metal-organic compounds

Hydrogen bonds in the framework of bis{2-[bis(2-aminoethyl)amino]-ethanol}nickel(II) diperchlorate

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The title molecule, $[Ni(C_6H_{17}N_3O)_2](ClO_4)_2$, possesses a crystallographic centre of symmetry at the Ni^{II} position. The coordination geometry around the Ni^{II} atom is distorted octahedral, consisting of six N atoms from two tripodal polyamine ligands, while the ethanol O atoms of the ligands remain uncoordinated. The crystal packing shows two-dimensional layers and an infinite three-dimensional framework which is stabilized by a hydrogen-bonded network.

Comment

Non-redox-active metals such as Ni^{II} and Zn^{II} are potentially of interest as hydrolytic cleaving agents of DNA, and their reactivity in model systems may lead to functional DNA cleaving molecules. Metal–polyamine complexes of Ni^{II} or Zn^{II} are frequently used as models for hydrolases. Among the polyamine ligands designed, tripodal polyamines are of special interest owing to their implication in a wide variety of biochemical and supramolecular systems (Mao *et al.*, 1993; Anderegg & Gramlich, 1994; Murthy & Karlin, 1993; Lu *et al.*, 1998). Some reported Ni^{II}–tripodal polyamine complexes exhibit very high hydrolytic activity towards phosphate esters and are potential artificial DNA-cut agents (De Rosch & Trogler, 1990; Tafesse *et al.*, 1993). In the course of our work on the synthesis of metal–asymmetric tripodal heteropoly-amine complexes, we obtained a new 1:2 $Ni^{II}L$ complex, (I), with a structure of firstly infinite two-dimensional layers, then an infinite three-dimensional framework stabilized by a hydrogen-bond network.

(I)
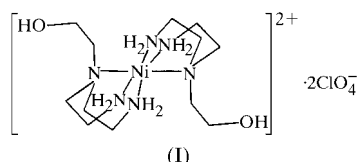
As depicted in Fig. 1, the Ni^{II} atom is located at the symmetry centre and exhibits a slightly distorted octahedral geometry consisting of six N atoms from two tripodal poly-amine ligands. Four primary amine N atoms form the equatorial plane in which the Ni^{II} atom lies almost in the middle with equal Ni^{II}—N distances [Ni^{II}—N2 = Ni^{II}—N2($-x$, $-y$, $-z$) = 2.122 (2) Å and Ni^{II}—N3 = Ni^{II}—N3($-x$, $-y$, $-z$) = 2.129 (2) Å], while the apical N atom (tertiary amine N atom) is a little bit further from the central Ni^{II} atom [Ni^{II}—N1 = Ni^{II}—N1($-x$, $-y$, $-z$) = 2.191 (2) Å]. All the N—Ni^{II}—N bond angles are in the range 82.32 (9)–91.17 (10)°. The $ClO_2O_3O_4O_5$ and $Cl'O_2'O_3'O_4'O_5'$ perchlorate anions are disordered, with occupancy factors of 0.50. Six kinds of hydrogen bonds occur in the structure. A hydrogen bond between the ethanol O1 atom and the amine N3 atom of an adjacent ligand [N3—H3A···O1($\frac{1}{2} - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$): N3···O1 3.11 Å and N3—H3A···O1 155°] is responsible for the formation of the two-dimensional sheet-like $Ni^{II}L_2$ cation polymers which spread along the $(1,0,\bar{1})$ plane to form an
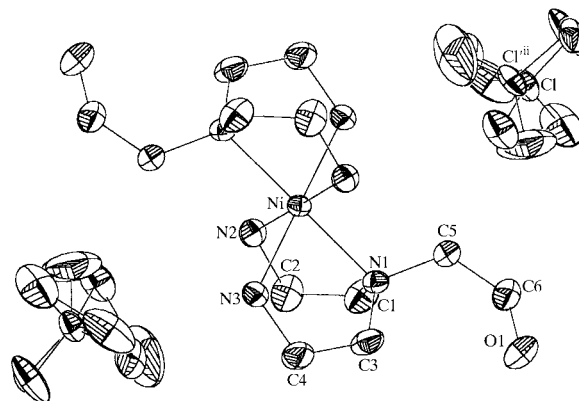

Figure 1
The molecular structure of (I) showing 30% probability displacement ellipsoids and atom-numbering scheme. H atoms have been omitted for clarity. [Symmetry code: (i) $-x$, $-y$, $-z$.]
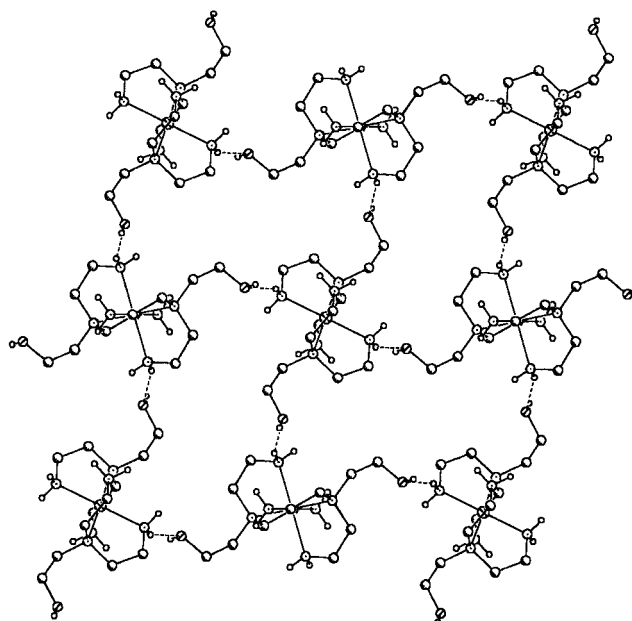

