

CHAPTER V

BIPYRAZINE/BIPYRIMIDINE COMPLEXES OF RUTHENIUM(II)- L AND OSMIUM(II)-L

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ABSTRACT : Different synthetic routes for mixed-tris complexes of type $[ML'L_2](ClO_4)_2 \cdot H_2O$ [$M = Ru$ (**4**) or Os (**5**); $L' = 2,2'$ -bipyrazine (bpyz) or $2,2'$ -bipyrimidine (bpym) and $L = 2$ -(phenylazo)pyridine (L^1) or 2 -(*m*-tolylazo)pyridine (L^2) have been found out. The chelates (**4** and **5**) have been characterised on the basis of spectroscopic and physicochemical results. Osmium complexes show a much lower wave number shift of $\nu(N=N)$ from the free ligand value (1425 cm^{-1}), indicating better π -donicity of the late member osmium compared to ruthenium. The single sharp methyl signal in $[RuL'L_2]^{2+}$ (**4**) ($L' = \text{bpyz}$ or bpym) is in line with the stereoretentivity of the solvolytic displacement reaction in ruthenium complexes. The corresponding osmium complexes exhibit three signals, two of which have equal heights, reflecting stereochemical rearrangement during halide substitution. The complexes display an intense metal-to-ligand charge transfer (MLCT) transition at $\sim 500\text{ nm}$ alongwith shoulders. A number of spin forbidden transitions are also observable in osmium complexes. In MeCN solutions the complexes display a nearly reversible one-electron oxidative response corresponding to metal(III) - metal(II) couple. Comparison of formal potential (E^0) with the reported value for pure tris complexes demonstrates that π -acceptance follows the order $\text{bipy} < \text{bpym} < \text{bpyz} < L$. On the negative side of SCE five consecutive one-electron ligand-based (L/L') reductions are observable within the available potential window.

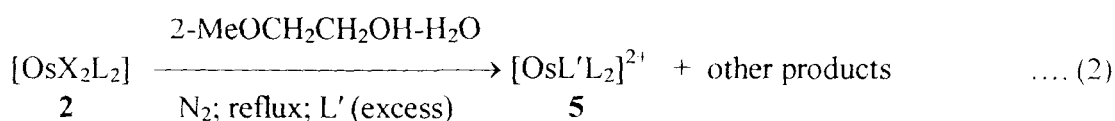
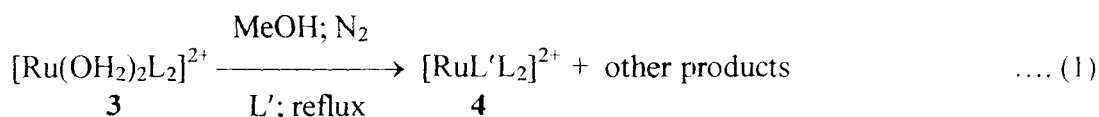
V.1 INTRODUCTION

The chemistry of 2-(aryloxy)pyridines (L; **1**), a non-innocent¹ N,N-chelating ligand in ruthenium²⁻⁸ and osmium⁹⁻¹² bound state is of special interest by several groups. The prime concern of these studies is to investigate the electron transfer properties of different complexes in varied oxidation states of the metal. The literature shows that ruthenium chemistry is well documented; however, corresponding osmium chemistry remains less studied. We were interested to explore the chemistry of osmium(II)-L that remains uninvestigated so far. In previous chapters we have examined the reaction behaviour of [OsX₂L₂] (**2**) (X = Cl or Br) towards monodentate anionic ligands like NO₂⁻, SCN⁻ and N₃⁻ (**Chapter III**) and neutral ligands like pyridine (py), pyrazine (pyz) and pyrazole (pzH) (**Chapter IV**). In this chapter we are investigating the reactions of **2** with two redox-active ligands^{1,13,14} (L') viz. 2,2'-bipyrazine (bpyz) and 2,2'-bipyrimidine (bpym). Successfully we have isolated complexes of the type [OsL'L₂]²⁺ from reaction between [OsX₂L₂], **2**, and L' in boiling aqueous 2-methoxyethanol. The corresponding ruthenium chemistry remains unexplored. So, for a comparative purpose we have also prepared ruthenium complexes, [RuL'L₂]²⁺, by reaction between solvento complex [Ru(OH₂)₂L₂]²⁺ (**3**) and L' in methanol. The details of synthesis and characterisation and redox stability of metal/ligand oxidation levels of these mixed-tris complexes, [ML'L₂]²⁺ [M = Ru (**4**)/Os (**5**)], are the subject matter of this chapter.

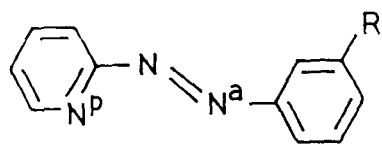
V.2 RESULTS AND DISCUSSION

A. SYNTHESIS

The convenient synthetic routes used for the preparation of ruthenium (**4**) and osmium (**5**) compounds are shown in **equations 1** and **2**, respectively. Different synthetic principles are

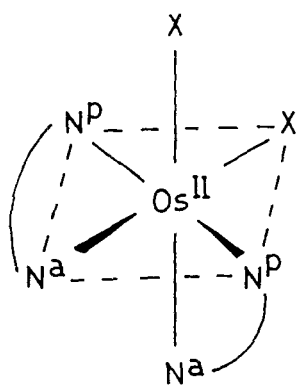


involved in reactions 1 and 2. This is due to the difference in use of starting materials for these two congeneric metal ions. The ease in availability⁵ of the blue diaquo species **3** with highly



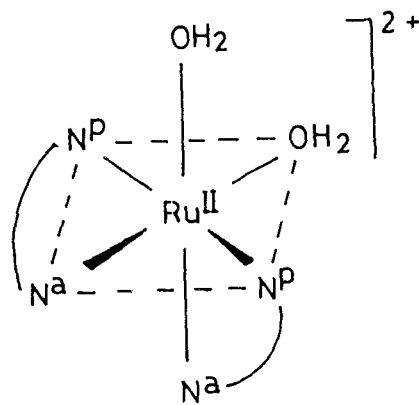
R = H; L¹
 R = Me; L²

L; 1



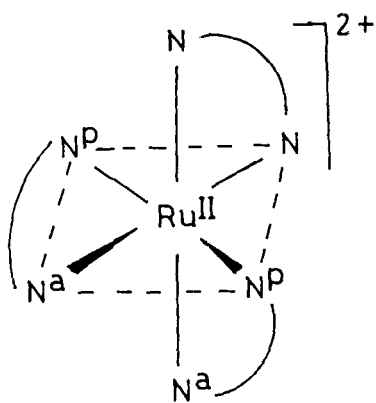
X = Cl, Br
 ctc

2

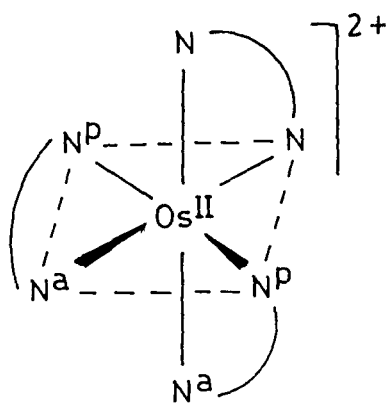


ctc

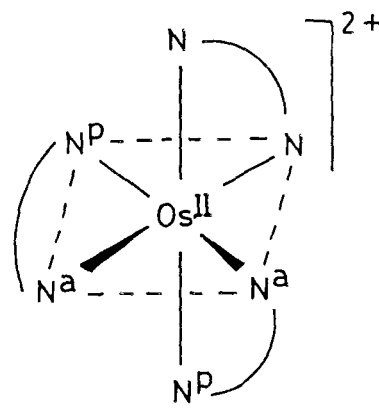
3



4



5'



5''

CHART V. 1

labile leaving group (H_2O) gives rise to facile reaction path. A 1:1.5 ratio of complex : ligand and use of MeOH (b.p., 338 K) as solvent ensure completion of the reaction within a short (2 h) time period. $[\text{RuL}'\text{L}_2]^{2+}$ was obtained in high yield through solvolytic displacement of the H_2O molecule from coordination zone followed by subsequent chelation by L' . On the other hand, lack of a route to obtain corresponding solvento complexes in osmium restricts use of labile centre(s). We had to use blue-violet dihalo complex **2** as a precursor. Further a ten-fold excess of L' along with a high boiling (b.p., 398 K) solvent like 2-methoxyethanol was needed for the completion of the reaction. The nucleophilic displacement of halide ions and subsequent chelation by L' furnished the mixed-tris complex. In MeOH the reaction does not proceed at all. The use of such drastic reaction conditions and prolonged boiling gives rise to extensive stereochemical rearrangement on substitution. Iterative separation by column chromatography did not afford pure isomers. On the contrary, a mild reaction condition in ruthenium yields stereoretentive products (see below; ^1H NMR results).

The new complexes (**4a** - **4d** and **5a** - **5d**) were characterised by elemental (C, H and N) analyses, solution electrical conductivities, spectroscopic (IR, NMR and UV-Vis) properties and electrochemical [cyclic voltammetry (CV), differential pulse voltammetry (DPV) and coulometry] results. The pertinent features are summarised in **Tables V.1 - V.7**. The air stable moisture-insensitive complexes are soluble in a range of common organic solvents like alcohols, dichloromethane, acetonitrile, dimethylformamide and dimethylsulfoxide and moderately soluble in water. In MeCN all the complexes (**4** and **5**) behave as 2:1 electrolytes which are reflected¹⁵ in high conductivity values (**Table V.1**).

