*Refinement*

Refinement on $F^2$
$R(F) = 0.0321$
$wR(F^2) = 0.1060$
$S = 1.065$
5562 reflections
441 parameters
H atoms were isotropically refined as riding atoms

$w = 1/[\sigma^2(F_o^2) + (0.0569P)^2 + 1.6054P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.361$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.305$ e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Ni7—B8 | 2.080 (4) | S1—C1 | 1.675 (3) |
| Ni7—B11 | 2.085 (3) | S2—C2 | 1.683 (3) |
| Ni7—B3 | 2.121 (3) | P1—B10 | 1.910 (3) |
| Ni7—B2 | 2.159 (4) | B8—O1 | 1.473 (4) |
| Ni7—S1 | 2.2056 (10) | B11—O2 | 1.483 (4) |
| Ni7—S2 | 2.2135 (10) | | |
| B8—Ni7—B11 | 95.50 (13) | B8—Ni7—S1 | 81.76 (10) |
| B8—Ni7—B3 | 48.73 (14) | B3—Ni7—S1 | 105.09 (10) |
| B11—Ni7—B3 | 86.72 (13) | B11—Ni7—S2 | 82.78 (9) |
| B8—Ni7—B2 | 88.47 (14) | B2—Ni7—S2 | 109.25 (10) |
| B11—Ni7—B2 | 48.19 (13) | S1—Ni7—S2 | 91.08 (4) |
| B3—Ni7—B2 | 49.63 (14) | | |

Data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *Manual*. Data reduction: *SDP-Plus* (Frenz, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai & Huttner, 1994). Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1444). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# *ortho*-Cycloboronation of a Thiobenzoate Cluster: $[(PPh_3)(PhCOS)_2NiB_{10}H_{10}]$.-$0.5C_6H_{14}$

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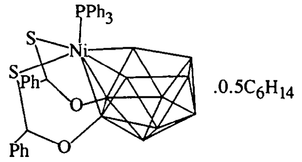
## Abstract

The title compound, 2,7:3,7-di($\mu$-thiobenzoato-*S*:*O*)-7-(triphenylphosphine-*P*)-8,9:10,11-di-$\mu H$-7-nickela-*nido*-undecaborane–hexane (1/0.5), $C_{32}H_{35}B_{10}NiO_2PS_2.0.5C_6H_{14}$, has been synthesized and characterized by X-ray diffraction analysis. The Ni atom is bound to one $PPh_3$ ligand, two S atoms and four B atoms of the $\{NiB_{10}\}$ cage. The *ortho*-cycloboronation of thiobenzoates produces two five-membered Ni—S—C—O—B rings.

## Comment

In some metallaboranes, there is *ortho*-cycloboronation of a metal ligand to the cluster. The groups of cyclization include the phosphine–phenyl ligand (Crook, Greenwood, Kennedy & McDonald, 1982; Bould, Greenwood, Kennedy & McDonald, 1982; Bould, Crook, Greenwood, Kennedy & Thornton-

Pett, 1990; Bould, Crook, Greenwood, Kennedy & McDonald, 1983; Elrington, Greenwood, Kennedy & Thornton-Pett, 1986), acetate (Fontaine, Greenwood, Kennedy, Thornton-Pett & Zheng, 1987) and $SCSNEt_2$ (Beckett, Greenwood, Kennedy & Thornton-Pett, 1985). We have reported previously the *ortho*-cycloboronation of benzoate (Yao *et al.*, 1995) and thiobenzoate (Dou *et al.*, 1997) clusters. The latter compound is $[(PhCOS)_2NiB_{10}H_8(PPh_3)]$, (I). Another example of an *ortho*-cycloboronated nickelaborane, $[(PPh_3)(PhCOS)_2NiB_{10}H_{10}].0.5(C_6H_{14})$, (II), is reported here.



