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Novel Palladium (II) and Platinum (II) Complex Salts Containing Carbazolium, Indolium and Pyrrolium Cations

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ABSTRACT

A new series of complex salts of the type $[RA]_2[MCl_4]$ [R=carbazole,indole or pyrrole,A=H or $PhCH_2$;M= Pd(II) or Pt(II)], were prepared and characterized by elemental analysis, molar conductance, IR and UV/Vis spectral studies and magnetic measurements.The results of UV/Vis spectral studies and magnetic measurements showed that the anions complexes have a square planar geometry.

املاح معقدات البلاديوم (II) والبلاتين (II) المحتوية على ايونات الكاربازوليوم، الاندوليوم والبايروليوم الموجبة

الملخص

يتضمن البحث تحضير مجموعة من الاملاح المعقدة الجديدة من النوع $[RA]_2[MCl_4]$ {حيث R= كاربازول او اندول او بايرول ، A=H او $PhCH_2$ و M=Pd(II) او Pt(II)} وتشخيصها بوساطة تقنيات التحليل الدقيق للعناصر والموصلية الكهربائية والاشعة تحت الحمراء والاشعة فوق البنفسجية/المرئية والقياسات المغناطيسية. اوضحت نتائج الاشعة فوق البنفسجية/المرئية والقياسات المغناطيسية ان الايونات المعقدة السالبة تتخذ شكل المربع المستوي.

INTRODUCTION

Among the various known room temperature molten salts were those obtained from a mixture of 1,3-dialkylimidazolium chloride and aluminium chloride. These salts received a special attention due to their wide applications, in electrochemistry (Hussey et al.,1979;Wilkes et al., 1982) and as solvents in two-phase catalytic oligomerization reactions (Sanders et al.,1986;Suarez et al.,1998). However applications of aluminum based ionic liquids were moisture sensitive. Most transition metal complexes and the organic substrates were not inert towards organo-aluminate compounds. Air and moisture stable molten salts can be obtained by substitution of the chloro-aluminate anion in 1-ethyl-3-ethylimidazolium aluminate by weakly complexing anions such as $[BF_4]^-$ or $[PF_6]^-$ (Earle and Seddon,2000).

A new class of complex salts of the type $[B][CdX_4]$, ($B=[Ni(en)_3]^{+2}$,$[Ni(bpy)_3]^{+2}$ or $[Ni(bpy)_2(H_2O)_2]^{+2}$ {en=ethylene diamine, bpy = 2,2`-bipyridine,$X=Cl^-,Br^-$} were reported (Chesnut et al., 1999). These salts have been prepared by mixing $[CdX_2]$ with the organoamine nickel salts $[B]X_2$. They were characterized by physicochemical methods and x-ray single crystal analysis.

The crystal structure of di-(tetramethylammonium) tetrachloro palladate (II) $[N(CH_3)_4]_2[PdCl_4]$ was studied (Heines and Keler , 2004). They found that the above complex salt was built up by a layered structure of isolated complex cations and anions.

The oxidative addition of 2-iodo-1,3,4,5-tetramethylimidazolium tetrafluoroborate to Platinum(0) has been successfully carried out to give trans- [Pt(I) (1,3,4,5-tetramethylimidazolin-2-ylidene) $(PPh_3)_2$] BF_4. The complex has been isolated as colourless crystals and its x-ray structure analysis was studied (MeGuinness et al., 2001).

Halide sulfur chelate cross transfer gave new bimetallic complex salts of the type $[Ni(S_2CNEt_2)(dppe)]_2[HgBr_4]$, $[Pt(S_2CNEt_2)(dppe)]_2[CdCl_4]$ and $[Pd(S_2CNBu^n{}_2)bipy][CdCl_4]$, the structures of which were characterized using x-ray diffraction (Exarchos et al., 2001).

The synthesis and characterization of new complex salts of palladium(II) and platinum (II) containing the carbazolium, indolium or pyrrolium cations (Fig 1) and their benzyl derivatives have been studied.

