

trans-[*N,N'*-Bis(salicylidene)cyclohexane-1,2-diaminato]nickel(II)–chloroform (1/1)

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In the title complex, *trans*-{2,2'-[cyclohexane-1,2-diylbis(nitri-*l*omethylidene)]diphenolato- κ^4 O,*N,N',O'*}nickel(II)–chloroform (1/1), [Ni(C₂₀H₂₀N₂O₂)]·CHCl₃, the Ni atom has a square-planar geometry, slightly tetrahedrally distorted. The Ni–N and Ni–O bonding distances are within the expected ranges for Ni–Schiff base derivatives. The diimine bridge has a *gauche* conformation with the cyclohexyl ring almost coplanar with the NiN₂O₂ plane. The complex molecules pack in dimers with an Ni···Ni distance of 3.59 (1) Å and form a three-dimensional structure displaying a herring-bone configuration. Channels are occupied by solvent molecules, which are involved in C–H···O hydrogen bonds with the ligand O atoms.

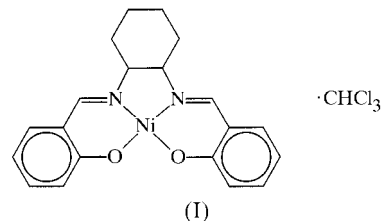
Comment

Nickel(II) complexes with N₂O₂ Schiff base ligands derived from salicylaldehyde have long been used as homogenous catalysts (Gosden *et al.*, 1978, 1981; Healy & Pletcher, 1980), and more recently, the preparation by oxidative electropolymerization of the metal complexes of metal salen-based modified electrodes prompted their use in heterogenous electrocatalysis (Dahm & Peters, 1996). Work in our laboratory has attempted to assess the role played by structural/electronic effects to control the redox chemistry of the Ni^{II} metal centres which may prove to be critical in the design and improvement of new catalysts.

The asymmetric unit of the title complex, (I), contains one [*N,N'*-bis(salicylidene)cyclohexane-1,2-diamine]nickel(II) molecule and a chloroform solvate molecule. Fig. 1 shows the molecular structure of the title compound with the atomic labelling scheme used.

The Ni atom adopts a square-planar coordination geometry, the N₂O₂ plane being slightly tetrahedrally distorted [maximum deviation of 0.044 (2) Å for both O1 and O2]. The

Ni atom is well within the plane [deviation of 0.002 (2) Å]. This geometry is very similar to the overall coordination geometry found in the corresponding optically active complex [Ni(–)chxn(sal)₂] (Wojtczak *et al.*, 1997) and its α,α' -Me derivative [Ni(–)chxn(hapi)₂] (Szlyk *et al.*, 1999), as well as in the *R,S* isomer of the latter (Azevedo *et al.*, 1994), whose



values are presented in Table 2. We have found that the coordination geometry is usually more tetrahedrally distorted when the substituents in the imine bridge are bulkier or the substitution is asymmetric, as in complexes [Ni(saltMe)] and [Ni(saldMe)] (Santos *et al.*, 2000), where the tetrahedral distortion has a high value of ± 0.124 Å even though the Ni atom is still within the mean least-squares plane (Ni is 0.0134 Å out of the plane).

Both the Ni–N and the Ni–O bonding distances [1.844 (3)/1.849 (3) and 1.840 (3)/1.842 (3) Å, respectively] are in good agreement with those observed in similar Schiff base Ni complexes and are similar to the average values found in a Cambridge Structural Database search for compounds having a cyclohexyl substituent in the imine bridge [values range from 1.848 (7) to 1.853 (6) Å; Allen *et al.*, 1983].

The dihedral angle between the two chelating ring systems is 6.1 (2)° and the angles between the N₂O₂ coordinating plane and the N1···O1 and N2···O2 planes are, respectively, 9.9 (2) and 4.0 (2)°, indicating a flat arrangement of the molecule. This is similar to the geometry of the two symmetry-independent molecules in the [Ni(–)chxn(sal)₂] complex (Wojtczak *et al.*, 1997) (see Table 2). These values are rather small compared with those found for [Ni(–)chxn(hapi)₂] (Szlyk *et al.*, 1999) and the corresponding *R,S* isomer (Azevedo *et al.*, 1994) (see Table 2), which show a larger distortion of the planar geometry, especially in the *R,S* isomer. This distortion is more pronounced in the α,α' -Me-substituted compounds due to the steric requirements imposed by the interaction between the H atoms of the cyclohexyl ring and the bulky methyl groups of the aromatic ring systems in the ligand.

