

## Different intermolecular interactions in azido[2-(diphenylphosphino)benzaldehyde semicarbazonato- $\kappa^2P,N^1,O$ ]nickel(II)

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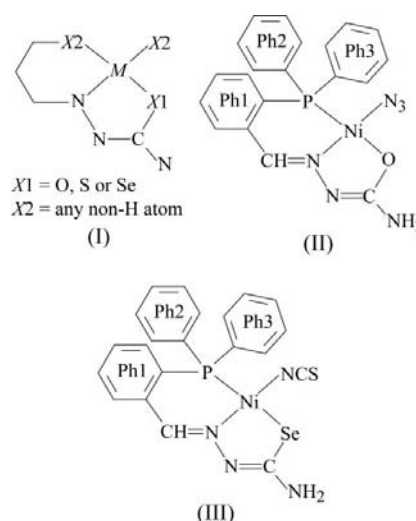
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The title compound,  $[\text{Ni}(\text{C}_{20}\text{H}_{17}\text{N}_3\text{OP})(\text{N}_3)]$ , is the first complex with a semicarbazide-based ligand having a P atom as one of the donors. The influence of the P atom on the deformation of the coordination geometry of the  $\text{Ni}^{\text{II}}$  ion is evident but less expressed than in the cases of complexes with analogous seleno- and thiosemicarbazide ligands. The torsion angles involving the two bonds formed by the P atom within the six-membered chelate ring have the largest values [ $\text{C}-\text{P}-\text{Ni}-\text{N} = 24.3(2)^\circ$  and  $\text{C}-\text{C}-\text{P}-\text{Ni} = -24.2(4)^\circ$ ], suggesting that the P atom considerably influences the conformation of the ring. Two types of  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bond connect the complex units into chains.

### Comment

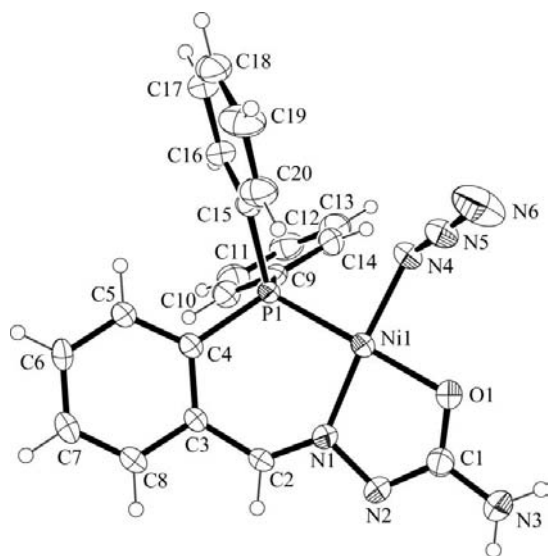
Semicarbazones, thiosemicarbazones and selenosemicarbazones and their metal complexes have been the subject of extensive investigations because of their potential pharmacological properties (Beraldo & Gambino, 2004; Gómez-Quiroga & Navarro Ranninger, 2004). Besides their relevance for biological studies, the structural diversity of these ligands, their good complexation abilities and the variety of their coordination modes have prompted the development of a very rich structural chemistry related to these compounds (Campbell, 1975; Padhyé & Kauffman, 1985; West *et al.*, 1991, 1993; Fanning, 1991; Dittes *et al.*, 1997; Casas *et al.*, 2000). The similarity in composition and structure which can be attained by the analogous semi-, thiosemi- and selenosemicarbazone ligands offers an opportunity for an investigation of the changes in metal–ligand bonding when the donor set is partly modified by a donor of different van der Waals radius (O, S and Se, respectively; Bondi, 1964). It also allows a comparison

