

maps, were refined isotropically. All calculations were performed on a VAX3400 computer at the Computer Center, Indian Association for the Cultivation of Science. Since all attempts to obtain suitable single crystals of (2) failed, the complex was examined by X-ray powder diffraction. Accurate d_{hkl} spacings (Å) were obtained from the powder pattern recorded on a Seifert XRD-3000P diffractometer at 295 K operating at 30 kV and 30 mA with a 2° min^{-1} scan rate. The results are summarized in Table 4. The initial cell parameters have been determined from powder data and accurate lattice parameters were obtained by least-squares refinement (Gabe, Le Page, Charland, Lee & White, 1989).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989) for (1). Cell refinement: *CAD-4 Software* for (1). Data reduction: *CAD-4 Software* for (1). Program(s) used to solve structures: *SHELX76* (Sheldrick, 1976) for (1). Program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993) for (1); *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1993) for (2). Molecular graphics: *ORTEPII* (Johnson, 1976) for (1). Software used to prepare material for publication: *SHELXL93* for (1).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: L11152). Services for accessing these data are described at the back of the journal.

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[*N,N'*-Bis(2-thiobenzylidene)-1,2-phenylenediaminato]nickel(II)†

WILBERTH J. J. SMEETS,^a ANTHONY L. SPEK,^a RICHARD K. HENDERSON,^b ELISABETH BOUWMAN^b AND JAN REEDIJK^b

^a*Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands, and*
^b*Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands. E-mail: spea@xray.chem.ruu.nl*

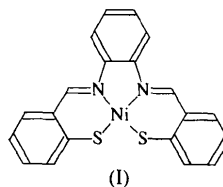
(Received 3 January 1997; accepted 23 June 1997)

Abstract

The title compound, $[\text{Ni}(\text{C}_{20}\text{H}_{14}\text{N}_2\text{S}_2)]$, was formed from a Schiff base reaction of 2-*tert*-butylthiobenzaldehyde with 1,2-phenylenediamine, followed by reaction with $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$. The square-planar NiN_2S_2 complex has Ni—N distances of 1.8992 (17) and 1.9014 (15) Å, and Ni—S distances of 2.1519 (6) and 2.1587 (6) Å. Molecules pack in layers with a tilt angle of 46.09 (1)°; the (001) packing plane is arranged so that the molecules in superimposed layers stack approximately perpendicular to each other.

Comment

Mononuclear NiN_2S_2 complexes are well known, but continue to be studied as models for the active sites in metalloenzymes, such as nickel hydrogenases (Ni-H₂ases) (Lancaster, 1988; Halcrow & Christou, 1994). The title complex, $[\text{Ni}(\text{tsalphen})]$, (I), and the related 4,5-dimethyl-1,2-phenylenediamino complex $[\text{Ni}(\text{tsaldimph})]$ (Henderson, Bouwman, Reedijk & Powell, 1996) were synthesized and characterized as part of research in modelling the active site of the Ni-H₂ase enzyme from *Desulfovibrio Gigas*, for which an X-ray structure was recently published (Volbeda *et al.*, 1995).



The title complex contains a square-planar Ni atom, coordinated by two imino N atoms and two thiolate S atoms. The asymmetric unit corresponds to one complete molecule. No use is made of the molecular

† Alternative name: {2,2'-[1,2-phenylenebis(nitrilomethylidene)]diphenolato-S,N,N',S'}nickel(II).

twofold axis in the packing (see below). Atoms N1, N2 and Ni1 define a plane from which S1 is displaced by 0.392 (1) Å in one direction and S2 by 0.394 (1) Å in the other. The planes generated by the two Schiff base moieties containing the 2-thiobenzylidene units are essentially planar to within 0.03 Å. The phenyl ring of the phenylenediamine moiety makes angles of 4.27 (9) and 9.67 (9)° with the two Schiff base moieties.

The present structure can be compared with two similar Ni complexes. The compound [(*N,N'*-*o*-phenylenedisalicylideneaminato-*N,N',O,O'*)nickel(II)], [Ni(salph)] (Radha, Seshasayee, Ramalingam & Aravamudan, 1985), is the NiN₂O₂ analogue of the title compound, in which the plane defined by N1, N2 and Ni has O1 0.015 Å above and O2 0.032 Å below it. This is considerably more planar than the title compound, an obser-

vation related to the smaller radius of oxygen. The compound [Ni(tsaldimph)] (Henderson *et al.*, 1996) contains a 4,5-dimethyl-1,2-phenylenediamino unit instead of a simple 1,2-phenylenediamino unit, with the molecular twofold axis coinciding with a crystallographic twofold axis. The coordination geometry around the Ni^{II} centre in [Ni(tsaldimph)] is more planar than the title complex, with the two S atoms deviating by only 0.202 (1) Å from the plane defined by Ni and the two coordinating N atoms.

