

# [NH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>NH<sub>3</sub>][Fe<sub>2</sub>{O<sub>3</sub>PC(CH<sub>3</sub>)(OH)(PO<sub>3</sub>H)}<sub>2</sub>]·2H<sub>2</sub>O: 一个新的二膦酸亚铁化合物的合成、结构与性质研究

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通过水热合成得到一个新的有机二膦酸亚铁化合物[NH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>NH<sub>3</sub>][Fe<sub>2</sub>{O<sub>3</sub>PC(CH<sub>3</sub>)(OH)(PO<sub>3</sub>H)}<sub>2</sub>]·2H<sub>2</sub>O, 该化合物包含阴离子型共价双链[Fe<sub>2</sub>{O<sub>3</sub>PC(CH<sub>3</sub>)(OH)PO<sub>3</sub>H}<sub>2</sub>]<sup>2-</sup>, 质子化的戊二胺和结晶水, 双链之间通过强氢键构成一个开放型的骨架结构。另外, 观察到亚铁离子之间存在弱铁磁性相互作用。

**关键词:** 二膦酸亚铁化合物    晶体结构    磁性    穆斯堡尔谱

**分类号:** 0614.81<sup>+</sup>1

## Synthesis, Structure and Properties of a New Iron (II) Diphosphonate: [NH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>NH<sub>3</sub>][Fe<sub>2</sub>{O<sub>3</sub>PC(CH<sub>3</sub>)(OH)(PO<sub>3</sub>H)}<sub>2</sub>]·2H<sub>2</sub>O

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Under hydrothermal conditions, a new iron (II) diphosphonate namely [NH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>NH<sub>3</sub>][Fe<sub>2</sub>{O<sub>3</sub>PC(CH<sub>3</sub>)(OH)(PO<sub>3</sub>H)}<sub>2</sub>]·2H<sub>2</sub>O was synthesized and structurally characterized. The compound contains covalent double chains of [Fe<sub>2</sub>{O<sub>3</sub>PC(CH<sub>3</sub>)(OH)PO<sub>3</sub>H}<sub>2</sub>]<sup>2-</sup>, charge balanced by the protonated pentamethylenediamine. The double chains are held together by very strong hydrogen bonds, forming a three-dimensional open network. Weak ferromagnetic coupling is observed for the compound.

**Keywords:** iron diphosphonate    crystal structure    magnetic property    Mössbauer spectra

## 0 Introduction

An increasing attention has been paid to the metal phosphonate chemistry in recent years, primarily due to their potential applications in ion exchanges, absorp-

tions and sensors<sup>[1~6]</sup>. A number of phosphonate compounds have been prepared, among which compounds with open framework or porous structures are of most interest<sup>[7~11]</sup>.

As an extension to our previous studies of template

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influences on directing the structures of transition metal phosphonates, based on 1-hydroxyethylidenediphosphonate [hedp,  $\text{O}_3\text{PC}(\text{CH}_3)(\text{OH})(\text{PO}_3\text{H})_2$ ]<sup>12-16</sup>. herein we report the structure and magnetic properties of a new iron-hedp compound  $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3^+][\text{Fe}_2^{II}(\text{O}_3\text{PC}(\text{CH}_3)(\text{OH})(\text{PO}_3\text{H})_2)_2] \cdot 2\text{H}_2\text{O}$  (1). To the best of our knowledge, iron phosphonate compounds reported so far are still rather limited in number, including  $\text{HFe}^{III}(\text{C}_n\text{H}_2\text{PO}_3\text{H})_2$ ,  $\text{HFe}^{II}(\text{RPO}_3)_2 \cdot \text{H}_2\text{O}$  ( $\text{R} = \text{C}_2\text{H}_5$ ,  $\text{C}_6\text{H}_5$ ),  $\text{HFe}^{II}(\text{CH}_3\text{PO}_3)_2$ <sup>17-19</sup>,  $\text{Fe}^{II}(\text{C}_3\text{H}_5\text{PO}_3) \cdot \text{H}_2\text{O}$ <sup>20</sup>,  $[\text{Fe}_2(\text{H}_2\text{O})_2(\text{O}_3\text{PCH}_2\text{PO}_3\text{H})_2] (\text{H}_2\text{O})_2$ <sup>21</sup>, and  $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3^+][\text{Fe}_2^{II}(\text{O}_3\text{PC}(\text{CH}_3)(\text{OH})(\text{PO}_3\text{H})_2)_2] \cdot \text{H}_2\text{O}$ <sup>15</sup>.

