

Synthesis and Characterization of New Iron Phosphatooxalates: [(S)-C₅H₁₄N₂][Fe₄(C₂O₄)₃(HPO₄)₂(H₂O)₂] and [(S)-C₅H₁₄N₂] [Fe₄(C₂O₄)₃(HPO₄)₂]

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Two new organically templated iron(II) phosphatooxalates, [(S)-C₅H₁₄N₂][Fe₄(C₂O₄)₃(HPO₄)₂(H₂O)₂] (1) and [(S)-C₅H₁₄N₂][Fe₄(C₂O₄)₃(HPO₄)₂] (2), have been synthesized under hydrothermal conditions and characterized by single-crystal X-ray diffraction and Mössbauer spectroscopy. Crystal data are as follows: compound 1, triclinic, *P*1 (No. 1), *a* = 7.6999(4) Å, *b* = 7.9542(4) Å, *c* = 9.8262(5) Å, α = 74.8444(7)°, β = 81.7716(8)°, γ = 85.4075(8)°, *V* = 574.34(8) Å³, *Z* = 1, and *R*1 = 0.0255; compound 2, monoclinic, *P*2₁ (No. 4), *a* = 7.5943(8) Å, *b* = 7.8172(8) Å, *c* = 18.318(2) Å, β = 99.111(2)°, *V* = 1073.8(3) Å³, *Z* = 2, and *R*1 = 0.0281. The structure of 1 consists of dimers of edge-sharing FeO₆ octahedra that are linked by phosphate and oxalate groups to generate a three-dimensional framework with intersecting tunnels parallel to the [100] and [010] directions. Diprotonated (S)-2-methylpiperazinium cations are located at the intersections of these tunnels. Compound 1 crystallizes as a minor product when a racemic mixture of 2-methylpiperazine is used in the synthesis, and can be prepared as a major product with a small amount of 2 if optically pure (S)-2-methylpiperazine is used. The structure of 2 is similar to that of 1 except that the coordination around the iron centers in the dimer are square pyramidal and octahedral. The two compounds are the first 3-dimensional phosphatooxalates containing a chiral amine.

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variety of means of connection. An interesting variant of the metal phosphates is obtained by incorporating the oxalate unit in the materials. A large number of phosphatooxalates of Fe (8–13), V (14), Al (15, 16), Ga (17–19), In (20), and Mn (21) have been reported during past few years. In this new class of organically modified inorganic materials, there have been relatively more reports on the Fe–PO–Ox system. All of these iron compounds adopt three-dimensional framework structures. Most of them consist of anionic frameworks templated with organic amines in protonated forms, while a few contain neutral frameworks without amine templates. In our continuing research on this system, we have discovered two novel iron phosphatooxalates templated with a chiral amine, [(S)-C₅H₁₄N₂][Fe₄(C₂O₄)₃(HPO₄)₂(H₂O)₂] (1) and [(S)-C₅H₁₄N₂][Fe₄(C₂O₄)₃(HPO₄)₂] (2). Most interestingly, only the chiral species acts as a template in 1, although a racemic mix of 2-methylpiperazine is used in the synthesis. Compound 2 crystallizes as a minor product when the chiral amine (S)-2-methylpiperazine is used as a template. To our knowledge, no three-dimensional metal phosphate-oxalate framework templated with a chiral amine has been reported before this work.

INTRODUCTION

Recently, many research activities have focused on the synthesis of new open-framework metal phosphates, owing to their diverse structural chemistry and potential applications (1). In the context of building open frameworks, it is also possible to use organic molecules in the skeleton (2–7). As compared with inorganic phosphates, the organic molecules have larger sizes of polyhedral centers and a wide

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EXPERIMENTAL SECTION

Synthesis. The compounds were synthesized hydrothermally in a 23-mL Teflon-lined autoclave under autogenous pressure. Reaction of a racemic mixture of 2-methylpiperazine (5 mmol), iron metal powder (3 mmol), H₃PO₄ (7 mmol), oxalic acid (4 mmol), and H₂O (10 mL) at 165°C for 3 days followed by slow cooling at 10°C/h to room temperature produced a small amount of red crystals of [(S)-C₅H₁₄N₂][Fe₄(C₂O₄)₃(HPO₄)₂(H₂O)₂] (1) and orange crystals of [(S)-C₅H₁₄N₂][Fe₄(C₂O₄)₃(HPO₄)₂] (2) as the major products. The filling rate of the bomb was about 50%. The initial and final pH values were 4.6 and 5.9,

respectively. The crystal that was selected for single-crystal X-ray diffraction contained (*S*)-2-methylpiperazinium cations. In theory $[(R)\text{-C}_5\text{H}_{14}\text{N}_2][\text{Fe}_4(\text{C}_2\text{O}_4)_3(\text{HPO}_4)_2(\text{H}_2\text{O})_2]$ should also crystallize as a minor product. A subsequent reaction using (*S*)-(+)-2-methylpiperazine instead of racemic 2-methylpiperazine produced compound **1** in a yield of about 70% and a small amount of orange crystals of $[(S)\text{-C}_5\text{H}_{14}\text{N}_2][\text{Fe}_4(\text{C}_2\text{O}_4)_3(\text{HPO}_4)_2]$ (**2**) (22). Energy dispersive X-ray analysis confirmed the presence of iron and phosphorus in all three compounds. Suitable crystals were selected for single-crystal X-ray structure determination. The red crystals were manually separated from the orange crystals to give pure **1** as judged by visual microscopic examination and by comparison of the X-ray powder pattern to the pattern simulated from the atomic coordinates derived from single-crystal study. Elemental analysis of **1** confirmed the stoichiometry. Analysis found the following: C, 16.1; H, 2.41; N, 3.38. Calculations were as follows: C, 16.2; H, 2.46; N, 3.42%.

