

CHAPTER III

**ISOMERIC $[\text{OsA}_2\text{L}_2]$ (A = NO_2^- , SCN^- or N_3^-) COMPLEXES :
SYNTHESIS, SPECTRA AND ELECTROCHEMISTRY**

CHAPTER III

ISOMERIC $[\text{OsA}_2\text{L}_2]$ ($\text{A} = \text{NO}_2^-$, SCN^- or N_3^-) COMPLEXES : SYNTHESIS, SPECTRA AND ELECTROCHEMISTRY

ABSTRACT : Both blue-violet (**2**) and red-violet (**3**), isomers of $[\text{OsX}_2\text{L}_2]$ [$\text{X} = \text{Cl}$ or Br and $\text{L} = 2\text{-(arylamino)pyridines (1)}$] react smoothly with A ($\text{A} = \text{NO}_2^-$, SCN^- or N_3^-) in boiling aqueous ethanol affording species of the type $[\text{OsA}_2\text{L}_2]$ (**5** and **6**, respectively). The complexes were characterised using microanalytical, spectroscopic and electrochemical results. **5** and **6** behave as non-electrolytes. IR spectra strongly suggest the *cis* geometry of OsA_2 moiety. ^1H NMR results (taking δ_{Me} as diagnostic probe) demonstrates the stereoretentivity of the reactions. Several spin-allowed and spin-forbidden transitions are observed in their electronic spectra. The complexes are redox-active and show one metal-centered oxidation and successive ligand-based reductions in MeCN solutions.

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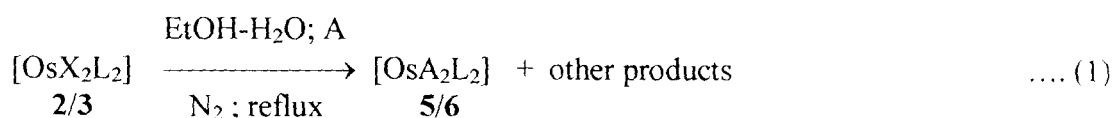
III.1 INTRODUCTION

In Chapter II we have discussed different facile synthetic routes for the preparation of isomeric¹⁻³ complexes (**2**, **3** and **4**) of type $[\text{OsX}_2\text{L}_2]$ [$\text{X} = \text{Cl}$ or Br ; $\text{L} = 2\text{-(arylazo)pyridines}$, **1**]. We are interested to establish the reactivity pattern of these complexes towards different monodentate and bidentate ligands. In this chapter we have examined reaction behaviour of the two isomeric *cis*-dihalobis complexes **2** (*cis, trans, cis; etc*) and **3** (*cis, cis, cis; ccc*) towards three monodentate anionic ligands like NO_2^- , SCN^- and N_3^- (A). Successfully we have isolated isomeric species of type $[\text{OsA}_2\text{L}_2]$ (**5** and **6**). No monosubstituted complexes of type $[\text{OsX(A)L}_2]$ could be isolated by changing the mole ratio of **2/3** and A. Here we report the details of synthesis and characterisation of these disubstituted complexes (**5** and **6**).

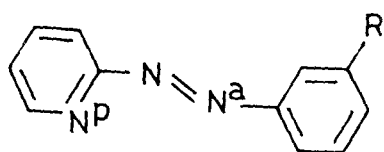
III.2 RESULTS AND DISCUSSION

A. SYNTHESIS

2-(Arylazo)pyridines namely 2-(phenylazo)pyridine (L^1) and 2-(*m*-tolylazo)pyridine (L^2) were prepared as described in the previous chapter. Dihalogeno complexes were synthesised as reported earlier¹. The synthetic details of the mixed ligand compounds of type $[\text{OsA}_2\text{L}_2]$ (A = NO_2^- , SCN^- or N_3^-) by the reaction of $[\text{OsX}_2\text{L}_2]$ and Na^+ or NH_4^+ salts of the appropriate anion in boiling aqueous ethanol under nitrogen are shown in **equation 1**. Reaction 1 did not progress by



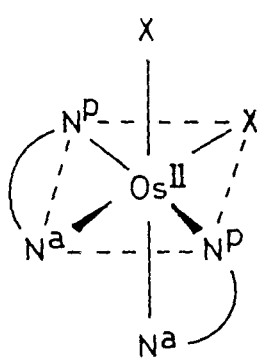
maintaining a logical 1:2 mole ratio for the dihalo complexes (**2** and **3**) and the ligand A. At least a five-fold excess of A was required for completion of the reaction in a reasonable time⁴. By changing the solvent from aqueous ethanol (b. p. 351 K) to aqueous 2-methoxyethanol (b. p. 398 K) the reaction got faster but isomeric homogeneity was lost due to severe reaction condition. In no case monosubstituted $[\text{OsX(A)L}_2]$ could be isolated. However during column chromatographic separation a very small band was eluted before separation of $[\text{OsA}_2\text{L}_2]$. This might be indicative of $[\text{OsX(A)L}_2]$ formation. Very small formation restricted its full characterisation.



R = H; L¹

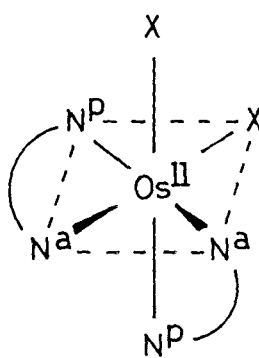
R = Me; L²

L; 1



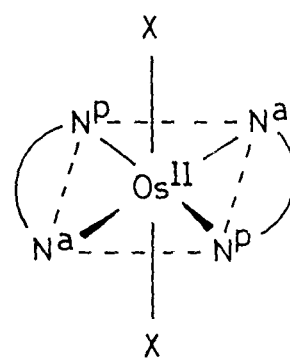
ctc

2 X = Cl or Br



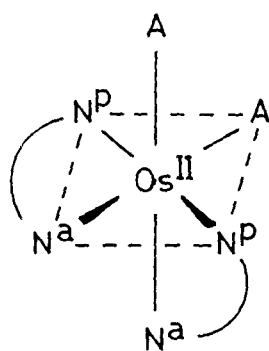
ccc

3



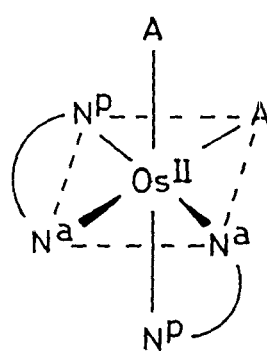
ttt

4



ctc

5



ccc

6

A = NO₂⁻, SCN⁻ or N₃⁻

CHART III.1

The complexes **5** and **6** were characterised by elemental (C, H and N) analyses, solution electrical conductivities, spectroscopic (IR, NMR and UV-Vis) properties and electrochemical [cyclic voltammetry (CV); differential pulse voltammetry (DPV) and coulometry] results (Tables III.1 - III.7). All the complexes are readily soluble in benzene, alcohols, chloroform, dichloromethane, acetonitrile and dimethylsulfoxide. Very low conductivity values indicate the non-electrolytic behaviour⁵ (Table III.1) of the compounds in MeCN and MeNO₂ solutions. Room temperature solid phase magnetic susceptibility measurements show that the complexes (**5** and **6**) are uniformly diamagnetic (t_{2g}^6 idealised; S = 0).

