

CHAPTER VII

ISOMERIC $[\text{Os}^{\text{III}}\text{X}_2\text{L}_2]^{1+}$ (X = Cl OR Br) COMPLEXES

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ABSTRACT : An efficient route for isolation of high potential isomeric complexes of type $[\text{Os}^{\text{III}}\text{X}_2\text{L}_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**4**, **5** and **6**) [$\text{X} = \text{Cl}$ or Br ; $\text{L} = 2\text{-(phenylazo)pyridine (L}^1\text{)}$ or $2\text{-(m-tolylazo)pyridine (L}^2\text{)}$] has been achieved by oxidising corresponding osmium(II) compounds (**1**, **2** and **3**, respectively) with concentrated HNO_3 . Reduction with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ reverts osmium(II) precursors. The cations have been isolated as crystalline perchlorate monohydrates. The complexes were characterised using spectroscopic, magnetic and physicochemical results. The synthetic routes are found to be stereoretentive. The low-spin (idealised t_{2g}^5 ; $S = \frac{1}{2}$) paramagnetic complex ions display characteristic osmium(III) EPR spectra in frozen (77 K) MeCN-PhMe. The isomeric complexes display characteristic multiple ligand-to-metal charge transfer bands and shoulders. A number of spin-forbidden and spin-allowed transitions are also observable. A blue-shift is seen in going from **6** to **5** via **4**. In dry MeCN solutions, the OsX_2N_4 unit exhibits irreversible $[\text{OsX}_2\text{L}_2]^{2+}/[\text{OsX}_2\text{L}_2]^{1+}$ and reversible $[\text{OsX}_2\text{L}_2]^{1+}/[\text{OsX}_2\text{L}_2]$ couples at ~ 1.8 and ~ 1.0 V versus saturated calomel electrode, respectively. The use of the complexes as oxidants is noted.

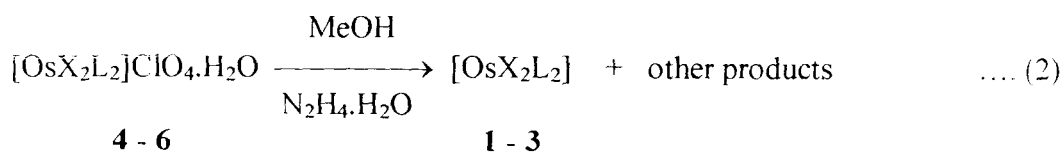
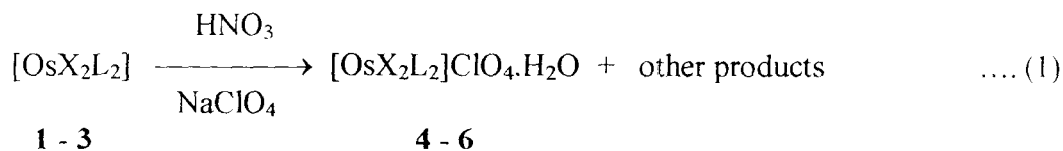
VII.1 INTRODUCTION

In recent years many studies¹⁻⁶ have been devoted to osmium(II) complexes with 2-(aryloxy)pyridine (L, **1**), an unsymmetrical, non-innocent⁷ N,N-bidentate chelator with azoimine (-N=N-C=N-) chromophore. Three isomeric dihalo species of types blue-violet *cis*, *trans*, *cis* (*etc.* **1**), red-violet *cis*, *cis*, *cis* (*ccc*, **2**) and blue *trans*, *trans*, *trans* (*ttt*, **3**) are obtainable by reaction of L with hexahaloosmate(IV) salt; no osmium(III) complexes appear to furnish in a pure state¹. The apparent high affinity of L towards the +2 state is reflected in the high formal potential (~1.0 V vs SCE) of the [Os^{III}X₂L₂]¹⁺/[Os^{II}X₂L₂] couple. In this chapter we examine the possibility of isolation of these three isomeric [OsX₂L₂] (**1**, **2** and **3**) (X = Cl or Br) species in the osmium(III) state. A series of isomeric complex ions of the type [Os^{III}X₂L₂]¹⁺ have been isolated as perchlorate monohydrate (**4**, **5** and **6**) via stereoretentive oxidations of the precursors (**1**, **2** and **3**, respectively) with concentrated nitric acid.

VII.2 RESULTS AND DISCUSSION

A. SYNTHESIS

The isomeric osmium(III) complexes of the general formula [Os^{III}X₂L₂]ClO₄.H₂O (**4**, **5** and **6**), were generally prepared by oxidising corresponding solid osmium(II) compounds [OsX₂L₂] (**1**, **2** and **3**) with concentrated nitric acid. Titrating the finely powdered sample for a few minutes under such conditions, followed by the addition of solid sodium perchlorate, yielded (almost quantitatively) a dark brown precipitate (**equation 1**). Chemical (hydrazine hydrate) or electrochemical (coulometry, potentiostated at 0.65 V vs SCE in MeCN) reduction of each isomeric salt furnishes the corresponding osmium(II) parent immediately (**equation 2**). The



interconversion in each pair of redox complex species [Os^{III}X₂L₂]¹⁺/[Os^{II}X₂L₂] occurs without stereochemical reorganisation in the coordination sphere (see below).

The osmium(III) complexes were characterised by elemental analyses, solution electrical conductivity and magnetic susceptibility measurements, IR, UV-Vis and EPR spectroscopic investigations and electrochemical studies (**Tables VII.1 - VII.8**). In the crystalline state all the compounds (**4, 5 and 6**) are one-electron paramagnets. The isomers are readily soluble in a range of common organic solvents like acetonitrile, chloroform, alcohols, dimethylformamide and dimethylsulphoxide giving rise to deep red solutions. In MeCN the salts exhibited the anticipated⁸ electrical conductivity (**Table VII.1**). Other pertinent results are summarised in **Tables VII.2 - VII.8**; all conform with the formulations of **4, 5 and 6**.

B. INFRARED SPECTRA

Selected IR frequencies are listed in **Table VII.2**. Characteristic spectral nature of each isomeric complex ion are shown in **Figures VII.1 - VII.3**. The very broad and structureless ν_3 band of ClO_4^- suggests⁹ the presence of perchlorate as a counter ion in the solid state as in solution (conductivity results). The N=N stretching frequency in **1, 2 and 3** are located at ~ 1280 , ~ 1275 and $\sim 1285 \text{ cm}^{-1}$. These values are systematically higher in corresponding isomeric osmium(III) complexes **4** ($\sim 1290 \text{ cm}^{-1}$), **5** ($\sim 1285 \text{ cm}^{-1}$) and **6** (1295 cm^{-1}). The free ligand $\nu(\text{N}=\text{N})$ value¹⁰ is 1425 cm^{-1} . The lowering of $\nu(\text{N}=\text{N})$ from free state to the complex is indicative of strong $d(\text{Os}) \rightarrow \pi^*(\text{L})$ back bonding. However the greater values in **4, 5 and 6** clearly demonstrate that osmium(III) is a weaker π -donor compared to osmium(II). Similar observations for $[\text{CuL}_2]^n$ ($n = +1, +2$) complexes have been reported ($n = +1$, $\nu(\text{N}=\text{N})$, ~ 1375 ; $n = +2$, $\nu(\text{N}=\text{N})$, $\sim 1412 \text{ cm}^{-1}$)¹¹. The $\nu(\text{C}=\text{N})$ value remains almost invariant at $\sim 1590 \text{ cm}^{-1}$ in all osmium(III) and osmium(II) complexes, reflecting¹² the effective π -bonding centre at the azo part of the azoimine ($-\text{N}=\text{N}-\overset{\text{I}}{\text{C}}=\text{N}-$) chromophore. $\nu(\text{Os}-\text{Cl})$ shifts to a higher frequency in going from osmium(II) to osmium(III) as the latter has greater charge.

The stereochemical assignment of the isomeric osmium(III) complexes (**4 - 6**) is revealed by close examination of their vibration spectra with those of the structural characteristics^{1,2} osmium(II) precursors (**1 - 3**). The spectrum of a compound belonging to type **4** is virtually superimposable on that of its precursor **1** in the $4000 - 300 \text{ cm}^{-1}$ range, except for lattice water ($\sim 3400 \text{ cm}^{-1}$) and ionic perchlorate bands (**Table VII.2**), and for small but distinct upward shifts of $\nu(\text{N}=\text{N})$ (in all) and $\nu(\text{Os}-\text{Cl})$ (for $\text{X} = \text{Cl}$ only) stretches. A similar relationship holds between the spectra of **2 and 5**, and **3 and 6** (see **Figures VII.1 - VII.3**). Again, a 1:1 correspondence

TABLE VII.1

Molar Conductivity data^a in MeCN at 298 K

Compound	Λ_M (ohm ⁻¹ cm ² mol ⁻¹)
ctc-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (4a)	150
ccc-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (5a)	155
ttt-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (6a)	150
ctc-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (4b)	150
ccc-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (5b)	150
ttt-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (6b)	155
ctc-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (4c)	155
ccc-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (5c)	155
ttt-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (6c)	150
ctc-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (4d)	155
ccc-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (5d)	150
ttt-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (6d)	150

^aSolute concentration, $\sim 10^{-3}$ M.

