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[*N*,*N'*-Bis(2-thiobenzylidene)-1,2-dimethyl-4,5-phenylenediaminato]nickel(II), Ni(tsaldimph)

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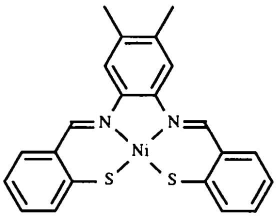
Abstract

{2,2'-[4,5-Dimethyl-1,2-phenylenebis(nitrilomethylidyne-*N*)]bis(thiophenolato-*S*)}nickel(II), [Ni($C_{22}H_{18}N_2S_2$)], is a square-planar NiN_2S_2 complex, formed from a Schiff base reaction of 2-*tert*-butylthiobenzaldehyde with 1,2-dimethyl-4,5-phenylenediamine, followed by coordination with nickel tetrafluoroborate. It crystallizes in the orthorhombic space group *Pbcn*, with Ni—N distances of 1.920 (3) Å and Ni—S distances of 2.174 (1) Å.

Comment

Mononuclear NiN_2S_2 complexes are well known but continue to be studied owing to their structural features which are of use in forming models for the active sites in metalloenzymes such as nickel hydrogenases (Ni-H_2ases) (Lancaster, 1988; Halcrow & Christou, 1994). The title complex, (I), was synthesized and characterized as part of research on modelling the active site of the Ni-H_2ase enzyme from *Desulfovibrio gigas*, for which an X-ray crystal structure was recently published (Volbeda *et al.*, 1995).



(I)

The title complex, Ni(tsaldimph) (Fig. 1), contains a square-planar Ni atom coordinated by two imino N atoms and two thiolate S atoms. The asymmetric unit corresponds to one half of the molecule, with the Ni atom sitting on the twofold axis along **b**. The rest of the molecule is generated by the symmetry operation $-x, y, \frac{1}{2} - z$, *i.e.* (i). The coordination geometry around the Ni^{II} centre is essentially planar with the Ni(1), N(1), N(1^{i}), S(1) and S(1^{i}) atoms defining a plane with a mean deviation of 0.079 Å. Within the crystal lattice, the molecules are arranged in a herringbone pattern, as illustrated in the packing diagram viewed down the *b* axis (Fig. 2).

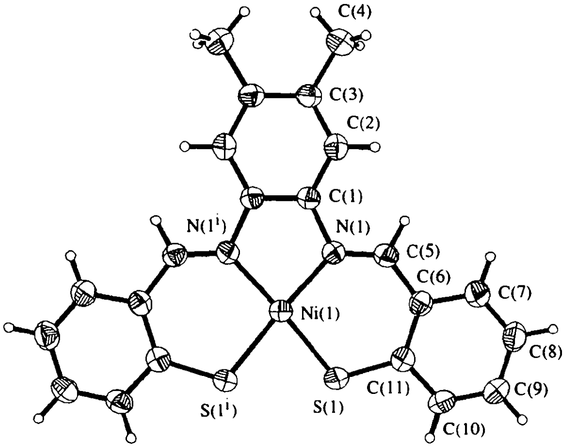


Fig. 1. A view of Ni(tsaldimph) with displacement ellipsoids drawn at the 50% probability level.

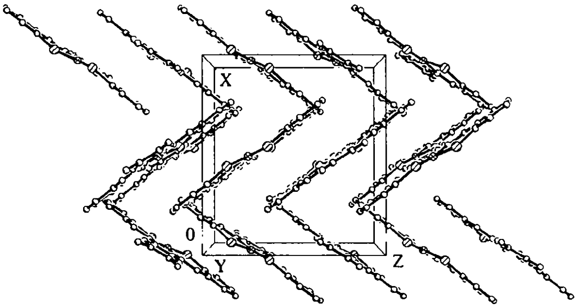


Fig. 2. Packing diagram of Ni(tsaldimph) viewed along the *b* axis. H atoms have been omitted for clarity.

Ni(tsaldimph) has been compared with two similar nickel structures. The [*N*,*N'*-bis(2-thiobenzenylidene)-ethylenediaminato]nickel(II) complex, [Ni(tsalen)] (Yamamura, Tadokoro, Tanaka & Kuroda, 1993), has a similar NiN_2S_2 coordination sphere around nickel, but the mean deviation from the NiN_2S_2 plane is smaller at 0.027 Å. The ethylenediamine bridge in this complex is not forced to be planar since there is no conjugation of electron density as in the title complex. This allows the bridge to be more flexible resulting in the NiN_2S_2 moiety being more planar. The complex (*N*,*N'*-*o*-phenylenedisalicylideneaminato-*N*,*N'*,*O*,*O'*)nickel(II), [Ni(salph)] (Radha, Seshasayee, Ramalingam, & Aravamudan, 1985), is very nearly an NiN_2O_2 analogue of the title complex. No atoms in

Ni(salph) lie on symmetry positions and the mean deviation from the plane generated by the NiN_2O_2 atoms is 0.010 Å. The phenyl-ring planes in Ni(tsaldimph) are inclined to the N_2S_2 plane at angles of 8.0 (1), 8.0 (1) and 3.7 (1)° for the two 2-thiobenzimine and the dimethylphenyl moieties, respectively. The equivalent planes in Ni(salph) make dihedral angles of 6.1, 7.3 and 3.2° with the N_2O_2 plane.

