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Key indicators

Single-crystal X-ray study
 $T = 170$ K
Mean $\sigma(\text{O}-\text{N}) = 0.002$ Å
 R factor = 0.022
 wR factor = 0.056
Data-to-parameter ratio = 16.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Diaquabis(1,1,4-trimethylthiosemicarbazide)-
nickel(II) dinitrate

The determination of the crystal structure of the title compound, $[\text{Ni}(\text{C}_4\text{H}_{11}\text{N}_3\text{S})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$, reveals a distorted octahedral geometry around the Ni centre, which lies on an inversion centre, with water molecules occupying the axial positions. Hydrogen bonding is observed between the 1,1,4-trimethylthiosemicarbazide NH groups and the nitrate anions, and also between the coordinated water molecules and the anions.

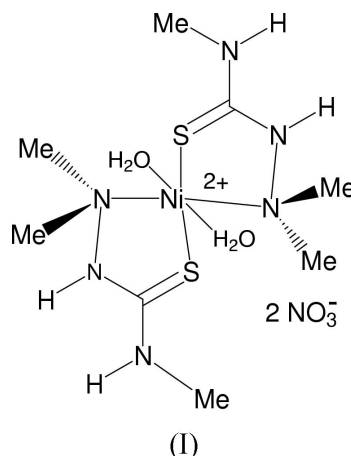
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Comment

The title compound, (I), was formed as part of our investigations into the crystal engineering of nickel bis(thiosemicarbazide) dicarboxylates, in which the Ni-containing cations and dicarboxylate anions are linked through charge-augmented hydrogen bonds (Allen *et al.*, 1999; Burrows *et al.*, 2000, 2004).



The asymmetric unit in (I) consists of a nickel(II) centre, to which is co-ordinated one 1,1,4-trimethylthiosemicarbazide ligand, *via* the S and dimethylamine N atoms, and one water molecule. A nitrate anion completes the asymmetric unit. The remainder of the molecular unit is generated by transformation through a crystallographic inversion centre, on which the metal is located. The structure of (I) is shown in Fig. 1.

The geometry around the Ni centre is distorted octahedral, with bond angles ranging from 82.95 (3) to 97.05 (3)°. Each nitrate anion forms hydrogen bonds to three separate Ni^{II} species. The presence of parallel N—H donors (*D*) on the 1,1,4-trimethylthiosemicarbazide ligand and parallel O acceptors (*A*) on the nitrates facilitates the formation of *DD:AA* interactions, graph set $R_2^2(8)$ (Etter, 1990), which link the cations and anions. Each of the remaining *AA* faces of the

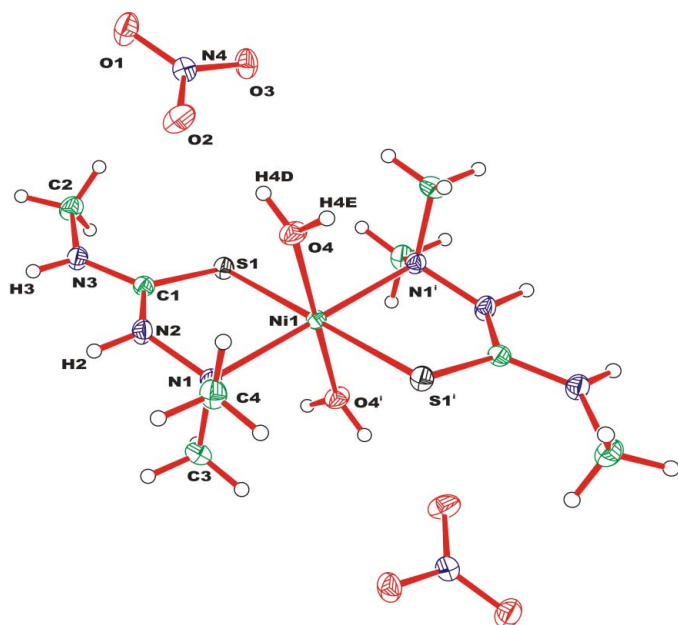


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by small spheres. [Symmetry code: (i) $x + 1, y + 1, z + 1$.]

