$$k_{ex} = k_0 + k_H[H^+]^2 \qquad (16)$$

16 000 s^{-1} and $k_H^{298} \approx 2000\ m^{-2}\ s^{-1}$ are roughly estimated from the experimental data (Table VI). As discussed already, TiO^{2+} is not likely to be responsible for the k_0 term in eq 16. Since the equilibrium between TiO^{2+} and $Ti(OH)_2{}^{2+}$ is $[H^+]$- and $[Ti(IV)]_{total}$-independent, the equilibrium constant remains unknown. On the basis of the stability of the TiO^{2+} yl bond it, however, seems to be unlikely that the concentration of $Ti(OH)_2{}^{2+}$ is large. This might be one reason for the fact that the dihydroxo species still has escaped any direct experimental proof.

We conclude that our results together with earlier work indicate that monomeric titanyl exists in aqueous acidic solution. The fact that TiO^{2+} exchanges its oxygen very fast is explained by a relatively easily protonated yl oxygen. This clearly indicates that monomeric titanyl is in equilibrium with other monomeric species, which most probably include $Ti(OH)_2{}^{2+}$ and $Ti^{4+}(aq)$.

Acknowledgment. We are grateful to Dr. F. P. Rotzinger (EPF Lausanne) for the donation of a sample of purified and analyzed $TiOSO_4 \cdot 2H_2O$ and to Dr. R. Humphry-Baker (EPF Lausanne, light scattering), Dr. L. Helm (Universitē de Lausanne, NMR), E. Cotelioglu (Universitē de Lausanne, computing), and V. Kasparek and C. Desponds (Universitē de Lausanne, FTIR) for their help with the instrumentation. We thank the Swiss National Science Foundation for financial support through Grant 2.854-0.85.

Registry No. TiO^{2+}, 12192-25-5; Ti, 7440-32-6; oxygen, 7782-44-7.

Supplementary Material Available: Details of the oligomer fits, listings of calculations on the potentiometric titrations, and details of the pK_a determinations (19 pages). Ordering information is given on any current masthead page.

Contribution from the Istituto Chimico "G. Ciamician" dell'Universitā, Bologna, Italy, Istituto FRAE-CNR, Bologna, Italy, and Institute of Inorganic Chemistry, University of Fribourg, Fribourg, Switzerland

Absorption Spectra, Electrochemical Behavior, Luminescence Spectra, and Excited-State Lifetimes of Mixed-Ligand Ortho-Metalated Rhodium(III) Complexes

Mauro Maestri,*[1] Diana Sandrini,[1] Vincenzo Balzani,*[1,2] Urs Maeder,[3] and Alex von Zelewsky[3]

Received July 25, 1986

We report results of an investigation on the absorption spectra, electrochemical behavior, luminescence spectra, and excited-state lifetimes of the $Rh(phpy)_2(bpy)^+$ and $Rh(thpy)_2(bpy)^+$ complexes, where $phpy^-$ and $thpy^-$ are the ortho-C-deprotonated forms of 2-phenylpyridine and 2-(2-thienyl)pyridine and bpy is 2,2′-bipyridine. The results obtained have been compared with those previously available for $Rh(bpy)_3{}^{3+}$ and for Pt(II) and Pt(IV) complexes containing the phpy and thpy ligands. On electrochemical oxidation, the two mixed-ligand complexes exhibit an irreversible wave at about +1.1 V and, on reduction, a reversible one-electron wave at −1.4 V. Besides ligand-centered bands in the UV region, the absorption spectra of the mixed-ligand complexes show intense bands at lower energy (λ_{max} = 367 nm for $Rh(phpy)_2(bpy)^+$ and 379 nm for $Rh(thpy)_2(bpy)^+$ that are assigned to metal-to-ligand (presumably, Rh → $phpy^-$ and Rh → $thpy^-$) charge-transfer transitions. Both complexes exhibit a strong and long-lived ($\tau \approx$ 0.17 and 0.50 ms for $Rh(phpy)_2(bpy)^+$ and $Rh(thpy)_2(bpy)^+$, respectively) luminescence emission at 77 K in rigid matrix, which is assigned as a triplet ligand-centered luminescence of the $phpy^-$ and $thpy^-$ ligands. For $Rh(phpy)_2(bpy)^+$, there is indication of some mixing of the emitting triplet ligand-centered state with a charge-transfer state. Emission lifetime and emission intensity decrease strongly in fluid solution. For $Rh(phpy)_2(bpy)^+$, no emission can be observed above 222 K, whereas $Rh(thpy)_2(bpy)^+$ is luminescent even at room temperature (τ = 1.0 μs). The results obtained, compared with those available for $Rh(bpy)_3{}^{3+}$, are consistent with a higher ligand field strength of the ortho-metalated ligands compared with that of bpy. Because of its redox and luminescence properties, $Rh(thpy)_2(bpy)^+$ promises to be a useful excited-state reactant and excited-state product in electron-transfer reactions.

Introduction

In the search for new luminescent compounds that can play the role of light absorption and/or light emission sensitizers,[4] we have studied the photophysical and photochemical properties of several Ru(II) diimine complexes.[5] Recently, we have extended our interest to ortho-metalated complexes that contain ligands similar to diimines and exhibit very interesting excited-state properties. Results concerning ortho-metalated Pt(II)[6] and Pt(IV)[7] complexes have already been presented.

