



Crystal structure and Hirshfeld surface analysis of the hydrated 2:1 adduct of piperazine-1,4-dium 3,5-dinitro-2-oxidobenzoate and piperazine

Veerappan Subha,^a Thangaraj Seethalakshmi,^{a*} Thangavelu Balakrishnan,^b M Judith Percino^c and Perumal Venkatesan^{d*}

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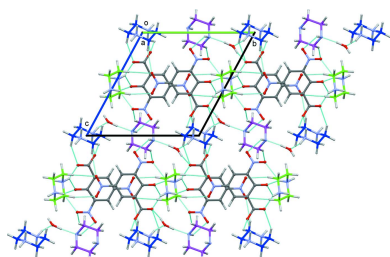
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^aPG and Research Department of Physics, Government Arts College (Autonomous and affiliated to Bharathidasan University, Tiruchirappalli), Thanthonimalai, Karur-639 005, Tamil Nadu, India, ^bCrystal Growth Laboratory, PG and Research department of Physics, Periyar EVR Government College (Autonomous and affiliated to Bharathidasan University, Tiruchirappalli), Tiruchirappalli-620 023, Tamil Nadu, India, ^cUnidad de Polímeros y Electrónica Orgánica, Instituto de Ciencias, Benemérita Universidad Autónoma de Puebla, Val3-Ecocampus Valsequillo, Independencia O2 Sur 50, San Pedro Zacachimalpa, 72960, Puebla, Mexico, and ^dDepartment of Chemistry, Srimad Andavan Arts and Science College (Autonomous), Tiruchirappalli-620 005, Tamil Nadu, India. *Correspondence e-mail: seethabala@gmail.com, venkat@andavancollege.ac.in

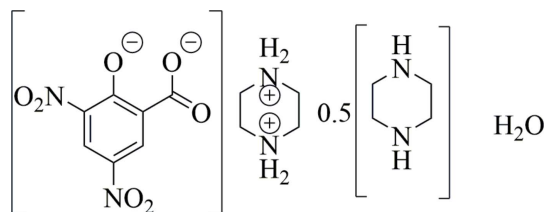
The crystal structure of the adduct piperazine-1,4-dium 3,5-dinitro-2-oxido-benzoate–piperazine–water (2/1/2) shows the existence of a 3,5-dinitrosalicylate dianion (DNSA²⁻) and a protonated piperazine-1,4-dium cation (PIP²⁺) along with a piperazine molecule. The formula of the title adduct in the asymmetric unit is 2C₄H₁₂N₂²⁺·2C₇H₂N₂O₇²⁻·C₄H₁₀N₂·2H₂O with Z = 1. The piperazine ring in the piperazine-1,4-dium cation and in the neutral piperazine molecule adopt chair conformations. All O atoms in the DNSA²⁻ moiety and the water molecule act as hydrogen-bonding acceptors for various intermolecular O–H···O, N–H···O and C–H···O interactions, which stabilize the crystal structure. Various supramolecular architectures formed by the different intermolecular interactions are discussed. The relative contribution of various intermolecular contacts is analysed with the aid of two-dimensional (full and decomposed) fingerprint plots, indicating that H···O/O···H (50.2%) and H···H (36.2%) contacts are the major contributors to the stabilization of the crystal structure.

1. Chemical context

3,5-Dinitrosalicylic acid (DNSA) is one of the most prevalent proton-donor molecules for forming organic salts with different Lewis bases. There are more than 150 examples found in the Cambridge Structural Database (CSD, Version 5.41, update of August 2020; Groom *et al.*, 2016) containing the DNSA moiety. Among them, there are 20 structures containing the neutral DNSA molecule with the rest being proton-transfer salts of the monoanion DNSA⁻ and the dianion DNSA²⁻. The loss of both acidic protons from the carboxylic acid (–COOH) and phenolic (–OH) groups in the DNSA molecule forms the DNSA²⁻ dianion. In general, the removal of the acidic proton from the –COOH group in DNSA [pK_a(COOH) = 2.2] would be expected to occur more readily than the removal of the proton from the phenolic –OH group [pK_a(OH) = 6.8]. Consequently, the DNSA molecule easily forms 1:1 proton-transfer salts with aliphatic amines (Smith *et al.*, 2002), monocyclic, polycyclic aromatic and heteroaromatic amines (Smith *et al.*, 2003, 2007), substituted primary and secondary anilines and phenylenediamines (Issa



et al., 1980, 1981; Hindawey *et al.*, 1980). However, 1:2 proton-transfer salts of DNSA containing the DNSA^{2-} dianion are much fewer in number. Briefly, the structurally characterized 1:2 proton-transfer salts were formed with ethylenediamine (EGUVAD; Smith *et al.*, 2002), cyclohexylamine (ROFLIJ; Gao *et al.*, 2014), piperidine (XEBFAM; Smith *et al.*, 2006) and diethylenetriamine (ZONBIP; Chen *et al.*, 2014). Among the four DNSA^{2-} salts, the asymmetric unit of ROFLIJ consists of two cyclohexylaminium cations and a DNSA^{2-} moiety while one dication (diethylenetriaminium dication in ZONBIP or ethylenediaminium dication in EGUVAD), DNSA^{2-} and one water molecule are found in the asymmetric unit of ZONBIP or EGUVAD. The dianions (DNSA^{2-}), mono anions (DNSA^{1-}), and partially substituted mono picrate anion along with three piperidinium cations and a water molecule are found in the asymmetric unit of XEBFAM. The crystal structures (EGUVAD, ROFLIJ, ZONBIP, and XEBFAM) of these DNSA^{2-} salts are mainly stabilized by $\text{N}-\text{H}\cdots\text{O}$, $\text{C}-\text{H}\cdots\pi$ and $\pi-\pi$ interactions. On the other hand, co-crystals of DNSA were reported with phenazine (Senthil Kumar *et al.*, 2002), urea or substituted ureas (Smith *et al.*, 1997, 2000; Bott *et al.*, 2000) and *trans*-1,4-dithiane-1,4-dioxide (Senthil Kumar *et al.*, 2002b). In this study, the crystal structure, Hirshfeld surface (HS) analysis, structural features, and various intermolecular interactions that exist in the monohydrated 1:1 adduct of bis(piperazine-1,4-dium) 3,5-dinitro-2-oxido-benzoate and piperazine (I) are reported. The various intermolecular interactions and the relative contribution of various intermolecular contacts are compared with a similar structure (XEBFAM).



