# Hydrothermal synthesis and crystal structure of a new inorganic/organic hybrid of scandium sulfate: $(H_2en)Sc_2(SO_4)_4 \cdot (H_2O)_{0.72}$

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## Abstract

The first organically templated layered structure of scandium sulfate, $(H_2en)Sc_2(SO_4)_4 \cdot (H_2O)_{0.72}$, (en = ethylenediamine) was synthesized by a hydrothermal method and characterized by single crystal X-ray diffraction. In the title compound, scandium ions are bridged by sulfate groups with a ratio of 1:2 into a $4_3^6$ layer structure. These layers are parallel packed and separated from each other by ethylenediammonium dications and water molecules. The title compound crystallizes in the monoclinic space group $P2/c$, with cell parameters $a = 8.5966(13)$ Å, $b = 5.1068(8)$ Å, $c = 18.847(3)$ Å, $\beta = 91.210(3)^\circ$, $V = 827.2(2)$ Å$^3$ and $Z = 2$. Refinement gave $R_1[I > 2\sigma(I)] = 0.0354$ and w$R_2[I > 2\sigma(I)] = 0.0878$. Thermogravimetric analysis indicates that this material is thermally stable to above 400 °C.
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*Keywords:* Hydrothermal synthesis; Layer; Inorganic/organic hybrid; Scandium sulfate; Crystal structure

## 1. Introduction

Following the discovery of zeolites, considerable research has focused on the synthesis of inorganic/organic hybrid compounds, especially organically templated inorganic open frameworks [1,2], due to their structural diversity as well as their potential applications in catalysis [3], gas storage [4], separation [5], ion-exchange [6], etc. One commonly employed research strategy is the replacement of silicon/aluminum with other elements that can function as building blocks for the construction of open frameworks, for example, by replacing $Si^{IV}O_2$ with $[M^{III}(SO_4)_2]^-$. Recent examples include organically templated metal sulfates of cadmium [7,8], iron [9], lanthanum [10–12] and uranium [13,14].

We are interested in the exploration of new types of porous materials that can be synthesized by the hydrothermal method with organic amines as structure directing entities. Robust frameworks can be prepared by linking octahedral metal centers with tetrahedral phosphate or sulfate anions. Phosphate frameworks have been more extensively studied. Scandium is relatively abundant in the earth's crust, yet it is perhaps the least studied first row transition element because of its high cost. Metal-organic [4,15–18] or inorganic/organic hybrid structures [19,20] of scandium are rarely seen in literature. Three-dimensional scandium phosphate frameworks have been templated by en (en = 1,2-diaminoethane or ethylenediamine) [(H$_2$en)$_8$ Sc$_8$(ScO$_2$)$_4$(PO$_4$)(HPO$_4$)$_{12}$ · 12H$_2$O [21], (H$_2$en)Sc$_2$(HPO$_4$)$_4$ [21,22] and (H$_2$en)$_2$Sc$_2$F$_6$(HPO$_4$)$_2$ [23]] and DABCO (1,4-diazabicyclo[2,2,2]octane) [(DABCO)Sc$_4$F$_2$(PO$_4$)$_4$ · 4H$_2$O [24]]. A CSD database [25] search for organically templated scandium sulfate compounds shows that two chain structures, [H$_3$N(CH$_2$)$_6$NH$_3$][Sc(H$_2$O)$_2$(SO$_4$)$_2$]$_2$ · 2H$_2$O and [C(NH$_2$)$_3$]$_3$[Sc(SO$_4$)$_3$] · 3H$_2$O [19], and only one open framework scandium sulfate/phosphate, Sc$_{56}$(SO$_4$)$_{98}$ (PO$_4$)$_{22}$ · [(C$_8$N$_4$H$_{24}$)$^{4+}$]$_{15}$ · 34H$^+$ · 57H$_2$O [20], were structurally characterized.

In this paper, we report a new layered scandium sulfate $(H_2en)Sc_2(SO_4)_4 \cdot (H_2O)_{0.72}$ that is templated by $(H_2en)^{+2}$ dications. The compound was hydrothermally synthesized and its crystal structure determined by single crystal X-ray diffraction. The as-synthesized product was also

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characterized by means of elemental analysis, powder X-ray diffraction, IR spectroscopy and thermogravimetric analysis (TGA).

