

## Ruthenium Complexes with 1,4,5,8-Tetraazaphenanthrene. Unusual Photophysical Behavior of the Tris-Homoleptic Compound

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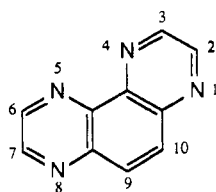
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The photophysical and electrochemical properties of the series of complexes  $\text{Ru}(\text{bpy})_n(\text{tap})_{3-n}^{2+}$  ( $n = 0-3$ ) (bpy = 2,2'-bipyridine; tap = 1,4,5,8-tetraazaphenanthrene) have been examined and compared with those of the other previously studied series. Although the mixed-ligand complexes seem to follow the same sequence of photophysical behaviors described in the literature for other series, the homoleptic  $\text{Ru}(\text{tap})_3^{2+}$  presents peculiar properties; it is the only one whose emission lifetime does not seem to be controlled by the nonradiative deactivation from the  $^3\text{MLCT}$  (metal-to-ligand-charge-transfer triplet), but by the intersystem crossing to the  $^3\text{MC}$  (metal-centered triplet) state, responsible for the photolability of the complex. The luminescence quenching by  $\text{Cl}^-$  ions and the emission lifetimes as a function of temperature, in absence and presence of  $\text{Cl}^-$ , suggest that there would be a dynamic coupling of the  $^3\text{MLCT}$  with the  $^3\text{MC}$  through a rapid equilibrium between those states, at least in acetonitrile.

### Introduction

$\text{Ru}(\text{bpy})_3^{2+}$  (bpy = 2,2'-bipyridine) is one of the molecules that has been the most extensively studied during this last decade.<sup>1a</sup> Its attractiveness as an efficient photosensitizer for electron-transfer reactions, and especially its potential use in water photocleavage systems, are at the origin of this intense scientific research. Therefore, it is now considered as the reference compound for studying the photophysics, photochemistry, and electrochemistry of other Ru complexes containing new ligands. The accepted photophysical model proposed for this complex constitutes a good basis for understanding the behavior of new complexes that are made in order to tune the properties of the photosensitizer according to the envisioned redox partner.<sup>2-8</sup> As a matter of fact, Balzani et al. in a recent review,<sup>2</sup> count no less than 200 polypyridine-like molecules able to complex ruthenium.

In our laboratory, we have been interested in two novel ligands:<sup>9-13</sup> 1,4,5,8,9,12-hexaazatriphenylene (=hat)<sup>14,15</sup> and 1,4,5,8-tetraazaphenanthrene (=tap).<sup>9</sup>



1,4,5,8-tetraazaphenanthrene (= tap)

The former was successfully complexed to ruthenium,<sup>16</sup> taking advantage of the three chelation sites of this ligand, so that we were able to prepare highly symmetric polymetallic complexes,  $[\text{Ru}(\text{bpy})_2]_n(\text{hat})^{2n+}$  ( $n = 1-3$ ).

The rather complicated photophysical behaviors observed with those complexes prompted us to study, as a first approach, the properties of the simpler monometallic tap complexes. We report here the results of this investigation.

### Experimental Section

The homoleptic complexes  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{Ru}(\text{tap})_3^{2+}$  were prepared according to published procedures,<sup>10,17</sup> and the heteroleptic complexes  $\text{Ru}(\text{bpy})_2(\text{tap})^{2+}$  and  $\text{Ru}(\text{bpy})(\text{tap})_2^{2+}$  were obtained by reacting 1 equiv of tap (or bpy) with 1 equiv of  $\text{Ru}(\text{bpy})_2\text{Cl}_2^{18}$  (or  $\text{Ru}(\text{tap})_2\text{Cl}_2$ ) as described by Belser et al.<sup>19</sup>

All the complexes were purified by ion exchange chromatography on Sephadex SP-C25 (eluent 0.1 M NaCl) and precipitated with a saturated aqueous solution of  $\text{KPF}_6$ . The  $\text{Ru}(\text{bpy})_n(\text{tap})_{3-n}(\text{PF}_6)$  complexes were obtained in 89, 53, 78, and 69% yields, respectively, for  $n = 0-3$ ;  $\text{Ru}(\text{bpy})_2(\text{tap})_2^{2+}$  required two purifications. Hexafluorophosphate salts of the complexes were used for all further experiments.

The  $^1\text{H}$  NMR spectra of the three tap complexes (Bruker, 250 MHz, in  $\text{CD}_3\text{CN}$ , versus TMS as an internal reference) are in full agreement

with the expected structures. Absorption spectra were recorded on a Varian Cary 219 UV-visible spectrophotometer; emission spectra were taken with a modified Applied Photophysics laser kinetic spectrometer, equipped with a Hamamatsu R928 photomultiplier tube; corrections of the emission spectra for the monochromator and the PMT response were achieved by measuring the spectrum of a standard lamp whose true emission spectrum was provided by the manufacturer (2000-W quartz-halogen lamp, Model M-217/220A from Optronics Laboratories).

Cyclic voltammetry was performed on a homemade platinum-disk electrode (approximate area  $\approx 20 \text{ mm}^2$ ) in acetonitrile; the potential of the working electrode, scanned at 200 mV/s between  $-2$  and  $+2$  V, was controlled by a homemade potentiostat versus a saturated calomel electrode (Radiometer K701) separated from the solution by a Tacussel bridge; the counter electrode was a large-area platinum grid. The supporting electrolyte was in all cases tetrabutylammonium hexafluorophosphate (Fluka puriss.).

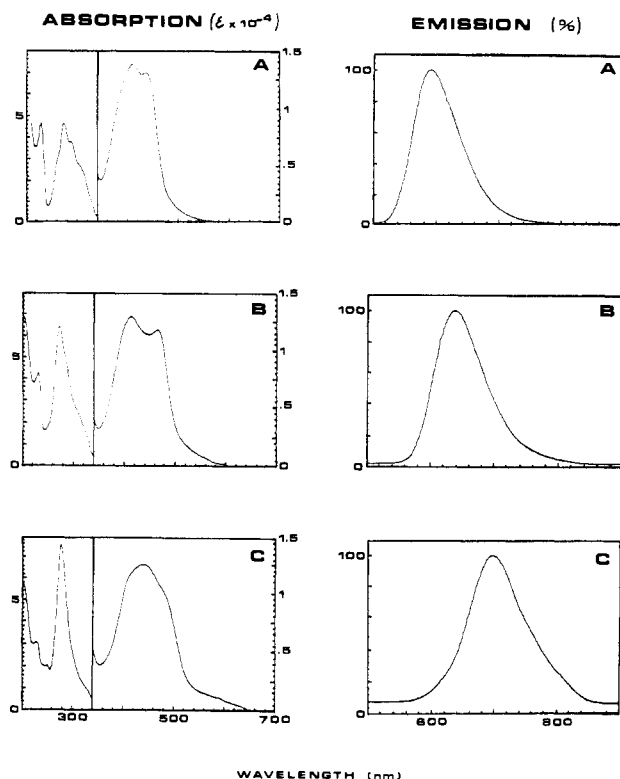
Acetonitrile (Aldrich Gold Label) was carefully distilled from  $\text{P}_2\text{O}_5$  and stored over molecular sieves. The solutions were deoxygenated by bubbling dry nitrogen for at least 20 min.

