(1S,2S)-[1,1'-Bis(4-methoxyphenyl)-3,3'-(1,2-cyclohexanediyldinitrilo)diprop-1-ene-thiolato-$\kappa^4 S,N,N',S'$]nickel(II)

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Key indicators

Single-crystal X-ray study
$T = 150$ K
Mean σ(C–C) = 0.005 Å
R factor = 0.068
wR factor = 0.169
Data-to-parameter ratio = 22.5

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

In the title compound, $[\mathrm{Ni}(\mathrm{C_{26}H_{28}N_2O_2S_2})]$, the three independent Ni[II] complex cations are conformational isomers. The Ni atom has a square-planar environment and is coordinated by two imine functions and two S atoms. The Ni—N and Ni—S bond lengths are in the ranges 1.893 (4)–1.909 (4) and 2.1527 (13)–2.1613 (12) Å, respectively.

Comment

Over the past few years, N_2S_2 and N_2O_2 ligands have been extensively investigated with regard to numerous applications in organic synthesis and medicine. Such ligands are of interest not only for optical sensors (Lee *et al.*, 2001) and liquid crystals (Lai *et al.*, 1998), but also as transition-metal-chelating agents for applications in nuclear medicine (Liu & Edwards, 1999; Auzeloux *et al.*, 2001; Benoist *et al.*, 1998, 1999; Dearling *et al.*, 1998) and asymmetric catalysis (Diltz *et al.*, 1997; Tommasino *et al.*, 2000). Several N_2S_2 and N_2O_2 ligands have already been synthesized and used as chelating agents (Charrier *et al.*, 2001). Our ongoing project to design new ligands by combining well known reactions and conducting high throughput evaluation in our laboratory led us to consider the synthesis of new tetradentate nickel complexes similar to the title compound, (I) (Mevellec *et al.*, 2001).

(I)
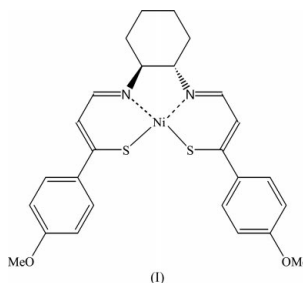
In many cases, thioxo ligands have been obtained by thionation of oxo analogues (Panova *et al.*, 1983). To avoid this delicate step, compound (I) was synthesized according to the slightly modified method of Quiniou (1981) and Charbonnel-Jobic *et al.* (1995) by reaction of a dithiolylium perchlorate with a diamine rather than by using thionating agents. Optically pure cyclohexanediammonium tartrate (SS, −) was used as a chiral source of cyclohexanediamine. Optical purity of the chiral ligand was confirmed by measuring the optical rotation. The corresponding chelate was obtained by reaction of nickel acetate. Although all spectroscopic methods (¹H and ¹³C NMR, IR, elemental analysis and mass spectroscopy) indicated that the correct complex had been formed, the exact structure of (I) could not be determined. In fact, two meso-meric forms (enaminothioketone and enethiolimine) can be considered for this chelate. ¹³C NMR analysis showed differ-
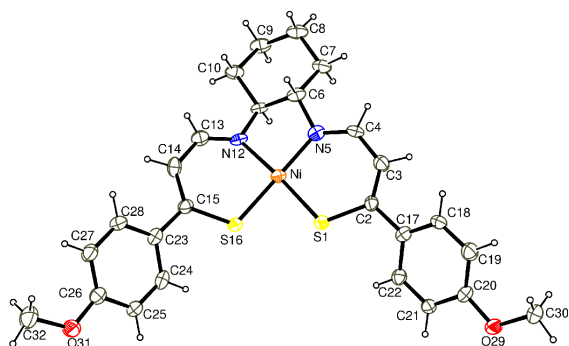
Figure 1
The molecular structure of one of the three independent molecules of (I) ('*a*' molecule), showing 50% probability displacement ellipsoids.