B. INFRARED SPECTRA

The infrared spectra of complexes **4** and **5** were recorded in the range 4000 - 300 cm^{-1} . Selected frequencies are given in **Table V.2** and **Figure V.1**. All the diperchlorate monohydrates display characteristic¹⁶ ionic perchlorate bands at ~ 1100 (ν_3) and ~ 620 (ν_2) cm^{-1} and a lattice water band at ~ 3400 cm^{-1} . $\nu(\text{C}=\text{N})$ at ~ 1590 cm^{-1} is invariably seen in all complexes. Osmium complexes show a much lower wave number shift of $\nu(\text{N}=\text{N})$ from free ligand value^{2b,17} (1425 cm^{-1}). This is indicative of greater π -donicity of the late member osmium compared to ruthenium. Again of bpyz and bpym complexes, the former has greater $\nu(\text{N}=\text{N})$ value which is in line^{13,14} with greater π -acceptance strength of bpyz. It is well documented² that the greater the

TABLE V. 1

Molar Electrical Conductivity Data^a in MeCN at 298 K

Compound	Λ_M (ohm ⁻¹ cm ² mol ⁻¹)
[Ru(bpyz)L ¹ ₂](ClO ₄) ₂ .H ₂ O (4a)	260
[Ru(bpyz)L ² ₂](ClO ₄) ₂ .H ₂ O (4b)	265
[Ru(bpym)L ¹ ₂](ClO ₄) ₂ .H ₂ O (4c)	260
[Ru(bpym)L ² ₂](ClO ₄) ₂ .H ₂ O (4d)	270
[Os(bpyz)L ¹ ₂](ClO ₄) ₂ .H ₂ O (5a)	240
[Os(bpyz)L ² ₂](ClO ₄) ₂ .H ₂ O (5b)	240
[Os(bpym)L ¹ ₂](ClO ₄) ₂ .H ₂ O (5c)	245
[Os(bpym)L ² ₂](ClO ₄) ₂ .H ₂ O (5d)	240

^aSolute concentration, ~ 10⁻³ M.

TABLE V. 2

Selected Infrared^{a-c} Frequencies (cm⁻¹)

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{N}=\text{N})$	$\nu(\text{ClO}_4)$
[Ru(bpyz)L ¹ ₂](ClO ₄) ₂ .H ₂ O (4a)	1595	1350	1090, 620
[Ru(bpyz)L ² ₂](ClO ₄) ₂ .H ₂ O (4b)	1595	1350	1085, 620
[Ru(bpym)L ¹ ₂](ClO ₄) ₂ .H ₂ O (4c)	1590	1345	1085, 620
[Ru(bpym)L ² ₂](ClO ₄) ₂ .H ₂ O (4d)	1590	1345	1090, 620
[Os(bpyz)L ¹ ₂](ClO ₄) ₂ .H ₂ O (5a)	1590	1315	1085, 620
[Os(bpyz)L ² ₂](ClO ₄) ₂ .H ₂ O (5b)	1595	1315	1085, 620
[Os(bpym)L ¹ ₂](ClO ₄) ₂ .H ₂ O (5c)	1590	1310	1085, 620
[Os(bpym)L ² ₂](ClO ₄) ₂ .H ₂ O (5d)	1595	1310	1090, 620

^aIn KBr discs (4000 - 300 cm⁻¹). ^bBands at ~ 1090 cm⁻¹ are due to ν_3 type (broad and strong) and at 620 cm⁻¹ are ν_2 type (sharp and strong). ^cLattice water band observable at ~ 3400 cm⁻¹.

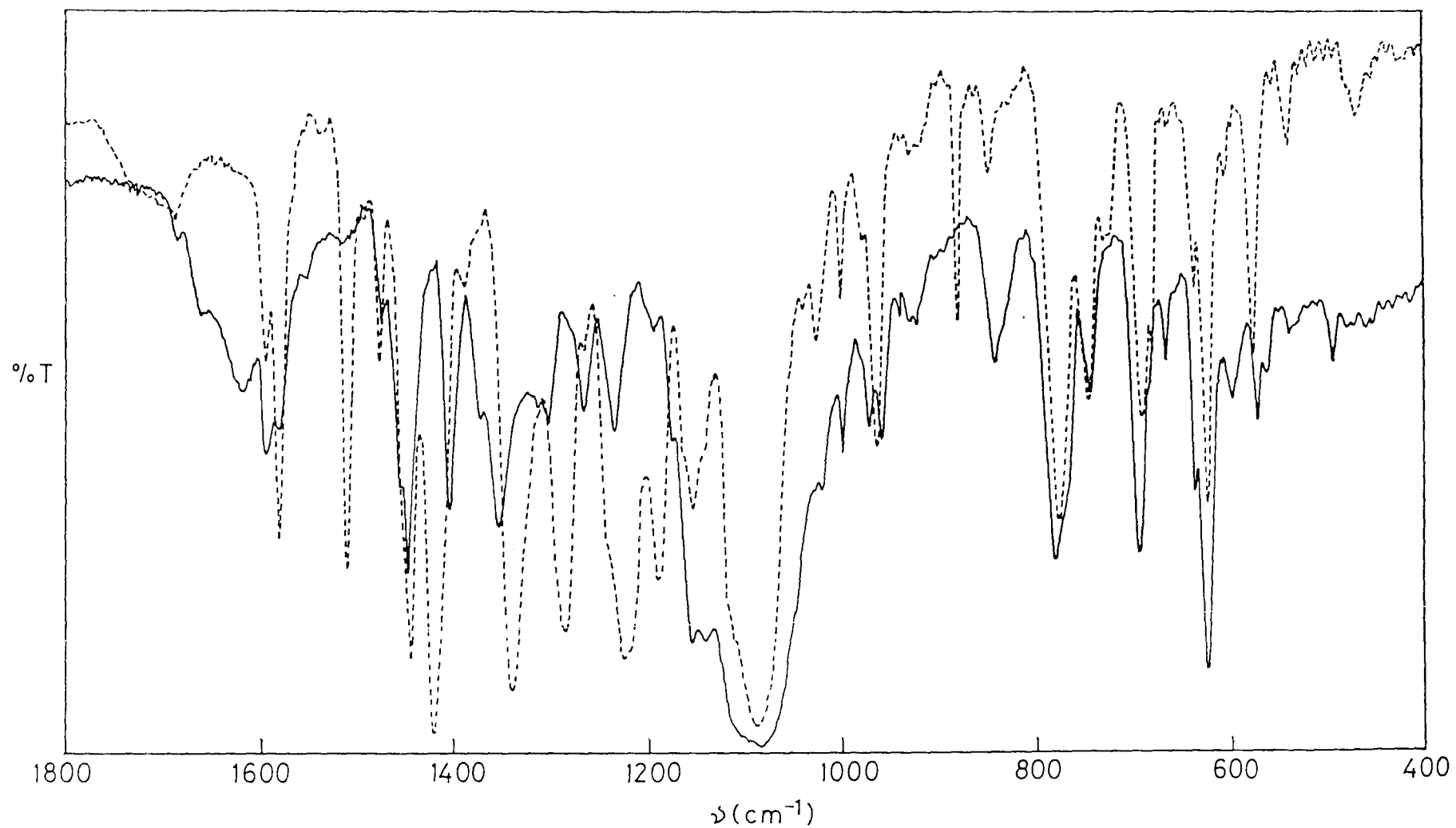


FIGURE V.1. IR SPECTRA OF (a) $[\text{Os}(\text{bpyz})\text{L}^2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (---) AND (b) $[\text{Ru}(\text{bpyz})\text{L}^2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (—) IN KBr DISC

π -acceptor strength of co-ligands, the less the π -back donation toward L and that the result is higher $\nu(\text{N}=\text{N})$ value.

C. ^1H NMR SPECTRA

^1H NMR investigation of selected complexes was made to solve the stereochemical problem of these tris complexes. The pertinent results are summarised in **Table V.3**. Representative spectral patterns are shown in **Figure V.2**. The methyl signal of L^2 is particularly useful in diagnosing the geometry of $[\text{ML}_2]^{2+}$ radicals. A single sharp methyl signal in $[\text{RuL}'\text{L}^2_2]^{2+}$ (**4**) ($\text{L}' = \text{bpyz}$ or bpym) at ~ 2.2 ppm is in line with the fact that the gross geometry of $[\text{RuL}^2_2]^{2+}$ and by inference $[\text{RuL}^1_2]^{2+}$ in these mixed-ligand complexes is the same as in the diaquo species **3**. It is then reasonable to assume that the reaction proceeds in a stereoretentive manner and the effective C_2 symmetry is retained. On the other hand, corresponding osmium complexes $[\text{OsL}'\text{L}^2_2]^{2+}$ (**5**) exhibit three signals – two of which have equal heights. This implies that $[\text{OsL}^2_2]^{2+}$ moiety and by inference $[\text{OsL}^1_2]^{2+}$ are certainly present both in *cis, trans, cis* (one signal with effective C_2 symmetry; **5'**) and *cis, cis, cis* (two signals with effective C_1 symmetry; **5''**) geometry. The ratio of *cis, trans, cis (cte)* and *cis, cis, cis (ccc)* depends on reaction time; by prolonging the period *cis, cis, cis* is the major component. The observations here are in line with the fact that during substitution of halide from relatively inert **2**, extensive stereochemical rearrangement occurs. It is of note that such observation was found^{9b} for tris chelate formation $[\text{OsL}_3]^{2+}$ from **2** under similar reaction condition.

