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Luminescent Dinuclear Complexes Containing Ruthenium(II)- and Osmium(II)-Terpyridine-Type Chromophores Bridged by a Rigid Biscyclometalating Ligand

**Marc Beley,[1a] Sandrine Chodorowski,[1a] Jean-Paul Collin,[1a] Jean-Pierre Sauvage,[1a]
Lucia Flamigni,[1b] and Francesco Barigelletti*,[1b]**

Laboratoire de Chimie Organo-Minerale, Faculté de Chimie, 1 rue Blaise Pascal, Université
Louis Pasteur, F-6700 Strasbourg, France, and Istituto FRAE-CNR, Via dé Castagnoli 1,
40126 Bologna, Italy

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The spectroscopic properties (UV–vis absorption and luminescence) of Ru(II)- and Os(II)-based mononuclear and dinuclear complexes containing terdentate terpyridine-type (ttp) and related cyclometalating (dpb$^-$, and tpbp^{2-}) ligands are reported [ttp is 4′-*p*-tolyl-2,2′:6′,2″-terpyridine, dpbH is di-*o*-pyridyl-1,3-benzene, tpbpH$_2$ is 3,3′,5,5′-tetrapyridylbiphenyl]. For the dinuclear species, [(ttp)M(tpbp)M′(ttp)]$^{2+}$, the biscyclometalating dianionic tpbp^{2-} ligand bridges the two metal centers, which are held at a fixed distance of 11 Å [M, M′ = Ru, Os]. The five complexes are weakly luminescent at room temperature, $\lambda_{max} \sim 790$ nm, $\phi \sim 4 \times 10^{-5}$, and $\tau \sim 4$ ns for the ruthenium complexes, and $\lambda_{max} \sim 820$ nm, and $\phi \sim 2\text{-}5 \times 10^{-6}$ for the osmium-containing complexes. The luminescence properties are compared to the electrochemical behavior and are discussed in terms of a high degree of covalency for the metal–ligand interaction. For the heterodinuclear [(ttp)Ru(tpbp)Os(ttp)]$^{2+}$ complex, the Ru → Os energy transfer step, which is exothermic by ~0.16 eV, is very efficient ($k_{en} \geq 2 \times 10^9$ s^{-1}), and luminescence only occurs from the Os-based component. The energy transfer takes place according to an exchange-type mechanism.

Introduction

Photoinduced processes in systems containing luminactive and electroactive subunits are of utmost interest for research in the field of supramolecular chemistry.[2,3] In these systems the component subunits, which display individual spectroscopic and electrochemical properties, are linked by saturated or unsaturated bridges. A proper organization of the components can give rise to sequences of light-induced elementary events. Thus, it is possible to mimic natural functions[4] or put artificial devices at work.[5] The bridge plays a key role because it is responsible for the intercomponent electronic coupling and, when sufficiently rigid, affords control of the geometry of the whole system.[2–4,6]

We are engaged in the investigation of light-induced energy and electron transfer processes in polynuclear complexes[7,8] (as well as charge separation in dyads and triads[9]), containing photoactive and electroactive Ru(II)– and Os(II)–bpy or –terpy type centers [bpy = 2,2′-bipyridine, terpy = 2,2′:6′,2″-terpyridine]. The use of terpy as chelating ligand proves useful from a geometrical point of view because the multicomponent system is linearly arranged if the chromophores are connected through the 4′-position of the terpy fragment.[7,9–12] In addition, by employing suitable intervening spacers, it is possible to vary the metal–metal distance on the nanometer scale.[13]

In order to achieve a certain control of the energy levels involved in the photoinduced processes, we wished to tune the electrochemical and spectroscopic properties of systems of the abovementioned type. One way to afford this tuning is to exploit the σ-donating properties of cyclometalating ligands.[14] A novel extension along this line is based on the use of biscyclometalating ligands as bridges, which can act as σ-donors toward both metal centers.[7]

In this contribution we report on the following mononuclear and dinuclear complexes (Chart 1): Ru(ttp)(dpb)$^+$ (**Ru**), Os(ttp)(dpb)$^+$ (**Os**), (ttp)Ru(tpbp)Ru(ttp)$^{2+}$ (**RuRu**), (ttp)Os(tpbp)Os(ttp)$^{2+}$ (**OsOs**), and (ttp)Ru(tpbp)Os(ttp)$^{2+}$ (**RuOs**) [ttp is 4′-*p*-tolyl-2,2′,6′,2″-terpyridine, dpbH is di-*o*-pyridyl-1,3-benzene, tpbpH$_2$ is 3,3′,5,5′-tetrapyridylbiphenyl].

