

CHAPTER IV

**SYNTHESIS AND CHARACTERISATION OF COMPLEXES OF
TYPE $[\text{OsX}(\text{B})\text{L}_2]^{1+}$ (X = Cl OR Br; B = HETEROCYCLIC BASES)**

CHAPTER IV

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ABSTRACT : The synthesis and characterisation of a series of complexes of the type $[\text{OsX}(\text{B})\text{L}_2]^{1+}$ (X = Cl or Br; B = heterocyclic bases like pyridine (py), pyrazine (pyz), and pyrazole (pzH), L = 2-(phenylazo)pyridine (L^1) or 2-(*m*-tolylazo)pyridine (L^2) are described. The cations have been isolated as crystalline perchlorate monohydrates after purification by column chromatography. The diamagnetic compounds display several spin-allowed and spin-forbidden MLCT transitions in the visible region. The electron transfer properties of the complexes are examined in MeCN solutions using CV, DPV and coulometry. The results are in conformity with the monocationic formulation $[\text{OsX}(\text{B})\text{L}_2]^{1+}$. The compounds undergo two successive one-electron oxidations corresponding to osmium(III) - osmium(II) and osmium(IV) - osmium(III) couples occurring at ~ 1.3 and ~ 2.3 V vs SCE. Four successive azo reductions are observable in the potential range -0.4 to -2.4 V.

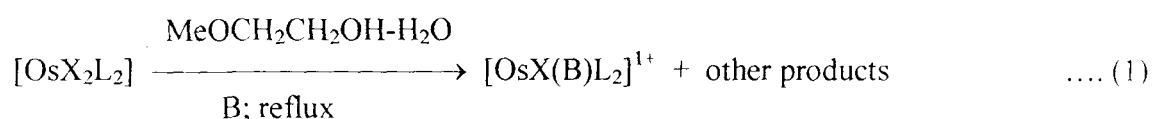
IV.1 INTRODUCTION

In the preceding chapter we have studied the reactivity of isomeric dihalogenobis complexes $[\text{OsX}_2\text{L}_2]$ (**2** and **3**) [$\text{X} = \text{Cl}$ or Br and L (**1**) = 2-(phenylazo)pyridine (L^1) or 2-(*m*-tolylazo)pyridine (L^2)] with monodentate anionic ligands A ($\text{A} = \text{NO}_2^-$, NCS^- and N_3^-). Cursory report¹ by Ghosh et al. involves a study of the reactivity of **2** with neutral or anionic (N,N), (N,O) and (O,O) bidentate ligands (D^{Z-}) furnishing tris complexes of the type $[\text{OsDL}_2]^{(2-Z)+}$ ($Z = 0 - 2$). However the reactivity of **2** towards monodentate neutral nitrogen donors has not been investigated. With this in mind we have examined this point with three neutral heterocyclic bases (B): pyridine (py), pyrazine (pyz) and pyrazole (pzH). This chapter describes the synthesis, characterisation and redox stability of metal/ligand oxidation states of a series of monosubstituted complexes of the type $[\text{OsX}(\text{B})\text{L}_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$.

IV.2 RESULTS AND DISCUSSION

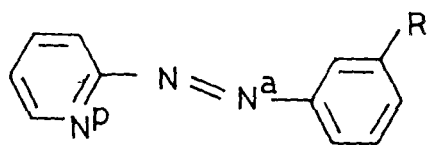
A. SYNTHESIS

Unsymmetrical non-innocent² (N,N)-chelating ligands L^1 and L^2 were prepared^{3,4} as described in the previous chapters. Dihalo complexes of type **2** were synthesised as discussed in **Chapter II** and the method⁵ of Ghosh et al. A series of complexes of general formula $[\text{OsX}(\text{B})\text{L}_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**4**) have been prepared (**equation 1**) by reacting $[\text{OsX}_2\text{L}_2]$ (**2**) with a



ten-fold excess of B in aqueous 2-methoxyethanol (2:1) followed by addition of a saturated solution of NaClO_4 . The reaction 1 proceeded slowly. Of the two chloro and bromo, the latter is more reactive. In all cases only one halide was substituted by the heterocyclic base. No dicationic species of type $[\text{OsB}_2\text{L}_2]^{2+}$ could be isolated even by using a very high excess of B or extending the reaction time >100 h. However during chromatographic purification of **4**, a very small orange band was left at the top of the column, which remained unmoved even using polar eluents.

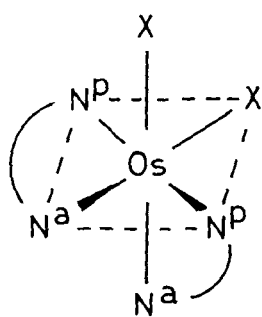
A similar result is given in the literature⁶ for the preparation of $[\text{OsX}(\text{py})(\text{bipy})_2]^{1+}$ and $[\text{Os}(\text{py})_2(\text{bipy})_2]^{2+}$ (bipy = 2,2'-bipyridine). The product obtained from the reaction between



R = H; L¹

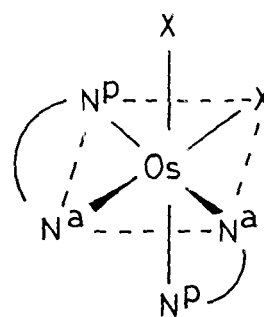
R = Me; L²

L; 1



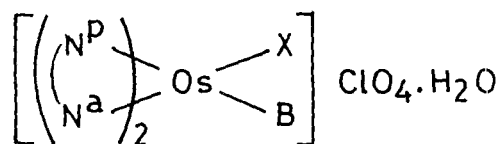
ctc

2



ccc

3



ClO₄·H₂O

4

STRUCTURES

$[\text{OsX}_2(\text{bipy})_2]$ ($X = \text{Cl}$ or Br) and py depends on the choice of the solvent and reaction time. In boiling ethanol-water (12 h), the monocationic $[\text{OsX}(\text{py})(\text{bipy})_2]^{1+}$ species is formed. However $[\text{Os}(\text{py})_2(\text{bipy})_2]^{2+}$ can be obtained if the reflux is continued for 70 h. Hence the halide in complex **2** is more inert towards substitution than is the analogous bipy complex. Tris and mixed-tris complexes (albeit in low yield) are reported to form by the reaction of **2** and bidentate (N,N) ligands such as L, bipy and phen (1,10-phenanthroline) under similar conditions with loss of both halogens, which is presumably due to chelate effect¹.