In this paper, we report the results of an investigation on the $Rh(phpy)_2(bpy)^+$ and $Rh(thpy)_2(bpy)^+$ complexes, where $phpy^-$ and $thpy^-$ are the ortho-C-deprotonated forms of 2-phenylpyridine and 2-(2-thienyl)pyridine and bpy is 2,2′-bipyridine (Figure 1). The results obtained have been compared with those previously available for $Rh(bpy)_3{}^{3+}$. Studies on the dichloro-bridged dimeric $[Rh(phpy)_2Cl]_2$ complex[8a] and on dimeric[8a] and monomeric[9,10]

---

(1) University of Bologna.

(2) Istituto FRAE-CNR.

(3) University of Fribourg.

(4) (a) Balzani, V.; Bolletta, F.; Ciano, M.; Maestri, M. *J. Chem. Educ.* **1983**, *60*, 447. (b) Balzani, V.; Bolletta, F. *Comments Inorg. Chem.* **1983**, *2*, 211.

(5) (a) Juris, A.; Balzani, V.; Belser, P.; von Zelewsky, A. *Helv. Chim. Acta* **1981**, *64*, 2175. (b) Juris, A.; Barigelletti, F.; Balzani, V.; Belser, P.; von Zelewsky, A. *Isr. J. Chem.* **1982**, *22*, 87. (c) Belser, P.; von Zelewsky, A.; Juris, A.; Barigelletti, F.; Balzani, V. *Gazz. Chim. Ital.* **1983**, *113*, 731. (d) Barigelletti, F.; Juris, A.; Balzani, V.; Belser, P.; von Zelewsky, A. *Inorg. Chem.* **1983**, *22*, 3335. (e) Juris, A.; Barigelletti, F.; Balzani, V.; Belser, P.; von Zelewsky, A. *Inorg. Chem.* **1985**, *24*, 202. (f) Balzani, V.; Juris, A.; Barigelletti, F.; Belser, P.; von Zelewsky, A. *Riken Q.* **1984**, *78*, 78. (g) Juris, A.; Belser, P.; Barigelletti, F.; von Zelewsky, A.; Balzani, V. *Inorg. Chem.* **1986**, *25*, 256. (h) Belser, P.; von Zelewsky, A.; Juris, A.; Barigelletti, F.; Balzani, V. *Gazz. Chim. Ital.* **1985**, *115*, 723.

(6) Maestri, M.; Sandrini, D.; Balzani, V.; Chassot, L.; Jolliet, P.; von Zelewsky, A. *Chem. Phys. Lett.* **1985**, *122*, 375.

(7) Chassot, L.; von Zelewsky, A.; Sandrini, D.; Maestri, M.; Balzani, V. *J. Am. Chem. Soc.* **1986**, *108*, 6084.

(8) (a) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 6647. (b) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. *Abstracts of Papers*, 6th International Symposium on the Photochemistry and Photophysics of Coordination Compounds, London, 1984; p 20.

(9) King, K. A.; Spellane, P. J.; Watts, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1431.

(10) King, K. A.; Finlayson, M. F.; Spellane, P. J.; Watts, R. J. *Riken Q.* **1984**, *78*, 97.

0020-1669/87/1326-1323$01.50/0 © 1987 American Chemical Society

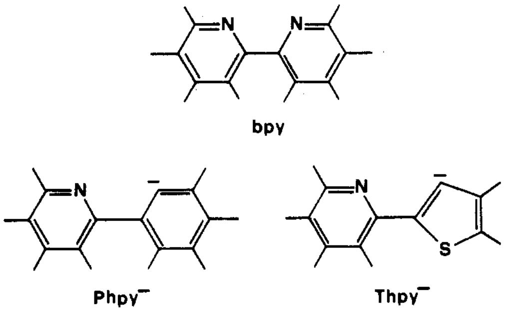

Figure 1. Structural formulas of the ligands.

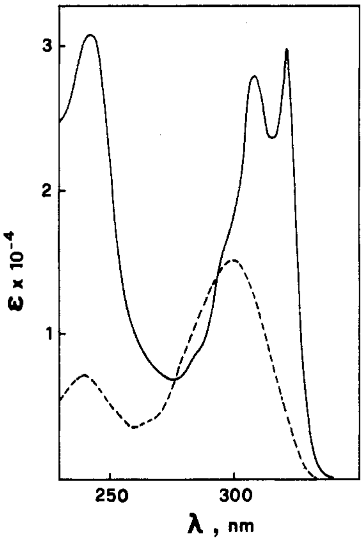

Figure 2. Absorption spectra of $Rh(bpy)_3^{3+}$ (—) in MeOH solution and $bpyH^+$ (- - -) in $MeOH-H_2SO_4$ solution, at room temperature.

ortho-metalated Ir(III) complexes have been reported by Watts and co-workers, who have also mentioned a ligand-centered emission from monomeric mixed-ligand ortho-metalated Rh(III) complexes.[8b] An investigation on the photochemical behavior of some ortho-metalated Pd(II) complexes has been recently reported by Wakatsuki et al.[11]

Experimental Section

The preparation, purification, and characterization of $Rh(bpy)_3^{3+}$,[12] $Rh(phpy)_2(bpy)^+$,[13] and $Rh(thpy)_2(bpy)^+$[13] as Cl^- or PF_6^- salts have been described elsewhere. Propionitrile and butyronitrile were purified according to literature methods and used in a 4:5 v/v mixture; in the following, this mixture will be simply called "nitrile". The other solvents and chemicals used were of the best commercial grade. When necessary, the solutions were deaerated by repeated freeze–pump–thaw cycles.