Because of the geometrical properties of the tpbp^{2-} bridge the metal–metal distance in the dinuclear complexes is fixed at 11 Å.[7] The synthesis and characterization of **RuOs**, which is suited for investigating the Ru → Os energy transfer (vide infra), as well as the luminescence results for the five complexes are reported

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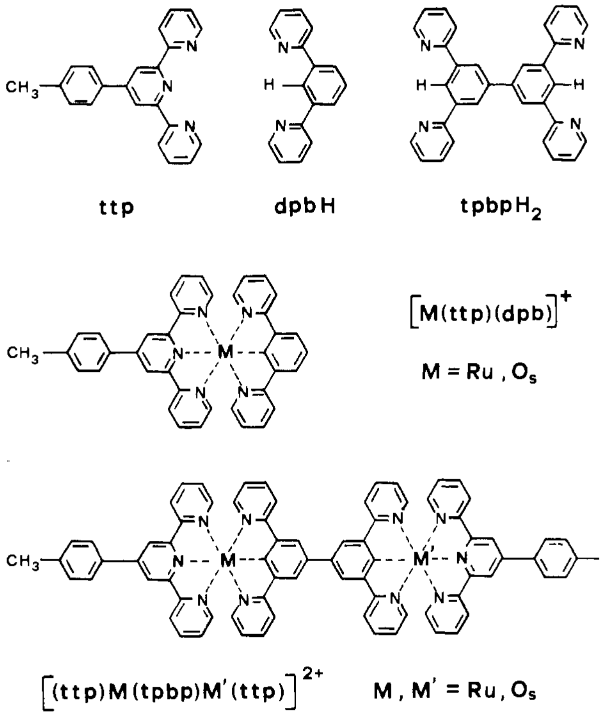
Chart 1



here for the first time. The synthesis, electrochemical behavior, and UV–vis absorption spectra for **RuRu** and **OsOs** have in part been described in conjunction with intervalence transfer studies.[7]

Experimental Section

Preparation of the Complexes. The complexes Ru(ttp)(dpb)$^+$ (**Ru**), Os(ttp)(dpb)$^+$ (**Os**), (ttp)Ru(tpbp)Ru(ttp)$^{2+}$ (**RuRu**), and (ttp)Os(tpbp)-Os(ttp)$^{2+}$ (**OsOs**) were prepared according to literature procedures.[7]

Ru(ttp)(tpbpH)(PF$_6$). A mixture of Ru(ttp)Cl$_3$[9b] (0.19 g, 0.36 mmol) and AgBF$_4$ (0.228 g, 1.117 mmol) in acetone (30 mL) was refluxed for 2 h under air. After cooling and filtration, the solvent was evaporated and the residue was dissolved in *n*-BuOH (50 mL). This solution was added dropwise, under argon, to a warm solution of tpbpH$_2$[15] (0.166 g, 0.36 mmol) in *n*-BuOH (100 mL) for 5 h. The reaction mixture was stirred under reflux for 3 h. After cooling, the solvent was removed and the residue was dissolved in CH$_3$CN (25 mL). The precipitate obtained by addition of an aqueous solution of KPF$_6$ (0.2 g in 100 mL of water) was washed successively with water (100 mL) and ether (50 mL). The product was purified by column chromatography (SiO$_2$; CH$_3$CN–aqueous solution of KNO$_3$ as eluent; yield 46%). ^{1}H NMR (200 MHz, CD$_3$CN): δ 9.04 (2H, s), 8.92 (2H, s), 8.78 (2H, d, 4.6 Hz), 8.67 (1H, s), 8.55 (4H, d, J = 8.2 Hz), 8.21 (4H, d, J = 8.0 Hz), 8.11 (4H, d, J = 8.2 Hz), 7.96 (2H, td, J = 7.6 and 1.8 Hz), 7.64 (2H, m), 7.61 (2H, m), 7.55 (2H, d, J = 8.1 Hz), 7.42 (2H, m), 7.32 (2H, m), 7.10 (4H, t, J = 8.0 Hz), 6.53 (2H, t, J = 6.1 Hz), 2.52 (3H, s). FAB-MS (nitrobenzyl alcohol matrix): m/z 886.0; Ru(ttp)(tpbpH)$^+$ requires 886.

