

Photochemical and electrochemical properties of tetranuclear Ru (II) complexes

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Abstract

The luminescent and redox active multinuclear Ru (II) Complex containing both electron poor (2,3-bis (2-pyridyl) pyrazine, 2,3-dpp) and electron rich (3,5-bis (pyridin-2yl)-1,2,4-triazole, Hppt) polypyridine bridging ligands has been synthesized. The novel complex is $[(\text{phen})_2 \text{Ru} (\mu\text{-bpt}) \text{Ru} (\mu\text{-2,3-dpp}) \text{Ru} (\text{Phen})_2]^{7+}$ (1:Phen=1,10-Phenanthroline) Its absorption spectrum, luminescence properties, and redox behavior have been studied and compared with the properties of parent complexes $[\text{Ru} (\mu\text{-2,3-dpp}) \text{Ru} (\text{Phen})_2]^{3+}$ (2) and $[(\text{Phen})_2 \text{Ru} (\mu\text{-bpt}) \text{Ru} (\text{Phen})_2]^{3+}$ (3). The absorption spectrum of 1 is dominated by ligand centered bands in the U.V. region and by metal to ligand CT bands in the visible region. Excited states and oxidation and reduction processes are localized in specific sites of the multicomponent structure. However, perturbations of each component on the redox and excited state properties, as well as electronic interactions between the chromospheres can be observed. Intercomponent energy transfer from the upper lying $(\mu\text{-bpt}) (\text{Phen}) \text{Ru} \rightarrow \text{Phen CT}$ excited state of the $\text{Ru} (\text{Phen})_2 (\mu\text{-bpt})^+$ component to the lower lying $(\text{Phen})_2 \text{Ru} \rightarrow \mu\text{-2,3-dpp CT}$ excited - state of the $\text{Ru} (\text{Phen})_2 (\mu\text{-2,3-dpp})^{2+}$ subunit(s) is efficient in fluid solution at room . And the process is not observed in a rigid matrix at 77 K. A two step energy transfer mechanism is proposed to explain the photophysical properties of the new complex.

Keywords: 2,3-dPP = 2,3-di Phenyl pyridyle, Phen = 1,10-Phenanthroline, μ bpt = μ -bipyridine, CT = Charge Transfer, MLCT = Metal Ligand charge Transfer

INTRODUCTION

Luminescent and redox active multinuclear complexes are currently the object of great interest on the basis of theoretical and potential practical applications. This family of complexes hold a central position in the design of supramolecular system capable of performing photoinduced energy migration and charge separation, with the ultimate aim of constructing devices for solar energy conversion and/or light driven information processing [1]. In our earlier communication we studied the electron transfer quenching of Ru (III) perchlorates with some poly tertiary arsines and phosphines [2]. We have also studied the specific solvation effects on emission properties of Bis (1,10-Phenanthroline), (3,5-dicarboxy-2,2' - bipyridine ruthenium (II) chloride [3].

A major class of luminescent and redox active multinuclear metal complexes is based on Ru (II)- Polypyridine building blocks connected by electron poor (i.e. with low lying π^* orbitals) bridging ligands. One of the most used bridging ligand is 2,3-bis (2 Pyridyl) pyrazine (2,3 dpp) [4]. A second class of luminescent multinuclear complexes is based on the same building blocks connected by anionic electron rich (with relatively high lying π orbitals) bridging ligands [5] An interesting difference between the two classes of multinuclear system is that electron poor bridging ligands can mediate metal-metal communication by a super exchange mechanism essentially based on low lying, empty π^* orbital of the

bridge (electron transfer pathway) [5] while electron rich bridges may take advantage of high lying full π orbitals.

We report the photophysical and electrochemical properties of the first luminescent and redox active multinuclear Ru (II) system in which both electron poor (2,3-dpp) and electron rich (3,5-bis (pyridine-2 yl)-1,2,4-triazolate bpt) polypyridine bridges are present. The formula of the complex is $[(\text{Phen})_2 \text{Ru} (\mu\text{-bpt}) \text{Ru} (\mu\text{-2,3-dpp}) \text{Ru} (\text{Phen})_2]^{7+}$ (1 Phen= 1,10-Phenanthroline, for the structural formula of ligands in Flg A). Comparison with the properties of parent complexes $[\text{Ru} (\mu\text{-2,3-dpp}) \text{Ru} (\text{Phen})_2]^{3+}$ (2) and $[(\text{Phen})_2 \text{Ru} (\mu\text{-bpt}) \text{Ru} (\text{Phen})_2]^{3+}$ (3) has also been made. (Ref.-7)

