Synthesis, properties and supramolecular structure of piperazinediium thiosulfate monohydrate[+]

BIKSHANDARKOIL R SRINIVASAN[a]*, ASHISH R NAIK[a], SUNDER N DHURI[a], CHRISTIAN NÄTHER[b] and WOLFGANG BENSCH[b]

[a]Department of Chemistry, Goa University, Goa 403 206, India

[b]Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel, Max-Eyth Straße 2, D-24118 Kiel, Germany
e-mail: srini@unigoa.ac.in

Abstract. Aqueous reaction of ammonium thiosulfate with piperazine (pip) results in the formation of the title compound $(pipH_2)[S_2O_3]\cdot H_2O$ **1** ($pipH_2$ = piperazinediium) in good yield. **1** was characterized by elemental analysis, IR, Raman and NMR spectra, X-ray powder pattern and its structure was determined. On heating at 100°C, **1** transforms to anhydrous piperazinediium thiosulfate **2**, which can be rehydrated to the monohydrate on exposure to moisture. The structure of **1** consists of two crystallographically independent piperazinediium $(pipH_2)^{2+}$ cations located on inversion centers, a thiosulfate anion and a lattice water. The organic cations, thiosulfate anion and lattice water are linked by six varieties of hydrogen bond namely O–H···O, O–H···S, N–H···O, N–H···S, C–H···O and C–H···S, leading to the formation of alternating layers of $(pipH_2)^{2+}$ cations and water linked thiosulfate chains. A comparative study of several compounds charge balanced by the piperazinediium cation is described.

Keywords. Piperazine; piperazinediium; rehydration; crystal structure; thiosulfate chain.

1. Introduction

A study of crystalline hydrates has classified the extended patterns of H-bonding involving chemical groups and water molecules.[1–3] Several reports have appeared in recent years describing several interesting structural features of crystalline hydrates.[4–19] Hydrated salts of organic amines exhibit interesting structural features such as a bilayer in 2-aminoanilinium perchlorate monohydrate,[12] sulfate anion helices in *o*-phenylenediammonium sulfate sesquihydrate,[13] a one-dimensional polymeric chain of water in [(3-aba)(dabcoH)(H_2O)_2] (3-aba = 3-aminobenzoate; dabco = 1,4-diazabicyclo[2,2,2]octane),[14] a water bridged cyclic dibromide unit in $(dbtmen)Br_2\cdot 2H_2O$ (dbtmen = *N,N′*-dibenzyl-*N,N,N′,N′*-tetramethylethylenediammonium),[15] a spiral-like anionic water chain containing a water dimer in $(dbtmen)Cl_2\cdot 3H_2O$[16], water pipe held up by a polyoxometalate supported transition metal complex[17] and linear water dimer in an alkaline earth 4-nitrobenzoate.[18]

In our research, we have investigated the supramolecular structure of compounds containing tetrahedral anions like tetrasulfidotungstate[19–22] $[WS_4]^{2-}$, tetrasulfidomolybdate[23–25] $[MoS_4]^{2-}$, monooxidotrisulfidotungstate[26] $[WOS_3]^{2-}$, etc. charge balanced by organic ammonium cations. Based on the structural analysis of several tetrasulfidometalates of the group VI metals, we have shown that organic ammonium tetrasulfidometalates exhibit a minimum of two varieties of H–bond namely N–H···S, and C–H···S, which can be increased to more varieties by incorporation of a lattice water as observed in $(MepipH_2)[WS_4]\cdot H_2O$ (MepipH_2 = 1-methylpiperazinediium).[19] We have shown[27] that the compounds $(pipH)_2[MS_4]$ (M = Mo, W; pipH = piperazin-1-ium) exhibit an intra- and intermolecular N–H···N interaction leading to an infinite chain of H-bonded $(pipH)^+$ cations which are further linked to $[MS_4]^{2-}$ anions with the aid of N–H···S and C–H···S bonds. In view of this, we are investigating the structural chemistry of compounds stabilized by cations

based on piperazine. In the present report, we describe the synthesis, properties and supramolecular structure of the title compound $(pipH_2)[S_2O_3]\cdot H_2O$ (**1**).

