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· Communication

Ionic Liquid of Choline Chloride/Malonic Acid as a Solvent in the Synthesis of Open-Framework Iron Oxalatophosphates

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Two new iron(III) oxalatophosphates, $Cs_2Fe(C_2O_4)_{0.5}(HPO_4)_2$ (**1**) and $CsFe(C_2O_4)_{0.5}(H_2PO_4)(HPO_4)$ (**2**), have been synthesized by using a low melting point eutectic mixture of choline chloride and malonic acid as a solvent and characterized by single-crystal X-ray diffraction and magnetic susceptibility. Crystal data are as follows: compound **1**, monoclinic, $P2_1/c$ (No. 14), $a = 8.5085(4)$ Å, $b = 12.7251(6)$ Å, $c = 9.8961(4)$ Å, $\beta = 107.117(1)°$, $V = 1024.01(8)$ Å^3, $Z = 4$, and $R_1 = 0.0264$; compound **2**, monoclinic, $P2_1/n$ (No. 14), $a = 8.0038(3)$ Å, $b = 10.2923(3)$ Å, $c = 11.4755(4)$ Å, $\beta = 100.507(1)°$, $V = 929.47(5)$ Å^3, $Z = 4$, and $R_1 = 0.0311$. The structure of **1** comprises FeO_6 octahedra connected by $HPO_4{}^{2-}$ tetrahedra and bisbidentate oxalate anions to form a 3D framework containing intersecting 12-ring channels, with the charge-compensating Cs^+ cations being located at the intersections of these channels. The structure of **2** consists of 2D layers of octahedral FeO_6, tetrahedral $H_2PO_4{}^-$ and $HPO_4{}^{2-}$ moieties, and bisbidentate oxalate ligands with the Cs^+ cations between the layers. They are the first examples for the use of ionic liquid as a solvent in the synthesis of metal oxalatophosphates.

The synthesis of open-framework metal phosphates has been extensively studied, owing to their potential applications in ion exchange and catalysis.[1] Recently, many research activities have focused on the synthesis of organic−inorganic hybrid compounds by incorporating organic ligands in the structures of metal phosphates. Compared with inorganic phosphates, the organic ligands have larger sizes and a wide variety of means of connection. This idea is currently used by a number of groups and leads to a large number of oxalatophosphates of transition metals and group 13 elements.[2] Most of them were synthesized in aqueous solutions under mild hydrothermal conditions with an organic template that guides the synthesis pathway toward particular structures.

Interestingly, $Mn_2(H_2PO_4)_2(C_2O_4)$ was prepared under hydrothermal conditions using "reagent" quantities only of water.[3]

Recent studies have shown that low melting point eutectic mixtures of quaternary ammonium salts with amides or carboxylic acids have unusual solvent properties.[4,5] There were reports on the preparation of open-framework aluminophosphates and metal phosphonate by using ionic liquids or eutectic mixtures. For example, 1-methyl-3-ethylimidazolium bromide (melting point 83 °C) and a choline chloride/urea eutectic mixture (melting point 12 °C) have been used in the preparation of aluminophosphate zeolite analogues.[6] Choline chloride/urea was used for the synthesis of a new coordination polymer, $Zn(O_3PCH_2CO_2)\cdot NH_4$.[7] The ionic liquids not only act as solvents but also provide the template cations around which the inorganic frameworks order. Because of the vanishingly low vapor pressure of ionic liquids, synthesis takes place at ambient pressure. The use of ionic liquids as solvents in the reaction was termed ionothermal synthesis to distinguish it from hydrothermal synthesis.[6] We have been interested in applying new synthetic methods to the exploratory synthetic and structural studies of new materials with open-framework structures. Here we present the first use of ionic liquid of choline chloride/malonic acid in the synthesis of two organic−inorganic hybrid compounds, $Cs_2Fe(C_2O_4)_{0.5}(HPO_4)_2$ (**1**) and $CsFe(C_2O_4)_{0.5}(H_2PO_4)(HPO_4)$ (**2**).

