

2669 reflections  
186 parameters  
All H atoms refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0347P)^2 + 0.3555P]$   
where  $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from  
*International Tables for  
Crystallography* (Vol. C)

*Acta Cryst.* (1999). **C55**, 1991–1993

## Tris(1,10-phenanthroline)nickel(II) dinitrate thiourea monohydrate

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(Received 17 March 1999; accepted 1 September 1999)

Table 1. Selected geometric parameters ( $\text{Å}$ ,  $^\circ$ )

Cu—N1	2.027 (2)	Cu—Cl1	2.3010 (8)
Cu—N2	2.039 (2)	Cu—Cl1'	2.7511 (9)
Cu—Cl2	2.2665 (7)	Cu—Cl2''	3.1325 (11)
N1—Cu—N2	87.28 (9)	Cl2—Cu—Cl1'	102.48 (3)
N1—Cu—Cl2	165.46 (7)	Cl1—Cu—Cl1'	87.59 (3)
N2—Cu—Cl2	94.90 (6)	N1—Cu—Cl2''	83.48 (6)
N1—Cu—Cl1	88.87 (6)	N2—Cu—Cl2''	82.66 (6)
N2—Cu—Cl1	171.11 (6)	Cl2—Cu—Cl2''	82.56 (3)
Cl2—Cu—Cl1	90.82 (3)	Cl1—Cu—Cl2''	104.87 (3)
N1—Cu—Cl1'	92.03 (6)	Cl1'—Cu—Cl2''	166.61 (2)
N2—Cu—Cl1'	84.53 (6)	Cu—Cl1—Cu'	92.41 (3)

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

Refined C—H distances are in the range 0.84 (3)–0.97 (3)  $\text{Å}$ .

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *MSCIAFC Diffractometer Control Software*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1995). Software used to prepare material for publication: *PLATON* (Spek, 1990).

This work was partially supported by CONICYT and CSIC (Uruguayan Organizations).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1092). Services for accessing these data are described at the back of the journal.

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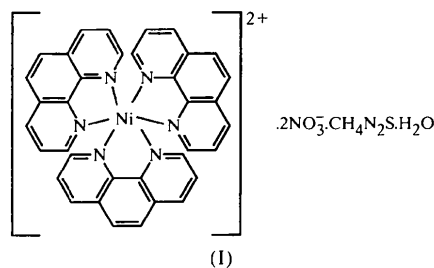
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## Abstract

The structure of the first nickel coordination complex with 1,10-phenanthroline (phen) containing thiourea as a cocrystallization molecule is reported. The title compound,  $[\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{NO}_3)_2 \cdot \text{CH}_4\text{N}_2\text{S} \cdot \text{H}_2\text{O}$ , crystallizes in the centrosymmetric space group  $C2/c$ . The crystal structure is formed by  $[\text{Ni}(\text{phen})_3]^{2+}$  cations, water and thiourea molecules positioned on a twofold axis, with the nitrate anions in general positions. The packing is directed by electrostatic interactions, stacking of phen molecules and hydrogen bonds between the crystallization molecules and the nitrate anions.

## Comment

This work reports the crystal structure of the compound tris(1,10-phenanthroline)nickel(II) dinitrate thiourea monohydrate, (I). The structure is composed of



$[\text{Ni}(\text{phen})_3]^{2+}$  cations, two nitrate anions, one water and one thiourea molecule per cation. Although the presence of thiourea has been reported in other cocrystal structures, there are no reports of its cocrystallization with phen or with other nickel complexes. The crystal structure is properly described in the centrosymmetric space group  $C2/c$  with the asymmetric unit comprising half of the  $[\text{Ni}(\text{phen})_3]^{2+}$  cationic complex, half of the cocrystallization solvates and one independent nitrate anion. The Ni atom, as well as the O51, C31 and S31 atoms, are positioned on a twofold axis of symmetry to maintain the necessary 1:2 cation–anion ratio. Tris(1,10-

phenanthroline) compounds have been described previously, in fact, the [Ni(phen)<sub>3</sub>]<sup>2+</sup> complex has been studied extensively (Butler & Snow, 1971; Frenz & Ibers, 1972; Abdel-Rahman *et al.*, 1995; Marek *et al.*, 1995; Decurtins *et al.*, 1996). In some of the compounds studied, the symmetry of the complex is described as approximately C<sub>2</sub>. The present is the first report of such a complex exhibiting exact C<sub>2</sub> symmetry. Fig. 1 shows the complex with the atom-labelling scheme.

