

Bis(thiosemicarbazido- κ^2N,S)nickel(II)–succinate–succinic acid (1/1/1)

Sheng-Li Li,^a Anwar Usman,^b Ibrahim A. Razak,^b Azhar A. Rahman,^b Hoong-Kun Fun,^{b*} Jie-Ying Wu,^c Yu-Peng Tian,^{d†} Min-Hua Jiang^e and Zu-Yao Chen^a

^aDepartment of Applied Chemistry, University of Science and Technology of China, Hefei 230026, People's Republic of China, ^bX-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, ^cDepartment of Chemistry, Anhui University, Hefei 230026, People's Republic of China, ^dState Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China, and ^eState Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China

† Department of Chemistry, Anhui University, Hefei 230026, People's Republic of China

Correspondence e-mail: hkfun@usm.my

Key indicators

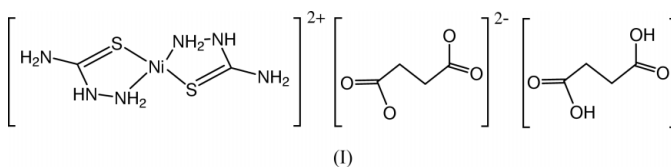
Single-crystal X-ray study
 T = 293 K
 Mean $\sigma(C-C)$ = 0.006 Å
 R factor = 0.065
 wR factor = 0.174
 Data-to-parameter ratio = 10.3

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

The title ternary complex, $[\text{Ni}(\text{CH}_5\text{N}_3\text{S})_2](\text{C}_4\text{H}_4\text{O}_4) \cdot \text{C}_4\text{H}_6\text{O}_4$, consists of a thiosemicarbazide-coordinated nickel cation, a succinate anion, and a neutral succinic acid molecule, all of which are centrosymmetric. The Ni atom is four-coordinated in a planar geometry by N and S atoms from two symmetry-related thiosemicarbazide ligands. In the crystal structure, the three components are effectively linked together by mutual electrostatic interactions and hydrogen-bonding interactions of the $\text{N}-\text{H} \cdots \text{O}$, $\text{C}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ types.

Comment

Crystal engineering based on the use of either coordination bonds or weaker intermolecular interactions has attracted great interest, and in the latter methodology, hydrogen bonding can influence the metal coordination geometry due to its relative strength and directionality (Russell *et al.*, 1997; Kawamoto *et al.*, 1996). Meanwhile, self-assembly is the most efficient means for the construction of highly organized structures and transition-metal-directed self-assembly *via* coordination has emerged as a new and major motif in supramolecular architecture (Zhang, Li, Chen *et al.*, 2000; Philp & Stoddart, 1996). Dicarboxylates constitute an important class of ligands in the formation of coordination polymers, and the chemistry of metal complexes containing S,N-bidentate ligands has been studied widely because of the structural features and particular properties of these compounds (Groeneman *et al.*, 1999; Fun *et al.*, 1996; West *et al.*, 1993). We have synthesized a series of complexes containing thiosemicarbazide ligands and appropriate dicarboxylates in order to study their potential non-linear optical properties. In the present paper, we report the crystal structure of the title compound, (I).



The structure of (I) consists of three fragments, namely the thiocarbazine-coordinated nickel(II) dication, a succinate anion and a neutral succinic acid molecule, all of which are centrosymmetric (Fig. 1). In contrast to related compounds (Zhang, Li, Nishiura *et al.*, 2000; Burrows *et al.*, 2000), the succinate anion here does not coordinate to the Ni atom but acts as a counter-ion in the structure, and mutual electrostatic interaction is expected.

The molecular structure of (I) shows that the Ni atom is four-coordinated by N and S atoms from two symmetry-

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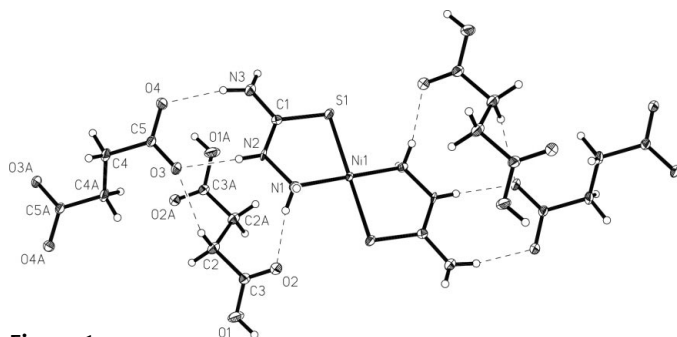


Figure 1
The structure of (I), showing ellipsoids at the 50% probability level and the atom-numbering scheme. Hydrogen bonds are indicated by dashed lines.

