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# Spectroscopic and electrochemical characterization of some Schiff base metal complexes containing benzoin moiety $\stackrel{\star}{\sim}$



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#### HIGHLIGHTS

- A series of complexes of Rh, Ru, Pd and Cu complexes of selected Schiff bases of benzoin was prepared.
- The electrode potential of the couple  $M^{3+}/M^{2+}$  of complexes is correlated to the nature of the d orbital's involved.
- The orbital's are HOMO consisting of  $d_{\chi^2-\gamma^2}$  and while LUMO consisting of the  $\pi^*$  orbital of ligand.
- The high value of  $Rh^{2+}/Rh^{3+}$  and  $Ru^{2+}/$ Ru<sup>3+</sup> couple can be explained in terms of the higher energy of  $d_{\chi^2-\gamma^2}$  compared to Pd.

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#### G R A P H I C A L A B S T R A C T

A series of benzoin Schiff bases and their complexes with Rh<sup>3</sup> <sup>+</sup>, Ru<sup>3+</sup>, Pd<sup>2+</sup>, Cu<sup>2+</sup> and Ni<sup>2+</sup>. The prepared and fully characterized. The proposed chemical structure of Rh<sup>3+</sup>, or Ru<sup>3+</sup> complexes are shown in Scheme I. Based upon the 10Dq values of the aformentioned O<sub>h</sub> BTS complexes, the stability of the complexes followed the order: [Ru(BTS)<sub>2</sub>]Cl > [Rh(BTS)<sub>2</sub>]Cl > [Cu<sub>2</sub>(BTS)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O]. Scheme I: Proposed structures of Rh<sup>3+</sup> or Ru<sup>3</sup> complexes of Schiff base BTS.



Introduction

#### ABSTRACT

The ligation behavior of bis-benzoin ethylenediamine (B<sub>2</sub>ED) and benzoin thiosemicarbazone (BTS) Schiff bases towards Ru<sup>3+</sup>, Rh<sup>3+</sup>, Pd<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> were determined. The bond length of M–N and spectrochemical parameters (10Dq,  $\beta$ , *B* and LFSE) of the complexes were evaluated. The redox characteristics of selected complexes were explored by cyclic voltammetry (CV) at Pt working electrode in non aqueous solvents. Au mesh (100 w/in.) optically transparent thin layer electrode (OTTLE) was also used for recording thin layer CV for selected Ru complex. Oxidation of some complexes occurs in a consecutive chemical reaction of an EC type mechanism. The characteristics of electron transfer process of the couples M<sup>2+</sup>/M<sup>3+</sup> and M<sup>3+</sup>/M<sup>4+</sup> (M = Ru<sup>3+</sup>, Rh<sup>3+</sup>) and the stability of the complexes towards oxidation and/or reduction were assigned. The nature of the electroactive species and reduction mechanism of selected electrode couples were assigned.

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### Schiff base compounds are well known to exhibit a wide range of applications in pharmaceutical, antimicrobial, anticarcenogenic reagents, industrial and analytical uses [1–4]. Thus, in the last few years Schiff base macrocyclic ligands and their complexes have received considerable interest [5–15]. The introduction of a transition metal ion into molecules containing a chromophore which is

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Fig. 1. Chemical structures of benzoin- thiosemicabazone (BTS), I and benzoin ethylenediamine ( $B_2ED$ ), II Schiff bases.



Fig. 2. Proposed structure of Rh<sup>3+</sup> or Ru<sup>3</sup> complex of Schiff base BTS. M = Ru or Rh.

based on the Schiff base group in many cases produces low color strength [16–20].

The redox properties include oxidation and reduction of the central metal ion and various oxidation and reduction of the ligands, and the process involve both the central atom and the ligand [21,22].The spectroscopic and electrochemical techniques provide an excellent approach for studying the redox behavior and the influence of the chromopheres in many types of metal complexes [21–25]. The redox behavior of benzoin Schiff bases and their transition metal complexes has special interest [26– 28]. Little informations on the redox properties of their coordination compounds are known.

The influence of metal ions in the spectroscopic and electrochemical behavior of Schiff bases metal complexes containing benzoin moiety is not well known. Thus, this article is focused on the spectroscopic and electrochemical characteristics of benzoin thiosemicarbazone, BTS and N,N-bis benzoin-ethylenediamine, B<sub>2</sub>ED Schiff bases (Fig. 1) and some of their Ru<sup>3+</sup>, Rh<sup>3+</sup>, Pd<sup>2+</sup>, Cu<sup>2+</sup> and Ni<sup>2+</sup>complexes. Nature of the electrode couples were also assigned.

#### Experimental

#### Reagents and materials

Analytical reagent grade chemicals were used as received. Tetrabutylammonium chloride (TBA<sup>+</sup>·Cl<sup>-</sup>) and tetrabutylammonium hexafluorophosphate TBA<sup>+</sup>·F<sub>6</sub><sup>-</sup>) (BDH Ltd., Poole, England) were used as supporting electrolyte in N,N'-dimethylformamide (DMF). BDH RhCl<sub>3</sub>, RuCl<sub>3</sub>·3H<sub>2</sub>O, PdCl<sub>2</sub>, CuCl<sub>2</sub> and Ni(CH<sub>3</sub>COO)<sub>2</sub> were used. DMF was chosen as a proper solvent, since it is easily purified and its functions as a better Lewis base. The Schiff bases and their metal chelates have significant solubility in DMF.

