

CHAPTER II

**SYNTHESIS AND ISOLATION OF ELUSIVE TRANS, TRANS,
TRANS-[OsX₂L₂] [X = Cl OR Br; L = 2-(ARYLAZO)PYRIDINES]**

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SYNTHESIS AND ISOLATION OF ELUSIVE TRANS, TRANS, TRANS-[OsX₂L₂] [X = Cl OR Br; L = 2-(ARYLAZO)PYRIDINES]

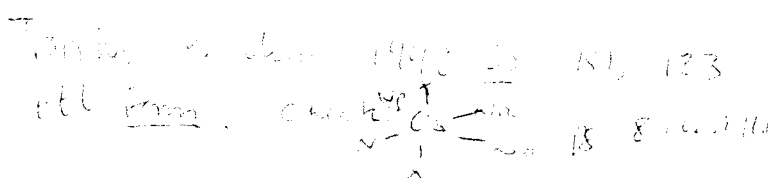
ABSTRACT : 2-(Arylazo)pyridines (L, **1**) is known to yield two isomeric complexes. blue-violet and red-violet [OsX₂L₂] (**2** and **4**, respectively) (X = Cl or Br) by reaction with (Et₄N)₂[OsX₆] (X = Cl or Br) in 2-methoxyethanol (b.p., 398 K). However, reaction in boiling methanol (b.p., 338 K) results a new isomer, blue [OsX₂L₂], **6**, along with **2** and **4**. The isomeric complexes have been separated by iterative column chromatographic filtration. The new isomer **6** was characterised using microanalytical, spectroscopic, magnetic and electrochemical results. The isomers **2** and **4** were identified by comparing their properties with authentic samples. The diamagnetic compounds (**2**, **4** and **6**) show distinctly different absorption bands in their electronic spectra (200 - 1400 nm) and characteristic E⁰ values (-2.0 to 1.6 V vs SCE) in the electrochemical measurements. A 1:1 correspondence in IR spectra of **2**, **4** and **6** is seen with corresponding ruthenium analogues suggesting cognate structures.

of Os complex

Os complex

II.1 II

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and Gh
type [M
6) (see
(N^a,N^a)



¹⁵⁻²⁰ has been
Goswami^{13,14}
complexes of
eric forms (2 -
(N^p,N^p) and
ccc), 4: trans.

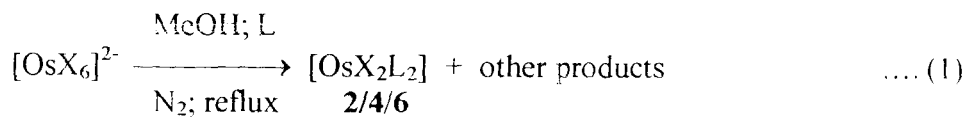
cis, cis (tcc), **5**; *trans, trans, trans (ttt)*, **6** respectively. Reaction of L with RuX₃ in boiling methanol furnishes three isomeric complexes of type [RuX₂L₂]. Chemical information^{1,5,13} and X-ray work¹² are in line with structures **2**, **4** and **6** (M = Ru). Among the three isomers one is green (**6**) and the other two are blue (**2** and **4**). However, L is known to yield only two isomeric complexes^{15,17} blue-violet (**2**) and red-violet (**4**) isomers of [OsX₂L₂] (X = Cl or Br) with (Et₄N)₂[OsX₆] (X = Cl or Br) in boiling 2-methoxyethanol (b.p., 398 K) and these are structurally characterised using X-ray study¹⁶; the isomeric form **6** obtainable in ruthenium, however, remains elusive in case of osmium. In this chapter, we have examined a new route towards isolation of this isomer. Changing the solvent 2-methoxyethanol to methanol (b.p., 338 K) and producing the reaction course less severe, we are able to prepare and isolate the elusive **6** (M = Os) along with **2** and **4**. This chapter presents the characterisation/identification of these isomeric products (**2**, **4** and **6**) using chromatographic, microanalytical, spectroscopic and electrochemical results and highlights the advantages of this new route.

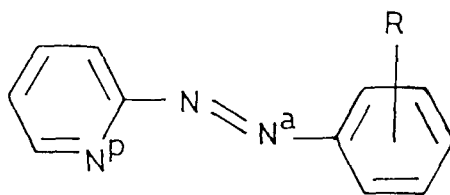
II.2 RESULTS AND DISCUSSION

A. SYNTHESIS

2-(Arylazo)pyridines were prepared^{1,2} by condensing 2-aminopyridine with appropriate nitrosoarene in highly alkaline solutions.

In boiling methanol (b.p., 338 K) under a dinitrogen atmosphere the reaction of L with (Et₄N)₂[OsX₆] (X = Cl/Br) in 2:1 ratio proceeded relatively slowly¹⁵ but smoothly affording a mixture of three isomers (**2**, **4** and **6**) of [OsX₂L₂] with a major yield of **6**. The general synthetic route is shown in **equation 1**. On concentrating the reaction mixture a dark solid mass resulted in



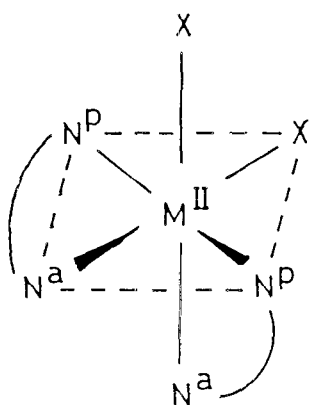


$R = H; L^1$

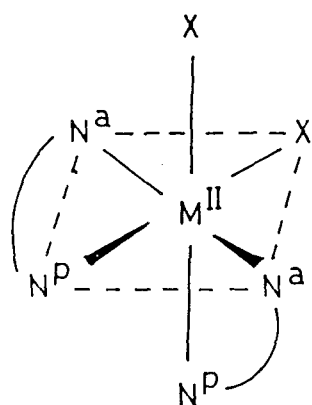
$R = m\text{-Me}; L^2$

$R = p\text{-Me}; L^3$

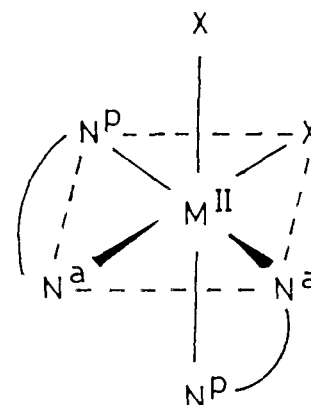
1



ctc, **2**

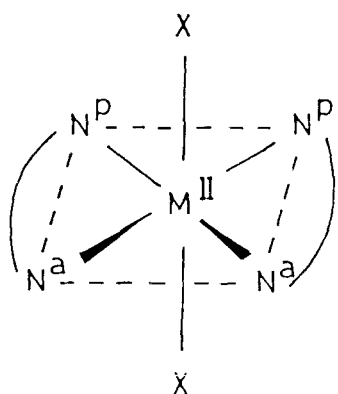


cct, **3**

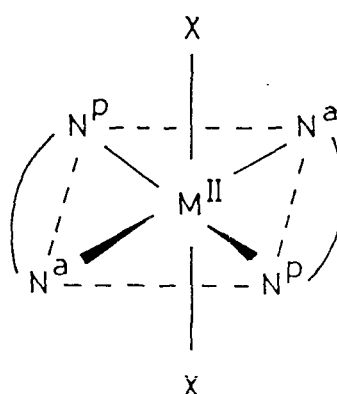


ccc, **4**

$M = Ru / Os$



tcc, **5**



ttt, **6**

Orientation in the order (X, X) (N^P, N^P) and (N^a, N^a)

Chart II.1

~80% yield, from which isomer **6** was obtained in ~40% after chromatographic filtration. Isomeric purity was tested by thin layer chromatography and ^1H NMR spectroscopy. The components were separated by iterative column chromatography. Even when L was used in excess of 2 mol, only $[\text{OsX}_2\text{L}_2]$ resulted, no tris complexes of the type $[\text{OsL}_3]^{2+}$ appeared to be formed. In the reaction 1, the stage at which the reduction of osmium(IV) species to osmium(II) dihalogeno compound occurred has not been elucidated. The alcoholic solvent presumably acts as a reducing agent.

The reported method¹⁵ using 2-methoxyethanol as solvent furnished only **2** and **4** which are thermodynamically more stable. The use of relatively low boiling solvent methanol ensures the isolation of kinetically^{1,5} controlled product **6** ($M = \text{Os}$). This view is strengthened by boiling pure **6** in 2-methoxyethanol that leads to formation of **2** and **4** together with concomitant loss of the former.

All the new complexes of type **6** were characterised by elemental (C, H and N) analyses, solution electrical conductivity and magnetic susceptibility measurements, spectroscopic (IR, NMR and UV-Vis) properties and electrochemical [cyclic voltammetry (CV), differential pulse voltammetry (DPV) and coulometry] results. The identities of **2** and **4** complexes were established by comparing their properties with authentic samples^{15,17}. The pertinent results are summarised in **Tables II.1 – II.7**. The complexes are highly soluble in common organic solvents like benzene, chloroform, dichloromethane, acetonitrile and sparingly soluble in alcohols, dimethylformamide and dimethylsulfoxide. In MeCN and MeNO₂ solutions, the complexes behave as non-electrolytes²¹ as is evident from very low conductivity values (**Table II.1**). This strongly suggests poor dissociation of the halides from the coordination sphere. Room temperature magnetic susceptibility measurements show that the complexes are diamagnetic with singlet (sharp ^1H NMR signals) (t_{2g}^6 idealised, $S = 0$) ground state.