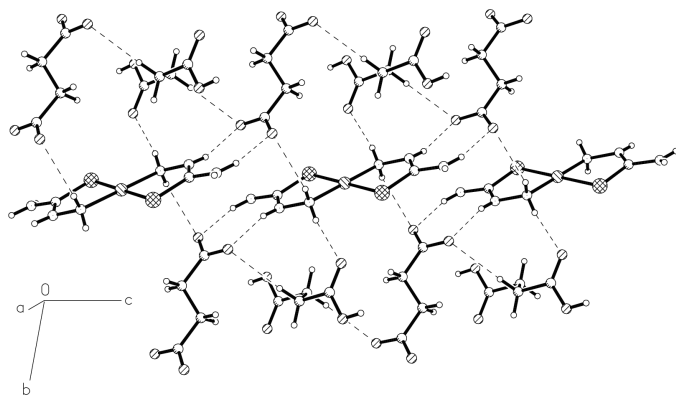


Figure 2
Packing diagram of the structure (I), showing the column formation parallel to the *c* direction. Hydrogen bonds are indicated by dashed lines.

related bidentate thiosemicarbazide ligands and the two pairs of Ni—N and Ni—S bonds are in a planar geometry. The Ni—S and Ni—N bond lengths are within normal ranges, and agree with those in *trans*-diaquabis(thiosemicarbazido- κ^2N,S)nickel(II) dimaleate dihydrate (Li *et al.*, 2003). The chelate N1—N2—C1—S1—Ni1 ring is slightly non-planar, tending towards an envelope conformation, with atom Ni1 displaced by 0.273 (1) Å from the N1/N2/C1/S1 plane. The C1—S1 and C1—N2 bonds length are intermediate between single and double bonds. These results suggest that electronic delocalization acts to some extent on the ligand upon complex formation. Within the succinate anion, the C—O bond distances are between single- and double-bond values compared with the corresponding values in succinic acid, implying that the negative charge on this moiety is delocalized over the two C—O bonds.

In the asymmetric unit, the succinate anion and succinic acid molecule are linked together by a C2—H2B···O3 hydrogen bond (Fig. 1 and Table 2), and are interconnected to the coordinated thiosemicarbazide ligands by three N—H···O hydrogen bonds, *viz.* N1—H1A···O2, N2—H2A···O3 and N3—H3A···O4, in which the thiosemicarbazide ligands act as hydrogen-bond donors. The molecules are interconnected into columns parallel to the *c* direction by an intermolecular N1—H1B···O4ⁱⁱ hydrogen bond (Table 2 and Fig. 2). The columns are further linked into a three-dimensional network by inter-

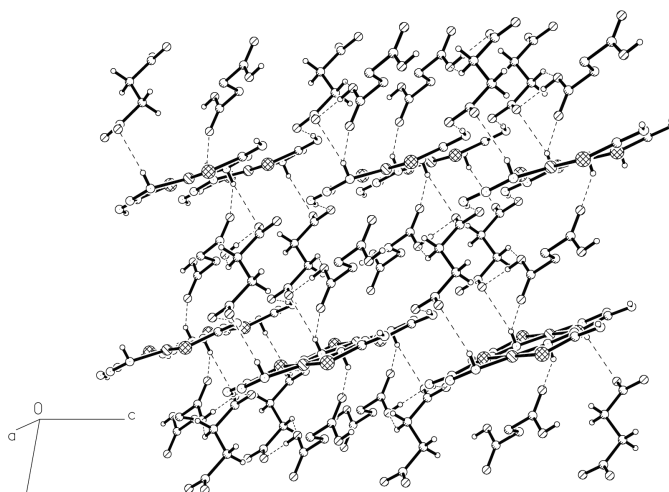


Figure 3
Packing diagram of the structure (I), showing the hydrogen bonds between the molecular columns. H atoms not involved in hydrogen bonds have been omitted for clarity.

molecular N—H···O, O—H···O, and C—H···O hydrogen bonds (Fig. 3), *viz.* N1—H1B···O2ⁱ, O1—H1O···O4ⁱⁱⁱ, N3—H3B···O3^{iv}, C4—H4A···O2^v and C4—H4B···O1^{vi} (see Table 2 for details and symmetry codes).

