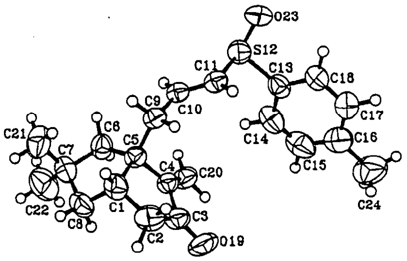

Fig. 1. View of the title compound with atom numbering.

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The Structure of 1,5-Bis(salicylidene)carbonohydrazide Monohydrate

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Abstract. $C_{15}H_{14}N_4O_3.H_2O$, $M_r = 316{\cdot}3$, orthorhombic, $C222_1$, $a = 12{\cdot}229\,(2)$, $b = 4{\cdot}553\,(1)$, $c = 27{\cdot}371\,(13)$ Å, $V = 1523{\cdot}98$ Å^3, $Z = 4$, molecular symmetry 2 (C_2), $D_m = 1{\cdot}39\,(1)$, $D_x = 1{\cdot}379$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}109$ mm^{-1}, $F(000) = 664$, $T = 298$ K. Final $R = 0{\cdot}042$ for 510 observed diffractometer data. The ligand as a whole is planar to within 0·081 (7) Å. The salicyl ring is planar to within 0·012 (7) Å with normal dimensions and is tilted by 3·0 (2)° from the remainder of the molecule. Bond lengths and angles suggest delocalization of π electrons in the part of the molecule adjacent to the salicyl ring. In addition to van der Waals forces, hydrogen bonding of the water O atom with the carbonyl O atom [O···O 2·730 (4) Å] stabilizes the molecular packing.

Introduction. Recently, Dutta & Hossain (1983) have synthesized bis(salicylidene)carbonohydrazide which acts a chelating ligand. Although several metal chelates of bis(salicylidene)thiocarbonohydrazide have been studied, there is no report on the complexing behaviour of its oxygen analogue. A number of coordination complexes of the latter ligand with nickel(II), cobalt(II), copper(II), oxovanadium(IV) and lead(II) have been synthesized. A comparison of the structural parameters of the free ligand with those of its metal complexes allows a discussion of the bonding in the metal complexes and hence a rationalization of some of their properties (Calligaris, Nardin & Randaccio, 1972).

Experimental. Title compound synthesized by mixing carbonohydrazide and salicylaldehyde and refluxing on a steam bath. Thin plate-shaped colourless crystals obtained by slow evaporation from alcohol at room

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temperature. D_m by flotation in aqueous $ZnSO_4$. Approximate lattice constants from rotation and Weissenberg photographs, accurate values by least squares from the 2θ values of 25 reflexions. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation; crystal *ca* 0·30 × 0·25 × 0·15 mm. Intensity data for $6{\cdot}0 \leq 2\theta \leq 45{\cdot}9°$; index range $0 \leq h \leq 13$, $0 \leq k \leq 4$, $0 \leq l \leq 30$; ω–2θ scan; three standard reflexions monitored periodically did not vary significantly during data collection; 641 independent reflexions, 510 $[I > 2\sigma(I)]$ employed for refinement; Lorentz–polarization corrections but no absorption or extinction correction. Structure solved using direct methods with *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) with 120 $|E|$ values $> 1{\cdot}3$ for phase determination; model completed by successive weighted Fourier syntheses; after isotropic full-matrix least-squares refinement, the H atoms (excluding phenolic and water H atoms) were included in calculated positions (C—H = 0·95 Å) and kept fixed during refinement; each H atom given the isotropic temperature factor of its associated non-H atom. A difference map at this stage revealed a peak close to 0·45, 0·5, 0·5, with maximum electron density 4·0 e Å^{-3}, and placed on twofold axis. This peak assigned to the O atom [called O(W)] of a molecule of water crystallization. Inclusion of one molecule of water in the formula provided better agreement between the calculated and measured densities. Block-diagonal least-squares refinement on F, anisotropic thermal parameters for non-H atoms, discontinued when all parameter shifts $<\sigma$. Final $R = 0{\cdot}042$, $wR = 0{\cdot}058$ for 510 observed reflexions. Weighting scheme based on modified $\sigma(F)$ (Seal & Ray, 1981) as follows: for $11{\cdot}41 < |F_o| \leq 14{\cdot}86$, $\sigma(F) = 0{\cdot}20|F_o|$; for $14{\cdot}86 < |F_o| \leq 18{\cdot}05$, $\sigma(F) = 0{\cdot}11|F_o|$; for $18{\cdot}05 < |F_o| \leq 21{\cdot}50$, $\sigma(F) = 0{\cdot}09|F_o|$; for $21{\cdot}50 < |F_o| \leq 25{\cdot}48$, $\sigma(F) = 0{\cdot}10|F_o|$; for $25{\cdot}48 < |F_o| \leq 31{\cdot}05$, $\sigma(F) = 0{\cdot}08|F_o|$; for $31{\cdot}05 < |F_o| \leq 37{\cdot}95$, $\sigma(F) = 0{\cdot}06|F_o|$; for $37{\cdot}95 < |F_o| \leq 48{\cdot}30$, $\sigma(F) = 0{\cdot}05|F_o|$; $48{\cdot}30 < |F_o| \leq 62{\cdot}90$, $\sigma(F) = 0{\cdot}04|F_o|$ and for $62{\cdot}90 < |F_o| \leq 102{\cdot}18$, $\sigma(F) = 0{\cdot}03|F_o|$. Phenolic and water H atoms could not be located and were not included in the structure-factor calculations. Final difference map was featureless, the max. peak being 0·2 and min. −0·3 e Å^{-3}. Final value of goodness of fit is 0·90. The thermal motion of the molecule is strongly anisotropic, with B_{33} larger than the other components for most of the atoms. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All computations performed on the Burroughs B 6700 computer of the Regional Computer Centre, Jadavpur University Campus, Calcutta, with program *XRAYARC* (Vickery, Bright & Mallinson, 1971). *EXFFT* and *SEARCH* of *MULTAN*78 used for weighted Fourier synthesis.