TGA and Mössbauer spectroscopy. Thermogravimetric analysis for **1** was carried out on a Perkin–Elmer TGA7 thermal analyzer under oxygen atmosphere in the range 30–900°C at a heating rate of 10°C/min. The X-ray powder pattern of the final decomposition product revealed the presence of $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ (23). The ^{57}Fe Mössbauer measurements were made on a constant-acceleration instrument at room temperature. Isomer shifts are reported with respect to an iron foil standard at 300 K.

Single-crystal X-ray diffraction. A suitable single crystal of each compound was selected for indexing and intensity data collection on a Siemens Smart-CCD diffractometer equipped with a normal focus, 3-kW sealed tube X-ray source at room temperature. Empirical absorption corrections were applied. The structures were solved by direct methods and difference Fourier syntheses. Bond-valence calculations indicate that all the Fe atoms are divalent and all phosphate ligands are HPO_4^{2-} (24). Compound **1** adopts a new structure, while the structure of **2** is closely related to that of $[\text{C}_4\text{H}_{12}\text{N}_2][\text{Fe}_4(\text{C}_2\text{O}_4)_3(\text{HPO}_4)_2]$, where $[\text{C}_4\text{H}_{12}\text{N}_2]^{2+}$ is a piperazinium cation (8). Compound **3** is isotopic to $[\text{C}_4\text{H}_{12}\text{N}_2][\text{Fe}_4(\text{C}_2\text{O}_4)_3(\text{HPO}_4)_2]$. All of the hydrogen atoms were positioned geometrically and refined using a riding model with fixed isotropic thermal parameters. The final cycles of least-squares refinement included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The reliability factors converged to $R1 = 0.0255$, $wR2 = 0.0727$, and $S = 1.075$ for **1** and $R1 = 0.0281$, $wR2 = 0.0744$, and $S = 1.020$ for **2**. The Flack x parameters were 0.0(2) and 0.05(2) for **1** and **2**, respectively, indicative of correct absolute structures. All calculations were performed using the SHELXTL Version 5.1 software package (25). The crystal data and structure refinement parameters for **1** and **2** are given in Table 1, the atomic

TABLE 1
Crystal Data and Structure Refinement Parameters for $[(S)\text{-C}_5\text{H}_{14}\text{N}_2][\text{Fe}_4(\text{C}_2\text{O}_4)_3(\text{HPO}_4)_2(\text{H}_2\text{O})_2]$ (**1**) and $[(S)\text{-C}_5\text{H}_{14}\text{N}_2][\text{Fe}_4(\text{C}_2\text{O}_4)_3(\text{HPO}_4)_2]$ (**2**)

	1	2
Empirical formula	$\text{C}_{11}\text{Fe}_4\text{H}_{20}\text{N}_2\text{O}_{22}\text{P}_2$	$\text{C}_{11}\text{Fe}_4\text{H}_{16}\text{N}_2\text{O}_{20}\text{P}_2$
Formula weight	817.63	781.6
Crystal color	red	orange
Crystal size, mm ³	0.25 × 0.15 × 0.1	0.6 × 0.15 × 0.1
Crystal system	triclinic	monoclinic
Space group	$P1$ (No. 1)	$P2_1$ (No. 4)
Unit cell dimensions	$a = 7.6999(4)$ $b = 7.9542(4)$ $c = 9.8262(5)$ $\alpha = 74.8444(7)$ $\beta = 81.7716(8)$ $\gamma = 85.4075(8)$ $V = 574.34(8)$	7.5943(8) 7.8172(8) 18.318(2) 90 99.111(2) 90 1073.8(3)
Z	1	2
D_{calcd} , g·cm ⁻³	2.364	2.413
T , °C	23	23
λ (MoK α), Å	0.71073	0.71073
μ , mm ⁻¹	2.73	2.91
$2\theta_{\text{max}}$, °	56	56.6
Index ranges	$-9 \leq h \leq 9$, $-10 \leq k \leq 10$ $-12 \leq l \leq 11$	$-10 \leq h \leq 9$, $-8 \leq k \leq 10$ $-22 \leq l \leq 23$
Data collected	5457	6826
Unique data	4243 [$F_o > 4\sigma(F_o)$]	3321 [$F_o > 4\sigma(F_o)$]
Number of variables	371	352
Goodness-of-fit	1.075	1.020
R indices [$F_o > 4\sigma(F_o)$]	$R1 = 0.0255$, $wR2 = 0.0725$	$R1 = 0.0281$, $wR2 = 0.0703$
R indices (all data)	$R1 = 0.0257$, $wR2 = 0.0727$	$R1 = 0.0357$, $wR2 = 0.0744$
Flack x parameter	0.0(2)	0.05(2)
$(\Delta\rho)_{\text{max, min}}$, e·Å ⁻³	0.49, -0.39	0.62, -0.35

