Structural and spectral characterization of a new

non-centrosymmetric organic thiosulfate

Bikshandarkoil R. Srinivasan[a], Savita Khandolkar[a], Rita Jyai[a], Krishnan Ravikumar[b],

Balasubramanian Sridhar[b], Subramanian Natarajan[c]

[a]Department of Chemistry, Goa University, Goa 403 206, INDIA.
 Email: srini@unigoa.ac.in Telephone: 0091-(0)832-6519316; Fax: 0091-(0)832-2451184
[b]Laboratory of X-ray Crystallography, CSIR-Indian Institute of Chemical Technology
Hyderabad, 500 007, INDIA.
[c]Department of Physics, Madurai Kamaraj University, Madurai -625 021, INDIA.

Abstract

Aqueous reaction of ammonium thiosulfate with ethylenediamine (en) results in the formation of the title compound $(enH_2)[S_2O_3]$ (**1**) (enH_2 = ethylenediammonium) in good yields. Compound **1** was characterized by analytical data, IR, Raman and NMR spectra, X-ray powder pattern and its crystal structure was determined. The structure of **1** which crystallizes in the non-centrosymmetric orthorhombic space group $P2_12_12_1$, consists of two crystallographically independent $(enH_2)^{2+}$ dications and two unique thiosulfate anions, which are interlinked by three varieties of H-bonding interactions, namely N-H···O, N-H···S, and C-H···O. ^1H and ^{13}C NMR spectra reveal the purity of **1** while its transparent nature can be evidenced from the UV-Vis-NIR spectral data. In compound **1** which exhibits SHG property, the infrared and Raman spectra confirm the presence of the organic dication and the thiosulfate anion.

Keywords: Ethylenediammonium; Thiosulfate; Crystal structure; Non-centrosymmetric; IR, Raman and NMR spectra

1. Introduction

Non-centrosymmetric solids are of current interest to researchers because they can exhibit several desirable physical properties including nonlinear optical activity (NLO) [1]. It is well-known that solids crystallize in one of 230 possible space groups, of which 65 (Sohncke space groups) do not possess mirror or inversion symmetry and are thus non-centrosymmetric [2, 3]. Although more than 70% of all known crystal structures in the Cambridge Structural Database (CSD) reside in the four centrosymmetric space groups *P2$_1$/c*, *P-1*, *C2/c* and *Pbca* in accordance with Kitaigorodskii's principle of close packing [4], it is interesting to note that two of the five most popular space groups in the CSD are the Sohncke space groups *P2$_1$2$_1$2$_1$* (7.6%) and *P2$_1$* (5.3%) which account for an eighth (~12.9%) of all known crystal structures [5].

Chiral molecules when crystallized from an enantiomerically pure solution must have a structure belonging to a Sohncke space group [6, 7], which can explain the use of naturally occurring L-amino acids or D-sugars or chiral compounds as reagents for the synthesis of new materials for NLO applications [1]. Unlike chiral molecules, achiral molecules can crystallize in both centrosymmetric and Sohncke space groups [2, 6]. Although it is not possible to accurately predict if a given achiral compound will crystallize in a Sohncke space group, based on a study of the CSD it has been reported that molecular flexibility plays a role in space group choice for achiral molecules [7]. While centrosymmetric space groups are the most likely preferred hosts for achiral compounds, several achiral molecules, for example sodium chlorate $NaClO_3$ [8, 9], $(enH_2)[SO_4]$ (enH_2 = ethylene-diammonium) [10] crystallizing in Sohncke space groups are well documented. It is to be noted that the chiral crystallization of sodium chlorate has been known for over 100 years [11], while the achiral compound $(enH_2)[SO_4]$ which crystallizes in the chiral space group *P4$_1$* has been of considerable interest in recent years [12-14].

A survey of the literature reveals that the $(enH_2)^{2+}$ unit is flexible and can exist in a variety of structural environments with different counter anions [10, 15-50]. In the family of achiral compounds containing $(enH_2)^{2+}$ as the charge balancing cation (Table 1), compounds crystallize in both centrosymmetric and Sohncke space groups. It is interesting to note that compounds of the type $(enH_2)[AB_4]$ where AB_4 is a tetrahedral dianion such as $[SO_4]^{2-}$, $[BeF_4]^{2-}$, $[CrO_4]^{2-}$ etc. (Entry Nos. 1-6 in Table 1) have a tendency to crystallize in a Sohncke space group. In the present work, we have charge balanced the acentric thiosulfate anion with the $(enH_2)^{2+}$ cation and the resulting product ethylenediammonium thiosulfate **1** crystallizes in the Sohncke space group $P2_12_12_1$. The synthesis, structural characterization, spectral and thermal properties of **1** is described in this paper.

Table 1
Geometry of achiral anions in compounds charge balanced by ethylenediammonium cations

No	Compound	Geometry of anion	Space group	Reference
1	$(enH_2)[SO_4]$	Tetrahedron	$P4_1$	10, 15
2	$(enH_2)[BeF_4]$	Tetrahedron	$P4_12_12$	16
3	$(enH_2)[CrO_4]$	Tetrahedron	$P2_12_12_1$	19
4	$(enH_2)[MoS_4]$	Tetrahedron	$P2_12_12_1$	17
5	$(enH_2)[WS_4]$	Tetrahedron	$P2_12_12_1$	18
6	$(enH_2)[ZnCl_4]$	Tetrahedron	$P2_12_12_1$	20
7	$(enH_2)[S_2O_3]$	Tetrahedron	$P2_12_12_1$	This work
8	$(enH_2)[MoO_4]$	Tetrahedron	$P\bar{1}$	21
9	$(enH_2)[CuCl_4]$	Tetrahedron	$P2_1/b$	22
10	$(enH_2)[MnCl_4]$	Tetrahedron	$P2_1/b$	22
11	$(enH_2)[CuBr_4]$	Tetrahedron	$P2_1/a$	23
12	$(enH_2)[WOS_3]$	Tetrahedron	$P2_1/n$	24
13	$(enH_2)[FPO_3]$	Tetrahedron	$Pbca$	36
14	$(enH_2)[Au(SO_3)_2(en)]_2$	Square planar	$P\bar{1}$	33
15	$(enH_2)[Cu(C_{10}H_2O_8)]\cdot2.5H_2O$	Square planar	$P2_1/c$	37
16	$(enH_2)[picrate]_2\cdot2H_2O$	Planar ring	$Pnma$	29
17	$(enH_2)[phthalate]$	Planar ring	$Pbca$	35
18	$(enH_2)_2[P_4O_{12}]\cdot H_2O$	Planar ring	$Pcca$	34
19	$(enH_2)[Cr_2O_7]$	Corner shared bitetrahedron	$C2/c$	19
20	$(enH_2)_2[Cr_2O_7][C_2O_4]$	Corner shared bitetrahedron	$C2/c$	38

