metal-organic papers

Tridecaaquadinitratohexasodium(I) bis[(*trans*-cyclohexane-1,2-diyldinitrilotetraacetato)nickelate(II)]

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In the title compound, $[Na_6(NO_3)_2(H_2O)_{13}][Ni(C_{14}H_{18}N_2O_8)]_2$, the edta-like tetraanionic unit uses two N and four O atoms to chelate to the Ni atom so that the $[Ni(C_{14}H_{18}N_2O_8)]^{2-}$ portion of the structure has the Ni atom in a *cis*–N_2O_4Ni octahedral geometry. The $[Na_6(NO_3)_2$-$H_2O)_{13}]^{4+}$ portion exists as a chain consisting of edge-sharing NaO_6 octahedra; there are four independent Na atoms in the asymmetric unit. The vertices are derived from the O atoms of water molecules, the O atom of the nitrate group as well as the O atoms of the $[Ni(C_{14}H_{18}N_2O_8)]^{2-}$ unit. The layer structure is consolidated by hydrogen bonds into a three-dimensional network. Two of the Na atoms and three of the water O atoms lie on special positions of site symmetry 2.

Comment

The *trans*-cyclohexane-1,2-diyldinitrilotetraacetate tetraanion behaves like the edta tetraanion in its chelating behavior; the anion uses its pair of N atoms and its four negatively charged carboxyl O atoms to chelate to first-row transition metal ions in, for example, potassium manganate(II) hydrate (Rettig & Trotter, 1973), tetraaquacopper(II) nickelate(II) trihydrate (Fuertes *et al.*, 1985, 1987), pentasodium aquavanadate(III) (Shimoi *et al.*, 1991), oxonium cobaltate(III) tetrahydrate (Antsyshkina *et al.*, 2000) and pentaaquasodium aquaferrate(III) (Seibig & van Eldik, 1998).

(I)
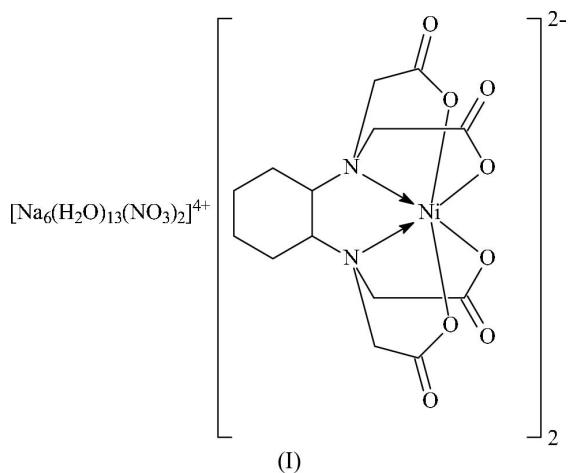
A similar binding mode is observed in the present sodium nickelate(II), (I); the four negative charges of the two nickelate ions are balanced by the charge of the cationic unit, which consists of six Na^I atoms, two nitrate units and 13 water molecules. The $[Na_6(NO_3)_2H_2O)_{13}]^{4+}$ cationic entity (Fig. 1) forms a chain motif of edge-sharing NaO_6 octahedra (Fig. 2). In the anionic $[Ni(C_{14}H_{18}N_2O_8)]^{2-}$ entity, the chelated Ni
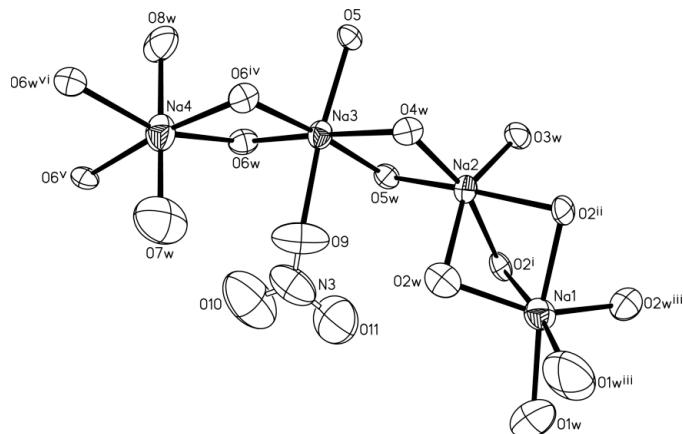
Figure 1
ORTEPII plot (Johnson, 1976) plot of a portion of the water-coordinated chain of Na atoms in (I). Atoms O2^i, O2^{ii}, O5, O6^{iv} and O6^v belong to [Ni(C$_{14}$H$_{18}$N$_2$O$_8$)]$^{2-}$ dianions. Displacement ellipsoids are drawn at the 50% probability level and H atoms are not shown. Symmetry codes are as given in Table 1.

