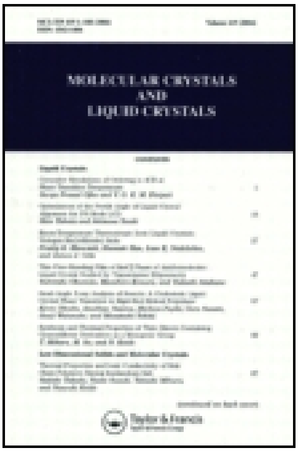

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Synthesis, Structure, and Magnetic Properties of Crystalline Coordination Polymers of Copper(II), $\{[Cu(CA)(H_2O)_2 (H_2O)\}_n$ AND $[Cu(CA)(MeOH)_{2\ n}$ (H_2CA; Chloranilic Acid)

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SYNTHESIS, STRUCTURE, AND MAGNETIC PROPERTIES OF CRYSTALLINE COORDINATION POLYMERS OF COPPER(II), $\{[Cu(CA)(H_2O)_2](H_2O)\}_n$ AND $[Cu(CA)(MeOH)_2]_n$ (H_2CA; CHLORANILIC ACID)

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Abstract Hydrogen bonded coordination polymers, $\{[Cu(CA)(H_2O)_2](H_2O)\}_n$, $[Cu(CA)(MeOH)_2]_n$ (H_2CA; chloranilic acid), and related polycrystalline analogs have been structurally and magnetically characterized. 1-Dimensional (1-D) weak antiferromagnetic exchange interaction ($J = -2.01$ cm^{-1}) was observed in $\{[Cu(CA)(H_2O)_2](H_2O)\}_n$, which has a 3-dimensional hydrogen bond network in the crystal. This polycrystalline form liberates the water molecules to be $[Cu(CA)]_n$, which is known as the Heisenberg antiferromagnet. Powder X-ray diffraction and thermal data show that the framework constructed by 1-D chains are so stable that water molecules readily come out without breaking the 1-D chains. Two types of coordination polymers ($[Cu(CA)(MeOH)_2]_n$ and $[Cu(CA)(MeOH)]_n$) containing axially coordinated MeOH have been prepared. $[Cu(CA)(MeOH)]_n$ has strong and anomalous antiferromagnetic exchange interactions in the crystal, indicating a new phase of Cu/CA systems, such as a mixed valence state, and if so the coordinated MeOH plays an important role to control physical properties of the polymers.

INTRODUCTION

Building 2-dimensional (2-D) copper complex-based layers is an important step to create systems having strongly correlated electrons, which would provide cooperative conductive and magnetic properties.[1] In order to afford higher spatial and electronic dimensionalities a crystalline coordination polymer is most useful in various assembled systems of copper.[2] Polyoxocarbons are a good candidate for ligands to provide transition metal coordination polymers. Especially, chloranilic acid (H_2CA) is known to be double bidentate ligand, providing one dimensional chains of various metal ions.[3-5] The background of this chemistry prompts us to utilize CA chains of copper as a building block of the high dimensional materials. A useful way is to fabricate 2-D coordination polymers by both 1-D polymers and additional bridging ligands. Very recently we have succeeded in the syntheses and the characterizations of a 2-D coordination polymer,

$[Cu(CA)(pz)]_n$ (pz = pyrazine) (**1**),[6] and hydrogen bonded polymers $\{[Cu(CA)(H_2O)_2](H_2O)\}_n$ (**2**),[7] and $[Cu(CA)(MeOH)_2]_n$ (**3**),[6] where the water and MeOH molecules are used to link the 1-D motifs with the aid of the hydrogen bonding. **1** can be obtained as both single crystal and polycrystalline phases. On the other hand, **2** and **3** are also obtained as single crystal phase but their polycrystalline forms indicate that the stoichiometry of water or methanol is different from that of **2** and **3**. This is associated with the liberation of coordinated and/or interstitial solvent molecules in between polymer chains. This manuscript concerns the structural and magnetic characterizations of **2**, **3**, and their polycrystalline analogs.

EXPERIMENTAL

The synthesis of **2** and **3** was described previously.[6,7] $[Cu(CA)]_n$ (**5**) was prepared according to the literature.[5]

Synthesis of $[Cu(CA)(MeOH)]_n$ (**4**)

To a methanol solution (10 ml) of *p*-chloranil (6×10^{-5} mol) was added a methanol solution (10 ml) of $[Cu(CH_3CN)_4]PF_6$ (6×10^{-5} mol) with stirring in a nitrogen atmosphere. Black precipitates began to form immediately. Calcd for $CuC_7H_4O_5Cl_2$: C, 27.29; H, 1.24 %. Found: C, 27.78; H, 1.33%.