TABLE VII. 2

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

Compound	$\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$	$\nu(\text{N}=\text{N})$	$\nu(\text{ClO}_4)^{\text{d}}$	$\nu(\text{Os}-\text{Cl})$
ctc-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (4a)	1590	1290	1080, 620	335, 320
ccc-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (5a)	1592	1285	1085, 620	330, 320
ttt-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (6a)	1590	1295	1084, 620	335
ctc-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (4b)	1595	1290	1085, 620	335, 320
ccc-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (5b)	1590	1285	1080, 620	330, 320
ttt-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (6b)	1592	1294	1085, 620	338
ctc-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (4c)	1592	1290	1085, 620	e
ccc-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (5c)	1590	1285	1086, 620	e
ttt-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (6c)	1592	1296	1084, 620	e
ctc-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (4d)	1594	1290	1080, 620	e
ccc-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (5d)	1592	1285	1085, 620	e
ttt-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (6d)	1590	1295	1082, 620	e

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

^cLattice water band at ~3400 cm⁻¹. ^dbroad band at ~1080 cm⁻¹ due to ν_3 transition; band at 620 cm⁻¹ due to ν_2 type. ^e $\nu(\text{Os}-\text{Br})$, not studied.

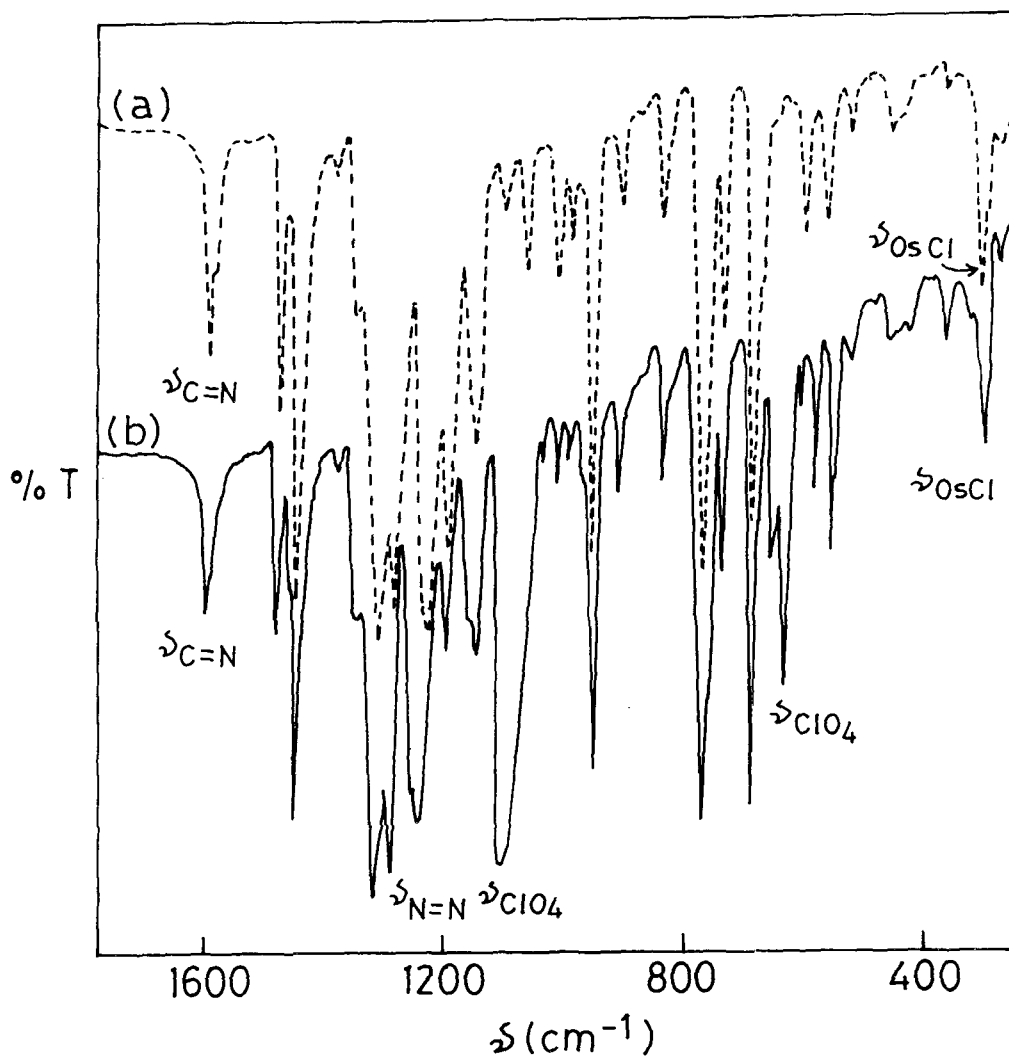


FIGURE VII.1. IR SPECTRA OF (a) $\text{ctc-}[\text{OsCl}_2\text{L}^1_2]$ (----) AND (b) $\text{ctc-}[\text{OsCl}_2\text{L}^1_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (—) IN KBr DISC

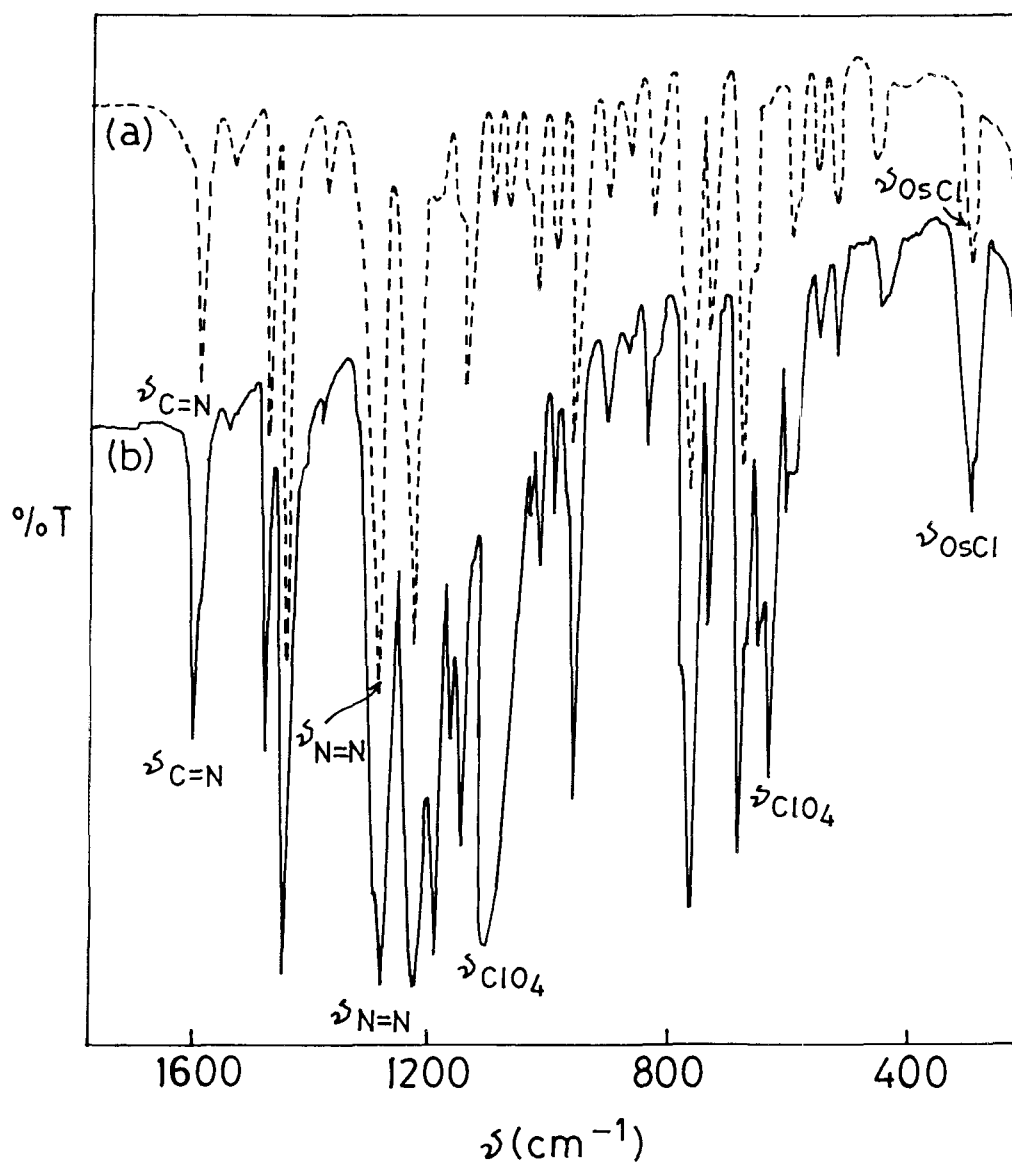


FIGURE VII.2. IR SPECTRA OF (a) $\text{ccc-}[\text{OsCl}_2\text{L}^1_2]$ (----) AND (b) $\text{ccc-}[\text{OsCl}_2\text{L}^1_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (—) IN KBr DISC