atom shows octahedral coordination (Fig. 3). The anionic and cationic portions are linked into layers *via* dative Na—O bonds, and the layers are linked into a three-dimensional network structure by hydrogen bonds (Table 2).

Experimental

trans-Cyclohexane-1,2-diyldinitrilotetraacetic acid (0.036 g, 0.1 mmol) and nickel nitrate hexahydrate (0.058 g, 0.2 mmol) were dissolved in a 1:1 water–ethanol mixture (20 ml). After the pH of the solution was adjusted to 6 by the addition of several drops of 1 *M* sodium hydroxide, the mixture was heated in Teflon-lined stainless steel Parr bomb at 433 K for 50 h. The bomb was cooled to room temperature at a rate of 5 K h^{-1}. Light green crystals were isolated from the solution in about 50% yield.

Crystal data
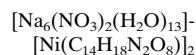
[Na$_6$(NO$_3$)$_2$(H$_2$O)$_{13}$]-	D_x = 1.700 Mg m^{-3}
[Ni(C$_{14}$H$_{18}$N$_2$O$_8$)]$_2$	Mo $K\alpha$ radiation
M_r = 1298.20	Cell parameters from 8026
Monoclinic, $C2/c$	reflections
a = 16.9182 (7) Å	θ = 2.5–28.3°
b = 29.388 (1) Å	μ = 0.90 mm^{-1}
c = 10.6777 (4) Å	T = 295 (2) K
β = 107.174 (1)°	Block, light green
V = 5072.2 (4) Å^3	0.40 × 0.25 × 0.20 mm
Z = 4	

Data collection

Bruker SMART APEX area-detector diffractometer	5669 independent reflections
φ and ω scans	4889 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	R_{int} = 0.034
SADABS (Bruker, 2002)	θ_{max} = 27.5°
T_{min} = 0.641, T_{max} = 0.840	h = −21 → 9
14674 measured reflections	k = −36 → 38
	l = −13 → 13

