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Bis{2-[2-(diethylamino)ethyliminomethyl]-4-nitrophenolato}dithiocyanatonickel(II) dihydrate

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.003 Å
R factor = 0.037
wR factor = 0.095
Data-to-parameter ratio = 18.0

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

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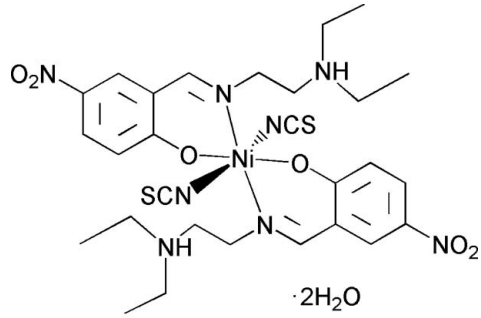
In the title centrosymmetric mononuclear nickel(II) compound, $[Ni(C_{13}H_{19}N_3O_3)_2(NCS)_2]\cdot 2H_2O$, the Ni^{II} atom lies on an inversion centre and is six-coordinated by two phenolate O and two imine N atoms from two Schiff base ligands, and by two terminal N atoms from two thiocyanate anions, forming an octahedral coordination. In the crystal structure, molecules are linked through intermolecular O—H···O, O—H···N and N—H···O hydrogen bonds, forming chains running along [101].

Comment

Urea is highly stable in aqueous solutions. To avoid the accumulation of urea, the enzyme urease (urea amidohydrolase, E·C. 3.5.1.5) catalyses the hydrolysis of urea to form ammonium carbamate 10^{14} times faster than the uncatalysed disproportionation of urea to yield ammonia and cyanic acid (Todd & Hausinger, 2000; Karplus *et al.*, 1997; Wolfenden & Snider, 2001). However, high concentrations of ammonia arising from these reactions, as well as the accompanying pH elevation, have important implications in medicine and agriculture (Mobley *et al.*, 1995; Mulvaney & Bremner, 1981; Zonia *et al.*, 1995). In 1926, the protein from jack bean seeds was the first enzyme to be crystallized (Sumner, 1926). Crystallographic analysis of the *Klebsiella aerogenes* enzyme first revealed a dinuclear nickel(II) active site with the two metal atoms bridged by a carbamylated lysine and a hydroxide (Jabri *et al.*, 1995; Pearson *et al.*, 1997). In order to mimic the urease structure and to investigate the novel urease inhibitor, the title new nickel(II) complex, (I), was synthesized and its crystal structure is reported here.



(I)

Compound (I) is a mononuclear nickel(II) complex (Fig. 1), which contains a bis{2-[2-(diethylamino)ethyliminomethyl]-4-nitrophenolato}dithiocyanatonickel(II) unit and two uncoordinated water molecules. The Ni^{II} atom, lying on an inversion centre, is six-coordinated by two Schiff base ligands

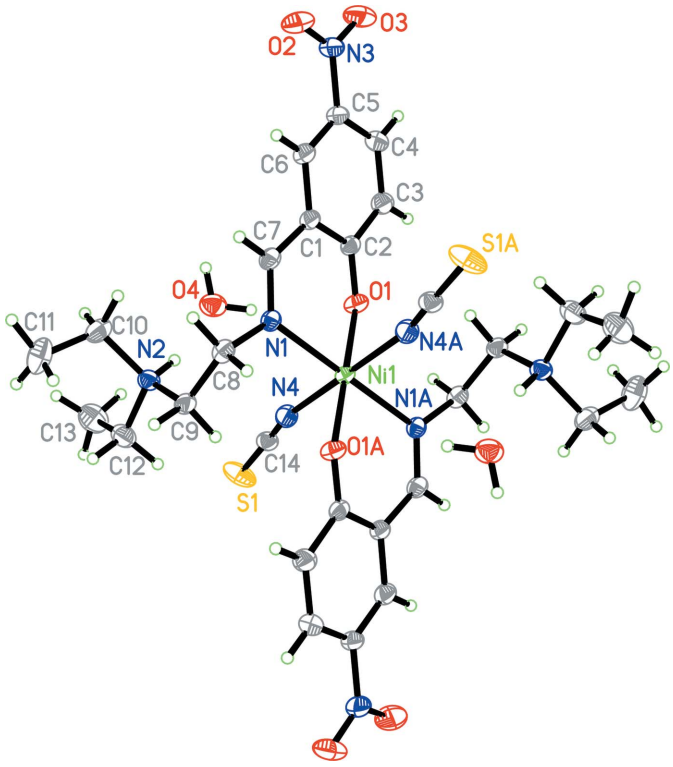


Figure 1
View of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms labelled with the suffix A and unlabelled atoms are generated by the symmetry code $(1-x, 1-y, 1-z)$.