The monosubstituted cationic complexes (**4**) were characterised by elemental analyses, solution electrical conductivity measurements, spectroscopic (IR, NMR and UV-Vis) properties and electrochemical results (**Tables** IV.1 - IV.6). All the complexes are highly soluble in common organic solvents like alcohols, dichloromethane, acetonitrile, dimethylformamide and dimethylsulfoxide and moderately soluble in water. The conductance values of **4** in acetonitrile solutions at 298 K lie in the $140 - 150 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ range (**Table** IV.1), consistent with the monocationic formulation⁷. Room temperature magnetic susceptibility measurements show that the complexes are uniformly diamagnetic (idealised t_{2g}^6 ; $S = 0$, singlet).

B. INFRARED SPECTRA

The most characteristic features of the IR spectra are given in the **Table** IV.2. A representative spectral nature is shown in **Figure** IV.1. All the perchlorate monohydrates display characteristic ionic perchlorate bands⁸ at ~ 1100 (ν_3) and 620 (ν_2) cm^{-1} and a lattice water band at ~ 3400 cm^{-1} . A sharp peak at ~ 320 cm^{-1} in the chloro complex is inferred to be $\nu(\text{Os}-\text{Cl})$ stretch from its absence in the bromo analogues. $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$ stretch is invariably observed at ~ 1595 cm^{-1} . $\nu(\text{N}=\text{N})$ stretch at ~ 1285 cm^{-1} is seen in all complexes; corresponding free ligand value appears⁹ at ~ 1425 cm^{-1} . The shift of $\nu(\text{N}=\text{N})$ towards lower frequency from that in free ligand indicates strong metal to ligand, $d(\text{Os}) \rightarrow \pi^*(\text{L})$, π -back bonding. In going from **2** to **4** the $\nu(\text{N}=\text{N})$ stretching frequency is shifted towards higher wavenumber value, reflecting less osmium-azo π -back bonding in the latter. If the ancillary ligand is a good π -acceptor, a competition arises for the osmium t_2 electrons resulting in less π -back donation¹⁰ to the $\text{N}=\text{N}$ π^* orbital¹¹. The $\nu(\text{N}=\text{N})$ frequencies of some related complexes^{1,5} are as follows : **2**, 1280; **4**, 1285; $[\text{Os}(\text{bipy})\text{L}_2]^{2+}$, 1300; $[\text{OsL}_3]^{2+}$, 1320 cm^{-1} . Evidently, $[\text{OsL}_3]^{2+}$ has the highest wave number value, reflecting the strength of competition in the order $\text{XL} < \text{XB} < \text{bipy} < \text{L}$.

TABLE IV.1

Molar Conductivity Data^a in MeCN at 298 K

Compound	Λ_M (ohm ⁻¹ cm ² mol ⁻¹)
[OsCl(py)L ¹ ₂]ClO ₄ .H ₂ O (4a)	140
[OsBr(py)L ¹ ₂]ClO ₄ .H ₂ O (4b)	145
[OsCl(py)L ² ₂]ClO ₄ .H ₂ O (4c)	150
[OsBr(py)L ² ₂]ClO ₄ .H ₂ O (4d)	145
[OsCl(pyz)L ² ₂]ClO ₄ .H ₂ O (4e)	150
[OsBr(pyz)L ² ₂]ClO ₄ .H ₂ O (4f)	145
[OsCl(pzH)L ² ₂]ClO ₄ .H ₂ O (4g)	150
[OsBr(pzH)L ² ₂]ClO ₄ .H ₂ O (4h)	140

^aSolute concentration, ~ 10⁻³ M.

TABLE IV. 2

Selected Infrared Frequencies^{a,b} in cm⁻¹

Compound	$\nu(\text{C}=\text{N}) + \nu(\text{C}=\text{C})^c$	$\nu(\text{N}=\text{N})^d$	$\nu(\text{ClO}_4)$	$\nu(\text{OsCl})$
[OsCl(py)L ¹ ₂]ClO ₄ .H ₂ O (4a)	1595	1285	1085, 620	320
[OsBr(py)L ¹ ₂]ClO ₄ .H ₂ O (4b)	1600	1286	1080, 620	e
[OsCl(py)L ² ₂]ClO ₄ .H ₂ O (4c)	1595	1286	1090, 620	322
[OsBr(py)L ² ₂]ClO ₄ .H ₂ O (4d)	1595	1285	1085, 620	e
[OsCl(pyz)L ² ₂]ClO ₄ .H ₂ O (4e)	1590	1286	1090, 620	324
[OsBr(pyz)L ² ₂]ClO ₄ .H ₂ O (4f)	1595	1285	1085, 620	e
[OsCl(pzH)L ² ₂]ClO ₄ .H ₂ O (4g)	1585	1285	1088, 620	320
[OsBr(pzH)L ² ₂]ClO ₄ .H ₂ O (4h)	1588	1287	1085, 620	e

^aIn KBr discs (4000 - 600 cm⁻¹) and polyethylene discs (600 - 300 cm⁻¹). ^bCharacteristics : ^c $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$, medium and sharp; ^d $\nu(\text{N}=\text{N})$, sharp and strong. ^eNot studied.