#### Apparatus

A Perkin–Elmer infrared (IR) model RXI-FT-IR system 55529 spectrometer  $(4000-200 \text{ cm}^{-1})$  was used for recording the spectra of the Schiff bases and their complexes in KBr disc. <sup>1</sup>H NMR spectra in d<sub>6</sub>-DMSO were recorded on a Brucker advance DPX 400 MHz model using TMS as an internal standard. AUnicam UV<sub>2-100</sub> Spectrometer was used for recording electronic spectra of the compounds. A Perkin Elmer T GA 7 FT thermo-gravimetric analyzer (0.0-1400 °C) coupled with thermal analysis controller TAC 7/DX were used for recording the thermogravimetric measurements in a nitrogen atmosphere (25–900.0 °C) at 5 °C min rate using Al<sub>2</sub>O<sub>3</sub> as a reference. A Portable Potentiostat wave generator model PP-2 (Oxford Electrodes) coupled with a Phillips 8043 X-Y recorder. The electrochemical cell assembly consists of Pt wires (0.5 mm id.-BAS model MW-1032) as working and counter electrodes and a double-junction Ag/AgCl, KCl( $3.0 \text{ mol } L^{-1}$ ) as a reference electrode. The reference electrode was separated from the bulk solution by a fritted-glass bridge filled with the solvent/supporting electrolyte mixture. Bioanalytical system Pt mesh (100 w/in.) was used in the fabrication of OTTLE cell as reported [29]. Thin layer cyclic voltammetry experiments were performed on a home-built OTTLE that utilized a light transparent Pt mesh (BAS, 100 w/in.) working electrode [29]. Molar conductance  $(\Lambda_m)$  in DMF was carried out YSI-conductometer, Model-32. Magnetic data were measured on a Jhonson-Matthey magnetis susceptibility balance.

#### Preparation of the Schiff bases and their complexes

The Schiff bases BTS and B<sub>2</sub>ED (Fig. 1) were prepared by the method of Offiong [2,3]. To a hot solution of benzoin (2.0 mmole) in ethanol (10 mL), two drops of glacial acetic acid and thiosemicarbazide (2.0 mmole) or ethylenediamine (1.0 mmole) in hot ethanol (10 mL) were added. The reaction mixtures were refluxed for 2 h under constant stirring. The produced pale yellow solid precipitates of B<sub>2</sub>ED and BTS were separated out, filtered off, washed with hot ethanol, recrystalized from ethanol and finally dried at 110 °C. <sup>1</sup>HNMR spectrum of BTS showed signals at  $\delta$  3.7, 7.05, 8.6, 7.94 ppm due to OH, NH, NH<sub>2</sub> and benzylidenimin protons, respectively [25]. <sup>1</sup>HNMR spectrum of B<sub>2</sub>ED showed signal at  $\delta$  5.4 ppm and was assigned to OH proton. Signals at  $\delta$  7.02, 7.54, 7.66 and 8.54 ppm were attributed to benzylidenimin protons [15]. Azomethine proton signal was observed at  $\delta$  8.02–8.7 ppm as a multiplet in both BTS and B<sub>2</sub>ED ligands.

Metal complexes were prepared by mixing an accurate weight (4.0 mmole) of the Schiff base in hot ethanol (10 mL) with RhCl<sub>3</sub>, RuCl<sub>3</sub>·3H<sub>2</sub>O, PdCl<sub>2</sub>, CuCl<sub>2</sub> or Ni(CH<sub>3</sub>COO)<sub>2</sub> (2.0 mmole) in ethanol (25 mL) for 2 h with constant stirring. The precipitates were filtered off, washed with hot ethanol, ether and dried under vacuum at 70 °C.

#### **Results and discussion**

The prepared Schiff bases and their metal complexes are listed in Table 1 together with their elemental analyses and colors. The complexes are red, brownish black, brownish green, green, blue and buff and have high melting points >200 °C owing to their inherent stability. The complexes are stable in air, insoluble in common organic solvents and are easily soluble in DMF. The structures of the complexes are in agreement with their stoichiometries (Table 1). Rh(BTS)<sub>2</sub>Cl and Ru(BTS)<sub>2</sub>Cl have molar conductances in the range 47–58  $\Omega^{-1}$  indicating formation of of complexes of 1:1 electrolytic nature [30]. [Pd(BTS)Cl], [Cu(BTS)Cl.2H<sub>2</sub>O], [Cu(B<sub>2</sub>ED)], [Ni(B<sub>2</sub>ED)] have molar conductance in the range 2.6–4.3  $\Omega^{-1}$  confirming formation of non-electrolyte complex species [30].

