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Key indicators

Single-crystal X-ray study
 T = 298 K
 Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$
 Disorder in solvent or counterion
 R factor = 0.057
 wR factor = 0.156
 Data-to-parameter ratio = 14.5

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

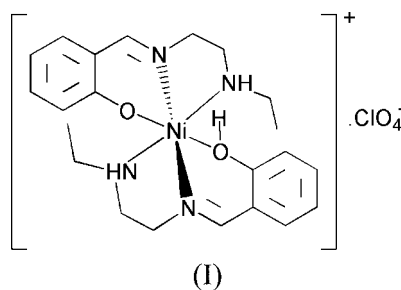
**{2-[2-(Ethylamino)ethyliminomethyl]phenol}-
 {2-[2-(ethylamino)ethyliminomethyl]phenolato}-
 nickel(II) perchlorate**

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In the title structure, $[\text{Ni}(\text{C}_{11}\text{H}_{15}\text{N}_2\text{O})(\text{C}_{11}\text{H}_{16}\text{N}_2\text{O})]\text{ClO}_4$, there are two independent ion pairs in the asymmetric unit. In each cation, the Ni^{II} atom is six-coordinated in a slightly distorted octahedral geometry by two phenolate O atoms, two imine N atoms and two amine N atoms from two Schiff base ligands, in one of which the phenolate O atom is protonated. In the crystal structure, anions and cations are linked through intermolecular O—H···O, N—H···O and weak C—H···O hydrogen bonds, forming one-dimensional chains containing hydrogen-bonded cation dimers.

Comment

The first enzyme to be crystallized was urease from jack bean seeds (Sumner, 1926). The crystal structure of the *Klebsiella aerogenes* enzyme revealed a dinuclear nickel(II) active site with the two metals bridged by a carbamylated lysine and a hydroxide group (Jabri *et al.*, 1995; Pearson *et al.*, 1997). In this structure, the coordination of one Ni atom is pseudo-tetrahedral and the other is distorted trigonal-bipyramidal. It is well known that urea is formed in large quantities as a product of the catabolism of nitrogen-containing compounds. Owing to its resonance stabilization, urea is highly stable in aqueous solutions. To avoid accumulation of urea, urease catalyses the hydrolysis of urea, forming ammonia and carbamate 10¹⁴ times faster than the uncatalysed elimination of urea, yielding ammonia and cyanic acid (Todd & Hausinger, 2000; Karplus *et al.*, 1997; Wolfenden & Snider, 2001). However, the 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 order to mimic the urease structure and to search for novel urease inhibitors, the title nickel(II) complex, (I), was synthesized and its crystal structure is reported here.



Complex (I) contains two independent mononuclear nickel(II) complex cations and two perchlorate anions in the asymmetric unit (Fig. 1). The two nickel(II) complex cations

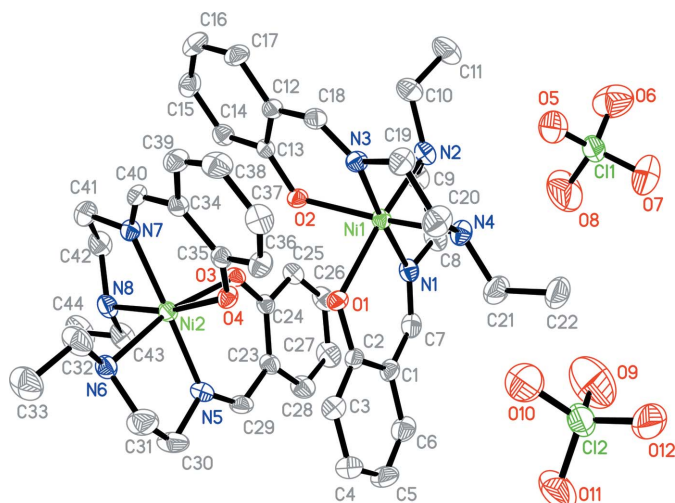


Figure 1
The asymmetric unit of (I), with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity and only the major component of the disordered perchlorate anion is shown.

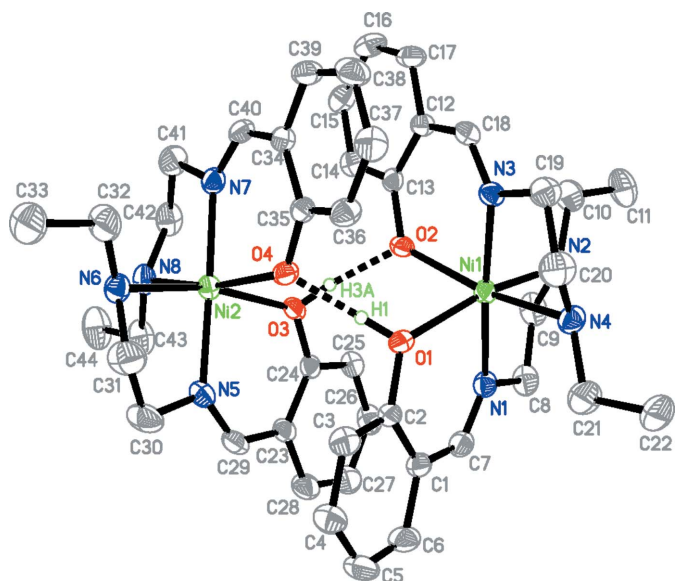


Figure 2
View of the O—H...O strong hydrogen bonds of the title complex.

