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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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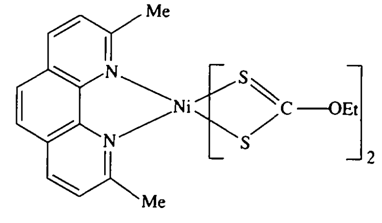
Abstract

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)°].

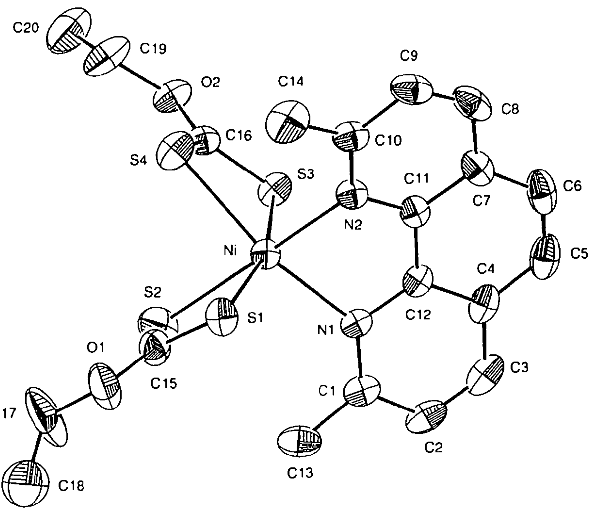


Fig. 1. Molecular structure showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.

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.

Crystal data

$[Ni(C_3H_5OS_2)_2(C_{14}H_{12}N_2)]$
$M_r = 509.35$
Monoclinic
$P2_1/c$
$a = 17.344\ (5)$ Å
$b = 8.336\ (5)$ Å
$c = 18.206\ (4)$ Å
$\beta = 117.63\ (1)°$
$V = 2332\ (2)$ Å^3
$Z = 4$
$D_x = 1.45$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.88–14.78°$
$\mu = 1.197$ mm^{-1}
$T = 296$ K
Plate
$0.95 \times 0.22 \times 0.06$ mm
Brownish

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (*TEXSAN*; Molecular Structure Corporation, 1985)
$T_{min} = 0.803$, $T_{max} = 1.000$
4551 measured reflections
4461 independent reflections

3260 observed reflections $[I > 3\sigma(I)]$
$R_{int} = 0.009$
$\theta_{max} = 25°$
$h = 0 \rightarrow 20$
$k = 0 \rightarrow 9$
$l = -21 \rightarrow 21$
3 standard reflections monitored every 300 reflections
intensity decay: 0.9%

Refinement

Refinement on F
$R = 0.053$
$wR = 0.069$
$S = 1.78$
3260 reflections
262 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.07$
$\Delta\rho_{max} = 0.85$ e Å^{-3}
$\Delta\rho_{min} = -0.69$ 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)