#### Table 1

Physical properties and analytical data (%) of the Schiff bases and their metal chelates. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)<sup>a</sup>

Compound No.	Compound	Color	Calculated (Found) (%)					
			С	Н	Ν	М		
1	BTS	Yellow	63.86 (64.20)	5.58 (5.71)	14.41 (14.23)	-		
2	B <sub>2</sub> ED	Yellow	80.88 (81.21)	6.47 (6.60)	6.35 (6.42)	-		
3	[Rh(BTS) <sub>2</sub> ]Cl	Red	49.61 (49.96)	3.54 (3.46)	11.30 (11.26)			
4	[Ru(BTS) <sub>2</sub> ]Cl	Brownish black	50.40 (50.72)	3.97 (4.10)	11.90 (11.80)	14.38 (14.50)		
5	[Pd(BTS)Cl]	Brownish green	42.30 (42.90)	3.36 (3.42)	9.84 (9.42)	25.70 (25.80)		
6	[Cu(BTS)Cl H <sub>2</sub> O]	Green	36.36 (36.42)	3.20 (3.12)	8.05 (7.9)	20.98 (21.20)		
7	$[Cu(B_2ED)]$	Blue	70.73 (70.85)	5.11 (5.24)	5.50 (5.67)	12.37 (12.7)		
8	[Ni(B <sub>2</sub> ED)]	Buff	70.48 (70.60)	4.85 (4.70)	5.36 (5.20)	11.38 (11.20)		

<sup>a</sup> Theoretical values are given in parentheses.

#### Table 2

Significant IR frequencies (cm <sup>-1</sup>	) and bond length of M—N (r, A	<ul> <li>of metal chelates with relevant</li> </ul>	bands of the free Schiff bases in brackets. <sup>a</sup>
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Complex No.	$\nu_a \ NH$	$\nu_{s} \ NH$	δ ΝΗ	vC=N	$v$ CN + $\delta$ NH	vCN + vN—N	vC=S	νМ—О	vM—N	vM—S	vM—Cl	$\Delta v$	r(Å)
3	3274 s (3420s)	3169 s	1610	1605 (1635)	1530	1085	840	520	474	362		35	2.6
4	3260 (3420s)	3170 s (3165)	1595 (1610)	1600 (1635)	1575 m (1505)	1120 (1125)	860 m (900)	545 m	480	369		30	2.73
5	3270 m (3420) s	3185	1610	1595 (1635)	1530	1130	895	510	465		330, 290	32	2.69
6	3285 m	3190	1612	1603 (1635)	1520	1139	760	495 s	450	342	345	55	2.27
7				1590 (1620)				490	430			30	2.73
8				1570 s (1620)				480 s	390 w			50	2.44

<sup>a</sup> s = strong, m = medium and br = broad,  $v_{OH}$  = 3420–3452 cm<sup>-1</sup>.

#### Infrared studies

The IR spectra of the Schiff base BTS and its metal complexes suggest that, the ligand BTS bind to metal ions in a a mononegative tridentate fashion through C=S, C=N and OH groups with deprotonation of OH. This behavior was achieved for Ru<sup>3+</sup>, Rh<sup>3+</sup>, Pd<sup>2+</sup> and Cu<sup>2+</sup> complexes based upon the following evidence: (i) the v(C=S) and v(C=N) bands are shifted to lower frequency by 10–35 and 30–40 cm<sup>-1</sup>, respectively and (ii) the third coordinating site v(OH) at 3420 cm<sup>-1</sup> is shifted by 15–20 cm<sup>-1</sup> to lower frequency (Table 2) suggesting involvement of azomethine nitrogen in coordination of ligand with Ru<sup>3+</sup>, Rh<sup>3+</sup>, Pd<sup>2+</sup> and Cu<sup>2+</sup> ions [31,32]. The bands observed at 495–545, 450–480 and 342–369 cm<sup>-1</sup> are assigned to v(M–O), v(M–N) and v(M–S) [31,32], respectively. The two bands in the range 310–300 cm<sup>-1</sup> in the spectra of [Pd(BTS)Cl], and [Cu(BTS)Cl·H<sub>2</sub>O] are assigned to vM–Cl vibration [31].

The significant IR frequencies of most relevant bands of the free Schiff base B<sub>2</sub>ED and its [Ni(B<sub>2</sub>ED)] and[Cu(B<sub>2</sub>ED)]complexes with their probable assignments are also given in Table 2. The IR spectrum of B<sub>2</sub>ED showed characteristic vibrations of C=N and OH groups at 1620 and 3452 cm<sup>-1</sup> [31,32], respectively. In the spectra of Ni<sup>2+</sup> and Cu<sup>2+</sup> complexes, the azomethine band (vC=N) was shifted to lower wavenumber (1595–1605 cm<sup>-1</sup>) whereas, the v(OH) is shifted by 10–15 cm<sup>-1</sup> to lower frequency upon complex formation suggesting involvement of C=N and OH groups in coordination [30]. Bands in the range 480–490, 390–430 and 330–345 cm<sup>-1</sup> of Ni<sup>2+</sup> and Cu<sup>2+</sup> complexes are assigned to vM–N and vM–O [31], respectively.