Note. $R1 = \sum |F_o| - |F_c| / \sum |F_o|$, $wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)] \}^{1/2}$, $w = 1 / [\sigma^2(F_o)^2 + (aP)^2 + bP]$, $P = [\text{Max}(F_o, 0) + 2(F_c)^2] / 3$, where $a = 0.0494$ and $b = 0.36$ for **1**, and $a = 0.0460$ and $b = 0$ for **2**.

coordinates are in Table 2, and selected bond distances are in Table 3. Crystal data for **3** are as follows: monoclinic, $P2_1/c$, $a = 7.5949(7)$ Å, $b = 7.8208(7)$ Å, $c = 18.326(2)$ Å, $\beta = 99.155(2)^\circ$, $V = 1074.6(3)$ Å³, $Z = 2$, $D_{\text{calc}} = 2.415$ g cm⁻³, $\lambda = 0.71073$ Å, 1878 absorption corrected reflections with $F_o > 4\sigma(F_o)$ measured at 23°C on an orange crystal ($2\theta_{\text{max}} = 56.4^\circ$), $R1 = 0.0365$, and $wR2 = 0.0982$.

RESULTS AND DISCUSSION

TGA and Mössbauer spectroscopy. TGA data for **1** in oxygen show a broad weight loss that begins at about 200°C, has a maximum rate at 350°C, and is complete above 700°C. The weight loss is attributed to dehydration of hydrogen phosphate groups, deprotonation of 2-methylpiperazinium cations, decomposition of oxalate anions, and

TABLE 2

Atomic Coordinates and Temperature Factors (\AA^2) for [(S)- $\text{C}_5\text{H}_{14}\text{N}_2$][$\text{Fe}_4(\text{C}_2\text{O}_4)_3(\text{HPO}_4)_2(\text{H}_2\text{O})_2$] (1) and [(S)- $\text{C}_5\text{H}_{14}\text{N}_2$][$\text{Fe}_4(\text{C}_2\text{O}_4)_3(\text{HPO}_4)_2$] (2)

Atom	x	y	z	U_{eq}^a
⟨Compound 1⟩				
Fe(1)	0.91140(6)	0.59482(6)	0.73064(5)	0.0140(1)
Fe(2)	0.59107(6)	0.31879(5)	0.83930(5)	0.0139(1)
Fe(3)	0.63062(6)	-0.35143(5)	0.21660(5)	0.0131(1)
Fe(4)	0.95213(6)	-0.07778(5)	0.10437(5)	0.0137(1)
P(1)	0.6915(1)	-0.1056(1)	0.8800(1)	0.0138(2)
P(2)	0.8456(1)	0.3428(1)	0.0718(1)	0.0120(2)
O(1)	0.7295(5)	0.4743(4)	0.6412(3)	0.0164(6)
O(2)	0.7907(4)	0.4163(4)	0.9226(3)	0.0180(7)
O(3)	0.1659(5)	0.6804(4)	0.7608(4)	0.0227(7)
O(4)	0.7853(5)	0.8081(4)	0.7682(3)	0.0226(7)
O(5)	0.0951(5)	0.3847(4)	0.7051(4)	0.0238(8)
O(6)	0.9593(5)	0.7177(4)	0.4968(3)	0.0229(7)
O(7)	0.7083(5)	0.0903(4)	0.8323(4)	0.0185(7)
O(8)	0.3597(4)	0.2711(4)	0.7527(4)	0.0206(7)
O(9)	0.4292(5)	0.5650(4)	0.8173(4)	0.0222(7)
O(10)	0.4278(4)	0.2688(4)	0.0459(3)	0.0309(7)
O(11)	0.8173(5)	-0.2406(4)	0.3049(4)	0.0205(7)
O(12)	0.7534(4)	-0.1822(4)	0.0266(3)	0.0174(7)
O(13)	0.3842(5)	-0.4268(4)	0.1634(4)	0.0224(7)
O(14)	0.7385(5)	-0.5737(4)	0.1813(3)	0.0220(7)
O(15)	0.4469(4)	-0.1448(4)	0.2435(3)	0.0192(7)
O(16)	0.5900(4)	-0.4801(4)	0.4500(3)	0.0217(7)
O(17)	0.8365(5)	0.1470(4)	0.1241(4)	0.0199(7)
O(18)	0.0757(5)	0.0253(4)	0.8883(3)	0.0328(8)
O(19)	0.4879(4)	-0.1382(4)	0.8967(3)	0.0189(6)
H(1P)	0.4504(4)	-0.0960(4)	0.8205(3)	0.0283
O(20)	0.0458(4)	0.3869(4)	0.0633(4)	0.0238(7)
H(2P)	0.0556(4)	0.4927(4)	0.0351(4)	0.0358
O(21)	0.1196(4)	-0.3127(4)	0.1103(4)	0.0206(7)
O(22)	0.1923(5)	-0.0185(4)	0.1753(4)	0.0252(8)
C(1)	0.7060(6)	0.5475(5)	0.5127(4)	0.0149(8)
C(2)	0.8429(6)	0.6869(5)	0.4313(4)	0.0151(8)
C(3)	0.2801(6)	0.5607(5)	0.7787(5)	0.0163(8)
C(4)	0.2430(6)	0.3912(5)	0.7410(4)	0.0152(8)
C(5)	0.2638(6)	-0.3097(5)	0.1537(5)	0.0162(8)
C(6)	0.3046(6)	-0.1421(6)	0.1933(5)	0.0172(9)
C(7)	0.2017(5)	0.0782(5)	0.4758(4)	0.0244(7)
H(7A)	0.2008(5)	-0.0118(5)	0.4242(4)	0.0293
C(8)	0.3067(6)	0.2285(5)	0.3786(5)	0.0284(9)
H(8A)	0.2506(6)	0.2767(5)	0.2936(5)	0.0341
H(8B)	0.3085(6)	0.3200(5)	0.4271(5)	0.0341
C(9)	0.5798(6)	0.0795(6)	0.4610(5)	0.032(1)
H(9A)	0.5963(6)	0.1626(6)	0.5143(5)	0.0384
H(9B)	0.6947(6)	0.0345(6)	0.4285(5)	0.0384
C(10)	0.4756(5)	-0.0672(5)	0.5556(4)	0.0271(7)
H(10A)	0.5352(5)	-0.1218(5)	0.6377(4)	0.0325
H(10B)	0.4654(5)	-0.1544(5)	0.5046(4)	0.0325
C(11)	0.0115(6)	0.1377(7)	0.5137(6)	0.038(1)
H(11A)	0.9486(6)	0.0410(7)	0.5747(6)	0.0573
H(11B)	0.9573(6)	0.1810(7)	0.4284(6)	0.0573
H(11C)	0.0092(6)	0.2287(7)	0.5619(6)	0.0573
N(1)	0.2946(5)	0.0017(4)	0.6035(4)	0.0275(8)
H(12A)	0.2331(5)	-0.0855(4)	0.6634(4)	0.0330
H(12B)	0.3038(5)	0.0838(4)	0.6498(4)	0.0330
N(2)	0.4901(4)	0.1672(4)	0.3383(3)	0.0274(6)
H(13A)	0.4881(4)	0.0933(4)	0.2831(3)	0.0329
H(13B)	0.5515(4)	0.2593(4)	0.2866(3)	0.0329

