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Ionothermal Synthesis of Metal Oxalatophosphonates with a Three-Dimensional Framework Structure: $Na_2M_3(C_2O_4)_3(CH_3PO_3H)_2$ (M = Fe^{II} and Mn^{II})

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Two isostructural transition-metal oxalatophosphonates, $Na_2M_3(C_2O_4)_3(CH_3PO_3H)_2$ (M = Fe^{II} and Mn^{II}), 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 ^{57}Fe Mössbauer spectroscopy. The 3D framework structure consists of a corner-sharing octahedral trimer that is linked with other trimers through two distinct oxalate ligands with unusual linkage types, phosphonate tetrahedra, and H bonds to form infinite channels along the [101] direction where the Na^+ cations are located. They are the first examples for the use of an ionic liquid as a solvent in the synthesis of metal oxalatophosphonates. Crystal data for the Fe compound follow: monoclinic, $P2_1/n$ (No. 14), $a = 5.8063(1)$ Å, $b = 10.3867(3)$ Å, $c = 14.8094(4)$ Å, $\beta = 96.926(1)°$, and $Z = 2$. Crystal data for the Mn compound are the same as those for the Fe compound except $a = 5.8734(9)$ Å, $b = 10.557(2)$ Å, $c = 14.863(2)$ Å, and $\beta = 96.691(2)°$.

Introduction

Many research activities have focused on the synthesis of organic−inorganic hybrid compounds by incorporating organic ligands in the structures of metal phosphates. A large number of metal oxalatophosphates of transition metals and main-group elements have been reported.[1] However, very few reports in the literature illustrate the use of oxalate anions forming part of the structure along with the phosphonate groups, although the chemistry of metal phosphonates has been extensively studied for many years. $Sn_2(O_3PCH_3)(C_2O_4)$ and $Sn_4(O_3PCH_2CH_2CO_2)_2(C_2O_4)$ are the first members of metal oxalatophosphonates.[2,3] The former has a 2D layer structure, and the latter adopts a 3D framework structure that consists of two different bifunctional linkers, phosphonopropionate and oxalate anions. Several lanthanide oxalate−aminophosphonate hybrids with 3D framework structures were also synthesized.[4] Recently, we reported the first organically templated metal oxalatophosphonate, $(C_3H_{12}N_2)_{0.5}$-$[Ga_3(C_2O_4)(CH_3PO_3)_4]\cdot0.5H_2O$, with a layer structure.[5] All of these oxalatophosphonates were synthesized in aqueous solutions under mild hydrothermal conditions.

Recently, there were reports on the preparation of coordination polymers and aluminophosphates by using ionic liquid dialkylimidazolium salts or a low-melting-point eutectic mixture of choline chloride and urea.[6−10] The ionic liquids can not only act as solvents but also provide the

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template ions around which the inorganic frameworks order. The use of an ionic liquid as a solvent in the reaction was termed ionothermal synthesis to distinguish it from hydrothermal synthesis.[7] We have been interested in applying new synthetic methods to the exploratory synthetic and structural studies of new materials with open-framework structures. Recently, we reported the first use of an ionic liquid of chlorine chloride/malonic acid in the synthesis of two new iron(III) oxalatophosphates, $Cs_2Fe(C_2O_4)_{0.5}(HPO_4)_2$ and $CsFe(C_2O_4)_{0.5}(H_2PO_4)(HPO_4)$.[11] We have extended the exploratory synthetic and structural studies to the class of metal oxalatophosphonates. This work describes the ionothermal synthesis and structural characterization by single-crystal X-ray diffraction of a new iron(II) oxalatophosphonate, $Na_2Fe_3(C_2O_4)_3(CH_3PO_3H)_2$ (denoted as **1**), and the Mn analogue, $Na_2Mn_3(C_2O_4)_3(CH_3PO_3H)_2$ (denoted as **2**), which have a 3D framework structure built of corner-sharing octahedral trimers, in addition to methylphosphonate groups and two distinct oxalate units. ^{57}Fe Mössbauer spectroscopy confirms the divalent state of the Fe ions in **1**.

