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The first organically templated linear metal selenate

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Abstract

An organically templated cadmium selenate of the formula $[enH_2][Cd(H_2O)_2(SeO_4)_2]$, **I**, has been synthesized by carrying out the reaction between CdO and H_2SeO_4 in the presence of the amine in aqueous medium at 80°C. The structure of **I** involves isolated infinite $[Cd(H_2O)_2(SeO_4)_2]^{2-}$ chains running along the *c*-axis, with the protonated ethylenediamine molecules between them. Crystal data for **I** are as follows: Monoclinic, space group $= C2/c$, $a = 10.5059(7)$, $b = 10.3605(7)$, $c = 10.6028(7)$ Å, $\beta = 94.666(2)°$, $V = 1150.25(13)$ Å^3, $z = 8$, $R_1 = 0.0237$, $wR_2 = 0.0500$ (for all data).

Keywords: Cadmium selenate; Organically templated material; One-dimensional structure; Kröhnkite-type chain and thermogravimetric analysis

1. Introduction

Apart from the aluminosilicate zeolites [1], the area of open-framework materials is largely dominated by metallophosphates [2]. An important objective in this area of research is to design compounds with novel framework structures and interesting physical properties. In this regard, a great number of different cations have been employed in combination with the PO_4^{3-} anion [2], or the analogous AsO_4^{3-} anion [2,3] to prepare open-framework phosphates or arsenates. The structural versatility that can be brought about by changing the anionic (oxy-anion) moiety of the framework, on the other hand, has not been explored sufficiently. We have been attempting to design inorganic open architectures making use of the oxy-anions of group 16, namely S and Se, specially the SO_4^{2-} anion. Thus, we have synthesized and characterized organically templated sulfates of Cd [4,5], V [6] and Fe [7–9], the last group showing interesting magnetic properties. The amine templated metal sulfate family has been extended to actinide and lanthanide elements with the report of 1-, 2- and 3-D uranium [10,11] and 2- and 3-D lanthanum [12] sulfates. In the case of oxy-anions of Se, an organically templated 2-D zinc selenite was first reported by Harrison et al. [13]. Organically templated 3-D iron(III) and zinc selenites were reported by us recently [14]. Both the organically templated and the organically linked vanadium selenites have been reported [15,16]. To our knowledge, no organically templated metal selenate has been reported thus far, although one would expect SeO_4^{2-} to form compounds structurally similar to those formed by SO_4^{2-}.

The oxy-anions of S and Se differ with respect to the stability of the oxidation states and their redox behavior [17]. While the most stable oxidation state of S is +VI as in SO_4^{2-}, that of Se is +IV (SeO_3^{2-} or $Se_2O_5^{2-}$). The reduction potential of the XO_4^{2-}/XO_3^{2-} couple is 0.03 V in alkaline medium in the case of Se and 0.119 V for S, and this has implications on the thermal decomposition and the relative stabilities of their compounds. It is, therefore, difficult to stabilize a metal selenate framework under the hydrothermal conditions specially in presence of amine templates. Furthermore, SeO_4^{2-} gets easily reduced to SeO_3^{2-} in solids, as in the case of $[C_2N_2H_8]_{0.5}ZnSeO_3$ [14] and $[DABCOH_2]_{0.5}[(VO)(HSeO_3)(SeO_3)] \cdot H_2O$ [15], where the starting Se source was H_2SeO_4. This behavior of the selenate anion in inorganic frameworks in the presence of organic amine templates has motivated the present investigation. In this paper, we report the first organically templated linear cadmium selenate, $[enH_2][Cd(H_2O)_2(SeO_4)_2]$, **I**.

