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Mixed 3,5-dinitrosalicylate(2–) and partial 3,5-dinitrosalicylate(1–) and picrate(1–) species in tris(piperidinium) bis(3,5-dinitrosalicylate) picrate monohydrate

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The crystal structure of the monohydrated proton-transfer compound of 3,5-dinitrosalicylic acid with piperidine shows the presence of dianionic 3,5-dinitrosalicylate species, as well as partial monoanionic 3,5-dinitrosalicylate and picrate species; the formula is $3C_5H_{12}N^+\cdot C_7H_3N_2O_7^-\cdot 0.79C_7H_2N_2O_7^{2-}\cdot 0.21C_6H_2N_3O_7^-\cdot H_2O$. All available proton-donor species, including the solvent water molecule, are involved in hydrogen-bonding interactions with O-atom acceptors on the anion species, giving a one-dimensional column polymer structure, with further structure extension through anion–anion π–π ring interactions.

Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.009 Å
Disorder in main residue
R factor = 0.055
wR factor = 0.211
Data-to-parameter ratio = 12.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

3,5-Dinitrosalicylic acid (DNSA) has proved to be particularly effective as a proton-donating acid species for stabilizing crystalline salts of Lewis bases. We have previously reported the crystal structures of a number of the compounds of DNSA with Lewis bases, including those with ammonia and aliphatic amines (Smith *et al.*, 2002; Smith, Wermuth & White, 2005), monocyclic aromatic amines (Smith *et al.*, 2003) and polycyclic heteroaromatic amines (Smith, Wermuth, Healy & White,

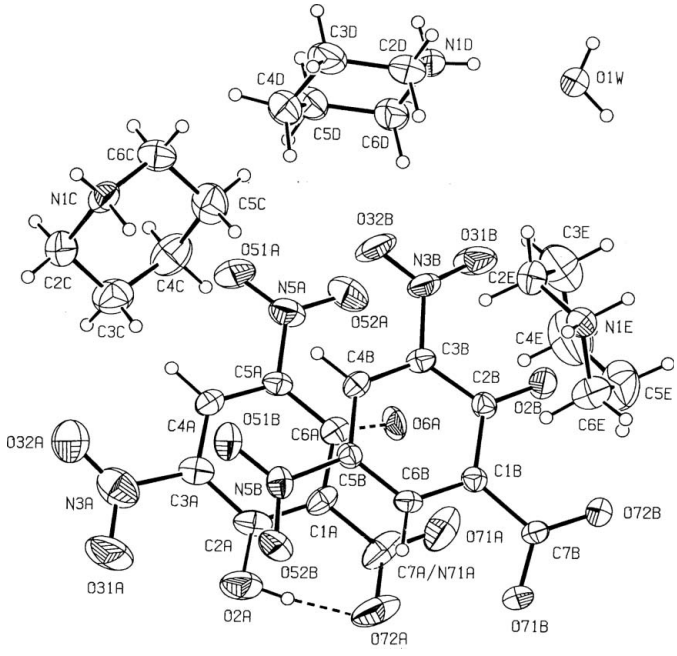
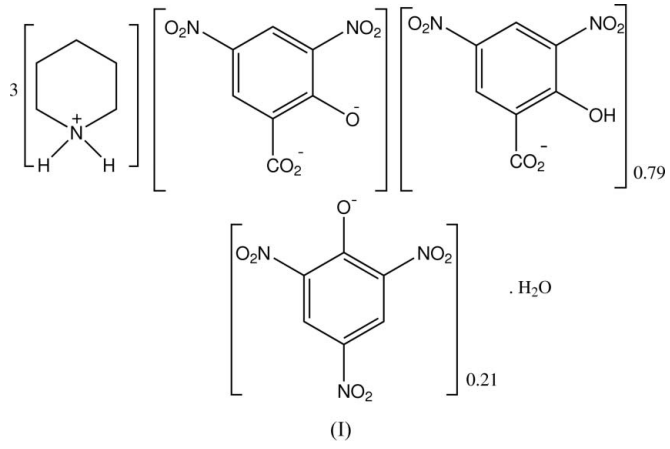


Figure 1
The molecular configuration and atom-numbering scheme for the two independent DNSA anions (*A* and *B*), the three PIP cations (*C*, *D*, *E*) and the water molecule in the asymmetric unit of (I). The atoms of the rotationally disordered phenolate group are O2*A* (79%) and O6*A* (21%). The alternative atoms H2*A* (21%) and H6*A* (79%) are not shown. Displacement ellipsoids are drawn at the 30% probability level.

