Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Iron-Chloranilate Intercalation Compounds: Synthesis, Crystal Structures, and Thermal Properties

M. K. Kabir [a], S. Kawata [a], K. Adachi [a], H. Tobita [b], N. Miyazaki [a], H. Kumagai [b], M. Katada [b] & S. Kitagawa [c]

[a] Department of Chemistry, Shizuoka University, 836 Oya, Shizuoka, 422-8529, Japan

[b] Department of Chemistry, Tokyo Metropolitan University, Minami Ohsawa, Hachiouji, Tokyo, 192-0397, Japan

[c] Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto, 606-8501, Japan

Version of record first published: 27 Oct 2006

Mol. Cryst. and Liq. Cryst., 2000, Vol. 341, pp. 491-496
Reprints available directly from the publisher
Photocopying permitted by license only

Iron-Chloranilate Intercalation Compounds: Synthesis, Crystal Structures, and Thermal Properties

M. K. KABIR[a*], S. KAWATA[a], K. ADACHI[a], H. TOBITA[b], N. MIYAZAKI[a], H. KUMAGAI[b], M. KATADA[b] and S. KITAGAWA[c]

[a]*Department of Chemistry, Shizuoka University, 836 Oya, Shizuoka 422–8529, Japan,* [b]*Department of Chemistry, Tokyo Metropolitan University, Minami Ohsawa, Hachiouji, Tokyo, 192–0397, Japan and* [c]*Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606–8501, Japan*

Hydrogen bond supported new iron-chloranilate assemblies, $\{(Hpy)[Fe(CA)_2(H_2O)_2](H_2O)\}_n$ (py = pyridine, H_2CA = chloranilic acid, $C_6H_2O_4Cl_2$) (**1**), and $[(phz)_2[Fe(CA)_2(H_2O)_2](H_2O)_2]_n$ (phz = phenazine, $C_{12}H_8N_2$) (**2**) have been synthesized and characterized. Compound **2** crystallizes in the monoclinic, space group *C2/m* (#12), with *a*= 29.135(6) Å, *b*= 16.886(6) Å, *c* = 15.017(5) Å, β = 165.907(1)°, *V* = 1798(2) Å^3, *Z* = 2. In both the compounds two chloranilate dianions and two water molecules are coordinated to the iron ion making anionic monomers $[Fe(CA)_2(H_2O)_2]^-$, which are the building blocks of the compounds. The coordination environment around the iron ion in the building block is a distorted octahedron, where two water molecules sit on the *trans* position to each other. $[Fe(CA)_2(H_2O)_2]^-$ anions form common layer structures, supported by hydrogen bonds. Hpy^+ are intercalated in between the layers of **1** by electrostatic and hydrogen bonding interactions and phz are intercalated in that of **2** by electrostatic interactions. DSC traces of **1** show anomaly at 174 K, indicating phase transition in the compound.

Keywords: intercalation compounds; chloranilate; stacking interaction

INTRODUCTION

Construction of transition metal complex based assemblies is currently of great interest due to their potential properties, such as magnetism, electrical conductivity, host-guest chemistry and catalysis[1,2]. Especially, 2-D metal

* Corresponding author

complexes provide fascinating system having molecule-based magnetic and electrical properties[3]. Our recent studies devoted to the synthesis and characterization of new metal chloranilate assemblies. Chloranilic acid (H_2CA = $C_6H_2O_4Cl_2$) is one of the oxocarbon families which provide 1-D chains and 2-D layers of various metal ions[3]. As a part of our research on metal chloranilate intercalation chemistry, we have synthesized and reported a series of common intercalation compounds $\{[M(CA)(H_2O)_2](G)\}_n$ (M = Fe^{2+}, Cu^{2+}, Co^{2+}, Mn^{2+}; G = H_2O, phz, etc.)[2,4,8]. The structures consist of 1-D chains $[M(CA)(H_2O)_2]_k$, which are the building blocks of the compounds and guest molecules. The chains make 2-D layers by hydrogen bonds where neutral guest molecules are introduced in between them. We have also synthesized iron chloranilate assemblies $\{(G)_m[Fe(CA)_2(H_2O)_2]\}_n$ (G = Hpy^+(**1**), H_2bpy^{2+} and $[Fe(Cp)_2]^+$)[3,5], where anionic monomers $[Fe(CA)_2(H_2O)_2]^-$ are the building blocks of the compounds which make 2-D layers by hydrogen bonds. The intercalation mode of the guest molecules and the role of the building blocks in the formation of metal complex assemblies are the object of this study. Crystal structure of new iron chloranilate compound $\{(phz)_2[Fe(CA)_2(H_2O)_2](H_2O)_2\}_n$ (**2**) and the thermal properties of **1** are described here.