B. INFRARED SPECTRA

IR spectra of all the complexes were recorded in KBr discs (4000 - 600 cm⁻¹) and in polyethylene discs (600 - 300 cm⁻¹). Only the pertinent results are considered here (Table III.2 and Figures III.1 and III.2). $\nu(\text{C}=\text{N})$ and $\nu(\text{N}=\text{N})$ modes of the complexed L are seen at ~1600 cm⁻¹ and >1280 cm⁻¹ respectively. The shift of $\nu(\text{N}=\text{N})$ towards higher frequency in going from [OsX₂L₂] to [OsA₂L₂] suggests less osmium-azo π -back bonding in the latter. The better π -acceptor behaviour of A compared to X results in less π -back donation⁶ toward azo fragment which is the effective π -acceptance centre⁷ of L. The thiocyanato complexes show two $\nu(\text{C}\equiv\text{N})$ modes below 2100 cm⁻¹ (at ~2065 and ~2080 cm⁻¹) which is in consistent with the *cis*-Os(NCS)₂ geometry having Os-N bonding⁸. The $\nu(\text{C}=\text{S})$ stretching mode is apparently obscured by the ligand absorptions. In azido complexes the antisymmetric N₃ stretch⁹ appears at ~2075 cm⁻¹ as a strong band perhaps containing components. The dinitro complexes exhibit sharp bands at ~1300, ~1320 and ~1370 cm⁻¹; the position and number of bands, indicate coordination through N as also their *cis* dispositions in the complexes¹⁰. Thus IR spectra are in line with the *cis* geometry of OsA₂ moiety. A close examination of the IR spectra of the *ctc*-[OsA₂L₂] with corresponding *ctc*-[OsX₂L₂] and the vibration spectra of the *ccc*-[OsA₂L₂] with corresponding *ccc*-[OsX₂L₂] leads to very helpful conclusion regarding the structures of [OsA₂L₂]. A 1:1 correspondence is seen in the range 4000 - 400 cm⁻¹, except for the frequency shift in the $\nu(\text{N}=\text{N})$ region, and appearance of A vibrations. The typical patterns are shown in Figures III.1 and III.2 with azido complexes.

TABLE III.1

Molar Conductivity data^a at 298 K

Compound	Λ_M (ohm ⁻¹ cm ² mol ⁻¹)	
	MeCN	MeNO ₂
ctc-[Os(NO ₂) ₂ L ¹ ₂] (5a)	5	4
ccc-[Os(NO ₂) ₂ L ¹ ₂] (6a)	7	5
ctc-[Os(NO ₂) ₂ L ² ₂] (5b)	5	4
ccc-[Os(NO ₂) ₂ L ² ₂] (6b)	6	5
ctc-[Os(NCS) ₂ L ¹ ₂] (5c)	4	3
ccc-[Os(NCS) ₂ L ¹ ₂] (6c)	6	4
ctc-[Os(NCS) ₂ L ² ₂] (5d)	5	4
ccc-[Os(NCS) ₂ L ² ₂] (6d)	7	5
ctc-[Os(N ₃) ₂ L ¹ ₂] (5e)	5	3
ccc-[Os(N ₃) ₂ L ¹ ₂] (6e)	7	4
ctc-[Os(N ₃) ₂ L ² ₂] (5f)	5	4
ccc-[Os(N ₃) ₂ L ² ₂] (6f)	6	5

^aSolute concentration, ~ 10⁻³ M.

TABLE III. 2

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

Compound	$\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})^{\text{c}}$	$\nu(\text{N}=\text{N})^{\text{d}}$
ctc-[Os(NO ₂) ₂ L ¹ ₂] (5a)	1595	1290
ccc-[Os(NO ₂) ₂ L ¹ ₂] (6a)	1590	1286
ctc-[Os(NO ₂) ₂ L ² ₂] (5b)	1595	1290
ccc-[Os(NO ₂) ₂ L ² ₂] (6b)	1590	1285
ctc-[Os(NCS) ₂ L ¹ ₂] (5c)	1592	1289
ccc-[Os(NCS) ₂ L ¹ ₂] (6c)	1590	1285
ctc-[Os(NCS) ₂ L ² ₂] (5d)	1590	1288
ccc-[Os(NCS) ₂ L ² ₂] (6d)	1590	1285
ctc-[Os(N ₃) ₂ L ¹ ₂] (5e)	1592	1289
ccc-[Os(N ₃) ₂ L ¹ ₂] (6e)	1595	1286
ctc-[Os(N ₃) ₂ L ² ₂] (5f)	1590	1288
ccc-[Os(N ₃) ₂ L ² ₂] (6f)	1595	1286

^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.

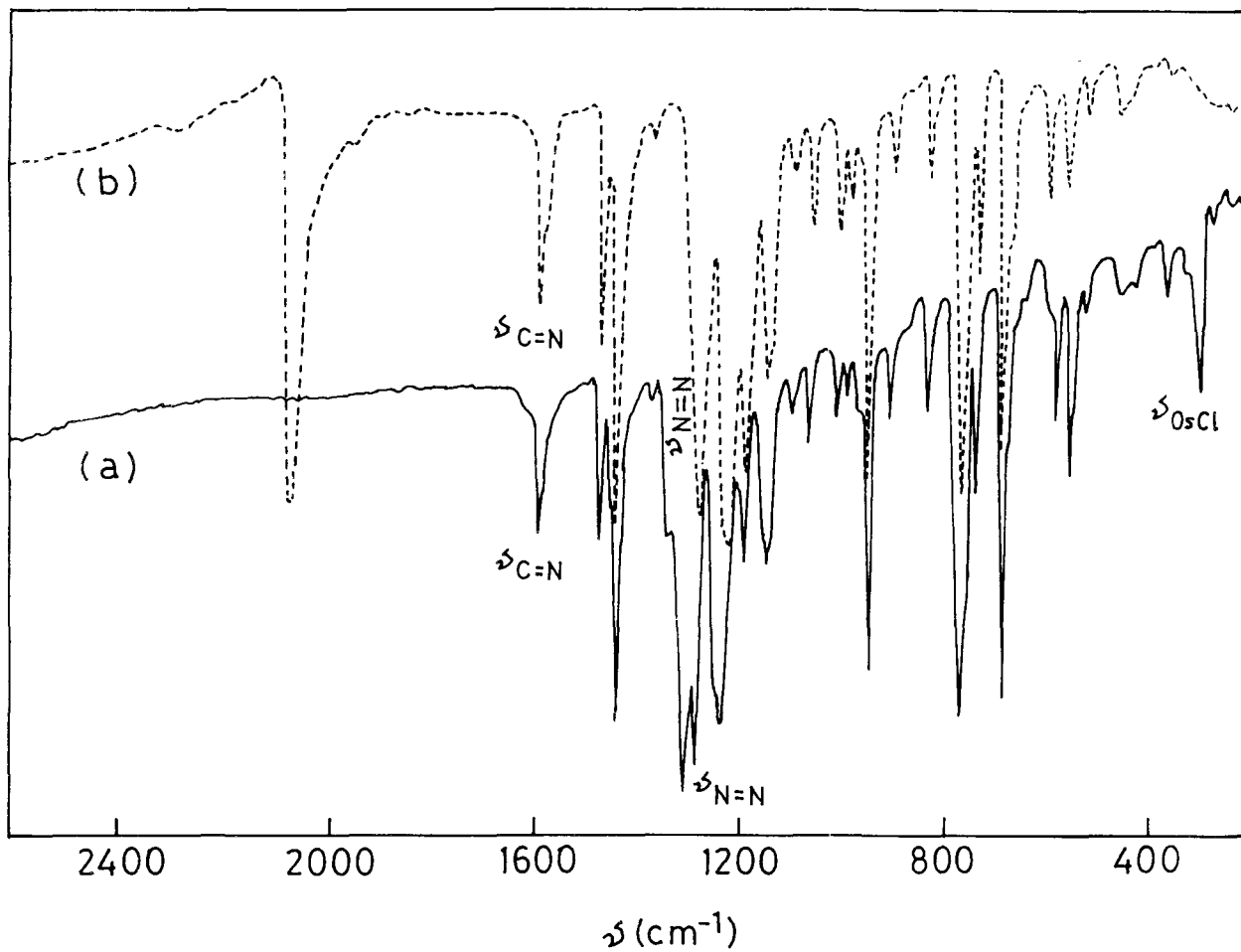


FIGURE III.1. IR SPECTRA OF (a) $\text{ctc-}[\text{OsCl}_2\text{L}'_2]$ (—) AND (b) $\text{ctc-}[\text{Os}(\text{N}_3)_2\text{L}'_2]$ (----)

