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Electrochemical and Photophysical Properties of New Triazole-Bridged Heterobimetallic Ruthenium–Rhodium and Ruthenium–Iridium Complexes

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The synthesis, characterization, and the electrochemical and photophysical properties of $[(bpy)_2Ru^{II}(bpt)Rh^{III}(ppy)_2]^{2+}$, $[(bpy)_2Ru^{II}(bpt)Ir^{III}(ppy)_2]^{2+}$, $\{[Rh^{III}(ppy)_2]_2(bpt)\}^+$, and $\{[Ir^{III}(ppy)_2]_2(bpt)\}^+$ are reported (Hppy = 2-phenylpyridine; bpy = 2,2′-bipyridine, Hbpt = 3,5-bis(pyridin-2-yl)-1,2,4-triazole). The $Ru(bpy)_2$ moiety is bound via N1 of the triazole ring, while the $M(ppy)_2$ center (M = Rh or Ir) is coordinated via the N4 of the triazole ring. The electrochemical measurements show that in the mixed-metal complexes the first oxidized metal is Ru and the first reduced ligand is bpy. The homobimetallic Ir and Rh complexes exhibit a bpt^--based reduction. The absorption spectra of the mixed-metal complexes exhibit both Ru → bpy and M → ppy^- transitions. The energies of these transitions are different from those of the their homobimetallic analogs. The emission observed for $\{[Rh(ppy)_2]_2(bpt)\}^+$ at 77 K corresponds to a ligand-centered excited state, while for the analogous iridium complex a charge-transfer emission, which involves the bpt^- ligand, is observed. In the mixed-metal complexes efficient energy transfer occurs from higher energy excited states centered on the $M(ppy)_2$ component to the lowest energy excited state, which is a metal-to-ligand charge transfer level localized on the $Ru(bpy)_2$ component.

Introduction

Ruthenium(II)–polypyridine complexes have been the subject of extensive research, in particular with respect to their electrochemical, photophysical, and photochemical properties.[2–6] The properties of the "simple" monometallic complexes are by now fairly well understood. Changing the ligand systems allows the properties of the complexes to be gradually changed in the desired direction (fine tuning). Due to the building block capabilities of the $Ru(bpy)_2$ moiety (bpy = 2,2′-bipyridine), a large number of interesting bimetallic and polymetallic ruthenium-containing systems have also been synthesized in recent years.[7–20]

Recently, we reported the properties of $[Ru(bpy)_2(bpt)]^+$ and $\{[Ru(bpy)_2]_2(bpt)\}^{3+}$ with Hbpt = 3,5-bis(pyridin-2-yl)-1,2,4-triazole.[8] It has been shown that the bridging bpt^- ligand exhibits unusual properties. Its lowest unoccupied molecular orbital (LUMO) is very high in energy and, as a result, the electrochemical and photophysical properties are based on bpy. Another feature of bpt^- is that the N1 site of the triazolate ligand has stronger σ-donor properties than the N4 site. This asymmetric

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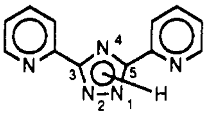


Hbpt

coordination environment is reflected in different oxidation potentials for $[(bpy)_2Ru(bpt)Os(bpy)_2]^{3+}$ (Ru coordinated via N1 and Os via N4 of the triazole ring) and $[(bpy)_2Os(bpt)Ru(bpy)_2]^{3+}$ (Ru bound through N4 and Os via N1).[8a,e] Furthermore, the ruthenium homobimetallic compound shows an unusually large separation of the oxidation potentials, which is only partially due to the asymmetric coordination. The results obtained suggested that a significant electronic communication between the metal centers is present, most likely via the highest occupied molecular orbital (HOMO) of the bridging bpt^- ligand.

