Bis(1,1,5,5-tetramethyl-2-thiobiuretato)nickel(II)

Jonathan D Crane* and Matthew Whittingham

Department of Chemistry, University of Hull, Cottingham Road, Kingston-upon-Hull HU6 7RX, England

Correspondence e-mail: j.d.crane@hull.ac.uk

Key indicators

Single-crystal X-ray study
$T = 150$ K
Mean σ(N–C) = 0.003 Å
Disorder in main residue
R factor = 0.030
wR factor = 0.060
Data-to-parameter ratio = 19.1

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

At 150 K, the title compound, [Ni($C_6H_{12}N_3OS$)$_2$], comprises a *cis* square-planar nickel(II) ion with two anionic bidentate 1,1,5,5-tetramethyl-2-thiobiurete ligands. All non-H atoms lie on a crystallographic mirror plane.
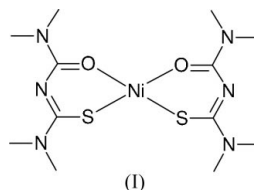
Comment

The title compound, (I), is the neutral homoleptic nickel(II) complex of the anionic bidentate 1,1,5,5-tetramethyl-2-thio-biuretate ligand. The complex is *cis* square-planar (Table 1) and all non-H atoms lie on a crystallographic mirror plane (Fig. 1).

(I)

In both of the ligands, the pattern of bond distances is similar to that observed for the corresponding homoleptic cobalt(III) complex reported by Crane & Whittingham (2004) and indicates that the formal negative charge is predominately localized on the S atom. The relatively long C—S and short C—O average bond lengths [1.747 (4) and 1.261 (3) Å] are consistent with mostly single- and double-bond character, respectively, and this bond localization is also reflected in the average C—N bond distances to the central N atom, *viz.* 1.323 (7) Å in the (iso)thiourea group and 1.348 (7) Å in the urea group.
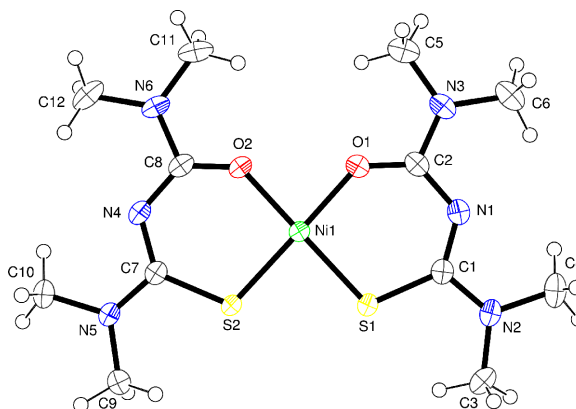

Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size. Only one of the disordered positions for each methyl group is shown.
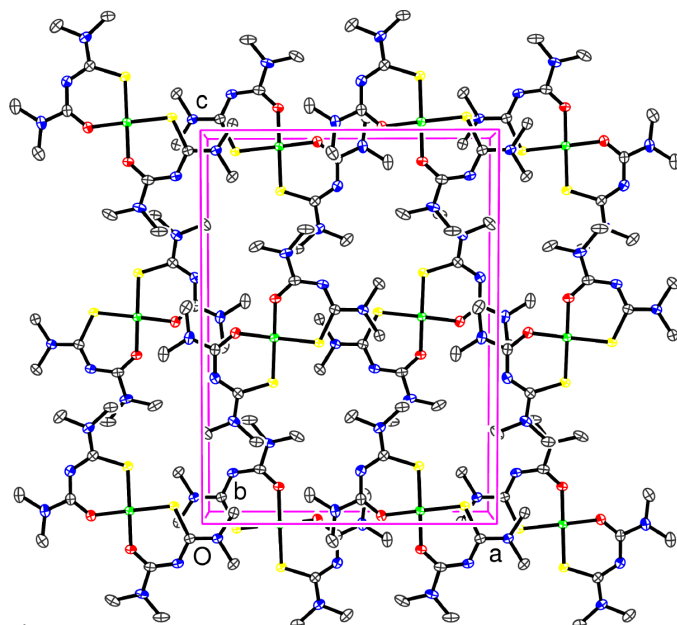
Figure 2
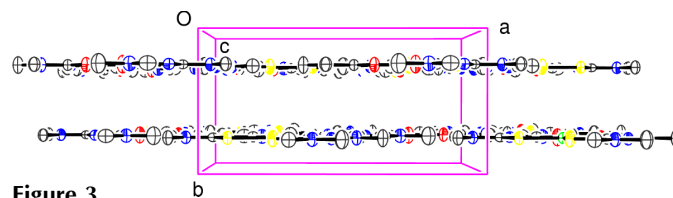The packing and unit cell of (I), viewed down the *b* axis. H atoms have been omitted.