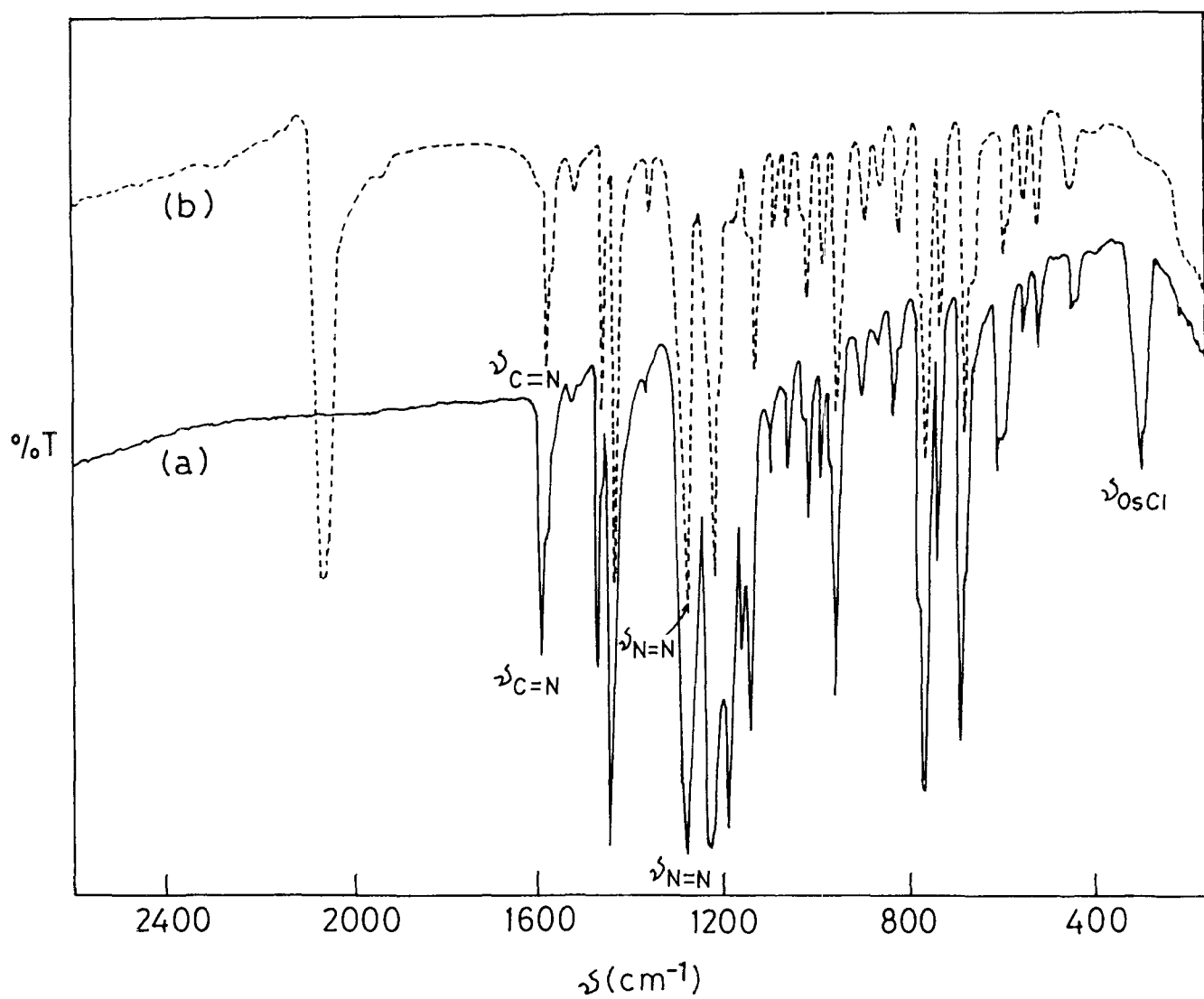


FIGURE III.2. IR SPECTRA OF (a) $\text{ccc-}[\text{OsCl}_2\text{L}^1_2]$ (—) AND (b) $\text{ccc-}[\text{Os}(\text{N}_3)_2\text{L}^1_2]$ (---)

C. ¹H NMR SPECTRA AND STEREOCHEMISTRY

¹H NMR results of L² complexes were used to examine the stereochemistry of **5** and **6**. Relevant chemical shifts are set in **Table III.3**. Spectral nature of the representative complexes are shown in **Figure III.3**. [OsA₂L₂] complexes obtained from **2** via reaction 1 show a single sharp methyl signal in CDCl₃ solutions. The complexes resulting from the reaction of A and **3** show two equally intense methyl signals (**Fig III.3**) demonstrating that OsL₂ group has the same symmetry as in **3**. Hence the reaction 1 is stereoretentive. It is reasonable to assume that this is



applicable to L¹ complexes also. Three signals are invariably present in the case of the products obtained from either **2** or **3** and A in aqueous 2-methoxyethanol. Two of the three signals have equal heights (see **Figure III.3**). This implies that [OsL₂]²⁺ moiety is certainly present both in *cis*, *trans*, *cis* (one signal) and *cis*, *cis*, *cis* (two signals) geometry in the order (A, A) (N^p, N^p) and (N^a, N^a) respectively. Evidently, *cis*, *cis*, *cis* is the major product. This is in line with the fact that during substitution extensive stereochemical rearrangement is occurring. A similar observation¹¹ was found for tris chelate formation from **2** in such a severe reaction condition.

D. CHARGE-TRANSFER SPECTRA

Spectral data in MeCN solutions are set in **Table III.4**. The complexes have several absorption bands and shoulders in the region 200 - 900 nm. Though solution colour of complexes **5** and **6** with a particular A is same (red-violet), the recorded spectra have sharp differences (**Figure III.4**). A characteristic feature of the red-violet solution is an intense band at ~500 nm. Weak absorptions at lower energies are also noticeable in all the complexes. A blue shift of these absorptions is found in going from **5** to **6**. These are assigned as metal-to-ligand charge transfer (MLCT) transitions, t₂(Os)→π*(L) within the framework of pseudooctahedral osmium(II) stereochemistry. The more intense absorptions at higher energies are presumably of spin-allowed type whereas the weaker ones at higher wavelengths could be due to spin-forbidden transitions which become partially allowed through strong spin-orbit coupling^{12,13} in a heavy metal like osmium. The transitions below 400 nm are of ligand origin as described in the earlier chapter.