D. CHARGE-TRANSFER SPECTRA

The electronic spectra of the complexes (**4** and **5**) in acetonitrile solutions are set in **Table V.4**. Representative spectral nature is shown in **Figure V.3**. The complexes give a characteristic absorption band at ~ 500 nm with a clearly defined shoulder at ~ 450 nm. In addition, a number of weak absorptions at lower energy are observed for osmium complexes, which may arise due to spin-forbidden singlet-triplet transitions being partially allowed through strong spin-orbit coupling^{18,19} in the heavy metal osmium. The intense transitions below 400 nm are presumably due to intra-ligand excitation and/or charge-transfer involving antibonding ligand levels higher than LUMO^{9,13,14}.

TABLE V. 3

¹H NMR Data^{a-c}

Compound	δ (Me), ppm
[Ru(bpyz)L ²] ₂ (ClO ₄) ₂ .H ₂ O (4b)	2.18
[Ru(bpym)L ²] ₂ (ClO ₄) ₂ .H ₂ O (4d)	2.17
[Os(bpyz)L ²] ₂ (ClO ₄) ₂ .H ₂ O (5b)	2.26, 2.11, 1.94
[Os(bpym)L ²] ₂ (ClO ₄) ₂ .H ₂ O (5d)	2.23, 2.09, 1.92

^aSiMe₄ is used as internal standard. ^bAromatic proton signals are not tabulated. ^cSolvent is (CD₃)₂SO.

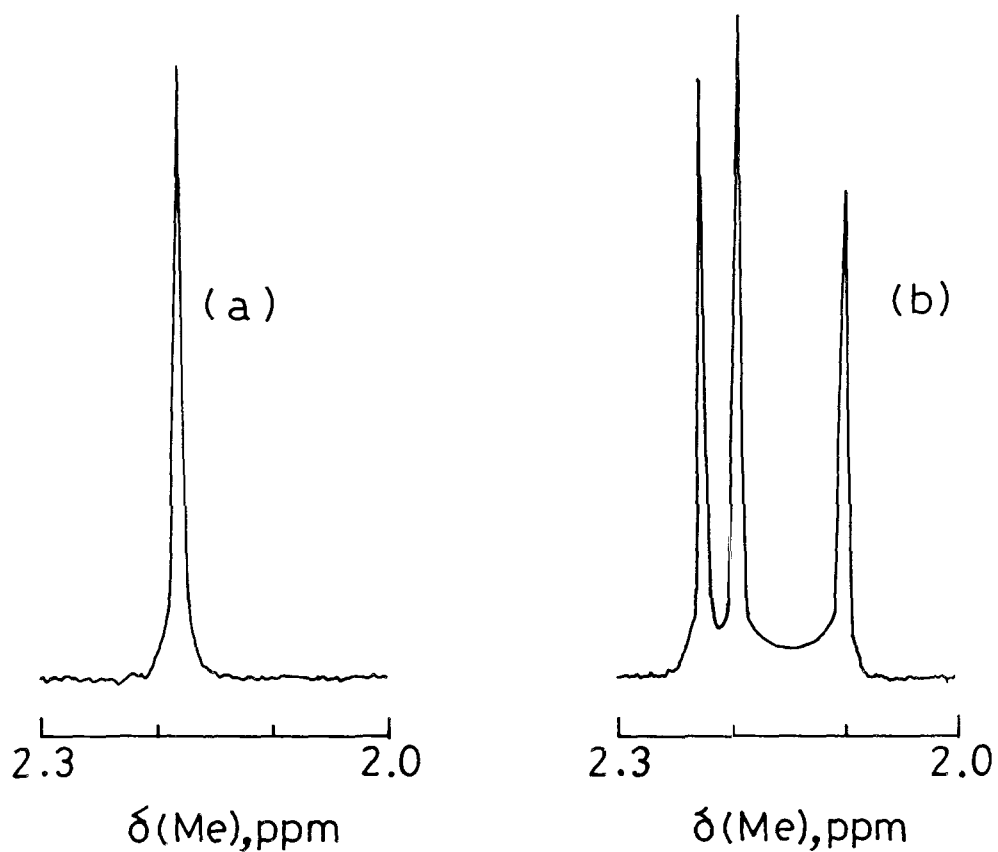


FIGURE V.2. ^1H NMR SPECTRA (Me SIGNALS) OF
(a) $[\text{Ru}(\text{bpyz})\text{L}^2_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ AND
(b) $[\text{Os}(\text{bpyz})\text{L}^2_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ IN CDCl_3

TABLE V. 4

Electronic Spectral Data^{a,b} at 298 K

Compound	λ_{\max} , nm (ϵ , M ⁻¹ cm ⁻¹)
[Ru(bpyz)L ¹ ₂](ClO ₄) ₂ .H ₂ O (4a)	501 (11,870), 470 ^c (8,870), 366 (24,060), 314 ^c (23,000), 288 (35,130)
[Ru(bpyz)L ² ₂](ClO ₄) ₂ .H ₂ O (4b)	500 (12,010), 470 ^c (8,490), 368 (25,010), 316 ^c (23,840), 290 (34,460)
[Ru(bpym)L ¹ ₂](ClO ₄) ₂ .H ₂ O (4c)	505 (12,080), 465 ^c (9,020), 372 (23,900), 312 ^c (22,080), 280 (32,890)
[Ru(bpym)L ² ₂](ClO ₄) ₂ .H ₂ O (4d)	507 (12,500), 468 ^c (8,460), 370 (24,300), 314 ^c (22,310), 284 (33,740)
[Os(bpyz)L ¹ ₂](ClO ₄) ₂ .H ₂ O (5a)	884 ^c (800), 757 ^c (1,800), 652 ^c (2,850), 521 (12,050), 457 ^c (7,490), 338 (24,990), 296 (22,630)
[Os(bpyz)L ² ₂](ClO ₄) ₂ .H ₂ O (5b)	886 ^c (840), 758 ^c (1,880), 652 ^c (2,910), 521 (12,190), 458 ^c (7,600), 338 (26,100), 294 (23,340)
[Os(bpym)L ¹ ₂](ClO ₄) ₂ .H ₂ O (5c)	890 ^c (900), 760 ^c (1,740), 660 ^c (2,490), 525 (11,960), 460 ^c (8,020), 340 (25,600), 292 (24,000)
[Os(bpym)L ² ₂](ClO ₄) ₂ .H ₂ O (5d)	890 ^c (960), 755 ^c (1,640), 655 ^c (2,170), 525 (12,050), 460 ^c (7,920), 340 (26,000), 290 (23,770)

^aSolvent, MeCN. ^bSolute concentration, $\sim 10^{-3}$ M. ^cShoulder.