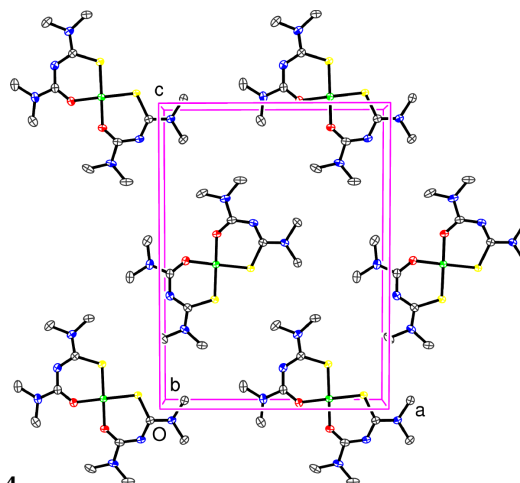**Figure 3**
The packing and unit cell of (I), viewed down the *c* axis.

Figure 4
The packing of one layer of molecules of (I), parallel to the *ac* plane. H atoms have been omitted.

The molecules are packed in layers (Figs. 3 and 4) perpendicular to the *b* axis, with an interlayer spacing of 3.5062 (3) Å. Of the shortest non-H interatomic contact distance between layers (Table 2), the shortest involving the S atoms is 3.5986 (5) Å for S2 and N5^i [symmetry code: (i) $-x$, $1 - y$, $-z$].

Experimental

The title compound, (I), was prepared by a variation of the method of Koenig *et al.* (1987). Dimethylcarbamyl chloride (1.08 g, 10 mmol) and potassium thiocyanate (0.97 g, 10 mmol) in acetonitrile (40 ml) were heated at reflux for 2 h. The solution was allowed to cool to room temperature and excess 40% aqueous dimethylamine (3.4 ml, 30 mmol) was added with stirring, followed after 15 min by nickel(II) acetate tetrahydrate (1.25 g, 5 mmol) and water (5 ml). After stirring for a further 15 min, the crude product was obtained as a purple powder by precipitation with methanol (200 ml), isolation by filtration and washing sequentially with water, methanol and diethyl ether. Suitable crystals were grown by recrystallization from dichloromethane/methanol: yield 1.07 g, 53%. Spectroscopic analysis: IR (KBr disk, cm^{-1}): ν 2921 (*w*), 1540 (*s*), 1481 (*s*), 1389 (*s*), 1357 (*s*), 1266 (*w*), 1198 (*w*), 1115 (*m*), 1031 (*m*), 734 (*m*), 474 (*w*); ^{1}H NMR (CDCl$_3$, p.p.m.): δ 3.18 (*br, s*, 6H), 3.08 (*br, s*, 6H), 2.96 (*s*, 6H), 2.87 (*s*, 6H); ^{13}C NMR (CDCl$_3$, p.p.m.): δ 171.3, 163.1, 40.1, 39.7, 37.4, 35.9. Analysis calculated for C$_{12}$H$_{24}$N$_6$NiO$_2$S$_2$: C 35.40, H 5.94, N 20.64, S 15.75%; found: C 35.49, H 6.03, N 20.49, S 15.71%.

