

Tetranuclear Bimetallic Complexes of Ruthenium, Osmium, Rhodium, and Iridium. Synthesis, Absorption Spectra, Luminescence, and Electrochemical Properties

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Abstract: Extension of the previously used "complexes-as-metals and complexes-as-ligands" synthetic strategy (*J. Am. Chem. Soc.* 1992, 114, 2944) to cyclometalated Rh(III) and Ir(III) complexes has allowed us to prepare four new tetranuclear bimetallic complexes (as PF₆⁻ salts): [Ru{μ-2,3-dpp}Rh(ppy)₂]₃⁵⁺ (RuRh₃), [Ru{μ-2,3-dpp}Ir(ppy)₂]₃⁵⁺ (RuIr₃), [Os{μ-2,3-dpp}Rh(ppy)₂]₃⁵⁺ (OsRh₃), and [Os{μ-2,3-dpp}Ir(ppy)₂]₃⁵⁺ (OsIr₃); 2,3-dpp = 2,3-bis(2-pyridyl)pyrazine, ppy = phenylpyridine anion. The absorption spectra, excited state properties, and electrochemical behaviors of the four novel complexes in CH₂Cl₂ solution have been investigated and compared with those observed for previously studied Ru(II)- and/or Os(II)-based tetranuclear complexes. All the complexes examined exhibit very intense ligand-centered (LC) absorption bands in the UV region and moderately intense metal-to-ligand charge-transfer (MLCT) bands in the visible region. The RuRh₃ and OsRh₃ complexes show a luminescence emission (at 77 K, λ_{max} = 645 and 789 nm, respectively) that can be assigned to the lowest ³MLCT level of the Ru-based and Os-based cores. For RuIr₃ and OsIr₃ complexes, the observed emissions (at 77 K, λ_{max} = 726 and 810 nm, respectively) are likely due to the peripheral Ir-based units in the former compound and to the Os-based core in the latter. All the compounds exhibit luminescence also at room temperature, where mixing of states of different orbital origin is more likely. Cyclic and differential pulse voltammetry experiments carried out in argon-purged dichloromethane solution at room temperature show that the RuRh₃, RuIr₃, and OsIr₃ complexes undergo three reversible reduction processes in the -0.3/-0.7 V (*vs* SCE) potential range, which correspond to the successive first reduction of the three bridging ligands in each complex. At more negative potentials (-1.1/-1.6 V), three other reduction waves are observed, assigned to the successive second reduction of each bridging ligand. The trend observed for the reduction waves of the various complexes is discussed. The reduction processes observed for OsRh₃ are irreversible. For the RuRh₃ and RuIr₃ complexes, irreversible oxidation waves are observed at +1.25 and +1.40 V, respectively. For the former compound, the process involves one electron and can be attributed to oxidation of the Ru ion, whereas for the RuIr₃, the process involves at least three electrons and therefore should concern the Ir peripheral units. For OsIr₃, a somehow reversible oxidation wave at +1.00 V, assigned to the one-electron oxidation of the central Os(II) ion, is followed by an irreversible, three-electron wave at +1.40 V, assigned to the one-electron oxidation of the three peripheral Ir-based units. In the case of OsRh₃, an irreversible one-electron oxidation at +0.75 V, assigned to the oxidation of the Os ion, is followed by an irreversible oxidation at +1.50 V, which involves more than one electron, and is therefore assigned to the oxidation of the peripheral Rh-based units. The successful synthesis of these new tetranuclear compounds shows that combination of N-N (bipyridine type) and C-N (cyclometalating type) chelating sites is a promising strategy to extend the number and the type of metals and/or ligands that can be incorporated in luminescent and redox-active complexes of high nuclearity.

Introduction

Much attention is currently devoted to the study of polynuclear metal complexes.^{2,3} The interest in these compounds is related not only to their large size but also to the variety of components that can be incorporated into the supramolecular array (i.e., the specific pieces of information, such as electronic excited states and redox levels, embedded in the array).^{3a} Interesting inves-

tigations along this line have been recently reported by several laboratories.⁴⁻⁹ In our studies on luminescent and redox-active polynuclear (up to 22 metal ions)¹⁰ complexes, we have used Ru(II) and Os(II) as metals, 2,3- and 2,5-bis(2-pyridyl)pyrazine (dpp) as bridging ligands, and 2,2'-bipyridine (bpy) and 2,2'-biquinoline (biq) as terminal ligands. Recently we have begun

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Table 1. Reaction Times, Yields, and Elemental Analyses for the New Compounds

compound	reaction time (h)	yields	elemental analyses (found (calcd))		
			C%	H%	N%
OsRh ₃	2.0	88%	45.7 (45.5)	2.8 (2.7)	8.7 (8.8)
RuRh ₃ ^a	1.5	90%	47.2 (46.9)	2.9 (2.8)	9.2 (9.1)
OsIr ₃	2.5	70%	41.6 (41.6)	2.6 (2.5)	7.9 (8.1)
RuIr ₃	2.5	73%	42.1 (42.0)	2.8 (2.7)	8.0 (8.2)

^a Elemental analysis calculated for RuRh₃·3H₂O.

a systematic study aimed to extend the number of different metals and/or ligands that can be incorporated in complexes of high nuclearity.¹¹