Physical Measurements

The Magnetic susceptibility data were recorded over the temperature range from 2 to 300K at 1 T with a SQUID susceptometer (Quantum Design, San Diego, CA) interfaced with an HP Vectra computer system. All data were corrected for diamagnetism which were calculated from Pascal's table. The TIP was assumed to be 60×10^{-6} cm^3mol^{-1}. ESR spectra were recorded at X-band frequency with a JEOL RE-3X spectrometer operating at 9.1-9.5 GHz. Resonance frequency was measured on an Anritsu MF76A microwave frequency counter. Magnetic fields were calibrated by an Echo Electronics EFM-2000AX NMR field meter. X-Ray powder diffraction data were collected on a MAC Science MXP18 automated diffractometer by using Cu Kα radiation. Thermal analyses were carried out with a Rigaku Thermoflex analyzer in a nitrogen atmosphere (heating rate: 1 K / min).

RESULTS AND DISCUSSION

Thermal and Magnetic Properties of **2**

The single crystal structure of **2** shows that infinite, straight chains formed by Cu(II) ions and the *bis*-chelating CA^{2-} anions are linked by hydrogen bondings between coordinated water molecules and the oxygen atoms of CA^{2-} anions, resulting in 2-D layers.[7] There are additional interstitial water molecules in between polymer chains. The water molecules are also hydrogen-bonded to the layers, forming a 3-D network in the crystal. The geometry around the copper atom is a distorted elongated octahedron involving the four oxygen atoms of two CA^{2-} anions and two oxygen atoms from two water molecules.

The ESR spectrum of **2** at 77 K consists of axial g values (2.404, and 2.085) indicating that the magnetic orbital is formed by $d_{x^2-y^2}$. Although no hyperfine structures were observed, the line-width appeared to be extremely narrow, indicating the exchange narrowing mechanism. The magnetic susceptibilities (χ_M) over temperatures of 2-300 K exhibit weak antiferromagnetic exchange coupling (J = -2.01 cm^{-1}, g = 2.12, and ρ = 7.12 %) on the basis of the Heisenberg linear chain theory, suggesting that the magnetic orbital $d_{x^2-y^2}$ of **2** is no longer simply parallel to chloranilate plane similar to that of **1**.[7] The experimental data below 5K, however, deviates substantially from the theoretical curve, possibly attributed to the onset of long-range three-dimensional ordering through the hydrogen bonding network in the crystal.

2 was also obtained as polycrystalline phase. Powder X-ray diffraction (XRD) pattern of the powdered sample is in good agreement with the simulated pattern reproduced from the F_c values of the calculated crystal structure (Fig. 1). **2** easily

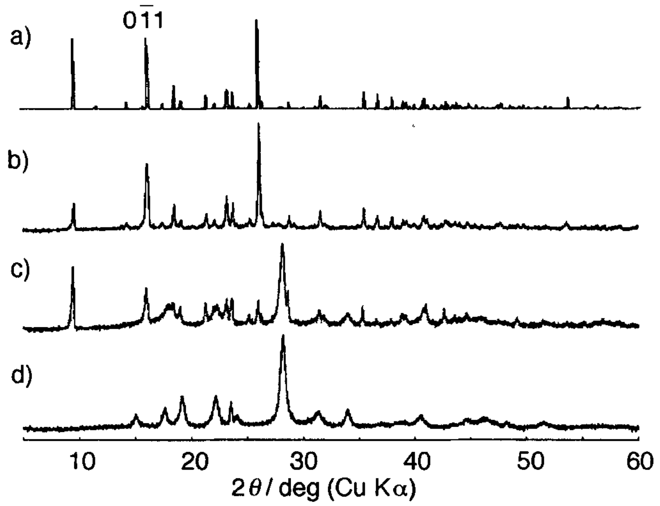

FIGURE 1 Powder X-ray diffraction patterns of (a) simulated from single crystal data of **2**, and the observed patterns of polycrystals dried (b) under atmosphere, (c) for one hour under reduced pressure at room temperature and (d) compound **5**, whose structure is proposed to be $[Cu(CA)]_n$.

