

***trans*-Diaquabis(thiosemicarbazido- κ^2N,S)nickel(II) dimaleate dihydrate**Sheng-Li Li,^a Anwar Usman,^b Ibrahim A. Razak,^b
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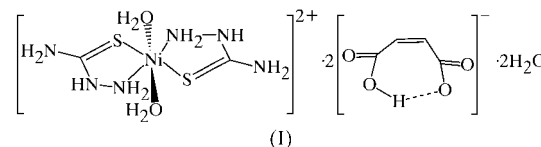
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In the title compound, $[\text{Ni}(\text{CH}_5\text{N}_3\text{S})_2(\text{H}_2\text{O})_2](\text{C}_4\text{H}_3\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, the Ni atom lies on a center of symmetry and is coordinated by N and S atoms from two thiosemicarbazide ligands and the O atoms of two water molecules in a distorted octahedral geometry. In the asymmetric unit, the three components are linked together by one O—H...O and two N—H...O hydrogen bonds. The packing is built from molecular ribbons parallel to the *b* direction, stabilized by intramolecular hydrogen bonds, and by one N—H...S and two N—H...O intermolecular hydrogen bonds. The ribbons are further connected into columns by N—H...O interactions and then into a three-dimensional network by three O—H...O hydrogen bonds.

Comment

Self-assembly is the most efficient means for the construction of highly organized structures. The study of self-assembly processes and properties of supramolecular systems and/or molecular aggregates in natural and non-natural systems (organic and inorganic systems) has attracted much interest (Lawrence *et al.*, 1995; Yaghi *et al.*, 1998). Meanwhile, there is considerable current interest in crystal engineering based on the use of either coordinative bonds (Blake *et al.*, 1999) or weaker intermolecular interactions. In the latter methodology, the hydrogen bond can influence the metal coordination geometry and adjust the structure of relative compounds because of the bond's relative strength, directionality, flexibility and dynamic character (Allen *et al.*, 1999; Russell *et al.*, 1997). The chemistry of metal complexes containing *S,N*-

bidentate ligands has been studied widely because of the structural features and particular properties of these complexes (Fun *et al.*, 1996; West *et al.*, 1993); dicarboxylates are an important class of ligands in the formation of coordination polymers (Heinze *et al.*, 1998; Groeneman *et al.*, 1999). As part of our studies of the synthesis and characterization of potential non-linear optical materials, we report here the crystal structure of the title compound, (I).



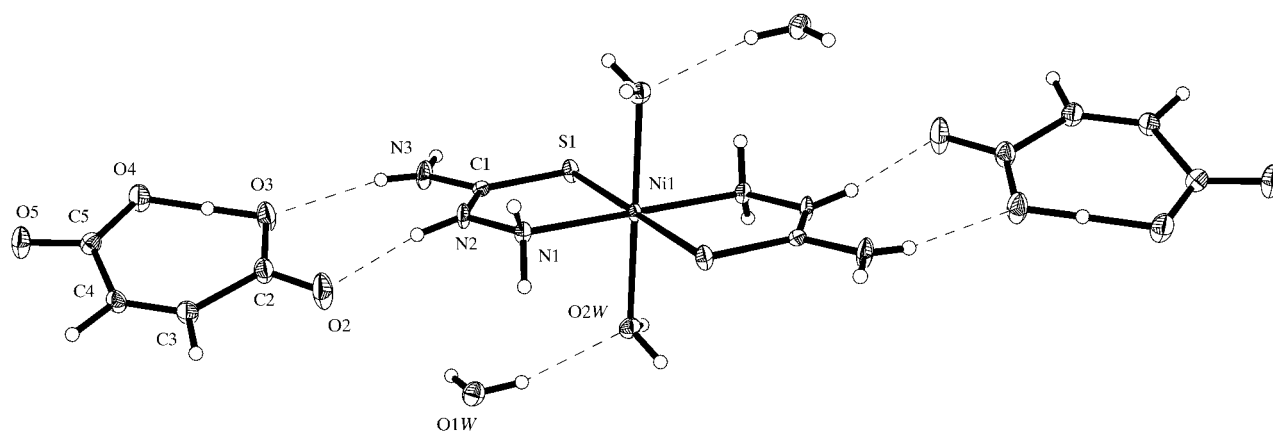
The structure of (I) consists of three independent fragments (Fig. 1), namely the dicarboxylate anion (maleate), the coordinated nickel(II) cation and water molecules. The structure differs from that of related compounds (Zhang *et al.*, 2000; Burrows *et al.*, 2000) in that the maleate moiety in (I) is not coordinated to the Ni atom but acts as an independent counter-ion, with mutual electrostatic interaction in the structure. This situation was also observed in our previous study (Li *et al.*, 2003) of the structure of bis(thiosemicarbazido- κ^3N,S)nickel(II)-succinate-succinic acid (1/1/1).