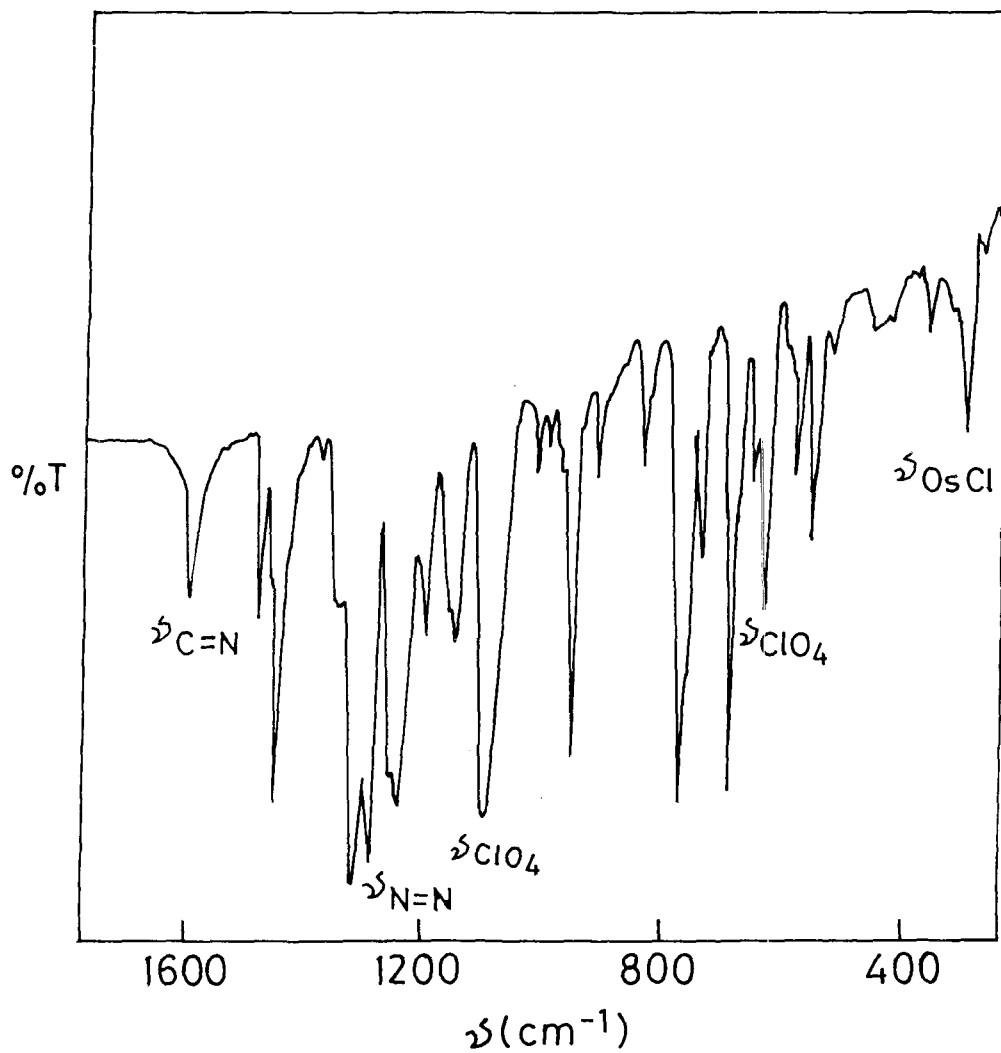


FIGURE IV.1. IR SPECTRUM OF $[OsCl(py)L_2]ClO_4 \cdot H_2O$
IN KBr DISC

C. CHARGE-TRANSFER SPECTRA

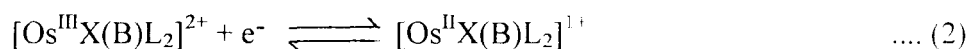
The complexes show multiple absorptions in the region 200 - 800 nm. Spectral data in MeCN solutions are set in **Table IV.3**. **Figure IV.2** shows major bands in a representative case. The red-violet solutions of **4** give characteristic absorptions at ~460, 500 and 750 nm, assigned to the metal-to-ligand charge-transfer (MLCT) transitions, $t_{2g}(\text{Os}) \rightarrow \pi^*(\text{L})$, within pseudooctahedral osmium(II) stereochemistry. More intense peaks at higher energies are presumably due to spin-allowed singlet-singlet transitions, whilst the weaker ones at higher wavelengths could be due to a singlet-triplet transitions being partially allowed through strong spin-orbit coupling^{12,13} for the heavy element osmium. A systematic shift of the bands to higher frequencies is observed on replacing the halo⁵ ligand by B. The presence of one heterocyclic base in **4** is expected to stabilise the t_2 level of osmium, hence shifting the absorptions to higher energy. The intense transitions below 400 nm are believed¹ to be due to intraligand excitation and/or charge-transfer involving antibonding ligand levels higher than the LUMO.

D. REDOX BEHAVIOUR

Electroactivity of the complexes was examined in MeCN solutions (0.1 M tetraethylammonium perchlorate, TEAP) using cyclic voltammetry (CV), differential pulse voltammetry (DPV) and coulometry. The DPV technique is particularly useful for observing responses close to solvent cut-off regions. The results are summarised in **Tables IV.4** and **IV.5**. Representative voltammograms are shown in **Figures IV.3 - IV.6**. All potentials are referenced to a saturated calomel electrode (SCE).

(a) Metal-centred oxidations

The positive side of SCE was scanned using a platinum working electrode. A nearly reversible (peak-to-peak separation, ΔE_p , 60 - 70 mV) one-electron oxidative response is observed (**Table IV.4**) assignable to osmium(III) - osmium(II) couple (**equation 2**). A multiple



scan cyclic voltammograms along with differential pulse of couple 2 is portrayed in **Figure IV.3**. One-electron stoichiometry of the electrode process was confirmed from constant potential coulometry of a selected complex (locked at 1.5 V for $[\text{OsCl}(\text{py})\text{L}_2]^{2+}\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**4c**): $n = 1.05$ where $n = Q/Q'$; Q' is the calculated coulomb count for one-electron transfer and Q , the coulomb count found after exhaustive electrolysis). The formal potential, E^0 lies at ~1.4 V. The

TABLE IV. 3

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

Compound	λ_{\max} , nm (ϵ , M ⁻¹ cm ⁻¹)
[OsCl(py)L ¹ ₂]ClO ₄ .H ₂ O (4a)	740 (1,580), 502 (10,250), 465 ^c (6,460), 342 (16,780), 300 (17,290), 242 ^c (8,820)
[OsBr(py)L ¹ ₂]ClO ₄ .H ₂ O (4b)	735 (1,540), 500 (10,390), 460 ^c (6,600), 340 (17,090), 304 (17,680), 242 ^c (9,320)
[OsCl(py)L ² ₂]ClO ₄ .H ₂ O (4c)	740 (1,690), 504 (10,120), 460 ^c (6,800), 340 (17,420), 300 (18,410), 244 ^c (8,950)
[OsBr(py)L ² ₂]ClO ₄ .H ₂ O (4d)	735 (1,600), 500 (10,630), 462 ^c (6,820), 340 (16,740), 300 (17,240), 246 ^c (7,460)
[OsCl(pyz)L ² ₂]ClO ₄ .H ₂ O (4e)	750 (1,350), 505 (10,120), 470 ^c (5,260), 350 (15,900), 314 (16,800), 230 ^c (6,420)
[OsBr(pyz)L ² ₂]ClO ₄ .H ₂ O (4f)	750 (1,210), 502 (10,250), 470 ^c (5,390), 350 (16,200), 310 (17,080), 235 ^c (6,960)
[OsCl(pzH)L ² ₂]ClO ₄ .H ₂ O (4g)	755 (1,470), 508 (10,330), 472 ^c (5,770), 345 (16,720), 315 (17,420), 238 ^c (7,330)
[OsBr(pzH)L ² ₂]ClO ₄ .H ₂ O (4h)	750 (1,330), 506 (10,580), 475 ^c (5,960), 348 (16,990), 318 (17,760), 240 ^c (7,510)