TABLE 2—Continued

Atom	x	y	z	U_{eq}^a
⟨Compound 2⟩				
Fe(1)	0.36475(9)	0.21560(9)	0.38359(4)	0.0150(2)
Fe(2)	0.7123(1)	0.95835(9)	0.43997(5)	0.0168(2)
Fe(3)	0.62826(9)	0.08735(9)	0.11549(4)	0.0157(2)
Fe(4)	0.2792(1)	0.34940(9)	0.05819(5)	0.0163(2)
P(1)	0.4497(1)	0.7285(2)	0.05537(7)	0.0132(3)
P(2)	0.5586(1)	0.5752(2)	0.44558(7)	0.0131(3)
O(1)	0.4313(5)	0.4615(5)	0.3938(2)	0.0175(8)
O(2)	0.1883(4)	0.0073(6)	0.3649(2)	0.0223(3)
O(3)	0.5769(4)	0.0964(6)	0.3403(2)	0.0189(9)
O(4)	0.4965(4)	0.5899(6)	0.5207(2)	0.0202(9)
O(5)	0.3014(4)	0.2595(6)	0.2614(2)	0.024(1)
O(6)	0.1386(4)	0.2909(6)	0.4456(2)	0.0212(9)
O(7)	0.5762(4)	0.7463(6)	0.4109(2)	0.0199(9)
O(8)	0.9421(5)	0.8960(6)	0.3957(2)	0.0216(9)
O(9)	0.8790(4)	0.1778(6)	0.4674(2)	0.0221(9)
O(10)	0.5819(5)	0.8350(5)	0.1075(2)	0.0193(9)
O(11)	0.8039(4)	0.2874(6)	0.1339(2)	0.0242(9)
O(12)	0.4095(4)	0.2010(6)	0.1572(2)	0.0197(9)
O(13)	0.4848(4)	0.2071(6)	0.0187(2)	0.0197(9)
O(14)	0.6898(4)	0.0420(6)	0.2367(2)	0.023(1)
O(15)	0.8558(4)	0.0157(6)	0.0497(2)	0.0212(9)
O(16)	0.4148(5)	0.5572(6)	0.0892(2)	0.0210(9)
O(17)	0.0522(4)	0.4052(5)	0.1088(2)	0.0191(9)
O(18)	0.1102(4)	0.1378(6)	0.0266(2)	0.0219(9)
O(19)	0.2629(5)	0.8231(6)	0.0431(2)	0.026(1)
H(1P)	0.2736(5)	0.9174(6)	0.0248(2)	0.0384
O(20)	0.7514(5)	0.4952(6)	0.4561(2)	0.0218(9)
H(2P)	0.7496(5)	0.4004(6)	0.4751(2)	0.0328
C(1)	0.9405(6)	0.2905(8)	0.1031(3)	0.016(1)
C(2)	0.9718(6)	0.1318(8)	0.0554(3)	0.016(1)
C(3)	0.0232(6)	0.1769(7)	0.4416(3)	0.017(1)
C(4)	0.0527(7)	0.0147(8)	0.3960(3)	0.019(1)
C(5)	0.4134(6)	0.1980(8)	0.2274(3)	0.016(1)
C(6)	0.5778(5)	0.1019(8)	0.2721(3)	0.017(1)
C(7)	0.8515(6)	0.6462(6)	0.2606(2)	0.022(1)
H(7A)	0.8288(6)	0.7552(6)	0.2838(2)	0.0269
C(8)	0.0569(7)	0.7920(7)	0.1871(3)	0.031(1)
H(8A)	0.0355(7)	0.9025(7)	0.2081(3)	0.0366
H(8B)	0.0819(7)	0.8100(7)	0.1373(3)	0.0366
C(9)	0.2162(7)	0.7041(7)	0.2343(3)	0.030(1)
H(9A)	0.2444(7)	0.5995(7)	0.2102(3)	0.0365
H(9B)	0.3194(7)	0.7787(7)	0.2386(3)	0.0365
C(10)	0.0105(7)	0.5609(7)	0.3060(3)	0.028(1)
H(10A)	0.9865(7)	0.5437(7)	0.3559(3)	0.0338
H(10B)	0.0281(7)	0.4494(7)	0.2850(3)	0.0338
C(11)	0.6881(7)	0.5366(7)	0.2552(3)	0.036(1)
H(11A)	0.5895(7)	0.5942(7)	0.2260(3)	0.0546
H(11B)	0.6610(7)	0.5158(7)	0.3039(3)	0.0546
H(11C)	0.7091(7)	0.4297(7)	0.2323(3)	0.0546
N(1)	0.8964(5)	0.6809(5)	0.1850(2)	0.0224(9)
H(12A)	0.9159(5)	0.5808(5)	0.1633(2)	0.0269
H(12B)	0.8026(5)	0.7318(5)	0.1572(2)	0.0269
H(2)	0.1774(5)	0.6635(6)	0.3088(2)	0.030(1)
H(13A)	0.1664(5)	0.7616(6)	0.3335(2)	0.0360
H(13B)	0.2694(5)	0.6045(6)	0.3339(2)	0.0360