Emission lifetimes were measured in the laser kinetic spectrometer already described, by exciting the samples at 337 nm with a Moletron UV-24 (8-ns pulse width) nitrogen laser. Signals were recorded with a digital oscilloscope (HP 54200 A), connected through an IEEE 488 interface to an HP 9816 S computer, and were averaged over at least 16 shots; base-line corrections were also introduced. Kinetic analysis of the

- (1) (a) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. (b) Kalyanasundaram, K. *J. Phys. Chem.* **1986**, *90*, 2285.
- (2) Juris, A.; Barigelletti, F.; Campagna, S.; Balzani, V.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.
- (3) Cook, M. J.; Thomson, A. J. *Chem. Br.* **1984**, 914.
- (4) Cook, M. J.; Lewis, A. P.; McAuliffe, G. S. G.; Thompson, A. J.; Gasper, J. L.; Robbins, D. G. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1293.
- (5) Alford, P. C.; Cook, M. J.; Lewis, A. P.; McAuliffe, G. S. G.; Skarda, V.; Thompson, A. J.; Gasper, J. L.; Robbins, D. J. *J. Chem. Soc., Perkin Trans. 2* **1985**, 705.
- (6) Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1617.
- (7) Crutchley, R. J.; Lever, A. B. P. *J. Am. Chem. Soc.* **1980**, *102*, 7129.
- (8) Crutchley, R. J.; Lever, A. B. P. *Inorg. Chem.* **1982**, *21*, 2276.
- (9) Nasielski-Hinkens, R.; Benedek-Vamos, M. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1229.
- (10) Kirsch-De Mesmaeker, A.; Nasielski-Hinkens, R.; Maetens, D.; Pauwels, D.; Nasielski, J. *Inorg. Chem.* **1984**, *23*, 377.
- (11) Kirsch-De Mesmaeker, A.; Maetens, D.; Nasielski-Hinkens, R. *J. Electroanal. Chem. Interfacial Electrochem.* **1985**, *182*, 123.
- (12) Kirsch-De Mesmaeker, A.; Maetens, D.; Nasielski-Hinkens, R. *Acta Chim. Hung.* **1985**, *119*, 245.
- (13) Masschelein, A.; Kirsch-De Mesmaeker, A. *Nouv. J. Chim.* **1987**, *11*, 329.
- (14) Nasielski-Hinkens, R.; Benedek-Vamos, M.; Maetens, D.; Nasielski, J. *J. Organomet. Chem.* **1981**, *217*, 179.
- (15) Nasielski, J.; Verhoeven, C.; Nasielski-Hinkens, R.; Praefcke, K.; Kohne, B.; Kohlschreiber, T.; Korinath, F. *Chimia* **1987**, *41*, 343.
- (16) Masschelein, A.; Kirsch-De Mesmaeker, A.; Verhoeven, C.; Nasielski-Hinkens, R. *Inorg. Chim. Acta* **1987**, *129*, L13.
- (17) Anderson, S.; Seddon, K. R. *J. Chem. Res., Synop.* **1979**, 74.
- (18) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.
- (19) Belser, P.; von Zelewsky, A. *Helv. Chim. Acta* **1980**, *63*, 1675.

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**Figure 1.** Absorption ( $M^{-1} \text{ cm}^{-1}$ ) and emission spectra (uncorrected) of  $\text{Ru}(\text{bpy})_n(\text{tap})_{3-n}^{2+}$  in water at room temperature: (A)  $n = 0$ ; (B)  $n = 1$ ; (C)  $n = 2$ .

traces was performed by nonlinear least-squares regression,<sup>20,21</sup> modified by a Marquard's algorithm.<sup>22</sup>

An Oxford Instruments DN 1704 nitrogen cryostat was used for the emission lifetime measurements as a function of temperature.

Flash-photolysis experiments were performed by using the same excitation source as for the emission lifetime measurements and a xenon lamp (250 W) as the monitoring source. Traces were recorded and transferred through the same detection system as used for the emission lifetime measurements.

Emission quantum yields were determined by integrating the corrected emission spectra over the frequencies. The optically dilute method was used;<sup>23</sup>  $\text{Ru}(\text{bpy})_3^{2+}$  in water under air was chosen as the standard lumiphore ( $\phi = 0.028^{24}$ ).

Photoreactions were followed by monitoring the emission intensity of the complexes as a function of time under steady-state irradiation at 435 nm; concentrations of the solutions degassed by freeze-pump-thaw cycles at a residual pressure lower than  $10^{-4}$  Torr were adjusted in order to get a same absorbed light intensity at the irradiation wavelength ( $\text{OD} = 1$ ). A second PMT was used to monitor the excitation intensity variations. This method for following the photoreactions was described previously in the literature<sup>49a</sup> and is based on the observation that the Ru complexes  $\text{Ru}(\text{L})_3^{2+}$ , after loss of a polypyridine ligand L (replaced by monodentate ligands such as  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{CN}$ , or  $\text{Cl}^-$ ), do no more luminesce. Thus the quantum yields of photoreactions (or photodechelation) were determined relatively to  $\text{Ru}(\text{bpy})_3^{2+}$  ( $\phi_D = 0.029$ , in  $\text{CH}_3\text{CN}$ , 2mM in  $(n\text{-C}_4\text{H}_9)_4\text{NCl}^{49}$ ), from the slopes at the origin of the curves of emission intensity versus time, normalized to a same excitation intensity, measured with the ferrioxalate actinometer.

## Results

**Spectroscopic and Electrochemical Properties.** Absorption and emission spectra of the three complexes  $\text{Ru}(\text{bpy})_n(\text{tap})_{3-n}^{2+}$  ( $n = 0-2$ ) are presented in Figure 1; spectroscopic data are given in Table I, with those of  $\text{Ru}(\text{bpy})_3^{2+}$  for comparison. While the absorption spectra are relatively insensitive to the nature of the solvent, the emission spectra are blue-shifted in acetonitrile

**Table I.** Spectroscopic Data for  $\text{Ru}(\text{bpy})_n(\text{tap})_{3-n}^{2+}$  ( $n = 0-3$ ):  $\lambda_{\text{max}}$ , nm ( $10^{-4}\epsilon$ ,  $M^{-1} \text{ cm}^{-1}$ )<sup>a</sup>

complex	Abs/ $\text{H}_2\text{O}$	Abs/ $\text{CH}_3\text{CN}$	Em/ $\text{H}_2\text{O}$	Em/ $\text{CH}_3\text{CN}$
$\text{Ru}(\text{bpy})_3^{2+}$	285 (6.97) 424 452 (1.20)	287 424 450	617	621
$\text{Ru}(\text{bpy})_2(\text{tap})^{2+}$	278 (7.61) 439 (1.24) 484	280 428 472	714	679
$\text{Ru}(\text{bpy})(\text{tap})_2^{2+}$	273 (6.43) 412 (1.40) 465 (1.28)	274 412 463	649	641
$\text{Ru}(\text{tap})_3^{2+}$	276 (4.68) 408 (1.37) 437 (1.30)	276 408 437	602	604

<sup>a</sup> Absorption (Abs) and corrected emission (Em) ( $\pm 3$  nm). Experimental error for  $\epsilon$  values:  $\pm 3\%$ .