TABLE III. 3

¹H NMR Data^{a-c} of L² Complexes

Compound	$\delta(\text{Me})$, ppm
ctc-[Os(NO ₂) ₂ L ² ₂] (5b)	2.20
ccc-[Os(NO ₂) ₂ L ² ₂] (6b)	2.14, 2.29
ctc-[Os(NCS) ₂ L ² ₂] (5d)	2.18
ccc-[Os(NCS) ₂ L ² ₂] (6d)	2.16, 2.31
ctc-[Os(N ₃) ₂ L ² ₂] (5f)	2.19
ccc-[Os(N ₃) ₂ L ² ₂] (6f)	2.13, 2.33

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

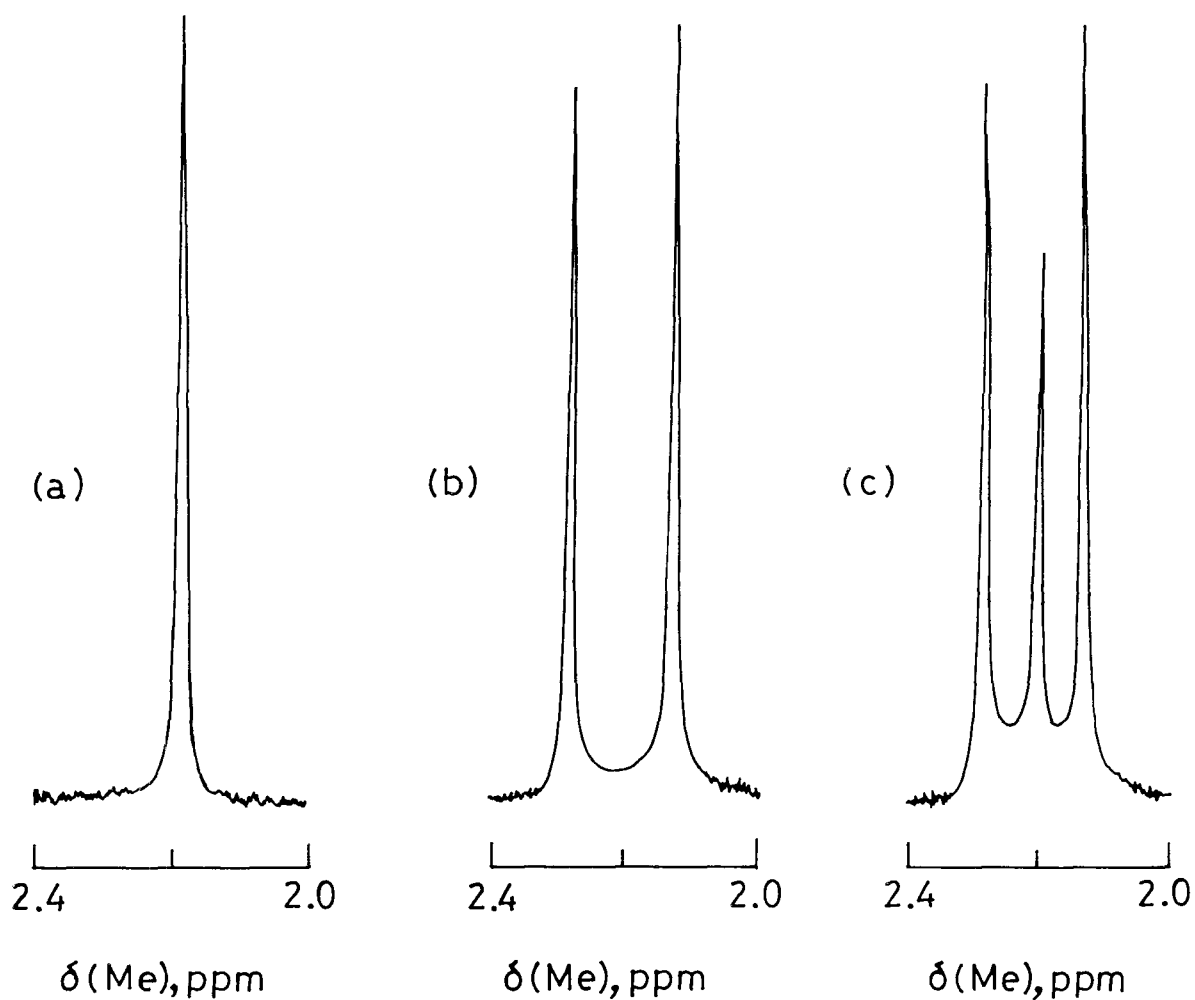


FIGURE III.3 ^1H NMR SPECTRA (Me SIGNALS) OF
 (a) *ctc*- $[\text{Os}(\text{NO}_2)_2\text{L}^2_2]$; (b) *ccc*- $[\text{Os}(\text{NO}_2)_2\text{L}^2_2]$; AND
 (c) MIXTURE OF *ctc*- AND *ccc*- $[\text{Os}(\text{NO}_2)_2\text{L}^2_2]$ IN CDCl_3

TABLE III. 4

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

Compound	λ_{max} , nm (ϵ , M ⁻¹ cm ⁻¹)
ctc-[Os(NO ₂) ₂ L ¹ ₂] (5a)	880 ^c (620), 740 ^c (1,110), 630 ^c (1,740), 510 (9,800), 340 (17,280), 300 (18, 590), 220 (24,170)
ccc-[Os(NO ₂) ₂ L ¹ ₂] (6a)	800 ^c (650), 705 ^c (1,300), 555 ^c (2,080), 500 (10,020), 332 (17,970), 300 (18, 850), 235 (24,430)
ctc-[Os(NO ₂) ₂ L ² ₂] (5b)	880 ^c (630), 746 ^c (1,140), 628 ^c (1,760), 510 (9,880), 338 (17,340), 300 (18, 660), 224 (24,580)
ccc-[Os(NO ₂) ₂ L ² ₂] (6b)	800 ^c (680), 700 ^c (1,380), 550 ^c (2,120), 500 (10,110), 335 (18,040), 300 (18, 910), 240 (24,920)
ctc-[Os(NCS) ₂ L ¹ ₂] (5c)	860 ^c (700), 730 ^c (1,040), 616 ^c (1,690), 505 (9,780), 338 (17,830), 300 (19,030), 230 (25,810)
ccc-[Os(NCS) ₂ L ¹ ₂] (6c)	790 ^c (730), 705 ^c (1,270), 548 ^c (1,790), 498 (9,940), 318 (18,010), 300 (19, 120), 238 (26,120)
ctc-[Os(NCS) ₂ L ² ₂] (5d)	860 ^c (710), 735 ^c (1,260), 620 ^c (1,800), 505 (9,910), 335 (18,050), 300 (19,220), 230 (26,000)
ccc-[Os(NCS) ₂ L ² ₂] (6d)	790 ^c (790), 700 ^c (1,390), 540 ^c (1,860), 498 (10,070), 320 (18,240), 300 (19, 390), 240 (26,540)
ctc-[Os(N ₃) ₂ L ¹ ₂] (5e)	868 ^c (660), 735 ^c (1,130), 630 ^c (1,700), 508 (9,480), 340 (17,390), 300 (17, 890), 228 (22,770)
ccc-[Os(N ₃) ₂ L ¹ ₂] (6e)	790 ^c (700), 708 ^c (1,180), 558 ^c (1,720), 500 (9,870), 335 (17,880), 300 (18, 020), 232 (23,660)
ctc-[Os(N ₃) ₂ L ² ₂] (5f)	865 ^c (690), 740 ^c (1,180), 625 ^c (1,780), 508 (9,590), 340 (17,530), 300 (18, 020), 230 (23,200)
ccc-[Os(N ₃) ₂ L ² ₂] (6f)	790 ^c (750), 700 ^c (1,270), 550 ^c (1,800), 500 (10,010), 330 (18,100), 300 (18, 230), 235 (23,970)

^aSolvent, MeCN. ^bSolute concentration, ~ 10⁻³ M. ^cShoulder.

