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Synthesis, Structure, and Antimicrobial Activity of Complexes of Pt(II), Pd(II), and Ni(II) with the Condensation Product of 2-(Diphenylphosphino)benzaldehyde and Semioxamazide

Vesna Radulović[1], **Alessia Bacchi**[2], **Giancarlo Pelizzi**[2], **Dušan Sladić**[3], **Ilija Brčeski**[3], and **Katarina Andjelković**[3,*]

[1] Institute of Chemistry, Technology and Metallurgy, Belgrade, Serbia and Montenegro
[2] Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, University of Parma, Parma, Italy
[3] Faculty of Chemistry, University of Belgrade, Belgrade, Serbia and Montenegro

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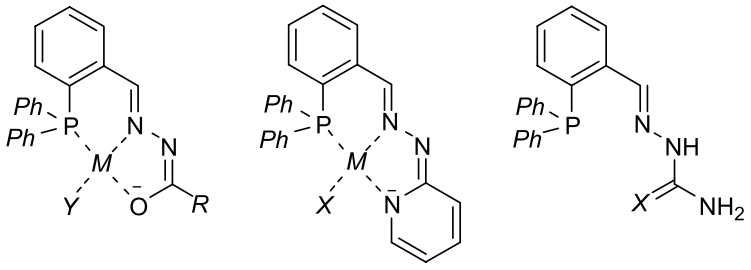
Summary. Complexes of Pt(II), Pd(II), and Ni(II) with the condensation derivative of 2-(diphenylphosphino)benzaldehyde and semioxamazide were synthesized, characterized, and their antimicrobial activity was evaluated. The ligand and the complexes were characterized by spectroscopic methods with the particular accent on NMR spectral analysis. For the palladium(II) complex, the crystal structure was determined by X-ray analysis. In all the complexes the ligand is coordinated as a tridentate *via* a P, N, O donor set. The Pd(II) and Pt(II) complexes have a square planar geometry, whereas the geometry of the Ni(II) complex is tetrahedral. The ligand showed antibacterial and antifungal activity, which was enhanced upon complexation.

Keywords. Antimicrobial activity; 2-(Diphenylphosphino)benzaldehyde derivative; Metal complexes; NMR spectroscopy; X-Ray structure determination.

Introduction

Transition metal complex compounds with organic polyfunctional ligands of hydrazone type, possessing various sets of donor atoms have been the subject of extensive research. Many such compounds and their complexes found application in catalysis of organic reactions [1–3], basic for modern industrial processes.

* Corresponding author. E-mail: kka@chem.bg.ac.yu



Scheme 1

Besides that, many substances of this type and their complexes exhibit a wide spectrum of biological activities [4–7].

It is well known that complexes with hydrazone type ligands having a phosphorus atom in the coordination sphere, namely square-planar Pd(II) and Ni(II) complexes with different derivatives of **1** (PNO chromophore) coordinated as tridentates in such a way that a six-membered and a five-membered ring around the central metal ion are formed (Scheme 1a), show a significant catalytic activity [3, 8, 9].

Similar complexes were obtained with ligands in which the coordinated oxygen was replaced by sulphur, resulting in change in catalytic activity, which also depends on the nature of the atom bound to the fourth coordination site. The correlation of activity with the leaving group activity of anions could be established only for complexes with PNO set of donor atoms [9].

The catalytic properties of analogous complexes with PNN set of donor atoms (Scheme 1b) were also studied [8].

Complexes of Ni(II), Cu(II), and Cu(I) with semi-, thiosemi-, and selenosemicarbazone of compound **1** (Scheme 1c) were synthesized with the aim to obtain biologically active compounds [10–12].

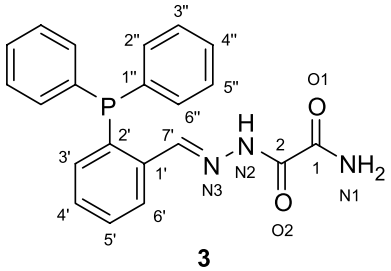
All investigated copper complexes have a square-planar geometry (PN*X* donor atom set) which also applies for the Ni(II) complexes, except for the complex with PNS set of donor atoms, which has a tetrahedral geometry.

