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Hydrogen bonding in proton-transfer compounds of 8-quinolinol (oxine) with aromatic sulfonic acids

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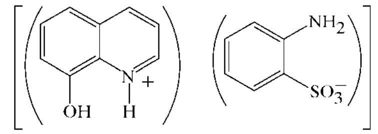
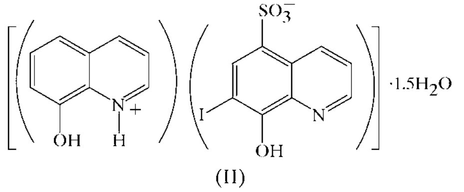
The crystal structures of the proton-transfer compounds of 8-quinolinol (oxine) with the aromatic sulfonic acids 2-aminobenzenesulfonic acid (orthanilic acid) and 8-hydroxy-7-iodoquinoline-5-sulfonic acid (ferron) have been determined. In both 8-hydroxyquinolinium 2-aminobenzenesulfonate, $C_9H_8NO^+\cdot C_6H_6NO_3S^-$, (I), and 8-hydroxyquinolinium 8-hydroxy-7-iodoquinoline-5-sulfonate sesquihydrate, $C_9H_8NO^+\cdot C_9H_5INO_4S^-\cdot 1.5H_2O$, (II), extensive hydrogen-bonding interactions, together with significant cation–cation [in (I)] and cation–anion [in (II)] π–π stacking associations, give rise to layered polymer structures.

Comment

8-Quinolinol (8-hydroxyquinoline, 8-HQ) is a particularly useful reagent (oxine) for metal complex formation, achieved through *N*,*O*-bidentate interaction, giving bis- and tris-chelate compounds, for example, $[Pd(8\text{-}HQ)_2]$ (Prout & Wheeler, 1966). Oxine will react with most metal types, but the values of the dissociation constants for the phenol O and the heterocyclic N-donor groups ($pK_{a1,2}$ = 4.9 and 10.8) provide the textbook example of a reagent that has wide interactive selectivity, particularly through pH control, giving numerous analytical chemical applications (Skoog *et al.*, 1988). The molecule also readily forms adducts, both with metal complex species, for example, $K^+\cdot(8\text{-HQ})^-\cdot(8\text{-HQ})$ and $K^+\cdot(8\text{-HQ})^-\cdot 2(8\text{-HQ})$ (Hughes & Truter, 1979), and with neutral compounds, for example, chloranil (1:1; Prout & Wheeler, 1967) and 1,3,5-trinitrobenzene (1:1; Castellano & Prout, 1971). In the presence of relatively strong organic acids, protonation of the heterocyclic N atom of oxine occurs and the resulting 8-HQ$^+$ cation provides structure extension through hydrogen-bonding interactions. Known structures of this type are those with salicylic acid (SA, a discrete 2:2 dimer; Singh *et al.*, 2000; Smith, Wermuth & White, 2003), 2-nitrobenzoic acid (1:1 monohydrate), 3,5-dinitrobenzoic acid (1:1 trihydrate) and 3,5-dinitrosalicylic acid (1:1; Smith *et al.*, 2001), 5-sulfosalicylic acid (1:1 monohydrate; Smith, Wermuth & White, 2004), and Kemp's triacid (*cis-cis*-1,3,5-trimethylhexane-1,3,5-tricarboxylic acid, a 1:1 anhydrate; Smith *et al.*, 2000). Adduct salts with SA $[(8\text{-HQ})^+\cdot(\text{SA})^-\cdot(8\text{-HQ})$; Jebamony & Muthiah, 1998] and 1,2,3-trihydroxybenzene $[(8\text{-HQ})^+\cdot(\text{THB})^-\cdot(8\text{-HQ})$; Singh *et al.*, 1994] are also known. It is also of interest that, with a number of these compounds, the formation reactions can proceed in the solid state (Rastogi *et al.*, 1977; Singh *et al.*, 1994, 1999, 2000).


