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A nickel complex with a tetradentate N_2S_2 Schiff base ligand

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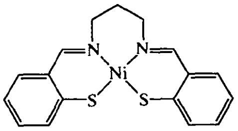
Abstract

The title compound, {2,2′-[1,3-propanediylbis(nitrilomethylidyne)]dibenzenethiolato(2−)-*S*,*N*,*N*′,*S*′}nickel(II) 1,4-dioxane 0.25-solvate, $[Ni(C_{17}H_{16}N_2S_2)]\cdot0.25C_4H_8O$, has the Ni^{II} atom coordinated by a tetradentate ligand through two N and two S atoms. The complex has a *cis* configuration, imposed by the chelate ligand, in a tetrahedrally distorted planar environment.

Comment

Ligands containing thiolate donors have attracted much attention in recent years due to their potential use as models for the active centre of metalloproteins, especially for nickel-dependent oxidoreductases, where a sulfur-rich environment for the metal has been proposed (Hausinger, 1997; Kolodziej, 1994). Nickel(II) complexes with tetradentate Schiff bases have been frequently used to probe the structural and electronic consequences of small modifications of the ligand skeleton, namely changes in the polymethylene bridge between the nitrogen donors and the introduction of substituents into the salicylate fragment. On the other hand, and in contrast to what is found for N_2O_2 Schiff bases, there have been no systematic studies on the structural modifications induced by small changes in the ligand skeleton for NiN_2S_2 complexes or by O/S replacement in this type of complex.

In the course of a systematic study on S/O replacement in nickel(II) complexes (de Castro *et al.*, 1997; Pereira *et al.*, 1998), we have prepared and studied the title compound, [Ni(t-salpd)]. Details of the physicochemical characterization will be published elsewhere (Gomes *et al.*, 1999). The X-ray structure (Fig. 1) shows that the asymmetric unit contains two independent nickel complex molecules and half a molecule of solvent (1,4-dioxane), which lies across a centre of inversion. Both complex molecules have a *cis*-N_2S_2 coordination sphere around the Ni^{II} atom, showing an approximately square-planar geometry, with a small tetrahedral distortion. The dihedral angles between the N—Ni—S coordination planes are 10.60 (3) and 7.64 (3)° for molecules *A* and *B*, respectively, and the maximum deviation of the Ni, N and S atoms from the N_2S_2 best plane is less than 0.144 (1) Å for molecule *A* and less than 0.101 (1) Å for molecule *B*. Metal–ligand bonds are within the expected range for Schiff base nickel(II) complexes. The analogous complex with a dimethylene bridge between nitrogen donors, [Ni(t-salen)], shows a very similar structure but with a smaller tetrahedral distortion (Yamamura *et al.*, 1993). The different tetrahedral distortion is reflected in the Ni—N bond lengths, which are clearly longer in the present compound, probably because of the higher stereochemical demand of the propylene bridge. The increase in Ni—N bond lengths due to the replacement of the dimethylene bridge by a trimethylene bridge is also observed in nickel(II) complexes with related N_2O_2 Schiff bases (Carrondo *et al.*, 1993; Drew *et al.*, 1985).



[Ni(t-salpd)]