In this work several new complexes of this type were synthesized and characterized with a particular accent on biological activity evaluation.

Results and Discussion

By condensation reaction, starting from compounds **1** and **2**, at $pH \sim 4$, 2-{(2*E*)-2-[2-(diphenylphosphino)benzylidene]hydrazino}-2-oxoacetamide (**3**) was obtained (Scheme 2).

This new ligand was used for preparation of Ni(II), Pd(II), and Pt(II) complexes (Schemes 3 and 4). Complexes of Pd(II) and Pt(II) were prepared by substitution reactions starting from $K_2[PdCl_4]$ and $K_2[PtCl_4]$, respectively, and the ligand **3**. The Ni(II) complex was obtained by direct synthesis from $Ni(NO_3)_2 \cdot 6H_2O$ and the ligand **3**.



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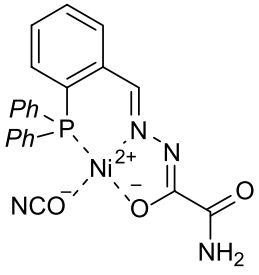
Scheme 2



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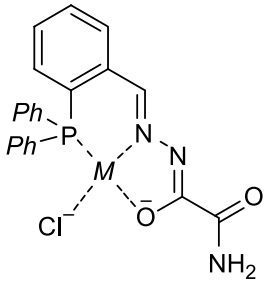
Scheme 3



M = Pd(II) complex **5**
M = Pt(II) complex **6**

Scheme 4

In the IR spectra of ligand **3** there is a characteristic band at $\bar{\nu} = 1577\,\mathrm{cm}^{-1}$ originating from the imino group (ν(C=N)), while the carbonyl bands are shifted to higher wavenumber ($1664\,\mathrm{cm}^{-1}$), compared to those in the IR spectrum of compound **2** ($1654\,\mathrm{cm}^{-1}$, ν(C=O) of the primary amide, and $1590\,\mathrm{cm}^{-1}$, ν(C=O) of the secondary amide).

Comparison of IR spectra of ligand **3** and complexes **4**, **5**, and **6** indicates the complex formation. Namely, bands originating from ν(C=O) vibrations are shifted toward higher frequences in the spectra of the complexes ($1687\,\mathrm{cm}^{-1}$ **4**, $1705\,\mathrm{cm}^{-1}$ **5**, $1710\,\mathrm{cm}^{-1}$ **6**). A new band appears in the complexes ($1478\,\mathrm{cm}^{-1}$ **4**, $1533\,\mathrm{cm}^{-1}$ **5**, $1540\,\mathrm{cm}^{-1}$ **6**), originating from $\nu(^{-}\mathrm{O}\text{–}\mathrm{C}{=}\mathrm{N})$ of the deprotonated hydrazide moiety