There are two independent essentially planar phen molecules (phen1 and phen2) coordinated to the Ni atom, but one of them is positioned on a twofold axis

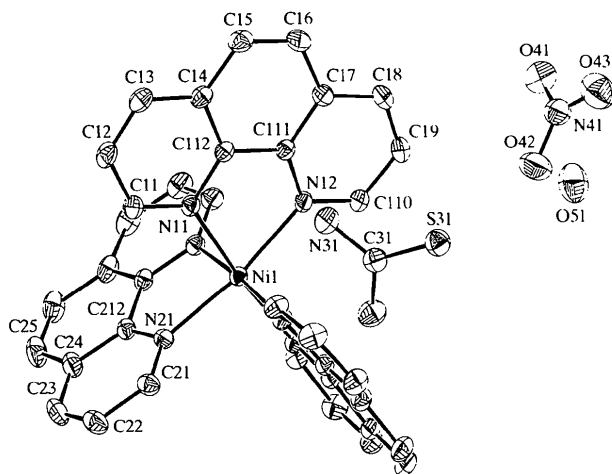


Fig. 1. ZORTEP (Zsolnai & Pritzkow, 1995) drawing showing the [Ni(phen)<sub>3</sub>]<sup>2+</sup> cation with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been excluded for clarity.

(phen2). Ni—N bond distances are in the expected range. The angle N—Ni—N with both N atoms belonging to the same phen moiety is close to 80° as expected, due to the fixed bite of phen. This rigid ligand forces the coordination sphere around nickel to be distorted from that of a regular octahedron. This is clearly evidenced by the *trans*-N—Ni—N angles of 171.93 (6) and 173.53 (8)°, far from the expected value for regular octahedral coordination. Table 1 shows selected geometrical parameters. The values of the dihedral angles of the phen planes are 88.09 (3) (phen1–phen2) and 84.38 (3)° (phen1–phen1<sup>i</sup>) [symmetry code: (i)  $-x, y, -z - \frac{1}{2}$ ], are near the ideal value expected for steric considerations.

Previous reports have described that [Ni(phen)<sub>3</sub>]<sup>2+</sup> units pack leaving holes or boxes for the anions and other small molecules (Decurtins *et al.*, 1996). In this structure, the holes are filled by the nitrate anions, the thiourea molecules and the water molecules. Marek *et al.* (1995) have reported the similar structure [Ni(phen)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>·2CHCl<sub>3</sub>·H<sub>2</sub>O, (II), where the holes are occupied by chloroform and water molecules. That structure is not related to the one described in this paper as it crystallizes in space group *P2<sub>1</sub>/n*. The interactions between proximal units of the complexes are the stacking of phen molecules. There are two stacking interactions with perpendicular distances between equivalent planes of 3.253 and 3.414 Å for phen1–phen1<sup>ii</sup> and phen2–phen2<sup>iii</sup>, respectively [symmetry codes: (ii)  $1-x, 1-y, 1-z$ ; (iii)  $\frac{1}{2}-x, \frac{1}{2}-y, -z$ ]. In spite of the similar composition, no stacking interactions are described in (II).

Geometrical parameters for the nitrate anion and the thiourea molecule are as expected. Relevant geometrical parameters of the thiourea are included in Table 1.

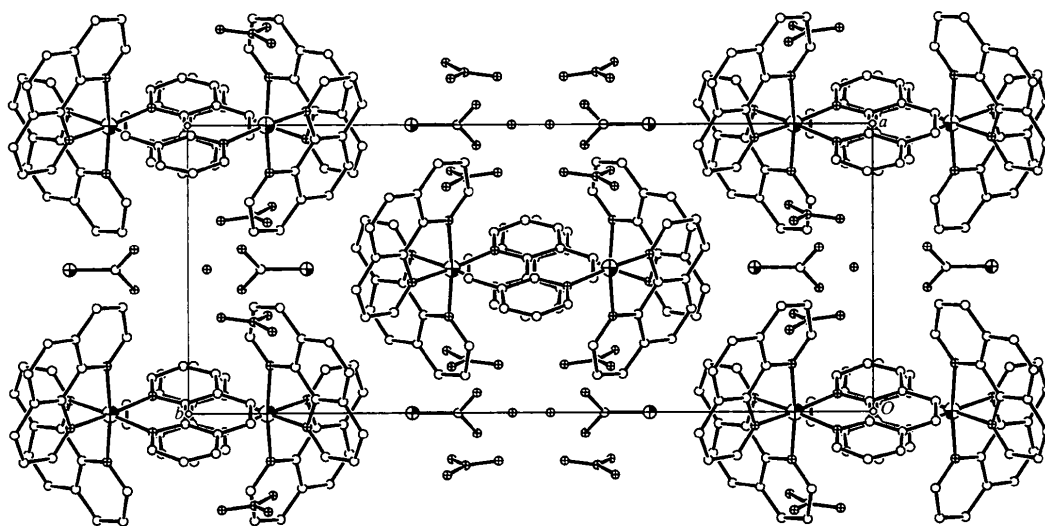


Fig. 2. View of the crystal packing and unit cell for the title compound. The arrangement shows the C centering clearly. Atoms were drawn as spheres of arbitrary radii. H atoms have been excluded for clarity.