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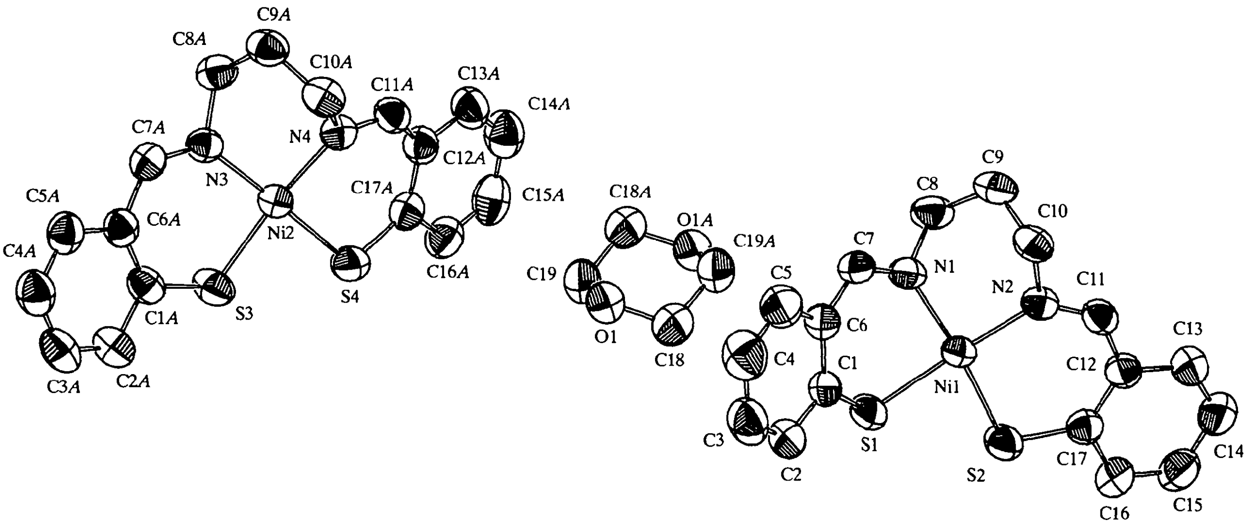

Fig. 1. The molecular structure of [Ni(t-salpd)] with the atom-labelling scheme. Displacement ellipsoids are plotted at the 50% probability level and H atoms have been omitted for clarity. The 1,4-dioxane solvate molecule is also shown.

The structural comparison of [Ni(t-salpd)] and [Ni(salpd)] (Drew *et al.*, 1985) shows that the replacement of S by O-atom donors in the metal coordination sphere leads only to minor structural changes. Apart from the obvious difference in Ni—S and Ni—O bond lengths, the most important difference in the molecular structure of these two complexes lies in the type of distortion from planarity; that in [Ni(salpd)] is not of the tetrahedral type, with the two Ni—N—O coordination planes folded and the Ni atom 0.12 Å out of the coordination plane. Whether this is due to a particular effect of the coordination sphere change or to crystal-packing forces is not clear. Tetrahedrally distorted structures for nickel(II) complexes with N_2O_2 Schiff bases are not very common, but they have been observed with ligands that have very high stereochemical demands (Azevedo *et al.* 1994). In contrast, nickel(II) complexes with N_2S_2 and N_2OS coordination spheres are commonly tetrahedrally distorted. This seems to point to a specific role of sulfur in determining this type of distortion, and may be rationalized by recalling that the lower π interaction between nickel and sulfur decreases the energy preference of nickel(II) for square-planar geometries.

A final comment regards the role of 1,4-dioxane in the crystal packing of [Ni(t-salpd)]. The crystal structure reveals that there are no interactions between Ni^{II} centres and that the molecules are aligned parallel to the [010] direction and form Ni1–Ni2–Ni2–Ni1 columnar arrangements separated by 1,4-dioxane molecules (Fig. 2), with the solvent molecules interacting with Ni1-labelled molecules of adjacent patterns, $O1(x, y-1, z)\cdots H13/H14$ and $O1(x, \frac{1}{2}-y, \frac{1}{2}+z)\cdots H16$.

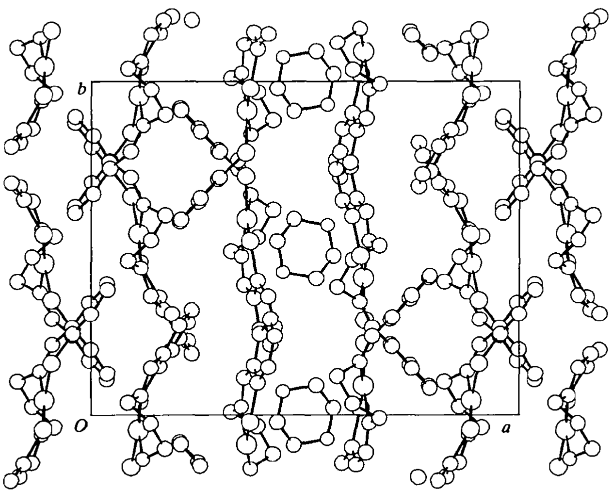

Fig. 2. A view of the crystal packing of [Ni(t-salpd)] down the *c* axis.