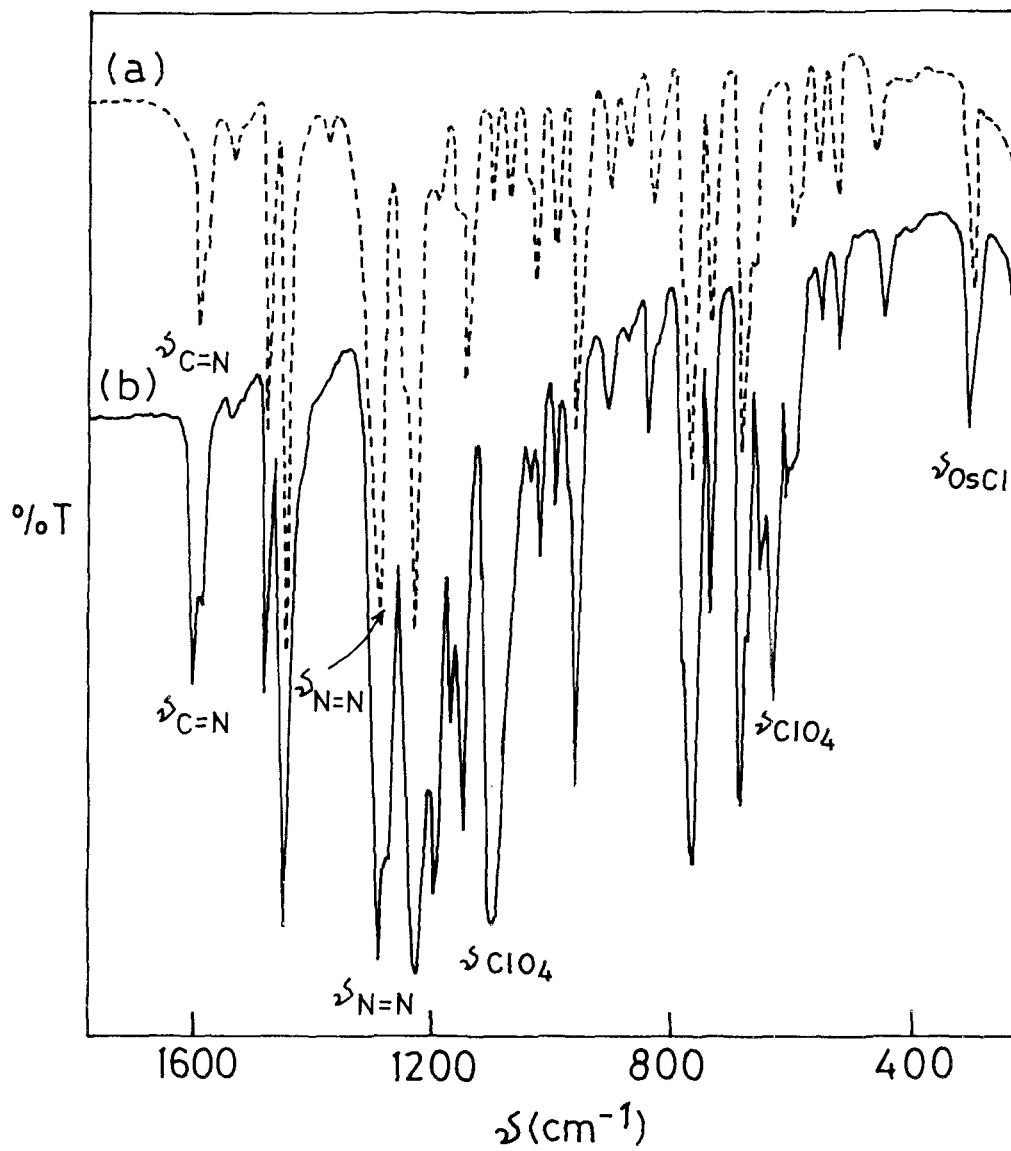


FIGURE VII.3. IR SPECTRA OF (a) $\text{ttt-}[\text{OsCl}_2\text{L}_2]$ (----) AND (b) $\text{ttt-}[\text{OsCl}_2\text{L}_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (—) IN KBr DISC

exists in the IR spectra of well characterised¹³ ruthenium(III) species $[\text{Ru}^{\text{III}}\text{X}_2\text{L}_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ belonging to formulations **4** - **6** and the oxidation products isolated from **1** - **3**.

C. MAGNETISM AND EPR SPECTRA

The room temperature magnetic moments of the complexes in solid state are listed in **Table VII.3**. The observed moments correspond to low-spin d^5 configuration (idealised t_{2g}^5 , $S = 1/2$) with a distinct orbital contribution. The cation $[\text{OsX}_2\text{L}_2]^{1+}$ is best described as having two-fold (C_2) rotational symmetry. Rhombic EPR spectra are therefore expected for all these osmium(III) complexes. At room temperature a very broad spectrum is obtained in solid phase and in acetonitrile-toluene (1:1) solution. However, two resonances (**Table VII.4**) are observable in frozen acetonitrile-toluene (1:1) glasses (77 K). A representative spectrum is shown in **Figure VII.4**. Such a two component¹⁴⁻¹⁶ resonance is often a characteristic rhombic structure associated with low-spin d^5 osmium(III) in a distorted octahedral environment. The third component occurs at high field and is often unobserved¹⁵.

D. CHARGE-TRANSFER SPECTRA

The complexes display multiple bands and shoulders in the 200 - 800 nm range. Spectral data in MeCN are set in **Table VII.5**. Representative spectral nature is shown in **Figure VII.5**. A characteristic feature of $[\text{OsX}_2\text{L}_2]^{1+}$ is a strong absorption at ~500 nm along with a shoulder at lower energy. This is assignable to the ligand-to-metal charge transfer (LMCT) transition within the framework of pseudooctahedral osmium(III) stereochemistry¹⁷. Though the visual colours of **4** - **6** are quite similar, the bands are blue shifted in going from **6** to **5** via **4**. The allowed transitions below 400 nm are probably of ligand origin and are considered in early chapters.

E. REDOX BEHAVIOUR

The electron transfer properties of the complexes in acetonitrile solutions (0.1 M in TEAP) were examined 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 in **Tables VII.6** and **VII.7**. Representative voltammograms are shown in **Figures VII.6** - **VII.9**. All potentials are referenced to a saturated calomel electrode (SCE).

TABLE VII. 3

Bulk Magnetic Moments^a of the Complexes

Compound	μ_{eff} (μ_{B})
ctc-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (4a)	1.91
ccc-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (5a)	1.88
ttt-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (6a)	1.89
ctc-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (4b)	1.86
ccc-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (5b)	1.92
ttt-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (6b)	1.88
ctc-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (4c)	1.85
ccc-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (5c)	1.87
ttt-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (6c)	1.89
ctc-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (4d)	1.91
ccc-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (5d)	1.92
ttt-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (6d)	1.89

^aIn solid state at 298 K.

TABLE VII. 4

EPR Results^{a,b} of the Complexes

Compound	g values	
	$g_{ }$	g_{\perp}
ctc-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (4a)	2.525	2.168
ccc-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (5a)	2.482	2.124
ttt-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (6a)	2.563	2.191
ctc-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (4b)	2.528	2.159
ccc-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (5b)	2.476	2.121
ttt-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (6b)	2.569	2.197
ctc-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (4c)	2.532	2.156
ccc-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (5c)	2.471	2.128
ttt-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (6c)	2.571	2.199
ctc-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (4d)	2.534	2.156
ccc-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (5d)	2.491	2.131
ttt-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (6d)	2.567	2.194

^aIn 1:1 MeCN-PhMe at 77K. ^bThe spectra were calibrated with the help of 1,1-diphenyl-2-picrylhydrazyl (DPPH).