## 2. Experimental

### 2.1. Preparation of $(H_2en)Sc_2(SO_4)_4 \cdot (H_2O)_{0.72}$

A mixture of $Sc_2O_3$ (130 mg, 0.94 mmol, Strem), $Na_2SO_4$ (295 mg, 2.08 mmol, Aldrich), en (0.24 mL, 215 mg, 3.58 mmol, Aldrich) and 10 mL distilled water was acidified to a pH value ~1–2 with 37% HCl. The mixture was then stirred for 30 min and transferred into a 23 mL Teflon lined Parr acid digestion bomb. The bomb was heated at 200 °C in an oven and held at that temperature for 3 days before being naturally cooled down to room temperature. Colorless plate-like crystals were collected by filtration and washed several times with distilled water. The crystals were stored in air for several hours prior to single crystal X-ray analysis and several months before completion of the bulk measurements. Yield: 90 mg (17% by Sc). Element analyses for $(H_2en)Sc_2(SO_4)_4 \cdot (H_2O)_{0.72}$ ($M_r = 549.05$): calculated (observed) C 4.37% (4.50%), H 2.10% (1.99%), N 5.10% (4.92%), S 23.36% (23.09%). FTIR data ($cm^{-1}$): 3115 (w), 1509 (w), 1347 (vw), 1221 (m), 1101 (s), 1077 (s), 1064 (s), 1053 (s), 769 (w), and 659 (m).

### 2.2. Single crystal X-ray diffraction and structure determination

The X-ray diffraction data for $(H_2en)Sc_2(SO_4)_4 \cdot (H_2O)_{0.72}$ were collected at 200 K on a Siemens SMART single crystal diffractometer equipped with a CCD area detector and a sealed-tube $MoK\alpha$ source (graphite monochromator, $\lambda = 0.7107$ Å). The detector frames were integrated by use of the program SAINT [26]. Systematic variations in the data were corrected by the analysis of replicate reflections using the program SADABS [27]. The structure was solved by the use of direct methods, while full-matrix least-squares refinement on $F^2$ (including all data) was performed, both using the SHELXTL package [28]. All hydrogen atoms (except for water) were included in idealized positions. All non-hydrogen atoms were refined anisotropically. Crystallographic data and refinement details for the title compound are summarized in Table 1. Relevant bond distances and angles are listed in Table 2.

### 2.3. Bulk measurements

These measurements are based on samples that were stored in air for several months. It is expected that some of the cocrystallized water was no longer present in the samples used for these measurements. X-ray powder diffraction (XPD) data were collected on a Rigaku Miniflex diffractometer with $CuK\alpha$ radiation in steps of

Table 1
Single crystal data and structure refinement details for $(H_2en)Sc_2(SO_4)_4 \cdot (H_2O)_{0.72}$

| | |
|---|---|
| Empirical formula | $C_2H_{11.44}N_2O_{16.72}S_4Sc_2$ |
| Formula weight | 549.26 |
| Space group | $P2/c$ |
| Crystal system | Monoclinic |
| $a$ (Å) | 8.5966(13) |
| $b$ (Å) | 5.1068(8) |
| $c$ (Å) | 18.848(3) |
| $\beta$ (deg) | 91.210(3) |
| $V$ (Å$^3$) | 827.2(3) |
| Calculated density (mg m$^{-3}$) | 2.205 |
| $Z$ | 2 |
| Absorption coefficient (mm$^{-1}$) | 1.417 |
| Temperature (K) | 200 |
| GOF | 1.032 |
| $R_{int}$ | 0.0279 |
| $R_1{}^a$ [$I > 2\sigma(I)$] (all data) | 0.0354/0.0526 |
| $wR_2{}^b$ [$I > 2\sigma(I)$] (all data) | 0.0878/0.0978 |