2. Structural commentary

The title compound crystallizes in the triclinic space group $P\bar{1}$ with $Z = 1$ with the asymmetric unit comprising two DNSA^{2-} ions, two protonated piperazine-1,4-dium cations, and a neutral piperazine molecule along with two water molecules and having the formula $2\text{C}_4\text{H}_{12}\text{N}_2^{2+}\cdot 2\text{C}_7\text{H}_2\text{N}_2\text{O}_7^{2-}\cdot 2\text{H}_2\text{O}$. The atom-numbering scheme and molecular structure of (I) are shown in Fig. 1. The distance between the phenolate oxygen atom, O7, and the carboxylate oxygen atom, O6, in the anion is 2.770 (2) Å and is comparable to that found earlier reported dianionic salts (2.735–2.912 Å). This, together with the absence of a locateable H atom between these oxygen atoms (O6 and O7) is good evidence for the existence of the dianion in this adduct. One of the nitro groups (N1, O1, and O2) and the phenolate oxygen atom, O7 are coplanar with the mean plane of the phenyl ring, while the second nitro group (N2, O3, and O4) and the carboxylate group (C7, O5, and O6)

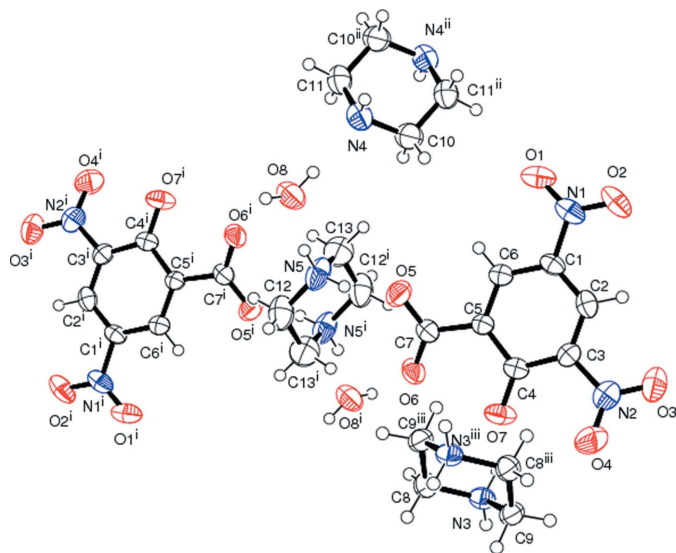


Figure 1

The molecular structure of the title adduct, (I), showing the atom-labelling scheme [symmetry codes: (i) $-x + 2, -y + 2, -z + 2$; (ii) $-x + 1, -y + 1, -z + 2$; (iii) $-x, -y + 2, -z + 1$]. Displacement ellipsoids are drawn at the 50% probability level.

are slightly twisted from the above plane. These twists are measured by the dihedral angles between the mean plane of the phenyl ring and those of the second nitro and carboxylate groups of 19.4 (3) and 24.4 (3)°, respectively, and by the C2–C3–N2–O4 and C6–C5–C7–O6 torsion angles of 161.1 (2)° and 156.6 (2)°, respectively. These slight twists of the nitro and carboxylate groups are due to the differences in the intermolecular hydrogen-bonding patterns in which the N2/O3/O4 and C7/O6/O7 groups participate as compared to the N1/O1/O2 group.

The piperazine rings in the piperazine-1,4-dium cations and the neutral piperazine molecule in (I) adopt chair conformations with puckering parameters (Cremer & Pople, 1975), $Q = 0.563$ (3) Å, $\theta = 180.0$ (3)°, $\varphi = 0^\circ$ for the the N3 ring, $Q = 0.571$ (3) Å, $\theta = 1.87$ (1)°, $\varphi = 0^\circ$ for the N5 ring and $Q = 0.517$ (3) Å, $\theta = 180.0$ (3)°, $\varphi = 0^\circ$ for the N4 ring in the neutral PIP molecule.

Additionally, we carried out a structural overlay study of the DNSA^{2-} units in the di-anionic salts found in (I), EGUVAD (Smith *et al.*, 2002), ROFLIJ (Gao *et al.*, 2014), ZONBIP (Chen *et al.*, 2014) and XEBFAM (Smith *et al.*, 2006) using the six carbon atoms in the phenyl ring in DNSA^{2-} as the basis. The DNSA^{2-} units in all five structures overlay quite well with one another. The maximum r.m.s.d. observed between any molecular pair is 0.0095 Å (for ROFLIJ and ZONBIP). However, the slight rotation of the nitro and carboxylate groups in the DNSA^{2-} unit (Fig. 2) may well be due to the oxygen atoms in these functional groups participating in different intermolecular interactions in their crystal structures as noted above.