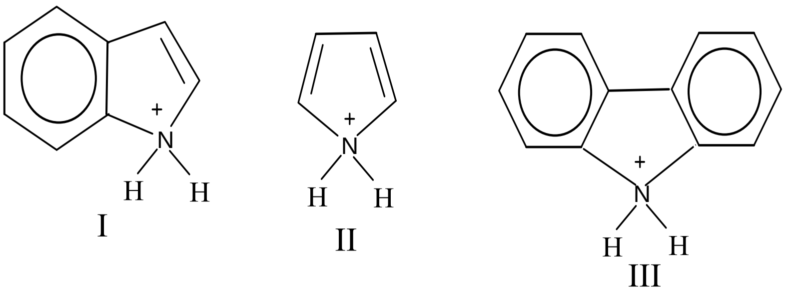


Fig 1: The organic cations used;Indolium(I),Pyrrolium(II), carbazolium (III).

EXPERIMENTAL

All reagents used were either analytical grade or chemically pure. Preparative work was carried out under dry nitrogen gas using standard schlenk techniques. Solvents were distilled from appropriate drying agents under nitrogen. IR spectra were recorded on a Perkin Elmer 580 B spectrophotometer in the 200-4000cm^{-1} range using CsI discs.Elemental analysis were carried out on a CHN analyzer type 1106 (Carlo Erba.; Germany). Melting points were measured on electrothermal melting point apparatus. Palladium and Platinum contents were determined spectrophotometrically using AA670. Conductivity measurements were made on a conductivity meter type PCM3-Jenway. Electronic spectra were recorded using a Shemadzu UV-160 spectrophotometer for 10^{-3}M solution of the complexes. Magnetic measurements were measured by a Brucker BM6 instrument at room temperature following the Faraday method.

Preparation of organic salts

2-Benzyl pyrrolium chloride (bpy)Cl (No.1)

A solution of pyrrole (0.67 g,0.01 mol) in ethanol (10 cm^3) was added dropwise to a solution of benzylchloride (1.26 g,0.01 mol) in ethanol (10 cm^3). Addition was continued for ca 30 min. The reaction mixture was refluxed for ca 2h, then left to stand at room temperature. The brown solid thus formed was filtered off, washed twice with ethanol (10 cm^3)and then dried under vacuum.

The analogous salts 2-benzylindoliumchloride (bind)Cl (No.4) and 2-benzylcarbazoliumchloride (bcarb)Cl (No.7) were prepared using similar methods.

Preparation of the complex salts $[bpy]_2[PdCl_4]$(No.2)

$PdCl_2$ (0.18 g,0.001 mol) in distilled water (10cm^3) was added drop wise to a solution of 2-benzyl pyrrolium chloride (0.35 g,0.002 mol) in acetonitrile (15 cm^3) . The mixture was refluxed for 2h, to give clear solution , which was allowed to cool at room temperature. The solid thus formed , was filtered off, washed with ethanol (10 cm^3) then diethyl ether (10 cm^3) and dried under vacuum.

The complex salts (Nos.3,5,6,8 and 9) were prepared similarly.

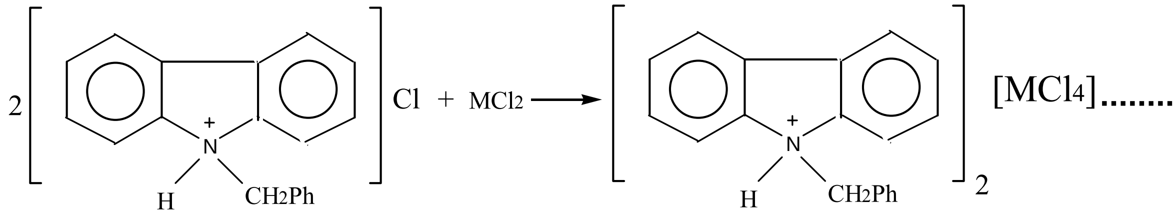
$[Hpy]_2[PdCl_4]$ (No.10)

A solution of $PdCl_2$ (0.18 g, 0.01 mol) in ethanol (10 cm^3) was added to a solution of pyrrole (0.14 g, 0.02 mol) in ethanol (10cm^3). Concentrated hydrochloric acid was added dropwise with stirring until pH of the solution was adjusted to 2.5-3.0. The mixture was stirred for 2h then left to stand at room temperature for 1 day. The solid thus formed was filtered off, washed with ethanol, diethylether and dried under vacuum.

The complex salts (Nos.11,12,13,14,15) were prepared using similar procedure.