B. INFRARED SPECTRA

The infrared spectra of all the complexes were recorded in 4000 - 300 cm^{-1} range (4000 - 600 cm^{-1} in KBr discs; 600 - 300 cm^{-1} in polyethylene discs). Selected frequencies are given in **Table II.2** and **Figures II.1 - II.3**. The $\nu(\text{N}=\text{N})$ stretching frequency in free L appears² at 1425 cm^{-1} . This is shifted to lower wave number in dihalo complexes [$\nu(\text{N}=\text{N})$: **2**, 1280 cm^{-1} ; **4**, 1275 cm^{-1} and **6**, 1285 cm^{-1}] indicating strong π -back bonding $d(\text{Os}) \rightarrow \pi^*(\text{L})$ in the ground state

TABLE II.1

Molar Conductivity data^a at 298 K

Compound	Λ_M (ohm ⁻¹ cm ² mol ⁻¹)	
	MeCN	MeNO ₂
ttt-[OsCl ₂ L ¹ ₂] (6a)	4	3
ttt-[OsBr ₂ L ¹ ₂] (6b)	5	4
ttt-[OsCl ₂ L ² ₂] (6c)	3	2
ttt-[OsBr ₂ L ² ₂] (6d)	5	3
ttt-[OsCl ₂ L ³ ₂] (6e)	4	3
ttt-[OsBr ₂ L ³ ₂] (6f)	3	3

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

TABLE II. 2

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

Compound	$\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})^{\text{c}}$	$\nu(\text{N}=\text{N})^{\text{d}}$	$\nu(\text{Os}-\text{Cl})^{\text{e}}$
ttt-[OsCl ₂ L ¹ ₂] (6a)	1590	1285	325
ttt-[OsBr ₂ L ¹ ₂] (6b)	1592	1286	f
ttt-[OsCl ₂ L ² ₂] (6c)	1595	1285	324
ttt-[OsBr ₂ L ² ₂] (6d)	1590	1286	f
ttt-[OsCl ₂ L ³ ₂] (6e)	1594	1285	322
ttt-[OsBr ₂ L ³ ₂] (6f)	1592	1286	f

^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; ^e $\nu(\text{Os}-\text{Cl})$, weak and sharp. ^f $\nu(\text{Os}-\text{Br})$, not studied.

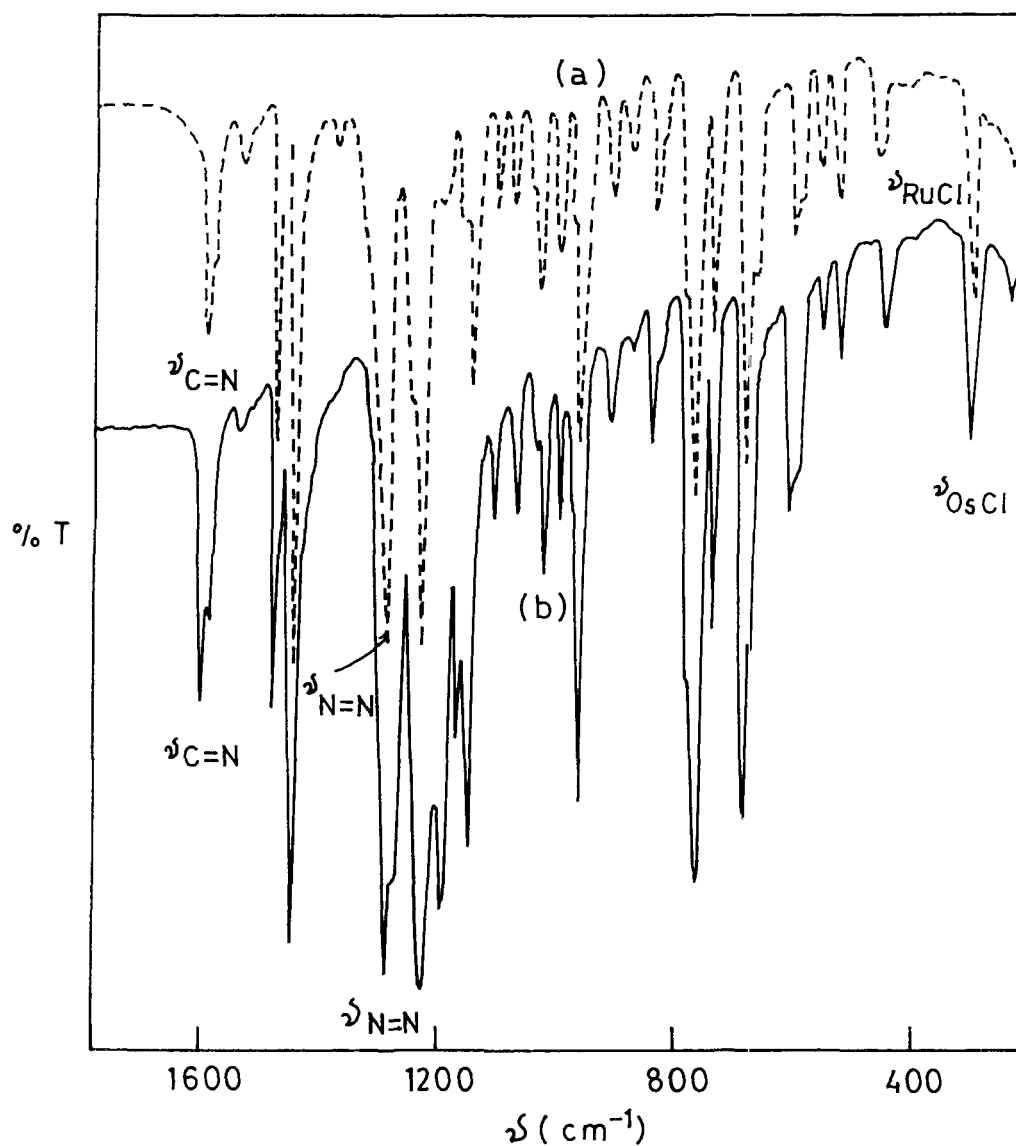


FIGURE II.1 IR SPECTRA OF ttt(6) ISOMER OF
 (a) $[\text{RuCl}_2\text{L}_2]$ (----) AND (b) $[\text{OsCl}_2\text{L}_2]$ (—)

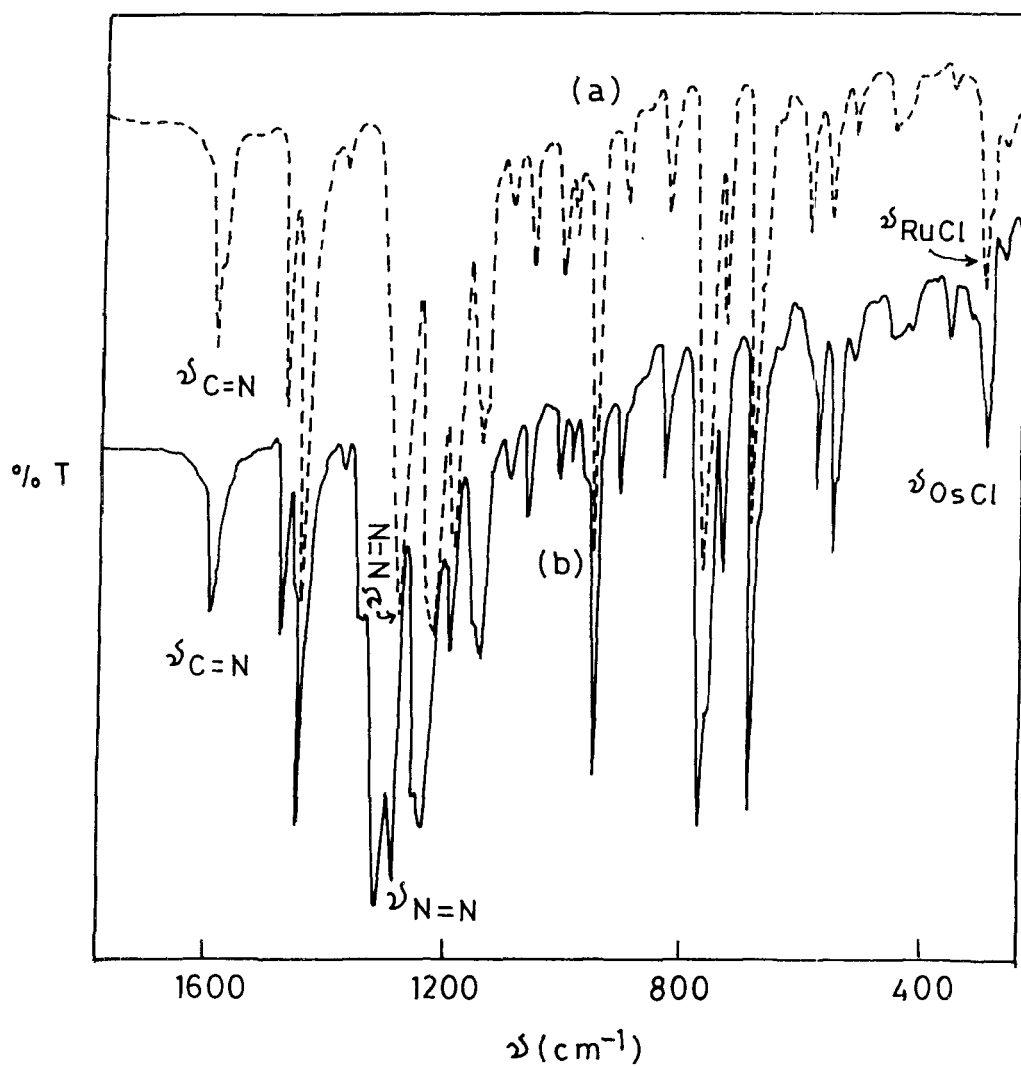


FIGURE II.2 IR SPECTRA OF ctc(2) ISOMER OF
 (a) [RuCl₂L₂](---) AND (b) [OsCl₂L₂](—)

