Preparation and Spectroscopic Characterization of Some Novel Schiff Base Complexes of Pd, Rh, and Ru

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Abstract:

A series of Schiff involving benzoin or 2-(1-hydroxy-2 – acetonaphthol) and thiosemicarbazone, o,o- phenylenediamine, aniline or o- bromoaniline and some of their palladium (II), rhodium (III) and ruthenium (II) complexes was prepared. Spectroscopic characterization of the prepared Schiff bases and their complexes were achieved. The spectrochemical parameters (10Dq, B, β 35) and the ligand field stabilization energy (LFSE) of some of the prepared complexes were calculated. The redox behavior of one of the prepared palladium (II) complexes was investigated employing bulk voltammetry in N, N'- dimethylformamide at different sweep rate.

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المستخلص:

تضمن البحث تحضير وتوصيف طيفي لبعض قواعد شيف و متراكباتها مع البلاديم والروثيم والروثيم تضمن البحث تحضير وتوصيف العديد من قواعد شيف من تكاثف مركب البنزوين (Benzoin) مع كل من: ثيوسيميكربازايد (Thiosemicarbazide) والفينيلين داى أمين (phenylenediamine) كلا على حدة والهيدرازونات المحضرة بتكاثف المركب 1-هيدروكسي-2- اسيتوفينون مع بعض الأمينات الأروماتية باستخدام طرق الطيف المختلفة و التحليل العنصرى(Elemental analysis). امكن ايضا تحضير وتوصيف بعض متراكبات هذه القواعد مع البلاديم والرديم والروثونيم. أمكن تحديد التركيب الكيميائي والفراغي للمتراكبات كما أمكن أيضا حساب بعض الدوال الطيفية (JDQ, B, β35, LFSE) المعبرة عن التركيب الإلكتروني والفراغي لبعض المتراكبات المحضرة. كما استخدام الفولتامتري الدائري في دراسة السلوك الكهروكيميائي لأحد متراكبات البلاديم قيد الدراسة بإستخدام قطب البلاتين الفعاال لتحديد إمكانية إختزال و أكسدة أيونات البلاديم إلى حالات التأكسد المختلفة.

1. Introduction:

Particular attention has been devoted to the Schiff bases and their metal chelates [1-5] in the last two decades. The Schiff base ligands are coordinated to the investigated metal ion through the azomethine nitrogen either alone or in combination with other electroactive sites such as oxygen and I or sulfur. This class of compounds is well known to exhibit a wide range of biological, industrial and analytical applications [5-8]. Schiff base macrocyclic ligands and their transition metal complexes have many applications in biochemistry, pharmaceutical, antimicrobial, antifungal, and anticarcenogenic reagents have received considerable interest [5-9]. Schiff bases involving thiosemicarbazones, ethylenediamine and their transition metal complexes have been reported in the last few years [10-16]. The importance of the Schiff bases involving thiosemicarbazones and their ability to inhibit the biosynthesis of DNA have been reported by Demertzi, et al [17]. The spectroscopic and electrochemical techniques provide an excellent approach for studying the redox behavior and the influence of the chromospheres in many types of metal complexes [18-24]. Cyclic voltammetry at bulk or thin layer electrodes at Au or Pt mesh transparent electrodes takes the advantages of rapid electrolysis and small-volume features for measuring the redox potentials of organic, biological molecules of slow electron transfer and metal complexes [22-24]. Therefore, the present study was focused on the synthesis, spectral and electrochemical studies on some Schiff bases containing e.g. benzoin or 2-(1- hydroxy-2-acetonaphthol) moiety and some of their complexes with Ru^{3+} , Rh^{3+} and Pd^{2+} . The spectroscopic parameters 10 Dq, B, β_{35} and LFSE of some of the

complexes are included. The redox behavior and stability of one of the palladium (II) complexes towards oxidation were explored employing cyclic voltammetry.

