

# {3,3'-[2,2'-(Ethylenedioxy)dibenzylidene]bis(*S*-methyl dithiocarbazate)}-nickel(II)

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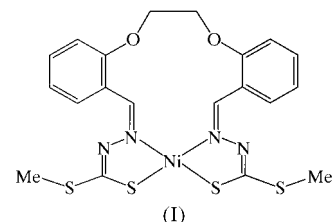
The tetradentate N<sub>2</sub>S<sub>2</sub> Schiff base ligand 3,3'-[2,2'-(ethylenedioxy)dibenzylidene]bis(*S*-methyl dithiocarbazate) (H<sub>2</sub>L), prepared by the condensation of *S*-methyl dithiocarbazate with 1,4-bis(2-formylphenyl)-1,4-dioxabutane in a 1:2 molar ratio, reacts with nickel acetate to form the title neutral metal complex, [Ni(C<sub>20</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>S<sub>4</sub>)]. The X-ray structure of the complex shows a distorted square-planar geometry around the Ni atom. The monomeric units are weakly associated into dimers *via* a long Ni···S interaction [3.569 (1) Å]. These dimeric units are then linked by C—H···S intermolecular contacts to form a polymeric chain along the *a* axis.

## Comment

Schiff base compounds derived from *S*-alkyl dithiocarbazate are of interest due to their pronounced biological activity against bacteria, viruses and cancer (Davies *et al.*, 1990; Kirschner *et al.*, 1966), and have stimulated interest in their coordination chemistry. In recent years, much work has been devoted to the synthesis and characterization of tetradentate sulfur–nitrogen ligands. As part of our continuing study of new chelating ligands containing mixed NS donors (Tian *et al.*, 1996, 1998), the synthesis and crystal structure of the title nickel(II) complex, (I), derived from a new N<sub>2</sub>S<sub>2</sub> tetradentate Schiff base ligand, are now described.

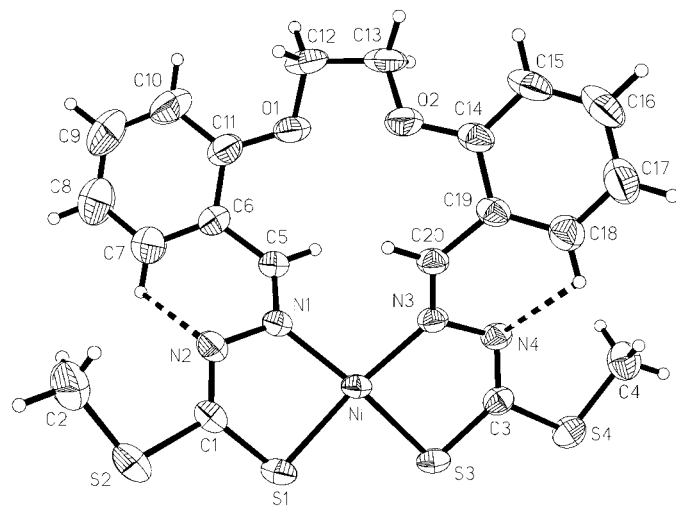
As shown in Fig. 1, the coordination system in (I) is a distorted square-planar configuration (Table 1), the non-planarity being shown by the fact that S1 and N3 are displaced on one side of the weighted least-squares plane through Ni by 0.052 (1) and 0.362 (2) Å, respectively, while S3 and N1 are displaced on the other side by 0.041 (1) and 0.364 (2) Å, respectively. The ligand deviates slightly from planarity, with a

dihedral angle of 11.16 (15)° between the phenyl rings. The twist is introduced by the –OCH<sub>2</sub>CH<sub>2</sub>O– bridge. The molecular conformation is influenced by C—H···N intramolecular hydrogen bonds (Table 2). The Schiff base ligand H<sub>2</sub>L is doubly deprotonated, thus acting as a double negatively charged tetradentate *NNSS*-chelate, coordinated to the Ni atom *via* both azomethine N atoms (N1 and N3), and both