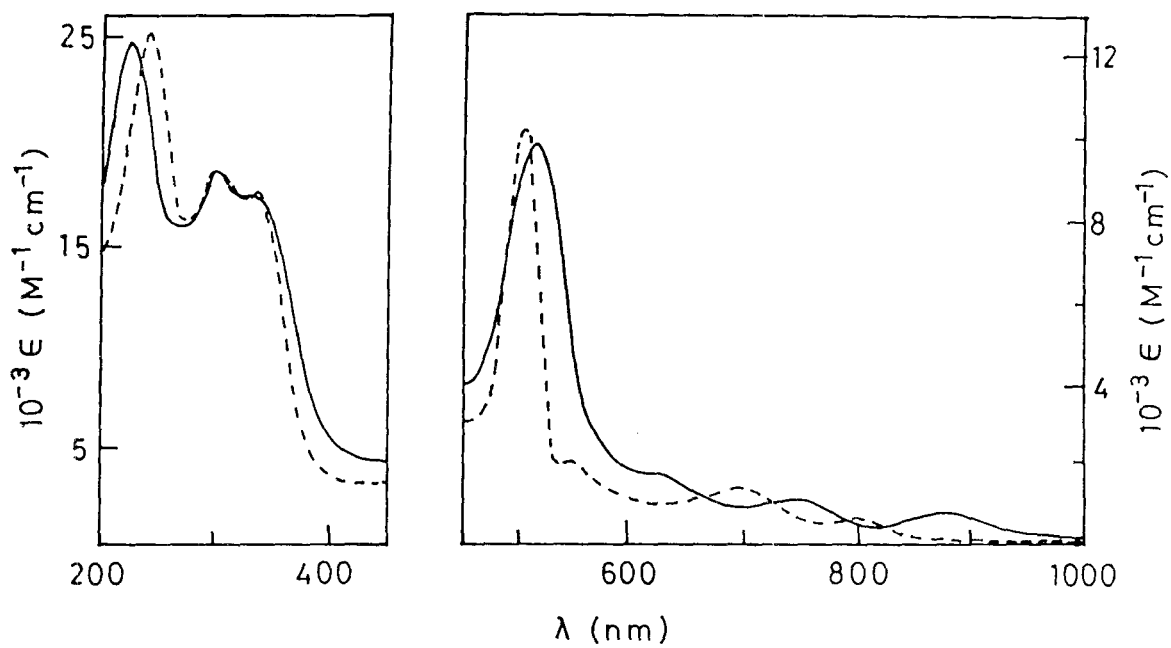


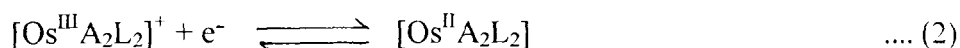
FIGURE III.4. ELECTRONIC SPECTRA OF (a) $ctc-[Os(NO_2)_2L_2^2]$ (—) AND (b) $ccc-[Os(NO_2)_2L_2^2]$ (---) IN MeCN AT 298 K

E. REDOX BEHAVIOR

Electroactivity of the complexes was studied in some detail (using CV, DPV and coulometry). Results are summarised in **Tables** III.5 and III.6. Selected voltammograms are represented in **Figures** III.5 - III.7. All potentials are referenced to a saturated calomel electrode (SCE).

(a) Metal-centred oxidation

The positive side of SCE was scanned using a platinum working electrode in MeCN solutions. Complexes **5** and **6** show one one-electron oxidative cyclic voltammetric response attributable to osmium(III) - osmium(II) couple as shown in **equation** 2. The peak-to-peak



separation lies in the range 100 - 120 mV indicating the quasi-reversible nature of the couple 2. Multiple scan cyclic voltammograms along with differential pulse of a selected complex is shown in **Figure** III.5. At higher scan rate the cathodic current increases its height indicating nearly reversible electron transfer in the CV time scale. One-electron stoichiometry of the complexes was ascertained from comparison of the current height of the standard one-electron transfer in the dihalo precursors, since attempted coulometry at the required high potentials led to continuous coulomb count. The formal potential lies in the 1.17 - 1.21 V potential range. In the precursor complexes **2** and **3**, the couple is observable at ~1.0 V. An anodic shift in potential value reflects the lowering of energy of metal t_2 level (HOMO) due to better⁶ π -acceptor behaviour of A compared to X.

(b) Ligand-based reductions

The negative side of SCE was scanned using a glassy carbon working electrode. The complexes **5** and **6** show three successive cyclic voltammetric reductive responses in the potential range, ~ -0.5 to -2.0 V. On scan reversal the corresponding anodic peaks of the first two steps, though of lower current height, are seen but for the last one it is unobservable (**Figure** III.6). Irreversibility of these responses at very lower potential indicates that the three-electron reduced product is not stable in the CV time scale, and some kind of chemical assistance is connected with the charge-transfer step. Since the LUMO of L can accommodate¹⁴ (discussed in the previous chapter) upto two electrons, four successive one-electron reductions are expected. Even in DPV experiments the fourth reduction is not observable in dry acetonitrile solutions (**Figure** III.7). It is very likely that the reduction at such negative potential leads to dissociation of the ligand for which the fourth one is not seen within the available potential window. The

TABLE III. 5

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

Compound	osmium(III) - osmium(II)			
	E_{pa} , V	E_{pc} , V	ΔE_p , mV	E^0 , V
ctc-[Os(NO ₂) ₂ L ¹ ₂] (5a)	1.26	1.16	100	1.21
ccc-[Os(NO ₂) ₂ L ¹ ₂] (6a)	1.25	1.14	110	1.20
ctc-[Os(NO ₂) ₂ L ² ₂] (5b)	1.24	1.14	100	1.19
ccc-[Os(NO ₂) ₂ L ² ₂] (6b)	1.23	1.13	100	1.18
ctc-[Os(NCS) ₂ L ¹ ₂] (5c)	1.30	1.18	120	1.24
ccc-[Os(NCS) ₂ L ¹ ₂] (6c)	1.27	1.16	110	1.22
ctc-[Os(NCS) ₂ L ² ₂] (5d)	1.28	1.16	120	1.22
ccc-[Os(NCS) ₂ L ² ₂] (6d)	1.24	1.13	110	1.19
ctc-[Os(N ₃) ₂ L ¹ ₂] (5e)	1.26	1.16	100	1.21
ccc-[Os(N ₃) ₂ L ¹ ₂] (6e)	1.24	1.14	100	1.19
ctc-[Os(N ₃) ₂ L ² ₂] (5f)	1.24	1.14	100	1.19
ccc-[Os(N ₃) ₂ L ² ₂] (6f)	1.22	1.12	100	1.17

