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The Dihydropyrimidine-2,4-(1*H*,3*H*)-dione Functionality: a Suitable Module for Novel Crown-containing Hydrogen-bonded Supramolecular Assemblies

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Two novel pyrimidine derivatives, 2-(2-methylphenyl)-2*H*-[1,2,3]triazolo[4,5-*d*]pyrimidine-5,7(4*H*,6*H*)-dione 3-oxide (H-PD) and 6-amino-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-ylsulfamic acid (H-PS), were synthesized and investigated as suitable ligands for co-crystallization with 1,10-diaza-18-crown-6 (DA18C6). Two solid compounds formulated as $[(H_2DA18C6)(PD)_2(H_2O)_4]$ (1) and $[(H_2DA18C6)(PS)_2(H_2O)_2]$ (2) have been shown by single-crystal structural analysis to be 2D and 3D networks, respectively, through extensive H-bonding intermolecular interactions. Both 1 and 2 incorporate the diaza-18-crown-6 units in the form of macrocyclic cations. In 1 the $(PD)^-$ anions deprotonated in the fourth position of the pyrimidine ring and water molecules are combined into 2D anionic sheets, the macrocyclic cations occupying the cavities in these sheets. In 2 the ensemble of donor and acceptor binding sites available in the 6-amino-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-ylsulfamate anions $(PS)^-$ facilitates their self-assembly into a double layer via diverse hydrogen bonds. Water molecules and H_2-1,10-diazonia-18-crown-6 cations bridge the neighboring layers thus providing the final 3D supramolecular architecture.

Keywords: Pyrimidine derivatives; Self-assembly; Crown spacer; Hydrogen bonding

INTRODUCTION

The design of new supramolecular architectures [1–3] requires the identification of the suitable supramolecular modules and the usage of such connectors in the assembly of organic and metal-containing networks. So far, consolidation of metal complexes has been achieved through syntheses of coordination polymers, and several 2D and 3D metal-containing frameworks have resulted in porous solids with channels and cavities [4–6]. The creation of ordered hydrogen-bonded networks also has attracted attention, and some intermolecular connectors have been utilized successfully for the linking of building blocks into diverse types of hydrogen-bonded architecture [7–9]. The dihydropyrimidine-2,4-(1*H*,3*H*)-dione functionality represents a supramolecular module that can generate infinite two-dimensional networks through complementary hydrogen bonds with the formation of a dimeric N—H···O(=C) supramolecular synthon (synthon **I** in Chart 1) [10–15], $R_2^2(8)$ graph set [16,17]. If it is combined with the additional H-binding sites (oxime, amine or sulfonamide moieties), we obtain access to 3D supramolecular architectures.

Recently [18] the novel dioxime, (4*Z*,5*E*)-pyrimidine-2,4,5,6(1*H*,3*H*)-tetraone 4,5-dioxime (**H_2-PTD**) was obtained by the interaction of 6-amino-5-nitrosopyrimidine-2,4(1*H*,3*H*)-dione with hydroxylamine hydrochloride. The structures of two complexes incorporating the corresponding monoanion, 6-hydroxyimino-2,4-dioxo-1,2,3,6-tetrahydropyrimidine-5(4*H*)-one oximate (Chart 2), deprotonated at one of the oxime groups, with H_2-1,10-diazonia-18-crown-6 (stoichiometry 1:2), and its ammonium salt in the complex with the *cis–syn–cis* isomer of dicyclohexano-18-crown-6

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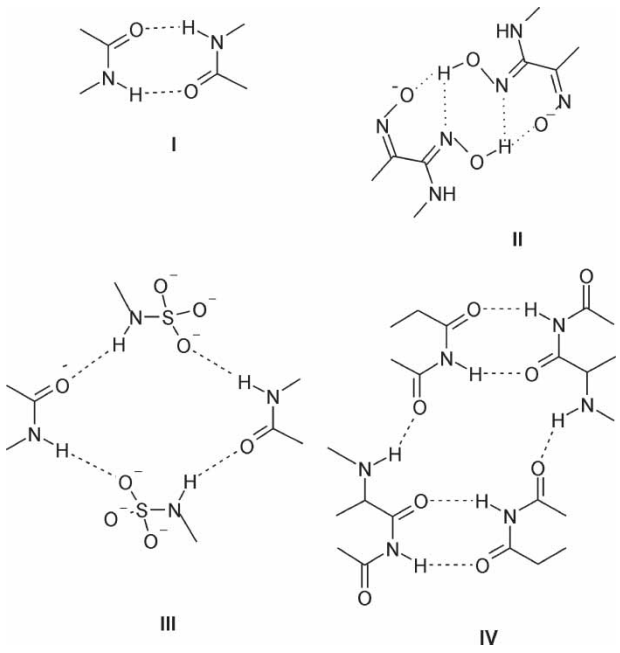


CHART 1 Supramolecular synthons found in dihydropyrimidine-2,4-(1*H*,3*H*)-dione derivatives.