21	$(enH_2)[Mn(SO_4)_2(H_2O)_4]$	Octahedron	$P\bar{1}$	30
22	$(enH_2)[Cd(SO_4)_2(H_2O)_4]$	Octahedron	$P\bar{1}$	39
23	$(enH_2)[Mg(SO_4)_2(H_2O)_4]$	Octahedron	$P\bar{1}$	40
24	$(enH_2)[Fe(SO_4)_2(H_2O)_4]$	Octahedron	$P\bar{1}$	41
25	$(enH_2)[Co(SO_4)_2(H_2O)_4]$	Octahedron	$P\bar{1}$	42
26	$(enH_2)[Cu(C_7H_3NO_4)_2(H_2O)_4]$ $\cdot 2H_2O$	Octahedron	$P\bar{1}$	43
27	$(enH_2)[TeCl_6]$	Octahedron	$P\bar{1}$	32
28	$(enH_2)[SnCl_6]$	Octahedron	$P\bar{1}$	32
29	$(enH_2)[HgCl_4]$	Corner sharing octahedron	$Pccn$	47
30	$(enH_2)[CdCl_4]$	Corner sharing octahedron	$P2_1/c$	50
31	$(enH_2)_5[Ce_2(SO_4)_9]$	Tricapped trigonal prism	$P\bar{1}$	44
32	$(enH_2)[Np_2F_{10}]$	Tricapped trigonal prism	$C2/c$	48
33	$(enH_2)[ICl_2]Cl$	Linear	$C2/c$	45
34	$(enH_2)[H_2PO_4]_2$	Tetrahedron	$P2_1/a$	25
35	$(enH_2)[HgBr_4] \cdot H_2O$	Tetrahedron	$P2_1/m$	46
36	$(enH_2)_2[ZnCl_4]Cl_2$	Tetrahedron	$Pnma$	26
37	$(enH_2)_2[CoCl_4]Cl_2$	Tetrahedron	$Pnma$	27
38	$(enH_2)_2[HgCl_4]Cl_2$	Square pyramid	$Pnma$	28
39	$(enH_2)[VTeO_5]_2$	An infinite layer	$P\bar{1}$	49
40	$(enH_2)_3[P_6O_{18}][Te(OH)_6]_2 \cdot 2H_2O$	Planar ring; octahedron	$P\bar{1}$	31

2.1 Material and Methods

Infrared spectra of the samples diluted in KBr were recorded in the region $4000 - 400$ cm^{-1} using a Shimadzu (IR Prestige-21) FT-IR Spectrometer, at a resolution of 4 cm^{-1}. Raman spectra were recorded using a model RFS 100/S Bruker instrument with a Nd: YAG laser operated at 1064 nm with a power output of 200 mW. The spectrum was recorded in the range 3500–100 cm^{-1} at a resolution of 4 cm^{-1}. The sample was finely powdered and pressed into a small depression on a metal disc and mounted on the sample compartment. The UV-Visible spectra of aqueous solutions of **1** were recorded in matched quartz cells using an Agilent 8453 UV–Visible spectrophotometer in the range 200–1100 nm. ^{1}H and ^{13}C NMR spectra were recorded in D_2O on a Bruker 300 MHz FT-NMR spectrometer. X-ray powder patterns were measured on a Rigaku Miniflex II powder diffractometer using

Cu-K$_\alpha$ radiation with a Ni filter. Simultaneous thermogravimetry (TG) and differential thermal analyses (DTA) of a powdered sample of **1** were performed in the temperature range of 25°C to 900°C, using a Netzsch STA-409 PC thermal analyzer, at a heating rate of 10 °C/min. The crucible used was of alumina (Al_2O_3), which also served as a reference for the sample. The second harmonic generation (SHG) conversion efficiency was tested using a modified setup of Kurtz and Perry as described previously [51].

2.2 Synthesis of (enH$_2$)[S$_2$O$_3$] 1

Method 1: Ammonium thiosulphate (7.419 g, 50 mmol) was dissolved in distilled water (~25 ml). To the clear solution obtained, 99.9% ethylenediamine (~4 ml) was added and the reaction mixture was filtered after ~ 1 h. The clear filtrate was left undisturbed for slow evaporation at room temperature. Transparent blocks separated out after ~5 days. The crystalline product was isolated by filtration, washed with ice-cold water followed by ether and dried in air to yield 6.89 g of compound **1** in 80% yield.

Method 2: Ethylenediamine dihydrochloride (6.65 g, 50 mmol) was dissolved in water (~25 ml). Into this, a solution of ammonium thiosulphate (7.41 g, 50 mmol) or sodium thiosulfate (6.20 g) dissolved in distilled water (~25 ml) was added. The reaction mixture was filtered and the clear filtrate was kept for slow evaporation at room temperature. Transparent blocks which separated after ~5 days were isolated by filtration as in method A, to yield 6.98 g of compound **1** in 79 % yield.

2.3 Crystal structure determination

The intensity data were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) by the ω-scan method. Preliminary lattice parameters and orientation matrices were obtained from

four sets of frames. Integration and scaling of intensity data were accomplished using the program SAINT [52]. The structure was solved by direct methods using SHELXS97 [53] and refinement was carried out by full-matrix least-squares technique using SHELXL97 [53]. Anisotropic displacement parameters were calculated for all non-hydrogen atoms. H atoms attached to the N atoms of the $(enH_2)^{2+}$ cation were located in a difference Fourier density map and refined isotropically. The H atoms of the methylene groups were located in a difference electron density map but were positioned geometrically and included as riding atoms, with C-H = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. Technical details of data acquisition and selected refinement results are listed in Table 2.

Table 2
Crystal data and structure refinement for $(enH_2)[S_2O_3]$ **1**

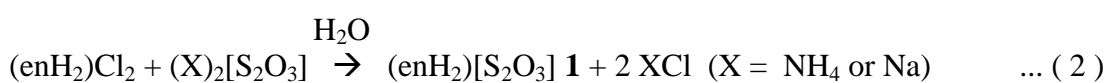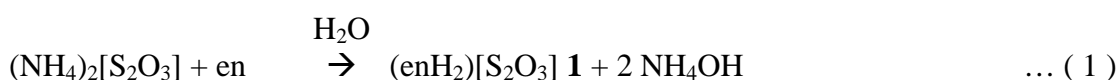|	
Empirical formula	$(C_2H_{10}N_2)^{2+} \cdot (S_2O_3)^{2-}$
Formula weight	174.24
Temperature	294(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic $P2_12_12_1$
Unit cell dimensions	a = 5.9125(6) Å
	b = 10.2280(9)Å
	c = 23.069(2) Å
	$\alpha = \beta = \gamma = 90^o$
Volume	1395.0(2)Å^3
Z, Calculated density	8,1.659 mg/m^3
Absorption coefficient	0.705 mm^{-1}
F(000)	736
Crystal size	0.15 x 0.14 x 0.06
θ range for data collection	1.77^o to 25°
Limiting indices	$-7 \leq h \leq 7$, $-12 \leq k \leq 12$, $-27 \leq l \leq 27$
Reflections collected /unique	13310 / 2452 [R(int) = 0.0217]
Completeness $\theta = 25.00^o$	100.0 %
Absorption correction	None

|	
Refinement method	Full- matrix least-squares on F^2
Data / restraints / parameters	2452 / 0 / 211
Goodness-of-fit on F^2	1.131
Final R indices [I>2σ(I)]	R1 = 0.0184, wR2 = 0.0534
R indices (all data)	R1 = 0.0187, wR2 = 0.0537
Absolute structure parameter	-0.02(6)
Largest diff. peak and hole	0.161 and -0.270 e.A^{-3}

