	7.26	1.36
	(33.13)	(27.73)	(12.52)	(2.63)	(7.30)	
$CuBr_{3/2}(OOCCH_2NH_3)$	24.73	46.32	9.15	1.84	5.36	1.31
	(24.59)	(46.37)	(9.30)	(1.95)	(5.42)	
$CuCl_2(OOCCH_2CH_2NH_3)_2\cdot H_2O$	19.18	21.67	21.71	4.86	8.44	1.35
	(19.22)	(21.44)	(21.80)	(4.88)	(8.47)	
$CuBr_2(OOCCH_2CH_2NH_3)_2\cdot H_2O$	15.28	37.90	17.07	3.85	6.68	1.35
	(15.15)	(38.09)	(17.18)	(3.88)	(6.68)	
$CuCl_2(OOCCH_2CH_2CH_2NH_3)_2\cdot 3/2H_2O$	17.38	19.40	26.42	5.82	7.70	1.33
	(17.28)	(19.28)	(26.13)	(5.76)	(7.62)	
$CuBr_2(OOCCH_2CH_2CH_2NH_3)_2\cdot 1/2H_2O$	14.56	36.55	21.40	4.35	6.26	1.33
	(14.49)	(36.44)	(21.91)	(4.37)	(6.39)	
$CuCl_2(OOCCH_2CH_2CH_2CH_2NH_3)_2\cdot 2H_2O$	15.85	18.15	29.45	6.42	6.87	1.33
	(15.70)	(17.52)	(29.67)	(6.47)	(6.92)	
$CuBr_2(OOCCH_2CH_2CH_2CH_2NH_3)_2$	14.00	35.22	26.01	4.88	6.10	1.28
	(13.89)	(34.92)	(26.25)	(4.85)	(6.12)	
$CuCl_2(OOCCH_2CH_2CH_2CH_2CH_2NH_3)_2\cdot 2H_2O$	14.70	16.42	33.00	6.97	6.45	1.32
	(14.68)	(16.38)	(33.30)	(6.99)	(6.47)	
$CuBr_2(OOCCH_2CH_2CH_2CH_2CH_2NH_3)_2\cdot 2H_2O$	12.15	30.55	27.48	5.61	5.37	1.29
	(12.18)	(30.63)	(27.63)	(5.80)	(5.37)	

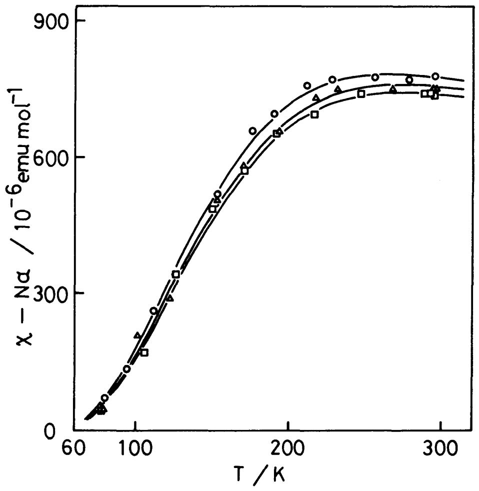

Fig. 1. Magnetic susceptibilities of the copper(II) chloride compounds with 3-aminopropionic (○), 4-aminobutyric (△) and 6-aminohexanoic (□) acids. The solid curve represents the Bleaney-Bowers equation.

susceptibility of binuclear copper(II) compounds (Bleaney-Bowers equation⁹⁾), using the following parameters: g=2.18 and $2J=-315\,\text{cm}^{-1}$, g=2.15 and $2J=-320\,\text{cm}^{-1}$, and g=2.15 and $2J=-324\,\text{cm}^{-1}$ for the compounds with 3-aminopropionic(β-alanine), 4-aminobutyric and 6-aminohexanoic acids, respectively, and $N\alpha=60\times10^{-6}$ emu mol^{-1} (1 emu mol$^{-1}=4\pi\times10^{-6}$ m^3 mol^{-1}). IR spectra of the solid complexes show the bands near 1520 and 1580 cm^{-1} connected with NH_3^+ deformations¹⁰⁾ in addition to the characteristic bands in the range 1430—1450 and 1600—1660 cm^{-1} connected with symmetric and unsymmetric stretching vibrations of the carboxyl groups.¹¹⁾ The obtained results show clear evidence for the presence of a dinuclear subunit, which contains four zwitterionic amino carboxylic acids bound with the copper(II) ions *via* carboxyl group like copper(II) acetate monohydrate. The axial positions seem to be occupied by halide ions, because there exists a slight difference in the magnetic moments between the chloride and bromide salts. It is consistent with the fact that the magnetic moments of the anhydrous compounds are not greatly different from those of the hydrated compounds, water being probably involved in hydrogen bonding in the packing of the molecules.

It has already been pointed out that the magnetic superexchange interaction in the dimeric carboxylates is related to the donor-acceptor character of bridging and axial ligands.¹²⁾ Although this relationship does not take into account the effect of the metal-ligand bond or steric effects in the axial ligand coordination, it has been supported experimentally¹³,¹⁴⁾ and shown to be consistent with the results of molecular orbital analyses of the bridged dimeric structure.¹⁵⁾ In this series of bridging ligands, the pK_a value varies from 2.36 for glycine to 3.53, 4.03, 4.27, and 4.43 for 3-aminopropionic, 4-aminobutyric, 5-aminovaleric and 6-aminohexanoic acids, respectively.¹⁶⁾ From Table 1, it can be seen that, except for the glycine compounds, the trend that magnetic moments in the series of the same halide salts increase as the acid strength of the ammonio carboxylic acids (pK_{a_1}) becomes stronger. This trend is consistent with the variation of singlet-triplet separation values($-2J$) determined for a series of chloride salts. X-Ray and magnetic susceptibility studies of the glycine compound $CuCl_{3/2}(OOCCH_2NH_3)$ have shown that this polymeric compound is composed of cupric dimeric subunits with an exchange integral $2J=-385\,\text{cm}^{-1}$.¹⁾ Although this strong antiferromagnetic interaction was explained by the presence of an electrophilic NH_3^+ group,¹⁾ a large number of magnetic data for copper(II) halogenoacetates¹⁷⁾ have shown that the σ-electron attracting effect produces a comparative decreasing magnetic interaction. The disobedience of the general trend suggests that the strong interaction in the glycine compound is attributable to steric effects or the coordination of the axial chlorine to a copper(I) ion. The fact that the magnetic moments of the chloride salts are higher than those of bromide salts indicates that the antiferromagnetic interaction in dimeric copper(II) carboxylate adducts tends to become stronger as the basicity of the added axial ligands becomes weaker.¹⁸⁾

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