**Table II.** Electrochemical Data for  $\text{Ru}(\text{bpy})_n(\text{tap})_{3-n}^{2+}$  ( $n = 0-3$ )<sup>a</sup>

complex	redn				oxidn
$\text{Ru}(\text{bpy})_3^{2+}$	-1.35	-1.54	-1.79	irr	+1.28
$\text{Ru}(\text{bpy})_2(\text{tap})^{2+}$	-0.88	-1.44	-1.63	irr	irr
$\text{Ru}(\text{bpy})(\text{tap})_2^{2+}$	-0.83	-1.01	-1.56	-1.72	+1.70
$\text{Ru}(\text{tap})_3^{2+}$	-0.75	-0.88	-1.10	-1.60	-1.80

<sup>a</sup> The redox potentials ( $\pm 20$  mV) were determined by cyclic voltammetry in acetonitrile on a platinum-disk electrode, from  $-2$  to  $+2$  V at 200 mV/s. The solutions were  $10^{-3}$  M in complex and  $10^{-1}$  M in  $(n\text{-Bu})_4\text{NPF}_6$  as supporting electrolyte. Potentials are given in V/SCE;  $\Delta E_p \approx 60$  mV. irr = irreversible wave.

**Table III**

(a) Emission Lifetimes of  $\text{Ru}(\text{bpy})_n(\text{tap})_{3-n}^{2+}$  ( $n = 0-3$ )<sup>a</sup>

complex	$\tau$ , ns			EtOH/MeOH	
	$\text{H}_2\text{O}$	$\text{D}_2\text{O}$	$\text{CH}_3\text{CN}$	293 K	77 K
$\text{Ru}(\text{bpy})_3^{2+}$	630 <sup>51</sup>	1090 <sup>47</sup>	855 <sup>51</sup>	376	4720
$\text{Ru}(\text{bpy})_2(\text{tap})^{2+}$	145	361	980	529	6755
$\text{Ru}(\text{bpy})(\text{tap})_2^{2+}$	778	1672	2134	1522	9680
$\text{Ru}(\text{tap})_3^{2+}$	223	222	68	85	10490

(b) Emission ( $\phi_{\text{em}}$ ) and Dechelation ( $\phi_D$ ) Quantum Yields of  $\text{Ru}(\text{bpy})_n(\text{tap})_{3-n}^{2+}$  ( $n = 0-3$ )<sup>b</sup>

complex	$\text{H}_2\text{O}$	$\text{CH}_3\text{CN}$	
	$\phi_{\text{em}}$	$\phi_{\text{em}}$	$\phi_D$
$\text{Ru}(\text{bpy})_3^{2+}$	0.042 <sup>47</sup>	0.062 <sup>51</sup>	0.029 <sup>49b</sup> (a)
$\text{Ru}(\text{bpy})_2(\text{tap})^{2+}$	0.003	0.042	(b)
$\text{Ru}(\text{bpy})(\text{tap})_2^{2+}$	0.040	0.174	0.025 (a)
$\text{Ru}(\text{tap})_3^{2+}$	0.014	0.007	0.095 (a)

<sup>a</sup> Experimental error lower than 3%; all the solutions degassed.

<sup>b</sup> Quantum yields of emission ( $\phi_{\text{em}}$ ,<sup>47,51</sup> approximate experimental error <20%) and quantum yields of dechelation ( $\phi_D$ ,<sup>49b</sup> approximate experimental error 10%) were determined relative to  $\text{Ru}(\text{bpy})_3^{2+}$  at room temperature, for degassed solutions (see Experimental Section). Key: (a) in  $\text{CH}_3\text{CN}$ , 2 mM in  $(n\text{-C}_4\text{H}_9)_4\text{NCl}$ ; (b) too low to be measured with accuracy.

compared to water, especially for  $\text{Ru}(\text{bpy})_2(\text{tap})^{2+}$ . These behaviors are characteristic of the expected charge-transfer nature of the excited state involved in the absorption and emission process, i.e. the excited MLCT state stabilized in polar solvents.<sup>38b</sup>

Concerning the electrochemical properties, one wave, corresponding to the  $\text{Ru}^{2+}/\text{Ru}^{3+}$  couple, is recorded for the four complexes ( $n = 0-3$ ) in the available potential range ( $-2$  to  $+2$  V/SCE; see Table II).  $\Delta E_p$  is near 60 mV, and the peak currents are all of the same order of magnitude; since the oxidation of  $\text{Ru}(\text{bpy})_3^{2+}$  has been attributed to a one-electron redox process,<sup>25,26</sup> we conclude

(20) Wentworth, W. E. *J. Chem. Educ.* **1965**, *42*, 96.

(21) Wentworth, W. E. *J. Chem. Educ.* **1965**, *42*, 162.

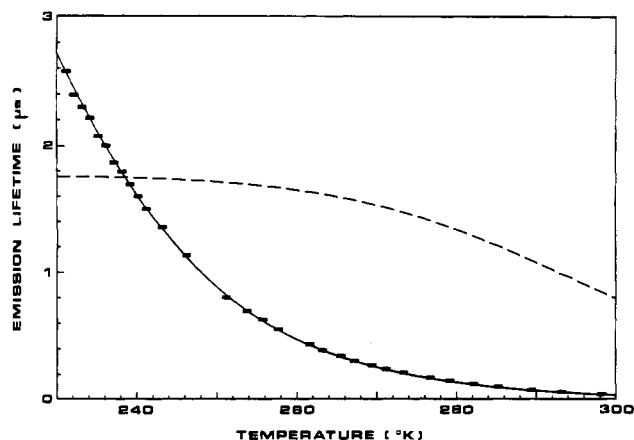
(22) Demas, J. N. *Excited State Lifetime Measurement*; Academic Press: New York, 1983.

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

(24) Nakamoru, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697.

(25) Tokel-Takvoryan, N. E.; Hemingway, R. E.; Bard, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 6582.

(26) Saiji, T.; Aoyagui, S. *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *58*, 104.



**Figure 2.** Emission lifetimes as a function of temperature for  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{Ru}(\text{tap})_3^{2+}$  ( $5 \times 10^{-5}$  M) in acetonitrile. Dashed line: curve for  $\text{Ru}(\text{bpy})_3^{2+}$  calculated with eq i and parameters of ref 51. Solid line: comparison of the temperature-dependent experimental lifetimes (experimental error bars are shown for each  $\tau$  measurement) with a computer-generated fit using eq i and the parameters ( $k'$ ,  $k^\circ$ ,  $\Delta E'$ ) in Table IV.

that the tap complexes are also reversibly oxidized and that the corresponding waves involve one electron.

