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Synthesis and Crystal Structure of the Nickel(II) Complex with 2-Diphenylphosphinobenzaldehyde 2-Quinolinylhydrazone

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Abstract—2-Diphenylphosphinobenzaldehyde 2-quinolinylhydrazone (HL) and its nickel(II) complex [Ni(L)(CH_3COO)] were synthesized. The structure of the complex was determined by X-ray diffraction. The nickel ion in the molecule of the complex has a square PNN'O donor environment. Owing to C–H···O intermolecular hydrogen bonds, centrosymmetric dimers are formed in the crystal.

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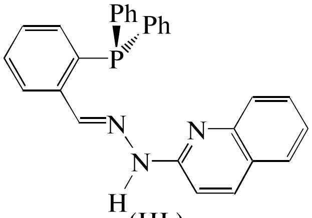
INTRODUCTION

In the last decades, transition metal complexes with hydrazones of polyfunctional carbonyl compounds have been subjects of vigorous research [1–5]. Depending on several factors, hydrazones can form mono-, bi-, or polynuclear complexes, which find use in homogeneous catalysis [6], medical and bioinorganic chemistry [8, 9], magnetochemistry [10], and so on. Of particular interest are polyfunctional hydrazone derivatives of 2-diphenylphosphinobenzaldehyde containing various sets of hard and soft donor atoms. Published data are available for some 3*d*- and 4*d*-metal complexes based on various aroylhydrazones [11–16] and derivatives of 2-diphenylphosphinobenzaldehyde semicarbazones [17, 18], thiosemicarbazones [19–21], and selenosemicarbazones [22]. Compounds of 2-diphenylphosphinobenzaldehyde hetarylhydrazones are much less studied. Only 2-di-phenylphosphinobenzaldehyde 2-pyridylhydrazone complexes with Cu(I), Ni(II), Fe(II), Pt(II), and Pd(II) were described in the literature [11, 23, 24].

As a continuation of our studies of transition metal complexes with hetarylhydrazones [25–27], we synthesized and structurally characterized nickel(II) complex with a tridentate PNN'-donor ligand, 2-diphenylphosphinobenzaldehyde 2-quinolinylhydrazone (HL) – [Ni(L)(CH_3COO)] (**I**).



(HL)

EXPERIMENTAL

Synthesis of HL A solution of 2-hydrazinoquinoline (0.005 mol) in ethanol (10 mL) was added to a hot solution of 2-diphenylphosphinobenzaldehyde (0.005 mol) in ethanol (15 mL), and the mixture was refluxed for 1 h and left overnight. The bright yellow amorphous precipitate was filtered off, washed with ethanol, and recrystallized from ethanol. Yield 65%. mp 110–112°C.

For $C_{28}H_{22}N_3P$

anal. calcd., %:	C, 77.94;	H, 5.14;	N, 9.74.
Found, %:	C, 77.61;	H, 5.26;	N, 9.81.

IR (ν, cm^{-1}): 3168 ν(NH), 1637, 1596 ν(C=N). ^1H NMR (DMSO-d_6; δ, ppm): 6.77–6.81 (m, 1H, CH_{arom}); 7.15–7.26 (m, 6H, CH_{arom}); 7.33–7.37 (m, 7H, CH_{arom}); 7.45–7.64 (m, 4H, CH_{arom}); 7.91 (d, 1H, $J = 9.0$ Hz, CH_{arom}); 7.98 br.s. (1H, CH_{arom}); 8.62 (d, 1H, $J_P = 3.0$ Hz, CH=N); 11.30 (s, 1H, NH). UV/Vis (DMSO; λ, nm (ε, L cm^{-1} mol^{-1})): 358 (31100).

[†] Deceasred.

Table 1. Crystallographic data and X-ray experiment and structure refinement details for complex **I**

Parameter	Value
M	548.20
Crystal size, mm	0.40 × 0.25 × 0.20
Temperature, K	120(2)
System	Monoclinic
Space group	$P2_1/n$
a, Å	10.5427(18)
b, Å	16.967(3)
c, Å	14.153(2)
β, deg	98.342(4)
V, Å^3	2504.9(7)
Z	4
ρ_{calcd}, g/cm^3	1.454
μ, mm^{-1}	0.872
F(000)	1136
Scan range of θ, deg	1.89–26.00
The number of measured reflections	21496
The ranges of reflection indices	$-13 \le h \le 13$, $-20 \le k \le 20$, $-17 \le l \le 17$
The number of independent reflections	4839
The number of reflections with $I > 2\sigma(I)$	2772
The number of refined parameters	335
GOOF (all reflections)	1.012
R_1 ($I > 2\sigma(I)$)	0.0549
wR_2 (all reflections)	0.1390
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.809/–0.595