Figure 2
A view of the two-dimensional network along the $(1,0,\bar{1})$ plane. Unrelated H atoms and perchlorate anions have been omitted for clarity.
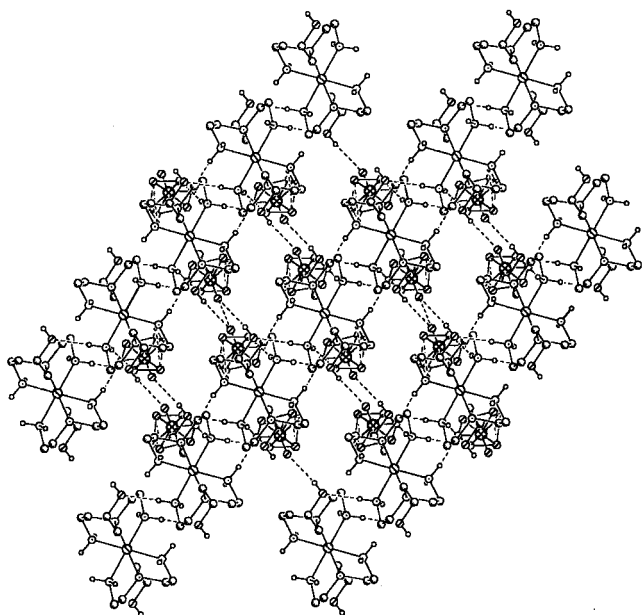
Figure 3
Packing diagram viewed down the *b* axis, showing the three-dimensional framework.

infinite network (see Fig. 2). Three kinds of additional hydrogen bonds exist inside the layer between the N atoms of the amine pods and the perchlorate anions: N2—H2A···O3($-x$, $-y$, $-z$), N2···O3 3.16 Å and N2—H2A—O3 161°; N3—H3B···O4($-x$, $-y$, $-z$), N3···O4 3.09 Å and N3—H3B···O4 155°; N3—H3B···O4′($-x$, $-y$, $-z$), N3···O4′ 3.04 Å and N3—H3B···O4′ 171°. The other two kinds of hydrogen bonds [O1—H1···O2(1 + x, y, z), O1···O2 2.9 Å and O1—H1···O2 168°; O1—H1···O2′(1 + x, y, z), O1···O2′ 3.04 Å and O1—H1—O2′ 162°] between the ethanol O atom and the perchlorate anions crosslink the layers into one three-dimensional framework, as is depicted in Fig. 2.

Experimental

The title compound was synthesized by mixing the ligand 2-[bis(2-aminoethyl)amino]ethanol (0.147 g, 1 mmol) and $Ni^{II}(ClO_4)_2 \cdot 6H_2O$ (0.366 g, 1 mmol) in water. Purple crystals were obtained upon evaporation of the solvent.

Crystal data

$[Ni(C_6H_{17}N_3O)_2](ClO_4)_2$	$D_x = 1.648$ Mg m^{-3}
$M_r = 552.06$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25
$a = 9.0260 (10)$ Å	reflections
$b = 12.623 (2)$ Å	$\theta = 2.95–16.23°$
$c = 10.6830 (10)$ Å	$\mu = 1.173$ mm^{-1}
$\beta = 113.900 (10)°$	$T = 298 (2)$ K
$V = 1112.8 (2)$ Å^3	Prism, purple
$Z = 2$	$0.50 \times 0.44 \times 0.32$ mm

Data collection

Siemens $P4$ diffractometer	$R_{int} = 0.016$
ω scans	$\theta_{max} = 25.50°$
Absorption correction: empirical	$h = 0 \rightarrow 10$
(North *et al.*, 1968)	$k = 0 \rightarrow 15$
$T_{min} = 0.598$, $T_{max} = 0.687$	$l = -12 \rightarrow 11$
2397 measured reflections	3 standard reflections
2061 independent reflections	every 97 reflections
1700 reflections with $I > 2\sigma(I)$	intensity decay: 2.25%

Table 1
Selected geometric parameters (Å, °).

Ni—N2	2.122 (2)	Ni—N1	2.191 (2)
Ni—N3	2.129 (2)		
N2—Ni—N3	91.17 (10)	N3—Ni—N1^i	98.18 (9)
N2—Ni—N1^i	97.68 (9)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^i	0.82 (3)	2.09 (3)	2.895 (14)	168 (5)
O1—H1···O2′^{i}	0.82 (3)	2.25 (3)	3.041 (18)	162 (4)
N2—H2A···O3^{ii}	0.90	2.29	3.156 (9)	161
N3—H3A···O1^{iii}	0.90	2.28	3.113 (4)	154
N3—H3B···O4^{ii}	0.90	2.25	3.089 (10)	155
N3—H3B···O4′^{ii}	0.90	2.15	3.038 (14)	171

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

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.037$	$\Delta\rho_{max} = 0.59$ e Å^{-3}
$wR(F^2) = 0.105$	$\Delta\rho_{min} = -0.39$ e Å^{-3}
$S = 1.064$	Extinction correction: *SHELXL*97
2061 reflections	(Sheldrick, 1997)
192 parameters	Extinction coefficient: 0.0079 (18)
H atoms constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0669P)^2$	
$+ 0.1837P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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