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

Table 2
Selected bond lengths (Å) and angles (deg) for $(H_2en)Sc_2(SO_4)_4 \cdot (H_2O)_{0.72}$

| | | | |
|---|---|---|---|
| Sc–O(3) | 2.041(2) | S(1)–O(3) | 1.469(2) |
| Sc–O(1)#1 | 2.069(2) | S(1)–O(2) | 1.474(2) |
| Sc–O(2)#2 | 2.076(2) | S(1)–O(1) | 1.482(2) |
| Sc–O(5) | 2.082(2) | S(2)–O(8) | 1.444(2) |
| Sc–O(7)#3 | 2.088(2) | S(2)–O(7) | 1.471(2) |
| Sc–O(6)#4 | 2.104(2) | S(2)–O(5) | 1.475(2) |
| S(1)–O(4) | 1.440(2) | S(2)–O(6) | 1.479(2) |
| | | | |
| O(3)–Sc–O(1)#1 | 91.90(8) | O(1)#1–Sc–O(6)#4 | 92.49(8) |
| O(3)–Sc–O(2)#2 | 95.61(9) | O(2)#2–Sc–O(5) | 88.41(8) |
| O(3)–Sc–O(5) | 175.97(9) | O(2)#2–Sc–O(7)#3 | 89.12(8) |
| O(3)–Sc–O(7)#3 | 87.09(8) | O(2)#2–Sc–O(6)#4 | 177.44(8) |
| O(3)–Sc–O(6)#4 | 86.80(9) | O(5)–Sc–O(7)#3 | 92.77(8) |
| O(1)#1–Sc–O(2)#2 | 88.28(8) | O(5)–Sc–O(6)#4 | 89.17(8) |
| O(1)#1–Sc–O(5) | 88.42(8) | O(7)#3–Sc–O(6)#4 | 90.17(8) |
| O(1)#1–Sc–O(7)#3 | 177.11(8) | | |
| | | | |
| S(1)–O(1)–Sc#1 | 141.25(11) | S(2)–O(5)–Sc | 143.18(13) |
| S(1)–O(2)–Sc#2 | 141.12(13) | S(2)–O(6)–Sc#4 | 141.16(13) |
| S(1)–O(3)–Sc | 158.56(15) | S(2)–O(7)–Sc#3 | 149.00(12) |

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

0.02° over the $3° < 2\theta < 40°$ angular range and a fixed-time counting of 2 s/step at room temperature. TGA was performed using a TA Instruments TGA 2950 thermogravimetric analyzer at a heating rate of 15 °C min$^{-1}$ in $N_2$ stream. Elemental analysis was performed by Midwest Microlab, Indianapolis, IN. FTIR spectra were collected on top of a germanium crystal using a Bruker Vertex 70 spectrometer equipped with a mercury cadmium telluride (MCT) detector and a Pike ATR accessory.

## 3. Results and discussion

The structure of the title compound consists of an infinite two-dimensional $[Sc(SO_4)_2]_n^{n-}$ network, ethylenediammonium cations for charge-compensation, and water molecules. The asymmetric unit contains one scandium(III) cation, two sulfate dianions, half of an $(H_2en)^{+2}$ dication, and a partially occupied, disordered water molecule (Fig. 1). The $(H_2en)^{+2}$ dication lies on a two-fold axis while the partially occupied water molecule is disordered over two sites related to each other by a two-fold rotation.

To the best of our knowledge, the title compound is the first layer structure of organically templated scandium sulfate. As shown in Fig. 2, scandium atoms are bridged by sulfate groups into an infinite layer structure parallel to the *ab*-plane. The unique scandium atom is approximately octahedrally coordinated by the oxygen atoms of six sulfate groups (three above the plane and three below). The Sc–O bond distances are between 2.041(2) and 2.104(2) Å, with an average value of 2.08(2) Å. These values are typical of Sc–O bonds, as seen, for example, in scandium formate which has a Sc–O distance of 2.0794(9) Å [29]. The O–Sc–O angles are approximately octahedral and range from 86.80(9)° to 95.61(9)°. In each sulfate group, three oxygen atoms are coordinated to scandium and one is terminal. For bridged oxygen atoms, the angles of S–O–Sc range from 141.12(13)° to 158.56(15)°. The S–O bonds containing terminal oxygen atoms are slightly shorter, 1.440(2) and 1.444(2) Å, than the bonds containing the coordinated oxygen atoms, 1.469(2) to 1.482(2) Å, as also observed in