## 1 Experimental

### 1.1 Materials and Methods

All the starting materials were reagent grade used as purchased. Elemental analyses were performed on a PE 240C elemental analyzer. Infrared spectra were recorded on a IFS66V spectrometer with pressed KBr pellets. Mössbauer spectrum was carried out with an Austin S-600 Mössbauer spectrometer using a <sup>57</sup>Cu/Pd source. The instrument was calibrated by a standard sample of  $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O}$  (SNP) at room temperature. The isomer shift was reported relative to SNP. Variable-temperature magnetic susceptibility data were obtained on polycrystalline sample (38.8mg) from 2 to ca. 300K in a magnetic field of 10kOe after zero-field cooling using a MagLab System 2000 magnetometer. Diamagnetic corrections were estimated from Pascal's constants<sup>22</sup>.

### 1.2 Synthesis of $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3^+][\text{Fe}_2(\text{O}_3\text{PC}(\text{CH}_3)(\text{OH})(\text{PO}_3\text{H})_2)_2] \cdot 2\text{H}_2\text{O}$ (1)

Hydrothermal treatment of a mixture of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (1mmol, 0.2787g), 50% hedpH<sub>4</sub> (1cm<sup>3</sup>), LiF (1mmol, 0.0265g) and  $\text{H}_2\text{O}$  (8cm<sup>3</sup>), adjusted by 1, 5-pentamethylenediamine to pH ≈ 3.5, at 140°C for 48h resulted in the monophasic colorless needle-like crystals. The crystals were further used for single crystal structure determination and property measurements. Anal. Calcd. for  $\text{C}_{10}\text{H}_{30}\text{Fe}_2\text{N}_2\text{O}_{16}\text{P}_4$ : C, 16.16; H, 4.88; N, 3.77%. Found: C, 16.25; H, 4.79; N, 3.74%. IR (KBr): 3653m, 3426s, 3260s(br), 1676m, 1628m, 1563m, 1530m, 1502m, 1474m, 1418w, 1371w, 1135s, 1006s, 924s, 901s, 793m, 669w, 568m, 497w.

462w, 416m, 407m · cm<sup>-1</sup>. Same compound can be obtained without the addition of fluoride. The compound is not stable and can be oxidized in air slowly, as suggested by its brown color on the crystal surfaces.

### 1.3 Crystallographic Studies

A single crystal with dimensions  $0.15 \times 0.06 \times 0.06$  mm was used for structural determination on a Siemens Smart-CCD diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073\text{\AA}$ ) at room temperature. Intensity data were collected in 1271 frames. The data were integrated using the Siemens SAINT program<sup>23</sup>, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Empirical absorption correction was applied.

The structure was solved by direct method and refined on  $F^2$  by full-matrix least squares using SHELXTL<sup>24</sup>. All non-hydrogen atoms except the C and N atoms in  $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3]^{\pm}$  were refined with anisotropic displacement parameters. The pentamethylenediammonium cations are disordered over two sites, each with occupancy factors fixed at 0.33333 and 0.16666, respectively. The C-C and C-N constraints were used in the further refinements. All hydrogen atoms except those in  $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3]^{\pm}$  were located in difference electron density maps and refined with the isotropic displacement parameters 1.2 or 1.4 times the preceding normal atoms. The hydrogen atoms in  $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3]^{\pm}$  were placed in calculated positions. The disordered C and N atoms and all hydrogen atoms were refined isotropically. Crystallographic data are summarized in Table 1, atomic coordinates in Table 2, and selected bond lengths and angles in Table 3.

