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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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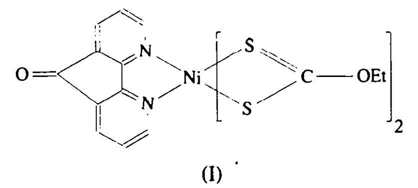
Abstract

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).

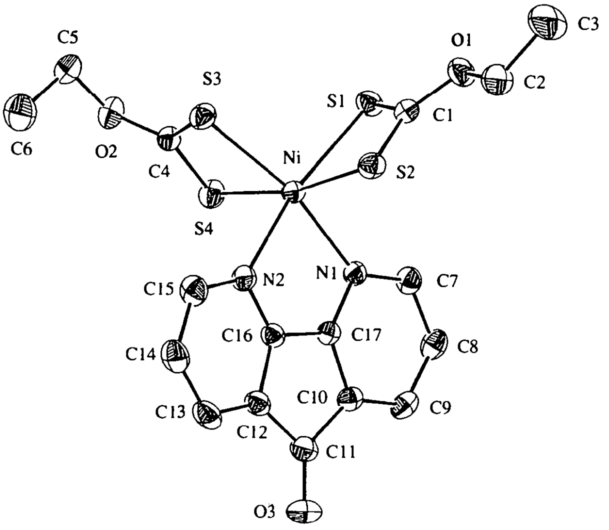


Fig. 1. Molecular structure showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.

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

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

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Monoclinic
$P2_1/n$
$a = 10.682$ (2) Å
$b = 12.742$ (2) Å
$c = 15.508$ (4) Å
$\beta = 103.51$ (1)°
$V = 2052.4$ (7) Å^3
$Z = 4$
$D_x = 1.56$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 10.68$–18.05°
$\mu = 1.359$ mm^{-1}
$T = 296$ K
Prism
0.45 × 0.42 × 0.32 mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (*TEXSAN*; Molecular Structure Corporation, 1985)
$T_{\min} = 0.929$, $T_{\max} = 1.000$
4001 measured reflections
3804 independent reflections

3321 observed reflections $[I > 3\sigma(I)]$
$R_{\rm int} = 0.023$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 15$
$l = -18 \rightarrow 18$
3 standard reflections monitored every 300 reflections intensity decay: 0.2%

Refinement

Refinement on F
$R = 0.029$
$wR = 0.045$
$S = 1.43$
3321 reflections
308 parameters
H-atom parameters refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.22$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ 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)*

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

	x	y	z	$B_{\rm eq}$
Ni	0.31444 (3)	0.22715 (2)	0.02043 (2)	2.95 (1)
S(1)	0.33730 (6)	0.28942 (5)	0.17057 (4)	3.71 (2)
S(2)	0.12436 (6)	0.33263 (5)	0.01945 (4)	3.74 (2)
S(3)	0.44193 (6)	0.36068 (4)	−0.02520 (4)	3.65 (2)
S(4)	0.52756 (6)	0.15112 (4)	0.03612 (4)	3.86 (2)
O(1)	0.1390 (2)	0.3962 (1)	0.1854 (1)	4.53 (8)
O(2)	0.6798 (2)	0.2867 (1)	−0.0077 (1)	4.43 (8)
O(3)	0.0694 (2)	−0.1689 (1)	−0.1782 (1)	5.47 (9)
N(1)	0.2286 (2)	0.0819 (1)	0.0477 (1)	3.01 (7)
N(2)	0.2488 (2)	0.1723 (1)	−0.1160 (1)	3.39 (7)
C(1)	0.1922 (2)	0.3439 (2)	0.1293 (2)	3.44 (9)
C(2)	0.0103 (3)	0.4400 (3)	0.1535 (3)	5.5 (1)
C(3)	−0.0168 (4)	0.5104 (5)	0.2236 (4)	8.5 (3)
C(4)	0.5590 (2)	0.2704 (2)	−0.0019 (1)	3.26 (9)
C(5)	0.7123 (3)	0.3841 (2)	−0.0476 (2)	4.9 (1)
C(6)	0.6911 (5)	0.3719 (3)	−0.1444 (2)	6.3 (2)
C(7)	0.2085 (2)	0.0288 (2)	0.1183 (1)	3.7 (1)
C(8)	0.1548 (2)	−0.0703 (2)	0.1121 (2)	4.0 (1)
C(9)	0.1177 (2)	−0.1209 (2)	0.0306 (2)	3.7 (1)
C(10)	0.1366 (2)	−0.0678 (2)	−0.0421 (1)	3.09 (8)
C(11)	0.1108 (2)	−0.0892 (2)	−0.1405 (2)	3.8 ((1)
C(12)	0.1499 (2)	0.0096 (2)	−0.1810 (1)	3.43 (9)
C(13)	0.1453 (3)	0.0447 (2)	−0.2658 (2)	4.5 (1)
C(14)	0.1949 (3)	0.1446 (2)	−0.2738 (2)	4.8 (1)
C(15)	0.2455 (3)	0.2048 (2)	−0.1999 (2)	4.3 (1)
C(16)	0.2006 (2)	0.0777 (2)	−0.1117 (1)	3.03 (8)
C(17)	0.1912 (2)	0.0314 (2)	−0.0287 (1)	2.78 (8)