METHODS AND MATERIALS

$[\text{Ru} (\text{Phen})_2 (\text{bpt})] (\text{PF}_6)_4$, $[\text{Cl}_2 \text{Ru} (\mu\text{-2,3-dpp}) \text{Ru} (\text{Phen})_2]_2 (\text{PF}_6)_4$, $[\text{Ru} (\mu\text{-2,3-dpp}) \text{Ru} (\text{Phen})_2]_3 (\text{PF}_6)_6$ and $[(\text{Phen})_2 \text{Ru} (\mu\text{-bpt}) \text{Ru} (\text{Phen})_2] (\text{PF}_6)_3$ were prepared according to the published method, details on equipment and method for spectroscopic photophysical and electrochemical and spectrochemical experiments have been reported [6]. All the solvents chemicals used. A.R. grade. Experimental errors in the reported data are as follows-Absorption maxima 2 nm, luminescence maxima 5 nm, molar absorption coefficients 10%, emission lifetimes 10%, emission quantum yields 20%, redox potentials 20 m V.

Synthesis

$[(\text{Phen})_2 \text{Ru} (\mu\text{-bpt}) \text{Ru} (\mu\text{-2,3-dpp}) \text{Ru} (\text{Phen})_2] (\text{PF}_6)_7$ (1)- The trinuclear complex ligand $[\text{Cl}_2 \text{Ru} (\mu\text{-2,3-dpp}) \text{Ru} (\text{Phen})_2]_2 (\text{PF}_6)_4$ (0.045 g, 0.021 m. mol) was dissolved in ethanol 95% (3 ml) and this was treated with 0.0008 g, 0.045 m mol of AgNO_3 in methanol (3ml) at room temp. The reaction mixture turned blue as the precipitate of AgCl formed. The solution was left stirring for 3 hours. The complex

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metal [Ru (Phen)₂ (bpt) (PF₆) (0.010g, 0.027m mol) was dissolved in ethylene glycol (3ml) and this was added to the mixture. The reaction was then left to reflux for 4 days. The mixture was then allowed to cool and the black AgCl was removed by centrifugation after which the remaining is reduce under to 3 ml. Water (5ml) and a few drops of a concentrated NH₄ PF₆ solution were then added. The dark precipitate was collected and washed with water and diethyl ether (25 ml each), The product was then recrystallized.

RESULTS

Complex [Ru (Phen)₂ (bpt)]⁺ was used as. the complex ligand species and as the complex metal partner [Cl₂Ru (μ-2,3-dpp) Ru (Phen)₂]₂⁴⁺ was employed in a ratio 1: 1.

The new complex is stable in solution under experimental conditions used for at least couple of weeks as demonstrated by the stability of its absorption spectrum. The electronic spectrum in acetonitrile solution (Figure B) in the U.V region (λ_{max} =285 nm, ϵ =156500M⁻¹ cm⁻¹) and a intense and broad absorption in the visible region (λ_{max} = 435nm, ϵ = 36600M⁻¹ cm⁻¹, λ_{max} = 535 nm, ϵ = 2700 M⁻¹ cm⁻¹).

At room in fluid solution, the complex 1 exhibits only one emission feature with a strictly monoexponential. The excitation

spectrum, recorded at the emission maximum, closely overlaps the absorption spectrum in region 360-740nm. At 77K in rigid glass, 1 exhibits two independent emission which show excitation wavelength dependence. The excitation wavelength is 420 nm. The emission spectrum peaks at 600 nm with a lower intensity component at 720 nm and the higher energy component was negligible. According to this excitation spectra measured at 600 nm and 720 nm are different each other. The luminescence spectra obtained upon excitation at 400 nm at room at 77 K are shown in the set of Fig C. Figure C shows emission spectra at 77 K recorded with two different wavelengths. Figure D shows 77 K corrected excitation spectra performed at two different emission wavelengths.. Spectroscopic and photophysical data are listed in Table-I.

