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The Magnetic Properties of $Cu(CH_3COO)_2 \cdot 2NH_4Cl$ and $NH_4Cu(HCOO)Cl_2$

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Synopsis. The temperature dependence of the magnetic susceptibility of $Cu(CH_3COO)_2 \cdot 2NH_4Cl$ obeys the Bleaney-Bowers equation, indicating the existence of the anionic copper(II) acetate dinuclear unit. The exchange integral, J/k, is equal to -205 K. For $NH_4Cu(HCOO)Cl_2$, the structure containing copper(II) formate layers connected by tetrachlorocuprate(II) bridges is presumed on the basis of the value of the Weiss constant.

It has been suggested that, in dinuclear copper(II) carboxylate adducts, the axial ligand (apical ligand of the square pyramidal coordination polyhedron) plays a role in determining the extent of spin-exchange interaction or the singlet-triplet separation ($-2J$).[1] Goodgame *et al.* have reported the magnetic properties of several dinuclear anionic copper(II) acetate complexes, $(R_4N)_2[Cu(CH_3COO)_2X]_2$ (X=NCS, NO_2, or Br).[2,3] However, insufficient data have been available to draw any precise conclusions regarding the role of the axial ligand in anionic copper(II) acetate complexes. In this work, we prepared three copper(II) acetate complexes, $Cu(CH_3COO)_2 \cdot 2KCl$, $Cu(CH_3COO)_2 \cdot 2NH_4Cl$, and $Cu(CH_3COO)_2 \cdot 3/2C_4H_9NH_3Cl$, and two copper(II) formate complexes, $KCu(HCOO)Cl_2$ and $NH_4Cu(HCOO)Cl_2$, and measured their magnetic susceptibilities in order to study the effect of the chloride ions upon the magnetic properties.

The compound with the stoichiometry of $Cu(CH_3COO)_2 \cdot n ACl$, where $n=2$ for $A=NH_4$ or K and $n=3/2$ for $A=n\text{-}C_4H_9NH_3$, was precipitated in large green crystals when an excess of ACl was added to a hot aqueous solution of copper(II) acetate monohydrate with a few drops of acetic acid and the mixture was allowed to stand overnight at *ca.* 5 °C in a refrigerator. The magnetic moments of these compounds 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 (Table 1).

The temperature dependence of the magnetic susceptibility of the $Cu(CH_3COO)_2 \cdot 2NH_4Cl$ complex over the 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 the theoretical curve calculated from the usual expression[5] for the susceptibility of the copper(II) ions in the copper(II) acetate dimer (Bleaney-Bowers equation), using the following parameters: $g=2.14$, $J/k=-205$ K, and $N\alpha=60\times10^{-6}$ emu/mol (1 emu/mol$=4\pi\times10^{-6}$ m^3/mol). The variation in the value of $-2J$ on the replacement of H_2O by Cl is too small to confirm the suggestion that the exent of spin-exchange interaction increases as the axial ligand becomes stronger as an electron donor.[6] However, the obtained result is consistent with the assumption that the anionic copper(II) acetate is constructed by replacing the water molecules in $[Cu(CH_3COO)_2 \cdot H_2O]_2$ with chloride ions.

We attempted to prepare the analogous formate complexes by the method described above. However, the compounds with the stoichiometry of $ACu(HCOO)Cl_2$, where $A=NH_4$ or K, were obtained as fine yellowish

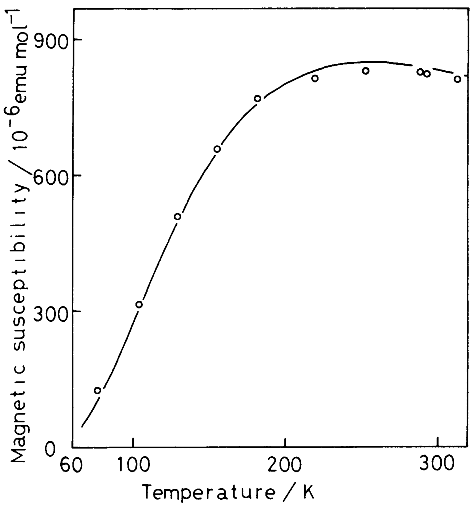

Fig. 1. Observed and calculated magnetic susceptibilities of $Cu(CH_3COO)_2 \cdot 2NH_4Cl$: experimental points and solid curve calculated by the Bleaney-Bowers equation.