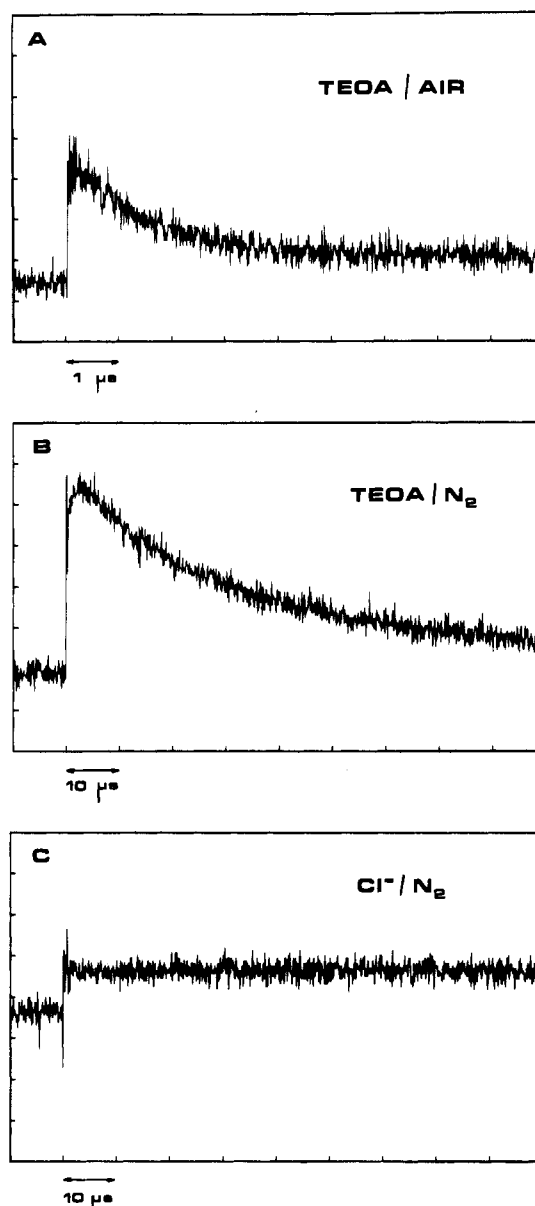
Waves corresponding to the reduction of the  $\text{Ru}^{2+}$  complexes have been characterized in the same way; the redox potentials are also given in Table II. It can be clearly seen from those data that the complexes become better oxidants when bipyridine is sequentially replaced by tetraazaphenanthrene; this is in agreement with the relative oxidizing power of the two ligands. The reduction wave intervals also follow this relative oxidizing power, as can be inferred from Table II, and are in agreement with reductions corresponding to orbitals mainly of ligand origin, as demonstrated previously for other polypyridine complexes.<sup>27-31</sup>

#### Emission Lifetimes and Quantum Yields of Luminescence.

Emission lifetimes and quantum yields of luminescence in various experimental conditions are given in Table III.

The three bipyridine-containing complexes all show longer emission lifetimes in acetonitrile than in water; this is usually explained by the fact that the OH vibrations of water play the role of energy acceptors and thus enhance radiationless decay.<sup>32</sup>

- (27) Heath, G. A.; Yellowlees, L. J.; Braterman, P. S. *J. Chem. Soc., Chem. Commun.* **1981**, 287.
- (28) Heath, G. A.; Yellowlees, L. J.; Braterman, P. S. *Chem. Phys. Lett.* **1982**, 92, 66.
- (29) Ohsawa, Y.; Hanck, K. W.; De Armond, M. K. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, 175, 229.
- (30) Tait, C. D.; Donohoe, R. J.; De Armond, M. K.; Wertz, D. W. *Inorg. Chem.* **1987**, 26, 2754.
- (31) Gex, J. N.; De Armond, M. K.; Manck, K. W. *J. Phys. Chem.* **1987**, 91, 251.
- (32) Meyer, T. J. *Pur Appl. Chem.* **1986**, 58, 1193.
- (33) Morris, D. E.; Hanck, K. W.; De Armond, M. K. *J. Am. Chem. Soc.* **1983**, 105, 3032.
- (34) Juris, A.; Belsler, P.; Barigelletti, F.; von Zelewsky, A.; Balzani, V. *Inorg. Chem.* **1986**, 25, 256.
- (35) Barigelletti, F.; Juris, A.; Balzani, V.; Belsler, P.; von Zelewsky, A. *J. Phys. Chem.* **1986**, 90, 5190.
- (36) Bryant, G. M.; Ferguson, J. E.; Powell, J. K. *J. Aust. J. Chem.* **1971**, 24, 257.
- (37) Bryant, G. M.; Ferguson, J. E. *Aust. J. Chem.* **1971**, 24, 275.
- (38) (a) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1982**, 21, 3967. (b) Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1984**, 23, 2098.
- (39) Ferguson, J.; Herren, F. *Chem. Phys.* **1983**, 76, 45.
- (40) Kirk, A. D.; Hoggard, P. E.; Porter, G. B.; Rockley, M. G.; Windsor, M. W. *Chem. Phys. Lett.* **1976**, 37, 199.
- (41) Demas, J. N.; Taylor, D. G. *Inorg. Chem.* **1979**, 18, 3177.
- (42) Lacky, D. E.; Panckuch, B. J.; Crosby, G. A. *J. Phys. Chem.* **1980**, 84, 2068.
- (43) Hager, G. D.; Crosby, G. A. *J. Am. Chem. Soc.* **1975**, 97, 7031.
- (44) Hager, G. D.; Watts, R. J.; Crosby, G. A. *J. Am. Chem. Soc.* **1975**, 97, 7037.



**Figure 3.** Flash photolysis of  $\text{Ru}(\text{tap})_3^{2+}$  ( $10^{-4}$  M) in acetonitrile monitored at 480 nm: (A) with TEOA ( $10^{-1}$  M) under air, 1  $\mu\text{s}/\text{division}$ ; (B) with TEOA ( $10^{-1}$  M) under  $\text{N}_2$ , 10  $\mu\text{s}/\text{division}$ ; (C) with  $\text{Et}_4\text{NCl}$  ( $10^{-2}$  M) under  $\text{N}_2$ , 10  $\mu\text{s}/\text{division}$ . Ordinate scales are 5 mV/division.

The importance of OH vibrations is confirmed by the solvent isotope effect when emission lifetimes that are shorter in water than in heavy water are compared.<sup>47,48</sup>

On the contrary,  $\text{Ru}(\text{tap})_3^{2+}$  is quite different from this point of view, since its emission lifetime is much shorter in acetonitrile than in water and, accordingly, there is no solvent isotope effect at all for this complex.