Experimental Section

Synthesis and Initial Characterization. An ionic liquid was prepared by heating a mixture of choline chloride and malonic acid in a 1:1 mole ratio at 80 °C and stirring until a homogeneous colorless liquid was formed. The melting point of the ionic liquid is 10 °C.[12] Ionothermal reaction of 1 mmol of $FeC_2O_4 \cdot 2H_2O$, 2 mmol of $CH_3PO(OH)_2$, 1 mmol of $H_2C_2O_4 \cdot 2H_2O$, and 2 mmol of NaOH in 3 g of the ionic liquid (123 mmol of choline chloride and malonic acid) in a 23-mL Teflon-lined autoclave at 160 °C for 3 days produced orange rod crystals of **1** as the major product along with a small amount of a colorless impurity phase. The reaction mixture contained about 23 mmol of H_2O because NaOH(aq) (5 M) is an aqueous solution and $FeC_2O_4 \cdot 2H_2O$ and $H_2C_2O_4 \cdot 2H_2O$ contain lattice H_2O molecules. The product was filtered by suction, washed with H_2O, and dried in a desiccator at room temperature. We did not study the dependence of the products on the amount of H_2O by evaporation of H_2O in the reaction mixture before the reaction or addition of H_2O to the reaction mixture. An orange crystal was selected for structure determination by single-crystal X-ray diffraction. The crystals were easily separated by hand sorting, and the purity of the sample for property measurements was confirmed by powder X-ray diffraction (Figure S1 in the Supporting Information). Elemental analysis of the sample confirmed the stoichiometry of **1**. (Found: C, 14.39; H, 1.41. Calcd for $C_8H_8O_{18}P_2Fe_3Na_2$: C, 14.392; H, 1.208.) The yield was 69% based on Fe. The colorless impurity phase is $Fe[(CH_3PO_3)(H_2O)]$, as indicated from powder X-ray diffraction.[13]

Colorless rod crystals of **2** were synthesized as a major product by heating a mixture of 1.3 mmol of $MnC_2O_4 \cdot 2H_2O$, 2 mmol of $CH_3PO(OH)_2$, 1.6 mmol of $H_2C_2O_4 \cdot 2H_2O$, and 2 mmol of NaOH in 3 g of the ionic liquid under the same reaction conditions. A crystal was selected for structure determination. The product always contained a small amount of an unidentified impurity phase, as indicated by powder X-ray diffraction. Manual separation of the impurity phase from the major product has not been achieved because both phases are colorless.

Table 1. Crystallographic Data for **1** and **2**

	1	**2**
chemical formula	$C_8H_8Fe_3Na_2O_{18}P_2$	$C_8H_8Mn_3Na_2O_{18}P_2$
a, Å	5.8063(1)	5.8734(9)
b, Å	10.3867(3)	10.557(2)
c, Å	14.8094(4)	14.863(2)
V, Å^3	886.60(4)	915.4(4)
Z	2	2
formula weight	667.61	664.88
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
T, °C	20	20
λ(Mo Kα), Å	0.710 73	0.710 73
D_{calc}, g·cm^{-3}	2.501	2.412
μ(Mo Kα), cm^{-1}	27.5	23.6
R1[a]	0.0310	0.0322
wR2[b]	0.0841	0.0848

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o,0) + 2(F_c)^2]/3$, where $a = 0.0406$ and $b = 0$ for **1** and $a = 0.0410$ and $b = 0.00$ for **2**.

Single-Crystal X-ray Diffraction. An orange rod crystal of dimensions 0.09 × 0.1 × 0.3 mm^3 for **1** and a colorless rod crystal of dimensions 0.01 × 0.06 × 0.15 mm^3 for **2** were selected for indexing and intensity data collection on Bruker CCD diffractometers. The data were collected at room temperature in 1270 frames with ω scans (width of 0.30° per frame). Empirical absorption corrections based on symmetry equivalence were applied ($T_{min,max} = 0.790$ and 0.959 for **1**; $T_{min,max} = 0.851$ and 0.954 for **2**). On the basis of systematic absences and successful solution and refinement of the structures, the space groups were determined to be $P2_1/n$ (No. 14) for both **1** and **2**. The structures were solved by direct methods and difference Fourier synthesis. The H atom in the hydroxyl group was located in difference Fourier maps and refined with a fixed isotropic thermal parameter. The H atoms in the methyl group were not located. The final cycles of least-squares refinement including atomic coordinates for all atoms and anisotropic thermal parameters for non-H atoms converged at $R1 = 0.0310$ and $wR2 = 0.0841$ for **1** and $R1 = 0.0322$ and $wR2 = 0.0848$ for **2**. All calculations were performed using the *SHELXTL*, version 5.1, software package.[14] Crystallographic data are summarized in Table 1.

Mössbauer Measurements. A Mössbauer spectrum was recorded on **1** at room temperature with a ^{57}Co/Rh source and a conventional constant-acceleration Mössbauer spectrometer. The spectrum was least-squares-fitted using the computer program MOSFIT.[15] The isomer shift values are relative to Fe metal at 293 K.

