NLO crystals of bis[1-(diaminomethylene)thiouron-1-ium] tartate(2–) hemihydrate and deuterated [1-(diaminomethylene)thiouron-1-ium] tartate(–)

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HIGHLIGHTS

- Protiated and deuterated crystals of 1-(diaminomethylene)thiouron-1-ium tartate were obtained.
- Hydrogen bonding motifs $R_2^1(6)$ and $R_2^2(8)$ in protiated and $R_1^1(5)$ and $R_2^1(6)$ in deuterated crystals are present.
- Both compounds crystallise in the non-centrosymmetric space groups and exhibit NLO properties.

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ABSTRACT

The protiated single crystals of bis[1-(diaminomethylene)thiouron-1-ium] tartate hemihydrate were grown using a solution growth technique. The deuterated single crystals of [1-(diaminomethylene)thiouron-1-ium] tartate(–) were obtained by threefold recrystallisation of protiated crystals. The protiated and deuterated compounds crystallise in the non-centrosymmetric space groups $P2_12_12$ and $P2_1$ of the orthorhombic and monoclinic systems, respectively. The conformation of the 1-(diaminomethylene)thiouron-1-ium cation in both structures is very similar and is almost planar. The double deprotonated tartate(2–) dianion in protiated crystals exhibits C_2 symmetry, while tartate(–) monoanion in deuterated crystals has C_1 symmetry. The oppositely charged components of the crystals, i.e. 1-(diaminomethylene)thiouron-1-ium cation and tartate(2–) dianion in protiated and 1-(diaminomethylene)thiouron-1-ium cation and tartate(–) monoanion, interact via different hydrogen bonding motifs: $R_2^1(6)$ and $R_2^2(8)$ in protiated and $R_1^1(5)$ and $R_2^1(6)$ in deuterated crystals forming 2:1 and 1:1 supramolecular complexes. These supramolecular complexes interact each other via $N-H\cdots O$ or $O-H\cdots O$ hydrogen bonds forming the 2D-layered structures. Both compounds were also characterised by IR-spectroscopy. The SHG efficiency relative to potassium dihydrophosphate (KDP) was found to be 0.77 and 0.82 for protiated and deuterated crystals, respectively.

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1. Introduction

Non-covalent intermolecular interactions are of fundamental importance for understanding of molecular recognition and self-organisation in supramolecular chemistry and biology [1–3]. The directional strong hydrogen bonds $O-H\cdots Y$ and $N-H\cdots Y$ ($Y=O, N$) between the molecules containing complementary array of the hydrogen bonding sites play an important role in molecular arrangement in solids [4–8].

The commercially available 2-imino-4-thiobiuret (Aldrich, CAS No. 2114-20-05) is in the fact the tautomeric form of 1-(diaminomethylene)thiourea as has been shown by the X-ray single crystal analysis [9]. Both tautomers are already considered to be useful building blocks in crystal engineering, since they contain active

hydrogen bonding sites. The 1-(diaminomethylene)thiourea contains the basic N atom with the lone-pair of electrons that can accept the proton forming positively charged cation, which with the oppositely charged units forms salts with the extended hydrogen bonded networks in solids [10–16]. Several materials based on the acid–base ionic and directional hydrogen-bonding interactions exhibit non-linear optical properties due to the relatively strong hyperpolarisability of the base-organic part of the crystals [17–21].

To explore the possibility of the 1-(diaminomethylene)thiourea to form new materials with the extended hydrogen-bonding patterns in solid with the non-linear optical properties (NLO), we investigate the supramolecular motifs in the crystal of bis[1-(diaminomethylene)thiouron-1-ium] tartate(2–) hemihydrate and the deuterated 1-(diaminomethylene)thiouron-1-ium tartate(–). Both materials were also characterised by the vibrational spectroscopy.

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2. Experimental

All materials were commercially available and used as received. Elemental analysis was carried out with a Perkin-Elmer 240 elemental analyser.