The asymmetric unit of (I) contains half of the complex molecule; the other half is related by a center of symmetry at atom Ni1. Atom Ni1 is six-coordinated by N, S and O atoms. Each of the two pairs of coordinated S and N atoms belongs to one of the two symmetry-related thiosemicarbazide ligands, in which the ligands act as an *N,S*-chelates, while the two coordinated O atoms belong to the symmetry-related water molecules. The $\text{NiN}_2\text{S}_2\text{O}_2$ group forms a distorted octahedral configuration. The linear $\text{O}2\text{W}-\text{Ni}1-\text{O}2\text{W}^i$ group [symmetry code: (i) $-x, 1-y, 1-z$] is nearly perpendicular to the basal $\text{N}1/\text{S}1/\text{N}1^i/\text{S}1^i$ plane, as evidenced by the angles subtended at atom Ni1 (Table 1). The coordinated bond lengths (Ni—O2W, Ni—N and Ni—S) are normal (Allen *et al.*, 1987), whereas the C—N and C—S bond distances in the thiosemicarbazide ligands are intermediate between single- and double-bond lengths. These C—N and C—S bonds suggest, to some extent, the electronic delocalization effect on the ligand upon complex formation.

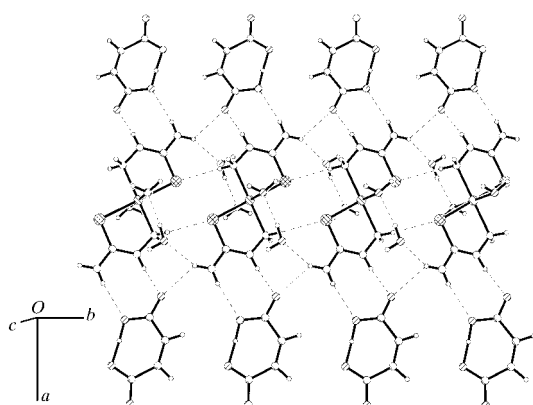
The thiosemicarbazide ligands are planar, with the coordinated Ni1 atom displaced by 0.054 (1) Å. The maleate anion is also planar, with maximum deviations of 0.028 (2) Å in opposite directions at atoms O2 and O3. Atoms O3 and O4 share one H atom, as indicated by the explicitly located H atom and the C2—O3 and C5—O4 bond lengths (Table 1), which are intermediate between the lengths of C—O single and double bonds. This H-atom position also maintains the planarity of the maleate anion.

In the asymmetric unit, the nickel cation, maleate anions and uncoordinated O1W water molecules are linked by $\text{N}2-\text{H}2 \cdots \text{O}2$, $\text{N}3-\text{H}3\text{A} \cdots \text{O}3$ and $\text{O}1\text{W}-\text{H}1\text{W}1 \cdots \text{O}2\text{W}$ hydrogen bonds (Fig. 1 and Table 2), in which the maleate anions and the aqua ligands act as hydrogen-bond acceptors.

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Figure 1

A view of the structure of (I), showing displacement ellipsoids at the 50% probability level and the atom-numbering scheme.


Figure 2

Packing diagram of (I), showing the ribbon formations.

In the crystal packing, the thiosemicarbazide ligands and the two water molecules play an important role in the intermolecular hydrogen bonding. The molecules are linked by three types of N—H...O bond, one N—H...S bond and three types of O—H...O bond (Table 2). The N1—H1A...O4ⁱⁱ, N1—H1B...S1ⁱⁱⁱ and N3—H3B...O1W^{iv} hydrogen bonds (see Table 2 for symmetry codes), together with the intramolecular hydrogen bonds, link the molecules into ribbons parallel to the *b* direction (Fig. 2). A chain therefore consists of three different hydrogen-bonded ring patterns (Bernstein *et al.*, 1995), namely those linking a maleate anion to a thiosemicarbazide ligand [graph set $R_2^2(8)$], those linking a maleate anion to two symmetry-related thiosemicarbazide ligands [$R_3^2(9)$], and those linking two symmetry-related thiosemicarbazide ligands [$R_2^2(8)$]. The water molecules can be considered as bridges between the thiosemicarbazide ligand and the central Ni atom of the adjacent asymmetric unit. Two adjacent ribbons are symmetrically connected by N3—H3B...O2^{iv} hydrogen bonds to form columns, and the columns are further connected into a three-dimensional network by O1W—H2W1...O5^v, O2W—H1W2...O1W^{vi} and O2W—H2W2...O5^{vii} hydrogen bonds (see Table 2 for symmetry codes).