Results and Discussion

As shown in Figure 1, the structure of **1** is constructed from $Fe^{II}O_6$ octahedra, methylphosphonate pseudotetrahedra, and oxalate units. Fe2 sits on an inversion center, and all other atoms are at general positions. Fe1 is coordinated by one bidentate oxalate chelate, three monodentate oxalate units, and one phosphonate tetrahedron. $Fe1O_6$, $Fe2O_6$, and

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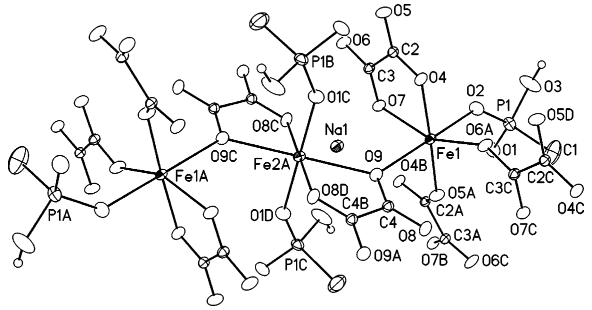

Figure 1. Building units of **1** showing the atom-labeling scheme. Thermal ellipsoids are shown at 50% probability.

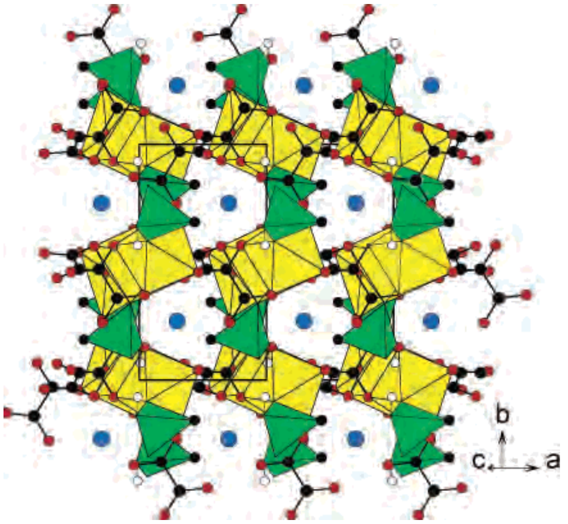

Figure 2. Polyhedral plot of the structure of **1** along the [101] direction. The yellow and green polyhedra represent FeO_6 octahedra and phosphonate tetrahedra, respectively. Large blue circles: Na ions. Black circles: C atoms. Red circles: oxalate O atoms. Small open circles: H atoms.

$C4_2O_4$ units share a common corner, O9. Fe2 is coordinated by two bidentate oxalate chelates and two phosphonate tetrahedra. Each $Fe2O_6$ octahedron shares trans corners with two $Fe1O_6$ octahedra to form trimeric units, which are connected by oxalate units, phosphonate tetrahedra, and H bonds to form infinite channels along the [101] direction where the Na^+ cations are located (Figure 2). There are two distinct oxalate ligands in the structure: $C2C3O_4$ is a monobidentate chelate to one Fe1 ion and a bismonodentate ligand to another two Fe1 ions, whereas $C4_2O_4$ is a bisbidentate chelate that bridges two Fe2 ions and a bismonodentate ligand to two Fe1 ions, with O9 therefore being three-coordinate (Figure 3). Bismonodentate and bisbidentate coordination by the same oxalate ligand has been observed in $Fe^{II}_4(PO_4)_2(C_2O_4)(H_2O)_2$ and $(C_4H_{12}N_2)[Fe^{II}_4(C_2O_4)_3(HPO_4)_2]$.[1a,b] To our knowledge, the unusual bismonodentate and monobidentate coordination by the same oxalate is observed for the first time. Both FeO_6 octahedra are distorted because of μ_2 coordination by the oxalate ligands (Fe1−O, 2.059−2.245 Å, ∠O4−Fe1−O7 = 76.25°; Fe2−O, 2.023−2.312 Å, ∠O8−Fe2−O9 = 73.18°). The longest Fe−O bonds involve the μ_3-O atom, O9, which is bonded to two Fe ions and one C atom. The octahedral distortion can be estimated by using the equation $\Delta = (1/6)\sum[(R_i - R_{av})/R_{av}]^2$, where R_i is the individual bond length and R_{av} is the average bond length.[16] The calculation results indicate that the distortion in $Fe2O_6$ ($\Delta = 29.9 \times 10^{-4}$) is much more pronounced than that in $Fe1O_6$ ($\Delta = 7.2 \times 10^{-4}$). Each CH_3-PO_3H unit is linked through two O atoms to two Fe ions belonging to two octahedral trimers. The hydroxyl group is H-bonded with an adjacent phosphonate O atom. The P−C bond length agrees well with those found in other metal phosphonates. The thermal ellipsoids of the hydroxyl O atom and the methyl C atom are elongated in a direction perpendicular to the P−OH and P−CH_3 bonds, respectively. The larger temperature parameters of the two atoms can be attributed to thermal vibration of the two-connected methylphosphonate group. The six-coordinate Na^+ ion is tightly bonded in the structural channel and is immobile, as indicated by short and regular Na−O bond lengths and nearly isotropic thermal vibrations. Compound **2** is isostructural with **1**. The unit-cell volume for **2** is significantly larger than that for **1** because Mn^{2+} is larger than Fe^{2+}. Another noticeable difference between the two compounds is that the octahedral distortions in **2** ($\Delta = 5.5 \times 10^{-4}$ for $Mn1O_6$ and 18.4×10^{-4} for $Mn2O_6$) are smaller than those in **1** because the d orbitals of Mn^{2+} are symmetrically occupied.