All H atoms bonded to donor atoms are involved in hydrogen bonds with O atoms of nitrate ions and water molecules. Table 2 lists the hydrogen-bonding geometry. Note that H51 is involved in two hydrogen bonds that can be described as a unique three-centered, or bifurcated, hydrogen bond. The sum of angles about H51 [O51—H51—O42 144 (5), O51—H51—O43 162 (5) and O42—H51—O43 53.6 (13)<sup>o</sup>] is 360 (7)<sup>o</sup> (Jeffrey & Saenger, 1991). The crystal packing and unit cell of (I) are shown in Fig. 2. Note the C centering, the stacking interactions between equivalent phen2 molecules and the anions and solvent molecules located in the holes left by the cations.

## Experimental

The title compound was obtained as a by-product of the synthesis of 1,10-phenanthroline and thiourea complexes of nickel. It crystallizes as prismatic orange single crystals of suitable size for X-ray data collection.

### Crystal data

[Ni(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>·  
CH<sub>4</sub>N<sub>2</sub>S·H<sub>2</sub>O

*M<sub>r</sub>* = 817.48

Monoclinic

*C*2/*c*

*a* = 11.2528 (16) Å

*b* = 25.346 (2) Å

*c* = 13.0637 (15) Å

β = 106.117 (9)<sup>o</sup>

*V* = 3579.5 (7) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.517 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Mo Kα radiation

λ = 0.71069 Å

Cell parameters from 25  
reflections

θ = 13.20–19.13<sup>o</sup>

μ = 0.667 mm<sup>-1</sup>

*T* = 293 (2) K

Prismatic

0.43 × 0.38 × 0.22 mm

Orange

### Data collection

Rigaku AFC-7S diffractometer

θ/2θ scans

Absorption correction:

ψ scan (Molecular

Structure Corporation,  
1993)

*T<sub>min</sub>* = 0.762, *T<sub>max</sub>* = 0.867

4312 measured reflections

4108 independent reflections

3418 reflections with

*I* > 2σ(*I*)

*R<sub>int</sub>* = 0.034

θ<sub>max</sub> = 27.49<sup>o</sup>

*h* = 0 → 14

*k* = 0 → 32

*l* = -16 → 16

3 standard reflections

every 150 reflections

intensity decay: 1.3%

### Refinement

Refinement on *F*<sup>2</sup>

*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.040

*wR* (*F*<sup>2</sup>) = 0.116

*S* = 1.028

4108 reflections

315 parameters

All H atoms refined

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0714*P*)<sup>2</sup>  
+ 1.9001*P*]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> = 0.001

Δρ<sub>max</sub> = 0.509 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.909 e Å<sup>-3</sup>

Extinction correction: none

Scattering factors from

*International Tables for  
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Ni1—N21	2.0701 (15)	S31—C31	1.695 (3)
Ni1—N12	2.0805 (15)	C31—N31	1.325 (3)
Ni1—N11	2.1060 (16)		
N21—Ni1—N21'	80.63 (9)	N12—Ni1—N11	79.81 (6)
N21—Ni1—N12	171.93 (6)	N21—Ni1—N11'	91.62 (6)
N21—Ni1—N12'	95.25 (6)	N12—Ni1—N11'	95.56 (6)
N12—Ni1—N12'	89.65 (9)	N11—Ni1—N11'	173.53 (8)
N21—Ni1—N11	93.31 (6)		

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

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N31—H31 <i>B</i> ...O51'	0.90 (4)	2.11 (4)	2.937 (5)	152 (3)
N31—H31 <i>A</i> ...O41''	0.83 (3)	2.25 (3)	3.064 (4)	164 (3)
O51—H51...O42	0.82 (6)	2.39 (5)	3.092 (4)	144 (5)
O51—H51...O43	0.82 (6)	2.33 (6)	3.115 (3)	162 (5)

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

All H atoms were refined; C—H distances are in the range 0.89 (3)–1.00 (2) Å.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *MSCIAFC Diffractometer Control Software*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1995). Software used to prepare material for publication: *PLATON98* (Spek, 1990).

The authors gratefully thank PEDECIBA–Química and CONICYT for financial aid and Dr Ricardo Baggio for helpful discussions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1088). Services for accessing these data are described at the back of the journal.

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