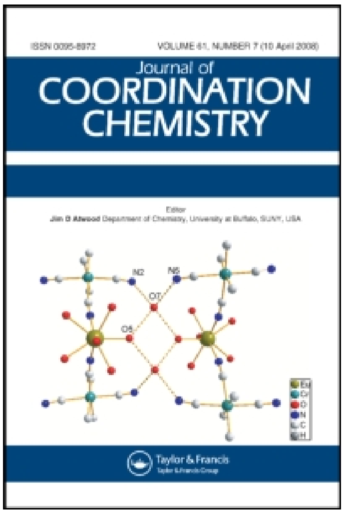

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TRANSITION METAL COMPLEXES WITH THIOSEMICARBAZIDE-BASED LIGANDS. PART 28. SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF THE FIRST PHOSPHORUS-BONDED THIOSEMICARBAZIDE COMPLEX: [2-(DIPHENYLPHOSPHINO) BENZALDEHYDE THIOSEMICARBAZONATO(1-)] PYRIDINENICKEL(II)-NITRATE

Vukadin M. Leovac[a]; Béla Ribár[a]; Gyula Argay[b]; Alajos Kálmán[b]; Ilija Brčeski[c]
[a] Faculty of Sciences, Trg. D. Obradovica, Novi Sad, Yugoslavia [b] Central Research Institute of Chemistry, Hungarian Academy of Sciences, Hungary [c] Faculty of Chemistry, University of Belgrade, Belgrade, Yugoslavia

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VUKADIN M. LEOVAC, BÉLA RIBÁR

Faculty of Sciences, Trg. D. Obradovica 3, 21000, Novi Sad, Yugoslavia

GYULA ARGAY, ALAJOS KÁLMÁN*

Central Research Institute of Chemistry, Hungarian Academy of Sciences, Budapest-114, P.O. Box 17, H-1525, Hungary

and ILIJA BRČESKI

Faculty of Chemistry, University of Belgrade, Studenski Trg. 16, P.O. Box 550 Belgrade, Yugoslavia

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The synthesis and crystal structure analysis of the diamagnetic complex [Ni(L)Py]NO_3 (L = the monoanion of the newly synthesized ligand 2-(diphenylphosphino)benzaldehyde thiosemicarbazone) are reported. The complex crystallizes in the space group $P2_1/n$ (No. 14) with $a = 8.533(1)$, $b = 29.123(3)$, $c = 10.627(a)$ Å, $\beta = 100.36(1)°$, $V = 2597.8(5)$ Å^3. As revealed by X-ray analysis, the 2-(diphenylphosphino)benzaldehyde thiosemicarbazone ligand deprotonated at N(3) acts as a monoanionic tridentate donor, coordinating through SNP. The core of the bulky $\{Ni[(C_6H_5)_2P\text{-}(C_6H_4CH{=}N\text{-}N{=}CS\text{-}NH_2)\cdot]\}^+$ cation is a slightly puckered

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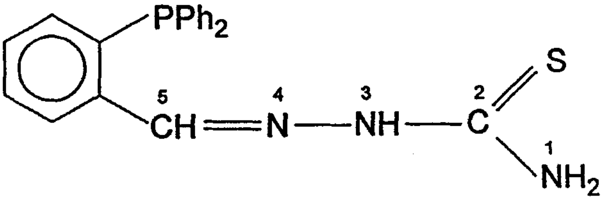
* Author for correspondence.

quadrangle formed around Ni^{2+} by SNP accompanied by a pyridine nitrogen. The dihedral angle of the atomic triangles S/N(4)/N(41) and P(2)/N(4)/N(41) is 18.0(4)°. The NO_3^- anions are well separated from the cations which may account for the observed disorder of the oxygen atoms.

Keywords: nickel(II) complex; 2-(diphenylphosphino)benzaldehydethiosemicarbazone; Schiff base; X-ray structure

INTRODUCTION

Coordination chemistry of the thiosemicarbazide-based ligands began with Jensen's work[1] in 1934, but interest in these compounds increased in the sixties after discovering that some of them show biological activity.[2] These ligands utilize sulfur, nitrogen and oxygen atoms[2-4] as donors. As far as we know, our newly synthesized 2-(diphenyl-*phosphino*)benzaldehyde thiosemicarbazone (**1**) is the first tridentate ligand in which beside S and the hydrazine nitrogen N(4), the third donor atom is phosphorus. The synthesis and crystal structure of the monoanion L of the complex $[Ni(L)Py]NO_3$ are presented in this manuscript. The synthesis of this new compound extends the range of thiosemicarbazide-based ligands, and its complexing properties to ions of other transition metals are under examination.