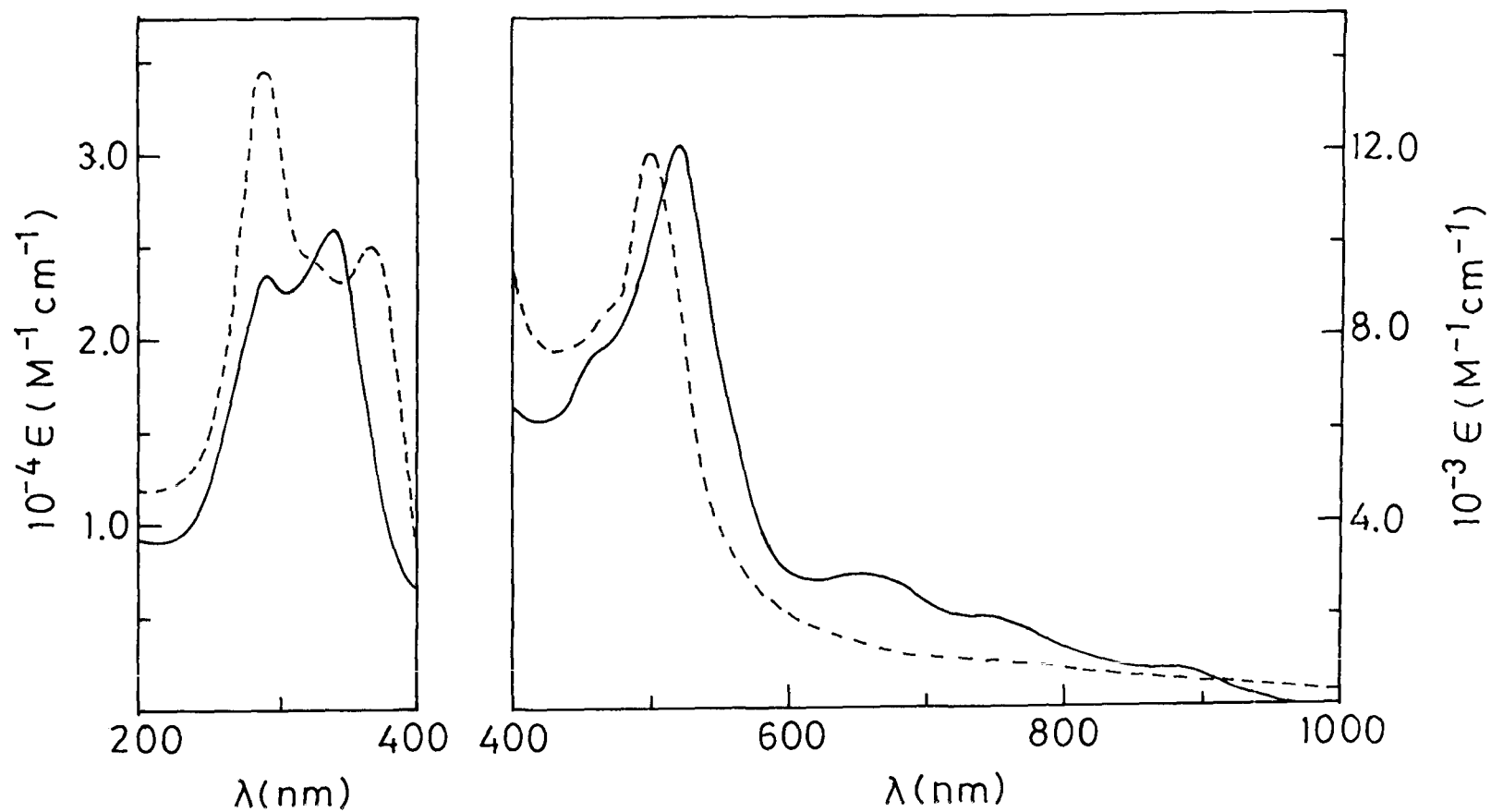


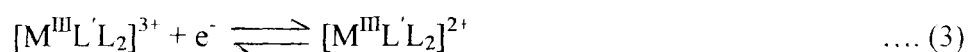
FIGURE V.3. ELECTRONIC SPECTRA OF $[\text{Ru}(\text{bpYZ})\text{L}^1_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (---) AND $[\text{Os}(\text{bpYZ})\text{L}^1_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (—) IN MeCN AT 298 K

E. REDOX BEHAVIOUR

The complexes are redox-active and show one metal-centred oxidation and several successive ligand-based reductions in MeCN solutions (0.1 M TEAP, solute concentration $\sim 10^{-3}$ M). The results are summarised in **Tables V.5** and **V.6**. Representative voltammograms are shown in **Figures V.4 - V.9**. The details of solvent, solute concentration and reference electrode are the same as in **Chapter IV**. The chelates are found to act as carriers¹ of complete or nearly complete electron-transfer series.

(a) Metal-centred oxidation

The positive side of SCE was scanned using a platinum working electrode. In CV, a nearly-reversible (peak-to-peak separation, $\Delta E_p = 80 - 100$ mV) one-electron oxidative response is observed at a platinum working electrode which corresponds to metal(III) - metal(II) couple as depicted in **equation 3**. Multiple scan cyclic voltammograms along with differential pulse of a



representative ruthenium (**Figure V.4**) and an osmium (**Figure V.5**) complexes are shown to have better knowledge about the nature of response. The one-electron stoichiometry of the couple in equation 3 was confirmed from comparison of current height of standard one-electron transfer system described in previous chapters, since constant potential electrolysis at such high potential results in a continuous coulomb count. The formal potential (E^0) lies in the range 1.6 to 2.1 V. The osmium(III) - osmium(II) couple has invariably (**Figure V.6**) a lower potential (~ 0.3 V) than the ruthenium(III) - ruthenium(II) couple in similar complexes, reflecting the relatively greater stability of the higher oxidation states in the heavier metal. Again from bpym to bpyz a definite shift to higher potential is observable (**Figure V.7**). This is in accord^{1,13,14} with the relative π -acceptance capacities of the two ligands. We know, E^0 of such metal-based electrode reaction primarily depends on the energy of the t_{2g} level. With the increase in π -stabilisation the energy of the t_{2g} level decreases resulting in a corresponding increase in E^0 value. The results from this study and the reported E^0 values for $M^{III}-M^{II}$ in pure tris complexes like $[Ru(bipy)_3]^{2+}$ (1.27²⁰ V), $[Ru(bpym)_3]^{2+}$ (1.69¹³ V), $[Ru(bpyz)_3]^{2+}$ (1.98¹³ V), $[RuL^2_3]^{2+}$ (2.23^{6a} V), $[Os(bipy)_3]^{2+}$ (0.81²¹ V), $[Os(bpyz)_3]^{2+}$ (1.52²² V), $[OsL^2_3]^{2+}$ (1.87^{9b} V) demonstrate that π -acceptance follows the order $bipy < bpym < bpyz < L$. Of course, L with azo-imine ($-N=N-\overset{\cdot}{C}=N-$) fragment has the highest π -acceptor strength and bipy with diimine ($-\overset{\cdot}{C}=N-\overset{\cdot}{C}=N-$) moiety, the lowest;

TABLE V. 5

Voltammetric Data^{a-c} in Acetonitrile at 298 K on the Positive Side of SCE

Compound	M(III) - M(II)			
	E_{pa} , V	E_{pc} , V	ΔE_p , mV	E^0 , V
[Ru(bpyz)L ¹ ₂](ClO ₄) ₂ .H ₂ O (4a)	2.15	2.05	100	2.10
[Ru(bpyz)L ² ₂](ClO ₄) ₂ .H ₂ O (4b)	2.13	2.02	110	2.08
[Ru(bpym)L ¹ ₂](ClO ₄) ₂ .H ₂ O (4c)	2.07	1.97	100	2.02
[Ru(bpym)L ² ₂](ClO ₄) ₂ .H ₂ O (4d)	2.06	1.96	100	2.01
[Os(bpyz)L ¹ ₂](ClO ₄) ₂ .H ₂ O (5a)	1.83	1.75	80	1.79
[Os(bpyz)L ² ₂](ClO ₄) ₂ .H ₂ O (5b)	1.81	1.73	80	1.77
[Os(bpym)L ¹ ₂](ClO ₄) ₂ .H ₂ O (5c)	1.74	1.66	80	1.70
[Os(bpym)L ² ₂](ClO ₄) ₂ .H ₂ O (5d)	1.73	1.65	80	1.69

^aConditions of experiments and parameters and relations used are the same as in Chapter II. ^bWorking electrode, platinum. ^cBoth CV and DPV results are set; the agreement between data obtained by two techniques is invariably good (within ± 5 mV).

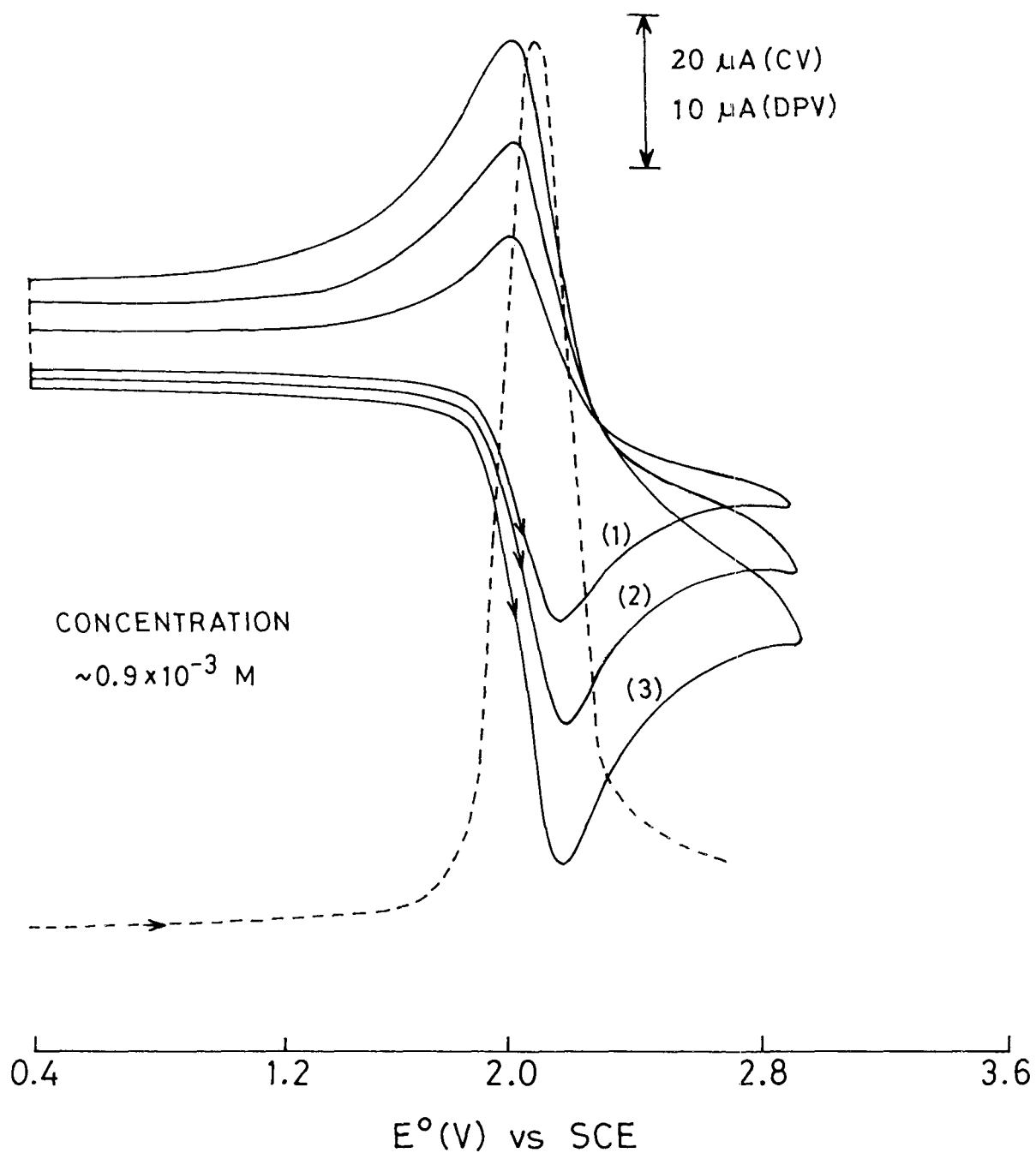


FIGURE V.4. VOLTAMMOGRAMS OF $[\text{Ru}(\text{bpyz})\text{L}^1\text{L}^2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ IN MeCN. SCAN RATES : FOR CV(—), (1) 50, (2) 100, (3) 200 mVs^{-1} ; FOR DPV(---), 10 mVs^{-1}