2. Experimental

2.1 *Materials and methods*

All the chemicals and solvents were used in this investigation as obtained from commercial sources with analytical purity. Far-IR spectra (range 80–500 cm^{-1}) were recorded using a Bruker IFS 66 infrared spectrometer MIR spectra were recorded in a KBr matrix using a Shimadzu (IR Prestige-21) FT-IR spectrometer and a ATI Mattson Genesis IR spectrometer in the range of 4000–400 cm^{-1}. Raman spectra were recorded in the region from 100 to 3500 cm^{-1} on a Bruker FRA 106 Fourier Transform Raman spectrometer. ^{1}H and ^{13}C NMR spectra were recorded in D_2O on a Bruker 300 MHz FT-NMR spectrometer. X-ray powder pattern were measured using a STOE Stadi-P diffractometer.

2.2 *Preparation of piperazinediium thiosulfate monohydrate*

A solution of piperazine (3·44 g, 40 mmol) in water (20 mL) was added to an aqueous solution of $(NH_4)_2[S_2O_3]$ (5·93 g, 40 mmol) in water (20 mL). The reaction mixture was filtered and the clear filtrate was heated on a water bath for ~15 min to expel ammonia gas. The reaction mixture was again filtered and left undisturbed. After a week, colourless blocks of **1** were obtained from the reaction mixture. The crystals were filtered, washed with a little ice-cold water and dried in air. Yield 6·1 g.

Anal. Calc. for $C_4H_{14}N_2O_4S_2$ (218·29): C, 22·01; H, 6·46; N, 12·83 S, 29·38 Found: C, 22·00; H, 6·51, N, 13·25; S 29·57%.

IR (KBr cm^{-1}): 3327(br) (ν_{O-H}), 2995 (br), 2862–2472(br), 2200, 1608, 1470, 1366, 1298, 1223, 1120 (ν_4), 1082(s), 1042 (m), 999 (ν_2), 965, 875, 659 (ν_3), 594, 534 (ν_5) 456 (ν_1), 337 (ν_6), 253, 219.

Raman (cm^{-1}): 3011, 2994, 2975, 2966, 2915, 1470, 1450, 1315, 1115 (ν_4), 1062, 1040, 968, 830, 819, 812, 655 (ν_3), 535 (ν_5), 453 (ν_1), 422, 350, 334 (ν_6), 128.

2.3 *Dehydration and rehydration studies*

A powdered sample of **1** (308 mg) was heated on a water bath for ~30 minutes. Afterwards the sample was weighed and the observed mass loss was found to be in good agreement for the loss of one mole of water per mole of the compound. The dehydrated compound **2** was exposed to moisture overnight, which resulted in the formation of **1** in quantitative yields.
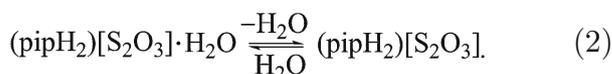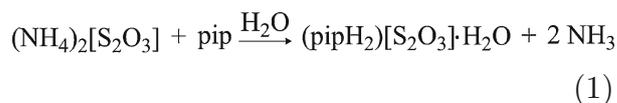
2.4 *X-ray crystal structure determination*

Intensity data for **1** were collected on a AED-II four circle diffractometer from STOE. The structure was solved with direct methods using SHELXS-97[28] and refinement was carried out against F^2 using SHELXL-97.[28] All non-hydrogen atoms were refined using anisotropic displacement parameters. The H atoms attached to the nitrogen atoms of the amine and the oxygen atom of the lattice water were located in difference map but were positioned with idealized geometry and refined using a riding model. Selected refinement results are listed in table 1.

3. Results and discussion

3.1 *Synthesis and spectroscopy*

Colourless blocks of compound **1** were synthesized in good yields by an aqueous reaction of ammonium thiosulfate with piperazine (eq. 1). The synthetic methodology is very similar to the one employed by us for other piperazinediium compounds like $(pipH_2)$ $[MS_4]$ (M=Mo[29], W[30]) and $(pipH_2)[CrO_4]$.[31] The reaction involves the displacement of ammonia (pK_a = 9·24) from ammonium thiosulfate by the stronger base piperazine (pK_a = 9·82) leading to the formation of **1**. The use of ammonium sulfate instead of the thiosulfate resulted in the formation of the corresponding sulfate monohydrate $(pipH_2)[SO_4]$ $\cdot H_2O$ in good yields. The synthesis of the sulfate monohydrate of pip has been previously reported[7] by a direct reaction of piperazine with sulfuric acid. The present synthesis of organic ammonium salts by the direct reaction of an ammonium salt with an organic base can be considered as a milder synthetic method.