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

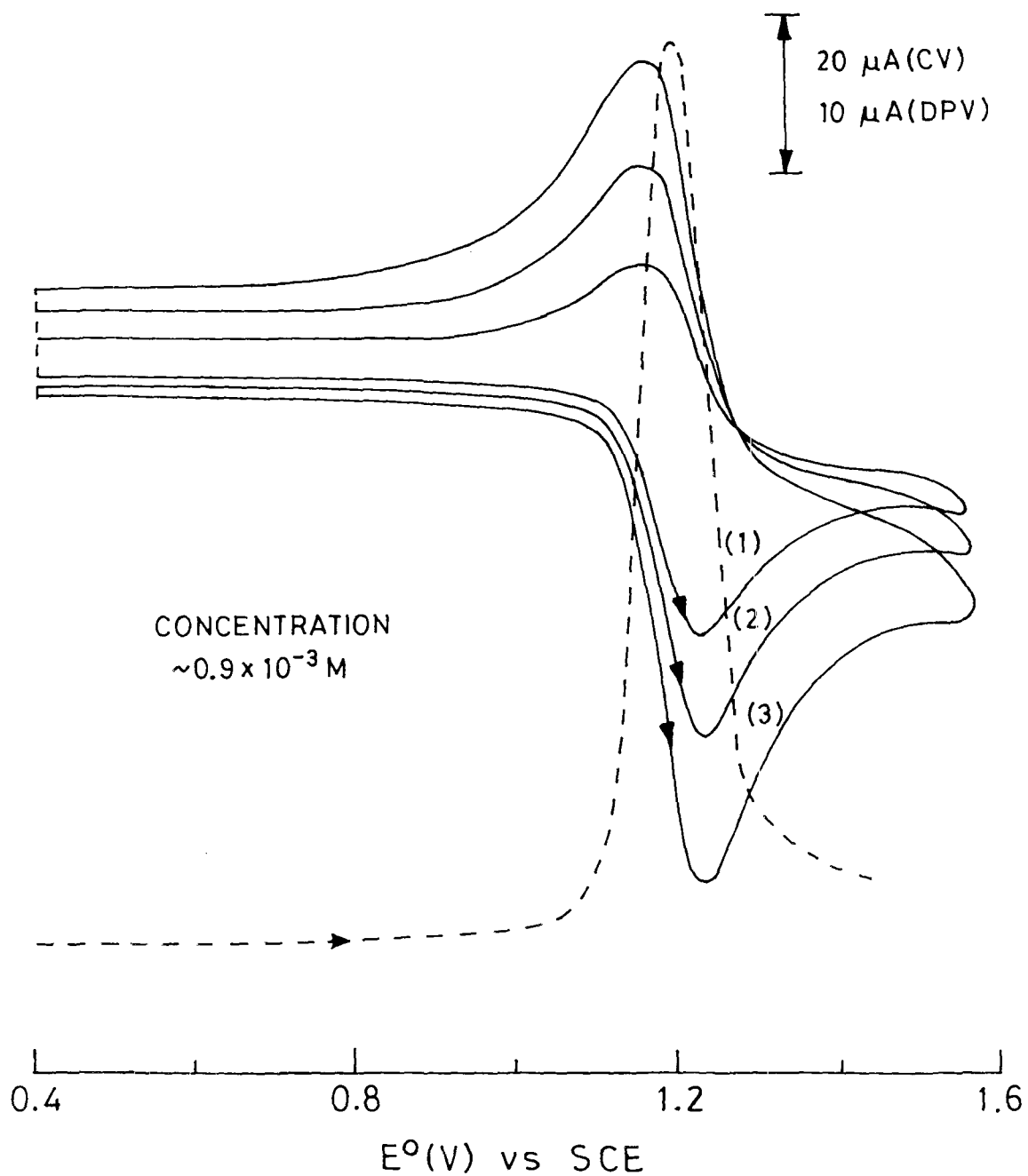


FIGURE III.5 VOLTAMMOGRAMS OF $\text{ctc-}[\text{Os}(\text{NO}_2)_2\text{L}_2]$ IN MeCN. SCAN RATES : FOR CV(—), (1) 50, (2) 100, (3) 200 mVs^{-1} ; FOR DPV(---), 10 mVs^{-1}

TABLE III. 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
ctc-[Os(NO ₂) ₂ L ¹ ₂] (5a)	0.51 (60)	0.90 (80)	1.89
ccc-[Os(NO ₂) ₂ L ¹ ₂] (6a)	0.52 (60)	0.90 (80)	1.91
ctc-[Os(NO ₂) ₂ L ² ₂] (5b)	0.54 (70)	0.92 (85)	1.96
ccc-[Os(NO ₂) ₂ L ² ₂] (6b)	0.53 (60)	0.89 (80)	1.98
ctc-[Os(NCS) ₂ L ¹ ₂] (5c)	0.52 (60)	0.91 (80)	1.88
ccc-[Os(NCS) ₂ L ¹ ₂] (6c)	0.53 (70)	0.92 (75)	1.91
ctc-[Os(NCS) ₂ L ² ₂] (5d)	0.50 (60)	0.88 (75)	1.92
ccc-[Os(NCS) ₂ L ² ₂] (6d)	0.54 (70)	0.90 (80)	1.97
ctc-[Os(N ₃) ₂ L ¹ ₂] (5e)	0.53 (70)	0.90 (85)	1.95
ccc-[Os(N ₃) ₂ L ¹ ₂] (6e)	0.52 (70)	0.88 (90)	1.94
ctc-[Os(N ₃) ₂ L ² ₂] (5f)	0.55 (70)	0.93 (90)	1.93
ccc-[Os(N ₃) ₂ L ² ₂] (6f)	0.51 (65)	0.89 (90)	1.97

^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.

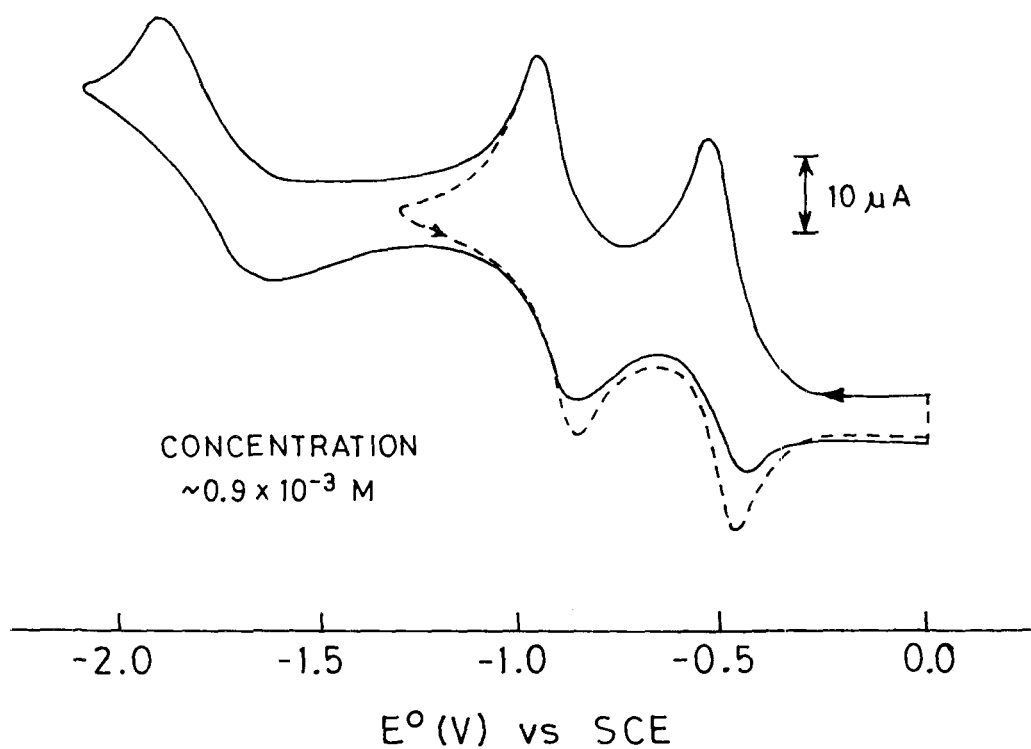


FIGURE III.6 CYCLIC VOLTAMMOGRAM OF $\text{ctc-}[\text{Os}(\text{NO}_2)_2\text{L}^1_2]$ IN MeCN. THE REPRESENTATION (---) SHOWS VOLTAMMOGRAM WHERE THE SCAN WAS REVERSED BEFORE REACHING THE THIRD REDUCTION WAVE