The quantum yields of emission (Table IIIb) follow more or less the same trends as the lifetimes in water and in acetonitrile. One could think a priori that  $\text{Ru}(\text{tap})_3^{2+}$  would be more similar to  $\text{Ru}(\text{bpz})_3^{2+}$  (bpz = 2,2'-bipyrazine) than to  $\text{Ru}(\text{bpy})_3^{2+}$ . However this is not the case; for  $\text{Ru}(\text{bpz})_3^{2+}$ , the higher quantum yield and longer lifetime of emission<sup>1b,49b</sup> are also in sharp contrast

- (45) Allsopp, S. R.; Cox, A.; Kemp, T. J.; Reed, W. J.; Carassiti, V.; Traverso, O. *J. Chem. Soc., Faraday Trans.* **1979**, 75, 353.
- (46) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1984**, 23, 3877.
- (47) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, 98, 4853.
- (48) Van Houten, J.; Watts, R. J. *Inorg. Chem.* **1978**, 17, 3381.
- (49) (a) Durham, B.; Caspar, V. J.; Nagle, J. K.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, 104, 4803. (b) Allen, G. H.; White, R. P.; Rillema, D. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1984**, 106, 2613.
- (50) Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1983**, 22, 2444.

to the low values found for  $\text{Ru}(\text{tap})_3^{2+}$ .

At low temperature (77 K), in an alcoholic mixture (EtOH–MeOH (4:1); Table IIIa),  $\text{Ru}(\text{tap})_3^{2+}$  has the longest lifetime of the series whereas, at room temperature, it is again deactivated much more rapidly than the complexes containing bipyridine. This observation prompted us to compare the temperature effect on the emission lifetimes of  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{Ru}(\text{tap})_3^{2+}$ ; Figure 2 shows the plot of the lifetime as a function of temperature for the two complexes. It is clear that a plateau value for  $\tau$  is already reached around 260 K for  $\text{Ru}(\text{bpy})_3^{2+}$  whereas, for  $\text{Ru}(\text{tap})_3^{2+}$ , the lifetime is still increasing at 230 K, the lowest temperature that can be reached before acetonitrile freezes. The two homoleptic complexes show thus quite different luminescence behaviors with temperature.

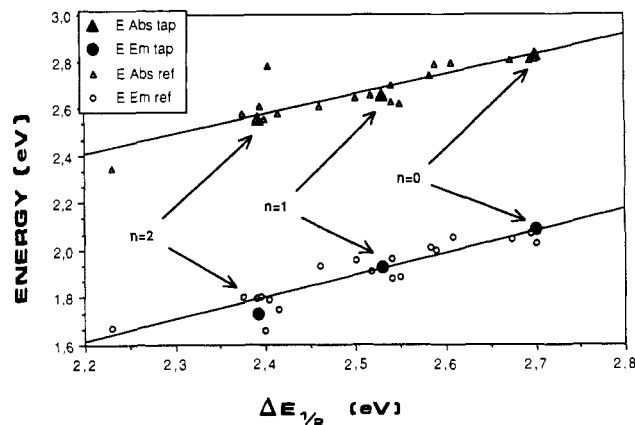
**Photoreactions in Acetonitrile.** In acetonitrile, emission of excited  $\text{Ru}(\text{tap})_3^{2+}$  is very efficiently quenched by chloride ions. Unfortunately, it is rather difficult to obtain a fully satisfactory Stern–Volmer plot because of the relatively low emission quantum yield and the short emission lifetime (68 ns; see Table IIIa) of this complex in this medium. Therefore, we obtained only an estimation of the quenching rate constant ( $2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) from the few lifetimes that we could measure. The excited heteroleptic complexes  $\text{Ru}(\text{bpy})_n(\text{tap})_{3-n}^{2+}$  ( $n = 1, 2$ ) in acetonitrile are much less sensitive, or not sensitive at all, to the addition of chloride ions ( $k_q \approx 6.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for  $n = 1$ ; unmeasurable for  $n = 2$ ).

The homoleptic excited complex  $\text{Ru}(\text{tap})_3^{2+}$  is such a strong oxidant that its reduction by  $\text{Cl}^-$  is thermodynamically possible; thus the quenching by  $\text{Cl}^-$  could stem from an electron-transfer process to the  $^3\text{MLCT}$ . In order to check this hypothesis, we have performed flash-photolysis experiments; the reduced complex  $\text{Ru}(\text{tap})_3^+$  was previously characterized by using a reversible reductive quencher<sup>13</sup> and has a maximum of absorption at 480 nm. Before examining the result of the quenching by  $\text{Cl}^-$ , we should first notice that, from the quenching of the excited complex by an irreversible reductant such as triethanolamine (TEOA), the reduced species is formed (Figure 3A,B) and can be reoxidized by oxygen; the lifetime of the transient  $\text{Ru}(\text{tap})_3^+$  is thus sensitive to the concentration of the oxidant, as shown by comparing parts A and B of Figure 3. In contrast, Figure 3C shows that the species resulting from the chloride quenching is rather stable, at least on a time scale of a few tens of a microsecond, and is insensitive to the oxygen concentration; thus this cannot be  $\text{Ru}(\text{tap})_3^+$ . The actual nature of this species is not clearly established up to now; it corresponds however to an intermediate product leading to a final compound absorbing also at 480 nm. This is concluded from the observation that the species formed in Figure 3C disappears on a longer time scale (within a few tens of a millisecond), giving rise to a permanent absorption at 480 nm.

In connection with these results from laser flash experiments, we also observed a rather high instability of  $\text{Ru}(\text{tap})_3^{2+}$  upon steady-state irradiation, when chloride ions are present in the acetonitrile solution, as compared to the other complexes of the series. This is quantitatively pointed out by comparing the quantum yields of photodechelation (or photoreaction) given in Table IIIb for the four complexes, and obtained by monitoring their normalized steady-state emission intensity as a function of time (see Experimental Section): from this comparison it is clear that  $\text{Ru}(\text{tap})_3^{2+}$  is the least stable.

That the decrease of luminescence intensity is accompanied (i) by the appearance of a new product absorbing bathochromically (480–500 nm) to the starting compound and (ii) by the release of a free tap ligand in the solution was shown previously for  $\text{Ru}(\text{tap})_3^{2+}$ ;<sup>11</sup> the photoproducted compound should thus correspond to a dechelation product and should be responsible for the permanent absorption at 480 nm observed after flash photolysis of  $\text{Ru}(\text{tap})_3^{2+}$  with  $\text{Cl}^-$ .

It is interesting at this stage to go back to the comparison with  $\text{Ru}(\text{bpz})_3^{2+}$ . Although the luminescence characteristics of  $\text{Ru}(\text{bpz})_3^{2+}$  are different from those of  $\text{Ru}(\text{tap})_3^{2+}$ , the flash-photolysis results obtained by Kalyanasundaram<sup>1b</sup> for the photoreaction of



**Figure 4.** Spectroelectrochemical correlation in absorption and emission for a series of polypyridine–ruthenium complexes taken from refs 2 and 29 and for the tap complexes  $\text{Ru}(\text{bpy})_n(\text{tap})_{3-n}^{2+}$  ( $n = 0-2$ ).  $\Delta E_{1/2}$  is the difference between the first oxidation and the first reduction potentials. Ordinates are energies corresponding to the most bathochromic visible transitions in absorption (Abs) and to the maximum of emission (Em).

