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Azido{4-bromo-2-[(2-diethylaminoethylimino)methyl]phenolato}nickel(II)

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.007 Å
R factor = 0.056
wR factor = 0.154
Data-to-parameter ratio = 18.1

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

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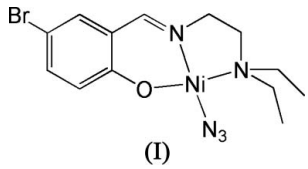
The title mononuclear nickel(II) complex, [Ni($C_{13}H_{18}BrN_2O$)N_3], contains two molecules in the asymmetric unit. Each Ni^{II} atom is four-coordinated by one phenolate O atom, one imine N atom and one amine N atom from a Schiff base ligand, and by one terminal N atom of an azide anion, forming a square-planar coordination. In the crystal structure, adjacent molecules are linked through C—H···N interactions, forming chains along the *a* axis.

Comment

Urea is formed in large quantities as a product of catabolism of nitrogen-containing compounds. Owing to its resonance stabilization, urea is highly stable in aqueous solutions. For example, urea spontaneously eliminates ammonia to form cyanic acid with a half-life of 3.6 years at 311 K. To avoid the accumulation of urea, the enzyme urease (urea amidohydrolase, E.C. 3.5.1.5), which is present in a variety of plants, selected fungi and a broad range of bacterial species, catalyzes the hydrolysis of urea to form ammonia and carbamate 10^{14} times faster than the uncatalyzed elimination 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 group (Jabri *et al.*, 1995; Pearson *et al.*, 1997). The coordination of one Ni atom is pseudo-tetrahedral and the other is distorted trigonal–bipyramidal. In order to mimic the urease structure and investigate the novel urease inhibitor, the title new nickel(II) complex, (I), was synthesized and its crystal structure is reported here.



(I)

The asymmetric unit of (I) contains a pair of mononuclear nickel(II) complex molecules (Fig. 1). Both the Ni^{II} atoms are four-coordinated by one phenolate O atom, one imine N atom and one amine N atoms from the Schiff base ligand, and by one terminal N atom of a coordinated azide anion. The four

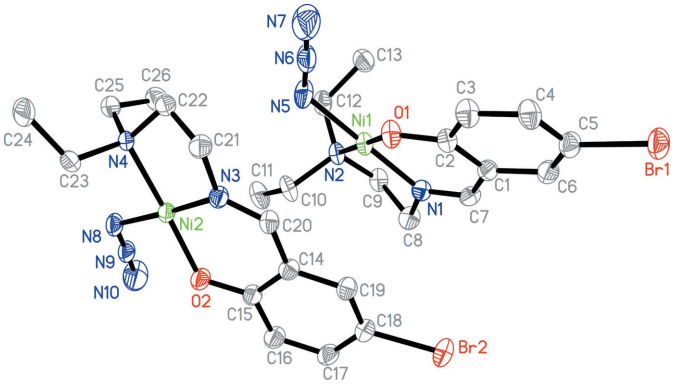


Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

coordinating atoms around each Ni^{II} centre are approximately coplanar, giving a square-planar geometry with an r.m.s. deviation of 0.016 (3) Å for the Ni1 complex [0.011 (3) Å for the Ni2 complex]. The bond lengths (Table 1) involving the Ni^{II} atoms are comparable with the corresponding values observed in other Schiff base nickel(II) complexes (You, 2005, 2006). The C7═N1 and C20═N3 bond lengths conform to the values for double bonds, while the C8—N1 and C21—N3 bond lengths conform to the values for single bonds. The bond angles around the Ni^{II} centres show slight deviation from ideal square-planar geometry (Table 1). The azide anions are nearly linear and show bent coordination modes with the Ni^{II} atoms (Table 1).

In the crystal structure, adjacent molecules are linked through C—H···N hydrogen bonds (Table 2) forming chains along the *a* axis.

Experimental

N,*N*-Diethylethane-1,2-diamine and 5-bromosalicylaldehyde were available commercially and were used without further purification. *N*,*N*-Diethylethane-1,2-diamine (0.1 mmol, 13.5 mg) and 5-bromosalicylaldehyde (0.1 mmol, 20.2 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 NaN_3 (0.1 mmol, 6.5 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 keeping the filtrate in air for 3 d, green block-shaped crystals were formed at the bottom of the vessel. Analysis found: C 38.93, H 4.60, N 17.60%; calculated for $C_{13}H_{18}BrN_5NiO$: C 39.14, H 4.55, N 17.56%.

Crystal data

$[Ni(C_{13}H_{18}BrN_2O)N_3]$
M_r = 398.94
Triclinic, $P\overline{1}$
a = 9.261 (1) Å
b = 10.178 (1) Å
c = 17.274 (2) Å
α = 100.90 (1)°
β = 100.88 (1)°
γ = 93.66 (1)°
V = 1561.7 (3) Å^3
Z = 4
D_x = 1.697 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3098 reflections
θ = 2.3–25.4°
μ = 3.81 mm^{-1}
T = 298 (2) K
Block, green
0.18 × 0.14 × 0.13 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scan
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.547, T_{max} = 0.638
13422 measured reflections
6917 independent reflections
4684 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 27.5°
$h = -10 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.154
S = 0.98
6917 reflections
383 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.086P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.10 e Å^{-3}
$\Delta\rho_{min}$ = −0.78 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—O1	1.826 (3)	Ni2—N8	1.898 (4)
Ni1—N1	1.848 (4)	Ni2—N4	1.957 (4)
Ni1—N5	1.901 (5)	N1—C7	1.288 (6)
Ni1—N2	1.962 (4)	N1—C8	1.463 (6)
Ni2—O2	1.827 (3)	N3—C20	1.280 (6)
Ni2—N3	1.850 (4)	N3—C21	1.463 (6)
O1—Ni1—N1	93.92 (16)	N3—Ni2—N8	177.23 (17)
O1—Ni1—N5	88.47 (18)	O2—Ni2—N4	177.95 (15)
N1—Ni1—N5	177.44 (18)	N3—Ni2—N4	87.13 (16)
O1—Ni1—N2	178.64 (14)	N8—Ni2—N4	90.13 (17)
N1—Ni1—N2	87.01 (17)	N5—N6—N7	176.5 (6)
N5—Ni1—N2	90.62 (19)	Ni1—N5—N6	120.5 (4)
O2—Ni2—N3	94.06 (16)	N8—N9—N10	176.6 (6)
O2—Ni2—N8	88.68 (16)	Ni2—N8—N9	121.3 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
C24—H24A···N10^{i}	0.96	2.49	3.407 (9)	160

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

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.93–0.97 Å, and with U_{iso}(H) values of 1.2 or 1.5 times U_{eq}(C). The highest peak is located 0.93 Å from atom Br2.

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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