(II)

Compound (II) is a *nido* 11-vertex $\{NiB_{10}\}$ cage, with the Ni atom in the open $NiB_4$ face. There are two five-membered rings, namely Ni7—S1—C1—O1—B2 and Ni7—S2—C2—O2—B3. The two rings are either side of the plane formed by atoms Ni7, B1 and B5. The Ni atom is bound to one $PPh_3$ group, two S atoms and four B atoms. The Ni7—B2 and Ni7—B3 distances (Table 1) are shorter than the corresponding Ni—B distances in $Ni(B_{10}H_{12})_2^{2-}$ (Guggenberger, 1972), while Ni7—B8 and Ni7—B11 are within the expected range. In compound (I), it is the Ni7—B8 [2.080 (4) Å] and Ni7—B11 [2.085 (3) Å] distances, not Ni7—B2 [2.159 (4) Å] and Ni7—B3 [2.121 (3) Å], that are shorter. This also demonstrates that *ortho*-cycloboronation can strengthen the Ni—B bonding.

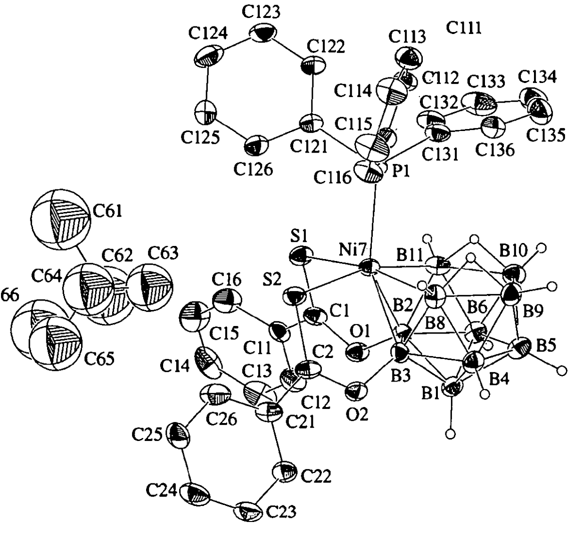


Fig. 1. The molecular structure showing 30% probability displacement ellipsoids. H atoms on C atoms have been omitted for clarity.

The distances between the Ni and two S atoms (Table 1) are longer than the Ni—S bond lengths in compound (I) [Ni7—S1 2.2135 (10) and Ni7—S2 2.2056 (10) Å]. This may be interpreted by steric effects owing to two Ni—S—C—O—B rings being on the same side of the cage [S1—Ni7—S2 87.86 (5)°]. The B—O distances in compounds (I) and (II) are essentially identical but longer than those reported for B—O*R* groups (Kennedy, 1986). This is attributed to the $p$–$\pi$ conjugation in the oxygen–carbon–sulfur system. A similar situation was observed in the acetate (Fontaine, Greenwood, Kennedy, Thornton-Pett & Zheng, 1987) and benzoate (Yao *et al.*, 1995) compounds. The B8 and B9 atoms, as well as B10 and B11, are bridged by H atoms at distances of 1.24 (4)–1.31 (4)°.

## Experimental

The synthesis of the title cluster was carried out by reaction of $[NiCl_2(PPh_3)_2]$ (0.6 mmol) and $(Et_4N)_2B_{10}H_{10}$ (0.6 mmol) with PhCOSH (1.2 mmol) in refluxing dichloromethane for 63 h under an atmosphere of dry nitrogen. The formed solution was reduced in volume and chromatographed using dichloromethane/light petroleum (4:1) as the eluting medium to give the black title compound at $R_f$ = 0.96. The product was recrystallized from *n*-hexane/dichloromethane solution.

*Crystal data*

$C_{32}H_{35}B_{10}NiO_2PS_2.0.5C_6H_{14}$
$M_r$ = 756.59
Monoclinic
$P2_1/n$
$a$ = 11.043 (5) Å
$b$ = 15.524 (3) Å
$c$ = 23.016 (3) Å
$\beta$ = 91.28 (2)°
$V$ = 3945 (2) Å$^3$
$Z$ = 4
$D_x$ = 1.274 Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda$ = 0.71073 Å
Cell parameters from 25 reflections
$\theta$ = 10.4–12.8°
$\mu$ = 0.670 mm$^{-1}$
$T$ = 294 (2) K
Prism
0.42 × 0.30 × 0.18 mm
Black