2.1. Preparation of bis[1-(diaminomethylene)thiourea-1-ium] tartate hemihydrate

Commercially available 2-imino-4-thiobiuret (amidinothiourea, Aldrich, CAS No. 2114-02-05, purity of 99 %), which is in fact the tautomeric form 1-(diaminomethylene)thiourea and L-tartaric acid (Aldrich, purity of 99.5%) were added to hot water in a molar proportion of 2:1. When the solution became homogeneous it was cooled slowly and kept at room temperature. After several days, transparent colourless orthorhombic crystals of $2(\text{C}_2\text{H}_7\text{N}_4\text{S}) \cdot (\text{C}_4\text{H}_4\text{O}_6) \cdot 0.5(\text{H}_2\text{O})$ were formed. Analysis: calculated for $\text{C}_8\text{H}_{19}\text{N}_8\text{O}_{6.5}\text{S}_2$: C, 24.31%; H, 4.83%; N, 28.33%; O, 26.30% and S, 16.23%. Found: C, 24.45%; H, 4.88%; N, 28.20%; O, 26.35% and S, 16.12%.

Deuterated D^{10} 1-(diaminomethylene)thiourea-1-ium tartate was prepared by the usual reaction with heavy water. The crystals of bis[1-(diaminomethylene)thiourea-1-ium] tartate hemihydrate were dissolved in heavy water, and were left in the atmosphere saturated with heavy water for 1 week in order to avoid the contamination of the crystals. Then the procedure was repeated twice. The obtained deuterated 1-(diaminomethylene)thiourea-1-ium tartate crystallises in the non-centrosymmetric space group ($P2_1$) of monoclinic system.

2.2. X-ray data collection

X-ray intensity data for the crystals were collected using graphite monochromatic $\text{Mo K}\alpha$ radiation on a four-circle κ geometry KUMA KM-4 diffractometer with a two-dimensional area CCD detector. The ω -scan technique with $\Delta\omega = 1.0^\circ$ for each image was used for data collection. The 930 images for six different runs covering over 99% of the Ewald sphere were performed. The unit cell parameters were refined by the least-squares methods. One image was used as a standard after every 50 images for monitoring of the crystal stability and data collection. No correction on the relative intensity variations was necessary. Data collections were made using the CrysAlis CCD program [22]. Integration, scaling of the reflections, correction for Lorentz and polarisation effects and absorption corrections were performed using the CrysAlis Red program [22]. The structures were solved by the direct methods using SHELXS-97 and refined using SHELXL-97 program [23]. The hydrogen atoms were located in difference Fourier maps and were refined. The final difference Fourier maps showed no peaks of chemical significance. Details of the data collection parameters, crystallographic data and final agreement parameters are collected in Table 1. Visualisation of the structure was made with the Diamond 3.0 program [24]. Selected geometrical parameters are listed in Table 2 and the geometry of hydrogen bonding interactions are collected in Table 3.

2.3. Vibrational spectra measurements

The vibrational measurements were carried out at room temperature. The Fourier transform infrared spectrum was recorded from Nujol mulls between 4000 and 400 cm^{-1} on a Bruker IFS 113 V FTIR.

2.4. Second harmonic generation (SHG)

Second harmonic generation properties were measured for the solid state samples at the fundamental wavelength (1064 nm) of a Q-switched Nd:YAG laser using the modified Kurtz–Perry method [25].

2.5. Thermal measurements

Thermal analysis was carried out on a Linseis L81 thermobalance apparatus with Pt crucibles. Powdered Al_2O_3 has been used as a reference. The measurements have been performed under static air atmosphere on heating from room temperature to 120°C at the heating rate of 5°C min^{-1} .

2.6. X-ray powder diffraction measurements

The rest of the samples left after thermogravimetric analyses were checked on a STOE powder diffractometer equipped with a linear position detector (PSD) [26] using $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.540562\text{ \AA}$) at room temperature.

3. Results and discussion

Good quality single crystals of bis[1-(diaminomethylene)thiourea-1-ium] tartate hemihydrate suitable for the X-ray analysis were obtained from water solution at 25°C . The deuterated D^{10} crystals were obtained by threefold recrystallisation of bis[1-(diaminomethylene)thiourea-1-ium] tartate hemihydrate from heavy water. However, the deuterated D^{10} crystals, in contrast to the orthorhombic protiated crystals, are monoclinic.