$$(NH_4)_2[S_2O_3] + pip \xrightarrow{H_2O} (pipH_2)[S_2O_3]\cdot H_2O + 2\,NH_3$$

$$(1)$$

$$(pipH_2)[S_2O_3]\cdot H_2O \underset{H_2O}{\overset{-H_2O}{\rightleftharpoons}} (pipH_2)[S_2O_3] \qquad (2)$$

Table 1. Crystal data and structure refinement for $(pipH_2)[S_2O_3] \cdot H_2O$ **1**.

Empirical formula	$(C_4H_{12}N_2)[S_2O_3] \cdot H_2O$ **1**
Formula weight (g mol^{-1})	218·29
Temperature (K)	293(2)
Wavelength (Å)	0·71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	$a = 12 \cdot 6176$ (9)
	$b = 6 \cdot 2329$ (9)
	$c = 12 \cdot 3786$ (16)
	$\beta = 102 \cdot 573(12)$
Volume (Å^3)	950·2(2)
Z	4
Density (calcd.) (mg/m^3)	1·526
Absorption coefficient (mm^{-1})	0·542
F(000)	464
Crystal size (mm^3)	0·3×0·25×0·15
Theta range for data collection (°)	1·65 to 28·02
Index ranges	$-16 \leq h \leq 16$, $-1 \leq k \leq 8$, $-16 \leq l \leq 2$
Reflections collected	3290
Independent reflections (R_{int})	2295 (0·0264)
Completeness to theta	99·6 %
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2295/0/116
Goodness-of-fit on F^2	0·978
Final R indices [$I>2\sigma$ (I)]	$R1=0 \cdot 0344$, $wR2=0 \cdot 0824$
R indices (all data)	$R1=0 \cdot 0760$, $wR2=0 \cdot 0915$
Extinction coefficient	0·0132(19)
Largest diff. peak and hole (e.Å^{-3})	0·317 and $-0 \cdot 280$
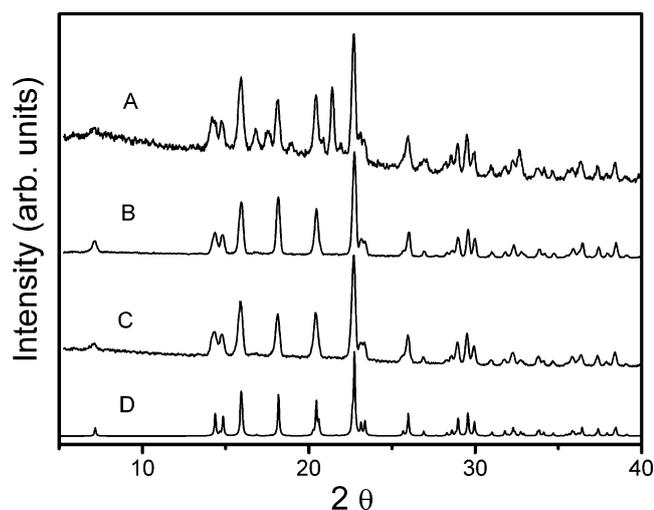
Figure 1. X-ray powder pattern of A) pristine **1**, B) **1** heated at 100°C, C) rehydrated compound and D) calculated powder pattern from single crystal data of **1**.
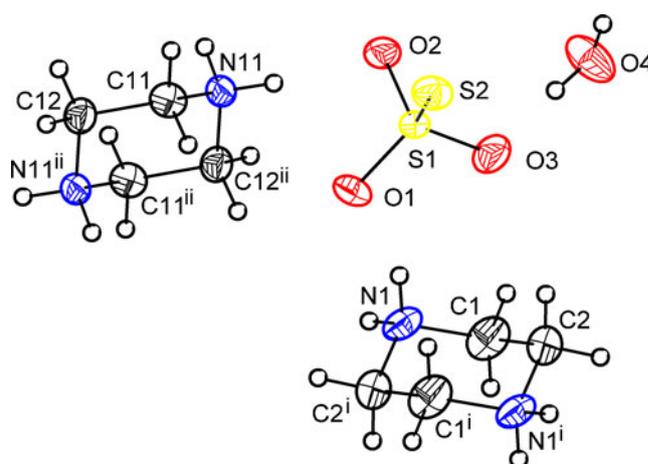
Figure 2. The crystal structure of $(pipH_2)[S_2O_3] \cdot H_2O$ **1**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at 50% probability level except for the H atoms, which are shown as circles of arbitrary radius. Symmetry codes: i) $-x+2$, $-y$, $-z+1$; ii) $-x+1$, $-y$, $-z+1$.

