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**Crystal Structure
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trans-Bis(thioacetato-*S*)bis(triphenylphosphine-*P*)nickel(II)

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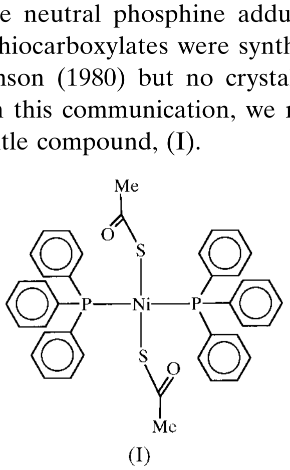
In the title compound, $[Ni(C_2H_3OS)_2(C_{18}H_{15}P)_2]$, the Ni atom lies on an inversion centre and the triphenyl phosphine and thioacetate ligands are bonded to the central Ni^{II} atom in a *trans* fashion, with Ni—S = 2.2020 (8) and Ni—P = 2.2528 (8) Å, and angle S—Ni—P = 92.47 (3)°.

Comment

We have been pursuing a systematic study of the chemistry of thiocarboxylates (Deivaraj & Vittal, 2000; Sampanthar *et al.*, 1999, and references therein). This ligand belongs to an interesting class of ligands that contain both soft and hard donor sites. Furthermore, the chemistry of thiocarboxylates has been relatively unexplored compared with that of thiolates or the analogous monochalcogenato ligands, such as monothiocarbamates. We have synthesized and determined the crystal structures of the anionic metal complexes of Mn, Co and Ni (Devy *et al.*, 1998). The synthesis of the neutral nickel thiobenzoate compound $[Ni\{S(O)CPh\}_2]$ was reported three decades ago (Savant & Gopalakrishnan, 1970; Melson, Crawford & Geddes, 1970) and the structure of $[Ni\{SC(O)Ph\}_2]_2\cdot 2EtOH$ determined (Melson, Greene & Bryan, 1970). The neutral phosphine adducts of the corresponding nickel thiocarboxylates were synthesized by Goodfellow & Stephenson (1980) but no crystal structures have been reported. In this communication, we report the crystal structure of the title compound, (I).



(I)

In the structure of the neutral compound, the central Ni^{II} atom lies on an inversion centre and is bonded to two PPh_3 and two $CH_3C(O)S^-$ anions in a *trans* fashion; the NiP_2S_2 moiety is necessarily planar, but is not exactly square [P—Ni—S 92.47 (3)°]. A view of the molecule is shown in Fig. 1 and selected bond distances and angles are given in Table 1. The Ni—P bond distance is normal. However, the Ni—S bond distance of 2.2020 (8) Å is shorter than the values of 2.419 (1) Å observed in $(Ph_4P)[Ni\{SC(O)Ph\}_3]$, (II) (Devy *et al.*, 1998), and 2.221 (5) to 2.230 (5) Å found in $[Ni\{SC(O)Ph\}_2]_2\cdot 2EtOH$, (III) (Melson, Greene & Bryan, 1970). In the latter compounds, the $Ph(O)CS^-$ anions act as a chelating ligand and, in addition, the C—S and C—O bonds acquire partial double-bond character. On the other hand, no such delocalization occurs in (I). This is reflected in the Ni—S, C—S and C—O bond distances. The S—C distance of 1.756 (4) Å is longer than those found in (II) [1.705 (4) Å] and (III) [1.70 (1)–1.72 (1) Å], and the C—O distance of 1.215 (4) Å is shorter than those found in (II) and (III). There appear to be no interactions between the Ni^{II} atom and the O atoms of the thioacetato ligands [Ni1···O1 3.312 (3) Å].

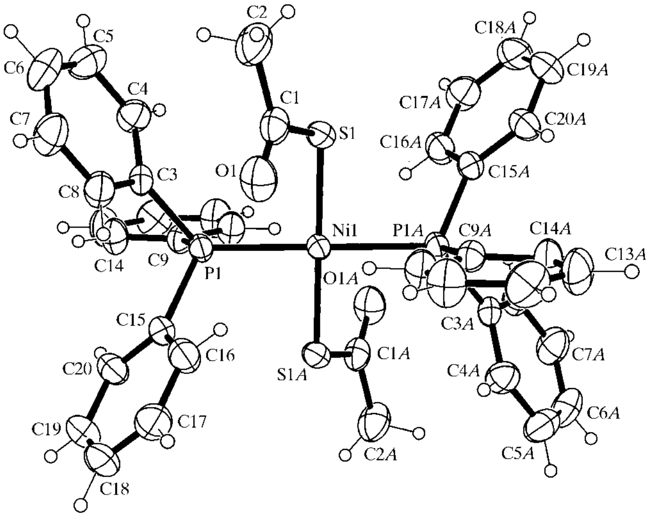


Figure 1
A view of the structure of (I) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as spheres of arbitrary radii.