(I)


(II)

8-Hydroxy-7-iodoquinoline-5-sulfonic acid (ferron) is chemically analogous to oxine, with potential for complex formation but with steric constraints because of the presence of the bulky 7-iodo substituent. Therefore, ferron gives a colour reaction with iron(III) but not with iron(II) (Vogel, 1964). The crystal structure determination of ferron (Merritt & Duffin, 1970; Balasubramanian & Muthiah, 1996) has confirmed the presence of a sulfonate–quinolinium zwitterion. We have reported the structure of the bis(guanidinium) monohydrate salt of ferron, in which deprotonation of both the sulfonic acid and the phenol groups has occurred (Smith, Wermuth & Healy, 2003), while in the structure of the 1:1 salt with 4,4′-bipyridine (Hemamalini *et al.*, 2004), only the sulfonate group is deprotonated. We have also determined the 1:1:1 ferron/urea/water adduct structure (Smith, Wermuth & Healy, 2004).

The crystal structures reported here are those of the products of the reaction of 8-hydroxyquinoline with

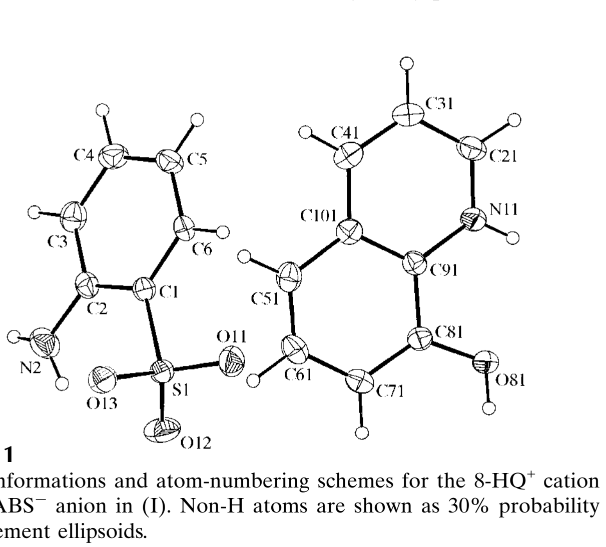


Figure 1
The conformations and atom-numbering schemes for the 8-HQ$^+$ cation and 2-ABS$^-$ anion in (I). Non-H atoms are shown as 30% probability displacement ellipsoids.

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2-aminobenzenesulfonic acid (orthanilic acid), namely 8-hydroxyquinolinium 2-aminobenzenesulfonate [(8-HQ)$^+$·(2-ABS)$^-$], (I), and with ferron, 8-hydroxyquinolinium 8-hydroxy-7-iodoquinoline-5-sulfonate sesquihydrate [(8-HQ)$^+$·$C_9H_6INO_4S\cdot1.5H_2O$], (II). As expected, in both compounds, proton transfer from the sulfonic acid group to the quinoline N atom of the oxine molecule occurs. Fig. 1 shows the atom-numbering scheme used for the 8-HQ$^+$ cation and the 2-aminobenzenesulfonate anion (2-ABS$^-$) in (I). A similar scheme is employed for the 8-HQ$^+$ cation in (II) (Fig. 2). Tables 1 and 2 list the geometric parameters for the hydrogen-bonding interactions in (I) and (II) and the symmetry codes used below.

Compound (I) exhibits a direct $N^+—H\cdots O^-_{sulfonate}$ interaction [N11—H11···O11 = 2.745 (4) Å; Fig. 3]. The 8-hydroxy substituent group of the 8-HQ$^+$ cation is strongly associated intermolecularly with a 2-ABS$^-$ sulfonate O atom [O81···O13^{ii} = 2.623 (3) Å]. As is usual for 8-HQ$^+$ cations, there is an intramolecular association between the quinolinium H atom and the phenol O atom [N11···O81 = 2.675 (4) Å], while in the 2-ABS$^-$ anion, the conformation of the sulfonate group is stabilized by $N_{amine}—H\cdots O$ and $C_{ring}—H\cdots O$ interactions [2.937 (5) and 2.875 (4) Å, respectively].