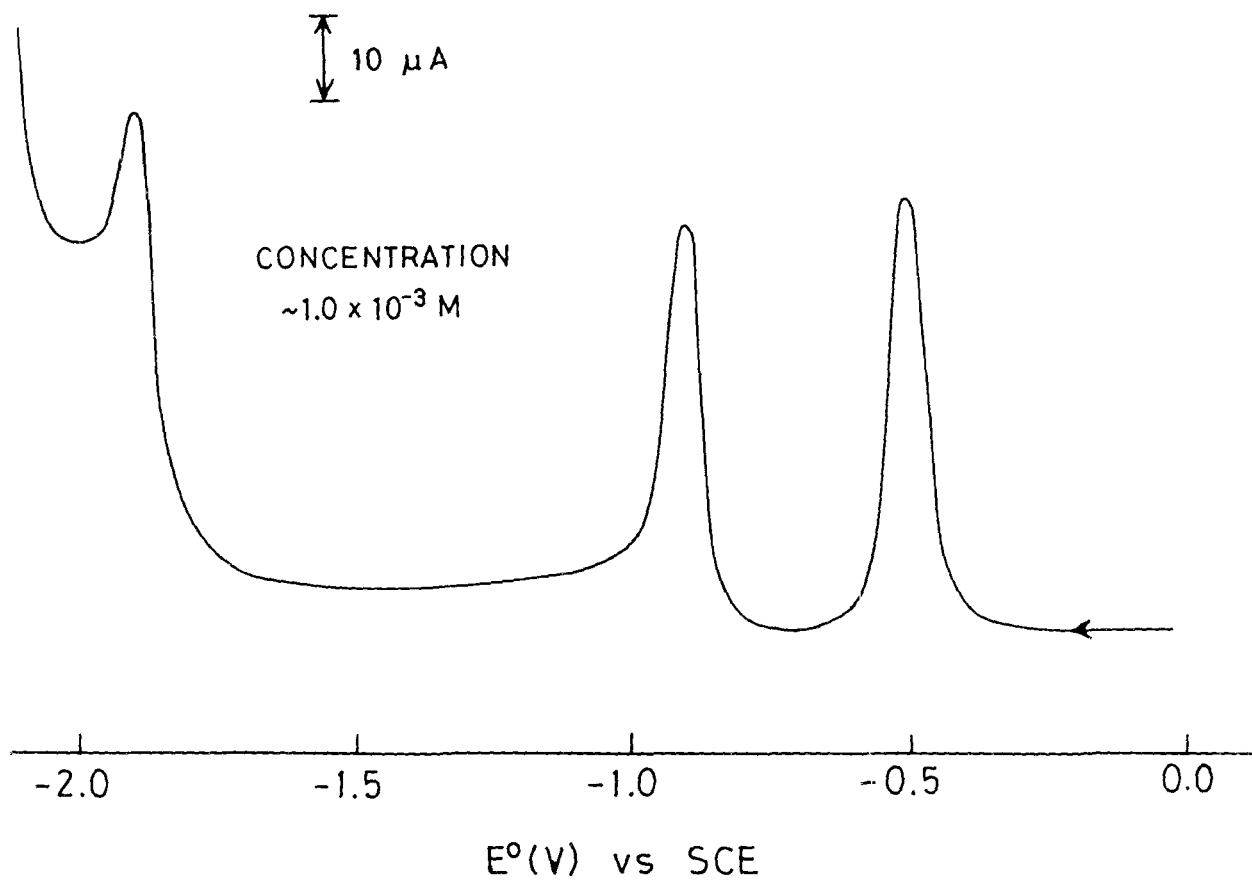


FIGURE III.7. DIFFERENTIAL PULSE VOLTAMMOGRAM OF $\text{ctc-}[\text{Os}(\text{NO}_2)_2\text{L}^1_2]$ IN MeCN. SCAN RATE, 10 mVs^{-1}

reductions involve electron transfer to azo fragment of the azoimine group as are described in the previous chapter. A comparison of current heights of these three reductive responses with that of the oxidation process (in couple 2) in DPV experiments is of help to ascertain the one-electron nature.

F. CONCLUSION

This work pertains to the chemistry of a series of stable osmium(II)-L complexes containing anionic monodentate N-donor ligands (A). Isomerically pure $[\text{OsA}_2\text{L}_2]$ compounds differing in the disposition of the OsL_2 group are isolated via stereoretentive reaction of A with $[\text{OsX}_2\text{L}_2]$ (**2/3**) in aqueous ethanol. The complexes provide unique opportunity for studying both metal-centred and ligand-based electron transfers. They have rich electronic spectra – displaying both spin-allowed and spin-forbidden charge-transfer transitions. In the next chapter we will describe the reaction behaviour of **2** towards some pyridine bases.

III.3 EXPERIMENTAL SECTION

A. PREPATION OF COMPOUNDS

(a) Chemicals, solvents and starting materials

The chemicals and solvents used for the preparative procedure were stated in **Chapter II**. The other chemicals used here are sodium nitrite, ammonium thiocyanate and sodium azide. BDH (India); ethanol, Bengal Chemicals (India). All other solvents and chemicals used were of reagent grade available commercially and were used without further purification.

(b) Ligands

(i) Nitrosobenzene and *m*-nitrosotoluene

These were prepared from nitrobenzene and *m*-nitrotoluene as described in the literature¹⁵.

(ii) 2-(Phenylazo)pyridine (L^1)

The preparative procedure is the same as described in **Chapter II**.

(iii) 2-(*m*-Tolylazo)pyridine (L^2)

This was prepared using the same procedure as described in **Chapter II**.

(c) Precursors

The isomeric dihalo complexes, *cis*, *trans*, *cis*-[OsX₂L₂] and *cis*, *cis*, *cis*-[OsX₂L₂] (**2** and **3**) (X = Cl or Br; L = L¹ or L²) were prepared following same procedure¹ as was used by Ghosh et al. Of the chloro and bromo, the latter were taken for the synthesis of **5a-5f** and **6a-6f** as the reactions were faster and better yields were obtainable.

(d) Complexes

(i) *Cis*, *trans*, *cis*-Dinitrobis[2-(phenylazo)pyridine]osmium(II), *ctc*-[Os(NO₂)₂L¹₂] (**5a**)

To a suspension of 0.1 g (0.139 mmol) of *cis*, *trans*, *cis*-[OsBr₂L¹₂] in 15 ml EtOH-H₂O (2:1) was added 0.05 g (0.72 mmol) of NaNO₂. The mixture was heated to reflux under dinitrogen atmosphere for 6 h. The red-violet solution was concentrated and then cooled. The precipitate thus formed was collected by filtration, washed thoroughly with water and dried. The solid was redissolved in a minimum of dichloromethane and was loaded on a silica gel (60 - 120 mesh; BDH, India) column (20 x 1 cm). A small blue-violet band was eluted first with dichloromethane. Finally the slow moving red-violet band was collected with benzene-acetonitrile (3:1). On slow evaporation of the eluant shining crystals of **5a** resulted; the yield was 0.072 g (80%).

(ii) *Cis*, *cis*, *cis*-Dinitrobis[2-(phenylazo)pyridine]osmium(II), *ccc*-[Os(NO₂)₂L¹₂] (**6a**)

6a was prepared using the same solvent, procedure and stoichiometry as in **5a** except that 0.1 g (0.139 mmol) of *ccc*-[OsBr₂L¹₂] instead of *ctc*-[OsBr₂L¹₂] was used. Yield, 0.077 g (85%).

(iii) *Cis*, *trans*, *cis*-Dinitrobis[2-(*m*-tolylazo)pyridine]osmium(II), *ctc*-[Os(NO₂)₂L²₂] (**5b**)

5b was isolated similarly as in **5a**. Here 0.1 g (0.134 mmol) of *ctc*-[OsBr₂L²₂] was taken instead of *ctc*-[OsBr₂L¹₂]. Yield, 0.071 g (80%).

(iv) *Cis*, *cis*, *cis*-Dinitrobis[2-(*m*-tolylazo)pyridine]osmium(II), *ccc*-[Os(NO₂)₂L²₂] (**6b**)

The preparative procedure was the same as described in the synthesis of **5b** except that 0.1 g (0.134 mmol) of *ccc*-[OsBr₂L²₂] was reacted with 0.05 g (0.72 mmol) of NaNO₂. Yield was 0.076 g (85%).

(v) *Cis, trans, cis-Dithiocyanatobis[2-(phenylazo)pyridine]osmium(II), ctc-[Os(NCS)₂L¹₂]* (**5c**)

To prepare **5c** 0.1 g (0.139 mmol) of *ctc*-[OsBr₂L¹₂] was reacted with 0.05 g (0.65 mmol) of NH₄NCS. The mixture was heated to reflux under dinitrogen atmosphere for 8 h. The red-violet solution was concentrated and cooled to have the desired product; yield, 0.075 g (80%).