(stoichiometry 1:1), were determined by X-ray analysis. In the first compound the $(\mathbf{H\text{-}PTD})^-$ anions are joined into dimers through O—H···N, and O—H···O hydrogen bonds, [synthon **II** in Chart 1, $R_2^2(6)$ and $R_2^2(14)$ graph sets], and alternate with macrocyclic cations in the chains sustained by N—H(crown)···O and N—H(crown)···N interactions. The chains are further consolidated into a 3D network via N—H···O(crown) hydrogen bonds. In the second complex the self-complementarity of the $(\mathbf{H\text{-}PTD})^-$ anions facilitates their assembly into chains via N—H···O [$R_2^2(8)$ graph set] (synthon **I** in Chart 1) O—H···N, $R_2^2(6)$ and O—H···O $R_2^2(14)$ (synthon **II** in Chart 1) interactions. The ammonium cations bridge each $(\mathbf{H\text{-}PTD})^-$ anion in the chain with the macrocycle, affording ribbons.

Two novel pyrimidine derivatives, 2-(2-methylphenyl)-2*H*-[1,2,3]triazolo[4,5-*d*]pyrimidine-5,7(4*H*,6*H*)-dione 3-oxide (**H-PD**) and 6-amino-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-ylsulfamic acid (**H-PS**) were synthesized and explored in the design of polymeric networks with 1,10-diaza-18-crown-6 spacer, complexes **1** and **2**.

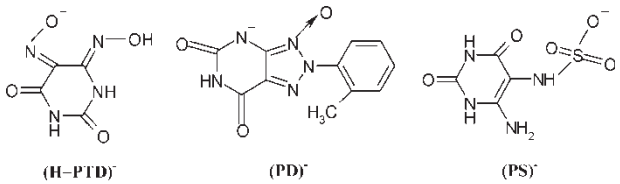


CHART 2 The anionic derivatives of dihydropyrimidine-2,4-(1*H*,3*H*)-dione incorporated in the co-crystals with crown ethers.

RESULTS AND DISCUSSION

The ternary complex **1** crystallizes in the monoclinic system, space group $P2_1/c$. Figure 1 displays an ORTEP drawing with the atom labels. The N(14) nitrogen atom in the $(\mathbf{PD})^-$ unit is deprotonated as was proved by the localization of two hydrogen atoms at the N(1) ammonium nitrogen of the crown molecule and an N(1)—H···N(14) 2.875(2) Å hydrogen bond. A search of the Cambridge Structural Database [19] for the deprotonated form of the barbital moiety identified six entries for barbital salts with metal ions or primary amines possessing similar geometry and conformation of the dioxopyrimidine ring [20–28]. In the $(\mathbf{PD})^-$ anion the triazole and pyrimidine rings and two carbonyl O-atoms, O(11) and O(12), form a practically planar system with a mean deviation of the atoms involved equal to 0.0264 Å. The dihedral angle between the least-squares plane through this bicyclic unit and the least-squares plane of the phenyl ring equals 106.5°. The dihedral angle between the least-squares planes through the heteroatoms of the macrocyclic cation and the pyrimidine ring equals 39.1°.

Two $(\mathbf{PD})^-$ anions and four water molecules are consolidated into a centrosymmetric association *via* four O(W)—H···O, two N—H···O(W), and two O—H(W)···O(W) hydrogen bonds, as shown in Fig. 2a. O(2W) behaves as an H-donor between two center-of-symmetry-related anions via O—H···O hydrogen bonds: O(2W)···O(13) 2.689(2), and O(2W)···O(11)$(-x, -y, -z+2)$ 2.826(2) Å (other interesting hydrogen bonded ring structures, even featuring crown-like architecture, exist [29–31]). The anions stack with an almost perfect overlap of the pyrimidine units with an interplane separation of 3.426 Å between the centers of the six-membered rings. Similar overlap has been observed for purine rings [32]. The O(1W) water molecule bridges the $(\mathbf{PD})^-$ anion and O(2W) molecule at distances of N(12)···O(1W) 2.943(2), and O(1W)···O(2W)$(-x, -y, -z+2)$ 2.874(3) Å. In Fig. 2a a nine-membered ring is observed, which is closed by three H-bonds. Water molecules themselves alternate in the chains running along the *c* direction, O(1W)···O(2W)$(-x, y+1/2, -z+3/2)$ 2.799(2) Å. Thus due to the (O1W) water molecules being shared between the neighboring $[(\mathbf{PD})_2(\mathrm{O2W})_2]^{2-}$ units, these associations are combined into infinite 2D anionic

