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**5-Nitrosalicylic Acid and its Proton-Transfer Compounds with Aliphatic Lewis Bases**

by

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## Abstract

The crystal structures of the proton-transfer compounds of 5-nitrosalicylic acid (5-nsa) with morpholine (morph), hexamethylenetetramine (hmt) and ethylenediamine (en) have been determined and their solid-state packing structures described. The compounds are [(morph)<sup>+</sup>(5-nsa)<sup>-</sup>] (1), [(hmt)<sup>+</sup>(5-nsa)<sup>-</sup> · H<sub>2</sub>O], (2) and [(en)<sup>2+</sup> 2(5-nsa)<sup>-</sup> · H<sub>2</sub>O], (3). In all compounds, protonation of the hetero-N of the Lewis base occurs. With (1), the 5-nsa anions and the morpholine cations lie respectively in or across crystallographic mirror planes and are linked within the planes by hydrogen bonding interactions through the aminium group and the carboxylic and phenolic oxygens of the anionic 5-nsa species giving a two-dimensional sheet polymer. Compound (2) is an unusual structure with the planar 5-nsa anions lying within pseudo mirror planes and cyclically linked by duplex water bridges through a single carboxylate oxygen into centrosymmetric dimers. The hmt cation molecules are disordered across the pseudo mirror and are strongly linked via N<sup>+</sup>-H...O hydrogen bonds only to the water molecules with peripheral weak hmt C-H...O hydrogen bonds extending the dimer within and between the dimer planes. Compound (3) is a network polymer comprising the 5-nsa anions, the en dianions and the water molecule in an extensive hydrogen-bonded structure.

## Introduction

The acid 5-nitrosalicylic acid (5-nsa) is similar to the analogous 3,5-dinitrosalicylic acid (dnsa) and has a comparable dissociation constant (p*K*<sub>a</sub> 2.14 *cf.* 2.18 for dnsa) and with most Lewis bases gives proton-transfer compounds. However, the quality of the crystalline proton-transfer products obtained with 5-nsa is poor by comparison so that the description of the modes of interaction of Lewis base cations with 5-nsa anions is negligible compared to those with dnsa where 36 have been crystallographically characterized.<sup>[1-4]</sup> The only reported proton-transfer structures of 5-nsa are with 3-amino-1*H*-1,2,4-triazole (3-at), [(3-at)<sup>+</sup>(5-nsa)<sup>-</sup>]<sup>[5]</sup> and with 8-aminoquinoline (8-aq), [(8-aq)<sup>+</sup>(5-nsa)<sup>-</sup>]<sup>[6]</sup> We have also reported the preparation of the 1:1 proton-transfer compounds with 8-hydroxyquinoline<sup>[7]</sup> and creatinine<sup>[8]</sup> but poor crystal quality precluded their determination by X-ray methods. Four non-transfer structures, with urea (ur), [(5-nsa)<sub>2</sub>(ur)]<sup>[9]</sup>, 1,1-diethylurea (deur), [(5-nsa)(deur)]<sup>[10]</sup> triphenylphosphine oxide (tppo), [(5-nsa)(tppo)]<sup>[11]</sup> and the 2:1 adduct with 2-imidazolidone (2-ida), [(5-nsa)(2-ida)<sub>2</sub>]<sup>[12]</sup> have been described by us.

The proton-transfer examples characterised crystallographically to date have been those with heteroaromatic Lewis bases so that we set out to complete a representative series containing Lewis base types not previously considered with 5-nsa but particularly those with aliphatic amines. From this we

hoped to obtain information which might explain why 5-nsa is so inferior to dnsa as a crystallization aid. Reported here are the preparations and crystal structure determinations of proton-transfer compounds of 5-nitrosalicylic acid with a set of Lewis bases comprising tetrahydro-2*H*-1,4-oxazine (morpholine = morph), 1,3,5,7-tetraazaadamantane (hexamethylenetetramine = hmt) and ethylenediamine (en). These compounds are respectively as follows: [(C<sub>4</sub>H<sub>10</sub>NO)<sup>+</sup>(C<sub>7</sub>H<sub>4</sub>NO<sub>5</sub>)<sup>-</sup>] (1), [(C<sub>6</sub>H<sub>13</sub>N<sub>4</sub>)<sup>+</sup>(C<sub>7</sub>H<sub>4</sub>NO<sub>5</sub>)<sup>-</sup> · H<sub>2</sub>O] (2) and [ {(CH<sub>2</sub>NH<sub>3</sub>)<sub>2</sub> }<sup>2+</sup> 2(C<sub>7</sub>H<sub>4</sub>NO<sub>5</sub>)<sup>-</sup> · H<sub>2</sub>O] (3).

