

catena-Poly[tris(ethylenediamine- κ^2N,N')nickel(II) [[trithiocyanato- κ^3N -sodium(I)]- μ -aqua- $\kappa^2O:O$]Liang Shen^{a*} and Zhi Min Jing^b^aDepartment of Chemistry, Hangzhou Teachers' College, Hangzhou 310012, People's Republic of China, and ^bCollege of Pharmaceutical Science, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China
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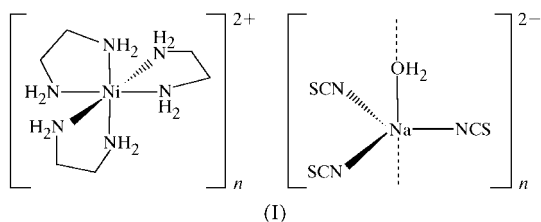
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The title complex, $\{[\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_3][\text{Na}(\text{NCS})_3(\text{H}_2\text{O})]\}_n$, consists of discrete $[\text{Ni}(\text{en})_3]^{2+}$ dications (en is ethylenediamine) and polymeric $[(\text{H}_2\text{O})_{0.5}\text{Na}(\text{NCS})_3(\text{H}_2\text{O})_{0.5}]_n^{2-}$ anions. The compound crystallizes in space group $P\bar{3}c1$. The Ni^{II} atom lies on a threefold axis and has a distorted octahedral coordination geometry. The Na^+ cation also lies on a site with imposed crystallographic threefold symmetry and is coordinated by the thiocyanate N atoms (the thiocyanates are in general positions), by one water molecule with crystallographically imposed 3_2 symmetry and by a second water molecule with crystallographically imposed $\bar{3}$ symmetry. The unique Na atom thus has trigonal-bipyramidal coordination. The O atoms of the water molecules bridge the Na^+ cations to form one-dimensional polymeric chains in the crystal structure. The $[\text{Ni}(\text{en})_3]^{2+}$ dications are distributed around and between the chains and are linked to them *via* $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds.

Comment

The Na^+ cation plays an important role in the growth of organisms and exists extensively in various kinds of organisms in the form of complexes of biological function. Research into the coordination environment of the Na^+ cation is conducive



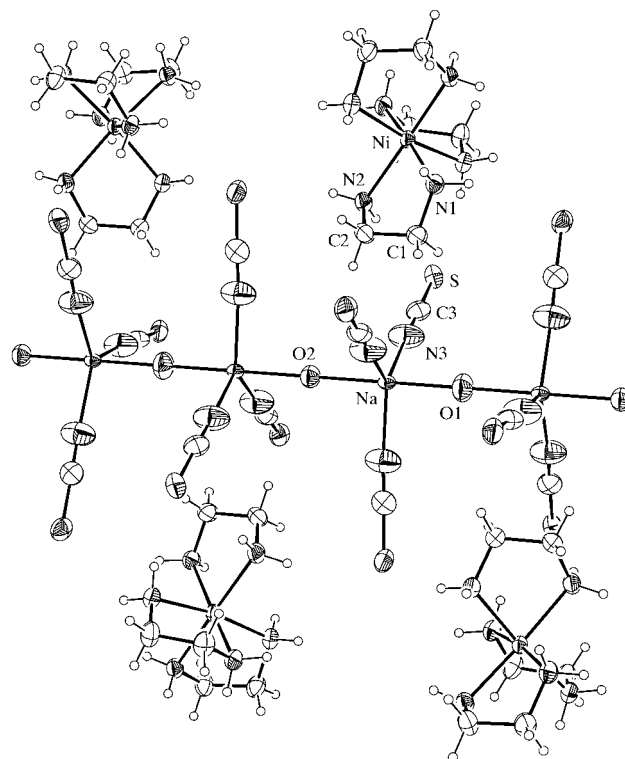
to further understanding of its biological function. The Na^+ cation usually forms four- or six-coordinated complexes (Goher & Mautner, 1994; Paixão *et al.*, 2000). Five-, seven- and eight-coordinated sodium complexes are relatively rare (Hauptmann *et al.*, 1999; Farrugia & Watson, 1999; Krishnakumar *et al.*, 2001). We report here the preparation and crystal

structure of the title five-coordinated Na complex, (I), which has trigonal-bipyramidal geometry.

