

CHAPTER VI

MIXED DIOXOLENE-L COMPLEXES OF OSMIUM(II)

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ABSTRACT : The reaction of both blue-violet (**2**) and red-violet (**3**) isomers of $[\text{OsX}_2\text{L}_2]$ [$\text{X} = \text{Cl}$ or Br and L (**1**) = 2-(phenylazo)pyridine (L^1) and 2-(*m*-tolylazo)pyridine (L^2)] with catechol and its substituted derivative (H_2Q) in boiling aqueous ethanol affords mixed-tris complexes of the type $[\text{OsQL}_2]$ (**4** and **5**, respectively). The complexes have been characterised by physicochemical, spectroscopic and magnetic results. From ^1H NMR spectra (taking δ_{Me} of L^2 as probe) the stereoretentivity of the reaction is proposed. The diamagnetic complexes display a number of spin-allowed and spin-forbidden charge transfer transitions in the 1200 - 200 nm region. Both **4** and **5** are electroactive and display six voltammetric responses — two oxidations and four reductions. EPR study of the coulometrically generated one-electron oxidation product suggests the involvement of semiquinone radical formation.

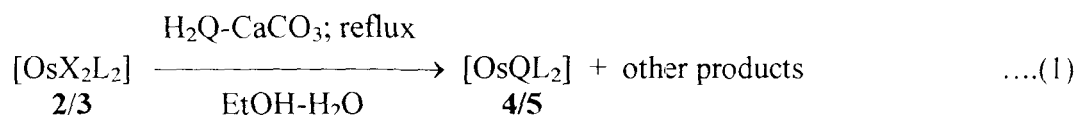
VI.1 INTRODUCTION

The quinone ligand system (H_2Q) has received much attention in the past few years¹⁻⁶ due to structural characterisation, identification of effective oxidation levels (hydroquinone, semiquinone and quinone) and the quite rich electrochemistry. The ruthenium and osmium chemistry of Q in combination with 2,2'-bipyridine (bpy)^{3,5} is well established. Similar chemistry of Q with L (**1**) in ruthenium⁶ bound state is reported. However, corresponding osmium chemistry remains unexplored. As a part of our program on the reaction behaviour of isomeric $[OsX_2L_2]$ ($X = Cl$ or Br) (**2** and **3**) towards different mono- and bidentate ligands, we have examined here reactivity of **2** and **3** towards two quinone ligands, catechol (H_2Q^1) and tetrachlorocatechol (H_2Q^2). Successful synthesis of the isomeric complexes of the type $[OsQL_2]$ (**4** and **5**) via stereoretentive reaction of $[OsX_2L_2]$ (**2** and **3**, respectively) with H_2Q and their spectroscopic and electrochemical properties are described below.

VI.2 RESULTS AND DISCUSSION

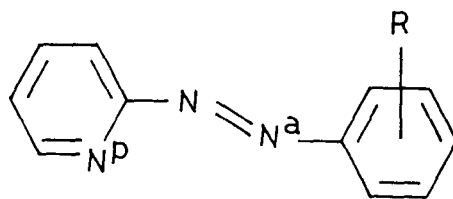
A. SYNTHESIS

Reaction of $[OsX_2L_2]$ with an excess of H_2Q , a dibasic acid, proceeds slowly but smoothly in boiling aqueous ethanol in the presence of suspended $CaCO_3$ (heterogeneous base), which neutralises⁷ the liberated acid. The reaction is shown in **equation 1**. To hasten the reaction, H_2Q



was used in five-fold excess. Of the two **2** and **3**, the latter is more reactive. With tetrachlorocatecholate the reaction time is shorter and even in the absence of a base the reaction completes, which is evidently due to better acidity of H_2Q^2 over H_2Q^1 . By changing the solvent matrix from aqueous ethanol (b.p., 351 K) to aqueous 2-methoxyethanol (b.p., 398 K), reaction 1 proceeds much faster, but isomeric homogeneity is lost (see below, ¹H NMR results). A mixture of **4** and **5** was obtained from either **2** or **3**. The presence of high boiling solvent 2-methoxyethanol (b.p., 398 K) is presumably one major responsible factor for the reorganisation in the OsL_2 coordination frame.

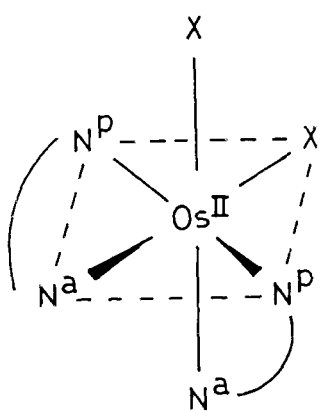
The complexes (**4** and **5**) were characterised by elemental (C, H and N) analyses, solution electrical conductivity measurements, spectroscopic (IR, NMR, EPR and UV-Vis) properties and



$R = H; L^1$

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

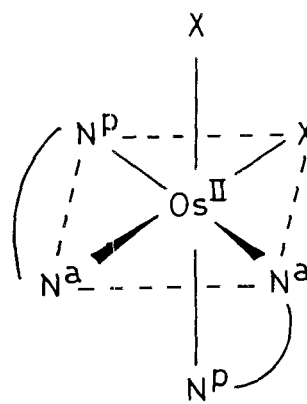
L; 1



$X = Cl, Br$

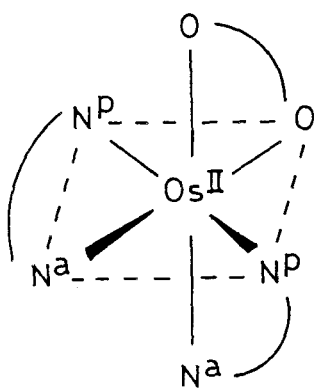
ctc

2

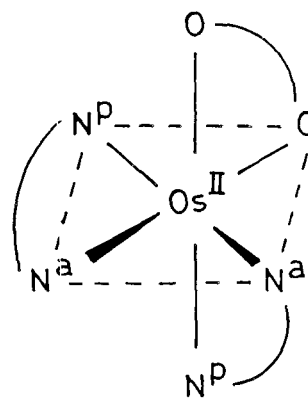


ccc

3



4



5

CHART VI.1

electrochemical results (**Tables** VI.1 - VI.7). The air stable moisture insensitive red complexes are soluble in common organic solvents like alcohols, chloroform, dichloromethane, acetonitrile and insoluble in water. In MeCN, **4** and **5** behave as non-electrolytes as reflected⁸ from their low conductivity values ($0 - 5 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$) at 298 K (**Table** VI.1). Room temperature magnetic susceptibility measurements show that the complexes **4** and **5** are uniformly diamagnetic (idealised t_{2g}^6 ; $S = 0$).

B. INFRARED SPECTRA

IR spectra of the complexes were recorded in KBr discs ($4000 - 300 \text{ cm}^{-1}$). The results are summarised in **Table** VI.2. Representative spectral nature is shown in **Figure** VI.1. Only the pertinent results are considered here. $\nu(\text{C}=\text{N})$ and $\nu(\text{N}=\text{N})$ modes of the complexed L are observed at $\sim 1590 \text{ cm}^{-1}$ and $>1280 \text{ cm}^{-1}$, respectively. The shift of $\nu(\text{N}=\text{N})$ towards higher frequency from $[\text{OsX}_2\text{L}_2]$ to $[\text{OsQL}_2]$ suggests⁹ less osmium-azo π -back bonding in the latter. Of the two **4** and **5**, the latter has $\nu(\text{N}=\text{N})$ frequency in lower energy position reflecting better π -acceptance properties of L in *cis, cis, cis* geometry over *cis, trans, cis* geometry as was the case¹⁰ in **2** [$\nu(\text{N}=\text{N}), 1280 \text{ cm}^{-1}$] and **3** [$\nu(\text{N}=\text{N}), 1275 \text{ cm}^{-1}$]. The typical metal bound $\nu(\text{C}-\text{O})$ of Q is seen at $\sim 1100 \text{ cm}^{-1}$. All other characteristic L vibrations are invariably seen in the $1600 - 600 \text{ cm}^{-1}$ range.