the case of $[H_3N(CH_2)_6NH_3][Sc(H_2O)_2(SO_4)_2]_2 \cdot 2H_2O$ and $[C(NH_2)_3]_3[Sc(SO_4)_3] \cdot 3H_2O$ [19]. The sulfate anions are approximately tetrahedral, with no significant geometrical differences between the two independent sulfate anions.

The layer structure corresponds to a topological net that is defined by three (sulfate) and six nodes (scandium) in a 2:1 ratio. The Sc···S separations are 3.3536(9) to 3.4505(9) Å. If all the bridge oxygen atoms were replaced by linear spacers and terminal oxygen atoms omitted, the
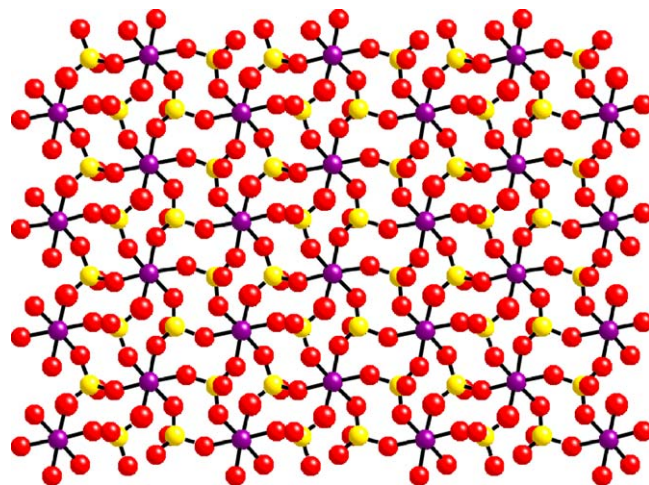


Fig. 2. A view of the anionic $[Sc(SO_4)_2]_n^{n-}$ layered structure with the four-membered rings, composed of corner sharing $SO_4$ and $ScO_6$ polyhedra, viewed along the *c*-axis. (Color online.) Scheme: oxygen (black), scandium (equatorial) and sulfur (white).
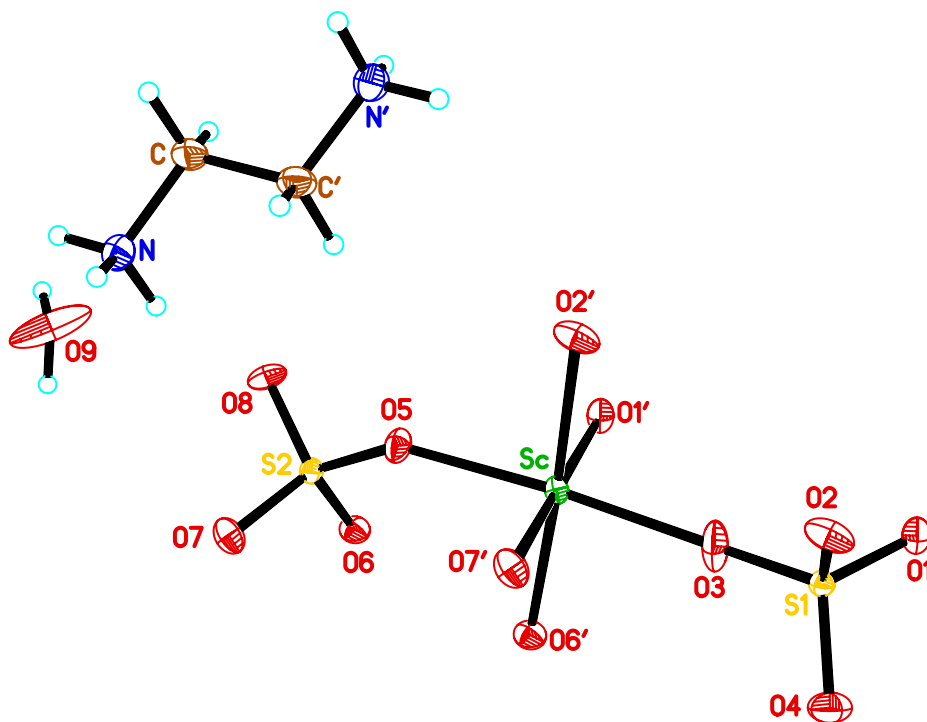