Cyclic and differential pulse voltammetry showed that the new complex (4) undergoes several redox processes in the potential window examined (+1.79/-2.00 V vs SCE)- The potential value and the number of electrons exchanged for each wave are given in Table-2.

Spectroelectrochemical oxidation of 1 was performed at 1.05 V vs Ag/AgCl in acetonitrile solution at room . 0.1 M TEAP was used as a supporting electrolyte, and a few drops of 6% HNO₃ were added to stabilize Ru (III) metal ion. Spectroscopic change resulting from the oxidation of R are shown in Fig E.

Table 1. Absorption Emission Data

No.	Complex Formula	abs. (298K) λ_{max} nm (ϵ , M ⁻¹ Cm ⁻¹) ^b	Luminescence (298K)			λ_{max} nm	τ , μ s
			λ_{max} nm ²	τ , ns	ϕ		
1	[(Phen) ₂ Ru (bpt) Ru {(dpp) Ru (Phen) ₂ }] ⁷⁺	530 (2650)	790	65	.001	590 710	4 – 0 1 – 6
2	[Ru{(dpp)Ru (Phen) ₂ }] ⁸⁺	535(4400)	800	65	.001	720	1 – 4
3	[(Phen) ₂ Ru (bpt) Ru (Phen)] ³⁺	450(8500)	645	90	.002	605	3.5

Table 2. Electro Chemical Data

No	Oxid ⁿ	Red ⁿ
1	+ 1.007 [1] (Ru A) + 1.54[2] (Ru B)	- 0.65 [1]; - 0.87 [1]; - 1.47[4]; - 1.70 [4]
2	+ 1.53 [3]	- 0.60[1]; - 0.75 [1]; - 1.20 [1]
3	+ 1.05 [1]; 1.32 [1]	- 1.40[2]; - 1.60 [1]; - 1.65[1]

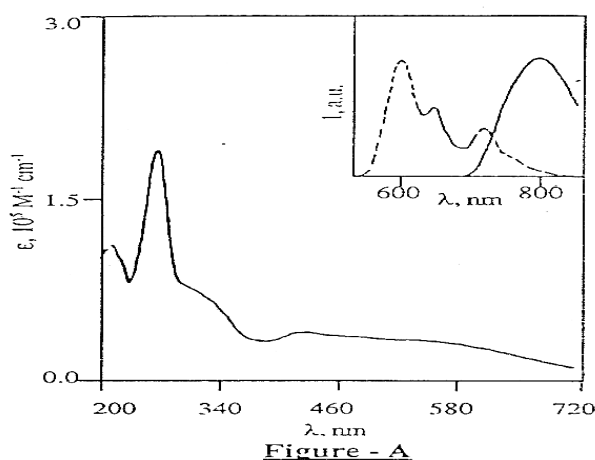


Fig A. Absorption spectrum in acetonitrile solution and (in set) luminescence spectra of 1 (solid line room temperature acetonitrile solution, dashed line, 77K MeOH/EtOH 4:1 rigid matrix λ_{exc} = 400 nm.

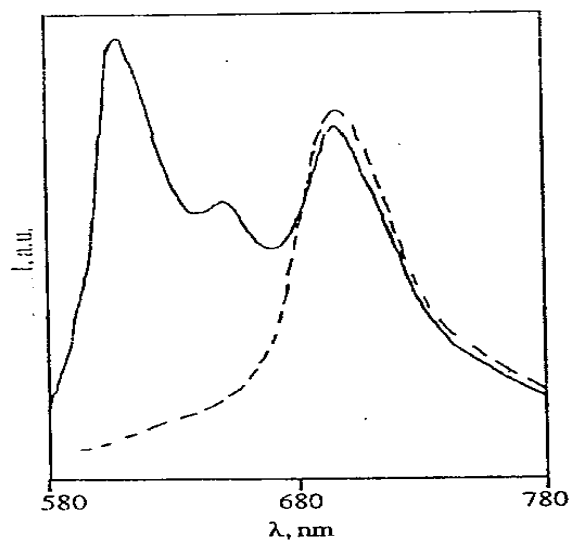
**Figure - B**

Fig B. Emission spectra of 1 in MeOH/EtOH 4:1 (v/v) rigid matrix at 77K. Solid line excitation wave length 420nm dashed line excitation wave length 530nm.