Table 1. ^{1}H and ^{13}C NMR chemical shifts in *DMSO*-d_6

	^{1}H NMR chemical shifts (ppm)
Ligand **3**	12.38 (s, 1H, N-2), 9.27 (d, 1H, $J = 4.8$ Hz, C-7′), 8.28 (s, 1H, N-1-H_a), 8.03 (m, 1H, C-6′), 7.93 (s, 1H, N-1-H_b), 7.3–7.7 (m, 9H, C-3′, C-2″, C-3″, C-5″, C-6″), 7.1–7.3 (m, 3H, C-4′, C-4″), 6.83 (m, 1H, C-5′)
Complex **5**	8.81 (d, 1H, $J = 4.2$ Hz, C-7′), 8.10 (m, 1H, C-6′), 7.86 (m, 1H, C-3′), 7.4–7.8 (m, 14H, N-1-H_a, N-1-H_b, C-4′, C-5′, C-2″, C-3″, C-4″, C-5″, C-6″)
Complex **6**	9.12 (s, 1H, C-7′), 8.15 (m, 1H, C-6′), 7.7–7.9 (m, 4H, C-3′, C-4′, N-1-H_a, N-1-H_b), 7.5–7.7 (m, 11H, C-5′, C-2″, C-3″, C-4″, C-5″, C-6″)
	^{13}C NMR chemical shifts (ppm)
Ligand **3**	162.1 (s, C-1), 157.2 (s, C-2), 135.9 (d, $^{2}J(C,P) = 10.0$ Hz, C-1′), 138.0 (d, $^{1}J(C,P) = 20.0$ Hz, C-2′), 133.5 (d, $^{2}J(C,P) = 13.6$ Hz, C-3′), 129.5 (d, $^{3}J(C,P) = 8.2$ Hz, C-4′), 126.3 (s, C-5′), 129.5 (d, $^{3}J(C,P) = 8.2$ Hz, C-6′), 148.6 (d, $^{3}J(C,P) = 25.4$ Hz, C-7′), 137.1 (d, $^{1}J(C,P) = 19.2$ Hz, C-1″), 133.7 (d, $^{2}J(C,P) = 19.1$ Hz, C-2″,6″), 129.1 (d, $^{3}J(C,P) = 5.8$ Hz, C-3″,5″), 130.7 (s, C-4″)
Complex **5**	161.9 (d, $^{4}J(C,P) = 7.2$ Hz, C-1), 169.3 (d, $^{3}J(C,P) = 4.6$ Hz, C-2), 136.2 (d, $^{2}J(C,P) = 18.2$ Hz, C-1′), 118.5 (d, $^{1}J(C,P) = 53.7$ Hz, C-2′), 134.0 (d, $^{2}J(C,P) = 10.9$ Hz, C-3′), 138.0 (d, $^{3}J(C,P) = 9.1$ Hz, C-4′), 135.0 (bs, C-5′), 134.0 (d, $^{3}J(C,P) = 9.1$ Hz, C-6′), 154.3 ($^{3}J(C,P) = 5.4$ Hz, C-7′), 127.9 (d, $^{1}J(C,P) = 61.0$ Hz, C-1″), 134.0 (d, $^{2}J(C,P) = 10.9$ Hz, C-2″,6″), 129.4 (d, $^{3}J(C,P) = 11.8$ Hz, C-3″,5″), 132.5 (d, $^{4}J(C,P) = 2.8$ Hz, C-4″)
Complex **6**	160.6 ($^{4}J(C,P) = 5.4$ Hz, C-1), 170.6 (poorly resolved doublet, C-2), 136.6 ($^{2}J(C,P) = 14.6$ Hz, C-1′), 117.9 (d, $^{1}J(C,P) = 62.8$ Hz, C-2′), 133.8 (d, $^{2}J(C,P) = 16.4$ Hz, C-3′), 138.0 (d, $^{3}J(C,P) = 10.0$ Hz, C-4′), 134.7 (bs, C-5′), 134.3 (d, $^{3}J(C,P) = 8.2$ Hz, C-6′), 154.0 (poorly resolved doublet, C-7′), 128.4 (d, $^{1}J(C,P) = 69.2$ Hz, C-1″), 133.9 (d, $^{2}J(C,P) = 10.9$ Hz, C-2″,6″), 129.3 (d, $^{3}J(C,P) = 11.8$ Hz, C-3″,5″), 132.3 (d, $^{4}J(C,P) = 2.8$ Hz, C-4″)

in the bound ligand in which there is electron delocalization [$-N^{-}-C{=}O \leftrightarrow -N{=}C-O^{-}$]. The ν(C=N) vibration band is only slightly shifted (1569 cm^{-1} **4**, 1571 cm^{-1} **5**, 1578 cm^{-1} **6**). In the complex **4** there is a band at 2212 cm^{-1} due to coordinated cyanate ion. In the spectra of all complexes as well as the ligand the position of the band corresponding to ν(C–P) vibrations is constant (1434 cm^{-1} **3**, 1434 cm^{-1} **4**, 1431 cm^{-1} **5**, 1433 cm^{-1} **6**).