The X-ray single crystal analysis of the protiated crystal shown that the both carboxyl groups of the tartaric acid are deprotonated (Fig. 1). In addition, the X-ray analysis revealed that only a half of the deprotonated tartate(2−) anion is independent, since it lies on the twofold symmetry axis. The water molecule also lies on the twofold symmetry axis. In the deuterated D^{10} crystals, as shown in the X-ray analysis, only one of two carboxyl groups of the tartaric acid is deprotonated, and it lies in the general position (Fig. 2). In the protiated crystal the oppositely charged units, i.e. 1-(diaminomethylene)thiourea-1-ium cation and tartate dianion interact via three $\text{N}=\text{H} \cdots \text{O}$ hydrogen bonds forming bis[1-(diaminomethylene)thiourea-1-ium] tartate molecular complex (Fig. 3). Whereas in the deuterated D^{10} crystals the 1-(diaminomethylene)thiourea-1-ium cation interacts with tartate monoanion via six different $\text{N}=\text{H} \cdots \text{O}$ hydrogen bonds with a three graphs of $R_2^2(5)$ and two graphs of $R_2^2(6)$ forming the 1:1 supramolecular motif (Fig. 2).

The conformation of the 1-(diaminomethylene)thiourea-1-ium cation in both crystals is only slightly deviated from a planar configuration. Both arms of the cation are slightly oppositely rotated around the C–N bonds involving the central N1 atom. The dihedral angle between the N1/C1/S1/N2 and N1/C2/N3/N4 planes is equal to $2.5(2)^\circ$ and $1.6(2)^\circ$ in the protiated and deuterated crystals, respectively. The rotation of the arms around the C–N1 bonds in both structures is significantly smaller than that in the crystal of neutral 1-(diaminomethylene)thiourea molecule ($22.2(1)^\circ$) [9]. Protonation of the neutral 1-(diaminomethylene)thiourea molecule causes a reduction in the steric effect of the lone pair of electron at the central N1 atom. The non-planar conformation of the neutral 1-(diaminomethylene)thiourea molecule and its protonated cation is also observed in the gas-phase structures as show by the *ab initio* molecular orbital calculations: 6.2° in the neutral molecule and 4.2° in the cation [9,11]. The currently available data on 1-(diaminomethylene)thiourea-1-ium salts show that the cat-

Table 1

Crystallographic data for bis[1-(diaminomethylene)thiuron-1-ium] tartate hemihydrate (**1**) and deuterated D¹⁰ 1-(diaminomethylene)thiuron-1-ium tartate (**2**).

	1	2
Empirical formula	(C ₂ H ₇ N ₄ S) ₂ C ₄ H ₄ O ₆ · 0.5H ₂ O	(C ₂ D ₇ N ₄ S) ₂ C ₄ H ₂ D ₃ O ₆
Formula weight (g mol ^{−1})	395.23	278.29
Crystal system	Orthorhombic	Monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 (No. 18)	<i>P</i> 2 ₁ (No. 4)
<i>a</i> (Å)	25.387(4)	5.7517(12)
<i>b</i> (Å)	4.8920(10)	7.0499(14)
<i>c</i> (Å)	6.6820(10)	13.737(3)
β (°)		90.84(3)
<i>V</i> (Å ³)	829.9(2)	557.0(2)
<i>Z</i>	2	2
<i>D</i> _{calc} / <i>D</i> _{obs} (g cm ^{−3})	1.583/1.58	1.659/1.65
μ (mm ^{−1})	0.370	0.317
Crystal size (mm)	0.28 × 0.24 × 0.21	0.34 × 0.25 × 0.21
Radiation type, wavelength, λ (Å)	Mo K α , 0.71073	Mo K α , 0.71073
Temperature (K)	295(2)	295(2)
θ range(°)	3.05–29.39	2.97–29.40
Absorption correction	Numerical, CrysAlis Red [22]	Numerical, CrysAlis Red [22]
<i>T</i> _{min} / <i>T</i> _{max}	0.9112/0.9455	0.9110/0.9427
Reflections collected/unique/observed	10160/2160/1620	7530/2726/1997
<i>R</i> _{int}	0.0291	0.0225
Refinement on	<i>F</i> ²	<i>F</i> ²
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.0325	0.0268
<i>wR</i> [<i>F</i> ² all reflections]	0.0568	0.0494
Goodness-of-fit, <i>S</i>	1.006	1.003
Flack parameter	0.11(7)	−0.05(5)
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ^{−3})	+0.309, −0.245	+0.173, −0.252

$$wR = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4 \}^{1/2}; w^{-1} = 1 / [\sigma^2(F_o^2) + (aP)^2] \text{ where } a = 0.022 \text{ and } a = 0.021 \text{ for } \mathbf{1} \text{ and } \mathbf{2}, \text{ respectively, and } P = (F_o^2 + 2F_c^2) / 3.$$

Table 2

Comparison of the bond lengths (Å) and angles (°) for bis[1-(diaminomethylene) thiuron-1-ium] tartate hemihydrate (**1**) and and deuterated D¹⁰ 1-(diaminomethylene) thiuron-1-ium tartate (**2**).