The frequency shift  $(\Delta v)$  in the IR data (Table 2) is dependent on the nature of the transition metal ion and/or ligand involved in chelation and change in the electrostatic field of the metal ions and the vibrational dipoles of ligand [31]. The metal ions (Ru<sup>3+</sup>, Rh<sup>3+</sup>) or (Ni<sup>2+</sup>, Pd<sup>2+</sup>, Cu<sup>2+</sup> have the same charge, therefore the distance between the metal ion and the coordinating center would be the main factor affecting band shifts. Thus, the magnitude of frequency shifts between metal ion and the coordinating group (vC=N) was used for determining bond length (r) employing the equation [32]:

$$\Delta v = \left(\frac{32\pi\alpha}{a^2}\right) \left(\frac{v_{x=y} - v_{x-y}}{l}\right) \exp\left(-2\pi\sqrt{\frac{2r}{a}}\right) \tag{1}$$

where  $\alpha$  is the bond polarisability,  $\Delta v$  the shift in the oscillator frequency ( $v_{\text{ligand}}-v_{\text{complex}}$ ), *a* the lattice constant of the metal ion used [33],  $v_x - v_y$  the frequency of the oscillator with single bond,  $v_x = v_y$  the frequency of the oscillator with double bond, and *l* is the length of the oscillator coordinated to the metal ion. The plot of log  $\Delta v$  vs. (r)<sup>1/2</sup> was linear. The values of (r) and M—N of the complexes are given in Table 2. The v(C=N) shift and the calculated bond length (M—N) of the C=N group upon coordination of BTS Schiff base follow the order:

$$Cu^{2+} < Pd^{2+} > Rh^{3+} > Ru^{3+}$$

The M–N frequencies decreased in the same order as the azomethine vibrations, revealing thereby decreasing in the strength of the metal nitrogen bond in the same order. The low value of *r* Cu–N is attributed to increase in the strength of electrostatic field of the Cu<sup>2+</sup> as a result of the small ionic radius of copper (II) ion.

### Electronic spectra

The electronic spectra of the Schiff bases BTS and B<sub>2</sub>ED showed one  $\pi \rightarrow \pi^*$  transition at ~35,570 cm<sup>-1</sup> and two  $n \rightarrow \pi^*$  bands at ~32,700 and 29,800 cm<sup>-1</sup>. These bands were shifted to higher wavenumbers on complex formation. The spectra and positions of the absorption bands of the complexes in DMF and in solid state at ambient temperature are not significantly different, showing no electronic or geometric changes and the compositions of the chromophores of the complexes are the same in DMF and in solid state and are stable [34]. The spectra of the complexes in DMF with their probable assignments and ligand field parameters (10Dq,  $\beta$ , *B* and LFSE) [34] are given in Table 3.

In the spectrum of  $[Rh(BTS)_2]Cl$ , three absorption bands at  $v_1 = 16,790$ ,  $v_2 = 28,620$  and  $v_3 = 39,420$  cm<sup>-1</sup> were observed with low molar extinction coefficients (Table 3). The complex was diamagnetic and it is consistent with O<sub>h</sub> symmetry of N and S atoms producing strong field. <sup>1</sup>H NMR spectrum in d<sub>6</sub>-DMSO showed signals at  $\delta$  7.07, 8.6, and 7.94 ppm assigned to NH, NH<sub>2</sub> and benzylidenimin protons, respectively [29]. The azomethine proton (CH=N) signal showed downfield shift at  $\delta$  8.16–8.7 ppm indicating involvement of azomethine in coordination. Thus, the first two bands were assigned to spin-allowed transitions for  $t_2^{5}g \ e^1g$  state in O<sub>h</sub> symmetry around Rh. Hence, the two peaks were assigned to  ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ , and  ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$  and charge transfer  ${}^{1}A_{1g} \rightarrow b$ ,  ${}^{1}T_{1u}$  transitions, respectively.

The interelectronic repulsion parameter *B* of  $[Rh(BTS)_2]Cl$  was about 59% of the free ion (*B* = 720 cm<sup>-1</sup>) (Table 3) indicating considerable orbital overlap with a strongly covalent metal–ligand bond character [34]. The low value of B is associated with a reduction in the effective nuclear charge (*Z*<sup>\*</sup>) on Rh<sup>3+</sup> ion [34]. The variation of *B* of 4 d metal ions with ionic charge (*Z*<sup>\*</sup>), and the number of d-electrons in the partially filled d-state (*q*) is given by the equation:

$$B = 742 + 28q = 50(Z^* + 1) - 500/(Z^* + 1)$$
<sup>(2)</sup>

The value of  $Z^*$  of Rh in [Rh(BTS)<sub>2</sub>]Cl complex was 0.75 below the formal value of trivalent metal ions. The nephelauxetic parameter  $\beta$  (0.58) of the complex indicated that, the ligand BTS lies is in the middle of the nephelauxetic of other nitrogen donor series indicating participation of BTS in a tridentate fashion (SNO) to Rh<sup>3+</sup>.