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

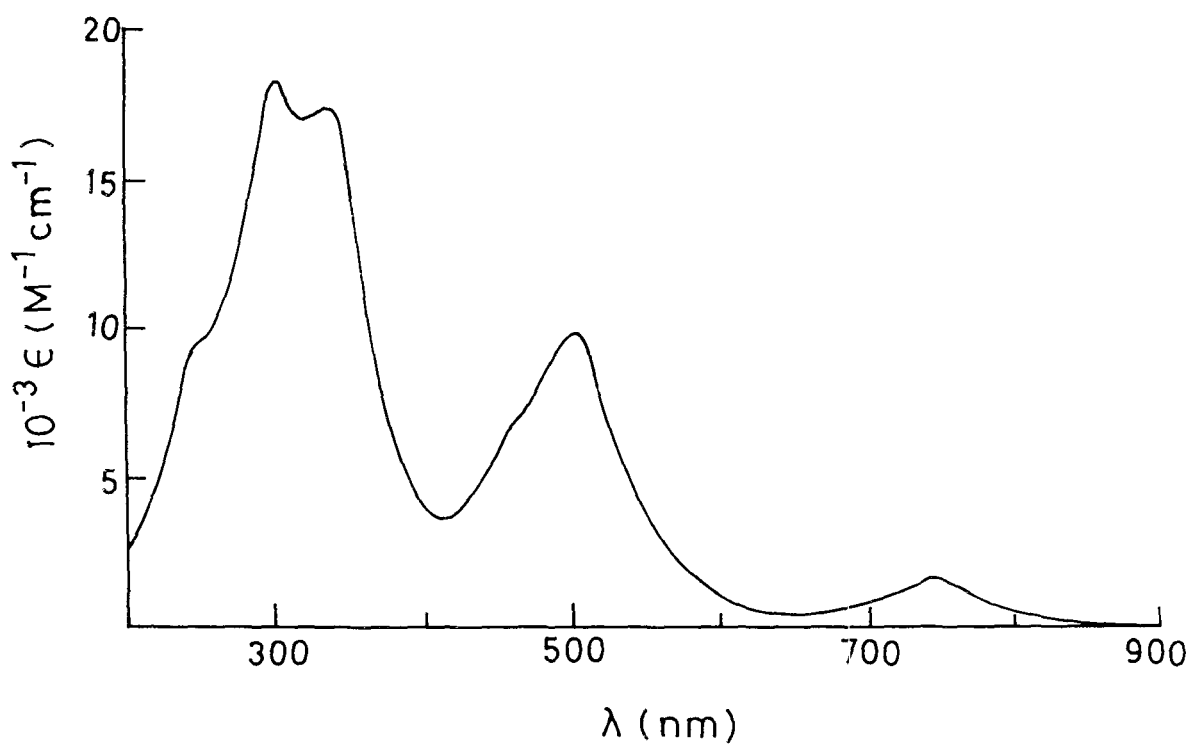


FIGURE IV.2. ELECTRONIC SPECTRA OF $[\text{OsCl}(\text{py})\text{L}_2]\text{ClO}_4 \cdot \text{H}_2\text{C}$ IN MeCN

TABLE IV. 4

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

Compound	Os(III) - Os(II) ^c	Os(IV) - Os(III) ^d
	E ⁰ , V (ΔE_p , mV)	E ⁰ , V
[OsCl(py)L ¹ ₂]ClO ₄ .H ₂ O (4a)	1.33 (60)	2.34
[OsBr(py)L ¹ ₂]ClO ₄ .H ₂ O (4b)	1.35 (60)	2.31
[OsCl(py)L ² ₂]ClO ₄ .H ₂ O (4c)	1.34 (60)	2.30
[OsBr(py)L ² ₂]ClO ₄ .H ₂ O (4d)	1.35 (60)	2.29
[OsCl(pyz)L ² ₂]ClO ₄ .H ₂ O (4e)	1.29 (70)	2.25
[OsBr(pyz)L ² ₂]ClO ₄ .H ₂ O (4f)	1.30 (70)	2.38
[OsCl(pzH)L ² ₂]ClO ₄ .H ₂ O (4g)	1.32 (70)	2.39
[OsBr(pzH)L ² ₂]ClO ₄ .H ₂ O (4h)	1.34 (70)	2.42

^aMeaning and units of symbols are the same as in the text and in Chapter II. ^bWorking electrode, platinum; supporting electrolyte, TEAP (0.1 M); solute concentration, $\sim 10^{-3}$ M. ^cBoth CV and DPV results are set; the agreement between data obtained by two techniques is invariably good (within ± 5 mV). ^dOnly DPV data.

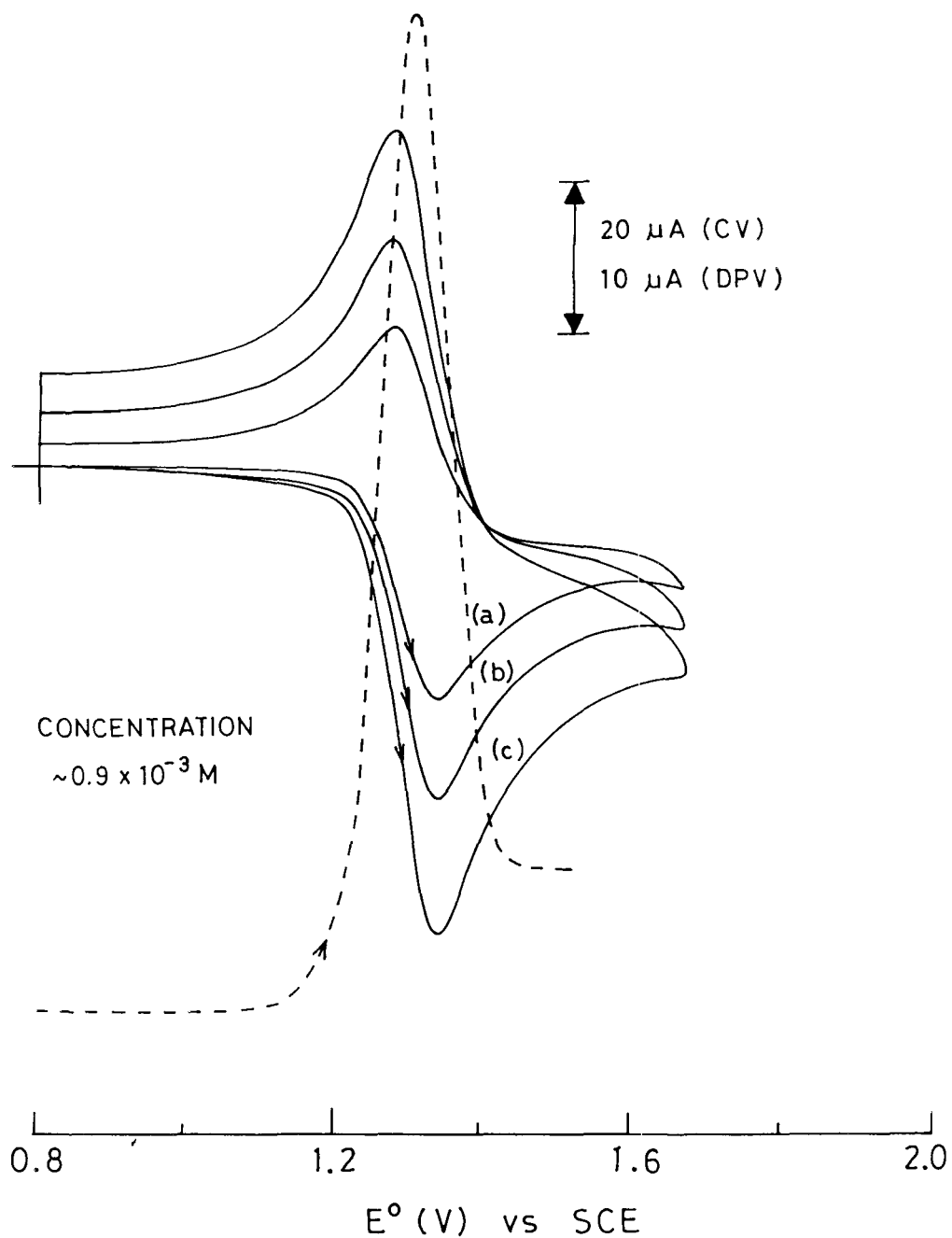
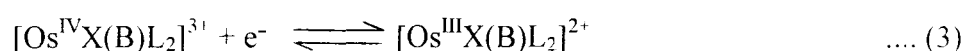