## 2 Results and Discussion

### 2.1 Description of the Structure

Compound 1 crystallizes in space group  $P2_1/c$ . It contains anionic double chains of  $[\text{Fe}_2(\text{O}_3\text{PC}(\text{CH}_3)(\text{OH})(\text{PO}_3\text{H})_2)_2]^{3-}$ , charge balanced by protonated pentamethylenediamine (Fig. 1 and 2). The double chain is constructed from two equivalent single chains by edge-sharing of the  $\{\text{FeO}_6\}$  octahedra. Within each single chain, the diphosphonate  $(\text{O}_3\text{PC}(\text{CH}_3)(\text{OH})(\text{PO}_3\text{H})_2)_2$

Table 1 Crystallographic Data

compound	1
formula	$C_{11}H_{16}N_2Fe_2O_1P_4$
M	657.93
crystal system	monoclinic
space group	$P2_1/c$
a/ $\text{\AA}$	5.5407(11)
b/ $\text{\AA}$	12.726(2)
c/ $\text{\AA}$	16.1371(4)
$\beta$ (°)	99.38(2)
V/ $\text{\AA}^3$	1122.71(4)
Z	2
D (g $\cdot \text{cm}^{-3}$ )	1.946
F(000)	676
$\mu(MoK\alpha) / \text{cm}^{-1}$	16.57
goodness of fit on $F^2$	1.053
$R_1$ , w $R_2$ [ $f > 2\sigma(f)$ ]	0.0350, 0.0892
(all data)	0.0441, 0.0922
( $\Delta\rho$ ) <sub>max</sub> , ( $\Delta\rho$ ) <sub>min</sub> ( $e \cdot \text{\AA}^{-3}$ )	0.433, -0.377

$$wR_2 = \sum |(F_0) - (F_1)| / \sum |F_0|$$

$$wR_2 = [\sum w(F_0^2 - F_1^2)^2 / \sum w(F_0^2)]^{1/2}$$

$(PO_3H)^{3-}$  bridges the Fe atoms in a bis(chelating) mode using O(1), O(2), O(4), O(5) and O(7) atoms. Therefore, the double chain structure can be viewed as a ladder with the  $\{Fe_2(\mu-O)_2\}$  as the rung and the

$\{O_3PC(CH_3)(OH)(PO_3H)\}^{3-}$  group as the rail (Fig. 1). The Fe atom, sitting at an inversion center, has a distorted octahedral geometry. The Fe-O bond lengths [2.057(3) ~ 2.338(3)  $\text{\AA}$ ] are comparable to those in the other Fe(II)-phosphonate compounds<sup>15~20</sup>. The Fe(1)···Fe(1B) distance over the  $\mu$ -O bridge is 3.417  $\text{\AA}$ , and the Fe(1)-O(4)-Fe(1B) angle is 101.3(1)°. The bond valence sum calculated for Fe is 1.97<sup>21</sup>.

The phosphonate oxygens in  $[O_3PC(CH_3)(OH)(PO_3H)]^{3-}$  in the title compound is singly protonated. Each phosphonate group presents one terminal bonding with a slightly longer P-O distance [P(1)-O(3) 1.541(3)  $\text{\AA}$ , P(2)-O(6) 1.540(3)  $\text{\AA}$ ]. The hydrogen atom must link the two terminal oxygen atoms in order to satisfy the valence of oxygen. Subsequently, a very strong hydrogen bond is found between the neighboring double chains with the O(3)···O(6') distance 2.454  $\text{\AA}$ . Hence a three-dimensional supra-molecular network structure is built up from hydrogen bonded  $[Fe_2^{II}(O_3PC(CH_3)(OH)(PO_3H))_2]^{3n-}$  double chains with one-dimensional channels generated along the [100] di-