The spectrum of [Ru(BTS)<sub>2</sub>]Cl displayed three bands at  $v_1 = 13,700, v_2 = 21,320$  and  $v_3 = 23,600$  cm<sup>-1</sup>. The  $\mu_{\text{eff}}$  of the complex was 1.94 BM, indicating a one electron paramagnetic of a low spin  $t_{2\alpha}^5$  (S = 1/2) O<sub>h</sub> symmetry around Ru (III) ion. Hence, the ground state  ${}^{2}T_{1g}$  of Ru (III) in an O<sub>h</sub> environment is arising from  $t_{2g}^5$  configuration [34]. The order of increasing energy of the first excited doublet levels is  ${}^{2}A_{2g}$  and  ${}^{2}T_{1g}$  arising from  $t_{2g}^{5}$   $e_{g}^{1}$  configura-tion. Hence, the first ( $\nu_{1}$ ) and third ( $\nu_{3}$ ) bands are assigned to the spin forbidden  ${}^{2}T_{1g} \rightarrow {}^{2}E_{2g}$  and  ${}^{2}T_{1g} \rightarrow {}^{2}A_{1g}$  whereas, the band at 21,320 cm<sup>-1</sup> is due to the spin allowed transitions  ${}^{2}T_{2g} \rightarrow {}^{2}A_{2g}$  of low spin d<sup>5</sup> Ru<sup>3+</sup> in  $O_h$  geometry, t<sup>5</sup><sub>2g</sub> [27–29]. B value was about 443 cm<sup>-1</sup> and 70% of the free ion (B = 630 cm<sup>-1</sup>) indicating considerable orbital overlap with a strongly covalent metal-ligand bond character [25]. The low values of 10Dq and B for  $Rh^{3+}$  and  $Ru^{3+}$ complexes (Table 3) may be attributed to participation of S in coordination [25]. The nephelauxetic parameter,  $\beta_{35}$  of Rh<sup>3+</sup> and Ru<sup>3+</sup> BTS complexes was 0.58 and 0.64, respectively. The 10Dq values (Table 3) are close to the range for RuN<sub>2</sub>O<sub>2</sub>S<sub>2</sub> [25]. Thus, the ligand BTS lies in middle range of the spectrochemical series. The decrease in B values of the two complexes compared to the free ions suggests strong covalent bonding between the donor site and the metal ions. The increase in the 10Dg, was associated with considerable electron delocalization in the complex [29-31]. A representative structure of Rh<sup>3+</sup> or Ru<sup>3+</sup> complex is proposed in Fig. 2. The electronic spectrum of [Pd(BTS)Cl] showed peaks at 20,449,

The electronic spectrum of [Pd(BTS)Cl] showed peaks at 20,449, 21,929 cm 24,043 and 26,666 cm<sup>-1</sup> (Table 3) with low extinction coefficient. The complex was diamagnetic and its <sup>1</sup>H NMR spectrum in d<sub>6</sub>-DMSO showed proton signals at  $\delta$  7.07, 8.6, 7.94; 8.4–8.9 ppm and were assigned to NH, NH<sub>2</sub>, benzylidenimin and CH=N

protons, respectively [29] indicating participation of OH and the CH=N groups. Thus, the two peaks at 20,449 and 21,929 cm<sup>-1</sup> were assigned to spin allowed transitions  ${}^{1}A_{2g} \rightarrow {}^{1}B_{g}$  and  ${}^{1}A_{1g} \rightarrow {}^{1}E_{g}$  in square planar-geometry [34]. Bands at 24,043 and 26,666 cm<sup>-1</sup> are assigned to CT or ligand bands [34].

The spectrum of [Cu(BTS)Cl H<sub>2</sub>O] showed three bands around 12,820 (br.), 25,440 and 34,366 cm<sup>-1</sup> (Table 3).  $\mu_{eff}$  was 1.8 B.M concluding formation of paramagnetic copper complex. Thus, broad band at 12,820 cm<sup>-1</sup> was assigned to  ${}^{2}E_{2g} \rightarrow {}^{2}T_{2g}$  transition in Oh symmetry [34]. The band at 25,440 cm<sup>-1</sup> was assigned to S  $\rightarrow$  Cu (II) LMCT, whereas the band at 34,366 cm<sup>-1</sup> was assigned to O  $\rightarrow$  Cu (II) LMCT and intraligand ( $n \rightarrow \pi^{*}$ ) charge transfer [34]. Thermal analysis of the complex showed well defined peak at 160 °C due to loss of water molecule suggesting water coordination to central copper (II).

Based upon the 10Dq values (Table 3) of the aformentioned  $O_h$  BTS complexes, the stability of the complexes followed the order [28]:

 $[Ru(BTS)_2]Cl > [Rh(BTS)_2]Cl > [Cu_2(BTS)_2Cl_2 \cdot 2H_2O]$ 

In the spectrum of [Cu(B<sub>2</sub>ED)], the broad bands at 14,700 cm<sup>-1</sup> (log  $\varepsilon$  = 1.6) and 16,650 cm<sup>-1</sup> were assigned to spin allowed <sup>2</sup>B<sub>1g</sub>  $\rightarrow$  <sup>2</sup>A<sub>1g</sub> ( $v_1$ ) ( $d_{\chi^2-\gamma^2} \rightarrow d_{Z^2}$ ) (10Dq) and <sup>2</sup>B<sub>1g</sub>  $\rightarrow$  <sup>2</sup>E<sub>g</sub> ( $v_3$ ) ( $d_{\chi^2-\gamma^2} \rightarrow d_{XZ}$ ,  $d_{XZ}$ ) transitions in square-planar geometry [34].  $\mu_{eff}$  of the complex was 1.76 B.M. and close to the spin moment for one un-unpaired electron confirming the proposed structure. The spectrum of [Ni(B<sub>2</sub>ED)] showed two bands at 21,270, 27,170 and 33,120<sub>(sh)</sub> cm<sup>-1</sup>. The complex was diamagnetic and its <sup>1</sup>H NMR spectrum showed signals at  $\delta$  7.02, 7.54, 7.66, 8.54 and 8.8 ppm confirming deprotonation of OH group upon coordination. The bands at 21,270, 27,170 and 33,120 (sh) cm<sup>-1</sup> are assigned to <sup>1</sup>A<sub>1g</sub>  $\rightarrow$  <sup>1</sup>A<sub>2g</sub> ( $v_3$ ) and <sup>1</sup>A<sub>1g</sub>  $\rightarrow$  <sup>1</sup>B<sub>2g</sub> ( $v_2$ ) and a CT transitions in a square-planar geometry [34], respectively.