(5-nsa)

(morph)

(hmt)

(en)

The crystal structures of the dnsa proton-transfer compounds with two of these bases (hmt and en) have been reported,<sup>[2]</sup> as well as that with 8-aminoquinoline<sup>[6]</sup> and the non-transfer adduct with urea.<sup>[8]</sup> Hexamethylenetetramine has utility as a structure-extending molecule or a molecule for adduct formation in both organic and coordination chemistry<sup>[13]</sup> although examples with organic acids are uncommon. The only known structures are a set of three non-transfer compounds with dicarboxylic acids [adipic (1:1), isophthalic (1:2 monohydrate) and 2,2'-thiosalicylic (1:1 hemihydrate)],<sup>[14]</sup> and a proton-transfer example with picric acid (1:1),<sup>[15]</sup> as well as the previously mentioned dnsa example (1:1).<sup>[2]</sup>

Other Lewis bases which were previously found to give good crystalline materials with dnsa, e.g. ammonia and a number of primary aliphatic amines,<sup>[2]</sup> as well as the hetero-aromatic examples (pyridine,<sup>[3]</sup> quinoline,<sup>[4]</sup> and the bifunctional polycyclic bases 1,10-phenanthroline<sup>[4]</sup> and 2,2'-bipyridine<sup>[4]</sup>) were found to give immediate precipitation of unmanageable products on reaction with 5-nsa so that the set reported here represents the rare isolation of crystalline products suitable for X-ray analysis.

## Discussion

All three compounds reported in this study have been confirmed as involving proton-transfer. This might be expected on the basis of the p*K*<sub>a</sub> values of the Lewis bases involved relative to that for 5-nsa (morpholine, 8.6; hexamethylenetetramine, 4.9; ethylenediamine, 9.9, 6.9). Figure 1

shows the molecular structure and atom numbering scheme used for the 5-nsa anion (molecule A) and the morph cation (molecule D) in compound (1), and for 5-nsa is the same as that used for all of the compounds reported here. With compound (3) where there are two independent 5-nsa anions, the second is B, while the cation molecule is molecule C. This scheme is also directly comparable to that used in our reported dnsa compounds. Lists of hydrogen-bonding interactions are given in Table 1.

*The individual structures*



The 1:1 proton-transfer compound of 5-nsa with morpholine, [(morph)<sup>+</sup>(5-nsa)<sup>-</sup>] has a repeating unit which comprises two independent half-molecules of 5-nsa<sup>-</sup> (molecules A and B) which lie across the crystallographic mirror planes at  $b = \frac{1}{4}$  and  $\frac{3}{4}$ , and two morph cations (molecules C and D) which lie in the same mirror planes. These cation and anion species are linked by hydrogen-bonding interactions between the protonated hetero-N and both carboxylate oxygens [N4D...O72A, 2.761(3)Å; N4D...O71A, 3.036(3) Å; N4D...O71B, 2.754(2)Å; N4C...O72A, 2.761(3)Å; N4C...72B, 2.806(3)Å]. Neither the morph<sup>+</sup> nor the 5-nsa<sup>-</sup> phenol oxygen atoms are involved in hydrogen bonding. The 5-nsa A and B anion molecules in the sheet structure generated partially superimpose down the  $b$  axis of the cell (Fig. 2), with a separation of  $b/2$  (3.435Å), with the resultant  $\pi-\pi$  interactions providing the only inter-plane association.