The inversion-related 8-HQ$^+$ cation rings form stacks that extend approximately along the *c* direction, with approximate superimposition of the C51/C61/C71/C81/C91/C101 six-membered rings. These have perpendicular separations of 3.40 (1) (intradimer) and 3.39 (1) Å (interdimer), with a ring-centroid separation of 3.78 (1) Å, which is strongly indicative of π–π interaction. These 'sandwich' dimers are similar to those found in the discrete dimeric 2:2 compound of oxine with salicylic acid (Smith, Wermuth & White, 2003), in which the intra- and interdimer separations are 3.34 and 3.40 Å, respectively (the ring-centroid separation is 3.58 Å). In this salicylate compound, the oxine rings are edge-linked by bis-salicylate cleats. In (I), the molecular pairs are peripherally linked to the sulfonate anions, forming sheets across the *ac* plane with only weak intersheet interactions [N2—H2*B*···O11^i = 3.402 (4) Å].

In (II), the protonated heterocyclic N atom of the 8-HQ$^+$ cation forms an intramolecular hydrogen bond with the phenol O atom similar to that in (I) [N11···O81 = 2.694 (6) Å; Fig. 4]. However, in contrast to the reaction in (I), the propagating interaction in (II) is with a water molecule [N11—H11···O1*W*^{iv} = 2.733 (5) Å] rather than with a sulfonate O atom. Although a direct $N^+—H\cdots O^-_{sulfonate}$ interaction is also found in the monohydrated compound of oxine with 5-sulfosalicylic acid (5-SSA; Smith, Wermuth & White, 2004), it is

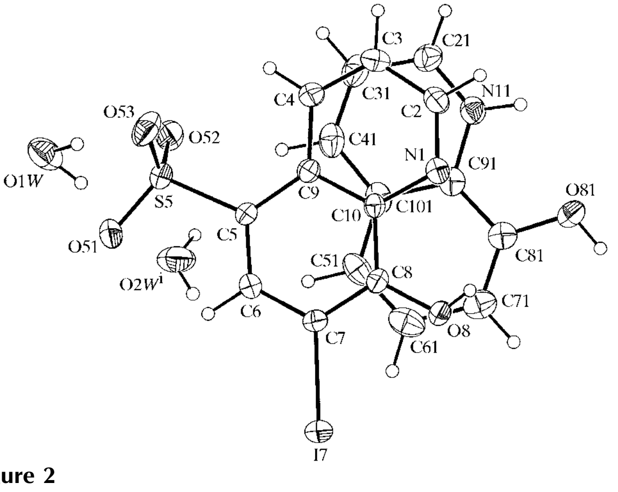

Figure 2

The conformation and atom-numbering scheme for (II), showing the 8-HQ$^+$ cation and ferron anion superimposition. Non-H atoms are shown as 30% probability displacement ellipsoids. [Symmetry code: (i) *x*, *y*, *z* − 1.]

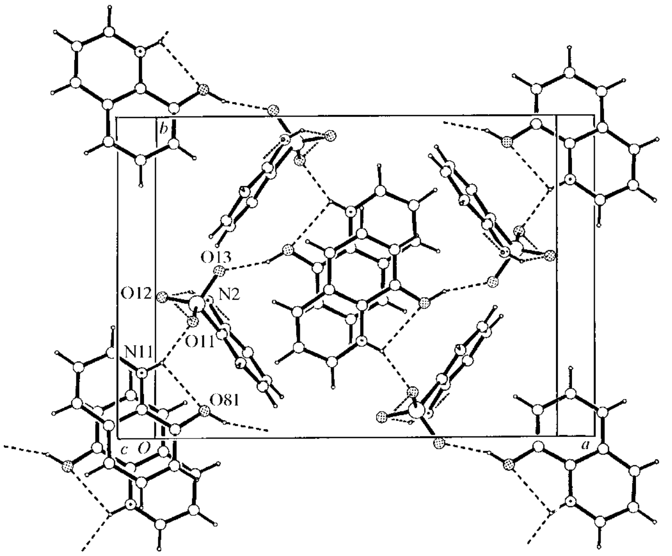

Figure 3

A perspective view of the packing of (I) in the unit cell, viewed down *c*, showing homomolecular stacks of oxine cations and hydrogen-bonding associations (broken lines).