FIGURE IV.3. VOLTAMMOGRAMS OF $[\text{OsCl}(\text{py})\text{L}_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ IN MeCN.
 SCAN RATES: FOR CV(—), (a) 50, (b) 100, (c) 200 mVs^{-1} ;
 FOR DPV(---), 10 mVs^{-1}

corresponding E^0 values in **2** is observable⁵ at ~ 1.0 V. This anodic shift reflects the lowering in energy of the osmium t_2 level (HOMO) resulting from the better π -acceptor properties of B over X. A similar increase¹⁴ in osmium(III) – osmium(II) potential is observed for the bipy complexes, viz. $[\text{OsX}_2(\text{bipy})_2]$ (~ 0.0 V) and $[\text{OsX}(\text{py})(\text{bipy})_2]^{1+}$ (~ 0.4 V). For the L complexes, strong osmium(II)-azo π -back bonding is no doubt a contributing factor in making E^0 values higher (~ 1 V) than the corresponding bipy analogues.

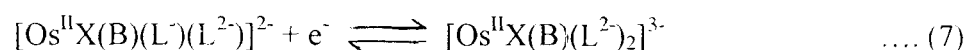
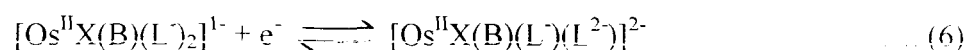
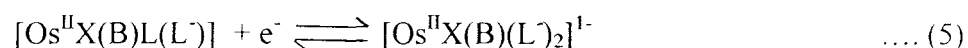
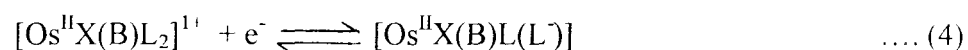
An additional one-electron oxidative response was observed under very carefully controlled experimental conditions. This is assignable to a higher oxidation as shown in **equation 3**.



Observation of this redox process at a higher potential near the solvent cut-off was best made with DPV (**Figure IV.4**) in dry acetonitrile. In the CV experiment the cathodic peak corresponding to couple 3 shows low currents. This might be due to formation of an unstable osmium(IV) species, which then undergoes further reaction.

(b) Ligand-based reductions

The negative side of SCE was scanned using a glassy carbon electrode (**Table IV.5**). In the -0.4 to -2.4 V potential range, four successive cathodic reductions are observable by CV. On scan reversal the corresponding anodic peaks of the first two steps are visible, albeit at lower current height; but those corresponding to the third and fourth reductions are ill-developed (**Figure IV.5**). This reflects some kind of chemical assistance connected with the charge-transfer steps. The LUMO of L can accommodate² upto two electrons. Hence four successive one-electron reductions are expected for the OsL_2^{2+} radical. These are clearly identifiable in the DPV experiments (**Figure IV.6**). The electrode processes are presumably due to the couples as shown in **equations 4 - 7**. One-electron stoichiometry of these reductions could not be ascertained by



direct coulometry experiments due to continuous accumulation of coulomb count at more cathodic of the E^0 value of couple 4. However the current heights of these reductions in DPV experiments are comparable to those of the oxidative steps on the positive side of SCE.