RESULTS AND DISCUSSION

Reactions of the organic salts [RA]Cl (R=H or $PhCH_2$;A=indole , pyrrole or carbazole) with the metal salts MCl_2 (M=Pd or Pt) in ethanol gave complex salts of the type $[RA]_2[MCl_4]$ in high yield, equation 1, 2.



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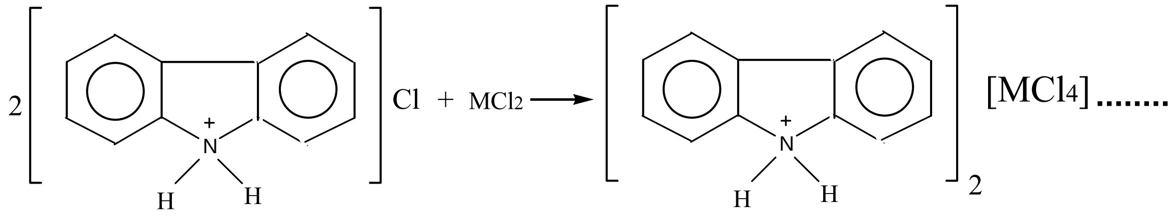

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The complex salts were identified by elemental analysis, IR,UV-vis spectra, magnetic susceptibility and conductivity measurements (Table 1 and 2).

The synthesized complex salts were microcrystalline solids and stable in the solid state as well as in solution. They are insoluble in most common organic solvents but soluble in dimethylsulfoxide (DMSO).

Conductivity data (Table 1) showed that all the complex salts were 2:1 electrolytes. Molar conductivities were also measured for the various salt concentration. Plots of Λ_e versus $N^{1/2}$ in Onsanger equation ($\Lambda_o=\Lambda_e \; A \; N^{1/2}$) were found to be linear over the concentration: 0.1 -1.0 mmol range.A and Λ_o values were found to be 330-345 $ohm^{-1}.cm^2.equiv^{-1}$ and 102-108 $ohm^{-1}.cm^2.equiv^{-1}$, respectively. These values a greed well with those reported for 2:1 electrolytes (Geary ,1971). Conductivity values were significantly higher than those reported for 1-n-butyl-3-methylimidazolium tetrachloroaluminate (Suarez et al., 1998), indicating that the interactions between the cations and anions were essentially electrostatic with small contributions of hydrogen bondings (Abdul-Sada et al., 1990).

The IR spectra of the organic salts showed bands at 2550-2603 and 1610-1625) cm^{-1} are assigned to $\upsilon(NH)^+$ (Buttrus and Adnan, 2005) and $\upsilon(C=N)$ (Bayoumi et al., 2001), respectively. The spectra of the complex salts also revealed the presence of the above bands at similar positions. The spectra showed two new bands at 290-310 and 330-340 cm^{-1} assigned to $\upsilon(M\text{-}Cl)$ in a square planar arrangements (Agarwal and Prasad ,2005). The magnetic data of the complex salts showed that they are diamagnetic as expected to a d^8-metal ion in a square planer arrangements (AL-Hayaly et al.,2005).

Electronic spectra of the prepared complex salts exhibited a number of overlap of intense bands in the UV-Vis region (Table 2). In a d^8 Pd(II) or Pt(II) one electron d-d transition was in the order of increasing energies $^1B_2g \longrightarrow {}^1B_1g, {}^1Eg \longrightarrow B_1g$, $^1A_1g \longrightarrow {}^1B_1g$ and $^1A_1g \longrightarrow {}^1Eg$ From these transitions only the highest energy had magnetic dipole forbidden to the extent that D_4h symmetry is maintained. Application of the above order on the electronic spectra of the present complex salts lead to the following assignments. The low intensity d-d bands at 833-460 nm were assigned to $^1A_1g \longrightarrow {}^1Eg$ and $^1A_1g \longrightarrow {}^1B_1g$ (Stoicesu et al., 2001). The charge transfer transition observed at 322-295nm suggested a square planar arrangement around metal ions (AL-Hayaly et al., 2002).

Acknowledgment

Dedicated to the memory of Prof. Talal A.K.AL-Allaf.