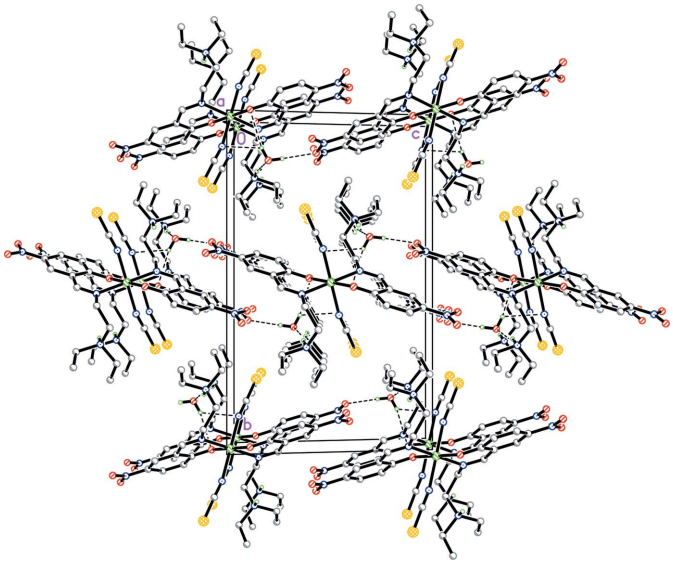


Figure 2
The crystal packing of (I). Intermolecular hydrogen bonds are shown as dashed lines.

and two thiocyanate anions, forming an octahedral coordination. Each Schiff base acts as a bidentate ligand and chelates to the Ni^{II} atom *via* the phenolate O and imine N atoms. The amine N atom of the Schiff base is protonated and not coordinated to the Ni atom. Each thiocyanate anion acts as a monodentate ligand and coordinates to the Ni atom *via* the terminal N atom. The bond lengths involving the Ni^{II} atom (Table 1) are comparable with the corresponding values observed in other Schiff base nickel(II) complexes (You, 2005, 2006). The C7═N1 bond length conforms to the value for a double bond, while the C8—N1 bond length conforms to the value for a single bond. The bond angles around the Ni^{II} centre show slight deviations from ideal octahedral geometry (Table 1). The thiocyanate anion is nearly linear and shows a bent coordination mode with the Ni^{II} atom. The nitro group is coplanar with the C1–C6 benzene ring, the dihedral angle between the two planes being 3.0 (2)°.

In the crystal structure, molecules are linked through intermolecular O—H···O, O—H···N and N—H···O hydrogen bonds (Table 2), forming chains running along [101] (Fig. 2).

Experimental

N,*N*-Diethylethane-1,2-diamine and 5-nitrosalicylaldehyde were available commercially and were used without further purification. *N*,*N*-Diethylethane-1,2-diamine (0.1 mmol, 13.5 mg) and 5-nitrosalicylaldehyde (0.1 mmol, 16.7 mg) were dissolved in MeOH (10 ml). The mixture was stirred at room temperature for 10 min to give a clear yellow solution. To this solution was added an aqueous solution (2 ml) of NH_4NCS (0.1 mmol, 7.6 mg) and an MeOH solution (5 ml) of $Ni(CH_3COO)_2{\cdot}4H_2O$ (0.1 mmol, 24.9 mg), with stirring. The resulting mixture was stirred for another 10 min at room temperature. After allowing the filtrate to stand in air for 8 d, green block-shaped crystals were formed at the bottom of the vessel. Analysis found: C 45.23, H 5.83, N 15.23%; calculated for $C_{28}H_{42}N_8NiO_8S_2$: C 45.35, H 5.71, N 15.11%.