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0885P)^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.064	$+ 18.9719P]$
$wR(F^2)$ = 0.182	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.10	$(\Delta/\sigma)_{max}$ = 0.001
5669 reflections	$\Delta\rho_{max}$ = 1.60 e Å^{-3}
358 parameters	$\Delta\rho_{min}$ = −0.69 e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Ni1—O1	2.085 (3)	Na2—O4w	2.319 (3)
Ni1—O3	2.034 (3)	Na2—O5w	2.425 (3)
Ni1—O5	2.066 (3)	Na3—O5	2.441 (3)
Ni1—O7	2.040 (3)	Na3—O6^{iv}	2.455 (3)
Ni1—N1	2.069 (3)	Na3—O9	2.474 (5)
Ni1—N2	2.062 (3)	Na3—O4w	2.384 (3)
Na1—O2^i	2.428 (4)	Na3—O5w	2.438 (3)
Na1—O1w	2.468 (8)	Na3—O6w	2.373 (3)
Na1—O2w	2.472 (4)	Na4—O6^{iv}	2.600 (3)
Na2—O2^i	2.608 (4)	Na4—O6w	2.401 (3)
Na2—O2^{ii}	2.363 (3)	Na4—O7w	2.22 (1)
Na2—O2w	2.454 (4)	Na4—O8w	2.378 (7)
Na2—O3w	2.398 (4)		
O1—Ni1—O3	94.5 (1)	O2^{ii}—Na2—O5w	163.4 (1)
O1—Ni1—O5	114.2 (1)	O2w—Na2—O3w	154.5 (1)
O1—Ni1—O7	86.2 (1)	O2w—Na2—O4w	89.4 (1)
O1—Ni1—N1	80.3 (1)	O2w—Na2—O5w	106.4 (1)
O1—Ni1—N2	162.2 (1)	O3w—Na2—O4w	114.5 (1)
O3—Ni1—O7	178.4 (1)	O3w—Na2—O5w	85.6 (1)
O3—Ni1—O5	89.4 (1)	O4w—Na2—O5w	84.2 (1)
O3—Ni1—N1	83.5 (1)	O5—Na3—O6^{iv}	93.6 (1)
O3—Ni1—N2	95.5 (1)	O5—Na3—O9	173.7 (2)
O5—Ni1—O7	89.0 (1)	O5—Na3—O4w	84.3 (1)
O5—Ni1—N1	164.4 (1)	O5—Na3—O5w	91.7 (1)
O5—Ni1—N2	80.7 (1)	O5—Na3—O6w	96.9 (1)
O7—Ni1—N1	98.1 (1)	O6^{iv}—Na3—O9	88.8 (2)
O7—Ni1—N2	84.2 (1)	O6^{iv}—Na3—O4w	97.5 (1)
N1—Ni1—N2	86.2 (1)	O6^{iv}—Na3—O5w	174.7 (1)
O2^i—Na1—O2^{ii}	80.6 (2)	O6^{iv}—Na3—O6w	85.5 (1)
O2^i—Na1—O1w	103.7 (2)	O9—Na3—O4w	89.6 (2)
O2^i—Na1—O1w^{iii}	171.6 (2)	O9—Na3—O5w	85.9 (2)
O2^i—Na1—O2w	83.2 (1)	O9—Na3—O6w	89.1 (2)
O2^i—Na1—O2w^{iii}	78.1 (1)	O4w—Na3—O5w	82.6 (1)
O1w—Na1—O1w^{iii}	73.1 (5)	O4w—Na3—O6w	176.8 (1)
O1w—Na1—O2w	109.4 (2)	O5w—Na3—O6w	94.4 (1)
O1w—Na1—O2w^{iii}	90.5 (3)	O6^{iv}—Na4—O6^v	171.8 (2)
O2w—Na1—O2w^{iii}	155.4 (2)	O6^{iv}—Na4—O6w	81.8 (1)
O2^i—Na2—O2^{ii}	78.2 (1)	O6^{iv}—Na4—O6w^{vi}	100.0 (1)
O2^i—Na2—O2w	79.9 (1)	O6^{iv}—Na4—O7w	85.9 (1)
O2^i—Na2—O3w	78.2 (1)	O6^{iv}—Na4—O8w	94.1 (1)
O2^i—Na2—O4w	164.2 (1)	O6w—Na4—O6w^{vi}	155.4 (2)
O2^i—Na2—O5w	87.7 (1)	O6w—Na4—O7w	102.3 (1)
O2^{ii}—Na2—O2w	79.7 (1)	O6w—Na4—O8w	77.7 (1)
O2^{ii}—Na2—O3w	83.2 (1)	O7w—Na4—O8w	180
O2^{ii}—Na2—O4w	111.5 (2)		

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 2 - z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $-x, y, \frac{3}{2} - z$; (iv) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (v) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (vi) $1 - x, y, \frac{3}{2} - z$.

