CHAPTER 1

Studies on Absorption Spectra, Electrochemical behaviour and Inter Component energy transfer of Dinuclear Ru (II) / Os (II) phenenthroline complexes.
INTRODUCTION

The study of the photochemical & photophysical properties of coordination compounds has received a great deal of attention since the 1960\textsuperscript{1}. The main reason for such a success is based on the fact that most of these complexes combine remarkable feature like; (i) ease of preparation; (ii) reversible electrochemical behavior; (iii) light absorption in the visible spectral region (VIS); (iv) long-lived electronically excited states; (v) intense luminescence. All these characteristics, make them attractive for the study of fundamental processes such as photo induced energy and electron transfer under diffusional (bimolecular) condition\textsuperscript{1,2} or within multicomponent (supramolecular) array\textsuperscript{3}. Development in these fields have been of great interest from the practical point of view since various application can be envisaged, including, solar energy conversion\textsuperscript{4}.

Ruthenium-polypyridyl complexes are one of the most widely studied chromophones for molecular light to chemical energy conversion because of their favorable photo-physical properties & chemical stability\textsuperscript{5,6}. A huge variety of mononuclear, oligomeric & polymeric assemblies of the [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} complex or closely related complexes have been prepared and in many cases, shown to efficiently capture & collect light energy\textsuperscript{5,7-11}. However nearly all such assemblies are limited to driving one-electron processes\textsuperscript{12}.

Interlocked macrocyclic species\textsuperscript{13,14} are very interesting from a photochemical & photophysical view point because of the properties
which originate from the electronic interactions of various sub-units\textsuperscript{15-22}. Catenanes that exhibit coordination ability\textsuperscript{15,23} can give rise to metal complexes where the photophysical & photochemical properties are profoundly affected by the nature of the coordinated metal\textsuperscript{24}. As far as light - and/or redox-induced functions are concerned, much attention is presently focussed on systems based on M(N-N)\textsubscript{3\textsuperscript{n}} building blocks, where M is a metal ion of the second or third transition row (in particular, Ru(II) & Os (II) and N-N is a bidentate bpy-type ligand (bpy = 2,2 - bipyridine)\textsuperscript{18}. This choice is justified by the outstanding excited-state & redox properties of the M (bpy)\textsubscript{2\textsuperscript{n}}, type complexes\textsuperscript{19}.

The use of bidenote phen-type ligands (Scheme 1 : is much more convenient from a geometric viewpoint\textsuperscript{24-26}. The price to pay on replacing bpy-type with phenanthroline ligands in Ru(II) complexes is a shorten excited-state life time and a much weaker luminescence intensity in fluid solution at room temperature\textsuperscript{26}. A systematic investigation of Ru(Phen)\textsubscript{3\textsuperscript{n}} type complexes have recently shown that this drawback can be at least in part overcome by using appropriate substituents e.g. (MeSO\textsubscript{3}).

Taking advantage of the structural properties of the H(Phen)\textsubscript{3\textsuperscript{n}} type complexes, we have synthesized a series of compound, where Ru(II) based and Os by one or two phenylene spacers\textsuperscript{27}. In such systems the metal-to-metal distance is 12, 15, 20\textsuperscript{A} depending upon the number of interposed para-phenylene spacers (n=0, 1 or 2 respectively). Because of the well-known energy difference between the lowest excited states of Ru (II) & Os (II) phen-type complexes\textsuperscript{28} electronic energy transfer is expected to occur from the Ru based to the Os-
based unit.

We report here the results of investigation of the excited state and redox properties of the prepared compounds. Energy transfer has been monitored by using stationary & time resolved luminescence spectroscopy. The role of phenylene spacer which has been recently investigated. In other systems is discussed, and it is shown that the electron exchange mechanism is responsible for the highly efficient-energy transfer from the Ru-based to the Os-based component.

EXPERIMENTAL SECTION

Preparation of the Compound [(Meph-phen₃) Ru (phen₃ - phen₃)] (PF₆)₂

Ru-(Meph-phen₃) Cl₃ (110 mg, 0.21 mmol) & AgBF₄ (125 mg, 0.64 mmol) were refluxed in air for 2 hrs. in acetone (50 ml). The reaction mixture was filtered to remove AgCl, DMF (100 ml) was added, and the acetone was evaporated. The resulting solution was slowly added, and the acetone was evaporated. The resulting solution was slowly added under Ar to a hot solution (80°C) of the ligand 1-10 phenenthroline (phen) (149 mg, 0.31 mmol) in DMF (100 ml). The mixture was refluxed under Ar for 1 hr. DMF was then evaporated under reduced pressure and acetonitrile (150 ml) & KPF₆ (400 mg) were added. The hexafluorophosphate salts of the complexes were precipitated by addition of water (150 ml) & evaporation of acetonitrile. The
Scheme 1

1. Ag⁺, Acetone
2. phen-(ph)₅-phen

Meph-phenOsCl₂

n = 0, 1, 2
precipitate obtained was washed with water (2 x 50 ml) & other (2 x 50 ml) & subjected to a silica gel column chromatography (eluent acetonitrile) to give 208 mg of pure complex (yield 80%).