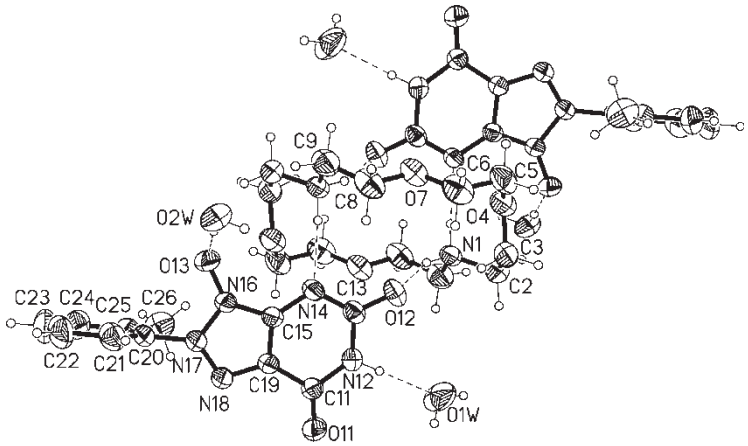


FIGURE 1 ORTEP drawing of **1** with atomic labelling; hydrogen bonds are represented by dashed lines. Thermal ellipsoids are scaled to the 50% probability level.

sheets developed parallel to the *bc* plane (Fig. 2b). The macrocyclic cations occupy the cavities within the sheets, and are held in position by ionic hydrogen bonds, $N(1)^{+}\cdots N(14)^{-}$ $(-x, -y, -z+1)$ 2.875(2) Å and $N(1)^{+}\cdots O(12)$ 2.764(2) Å (Fig. 3). The corrugated layers are packed along the *a* direction with only van der Waals contacts between them, the toluene substituents of $(\mathbf{PD})^{-}$

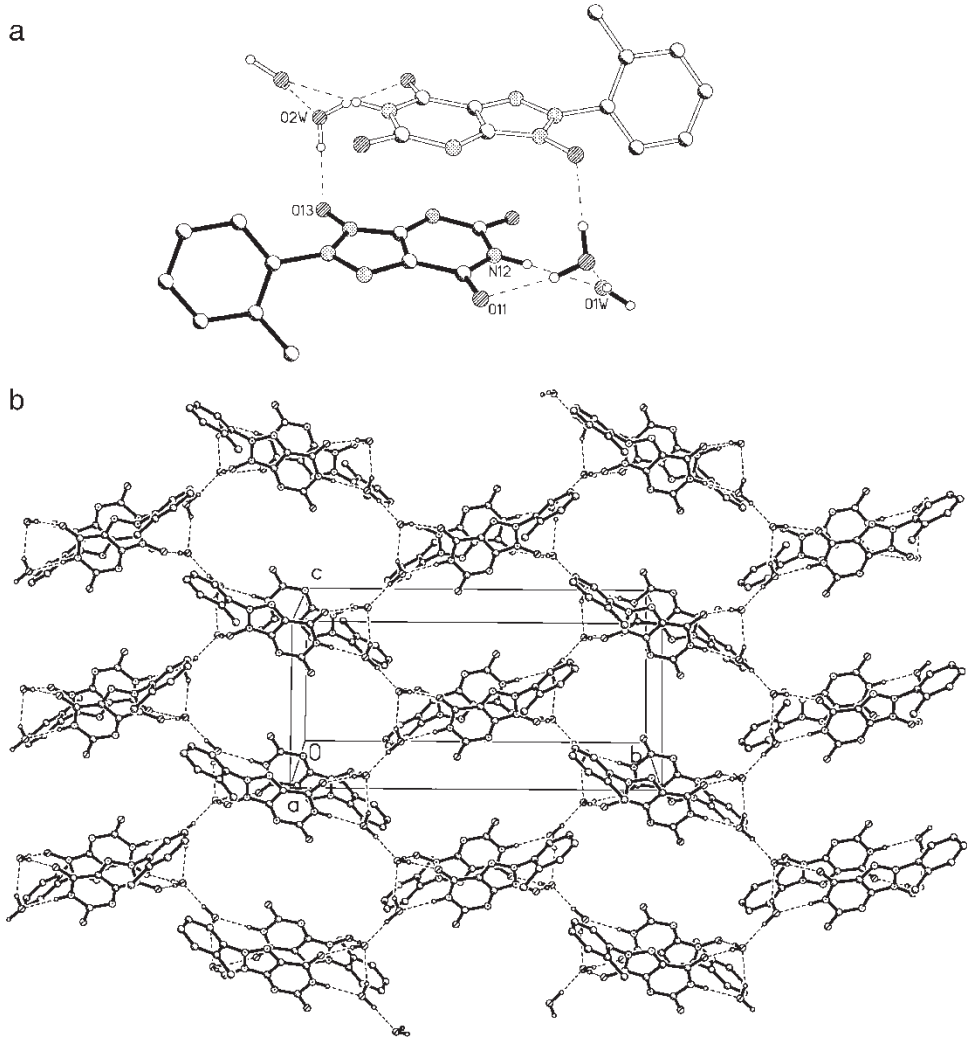


FIGURE 2 (a) Side view of the $[(\mathbf{PD})_2)H_2O)_4]^{2-}$ association in **1**. Non-functional hydrogen atoms are omitted for clarity. The darker lines indicate bonds in the molecule that are closer to the viewer. (b) View of the hydrogen-bonded anionic sheet in **1**. The cations of 1,10-diazonia-18-crown-6 are omitted.