	1	2
<i>1-(Diaminomethylene) thiuron-1-ium cation</i>		
C1–S1	1.6786(17)	1.6646(17)
C1–N1	1.375(2)	1.377(2)
C1–N2	1.316(2)	1.317(2)
C2–N1	1.352(2)	1.360(2)
C2–N3	1.316(3)	1.315(2)
C2–N4	1.313(2)	1.290(2)
N2–C1–N1	112.50(15)	112.60(15)
N2–C1–S1	122.74(13)	122.30(13)
N1–C1–S1	124.76(13)	125.07(13)
C2–N1–C1	131.11(16)	130.71(15)
N4–C2–N3	120.15(19)	120.03(17)
N4–C2–N1	116.05(19)	123.32(15)
N3–C2–N1	123.80(17)	116.66(16)
C1–N1–C2–N3	1.6(3)	177.4(2)
<i>Tartate(2−) dianion in 1 and tartate(−) monoanion in 2</i>		
O1–C3	1.2388(19)	1.2539(19)
O2–C3	1.263(2)	1.2503(19)
C3–C4	1.527(2)	1.523(2)
O3–C4	1.4226(19)	1.415(2)
C4–C4 ⁱ (C4–C5 in 2)	1.518(3)	1.524(2)
(C5–O5 in 2)		1.4058(19)
(C5–C6 in 2)		1.508(2)
(C6–O8 in 2)		1.2176(18)
(C6–O7 in 2)		1.3040(18)
O2–C3–O1	125.61(16)	123.91(15)
(O8–C6–O7 in 2)		123.58(15)

Symmetry code: (i) −*x*, −*y*, *z*.

ion twisting conformation may differ when different anions are used and dependent on the hydrogen bonding. For example, the greatest twisting angle is observed in 1-(diaminomethylene)thiuron-1-ium chloride (22.9(1)°) and bromide (15.2(1)°) [11]. In the other known salts the twisting angle ranges from 1.4(1)° in perchlorate to 9.8(1)° in hydrogen sulphate [10]. The C1–S1 bond

(Table 2) in both structures is slightly longer than the typical C=S double bond as observed in the thioformaldehyde CH₂C=S (1.6019(8) Å) [27], which represents 100% double bond character, and is shorter than the value of ~1.74 Å as observed is several thio- late anions that represent 50% double bond character [28]. Thus in the present structures the bond order of C1–S1 bond is intermedi- ate between 2 and 1.5. The three C–N bond lengths linking the amine groups are shorter by ~0.07 Å than the C–N bonds involving the central N1 atom (Table 2). The planarity of the amine groups points to the *sp*² hybridisation of the *p* orbitals of the nitrogen atoms. This indicates that the lone pair of electrons occupies the *p* orbital. In addition, the *p* orbitals of the C, S and N1 atoms form- ing the π bond of the C1–S1 and C2–N1 double bonds could be delocalised over the C–N bonds linking the amine groups, due to symmetry of the *p* orbitals. In result the shortening of the C–N bonds linking the amine groups and elongation of the C C–N bonds involved the central N1 atoms are observed.

The conformation of the anionic part of the crystals, i.e. tar- tate(2−) dianion in protiated and tartate(−) monoanion in the deu- terated crystal is different. In protiated crystal the torsion angle of the carbon chain C3–C4–C4ⁱ–C3ⁱ is equal to −175.1(2)°, and the anion exhibits the *C*₂ symmetry. In deuterated crystal the symme- try of the tartate(−) monoanion is *C*₁ and the torsion angle describ- ing the conformation of the carbon chain C3–C4–C5–C6 is equal to 165.7(2)°. The deprotonated COO[−] group lies in the plane of C3/C4/O3 (the torsion angle O2–C3–C4–O3 = 0.5(2)°), while the non-dissociated COOD (D = deuter, in deuterated crystal) is in- clined by 8.9(2)° to the respective C6/C5/O5 plane (the torsion an- gle O8–C6–C5–O5 = 8.9(2)°). In the protiated crystal due to *C*₂ symmetry of the tartate(2−) dianion the COO[−] groups are inclined to the respective C3/C4/O3 and symmetrically equivalent planes by 6.1(2)°. A similar conformation of the carbon chain is observed in the crystal of (+)-tartaric acid, the respective torsion angles are −175.4(1)° and 4.8(1)° for the C–C–C–C chain and for O–C–C–O describing the orientation of the both COOH groups in relation the plane [29].

