

[*N,N'*-Bis(salicylidene)-1,3-propane-diaminato](methanol)(thiocyanato)nickel(II)**Zhong-Lu You,^{a,b} Hai-Liang Zhu^{a,b*} and Wei-Sheng Liu^b**^aDepartment of Chemistry, Fuyang Normal College, Fuyang Anhui 236041, People's Republic of China, and ^bDepartment of Chemistry, Lanzhou University, Lanzhou 730000, People's Republic of China

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Key indicators

Single-crystal X-ray study

 $T = 298\text{ K}$ Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$

Disorder in main residue

 R factor = 0.036 wR factor = 0.107

Data-to-parameter ratio = 14.1

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

The title compound, $[\text{Ni}(\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_2)(\text{NCS})(\text{CH}_4\text{O})]$, is a mononuclear nickel(II) complex. The Ni^{II} atom has a slightly distorted octahedral geometry, coordinated by two N and two O atoms of the Schiff base ligand, and one terminal N atom from a thiocyanate anion, together with a methanol molecule. In the crystal structure, the complex forms centrosymmetric $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonded dimers. The symmetry-related dimers are linked by weak $\text{O}-\text{H}\cdots\text{S}$ hydrogen bonds to form layers parallel to the bc plane.

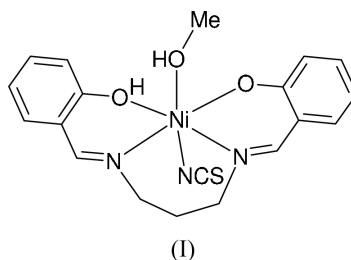
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Comment

Transition metal compounds containing Schiff base ligands have been of great interest for many years (Yamada, 1999). These compounds play an important role in the coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures. Since nickel compounds are present in the active sites of urease, and are used extensively in the design and construction of new magnetic materials, the study of nickel compounds is of great interest in various aspects of chemistry (Karplus & Pearson, 1997; Zhu *et al.*, 1999, 2001). Recently, we have reported a few Schiff base complexes (You, Lin *et al.*, 2003; You, Qu *et al.*, 2003; You *et al.*, 2004). As an extension of our work on the structural characterization of the Schiff base complexes, a mononuclear nickel(II) compound, (I), is reported here.



The title compound, (I), is an electronically neutral mononuclear nickel(II) compound (Fig. 1). The Ni^{II} atom in the compound is in an octahedral geometry and is coordinated by one Schiff base ligand, one thiocyanate anion, and one methanol molecule. The Schiff base acts as a tetradentate ligand and ligates to the Ni atom through two phenolate O atoms and two imine N atoms. The thiocyanate anion is a monodentate ligand and coordinates to the nickel *via* the terminal N atom. The three *trans* angles at Ni are all close to 180° (Table 1). The other angles are close to 90° , varying from

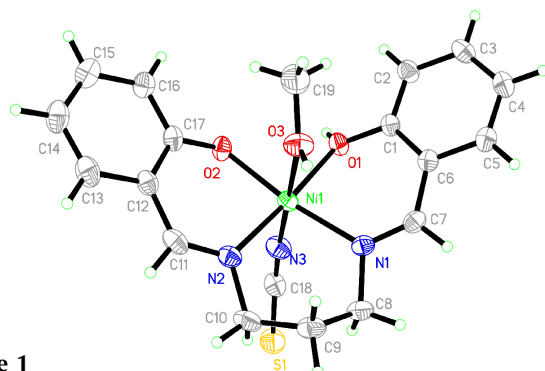


Figure 1
The structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. Only the major component of the disordered S atom is shown.