liberates water molecules, and the XRD patterns have shown that the $[Cu(CA)]_n$ (**5**)[4] could be obtained by drying procedures. Drying under reduced pressure causes decrease of $0\bar{1}1$ diffraction peak intensity, suggesting that the liberation of the water molecules results in the compression of the channels. In order to examine the water-liberation process, the thermogravimetric (TG) measurements have been carried out. The curve clearly shows that a rapid change of **2** takes place up to 400K (Fig. 2). The liberation of three water molecules accounts for 17 % weight loss. The obtained species in the intermediate range 400 - 600 K is thus assigned to a binary compound, **5**, which has been demonstrated by IR spectrum and the elemental analysis. Thus the process of the liberation corresponds to an equation (1). Since **5** is known to have 1-D ribbon structure,

$$\{[Cu(CA)(H_2O)_2](H_2O)\}_n\ (\mathbf{2}) \rightarrow [Cu(CA)]_n\ (\mathbf{5}) + 3H_2O \qquad (1)$$

there are no substantial changes in the 1-D structure during the liberation of waters from **2**. The framework with channels constructed by these 1-D chains are so stable that no significant destruction of the chain structure occurs upon the release of both coordinated and interstitial water molecules. Moreover, this host-guest phenomenon is greatly associated with the long-range structural order for single crystal phase.

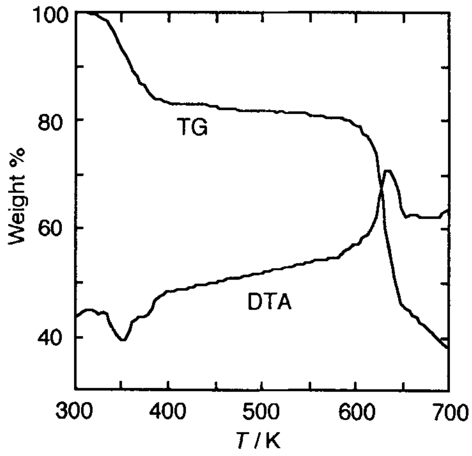

FIGURE 2 TG-DTA curves of **2**.

Magnetic Characterization of 4

Two types of CA-bridged coordination polymers (**3** and **4**) containing axially coordinated MeOH have been prepared. Their synthetic procedures have been uniquely developed: a cuprous complex, $[Cu(CH_3CN)_4]PF_6$, is used as a starting material instead of Cu(II) salts.[5] The oxidation of Cu(I) ion is an important step to form **3**. *p*-Chloranil was used as a starting material, which is readily converted to chloranilic acid in the presence of copper(I) species. Similarly, polynuclear Pr(III) complex of chloranilic acid, $[Pr(CA)_3(EtOH)_3]$, has also been obtained by slow hydrolysis of *o*-chloranil ($C_6Cl_4O_2$), a chlorinated benzoquinone that is easily reduced to the semiquinone and finally the catecholate.[8] Practically, very slow growing of crystals is a key step to get good single crystals of **3**, so we chose a copper(I) complex of thiochrome as a starting material. On the other hand, polycrystalline compound **4** is obtained by the rapid mixing of $[Cu(CH_3CN)_4]PF_6$ with *p*-chloranil in MeOH. However, the composition in methanol of **4** is different from that of **3**.

Single crystals of **3** afford the 2-D layers in which the straight 1-D $[Cu(CA)(MeOH)_2]_n$ chains are linked by two hydrogen bonds, whose structure is illustrated in Figure 3. In the region of CA ligand absorptions the IR spectrum of **4** shows a striking resemblance to that of **3**, sharp and strong carbonyl stretching bands shifting to 1490 cm^{-1} in both cases dissimilar to that of metal-free H_2CA. This exhibits the presence of bridging CA^{2-} ligands in **4**, affording 1-D structure as well as **3**. Elemental analysis data appears to show that only one methanol molecule coordinates to Cu^{2+} ion. Other polymer structure having the mixed-motifs of $\{Cu(CA)(MeOH)_2\}$ and $\{Cu(CA)\}$ is not excluded at the present stage.

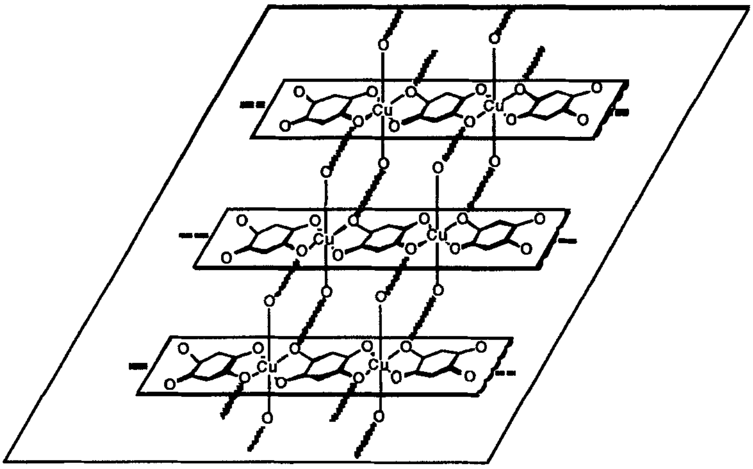

FIGURE 3 Schematic illustration of the structure of **3**.

