

Hydrothermal synthesis and crystal structure of a three-dimensional metal selenite containing double helical chains: $\text{Fe}_3(\text{H}_2\text{O})(\text{SeO}_3)_3$

Dongrong Xiao, Yu Hou, Enbo Wang,* Haiyan An, Jian Lü, Yangguang Li, Lin Xu, and Changwen Hu

Institute of Polyoxometalate Chemistry, Department of Chemistry, Northeast Normal University, Changchun, Jilin 130024, People's Republic of China

Received 7 January 2004; accepted 9 April 2004

Abstract

A novel three-dimensional (3D) transition metal selenite $\text{Fe}_3(\text{H}_2\text{O})(\text{SeO}_3)_3$ (**1**) has been hydrothermally synthesized and characterized by the elemental analyses, IR spectrum, TG analysis and the single-crystal X-ray diffraction. Compound **1** crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 8.0916(16)$ Å, $b = 8.2089(16)$ Å, $c = 8.5679(17)$ Å, $\alpha = 69.21(3)^\circ$, $\beta = 62.74(3)^\circ$, $\gamma = 67.16(3)^\circ$, $Z = 2$, and $R_1[I > 2\sigma(I)] = 0.0379$. Compound **1** exhibits an interesting 3D framework formed by $\{\text{FeO}_6\}$ octahedra and $\{\text{SeO}_3\}$ trigonal pyramids via the corner- and/or edge-sharing mode. Furthermore, compound **1** consists of left-handed and right-handed helical chains, which are further entangled to form the double helical chains.

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Keywords: Metal selenite; Helical chains; Hydrothermal synthesis; Crystal structure

1. Introduction

Microporous inorganic materials including zeolites, aluminum phosphates, and transition metal phosphates are particularly important for their applications as molecular sieves, desiccants, ion exchangers, and catalysts [1,2], and thus they have been studied in detail in the past decades. An important objective in this area of research is to design compounds with novel framework structures. In this regard, a large variety of transition metal cations have been combined with PO_4^{3-} anion to prepare open-framework phosphates [1]. In contrast to the rich structural chemistry of transition metal phosphates, the $\{M/X/O\}$ system (M = transition metal, X = S, Se or Te) remains relatively undeveloped. Recent researches indicate that the structural versatility not only can be brought about by changing the cations, but also can be brought about by changing the anionic moiety of the framework [3–7]. On the basis of the latter mode, we have been attempting to design inorganic architectures making use of the oxy-anions of group 16,

namely S, Se and Te [8]. Furthermore, it is noteworthy that the ubiquitous presence of a stereochemically active lone-pair of electrons on the Se(IV) centers can play a substantial role in the crystalline architectures of this family of compounds [7]. In fact, the entire structure is affected by the requirement for “empty” space to accommodate the selenium lone-pair electrons [7]. Thus, it can be presumed that the combination of the inherently asymmetric $[\text{SeO}_3]^{2-}$ group with the transition metal may result in a rich structural chemistry of transition metal selenites.

Among the large amount of reported work, the design and synthesis of inorganic materials with helical structures are of particular interest and of great challenge [9–13]. In this work, we report the hydrothermal synthesis and crystal structure of a novel 3D transition metal selenite $\text{Fe}_3(\text{H}_2\text{O})(\text{SeO}_3)_3$ (**1**), which consists of left-handed and right-handed helical chains. Furthermore, compound **1** exhibits a novel 3D Fe–O–Fe framework grafted with the selenium atoms. It is noteworthy that the transition metal complex containing 3D M –O– M framework may exhibit many of the cooperative effects well known in the transition metal oxides and good thermal stability [14].

*Corresponding author. Fax: +86-431-568-4009.

E-mail address: wangbenbo@public.cc.jl.cn (E. Wang).

2. Experimental section

2.1. General procedures

All the chemicals were commercially purchased and were used without further purification. Fe, and Se were determined by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectrum was recorded in the range 400–4000 cm^{-1} on an Alpha Centaur FT/IR Spectrophotometer using KBr pellets. TG analysis was performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10°C · min⁻¹.