In this contribution we wish to report the properties of heterobimetallic systems with $Ru(bpy)_2$ bound via N1 and $Rh(ppy)_2$/$(Ir(ppy)_2$ bound via N4 (Hppy = 2-phenylpyridine)). It is known that $[Rh(ppy)_2(L)]^+$ compounds exhibit a ligand-centered (LC) ppy-based emission,[21] while the $[Ir(ppy)_2(L)]^+$ analogs show a metal-to-ligand charge-transfer (MLCT) luminescence[22] (L = bidentate NN ligand, such as bpy). Of interest in the compounds reported is the nature of the emitting excited states and in particular how they are affected by the presence of $Ru(bpy)_2$ moieties and the bridging bpt^- ligand. To assess these effects, the properties of the complexes reported here will be compared with those of some monometallic analogs. Also the properties will be compared with recently reported heterobimetallic complexes which contain the $Ru(bpy)_2(bpt)$ moiety and $Rh(PPh_3)_2H_2$ or $Ir(PPh_3)_2H_2$ components bound via N4 to the bpt^- ligand.[13c]

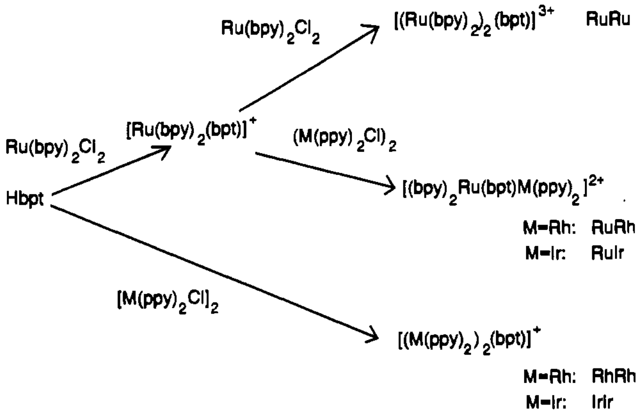
Experimental Section

Synthesis and Materials. 3,5-Bis(pyridin-2-yl)-1,2,4-triazole (Hbpt) was prepared as described previously.[8a] *cis*-$[Ru(bpy)_2Cl_2]\cdot 2H_2O$ was prepared according to literature methods from $RuCl_3\cdot xH_2O$ and bpy.[23] $[Ru(bpy)_2(bpt)]PF_6\cdot{}^1/_2H_2O$ (**Ru**) and $\{[Ru(bpy)_2]_2(bpt)\}(PF_6)_3$ (**RuRu**) have been prepared as described previously.[8a]

Heterobimetallic Compounds. A 0.25-mmol sample of $[Ru(bpy)_2(bpt)]^+$ [8a] was dissolved in 50 mL of 2-methoxyethanol. A 0.25-mmol sample of $[Rh(ppy)_2Cl]_2$[21e] or $[Ir(ppy)_2Cl]_2$[22a] was added, and the mixture was heated to reflux for 48 h. After being cooled to room temperature, the volume of the filtered solution was reduced by evaporation to 25%. The solution was then added to an excess of aqueous NH_4PF_6. The precipitate was filtered off, dissolved in acetone and purified by column chromatography (neutral Al_2O_3; EtOH as eluent; height of Al_2O_3, 20 cm; width of column, 2 cm). The product was recrystallized from water/acetone (1:1 v/v) or water/CH_3CN (1:1 v/v). Anal. Calcd for $[(bpy)_2Ru(bpt)Rh(ppy)_2](PF_6)_2$ (**RuRh**): C, 48.52; H, 3.02; N, 11.52; P, 4.63. Found: C, 48.72; H, 3.13; N, 11.19; P, 4.52. Anal. Calcd for $[(bpy)_2Ru(bpt)Ir(ppy)_2](PF_6)_2\cdot H_2O$ (**RuIr**): C, 44.91; H, 2.91; N, 10.67. Found: C, 44.69; H, 2.69; N, 10.40.

Homobimetallic Compounds. A 0.25-mmol sample of $[M(ppy)_2Cl]_2$ (M = Rh[21e] or Ir[22a]) and 0.4 mmol of Hbpt were heated at reflux for 6 h in 50 mL of CH_2Cl_2/EtOH (2:1 v/v). After being cooled to room temperature, the solution was evaporated to 10 mL and added to an excess of aqueous NH_4PF_6. The crude product was filtered off and recrystallized from water/acetone (1:1 v/v). Anal. Calcd for $\{[Rh(ppy)_2]_2(bpt)\}(PF_6)\cdot$acetone (**RhRh**): C, 56.79; H, 3.72; N, 10.10; P, 2.48. Found: C, 56.68; H, 3.75; N, 9.99; P, 2.51. Anal. Calcd for $\{[Ir(ppy)_2]_2(bpt)\}(PF_6)\cdot$acetone (**IrIr**): C, 49.68; H, 3.15; N, 8.84. Found: C, 49.40; H, 3.33; N, 8.91.