2- Experimental:

2.1. Reagents and materials

All chemicals and solvents used were of analytical reagent grade and were used without further purification. All containers used were pre-cleaned by soaking in nitric acid (20 %w/v) and rinsed with de-ionized water before use. The reagents benzoin, 2-(1- hydroxy-2-acetonaphthol), thiosemicarbazize, o, o-phenylenediamine, aniline and bromoaniline were obtained from BDH (Poole, England). The salts Rh(NO₃)₃.2H₂ O, Ru Cl₃.2H₂O and Pd Cl₂ were obtained from Aldrich, France.

2.2. Physical measurements

Infrared (IR) spectra (200-400 cm $^{-1}$) as KBr discs were measured on a Matson 500 FT-IR spectrometer at room temperature. A Perkin Elmer (Lambda EZ-210) double beam spectrophotometer (190-1100 nm) with 1cm (path width) quartz cell was used for recording the electronic spectra of the complexes and their chelates. 1 H NMR in DMSO-d₆ and electronic spectra in CH₂Cl₂ ($\sim 5 \times 10^{-4}$ M) were recorded on a Varian Gemini VM-200 and a Unicam UV₂₋₁₀₀ UV-visible spectrometers, respectively. The cyclic voltammetric measurements were performed on a Metrohm 746 VA trace analyzer and 747 VA stand. A three-compartment borosilicate (Metrohm) voltammetric cell (10 mL) configuration system incorporating Pt working electrode, double-junction Ag/AgCl,(3M KCl), as a reference and platinum wire (BAS model MW-1032) as counter electrodes was used, respectively. CEM microwave system (Mars model, 907500, USA) and digital pH-

meter (model MP220, Metter Toledo) were used for sample digestion of the prepared metal complexes and pH measurements. Teflon digestion vessel (HP 500) was used for the digestion of the sample in the microwave system for metal determination. A Perkin-Elmer Analyst TM 800, USA atomic absorption spectrometer (AAS) was used for measuring the concentration of the ruthenium, rhodium and palladium under instrument's optimum settings at 0.5 slit width.

2.3. Preparation of the Schiff bases

2.3.1. Preparation of the Schiff bases involving benzoin moiety:

In ethanol (40-50 mL), an accurate weight of benzoin (4.0 mmol) is refluxed with thiosemicarbazide, or o, o-phenylenediamine (8.0 mmole) under constant stirring for 3h. The refluxed solutions were concentrated by removal one/ third of the solvent and cooled. The produced yellow polycrystalline precipitates were separated out, filtered off, washed thoroughly with hot ethanol to remove any nonspecifically material. The Schiff bases were re crystallized from ethanol as pale solid yellow crystals, dried under vacuum at 50 °C and in an oven at 110 °C and finally stored in desiccators.

2.3.2. Preparation of the Schiff bases involving 2-(1- hydroxy-2-acetonaphthol) moiety:

In ethanol (20-30- mL), an accurate weight of the carbonyl compound 2-(1- hydroxy-2-acetonaphthol) (10 mmole) is refluxed with aniline or 3- bromoaniline (4.0 mmole) under constant stirring for 3h. On concentrating the reaction solutions, cooling, polycrystalline pale dark yellow precipitates were separated out. The produced precipitates of the Schiff bases were then separated out, filtered off, washed thoroughly with hot ethanol, ether and

finally crystallized from ethanol. The resultants solids as pale solid yellow crystals, dried under vacuum at 50 °C and in an oven at 110 °C and finally stored in desiccators.

2.4-Preparation of the Schiff base metal complexes:

To an accurate weight of the Schiff base (3.0 mmole) in hot ethanol (10.0 mL), ruthenium tri chloride trihydrate, palladium chloride or rhodium (III) chloride (1.0 mmole) in ethanol (15 mL) was added. Immediate brownish black, brownish green, red and brownish green precipitates were formed with Ru³⁺, Pd²⁺ and Rh³⁺. The reaction mixtures were refluxed for one hour under constant stirring. The precipitates formed were then separated out, filtered off, washed with ethanol and finally dried under vacuum at 60-70 °C and finally stored in desiccators' over anhydrous CaCl₂.