The molecular structure of (I) is shown in Fig. 1. The complex comprises discrete $[\text{Ni}(\text{en})_3]^{2+}$ cations (en is ethylenediamine) and polymeric $[(\text{H}_2\text{O})_{0.5}\text{Na}(\text{NCS})_3(\text{H}_2\text{O})_{0.5}]_n^{2-}$ anion chains. The Ni^{II} atom lies on a threefold axis and has slightly distorted octahedral geometry, being coordinated by six N atoms from three ethylenediamine ligands. All bond lengths and angles involving the Ni atom are similar to those found in comparable complexes (*e.g.* Huang & Huang, 1984).

The Na atom in the anion lies on a threefold axis and has trigonal-bipyramidal coordination geometry, with the equatorial positions occupied by the three N atoms of three symmetry-related thiocyanate anions and the axial positions by the O atoms of the bridging water molecules. The thiocyanate ion is in a general position. Water atom O1 lies on a site with crystallographic 3_2 symmetry, while water atom O2 lies on a site with crystallographic $\bar{3}$ symmetry.

The $\text{N}-\text{Na}-\text{N}$ angles are $120(2)^\circ$ and the $\text{Na}-\text{O}2$ bond [$2.1719(18) \text{ \AA}$] is slightly longer than $\text{Na}-\text{O}1$ [$2.1224(18) \text{ \AA}$]. These $\text{Na}-\text{O}$ distances in (I) are significantly shorter than the $\text{Na}-\text{O}(\mu\text{-aqua})$ distances in other water O-bridged complexes, *e.g.* $[\text{NaMn}(\text{pyz})(\text{N}_3)(\text{H}_2\text{O})]$ [$2.455(2) \text{ \AA}$; pyz is pyrazine; Goher *et al.*, 1993] and $[\text{NaCu}\{\text{C}_6\text{H}_3(\text{COO})_3\}(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$ [$2.469(2) \text{ \AA}$; Chui *et al.*, 1999]. $\text{Na}-\text{O}$ distances of $2.366(4)$ and $2.375(4) \text{ \AA}$ were found in $[\text{NaCu}(\text{pic})_2(\text{N}_3)(\text{H}_2\text{O})_2]_n$ (pic is picolinate; Goher & Mautner, 1994). The $\text{Na}-\text{N}-\text{C}$ angle in (I) is $175.8(5)^\circ$, deviating slightly from the expected value of 180° . The other thiocyanate dimensions are normal.

**Figure 1**

The molecular structure of (I), showing the atom-numbering scheme and 35% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

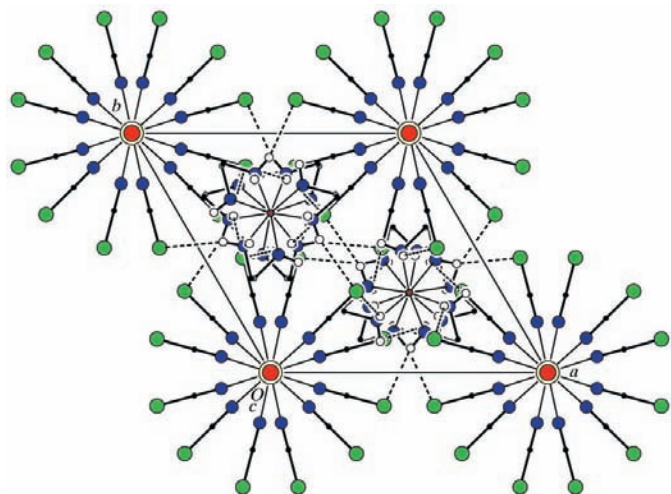


Figure 2
A packing diagram for (I), projected along the c direction. Some of the hydrogen bonds are shown by dashed lines.

