Curtis, M. D., Shiu, K.-B. & Butler, W. M. (1986). *J. Am. Chem. Soc.* **108**, 1550–1561.
Fachinetti, G., Fochi, G. & Floriani, C. (1977). *J. Chem. Soc. Dalton Trans.* pp. 1946–1952.
Grotjahn, D. B. & Lo, H. (1995). *Organometallics.* In the press.
Grotjahn, D. B., Lo, H. & Groy, T. L. (1996). *Acta Cryst.* C**52**, 300–302.
Lahuerta, P., Latorre, J., Sanaú, M., Cotton, F. A. & Schwotzer, W. (1988). *Polyhedron*, **7**, 1311–1316.
Leeaphon, M., Fanwick, P. E. & Walton, R. A. (1991). *Inorg. Chem.* **30**, 4986–4995.
Lindner, E., Wang, Q., Mayer, H. A., Fawzi, R. & Steimann, M. (1993). *Organometallics*, **12**, 1865–1870.
Milstein, D., Fultz, W. C. & Calabrese, J. C. (1986). *J. Am. Chem. Soc.* **108**, 1336–1338.
Morrison, E. C., Palmer, C. A. & Tocher, D. A. (1988). *J. Organomet. Chem.* **349**, 405–411.
Redhouse, A. D. (1982). *Structure of Organometallic Compounds. The Chemistry of the Metal–Carbon Bond*, Vol. 1, pp 1–41. New York: Wiley.
Rodman, G. S. & Mann, K. R. (1985). *Inorg. Chem.* **24**, 3507–3508.
Roper, W. R., Taylor, G. E., Waters, J. M. & Wright, L. J. (1979). *J. Organomet. Chem.* **182**, C46–C48.
Sheldrick, G. M. (1990*a*). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1990*b*). *SHELXTL/PC User's Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1989). *P3/PC Diffractometer Program.* Version 3.13. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Steed, J. W. & Tocher, D. A. (1992). *J. Chem. Soc. Dalton Trans.* pp. 2765–2773.

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Bis[*O*-(4-methylcyclohexyl) dithiocarbonato-*S*,*S*′]nickel(II)

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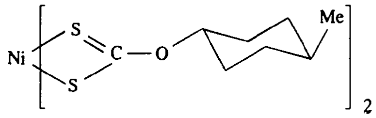
Abstract

The Ni atom in the title compound, [Ni($C_7H_{13}OCS_2$)$_2$], lies on an inversion centre and adopts square-planar coordination geometry defined by the four S atoms of the two dithiocarbonato (xanthate) ligands. The lengths of the two independent Ni—S bonds are equal [2.205 (1) Å].

Comment

Extensive studies have been carried out on the crystal structures, thermal decomposition and spectroscopic properties of alkyl xanthate nickel(II) complexes (Prisyazhnyuk, Bel'skii & Kolchinskii, 1987; Mizota, Fujii & Asahina, 1980; Ballester & Perpinan, 1988). Square-planar xanthate nickel(II) complexes can form adducts using the vacant coordination sites and they readily form clathrates capable of containing a variety of guest molecules (Gable, Hoskins & Winter, 1985; Pang, Lucken & Bernardinelli, 1990). They also have wide technological applications, for example, as oil additives and antioxidants for polyolefins (Klibanov, Dzottsoev & Bushe, 1989; Al-Malaika & Scott, 1983). In an attempt to create a host capable of accepting larger guest molecules, we have prepared the title complex, (I), which is chemically very similar to [Ni($C_2H_5OCS_2$)$_2$] (Prisyazhnyuk *et al.*, 1987), and determined its crystal structure.



