CRYSTAL STRUCTURE AND HIRSHFELD SURFACE ANALYSIS OF 2,4-DIAMINO-6-PHENYL-1,3,5-TRIAZIN-1-IUM PERCHLORATE

STRUCTURA CRISTALĂ ȘI ANALIZA SUPRAFEȚEI HIRSHFELD A 2,4-DIAMINO-6-PHENYL-1,3,5-TRIAZIN-1-IUM PERCHLORATULUI

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Summary. *Synthesis and characterization of new organic salt, 2,4-diamino-6-phenyl-1,3,5-triazin- 1-ium perchlorate (LH)(ClO_4), in which NH ···O(N) hydrogen bonds play an essential role in stabilizing the crystal structure, were highlighted in the present study. The crystal structure was determined using single-crystal X-ray diffraction analysis, which reveals that the title compound crystallizes in the monoclinic centrosymmetric space group $P2_1/c$ and contains one cation and one anion in the asymmetric unit. The unit cell parameters are a =13.8011(13) Å, b = 5.0674(5) Å, c = 16.6411(13) Å, and β = 91.930(9)˚. Also, the composition $C_9H_{10}ClN_5O_4$, of the discussed compound was confirmed by FTIR spectroscopy. From this research a decisive influence of hydrogen bonds on stability of the reported crystal is evidenced. The distribution of all types of intermolecular interactions was assessed by the Hirschfeld surface analysis method.*

Keywords*: organic salt, 2,4-Diamino-6-phenyl-1,3,5-triazine-1-ium, crystal structure, Hirshfeld surface analysis.*

INTRODUCTION

The association of organic adducts, containing 1,3,5-triazines, with various types of biological activities [1, p.40] such as antimicrobial [2, p.348], anticancer [3, p.3, 4, p.3301]

and antiviral ones [5, p.1231] has accelerated the rate of progress in synthesizing new 1,3,5-triazine derivatives. Apart from biological activities, compounds containing 1,3,5-triazine entities are of specific interest due to their nonlinear optical response with high potential [6, p.110370, 7, p.220]. Triazine derivatives are also used as building blocks for the creation of hybrid organic /inorganic framework architectures [8, p.9046].

2,4-Diamino-6-phenyl-1,3,5-triazine is a popular heterotopic molecule extensively used today as a universal ligand for the synthesis of metal complexes with diverse structural architectures [9, p.3568, 10, p.4813, 11, p.348] and supramolecular aggregates [12, p.30102, 13, p.04681].

The survey of CSD (Con Quest Version 2024.1.0) showed that in the metal-free compounds the L/LH^+ entities were able to successfully cocrystallize with mono- or dicarboxylic acids or pharmaceuticals, thus revealing their potential as H-donor/acceptor in the environment either as a neutral molecule or as a monocation. In the latter case, the L-base is protonated either at one of the nitrogen atoms of the triazine cycle or at the terminal amino group.

The triazine ligand used both as a main ligand and as an auxiliary ligand is interesting due to the fact that not only the amino groups of the triazine ring can form hydrogen bond interactions with oxygen atoms, nitrogen atoms or solvent molecules [14, p.137, 9, p.3568] , but also triazine and benzene rings are able to generate π…π stacking interactions [12, p.30102].

MATERIALS AND METHODS

All reagents were purchased from commercial sources and used without further purification. The IR spectra were recorded on a FTIR Spectrum-100 Perkin Elmer spectrometer in the range of 4000–650 cm^{-1}. X-ray single crystal data were collected at room temperature 293(2) K on an Xcalibur E diffractometer equipped with a charge-coupled device (CCD) area detector and a graphite monochromator utilizing MoKα radiation (λ=0.71073 Å)

Synthesis of (LH)(ClO_4)

0.018 g (0.1 mmol) of 2,4-diamino-6-phenyl-1,3,5-triazine (LH) was dissolved in 8 ml C_2H_5OH and stirred until dissolved at temperature 80°C, then citric acid was added, further stirring the solution at the same temperature. To the resulting solution was added 0.031 g (0.1 mmol) $Cd(ClO_4)_2 \cdot 2H_2O$ salt and stirred until completely dissolved. After 64 days, colorless crystals precipitated on the walls of the vessel. The collected crystals were washed with ethanol and dried under vacuum. (Yield: 64%).