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2. Experimental

2.1. Synthesis and initial characterization

The title compound, $[enH_2][Cd(H_2O)_2(SeO_4)_2]$, **I**, was synthesized in aqueous medium at 80°C from a solution containing ethylenediamine (en) as the templating amine. In a typical synthesis, 0.1284 g of CdO (s.d. fine chem. Ltd.) was dispersed in 10 mL of deionized water taken in 100 mL beaker. To this solution was added 0.77 mL of selenic acid (Aldrich, 40 wt%) followed by 0.06 mL of ethylenediamine (Aldrich, 99%), and the whole solution was stirred for 15 min. The final colorless clear solution, with the molar composition $1CdO{:}3H_2SeO_4{:}1en{:}555.5H_2O$, was concentrated on water bath at 80°C for 4 h. The solution was then allowed to cool at room temperature. A large number of needle-like crystals were recovered by filtration. No significant change occurred in the initial pH of 2 over the formation of the product. The product was washed with minimum amount of water, as excess of water destroyed the crystallinity of the product. After drying the product at the ambient conditions, the yield was found to be 64% based on cadmium. An acidic pH and mild reaction conditions (80°C and 4 h time) are two important factors to avoid reduction of the SeO_4^{2-} species. Initial characterization was carried out by powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), Energy Dispersive X-ray Analysis (EDAX) and IR spectroscopy. EDAX indicated the ratio of Cd and Se to be 1:2.

2.2. Single crystal structure determination

A suitable single crystal of the compound **I** was selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate (super glue) adhesive. Single crystal structure determination by X-ray diffraction was performed with a Siemens smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. A hemisphere of intensity data was collected at room temperature in 1321 frames with ω scans (width of 0.30° and exposure time of 20 s per frame) in the 2θ range 5.5–46.48°. The structure was solved by direct methods using SHELXS-86 [18], which readily established the heavy atom positions (Cd and Se) and facilitated the identification of the light atoms (O) from difference Fourier maps. An empirical absorption correction based on symmetry equivalent reflections was applied using SADABS program [19]. Other effects, such as absorption by the glass fiber etc., were corrected for. All the hydrogen positions were initially observed in the difference Fourier maps, but for the final refinement the hydrogen atoms of the amine were placed geometrically and held in the riding mode. The hydrogen atoms of the bonded water (O3) were refined, keeping them in their located positions. The last cycle of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full-matrix-least-squares structure refinement against $|F^2|$ was carried out using SHELXTL-PLUS package of programs [20]. The details of the final refinements are given in Table 1. The final atomic coordinates, selected bond distances and angles for I are given in Tables 2 and 3. The powder X-ray diffraction pattern of the bulk is in agreement with the one simulated by the single crystal. A least-square-fit [21] of the powder XRD (Cu$K\alpha$) lines of the bulk sample of **I**, using the $h\,k\,l$ indices generated from single crystal X-ray data, gave the following cell: $a = 10.4915(4)$ Å, $b = 10.3443(2)$ Å, $c = 10.5667(7)$ Å, $\beta = 94.6418(3)°$, which is in good agreement with that determined by single crystal XRD. The infrared spectrum of **I** was recorded with a Bruker 66v/S spectrometer taking the sample as KBr pellet. The spectrum showed characteristic absorption bands at 839, 877 cm^{-1} due to the stretching vibrations and at 410, 439 cm^{-1} due to the bending vibrations of SeO_4 group. The bending vibrations of the amine and the water molecules appear in the

Table 1
Crystal data and structure refinement parameters for **I**, $[enH_2][Cd(H_2O)_2(SeO_4)_2]$

Empirical formula	$C_2H_{14}CdN_2O_{10}Se_2$
Crystal system	Monoclinic
Space group	$C2/c$
A (Å)	10.5059(7)
b (Å)	10.3605(7)
c (Å)	10.6028(7)
α (deg)	90.0
β (deg)	94.666(2)
γ (deg)	90.0
Volume (Å^3)	1150.25(13)
Z	8
Formula mass	496.48
ρ_{calc} ($g\,cm^{-3}$)	2.867
λ (Mo$K\alpha$) Å	0.71073
μ (mm^{-1})	8.275
θ range (deg)	2.77–23.24
Total data collected	2332
Index ranges	$-11 \leqslant h \leqslant 6$, $-11 \leqslant k \leqslant 11$, $-11 \leqslant l \leqslant 11$
Unique data	824
Observed data ($\sigma > 2\sigma(I)$)	753
Refinement method	Full-matrix least-squares on $\lvert F^2 \rvert$
R indices $[I > 2\sigma(I)]$	$R_1 = 0.0206$, $wR_2 = 0.0487$
R indices (all data)	$R_1 = 0.0237$, $wR_2 = 0.0500$[a]
Goodness of fit (S)	1.080
No. of variables	87
Largest difference map peak and hole $e\,Å^{-3}$	0.451 and −0.383

