N	0.1825 (3)	−1/4	−0.3051 (5)	0.0273 (10)
Cl	0.2255 (3)	−0.0790 (6)	−0.2521 (6)	0.0397 (10)
C2	0.1671 (4)	−1/4	−0.4853 (7)	0.0378 (14)

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

Ni—O	2.055 (3)	N—C2	1.482 (8)
Ni—Cl2	2.4123 (8)	N—C1	1.483 (5)
Ni—Cl1	2.4637 (8)		
O—Ni—Cl2′	90.72 (9)	Cl1—Ni—Cl1′	180.0
O′—Ni—Cl2′	89.28 (9)	Niⁱⁱ—Cl1—Ni	93.25 (4)
O—Ni—Cl1	89.53 (8)	Ni—Cl2—Niⁱⁱⁱ	95.86 (4)
O′—Ni—Cl1	90.47 (8)	C2—N—C1	111.7 (3)
Cl2′—Ni—Cl1	84.32 (3)	C1—N—C1ⁱˣ	111.4 (5)
Cl2—Ni—Cl1	95.68 (3)		

Symmetry codes: (i) −x, −y, −z; (ii) −x, y − ½, −z; (iii) −x, ½ + y, −z; (iv) x, −½ − y, z.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O—H3A···Cl3	0.87 (5)	2.32 (5)	3.111 (3)	150 (4)
O—H3B···Cl3	0.77 (4)	2.41 (4)	3.153 (3)	163 (4)
N—H1···O	0.75 (5)	2.49 (4)	3.082 (5)	138 (4)
N—H1···Cl1	0.75 (5)	2.80 (5)	3.344 (4)	132 (5)

The quality of the single crystals, initial cell parameters and symmetry information were determined from DeJong and Buerger photographs taken at 293 K. The largest feature in the final difference electron-density map was 0.58 e Å⁻³ at a distance of 0.99 Å from Cl3. Every H atom was clearly resolved in the Δρ maps.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-FOR/CADSEX* (Keller, 1981). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEPIII* (Johnson & Burnett, 1997).

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Transition Metal Complexes with Thiosemicarbazide-Based Ligands. 33. [4-(2-Diphenylphosphino-α-ethoxy-benzyl-P)-3-methyl-1-salicylidene-isothiosemicarbazido-N¹,N⁴,O]nickel(II)

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Abstract

The title compound, [Ni(C₃₀H₂₈N₃O₂PS)], is the first example of a transition metal complex involving a thiosemicarbazide-based tetradentate ligand with a P atom in its coordination sphere. The Ni atom in the complex has a distorted square-planar configuration formed by N₂OP donor atoms. It can be concluded from the structure that the formation of the complex involved addition across the azomethine group, which is the first time this has been observed for this class of ligands.

Comment

A large number of complexes involving thiosemicarbazide-based ligands of different denticity with O, S and N as donor atoms have been described (Jensen & Rancke-Madsen, 1934; Campbell, 1975; Padhye & Kauffman, 1985; West *et al.*, 1991). In a recent paper (Leovac *et al.*, 1996), we described a nickel(II) complex of an O,N,P-tridentate 2-(diphenylphosphino)-thiosemicarbazone, the first thiosemicarbazide-derived ligand to contain a P atom. It is well known that the NH₂ group of the thiosemicarbazide and the S-alkylisothiosemicarbazide fragment of tridentate semicarbazones takes part in the common condensation reaction with carbonyl compounds only in the presence of a metal ion acting as template, the products being complexes with corresponding tetradentate ligands.

This paper describes the structure of the title complex, (I), in which the ligand is a condensation product of co-ordinated salicylaldehyde S-methylisothiosemicarbazone and 2-(diphenylphosphino)benzaldehyde. The determination of the structure of the complex has shown that the condensation reaction takes place with the addition of EtOH across the azomethine C4—N3 bond. This addition has been detected for only one thiosemicarbazide-based complex so far (Leovac et al., 1988), in which the azomethine group participates in the structure of the five-membered chelate ring. No example of this addition in which an azomethine group participates in the structure of a six-membered chelate ring has been found until now.