C. ¹H NMR SPECTRA

¹H NMR investigations of selected complexes were made in order to solve the stereochemical question in **4** and **5**. The L^2 methyl signal (δ_{Me}) is particularly useful in this regard. Relevant results are shown in **Table** VI.3 and **Figure** VI.2. A single sharp methyl signal at $\sim 2.2 \text{ ppm}$ is observed for *cis, trans, cis*- $[\text{OsQL}_2]$ (**4**) complexes obtained from **2** via reaction 1. Thus the two-fold axis of **2** is retained in the product. Mixed-tris $[\text{OsQL}_2]$ (**5**) complexes resulting from the reaction of H_2Q and **3** show two equally intense methyl signals at ~ 2.2 and $\sim 2.3 \text{ ppm}$ (**Figure** VI.2) demonstrating that $[\text{OsL}_2]$ group has the same symmetry as in **3**. Thus the transformations **2**→**4** and **3**→**5** in reaction 1 proceeds in a stereoretentive manner. A change in solvent from ethanol to 2-methoxyethanol occurs with reorganisation in the coordination sphere leading to a mixture of both *ctc* and *ccc* isomers (see **Figure** VI.2) of $[\text{OsQL}_2]$. Considering the mild

TABLE VI.1

Molar Conductivity data^a in MeCN at 298 K

Compound	Λ_M (ohm ⁻¹ cm ² mol ⁻¹)
ctc-[OsQ ¹ L ¹ ₂] (4a)	5
ccc-[OsQ ¹ L ¹ ₂] (5a)	4
ctc-[OsQ ¹ L ² ₂] (4b)	5
ccc-[OsQ ¹ L ² ₂] (5b)	4
ctc-[OsQ ² L ¹ ₂] (4c)	6
ccc-[OsQ ² L ¹ ₂] (5c)	5
ctc-[OsQ ² L ² ₂] (4d)	6
ccc-[OsQ ² L ² ₂] (5d)	6

^aSolute concentration, ~ 10⁻³ M.

TABLE VI. 2

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

Compound	$\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})^c$	$\nu(\text{N}=\text{N})^d$	$\nu(\text{C}-\text{O})^e$
ctc-[OsQ ¹ L ¹ ₂] (4a)	1592	1288	1102
ccc-[OsQ ¹ L ¹ ₂] (5a)	1590	1285	1102
ctc-[OsQ ¹ L ² ₂] (4b)	1590	1290	1100
ccc-[OsQ ¹ L ² ₂] (5b)	1588	1286	1102
ctc-[OsQ ² L ¹ ₂] (4c)	1588	1288	1102
ccc-[OsQ ² L ¹ ₂] (5c)	1592	1285	1104
ctc-[OsQ ² L ² ₂] (4d)	1590	1290	1103
ccc-[OsQ ² L ² ₂] (5d)		1286	1104

^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 $\nu(\text{C}-\text{O})$, sharp and strong.

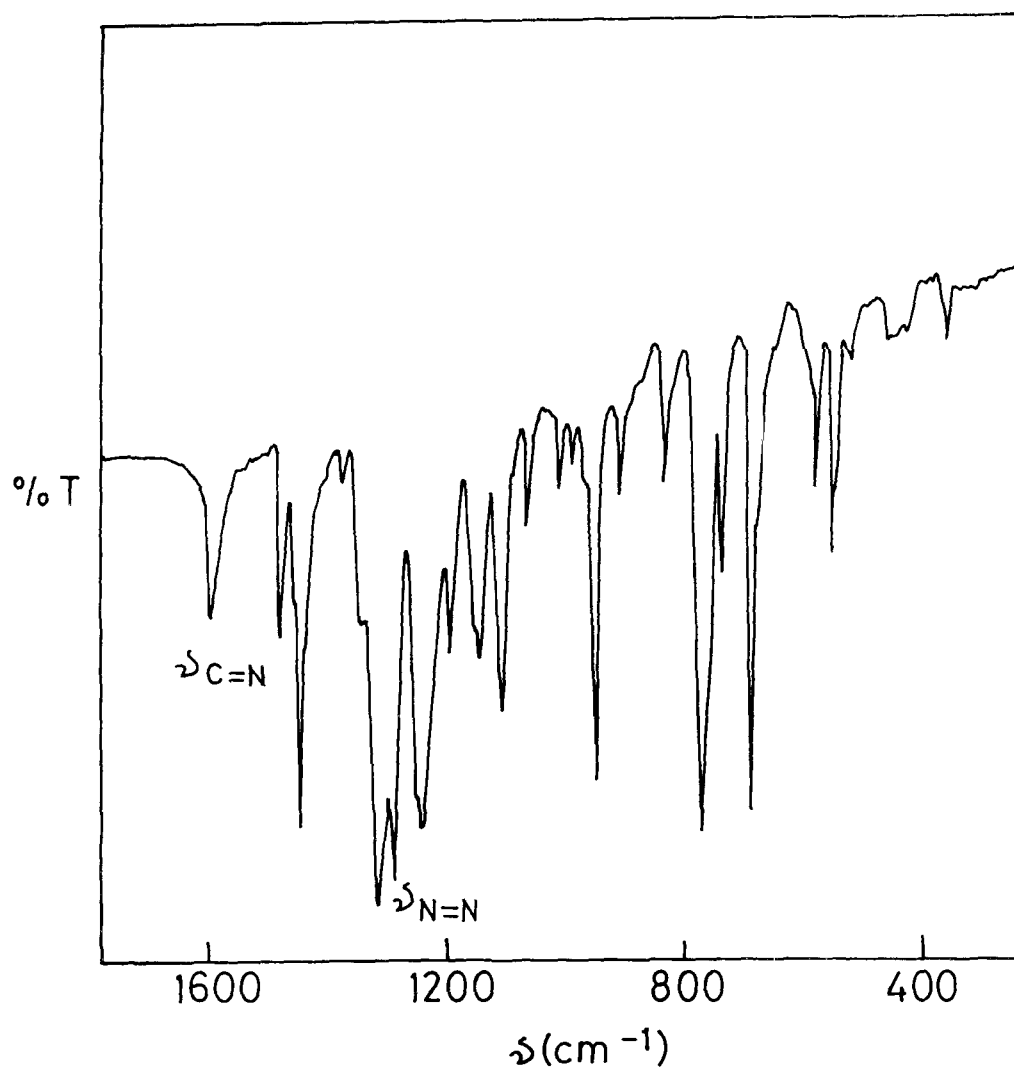


FIGURE VI.1. IR SPECTRUM OF $ctc-[OsQ^2L^2_2]$ IN KBr DISC

TABLE VI. 3

 ^1H NMR Data^{a-c} of L^2 Complexes

Compound	(ppm)
ctc- $[\text{OsQ}^1 \text{L}^2_2]$ (4b)	2.23
ccc- $[\text{OsQ}^1 \text{L}^2_2]$ (5b)	2.16, 2.29
ctc- $[\text{OsQ}^2 \text{L}^2_2]$ (4d)	2.29
ccc- $[\text{OsQ}^2 \text{L}^2_2]$ (5d)	2.21, 2.35

^a SiMe_4 used as internal standard. ^bAromatic proton signals not tabulated. ^cSolvent, CDCl_3 .