The hydrated compound of 5-nsa with hexamethylenetetramine [(hmt)<sup>+</sup>(5-nsa)<sup>-</sup> · H<sub>2</sub>O] is based on a centrosymmetric dimer comprising two planar 5-nsa anion molecules linked *via* symmetric bis-water bridges but involving only one carboxylate oxygen (O71) [O1W-H11W...O71, 2.766(3)Å:  $x, y, z$ ; O1W-H12W...O71<sup>a</sup>, 2.744(3)Å:  $a = 1 - x, 1 - y, 1 - z$ ]. This gives a cyclic R<sup>4</sup><sub>2</sub>(8) association [O71-O1W-O71<sup>a</sup>, 99.4(1)<sup>o</sup>; O1W-O71-O1W<sup>a</sup>, 80.6(1)<sup>o</sup>] (Fig. 3). The dimers lie essentially in the  $ac$  planes at  $b = 0, \frac{1}{2}$  and are the pseudo-mirror planes of the false  $C$ -centred structure (Fig. 4) which gave rise to the initial structural anomaly, explained under Experimental. The hmt cation molecules are disordered across the pseudo-mirror planes and are linked by only one strong hydrogen bond through the protonated hmt-N to the water molecule [N5B-H5B...O1W, 2.726(3)Å:  $x, y, z$ ]. The resulting tetramers are weakly linked within and between the pseudo-mirror plane by weak C-H (hmt)...O hydrogen bonds involving all 5-nsa oxygen-acceptor types, including the second carboxylate-O, O72.

This structure has no precedent among either 5-nsa or dnsa proton-transfer compounds where

primary cation-anion interaction involves direct N<sup>+</sup>-H...O (carboxylate) hydrogen bonding. A very different type of interaction is also found in the 1:1 compound with dnsa, [(hmt)<sup>+</sup>(dnsa)<sup>-</sup>] where the association is three-centred about the aminium proton to both the phenolic and nitro oxygen acceptors of dnsa, and is linearly extended through only one hmt C-H...O (nitro) hydrogen bond.<sup>[2]</sup>

$\{[(\text{CH}_2\text{NH}_3)_2]^{2+} 2(\text{C}_7\text{H}_2\text{N}_2\text{O}_7)^- \cdot \text{H}_2\text{O}\}$  (3). With the structure of the 2:1 compound of 5-nitrosalicylic acid with ethylenediamine, [(en)<sup>2+</sup> 2(5-nsa)<sup>-</sup> · H<sub>2</sub>O] (3), two 5-nsa anions (A and B) result from protonation of the en molecule (Fig. 5). This en<sup>2+</sup> species, which adopts an eclipsed rather than an extended conformation [torsion angle N1-C11-C21-N2, -66.5(7)<sup>o</sup>] gives a total of nine hydrogen-bonding interactions to oxygen acceptors, three to N1 and six to N2. These include a primary direct N<sup>+</sup>-H...O(carboxyl) interaction [N1-H2...O71, 2.773(8) Å], two to water molecules [2.877(8), 2.924(8) Å], and an asymmetric three-centre hydrogen-bonding association to a B-anion carboxylate group [2.781(7), 3.309(7) Å]. The water molecule also forms hydrogen bonds to both a B-molecule carboxyl-O [2.872(7) Å] and a nitro-O [2.867(7) Å]. The resulting structure comprises stacks of 5-nsa anions down the *c* cell direction, linked peripherally through the en cations and the water molecules, giving a three-dimensional hydrogen-bonded polymer structure (Fig. 6).

By comparison, the structure of the 1:1 hydrate compound of dnsa with en, [(en)<sup>2+</sup> (dnsa)<sup>2-</sup> · H<sub>2</sub>O]<sup>[2]</sup>, represented the first and only occurrence of the dianionic dnsa species and had an unusual primary symmetric duplex cyclic association between a hydrogen of each protonated amine group of the en cation and both a carboxylate and a phenolate oxygen of a dnsa anion. However, the total of eight associations involving the six aminium protons gave a similar three-dimensional structure to that in (3). *Conformational features of the 5-nsa species.*

