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A New Nickel(II) Complex Derived From Bisthiocarbohydrazone: Synthesis, Characterization, Crystal Structure and Antioxidant Activity

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ABSTRACT

A new complex with composition [Ni(L)(PPh$_3$)] (PPh$_3$ = triphenylphosphine) was obtained from the reaction of 1,5-bis(salicylidene)thiocarbohydrazone (L) with an equimolar amount of [NiCl$_2$(PPh$_3$)$_2$]. The complex was identified by FT-IR, ^{1}H NMR and UV-Vis spectroscopic methods and elemental analysis. The solid state structure of [Ni(L)(PPh$_3$)] was established by X-ray diffraction analysis. It was determined that the complex, whose nickel center has a distorted square planar configuration, crystallizes in the monoclinic space group I2/c. Bisthiocarbohydrazone (L) binds to the nickel center through its phenolate O, azomethine N and thioenolate S atoms in a dianionic tridentate mode. The antioxidant capacity of L and Ni(II) complex was examined using the CUPRAC (cupric reducing antioxidant capacity) method. Also, the DPPH (1,1-Diphenyl-2-picrylhydrazyl) method was used to test free radical scavenging activity of the compounds. Antioxidant activity results showed that L exhibited better activity than Ni(II) complex.

Keywords: Thiocarbohydrazone, Nickel(II) complex, Triphenylphosphine, Crystal structure, Antioxidant activity.

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Introduction

Compounds with C=S and C-SH groups are substantial organic compounds as they are potential donor ligands for transition metal ions [1, 2]. Thiocarbohydrazide is a compound with two hydrazine and one thione group. Thiocarbohydrazide is a precursor compound in the formation of macrocyclic ligands for the binding of a wide variety of metals [3, 4]. The hydrazine groups of thiocarbohydrazide can react with aldehydes or ketones to form bis- or monothiocarbohydrazones [5, 6]. Thiocarbohydrazones have the ability to form chelates with various metal ions through donor groups originating from both thiocarbohydrazide and aldehyde or ketone molecules [7]. Thiocarbohydrazones and their metal complexes have some activities or features such as antitumor, antioxidant, antimicrobial, antiviral, antitubercular, physicochemical, carbonic anhydrase and acetylcholinesterase inhibitors, electrochemical and corrosion inhibitors [8, 9]. Thiocarbohydrazones can also be used for the extraction and sensing of heavy metal ions [10, 11].

Nickel(II) complexes containing S and N donor ligands are of great interest because some enzymes such as hydrogenases and carbon monoxide dehydrogenases have nickel complexes in their active sites [12].

Phosphine-based ligands are among the important compounds as they exhibit significant efficiency in transition metal-catalyzed reactions. The development of suitable new phosphine ligands to make a reaction more efficient is an important aspect in catalyst development [13, 14]. These compounds also have important bioactivities such as antitumor, antiviral, antifungal, antibacterial and antioxidant [15, 16].

Reactive oxygen species (ROS) produced in high concentrations cause adverse changes in lipids, proteins and DNA components. The disruption of the balance between the detoxification of ROS and the production and accumulation of these reagents is called "oxidative stress". Oxidative stress causes some diseases such as cancer, hypertension, neurological disorders and diabetes. Antioxidants, which are effective in eliminating the detrimental effects of ROS, can protect cells from the formation of diseases caused by oxidative stress [17, 18]. So, in this study, a new Ni(II) complex was synthesized from 1,5-bis(salicylidene)thiocarbohydrazone (L) and [NiCl$_2$(PPh$_3$)$_2$] in order to test its potential antioxidant activity. L and Ni(II) complex were characterized using FT-IR, ^{1}H NMR, UV-Vis spectroscopies and elemental analysis. The antioxidant activities of the compounds were also examined using DPPH and CUPRAC methods.

Materials and Methods

Thiocarbohydrazide was gained as described in the previously published procedure [19]. All other chemicals and solvents were purchased and used as received. IR and ^{1}H NMR spectra, UV-Vis data (in 4 x 10^{-5} M DMSO), elemental analysis and magnetic moment measurements were obtained using an Agilent Cary 630 FTIR, a Varian UNITY INOVA 500

MHz NMR device, a Shimadzu 2600 UV-Vis spectrophotometer, a Thermo Finnigan Flash EA 1112 elemental analyzer and a Sherwood Scientific MK I model device, respectively.