of the extent of the deformation of the metal coordination environment caused by different donor sets, as well as the effect on the manner of intermolecular association. According to a survey of the Cambridge Structural Database (CSD, Version 3.2; Allen, 2002), among the 201 crystal structures containing the fragment (I) (see scheme), there are only six which have a P atom as the  $X_2$  donor coordinated to a metal atom (Brčeski *et al.*, 2004; Castineiras & Pedrido, 2008; Abram *et al.*, 2000; Argay *et al.*, 2000; Leovac *et al.*, 1996; You *et al.*, 1997). The title complex,  $[\text{NiL}(\text{N}_3)]$  [ $\text{HL} = 2$ -(diphenylphosphino)benzaldehyde semicarbazone], (II), represents the first complex with a semicarbazone-based ligand ( $X_1 = \text{O}$ ) which, besides the standard N- and O-atom donors, involves a P atom as the third donor in the coordination environment of the metal.



In the crystal structure of (II), the  $\text{Ni}^{\text{II}}$  centre occupies a distorted square-planar environment formed by atoms P1, N1 and O1 of the deprotonated semicarbazone ligand and azide atom N4 (Fig. 1). While in the cases of the complexes with equivalent Se and S ligands,  $[\text{NiL}'(\text{NCS})]$  [ $\text{HL}' = 2$ -(diphenylphosphino)benzaldehyde selenosemicarbazone], (III) (Brčeski *et al.*, 2004), and  $[\text{NiL}''(\text{py})]\text{NO}_3$  [ $\text{HL}'' = 2$ -(diphenylphosphino)benzaldehyde thiosemicarbazone and py is pyridine] (Leovac *et al.*, 1996), considerable deviation of the P atom from the mean planes defined by Ni1 and the rest of the coordinated atoms has been reported [0.494(3) and 0.683(3) Å, respectively], in the present case, for the same reference plane, the deviation of P1 is less expressed and equal to 0.079(4) Å. If the mean reference plane is defined by atoms O1, N1, P1 and N4, the metal atom is significantly displaced by 0.069(2) Å, which is somewhat smaller than the displacement of the P1 atom from the mean plane through atoms O1, N1, N4 and Ni1.

Selected geometric parameters for (II) are given in Table 1. It is worth noting that three metal–ligand bonds (one  $\text{Ni}-\text{O}$  and two  $\text{Ni}-\text{N}$ ) have almost identical lengths, while  $\text{Ni}-\text{P}$  is longer, as expected. Comparison of this geometry with related Ni complexes having Se and S ligands points to substantial shortening of the  $\text{Ni1}-\text{P1}$  bond by 0.048(1) and 0.041(6) Å, respectively. Similarly, the  $\text{Ni1}-\text{N1}$  bond in (II) is on average

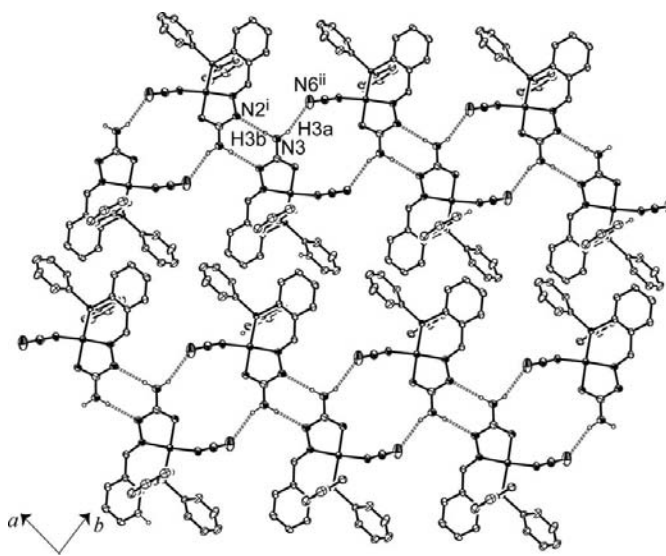

**Figure 1**

A view of the molecule of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

0.024 (7) Å shorter than those in the previously characterized complexes. This finding suggests that the presence of the O atom as a donor instead of S or Se induces stronger binding of the ligand in general.