Experimental

Compound (I) was prepared by the self-assembly synthesis method. Solutions of nickel chloride hexahydrate, maleic acid and thiosemicarbazide in methanol/water (1:1 *v/v*) were mixed with stirring. The pH of the mixture was maintained at 4.8–5.0. The solution was filtered and evaporated slowly at room temperature in air. Single crystals of (I) suitable for X-ray analysis were obtained after one week.

Crystal data

[Ni(CH₃N₃S)₂(H₂O)₂](C₄H₃O₄)₂·
2H₂O
M_r = 543.18
Monoclinic, *P*2₁/*c*
a = 13.0487 (3) Å
b = 5.9574 (1) Å
c = 14.0254 (3) Å
β = 109.078 (1)°
V = 1030.40 (4) Å³
Z = 2

D_x = 1.751 Mg m⁻³
Mo *Kα* radiation
Cell parameters from 5224
reflections
θ = 3.0–28.3°
μ = 1.22 mm⁻¹
T = 183 (2) K
Wedge, blue
0.52 × 0.46 × 0.22 mm

Data collection

Siemens SMART CCD area-
detector diffractometer
ω scans
Absorption correction: empirical
(*SADABS*; Sheldrick, 1996)
*T*_{min} = 0.570, *T*_{max} = 0.776
5956 measured reflections

2521 independent reflections
2162 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.084
*θ*_{max} = 28.3°
h = −9 → 17
k = −7 → 7
l = −18 → 18

Table 1

Selected geometric parameters (Å, °).

Ni1—N1	2.0747 (18)	N2—C1	1.329 (3)
Ni1—O2W	2.1666 (16)	N3—C1	1.330 (3)
Ni1—S1	2.3627 (5)	O3—C2	1.298 (3)
S1—C1	1.709 (2)	O4—C5	1.279 (3)
N1—N2	1.415 (3)	O5—C5	1.241 (3)
N1—Ni1—O2W ⁱ	93.39 (7)	O2W ⁱ —Ni1—S1	90.72 (5)
N1—Ni1—O2W	86.61 (7)	O2W—Ni1—S1	89.28 (5)
N1—Ni1—S1	84.85 (5)	C1—S1—Ni1	96.23 (7)
N1 ⁱ —Ni1—S1	95.15 (5)	N2—N1—Ni1	114.70 (13)

Symmetry code: (i) $-x, 1 - y, 1 - z$.

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

D—H...A	D—H	H...A	D...A	D—H...A
O3—H34...O4	1.10 (4)	1.32 (4)	2.423 (2)	177 (2)
N1—H1A...O4 ⁱⁱ	0.84 (3)	2.45 (3)	3.137 (3)	140 (2)
N1—H1B...S1 ⁱⁱⁱ	0.94 (3)	2.55 (3)	3.438 (2)	157 (2)
N2—H2...O2	0.87 (3)	1.90 (3)	2.756 (3)	170 (4)
N3—H3A...O3	0.81 (4)	2.23 (4)	3.038 (3)	169 (4)
N3—H3B...O1W ^{iv}	0.88 (3)	2.30 (4)	3.073 (3)	148 (3)
N3—H3B...O2 ^{iv}	0.88 (3)	2.41 (3)	2.985 (3)	123 (3)
O1W—H1W1...O2W	0.86 (3)	2.12 (3)	2.959 (3)	165 (3)
O1W—H2W1...O5 ^v	0.84 (3)	1.93 (3)	2.762 (3)	169 (3)
O2W—H1W2...O1W ^{vi}	0.91 (4)	1.81 (4)	2.716 (3)	172 (4)
O2W—H2W2...O5 ^{vii}	0.87 (4)	1.91 (4)	2.775 (3)	174 (4)

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

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.110$
 $S = 1.00$
 2521 reflections
 189 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0314P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.77 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -1.28 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXTL97*
 Extinction coefficient: 0.032 (3)

All H atoms were located in difference Fourier maps and were refined isotropically. The U_{iso} values of atoms H1W2 and H34 were fixed because these values became too large during refinement. The C—H, O—H and N—H bond lengths are in the ranges 0.93 (3)–0.96 (3), 0.86 (4)–1.10 (4) and 0.82 (3)–0.94 (3) Å, respectively. Atom H34 is shared between atoms O3 and O4 of the maleate anion, with O3—H34 and O4—H34 distances of 1.10 (4) and 1.32 (4) Å, respectively. Owing to the poor quality of the crystal, the R_{int} value was 0.084. The highest peak and deepest hole in the difference map were located 0.93 and 0.77 Å, respectively, from atom Ni1.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINTE* (Siemens, 1996); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1111). Services for accessing these data are described at the back of the journal.

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