2005). The acid strength of DNSA (pK_{a1} 2.2) means that reaction with most amines results in the formation of 1:1 proton-transfer salts. Although the phenolic substituent group achieves enhanced acidity due to the presence of the nitro substituents (pK_{a2} 6.8), making DNSA analogous to picric acid, among the crystallographically characterized compounds of DNSA there is only one in which the dianionic species is found (ethylenediaminium 3,5-dinitrosalicylate monohydrate; Smith *et al.*, 2002). The 1:1 stoichiometric reaction of DNSA with the strong Lewis base hexahydropyridine (piperidine, PIP; pK_a 11.1) in ethanol–water might be expected to give the usual 1:1 salt, such as is found in the structure of the analogous piperidinium picrate (Saminathan *et al.*, 2005). However, the crystal structure of the product from this reaction showed an unusual compound containing both DNSA(2−) and DNSA(1−) species, as well as partial superimposed picrate(1−) substitution for DNSA(1−) anions. The structure of this compound, $3C_5H_{12}N^+\cdot C_7H_2N_2O_7^{2-}\cdot 0.79C_7H_3N_2O_7^-\cdot 0.21C_6H_2N_3O_7^-\cdot H_2O$, (I), is reported here.



(I)

The two DNSA anion species [monoanion *A* (with the picrate anion superimposed) and dianion *B*], the three PIP cation species (*C*, *D* and *E*) and the solvent water molecule in (I) are shown in Fig. 1. The DNSA *A*– species is the commonly formed monoanion, with the expected intramolecular hydrogen bond between the carboxylate and phenolic groups, with the H atom localized on the phenol group [O···O 2.586 (8) Å]. There is partial replacement of the *A* anion by a structurally similar picrate(1−) species (DNSA:PIC = 0.79:0.21), suggested by the unsatisfactory refinement of the model which involved the presence of a positionally disordered phenolic –OH group at C2 of the DNSA species [site-occupancy factor 0.79 (2)] as an alternative to the phenolate O atom at C6 of the picrate species [site-occupancy factor 0.21 (2)]. Analogous structures have previously been reported for 1*H*-nicotinaminium 3,5-dinitrosalicylate (Koman *et al.*, 2003) and the non-transfer adduct with urea (Smith *et al.*, 1997), but both of these have rotational disorder about the C1···C6 ring vector of the DNSA anion.

In the formation of (I), it is assumed that picric acid is present as a minor impurity in the DNSA reagent, where it is a common by-product from the nitration of salicylic acid in the usual synthesis of DNSA (Huebner, 1879). The presence of picrate is justified in the structure analysis by the satisfactory refinement of the model and confirmed by the elemental analysis. Further evidence lies in the precedence of the structure of anilinium picrate (Smith *et al.*, 2004), which was found as minor morphologically different co-crystals among those of anilinium 3,5-dinitrosalicylate (Smith *et al.*, 2003). The stereochemical differences between the superimposed picrate-nitro and DNSA-carboxyl substituent groups at C1 (*e.g.* C—N *cf.* C—C and N—O *cf.* C—O bond distances and associated bond angles) are apparent in significant vibrational disorder, particularly with the O atoms of the groups. Furthermore, there is also considerable thermal disorder in the C atoms of the PIP cation rings.

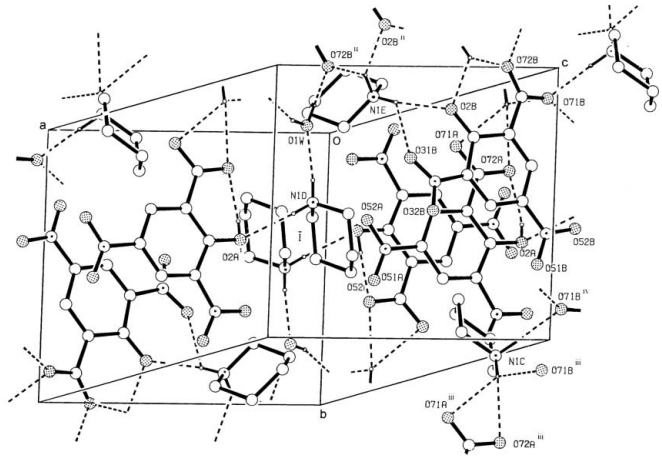


Figure 2
A perspective view of the packing of (I) in the unit cell, showing hydrogen-bonding associations as dashed lines. The minor component of the disordered phenolate group has been omitted, as have the non-interacting H atoms on all species. For symmetry codes, see Table 1.