[a] $W = 1/[\sigma^2(F_o)^2 + (0.0190P)^2 + 0.5334P]$ where $P = [F_o^2 + 2F_c^2]/3$.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **I**, $[enH_2][Cd(H_2O)_2(SeO_4)_2]$

Atoms	x	y	z	U_{eq} [a]
Cd(1)	0	1216(1)	2500	18(1)
Se(1)	−1918(1)	−195(1)	4773(1)	15(1)
O(1)	−994(3)	−286(3)	3609(3)	27(1)
O(2)	−1503(3)	−1322(3)	5809(3)	24(1)
O(3)	−1169(4)	3038(4)	3058(4)	27(1)
O(4)	−1870(3)	1241(3)	5400(3)	25(1)
O(5)	−3392(3)	−479(3)	4208(3)	24(1)
N(1)	5037(3)	−8190(4)	4261(3)	23(1)
C(1)	4470(4)	−8261(5)	2940(4)	23(1)
Hydrogen coordinates				
H				
H(1)	4417(3)	−8190(4)	4786(3)	34
H(2)	5493(3)	−7469(4)	4368(3)	34
H(3)	5542(3)	−8870(4)	4425(3)	34
H(4)	3913(4)	−7527(5)	2757(4)	28
H(5)	3966(4)	−9042(5)	2818(4)	28
H(6)	−1778(50)	3149(53)	3424(50)	34(17)
H(7)	−1348(58)	3546(59)	2472(60)	54(21)

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

Table 3
Selected bond distances and angles in **I**, $[enH_2][Cd(H_2O)_2(SeO_4)_2]$

Moiety	Distance (Å)	Moiety	Angle (deg)
Cd(1)–O(1)$^{\#1}$	2.257(3)	O(1)$^{\#1}$–Cd(1)–O(1)	92.8(2)
Cd(1)–O(1)	2.257(3)	O(1)$^{\#1}$–Cd(1)–O(2)$^{\#2}$	97.01(11)
Cd(1)–O(2)$^{\#2}$	2.293(3)	O(1)–Cd(1)–O(2)#2	86.80(11)
Cd(1)–O(2)$^{\#3}$	2.293(3)	O(1)$^{\#1}$–Cd(1)–O(2)$^{\#3}$	86.80(11)
Cd(1)–O(3)$^{\#1}$	2.354(4)	O(1)–Cd(1)–O(2)$^{\#3}$	97.01(11)
Cd(1)–O(3)	2.354(4)	O(2)$^{\#2}$–Cd(1)–O(2)$^{\#3}$	174.49(14)
Se(1)–O(4)	1.629(3)	O(1)$^{\#1}$–Cd(1)–O(3)$^{\#1}$	98.59(13)
Se(1)–O(1)	1.634(3)	O(1)–Cd(1)–O(3)$^{\#1}$	163.11(13)
Se(1)–O(2)	1.638(3)	O(2)$^{\#2}$–Cd(1)–O(3)$^{\#1}$	79.50(11)
Se(1)–O(5)	1.641(3)	O(2)$^{\#3}$–Cd(1)–O(3)$^{\#1}$	96.04(11)
		O(1)$^{\#1}$–Cd(1)–O(3)	163.11(13)
		O(1)–Cd(1)–O(3)	98.58(13)
		O(2)$^{\#2}$–Cd(1)–O(3)	96.04(11)
		O(2)$^{\#3}$–Cd(1)–O(3)	79.50(11)
		O(3)$^{\#1}$–Cd(1)–O(3)	73.3(2)
		O(4)–Se(1)–O(1)	111.2(2)
		O(4)–Se(1)–O(2)	112.3(2)
		O(1)–Se(1)–O(2)	108.8(2)
		O(4)–Se(1)–O(5)	108.1(2)
		O(1)–Se(1)–O(5)	108.3(2)
		O(2)–Se(1)–O(5)	108.0(2)
		Se(1)–O(1)–Cd(1)	133.0(2)
		Se(1)–O(2)–Cd(1)$^{\#2}$	128.2(2)
Organic moiety			
N(1)–C(1)	1.479(5)	N(1)–C(1)–C(1)$^{\#4}$	109.0(4)
C(1)–C(1)$^{\#4}$	1.509(8)		