(ttp)Ru(tpbp)Os(tpp)(PF$_6$)$_2$ (RuOs). A mixture of Ru(ttp)(tpbpH)-(PF$_6$) (0.12 g, 0.12 mmol) and Os(ttp)Cl$_3$[16] (0.075 g, 0.12 mmol) in *n*-BuOH (120 mL) was refluxed under argon for 20 h. After evaporation of *n*-BuOH, the black residue was dissolved in CH$_3$CN (20 mL). This solution was treated with an aqueous solution of KPF$_6$ (0.4 g in 100 mL of water). The precipitate obtained was washed with water (100 mL) and ether (50 mL). The mixture of complexes was separated by silica gel chromatography. Elution with KNO$_3$ in an acetone–water mixture (90:10, KNO$_3$ 0.5 M) gave **RuOs** as a deep brown solid (0.098 g, 60%). ^{1}H NMR (200 MHz, CD$_3$CN): δ 9.04 (6H, s), 8.94 (2H, s), 8.62 (4H, d, J = 8.2 Hz), 8.46 (4H, m), 8.12 (4H, t, J = 7.8 Hz), 7.66 (12H, m), 7.28 (4H, d, J = 4.3 Hz) 7.18 (4H, d, J = 4.3 Hz), 7.0 (6H, m), 6.70 (4H, m), 2.55 (3H, s) 2.53 (3H, s). FAB-MS (nitrobenzyl alcohol matrix): m/z = 1545.2; (ttp)Ru(tpbp)Os(ttp)(PF$_6$)$^+$ requires 1545.

Equipment and Methods. The instruments and procedures used to obtain ^{1}H NMR spectra, mass spectra, and cyclic voltammograms have been described in a previous paper.[9b]

Absorption spectra were measured in acetonitrile solution at room temperature with a Perkin-Elmer Lamdba 9 spectrophotometer. Luminescence experiments were performed in deaerated butyronitrile solutions at the indicated temperatures. The butyronitrile solvent was freshly distilled, and deaeration of the samples was accomplished by repeated freeze–pump–thaw cycles. Uncorrected luminescence spectra were obtained with a Spex Fluorolog II spectrofluorimeter, and uncorrected band maxima are used throughout. Correction of the luminescence profile was performed by using software provided by the firm. Luminescence quantum yields were evaluated by comparing areas under the corrected luminescence profiles on an energy scale and with reference to ϕ = 0.005 for Os(bpy)$_3$$^{2+}$,[17]. The experimental uncertainty in the band maxima for absorption and luminescence spectra is 2 nm; that in the luminescence intensity is 30%.

Luminescence decay measurements were performed with an IBH single photon counting equipment or with a laser-based system. In the former case, the operating lamp employed deuterium and excitation and emission wavelengths were selected with monochromators or optical filters. In the latter case, the apparatus was based on a mode-locked, cavity-dumped Nd:YAG laser (Continuum PY62-10) and a streak camera (Hamamatsu C1587) equipped with a fast single sweep unit (M1952). Excitation was at 532 nm, and pulse duration was 35 ps. The light emitted was collected and fed into the entrance of a spectrograph (HR 250 Jobin-Yvon) and then focused on the slit of the streak camera. Acquisition of the streak images was performed via cooled CCD camera (Hamamatsu C3140). In both cases, the processing software was based on iterative nonlinear least-squares procedures[18] and was running on PCs connected to the equipment. The time resolutions of the single photon spectrometer and of the laser-based system are estimated to be 200 and 30 ps, respectively, and the uncertainty in the evaluated lifetimes is 10%.

Results and Discussion

The homodinuclear complexes (ttp)M(tpbp)M(ttp)$^{2+}$ (M = Ru or Os) can be prepared by oxidative coupling of their corresponding mononuclear complex.[7] This procedure, applied to stoichiometric amounts of Ru and Os mononuclear complexes, is expected to lead to a mixture of homo and heterodinuclear complexes (**RuRu, OsOs,** and **RuOs**). These compounds would display exactly the same retention times by silica gel chromatography and would thus be virtually impossible to separate. In order to avoid these difficulties, a sequential method based on the use of the bridging ligand dpbpH$_2$[15] has been preferred. The reaction of Ru(ttp)(acetone)$_3$$^{2+}$ with an excess of dpbpH$_2$ gave (ttp)Ru(tpbpH)$^+$ in 46% yield. In a second step, the reaction between this complex and Os(ttp)Cl$_3$ afforded the heterodinuclear **RuOs** complex in appreciable yield (60%).