Table 3
Hydrogen-bond geometry (Å, °).

(a) Bis[1-(diaminomethylene)thiuron-1-ium] tartate hemihydrate ^a				
D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...O2	0.88(2)	1.82(2)	2.697(2)	172(2)
N2—H21...O1	0.89(2)	2.09(2)	2.958(2)	166(2)
N2—H22...S1 ⁱⁱ	0.82(2)	2.65(2)	3.408(2)	154(2)
N3—H31...O1 ⁱⁱⁱ	0.82(2)	2.17(2)	2.974(2)	168(2)
N3—H32...S1	0.93(2)	2.28(2)	3.019(2)	136(2)
N3—H32...S1 ^{iv}	0.93(2)	2.91(2)	3.586(2)	131(2)
N4—H41...O3 ⁱⁱⁱ	0.85(2)	2.14(2)	2.836(2)	139(2)
N4—H41...O1 ⁱⁱⁱ	0.85(2)	2.61(2)	3.333(3)	144(2)
N4—H42...O2	0.94(3)	2.31(2)	3.072(2)	138(2)
O3—H3...N4 ^v	0.82(2)	2.40(1)	2.836(2)	114(2)
O4—H40...N4 ^{vi}	0.82(2)	2.50(6)	3.194(2)	144(2)
(b) Deuterated D ¹⁰ 1-(diaminomethylene)thiuron-1-ium tartate ^b				
D—D...A	D—H	D...A	D...A	D—D...A
N1—D1...O5	0.86(2)	2.16(2)	2.891(2)	143(2)
N1—D1...O3	0.86(2)	2.28(2)	3.024(2)	146(2)
N2—D2A...O2	0.76(2)	2.34(2)	3.016(2)	149(2)
N2—D2A...O3	0.76(2)	2.57(2)	3.216(2)	144(2)
N2—D2B...S1 ⁱ	0.83(2)	2.75(2)	3.472(2)	147(2)
N3—D3A...O1 ⁱⁱ	0.94(2)	1.96(2)	2.882(2)	171(2)
N3—D3B...O8	0.78(2)	2.29(2)	2.999(2)	152(2)
N3—D3B...O5	0.78(2)	2.54(2)	3.140(2)	135(2)
N4—D4A...O2 ⁱⁱ	0.85(2)	2.11(2)	2.935(2)	162(2)
N4—D4B...S1	0.87(2)	2.31(2)	3.007(2)	138(2)
O3—D31...O8 ⁱⁱⁱ	0.77(2)	2.04(2)	2.790(2)	165(2)
O5—D51...O2 ^{iv}	0.80(2)	1.90(2)	2.700(2)	171(2)
O7—D71...O1 ^v	0.90(2)	1.65(2)	2.542(2)	174(2)

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

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

Fig. 1. A view of bis[1-(diaminomethylene)thiuron-1-ium] tartate(2-) hemihydrate showing displacement ellipsoids at the 50% probability level and H atoms as a sphere of arbitrary radii. Dashed lines represent the hydrogen bonds.

