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Salicylaldoxime-III at 150 K

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.033
wR factor = 0.079
Data-to-parameter ratio = 9.7

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

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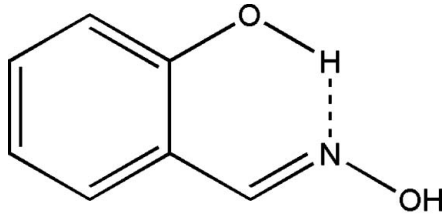
Salicylaldoxime derivatives crystallize in either hydrogen-bonded ring or chain motifs. A polymorph of the parent compound, salicylaldoxime, characterized by ring formation, has been known for some time. We now report a new polymorph of salicylaldoxime (2-hydroxybenzaldehyde oxime, $C_7H_7NO_2$), which exhibits chain formation and which has two molecules per asymmetric unit. π–π stacking interactions occur between the chains. We refer to this polymorph as salicylaldoxime-III.

Comment

Salicylaldoximes bearing branched alkyl chains are used as extractants to effect the separation and concentration operations in the hydrometallurgical recovery of copper, accounting for around 30% of annual production (Kordosky, 2002). The $N_2O_2^{2-}$ donor set in bis-salicylaldoxime complexes is stabilized by interligand hydrogen bonds, forming a pseudo-macrocyclic arrangement (*e.g.* Fig. 1*a*). The high selectivity of salicylaldoximes for copper over other metal ions is the result of the compatibility of the size of the cavity at the centre of the pseudo-macrocycle and the ionic radius of Cu^{2+} (Smith *et al.*, 2002).



(1)

The crystal structure of the parent compound salicylaldoxime, (1), was determined using X-ray diffraction by Pfluger & Harlow (1973) [Cambridge Structural Database (CSD, Version 5.27; Allen, 2002) refcode SALOXM]. We refer to the phase investigated by these workers as salicylaldoxime-I. We have recently shown that salicylaldoxime-I undergoes a phase transition at 5.3 GPa to a second phase, salicylaldoxime-II (Wood *et al.*, 2006).

Salicylaldoxime-I crystallizes in space group $P2_1/n$. Pairs of molecules, related by inversion centres, form intermolecular O—H···O hydrogen bonds to produce a dimer (Fig. 1*b*), for which the graph-set descriptor is $R_4^4(10)$ (Bernstein *et al.*, 1995). This dimeric form closely resembles the pseudo-macrocyclic arrangement observed in metal complexes, and is only observed in the free ligands in the solid state in salicylaldoxime derivatives which carry small substituents [*e.g.* CSD

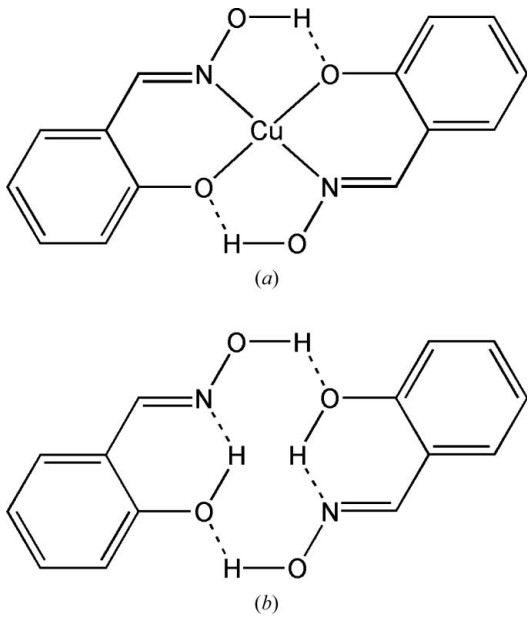


Figure 1
Pseudomacrocycle formation by salicylaldoxime. (*a*) Salicylaldoxime complexation by copper(II). (*b*) Hydogen-bonded dimers formed in the crystal structure of salicylaldoxime-I. Dashed lines indicate hydrogen bonds.