The difficulty of this task rests on the fact that, for each type of metal, specific types of ligands must be chosen in order to assure chemical stability and to confer the desired excited state and redox properties. With metals like Rh(III), Ir(III), Pd(II), Pt(II), and Pt(IV), N–N (bipyridine-type) chelating ligands are not fully satisfactory, whereas C–N (cyclometalating) chelating ligands give rise to stable and quite interesting species.^{12–14} For example, attempts to prepare [Ir(bpy)₃]³⁺ led to formation of [Ir(bpy)₂(bpy-C³)]²⁺ where a bpy ligand is cyclometalating.¹² We are therefore extending the “complexes-as-metals and complexes-as-ligands” synthetic strategy^{10,15} to Rh(III), Ir(III), Pd(II), Pt(II), and Pt(IV) metals and to cyclometalating chelating sites both as terminal ligands and as components of bridging ligands. As a first step along this direction, we report here the synthesis and characterization of four new tetranuclear bimetallic complexes involving Rh(III)- and Ir(III)-based units which contain the cyclometalating phenylpyridine anion (ppy⁻) as a terminal ligand. The electrochemical and excited state properties of the new complexes have been investigated and compared with those of previously studied^{13,14} tetranuclear complexes.

Experimental Section

Materials and Methods. The preparations of the precursor complexes [Os(2,3-dpp)₃]²⁺¹⁶ and [Ru(2,3-dpp)₃]²⁺^{17,18} as well as the details and procedures for elemental analyses and IR, absorption, and luminescence spectra and lifetimes have been previously reported.^{3a,17} The complexes [Ir(ppy)₂Cl]₂¹⁹ and [Rh(ppy)₂Cl]₂²⁰ were prepared by following literature procedures.

Preparation of the Complexes. [Ru{(μ-2,3-dpp)Ir(ppy)₂}]₃(PF₆)₅ (RuIr₃) was obtained by slowly adding (20 min) a solution of [Ru(2,3-dpp)₃](PF₆)₂ (0.020 g, 0.018 mmol) in dichloromethane (6 mL) to a refluxing solution of [Ir(ppy)₂Cl]₂ (0.032 g, 0.028 mmol) in the same solvent (3 mL). The reaction mixture turned immediately from yellow to red brown. After the mixture was refluxed for 2.5 h, it was cooled to room temperature and a saturated solution of NH₄PF₆ in ethanol (1.5

mL) was added. The mixture was rotary evaporated in vacuo until the precipitation was complete. The product was filtered off, dissolved in dichloromethane, and reprecipitated with ethanol. The last operation was repeated, and the brown solid, after being washed with diethyl ether, was vacuum-dried (yield 0.040 g, 73%).

The synthetic procedures used to obtain the other tetranuclear complexes were very similar to that described above. The reactant quantities employed and the colors of the new compounds were as follows.

[Ru{(μ-2,3-dpp)Rh(ppy)₂}]₃(PF₆)₅ (RuRh₃). Employed quantities: [Rh(ppy)₂Cl]₂ (0.040 g, 0.041 mmol), [Ru(2,3-dpp)₃](PF₆)₂ (0.030 g, 0.027 mmol). Color: red brown.

[Os{(μ-2,3-dpp)Ir(ppy)₂}]₃(PF₆)₅ (OsIr₃). Employed quantities: [Ir(ppy)₂Cl]₂ (0.044 g, 0.038 mmol), [Os(2,3-dpp)₃](PF₆)₂ (0.030 g, 0.025 mmol). Color: dark brown.

[Os{(μ-2,3-dpp)Rh(ppy)₂}]₃(PF₆)₅ (OsRh₃). Employed quantities: [Rh(ppy)₂Cl]₂ (0.031 g, 0.032 mmol), [Os(2,3-dpp)₃](PF₆)₂ (0.025 g, 0.021 mmol). Color: dark brown.

All the prepared compounds have been characterized by elemental and TLC analyses, IR spectra, and reactivity toward methylation (excess of (CH₃)₃OBF₄ refluxing in dry dichloroethane for 30 min). The characteristic IR bands of ppy⁻ are observed in the 1580–1610 cm⁻¹ region, the modified structure of the ppy⁻ band system in the 1480–1410 cm⁻¹ region is consistent with the presence of the μ-2,3-dpp bands in the same region, while no band of unbridged 2,3-dpp ligands (990 cm⁻¹) is observed. Table 1 shows reaction times, yields, and elemental analyses of the new compounds.

