$[NH_3(CH_2)_4NH_3]Fe_2[CH_3C(OH)(PO_3)(PO_3H)]_2{\cdot}2H_2O$: A Novel Iron(II) Diphosphonate with a Supramolecular Open Network Structure

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Increased attention has been paid to transition metal phosphonates in recent years due to their potential applications in ion exchange, absorption, and sensors.[1−3] Usually, the metal phosphonates adopt layered or pillared layered structures, with the organic groups filling in between the inorganic layers.[4,5] Other structural types have also been observed in some phosphonates, among which the porous structure is of particular interest.[6−8] We are currently interested in searching for new transition metal diphosphonates, based on 1-hydroxyethylidenediphosphonate [$CH_3C(OH)(PO_3)_2$, hedp], with possibly microporous frameworks. The effort has resulted in the preparation of a mixed-valence copper(I/II) compound $Na_2Cu_{15}(hedp)_6(OH)_2(H_2O)$[9] with a three-dimensional open-framework structure. As an extension to our previous work, herein we report the hydrothermal synthesis and characterization of an Fe(II) diphosphonate, $[NH_3(CH_2)_4NH_3]Fe_2(hedpH)_2{\cdot}2H_2O$, **1**, with a new structure type. It is worth noting that only a few examples of iron monophosphonates with lamellar structures have been described by Bujoli et al., including $HFe^{III}(C_6H_5PO_3H)_4$, $HFe^{III}(RPO_3)_2{\cdot}H_2O$ ($R = C_2H_5$, C_6H_5), $HFe^{III}(CH_3PO_3)_2$,[10−12] and $Fe^{II}(C_2H_5PO_3){\cdot}H_2O$.[13]

The title compound **1** was prepared by hydrothermal treatment of a mixture of $FeSO_4{\cdot}7H_2O$ (1 mmol, 0.2776 g), 50% hedpH_4 (1 cm^3), LiF (1 mmol, 0.0256 g), and H_2O (8 cm^3), adjusted by 1,4-butylenediamine to pH = 3, at 140 °C for 48 h. The colorless needles were collected as a monophasic material.[14] A suitable crystal was selected for an X-ray crystallographic study.[15] The structure of **1** can be best described by a supramolecular open network, built up from the strongly hydrogen-bonded covalent chains. Figure 1 depicts a fragment of the chain with the atomic labeling scheme, which contains centrosymmetric dimer units of $[Fe_2(hedpH)_2]^{2-}$. In this dimer unit, each Fe atom adopts a distorted octahedral coordination geometry with the six O atoms from three equivalent hedpH^{3-} ligands. The Fe−O bond lengths fall in the range 2.066(2)−2.312(2) Å, close to those in $Fe^{II}(C_2H_5PO_3){\cdot}H_2O$ [2.05(1)−2.35(1) Å].[13] The bond valence sum for Fe is 1.98.[16] The hedpH^{3-} ligand is bis-chelated and bridges the Fe atoms through the O(1), O(2), O(4), and O(5) atoms from phosphonate moieties and O(7) from the hydroxy group. The O(4) atom serves as a μ_3 bridging ligand which links the two iron octahedra through edge sharing, thus forming infinite double chains along the [100] direction (Figure 1). The Fe1···Fe1A distance is 3.354 Å. The P−O(Fe) lengths [1.504(2)−1.524(2) Å] are comparable to those in $Na_2Cu_{15}(hedp)_6(OH)_2(H_2O)$ [1.501(9)−1.525(8) Å].[9] Between the chains, there exists a very strong hydrogen-bonding interaction through O(3) and O(6). The O(3)···O(6^i) distance is 2.427(2) Å, and the O(3)−H(11)···O(6^i) bond angle is 170.2° (symmetry code for i: $2 - x$, $0.5 + y$, $0.5 - z$). Very strong hydrogen bonds have been observed in $CsMnHP_3O_{10}$