Discussion. The final coordinates are given in Table 1* and bond lengths and angles in Table 2. The labelling sequence in the molecule is given in Fig. 1.

The ligand as a whole is not quite planar, the maximum deviation of atoms from the least-squares plane is 0·081 (7) Å. However, the salicyl ring is strictly planar, the maximum deviation of an atom from the least-squares plane being 0·012 (7) Å. Bond distances and angles in the salicyl ring are satisfactory (mean C—C distance 1·388 Å) and it is tilted slightly from the remainder of the molecule [dihedral angle 3·0 (2)°]. The N—N distance is similar to those found in $[Ni(C_{19}H_{14}N_3O_2)_2].H_2O$ (Seth & Chakraborty, 1984) and is intermediate between single- and double-bond

Table 1. *Final fractional coordinates* (×10^4) *and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

$$B_{eq} = (B_{11} + B_{22} + B_{33})/3.$$

	x	y	z	B_{eq}(Å^2)
C(1)*	6772 (6)	10000	5000	3·9
C(2)	7482 (4)	5075 (12)	4073 (2)	4·0
C(3)	7056 (4)	3162 (13)	3702 (2)	3·9
C(4)	5928 (4)	2849 (13)	3616 (2)	4·6
C(5)	5575 (5)	1074 (16)	3236 (2)	5·9
C(6)	6300 (6)	−466 (15)	2954 (2)	5·6
C(7)	7419 (6)	−232 (15)	3037 (2)	5·4
C(8)	7777 (5)	1579 (13)	3407 (2)	4·7
N(1)	7377 (3)	8328 (10)	4696 (2)	4·0
N(2)	6866 (3)	6518 (10)	4363 (2)	4·0
O(1)*	5748 (4)	10000	5000	5·1
O(2)	5167 (3)	4270 (11)	3894 (2)	6·4
O(W)*	4515 (4)	5000	5000	5·1

* Atom at special position.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)—N(1)	1·350 (6)	C(1)—O(1)	1·253 (8)
C(2)—C(3)	1·434 (8)	C(2)—N(2)	1·278 (7)
C(3)—C(4)	1·407 (7)	C(3)—C(8)	1·397 (8)
C(4)—C(5)	1·387 (9)	C(4)—O(2)	1·365 (7)
C(5)—C(6)	1·368 (10)	C(6)—C(7)	1·39 (10)
C(7)—C(8)	1·376 (8)	N(1)—N(2)	1·377 (6)

N(1)—C(1)—O(1)	123·3 (4)	C(3)—C(2)—N(2)	122·6 (5)
C(2)—C(3)—C(4)	122·4 (5)	C(2)—C(3)—C(8)	119·6 (5)
C(4)—C(3)—C(8)	118·0 (5)	C(3)—C(4)—C(5)	119·3 (5)
C(3)—C(4)—O(2)	121·8 (5)	C(5)—C(4)—O(2)	118·9 (5)
C(4)—C(5)—C(6)	121·4 (6)	C(5)—C(6)—C(7)	120·4 (6)
C(6)—C(7)—C(8)	118·6 (6)	C(3)—C(8)—C(7)	122·3 (5)
C(1)—N(1)—N(2)	119·8 (4)	C(2)—N(2)—N(1)	116·9 (4)

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters, least-squares-planes calculations and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43692 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

lengths, indicating that the azo group is involved in resonance. The character of the azo bond is influenced by a number of factors, including the nature of the ligand, the resonance possibility of the ligand and, for metal complexes, the electron-withdrawing power of the metal.