3. Results and discussion

3.1. Synthesis

Colourless blocks of compound **1** were synthesized in good yields by an aqueous reaction of ammonium thiosulfate with ethylenediamine (en) followed by slow evaporation of the reaction mixture (eq. 1). Crystalline blocks which are as long as 1 cm (Fig. S1) can be grown by this procedure. The synthetic protocol is similar to the one employed for other $(enH_2)^{2+}$ compounds like $(enH_2)[MS_4]$ (M = Mo, W) [17, 18], $(enH_2)[CrO_4]$ [19] and $(enH_2)[WOS_3]$ [24]. The reaction involves the displacement of the weaker base ammonia (pka = 9.24) from ammonium thiosulfate by the stronger base en (pka = 10.09) leading to the formation of **1**.

$$(NH_4)_2[S_2O_3] + en \quad \xrightarrow{H_2O} \quad (enH_2)[S_2O_3]\ \mathbf{1} + 2\ NH_4OH \qquad \qquad \dots (\,1\,)$$

$$(enH_2)Cl_2 + (X)_2[S_2O_3] \quad \xrightarrow{H_2O} \quad (enH_2)[S_2O_3]\ \mathbf{1} + 2\ XCl\ \ (X = NH_4\ or\ Na) \qquad \dots (\,2\,)$$

Alternatively compound **1** can also be prepared by the slow evaporation of aqueous solutions containing ethylenediamine dihydrochloride and ammonium or sodium thiosulfate (eq. 2) in stoichiometric amounts. Both methods can also be used to synthesize the closely related compound $(enH_2)[SO_4]$ by using ammonium sulfate instead of the thiosulfate in eqs. 1 and 2. The observed unit cell parameters ($a = b = 5.996(1)$Å; $c = 18.056(4)$Å; $\alpha = \beta = \gamma = 90^o$; $V = 648.6(3)$ Å^3) of $(enH_2)[SO_4]$ prepared according to

equation 1 are in very good agreement with literature values [15]. It is to be noted that the synthesis of $(enH_2)[SO_4]$ has been earlier reported by a direct reaction of en with sulfuric acid [15]. Compound **1** is soluble in water and insoluble in most common organic solvents. The identical nature of the products obtained from the two methods was confirmed by a comparison of the X-ray powder pattern of the products (Fig. 1). The phase purity of the product in both methods was further confirmed by their identical infrared, Raman and optical spectra (Fig. S2).
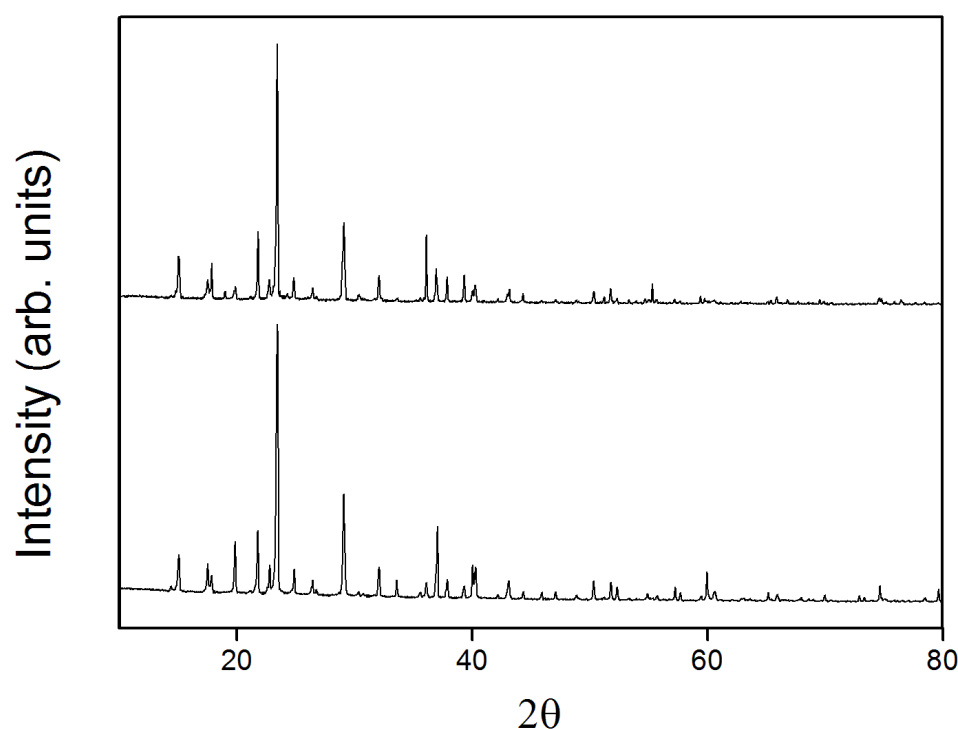

Fig. 1. X-ray powder pattern of products from method 1(top) and method 2 (bottom)

3.2. Description of crystal structure of 1

The title compound **1** crystallizes in the non-centrosymmetric orthorhombic space group $P2_12_12_1$ with all atoms situated in general positions. The crystal structure of **1** consists of two crystallographically independent ethylenediammonium dications and two unique thiosulfate anions (Fig. 2). Unlike in $(enH_2)[SO_4]$ where the $(enH_2)^{2+}$ cation adopts a chiral gauche conformation (Fig. S3), both the unique $(enH_2)^{2+}$ cations in **1** exhibit an anti