In the unit cell, two piperazine-1,4-dium cations and one DNSA^{2-} anion are linked *via* N3–H3B \cdots O7, N3–H3B \cdots O4 and N5–H5B \cdots O5 hydrogen bonds (Table 1). Furthermore, the second piperazine-1,4-dium cation is linked

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O8—H8D \cdots O6 ⁱ	0.84 (4)	1.98 (4)	2.807 (3)	173 (4)
N3—H3A \cdots O6 ⁱⁱ	0.90 (2)	1.92 (2)	2.752 (3)	153 (3)
N3—H3A \cdots O7 ⁱⁱⁱ	0.90 (2)	2.33 (3)	2.940 (3)	125 (2)
N3—H3B \cdots O4 ⁱⁱⁱ	0.90 (2)	2.50 (2)	3.142 (3)	129 (2)
N3—H3B \cdots O7 ⁱⁱⁱ	0.90 (2)	1.84 (2)	2.696 (3)	157 (3)
N4—H4 \cdots O3	0.860 (17)	2.59 (2)	3.304 (3)	141 (2)
N5—H5A \cdots O8	0.900 (17)	1.83 (2)	2.712 (3)	166 (3)
N5—H5B \cdots O5 ^{iv}	0.918 (17)	1.74 (2)	2.637 (3)	165 (3)
O8—H8C \cdots N4	0.84 (4)	1.88 (4)	2.717 (3)	169 (3)
C8—H8A \cdots O1	0.97	2.49	3.369 (3)	151
C9—H9B \cdots O2	0.97	2.67	3.482 (3)	141
C12—H12A \cdots O2 ^v	0.97	2.58	3.455 (4)	151
C12—H12B \cdots O5 ⁱ	0.97	2.59	3.353 (4)	136

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

to a piperazine molecule through a water molecule *via* N5—H5A \cdots O8 and O8—H8C \cdots N4 hydrogen bonds.

3. Supramolecular features

The O1–O4 oxygen atoms in both nitro groups and the oxygen atoms in the carboxylate (O6 and O7) and the phenolate groups (O8) in the DNSA²⁻ ion act as acceptors for various intermolecular N—H \cdots O and C—H \cdots O interactions (Table 1). The atoms O1 and O2 in one nitro group form C8—H8A \cdots O1 and C9—H9B \cdots O2 hydrogen bonds, which link neighbouring DNSA²⁻ and PIP²⁺ ions with $R_2^2(8)$ motifs. The O6 and O7 atoms (from phenolate and carboxylate groups) form a cyclic bidentate hydrogen bond with the H3A—N3 unit N3—H3A \cdots O6 and N3—H3A \cdots O7 with an $R_1^2(6)$ motif. This $R_1^2(6)$ motif is a common one in proton-transfer compounds of DNSA and it helps to extend their secondary structures (Smith *et al.*, 2007). These two ring motifs [$R_2^2(8)$ and $R_1^2(6)$] link a DNSA²⁻ anion and one of the PIP²⁺ cations

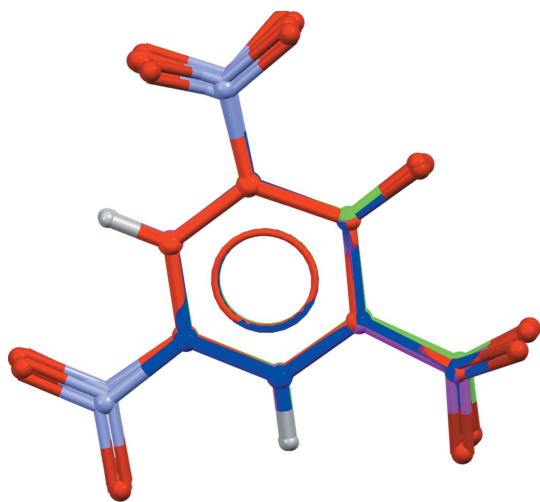


Figure 2
Superimposition of DNSA²⁻ units in (I) and its analogs [colour codes: EGUVD (green), ROFLIJ (blue), ZONBIP (red) and XEBFAM (magenta)].

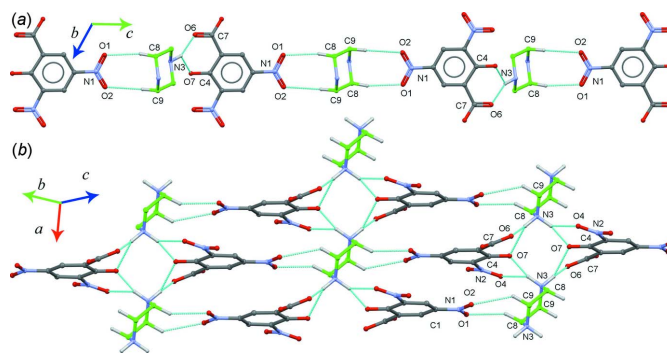


Figure 3
(a) Part of the crystal structure of (I) showing the $R_2^2(8)$ and $R_1^2(6)$ motifs formed by intermolecular N—H \cdots O and C—H \cdots O hydrogen bonds (see Table 1), which link the neighbouring anionic unit (DNSA²⁻) and cationic moiety (PIP²⁺) into a molecular chain, which propagates parallel to the c axis. (b) Part of the crystal structure of (I) showing the sheet-like architecture.

into a molecular chain, which propagates parallel to the c axis (Fig. 3a). Furthermore, N3—H3A \cdots O6, N3—H3A \cdots O7, N3—H3B \cdots O4 and N3—H3B \cdots O7 interactions link two neighbouring molecular chains through the PIP²⁺ cations into a sheet-like architecture containing two $R_1^2(6)$ motifs. Also involved is a weak C9—H9B \cdots O2 interaction (Fig. 3 b) which, although quite long, has precedent in recent work (Sosa-Rivadeneira *et al.*, 2020). The water molecule links the second piperazine-1,4-dium cation and a piperazine molecule, PIP through O8—H8C \cdots N4 and N5—H5A \cdots O8 hydrogen bonds to form a molecular chain (Fig. 4). Additional O—H \cdots O, N—H \cdots O and C—H \cdots O hydrogen bonds produce a three-dimensional framework (Fig. 5).