- $[(\text{Meph-phen}_3) \text{ Ru (phen}_3\text{-ph-phen}_3)(\text{PF}_6)_2]$. The same procedure as a above was used (Yield, 79%).

- $[(\text{Meph-phen}_3) \text{ Ru (phen}_3\text{(ph)}_2\text{ phen}_3)(\text{PF}_6)_2]$. The same experimental procedure was used (Yield, 80%).

- $[(\text{MeO}_2\text{S-phen}_3) \text{ Ru (phen}_3\text{(ph)}_2\text{ phen}_3)(\text{PF}_6)_2]$. The same experimental procedure as above was used (Yield, 65%).

- $[(\text{Meph-phen}_3) \text{ Ru (phen}_3\text{-phen}_3\text{ Os (phen}_3\text{-ph Me})(\text{PF}_6)_4]$ (1)

$[(\text{Meph-phen}_3) \text{ Ru (phen}_3\text{-phen}_3\text{)} (\text{PF}_6)_2$ (67 mg, 0.056 mmol) and (Meph - phen) OsCl$_3$ (35 mg, 0.056 mmol) were refluxed under argon in butanol (50ml) for 7 hrs. After removing the solvent, acetonitrile (100 ml) and KPF$_6$ (200mg) were added. The hexafluorophosphate salts were precipitated by addition of water (150 ml) and evaporation of acetonitrile. The precipitate was washed with water (2x50ml) and other (2x50ml) and subjected to silicon gel chromatography (eluent, acetonitrile and 10% aqueous KNO$_3$ 80.4M) to give 26 mg of complex 1 (yield 20%) and a by-product (Meph-phen$_3$) Ru (phen$_3$ - phen$_3$) OsCl$_3$ (PF$_6$)$_2$ (Yield 15%) which was characterised by FAB - MS (nitrobenzyl alcohol matrix).

$[(\text{Meph-phen}_3) \text{ Ru (phen}_3\text{- (ph) phen}_3\text{ Os (phen}_3\text{-phMe})(\text{PF}_6)_4$ (2). This compound was prepared in an analogous way to 1 (Yield-32%).

$[(\text{Meph-phen}_3) \text{ Ru (phen}_3\text{- (ph)}_2\text{ phen}_3\text{ Os (phen}_3\text{-phMe)]]$
(PF₆)₄ (3). The same experimental procedure as for 1 & 2 was used (Yield-15%).

\[ \text{[(MeO₂S - phen₃) Ru (Phen₃ - phen₃) (PF₆)₂]} \] - A suspension of phen₃-phen₃ (0.10 mmol), (10ml) & Ru [Ru (Me SO₂ phen₃) Cl₃ (0.09 mmol) in 1, 2-ethanediol (10ml) was refluxed for 20 min. The red solution was allowed to cool, and 10 ml. of water was added along with an excess of methanolic [NH₄] [PF₆]. The precipitate was collected by filtration and redissolved in the minimum volume of acetonitrile for column chromatography (silica; acetonitrile, saturated aqueous KNO₃, water (7:1:0.5 v/v) as eluent). The main range product fraction was collected, and water (25ml) and excess methanolic [NH₄] [PF₆] were then added. The mixture was then reduced in volume in vacuo to precipitate. The complex as the hexafluorophosphate salt. Recrystallization from acetone - methanol or acetonitrile water gave the complex as an analytically pure red powder in 25 - 45% yield.

\[ \text{[(MeO₂S-phen₃) Ru (phen₃-ph-phen₃) (PF₆)₂]} \] (0.12g, 0.22 mmol) of phen₃-ph-phen₃ and Ru (MeO₂S-phen₃) Cl₃ (0.110g, 0.21 mmol) in 1, 2-ethanediol (10 cm³) was refluxed for 45 minutes and the red solution cooled. Water (10ml) was added, along with an excess of methanolic [NH₄] [PF₆], and the precipitate was redissolved in the minimum volume of acetonitrile for column chromatography on silica (column 16cm., 3cm. wide; acetonitrile, saturated aqueous KNO₃, water (7:1:0.5 v/v) as eluent). The main range product fraction was collected
Scheme 2
and water (25ml) and excess Methanolic (NH₄) [PF₆] were added. The mixture
was reduced in volume in vacuo to precipitate the complex as the hexafluoro
phosphate salt. Recrystallization from 1:1 acetone methanol gave [(MeO₂S
phen₃) Ru (phen₃ - ph - phen₃) [PF₆]₂] as an analytically pure brown powder
(0.065 of 22%).

[(MeO₂ phen₃) Ru (phen₃ - phen₃) Os (phen₃)] [PF₆]₄ (4).

A suspension of Os-(phen₃)Cl₃ (21 mg, 0.04 mmol) &
[MeO₂S-tpy] Ru (phen₃ - phen₃)] (PF₆)₂ (45 mg, 0.04 mmol) in 1, 2-
etharediol (10ml) was refluxed for 1 hr. The purple-brown solution
was cooled & water (10ml) & an excess of Methanolic NH₄PF₆ were
added. The precipitated hexafluorophosphate salts were dissolved in
the minimum volume of acetonitrile and chromatographed on silica
(acetonitrile, saturated aqueous potassium nitrate, water (7:1:0.5 v/v) as
eluent) to give 15mg of pure complex (Yield 20%).