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* $\psi$ scans (North, Phillips & Mathews, 1968)
$T_{min}$ = 0.748, $T_{max}$ = 0.886
7413 measured reflections
6933 independent reflections

4959 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.0213
$\theta_{max}$ = 25°
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 27$
3 standard reflections frequency: 60 min intensity decay: 0.1%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.0428
$wR(F^2)$ = 0.1578
$S$ = 0.986
6933 reflections
463 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0963P)^2 + 5.395P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.018$
$\Delta\rho_{max}$ = 0.645 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.629 e Å$^{-3}$

H atoms were isotropically refined as riding atoms

Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Ni7—B3 | 2.087 (4) | Ni7—P1 | 2.3343 (13) |
| Ni7—B2 | 2.092 (4) | S2—C2 | 1.680 (4) |
| Ni7—B8 | 2.168 (4) | S1—C1 | 1.664 (4) |
| Ni7—B11 | 2.203 (4) | B3—O2 | 1.463 (5) |
| Ni7—S1 | 2.2735 (11) | B2—O1 | 1.486 (4) |
| Ni7—S2 | 2.3118 (13) | | |
| B3—Ni7—B2 | 49.8 (2) | B3—Ni7—S2 | 81.83 (12) |
| B3—Ni7—B8 | 49.8 (2) | B2—Ni7—S2 | 115.09 (12) |
| B2—Ni7—B8 | 86.8 (2) | B8—Ni7—S2 | 91.22 (13) |
| B3—Ni7—B11 | 86.3 (2) | S1—Ni7—S2 | 87.86 (5) |
| B2—Ni7—B11 | 48.5 (2) | B8—Ni7—P1 | 96.38 (13) |
| B8—Ni7—B11 | 89.9 (2) | B11—Ni7—P1 | 94.18 (12) |
| B3—Ni7—S1 | 119.15 (12) | S1—Ni7—P1 | 94.67 (4) |
| B2—Ni7—S1 | 83.49 (11) | S2—Ni7—P1 | 102.13 (4) |
| B11—Ni7—S1 | 87.82 (12) | | |

Considering both $R$ and $U_{\rm eq}$, the site-occupation factor of the hexane solvent molecule was estimated as 0.5.

Data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *Manual*. Data reduction: *SDP-Plus* (Frenz, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai & Huttner, 1994). Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1447). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# A (4-Ethylpyridine)(*N*-salicylideneglycinato)copper(II) Tetramer

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## Abstract

The title compound, *cyclo*-tetrakis[(4-ethylpyridine-*N*)(*N*-salicylideneglycinato-*O*,*N*,*O*′:*O*″)copper(II)], [Cu($C_9H_7NO_3$)($C_7H_9N$)]$_4$, adopts a square-pyramidal Cu$^{II}$ coordination with the tridentate *N*-salicylideneglycinato Schiff base dianion (TSB$^{2-}$) and the 4-ethylpyridine ligand bound in the basal plane. The apex of the pyramid is occupied by a carboxylic O atom from the neighbouring chelate at an apical distance of 2.458 (2) Å. Four such molecules build a tetrameric unit, in which all copper positions are magnetically non-equivalent. The unit cell contains four tetramers.

## Comment

Copper(II) complexes with the tridentate Schiff base dianion of the *N*-salicylideneaminoalkanoate type (TSB$^{2-}$) represent a relatively simple model for studies of cooperative bonding effects, which can be investigated by electron paramagnetic resonance (EPR) spectroscopy. In these complexes, which are of the general type [Cu(TSB)($L$)]$_n$ (Warda, 1994), three donor atoms (O, N and O) of the Schiff base and a fourth donor atom from the neutral ligand $L$ (N, O or S) normally define the base of a square pyramid. For isolated (monomeric) structures, the copper coordination can be square planar or square pyramidal when a neutral donor ligand is located in the apical site ($n$ = 1; Warda, Friebel, Sivý, Plesch & Švajlenová, 1996). Polymeric structures ($n$ = ∞) result when the apical position is occupied by a carboxylic O atom from an adjacent molecule to make

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