Table 2. Selected bond lengths and angles (Å, °) for $(pipH_2)[S_2O_3]\cdot H_2O$ **1**.

S(1)–O(3)	1·4626(16)	S(1)–O(1)	1·4838(14)
S(1)–O(2)	1·4804(14)	S(1)–S(2)	1·9837(8)
O(3)–S(1)–O(2)	111·20(9)	O(3)–S(1)–S(2)	110·38(8)
O(3)–S(1)–O(1)	108·61(9)	O(2)–S(1)–S(2)	108·42(7)
O(2)–S(1)–O(1)	108·46(9)	O(1)–S(1)–S(2)	109·74(7)
N(1)–C(1)	1·477(3)	N(11)–C(12)[ii]	1·485(3)
N(1)–C(2)[i]	1·482(3)	N(11)–C(11)	1·489(3)
C(1)–C(2)	1·507(4)	C(11)–C(12)	1·508(3)
C(2)–N(1)[i]	1·482(3)	C(12)–N(11)[ii]	1·485(3)
C(1)–N(1)–C(2)[i]	111·19(17)	C(12)[ii]–N(11)–C(11)	111·65(16)
N(1)–C(1)–C(2)	110·4(2)	N(11)–C(11)–C(12)	109·65(18)
N(1)[i]–C(2)–C(1)	110·1(2)	N(11)[ii]–C(12)–C(11)	110·38(16)

Symmetry transformations used to generate equivalent atoms: i) −x+2,−y,−z+1 ;
ii) −x+1,−y,−z+1

The ^1H NMR spectrum of **1** in D_2O exhibits a single sharp signal at 3·47 ppm assignable for the equivalent methylene protons and the single sharp ^{13}C resonance at 40·4 ppm indicates the equivalence of the carbon atoms in **1**. Thus the equivalent carbon atoms indicate diprotonation of pip, which was further confirmed by the elemental analytical data. The several signals in the mid IR spectra, many of which are also observed in the free amine pip, clearly indicate the presence of pip in **1** and **2**. For the $[S_2O_3]^{2-}$ anion, with a C_{3v} symmetry the fundamental frequencies are expected[32] at the following wavenumbers: $\nu(S-S)$ (ν_1, A_1), 447; $\nu_s(SO_3)$ (ν_2, A_1), 1004; $\delta_s(SO_3)$ (ν_3, A_1), 670; $\nu_{as}(SO_3)$ (ν_4, E), 1106;

$\delta_{as}(SO_3)$ (ν_5, E), 538; $\rho(SO_3)$ (ν_6, E), 339. All these vibrations are observed in the title compound in its IR and Raman spectra (for assignment see experimental data) in the expected region and thus unambiguously indicate the presence of a free thiosulfate. The strong and broad signal centered at around 3327 cm^{-1} assignable for the O–H stretching vibration indicates the presence of water in **1**. This assignment gains credence based on a comparison of the IR spectra of **1** and the anhydrous compound **2** and the rehydrated compound (Supplementary figure 1). The IR spectrum of **2** is identical to that of **1** excepting the disappearance of the O–H vibration. Further, the anhydrous compound **2** exhibits sharp signals in its powder

Table 3. H-bonding geometry (Å, °) for $(pipH_2)[S_2O_3]\cdot H_2O$ **1**.