[(MeO₂S phen₃) Ru (phen₃ - ph - phen₃) Os (phen₃)][PF₆]₄ (5). This
was prepared in an analogous way to 4 (Yield 18%).

[(MeO₂S-phen₃) Ru (phen₃(ph)₂ phen₃) Os (phen₃-phMe)] [PF₆]₄(6). The
same procedure as for 1 was used (Yield, 10%).

RESULT & DISCUSSION

The general preparation of the ruthenium-osmium
dinuclear complex is given in scheme-2. The key complex
(Meph(phen)₃ Ru (phen₃(ph) phen₃) for the synthesis
heterodinuclear compound can be obtained by reaction of a labile solvated
<table>
<thead>
<tr>
<th>Ligand centered</th>
<th>$\lambda_{\text{max}}, \text{nm} (\varepsilon, \text{M}^{-1} \text{cm}^{-1})$</th>
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<tr>
<td><a href="PF$_6$">(MePh-phen),Ru(phen,-phen),O(phen,-phMe)</a>$_4$</td>
<td>288(130 000)</td>
</tr>
<tr>
<td><a href="PF$_6$">(MePh-phen),Ru(phen,-(phphen),O(phen,-phMe)</a>$_4$</td>
<td>288(113 000)</td>
</tr>
<tr>
<td><a href="PF$_6$">(MePh-phen),Ru(phen,-(ph),phen),O(phen,-phMe)</a>$_4$</td>
<td>284(112000)</td>
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<tr>
<td><a href="PF$_6$">(MeO$_2$-phen),Ru(phen,-phen),O(phen)</a>$_4$</td>
<td>275(69700)</td>
</tr>
<tr>
<td><a href="PF$_6$">(MeO$_2$S-phen),Ru(phen,-ph-phen),O(phen)</a>$_4$</td>
<td>275(73500)</td>
</tr>
<tr>
<td><a href="PF$_6$">(MeO$_2$S-phen),Ru(phen,-(ph),phen),O(phen,-phMe)</a>$_4$</td>
<td>275(79200)</td>
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</table>
ruthenium precursor (Meph-phen₃) Ru (acetone)₂ with an excess of bridging ligand. In a second step, the ruthenium complex bearing a free phen₃ site is allowed to react with (Meph-phen₃)OsCl₃. This very insoluble compound is used without further purification. In fact, attempts to remove the chloride ions with Ag⁺ was in conclusive. Depending upon the starting sample two other ruthenium-osmium complexes could be isolated in low yield: a dinuclear compound where the Os was coordinated to three Cl atoms on a trinuclear complex (Scheme 3). Their formation seems to indicate the polymerise nature of the poorly defined starting complex of (Meph-phen₃)OsCl₃.

The six novel dinuclear compounds can be grouped into two families. The first one (1-3) contains (Meph-phen₃) Ru and Os (phen₃ - phMe)₂, units connected by phen₃ (ph)ₙ phen₃ (n = 1, 1, 2) bridging ligands. The second family (4-6) differs from the first one two reasons (I) in the Ru moiety, the meph substituent on the 4' position of the external phen₃ ligand has been replaced by the strong π electron acceptor MeO₂S group. (II) in 4 & 5 in the Os moiety the Meph substituent. On the 4' position of the external phen₃ ligand has been replaced by hydrogen (in 6, the Os moiety has not been varied). Comparison of the results obtained for complexes of the same facily allows us to discuss the problem of electronic interaction through the different bridge. Comparison of the results obtained for members of the two families which contain the same bridging ligand can yield information on the change in the inter-component interception on changing the substituent on the external phen₃ ligands.
ABSORPTION SPECTRA

The visible parts of the absorption spectra of the novel dinuclear compounds 4, 5 & 6 are shown in Fig. 2 & the absorption maxima of all the complexes & of some reference compounds are collected in Table-1. The absorption spectra of the dinuclear species of the same family are considerably different in the visible region, even though the spacers do not absorb in that region. For both families, the bands in the visible region are metal to ligand charge transfer (MLCT) in character. They move to lower energy as the metal-metal separation distance, decreases. A comparison with the available data for the mononuclear components. (Table-1) can help in understanding the reason for this trend. For example, in the M (phen)$_2$$^{12}$ & Mphen$_3$-phMe)$_2$$^{12}$ reference compounds the value of $\lambda_{max}$ of the MLCT band does not depend on whether M is Ru or Os, whereas for the complexes of the same metal the Meph substituent displaces $\lambda_{max}$ to lower energy. In compound 3 which is made of Ru & Os units very similar to the M (Os phen$_3$ - phMe)$_2$$^{12}$ reference compounds. $\lambda_{max}$ is shifted to lower energy compared with M (phen$_3$ - ph Me)$_2$$^{12}$. On passing to 2 & 1, $\lambda_{max}$ moves further to the red. This behaviour suggests that the accepter orbital of the MLCT transition is located on the phen$_3$ ligands belonging to the bridge, as will be clearly shown by the electrochemical results (vide infra).