Visible light absorption in complexes of the Ru(II)– and Os(II)–polypyridine families leads to formation of low-lying ^{1}MLCT excited states.[19] After intersystem crossing, formally triplet MLCT luminescent levels are populated. The energy ordering of the various ^{3}MLCT levels is as follows: (i) those based on ruthenium lie at higher energy than those based on osmium as the latter is easier to oxidize, and (ii) in mixed-ligand mononuclear complexes, the lowest lying MLCT level involves the ligand(s) easier to reduce. In polynuclear complexes, each metal-centered chromophore can be viewed as a mixed-ligand unit, incorporating terminal and bridging ligands. For this reason, in order to investigate the role played by the electronic and geometric factors in light-induced intercomponent energy and electron transfer processes within polynuclear complexes, it is of relevance to know whether peripheral or bridging ligands are involved in the lowest-

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Table 1. Ground-State Absorption Maxima[a]

	λ_{max}, nm (ϵ, M^{-1} cm^{-1})				
$Ru(ttp)(dpb)^+$	286 (43 000)		504 (10 800)	550 (8250)	
$Ru(ttp)(tpbp)Ru(ttp)^{2+}$	287 (109 000)		512 (30 600)	547 (29 350)	
$Os(ttp)(dpb)^+$	288 (48 000)	373 (14 000)	503 (13 650)	537 (13 000)	765 (2000)
$Os(ttp)(tpbp)Os(ttp)^{2+}$	290 (122 000)	372 (45 000)	513 (35 500)	541 (37 250)	770 (4500)
$Ru(ttp)(tpbp)Os(ttp)^{2+}$	288 (119 000)	368 (42 000)	511 (35 450)	542 (35 700)	770 (2700)
$Ru(ttp)_2^{2+}$ [b]	284 (68 000)	310 (76 000)	490 (28 000)		
$Os(ttp)_2^{2+}$ [c]	286 (58 000)	314 (68 000)	490 (26 000)		667 (6600)

[a] CH_3CN solutions, room temperature. For some complexes, slightly different values are reported in ref 7. [b] Reference 9b. [c] Reference 9c.

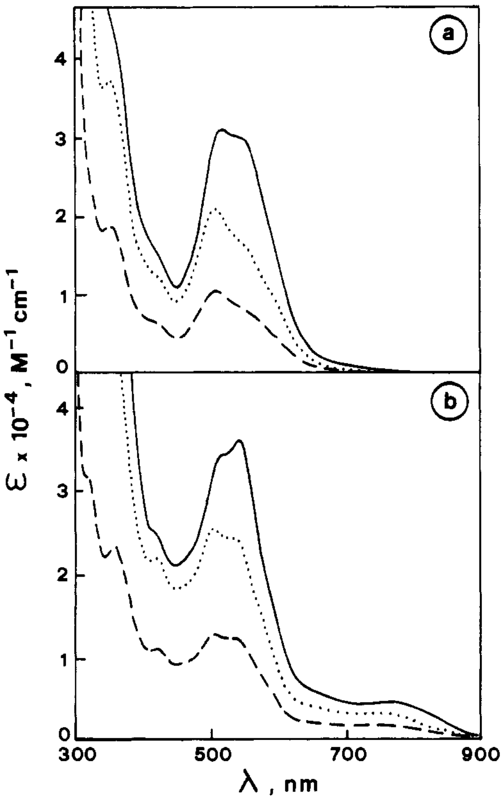

Figure 1. Room temperature absorption spectra of CH_3CN solutions of (a) 2 × 10^{-5} M **Ru** (– –), 4 × 10^{-5} M **Ru** (2**Ru**, ···), and 2 × 10^{-5} M **RuRu** (—); (b) 2 × 10^{-5} M **Os** (– –), 4 × 10^{-5} M **Os** (2**Os**, ···), and 2 × 10^{-5} M **OsOs** (—).

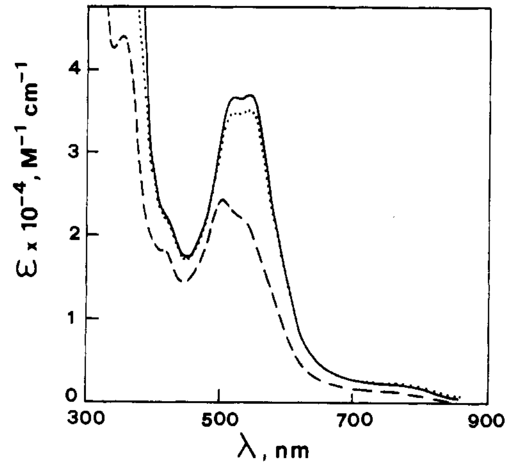

Figure 2. Room temperature absorption spectra of CH_3CN solutions of a 1:1 mixture (2 × 10^{-5} M each) of **Ru** and **Os** (**Ru** + **Os**, –P–), a 1:1 mixture (1 × 10^{-5} M each) of **RuRu** and **OsOs** ($^1/_2$[**RuRu**+**OsOs**], ···), and 2 × 10^{-5} M **RuOs** (—).