2.2. Hydrothermal synthesis

In a typical synthesis procedure for **1**, a mixture of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (1 mmol), SeO_2 (1 mmol), and 9 mL of H_2O was stirred for 30 min in air. The starting pH value was adjusted to 4.0 by the addition of ethylenediamine. The mixture was then sealed in an 18 mL Teflon-lined autoclave, which was heated to 160°C for 120 h. After slow cooling to room temperature, the resulting dark red block crystals **1** were filtered off, washed with distilled water, and dried at ambient temperature (yield: ca. 85% based on Fe). Elemental analyses results of the dark red crystals are consistent with the stoichiometry of **1**. Calc. for $\text{Fe}_3\text{H}_2\text{O}_{10}\text{Se}_3$ **1**: Fe, 29.6; Se, 41.8%. Found: Fe, 29.5; Se, 41.9%. FT/IR data (cm^{-1}) for **1**: 3445(s), 1644(m), 688(s), 675(s), 553(m), 505(m), 468(m), 438(m), 425(m), 416(m), 412(m).

2.3. X-ray crystallography

The structure of compound **1** was determined by single-crystal X-ray diffraction. A dark red single crystal of **1** with dimensions 0.49 × 0.38 × 0.33 mm was mounted on a glass fiber. The data were collected on a Rigaku R-AXIS RAPID IP diffractometer with $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) at 293 K in the range of $2.74 < \theta < 27.47^\circ$. Numerical absorption correction was applied. The structure was solved by the direct method and refined by the full-matrix least-squares on F^2 using the SHELXL-97 software [15]. All the non-hydrogen atoms were refined anisotropically. On the basis of bond valence sum calculations [16], OW1 was found to be considerably undersaturated. Since two hydrogen atoms must be included to balance the charge, and a valence sum of 0.44 was calculated for OW1, it is probable that OW1 is a water molecule. The hydrogen atoms were not located. A total of 2974 (1963 unique, $R_{\text{int}} = 0.0483$) reflections were measured ($-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $-11 \leq l \leq 11$). Structure solution and the refinement based on 1963 independent reflections and 148 parameters gave $R_1(wR_2) = 0.0379$ (0.1088) $\{R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}\}$.

Table 1
Crystal data and structure refinement for **1**

Chemical formula	$\text{Fe}_3\text{H}_2\text{O}_{10}\text{Se}_3$
Formula weight	566.45
T (K)	293(2)
λ (Å)	0.71073
Space group	$P\bar{1}$
a (Å)	8.0916(16)
b (Å)	8.2089(16)
c (Å)	8.5679(17)
α (deg)	69.21(3)
β (deg)	62.74(3)
γ (deg)	67.16(3)
V (Å ³)	455.21(16)
Z	2
Dc (g/cm ³)	4.133
μ (mm ⁻¹)	16.751
$R_1^a [I > 2\sigma(I)]$	0.0379
$wR_2^b [I > 2\sigma(I)]$	0.1088

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}.$$

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**

	x	y	z	U_{eq}
Se(3)	4354(1)	2661(1)	2613(1)	8(1)
Se(2)	1765(1)	1694(1)	7981(1)	9(1)
Se(1)	2032(1)	8325(1)	4356(1)	8(1)
Fe(4)	3460(1)	4630(1)	7012(1)	6(1)
Fe(3)	2834(1)	6436(1)	1102(1)	7(1)
Fe(2)	5000	0	0	5(1)
Fe(1)	0	5000	5000	6(1)
O(9)	5466(6)	1955(6)	640(6)	11(1)
O(8)	4006(6)	6745(6)	4727(6)	12(1)
O(7)	1328(6)	7136(6)	3583(6)	13(1)
O(6)	2146(6)	3947(6)	2583(6)	11(1)
O(5)	1906(6)	3587(6)	6259(6)	12(1)
O(4)	3026(6)	2123(6)	8852(6)	10(1)
O(3)	-497(6)	2226(6)	9513(6)	14(1)
OW1	811(6)	6301(7)	8100(6)	18(1)
O(2)	2912(6)	9818(6)	2532(6)	14(1)
O(1)	5373(6)	4438(6)	1743(6)	11(1)

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

A summary of crystal data and structure refinement for compound **1** is provided in Table 1. The atomic coordinates and equivalent isotropic displacement parameters for **1** are given in Table 2. The selected bond lengths and angles are listed in Table 3. Crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters were available in supplementary crystallographic data (CSD reference number: 413607).