D–H···A	D(D–H)	d(H···A)	<DHA	D(D···A)	Symmetry code
N1-H1A···O4	0·900	1·786	174	2·683	x, −y−1/2, z+1/2
N1-H1B···O1	0·900	1·989	157	2·839	x, y, z
N1-H1B···O3	0·900	2·581	141	3·327	x, y, z
N1-H1B···S1	0·900	2·794	172	3·687	x, y, z
N11-H11A···O2	0·900	2·230	141	2·985	−x+1, y−1/2
N11-H11A···S2	0·900	2·509	145	3·290	−x+1, y−1/2
N11-H11A···S1	0·900	2·880	171	3·771	−x+1, y−1/2
N11-H11B···O2	0·900	1·917	173	2·813	x, y, z
N11-H11B···S1	0·900	2·713	154	3·543	x, y, z
N11-H11B···O1	0·900	2·50	121	3·062	x, y, z
O4-H1O4···O3	0·881	1·848	172	2·724	x, y, z
O4-H1O4···S1	0·881	2·912	155	3·728	x, y, z
O4-H2O4···O1	0·747	2·037	171	2·777	x, −y+1/2, z−1/2
C2-H2B···O3	0·970	2·462	141	3·274	x, y, z
C1-H1C···S2	0·970	2·903	139	3·689	x, y−1, z
C2-H2A···O3	0·970	2·681	151	3·561	−x+2, y−1/2, −z+1/2
C2-H2A···S2	0·970	2·94	144	3·771	−x+2, y−1/2, −z+1/2

pattern indicating its crystalline nature. The X-ray powder pattern of the rehydrated compound is identical to that of the starting material **1** indicating that compound **1** can be reversibly hydrated (eq. 2). The theoretical powder pattern of **1** calculated from the structure data (figure 1) is identical to that of the pattern of the bulk sample indicating the formation of a monophasic material.

3.2 *Description of crystal structure of (pipH$_2$)[S$_2$O$_3$]. H$_2$O 1*

The crystal structure of **1** consists of two crystallographically independent piperazindiium cations located on inversion centers, a tetrahedral thiosulfate anion and a lattice water situated in general positions (figure 2). The cyclic organic cations adopt a chair conformation and both the N atoms in each of the crystalographically independent cations are protonated. Unlike the earlier reported compounds (pipH)$_2$[MS$_4$] (M = Mo, W)[27] which exhibit a short and a long C–N bond distance in view of the monoprotonation of pip, the C–N bond distances of **1** scatter in a very narrow range clearly indicating the diprotonation of the organic diamine. In one of the cations (N1) the C–N distances vary from 1·477(3) to 1·482(3) Å, while in the other cation (N11) the C–N bond lengths range between 1·485(3) and 1·489(3) Å (table 2). The observed bond distances and the bond angles of the organic cations are in agreement with reported values for compounds containing the (pipH$_2$)$^{2+}$ ion.[29–31,33] For the tetrahedral thiosulfate anion the O–S–O and the O–S–S bond angles range from 108·42(7) to 111·20(9)°. The S–O bond lengths range from 1·4626(16) to 1·4838(14) Å (table 2), while the S–S bond distance is longer at 1·9837(8) Å.

3.3 *Secondary interactions in 1*

Based on the structural analysis of several tetrahedral tetrasulfidometalates of the group VI metals which exhibit a minimum of two types of H-bonding namely N–H⋯S, and C–H⋯S and the observed secondary interactions in (C$_6$H$_{18}$N$_3$)[MoS$_4$].½ H$_2$O[23] (N–H⋯O, C–H⋯S, O–H⋯S, N–H⋯S), and (enH$_2$)[WOS$_3$][26] where en = ethylenediamine (N–H⋯S, C–H⋯S, N–H⋯O, C–H⋯O), it was postulated that a combination of an organic ammonium cation, a tetrahedral dianion with an imposed asymmetry and a lattice water can lead to the observation of more varieties of H-bond in a single compound. The tetrahedral thiosulfate ion which contains more than one type of terminal H-acceptors