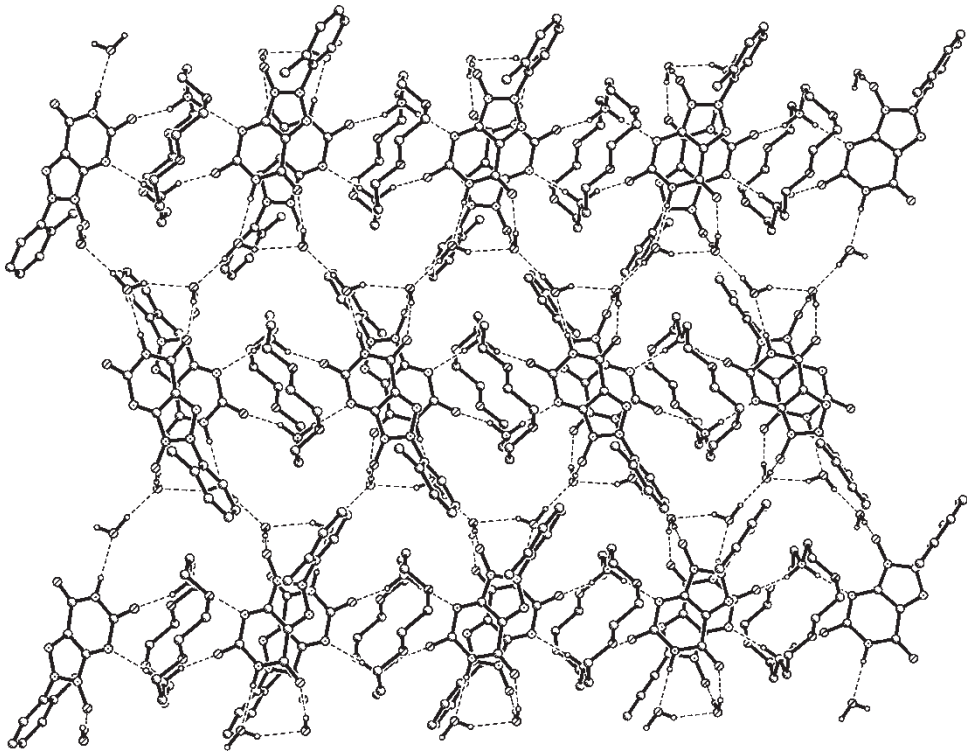


FIGURE 3 Layer in **1**. Macrocyclic cations are imprisoned in the cavities of the anionic network. Non-functional hydrogen atoms are omitted for clarity.

anions being oriented inside the voids between the layers.

The ternary complex **2** crystallizes in the triclinic system, space group $P\bar{1}$. Figure 4 displays an ORTEP drawing with atom labels. The components are held together by N—H···O and O—H···O ionic hydrogen bonds, $N(1)^{+}\cdots O(12)$ 2.927(2), and $O(1W)\cdots O(15)^{-}$ 2.844(4) Å. The hydrogen atoms of the ammonium functionalities of the macrocyclic cation are oriented outside the cavity and are involved in N—H(crown)···O(=C) hydrogen bonds with the four nearest $(\mathbf{PS})^{-}$ anions. A search of the CSD [19] for the protonated form of 1,10-diaza-18-crown-6, H_2-1,10-diazonia-18-crown-6, identified 37 entries with different orientations of ammonium hydrogen atoms with respect to the macrocyclic cavity. In only nine complexes was out-of-cavity coordination of ammonium functionalities found [33–41]. The mutual arrangement of the crown spacer and $(\mathbf{PS})^{-}$ anion in **2** is described by the dihedral angle between the least-squares plane of the crown heteroatoms and the pyrimidine ring, which is equal to 35.2(4)°.

Two $(\mathbf{PS})^{-}$ anions related by an inversion center are combined into a dimer of barrel-like

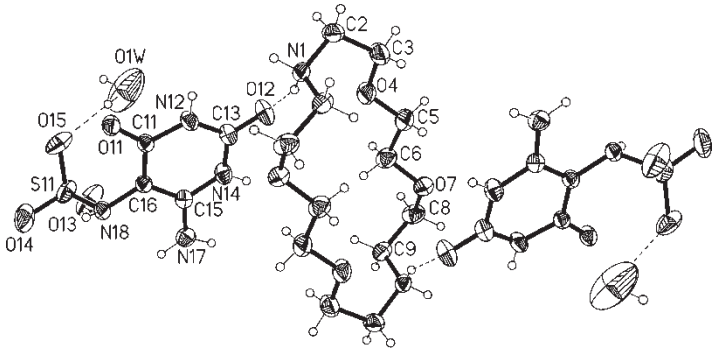


FIGURE 4 ORTEP drawing of **2** with atomic labelling; hydrogen bonds are represented by dashed lines. Thermal ellipsoids are scaled to the 50% probability level.