The C(1)—N(1) bond length, 1·350 (6) Å, is comparable to 1·334 (12), 1·329 (11) Å for the analogous bond in the two independent molecules in 1,5-diphenylcarbazone (Blaton, Peeters, De Ranter & Willems, 1979). The C—N distance is about 0·10 Å shorter than that expected for an N—C(sp^2) single bond while the C(2)—C(3) distance of 1·434 (8) Å is rather shorter than a C(sp^2)—C(sp^2) single-bond length. This indicates a delocalization of π electrons, which is in accordance with the suggestion of Burke-Laing & Laing (1976) that the π electrons on N in a C—N bond are delocalized if this atom is involved in three σ bonds, especially if an N—H group is present (because intermolecular hydrogen bonding facilitates delocalization), or if a C=O group is adjacent.

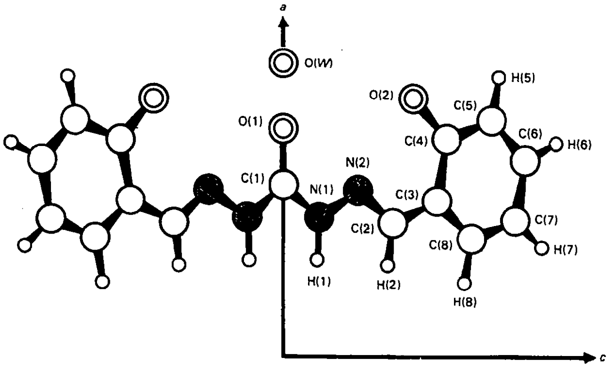

Fig. 1. View of the molcule along **b** showing the atom-numbering scheme. O(W) is situated on a different twofold axis from C(1) and O(1). C(1) and O(1) lie on the twofold axis at $y = 0$, $z = \frac{1}{2}$; O(W) lies on the twofold axis at $y = \frac{1}{2}$, $z = \frac{1}{2}$.

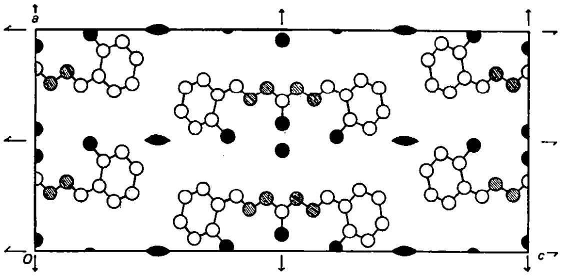

Fig. 2. Molecular packing viewed along **b**. H atoms have been omitted for clarity. C, N and O atoms are depicted by open circles, shaded circles and black circles respectively.

The C(sp^2)—O(sp^2) bond length [1·253 (8) Å] is slightly longer than a C=O double bond. A similar result has been obtained in related compounds such as carbonohydrazide [1·242 (2) Å] (Domiano, Pellinghelli & Tiripicchio, 1972). The C(sp^2)—N(sp^2) length, 1·278 (7) Å, is in good agreement with that in α-(1-phenylethylimino)benzyl phenyl ketone (Fonseca, Martínez-Carrera & García-Blanco, 1979). The C(sp^2)—O(sp^3) distance of 1·365 (7) Å is near the expected value.

Fig. 2 shows the contents of the unit cell projected along **b**. In the structure, a molecule of water of crystallization ($B_{eq} = 5{\cdot}1$ Å^2), lying on the twofold axis at $y = \frac{1}{2}$, $z = \frac{1}{2}$, is hydrogen bonded to O(1) of two ligand molecules lying on the twofold axes at $y = 0$, $z = \frac{1}{2}$ and $y = 1$, $z = \frac{1}{2}$. The H atoms attached to O(W) are not well resolved; but, judging from the O···O distance [2·730 (4) Å], a hydrogen bond may be assumed to exist and stabilize the ligand. Evidently the above intermolecular hydrogen bond in addition to the usual van der Waals forces stabilize the molecular packing. There are no unusually short intermolecular contacts so that packing forces are unlikely to influence the geometry of the molecule to an appreciable extent.

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