

**{*N,N'*-Bis[2-(methylsulfanyl)phenyl]pyridine-2,6-dicarboxamidato(2-)}nickel(II)****Sheng-Gui Liu, Yi-Zhi Li,\*  
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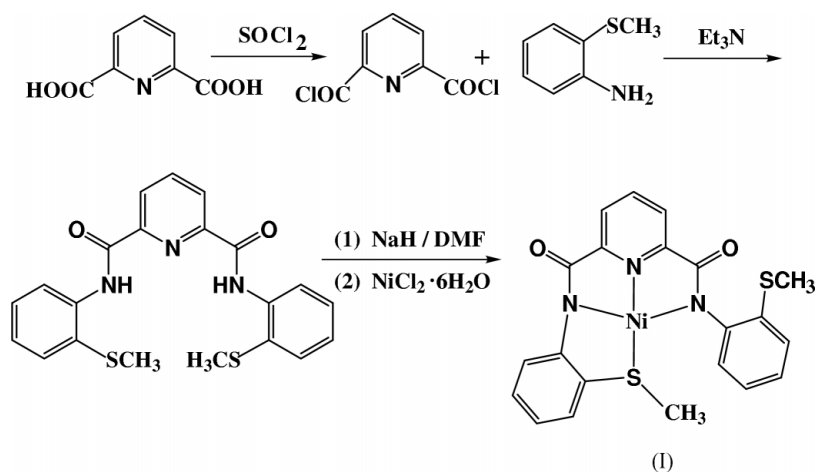
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**Key indicators**Single-crystal X-ray study  
 $T = 293\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$   
 $R$  factor = 0.052  
 $wR$  factor = 0.132  
Data-to-parameter ratio = 14.5For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

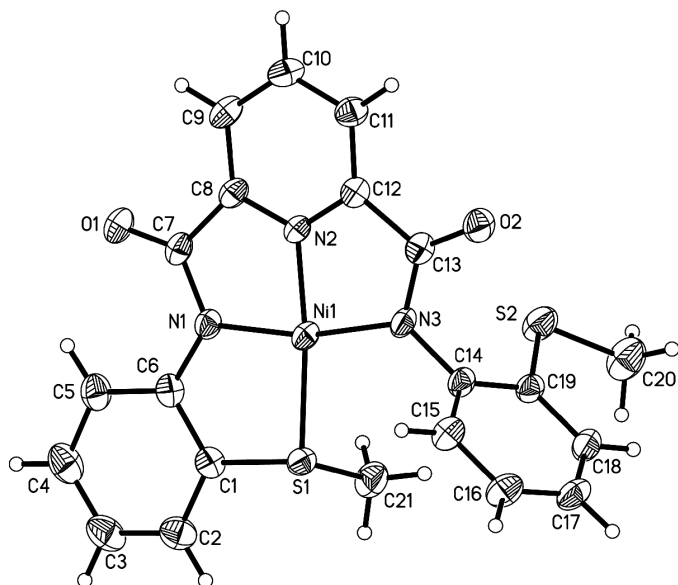
In the molecule of the title complex,  $[\text{Ni}(\text{C}_{21}\text{H}_{17}\text{N}_3\text{O}_2\text{S}_2)]$ , the Ni atom is coordinated by three N atoms and one S atom of the pyridine-2,6-dicarboxamide ligand. The geometry around the  $\text{Ni}^{\text{II}}$  atom is approximately square planar. The crystal structure is stabilized by weak  $\pi-\pi$  and  $\text{C}-\text{H}\cdots\text{O}$  intermolecular interactions.

