Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Salicylaldoximium 3,5-dinitrosalicylate dihydrate

Graham Smith,[a]* Urs D. Wermuth[a] and Jonathan M. White[b]

[a]Centre for Instrumental and Developmental Chemistry, Queensland University of Technology, GPO Box 2434, Brisbane 4001, Australia, and [b]School of Chemistry, The University of Melbourne, Parkville 3052, Australia

Correspondence e-mail: g.smith@qut.edu.au

Received 14 October 2002
Accepted 22 October 2002
Online 31 October 2002

Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
R factor = 0.048
wR factor = 0.110
Data-to-parameter ratio = 10.4

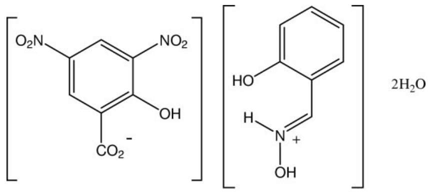
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The crystal structure of the dihydrate of the 1:1 proton-transfer compound of 3,5-dinitrosalicylic acid with 2-hydroxybenzaldehyde oxime (salicylaldoxime), $C_7H_8NO_2^+\cdot C_7H_3N_2O_7^-\cdot 2H_2O$, is a three-dimensional hydrogen-bonded polymer. In this, the oxime-N atom of salicylaldoxime is protonated and, together with the adjacent O—H group, gives primary cyclic asymmetric hydrogen-bonding associations with both carboxyl O atoms of the acid. These, together with hydrogen-bonding interactions among all species present, including the two water molecules, give an essentially planar ten-membered ring. Peripheral hydrogen bonding also links the water molecules to carboxyl and nitro-O atoms, giving rise to a three-dimensional polymer structure.

Comment

3,5-Dinitrosalicylic acid (DNSA) (pK_a = 1.8) is a sufficiently strong acid to protonate most amines with which it reacts (Issa *et al.*, 1980). Most compounds involving this molecule are, therefore, proton-transfer types, while others involving bases with particularly small pK_a values may form molecular complexes, which may or may not involve π–π stacking and electron transfer. The 1:1 adduct of the weak base phenazine (pK_a = 1.2) (Kumar *et al.*, 2002) is a rare example of a crystallographically characterized DNSA–Lewis base compound in which no proton transfer or electron transfer occurs. Other neutral DNSA complexes involving non-Lewis bases are more common, *e.g.* with urea (Smith *et al.*, 1997) and 1,1-diethylurea (Smith *et al.*, 2000) (both 1:1), and the pseudo-polymorphic solvate structures with water (two polymorphs: Smith *et al.*, 1995; Kumar *et al.*, 1999), 1,4-dioxane (four polymorphs: Kumar *et al.*, 1999) and *tert*-butyl alcohol (one polymorph: Kumar *et al.*, 1999). It was considered that, with a weak base such as an oxime, proton transfer may not occur with common carboxylic acids, *e.g.* the acetophenone oxime–benzoic acid compound (Maurin *et al.*, 1993) is non-transfer. Salicylaldoxime (SALOX) is a common analytical reagent used for the selective precipitation of copper(II) and palladium(II) (Vogel, 1964), achieved *via* formation of neutral square-planar bis-chelate complexes through both the phenolate-O (pK_a = 9.1) and the neutral oxime-N donor atoms. The structures of these complexes of SALOX with copper(II) (Jarski & Lingafelter, 1964) and palladium(II) (Pfluger *et al.*, 1970) are known, together with that of nickel(II), which is isomorphous with the Pd complex (Srivastava *et al.*, 1967). Examples of complexes involving these, as well as other metals and often with mixed ligands, *e.g.* platinum(II) (Kaplan *et al.*, 2001), nickel(II) (Lalia-Kantouri *et al.*, 1999) and tin(IV) (Willem *et al.*, 1996; Mercier *et al.*, 1998) are also known.

With SALOX, the protonation of the oxime-N atom (pK_a = 11.4) might be considered feasible, particularly in the presence of carboxylic acids such as DNSA. This was found to be the case with the 1:1 compound reported here, obtained from the reaction of DNSA with SALOX, the dihydrate $\text{SALOX}^+\cdot\text{DNSA}^-\cdot2H_2O$, (I).



(I)

In (I), the oxime-N atom of SALOX is protonated and is subsequently involved in a three-centred hydrogen-bonding interaction: an intramolecular hydrogen bond with the phenolic O atom of SALOX [N71—H71*A*···O21 2.645 (2) Å] and an intermolecular hydrogen bond to a carboxylate O atom [N71—H71*A*···O72 2.808 (2) Å] (Fig. 1). This intramolecular association in SALOX in (I) is similar to that found in the hydrogen-bonded cyclic dimeric structure of the parent oxime (Pfluger & Harlow, 1973). Completing an asymmetric cyclic $R^2_2(7)$ association in (I) is a strong O—H(oxime)···O(carboxyl) hydrogen bond [O81—H81···O71 2.556 (2) Å]. The two water molecules, together with the SALOX cation and the DNSA anion, complete a ten-membered and essentially planar hydrogen-bonded ring. This is extended peripherally in the *b*-axis direction, through the water molecules [O1*W*···O71$^{\text{i}}$; symmetry code: (i) x, $1 + y$, z] and *via* an *n*-glide operation [O2*W*···O32$^{\text{ii}}$; symmetry code: (ii) $-x + \frac{1}{2}$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$] (Fig. 2 and Table 1), to give a three-dimensional polymer structure.

