Synthesis and Crystal Structure of *N*-Salicylidene-2-hydroxy-5-chlorobenzylamine

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The title compound, *N*-salicylidene-2-hydroxy-5-chlorobenzylamine, was synthesized and the crystal structure was determined by the single-crystal X-ray diffraction method at 90 K. It crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.2114(15) \text{ \AA}$, $b = 12.5960(17) \text{ \AA}$, $c = 8.5169(12) \text{ \AA}$, $\beta = 96.039(2)^\circ$, $V = 1196.1(3) \text{ \AA}^3$, $D_x = 1.453 \text{ g/cm}^3$, and $Z = 4$. The $R1$ and $wR2$ values are 0.0358 and 0.0949, respectively, for 2805 reflections. The molecule is not planar with a dihedral angle between the two aromatic rings of $66.51(3)^\circ$.

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o-(Salicylideneaminomethyl)phenol and its substituted derivatives, which have two phenolic oxygen and one imino-nitrogen donor atoms, are unique tridentate ligands, giving mononuclear manganese(IV)¹ and vanadium(IV)² complexes and dinuclear vanadium(V),² iron(III),³ and copper(II)⁴ complexes with a meridional *O,N,O*-chelating. Although these ligands were originally synthesized by Yamaguchi many years ago,⁵ the structures have never been elucidated by X-ray crystal structure analysis, possibly because of a difficulty in crystallizing the Schiff-bases. In this study, we successfully isolated crystals of the title compound (Fig. 1, I) as one of these ligands, and determined the crystal structure.

2-Hydroxy-5-chlorobenzylamine (18 mg, 0.11 mmol) was dissolved in ethanol (2 cm³). To this solution was added salicylaldehyde (13 mg, 0.11 mmol) dissolved in 1 cm³ of ethanol, and the mixture was heated with stirring for 2 h, and then left at room temperature. The resulting yellow precipitate was filtered off. Yellow crystals suitable for X-ray crystallography were obtained by slow evaporation of the filtrate.

A preliminary examination was made, and data were collected on a Bruker CCD X-ray diffractometer (SMART APEX) using graphite-monochromated Mo- K_α radiation. Crystal data and details concerning data collection are given in Table 1. The

structures were solved by direct methods and refined by full-matrix least-squares methods. All of the hydrogen atoms were located from subsequent difference Fourier maps and refined. All of the calculations were carried out on a Pentium IV Windows 2000 computer utilizing the SHELXTL software package. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposit number CCDC-679448. Copies of the data can be obtained free of

Table 1 Crystal and experimental data

Chemical formula: C ₁₄ H ₁₂ ClNO ₂
Formula weight = 261.70
$T = 90 \text{ K}$
Crystal system: monoclinic
Space group: $P2_1/c$
$a = 11.2114(15) \text{ \AA}$
$b = 12.5960(17) \text{ \AA}$
$c = 8.5169(12) \text{ \AA}$
$V = 1196.1(3) \text{ \AA}^3$
$Z = 4$
$D_x = 1.453 \text{ g/cm}^3$
Radiation: Mo K_α ($\lambda = 0.71073 \text{ \AA}$)
$\mu(\text{Mo } K_\alpha) = 0.311 \text{ mm}^{-1}$
$F(000) = 544$
Crystal size = $0.40 \times 0.30 \times 0.30 \text{ mm}^3$
No. of reflections collected = 7348
No. of independent reflections = 2805
θ range for data collection: 1.83 to 28.66°
Data/Restraints/Parameters = 2805/0/211
Goodness-of-fit on $F^2 = 1.064$
R indices [$I > 2\sigma(I)$]: $R1 = 0.0339$, $wR2 = 0.0932$
R indices (all data): $R1 = 0.0358$, $wR2 = 0.0949$
$(\Delta\sigma)_{\text{max}} = 0.000$
$(\Delta\rho)_{\text{max}} = 0.388 \text{ e \AA}^{-3}$
$(\Delta\rho)_{\text{min}} = -0.208 \text{ e \AA}^{-3}$
Measurement: Bruker Smart APEX CCD diffractometer
Program system: SHELXTL
Structure determination: direct methods (SHELXS-97)
Refinement: full matrix least-squares (SHELXL-97)
CCDC deposition number: 679448

Fig. 1 Chemical structure.

