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Solid-state supramolecular structure formed between the 1-(diaminomethylene)thiourea and mellitic acid

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ABSTRACT

The single crystals of hexakis(1-(diaminomethylene)thiouron-1-ium) benzene-1,2,3,4,5,6-hexacarboxylate (mellitate(6-)) tetrahydrate suitable for the X-ray analysis were grown using a solution growth technique at room temperature. The compound crystallises in centrosymmetric space group of the triclinic system. The conformation of six crystallographically independent 1-(diaminomethylene) thiouron-1-ium cations is not strictly planar, but twisted. Both planar arms of the cations are oppositely rotated by 6.1(1) ÷ 20.9(1)° around the C–N bonds involving the central N atom. All of the carboxylate groups of mellitate(6-) anion are inclined to the plane of aromatic six-membered carbon ring by 43.0(1) ÷ 72.0(1)°. Oppositely charged components i.e. 1-(diaminomethylene)thiouron-1-ium cations and mellitate(6-) anion interact each other via N–H···O hydrogen bonds forming hexakis(1-(diaminomethylene)thiouron-1-ium) mellitate units that further interact with the water molecules forming hexakis(1-(diaminomethylene)thiouron-1-ium) mellitate tetrahydrate supramolecular architecture. Hirshfeld surface and the analysis of 2D fingerprint plots are used for illustrate both qualitatively and quantitatively interactions between the units governing the supramolecular assemblies. The compound was also characterised by vibrational spectroscopy. The vibrational assignment have been supported by the isotopic frequency shift.

1. Introduction

The study of the crystalline compounds in the context of supramolecular chemistry plays a very important and fundamental role in many branches of science including molecular recognition and aggregation, molecular biology, pharmaceutic and nanotechnology, since the properties of these materials are influenced by the crystalline structure [1,2].

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 [3–10]. The prediction of the supramolecular structure with the specific desirable properties of the product from the structures of the substrates remain of ultimate goal of the investigations [11,12]. Understanding of the interactions between the molecules in the context of design of new supramolecular architectures is rapidly extending research branch of materials science [13,14]. 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 [15–17]. 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 [18–20]. The components containing complementary arrays of hydrogen bonding sites are widely used in crystal engineering for obtaining supramolecular architectures with predictable structures. The carboxylic acids are popular choice for supramolecular synthons in supramolecular crystals because of the directionality and predictability of their interactions. Besides the carboxylic group, other function groups like as sulfonic [21,22], phosphonic [23–28] and silanol [28,29] are also attractive for supramolecular assemblies.

The aromatic carboxylic acids containing three or more carboxylic groups linked to aromatic ring, like 1,3,5-benzenetricarboxylic acid (trimesic acid) or 1,2,4,5-benzenetetracarboxylic acid (pyromelllitic acid), have been used as building blocks for supramolecular synthesis [30–38]. However, the mellitic acid containing six carboxyl groups (1,2,3,4,5,6-

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benzenehexacarboxylic acid) was used very rarely as building blocks for supramolecular synthesis [39–41]. Therefore in the present work, the self-assembly solid state structure formed between the mellitic acid 1-(diaminomethylene)-thiourea is investigated (Scheme 1).

The commercially available 2-imino-4-thiobiuret (Aldrich, CAS No. 2114-02-5) is, as has been shown by the X-ray single crystal analysis, its tautomeric form of 1-(diaminomethylene)thiourea [42]. Both tautomer's are already used as a building blocks for supramolecular synthesis, since they contain active hydrogen bonding sites. In addition they can act as *N,N*- or *N,S*-coordinating ligands forming several types of complexes with metal ions [43–45].

2. Experimental

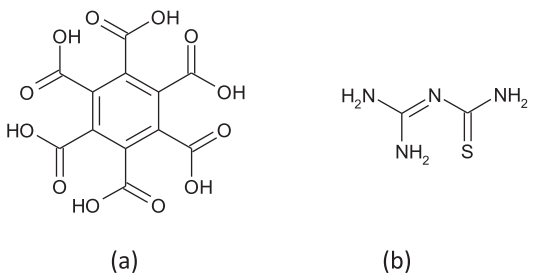
2-imino-4-thiobiuret (99%), which is in the fact the tautomeric form 1-(diaminomethylene)-thiourea and the mellitic acid (99%) were commercially available (Aldrich-Sigma) and was used as received. Elemental analysis was carried out with a Perkin-Elmer 240 elemental analyser.