(I)
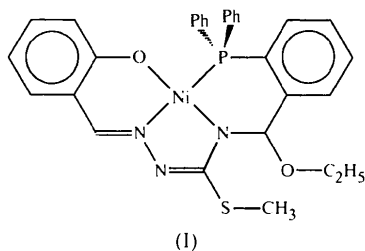
The Ni atom has distorted square-planar coordination geometry. The greatest deviation is shown by the P atom, which deviates from the least-squares plane through Ni, O1, N1 and N3 by 0.280 (3) Å. The structure contains three condensed chelate rings in the form of a six-membered ring fused to a five-membered ring, which is in turn fused to a puckered six-membered ring. The six-membered chelate ring containing the O1 atom and the five-membered chelate ring are planar. However, the six-membered chelate ring containing the P atom assumes an unusual boat conformation. According to a Boeyens diagram, the endocyclic torsion angles are equivalent to a $B_{4,1}$ form (Boeyens, 1978). (The P atom was taken as the first atom in the ring.)
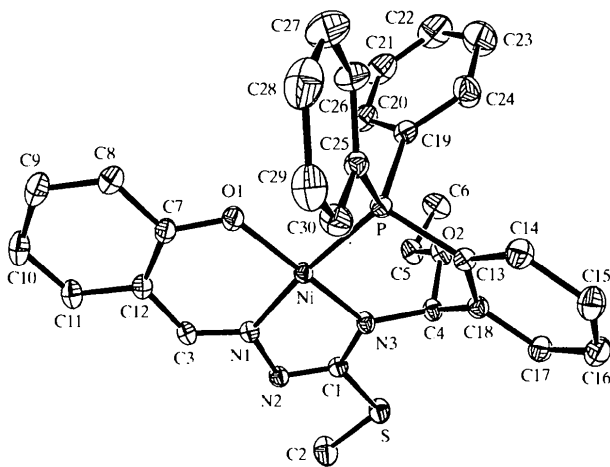

Fig. 1. A perspective view of the title complex with 40% probability ellipsoids. H atoms have been omitted for clarity.

The bond lengths and angles in the ligand are in accordance with those in other metal complexes containing thiosemicarbazide-based tetradentate ligands for which the structures have been determined. However, the N2—C1 [1.316 (3) Å] and C1—N3 [1.345 (3) Å] bond lengths are not typical compared with other thiosemicarbazide-based complexes, suggesting that electron delocalization occurs in the N2—C1—N3 fragment. There are no intermolecular hydrogen bonds in the structure.

Experimental

The starting complex [Ni(HL)py]Cl.0.5py (where HL is the monoanion of salicylaldehyde S-methylisothiosemicarbazone and py is pyridine) was prepared according to the procedure described by Leovac et al. (1984). The title complex results from a template synthesis, i.e. the reaction between a warm ethanolic solution of [Ni(HL)py]Cl.0.5py and 2-(diphenylphosphino)benzaldehyde. Single crystals suitable for X-ray data collection were obtained by recrystallization from warm ethanol.

Crystal data

[Ni(C$_{30}$H$_{28}$N$_3$O$_2$PS)]	Mo $K\alpha$ radiation
$M_r = 584.29$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 5224
$P\bar{1}$	reflections
$a = 9.1720 (2)$ Å	$\theta = 10.00–33.15°$
$b = 12.2492 (3)$ Å	$\mu = 0.872$ mm^{-1}
$c = 12.9400 (3)$ Å	$T = 293 (2)$ K
$\alpha = 90.7376 (5)°$	Prismatic
$\beta = 104.7757 (4)°$	$0.20 \times 0.18 \times 0.13$ mm
$\gamma = 101.3404 (6)°$	Dark red
$V = 1375.24 (6)$ Å^3	
$Z = 2$	
$D_x = 1.411$ Mg m^{-3}	
$D_m = 1.40$ Mg m^{-3}	
D_m measured by flotation in n-hexane/CCl$_4$	

Data collection

Siemens SMART CCD diffractometer	7583 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.014$
Absorption correction:	$\theta_{max} = 33.15°$
SADABS (Sheldrick, 1996)	$h = -14 \rightarrow 13$
$T_{min} = 0.839$, $T_{max} = 0.893$	$k = -18 \rightarrow 18$
13 857 measured reflections	$l = 0 \rightarrow 19$
8390 independent reflections	Intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2$
$R(F) = 0.049$	$+ 1.1845P]$
$wR(F^2) = 0.099$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.244$	$(\Delta/\sigma)_{max} = 0.001$
7556 reflections	$\Delta\rho_{max} = 0.334$ e Å^{-3}
343 parameters	$\Delta\rho_{min} = -0.294$ e Å^{-3}
H-atom parameters constrained	Extinction correction: none
	Scattering factors from International Tables for Crystallography (Vol. C)