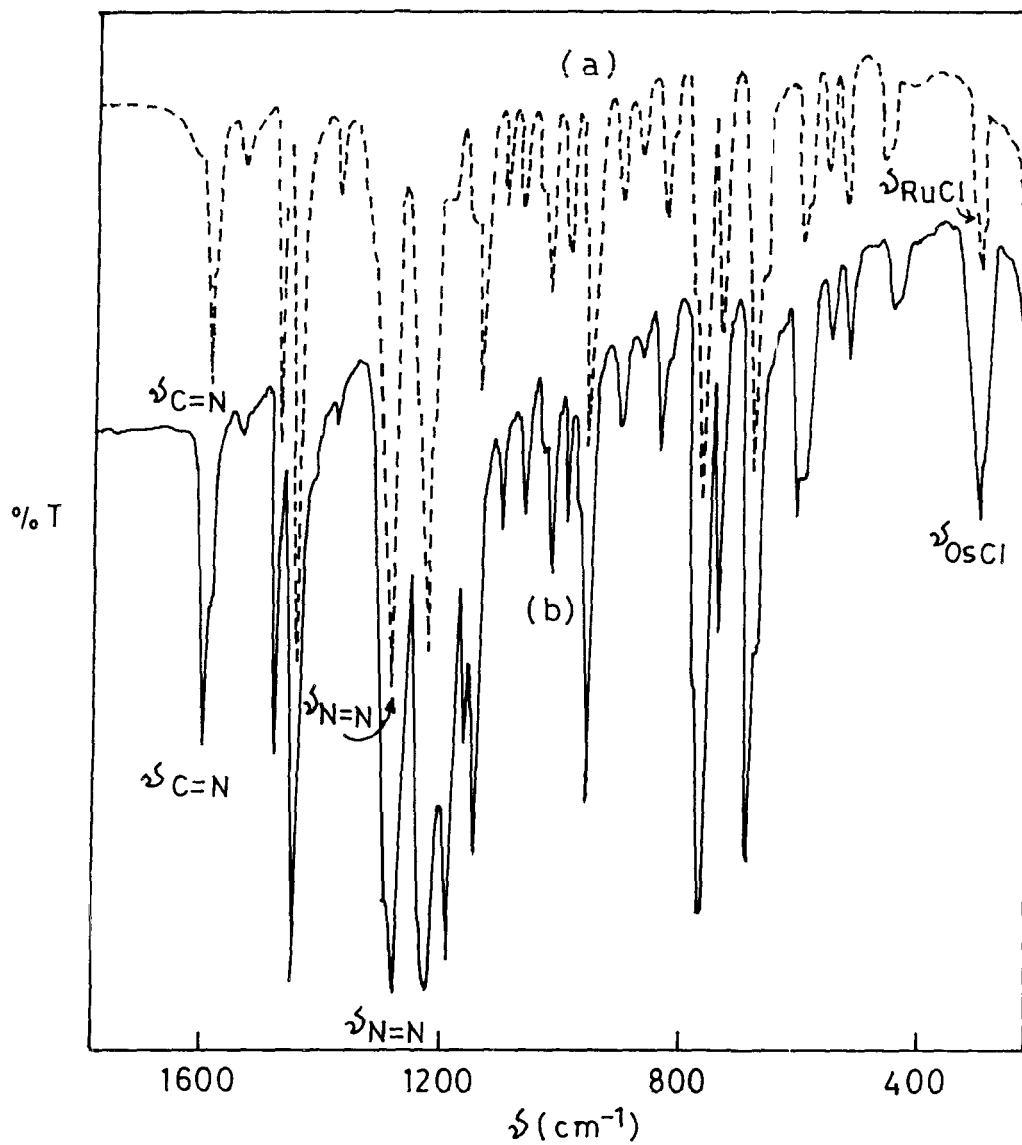


FIGURE II.3 IR SPECTRA OF $\text{ccc}(4)$ ISOMER OF
 (a) $[\text{RuCl}_2\text{L}_1^2]$ (---) AND (b) $[\text{OsCl}_2\text{L}_1^2]$ (—)

of osmium(II). Of the three, the isomer **4** has the largest shift of the $\nu(\text{N}=\text{N})$ towards lower frequency. Evidently, this is dependent on the mutual disposition of donor centres in the coordination sphere. A similar shift in $\nu(\text{N}=\text{N})$ frequencies has also been observed in the L complexes of Ru(II)^{1,5}, Fe(II)²², Cu(I)²³ and other low-valent transition metal L-complexes²⁴. The $\nu(\text{N}=\text{N})$ frequencies are the lowest in osmium(II)-L complexes among those of all L complexes reported so far. Clearly osmium(II) is the strongest π -donor. $\nu(\text{C}=\text{N})$ value remains almost invariant at $\sim 1590\text{ cm}^{-1}$ in all the three isomers, reflecting the effective π -bonding centre at the azo part of the azoimine ($-\text{N}=\text{N}-\overset{\text{I}}{\text{C}}=\text{N}-$) chromophore. The OsCl_2 species show a single, sharp and strong band at $\sim 320\text{ cm}^{-1}$, which is absent in the corresponding dibromo complexes. This strongly suggests that the OsCl_2 group and by inference the OsBr_2 moiety are *trans* with linear MX_2 orientation.

The stereochemical assignment of the isomeric complexes is made by close examination of their vibration spectra and the well-characterised ruthenium analogues. A 1:1 correspondence (see **Figures II.1 - II.3**) in the IR spectra is noticed of these three isomers with the corresponding ruthenium compounds. The spectra of the blue isomer of $[\text{OsX}_2\text{L}_2]$ and the green isomer of $[\text{RuX}_2\text{L}_2]$ are nearly superimposable in the range $4000 - 300\text{ cm}^{-1}$ except for frequency shift particularly in the $\nu(\text{N}=\text{N})$ region (**Figure II.1**). A similar relationship holds (**Figures II.2 and II.3**) between the other two isomers of the congeneric elements.

C. ¹H NMR SPECTRA

The ¹H NMR spectra of selected complexes are examined to determine the stereochemistry of the complexes unequivocally. The methyl signals of L^2 and L^3 complexes (**Table II.3**) are particularly useful in this context. A single sharp signal is observed for $[\text{OsX}_2\text{L}_2]$ ($\text{L} = \text{L}^2$ or L^3) near $\sim 2.15\text{ ppm}$ (**Figure II.4**; with $\text{X} = \text{Cl}$, $\text{L} = \text{L}^2$). Thus an effective C_2 symmetry in **6** is present. So taking the advantage of IR results along with NMR data structure **6** is the most probable formulation. Steric crowding in **5** is obviously in the contrary towards this formulation. The isomers **2** and **4** show one and two methyl signals (see **Figure II.4**) respectively as expected.

D. ELECTRONIC SPECTRA

The complexes display multiple absorption bands and shoulders in the $200 - 1400\text{ nm}$ range. Results in MeCN solutions are given in **Table II.4** and **Figure II.5**. Major absorptions occur in

TABLE II. 3

¹H NMR Data^{a-c} of L² and L³ Complexes

Compound	$\delta(\text{Me})$, ppm
ttt-[OsCl ₂ L ² ₂] (6c)	2.16
ttt-[OsBr ₂ L ² ₂] (6d)	2.18
ttt-[OsCl ₂ L ³ ₂] (6e)	2.16
ttt-[OsBr ₂ L ³ ₂] (6f)	2.17

^aSiMe₄ used as internal standard. ^bAromatic proton signals not tabulated.^cSolvent, CDCl₃.

