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The Magnetic Properties of the Ammonium Chloride Adducts of Copper(II) Chloroacetates

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Sinopsis. Various ammonium chloride adducts of copper(II) chloroacetate and copper(II) dichloroacetate were prepared. The variable-temperature magnetic susceptibilities of the dimethylammonium chloride adducts obey the Bleaney-Bowers equation, indicating the existence of the copper(II) acetate type of dinuclear moiety in their crystals. The effect of the counter cations on their magnetic moments was discussed.

A large number of dinuclear copper(II) carboxylate adducts, $[Cu(RCOO)_2\cdot L]_2$, have been studied to elucidate the factors influencing the magnetic properties in these compounds. In particular, the effects of the carboxylate substituent R and of the axial ligand L upon the strength of the spin-exchange interaction or singlet-triplet separation($-2J$) have been extensively investigated.[1] However, both the variation of surrounding ions around the dinuclear molecule and the crystal packing must also affect the magnetic properties. Goodgame *et al.* reported the preparation and magnetic properties of some dinuclear anionic copper(II) acetate complexes, $\{(CH_3)_4N\}_2[Cu(CH_3COO)_2X]_2$ (X= NCS, NO_2, or Br).[2,3] Because the counter cation can be easily replaced, these anionic dinuclear copper(II) compounds are appropriate to examine the effect of the surrounding ions but only insufficient data have been available. Here, we report the preparation and magnetic properties of the various ammonium chloride adducts of copper(II) chloroacetate and copper(II) dichloroacetate.

The compound with the stoichiometry of $Cu(ClCH_2COO)_2\cdot n$ACl, where $n=2$ for $A=NH_4$ and $n=1$ for $A=(CH_3)_2NH_2$ and CH_3NH_3, was precipitated in green crystals when an excess of ACl was added to a hot aqueous solution of copper(II) chloroacetate with a small amount of chloroacetic acid, and then the mixture was allowed to stand for a few minutes. The dichloroacetate compond $Cu(Cl_2CHCOO)_2\cdot n$ACl, where $n=5/7$ for $A=(CH_3)_2NH_2$ and $n=3/2$ for $A=(CH_3)_3NH$, was also obtained in a similar way.

The magnetic moments of these compounds (Table 1) were evaluated from their susceptibilities observed at room temperature and the relevant Pascal constants.[4] They are low and practically the same as that of copper(II) acetate monohydrate (1.40 BM at 21 °C).[5] The temperature dependence of the magnetic susceptibilities of the dimethylammonium chloride adducts of copper(II) chloroacetate and copper(II) dichloroacetate over the temperature range of 77—300 K (Fig. 1) was also found to correspond well with the known behavior of copper(II) acetate monohydrate. A reasonably good agreement was found between the experimental results and a theoretical curve calculated from the usual expression[6] for the susceptibility of the copper(II) ions in the copper(II) acetate dimer (Bleaney-Bowers equation), using the following parameters: $g=2.19$ and $2J=-278$ cm^{-1} for the chloroacetate compound and $g=2.21$ and $2J=-271$ cm^{1} for the dichloroacetate compound, respectively, and $N\alpha=60\times10^{-6}$ emu/mol (1 emu/mol$=4\pi\times10^{-6}$ m^3/mol). The result obtained is consistent with the assumption that all have the familiar bridged dimeric copper(II) acetate monohydrate structure. Although the chloride ion has a tendency to displace the bridging carboxylate, the anionic dinuclear copper(II) carboxylate is constructed by the axial coordination of a chloride ion with the exception of the dimethylammonium chloride adduct of copper(II) dichloroacetate and the tetramethylammonium chloride adduct of copper(II) chloroacetate. Garner and Senior[7] reported that the reaction of molybdenum(II) trifluoroacetate with tetraethylammonium halides resulted in the formation of the hemi- and mono-adducts, $\{(C_2H_5)_4N\}$, $[Mo_2(CF_3COO)_4X]$, and $\{(C_2H_5)_4N\}_2[Mo(CF_3COO)_2X]_2$, and suggested that the adducts are more stable than the neutral molecule, presumably due in large measure to the lattice energy of these salts. This is also the case for copper(II) carboxylate, and the $(NH_4)_2ZnCl_4$ adduct of copper(II) chloroacetate (1.41 BM at 28 °C) can be isolated easily.[8] From the Table 1 and the magnetic data of the corresponding acetate adducts,[9] the following trends in the magnetic properties can be seen. First, the magnetic moments in the series of the same ammonium chloride adducts increase as the acid strength of the parent carboxylic acids become stronger, which is attributed to the fact that the stronger carboxlylic acid has a tendency to elongate the bridging Cu-O-C-O-Cu length.[1] The IR spectra, assigned by a comparison with the spectra of the corresponding pyridine adducts, show absorption bands characteristic of Cu-Cl stretching vibrations, except for the dimethylammonium chloride adduct of copper(II)