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Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$). U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor

Atom	x	y	z	U_{eq}
Cl(1)	2161(1)	4582(1)	469(1)	24(1)
O(1)	756(1)	8972(1)	1577(1)	21(1)
O(2)	-1913(1)	9618(1)	-185(1)	21(1)
N(1)	-1503(1)	8000(1)	1635(1)	18(1)
C(1)	442(1)	7139(1)	1868(1)	17(1)
C(2)	1111(1)	7970(1)	1300(1)	17(1)
C(3)	2083(1)	7746(1)	466(1)	19(1)
C(4)	2397(1)	6700(1)	208(2)	19(1)
C(5)	1743(1)	5891(1)	794(1)	18(1)
C(6)	768(1)	6093(1)	1617(1)	18(1)
C(7)	-633(1)	7411(1)	2707(2)	19(1)
C(8)	-2588(1)	7704(1)	1187(1)	18(1)
C(9)	-3369(1)	8284(1)	71(1)	18(1)
C(10)	-2978(1)	9256(1)	-587(1)	18(1)
C(11)	-3810(1)	9770(1)	-1712(2)	23(1)
C(12)	-4921(1)	9348(1)	-2146(2)	25(1)
C(13)	-5286(1)	8385(1)	-1514(2)	25(1)
C(14)	-4519(1)	7872(1)	-413(2)	23(1)

Fig. 2 ORTEP view of the title compound, showing the labeling scheme of the non-H atoms. The thermal ellipsoids are shown at the 50% probability level.

Table 3 Selected bond distances ($\text{\AA}$), angles ($^\circ$), and torsion angles ($^\circ$)

Cl(1)-C(5)	1.7438(13)	N(1)-C(7)	1.4654(16)
O(1)-C(2)	1.3517(15)	C(1)-C(7)	1.5036(17)
O(2)-C(10)	1.2905(15)	C(8)-C(9)	1.4251(17)
N(1)-C(8)	1.2910(16)		
C(8)-N(1)-C(7)	125.64(11)	N(1)-C(7)-C(1)	109.51(10)
O(1)-C(2)-C(3)	122.65(11)	N(1)-C(8)-C(9)	122.85(11)
O(1)-C(2)-C(1)	117.27(11)	O(2)-C(10)-C(11)	122.76(12)
C(4)-C(5)-Cl(1)	118.66(10)	O(2)-C(10)-C(9)	120.76(11)
C(6)-C(5)-Cl(1)	119.60(10)		
C(1)-C(7)-N(1)-C(8)	119.47(13)	C(7)-N(1)-C(8)-C(9)	-176.32(11)
C(6)-C(1)-C(7)-N(1)	-118.04(12)	N(1)-C(8)-C(9)-C(14)	176.66(12)
C(2)-C(1)-C(7)-N(1)	60.56(14)	N(1)-C(8)-C(9)-C(10)	-1.41(19)
O(1)-C(2)-C(1)-C(7)	1.37(16)	O(2)-C(10)-C(9)-C(8)	0.25(18)

charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). The final atomic coordinates and equivalent isotropic displacement parameters for non-H atoms are listed in Table 2.

The molecular structure drawn by ORTEP is shown in Fig. 2. Selected bond distances and angles are given in Table 3. The N1-C7 distance is 1.4654(16) $\text{\AA}$, which is normal for a single bond, while the N1-C8 bond length of 1.2910(16) $\text{\AA}$ shows a double-bond character, although the two benzene rings are delocalized. The C7, N1, C8, and C9 moiety is essentially flat

Fig. 3 Packing diagram of the title compound, showing hydrogen bondings (dashed lines).

Table 4 Hydrogen-bonding geometry ($\text{\AA}$, $^\circ$)

D-H...A	D-H ($\text{\AA}$)	H...A ($\text{\AA}$)	D...A ($\text{\AA}$)	D-H...A ($^\circ$)
N(1)-H(2A)...O(2)	0.88(2)	1.85(2)	2.573(1)	137.4(15)
N(1)-H(2A)...O(1)	0.88(2)	2.31(2)	2.818(1)	116.7(14)
O(1)-H(1A)...O(2) ⁱ	0.85(2)	1.72(2)	2.562(1)	174.5(23)

Symmetry code: (i) $-x, -y+2, -z$.

(r.m.s. deviation from the mean plane is 0.019 $\text{\AA}$), which is consistent with the sp^2 hybrid character of the N atom. In fact, the d-Fourier map shows that a hydrogen atom is close to N1 atom with a distance of 0.88(2) $\text{\AA}$, rather than the O2 atom, which forms an intramolecular hydrogen bond, suggesting structure II in Fig. 1. The torsion angles around C7, C1-C7-N1-C8, C6-C1-C7-N1, and C2-C1-C7-N1 (Table 3) show that this molecule twists a little at the C7 atom, giving a dihedral angle of the aromatic rings containing C1 and C9 of 66.51(3) $^\circ$. This structural feature may be in harmony with the coordination to metal ion in a meridional fashion of this ligand. In the crystal, the molecules are connected by O-H...O hydrogen bonds, forming a dimer structure (Fig. 3). The hydrogen-bonding parameters are summarized in Table 4.

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