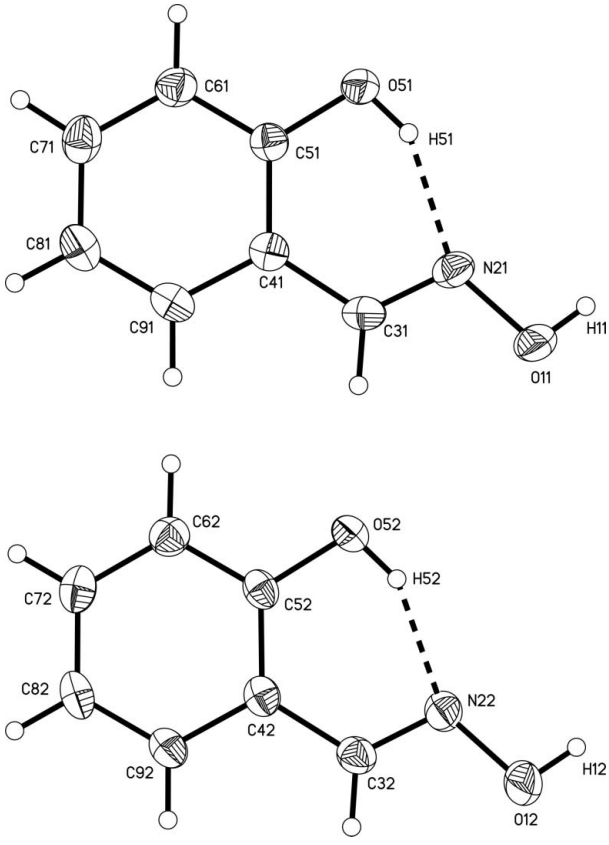


Figure 2
The two molecules comprising the asymmetric unit of salicylaldoxime-III. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as circles of arbitrary radii. Dashed lines indicate hydrogen bonds.

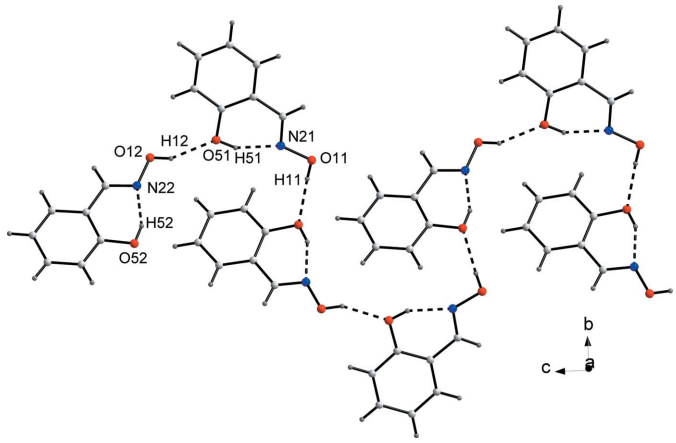


Figure 3
Hydrogen-bonded chains in salicylaldoxime-III. Dashed lines indicate hydrogen bonds.

refcodes ABULIT (Xu *et al.*, 2004) and CLSALX (Simonsen *et al.*, 1961)]. Bulky alkyl substituents lead to hydrogen-bonded chain motifs in preference to rings [*e.g.* CSD refcodes HEPKET10 (Koziol & Kosturkiewicz, 1984) and HELBOP (Maurin, 1994)].

We now report the crystal structure of a third polymorph of salicylaldoxime, salicylaldoxime-III, obtained under ambient conditions by recrystallization from a solution of hexane and chloroform. Weissenberg photographs, taken using a crystal of salicylaldoxime obtained from alcohol, were indexed by Merritt & Schroeder (1956) on the basis of an orthorhombic cell with dimensions a = 12.69, b = 13.51 and c = 7.98 Å, although no coordinates were determined. These cell dimensions closely resemble those determined here for salicylaldoxime-III. In the same paper, the authors report a powder pattern, which Pfluger & Harlow (1973) claim actually corresponds to the monoclinic form, salicylaldoxime-I. However, a powder pattern simulated (using *PLATON*; Spek, 2006) on the basis of the structural parameters reported here for phase III more closely resembles the data reported by Merritt & Schroeder (1956) than the pattern calculated for phase I (sourcing coordinates from CSD refcode SALOXM). For example, the first six simulated d spacings for form III are 6.89, 6.36, 5.89, 5.74, 5.04 and 4.61 Å; the corresponding data for phase I are 9.59, 6.54, 6.26, 4.82, 4.71 and 4.50 Å, while the data reported by Merritt & Schroeder are 6.76, 6.32, 5.99, 5.68, 5.10 and 4.58 Å. We therefore disagree with Pfluger & Harlow's conclusion regarding the pattern reported by Merritt & Schroeder.