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

Ni—N(1)	2.151 (2)	Ni—N(2)	2.182 (2)
Ni—S(1)	2.4175 (8)	Ni—S(2)	2.4315 (8)
Ni—S(3)	2.3882 (7)	Ni—S(4)	2.4330 (8)
S(1)—C(1)	1.682 (2)	S(2)—C(1)	1.694 (2)
S(3)—C(4)	1.675 (2)	S(4)—C(4)	1.692 (2)
C(1)—O(1)	1.326 (3)	C(4)—O(2)	1.331 (3)
S(1)—Ni—S(2)	73.81 (3)	S(1)—Ni—N(1)	92.55 (5)
N(1)—Ni—N(2)	81.97 (7)	S(1)—Ni—N(2)	167.43 (5)
S(2)—Ni—N(1)	94.75 (5)	N(1)—Ni—S(3)	166.02 (5)
S(2)—Ni—N(2)	95.28 (6)	S(4)—Ni—N(2)	92.91 (5)
S(3)—Ni—N(2)	90.98 (5)	S(1)—Ni—S(3)	96.92 (3)
S(4)—Ni—N(1)	94.01 (5)	S(1)—Ni—S(4)	98.77 (3)
S(2)—Ni—S(4)	168.75 (2)	S(2)—Ni—S(3)	97.91 (3)
S(3)—C(4)—S(4)	119.5 (1)	S(1)—C(1)—S(2)	119.2 (1)
Ni—S(2)—C(1)	83.10 (8)	Ni—S(1)—C(1)	83.77 (8)
Ni—S(4)—C(4)	82.25 (8)	Ni—S(3)—C(4)	84.00 (8)
S(3)—Ni—S(4)	74.22 (2)		

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* program (Beurskens, 1984). H-atom positions were initially fixed geometrically with C—H = 0.95 Å, but were included in the subsequent 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: MU1213). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(2,9-Dimethyl-1,10-phenanthroline-N^1,N^{10})-bis(O-ethyl dithiocarbonato-S,S')nickel(II)

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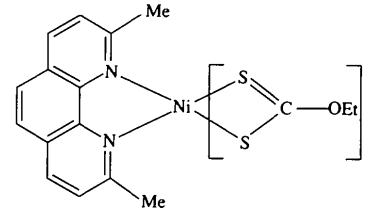
(*Received 10 July 1995; accepted 1 August 1995*)

Abstract

The crystal structure of [Ni($C_2H_5OCS_2$)$_2$($C_{14}H_{12}N_2$)], *cis*-[Ni(EtXA)$_2$(2,9-dmphen)] (EtXA = ethyl xanthate, 2,9-dmphen = 2,9-dimethyl-1,10-phenanthroline), containing a distorted octahedral NiS_4N_2 core, is reported. The Ni—S bond lengths range from 2.376 (2) to 2.522 (2) Å and the Ni—N bond lengths are 2.107 (4) and 2.153 (3) Å, while the N(1)—Ni—N(2) chelate angle is 78.3 (1)°.

Comment

Clathrate compounds and molecular inclusion phenomena have been used widely in a variety of fields, such as chemistry, biochemistry, physics, mineralogy, pharmacology and applied fields related to agriculture, medicine and the chemical industry. Of these inclusion compounds, inorganic and metal-complex hosts have attracted considerable attention in recent years, due in part to inclusion formation affecting the physicochemical properties of the guest (Harata, 1993). The crystal structures of the inclusion compounds [Ni(EtXA)$_2$(2,2'-dpa)].C_6H_6 and [Ni(BuXA)$_2$(4,4'-dm-2,2'-bipy)].2CCl_4 (2,2'-dpa = 2,2'-dipyridylamine, BuXA = butyl xanthate, 4,4'-dm-2,2'-bipy = 4,4'-dimethyl-2,2'-bipyridyl) have been described and the structure of [Ni(EtXA)$_2$(4,4'-dm-2,2'-bipy)].2CCl_4 has been reported (Gable, Hoskins & Winter, 1985; Pang, Lucken & Bernardinelli, 1990). We report here the crystal structure of the host molecule, [Ni(EtXA)$_2$(2,9-dmphen)], (I).



(I)

The Ni atom in (I) is six-coordinate, being surrounded by two chelating xanthate ligands and one chelating 2,9-dmphen ligand. The Ni—S bond lengths in (I) are in good agreement with those found in [Ni(EtXA)$_2$(2,2'-dpa)].C_6H_6 [2.416 (2)–2.520 (2) Å] and [Ni(EtXA)$_2$-(4,4'-dm-2,2'-bipy)].2CCl_4 [2.456 (3)–2.442 (4) Å] (Gable *et al.*, 1985; Pang *et al.*, 1990). Furthermore, the N(1)—Ni—N(2) bond angle in (I) is consistent with that in [Ni(EtXA)$_2$(2,2'-dpa)].C_6H_6 [87.61 (9)°].

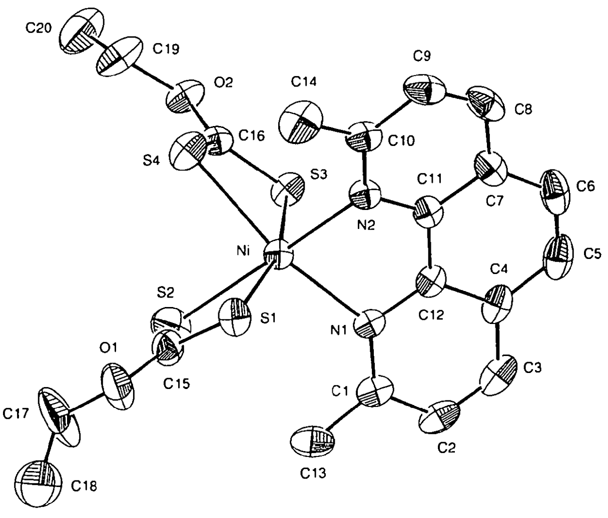


Fig. 1. Molecular structure showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.

Experimental

Bis(O-ethyl dithiocarbonato-S,S')nickel(II) was dissolved in EtOH/$CHCl_3$ and 2,9-dimethylphenanthroline in EtOH solution was added dropwise until the colour changed from brown to greenish. Crystals were obtained by evaporation at room temperature for one week.