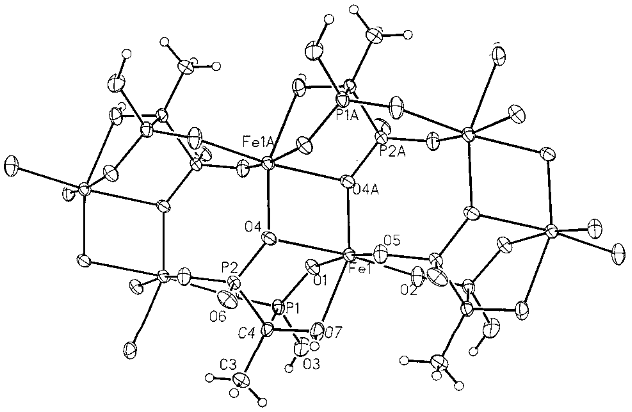

Figure 1. Fragment of the chain with atomic labeling scheme (50% probability) in **1**.

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(14) Elemental anal. Found (calcd) for $C_8H_{28}Fe_2N_2O_{16}P_4$: C, 14.96 (14.92); H, 4.20 (4.38); N, 4.20 (4.35). Yield: 60% based on Fe.

(15) Crystal data for $(C_4H_{14}N_2)[Fe_2(C_2H_5P_2O_7)_2]{\cdot}2H_2O$: monoclinic, space group $P2_1/c$, $a = 5.5362(2)$ Å, $b = 12.8676(5)$ Å, $c = 15.4337(5)$ Å, $\beta = 99.279(1)°$, $V = 1085.07(7)$ Å^3, $Z = 2$, $M_r = 643.90$, $D_c = 1.971$ g cm^{-3}, $F(000) = 660$, μ(Mo Kα) = 17.12 cm^{-1}, $\lambda = 0.710\ 73$ Å, crystal dimensions 0.5 × 0.1 × 0.1 mm. The crystal was mounted on a Siemens Smart-CCD diffractometer equipped with a normal focus, 3 kW sealed tube X-ray source. Intensity data were collected ($2\theta_{max} = 55.9°$) in 1271 frames with increasing ω (width of 0.30° per frame). Number of measured and observed reflections [$I > 2\sigma(I)$]: 2364, 1981 ($R_{int} = 0.0281$). Empirical absorption correction was applied using the SADABS program ($T_{min,max} = 0.839$, 0.966). The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL.[24] All of the non-hydrogen atoms were refined anisotropically. The H atoms were located from the electron density maps and refined isotropically. $(\Delta\rho)_{max,min} = 0.453$, -0.313 e Å^{-3}. R1 = 0.0245, wR2 = 0.0624, GOF = 1.007.

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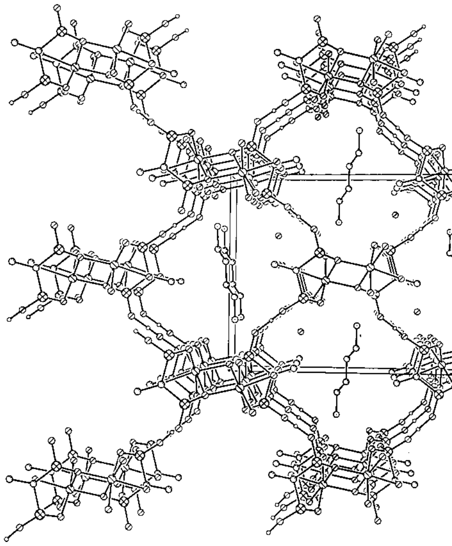

Figure 2. Crystal packing of **1** viewed along the [100] direction. All H atoms except H(11) are omitted for clarity.