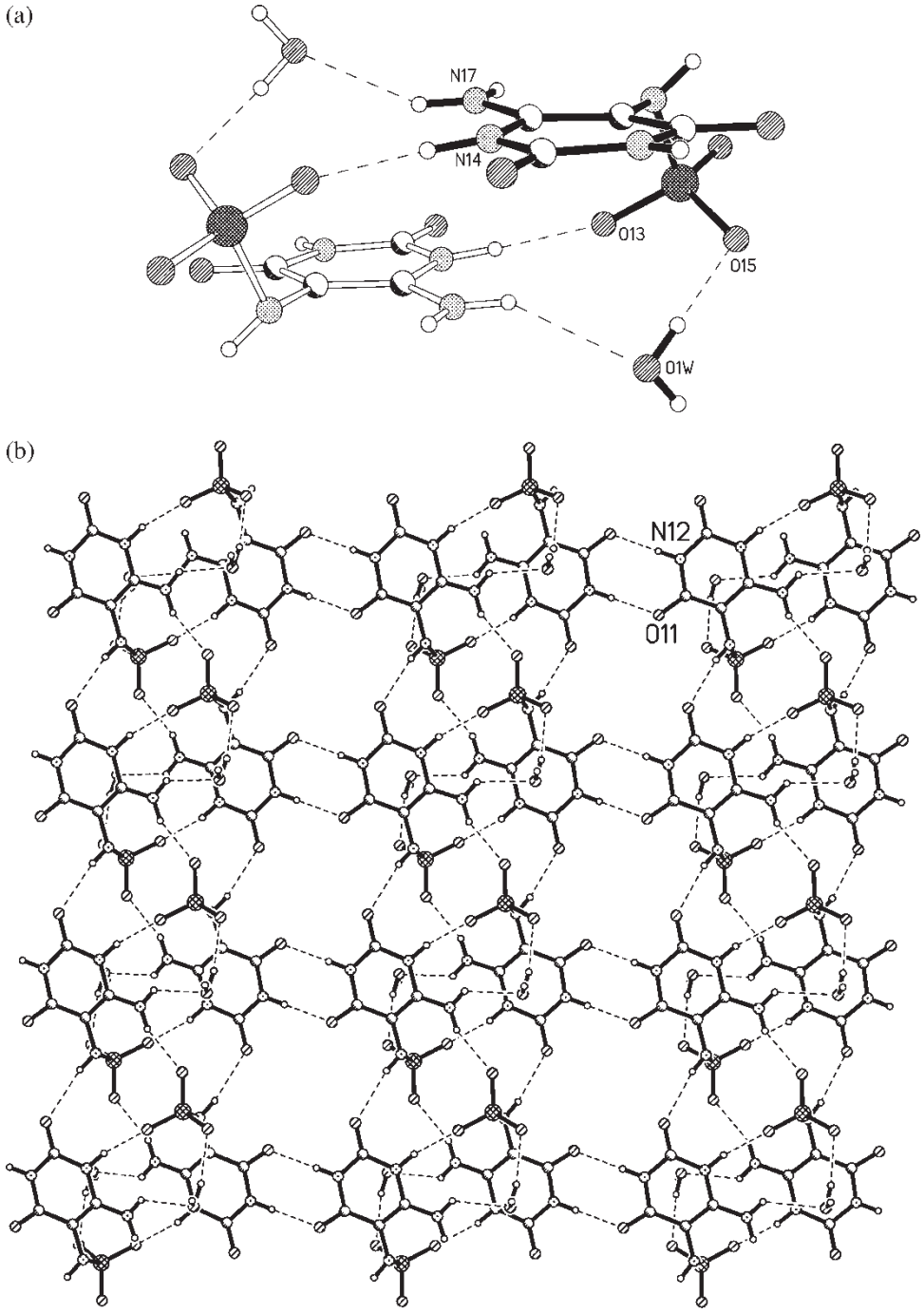


FIGURE 5 (a) View of the $[(\mathbf{PS})_2(H_2O)_2]^{2-}$ centrosymmetric heterotetramer in **2**. The darker lines indicate bonds in the molecule that are farther from the viewer. (b) Hydrogen-bonded anionic layer in **2**, parallel to the (011) plane.

shape, in which the 'top' and 'bottom' are formed by the planar pyrimidine rings, while the oppositely oriented $N{-}SO_3^-$ covalent bonds, with the bond angle at N(18) equal to 116.1(1)°, serve as its 'walls'. The $N{-}H\cdots O$ hydrogen bond $N(14)\cdots O(13)(-x-1,\ -y+1,\ -z+3)$ 2.776(2) Å, is situated practically in the plane of the pyrimidine unit (Fig. 5a). The $(\mathbf{PS}^-)_2$ dimer and two water molecules generate a special supramolecular entity, $[(\mathbf{PS})_2(O1W)_2]^{2-}$ (Fig. 5a) that is additionally stabilized by two H-bonds, $N(17)\cdots O(1W)(-x-1,\ -y+1,\ -z+3)$ 3.187(3), and $O(1W)\cdots O(15)$ 2.844(3) Å. The resulting 10-membered H-bonded cycle with the participation of the O(1W) molecule is closed by three hydrogen bonds. The neighboring $[(\mathbf{PS})_2(H_2O)_2]^{2-}$ heterotetramers joined via shared SO_3^- groups form thick double chains propagated along the *b* direction