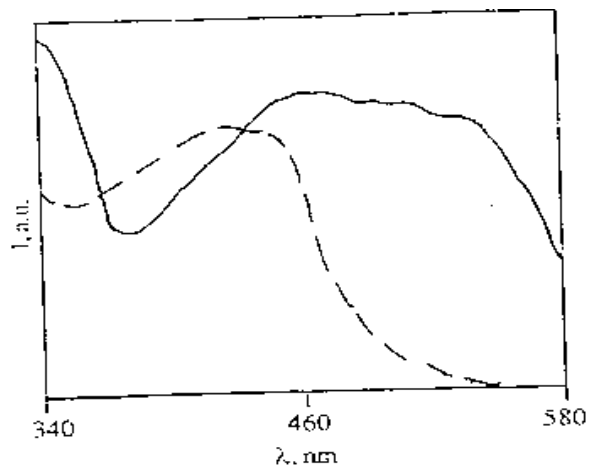
**Figure C**

Fig C. Corrected excitation spectra of 1 in MeOH/EtOH 4:1 (v/v) rigid matrix at 77K. Solid line emission wave length 720 nm dashed line emission wave length 600 nm

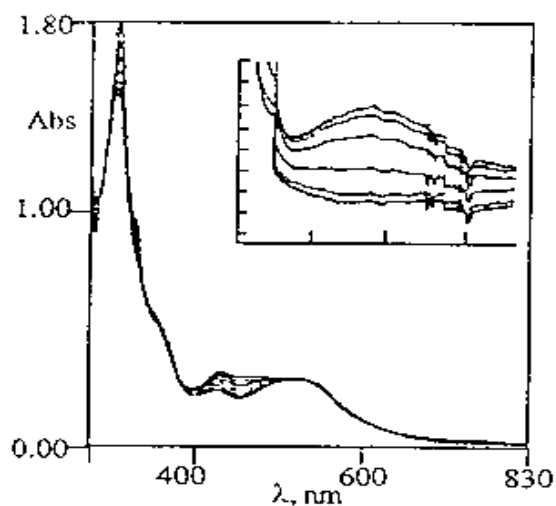


Fig D. Spectroscopic changes on electro chemical oxidation of 1: Oxidation potential 1.05 V vs Ag/AgCl; supporting electrolyte 0.1 M TEAP, solvent acetonitrile, a few drop of 6% HNO_3 were added to stabilized the Ru (III) metal-based component scans were taken at regular intervals over a period of 300 min.

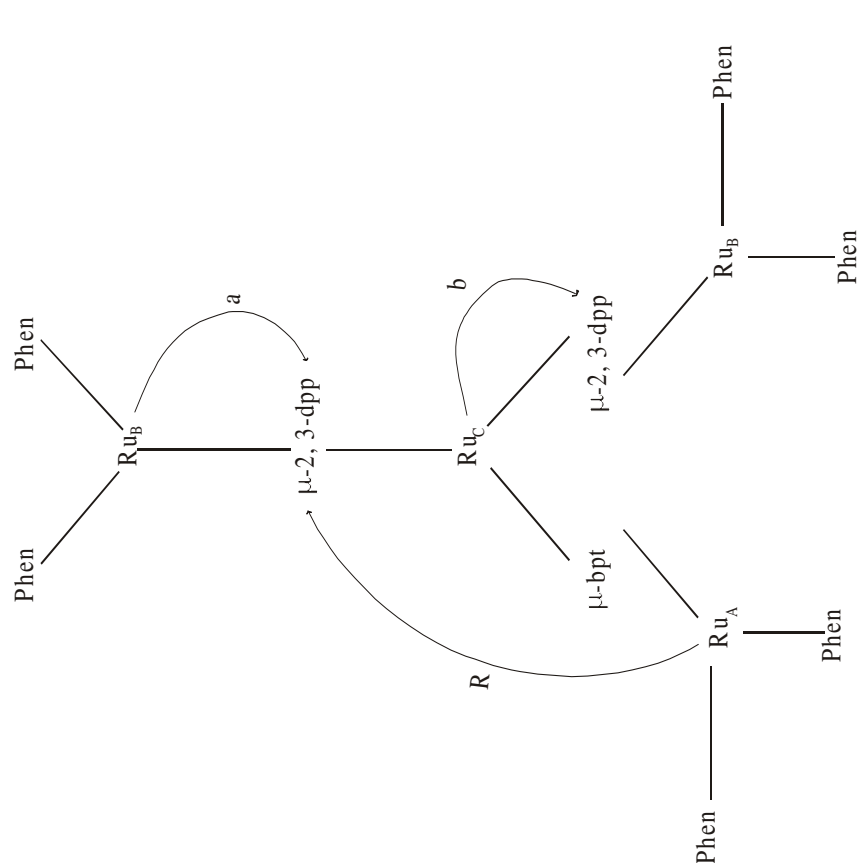


Figure-E :- Lowest energy electronic transitions occurring 1 (only transitions relevant to the discussion are represented R is the “remote” transition reported in the text.