Crystal data

[Ni(C$_6$H$_{12}$N$_3$OS)$_2$]	Mo $K\alpha$ radiation
$M_r = 407.20$	Cell parameters from 10003
Orthorhombic, *Pnma*	reflections
$a = 13.9350$ (10) Å	$\theta = 2.2$–30.0°
$b = 7.0123$ (5) Å	$\mu = 1.32$ mm^{-1}
$c = 18.4739$ (18) Å	$T = 150$ (2) K
$V = 1805.2$ (3) Å^3	Plate, purple
$Z = 4$	0.20 × 0.18 × 0.02 mm
$D_x = 1.498$ Mg m^{-3}	

Data collection

Stoe IPDS-II area-detector	2820 independent reflections
diffractometer	1936 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.065$
Absorption correction: numerical	$\theta_{max} = 30.0°$
(*X-SHAPE*; Stoe & Cie, 2001)	$h = -16 \rightarrow 19$
$T_{min} = 0.630$, $T_{max} = 0.751$	$k = -9 \rightarrow 9$
18236 measured reflections	$l = -25 \rightarrow 25$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0271P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.030$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$wR(F^2) = 0.060$	$(\Delta/\sigma)_{max} = 0.001$
$S = 0.87$	$\Delta\rho_{max} = 0.36$ e Å^{-3}
2820 reflections	$\Delta\rho_{min} = -0.26$ e Å^{-3}
148 parameters	Extinction correction: *SHELXL*97
H-atom parameters constrained	Extinction coefficient: 0.0017 (3)

Table 1
Selected geometric parameters (Å, °).

Ni1—O1	1.8694 (17)	N1—C1	1.316 (3)
Ni1—O2	1.8634 (15)	N1—C2	1.355 (3)
Ni1—S1	2.1374 (7)	N2—C1	1.353 (3)
Ni1—S2	2.1386 (7)	N3—C2	1.351 (3)
S1—C1	1.743 (2)	N4—C7	1.329 (3)
S2—C7	1.750 (2)	N4—C8	1.341 (3)
O1—C2	1.261 (3)	N5—C7	1.333 (3)
O2—C8	1.260 (3)	N6—C8	1.366 (3)
O1—Ni1—S1	95.16 (6)	C2—O1—Ni1	133.73 (16)
O2—Ni1—S2	94.65 (6)	C8—O2—Ni1	134.24 (17)
O1—Ni1—O2	84.45 (8)	C1—N1—C2	123.6 (2)
S1—Ni1—S2	85.75 (3)	C7—N4—C8	123.39 (19)
O1—Ni1—S2	179.10 (6)	N1—C1—S1	129.24 (18)
O2—Ni1—S1	179.60 (7)	O1—C2—N1	129.2 (2)
C1—S1—Ni1	109.05 (8)	N4—C7—S2	128.39 (18)
C7—S2—Ni1	109.52 (8)	O2—C8—N4	129.8 (2)

Table 2
Interlayer contact distances (Å) less than 3.6 Å for non-H atoms.

S2···N5[i]	3.5986 (5)	N6···C3[iii]	3.5470 (6)
C2···C5[ii]	3.5161 (4)	N2···C12[iv]	3.5622 (7)

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

All H atoms were initially located in a difference Fourier map. The methyl H atoms were constrained to an ideal geometry, with a C—H distance of 0.98 Å, and $U_{iso}(H)$ was set to $1.2U_{eq}(C)$, but each group was allowed to rotate freely about its X—C bond. In their final positions, none of the methyl groups accords with the crystallographic mirror symmetry and hence each methyl group is disordered 50:50 about the mirror plane.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2001); program(s) used to solve structure: *X-STEP*32 (Stoe & Cie, 2001) and *WinGX* (Farrugia, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* and *PLATON* (Spek, 2001).

References

Crane, J. D. & Whittingham, M. (2004). *Acta Cryst.* E**60**, m350–m351.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Koenig, K. H., Kaul, L., Kuge, M. & Schuster, M. (1987). *Liebigs Ann. Chem.* pp. 1115–1116.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (2001). *PLATON*. University of Utrecht, The Netherlands.
Stoe & Cie (2001). *X-AREA*, *X-RED*, *X-SHAPE* and *X-STEP*32. Stoe & Cie GmbH, Darmstadt, Germany.