$\text{Ru}(\text{bpz})_3^{2+}$  show striking similarities with those for  $\text{Ru}(\text{tap})_3^{2+}$ . However there are two major differences: (i) the absorbance that appears after the laser pulse stems from an intermediate for  $\text{Ru}(\text{tap})_3^{2+}$  and is attributed to a stable photoproduct for  $\text{Ru}(\text{bpz})_3^{2+}$ ; (ii) the quantum yield of photodechelation  $\phi_D$  (Table IIIb) is much smaller for  $\text{Ru}(\text{tap})_3^{2+}$  than for  $\text{Ru}(\text{bpz})_3^{2+}$ .<sup>49b</sup>

## Discussion

**Electrochemistry and Spectroscopy.** It has been shown for  $\text{Ru}(\text{bpy})_3^{2+}$ <sup>25,26</sup> that oxidation corresponds to removal of an electron from the  $t_{2g}$  orbital, which is essentially of metal origin, and that the reduction waves imply  $\pi^*$  orbitals belonging to the ligand network. At low temperatures, it is even possible to add reversibly up to six electrons onto  $\text{Ru}(\text{bpy})_3^{2+}$ <sup>29</sup> with two electrons localized on each bipyridine ligand.<sup>28,29,31,33</sup>

In that respect,  $\text{Ru}(\text{tap})_3^{2+}$  is similar to  $\text{Ru}(\text{bpy})_3^{2+}$ , with however a shift of its redox potentials toward more positive values, which is consistent with the relative oxidizing power of the two ligands and which allows the observation of up to five reduction waves at room temperature for the homoleptic tap complex (see Table II).

The assignment of reductions to ligand orbitals is confirmed by their sequence within the series of the bpy–tap complexes. Thus, for  $\text{Ru}(\text{bpy})_2(\text{tap})^{2+}$ , it is likely that tap is reduced first, before the bipyridines; similarly, one reduces the two tap ligands before reducing bipyridine in  $\text{Ru}(\text{bpy})(\text{tap})_2^{2+}$ .

If the orbitals involved in the electronic transitions and in electrochemistry are the same or, in other words, if the HOMO is one of the metal-centered  $d\pi$  orbitals and the LUMO is one of the ligand  $\pi^*$  orbitals, then the energy of the transition (in absorption or in emission) shall be correlated to the difference between the first reduction and the first oxidation potential. This is generally the case for most of the polypyridine–ruthenium complexes; the fact that a complex obeys the same correlation is thus good experimental evidence in favor of an MLCT electronic transition.<sup>2,29,34</sup>

In this respect, it is interesting to notice that using an isomer of tap, taphen (taphen = dipyrido[3,2-c:2',3'-e]pyridazine), described by Balzani et al.,<sup>34,35</sup> leads to problems arising from the symmetry of the orbitals involved and resulting in significant deviations from the spectroelectrochemical correlation. This could also be expected for the tap complexes, however, as shown by the spectroelectrochemical correlation in Figure 4 for the three tap complexes and for some other polypyridine–Ru complexes from the literature;<sup>2,29</sup> our complexes fit the lines for both emissions and absorptions. We can thus conclude that, contrary to taphen derivatives, the tap complexes behave normally; the visible absorption is due to MLCT transitions, and emission stems from MLCT excited states.

Table IV. Temperature Effect on Emission Lifetimes in Acetonitrile<sup>a</sup>

complex in CH <sub>3</sub> CN <sup>b</sup>	10 <sup>-4</sup> (k <sub>r</sub> + k <sub>nr</sub> ), s <sup>-1</sup>	10 <sup>-4</sup> k <sub>r</sub> , s <sup>-1</sup>	10 <sup>-4</sup> k <sub>nr</sub> , s <sup>-1</sup>	10 <sup>-4</sup> k'(298 K), s <sup>-1</sup>	10 <sup>-13</sup> k <sup>∞</sup> , s <sup>-1</sup>	ΔE', cm <sup>-1</sup>	φ <sub>dd</sub> (298 K)
Ru(bpy) <sub>3</sub> <sup>2+</sup> <sup>51</sup>	55.7	7.7	48	58	5.8	3800	0.5
Ru(tap) <sub>3</sub> <sup>2+</sup>	17.6	10.3	7.6	171	7.3	3150	0.91
Ru(tap) <sub>3</sub> <sup>2+</sup> + Cl <sup>-c</sup>	17.8			628	21	3100	0.97

<sup>a</sup> Comparison of Ru(bpy)<sub>3</sub><sup>2+</sup> and Ru(tap)<sub>3</sub><sup>2+</sup> in absence and in presence of Cl<sup>-</sup>; the values are obtained by fitting the temperature dependence of the emission lifetimes to eq i from 300 to 230 K. <sup>b</sup> Estimated errors. ΔE', ±50 cm<sup>-1</sup>; k<sub>r</sub> and k<sub>nr</sub>, ±15%; k<sup>∞</sup>, ±20%. k<sub>r</sub> has been determined from the emission quantum yield and lifetime at room temperature. <sup>c</sup> Concentration in Et<sub>4</sub>NCl = 7.5 × 10<sup>-4</sup> M; under these conditions it is not possible to determine accurately φ<sub>em</sub> because it is too low; therefore, only the sum k<sub>r</sub> + k<sub>nr</sub> is available.

**Emission Lifetimes.** The emission lifetimes of Ru(tap)<sub>3</sub><sup>2+</sup> show peculiar behaviors as compared with the other complexes of the series; we will try to explain those differences with the photophysical scheme usually accepted for the polypyridine-ruthenium complexes.

It has been shown<sup>36-41</sup> that when Ru(bpy)<sub>3</sub><sup>2+</sup> is excited in its visible absorption band, an <sup>1</sup>MLCT state is populated, which rapidly crosses over, with a quantum yield of about 1, to a manifold of emitting triplet states. Those states are so close in energy (a few tens of a reciprocal centimeter) that one has to lower the temperature to 4.2 K to distinguish them.<sup>42-46</sup> At room temperature, it is reasonable to consider only one <sup>3</sup>MLCT since the state manifold is in rapid equilibrium in this condition. This <sup>3</sup>MLCT can decay radiatively and nonradiatively; the latter process may involve in certain cases energy transfers to the solvent, with hydroxylated solvents for instance.<sup>32</sup> But one important mode of nonradiative deactivation involves another excited state, metal centered, which is believed to be responsible for ligand loss processes.<sup>32,47,48</sup>

For the heteroleptic complexes (Table III), the luminescence lifetimes and the quantum yields of emission and of dechelation show trends similar to those observed for other series of complexes.<sup>49</sup> This would suggest that their photophysical mechanisms would be comparable to those discussed previously in the literature,<sup>49b</sup> on the basis of the scheme described above.

What are the peculiarities of Ru(tap)<sub>3</sub><sup>2+</sup> as compared to the other complexes of the series? First, its emission lifetime is shorter in acetonitrile than in water, whereas all the other complexes studied here present a shorter lifetime in water, as expected from the already mentioned role of the hydroxyl functions of this solvent, and next, it shows no solvent isotope effect at all; thus, its emission lifetime seems to be controlled by a completely different mechanism.

Several other experimental data underline other peculiarities of this complex, which are helpful in order to determine the photophysical mechanism associated with this compound; only the more characteristic behavior in *acetonitrile* will be discussed in the following.