Scheme I. Schematic Outline of the Synthesis of the Dinuclear Complexes



Physical Measurements. Electronic absorption spectra were recorded in ethanol with a Perkin-Elmer 330 or a Varian DMS 200 spectrophotometer. The emission spectra were obtained with a Perkin-Elmer LS 5 instrument. The emission lifetimes were measured by an Edinburgh 199 DS single-photon-counting instrument. Single exponential decays were obtained in all cases (estimated uncertainty on the lifetime values < 10%).

The differential pulse polarography (DPP) measurements and the cyclic voltammograms (CV) were carried out on an EG&G PAR C Model 303 instrument with an EG&G 384 B polarographic analyzer. The scan rate was 4 mV/s for the DPP experiments with a pulse height of 20 mV. For the cyclic voltammograms the scan rate was 100 mV/s. A saturated calomel electrode (SCE) was used as a reference. The electrolyte used was acetonitrile, containing 0.1 M tetrabutylammonium perchlorate (TBAP). Elemental analyses were carried out at University College Dublin.

Results

An outline of the synthetic path used to prepare the homobimetallic and heterobimetallic complexes is shown in Scheme I. Unfortunately, pure monometallic $[Rh(ppy)_2(Hbpt)]^+$ and $[Ir(ppy)_2(Hbpt)]^+$ compounds could not be isolated. In all fractions obtained, some bimetallic products always were found to be present and could not be eliminated by recrystallization or column chromatography. The X-ray structure[8] of $[Ru(bpy)_2(bpt)](PF_6)\cdot{}^1/_2H_2O$ shows that the $Ru(bpy)_2$ moiety is bound via N1 of the bpt^- ligand. Therefore, by refluxing $[Ru(bpy)_2(bpt)]^+$ with $[Rh(ppy)_2Cl]_2$ or $[Ir(ppy)_2Cl]_2$, the $M(ppy)_2$ group can only bind via N4 (Figure 1), as isomerism is known not to occur in these systems. The electrochemical properties of the compounds obtained are listed in Table I. For comparison, the oxidation and reduction potentials of $\{[Ru(bpy)_2]_2(bpt)\}^{3+}$ have also been included. Figure 2 shows the differential pulse polarogram of the **RuIr** complex. The $Ru(bpy)_2$-centered oxidation is reversible in all cases, as shown by the cyclic voltammetry results (peak-to-peak separation < 100 mV; $i_a/i_c = 1$). On the other hand, the $Rh(ppy)_2$- and $Ir(ppy)_2$-based oxidation processes are irreversible in all cases. As shown in Table I, the first reduction process is always reversible while the subsequent waves can be irreversible depending on the specific complex.

The UV–vis absorption data are presented in Table II. Figure 3 shows the UV–vis spectra of the **RuRu**, **RuRh**, and **RhRh** complexes in ethanol. All complexes are luminescent at 77 K and, except for the **RhRh** compound, even in fluid solution at room temperature. Table III contains the emission maxima and lifetimes of the complexes. Figure 4 shows the emission spectra of **RuRh** and **RhRh** obtained at 77 K. For the **RuRh** and **RuIr**

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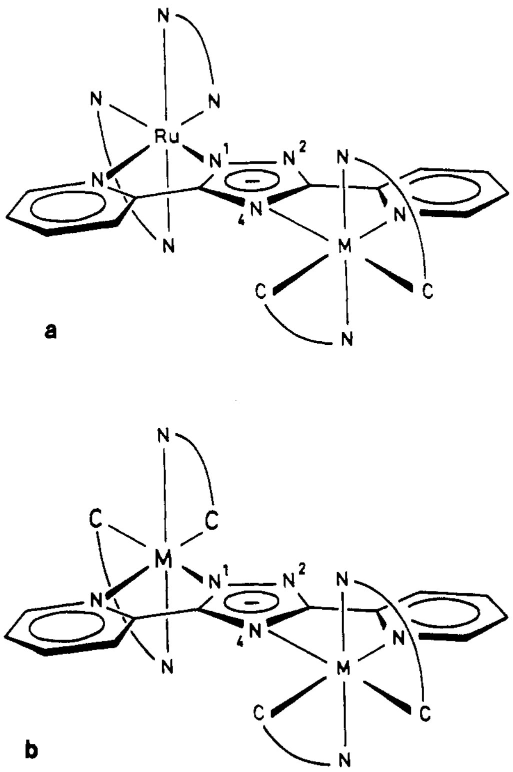