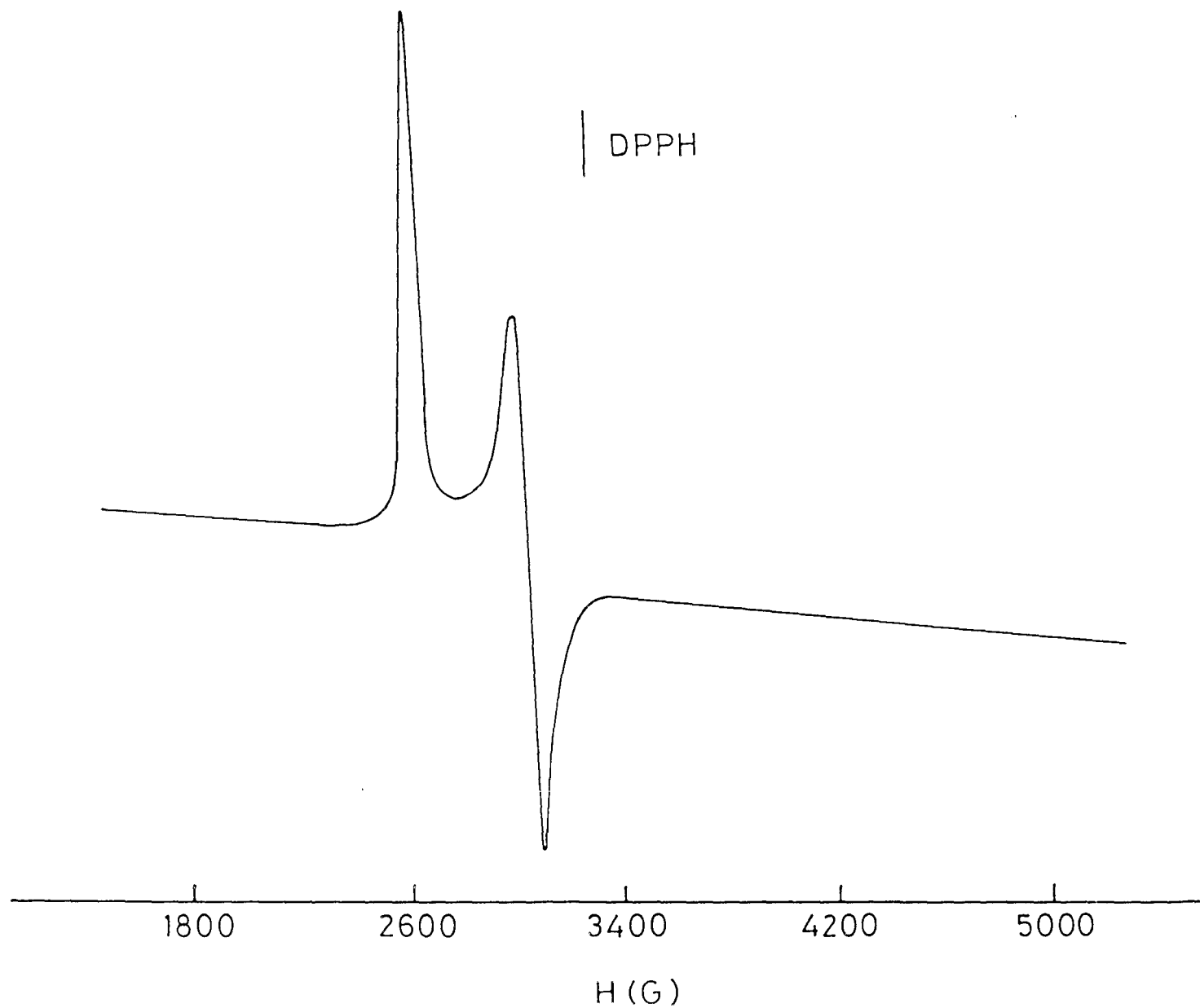


FIGURE VII.4. X-BAND EPR SPECTRUM OF $ctc-[OsCl_2L_2](ClO_4).H_2O$ IN MeCN-PhMe GLASS (77 K). (DPPH = 1,1-DIPHENYL-2-PICRYLHYDRAZYL)

TABLE VII. 5

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

Compound	λ_{max} , nm (ϵ , M ⁻¹ cm ⁻¹)
ctc-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (4a)	780 ^c (1,240), 505 (7,290), 322 (16,120), 236 (20,370)
ccc-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (5a)	760 ^c (1,390), 490 (8,150), 310 (18,250), 260 (22,490), 230 (28,180)
ttt-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (6a)	820 ^c (1,160), 515 (7,050), 330 (15,590), 280 (21,240), 240 (26,170)
ctc-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (4b)	778 ^c (1,320), 505 (7,460), 324 (16,800), 234 (20,850)
ccc-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (5b)	762 ^c (1,460), 490 (8,220), 315 (19,100), 265 (23,240), 232 (29,000)
ttt-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (6b)	825 ^c (1,030), 515 (7,370), 334 (16,160), 275 (21,510), 238 (26,550)
ctc-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (4c)	780 ^c (1,260), 505 (7,340), 322 (16,940), 236 (20,940)
ccc-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (5c)	760 ^c (1,390), 490 (8,390), 310 (19,340), 260 (23,370), 230 (29,240)
ttt-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (6c)	820 ^c (1,230), 515 (7,190), 332 (15,730), 278 (21,400), 240 (26,320)
ctc-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (4d)	776 ^c (1,280), 505 (7,620), 322 (17,130), 236 (21,310)
ccc-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (5d)	764 ^c (1,390), 490 (8,520), 310 (19,470), 260 (23,440), 230 (29,450)
ttt-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (6d)	824 ^c (1,300), 515 (7,580), 330 (16,430), 276 (21,770), 235 (26,640)

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

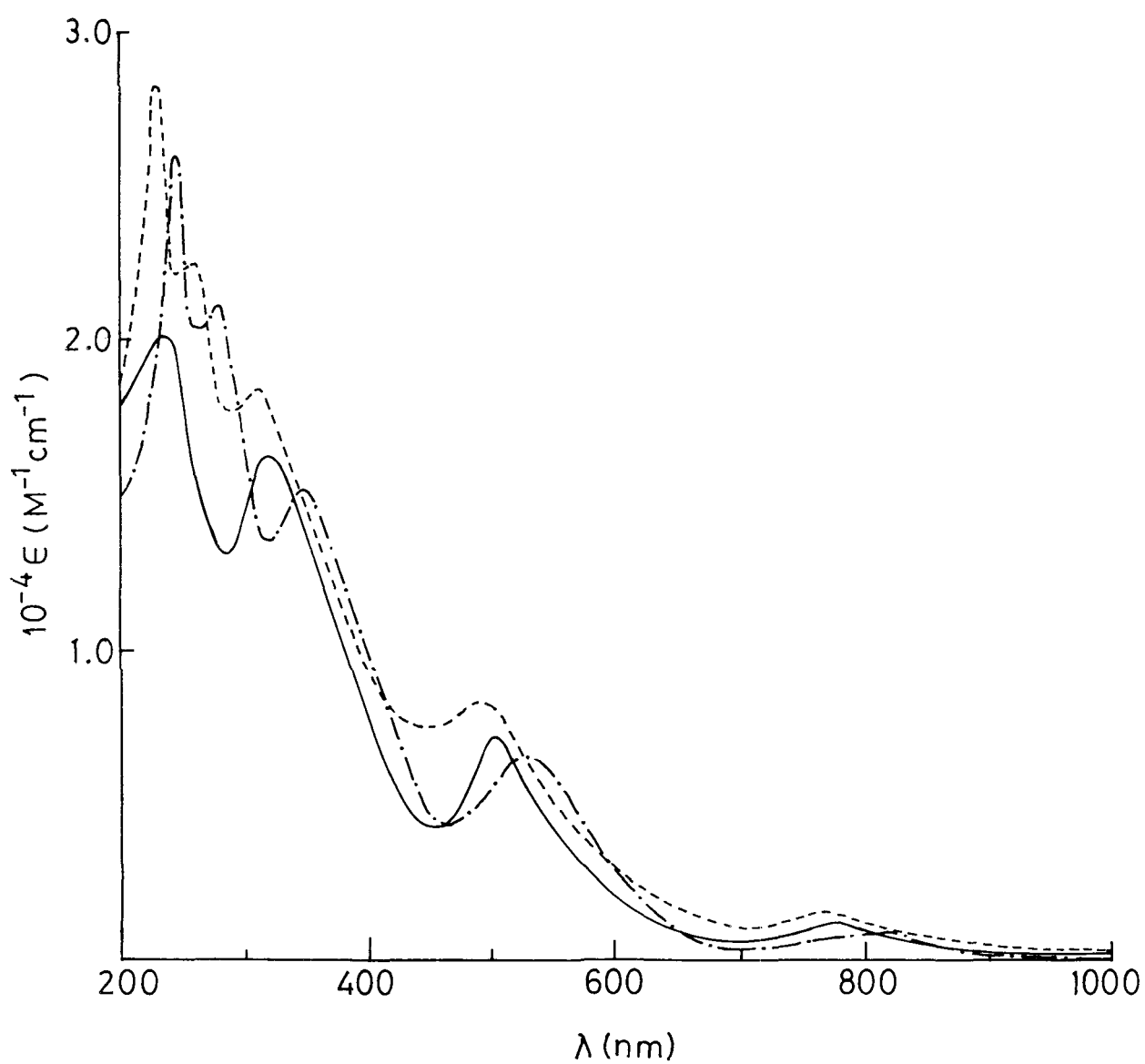
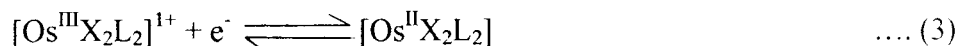