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Ionic liquids were prepared by heating a mixture of choline chloride (Acros 99%) and malonic acid (Sigma 99%) in a 1:1 mole ratio at 80 °C and stirring until a homogeneous colorless liquid was formed. Ionothermal reaction of $FeCl_3 \cdot 6H_2O$, H_3PO_4, $H_2C_2O_4 \cdot 2H_2O$, CsOH, and 1,4-bis(3-aminopropyl)piperazine (APPIP) in the molar ratio of 0.8:2:1:2:1 in 3 g of the ionic liquid in a 23-mL Teflon-lined autoclave at 130 °C for 1 day produced pale-green taperlike crystals of **1** in 78% yield based on iron. The reaction mixture contained some water because $H_3PO_4(aq)$ (85%) and CsOH-(aq) (50%) are aqueous solutions. A crystal was selected for structure determination by single-crystal X-ray diffraction.[8] The bulk product was monophasic as judged by the total consistency of its X-ray powder pattern with that simulated from the atomic coordinates derived from single-crystal X-ray study. We subsequently found that APPIP was not incorporated into the resulting iron oxalatophosphate framework and that a pure product could not be obtained in the absence of the organic amine additive. Elemental analysis confirmed the carbon content. Anal. Found: C, 2.19%. Calcd: 2.15%. Thermogravimetric analysis (TGA) was performed by heating the sample in flowing oxygen from 50 to 900 °C at 10 °C/min. The TGA curve for **1** shows a one-step weight loss between 375 and 450 °C, which corresponds to the loss of H_2O, $^1/_2CO$, and $^1/_2CO_2$ (obsd, 9.79%; calcd, 9.68%). Colorless plate crystals of **2** were synthesized by heating a mixture of $FeCl_3 \cdot 6H_2O$, H_3PO_4, $H_2C_2O_4 \cdot 2H_2O$, and CsOH in the molar ratio of 0.8:2:1:1 in 3 g of the ionic liquid under the same reaction conditions. The yield was 67% based on iron. A crystal was selected for structure determination.[9] The purity of the bulk product was confirmed by powder X-ray diffraction. Anal. Found: C, 2.93%. Calcd: 2.82%. The TGA curve for **2** shows a broad weight loss between 200 and 500 °C, which corresponds to the loss of $^3/_2H_2O$, $^1/_2CO$, and $^1/_2CO_2$ (obsd, 14.59%; calcd, 14.79%). The final decomposition product was $CsFeP_2O_7$,[10] as indicated by powder X-ray diffraction. Attempts to prepare the two compounds in aqueous solutions were unsuccessful.

An ion-exchange experiment was performed by stirring **1** with concentrated NaCl(aq) at 50 °C for 1 day. The framework structure was retained after ion exchange, as indicated by powder X-ray diffraction. Sodium content

(8) Crystal data for **1**: $Cs_2Fe(C_2O_4)_{0.5}(HPO_4)_2$, pale-green taperlike crystal of dimensions $0.31 \times 0.19 \times 0.13$ mm, $T = 293$ K, monoclinic, $P2_1/c$ (No. 14), $a = 8.5085(4)$ Å, $b = 12.7251(6)$ Å, $c = 9.8961(4)$ Å, $\beta = 107.117(1)°$, $V = 1024.01(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 3.617$ g cm^{-3}, $\lambda = 0.710 73$ Å, $\mu = 88.3$ cm^{-1}, 2540 unique reflections with $I > 2\sigma(I)$ ($2\theta_{max} = 56.58°$, $R_{int} = 0.0387$), R1 = 0.0264, wR2 = 0.0629. The H atoms were not located. The final cycles of least-squares refinement included atomic coordinates and anisotropic thermal parameters for all atoms.
(9) Crystal data for **2**: $CsFe(C_2O_4)_{0.5}(H_2PO_4)(HPO_4)$, colorless plate crystal of dimensions $0.13 \times 0.09 \times 0.02$ mm, $T = 293$ K, monoclinic, $P2_1/n$ (No. 14), $a = 8.0038(3)$ Å, $b = 10.2923(3)$ Å, $c = 11.4755(4)$ Å, $\beta = 100.507(1)°$, $V = 929.47(5)$ Å^3, $Z = 4$, $D_{calcd} = 3.042$ g cm^{-3}, $\lambda = 0.710 73$ Å, $\mu = 58.6$ cm^{-1}, 2318 unique reflections with $I > 2\sigma(I)$ ($2\theta_{max} = 56.54°$, $R_{int} = 0.0688$), R1 = 0.0311, wR2 = 0.0760. The H atoms were located from difference Fourier maps. The final cycles of least-squares refinement included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The atomic coordinates and isotropic thermal parameters for H atoms were fixed.
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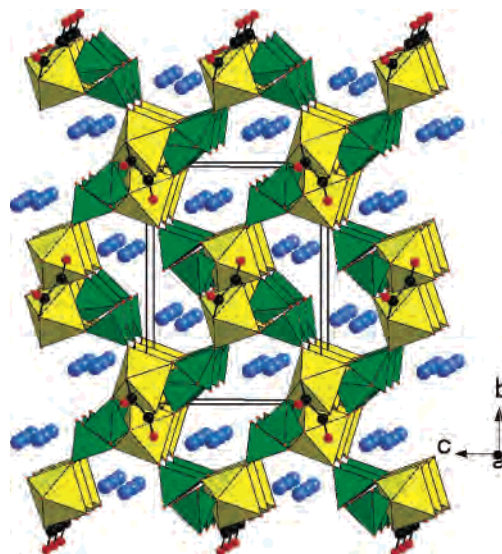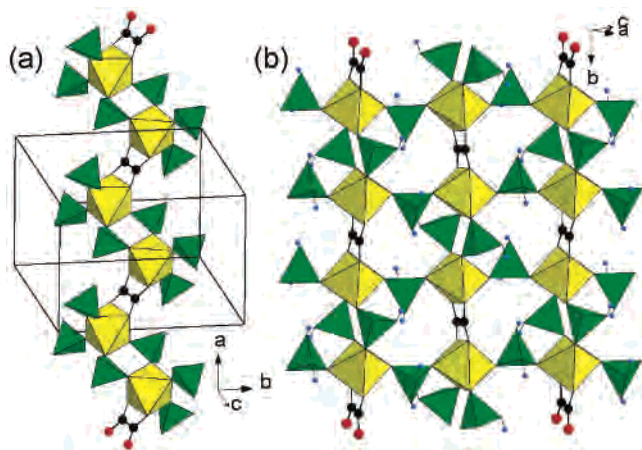
Figure 1. Polyhedral plot of the structure of **1** along the *a* axis. The yellow and green polyhedra represent FeO_6 octahedra and phosphate tetrahedra, respectively. Blue circles: Cs atoms. Black circles: C atoms. Red circles: O atoms.