3. Results and discussion

In view of the role of M-O and M-N bonds in the initiation of some biochemical reactions and catalytic activity, interaction of transition metal ions with some chelating agents e.g. Schiff bases derived from benzoin or 2-(1- hydroxy-2-acetonaphthol are of greet importance [24, 43]. The prepared Schiff base ligands, their abbreviations, IUPAC nomenclature and their percent yield are summarized in Table 1. The physical properties and analytical data of the prepared Schiff bases are listed in Tables 2. On the other hand, the physical properties and analytical data of the prepared Schiff bases and the prepared complexes of palladium (II), ruthenium (III) and rhodium (III) are listed in Table 3. The Schiff base and the complexes are colored, stable and have moderate melting points owing to their inherent stability.

3.1. Spectroscopic characterization:

The most significant IR frequencies of the free Schiff bases as well as their metal complexes in the range 200- 4000 cm⁻¹ with their probable assignments are summarized in Table 4. The IR spectra of the complexes showed a large number of bands most of them generated by aromatic and aliphatic substituents. It is not easy task to extract bands resulting mainly from the Schiff base ligand. The bands are possibly coupled to the aromatic ring vibrations and it is far from accurate to describe them as pure modes as v (C=N) vibrations. The C=N, band in the range 1604-1629(s) cm⁻¹ of the free Schiff bases HRSB is shifted to lower wave numbers (1600- 1615 cm⁻¹) in the complexes, indicating participation of the azomethine nitrogen[25]. Thus, the Schiff bases HRSB are coordinated to the tested metal ions via the C=N nitrogen and the OH oxygen. This assignment is further supported by the appearance of new bands in the far IR at regions 1208-1255, 510-540 and 480 cm⁻¹ due to the ν (C-O), ν (M-O), ν (M-N) vibrations, respectively[26]. The strong bands observed at 3425(s) and 3260(s) is tentatively assigned to v OH and v NH of the Schiff base. The former band was disappeared upon coordination suggesting bonding of hydroxyl group oxygen [25, 26]. The bridging sites in the metal complexes were determined by careful comparison of the IR spectra of the ligand and its deprotonation of the hydroxyl group and the involvement of the OH in metal chelation [15, 16]. The observed far IR bands in the region 485-490 cm⁻¹ in the spectra of the complexes which are absent in the IR spectra of the free Schiff bases are assigned to metal- oxygen, v (M-O) vibration [16, 17]. The bands observed at 390 cm⁻¹ and 290 cm⁻¹ are assigned to v (Ru-Cl) terminal and bridging [12, 14]. The IR spectral data of the complexes with the most probable assignments are given in Table 2.3. The data showed that, the ligand acts as a monobasic bidentate ligand via the OH of its enol form and the carbonyl group. The modes of chelation are supported by the following evidences: i- the large shift

(60-70 cm⁻¹) in the vibration mode of the carbonyl group (vC=O) to the lower wave numbers indicating strong chelation with the metal ions; ii- the existence of the strong C=C band at 1615 cm⁻¹ and finally iii- the appearance of new bands in the lower frequency region at 490-521 cm⁻¹ due to M-O [50]

3.2. Electronic spectra and spectrochemical parameters of the complexes

The electronic spectra of the prepared complexes were critically investigated solid state and in DMF solution at ambient temperature. The positions of the absorption bands were not significantly different from those in the solid state, showing that no electronic or geometric change of the species in dissolution in DMF and the composition of the chromophores of the compounds are the same in solution and in solid state. The solution electronic spectra of some of the complexes with their probable assignments are given in Table 5. The ligand field parameters (10Dq, β_{35} , B and LFSE) for some of the complexes are also given in Table5. In the spectrum of rhodium complexes Rh(BTSC)₃ and Rh(BBPD)₃ three well defined bands were observed in the region at 16760- 16790, 28620-29155 and 38574-39420 cm⁻¹. The first two bands were safely assigned to $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$ d-d transition, respectively in octahedral symmetry [27].

