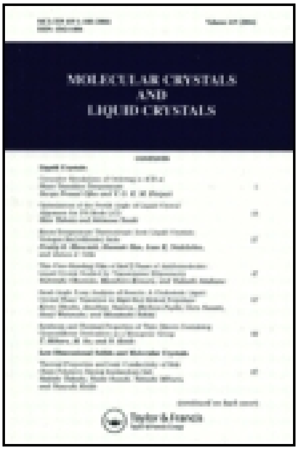

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Hydrogen Bond-Supported Two-Dimensional Layers Of Iron(I?) and Copper(II) Complexes Of Chloranilate. Their Crystal Structures And Magnetic Properties

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HYDROGEN BOND-SUPPORTED TWO-DIMENSIONAL LAYERS OF IRON(III) AND COPPER(II) COMPLEXES OF CHLORANILATE. THEIR CRYSTAL STRUCTURES AND MAGNETIC PROPERTIES

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Abstract New hydrogen bond-supported layer compounds of $\{[Fe(Cp)_2][Fe(CA)_2(H_2O)_2]\}$ (**1**) (H_2CA = chloranilic acid; Cp = cyclopentadienyl anion) and $[Cu_2(CA)_2(H_2O)_2(bpm)]$ (**2**) (bpm = 2,2'-bipyrimidine) have been synthesized and characterized. The crystal structure of **1** consists of layers of $[Fe(CA)_2(H_2O)_2]^-$ anion and columns of $[Fe(Cp)_2]^+$ cations which are intercalated in between the two layers. The iron atom in $[Fe(CA)_2(H_2O)_2]^-$ displays a six-coordinate geometry with two chelating CA^{2-} and water molecules, linked to each other by hydrogen bonds (the distance of 2.67 Å) between the water molecules and the oxygen atoms of CA^{2-} on the adjacent molecules. The ^{57}Fe-Mössbauer spectrum shows the Fe(III) state with $S = 5/2$ and 1/2 for $[Fe(CA)_2(H_2O)_2]^-$ and $[Fe(Cp)_2]^+$, respectively. The compound **2** has a hydrogen bond-supported layer structure as well as **1**, however, dissimilar to **1** because of no intercalated molecules. **1** shows intermolecular antiferromagnetic interactions between $[Fe(CA)_2(H_2O)_2]^-$ molecules and/or $[Fe(Cp)_2]^+$ molecules while in the case of **2** the intramolecular antiferromagnetic interaction occurs predominantly in the dimeric molecule.

INTRODUCTION

Advent of molecule-based magnets and conductors prompted us to search for novel 2- and 3-dimensional (2- and 3-D) compounds based on transition metal complexes, which have interesting cooperative effects.[1,2] Especially, 2-D copper and iron complexes provide fascinating system to realize a new magnetic and conductive phase. In order to obtain these compounds the rational synthesis should be developed. In this respect, metal complex-based layer compounds intercalating organometallic molecules, such as ferrocene derivatives which are known to be an element of molecule-based magnets,[3] are one of the candidates to provide novel solid state properties. Polyoxocarbons are well-known to be double bidentate ligands, and to provide transition metal or alkaline earth polymers. Chloranilic acid (H_2CA) is one of the family, affording one dimensional chains of various metal ions.[4-8] Very recently we have succeeded in the synthesis and the characterization of 2-D coordination polymers having hydrogen bonding link, $\{[Cu(CA)(H_2O)_2](H_2O)\}_n$ and $[Cu(CA)(MeOH)_2]_n$.[6-8] Throughout these studies we have developed architecture of higher dimensional metal complex layer structures by using hydrogen bond. In this report, the syntheses, structures and magnetic properties of iron(III) and copper(II) complexes with 2-D network linked by hydrogen bonds are described. Especially, the iron layered compound presented here intercalates ferricenium cations, which is a novel type of intercalation compounds.

EXPERIMENTAL

Synthesis.

$\{[Fe(Cp)_2][Fe(CA)_2(H_2O)_2]\}_n$ (**1**): An aqueous solution (10 mL) of ferricenium hexafluorophosphate (6×10^{-5} mol) was transferred to a glass tube, then an ethanol-H_2O (1:1) solution (10 mL) of H_2CA (6×10^{-5} mol) was poured into the tube without mixing the two solutions. Black plate crystals began to form at ambient temperature in three days.

$[Cu_2(bpm)(CA)_2(H_2O)_2]$ (**2**): An ethanol-H_2O (1:1) solution (5 ml) of copper perchlorate (5×10^{-5} mol) was transferred to a glass tube, then an aqueous solution(5 ml) of bpm (5×10^{-5} mol) and chloranilic acid (5×10^{-5} mol) was poured into the tube without mixing the two solutions. Dark gray plate crystals began to form in a week.

