

P	0.7327 (1)	-0.11240 (4)	0.8548 (1)	3.99 (4)
O(1)	0.7209 (3)	-0.2022 (1)	0.8647 (3)	5.2 (1)
O(2)	0.5536 (3)	-0.1054 (1)	0.7429 (3)	5.7 (1)
N(1)	0.8518 (3)	0.0886 (1)	0.8885 (2)	3.3 (1)
N(2)	0.5255 (4)	0.2240 (2)	0.9188 (3)	4.9 (1)
C(1)	0.7336 (4)	0.1254 (2)	0.9302 (3)	3.2 (1)
C(2)	0.6419 (4)	0.1877 (2)	0.8667 (3)	3.6 (1)
C(3)	0.6773 (5)	0.2130 (2)	0.7521 (4)	4.8 (2)
C(4)	0.7946 (5)	0.1750 (2)	0.7068 (4)	5.1 (2)
C(5)	0.8806 (4)	0.1135 (2)	0.7756 (3)	4.2 (1)
C(6)	0.8567 (5)	-0.2455 (2)	0.9560 (5)	6.0 (2)
C(7)	0.8140 (6)	-0.3272 (2)	0.9377 (5)	6.6 (2)
C(8)	0.4778 (6)	-0.0334 (3)	0.6971 (5)	7.4 (2)
C(9)	0.3026 (7)	-0.0426 (3)	0.6156 (6)	9.1 (3)

Table 2. Selected geometric parameters (Å, °)

Ni—N(1)	2.103 (3)	Ni—N(1')	2.103 (3)
Ni—S(1)	2.491 (2)	Ni—S(1')	2.491 (2)
Ni—S(2)	2.505 (3)	Ni—S(2')	2.505 (3)
P—S(1)	1.977 (2)	P—O(2)	1.582 (3)
O(1)—C(6)	1.446 (5)	O(2)—C(8)	1.430 (5)
N(1)—Ni—N(1')	180.00	S(1)—Ni—S(2)	81.58 (7)
N(1)—Ni—S(1)	89.71 (9)	N(1')—Ni—S(2)	90.1 (1)
N(1)—Ni—S(2)	89.9 (1)	S(1)—Ni—N(1')	90.29 (9)
S(1)—P—S(2)	111.52 (8)	O(1)—P—O(2)	93.8 (2)
O(1)—P—S(1)	112.2 (1)	O(2)—P—S(2)	112.2 (1)

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

Data were collected using *CONTROL* software (Molecular Structure Corporation, 1988). The structure was solved by direct methods using *MITHRIL* (Gilmore, 1983); the heavy atom Ni was located in an *E* map and the remaining non-H atoms were located using *DIRDIF* (Beurskens, 1984). H atoms were placed in geometrically calculated positions ($C-H = 0.95 \text{ \AA}$) and 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. 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 Major Project from the State Science and Technology Commission, and the National Science Foundation of China, as well as the State Key Laboratory of Tribology of Tsinghua University.

Lists of structure factors, torsion angles, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving H atoms have been deposited with the IUCr (Reference: AB1261). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Adduct of Bis(*O,O'*-dibutyl dithiophosphato)nickel(II) with Isoquinoline

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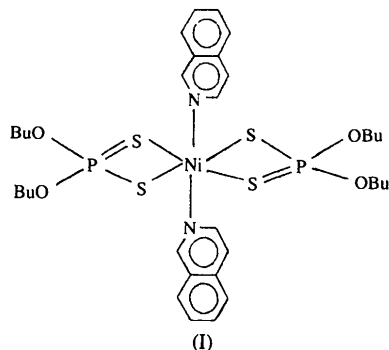
Abstract

In the title compound, $[\text{Ni}\{(\text{C}_4\text{H}_9\text{O})_2\text{PS}_2\}_2(\text{C}_9\text{H}_7\text{N})_2]$, the metal atom is coordinated in a distorted octahedral arrangement with the central Ni atom lying in the plane formed by the four S atoms and with the two isoquinoline moieties in *trans* positions. The Ni—S bond distances are 2.491 (3) and 2.498 (2) Å and the Ni—N distances are 2.103 (4) Å.