Table 2. Extended Hückel Calculations of MO Properties for the Ligands[a]

	LUMO of the ligand	
L	energy, eV	non-zero overlap for $d_M \rightarrow$ LUMO transitions
ttp	–9.88	$d_{yz} \rightarrow \pi_y{}^b$ ($b_1 \times b_1$, z allowed)
dpb^-	–9.42	$d_{xy} \rightarrow \pi_{xy}{}^b$ ($a_2 \times a_2$, z allowed)
$tpbp^{2-}$ [c]	–9.45	$d_{xy} \rightarrow \pi_{xy}{}^b$ ($a_2 \times a_2$, z allowed)

[a] Results are for planar ligands. The ligand symmetry is C_{2v}, the ligand plane is xz, and z coincides with the C_2 axis of the ligand, i.e. the long axis of the dinuclear species. [b] The symmetry label corresponds to the LUMO properties on the chelating positions. [c] From X-ray studies, the torsional angle between the halves of the biphenyl core of tpbp is 22.2°.[7] However we have found that the energy of the LUMO is only slightly affected by this variation in geometry.

lying MLCT excited state.[20] In an attempt to obtain this piece of information, we will make use of spectroscopic data related to the MLCT transitions (visible absorption and luminescence) and of electrochemical properties.

Spectroscopy. Figures 1 and 2 show the absorption spectra in the visible region of the five complexes, as obtained from 2 × 10^{-5} M CH_3CN solutions. From Figures 1 and 2, one sees that (i) the spectra of **RuRu**, **OsOs**, and **RuOs** do not coincide with the sum of the spectra of the component subunits, **Ru** and **Os**, although (ii) the absorption spectrum corresponding to $^1/_2$ (**RuRu** + **OsOs**) closely resembles that of **RuOs** (Figure 2). This points to a sizable interaction between the two metal centers, likely due to metal–ligand mixing. Actually, from intervalence studies on the $Ru^{II}Ru^{III}$ dinuclear species,[7a] it was found that 23% of electron charge is redistributed in the ground state from the Ru^{II} to the Ru^{III} center, consistent with a high degree of covalency for the Ru–tpbp interaction.

The spectra of Figures 1 and 2 display two bands, at 503–513 and 537–550 nm (Table 1) whose molar absorption extinction coefficients are as expected for singlet–singlet M → L CT transitions ($\epsilon \sim 10^4$ M^{-1} cm^{-1}).[19] According to a simplified description, the bands could be ascribed to MLCT transitions involving the lowest unoccupied molecular orbital (LUMO) of the ttp or the cyclometalating ligands, M → $LUMO_{ttp}$ and M → $LUMO_{dpb/tpdp}$, respectively. For **RuRu**, **OsOs**, and **RuOs** the resulting CT state would be localized on the periphery or between the two metal centers, respectively.[20]

An estimate of the energy ordering of the LUMO for ttp, dpb^-, and $tpbp^{2-}$, as obtained from EHMO calculations,[21] is $LUMO_{ttp} < LUMO_{dpb} < LUMO_{tpbp}$, Table 2. On this basis, one expects that the transition involving ttp occurs at lower energy than that involving dpb^- or $tpbp^{2-}$. A nonzero overlap between metal-centered and LUMO (ligand-centered) orbitals is found in all cases (Table 2), and according to current theories,[22] intense CT optical transitions are expected to involve either the peripheral ttp ligand and the cyclometalating ligands. These results suggest

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Table 3. Luminescence Data[a]

	298 K				77 K	
	λ_{max}, nm	τ, ns	I_{rel}	ϕ[b]	λ_{max}, nm	τ, μs
Ru(ttp)(dpb)$^+$	784	4.5	100	4.5×10^{-5}	752	0.48
Ru(ttp)(tpbp)Ru(ttp)$^{2+}$	798	3.96	81	3.7×10^{-5}	762	0.44
Os(ttp)(dpb)$^+$	824	[c]	12	5.4×10^{-6}	832	[c]
Os(ttp)(tpbp)Os(ttp)$^{2+}$	820	[c]	5	2.4×10^{-6}	[c]	[c]
Ru(ttp)(tpbp)Os(ttp)$^{2+}$	816	[c]	12	5.4×10^{-6}	834	[c]
Ru(ttp)$_2^{2+}$	640[d]	0.95[d]		3.2×10^{-5} [d]	628	11.0
Os(ttp)$_2^{2+}$	734[e]	220[e]		2.0×10^{-2} [e]	730	2.8

[a] Butyronitrile deareated solutions. [b] Relative to Os(bpy)$_3^{2+}$, $\phi = 0.005$.[17] Excitation of isoabsorptive solutions was performed at 500 nm. [c] Too weak to detect. [d] Reference 13. [e] Reference 9c.