Table 2. Selected interatomic distances and bond angles in the coordination polyhedra of nickel atoms in the molecule of **I**

Bond	d, Å	Bond	d, Å
Ni(1)–N(3)	1.865(3)	Ni(1)–N(1)	1.947(3)
Ni(1)–O(2)	1.883(3)	Ni(1)–P(1)	2.1660(12)
Angle	**ω, deg**	**Angle**	**ω, deg**
N(3)Ni(1)O(2)	173.68(13)	N(3)Ni(1)P(1)	94.60(11)
N(3)Ni(1)N(1)	83.75(14)	O(2)Ni(1)P(1)	82.78(9)
O(2)Ni(1)N(1)	99.93(13)	N(1)Ni(1)P(1)	168.73(11)

Table 3. Characteristics of intermolecular hydrogen bonds C–H···O in the crystal of complex **I***

C–H···O	Distance, Å**		CHO angle, deg
	H···O	C···A	
C(2)–H(2A)···O(2)	2.20	2.975(5)	141
C(24)–H(24A)···O(2)	2.33	3.088(5)	138
C(5)–H(5A)···O(1)^{i}	2.45	3.317(6)	156
C(10)–H(10A)···O(1)^{ii}	2.46	3.314(5)	153
C(16)–H(16A)···O(1)^{ii}	2.48	3.315(5)	150

* Crystallographic positions: ^{i} $5/2 - x$, $-1/2 + y$, $3/2 - z$; ^{ii} $2 - x$, $-y$, $2 - z$.

** C–H is 0.93 Å.

Synthesis of I. A hot solution of nickel(II) acetate (0.002 mol) in methanol (20 mL) was added to a hot solution of HL (0.002 mol) in methanol (20 mL). The mixture was refluxed for 4 h and the precipitate was washed with hot methanol, dried in vacuum, and recrystallized from DMSO. Yield 45%.

For $C_{30}H_{24}N_3NiO_2P$

anal. calcd., %:	C, 65.73;	H, 4.41;	N, 7.66.
Found, %:	C, 65.39;	H, 4.28;	N, 7.47.

IR (ν, cm^{-1}): 1628, 1595 ν(C=N). ^{1}H NMR (DMSO-d$_6$; δ, ppm): 2.72 (s, 1H, CH_3); 6.92 (m, 1H, CH_{arom}); 7.13 (br.s., 3H, CH_{arom}); 7.28 (br.s., 1H, CH_{arom}); 7.38 (br.s., 1H, CH_{arom}); 7.45–7.57 (m, 5H, CH_{arom}); 7.79–7.99 (m, 9H, CH_{arom}); 8.36 (d, 1H, J_P = 3.0 Hz, CH=N). UV/Vis (DMSO, λ, nm (ε, L cm^{-1} mol^{-1})): 355)): 355 (7900), 510 (3300).

The ^{1}H NMR spectra were recorded in DMSO-d$_6$ on a Varian Unity 300 spectrometer (300 MHz) in the pulse FT mode using HMDS as the internal standard. IR spectra were measured on a Varian Scimitar 1000 FT-IR instrument at 400–4000 cm^{-1} for mineral oil mulls.

X-ray diffraction analysis of **I** was performed on a Bruker SMART 1000 CCD diffractometer (MoK_α, λ = 0.71073 Å, graphite monochromator). The initial array of measured reflection intensities was processed using SAINT [28] and SADABS [29] software. The structure was solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms on F^2_{hkl}. The hydrogen atoms were placed in geometrically calculated positions and refined using the riding model

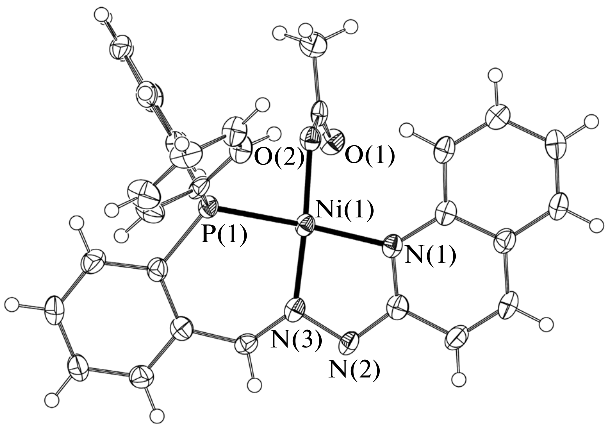


Fig. 1. General view of the molecule of complex **I** with atoms being represented by atom displacement ellipsoids with 50% probability.