Structure (1)

EXPERIMENTAL

Ligand HL

An equimolar mixture (2.0 mmol) of thiosemicarbazide (0.18 g) (Merck) and 2-(diphenylphosphino) benzaldehyde (0.58 g) prepared according to a known procedure,[5] was refluxed for 1 h in absolute EtOH (10 cm^3). After cooling, the white crystals obtained were separated by filtration and washed with EtOH. Yield: 0.63 g (86%). M.p. of the product recrystallized from warm EtOH was 226°C. *Anal.* calcd for $C_{20}H_{18}N_3PS$

($M_r = 363.40$): C, 66.10; H, 4.99; N, 11.56%. Found: C, 65.65; H, 5.38; N, 11.34%. The product was used in the synthesis of the nickel complex without recrystallization.

[Ni(L)Py]NO$_3$

A mixture of the ligand *HL* (0.12 g; 0.3 mmol) and $Ni(NO_3)_2 \cdot 6H_2O$ (0.15 g; 0.5 mmol) was dissolved by heating in MeOH (5 cm^3) and then Py (0.5 cm^3) was added to it. After 48 h, the brown crystals were separated by filtration and washed with MeOH and Et_2O. Yield: 0.10 g (54%). *Anal.* calcd for $NiC_{25}H_{22}N_5O_3PS$ ($M_r = 562.22$) (%): C, 53.41; H, 3.94; N, 12.46. Found: C, 53.75; H, 3.78; N, 12.18. Samples used for elemental analysis were dried in air and the C, H and N contents were determined by standard micromethods.

Physical Measurements

Air dried samples were also used for physical measurements. Magnetic susceptibilities (check of diamagnetism) were carried out on a magnetic susceptibility balance MSB-MKI (Scherwood Scientific Ltd., Cambridge UK). Infrared spectra (KBr disc and $CHCl_3$ solution) were recorded on a Perkin-Elmer Infracord 457 spectrophotometer. Molar conductivity of a 10^{-3} mol dm^{-3} MeOH solution was measured by a Jenway 4010 digital conductivity meter. Melting points were determined on a Boetius HPMK 05 apparatus without correction.

X-ray Crystallography

The title compound (F.W.562.22) is monoclinic, space group $P2_1/n$ (No. 14) with $a = 8.533(1)$, $b = 29.123(3)$, $c = 10.627(1)$ Å, $\beta = 100.36(1)°$ $V = 2597.8(5)$ Å^3. $Z = 4$, $D_{calc} = 1.437$ g.cm^{-3}, $F(000) = 1160$, $\mu = 2.717$ mm^{-1}.

A single crystal of dimensions $0.16 \times 0.14 \times 0.06$ mm was mounted on an Enraf-Nonius turbo-CAD-4 diffractometer equipped with graphite monochromator. Intensities were recorded with CuKα radiation ($\lambda = 1.5418$Å) using ω-2θ scan technique in the range $3.03 < \theta < 75.15°$. Three standard reflections were monitored every hour; no decay correction was applied. Cell constants were determined by least squares refinement of diffractometer angles for 25 automatically centered reflections collected in the range $25.0 < \theta < 33.4°$. Details are given in Table 1.

TABLE 1 Crystal data and structure refinement for RBTSC

Identification code	rbt13
Empirical formula	$C_{25}H_{22}N_5NiO_3PS$
Formula weight	562.22
Temperature	293(2) K
Wavelength	1.54180 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
a(Å)	8.533(1)
b(Å)	29.123(3)
c(Å)	10.627(1)
α(°)	90
β(°)	100.36(1)
γ(°)	90
V Å^3	2597.8(5)
Z	4
Density (calculated)	1.437 Mg/m^3
Absorption coefficient	2.717 mm^{-1}
F(000)	1160
Crystal size	0.16 x 0.14 x 0.06 mm
Theta range for data collection	3.03 to 75.15°
Index ranges	0< = h< = 10, -36< = k< = 0, -3< = l< = 13
Reflections collected	5726
Independent reflections	5370 [R(int) = 0.0269]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5370/224/324
Goodness-of-fit on F^2	1.072
Final R indices [I>2σ(I)]	$R1 = 0.0787$, $wR2 = 0.1672$
R indices (all data)	$R1 = 0.1700$, $wR2 = 0.2357$
Extinction coefficient	0.00022(11)
Largest diff. peak and hole	0.611 and -0.613 e.Å^3