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

Ni—O1	1.8369 (15)	O2—C5	1.426 (3)
Ni—N1	1.853 (2)	N1—C3	1.300 (3)
Ni—N3	1.864 (2)	N1—N2	1.398 (2)
Ni—P	2.1829 (6)	N2—C1	1.316 (3)
S—C1	1.767 (2)	N3—C1	1.345 (3)
S—C2	1.783 (3)	N3—C4	1.451 (3)
P—C25	1.815 (2)	C3—C12	1.430 (3)
P—C19	1.816 (2)	C4—C18	1.510 (3)
P—C13	1.821 (2)	C5—C6	1.493 (4)
O1—C7	1.320 (3)	C7—C12	1.404 (3)
O2—C4	1.417 (3)		
O1—Ni—N1	95.52 (7)	N2—N1—Ni	117.03 (13)
O1—Ni—N3	176.60 (8)	C1—N2—N1	107.3 (2)
N1—Ni—N3	82.55 (8)	C1—N3—C4	120.6 (2)
O1—Ni—P	88.68 (6)	C1—N3—Ni	111.08 (13)
N1—Ni—P	173.05 (5)	C4—N3—Ni	127.87 (14)
N3—Ni—P	93.52 (6)	N2—C1—N3	122.0 (2)
C1—S—C2	101.69 (12)	N2—C1—S	117.0 (2)
C25—P—C19	105.07 (10)	N3—C1—S	121.0 (2)
C25—P—C13	106.81 (10)	N1—C3—C12	123.8 (2)
C19—P—C13	104.18 (9)	O2—C4—N3	113.2 (2)
C25—P—Ni	117.57 (8)	O2—C4—C18	104.9 (2)
C19—P—Ni	113.07 (7)	N3—C4—C18	113.1 (2)
C13—P—Ni	109.15 (7)	O2—C5—C6	108.4 (2)
C7—O1—Ni	126.49 (15)	O1—C7—C12	124.6 (2)
C4—O2—C5	114.2 (2)	O1—C7—C8	117.6 (2)
C3—N1—N2	115.9 (2)	C7—C12—C3	122.4 (2)
C3—N1—Ni	127.1 (2)	C18—C13—P	118.7 (2)
N3—Ni—P—C13	−31.11 (8)	Ni—P—C13—C18	39.4 (2)
P—Ni—N3—C4	−12.7 (2)	P—C13—C18—C4	3.3 (3)
Ni—N3—C4—C18	59.0 (2)	N3—C4—C18—C13	−55.1 (3)

The data collection nominally covered over a full hemisphere of reciprocal space by a combination of six sets of exposures with the area detector held at two 2θ swing angles (25 and 53°). The reciprocal space was scanned by 0.1° ω steps at a different φ for each set of exposures. The detector was placed at a distance of 5.02 cm from the crystal. Crystal decay was monitored by repeating the initial 70 frames at the end of data collection and analysing the duplicate reflections (*SADABS*; Sheldrick, 1996). No decay was observed. The structure was solved by Patterson and difference Fourier methods and refined by full-matrix least-squares methods. All H atoms were found in the difference Fourier map, but they were placed at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the parent atom.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SDP* (Frenz, 1982). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEX3* (McArdle, 1994). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1226). Services for accessing these data are described at the back of the journal.

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Aqua(2,4-dimethylpyridine-*N*)(*N*-salicylideneglycinato-*O*,*N*,*O*′)copper(II)

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Abstract

The Cu^{II} atom of the title complex, [Cu(C$_9$H$_7$NO$_3$)-(C$_7$H$_9$N)(H$_2$O)], has a square-pyramidal coordination sphere with a tridentate *N*-salicylideneglycinato Schiff base dianion and a 2,4-dimethylpyridine ligand bound in the basal plane. The apex of the pyramid is occupied by an O atom from the coordinated water molecule at an apical distance of 2.416 (2) Å. The monomeric moieties in the crystal are stabilized through hydro-