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Two-dimensional hydrogen-bonded networks in 1-(diaminomethylene)thiouron-1-ium nitrate and bis[1-(diaminomethylene)thiouron-1-ium] phosphonate monohydrate

Jan Janczak[a]* and Genivaldo Julio Perpétuo[b]

[a]Institute of Low Temperatures and Structures Research, Polish Academy of Sciences, PO Box 1410, 50-950 Wrocław, Poland, and [b]Departamento de Fisica, Instituto de Ciências Exatas e Biológicas, Universidade Federal de Ouro Preto, CEP 35.400-000, Ouro Preto, MG, Brazil
Correspondence e-mail: j.janczak@int.pan.wroc.pl

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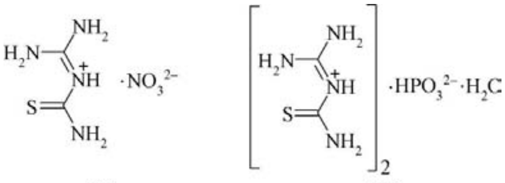
Crystals of the title compounds, $C_2H_7N_4S^+\cdot NO_3^-$, (I), and $2C_2H_7N_4S^+\cdot HPO_3^{2-}\cdot H_2O$, (II), are built up from 1-(diaminomethylene)thiouron-1-ium cations and nitrate anions in (I), and from phosphonate anions and water molecules in (II). In both crystals, the cations and anions are linked together *via* N—H···O hydrogen bonds. The 1-(diaminomethylene)thiouron-1-ium cations exhibit a twisted conformation. Both arms of the cations are planar and are turned in opposite directions around the C—N bond involving the central N atom. Hydrogen-bonding interactions join oppositely charged units into layers in the nitrate salt and into double layers in the phosphonate monohydrate salt. In addition, the structures are stabilized by π–π interactions between the delocalized π bonds of the cations. The significance of this study lies in the illustration of the differences between the supramolecular aggregations in the nitrate and phosphonate salts of a small organic molecule. The different geometries of the counter-ions and their different potential for hydrogen-bond formation results in markedly different hydrogen-bond arrangements.

Comment

As a continuation of our studies on 1-(diaminomethylene)thiourea and its imino tautomer, *i.e.* 2-imino-4-thiobiuret, whose utility has been described previously (Janczak & Perpétuo, 2008*a*,*b*; Perpétuo & Janczak, 2008), we have investigated the crystal structures of 1-(diaminomethylene)thiouron-1-ium nitrate, (I), and bis[1-(diaminomethylene)thiouron-1-ium] phosphonate monohydrate, (II).

The asymmetric unit of (I) consists of a 1-(diaminomethylene)thiouron-1-ium cation and a nitrate anion (Fig. 1*a*), while the asymmetric unit of (II) consists of two 1-(diaminomethylene)thiouron-1-ium cations, one phosphonate dianion and a water molecule (Fig. 1*b*). The cations in these crystals are not strictly planar but are twisted. Both arms of each cation are rotated relative to the central N atom. The dihedral angle between the N1/C2/N3/N4 and N1/C1/N2/S1 planes is 7.2 (1)° in (I), while the equivalent angles in (II) are 9.1 (1) and 3.7 (1)° for the independent *M*1 and *M*2 units, respectively (for the *M*1 unit the planes are N11/C12/N13/N14 and N11/C11/N12/S11, and for *M*2 the planes are N21/C22/N23/N24 and N21/C21/N22/S21). For comparison, the neutral molecule of 1-(diaminomethylene)thiourea also has a twisted conformation, with a dihedral angle of 2.1 (1)° (Janczak & Perpétuo, 2008*a*)



(I) (II)

The respective C—N and C═S bond lengths in (I) and in both independent cations in (II) are very similar. The average C—N distance involving the central N atom [1.374 (12) Å] is significantly longer than the average of the other C—N bond lengths linking the amine groups [1.313 (9) Å]. The lengths of the C═S bonds in these salts are intermediate between the pure double C═S bond length [1.6109 (8) Å; Johnson *et al.*, 1971] and the distance of *ca* 1.74 Å which represents 50% double-bond character (Abrahams, 1956; Allen *et al.*, 1987).