nitrate is involved in a single O—H···O interaction with coordinated water molecules

The combination of the *DD:AA* hydrogen bonds with one such O—H···O interaction results in the formation of ‘slipped’ hydrogen-bonded chains along the crystallographic *a* axis, as illustrated in Fig. 2. Within the chains are hydrogen-bonded rings of graph set $R_4^2(16)$. The ‘slipped’ description of these chains is relative to chains observed in networks formed from reactions with linear dicarboxylates, such as fumarate or terephthalate, where the cations are linked solely *via DD:AA* interactions to the anion carboxylate groups (Allen *et al.*, 1999; Burrows *et al.*, 2004). The formation of the three-dimensional structure is facilitated by the second O—H···O interaction, graph set $R_6^5(23)$, illustrated in Fig. 3. Thus all of the hydrogen-bond donors are satisfied. By contrast, not all of the hydrogen-bond acceptors available to the O atoms of the nitrate anion are utilized, O2 being the only atom to form two interactions, with atoms H3 and H4B. In the cases of atoms O1 and O3, only one hydrogen bond is formed. Details of the hydrogen bonding are given in Table 1.

Experimental

Equimolar aqueous solutions of bis(1,1,4-trimethylthiosemicarbazide)nickel(II) nitrate (Burrows *et al.*, 2004) and the sodium salt of either succinic or itaconic acid were allowed to evaporate slowly over a period of two weeks. In both cases, the formation of green crystals of (I) resulted. Analysis by single-crystal X-ray diffraction revealed the identity of the products and confirmed that the dicarboxylate was not incorporated into the crystalline material in either case.

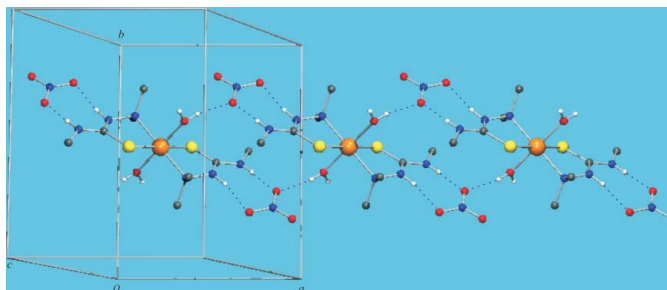


Figure 2
Interactions (dashed lines) forming hydrogen-bonded chains in (I).

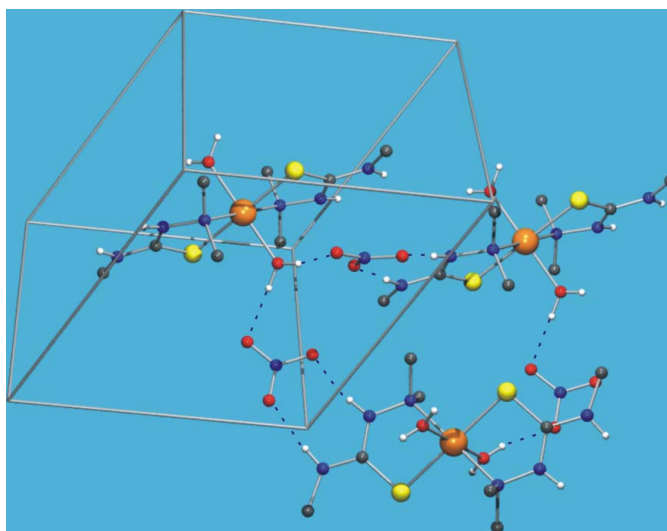


Figure 3
Hydrogen-bond interactions (dashed lines) in the formation of the $R_6^5(23)$ graph set.