4. Hirshfeld surface analysis

Crystal Explorer 17.5 (Turner *et al.*, 2017) was used to calculate the Hirshfeld surfaces (HS; McKinnon *et al.*, 1998, 2004) of the title adduct and generate two-dimensional fingerprint plots (full and decomposed, 2D-FP; Spackman & McKinnon, 2002; Spackman & Jayatilaka, 2009). The HS and 2D-FP were used to provide additional information and to quantify the intermolecular interactions using distinct colours and intensities to indicate short and long contacts, as well as the relative contribution of the different interactions in the solid-state (Venkatesan *et al.*, 2015, 2016). The HS is plotted over d_{norm} in the range -0.7438 to 1.3459 a.u. and two views (front and back) of the HS are shown in Fig. 6. Bright-red spots on the HS confirm the existence of hydrogen-bonding contacts in the

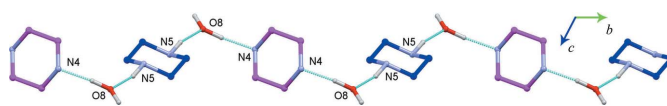


Figure 4
Part of the crystal structure of (I) showing the molecular chain, formed by O8—H8C \cdots N4 and N5—H5A \cdots O8 hydrogen bonds, which propagates parallel to the b axis.

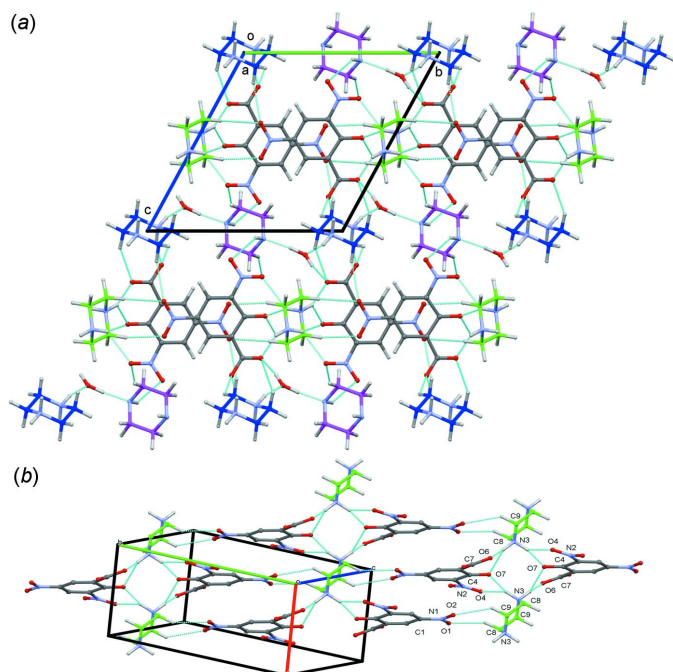


Figure 5
Crystal packing of (I), (a) viewed along the *a* axis and (b) viewed along the *c* axis.

crystal structure. The 2D FP plots show that the relative contributions of the various non-covalent contacts (Fig. 7). $O\cdots H$ contacts contribute most (50.2%) to the crystal packing while the second significant contact is $H\cdots H$, which contributes 36.2%. The relative contributions of $C\cdots O$, $C\cdots H$, $N\cdots H$, $C\cdots N$ and $C\cdots C$ contacts are 4.6%, 2.9%, 2.7%, 1.7% and 1.0%, respectively. In the XEBFAM structure, the relative contributions of $O\cdots H$, $H\cdots H$, $C\cdots O$, $C\cdots H$, $N\cdots H$, $C\cdots N$ and $C\cdots C$ contacts are 49.7%, 37.6%, 3.6%, 2.7%, 1.3%, 0.7%, and 2.1%, respectively. The relative contribution of various interatomic contacts in XEBFAM and the title adduct (I) are similar, even though the compounds have different compositions as discussed earlier.

5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.41, update of August 2020; Groom *et al.*, 2016) using *Conquest* (Bruno *et al.*, 2002) for the neutral DNSA molecule

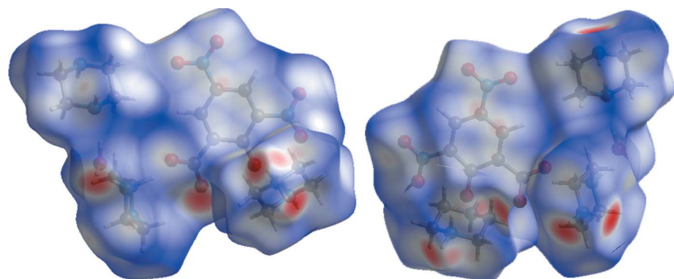


Figure 6
Two different views of the Hirshfeld surface of (I).