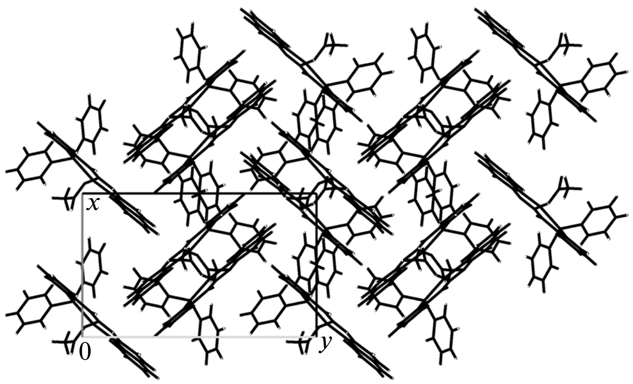


Fig. 2. Packing of the molecules of complex **I** in the crystal (view along the crystallographic axis *z*).

(U_{iso}(H) = nU_{iso}(C), where $n = 1.5$ for methyl carbons and $n = 1.2$ for other C atoms). All calculations were carried out by SHELXTL software [30]. The structure was analyzed using PLATON program [31].

X-ray experiment details and crystallographic data are summarized in Table 1, selected interatomic distances and bond angles are in Table 2, and parameters of C–H···O hydrogen bonds are given in Table 3. The atom coordinates and thermal factors are deposited with the Cambridge Crystallographic Data Centre (no. 950913: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The composition and structure of the isolated compounds were established from data of elemental analysis, IR and ^{1}H NMR spectroscopy, and X-ray diffraction (for **I**). The positions of the ν(NH) absorption band in the IR spectrum and the NH proton signal in the ^{1}H NMR spectrum of HL suggest that the compound exists as the hydrazone tautomer [11, 24, 27]. The signal of the NH proton is fully suppressed by addition of D_2O, indicating its exchange nature.

The reaction of hydrazone HL with nickel(II) acetate in methanol yields complex **I**. The complex is diamagnetic, which attests to a square environment of the nickel ion [32]. The absence of the NH-proton signal in the ^{1}H NMR spectrum and the ν(NH) absorption band in the IR spectrum of the complex points to the monodeprotonated form of hydrazone HL coordinated to nickel.

The structure of complex **I** was determined by X-ray diffraction; the single crystal was obtained by recrystallization from DMSO. The Ni coordination polyhedron is a slightly distorted square formed by P(1), heterocyclic N(1) and azomethine N(3) nitrogen atoms, and the O(2) atom of the carboxy group (Fig. 1). The five-membered chelate ring in the molecule has an envelope conformation in which the flap, the nickel atom, deviates from the mean plane of the other four atoms by 0.145 Å. The six-membered chelate ring is also somewhat distorted due to folding along the N(3)–P(1) line, resulting in deviation of the nickel atom from the plane of other atoms by 0.242 Å.

The monodeprotonated hydrazone HL residue in complex **I** is nearly planar. This is due to the presence of extended chain of conjugated bonds, which is confirmed by alternation of short and long carbon–carbon and carbon–nitrogen bonds [33]. The dihedral angle between the mean planes of the benzene and phthalazine rings is only 1.84°, while that between the planes of the phenyl rings attached to phosphorus is 84.42°. This type of orientation of phenyl groups is found in all 2-diphenylphosphinobenzaldehyde hydrazone complexes described previously by X-ray diffraction [11–24].

The molecule of the complex has intramolecular hydrogen bonds (HBs), C–H···O [34], which involve the O(2) atom (Table 3). The O(1) atom has three more intermolecular HBs, C–H···O, giving rise to centrosymmetric dimers in the crystal (Fig. 2).

The reaction of hydrazone HL with copper(II) salts is accompanied by its oxidation, resulting in copper(I) compounds; however, preparative isolation of the reaction products failed.

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