Fig. 1. Atomic numbering scheme of $(H_2en)Sc_2(SO_4)_4 \cdot (H_2O)_{0.72}$. Thermal ellipsoids are drawn at the 50% probability level. Atoms with primes are related by symmetry. (Color online.)
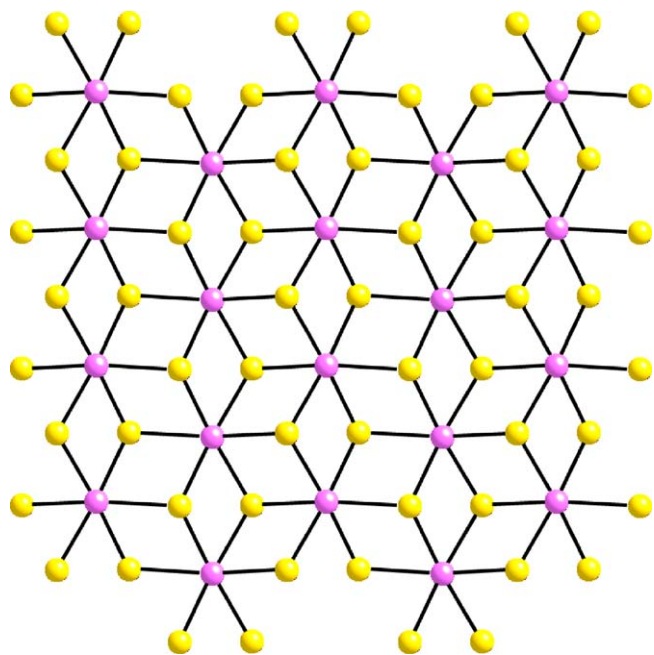
Fig. 3. A $4_3^6$ network can be identified in the structure by omitting all oxygen atoms and directly connecting Sc (white) and S (black) atoms. (Color online.)

layer could be mapped onto a two-dimensional net with a $4_3^6$ topology (see Fig. 3), analogous to the well-known $CdCl_2$ type. The same layer structure also exists in compounds such as $ASc(SO_4)_2$ ($A$ = K, Rb, Cs) [30] and $KAl(SO_4)_2$ [31].

Fig. 4 presents a view of the title compound along the $b$-axis (edge-on to the layers). The layers are stacked in an $ABAB$ fashion with an interlayer distance of 9.424(2) Å, where $A$ and $B$ represent two orientations of the layer related to each other by the c-glide operation. $(H_2en)^{+2}$ dications and disordered, partially occupied water molecules reside between anionic $[Sc(SO_4)_2]_n^{n-}$ sheets. N–H···O (N···O distances of 2.882(3), 2.885(3) and 2.914(3) Å) and O···H–O hydrogen bonds (O···O distance of 2.967(17) Å) stabilize the network [32,33]. The hydrogen-bond information is summarized in Table 3.