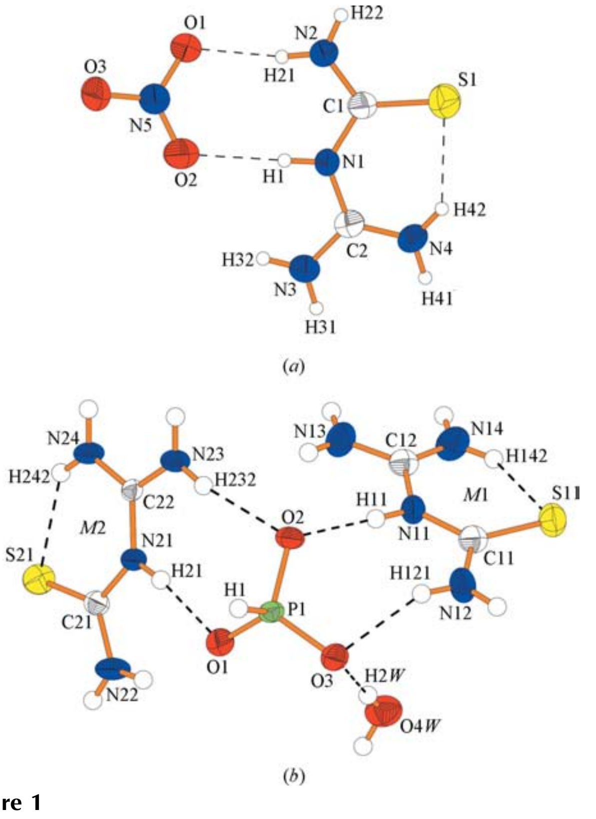


Figure 1
A view of (*a*) (I) and (*b*) (II), showing the atom-labelling schemes. Displacement ellipsoids are shown at the 50% probability level.

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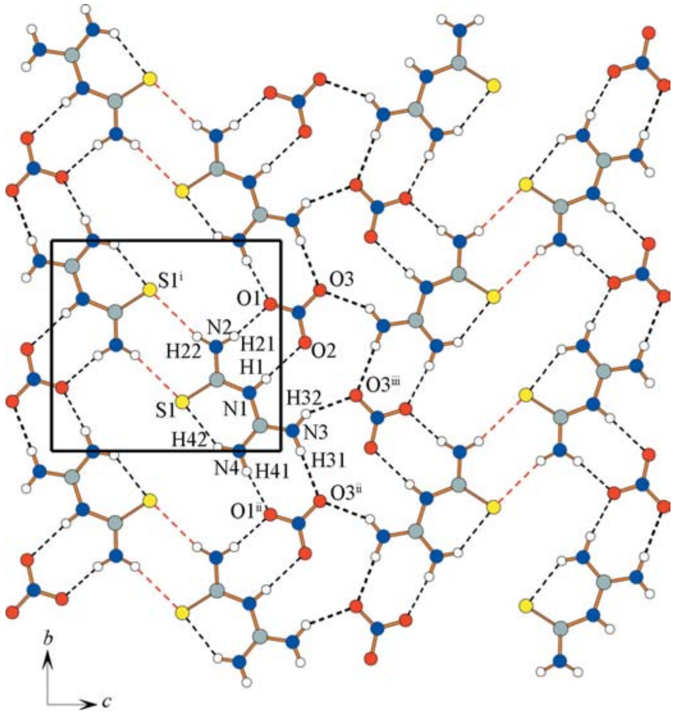

Figure 2
A view of the hydrogen-bonded layers in (I). Symmetry codes are as in Table 1.

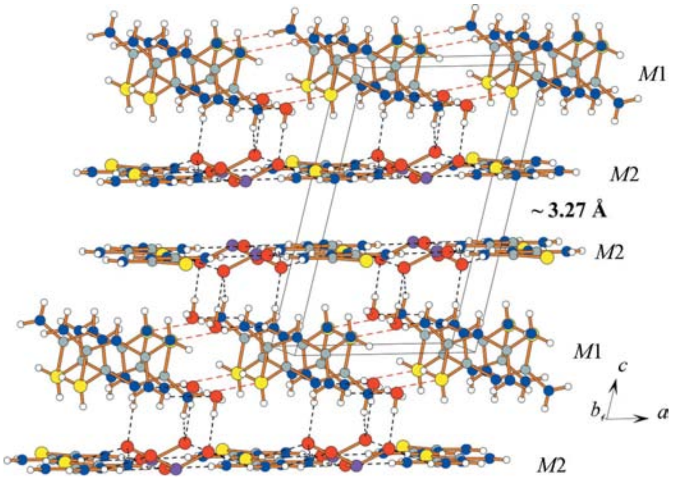

Figure 3
A view of the crystal packing of (II), showing N—H···O and O—H···O hydrogen-bonded double layers.