$^{\#1}-x, y, -z+1/2$; $^{\#2}-x, -y, -z+1$; $^{\#3}x, -y, z-1/2$; $^{\#4}-x+1, y, -z+1/2$.

1514–1626 cm^{-1} region, with the stretching vibrations appearing in the 2550–3403 cm^{-1} region.

3. Results and discussion

The structure of **I** consists of one-dimensional polymeric anions of the formula $[Cd(H_2O)_2(SeO_4)_2]^{2-}$, with charge compensation being achieved by the presence of the protonated ethylenediamine. The asymmetric unit of **I** contains 17 independent non-hydrogenic atoms, which include one cadmium, sitting in a special position with 0.5 occupancy and one crystallographically distinct selenium atom (Fig. 1a). The cadmium atom is octahedrally coordinated by 6 oxygen atoms, four from SeO_4^{2-} units and two from water molecules which are *cis* to each other. Out of the six oxygen atoms of the CdO_6 octahedron, four forms Cd–O–Se linkages with four crystallographically unique Se atoms (ave. Cd–O–Se = 130.5°) and the remaining two as terminal Cd–OH_2 bonds. The Se atoms are tetrahedrally coordinated by oxygen atoms as expected. Out of the four oxygen atoms around each Se, two involve in Se–O–Cd connectivities, the other two forming terminal Se = O bonds, as indicated by the short Se–O bonds. The Cd–O bond lengths are in the range 2.257(3)–2.293(3) Å with a fairly distorted CdO_6 octahedra where the longer bond lengths belong to the Cd–OH_2 bonds. The average Cd–O and Se–O bond lengths [$(Cd–O)_{av}$ = 2.304 Å, $(Se1–O)_{av}$ = 1.636 Å] agree with those reported for cadmium selenates in Refs. [22,23].

The strictly alternating $Cd(H_2O)_2O_4$ and SeO_4 units form four-membered rings linked through their corners forming one-dimensional chains along the *c*-axis (Fig. 1b). The ethylenediammonium cations are located between the chains and connect them through N–H···O

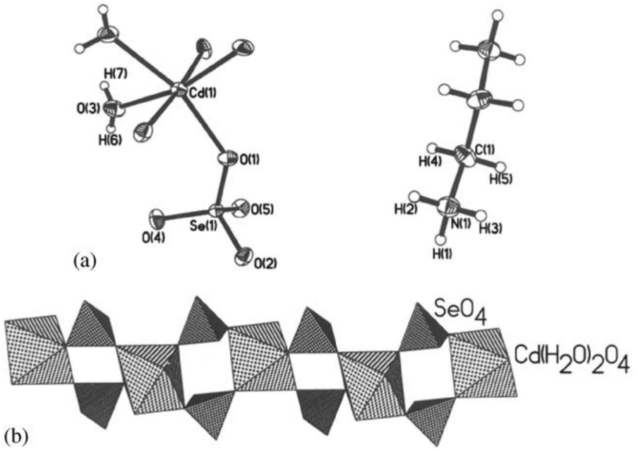

Fig. 1. (a) ORTEP plot of $[enH_2][Cd(SeO_4)_2(H_2O)_2]$, **I**. Asymmetric unit is labeled. Thermal ellipsoids are given at 50% probability. (b) Polyhedral structure of the $[Cd(H_2O)_2(SeO_4)_2]^{-2}$ chain along the *c*-axis.