The hydrogen bonding pattern involving the tartate(2-) or tartate(-) anions is considerably different. In protiated crystals the tartate(2-) dianion interacts with two 1-(diaminomethylene)thiuron-1-ium cations via two pairs of different motifs. One of them is $R_2^2(8)$ that is formed by donation to the COO⁻ group from amine and imine groups of the 1-(diaminomethylene)thiuron-1-ium cation. The other motif is $R_2^1(6)$ is formed by donation of amine and imine groups to the one oxygen atom (O2) of the carboxylate group. These motifs link the tartate(2-) dianion with two cations forming bis[1-(diaminomethylene)thiuron-1-ium] tartate supramolecular complex (Fig. 3). These 2:1 supramolecular complexes related by a translation along the *c*-axis and *b*-axis interact via two pairs of N—H...O hydrogen bonds forming two-dimensional layer aligned parallel to the (100) crystallographic plane (Fig. 4). The presence of the sulphur atom in the 1-(diaminomethylene)thiuron-1-ium

Fig. 2. A view of deuterated D¹⁰ 1-(diaminomethylene)thiuron-1-ium tartate showing displacement ellipsoids at the 50% probability level.

cation raises the question of whether there are hydrogen bonds with the S as an acceptor, although the importance of such interactions has been questioned [30]. Nevertheless, there are authors motivated by the high content of sulphur in biological systems who claim to utilise the D—H...S interactions (D = donor) in the crystal engineering. The N—H...S interactions have been utilised for design supramolecular arrangement of thiourea derivatives [31]. Thus such N—H...S intramolecular interactions seem to be present in the bis[1-(diaminomethylene)thiuron-1-ium] tartate structure (Table 3). Besides, the N—H...S intramolecular interactions, the weak N—H...S intermolecular interactions in the present structure are also exist. These weak N—H...S intermolecular interactions link the 2D-layers forming a three-dimensional network. In the 2D-layers, the one dimensional channels with the solvated water molecules along the *b*-axis are observed (Fig. 4). The water molecules are relatively weak interact with the layers and they can be easy removed from the crystalline structure at ~95 °C. The weight loss of ~2.3% was registered by the thermogravimetric analysis and is in agreement with the loss of water molecules from the crystal (2.28%). After TG analysis the crystals were not suitable for the single crystal X-ray analysis. However, the lattice parameters obtained by the X-ray powder diffraction technique do not change significantly (orthorhombic, $a = 25.362$, $b = 4.886$ and $c = 6.663$ Å), therefore we suppose that the layered structure is preserved.

In the deuterated crystal the tartate(-) monoanion interacts with 1-(diaminomethylene)thiuron-1-ium cation via five hydrogen bonding motifs. Three of them are $R_1^1(5)$ and the other two are $R_2^1(6)$. One of three $R_1^1(5)$ motif is formed by donation of hydrogen from imine group of the cation to the both oxygen atoms (O3 and O5) of hydroxyl groups, the other two $R_1^1(5)$ motifs are formed by donation of the H atoms from the amine groups to the hydroxyl groups and to one of the oxygen atom of the COO⁻ and COOH groups of the tartate(-) anion. The other two $R_2^1(6)$ motifs are formed by donation of H atoms from amine and imine groups of the cation to the same oxygen atoms of hydroxyl groups of the anion (Fig. 5). In all hydrogen bonding motifs in the structure the H atoms are involved in the bifurcate hydrogen bonds. In the deuterated crystal the tartate(-) monoanions, in contrast to the tartate(2-) dianions in the protiated crystals in which they are

Fig. 3. A view of bis[1-(diaminomethylene)thiuron-1-ium] tartate(2-) hemihydrate showing the $R_2^1(6)$ and $R_2^2(8)$ graphs of hydrogen bonds.

Fig. 4. A view along b -axis of the crystal packing of bis[1-(diamino-methylene)-thiuron-1-ium] tartate(2-) hemihydrate showing the 2D-layers parallel to (100) plane.

Fig. 5. A view of 2D-layer of tartate(-) anions showing the $R_2^2(10)$ and $R_4^4(20)$ graphs of hydrogen bonds.

Fig. 6. The crystal packing of deuterated D^{10} 1-(diaminomethylene)thiuron-1-ium tartate showing the 2D-layers parallel to (001) plane.