Single crystals of $[Ni(L)(PPh_3)]$ were obtained by slow evaporation of a methanol+dichloromethane+DMSO solution of the solid complex. A Bruker APEX II CCD diffractometer was used for data collection at room temperature. Structure solution and refinement were performed with the SHELXT [20] and SHELXL [21] programs. Indexing, data reduction and integration were performed using APEX2 [22] and SAINT [23]. The crystallographic data of $[Ni(L)(PPh_3)]$ are given in Table 1. The selected bond angles and distances are listed in Table 2.

Synthesis of 1,5-bis(salicylidene)thiocarbohydrazone (L)

1,5-bis(salicylidene)thiocarbohydrazone (L) was obtained according to our published procedure (Figure 1) [24].

Color: Light yellow. Yield: 85%. M.p.: 190-191 °C. Calc. for $C_{15}H_{14}N_4O_2S$ (314.36 g mol^{-1}): C: 57.31, H: 4.49, N: 17.82, S: 10.20%; found: C: 57.50, H: 4.46, N: 17.84, S: 10.28%. IR (cm^{-1}): ν(OH) 3195, ν(NH) 3133, ν(C=N) 1613, ν(C=S) 1240. ^{1}H NMR (500 Mhz, DMSO-d_6, ppm): 11.70 (s, 2H, -OH), 11.62 (s, 1H, -NH), 10.62 (s, 1H, -NH), 8.67 (s, 2H, -CH=N-), 7.35-6.89 (m, 8H, aromatic H). UV-Vis [λ_{max} (log ε), nm (dm^3 cm^{-1} mol^{-1})]: 251 (3.90) $\pi\rightarrow\pi^*$, 302 (4.19) $\pi\rightarrow\pi^*$, 351 (4.53) $n\rightarrow\pi^*$, 367 (4.43) $n\rightarrow\pi^*$.

Synthesis of 1,5-bis(salicylidene)thiocarbohydrazone-triphenylphosphine-nickel(II) [Ni(L)(PPh$_3$)]

A solution of $[NiCl_2(PPh_3)_2]$ (0.654 g, 1 mmol) in ethanol (10 mL) was added to a stirring solution of L (0.314 g, 1 mmol) in ethanol (10 mL) and dichloromethane (5 mL). 2 drops of triethylamine were added to the mixture and the mixture was stirred under reflux for 5 h to give a red solution. Red colored product was obtained by slow evaporation. The product was filtered and washed with ethanol and dried under vacuum (Figure 1).

Color: Dark red. Yield: 54%. M.p.: 242-244 °C. Calc. for $C_{33}H_{27}N_4NiO_2PS$ (633.32 g mol^{-1}): C: 62.58, H: 4.30, N: 8.85, S: 5.06%; found: C: 62.33, H: 4.12, N: 8.64, S: 4.91%. IR (cm^{-1}): ν(OH) 3185, ν(NH) 3116, ν(C=N) 1617 and 1598, ν(PPh_3) 1433, 1096, 737, 690. ^{1}H NMR (500 Mhz, DMSO-d_6, ppm): 11.53 (s, 1H, -OH), 10.71 (s, 1H, -NH), 8.50 (s, 1H, -CH=N-), 8.09 (s, 1H, -CH=N-), 7.76-5.75 (m, 23H, aromatic H). UV-Vis [λ_{max} (log ε), nm (dm^3 cm^{-1} mol^{-1})]: 257 (4.47) $\pi\rightarrow\pi^*$, 287 (4.34) $\pi\rightarrow\pi^*$, 339 (4.29) $n\rightarrow\pi^*$, 387 (4.36) $n\rightarrow\pi^*$ and 435 (4.22) LMCT.

