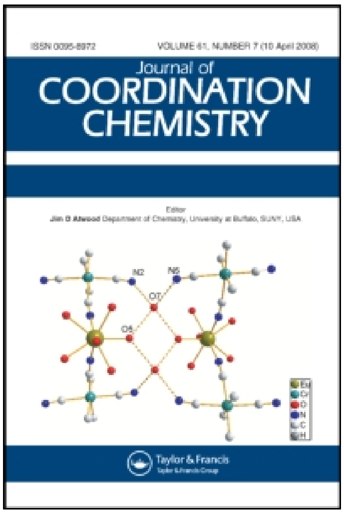

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Structural effects of lone-pair electrons: a novel three-dimensional, open-framework metal selenite constructed from $\{CoSeO_3\}_n$ double helical chains linked via ethylenediamine pillars

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Structural effects of lone-pair electrons: a novel three-dimensional, open-framework metal selenite constructed from $\{CoSeO_3\}_n$ double helical chains linked via ethylenediamine pillars

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A novel three-dimensional, open-framework selenite $[H_2N(CH_2)_2NH_2]_{0.5} \cdot CoSeO_3$ (**1**) has been hydrothermally synthesized and characterized by elemental analyses, IR spectrum, XPS spectrum, TG analysis and single crystal X-ray diffraction. Compound **1** crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 6.6018(14)$ Å, $b = 9.2559(19)$ Å, $c = 7.9097(16)$ Å, $\beta = 113.56(3)^\circ$, $V = 443.02(16)$ Å^3, and $Z = 4$. Compound **1** exhibits an interesting three-dimensional open-framework structure constructed from unique $\{CoSeO_3\}_n$ layers aggregated from double helical chains pillared by en ligands. Furthermore, the open framework of **1** possesses three types of one-dimensional channels, in which the triangular channel is particularly rare in covalently bonded microporous materials.

1. Introduction

The rational design of open-framework and microporous materials has attracted increasing attention in recent years because of their traditional applications in catalysis, separation, and ion-exchange, as well as their expected future uses as hybrid composite materials in fields such as sensors and microdevices [1–8]. An important research target in this area is to design zeolite-type materials with new framework topologies or chemical compositions. As a result, a large variety of cations have been used to combine with the PO_4^{3-} anion to prepare open-framework phosphates [1–4]. Recent research indicates that structural versatility can also be brought about by changing the anionic moiety of the framework [9–23] and many open-framework arsenates and germinates have also been reported [19–23]. Little has been done on the {MxLy/X/O} system (M = transition metal, L = organic ligand, X = Se or Te).

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Sparked by the merits of Se and Te in optical materials, we have been attempting to design organic–inorganic hybrid materials by using oxy-anions of group 16 elements [24–26]. Composites containing Se(IV) are of interest due to the possible role of the lone pair of electrons as an invisible structure-directing agent. In fact, the entire structure is affected by the requirement for 'empty' space to accommodate the selenium lone-pair electrons [17–18]. Furthermore, the stereochemically active lone-pair electrons on the Se(IV) centers generally lead to formation of an inherently asymmetric $[SeO_3]^{2-}$ anion. The stereochemically active lone-pair electrons possessed by Se(IV) may induce noncentrosymmetric structures with interesting physical properties, such as nonlinear optical second harmonic generation (SHG) [12, 15].

Designed open-framework materials with helical structures are particularly interesting and are a great challenge [27–36]. Nevertheless, the occurrence of inorganic materials with helical character is particularly rare. Hitherto, only a few open-framework metal phosphates and phosphites are known to have such structural features [27–29]. Gier *et al.* [30] reported cross-linked helical pores in the UCSB-7 frameworks. Rao's group reported an open-framework zinc phosphate $[\{NH_3(CH_2)_2NH_2(CH_2)_2NH_3\}\{Zn_4(PO_4)_3(HPO_4)\}] \cdot H_2O$ [31] containing intersecting helical channels. Kniep *et al.* and Yilmaz *et al.* have prepared metal borophosphates containing 6_1 or 6_5 helices [32, 33]. In this work, we report the synthesis and structure of a new three-dimensional (3D) open-framework cobalt selenite, $[H_2N(CH_2)_2NH_2]_{0.5} \cdot CoSeO_3$ (**1**), which contains left-handed and right-handed helical chains. Furthermore, the open framework of **1** possesses three types of one-dimensional (1D) channels, among which the triangular channel is rarely reported.

2. Experimental

2.1. *General procedures*

All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Co and Se were determined by a PLASMA-SPEC(I) ICP atomic emission spectrometer. XPS analysis was performed on a VG ESCALABMKII spectrometer with an Mg$K\alpha$ (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2×10^{-6} Pa during the analysis. An IR spectrum was recorded in the range 400–4000 cm^{-1} on an Alpha Centauri 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 $10^\circ C\,min^{-1}$.