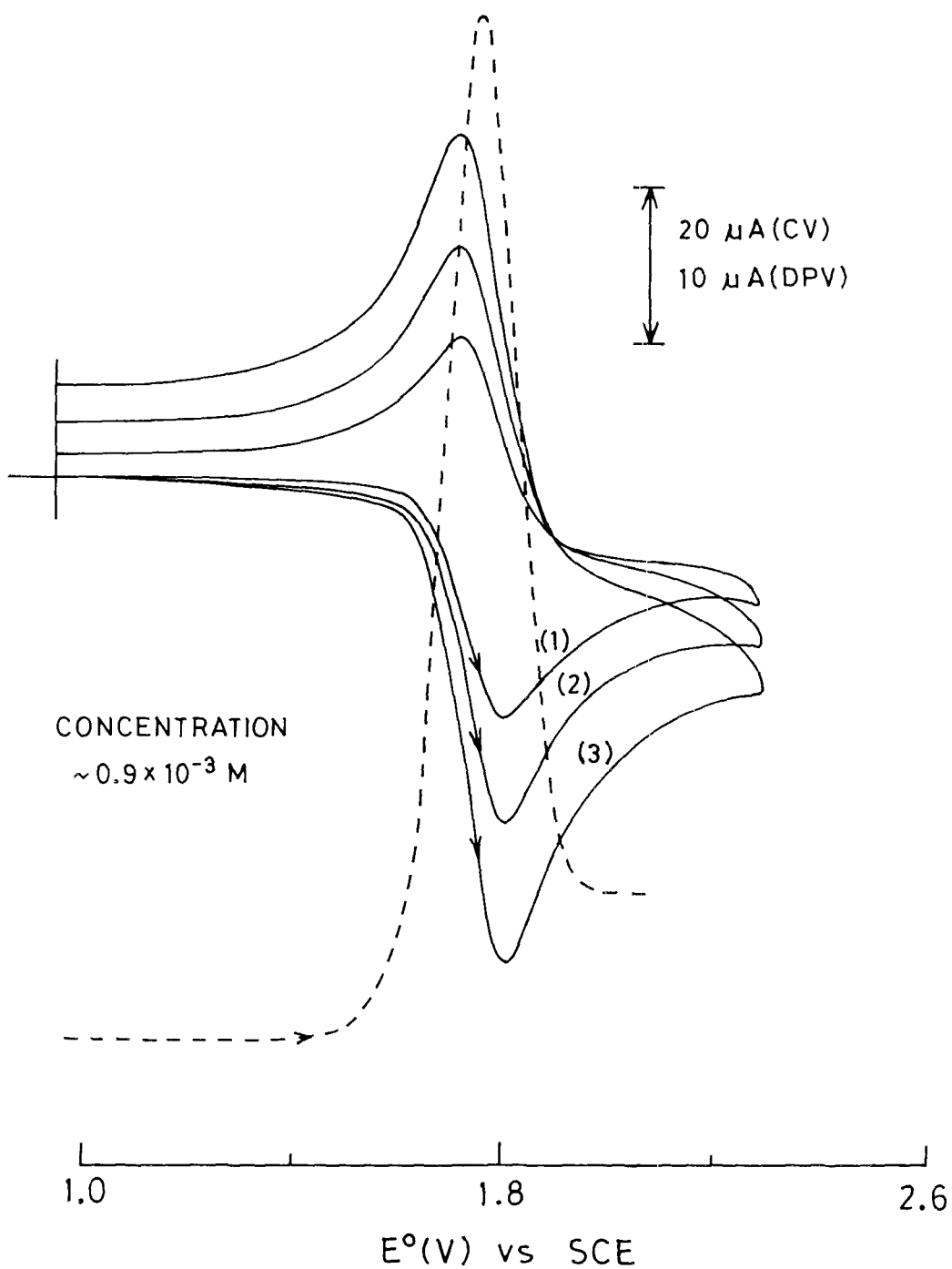


FIGURE V.5. VOLTAMMOGRAMS OF $[\text{Os}(\text{bpyz})\text{L}_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ IN MeCN. SCAN RATES: FOR CV(—), (1) 50, (2) 100, (3) 200 mVs^{-1} ; FOR DPV(---), 10 mVs^{-1}

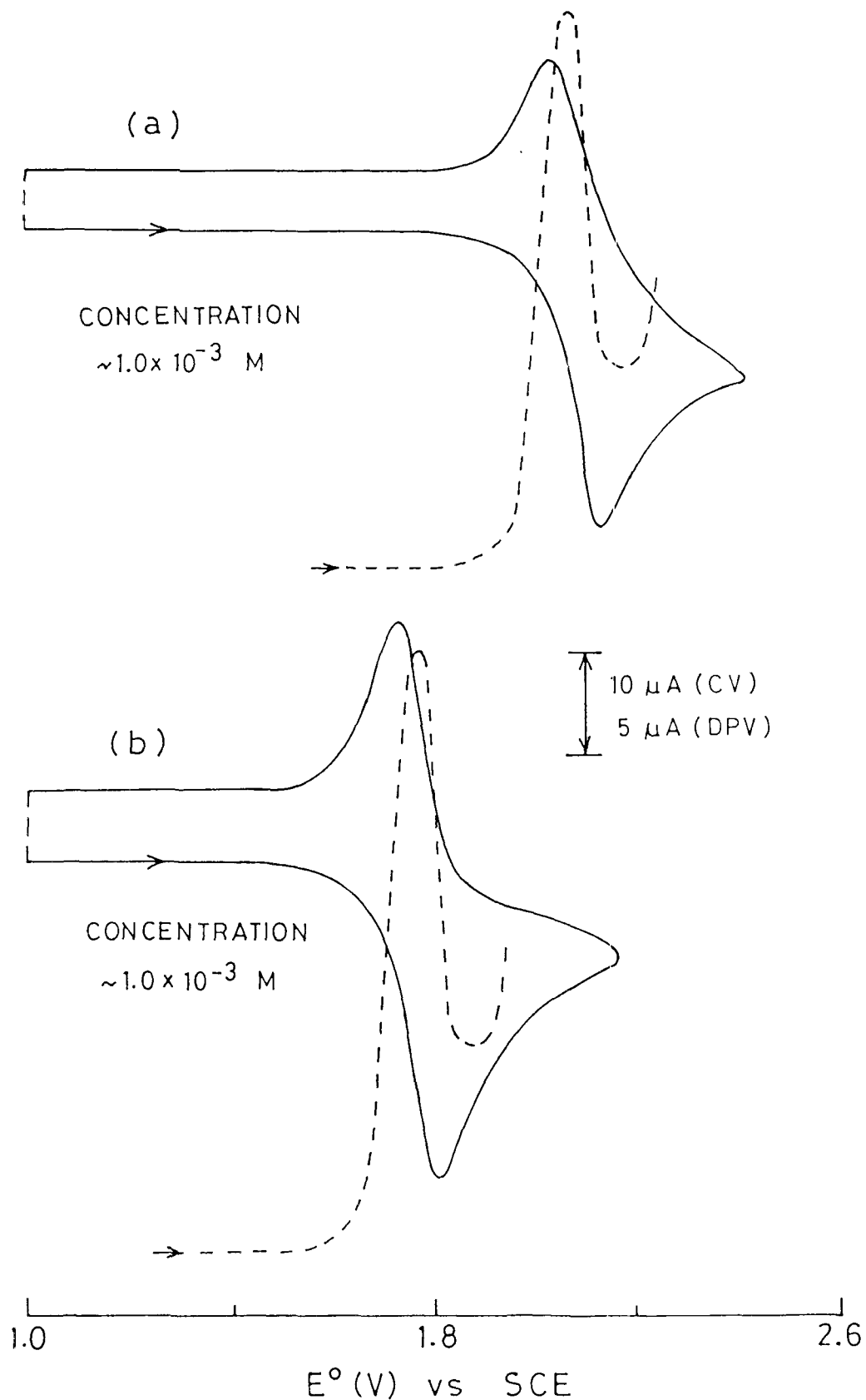


FIGURE V.6. VOLTAMMOGRAMS OF (a) $[\text{Ru}(\text{bpyz})\text{L}^2_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ AND (b) $[\text{Os}(\text{bpyz})\text{L}^2_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ IN MeCN. SCAN RATES: FOR CV(—), 50 mVs^{-1} ; FOR DPV(---), 10 mVs^{-1}