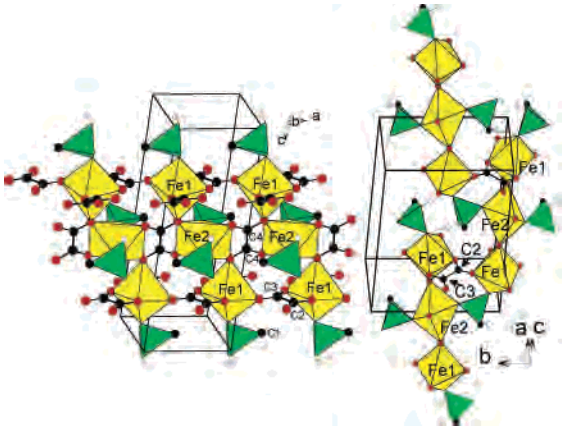

Figure 3. Sections of the structure of **1** showing the connectivity between the corner-sharing octahedral trimers. Dashed lines represent H bonds.

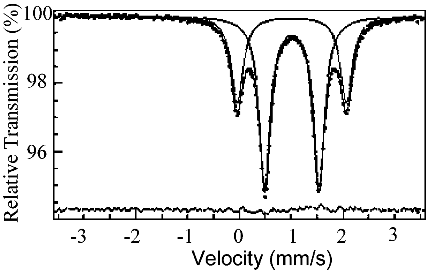

Figure 4. Powder ^{57}Fe Mössbauer spectrum of **1** recorded at 293 K.

The Mössbauer spectrum (Figure 4) was least-squares-fitted with two doublets as expected from crystallographic studies. The obtained parameters are δ(isomer shift) = 1.13(1) mm s^{-1}, ΔE_Q(quadrupole splitting) = 1.05(1) mm s^{-1}, and Γ(full width at half-height) = 0.26(1) mm s^{-1} for site 1 and δ = 1.12(1) mm s^{-1}, ΔE_Q = 2.11(1) mm s^{-1}, and Γ = 0.28(1) mm s^{-1} for site 2. The isomer shift values are relative to Fe metal at 293 K. The observed relative areas lead to a

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ratio of site 1:site 2 = 64:36, in agreement with the existence of two Fe crystallographic sites in a proportion of 2:1. The isomer shifts for both sites are characteristic of Fe^{II}. The usual ranges of isomer shifts in oxides are 0.29−0.50 and 1.03−1.28 mm s^{-1} for Fe^{III} and Fe^{II} in six coordination, respectively.[17] The site with larger ΔE_Q (2.11 mm s^{-1}) can be assigned to Fe2 because it has a larger octahedral distortion.

In summary, an iron(II) oxalatophosphonate and the Mn analogue have been synthesized by an ionothermal method. Their structures are characterized by single-crystal X-ray diffraction and Mössbauer spectroscopy. The 3D framework structure consists of corner-sharing octahedral trimers that are connected by phosphonate groups and two types of oxalate ligands with unusual linkage modes. In the course of our hydrothermal synthesis of metal oxalate−organophosphonates, we noted that all compounds form very thin, flat, easily separated sheets, indicating that they have 2D layer structures. The title compounds are the first examples of the use of an ionic liquid as a solvent in the synthesis of metal oxalatophosphonates. In addition, they are the first oxalate−methylphosphonates with a 3D framework structure. Altering the solvent from H_2O to an ionic liquid can change the chemistry of the system. This work shows that ionothermal synthesis is a new route for preparing new organic−inorganic hybrid compounds.

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

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