hydrogen bonds to form layers along the *b*-axis (Fig. 2a). These layers are stacked over one another to form the 3-D crystalline assembly. When viewed along the *a*-axis, the chains are placed parallel to each other with no inter-chain interaction (Fig. 2b). The organoammonium ions grafted onto the bending of the $[Cd(H_2O)_2(SeO_4)_2]^{2-}$ chain through N–H···O and C–H···O bonds. The zig-zag nature of the chain is caused by the *cis* orientation of the water molecules. Another layered network, formed by O–H···O hydrogen bonds between the bonded water molecules and the oxygens of the selenate ions, can be discerned when viewed along the [1−10] direction (Fig. 3). Details of the hydrogen bonding interactions in **I** are listed in Table 4.

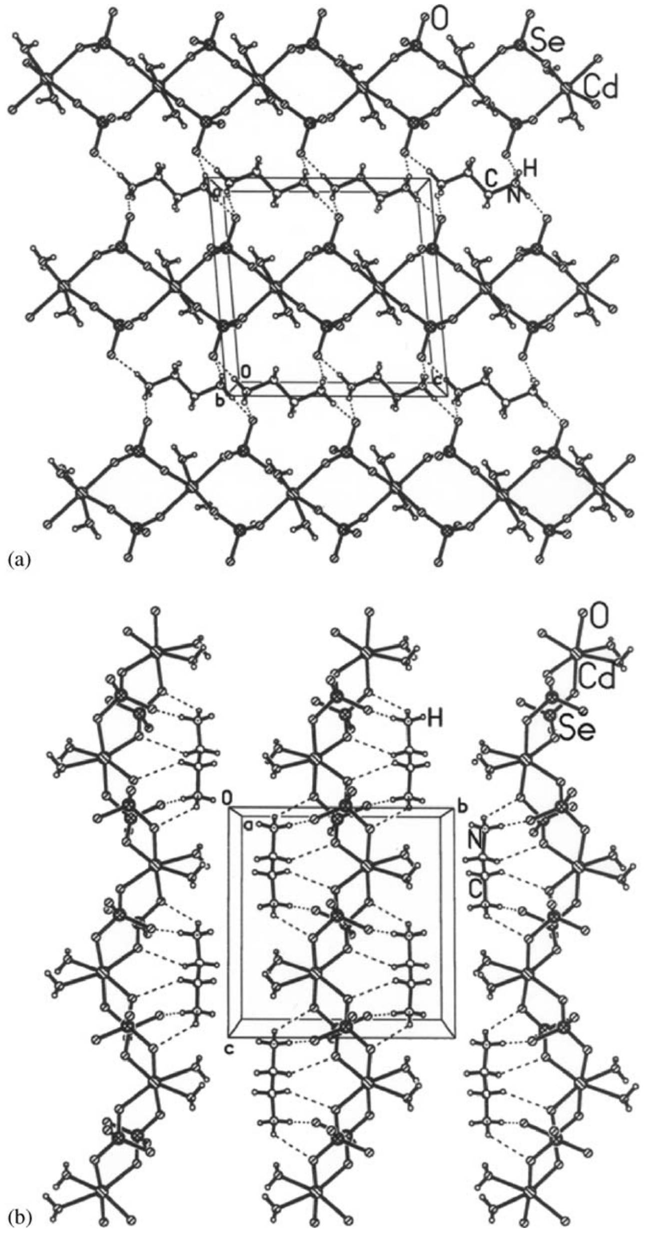

Fig. 2. (a) Structure of **I** along the *b*-axis showing the layer-network. Dotted lines indicate hydrogen bonding between the amine and the chain. (b) Structure of **I** along the *a*-axis.