The B value obtained for this complex is of the order of 59% of the free ion (B = 720 cm⁻¹). These data suggest considerable orbital overlap with a strong covalency character in the metal-ligand sigma bond. The low value of B may also be associated with the reduction in the effective cationic charge [19]. The electronic spectrum of the two ruthenium (II) complexes Ru(Bntsc)Cl and Ru(BBPD)₃ showed three well defined bands at 1237-12460, 21320-22059 and 24230-24860 cm⁻¹. The first and third bands have been assigned to the spin forbidden transitions ${}^2T_{1g} \rightarrow {}^2E_g$ and ${}^2T_{1g} \rightarrow {}^2A_{1g}$ d-d transitions in octahedral

symmetry [18, 27]. The band observed at 21850 cm⁻¹ was safely assigned to the spin allowed transition ${}^2T_{2g} \rightarrow {}^2A_{2g}$ of Ru(III) in octahedral environment [16]. The separation energy between the first and the second transitions corresponds to 8B [10, 12]. Thus, the value of the crystal field splitting energy (10Dq) can be calculated from the ratio Dq / B.. The values of 10Dq and the nephelauxetic parameter, β were found therefore equal 5.1 and 0.64 in the middle nitrogen and oxygen and donor atom, respectively.

The cyclic voltammetry (CV) of the complex Pd (BTSC)Cl in DMF-TBA⁺Cl⁻ showed diffuse, irreversible and successive two one electron reductions and one quasi-reversible one electron oxidation. The observed $E_{p,c}$ at -0.67 V coupled with an $E_{p,a}$ at -0.09 V with $\Delta E_p = 0.58$ V is safely assigned to the irreversible one-electron transfer Pd^{2+}/Pd^+ via the reduction; $[Pd(BTSC)Cl]/[Pd(BTSC)Cl]^-$ [18, 19]. The ratio of the $i_{p,a}/v^{1/2}$ where v is the sweep rate (mV/s) decreased up to a constant value at v > 200 mV/sec and the $i_{p,a}/i_{p,c}$ ratios for this couple were found less than one at scan rates ≤ 100 mV/sec and progressively increased reaching unity at $v \geq 200$ mV/sec. Thus, the electrode couple is consistent with a coupled chemical reaction that takes place after the charge transfer process, EC_i mechanism [28, 29]. The irreversible nature of the couple Pd^{2+}/Pd^+ could be due to the rupture of Pd-Cl as a result of the strong chelating effect of the Schiff base BTSC. Attempts to establish the nature of the palladium (I) reduction products were unsuccessful, most likely because of their propensity for dimerization through the formation of metal-metal bond [30]. The electrode couple with $E_{p,a}$ +1.55 V, $E_{p,c}$ –0.07 V and $\Delta E_p = 1.62$ V is most likely attributed to the irreversible redox reaction.

4. Conclusion:

The present study provides a very useful set of data on the Schiff bases involving the carbonyl compounds namely benzoin and 1-hydroxy-2-acetonaphthone and their metal complexes of palladium (II), rhodium (III) and ruthenium (III). The study will be helpful for conducting a pre feasibility investigation to exploit the use such class of Schiff bases and their complexes with ruthenium (III) and palladium (II) and their possible application as good oxidant for some aldehydes, ketones and olefins. The developed procedures could be extended to be carried out employing thin layer voltammetry at gold or platinum mesh working electrodes are to able to investigate the electronic spectra of various intermediates generated in the test solution in the electrochemical cell.

