O21—Zn1—O25	85.3 (2)	C5—N9—C18	111.9 (4)
O17—Zn1—O21	165.9 (2)	N8—C10—C11	109.0 (5)
O13—Zn1—O21	86.5 (2)	C10—C11—O12	118.1 (5)
N9—Zn1—O25	79.9 (2)	C10—C11—O13	116.0 (5)
N9—Zn1—O17	102.3 (2)	O12—C11—O13	125.9 (6)
N8—Zn1—O25	148.5 (2)	C5—C4—N8	118.9 (5)
N8—Zn1—O17	79.2 (2)	C6—C5—N9	121.5 (5)
N8—Zn1—N9	80.3 (2)	C4—N8—C10	113.9 (5)
O17—Zn1—O25	81.4 (2)	C5—N9—C22	114.4 (5)
O13—Zn1—O25	128.2 (2)	C18—N9—C22	110.5 (4)
O13—Zn1—O17	98.0 (2)	C10—C11—O13	116.0 (5)
N9—Zn1—O21	79.9 (2)	O12—C11—O13	125.9 (5)
N9—Zn1—O13	147.8 (2)	C10—C11—O12	118.1 (5)
N8—Zn1—O21	114.8 (2)	N8—C14—C15	113.8 (4)
N8—Zn1—O13	79.2 (2)	C14—C15—O17	118.3 (5)
O20—Zn2—O24	87.0 (2)	O16—C15—O17	124.4 (6)
O24—Zn2—O3*W*	97.4 (2)	C18—C19—O21	118.3 (5)
O24—Zn2—O1*W*	171.1 (2)	C22—C23—O25	118.2 (5)
O20—Zn2—O3*W*	174.6 (2)	O24—C23—O25	123.4 (5)
O20—Zn2—O1*W*	86.4 (2)	Zn1—N9—C5	110.2 (3)
O2*W*—Zn2—O4*W*	177.7 (2)	Zn1—O25—C23	114.6 (4)
O1*W*—Zn2—O4*W*	93.7 (2)	Zn1—O21—C19	113.6 (4)
O1*W*—Zn2—O2*W*	84.2 (2)	C18—N9—Zn1	108.0 (4)
O24—Zn2—O4*W*	92.3 (2)	Zn1—N8—C10	101.9 (4)
O24—Zn2—O2*W*	89.6 (2)	C14—C15—O16	117.2 (5)
O20—Zn2—O4*W*	89.7 (2)	N9—C18—C19	114.3 (5)
O20—Zm2—O2*W*	89.1 (2)	N9—C22—C23	109.8 (5)
O3*W*—Zn2—O4*W*	87.0 (2)	C22—C23—O24	118.4 (5)
O2*W*—Zn2—O3*W*	94.0 (2)	O20—C19—O21	126.6 (6)
O1*W*—Zn2—O3*W*	89.5 (2)	C4—N8—Zn1	110.7 (3)
C3—C4—N8	121.4 (5)	Zn1—N9—C22	101.1 (3)
C4—C5—N9	119.4 (5)	Zn1—N8—C14	107.3 (3)
C4—N8—C14	111.6 (5)	Zn1—O13—C11	115.8 (4)
C10—N8—C14	110.8 (5)	Zn1—O17—C15	116.6 (4)

Calculated positions were used for the H atoms of the organic skeleton, all were refined will a common overall isotropic displacement parameter.

Data collection and cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *XRAY System* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Structure solution: *SHELXS*86 (Sheldrick, 1985). Structure refinement: *SHELX*76 (Sheldrick, 1976). Software used to obtain parameters of interest: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1187). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 1552–1554

Bis(phenylthiolato-*S*)bis(tri-*n*-butylphosphine-*P*)nickel(II), $[Ni(SPh)_2(P^nBu_3)_2]$

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Abstract

The title compound, $[Ni(C_6H_5S)_2(C_{12}H_{27}P)_2]$, was isolated from the reaction of $NiCl_2.6H_2O$, NaSPh and P^nBu_3 in MeOH. The molecule possesses a crystallographic inversion center at the Ni atom which is fourfold coordinated by two P and two S atoms with almost square-planar geometry. The Ni—S and Ni—P distances are 2.217 (2) and 2.245 (2) Å, respectively.

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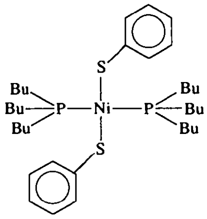
Comment

Nickel compounds with mixed sulfur and phosphine ligands have attracted attention because of their relevance and importance to a wide variety of chemical and industrial systems. We have recently reported a series of such compounds: [Ni(S-*p*-tolyl)$_2$(P^{n}Bu$_3$)$_2$] (Jiang, Wei, Lei, Huang, Hong & Liu, 1991), [Ni$_2$(PPh$_3$)$_2$(SC$_2$H$_4$S)$_2$] (Cao, Huang, Lei, Hong & Liu, 1992) and [Ni$_2$(PPh$_3$)$_2$(SC$_3$H$_6$S)$_2$] (Cao, Huang, Lei, Kang, Hong & Liu, 1992). Herein, we report the crystal structure of [Ni(P^{n}Bu$_3$)$_2$(SPh)$_2$], (I).