The usual intramolecular hydrogen bond is found between the phenolic H atom and a carboxylate-O atom of DNSA [O2—H2···O72 2.431 (2) Å], making this one of the minority examples among proton-transfer compounds of DNSA, where the proton is located on the phenol group rather than the carboxyl group (Smith *et al.*, 2002, 2002*a*,*b*).

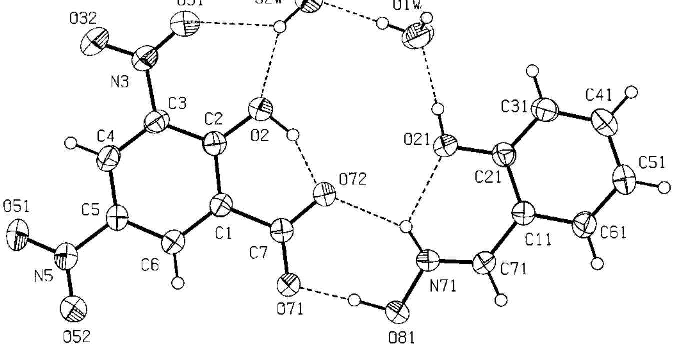


Figure 1
The molecular structure and atom-labelling scheme for the individual DNSA^-, SALOX^+ and water molecules in (I). Non-H atoms are drawn as 40% probability ellipsoids

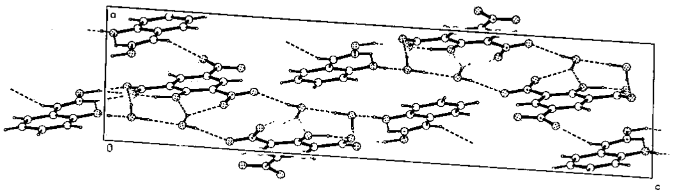


Figure 2
Perspective view of the packing in the unit cell, showing hydrogen-bonding associations as broken lines.

Experimental

The synthesis of the title compound, (I), was carried out by heating 1 mmol quantities of 3,5-dinitrosalicylic acid (DNSA) and 2-hydroxybenzaldehyde oxime (salicylaldoxime = SALOX) in 50 ml of 80% ethanol/water for 10 min under reflux. After concentration to *ca* 30 ml, partial room-temperature evaporation of the hot-filtered solution gave yellow crystals (m.p. 375.5–379.0 K), suitable for X-ray analysis.

Crystal data

$C_7H_8NO_2^+\cdot C_7H_3N_2O_7^-\cdot2H_2O$
M_r = 401.29
Monoclinic, $P2_1/n$
a = 7.0077 (4) Å
b = 8.5126 (5) Å
c = 28.5138 (15) Å
β = 92.979 (1)°
V = 1698.66 (17) Å^3
Z = 4

D_x = 1.569 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9872 reflections
θ = 2.5–25.0°
μ = 0.14 mm^{-1}
T = 295 (2) K
Block, yellow
0.50 × 0.30 × 0.10 mm

Data collection

Bruker CCD area detector diffractometer
φ and ω scans
Absorption correction: none
11631 measured reflections
2985 independent reflections

2898 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 25.0°
$h = -8 \rightarrow 8$
$k = -10 \rightarrow 10$
$l = -33 \rightarrow 33$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.110
S = 1.21
2985 reflections
286 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0322P)^2 + 0.9115P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}}$ = 0.003
$\Delta\rho_{\text{max}}$ = 0.28 e Å^{-3}
$\Delta\rho_{\text{min}}$ = −0.20 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0094 (12)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*A*···O71$^{\text{i}}$	0.93 (4)	1.95 (4)	2.853 (2)	164 (3)
O1*W*—H1*B*···O2*W*	0.89 (3)	1.84 (3)	2.733 (3)	178 (3)
O2—H2···O72	1.07 (3)	1.40 (3)	2.431 (2)	161 (3)
O2*W*—H2*A*···O2	0.94 (4)	1.98 (4)	2.822 (3)	148 (3)
O2*W*—H2*A*···O31	0.94 (4)	2.17 (4)	2.911 (3)	134 (3)
O2*W*—H2*B*···O32$^{\text{ii}}$	0.80 (4)	2.15 (4)	2.947 (3)	173 (4)
O21—H21···O1*W*	0.91 (3)	1.68 (3)	2.590 (2)	176 (3)
N71—H71*A*···O21	0.92 (3)	2.05 (3)	2.645 (2)	121 (2)
N71—H71*A*···O72	0.92 (3)	2.00 (3)	2.808 (2)	145 (2)
O81—H81···O71	1.02 (3)	1.54 (3)	2.556 (2)	177 (2)
O81—H81···O72	1.02 (3)	2.50 (3)	3.162 (2)	121.9 (18)
C71—H71···O52$^{\text{iii}}$	0.93	2.39	3.280 (3)	160