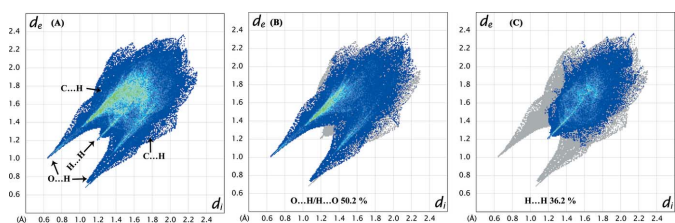


Figure 7
The two-dimensional fingerprint plots for (I): (A) a complete unit (various types of contacts are indicated); (B) $H\cdots H$ contacts and (C) $O\cdots H/H\cdots O$ contacts.

found 20 structures of co-crystals, including those with urea (NUHYAQ; Smith *et al.*, 1997), *trans*-1,4-dithiane-1,4-dioxide (OGAHEJ; Senthil Kumar *et al.*, 2002a), 4-(dimethylamino)-benzaldehyde (SUYYIW; Jin *et al.*, 2016) and dioxane (GORXAM, GORXAM01, GORXEQ, GORXEQ01; Senthil Kumar *et al.*, 1999). For monoanions of DNSA, a total of 62 structures containing the carboxylate (COO^-) moiety and 70 containing the phenolate anion (O^-) were found. As mentioned earlier, the removal of the carboxylic acid proton is expected to be easier than the removal of the proton from the phenolic $-OH$ group in DNSA so it is somewhat surprising that the number of crystal structures containing phenolate ions is larger than those containing carboxylate ions. These seemingly conflicting results may suggest that the formation and stability of the salts with phenolate ions of the DNSA moiety is governed by intermolecular interactions in the crystal. However, it has been pointed out (Fábry, 2018), that since the monoanions generally contain a hydrogen atom bridging between the the carboxylate and phenolate oxygen atoms, how one formulates the anion (carboxylate or phenolate) depends critically on how this hydrogen atom is treated in the refinement so that some of the reported phenolate structures may actually be carboxylates.

As mentioned earlier, there are four structures of the dianionic salt of DNSA, which are formed with ethylenediamine (EGUVAD; Smith *et al.*, 2002), cyclohexylamine (ROFLIJ; Gao *et al.*, 2014), piperidine (XEBFAM; Smith *et al.*, 2006) and diethylenetriamine (ZONBIP; Chen *et al.*, 2014). The cation (ethylenediaminium or 2,2'-imino-diethanaminium) and dianion ($DNSA^{2-}$) along with a water molecule are connected *via* intermolecular $O-H\cdots O$, $N-H\cdots O$ and $C-H\cdots O$ interactions in the asymmetric unit of EGUVAD and ZONBIP. An $N-H\cdots O$ hydrogen bond connects the cyclohexylaminonium moiety and the dianion in ROFLIJ, while the piperazine-1,4-dium cations form a mixed salt with the dianion and monoanion of 3,5-dinitrosalicylate along with a picrate anion in XEBFAM. The cation and anions are linked *via* $O-H\cdots O$, $N-H\cdots O$ and $C-H\cdots O$ interactions in XEBFAM.

6. Synthesis and crystallization

The title adduct was synthesized from 3,5-dinitrosalicylic acid (1 mmol, 228 mg) and piperazine (5 mmol, 426 mg, 0.5 mL)

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_4H_{12}N_2^{2+} \cdot C_7H_2N_2O_7^{2-} \cdot 0.5C_4H_{10}N_2 \cdot H_2O$
M_r	375.35
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	296
a, b, c (Å)	6.6211 (16), 11.891 (3), 12.389 (3)
α, β, γ (°)	116.320 (5), 98.878 (5), 98.390 (5)
V (Å ³)	838.1 (3)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.12
Crystal size (mm)	0.20 × 0.18 × 0.15
Data collection	
Diffractometer	Bruker Kappa APEXII
Absorption correction	Multi-scan (SADABS; Bruker, 2012)
T_{min}, T_{max}	0.834, 0.942
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15411, 3265, 1835
R_{int}	0.067
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.615
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.049, 0.133, 1.02
No. of reflections	3265
No. of parameters	264
No. of restraints	7
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.24, -0.21

Computer programs: APEX2, SAINT and XPREP (Bruker, 2012), SHELXT2014/5 (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b), Mercury (Macrae et al., 2020) and PLATON (Spek, 2020).

dissolved in 50 mL of methanol and stirred well for 6 h. The homogeneous solution was filtered and the solution was allowed to evaporate slowly at room temperature. Red block-like crystals suitable for single X-ray diffraction were harvested after a growth period of 10 days.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The amino H atoms and O-bound H atoms were refined with DFIX instructions. The C-bound H atoms were included in calculated positions and treated as riding atoms: C–H = 0.93–0.98 Å, O–H = 0.82 Å with $U_{iso}(H) = 1.2U_{eq}(C)$ and $U_{iso}(H) = 1.5U_{eq}(O)$.

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supporting information

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Crystal structure and Hirshfeld surface analysis of the hydrated 2:1 adduct of piperazine-1,4-dium 3,5-dinitro-2-oxidobenzoate and piperazine

Veerappan Subha, Thangaraj Seethalakshmi, Thangavelu Balakrishnan, M Judith Percino and Perumal Venkatesan

Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *APEX2* and *SAINT* (Bruker, 2012); data reduction: *SAINT* and *XPREP* (Bruker, 2012); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *PLATON* (Spek, 2020).

Bis(piperazine-1,4-dium)-3,5-dinitro-2-oxidobenzoate–piperazine (1/1)

Crystal data

$C_4H_{12}N_2^{2+} \cdot C_7H_2N_2O_7^{2-} \cdot 0.5C_4H_{10}N_2 \cdot H_2O$

$M_r = 375.35$

Triclinic, $P\bar{1}$

$a = 6.6211$ (16) Å

$b = 11.891$ (3) Å

$c = 12.389$ (3) Å

$\alpha = 116.320$ (5)°

$\beta = 98.878$ (5)°

$\gamma = 98.390$ (5)°

$V = 838.1$ (3) Å³

$Z = 2$

$F(000) = 396$

$D_x = 1.487$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2314 reflections

$\theta = 3.2$ – 20.9 °

$\mu = 0.12$ mm⁻¹

$T = 296$ K

BLOCK, orange

$0.20 \times 0.18 \times 0.15$ mm

Data collection

Bruker Kappa APEXII

diffractometer

Radiation source: fine-focus sealed tube

ω and φ scan

Absorption correction: multi-scan

(SADABS; Bruker, 2012)

