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Structural and spectroscopic characterization of bis[1-(diaminomethylene)thiouron-1-ium] naphthalene-1,5-disulfonate

Marcela C. Felix [a], Genivaldo J. Perpétuo [a], Jan Janczak [b, *]

[a] Instituto de Ciências Exatas e Biológicas, Universidade Federal de Ouro Preto, MG, Brazil
[b] Institute of Low-Temperature and Structure Research, Polish Academy of Sciences, PO Box 1410, 50950, Wrocław, Poland

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ABSTRACT

Single crystals of bis[1-(diaminomethylene)thiouron-1-ium] naphthalene-1,5-disulfonate (**1**) are grown using growth solution technique. The compound crystallizes in the centrosymmetric C2/c space group of the monoclinic system with four molecules per unit cell. The arrangement of oppositely charged units, i.e. 1-(diaminomethylene)thiouron-1-ium cations and naphthalene-1,5-disulfonate anions in the crystal is mainly determined by the ionic and the N–H···O hydrogen bonding interactions. Hirshfeld surface and the analysis of 2D fingerprint plots are illustrating both qualitatively and quantitatively interactions governing the supramolecular arrangement. The compound was also characterized by FT-IR and Raman spectroscopies. The vibrational assignment of the characteristic bands of the functional groups have been supported by the isotopic frequency shift.

1. Introduction

The study of crystalline compounds in context of supramolecular chemistry promotes an interface of different areas like the pharmaceutic and nanotechnology industries, since the properties of materials are influenced by crystalline structure [1]. Intermolecular interactions play a very important role in crystal engineering of organic molecules including two or more components in formation of supramolecular self-assembly and the crystal packing of supramolecules in the three-dimensional space [2–9]. The hydrogen-bonding is an important driving force for supramolecular assemblies between the organic molecules due to its abundance, strength, and specific relative directional properties [10–12]. In this context, Etter el al. develop empirical hydrogen-bond rules for determining preferred modes of hydrogen-bonding pattern, which is an effective approach for structural design and prediction [13–15].

Supramolecular synthesis based on a combination of ionic and hydrogen bonding interactions between the organic acid-base adducts or salts yelds several kinds od self-assembly supramolecular frameworks in solids [16–20]. The work is a continuation of the study of supramolecular solid-state architectures formed by self-assembly of thiourea derivates [21–25]. The thiourea derivates can form multiple hydrogen bonds and are useful as building blocks in supramolecular synthesis.

A naphthalene ring is one of the most important aromatic platforms for organic functional ligands. It is usually substituted with functional groups accessible for intermolecular interactions, that is, coordination or hydrogen bonding. If a functional group is considered, the most widely explored one is the carboxylic group. Disubstituted 1,4- and 1,5- by carboxylic groups naphthalene platform is important in supramolecular synthesis as planar rigid linkers. It is quite different when the carboxylic groups is substituted by the sulfonic groups (-SO_3H) due to its tetrahedral geometry that makes some additional flexibility in comparison to carboxylic group [26–28].

In the present work, we report the solid-state structure formed by self-assembly of 1,5-naphthalene disulfonic acid and 1-(diaminomethylene)thiourea (Scheme 1) from a water solution.

2. Experimental

The 2-imino-4-thiobiuret (99%) and naphthalene-1,5-disulfonic acid tetrahydrate (97%) were commercially available (Aldrich) and used as received. Elemental analysis was carried out with a Perkin-

* Corresponding author.
E-mail address: j.janczak@int.pan.wroc.pl (J. Janczak).

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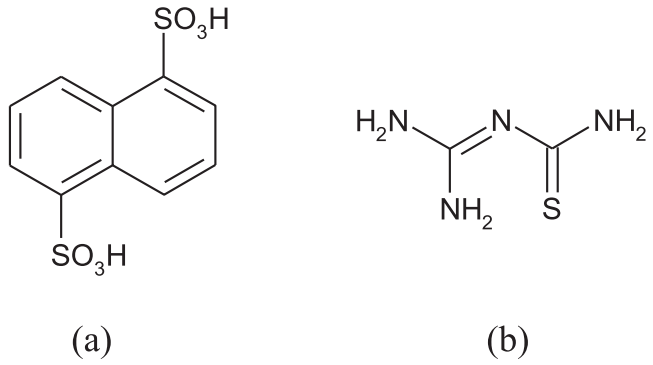

Scheme 1. Components of the analysed crystal: 1,5-naphthalene disulfonic acid (a) and 1-(diaminomethylene)thiourea (b).

Elmer 240 elemental analyzer.

2.1. Preparation of *1*

Commercially available 2-imino-4-thiobiuret (Aldrich, CAS No. 2114-02-05), which is in the fact the tautomeric form, 1-(diaminomethylene)thiourea [29] and the naphthalene-1,5-disulfonic acid tetrahydrate (Aldrich, CAS Number 211366-30-2) were added to hot water in a molar proportion of 2:1. When the solution became homogenous it was cooled slowly and kept at room temperature. After several days, transparent colourless crystals were formed. The crystals have been separated by filtration and dried in air. Analysis: Calc. for $C_{14}H_{20}N_8O_6S_4$: C, 32.05; N, 21.26; O, 18.30; S, 24.45 and H, 3.84%. Found: C, 31.88; N, 21.32; O, 18.63; S, 24.39 and H, 3.78%.

