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Bis[*N,N*-diisobutyl-*N'*-(2-thienylcarbonyl)-thioureato]nickel(II)

Ligia R. Gomes,^a Luis M. N. B. F. Santos,^b B. Schröder,^b Ch. Wagner^c and John N. Low^{d*}

^aCBFC—Faculdade de Ciências da Saúde, Escola Superior de Saúde da UFP, Universidade Fernando Pessoa, Rua Carlos da Maia, 296, P-4200-150 Porto, Portugal, ^bDepartment of Chemistry, Faculty of Science, Rua do Campo Alegre, 687, P-4169-007 Porto, Portugal, ^cUniversität Halle–Wittenberg, Institut für Anorganische Chemie, Kurt-Mothes-Strasse 2, 06120 Halle, Germany, and ^dDepartment of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland

Correspondence e-mail: lrgomes@ufp.pt

Key indicators

Single-crystal X-ray study
 T = 290 K
 Mean $\sigma(\text{C}-\text{C}) = 0.008 \text{ \AA}$
 Disorder in main residue
 R factor = 0.038
 wR factor = 0.099
 Data-to-parameter ratio = 16.1

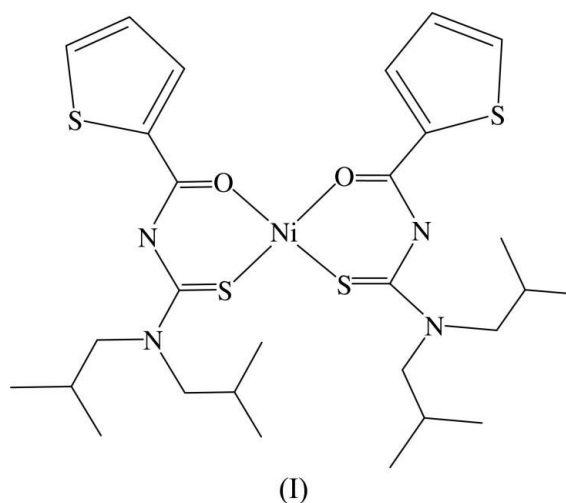
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title complex, $[\text{Ni}(\text{C}_{14}\text{H}_{21}\text{N}_2\text{OS}_2)_2]$, the Ni^{II} ion is in a square-planar coordination environment. The ligands assume a *cis* arrangement with respect to each other around the Ni^{II} ion, which lies on a crystallographic twofold rotation axis running parallel to the *c* axis. The title complex is isostructural with the copper(II) analogue.

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Comment

This work is part of an extensive study of the thermochemistry of 1,3-ligand systems with *S,O,N*-coordinating atoms aimed at helping to elucidate the binding process in complexes with transition metal ions.



The title complex, (I), exhibits a square-planar geometry with an S_2O_2 coordination environment, in which the ligands assume a *cis* arrangement with respect to each other. The Ni atom lies on a crystallographic twofold rotation axis. A similar coordination mode around the metal ion has been already reported for other related complexes (Ribeiro da Silva *et al.*, 2003; Richter *et al.*, 1980; Seidelmann *et al.*, 1995). The isostructural copper(II) complex, (II), is reported in the following paper (Gomes, Santos, Schröder, Wagner & Low, 2007).

The molecular structure of (I) is shown in Figs. 1 and 2. The main bond lengths are given in Table 1. The metal–oxygen and metal–sulfur bond lengths are of the same order of magnitude as for previously reported structures (Ribeiro da Silva *et al.*, 2003). When compared with the values for the free ligand (Gomes, Santos, Schröder & Wagner, 2007) (listed second in the following sequence of paired values), the N1–C21 [1.321 (5)/1.383 (3) Å] and N1–C6 [1.334 (5)/1.421 (3) Å] bonds are shorter while C6–S2 [1.738 (4)/1.677 (2) Å] and