The packing characteristics in the title compound and in [Ni(tsaldimph)] (Henderson *et al.*, 1996) are similar. Molecules pack in layers with tilt angles of 46.09 (1) and 35.75 (2)° to the packing plane. Molecules in the (001) plane pack parallel, while those in successive layers in the *c*-axis direction are approximately perpendicular (Fig. 2).

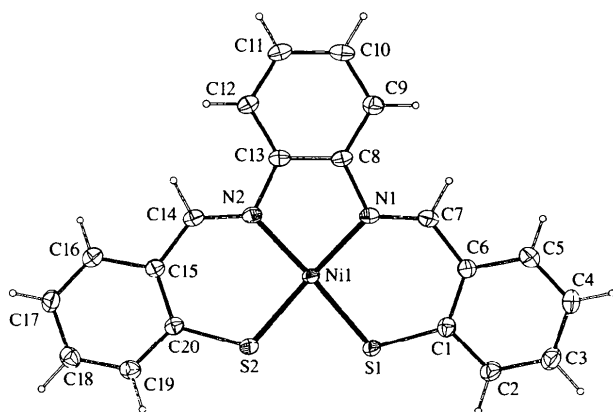


Fig. 1. Displacement ellipsoid plot (50% probability) of the title compound. H atoms are shown as small spheres of arbitrary radii.

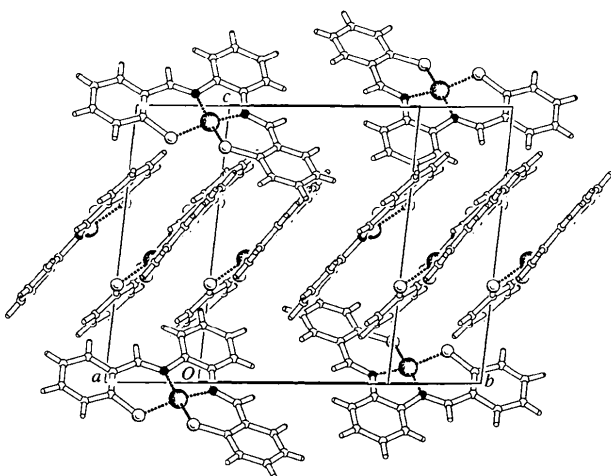


Fig. 2. Packing diagram illustrating the packing on (001), the non-planarity of the molecule and the non-crystallographic twofold molecular symmetry. The *b* axis runs to the right with the *c* axis vertically upwards.

Experimental

All procedures were performed in a nitrogen atmosphere using degassed solvents and Schlenk techniques. 2-*tert*-Butylthiobenzaldehyde was prepared according to the literature procedure of Meth-Cohn & Tarnowski (1978). To a solution of 2-*tert*-butylthiobenzaldehyde (0.41 g, 2.11 mmol) in dry toluene (10 ml) was added a solution of 1,2-phenylenediamine (0.13 g, 1.06 mmol) in dry toluene (10 ml) and the mixture was heated under reflux for 2 h in the presence of CaSO₄ as a drying agent. The resultant bright yellow solution was filtered and the solvent evaporated, leaving a bright yellow oil. The crude yellow oil was dissolved in 98% ethanol (10 ml) and a solution of Ni(BF₄)₂·6H₂O (0.34 g, 1.0 mmol) in ethanol (10 ml) was added. The mixture was heated under reflux for 1.5 h during which time the solution turned dark and a dark brown precipitate began to form. On cooling, the dark brown precipitate was collected on microfibre filter paper [0.18 g 45% yield based on Ni(BF₄)₂]. X-ray quality crystals were obtained by recrystallization from dimethylformamide/chloroform. Calculated microanalysis for C₂₀H₁₄N₂NiS₂: C 59.41, H 3.49, N 6.93, S 15.83%; found: C 59.18, H 3.55, N 6.63%. ¹H NMR (DMSO; 2-D ¹H ¹H COSY spectrum): δ 9.42 (2H, *s*, H7), 8.27 (2H, *d* of *t*, *J* = 3.5 and 10 Hz, H9), 7.96 (2H, *dd*, *J* = 1.4 and 8 Hz, H2), 7.65 (2H, *d*, *J* = 8 Hz, H5), 7.50 (2H, *d* of *t*, *J* = 3.5 and 10 Hz, H10), 7.33 (*t* of *d*, *J* = 1.5 and 7 Hz, H4), 7.14 (*t* of *d*, *J* = 0.7 and 7 Hz, H3).