discrete, are interact each other via different hydrogen bonding motifs forming a 2D-layer parallel to the (001) crystallographic plane. One of the motifs is $R_2^2(10)$ that is formed between the translationally equivalents tartate(−) anions via two $O-H \cdots O$ hydrogen bonds between the hydroxyl groups and one of oxygen atoms of COO^- and $COOH$ groups. The other motif in the 2D-layer is $R_4^4(20)$ and is formed by four tartate(−) anions related by a screw axis and translation along the a -axis. The large $R_4^4(20)$ hydrogen bonding motif is formed by four $O-H \cdots O$ hydrogen bonds. Two of them are formed between the hydroxyl groups as donors and O2 and O8 atoms of COO^- and $COOH$ groups as acceptors, and the other two are formed between the $COOH$ groups as donors and the COO^- groups as acceptors between the tartate(−) anions related by a screw axis. The arrangement of the oppositely charged

units, 1-(diaminomethylene)thiuron-1-ium cations and tartate(−) monoanions, is mainly determined by the ionic and directional $O-H \cdots O$ and $N-H \cdots O$ hydrogen bonds and to a lesser degree by the van der Waals forces forming a layered structure (Fig. 6). The neighbouring 2D-layers interact via van der Waals forces and by weak $N-H \cdots S$ hydrogen bonds.

The second harmonic generation properties were measured on crystalline samples that were irradiated at 1064 nm and the second harmonic beam power diffused by the samples at 532 nm were measured as a function of the fundamental beam power. The SHG efficiency relative to KDP was found to be 0.77 and 0.82 for protiated and deuterated D^{10} crystals, respectively.

The FT-IR spectra of bis[1-(diaminomethylene)thiuron-1-ium] tartate(2−) hemihydrate and the deuterated 1-(diaminomethyl-

Fig. 7. Room temperature FTIR spectrum of bis[1-(diaminomethylene)thiuron-1-ium] tartate(2−) hemihydrate.

Fig. 8. Room temperature FTIR spectrum of deuterated D¹⁰ 1-(diaminomethylene)thiouron-1-ium tartate(–).

ene)thiouron-1-ium tartate(–) are shown in Figs. 7 and 8, respectively. The bands corresponding to the vibration of the functional groups were identified with the aid of infrared correlation charts [32,33]. In addition, the spectra are compared with the spectra of 1-(diaminomethylene)thiourea [15] and of tartaric acid [34–36] as well as of tartate(2–) and tartate(–) salts [37–42]. The title compounds have several functional and skeletal groups such as three NH₂ (or ND₂) C=S, C–N–C, N–C–N and N–C–S groups in the cation and COO[–], (COOD), OH or OD, C–C, C–C–C and C–H in the anion. The tartate(2–) dianion in protiated crystals has C₂ symmetry, while the tartate(–) monanion in deuterated crystals exhibits lower symmetry (C₁), and the splitting of the vibrations modes is expected. A careful inspection of the IR spectrum (Fig. 8) shows medium-strong intensity bands in the spectral range of 3500 and 3000 cm^{–1} that can be attributed to the asymmetric and symmetric stretching of three NH₂ groups of the 1-(diaminomethylene)thiouron-1-ium cation as well as to stretching vibration of hydroxyl groups of tartate(2–) dianion and the hydrated water molecule. These bands, as expected, are shifted in the IR spectrum of deuterated sample (Fig. 8) to the spectral region of 2600–2200 cm^{–1}. The strong narrow band at 1709 cm^{–1} in the IR spectrum of protiated sample is assigned to the stretching of imine bond of the cation, since a similar band is observed in some imines and their salts [43]. In addition, the band of imine group of the deuterated sample is shifted, as expected, to the 1263 cm^{–1} (Fig. 8). The X-ray data reveal that the all NH₂ groups of 1-(diaminomethylene)thiouron-1-ium cation in the protiated crystals are involved in the N–H···O hydrogen bonds with N···O distances ranging from 2.697(2) to 3.072(2) Å. This reveals as a broad band at ~2700 cm^{–1}, which is shifted to ~1900 cm^{–1} in the spectrum of deuterated crystals in which the amine groups ND₂ are involved in the N–D···O hydrogen bonds with N···O distances ranging from 2.891(2) to 3.216(2) Å. Additionally, the broad band in the region of 1400–1100 cm^{–1} that overlaps with ν(C–N) of the cation points the presence of the N–H···O hydrogen bonds. The ν_a(CO₂) and ν_s(CO₂) bands of tartate anion in the IR spectrum of bis[1-(diaminomethylene)thiouron-1-ium] tartate hemihydrate are observed at 1621 and 1514 cm^{–1}, respectively, which can be also found in the spectrum of deuterated crystals (Fig. 8). The ν(C=S) band of the 1-(diaminomethylene)thiouron-1-ium cation, similar as in thiourea, is observed at ~730 cm^{–1} in both samples, while in several thio-

urea metal complexes the ν(C=S) band is observed in the range 715–700 cm^{–1} [44]. The observed frequencies of the most prominent bands and their assignments for the protiated and deuterated samples are listed in Table 4.