FIGURE VII.5. ELECTRONIC SPECTRA OF $ctc-[OsCl_2L^1_2]ClO_4 \cdot H_2O$ (—), $ccc-[OsCl_2L^1_2]ClO_4 \cdot H_2O$ (----) AND $ttt-[OsCl_2L^1_2]ClO_4 \cdot H_2O$ (-·-) IN MeCN

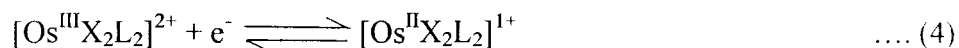
(a) Metal-centred electron transfers

Each isomeric osmium(III) species exhibits a reversible one-electron cyclic voltammetric reductive response in the potential range 0.8 to 1.0 V vs SCE, due to the electrode reaction in **equation 3**. The response is a reductive one. A multiple scan cyclic voltammogram



along with differential pulse of a particular isomer (compound of type **4**) is shown in **Figure VII.6**. The one-electron stoichiometry of the couple was confirmed from constant potential coulometry for some selected compounds (see **Table VII.6**). A systematic anodic shift of the potential is observed in going from **6** to **4** via **5**. Under an identical set of experimental conditions this voltammogram is superimposable to that of the corresponding osmium(II) counterparts, except in the mode of response which depends on the nature of the bulk solutions. This is in line with the fact that the process in **equation 3** is stereoretentive. After exhaustive one-electron constant-potential reduction of **4 - 6** potentiostated at 0.65 V, the reduced solutions are blue-violet, red-violet and blue in colour, respectively. Cyclic voltammograms of these solutions are again completely coincident with the initial ones, except for the inversion of the response.

An additional irreversible oxidative response at ~1.8 V is seen in all complexes under very carefully controlled experimental conditions. This is presumably due to the electrode reaction as shown in **equation 4**. Observation of this redox process at a higher potential near the solvent



cut-off was best made with DPV in dry acetonitrile. A similar behaviour is also seen for the osmium(II) analogues. A representative voltammogram containing both couples 3 and 4 is shown in **Figure VII.7**. The one-electron stoichiometry of the couple 4 could not be assigned by constant potential coulometry due to continuous accumulation of coulomb count. This high potential is in line with the fact that osmium(IV) species are not possible to obtain in solid state.

(b) Ligand-based reductions

The negative side of SCE was scanned using a glassy carbon electrode. Essentially the same voltammetric responses are obtained as is seen in the osmium(II) precursors described in **Chapter II**. The results are summarised in **Table VII.7**. Representative voltammograms are shown in **Figures VII.8** and **VII.9**. The complexes show three reductive responses in CV, but by careful DPV experiments all the four expected reductions are clearly seen. Comparison of current heights of these responses with that of the couple 3 is helpful in assigning one-electron

TABLE VII. 6

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

Compound	Os(III) - Os(II)	Os(IV) - Os(III)
	E^0 , V (ΔE_p , mV)	E^0 , V (ΔE_p , mV)
ctc-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (4a)	0.97 (60)	1.73 (160)
ccc-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (5a)	0.94 (60)	1.80 (170)
ttt-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (6a)	0.86 (60)	1.65 (160)
ctc-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (4b)	0.96 ^{d,e} (60)	1.76 (160)
ccc-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (5b)	0.93 ^{d,f} (60)	1.79 (170)
ttt-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (6b)	0.85 ^{d,g} (60)	1.62 (160)
ctc-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (4c)	0.96 (60)	1.78 (160)
ccc-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (5c)	0.94 (60)	1.77 (170)
ttt-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (6c)	0.84 (60)	1.64 (160)
ctc-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (4d)	0.96 (60)	1.72 (160)
ccc-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (5d)	0.94 (60)	1.81 (170)
ttt-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (6d)	0.83 (60)	1.61 (160)

^aMeaning and units of symbols are the same as in the text. ^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). ^dConstant potential coulometry (oxidation done at potential $E^0 + 200$ mV) : $n = Q/Q'$ where Q' is the calculated coulomb count for one-electron transfer and Q is the coulomb count found after exhaustive electrolysis of 0.01 mmol of the solute. ^e $n = 1.03$. ^f $n = 1.02$. ^g $n = 1.02$.

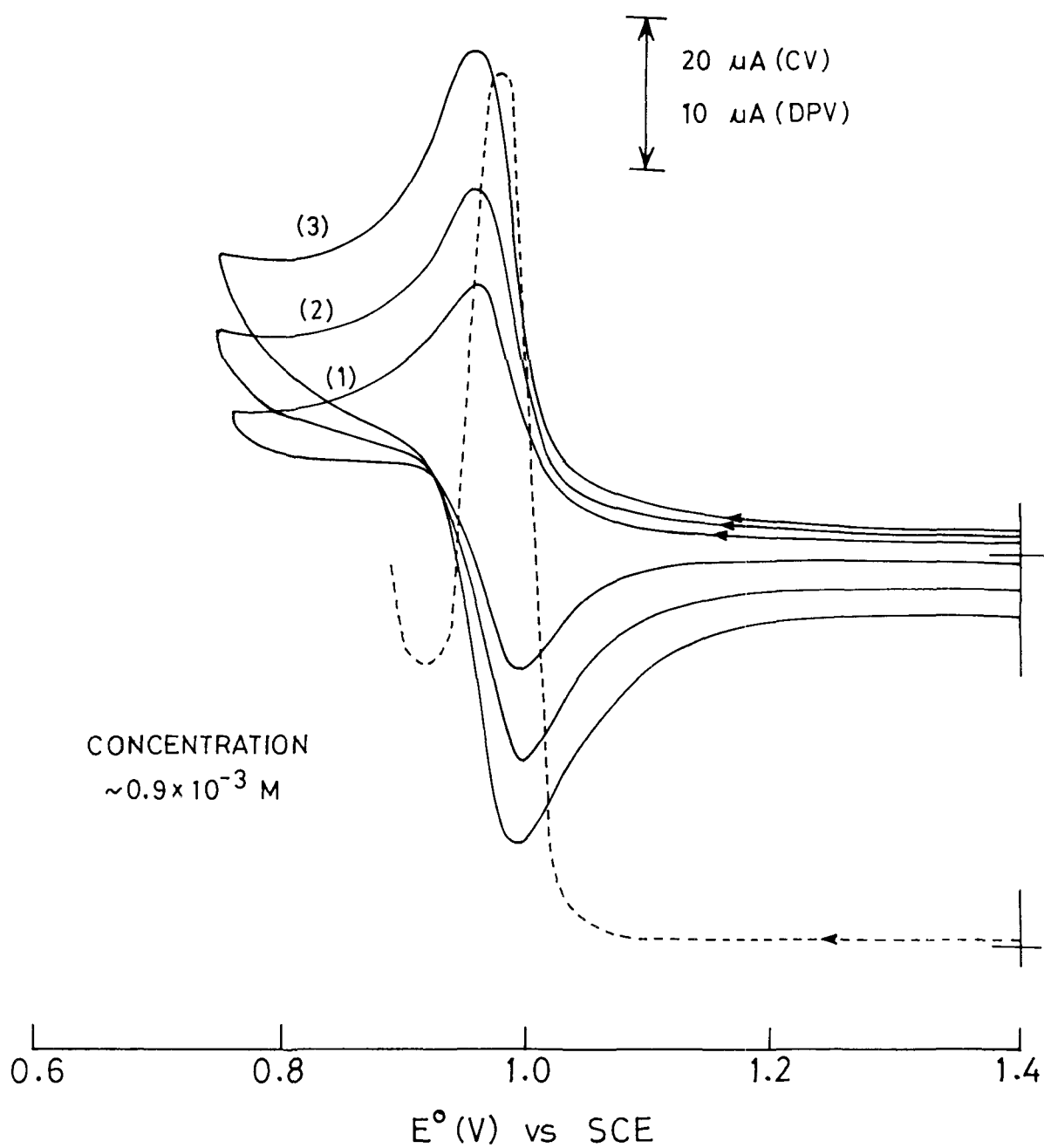


FIGURE VII.6. VOLTAMMOGRAMS OF $\text{ctc-}[\text{OsCl}_2\text{L}^1_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ IN MeCN. SCAN RATES : FOR CV(—), (1) 50, (2) 100, (3) 200 mVs^{-1} ; FOR DPV(---), 10 mVs^{-1}