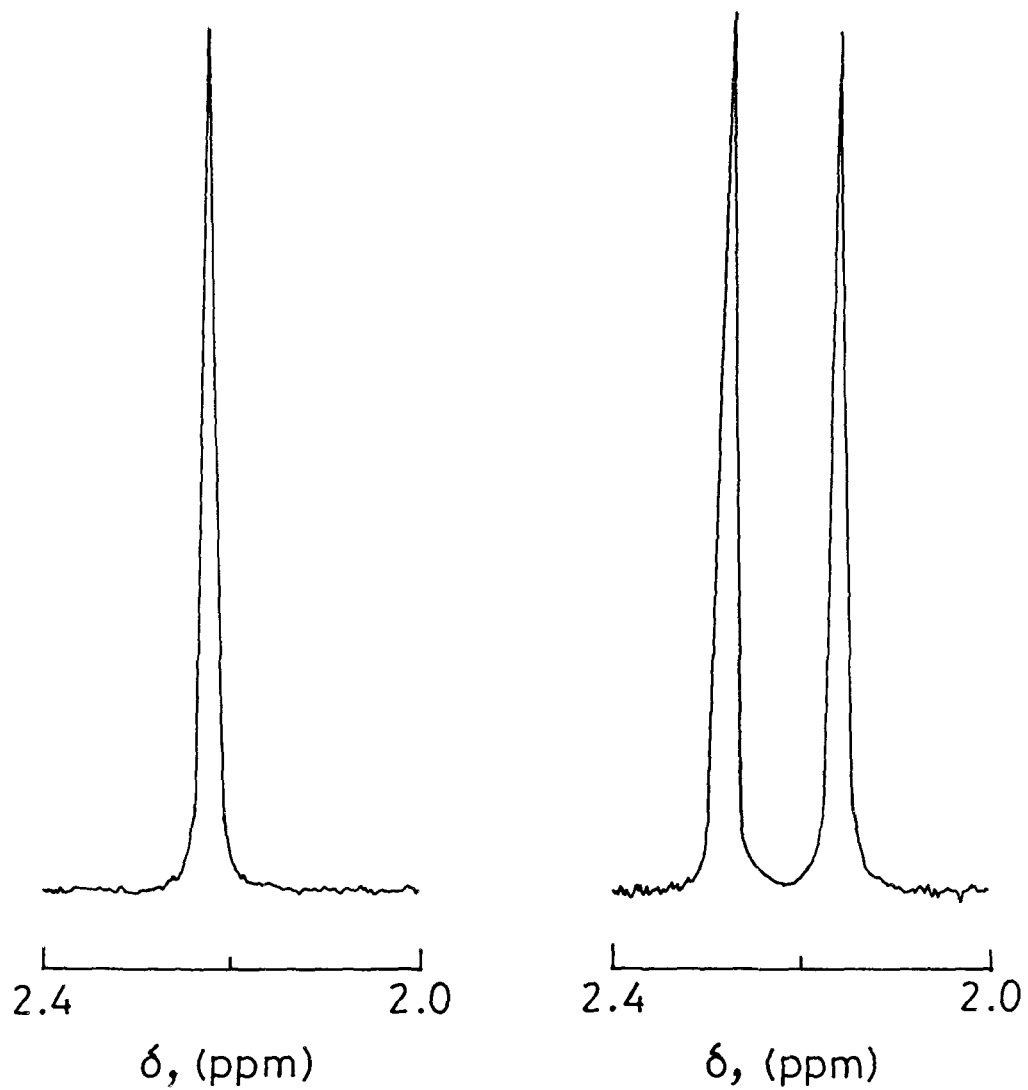


FIGURE VI.2. ^1H NMR SPECTRA (Me SIGNALS) OF $\text{ctc-}[\text{OsQ}^1\text{L}^2_2]$ IN CDCl_3

reaction conditions in ethanol over to 2-methoxyethanol, the mononuclear complex **4/5** is expected to have the same gross geometry as in **2/3**.

D. CHARGE-TRANSFER SPECTRA

The complexes exhibit several absorptions bands and shoulders in the 1200 - 200 nm region. Spectral data are set in **Table VI.4** and representative spectral pattern is shown in **Figure VI.3**. Though solution colour of the complexes **4** and **5** with a particular Q is same (orange-red), the recorded spectra have sharp difference. A characteristic feature of the orange-red solution is an intense band at ~550 nm with a shoulder at ~425 nm. A number of weak spin-forbidden^{11,12} transitions at lower energies are also observable in all complexes. These are assigned to be metal-to-ligand charge transfer (MLCT) transitions within the framework of pseudooctahedral osmium(II) geometry. The strong bands at higher energies could be due to intraligand $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions described in earlier chapters.

E. REDOX BEHAVIOUR

The electroactivity of the complexes was examined in MeCN solutions using voltammetry (CV and DPV) and coulometry at a platinum and a glassy carbon working electrodes. The results are summarised in **Tables VI.5** and **VI.6**. Representative voltammograms are portrayed in **Figures VI.4**, **VI.5**, **VI.7** and **VI.8**. The DPV technique is particularly useful in observing responses close to solvent cut-off regions.

(a) Oxidations

The complexes exhibit two successive oxidative responses at ~0.4 - 0.8 V and 1.0 - 1.3 V ranges. The responses (**equations 2** and **3**) are reproducible with no trace of decomposition after



a number of cycles. The voltammetric nature of the electrode reaction in couple 2 is shown in **Figure VI.4**. One-electron nature of this couple was confirmed from constant potential electrolyses and that of 3 from a comparison of current height (**Figure VI.5**) with that of couple 2 in DPV experiments. The substituent on Q has strong effect on the potential of couple 2 reflecting involvement of hydroquinone to semiquinone oxidation. The EPR spectrum of

TABLE VI. 4

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

Compound	λ_{max} , nm (ϵ , M ⁻¹ cm ⁻¹)
ctc-[OsQ ¹ L ¹ ₂] (4a)	1110 (790), 960 ^c (1,620), 805 (2,510), 715 ^c (2,090), 560 (7,480), 440 ^c (6,950), 372 (14,410), 310 (21,250)
ccc-[OsQ ¹ L ¹ ₂] (5a)	1102 (820), 955 ^c (1,680), 795 (2,560), 710 ^c (2,250), 555 (7,520), 425 ^c (7,190), 358 ^c (14,610), 310 (21,290)
ctc-[OsQ ¹ L ² ₂] (4b)	1115 (840), 965 ^c (1,670), 805 (2,670), 715 ^c (2,270), 560 (7,700), 440 ^c (7,300), 375 ^c (14,700), 310 (21,780)
ccc-[OsQ ¹ L ² ₂] (5b)	1105 (860), 958 ^c (1,770), 795 (2,780), 710 ^c (2,340), 555 (7,790), 430 ^c (7,420), 360 ^c (14,870), 310 (21,910)
ctc-[OsQ ² L ¹ ₂] (4c)	1075 (1,050), 942 ^c (1,930), 773 (3,010), 690 ^c (2,570), 540 (7,870), 420 ^c (7,520), 350 (14,810), 310 (21,950)
ccc-[OsQ ² L ¹ ₂] (5c)	1066 (1,160), 935 ^c (2,040), 762 (3,350), 678 (2,650), 535 (7,840), 406 (7,640), 350 ^c (14,920), 309 (22,210)
ctc-[OsQ ² L ² ₂] (4d)	1080 (1,120), 945 ^c (2,040), 775 (3,400), 690 ^c (2,690), 540 (8,010), 420 ^c (7,800), 355 ^c (15,120), 310 (22,800)
ccc-[OsQ ² L ² ₂] (5d)	1070 (1,240), 940 ^c (2,110), 765 (3,520), 680 ^c (2,730), 535 (8,190), 410 ^c (7,890), 350 ^c (15,300), 308 (22,840)