Crystal data

$[\text{Ni}(\text{C}_4\text{H}_{11}\text{N}_3\text{S})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$
 $M_r = 485.20$
 Monoclinic, $P2_1/c$
 $a = 9.464(2) \text{ \AA}$
 $b = 12.358(2) \text{ \AA}$
 $c = 9.775(2) \text{ \AA}$
 $\beta = 117.7671(13)^\circ$
 $V = 1011.60(4) \text{ \AA}^3$
 $Z = 2$

$D_x = 1.593 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 1024 reflections
 $\theta = 4.1\text{--}27.5^\circ$
 $\mu = 1.22 \text{ mm}^{-1}$
 $T = 170(2) \text{ K}$
 Block, green
 $0.30 \times 0.30 \times 0.30 \text{ mm}$

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (Blessing, 1995)
 $T_{\min} = 0.697, T_{\max} = 0.697$
 15 566 measured reflections

2317 independent reflections
 2203 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$
 $\theta_{\max} = 27.5^\circ$
 $h = -12 \rightarrow 12$
 $k = -15 \rightarrow 16$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.056$
 $S = 1.06$
 2317 reflections
 144 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0213P)^2 + 0.4059P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.26 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.26 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.0133 (16)

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H4A \cdots O3 ⁱ	0.862 (15)	1.913 (15)	2.7703 (14)	173 (2)
O4—H4B \cdots O2	0.847 (15)	1.875 (16)	2.7074 (14)	167 (2)
N2—H2 \cdots O1 ⁱⁱ	0.866 (13)	2.103 (14)	2.9565 (16)	168.6 (15)
N3—H3 \cdots O2 ⁱⁱ	0.867 (13)	1.990 (14)	2.8551 (15)	175.6 (15)

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

The positions of the water, amino and amido H atoms were located in a difference map and refined isotropically, subject to a distance restraint of 0.89 (2) Å. H atoms on all C atoms were included in calculated positions, constrained to an ideal geometry with C—H distances of 0.98 Å and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. Each group was allowed to rotate freely about its C—N bond.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL* (Bruker, 2001), *printCIF* and local programs.

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supporting information

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Diaquabis(1,1,4-trimethylthiosemicarbazide)nickel(II) dinitrate

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Crystal data

[Ni(C₄H₁₁N₃S)₂(H₂O)₂](NO₃)₂

M_r = 485.20

Monoclinic, *P*2₁/*c*

Hall symbol: -*P* 2ybc

a = 9.4640 (2) Å

b = 12.3580 (2) Å

c = 9.7750 (2) Å

β = 117.7671 (13)°

V = 1011.60 (4) Å³

Z = 2

F(000) = 508

D_x = 1.593 Mg m⁻³

Mo *K*α radiation, λ = 0.71070 Å

Cell parameters from 1024 reflections

θ = 4.1–27.5°

μ = 1.22 mm⁻¹

T = 170 K

Block, green

0.30 × 0.30 × 0.30 mm

Data collection

Nonius KappaCCD area-detector
diffractometer

Radiation source: sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

from symmetry-related measurements

(Blessing, 1995)

T_{min} = 0.697, *T_{max}* = 0.697

15566 measured reflections

2317 independent reflections

2203 reflections with *I* > 2σ(*I*)

R_{int} = 0.025

θ_{\max} = 27.5°, θ_{\min} = 4.1°

h = -12→12

k = -15→16

l = -12→12

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.022

wR(*F*²) = 0.056

S = 1.06

2317 reflections

144 parameters

4 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: geom & difmap

H atoms treated by a mixture of independent
and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0213*P*)² + 0.4059*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.26 e Å⁻³

Δρ_{min} = -0.26 e Å⁻³

Extinction correction: SHELXL97 (Sheldrick,
1997), *F_c** = *kF_c*[1 + 0.001*xF_c*²λ³/sin(2θ)]^{-1/4}