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1w—H1w1⋯O4^{vii}	0.82	2.27	2.660 (9)	109
O2w—H2w1⋯O11	0.82	2.00	2.797 (8)	165
O2w—H2w2⋯O4^{iv}	0.82	2.01	2.817 (6)	170
O4w—H4w1⋯O6	0.82	2.08	2.800 (4)	147
O4w—H4w2⋯O3^{iv}	0.82	1.99	2.803 (4)	172
O5w—H5w1⋯O7^i	0.82	1.98	2.778 (4)	164
O5w—H5w2⋯O8	0.82	2.27	3.053 (5)	159
O6w—H6w1⋯O8^i	0.82	2.01	2.789 (4)	159
O6w—H6w2⋯O1	0.82	2.03	2.845 (4)	170
O7w—H7w⋯O9^{vi}	0.82	2.36	3.130 (7)	156
O7w—H7w⋯O10^{vi}	0.82	2.32	3.04 (1)	146
O8w—H8w⋯O1	0.82	2.09	2.899 (4)	172

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 2 - z$; (iv) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (vi) $1 - x, y, \frac{3}{2} - z$; (vii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$.

Carbon-bound H atoms were positioned geometrically (C—H = 0.95 Å) and were allowed to ride on their parent C atoms, with the

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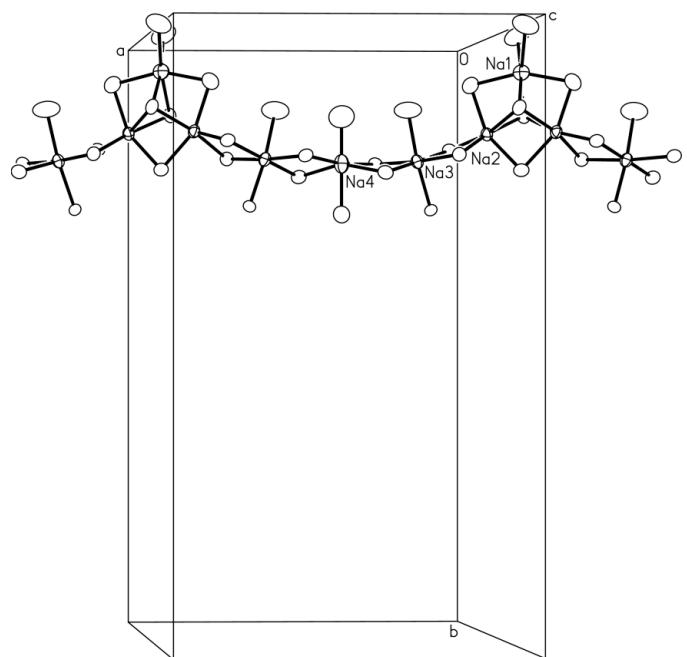
Figure 2
ORTEPII plot (Johnson, 1976) of the chain of NaO$_6$ octahedra.

Figure 3
ORTEPII plot (Johnson, 1976) illustrating the geometry of the Ni atom in the [Ni(C$_{14}$H$_{18}$N$_2$O$_8$)]$^{2-}$ anion. Displacement ellipsoids are drawn at the 50% probability level and H atoms as spheres of arbitrary radii.

displacement parameters set at 1.2 times U_{eq} of their parent atoms. A somewhat longer C—H distance used as the default (0.97 Å for the methine and 0.96 Å for the methylene distance) led to H···H interactions of less than 2 Å with the H atoms of the O1w water molecule. Of the eight water molecules, H atom positions were similarly generated for those connected to the Na atoms, except for the O1w molecule. Molecules O7w and O8w each have only one independent H atom; the OH group was rotated to fit the electron density; O—H = 0.82 Å and U_{iso}(H) = 1.2U_{eq}(O). Those on the terminal O1w molecule could not be generated, and were instead placed in chemically sensible positions so that the atoms were at least 2 Å from other H atoms. The final difference Fourier map had a large peak at 2.1 Å from Na1 and 1.5 Å from O1w on a special position; as the O1w atom was not disordered, attempts to refine this peak as a disorder component of the O1w atom did not lead to any meaningful outcome.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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