The non-H atoms in the thioacetato ligand are planar [r.m.s. deviation 0.0006 (8) Å] and the thioacetato plane makes an angle of 67.42 (8)° with the NiP_2S_2 plane. It is interesting to note that the C3—P1—C9 and C3—P1—C15 angles are shorter than the C9—P1—C15 angle. Further, the Ni1—P1—C3 angle is larger than the other two Ni—P—C angles. It is evident that the phenyl ring with the *ipso* C3 atom in PPh_3 is pushed away in order to minimize contacts with the thioacetato ligand.

Experimental

Compound (I) was obtained by reacting $[Ni\{SC(O)Me\}_2]$ with 2 molar equivalents of PPh_3 in CH_2Cl_2 solution. Single crystals of (I) were obtained by slow diffusion of diethyl ether into a dichloromethane solution of (I).

Crystal data

$[Ni(C_2H_3OS)_2(C_{18}H_{15}P)_2]$
$M_r = 733.46$
Triclinic, $P\bar{1}$
$a = 9.7364\ (5)$ Å
$b = 10.2509\ (5)$ Å
$c = 10.9197\ (6)$ Å
$\alpha = 106.1411\ (13)^\circ$
$\beta = 111.2595\ (14)^\circ$
$\gamma = 107.593\ (2)^\circ$
$V = 871.18\ (13)$ Å^3
$Z = 1$
$D_x = 1.398$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2519 reflections
$\theta = 2.22$–29.25°
$\mu = 0.804$ mm^{-1}
$T = 293\ (2)$ K
Block, red
0.20 × 0.18 × 0.09 mm

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.848$, $T_{\max} = 0.930$
4485 measured reflections
2969 independent reflections
2347 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\max} = 25^\circ$
$h = -9 \rightarrow 11$
$k = -10 \rightarrow 12$
$l = -12 \rightarrow 12$

Table 1
Selected geometric parameters (Å, °).

Ni1—S1	2.2020 (8)	P1—C3	1.837 (3)
Ni1—P1	2.2528 (8)	P1—C9	1.828 (3)
S1—C1	1.756 (4)	P1—C15	1.835 (3)
O1—C1	1.215 (4)	Ni1—O1	3.312 (3)
C1—C2	1.512 (5)		
S1—Ni1—P1	92.47 (3)	C9—P1—C3	100.30 (15)
C1—S1—Ni1	107.37 (12)	C15—P1—C3	101.98 (14)
O1—C1—C2	121.8 (3)	C3—P1—Ni1	123.81 (10)
O1—C1—S1	124.5 (3)	C9—P1—Ni1	108.91 (11)
C2—C1—S1	113.7 (3)	C15—P1—Ni1	111.73 (11)
C9—P1—C15	108.98 (15)		

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.106$
$S = 1.028$
2969 reflections
215 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 0.3131P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.31$ e Å^{-3}

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1594). Services for accessing these data are described at the back of the journal.

References

Deivaraj, T. C. & Vittal, J. J. (2000). *Inorg. Chem.* **39**, 1028–1034.
Devy, R., Vittal, J. J. & Dean, P. A. W. (1998). *Inorg. Chem.* **37**, 6939–6941.
Goodfellow, J. A. & Stephenson, T. A. (1980). *Inorg. Chim. Acta*, **41**, 19–24.
Melson, G. A., Crawford, N. P. & Geddes, B. J. (1970). *Inorg. Chem.* **9**, 1123–1126.
Melson, G. A., Greene, P. T. & Bryan, R. F. (1970). *Inorg. Chem.* **9**, 1116–1122.
Sampanthar, J. T., Deivaraj, T. C., Vittal, J. J. & Dean, P. A. W. (1999). *J. Chem. Soc. Dalton Trans.* pp. 4419–4423.
Savant, V. V. & Gopalakrishnan, J. (1970). *Inorg. Chem.* **9**, 748–751.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Siemens (1994). *SHELXTL*. Release 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1996). *SMART*. Version 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.