In the ^{1}H NMR spectrum of ligand **3** (Table 1), the signal of the aldehyde proton of **1** disappears, and is replaced by the signal of hydrazone CH at 9.27 ppm. This signal is a doublet ($J = 4.8$ Hz) due to coupling of the imine proton with phosphorus.

The ligand structure was also confirmed by ^{13}C NMR spectrum (Table 1) in which there is a signal of the hydrazone carbon coupled to phosphorus at 148.6 ppm instead of the aldehyde carbon in compound **1** at 191.7 ppm. The assignment of ^{13}C NMR resonances both in the ligand and in the complex was performed using literature data [13] and DEPT spectral data.

From the ^{1}H NMR spectra of complexes **5** and **6** (Table 1) it can be seen that ligand **3** is coordinated in monodeprotonated form, since the signal of hydrazide NH at 12.38 ppm is absent.

This deprotonation increases electron density at the hydrazide oxygen, facilitating coordination. In the spectra of **5** and **6** chemical shifts of aromatic protons have generally higher values, due to electron withdrawal by the coordinated metal ion. The signal of CH from the hydrazone function is shifted upfield in both complexes.

The ^{13}C NMR spectra (Table 1) provide evidence that in complexes **5** and **6** coordination sites are the phosphorus atom, the hydrazone nitrogen (N-3), and the hydrazide oxygen (O-2).

The consequence of coordination through N-3 is a strong downfield shift of the hydrazone carbon C-7′, and of the *para*-carbon C-4′. Due to coordination *via* the hydrazide oxygen, there is a strong downfield shift of the corresponding carbon C-2. Coordination through phosphorus can be evidenced by strong upfield shifts of signals of carbon atoms directly bound to phosphorus (C-2′ and C-1″), and by downfield shifts of carbons *para* to phosphorus (C-5′, C-4″). Another interesting feature of the spectra is splitting of signals of carbonyl carbons C-1 and C-2 in the complexes, which are singlets in the spectra of ligand **3**. These carbons are in remote positions from the phosphorus atom in ligand **3** and there is no coupling. However, in complexes **5** and **6**, due to coordination *via* O-2, C-2 and C-1 are separated from phosphorus by three and four bonds, respectively, and the signals are split.

Low values of electric conductivity indicate that all complexes are neutral, *i.e.* that the bound ligand is monodeprotonated.

Magnetic measurements of complex **4** indicate that it is paramagnetic with tetrahedral geometry.

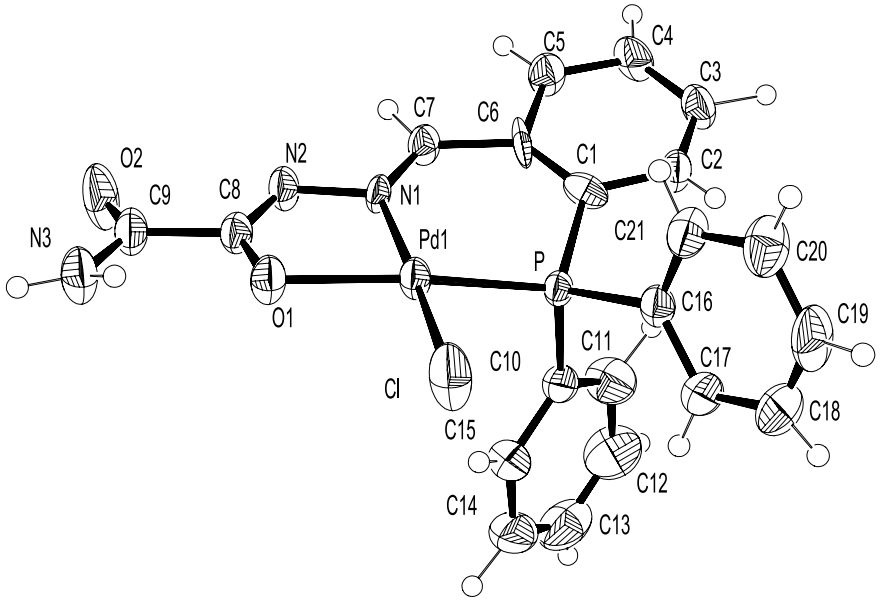


Fig. 1. Perspective view of the molecular structure of complex **5**, showing atom numbering and thermal displacement ellipsoids (50% probability level)