Coordination of the tridentate ligand to the metal atom in (II) results in the formation of two fused chelate rings, one five-membered (semicarbazide) and the other six-membered [(2-diphenylphosphino)benzaldehyde]. The five-membered chelate ring is nearly planar, with an r.m.s. deviation of the constituent atoms of 0.057 Å. The six-membered ring, on the other hand, exhibits considerable deviation of its atoms from the mean plane (0.136 Å). The ring-puckering parameters defined for the atom sequence P1–C4–C3–C2–N1–Ni1 are  $\theta = 62.0 (8)^\circ$ ,  $\varphi = -20.1 (8)^\circ$  and  $Q = 0.337 (3) \text{ \AA}$  (Cremer & Pople, 1975). A similar deformation of the six-membered chelate ring containing the P atom was observed and explained in more detail in a previous report (Brčeski *et al.*, 2004), and it has also been described in other structural reports (Drašković *et al.*, 2006; Bogdanović *et al.*, 1998). The P atom is the only atom in the chelate ligand which has four bonds and these bonds are in a distorted tetrahedral arrangement. The Ni–P1–C4 angle of  $111.95 (13)^\circ$  is in contrast with the planar form of the ring, which requires a wider angle of about  $125^\circ$ . Considering also that atoms N1, C2, C3 and C4 are  $sp^2$ -hybridized and prefer a planar geometry, the most pronounced deformation of the corresponding chelate ring is evident in the torsion angles involving the two bonds formed by P1, *viz.* C–P–Ni–N =  $24.3 (2)^\circ$  and C–C–P–Ni =  $-24.2 (4)^\circ$ . The other torsion angles within this chelate ring are below  $12^\circ$ . The torsion angles involving P1 in (II) are, however, smaller than in (III) [ $29.6 (1)^\circ$  and  $27.1 (1)^\circ$ , respectively] and  $[\text{NiL}''(\text{py})]\text{NO}_3$  [ $31.5 (2)^\circ$  and  $25.1 (2)^\circ$ , respectively].

The crystal structure arrangement of (II) is dominated by two relatively strong N–H...N hydrogen bonds (Table 2).


**Figure 2**

A segment of the crystal packing of (II), viewed approximately along the *c* axis, displaying two chains of molecules generated by N–H...N hydrogen bonds separated by regions of accumulated phenyl rings. See Table 2 for symmetry codes.

Both of these interactions connect centrosymmetrically related molecules into two types of dimers and further into chain of dimers (Fig. 2). The stronger N3–H3B...N2 hydrogen bond engages the semicarbazide parts of a neighbouring complex molecule, forming a cyclic centrosymmetric  $R_2^2(8)$  motif (Etter, 1990) centred at  $(0, 0, \frac{1}{2})$ . In the second dimer, the same N3 atom acts as a hydrogen-bond donor *via* atom H3A to terminal azide N6 atom. This pair of interactions therefore results in a centrosymmetric macrocyclic  $R_2^2(16)$  motif, centred at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . In the further arrangement of (II), neighbouring chains of dimers mutually orient their diphenylphosphine groups (Fig. 2), probably giving rise to C–H... $\pi$  interactions, as some of the perpendicular distances from H atoms to phenyl ring planes do not exceed 2.8 Å (Desiraju & Steiner, 1999). It should also be mentioned that in the crystal packing of the complex units, the chelate rings which represent widely delocalized systems have a parallel arrangement, resulting in very weak  $\pi$ -stacking interactions. The mean planes of these rings are at a distance of 3.7 Å from each other and the shortest distance of 3.42 Å was observed between atoms C3 and O1 (see Fig. S1 in the supplementary material).