The absorption spectra were recorded with a Kontron Uvikon 860 spectrophotometer, and the emission spectra were obtained with a Perkin-Elmer LS5 spectrofluorometer equipped with a Hamamatsu R928 phototube. Emission lifetimes were measured with a JK system 2000 neodymium YAG/DLPY 4 laser (third harmonic; pulse half-width 25 ns). Single exponential decays were obtained in all cases (estimated errors <10%). Emission quantum yields were estimated with the optically diluted method[14] using $Ru(bpy)_3^{2+}$ in aerated aqueous solution as a standard ($\Phi_{em} = 0.028$).[15]

Electrochemical measurements were carried out by using a Metrohm E/506 Polarecord, a Metrohm E/612 VA scanner, and a Hewlett-Packard 7044 X-Y recorder. Cyclic voltammograms were obtained in dimethylformamide (DMF) solution under argon atmosphere by using a stationary platinum-disk working electrode, a platinum counter electrode, and an Ag/0.01 M $AgNO_3$ reference electrode, with TBAP as supporting electrolyte. The scanning speed was 100 mV s^{-1}. The redox potentials of $Ru(bpy)_3^{2+}$ under the same experimental conditions were used as a secondary reference for the redox potentials of the new complexes.[5a]

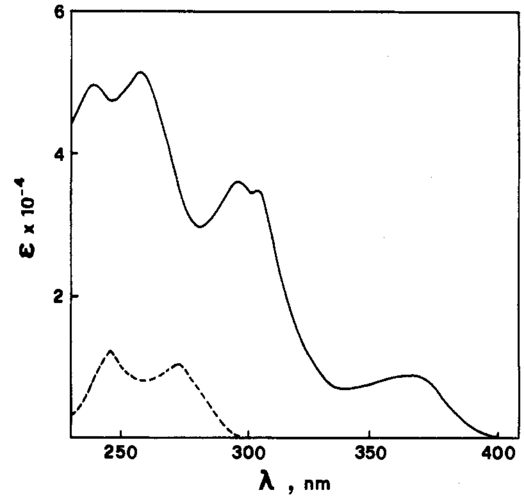

Figure 3. Absorption spectra of $Rh(phpy)_2(bpy)^+$ (—) in MeOH solution and phpyH (- - -) in $MeOH-H_2SO_4$ solution, at room temperature.

Table I. Absorption and Emission Data for the Rh Complexes and Their Protonated Free Ligands

	absorption[a]		emission[b]			
			293 K		77 K	
	λ_{max}, nm	$\epsilon \times 10^{-3}$	λ_{max},[c] nm	τ, μs	λ_{max},[c] nm	τ, ms
$Rh(bpy)_3^{3+}$	241 307 320	31 28 30	460[d]	<0.015[d]	448	2.0[e]
$Rh(phpy)_2(bpy)^+$	239 257 297 367	53 55 36 8	454[f]	<0.05	454	0.17
$Rh(thpy)_2(bpy)^+$	263 295 379	26 31 9	526 565	1	521	0.5
$bpyH^+$	240[g] 301	7.1[g] 15.6			436[h]	1010[i]
phpyH	247[g] 274	11.1[g] 8.9			430[j]	>100
thpyH	263[g] 303	7.8[g] 13.2			486[j]	35

[a] MeOH solution at 293 K, unless otherwise noted. [b] Nitrile solution. [c] λ of the high-energy feature of the phosphorescence emission. [d] Acetonitrile solution, 263 K; ref 25. [e] 2.2 ms in 5:1 EtOH–MeOH; ref 18. [f] 222 K; no emission detectable at higher temperature. [g] EtOH–water (Wynberg, H.; van Bergen, T. J.; Kellog, R. M. *J. Org. Chem.* **1969**, *34*, 3175). In the same reference the absorption maxima of the diprotonated ligands $phpyH_2^+$ (λ_{max} = 242, 295 nm; ϵ_{max} = 8700, 13 800) and $thpyH_2^+$ (λ_{max} = 268, 334 nm; ϵ_{max} = 6700, 15 300) are also reported. For the absorption maximum of $bpyH_2^{2+}$ (λ_{max} = 290 nm; ϵ_{max} = 15 200), see: Westheimer, F. H.; Benfey, O. T. *J. Am. Chem. Soc.* **1956**, *78*, 5310. [h] $MeOH-H_2SO_4$. [i] See ref 28. [j] The highest energy feature of the emission spectrum of the diprotonated ligand is red-shifted by ~10 nm.

Results

The absorption spectra of $Rh(bpy)_3^{3+}$, $Rh(phpy)_2(bpy)^+$, and $Rh(thpy)_2(bpy)^+$ at room temperature are shown in Figures 2–4, together with the spectra of the uncoordinated ligands $bpyH^+$, phpyH, and thpyH (see also Table I). The spectra of $bpyH_2^{2+}$, $phpyH_2^+$, and $thpyH_2^+$ were also recorded; their absorption maxima and the corresponding extinction coefficients are shown in footnote *g* of Table I.

---

(11) Wakatsuki, Y.; Yamazaki, H.; Grutsch, P. A.; Santhanam, M.; Kutal, C. *J. Am. Chem. Soc.* **1985**, *107*, 8153.