In summary, elemental analysis, spectral data, molar conductivity, and magnetic measurements show that complex **4** has a tetrahedral geometry, and that **5** and **6** have a square planar geometry.

The confirmation of the structure of complex **5** was obtained by X-ray crystal analysis.

The molecular structure of complex **5** determined by single crystal X-ray diffractometry is shown in Fig. 1, along with the labeling scheme.

Table 2 reports the most relevant bond lengths and angles relative to Pd coordination.

The monodeprotonated ligand **3** acts as a PNO tridentate chelating agent towards the Pd atom, which completes its square planar coordination by bonding to a Cl atom, *trans* to the nitrogen donor. The overall geometry of the chelated system is close to planar (maximum deviation within 0.55 Å), apart from the terminal diarylphosphine group. However, as usually observed in this class of complexes [14, 15], the P atom lies significantly out (0.64 Å) of the average molecular plane (maximum deviation within 0.28 Å when P is excluded from calculation). The PNO coordination generates a five-membered and a six-membered chelation ring;

Table 2. Most relevant bond lengths [Å] and angles [°] for complex **5**

Pd(1)–N(1)	2.003(4)
Pd(1)–O(1)	2.085(3)
Pd(1)–P	2.198(1)
Pd(1)–Cl	2.279(1)
N(1)–C(7)	1.269(6)
N(1)–N(2)	1.408(5)
N(2)–C(8)	1.302(6)
N(3)–C(9)	1.339(7)
O(1)–C(8)	1.289(6)
O(2)–C(9)	1.204(7)
C(1)–C(6)	1.310(8)
C(6)–C(7)	1.473(6)
C(8)–C(9)	1.536(7)
N(1)–Pd(1)–O(1)	79.8(1)
N(1)–Pd(1)–O(1)	93.5(1)
O(1)–Pd(1)–P	167.2(1)
N(1)–Pd(1)–Cl	175.1(1)
O(1)–Pd(1)–Cl	96.4(1)
P–Pd(1)–Cl	90.71(5)
C(7)–N(1)–N(2)	114.9(4)
C(7)–N(1)–Pd(1)	132.0(3)
N(2)–N(1)–Pd(1)	113.1(3)
C(8)–N(2)–N(1)	111.9(4)
C(8)–O(1)–Pd(1)	107.4(3)
C(1)–C(6)–C(7)	133.0(6)
N(1)–C(7)–C(6)	123.9(5)
O(1)–C(8)–N(2)	127.2(4)
O(1)–C(8)–C(9)	117.9(4)