Figure 1. Schematic representation of the structures of the $[(bpy)_2Ru(bpt)M(ppy)_2]^{2+}$ (M = Rh or Ir) (a) and of $\{[M(ppy)_2]_2(bpt)\}^+$ (M = Rh or Ir) (b) complexes.

Table I. Electrochemical Data[a] for the Bimetallic Complexes

compound	$E_{1/2}$(ox)		$E_{1/2}$(red)				
RuRu	$+1.04^b$	$+1.34^b$	$-1.40^{b,c}$	-1.62^b	-1.67^b	-2.22^d	-2.33^d
RuRh	$+1.03^b$	$+1.39^c$	-1.42^b	-1.65^b	-2.03^b	-2.26^d	-2.49^d
RuIr	$+1.05^b$	$+1.35^d$	-1.42^b	-1.66^b	-1.98^b	-2.27^d	
RhRh	$+1.36^d$	$+1.83^d$	-1.92^b	-2.12^d	-2.29^d	-2.48^d	
IrIr	$+1.13^d$	$+1.30^d$	-1.80^b	-2.12^d	-2.29^d	-2.44^d	

[a] In CH_3CN containing 0.1 M TBAP; values are in V vs. SCE; all values are ±0.02 V. [b] Reversible wave. [c] Bielectronic wave. [d] Irreversible wave.

compounds, corrected excitation spectra recorded at room temperature made clear that the intensity of the 635-nm emission does not depend on the excitation wavelength ($\lambda_{exc} > 350$ nm).

Discussion

Electrochemistry. Inspection of the data listed in Table I reveals that the first oxidation potentials of **RuRu**, **RuRh**, and **RuIr** are reversible and very similar. This indicates that in all cases the first oxidation process concerns $Ru(bpy)_2$. Such a conclusion is in agreement with the finding that the first oxidation potentials of the **IrIr** and **RhRh** complexes are significantly higher that those of the ruthenium-containing complexes.

The first oxidation potential of the **IrIr** complex is very similar to the oxidation potential observed for $[Ir(ppy)_2(4Mptr)]^+$ (4Mptr = 4-methyl-3(pyridin-2-yl)-1,2,4-triazole), where the $Ir(ppy)_2$ moiety is also bound via N1(2) of the triazole ring.[24] The second oxidation potential is significantly higher. This may be caused by a number of effects, such as (i) increased charge of the complex (electrostatic effect), (ii) different coordination environment (N4 of the triazole ring is a weaker σ donor than the N1 site[8b,c]), and (iii) delocalization of the charge through the triazolate bridge.[11a]