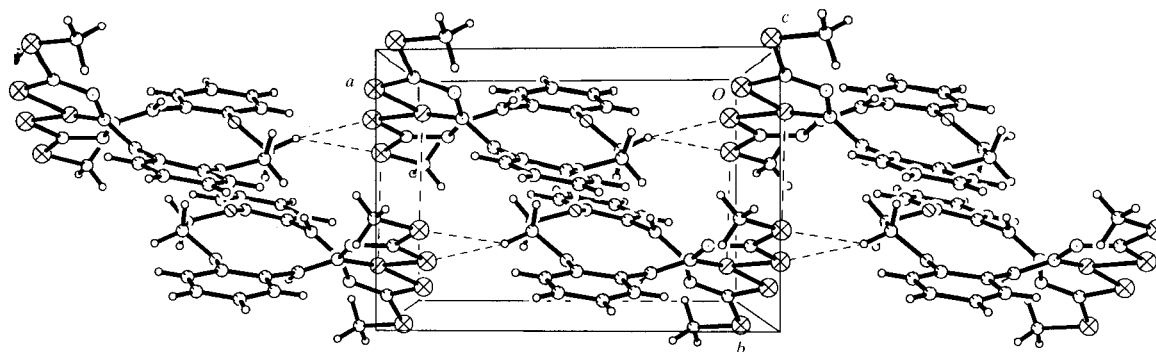
thiolate S atoms (S1 and S3). The Ni–N and Ni–S bond lengths compare well with those found in other related nickel(II) Schiff base complexes (Tian *et al.*, 1996, 1998). The lengths of C1–S1 and C3–S3 indicate single bonds, whereas those of C1–N2 and N4–C3 indicate double bonds, compared with those in the free ligand *S*-methyl *N*-[4-(dimethylamino)benzylidene]dithiocarbazate (Zhao *et al.*, 1997), where the single C–N bond is 1.333 (5) Å and the double C=S bond is 1.663 (4) Å.

Unlike *ML*<sub>2</sub> (where *M* is Ni<sup>II</sup> and *HL* is an *NS*-bidentate Schiff base derived from *S*-methyl dithiocarbazate; Fun *et al.*, 1996), in the case of (I), atoms N1, N3, S1 and S3 are coordinated to the Ni atom in a *cis* fashion, since the two bulky dithiocarbazate groups are preorganized, bridged by the –OCH<sub>2</sub>CH<sub>2</sub>O– group. When coordinated in this manner, the molecule of (I) is so congested that the two dithiocarbazate groups are not completely equivalent and a centrosymmetric packing is adopted to reduce the steric hindrance in the unit cell. The ligand forms three puckered chelate rings about the Ni atom, two of five members and one of thirteen. The first



**Figure 1**

The structure of compound (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as small spheres of arbitrary radii.


**Figure 2**

The packing diagram of (I) viewed down the *c* axis, showing the polymeric structure of the dimeric units along the *a* axis.

two are not equal in their total puckering amplitude,  $Q_T$  (Cremer & Pople, 1975) being 0.271 (1) and 0.168 (1) Å for the Ni/S1/C1/N2/N1 and Ni/S3/C3/N4/N3 rings, respectively, while  $Q_T$  is 0.956 (2) Å for the 13-membered N1/C5...C20/N3 ring. In this last ring, there is a local pseudo-twofold axis running between Ni and the midpoint of the C12—C13 bond, the ring distortion being mainly caused by steric hindrance [O1...O2 2.605 (2), C5...C20 3.232 (3), H5A...H20A 2.39 and N1...N3 2.925 (2) Å]. The conformation of the Ni/S1/C1/N2/N1 ring is such as to have two local pseudo-twofold axes, one running between atom N2 and the midpoint of the Ni—S1 bond, the other between atom C1 and the midpoint of the Ni—N1 bond, while in the Ni/S3/C3/N4/N3 ring, there is a local pseudo-mirror between Ni and the midpoint of C3—N4.

The two methyl groups (S2—C2 and S4—C4) are *trans* with respect to the S1—C1 and S3—C3 bonds, as defined by the S1—C1—S2—C2 [179.3 (2)°] and S3—C3—S4—C4 [−177.2 (1)°] torsion angles. It should be noted that the Ni atom is weakly coordinated by the S atom from another molecule in the unit cell [Ni...S4<sup>i</sup> 3.569 (1) Å; symmetry code: (i) 2 − *x*, −*y*, −*z*], thus giving rise to a dimer. These dimeric units are connected by intermolecular contacts [S3...H13B<sup>ii</sup> 2.904 Å and S4...H13B<sup>ii</sup> 2.933 Å; symmetry code: (ii) 1 + *x*, *y*, *z*] to form a polymeric chain along the *a* axis (Fig. 2).

