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Hexaaquanickelate(II) bis(thiodiacetato-κ^3O,S,O')-nickel(II) tetrahydrate

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Key indicators

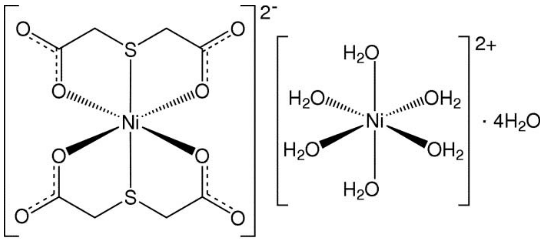
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
Disorder in solvent or counterion
R factor = 0.021
wR factor = 0.061
Data-to-parameter ratio = 17.5

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

The title compound, $[Ni^{II}(H_2O)_6][Ni^{II}(C_4H_4O_4S)_2]\cdot 4H_2O$, consists of $[Ni^{II}(H_2O)_6]^{2+}$ complex dications, $[Ni^{II}(C_4H_4O_4S)_2]^{2-}$ complex dianions and non-coordinated water molecules. In the complex dianion, two thiodiacetate dianions coordinate to the Ni^{II} ion in a *fac*-SO_2-tridentate chelating mode, resulting in a distorted octahedral *trans*-NiO_4S_2 coordination geometry. The crystal structure is stabilized by an extensive O—H···O hydrogen-bonding network.

Comment

Thiodiacetate (TDA) dianions can display a large variety of coordination modes to metal cations, including through the terminal carboxyl group O atoms or the central S atom. To study the factors affecting the configuration of TDA, the title compound, (I), has been prepared and its crystal structure has been determined.



(I)

Compound (I) contains Ni^{II} complex dications, Ni^{II} complex dianions and non-coordinated water molecules (Fig. 1 and Table 1). Two TDA dianions tridentately chelate to Ni1 in a facial manner, generating a distorted octahedral *trans*-NiO_4S_2

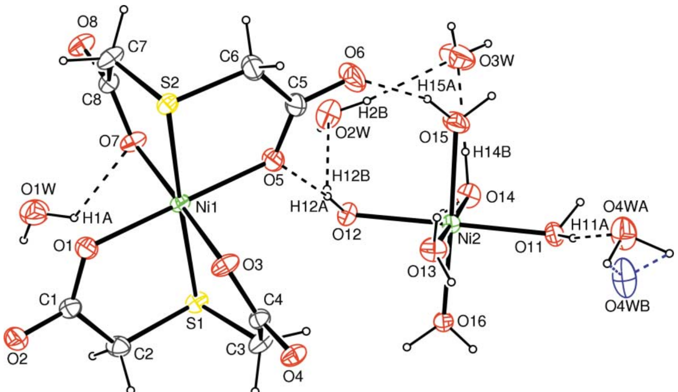


Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids. Blue dashed lines show one of the disordered components and black dashed lines indicate hydrogen bonds.

coordination geometry, as seen previously for related systems.

The two five-membered chelate rings of each TDA are nearly perpendicular to each other, with dihedral angles of 86.29 (5) and 85.59 (5)° for S1-TDA and S2-TDA, respectively. A similar situation was found in potassium bis(thiodiacetato-κ^3O,O',S)nickelate(II) trihydrate (Delaunay *et al.*, 1976).

Both the five-membered O1-ring (the chelate ring containing atom O1) and O7-ring display envelope configurations, with atoms Ni1 and S2 lying in the flap positions, 0.204 (4) and 0.366 (4) Å, respectively, out of the mean plane formed by the other four atoms. The five-membered O3-ring is twisted about the Ni1—S1 bond, with atom S1 displaced by 0.422 (9) Å from the plane formed by atoms C3, C4 and O3, and Ni1 displaced by −0.184 (9) Å from this plane. Conversely, the O5-ring is nearly planar, the maximum atomic deviation being 0.0253 (18) Å for atom C6.

The Ni2 complex dication displays an octahedral NiO_6 coordination geometry, formed by six water molecules.

A network of O—H···O hydrogen bonding helps to stabilize the molecular packing (Table 2 and Fig. 2). These hydrogen bonds variously link cations and anions, cations and water molecules, and anions and water molecules.

Experimental

The starting chemicals were of analytical grade and were used as received. $NiCl_2\cdot6H_2O$ (0.47 g, 2 mmol) was added to a water–ethanol solution (20 ml, 1:3 *v*/*v*) of Na_2CO_3 (0.21 g, 2 mmol) and H_2TDA (0.30 g, 2 mmol). The mixture was refluxed for 5 h and filtered after being cooled to room temperature. The filtrate was left to stand at room temperature and green single crystals of (I) were obtained after about one week.