conformation (Fig. 3). The observed bond angles of the unique organic dications (Table 3) are in the normal range and are in agreement with other compounds containing the same cation. The nearly equivalent C-N distances (1.477(3) and 1.479(2) Å in the first cation; 1.469(2) and 1.475(2) Å in the second cation) indicate the diprotonation of the organic diamine (Table 3). In the tetrahedral thiosulfate anions, the observed O-S-O and the O-S-S bond angles (Table 3) indicate a distortion of the $\{S_2O_3\}$ tetrahedron. The S-O bond lengths in the first unique anion range from 1.455(1) to 1.472(1) Å, while the S-S bond distance is 1.981(1) Å (Table 3). For the second unique thiosulfate anion the S-O bond distances range from 1.462(1) to 1.479(1) Å, while the S11-S12 bond length is 1.984(1) Å.
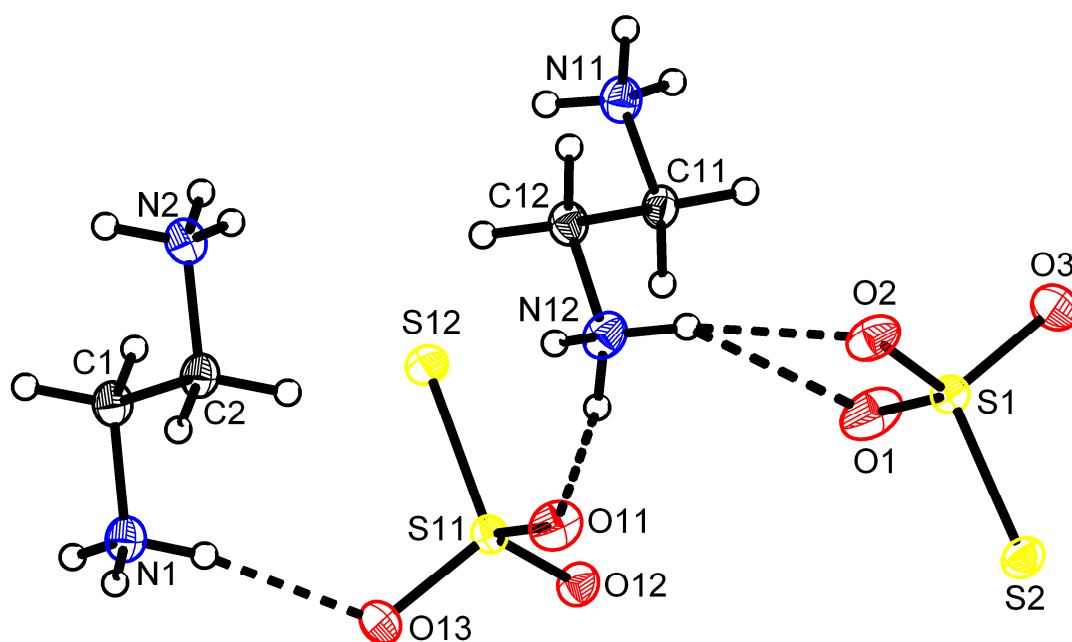
Fig. 2. Molecular structure of $(enH_2)[S_2O_3]$ **1**, showing atom labeling scheme. Thermal ellipsoids are drawn at the 30 % probability level excepting for H atoms, which are shown as circles of arbitrary radius. Intramolecular H-bonding is shown by dashed lines.
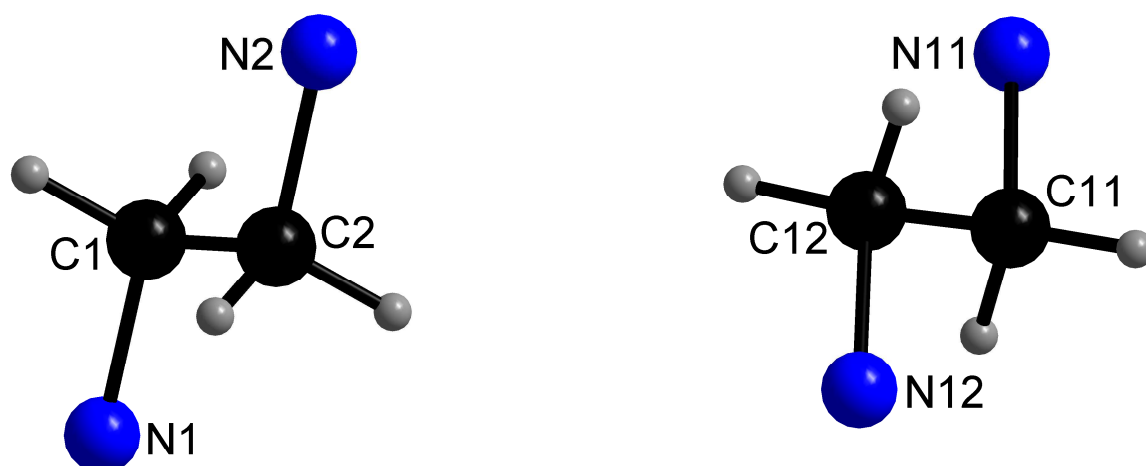
Fig. 3. The anti conformation of the unique $(enH_2)^{2+}$ cations in $(enH_2)[S_2O_3]$ **1**. Note that the N1 (or N11) atom is trans to N2 (or N12) in each of the dications. For clarity the H atoms on N are not shown.

Table 3
Selected bond lengths and bond angles (Å, °) for $(enH_2)[S_2O_3]$ **1**

Bond lengths			
S(1)-O(1)	1.455(1)	S(11)-O(11)	1.462(1)
S(1)-O(2)	1.466(1)	S(11)-O(12)	1.477(1)
S(1)-O(3)	1.472(1)	S(11)-O(13)	1.479(1)
S(1)-S(2)	1.981(1)	S(11)-S(12)	1.984(1)
C(1)-N(1)	1.479(2)	C(11)-N(11)	1.469(2)
C(1)-C(2)	1.514(2)	C(11)-C(12)	1.510(2)
C(2)-N(2)	1.477(3)	C(12)-N(12)	1.475(2)
Bond angles			
O(1)-S(1)-O(2)	109.5(1)	O(11)-S(11)-O(12)	109.1(1)
O(1)-S(1)-O(3)	109.0(1)	O(11)-S(11)-O(13)	109.3(1)
O(2)-S(1)-O(3)	109.0(1)	O(12)-S(11)-O(13)	109.0(1)
O(1)-S(1)-S(2)	111.2(1)	O(11)-S(11)-S(12)	111.5(1)
O(2)-S(1)-S(2)	109.2(1)	O(12)-S(11)-S(12)	108.6(1)
O(3)-S(1)-S(2)	109.0(1)	O(13)-S(11)-S(12)	109.3(1)
N(1)-C(1)-C(2)	109.9(1)	N(11)-C(11)-C(12)	110.1(1)
N(2)-C(2)-C(1)	109.4(1)	N(12)-C(12)-C(11)	109.8(1)