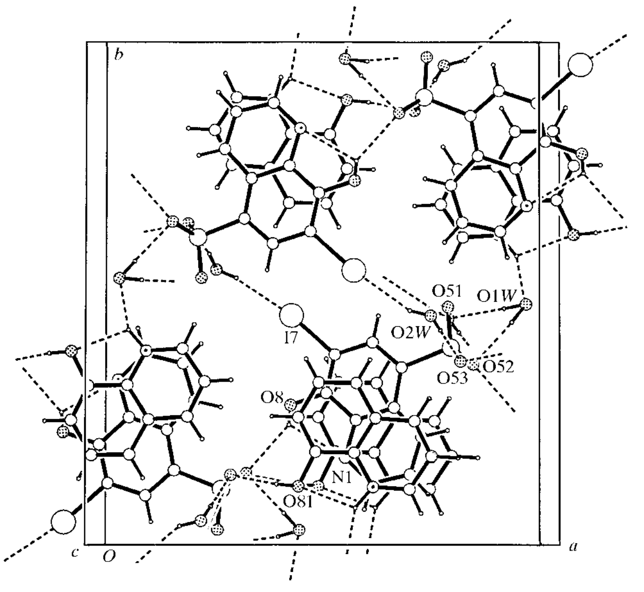

Figure 4

A perspective view of the packing of (II) in the unit cell, viewed down *c*, showing the 8-HQ$^+$-cation–ferron-anion stacks linked through hydrogen-bonding interactions (broken lines) also involving the water molecules.

more usual that, in the hydrated 5-SSA compounds with the quinoline-type Lewis bases, this primary interaction is with a water molecule. The ferron anion molecules have an intramolecular aromatic $\text{C6—H6}\cdots\text{O51}_{\text{sulfonate}}$ contact [2.823 (6) Å], while a short intermolecular $\text{O}W2\cdots\text{I7}^{\text{vi}}$ contact [3.17 (1) Å] is also present.

The molecules of (II) form stacks of alternating 8-HQ$^+$ cations and ferron anions, having approximate superimposition of the six-membered rings N11/C21/C31/C41/C101/C91 and N1/C2/C3/C4/C9/C10, with perpendicular separations of 3.51 (1) (intradimer) and 3.40 (1) Å (interdimer), also indicative of significant π–π interaction. These stacks form along the *c* axis and are linked by the previously described hydrogen bonds, as well as by a number of other associations involving the water molecules. This stacking phenomenon is consistent with perfect crystal cleavage perpendicular to the short [6.977 (4) Å] *c* axis. The presence of a hemihydrate molecule (O2*W*) is consistent with some lability in this molecule, although it is strongly associated in the crystal and only minor crystal decomposition (1.1%) was observed during data collection.

Experimental

The title compounds were synthesized by heating under reflux 1 mmol quantities of 8-quinolinol and either 2-aminobenzenesulfonic acid [for (I)] or 8-hydroxy-7-iodoquinoline-5-sulfonic acid [for (II)] in 50% ethanol/water (50 ml) for 10 min. After concentration to *ca* 30 ml, partial room-temperature evaporation of the hot-filtered solutions gave large pale-brown crystal blocks of (I) (m.p. 454.6–454.7 K) and large yellow prisms of (II) (m.p. 475.7–478.7 K).