Equipment. Infrared spectra (KBr pellets) were obtained by means of a Perkin-Elmer 1330 spectrometer. Elemental analyses were performed by using a Carlo Erba 1106 apparatus. ¹H NMR spectra were obtained by a Varian Gemini (200 MHz) in CDCl₃ solution. Spectroscopic measurements were carried out in CH₂Cl₂ deaerated solutions. Absorption spectra were obtained at room temperature by means of a Perkin-Elmer λ-6 spectrophotometer. Luminescence spectra were obtained with a Perkin-Elmer LS-50 spectrofluorimeter. Emission lifetimes were measured with Edinburgh 199 single-photon counting equipment. Emission quantum yields were measured at room temperature (20 °C) with the optically dilute method,²¹ calibrating the spectrofluorimeter with a standard lamp. [Ru(bpy)₃]²⁺ in aerated aqueous solution was used as a quantum yield standard, assuming a value of 0.028.²² Electrochemical measurements were carried out in argon-purged CH₂Cl₂ at room temperature with a PAR 273 multipurpose instrument interfaced to a PC. The working electrode was a Pt microelectrode or a glassy carbon (8 mm², Amel) electrode. The counter electrode was a Pt wire, and the reference electrode was a SCE separated with a fine glass frit. The concentration of the complexes was 7 × 10⁻⁴ M. Tetrabutylammonium perchlorate was used as the supporting electrolyte, and its concentration was 0.05 M. Cyclic voltammograms were usually obtained at scan rates of 50, 100, and 500 mV/s. For reversible processes, half-wave potentials (*v*s SCE) were calculated as an average of the cathodic and anodic peaks.

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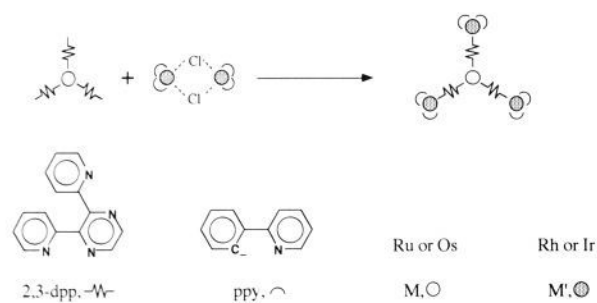
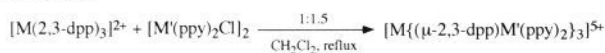
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Scheme 1



The criteria for reversibility were the separation between cathodic and anodic peaks, the close to unity ratio of the intensities of the cathodic and anodic currents, and the constancy of the peak potential on changing the scan rate. The number of exchanged electrons was measured with differential pulse voltammetry (DPV) experiments performed with a scan rate of 20 mV/s, a pulse height of 75 mV, and a duration of 40 ms. The procedure for the calibration of the number of electrons corresponding to the various redox waves has been described in detail.^{3a,23} Experimental errors in the reported data are as follows: absorption maxima, 2 nm; emission maxima, 5 nm; emission lifetimes, 10%; emission quantum yields, 20%; redox potentials, 20 mV. As far as molar absorption coefficients are concerned, the uncertainty in their absolute values is $\sim 10\%$ because of the highly diluted solutions used (10^{-5} – 10^{-4} M).

Results and Discussion

Synthesis. The cleavage of the dinuclear cyclometalated chloro-bridged Rh(III) and Ir(III) complexes by diimine ligands, and therefore the possibility of using these species as “complex metals”, is well-known.^{12,13} In our case, instead of a simple diimine ligand, we have used a mononuclear “complex ligand” which contains three free chelating sites $[M(2,3\text{-dpp})_3]^{2+}$, $M = \text{Ru(II), Os(II)}$; Scheme 1).

In principle, dinuclear and trinuclear complexes could be formed as byproducts due to uncomplete saturation of the chelating sites of the mononuclear complex ligand $[M(2,3\text{-dpp})_3]^{2+}$. The reaction was carried on until complete disappearance of cyclometalating precursors was observed in TLC analysis, indicating that the reaction went to completion. The presence of binuclear and trinuclear byproducts would have caused the appearance of the characteristic band at 990 cm^{-1} of the unbridged 2,3-dpp in the IR spectrum.^{3a} No such band was observed. In a further attempt to detect the presence of species not fully reacted (i.e., binuclear and trinuclear complexes), we have checked the reactivity of the purified product to methylation under conditions in which $[\text{Ru}(\text{bpy})_2(2,3\text{-dpp})]^{2+}$ is fully methylated. No CH_3 signal appeared in the $^1\text{H NMR}$ analysis. Blank experiments on mixtures of $[\text{Ru}(\text{bpy})_2(2,3\text{-dpp})]^{2+}$ and compounds not carrying unsaturated chelating sites allowed us to establish that 3% of unsaturated chelating sites could be easily revealed.

By using the strategy shown in Scheme 1, it is possible to obtain supramolecular systems containing different metals (Ru(II), Os(II), Rh(III), Ir(III)) and different ligands (diimine-bridged ligands and cyclometalated terminal ligands). By choosing the appropriate cyclometalated and diimine-type syntheses, we have set up the synthesis of four new mixed-metal and mixed-ligand tetranuclear complexes with easy and very efficient one-pot reactions. From a general point of view, it can be noted that in reactions between complex metals and complex ligands it is the chemical nature of the former that mainly determines reaction time and yield. In our case the lower reactivity of Ir(III) with respect to Rh(III) clearly reflects on the longer reaction

times and smaller yields (Table 1). The greater reactivity of Ru(II) compared to Os(II) influences the reaction to a lesser extent.

The new tetranuclear species are unstable in coordinating solvents like acetonitrile because of solvolysis reactions yielding the precursor complex ligands and solvated cyclometalated species, as already reported by other authors.¹² Therefore, we have studied the properties of the new tetranuclear complexes in dichloromethane, where these species are fairly stable, as shown by the constancy of their absorption spectra for at least 24 h.