The elongation of the C=S bond and the shortening of the C—NH_2 bonds indicate partial delocalization of the π bonds (C=S and C=N) over the whole 1-(diaminomethylene)thiouron-1-ium cation. The anionic species of (I) and (II) exhibit a slightly distorted C_{3h} geometry for the NO_3^- anion and C_{3v} geometry for the HPO_3^{2-} anion, with N—O and P—O bond lengths and angles typical of those found in several crystals of this type (Allen, 2002).

In the crystal structures of (I) and (II), the oppositely charged units are linked through hydrogen bonds. In both crystals, 1-(diaminomethylene)thiouron-1-ium cations, related by inversion, are linked *via* a pair of N—H···S hydrogen bonds (Tables 1 and 2), forming $R_2^2(8)$ dimeric structures. In (I), these dimers are linked by NO_3^- anions *via* N—H···O hydrogen bonds into layers that lie parallel to the $(30\overline{1})$ plane (Fig. 2). The layers are separated by a distance of ~3.37 Å. In (II), the dimers of the independent *M*1 and *M*2 units are located essentially perpendicular, for $(M1)_2$, and parallel, for $(M2)_2$, to the (001) plane (Fig. 3). Within one layer, the *M*2 dimeric cations are interconnected by HPO_3^{2-} anions *via* N—H···O hydrogen bonds, while in the second layer, *M*1 dimers are linked *via* N—H···O interactions with water molecules as well as with HPO_3^{2-} anions. The dimeric units of *M*1 and *M*2 are arranged into layers located parallel to the (001) crystallographic plane at $z = 0$ (*M*1 layer) and at $z = 0.50\,(15)$ (*M*2 layer) (Fig. 3). The layer of *M*1 units is surrounded by two layers of *M*2 units, forming a sheet parallel to the (001) plane (Fig. 3). Adjacent *M*2 sheets are separated by a distance of ~3.27 Å. Owing to the partial delocalization of the π electrons of the double C=S and N21=C22 bonds of the *M*2 cation over the whole cation, the π–π interaction between the *M*2 units stabilizes the structure and makes it more planar than the *M*1 unit [the greatest deviations of the non-H atoms observed in the *M*2 cation are 0.042 (2) Å, while in the *M*1 cation they are 0.122 (2) Å]. The distance of 3.27 Å between the layers of *M*2 units lies approximately halfway between the sum of the van der Waals radii for C atoms of π-interacting aromatic rings (~3.4 Å) and the distance of 3.08 Å at which the steric interactions between the π systems become predominantly repulsive (Pauling, 1960; Scheidt & Lee, 1987).

This study illustrates the usefulness of 1-(diaminomethylene)thiourea in crystal engineering for developing supramolecular structures. Protonation of the molecule at the central N atom increases to seven the number of hydrogen-bond donors. Depending on the form of the anion, hydrogen-bond interactions lead to the formation of layers in the nitrate salt or double layers in the phosphonate salt.

Experimental

Crystals of (I) and (II) were obtained from 2-imino-4-thiobiuret (purchased from Aldrich, 99% purity) dissolved in 5% aqueous solutions of the respective acids (HNO_3 or H_3PO_3). After several days at room temperature, crystals suitable for analysis were formed.