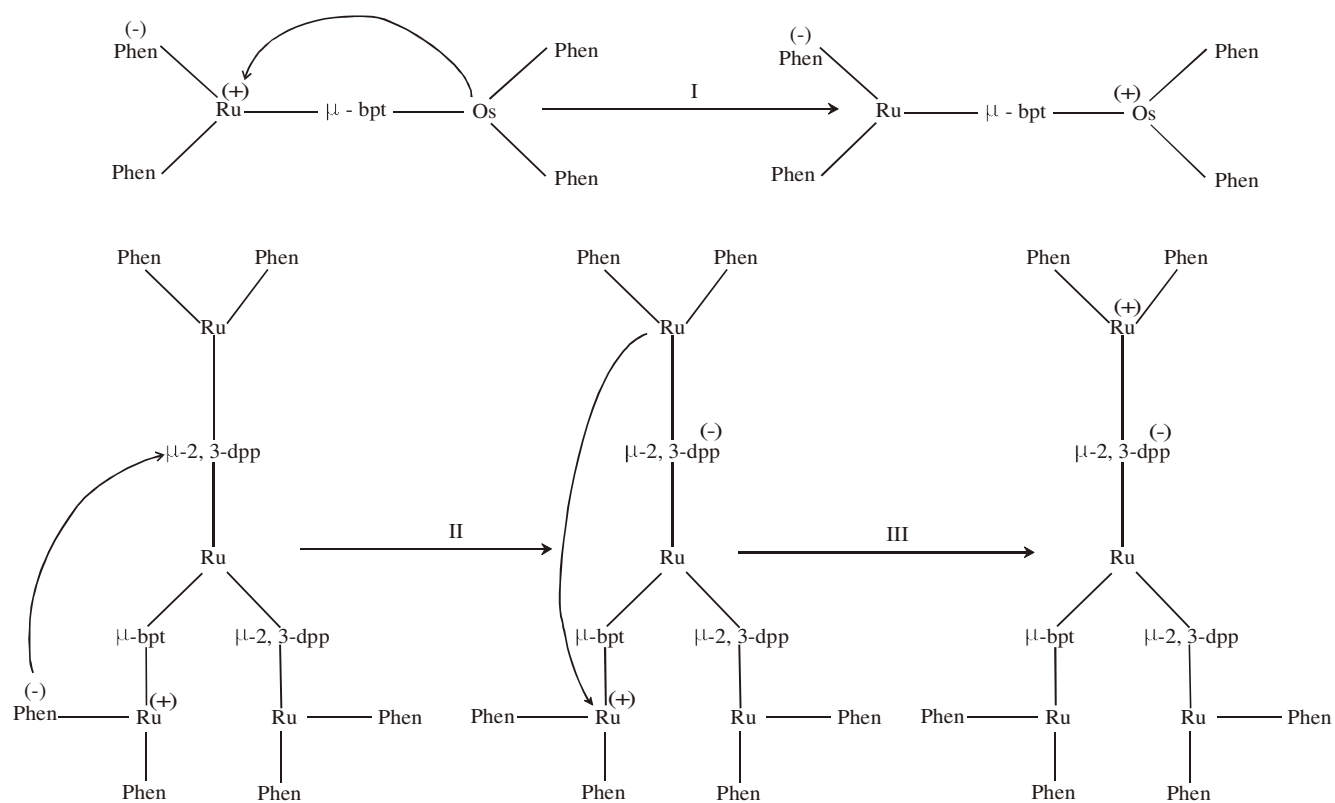


Figure-F :- Electron transfer processes which are proposed to be involved in 4 and 1 to mediate intercomponent energy transfer processes (see text).

