

# {*N,N'*-Bis[3-methoxymethyl-5-methyl-salicylidene]-(*R,R*)-1,2-diphenylene-diamino}nickel(II)

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## Key indicators

Single-crystal X-ray study

*T* = 295 K

Mean  $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$

*R* factor = 0.043

w*R* factor = 0.100

Data-to-parameter ratio = 19.3

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

In the title compound, 6,6'-bis(methoxymethyl)-4,4'-dimethyl-2,2'-[1,2-diphenyl-1,2-ethanediylbis(nitrilomethylidyne)]diphenol, [ $\text{Ni}(\text{C}_{34}\text{H}_{34}\text{N}_2\text{O}_4)$ ], there are two independent molecules per asymmetric unit; both have a twofold axis. These molecular structures are two rotamers in the presence of steric repulsions between the ether groups, and the coordination geometry around the  $\text{Ni}^{\text{II}}$  atom is slightly tetrahedrally distorted square planar. The rotamers are stacked alternately along the *c* axis.

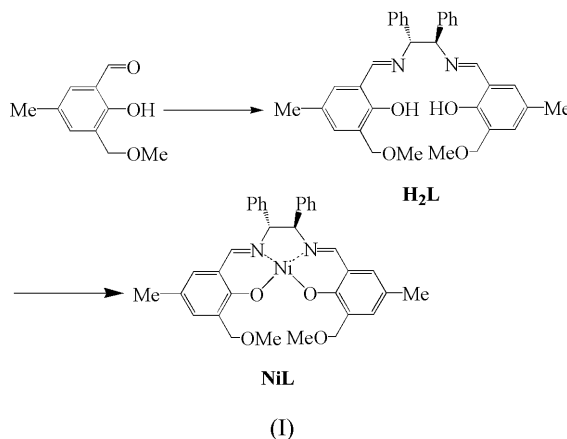
Received 23 September 2003

Accepted 2 October 2003

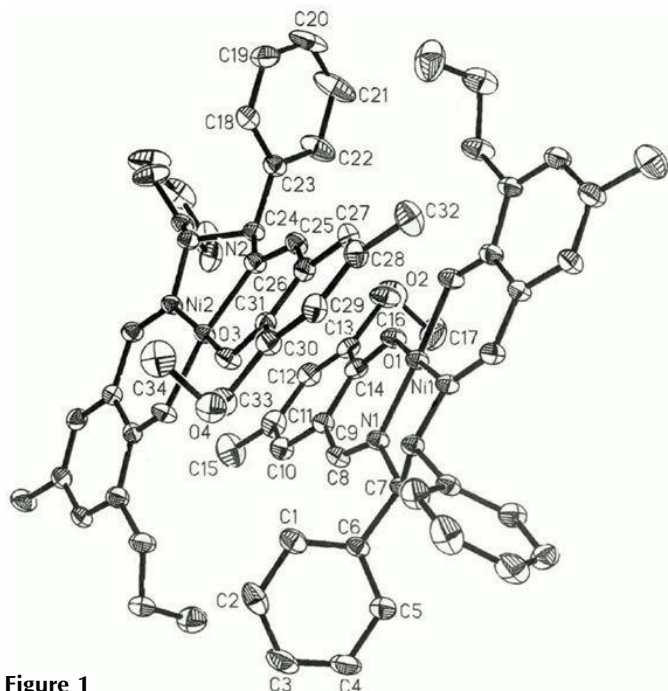
Online 7 October 2003

## Comment

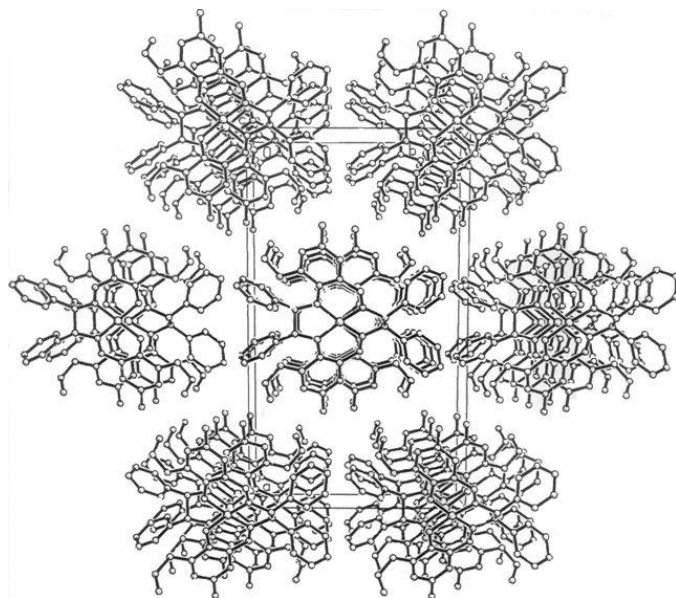
Metal complexes with a salen-type ligand have attracted much interest in recent decades because of their excellent unique asymmetric catalytic activity. Further research on salen-type complexes is very important in order to accelerate the development of their use in asymmetric catalyses. In asymmetric catalytic epoxidation of *trans*-olefins, introducing new chirality at the 3,3'-positions of the salen ligand is very important for the e.e. of the products (Hosoya *et al.*, 1994; Zhang *et al.*, 1990). Our group developed a cheap and easy method to synthesize new salen-type ligands with long ether residues at the 3,3'-positions for the purpose of introducing new chirality (Wu *et al.*, 2001). Due to the bulky effect, the two ether groups cannot be on the same side of the coordination plane and each salicylic phenyl residue may tilt in the same direction as its own ether residue. If the 3,3'-ether groups can swing up and down freely, the rotamers cannot be stable. If they can be on the same side, another rotamer can occur (three rotamers occur). This paper reports the molecular and crystal structure of the title compound, (I).



In the asymmetric unit, there are two independent molecules, each of which has a twofold axis (Fig. 1 and Table 1). Each  $\text{Ni}^{\text{II}}$  atom is coordinated by two O and two N atoms, forming a slightly tetrahedrally distorted square-planar



**Figure 1**  
A view of the two independent molecules of (I), showing 25% probability displacement ellipsoids for non-H atoms. Unlabelled atoms are related to labelled atoms by a twofold axis.



**Figure 2**  
The crystal packing of (I), viewed approximately down the *c* axis.