Because of the presence of the intramolecular hydrogen bond between the carboxylate group and the phenol group in all examples, it is generally expected and found, that the carboxylate group is essentially coplanar with the benzene ring {torsion angle C2-C1-C7-O71, 175<sup>o</sup> [compound (3)] to 180<sup>o</sup> [compound (1)]}. This feature is similar to that found in salicylic acid<sup>[16]</sup> and in the previously reported structures proton-transfer compounds of 5-nsa. The O...O separation for the present set [(1)-(3)] is essentially invariable [range: 2.489-2.509 Å], expected because of the planarity of the hydrogen-bonded carboxylate unit, and is generally contracted slightly compared to the non-transfer examples [range: 2.547-2.604 Å; mean: 2.588 Å], as a result of deprotonation. These values compare with the longer distance for salicylic acid [2.640 Å].<sup>[16]</sup> Among the overall proton-transfer series, there is one anomalous

long value (2.633Å) for the 8-aminoquinoline compound.<sup>[6]</sup> The reason for this can only be speculated upon, and is probably because of the nature of the hydrogen bonding associated with the unusual one-dimensional zig zag structure which does not involve the phenolic group. All other structures have some secondary hydrogen-bonding interactions in their makeup, involving the phenolic group usually in a facial relationship.

In addition, with all known compounds, the proton is located on the phenolic-O within the intramolecular hydrogen bond and in this respect differs from the majority of the dnsa proton-transfer compounds where the proton is *anti*-located on the carboxyl-O in *ca.* 70% of the examples. The reason for this difference has to be associated with the presence of the *ortho*-related nitro group. This process is influenced by the stereochemical features of the important interacting groups of dnsa, viz. the *ortho*-related carboxylic acid, phenol and nitro groups and their availability for proximal-group interaction. *The nitro group at C5.* The 5-nitro group varies little conformationally within this set of compounds [torsion angle C4-C5-N5-O52: 180° (1), 179.8(2)° (2), 175.4(6), 177.9(6)° (3)] and is similar to the range for the overall series of 5-NSA compounds<sup>[12]</sup>, reflecting the general absence of intermolecular hydrogen-bonding interactions involving this group. This is also similar to the dnsa series where the maximum deviation from planarity for this torsion angle is 19.6° in the compound with quinaldic acid<sup>[4]</sup> but is more typically <10°. However, the torsion angle variation for the more associative nitro substituent at C3 in the set of dnsa compounds is much greater with a maximum value of 25.5° in the compound with pyridine compound<sup>[3]</sup> with a typical value closer to 20°.

## Conclusions

5-Nitrosalicylic acid, like the analogous 3,5-dinitrosalicylic acid has a comparable ability to protonate the nitrogen functional group of most Lewis bases. For the dnsa compounds, there is with one exception, formation of primary direct aminium N<sup>+</sup>-H...O (carboxyl) hydrogen-bonding interactions, together with secondary propagating interactions as part of the structure-making process. This primary interaction may be absent with 5-nsa compounds and be replaced as in (2) by N<sup>+</sup>-H...O(water)-type interactions, while there is an inability to form comparable secondary hydrogen-bonding associations. This is considered as being due to the absence in 5-nsa of the second nitro group at C3. Because of this absence, the common proximal-group interactions involving carboxyl, phenol and nitro oxygen acceptors, which in dnsa has resulted in the structural characterization of 36 proton-transfer compounds,<sup>[1-4, 16]</sup> cannot occur. As with the dnsa compounds there are, in addition, fewer extending interactions involving the 5-nitro oxygen acceptors while the nitro group itself shows a lesser tendency

to become a more flexible proton acceptor through rotation of the oxygen atoms out of the plane of the parent ring. This means that the overall 5-nsa molecule remains planar [(1) and (2)] or essentially so and lacks the flexibility of dnsa. For these reasons 5-nsa structures often require the introduction of molecules of lattice water for structure-making to proceed, a feature which is rare in dnsa structures.