The cations and anions are interlinked by intra and intermolecular hydrogen bonding. The entire molecular surface of **1** is decorated with hydrogen-bond donors and acceptors, with all H-atoms functioning as H-donors for the terminal O and S atoms of the unique thiosulfate anions, resulting in two varieties of H-bonds namely N-H⋯O and N-H⋯S. A total of seventeen interactions comprising of fifteen N-H⋯O and two N-H⋯S are observed. All these contacts are shorter than the sum of their van der Waals radii (Table 4). The four intramolecular N-H⋯O bonds serve to link the constituents of the asymmetric unit (Fig. 2). The molecules are further extended into an intricate H-bonded network with the aid of N-H⋯O and N-H⋯S intermolecular interactions. It is observed that each unique $(enH_2)^{2+}$ dication is H-bonded to six symmetry related thiosulfate anions (Fig. S4). However, the first cation (C1, C2) differs from the second (C11, C12) in that it exhibits two C-H⋯O interactions. It is interesting to note that the O3 and O13 atoms of the unique thiosulfate ions which exhibit the longest S-O bond distance of 1.472(1) and 1.479(1) Å respectively are each involved in a C-H⋯O interaction, in addition to two N-H⋯O bonds. Like the cations, each unique anion is H-bonded to six different $(enH_2)^{2+}$ dications (Fig. S5). The net result of the H-bonding interactions is the formation of a three dimensional H-bonded network, with the organic cations and thiosulfate anions organized into alternating layers (Fig. 4).
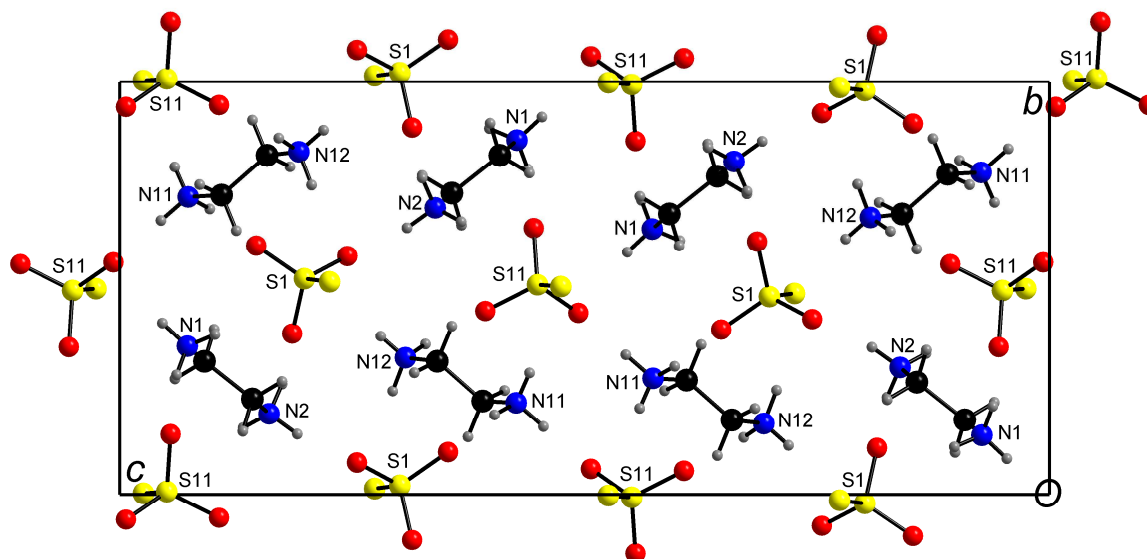
Fig. 4. A view along *a* axis of the crystallographic packing of (enH₂)[S₂O₃] **1** showing the alternating layers of cations and anions. For clarity H-bonding interactions are not shown.

Table 4

Hydrogen-bonding geometry (Å and °) for $(enH_2)[S_2O_3]$ **1**

D-H⋯A	d(D-H)	d(H⋯A)	d(D⋯A)	<(DHA)
N(12)-H(12N)⋯O(3)[i]	0.82(3)	2.49(2)	3.137(2)	137(2)
N(12)-H(12N)⋯O(2)[i]	0.82(3)	2.29(3)	3.039(2)	152(2)
N(12)-H(11N)⋯O(1)	0.91(3)	2.56(3)	3.116(2)	120(2)
N(12)-H(11N)⋯O(2)	0.91(3)	2.14(3)	3.045(2)	171(2)
N(12)-H(10N)⋯O(11)	0.91(3)	1.96(3)	2.832(2)	161(2)
N(11)-H(9N)⋯O(1)[ii]	0.90(3)	1.90(3)	2.791(2)	170(2)
N(11)-H(8N)⋯O(11)[ii]	0.85(2)	2.57(2)	3.116(2)	123(2)
N(11)-H(8N)⋯O(12)[ii]	0.85(2)	2.21(2)	3.029(2)	161(2)
N(11)-H(7N)⋯S(12)[iii]	0.90(2)	2.59(2)	3.412(2)	152(2)
N(11)-H(7N)⋯O(12)[iii]	0.90(2)	2.23(2)	2.946(2)	136(2)
N(2)-H(6N)⋯O(2)[i]	0.86(2)	2.32(2)	2.978(2)	134(2)
N(2)-H(5N)⋯S(2)[iv]	0.93(2)	2.92(2)	3.626(2)	134(2)
N(2)-H(5N)⋯O(3)[iv]	0.93(2)	1.97(3)	2.847(2)	158(2)
N(2)-H(4N)⋯O(13)[ii]	0.84(3)	2.09(3)	2.893(2)	160(2)
N(1)-H(3N)⋯O(12)[v]	0.85(2)	2.08(2)	2.889(2)	159(2)
N(1)-H(2N)⋯O(13)	0.89(2)	1.98(2)	2.848(2)	164(2)

N(1)-H(1N)···O(3)^{vi}	0.85(2)	2.11(2)	2.922(2)	160(2)
C(1)-H(1B)···O(13)^{ii}	0.97	2.682	3.408(2)	132
C(2)-H(2A)···O(3)^{vi}	0.97	2.45	3.212(2)	135

Symmetry transformations used to generate equivalent atoms:
 i) -x+1, y-1/2, -z+1/2 ; ii) x-1, y, z ; iii) x-1/2, -y+3/2, -z ; iv) x-1, y-1, z ;
 v) x-1/2, -y+1/2, -z ;   vi) x, y-1, z