3. Results and discussion

3.1. Synthesis

Hydrothermal synthesis has recently been proved to be a useful technique in the preparation of solid-state

Table 3
Selected bond lengths (Å) and angles (deg) for **1**

Fe(1)–O(5)	2.033(4)	Fe(1)–O(7)	2.112(4)
Fe(1)–O(5)#2	2.033(4)	Fe(1)–O(6)#2	2.205(4)
Fe(1)–O(7)#2	2.112(4)	Fe(1)–O(6)	2.205(4)
Fe(2)–O(2)#3	2.047(4)	Fe(2)–O(9)#5	2.074(4)
Fe(2)–O(2)#4	2.047(4)	Fe(2)–O(4)#6	2.149(4)
Fe(2)–O(9)	2.074(4)	Fe(2)–O(4)#7	2.149(4)
Fe(3)–O(3)#2	1.987(4)	Fe(3)–O(6)	2.118(4)
Fe(3)–O(9)#3	1.999(5)	Fe(3)–O(1)	2.234(4)
Fe(3)–O(7)	2.070(5)	Fe(3)–O(1)#3	2.398(4)
Fe(4)–O(4)	2.143(4)	Fe(4)–OW1	2.035(4)
Fe(4)–O(1)#1	2.164(4)	Fe(4)–O(8)#1	2.073(4)
Fe(4)–O(5)	2.168(4)	Fe(4)–O(8)	2.106(5)
Se(1)–O(2)	1.658(4)	Se(2)–O(3)	1.688(4)
Se(1)–O(8)	1.703(4)	Se(2)–O(4)	1.699(4)
Se(1)–O(7)	1.718(4)	Se(2)–O(5)	1.721(5)
Se(3)–O(6)	1.693(4)	Se(3)–O(1)	1.721(4)
Se(3)–O(9)	1.703(4)		
O(6)–Se(3)–O(9)	103.3(2)	O(3)–Se(2)–O(4)	100.9(2)
O(6)–Se(3)–O(1)	95.5(2)	O(3)–Se(2)–O(5)	105.0(2)
O(9)–Se(3)–O(1)	93.6(2)	O(4)–Se(2)–O(5)	94.5(2)
O(2)–Se(1)–O(7)	103.5(2)	O(2)–Se(1)–O(8)	105.0(2)
O(8)–Se(1)–O(7)	100.8(2)	O(8)#1–Fe(4)–O(1)#1	100.24(16)
OW1–Fe(4)–O(8)#1	164.41(17)	O(8)–Fe(4)–O(1)#1	90.99(17)
OW1–Fe(4)–O(8)	88.22(18)	O(4)–Fe(4)–O(1)#1	101.47(16)
O(8)#1–Fe(4)–O(8)	79.75(18)	OW1–Fe(4)–O(5)	84.02(17)
OW1–Fe(4)–O(4)	99.05(18)	O(8)#1–Fe(4)–O(5)	87.69(17)
O(8)#1–Fe(4)–O(4)	90.70(17)	O(8)–Fe(4)–O(5)	97.31(17)