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### Experimental

Compounds (1)-(3) were prepared using equimolar amounts (0.10 mmol) of 5-nitrosalicylic acid with the appropriate Lewis base (morpholine, hexamethylenetetramine and ethylenediamine). All preparations involved the heating under reflux of the two components in 50 cm<sup>3</sup> of 80% EtOH/H<sub>2</sub>O for 10 min. Volume reduction to *ca.* 40 cm<sup>3</sup> followed by partial or total room temperature evaporation of the hot-filtered solutions gave yellow prismatic crystals of (1), (2) and (3) respectively, suitable for X-ray examination. For (1) (m.p. 172.3-172.6°C); for (2) (m.p. 184.7-186.6°C); for (3) (m.p. 138.5-140.6°C). Preparations using a number of the other Lewis bases which previously gave good crystalline products with dnsa resulted mainly in the immediate formation of insoluble non-crystalline or microcrystalline products. These were not examined further, beyond trying different solvent mixtures to promote crystallization.

### Crystallography

#### Crystal Data

(1) [(C<sub>4</sub>H<sub>10</sub>NO)<sup>+</sup>(C<sub>7</sub>H<sub>4</sub>NO<sub>5</sub>)<sup>-</sup>], CCDC 235883, mol. wt. 270.24, orthorhombic, space group *Pnma* (no. 62), *a* 21.1285(15), *b* 6.8695(5), *c* 17.2642(13) Å, *V* 2505.8(3) Å<sup>3</sup>, *F*(000) 1136, *D<sub>c</sub>* (*Z* = 8) 1.430 g cm<sup>-3</sup>,  $\mu$ (Mo K $\alpha$ ) 1.18 cm<sup>-1</sup>, temperature 295(2) K. 12897 reflections measured, 2404 unique (*R*<sub>int</sub> 0.043) [22<sub>max</sub> 50°: -21 ≤ *h* ≤ 25; -5 ≤ *k* ≤ 8; -20 ≤ *l* ≤ 20]. Final *R* 0.045 (*F*); *wR*<sup>2</sup> 0.114 (*F*<sup>2</sup>) [1644 reflections with *I* > 2.0  $\Phi$ (*I*) for 233 refined parameters]; *S* 0.982; residual electron density (max/min) 0.17/-0.18 e Å<sup>-3</sup>; crystal size 0.40 x 0.30 x 0.20 mm.

(2) [(C<sub>6</sub>H<sub>13</sub>N<sub>4</sub>)<sup>+</sup>(C<sub>7</sub>H<sub>4</sub>NO<sub>5</sub>)<sup>-</sup> · H<sub>2</sub>O], CCDC 235884, mol. wt. 341.33, monoclinic, space group *P2<sub>1</sub>/c* (no. 14), *a* 12.2904(2), *b* 6.5494(1), *c* 19.8052(4) Å,  $\beta$  107.763(1)°, *V* 1518.2(3) Å<sup>3</sup>, *F*(000)



1440,  $D_c$  ( $Z = 4$ )  $1.493 \text{ g cm}^{-3}$ ,  $:(\text{Mo K}\alpha) 1.20 \text{ cm}^{-1}$ ,  $T 293(2) \text{ K}$ . 22987 reflections measured, 2421 unique ( $R_{\text{int}} 0.041$ ) [ $2\theta_{\text{max}} 55^\circ$ :  $-14 \leq h \leq 14$ ;  $-7 \leq k \leq 7$ ;  $-23 \leq l \leq 23$ ]. Final  $R 0.053$  ( $F$ );  $R_w 0.094$  ( $F$ ) [1892 reflections with  $I > 3.0 \Phi(I)$  for 169 refined parameters];  $S 2.01$ ; residual electron density (max/min)  $0.33/-0.24 \text{ e } \Delta^{-3}$ ; crystal size  $0.50 \times 0.35 \times 0.25 \text{ mm}$ .