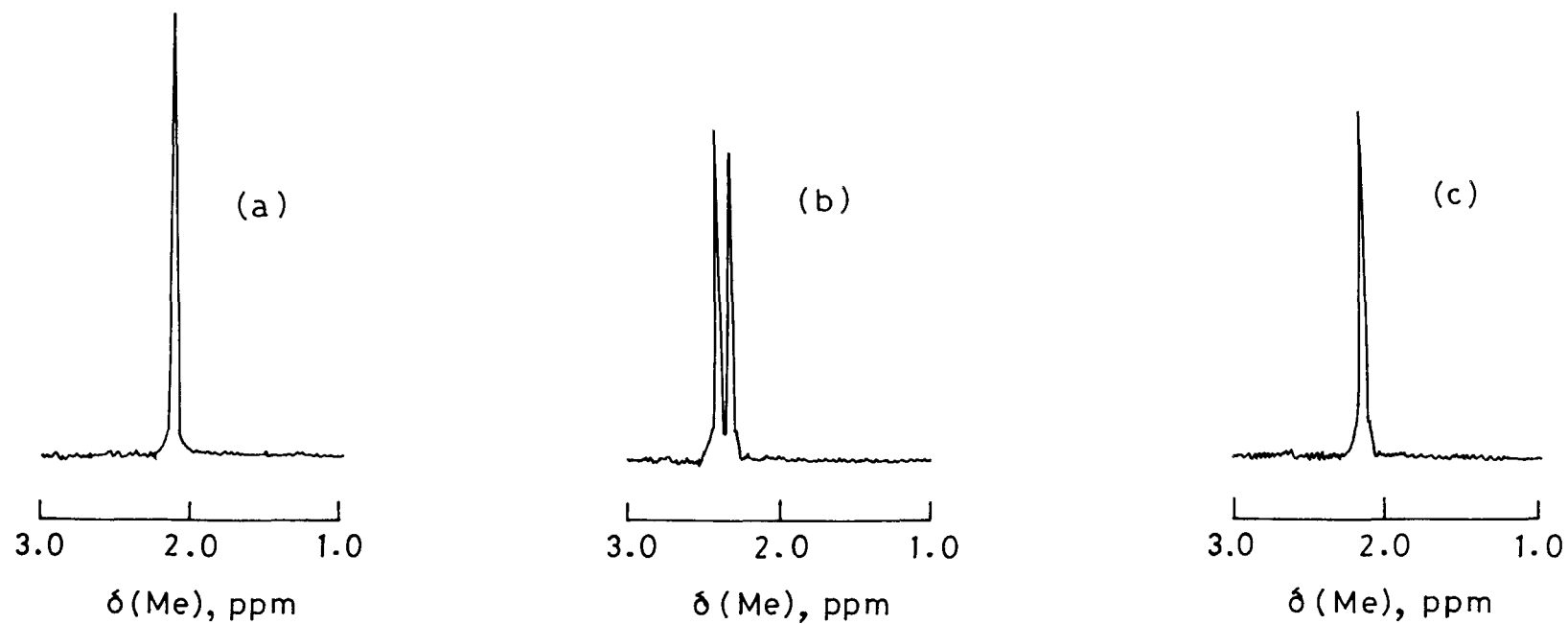


FIGURE II.4 ^1H NMR SPECTRA (Me SIGNALS) OF (a) $\text{ctc-}[\text{OsCl}_2\text{L}_2]$, (b) $\text{ccc-}[\text{OsCl}_2\text{L}_2]$ AND (c) $\text{ttt-}[\text{OsCl}_2\text{L}_2]$ IN CDCl_3

TABLE II. 4

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

Compound	λ_{\max} , nm (ϵ , M ⁻¹ cm ⁻¹)
ttt-[OsCl ₂ L ¹ ₂] (6a)	1325 (250), 925 ^c (190), 685 (3,550), 595 (8,380), 570 ^c (7,530), 500 ^c (3,980), 395 (5,960), 320 ^c (7,530), 280 (12,900)
ttt-[OsBr ₂ L ¹ ₂] (6b)	1322 (270), 920 ^c (210), 685 (3,720), 595 (8,570), 565 ^c (7,810), 500 ^c (4,010), 392 (6,060), 320 ^c (7,800), 280 (13,200)
ttt-[OsCl ₂ L ² ₂] (6c)	1324 (290), 922 ^c (220), 684 (3,840), 595 (8,640), 568 ^c (7,920), 504 ^c (4,090), 395 (6,170), 322 ^c (7,920), 280 (13,330)
ttt-[OsBr ₂ L ² ₂] (6d)	1320 (320), 920 ^c (230), 684 (3,920), 595 (8,820), 565 ^c (8,010), 502 ^c (4,210), 394 (6,290), 320 ^c (7,950), 280 (13,420)
ttt-[OsCl ₂ L ³ ₂] (6e)	1325 (280), 924 ^c (210), 682 (3,900), 595 (8,910), 566 ^c (8,070), 500 ^c (4,170), 395 (6,200), 322 ^c (7,860), 280 (13,400)
ttt-[OsBr ₂ L ³ ₂] (6f)	1322 (300), 920 ^c (250), 682 (4,040), 595 (8,980), 564 ^c (8,120), 500 ^c (4,210), 392 (6,410), 320 ^c (7,920), 280 (13,510)

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

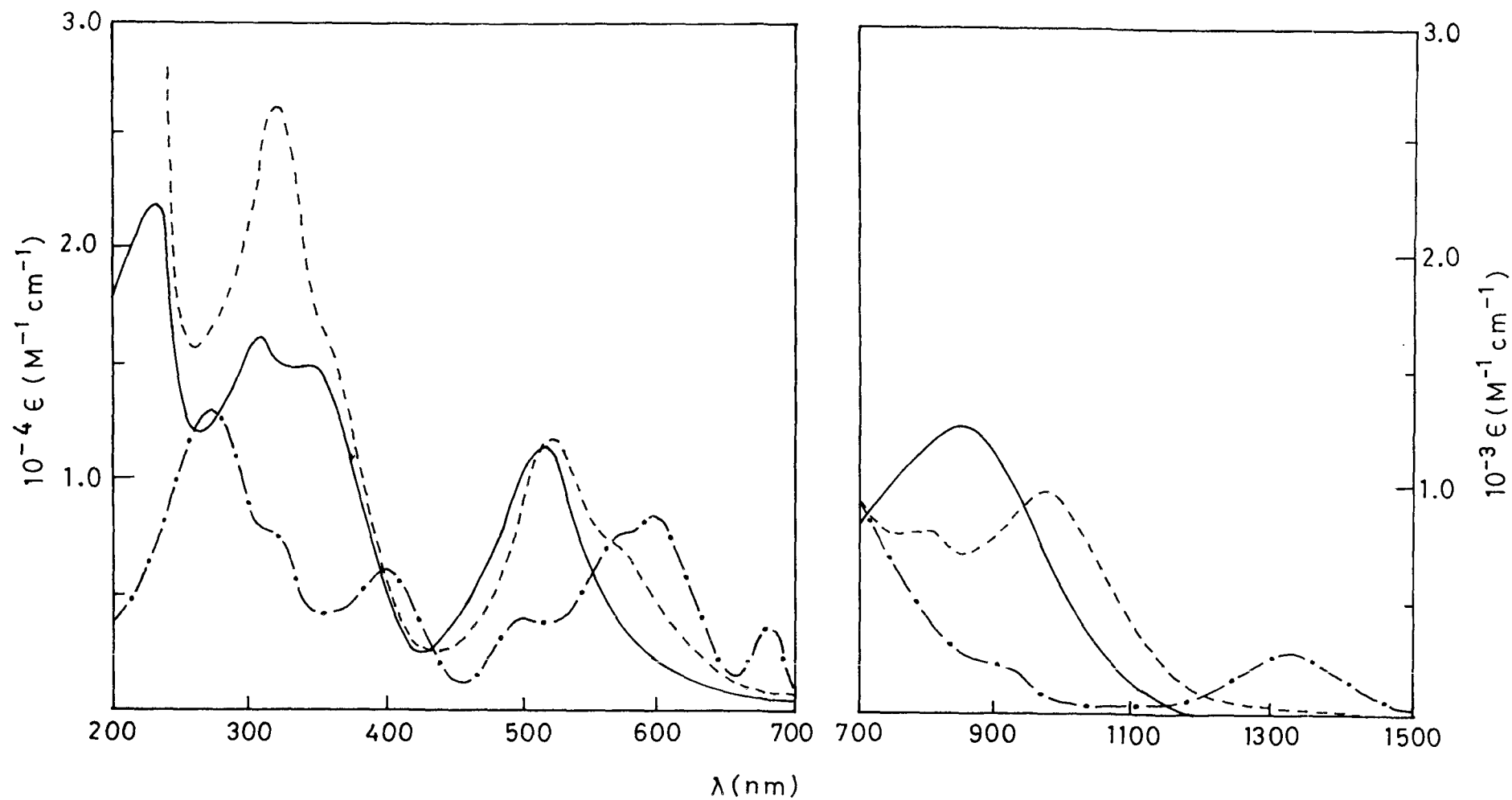


FIGURE II.5 ELECTRONIC SPECTRA OF $\text{ctc-}[\text{OsCl}_2\text{L}'_2]$ (---), $\text{ccc-}[\text{OsCl}_2\text{L}'_2]$ (—) AND $\text{ttt-}[\text{OsCl}_2\text{L}'_2]$ (-.-.) IN MeCN AT 298 K

three distinct regions: below 400, 500 - 700 and 900 - 1400 nm. Free 2-(arylo)pyridine ligands display absorption bands at 440 nm and 320 nm. These can be respectively assigned^{1,5} to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions centred primarily on the azo group. Hence the transition below 400 nm are probably of ligand origin.