Crystal data

$[Ni(H_2O)_6][Ni(C_4H_4O_4S)_2]\cdot4H_2O$
$M_r = 593.84$
Monoclinic, *Cc*
$a = 18.8369\ (5)$ Å
$b = 13.4729\ (3)$ Å
$c = 8.9472\ (2)$ Å
$\beta = 101.639\ (8)°$
$V = 2224.00\ (11)$ Å^3
$Z = 4$
$D_x = 1.774$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9212 reflections
$\theta = 1.9$–$27.5°$
$\mu = 1.96$ mm^{-1}
$T = 295\ (3)$ K
Block, green
0.46 × 0.40 × 0.31 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.408$, $T_{max} = 0.543$
10303 measured reflections
4886 independent reflections
4779 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 27.5°$
$h = -24 \rightarrow 24$
$k = -17 \rightarrow 17$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.061$
$S = 1.07$
4886 reflections
280 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0445P)^2 + 0.5706P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.52$ e Å^{-3}
Absolute structure: Flack (1983), 2338 Friedel Pairs
Flack parameter: 0.135 (8)

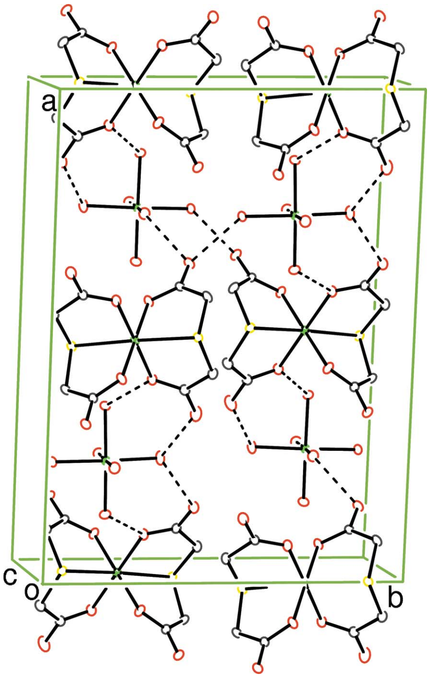


Figure 2
A packing diagram for (I), showing intermolecular O···O hydrogen-bonding contacts as dashed lines. The non-coordinated water molecules and H atoms have been omitted for clarity.

Table 1
Selected bond lengths (Å).

Ni1—O1	2.0365 (18)	Ni2—O11	2.0359 (17)
Ni1—O3	2.0257 (17)	Ni2—O12	2.0611 (16)
Ni1—O5	2.0404 (18)	Ni2—O13	2.0664 (19)
Ni1—O7	2.0386 (17)	Ni2—O14	2.0899 (18)
Ni1—S1	2.4194 (6)	Ni2—O15	2.0495 (18)
Ni1—S2	2.4132 (6)	Ni2—O16	2.0022 (16)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*A*···O7	0.83	2.40	2.947 (3)	124
O1*W*—H1*B*···O2^{i}	0.92	2.14	2.747 (3)	123
O2*W*—H2*A*···O3^{ii}	0.88	1.83	2.690 (3)	164
O2*W*—H2*B*···O3*W*	0.81	2.04	2.847 (4)	172
O3*W*—H3*A*···O6^{iii}	0.82	2.13	2.854 (4)	148
O3*W*—H3*B*···O1*W*^{iv}	0.84	2.02	2.774 (4)	150
O4*WA*—H4*A*···O2*W*^{v}	0.98	1.90	2.836 (4)	160
O4*WA*—H4*B*···O7^{v}	0.84	2.02	2.795 (4)	153
O11—H11*A*···O4*WA*	0.95	1.79	2.722 (4)	167
O11—H11*B*···O1^{iv}	0.93	1.79	2.721 (3)	172
O12—H12*A*···O5	0.90	1.84	2.734 (2)	171
O12—H12*B*···O2*W*	0.87	1.96	2.750 (3)	150
O13—H13*A*···O1*W*^{v}	0.83	2.05	2.811 (3)	152
O13—H13*B*···O8^{v}	0.81	2.00	2.812 (3)	175
O14—H14*A*···O4^{ii}	0.87	1.94	2.801 (3)	167
O14—H14*B*···O3*W*	0.89	1.96	2.843 (3)	175
O15—H15*A*···O6	0.86	1.87	2.699 (4)	161
O15—H15*B*···O2^{iv}	0.87	1.94	2.789 (3)	165
O16—H16*A*···O4^{i}	0.88	1.80	2.677 (3)	175
O16—H16*B*···O8^{vi}	0.85	1.83	2.675 (3)	176

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

The anion and cation in (I) closely conform to space-group symmetry $C2/c$ (Ni1 and Ni2 would possess $\overline{1}$ and 2 site symmetries, respectively), but this higher symmetry is broken by the non-coordinated water molecules. The occupancies of the disordered atoms O4*WA* and O4*WB* converged to 0.64 (2) and 0.36 (2), respectively (sum constrained to unity). They were fixed at 0.64 and 0.36 in the final cycles of refinement. The common H atoms of the disordered water molecule O4*WA*/O4*WB* were located in a difference Fourier map and included in the structure-factor calculations with fixed positional parameters and isotropic displacement parameters $U_{\rm iso}$(H) = 0.05 Å^2. The H atoms of the other water molecules were located in difference maps and refined as riding in their as-found relative positions, with a fixed $U_{\rm iso}$ of 0.05 Å^2. Other H atoms were placed in calculated positions, with C—H = 0.97 Å, and were included in the final cycles of refinement in the riding mode, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(carrier).

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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