Compound (I)

Crystal data

$C_9H_8NO^+\cdot C_6H_6NO_3S^-$
$M_r = 318.34$
Monoclinic, $P2_1/a$
$a = 16.030$ (4) Å
$b = 11.726$ (3) Å
$c = 7.7024$ (15) Å
$\beta = 100.298$ (17)°
$V = 1424.5$ (6) Å^3
$Z = 4$

$D_x = 1.484$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12.7$–$17.1°$
$\mu = 0.25$ mm^{-1}
$T = 298$ (2) K
Fragment, pale brown
0.40 × 0.20 × 0.10 mm

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (*TEXSAN for Windows*; Molecular Structure Corporation, 1999)
$T_{\min} = 0.942$, $T_{\max} = 0.976$
3780 measured reflections
3265 independent reflections

2047 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.053$
$\theta_{\max} = 27.5°$
$h = -8 \rightarrow 20$
$k = -15 \rightarrow 6$
$l = -10 \rightarrow 9$
3 standard reflections every 150 reflections intensity decay: 0.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.163$
$S = 0.90$
3265 reflections
212 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 3.934P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.011 (2)

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D$$\cdots$$A$	D—H$\cdots$$A$
N2—H2*A*$\cdots$O12	0.83 (3)	2.26 (4)	2.937 (5)	139 (3)
N2—H2*B*$\cdots$O11$^{\text{i}}$	0.86 (4)	2.60 (4)	3.402 (4)	157 (3)
N11—H11$\cdots$O81	0.85 (3)	2.35 (4)	2.675 (4)	103 (3)
N11—H11$\cdots$O11	0.85 (3)	1.95 (4)	2.745 (4)	155 (3)
O81—H81$\cdots$O13$^{\text{ii}}$	0.84 (3)	1.81 (3)	2.623 (3)	161 (3)
C6—H6$\cdots$O11	0.96	2.46	2.875 (4)	106

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

Compound (II)

Crystal data

$C_9H_8NO^+\cdot C_9H_5INO_4S^-\cdot 1.5H_2O$
$M_r = 523.30$
Monoclinic, $P2_1/a$
$a = 15.857$ (4) Å
$b = 17.667$ (7) Å
$c = 6.977$ (4) Å
$\beta = 95.78$ (4)°
$V = 1944.5$ (14) Å^3
$Z = 4$

$D_x = 1.791$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12.6$–$16.6°$
$\mu = 1.80$ mm^{-1}
$T = 298$ (2) K
Block, yellow
0.50 × 0.50 × 0.35 mm

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (*TEXSAN for Windows*; Molecular Structure Corporation, 1999)
$T_{\min} = 0.434$, $T_{\max} = 0.533$
5029 measured reflections
4473 independent reflections

3424 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.068$
$\theta_{\max} = 27.5°$
$h = -9 \rightarrow 20$
$k = 0 \rightarrow 22$
$l = -9 \rightarrow 9$
3 standard reflections every 150 reflections intensity decay: 1.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.158$
$S = 0.89$
4473 reflections
291 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 7.5983P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 1.55$ e Å^{-3}
$\Delta\rho_{\min} = -1.30$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0024 (6)

Table 2
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D$$\cdots$$A$	D—H$\cdots$$A$
O1*W*—H1*A*$\cdots$O52	0.97 (6)	1.96 (6)	2.882 (6)	156 (5)
O1*W*—H1*B*$\cdots$O2*W*$^{\text{i}}$	0.97 (6)	2.22 (6)	3.175 (11)	169 (5)
O2*W*—H2*A*$\cdots$I7$^{\text{vi}}$	0.79 (6)	2.44 (7)	3.169 (10)	155 (7)
O2*W*—H2*B*$\cdots$O53	0.90 (6)	1.94 (6)	2.848 (11)	180 (6)
O8—H8$\cdots$N1	0.86 (9)	2.26 (7)	2.687 (5)	111 (5)
O8—H8$\cdots$O52$^{\text{iii}}$	0.86 (9)	2.13 (8)	2.836 (5)	139 (6)
N11—H11$\cdots$O81	0.96 (7)	2.26 (7)	2.694 (6)	107 (5)
N11—H11$\cdots$O1*W*$^{\text{iv}}$	0.96 (7)	1.86 (7)	2.733 (5)	150 (6)
O81—H81$\cdots$O53$^{\text{v}}$	0.86 (6)	1.80 (6)	2.656 (5)	175 (5)
C6—H6$\cdots$O51	0.95	2.38	2.823 (6)	108

Symmetry codes: (i) $x, y, z-1$; (iii) $x-\frac{1}{2}, \frac{1}{2}-y, z$; (iv) $\frac{3}{2}-x, y-\frac{1}{2}, -z$; (v) $x-\frac{1}{2}, \frac{1}{2}-y, z-1$; (vi) $1-x, 1-y, 1-z$.