Physical Measurements.

Magnetic susceptibility data were recorded over the temperature range from 2 to 300 K at 1 T with a SQUID susceptometer (Quantum Design, San Diego, CA). All data were corrected for diamagnetism which were calculated from Pascal's table. The TIP was assumed to be 60×10^{-6} cm^3 mol^{-1} for copper(II) ion. The ^{57}Fe Mössbauer spectra were obtained by using an Wissel Mössbauer spectrometer with a proportional counter. A ^{57}Co(Rh) source moving in a constant-acceleration mode was used for the measurements. The velocity scale was calibrated by using a metallic iron-foil spectrum. The isomer shifts (I.S.) and the quadrupole splitting (Q.S.) were obtained by least-squares fitting of the Mössbauer data to Lorentzian line shapes.

Crystallographic Data Collection and Refinement of the Structure.

For each compound, a suitable crystal was chosen and mounted on glass fibers with epoxy resin. Data collections were carried out on a Rigaku AFC7R. The structures were solved by direct methods (Rigaku TEXSAN crystallographic software package of Molecular Structure Corporation). Full-matrix least-squares refinements were carried out with anisotropic thermal parameters for all non-hydrogen atoms. The final cycle of full-matrix least-squares refinement was based on No and n variable parameters and converged with unweighted agreement factors of $R = \Sigma||Fo|-|Fc||/\Sigma|Fo|$, $Rw = [\Sigma(|Fo|-|Fc|)^2 / \Sigma w |Fo|^2]^{1/2}$ where $w = 4Fo^2 / \sigma^2(Fo^2)$. Crystal Data of **1**. $Fe_2Cl_4O_{10}C_{22}H_{14}$, M = 681.77, monoclinic, space group C 2/m (#14), a = 7.088(3)Å, b = 16.955(5)Å, c = 9.853(3)Å, β = 96.43(3)°, V = 1176.6(6) $Å^3$, Z = 2, Dc = 1.924 g / cm^3, λ (Mo Kα) = 0.71069 Å, F (000) = 672.00, μ (MoKα) = 17.44 cm^{-1}, T = 23°C. Specimen size: 0.20 x 0.20 x 0.30 mm. 2θmax = 55.1°; N, No ($I > 3\sigma(I)$) = 1407, 829; n = 94; R ,Rw = 0.051, 0.055. Crystal Data of **2**. $Cu_2Cl_4O_{10}N_4C_{20}H_{10}$, M = 735.22, monoclinic, space group P 2_1/n (#14), a = 9.677(2)Å, b = 8.214(2)Å, c = 15.157(2)Å, b = 101.26(1)°, V = 1181.5(4) $Å^3$, Z = 2, Dc = 2.066 g / cm^3, λ (Mo Kα) = 0.71069 Å, F (000) = 728.00, μ (Mo,Kα) = 23.20 cm^{-1}, T = 23°C. Specimen size: 0.20 x 0.20 x 0.10 mm. 2θmax = 55.1; N, No ($I > 3\sigma(I)$) = 2938, 1144; n = 182; R, Rw = 0.054, 0.046.

RESULTS AND DISCUSSION

Synthesis and Crystal Structure of 1.

Compound **1** was readily isolated as the major product from the reaction of $[Fe(Cp)_2]PF_6$ and H_2CA in ethanol-water mixture. It has been well established that ferricenium cation is unstable in the presence of acid. The ferricenium cation decomposes in the acidic condition to afford Fe(III) aquo ion, which react with chloranilic acid. The structure of complex **1** consists of $[Fe(CA)_2(H_2O)_2]^-$ and $[Fe(Cp)_2]^+$ mononuclear units. ORTEP drawings of the structures around the two molecules in **1** with the atom numbering scheme is shown in FIGURE 1, where the iron atoms sit on the crystallographic inversion centers. The geometry around Fe(1) of $[Fe(CA)_2(H_2O)_2]^-$ is a distorted elongated octahedron involving the four oxygen atoms of two CA^{2-} anions and two oxygen atoms from two water molecules. There are two Fe-O distances; 1.983(6) Å (Fe-O(CA^{2-} oxygen)) and 2.065(9) Å (Fe-O(water)). Therefore the environment of the Fe(2) atom consists of the four short in-plane bonds and the two long axial bonds, giving rise to a "4 + 2" type of configuration, and the iron atom sits on the equatorial plane. The symmetrical coordination of the CA^{2-} dianion is also recognized from the same C-O distances, 1.26(1) Å and 1.22(1) Å for coordinated and for uncoordinated moieties, respectively, which are similar to those reported for a metal-free chloranilate dianion (1.243(7) and 1.253(7) Å).[9,10] These structural features support an enediol form for the symmetrical bidentate chloranilate. The coordination geometry around Fe(1) shows near D_{5d} symmetry, consisting of two cyclopentadienyl anions. These ferricenium ions are stacked with the Cp planes parallel to each other along a -axis, the distance of the nearest-neighbor Fe(1)•••Fe(1') being 7.09 Å. The shortest inter-cyclopentadienyl ring distance is 3.9Å along c -axis. Crystal packing structure consists of a stacking column of ferricenium cations and hydrogen bond supported sheets, $\{[Fe(CA)_2(H_2O)_2]^-\}_n$, which spread out along ab-plane (FIGURE 2). The hydrogen bond