are linked together by strong intermolecular O1—H1...O4 and O3—H3A...O2 hydrogen bonds (Fig. 2). Both Ni^{II} atoms are six-coordinated by one phenolate and one phenol O atoms, two imine N atoms and two amine N atoms from two Schiff base ligands, forming slightly distorted octahedral coordination geometries. The bond lengths around the Ni^{II} atoms are the same within experimental error, ranging from 2.031 (3) to 2.150 (3) Å for Ni1, and from 2.022 (3) to 2.153 (3) Å for Ni2 (Table 1). The largest deviations of the *cis* bond angles from those expected for an ideal octahedral geometry are N3—Ni1—N4 and N3—Ni1—O1 for Ni1, and N7—Ni2—N8 and N5—Ni2—N8 for Ni2.

In the crystal structure, the ions are linked to the Ni^{II} cations through intra- and intermolecular N—H...Cl hydrogen bonds (Table 2). The molecules are further linked

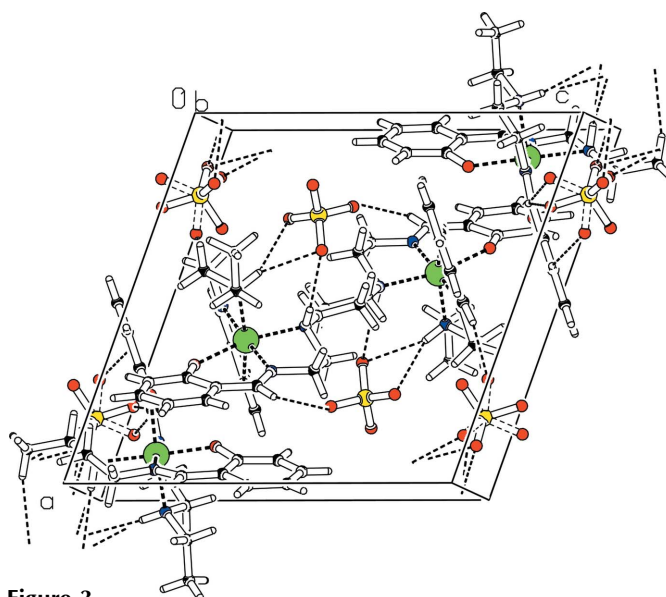


Figure 3
Partial packing plot (Spek, 2003) of (I), showing intermolecular hydrogen bonds as dashed lines. Colour codes: green Ni, yellow Cl, red O, blue N and black C.

through intermolecular N—H...O and C—H...O hydrogen bonds, forming one-dimensional chains (Table 2 and Fig. 3).

Experimental

N-Ethylethane-1,2-diamine and salicylaldehyde are available commercially and were used without further purification. *N*-Ethylethane-1,2-diamine (0.1 mmol, 8.8 mg) and salicylaldehyde (0.1 mmol, 12.1 mg) were dissolved in MeOH (10 ml). The mixture was stirred at room temperature for 30 min to give a clear yellow solution. To this solution was added an aqueous solution (5 ml) of Ni(ClO₄)₂·7H₂O (0.1 mmol, 38.4 mg) with stirring. The resulting mixture was stirred for another 30 min at room temperature. After leaving the filtrate to stand in air for 7 d, green block-shaped crystals of (I) were formed at the bottom of the vessel. Analysis, found: C 48.63, H 5.50, N 10.51%; calculated for C₂₂H₃₁ClN₄NiO₆: C 48.78, H 5.77, N 10.34%.

Crystal data

[Ni(C ₁₁ H ₁₅ N ₂ O)(C ₁₁ H ₁₆ N ₂ O)]ClO ₄	$V = 2472.9 (7) \text{ \AA}^3$
$M_r = 541.67$	$Z = 4$
Triclinic, $P\bar{1}$	$D_x = 1.455 \text{ Mg m}^{-3}$
$a = 13.813 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 13.850 (2) \text{ \AA}$	$\mu = 0.94 \text{ mm}^{-1}$
$c = 13.979 (2) \text{ \AA}$	$T = 298 (2) \text{ K}$
$\alpha = 100.24 (2)^\circ$	Block, green
$\beta = 106.14 (2)^\circ$	$0.25 \times 0.10 \times 0.10 \text{ mm}$
$\gamma = 98.45 (2)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	19417 measured reflections
ω scans	9586 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	6741 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.800$, $T_{\max} = 0.912$	$R_{\text{int}} = 0.042$
	$\theta_{\text{max}} = 26.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.157$
 $S = 1.03$
 9586 reflections
 663 parameters
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.076P)^2 + 0.0425P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.81 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.62 \text{ e } \text{Å}^{-3}$

Table 1
 Selected geometric parameters (Å, °).