O(8)–Fe(4)–O(4)	165.53(16)	O(4)–Fe(4)–O(5)	71.25(16)
OW1–Fe(4)–O(1)#1	89.77(17)	O(1)#1–Fe(4)–O(5)	169.45(17)
O(3)#2–Fe(3)–O(9)#3	98.91(18)	O(7)–Fe(3)–O(1)	95.90(17)
O(3)#2–Fe(3)–O(7)	89.32(18)	O(6)–Fe(3)–O(1)	70.94(16)
O(9)#3–Fe(3)–O(7)	111.87(17)	O(3)#2–Fe(3)–O(1)#3	91.91(16)
O(3)#2–Fe(3)–O(6)	99.38(17)	O(9)#3–Fe(3)–O(1)#3	68.52(16)
O(9)#3–Fe(3)–O(6)	156.31(16)	O(7)–Fe(3)–O(1)#3	178.64(17)
O(7)–Fe(3)–O(6)	83.30(17)	O(6)–Fe(3)–O(1)#3	95.91(16)
O(3)#2–Fe(3)–O(1)	168.27(18)	O(1)–Fe(3)–O(1)#3	82.78(15)
O(2)#3–Fe(2)–O(2)#4	180.0(4)	O(9)#3–Fe(3)–O(1)	88.91(17)
O(2)#3–Fe(2)–O(9)	95.35(17)	O(2)#4–Fe(2)–O(4)#6	92.31(17)
O(2)#4–Fe(2)–O(9)	84.65(17)	O(9)–Fe(2)–O(4)#6	88.41(16)
O(2)#3–Fe(2)–O(9)#5	84.65(17)	O(9)#5–Fe(2)–O(4)#6	91.59(16)
O(2)#4–Fe(2)–O(9)#5	95.35(17)	O(2)#3–Fe(2)–O(4)#7	92.31(17)
O(9)–Fe(2)–O(9)#5	180.0(2)	O(2)#4–Fe(2)–O(4)#7	87.69(17)
O(2)#3–Fe(2)–O(4)#6	87.69(17)	O(9)–Fe(2)–O(4)#7	91.59(16)
O(4)#6–Fe(2)–O(4)#7	180.0(2)	O(9)#5–Fe(2)–O(4)#7	88.41(16)
O(5)–Fe(1)–O(5)#2	180.0	O(7)–Fe(1)–O(6)#2	99.70(17)
O(5)–Fe(1)–O(7)#2	86.33(17)	O(5)–Fe(1)–O(6)	89.19(16)
O(5)#2–Fe(1)–O(7)#2	93.67(17)	O(5)#2–Fe(1)–O(6)	90.81(16)
O(5)–Fe(1)–O(7)	93.67(17)	O(7)#2–Fe(1)–O(6)	99.70(17)
O(5)#2–Fe(1)–O(7)	86.33(17)	O(7)–Fe(1)–O(6)	80.30(17)
O(7)#2–Fe(1)–O(7)	180.000(1)	O(6)#2–Fe(1)–O(6)	180.0
O(5)–Fe(1)–O(6)#2	90.81(16)	O(5)#2–Fe(1)–O(6)#2	89.19(16)
O(7)#2–Fe(1)–O(6)#2	80.30(17)		