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3
Selected Bond Lengths (Å) for [(S)-C₅H₁₄N₂][Fe₄(C₂O₄)₃(HPO₄)₂(H₂O)₂] (1) and [(S)-C₅H₁₄N₂][Fe₄(C₂O₄)₃(HPO₄)₂] (2)

〈Compound 1〉			
Fe(1)–O(1)	2.159(3)	Fe(1)–O(2)	2.179(3)
Fe(1)–O(3)	2.208(3)	Fe(1)–O(4)	1.979(3)
Fe(1)–O(5)	2.144(3)	Fe(1)–O(6)	2.239(6)
Fe(2)–O(1)	2.194(3)	Fe(2)–O(2)	2.126(3)
Fe(2)–O(7)	1.977(3)	Fe(2)–O(8)	2.180(3)
Fe(2)–O(9)	2.214(3)	Fe(2)–O(10)	2.188(3)
Fe(3)–O(11)	2.134(3)	Fe(3)–O(12)	2.139(3)
Fe(3)–O(13)	2.205(4)	Fe(3)–O(14)	1.985(3)
Fe(3)–O(15)	2.126(3)	Fe(3)–O(16)	2.241(3)
Fe(4)–O(11)	2.221(3)	Fe(4)–O(12)	2.117(3)
Fe(4)–O(17)	1.967(3)	Fe(4)–O(18)	2.173(3)
Fe(4)–O(21)	2.176(3)	Fe(4)–O(22)	2.193(4)
P(1)–O(4)	1.512(3)	P(1)–O(7)	1.516(3)
P(1)–O(12)	1.538(3)	P(1)–O(19)	1.588(3)
P(2)–O(2)	1.536(3)	P(2)–O(14)	1.520(3)
P(2)–O(17)	1.511(3)	P(2)–O(20)	1.594(3)
O(19)–H(1P)	0.82	O(20)–H(2P)	0.82
C(1)–O(1)	1.277(5)	C(1)–O(16)	1.219(5)
C(1)–C(2)	1.569(3)	C(2)–O(6)	1.249(6)
C(2)–O(11)	1.261(5)	C(3)–O(3)	1.238(6)
C(3)–O(9)	1.265(6)	C(3)–C(4)	1.545(5)
C(4)–O(5)	1.248(6)	C(4)–O(8)	1.253(6)
C(5)–O(13)	1.256(6)	C(5)–O(21)	1.249(6)
C(5)–C(6)	1.549(5)	C(6)–O(15)	1.261(6)
C(6)–O(22)	1.250(6)	C(7)–C(8)	1.528(5)
C(7)–C(11)	1.527(6)	C(7)–N(1)	1.499(5)
C(7)–H(7A)	0.98	C(8)–N(2)	1.489(5)
C(8)–H(8A)	0.97	C(8)–H(8B)	0.97
C(9)–C(10)	1.496(6)	C(9)–N(2)	1.463(6)
C(9)–H(9A)	0.97	C(9)–H(9B)	0.97
C(10)–N(1)	1.513(5)	C(10)–H(10A)	0.97
C(10)–H(10B)	0.97	C(11)–H(11A)	0.96
C(11)–H(11B)	0.96	C(11)–H(11C)	0.96
N(1)–H(12A)	0.90	N(1)–H(12B)	0.90
N(2)–H(13A)	0.90	N(2)–H(13B)	0.90
〈Compound 2〉			
Fe(1)–O(1)	1.989(4)	Fe(1)–O(2)	2.102(4)
Fe(1)–O(3)	2.120(3)	Fe(1)–O(4)	2.137(4)
Fe(1)–O(5)	2.240(4)	Fe(1)–O(6)	2.281(3)
Fe(2)–O(3)	2.227(4)	Fe(2)–O(4)	2.111(3)
Fe(2)–O(7)	1.981(4)	Fe(2)–O(8)	2.094(4)
Fe(2)–O(9)	2.144(4)	Fe(3)–O(10)	2.005(4)
Fe(3)–O(11)	2.049(4)	Fe(3)–O(12)	2.129(3)
Fe(3)–O(13)	2.143(4)	Fe(3)–O(14)	2.224(4)
Fe(3)–O(15)	2.326(3)	Fe(4)–O(12)	2.247(4)
Fe(4)–O(13)	2.134(4)	Fe(4)–O(16)	1.959(4)
Fe(4)–O(17)	2.127(3)	Fe(4)–O(18)	2.117(4)
P(1)–O(10)	1.520(4)	P(1)–O(13)	1.527(3)
P(1)–O(16)	1.517(4)	P(1)–O(19)	1.584(4)
P(2)–O(1)	1.527(4)	P(2)–O(4)	1.528(3)
P(2)–O(7)	1.496(4)	P(2)–O(20)	1.576(4)