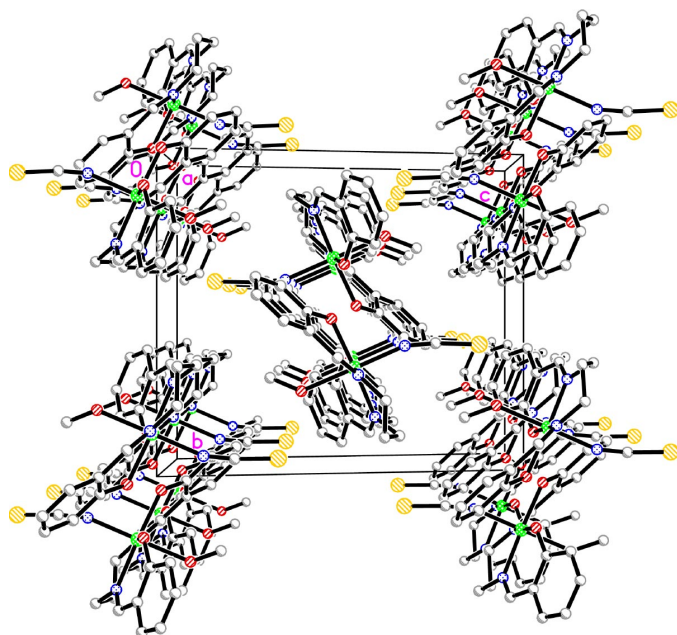


Figure 2
The crystal packing of (I), viewed along the *a* axis. H atoms have been omitted for clarity.

85.59 (8) to 95.64 (10)°, which indicates a slightly distorted octahedral geometry of the Ni atom. The six bond distances around the Ni atom are similar, ranging from 2.014 (2) to 2.163 (2) Å. The Ni—O(phenolate) bond lengths [2.054 (2) Å for Ni1—O1 and 2.014 (2) Å for Ni1—O2] are comparable to the value of 2.038 (2) Å observed by us in a Schiff base nickel(II) compound (You, Xiong *et al.*, 2003). The Ni1—O1 bond length of 2.054 (2) Å is a little longer than the Ni1—O2 bond distance of 2.014 (2) Å, which is probably due to the presence of the H atom on O1, while there is no H atom on O2. The presence of the H atom on O1 leads to the weaker interaction between Ni1 and O1 than that between Ni1 and O2. The average Ni—N(imine) bond distance of 2.043 (3) Å is a little shorter than the value of 2.068 (3) Å observed in the nickel compound cited above. The Ni1—O3 bond distance of 2.163 (2) Å is a little shorter than the corresponding bond length of 2.178 (6) Å observed in a similar Schiff base nickel(II) complex (Tatar *et al.*, 2002). The Ni1—N3 bond

distance of 2.056 (3) Å is a little shorter than the value of 2.121 (4) Å observed in a thiocyanate–nickel(II) complex we reported recently (Zhu *et al.*, 2003). The conformation of the six-membered ring containing the nickel, azomethine N atoms and three C atoms of the connecting 1,3-diaminopropane is an asymmetric chair. The torsion angles N1—C8—C9—C10 and N2—C10—C9—C8 are 71.9 (4) and –72.4 (4)°, respectively. The dihedral angle between the two benzene rings is 56.6 (3)°.

In the crystal structure, the complex forms centrosymmetric O—H···O hydrogen-bonded dimers. The symmetry-related dimers are linked by weaker O—H···S hydrogen bonds to form layers parallel to the *bc* plane (Fig. 2 and Table 2).

Experimental

Salicylaldehyde (2.0 mmol, 244 mg) and 1,3-diaminopropane (1.0 mmol, 74 mg) were dissolved in methanol (10 ml). The mixture was stirred at room temperature for 1 h to give a yellow precipitate of H₂L, where H₂L is *N,N'*-bis(2-hydroxyphenylmethenylimino)-1,3-diaminopropane. The precipitate was filtered off, washed three times with methanol and dried in a vacuum desiccator containing anhydrous CaCl₂ (yield 85.8%). Analysis found: C 72.38, H 6.50, N 9.85%; calculated for C₁₇H₁₈N₂O₂: C 72.32, H 6.43, N 9.92%. To a methanol solution (10 ml) of Ni(ClO₄)₂·7H₂O (1.0 mmol, 383 mg) was added a methanol solution (20 ml) of H₂L (282.0 mg, 1.0 mmol) and a methanol solution (10 ml) of ammonium thiocyanate (76.1 mg, 1.0 mmol), with stirring. The mixture was stirred for 1 h at room temperature and then filtered. After keeping the filtrate in air for 13 d, green block-shaped crystals were formed at the bottom of the vessel on slow evaporation of the solvent. The crystals were isolated, washed three times with methanol and dried in a vacuum desiccator using P₄O₁₀ (yield 62.3%). Analysis found: C 52.98, H 5.01, N 9.70%; calculated for C₁₉H₂₁N₃O₃SNi: C 53.05, H 4.92, N 9.77%.