(I)

The central Ni atom in (I) is coordinated to a square-planar array of four S atoms. The structure differs from that of [Ni($C_2H_5OCS_2$)$_2$] in which there are two crystallographically independent molecules, with four strong equatorial Ni—S bonds in each molecule and two weak axial bonds to S atoms in other molecules which give each Ni atom distorted octahedral coordination; these octahedra share edges to form a chain structure (Mizota *et al.*, 1980). The four Ni—S bond distances in (I) are equal at 2.205 (1) Å. The Ni—S distances show much greater variation in the five-coordinate complexes Ni($C_2H_5OCS_2$)$_2$.P(C_6H_5)$_3$ [2.225 (2)–2.654 (3) Å] and Ni($C_6H_{11}OCS_2$)$_2$.P(MePh$_2$) [2.210 (2)–2.722 (4) Å], in each of which the Ni atom adopts distorted square-pyramidal coordination geometry, one P and three S atoms describing an approximate basal plane with the apical position being occupied by an S atom from an asymmetrically coordinated xanthate ligand (Tiekink & Winter, 1986; Ballester, Gutierrez-Alonso, Perpinan, Gutierrez-Puebla & Ruiz-Valero, 1990). As expected, almost equivalent S—C bond lengths of 1.692 (3) and 1.696 (3) Å are observed in (I).

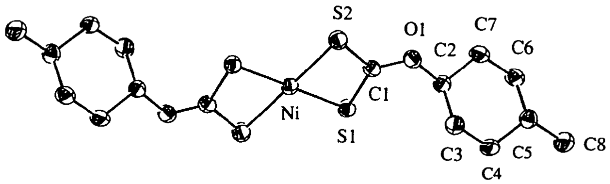


Fig. 1. Molecular structure showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.

Experimental

A solution of 150 ml of ethanol containing 0.0171 mol of [Ni($C_2H_5O_2$)$_2$].4H_2O was added, with stirring, to 0.0342 mol of sodium 4-methylcyclohexylxanthate in 170 ml of 50% ethanol. The precipitate was filtered off, washed with three portions of water and dried in vacuum. Recrystallization was from $CHCl_3$/EtOH.

Crystal data

[Ni($C_8H_{13}OS_2$)$_2$]
$M_r = 437.32$
Triclinic
$P\bar{1}$
$a = 6.442\ (3)$ Å
$b = 8.230\ (1)$ Å
$c = 10.631\ (3)$ Å
$\alpha = 106.94\ (2)°$
$\beta = 98.28\ (3)°$
$\gamma = 106.12\ (3)°$
$V = 502.2\ (3)$ Å^3
$Z = 1$
$D_x = 1.45$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.78–14.51°$
$\mu = 1.374$ mm^{-1}
$T = 296$ K
Prism
0.36 × 0.16 × 0.10 mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (*TEXSAN*; Molecular Structure Corporation, 1985)
$T_{\min} = 0.975$, $T_{\max} = 0.996$
1947 measured reflections
1773 independent reflections

1458 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.011$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 7$
$k = -9 \rightarrow 9$
$l = -12 \rightarrow 12$
3 standard reflections monitored every 300 reflections intensity decay: 4.0%

Refinement

Refinement on F
$R = 0.036$
$wR = 0.047$
$S = 1.35$
1458 reflections
106 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.44$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Ni	1	0	0	3.56 (2)
S(1)	0.7852 (1)	0.1656 (1)	0.04526 (8)	4.16 (3)
S(2)	1.2086 (1)	0.2092 (1)	0.19375 (9)	4.76 (3)
O(1)	1.0150 (4)	0.4451 (3)	0.2740 (2)	4.73 (7)
C(1)	0.9985 (5)	0.2949 (4)	0.1828 (3)	3.8 (1)
C(2)	0.8336 (5)	0.5216 (4)	0.2645 (3)	3.9 (1)
C(3)	0.8572 (6)	0.6238 (5)	0.1685 (3)	4.7 (1)
C(4)	0.6888 (6)	0.7220 (5)	0.1723 (3)	5.0 (1)
C(5)	0.7164 (6)	0.8494 (4)	0.3132 (3)	4.5 (1)
C(6)	0.6937 (7)	0.7427 (6)	0.4082 (3)	5.8 (1)
C(7)	0.8559 (8)	0.6401 (6)	0.4057 (3)	6.5 (2)
C(8)	0.5554 (7)	0.9529 (6)	0.3164 (4)	6.1 (2)

Table 2. *Selected geometric parameters* (Å, °)