The title compound is different from the two previously reported scandium sulfate chain structures [19]. Each sulfate group in $(H_2en)Sc_2(SO_4)_4 \cdot (H_2O)_{0.72}$ bridges three scandium atoms into two dimensional sheets, while in both chain structures, the sulfate group bridges only two scandium atoms. Hydrothermal conditions may be one of the reasons for this high number of connections because the two compounds with chain structures were crystallized at room temperature. Another contributing factor may be the scandium-to-sulfate ratio present during crystallization. In the present case, a $Sc^{3+}:SO_4^{2-}$ molar ratio of approximately 1:1 was used, while in the case of the chain compounds, an approximately two-fold excess of sulfate was present. Highly acidic conditions are necessary to facilitate the decomposition of the scandium oxide and promote crystal growth. It is likely that the pH of the
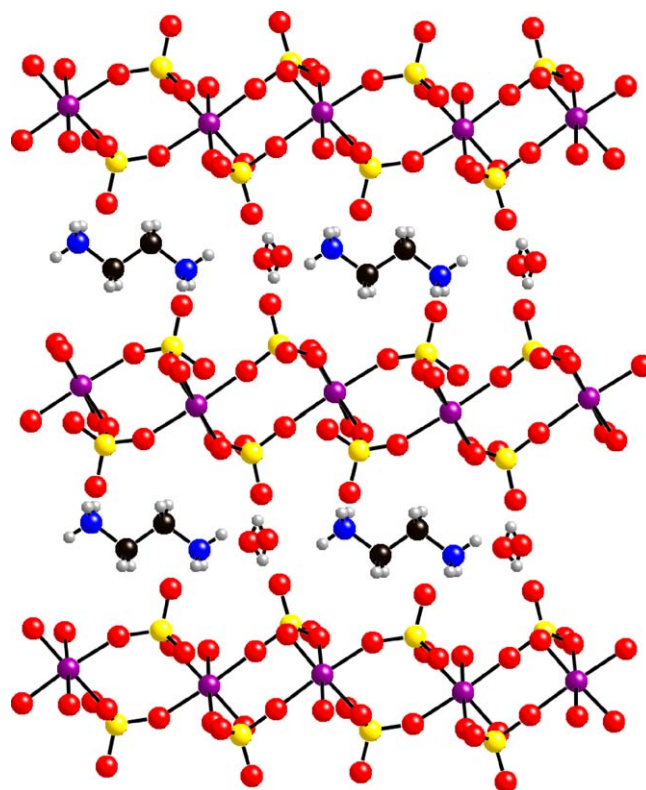


Fig. 4. A view of the title compound viewed approximately along the $b$-axis. (Color online.) Sulfur (large white), oxygen (black), carbon (filled equatorial), nitrogen (striped), scandium (equatorial) and hydrogen (small white).

Table 3
Hydrogen bonds for $(H_2en)Sc_2(SO_4)_4 \cdot (H_2O)_{0.72}$ (Å and deg)

| D–H···A | $d$(D–H) | $d$(H···A) | $d$(D···A) | <(DHA) |
|---|---|---|---|---|
| N–H(1)···O(4)#1 | 0.91 | 2.00 | 2.885(3) | 165 |
| N–H(1)···O(9) | 0.91 | 2.60 | 3.096(16) | 115 |
| N–H(2)···O(8)#2 | 0.91 | 2.05 | 2.914(3) | 159 |
| N–H(3)···O(8) | 0.91 | 2.01 | 2.882(3) | 161 |
| O(9)–H(6)···O(4)#3 | 0.819(19) | 2.34(3) | 2.967(17) | 133(5) |

Symmetry transformations used to generate equivalent atoms: #1: $x - 1$, $-y + 1$, $z - 1/2$; #2: $x$, $y + 1$, $z$; #3: $x - 1$, $-y$, $z - 1/2$.
The hydrogen atoms of the $(H_2en)^{+2}$ dication were placed in idealized positions and thus no uncertainties are given.

crystallization solution will affect the growth dynamics, possibly including the topology. The cocrystallized cation is also expected to play a significant role in templating the anionic framework and may ultimately determine its dimensionality.