General Properties. The spectroscopic and electrochemical behaviors of transition metal complexes and of organometallic compounds are usually discussed with the assumption that the ground state as well as the excited and redox states involved to interpret the observed properties can be described by a localized molecular orbital configuration.^{12,24,25} With such an assumption, the various spectroscopic transitions are classified as metal-centered (MC), ligand-centered (LC), or charge-transfer (either metal-to-ligand (MLCT) or ligand-to-metal (LMCT)) and the oxidation and reduction processes are classified as metal- or ligand-centered. This simplified picture, of course, is no longer applicable if there is a large degree of covalency in the metal–ligand bonds of the ground state complex and if excited state configurations of different natures are sufficiently close in energy to be intermixed. In the polypyridine-type complexes, the above described approximation is substantially valid. In the cyclometalated complexes, however, the metal–C σ bonds can exhibit a large degree of covalency and the LC and MLCT configurations often lie very close in energy. For these reasons, the localized molecular orbital approach can only be used as a crude approximation and the interpretation of the properties of cyclometalated complexes is not straightforward.^{12,13} Comparison of the results obtained for different ligands or for different metals may be very useful to reach a correct interpretation. On these bases, Kirsch-De Mesmaeker, Watts, and co-workers²⁶ have recently arrived at the conclusion that in the $[\text{Rh}(\text{ppy})_2(\text{TAP})]^{+}$ and $[\text{Rh}(\text{ppy})_2(\text{HAT})]^{2+}$ complexes (where TAP and HAT are the N–N chelating ligands 1,4,5,8-tetraazaphenanthrene and 1,4,5,8,9,12-hexaazatriphenylene, respectively) the HOMO involved in the oxidation process and in the lowest-lying charge-transfer excited state is a covalent metal–C σ -bonding orbital. The lowest-energy excited state would therefore involve a transition from such a σ bond orbital to a π^* orbital of a ligand (σ bond to ligand charge-transfer, SBLCT).

In our tetranuclear complexes, we have two types of units (Scheme 1), i.e. a core which is expected to exhibit the classical properties of the Ru(II)– or Os(II)–polypyridine complexes and three peripheral units which should display the more complex behavior of cyclometalated species. Reciprocal perturbation of the two types of units must also be taken into account.

Electrochemical Behavior. Because of the relative instability of the new complexes in coordinating solvents, the experiments were carried out in dichloromethane with tetrabutylammonium perchlorate as the supporting electrolyte (potential window from -1.7 to $+1.7$ V vs SCE). Except for OsRh_3 , several reversible reduction processes have been observed. The oxidation behavior, however, is less clean. The results obtained have been gathered in Table 2. The cyclic and differential pulse voltammograms for the reduction of OsIr_3 and RuIr_3 are shown in Figure 1.

From a great number of investigations on mononuclear and polynuclear complexes containing polypyridine-type (N–N) chelating sites, it is well-known that oxidation processes are metal-centered and reduction processes are ligand-centered.²⁵ On passing to mixed-ligand complexes which contain N–N and C–N

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Table 2. Electrochemical Results in Argon-Purged CH₂Cl₂ Solution at Room Temperature^a

complex	E_{ox} [n] ^b		E_{red} [n] ^b					
RuRh ₃	+1.25 ^c [~1]		-0.48 [1]	-0.60 [1]	-0.70 [1]	-1.19 [1]	-1.37 [1]	~-1.60 ^d
RuIr ₃	+1.40 ^c [~3.5]		-0.44 [1]	-0.55 [1]	-0.65 [1]	-1.12 [1]	-1.29 [1]	~-1.53 ^d
OsIr ₃	+1.00 [<1]	+1.40 ^c [3]	-0.32 [1]	-0.49 [1]	-0.67 [1]	-1.11 [1]	-1.29 [1]	~-1.44 ^{d,e}
OsRh ₃	+0.75 ^c [1]	+1.50 ^c [>1]	-0.35 ^c	-0.54 ^c	-0.82 ^c			

^a Potentials in V vs SCE. Unless otherwise noted, the waves are reversible; for irreversible waves, the potential is evaluated from the DPV peaks.

^b Number of exchanged electrons is given in brackets. ^c Irreversible wave. ^d A not well characterized wave. ^e Another not well characterized wave follows at ~-1.60 V.

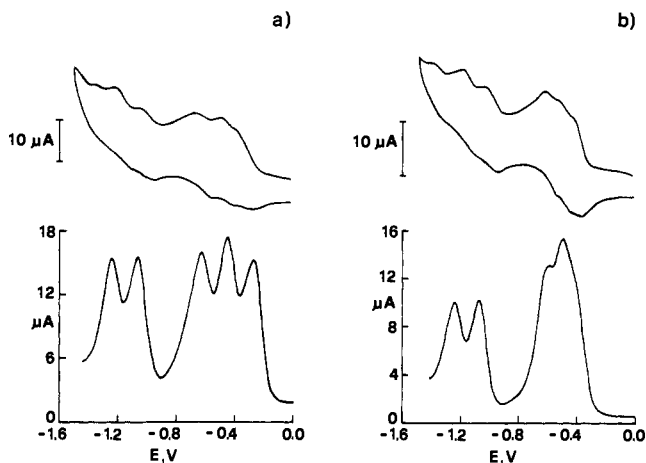


Figure 1. Cyclic and differential pulse voltammograms for OsIr₃ (a) and RuIr₃ (b) in argon-purged CH₂Cl₂ at room temperature.