release of organic components, giving Fe₄(P₂O₇)₃ and Fe₂O₃ as the final products. The observed total weight loss of 46.8% is close to the calculated value 47.5% according to

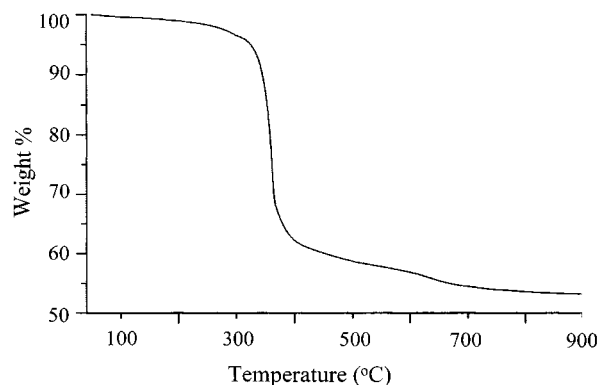
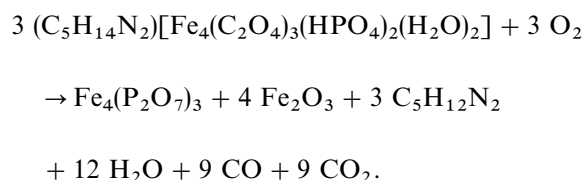


FIG. 1. Thermogravimetric analysis of **1** in flowing oxygen at 10°C min⁻¹.

the equation



A sample of **1** was heated in air at 220°C for 4 h. A powder X-ray diffraction of the product indicated that it was amorphous and **1** was not transformed to **2**.

The room temperature ⁵⁷Fe Mössbauer spectrum of **1** was least-squares fitted by one doublet (Fig. 2). The obtained parameters are δ (isomer shift) = 1.20 mm s⁻¹, ΔE_Q (quadrupole splitting) = 2.65 mm s⁻¹, and Γ (full-width at half-height) = 0.34 mm s⁻¹. The large quadrupole splitting corresponds to large octahedral distortion. The isomer shift is characteristic of high-spin Fe^{II}. According to Menil, 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 (26). Therefore, the valence of the iron atoms in **1** is confirmed by Mössbauer spectroscopy.

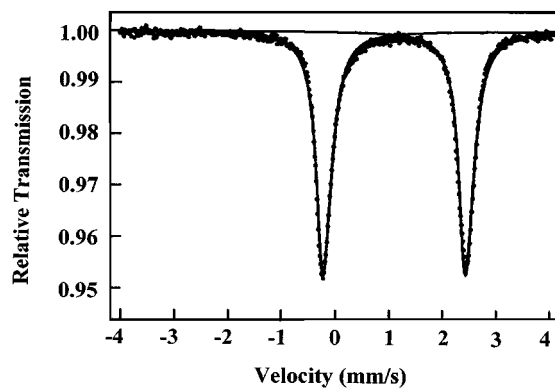


FIG. 2. Mössbauer spectroscopy of **1** at 300 K.