The fabrication of 3D frameworks may be possible through appropriate synthetic conditions and molecular templates. For the construction of 3D scandium sulfate frameworks, a higher number of connections between scandium and sulfate groups may be desirable, although it is possible to build 3D networks with the same number of connections. For example, in the analogous, but 3D
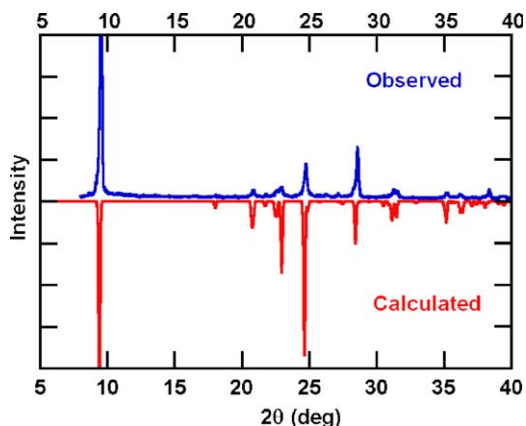
Fig. 5. XPD of $(H_2en)Sc_2(SO_4)_4 \cdot (H_2O)_{0.72}$ at room temperature. The calculated pattern (200 K) is shown inverted for easy comparison.



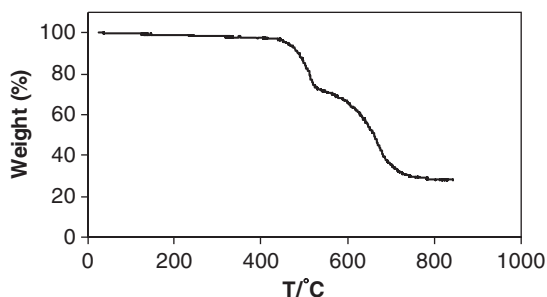Fig. 6. TGA curve of $(H_2en)Sc_2(SO_4)_4 \cdot (H_2O)_{0.72}$.

$(H_2en)Sc_2(HPO_4)_4$ [21,22] compound, the $HPO_4^{2-}$ tetrahedron is linked to two scandium octahedra within the same layer and one in the adjacent layer with the fourth apex (–OH) being terminal.

The bulk properties of the title compound were further characterized by XPD. As illustrated in Fig. 5, the major peaks that are obtained from XPD are in good agreement with those calculated from single crystal data. The minor differences of intensity between the observed and calculated patterns may be caused by several factors, including: (1) The powder pattern was obtained at room temperature while the single crystal data was collected at 200 K. (2) The single crystal data were collected shortly after harvesting the crystals while the powder pattern was collected on a sample that had been stored in air for several months, potentially resulting in different water content. (3) Possible preferred orientation of the crystallites in the XPD can affect the relative intensities.

As revealed by TGA in Fig. 6, the title compound is thermally very stable. Below 400 °C, a weight loss of 2.6% occurs, which if attributed to water, corresponds to water occupancy of about 0.8 (in good agreement with the 0.72 occupancy determined by X-ray diffraction). A two-step weight loss was observed between 400 and 750 °C. The first step, between 400 and 525 °C corresponds to an additional weight loss of about 24%. Although attributed to the decomposition and loss of the organic component, this step

is greater than would be expected for the simple loss of ethylenediammonium (11%) and must therefore include some decomposition of the sulfate anions. The weight loss between 525 and 750 °C accounts for about 44% of the total mass and is attributed to a sulfur-containing species. Although we are not able to identify the exact decomposition products, the total weight loss is about 73% which is in good agreement with the assumption that the final product is $Sc_2O_3$ (calculated weight loss at about 75%).

## 4. Conclusion

The first organically templated layered scandium sulfate was successfully synthesized by the hydrothermal method. Scandium ions are bridged by sulfate groups with a ratio of 1:2 into the $4_3^6$ net typified by $CdCl_2$. Charge compensating $(H_2en)^{+2}$ organic templates are located between the layers with hydrogen bonding to the scandium sulfate anionic layer. This compound is stable up to 400 °C.

## Supplemental material

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary Publication No. CCDC 293508. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44)1223 336-033; WWW: http://www.ccdc.cam.ac.uk/products/csd/request/).

## Acknowledgments

## Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2006.02.006.