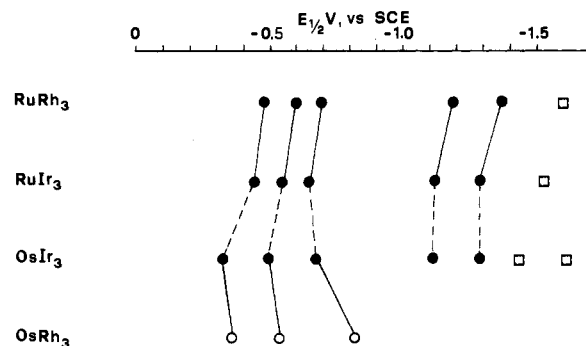


Figure 2. Correlations of the reduction waves (Table 2). Full and open circles indicate reversible and irreversible processes, respectively. Open squares represent not well characterized waves (see text).

(cyclometalating) chelating sites, the oxidation potential of the metal is known to move toward less positive values and the first reduction process is known to take place on the polypyridine ligands.^{12,13}

Reduction Processes. Cyclic voltammetry experiments showed that five successive reversible processes take place for RuRh₃, RuIr₃, and OsIr₃. A sixth (and also a seventh for OsIr₃) wave, not well characterized concerning the number of electrons involved, can be seen at more negative potentials (Table 2). For OsRh₃, three irreversible processes are observed, followed by other undefined waves. The first five reversible processes that take place for RuRh₃, RuIr₃, and OsIr₃ involve one electron each, as is clearly shown by differential pulse voltammetry experiments (Figure 1). The correlation diagram of Figure 2 shows that, if we consider also the sixth (not well defined) wave, the reduction processes of RuRh₃, RuIr₃, and OsIr₃ can be grouped into two "triplets". Since bridged 2,3-dpp is much easier to reduce than the cyclometalating ligands, it is straightforward to assign the first three reversible waves to successive one-electron reduction of the three bridging ligands. The separation between these successive peaks is smaller than that observed for the successive

one-electron reduction of the three ligands in [Ru(2,3-dpp)₃]²⁺,^{10b} [Os(2,3-dpp)₃]²⁺,¹⁶ [Ru{(μ-2,3-dpp)Ru(bpy)₂}₃]⁸⁺,^{9,17} and [Os{(μ-2,3-dpp)Ru(bpy)₂}₃]⁸⁺.¹⁶ The scheme of Figure 2 shows that the three reduction peaks move to less negative potentials on passing from RuRh₃ to RuIr₃. This behavior, which is apparently exhibited also by the corresponding Os complexes, indicates that in the Ir-containing complexes it is slightly easier to delocalize the charge of the incoming electrons, in agreement with the less covalent nature of the Ir-C⁻ bond (compared to the Rh-C⁻ one), which leaves the metal ion more positive.²⁶ On changing the central metal from Ru to Os, a shift of the first reduction potential toward less negative values is observed, as expected because of the well-known ability of Os to delocalize π electrons. This also explains why the shift becomes smaller for the second electron and reverses for the third one. In fact, when two or three bridging ligands are reduced, the electron repulsion is stronger for the more delocalizing Os-based cores. The larger ability of Os to delocalize the electron added around the central metal (and therefore to increase the repulsion between the electrons added in the bridging ligands) could also be invoked to explain the larger separation of the three peaks.

The fourth reduction wave is noticeably displaced to more negative potentials compared to the first three waves, while is close to the fifth and the sixth ones (Figure 2, Table 2). This indicates that the fourth, fifth, and sixth reduction processes correspond to second reduction of the three bridging ligands. Interestingly, from a comparison of the trend of first and second vs fourth and fifth waves of RuRh₃, RuIr₃, and OsIr₃, it is clear that second reduction of the bridging ligand is less affected by the nature of the internal metal (Ru vs Os) compared to what happens upon first reduction. This suggests that the first reduction process concerns the inner moiety of the 2,3-dpp bridging ligand (i.e., the chelating site directly coordinated to the central Ru or Os ion). As far as the second reduction process is concerned, two hypotheses can be made: (i) the process concerns the outer moiety (i.e., the chelating site directly coordinated to the peripheral cyclometalated Rh or Ir unit); (ii) after the first reduction, a rearrangement occurs, leading to a more planar and conjugated bridging ligand, so that the anionic charge can be more highly delocalized. As this rearrangement will be expected to increase significantly the electronic coupling of the inner metal to the outer ones, the extra increase of delocalization afforded by osmium would become relatively less important in the second reduction than in the first.²⁷

The irreversible behavior of OsRh₃ indicates that the reduced forms of the complex are unstable. Instability toward reduction is an expected result for all of these complexes because extra electrons on the bridging ligands prevent back-donation from the cyclometalated metal to the bridging 2,3-dpp. This causes a weakening of the strength of the already weak (see above) bonds between bridging ligands and outer metals. The reason why the instability for OsRh₃ is already evident on first reduction is not clear.