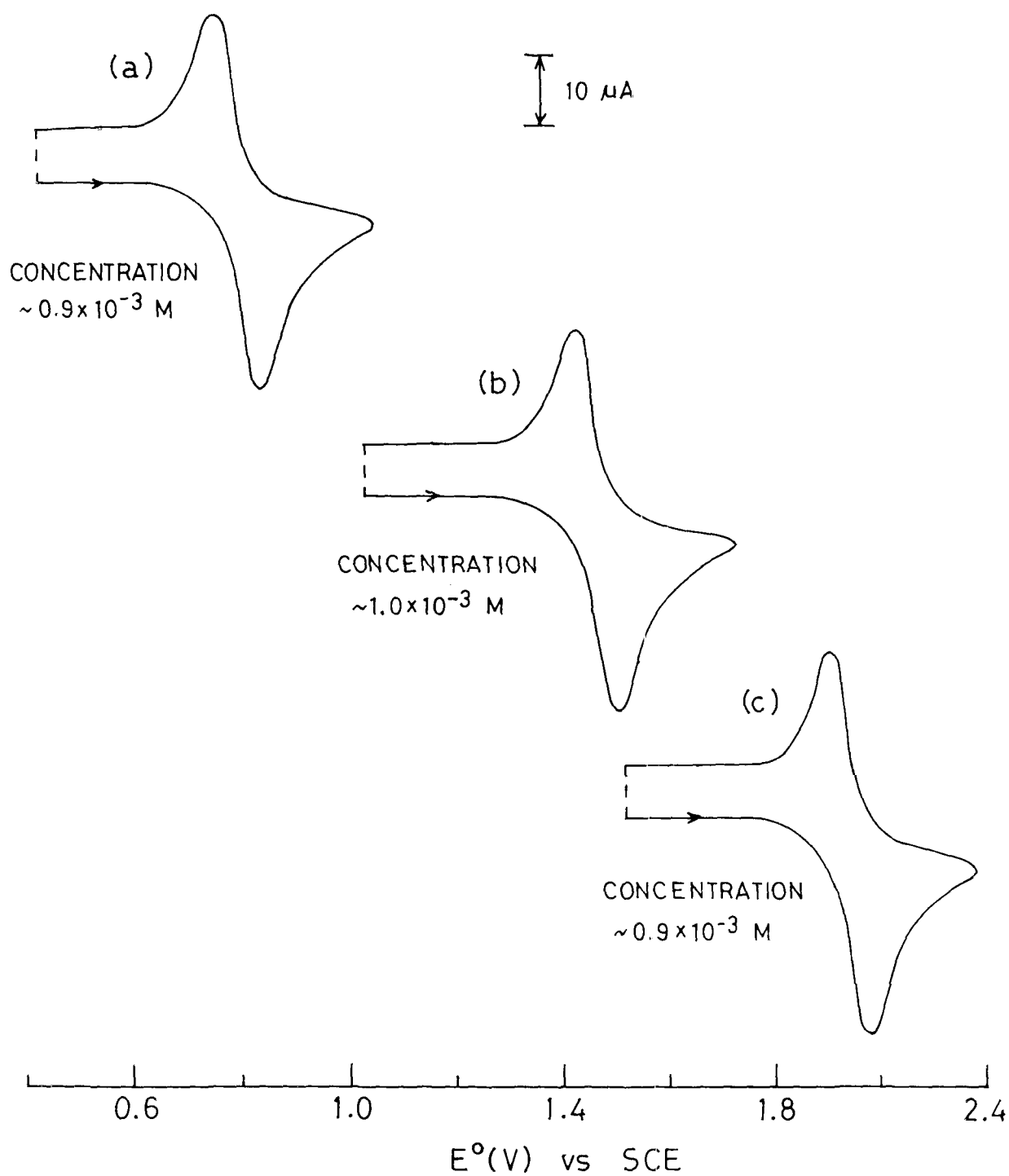


FIGURE V.7. CYCLIC VOLTAMMOGRAMS OF (a) $[\text{Os}(\text{bpy})_3]^{2+}$, (b) $[\text{Os}(\text{bpyz})_3]^{2+}$ AND (c) $[\text{OsL}_2^3]^{2+}$

bpy_m and bpy_z are of intermediate strengths and relative order depends on the position of heteroatoms within the ring.

(b) Ligand-based reductions

The negative side of SCE was scanned using a platinum and a glassy carbon electrodes. Better results are obtained with the latter. The LUMO (π^* level) of L and L' can accommodate¹ upto two electrons. Six successive one-electron reductions are therefore expected in $[\text{ML}'\text{L}_2]^{2+}$ species. Five consecutive one-electron (on comparison of current height with $\text{M}^{\text{III}}-\text{M}^{\text{II}}$ couple on the positive side of SCE) reductions are, however observable within the available potential window (**Figures V.8 and V.9**). Some systematic observations are noticed on analysis of these results. Bpy_z complexes are reduced at a more positive potential than bpy_m analogues. Similar behaviour is reported in the first reduction of the free ligands (bpy_z -1.76¹³ and bpy_m -1.99¹⁴ V). The corresponding potential in L is the lowest of all (-1.31^{6a} V). These demonstrate that in mixed ligand complexes, the first reduction process involves L. In going from ruthenium to osmium compounds an anodic shift is invariably observed for these reduction processes. Obviously, the effect of metal to lower the energy of ligand π^* level is different.

F. CONCLUSION

The feasibility of using $[\text{Ru}(\text{OH}_2)_2\text{L}_2]^{2+}$ and $[\text{OsX}_2\text{L}_2]$ for the synthesis of $[\text{ML}'\text{L}_2]^{2+}$ complexes has been established. The synthetic results reflect the substitutional inertness of X's in $[\text{OsX}_2\text{L}_2]$; extensive stereochemical rearrangements do occur in the reaction conditions used. They display rich electronic spectra – particularly the osmium complexes exhibiting both spin-allowed and spin-forbidden transitions. The complexes provide unique opportunity for studying both metal-centred and ligand-based electron transfers and constitute a well-characterised group where a nearly-complete redox series is observed with one one-electron metal-centred oxidation and five successive one-electron ligand-based reductions. The non-innocent L with azo-imine ($-\text{N}=\text{N}-\overset{|}{\text{C}}=\text{N}-$) and L' with diimine ($-\text{N}=\text{C}-\overset{|}{\text{C}}=\text{N}-$) functions provide π^* orbital to accommodate the electrons in the reduction processes.

TABLE V. 6

Voltammetric Data^{a,b} in MeCN at 298 K on the Negative Side of SCE

Compound	$-E^0$, V (E_p , mV)				
	r_1	r_2	r_3	r_4	r_5^c
[Ru(bpyz)L ¹ ₂](ClO ₄) ₂ .H ₂ O (4a)	0.16 (60)	0.50 (70)	1.15 (90)	1.60 (110)	2.04
[Ru(bpyz)L ² ₂](ClO ₄) ₂ .H ₂ O (4b)	0.17 (60)	0.53 (70)	1.15 (90)	1.62 (110)	2.06
[Ru(bpym)L ¹ ₂](ClO ₄) ₂ .H ₂ O (4c)	0.19 (65)	0.60 (80)	1.32 (95)	1.72 (120)	2.10
[Ru(bpym)L ² ₂](ClO ₄) ₂ .H ₂ O(4d)	0.19 (65)	0.62 (80)	1.34 (95)	1.69 (120)	2.12
[Os(bpyz)L ¹ ₂](ClO ₄) ₂ .H ₂ O (5a)	0.08 (60)	0.35 (60)	1.12 (90)	1.50 (110)	2.18
[Os(bpyz)L ² ₂](ClO ₄) ₂ .H ₂ O (5b)	0.09 (60)	0.37 (65)	1.14 (90)	1.54 (110)	2.20
[Os(bpym)L ¹ ₂](ClO ₄) ₂ .H ₂ O (5c)	0.14 (60)	0.45 (70)	1.30 (90)	1.61 (120)	2.32
[Os(bpym)L ² ₂](ClO ₄) ₂ .H ₂ O (5d)	0.15 (60)	0.48 (70)	1.32 (90)	1.63 (120)	2.30

^aMeaning and units of symbols are the same as in Chapter II. ^bWorking electrode, glassy carbon; supporting electrolyte, TEAP (0.1 M); solute concentration, $\sim 10^{-3}$ M. ^cDPV results.