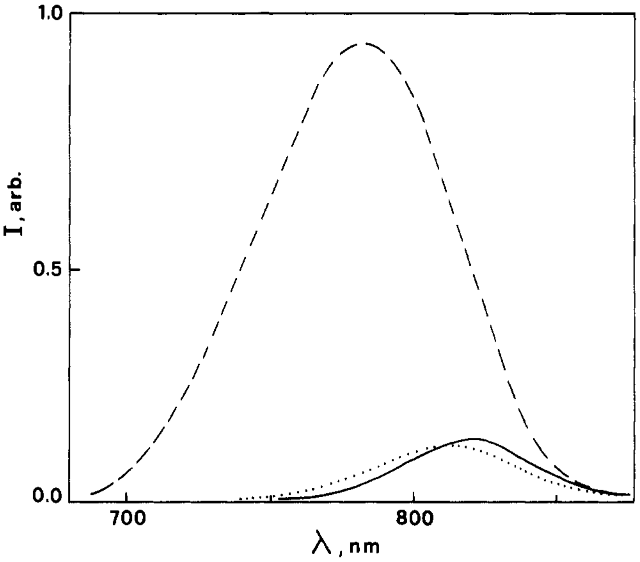

Figure 3. Room temperature luminescence spectra of isoabsorptive (λ_{exc} = 500 nm) butyronitrile solutions of **Ru** (– –), **RuOs** (···), and **Os** (—).

that it is possible to use the available absorption spectra to check the predicted energy ordering for the MLCT transitions (see below).

The spectra of the complexes containing the Os(II)-based component display additional bands at 765–770 nm (Table 1), which are ascribed to direct population of ^{3}MLCT excited states.[19b]

In Figure 3 are depicted luminescence spectra for **Ru**, **RuOs**, and **Os**, and Table 3 lists luminescence band maxima, relative intensities, and lifetimes. For comparison purposes, results for Ru(ttp)$_2^{2+}$ and Os(ttp)$_2^{2+}$ complexes are also included in the table. From Table 3, one sees that the luminescent energy level for the cyclometalated complexes undergoes a bathochromic shift with respect to what happens for their noncyclometalated counterparts. In addition, it is found that at room temperature **Ru**[23] and **RuRu** exhibit a slightly stronger luminescence than Ru(ttp)$_2^{2+}$, and that **Os**, **OsOs**, and **RuOs** are very weak emitters ($\phi \sim$ 2-5 $\times$ 10^{-6}), at odd with Os(ttp)$_2^{2+}$ (ϕ = 0.02[9c]).

These results can be discussed in terms of the σ-donating ability of cyclometalating ligands,[14] which is responsible for (i) a lowering of the luminescent MLCT energy levels for the cyclometalated complexes with respect to the related non-cyclometalated complexes, and (ii) an increase in energy separation between the MLCT levels and higher lying, thermally populated, nonluminescent MC levels.[24] Because of point (i) above, the decreased energy gap between the luminescent level and the ground state is expected to result in a faster deactivation through radiationless paths.[25] However, because of point (ii) above, for complexes of the Ru(II) family, the MC levels become less accessible[11a,19] and a more intense room temperature luminescence is expected in cyclometalated than in related non-cyclometalated complexes. No such effect is expected for Os(II)-based complexes as the MLCT–MC energy separation is large enough to prevent thermal population of the MC levels even in non-cyclometalated complexes.[9c]

In an attempt to clarify whether the lowest energy MLCT level involves ttp or the cyclometalating ligand, one can compare the absorption and luminescence spectra of the mononuclear and dinuclear species. In general terms, two types of behavior are usually registered,[20,26] according to what follows. (i) If the cyclometalating ligand (which plays the role of bridging ligand in the dinuclear species) is the one involved in the lowest MLCT level, the absorption (and luminescence) band will move to lower energy on going from the mononuclear complex to the dinuclear complex. This effect is due to the stabilizing influence of the added metal center on the LUMO level of the bridging ligand. (ii) If the ttp ligand (which plays the role of terminal ligand in the dinuclear species) is the one involved in the MLCT level, the addition of the second metal center will cause a raising of the energy of the MLCT transition.[26]

For the two singlet–singlet absorption bands in the visible region (Table 1), on passing from **Ru** to **RuRu** one sees that the 504-nm band apparently moves to 512 nm and that the 550-nm band moves to 547 nm. The former seems therefore ascribable to a Ru → dpb/tpbp transition (case (i) above), while the latter should correspond to a Ru → ttp transition (case (ii) above). For **Os**, **OsOs**, and **RuOs**, a less clear behavior is found, as both absorption bands move to lower energy.