Crystal data

[Ni(C₁₇H₁₇N₂O₂)(NCS)(CH₄O)]
M_r = 430.16
 Monoclinic, *P*2₁/*c*
a = 10.508 (3) Å
b = 12.998 (4) Å
c = 15.266 (5) Å
 β = 104.201 (4)°
V = 2021.4 (11) Å³
Z = 4

D_x = 1.413 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 3659 reflections
 θ = 3.8–24.1°
 μ = 1.09 mm⁻¹
T = 298 (2) K
 Block, green
 0.41 × 0.37 × 0.33 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.651, *T_{max}* = 0.701
 10 472 measured reflections

3574 independent reflections
 2699 reflections with *I* > 2σ(*I*)
R_{int} = 0.028
 θ_{max} = 25.0°
h = –12 → 12
k = –12 → 15
l = –18 → 18

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.036
wR (*F*²) = 0.107
S = 1.01
 3574 reflections
 253 parameters

H-atom parameters constrained
w = 1/[σ²(*F_o*²) + (0.0626*P*)²]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.40 e Å⁻³
 Δρ_{min} = –0.32 e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Ni1—O2	2.014 (2)	Ni1—O1	2.054 (2)
Ni1—N1	2.041 (3)	Ni1—N3	2.056 (3)
Ni1—N2	2.045 (3)	Ni1—O3	2.163 (2)
O2—Ni1—N1	171.89 (9)	N2—Ni1—N3	90.55 (11)
O2—Ni1—N2	89.46 (9)	O1—Ni1—N3	91.85 (10)
N1—Ni1—N2	95.64 (10)	O2—Ni1—O3	85.59 (8)
O2—Ni1—O1	87.14 (8)	N1—Ni1—O3	88.12 (9)
N1—Ni1—O1	87.51 (9)	N2—Ni1—O3	89.92 (10)
N2—Ni1—O1	175.97 (9)	O1—Ni1—O3	87.66 (8)
O2—Ni1—N3	94.02 (10)	N3—Ni1—O3	179.39 (10)
N1—Ni1—N3	92.23 (11)		

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3...S1 ⁱ	0.93	2.44	3.352 (10)	166
O3—H3...S1 ⁱ	0.93	2.41	3.309 (3)	163
O1—H1A...O2 ⁱⁱ	0.85	1.63	2.462 (3)	166

Symmetry codes: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $1 - x, -y, -z$.

During the final stages of the refinement, the highest difference peak ($1.37 \text{ e } \text{\AA}^{-3}$, 1.20 \AA from S1) was found to be much larger than the absolute value of the deepest hole ($-0.91 \text{ e } \text{\AA}^{-3}$, 0.88 \AA from S1). The positions of these peaks and the largest displacement parameters for S1 suggested disorder. The occupancies of the disordered positions S1/S1' were initially refined and later fixed at 67/33%. After checking their presence in a difference map, all the H atoms were placed in geometrically idealized positions and allowed to ride on their parent atoms, with O—H and C—H distances of 0.85–0.93 and

0.93–0.97 Å, respectively. The $U_{\text{iso}}(\text{H})$ value for atom O1 was fixed at 0.08 \AA^2 and those for the remaining H atoms were set equal to $1.2U_{\text{eq}}(\text{parent atom})$ [for methyl H atoms, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$].

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

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