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

	x	y	z	B_{eq}
Ni	0.77538 (3)	0.24231 (6)	0.47462 (3)	3.73 (2)
S(1)	0.68968 (8)	0.0824 (1)	0.35652 (8)	5.19 (5)
S(2)	0.6728 (1)	0.4268 (2)	0.3659 (1)	6.81 (7)
S(3)	0.82527 (7)	0.4497 (1)	0.58124 (7)	4.60 (5)
S(4)	0.66572 (9)	0.2688 (1)	0.5285 (1)	5.62 (6)
O(1)	0.5701 (3)	0.2383 (5)	0.2387 (2)	9.0 (2)
O(2)	0.7097 (2)	0.5249 (4)	0.6258 (2)	5.2 (1)
N(1)	0.8932 (2)	0.2553 (3)	0.4629 (2)	3.7 (1)
N(2)	0.8524 (2)	0.0651 (4)	0.5595 (2)	4.0 (1)
C(1)	0.9132 (3)	0.3276 (5)	0.4091 (3)	4.5 (2)
C(2)	0.9997 (4)	0.3531 (6)	0.4263 (4)	5.6 (2)
C(3)	1.0658 (3)	0.3046 (6)	0.4978 (4)	5.9 (2)
C(4)	1.0484 (3)	0.2181 (5)	0.5553 (3)	4.7 (2)
C(5)	1.1145 (3)	0.1546 (7)	0.6307 (4)	6.1 (2)
C(6)	1.0938 (3)	0.0635 (6)	0.6797 (3)	6.1 (2)
C(7)	1.0054 (3)	0.0290 (5)	0.6581 (3)	5.0 (2)
C(8)	0.9792 (4)	−0.0756 (6)	0.7028 (3)	6.2 (2)
C(9)	0.8950 (4)	−0.1159 (6)	0.6732 (3)	6.1 (2)
C(10)	0.8309 (3)	−0.0450 (5)	0.5993 (3)	4.8 (2)
C(11)	0.9384 (3)	0.0977 (5)	0.5863 (2)	3.9 (2)
C(12)	0.9603 (3)	0.1965 (4)	0.5344 (3)	3.8 (2)
C(13)	0.8427 (4)	0.3760 (7)	0.3263 (3)	6.5 (3)
C(14)	0.7402 (4)	−0.0989 (6)	0.5653 (4)	7.7 (3)
C(15)	0.6363 (3)	0.2537 (6)	0.3125 (3)	5.7 (2)
C(16)	0.7294 (3)	0.4196 (5)	0.5819 (3)	4.1 (2)
C(17)	0.5221 (7)	0.381 (1)	0.1952 (5)	16.0 (6)
C(18)	0.4953 (7)	0.378 (1)	0.1134 (7)	14.7 (7)
C(19)	0.6246 (4)	0.5141 (7)	0.6239 (4)	7.7 (3)
C(20)	0.6049 (5)	0.667 (1)	0.6521 (5)	10.0 (4)

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

Ni—S(1)	2.376 (2)	Ni—S(2)	2.487 (2)
Ni—S(3)	2.440 (2)	Ni—S(4)	2.522 (2)
Ni—N(1)	2.153 (3)	Ni—N(2)	2.107 (4)
S(1)—C(15)	1.689 (5)	S(2)—C(15)	1.691 (5)
S(3)—C(16)	1.687 (4)	S(4)—C(16)	1.657 (4)
O(1)—C(15)	1.308 (6)	O(2)—C(16)	1.336 (5)
N(1)—Ni—N(2)	78.3 (1)	S(3)—C(16)—S(4)	119.8 (3)
S(3)—Ni—S(4)	71.31 (6)	S(1)—Ni—S(2)	73.18 (6)
S(4)—Ni—N(2)	96.6 (1)	S(3)—Ni—N(2)	92.5 (1)
S(4)—Ni—N(1)	162.9 (1)	S(3)—Ni—N(1)	92.4 (1)
S(2)—Ni—N(1)	104.7 (1)	S(1)—Ni—N(1)	99.3 (1)
S(2)—Ni—N(2)	173.6 (1)	S(1)—Ni—N(2)	100.8 (1)
S(1)—Ni—S(4)	97.74 (6)	S(1)—Ni—S(3)	163.75 (5)
S(2)—Ni—S(3)	93.04 (6)	S(2)—Ni—S(4)	82.13 (7)
Ni—N(1)—C(12)	108.4 (2)	Ni—N(2)—C(11)	109.9 (3)
Ni—S(2)—C(15)	82.4 (2)	Ni—S(1)—C(15)	86.0 (2)
Ni—S(3)—C(16)	85.1 (2)	S(1)—C(15)—S(2)	118.2 (3)

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 fixed geometrically with C—H = 0.95 Å, but were not included in the calculations. 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.

This work was supported by a grant for a Key Research Project from the State Science and Technology Commission and the National Nature Science Foundation of China.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1214). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Pang, L., Lucken, E. A. C. & Bernardinelli, G. (1990). *J. Am. Chem. Soc.* **112**, 8754–8764.