DISCUSSION

Redox Behaviour

Redox process of Ru (II) polypyridine complexes are known to be metal centered and ligand centered. In the multi component species 1 studied here there are three different types of metal (FigA) centered respectively [7]. As polyphenanthrene ligands are concerned reduction potential should shift to more negative values in the series μ -2,3-dpp, Phen, μ -bpt [8].

The oxidation pattern of 1 exhibits two reversible oxidation waves, with $E_{1/2}$ at + 1.09 and + 1.55V respectively (Table-2). The intensity of the wave at more positive potential is twice that of the other one. On the basis of above consideration, the first wave is attribute to oxidation of Ru_A and the second wave is assigned to simultaneous to one electron oxidation of the both Ru_B metals. Oxidation of the central Ru_C metal is expected from the potential window investigated [9]. The oxidation of the $(Phen)_2 Ru (\mu$ -dpp)⁺ subunit in 1 is slightly shifted to more positive potentials with respect to oxidation of the corresponding subunit in 3 (+ 1.09vs + 1.04). Such a shift is justified by considering the different electron withdrawing properties of the $[(phen)_2 Ru (\mu$ -2,3dpp)] Ru^{6+} and $(Phen)_2 Ru^{2+}$ subunits which coordinate the $(\mu$ -dpt) $Ru (Phen)_2^{2+}$ moiety. Most likely the third and fourth waves also comprise the successive second reduction of the μ -2,3-dpp bridges [10]. The coordination sphere of central metal moves the μ -2,3- dpp ligands reduction to more negative potentials in 1 with respect to corresponding reduction in table 2. This effects in $E_{1/2}$ values in acetonitrile potentials vs SCE. Working electrode glassy carbon electrode. The figures in brackets refer to the number of electrons exchanged. All the redox processes are reversible unless otherwise stated. Typical compounds concentration 5×10^{-4} M. Oxidation assignments are reported parentheses. Metal atoms are indicated as in Fig A. In case of quasi reversible process, the potential refers to anodic peak. All the redox processes, at which the potential refers to anodic peak data forms, [11] are important for the μ -2,3 dpp than for the first one (compare-0.63 vs 0.61v for the first reduction in 1 and 2 respectively, with -0.76 and - 0.88V for the Second reduction Table 1. The reason is that the second reduction in 1 can not be stabilized by electron delocalization upon the other. The negatively charged bridges contrary to what happens for the second reduction of 2 [12].

Absorption spectrum, Luminescence properties and intercomponent transfer processes

The . U.V. region of the absorption spectrum of 1 is dominated by the strong ligand centered (LC) transitions of Phen ligands, which are known to be found at about 280 nm [13].

Because of the multicomponent nature of the complex, a number of different metal to ligand charge transfer (MLCT) bands are expected such as transition a, b, c and d. (leaving aside higher energy transitions involving the anionic bridge and remote C T transitions such as r) represented in Fig-F. On the basis of electrochemical data, the energies of such transitions should increase in the series $a < b < c < d$ (the energy order for relative energies of b and c is uncertain). The only useful information which can be obtained from best fitting analysis in the presence of a low energy broad band (ϵ_{max} about $4000 M^{-1} cm^{-1}$, half width about $1500 cm^{-1}$) centered in the range 640-660 nm. which could be assigned to the remote C T transitions r shown in Fig F. The strong uncertainties

on the spectral fittings limit further discussion of this band.

The luminescence of 1 at room in fluid solution is quite similar to that of parent compound-2 (Table-I) indicating the same luminescent level for both compounds, that is the $(Phen)_2 Ru \rightarrow \mu$ -2,3- dpp (i.e. $Ru \rightarrow \mu$ - 2, 3- dpp) C T excited state (Figure-F).

The similarity in visible region of the excitation and absorption spectra in acetonitrile fluid solution at room demonstrated that at this efficient intercomponent energy transfer occurs from the upper lying $(\mu$ -bpt) $(Phen)_2 Ru \rightarrow Phen$ (i.e. $Ru_A \rightarrow Phen$) CT excited state of $Ru (Phen)_2 (\mu$ - bpt)⁺ component to the lower lying $Ru_B \rightarrow \mu$ 2, 3-dpp CT excited state of the $Ru (Phen)_2 (\mu$ -2, 3-dpp)²⁺ subunit(s) (the driving force of process G, is-0.34eV) [14].