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

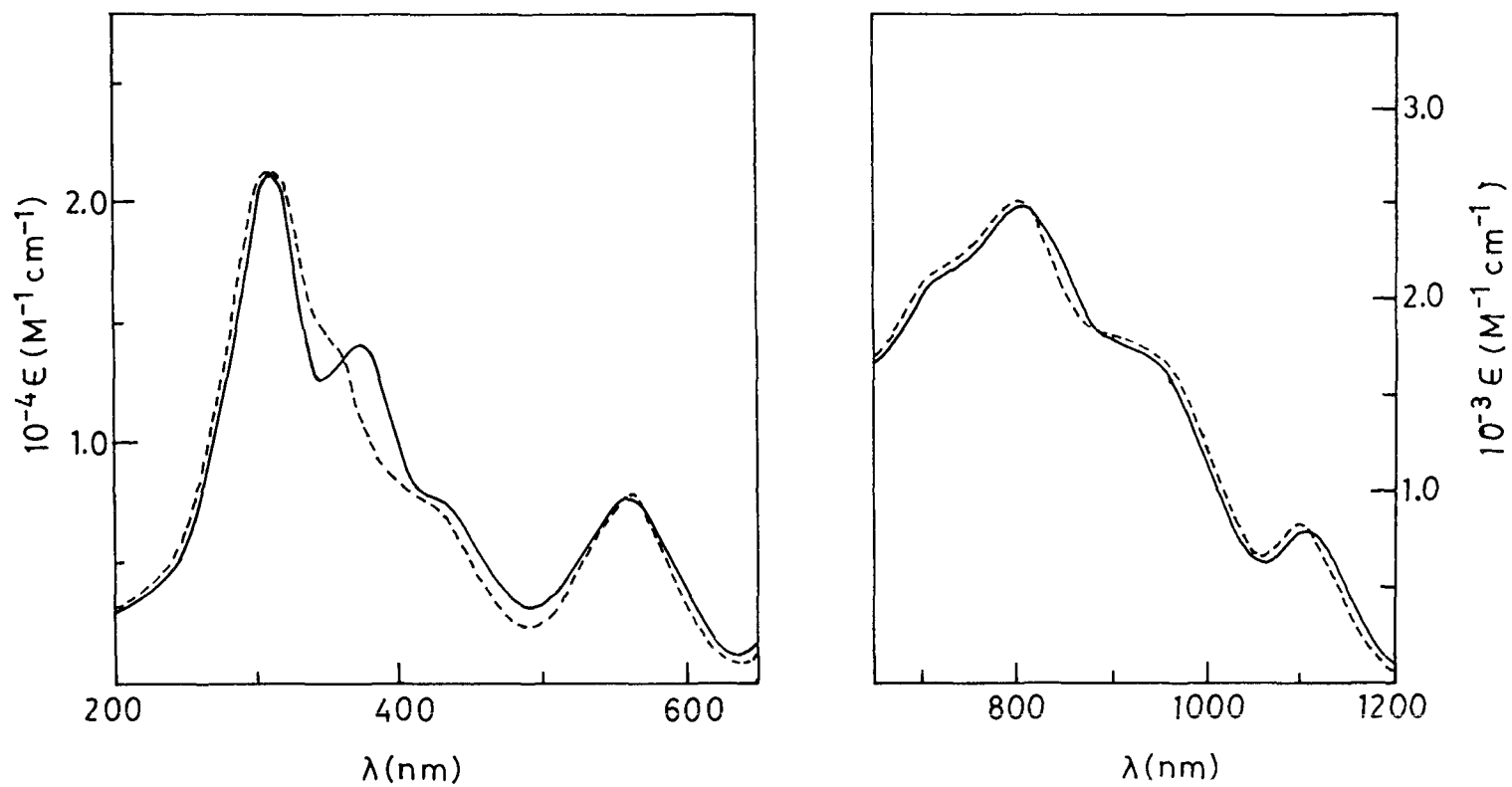


FIGURE VI.3. ELECTRONIC SPECTRA OF *ctc*-[OsQ¹L¹₂] (—) AND *ccc*-[OsQ¹L¹₂] (- - -) IN MeCN AT 298 K

TABLE VI. 5

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

Compound	q - sq	Os(III) - Os(II)
	E ⁰ , V (ΔE_p , mV)	E ⁰ , V (ΔE_p , mV)
ctc-[OsQ ¹ L ¹ ₂] (4a)	0.39 (60)	1.01 (100)
ccc-[OsQ ¹ L ¹ ₂] (5a)	0.39 (60)	0.99 (100)
ctc-[OsQ ¹ L ² ₂] (4b)	0.39 ^{de} (60)	1.00 (100)
ccc-[OsQ ¹ L ² ₂] (5b)	0.39 (60)	0.98 (100)
ctc-[OsQ ² L ¹ ₂] (4c)	0.82 ^{df} (60)	1.20 (110)
ccc-[OsQ ² L ¹ ₂] (5c)	0.82 (60)	1.18 (110)
ctc-[OsQ ² L ² ₂] (4d)	0.82 (60)	1.19 (110)
ccc-[OsQ ² L ² ₂] (5d)	0.82 (60)	1.16 (110)

^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 $n = 1.01$. ^f $n = 1.03$.