#### Redox behavior of metal complexes

The CV data of selected complexes vs. Ag/AgCl electrode at 50 mV s<sup>-1</sup> sweep rate ( $\nu$ ) are summarized in Table 4. Representative CV of [Rh(BTS)<sub>2</sub>]Cl complex in DMF-TBA<sup>+</sup>Cl<sup>-</sup> is shown in Fig. 3. In the CV of [Rh(BTS)<sub>2</sub>]Cl, one cathodic peak ( $E_{p,c}$ ) at -0.86 V coupled with one anodic peak ( $E_{p,a}$ ) at -0.2 V with potential–potential separation ( $\Delta E_p = E_{p,a} - E_{p,c}$ ) of 0.66 V were observed The number of electron transfer was calculated from charge–time curve of controlled potential coulometry (CPC) at the potential of the limiting current plateau of cathodic peak under N<sub>2</sub> atmosphere at Pt net electrode under the same experimental conditions. The complex was reduced by a potential step from -0.2 V to -0.9 V and the number of electron transfer was calculated using the equation:

$$Q_{\rm F} = Q_{\rm T} - Q_{\rm B} = n \rm FVc \tag{3}$$

where Q is the charge in coulomb,  $Q_F$  the faradic charge required for complete electrolysis of the complex in solution,  $Q_T$  the faradic charge required for complete electrolysis of the test solution which was measured by extrapolating the linear of the curve to zero time,  $Q_B$  the faradic charge required for complete electrolysis of the supporting electrolyte only, V the volume of the test solution in the cell in liter, C the concentration of the test solution, mol L<sup>-1</sup> and F is the Faraday's number, 96,485 C/equiv. A value of one electron transfer was computed from charge–time curve. One electron nature of this couple was also established by comparing the displayed current height with similar analogous of Rh (III) complexes [24]. The irreversible nature of the couple was confirmed from the observed increase in  $\Delta E_p$  on rising scan rate.

The product of the number of electron transfer involved in the reduction step ( $n\alpha$ ) and the corresponding charge transfer coeffi-

# Table 3 Electronic spectral data (cm<sup>-1</sup>) of the complexes with band assignments and ligand field parameters (Dq) in DMF.

Complex	Band position $(cm^{-1})\times 10^{-3}$	Assignments	$10 Dq \times 10^{-3} cm^{-1} \label{eq:mass_star}$	<i>B</i> (cm <sup>-1</sup> )	$\beta_{35}$	LFSE $(cm^{-1})$
[Rh(BTS) <sub>2</sub> ]Cl	16.79 (v <sub>1</sub> ) 28.62 (v <sub>2</sub> ) 39.42 (v <sub>3</sub> )	$\label{eq:constraint} \begin{array}{l} {}^1A_{1g} \rightarrow {}^1T_{1g} \\ {}^1A_{1g} \rightarrow {}^1T_{2g} \\ {}^1A_{1g} \rightarrow b, {}^1T_{1u} \end{array}$	24.260	424.8	0.58	10.62
[Ru(BTS) <sub>2</sub> ]Cl	13,700 21.32 24.86	$\label{eq:target} \begin{array}{c} {}^2T_{1g} \rightarrow {}^2E_{2g} \\ {}^2T_{2g} \rightarrow {}^2A_{2g} \\ {}^2T_{1g} \rightarrow {}^2A_{1g} \end{array}$	27.342	443	0.70	16.67
[Pd(BTS)Cl]	20.449 21.929 24.043 26.664	$\label{eq:constraint} \begin{array}{l} {}^1A_{1g} \rightarrow {}^1A_{2g} \\ {}^1A_{1g} \rightarrow {}^1B_{1g} \\ {}^1A_{1g} \rightarrow {}^1E_g \end{array}$				
[Cu(BTS)Cl H <sub>2</sub> O]	12.82 25.44 34.36	$\label{eq:E2g} \begin{array}{l} {}^2E_{2g} \rightarrow {}^2T_{2g} \\ S \rightarrow Cu \\ n \rightarrow \pi^* \end{array}$	12.820			
[Cu(B <sub>2</sub> ED)]	14.70 16.65 27.47 (sh) 28.65	$\label{eq:B1g} \begin{array}{l} {}^2B_{1g} \rightarrow {}^2A_{1g} \\ {}^2B_{1g} \rightarrow {}^2E_g \\ CT, \ d \rightarrow \pi^* \\ IL \ (CT) \end{array}$	14.700			
[Ni(B <sub>2</sub> ED)]	21.27 27.17 33.12	$\label{eq:constraint} \begin{array}{l} {}^{1}A_{1g} \rightarrow {}^{1}E_{g} \\ {}^{1}A_{1g} \rightarrow {}^{1}B_{2g} \\ IL \ (CT) \end{array}$				

#### Table 4

Bulk and thin layer cyclic voltammetric data of selected complexes at 100 mV/s in DMF-TBA+Cl- vs. Ag/AgCl reference electrode.<sup>a</sup>