(Fig. 5b, synthon **III** in Chart 1) and are stabilized due to the interactions between the anions related by the translation, N(18)···O(12)(x, $y+1$, z) 3.155(2) Å, and by the inversion center, N(17)···O(14)($-x-1$, $y+2$, $-z+3$) 2.887(2) Å. The mode of the involvement of the SO_3^- group in the binding with the topologically non-complementary donor centers in **2** is rather different from that found for this group in the guanidinium alkene- (arene)sulfonates where both guanidinium cations and sulfonate anions possess a common threefold axis molecular topology [42,43]. These double chains are further interlinked into a 2D sheet (Fig. 5b) via the centrosymmetric N—H···O═C supramolecular synthon **I** [Chart 1, $R_2^2(8)$ graph set], N(12)···O(11)($-x$, $-y+1$, $-z+2$) 2.793(2) Å, which is realized in the plane of the pyrimidine ring and is traditional for barbiturates [24–32]. This synthon alternates with another centrosymmetric synthon **IV** [$R_4^4(18)$ graph set], where, besides the two above-mentioned H-bonds, two other symmetry-related interactions, N(14)···O(13)($-x-1$, $-y+1$, $-z+3$) 2.776(2) Å, close the 18-membered ring. The final anionic corrugated sheets are propagated parallel to the (111) plane. As is evident, only N—H···O interactions are responsible for the sheet organization. The sheets seem to be rather rigid, because both ionic and conventional hydrogen bonds contribute to their stability. Two water molecules, related by an inversion center and having a separation O(1W)···O(1W)($-x-1$, $-y+1$, $-z+2$) of 2.953(6) Å, join the neighboring sheets along the *a* direction. Crown spacers also behave as the bridges between the neighboring layers and participate in hydrogen bonds with the four $(\mathbf{PS})^-$ anions closest to them, N(1)···O(12) 2.927(2) (single H-bond), N(1)···O(11)($-x$, $-y+1$, $-z+2$) 2.870(2), N(1)···O(15)($-x$, $-y+1$, $-z+2$) 2.889(2) Å (bifurcated H-bond). Thus, each macrocyclic cation occupies the cavity that is restricted by four $(\mathbf{PS})^-$ anions and four water molecules.

In summary, modified pyrimidinedione functionalities represent suitable connectors, which, together with the diaza-18-crown-6 spacer, are capable of generating ordered networks: 2D sheets (**1**) or 3D network (**2**). The planar active moiety of the $(\mathbf{PD})^-$ anion is capable of ensuring only 2D architecture in the co-crystal with diaza-18-crown-6. The self-assembly of $(\mathbf{PS})^-$ anions, rich in donor and acceptor centers, provides thick double layers which are further combined into 3D networks via macrocyclic spacers and water molecules.

EXPERIMENTAL

H-PD was synthesized in accordance with the route suggested [44]. **H-PS** was obtained by boiling aqueous [1,2,5]thiadiazole[3,4-*d*]pyrimidine-5,7-dione 1-oxide [45]. *N*-Oxides of 1,2,5-thiadiazoles represent a rather unexplored family of the ligands. Under the conditions of the hydrolysis, rearrangement of the *N*-oxide [1,2,5]thiadiazole[3,4-*d*]pyrimidine-5,7-dione occurs. A possible mechanism includes transformation of the cyclic *N*-oxide into the six-membered cycle and subsequent rearrangement of the ester hydroxylamine in the sulfamine group in accordance with Scheme 1.

General Procedures for Synthesis of 1 and 2

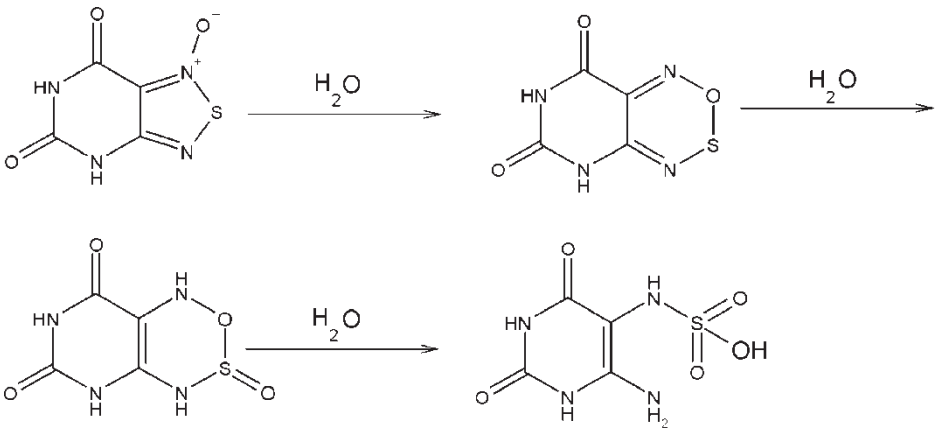
(**1**) **H-PD** (26 mg, 0.1 mmol) and diaza-18-crown-6 (26 mg, 0.1 mmol) were dissolved in the minimal amount of 50% methanol at the boiling temperature of the solution. The precipitate was filtered off, and recrystallized from 30% methanol. Long colorless crystals deposited from solution. Mp = 230°C (decomp.) (Found: C 47.92, H 6.12, N 19.76. Calc. for $C_{34}H_{52}N_{12}O_{14}$: C 47.88, H 6.15, N 19.71%)