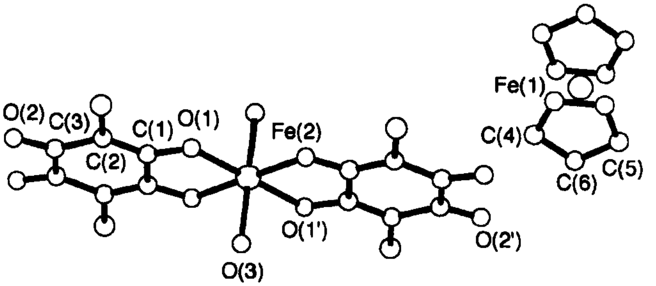

FIGURE 1 ORTEP view of the cationic and anionic units of 1. Important bond distances(Å) and angles(°); Fe(1)-C(4), 1.98(3); Fe(1)-C(5), 2.04(2); Fe(1)-C(6), 2.02(2); Fe(2)-O(1), 1.983(6); Fe(2)-O(3), 2.065(9); O(1)-Fe(2)-O(1'), 99.7(3); O(1)-Fe(2)-O(1'), 180.00; O(1)-Fe(2)-O(1'), 80.3(3); O(1)-Fe(2)-O(3), 91.7(3); O(1)-Fe(2)-O(3'), 88.3(3)

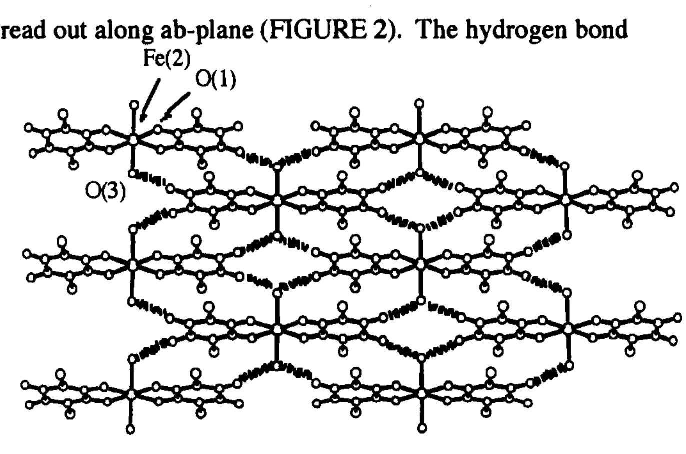

FIGURE 2 Crystal structure of 1; view onto the ab-plane. The dashed lines denote the hydrogen bonds.

(O(2)-O(3'); 2.67 Å) occurs between the coordinated water and the oxygen atom of CA^{2-} anion on the adjacent molecule, and links the molecule to form a sheet. The similar connectivity of the hydrogen bonding network has been found in compound **2** (vide infra). Interestingly, $\{[Fe(CA)_2(H_2O)_2]^-\}_n$ sheets sandwich ferricenium cations to result in a novel stoichiometric intercalation compound.

Crystal Structure of **2**.

The molecular structure of compound **2** shows a bpm-bridged dicopper unit, which has the crystallographic inversion center at the midpoint of the C(10)-C(10') vector of the bpm (FIGURE 3). Each copper atom has a five-coordinate CuN_2O_3 chromopher with a slightly distorted square pyramidal coordination geometry with the two bpm nitrogen atoms, two chloranilate oxygen atoms in the basal plane, and a water molecule in the apical position. The copper atom is displaced by 0. 245 Å from the least-squares plane defined by the N(1), O(1), O(2), and N(2) atoms. The dihedral angle between the mean equatorial plane of copper and the mean plane of the bridging bpm ligand is 7.2° The intramolecular metal-metal separation is 5.35 Å, the shortest observed for bpm-bridged dinuclear copper(II) complexes.[11,12] The chloranilate group act as a symmetrically bidentate ligand, indicating an enediol form similar to that in **1**. Interestingly, the coordinated water molecule is hydrogen-bonded to uncoordinated chloranilate oxygen atoms on the two nearest neighbor molecules (2.75 Å and 2.78 Å), forming a two dimensional sheet which spreads out along ab-plane (FIGURE 4). This hydrogen bond network is similar to that of **1**, but dissimilar because **2** has no intercalated molecules. The inter layer distance is 7.6Å.