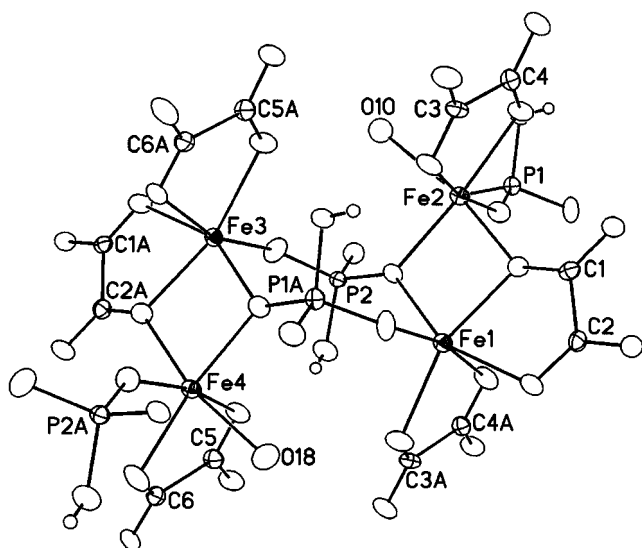


FIG. 3. A fragment of the structure of **1** (50% thermal ellipsoids) showing the basic structural building units. O(10) and O(18) are water oxygen atoms.

Description of the structures. The local coordinations of the framework atoms in **1** are shown in Fig. 3. It comprises FeO_6 , HPO_4 , and C_2O_4 moieties. All the four distinct Fe^{II} atoms are in six-coordination with a distorted octahedral geometry, but they do not display the same environment. Both Fe(1) and Fe(3) are coordinated by two bidentate oxalate and two phosphate units, while both Fe(2) and Fe(4) by one bidentate oxalate, one monodentate oxalate, two phosphate units, and one terminal water molecule. The coordination by bidentate oxalate leads to highly distorted octahedra for all four iron atoms, as indicated by the wide range of Fe–O bond lengths and small O–Fe–O bond angles subtended by the oxalate ligand, which also accounts for the large quadrupole splitting in the Mössbauer spectrum. There are three independent oxalate ligands in the structure: C(1)C(2)O₄ is a bridging bidentate ligand to both Fe(1) and Fe(3) as well as a monodentate ligand to Fe(2) or Fe(4), whereas the other two oxalates act only as bidentate ligands that bridge Fe(1) and Fe(2) or Fe(3) and Fe(4). The two distinct phosphorus atoms are all tetrahedrally coordinated and linked through three oxygens to four adjacent iron atoms, with the fourth coordination site in either case corresponding to a terminal P–OH group. One of the three oxygen atoms connects two iron atoms. The O–H groups are involved in hydrogen bonding as inferred from the short O...O distances (O(20)...O(21) = 2.67 Å and O(19)...O(9) = 2.76 Å).

The structural feature of **1** is the presence of an edge-sharing dimer formed of two Fe^{II} -centered FeO_6 octahedra. The oxygen atoms involved in the shared edge serve as corners for HPO_4 and C_2O_4 ligands. The dimer alternates with the HPO_4 group, and each HPO_4 connects three

dimers, thus forming a double chain parallel to the *b* axis (Fig. 4). Each double chain is linked to four others by oxalate ligands to generate a three-dimensional framework that delimits intersecting channels running along the [010] and [100] directions. Within the channels parallel to [010] are eight-membered rings containing four iron–oxygen octahedra and four oxalate units, whereas the other channels, parallel to [100], are delimited by eight-ring apertures containing four iron–oxygen octahedra, two phosphate tetrahedra, and two oxalate units. The (*S*)-2-methylpiperazinium cations are located at the intersections of these channels and are hydrogen-bonded to framework oxygen atoms. One of the nitrogen atoms of the cation, N(1), is hydrogen-bonded to O(3) at 2.79 Å, but the other nitrogen has no close oxygen neighbors.

The local coordinations of the framework atoms in **2** are shown in Fig. 5. It comprises FeO_6 , FeO_5 , HPO_4 , and C_2O_4 moieties. The iron atoms show two different coordination spheres. The FeO_6 environment of Fe(1) and Fe(3) is similar to that of Fe(1) and Fe(3) in **1**; namely, the iron atom is coordinated by two bidentate oxalate and two phosphate units. In contrast Fe(2) and Fe(4) in **2** are in five-fold coordination with a square pyramidal geometry. Of the five oxygen atoms, two belong to two phosphate groups and two to a bidentate oxalate unit, while the remaining oxygen, which is at the apex of the pyramid, is from a monodentate oxalate unit. The four basal ligand atoms and the iron atom are nearly coplanar. The axial bond is longer than the equatorial bonds, as is commonly found. The structural feature of **2** is also an edge-sharing dimer formed of two iron–oxygen polyhedra. Each FeO_6 octahedron shares an edge with a FeO_5 square pyramid to form a dimer that is linked by phosphate and oxalate ligands to adjacent dimers to form

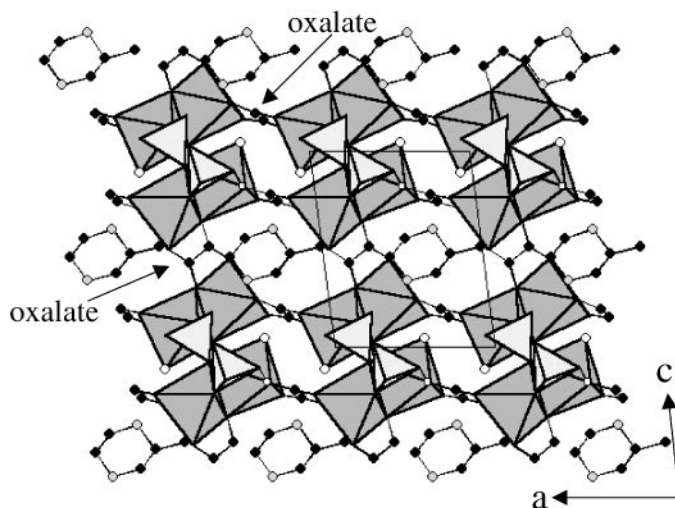


FIG. 4. A polyhedral view of the structure of **1** along the [010] direction. Solid circles, carbon atoms; stippled circles, nitrogen atoms; large open circles, water oxygen atoms; small open circles, hydrogen atoms.