(I)

The molecule possesses a crystallographic inversion center at the Ni atom which is surrounded by two *trans* P and two *trans* S atoms in an almost square-planar arrangement. The Ni—S bond length [2.217 (2) Å] is shorter than that (2.287 Å) found in the sulfur-ligated tetrathiolato complex [Ni(SPh)$_4$]$^{2-}$ (Swenson, Baenziger & Coucouvanis, 1978) and similar to that (2.213 Å) in [Ni(S-*p*-tolyl)$_2$(P^{n}Bu$_3$)$_2$] (Jiang, Wei, Lei, Huang, Hong & Liu, 1991). The Ni—P bond length [2.245 (2) Å] is similar to that (2.237 Å) found in [Ni(S-*p*-tolyl)$_2$(P^{n}Bu$_3$)$_2$]. All the butyl groups of the phosphine ligands adopt the normal zigzag (all *trans*) conformation of the C atoms, leading to an approximately coplanar arrangement of the C atoms in each butyl group. Fig. 1 depicts the structure of the title compound.

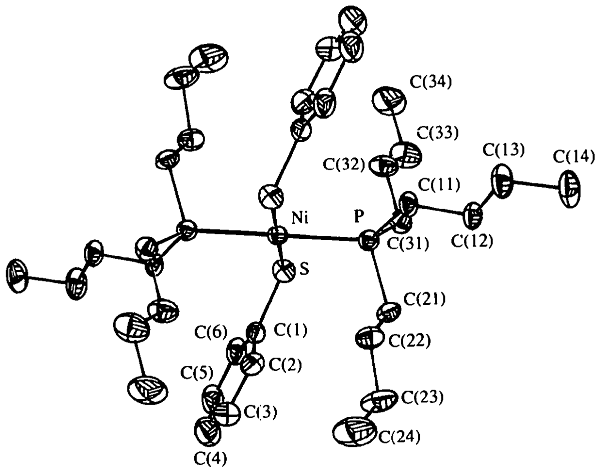


Fig. 1. Structure of [Ni(SPh)$_2$(P^{n}Bu$_3$)$_2$] with displacement ellipsoids plotted at the 30% probability level.

Experimental

The title compound was obtained from the reaction of NiCl$_2$.6H$_2$O, NaSPh, and P^{n}Bu$_3$ (molar ratio 1:2:2) in MeOH and recrystallized from CH$_2$Cl$_2$ solution.

Crystal data

[Ni(C$_6$H$_5$S)$_2$(C$_{12}$H$_{27}$P)$_2$]
M_r = 681.70
Triclinic
$P\bar{1}$
a = 10.259 (3) Å
b = 12.016 (4) Å
c = 8.420 (3) Å
α = 93.23 (3)°
β = 96.52 (3)°
γ = 78.22 (2)°
V = 1008.93 Å^3
Z = 1
D_x = 1.122 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 20 reflections
θ = 6–12°
μ = 0.68 mm^{-1}
T = 296 K
Rectangular
0.7 × 0.5 × 0.4 mm
Brown–red

Data collection

MSC/Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (ψ scans and refinement from ΔF)
$T_{\min}$ = 0.891, $T_{\max}$ = 1.000
3750 measured reflections
3689 independent reflections

2788 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int}$ = 0.025
$\theta_{\max}$ = 25°
$h = 0 \rightarrow 12$
$k = 13 \rightarrow 14$
$l = -10 \rightarrow 9$
3 standard reflections monitored every 250 reflections
intensity decay: none

Refinement

Refinement on F
R = 0.050
wR = 0.063
S = 1.55
2788 reflections
187 parameters
H atoms not located
Unit weights applied

$(\Delta/\sigma)_{\max}$ = 0.10
$\Delta\rho_{\max}$ = 0.43 e Å^{-3}
$\Delta\rho_{\min}$ = −0.42 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Ni	0	0	0	3.19 (3)
S	0.1380 (3)	−0.0785 (2)	0.2035 (3)	4.25 (6)
P	−0.0769 (2)	0.1383 (2)	0.1761 (3)	3.42 (5)
C(1)	0.0947 (10)	−0.2074 (7)	0.2421 (10)	4.2 (2)
C(2)	−0.0360 (10)	−0.2264 (8)	0.2016 (10)	5.6 (3)
C(3)	−0.0666 (10)	−0.3349 (9)	0.2301 (10)	7.3 (3)
C(4)	0.0306 (10)	−0.4198 (9)	0.3025 (10)	8.4 (4)
C(5)	0.160 (2)	−0.3996 (9)	0.3437 (10)	8.1 (4)
C(6)	0.1946 (10)	−0.2923 (8)	0.3145 (10)	5.7 (3)
C(11)	−0.1875 (10)	0.2681 (7)	0.1022 (10)	4.2 (2)
C(12)	−0.2508 (10)	0.3530 (7)	0.2320 (10)	4.6 (2)
C(13)	−0.3435 (10)	0.4557 (8)	0.1456 (10)	6.1 (3)
C(14)	−0.4056 (10)	0.5472 (9)	0.2710 (10)	7.4 (3)