Ni—S(1)	2.205 (1)	Ni—S(2)	2.205 (1)
S(1)—C(1)	1.692 (3)	S(2)—C(1)	1.696 (3)
O(1)—C(1)	1.296 (4)	O(1)—C(2)	1.477 (4)
S(1)—Ni—S(2)	79.46 (4)	S(2)—Ni—S(2$^{\rm i}$)	180.00
C(1)—S(1)—Ni	83.9 (1)	C(1)—S(2)—Ni	83.9 (1)
S(1)—C(1)—S(2)	112.7 (2)	C(1)—O(1)—C(2)	120.2 (2)

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

Data collection was performed using *CONTROL* software (Molecular Structure Corporation, 1986). The structure was solved by direct methods using *MITHRIL* (Gilmore, 1983); the Ni atom was located in an E map and the remaining non-H atoms were located using the *DIRDIF* (Beurskens, 1984) program. H atoms were placed in geometrically calculated positions with C—H = 0.95 Å, but were not included in the refinement. The structure was refined by full-matrix least-squares techniques with anisotropic displacement parameters for all non-H atoms. All calculations were performed on a VAX3100 computer using the *TEXSAN* (Molecular Structure Corporation, 1985) program package.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1211). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Al-Malaika, S. & Scott, G. (1983). *Eur. Polym. J.* **19**, 241–246.
Ballester, L., Gutierrez-Alonso, A., Perpinan, M. F., Gutierrez-Puebla, E. & Ruiz-Valero, C. (1990). *Polyhedron*. **9**, 1341–1343.
Ballester, L. & Perpinan, M. F. (1988). *J. Chem. Educ.* **65**, 362–364.
Beurskens, P. T. (1984). *DIRDIF. Direct Methods for Difference Structures – an Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors.* Technical Report 1984/1. Crystallography Laboratory, Toernooiveld, 6526 ED Nijmegen, The Netherlands.
Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Tables 2.2A and 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Gable, R. W., Hoskins, B. F. & Winter, G. (1985). *Inorg. Chim. Acta*, **96**, 151–159.
Gilmore, C. J. (1983). *MITHRIL. Computer Program for the Automatic Solution of Crystal Structures from X-ray Data.* Department of Chemistry, University of Glasgow, Scotland.
Klibanov, E. L., Dzottsoev, A. B. & Bushe, N. A. (1989). *Trenie Iznos Mash.* **10**, 1083–1086.
Mizota, T., Fujii, Y. & Asahina, H. (1980). *Technol. Rep. Yamaguchi Univ.* **2**, 389–398.
Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1986). *CONTROL. An Automatic Package for Rigaku AFC Single Crystal Diffractometers.* Revised 1988. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Pang, L., Lucken, E. A. C. & Bernardinelli, G. (1990). *J. Am. Chem. Soc.* **112**, 8754–8764.
Prisyazhnyuk, A. I., Bel'skii, V. K. & Kolchinskii, E. V. (1987). *Koord. Khim.* **13**, 977–978.
Tiekink, E. R. T. & Winter, G. (1986). *Aust. J. Chem.* **39**, 813–816.

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(4,5-Diazafluoren-9-one-N^4,N^5)bis(O-ethyl dithiocarbonato-S,S')nickel(II)

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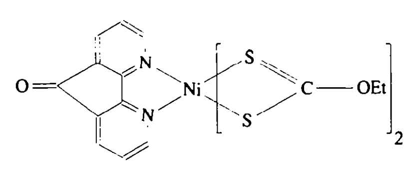
Abstract

The Ni atom in the title compound, $[Ni(C_2H_5OCS_2)_2(C_{11}H_6N_2O)]$, has a distorted octahedral environment defined by two chelating xanthate anions and one chelating 4,5-diazafluoren-9-one ligand. The Ni—S bond lengths range from 2.3882 (7) to 2.4330 (8) Å and the two Ni—N bond lengths are 2.151 (2) and 2.182 (2) Å.