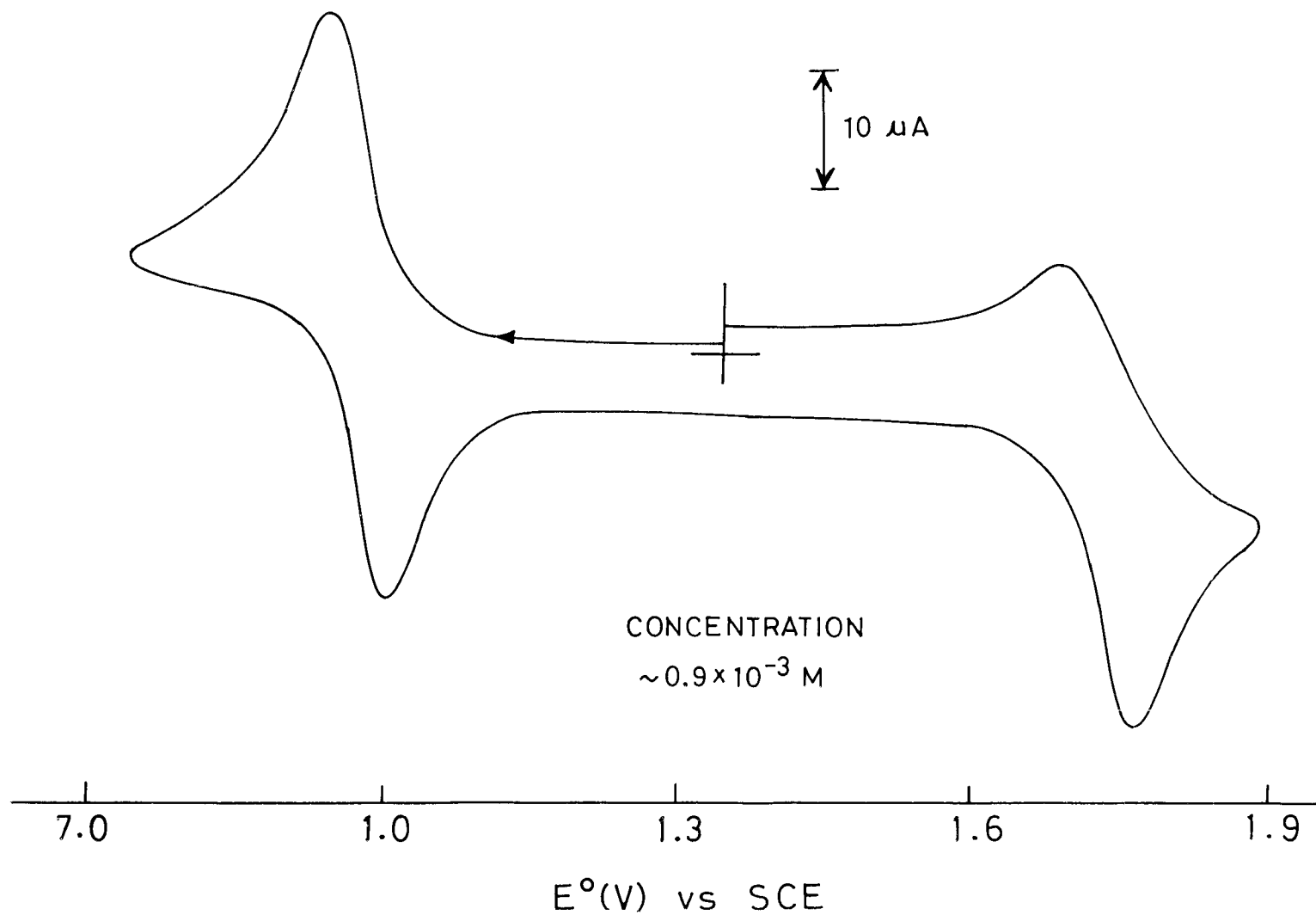


FIGURE VII.7. CYCLIC VOLTAMMOGRAM OF $\text{ctc-}[\text{OsCl}_2\text{L}^1_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ IN MeCN

TABLE VII. 7

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
ctc-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (4a)	0.52 (80)	0.83 (150)	1.51	1.94
ccc-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (5a)	0.54 (80)	0.87 (160)	1.56	1.96
ttt-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (6a)	0.55 (80)	0.88 (160)	1.52	1.92
ctc-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (4b)	0.56 (80)	0.89 (160)	1.54	2.01
ccc-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (5b)	0.58 (80)	0.90 (170)	1.58	2.02
ttt-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (6b)	0.59 (80)	0.92 (170)	1.60	2.00
ctc-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (4c)	0.55 (80)	0.90 (170)	1.53	2.02
ccc-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (5c)	0.57 (80)	0.92 (170)	1.56	2.03
ttt-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (6c)	0.58 (80)	0.91 (160)	1.57	2.02
ctc-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (4d)	0.56 (80)	0.89 (160)	1.56	1.99
ccc-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (5d)	0.58 (80)	0.91 (170)	1.59	2.03
ttt-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (6d)	0.59 (80)	0.93 (170)	1.60	2.00

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

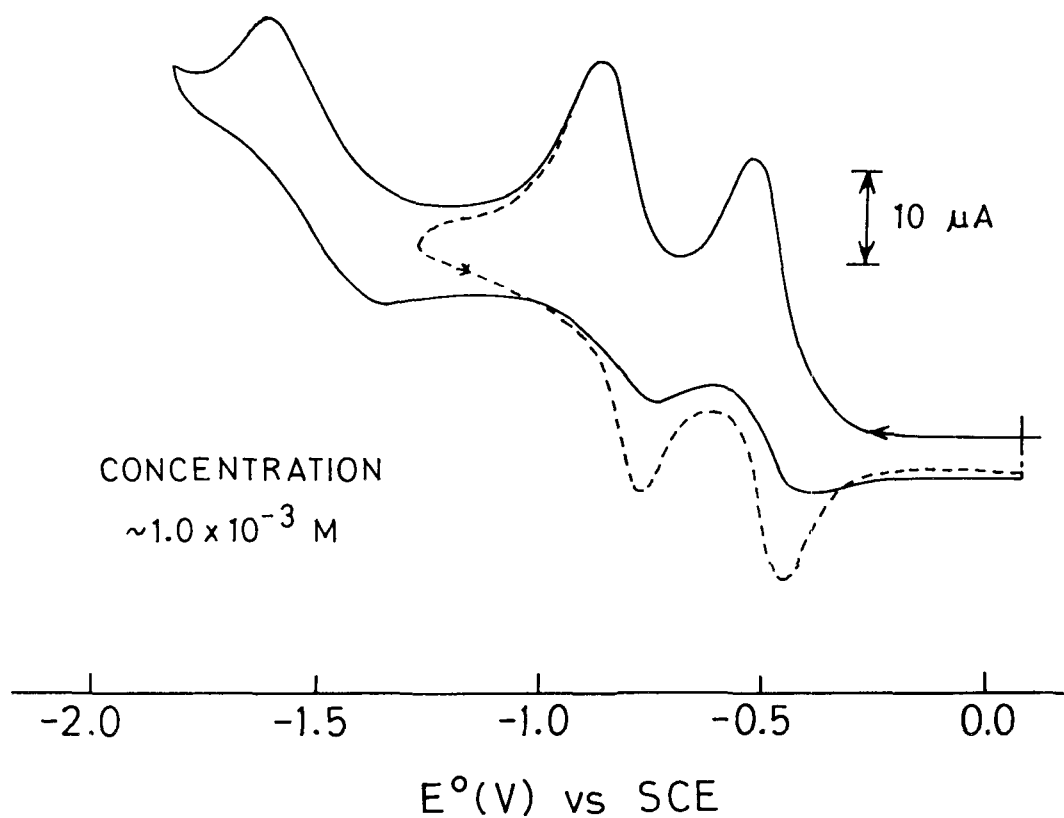


FIGURE VII.8. CYCLIC VOLTAMMOGRAM OF $\text{ttt-}[\text{OsCl}_2\text{L}_2]\text{ClO}_4 \cdot \text{H}_2\text{C}$ IN MeCN. THE PRESENTATION(----) SHOWS VOLTAMMOGRAM WHERE THE SCAN WAS REVERSED BEFORE REACHING THE THIRD REDUCTION WAVE

