rac-Bis[*μ*-N-salicylidene-*N'*-(*α*-phenylsulfanyl-methyl-2-oxidobenzyl)propylenediamine-*N,N',O,O,O'*]nickel(II) dichloromethane solvate

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The title compound, [Ni$_2$(C$_{24}$H$_{24}$N$_2$O$_2$S)$_2$]·CH$_2$Cl$_2$, is a centrosymmetric dimer. The Ni atoms are octahedrally coordinated by three O, one S and two N atoms. An intramolecular N—H···O hydrogen bond also connects the monomers.

## Comment

The title compound, (I), is a pentadentate dihydrosalen Ni^{II} complex with a thioether S atom positioned at an axial coordination site of the Ni atom. The two N atoms of the ligand are connected by a trimethylene bridge. The synthesis and the structural and chemical properties of the analogous Ni complex carrying two methylene groups between the N atoms have been published previously (Berkessel *et al.*, 1990; Berkessel *et al.*, 1993).

(I)
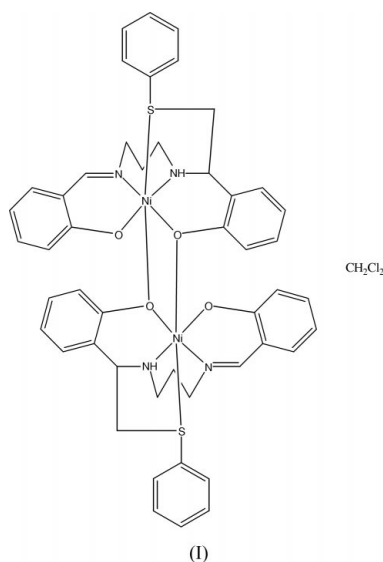
It is particularly noteworthy that the dimethylene complex reacts with atmospheric oxygen, with concomitant formation of Ni$_{salen}$ and selective removal of the thioether side chain. Obviously, the electron density provided by the ligand plays a crucial role in the ability of the complex to interact with molecular oxygen. The trimethylene complex was synthesized to probe the effect of diminished electron density at the central Ni atom. In fact, the trimethylene complex, (I), while being structurally similar to the dimethylene complex, is completely stable in air.

Compound (I) is a centrosymmetric dimer. The Ni atoms are octahedrally coordinated by three O, one S and two N atoms. The geometric parameters are in the same range as those in the 'dimethylene complex'. The Ni—Nsp^2 bond is
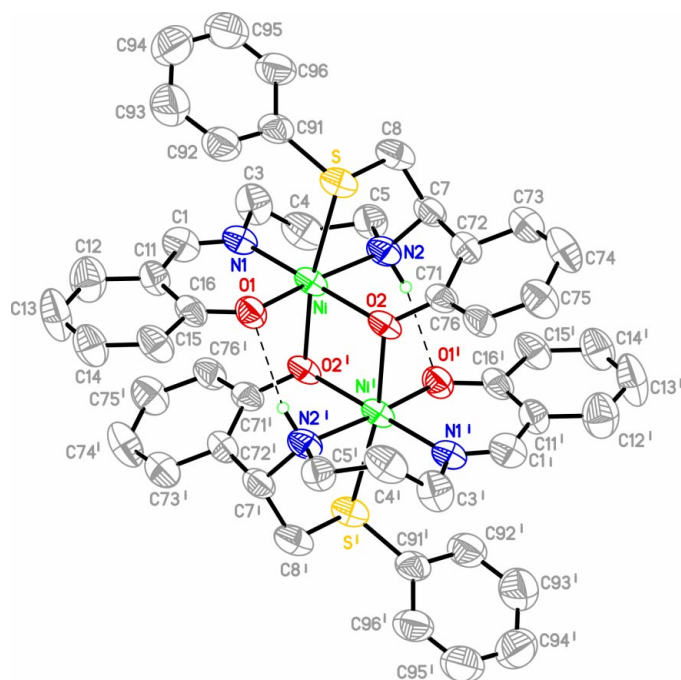
Figure 1
Perspective view of the title compound, with the atom-numbering scheme; displacement ellipsoids are at the 50% probability level. H atoms have been omitted for clarity. The disordered CH_2Cl_2 molecule is not shown. [Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.]

shorter than the $Ni—Nsp^3$ bond. The axial Ni—O bond *trans* to the Ni—S bond is the longest Ni—O bond (Table 1). An intramolecular N—H···O hydrogen bond provides a further stabilizing interaction between the monomeric units in the dimer.