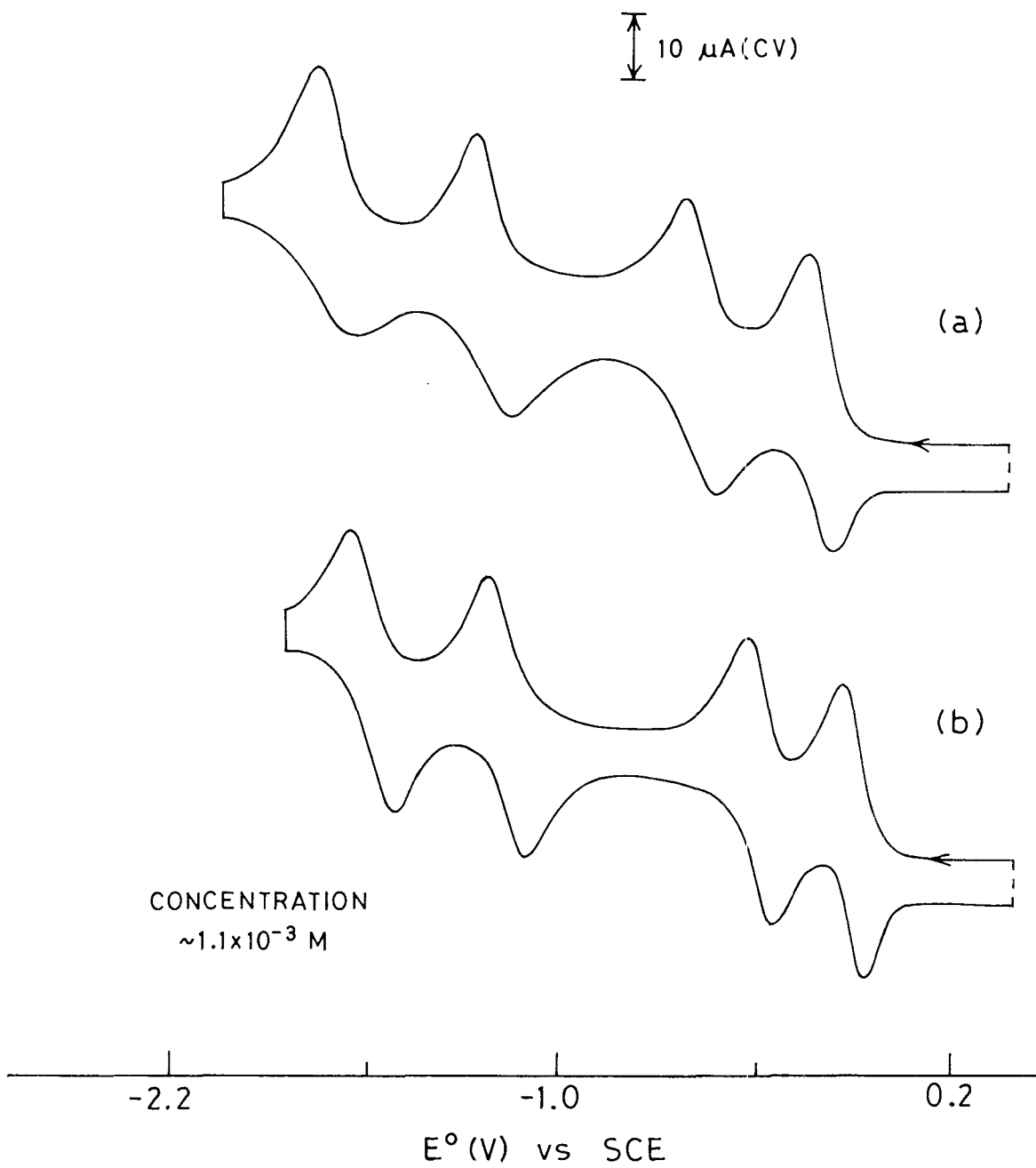


FIGURE V.8. CYCLIC VOLTAMMOGRAMS OF (a) $[\text{Ru}(\text{bpyz})\text{L}_2^2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ AND (b) $[\text{Os}(\text{bpyz})\text{L}_2^2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ IN MeCN. SCAN RATE, 50 mVs^{-1}

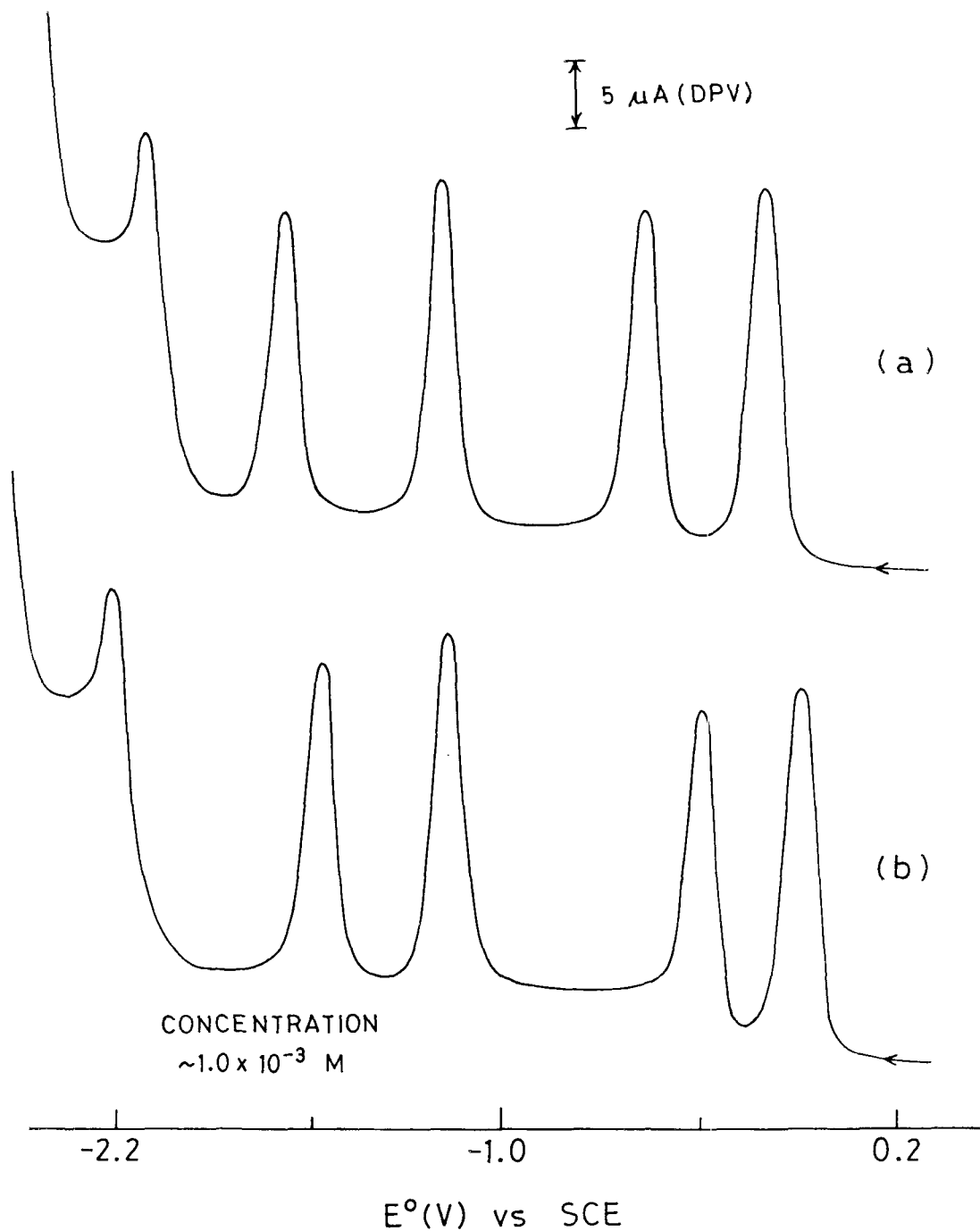


FIGURE V.9. DIFFERENTIAL PULSE VOLTAMMOGRAMS OF
 (a) $[\text{Ru}(\text{bpyz})\text{L}_2^2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ AND (b) $[\text{Os}(\text{bpyz})\text{L}_2^2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$
 H_2O IN MeCN. SCAN RATE, 10 mVs^{-1}

V.3 EXPERIMENTAL SECTION

A. PREPARATION OF COMPOUNDS

(a) Chemicals, solvents and starting materials

The chemicals and solvents used for the preparative procedure are stated in **Chapters II - IV**. The other chemicals used here are ruthenium trichloride, Arora-Matthey (India); silver perchlorate, Sigma (USA); 2,2'-bipyrazine, 2,2'-bipyrimidine, Aldrich (USA); perchloric acid, E. Merck (India); tetraethylammonium bromide, Fluka AG (Switzerland).

$\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ was converted to $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ by repeated evaporation²³ to dryness with concentrated hydrochloric acid. All other chemicals and solvents used for the preparation of ligands and complexes are of reagent grade available commercially.

(b) Ligands

The preparative procedures of 2-(phenylazo)pyridine (L^1) and 2-(*m*-tolylazo)pyridine (L^2) are same as described in the previous chapters.

(c) Precursors

(i) *cis, trans, cis-Dichlorobis[2-(phenylazo)pyridine]ruthenium(II)*, $[\text{RuCl}_2L^1_2]$

Literature method^{3a} was used to prepare this dihalogeno complex in which $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and L^1 was refluxed in methanol under dinitrogen atmosphere. This particular isomer was isolated by chromatographic filtration on a silica gel column.

(ii) *cis, trans, cis-Dichlorobis[2-(*m*-tolylazo)pyridine]ruthenium(II)*, $[\text{RuCl}_2L^2_2]$

This was prepared similarly as in $[\text{RuCl}_2L^1_2]$ except that L^2 instead of L^1 was used. Similar processing was used to have the pure isomer.