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Carbonyl(η^4-1,3-cyclohexadiene)[(η^5,κN)-2-methylaminoethylcyclopentadienyl]-molybdenum(II) Hexafluorophosphate

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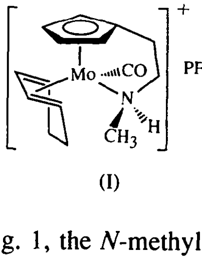
(Received 23 February 1993; accepted 24 July 1995)

Abstract

The pseudotetrahedral structure of [Mo($C_8H_{12}N$)(C_6H_8)(CO)]PF_6 has a *transoid* CH_3—N—Mo—CO arrangement. The amino group coordinates to the Mo atom intramolecularly, causing the side chain to bend away from the cyclopentadienyl plane by about 9.3°.

Comment

The title compound, carbonyl(η^4-1,3-cyclohexadiene)[(η^5,κN)-2-methylaminoethylcyclopentadienyl]molybdenum(II) hexafluorophosphate, (I), was obtained in about 10% yield during the preparation of the corresponding *N*,*N*-dimethyl complex (Wang & Wen, 1992). The structure determination was undertaken in order to verify that demethylation had occurred and also to establish the relative stereochemistry of the methyl and carbonyl groups.



(I)

As shown in Fig. 1, the *N*-methyl group points away from the carbonyl group to minimize steric interaction. The torsion angles C7—C2—C3—C4 of −170.6 (10) and C7—C2—C6—C5 of 170.7 (9)° suggest that the C7—C2 bond is bent away from the cyclopentadienyl plane by about 9.3°. The cyclohexadiene ring has a boat conformation with two planes, C11—C12—C13—C14 and C14—C15—C16—C11, inclined at an angle of about 45° to each other. The linear Mo—C1—O1 moiety [173.8 (5)°] resides on the top of the *exo*-η^4-cyclohexadiene group. The Mo—N bond length [2.282 (5) Å] is slightly shorter (0.1 Å) than those observed in similar complexes (Wang & Wen, 1992; Wang, Lee, Chou & Ong, 1992).

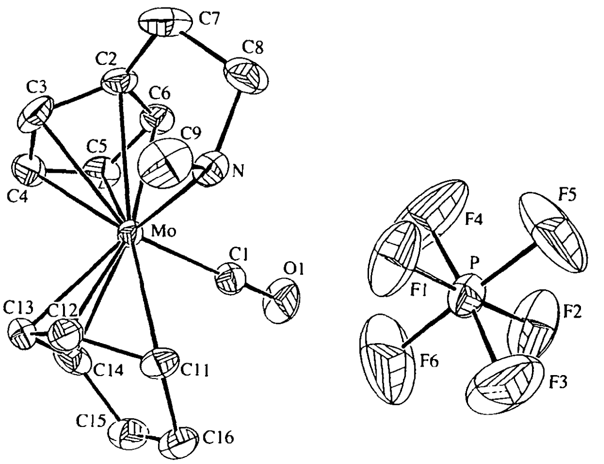


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of [Mo($C_8H_{12}N$)(C_6H_8)(CO)]PF_6. Displacement ellipsoids are shown at the 30% probability level.

Experimental

Crystals of carbonyl(η^4-1,3-cyclohexadiene)[(η^5,κN)-2-methylaminoethylcyclopentadienyl]molybdenum(II) hexafluorophosphate were obtained from acetone/dichloromethane solution.

Crystal data

[Mo($C_8H_{12}N$)(C_6H_8)(CO)]-PF_6
M_r = 471.23
Monoclinic
$P2_1/n$
a = 9.5234 (20) Å
b = 14.528 (5) Å
c = 12.913 (3) Å
β = 99.58 (2)°
V = 1761.6 (8) Å^3
Z = 4
D_x = 1.777 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 7.43–17.54°
μ = 0.898 mm^{-1}
T = 295 K
Prism
0.39 × 0.38 × 0.34 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min}$ = 0.968, $T_{\max}$ = 0.998
2449 measured reflections
2290 independent reflections

2026 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int}$ = 0.022
$\theta_{\max}$ = 22.5°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 15$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity decay: 1%