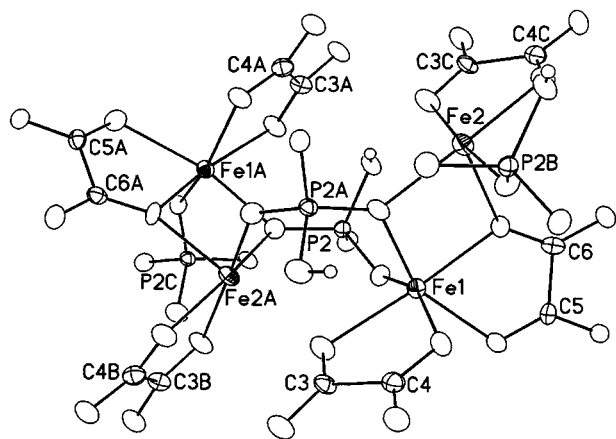


FIG. 5. A fragment of the structure of **2** (50% thermal ellipsoids) showing the basic structural building units.

a double chain in the same connection scheme as that in **1**. Each double chain rides on a 2_1 -screw axis and is connected to four others, generating intersecting channels running parallel to $[010]$ and $[100]$ (Fig. 6). Within channels there are also eight-ring windows formed by the edges of iron-oxygen polyhedra, phosphate tetrahedral, and oxalate units. Diprotonated (*S*)-2-methylpiperazinium cations are locked in their positions at the intersections of the channels by hydrogen bonds to phosphate oxygens ($N(1) \cdots O(10) = 2.84 \text{ \AA}$ and $N(2) \cdots O(1) = 2.77 \text{ \AA}$). Compound **3**, $[\text{C}_5\text{H}_{14}\text{N}_2][\text{Fe}_4(\text{C}_2\text{O}_4)_3(\text{HPO}_4)_2]$, crystallizes in the centrosymmetric space group $P2_1/c$ and is isotopic to $[\text{C}_4\text{H}_{12}\text{N}_2][\text{Fe}_4(\text{C}_2\text{O}_4)_3(\text{HPO}_4)_2]$, where the organic molecule is a diprotonated piperazinium cation. The organic molecules in **3** are found to be disordered because of the simultaneous

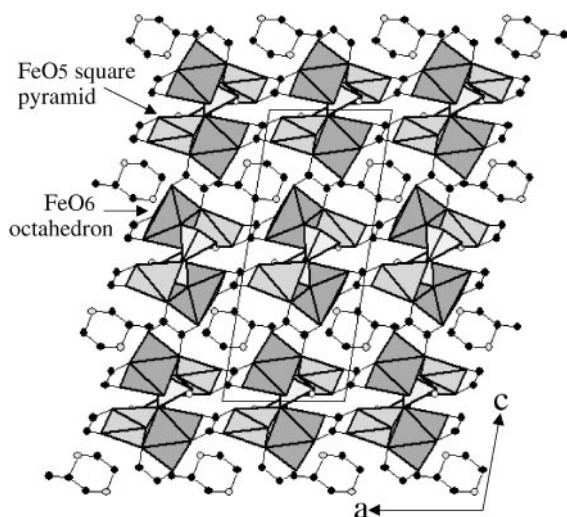


FIG. 6. A polyhedral view of the structure of **2** along the $[010]$ direction. Solid circles, carbon atoms; stippled circles, nitrogen atoms; small open circles, hydrogen atoms.

presence of (*R*)- and (*S*)-2-methylpiperazinium cations in the structural channels. The connection of the building units in **3** is essentially the same as that in **2**.

The title compounds are new members of a family of hybrid framework structures. They are the first 3-dimensional phosphatooxalates containing a chiral amine. The structure of **1** contains coordinated water molecules and six-coordinate iron atoms, whereas **2** comprises five- and six-coordinate iron atoms. Although the framework compositions are different, their structures are closely related and the connection schemes of the building units are similar. Both compounds contain diprotonated (*S*)-2-methylpiperazinium cations in the structural tunnels. Compound **2** can also be formed with piperazine or a racemic mix of 2-methylpiperazine present as part of the structure. In contrast only the chiral species act as templates in compound **1**. This implies that the chirality of the organic amine is transferred to the host structure. The material may be potentially useful if the framework does not collapse and if the chirality remains when the templates are removed. However, attempts to remove or exchange the templates have not been successful probably because the framework contains terminal P-OH groups and coordinated water molecules, and the organic cations form strong interactions with the framework, and as a result, they are necessary to maintaining the integrity of the crystal structure. Therefore, the practical value of this material is very limited. The synthesis of a chiral microporous material using chiral amine as a structure-directing agent is a significant challenge. Further work on this theme is in progress.

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