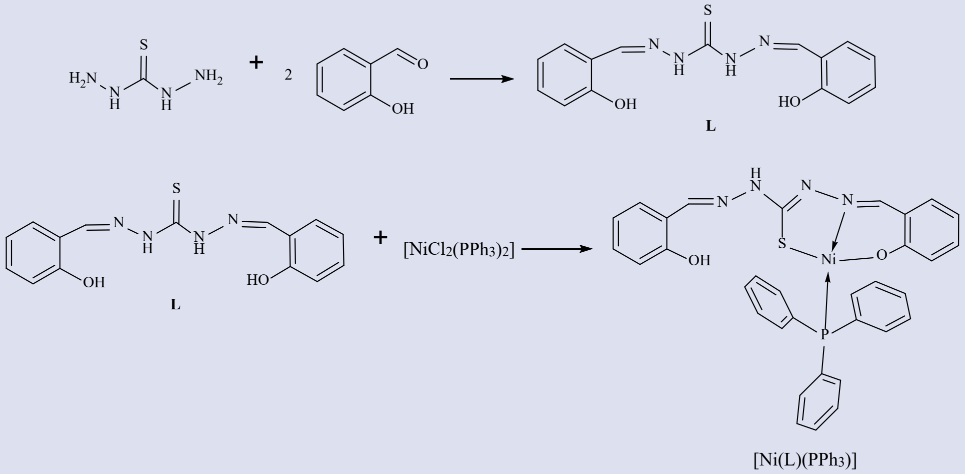

Figure 1. The general synthesis of L and Ni(II) complex.

Determination of Antioxidant Activity by DPPH and CUPRAC Assays

The DPPH radical scavenging activities of L and Ni(II) complex were determined by the method of Brand-Williams et al. with minor changes [25]. 2 mL of 10^{-4} M DPPH in ethanol, 1 mL of 10^{-4} M of the sample in ethanol (containing 1% DMSO) and (1-x) mL of ethanol were added to a glass test tube. The mixture was incubated for 30 min at 25 °C. Then, the absorbance values of the solutions in test tubes were measured against ethanol at 515 nm. The control solution consisted of a mixture of DPPH solution (2 mL) and ethanol (2 mL). Trolox was used as the reference compound. The radical scavenging activity was computed from this equation: % DPPH radical scavenging activity = $[A_{control} - A_{sample} / A_{control}] \times 100$, where $A_{control}$ is the absorbance of the control solution and A_{sample} is the absorbance of the sample-radical mixture solution.

Antioxidant capacities of L and Ni(II) complex were determined by CUPRAC method [26]. 1 mL of 10^{-2} M $CuCl_2.2H_2O$ in water, 1 mL of 7.5 x 10^{-3} M neocuproine in ethanol, 1 mL of 1 M NH_4Ac in water, x mL of 10^{-4} M sample in ethanol (containing 1% DMSO) and (1.1 - x) mL of water were added to a glass test tube. The mixture was incubated for 30 min at 25 °C. Then, the absorbance values of the solutions in test tubes were recorded at 450 nm. The results were given as TEAC (trolox equivalent antioxidant capacity) coefficient. TEAC values were calculated by dividing the molar absorptivity (Ɛ) of the compounds by that of Trolox (ε_{trolox} = 1.67 x 10^4 L mol^{-1} cm^{-1}).

Results and Discussion

Synthesis and Spectral Features

1,5-bis(salicylidene)thiocarbohydrazone (L) was obtained by the reaction of thiocarbohydrazide with salicylaldehyde in a mole ratio of 1:2. The reaction of L (1 mmol) with [$NiCl_2(PPh_3)_2$] (1 mmol) resulted in the formation of the Ni(II) complex {[Ni(L)(PPh_3)]}. [Ni(L)(PPh_3)] is soluble in DMF, DCM and DMSO solvents. The μ_{eff} measurement showed that the complex is diamagnetic. The elemental analysis and spectroscopic data agree with the proposed molecular formula of L and Ni(II) complex.

The characteristic bands of OH and NH groups were seen at 3195 and 3133 cm^{-1} in the IR spectrum of L. These bands, whose intensity decreased after complex formation, were observed at 3185 and 3116 cm^{-1} in the spectrum of [Ni(L)(PPh_3)]. The appearance of these bands in the spectrum of the complex supports that one of the OH and NH groups of L did not participate in the formation of the complex. The fact that the band seen in the spectrum of L and attributed to ν(C=S) did not appear in the spectrum of [Ni(L)(PPh_3)] can be explained as one NH group and the C=S group form C-SH by tautomerism. The shift of one of the bands of the azomethine groups in the spectrum of L to a lower wave number (1598 cm^{-1}) in the spectrum of [Ni(L)(PPh_3)] indicates the coordination of one of the azomethine nitrogen atoms with the metal atom. In the spectrum of [Ni(L)(PPh_3)], characteristic peaks of triphenylphosphine were also observed at 1433, 1096, 737, 690 cm^{-1}, respectively [24, 27, 28]. IR spectrum of [Ni(L)(PPh_3)] is given in Figure S1.