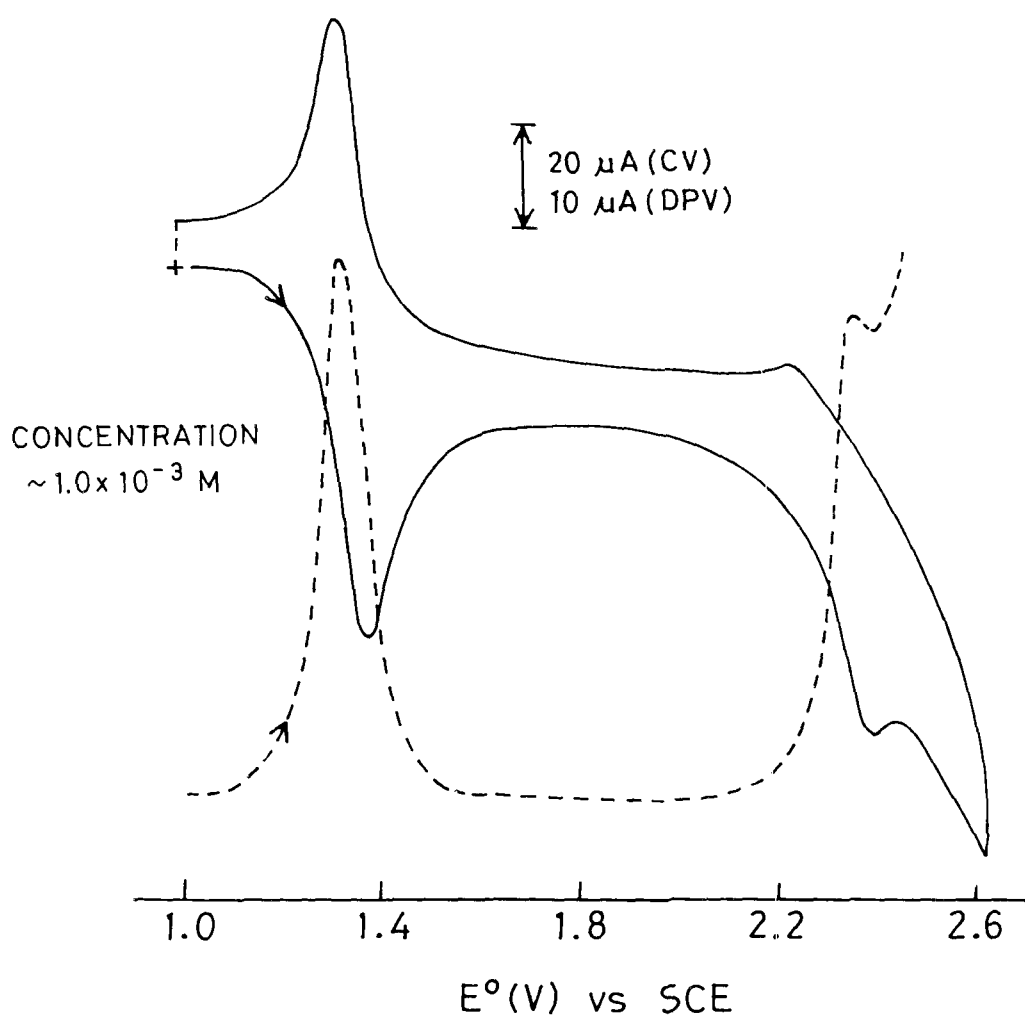


FIGURE IV.4. VOLTAMOGRAMS OF $[\text{OsCl}(\text{py})\text{L}_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ IN MeCN. SCAN RATES: FOR CV(—), 50 mVs^{-1} ; FOR DPV(---), 10 mVs^{-1}

TABLE IV. 5

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

Compound	-E ⁰ , V			
	r ₁	r ₂	r ₃ ^d	r ₄ ^d
[OsCl(py)L ¹ ₂]ClO ₄ .H ₂ O (4a)	0.46 (70)	0.85 (120)	1.51	2.18
[OsBr(py)L ¹ ₂]ClO ₄ .H ₂ O (4b)	0.43 (80)	0.80 (120)	1.50	2.24
[OsCl(py)L ² ₂]ClO ₄ .H ₂ O (4c)	0.45 (70)	0.81 (120)	1.51	2.26
[OsBr(py)L ² ₂]ClO ₄ .H ₂ O (4d)	0.44 (70)	0.79 (130)	1.49	2.20
[OsCl(pyz)L ² ₂]ClO ₄ .H ₂ O (4e)	0.48 (80)	0.85 (130)	1.57	2.32
[OsBr(pyz)L ² ₂]ClO ₄ .H ₂ O (4f)	0.47 (80)	0.84 (120)	1.58	2.31
[OsCl(pzH)L ² ₂]ClO ₄ .H ₂ O (4g)	0.45 (80)	0.82 (120)	1.53	2.19
[OsBr(pzH)L ² ₂]ClO ₄ .H ₂ O (4h)	0.48 (80)	0.84 (120)	1.55	2.25

^aMeaning and units of the symbols are the same as in the text and Chapter II. ^bWorking electrode, glassy carbon; supporting electrolyte, TEAP (0.1 M); solute concentration, ~ 10⁻³ M. ^cUnless otherwise stated both CV and DPV results are set; the agreement between data obtained by two techniques is invariably good (within ± 5 mV). ^dOnly DPV results.

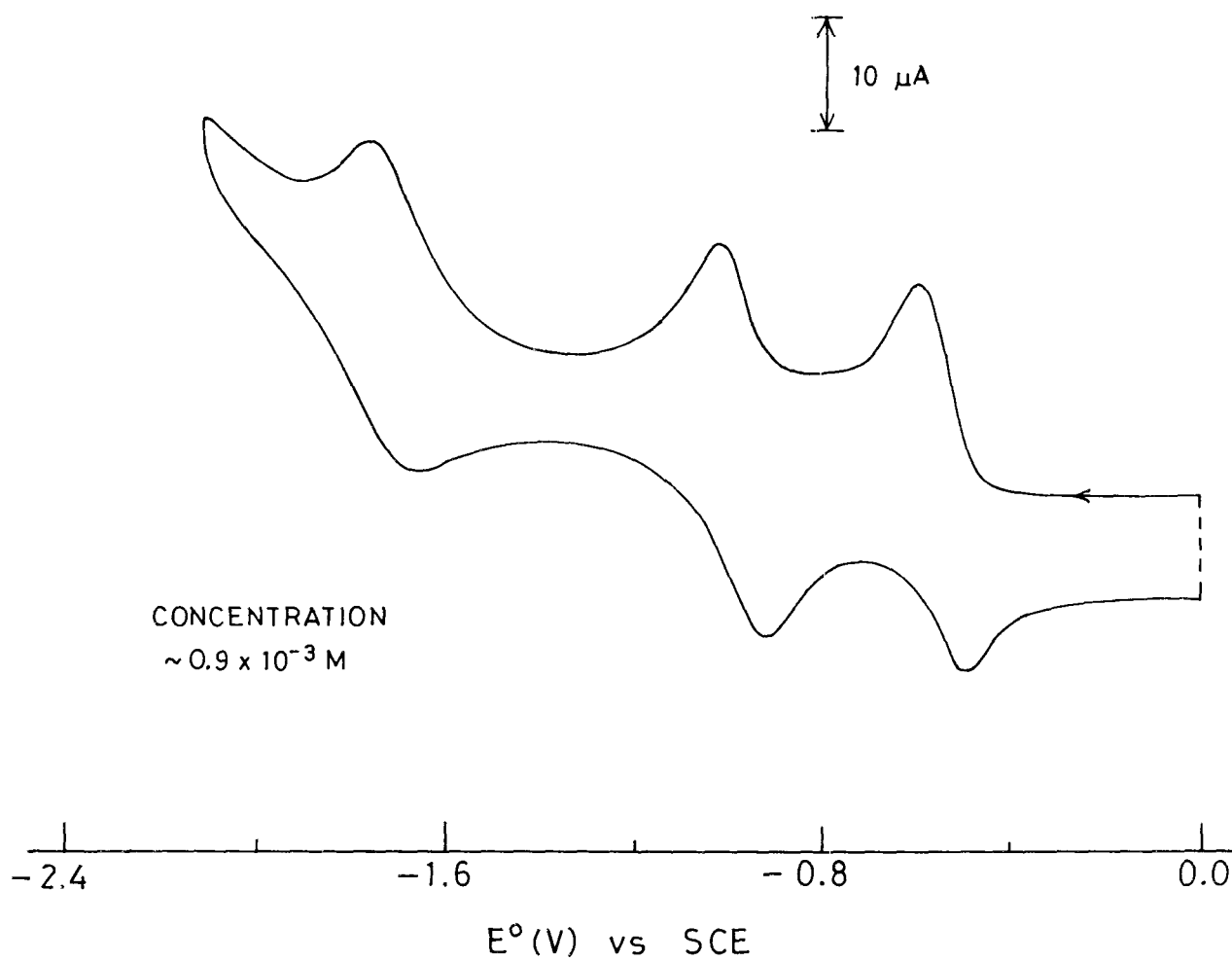


FIGURE IV.5. CYCLIC VOLTAMMOGRAM OF $[\text{OsCl}(\text{py})\text{L}_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ IN MeCN
SCAN RATE, 50 mVs^{-1}