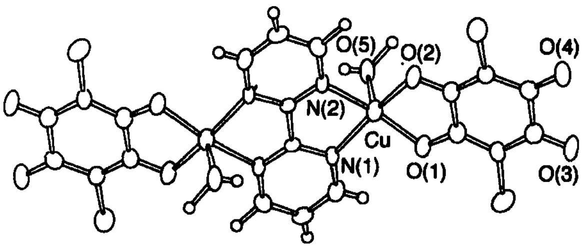

FIGURE 3 ORTEP view of the dimeric unit of **2**. Important bond distances(Å) and angles(°); Cu(1)-O(1), 1.907(8); Cu(1)-O(2),1.907(6); Cu(1)-O(5), 2.274(8); Cu(1)-N(1), 1.997(6); Cu(1)-N(2), 2.025(8); O(1)-Cu(1)-N(1), 94.1(3); O(1)-Cu(1)-N(2), 165.7(3); O(1)-Cu(1)-O(5), 104.6(3); O(2)-Cu(1)-N(1), 165.5(3); O(2)-Cu(1)-N(2), 94.6(3); O(2)-Cu(1)-O(5), 103.0(3); N(1)-Cu(1)-O(5), 91.4(3); N(1)-Cu(1)-O(5), 91.4(3)

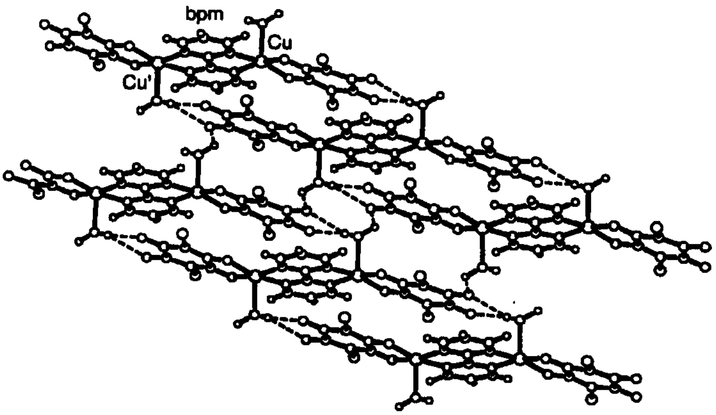

FIGURE 4 Crystal structure of **2**; view onto the ab plane. The dashed lines denote the hydrogen bonds.

Magnetic Properties.

The ^{57}Fe-Mössbauer spectrum of the polycrystalline sample of **1** consists of one singlet

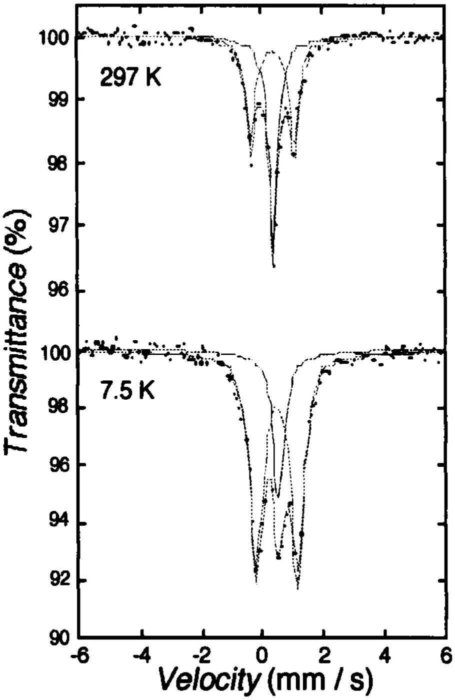

FIGURE 5 Mössbauer spectrum of compound **1**. The dots show the experimental data and the lines denote fitted curve.