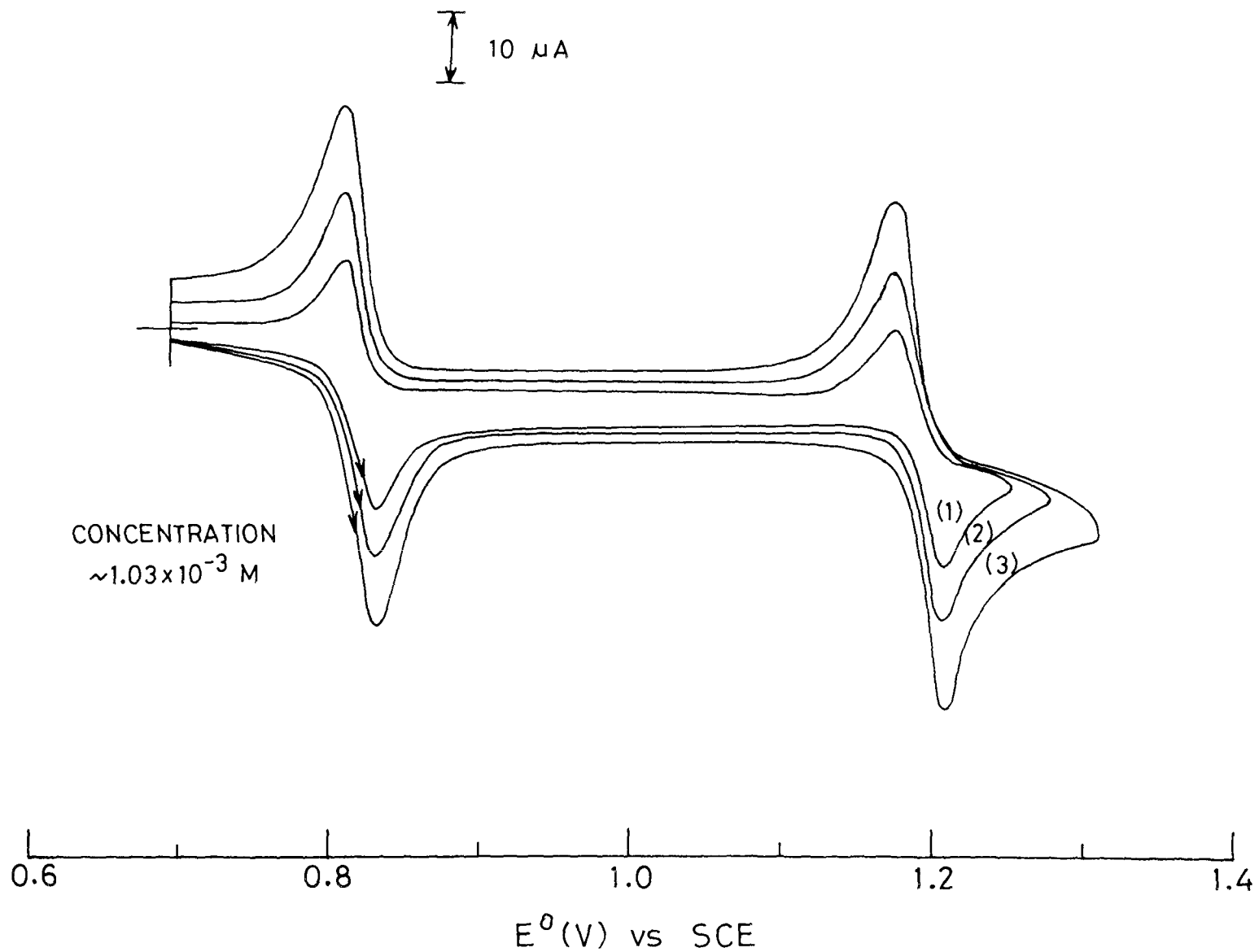


FIGURE VI.4. CYCLIC VOLTAMMOGRAMS OF $ctc-[OsQ^2L_2^2]$ IN MeCN.
SCAN RATES: (1) 50, (2) 100, (3) 200 mVs^{-1}

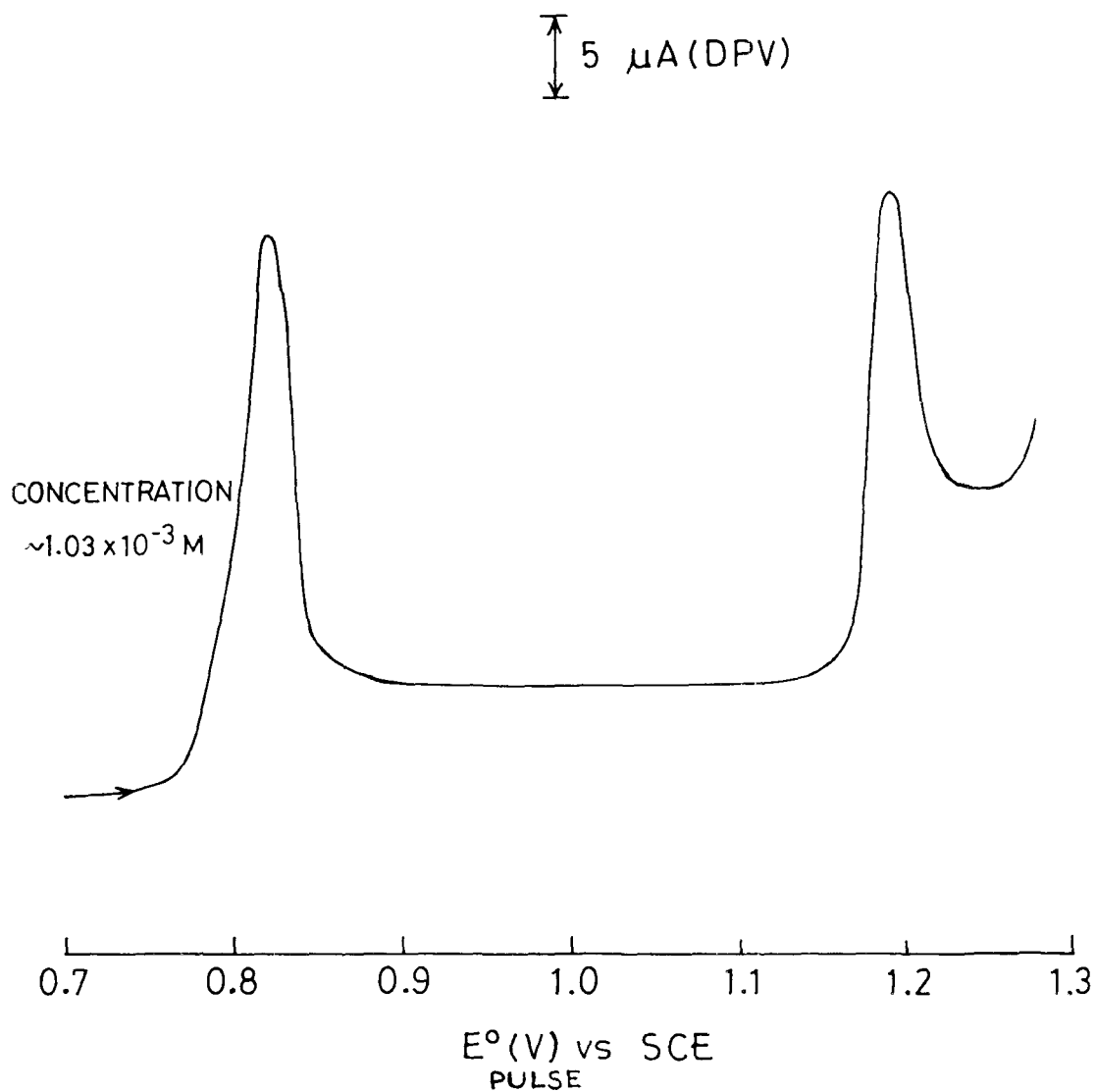
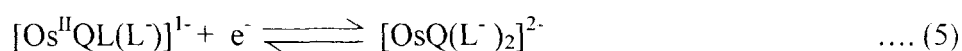
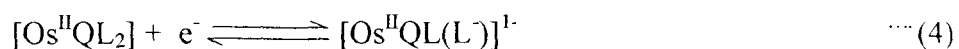


FIGURE VI.5. DIFFERENTIAL PULSE VOLTAMMOGRAM OF ctc-[OsQ²L₂] IN MeCN. SCAN RATE : 10 mVs⁻¹

coulometrically one-electron oxidised product of **4/5** in frozen (77 K) dichloromethane glass displays almost isotropic nature with g value close to 2 (**Figure VI.6**) corroborates this assignment. It is well-established^{5d} that complexes containing semiquinone ligands that are not magnetically coupled with other paramagnetic centres in the molecule generally have g values close to 2. Here the excellent π -acceptor L stabilises osmium(II) state. The potential of couple 3 is not so sensitive (see **Table VI.5**) from a change of substituent on Q network.