The intercomponent energy transfer appears to be efficient at 77 K in rigid matrix where two emission with essentially the typical lifetime of $(Phen)_2 Ru$ (bptt and $^*(Phen)_2 Ru(\mu$ -bptt)⁺ and $(Phen)_2 Ru(\mu$ -2,3 dpp)²⁺ component are found (Table-1).

We are suggesting that $(Phen)_2 Ru (\mu$ -bpt)⁺ $Ru (\mu$ -bpt)⁺ and $(Phen)_2 Ru (\mu$ -2,3dpp)²⁺ component can be regarded as 'isolated' component of supramolecule 1 at 77 K. This furthermore supported by considering the low temp excitation and emission spectra (Fig C and Fig D), from emission spectra performed & different excitation in the 420-460 nm region (the region in which that absorption on the Ru_A based chromophore is relatively more important [15]) yields an emission maximum at about 650 nm is due to vibrational progression of the $Ru \rightarrow Phen$ C T emission band at 77 K while 530 nm excitation (i.e. in the absorption bands due to Ru_B - based chromophore is responsible for lower energy emission. It should also be noted that the corrected emission spectra of 1 (Visible maximum at 430 nm, Fig D) is significantly different from that of parent mononuclear complex $[(Phen)_2 Ru (bpt) Ru (Phen)_2 (bpt)]^{3+}$. This definitively excluding the hypothesis of the presence of the species as the origin of the high energy emission.

Luminescence lifetimes measured at 580 and 760 nm (excitation wave length 337 nm in both cases), yields exponential decays of 4.0 and 1.6 μs respectively. Typical of 'Isolated' $Ru \rightarrow \mu$ -2,3- dpp and of $Ru \rightarrow \mu$ -2,3-dpp C T excited states are shown (Table 1). The spectral separation between the two emissions evidently permits spectral resolution of lifetimes. The resolved emission spectra confirms the attribution of the emission bands, showing that the high energy emission is the longer lived one.

The 77 K results are quite surprising on considering that intercomponent energy transfer is efficient even at 77 K in parent complex such as $[(Phen)_2 Ru (\mu$ -bpt) Os $(Phen)_2^{3+}$ [6] and $[Phen)_2 Ru (\mu$ -2,5dpp) Ru $\{(\mu$ -2,3-dpp) $Ru (Phen)_2\}_2^{8+}$. In particular $Ru \parallel Phen$ CT excited state is totally quenched in 4 by energy transfer with sensitization of the Os $\rightarrow bpy$ CT level at both room temp and 77 K.

We propose that the different behavior of 1 and 4 as far as the temp difference of the energy transfer are taken into account. Intercomponent energy transfer in multinuclear metal complexes can occur by an electron exchange (Dexter) mechanism. However in many cases the boundaries between energy and electron transfer can be efficiently mediated by electron transfer step.

In case 4 electron transfer from $(bpy)_2 Os (\mu$ -bpt)⁺ subunit to the excited Ru- based component (Fig G Process I) could be the first step of a two step mechanism which would speed the overall $Ru \rightarrow Phen$ to Os $\parallel bpy$ energy transfer process. / is expected to be fast there is a good communication between the metals [16]. The high electronic coupling furthermore suggest that the reorganization energy should be relatively low because of the large electronic

coupling also, the small reorganization energy suggest that the mechanism is also expected to be efficient at 77 K.

In **1** the analogous reductive electron transfer process is forbidden for energy reasons. However a two step energy transfer could occur by oxidative electron transfer from $^*(\text{Phen})_2 \text{Ru}(\mu\text{-bpt})^+$ subunit to a $(\mu\text{-2,3-dpp}) \text{Ru}(\text{Phen})_2^{2+}$ component (Fig G process II) with production of 'remote' CT level (this level corresponds to transition r in Fig F), Process II is isoenergetic by 0.34 eV and could derive the overall process. In fact, the remote' CT level would undergo to a second electron transfer (Fig F process III) to ultimately yield the luminescent triplet $^*(\text{Phen})_2 \text{Ru}(\mu\text{-2,3dpp})^{2+}$ excited state. Electronic coupling for the long range electron transfer II should be much lower than for I. Furthermore the reorganization energy produce larger temperature and medium effects on the efficiency of electron transfer mechanism **1** would translate in a high nuclear barrier and could explain the inefficiency of the intercomponent transfer process in rigid matrix at 77 K.