[O···O distance 2.372(12) Å][17] and many hydrogen phosphates such as $CaHPO_4$.[18] Consequently, comparing with the protonated P−O(H) [1.561(2), 1.571(2) Å] and the pendant P═O [1.502(2), 1.514(2) Å] distances in $[NH_3(CH_2)_4NH_3]Ni(hedpH_2)_2(H_2O)_2$,[19] the bond length of P(1)−O(3)(H) [1.549(2) Å] in **1** is significantly shorter whereas that of the P(2)═O(6) [1.538(2) Å] is much longer. A three-dimensional supramolecular framework is therefore constructed by the assembly of $[Fe_2(hedpH)_2]_n^{2n-}$ chains through strong hydrogen bonding, with one-dimensional channels created along the *a* axis (Figure 2). The $[NH_3(CH_2)_4NH_3]^{2+}$ cations and water molecules reside in the channels with extensive hydrogen-bonding interactions. The three shortest N···O distances are 2.789(3), 2.788(2), and 2.824(2) Å for N(1)···O(1), N(1)···O(6^{ii}), and N(1)···O(5^{ii}) (symmetry code for ii: $1 - x, -y, -z$), respectively. The bond lengths and angles for $[NH_3(CH_2)_4NH_3]^{2+}$ are normal.

The infrared spectrum of **1** exhibits a series of bands in the 1000−1200 cm^{-1} range associated with PO_3 group vibrations. The broad band appearing around 3000 cm^{-1} is due to O−H stretching of hydrogen-bonded hydroxyl groups including water molecules and protonated phosphonates.[20] The thermal analysis shows a weight loss (5.7%) in the temperature range 160−250 °C, corresponding to the release of two molecules of water (calcd 5.6%). Further weight loss (15.0%) between 280 and 460 °C is larger than that calculated for the removal of one molecule of 1,4-butylenediamine (13.7%), suggesting the collapse of the structure at higher temperature. The room temperature Mössbauer spectrum confirms the presence of ferrous ion. The least-squares fit of one doublet resulted in the parameters δ (isomer shift) = 1.41 mm/s and ΔE_Q (quadrupole splitting) = 1.01 mm/s, which are typical of a high-spin Fe(II).[21] The temperature dependent molar magnetic susceptibility measurement of **1** reveals that the magnetic moment at 300 K is 7.92 μ_B per molecule, which agrees with the expected spin-only value for two high-spin Fe(II) centers ($\mu_{eff} = 7.62\ \mu_B$ for $g = 2.2$). On cooling from room temperature, the gradual increasing of $\chi_m T$ indicates a dominant ferromagnetic exchange down to 36 K, which is confirmed by a positive Weiss constant (+10.4 K) determined in the temperature range 100−300 K. It has been suggested that the Fe−X−Fe angles close to 90° promote ferromagnetic exchange coupling in diferrous compounds.[22] The ferromagnetic exchange in **1** could be caused by the relatively small Fe(1)−O(4)−Fe(1A) angle [99.83(5)°]. The sharp decrease of $\chi_m T$ below 36 K is attributed to the zero-field splitting of the ground state. Similar phenomena have been observed in several other μ-O or μ-X (X = F, Cl) bridged diiron(II) complexes [Fe−O(X)−Fe angles 91.9−101.7°].[22,23] Compound **1** is not stable and oxidized slowly by exposure to air for several days; the oxidation can be recognized from the sample's light brown color. The Mössbauer spectrum of the fully oxidized sample shows a doublet with parameters δ (isomer shift) = 0.28 mm/s and ΔE_Q (quadrupole splitting) = 0.41 mm/s.

The structure of **1** is apparently different from that of the mononuclear species $[NH_3(CH_2)_4NH_3]Ni(hedpH_2)_2(H_2O)_2$,[19] although the same organic template is employed. Such a structural difference could originate from the versatile coordination abilities of Fe(II) compared with Ni(II). However, it has to be noted that the template may play an important role in directing the structure of the title compound and, further, stabilizing an Fe(II) oxidation state. Further work is in progress to investigate the template role in directing the structures of Fe−hedp compounds and in stabilizing different oxidation states of iron.

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Supporting Information Available: Plots of XRD, IR, TGA, Mössbauer spectra, and magnetic susceptibility. An X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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