**Electrochemical Behaviour** - Electrochemical results obtained for the six
Fig. 2: Absorption spectra (room temperature, butyronitrile solution) of $\text{MeO}_2\text{S-phen}_2$ Ru (phen$_2$-phen$_2$) Os (phen$_2$)$_{3-4}$ (4), $\text{MeO}_2\text{S-phen}_2$ Ru (phen$_2$-ph-phen$_2$) Os (phen$_2$)$_{3-4}$ (5) and $\text{MeO}_2\text{S-phen}_2$ Ru (phen$_2$-ph$_2$-phen$_2$) Os (phen$_2$)$_{3-4}$ (6)

Fig. 3: Luminescence spectra (room temperature, isoabsorptive butyronitrile solutions, $\lambda_{\text{max}}$ 500 nm) of ($\text{MeO}_2\text{S-phen}_2$) Ru (phen$_2$-phen$_2$) Os (phen$_2$)$_{3-4}$ (4), $\text{MeO}_2\text{S-phen}_2$ Ru (phen$_2$-ph-phen$_2$) Os (phen$_2$)$_{3-4}$ (5) and $\text{MeO}_2\text{S-phen}_2$ Ru (phen$_2$-ph$_2$-phen$_2$) Os (phen$_2$)$_{3-4}$ (6) and the reference compound Ru(phen$_2$-SO$_2$-Me)$_{3-2}$.
novel dinuclear compounds are gathered in Table-2 together with the results available for the reference mononuclear species. Several interesting corelations emerge from the examination of this set of data concerning the mononuclear compounds one can notice that (I) Ru is oxidised at much more positive potentials than Os; (II) The ligands are reduced to similar potentials in the Ru & Os compounds; (III) The Meph substituent moves the oxidation potential to slightly less positive values and the reduction potential to slightly less negative values; and (IV) The MeO₂S substituent makes the oxidation potential much more positive & the reduction potential much less negative.

Compound 1 shows two reversible oxidation waves, which can be straight forwardly assigned to the Os-based (+0.95V) & Ru based (+1.32V) moieties. The oxidation potential of the Os-based moiety is practically the average of the oxidation potential of the Os (phen)₃⁺² & Os (Meph - phen)₃⁺², model compounds. For the Ru based moiety, the oxidation potential is slightly higher than those of the corresponding model compounds as expected because of the electron acceptor properties of the already oxidized (+3 charge) Os-based moiety. As one can see from Table-2, the first reduction potential of 1 is much less negative than the first reduction potential of the parent compounds. This indicates that the LUMO orbital of the dinuclear complex is located on the bridging ligand where the two phen units interact strongly, as is also shown by the absorption spectra (vide supra). The second reduction potential is very close to the first reduction potential of the parent compound. This would indicate that either the second reduction process of 1 concerns again. The bridge of the monoreduced bridge does not affect the reduction of an external Meph - phen ligand. In the second case, however, independent simultaneous
<table>
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<th>Compounds</th>
<th>$E_{\text{ox}}^{\text{II}}$ (Ru)</th>
<th>$E_{\text{ox}}^{\text{I}}$ (Os)</th>
<th>$E_{\text{red}}^{\text{I}}$</th>
<th>$E_{\text{red}}^{\text{II}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="PF%E2%82%86">(Meph-phen₂,Ru(phen₂,phen₃)Os(phen₃,phMe)</a>₄</td>
<td>+1.27(60)</td>
<td>+0.90(60)</td>
<td>-1.01(70)</td>
<td>-1.28(60)</td>
</tr>
<tr>
<td><a href="PF%E2%82%86">(Meph-phen₂,Ru(phen₂,phphen₃)Os(phen₃,phMe)</a>₄</td>
<td>+1.25(60)</td>
<td>+0.90(60)</td>
<td>-1.20(100)</td>
<td>-1.43(120)</td>
</tr>
<tr>
<td><a href="PF%E2%82%86">(Meph-phen₂,Ru(phen₂,ph)₂phen₃)Os(phen₃,phMe)</a>₄</td>
<td>+1.24(70)</td>
<td>+0.90(60)</td>
<td>-1.22(80)</td>
<td>-1.44(100)</td>
</tr>
<tr>
<td><a href="PF%E2%82%86">(MeO₂S-phen₂,Ru(phen₃,phen₂)Os(phen₃)</a>₄</td>
<td>+1.44(105)</td>
<td>+0.99(110)</td>
<td>-0.95(90)</td>
<td>-1.09(90)</td>
</tr>
<tr>
<td><a href="PF%E2%82%86">(MeO₂S-phen₂,Ru(phen₃,ph-phen₂)Os(phen₃)</a>₄</td>
<td>+1.39(105)</td>
<td>+0.94(110)</td>
<td>-1.01(75)</td>
<td>-1.20(60)</td>
</tr>
<tr>
<td>(MeO₂S-phen₂,Ru(phen₃,(ph)₂,phen₂)Os(phen₃,phMe)](PF₆)₄</td>
<td>+1.31960</td>
<td>+0.90(60)</td>
<td>-1.00(60)</td>
<td>-1.20(60)</td>
</tr>
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</table>

*a* Acetonitrile solution, 0.1 M Bu₄NBF₄, room temperature potential in V, vs SCE; The literature data have been converted by adding 0.38 V; the values in the parentheses are differences between the anodic and cathodic peaks of the CV waves.
reduction of the two external ligands would be expected.