A total of 5726 reflections was collected of which, after conventional data reduction, 5370 [R(int) = 0.0547] were unique, non-zero and not systematically absent. Due to the low quality of the crystal (and no better one could be selected for a new second data collection) the number of the observed reflections is only 2481 with $I > 2\sigma(I)$. The crystallographic phase problems were solved by direct methods using the program SHELXS86.[6] At the end of the refinement with isostropic atomic displacement parameters an empirical absorption correction with program DIFABS[7] was calculated. The minimum and the maximum transmission factors were 0.798 and 1.100 respectively. This increased the number of observed reflections by 154. Full matrix least squares refinement for 324 parameters minimized $\Sigma w(\Delta F^2)^2$ with $w = 1/[\sigma^2(F_o^2) + (0.0764P)^2 + 6.74P]$ where $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$ and resulted in the final R values: $R = 0.078$, R(total) = 0.17, $S = 1.072$. The nitrate oxygen atoms show positional disorder. For each two well-separated positions were refined with an occupancy factor of 0.5. For the H atom coordinates a riding model refinement was applied. The hydro-

TABLE 2 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	*y*	*z*	U(eq)
Ni	7604(1)	1300(1)	8692(1)	39(1)
P(2)	9047(2)	1280(1)	7203(2)	40(1)
S	5606(2)	1323(1)	9692(2)	49(1)
N(1)	4197(7)	569(2)	10293(6)	57(2)
C(2)	5356(8)	736(2)	9756(7)	45(2)
N(3)	6330(6)	440(2)	9342(5)	46(1)
N(4)	7544(6)	652(2)	8813(5)	42(1)
C(5)	8554(8)	348(2)	8570(7)	52(2)
C(6)	9953(8)	408(2)	7968(7)	46(2)
C(7)	10955(9)	13(3)	8006(8)	61(2)
C(8)	12315(9)	24(3)	7487(8)	67(2)
C(9)	12710(10)	413(3)	6897(9)	71(2)
C(10)	11750(9)	799(3)	6821(8)	63(2)
C(11)	10370(8)	793(2)	7345(7)	45(2)
C(21)	7706(8)	1209(2)	5674(6)	45(2)
C(22)	8246(10)	1224(2)	4518(7)	54(2)
C(23)	7217(12)	1166(3)	3358(7)	66(2)
C(24)	5614(12)	1091(3)	3387(8)	70(2)
C(25)	5062(10)	1074(3)	4511(7)	63(2)
C(26)	6088(8)	1138(2)	5672(6)	47(2)
C(31)	10206(8)	1789(2)	7048(7)	47(2)
C(32)	11650(9)	1860(3)	7919(8)	60(2)
C(33)	12357(10)	2284(3)	7909(8)	65(2)
C(34)	11762(12)	2634(3)	7132(10)	82(3)
C(35)	10329(13)	2567(3)	6305(9)	75(3)
C(36)	9567(10)	2151(2)	6254(7)	53(2)
N(41)	7616(6)	1950(2)	8665(5)	43(1)
C(42)	8793(9)	2188(2)	9377(7)	53(2)
C(43)	8816(10)	2658(3)	9343(8)	66(2)
C(44)	7626(11)	2896(3)	8583(9)	73(2)
C(45)	6418(10)	2655(3)	7836(8)	62(2)
C(46)	6452(8)	2186(2)	7920(7)	52(2)
N(50)	943(8)	1182(2)	1322(8)	68(2)
O(1)	-361(14)	1381(4)	1219(14)	77(4)
O(2)	1593(17)	988(5)	2291(13)	88(4)
O(3)	1081(21)	1085(6)	229(14)	122(6)
O(1A)	31(18)	1402(5)	1850(16)	97(5)
O(2A)	1604(20)	821(5)	1702(17)	116(6)
O(3A)	1659(21)	1385(6)	544(17)	132(6)

occupany factors O(1),···O(3A) are 0.5

gen positions, except those pertaining to the C(6)-side chain, were generated from assumed geometries; while the others were checked repeatedly from difference maps. The lowest and highest peaks in the final $\Delta\rho$ map were −0.61 and 0.61 e.Å.$^{-3}$ Scattering factors were taken from standard tables incorporated in the program SHELXL93.[8] Fractional atomic coordinates of non-hydrogen atoms and equivalent atomic displacement