2.2. *Preparation*

In a typical synthesis procedure for **1**, a mixture of $CoCl_2 \cdot 6H_2O$ (0.5 mmol), SeO_2 (1 mmol), ethylenediamine (en) (0.2 mL) and H_2O (7 mL) was stirred for 30 min in air. The mixture was then sealed in a 15 mL, Teflon-lined autoclave, which was heated to 110°C for 36 h. After slow cooling to room temperature, purple block crystals of **1** were filtered off, washed with distilled water and dried at ambient temperature (yield: *ca.* 75% based on Co). The powder X-ray diffraction pattern of the bulk product is in good agreement with the calculated pattern based on results from single-crystal

X-ray diffraction (figure S4). Elemental analyses of the purple crystals are consistent with the stoichiometry of **1**. Calcd for CH_4CoNO_3Se(%): C, 5.56; H, 1.87; Co, 27.29; N, 6.49; Se, 36.57. Found: C, 5.64; H, 1.93; Co, 27.17; N, 6.55; Se, 36.69. FT/IR data (cm^{-1}): 3424(m), 3232(s), 3145(m), 2954(w), 2893(w), 1605(s), 1468(m), 1333(m), 1177(s), 1111(w), 1026(s), 814(m), 776(m), 740(s), 689(w), 511(m), 486(w).

2.3. *X-ray crystallography*

A purple single crystal of **1** with dimensions $0.55 \times 0.49 \times 0.31$ mm was mounted on a glass fiber capillary. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo–Kα ($\lambda = 0.71073$ Å) at 293 K in the range of $3.35 < \theta < 28.13°$. A numerical absorption correction was applied. A total of 3044 (1005 unique, $R_{\text{int}} = 0.0741$) reflections were measured ($-8 \le h \le 8$, $-12 \le k \le 12$, $-10 \le l \le 10$).

The structure of **1** was solved by the direct method and refined by full-matrix least squares on F^2 using the SHELXL-97 software [37, 38]. All of the non-hydrogen atoms were refined anisotropically. Positions of hydrogen atoms attached to nitrogen were located from the Fourier difference maps, and those attached to carbon atoms were fixed at their ideal positions. A summary of crystal data and structure refinement for compound **1** is provided in table 1. The selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Structure description*

Single crystal X-ray diffraction analysis reveals that the structure of **1** is constructed from $\{CoSeO_3\}_n$ layers, which consist of interconnected left- and right-handed

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

Empirical formula	CH_4CoNO_3Se
Formula weight	215.94
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 6.6018(14)$ Å; $\alpha = 90°$ $b = 9.2559(19)$ Å; $\beta = 113.56(3)°$ $c = 7.9097(16)$ Å; $\gamma = 90°$
Volume	443.02(16) Å ^{3}
Z	4
Dc	3.238 $g\,cm^{-3}$
Absorption coefficient	11.964 mm^{-1}
θ range for data collection	3.42 to 28.13°
Limiting indices	$-8 \le h \le 8$, $-12 \le k \le 12$, $-10 \le l \le 10$
Reflections collected	3044
Independent reflections	1005 [R(int) = 0.0741]
Completeness to $\theta = 28.13°$	92.4%
Data/restraints/parameters	1005/0/73
Goodness-of-fit on F^2	1.072
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0387$, w$R_2 = 0.0970$
R indices (all data)	$R_1 = 0.0420$, w$R_2 = 0.0989$

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Co(1)–O(1)#1	1.922(3)	Co(1)–O(3)	1.986(3)
Co(1)–O(2)#2	1.974(3)	Co(1)–N(1)	1.990(4)
Se(1)–O(1)	1.657(3)	Se(1)–O(2)	1.661(3)
Se(1)–O(3)	1.670(3)		
O(1)#1–Co(1)–O(2)#2	100.98(14)	O(1)#–Co(1)–N(1)	110.41(16)
O(1)#1–Co(1)–O(3)	119.25(17)	O(2)#–Co(1)–N(1)	96.39(14)
O(2)#2–Co(1)–O(3)	98.17(13)	O(3)–Co(1)–N(1)	123.90(15)
O(2)–Se(1)–O(1)	103.64(18)	O(1)–Se(1)–O(3)	100.33(18)
O(2)–Se(1)–O(3)	96.83(17)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+1/2$, $y-1/2$, $-z+1/2$; #2 $x-1/2$, $-\mathrm{y}+1/2$, $z-1/2$; #3 $-x+1/2$, $y+1/2$, $-z+1/2$; #4 $x+1/2$, $-y+1/2$, $z+1/2$; #5 $-x+1$, $-y+1$, $-z$.

