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Synthesis and Characterization of Palladium(II) Complexes with 2-(2'-hydroxylphenyl)benzoxazole, 2-(2'-hydroxyl phenyl)benzothiazole or the Mixed Ligands

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ABSTRACT

Na_2PdCl_4 reacts with 2-(2'-hydroxylphenyl)benzoxazole (Hpbo), 2-(2'-hydroxyl phenyl)benzothiazole (Hpbt) or the mixed ligands (Hpbo) and (Hpbt) in methanol to give trans-$[PdCl_2(Hpbo)_2]$, trans-$[PdCl_2(Hpbt)_2]$ or trans-$[PdCl_2(Hpbo)(Hpbt)]$, respectively the benzoxazole or benzothiazole ligands behave as monodentate ligands coordinated to palladium through the N-heterocyclic atom. Treatment of the prepared Palladium complexes with triethylamine in methanol gave trans-$[Pd(pbo)_2]$, trans-$[Pd(pbt)_2]$ or trans-[Pd(pbo)(pbt)] respectively. The deprotonated benzoxazole or benzothiazole ligands coordinated to Palladium as bidentate chelate ligands bonded through the N-heterocyclic atom and the anionic oxygen atom of the hydroxyl group.

The prepared complexes were characterized by conductivity measurements, the elemental analysis CHN, infrared and ^1H n.m.r. spectra.

Key word: Benzoxazole complexes, Benzothiazole complexes, Mixed ligands, Palladium complexes.

INTRODUCTION

Currently there is a considerable interests in the coordination chemistry of heterocyclic ligands contain nitrogen, oxygen and sulfur donors[1-10]. Partially because of the biological significance of such ligands. Thus benzothiazole derivatives are key components in the bioactive compounds of both natural and synthetic origin. However benzoxazoles are important biological substances, covering an extensive spectrum of essential and selective antimicrobial activities [11-16]. In addition to their biological importance they are strongly coordinating agents and form stable complexes with various transition metal ions [17]. The biological activity of these ligands increase on complex formation with metal ions [18,19]. It is believed that they react selectively toward certain biological system[20].

The use of biological ligands with hard base characters for chelation of heavy metals like uranium, thorium or lanthanides has been a subject of interest of some research groups [21-25] as those kinds of ligands generally produce very stable

chelate complexes. This makes them highly appropriates for therapeutic development of clinical chelators in safety procedures related to contamination through natural and depleted thorium and uranium and in similar chemoprevention processes against uranium, thorium heavy metals intoxication.

In view of the above mentioned importance of these ligands and their complexes and as a continuous of our interests in synthesis of new complexes with heterocyclic ligands containing nitrogen, oxygen or sulfur donors [26-30] we report here the syntheses and characterization of palladium(II) complexes with 2-(2ᵉ-hydroxylphenyl)benzoxazole (Hpbo), 2-(2ᵉ-hydroxylphenyl)benzothiazole (Hpbt) and mixed ligands (Hpbo) and (Hpbt).

EXPERIMENTAL

General

The experimental techniques were the same as those used in our recent paper from this laboratory [31].

Starting materials

The compounds 2-(2'-hydroxylphenyl)benzoxazole, 2-(2'-hydroxylphenyl) benzothiazole and Na_2PdCl_4 were commercial products and were used as supplied.

Synthesis of the complexes

trans-[$PdCl_2(Hpbo)_2$] (1)

A suspended mixture of Na_2PdCl_4 (0.074g, 0.25mmol) and Hpbo (0.10g, 0.5mmol) in methanol (5ml) was stirred at room temperature for 3h .The produce yellow solid was filtered off washed with cold methanol and dried under vacuum (0.12g , 82% yield).

Complex 3 was prepared and isolated in a similar manner.

trans-[$Pd(pbo)_2$] (2)

NEt_3 (0.02g, 0.2mmol) was added to a suspension of trans-[$PdCl_2(Hpbo)_2$] (0.10g, 0.1mmol) in methanol (5ml).The mixture was stirred for 3h during this period the colour of the mixture changed from yellow to orange. The produce orange solid was filtered off washed with cold methanol, dried in a vacuum oven and recrystallized from $CHCl_3$ to give the product as orange crystals (0.08g, 90% yield).