The NCCN torsion angle of -44.7 (4)° defines a *gauche* conformation of the imine bridge, similar to the complexes mentioned above (see Table 2). Atoms C3 and C8 are positioned on opposite sides of the N₂O₂ plane, -0.413 (6) and 0.284 (6) Å from it, respectively. A similar arrangement of the bridging C atoms has also been observed in the [Ni(–)chxn(sal)₂] complex (Wojtczak *et al.*, 1997), while in both methylated derivatives (Szlyk *et al.*, 1999; Azevedo *et al.*, 1994), the bridging C atoms are on the same side of the N₂O₂ plane. The steric effects in the α,α' -Me-substituted compounds affect also the cyclohexyl ring orientation, which is best described by the dihedral angle between its best plane and

N_2O_2 coordination plane. This dihedral angle is much larger in the substituted complexes, 34.7° in the $[\text{Ni}(-)\text{chxn}(\text{hapi})_2]$ complex (Szyk *et al.*, 1999) and 73.2° in the R,S isomer (Azevedo *et al.*, 1994) compared with $8.4(3)^\circ$ in the title structure and 11.0° in the $[\text{Ni}(-)\text{chxn}(\text{sal})_2]$ complex (Wojtczak *et al.*, 1997), showing a very small tilt of the central fragment of the ligand towards the potential axial ligand. When comparing these values, it should be noted that the R,S isomer used here for comparison is the *cis* isomer of the methylated derivative.

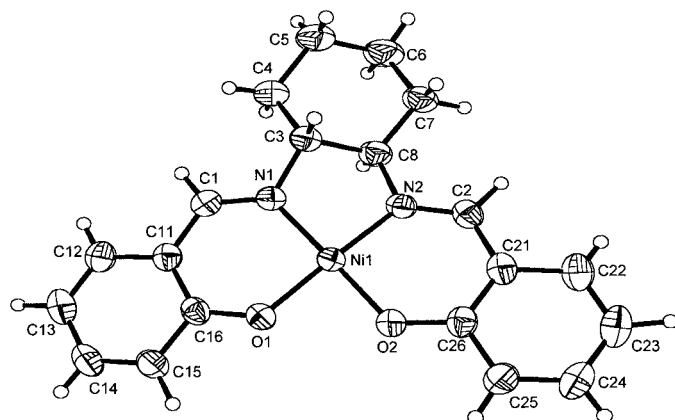


Figure 1
ORTEPII (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

The crystal packing of the title compound involves the pairing of two symmetry-related complex molecules (symmetry code: $1 - x, 2 - y, -z$) to form dimers. Such an arrangement has also been observed in other Ni Schiff base structures (Azevedo *et al.*, 1994; Encan *et al.*, 1997; Manfredotti & Gusatini, 1983; Akhtar, 1981). In the optically active derivative of the title compound (Wojtczak *et al.*, 1997), the dimer is formed by a non-crystallographic twofold axis. The observed distance $\text{Ni} \cdots \text{Ni}'$ of $3.59(1) \text{ \AA}$ is in the same order of magnitude as the values found in the complexes mentioned above [range $3.201\text{--}3.582(1) \text{ \AA}$]. The dimers stack along **b** with a dimer–dimer distance of $7.91(3) \text{ \AA}$. In the methylated derivatives as well as on other complexes with bulky substituents in the imine bridge (Allen *et al.*, 1983), the formation of dimers is not observed.

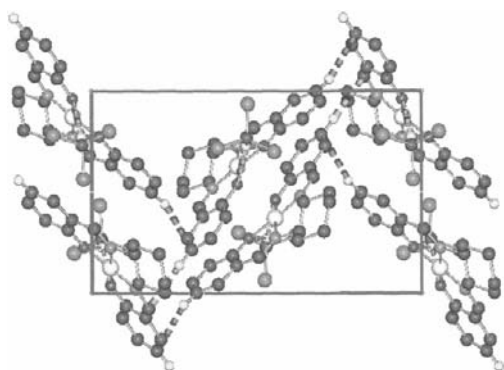


Figure 2
SCHAKAL (Keller, 1997) diagram of the crystal packing along **a** showing the herring-bone arrangement of the complex molecule.

When viewed along the crystallographic *a* axis, the relative orientation of the complex molecules exhibits a herring-bone configuration (Fig. 2). This arrangement is stabilized by short $\text{C}—\text{H} \cdots \text{C}$ intermolecular interactions [$\text{C}23—\text{H}23 \cdots \text{C}2$ $2.71(4) \text{ \AA}$ and $\text{C}13—\text{H}13 \cdots \text{C}23$ $2.76(5) \text{ \AA}$].