Evidence for the presence of the dianionic species in the DNSA *B* species, as suggested from the unusual compound stoichiometry, lies not only in the absence of a locatable intramolecular hydrogen-bonded H atom but also in the stereochemical features of the dianion. In the only example of the dianion among DNSA proton-transfer compounds with Lewis bases, the previously mentioned ethylenediaminium salt (Smith *et al.*, 2002), the absence of the intramolecular hydrogen bond results, as expected, in a significant expansion of the O2···O72 distance to 2.696 (2) Å. This value is comparable with that for the *B* anion [2.739 (6) Å]. Furthermore, this absence also means the disappearance of the usual coplanarity of the hydrogen-bonded carboxyl group and the benzene ring, *e.g.* in the *B* anion, the C2—C1—C7—O71 torsion angle is −165.8 (4)°, compared with 157.7 (2)° in the ethylenediaminium salt (Smith *et al.*, 2002) and 176.7 (5)° in the *A* anion.

All three piperidinium species (*C*, *D*, *E*) are complementarily protonated, as confirmed by the ready location and refinement of the H atoms and their subsequent involvement in hydrogen-bonding interactions (Table 1). These include two separate asymmetric three-centre $R_1^2(6)$ associations (Bern-

stein *et al.*, 1995) between the two H atoms of a PIP *E* cation and the proximal acceptor groups of separate inversion-related dianionic DNSA *B* species. The first of these interactions is with carboxyl and phenolate O-atom acceptors [N1*E*—H11*E*···O72*B*^{ii} 2.908 (7) ° and N1*E*—H11*E*···O2*B*^{ii} 2.782 (6) Å; symmetry code: (ii) $1-x, -y, 2-z$; Table 1]. The second involves the same phenolate O atom and a nitro O-atom acceptor [N1*E*—H12*E*···O2*B* 2.794 (7) Å and N1*E*—H12*E*···O31*B* 3.184 (7) Å; Table 1]. Another weak association involving one of the PIP aminium H atoms is four-centred, to both *A*- and *B*-anion O-atom acceptors [N1*C*—H11*C*···O71*A*^{iii}/O72*A*^{iii}/O71*B*^{iii}; symmetry code: (iii) $x, y+1, z$; Table 1], while the water molecule also acts as both a donor and an acceptor, linking the molecules into a one-dimensional column structure extending along the *a* direction (Fig. 2). There is also partial DNSA anion (*A*)–anion (*A*) (inversion related) and anion (*A*)–anion (*B*) ring overlap [ring centroid separation and inter-plane dihedral angle: *A*–*A* 3.632 (3) Å and 0°; *A*–*B* 3.864 (4) Å and 3.4 (1)°], indicating some π–π interaction and giving structure extension down the *c* axis (Fig. 3).

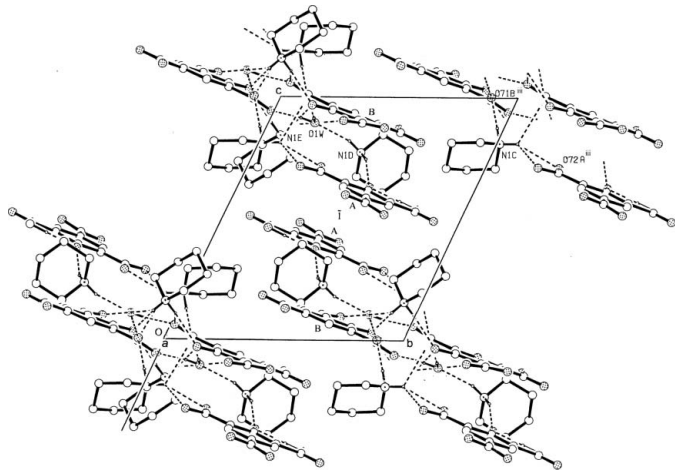


Figure 3
Polymer columns and inter-column π–π ring interactions (dashed lines) in the unit cell of (I), viewed down the *a* direction.