X-ray data collection and structure determination

Diffraction measurements were carried out on an Xcalibur E diffractometer equipped with a CCD area detector and a graphite monochromator utilizing MoKα (λ = 0.71073 Å) radiation at room temperature. The data were collected and processed using

the program CrysAlisPro [16, p.117] and the intensities were corrected for Lorentz and polarization effects as well as for empirical absorption based on the multi-scan technique. All calculations to solve the structure and to refine the model proposed were carried out with the programs SHELXS-2014 and SHELXL-2014 [17, p.6, 18, p.24]. Structure solution met no difficulties and no indication for the unresolved disordering. The C-bound H-atoms were positioned geometrically and treated as riding atoms using SHELXL default parameters with $U_{iso}(H) = 1.2U_{eq}(C)$, the N-bound H-atoms were found from differential Fourier maps at the intermediate stages of the refinement and their positions were restrained during the refinement. Crystal data for title compound: Mr = 287.67, monoclinic, space group $P2_1/c$, a = 13.8011(13), b = 5.0674(5), c =16.6411(13) Å; β = 91.930(9)°; V =1163.14(18) A^3; Z = 4; D_{calc} = 1.643 Mg m^{-3}; $F(000)$ =592; μ = 0.349 mm^{-1}; R_1 = 0.0649, wR_2 = 0.0837 for 2037 independent reflections with $I > 2\sigma(I)$; R_1 = 0.1296, wR_2 = 0.0997 for all 3793 independent reflections. CIF file was deposited in Cambridge Crystallographic Data Centre (CCDC) (https://www.ccdc.cam.ac.uk/structures/) with the CCDC deposition number 2368139.

IR spectroscopy

The IR plots for the free L-base and the title adduct are shown in Fig. 1 and indicate that the principal IR bands typical for the free L-base were also registered in the title salt and summarized in Table 1. The N-H stretching frequencies were registered in the range 3507-3175 cm^{-1} for L-base and 3561-3199 cm^{-1}, for the title compound. The N-H bending mode (scissoring) appears as a medium to strong intensity (broad) band in the range from 1621 to 1294 cm^{-1} for the ligand and 1717–1433 cm^{-1} for (LH)(ClO_4), overlapping with the aromatic C=C ring absorption, which also appear in this region, as well as the presence of a C-H bend at the methylene group. The C-N stretching absorption occurs in the region from 1388 to 1270 cm^{-1} as a medium to strong band. Deformation vibrations of aliphatic and aromatic C-H groups are present in the region of 900 cm^{-1} for the L-base and 1066 cm^{-1} for the title compound. A strong signal in the title adduct at 1066 cm^{-1} can be assigned to the stretching vibration of Cl-O bond in perchlorate anion.

Table 1. Main IR bands for compounds L and (LH)(ClO_4)

Stripes functions	**ν, cm^{-1}**	
	L	(LH)(ClO_4)
ν_{as}(N-H)	3507	3561
ν_s(N-H)	3372	3409
ν_{as}(C-H)	1694	1717
ν_s(C-H)	1621	1637
$\delta(NH_2)$	1490	1451

ν_{ring}	1578	1574
ν_{as}(C-N)	1294	1297
ν_{s}(C-N)	1276	1271
δ(CH)	900	1066
ν_{as}(Cl-O)	-	1066

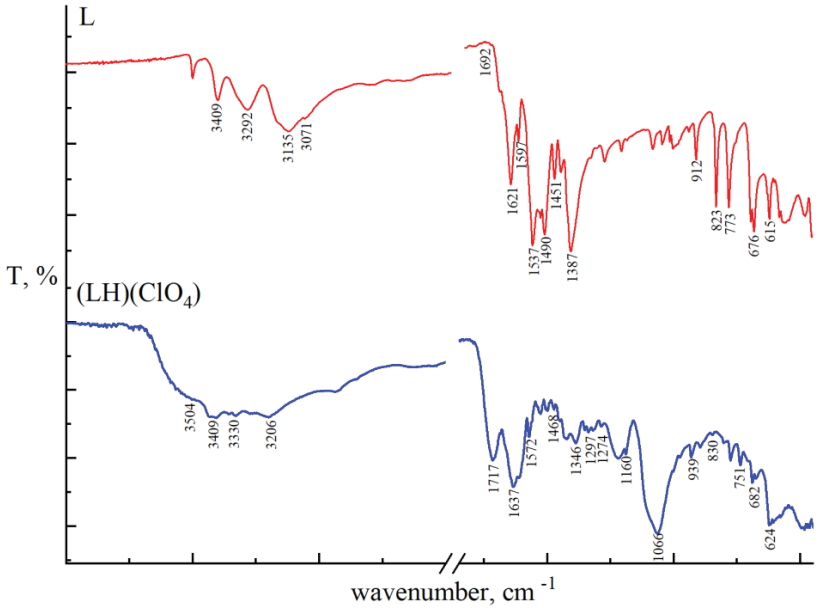
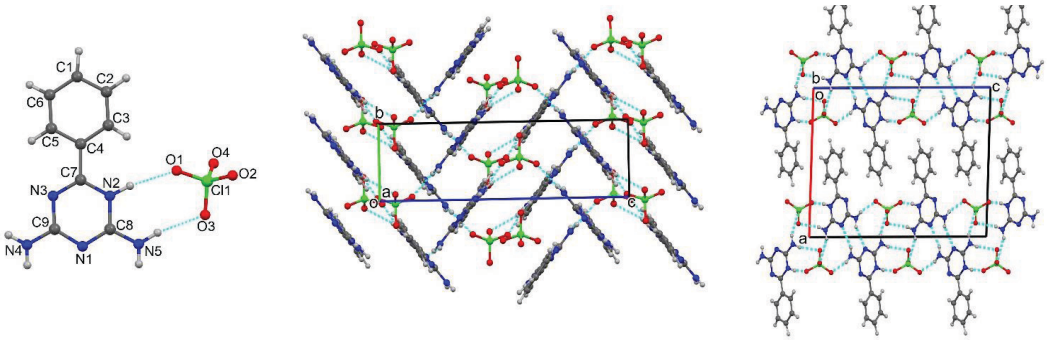