(12) Harris, C. M.; McKenzie, E. D. *J. Inorg. Nucl. Chem.* **1963**, *25*, 171.

(13) (a) Maeder, U.; Jenny, T.; von Zelewsky, A. *Helv. Chim. Acta* **1986**, *69*, 1085. (b) Maeder, U. Ph.D. Thesis, in preparation. (c) The $Rh(thpy)_2(bpy)^+$ complex is known[13a] to have the carbon atoms of the two $thpy^-$ ligands in a cis relationship and the nitrogen atoms of the same ligands in a trans relationship.

(14) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

(15) Nakamuru, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697.

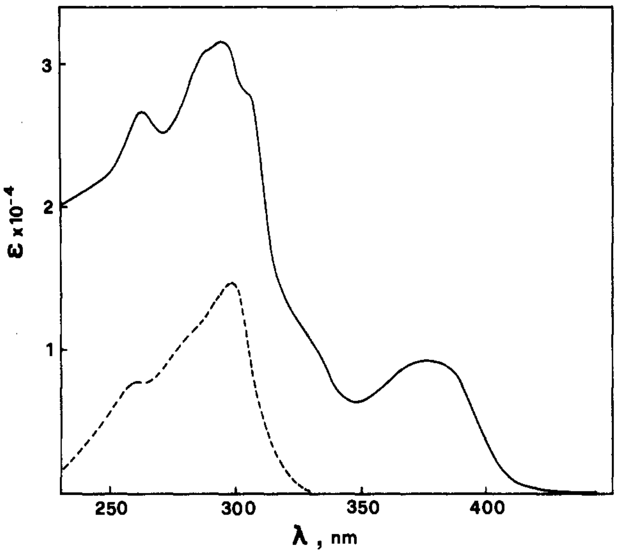

Figure 4. Absorption spectra of $Rh(thpy)_2(bpy)^+$ (—) in MeOH solution and thpyH (- - -) in $MeOH-H_2SO_4$ solution, at room temperature.

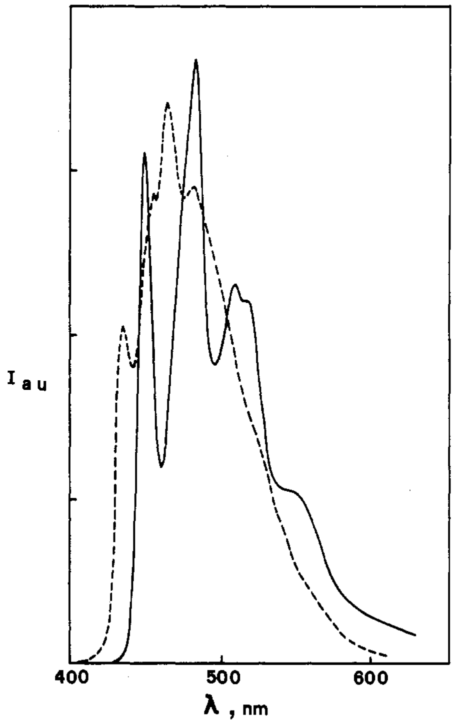

Figure 5. Emission spectra in rigid matrix at 77 K of $Rh(bpy)_3^{3+}$ (—) and $bpyH^+$ (- - -).

Table II. Ground- and Excited-State Redox Properties[a]

	E_{ox},[b] V	E_{red},[c] V	E_{00},[d] eV	$^*E_{ox}$,[e] V	$^*E_{red}$,[e] V
$Rh(phpy)_2(bpy)^+$	~+1.1	−1.41	2.73	~−1.6	+1.32
$Rh(thpy)_2(bpy)^+$	~+1.1	−1.42	2.38	~−1.3	+0.98

[a] All potentials are in DMF relative to NHE (see Experimental Section). [b] E_p for oxidation of the complex (irreversible). [c] $E_{1/2}$ for the reduction of the complex, except as otherwise noted. [d] Zero–zero excited-state energy, taken as the energy of the highest energy feature of the emission spectrum at 77 K. [e] Estimated from the oxidation or reduction potential of the ground-state and the zero–zero excited-state energies, as indicated in ref 31.

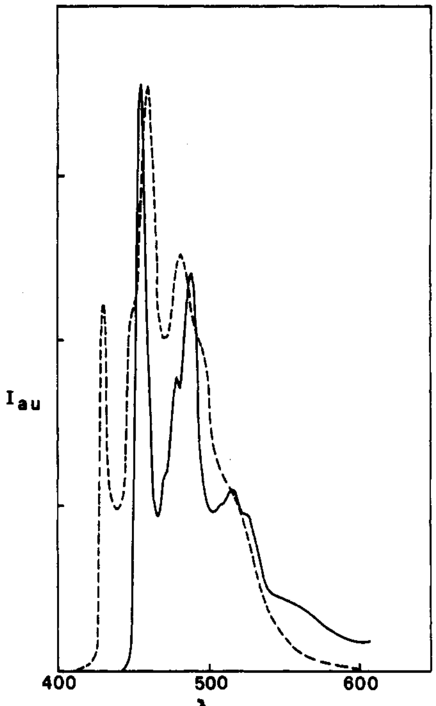

Figure 6. Emission spectra in rigid matrix at 77 K of $Rh(phpy)_2(bpy)^+$ (—) and phpyH (- - -).

