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Bis(4-hydroxy-3-methoxybenzaldehyde thiosemicarbazonato-N^1,S)-nickel(II) tetraethanol solvate

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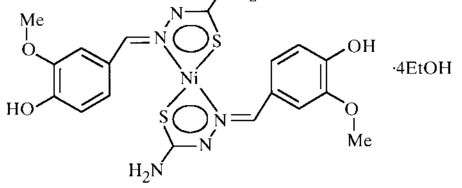
The title complex crystallizes as a tetraethanol solvate, $[\mathrm{Ni(C_9H_{10}N_3O_2S)_2}]\cdot4\mathrm{C_2H_6O}$, with the metal on a centre of inversion. Two singly deprotonated ligands coordinate the metal atom in a planar fashion. The metal complexes are organized into layers by an extended network of hydrogen bonds involving the NH_2 groups, the phenolic OH groups and the solvent molecules.

Comment

Transition metal complexes with thiosemicarbazones possess important biological activities, and antimalarial, antiviral and antibacterial activities have been proved for various representatives of this class of compounds (West *et al.*, 1991). Nevertheless, structural studies are comparatively rare and predominantly deal with complexes having tridentate thiosemicarbazones. To our knowledge, there is only one report on a transition metal complex with the fairly hydrophilic bidentate 4-hydroxy-3-methoxybenzaldehyde thiosemicarbazone (vanilline thiosemicarbazone, Hvtsc; Ortner & Abram, 1998), whereas the coordination chemistry of the isomeric but potentially tridentate ligand 2-hydroxy-3-methoxybenzaldehyde thiosemicarbazone is better known (Cui & Hu, 1994*a*,*b*; Agarwala & Hingorani, 1997; Offiong *et al.*, 1996). We describe herein the structure of the neutral nickel(II) complex $[\mathrm{Ni(vtsc)_2}]$, (I), which contains two chelate-bonded vanilline thiosemicarbzonato ligands.



(I)

The structure consists of $[\mathrm{Ni(vtsc)_2}]$ molecules (Fig. 1) with the metal on a centre of inversion and hydrogen-bonded molecules of ethanol solvent. The organic ligands are deprotonated at the azomethine position and bonded to the metal *via* the S and N3 atoms forming five-membered chelate rings. This results in an almost planar coordination, with a maximum deviation of 0.161 (1) Å from the least-square plane formed by Ni, S, C1, N2 and N3 (r.m.s. deviation 0.1189 Å). The hydroxyl group remains protonated and does not contribute to the coordination of the metal. A comparison of the bond lengths found for $[\mathrm{Ni(vtsc)_2}]$ with those in the $[\mathrm{Au(Hdamp)Cl(vtsc)}]^+$ cation [Hdamp is 2-(dimethylammoniummethyl)phenyl; Ortner & Abram, 1998] indicates a considerably higher degree of delocalization of electron density inside the chelate rings of the nickel compound under study. This is reflected by the C1—S bond length of 1.726 (3) Å (Table 1) which lies between the values of isolated C—S single and double bonds, whereas a C—S bond of 1.76 Å with almost single-bond character has been found for the gold compound. The same is true for the C,N skeletons of the thiosemicarbazone moieties which show nearly equal bonds for (I), whereas alternating short and long values are observed for the gold complex. An unusually short C—C bond length is observed in one of the solvent molecules which is probably due to thermal motion and/or disorder.

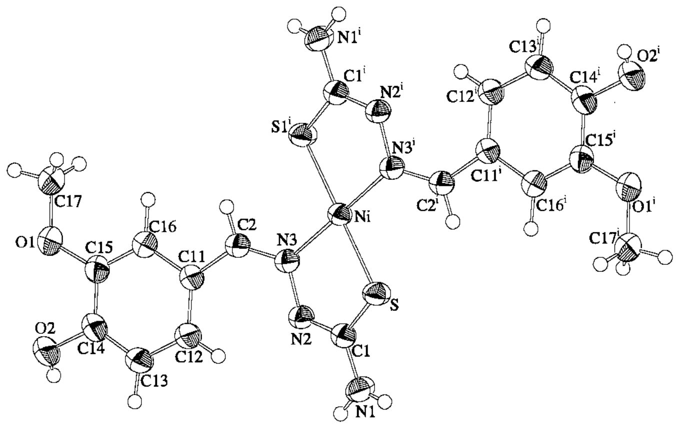


Figure 1
ZORTEP diagram (Zsolnai, 1997) of the molecular structure of $[\mathrm{Ni(vtsc)_2}]$ showing 50% probability displacement ellipsoids. [Symmetry code: (i) $-x$, $-y$, $-z$.]

The triclinic unit cell contains four molecules of the solvate ethanol. Hydrogen bridges between the complex molecules and two symmetry-related ethanol molecules form a two-dimensional arrangement. These layers are interconnected by additional hydrogen bonds between H30 and the N atoms of the thiosemicarbazone backbone of a complex molecule of the neigbouring layer. The hydrogen-bonding parameters are summarized in Table 2.

Experimental

$[\mathrm{Ni(vtsc)_2}]$ was prepared as previously reported (Akinchan *et al.*, 1992). Brown column-shaped single crystals of the sparingly soluble complex have been obtained from slow cooling of a concentrated ethanol solution.

Table 1
Selected geometric parameters (Å, °).

Ni—N3	1.908 (2)	N2—N3	1.401 (3)
Ni—S	2.1799 (7)	N3—C2	1.301 (3)
S—C1	1.726 (3)	C2—C11	1.452 (4)
N2—C1	1.317 (3)		
N3—Ni—S	85.42 (7)	N2—N3—Ni	119.40 (16)
C1—S—Ni	95.44 (9)	N2—C1—S	122.6 (2)
C1—N2—N3	112.2 (2)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O30^{i}	0.87	2.07	2.930 (3)	168
O20—H20···O2^{ii}	0.83	2.02	2.753 (3)	146
O2—H2A···O20	0.83	1.91	2.705 (3)	160
N1—H1B···O30^{iii}	0.87	2.19	3.023 (3)	161
O30—H30···N2^{iv}	0.83	2.01	2.838 (3)	174
O30—H30···N3^{iv}	0.83	2.63	3.360 (3)	147

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1-x, 1-y, 1-z$; (iii) $x-1, y, z-1$; (iv) $x, y, 1+z$.

Crystal data

$[Ni(C_9H_{10}N_3O_2S)_2]\cdot 4C_2H_6O$
M_r = 691.50
Triclinic, $P\overline{1}$
a = 6.894 (1) Å
b = 10.675 (1) Å
c = 11.878 (2) Å
α = 73.19 (1)°
β = 79.75 (1)°
γ = 84.91 (1)°
V = 822.8 (2) Å^3
Z = 1
D_x = 1.396 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 18.22–26.69°
μ = 2.496 mm^{-1}
T = 203 (2) K
Column, brown
0.30 × 0.25 × 0.25 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scans (*SDP*; Frenz, 1983)
T_{min} = 0.503, T_{max} = 0.536
3560 measured reflections
2792 independent reflections
2695 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 64.93°
$h = -1 \rightarrow 8$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$
3 standard reflections every 200 reflections intensity decay: 1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.152
S = 1.086
2792 reflections
197 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0940P)^2 + 0.5715P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.65 e Å^{-3}
$\Delta\rho_{min}$ = −0.59 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0154 (19)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *SET*4 in *SDP* (Frenz, 1983); data reduction: *SDP*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1098). Services for accessing these data are described at the back of the journal.

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