(3)  $[(\text{C}_2\text{H}_{10}\text{N}_2)^{2+} 2(\text{C}_7\text{H}_4\text{NO}_5)^- \cdot \text{H}_2\text{O}]$ , CCDC 235885, mol. wt. 444.36, triclinic, space group  $P-1$  (no. 2),  $a 10.813(4)$ ,  $b 13.508(5)$ ,  $c 6.678(6) \text{ \AA}$ ,  $\alpha 90.58(5)$ ,  $\beta 96.33(5)$ ,  $\gamma 93.16(3)^\circ$   $V 968(1) \text{ \AA}^3$ ,  $F(000) 464$ ,  $D_c$  ( $Z = 2$ )  $1.525 \text{ g cm}^{-3}$ ,  $:(\text{Mo K}\alpha) 1.31 \text{ cm}^{-1}$ ,  $T 298(2) \text{ K}$ . 4052 reflections measured, 3386 unique ( $R_{\text{int}} 0.037$ ) [ $2\theta_{\text{max}} 50^\circ$ :  $-12 \leq h \leq 12$ ;  $-16 \leq k \leq 16$ ;  $-7 \leq l \leq 4$ ]. Final  $R 0.067$  ( $F$ );  $wR2 0.213$  ( $F^2$ ) [1716 reflections with  $I > 2.0 \Phi(I)$  for 293 refined parameters];  $S 1.04$ ; residual electron density (max/min)  $0.33/-0.32 \text{ e } \Delta^{-3}$ ; crystal size  $0.50 \times 0.20 \times 0.10 \text{ mm}$ .

### **Data Collection, Structure Solution and Refinement**

X-ray diffraction data for (1) were collected on a Bruker SMART CCD detector-equipped diffractometer while data for (3) were collected on a Rigaku AFC 7R diffractometer. Graphite crystal monochromatized Mo K $\alpha$  radiation ( $8 0.71073 \text{ \AA}$ ) was used in all cases, for the Rigaku instrument from a 12 kW rotating anode source. For (2), an initial data set was also collected on the Rigaku diffractometer for a  $C$ -centred cell and subsequent structure solution and partial refinement indicated a structural problem possibly due to disorder. Subsequent re-examination of the crystal using a CCD-detector diffractometer at the RSC at Canberra revealed subsets of data in a primitive monoclinic cell, missed in the previous data collection so that a new data set was collected. Treatment of the problem of refinement of this structure is given later\*. No crystal instability was in evidence with any of the compounds. Data were corrected for Lorentz and polarization effects and for extinction but not for absorption. The structures were solved by direct methods and refined using full-matrix least-squares (on  $F^2$ ) [SHELXTL-97<sup>[18]</sup>, for (1) or SHELX-97<sup>[19]</sup>, for (3) in the latter case using the TeXsan system<sup>[19]</sup>]. Anisotropic thermal parameters were used for all non-hydrogen atoms. The values for  $A$  and  $B$  in the weighting scheme  $w = [\Phi^2 (F_o^2) + (AP)^2 + BP]^{-1}$  were (0.081, 0.0) (1), (0.040, 0.0) (2) and (0.100, 3.00) (3) {where  $P = [( \max. F_o^2, 0) + 2(F_c^2)]/3$ }. Hydrogen atoms were either located by difference methods if potentially involved in hydrogen-bonding interactions, and both positional and thermal parameters were refined, or were included at calculated positions as riding models. For all compounds:  $R1 = (\Gamma * F_o^* - * F_c^* ) / \Gamma * F_o^*$ ;  $wR2 = (\Gamma w(F_o^2 - F_c^2)^2 / \Gamma w(F_o^2)^2)^{1/2}$

For compound (2), an initial solution in the space group  $C2/m$  indicated an ordered 5-nsa anion