namely O and S has a C$_{3v}$ symmetry and is thus similar to the [WOS$_3$]$^{2-}$ ion. Compound **1** contains no less than seven hydrogen bond donors (two independent ammonium cations, four methylene groups and a lattice water) and two H-acceptors namely thiosulfate and crystal water. The thiosulfate anion provides several acceptor sites and the entire molecular surface is decorated with hydrogen-bond donors and acceptors. An analysis of the crystal structure of **1** reveals the presence of six varieties of H–bonds, namely O–H⋯O, O–H⋯S, N–H⋯O, N–H⋯S, C–H⋯O and C–H⋯S. A total of seventeen short contacts comprising of six N–H⋯O, four N–H⋯S, two O–H⋯O, one O–H⋯S, two C–H⋯O, and two C–H⋯S, are observed in **1,** and all these contacts are shorter than the sum of their van der Waals radii (table 3). The D-H-A angles vary from 121 to 174°. One of the H atoms attached to N1 (H1A), and the H atoms attached to C1 and C2 function as singly shared H-donors while the other H atoms are either
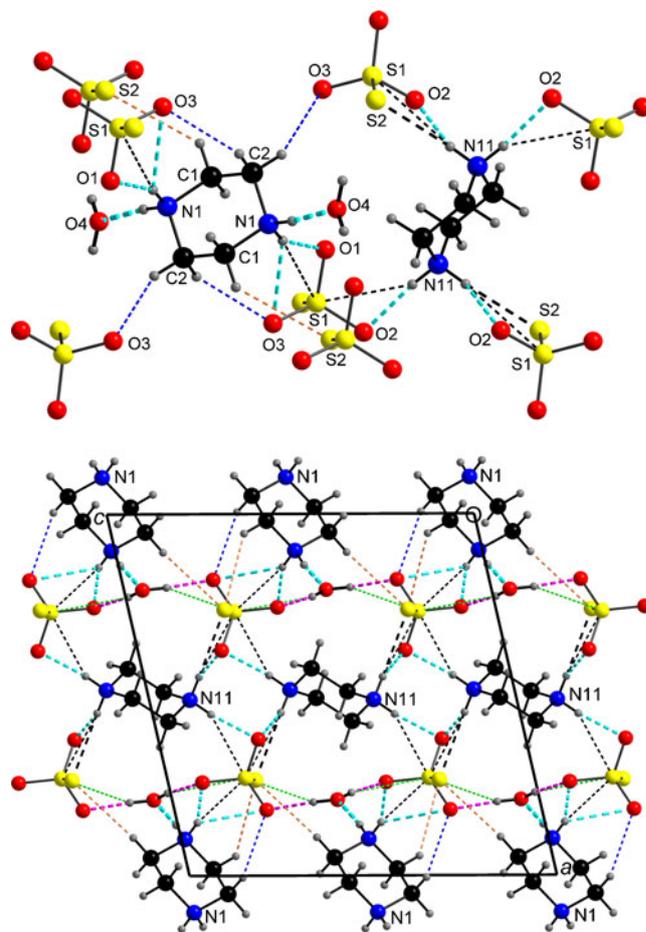
Figure 3. H-bonding situation around the unique cations (top). For symmetry relationship see table 3. A view along b axis, showing the crystallographic packing of **1** depicting all the six varieties of H-bonding interactions (bottom).

bifurcated or trifurcated donors. Each thiosulfate anion is H-bonded to five different piperazinediium cations and two crystal water molecules with the aid of O–H···O, O–H···S, N–H···O, N–H···S, C–H···O and C-H···S interactions (Supplementary figure 2). One of the crystallographically independent cations (N1) is H-bonded to six different thiosulfate anions and two water molecules with the aid of N–H···O, N–H···S, C–H···O and C–H···S interactions, while the other unique cation (N11) is linked to four thiosulfate anions but not with water via N–H···O and N–H···S interactions (figure 3). The lattice water serves to link the thiosulfate anions into a chain by H-bonding with two different anions with the aid of two short O–H···O and one O–H···S interactions and is further H-bonded to one of the cations via a short N–H···O interaction (Supplementary figure 3). As a result of the H-bonding interactions, the cations and the water linked thiosulfate chains are organized into alternating layers (figure 3). The C–H···O, C–H···S as well as the N11–H···O interactions provide links between the layers of crystallographically independent cations resulting in the formation of an intricate three-dimensional H-bonded network.