Comment

In recent years, adducts of nickel(II) dialkyl dithiophosphate with neutral nitrogen bases have received increasing attention, partly because of the reactivity of a variety of nitrogen bases with nickel(II) dialkyl dithiophosphate in solution (Liu *et al.*, 1991; You, Xiong, Dong & Huang, 1994; You *et al.*, 1991). Furthermore, the amines in lubricating oil have a great influence on the properties of metal dialkyl dithiophosphate additives (Shiomi, Tokashiki, Tomizawa

& Kuribayashi, 1989). It is interesting to investigate further the interaction between metal dialkyl dithiophosphates and amines. We report here the crystal structure of [Ni{(C₄H₉O)₂PS₂}₂(C₉H₇N)₂], (I), which displays octahedral geometry (Liu, Lin, Xu, Yu & You, 1987).



A perspective view of the title adduct with the atomic numbering scheme is shown in Fig. 1. The Ni atom lies on a crystallographic centre of symmetry and has distorted octahedral coordination from two isoquinoline ligands and two *O,O'*-dibutyl dithiophosphate bidentate ligands. The isoquinoline ring is almost planar; the mean deviation from the best plane is 0.0224 Å. The plane through Ni, S₂ and P is almost perpendicular to the plane of the isoquinoline ring, forming a dihedral angle of 89.05°. The S(1)—Ni—S(2) angle is 81.53 (8)°, which is in reasonable agreement with that of [Ni{(C₂H₅O)₂PS₂}₂py₂] [81.7 (1)°; Ooi & Fernando, 1967] and that of [Ni{(C₄H₉O)₂PS₂}₂py₂] [81.53 (8)°; Lju *et al.*, 1987]. Similarly, the Ni—N [2.103 (4) Å] and Ni—S [2.491 (3)—2.498 (2) Å] bond lengths are basically consistent with those of [Ni{(C₂H₅O)₂PS₂}₂py₂] [2.11 (1) and 2.49 (1)—2.50 (1) Å] and [Ni{(C₄H₉O)₂PS₂}₂py₂] [2.116 (4) and 2.486 (1)—2.511 (1) Å]. The terminal C atom, C24, of one of the butyl groups was found to be disordered.

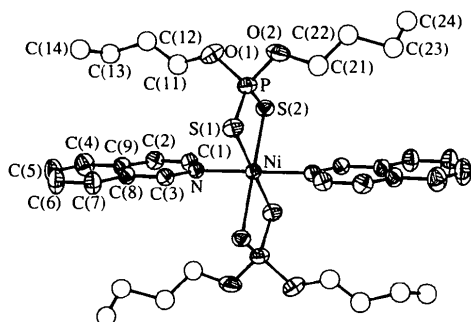


Fig. 1. Molecular structure of (I) showing 50% probability displacement ellipsoids for non-H atoms except for the C atoms of the butyl chains which are represented by spheres of arbitrary radii. H atoms are omitted for clarity.

Experimental

[Ni{(C₄H₉O)₂PS₂}₂] was dissolved in ethanol and excess isoquinoline was added until the colour of the solution changed from purple to green. Green column crystals of the title adduct were obtained by evaporation at room temperature for two weeks.

Crystal data

[Ni(C₈H₁₈O₂PS₂)₂(C₉H₇N)₂]
M_r = 799.67
 Monoclinic
*P*2₁/*c*
a = 6.860 (8) Å
b = 18.938 (2) Å
c = 16.224 (4) Å
 β = 92.78 (7)°
V = 2105 (2) Å³
Z = 2
D_x = 1.26 Mg m⁻³

Mo K α radiation
 λ = 0.71069 Å
 Cell parameters from 25 reflections
 θ = 10.20–11.70°
 μ = 0.761 mm⁻¹
T = 296 K
 Column
 0.42 × 0.18 × 0.12 mm
 Green

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: refined from ΔF (DIFABS; Walker & Stuart, 1983)
T_{min} = 0.76, *T_{max}* = 1.00
 4171 measured reflections
 3832 independent reflections
 2341 observed reflections
 [*I* > 3 σ (*I*)]