Complex	A								
	Couple I			Couple II			Couple III		
	E <sub>p,c</sub>	E <sub>p,a</sub>	$\Delta E_{\rm p}$	E <sub>p,c</sub>	E <sub>p,a</sub>	$\Delta E_{\rm p}$	E <sub>p,c</sub>	$E_{\rm p,a}$	$\Delta E_{\rm p}$
[Rh(BTS) <sub>2</sub> ] Cl [Ru(BTS) <sub>2</sub> ]Cl	-0.86 (-0.5) -1.22	$-0.2 \ (-0.06) \\ -0.24$	0.66 (0.44) 0.98	0.04 (0.02)	1.5 (0.5) 1.68	1.46 (0.48)	-1.3		
[Ru(BTS) <sub>2</sub> ]Cl* [Cu <sub>2</sub> (BTS)Cl H <sub>2</sub> O]	$-0.71 \ (-0.54) \\ -0.41$	-0.13 (-0.22) -0.2	0.58 (0.32) 0.21	0.29	0.73 (0.68) 0.55	0.44	-1.14	1.56	2.7
[Cu(B <sub>2</sub> ED)]	-0.32	-0.11	0.21	0.5	0.85	0.35	-1.13		

<sup>a</sup> Electrochemical data of OTTLE experiments are given in parantheses.





**Fig. 4.** Plot of  $E_{p,c}$  of the redox couple  $Rh^{3*}/Rh^{2*}$  vs. log v of  $[Rh(BTS)_2]Cl$   $(1 \times 10^{-3} \text{ mol } L^{-1})$  in DMF-TBA\*Cl<sup>-</sup>  $(1 \times 10^{-2} \text{ mol } L^{-1})$  at Pt electrode vs. Ag/AgCl electrode.

Fig. 3.	CVof $[Rh(BTS)_2]Cl (1 \times 10^{-3} \text{ mol } L^{-3})$	<sup>-1</sup> ) in DMF-TBA <sup>+</sup> Cl <sup>-</sup> (1 × 10 <sup>-2</sup> r	nol L <sup>-1</sup> ) at
50 mV	s <sup>-1</sup> scan rate at Pt electrode vs. Ag	/AgCl electrode.	

cient ( $\alpha$ ) was calculated from the linear dependence of cathodic peak potential ( $E_{p,c}$ ) vs. log v (Fig. 4) using the equation:

$$\Delta E_{\rm p,c}/\Delta logv = -29.58/\alpha n_{\alpha} \tag{4}$$

Assuming n = 1, the value of  $\alpha$  was found 0.56 in the range expected for irreversible one-electron transfer step [35,36]. Thus, electron transfer nature of the complex can be expressed by the irreversible metal-based reduction (Rh<sup>3+</sup>/Rh<sup>2+</sup>) couple [37,38] as given in the following equation:



Fig. 5. CV of  $[Ru(BTS)_2]Cl$   $(1 \times 10^{-3} \text{ mol } L^{-1})$  in DMF TBA<sup>+</sup>Cl<sup>-</sup> (A, B) and DMF-TBA<sup>+</sup>PF<sub>6</sub><sup>-</sup> (C) at 100 mV/s at Pt electrode vs. Ag/AgCl electrode.



Fig. 6. CV of  $[Cu(B_2ED)]~(1\times 10^{-3}~mol~L^{-1})$  in DMF TBA\*Cl^ at 100 mV/s at Pt electrode vs. Ag/AgCl electrode.

$$[Rh^{III}(BTS)_2]Cl^0 + e^- \rightarrow [Rh^{II}(BTS)^2]Cl^-$$
(5)

The reduction peak current,  $(i_{p,c})$  of the couple increased on increasing the scan rate from v = 10 to  $100 \text{ mV s}^{-1}$  and the anodic/catodic peak currents ratios  $(i_{p,a}/i_{p,c})$  were less than unity and gradually increases to unity on increasing scan rate. Plot of  $i_{p,c}$  vs.  $v^{1/2}$  was linear indicating diffusion-controlled electrochemical process [36]. The current function  $(i_{p,a}/v^{1/2})$  approximately remains constant along the whole range of scan rate indicating that a coupled chemical reaction of EC mechanism type takes place [38,39. Based on the CV of other analogous of Rh (III) complexes [35], the observed couple with an ill defined  $E_{p,c}$  at 0.04 V,  $E_{p,a} = +1.5$  V and  $\Delta E_p = 1.46$  V was tentatively assigned as metal based oxidation of Rh<sup>3+</sup>/Rh<sup>4+</sup>. The plot of the current ratio  $(i_{p,a}/i_{p,c})$  vs.  $v^{1/2}$  was linear and parallel

to the X axe ( $v^{1/2}$ ), suggesting a negligible adsorption on the electrode surface [35].