In the ^{1}H NMR spectrum of L, one of the peaks corresponding to two $OH_{phenolic}$ protons at 11.70 ppm was observed at 11.53 ppm, corresponding to a single OH phenolic proton in the NMR spectrum of [Ni(L)(PPh_3)]. This indicates that one of the OH groups of L is bonded to the nickel(II) ion by deprotonation. The spectrum of L exhibited two NH signals at 11.62 and 10.62 ppm. In the spectrum of [Ni(L)(PPh_3)], only one NH signal was found at 10.71 ppm. The disappearance of one of the H atoms of the two NH groups indicates the deprotonation of the H atom in the NH group through the sulfur atom by tautomerism. One of the signals belonging to the two azomethine protons at 8.67 ppm in the spectrum of L shifted to 8.09 ppm after the formation of the complex. This indicates the coordination of one of the azomethine groups of L to the nickel(II) ion [24, 29, 30]. ^{1}H NMR spectrum of [Ni(L)(PPh_3)] is given in Figure S2.

The UV-Vis spectrum of L exhibited two absorptions at 251 and 302 nm corresponding to $\pi\rightarrow\pi^*$ transitions of aromatic rings. These bands were seen at 257 and 287 nm in the spectrum of [Ni(L)(PPh_3)]. Other bands at 351 and 367 nm in the spectrum of L are assigned to $n\rightarrow\pi^*$ transitions of the C=N and C=S groups. These bands appear at 339 and 387 nm in the spectrum of [Ni(L)(PPh_3)]. This can be interpreted that the metal atom is coordinated to the ligand via the azomethine nitrogen and sulfur atoms. In addition, the band attributed to the charge transfer transition (LMCT) was observed at 435 nm in the spectrum of [Ni(L)(PPh_3)] [27, 31, 32]. UV-Vis spectrum of [Ni(L)(PPh_3)] is given in Figure S3.

Crystal Structure Interpretation

Crystallographic analysis results showed that [Ni(L)(PPh_3)] crystallizes in the I2/c space group and as a monoclinic crystal system. The molecular structure of [Ni(L)(PPh_3)] is shown in Figure 2. The asymmetric unit of the complex contains two crystallographically independent [Ni(L)(PPh_3)] molecules with almost similar parameters. In the complex, bisthiocarbohydrazone (L) is coordinated to nickel(II) ion by using its phenolic O, azomethine N and thiolate S atoms and acted as a dibasic tridentate donor by forming six and five-membered rings with O2-Ni1-N4, O4-Ni2-N8 and N4-Ni1-S1, N8-Ni2-S2 angles of 95.3(2)°, 94.8(2)° and 87.59(17)°, 87.81(17)°. These angles are similar to those observed in related Ni(II) complexes [30, 33, 34]. Fourth coordination site is completed by the phosphorus atom of PPh_3 molecule and the variation in the bonding parameters indicates that there is a distorted square planar geometry around the nickel(II) ion. Ni1-S1 [2.139(3) Å], Ni2-S2 [2.135(3) Å], Ni1-O2 [1.843(4) Å], Ni2-O4 [1.844(4) Å], Ni1-N4 [1.892(5) Å], Ni2-N8 [1.888(5) Å], Ni1-P1 [2.210(2) Å] and Ni2-P2 [2.228(2) Å] bond distances are within normal ranges and are in good agreement with those found in four-coordinate Ni(II) complexes containing triphenylphosphine [15, 35, 36]. C-S bond distances are 1.737(6) Å and 1.748(6) Å, indicating that free bisthiocarbohydrazone (L) is bound to metal in the thiolate form [37]. Finally, the crystal structure of [Ni(L)(PPh_3)] is stabilized by weak and moderately bound intramolecular and intermolecular hydrogen bonds (Table 3).