The following complexes were prepared and isolated in a similar manner (4) and (6).

trans-[$PdCl_2$(Hpbo)(Hpbt)] (5)

Methanol (10ml) was added to a solid mixture of Hpbt (0.051g, 0.2mmol), Hpbo (0.046g, 0.2mmol) and Na_2PdCl_4 (0.059g, 0.2mmol). The resulting mixture was stirred at room temperature for 3h to give a yellow solid, which was filtered off washed with cold methanol and dried in a vacuum oven (0.11g, 89%yield)

RESULTS AND DISCUSSION

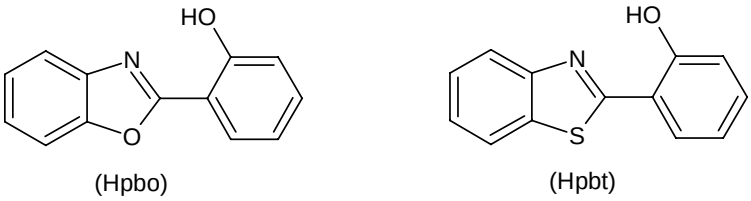
Synthesis of the complexes

Treatment of Na_2PdCl_4 with two mole equivalent of 2-(2'-hydroxylphenyl) benzoxazole (Hpbo) or 2-(2'-hydroxylphenyl)benzothiazole (Hpbt) in methanol gave complexes of the type trans-[$PdCl_2(Hpbo)_2$] (1) or trans-[$PdCl_2(Hpbt)_2$] (3) respectively Fig (1). The ligands Hpbo or Hpbt were coordinated as monodentate ligands to palladium through the heterocyclic N-atom. Mixed ligands complex of the type trans-[$PdCl_2$(Hpbo)(Hpbt)] was also prepared by treatment of Na_2PdCl_4 with one mole equivalent of (Hpbo) followed by (Hpbt).

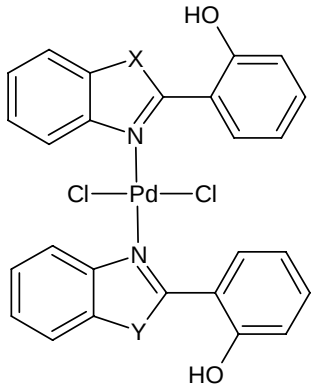
The prepared complexes are stable at room temperature, soluble in DMSO solvent but are insoluble in other common organic solvent such as CH_2Cl_2,$CHCl_3$, MeOH or EtOH.

Complex (1) has been reported previously [32]. It has been made starting with a rather different starting palladium compound, trans-bis(benzonitrile)dichloro palladium(II), and a long reaction time (20 days).

Attempts to displace the chloride ions of the above complexes with saccharinate ion by treatment with sodium saccharinate [33] were unsuccessful and always the starting complexes were obtained. It might be the stirric effect caused by the (hydroxyl groups prevent such reaction to occur.



(Hpbo) (Hpbt)



(1) X=Y=O
(3) X=Y=S
(5) X=O,Y=S

Fig.1. structures of the ligands and the prepared complexes

Treatment of the prepared palladium complexes (1) and (5) with triethylamine in methanol gave the chelated palladium complexes of the type trans-[$Pd(pbo)_2$], trans-[$Pd(pbt)_2$] or trans-[Pd(pbo)(pbt)] respectively Fig (2). The deprotonated anion ligands pbo or pbt behave as chelate ligands coordinated to palladium through the N-atom of the heterocyclic ring at the O-atom of the deprotonated OH group.