3.4 *Comparative study of compounds charge balanced by (pipH$_2$)$^{2+}$ cation*

The availability of structure data for several compounds[7,27,29–31,33–36] containing the (pipH$_2$)$^{2+}$ cation

(table 4) permits a comparative study, the details of which are described here. It is interesting to note that several piperazinediium compounds containing dinegative tetrahedral anions crystallize in centrosymmetric space groups while five tetrahalometaltes (pipH$_2$)[MX$_4$] (M = Zn, Cd or Hg; X = Br or I) crystallize in the non-centrosymmetric space group $P2_12_12_1$. All compounds listed in table 4, exhibit H-bonding interactions between the cation and anion, with the organic cations serving as H-donors, and the anion functioning as H-acceptors. Of all these compounds, **1** is unique in that it exhibits six varieties of H-bonds as described above. For many piperazinediium compounds (see table 4) a single type of H-bond N–H···X (X = O, S or Cl) is observed and a maximum of three varieties of H-bonds namely O–H···O, N–H···O, C–H···O, has been reported for (pipH$_2$)(SO$_4$)·H$_2$O[7]. The supramolecular structure of (pipH$_2$)(SO$_4$)·H$_2$O is very similar to that of **1,** in that it exhibits alternating layers of piperazinediium cations and water linked sulfate chains. Interestingly (pipH$_2$)(SO$_4$)·H$_2$O exhibits an identical behaviour like compound **1** in that it can be dehydrated to the anhydrous (pipH$_2$)(SO$_4$) by heating on a water bath and the anhydrous compound can be rehydrated as evidenced by infrared spectra. The replacement of an oxygen atom by a sulfur atom in the thiosulfate in **1** has resulted in three additional H-bridges namely N–H···S, O–H···S and C–H···S. While the N–H···S and

Table 4. Comparative structural features of piperazinediium compounds.

Compound	Space group	Secondary interactions	Ref.
(pipH$_2$)[MoS$_4$]	$P2_1/c$	N–H···S, C–H···S	29
(pipH$_2$)[WS$_4$]	$P2_1/c$	N–H···S, C–H···S	30
(pipH$_2$)[CrO$_4$]	$P2_1/n$	N–H···O, C–H···O	31
(pipH$_2$)[Cr$_2$O$_7$]	$P2_1/c$	N–H···O, C–H···O	33
(pipH)$_2$[MoS$_4$]	$P\bar{1}$	N–H···S, N–H···N, C–H···S	27
(pipH)$_2$[WS$_4$]	$P\bar{1}$	N–H···S, N–H···N, C–H···S	27
(pipH$_2$)[ZnBr$_4$]	$P2_12_12_1$	N–H···Br	34
(pipH$_2$)[ZnI$_4$]	$P2_12_12_1$	N–H···I	34
(pipH$_2$)[HgBr$_4$]	$P2_12_12_1$	N–H···Br	34
(pipH$_2$)[HgI$_4$]	$P2_12_12_1$	N–H···I	34
(pipH$_2$)[CdI$_4$]	$P2_12_12_1$	N–H···I	35
(pipH$_2$)[CdBr$_4$]·H$_2$O	$P2_1/c$	N–H···O, N–H···Br, O–H···Br,	36
(pipH$_2$)[CoCl$_4$]·H$_2$O	$P2_1/a$	N–H···Cl, O–H···Cl, C–H···Cl	37
(pipH$_2$)[SeO$_4$]·H$_2$O	$P2_1/n$	N–H···O, O–H···O	37
(pipH$_2$)[SO$_4$]·H$_2$O	$P2_1/n$	N–H···O, O–H···O, C–H···O	7
(pipH$_2$)[S$_2$O$_3$]·H$_2$O	$P2_1/c$	N–H···O, N–H···S, O–H···O, O–H···S, C–H···O, C–H···S	This work

Abbreviations: (pipH$_2$) = piperazinediium; (pipH) = piperazin-1-ium

C–H···S interactions in **1** are inter-layer interactions linking the anionic thiosulfate layer with the adjacent layer of organic cations, the observed weak O–H···S interaction is an intra-layer interaction between the anion and crystal water.

4. Conclusions

In summary, we have described the synthesis, properties and structural characterization of piperazinediium thiosulfate monohydrate, the supramolecular structure of which exhibits six varieties of H-bond.

Supplementary information

CCDC 621627 contains the supplementary crystallographic data for the structure of compound **1** reported in this paper. This can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre 12 Union Road, Campbridge CB2 1EZ, UK. (fax: (+44) 1223-336-033 or email: deposit@ccdc.cam.ac.uk).