**1. Temperature Effect on Emission Lifetime.** Van Houten et al.,<sup>47,48</sup> and later Meyer et al.,<sup>32,49-51</sup> have proposed eq i for an-

$$\tau^{-1}(T) = k_r + k_{nr} + k'(T) \quad k'(T) = k^\infty \exp(-\Delta E'/RT) \quad (i)$$

alyzing the temperature dependence of the Ru(bpy)<sub>3</sub><sup>2+</sup> emission lifetime, where k<sub>r</sub> and k<sub>nr</sub> are the radiative and nonradiative decay constants of the emissive <sup>3</sup>MLCT, respectively, and where the exponential term represents a temperature-dependent intersystem crossing to the <sup>3</sup>MC excited state.

If such an analysis is applied to the data obtained with Ru(tap)<sub>3</sub><sup>2+</sup> (Figure 2), from its emission lifetime dependence with temperature, the values of k<sub>r</sub> + k<sub>nr</sub>, k<sup>∞</sup>, and ΔE' can be approximated by nonlinear least-squares adjustments<sup>20,21</sup> of the parameters of eq i to the experimental data (Table IV). Furthermore, assuming that the intersystem crossing quantum yield from the excited singlet to the <sup>3</sup>MLCT is equal to 1, k<sub>r</sub>, the radiative rate constant, can be determined from φ<sub>em</sub> and τ<sub>em</sub>; from the sum k<sub>r</sub> + k<sub>nr</sub>, the nonradiative rate constant k<sub>nr</sub> can then be obtained. The values of all these parameters are given in Table IV; it turns out that the sum k<sub>r</sub> + k<sub>nr</sub> is lower for Ru(tap)<sub>3</sub><sup>2+</sup> than for Ru(bpy)<sub>3</sub><sup>2+</sup>, which supports the idea that the short lifetime of the tap complex is mainly due to other processes than pure deactivation through vibrational cascades and emission toward

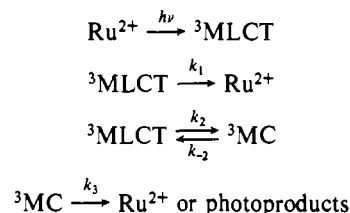
the ground state. The only possibility, if eq i is accepted as such, would be of course that k'(T) controls the emission, thus the crossing-over to the <sup>3</sup>MC. Since φ<sub>dd</sub>, defined by eq ii as the fraction

$$\phi_{dd} = \tau(T) k^\infty \exp(-\Delta E'/RT) \quad (ii)$$

of the MLCT triplets deactivating via the MC triplet, is almost the double for Ru(tap)<sub>3</sub><sup>2+</sup>, it is likely that the luminescence lifetime is indeed controlled by k'. Interestingly, from Table IV, one can also observe that it is mainly the lower energy barrier (ΔE') which enhances the crossing-over rather than the preexponential factor of the temperature-dependent term of eq i. Moreover, the fact that k<sub>nr</sub> is of the same order of magnitude as k<sub>r</sub> for Ru(tap)<sub>3</sub><sup>2+</sup>, while it is much larger than k<sub>r</sub> for Ru(bpy)<sub>3</sub><sup>2+</sup>, explains why at 77 K, when the crossing-over to the <sup>3</sup>MC is inhibited, the luminescence lifetime of Ru(tap)<sub>3</sub><sup>2+</sup> becomes longer than that of Ru(bpy)<sub>3</sub><sup>2+</sup>, whereas it is the opposite at room temperature (Table IIIa).

**2. Mechanism and Effect of Chloride Ions.** The next question that should be addressed concerns whether the crossing-over from the <sup>3</sup>MLCT toward the <sup>3</sup>MC is via an irreversible process or, on the other hand, via a rapid equilibrium between those two states.

The following mechanism can be proposed at this stage:



where k<sub>1</sub> = k<sub>r</sub> + k<sub>nr</sub> and where k<sub>3</sub> stands for a global rate constant, representing all the *leaks* from the <sup>3</sup>MC state such as the non-radiative decay to the ground state and the reactions of the <sup>3</sup>MC (with Cl<sup>-</sup> and/or CH<sub>3</sub>CN).

Assuming a steady-state concentration for the <sup>3</sup>MC, the temperature-dependent deactivation through this state is then given by

$$k'(T) = k_2 k_3 / (k_{-2} + k_3) \quad (iii)$$

Two limiting cases are to be considered: (i) k<sub>-2</sub> ≫ k<sub>3</sub> and then k'(T) ≈ k<sub>3</sub>(k<sub>2</sub>/k<sub>-2</sub>), which is the case of a rapid equilibrium between <sup>3</sup>MC and <sup>3</sup>MLCT; (ii) k<sub>-2</sub> ≪ k<sub>3</sub> and then k'(T) ≈ k<sub>2</sub>, which is the case of an irreversible crossing to <sup>3</sup>MC. It is clear that the reactions of the <sup>3</sup>MC (affecting the global constant k<sub>3</sub>) could influence the emission lifetime of the <sup>3</sup>MLCT, only through the *rapid equilibrium*.

We have seen that Cl<sup>-</sup> quenches efficiently the emission of Ru(tap)<sub>3</sub><sup>2+</sup>, giving rise to an intermediate of a few tens of a millisecond that is not Ru(tap)<sub>3</sub><sup>+</sup> but corresponds most probably to a species leading to a stable dechelation product or products. Actually, the exact nature of this species is not really relevant to our discussion, since we focus our interest on the kinetic steps preceding the formation of the dechelation product(s). Thus, on the basis of these observations in flash photolysis, it might be possible that the decrease of luminescence lifetime would stem from a decrease of the <sup>3</sup>MC lifetime due to its reaction with Cl<sup>-</sup>, affecting the global k<sub>3</sub> value and increasing the photoreaction quantum yield. This hypothesis of course would be valid only if (i) the <sup>3</sup>MC is in equilibrium with the <sup>3</sup>MLCT, as stated previously, and if (ii) the first step leading to dechelation product(s) is a bimolecular process depending on the Cl<sup>-</sup> concentration. Such

a process is probable in an organic solvent, where the chances of a static quenching of the  $^3\text{MC}$  by  $\text{Cl}^-$  within an ion pair are increased. In agreement with this is the fact that, in water, we have not observed any quenching of  $\text{Ru}(\text{tap})_3^{2+}$  by  $\text{Cl}^-$  even with concentrations as high as 1 M.

The mechanism proposed above has already been mentioned previously in the literature,<sup>49</sup> without however giving experimental evidence in its favor. In our case, the results are in agreement with the proposed equilibrium; however no definite proof has been established up to now.

**3. Combined Temperature and  $\text{Cl}^-$  Effects.** The comparison of the lifetime dependence of  $\text{Ru}(\text{tap})_3^{2+}$  on temperature, in the absence and in the presence of  $\text{Cl}^-$ , provides much more information on the system and allows us to draw more definite conclusions.

The parameters of eq i derived from these experiments are also given in Table IV; we shall examine the effect of  $\text{Cl}^-$  on each of them.