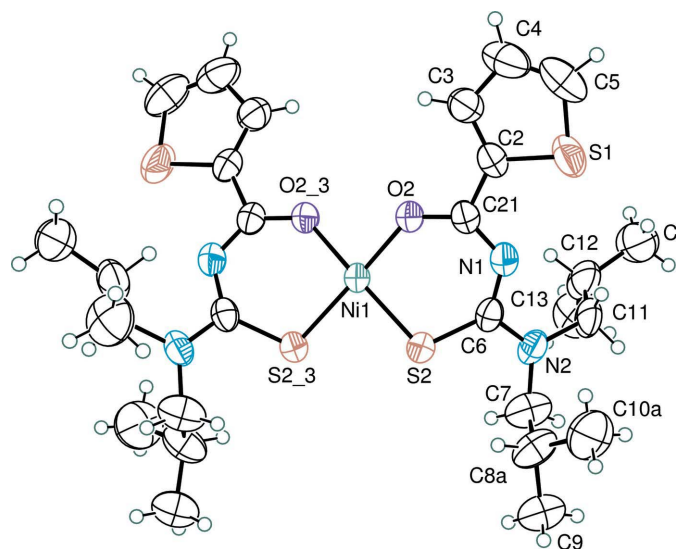


Figure 1
The molecular structure of (I), showing the major component of disorder and the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: $(_3) 1 - x, 1 - y, -z$.]

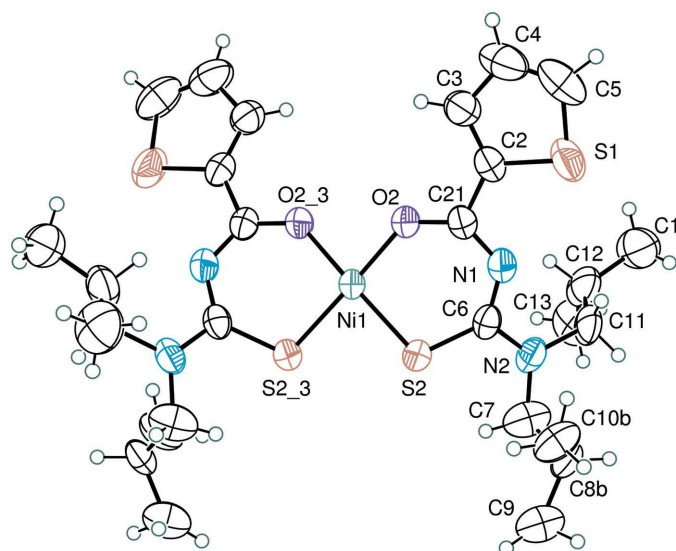


Figure 2
The molecular structure of (I), showing the minor component of disorder and the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: $(_3) 1 - x, 1 - y, -z$.]

C21–O2 [1.261 (5)/1.218 (3)], involving the coordinated O and S atoms, are longer. These observations suggest that the electrons in the C6–N1–C5 system are more delocalized in the complex.

In the crystal structure, the molecule at (x, y, z) is hydrogen bonded to the molecule at $(y, 1 - x, 2 - z)$, forming a hydrogen-bonded $R_4^2(20)$ ring (Bernstein *et al.*, (1995), in which atom C3 in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* H3, to atom O2 in the molecule at $(y, 1 - x, 2 - z)$, C3 in the molecule at $(y, 1 - x, 2 - z)$ acts as a hydrogen-bond donor to atom O2 in the molecule at $(1 - x, 1 - y, z)$, C3 in the molecule at $(1 - x, 1 - y, z)$ acts as hydrogen-bond donor to O2 in the molecule at $(1 - y, x, 2 - z)$ and, finally, C3 in the molecule at $(1 - y, x, 2 - z)$ acts as a