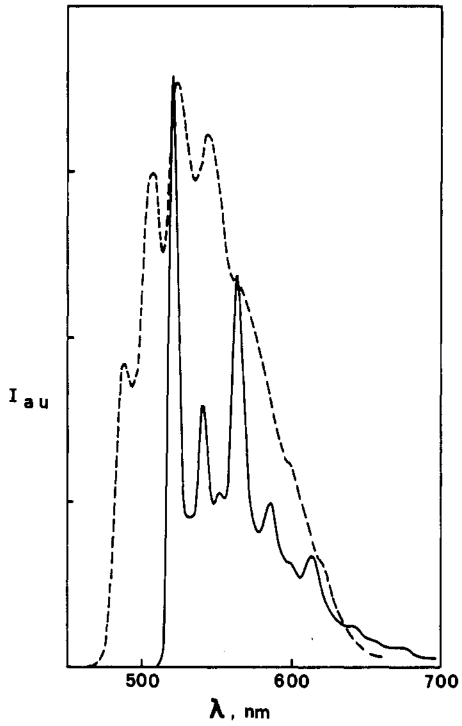

Figure 7. Emission spectra in rigid matrix at 77 K of $Rh(thpy)_2(bpy)^+$ (—) and thpyH (- - -).

Figures 5–7 show the luminescence spectra of the three complexes and of their uncoordinated ligands at 77 K in nitrile solution. No evidence for dual emission was obtained for all the complexes examined. Table I summarizes the main features of the absorption and emission spectra and shows the emission lifetimes of the three complexes and their ligands. In all cases, the luminescence decay was strictly exponential.

As previously reported,[16a] $Rh(bpy)_3^{3+}$ undergoes an irreversible two-electron reduction at slow sweep rates, followed by two reversible waves. At rapid sweep rates, the first reduction wave exhibits a quasi-reversible behavior.[16] This first reduction is followed by a moderately fast elimination of one bpy ligand. For

---

(16) (a) Kew, G.; DeArmond, M. K.; Hanck, K. *J. Phys. Chem.* **1974**, *78*, 727. (b) Creutz, C.; Keller, A.; Sutin, N.; Zipp, A. P. *J. Am. Chem. Soc.* **1982**, *104*, 3618.

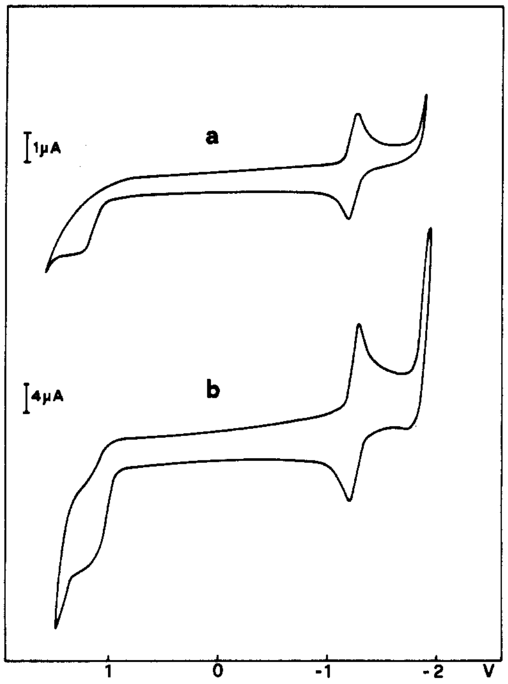

Figure 8. Cyclic voltammograms of $Rh(phpy)_2(bpy)^+$ (a) and $Rh(thpy)_2(bpy)^+$ (b) in DMF (sweep rate 100 mV s^{-1}; room temperature; Pt working electrode; tetrabutylammonium perchlorate, 0.1 M).

$Rh(phpy)_2(bpy)^+$ and $Rh(thpy)_2(bpy)^+$ in DMF solution only a one-electron reversible reduction wave is observed, even at low sweep rate (Figure 8). On oxidation, the two complexes show an irreversible wave. The ground- and excited-state redox properties of the two complexes are summarized in Table II.

Solutions of the complexes in acetonitrile or other solvents were stable both in the dark and under laboratory light. Irradiation of $Rh(phpy)_2(bpy)^+$ and $Rh(thpy)_2(bpy)^+$ in nitrile solution with 313-nm light for several hours did not cause any photochemical reaction. The luminescence emission in fluid solution was strongly quenched by dioxygen. For $Rh(thpy)_2(bpy)^+$, the emission quantum yield at room temperature was estimated to be $\leq 10^{-4}$.

Discussion

The $thpy^-$ and $phpy^-$ ligands are structurally similar to bpy. The main difference consists in their higher ligand field strength due to the strong σ-donor ability of C^-.[8] This also lowers the energy of the metal-to-ligand charge-transfer (MLCT) excited states because of the increase in the electron density on the metal.

Electrochemistry. As shown in Figure 8, both $Rh(phpy)_2(bpy)^+$ and $Rh(thpy)_2(bpy)^+$ exhibit a reversible one-electron reduction ($E_{1/2} = -1.41$ and -1.42 V vs. NHE, respectively). This behavior contrasts sharply with that of $Rh(bpy)_3^{3+}$, which undergoes an irreversible two-electron reduction process at about −0.8 V, leading to $Rh(bpy)_2^+$.[16] This suggests that reduction of $Rh(phpy)_2(bpy)^+$ and $Rh(thpy)_2(bpy)^+$ is a ligand-centered process, instead of a metal-centered process as in $Rh(bpy)_3^{3+}$. This is in agreement with the expected higher ligand field strength of $phpy^-$ and $thpy^-$.