3.3. NMR and UV-Vis spectra

The ^{1}H NMR spectrum of **1** in D_2O exhibits a single sharp signal at 3.2 ppm, assignable to the equivalent methylene protons (Fig. S6). No signal is observed for the equivalent protons of the $–NH_3$ group due to their rapid exchange with D_2O. The single sharp signal is a clear evidence for the purity of **1**. A single sharp ^{13}C resonance at 36.5 ppm (Fig. S6) indicates the equivalence of the carbon atoms in **1**. Thus the equivalent carbon atoms indicate diprotonation of en, which was further confirmed by a gravimetric analysis of ethylenediammonium content as the insoluble $(enH_2)[BPh_4]_2$ salt. The UV-Vis-NIR spectrum of **1** (Fig. S7) reveals the transparent nature of the title compound as no absorption signals are observed above 215 nm. Such a transparent behavior is a desirable characteristic of non-centrosymmetric materials for possible applications.
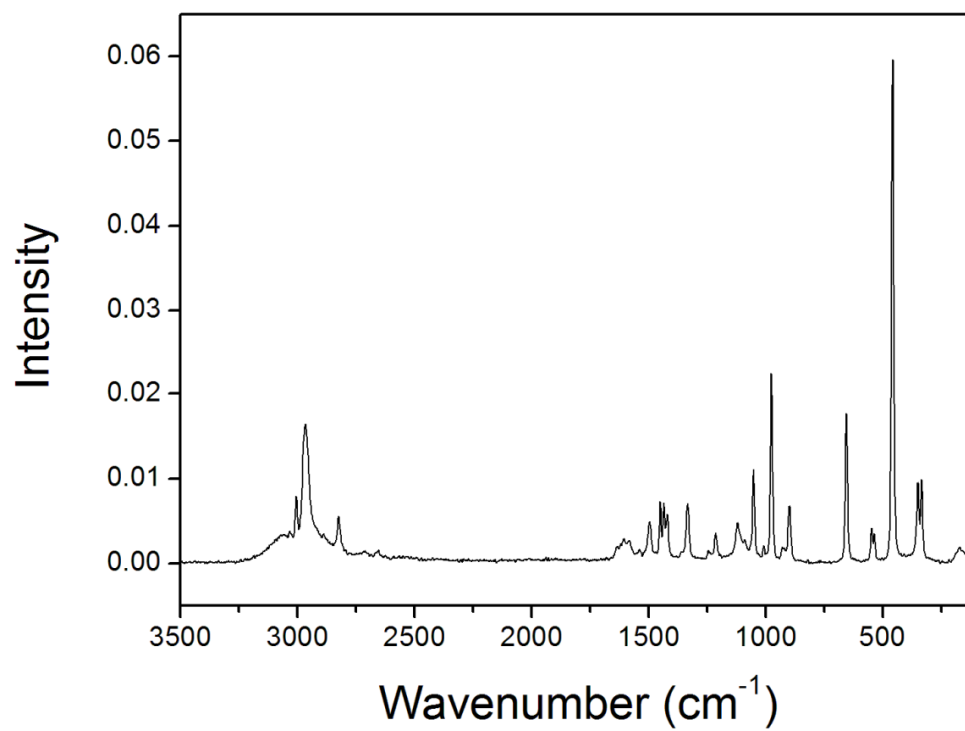
3.4 Infrared and Raman Spectra

A combination of infrared and Raman spectra has been used to characterize the functional groups in **1**. The assignments for the observed signals in the infrared and Raman spectra (Fig. 5 and 6) are made based on a comparison of the reported spectral data of compounds containing the $(enH_2)^{2+}$ cation and the thiosulfate anion [54, 55] and listed in Table 5. The $(enH_2)^{2+}$ ion has 36 normal modes of vibration which in the trans conformation would be distributed between the irreducible representations of this group as $11A_g + 8A_u + 7 B_g +$

10 B_u. The strong signals at 3055 and 2966 cm^{-1} in the IR and Raman spectra respectively can be assigned to the antisymmetric and symmetric N-H stretching vibrations, while the peaks at 1581 and 1500 cm^{-1} in IR are assigned to antisymmetric and symmetric N-H bending vibrations. The IR bands due to the wagging and twisting modes of the -CH$_2$ unit are observed at 1330 cm^{-1} and 1211 cm^{-1}, respectively, in infrared spectrum. The observed spectral data of **1** is in agreement with those reported for (enH$_2$)[CdCl$_4$] [56]. The tetrahedral [S$_2$O$_3$]$^{2-}$ anion has C$_{3v}$ symmetry and six normal modes of vibration (3A$_1$ + 3 E) all of which are both IR and Raman active, are expected [55]. All these fundamental frequencies are expected at the following wavenumbers: ν_s(SO$_3$) (ν_1, A$_1$), 995; ν(S-S) (ν_2, A$_1$), 446; δ_s(SO$_3$) (ν_3, A$_1$), 669; ν_{as}(SO$_3$) (ν_4, E), 1123; δ_{as}(SO$_3$) (ν_5, E), 541; ρ(SO$_3$) (ν_6, E), 335. As the IR spectrum has been investigated up to 400 cm^{-1} the (ν_6, E) vibration of the anion is absent. However this signal is observed in the Raman spectrum at 334 cm^{-1}. All IR and Raman vibrations are observed in the title compound in the expected region and thus unambiguously confirm the presence of a free thiosulfate ion in **1**. The symmetric stretching S-S vibration of the {S$_2$O$_3$} unit appears as an intense signal at 457 cm^{-1} in the Raman spectrum and at the same frequency in the IR. It has been reported that the S-S stretching vibration of an organic thiosulfate namely piperazinediium thiosulfate [56] occurs at 456 cm^{-1}.
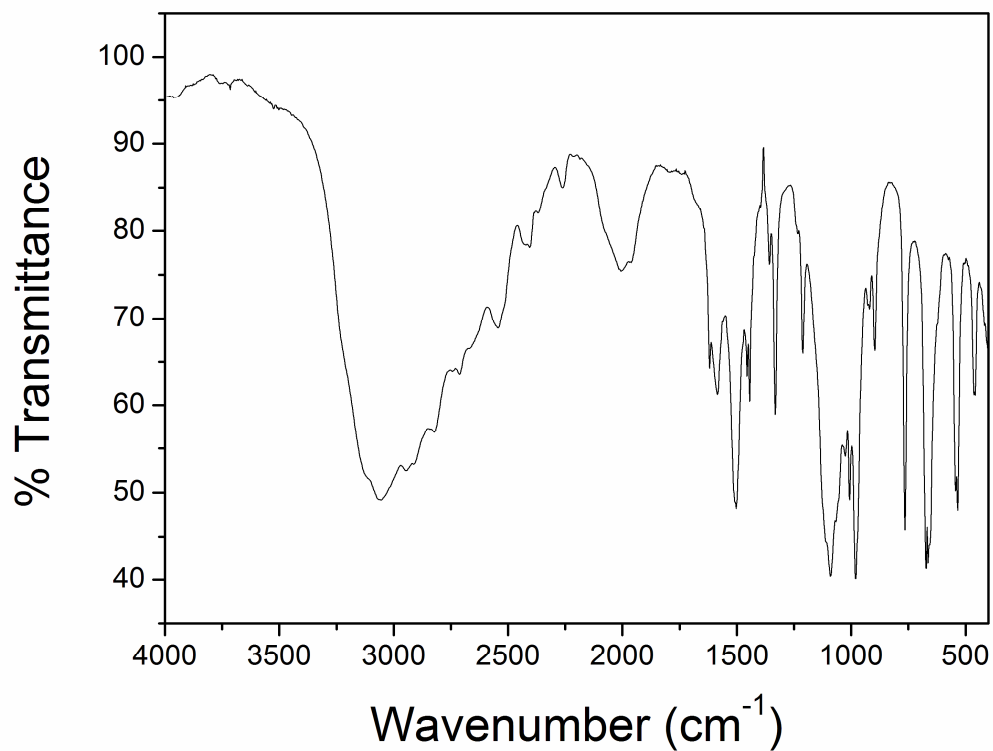
Fig. 5. Infrared spectrum of (enH$_2$)[S$_2$O$_3$] **1**.