C(21)	−0.1735 (9)	0.0792 (8)	0.3112 (10)	4.3 (2)
C(22)	−0.2978 (9)	0.0431 (8)	0.2131 (10)	4.9 (2)
C(23)	−0.3634 (10)	−0.0238 (10)	0.3262 (10)	7.7 (3)
C(24)	−0.4779 (10)	−0.0721 (10)	0.2297 (20)	10.0 (4)
C(31)	0.0507 (9)	0.1894 (7)	0.3201 (10)	4.2 (2)
C(32)	0.1555 (10)	0.2317 (8)	0.2270 (10)	5.7 (3)
C(33)	0.2664 (10)	0.2643 (10)	0.3455 (10)	7.1 (3)
C(34)	0.3699 (10)	0.3053 (10)	0.255 (2)	9.6 (4)

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

Ni—S	2.217 (2)	P—C(11)	1.825 (7)
Ni—P	2.245 (2)	P—C(21)	1.848 (8)
S—C(1)	1.754 (8)	P—C(31)	1.855 (7)
S—Ni—S^{i}	180	Ni—S—C(1)	108.4 (3)
S—Ni—P	86.29 (8)	Ni—P—C(11)	119.1 (2)
S—Ni—P^{i}	93.71 (8)	Ni—P—C(21)	108.1 (3)
P—Ni—P^{i}	180	Ni—P—C(31)	116.4 (3)

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

Intensity data used in the refinements were corrected for Lorentz–polarization factors, linear decay and absorption based on ψ scans and refinement from ΔF (*DIFABS*; Walker & Stuart, 1983). All non-H atoms were refined with anisotropic displacement parameters.

Data collection and refinement: *CONTROL* (Molecular Structure Corporation, 1988). Data reduction: *SDP/VAX* (Enraf–Nonius, 1989). Structure solution: direct methods using *MULTAN*11/82 (Main *et al.*, 1982). Structure refinement: *LSFM* (B. A. Frenz & Associates Inc., 1985). Molecular graphics: *ORTEP*II (Johnson, 1976). Preparation of material for publication: *SDP/VAX*.

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BK1083). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Benzoato[hydrotris(3-phenylpyrazol-1-yl-N^2)borato]zinc(II)

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Abstract

The structure of the title complex, [Zn{HB(C$_9$H$_7$N$_2$)$_3$}(C$_7$H$_5$O$_2$)], has been determined; the central Zn atom is coordinated in a distorted tetrahedral environment by three N atoms, one from each pyrazole ring [Zn—N 2.038 (5)–2.084 (5) Å], and by a benzoate O atom [Zn—O 1.935 (5) Å]. A hydrophobic pocket is formed around the fourth coordination site of the Zn atom by the phenyl substituent on each pyrazole ring; this pocket is occupied by the benzoate ligand.

Comment

Since the active site of carbonic anhydrase comprises a Zn$^{\rm II}$ atom coordinated to three histidine imidazole groups, the use of hydrotris(pyrazol-1-yl)borato ligands has become increasingly popular in synthetic inorganic and bioinorganic chemistry (Trofimenko, 1993). In recent reports, significantly bulky ligands such as hydrotris[(3-phenyl- or *tert*-butyl)pyrazol-1-yl]borato (*L*), will allow [Zn*L*]$^+$ formation (Trofimenko, Calabrese & Thompson, 1987; Looney, Han, McNeill & Parkin, 1993; Alfasser, Ruf, Trofimenko & Vehrenkamp, 1993), while the most commonly used of such ligands, hydrotris(3,5-dimethyl or unsubstituted pyrazolyl)borato (L'), will form ZnL'_2. Since the Zn$^{\rm II}$ in the biological system is almost always coordinated in a tetrahedral fashion, [Zn*L*]$^+$ is much more interesting, and the fourth, the 'mformat a: functional', site can be occupied by a small ligand, such as water, *R*—COO$^-$, OH$^-$ or NO$_3^-$. This work reports the synthesis and crystal structure of novel benzoato[hydrotris(3-phenylpyrazol-1-yl)borato]zinc(II), (I), where the fourth ligand is a benzoate ion.

Fig. 1 shows the molecular structure of [Zn{HB(3-Phpz)$_3$}(OBz)]. Each distance between the central Zn$^{\rm II}$ and the three N-atom sites in the tridentate ligand HB(3-Phpz)$_3^-$ is longer than the distance between Zn and O of the monodentate benzoate ion (see Table 2) by *ca* 0.1 Å. All values of the N—Zn—N bond angles range between 90.0 (2) and 97.0 (2)°, and those of N—Zn—O from 113.4 (2) to 131.3 (2)°. Thus, the geometry around

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