Oxidation Processes. As mentioned above, the Os(II)- and Ru(II)- polypyridine complexes undergo reversible metal-centered oxidation, whereas the oxidations of polypyridine-

(27) The authors would like to thank one of the reviewers for having suggested the second hypothesis.

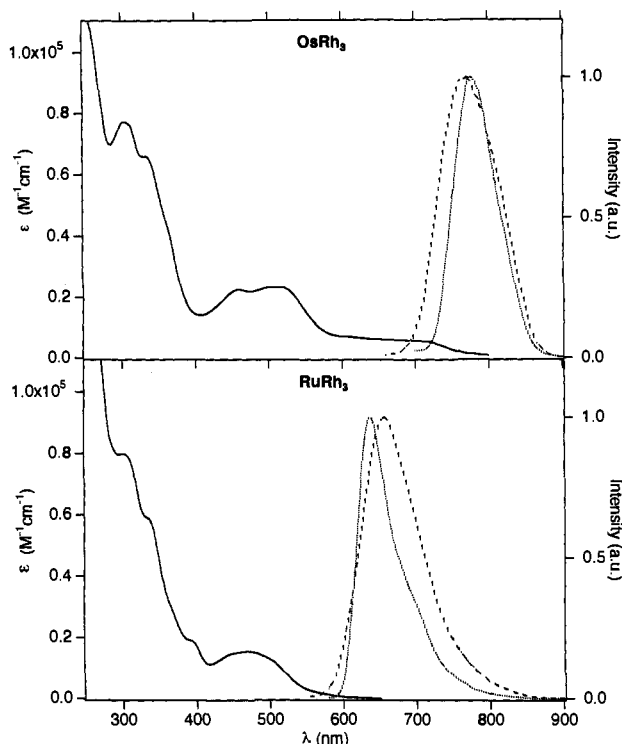


Figure 3. Absorption spectrum at room temperature (full line) and uncorrected luminescence spectra at room temperature (dashed line) and at 77 K (dotted line) of OsRh₃ and of RuRh₃ in CH₂Cl₂.

cyclometalated mixed-ligand complexes are usually irreversible for Rh(III) and sometimes also for Ir(III).^{12,13,26} The oxidation pattern of OsIr₃ shows a first reversible process at +1.00 V and a second multielectronic irreversible process at +1.40 V (Table 2). On the basis of the relative intensities of the DPV peaks, we assign the first wave to one-electron oxidation of the central metal and the second wave to one-electron oxidation of the three peripheral Ir-based units. This assignment is also consistent with the potential value expected for oxidation of Os(II).²⁸ In the OsRh₃ compound one expects a less positive oxidation potential of the Os core because of a larger back-donation from the cyclometalated moieties. The irreversible oxidation process at +0.75 V can thus be assigned to oxidation of the Os core.²⁹ The successive multielectron oxidation process (Table 2) can be reasonably assigned to simultaneous one-electron oxidation of the three independent cyclometalated moieties.

Since Ru(II) is much more difficult to oxidize than Os(II),^{12b,30} the one-electron, irreversible oxidation wave at +1.25 V for RuRh₃ is consistent with the oxidation of the Ru core. For RuIr₃, oxidation of Ru is expected to move to more positive potentials and is likely to merge into the multielectronic wave observed at +1.40 V, which should concern oxidation of the peripheral units. As mentioned above, the nature of the orbital of the cyclometalated unit involved in the oxidation process is difficult to establish. As recently discussed by Kirsch-De Mesmaeker, Watts, and co-workers for the case of similar Rh- and Ir-cyclometalated

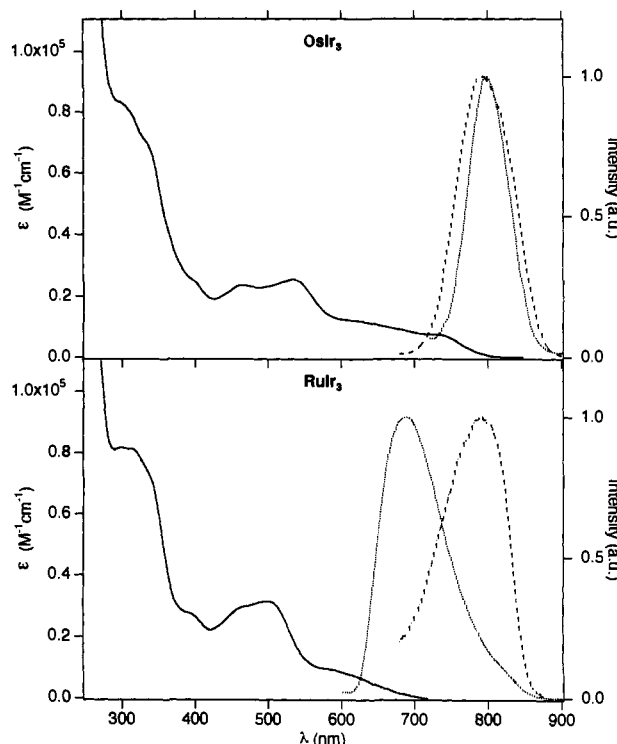


Figure 4. Absorption spectrum at room temperature (full line) and uncorrected luminescence spectra at room temperature (dashed line) and at 77 K (dotted line) of OsIr₃ and of RuIr₃ in CH₂Cl₂.

complexes,²⁶ the HOMO could be a metal t_{2g} or a metal–ligand (C^-) σ -bonding orbital.