Experimental

The title compound was synthesized by heating 1 mmol quantities of 3,5-dinitrosalicylic acid (DNSA) and hexahydropyridine (piperidine, PIP) in 80% ethanol–water (50 ml) for 10 min under reflux. After concentration to *ca* 30 ml, total room-temperature evaporation of the hot-filtered solution gave yellow crystal plates of (I) (m.p. 419–424 K). Analysis found: C 47.6, H 6.0, N, 13.6%; calculated for $C_{28.79}H_{42.79}N_{7.21}O_{15}$: C 47.4, H 5.9, N 13.8%.

Crystal data

$3C_5H_{12}N^+\cdot C_7H_2N_2O_7^{2-}\cdot 0.79C_7H_3N_2O_7^-\cdot 0.21C_6H_2N_3O_7^-\cdot H_2O$
$M_r = 729.91$
Triclinic, $P\overline{1}$
$a = 12.5457$ (15) Å
$b = 12.903$ (2) Å
$c = 13.1415$ (17) Å
$\alpha = 67.63$ (1)°
$\beta = 89.012$ (10)°
$\gamma = 64.41$ (1)°
$V = 1746.4$ (5) Å^3
$Z = 2$
$D_x = 1.388$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 17 reflections
$\theta = 10.1$–16.3°
$\mu = 0.11$ mm^{-1}
$T = 297$ (2) K
Cut block, yellow
0.30 × 0.25 × 0.20 mm

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
7072 measured reflections
6147 independent reflections
2203 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 25.0°$
$h = -14 \rightarrow 7$
$k = -15 \rightarrow 13$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 150 min
intensity decay: 2.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.211$
$S = 0.89$
6147 reflections
507 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.2218P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2*A*—H21*A*···O72*A*	0.96 (5)	1.62 (5)	2.586 (8)	177 (5)
O1*W*—H1*W*···O71*B*^{i}	0.80 (8)	2.03 (8)	2.801 (7)	163 (6)
O1*W*—H2*W*···O72*B*^{ii}	0.85 (7)	1.85 (7)	2.693 (7)	175 (6)
N1*C*—H11*C*···O71*A*^{iii}	0.95 (5)	2.46 (5)	3.146 (8)	131 (5)
N1*C*—H11*C*···O72*A*^{iii}	0.95 (5)	2.35 (5)	3.165 (8)	146 (5)
N1*C*—H11*C*···O71*B*^{iii}	0.95 (5)	2.55 (5)	3.156 (7)	122 (4)
N1*C*—H12*C*···O71*B*^{iv}	0.95 (6)	1.86 (6)	2.797 (6)	168 (6)
N1*D*—H11*D*···O2*A*^{i}	0.95 (7)	1.99 (6)	2.892 (8)	158 (5)
N1*D*—H12*D*···O1*W*	0.97 (8)	1.74 (8)	2.704 (8)	171 (8)
N1*E*—H11*E*···O2*B*^{ii}	0.97 (7)	1.92 (7)	2.782 (6)	138 (6)
N1*E*—H11*E*···O72*B*^{ii}	0.97 (7)	2.12 (8)	2.908 (7)	139 (6)
N1*E*—H12*E*···O2*B*	0.88 (6)	1.95 (6)	2.794 (7)	162 (6)
N1*E*—H12*E*···O31*B*	0.88 (6)	2.57 (6)	3.184 (7)	126 (5)

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

Partial substitution of the picrate anion for the structurally similar 3,5-dinitrosalicylate(1−) (*A*) species was suggested by the partial occupancy of the non-superimposed phenolic group in *A* [atom O2*A*, site-occupancy factor 0.79 (2)], with an alternative site corresponding to the phenolate O atom of the picrate anion [atom O6*A*, site-occupancy factor 0.21 (2)]. There is a corresponding shared occupancy at the C7*A* site [C = 0.79 (2) and N = 0.21 (2)]. The occupancy factors for atoms O2*A* and O6*A* were obtained by least-squares refinement. Further evidence for the presence of picrate was obtained from elemental analysis and from the precedence of compounds synthesized from 3,5-dinitrosalicylic acid (Smith *et al.*, 2004). H atoms involved in hydrogen-bonding interactions, including the phenolic H atom of the DNSA *A* anion, were located by difference methods and their positional and isotropic displacement parameters were refined. Other H atoms were positioned geometrically and treated as riding in the refinement, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

PLATON (Spek, 2003); software used to prepare material for publication: *PLATON*.

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