The sum of  $k_r + k_{nr}$  is not affected by  $\text{Cl}^-$ , within the experimental errors; consequently, the observed luminescence quenching by  $\text{Cl}^-$  does not stem from a quenching of the  $^3\text{MLCT}$ , for example by electron transfer, as one could think a priori. In contrast, the values of  $k'$  and  $\phi_{\text{dd}}$  are increased by  $\text{Cl}^-$ , showing thus that  $\text{Cl}^-$  plays some role in the crossing-over to the  $^3\text{MC}$ ; if we compare the  $\Delta E'$  values, it does not seem that  $\text{Cl}^-$  has an effect on the energy barrier, which remains constant, taking into account the experimental error on  $\Delta E'$ . As shown by comparing the preexponential factors values, it is clear that  $\text{Cl}^-$  increases  $k^\infty$  by a factor of 3. In the case of an irreversible process,  $k^\infty$  should be equal to the preexponential factor of the rate constant  $k_2$ , corresponding to the crossing to the  $^3\text{MC}$ ; an effect of  $\text{Cl}^-$  on this factor would be difficult to explain. On the contrary, in the case of an equilibrium,<sup>32,49-51</sup>  $k^\infty$  would then be equal to  $k_3$ , the global constant containing the different factors contributing to the decay of  $^3\text{MC}$ ; in that case, it becomes easier to explain the enhancement of the  $^3\text{MC}$  decay by  $\text{Cl}^-$ . The reaction of  $\text{Cl}^-$  with  $^3\text{MC}$  would be so rapid (static quenching) that it would shift the equilibrium toward the reacting  $^3\text{MC}$ , leading to photoproducts. At this stage, it is useless to try to correlate some rate constant of reaction deriving from  $k^\infty$  ( $k_3$ ) with the approximate quenching rate constant that we found for the luminescence quenching by  $\text{Cl}^-$  ( $2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ); indeed, if the photophysical mechanism that we propose is

correct,  $\tau_0/\tau$  versus the concentration of  $\text{Cl}^-$  does not correspond to a simple Stern-Volmer plot but to a more complicated function that we cannot test experimentally for the reasons mentioned before.

If we return to the comparison between  $\text{Ru}(\text{tap})_3^{2+}$  and  $\text{Ru}(\text{bpz})_3^{2+}$ , we may conclude the following. Taking into account the published data on  $\text{Ru}(\text{bpz})_3^{2+}$ <sup>49b</sup> and our data on  $\text{Ru}(\text{tap})_3^{2+}$ , it seems that the photophysics of  $\text{Ru}(\text{bpz})_3^{2+}$  would be intermediate between that of  $\text{Ru}(\text{tap})_3^{2+}$  and that of  $\text{Ru}(\text{bpy})_3^{2+}$ . As mentioned previously, the flash-photolysis results<sup>1b</sup> indicate some similarities between  $\text{Ru}(\text{bpz})_3^{2+}$  and  $\text{Ru}(\text{tap})_3^{2+}$ . However one cannot conclude that the photophysical mechanism is the same (equilibrium between  $^3\text{MLCT}$  and  $^3\text{MC}$ ) because the lifetime dependence on temperature has not been measured for  $\text{Ru}(\text{bpz})_3^{2+}$ . The two striking differences between the photochemistries of  $\text{Ru}(\text{bpz})_3^{2+}$  and  $\text{Ru}(\text{tap})_3^{2+}$  (lower  $\phi_D$  and intermediate photodechelation product) could easily be explained: after the first photochemical breaking of the N-Ru bond from the  $^3\text{MC}$  states of the complexes, the nitrogen of the rigid and planar tap ligand would coordinate back to the metal more easily than the nitrogen of the more flexible bpz ligand.

### Conclusion

The study presented here points out the interesting photophysical behavior of  $\text{Ru}(\text{tap})_3^{2+}$  in its  $^3\text{MLCT}$  excited state. The results suggest, more especially the dependence of the luminescence lifetime on temperature, in absence and presence of  $\text{Cl}^-$ , that the  $^3\text{MLCT}$  state is dynamically coupled to the  $^3\text{MC}$  through a rapid equilibrium, at least in acetonitrile. On the other hand, the two other members of the series of tap complexes  $\text{Ru}(\text{bpy})_n(\text{tap})_{3-n}^{2+}$  ( $n = 1, 2$ ) present properties similar to those already described for other series of heteroleptic complexes (with bpy and bipyrazine for instance<sup>49</sup>), as is evidenced from their "classical" dependence of luminescence lifetime on solvent and temperature (room temperature versus 77 K). This peculiar behavior of  $\text{Ru}(\text{tap})_3^{2+}$  makes it very sensitive to its close environment, so that this complex is an ideal probe to test different microenvironments of different polymers such as the ion exchanger Sephadex SP-C25 or Nafion membranes, which are currently under investigation.

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## Pseudopotential Investigations on the Molecules $\text{Cu}_2\text{Si}_2$ , $\text{Cu}_2\text{Sn}_2$ , $\text{Cu}_4\text{Si}_4$ , and $\text{Cu}_4\text{Sn}_4$

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Pseudopotential calculations have been performed to obtain the binding energy and the equilibrium geometry of the clusters  $\text{Cu}_2\text{X}_2$  and  $\text{Cu}_4\text{X}_4$  with  $\text{X} = \text{Si}$  and  $\text{Sn}$ . Several possible structures have been taken into account. The equilibrium structures are the butterfly arrangement for the  $\text{Cu}_2\text{X}_2$  clusters and the heterocubane arrangement for the  $\text{Cu}_4\text{X}_4$  clusters. For the latter ones a new competitive structure with copper atoms in  $\mu_2$ -bridging positions is found. The bonding situation has been analyzed by means of population analysis, internally consistent self-consistent-field energies, and localized orbitals. For simulating the lower valence of the X atoms, we have performed molecular calculations where the corresponding valence s orbitals are kept frozen. The "inert pair effect" and multicenter contributions to chemical bonding are discussed.

### Introduction

In the last three decades the interest on mixed clusters of group 11 and group 14 elements has been increasing due to their importance in areas like catalysis, crystal growth, semiconductors, and intermetallic phases.<sup>1-5</sup> Up to now the bulk of experimental data of these mixed clusters exists for the clusters containing the

heavier elements of both groups;<sup>6-10</sup> however, neither experimental nor theoretical work about their structure has been published. For

- (1) Sinfelt, J. H. *J. Catal.* **1973**, *29*, 308; *Acc. Chem. Res.* **1977**, *10*, 15.
- (2) Yacaman, M. J.; Dominguez, J. M. *J. Catal.* **1981**, *67*, 475.
- (3) Abraham, F. F. *Homogeneous Nucleation Theory*; Academic Press: New York, 1974.
- (4) Baetzold, R. C.; Mack, R. E. *J. Chem. Phys.* **1975**, *62*, 1513.
- (5) Gates, B. C.; Lieto, J. *Chem. Technol.* **1980**, *10*, 195, 248.
- (6) Gingerich, K. A.; Hague, R.; Kingcade, J. E. *Thermochim. Acta* **1978**, *30*, 61.

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