(vi) *Cis, cis, cis-Dithiocyanatobis[2-(phenylazo)pyridine]osmium(II), ccc-[Os(NCS)₂L¹₂]* (**6c**)

6c was prepared using the same procedure as described in the formation of **5c** except that 0.1 g (0.139 mmol) of *ccc*-[OsBr₂L¹₂] was reacted with 0.05 g (0.65 mmol) of NH₄NCS. The yield was 0.08 g (85%).

(vii) *Cis, trans, cis-Dithiocyanatobis[2-(*m*-tolylazo)pyridine]osmium(II), ctc-[Os(NCS)₂L²₂]* (**5d**)

The preparative procedure was the same as in the preparation of **5c** except that 0.1 g (0.134 mmol) of *ctc*-[OsBr₂L²₂] was reacted 0.05 g (0.65 mmol) of NH₄NCS; yield, 0.075 (80%).

(viii) *cis, cis, cis-Dithiocyanatobis[2-(*m*-tolylazo)pyridine]osmium(II), ccc-[Os(NCS)₂L²₂]* (**6d**)

6d was prepared using the same reaction stoichiometry and conditions as in **5d** except that *ctc*-[OsBr₂L²₂] was replaced by *ccc*-[OsBr₂L²₂]; yield, 0.08 g (85%).

(ix) *Cis, trans, cis-Diazidobis[2-(phenylazo)pyridine]osmium(II), ctc-[Os(N₃)₂L¹₂]* (**5e**)

To isolate **5e** 0.1 g (0.139 mmol) of *ctc*-[OsBr₂L¹₂] was reacted with 0.05 g (0.77 mmol) of NaN₃. The mixture was refluxed under dinitrogen atmosphere for 8 h. The red-violet solution was processed as in **5a** or **5c** to have analytically pure **5e**. The yield was 0.069g (80%).

(x) *Cis, cis, cis-Diazidobis[2-(phenylazo)pyridine]osmium(II), ccc-[Os(N₃)₂L¹₂]* (**6e**)

6e was prepared following the similar procedure as in **5e** except that *ctc*-[OsBr₂L¹₂] was replaced by *ccc*-[OsBr₂L¹₂]; yield, 0.073 g (85%).

(xi) *Cis, trans, cis-Diazidobis[2-(*m*-tolylazo)pyridine]osmium(II), ctc-[Os(N₃)₂L²₂]* (**5f**)

To prepare **5f** the same procedure was followed as in *ctc*-[Os(N₃)₂L¹₂] (**5e**). Here 0.1 g (0.134 mmol) of *ctc*-[OsBr₂L²₂] was reacted with 0.05 g (0.77 mmol) of NaN₃; yield 0.074 g (80%).

(xii) *Cis, cis, cis-Diazidobis[2-(m-tolylazo)pyridine]osmium(II), $ccc-[Os(N_3)_2L^2_2]$ (6f)*

The preparative procedure was the same as in *ctc*- $[Os(N_3)_2L^2_2]$ (**5f**). Here the *ctc*- $[OsBr_2L^2_2]$ isomer was replaced by *ccc*- $[OsBr_2L^2_2]$; yield 0.078 g (85%).

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 III.7**.

C. PHYSICAL MEASUREMENTS

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

TABLE III. 7

Characterisation Data

Compound	%C		%H		%N	
	Calcd	Found	Calcd	Found	Calcd	Found
ctc-[Os(NO ₂) ₂ L ¹ ₂] (5a) C ₂₂ H ₁₈ N ₈ O ₄ Os	40.7	40.5	2.8	2.9	17.3	17.4
ccc-[Os(NO ₂) ₂ L ¹ ₂] (6a) C ₂₂ H ₁₈ N ₈ O ₄ Os	40.7	40.8	2.8	2.9	17.3	17.2
ctc-[Os(NO ₂) ₂ L ² ₂] (5b) C ₂₄ H ₂₂ N ₈ O ₄ Os	42.6	42.3	3.3	3.2	16.6	16.7
ccc-[Os(NO ₂) ₂ L ² ₂] (6b) C ₂₄ H ₂₂ N ₈ O ₄ Os	42.6	42.4	3.3	3.3	16.6	16.7
ctc-[Os(NCS) ₂ L ¹ ₂] (5c) C ₂₄ H ₁₈ N ₈ S ₂ Os	42.9	42.5	2.7	2.8	16.6	16.3
ccc-[Os(NCS) ₂ L ¹ ₂] (6c) C ₂₄ H ₁₈ N ₈ S ₂ Os	42.9	43.0	2.7	2.6	16.6	16.8
ctc-[Os(NCS) ₂ L ² ₂] (5d) C ₂₆ H ₂₂ N ₈ S ₂ Os	44.6	44.2	3.2	3.2	16.0	16.1
ccc-[Os(NCS) ₂ L ² ₂] (6d) C ₂₆ H ₂₂ N ₈ S ₂ Os	44.6	44.4	3.2	3.1	16.0	16.2
ctc-[Os(N ₃) ₂ L ¹ ₂] (5e) C ₂₂ H ₁₈ N ₁₂ Os	41.2	40.8	2.8	2.6	26.2	26.5
ccc-[Os(N ₃) ₂ L ¹ ₂] (6e) C ₂₂ H ₁₈ N ₁₂ Os	41.2	41.4	2.8	2.8	26.2	26.0
ctc-[Os(N ₃) ₂ L ² ₂] (5f) C ₂₄ H ₂₂ N ₁₂ Os	43.1	43.4	3.3	3.4	25.1	25.6
ccc-[Os(N ₃) ₂ L ² ₂] (6f) C ₂₄ H ₂₂ N ₁₂ Os	43.1	43.6	3.3	3.5	25.1	25.5

REFERENCES

1. B. K. Ghosh, S. Goswami and A. Chakravorty, *Inorg. Chem.*, 1983, **22**, 3358.
2. B. K. Ghosh, *Ph. D. Thesis*, The Jadavpur University, 1985.
3. A. K. Mahapatra, B. K. Ghosh, S. Goswami and A. Chakravorty, *J. Indian Chem. Soc.*, 1986, **63**, 101.
4. (a) F. P. Dwyer, H. A. Goodwin and E. C. Gyarmas, *Aust. J. Chem.* 1963, **16**, 42, 544; (b) D. A. Buckingham, F. P. Dwyer, H. A. Goodwin and A. M. Sargeson, *Aust. J. Chem.* 1964, **17**, 315, 325.
5. W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
6. R. A. Krause and K. Krause, *Inorg. Chem.*, 1982, **21**, 1714.
7. S. Wolfgang, T. C. Streckas, H. D. Gafney, R. A. Krause and K. Krause, *Inorg. Chem.*, 1984, **23**, 2650.
8. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edn, John Wiley, New York, 1978, p 270.
9. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edn, John Wiley, New York, 1978, p 278.
10. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edn, John Wiley, New York, 1978, p 220.
11. B. K. Ghosh, A. Mukhopadhyay, S. Goswami, S. Ray and A. Chakravorty, *Inorg. Chem.*, 1984, **23**, 4633.
12. (a) B. J. Pankuch, D. E. Lacky and G. A. Crosby, *J. Phys. Chem.*, 1980, **84**, 2061; (b) S. Decurtins, F. Felix, J. Ferguson, H. U. Güdel and A. Ludi, *J. Am. Chem. Soc.*, 1980, **102**, 4102.
13. E. M. Kober and T. J. Meyer, *Inorg. Chem.*, 1982, **21**, 3967.
14. B. K. Ghosh and A. Chakravorty, *Coord. Chem. Rev.*, 1989, **95**, 239.
15. (a) B. S. Raghavendra and A. Chakravorty, *Indian. J. Chem. Sect. A*, 1976, **14A**, 166; (b) B. S. Raghavendra, *Ph. D. Thesis*, Indian Institute of Technology, Kanpur, 1977.