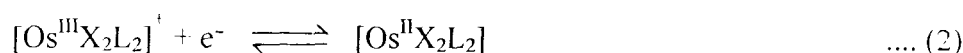
Blue solutions of type **6** complexes have an intense band at ~595 nm with a clearly defined shoulder at relatively higher and lower energy range. Additionally in the 900 - 1400 nm region weak transitions are also observable. These are assigned to MLCT transitions, $Os(t_2) \rightarrow L(\pi^*)$. The more intense bands at higher energies are believed to be spin-allowed singlet-singlet transitions while the weaker bands at lower energies could be the corresponding singlet-triplet transitions made partially allowed by the strong spin-orbit coupling²⁵⁻²⁷ in heavier atom osmium. A systematic blue shift (**Figure II.5**) is observed in going from type **6** (*III*) complexes to type **4** (*ccc*) compounds via **2** (*ctc*).

E. REDOX PROPERTIES

The electron transfer properties of the complexes were examined in acetonitrile solutions using cyclic voltammetry (CV), differential pulse voltammetry (DPV) and coulometry. Tetraethylammonium perchlorate, TEAP was used as the supporting electrolyte and platinum/glassy carbon as the working electrode. Redox responses at solvent cut-off were best identifiable by careful DPV experiments. Results are collected in **Tables II.5** and **II.6**. Representative voltammograms are shown in **Figures II.6 - II.9**. The 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 in MeCN (0.1 M TEAP) solutions. Complexes **6** display one one-electron cyclic voltammetric response near 0.8 V. The voltammogram is reproducible with no trace of decomposition after a number of cycles. Since free L does not undergo electron transfer in the above range, the responses are presumably due to osmium(III)-osmium(II) couple as depicted in **equation 2**. The formal potential, E^0 ,



calculated as the average of the cathodic (E_{pc}) and anodic (E_{pa}) peak potentials (**equation 3**) are

$$E^0 = 0.5(E_{pc} + E_{pa}) \quad \dots (3)$$

in **Table II.5**. **Figure II.6** shows the multiple scan cyclic voltammograms of **6** along with its differential pulse. The cathodic and anodic currents are of equal heights ($i_{pc} = i_{pa}$) and vary as the square root of the scan rate. The peak-to-peak separation (ΔE_p) lies in the range 60 - 70 mV at a scan rate (v) of 50 mVs^{-1} showing that the electrode process in couple 2 is evidently reversible to nearly reversible in nature. The one-electron stoichiometry of this couple was confirmed by constant potential coulometry at a potential $\sim 200 \text{ mV}$ more anodic than its E^0 (**Table II.5**) value.

The potentials of couple 2 for type **2** and **4** complexes are shifted towards more anodic values (for **2**, E^0 , $\sim 0.96 \text{ V}$; for **4**, E^0 , $\sim 0.94 \text{ V}$). This is in line with degree of osmium(II)- π^*L (azo) back bonding.

A second one-electron anodic response (**equation 4**) occurs at $\sim 1.6 \text{ V}$ close to the solvent cut-off limit. The corresponding cathodic peak is observed, but it is not as well-defined as in the

$$[\text{Os}^{\text{IV}}\text{X}_2\text{L}_2]^{2+} + e^- \rightleftharpoons [\text{Os}^{\text{III}}\text{X}_2\text{L}_2]^+ \quad \dots (4)$$

anodic peak and its height is smaller. The diminished current height of the cathodic response indicates that the osmium(IV) species may not be very stable. The one-electron character of couple 4 could not be assigned through direct coulometry experiments, since constant potential electrolysis at more anodic of E^0 value leads to continuous accumulation of coulomb count which obscures the detailed study of this process. However, comparison of the current heights (**Figure II.7**) with couple 2 in DPV experiments is helpful in ascertaining its one-electron nature. For a comparison of the nature of redox processes in these isomers (**2**, **4** and **6**), the voltammograms are set in **Figure II.7**.

(b) Ligand-based reductions

The negative side of SCE was scanned at both platinum and glassy carbon as working electrodes. Better results were obtained with the latter. The results are summarised in **Table II.6**.

The free ligand 2-(phenylazo)pyridine, L^1 shows two quasi-reversible cyclic voltammetric responses with¹³ peak-to-peak separation in the range 120 - 150 mV. Since no other reduction is observed, the non-degenerate lowest unoccupied molecular orbital (LUMO) is well separated from the next higher unoccupied molecular orbital (UMO). On comparison of couples 5 and 6 with those of 2,2'-bipyridine (bpy) on the one hand and aromatic azo ligands on the other¹¹, it emerges that the electron-accepting LUMO of L is primarily azo in character and couples 5 and 6



TABLE II. 5

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)
ttt-[OsCl ₂ L ¹ ₂] (6a)	0.86 ^{fg} (70)	1.64 (170)
ttt-[OsBr ₂ L ¹ ₂] (6b)	0.85 (70)	1.62 (170)
ttt-[OsCl ₂ L ² ₂] (6c)	0.84 (60)	1.64 (160)
ttt-[OsBr ₂ L ² ₂] (6d)	0.82 ^{fh} (60)	1.59 (160)
ttt-[OsCl ₂ L ³ ₂] (6e)	0.84 (60)	1.62 (160)
ttt-[OsBr ₂ L ³ ₂] (6f)	0.83 (60)	1.58 (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). ^dIn CV : scan rate, 50 mVs⁻¹; $E^0 = 0.5(E_{pc} + E_{pa})$ where E_{pc} and E_{pa} are cathodic and anodic peak potentials, respectively; ΔE_p is the peak-to-peak separation. ^eIn DPV : scan rate, 10 mVs⁻¹; modulation amplitude (ΔE), 25 mV; $E^0 = E_p + 0.5(\Delta E)$ where E_p is DPV peak potential. ^fConstant 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. ^g $n = 1.03$. ^h $n = 1.02$.

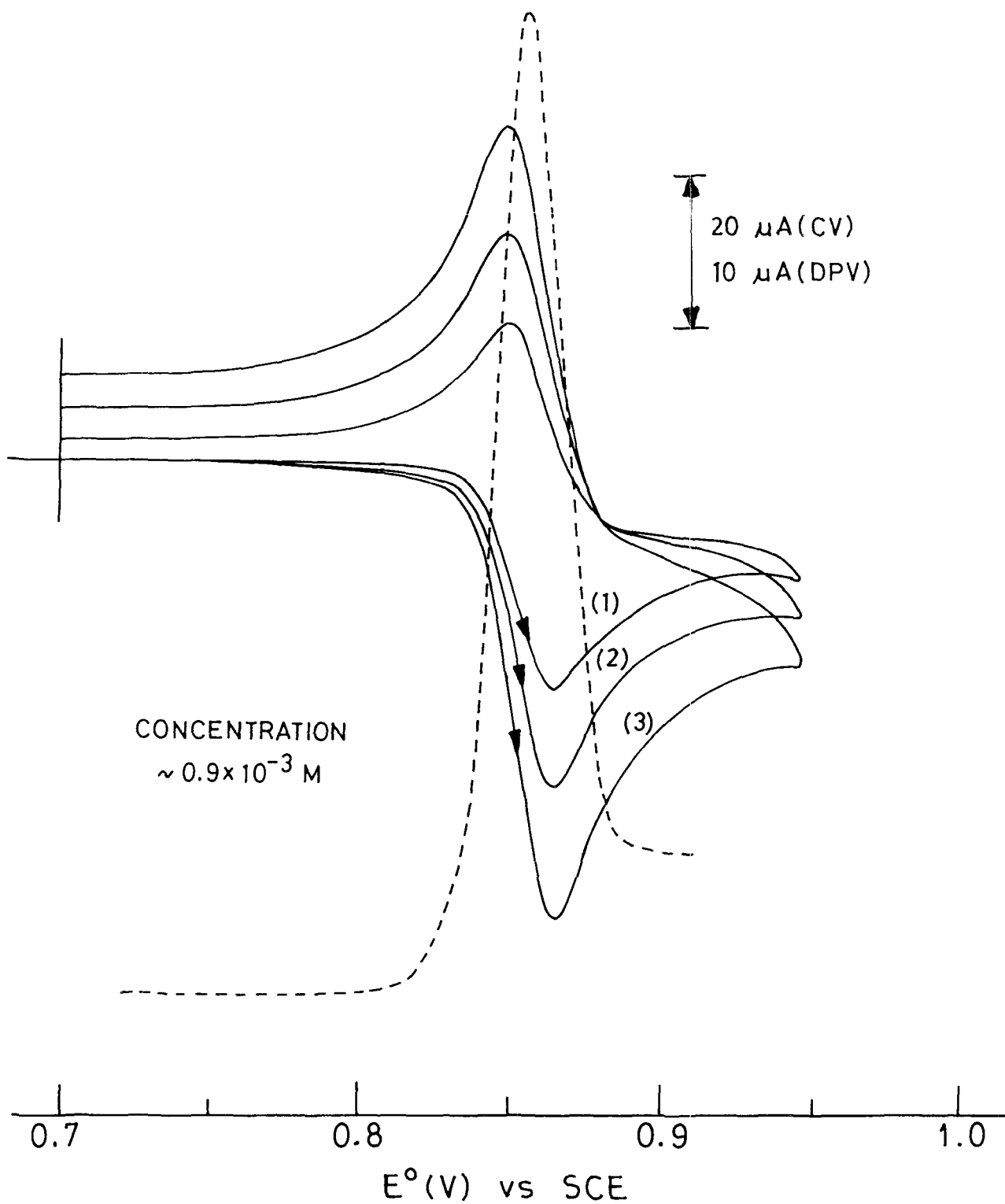


FIGURE II.6. VOLTAMMOGRAMS OF $\text{ttt-}[\text{OsCl}_2\text{L}^1_2]$ IN MeCN. SCAN RATES: FOR CV(—), (1) 50, (2) 100, (3) 200 mVs^{-1} ; FOR DPV(---), 10 mVs^{-1}