Table 2 Atomic Coordinates and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2$ ) for 1

atom	x	y	z	$U(eq)$	atom	x	y	z	$U(eq)$
Fe(1)	0.3839(1)	0.0512(1)	0.0831(1)	0.021(1)	P(1)	0.8913(2)	0.1483(1)	0.1579(1)	0.021(1)
P(2)	0.8966(2)	-0.0831(1)	0.1176(1)	0.019(1)	O(1)	0.6644(5)	0.1627(2)	0.0924(2)	0.023(1)
O(2)	1.1358(5)	0.1589(2)	0.1284(2)	0.029(1)	O(3)	0.8674(6)	0.2245(3)	0.2304(2)	0.034(1)
O(4)	0.6829(5)	-0.0609(2)	0.0477(2)	0.022(1)	O(5)	1.1501(5)	-0.0714(2)	0.0950(2)	0.026(1)
O(6)	0.8604(6)	-0.1937(2)	0.1522(2)	0.031(1)	O(7)	0.6122(6)	0.0095(3)	0.2139(2)	0.026(1)
O(1W)	0.5703(8)	-0.1612(3)	0.3092(3)	0.057(1)	C(2)	1.0448(8)	-0.0026(4)	0.2798(3)	0.027(1)
C(1)	0.8656(7)	0.0141(4)	0.1993(3)	0.020(1)	N(1)	0.5860(40)	0.2552(11)	-0.0693(13)	0.017(2)
N(2)	0.3770(40)	0.7429(10)	0.0570(11)	0.017(2)	C(11)	0.7420(30)	0.3477(11)	-0.0718(13)	0.058(2)
C(12)	0.6730(30)	0.4448(12)	-0.0309(13)	0.058(2)	C(13)	0.4250(30)	0.4553(11)	-0.0058(12)	0.058(2)
C(14)	0.3200(30)	0.5650(11)	-0.0026(11)	0.058(2)	C(15)	0.3930(40)	0.6296(10)	0.0738(10)	0.058(2)
N(2)	0.6750(50)	0.2457(16)	-0.0782(19)	0.017(2)	N(22)	0.3850(50)	0.7281(15)	0.1045(15)	0.017(2)
C(21)	0.7190(50)	0.3500(20)	-0.0400(30)	0.058(2)	C(22)	0.4730(50)	0.3837(17)	-0.0190(20)	0.058(2)
C(23)	0.4250(60)	0.4984(18)	-0.0287(15)	0.058(2)	C(24)	0.4020(70)	0.5468(17)	0.0557(18)	0.058(2)
C(25)	0.5140(60)	0.6546(19)	0.0580(20)	0.058(2)					

$U(eq)$  is defined as one third of the trace of the orthogonalized  $U_{eq}$  tensor.

Table 3 Selected Bond Lengths ( $\text{\AA}$ ) and Angles (°) for 1

Fe(1)-O(5A)	2.057(3)	Fe(1)-O(4B)	2.088(3)	Fe(1)-O(1)	2.091(3)	Fe(1)-O(2A)	2.152(3)
Fe(1)-O(4)	2.327(3)	Fe(1)-O(7)	2.338(3)	P(1)-O(2)	1.513(3)	P(1)-O(1)	1.516(3)
P(1)-O(3)	1.541(3)	P(1)-C(1)	1.848(5)	P(2)-O(5)	1.515(3)	P(2)-O(4)	1.523(3)
P(2)-O(6)	1.540(3)	P(2)-C(1)	1.835(5)				
O(5A)-Fe(1)-O(4B)	97.37(12)	O(5A)-Fe(1)-O(1)	168.48(12)	O(4B)-Fe(1)-O(1)	92.27(12)	O(5A)-Fe(1)-O(2A)	90.28(12)
O(4B)-Fe(1)-O(2A)	106.76(12)	O(1)-Fe(1)-O(2A)	92.97(12)	O(5A)-Fe(1)-O(4)	92.42(11)	O(4B)-Fe(1)-O(4)	78.68(12)
O(1)-Fe(1)-O(4)	83.27(11)	O(2A)-Fe(1)-O(4)	173.57(11)	O(5A)-Fe(1)-O(7)	90.02(12)	O(4B)-Fe(1)-O(7)	155.13(12)
O(1)-Fe(1)-O(7)	78.63(12)	O(2A)-Fe(1)-O(7)	96.87(12)	O(4)-Fe(1)-O(7)	77.30(11)	P(1)-O(1)-Fe(1)	119.39(17)
P(2)-O(4)-Fe(1B)	138.5(2)	P(2)-O(4)-Fe(1)	115.51(17)	Fe(1B)-O(4)-Fe(1)	101.32(12)	C(11)-O(7)-Fe(1)	103.7(2)

Symmetry transformations used to generate equivalent atoms: A:  $x+1, y, z$ ; B:  $-x+1, -y, -z$ .