Crystal data

[Ni(C₂₀H₁₄N₂S₂)]
M_r = 405.17
 Monoclinic
*P*2₁/*c*
a = 6.9518 (5) Å
b = 17.6990 (13) Å
c = 13.5035 (11) Å
 β = 100.520 (6)°
V = 1633.5 (2) Å³
Z = 4
D_x = 1.648 Mg m⁻³
D_m not measured

Mo K α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 11.6–14.1°
 μ = 1.45 mm⁻¹
T = 150 K
 Block
 0.48 × 0.45 × 0.30 mm
 Dark brown

Data collection

Enraf–Nonius CAD-4T 3215 reflections with
 diffractometer on rotating $I > 2\sigma(I)$
 anode source $R_{\text{int}} = 0.026$
 ω scans $\theta_{\text{max}} = 27.42^\circ$
 Absorption correction: $h = -6 \rightarrow 9$
 ψ scan (North, Phillips $k = 0 \rightarrow 22$
 & Mathews, 1968) $l = -17 \rightarrow 17$
 $T_{\text{min}} = 0.600$, $T_{\text{max}} = 0.670$ 3 standard reflections
 4026 measured reflections frequency: 60 min
 3703 independent reflections intensity decay: 5%

Refinement

Refinement on F^2 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $R(F) = 0.029$ $\Delta\rho_{\text{max}} = 0.41 \text{ e } \text{Å}^{-3}$
 $wR(F^2) = 0.071$ $\Delta\rho_{\text{min}} = -0.34 \text{ e } \text{Å}^{-3}$
 $S = 1.066$ Extinction correction: none
 3703 reflections Scattering factors from
 240 parameters *International Tables for*
 H atoms: see below *Crystallography* (Vol. C)
 $w = 1/[\sigma^2(F_o^2) + (0.0471P)^2$
 $+ 1.1696P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Table 1. Selected geometric parameters (Å, °)

Ni1—S1	2.1519 (6)	S2—C20	1.736 (2)
Ni1—S2	2.1587 (6)	N1—C7	1.302 (3)
Ni1—N1	1.8992 (17)	N1—C8	1.436 (3)
Ni1—N2	1.9014 (15)	N2—C13	1.432 (2)
S1—C1	1.728 (2)	N2—C14	1.297 (3)
S1—Ni1—S2	81.85 (2)	S2—Ni1—N1	168.99 (5)
S1—Ni1—N1	97.08 (5)	S2—Ni1—N2	96.78 (5)
S1—Ni1—N2	168.93 (5)	N1—Ni1—N2	86.34 (7)

The crystal used for data collection was cut to size in inert oil from a cluster of cube-shaped crystals. Attempts to use a face-indexed correction for absorption (de Meulenaer & Tompa, 1965) were unsatisfactory in detail but indicated a transmission range of 0.54–0.67. A more reasonable correction was possible on the basis of three close-to-axial ψ scans with the North, Phillips & Mathews (1968) method as implemented in *PLATON97* (Spek, 1990). The correction range was scaled on the value of T_{max} given above. H atoms were taken into account at calculated positions (restrained to C—H = 0.95 Å) and refined riding on their carrier atoms with $U_{\text{iso}} = 1.2U_{\text{eq}}$ of their attached atom. The structure was checked for possible higher symmetry using the *MISSYM* algorithm as implemented in *PLATON97*. The molecular twofold axis does not coincide with a lattice translation.

Data collection: locally modified *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *SET4* (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1997). Program(s) used to solve structure: *DIRDIF96* (Beurskens *et al.*, 1996). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *PLATON97*. Software used to prepare material for publication: *PLATON97*.

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Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1141). Services for accessing these data are described at the back of the journal.

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Bis(4-benzylpiperidinium) Tetrachloro-mercurate

ROLAND SPENGLER,^a FATMA ZOUARI,^b ABDELHAMID BEN SALAH^b AND HANS BURZLAFF^a

^a*Institut für Angewandte Physik, Lehrstuhl für Kristallographie, Universität Erlangen-Nürnberg, Bismarckstraße 10, D-91054 Erlangen, Germany, and* ^b*Faculté des Sciences, Département de Chimie, Université de Sfax, Rte. de Soukra, 3038 Sfax, Tunisia. E-mail: roland.spengler@krist.uni-erlangen.de*

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Abstract

The title compound, (C₁₂H₁₈N)₂[HgCl₄], contains a distorted tetrachloromercurate tetrahedron, with Hg—Cl distances ranging from 2.424 (3) to 2.614 (2) Å.