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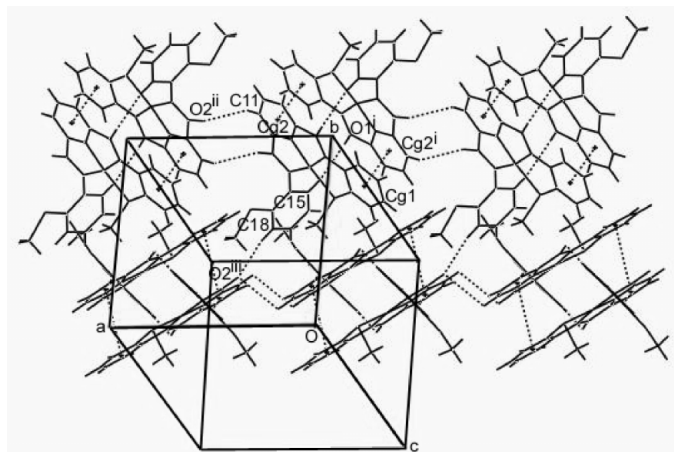
Nickel complexes with *N,S*-donor chelate ligands have received much attention in recent years. As well as being employed as models of metalloenzymes such as  $[\text{NiFe}]$ -hydrogenases (Marganian *et al.*, 1995), some of the complexes have been found to have pharmacological and catalytic properties (Brückner *et al.*, 2000; Harrop *et al.*, 2003). In order to develop further the coordination chemistry of nickel complexes with *N,S*-donor chelate ligands, we have synthesized a nickel complex based on the ligand *N,N'*-bis[2-(methylsulfanyl)phenyl]pyridine-2,6-dicarboxamide,  $L^{2-}$ , which contains deprotonated carboxamide nitrogen and sulfur as donor atoms.



The title complex, (I), was obtained from reaction of  $L^{2-}$  and  $\text{NiCl}_2$  in DMF solution in high yield. The absence of  $\nu(\text{NH})$  ( $3170\text{ cm}^{-1}$ ) in the IR spectrum confirms that the ligand is coordinated to the Ni atom in the deprotonated form. The  $\text{C}=\text{O}$  stretching vibration for the complex is at  $1635\text{ cm}^{-1}$ , lower than that in the free ligand  $\text{H}_2L$  ( $1676\text{ cm}^{-1}$ ). Such behavior is also observed in another deprotonated amide complex (Patra *et al.*, 2000). Compared to the UV spectrum of the free ligand, there is a new absorption band at  $342\text{ nm}$  for the complex, which is caused by a ligand-to-metal charge transfer transition.



**Figure 1**  
The molecular structure of (I), with anisotropic displacement ellipsoids drawn at the 30% probability level.



**Figure 2**  
The packing of the complex. The dashed lines show weak  $\pi$ - $\pi$  and C-H $\cdots$ O interactions, as detailed in Table 2 and the main text.

The molecular structure of the title complex is shown in Fig. 1. It is a mononuclear complex. The geometry around the central Ni atom is approximately square planar (r.m.s. deviation = 0.022 Å). Three of the coordination sites are occupied by N atoms from two amidate moieties and one pyridine ring; the fourth donor is an S atom. The C1–C6 benzene ring, the central pyridine ring and the two carboxamide groups are coplanar with the nickel coordination plane, which makes a dihedral angle of 75.74 (8)° with the other benzene ring, C14–C19. The average Ni–N<sub>amide</sub> distance [1.8685 (2) Å] is appreciably longer than that for Ni–N<sub>py</sub> [py is pyridine; 1.821 (2) Å], because of the steric requirement of the rigid ligand. This behavior has also been observed in an NiN<sub>3</sub>O square-planar complex (Kawamoto *et al.*, 1998). The Ni1–S1 bond distance is shorter than that observed in another complex [2.1988 (9) and 2.1740 (9) Å; Brückner *et al.*, 2000]. The bond lengths for C7–O1 and C13–O2 are only slightly

shorter than those reported for a C=O bond [1.234 (6) and 1.242 (6) Å; Redmore *et al.*, 1997]. Subtle changes within a ligand framework may result in entirely different structures when coordinated to a metal center. An NiN<sub>6</sub> compressed octahedral coordination for 2,6-bis(*N*-phenylcarbamoyl)pyridine has been reported (Patra & Mukherjee, 1999).

The crystal packing of the title complex is shown in Fig. 2. Two adjacent molecules form a dimer in the head-to-head fashion by two weak interactions; one is an intermolecular  $\pi$ - $\pi$  interaction between the pyridine ring and the C1–C6 benzene ring [the distance Cg1 $\cdots$ Cg2<sup>i</sup> is 3.691 (16) Å; symmetry code: (i)  $-x, 2-y, -z$ ; Cg1 is the center of the benzene ring and Cg2 is the center of the pyridine ring], and the other is an intermolecular weak interaction C15–H15 $\cdots$ O1<sup>i</sup> (Table 2). In the dimer, the Ni1 $\cdots$ Ni1<sup>i</sup> distance is 4.2943 (11) Å. In the crystal structure, these dimers form a two-dimensional layer through two further weak interactions (see Table 2).