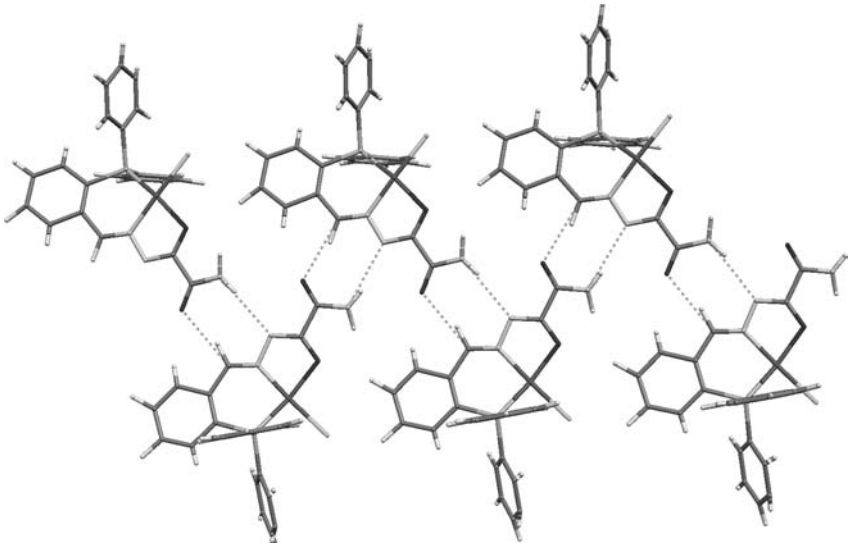


Fig. 2. Array of hydrogen bonded complexes **5** in the crystal packing, based on C–H···O and N–H···N hydrogen bonds (dotted)

the former is planar within 0.05 Å, while the latter is relevantly puckered (*Cremer* and *Pople* parameters [16]: total amplitude QT = 0.34, spherical polar angle $\theta 2 = 58^\circ$), due to the above described deviation of the P atom from the coordination plane. The coordination bonds lengths (Table 2) are in agreement with those observed in two closely related Pd complexes [14, 15], where the terminal –C(O)–NH_2 group is replaced by a phenyl substituent.

The crystal packing of complex **5** (Fig. 2) is based on the association in chains by weak CH···O (C7–H···O2 (3/2-x, y-1/2, 3/2-z), C···O = 3.150(6) Å, C–H···O = 157(4)°) and NH···N hydrogen bonds (N3–H···N2 (3/2-x, 1/2 + y, 3/2-z), N···N = 3.405(6) Å, N–H···N = 150(6)°).

Antibacterial activity of the ligand and the complexes was tested against *Gram* positive bacteria *Staphylococcus aureus* ATCC 6538, and *Gram* negative bacteria *Escherichia coli* ATCC 35218 and *Salmonella enteritidis* ATCC 13076, while antifungal activity was tested against *Candida albicans* (clinical isolate) (Table 3).

Table 3. Minimal inhibitory concentration (m*M*) of the investigated compounds to selected microorganisms

Compound	*S. aureus*	*E. coli*	*S. enteritidis*	*C. albicans*
3	1.61	1.61	1.61	1.07
4	0.78	0.59	0.59	0.59
5	0.77	0.77	0.77	0.77
6	0.66	0.66	0.66	0.66
K_2PtCl_4	1.93	1.45	1.45	1.45
K_2PdCl_4	2.45	1.23	1.83	1.23
DMSO	–	–	–	–
Control	0.57	1.14	1.14	1.93

Minimal inhibitory concentrations (*MIC*) of both the ligand and the complexes were of the same order of magnitude as for ampicillin and bifonazole against bacteria and fungi, respectively. The complexes with ligand **3** were more active than either the ligand **3** or the tetrachloro complexes, but there was no significant difference in activities of complexes of different metals.

Experimental

Physical Measurements

Magnetic moment was determined using the magnetic balance MSB-MK1 (Sherwood Scientific Ltd. Cambridge, UK), at room temperature (25°C) with $Hg[Co(SCN)_4]$ as calibrant; diamagnetic corrections were calculated from *Pascal's* constants. IR spectra were recorded on Perkin-Elmer FT-IR 1725X spectrophotometer by the KBr technique. NMR spectra were obtained in *DMSO*-d_6 using Varian-Gemini 2000 spectrometer (^{1}H at 200 MHz, ^{13}C at 50.3 MHz). Chemical shifts (δ) are given in ppm using *TMS* (tetramethylsilane) as internal standard. Melting points (uncorrected) were determined using Büchi instrument. Elemental analysis (C, H, N) was performed by the standard micromethod at the Center for Instrumental Analysis of the Faculty of Chemistry, University of Belgrade, using the ELEMENTAR Vario ELIII C.H.N.S/O analyser. The results of elemental analysis were found to be in good agreement with the calculated values. Molar conductivity of *DMF* solutions (concentration range 10^{-4} to 10^{-3} mol/dm^3) was measured at room temperature (25°C) on the digital conductometer JENWAY 4009.