Experimental

Solutions of nickel chloride hexahydrate, succinic acid and thiosemicarbazide in methanol–water (volume ratio 1:1) were mixed together with stirring. The pH of the resulting solution was controlled at 4.8–5.0. The solution was then filtered and slowly evaporated at room temperature in air. After one week, wedge-shaped blue single crystals of (I) suitable for X-ray diffraction analysis were obtained.

Crystal data

[Ni(CH ₃ N ₃ S) ₂](C ₄ H ₄ O ₄)·C ₄ H ₆ O ₄	<i>Z</i> = 1
<i>M_r</i> = 475.15	<i>D_x</i> = 1.794 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 6.3886 (3) Å	Cell parameters from 2847 reflections
<i>b</i> = 8.4876 (3) Å	θ = 2.5–29.5°
<i>c</i> = 8.9485 (3) Å	μ = 1.40 mm ⁻¹
α = 102.688 (1)°	<i>T</i> = 293 (2) K
β = 107.056 (1)°	Block, brown
γ = 98.926 (1)°	0.50 × 0.40 × 0.30 mm
<i>V</i> = 439.83 (3) Å ³	

Data collection

Siemens SMART CCD area-detector diffractometer	1521 independent reflections
ω scans	1350 reflections with <i>I</i> > 2 σ (<i>I</i>)
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	<i>R</i> _{int} = 0.064
<i>T</i> _{min} = 0.525, <i>T</i> _{max} = 0.658	θ _{max} = 25.0°
2494 measured reflections	<i>h</i> = -6 → 7
	<i>k</i> = -10 → 9
	<i>l</i> = -10 → 10

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.1198P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.065$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.174$	$(\Delta/\sigma)_{\max} < 0.001$
<i>S</i> = 1.01	$\Delta\rho_{\max} = 0.79 \text{ e \AA}^{-3}$
1521 reflections	$\Delta\rho_{\min} = -1.74 \text{ e \AA}^{-3}$
148 parameters	Extinction correction: <i>SHELXTL</i>
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.055 (16)

Table 1

Selected geometric parameters (Å, °).

Ni1—N1	1.910 (3)	N3—C1	1.325 (5)
Ni1—S1	2.1784 (9)	O1—C3	1.306 (5)
S1—C1	1.722 (4)	O2—C3	1.223 (5)
N1—N2	1.430 (4)	O3—C5	1.257 (5)
N2—C1	1.318 (5)	O4—C5	1.266 (5)
N1—Ni1—S1	87.92 (10)	N1 ^{vii} —Ni1—S1	92.08 (10)

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

Table 2

Hydrogen-bonding geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1A...O2	0.84 (4)	2.06 (4)	2.892 (4)	168 (4)
N1—H1B...O2 ⁱ	0.84 (4)	2.32 (4)	3.061 (4)	147 (4)
N1—H1B...O4 ⁱⁱ	0.84 (4)	2.56 (4)	3.147 (5)	128 (4)
O1—H1O...O4 ⁱⁱⁱ	0.88 (5)	1.63 (5)	2.516 (5)	177 (6)
N2—H2A...O3	0.84 (5)	1.98 (5)	2.763 (5)	156 (5)
N3—H3A...O4	0.89 (7)	1.99 (7)	2.866 (5)	167 (6)
N3—H3B...O3 ^{iv}	0.81 (7)	2.14 (7)	2.948 (6)	173 (6)
C2—H2B...O3	0.97	2.57	3.496 (5)	159
C4—H4A...O2 ^v	0.97	2.58	3.514 (5)	161
C4—H4B...O1 ^{vi}	0.97	2.53	3.285 (6)	135

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

The H atoms attached to N and O atoms were located in a difference Fourier map and were refined isotropically, whereas those attached to C atoms were fixed geometrically and treated as riding atoms, with C—H distances = 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The large maximum and minimum principal axis ADP ratio (3.10) for atom N2 may indicate unresolved disorder. The maximum and minimum electron density peaks are located at 0.96 and 0.88 Å⁻³, respectively, from Ni1.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; 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, 2003).

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