The CV of  $[Ru(BTS)_2]Cl$  in DMF-TBA<sup>+</sup>Cl<sup>-</sup> at Pt electrode at 100 mV s<sup>-1</sup> showed  $E_{p,c}$  at -1.22 V coupled with an  $E_{p,a}$  = +1.5 V at -0.24 V with  $\Delta E_p$  = 0.98 V (Fig. 5A and B). CPC under N<sub>2</sub> at a Pt net electrode at the same experimental conditions showed one electron transfer. On increasing the scan rate > 200 mV s<sup>-1</sup>, the  $E_{p,c}$  was shifted cathodically, while  $E_{p, a}$  shifted anodically confirming irreversible nature of the couple. At a scan rate < 200 mVs<sup>-1</sup>, the  $\delta E_p$  values between the two counter peaks ( $E_{p, a}$ ,  $E_{p, c}$ ) decreased on lowering the scan rate. Thus, the couple was assigned to the irreversible reduction couple Ru<sup>3+</sup>/Ru<sup>2+</sup> [39,40]. Plot of  $i_{p,c}$  vs.  $v^{1/2}$  was linear indicating that, the electrode reaction is diffusion controlled process and mass transfer is limited [38]. Based on CPC of  $E_{p,a}$  at 1.68 V and comparison with other analogs of Ru<sup>3+</sup> complexes [37,38], the couple was assigned to irreversible Ru<sup>3+</sup>/Ru<sup>4+</sup>.

Thin layer CV using OTTLE cell of  $[Ru(BTS)_2]Cl$  (Fig. 5C) showed two  $E_{p,c}$  at -0.71 and 0.29 V coupled with two  $E_{p,a}$  at -0.13 and 0.73 V with  $\Delta E_p = 0.58$  and 0.44 vs. Ag/AgCl electrode (Table 4), respectively.  $E_{p,c}$  at -0.71 V was assigned to Ru<sup>III</sup>/Ru<sup>II</sup> couple as follows:

$$[Ru^{III}(BTS)_2]Cl + e^- \rightarrow [Ru^{II}(BTS)_2]Cl$$
(6)

CPC under N<sub>2</sub> gas at a Pt electrode on the limiting current plateau of the second couple revealed one electron transfer. Thus, the couple of  $E_{p,c} = 0.29$  V and  $E_{p,a} = 0.73$  V V (Fig. 5C) was assigned to Ru<sup>3+</sup>/Ru<sup>4+</sup> couple [27,28].

The CV data of [Cu(B<sub>2</sub>ED)] and [Cu(BTS)Cl.H<sub>2</sub>O at 100 mV s<sup>-1</sup> are given in Table 4 and representative CV of [Cu(B<sub>2</sub>ED)] is shown in Fig. 6. CV showed one  $E_{p,c} = -0.32$  V,  $E_{p,a} = -0.11$  V and  $\Delta E_p = 0.21$  -V (Table 4) and CPC of this couple revealed one-electron transfer step. On increasing the scan rate, a slight shift on the potentials of  $E_{p,a}$  and  $E_{p,c}$  was noticed, while  $i_{p,a}$  became smaller relative to  $i_{p,c}$  on decreasing scan from 100 to 10 mV s<sup>-1</sup>. Analysis of  $i_{p,c}$  = f  $(v^{1/2})$  and  $E_{p,c} = f(\log v)$  is consistent with diffusion-controlled electro-chemical process. Thus, the couple was assigned to Cu<sup>2+</sup>/Cu<sup>+</sup> with CE mechanism [40]. Based on CPC data, the couple with  $E_{p,c} = +0.5 \text{ V}, E_{p,a} = +0.85 \text{ V}$  and  $\Delta E_p = 0.35 \text{ V}$  was safely assigned to irreversible  $\text{Cu}^{2+}/\text{Cu}^{3+}$  couple [41]. Change from  $\text{Cu}(\text{II}) \rightarrow \text{Cu}(\text{III})$ state (d<sup>8</sup> low spin) involves a drastic reduction of the metal ion radius and no changes in the geometries of Cu<sup>2+</sup>/Cu<sup>3+</sup> complexes in solution. The more positive values of  $E_{p,a}$  (Table 4) the more difficulty in stabilizing Cu (III) state for both copper (II) complexes. The values of  $E_{p,c}$  for  $Cu^{2+}/Cu^{+}$  couple (Table 4) revealed the difficulty in reducing Cu(II) ion in both complexes.

The potential of the redox couples of Rh<sup>3+</sup>, Ru<sup>3+</sup>, Pd<sup>2+</sup> and Cu<sup>2+</sup> of BTS complexes may be related to the nature of the orbitals involved in the redox processes. These orbitals are HOMO consisting predominately of the  $d_{\chi^2-\gamma^2}$  and LUMO consisting of  $\pi^*$  orbital of BTS. The high positive value of the couple Rh<sup>2+</sup>/Rh<sup>3+</sup> or Ru<sup>2+</sup>/Ru<sup>3+</sup> (Table 4) compared to the corresponding couples was explained in terms of the higher energy of  $d_{\chi^2-\gamma^2}$  in Pd than in Rh or Ru [42]. Thus, the changes in  $E_{1/2}$  are strongly related to changes in the electrophilic properties of the metal ions. Within the context of ligand field theory, the correlation between  $E_{1/2}$  of these couples and the size of the metal ion involved has been attributed to the spherical potential generated by the electron density of the donor atoms in the antibonding d-orbitals as reported by Lintvedt and Fenton [43].

### 4. Conclusion

BTS complexes with  $Rh^{3+}$ ,  $Ru^{3+}$  and  $Cu^{2+}$  are six-coordinate octahedral. The M (II) and M (III) complexes may be used as one-electron redox reagents, since the former is a strong reducing agent and the latter is strong oxidizing agent. The low  $\Delta E_p$  in the OTTLE cell for the redox couples favor reversibility as compared to bulk CV.

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