Table 4 Hydrogen Bonds ( $\text{\AA}$ ,  $^\circ$ ) for **1**

D - H $\cdots$ A	$d(\text{D-H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle(\text{DHA})$	D - H $\cdots$ A	$d(\text{D-H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle(\text{DHA})$
O(3) - H(3) $\cdots$ O(6) <sup>a</sup>	0.78(5)	1.68(5)	2.454(4)	170(6)	O(7I) - H(7I) $\cdots$ O(1W)	0.77(5)	1.93(5)	2.693(5)	176(6)
O(1W) - H(1WA) $\cdots$ O(3) <sup>a</sup>	0.90(6)	2.0416	2.811(5)	143(6)	O(1W) - H(1WB) $\cdots$ O(2) <sup>a</sup>	0.94(6)	2.03(7)	2.894(5)	151(5)
N(1) - H(1A) $\cdots$ O(5) <sup>a</sup>	0.89	2.01	2.82(2)	151.3	N(1) - H(1B) $\cdots$ O(6) <sup>a</sup>	0.89	2.00	2.730(17)	138.6
N(1) - H(1C) $\cdots$ O(1I)	0.89	1.98	2.83(2)	159.8	N(2I) - H(2I2C) $\cdots$ O(1I) <sup>a</sup>	0.89	2.11	2.671(17)	120.6
N(2I) - H(2IC) $\cdots$ O(6) <sup>a</sup>	0.89	2.22	3.08(2)	164.2	N(2I) - H(2IE) $\cdots$ O(1I)	0.89	2.20	2.96(3)	142.9

Symmetry transformations used to generate equivalent atoms: i:  $-x+1, -y, -z$ ; ii:  $-x+2, y+1/2, -z+1/2$ ; iii:  $-x+1, y-1/2, -z+1/2$ ; iv:  $-x+2, y-1/2, -z+1/2, v: -x+2, -y, -z$ ; vi:  $-x+1, -y+1, -z$ .

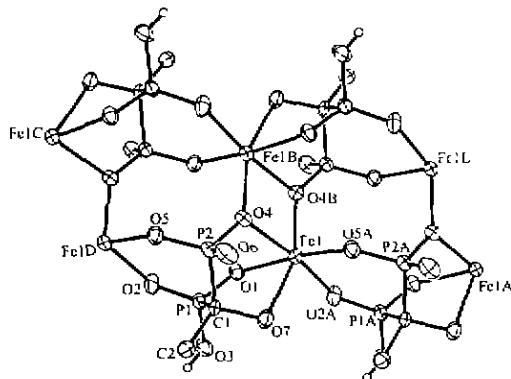


Fig. 1 A fragment of the double chain in **1** with atomic labeling scheme (50% probability)

All H atoms except H(3) are omitted for clarity.

reaction (Fig. 2). The disordered  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]^{2+}$  cations and water molecules reside in the channels with extensive hydrogen bonding interactions (Table 4). Compound **1** is isostructural to  $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3][\text{Fe}_2^{II}\{\text{O}_3\text{PC}(\text{CH}_3)(\text{OH})(\text{PO}_3\text{H})\}_2]\cdot\text{H}_2\text{O}$ , previously reported by us as a communication<sup>[15]</sup>.

## 2.2 Mössbauer Spectrum

The room temperature Mössbauer spectrum for the title compound is shown in Fig. 3. It can be least-squares fitted with one doublet corresponding to the one type of iron components. The parameters  $\delta$  (isomer shift) and  $\Delta E_0$  (quadrupole splitting) obtained are 1.63 and  $1.35 \text{ mm} \cdot \text{s}^{-1}$ , respectively, typical of high-spin Fe(II) ions<sup>[26, 27]</sup>. The result agrees well with the magnetic measurements.