TABLE 3 Relevant bond lengths (Å) and angles (°)

Ni-N(4)	1.892(5)	P(2)-C(11)	1.802(7)	N(1)-C(2)	1.321(8)
Ni-N(41)	1.895(5)	P(2)-C(31)	1.807(6)	C(2)-N(3)	1.327(8)
Ni-S	2.167(2)	P(2)-C(21)	1.823(7)	N(3)-N(4)	1.407(7)
Ni-P(2)	2.173(2)	S-C(2)	1.723(7)	N(4)-C(5)	1.294(8)

N(4)-Ni-N(41)	176.5(2)	N(1)-C(2)-S	119.4(5)
N(4)-Ni-S	87.9(2)	C(2)-N(3)-N(4)	113.4(5)
N(41)-Ni-S	89.0(2)	C(5)-N(4)-N(3)	110.2(5)
N(4)-Ni-P(2)	92.8(2)	C(5)-N(4)-Ni	129.9(5)
N(41)-Ni-P(2)	90.6(2)	N(3)-N(4)-Ni	119.7(4)
S-Ni-P(2)	163.1(1)	N(4)-C(5)-C(6)	129.1(6)
C(11)-P(2)-C(31)	107.9(3)	C(6)-C(11)-P(2)	117.8(5)
C(11)-P(2)-C(21)	105.6(3)	C(10)-C(11)-P(2)	121.4(6)
C(31)-P(2)-C(21)	106.1(3)	C(22)-C(21)-P(2)	122.0(6)
C(11)-P(2)-Ni	112.8(2)	C(26)-C(21)-P(2)	118.7(5)
C(31)-P(2)-Ni	115.9(2)	C(36)-C(31)-P(2)	120.8(6)
C(21)-P(2)-Ni	107.8(2)	C(32)-C(31)-P(2)	119.1(5)
C(2)-S-Ni	95.9(2)	C(42)-N(41)-Ni	121.0(5)
N(3)-C(2)-N(1)	117.7(6)	C(46)-N(41)-Ni	121.0(5)
N(3)-C(2)-S	122.8(5)		

parameters are given in Table 2. Relevant bond distances and angles are listed in Table 3 and the atomic numbering scheme is shown in Figure 1.

DISCUSSION

Synthesis and Physicochemical Characterization of the Ligand and the Complex

As in the reactions with a variety of primary mono- and di-amines,[9] in the warm EtOH solution the formyl group of 2-(diphenylphosphino)benzaldehyde readily undergoes a condensation reaction with thiosemicarbazide giving the Shiff base 2-(diphenylphosphino)-benzaldehyde thiosemicarbazone in a high yield. Besides chemical analysis, the condensation is substantiated by the absence of the carbonyl ν(CO) band in the IR spectrum of the ligand (KBr) which in the case of the ligand-precursor is observed as a doublet at 1680 and 1665 cm^{-1}. Similar to other thiosemicarbazones[10] the ν(SH) is also absent indicating the predominance of the thioketo form in the crystalline ligand. In contrast, in the IR spectrum of a $CHCl_3$ solution, a band of medium intensity observed at 2380 cm^{-1} suggests, that in equal amounts, both thioketo and thioenol forms are present.