Table 1: Color, M.P., Yield, Elemental analysis and conductivity of complexes (1)-(6)

Seq.	Compd	Color	m.p.	Yield	Found (cal.)%			Λ ($ohm^{-1}.cm^2.mol^{-1}$)	
			°C	%	C	H	N	DMSO	$CHCl_3$
1.	$[PdCl_2(Hpbo)_2]$	Yellow	288-290	82	52.07 (52.1)	3.03 (3.1)	4.67 (4.7)	0.02	-
2.	$[Pd(pbo)_2]$	Orange	297-300	91	59.27 (59.05)	3.06 (3.07)	5.32 (5.24)	-	0.00
3.	$[PdCl_2(Hpbt)_2]$	Yellow	256-258	78	49.42 (49.25)	2.87 (2.88)	4.43 (4.14)	0.01	-
4.	$[Pd(pbt)_2]$	Orange	>315	94	55.87 (55.95)	2.89 (2.70)	5.01 (4.72)	-	0.00
5.	$[PdCl_2(Hpbo)$ (Hpbt)]	Yellow	265-268	89	50.71 (50.78)	2.95 (2.78)	4.55 (4.35)	0.01	-
6.	[Pd(pbo)(pbt)]	Orange	285-287	50	57.52 (57.58)	2.97 (2.88)	5.16 (5.31)	-	0.00

Table 2: I.r. spectra date (cm^{-1}) of the ligands and complexes (1)-(6)

Seq.	Compound	ν(OH)	ν(Ar-H)	ν(C=N)	ν(C=C)	ν(C-O)	ν_{as}(COC)	ν(CSC)	δ(CH)	ν(Pd-Cl)	ν(Pd-N)	ν(Pd-O)
	Hpbo	3190_b	3058_m	1631_s	$1595_s 1485_s$	1253_s	1155_m	—	750_s	—	—	—
1.	$[PdCl_2(Hpbo)_2]$	3299_b	3064_m	1606_s	$1550_s 1487_s$	1261_s	1197_m	—	752_s	338_s	485_m	—
2.	$[Pd(pbo)_2]$	—	3056_m	1604_s	1531_m	1253_s	1193_w	—	746_s	—	480_m	420_m
	Hpbt	3163_b	3000_m	1620_s	$1605_s 1487_s$	1300_s	—	1106_m	756_s	—	—	—
3.	$[PdCl_2(Hpbt)_2]$	3390_b	3006_m	1600_s	1508_m	1307_m	—	1105_m	756_s	342_s	480_m	—
4.	$[Pd(pbt)_2]$	—	3058_m	1596_s	$1542_s 1487_s$	1290_w	—	1141_w	748_s	—	515_m	440_m
5.	$[PdCl_2(Hpbo)(Hpbt)]$	3284_b	3070_w	1600_m	$1546_m 1500_m$	$1259_w 1299_w$	1209_w	1108_w	752_s	335_s	474_m	—
6.	[Pd(pbo)(pbt)]	—	3062_m	1604_s	$1537_s 1463_s$	1251_s	1225_w	1160_w	746_s	—	480_m	433_m

b = broad, m = medium, s = strong, w = weak

The prepared chelated complexes are soluble in $CHCl_3$ or CH_2Cl_2 but insoluble in MeOH or EtOH solvents.

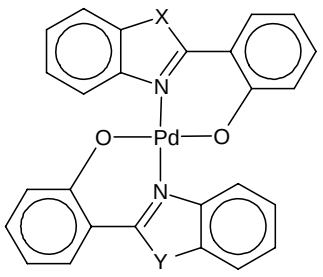
Attempts to open the chelate ring in the above chelate palladium complexes (2,4,6) with diphosphine such as dppm or dppe in a similar way to that reported for other chelate complexes [26], were unsuccessful and always the starting complexes were obtained.This probably reflect the high stability of chelate ring to be open by diphosphine.

Characterization of complexes

The prepared complexes were identified by Elemental analysis, i.r. spectra, conductivity measurements and ^{1}H nmr. spectra and their data are listed in Tables (1-3). The molar conductivity of complexes in DMSO or $CHCl_3$ is low enough to suggest that they are non-electrolytes [34].