EXPERIMENTAL

Synthesis of $\{(phz)_2[Fe(CA)_2(H_2O)_2](H_2O)_2\}_n$ (**2**)

An aqueous solution (1 mL) of chloranilic acid (5 x 10^{-3} M) was transferred to a glass tube, then an ethanol-water (1:1) solution (1 mL) of phenazine (5 x 10^{-3} M) and an ethanolic solution (1 mL) of iron chloride hexahydrate (5 x 10^{-3} M) was poured into the tube without mixing the three solutions. Black crystals began to form at ambient temperature in 6 months.

Crystallographic Data Collection and Refinement of the Structure **2**.

A suitable crystal was chosen and mounted on glass fiber with epoxy resin. Data collection of compound **2** was carried out on Mac Science MXC3 automatic diffractometer. The structure was 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 $R = \Sigma||F_o| - |Fc|| / \Sigma|F_o|$, $Rw = [\Sigma(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$ where $w = 1/\sigma^2(F_o) = [\sigma_c^2(F_o) + p^2/4\ F_o^2]^{-1}$. Crystal Data of **2**. $FeC_{16}O_{12}Cl_4N_4H_{24}$, fw = 902.26, monoclinic, space group *C2/m* (#12), with a = 29.135(6) Å, b = 16.886(6) Å, c = 15.017(5) Å, β = 165.907(1)° , V = 1798(2) Å^3, Z = 2, T = 23℃, μ(Mo Kα) = 7.88 cm^{-1}, λ(Mo Kα) = 0.71069 Å, n = 137; N, No ($I > 3\sigma(I)$) = 2134, 1414; R, Rw = 0.041, 0.055.

Physical Measurements

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 shift (I.S.) and the quadruple splitting (Q.S.) were obtained by least-squares fitting of the Mössbauer data to Lorentzian line shapes. Differential scanning calorimetry (DSC) was carried out with a Seiko Instruments SSC5200 thermo-analyzer in nitrogen atmosphere (heating rate: 2-5 K/min).

RESULTS AND DISCUSSION

Crystal Structure of **2**

Crystal structure of **2** is shown in Figure 1. Four oxygen atoms of two CA^{2-} anions and two oxygen atoms from two water molecules are coordinated to the iron ion making the $[Fe(CA)_2(H_2O)_2]^-$ monomer, which is the building block of **2**. The geometry around the iron ion is a distorted octahedron, where the two water molecules sit on the *trans* position to each other. There are two types of Fe-O bonds; Fe-O(1): 1.996(2) Å and Fe-O(3): 2.035(3) Å. This coordination geometry is similar to those of $\{[Fe(Cp)_2][Fe(CA)_2(H_2O)_2]\}_n$ and **1**[3,5]. In **2**, the $[Fe(CA)_2(H_2O)_2]^-$ anions make 2-D layer by hydrogen bond, which occur between the coordinated water molecules and the terminal oxygens of CA^{2-} (O(2)-O(3); 2.655(9) Å). The layer spreads along the [2,0,-1] plane. Moreover, the CA^{2-} planes are stacked over each other with the nearest neighbor C-C distance of 3.656(4) Å. The phz molecules are also stacked over each other with a nearest neighbor N-C distance of 3.470(11) Å to make columns, which