Acknowledgements

References

1. Infantes L and Motherwell S 2002 *Cryst. Eng. Commun.* **4** 454
2. Infantes L, Chisholm J and Motherwell S 2003 *Cryst. Eng. Commun.* **5** 480
3. Mascal M, Infantes L and Chisholm J 2006 *Angew. Chem. Int. Ed. Engl.* **45** 32
4. Das M C, Maity S B and Bharadwaj P K 2009 *Curr. Opi. Solid State Mater. Sci.* **13** 76
5. Supriya S and Das S K 2003 *J. Cluster Sci.* **14** 337
6. Das M C, Ghosh S K and Bharadwaj P K 2009 *Dalton Trans* 1644
7. Jayaraman K, Choudhory A and Rao C N R 2002 *Solid State Sci.* **4** 413
8. Ghosh S K and Bharadwaj P K 2004 *Angew. Chem. Int. Ed. Engl.* **43** 3577
9. Prasad T K and Rajasekharan M V 2006 *Cryst Growth Des.* **6** 488
10. Neogi S and Bharadwaj P K 2005 *Inorg. Chem.* **44** 816
11. Manikumari S, Shivaiah V and Das S K 2002 *Inorg. Chem.* **41** 6953
12. Raghavaiah P, Supriya S and Das S K 2005 *Cryst. Eng. Commun.* **7** 167
13. Raghavaiah P, Supriya S and Das S K 2006 *Chem. Commun.* 2762
14. Banerjee S and Murugavel R 2004 *Cryst. Growth Des.* **4** 545
15. Srinivasan B R, Dhuri S N, Sawant J V, Näther C and Bensch W 2006 *J. Chem. Sci.* **118** 211
16. Srinivasan B R, R Mhalsikar G, Rane K S, Näther C and Bensch W 2007 *J. Chem. Sci.* **119** 21
17. Shivaiah V, Chatterjee T, Srinivasu K and Das S K 2007 *Eur. J. Inorg. Chem.* 231
18. Srinivasan B R, Raghavaiah P and Sawant J V 2007 *Acta Crystalogr.* **63E** m2251
19. Srinivasan B R, Naik A R, Näther C and Bensch W 2010 *Indian J Chem* **49A** 437
20. Srinivasan B R, Naik A R, Dhuri S N, Näther C and Bensch W 2009 *Polyhedron* **28** 3715
21. Srinivasan B R, Näther C, Dhuri S N and Bensch W 2006 *Polyhedron* **25** 3269
22. Srinivasan B R, Naik A R , Näther C and Bensch W 2007 *Z. Anorg. Allg. Chem.* **633** 582
23. Srinivasan B R, Dhuri S N, Naik A R, Näther C and Bensch W 2008 *Polyhedron* **27** 25
24. Srinivasan B R, Girkar S V, Näther C and Bensch W 2009 *J. Coord. Chem.* **62** 3559
25. Srinivasan B R, Girkar S V, Näther C and Bensch W 2010 *J. Coord. Chem.* **63** 931
26. Srinivasan B R, Naik A R, Näther C and Bensch W 2007 *Acta Crystallogr.* **C63** m81
27. Srinivasan B R, Naik A R, Poisot M, Näther C and Bensch W 2009 *Polyhedron* **28** 1379
28. Sheldrick G M 2008 *Acta Crystallogr.* **A64** 112
29. Srinivasan B R, Dhuri S N, Poisot M, Näther C and Bensch W 2005 *Z Naturforsch* **59b** 1083
30. Srinivasan B R, Dhuri S N, Poisot M, Näther C and Bensch W 2005 *Z. Anorg. Allg. Chem.* **631** 1087
31. Srinivasan B R, Näther C and Bensch W 2003 *Acta Crystallogr.* **E59** m639
32. Tobon-Zapata G E, Etcheverry S B and Baran E J 1997 *Spectrochim Acta* **53A** 183
33. Srinivasan B R, Naik A R, Näther C and Bensch W 2004 *Acta Crystallogr.* **E60** m1384
34. Ishira H, Horiuchi K, Svoboda I, Fuess H, Gesing T M, Buhl J C and Terao H 2006 *Z. Naturforsch* **61b** 69
35. Ishira H, Horiuchi K, Gesing T M, Dou S, Buhl J C and Erk P 2002 *Z. Naturforsch.* **57b** 503
36. Qui D T and Palacios E 1990 *Acta Crystallogr.* **C46** 1212
37. Havlicek D, Plocek J, Nemec I, Gyepes R and Micka Z 2000 *J. Solid State Chem.* **150** 305