H atoms potentially involved in hydrogen-bonding interactions were located by difference methods and their positional and isotropic displacement parameters were refined. Other H atoms were included in the respective refinements at calculated positions (C—H = 0.95 Å) as riding atoms, with $U_{\text{iso}}(\text{H})$ values fixed at $1.2U_{\text{eq}}(\text{C})$. The large difference electron-density maximum and minimum for (II) are adjacent to the I atom.

For both compounds, 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: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON for Windows* (Spek, 1999); software used to prepare material for publication: *PLATON for Windows*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1460). Services for accessing these data are described at the back of the journal.

References

Balasubramanian, T. & Muthiah, P. T. (1996). *Acta Cryst.* C**52**, 2072–2073.

Castellano, E. E. & Prout, C. K. (1971). *J. Chem. Soc. A*, pp. 550–553.

Hemamalini, M., Muthiah, P. T., Bocelli, G. & Cantoni, A. (2004). *Acta Cryst.* C**60**, o284–o286.

Hughes, D. L. & Truter, M. R. (1979). *J. Chem. Soc. Dalton Trans.* pp. 520–527.

Jebamony, J. R. & Muthiah, P. T. (1998). *Acta Cryst.* C**54**, 539–540.

Merritt, L. L. Jr & Duffin, B. (1970). *Acta Cryst.* B**26**, 734–744.

Molecular Structure Corporation (1999). *MSC/AFC Diffractometer Control Software* and *TEXSAN for Windows* (Version 1.06). MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.

Prout, C. K. & Wheeler, A. G. (1966). *J. Chem. Soc. A*, pp. 1286–1290.

Prout, C. K. & Wheeler, A. G. (1967). *J. Chem. Soc. A*, pp. 469–475.

Rastogi, R. P., Singh, N. B. & Singh, R. P. (1977). *Indian J. Chem. Sect. A*, **15**, 941–946.

Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.

Singh, N. B., Singh, N. P., Kumar, V. A. & Nethaji, M. (1994). *J. Chem. Soc. Perkin Trans.* 2, pp. 361–366.

Singh, N. B., Singh, R. & Singh, K. (1999). *Mol. Cryst. Liq. Cryst.* **333**, 269–289.

Singh, N. B., Singh, R. & Singh, K. (2000). *Z. Phys. Chem.* **214**, 179–186.

Skoog, D. A., Holler, D. M. & West, F. J. (1988). *Analytical Chemistry*, 5th ed., pp. 76–77. New York: Saunders.

Smith, G., Wermuth, U. D. & Healy, P. C. (2003). *Acta Cryst.* E**59**, o1455–o1457.

Smith, G., Wermuth, U. D. & Healy, P. C. (2004). *Acta Cryst.* E**60**, o687–o689.

Smith, G., Wermuth, U. D. & White, J. M. (2000). *J. Chem. Soc. Chem. Commun.* pp. 2349–2350.

Smith, G., Wermuth, U. D. & White, J. M. (2001). *Aust. J. Chem.* **54**, 171–175.

Smith, G., Wermuth, U. D. & White, J. M. (2003). *CrystEngComm*, **5**, 58–61.

Smith, G., Wermuth, U. D. & White, J. M. (2004). *Acta Cryst.* C**60**, o575–o581.

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

Vogel, A. I. (1964). *Textbook of Macro and Semi-Micro Qualitative Inorganic Analysis*, 4th ed., p. 266. London: Longmans.