are introduced in between the layers by electrostatic interaction. The geometry of the intercalated phenazine molecules are similar to that of the pure or complex-forming phenazines[6,7]. To satisfy the neutral condition, two phz molecules need 1+ charge, which maybe gained by radical formation during intercalation. The interstitial water molecules sit in between the phenazine columns by making hydrogen bonds with the uncoordinated nitrogen atoms of phz (N-O(4), 2.85(1) Å). The exact positions of the water molecules are not ascertained due to their disorder. The structural feature of **2** is different from that of $\{[Fe^{II}(CA)(H_2O)_2](G)\}_n$[4], which are constructed from 1-D chains and guest molecules. Chains make layers by hydrogen bonds where guest molecules are introduced by hydrogen bonding interaction. The oxidation states of the metal

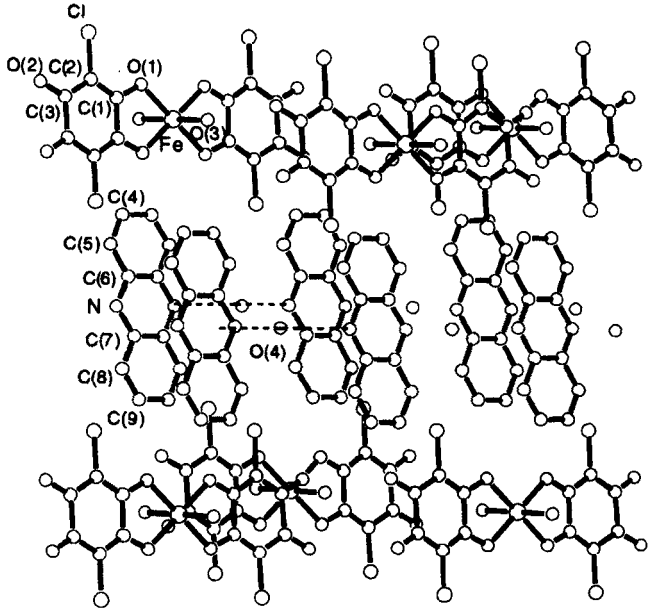

Figure 1. Crystal structure of $\{(phz)_2[Fe(CA)_2(H_2O)_2](H_2O)_2\}_n$. Selected Bond Distances (Å) and Angles (°) are as follows: Fe-O(1), 1.996(2); Fe-O(3), 2.035(3); C(1)-O(1), 1.281(3); C(3)-O(2), 1.227(4); N-C(6), 1.349(4); N-C(7), 1.350(5); C(5)-C(6), 1.418(5); C(7)-C(8), 1.420(5); N-O(4), 2.85(1); O(1)-Fe-O(1'), 80.6(1); O(1)-Fe-O(3), 88.20(10); C(6)-N(1)-C(7), 118.4(3). Dotted lines indicate hydrogen bonding.

ions is one of the important factors that make a difference in the building block approaches of $\{[Fe^{II}(CA)(H_2O)_2](G)\}_n$ and **2**. The ^{57}Fe Mössbauer spectra of **1** consists of one quadrupole doublet with $I.S.$ = 0.41 mm/s and $Q.S.$ = 0.83 mm/s, indicating that the oxidation state of iron is three. The coordination environment around the iron ion and the formation of the common layers similar to **1** and $\{[Fe(Cp)_2][Fe(CA)_2(H_2O)_2]\}_n$, indicates that the iron ion in **2** has the oxidation state of three, also. Therefore, an important conclusion can be drawn from these features that the oxidation state of the metal ions determines the nature of the building blocks in the intercalation compounds, and the building blocks determine whether the guest molecules will be included as neutral, radical or charged.

Thermal Properties

DSC traces of **1** show one thermal anomaly at 174 K upon heating. In the compound **1** the Hpy^+ cations with interstitial water molecules are anchored alternatively to the layers by making hydrogen bonds with the coordinated oxygens of chloranilate anions[5]. The intercalated Hpy^+ cations can move in the channel created by chlorine atoms of the coordinated CA^{2-} anions. Thus the anomaly in DSC traces are attributed to the structural phase transition caused by the reorientation of the Hpy^+ cations. On the other hand, in the case of $\{(H_2bpy)[Fe(CA)_2(H_2O)_2]_2(H_2O)_2\}_n$ (bpy = 4,4′-bipyridine)[5], no DSC peak is observed. H_2bpy^{2+} cations are intercalated and held tightly by both of its protonated nitrogens supported by electrostatic, hydrogen bonding and stacking interactions. At lower temperatures, H_2bpy^{2+} molecules have no ability to be rearranged or displaced from their positions. These results suggest that the flexibility of the layers and the crystal dynamics of the intercalation compounds depend on the hydrogen bonding ability of the guest molecules.