Fig. 1. Comparison of IR plots for L and title compound

RESULTS AND DISCUSSION

We report here the synthesis, spectroscopic characterization and crystal structure of the title compound, arising from ion-pairing and hydrogen bonding. Single-crystal X-ray diffraction analysis revealed that the title compound crystallizes in the centrosymmetric monoclinic $P2_1/c$ space group, and the asymmetric unit comprises salt-like aggregate $(LH)(ClO_4)$, as one triazinium cation, $(LH)^+$, and one perchlorate anion. In the crystal, the L-base is additionally protonated at triazine nitrogen atom N2, placed between the amino-group and phenyl substituent. This protonation is represented by an increase in the corresponding bond angle, C7–N2–C8 being equal to 119.4(4)° compared to the angles at unprotonated N-atoms, N1 and N3 with the corresponding bond angles of C8–N1–C9 = 115.8(4)° and C7–N3–C9 =117.4(4)°. The planar conformation of the LH^+ cation is indicated by the values of interplanar angle 6.04° between the triazine and phenyl rings and by the torsion angles C3–C4–C7–N2/C5–C4–C7–N3 with values -6.44/-5.14°.

The crystal structure is stabilized by four NH…O and one NH…N hydrogen bonds (Table 1). The counter-charged species are interconnected by four unique intermolecular *N–H*···O hydrogen bonds in such a way that each tetrahedral ClO_4^- anion in a tripod mode holds around three LH^+ cations. The LH^+ cations linked by the two-fold screw axis are associated in the homomeric helical chain via NH…N hydrogen bond. Interconnection of these H-bonded motifs resulted in the H-bonded layer restricted by the phenyl substituents (Fig. 2b). These layers pack in the interdigitated mode with π-π stacking interactions between the phenyl residues that belong to the neighboring layers (Fig. 2c).



a **b** **c**

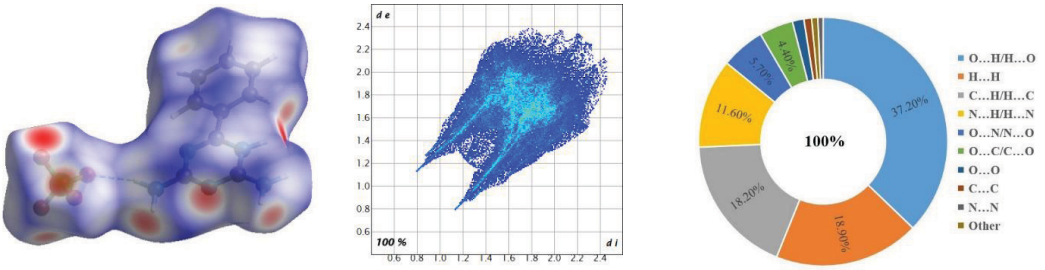
Fig. 2. a) Content of the asymmetric unit in the title compound. b) fragment of H-bonded layer; c) packing of the layers