Table 4. Crystal data and structure refinement for complex **5**

Empirical formula	$C_{21}H_{17}ClN_3O_2PPd$
Formula weight	516.20
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P\ 2_1/n$
Unit cell dimensions	$a = 12.405$ Å $\quad \beta = 109.403°$
	$b = 10.4254$ Å
	$c = 16.5090$ Å
Volume	2013.8(3) Å^3
Z	4
Density (calculated)	1.703 Mg/m^3
Absorption coefficient	1.157 mm^{-1}
$F(000)$	1032
Crystal size	$0.1 \times 0.07 \times 0.05$ mm^3
θ range for data collection	1.80 to 27.49°
*I*ndex ranges	$-15 \le h \le 15,\ -13 \le k \le 13,\ -20 \le l \le 20$
Reflections collected	20953
Independent reflections	4517 [R(int) = 0.0313]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4517/0/330
Goodness-of-fit on F^2	1.127
Final R indices [$I > 2$sigma(I)]	$R1 = 0.0513$, $wR2 = 0.1235$
R indices (all data)	$R1 = 0.0640$, $wR2 = 0.1300$
Largest ΔF maximum/minimum	2.376/−1.025 e.Å^{-3}

Crystallographic analysis: single crystal X-ray diffraction studies: MoKα radiation ($\lambda = 0.71073$ Å), $T = 293$ K, was used for data collection (SMART AXS 1000 CCD diffractometer). *Lorentz*, polarization, and absorption corrections were applied [17]. The structure was solved by direct methods using SIR97 [18] and refined by full-matrix least-squares on all F^2 using SHELXL97 [19], implemented in the WingX package [20]. Hydrogen atoms were located on *Fourier* difference maps and refined isotropically. Anisotropic displacement parameters were refined for all non-hydrogen atoms. Hydrogen bonds have been analyzed with SHELXL97 [19] and PARST97 [21]. Table 4 reports details of structure determination and refinement. In the discussion of the results, extended use has been made of the software of the Cambridge Structural Database (CSD) [22].

Complete list of coordinates, bond lengths, bond angles, and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Center (CCDC 283325).

Antimicrobical Activity Determination

The antimicrobical activity was determined by microdilution method. The following microorganisms were used: *Escherichia coli* ATCC 35218, *Salmonella enteritidis* ATCC 13076, *Staphylococcus aureus* ATCC 6538, and *Candida albicans* (clinical isolates) from Mycoteca of the Mycological Laboratory, Department of Plant Physiology, Institute for Biological Research, Belgrade. Test microorganisms were cultivated overnight at 37°C in TSB medium (Tryptic Soy Broth Biolife). Suspensions containing $\sim 10^9$ cells/cm^3 were used.

MIC determinations were performed by a serial dilution technique using 96-well microtitre plates. The compounds investigated were dissolved in nutrition broth (TSB) with microorganisms inocula. The microplates were incubated for 24 h at 37°C, after which 50 mm^3 of 0.2 mg/cm^3 solution of *INT* (*p*-iodonitrotetrazolium violet) were added to each row and the plate was returned to the incubator for 1 h to ensure adequate colour development. Inhibition of growth was indicated by a clear solution or absence of colour reaction [23]. The corresponding concentration was taken as the *MIC* of the compounds. Bifonazole was used as a positive control for *C. albicans*, and ampicillin for bacterial species.

2-{(2E)-2-[2-(Diphenylphosphino)benzylidene]hydrazino}-2-oxoacetamide

(**3**, $C_{21}H_{18}N_3O_2P \cdot 1/2C_2H_5OH$)