ences in chemical shifts for CHα (or CH$_2\alpha$) and C—S between the free ligand and chelate (I). In fact, the chemical shift for C=S changed from 206.6 p.p.m. to 163.2 p.p.m. This variation could have been due to a decrease in bond order, confirming the preferred imine form for the metal chelate complex. Analysis of the X-ray structure allowed us to opt for the enethiolimine form (see Fig. 1). The C15—S16 and C2—S1 bond lengths are, in fact, characteristic of a single bond (>> 1.71 Å). Similarly, C13—N12 and C4—N5 correspond to imine and not amine bonds. Finally, distances C2—C3 and C14—C15 (1.37 and 1.36 Å, respectively) correspond to classical Csp^2—Csp^2 bond values. Structural analysis showed a chair conformation for the cyclohexane, whereas the molecular core containing the Ni atom is nearly flat. However, the aromatic groups are shifted relative to the central plane of the metal complex, giving it an arc shape.

Experimental

A mixture of diastereoisomerically pure *trans*-cyclohexane-1,2-diammonium tartrate (SS, −) (0.871 g, 3.6 mmol), potassium hydroxide (0.384 g, 3.3 mmol) and water (10 ml) was stirred for 1 h at room temperature. To this solution was added dithiolylium perchlorate (0.925 g, 3 mmol) in ethanol (30 ml), and the resulting mixture was stirred for 24 h at room temperature. The solution was then extracted with dichloromethane and evaporated under reduced pressure. The residue was purified by silica-gel chromatography (dichloromethane) and crystallized from ethanol, yielding the free ligand as a red solid. A 50 ml round-bottomed flask equipped with a magnetic stirrer was loaded with a solution of the ligand (0.4 mmol) in chloroform (3 ml). To this solution was added dropwise nickel acetate (0.6 mmol) in methanol (10 ml), and the resulting mixture was stirred for 24 h at room temperature. The resulting solid was then filtered off and washed with methanol. Single crystals suitable for X-ray analysis were obtained by slow evaporation at room temperature of a methanol solution.

Crystal data

[Ni(C$_{26}$H$_{28}$N$_2$O$_2$S$_2$)]
$M_r = 523.3$
Orthorhombic, $P2_12_12_1$
$a = 7.8637$ (4) Å
$b = 29.1592$ (9) Å
$c = 31.2637$ (9) Å
$V = 7168.7$ (5) Å^3
$Z = 12$
$D_x = 1.45$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 5378 reflections
$\theta = 2.9$–30.0°
$\mu = 1.01$ mm^{-1}
$T = 150$ K
Thick plate, purple
$0.33 \times 0.21 \times 0.05$ mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: Gaussian (JANA2000; Petricek & Dusek, 2000)
$T_{min} = 0.794$, $T_{max} = 0.951$
44 477 measured reflections

20 073 independent reflections
16 068 reflections with $I > 3\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 30.0°$
$h = -11 \rightarrow 10$
$k = -40 \rightarrow 41$
$l = -43 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 3\sigma(F^2)] = 0.068$
$wR(F^2) = 0.169$
$S = 2.24$
20 073 reflections
893 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(I) + 0.001296I^2]$
$(\Delta/\sigma)_{max} = 0.027$

$\Delta\rho_{max} = 1.01$ e Å^{-3}
$\Delta\rho_{min} = -0.87$ e Å^{-3}
Extinction correction: B—C type 1 Lorentzian isotropic (Becker & Coppens, 1974)
Extinction coefficient: 20.5 (14)
Absolute structure: Flack (1983), 8572 Friedel pairs
Flack parameter = 0.046 (15)

Table 1
Selected geometric parameters (Å).

NiA—S1A	2.1584 (11)	NiB—N12B	1.905 (3)
NiA—N5A	1.897 (3)	NiB—S16B	2.1604 (11)
NiA—N12A	1.907 (3)	NiC—S1C	2.1569 (11)
NiA—S16A	2.1578 (12)	NiC—N5C	1.909 (3)
NiB—S1B	2.1537 (11)	NiC—N12C	1.909 (3)
NiB—N5B	1.903 (3)	NiC—S16C	2.1560 (12)

H atoms were positioned geometrically and refined as riding, with U_{iso}(H) = 1.2U_{eq}(carrier atom) (C—H = 1.00 Å).

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1995); program(s) used to refine structure: *JANA*2000 (Petricek & Dusek, 2000); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *JANA*2000.

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