Table 1. Analytical data and effective magnetic moments at 27 °C

Compound	Cu(%) Calcd	Cu(%) Found	Cl(%) Calcd	Cl(%) Found	μ_{eff}(BM)
$Cu(ClCH_2COO)_2\cdot 2NH_4Cl$	17.88	18.09	19.84	19.69	1.42
$Cu(ClCH_2COO)_2\cdot CH_3NH_3Cl$	19.98	20.06	11.15	11.22	1.43
$Cu(ClCH_2COO)_2\cdot (CH_3)_2NH_2Cl$	19.14	19.22	10.67	10.83	1.42
$Cu(ClCH_2COO)_2\cdot 1/3(CH_3)_4NCl\cdot H_2O$	20.83	20.93	3.87	3.72	1.41
$Cu(Cl_2CHCOO)_2\cdot 5/7(CH_3)_2NH_2Cl$	16.82	16.84	6.70	6.57	1.47
$Cu(Cl_2CHCOO)_2\cdot 3/2(CH_3)_3NHCl$	13.73	13.74	11.49	11.35	1.50

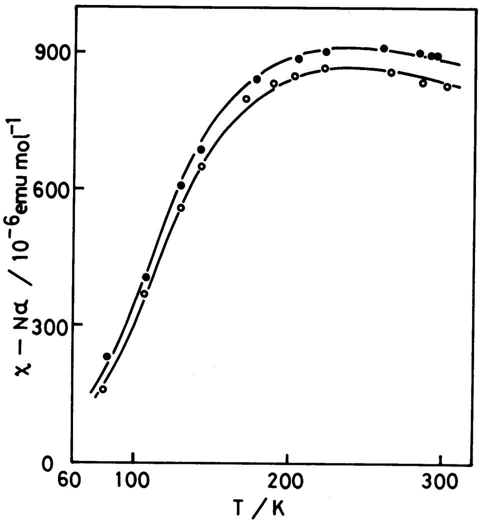

Fig. 1. Magnetic susceptibilities of the dimethylammonium chloride adducts of copper(II) chloroacetate (white circles) and copper(II) dichloroacetate (black circles). The solid curve represents the Bleaney-Bowers equation.

dichloroacetate which shows the complicated spectrum in the region of 276—317 cm^{-1} in agreement with its complicated stoichiometry. The observation of a band shift for the Cu-Cl stretching to the higher frequency, from 232—234 cm^{-1} of the acetates to 260—264 cm^{-1} of the chloroacetates suggests the stronger axial coordination in the chloroacetates. This is consistent with the fact that there is a movement of the copper atom out of the basal plane of its square pyramidal coordination polyhedron when the acid strength increases.[1,10)] Secondly, since the difference in the magnetic moments between the chloride adducts (1.38—1.41 BM at 17 °C for the acetates and 1.41—1.43 BM at 27 °C for the chloroacetates, respectively) and the hydrates (1.40 BM at 21 °C for the acetate[5)] and 1.45 BM at 24 °C for the chloracetate[11)]) is very small, it was difficult to evaluate the effect of the axial ligands. Thirdly, even for the same carboxylate compounds, there are slight differences in the observed magnetic moments of the chloride adducts (1.39—1.41 BM for the ammonium chloride adducts and 1.38 BM for the potassium chloride adduct of copper(II) acetate[9)]). This fact suggests that the hydrogen bonds to the bridging carboxylate and the cation affect the magnetic property in addition to the packing effect. The amount of the scattering seems to increase as the parent carboxylic acids become stronger.

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