Absorption Spectra. The intense absorption bands shown by the three complexes in the UV region can be due to LC (ligand-centered) and/or CT (charge-transfer) transitions. To make a correct assignment, comparison with the spectra of the free (uncoordinated) ligands or, better, with complexes where CT bands cannot occur is most useful. For the free ligands (Figure 1) the nonprotonated (bpy, $phpy^-$, $thpy^-$), monoprotonated ($bpyH^+$, phpyH, thpyH), and diprotonated ($bpyH_2^{2+}$, $phpyH_2^+$, $thpyH_2^+$) species could be considered. We believe that the diprotonated forms are not good models because they are presumably in a skew conformation. Between the nonprotonated and monoprotonated forms, the latter should better reflect the situation of the coordinated ligands, at least in the case of $phpy^-$ and $thpy^-$ complexes where a strong C–Rh σ-donor bond is present. As previously discussed by several authors,[17-19] the high-intensity bands that appear in the UV spectrum of $Rh(bpy)_3^{3+}$ can be assigned to perturbed ligand-centered transitions, by analogy with the spectrum of $Zn(bpy)_3^{2+}$.[20] The lowest energy singlet d–d (metal-centered, MC) band is expected to lie below 300 nm.[21,22] No spin-allowed metal-to-ligand charge-transfer (MLCT) band appears in the $Rh(bpy)_3^{3+}$ spectrum.

$Rh(phpy)_2(bpy)^+$ and $Rh(thpy)_2(bpy)^+$ exhibit bands in the UV region that can be attributed to $phpy^-$ and bpy (or $thpy^-$ and bpy) LC transitions (Figures 3 and 4). Pt(IV) complexes containing $phpy^-$ and $thpy^-$, where MLCT transitions cannot occur at low energy, show the lowest LC bands at 307 nm for $phpy^-$ and 344 nm for $thpy^-$.[7] It follows that the broad, intense band with maximum at 367 nm for $Rh(phpy)_2(bpy)^+$ and 379 nm for $Rh(thpy)_2(bpy)^+$ cannot be assigned to LC transitions. Neither can they be assigned to a MC transition because of their high intensity and also because of the fact that the ligand field strength for $Rh(phpy)_2(bpy)^+$ and $Rh(thpy)_2(bpy)^+$ is even higher than for $Rh(bpy)_3^{3+}$ (vide supra). It follows that the only possible assignments for these bands are (a) Rh → $phpy^-$ and Rh → $thpy^-$ CT transitions and (b) the Rh → bpy CT transition. Assignment a is supported by the finding of similar bands in the $[Rh(phpy)_2Cl]_2$ and $[Ir(phpy)_2Cl]_2$ dimers[8] and in the $Pt(phpy)_2$ and $Pt(thpy)_2$ complexes,[6] where bpy is not present. For the latter couple of complexes, the Pt → $thpy^-$ band is ~1000 cm^{-1} red-shifted compared to the Pt → $phpy^-$ band, as would be the case for $Rh(phpy)_2(bpy)^+$ and $Rh(thpy)_2(bpy)^+$ (Figures 3 and 4 and Table I). Assignment b seems less likely, but it cannot be ruled out because the strong σ-donor ability of $phpy^-$ and $thpy^-$ is expected to increase the negative charge on the metal and thus to decrease the energy of the Rh → bpy CT transition, compared to what happens in $Rh(bpy)_3^{3+}$. It is also possible that both types of transitions contribute to the observed absorption.[23]

Emission Spectra and Lifetimes. The luminescence emission of $Rh(bpy)_3^{3+}$ was only observed at low temperature (Table I). This emission has previously been assigned[18,19] to a ^3LC $\pi \rightarrow \pi^*$ excited state, on the basis of the long emission lifetime and some similarity with the phosphorescence emission of the uncoordinated bpy ligand. It should be noticed that the emission spectrum of $Zn(bpy)_3^{3+}$[20] (where no MC or MLCT excited states can be present at low energy) is quite similar to that of $Rh(bpy)_3^{3+}$, confirming that the emission of the latter complex can also be assigned as LC. For $Rh(phen)_3^{3+}$, the luminescence emission at 77 K is also due to a ^3LC excited state,[18,19] but at high temperature, dual emission from ^3LC and ^3MC is observed.[21,24] Several authors[21,25,26] agree on the facts that in $Rh(bpy)_3^{3+}$ and $Rh(phen)_3^{3+}$ the lowest energy excited state is a ^3LC state and that at a comparable or not much higher energy there is a distorted ^3MC state.

For $Rh(phpy)_2(bpy)^+$ and $Rh(thpy)_2(bpy)^+$, it is expected that the MC excited states lie at higher energies than for $Rh(bpy)_3^{3+}$ because of the higher σ-donor ability of C^- compared to that of N. The highly structured emissions of $Rh(phpy)_2(bpy)^+$ and $Rh(thpy)_2(bpy)^+$ (Figures 6 and 7) clearly agree with the expectation that ^3MC cannot be the emitting excited state. The relatively long excited-state lifetimes (Table I) point to a ^3LC assignment, but a ^3MLCT assignment should also be taken into account because of the presence of MLCT absorption bands at

---

(17) Carstens, D. H. W.; Crosby, G. A. *J. Mol. Spectrosc.* **1970**, *34*, 113.