## 2.3 Magnetic Properties

Fig. 4 shows the temperature dependent molar magnetic susceptibilities in the forms of  $\chi_{\text{M}}$  and  $\chi_{\text{M}}T$  vs  $T$  plots for **1**. The effective magnetic moment at 298 K (6.16  $\mu_{\text{B}}$  per Fe) is much higher than the spin-only value of 4.90  $\mu_{\text{B}}$  for  $S=2$ , attributed to the orbital contribution of high spin Fe(II) ions. The Weiss constant, determined in the temperature range 100 to 300K, is +22.7K, suggesting a weak ferromagnetic

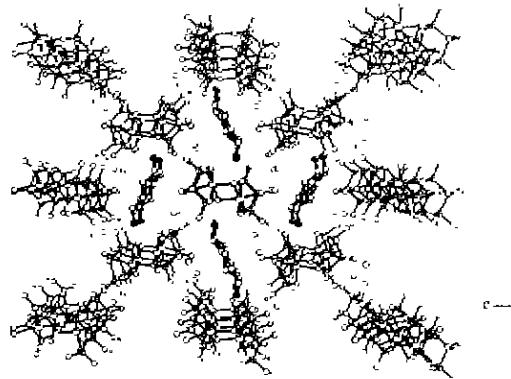


Fig. 2 Crystal packing of **1** viewed along  $a$ -axis  
All H atoms except H(3) are omitted for clarity

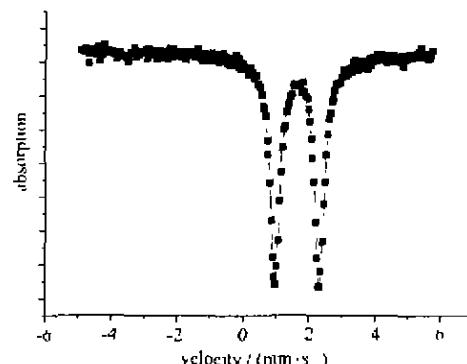
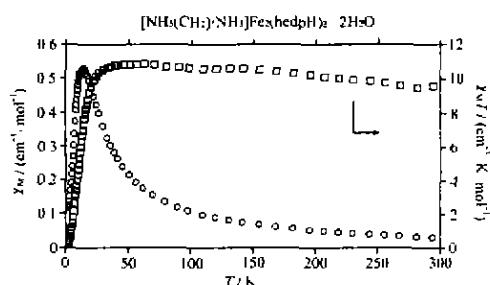


Fig. 3 Mössbauer spectrum for **1**  
exchange between the magnetic centers. The ferromagnetic interaction is confirmed by the slow increasing of  $\chi_{\text{M}}T$  on cooling from room temperature before a maximum is reached at 62K. Below 62K, the  $\chi_{\text{M}}T$  value drops rapidly which could be caused by the zero-field splitting of the ground state. According to the structure mentioned above, compound **1** contains a double chain structure linked by strong hydrogen bonds. Within the double chain, there exists oxygen bridged  $\{\text{Fe}_2\text{O}_2\}$  dimers. The dimers are further connected by O-P-O bridges. As the O-P-O bridge is usually not efficient in mediating the magnetic interactions because of electron localization, the dominant

Fig. 4  $\chi_M$  and  $\chi_M/T$  vs  $T$  plots for 1

ferromagnetic coupling observed in 1 should be mainly attributed to the  $\{Fe_2O_2\}$  dimers. The theoretical fitting using an isotropic dimer model for  $S = 2$ , based on the data in the temperature range 60 ~ 300K, led to parameters  $g = 2.56$ ,  $J = +1.21 cm^{-1}$ . A similar fitting based on the data in the whole temperature range was not successful. Ferromagnetic exchange couplings are also observed in the other  $\mu$ -O or  $\mu$ -X ( $X = F, Cl$ ) bridged diferrous complexes where the Fe-O(X)-Fe angles fall in the range 91.9 to 101.7° [15, 28, 29]. The Fe-O-Fe angle in 1 is 101.3°.

In summary, this paper reports a new iron (II) diphosphonate chain compound,  $[NH_3(CH_2)_4NH_3][Fe_2\{O_3PC(CH_3)(OH)(PO_3H)\}_2] \cdot 2H_2O$ . The very strong inter-chain hydrogen bonds connect the chains into an open network structure. A dominant ferromagnetic interaction is observed.

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