## References

[1] A.K. Cheetham, G. Ferey, T. Loiseau, Angew. Chem. Int. Ed. Engl. 38 (1999) 3268.
[2] M.E. Davis, Nature (London) 417 (2002) 813.
[3] J.S. Chang, J.S. Hwang, S.H. Jhung, S.E. Park, G. Ferey, A.K. Cheetham, Angew. Chem. Int. Ed. Engl. 43 (2004) 2819.
[4] J. Perles, M. Iglesias, M.A. Martin-Luengo, M.A. Monge, C. Ruiz-Valero, N. Snejko, Chem. Mater. 17 (2005) 5837.
[5] S.M. Kuznicki, V.A. Bell, S. Mair, H.W. Hillhouse, R.M. Jacubinas, C.M. Braunbarth, B.H. Toby, M. Tsapatsis, Nature (London) 412 (2001) 720.
[6] A. Clearfield, Solvent Extr. Ion Exch. 18 (2000) 655.

[7] A. Choudhury, J. Krishnamoorthy, C.N.R. Rao, Chem. Commun. (2001) 2610.

[8] G. Paul, A. Choudhury, C.N.R. Rao, Dalton Trans. (2002) 3859.

[9] G. Paul, A. Choudhury, C.N.R. Rao, Chem. Commun. (2002) 1904.

[10] T. Bataille, D. Louer, J. Mater. Chem. 12 (2002) 3487.

[11] Y. Xing, Z. Shi, G. Li, W. Pang, Dalton Trans. (2003) 940.

[12] Y. Xing, Y. Liu, Z. Shi, H. Meng, W. Pang, J. Solid State Chem. 174 (2003) 381.

[13] M. Doran, A.J. Norquist, D. O'Hare, Chem. Commun. (2002) 2946.

[14] A.J. Norquist, P.M. Thomas, M.B. Doran, D. O'Hare, Chem. Mater. 14 (2002) 5179.

[15] J.S. Brodkin, B.M. Foxman, J. Chem. Soc. Chem. Commun. (1991) 1073.

[16] J. Perles, M. Iglesias, C. Ruiz-Valero, N. Snejko, Chem. Commun. 2003 (2003) 346.

[17] S.R. Miller, P.A. Wright, C. Serre, T. Loiseau, J. Marrot, G. Ferey, Chem. Commun. (2005) 3850.

[18] D.L. Long, R.J. Hill, A.J. Blake, N.R. Champness, P. Hubberstey, C. Wilson, M. Schroder, Chem. Eur. J. 11 (2005) 1384.

[19] A.B. Ilyukhin, S.P. Petrosyants, Russ. J. Inorg. Chem. 11 (2004) 1232.

[20] I. Bull, P.S. Wheatley, P. Lightfoot, R.E. Morris, E. Sastre, P.A. Wright, Chem. Commun. (2002) 1180.

[21] I. Bull, V. Young, S.J. Teat, L. Peng, C.P. Grey, J.B. Parise, Chem. Mater. 15 (2003) 3818.

[22] D. Riou, F. Fayon, D. Massiot, Chem. Mater. 14 (2002) 2416.

[23] B. Ewald, S. Natarajan, Y. Prots, R. Kniep, Z. Kristallogr. NCS 219 (2004) 335.

[24] H. Park, I. Bull, L. Peng, J. Young, G. Victor, C.P. Grey, J.B. Parise, Chem. Mater. 16 (2004) 5350.

[25] F.H. Allen, Acta Crystallogr. B 58 (2002) 380.

[26] SAINT, Version 6.28a; Bruker AXS, Inc., Madison, WI, USA, 1996.

[27] G.M. Sheldrick, SADABS, Version 2.03a, Bruker AXS, Inc., Madison, WI, USA, 2001.

[28] G.M. Sheldrick, SHELXTL, Version 6.12; Bruker AXS Inc., Madison, WI, USA, 2001.

[29] A.B. Ilyukhin, S.P. Petrosyants, Acta Crystallogr. E 60 (2004) m151.

[30] F.M. Korytnaya, S.N. Putilin, A.N. Pokrovskii, Russ. J. Inorg. Chem. 28 (1983) 968.

[31] J.M. Manoli, P. Herpin, G. Pannetier, Bull. Soc. Chim. Fr. (1970) 98.

[32] J. Emsley, Chem. Soc. Rev. 9 (1980) 91.

[33] G.R. Desiraju, T. Steiner, The weak hydrogen bond, in: Structural Chemistry and Biology, Oxford University Press, New York, 1999.