Compound (I)

Crystal data

$C_2H_7N_4S^+\cdot NO_3^-$
$M_r = 181.19$
Monoclinic, $P2_1/n$
$a = 9.776\,(2)$ Å
$b = 8.3320\,(17)$ Å
$c = 10.003\,(2)$ Å
$\beta = 115.08\,(3)°$
$V = 738.0\,(3)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.41$ mm^{-1}
$T = 295$ K
0.36 × 0.32 × 0.14 mm

Data collection

Kuma KM-4 diffractometer with an area CCD detector
Absorption correction: numerical (*CrysAlis RED*; Oxford Diffraction, 2006)
$T_{min} = 0.865$, $T_{max} = 0.942$
8419 measured reflections
1915 independent reflections
1307 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2	0.86	2.11	2.9627 (16)	171
N2—H21···O1	0.86	1.94	2.7938 (16)	169
N2—H22···S1^{i}	0.86	2.63	3.4717 (14)	165
N3—H31···O3^{ii}	0.86	2.14	2.9903 (17)	169
N3—H32···O3^{iii}	0.86	2.16	2.9268 (18)	149
N4—H41···O1^{ii}	0.86	2.07	2.8927 (16)	160
N4—H42···S1	0.86	2.30	2.9962 (14)	139

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x, y-1, z$; (iii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{5}{2}$.

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11···O2	0.87	1.87	2.728 (3)	173
N12—H121···O3	0.86	2.09	2.862 (3)	149
N12—H122···S11^{i}	0.86	2.59	3.444 (2)	170
N14—H141···O4*W*^{ii}	0.86	2.05	2.846 (3)	153
N14—H142···S11	0.86	2.30	2.984 (3)	137
N13—H131···O4*W*^{ii}	0.86	2.31	3.037 (3)	142
N13—H131···O4*W*^{iii}	0.86	2.44	3.104 (3)	134
N13—H132···O2	0.86	2.49	3.188 (3)	139
N21—H21···O1	0.87	1.88	2.729 (3)	165
N22—H221···O1	0.86	2.22	2.976 (3)	146
N22—H222···O2^{iv}	0.86	2.12	2.948 (3)	163
N24—H241···O1^{iii}	0.86	2.14	2.970 (3)	162
N24—H242···S21	0.86	2.27	2.969 (2)	139
N23—H231···O3^{iii}	0.86	2.05	2.846 (3)	154
N23—H231···S21^{v}	0.86	2.84	3.345 (2)	119
N23—H232···O2	0.86	2.09	2.923 (3)	164
O4*W*—H1*W*···S11^{vi}	0.82	2.68	3.399 (2)	147
O4*W*—H2*W*···O3	0.82	1.88	2.698 (3)	178

Symmetry codes: (i) $-x+1, -y-1, -z+2$; (ii) $-x, -y, -z+2$; (iii) $x-1, y, z$; (iv) $x, y+1, z$; (v) $x, y-1, z$; (vi) $-x+1, -y, -z+2$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$	104 parameters
$wR(F^2) = 0.087$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{\max} = 0.18$ e Å^{-3}
1915 reflections	$\Delta\rho_{\min} = -0.16$ e Å^{-3}

Compound (II)

Crystal data

$2C_2H_7N_4S^+\cdot HPO_3^{2-}\cdot H_2O$	$\gamma = 85.842 (14)°$
$M_r = 336.35$	$V = 698.1 (2)$ Å^3
Triclinic, $P\overline{1}$	$Z = 2$
$a = 7.6109 (12)$ Å	Mo $K\alpha$ radiation
$b = 7.8771 (14)$ Å	$\mu = 0.52$ mm^{-1}
$c = 12.758 (2)$ Å	$T = 295$ K
$\alpha = 72.700 (16)°$	0.38 × 0.27 × 0.22 mm
$\beta = 72.961 (15)°$	

Data collection

Kuma KM-4 diffractometer with an area CCD detector	$T_{\min} = 0.850$, $T_{\max} = 0.923$
Absorption correction: numerical (*CrysAlis RED*; Oxford Diffraction, 2006)	8542 measured reflections 3529 independent reflections 1950 reflections with $I > 2\sigma(I)$ $R_{\rm int} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.089$	
$S = 1.00$	
3529 reflections	$\Delta\rho_{\max} = 0.43$ e Å^{-3}
188 parameters	$\Delta\rho_{\min} = -0.35$ e Å^{-3}

The H atom of the HPO_3^{2-} anion was located from a difference Fourier map and refined freely to P1—H1 = 1.36 (2) Å. All other H atoms were located from difference Fourier maps and were constrained [N—H = 0.86 Å with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(N), and O—H = 0.82 Å with $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(O)].

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3078). Services for accessing these data are described at the back of the journal.

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