A mixture of 370 mg (1.27 mmol) **1** and 130 mg (1.26 mmol) **2** was dissolved, by heating, in 35 cm^3 ethanol, *pH* was adjusted to ~4 with a few drops of hydrochloric acid and it was refluxed for 45 min. The solution was left to stand at room temperature for 24 h. White flaky crystals were filtered off and purified by recrystallization from 45 cm^3 ethanol. The solution was left again to stand at room temperature for 24 h, after which it was filtered. Yield 400 mg (78.90%); mp 232–233°C; IR (KBr): $\bar{\nu} = 3567$(w), 3426(w), 3052(w), 3005(w), 1695(vs), 1676(vs), 1584(w), 1558(s), 1460(s), 1432(s), 1294(s), 1198(s), 1124(s), 1092(s), 1068(s), 1024(w), 845(s), 752(vs), 698(vs), 672(s), 508(s), 450(s), 409(s) cm^{-1}; ^{1}H and ^{13}C NMR spectral data for **3** are listed in Table 1.

Preparation of the Nickel(II) Complex (**4**, $C_{22}H_{21}N_4NiO_5P$)

A mixture of 190 mg (0.65 mmol) $Ni(NO_3)_2 \cdot 6H_2O$ and 250 mg (0.63 mmol) **3** was dissolved, by heating at 50°C, in 45 cm^3 methanol and then the solution of NaOCN, prepared by dissolving 180 mg (0.62 mmol) with heating in 30 cm^3 methanol, was added to it. The color of the solution changed from brown to reddish. The mixture was refluxed for 45 min. The solution was left to stand at room temperature for three days. The brown precipitate was filtered off and washed with a small portion of methanol. Yield 190 mg (59.38%); IR (KBr): $\bar{\nu} = 3408$(w), 3310(w), 3053(w), 2212(vs), 1687(s), 1569(vs), 1478(w), 1434(s), 1316(s), 751(s), 699(s) cm^{-1}; μ_{eff} (293 K) = 2.80 μ_B, $\Lambda_M = 0.06\,\Omega^{-1}\,\text{cm}^2\,\text{mol}^{-1}$.

Preparation of the Palladium(II) Complex (**5**, $C_{21}H_{17}ClN_3O_2PPd$)

190 mg (0.48 mmol) **3** were dissolved, by heating at 65°C, in 40 cm^3 ethanol. After that, a solution of $K_2[PdCl_4]$, prepared by dissolving 160 mg (0.49 mmol) in 20 cm^3 H_2O with gentle heating, was added

to it. Right after that, the mixing temperature was decreased to 57°C, and the mixture was heated at that temperature for 45 min. The solution was left to stand at room temperature for three days. Yellow monocrystals were filtered off and washed with a small amount of ethanol. Yield 190 mg (80%); IR (KBr): $\bar{\nu} = 3475$(s), 3389(w), 3300(w), 3251(w), 1705(s), 1571(s), 1533(vs), 1480(w), 1431(w), 1387(w), 1275(s), 748(w), 698(s), 546(s), 514(s) cm^{-1}; $\Lambda_M = 20.08\ \Omega^{-1}\,cm^2\,mol^{-1}$; ^1H and ^{13}C NMR spectral data for **5** are listed in Table 1.

Preparation of the Platinum(II) Complex (**6**, $C_{21}H_{17}ClN_3O_2PPt$)
200 mg (0.50 mmol) **3** were dissolved, by heating at 65°C, in 40 cm^3 ethanol. After that, a solution of $K_2[PtCl_4]$, prepared by dissolving 210 mg (0.51 mmol) in 20 cm^3 H_2O, was added to it. Immediately after that, the mixing temperature was decreased to 50°C and the solution was stirred for 15 min and stirred without heating for 30 min more. The solution was left to stand at room temperature for three days. The yellow–brown crystals were filtered off and washed with a small portion of ethanol. Yield 190 mg (85.71%); IR (KBr): $\bar{\nu} = 3479$(s), 3324(w), 3261(w), 1710(vs), 1578(s), 1540(vs), 1481(w), 1433(s), 1385(w), 1273(s), 1100(w), 707(s), 694(s), 556(s), 516(s), 497(s) cm^{-1}; $\Lambda_M = 17.56\ \Omega^{-1}\,cm^2\,mol^{-1}$; ^1H and ^{13}C NMR spectral data for **6** are listed in Table 1.

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