Table 4

FT IR spectral data for protiated bis[1-(diaminomethylene)thiouron-1-ium] tartate(2–) hemihydrate and deuterated 1-(diaminomethylene)thiouron-1-ium tartate(–).

Protiated, ν (cm ^{–1})	Deuterated, ν (cm ^{–1})	Assignment
3410s	2558m	OH or OD
3387s	2523m	ν _a (NH ₂) or ν _a (ND ₂) asym stretch
3361m	2458m	ν _a (NH ₂) or ν _a (ND ₂) asym stretch
3342s	2397m	ν _a (NH ₂) or ν _a (ND ₂) asym stretch
3285s	2366s	OH or OD
3185m	2316m	ν _s (NH ₂) or ν _s (ND ₂) sym stretch
3123m	2298m	ν _s (NH ₂) or ν _s (ND ₂) sym stretch
3118m	2280m	ν _s (NH ₂) or ν _s (ND ₂) sym stretch
1717s	1263m	Imine bond stretch
1666m	1669	ν _a (CO ₂)
1621s	1625s	ν _a (CO ₂)
1514m	1516m	ν _s (CO ₂)
1462m	1458s	ν(C–N)
1426w	1400	γ(C–C) overlapped with Nujol
1377m	1019m	OH (OD) in-plane bend
1366m		ν(C–N) overlapped with Nujol
1341m	1323m, 1312m	
1290m	959w	δ(NH ₂), δ(ND ₂)
1237w	1195w	
1164w	870w	δ(NH ₂), δ(ND ₂)
1132w	1142m	γ(NH ₂)
	1110m	
1079m	1071w	
988w		
971w		γ(C–N)
914w	912w	δ(O–C–O) overlapped with ν(C–C)
	882w	
839w	801w	
746m	760w	γ(C–C)
726m	720m	ν(C=S)
696m	700s	
623m	680s	τ(NH ₂), ω(NH ₂)
584m	585w	Skeletal C–N–C, N–C–N
520w	521w	δ(C–COO)

4. Conclusion

The protiated single crystals of bis[1-(diaminomethylene)thiuron-1-ium] tartate(2−) hemihydrate were grown using a solution growth technique. The oppositely charged units, i.e. 1-(diaminomethylene)thiuron-1-ium cation and tartate dianion interact via two pairs of almost linear N—H...O hydrogen bonds with a graphs of $R_2^1(6)$ and $R_2^2(8)$ forming bis[1-(diaminomethylene)thiuron-1-ium] tartate(2−) supramolecular complex. The arrangement of these supramolecular complex units in the crystal is mainly determined by the N—H...O hydrogen bonds forming 2D-layered structure. In the deuterated crystals the tartate(−) monoanion interacts with 1-(diamino-methylene)thiuron-1-ium cation via five hydrogen bonding motifs. Three of them are $R_1^2(5)$ and the other two are $R_2^1(6)$ forming 1:1 hydrogen bonded supramolecular complex. In the deuterated crystal the tartate(−) monoanions, in contrast to the tartate(2−) dianions in the protiated crystals in which they are discrete, are interact each other via different hydrogen bonding motifs, $R_2^2(10)$ and $R_4^4(20)$, forming a 2D-layer parallel to the (001) crystallographic plane. The SHG efficiency relative to KDP was found to be 0.77 and 0.82 for protiated and deuterated crystals, respectively. Comparison of the IR spectra of protiated bis[1-(diaminomethylene)thiuron-1-ium] tartate(2−) hemihydrate with the deuterated 1-(diaminomethylene)thiuron-1-ium tartate(−) clearly shows marked differences in the regions of vibrations of the amine and imine groups as well as in the region of the N—H...O hydrogen bonds.

Appendix A. Supplementary material

Additional material comprising full details of the X-ray data collection and final refinement parameters including anisotropic thermal parameters and full list of the bond lengths and angles have been deposited with the Cambridge Crystallographic Data Center in the CIF format as supplementary publications no. CCDC 874067 and 874068 for deuterated and protiated crystals. Copies of the data can be obtained free of charge on the application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK, (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molstruc.2012.07.034>.

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