Fig. 6. Raman spectrum of (enH$_2$)[S$_2$O$_3$] **1**.

Table 5

Assignments of infrared and Raman bands

| Infrared (in cm^{-1})	Raman (in cm^{-1})	Tentative Assignments
3055^b	3005^{vw}	NH$_3^{+}$ asym. str
2945^{vw}	2966^s	NH$_3^{+}$ sym. str
2819^{vw}	2847^w	CH$_2$ sym. str
1581^m	1495^w	NH$_3^{+}$ asym. def
1500^s	1450^m	NH$_3^{+}$ sym. def
1442^w	-	CH$_2$ def
1330^s	1333^m	CH$_2$ wag
1211^m	1213^{vw}	CH$_2$ twist
1087^s	1121^w	S-O asym. str
1006^w	1051^m	S-O sym. str
979^s	976^s	C-N str
898^w	899^w	NH$_3^{+}$ rock
763^s	-	CH$_2$ rock
665^s	656^s	S-O sym. def
534^s	548^w	S-O asym. def
457^s	457^s	S-S str
-	334^m	S-O rock

s: strong, b: broad, m: medium, w: weak, vw: very weak, sym: symmetric, asym: antisymmetric, str: stretch, wag: wagging, def: deformation.

3.5 Thermal and NLO studies

The TG-DTA thermogram of **1** (Fig. 7) exhibits the first endothermic event with a peak in the DTA at 225 ^{o}C. The TG curve is parallel to the X-axis till ~180°C. The endothermic peak at 225 °C accompanied by a rapid drop in mass can be attributed to decomposition of **1**. In the absence of mass spectral data of the emitted fragments, no detailed description of

the thermal decomposition processes can be made. However, the related sulfate compound $(enH_2)[SO_4]$ is thermally more stable than **1** as it decomposes at 360 ^{o}C [15]. It has been reported by Rao and coworkers that an analogous non-centrosymmetric compound ethylenediammonium sulfate which crystallizes in the tetragonal *P4₁* space group exhibits weak NLO properties (2.3% of urea) [15]. A preliminary study of the second harmonic generation (SHG) property of a finely powdered sample of **1** was made by the Kurtz and Perry technique [57] by irradiating the sample with a near infrared laser beam of wavelength 1064 nm. The compound $(enH_2)[S_2O_3]$ exhibited SHG properties in the form of green emission.
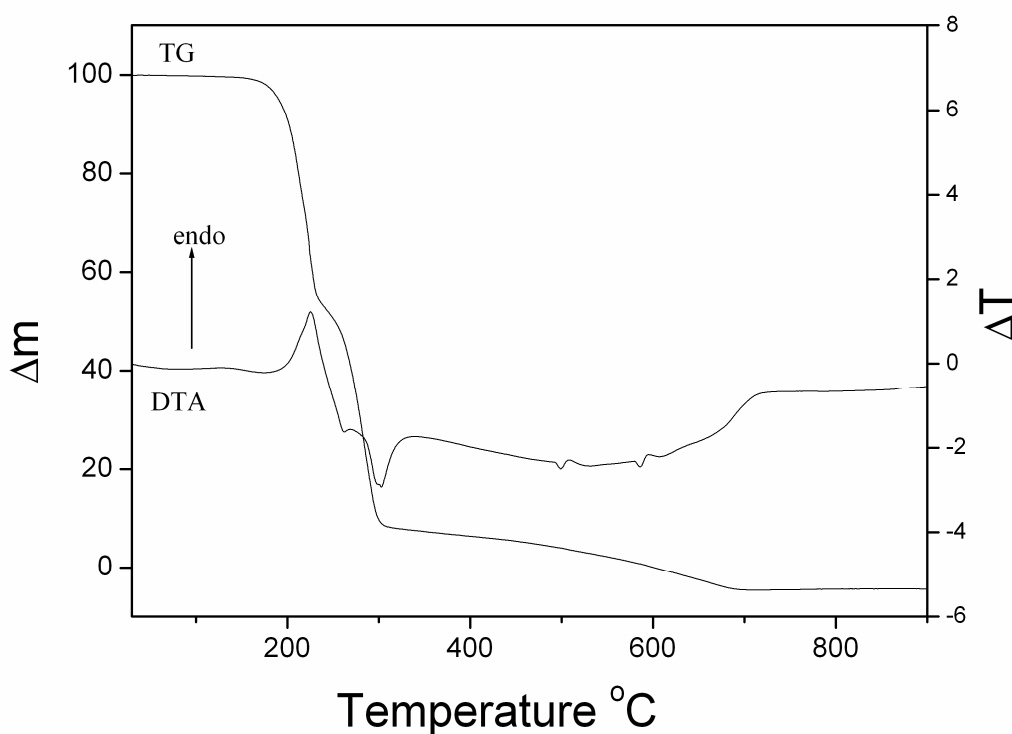
Fig. 7. TG-DTA thermogram of $(enH_2)[S_2O_3]$ **1**.

4. Conclusions

The compound ethylenediammonium thiosulfate **1** described in this work is an achiral molecule crystallizing in a non-centrosymmetric space group and exhibits SHG property. Compound **1** which can be prepared under mild reaction conditions is a new addition to the growing list of structurally characterized ethylenediammonium compounds. ^{1}H and ^{13}C NMR spectra reveal the spectral purity of **1**, while the presence of the organic cation and the thiosulfate anion are confirmed from the characteristic IR and Raman spectra.

Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structure of (enH$_2$)[S$_2$O$_3$] **1** reported herein have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 888779. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK. (fax: +44-(0)1223-336033 or email: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at ***.

References

[1] D.S. Chemla and J. Zyss, (Eds.), Nonlinear Optical Properties of Organic Molecules and Crystals, Vol. 1 and Vol. 2, Academic Press, New York, 1987.

[2] H.D. Flack, Helv. Chim. Acta 86 (2003) 905-921.

[3] M. Sakamoto, Chem. Eur. J. 3 (1997) 684-689.

[4] A. I. Kitaigorodskii, Organic Chemical Crystallography, Consultant's Bureau, New York, 1961.

[5] http://www.ccdc.cam.ac.uk/products/csd/statistics/

[6] J. Jacques, A. Collet, S.H. Wilen, 'Enantiomers, Racemates and Resolutions'. New York, John Wiley, 1981; J. Jacques, A. Collet, Reissue with corrections, Krieger, Malabar, FL, USA, 1994.

[7] E. Pidcock, Chem. Commun. (2005) 3457-3459.

[8] S.C. Abrahams, J.L. Bernstein, Acta Crystallogr. B33 (1977) 3601-3604.