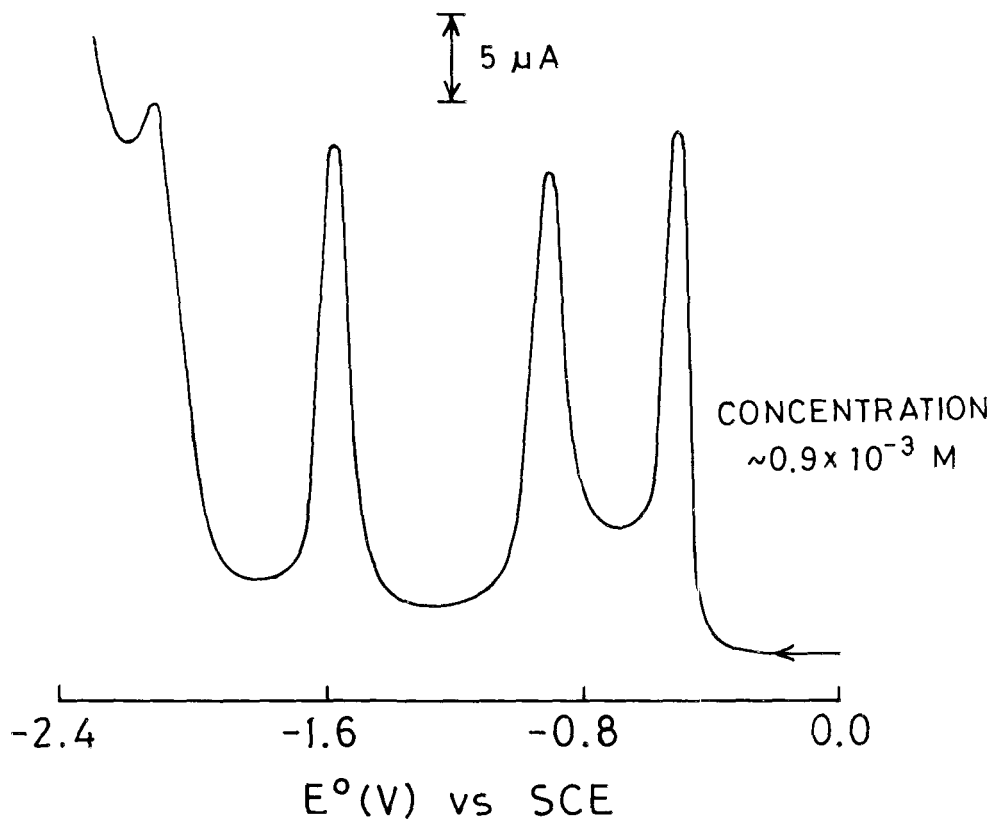


FIGURE IV.6. DIFFERENTIAL PULSE VOLTAMMOGRAM OF $[\text{OsCl}(\text{py})\text{L}_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ IN MeCN. SCAN RATE, 10 mVs^{-1}

Comparison of the electrochemical behaviour of **2** and **4** is instructive. The change of ancillary ligand from X to B shifts the osmium(III) - osmium(II) potential by ~ 0.4 V. By contrast, the variation in the first reductive response is smaller (upto 0.15 V). This suggests that the reaction centre in the reductive step is far from X/B. Again the potential values of **4** are also consistent with the monocationic formulation, considering the osmium(III) - osmium(II) potentials of the two series of complexes^{1,5,14}: $[\text{OsX}_2(\text{bipy})_2]$, ~ 0.0 V; $[\text{OsX}(\text{py})(\text{bipy})_2]^{1+}$, ~ 0.4 V; $[\text{Os}(\text{py})_2(\text{bipy})_2]^{2+}$, ~ 0.75 V; $[\text{Os}(\text{bipy})_3]^{2+}$, ~ 0.81 V; $[\text{OsX}_2\text{L}_2]$, ~ 1.0 V; $[\text{OsX}(\text{py})\text{L}_2]^{1+}$, ~ 1.4 V. $[\text{Os}(\text{bipy})\text{L}_2]^{2+}$, ~ 1.65 V. This strongly suggests that for the elusive $[\text{Os}(\text{py})_2\text{L}_2]^{2+}$ the potential of the osmium(III) - osmium(II) couple should be close to 1.6 V.

E. CONCLUSION

All the results conform to the monocationic formulation $[\text{OsX}(\text{B})\text{L}_2]^{1+}$. The synthetic results reflect the substitutional inertness of the second halogen. The complexes are rich in both spin-allowed and spin-forbidden metal-to-ligand charge transfer transitions, and exhibit two metal centred oxidations at high potentials and four azo-based reductions in successive one-electron transfer steps. Thus a nearly complete electron transfer series is formed in successive six one-electron transfer steps. The role of strong osmium-azo π -back bonding is reflected in the spectral and electrochemical properties. In the next chapter we will explore the chemistry of 2,2'-bipyrazine (bpyz) and 2,2'-bipyrimidine (bpym), two redox-active ligands in combination with osmium(II)-L.

IV.3 EXPERIMENTAL SECTION

A. PREPARATION OF COMPOUNDS

(a) Chemicals, solvents and starting materials

The chemicals and solvents used for the preparative procedure were stated in **Chapters II** and **III**. The other chemicals used are : pyridine, SD (India); pyrazole, pyrazine, Aldrich (USA). Isomeric $[\text{OsX}_2\text{L}_2]$ (**2**) (X = Cl or Br; L = L¹ or L²) were prepared as reported earlier⁵.

(b) Ligands

2-(Phenylazo)pyridine (L¹) and 2-(*m*-tolylazo)pyridine (L²) were prepared following the procedure^{3,4} described in **Chapter II**.

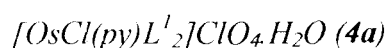
(c) Precursors

The dihalo complexes *cis, trans, cis*-[OsX₂L₂] (**2**) (X = Cl or Br; L = L¹ or L²) were prepared following same procedure⁵ as was used by Ghosh et al.