Absorption Spectra. As mentioned above, our compounds can be viewed as made of two types of chromophores, the Os(II)- or Ru(II)-based polypyridine core and the peripheral Rh(III)- or Ir(III)-based polypyridine cyclometalated units (Scheme 1). For a discussion of the cores, the localized MO approach can be used. In Figures 3 and 4, it is in fact possible to assign the two absorption peaks (or shoulders) in the 300–350 nm region to the $\pi-\pi^*$ ligand-centered ($\mu-2,3\text{-dpp}$) transitions, the broad absorption in the 400–550 nm region to the spin-allowed $M \rightarrow (\mu-2,3\text{-dpp})$ ($M = \text{Ru}$ or Os) MLCT transitions, and for the Os complexes, the broad and weaker absorptions at wavelengths higher than 600 nm to the corresponding spin-forbidden MLCT transitions. As far as the peripheral cyclometalated units are concerned, the localized MO approach may no longer be valid and transitions between poorly localized orbitals can play a fundamental role. Anyway, the spectra of the [Rh(ppy)₂(bpy)]⁺ and [Ir(ppy)₂(bpy)]⁺ model compounds¹² show that these units do not exhibit intense absorption bands at wavelengths higher than 300 nm. In fact, in Figures 3 and 4, no spectral features can clearly be assigned to the peripheral cyclometalated units, except the strong band around 260 nm (ppy⁻ LC transition) and the tail at $\lambda > 600$ nm in RuIr₃ (Ir-based spin-forbidden transitions, *vide infra*).

Luminescence. The uncorrected luminescence spectra of the four novel compounds are shown in Figures 3 and 4, and the

Table 3. Absorption and Emission Properties of the New Compounds^a

compound	absorption		room temperature emission			77 K emission	
	λ (nm) ^b	ϵ (M ⁻¹ cm ⁻¹)	λ (nm)	τ (ns)	Φ	λ (nm)	τ (μ s)
OsRh ₃	515	23 300	821	55	0.0058	789	0.62
RuRh ₃	471	15 400	681	330	0.018	645	1.05/3.40 ^c
OsIr ₃	534	25 400	825	5.2	4.5×10^{-4}	810	0.43
RuIr ₃	499	31 500	812	2.2	1.5×10^{-4}	726	0.57/1.71 ^c

^a Data in deaerated dichloromethane solution, unless otherwise noted. Emission maxima are corrected for photomultiplier response. Experimental uncertainties are as follows: absorption maxima, ± 2 nm; emission maxima, ± 4 nm; luminescence lifetime, 10%; quantum yields, 20%. ^b Maximum of the lowest-energy ¹MLCT band. ^c Double-exponential decay (see text).

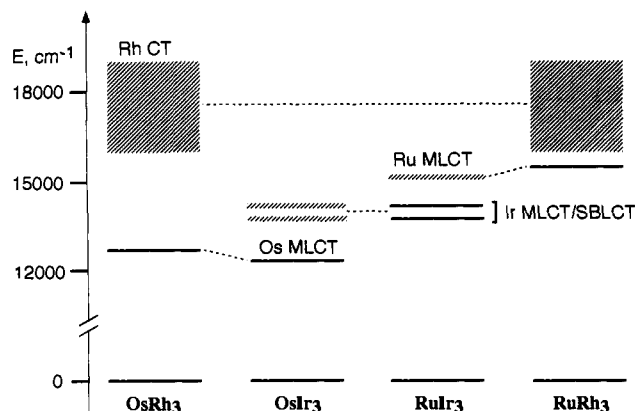


Figure 5. Schematic energy level diagram. Spectroscopically observable levels are indicated with a full line; the estimated positions of directly unobservable levels are shaded.

corrected luminescence maxima, lifetimes, and quantum yields are gathered in Table 3. In an attempt to better rationalize the emission behavior of the four compounds, we have tried to schematize the energy ordering at 77 K of the low-energy excited states (Figure 5).

The lowest luminescent excited state of the core is expected to be a $^3\text{MLCT}$ level (which in the Os(II) complex should lie $\sim 2000\text{ cm}^{-1}$ lower than in the Ru(II) complex),^{3a} whereas for the peripheral units, the ordering of the low-energy excited states is not easy to define. ^3LC , $^3\text{MLCT}$, and even a SBLCT (C-metal σ bond to π^* ligand charge-transfer, *vide supra*)^{12,26} can lie very close in energy. Luminescence from levels receiving contributions from different electronic configurations^{12,13} or even from two different types of levels²⁶ has been reported.