(18) DeArmond, M. K.; Hillis, J. E. *J. Chem. Phys.* **1971**, *54*, 2247.

(19) Crosby, G. A.; Elfring, W. H., Jr. *J. Phys. Chem.* **1976**, *80*, 2206.

(20) Ohno, T.; Kato, S. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2953.

(21) Bolletta, F.; Rossi, A.; Barigelletti, F.; Dellonte, S.; Balzani, V. *Gazz. Chim. Ital.* **1981**, *111*, 155.

(22) Josephsen, J.; Schaffer, C. E. *Acta Chem. Scand., Ser. A* **1977**, *A31*, 813.

(23) Preliminary results on the absorption spectra of the analogous complexes where bpy is replaced by biq (2,2′-biquinoline) support assignment a.

(24) Dual emission has not been found by Nishizawa et al.,[25] but it has been confirmed by luminescence and excited-state absorption studies carried out by Scandola et al. on $Rh(phen)_3^{3+}$[26] and $Rh(phen)_2X_2^{2+}$[27] complexes.

(25) Nishizawa, M.; Suzuki, T. M.; Sprouse, S.; Watts, R. J.; Ford, P. C. *Inorg. Chem.* **1984**, *23*, 1837.

(26) Indelli, M. T.; Cairoli, A.; Scandola, F. *J. Phys. Chem.* **1984**, *88*, 2685.

(27) Scandola, F.; et al., private communication.

relatively low energies (Figures 3 and 4).

For $Rh(thpy)_2(bpy)^+$, the assignment of the luminescence emission to a ^3LC excited state centered on the $thpy^-$ ligand can be confidently made after considerations of the following data:

(i) The emission spectrum is slightly displaced in energy ($\sim$500 cm^{-1}) and identical in shape compared to that of $Pt(thpy)_2(CH_2Cl)Cl$,[7] whose lowest excited state is certainly a ^3LC state localized on the $thpy^-$ ligand.

(ii) The emission lifetime at 77 K (500 μs) is longer than that of the $Pt(thpy)_2(CH_2Cl)Cl$ complex (340 μs),[7] as expected for a spin-forbidden LC emission that is perturbed by a lighter metal.

(iii) From the emission lifetime (1 μs) and the luminescence quantum yield ($\leq 10^{-4}$) at room temperature, the radiative lifetime is estimated to be $\geq 10^{-2}$ s, a figure expected for a perturbed ^3LC emission and inconsistent with a ^3MLCT emission: for $Rh(bpy)_3^{3+}$[28] and $Pt(thpy)_2(CH_2Cl)Cl$,[7] which are "bona fide" ^3LC emitters, the radiative lifetime is $\sim 5 \times 10^{-3}$ s^{-1}, whereas for $Ru(bpy)_3^{2+}$[29] and $Pt(thpy)_2$,[6] which are ^3MLCT emitters, the radiative lifetime is $\sim 1 \times 10^{-5}$ s^{-1}.

(iv) Assuming that the splitting between the energies of the absorption and emission maxima for MLCT excited states is of the order of 5000 cm^{-1}, as for $Ru(bpy)_3^{2+}$[5f] and $Pt(thpy)_2$,[6] and taking the absorption at 379 nm as a singlet MLCT band, we expected the ^3MLCT emission to occur at $\sim$475 nm, whereas the emission is actually observed at 521 nm (Figure 7).

For $Rh(phpy)_2(bpy)^+$, the assignment of the luminescence emission is a little less straightforward. In favor of a ^3LC $phpy^-$ emission are the following results: (i) the quite similar (but not identical) shapes of the spectra of $Rh(phpy)_2(bpy)^+$ and of the bona fide ^3LC $phpy^-$ emitter $Pt(phpy)_2(CH_2Cl)Cl$[7] and the same small red shift of the emission of the Rh complex, compared to the Pt complex, as is the case for $Rh(thpy)_2(bpy)^+$ compared with $Pt(thpy)_2(CH_2Cl)Cl$; (ii) the different shapes of the emission spectra of $Rh(phpy)_2(bpy)^+$ and $Rh(bpy)_3^{3+}$ (Figures 5 and 6), which disfavors a ^3LC bpy assignment; (iii) the fact that the emission lifetime at 77 K is considerably longer than that of ^3MLCT excited states (1–10 μs)[5,18,19] and even than that of $[Rh(phpy)_2Cl]_2$ (93 μs), which has previously been assigned as a ^3LC $phpy^-$ emission.[8]

However, the fact that the lifetime of the $Rh(phpy)_2(bpy)^+$ emission at 77 K (170 μs) is shorter than that of $Rh(thpy)_2(bpy)^+$ and also than that of $Pt(phpy)_2(CH_2Cl)Cl$ (300 μs),[7] in spite of the fact that Rh is lighter than Pt, suggests that the ^3LC $phpy^-$ state responsible for the $Rh(phpy)_2(bpy)^+$ emission has to be somewhat mixed with a CT level. Support for a mixing between LC and CT levels also comes from the observation that, with the same assumptions as those made in point iv above for $Rh(thpy)_2(bpy)^+$, emission from a ^3MLCT level is indeed expected to lie more or less at the same wavelength as that of the observed emission band.