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

o1316 Graham Smith *et al.* • $C_7H_8NO_2^+\cdot C_7H_3N_2O_7^-\cdot2H_2O$ *Acta Cryst.* (2002). E**58**, o1315–o1317

H atoms involved in hydrogen-bonding interactions (H2, H1*A*, H1*B*, H2*A*, H2*B*, H71*A* and H81) were located in difference maps and their positional and isotropic displacement parameters refined. Other H atoms were included in the refinement at calculated positions in the riding-model approximation. For refined H atoms, the oxime N—H distance is 0.92 (3) Å, the hydroxyl O—H range is 0.91 (3)–1.07 (3) Å and the water O—H range is 0.80 (4)–0.94 (4) Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* for Windows (Spek, 1999); software used to prepare material for publication: *SHELXTL*.

The authors acknowledge financial support from the Centre for Instrumental and Developmental Chemistry (Queensland University of Technology) and the University of Melbourne.

References

Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (1999). *SAINT*. Version 6.02. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2000). *SMART*. Version 5.55. Bruker AXS Inc., Madison, Wisconsin, USA.

Issa, Y. M., Hindawey, A. M., Issa, R. M. & Nassar, A. G. M. (1980). *Rev. Roum. Chim.* **25**, 1535–1541.

Jarski, M. A. & Lingafelter, E. C. (1964). *Acta Cryst*, **17**, 1109–1112.

Kaplan, S. F., Kukushkin, V. Y., Shova, S., Suwinska, K., Wagner, G. & Pombeiro, A. J. L. (2001). *Eur. J. Inorg. Chem.* pp. 1031–1038.

Kumar, V. S. S., Kuduva, S. S. & Desiraju, G. R. (1999). *J. Chem. Soc.Perkin Trans.* 2, pp. 1069–1073.

Kumar, V. S. S., Kuduva, S. S. & Desiraju, G. R. (2002). *Acta Cryst.* E**58**, o865–o866.

Lalia-Kantouri, M., Hatzidimitriou, A. & Uddin, M. (1999). *Polyhedron*, **18**, 3441–3450.

Maurin, J. K., Winnicka-Maurin, M., Paul, I. C. & Curtin, D. Y. (1993). *Acta Cryst.* B**49**, 90–96.

Mercier, F. A. G., Meddour, A., Gielen, M., Biesemans, M., Willem, R. & Tiekink, E. R. T. (1998). *Organometallics*, **17**, 5933–5936.

Pfluger, C. E. & Harlow, R. L. (1973). *Acta Cryst.* B**29**, 2608–2609.

Pfluger, C. E., Harlow, R. L. & Simonsen, S. H. (1970). *Acta Cryst.* B**26**, 1631–1633.

Smith, G., Baldry, K. A., Byriel, K. A. & Kennard, C. H. L. (1997). *Aust. J. Chem.* **50**, 727–736.

Smith, G., Coyne, M. G., & White, J. M. (2000). *Aust. J. Chem.* **53**, 203–208.

Smith, G., Lynch, D. E., Byriel, K. A. & Kennard, C. H. L. (1995). *Aust. J. Chem.* **48**, 1133–1149.

Smith, G., Wermuth, U. D., Bott, R. C., Healy, P. C. & White, J. M. (2002). *Aust. J. Chem.* **55**, 349–356.

Smith, G., Wermuth, U. D., Healy, P. C. & White, J. M. (2002*a*). *Aust. J. Chem.* Submitted.

Smith, G., Wermuth, U. D., Healy, P. C. & White, J. M. (2002*b*). *J. Chem. Crystallogr.* Submitted.

Spek, A. L. (1999). *PLATON* for Windows. September 1999 Version. University of Utrecht, The Netherlands.

Srivastava, R. C., Lingafelter, E. C. & Jain, P. C. (1967). *Acta Cryst.* **22**, 922–923.

Vogel, A. I. (1964). *Textbook of Macro and Semi-Micro Qualitative Inorganic Analysis*, 4th ed., p. 227. London: Longmans.

Willem, R., Bouhdid, A., Kayser, F., Delmotte, A., Gielen, M., Martens, J. C., Biesemans, M., Mahieu, B. & Tiekink, E. R. T. (1996). *Organometallics*, **15**, 1920–1929.

Acta Cryst. (2002). E**58**, o1315–o1317 Graham Smith *et al.* • $C_7H_8NO_2^+ \cdot C_7H_3N_2O_7^- \cdot 2H_2O$ **o1317**