Table 1. Hydrogen bond distances (Å) and angles (°) in the title compound

D–H···A	d(H···A), Å	d(D···A), Å	∠DHA, °	Symmetry operation for acceptor
N(2)-H(2N)···O(1)	2.02(4)	2.921(5)	165(3)	*x*, -*y*+3/2, *z*+1/2
N(4)-H(4NA)···O(4)	2.27(4)	3.099(5)	163(4)	*x*, *y*, *z*
N(4)-H(4NB)···N(1)	2.31(4)	3.104(5)	158(4)	-*x*, *y*-1/2, -*z*+1/2
N(5)-H(5NA)···O(3)	2.19(4)	3.063(5)	164(4)	*x*, -*y*+3/2, *z*+1/2
N(5)-H(5NB)···O(2)	2.40(4)	3.119(5)	145(4)	-*x*, *y*+3/2, -*z*+1/2

Hirshfeld surface analysis [18, p.20] and two-dimensional fingerprint plots are useful tools for describing the surface characteristics of the crystal structure and were generated using CrystalExplorer 3.0 [19, p.1008]. The normalized contact distance (d_{norm}) is based on the distances from the nearest atom inside (d_i) and outside (d_e) the surface. The three-dimensional d_{norm} surface of the title compound is shown in Fig. 3a. The red points represent closer contacts and negative d_{norm} values on the surface corresponding to N—H···O and N—H···N interactions. Two-dimensional fingerprint plots are shown in Fig. 4. The O···H interactions (37.2%) and H···H (18.9%) interactions make the highest

contributions with the C···H (18.2%), N···H (11.6%), O···N (5.7%) and C···O (4.4%) contacts also making significant contributions to the Hirshfeld surface.



a **b** **c**

Fig. 3. a) View of the three-dimensional Hirshfeld surface of the title compound. b) Two-dimensional fingerprint plot for all interactions. c) The diagram of the distribution of the principal intermolecular interactions

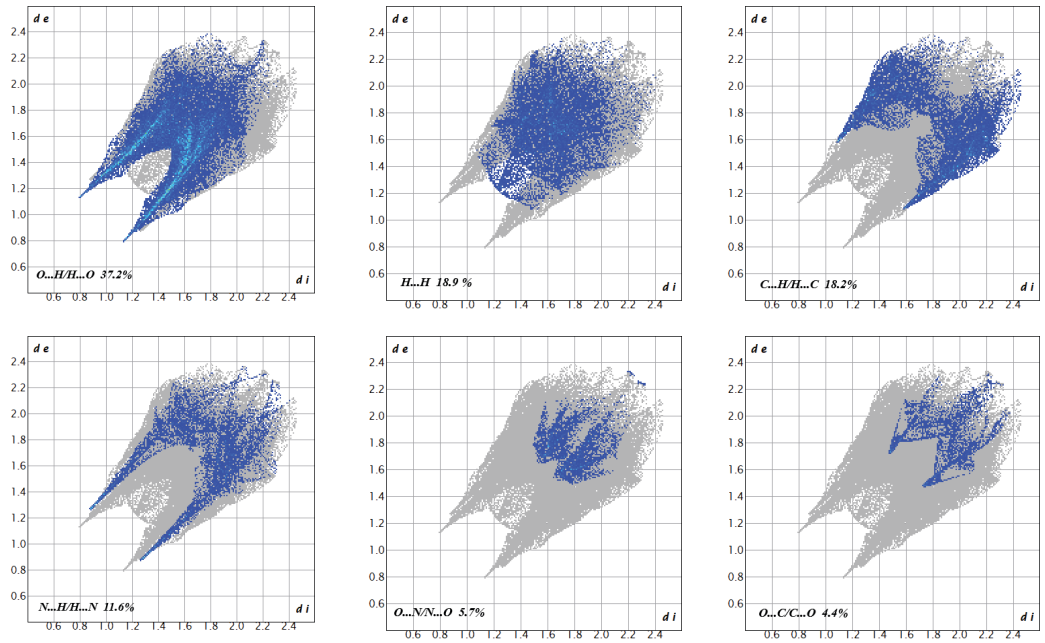


Fig. 4. Two-dimensional fingerprint plots for the title compound

CONCLUSIONS

An attempt to obtain a mixed-ligand Cd(II)-based coordination compound with involvement of diamino-substituted triazine derivative, resulted in novel organic-inorganic hybrid salt, 2,4-diamino-6-phenyl-1,3,5-triazin-1-ium perchlorate $(LH)(ClO_4)$,

whose structure has been confirmed by single crystal X-ray structural analysis. The NH...O(ClO_4) and NH…N hydrogen bonds are the main driving forces to stabilise the layered structural motif with π-π stacking interactions between the phenyl substituents from adjacent layers. Hirshfeld surface analysis that complemented the X-ray study, specified the quantitative distribution of weak interactions in the crystal. The present study extends our knowledge about specific interactions and association patterns in the adducts with participation of 2,4-diamino-6-phenyl-1,3,5-triazine.

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