$T_{\min} = 0.834$, $T_{\max} = 0.942$

15411 measured reflections

3265 independent reflections

1835 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.067$

$\theta_{\max} = 25.9$ °, $\theta_{\min} = 1.9$ °

$h = -8 \rightarrow 8$

$k = -14 \rightarrow 14$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.133$

$S = 1.02$

3265 reflections

264 parameters

7 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2 + 0.1429P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.24 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$

Extinction correction: *SHELXL2018/3*
 (Sheldrick 2015b),
 $Fc^* = kFc[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.022 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.2400 (4)	0.4979 (2)	0.4846 (2)	0.0331 (6)
C2	0.1716 (4)	0.5004 (2)	0.3755 (2)	0.0376 (6)
H2	0.097021	0.424987	0.303896	0.045*
C3	0.2150 (4)	0.6162 (3)	0.3737 (2)	0.0353 (6)
C4	0.3382 (4)	0.7355 (2)	0.4796 (2)	0.0335 (6)
C5	0.4064 (4)	0.7254 (2)	0.5918 (2)	0.0303 (6)
C6	0.3534 (4)	0.6100 (2)	0.5917 (2)	0.0325 (6)
H6	0.394113	0.606279	0.665144	0.039*
C7	0.5309 (4)	0.8402 (2)	0.7123 (2)	0.0362 (6)
C8	0.1947 (4)	0.0896 (2)	0.5817 (2)	0.0388 (7)
H8A	0.166572	0.172139	0.595530	0.047*
H8B	0.336846	0.105846	0.628741	0.047*
C9	-0.0406 (4)	-0.0246 (3)	0.3735 (2)	0.0379 (7)
H9A	-0.048896	-0.081723	0.286864	0.046*
H9B	-0.077271	0.053723	0.379768	0.046*
C10	0.4553 (5)	0.5527 (3)	-0.0810 (3)	0.0530 (8)
H10A	0.593339	0.595334	-0.079123	0.064*
H10B	0.351574	0.562706	-0.138468	0.064*
C11	0.5558 (5)	0.5896 (3)	0.1283 (3)	0.0519 (8)
H11A	0.517856	0.623969	0.207334	0.062*
H11B	0.699858	0.634402	0.142542	0.062*
C12	0.9027 (5)	1.0964 (3)	0.0763 (3)	0.0663 (9)
H12A	0.991252	1.127416	0.158769	0.080*
H12B	0.793302	1.143558	0.084060	0.080*
C13	0.9676 (5)	0.8797 (3)	0.0037 (3)	0.0660 (9)
H13A	0.899018	0.788492	-0.035061	0.079*
H13B	1.058073	0.903815	0.083872	0.079*
N1	0.1911 (3)	0.3784 (2)	0.4897 (3)	0.0448 (6)
N2	0.1279 (4)	0.6133 (3)	0.2575 (2)	0.0498 (6)
N3	0.1777 (3)	0.0079 (2)	0.4483 (2)	0.0366 (6)
N4	0.4177 (4)	0.6159 (2)	0.0429 (2)	0.0492 (6)
N5	0.8059 (4)	0.9568 (3)	0.0213 (2)	0.0594 (8)
O1	0.2522 (3)	0.37951 (19)	0.5894 (2)	0.0588 (6)
O2	0.0900 (3)	0.28024 (19)	0.3949 (2)	0.0618 (6)
O3	0.0716 (3)	0.5083 (2)	0.16184 (19)	0.0659 (6)

