Crystal Structure of *N,N'*-Bis(2-chlorobenzylidene)ethylenediamine

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The crystal structure of *N,N'*-bis(2-chlorobenzylidene)ethylenediamine, C₁₆H₁₄Cl₂N₂, has been determined. The molecule possesses a crystallographically imposed center of symmetry. In the crystal packing, the molecules are linked *via* weak intermolecular C–H...N and C–H...Cl hydrogen bonds.

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Schiff-base ligands are able to coordinate metals through imine nitrogen and another group, usually linked to the aldehyde. Modern chemists still prepare Schiff bases, and nowadays active and well-designed Schiff-base ligands are considered to be “privileged ligands”. In fact, Schiff bases are able to stabilize many different metals in various oxidation states, controlling the performance of metals in a large variety of useful catalytic transformations. Schiff bases and their metal complexes play a key role in understanding the coordination chemistry of transition-metal ions.¹ In particular, the bidentate ligands containing imine groups have been used as modulators of structural and electronic properties of transition metal centres. The diversity in the coordination environment and the structures of these complexes mainly depend on the type of Schiff-base ligand.² As a prerequisite for these applications, a detailed structural study of this ligand and its substituted derivatives is needed. However, the crystal structural analysis of the Schiff-base ligand is not easy because of the very small size and poor quality of the crystals, which have proved to be twinned.

We report here on the synthesis and crystal structure of the title compound (I) with the aim of confirming its structural properties, and gaining further insight into its coordinating properties toward various transition-metal ions. A schematic drawing of the molecule described in this paper is given in Fig. 1.

The compound (I) was prepared by a facile and convenient method. Ethylenediamine (0.3 mmol, 18 mg) and 2-

chlorobenzaldehyde (0.6 mmol, 84 mg) were dissolved in chloroform (10 ml). The mixture was stirred at room temperature for 4 h. Recrystallization from a methanol and acetonitrile (1:1) solution afforded small yellow crystals.

An initial diffraction pattern was obtained using a Bruker SMART 1K CCD diffractometer and graphite-monochromated Mo K_α radiation. Attempts to solve the structure from these data failed, because the compound yielded only very small crystals. Thus, synchrotron X-ray radiation was required to generate a sufficiently strong diffracted intensity for their characterization by single-crystal diffraction analysis. An attempt to use synchrotron data obtained by using a 0.01 × 0.01 × 0.01 mm³ crystal with a Bruker APEX2 CCD diffractometer

Table 1 Crystal data experimental data

Formula: C ₁₆ H ₁₄ Cl ₂ N ₂	
Formula weight = 305.19	
Crystal system: monoclinic	
Space group: <i>Cc</i>	<i>Z</i> = 8
<i>a</i> = 10.329(5) Å	
<i>b</i> = 10.239(5) Å	
<i>c</i> = 26.633(13) Å	
β = 99.554(6)°	
<i>V</i> = 2777(2) Å ³	
<i>D_x</i> = 1.460 g/cm ³	
No. of reflections used = 4814	
2 θ _{max} = 59.06°	
μ = 0.595 mm ⁻¹	
<i>T</i> = 120(2) K	
λ (synchrotron) = 0.7848 Å	
<i>R</i> = 0.1180	
<i>wR</i> = 0.3011	
($\Delta\rho$) _{max} = 0.013	
($\Delta\rho$) _{max} = 1.11 e Å ⁻³	
($\Delta\rho$) _{min} = -0.72 e Å ⁻³	
Measurements: Bruker APEX2 CCD	
Program system: APEX2 and SAINT	
Structure determination: direct methods (SHELXTL)	
Refinement: full-matrix least-squares	

Full crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 625978.

Fig. 1 Chemical structural diagram of *N,N'*-bis(2-chlorobenzylidene)ethylenediamine, (I).

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Fig. 2 Perspective views of the two crystallographically independent molecules in the title compound (I). Displacement ellipsoids are drawn at the 50 % probability level.