(**2**) [1,2,5]Thiadiazole[3,4-*d*]pyrimidine-5,7-dione 2-oxide (186 mg, 1 mmol) was dissolved in the minimal amount of boiling water. The solution became purple and then bleached. The hot solution was filtered, and cooled till the crystals precipitated. The precipitate of 6-amino-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-ylsulfamic acid (**H-PS**) was filtered off, mixed with diaza-18-crown-6 (262 mg, 1 mmol), dissolved in boiling water and filtered off. Long colorless crystals precipitated from solution. Mp = 227°C (Found: C 32.31, H 5.76, N 18.93, S 8.69. Calc. for $C_{20}H_{42}N_{10}O_{16}S_2$: C 32.34, H 5.70, N 18.86, S 8.63%).

X-ray Crystallography[†]

The X-ray data were collected on a Bruker AXS Smart single crystal diffractometer with CCD area detector at room temperature for **1** and 150 K for **2**. The structures were solved by direct methods with the software SHELXTL-NT V5.1 inserted into the Bruker AXS software [46]. The refinement of both structures proceeded similarly using SHELX-97 software [47]. The non-hydrogen atoms of the asymmetric unit were refined anisotropically (full-matrix least squares method on F^2). C-Bound H-atoms were placed in calculated positions with their isotropic displacement parameters riding on those of parent atoms, while the N- and O-bound H-atoms were found from

[†]Crystallographic files in CIF format for **1** and **2** are available free from the author. They have also been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 188811 and CCDC 188812.



SCHEME 1 The route of transformation of *N*-oxide [1,2,5]-thiadiazole-[3,4-*d*]pyrimidine-5,7-dione under hydrolysis conditions.

differential Fourier maps and refined without any constraints, except H-atoms of the O(1W) molecule in **2** which, because of their disorder, were refined in the rigid model. The ORTEP structures for **1** and **2** are shown in Figs. 1 and 4, the geometric parameters for the H-bonds are given in Table I. The crystal packing of **2** is shown in Fig. 6.

(**1**): Crystal data: $C_{34}H_{52}N_{12}O_{14}$, $M_r = 852.88$, monoclinic, space group $P2_1/c$, $a = 10.370(2)$, $b = 21.582(4)$, $c = 9.709(2)$Å, $\beta = 108.00(3)°$, $V = 2066.6(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.374\,Mg/mm^{-3}$, $\mu = 0.108\,mm^{-1}$, $F(000) = 904$, wavelength 0.71073 Å. A colorless prism with dimensions $0.15 \times 0.20 \times 0.25\,mm^3$ was measured with a Bruker Smart AXS CCD, θ range for data collection 1.89–30.25°. A total of 28793 reflections were measured, of which 5776 were unique ($R_{int} = 0.0268$). Weighting scheme $w = 1/[S^2(F_o^2) + (0.0622P)^2 + 0.4615P]$, where $P = (F_o^2 + 2F_c^2)/3$. Goodness of fit on F^2 was 1.055. Final R indices $[I > 2\sigma(I)]$ $R_1 = 0.0483$, $wR_2 = 0.1298$. Largest difference Fourier peak and hole 0.615 and -0.287 e Å^{-3}.

(**2**): Crystal data: $C_{20}H_{42}N_{10}O_{16}S_2$, $M_r = 742.76$, triclinic, space group $P\bar{1}$, $a = 10.608(2)$, $b = 7.718(2)$, $c = 10.439(2)$ Å, $\alpha = 85.77(3)$, $\beta = 65.68(3)$, $\gamma = 82.41(3)°$, $V = 771.8(3)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.598\,Mg/mm^{-3}$, $\mu = 0.264\,mm^{-1}$, $F(000) = 392$, wavelength 0.71073 Å. A colorless prism with dimensions $0.20 \times 0.20 \times 0.30\,mm^3$ was measured with a Bruker Smart AXS CCD, θ range for data collection 2.12–30.34°. A total of 10852 reflections were measured, of which 4177 were unique ($R_{int} = 0.0156$). Weighting scheme $w = 1/[S^2(F_o^2) + (0.0703P)^2 + 0.1698P]$, where $P = (F_o^2 + 2F_c^2)/3$. Goodness of fit on F^2 was 1.060. Final R indices $[I > 2\sigma(I)]$ $R_1 = 0.0406$, $wR_2 = 0.1141$. Largest difference Fourier peak and hole 0.400 and -0.640 e Å^{-3}.