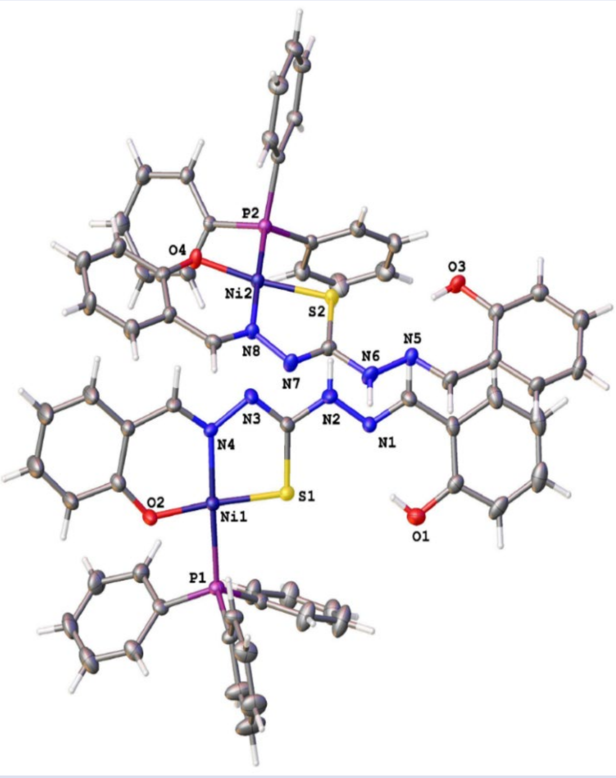

Figure 2. The molecular structure of [Ni(L)(PPh_3)] with hetero atom numbering scheme.

Table 1. Crystal data and structure refinement parameters for $[Ni(L)(PPh_3)]$.

CCDC	2196021
Empirical formula	$C_{33}H_{27}N_4NiO_2PS$
Formula weight	633.31
Temperature (K)	298
Crystal system	Monoclinic
Space group	I2/c
a (Å)	27.95(3)
b (Å)	7.852(10)
c (Å)	57.84(7)
α (°)	90
β (°)	102.08(5)
γ (°)	90
Volume (Å^3)	12413(26)
Z	16
Crystal size (mm^3)	0.707 × 0.14 × 0.062
Wavelength (Å)	0.71073
D_{calc} (g.cm^{-3})	1.356
μ (mm^{-1})	0.780
F(000)	5248.0
θ range for data collection (°)	2.88 to 49.998
Index ranges	$-32\leq h\leq 32$, $-9\leq k\leq 9$, $-68\leq l\leq 68$
Reflections collected	36995
Independent reflections	10908
Data/restraints/parameters	10908/0/759
Goodness-of-fit on F^2 (S)	0.909
Final R indexes [I ≥ 2σ(I)]	R_1 = 0.0693, wR_2 = 0.1255
Final R indexes [all data]	R_1 = 0.1862, wR_2 = 0.1539
Largest diff. peak/hole (e.Å^{-3})	0.51/-0.53

Table 2. The selected bond lengths (Å) and angles (°) of $[Ni(L)(PPh_3)]$.

Bond lengths (Å)		Bond angles (°)	
Ni1—S1	2.139(3)	S1—Ni1—O2	175.14(14)
Ni2—S2	2.135(3)	S2—Ni2—O4	173.26(13)
Ni1—O2	1.843(4)	N4—Ni1—P1	177.48(16)
Ni2—O4	1.844(4)	N8—Ni2—P2	176.25(15)
Ni1—N4	1.892(5)	O2—Ni1—P1	86.50(15)
Ni2—N8	1.888(5)	O4—Ni2—P2	86.72(14)
Ni1—P1	2.210(2)	O2—Ni1—N4	95.3(2)
Ni2—P2	2.228(2)	O4—Ni2—N8	94.8(2)
N4—N3	1.415(6)	S1—Ni1—P1	90.69(9)
N8—N7	1.410(6)	S2—Ni2—P2	91.03(10)
N2—N1	1.351(6)	S1—Ni1—N4	87.59(17)
N6—N5	1.380(6)	S2—Ni2—N8	87.81(17)
C8—S1	1.737(6)		
C41-S2	1.748(6)		

Table 3. Geometric values for hydrogen bonds for $[Ni(L)(PPh_3)]$.