Table 1. Analytical data and effective magnetic moments at 17 °C

Compound	Cu (%)		Cl (%)		μ_{eff}/BM
	Calcd	Found	Calcd	Found	
$Cu(CH_3COO)_2 \cdot 2KCl$	19.21	19.16	21.44	21.29	1.38
$Cu(CH_3COO)_2 \cdot 2NH_4Cl$	22.02	22.05	24.57	24.76	1.39
$Cu(CH_3COO)_2 \cdot 3/2C_4H_9NH_3Cl$	18.34	18.45	15.35	15.17	1.41
$KCu(HCOO)Cl_2$	29.07	29.12	32.44	32.27	1.78
$NH_4Cu(HCOO)Cl_2$	32.46	32.17	35.90	35.81	1.77

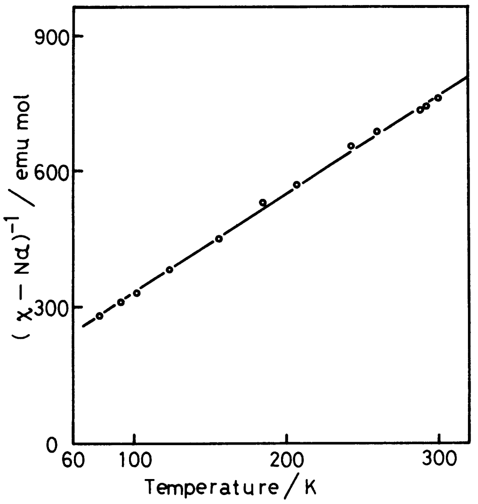

Fig. 2. A plot of inverse susceptibility data *vs.* temperature for the complex $NH_4Cu(HCOO)Cl_2$. The solid line shows the Curie-Weiss behavior.

green crystals. The room-temperature magnetic moments determined for these formates are slightly lower than those found for paramagnetic copper(II) compounds, indicating the existence of antiferromagnetic interactions among the copper(II) ions. Their values, however, are obviously different from those of dimeric copper(II) formate adducts with pyridine,[7,8] urea,[9] or thiocyanate ions.[2] The composition suggests that these compounds are 1 : 1 complexes between copper(II) formate and tetrachlorocuprates(II), $Cu(HCOO)_2 \cdot A_2CuCl_4$. This formulation is supported by the fact that these crystals can be obtained more efficiently by concentrating an aqueous solution of $Cu(HCOO)_2 \cdot 2H_2O$ and $A_2CuCl_4 \cdot 2H_2O$ on a water bath.

The temperature dependence of the magnetic susceptibility of the $NH_4Cu(HCOO)Cl_2$ complex over the range of 77—300 K (Fig. 2) obeys the Curie-Weiss law when the following parameters are used: $g=2.21$ and $\Theta=-52.8$ K. The value of the weiss constant for this compound is almost half of the value for $Cu(HCOO)_2 \cdot 4H_2O$,[10] the X-ray crystal analysis of which has indicated that the metal ions are bridged in anti-anti-bonding arrangements of Cu-O-C-O-Cu links to form a two-dimensional lattice.[11] It is known that half of the water molecules interposed between the copper(II) formate layers can be replaced by urea[12] or pyridine,[8] and that the resultant compound has essentially the same configuration as does tetrahydrate. These facts suggest that the present formates are also formed by interposing A_2CuCl_4 between the copper(II) formate layers, because the paramagnetic ions between layers seem to diminish the value of the Weiss constant. Martin and Waterman[10] have suggested that the adduct ligands which most effectively reduce the residual charge on the copper(II) ion may favour a syn-syn-bonding arrangement of the Cu-O-C-O-Cu links, but the importance of the packing effects was also pointed out.[13] The above-mentioned structure can be explained by this packing effect.

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