(b) Reductions

The negative side of SCE was scanned using a glassy carbon working electrode. The results are set in **Table VI.6** and representative voltammetric natures are represented in **Figures VI.7** and **VI.8**. The first two reductions are reproducible (in CV, **Figure VI.7**) with current height comparable to that of couple 2 indicating involvement of one-electron transfer. The redox processes are depicted in **equations 4** and **5**. The third and fourth reductions are irreversible,



which may be due to some kind of chemical assistance connected with the charge transfer at such lower potentials. These are best observable in DPV experiments (**Figure VI.8**). The substituents in Q have no effect on the potentials of these electrode processes indicating reaction centres far from Q.

F. CONCLUSION

We are successful in isolating isomeric $[\text{OsQL}_2]$ complexes. The compounds are formed in stereoretentive routes. They show rich electronic spectra – very much characteristic of two different isomeric entities. Within the available potential window the complexes display rich electrochemistry pertaining electron transfers from/to Q, L and the metal : (a) hydroquinone to semiquinone oxidation, (b) osmium(II) to osmium(III) transformation, and (c) four successive L-based reductions. Thus a nearly-complete electron transfer series is formed. The presence of strong π -acceptor L stabilises osmium(II)-hydroquinone state; however, osmium(II)-semiquinone can be generated in solution and is characterised by conjunctive benefit of spectroscopic and electrochemical studies.

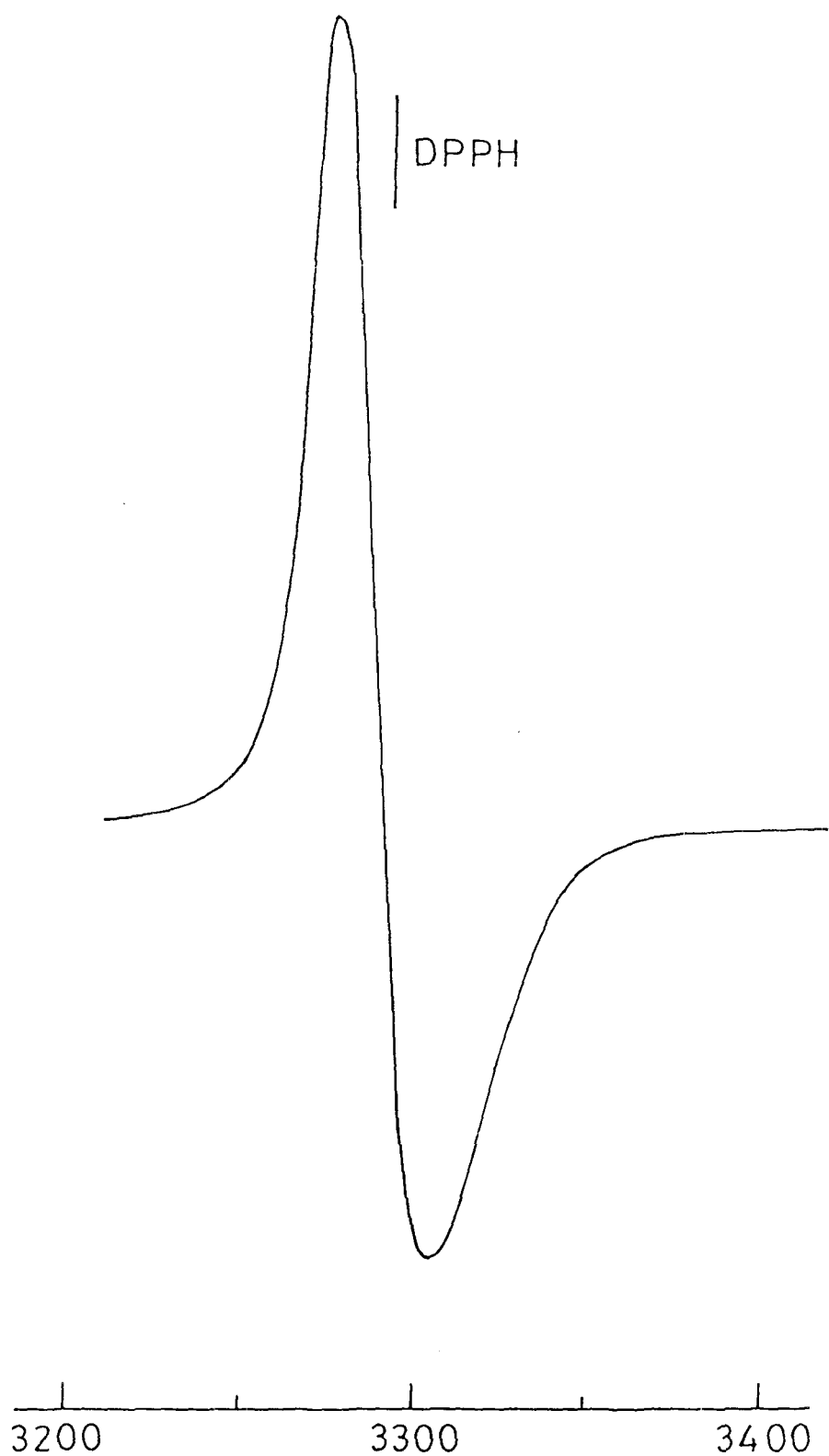


FIGURE VI.6. EPR SPECTRUM OF ONE-ELECTRON
OXIDISED PRODUCT OF $[OsQ^1L_2]$ IN
 CH_2Cl_2 GLASS (77 K)
(DPPH = 1,1-DIPHENYL-2-PICRYLHYDRAZYL)

TABLE VI. 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	r_4^d
ctc-[OsQ ¹ L ¹ ₂] (4a)	0.43 (60)	0.80 (90)	1.48 (120)	2.02
ccc-[OsQ ¹ L ¹ ₂] (5a)	0.41 (60)	0.78 (90)	1.46 (120)	2.00
ctc-[OsQ ¹ L ² ₂] (4b)	0.45 (60)	0.82 (90)	1.49 (120)	2.01
ccc-[OsQ ¹ L ² ₂] (5b)	0.43 (60)	0.80 (90)	1.46 (120)	2.03
ctc-[OsQ ² L ¹ ₂] (4c)	0.36 (60)	0.75 (80)	1.42 (110)	1.91
ccc-[OsQ ² L ¹ ₂] (5c)	0.34 (60)	0.72 (80)	1.40 (110)	1.92
ctc-[OsQ ² L ² ₂] (4d)	0.36 (60)	0.74 (80)	1.41 (110)	1.90
ccc-[OsQ ² L ² ₂] (5d)	0.33 (60)	0.73 (80)	1.39 (110)	1.91

^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.