Symmetry transformations used to generate equivalent atoms: #1, $-x+1, -y+1, -z+1$; #2, $-x, -y+1, -z+1$; #3, $-x+1, -y+1, -z$; #4, $x, y-1, z$; #5 $-x+1, -y, -z$; #6, $x, y, z-1$; #7, $-x+1, -y, -z+1$; #8, $x, y, z+1$; #9, $x, y+1, z$.

oxides. In a specific hydrothermal process, many factors can affect the formation and crystal growth of products, such as the type of initial reactants, starting concentration, pH value, reaction time and temperature. In our

case, the pH value of the reaction system was crucial for the crystallization of products. Indeed, compound **1** only forms in a limited pH range (3.5–4.5), whereas no product could be obtained out of this pH range. On the other hand, the role of ethylenediamine as the reducing agent is critical in the formation of compound **1**, although ethylenediamine is not incorporated into the final structure.

3.2. Structure description

The single-crystal X-ray diffraction analysis reveals that compound **1** consists of a novel three-dimensional (3D) framework constructed from $\{\text{FeO}_6\}$ octahedra and $\{\text{SeO}_3\}$ trigonal pyramids via corner- and/or edge-sharing mode. The asymmetric unit of **1** (Fig. 1) shows four crystallographically independent Fe atoms and three crystallographically independent Se atoms. All Fe sites exhibit distorted octahedral coordination geometries. The Fe–O bond lengths are in the range of 1.987(4)–2.398(4) Å and the O–Fe–O bond angles vary from 68.52(16)° to 180.0(4)°. All Se atoms show trigonal pyramidal geometries with a lone-pair electron. The average Se–O bond length is 1.700(8) Å. The O–Se–O bond angles are in the range of 93.6(2)–105.0(2)°. The bond valence sum calculations [16] give the values of 2.17, 2.30, 2.18 and 2.16 for Fe(1), Fe(2), Fe(3) and Fe(4), respectively, showing that all Fe sites are in the +2 oxidation state. Also, the calculations show the value of 4.14, 4.02 and 3.99 for Se(1), Se(2) and Se(3), respectively, indicating that all Se sites are in the +4 oxidation state.

As shown in Fig. 2, the $\{\text{Fe}(1)\text{O}_6\}$ octahedra and $\{\text{Fe}(3)\text{O}_6\}$ octahedra connect with each other in the edge-sharing mode to form infinite chains. Two $\{\text{Fe}(4)\text{O}_6\}$ octahedra share an edge to give rise to a Fe_2O_{10} moiety, which links the chains via corner-sharing to form a two-dimensional (2D) network (Fig. 2). All 2D networks are parallel to *ac* plane and adjacent 2D networks are connected together by $\{\text{Fe}(2)\text{O}_6\}$ octahedra through corner-sharing to produce the 3D Fe–O–Fe framework (Fig. S1 and Fig. S2). As shown in Figs. 3a and b, the selenium atoms are grafted onto the 3D Fe–O–Fe framework, resulting in two types of 8-ring channels ($8\{\text{FeO}_6\}$ octahedra). It is noteworthy that the lone-pair electrons of the Se(IV) species appear to point into the channels (Fig. 3b), which further confirms that the structures of metal selenites are affected by the requirement for “empty” space to accommodate the selenium lone-pair electrons. The most interesting structural feature of compound **1** is that all $\{\text{FeO}_6\}$ octahedra are connected with each other to form the right-handed and left-handed helical chains (Fig. 4), which are further entangled to form the double helical chains along *a*-axis (Fig. S3).

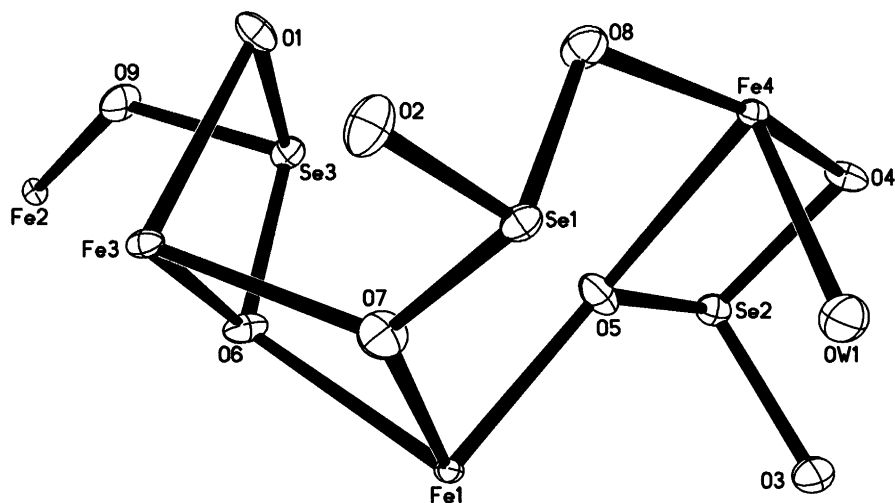


Fig. 1. ORTEP drawing of compound **1** with thermal ellipsoids at 50% probability.