Salicylaldoxime-III is characterized by the formation of hydrogen-bonded chains rather than hydrogen-bonded rings. There are two molecules in the asymmetric unit of salicylaldoxime-III (Fig. 2), which alternate along a hydrogen-bonded chain formed by intermolecular oximic O—H···O hydrogen bonds (Fig. 3). The chains run along the crystallographic c axis, being generated by a ..2_1 operation. Intramolecular phenolic O—H···N hydrogen bonds are also formed (Fig. 3).

The chains interact with each other *via* π–π stacking contacts formed between two symmetry-independent molecules. Within these stacking interactions, the atoms forming the phenyl ring of molecule 2 (based on O12 *etc*.) lie between 3.394 (2) and 3.519 (2) Å from the mean plane of molecule 1 (based on O11). The dihedral angle between the two phenyl planes is 2.69 (5)°.

Experimental

Salicylaldoxime was obtained from Acros. The solid was dissolved in chloroform and enough hexane was added to induce precipitation of a small quality of solid. Chloroform was added to redissolve the precipitated solid, and the solution was filtered into a small beaker through glass wool. Crystals of salicylaldoxime grew on allowing the solution to evaporate over the course of 5 d at room temperature.

Crystal data

$C_7H_7NO_2$
M_r = 137.14
Orthorhombic, $P2_12_12_1$
a = 7.6691 (2) Å
b = 12.7162 (3) Å
c = 13.3652 (3) Å
V = 1303.40 (5) Å^3
Z = 8
D_x = 1.398 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 150 K
Block, colourless
0.42 × 0.25 × 0.18 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2006)
T_{min} = 0.740, T_{max} = 0.980
15665 measured reflections
1886 independent reflections
1618 reflections with $I > 2\sigma(I)$
R_{int} = 0.061
θ_{max} = 28.9°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.079
S = 0.94
1886 reflections
194 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F^2) + (0.04P)^2]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}
Extinction correction: Larson (1970), equation 22
Extinction coefficient: 2.2 (2) × 10^2

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

D—H···A	D—H	H···A	D···A	D—H···A
O11—H11···O52^{i}	0.81 (2)	2.01 (2)	2.8137 (17)	176 (2)
O12—H12···O51^{ii}	0.87 (2)	1.99 (2)	2.7945 (18)	155 (2)
O51—H51···N21	0.86 (2)	1.85 (2)	2.6384 (18)	152 (2)
O52—H52···N22	0.85 (2)	1.84 (2)	2.6285 (18)	153.4 (19)

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

H atoms on O atoms (H11, H51, H12 and H52) were found in a difference Fourier map and their positions refined, subject to O—H distance restraints of 0.84 (5) Å and with U_{iso}(H) = 1.2U_{eq}(O). The remaining H atoms were positioned geometrically and constrained to ride on their host atoms, with C—H = 0.93–0.96 Å and with U_{iso}(H) = 1.2U_{eq}(C).

Data on this light-atom structure were collected with Mo $K\alpha$ radiation, and dispersion effects are negligible. The absolute configuration of the crystal used for data collection has not been determined in this study. Friedel pairs were merged.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT*; data reduction: *SAINT* (Bruker, 2003); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *DIAMOND* (Brandenburg, 2006) and *XP* (Sheldrick, 1997); software used to prepare material for publication: *CRYSTALS* and *PLATON* (Spek, 2006).

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