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 (1.05 g, 5.38 mmol) in 25 ml ethanol (98%) was added a solution of 1,2-dimethyl-4,5-phenylenediamine (0.366 g, 2.69 mmol) in 25 ml ethanol (98%) and the mixture heated under reflux for 1 h in the presence of $CaSO_4$ (drying agent). The resulting bright-yellow solution was filtered and the solvent evaporated. The resulting yellow solid was recrystallized from hexane. ^{1}H NMR ($CDCl_3$): δ 9.26 (2H, *s*, CH=N), 8.34–8.29, 7.59–7.38 (8H, *m*, H7–H10), 6.97 (2H, *s*, H2), 2.33 (6H, *s*, CH_3), 1.22 (18H, *s*, ^{t}Bu). A solution of the ligand (0.2 g, 0.4 mmol) in 5 ml ethanol (98%) was prepared and added a solution of $Ni(BF_4)_2.6H_2O$ (0.14 g, 0.4 mmol) in 5 ml ethanol (98%) and the mixture was heated under reflux for 1 h. After 10 min of heating, the solution had turned a dark-brown colour. On cooling, a dark-brown precipitate formed and was collected by filtration. X-ray quality crystals were obtained by recrystallization from dimethylformamide. Calculated microanalysis for $C_{22}H_{18}N_2NiS_2$: C 60.99, H 4.19, N 6.47, S 14.80%; found: C 60.55, H 4.23, N 6.35, S 14.07%. ^{1}H NMR ($CDCl_3$): δ 8.82 (2H, *s*, CH=N), 7.72–6.97 (10H, *m*, H2 and H7–H10), 2.25 (6H, *s*, CH_3).

Crystal data

$[Ni(C_{22}H_{18}N_2S_2)]$
$M_r = 433.22$
Orthorhombic
Pbcn
$a = 12.578\ (2)$ Å
$b = 12.848\ (2)$ Å
$c = 11.505\ (2)$ Å
$V = 1859.4\ (5)$ Å^3
$Z = 4$
$D_x = 1.548$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10–25°$
$\mu = 1.28$ mm^{-1}
$T = 291$ K
Needle
0.30 × 0.10 × 0.08 mm
Dark brown

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: semi-empirical *via* ψ scan (*SHELXTL-Plus*; Sheldrick, 1990)
$T_{min} = 0.84$, $T_{max} = 0.90$
1905 measured reflections
1645 independent reflections

1152 observed reflections $[F > 6\sigma(F)]$
$R_{int} = 0.01$
$\theta_{max} = 25°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 14$
$l = -13 \rightarrow 0$
3 standard reflections monitored every 150 reflections
intensity decay: none

Refinement

Refinement on *F*
$R = 0.0328$
$wR = 0.0454$
$S = 1.08$
1152 reflections
123 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.001F^2]$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ni(1)	0	0.5776 (1)	1/4	0.031 (1)
S(1)	0.0487 (1)	0.7083 (1)	0.1425 (1)	0.045 (1)
N(1)	0.0589 (2)	0.4673 (2)	0.1574 (2)	0.031 (1)
C(1)	0.0311 (3)	0.3643 (3)	0.2003 (3)	0.031 (1)
C(2)	0.0610 (3)	0.2673 (3)	0.1516 (3)	0.039 (2)
C(3)	0.0307 (3)	0.1716 (3)	0.1985 (3)	0.040 (2)
C(4)	0.0646 (4)	0.0696 (3)	0.1422 (4)	0.066 (2)
C(5)	0.1188 (3)	0.4722 (3)	0.0665 (3)	0.036 (2)
C(6)	0.1591 (3)	0.5632 (3)	0.0073 (3)	0.035 (2)
C(7)	0.2270 (3)	0.5443 (3)	−0.0874 (3)	0.044 (2)
C(8)	0.2709 (3)	0.6250 (3)	−0.1495 (3)	0.047 (2)
C(9)	0.2476 (3)	0.7296 (3)	−0.1207 (3)	0.043 (2)
C(10)	0.1816 (3)	0.7517 (3)	−0.0297 (3)	0.042 (2)
C(11)	0.1353 (3)	0.6694 (3)	0.0358 (3)	0.035 (2)

Table 2. *Selected geometric parameters (Å, °)*

Ni(1)—S(1)	2.174 (1)	Ni(1)—N(1)	1.920 (3)
S(1)—Ni(1)—N(1)	98.4 (1)	Ni(1)—S(1)—C(11)	111.2 (1)
S(1)—Ni(1)—S(1^{i})	78.8 (1)	Ni(1)—N(1)—C(1)	112.9 (2)
S(1)—Ni(1)—N(1^{i})	173.7 (1)	Ni(1)—N(1)—C(5)	129.7 (2)
N(1)—Ni(1)—N(1^{i})	85.0 (2)		

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

The title structure was solved by direct methods and refined by a full-matrix least-squares approach using the *SHELXTL-Plus* (Sheldrick, 1990) software package. All non-H atoms were readily located and refined with anisotropic displacement parameters. H atoms were located after successive cycles of least-squares refinement and constrained to idealized positions at a fixed distance of 0.96 Å from their parent C atoms.