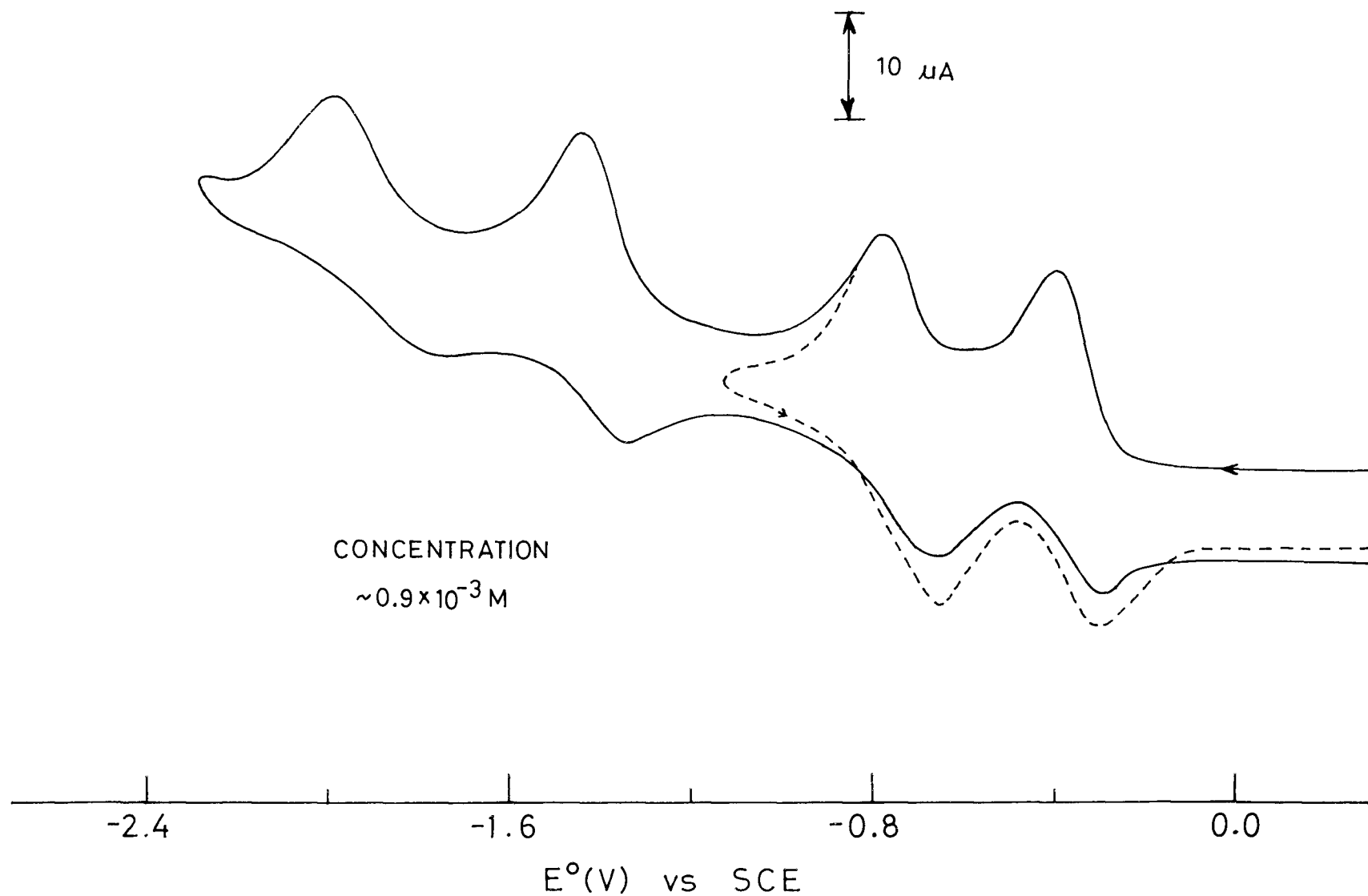


FIGURE VI.7. CYCLIC VOLTAMMOGRAM OF $\text{ctc-}[\text{OsQ}^2\text{L}_2^2]$ IN MeCN. THE PRESENTATION(---) SHOWS VOLTAMMOGRAM WHERE THE SCAN WAS REVERSED BEFORE REACHING THE THIRD REDUCTION WAVE

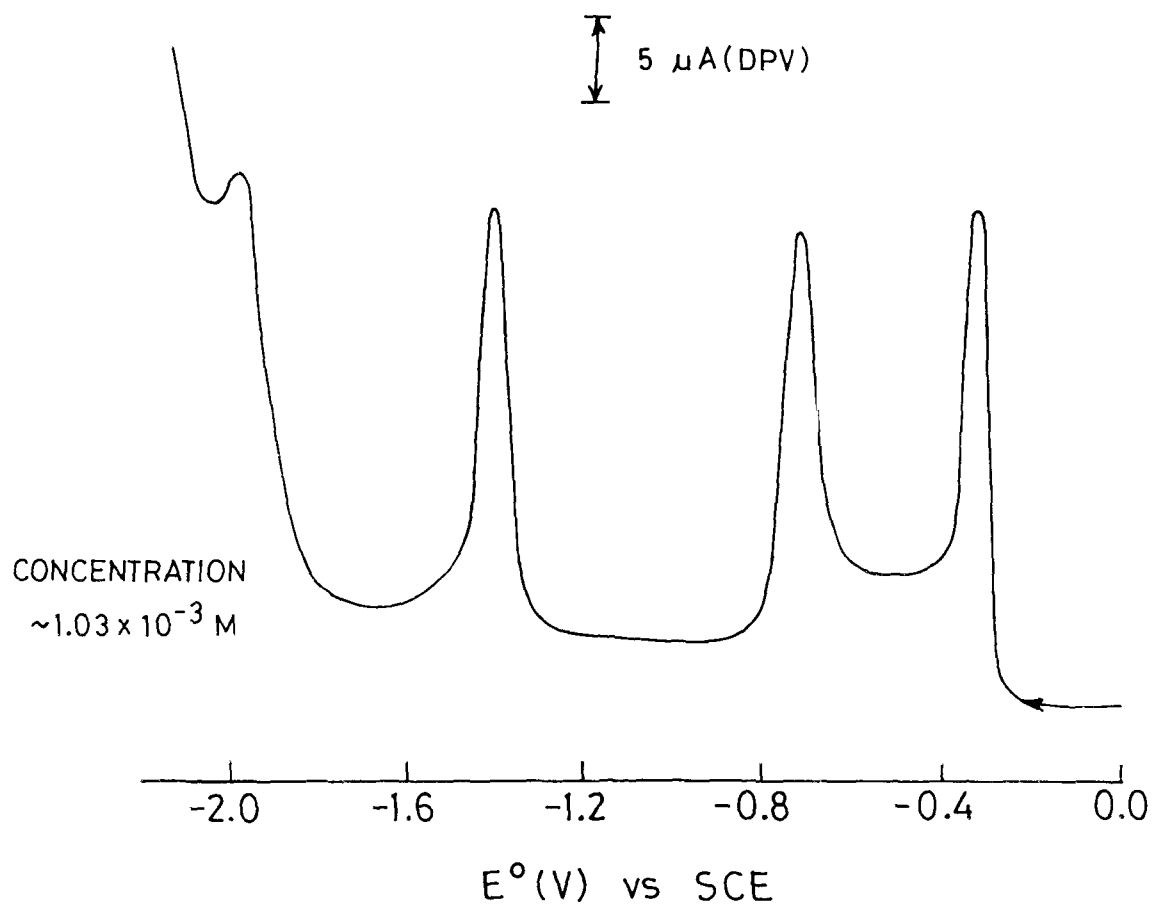


FIGURE VI.8. DIFFERENTIAL PULSE VOLTAMMOGRAM OF $ctc-[OsQ^2L^2_2]$ IN MeCN. SCAN RATE 10 mVs^{-1}

VI.3 EXPERIMENTAL SECTION

A. PREPARATION OF COMPOUNDS

(a) Chemicals, solvents and starting materials

The sources of chemicals and solvents are as described in the previous chapters. The other chemicals used are CaCO₃, SD (India); catechol, SD (India); tetrachlorocatechol, Aldrich (USA); ethanol, Bengal Chemicals (India); 2-methoxyethanol, Lancaster (UK). All chemicals were of analytical grade and were used without further purification. The synthetic reactions were carried out under dry dinitrogen and the final work-up was done in air.