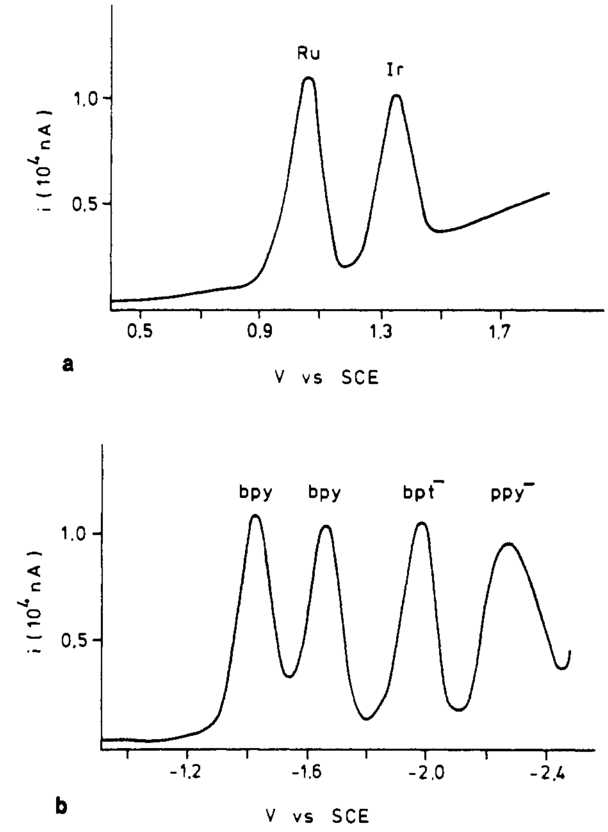

Figure 2. Differential pulse polarograms for the $[(bpy)_2Ru(bpt)Ir(ppy)_2]^{2+}$ (**RuIr**) complex measured in acetonitrile containing 0.1 M TBAP: (a) oxidation waves; (b) reduction waves.

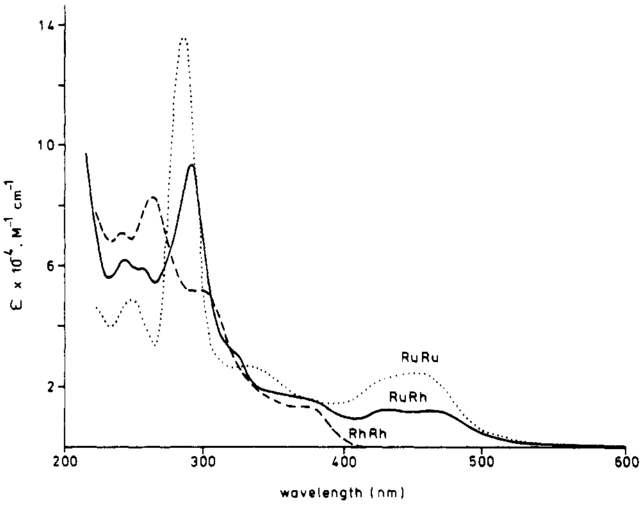

Figure 3. UV-vis absorption spectra of $[(bpy)_2Ru(bpt)Ru(ppy)_2]^{2+}$ (**RuRh**) (—), $\{[Rh(ppy)_2]_2(bpt)\}^+$ (**RhRh**) (- - -), and $\{[Ru(bpy)_2]_2(bpt)\}^{3+}$ (**RuRu**) (· · ·) measured in ethanol at room temperature.

Table II. UV–Vis Absorption Data[a] for the Bimetallic Complexes, Measured in Ethanol

compound	λ_{max}/nm ($\epsilon/10^4$ M^{-1} cm^{-1})					
RuRu	453 (1.8)	330 (1.8)	288 (14.7)	244 (3.6)		
RuRh	455 (1.0)	432 (1.0)	370 (1.3)	320 (2.6)	290 (8.2)	242 (5.4)
RuIr	465 (1.2)	424 (1.5)	380 (1.5)	320 (3.4)	290 (9.6)	255 (6.3)
RhRh	375 (0.9)	300 (4.4)	263 (7.0)	240 (6.1)		
IrIr	420 (0.1)	380 (0.8)	300 (3.7)	258 (6.3)		

[a] Ethanol solution; experimental uncertainties: λ_{max} ± 2 nm; ε ± 5%.

The **RhRh** complex shows higher oxidation potentials than observed for the analogous iridium compound. The first (irreversible) oxidation potential has a value similar to those observed for other $[Rh(ppy)_2(L)]^+$ complexes (L = various substituted

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Table III. Emission Maxima and Excited-State Lifetime[a] of the Bimetallic Compounds

	298 K		77 K	
compound	λ_{max}/nm	τ/μs	λ_{max}/nm	τ/μs
RuRu	648	0.10	608	3.6
RuRh	636	0.13	601[b]	4.6
RuIr	635	0.13	600	4.7
RhRh			458	160
IrIr	484	0.07	473	4.8

[a] Methanol–ethanol 4:1 v/v; λ_{Exc} = 300 nm. [b] A weak emission around 450 nm is also observed with a lifetime of ~160 μs; see text.