Probably the most interesting result concerning the crystal structures of (II) and complexes with analogous ligands is obtained by comparison of the intermolecular interactions in (II) and (III). Although the coordination environments of the corresponding Ni atoms in (II) and (III) differ in half the atoms [P, N, O and azide N in (II), and P, N, Se and thiocyanate N in (III)], and in (III) the voluminous Se atom takes the place of the much smaller O-atom donor, these two complexes arrange in very similar ways (see Fig. S2 in the supplementary material). Complex (III) also displays two main structural motifs,  $R_2^2(8)$ , which here involves the N-atom donors and

acceptors from the analogous selenosemicarbazide fragment, and the larger  $R_2^2(16)$  motif, where the role of the acceptor is delegated to the S atom of the linear thiocyanate ligand. Finally, as in the case of (II), the bulky diphenylphosphine groups tend to accumulate in separate regions.

## Experimental

A mixture of 2-(diphenylphosphino)benzaldehyde semicarbazone (100 mg) and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (100 mg) was dissolved in MeOH (6 ml) with heating. To this solution, a warm solution of  $\text{NaN}_3$  (35 mg) in MeOH (4 ml) was added. A white snow-like precipitate was readily formed which, after 24 h, transformed into red single crystals of complex (II). The crystals were filtered off and washed with MeOH (yield 140 mg).

### Crystal data

$[\text{Ni}(\text{C}_{20}\text{H}_{17}\text{N}_3\text{O})\text{P}(\text{N}_3)](\text{N}_3)$	$\gamma = 67.556$ (19) $^\circ$
$M_r = 447.08$	$V = 964.7$ (4) $\text{\AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.8700$ (15) $\text{\AA}$	Mo $K\alpha$ radiation
$b = 10.004$ (3) $\text{\AA}$	$\mu = 1.11$ $\text{mm}^{-1}$
$c = 12.870$ (2) $\text{\AA}$	$T = 293$ K
$\alpha = 69.993$ (19) $^\circ$	$0.30 \times 0.28 \times 0.25$ mm
$\beta = 70.598$ (14) $^\circ$	

### Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.025$
4745 measured reflections	3 standard reflections
4206 independent reflections	frequency: 60 min
2877 reflections with $I > 2\sigma(I)$	intensity decay: none

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$	262 parameters
$wR(F^2) = 0.169$	H-atom parameters constrained
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.92$ e $\text{\AA}^{-3}$
4206 reflections	$\Delta\rho_{\text{min}} = -0.95$ e $\text{\AA}^{-3}$

All H atoms were found in a difference Fourier map; they were then placed in geometrically calculated positions and refined using a riding model, with N–H = 0.86  $\text{\AA}$  and C–H = 0.93  $\text{\AA}$ , and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent})$ .

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999), *PLATON* (Spek, 2009) and *PARST* (Nardelli, 1983, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3164). Services for accessing these data are described at the back of the journal.

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Ni1–N1	1.871 (3)	P1–C9	1.826 (4)
Ni1–N4	1.872 (4)	N1–C2	1.285 (5)
Ni1–O1	1.872 (3)	N1–N2	1.401 (5)
Ni1–P1	2.1306 (11)	N2–C1	1.327 (6)
P1–C4	1.799 (4)	N3–C1	1.335 (6)
P1–C15	1.811 (4)	O1–C1	1.297 (5)
N1–Ni1–O1	84.20 (14)	C4–P1–Ni1	111.95 (13)
N4–Ni1–O1	92.28 (15)	C15–P1–Ni1	117.29 (15)
N1–Ni1–P1	94.74 (11)	C9–P1–Ni1	110.42 (13)
N4–Ni1–P1	88.49 (13)	C4–P1–C15	106.06 (18)
O1–Ni1–P1	175.49 (11)	C4–P1–C9	105.94 (19)
N1–Ni1–N4	174.91 (17)	C15–P1–C9	104.32 (19)

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
$\text{N3---H3B}\cdots\text{N2}^i$	0.86	2.27	3.051 (7)	152
$\text{N3---H3A}\cdots\text{N6}^{ii}$	0.86	2.44	3.254 (8)	158

Symmetry codes: (i)  $-x + 2, -y, -z + 1$ ; (ii)  $-x + 1, -y + 1, -z + 1$ .

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