molecule lying within the mirror plane and a disordered and uninterpretable hmt cation lying across the plane. This problem could not be resolved in the lower space group  $Cm$  (best  $R$  ca. 8%)., The structure solution was subsequently obtained using the  $k+l$  even subset of reflections with the CCD data set (with transformed axes) in the space group  $A2/m$  (non standard setting of  $C2/m$ ). Space group  $P2_1/c$  is a subgroup of this space group and a structure in this space group was obtained by ordering the  $A2/m$  structure and then refining it. The  $-1$  site of  $P2_1/c$  coincides with the  $2/m$  site of  $A2/m$ . The  $2_1$  screw relates anions packed perpendicular to  $\mathbf{b}^*$ . Having chosen between mirror related positions for the hmt cation the water oxygen O1W was chosen so as to allow a hydrogen bond to the N5B atom of the cation. A difference electron density map showed a hydrogen between these two atoms, which refined to be attached to N5B. The anisotropic refinement in  $P2_1/c$  used a number of constraints and restraints and used the program *RAELSO0*.<sup>[20]</sup> The central ring of the anion was constrained to be planar but this plane was allowed to rotate and translate. H atoms in the anion were allowed to refine subject to the constraint that they were coplanar with the ring. The constraints were achieved by using refinable local coordinates defined relative to a refinable orthonormal axial system.<sup>[21]</sup> The water-O and the attached H atoms were unconstrained while those in the cation were unconstrained. However, after seeing the answer a weak restraint on differences between N-C distances to approach zero was applied. This was done in two sets: (i) the three distances involving N5B (average N-C distance 1.511(2) Å) and (ii) the other nine distances (average N-C distance 1.456(2) Å, range 1.437 - 1.466 Å). The atomic displacement parameters for the ions were initially modelled using 15 *TLX* rigid body parameter sets.<sup>[21]</sup> Additional libration of the  $\text{CO}_2^-$  and  $\text{NO}_2$  groups of the anion about the bonds attaching them to the six-membered ring were included. It was found that a librational model adequately described the cation, but left unexplained peaks in the region of the cation and in addition the refinement of the H atom positions of the cation misbehaved. It was decided to fix these hydrogens in sensible positions after each refinement cycle, and fix their thermal parameters according to the last *TLX* refinement. Increments to the anisotropic displacement parameters of the non-hydrogen atoms were then allowed to refine independently reducing the  $R(F)$  values by about 0.01. Errors are calculated using the inverse of the least squares matrix used in the refinement and assume the appropriateness of the model and the various constraints and restraints used in the refinement.

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## Figures

- Figure 1.** Atom numbering scheme for the individual 5-nsa anion (molecule A) and morpholine cation (molecule D) species in (1). Atoms are shown as 30% probability ellipsoids.<sup>[22]</sup> The same scheme is used for the B and C molecules in (1) and the 5-nsa species in compounds (2) and (3). Atoms C2Da and C3Da are mirror-related to C2D and C3D.
- Figure 2.** Packing of (1) in the unit cell viewed down *b*. Hydrogen-bonding associations are shown as broken lines.
- Figure 3.** The hydrogen-bonded tetramer units of (2) showing the naming scheme and the duplex water bridges.
- Figure 4.** Partial packing of (2) in the unit cell viewed down *a* showing the pseudo mirror plane containing the 5-nsa anions.
- Figure 5.** The two 5-nsa anions (molecules A and B), the en cation and the water molecule in (3).
- Figure 6.** Perspective view of the packing of (3) in the unit cell viewed down *c*.

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**TABLE 1** Hydrogen-bonding associations ( $\Delta^{\circ}$ ) for compounds (1), (2) and (3)

(1)

| D   | H    | A    | D-H      | H...A    | D A       | D-H...A |
|-----|------|------|----------|----------|-----------|---------|
| O2A | H2A  | O71A | 0.96 (3) | 1.60 (3) | 2.503 (3) | 154 (3) |
| O2B | H2B  | O71B | 0.95 (3) | 1.57 (3) | 2.492 (4) | 165 (3) |
| N4C | H41C | O72B | 0.98 (3) | 1.71 (3) | 2.654 (3) | 162 (3) |
| N4D | H41D | O71B | 0.98 (3) | 1.78 (3) | 2.754 (3) | 172 (3) |
| N4C | H42C | O72A | 0.98 (3) | 1.85 (3) | 2.806 (3) | 164 (3) |
| N4D | H42D | O71A | 1.02 (3) | 2.49 (3) | 3.036 (3) | 113 (2) |
| N4D | H42D | O72A | 1.02 (3) | 1.75 (3) | 2.761 (3) | 173 (2) |
| C2C | H21C | O52B | 0.97     | 2.36     | 3.204 (4) | 145     |
| C3D | H32D | O71A | 0.97     | 2.57     | 3.214 (4) | 124     |