(iii) *cis, trans, cis-Diaquobis[2-(phenylazo)pyridine]ruthenium(II) diperchlorate monohydrate*, $[\text{Ru}(\text{OH}_2)_2L^1_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$

Published method^{5b} was used to prepare the diaquo complex. A mixture of *cis*- $[\text{RuCl}_2L^1_2]$ and AgClO_4 in water was heated to reflux for 2 h. Precipitated AgCl was filtered off through a fine glass-frit. Excess NaClO_4 was added to the filtrate. The desired complex crystallised after 12 h in a refrigerator. This was dried in vacuo over P_4O_{10} .

(iv) *cis, trans, cis-Diaquobis[2-(m-tolylazo)pyridine]ruthenium(II)diperchlorate monohydrate*,
 $[Ru(OH_2)_2L^2_2](ClO_4)_2.H_2O$

This was isolated using the same procedure as in the above case except that *ctc*- $[RuCl_2L^2_2]$ instead of *ctc*- $[RuCl_2L^1_2]$ was used as the starting material.

(v) *cis, trans, cis-Dihalogenobis[2-(phenylazo)pyridine]osmium(II)*, $[OsX_2L^1_2]$ ($X = Cl, Br$)

This was prepared as described in **Chapter II**.

(vi) *cis, trans, cis-Dihalogenobis[2-(m-tolylazo)pyridine]osmium(II)*, $[OsX_2L^2_2]$ ($X = Cl, Br$)

The preparative procedure of this is the same as in *ctc*- $[OsX_2L^1_2]$.

(d) Complexes

The ruthenium and osmium complexes were prepared following separate procedures. The details are given below. Yields varied in the range 70 - 80%. Osmium complexes show relatively lower yield. A ten-fold excess of L' was needed for the synthesis of osmium complexes.

(i) *(2,2'-Bipyrazine)bis[2-(phenylazo)pyridine]ruthenium(II) diperchlorate monohydrate*,
 $[Ru(bpyz)L^1_2](ClO_4)_2.H_2O$ (**4a**)

Dinitrogen was purged for 15 min through a blue-violet solution of 0.1 g (0.139 mmol) of *ctc*- $[Ru(OH_2)_2L^1_2](ClO_4)_2.H_2O$ (**3**) in 15 ml methanol. To this 0.038 g (0.24 mmol) of bpyz was added and the mixture was heated at reflux under nitrogen atmosphere for 2 h. The colour gradually changed to red. On partial evaporation followed by addition of $NaClO_4$, dark crystals started depositing. Quantitative precipitation was obtained by chilling for 6 h in a refrigerator. The precipitate collected by filtration was washed thoroughly with cold methanol and finally with diethyl ether. This was dried in vacuo over P_4O_{10} . Analytical purity was obtained after recrystallisation from MeOH- H_2O (3:1). The yield was 0.094 g (80%).

(ii) *(2,2'-Bipyrazine)bis[2-(m-tolylazo)pyridine]ruthenium(II) diperchlorate monohydrate*,
 $[Ru(bpyz)L^2_2](ClO_4)_2.H_2O$ (**4b**)

The procedure was the same as in the preparation of **4a** except that 0.1 g (0.134 mmol) of *ctc*- $[Ru(OH_2)_2L^2_2](ClO_4)_2.H_2O$ was allowed to react with 0.035 g (0.22 mmol) of bpyz; yield, 0.093 g (80%).

(iii) (2,2'-Bipyrimidine)bis[2-(phenylazo)pyridine]ruthenium(II) diperchlorate monohydrate,
 $[Ru(bpym)L^1_2](ClO_4)_2.H_2O$ (**4c**)

4c was prepared [yield, 0.094 g (80%)] following the same procedure as described in **4a** using 0.1 g (0.139 mmol) of *ctc*- $[Ru(OH_2)_2L^1_2](ClO_4)_2.H_2O$ and 0.038 g (0.24 mmol) of bpym.

(iv) (2,2'-Bipyrimidine)bis[2-(*m*-tolylazo)pyridine]ruthenium(II) diperchlorate monohydrate,
 $[Ru(bpym)L^2_2](ClO_4)_2.H_2O$ (**4d**)

The same procedure and reaction stoichiometry as in **4a** formation was adopted to synthesise **4d**. Here 0.035 g (0.22 mmol) of bpyz was allowed to react with 0.1 g (0.134 mmol) of *ctc*- $[Ru(OH_2)_2L^2_2](ClO_4)_2.H_2O$. The yield was 0.093 g (80%).

(v) (2,2'-Bipyrazine)bis[2-(phenylazo)pyridine]osmium(II) diperchlorate monohydrate,
 $[Os(bpyz)L^1_2](ClO_4)_2.H_2O$ (**5a**)

To a suspension of 0.1 g (0.139 mmol) of *ctc*- $[OsBr_2L^1_2]$ in 30 ml 2-methoxyethanol-water (2:1) was added 0.253 g (1.6 mmol) of bpyz, and the mixture was heated at reflux for 12 h under dinitrogen. An orange-red solution gradually appeared with the progress of the reaction. This was evaporated on a steam-bath and the residue was washed several times with diethylether. After redissolving the solid in MeCN a saturated aqueous solution of NaClO₄ was added and the whole reaction mixture was evaporated slowly in air. The precipitate was collected by filtration, washed with chilled water and dried over P₄O₁₀. This was dissolved in a minimum of dichloromethane and subjected to chromatography on an alumina (Merck, India) column (20 × 1 cm). A small blue-violet band of unreacted $[OsBr_2L^1_2]$ was rejected. The slower moving orange-red band was eluted with PhH-MeCN (1:1) and on slow evaporation of the eluant the desired compound (**5a**) resulted in 70% yield (0.091 g).

(vi) (2,2'-Bipyrazine)bis[2-(*m*-tolylazo)pyridine]osmium(II) diperchlorate monohydrate,
 $[Os(bpyz)L^2_2](ClO_4)_2.H_2O$ (**5b**)

The complex **5b** was prepared using the same reaction stoichiometry and the procedure as in **5a** except that 0.1 g (0.134 mmol) of *ctc*- $[OsBr_2L^2_2]$ was reacted with 0.242 g (1.53 mmol) of bpyz. The yield was 0.09 g (70%).

(vii) (2,2'-Bipyrimidine)bis[2-(phenylazo)pyridine]osmium(II) diperchlorate monohydrate,
 $[Os(bpym)L^1_2](ClO_4)_2 \cdot H_2O$ (**5c**)

The preparation of **5c** was essentially the same as in **5a**. Here 0.1 g (0.139 mmol) of *cis*- $[OsBr_2L^1_2]$ was reacted with 0.253 g (1.6 mmol) of bpym. The yield was 0.091 g (70%).

(viii) (2,2'-Bipyrimidine)bis[2-(*m*-tolylazo)pyridine]osmium(II) diperchlorate monohydrate,
 $[Os(bpym)L^2_2](ClO_4)_2 \cdot H_2O$ (**5d**)

5d was prepared [yield 0.09 g (70%)] following the same reaction stoichiometry and conditions as in **5a** except that 0.1 g (0.134 mmol) of *cis*- $[OsBr_2L^2_2]$ was reacted with 0.242 g (1.53 mmol) of bpym.

B. CHARACTERISATION OF COMPLEXES

The complexes were characterised by microanalyses (carbon, hydrogen and nitrogen). Results obtained with the help of a Perkin-Elmer Model 240 C Elemental Analyser are set in **Table V.7**.

C. PHYSICAL MEASUREMENTS

This was done as described in **Chapters II - IV**.

TABLE V. 7

Characterisation Data

Compound	%C		%H		%N	
	Calcd	Found	Calcd	Found	Calcd	Found
[Ru(bpyz)L ¹ ₂](ClO ₄) ₂ .H ₂ O (4a) C ₃₀ H ₂₆ N ₁₀ O ₉ Cl ₂ Ru	42.8	43.1	3.1	3.1	16.6	16.8
[Ru(bpyz)L ² ₂](ClO ₄) ₂ .H ₂ O (4b) C ₃₂ H ₃₀ N ₁₀ O ₉ Cl ₂ Ru	44.1	44.4	3.5	3.6	16.1	16.2
[Ru(bpym)L ¹ ₂](ClO ₄) ₂ .H ₂ O (4c) C ₃₀ H ₂₆ N ₁₀ O ₉ Cl ₂ Ru	42.8	42.6	3.1	3.2	16.6	16.5
[Ru(bpym)L ² ₂](ClO ₄) ₂ .H ₂ O (4d) C ₃₂ H ₃₀ N ₁₀ O ₉ Cl ₂ Ru	44.1	43.9	3.5	3.5	16.1	16.3
[Os(bpyz)L ¹ ₂](ClO ₄) ₂ .H ₂ O (5a) C ₃₀ H ₂₆ N ₁₀ O ₉ Cl ₂ Os	38.7	38.7	2.8	2.9	15.0	15.4
[Os(bpyz)L ² ₂](ClO ₄) ₂ .H ₂ O (5b) C ₃₂ H ₃₀ N ₁₀ O ₉ Cl ₂ Os	40.0	40.2	3.2	3.0	14.6	14.6
[Os(bpym)L ¹ ₂](ClO ₄) ₂ .H ₂ O (5c) C ₃₀ H ₂₆ N ₁₀ O ₉ Cl ₂ Os	38.7	38.9	2.8	2.8	15.0	15.1
[Os(bpym)L ² ₂](ClO ₄) ₂ .H ₂ O (5d) C ₃₂ H ₃₀ N ₁₀ O ₉ Cl ₂ Os	40.0	40.5	3.1	3.2	14.6	14.5

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