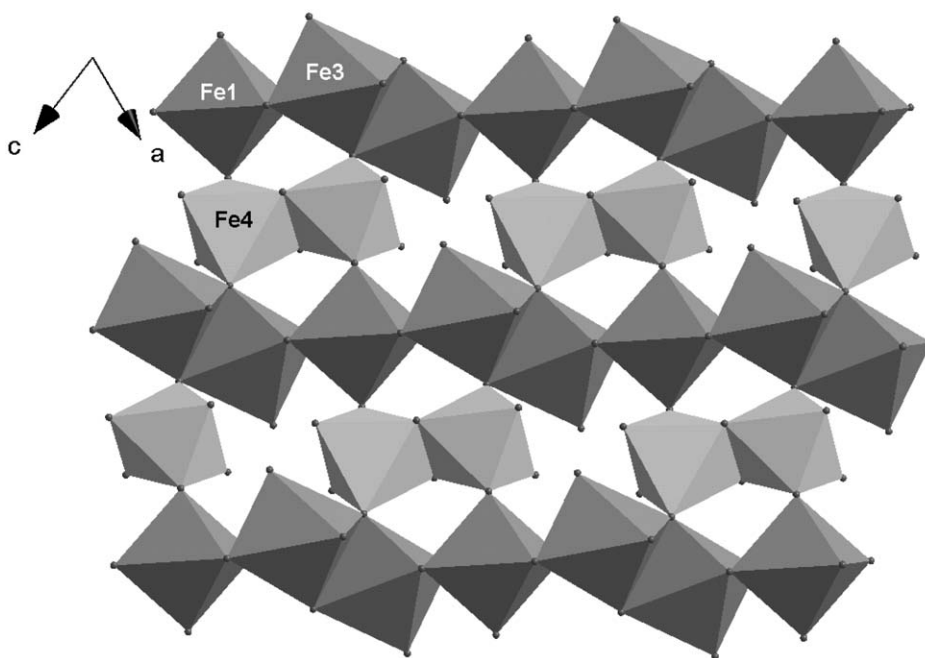


Fig. 2. Polyhedral representation of the 2D Fe/O network in **1**.

3.3. FT-IR spectroscopy

In the infrared spectrum of compound **1** (as shown in Fig. S4), the strong bands at 688 and 675 cm^{-1} could be due to the $\nu(\text{SeO}_3)^{2-}$ vibrations. The peaks around 553, 505, 468, 438, and 425 cm^{-1} are ascribed to the $\delta(\text{SeO}_3)^{2-}$ vibrations. Bands at the 3446 and 1644 cm^{-1} are attributed to the characteristic peaks of the water molecules.

3.4. Thermal analysis

The TG curve of compound **1** (Fig. 5) exhibits two steps of weight losses. The first weight loss is 3.41% in the temperature range of 370–425 $^{\circ}\text{C}$, corresponding to

the loss of H_2O . The second weight loss of 58.37% from 505 $^{\circ}\text{C}$ to 680 $^{\circ}\text{C}$ is assigned to the release of selenium dioxides. The residue was FeO. The whole weight loss (61.78%) is in agreement with the calculated value (61.95%). The sample does not lose weight at temperatures higher than 640 $^{\circ}\text{C}$. The thermal stability of compound **1** is interestingly high compared to other metal selenites. We attribute this exceptional stability to the 3D $M\text{--O--}M$ framework of compound **1**.

4. Conclusions

In summary, we have prepared a novel 3D transition metal selenite $\text{Fe}_3(\text{H}_2\text{O})(\text{SeO}_3)_3$ (**1**), which exhibits a