and one doublet absorption, with parameters, I.S. = 0.43 mm /s for the singlet and I.S. = 0.40 mm /s and Q.S. = 1.38 mm /s for the doublet (FIGURE 5). These values and the coordination environments of the irons indicate that the Fe(III) state with S = 5/2 and 1/2 for $[Fe(CA)_2(H_2O)_2]^-$ and $[Fe(Cp)_2]^+$, respectively. The magnetic susceptibilities (χ) were measured over temperatures of 2 - 300 K. The χ T value of **1** at 300K is nearly equal to the calculated spin-only value of 2.376 (mean value of S = 1/2 and S = 5/2; g = 2). However, χT decreases slightly with decreasing temperature and shows rapid decrease at lower temperature to 0.8 (2K). 1 / χ shows that **1** does not followed a simple Curie-Weiss law (FIGURE 6). Furthermore, **1** is EPR inactive in the temperature range of 7 to 300 K, indicating the presence of intermolecular iron-iron magnetic

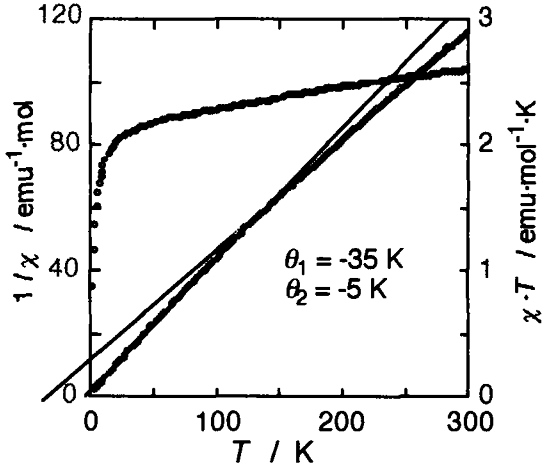

FIGURE 6 Plots of observed $1/\chi$ and χT vs. T. The open circles denote observed data and the two lines show the Curie-Weiss analysis at low and high temperature regions.

interaction. On the other hand, the temperature dependence of the magnetic susceptibility of **2** is interpreted by a simple Bleany-Bowers equation[2] for a dinuclear copper(II) complex ($J = -97\ cm^{-1}$), where J is the singlet-triplet energy gap defined by the Hamiltonian $H = -J\ S1 \cdot S2$ with $S1 = S2 = 1/2$, thus there is no significant inter-molecular interaction in the solid. The trend in **1** implies that there exists an anomalous antiferromagnetic interaction; the pathways for this interaction could be those between $\{[Fe(CA)_2(H_2O)_2]^-\}_n$ through hydrogen bonds in the layer, and/or stacked-column of $[Fe(Cp)_2]^+$.

In this study, we have synthesized crystalline two dimensional hydrogen bond-supported layers composed of the mononuclear iron(III) units and dinuclear copper(II) units as building blocks. Hydrogen-bond formations between transition metal complexes are proved to be useful for assemblages with extended arrays with tuning metal-metal separation. On the basis, it would be possible to create new materials if the hydrogen bonded sheets are able to intercalate organic or organometallic molecules which have conducting and/or photosensitized properties.

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REFERENCES

1)Gatteschi, D.; Kahn, O.; Miller, J. S.; Palacio, F. Magnetic Molecular Materials; Dordrecht: 1991.

2)Kahn, O. Molecular Magnetism, VCH: 1992.

3)Miller, J. S.; Epstein, A. J. Angew. Chem. Int. Ed. Engl. 33, 385, (1994)

4)Verdaguer, M.; Michalowicz, A.; Alberding, N.; Girerd, J. J.; Kahn, O. Inorg. Chem. , 19, 3271,(1980)

5)Wrobleski, J. T.; Brown, D. B. Inorg. Chem. 18, 2738. (1979)

6)Kawata, S.; Kitagawa, S.; Kondo, M.; Furuchi, I.; Munakata, M. Angew. Chem. Int. Ed. Engl. 1994, 33, (1759)

7)Kawata, S.; Kitagawa, S.; Kondo, M.; Katada, M. Synth. Metals , 71, 1917, (1995)

8)Kawata, S.; Kitagawa, S.; Furuchi, I.; Kudo, C.; Kamesaki, H.; Kondo, M.; Katada, M.; Munakata, M. Mol.Cryst.Liq.Cryst. , 274, 179. (1995)

9)Andersen, E. K. Acta Cryst. , 22, 191, (1967)

10)Calvo, M. A.; Lanfredi, A. M. M.; Oro, L. A.; Pinillos, M. T.; Tejel, C.; Tiripicchio, A.; Ugozzoli, F. Inorg. Chem. , 32, 1147,(1993)

11)Castro, I.; Sletten, S.; Glærum, L. K.; Lloret, F.; Faus, J.; Julve, M. J. Chem. Soc. Dalton Trans.,, 2777, (1994) references therein.

12)De Muno, G.; Julve, M.; Lloret, F.; Cano, J.; Caneschi, A. Inorg. Chem. , 34 , 2048, (1995)