Table 2 Selected bond distances(Å) and angles (°)

N1-C8	1.419(18)	C1-C11	1.717(12)
N1-C7	1.271(16)	C16-C12	1.760(11)
N2-C10	1.239(15)	C17-C13	1.719(11)
N2-C9	1.460(16)	C32-C14	1.799(12)
N3-C24	1.46(2)	C24-C25	1.557(19)
N3-C23	1.296(16)	C8-C9	1.574(15)
N4-C25	1.476(14)	C6-C7	1.459(18)
N4-C26	1.217(17)	C10-C11	1.527(15)
C7-N1-C8	115.5(12)	C6-C7-N1	122.1(12)
C9-N2-C10	117.9(10)	N2-C9-C8	110.7(10)
C23-N3-C24	117.8(11)	N4-C25-C24	108.6(10)
C25-N4-C26	118.1(10)	C11-C1-C6	121.0(9)

on Station 16.2 SMX at the Synchrotron Radiation Source (SRS) at Daresbury, UK was successful. The wavelength was 0.7848 Å.³ The unit-cell parameters were determined using APEX2, and refined based on the positions of all strong reflections using SAINT.⁴ An absorption correction was unnecessary for this small crystal, but SADABS⁵ was used to correct for synchrotron beam decay. The structure was solved by direct methods using SIR97⁶ and refined by full-matrix least-squares on F^2 using SHELXTL with 244 restraints.⁷ H atoms were placed in calculated positions, with C-H distances of 0.95–0.99 Å, and treated as riding atoms, with $U_{\text{iso}}(\text{H}) = 1.3 U_{\text{eq}}(\text{C})$. The crystal and experimental data are summarized in Table 1. The crystal was found to be non-merohedrally twinned, with a contribution of the minor component of 11.8(4)%. Furthermore, it was inversion twinned, with an enantiopole parameter of 0.5(2), the standard uncertainty being rather high for this poor-quality crystal.

The structure analysis of compound (I) reveals the asymmetric unit of the crystal structure to contain two symmetry-independent molecules (Fig. 2) with some differences in the bond lengths, angles and torsion angles [for example, we can compare the torsion angles $\text{C10-N2-C9-C8} = 123.8(11)^\circ$ and $\text{C7-N1-C8-C9} = -122.9(11)^\circ$ with the corresponding angles $\text{C26-N4-C25-C24} = -118.8(12)^\circ$ and $\text{C23-N3-C24-C25} = 122.0(11)^\circ$ in the other molecule].

Table 3 Hydrogen-bond geometry (Å, °)

D-H...A	D-H	H...A	D...A	D-H...A
C21-H21A...N3	0.95	2.59	2.865	97
C28-H28A...N4	0.95	2.61	2.870	96
C5-H5A...N1	0.95	2.60	2.873	97
C12-H12A...N2	0.95	2.60	2.865	96
C7-H7A...Cl1	0.95	2.72	3.076	103
C10-H10A-Cl2	0.95	2.76	3.083	101
C23-H23A...Cl3	0.95	2.67	3.057	105
C26-H26A...Cl4	0.95	2.69	3.099	107

In compound (I), two 2-chlorobenzylidene groups are bridged by ethylenediamine *via* two C=N double bonds in an extended conformation. The N1-C8 and N1-C7 bond lengths are 1.419(18) and 1.271(16) Å (Table 2), which are typical values of C-N and C=N bonds, respectively. The crystals are held together by hydrogen bonds between secondary CH groups and N and Cl atoms in the neighbouring molecules (Table 3).⁸

The small crystal size and poor quality lead to a structure of relatively low precision; as a result, some atomic displacement ellipsoids have elongated shapes, and chemically equivalent geometrical parameters show some differences, though these are generally not large compared with the standard uncertainties. A least-squares fit of the two molecules, excluding H atoms, gives an r.m.s. deviation of 0.140 Å; this is reduced to 0.045 Å for the central chain linking the two rings, indicating that the two molecules are very similar, the main difference being in small twists of the rings relative to the linking chain.

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