When one of two phenylene spacers are interposed between the Ru-based & Os-based units, the oxidation potential of the Os-based moiety is not affected the small decrease of the oxidation potential of the Ru-based moiety may reflect the decrease of the electron-acceptor effect of the already oxidized, Os-based moiety with increasing distance. The effect of the ph spacers is much more dramatic on the reduction potentials. In 2 the first reduction wave occurs at a potential more negative than that of 1, but still slightly more positive than that of the parent compounds. It seems likely, therefore that the first reduction process again involves the bridging ligand. The big difference with respect to 1 is that in 2 the two phen moieties of the bridging ligand do not interact strongly with each other because of the presence of the phenylene spacers, so that the LUMO of the two inner ligands lies at energies much closer to that in 2 the first reduction wave involves two electrons. In other words, the second reduction process in 2 occurs at a potential almost coincident to that of the first one and less negative than the second process of 1. This would exclude the possibility that the first and second reduction processes of 2 concern the two moieties of the bridging ligand or the two ligands of the same metal-based unit. In order to reduce electron repulsion, in fact, the two electron reduced species of 2 would correspond to the one-electron reduction of an bridging ph-phen, unit and of an external Meph - phen, ligand, coordinated to different metal centers. Further reduction of 2 (Table-2) involves again two electrons at almost the same potential. This means that such processes involve uncoupled sites i.e. ligands units not directly linked and belonging to different metals in agreement with the above discussion.
Table 3  Luminescence Data

<table>
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<tr>
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<th>293K</th>
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<th>77K</th>
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<tbody>
<tr>
<td></td>
<td>Ru-based</td>
<td>Os-Based</td>
<td>Ru-based</td>
<td>Os-based</td>
</tr>
<tr>
<td></td>
<td>(\nu_{\text{max}}, \text{cm}^{-1})</td>
<td>(\tau, \text{ns})</td>
<td>(\nu_{\text{max}}, \text{cm}^{-1})</td>
<td>(\tau, \text{ns})</td>
</tr>
<tr>
<td>1. (Me ph-phen)Ru(phen1-phen2)Os(phen1-phMe)(PF_6)_4</td>
<td>e</td>
<td>i</td>
<td>12 500</td>
<td>110</td>
</tr>
<tr>
<td>2. (Me ph-phen)Ru(phen1)-(ph)phen2)Os(phen1-phMe)(PF_6)_4</td>
<td>e</td>
<td>i</td>
<td>13 400</td>
<td>190</td>
</tr>
<tr>
<td>3. (Me ph-phen)Ru(phen1-(ph)phen2)Os(phen1-phMe)(PF_6)_4</td>
<td>e</td>
<td>i</td>
<td>13 550</td>
<td>200</td>
</tr>
<tr>
<td>4. (MeO, phen)Ru(phen1-phen2)Os(phen1)(PF_6)_4</td>
<td>e</td>
<td>i</td>
<td>12 600</td>
<td>130</td>
</tr>
<tr>
<td>5. (MeO, S-phen)Ru(phen1-phen2)Os(phen1)(PF_6)_4</td>
<td>e</td>
<td>i</td>
<td>13 475</td>
<td>213</td>
</tr>
<tr>
<td>6. (MeO, S-phen)Ru(phen1-(ph)phen2)Os(phen1-phMe)(PF_6)_4</td>
<td>e</td>
<td>i</td>
<td>13 550</td>
<td>219</td>
</tr>
</tbody>
</table>

\(^b\) relative luminescence intensity with \(\lambda_{\text{max}} = 500 \text{ nm}\). At this excitation wavelength only the Ru-based and Os based units of the dinuclear complexes are excited in an approximately 1:1 ratio (see fig 2 & 3).

\(^c\) relative luminescence intensity with \(\lambda_{\text{max}} = 650 \text{ nm}\). At this excitation wavelength only the Os-based units of the dinuclear complexes are excited.
on the first two reduction processes.

In compound 3 the Ru-based & Os-based oxidation potentials are very close to those of 2 (and 1), showing that interposition of another ph spacer does not substantially affect the metal-metal interaction that as well have seen above, is already small in 1. As far as reduction in concerned, one can notice again two well-separated waves, each corresponding to two almost equivalent sites. Therefore, the two observed waves should not correspond to inner-inner & outer-outer ligand couples, but rather to two inner-outer ligand couples, in agreement with the conclusion drawn above for 2.

The oxidation potential of the Os-based moiety of 4 is slightly more positive than that of the Os (phen)$_3^{12}$. Model compared, contrary to what happens for 1 (vide supra). This is likely to be related to the presence of the strongly electron-withdrawing MeO$_2$S substituent on the outer phen ligand of the Ru-based moiety. The oxidation potential of the Ru-based moiety of 4 is much more positive than the average of the oxidation potentials of the (Ru Phen)$_6^{12}$ & Ru (phen - So$_2$Me)$_2^{12}$ model compounds because of electron-withdrawing effect of the already oxidized Os-based moiety. Interestingly, the first oxidation potential of the model symmetrical dinuclear compound (MeO$_2$S-phen) Ru (phen$_3$-phen$_3$) Ru (phen$_3$-So$_2$Me)$_2$ (+1.49V) is very close to that of the Ru-based moiety of 4 (i.e., to its second oxidation potential), indicating that the Os(phen)$_3^{12}$ & Ru (phen$_3$-So$_2$Me)$_2$ terminator units show very similar electronic effects.