Table 1: Physical and molar conductivity data compound (1-15)

Compound	M.p (ºc)	Colour	Yield (%)	Analysis found (calcd.) %				C
				C	H	N	M	
py]Cl	180 d	brown	91	68.2(68.2)	6.2(6.2)	7.2(7.2)	----	
py]$_2$[PdCl$_4$]	270	brown	85	46.8(46.9)	4.2(4.3)	5.0(5.0)	18.8(18.8)	
py]$_2$[PtCl$_4$]	225	brown	80	40.4(40.4)	3.9(3.7)	4.4(4.3)	29.8(29.9)	
ind]Cl	115	brown	95	73.9(73.9)	5.7(5.8)	5.7(5.8)	---	
ind]$_2$[PdCl$_4$]	214	brown	87	52.2(52.0)	3.9(4.0)	8.3(8.1)	15.2(15.4)	
ind]$_2$[PtCl$_4$]	149	Pale brown	78	45.7(45.5)	3.3(3.5)	7.1(7.1)	24.6(24.7)	
carb]Cl	210	Pale brown	95	71.1(71.1)	4.4(4.4)	6.9(6.9)	---	
carb]$_2$[PdCl$_4$]	129 d	Dark brown	83	40.6(40.4)	5.6(5.7)	9.8(9.9)	18.7(18.8)	
carb]$_2$[PtCl$_4$]	223 d	Pale brown	79	34.9(34.9)	4.8(4.9)	8.5(8.6)	29.6(29.9)	
Ipy]$_2$[PdCl$_4$]	300 d	Black	80	25.0(25.0)	3.2(3.1)	7.3(7.3)	27.4(27.6)	
Ipy]$_2$[PtCl$_4$]	280 d	Black	75	20.2(20.3)	2.5(2.5)	5.9(5.9)	41.2(41.2)	
Iind]$_2$[PdCl$_4$]	245 d	Black	79	39.4(39.7)	3.3(3.3)	5.7(5.7)	21.8(21.9)	
Iind]$_2$[PtCl$_4$]	225 d	brown	95	33.4(33.5)	2.7(2.8)	3.8(3.9)	34.2(34.0)	
Icarb]$_2$[PdCl$_4$]	250	Dark brown	85	49.2(49.3)	3.4(3.4)	4.7(4.8)	18.0(18.2)	
Icarb]$_2$[PtCl$_4$]	300	Black	90	42.7(42.8)	2.9(3.0)	4.1(4.2)	28.8(29.0)	

d = Decomposition temperature

Table 2: IR and electronic spectral data for the compounds (1-15).

Comp.	υ(NH)	υ(C=N)	υ(M-Cl)	λ_{max} (nm)	Assignments

1	2560_S	1628_S	---	311	----
2	2530_S	1624_S	$290_w,330_w$	301 790	${}^1A_1g \rightarrow {}^1Eg$
3	2550_S	1620_S	$295_w,320_w$	294 790	${}^1A_1g \rightarrow {}^1Eg$
4	2598_m	1620_S	----	332	
5	2590_m	1621_S	$298_w,345_w$	486 785	${}^1A_1g \rightarrow {}^1B_1g$ ${}^1A_1g \rightarrow {}^1Eg$
6	2595_m	1624_S	300,350	294 483 830	${}^1A_1g \rightarrow {}^1B_1g$ ${}^1A_1g \rightarrow {}^1Eg$
7	2603_m	1625_S	----	319	
8	2600_m	1628_S	310,345	322 791	c.t. ${}^1A_1g \rightarrow {}^1Eg$
9	2602_w	1623_S	300,341	313 830	c.t. ${}^1A_1g \rightarrow {}^1Eg$
10	2540_m	1625_S	290,335	301 830	c.t. ${}^1A_1g \rightarrow {}^1Eg$
11	2550_m	1628_S	300,341	311 833	c.t. ${}^1A_1g \rightarrow {}^1Eg$
12	2580_m	1630_m	295,345	298 746	c.t. ${}^1Ag \rightarrow {}^1Eg$
13	2575_m	1625_S	290,341	295 825	c.t. ${}^1A_1g \rightarrow {}^1Eg$
14	2560_w	1630_S	300,340	294 773	c.t. ${}^1A_1g \rightarrow {}^1Eg$
15	2555_w	1631_w	295,345	294 786	c.t. ${}^1A_1g \rightarrow {}^1Eg$

S = strong , m=medium,w=weak
c.t.= charge transfer

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