The deuterated analogue of bis[1-(diaminomethylene)thiouron-1-ium] naphthalene-1,5-disulfonate was prepared by usual reaction with heavy water. The crystals of **1** were dissolved in heavy water and was left in the atmosphere saturated with heavy water for two weeks in order to avoid the contamination of the crystals, than the procedure was repeated twice.

2.2. Single crystal X-ray data collection

X-ray intensity data for the crystal were collected using graphite monochromatic MoKα 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. One image was used as a standard after every 40 images for monitoring of the crystal stability and data collection, and no correction on the relative intensity variations was necessary. Data collections were made using the CrysAlis CCD program [30]. Integration, scaling of the reflections, correction for Lorenz and polarisation effects and absorption corrections were performed using the CrysAlis Red program [30]. The structure was solved by the direct methods using SHELXS97 [31] and refined using SHELXL-2014 program [32]. Aromatic hydrogen atoms were placed in their geometrical positions and the hydrogen atoms joined to nitrogen 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. Selected geometrical parameters are listed in Table 2 and the geometry of hydrogen bonding interactions are collected in Table 3. Visualisation of the structure was made with the Diamond 3.0 program [33].

Table 1
Crystallographic data for **1**.

Empirical formula	$(C_2H_7N_4S)_2[C_{10}H_6(SO_3)_2]$
Formula weight ($g\cdot mol^{-1}$)	524.62
Crystal system, space group	Monoclinic, C 2/c (No. 15)
a (Å)	32.4476(6)
b (Å)	8.1602(2)
c (Å)	8.3878(2)
β (°)	104.098(2)
V (Å^3)	2154.02(9)
Z	4
D_{calc}/D_{obs} ($g\cdot cm^{-3}$)	1.618/1.61
μ (mm^{-1})	0.493
F(000)	1088
Crystal size (mm)	0.28 × 0.24 x 0.18
Radiation type, wavelength, λ (Å)	Mo *Kα*, 0.71073
Temperature (K)	295 (2)
θ range(°)	3.04 ÷ 28.95
Absorption correction	multi-scan
T_{min}/T_{max}	0.943/1.000
Reflections collected/unique/observed	27018/2820/2534
R_{int}	0.0191
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0264
w*R*(F^2 all reflections)	0.0680
Goodness-of-fit, *S*	1.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	+0.285, −0.242

$wR = \{\Sigma\ [w(F_o^2-F_c^2)^2]/\Sigma wF_o^4\}^{½}$; $w^{-1} = [\sigma^2(F_o^2) + (0.0345P)^2 + (1.5419P)]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 2
Selected bond lengths (Å) and angles (°) for **1**.

S1—C1	1.6807(13)	N2—C1—N1	112.44(11)
C1—N2	1.3144(17)	N2—C1—S1	122.02(10)
C1—N1	1.3804(16)	N1—C1—S1	125.54(9)
N1—C2	1.3616(15)	C2—N1—C1	130.17(11)
C2—N3	1.3070(17)	N3—C2—N4	121.23(12)
C2—N4	1.3184(17)	N3—C2—N1	122.64(12)
S2—O1	1.4522(9)	N4—C2—N1	116.12(12)
S2—O3	1.4562(9)	O1—S2—O3	113.46(5)
S2—O2	1.4656(9)	O3—S2—O2	111.30(5)
S2—C4	1.7853(11)	O1—S2—C4	106.93(5)
C3—C7^i	1.4207(15)	O3—S2—C4	105.97(5)
C3—C3^i	1.432(2)	O2—S2—C4	107.33(5)
C3—C4	1.4330(15)	C7^i—C3—C3^i	118.71(12)
C4—C5	1.3667(16)	C7^i—C3—C4	123.31(9)
C5—C6	1.4090(16)	C3^i—C3—C4	117.98(12)
C6—C7	1.3618(17)	C5—C4—C3	121.2(1)
		C5—C4—S2	117.41(8)
		C3—C4—S2	121.36(8)
		C4—C5—C6	120.32(11)
		C7—C6—C5	120.37(11)
		C6—C7—C3^i	121.42(10)

Symmetry code: (*i*) 0.5-x, 0.5-y, 1-z.

Table 3
Hydrogen bonding geometry (Å,°) for **1**.

D-H···A	D-H	H···A	D···A	D-H···A
N1—H1N···O3^i	0.85(2)	1.97(3)	2.8147(14)	172.2(15)
N2—H2N···O2^i	0.83(2)	2.20(2)	2.9867(15)	158.9(16)
N2—H3N···S1^{ii}	0.83(2)	2.57(2)	3.3872(12)	169.5(15)
N3—H4N···O2	0.77(2)	2.12(2)	2.8646(15)	163.4(18)
N3—H5N···S1	0.86(2)	2.26(2)	2.9950(14)	143.0(16)
N4—H6N···O2^{iii}	0.85(2)	2.32(2)	2.9305(15)	129.2(17)
N4—H6N···O3^i	0.85(2)	2.43(2)	3.1238(16)	139.4(17)
N4—H7N···O1	0.82(2)	2.12(2)	2.9355(16)	176.1(17)

Symmetry codes: (*i*) x, 1 + y, z; (*ii*) -x, 2-y, 1-z; (*iii*) x, 1-y, −0.5 + z.