R_{int} = 0.031
 θ_{\max} = 25°
h = 0 → 8
k = -22 → 0
l = -19 → 19
 3 standard reflections monitored every 300 reflections
 intensity decay: 7.0%

Refinement

Refinement on *F*
R = 0.049
 ωR = 0.058
S = 1.27
 2341 reflections
 213 parameters
 H-atom parameters not refined
 $w = 1/\sigma^2(F)$

(Δ/σ)_{max} = 0.15
 $\Delta\rho_{\max}$ = 0.33 e Å⁻³
 $\Delta\rho_{\min}$ = -0.30 e Å⁻³
 Extinction correction: none
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

*B*_{iso} for C24 and C24'; *B*_{eq} = (8 $\pi^2/3$) $\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$ for others.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} / <i>B</i> _{iso}
Ni	1/2	0	0	3.76 (4)
S(1)	0.3851 (2)	0.07818 (7)	0.11175 (8)	5.24 (6)
S(2)	0.8159 (2)	0.05903 (7)	0.03866 (8)	5.12 (6)
P	0.6598 (2)	0.10935 (7)	0.11977 (9)	5.36 (7)
O(1)	0.6800 (6)	0.1923 (2)	0.1137 (3)	7.1 (2)
O(2)	0.7533 (6)	0.1042 (2)	0.2109 (2)	7.7 (2)
N	0.4374 (5)	0.0802 (2)	-0.0870 (2)	4.1 (2)
C(1)	0.5698 (7)	0.0994 (3)	-0.1436 (3)	4.8 (2)
C(2)	0.5339 (7)	0.1522 (3)	-0.1985 (3)	5.5 (3)
C(3)	0.2689 (6)	0.1133 (2)	-0.0896 (3)	4.4 (2)
C(4)	0.311 (1)	0.2458 (3)	-0.2560 (4)	7.1 (3)
C(5)	0.136 (1)	0.2771 (3)	-0.2547 (4)	8.3 (4)
C(6)	-0.0014 (9)	0.2563 (3)	-0.1994 (5)	8.2 (4)
C(7)	0.0383 (7)	0.2034 (3)	-0.1454 (4)	6.3 (3)

C(8)	0.2198 (7)	0.1688 (3)	-0.1442 (3)	4.8 (2)
C(9)	0.3593 (7)	0.1893 (3)	-0.2012 (3)	5.1 (2)
C(11)	0.636 (2)	0.2291 (4)	0.0402 (6)	16.4 (8)
C(12)	0.622 (3)	0.2978 (6)	0.0390 (8)	21 (1)
C(13)	0.552 (4)	0.3362 (8)	-0.034 (1)	24 (2)
C(14)	0.433 (6)	0.379 (2)	-0.032 (2)	42 (4)
C(21)	0.769 (2)	0.0368 (5)	0.2507 (5)	14.5 (7)
C(22)	0.936 (3)	0.0321 (7)	0.307 (1)	22 (1)
C(23)	1.023 (3)	-0.043 (2)	0.330 (2)	29 (2)
C(24)	1.171 (7)	-0.031 (2)	0.358 (3)	25 (2)
C(24')	0.897 (7)	-0.049 (3)	0.369 (3)	23 (2)

Table 2. Selected geometric parameters (Å, °)

Ni—N	2.103 (4)	Ni—S(1)	2.498 (2)
Ni—S(2)	2.491 (3)	P—S(1)	1.973 (3)
P—S(2)	1.981 (2)	P—O(1)	1.581 (4)
P—O(2)	1.587 (4)	N—C(1)	1.371 (5)
N—C(3)	1.315 (5)	O(1)—C(11)	1.40 (1)
O(2)—C(21)	1.43 (1)		
N—Ni—N'	180.00	S(1)—Ni—S(2)	81.53 (8)
N—Ni—S(1)	89.9 (1)	N—Ni—S(2)	89.5 (1)
S(1)—P—S(2)	111.0 (1)	O(1)—P—O(2)	94.9 (2)

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

Data collection was performed using *CAD-4 Software* (Enraf-Nonius, 1989). The ω -scan width was $(0.45 + 0.35 \tan \theta)^\circ$ and the scan speed was $1-5.46^\circ \text{ min}^{-1}$. The structure was solved by direct methods and difference syntheses, and refined with anisotropic displacement parameters for all non-H atoms except C24, which was found to be disordered. Calculations were performed on a VAX3100 computer using the *TEXSAN* (Molecular Structure Corporation, 1985) program package. Molecular graphics were prepared using *ORTEPII* (Johnson, 1976).