Excited-State Properties in Fluid Solution. It is well-known that excited states having sufficiently long lifetimes can be used as reactants in energy- and electron-transfer processes in fluid solution.[30-36] Such excited-state reactions, which are extremely important for the development of kinetic theories[33,36-38] as well as for practical applications,[39-41] can be best monitored by luminescence measurements. Luminescent compounds that can undergo reversible oxidation and/or reduction processes are also useful for generating light in chemiluminescent and electrochemiluminescent processes.[4] From this point of view, $Rh(bpy)_3^{3+}$ is a compound of no practical value because of the lack of luminescence in fluid solution, the extremely short excited-state lifetime (<15 ns),[25] and the irreversible redox behavior.[16] Most of these drawbacks have their origin in the relative energies of the ^3LC and ^3MC excited states. The presence of a low-energy ^3MC level offers a fast deactivation channel at room temperature to the intrinsically long-lived and luminescent ^3LC level.[20,25,26] Furthermore, in the reduced form the availability of a low-energy $\sigma_M(e_g)$ orbital facilitates ligand dissociation. When bpy is replaced by its ortho-metalating analogue $phpy^-$, the ligand field strength increases because of the stronger σ-donor ability of C^-. This moves the $\sigma_M(e_g)$ orbitals to higher energy, making this orbital unavailable for the reduction process, as is shown by the reversible reduction behavior of $Rh(phpy)_2(bpy)^+$. The ^3MC excited state is also expected to move to higher energy, but apparently not enough to prevent its population (with the consequent fast luminescence decay) at high temperature, as is shown by the lack of luminescence emission at 293 K (Table I). When bpy is replaced by $thpy^-$, which has presumably a ligand field strength similar to that of $phpy^-$; the $\sigma_M(e_g)$ orbitals move again to higher energy, as indicated by the reversible reduction behavior. Furthermore, $thpy^-$ has an intrinsic ^3LC level that lies at a much lower energy than that of $phpy^-$ (Table I), so that the energy gap between ^3MC is likely to be much higher in $Rh(thpy)_2(bpy)^+$ than in $Rh(phpy)_2(bpy)^+$, as indicated by the long emission lifetime of the luminescence emission of $Rh(thpy)_2(bpy)^+$ (Table I). Thus, because of its excited-state energy, reversible reduction behavior, strong excited-state reducing and oxidizing power (Table II), long excited-state lifetime, and room-temperature luminescence, $Rh(thpy)_2(bpy)^+$ promises to be a useful excited-state reactant for energy-transfer and electron-transfer processes, as well as a useful (i.e. light-emitting) excited-state product in chemiluminescent and electrochemiluminescent reactions.

Conclusion

The mixed-ligand $Rh(phpy)_2(bpy)^+$ and $Rh(thpy)_2(bpy)^+$ complexes are strongly emitting and long-lived luminescent compounds in rigid matrix at 77 K. $Rh(thpy)_2(bpy)^+$ maintains a nonnegligible luminescence and a long lifetime also in fluid solution at room temperature. For both complexes, emission is assigned as triplet ligand-centered luminescence of the $phpy^-$ or $thpy^-$ ligands. For $Rh(phpy)_2(bpy)^+$, there is evidence for some mixing between the emitting ^3LC excited state and a ^3MLCT level. The energy gap between the lowest ^3LC and ^3MC excited states is expected to be higher in the $thpy^-$ complex, as indicated by the long lifetime of the excited $Rh(thpy)_2(bpy)^+$ complex at room temperature. Both complexes undergo a reversible one-electron reduction, which is consistent with the ligand-localized nature of the lowest energy unoccupied orbitals. Because of its spectroscopic and redox properties, $Rh(thpy)_2(bpy)^+$ is a strong reductant and a relatively strong oxidant in the excited state, and because of its long lifetime and sufficiently strong luminescence at room temperature it promises to be a useful excited-state reactant in energy- and electron-transfer processes, as well as a useful excited-state product for chemiluminescent and electrochemiluminescent reactions.

Acknowledgment. We thank G. Gubellini and V. Cacciari for technical assistance. This work was supported by the Ministero della Pubblica Istruzione and Consiglio Nazionale delle Ricerche of Italy and by the Swiss National Science Foundation.

Registry No. $Rh(phpy)_2(bpy)^+$, 106266-44-8; $Rh(thpy)_2(bpy)^+$, 107053-32-7.

---

(28) Hillis, J. E.; DeArmond, M. K. *J. Lumin.* **1971**, *4*, 273.

(29) Demas, J. N.; Taylor, D. G. *Inorg. Chem.* **1979**, *18*, 3177.

(30) Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Laurence, G. S. *Coord. Chem. Rev.* **1975**, *15*, 321.

(31) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1.

(32) Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717.

(33) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159.

(34) Endicott, J. F.; Kumar, K.; Ramasani, T.; Rotzinger, F. P. *Prog. Inorg. Chem.* **1983**, *30*, 141.

(35) Watts, R. J. *J. Chem. Educ.* **1983**, *60*, 834.

(36) Meyer, T. J. *Prog. Inorg. Chem.* **1983**, *30*, 94.

(37) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.

(38) Sutin, N.; Creutz, C. *J. Chem. Educ.* **1983**, *60*, 809.

(39) Rabani, J., Ed. *Photochemical Conversion and Storage of Solar Energy*; Weizmann: Jerusalem, 1982.

(40) Graetzel, M., Ed. *Energy Resources by Photochemistry and Catalysis*; Academic: London, 1983.

(41) Chanon, M.; Tobe, M. L. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 1.