The first oxidation potential of 5 is less positive than that of 4 because of the smaller interaction with the Ru-based electron acceptor moiety. The decrease in the oxidation potential of the Ru-based moiety is to be
attributed to the smaller electron withdrawing effect of the already oxidized Os-based moiety (again, the first oxidation potential of the symmetric dinuclear Ru compound is identical to that of the Ru-based moiety of 5). Insertion of another ph spacer (compound 6) would be expected to have a smaller effect, but it must also be considered that in going from 4 and 5 to 6 a Mephe-phen₃ substituent has been placed on the outer phen ligand of Os.

The first reduction potential of 4 is slightly less negative than that of 1 (where, as we have seen above, reduction takes place on the bridge) & very close to the first reduction potential of Ru (MeO₂S-phen)₃⁺². Therefore, it is difficult to say whether the first reduction process takes place in the bridge or in the outer ligand of Ru. The second reduction process is much closer to the first on than in 1. Therefore, it can be concluded that in the two electron reduced species the two reduced sites are the outer Ru-ligand and the inner ligand on the Os side. The first reduction process of 5 can straightforwardly be assigned to the outer ligand of Ru, and the second one to the inner ligand of Os. The same assignment can be done for 6. The first reduction process, in fact, occurs at almost the same potential in 5 & 6, suggesting & that it does not concern. The bridge (compare with the behaviour of 1-3), and the second reduction potential becomes more negative in going from 5 to 6, while the reverse would be expected for reduction on the outer ligand of Os.

LUMINESCENCE PROPERTIES

All the data concerning the luminescence behaviour of the dinuclear
complexes and of the reference compounds are collected in Table-3. The emission spectra at room temperature of compounds 4-6 are shown in Fig. 3 together with the spectrum of Ru(MeO₂S - phen)₃⁺².

All the Ru reference compounds exhibit a strong and long-lived luminescence at 77K & the Ru complexes bearing Meph or MeO₂S substituents in the 4 position exhibit luminescence also at room temperature. In no case, however is Ru-based luminescence observed for the dinuclear compounds (see, for exp. Fig. 3 & 4), because of quenching processes whose nature will be discussed in the next section. Given the instrumental characteristics of our equipment, we estimate that the lifetime of the Ru-based unit is <20 ps²⁹. The present discussion therefore, concern the Os-based luminescence of the dinuclear compounds, for which the following corelations can be observed.

(1) For 1 & 4 the luminescence band is substantially red shifted compared to that of Os (phen)_3⁺² & Os (Meph-phen)_3⁺² reference compounds. This shows that the lowest excited state of 1 & 4 involves a CT transition from Os (II) to the phen₃-phen₃ bridging ligand, in agreement with the electrochemical results.

(2) In going from 1 to 2 and 3 and from 4 to 5 and 6, the luminescence band moves to higher energies, but does not reach the energy of the Os(II) model compounds. This suggest that the lowest excited state concerns the bridging ligands in all the dinuclear compounds.

(3) In all cases, there is a blue shift in going from fluid solution to rigid matrix. This expected behaviour for CT excited states is due to the lack of solvent repolarization in rigid matrix²⁸. This effect should
increase with increasing change in the dipole moment caused by the
CT transition. In 1 & 4 the blue shift is much larger than in the
reference compounds, which is consistent with the expected larger
variation in the dipole moment when the CT transition involves the
phen$_3$-phen$_3$ bridging ligand. As expected, the blue shift decreases
when the interaction between the two halves of the bridging ligand
decreases because of the introduction of one or two ph spacers.

The emission bands of 1 and 2 at room temperature are red shifted
with respect to those 4 & 5, respectively, as expected from the
electrochemical data.

The electrochemical data show that for 6 the site easier to oxidize
(i.e. Os) is far away from the site easier to reduce (i.e. the outer
MeO$_3$S - phen$_3$ ligand of Ru). This would suggest that the lowest
excited state of 6 corresponds to a "remote" MLCT transition. This,
however, does not seem to be the case since the luminescence
behaviour of 6 is exactly the same as that of 3, where low energy
remote' MLCT transitions are not present and Os is coordinated to
the same ligands as in 6. It should be recalled in fact, that a
remote CT level is destabilized with respect to a proximate one by
the smaller electrostatic repulsion.

Looking at the luminescence lifetimes, there is clearly a
relationship with the energy of the emitting level both at 77K and at
room temperature, as expected for radiationless processes governed by
the energy gap rule$^{28,30}$. The relative luminescence intensities, however, are not
Fig. 4: Normalised luminescence spectra (butyronitrile solutions, $\lambda_{\text{exc}}$ 500 nm) at 77K in of (MeO,S-phen,), Ru (phen,phen,) Os (phen,)$^\text{II}$ (4), MeO,S-phen,) Ru (phen,phen,) Os (phen,)$^\text{IV}$ (5) and MeO,S-phen,) Ru (phen,phen,) Os (phen,)$^\text{IV}$ (6) and the reference compound Ru(phen,SO$_2$-Me)$_2$.$^\text{12}$
linearly related to the luminescence lifetimes. For example, in passing from Os (Meph-phen)$_3^{12}$ to 1 and 4, the luminescence intensity decreases by a factor of $\sim 16$, whereas the lifetime decreases only by a factor of $\sim 2$. This indicates that the radiative rate constant is much smaller in 1 and 4 than in the mononuclear compound. This also happens, but to a much smaller degree, for the other dinuclear species. It is clear that the inter-position of a second ph spacer has a much smaller effect than interposition of a second ph spacer has a much smaller effect than interposition of the first one.