Data collection: *TEXSAN* (Molecular Structure Corporation, 1993). Cell refinement: *TEXSAN*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *PLATON* (Spek, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1114). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Dinuclear Nickel(II) Compound: *μ*-{*N*,*N*,*N*′,*N*′-Tetrakis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]-1,2-ethylenediamine}-bis[aqua(nitrato-*O*,*O*′)nickel(II)] Dinitrate Dimethanol Solvate

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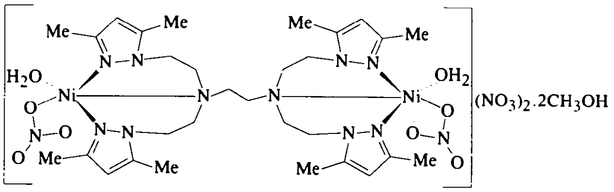
Abstract

The title compound, $[Ni_2(NO_3)_2(C_{30}H_{48}N_{10})(H_2O)_2]$-$(NO_3)_2.2CH_3OH$, contains a doubly charged cation which lies across an inversion center. The hexadentate ligand *N*,*N*,*N*′,*N*′-tetrakis[2-(3,5-dimethyl-1-pyrazolyl)-ethyl]-1,2-ethylenediamine (tped) holds two Ni^{II} ions at a distance of 6.3721 (13) Å. A distorted octahedron around each Ni^{II} ion is defined by two pyrazole N atoms of tped at distances of 2.023 (4) and 2.048 (4) Å, one amine N atom of tped at a distance of 2.161 (4) Å, two O atoms of a chelating nitrate anion at distances of 2.144 (3) and 2.205 (4) Å, and a water O atom at a distance of 2.032 (4) Å. A one-dimensional hydrogen-bonding network running along the *a* axis connects the methanol molecule of crystallization to the nitrato and aqua ligands of different cations, and an aqua ligand to the non-coordinated nitrate ion. The structure is essentially isomorphous with the previously reported Cu^{II} analog [Driessen, Haanstra & Reedijk (1992). *Acta Cryst.* C**48**, 1585–1587], the main differences being that NO_3 is involved in bidentate coordination to Ni^{II} and in a bifurcated hydrogen bond with methanol, whereas in the Cu^{II} complex, it is monodentate and only one of its O atoms hydrogen bonds to methanol.

Comment

The pyrazole group is employed as a substitute for imidazole in transition metal compounds used to model the active sites in metalloproteins (Kitajima & Moro-oka, 1994). Several pyrazole derivatives have been designed and synthesized for this purpose (Driessen, 1982; Bol, Driessen & Reedijk, 1995). The current X-ray study of the title compound, (I), was undertaken in order to establish the detailed coordination structure of the Ni^{II} analog of the previously reported Cu^{II} complex (Driessen, Haanstra & Reedijk, 1992), since it was thought possible that a nitrato ligand might bridge the two Ni^{II} centers.



(I)

The title compound (Figs. 1 and 2) contains a doubly charged cation residing on an inversion centre, with the asymmetric unit comprising half a cation, an NO_3^- anion and a methanol molecule. The Ni^{II} ion is in a distorted octahedral environment formed by two pyrazole N atoms and the amine N atom of tped, an O atom of a water molecule and two O atoms of one of the nitrate anions. The Ni—N and Ni—O bond lengths are comparable to values found in related compounds (Driessen, Haanstra & Reedijk, 1992; Claramunt, Domiano, Elguero, & Lavandera, 1989; Kleywegt, Wiesmeijer, van Driel, Driessen, Reedijk & Noordik, 1985).

The analogous hexadentate N-donor ligand *N*,*N*,*N*′,*N*′-tetrakis(1-pyrazolylmethyl)-1,2-ethylenediamine forms coordination compounds with transition metals in which the N(pyrazole)–metal ion–N(amine) bond angles are significantly smaller than 90° due to the three-bond bite of this ligand (Hulsbergen, Driessen, Reedijk & Verschoor, 1984). With tped regular octahedral, N(pyrazole)-to-N(amine) angles can be expected since four-bond bites are involved (Driessen, Haanstra & Reedijk, 1992) and, indeed, these angles range from 90.33 (15) to 96.42 (16)°. The bidentate nitrate ion,