TABLE I Geometry of the selected hydrogen bonds in aggregates **1** and **2**

D—H···A	*r*(H···A) (Å)	*r*(D···A) (Å)	∠(DH···A) (°)	Symmetry transformation for H-acceptor
1				
N(1)—H(1N1)···O(12)	1.82(2)	2.765(2)	160(2)	*x*, *y*, *z*
N(1)—H(2N1)···N(14)	1.94(2)	2.866(2)	175(2)	$-x, -y, -z+1$
N(12)—H(12N)···O(1W)	2.06(2)	2.943(2)	178(2)	*x*, *y*, *z*
O(1W)—H(1W1)···O(2W)	1.87(4)	2.797(2)	171(3)	$-x, y+1/2, -z+3/2$
O(1W)—H(2W1)···O(2W)	2.16(4)	2.878(2)	153(4)	$-x, -y, -z+2$
O(2W)—H(1W2)···O(11)	1.99(3)	2.825(2)	165(2)	$-x, -y, -z+2$
O(2W)—H(2W2)···O(13)	1.82(3)	2.691(2)	177(2)	*x*, *y*, *z*
2				
N(1)—H(1N1)···O(12)	2.08(2)	2.928(2)	163(2)	*x*, *y*, *z*
N(1)—H(2N1)···O(11)	2.08(2)	2.870(2)	150(2)	$-x, -y+1, -z+2$
N(1)—H(2N1)···O(15)	2.32(2)	2.889(2)	123(2)	$-x, -y+1, -z+2$
N(12)—H(12A)···O(11)	1.92(2)	2.793(2)	177(2)	$-x, -y+1, -z+2$
N(14)—H(14A)···O(13)	1.88(2)	2.775(2)	167(2)	$-x-1, -y+1, -z+3$
N(17)—H(17A)···O(14)	2.08(2)	2.887(2)	152(2)	$-x-1, -y+2, -z+3$
N(17)—H(17B)···O(1W)	2.50(2)	3.183(3)	135(2)	$-x-1, -y+1, -z+3$
N(17)—H(17B)···O(13)	2.60(2)	3.307(2)	138(2)	$-x-1, -y+1, -z+3$
N(18)—H(18N)···O(12)	2.31(2)	3.155(2)	169(2)	$x, y+1, z$
O(1W)—H(1W1)···O(1W)	2.18(5)	2.958(6)	151(3)	$-x-1, -y+1, -z+2$
O(1W)—H(2W1)···O(15)	1.99(2)	2.842(4)	174(3)	*x*, *y*, *z*

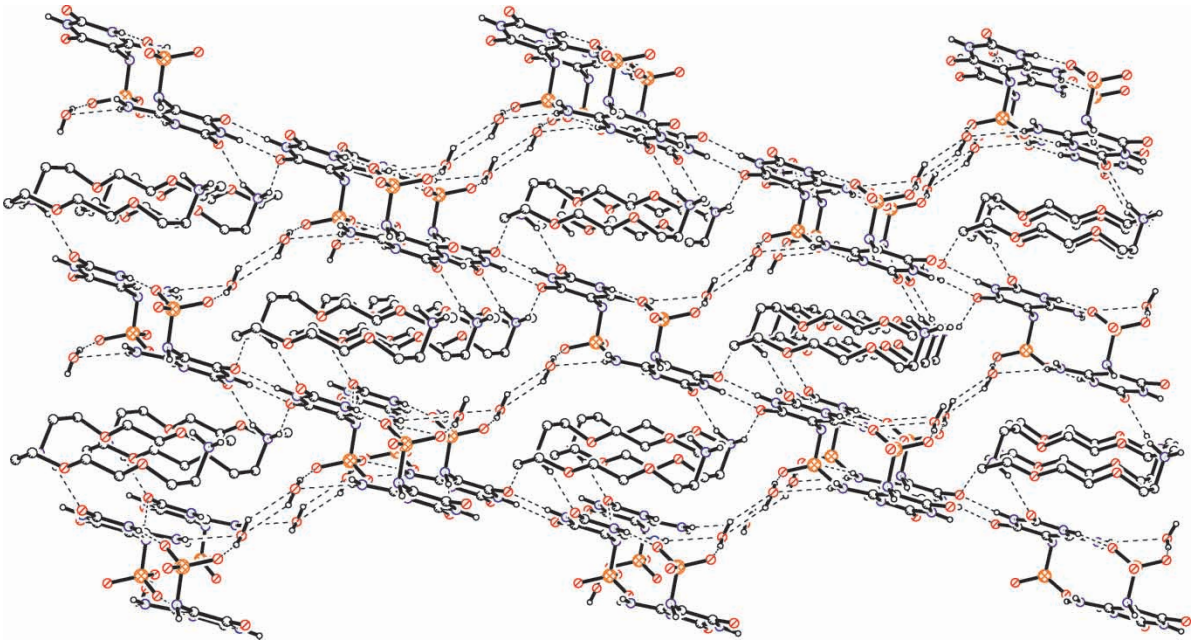


FIGURE 6 Crystal packing in **2**. Non-functional hydrogen atoms are omitted for clarity. Red: oxygen, blue: nitrogen, yellow: sulfur.

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