[9] R.M. Pagni, R.N. Compton, Cryst. Growth Des. 2 (2002) 249-253.

[10] Y. Okaya, J. Nitta, Acta Crystallogr. 5 (1952) 564-570.

[11] F.S. Kipping, W.J. Pope, J. Chem. Soc. Trans. 73 (1898) 606-617.

[12] L. Koby, J.B. Ningappa, M. Dakessian, L.A. Cuccia, J. Chem. Ed. 82 (2005) 1043-1045.

[13] P.S.M. Cheung, J. Gagnon, J. Surprenant, Y. Tao, H. Xu, L.A. Cuccia, Chem. Commun. (2008) 987-989.

[14] P.S.M. Cheung, L.A. Cuccia, Chem. Commun. (2009) 1337-1338.

[15] K. Jayaraman, A. Choudhury, C.N.R. Rao, Solid State Sci. 4 (2002) 413-422.

[16] Y.L. Fur, S. Aleonard, M.F. Gorius, Acta Crystallogr. C47 (1991) 949-951.

[17] B.R. Srinivasan, B.K. Vernekar, K. Nagarajan, Indian J. Chem. 40A (2001) 563-567.

[18] B.R. Srinivasan, S.N. Dhuri, C. Näther, W. Bensch, Acta Crystallogr. E58 (2002) m622-m624.

[19] B.R. Srinivasan, S.N. Dhuri, C. Näther, W. Bensch, Indian J. Chem. 42A (2003) 2735-2741.

[20] W.T.A. Harrison, Acta Crystallogr. E61 (2005) m1951-m1952.

[21] W. Bensch, P. Hug, R. Emmenegger, A. Reller, H.R. Oswald, Mat Res Bull 22 (1987) 447-454.

[22] K. Tichỷ, J. Beneš and W. Hälg, H. Arend, Acta Crystallogr. B34 (1978) 2970-2981.

[23] K. Halvorson, R D. Willett, Acta Crystallogr. C44 (1988) 2071-2076.

[24] B.R. Srinivasan, A.R. Naik, C. Näther, W. Bensch, Acta Crystallogr. C63 (2007) m81-m84.

[25] S. Kamoun, A. Jouini, M. Kamoun, A. Daoud, Acta Crystallogr. C45 (1989) 481-482.

[26] D.H. He, Y.Y. Di, B. Wang, W.Y. Dan, Z.C. Tan, Thermochim. Acta 506 (2010) 41-46.

[27] H.W. Smith, W.J. Stratton, Inorg. Chem 16 (1977) 1640–1645.

[28] H. Wen, S. E. Miller, D. A. House, V. McKee, W. T. Robinson, Inorg. Chim. Acta 193 (1992) 77-85. See also R. Spengler, R. Zouari, A. Ben Salah, H. Zimmermann, H. Burzlaff, *Acta Cryst.* (1998). C54, IUC9800034 http://dx.doi.org/10.1107/S0108270198099491

[29] J.P. Jasinski, R.J. Butcher, Q.N.M. Hakim Al-arique, H.S. Yathirajan, B. Narayana, Acta Crystallogr. E67 (2011) o637-o638.

[30] S. Chaabouni, S. Kamoun, A. Daoud, T. Jouini, Acta Crystallogr. C52 (1996) 505-506.

[31] M.T. Averbuch-Pouchot, A. Durif, Acta Crystallogr. C46 (1990) 2236-2238.

[32] W. Abriel, Acta Crystallogr. B42 (1986) 449-453.

[33] A. Dunand , R. Gerdil, Acta Crystallogr. B31 (1975) 370-374

[34] M.T. Averbuch-Pouchot, A. Durif, J.C. Guitel, Acta Crystallogr. C45 (1989) 428-430.

[35] S.H. Edwards, I.A. Kahwa, J.T. Mague, Acta Crystallogr. E57 (2001) o20-o21.

[36] J. Fábry, M. Dusek, R. Krupková, P. Vanek, Acta Crystallogr. E62 (2006) o3217-3219.

[37] M. Rafizadeh, V. Amani, L. Dehghan, F. Azadbakht, E. Sahlolbei, Acta Crystallogr. E63 (2007) m1841- m1842.

[38] R. Ben Smail, H. Chebbi, A. Driss, Acta Crystallogr. E63 (2007) m1859- m1860.

[39] W. Rekik, H. Naïli, T. Mhiri, T. Bataille, Acta Crystallogr. E67 (2011) m1176-m1177.

[40] W. Rekik, H. Naïli, T. Mhiri, T. Bataille, Acta Crystallogr. E65 (2009) m1404-m1405.

[41] P. Held, Acta Crystallogr. E59 (2009) m197- m198.

[42] P. Leyva-Bailen, A. V. Powell, P. Vaqueiro, Acta Crystallogr. E63 (2007) m2643-m2644.

[43] A. Dorazco-Gonzalez, R. A. Toscano, V. Gómez-Vidales, J. Valdés-Martínez, Acta Crystallogr. E62 (2007) m1027- m1029.

[44] N. Jabeen, S. Ahmad, A. F. Meer, I. U. Khan, S. W. Ng, Acta Crystallogr. E66 (2010) m797- m798.

[45] L.-Z. Chen Acta Crystallogr. E65 (2009) o2625- o2625.

[46] B. T. Gowda, S. Foro, H. Terao, H. Fuess, Acta Crystallogr. E65 (2009) m946- m946.

[47] A.B. Salah, A. Daoud, G. Constant, J. Jaud, J. Galy, Acta Crystallogr. C39 (1983) 63- 66.

[48] T. A. Sullens, P. M. Almond, T. E. Albrecht-Schmitt, Acta Crystallogr. E60 (2004) m973-m975.

[49] K. Jung, H. Kim, H. Yun, J. Do, Z. Anorg. Allg. Chem 632 (2006) 1582-1585.

[50] A. Lamhamdi, E. Mejdoubi, K. Fejfarová, M. Dusek, B. El Bali, Acta Crystallogr. E65 (2009) m215-m216.

[51] K. Moovendaran, B.R. Srinivasan, J.K. Sundar, S.A.M.B. Dhas, S. Natarajan, Spectrochim. Acta A92 (2012) 388-391.

[52] Bruker (2001). SAINT and SMART. Bruker AXS Inc., Madison, Wisconsin, USA.

[53] G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112-122.

[54] I.A. Oxton, O. Knop, J. Mol. Struc. 43 (1978) 17-28.

[55] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds Part A: Theory and Applications in Inorganic Chemistry, sixth ed., John Wiley New Jersey, 2009, pp. 204-205.

[56] B.R. Srinivasan, A.R. Naik, S.N. Dhuri, C. Näther, W. Bensch, J. Chem. Sci. 123 (2011) 55-61.

[57] S. K. Kurtz, T. T. Perry, J. Appl. Phys 39 (1968) 3798-3813.