## Experimental

1,4-Bis(2-formylphenyl)-1,4-dioxabutane (1.25 g; Armstrong & Lindoy, 1975) was dissolved in hot absolute ethanol (30 ml). A yellow precipitate was formed when a solution of *S*-methyl dithiocarbazate (1.22 g; Akbar Ali & Tarafdar, 1977) in absolute ethanol (30 ml) was added to this solution. The reaction mixture was stirred and refluxed for 3 h. After filtration, the product, H<sub>2</sub>L, was washed with hot ethanol. The H<sub>2</sub>L ligand (0.36 g, 1 mmol) was suspended in ethanol (10 ml) in the presence of dimethylformamide (2 ml). To this suspension, a solution of [Ni(CH<sub>3</sub>COO)<sub>2</sub>]·2H<sub>2</sub>O (1 mmol) in ethanol (10 ml) was added dropwise under reflux and stirring. The reaction lasted until the yellow suspension completely disappeared and a deep-blue crystalline precipitate, (I), was formed instead. The mixture was filtered while still hot and the product was washed with hot ethanol. Single crystals of (I) suitable for X-ray analysis were

obtained by slow evaporation from a methylene dichloride solution at room temperature.

### Crystal data

[Ni(C<sub>20</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>S<sub>4</sub>)]  
 $M_r = 535.35$   
 Monoclinic,  $P2_1/c$   
 $a = 11.1188$  (1) Å  
 $b = 7.6413$  (1) Å  
 $c = 27.4773$  (1) Å  
 $\beta = 99.065$  (1)°  
 $V = 2305.37$  (4) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.542$  Mg m<sup>−3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 8192 reflections  
 $\theta = 2.77$ – $33.17$ °  
 $\mu = 1.229$  mm<sup>−1</sup>  
 $T = 293$  (2) K  
 Plate, dark blue  
 0.45 × 0.30 × 0.06 mm

### Data collection

Siemens SMART CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: empirical (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.608$ ,  $T_{\max} = 0.930$   
 14 690 measured reflections

5277 independent reflections  
 4356 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.028$   
 $\theta_{\text{max}} = 27.5$ °  
 $h = -13 \rightarrow 14$   
 $k = -9 \rightarrow 8$   
 $l = -35 \rightarrow 35$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.080$   
 $S = 1.050$   
 5277 reflections  
 280 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0296P)^2 + 0.9504P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.32$  e Å<sup>−3</sup>  
 $\Delta\rho_{\text{min}} = -0.27$  e Å<sup>−3</sup>

After checking their presence in the difference map, all H atoms were geometrically fixed and allowed to ride on the atoms to which they were attached, with  $U_{\text{iso}} = 1.2U_{\text{eq}}$  for the aromatic parent atoms and  $1.5U_{\text{eq}}$  for the methyl C atoms, and with C—H = 0.93 Å.

**Table 1**

Selected geometric parameters (Å, °).

Ni—N1	1.912 (2)	S3—C3	1.731 (2)
Ni—N3	1.917 (2)	N1—C5	1.293 (3)
Ni—S3	2.1471 (6)	N2—C1	1.291 (3)
Ni—S1	2.1668 (6)	N4—C3	1.296 (2)
S1—C1	1.732 (2)		
N1—Ni—N3	99.64 (7)	N1—Ni—S1	85.97 (5)
N3—Ni—S3	86.55 (5)	S3—Ni—S1	90.29 (2)
Ni—N1—C5—C6	168.3 (2)	Ni—N3—C20—C19	167.2 (2)

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C7–H7A $\cdots$ N2	0.93	2.50	2.902 (4)	106
C18–H18A $\cdots$ N4	0.93	2.47	2.917 (3)	109

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINTE* (Siemens, 1996); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1503). Services for accessing these data are described at the back of the journal.

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