The thermogravimetric analysis (TGA) of **I** was carried out under constant flow of N_2 at a heating rate of 5°C/min in the temperature range 30–950°C. The TGA curve (Fig. 4) consists of mainly two stages of weight loss. The first major weight loss (61.57%) occurs in a broad temperature range of 160–480°C and then followed by a tail stretching from 600°C to 900°C which involves 14.43% weight loss. The thermal decomposition mechanism of **I** seems to be complicated. The first stage of weight loss can be explained by taking into account the removal of amine, water molecules and SeO_2 (calc. 60.70%, steps 1 and 2 in Table 5). The weight loss in the first stage is nearly continuous while in the case of organically templated cadmium sulfates the removal of amine is marked by a clear step [5], a difference between the sulfates and the selenates mentioned earlier. At this stage, the sample transforms to a mixture of basic cadmium selenite $[2CdO \cdot CdSeO_3]$ and $CdSeO_3$. On further heating, the mixture decomposes to another basic selenite $[4CdO \cdot CdSeO_3]$ with the removal of SeO_2, eventually dissociating to a mixture of CdO and CdSe (JCPDS file, card nos: 05-0640 and 08-0459) as indicated by the PXRD of the residue at 950°C. The probable steps of weight loss are described in Table 5. The thermal decomposition via the basic selenite route has been observed in the case of $PbSeO_3$ [24,25] but the reduction to selenide is unusual.

While **I** is the first example of an organically templated open-framework cadmium selenate, a similar chain topology occurs in the mineral kröhnkite, $Na_2[Cu(SO_4)_2(H_2O)_2]$ [26]. Several naturally occurring minerals as well as synthetic compounds with related structures are known [23,27]. Fleck et al. [27] have recently reviewed compounds with the kröhnkite-type chain topology and have attempted to give a structural classification. The structure of the kröhnkite-type infinite chains is composed of a more or less distorted MO_6 octahedra corner-linked with XO_4 tetrahedra ($X = $ S, Se, Mo etc.), the remaining two opposite corners in *trans* position being occupied by the water molecules. Each tetrahedron connects the neighboring octahedra, thereby forming an infinite $[M(XO_4)_2(H_2O)_2]$ chain. Following Fleck et al. [27], **I** can be considered as a kröhnkite-like chain rather than kröhnkite-type chain. The main difference is that in **I**, two water molecules in the CdO_6 octahedron are located in adjacent corners (*cis*). In kröhnkite-type compounds, the water molecules are present in *trans* positions. This is the reason why the chains in **I** are twisted rather than being straight as in true kröhnkite-type chains. Such examples are found in minerals such as $Cs[Tl^{+3}(SO_4)_2] \cdot 2H_2O$ [28], $Cs[In^{+3}(SO_4)_2] \cdot 2H_2O$ [29] and $Cs[In^{+3}(SeO_4)_2] \cdot 2H_2O$ [30]. Most of these compounds possess lower symmetries and only a few are known to possess higher symmetries.

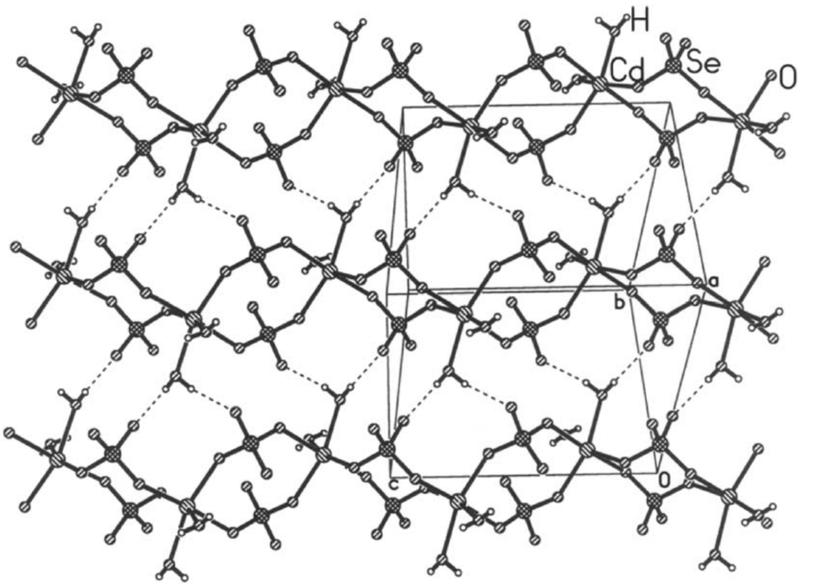

Fig. 3. Layered structure formed by chain–chain interactions along the [1−10] direction.