The geometry around the copper atom of **3** is a distorted elongated octahedron. The four chloranilate oxygen and the copper atoms form a basal plane, thus the magnetic orbital lies in the plane, dissimilar to the case of **1** and **2**. On this basis the magnetic orbitals of **4** may also lie in the basal plane if the expected geometry around copper atom is not significantly different.

The polycrystalline powder ESR of **4** at 15 K appears broad line spectrum around $g = 2$ region (Fig. 4). The line shape is different from those of other CA^{2-} bridged polymers (**1** and **2**), which show the spectra having narrow line width, indicative of a exchange mechanism different from that of **4**. The magnetic susceptibilities (χ_M) were measured over temperatures of 2-300K. $\chi_M T$ curve shows sharp decreases at higher temperature (Fig. 5). Above 150 K the data are approximately described by a Curie-Weiss law with an antiferromagnetic Weiss constant of 365 K. Furthermore, $1 / \chi$ curve diverges from the linear line below 150 K, indicative of the presence of strong and

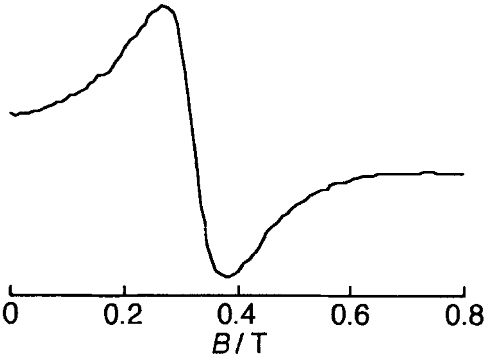

FIGURE 4 ESR spectrum of **4** at 15K (ν = 9.15056GHz).

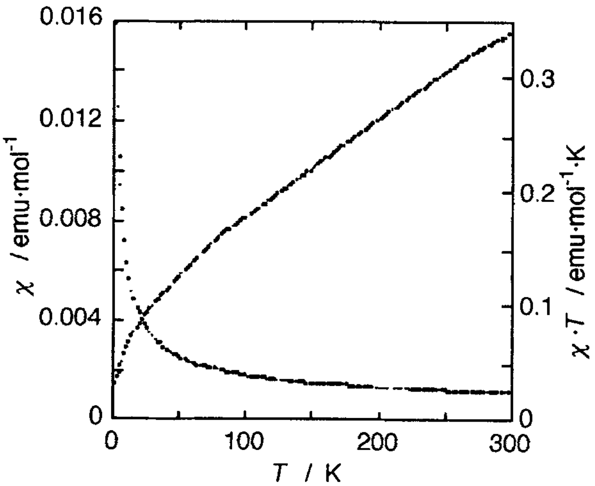

FIGURE 5 Temperature dependence of magnetic susceptibility of **4**.

anomalous antiferromagnetic exchange interactions in the crystal. This feature is also different from the magnetic behavior of **5**, which has a magnetic interaction through CA^{2-} ($J = -24.5cm^{-1}$).[5] The magnetic orbital of **5** is d_{x2-y2} parallel to the CA^{2-} plane similar to the case of **4**. These discrepancies indicates that the polycrystalline compound of **4** is a new phase in Copper/CA systems, such as a mixed valence state or a partially reduced structure, and if so the coordinated MeOH plays an important role to control physical properties of the polymers.[9]

CONCLUSION

Coordination polymers are the better candidate for the novel magnetic materials. However, the synthetic strategies of them are still sparse. We reported thermal properties $\{[Cu(CA)(H_2O)_2](H_2O)\}_n$, and the magnetic behavior of $[Cu(CA)(MeOH)]_n$, which is constructed according to the new synthetic procedure. The fabrication of higher dimensional coordination polymers from a 1-D Cu-CA chain has demonstrated to be quite useful to obtain the novel magnetic systems. Axial ligands can control the exchange interaction not only in the 1-D chain but also in crystal by the coordination interaction and hydrogen bonding. Furthermore, the valence state of the metals may be controlled by the additional axial ligands to form the novel magnetic structure.

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