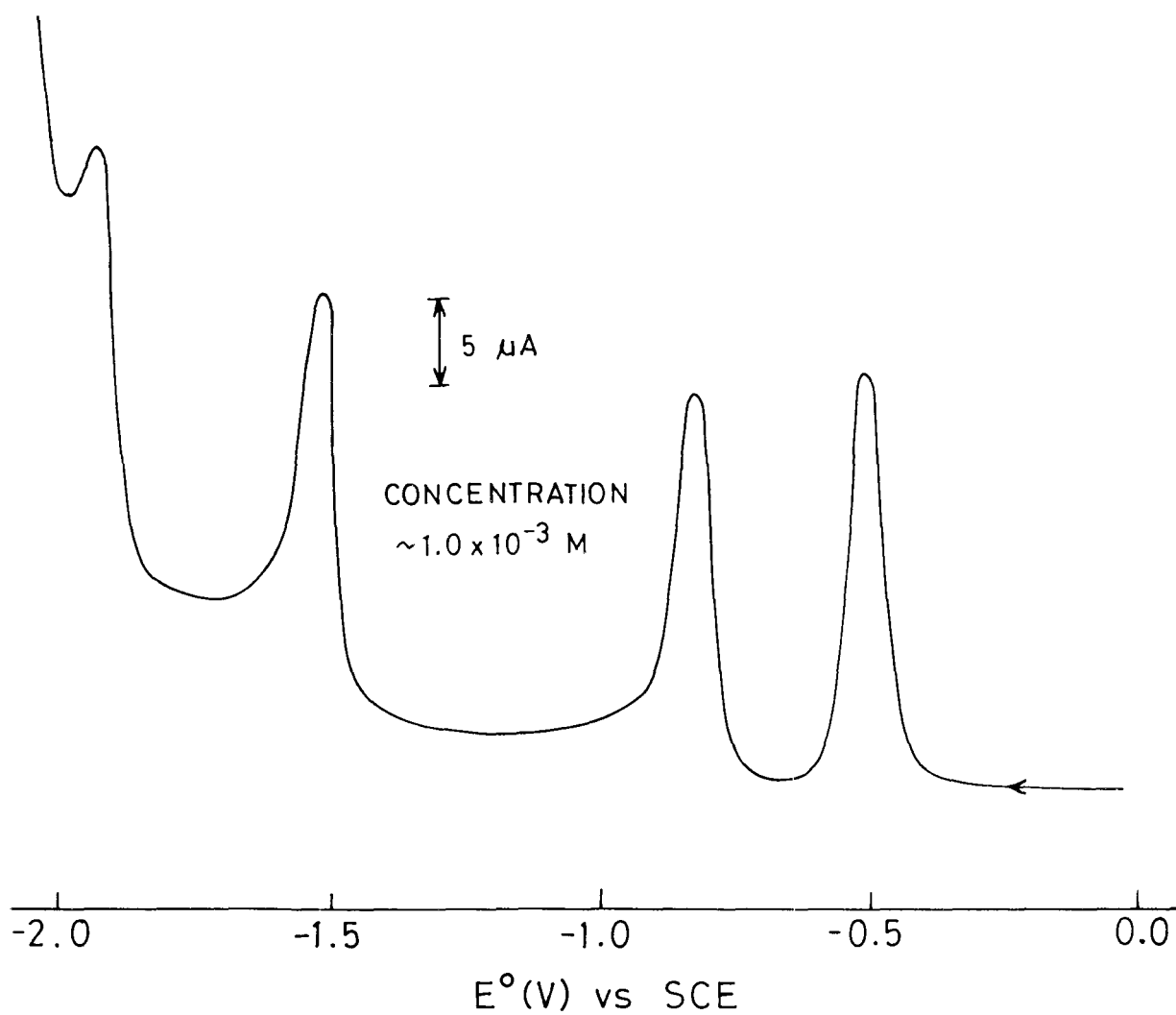
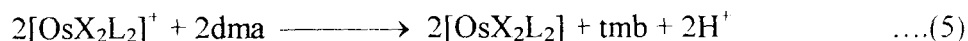


FIGURE VII.9. DIFFERENTIAL PULSE VOLTAMMOGRAM OF $\text{ttt-}[\text{OsCl}_2\text{L}_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ IN MeCN. SCAN RATE 10 mVs^{-1}

nature of the processes. The electron transfers involve successive reductions of metal bound L as already described in **Chapter II**. A nearly complete electron transfer series¹⁸ is formed exhibiting two metal centred redox reactions and four ligand-based responses in successive one-electron transfer steps.

F. USE AS OXIDANTS

Isomeric $[\text{OsX}_2\text{L}_2]^{1+}$ species oxidise N,N-dimethylaniline (dma) in MeCN solutions -- themselves being reduced to the corresponding $[\text{OsX}_2\text{L}_2]$ precursors. The resultant solutions exhibit the characteristic voltammogram¹⁹ of N,N,N',N'-tetramethylbenzidine (tmb) evidently formed by oxidative coupling as depicted in **equation 5**. Addition of **4**, **5** or **6** to a hydroquinone



(cat) solution in MeCN instantaneously yields the characteristic blue, blue-violet or red-violet colour of **1**, **2** or **3**, respectively; the solution display a strong EPR signal of semiquinone (sq) radical²⁰ centred at $g = 2.006$. The EPR spectra corresponding to osmium(III) cation is absent. Spectrophotometric titration using the intensity of the band of the complex **4** ($X = \text{Cl}$) at 505 nm establishes that the reaction has 1:1 stoichiometry as in **equation 6**. An electrocatalytic effect,



quite significant on cyclic voltammetry time-scale, has been observed in MeCN solution using 1,2-naphthoquinone monoxime (Hnqo) and complex **1** in voltammograms of this mixture. the anodic current at ~ 1 V is substantially greater than the sum of those of the two individual components. This is rationalised by the fact that electrogenerated **4** (from anodic oxidation of **1**) oxidises Hnqo and an iminoxy radical ($g = 2.005$; $A_N = 28$ G)²¹ is formed with regeneration of **1**: the latter is reoxidised and plays a role as electrocatalyst. With an increase in the concentration of Hnqo, the effect seems to be pronounced.

G. CONCLUSION

Our goal for obtaining isomeric $[\text{Os}^{\text{III}}\text{X}_2\text{L}_2]^{1+}$ ion in pure state has made with success. The available spectroscopic and electrochemical results are in full consonance with stereoretentive transformations. The complexes are rich in both spin-allowed and spin-forbidden LMCT transitions, and exhibit one metal-centred oxidation, one metal-centred reduction and four azo-based reductive responses in successive one-electron transfer steps. Finally the high formal

potential and substitutional inertness and stereochemical rigidity make these species good one electron oxidants.

VII.3 EXPERIMENTAL SECTION

A. PREPARATION OF COMPOUNDS

(a) Chemicals, solvents and starting materials

The chemicals and their sources are as follows : 1,1-diphenyl-2-picryl-hydrazyl, Aldrich (USA); nitric acid, SD (India), hydrazine hydrate, Loba (India). All other chemicals and solvents used here are either described in previous chapters or of analytical grade unless otherwise stated.

(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

Isomeric $[\text{OsX}_2\text{L}_2]$ complexes were prepared using reported procedure¹ and as described in Chapter II.

(d) Complexes

Isolation of the isomeric dihalobis[2-(arylozo)pyridine]osmium(III) perchlorate monohydrate, $[\text{OsX}_2\text{L}_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**4**, **5** and **6**) from the corresponding osmium(II) isomers of $[\text{OsX}_2\text{L}_2]$ (**1**, **2** and **3**) and conversion of the former to the latter, were made by using the general procedure described below. The yields ranged from 80 - 90%.

(i) *Cis, trans, cis-Dichlorobis[2-(phenylazo)pyridine]osmium(III) perchlorate monohydrate, ctc-[OsCl₂L¹₂ClO₄H₂O (4a)*

To a finely powdered sample of 0.2 g (0.319 mmol) of *ctc*- $[\text{OsCl}_2\text{L}^1_2]$ in a small beaker was added concentrated nitric acid (5 ml) dropwise with constant tituration using a glass rod. The process was continued for 15 min during which time the compound dissolved to produce a bright red solution with the evolution of brown fumes. To this was added sodium perchlorate (0.5 g) under constant stirring. Dark crystals started to deposit. For quantitative precipitation the mixture was kept in a refrigerator for 2 h. The dark needles, which separated on cooling, were filtered off

and washed with chilled water containing a mixture of nitric acid and sodium perchlorate. Analytically pure solid was obtained after drying in *vacuo* over P₄O₁₀. The yield was 0.195 g (82%).