Comment

Bipyridine-like ligands such as 4,5-diazafluorene and 4,5-diazafluorene-9-one have been used widely in photochemistry because the bipyridine nucleus is distorted in such a manner as to reduce the nitrogen–metal overlap. Hence, these ligands are effectively lower than bipyridine in the spectrochemical series, which translates into an energetic lowering of any ligand-field states (Henderson, Fronczek & Cherry, 1984; Shi, You, Li, Xiong & Yu, 1995). Although the structure of 4,5-diazafluoren-9-one has been reported (Fun, Sivakumar, Zhu & You, 1995), its complexes with metals have received relatively little attention (Shi *et al.*, 1995; Zhu, Wang, You, Yang & Huang, 1992). As a continuation of our investigation of the reactions of 4,5-diazafluoren-9-one with transition metal complexes, we have determined the crystal structure of $[Ni(C_2H_5OCS_2)_2(C_{11}H_6N_2O)]$, (I).



(I)

The Ni atom in (I) is coordinated to four S atoms and two *cis* N atoms which form a distorted octahedron. The structure resembles those of $[Ni(EtXA)_2(2,2'\text{-dpa})].C_6H_6$ and $[Ni(EtXA)_2(4,4'\text{-dm-}2,2'\text{-bipy})].2CCl_4$ (where 2,2'-dpa = 2,2'-dipyridylamine, EtXA = ethyl xanthate and 4,4'-dm-2,2'-bipy = 4,4'-dimethyl-2,2'-bipyridyl) (Gable, Hoskins & Winter, 1985; Pang, Lucken & Bernardinelli, 1990), which have similar Ni—S bond lengths, and differs from those of $Ni(C_2H_5OCS_2)_2.PPh_3$ and $Ni(C_6H_{11}OCS_2)_2.PMePh_2$ where the metal coordination is square pyramidal (Tienkink & Winter, 1986; Ballester, Gutierrez-Alonso, Perpinan, Gutierrez-Puebla & Ruiz-Valero, 1990). The Ni—N bond distances in (I) are somewhat longer than those in $[Ni(EtXA)_2(2,2'\text{-dpa-}C_6H_6)]$ [2.067 (5)–2.074 (5) Å] and $[Ni(EtXA)_2(4,4'\text{-dm-}2,2'\text{-bipy})].2CCl_4$ [2.068 (8)–2.073 (9) Å] (Gable *et al.*, 1985; Pang *et al.*, 1990), presumably for steric reasons. Similarly, the N(1)—Ni—N(2) bond angle is more acute than the corresponding angles [87.61 (9)°] in $[Ni(EtXA)(2,2'\text{-dpa})].C_6H_6$ (Gable *et al.*, 1985).

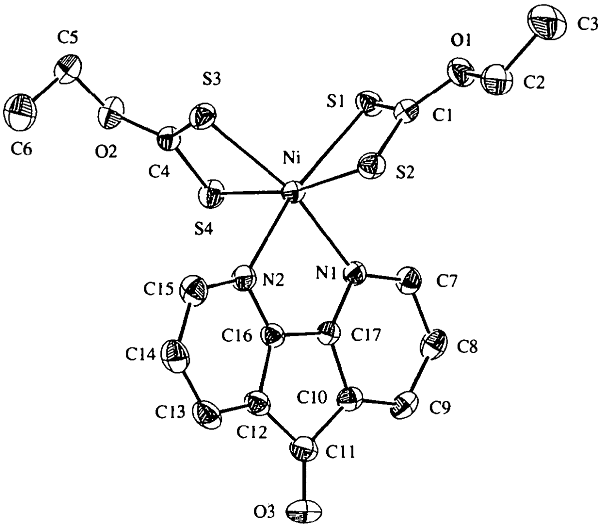


Fig. 1. Molecular structure showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.

Experimental

Bis(O-ethyl dithiocarbonato-S,S')nickel(II) was dissolved in $EtOH/CHCl_3$ and 4,5-diazafluoren-9-one in EtOH solution was added dropwise until the colour changed from brown to yellowish. Crystals were obtained after the solution evaporated at room temperature.

Crystal data

$[Ni(C_3H_5OS_2)_2(C_{11}H_6N_2O)]$	Mo $K\alpha$ radiation
$M_r = 483.27$	$\lambda = 0.71073$ Å