Experimental

The title compound was prepared according to published procedures (Dutton *et al.*, 1988) and purified by recrystallization from dichloromethane/methanol (4:1 *v*/*v*). Slow evaporation of a 1,4-dioxane solution afforded prismatic single crystals of suitable quality for analysis. Analysis: C 54.38, H 4.57, N 7.45%; $C_{17}H_{16}N_2NiS_2$ requires C 54.98, H 4.34, N 7.54%.

Crystal data

$[Ni(C_{17}H_{16}N_2S_2)]\cdot$
$0.25C_4H_8O$
$M_r = 393.17$
Monoclinic
$P2_1/c$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 1580 reflections
$\theta = 4.8–28.2°$

$a = 17.000\,(2)$ Å
$b = 14.369\,(2)$ Å
$c = 13.485\,(2)$ Å
$\beta = 91.32\,(1)^\circ$
$V = 3293.1\,(8)$ Å^3
$Z = 8$
$D_x = 1.586$ Mg m^{-3}
D_m not measured

$\mu = 1.435$ mm^{-1}
$T = 298\,(2)$ K
Block
$0.5 \times 0.4 \times 0.2$ mm
Brown

Data collection

Stoe IPDS diffractometer
Area-detector scans
Absorption correction: numerical (*X-RED* in *IPDS*; Stoe & Cie, 1996)
$T_{\min} = 0.778$, $T_{\max} = 0.891$
32 839 measured reflections
8343 independent reflections
6272 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.044$
$\theta_{\max} = 29.49^\circ$
$h = -23 \rightarrow 22$
$k = -18 \rightarrow 19$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.121$
$S = 1.215$
7704 reflections
569 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0400P)^2 + 1.6555P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.432$ e Å^{-3}
$\Delta\rho_{\min} = -0.454$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0087 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ni1—N1	1.909 (2)	Ni2—N4	1.913 (2)
Ni1—N2	1.916 (2)	Ni2—N3	1.919 (2)
Ni1—S2	2.1454 (8)	Ni2—S3	2.1610 (9)
Ni1—S1	2.1733 (8)	Ni2—S4	2.1686 (9)
S1—C1	1.708 (3)	S3—C1*A*	1.712 (3)
S2—C17	1.731 (3)	S4—C17*A*	1.721 (3)
N2—C11	1.291 (4)	N3—C7*A*	1.270 (4)
N2—C10	1.462 (4)	N3—C8*A*	1.472 (4)
N1—C7	1.265 (4)	N4—C11*A*	1.267 (4)
N1—C8	1.452 (4)	N4—C10*A*	1.445 (4)
N1—Ni1—N2	90.70 (10)	N4—Ni2—N3	90.67 (10)
N2—Ni1—S2	96.66 (7)	N3—Ni2—S3	94.36 (8)
N1—Ni1—S1	90.07 (8)	N4—Ni2—S4	92.36 (8)
S2—Ni1—S1	83.60 (3)	S3—Ni2—S4	83.14 (4)

Data collection: *EXPOSE* in *IPDS* (Stoe & Cie, 1996). Cell refinement: *CELL* in *IPDS*. Data reduction: *INTEGRATE* in *IPDS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1011). Services for accessing these data are described at the back of the journal.

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(5,6-Dimethyl-1,10-phenanthroline)(nitrato)(salicylaldehydato)copper(II)

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Abstract

The Cu$^{\rm II}$ ion of the title complex, (5,6-dimethyl-1,10-phenanthroline-*N*,*N*′)(2-formylphenolato-*O*,*O*′)(nitrato-*O*)copper(II), $[\mathrm{Cu(C_7H_5O_2)(NO_3)(C_{14}H_{12}N_2)}]$, displays a slightly distorted square-pyramidal coordination site, where one O atom from the nitrate ion is coordinated in the apical position [at 2.239 (2) Å], and both O atoms from the salicylaldehydate [at 1.893 (2) and 1.963 (2) Å] and both N atoms from the phenanthroline molecule [at 1.995 (2) and 2.005 (2) Å] define its base. The five-membered chelate ring ($\mathrm{CuC_2N_2}$) in the phenanthroline