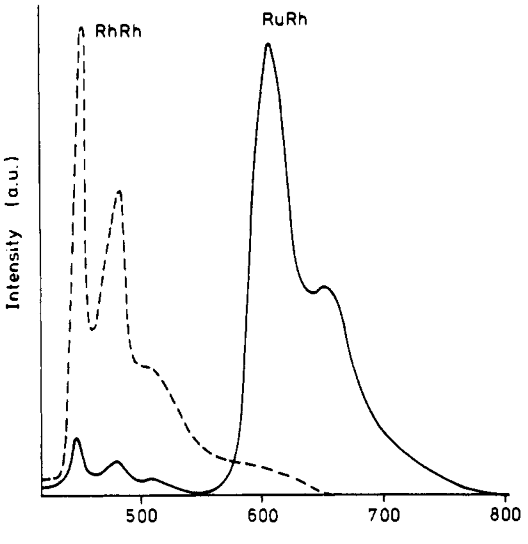

Figure 4. Emission spectra of $[(bpy)_2Ru(bpt)Ru(ppy)_2]^{2+}$ (**RuRh**) and $\{[Rh(ppy)_2]_2(bpt)\}^+$ (**RhRh**) in EtOH/MeOH at 77 K.

pyridyltriazole ligands).[21f] Interestingly, the difference between the oxidation potentials of the **RhRh** complex is much larger than in the case of the **IrIr** compound. Such a large difference has also been observed for $\{[Ru(bpy)_2]_2(bpt)\}^{3+}$ with respect to $\{[Os(bpy)_2]_2(bpt)\}^{3+}$, and it has been attributed to a larger electron delocalization for the **RuRu** complex.[8a,17a] The interaction in the mixed-valence complexes between the M(III) center and the electron-rich HOMO of the bridge reduces the electron density present on the other coordination center for the second metal ion. As ruthenium(III) is a better π-acceptor than osmium(III), this effect is more pronounced for ruthenium than for osmium. This effect could also explain the different behavior of the **RhRh** and **IrIr** complexes.

It should be noted that, due to the irreversible character of the oxidation processes, the properties of the mixed-valence $M^{IV}M^{III}$ (M = Rh, Ir) complexes could not be studied.

The first two reduction waves in mixed-ligand $[Rh(ppy)_2(L)]^+$ complexes are L based, where L = bipyridine,[21d] biquinoline,[21c] and various pyridyltriazoles.[21f] The reduction waves observed below –2.2 V have been assigned to ppy-based reductions.[21c,f] The $Ru(bpy)_2$-containing complexes (**RuRu**, **RuRh**, and **RuIr**) show reversible reduction waves at –1.4 and –1.65 V. As discussed previously,[8] the first two waves observed for **RuRu** are bpy-based reductions. The similar values of the first two reduction potentials suggest a first bpy-based reduction also in the case of **RuRh** and **RuIr**. The third reduction of these heterobimetallic compounds, observed around –2 V, can therefore be assigned to a bpt$^-$-based reduction. This is in agreement with previous conclusions[8] that the LUMO of bpt$^-$ is at higher energy than that of bpy. MacQueen and Petersen have also concluded that bpt$^-$ is more difficult to reduce than bpy for the $[(bpy)_2Ru(bpt)M(PPh_3)_2H_2]^{2+}$ complexes (M = Rh and Ir).[13c] The irreversible reduction waves below –2.2 V have been assigned to ppy$^-$-based reduction.

For the **RhRh** and **IrIr** complexes, the first reversible reduction wave at –1.92 and –1.80 V, respectively, can be assigned to bpt$^-$-based reduction, and the subsequent waves, to ppy$^-$-based reduction.

Absorption Spectra. The homobimetallic **RhRh** complex exhibits UV absorption bands at the same energy as observed previously for a series of $[Rh(ppy)_2(L)]^+$ complexes, where L = bipyridine, biquinoline, and pyridyltriazole.[21c,d,f] These bands have been assigned to Rh → ppy$^-$ charge-transfer transitions. The **RuRu** complex shows intense absorption bands in the visible region, due to Ru → bpy charge-transfer transitions.[4] The mixed-metal **RuRh** complex shows features of both Ru → bpy (455 and 432 nm) and Rh → ppy$^-$ (370 nm) transitions. Also the **RuIr** compound exhibits both Ru → bpy and Ir → ppy$^-$ transitions. The **IrIr** complex exhibits strong ^{3}LC-centered bands at 258 and 300 nm and a MLCT band at 380 nm.[21a] The very intense bands in the UV region observed for all complexes have been assigned to $\pi \rightarrow \pi^*$ transitions located on the bpy, ppy$^-$, and bpt$^-$ ligands.[4,8,21,22]