The channels in the herring-bone arrangement are occupied by solvent molecules which are stabilized by $\text{C}—\text{H} \cdots \text{O}$ hydrogen bonds between the two O atoms of the ligand and the CH group of the chloroform molecule. The CHCl_3 displays bifurcated asymmetric $\text{C}—\text{H} \cdots \text{O}$ intermolecular contacts of $2.36(3) \text{ \AA}$ for $\text{C}10—\text{H}10 \cdots \text{O}1$ and $2.41(3) \text{ \AA}$ for $\text{C}10—\text{H}10 \cdots \text{O}2$, with angles of $144(4)$ and $152(5)^\circ$, respectively.

Experimental

The title nickel(II) complex was prepared by standard procedures (Santos *et al.*, 2000). An ethanolic solution of the Schiff base was added to a solution of nickel(II) acetate in ethanol and the resulting mixture refluxed. After cooling, a red–brown solid was filtered off, washed with ethanol and diethyl ether, and dried under vacuum. Diffraction-quality crystals were obtained by slow diffusion of ethanol and chloroform. The 1,2-diaminocyclohexane ligand (from Aldrich) used to prepare the Schiff base derivative H_2salhd was a mixture of the *cis* and *trans* isomers. As established by the X-ray crystallographic analysis, the crystals obtained were of the *trans* isomer.

Crystal data

$[\text{Ni}(\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2)] \cdot \text{CHCl}_3$
 $M_r = 498.46$
 Monoclinic, $P2_1/n$
 $a = 13.249(4) \text{ \AA}$
 $b = 10.086(9) \text{ \AA}$
 $c = 16.695(5) \text{ \AA}$
 $\beta = 101.99(2)^\circ$
 $V = 2182(2) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.52 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 12\text{--}14^\circ$
 $\mu = 1.276 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Parallelepiped, orange
 $0.20 \times 0.04 \times 0.03 \text{ mm}$

Data collection

Enraf–Nonius MACH3 diffractometer
 ω – 2θ scans
 8599 measured reflections
 3839 independent reflections
 3068 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$
 $\theta_{\text{max}} = 25.02^\circ$

$h = -15 \rightarrow 15$
 $k = -1 \rightarrow 11$
 $l = -19 \rightarrow 19$
 3 standard reflections every 240 reflections
 frequency: 90 min

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.156$
 $S = 1.060$
 3839 reflections
 346 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.079P)^2 + 3.473P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.041$
 $\Delta\rho_{\text{max}} = 0.91 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.78 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Ni1—O1	1.840(3)	N1—C1	1.284(5)
Ni1—O2	1.842(3)	N1—C3	1.487(5)
Ni1—N1	1.844(3)	N2—C2	1.289(5)
Ni1—N2	1.849(3)	N2—C8	1.475(5)
O1—Ni1—O2	83.52(13)	O1—Ni1—N2	177.09(13)
O1—Ni1—N1	94.87(13)	O2—Ni1—N2	95.21(14)
O2—Ni1—N1	176.77(14)	N1—Ni1—N2	86.52(14)

Table 2

Comparison of the geometric parameters of similar Schiff base Ni complexes (\AA , $^\circ$).

D1 is the maximum deviation from the N_2O_2 plane; *D2* is the deviation of the Ni atom from the least-squares N_2O_2 plane; *A1* is the dihedral angle between the two chelating rings; *A2* is the angle between the N_2O_2 plane and the $\text{N1}\cdots\text{O1}$ plane; *A3* is the angle between the N_2O_2 plane and the $\text{N2}\cdots\text{O2}$ plane; *A4* is the $\text{N}-\text{C}-\text{C}-\text{N}$ torsion angle.

(I)	$[\text{Ni}(-)\text{chxn}(\text{sal})_2]$	$[\text{Ni}(-)\text{chxn}(\text{hapi})_2]$	$[\text{Ni}(\alpha,\alpha'\text{-Mesalhd})]$
<i>D1</i>	0.044 (2)	± 0.08	± 0.0039
<i>D2</i>	0.002 (2)	0.06	-0.029
<i>A1</i>	6.1 (2)	8.9 (3)/10.3 (2)	43.5 (1)
<i>A2</i>	9.9 (2)	4.0 (2)/7.3 (2)	24.9 (2)
<i>A3</i>	4.0 (2)	4.9 (3)/4.7 (2)	19.0 (2)
<i>A4</i>	-44.7 (4)	-46.3 (6)/ -46.1 (6)	-39.0 (5)

All H atoms were refined isotropically [$\text{C}-\text{H}$ distance range 0.80 (5)–1.14 (6) \AA].

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SORTX* (McArdle, 1995), *ORTEPII* (Johnson, 1976) and *SCHAKAL* (Keller, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1056). Services for accessing these data are described at the back of the journal.

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