(b) Ligands

2-(Phenylazo)pyridine (L¹) and 2-(*m*-tolylazo)pyridine (L²) were prepared using the same procedure as described in Chapter II.

(c) Precursors

The isomeric dihalo complexes, *cis*, *trans*, *cis*-[OsX₂L₂] (**2**) and *cis*, *cis*, *cis*-[OsX₂L₂] (**3**) (X = Cl or Br; L = L¹ or L²) were prepared following same procedure¹⁰ as was used by Ghosh et al. Of the chloro and bromo, the latter is more reactive; so it was used for the preparations of isomeric [OsQL₂] compounds.

(d) Complexes

(i) *Cis*, *trans*, *cis*-Catecholato-bis[2-(phenylazo)pyridine]osmium(II), *ctc*-[OsQ¹L¹₂] (**4a**)

To a suspension of 0.1 g (0.139 mmol) of *ctc*-[OsBr₂L¹₂] and 0.14 g (1.4 mmol) of CaCO₃ in 30 ml aqueous ethanol (2:1) was added 0.15 g (1.36 mmol) H₂Q¹. The mixture was heated at reflux under dinitrogen atmosphere for 6 h. The initial blue-violet solution changed to red, which was filtered through a fine glass frit and was evaporated under reduced pressure. The residue was washed copiously with Et₂O and redissolved in a minimum of CH₂Cl₂ and was loaded on a silica gel (60 - 120 mesh) column (20 × 1 cm). A small blue-violet band was eluted first with dichloromethane. Finally the slow moving red band of the desired compound was collected with PhH-MeCN (4:1). On slow evaporation of this solution resulted in dark red crystals that were separated by filtration, washed with chilled water and dried in vacuo over P₄O₁₀ to yield analytically pure **4a**. The yield was 0.055 g (60%).

(ii) *Cis, cis, cis-Catecholabis[2-(phenylazo)pyridine]osmium(II), ccc-[OsQ¹L¹]₂ (5a)*

5a was prepared [yield 0.055 g (60%)] following the same procedure and reaction stoichiometry as described in **4a** preparation except that 0.1 g (0.139 mmol) of *ccc*-[OsBr₂L¹]₂ was reacted with 0.15 g (1.36 mmol) of H₂Q¹.

(iii) *Cis, trans, cis-Catecholabis[2-(m-tolylazo)pyridine]osmium(II), ctc-[OsQ¹L²]₂ (4b)*

The procedure was the same as in the preparation for **4a** except that 0.1 g (0.134 mmol) of *ctc*-[OsBr₂L²]₂ was allowed to react with 0.15 g (1.36 mmol) of H₂Q¹. The yield was 0.057 g (60%).

(iv) *Cis, cis, cis-Catecholabis[2-(m-tolylazo)pyridine]osmium(II), ccc-[OsQ¹L²]₂ (5b)*

The preparative procedure for **5b** was the same as described in **5a** preparation. Here 0.1 g (0.134 mmol) of *ccc*-[OsBr₂L²]₂ was reacted with 0.15 g (1.36 mmol) of H₂Q¹. The yield was 0.057 g (60%).

(v) *Cis, trans, cis-Tetrachlorocatecholabis[2-(phenylazo)pyridine]osmium(II), ctc-[OsQ²L¹]₂ (4c)*

To prepare **4c** the same procedure and reaction stoichiometry was followed as described in **4a** formation. Here 0.1 g (0.139 mmol) of *ctc*-[OsBr₂L¹]₂ was allowed to react with 0.15 g (0.61 mmol) of H₂Q². The yield was 0.073 g (65%).

(vi) *Cis, cis, cis-Tetrachlorocatecholabis[2-(phenylazo)pyridine]osmium(II), ccc-[OsQ²L¹]₂ (5c)*

5c was prepared [yield 0.073 g (65%)] using the same procedure and reaction stoichiometry as described in **5a** preparation except that 0.1 g (0.139 mmol) of *ccc*-[OsBr₂L¹]₂ was reacted with 0.15 g (0.61 mmol) of H₂Q².

(vii) *Cis, trans, cis-Tetrachlorocatecholabis[2-(m-tolylazo)pyridine]osmium(II), ctc-[OsQ²L²]₂ (4d)*

The same procedure and reaction stoichiometry as in **4a** preparation was adopted except that 0.1 g (0.134 mmol) of *ctc*-[OsBr₂L²]₂ was reacted with 0.15 g (0.61 mmol) of H₂Q². The yield was 0.072 g (65%).

(viii) *Cis, cis, cis-Tetrachlorocatecholobis[2-(*m*-tolylazo)pyridine]osmium(II),
ccc-[OsQ²L²]**(5d)***

To prepare **5d** the same procedure and reaction stoichiometry was followed as described in **5b** formation. Here 0.1 g (0.134 mmol) of *ctc*-[OsBr₂L²]₂ was replaced by 0.1 g (0.134 mmol) of *ccc*-[OsBr₂L²]₂. The yield was 0.072 g (65%).

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 VI.7**.

C. PHYSICAL MEASUREMENTS

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). All other measurements are done as described in the previous chapters.

TABLE VI. 7

Characterisation Data

Compound	%C		%H		%N	
	Calcd	Found	Calcd	Found	Calcd	Found
ctc-[OsQ ¹ L ¹ ₂] (4a) C ₂₈ H ₂₂ N ₆ O ₂ Os	50.6	50.8	3.3	3.3	12.6	12.3
ccc-[OsQ ¹ L ¹ ₂] (5a) C ₂₈ H ₂₂ N ₆ O ₂ Os	50.6	50.5	3.3	3.2	12.6	12.6
ctc-[OsQ ¹ L ² ₂] (4b) C ₃₀ H ₂₆ N ₆ O ₂ Os	52.0	51.7	3.8	3.6	12.1	11.8
ccc-[OsQ ¹ L ² ₂] (5b) C ₃₀ H ₂₆ N ₆ O ₂ Os	52.0	52.2	3.8	3.8	12.1	12.3
ctc-[OsQ ² L ¹ ₂] (4c) C ₂₈ H ₁₈ N ₆ O ₂ Cl ₄ Os	41.9	50.4	2.3	2.5	10.4	10.4
ccc-[OsQ ² L ¹ ₂] (5c) C ₂₈ H ₁₈ N ₆ O ₂ Cl ₄ Os	41.9	41.7	2.3	2.3	10.4	10.1
ctc-[OsQ ² L ² ₂] (4d) C ₃₀ H ₂₂ N ₆ O ₂ Cl ₄ Os	43.4	43.4	2.7	2.9	10.1	10.4
ccc-[OsQ ² L ² ₂] (5d) C ₃₀ H ₂₂ N ₆ O ₂ Cl ₄ Os	43.4	43.6	2.7	2.9	10.1	9.8

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