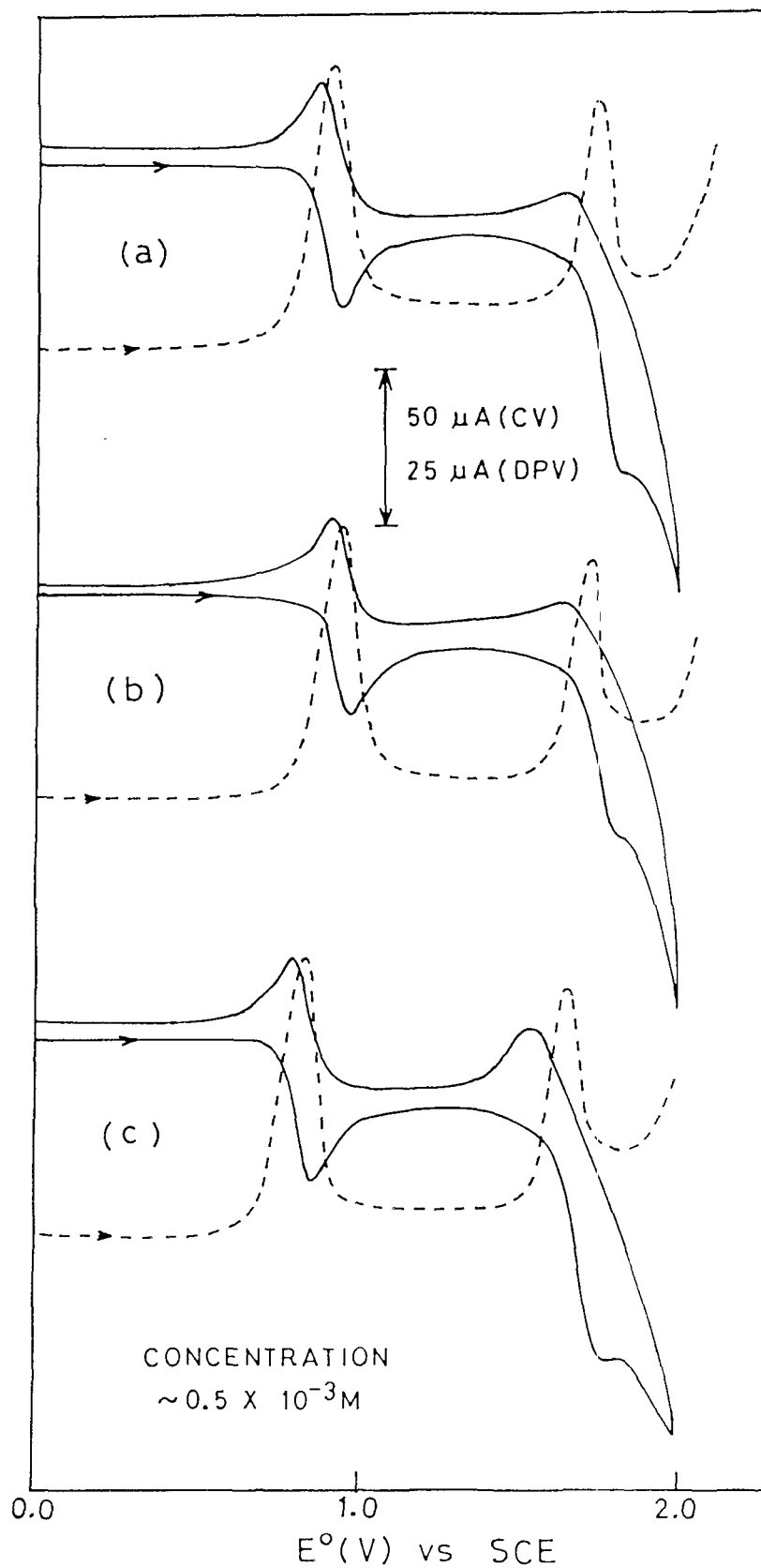


FIGURE II.7. VOLTAMMOGRAMS OF (a) $\text{ccc-}[\text{OsCl}_2\text{L}^1_2]$, (b) $\text{ctc-}[\text{OsCl}_2\text{L}^1_2]$ AND (c) $\text{ttt-}[\text{OsCl}_2\text{L}^1_2]$ IN MeCN. SCAN RATES: FOR CV (—), 50 mVs^{-1} ; FOR DPV (---), 10 mVs^{-1}

TABLE II. 6

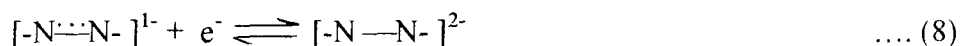
Voltammetric Data^{a,c} in MeCN on the negative Side of SCE at 298 K

Compound	-E ⁰ , V (ΔE_p , mV)			
	r ₁	r ₂	r ₃ ^d	r ₄ ^d
ttt-[OsCl ₂ L ¹ ₂] (6a)	0.52 (80)	0.83 (150)	1.51	1.94
ttt-[OsBr ₂ L ¹ ₂] (6b)	0.54 (80)	0.87 (160)	1.56	1.96
ttt-[OsCl ₂ L ² ₂] (6c)	0.56 (80)	0.89 (160)	1.54	2.01
ttt-[OsBr ₂ L ² ₂] (6d)	0.58 (80)	0.90 (170)	1.58	2.02
ttt-[OsCl ₂ L ³ ₂] (6e)	0.55 (80)	0.90 (170)	1.53	2.02
ttt-[OsBr ₂ L ³ ₂] (6f)	0.58 (80)	0.91 (170)	1.59	2.03

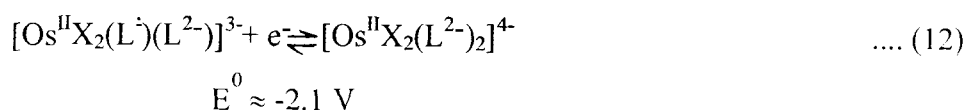
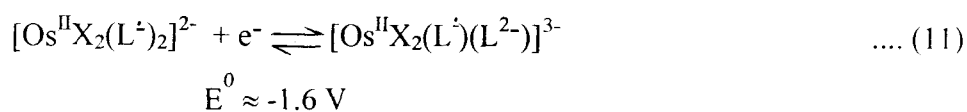
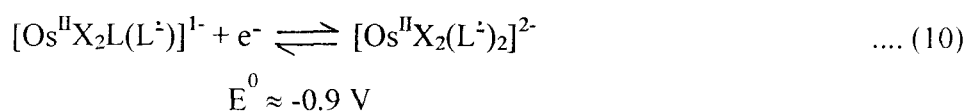
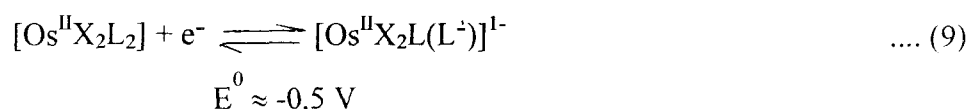
^aMeaning and units of the symbols are the same as in the text. ^bWorking electrode, glassy carbon; supporting electrolyte, TEAP (0.1 M); solute concentration, $\sim 10^{-3}$ M. ^cUnless otherwise stated both CV and DPV results are set; the agreement between data obtained by two techniques is invariably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



essentially corresponds to processes 7 and 8 respectively.