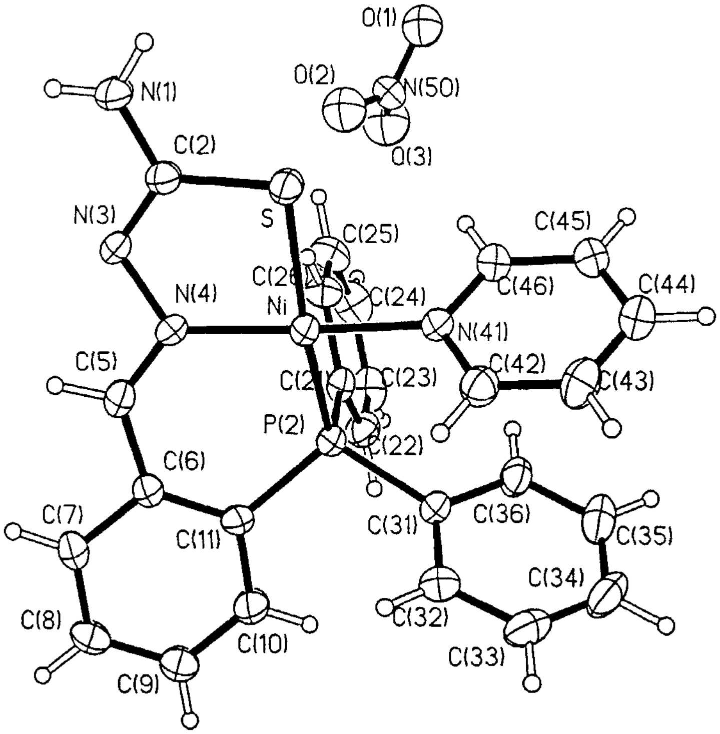
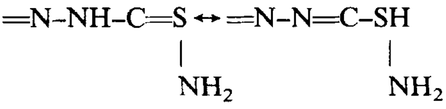


FIGURE 1 A view of the complex with atomic numbering


$$=N-NH-\underset{\underset{\displaystyle NH_2}{|}}{C}=S \leftrightarrow =N-N=\underset{\underset{\displaystyle NH_2}{|}}{C}-SH$$

Scheme 1

The isolated ligand is a white substance stable in air, poorly soluble in MeOH and EtOH more soluble in DMF and insoluble in water.

Reaction of warm MeOH solutions of $Ni(NO_3)_2$ and 2-(diphenylphosphino) benzaldehyde thiosemicarbazone (HL) in the presence of pyrimidine gave brown crystals of $[Ni(L)Py]NO_3$. The complex is stable in air, soluble in polar organic solvents, but insoluble in water. The molar conductivity of its MeOH solution ($\lambda_M = 80.0$ S cm^2 mol^{-1}) corresponds to a 1:1 type electrolyte[11] and is in accordance with its coordination formula. This means that the NO_3 group is not coordinated; this conclusion is also supported by the presence of the characteristic $\nu(NO_3)$ band at 1385 cm^{-1} in the IR spectrum.[12] The slightly bent coordination quadrangle formed around Ni^{2+} is closed by a pyridine molecule. Ligand deprotonation is facilitated by the synthesis conditions, *i.e.* by the presence of an excess of pyridine as a proton acceptor. The ν(CS) band observed at 810 cm^{-1} in the ligand spectrum, due to complexation (*i.e.* the S-coordination of the ligand) is shifted to lower energy (750 cm^{-1}). Finally, it should be noted that in accordance with its square-planar structure established by X-ray diffraction, the compound is diamagnetic.

Crystal Structure of $[Ni(L)Py]NO_3$

The core of the bulky $\{Ni[(C_6H_5)_2P\text{-}(C_6H_4CH{=}N\text{-}N{=}CS\text{-}NH_2)]\}^+$ cation is a slightly puckered quadrangle (Figure 1) formed around Ni^{2+} by the enolized sulfur atom, N(4) from the hydrazine moiety and the phosphorus atom P(2), accompanied by a pyridine nitrogen N(41) with non-bonded distances of S–N(4) = 2.824(5), N(4)–P(2) = 2.951(5), P(2)–N(41) = 2.897(6) and N(41)–S = 2.854(5) Å, respectively. The mean deviation of the four ligand atoms from their least-squares plane is 0.170(4) Å, while the metal ion is separated from this plane by 0.149(5) Å in the direction of the N(4)···N(41) vector [N(4)–Ni–N(41) = 176.5(4)° *vs* S–Ni–P(2) = 163.1(1)°]. The corresponding dihedral angle formed by the atomic triangles S/N(4)/N(41) and P(2)/N(4)/N(41) is 18.0(4).° The site of deprotonation at N(3) is underscored by the hydrogen bond pair formed around the centre of symmetry at (½,0,1) with the terminal $N(1)H_2$ group acting as donor to N(3) which plays the acceptor role [D····A = 3.008(8), H···A = 2.15(1) Å, ∠DH···A = 174.5(2)°]. The oxygen atoms are well separated from the cation which may account for their positional disorder (Figure 1).

Supplementary Material

Tables of bond distances and angles, atomic parameters (including H atoms), atomic displacement parameters and structure factors are available from Alajos Kálmán upon request.

Acknowledgements

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