Extinction coefficient: 0.0133 (16)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.5000	0.5000	0.5000	0.01900 (9)
S1	0.45094 (4)	0.47524 (3)	0.71566 (4)	0.02431 (10)
O1	0.01934 (13)	0.22074 (10)	0.58796 (14)	0.0439 (3)
O2	0.09424 (12)	0.32177 (9)	0.45410 (13)	0.0415 (3)
O3	0.24872 (12)	0.19351 (9)	0.59396 (12)	0.0354 (2)
O4	0.30050 (12)	0.40960 (8)	0.36503 (12)	0.0301 (2)
H4A	0.280 (2)	0.3818 (16)	0.2767 (19)	0.056 (6)*
H4B	0.246 (2)	0.3740 (16)	0.398 (2)	0.061 (6)*
N1	0.33577 (12)	0.63500 (9)	0.45151 (12)	0.0229 (2)
N2	0.23053 (14)	0.61040 (10)	0.51535 (13)	0.0275 (2)
H2	0.1510 (17)	0.6543 (13)	0.4910 (19)	0.032 (4)*
N3	0.18327 (14)	0.54724 (10)	0.70802 (13)	0.0276 (2)
H3	0.0975 (17)	0.5861 (13)	0.6625 (18)	0.031 (4)*
N4	0.12171 (13)	0.24468 (9)	0.54663 (12)	0.0265 (2)
C1	0.27924 (15)	0.54831 (10)	0.64284 (14)	0.0224 (2)
C2	0.20559 (18)	0.47758 (13)	0.83646 (17)	0.0328 (3)
H2A	0.1880	0.4021	0.8019	0.049*
H2B	0.1292	0.4978	0.8735	0.049*
H2C	0.3146	0.4860	0.9205	0.049*
C3	0.41701 (18)	0.73925 (11)	0.51787 (18)	0.0325 (3)
H3A	0.3370	0.7965	0.4923	0.049*
H3B	0.4889	0.7575	0.4746	0.049*
H3C	0.4788	0.7325	0.6305	0.049*
C4	0.23263 (17)	0.64895 (12)	0.28301 (16)	0.0315 (3)
H4C	0.1528	0.7051	0.2653	0.047*
H4D	0.1786	0.5805	0.2381	0.047*
H4E	0.2983	0.6705	0.2343	0.047*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.01794 (13)	0.01924 (14)	0.01906 (13)	-0.00020 (7)	0.00798 (10)	-0.00053 (7)
S1	0.02300 (17)	0.02794 (18)	0.02205 (17)	0.00512 (12)	0.01056 (13)	0.00483 (12)
O1	0.0389 (6)	0.0526 (7)	0.0514 (7)	0.0139 (5)	0.0305 (5)	0.0202 (5)
O2	0.0262 (5)	0.0448 (6)	0.0486 (7)	0.0051 (4)	0.0132 (5)	0.0236 (5)
O3	0.0315 (5)	0.0403 (6)	0.0359 (5)	0.0147 (4)	0.0169 (4)	0.0088 (4)

O4	0.0284 (5)	0.0326 (5)	0.0300 (5)	-0.0108 (4)	0.0143 (4)	-0.0081 (4)
N1	0.0239 (5)	0.0238 (5)	0.0234 (5)	0.0027 (4)	0.0130 (4)	0.0038 (4)
N2	0.0248 (5)	0.0316 (6)	0.0307 (6)	0.0097 (5)	0.0168 (5)	0.0096 (5)
N3	0.0261 (6)	0.0310 (6)	0.0291 (6)	0.0056 (5)	0.0157 (5)	0.0059 (5)
N4	0.0259 (5)	0.0287 (6)	0.0225 (5)	0.0022 (4)	0.0093 (4)	-0.0002 (4)
C1	0.0229 (6)	0.0216 (6)	0.0223 (6)	-0.0006 (5)	0.0102 (5)	-0.0008 (5)
C2	0.0353 (8)	0.0380 (8)	0.0308 (7)	-0.0002 (6)	0.0203 (6)	0.0055 (6)
C3	0.0374 (7)	0.0209 (7)	0.0404 (8)	0.0020 (5)	0.0193 (6)	0.0005 (5)
C4	0.0314 (7)	0.0369 (8)	0.0255 (7)	0.0107 (6)	0.0127 (6)	0.0099 (6)

Geometric parameters (Å, °)