Experimental

The synthesis of (I) was carried out by a route analogous to that reported by Berkessel *et al.* (1990).

Crystal data

$[Ni_2(C_{24}H_{24}N_2O_2S)_2]\cdot CH_2Cl_2$	$D_x = 1.460$ Mg m^{-3}
$M_r = 1011.37$	Cu $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 25
$a = 25.380$ (2) Å	reflections
$b = 7.976$ (1) Å	$\theta = 20–30°$
$c = 22.950$ (2) Å	$\mu = 3.33$ mm^{-1}
$\beta = 97.82$ (1)°	$T = 293$ K
$V = 4602.6$ (8) Å^3	Block, green
$Z = 4$	$0.40 \times 0.30 \times 0.20$ mm

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.095$
diffractometer	$\theta_{max} = 55.0°$
ω scans	$h = -25 \rightarrow 25$
Absorption correction: ψ scan	$k = -8 \rightarrow 2$
(North *et al.*, 1968)	$l = 0 \rightarrow 22$
$T_{min} = 0.327$, $T_{max} = 0.518$	3 standard reflections
3487 measured reflections	frequency: 90 min
2855 independent reflections	intensity decay: 2.3%
2268 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.127$	$w=1/[\sigma^2(F_o^2) + (0.2P)^2]$
$wR(F^2) = 0.333$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.41$	$(\Delta/\sigma)_{max} < 0.001$
2855 reflections	$\Delta\rho_{max} = 1.66$ e Å^{-3}
294 parameters	$\Delta\rho_{min} = -1.20$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni—O1	2.000 (5)	Ni—N2	2.095 (6)
Ni—N1	2.015 (7)	Ni—O2^i	2.107 (5)
Ni—O2	2.076 (5)	Ni—S	2.536 (2)
O1—Ni—N1	91.7 (2)	O2—Ni—O2^i	83.8 (2)
O1—Ni—O2	88.8 (2)	N2—Ni—O2^i	92.4 (2)
N1—Ni—O2	179.4 (3)	O1—Ni—S	92.68 (17)
O1—Ni—N2	171.7 (2)	N1—Ni—S	94.5 (2)
N1—Ni—N2	96.0 (3)	O2—Ni—S	85.89 (15)
O2—Ni—N2	83.5 (2)	N2—Ni—S	83.79 (19)
O1—Ni—O2^i	89.7 (2)	O2^i—Ni—S	169.32 (16)
N1—Ni—O2^i	95.8 (2)		

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.

Table 2
Hydrogen-bonding geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N2—H2N···O1^i	0.91	2.13	2.996 (9)	160

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.

H atoms were refined with fixed individual displacement parameters [$U_{iso}(H) = 1.2U_{eq}(C,N)$] using a riding model, with N—H = 0.91 Å, $C_{aromatic}$—H = 0.93 Å, $C_{methylene}$—H = 0.97 Å and $C_{tertiary}$—H = 0.98 Å. The C atom of the dichloromethane molecule is located on a twofold rotation axis. As a result, the Cl- and H-atom sites are only half occupied. The low precision of the structure is probably due to the low 2θ value. The high R factor, on the other hand, could be attributed to the contribution of the disordered solvent to the reflection data. However, omitting the contribution of the disordered solvent using the SQUEEZE option in *PLATON* (Spek, 2003) did not improve the result. A check for twinning did not yield a suitable twin law. Publication of the structure is nevertheless justified because of the comparison with the dimethylene complex (Berkessel *et al.*, 1990). The maximum density peak in the final difference Fourier map lies close (1.22 Å) to the Ni atom, as does the second peak (1.33 e Å^{-3}, 1.12 Å). The third, fourth and fifth peaks (1.3, 1.2 and 1.19 e Å^{-3}, respectively) lie close to the disordered solvent. The deepest hole lies 1.15 Å from the Ni atom.

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