The complexes (6) show successive multiple reductive responses in the potential range ~ -0.5 to -2.1 V in MeCN solutions. Due to the positive charge of the metal ion the formal potential for the first reduction of L in osmium complexes is uniformly more positive than that of the free L. The LUMO (π^* level) of L can accommodate¹¹ upto two electrons. Four successive one-electron reductions are therefore expected in $[\text{OsX}_2\text{L}_2]$. In CV only the first three responses are observed. The cathodic and anodic current heights of the first two responses are comparable, but the third response shows very low anodic current (**Figure II.8**) which is indicative of some kind of chemical assistance associated with the charge transfer within the CV time scale. However all the four reductions are observed in DPV experiments (**Figure II.9**) These involve successive reductions of metal bound L as depicted in **equations 9 - 12** :



F. CONCLUSION

We are now able to find out a very facile synthetic route for the isolation of the elusive isomer **6** of $[\text{OsX}_2\text{L}_2]$. So all the three isomers as were found in ruthenium are obtainable for its congener osmium by the judicious choice of reaction condition. The complexes show rich electronic spectral absorptions exhibiting both high intensity spin-allowed and reasonable

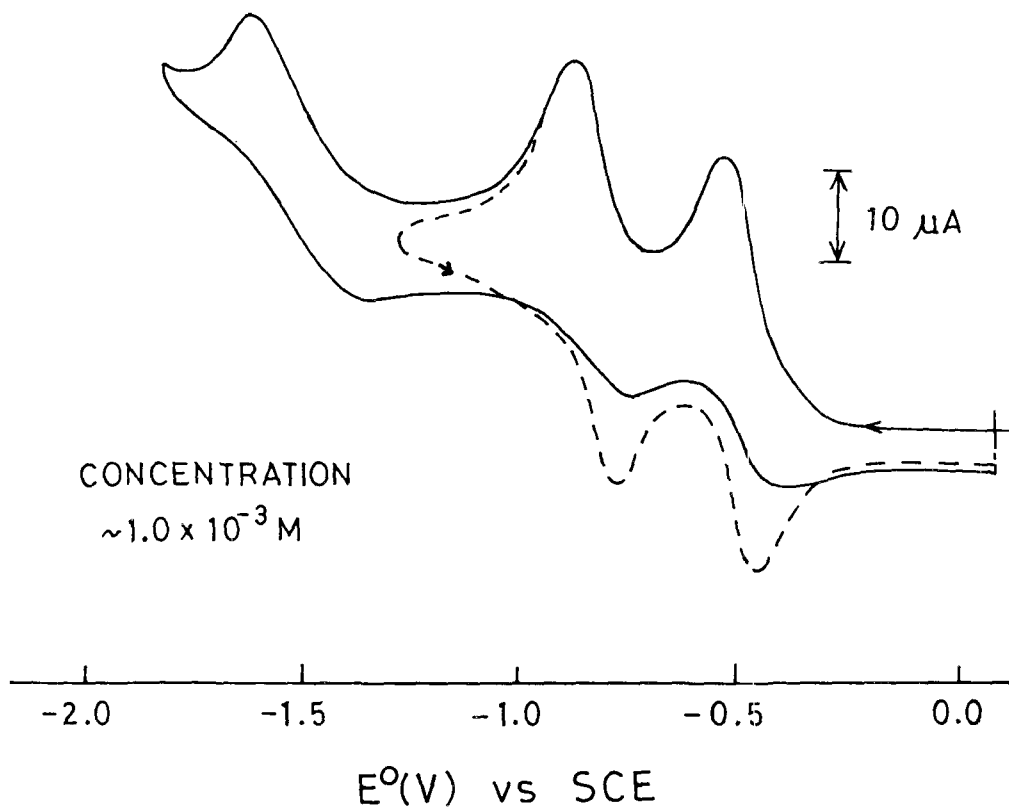


FIGURE II.8. CYCLIC VOLTAMMOGRAM OF $\text{ttt-}[\text{OsCl}_2\text{L}_2^1]$ IN MeCN. THE PRESENTATION (---) SHOWS VOLTAMMOGRAM WHERE THE SCAN WAS REVERSED BEFORE REACHING THE THIRD REDUCTION WAVE

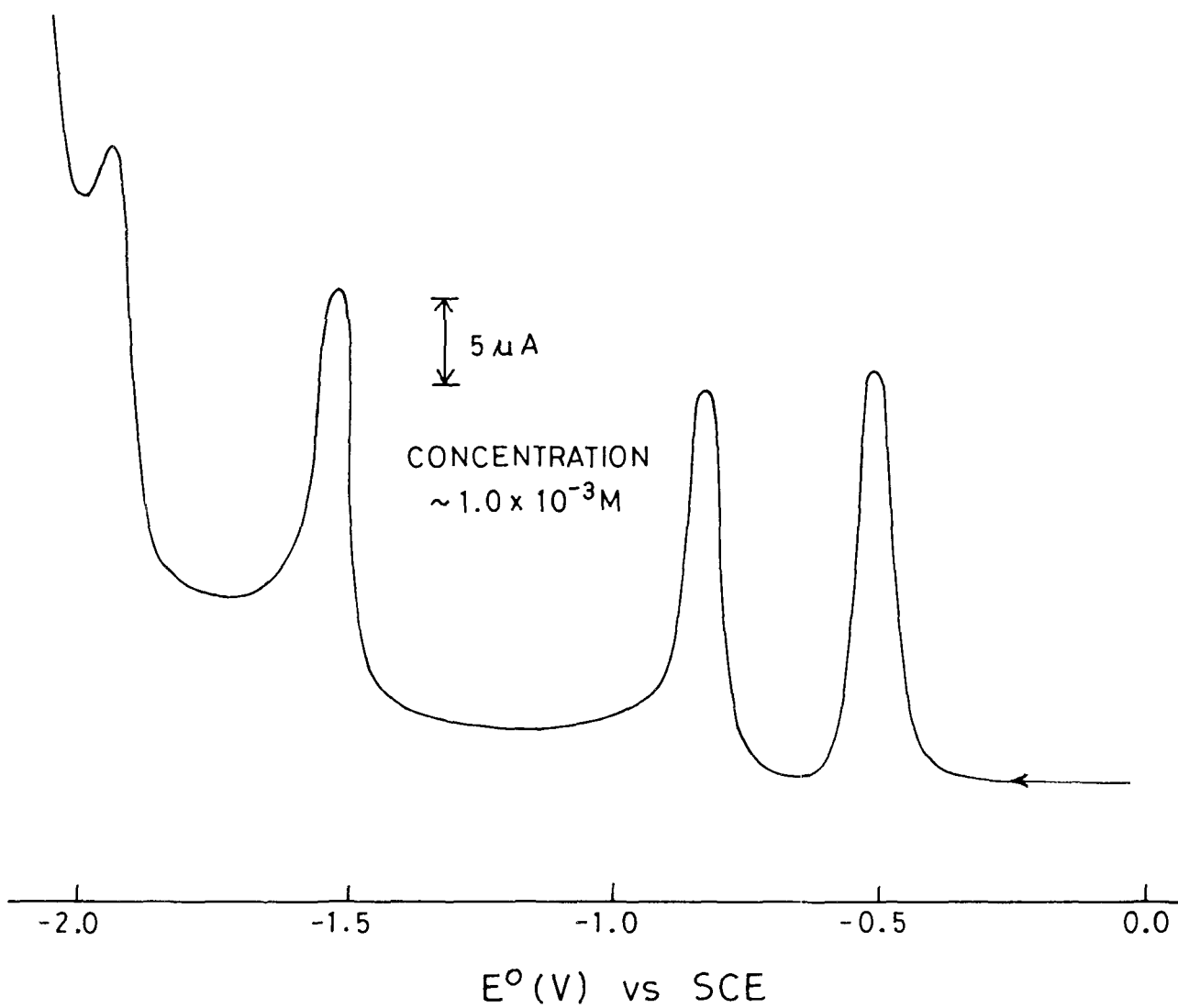


FIGURE II.9 DIFFERENTIAL PULSE VOLTAMMOGRAM OF $\text{ttt-}[\text{OsCl}_2\text{L}_2]$ IN MeCN. SCAN RATE 10 mVs^{-1}

intensity spin-forbidden transitions. The compounds display both metal-centred oxidations and successive ligand based reductions; a nearly complete electron transfer series is formed involving two one-electron metal-centred oxidations and four successive one-electron ligand-based reductions. The isomer **6** can be easily converted to **2** and **4** together by refluxing in a high boiling alcohol like 2-methoxyethanol. However, the interconversion **6**→**2/4** is not possible applying thermal, electrochemical and photochemical methods. We are now interested to synthesise a variety of mixed ligand complexes by examining the reactions of these isomeric complexes towards different neutral and anionic ligands of varied ligation motifs and strengths.

II. 3 EXPERIMENTAL SECTION

A. PREPATION OF COMPOUNDS

(a) Chemicals, solvents and starting materials

The chemicals and their sources are as follows : nitrobenzene, Lab-chem Industries (India); *m*-nitrotoluene and *p*-nitrotoluene, E. Merck (India); 2-aminopyridine, Coch-light Lab (UK); ammonium chloride, ammonium bromide, potassium chloride, potassium bromide, Loba-Chemie (India); sodium dithionite, sodium bicarbonate, sodium hydroxide, charcoal, SD (India); zinc dust, BDH (UK); sodium dichromate, CDH (India); phosphorous pentoxide, BDH (India); ethanol, Bengal Chemicals (India); chloroform, SD (India); 2-methoxyethanol, E. Merck (India); dichloromethane, methanol, acetone, acetonitrile, dimethylformamide, dimethylsulfoxide, nitromethane, E. Merck (India); anhydrous calcium chloride, SD (India); lithium carbonate, mercurous chloride, potassium permanganate, ferrous sulphate, SRL (India); sulphuric acid, hydrochloric acid, hydrobromic acid, perchloric acid, E. Merck (India); calcium hydride, Riedel (Germany); tetraethylammonium bromide, Fluka AG (Switzerland); 1,1-diphenyl-2-picrylhydrazyl, Aldrich (USA); silica-gel for column chromatography, SD (India).