(ii) *Cis, cis, cis-Dichlorobis[2-(phenylazo)pyridine]osmium(III) perchlorate monohydrate, ccc-[OsCl₂L¹₂]ClO₄·H₂O (5a)*

The procedure was the same as in the formation of **4a**. Here 0.2 g (0.319 mmol) of *ccc*-[OsCl₂L¹₂] was taken for the preparation of **5a**. The yield was 0.199 g (84%).

(iii) *Trans,trans,trans-Dichlorobis[2-(phenylazo)pyridine]osmium(III) perchlorate monohydrate, ttt-[OsCl₂L¹₂]ClO₄·H₂O (6a)*

0.2 g (0.319 mmol) of *ttt*-[OsCl₂L¹₂] was taken, titrated with concentrated nitric acid (5 ml) and processed following the procedure as described in **4a**. The yield was 0.201 g (85%).

(iv) *Cis, trans, cis-Dichlorobis[2-(m-tolylazo)pyridine]osmium(III) perchlorate monohydrate, ctc-[OsCl₂L²₂]ClO₄·H₂O (4b)*

Here 0.2 g (0.305 mmol) of *ctc*-[OsCl₂L²₂] was taken for the synthesis of **4b**. The remaining procedure was same as in **4a** preparation. Yield, 0.188 g (80%).

(v) *Cis, cis, cis-Dichlorobis[2-(m-tolylazo)pyridine]osmium(III) perchlorate monohydrate, ccc-[OsCl₂L²₂]ClO₄·H₂O (5b)*

The same procedure and reaction stoichiometry as in **5a** formation was adopted except that *ccc*-[OsCl₂L¹₂] was replaced by *ccc*-[OsCl₂L²₂]; yield 0.2 g (85%).

(vi) *Trans, trans, trans-Dichlorobis[2-(m-tolylazo)pyridine]osmium(III) perchlorate monohydrate, ttt-[OsCl₂L²₂]ClO₄·H₂O (6b)*

6b was prepared following the same procedure and reaction stoichiometry as described in **6a** preparation except that 0.2 g (0.305 mmol) of *ttt*-[OsCl₂L²₂] was taken instead of 0.2 g (0.269 mmol) *ttt*-[OsCl₂L¹₂]. The yield was 0.202 g (86%).

(vii) *Cis, trans, cis-Dibromobis[2-(phenylazo)pyridine]osmium(III) perchlorate monohydrate.*

ctc-[OsBr₂L¹₂]ClO₄·H₂O (4c)

4c was prepared [yield, 0.191 g (82%)] using the same procedure as described in **4a** except that 0.2 g (0.284 mmol) *ctc*-[OsBr₂L¹₂] was taken for the synthesis.

(viii) *Cis, cis, cis-Dibromobis[2-(phenylazo)pyridine]osmium(III) perchlorate monohydrate.*

ccc-[OsBr₂L¹₂]ClO₄·H₂O (5c)

To prepare **5c** the same procedure was followed as in **5a** except that *ccc*-[OsBr₂L¹₂] was taken instead of *ccc*-[OsCl₂L¹₂]; yield 0.198 g (85%).

(ix) *Trans, trans, trans-Dibromobis[2-(phenylazo)pyridine]osmium(III) perchlorate*

monohydrate, ttt-[OsBr₂L¹₂]ClO₄·H₂O (6c)

To synthesise **6c** the same procedure and reaction stoichiometry was followed as described in **6a**. Here 0.2 g (0.284 mmol) of *ttt*-[OsBr₂L¹₂] was taken for the preparation; yield, 0.208 g (90%).

(x) *Cis, trans, cis-Dibromobis[2-(m-tolylazo)pyridine]osmium(III) perchlorate monohydrate.*

ctc-[OsBr₂L²₂]ClO₄·H₂O (4d)

To prepare **4d** the same procedure was followed as in **4b**. Here 0.2 g (0.269 mmol) of *ctc*-[OsBr₂L²₂] was taken for its synthesis. The yield was 0.208 g (90%).

(xi) *Cis, cis, cis-Dibromobis[2-(m-tolylazo)pyridine]osmium(III) perchlorate monohydrate.*

ccc-[OsBr₂L²₂]ClO₄·H₂O (5d)

5d was prepared [yield 0.208 g (90%)] using the same procedure as described in **5b** except that 0.2 g (0.269 mmol) *ccc*-[OsBr₂L²₂] was taken instead of *ccc*-[OsCl₂L²₂].

(xii) *Trans,trans,trans-Dibromobis[2-(m-tolylazo)pyridine]osmium(III) perchlorate*

monohydrate, ttt-[OsBr₂L²₂]ClO₄·H₂O (6d)

The same procedure and reaction stoichiometry as in **6b** formation was followed except that *ttt*-[OsCl₂L²₂] was replaced by *ttt*-[OsBr₂L²₂]. The yield was 0.2139 g (92%).

Conversion : $[OsX_2L_2]^{1+} \longrightarrow [OsX_2L_2]$

All the osmium(III) complexes were converted to their osmium(II) precursors following a general procedure. Details for a *ctc* isomer is described below.

To a methanolic (10 ml) solution of 0.1 g (0.134 mmol) *ctc*- $[OsCl_2L^1_2]ClO_4 \cdot H_2O$, hydrazine hydrate (0.01 g, 0.2 mmol) in acetonitrile (5 ml) was added dropwise with constant stirring. The red solution, which immediately changed to blue-violet, was filtered through a fine glass frit. After removal of solvent under reduced pressure, the residue was washed with water (15 ml) and extracted into dichloromethane (30 ml). Slow evaporation under aerobic conditions quantitatively yielded shining crystals of the corresponding osmium(II) species.

Caution !

The synthesis described above involves the use of perchlorate as the counter ion. Heavy metal perchlorate salts with organic ligands are potentially explosive. Due care must be exercised in mixing with acids and in using a stirring rod or spatula to mechanically agitate the solid, although we have not encountered any problem by taking small quantities of samples at a time.

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 VII.8**.

C. PHYSICAL MEASUREMENTS

The details of measurements are described in **Chapter II**. Magnetic susceptibilities were measured (in solid state at 298 K) with a PAR 155 vibrating sample magnetometer fitted with a Walker Scientific L 75 FBAL magnet. EPR spectra were run on a Varian 109C E-line X-band spectrometer fitted with a quartz Dewar for measurements at 77 K (liquid nitrogen).

TABLE VII. 8

Characterisation Data

Compound	%C		%H		%N	
	Calcd	Found	Calcd	Found	Calcd	Found
ctc-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (4a) C ₂₂ H ₂₀ N ₆ O ₅ Cl ₃ Os	35.5	35.3	2.7	2.7	11.3	11.3
ccc-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (5a) C ₂₂ H ₂₀ N ₆ O ₅ Cl ₃ Os	35.5	35.6	2.7	2.7	11.3	11.2
ttt-[OsCl ₂ L ¹ ₂]ClO ₄ .H ₂ O (6a) C ₂₂ H ₂₀ N ₆ O ₅ Cl ₃ Os	35.5	35.8	2.7	2.7	11.3	11.4
ctc-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (4b) C ₂₄ H ₂₄ N ₆ O ₅ Cl ₃ Os	37.3	37.4	3.1	3.2	10.9	11.0
ccc-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (5b) C ₂₄ H ₂₄ N ₆ O ₅ Cl ₃ Os	37.3	37.2	3.1	3.1	10.9	10.7
ttt-[OsCl ₂ L ² ₂]ClO ₄ .H ₂ O (6b) C ₂₄ H ₂₄ N ₆ O ₅ Cl ₃ Os	37.3	37.6	3.1	3.0	10.9	10.9
ctc-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (4c) C ₂₂ H ₂₀ N ₆ O ₅ Br ₂ ClOs	31.7	31.4	2.4	2.3	10.1	9.9
ccc-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (5c) C ₂₂ H ₂₀ N ₆ O ₅ Br ₂ ClOs	31.7	31.9	2.4	2.5	10.1	10.3
ttt-[OsBr ₂ L ¹ ₂]ClO ₄ .H ₂ O (6c) C ₂₂ H ₂₀ N ₆ O ₅ Br ₂ ClOs	31.7	32.0	2.4	2.4	10.1	9.9
ctc-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (4d) C ₂₄ H ₂₄ N ₆ O ₅ Br ₂ ClOs	33.4	33.5	2.8	2.8	9.7	9.8
ccc-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (5d) C ₂₄ H ₂₄ N ₆ O ₅ Br ₂ ClOs	33.4	33.3	2.8	2.8	9.7	9.9
ttt-[OsBr ₂ L ² ₂]ClO ₄ .H ₂ O (6d) C ₂₄ H ₂₄ N ₆ O ₅ Br ₂ ClOs	33.4	33.1	2.8	2.8	9.7	9.8

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