INTERCOMPONENT ENERGY TRANSFER

As we have seen in the previous section, the potentially, luminescent Ru-based units do not show any appreciable emission in the dinuclear compounds (Table-3, Fig. 3 & 4), indicating that they are quenched by the connected Os-based units. In order to see whether this quenching is accompanied by sensitization of the luminescence of the Os-based units, the following experiments were performed. Isoabsorptive solutions of Os (Meph-phen)$_3^{12}$ and of the six dinuclear compounds were excited with 650 nm light, which in the dinuclear compounds is absorbed only by the Os-based moieties (see e.g., Fig. 2 Table-1). The relative intensity values obtained for the Os-based emission are shown in Table-3. The isoabsorptive solutions of the same compounds were excited at 500 nm, where in the dinuclear compounds approximately 50% of the absorbed light concerns the Ru-based units (Fig. 2, Table-1). The relative values of the Os-based luminescence intensity obtained under the latter experimental conditions are also shown in Table-3. One can see
the two sets of intensity values are identical with in experimental conditions are
also shown in Table-3. One can see that the two set of intensity values are
identical with in experimental error (estimated to about 50%). This indicates
that in each dinuclear compound the excitation energy absorbed by the Ru-
based unit is quantitatively transferred to the connected Os-based unit.

The energy-transfer rate constant can be estimated eq. 1 or 2, where
\( \tau^0 \) & \( I^0 \) are the luminescence lifetime and intensity of a suitable model
compound and \( \tau \) and \( I \) are the Ru-based luminescence lifetime and intensity of
the dinuclear compound:

\[
K_{en} = I / \tau^0 - I / \tau^1 \tag{1}
\]

\[
K_{en} = (I / \tau^0) \cdot (I^0 / I-1) \tag{2}
\]

For 3, an appropriate model compound is Ru (Meph-phen)\(_3\)^{2+} which
shows \( \tau^0 = 0.85 \) ns. By using eq. 1, with the estimated upper but \( \tau = 20 \) ps
(vide supra) a lower limit of 6x10\(^{10}\) S\(^{-1}\) is obtained for \( K_{en} \). Since \( I^0 \) is at least
10 times larger than \( I \). The lower limit obtained from eq. 2 is 1 x 10\(^{10}\) S\(^{-1}\).

For 6 an appropriate model compound (e.g. (Me \( O_2 \) S - phen\(_3\)) Ru (phen\(_3\) -
phMe\(^+\))\(^{2+}\) is not available but from the data obtained for Ru (Me \( O_2 \) S-phen\(_3\))\(^{2+}\)
and Ru (Meph - phen)\(_3\)^{2+} (Table-3) one can assume that \( \tau^0 \) is longer than 1 ns
and \( I^0 \) is at least 3 times larger than that of Ru (Meph - phen)\(_3\)^{2+} and therefore
at least 30 times larger than \( I \). Using these data, from eqn. (1) & (2), one
gets lower but values of 5x10\(^{10}\) and 3x10\(^{10}\) S\(^{-1}\) for \( K_{en} \), respectively. Since 3
& 6 are the compounds which contain the longest bridges, in the other
dinuclear compounds. The energy-transfer process is ever faster. It is worth
noticing that the energy transfer rate constant in 3 is atleast 1000 times larger
than that found recently for Ru (phen)$_3^{2+}$ and Os (phen)$_3^{2+}$ chromophore separated by riding non-conjugated bridges with a metal-metal distance of 18Å.

Energy transfer can take place by coulombic (Forster$^{31}$) and exchange mechanisms. In the former one the main contribution to the rate constant comes from the dipole - dipole interaction between donor and acceptor. The rate constant according to this mechanism can be calculated from spectroscopic and structural parameters by using eqs. 3 & 4:

\[
K_{en} = 1 / \tau_{0} (R_{0} / i)^{6}
\]

\[
R_{0}^{6} = 5.87 \times 10^{-25} \phi / n^4 \int F(v) (- (v)v^{-1}dv
\]

$R_{0}$ is the so-called critical radius, i.e. the distance at which the energy transfer rate and the intrinsic deactivation rate of the donor are equal (50% transfer efficiency), v is the frequency (cm$^{-1}$) and n, $\phi$, and $\tau$ are the refractive index of the solvent, the luminescence quantum yield of the donor, and the donor-acceptor distance respectively. In eq. 4 the spectral overlap integral of the donor luminescence and acceptor absorption is calculated to be 9.8 x 10$^{-14}$ M$^{-1}$ Cm$^{-1}$ for 3. From eq. 4, $R_{0}$ is 9.1 Å for 3, which is a value considerably smaller than the metal-metal distance (10Å). In other words, the calculated rate constant over a 20Å distance (eq. 3) is 9.3 x 10$^{6}$ S$^{-1}$, i.e., at least 3 orders of magnitude smaller than the lower limit for the estimated experimental rate constant. It should be noted that the metal-metal distance is likely to be a structural parameter not fully appropriate for this type of calculations since the MLCT states involved in the energy transfer process are not localized on the metals but extend considerably over the bridging ligand. For example, if the effective distance is 10Å, the calculated rate constant would be about 100 times larger. In conclusion, it seems reasonable to admit
that the coulombic contribution could not account for the fast energy transfer processes observed experimentally.