structure. The dihedral angle between the N1/Ni1/O1 and N1<sup>i</sup>/Ni/O1<sup>i</sup> chelate planes is 3.91 (8)°, and that between the N2/Ni2/O3 and N2<sup>ii</sup>/Ni2/O3<sup>ii</sup> planes is 12.93 (4)° [symmetry codes: (i) 1 - *x*, *y*, -*z*; (ii) 1 - *x*, *y*, 1 - *z*]. The ether group (methoxymethyl) and its symmetry-related counterpart do not appear on the same side of the coordination plane due to steric repulsion. As a result, two rotamers occur. In the Ni1 complex, the O2/C17 moiety is on the same side as the H atom on the closer chiral atom C7, whereas in the Ni2 complex, the O4/C34 moiety is on the opposite side to the H atom on the

closer chiral atom C24. The salicylic benzene rings are tilted in the same orientation as their own ether group from the coordination plane. In order to distinguish the rotamers, we denote the Ni1 and Ni2 complexes as *P* and *M* (plus and minus) configurations, respectively (Cahn *et al.*, 1966; Miguel *et al.*, 2003). In the crystal structure, the two rotamers are stacked alternately along the *c* axis (Fig. 2).

## Experimental

The ligand (H2L) was prepared as follows: 2-formyl-6-(methoxymethyl)-4-methylphenol (2 mol) was dissolved in 5 ml ethanol and 5 ml ethanol solution of (*R,R*)-1,2-diphenylethandiamine (2 mmol) was added slowly. The resulting mixture was stirred and refluxed for 2 h. The ethanol was evaporated and a yellow oil was obtained. The residue was chromatographed on silica gel (ethyl acetate–petroleum ether = 40:1–10:1) to give yellow solid (yield 99%; m.p. 330–331 K). IR (KBr, cm<sup>-1</sup>): 2900–2600 (*s, br*), 1628 (*vs*), 1602 (*s*), 1460 (*s*), 1263 (*m*), 1119 (*m*), 1092 (*m*); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.23 (*s*, Ar–CH<sub>3</sub>, 6H), 3.46 (*q*, –OCH<sub>3</sub>, 6H), 4.56 (*s*, Ar–CH<sub>2</sub>OR, 4H), 4.69 [*s*, =NCH(C<sub>6</sub>H<sub>5</sub>)–, 2H], 6.91 (*s*, C<sub>6</sub>H–H, 2H), 7.19 (*m*, C<sub>6</sub>H<sub>5</sub> + C<sub>6</sub>H–H, 12H), 8.32 (*s*, –CH=N, 2H), 13.37 (*s*, –OH, 2H); FAB–MS: *m/z* = 537(*M*<sup>+</sup> + 1). An ethanol solution (2 ml) of Ni(OAc)<sub>2</sub> (1.1 mmol) was added to the yellow ethanol solution (5 ml) of H<sub>2</sub>L (1 mmol). The resulting solution was refluxed for 2 h and then cooled to room temperature. The precipitate was collected by filtration, washed with ethanol and dried in a vacuum (90% yield; m.p. 512 K). The crystals of NiL, (I), were grown from an ethanol solution at room temperature. Analysis found: C 68.63, H 5.87, N 4.90%; calculated: C 68.83, H 5.78, N 4.72%. IR (KBr, cm<sup>-1</sup>): 1620 (*vs*), 1545 (*vs*), 1444 (*vs*), 1227 (*m*), 1103 (*m*); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.17 (*s*, Ar–CH<sub>3</sub>, 6H), 3.54 (*q*, –OCH<sub>3</sub>, 6H), 4.61 (*s*, Ar–CH<sub>2</sub>OR, 4H), 4.43 [*s*, =NCH(C<sub>6</sub>H<sub>5</sub>)–, 2H], 6.68 (*s*, C<sub>6</sub>H–H, 2H), 7.18–7.90 (*m*, C<sub>6</sub>H<sub>5</sub> + C<sub>6</sub>H–H, 12H), 7.92 (*s*, –CH=N, 2H).