analysis using atomic absorption spectroscopy and TGA of the ion-exchange product showed that about 10% of Cs^+ cations were replaced by Na^+ and the composition of the product was $Cs_{1.8}Na_{0.2}Fe(C_2O_4)_{0.5}(HPO_4)_2 \cdot xH_2O$. The magnetic susceptibilities for both **1** and **2** follow the Curie−Weiss law at high temperature (Figures S3 and S4 in the Supporting Information). The $\chi_M T$ values for both compounds decrease with decreasing temperature, indicating that the strongest magnetic interaction between Fe atoms is antiferromagnetic. The effective magnetic moments at 300 K are 5.71 and 5.38 μ_B/Fe for **1** and **2**, respectively, which are smaller than the spin-only value for the Fe^{3+} ion because of anitferromagnetic interaction. A fit of the data from 70 to 300 K to the equation $\chi_M = C/(T - \theta)$ results in $C = 4.78$ and 4.81 cm^3·K/mol and $\theta = -49$ and -96 K for **1** and **2**, respectively. Compound **1** shows complicated phase transitions below about 20 K, whereas **2** is antiferromagnetically ordered at about 50 K and shows phase transitions below about 30 K.

The structure of **1** consists of $Fe^{III}O_6$ octahedra connected by coordinating $C_2O_4^{2-}$ and HPO_4^{2-} anions to form intersecting tunnels parallel to the [100] and [001] directions, with the Cs^+ cations being located at the intersections of these tunnels. The tunnel parallel to [100] has a window formed by the edges of six FeO_6 octahedra and six phosphate tetrahedra (Figure 1). The other type of tunnel also has a 12-membered window formed by six octahedra, four tetrahedra, and two oxalate units. The $C_2O_4^{2-}$ anions act as a bis-bidentate ligand to Fe atoms to form dimers, which are connected by $HP(1)O_4^{2-}$ tetrahedra to form infinite chains along the [100] direction (Figure 2a). Because the two $HP(1)O_4^{2-}$ tetrahedra and oxlate unit have a cis arrangement, the chain is zigzag. The $HP(2)O_4^{2-}$ tetrahedra, positioned between the chains, join the Fe atoms from adjacent chains, generating the 3D-framework structure. The FeO_6 octahedron is highly distorted because of μ_2 coordination by the oxalate ligands [Fe(1)−O, 1.917−2.146 Å, ∠O(9)−Fe(1)−O(10),

Figure 2. (a) Section of an infinite chain in **1** viewed along the *a* axis. (b) Section of a layer in **2** viewed in a direction approximately parallel to [10$\bar{1}$] direction.
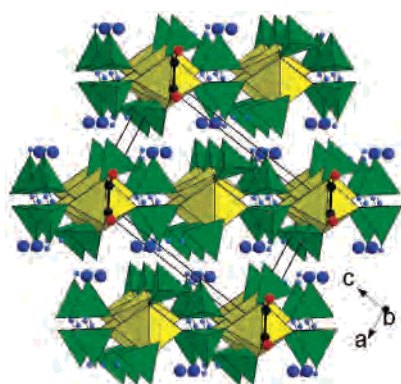

Figure 3. Polyhedral plot of the structure of **2** along the *b* axis. The yellow and green polyhedra represent FeO_6 octahedra and phosphate tetrahedra, respectively. Large blue circles: Cs atoms. Black circles: C atoms. Small blue circles: H atoms.