The Dexter-type energy transfer mechanism is described as a double exchange of electrons between donors and acceptor. Its occurrence is therefore related to direct or super exchange mediated electronic interaction between the two partners. The rate constant of energy transfer via The Dexter Mechanism can be expressed in the nonadiabatic limit as in eq. 5. \( \nu_{en} \) and \( \Delta G^\circ \) can be obtained from eq. 6 & 7, respectively

\[
K_{en} = \nu_{en} \exp \left(-\frac{\Delta G^\circ}{RT}\right) \tag{5}
\]

\[
\nu_{en} = \left[2 \left( \frac{H_{en}}{h} \right) \left( \pi^2 / \lambda \right) RT \right]^{1/2} \tag{6}
\]

\[
\Delta G^\circ = \left( \lambda / 4 \right) \left( 1 + \Delta G^0 / \lambda \right)^2 \tag{7}
\]

Following the usual assumptions the free energy charge \( \Delta G^0 \) can be expressed by the difference between the spectroscopic energies of the donor & acceptor (Ca 2000 Cm\(^{-1}\) for 3, as estimated from the energy of the emission maxima of the model compounds at 77K), and the reorganization energy \( \lambda \) (Ca 1000 Cm\(^{-1}\)) can be estimated from the spectroscopic stokes shift (Tables 1 & 3) of the acceptor (That for the donor should be approximately the same).

This yields a value of about 0.3 for the exponential term for eq. 5. In other words, \( K_{en} \) is almost equal to \( \nu_{en} \) value of 10\(^{10}\) s\(^{-1}\) (i.e. on the order of the lower limit experimentally estimated for the energy-transfer rate constant in 3), an electronic interaction energy of less than 4 Cm\(^{-1}\) (i.e. Ca 0.5 mV) is sufficient. This discussion above of the electrochemical behaviour clearly shows that the interaction energy between the two moieties of 3 is likely to be much larger than 0.5 mV. Therefore, we can conclude that the very efficient electronic energy transfer observed in the examined complexes can be
accounted for by a Dexter Mechanism.

In conclusion, fast energy transfer takes place in our dinuclear complexes, most likely via the Dexter Mechanism, even when the two M (phen)$_3$ chromophores are separated by two phenylene bridges. This result is consistent with the recent findings by McLendon and co-workers$^{37}$ of the small effect of phenylene spacers in decreasing electronic coupling between electron donor / electron acceptor bisporphyrin compounds and by Mataga and co-workers$^{38}$ of fast singlet-singlet energy transfer between porphyrins through two phenylene spacers. Efficient electronic communication through phenylene bridges is also shown by the presence intervalence bands in (Mephe - phen$_3$) Ru$^{III}$ (phen$_3$(ph)$_2$ phen$_3$) - Ru$^{III}$ (phen$_3$ - phMe)$_2$ (interaction energy Ca. 170 Cm$^{-1}$)$^{34}$ and (NH$_3$)$_5$ Ru$^{II}$ (Py (Ph)$_2$ Py) Ru$^{III}$ (NH$_3$)$_5$.$^{35,39}$

From the theoretical viewpoint, the effect of bridging phenylene spacers has been discussed by Onuchic & Beratan$^{40}$. The basic assumption of their model is that the exchange integral within the aromatic ring is much larger than that between rings, since conjugation between the rings is broken at the ring function due to non bonded interaction which force the phenanthroline into a non-planar geometry. In an investigation of electron transfer in bis-porphyrin compounds with different biphenylene spacers, McLendon & Co-workers$^{37a}$ found that when the dihedral angle between the two phenylene spacers is varied from 0° to 50° (The known geometry of phenanthroline), a 7-fold decrease in the electron transfer rate constant is observed, in fair agreement with a decay factor of less than 10 per ring predicted by the theoretical model$^{40}$. In terms of distance (which in the above model would not be an appropriate parameter). The rate constant for electron-transfer processes in
bis-porphyrin donor / acceptor compounds with one two, and three phenylene spacers expressed as

\[ K = A_0 \exp(-\beta r) \]

Yielded a value of \( \beta = 0.4 \ A^{0.1} \) to be compared with values around \( 1A^{0.1} \) obtained for aliphatic spacers\(^{41,42} \). Since in our compounds with \( n=0 \) the electronic coupling is relatively strong as shown by the spectroscopic and electrochemical results, introduction of one or two phenylene spacers cannot be expected to fully insulate the Ru-based from the Os-based moiety. The high rate of electronic energy transfer, therefore, is not at all surprising.
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