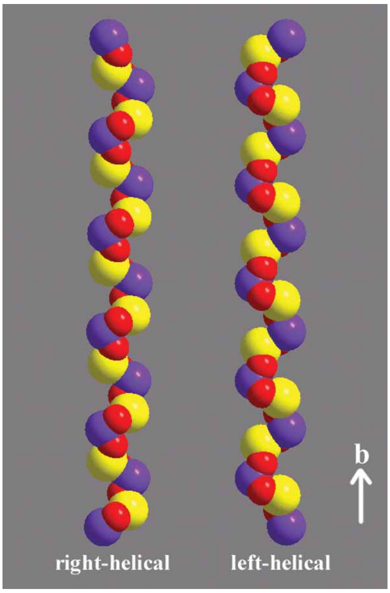

Figure 1. A space-filling view of the left-handed, right-handed helical chains (colour code: Co, yellow; Se, purple; O, red).

helical chains, pillared by en molecules into a 3D open framework. The asymmetric unit of **1** (figure S6) shows one crystallographically independent Co atom and one crystallographically independent Se atom. The Co center adopts a tetrahedral geometry, coordinated by one nitrogen donor (Co–N 1.990(4) Å) of en, three oxygen atoms (Co–O 1.922(3)–1.986(3) Å) of SeO_3 units. The Se atom adopts a characteristic pyramidal coordination, with the lone pair of electrons presumed to occupy the fourth tetrahedral vertex. The CoO_3N tetrahedra and SeO_3 pyramids are connected with each other by corner-sharing oxygen atoms to form the left- and right-handed helical chains (figure 1), which are further interconnected through O(2) atoms to produce double helical chains (figure S1). The central axis of each helical chain is a twofold screw axis along the crystallographic *b* axis. The pitch of the helix is equal to the unit cell repeat length. By inspection of the structure of **1**, the formation of the helix may be attributed to two features in this compound. One is that the en molecules, acting as a pillar, may induce a helical array of the –Co–O–Se– chains.

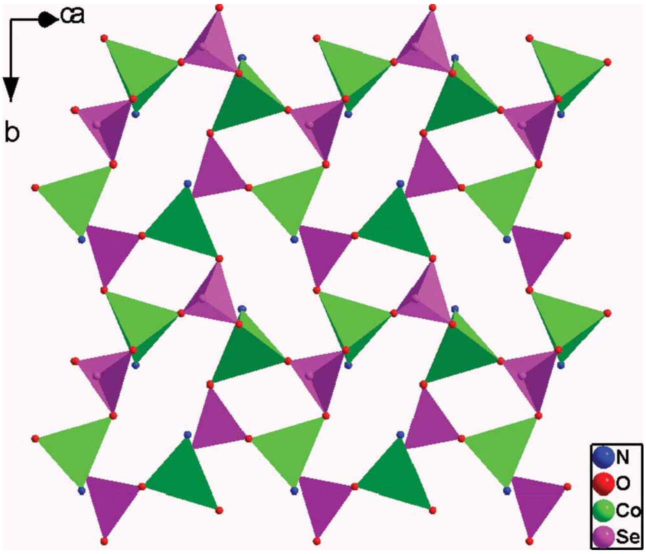

Figure 2. Polyhedral representation of the 2D inorganic cobalt selenite layer in **1** viewing along $[10\bar{1}]$ direction.

A similar phenomenon has also been observed in $[M(4,4'\text{-bpy})_2][(VO_2)_2(HPO_4)_4]$ (M=Co, Ni) [28] and $(C_5H_6N_2)Zn(HPO_3)$ [29]. The other is that the selenium lone-pair electrons may also impose an extra-force to the –Co–O–Se– chains due to the requirement for 'empty' space. Further understanding of the role of the organic amine molecules and the lone-pair electrons in determining the helical structures will be very important in the rational design and synthesis of open-framework metal selenites with helical character.

As shown in figure 2, the inorganic $\{CoSeO_3\}_n$ layer in **1** contains four- and eight-membered rings. Each eight-membered ring is surrounded by four four-membered rings and four eight-membered rings, and each four-membered ring shares all edges with four eight-membered rings to produce a 4.8^2-net sheet propagating normal to [101]. Interestingly, adjacent $\{CoSeO_3\}_n$ layers are covalently connected by en molecules to generate a 3D structure. The en molecules thus act as pillars through end-to-end (Co–en–Co) connectivity and create three types of 1D channels (figure 3, figure 4 and figure S7). Of the many noteworthy features in the structure of **1**, the triangular channel is unusual. In comparison with other shaped channels – such as square, rectangular, and honeycomb – often observed in 3D covalently bonded microporous materials, the triangular channel is rarely reported. The formation of this unique triangular channel may be attributed to the role of the lone pair of electrons as an invisible structure-directing agent. As shown in figure 3, the lone-pair electrons of the Se(IV) species appear to point into the triangular channels, further confirming that the structures of metal selenites are profoundly affected by the requirement for 'empty' space to accommodate the selenium lone-pair electrons.