(2)

| D    | H    | A                 | D-H      | H...A    | D A       | D-H...A |
|------|------|-------------------|----------|----------|-----------|---------|
| O2A  | H2A  | O72A              | 1.00 (4) | 1.56 (4) | 2.509 (3) | 156 (3) |
| N5B  | H5B  | O1W               | 0.99 (4) | 1.74 (4) | 2.726 (3) | 177 (3) |
| O1W  | H11W | O71A              | 0.87 (3) | 1.90 (3) | 2.766 (3) | 171 (3) |
| O1W  | H12W | O71A <sup>a</sup> | 1.04 (4) | 1.74 (4) | 2.744 (3) | 160 (3) |
| C10B | H10B | O72A              | 1.00     | 2.51     | 3.293 (3) | 135     |
| C2B  | H21B | O51A <sup>b</sup> | 1.00     | 2.57     | 3.419 (3) | 143     |
| C2B  | H22B | O52A <sup>c</sup> | 1.00     | 2.52     | 3.519 (4) | 179     |
| C6B  | H61B | O71A <sup>a</sup> | 1.00     | 2.59     | 3.460 (4) | 145     |
| C8B  | H82B | O2A <sup>d</sup>  | 1.00     | 2.42     | 3.266 (3) | 142     |

a = 1-x, 1-y, 1-z; b = 1-x, -1/2+y, 1/2-z; c = -1+x, 1/2-y, -1/2+z; d = -x, 1-y, 1-z

(3)

| D   | H    | A                 | D-H      | H...A    | D A       | D-H...A |
|-----|------|-------------------|----------|----------|-----------|---------|
| O2A | H2A  | O72A              | 1.04 (9) | 1.55 (9) | 2.505 (6) | 149 (8) |
| O2B | H2B  | O72B              | 1.00 (7) | 1.65 (7) | 2.489 (6) | 139 (6) |
| O2A | H2A  | O72A <sup>a</sup> | 1.04 (9) | 2.56 (9) | 3.222 (7) | 121 (6) |
| N1  | H11  | O1W               | 0.98 (7) | 1.93 (7) | 2.877 (8) | 162 (6) |
| O1W | H11W | O52B <sup>b</sup> | 0.99 (9) | 1.88 (9) | 2.867 (7) | 180 (8) |
| N1  | H12  | O71A              | 1.05 (7) | 1.73 (7) | 2.773 (7) | 173 (6) |
| O1W | H12W | O72B <sup>c</sup> | 0.95 (8) | 1.92 (8) | 2.872 (7) | 179 (7) |
| N1  | H13  | O72B <sup>d</sup> | 0.89 (8) | 2.04 (8) | 2.916 (8) | 168 (7) |
| N2  | H21  | O71B <sup>d</sup> | 0.95 (7) | 1.86 (7) | 2.781 (7) | 161 (7) |
| N2  | H21  | O72B <sup>d</sup> | 0.95 (7) | 2.52 (8) | 3.309 (7) | 140 (6) |
| N2  | H22  | O72A <sup>e</sup> | 0.96 (8) | 2.01 (8) | 2.882 (7) | 150 (6) |
| N2  | H22  | O51A <sup>f</sup> | 0.96 (8) | 2.46 (7) | 2.984 (8) | 114 (5) |
| N2  | H23  | O1W <sup>e</sup>  | 0.96 (8) | 2.15 (8) | 2.924 (8) | 137 (6) |
| N2  | H23  | O2A <sup>g</sup>  | 0.96 (8) | 2.40 (8) | 3.022 (7) | 122 (6) |
| C4B | H4B  | O71A              | 0.95     | 2.45     | 3.397 (8) | 172     |
| C11 | H111 | O2A <sup>a</sup>  | 0.95     | 2.52     | 3.443 (9) | 164     |
| C11 | H112 | O2B <sup>h</sup>  | 0.95     | 2.47     | 3.138 (8) | 127     |
| C21 | H212 | O51A <sup>f</sup> | 0.95     | 2.46     | 3.108 (8) | 126     |

a = 1-x, 2-y, 1-z; b = 1-x, 1-y, 1-z; c = -x, 1-y, 1-z; d = -x, 1-y, -z; e = x, y, -1+z; f = -x, 2-y, -z; g = 1-x, 2-y, -z; h = 1+x, y, z.