It was not possible to locate the water H atoms, which have to be disordered because of the imposed 32 and $\bar{3}$ symmetry at the water O atoms. In the crystal structure of (I), the O atoms of the water molecules bridge Na^+ cations to form infinite $-\text{O}-\text{Na}-\text{O}-\text{Na}-$ chains, in which the monomer is the $[(\text{H}_2\text{O})_{0.5}\text{Na}(\text{NCS})_3(\text{H}_2\text{O})_{0.5}]^{2-}$ anion. The space-group symmetry ensures that adjacent $[\text{Na}(\text{NCS})_3]^{2-}$ moieties in the polymeric chains are arranged in a staggered stacking fashion along the c axis (Fig. 2). The $[\text{Ni}(\text{en})_3]^{2+}$ dications connect the $[(\text{H}_2\text{O})_{0.5}\text{Na}(\text{NCS})_3(\text{H}_2\text{O})_{0.5}]^{2-}$ anion chains by both electrostatic and hydrogen-bond interactions, involving the N—H moieties of the en ligands and the S atoms of the thiocyanate groups, forming a three-dimensional network.

Experimental

To an aqueous solution (15 ml) of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.37 g, 1 mmol) and ethylenediamine (0.18 g, 3 mmol), an aqueous solution (15 ml) of NaNCS (0.24 g, 3 mmol) was added with stirring. After stirring for 30 min at room temperature, the resulting purple solution was filtered. Purple single crystals of (I) were obtained by slow evaporation of the filtrate over a period of one week.

Crystal data

$[\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_3][\text{Na}(\text{NCS})_3(\text{H}_2\text{O})]$	Mo $K\alpha$ radiation
$M_r = 454.27$	Cell parameters from 22 reflections
Trigonal, $P\bar{3}c1$	
$a = 11.588$ (1) Å	$\theta = 3.1\text{--}16.1^\circ$
$b = 11.588$ (1) Å	$\mu = 1.32$ mm $^{-1}$
$c = 17.177$ (2) Å	$T = 293$ (2) K
$V = 1997.5$ (3) Å 3	Prism, purple
$Z = 4$	$0.48 \times 0.46 \times 0.40$ mm
$D_x = 1.511$ Mg m $^{-3}$	

Data collection

Siemens P4 diffractometer	$R_{\text{int}} = 0.025$
ω scans	$\theta_{\text{max}} = 27^\circ$
Absorption correction: empirical (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 14$
$T_{\text{min}} = 0.552$, $T_{\text{max}} = 0.589$	$k = -14 \rightarrow 1$
3084 measured reflections	$l = 0 \rightarrow 21$
1462 independent reflections	3 standard reflections
1001 reflections with $I > 2\sigma(I)$	every 97 reflections
	intensity decay: 1.8%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0680P)^2 + 1.1204P]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.130$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.50$ e Å $^{-3}$
1462 reflections	$\Delta\rho_{\text{min}} = -0.29$ e Å $^{-3}$
75 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.0111 (14)

Table 1

Selected geometric parameters (Å, °).

Ni—N1	2.123 (3)	Na—O2	2.1719 (18)
Ni—N2	2.125 (3)	Na—N3	2.163 (5)
Na—O1	2.1224 (18)		
N1—Ni—N2	81.61 (10)	N1—Ni—N2 ⁱⁱ	171.19 (10)
N1—Ni—N1 ⁱ	92.15 (10)	O1—Na—N3	90.46 (16)
N1 ⁱⁱ —Ni—N2	94.28 (11)		

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

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1A \cdots S ⁱ	0.90	2.83	3.504 (3)	132
N1—H1B \cdots S ⁱⁱ	0.90	2.83	3.681 (3)	159
N2—H2A \cdots S ⁱⁱⁱ	0.90	2.72	3.518 (3)	148
N2—H2B \cdots S	0.90	2.96	3.836 (3)	165

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

The systematic absences and Laue symmetry allowed the space group to be either $P\bar{3}c1$ or $P3c1$; $P\bar{3}c1$ was selected and confirmed by the analysis. The eight H atoms of the unique en ligand were allowed for as riding atoms ($C-H = 0.97$ Å and $N-H = 0.90$ Å). It was not possible to locate the water H atoms on the 32 and $\bar{3}$ special positions.

Data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *SHELXTL-Plus* (Sheldrick, 1990a); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990b); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1666). Services for accessing these data are described at the back of the journal.

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