By taking into account the luminescence properties for the ruthenium complexes, one sees that the emission band maximum moves to slightly lower energy on passing from **Ru** to **RuRu** (from λ = 784 to λ = 798 nm, respectively). This is not in accord with the hypsochromic shift exhibited by the lowest energy absorption band (from 550 to 547 nm). In addition, for the osmium complexes the trend in the luminescence maxima appears reversed with respect to what happens for the ruthenium complexes (see Table 3).

We conclude that, for the series of examined complexes, the usual approach based on a simple localized description of the MLCT excited states for the interpretation of the spectroscopic results does not provide a clearcut indication concerning the type of ligand (ttp or cyclometalating) involved in the lowest lying excited levels. This is related to the high degree of covalency for the metal-ligand interaction, as evidenced by the electrochemical data discussed below.

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(23) A Ru-based complex incorporating a related cyclometalating ligand, phenylbipyridine, has been previously reported, see: Collin, J.-P.; Beley, M.; Sauvage, J.-P.; Barigelletti, F. *Inorg. Chim. Acta* **1991**, *185*, 91.

(24) Very weak luminescence for MC excited states has been occasionally reported; see, for instance: Bolletta, F.; Rossi, A.; Barigelletti, F.; Dellonte, S.; Balzani, V. *Gazz. Chim. Ital.* **1981**, *111*, 155.

(25) (a) Englman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 1459. (b) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630. (c) Barkawi, K. R.; Murtaza, Z.; Meyer, T. J. *J. Phys. Chem.* **1991**, *95*, 47.

(26) (a) Barigelletti, F.; De Cola, L.; Balzani, V.; Hage, R.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *Inorg. Chem.* **1989**, *28*, 4344. (b) Barigelletti, F.; De Cola, L.; Balzani, V.; Hage, R.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *Inorg. Chem.* **1991**, *30*, 641.

Table 4. Electrochemical Potentials[a]

	E_{ox}, V		E_{red}, V
$Ru(ttp)(dpb)^{+}$ [b]	+0.485		–1.61
$Ru(ttp)(tpbp)Ru(ttp)^{2+}$ [b]	+0.34	+0.50	–1.55
$Os(ttp)(dpb)^{+}$ [b]	+0.335		–1.60
$Os(ttp)(tpbp)Os(ttp)^{2+}$ [b]	+0.22	+0.34	–1.53
$Ru(ttp)(tpbp)Os(ttp)^{2+}$	+0.29	+0.51	–1.48
$Ru(ttp)_2^{2+}$ [c]	+1.25		–1.24
$Os(ttp)_2^{2+}$ [d]	+0.89		–1.17

[a] CH_3CN solutions, vs SCE. [b] Reference 7. [c] Reference 9b. [d] Reference 9c.

Electrochemistry. Table 4 reports electrochemical potentials for the series of investigated complexes. From these data one sees that substitution of a cyclometalating ligand for a ttp ligand has remarkable electronic consequences. For instance, on passing from $Ru(ttp)_2^{2+}$ to **Ru** the metal-centered oxidation potential changes by 0.77 V (from 1.25 to 0.485 V, respectively). Similarly, on passing from $Os(ttp)_2^{2+}$ to **Os** the oxidation potential changes by 0.56 V (from 0.89 to 0.335 V, respectively). For **RuRu** and **OsOs**, the change in first oxidation potential relative to $Ru(ttp)_2^{2+}$ and $Os(ttp)_2^{2+}$ amounts to 0.91 and 0.67 V, respectively. It is interesting to notice that the ligand-centered reduction is also dramatically affected by the introduction of the cyclometalating ligand. Actually, first reduction for $Ru(ttp)_2^{2+}$ and $Os(ttp)_2^{2+}$ occurs at –1.24 and –1.17 V, respectively, while it occurs at –1.61 and –1.60 V for **Ru** and **Os**, respectively, and at –1.55 and –1.53 V for **RuRu** and **OsOs**, respectively.[27]

The electrochemical results indicate that the σ-donating properties of dpb^- and $tpbp^{2-}$ strongly affect *both* the metal center(s) *and* the ttp ligand(s), the latter becoming more difficult to reduce by at least 0.3–0.4 V. A possible consequence of this redistribution of electronic density is that the energy level of the LUMO of ttp might increase (whereas that of dpb^- and $dpbp^{2-}$ might decrease), by such an extent that the prediction based on the EHMO calculations of Table 2 (lower energy for M→ttp optical transition) is no longer valid.