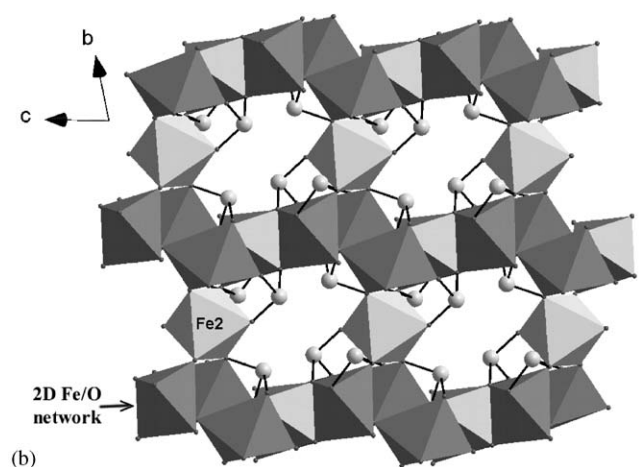
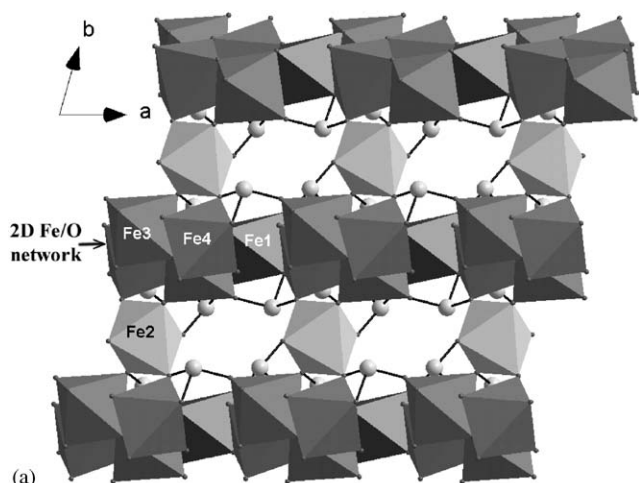


Fig. 3. (a) View of the 3D structure of **1** along the *c*-axis. (b) View of the 3D structure of **1** along the *a*-axis.

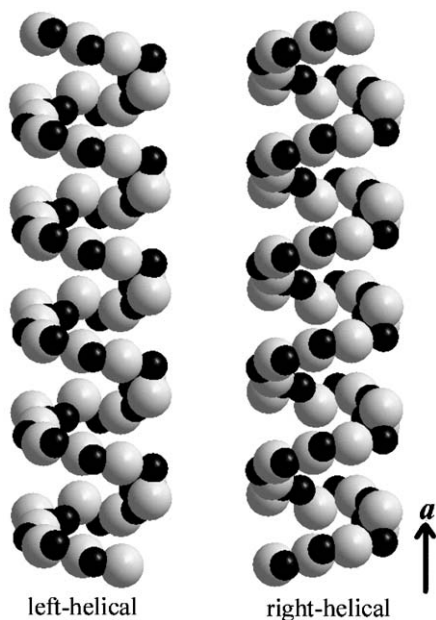


Fig. 4. Space-filling view of the left-handed and right-handed helical chains along *a* exhibited by **1**.

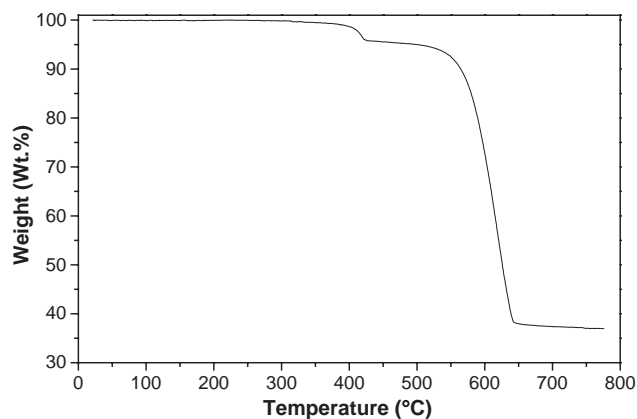


Fig. 5. TG curve of compound **1**.

novel 3D Fe–O–Fe framework grafted with the selenium atoms. The title compound consists of left-handed and right-handed helical chains, which are further entangled to produce the double helical chains. The successful isolation of **1** further confirms the observation that the stereochemically active lone-pair of electrons on the Se(IV) centers may profoundly influence the structure of the metal selenites framework. This work also shows that the hydrothermal synthesis is a powerful method to obtain novel structural materials.

Acknowledgments

This work was financially supported by the National Science Foundation of China (20171010).

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