77.9°]. Both $HP(1)O_4$ and $HP(2)O_4$ groups coordinate to two Fe atoms through two O donors; the hydroxyl group and the pendant $P(1)-O(3)$ and $P(2)-O(7)$ project into the tunnels. All hydroxyl groups are involved in hydrogen bonding, as inferred from the short O···O distances between adjacent tetrahedra.

The structure of **2** consists of $Fe^{III}O_6$ octahedra connected by coordinating $C_2O_4^{2-}$, $H_2PO_4^{-}$, and HPO_4^{2-} anions to form macroanionic layers in the (10$\bar{1}$) plane, with the Cs^+ cations residing between the layers (Figure 3). Each layer consists of eight-membered windows formed by the edges of four FeO_6 octahedra, three phosphate tetrahedra, and one oxalate unit (Figure 2b). Adjacent layers are aligned such that straight channels along the [100] direction are formed. The $C_2O_4^{2-}$ anions also act as a bis-bidentate ligand to Fe atoms to form dimers, which are connected by $HP(2)O_4^{2-}$ tetrahedra to form infinite chains along the [010] direction. Because the two $HP(2)O_4^{2-}$ tetrahedra and oxlate unit have a mutual trans arrangement, the chain is nearly linear. The $H_2P(1)O_4^{-}$ tetrahedra, positioned between the chains, join the Fe atoms from adjacent chains, generating the 2D-layer structure. The FeO_6 octahedron is also distorted because of μ_2 coordination by the oxalate ligands [$Fe(1)-O$, 1.928–2.125 Å, $\angle O(9)-Fe(1)-O(10)$, 78.2°]. Both $H_2P(1)O_4$ and $HP(2)O_4$ groups coordinate to two Fe atoms through two O donors; the

hydroxyl groups project into the interlayer space or to the eight-membered window within a layer. All hydroxyl groups are involved in hydrogen bonding.

Both iron(II) and iron(III) oxalatophosphates are common, whereas only one mixed-valence iron compound has been reported.[2i] Almost all oxalatophosphates in the literature contain organic ammonium ions as templates or charge-compensating cations. We have previously reported a potassium compound, $K_2[Ga_4(C_2O_4)(PO_4)_4]\cdot2H_2O$,[11] which was prepared under hydrothermal conditions. The structure consists of GaO_6 octahedra and GaO_4 tetrahedra connected by coordinating oxalate and phosphate anions to generate intersecting channels in the 3D framework. To our knowledge, the title compounds are the second examples of oxalatophosphates containing alkali metals as countercations. Both structures consist of infinite chains of oxalate-bridging dimers of an FeO_6 octahedron, which is a common structural building unit in metal oxalatophosphates. Within a chain, every octahedron has two terminal O atoms that act as common vertexes to two bridging HPO_4 tetrahedra. If the two bridging phosphates of every octahedron are in positions cis to the oxalate unit, the result is a 3D-framework structure as observed in **1**. In contrast, a 2D-layer structure as observed in **2** is formed when the two bridging phosphate tetrahedra are trans to the oxalate unit. The reaction mixture for **2** is expected to be more acidic as compared with **1** because 2 mmol of CsOH and 1 mmol of the organic amine APPIP were added in the reaction mixture for **1**. Therefore, compound **2** contains a H_2PO_4 group, while **1** contains HPO_4 only.

The title compounds are the first examples of the use of ionic liquid as a solvent in the synthesis of metal oxalatophosphates. The same compounds could not be achieved from hydrothermal synthesis under similar reaction conditions, indicating that ionic liquid plays a vital role in the crystallization of one desired compound. The ionothermal approach reported here is a new route for new compounds in metal oxalate–phosphate (or phosphonate) systems. For example, we have also synthesized an iron(II) oxalatophosphonate, which consists of corner-sharing octahedral trimers.[12] Further work on the ionothermal synthesis of new materials with open-framework structures is in progress.

Supporting Information Available: Crystallographic data for **1** and **2** in CIF format, X-ray powder patterns, and magnetic measurement results. This material is available free of charge via the Internet at http://pubs.acs.org.

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