Energy Transfer in RuOs. The three complexes containing the osmium center, **Os**, **OsOs**, and **RuOs**, exhibit luminescence band maxima centered at ~820 nm, and comparable luminescence intensities, Table 3. As in each case excitation was performed at 500 nm one concludes that for **RuOs** (where the Ru-based chromophore absorbs ~50% of the light) an efficient Ru → Os energy transfer takes place. As can be judged from the luminescence band maxima of **Ru** and **Os**, this step is exothermic by ~0.16 eV and leads to population of an osmium-centered excited state,[28] which is the final state responsible for the luminescence (Figure 3). For **Ru** the luminescence lifetime is 4.5 ns, and taking into account that for **RuOs** no residual Ru-based luminescence intensity is detected (within the experimental error of 10%), the energy transfer rate is estimated to be $\geq 2 \times 10^9$ s^{-1}. As the luminescence was too weak, we were unable to obtain a more precise value with our laser-based system.

Two types of mechanism for energy transfer are described in the literature, the dipole–dipole[29] and the exchange (contact)[30] transfer. According to the dipole–dipole (Förster) treatment,[29] one evaluates the overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor, as taken on an energy scale. In this way, it is possible to obtain the critical transfer radius, R_0, for which the energy transfer efficiency is 50%, and the energy transfer rate, k_{ET}^F, eq 1.

$$R_0^{\,6} = 5.87 \times 10^{-25}\phi_D/n^4 \int F_D(\bar{\nu})\epsilon_A(\bar{\nu})\,d\bar{\nu}/\bar{\nu}^4 \qquad (1a)$$

$$k_{ET}^{\ F} = (1/\tau_D)(R_0/r)^6 \qquad (1b)$$

In eq 1 ϕ_D, $F_D(\bar{\nu})$ and τ_D are the luminescence quantum yield, the normalized luminescence spectrum, and the luminescence lifetime of the donor, respectively, n is the refractive index of the solvent, $\epsilon_A(\bar{\nu})$ is the absorption spectrum of the acceptor, and r is the distance separation between the chromophores. For **RuOs** we assume that the donor and the acceptor are the $Ru(ttp)(dpb)^+$ ($\phi_D = 4.5 \times 10^{-5}$, and $\tau_D = 4.5$ ns, Table 3), and the $Os(ttp)(dpb)^+$ moieties, respectively, and that the chromophore–chromophore separation corresponds to the metal–metal separation, $r = 11$ Å.[31] From the available spectral quantities the overlap integral of eq 1 is evaluated as 5.5×10^{-14} M^{-1} cm^3. By using the mentioned photophysical data we find $R_0 = 8.8$ Å, and $k_{ET}^F = 5.6 \times 10^7$ s^{-1} at r = 11 Å. Clearly this finding rules out the Förster mechanism as responsible for the energy transfer in **RuOs**, which takes place at $k_{ET} \geq 2 \times 10^9$ s^{-1}. The exchange (Dexter) transfer[30] is therefore the mechanism most likely to operate in this case.

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(27) The electrochemical potentials are expected to be affected by the charge of a complex. For instance, on passing from the homoleptic $Ru(ttp)_2^{2+}$ and $Os(ttp)_2^{2+}$ complexes to the heteroleptic **Ru** and **Os** complexes the charge changes from 2+ to +1. Such a charge effect can be estimated by considering that for the $Ru(bpy)_3^{2+}$ and $Ru(bpy)_2(bpt)^+$ complexes the bpy centered reduction changes by 0.12 V (from –1.35 to –1.47 V, respectively) on passing from the 2+ homoleptic complex to the +1 heteroleptic complex[26a] [bpt^- is bipyridyltriazole, a negatively charged, noncyclometalating ligand].

(28) The excitation spectrum of **RuOs** satisfactorily overlaps with its absorption spectrum. However, this result cannot be used as a clear evidence for a Ru → Os energy transfer because the bands of the **Ru** and **Os** components (i) overlap to a large extent and (ii) do not show additive properties.

(29) Förster, Th.H. *Discuss. Faraday Soc.* **1959**, *27*, 7.

(30) Dexter, D. C. *J. Chem. Phys.* **1953**, *21*, 836.

(31) This represents a somewhat crude assumption as we have seen that the metal-based components of the dinuclear complexes loose part of their individual properties. However, the fact that the luminescence properties of **RuOs** can be described as Os-based justifies this approach. Of course, the strong electronic interaction between the Ru- and Os-based components of **RuOs** is consistent with the conclusion that energy transfer takes place *via* an exchange- (contact-type) mechanism, see text.