## Experimental

All the chemicals were of AR grade reagent. CH<sub>2</sub>Cl<sub>2</sub> and DMF were dried over CaH<sub>2</sub> and distilled before use. Pyridine-2,6-dicarboxylic acid (3.34 g, 20 mmol) was refluxed in 10 ml thionyl chloride for 8 h. Excess thionyl chloride was removed under vacuum. After cooling to room temperature, 2-(methylthio)aniline (5.56 g, 40 mmol) and triethylamine (3 ml) in CH<sub>2</sub>Cl<sub>2</sub> (40 ml) were added to the solution of the residue in dry CH<sub>2</sub>Cl<sub>2</sub> (30 ml). After the mixture had been stirred for 2 h at ambient temperature, the precipitated white solid was collected by filtration, washed with water and dried *in vacuo*. The product was recrystallized from ethanol to give the ligand H<sub>2</sub>L (yield: 7.40 g, 90.5%). Analysis calculated for C<sub>21</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub>: C 61.54, H 4.64, N 10.26%; found: C 61.62, H 4.63, N 10.29%. IR (KBr pellets, cm<sup>-1</sup>): 3450, 3170, 1676, 1655, 1585, 1533, 1458, 1257, 1073, 768.

The ligand H<sub>2</sub>L (257 mg, 0.63 mmol) and NaH (30 mg, 1.25 mmol) in 10 ml *N,N*-dimethylformamide (DMF) were added to a solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (74 mg, 0.315 mmol) in DMF (5 ml) with stirring. The resulting red solution was stirred for 15 min at room temperature. Exposure of the solution to the air for a week gave red single crystals suitable for structure determination (yield: 180 mg, 69.20%). Analysis calculated for C<sub>21</sub>H<sub>19</sub>N<sub>3</sub>NiO<sub>2</sub>S<sub>2</sub>: C 54.05, H 3.65, N 9.00%; found: C 54.13, H 3.63, N 9.04%. IR: (KBr pellets, cm<sup>-1</sup>): 3445, 1635, 1578, 1466, 1360, 750. UV (DMF): 342 nm.

### Crystal data

[Ni(C<sub>21</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub>)]  
*M<sub>r</sub>* = 466.21  
 Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 11.430 (2) Å  
*b* = 11.406 (2) Å  
*c* = 15.087 (3) Å  
 $\beta$  = 96.765 (4)°  
*V* = 1953.2 (6) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.585 Mg m<sup>-3</sup>  
 Mo K $\alpha$  radiation  
 Cell parameters from 775 reflections  
 $\theta$  = 2.5–25.0°  
 $\mu$  = 1.23 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Prism, red  
 0.32 × 0.22 × 0.20 mm

### Data collection

Bruker SMART APEX CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Bruker, 2000)  
*T<sub>min</sub>* = 0.669, *T<sub>max</sub>* = 0.782  
 10243 measured reflections

3834 independent reflections  
 3039 reflections with *I* > 2 $\sigma$ (*I*)  
*R<sub>int</sub>* = 0.066  
 $\theta_{max}$  = 26.0°  
*h* = -8 → 14  
*k* = -14 → 13  
*l* = -18 → 18

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.052$   
 $wR(F^2) = 0.132$   
 $S = 0.92$   
 3834 reflections  
 264 parameters  
 H-atom parameters constrained

$$w = 1/(\sigma^2(F_o^2) + (0.07P)^2 + 1.55P)$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.87 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.83 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Ni1—N2	1.821 (3)	Ni1—N3	1.876 (3)
Ni1—N1	1.861 (3)	Ni1—S1	2.1535 (10)
N2—Ni1—N1	83.88 (13)	N2—Ni1—S1	173.58 (10)
N2—Ni1—N3	83.42 (13)	N1—Ni1—S1	89.88 (10)
N1—Ni1—N3	167.19 (13)	N3—Ni1—S1	102.85 (10)

Table 2

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C15—H15 $\cdots$ O1 <sup>i</sup>	0.93	2.36	3.272 (6)	168
C11—H11 $\cdots$ O2 <sup>ii</sup>	0.93	2.77	3.134 (5)	105
C18—H18 $\cdots$ O2 <sup>iii</sup>	0.93	2.32	3.235 (5)	167

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

H atoms were positioned geometrically and constrained as riding atoms, with C—H distances of 0.93–0.96  $\text{\AA}$  and  $U_{\text{iso}}(\text{H})$  set to 1.2–1.5  $U_{\text{eq}}$  of the parent atom.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *MERCURY* (Version 1.2.1; Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXTL*.

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