D-H···A	D-H [Å]	H···A [Å]	D···A [Å]	D-H···A [°]
O1-H1···N1	0.820(4)	1.918(5)	2.634(7)	145.3(4)
O3-H3A···N5	0.820(4)	1.924(5)	2.636(7)	144.6(3)
N2-H2···S2	0.860(6)	2.700(3)	3.335(6)	131.8(4)
N6-H6A···S1^{i}	0.860(6)	2.784(3)	3.446(7)	135.0(4)
O3-H3A···S2	0.820(4)	2.911(3)	3.616(5)	145.5(3)
C35-H35···O3^{ii}	0.931(7)	2.608(5)	3.507(9)	162.4(4)
C53-H53···S2^{iii}	0.930(8)	3.002(3)	3.820(9)	147.7(5)
O1-H1···S1	0.820(4)	3.015(3)	3.723(6)	146.0(4)

Symmetry codes: (i) +x, -1+y, +z; (ii) 1-x, +y, ½-z; (iii) +x, 1+y, +z.

Antioxidant Properties

The total antioxidant capacity of L and Ni(II) complex was determined using the CUPRAC method. When the TEAC values (Table 4) are examined, it is seen that the total antioxidant capacity of both L and Ni(II) complex is better than Trolox ($TEAC_{trolox}$ = 1). Also, L (TEAC = 3.54 ± 0.719) exhibits higher activity than $[Ni(L)(PPh_3)]$ (TEAC = 2.58 ± 0.107). The free radical scavenging activity (Table 5) of $[Ni(L)(PPh_3)]$ is also lower than that of L, which is parallel with the antioxidant capacity results. The position and number of OH groups and the contribution of NH groups are factors that affect the antioxidant activity of thiocarbohydrazone [38, 39]. Therefore, we can say that the decrease in the number of OH and NH groups in L by complexation is the reason why the antioxidant activity of $[Ni(L)(PPh_3)]$ is lower than that of L.

Table 4. The TEAC values of the compounds.

Compounds	TEAC	Correlation coeff. (r)
L	3.54 ± 0.719	0.9939
$[Ni(L)(PPh_3)]$	2.58 ± 0.107	0.9997

$TEAC_{Trolox}$ = 1.00.

Table 5. % free radical scavenging activities of the compounds.

Compounds	Free Radical Scavenging Activity (%)
L	77.84 ± 0.19
$[Ni(L)(PPh_3)]$	63.65 ± 3.28
Trolox	82.33 ± 2.95

Conclusion

A new Ni(II) complex was synthesized from 1,5-bis(salicylidene)thiocarbohydrazone (L) and $[NiCl_2(PPh_3)_2]$ and its structure was characterized by various spectroscopic methods and elemental analysis. The distorted square planar geometry around the nickel center with surrounding ONSP atoms was confirmed by single crystal crystallographic results. The X-ray diffraction analysis showed that L binds with nickel(II) ion in a tridentate mode through N atom of the azomethine, O atom of the hydroxyl group and S atom in $[Ni(L)(PPh_3)]$. The fourth coordination was completed with a phosphorus atom of triphenylphosphine co-ligand. The examination of the antioxidant activities of L and its Ni(II) complex by various antioxidant assays (CUPRAC and DPPH methods) disclosed that L exhibited higher antioxidant capacity and free radical scavenging abilities compared to the Ni(II) complex. The antioxidant potential of phenolic compounds depends on the number and arrangement of the hydroxyl groups in the molecules of interest. Also, the presence of NH and SH groups contributes to antioxidant properties. So, we can say that the excess of OH and NH groups in L is the reason why L has higher antioxidant activity compared to Ni(II) complex. In conclusion, L and Ni(II) complex with good antioxidant activity can be used for therapeutic purposes to eliminate radical oxygen species formed as a result of some metabolic diseases.

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I dedicate this paper to Prof. Dr. Ayşe ERÇAĞ, the mentor of my research career.

Conflicts of Interest

There are no conflicts of interest in this work.

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