Luminescence Properties. The **RhRh** complex shows a high-energy, highly-structured luminescence band at 77 K that can be assigned to a triplet ligand-centered (^{3}LC) ppy$^-$-based emission (see Figure 4).[21] The long luminescence lifetime (0.16 ms) supports this assignment since ^{3}MLCT luminescence usually has a lifetime of a few microseconds. No emission could be detected for the **RhRh** complex at room temperature in fluid solution. This is in agreement with observations made previously for other $Rh(ppy)_2$ complexes[21] where deactivation has been attributed to ^{3}MC excited states.

The **IrIr** complex exhibits a lower energy emission, the luminescence is shorter lived, and the luminescence band is less structured compared to that of the **RhRh** complex. Comparison with other $[Ir(ppy)_2(L)]^+$ complexes suggests that this emission can be assigned to a ^{3}MLCT excited state. The **IrIr** luminescence is still present at room temperature, at the same energy as at 77 K. In general a red shift of the MLCT emission band in a polar solvent is observed with increasing temperature. This is caused by melting of the solvent glass which allows the solvent molecules to relax to their most favorable geometry after light excitation. This phenomenon is expected to be more pronounced when the charge-transfer transition involves ligands which are in direct contact with the solvent (like the ppy$^-$ ligands). The absence of a red shift suggests therefore that the emission originates from a triplet Ir → bpt$^-$ CT level. The perturbation of the solvent may be quite small for a bpt$^-$-based CT emission, because the bridging ligand is shielded from the solvent by the two bulky $Ir(ppy)_2$ moieties. The less negative bpt$^-$-based reduction potential observed for **IrIr** supports this assumption; i.e., the lowest ^{3}MLCT emission involves the ligand with its π^* orbital at lower energy. This appears to be the first reported example of a transition metal complex in which the bpt$^-$ ligand is directly involved in the luminescence process.

The mixed-metal **RuRh** and **RuIr** complexes could in principle exhibit a Ru-based emission and a Rh/Ir-based emission at higher energy if no communication between the two chromophoric groups is present. By excitation of the **RuRh** complex at 77 K, a strong emission at 601 nm and a very weak emission at ~450 nm have been observed (Figure 4). The energy, shape, and lifetime of the low-energy band indicate a ^{3}MLCT luminescence, originating from the $Ru(bpy)_2$ center. The intensity ratio of the two luminescence bands depends on the excitation energy. Excitation of an equimolar mixture of **RuRh** and **RhRh** at 370 nm (where they have the same extinction coefficient) results in the presence of a ^{3}LC emission at 458 nm for the **RhRh** complex which is at least 10 times more intense than the luminescence observed for the **RuRh** complex under the same experimental conditions. This shows that at least 90% of the Rh-based luminescence is quenched in the **RuRh** complex. The remaining 10% of the Rh-based

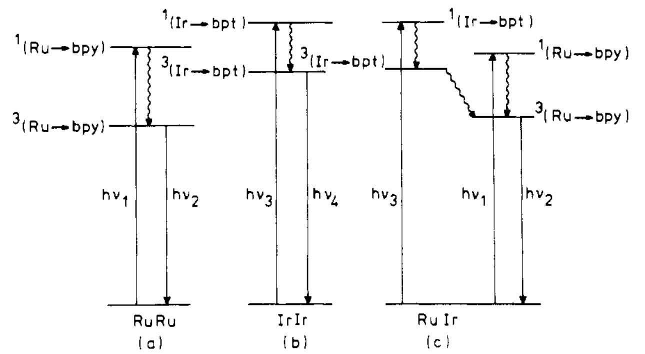

Figure 5. Schematic energy-level diagrams: (a) homobimetallic $\{[Ru(bpy)_2]_2(bpt)\}^{3+}$; (b) homobimetallic $\{[Ir(ppy)_2]_2(bpt)\}^{+}$; (c) heterobimetallic $[(bpy)_2Ru(bpt)Ir(ppy)_2]^{+}$. Each excited state is indicated by the corresponding electronic transition.