Crystal data

$[Ni(C_{13}H_{19}N_3O_3)_2(NCS)_2]{\cdot}2H_2O$
$M_r = 741.53$
Monoclinic, $P2_1/c$
$a = 6.909$ (1) Å
$b = 20.183$ (2) Å
$c = 12.554$ (1) Å
$\beta = 102.84$ (1)°
$V = 1706.8$ (3) Å^3
$Z = 2$
$D_x = 1.443$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5943 reflections
$\theta = 2.6$–27.8°
$\mu = 0.75$ mm^{-1}
$T = 298$ (2) K
Block, green
0.27 × 0.23 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.823$, $T_{max} = 0.865$
14641 measured reflections
4052 independent reflections
3459 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 28.3°$
$h = -9 \rightarrow 9$
$k = -25 \rightarrow 26$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.095$
$S = 1.04$
4052 reflections
225 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0481P)^2 + 0.596P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—O1	2.026 (2)	N1—C7	1.280 (2)
Ni1—N4	2.093 (2)	N1—C8	1.468 (2)
Ni1—N1	2.106 (2)		
O1—Ni1—O1^{i}	180	O1—Ni1—N1^{i}	92.90 (6)
O1—Ni1—N4^{i}	91.59 (6)	N4—Ni1—N1^{i}	85.73 (6)
O1—Ni1—N4	88.41 (6)	N1—Ni1—N1^{i}	180
N4^{i}—Ni1—N4	180	C14—N4—Ni1	165.79 (16)
O1—Ni1—N1	87.10 (6)	N4—C14—S1	178.61 (18)
N4—Ni1—N1	94.27 (6)		

Symmetry code: (i) $-x+1, -y+1, -z+1$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4A···O3^{ii}	0.85 (1)	2.09 (1)	2.931 (2)	175 (3)
O4—H4B···O1	0.85 (1)	2.40 (1)	3.227 (2)	165 (3)
O4—H4B···N4	0.85 (1)	2.52 (2)	2.992 (2)	116 (2)
N2—H2···O4	0.90 (1)	2.01 (1)	2.893 (2)	167 (3)

Symmetry code: (ii) $-x, -y+1, -z$.

The amino and water H atoms were located in a difference Fourier map and refined isotropically, with the N—H, O_w—H and $H_w\cdots H_w$ distances restrained to 0.90 (1), 0.84 (1) and 1.37 (2) Å, respectively. The C-bound H atoms were placed in idealized positions and constrained to ride on their parent C atoms, with C—H distances in the range 0.93–0.97 Å and with U_{iso}(H) = 1.2 or 1.5 times U_{eq}(C).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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References

Bruker (1998). *SMART* (Version 5.628) and *SAINT* (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.
Jabri, E., Carr, M. B., Hausinger, R. P. & Karplus, P. A. (1995). *Science*, **268**, 998–1004.
Karplus, P. A., Pearson, M. A. & Hausinger, R. P. (1997). *Acc. Chem. Res.* **30**, 330–337.
Mobley, H. L. T., Island, M. D. & Hausinger, R. P. (1995). *Microbiol. Rev.* **59**, 451–480.
Mulvaney, R. L. & Bremner, J. M. (1981). *Soil Biochemistry*, Vol. 5, edited by E. A. Paul & J. N. Ladd, pp. 153–196. New York: Marcel Dekker Inc.
Pearson, M. A., Michel, L. O., Hausinger, R. P. & Karplus, P. A. (1997). *Biochemistry*, **36**, 8164–8172.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*a*). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Sumner, J. B. (1926). *J. Biol. Chem.* **69**, 435–441.
Todd, M. J. & Hausinger, R. P. (2000). *Biochemistry*, **39**, 5389–5396.
Wolfenden, R. & Snider, M. J. (2001). *Acc. Chem. Res.* **34**, 938–945.
You, Z.-L. (2005). *Acta Cryst.* E**61**, m1963–m1964.
You, Z.-L. (2006). *Z. Anorg. Allg. Chem.* **632**, 664–668.
Zonia, L. E., Stebbins, N. E. & Polacco, J. C. (1995). *Plant Physiol.* **107**, 1097–1103.