(d) Complexes

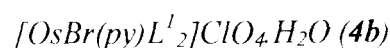
The monosubstituted complexes [OsX(B)L₂]ClO₄·H₂O (**4**) were prepared by the general procedure as described below. The yields varied in the range 60 - 80%.

(i) *Chloropyridinebis[2-(phenylazo)pyridine]osmium(II) perchlorate monohydrate.*



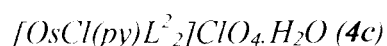
To a suspension of 0.1 g (0.159 mmol) of *cis*-[OsCl₂L¹₂] in 2:1 2-methoxyethanol-water (25 ml) 0.126 g (1.59 mmol) of pyridine was added, and the mixture was boiled under reflux for 12 h. The resulting red-violet solution was evaporated on steam-bath and the residue was dried in vacuo, washed several times with benzene and redissolved in 10 ml 2:1 MeCN-H₂O saturated with NaClO₄. The solution was evaporated slowly in air. The precipitate, collected by filtration, washed thoroughly with chilled water, dried and chromatographed on an alumina (E. Merck, India) column (20 × 1 cm). At first a small blue-violet solution was eluted with dichloromethane, followed by a red-violet band eluted with 1:1 PhH-MeCN. On slow evaporation of the eluant crystals of the desired compound (**4**) resulted. Analytical purity was obtained after drying in vacuo over P₄O₁₀. The yield was 0.09 g (72%).

(ii) *Bromopyridinebis[2-(phenylazo)pyridine]osmium(II) perchlorate monohydrate.*



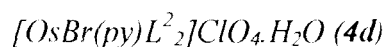
4b was prepared using the same procedure as described in **4a** except that 0.1 g (0.139 mmol) *cis*-[OsBr₂L¹₂] was reacted with 0.11 g (1.4 mmol) pyridine. The yield was 0.116 g (78%).

(iii) *Chloropyridinebis[2-(*m*-tolylazo)pyridine]osmium(II) perchlorate monohydrate.*



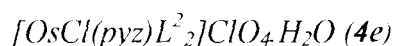
The procedure was the same as in the preparation of **4a** except that 0.1 g (0.153 mmol) of *cis*-[OsCl₂L²₂] was allowed to react with 0.126 g (1.6 mmol) of pyridine. The yield was 0.087 g (70%).

(iv) *Bromopyridinebis[2-(m-tolylazo)pyridine]osmium(II) perchlorate monohydrate.*



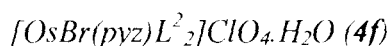
The preparative procedure for **4d** was the same as described in **4a**. Here 0.1 g (0.134 mmol) of *cis*- $[\text{OsBr}_2\text{L}^2_2]$ was reacted with 0.106 g (1.34 mmol) of pyridine: yield, 0.085 g (74%).

(v) *Chloropyrazinebis[2-(m-tolylazo)pyridine]osmium(II) perchlorate monohydrate.*



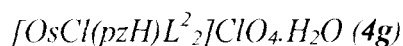
The same procedure and reaction stoichiometry as in **4a** preparation were followed. Here 0.1 g (0.153 mmol) of *cis*- $[\text{OsCl}_2\text{L}^2_2]$ was reacted with 0.122 g (1.53 mmol) of pyrazine. The yield was 0.09 g (70%).

(vi) *Bromopyrazinebis[2-(m-tolylazo)pyridine]osmium(II) perchlorate monohydrate.*



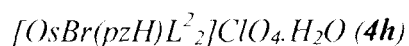
4f was prepared using the same solvent, procedure and reaction stoichiometry as in **4a** except that 0.1 g (0.134 mmol) of pyrazine was used; yield, 0.085 g (74%).

(vii) *Chloropyrazolebis[2-(m-tolylazo)pyridine]osmium(II) perchlorate monohydrate.*



To prepare **4g** the same procedure was followed as in **4a**. Here 0.1 g (0.153 mmol) of *cis*- $[\text{OsCl}_2\text{L}^2_2]$ was reacted with 0.104 g (1.53 mmol) pyrazole. The yield was 0.076 g (64%).

(viii) *Bromopyrazolebis[2-(m-tolylazo)pyridine]osmium(II) perchlorate monohydrate.*



The cationic complex **4h** was prepared using the procedure described in the preparation of **4a**. Here 0.1 g (0.134 mmol) of *cis*- $[\text{OsBr}_2\text{L}^2_2]$ was reacted with 0.09 g (1.34 mmol) of pyrazole: yield, 0.076 g (70%).

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 IV.6**.

C. PHYSICAL MEASUREMENTS

This was done as described in **Chapters II and III**.

TABLE IV. 6

Characterisation Data

Compound	%C		%H		%N	
	Calcd	Found	Calcd	Found	Calcd	Found
[OsCl(py)L ¹ ₂]ClO ₄ .H ₂ O (4a) C ₂₇ H ₂₅ N ₇ O ₅ Cl ₂ Os	41.1	41.3	3.2	3.3	12.4	12.6
[OsBr(py)L ¹ ₂]ClO ₄ .H ₂ O (4b) C ₂₇ H ₂₅ N ₇ O ₅ ClBrOs	38.9	38.8	3.0	3.0	11.8	11.8
[OsCl(py)L ² ₂]ClO ₄ .H ₂ O (4c) C ₂₉ H ₂₉ N ₇ O ₅ Cl ₂ Os	42.6	42.5	3.6	3.6	12.0	12.1
[OsBr(py)L ² ₂]ClO ₄ .H ₂ O (4d) C ₂₉ H ₂₉ N ₇ O ₅ ClBrOs	40.4	40.3	3.4	3.5	11.4	11.3
[OsCl(py _z)L ² ₂]ClO ₄ .H ₂ O (4e) C ₂₇ H ₂₉ N ₇ O ₅ Cl ₂ Os	41.1	40.9	3.5	3.4	13.7	13.7
[OsBr(py _z)L ² ₂]ClO ₄ .H ₂ O (4f) C ₂₇ H ₂₉ N ₇ O ₅ ClBrOs	39.0	38.8	3.3	3.3	13.0	13.3
[OsCl(pzH)L ² ₂]ClO ₄ .H ₂ O (4g) C ₂₆ H ₂₄ N ₈ O ₅ Cl ₂ Os	39.5	39.2	3.1	3.1	14.2	14.3
[OsBr(pzH)L ² ₂]ClO ₄ .H ₂ O (4h) C ₂₆ H ₂₄ N ₈ O ₅ ClBrOs	37.4	37.2	2.9	3.0	13.4	13.6

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