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Table 1. List of the abbreviations, IUPAC nomenclature and the percent yield (%) prepared Schiff bases

Schiff base	Abbreviation	IUPAC name and percent (%) yield		
1	BTSC	Benzoin thiosemcarbazone (70.6%)		
2	BBPD	Bis benzoin- <i>O,O</i> -phenylene diamine, (79.6%)		
3	HBSB	2-(1- Hydroxy-2-aceto naphthol)-iminobenzene, (90.7 %)		
4 HBrSB		2-(1- Hydroxy-2-acetonaph thol)-iminbromo obenzene (82.3%)		

Table 2. Physical properties and analytical data (%) of the prepared Schiff bases

Schiff base	Color	Calculated (Found), %				
		C	Н	N		
BTSC	Yellow	63.6	5.34	14.61		
		(64.2)	(5.71)	(14.23)		
BBPD	Yellow	88.5	5.75	5.85		
BBIB	V100-100-100-100-100-100-100-100-100-100	(87.8)	(6.20)	(6.32)		
HBSB	Pale	82.7	5.8	5.4		
ПВЗВ	yellow	(81.8)	(4.9)	(5.4)		
HBrSB	Pale	63.5 0	4.2	4.1		
	yellow	(64. 2)	(4.2)	(4.1)		

Table 3. Physical properties and analytical data (%) of the chelating agents and their metal chelates:

Complex	Complex	Color	Calculated (Found), %					
no			С	Н	N	M		
1	Pd(HBSB) ₂ .2 H ₂ O	Green	65.7 (65.4)	5.5 (5.1)	4.05 (4.10)	15.3 (15.0)		
2	Pd(HBrSB) ₂ .2 H ₂ O	Green	65.2 (65.1)	4.9 (5.1)	4.20 (4.10)	16.1 (16.2)		
3	Pd(BTSC)Cl	Brown	42.3	3.3	9.8	24.9		
		7	(42.9)	(3.4)	(9.4)	(25.8)		
4	Pd(BBPD) ₂	Green	37.6	3.5	8.6	19.6		
			(36.4)	(3.2)	(7.9)	(21.2)		
5	Rh(BTSC) ₃	Purple	49.31	3.96	3.64			
6	Rh(BBPD) ₃	Downlas	(49.96	(3.46	(3.2)			
O	KII(BBFD)3	Purple	52.31 (51.1)	4.3 (4.9)	3.9 (4.1)			
7	Ru(BBPD) ₃	Green	48.3.	4.9	4.2			
8	Ru(BTSC) ₂ Cl ₂	Green- violet	(49.1) 50.10 (50.7)	(4.3) 3.92 (4.10)	(4.1) 11.6 (11.26)	14.30 (14.50)		

Table 4. Infrared Spectral data of the prepared complexes

Complex no. v OH	v _a NH v _s N	v _s NH	δ ΝΗ	v C=N	v CN+	v CN+	v C=S	v M-O	v M-N	
		VS 1 111			δ ΝΗ	v N-N				
1	3452 s	3260 s	3165 s	1610 sh	1615 s	1505	1125	3	510	470
2	3420 br	3270 s	3185 s	1605	1610	1515			543	466
3		3265 s	3170 s	1595	1605	1575 m	1120	860 m	545 m	480
4		3274 s	3169 s	1610	1600	1530	1085		520	474
5		3270 m	3185	1610	1603	1530	1130	895	510	465
6		3285 m	3190	1612	1580	1520	1139		495 s	450
7		3164	3274	1620	1590				490	431
8		3215	_	1612	1570 s			843	485 s	390 w

Table 5. Electronic spectral data (cm⁻¹) of some of the complexes with ligand field parameters in DMF and the most probable band assignments

Compound no.	Bands (cm ⁻¹) x 10 ³	Assignments	10Dq	В	β ₃₅	LFSE (cm ⁻¹)
6	12.46	$^{2}\mathrm{T}_{1g} \rightarrow ^{2}\mathrm{E}_{2g}$	56.48	1107.5	0.64	16.67
	21.32	$^{2}T_{2g} \rightarrow ^{2}A_{2g}$				
	24.86	$^{2}T_{1g} \rightarrow ^{2}A_{1g}$				
8	16.79 (v ₁)	$^{I}A_{1g} \rightarrow {}^{I}T_{1g}$	24.26	424.8	0.58	10.62
	$28.62 (v_2)$	$^{1}A_{1g} \rightarrow {}^{1}T_{2g}$				
1	$39.42 (v_3)$	$^{1}A_{1g} \rightarrow b, ^{1}T_{1u}$				