Ni1—N3	2.031 (3)	Ni2—N5	2.022 (3)
Ni1—N1	2.037 (3)	Ni2—N7	2.031 (3)
Ni1—O2	2.110 (3)	Ni2—O4	2.098 (3)
Ni1—O1	2.134 (3)	Ni2—O3	2.114 (3)
Ni1—N2	2.146 (4)	Ni2—N6	2.146 (3)
Ni1—N4	2.150 (3)	Ni2—N8	2.153 (3)
N3—Ni1—N1	176.64 (12)	N5—Ni2—N7	178.45 (12)
N3—Ni1—O2	84.89 (11)	N5—Ni2—O4	94.04 (12)
N1—Ni1—O2	97.26 (11)	N7—Ni2—O4	86.61 (12)
N3—Ni1—O1	98.53 (12)	N5—Ni2—O3	85.69 (12)
N1—Ni1—O1	84.27 (12)	N7—Ni2—O3	95.75 (12)
O2—Ni1—O1	84.79 (10)	O4—Ni2—O3	86.69 (10)
N3—Ni1—N2	95.92 (14)	N5—Ni2—N6	82.08 (14)
N1—Ni1—N2	81.40 (14)	N7—Ni2—N6	96.50 (14)
O2—Ni1—N2	93.31 (12)	O4—Ni2—N6	91.87 (12)
O1—Ni1—N2	165.19 (12)	O3—Ni2—N6	167.56 (12)
N3—Ni1—N4	81.40 (13)	N5—Ni2—N8	97.46 (14)
N1—Ni1—N4	96.64 (13)	N7—Ni2—N8	81.97 (14)
O2—Ni1—N4	165.62 (12)	O4—Ni2—N8	167.99 (12)
O1—Ni1—N4	92.94 (13)	O3—Ni2—N8	90.74 (12)
N2—Ni1—N4	92.41 (14)	N6—Ni2—N8	93.11 (13)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots O4	0.86 (3)	1.60 (3)	2.457 (4)	180 (6)
O3—H3A \cdots O2	0.84 (4)	1.61 (5)	2.448 (3)	172 (5)
N4—H4A \cdots O5	0.89 (4)	2.37 (4)	3.247 (6)	167 (4)
N6—H6A \cdots O10 ^j	0.90 (5)	2.52 (2)	3.411 (13)	174 (5)
N6—H6A \cdots O10 ⁱ	0.90 (5)	2.27 (2)	3.16 (2)	174 (5)
N2—H2 \cdots O8	0.89 (4)	2.52 (3)	3.316 (7)	149 (4)
N2—H2 \cdots O5	0.89 (4)	2.36 (2)	3.186 (6)	154 (5)
N8—H8 \cdots O10 ⁱ	0.90 (3)	2.57 (3)	3.337 (10)	143 (4)
N8—H8 \cdots O11 ⁱ	0.90 (3)	2.33 (2)	3.202 (5)	162 (5)
C8—H8B \cdots O8	0.97	2.50	3.325 (7)	143
C18—H18 \cdots O6 ⁱⁱ	0.93	2.60	3.500 (7)	163 (4)
C29—H29 \cdots O12 ⁱⁱⁱ	0.93	2.54 (3)	3.410 (7)	155 (4)

Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $-x + 1, -y, -z + 1$; (iii) $x, y, z - 1$.

Atoms H1, H2, H3A, H4A, H6A and H8 were located in a difference Fourier map and refined isotropically, with O—H distances restrained to 0.85 (1) Å, N—H distances restrained to 0.90 (1) Å and $U_{\text{iso}}(\text{H})$ values fixed at 0.08 Å². The other H atoms were placed in calculated positions and constrained to ride on their parent atoms, with C—H distances in the range 0.93–0.97 Å, and with $U_{\text{iso}}(\text{H})$ set at 1.2 $U_{\text{eq}}(\text{C})$, or 1.5 $U_{\text{eq}}(\text{C})$ for methyl H atoms. Atoms O9, O10 and O12 of one perchlorate anion are disordered over two distinct sites with refined occupancies of 0.675 (3) and 0.325 (3). The Cl—O distances in the disordered components were restrained to 1.41 (1) Å, and the O \cdots O distances were restrained to be equal. The U^{ij} components of atoms O8 and O12' were restrained to isotropic behaviour.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; 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* and *PLATON* (Spek, 2003).

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