## Crystal data

[Ni(C<sub>34</sub>H<sub>34</sub>N<sub>2</sub>O<sub>4</sub>)]  
*M<sub>r</sub>* = 593.34  
Monoclinic, *C*2  
*a* = 24.101 (3) Å  
*b* = 13.760 (1) Å  
*c* = 8.989 (1) Å  
β = 100.87 (1)°  
*V* = 2927.3 (5) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.346 Mg m<sup>-3</sup>  
Mo *K*α radiation  
Cell parameters from 29 reflections  
θ = 3.0–14.2°  
μ = 0.70 mm<sup>-1</sup>  
*T* = 295 (2) K  
Block, brown  
0.52 × 0.40 × 0.32 mm

## Data collection

Siemens *P4* diffractometer  
ω scans  
Absorption correction: ψ scan  
(*SHELXTL*; Siemens, 1996)  
*T<sub>min</sub>* = 0.738, *T<sub>max</sub>* = 0.798  
7965 measured reflections  
7242 independent reflections  
5073 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.014  
θ<sub>max</sub> = 28.3°  
*h* = –32 → 32  
*k* = –18 → 18  
*l* = –11 → 11  
3 standard reflections  
every 97 reflections  
intensity decay: 2.5%

## Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.043  
*wR* (*F*<sup>2</sup>) = 0.100  
*S* = 0.96  
7242 reflections  
376 parameters  
H-atom parameters constrained  
*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0454*P*)<sup>2</sup>]  
where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> = 0.001  
Δρ<sub>max</sub> = 0.47 e Å<sup>-3</sup>  
Δρ<sub>min</sub> = –0.27 e Å<sup>-3</sup>  
Extinction correction: *SHELXTL*  
Extinction coefficient: 0.00045 (13)  
Absolute structure: Flack (1983),  
3473 Friedel pairs  
Flack parameter = 0.038 (15)

**Table 1**

Selected geometric parameters (Å, °).

Ni1—O1	1.835 (3)	Ni2—N2	1.849 (4)
Ni1—N1	1.862 (3)	Ni2—O3	1.866 (3)
O1—C14	1.313 (5)	O3—C31	1.320 (5)
N1—C8	1.274 (5)	N2—C25	1.288 (5)
C8—C9	1.407 (6)	C25—C26	1.434 (6)
O1 <sup>i</sup> —Ni1—O1	85.22 (18)	N2—Ni2—N2 <sup>ii</sup>	85.5 (2)
O1—Ni1—N1	94.26 (11)	N2—Ni2—O3	95.25 (11)
O1—Ni1—N1 <sup>i</sup>	177.07 (17)	N2—Ni2—O3 <sup>ii</sup>	170.48 (15)
N1—Ni1—N1 <sup>i</sup>	86.4 (2)	O3—Ni2—O3 <sup>ii</sup>	85.58 (18)

Symmetry codes: (i) 1 - x, y, -z; (ii) 1 - x, y, 1 - z.

*PLATON/ADDSYM* (Spek, 2002) suggested a pseudo-center of symmetry and pseudo-space group *C2/c*. However, this was rejected, since the title compound has chiral atoms C7 and C24 in an *R* configuration. The positions of all H atoms were fixed geometrically with distances to H atoms in the range 0.92–0.98 Å and given  $U_{\text{iso}}$  values 1.2–1.5 times the  $U_{\text{eq}}$  value of the parent atom.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1996); program(s)

used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was supported by the Science Foundation of Gansu Province of China (No. ZR001-A25-001-Z).

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