This work was supported by a grant for a Major Project from the State Science and Technology Commission, and the National Science Foundation of China, as well as the State Key Laboratory of Tribology of Tsinghua University.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data and complete geometry have been deposited with the IUCr (Reference: CR1171). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two Cobaltacyclopentadiene Complexes and One Cyclobutadiene Complex

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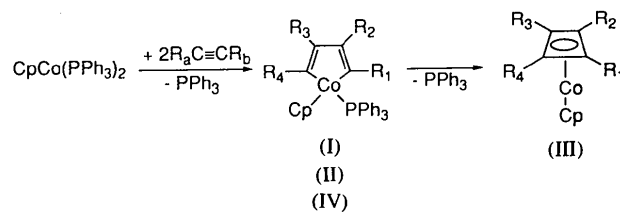
(Received 26 October 1993; accepted 9 May 1995)

Abstract

The structures of three cobalt complexes, [1,4-bis(1-propynyl)-2,3-dimethyl-1,3-butadiene-1,4-diyl](η^5 -cyclopentadienyl)(triphenylphosphine)cobalt, $[\text{Co}(\text{C}_5\text{H}_5)(\text{C}_{12}\text{H}_{12})(\text{C}_{18}\text{H}_{15}\text{P})]$, (η^5 -cyclopentadienyl)[2,4-diphenyl-1,3-bis(phenylethynyl)-1,3-butadiene-1,4-diyl](triphenylphosphine)cobalt, $[\text{Co}(\text{C}_5\text{H}_5)(\text{C}_{32}\text{H}_{20})(\text{C}_{18}\text{H}_{15}\text{P})]$, and $\{\eta^4$ -1,3-bis(trimethylsilyl)-2,4-bis[4'-(trimethylsilyl)ethynyl]biphenyl-4-yl]cyclobutadiene}(η^5 -cyclopentadienyl)cobalt, $[\text{Co}(\text{C}_5\text{H}_5)(\text{C}_{44}\text{H}_{52}\text{Si}_4)]$, have been determined by single-crystal X-ray diffraction.

Comment

Dialkynylcobaltacyclopentadiene complexes were obtained from the reaction of $(\text{C}_5\text{H}_5)\text{Co}(\text{PPh}_3)_2$ with conjugated diacetylenes. In order to identify geometric isomers, X-ray structure analyses have been carried out. The syntheses and electrochemical properties of the complexes have been published elsewhere (Shimura *et al.*, 1995).



(I) $\text{R}_1 = \text{R}_4 = \text{C}\equiv\text{C-Me}$, $\text{R}_2 = \text{R}_3 = \text{Me}$

(II) $\text{R}_1 = \text{R}_3 = \text{C}\equiv\text{C-Ph}$, $\text{R}_2 = \text{R}_4 = \text{Ph}$

(III) $\text{R}_1 = \text{R}_3 = \text{SiMe}_3$, $\text{R}_2 = \text{R}_4 = \text{C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-C}\equiv\text{C-SiMe}_3$

(IV) $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{R}_4 = \text{C}_6\text{F}_5$ (Gastinger *et al.*, 1976)

Complex (I), [1,4-bis(1-propynyl)-2,3-dimethyl-1,3-butadiene-1,4-diyl](η^5 -cyclopentadienyl)(triphenylphosphine)cobalt, has chemical mirror symmetry through the Co—P axis and the midpoint of C2—C3. The two $\text{—C}\equiv\text{C—Me}$ groups are bonded to C1 and C4 of the metallacycle.