The strong differences in the luminescence properties (energy, lifetime, quantum yield) of OsRh₃ and RuRh₃ (Figure 3, Table 3) clearly rule out the involvement of the same peripheral Rh-based unit in the luminescence of these compounds. Furthermore, the luminescence properties of OsRh₃ (including band shape and energy shift in going from fluid solution to rigid matrix) are typical of Os(II)-polypyridine units (for example, for [Os(μ -2,3-dpp)Ru(bpy)₂]₃⁸⁺ in dichloromethane fluid solution at room temperature, $\lambda_{\text{max}} = 850\text{ nm}$ and $\tau = 36\text{ ns}$).¹¹ The slight blue shift of the Os-core emission on passing from [Os(μ -2,3-dpp)Ru(bpy)₂]₃⁸⁺ to OsRh₃ can be assigned to the different "electron acceptor" properties of the peripheral [Rh(ppy)₂]⁺ units compared to [Ru(bpy)₂]²⁺ ones. In cyclometalated complexes, the Rh-based CT levels lie at much higher energy than the corresponding Ir-based CT levels (from 2000 to 5000 cm^{-1}).^{12a,26} As we will see below, the lowest Ir-based CT level in RuIr₃ lies at $\sim 14\,000\text{ cm}^{-1}$, which places the lower limit of the Rh-based CT levels in OsRh₃ and RuRh₃ at $\sim 16\,000\text{ cm}^{-1}$. Therefore, there is no doubt that the lowest excited state of OsRh₃ is the core-localized $^3\text{MLCT}$ level.

(28) The potential for oxidation of Os(II) in OsIr₃ is expected to be less positive than that in Os(μ -2,3-dpp)Ru(bpy)₂]₃⁸⁺ (+1.25 V)¹⁶ because in the former compound the peripheral units are less electron withdrawing.

(29) On the basis of the known reversibility of the oxidation processes of the Os(II)- and Ru(II)-polypyridine compounds, one could expect a reversible oxidation for the metal core. This is in fact what is found for OsIr₃. Oxidation of the core in these tetranuclear species, however, causes a weakening of the bridging ligand-cyclometalated metal ion bond because of reduced σ donor properties of the chelating site of the bridge coordinated to Rh(III) or Ir(III) ions. Reversibility of core oxidation is therefore related to the rate constant of the breaking of the Rh(III)- (or Ir(III)-) bridging ligand bond. This rate is expected to be higher for Rh(III) vs Ir(III) and for Ru(II) vs Os(II). This is likely the reason why the oxidation of the core is irreversible in the other three tetranuclear compounds.

(30) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193.

For RuRh₃, problems may arise in the assignment of the luminescence band because the Ru-based and Rh-based CT levels could overlap (Figure 5). The observed luminescence properties are those expected for the Ru(II)-polypyridine core, and the changes observed in going from OsRh₃ to RuRh₃ (Table 3) are exactly those expected for Os-based and Ru-based luminescent polypyridine complexes.^{25,30} However, the nonexponential decay observed at 77 K (Table 3) suggests that two different levels could be involved, at least at low temperature.

For the OsIr₃ and RuIr₃ compounds, core- and peripheral-based excited states are expected to be very close in energy. As far as OsIr₃ is concerned, the luminescence data at 77 K suggest an assignment of the lowest excited state to the Os core. This is in agreement with the electrochemical data (*vide supra*) which show that Os(II) is oxidized at less positive potentials than Ir(III) and the μ -2,3-dpp is first reduced on the Os side. In going to room temperature, the Ir (SBLCT) level is expected to undergo a much larger red shift than the Os (MLCT) level, so that which level is the lowest one is difficult to say. Some experimental features (e.g., the band width) would indicate an Os (MLCT) assignment, whereas the lifetime and the quantum yield, when compared to the values shown by OsRh₃ and RuIr₃ (*vide infra*), would suggest an Ir (SBLCT) assignment.

RuIr₃ (Figure 4) shows a luminescence behavior quite different from that of RuRh₃ (Figure 3). At 77 K, the luminescence band of RuIr₃ is very large (half-width $\sim 2500\text{ cm}^{-1}$, to be compared with $\sim 1600\text{ cm}^{-1}$ for OsRh₃), indicating the contribution from two different emitting levels. This is consistent with the double exponential decay observed for this emission (Table 3). The difference in emission energies at 77 K between OsRh₃ and OsIr₃ ($\sim 300\text{ cm}^{-1}$) can be taken as an estimate of the effect of peripheral units on the energy of the lowest MLCT level of the core. Using this value and the experimental emission energy of RuRh₃, the lowest Ru-based $^3\text{MLCT}$ level of RuIr₃ should lie significantly higher than the observed luminescent levels. Luminescence can thus be assigned to the peripheral Ir-based units. A very similar dual emission, assigned to two different Ir-based (ML and SBL) CT levels, has recently been observed for [Ir(ppy)₂(HAT)]⁺.²⁶ On going from 77 K to room temperature, both MLCT and SBLCT levels are expected to decrease in energy; this effect should be particularly significant for the SBLCT level, which carries a more pronounced CT character.²⁶ The large red shift of the emission energy of RuIr₃ on passing from 77 K to room temperature (1470 cm^{-1}) compared to the red shift exhibited by the other complexes of this series (i.e., 490 cm^{-1} for OsRh₃, a pure MLCT emitter) suggests a pure Ir(SBLCT) emission at room temperature. For mononuclear Ir(III) cyclometalated complexes, the orbital nature of the lowest excited state can be inferred from the electrochemical behavior (reversible oxidation process/MLCT lowest excited state; irreversible oxidation process/SBLCT lowest excited state).²⁶ In our case, such a correlation is not straightforward because of the presence of different metal centers.

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