In order for the two step mechanism to operate, electron transfer from the remote CT level to produce $^*(\text{Phen})_2 \text{Ru}(\mu\text{-2,3 dpp})^{2+}$ (process III in Fig G) should be relatively fast inspite of the fact that this process is almost isoenergetic [17]. Actually, a whole transfer superexchange mechanism involving the anionic bpt bridge, the central Ru metal and the reduced 2,3 dpp bridge (i.e. another anionic bridge) is expected to yield a strong long distance metal-metal communication between the oxidized Ru (III) of the $(\text{Phen})_2 \text{Ru}(\mu\text{-bpt})$ component and the donor Ru (II) metal of the reduced $(\mu\text{-2,3dpp}) \text{Ru}(\text{Phen})_2$ Unit [18]. Anionic bridging ligands are indeed known to promote strong metal-metal interaction in multicomponent system [19,20]. The presence of the anionic bridge would therefore be decisive to obtain such a strong communication and speed up the second electron transfer step [20]. Further more competitive direct charge recombination from the 'remote' CT level to the ground state should probably lie in the Marcus inverted region ($\lambda \sim 1.73$ eV) and is expected to be not very fast.

Spectroelectrochemical oxidation

Because of the high number of redox sites which are present in **1** and in similar multicomounds. Spectroelectrochemical investigation on these species are quite interesting and can provide useful information on the contribution of the various MLCT transition to the 'Visible' absorption on the extent of the electronic interaction between the metal base chromophores. As the first step towards this direction here we will discuss the spectrum of the singly oxidized form of the title compound.

Spectroelectrochemical oxidation of **1** was performed at 1.05V Vs Ag/AgCl in acetonitrile at room temp. At this potential only oxidation of Ru_A occurs (see redox reaction): Clean isobestic points at about 640, 330 and 280nm were maintained during the course of the oxidation process (Fig F) On reduction back to 0V, the initial spectrum is almost totally recurred showing the reversibility of process. The main spectral change (Fig E) can be interpreted as follows.

The decrease of the absorption in the region around 430 nm is mainly due to disappearing of $\text{Ru}_A \rightarrow \text{phen}$ CT transitions (transition c in Fig F) and a minor extent of $\text{Ru}_A \rightarrow \mu\text{-bpt}$ CT transition expected in the region 330-400 nm [8]. The decrease of phen-centered absorption peaking at 285 nm with the contemporary increase of the absorption in the region 300-330 nm is due to the red shift of the ligand-centered transitions. Actually phen centered

transition in $[\text{Ru}(\text{phen})_3]^{3+}$ occurs at lower energies than the corresponding transition in $[\text{Ru}(\text{phen})_3]^{2+}$ [21]. Increased absorption at $\lambda > 660$ nm is probably due to LMCT transitions (i.e. $\mu\text{-bpt} \rightarrow \text{Ru}_A^{\text{III}}$ CT).

Interestingly an infrared absorption band appears ($\lambda_{\text{max}} = 1370\text{nm}$, $\epsilon_{\text{max}} = 1870 \text{ M}^{-1}$, half width = 3690cm^{-1}) intervalence transfer transition ($\text{Ru}_c^{\text{II}} - \text{Ru}_A^{\text{III}}$ CT) By using the common Hush equation [22] to calculate the electronic delocalization coefficient ∇^2 between the redox centres Ru_c and Ru_A , a value of 0.010 was obtained (the $\text{Ru}_c - \text{Ru}_A$ distance is assumed to be 6.18Å.) The fact that the ∇^2 value is much smaller than the unity confirms the supramolecular nature of **1** in that the valences can be considered trapped [23].

CONCLUSION

The first polynuclear luminescent and redox active complex (**1**) in which both electron rich and electron poor polyphenanthroline bridging ligands are present has been prepared and its spectroscopic photophysical and electrochemical properties have been studied and oxidation reduction process are localized in specific sites of multicomponent structure. However perturbations of each complex on the other subunit of multinuclear system can be evidenced as well as electronic interaction between the metal-based complex. Intercomponent energy transfer is efficient in **1** in fluid solution at room whereas the process is not observed in rigid matrix at 77 K. An energy transfer process has been proposed to rationalize the photophysical properties.

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