O4	0.1115 (4)	0.7148 (2)	0.25659 (19)	0.0693 (7)
O5	0.5161 (3)	0.83365 (19)	0.80899 (17)	0.0578 (6)
O6	0.6420 (3)	0.93523 (17)	0.71300 (16)	0.0481 (5)
O7	0.3856 (3)	0.84047 (17)	0.47722 (17)	0.0499 (5)
O8	0.5428 (4)	0.8759 (3)	0.1338 (2)	0.0634 (7)
H8C	0.489 (6)	0.796 (4)	0.102 (3)	0.089 (13)*
H8D	0.486 (6)	0.928 (4)	0.182 (4)	0.102 (16)*
H3A	0.267 (4)	0.045 (2)	0.418 (3)	0.069 (10)*
H3B	0.224 (4)	−0.0629 (19)	0.438 (2)	0.058 (9)*
H4	0.291 (3)	0.582 (3)	0.039 (3)	0.061 (10)*
H5A	0.726 (4)	0.943 (3)	0.069 (2)	0.086 (12)*
H5B	0.712 (4)	0.927 (3)	−0.0537 (18)	0.083 (12)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0281 (14)	0.0283 (14)	0.0472 (17)	0.0077 (11)	0.0161 (12)	0.0193 (13)
C2	0.0297 (14)	0.0347 (15)	0.0386 (16)	0.0071 (12)	0.0120 (12)	0.0082 (13)
C3	0.0316 (14)	0.0434 (17)	0.0343 (15)	0.0110 (12)	0.0105 (12)	0.0202 (14)
C4	0.0272 (14)	0.0344 (15)	0.0453 (16)	0.0096 (12)	0.0129 (12)	0.0227 (14)
C5	0.0288 (14)	0.0316 (14)	0.0349 (15)	0.0091 (11)	0.0129 (11)	0.0174 (13)
C6	0.0284 (13)	0.0352 (15)	0.0404 (16)	0.0104 (12)	0.0143 (12)	0.0209 (14)
C7	0.0346 (15)	0.0327 (15)	0.0416 (17)	0.0087 (12)	0.0139 (13)	0.0164 (14)
C8	0.0344 (15)	0.0385 (16)	0.0378 (17)	0.0012 (12)	0.0044 (12)	0.0170 (14)
C9	0.0399 (16)	0.0409 (16)	0.0346 (15)	0.0057 (12)	0.0073 (12)	0.0212 (14)
C10	0.057 (2)	0.0492 (19)	0.057 (2)	0.0128 (15)	0.0165 (16)	0.0281 (17)
C11	0.0501 (18)	0.0477 (19)	0.0454 (18)	0.0058 (15)	0.0065 (15)	0.0150 (16)
C12	0.054 (2)	0.068 (2)	0.052 (2)	0.0006 (17)	0.0126 (17)	0.0117 (18)
C13	0.053 (2)	0.071 (2)	0.067 (2)	−0.0030 (18)	0.0156 (18)	0.032 (2)
N1	0.0357 (14)	0.0330 (15)	0.0707 (19)	0.0119 (11)	0.0243 (13)	0.0244 (15)
N2	0.0439 (15)	0.0615 (18)	0.0459 (17)	0.0146 (13)	0.0126 (12)	0.0261 (16)
N3	0.0358 (13)	0.0362 (14)	0.0446 (15)	0.0078 (11)	0.0133 (11)	0.0241 (12)
N4	0.0466 (16)	0.0431 (15)	0.0527 (16)	0.0098 (13)	0.0149 (13)	0.0180 (13)
N5	0.0428 (16)	0.081 (2)	0.0382 (16)	−0.0074 (15)	0.0115 (14)	0.0208 (16)
O1	0.0646 (14)	0.0533 (14)	0.0814 (16)	0.0181 (11)	0.0241 (12)	0.0485 (13)
O2	0.0579 (14)	0.0295 (12)	0.0816 (16)	0.0017 (10)	0.0193 (12)	0.0146 (12)
O3	0.0694 (15)	0.0694 (16)	0.0389 (13)	0.0079 (12)	0.0052 (11)	0.0141 (12)
O4	0.0837 (17)	0.0753 (17)	0.0616 (15)	0.0283 (13)	0.0092 (12)	0.0435 (14)
O5	0.0679 (14)	0.0570 (13)	0.0370 (12)	−0.0114 (10)	0.0063 (10)	0.0226 (11)
O6	0.0558 (12)	0.0350 (11)	0.0451 (12)	−0.0015 (9)	0.0207 (9)	0.0130 (9)
O7	0.0409 (11)	0.0458 (12)	0.0705 (14)	0.0011 (9)	0.0020 (10)	0.0408 (11)
O8	0.0809 (18)	0.0400 (15)	0.0751 (18)	0.0151 (14)	0.0457 (14)	0.0240 (14)

Geometric parameters (Å, °)

C1—C2	1.373 (3)	C10—H10A	0.9700
C1—C6	1.390 (3)	C10—H10B	0.9700
C1—N1	1.442 (3)	C11—N4	1.460 (3)

C2—C3	1.376 (3)	C11—H11A	0.9700
C2—H2	0.9300	C11—H11B	0.9700
C3—C4	1.443 (3)	C12—N5	1.478 (4)
C3—N2	1.448 (3)	C12—C13 ⁱⁱⁱ	1.497 (4)
C4—O7	1.257 (3)	C12—H12A	0.9700
C4—C5	1.455 (3)	C12—H12B	0.9700
C5—C6	1.366 (3)	C13—N5	1.488 (4)
C5—C7	1.503 (3)	C13—H13A	0.9700
C6—H6	0.9300	C13—H13B	0.9700
C7—O6	1.251 (3)	N1—O2	1.227 (3)
C7—O5	1.251 (3)	N1—O1	1.232 (3)
C8—N3	1.475 (3)	N2—O3	1.232 (3)
C8—C9 ⁱ	1.507 (3)	N2—O4	1.233 (3)
C8—H8A	0.9700	N3—H3A	0.903 (16)
C8—H8B	0.9700	N3—H3B	0.900 (16)
C9—N3	1.484 (3)	N4—H4	0.860 (17)
C9—H9A	0.9700	N5—H5A	0.900 (17)
C9—H9B	0.9700	N5—H5B	0.918 (17)
C10—N4	1.461 (3)	O8—H8C	0.84 (4)
C10—C11 ⁱⁱ	1.510 (4)	O8—H8D	0.84 (4)
C2—C1—C6	120.9 (2)	N4—C11—H11A	108.9
C2—C1—N1	120.0 (2)	C10 ⁱⁱ —C11—H11A	108.9
C6—C1—N1	119.1 (2)	N4—C11—H11B	108.9
C1—C2—C3	119.0 (2)	C10 ⁱⁱ —C11—H11B	108.9
C1—C2—H2	120.5	H11A—C11—H11B	107.7
C3—C2—H2	120.5	N5—C12—C13 ⁱⁱⁱ	110.2 (3)
C2—C3—C4	123.4 (2)	N5—C12—H12A	109.6
C2—C3—N2	116.1 (2)	C13 ⁱⁱⁱ —C12—H12A	109.6
C4—C3—N2	120.5 (2)	N5—C12—H12B	109.6
O7—C4—C3	123.7 (2)	C13 ⁱⁱⁱ —C12—H12B	109.6
O7—C4—C5	121.7 (2)	H12A—C12—H12B	108.1
C3—C4—C5	114.5 (2)	N5—C13—C12 ⁱⁱⁱ	110.0 (3)
C6—C5—C4	120.6 (2)	N5—C13—H13A	109.7
C6—C5—C7	117.2 (2)	C12 ⁱⁱⁱ —C13—H13A	109.7
C4—C5—C7	122.2 (2)	N5—C13—H13B	109.7
C5—C6—C1	121.6 (2)	C12 ⁱⁱⁱ —C13—H13B	109.7
C5—C6—H6	119.2	H13A—C13—H13B	108.2
C1—C6—H6	119.2	O2—N1—O1	122.8 (2)
O6—C7—O5	123.4 (2)	O2—N1—C1	118.6 (3)
O6—C7—C5	120.5 (2)	O1—N1—C1	118.5 (2)
O5—C7—C5	116.1 (2)	O3—N2—O4	121.8 (2)
N3—C8—C9 ⁱ	110.7 (2)	O3—N2—C3	118.6 (2)
N3—C8—H8A	109.5	O4—N2—C3	119.7 (3)
C9 ⁱ —C8—H8A	109.5	C8—N3—C9	111.2 (2)
N3—C8—H8B	109.5	C8—N3—H3A	113.0 (19)
C9 ⁱ —C8—H8B	109.5	C9—N3—H3A	109.0 (18)
H8A—C8—H8B	108.1	C8—N3—H3B	108.8 (17)