Osmic acid was obtained from Johnson Matthey and Co. Ltd. (UK) and was converted to $(\text{NH}_4)_2[\text{OsX}_6]$ ($\text{X} = \text{Cl}$ or Br) following reported procedures²⁸. $(\text{NH}_4)_2[\text{OsCl}_6]$ was obtained by reacting OsO_4 with concentrated HCl in presence of Fe^{2+} ion as catalyst followed by metathesis with NH_4Cl . Direct reaction of OsO_4 with 47% HBr afforded $\text{H}_2[\text{OsBr}_6]$; metathesis of the latter with NH_4Br resulted dark crystals of $(\text{NH}_4)_2[\text{OsBr}_6]$. $(\text{Et}_4\text{N})_2[\text{OsX}_6]$ ($\text{X} = \text{Cl}$ or Br) was prepared by metathesis of $(\text{NH}_4)_2[\text{OsX}_6]$ and tetraethylammonium perchlorate (TEAP) in aqueous solution.

(b) Ligands*(i) Nitrosobenzene, m-nitrosotoluene and p-nitrosotoluene*

Nitrosobenzene was prepared from nitrobenzene, *m*-/*p*-nitrosotoluene was isolated from *m*-/*p*-nitrotoluene following the reported procedure as described in the literature²².

(ii) 2-(Phenylazo)pyridine (L¹)

5.1 g of 2-(amino)pyridine was added to a warm 50% NaOH solution (50 ml). The mixture was gently heated^{1,2} to 323 K after adding 15 ml of benzene; 6 g nitrosobenzene was then added portion wise. The mixture was stirred at 323 K for 10 h. The resulting solution was then extracted several times with benzene. The dark brown solution was boiled with charcoal and filtered. The filtrate (~25 ml) was concentrated and was then subjected to column chromatography on a silica-gel (60 - 120 mesh, BDH) column (40 × 1 cm) eluting with benzene. The lowermost green band was rejected. The orange band was collected. The evaporation yielded a red liquid of 2-(phenylazo)pyridine. Yield was 70%.

(iii) 2-(m-Tolylazo)pyridine (L²)

It was similarly prepared in good yield (~65%) by using *m*-nitrosotoluene instead of nitrosobenzene described above.

(iv) 2-(p-Tolylazo)pyridine (L³)

2-(*p*-Tolylazo)pyridine was also prepared in a similar manner described above using *p*-nitrosotoluene instead of nitrosobenzene, and 2-(amino)pyridine. Yield was 60%.

(c) Authentic samples (2 and 4)*(i) ctc-[OsX₂L₂] (2) and ccc-[OsX₂L₂] (4)*

These were prepared using the procedure of Ghosh et al¹⁵. (Et₄N)₂[OsX₆] (X = Cl/Br) was refluxed in 2-methoxyethanol under N₂ with appropriate L. The red-violet solution was concentrated slowly and kept in the refrigerator overnight. The shining *ctc*-isomer **2** precipitated out, which was collected by filtration. From the filtrate the *ccc*-isomer **4** was isolated by column chromatographic separation.

(d) Complexes*(i) Trans, trans, trans-Dichlorobis[2-(phenylazo)pyridine]osmium(II), ttt-[OsCl₂L¹₂] (6a)*

Dinitrogen was purged for 15 min through a suspension of 0.33 g (0.5 mmol) of (Et₄N)₂[OsX₆] in 50 ml of methanol. Following this 0.2 g (1.09 mmol) of L¹ in 5 ml methanol was added dropwise. The mixture was then heated to reflux under dinitrogen atmosphere for 12 h. During this period the suspension dissolved resulting a blue-violet solution. This was then concentrated under reduced atmosphere resulting a dark mass, which was redissolved in a minimum volume of dichloromethane and was subjected to column chromatography on a silica gel (60 - 120 mesh, BDH) column (30 X 1 cm). The blue band was first eluted with benzene. The blue-violet band was collected using 1:1 PhH-CH₂Cl₂ as eluent. For the red-violet band eluent was 9:1 PhH-MeCN. Crystalline **6a** resulted on slow evaporation of the blue eluant at room temperature. The yield was 0.125 g (40%).

(ii) Trans, trans, trans-Dibromobis[2-(phenylazo)pyridine]osmium(II), ttt-[OsBr₂L¹₂] (6b)

This was prepared using the same reaction stoichiometry and condition as in the preparation of **6a** except that 0.45 g (0.5 mmol) of (Et₄N)₂[OsBr₆] was reacted with 0.2 g (1.09 mmol) of L¹. The reaction was faster than that in **6a** (reaction time 6 h). The yield was 0.161 g (40%).

(iii) Trans, trans, trans-Dichlorobis[2-(m-tolylazo)pyridine]osmium(II), ttt-[OsCl₂L²₂] (6c)

The procedure was the same as in the preparation of **6a** except that 0.32 g (0.5 mmol) of (Et₄N)₂[OsCl₆] was reacted with 0.2 g (1.01 mmol) of L². The reaction time was 12 h. The yield was 0.147 g (45%).

(iv) Trans, trans, trans-Dibromobis[2-(m-tolylazo)pyridine]osmium(II), ttt-[OsBr₂L²₂] (6d)

The same solvent, procedure and reaction stoichiometry as described in the preparation of **6a** were adopted except that 0.45 g (0.5 mmol) of (Et₄N)₂[OsBr₆] was reacted with 0.22 g (1.11 mmol) of L². The yield was 0.186 g (50%).

(v) Trans, trans, trans-Dichlorobis[2-(p-tolylazo)pyridine]osmium(II), ttt-[OsCl₂L³₂] (6e)

6e was prepared using the same procedure as described in **6a** except that 0.20 g (1.01 mmol) of L³ was reacted with 0.32 g (0.5 mmol) of (Et₄N)₂[OsCl₆]; yield is 0.147 g (45%).

(vi) *Trans, trans, trans-Dibromobis[2-(p-tolylazo)pyridine]osmium(II), ttt -[OsBr₂L³]₂ (6f)*

The same preparative procedure was followed for **6f** as described in **6a**. Here 0.20 g (1.01 mmol) of L³ was reacted with 0.45 g (0.5 mmol) of (Et₄N)₂[OsBr₆]. The yield was 0.186 g (50%).

(e) Conversion : 6→2/4

An alcoholic solution of **6**, charged with dinitrogen, was heated to reflux. Blue colour gradually changed to blue-violet and finally to red-violet. The composition of the reaction mixture was monitored by thin layer chromatography, and after 12 h this was evaporated under reduced pressure. The solid mass was dried, redissolved in a minimum volume of dichloromethane and was chromatographed on a silica gel column in benzene as described earlier. The blue-violet **2** was obtained eluting with 1:1 PhH-CH₂Cl₂ and the red-violet **4**, with 9:1 PhH-MeCN. The two isomers were identified by comparing their spectroscopic, magnetic and physicochemical properties of authentic samples¹⁵.

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 II.7**.

C. PHYSICAL MEASUREMENTS

Solution electrical conductivities (in MeCN, solute concentration $\sim 10^{-3}$ M) and electronic (in MeCN, solute concentration $\sim 10^{-3}$ M), IR spectra (KBr discs, 4000 - 600 cm⁻¹; polyethylene discs, 600 - 300 cm⁻¹) were recorded using a Philips PR 9500 conductivity bridge, Hitachi 330/Shimadzu UV 160A spectrophotometer and Perkin-Elmer 783 spectrometer, respectively. 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). Microanalyses (C, H and N) were done with a Perkin-Elmer 240 C elemental analyser. Electrochemical studies were performed (in MeCN at 298 K) under dry N₂ with a PAR 370-4 electrochemistry system incorporating a Model 174 A polarographic analyser, a 175 Universal Programmer, a Model 173 potentiostat, a model 179 digital coulometer, an RE0074

X-Y recorder and a model 377 A cell system. A planar Beckman Model 39273 platinum-inlay or PAR G0021 glassy carbon working electrode, a platinum wire auxiliary electrode and an aqueous calomel reference electrode (SCE) were used in three-electrode measurements. A platinum-wire gauge working electrode was used in coulometric experiments. In cyclic voltammetry (CV) the following parameters and relation were used : scan rate (v), 50 mVs^{-1} ; formal potential $E^0 = 0.5(E_{\text{pa}} + E_{\text{pc}})$ where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; ΔE_p is the peak-to-peak separation. For differential pulse voltammetry (DPV) : scan rate (v), 10 mVs^{-1} ; modulation amplitude (ΔE), 25 mV ; $E^0 = E_p + 0.5(\Delta E)$ where E_p is the DPV peak potential. The agreement between E^0 data obtained by the two techniques was good (within $\pm 5 \text{ mV}$). In constant potential coulometry experiments (oxidation done at potential $E^0 + 200 \text{ mV}$ and reduction, at $E^0 - 200 \text{ mV}$); $n = Q/Q'$ where Q' is the calculated coulomb count for one-electron transfer and Q is coulomb count found after exhaustive electrolysis of 0.01 mmol of solute. The potentials are referenced to a saturated calomel electrode (SCE) and are uncorrected for the junction contributions.

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