emission can be due either to incomplete quenching in the **RuRh** species or to the presence of small amounts of a Rh-containing emitting impurity. Since the intensity quenching of the 458-nm band is not accompanied by a quenching in the luminescence lifetime, which remains ~160 μs, we believe that the hypothesis of a luminescent impurity is more likely. At room temperature, only the Ru-based ^{3}CT emission can be observed, as expected because of the general lack of luminescence for Rh-based complexes under such experimental conditions. The **RuIr** complex shows only Ru-based ^{3}MLCT luminescence both at room temperature and at 77 K.

The results described above show that the Rh- and Ir-based components, which are luminescent in the homobimetallic compounds, undergo a quenching process in the mixed-metal **RuRh** and **RuIr** compounds. In principle, the observed quenching may occur via electron or via energy transfer. The spectroscopic and electrochemical data indicate that electron transfer quenching is endoergonic for the **RuRh** complex (to a first approximation, by 0.05 eV) and only marginally exoergonic (to a first approximation, by 0.08 eV) in the case of the **RuIr** complex (Tables I and III). It is therefore unlikely that electron transfer can play an important role. On the other hand, the occurrence of energy transfer is demonstrated by the luminescence results. For both the heterometallic compounds, in fact, corrected excitation spectra at room temperature showed that the Ru-based luminescence intensity does not depend on the excitation wavelength.

The excited-state processes which have been observed for the **RuRu**, **IrIr**, and **RuIr** systems have been schematically depicted in Figure 5. An estimate of the room temperature energy-transfer rate can be obtained by considering that the lifetime of the luminescent ^{3}MLCT level for the **IrIr** complex is 0.07 μs. Since the Ir-based luminescence intensity in the **RuIr** compound decreases to less than 1% of that of the **IrIr** complex, the energy transfer rate must be more than 100 times higher than 1/0.13 μs^{-1}, i.e. $>7 \times 10^8$ s^{-1}. For the **RuRh** complex a similar evaluation cannot be done because of the above-mentioned presence of a luminescent impurity. Nevertheless, the results obtained show that the energy-transfer process is at least 90% efficient at 77 K.

An efficient energy transfer from the high-energy $M(ppy)_2$ center to the lower energy $Ru(bpy)_2$ unit in the **RuRh** and **RuIr** complexes is consistent with recent results obtained for similar compounds.[8f,13c] For $[(bpy)_2Ru(bpt)M(PPh_3)_2H_2]^{2+}$ (M = Rh, Ir) efficient energy transfer has been found from the higher energy $M(PPh_3)_2H_2$ unit to the lower energy $Ru(bpy)_2$ unit,[13c] and for the two $[(bpy)_2Ru(bpt)Os(bpy)_2]^{3+}$ and $[(bpy)_2Os(bpt)Ru(bpy)_2]^{3+}$ isomers efficient energy transfer occurs from the higher energy Ru-based to the lower energy Os-based moieties.[8f]

Mediation of Energy Transfer via the bpt$^-$ Bridge. As shown previously for other anionic ligands,[18,26-28] the metal-metal interaction can be significantly enhanced through the HOMO of the bridge. An efficient mixing of the dπ metal orbitals with filled π orbitals of the bridge can cause a strong coupling between the metal centers (superexchange mechanism via hole-transfer). It has recently been suggested that for bimetallic complexes based on bpt$^-$ the hole-transfer mechanism is of major importance.[8b,c] Similar conclusions were reached by studying the analogous 3,5-bis(pyrazin-2-yl)-1,2,4-triazolate (bpzt$^-$)[29] complex. Although the lowest π* orbital of bpzt$^-$ is much lower in energy than that of bpt$^-$, the coupling between the metal centers is approximately the same for both complexes. This shows that the coupling via the LUMO is of minor importance for the bpt$^-$/bpzt$^-$ complexes. It is therefore expected that also for the mixed-metal **RuRh** and **RuIr** complexes the coupling takes place via the HOMO of the bridging ligand.

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