Intercalation Modes of the Guest Molecules

We have synthesized iron-chloranilate intercalation compounds with different guest molecules. Hpy^+, phz and $[Fe(Cp)_2]^+$ are the intercalated guest molecules of the compounds **1**, **2** and $\{[Fe(Cp)_2][Fe(CA)_2(H_2O)_2]\}_n$, respectively. In the common anionic layers of the above three compounds, cationic guest molecules are introduced by electrostatic interaction, which is the common binding force for these intercalation systems. Hpy^+ cations with interstitial water molecules are

included by electrostatic interaction in the channels created by chlorine atoms of the coordinated CA^{2-} anions. Hpy^{+} has one nitrogen atoms by which it is anchored alternatively to the nearest layers by hydrogen bonding interaction. $[Fe(Cp)_2]^{+}$ cations are intercalated as sandwiched structures in the hydrogen bonded sheets only by stacking and electrostatic interaction as they have no site for hydrogen bonding. In **2**, phz molecules are included as stacking column by electrostatic interaction with the layers. The phz makes hydrogen bonding with interstitial water molecules, not with layers. In $\{[M(CA)(H_2O)_2](G)\}_n$, there is no electrostatic interaction in the introduction of the neutral guest molecules. These features conclude that the intercalation mode of the guest molecules is guided by their binding nature. Another important aspect of the compounds is the flexibility of the layer structures. The interlayer distances of the compounds **1**, $\{[Fe(Cp)_2][Fe(CA)_2(H_2O)_2]\}_n$ and **2** are 8.91 Å, 9.85 Å and 14.57 Å respectively. These variations of the distances correlate well with the size of the guest molecules, suggesting that $[Fe(CA)_2(H_2O)_2]$ is a good motif which is able to make flexible layers for the intercalation of various types of guest molecules.

Acknowledgements

This research was supported by a Grant-in-Aid for Scientific Research (No. 10640541) and by a Grant-in-Aid for Scientific Research on Priority Areas (No. 10149101, Metal-assembled Complexes) from Ministry of Education, Science, Sports and Culture, Japan.

References

[1] L. Ouahab, *Chem. Mater.*, **9,** 1909 (1997).
[2] S. Kawata, S. Kitagawa, H. Kumagai, C. Kudo, H. Kamesaki, T. Ishiyama, R. Suzuki, M. Kondo, and M. Katada. *Inorg. Chem.*, **35,** 4449 (1996).
[3] S. Kawata, H. Kumagai, S. Kitagawa, K. Honda, M. Enomoto, and M. Katada, *Mol. Cryst. Liq. Cryst.*, **286,** 51–58 (1996).
[4] S. Kawata, S. Kitagawa, H. Kumagai, T. Ishiyama, K. Honda, H. Tobita, K. Adachi, and M. Katada, *Chem. Mater.*, **10,** 3902–3912 (1998).
[5] M. K. Kabir, N. Miyazaki, S. Kawata, K. Adachi, H. Kumagai, K. Inoue, S. Kitagawa and K. Iijima, *Coordination Chemistry Reviews*, (1999) in press.
[6] K. Wo'zniak, B. Kariuki and W. Jones, *Acta Cryst.*, **C47**, 1113 (1991).
[7] N. Karl, W. Ketterer and J. J. Stezowski, *Acta Cryst.*, **B38,** 2917 (1982).
[8] S. Kawata, S. Kitagawa, M. Kondo, I Furuchi, and M. Munakata, *Angew. Chem. Int. Ed. Engl.*, **33,** 1759 (1994).