N3—C9—C8 ⁱ	110.8 (2)	C9—N3—H3B	112.4 (18)
N3—C9—H9A	109.5	H3A—N3—H3B	102.2 (19)
C8 ⁱ —C9—H9A	109.5	C11—N4—C10	110.1 (2)
N3—C9—H9B	109.5	C11—N4—H4	106.5 (19)
C8 ⁱ —C9—H9B	109.5	C10—N4—H4	108 (2)
H9A—C9—H9B	108.1	C12—N5—C13	111.6 (2)
N4—C10—C11 ⁱⁱ	113.1 (2)	C12—N5—H5A	110 (2)
N4—C10—H10A	109.0	C13—N5—H5A	111 (2)
C11 ⁱⁱ —C10—H10A	109.0	C12—N5—H5B	111 (2)
N4—C10—H10B	109.0	C13—N5—H5B	109 (2)
C11 ⁱⁱ —C10—H10B	109.0	H5A—N5—H5B	104 (2)
H10A—C10—H10B	107.8	H8C—O8—H8D	119 (4)
N4—C11—C10 ⁱⁱ	113.3 (2)		
C6—C1—C2—C3	-0.7 (4)	C4—C5—C7—O6	-25.2 (4)
N1—C1—C2—C3	178.2 (2)	C6—C5—C7—O5	-23.2 (3)
C1—C2—C3—C4	3.0 (4)	C4—C5—C7—O5	155.0 (2)
C1—C2—C3—N2	-176.6 (2)	C2—C1—N1—O2	0.7 (3)
C2—C3—C4—O7	177.0 (2)	C6—C1—N1—O2	179.6 (2)
N2—C3—C4—O7	-3.4 (4)	C2—C1—N1—O1	-179.0 (2)
C2—C3—C4—C5	-2.6 (3)	C6—C1—N1—O1	-0.1 (3)
N2—C3—C4—C5	177.0 (2)	C2—C3—N2—O3	-18.7 (3)
O7—C4—C5—C6	-179.7 (2)	C4—C3—N2—O3	161.7 (2)
C3—C4—C5—C6	-0.1 (3)	C2—C3—N2—O4	161.1 (2)
O7—C4—C5—C7	2.1 (4)	C4—C3—N2—O4	-18.5 (4)
C3—C4—C5—C7	-178.2 (2)	C9 ⁱ —C8—N3—C9	56.3 (3)
C4—C5—C6—C1	2.3 (3)	C8 ⁱ —C9—N3—C8	-56.4 (3)
C7—C5—C6—C1	-179.4 (2)	C10 ⁱⁱ —C11—N4—C10	-52.3 (3)
C2—C1—C6—C5	-2.0 (4)	C11 ⁱⁱ —C10—N4—C11	52.1 (3)
N1—C1—C6—C5	179.1 (2)	C13 ⁱⁱⁱ —C12—N5—C13	57.4 (4)
C6—C5—C7—O6	156.6 (2)	C12 ⁱⁱⁱ —C13—N5—C12	-57.4 (4)

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O8—H8D \cdots O6 ^{iv}	0.84 (4)	1.98 (4)	2.807 (3)	173 (4)
N3—H3A \cdots O6 ^v	0.90 (2)	1.92 (2)	2.752 (3)	153 (3)
N3—H3A \cdots O7 ^v	0.90 (2)	2.33 (3)	2.940 (3)	125 (2)
N3—H3B \cdots O4 ^{vi}	0.90 (2)	2.50 (2)	3.142 (3)	129 (2)
N3—H3B \cdots O7 ^{vi}	0.90 (2)	1.84 (2)	2.696 (3)	157 (3)
N4—H4 \cdots O3	0.860 (17)	2.59 (2)	3.304 (3)	141 (2)
N5—H5A \cdots O8	0.900 (17)	1.83 (2)	2.712 (3)	166 (3)
N5—H5B \cdots O5 ^{vii}	0.918 (17)	1.74 (2)	2.637 (3)	165 (3)
O8—H8C \cdots N4	0.84 (4)	1.88 (4)	2.717 (3)	169 (3)
C8—H8A \cdots O1	0.97	2.49	3.369 (3)	151
C9—H9B \cdots O2	0.97	2.67	3.482 (3)	141

C12—H12A···O2 ^{viii}	0.97	2.58	3.455 (4)	151
C12—H12B···O5 ^{iv}	0.97	2.59	3.353 (4)	136

Symmetry codes: (iv) $-x+1, -y+2, -z+1$; (v) $-x+1, -y+1, -z+1$; (vi) $x, y-1, z$; (vii) $x, y, z-1$; (viii) $x+1, y+1, z$.