2.1. Preparation of hexakis(1-(diaminomethylene)thiouron-1-ium) mellitate tetrahydrate (**1**)

1-(diaminomethylene)-thiourea (0.5042 g) and mellitic acid (0.1711 g) were added to hot water (molar proportion of 6:1). When the solution became homogenous it was cooled and kept at room temperature. After several days, well-developed colourless crystals suitable for the X-ray analysis were formed. The crystals have been separated by filtration and dried in air. Analysis. Calculated for $C_{24}H_{50}N_{24}O_{16}S_6$: C, 25.66; H, 4.49; N, 29.93; O, 22.79 and S, 17.13%. Found: C, 25.52; H, 4.44; N, 29.89; O, 22.98 and S, 17.23%.The deuterated analogue of **1** 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 several days in order to avoid the contamination of the crystals. Then 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. 41201 reflections (11472 independent, $R_{int} = 0.0672$) were measured. Data collections were made at 100(1)K using the CrysAlis CCD program [46]. Integration, scaling of the reflections, correction for Lorenz and polarisation effects and absorption corrections were performed using the CrysAlis Red program [46]. The structure was solved by the direct methods using SHELXS97 [47] and refined using SHELXL-2014 program [48]. The hydrogen atoms of amine and imine groups were located in difference Fourier maps and were refined with $U_{iso} = 1.2U_{eq}(N)$ and the H atoms of water molecules (O14 and O15) were refined while the H atoms of water (O13 and O16) molecules were constrained with O–H distance of 0.85 Å and with the $U_{iso}(H) = 1.5U_{iso}(O)$. The final difference Fourier maps showed no peaks of chemical significance. The largest peaks on the final Δρ map were +0.684 and −0.496 eÅ^{-3}. 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 [49].



Scheme 1. Mellitic acid (a) and 1-(diaminomethylene)-thiourea (b).

2.3. Powder X-ray diffraction (XRPD)

Powder X-ray diffraction patterns of the powdered protonated and deuterated analogue of **1** were checked on a PANanalytical X'Pert diffractometer equipped with a CuKα radiation source (λ = 1.54182 Å). The diffraction data were recorded in the 2è range of 5 ÷ 45° at room temperature. The powder diffraction patterns of H- and D-compounds are included in Supporting Materials (Fig. S1). The obtained deuterated analogue of **1** crystallizes similar as H-compound in the same space group of triclinic system, with quite similar lattice parameters.

2.4. Vibrational spectra measurements

The vibrational measurements of H-and D-compounds 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. The Fourier Transform Raman spectrum was recorded on a FRA-106 attached to the Bruker 113 V

Table 1
Crystallographic data for hexakis(1-(diaminomethylene)thiouron-1-ium)mellitate tetrahydrate.

Empirical formula	$C_{24}H_{50}N_{24}O_{16}S_6$
Formula weight (g·mol^{-1})	1123.24
Crystal system, space group Temperature (K)	triclinic, *P-1* (No. 2) 100(1)
a (Å)	7.6147(4)
b (Å)	11.8076(5)
c (Å)	26.3891(11)
α (°)	90.503(5)
β (°)	96.166(4)
γ (°)	99.467(4)
V (Å^3)	2325.98(19)
Z	2
D_{calc}/D_{obs} (g·cm^{-3})	1.604/1.60
μ (mm^{-1})	0.386
F(000)	1172
Crystal size (mm)	0.29 × 0.27 × 0.22
Radiation type, wavelength, λ (Å)	Mo *Kα*, 0.71073
Temperature (K)	100(1)
θ range(°)	2.787 ÷ 29.605
Absorption correction	multi-scan
T_{min}/T_{max}	0.977/1.000
Reflections collected/unique/observed	41201/11472/7203
R_{int}	0.0662
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0578
$wR(F^2$ all reflections)	0.1059
Goodness-of-fit, *S*	1.01
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	+0.684, −0.496

$wR = \{\Sigma\ [w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.0304P)^2 + 0.4863P$ where $P = (F_o^2 + 2F_c^2)/3$.