Table 4
The most probable hydrogen bonding parameters in **I**, $[enH_2][Cd(H_2O)_2(SeO_4)_2]$

D–H⋯*A*	*D*⋯*A*	*D*–H⋯A
N(1)—H(1)⋯O(5)	2.825(5)	138.7(5)
N(1)—H(2)⋯O(4)	2.793(5)	164.0(4)
N(1)—H(3)⋯O(5)	2.892(5)	162.2(4)
O(3)—H(6)⋯O(4)	2.833(5)	167(5)
O(3)—H(7)⋯O(5)	2.858(5)	168(6)
C(1)—H(4)⋯O(1)	3.209(6)	130.8(4)

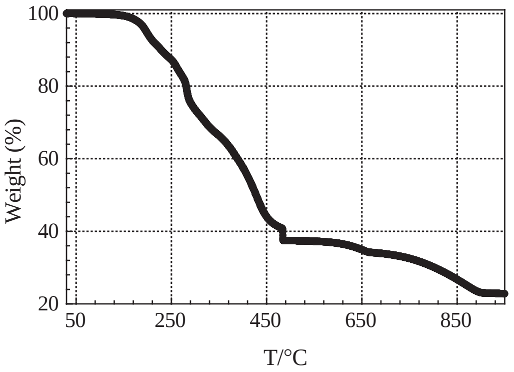

Fig. 4. TGA curve of **I**.

Table 5
The probable steps in the thermal decomposition of **I**

Steps	Probable decomposition pathways	Temp.	Wt. loss (%)
1	$5[enH_2][Cd(H_2O)_2(SeO_4)_2] \rightarrow 5en\uparrow + 15H_2O\uparrow + SeO_2\uparrow + 5O_2\uparrow + 5CdSeO_3$	160–480	Obs. = 61.57
2	$5CdSeO_3 \rightarrow 2CdO \cdot CdSeO_3 + 2CdSeO_3 + 2SeO_2\uparrow$		Theo. = 60.7
3	$2CdO \cdot CdSeO_3 + 2CdSeO_3 \rightarrow 4CdO \cdot CdSeO_3 + 2SeO_2\uparrow$	600–900	Obs. = 14.43*
4	$4CdO \cdot CdSeO_3 \rightarrow 4CdO + CdSe + SeO_2\uparrow + 1/2O_2\uparrow$		Theo. = 10.4

The slight discrepancy in steps 3 and 4 between the theoretical and the observed values could be due to the fact that $CdSeO_3$ (step 4) may convert partially to the oxide with the rest being reduced to the selenide.

Compound **I** is only the third example of such compound with the space group $C2/c$.

A few organically templated zinc, aluminum and cobalt phosphates with one-dimensional linear chain structures similar to **I** are known [31–33]. In these phosphates, the four-membered rings are formed by the corner-sharing $MO_4 (M = \mathrm{Zn, Al, Co})$ tetrahedra and the PO_4 tetrahedra, instead of the CdO_6 octahedra and the SeO_4 tetrahedra as in the present case. A mechanism proposed for the formation of open-framework phosphates considers the corner-shared chains to be an important building unit [34]. Such corner-shared chains have been transformed into 3-D structures by introducing divalent cations [35]. The kröhnkite-type chain is likely to constitute a building unit in the formation of naturally occurring minerals such as yavapaiite, merwinite and bafertisite [36–38]. These minerals contain sheets which may be formed by linking kröhnkite-type chains.

4. Conclusions

Synthesis of an amine-templated cadmium selenate, $[enH_2][Cd(H_2O)_2(SeO_4)_2]$, with a linear chain structure has been accomplished. The similarity of the chain structure to that of kröhnkite and the known ability of the linear chain phosphates to transform to higher dimensional structures, suggest that it should be possible to synthesize 2-D and 3-D metal selenates, suitably templated by organic amines.

Acknowledgments

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