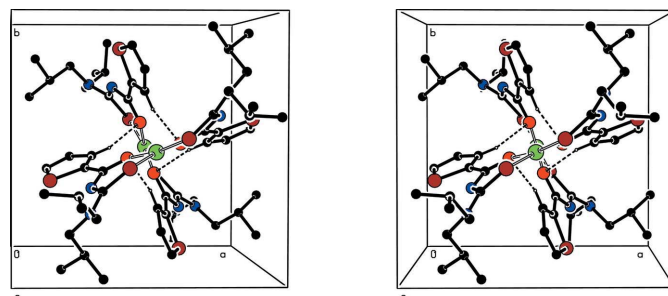


Figure 3
Stereoscopic view of the hydrogen-bonded complex. H atoms not involved in the hydrogen bonding are omitted for clarity. Only the major component of disorder is shown. Hydrogen bonds are shown as dashed lines.

hydrogen-bond donor to O2 in the molecule at (x, y, z) (Table 2 and Fig. 3).

Experimental

The preparation of the title complex was carried out according to the general procedure of Beyer *et al.* (1975). The compound was filtered off and washed with ethanol. The precipitate was recrystallized from chloroform/ethanol (1:4), resulting in red–violet–dark-brown crystals. X-ray quality single crystals were obtained by slow evaporation of methanol solutions of (I). The purity of the synthesized compounds was verified by elemental analysis. Found (%w) for $C_{28}H_{42}N_4NiNO_2S_4$: C 51.7, H 6.4, N 8.7, O 5.0, S 19.7; calculated (%w): C 51.45, H 6.48, N 8.6, O 4.90, S 19.62;

Crystal data

[Ni(C₁₄H₂₁N₂OS₂)₂]
 $M_r = 653.60$
Tetragonal, $I\bar{4}$
 $a = 13.077$ (9) Å
 $c = 20.44$ (2) Å
 $V = 3495$ (5) Å³

$Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.82$ mm⁻¹
 $T = 290$ (2) K
 $0.3 \times 0.2 \times 0.1$ mm

Data collection

Stoe Stadi-4 diffractometer
Absorption correction: ψ scan
(North *et al.*, 1968)
 $T_{\min} = 0.790$, $T_{\max} = 0.922$
3040 measured reflections
2957 independent reflections

2785 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$
16 standard reflections
frequency: 60 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.099$
 $S = 1.08$
2957 reflections
184 parameters
H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.52$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.60$ e Å⁻³
Absolute structure: Flack (1983),
1653 Friedel pairs
Flack parameter: 0.003 (15)

Table 1

Selected bond lengths (Å).

Ni1–O2	1.872 (3)	N1–C6	1.334 (5)
Ni1–S2	2.1549 (17)	C6–N2	1.341 (5)
C21–O2	1.261 (5)	C6–S2	1.738 (4)
C21–N1	1.321 (5)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C3-H3\cdots O2^i$	0.93	2.35	3.204 (6)	153

Symmetry code: (i) $y, -x + 1, -z + 2$.

H atoms bonded to C atoms were refined with standard distances (0.93 Å for aromatic and 0.98, 0.96 and 0.97 Å, for tertiary, secondary and primary aliphatic groups, respectively), with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl groups and $U_{iso}(H) = 1.2U_{eq}(C)$ for all others. Atoms C8 and C10 of the isobutyl group are disordered over two sites with refined occupancies of 0.627 (12) and 0.373 (12), respectively. The H atoms on C7, C8, C9 and C10 were calculated on the basis of this disorder. Those for methyl atoms C9 and C10 were calculated as six equally spaced half-occupancy H atoms. The C–C bond distances within the disordered isobutyl group were restrained to 1.520 (5) Å. There is a solvent-accessible void in the structure of volume 59 Å³, corresponding to 1.7% of the unit-cell volume. No discernible peaks could be found in the void.

Data collection: *IPDS Software* (Stoe & Cie, 1996); cell refinement: *CELL* (Burzlaff, 1996); data reduction: *INTEGRATE* in *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

X-ray data were collected at the Institut für Anorganische Chemie, University Universität Halle–Wittenberg. BS thanks

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