Ni1—S1	2.3802 (3)	N2—H2	0.866 (13)
Ni1—S1 ⁱ	2.3802 (3)	N2—C1	1.3487 (16)
Ni1—O4	2.0573 (10)	N3—H3	0.867 (13)
Ni1—O4 ⁱ	2.0573 (10)	N3—C1	1.3305 (16)
Ni1—N1	2.1765 (10)	N3—C2	1.4543 (18)
Ni1—N1 ⁱ	2.1765 (10)	C2—H2A	0.9800
S1—C1	1.6985 (13)	C2—H2B	0.9800
O1—N4	1.2467 (15)	C2—H2C	0.9800
O2—N4	1.2547 (15)	C3—H3A	0.9800
O3—N4	1.2412 (14)	C3—H3B	0.9800
O4—H4A	0.862 (15)	C3—H3C	0.9800
O4—H4B	0.847 (15)	C4—H4C	0.9800
N1—N2	1.4328 (14)	C4—H4D	0.9800
N1—C3	1.4857 (17)	C4—H4E	0.9800
N1—C4	1.4823 (17)		
S1—Ni1—S1 ⁱ	180.0	H3—N3—C1	115.7 (11)
S1—Ni1—O4	89.93 (3)	H3—N3—C2	119.7 (11)
S1 ⁱ —Ni1—O4	90.07 (3)	C1—N3—C2	124.22 (12)
S1 ⁱ —Ni1—O4 ⁱ	89.93 (3)	O1—N4—O2	118.85 (11)
S1—Ni1—O4 ⁱ	90.07 (3)	O1—N4—O3	121.48 (11)
S1—Ni1—N1	82.95 (3)	O2—N4—O3	119.67 (11)
S1 ⁱ —Ni1—N1 ⁱ	82.95 (3)	S1—C1—N2	122.56 (9)
S1 ⁱ —Ni1—N1	97.05 (3)	S1—C1—N3	121.82 (10)
S1—Ni1—N1 ⁱ	97.05 (3)	N2—C1—N3	115.62 (11)
O4—Ni1—O4 ⁱ	180.00 (5)	N3—C2—H2A	109.5
O4—Ni1—N1	85.85 (4)	N3—C2—H2B	109.5
O4—Ni1—N1 ⁱ	94.15 (4)	N3—C2—H2C	109.5
O4 ⁱ —Ni1—N1 ⁱ	85.85 (4)	H2A—C2—H2B	109.5
O4 ⁱ —Ni1—N1	94.15 (4)	H2A—C2—H2C	109.5
N1—Ni1—N1 ⁱ	180.0	H2B—C2—H2C	109.5
Ni1—S1—C1	95.96 (4)	N1—C3—H3A	109.5
Ni1—O4—H4A	124.9 (14)	N1—C3—H3B	109.5
Ni1—O4—H4B	125.0 (15)	N1—C3—H3C	109.5
H4A—O4—H4B	106 (2)	H3A—C3—H3B	109.5
Ni1—N1—N2	108.26 (7)	H3A—C3—H3C	109.5

Ni1—N1—C3	113.44 (8)	H3B—C3—H3C	109.5
Ni1—N1—C4	111.40 (8)	N1—C4—H4C	109.5
N2—N1—C3	108.49 (10)	N1—C4—H4D	109.5
N2—N1—C4	106.09 (10)	N1—C4—H4E	109.5
C3—N1—C4	108.85 (11)	H4C—C4—H4D	109.5
N1—N2—H2	116.0 (11)	H4C—C4—H4E	109.5
N1—N2—C1	121.02 (10)	H4D—C4—H4E	109.5
H2—N2—C1	119.3 (11)		

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

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O4—H4A \cdots O3 ⁱⁱ	0.86 (2)	1.91 (2)	2.7703 (14)	173 (2)
O4—H4B \cdots O2	0.85 (2)	1.88 (2)	2.7074 (14)	167 (2)
N2—H2 \cdots O1 ⁱⁱⁱ	0.87 (1)	2.10 (1)	2.9565 (16)	169 (2)
N3—H3 \cdots O2 ⁱⁱⁱ	0.87 (1)	1.99 (1)	2.8551 (15)	176 (2)

Symmetry codes: (ii) $x, -y+1/2, z-1/2$; (iii) $-x, -y+1, -z+1$.