Nuclear magnetic resonance

The ^{1}H-nmr data of the prepared complexes are given in Table 3. The ^{1}H-nmr spectra of complexes trans-$[PdCl_2(Hpbo)_2]$ (1), trans-$[PdCl_2(Hpbt)_2]$ (3) showed a broad singlet each at δH=11.20 and 11.54 ppm a singed to the hydroxyl proton in complexes (1) and (2) respectively, while trans-$[PdCl_2(Hpbo)(Hpbt)]$ (5) showed two broad singlets at δH=11.18 and 11.58 ppm assigned to two different hydroxyl protons of the two ligands (Hpbo) and (Hpbt) respectively. The phenyl protons appeared within the δH=7.0-8.026 ppm ring. Integration showed that the ratio of the OH: aromatic protons are 1:8.



(2) X=Y=O
(4) X=Y=S
(6) X=O,Y=S

Fig. 2. Structures of the prepared chelate complexes (4)-(6)

Table 3: ^{1}H-nmr data for complexes (1)-(6)

	Seq.	Complexes	Solvent (phenyl)	δH p.p.m. OH
1.	$[PdCl_2(Hpbo)_2]$	DMSO	8.026-7.078	11.201
2.	$[Pd(pbo)_2]$	$CDCl_3$	7.937-6.721	-
3.	$[PdCl_2(Hpbt)_2]$	DMSO	8.11-7.06	11.54
4.	$[Pd(pbt)_2]$	$CDCl_3$	7.987-6.960	-
5.	$[PdCl_2(Hpbo)(Hpbt)]$	DMSO	8.146-6.973	11.18-11.58
6.	[Pd(pbo)(pbt)]	$CDCl_3$	8.001-6.704	-

The hydroxyl signals disappeared in the spectra of the chelated complexes (2), (4) and (6) confirming the deprotontion of the hydroxyl protons. The aromatic protons appeared within the chemical shift δH=6.70-8.0 ppm.

On the basis of the above n.m.r. data and other identification data given in Tables 1 and 2, the structures shown in Figs. 1 and 2 have been suggested.

Infrared spectra

The i.r. data of the prepared complexes are given in Table 2. The i.r. spectra of complexes 1, 3 and 5 have a broad medium intensity bond centered at 3299, 3390 and 3284 cm^{-1} respectively due to the vibration of the hydroxyl group u(OH).

The spectra also showed a strong bond at 338, 342 and 335 cm^{-1} assigned to ν(Pd-Cl) in a trans arrangement around palladium [35,36]. The ν(OH) and (Pd-Cl) bands disappeared in the spectra of complexes (2), (4) and (6) and a new medium intensity band at around 420-433 cm^{-1} appeared. This band assigned to ν(Pd-O) [37].The spectra of the prepared complexes (1)-(6) showed a medium to strong band at 1596-1606 cm^{-1} shifted to a lower frequency from that in the corregonding free ligands. This band assigned to ν(C=N) of the heterocyclic coordinated to palladium through the N-atom [38]. Further evidence came from the appearance of a new medium intarsity band at 474-485 cm^{-1} which was absent in the spectra of the ligands this band assigned to ν(Pd-N).

CONCLUSIONS

In summary reaction of Na_2PdCl_4 with two mole equivalents of (Hpbo), (Hpbt) or the mixed ligands (Hpbo) and (Hpbt) in methanol gave complexes of the type trans-$[PdCl_2(Hpbo)_2]$, trans-$[PdCl_2(Hpbt)_2]$ or trans-$[PdCl_2(Hpbo)(Hpbt)]$. These complexes do not seem to react with sodium saccharinate.

Treatment of the prepared complexes with triethylamine gave the chelate complexes trans-$[Pd(pbo)_2]$, trans-$[Pd(pbt)_2]$ and trans-[Pd(pbo)(pbt)]. These complexes failed to react with diphosphine such as dppm or dppe.

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