Bond valence sum calculations [39] indicate that the Se site is in the +4 oxidation state in **1**. This result is also supported by the XPS measurement of **1** in the energy regions of Se_{3d}. The XPS spectrum shows one peak at 58.1 eV as shown in figure S2,

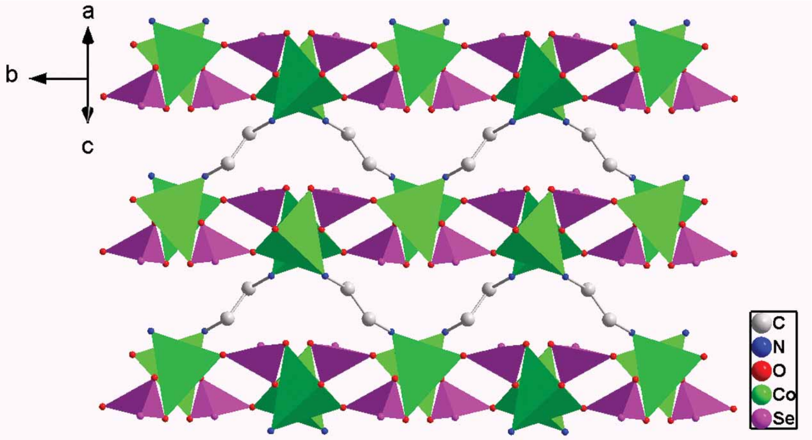

Figure 3. View of the 3D open-framework of **1** along [101] direction, showing the triangular channels.

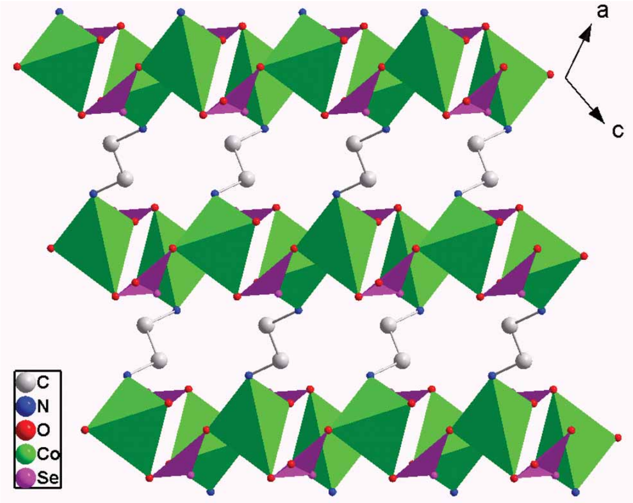

Figure 4. View of the 3D open framework of **1** along the *b* axis direction. All hydrogen atoms are omitted for clarity.

attributable to Se^{4+}. The bond valence analysis also shows that the Co site is in the +2 oxidation state. These results are consistent with charge balance considerations.

3.2. *FT-IR spectroscopy*

In the infrared spectrum of compound **1** (as shown in figure S5). The bands around 814, 776, 740, and 689 cm^{-1} could be due to the $\nu(SeO_3)^{2-}$ vibrations [40]. The peaks at 512, 485 and 459 cm^{-1} are ascribed to the $\delta(SeO_3)^{2-}$ vibrations [40]. Bands in the 3424–1026 cm^{-1} regions in the infrared spectrum of compound **1** are attributed to characteristic peaks of en groups.

3.3. *TG analyses*

The thermal gravimetric (TG) curve (as shown in figure S3) of **1** in the temperature range of 30–800°C displays complex multi-step weight loss. The total weight loss of 65.69% is in good agreement with the calculated value of 65.32%. The weight loss of 14.04% at 210–280°C corresponds to the loss of en groups (Calcd 13.94%). The weight loss of 51.65% at 280–760°C arises from the release of selenium dioxides (Calcd 51.38%).

4. Conclusions

In conclusion, we have prepared and structurally characterized a novel 3D inorganic–organic hybrid metal selenite, which features an open-framework structure built of $\{CoSeO_3\}_n$ layers aggregated from double helical chains pillared by en ligands. Furthermore, the open framework of **1** has an unusual triangular channel. It is believed that the organoamine ligands and the lone-pair electrons are important for the formation of both the helical chains and multi-direction channels. Hence, the successful isolation of **1** not only confirms the observation that the stereochemically active lone-pair of electrons on the Se(IV) centers may profoundly influence the structure of the metal selenite framework, but also provides an interesting matrix for the design and synthesis of helical metal selenite materials.

Supplementray material

CCDC reference number: 261158.

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