This triplet is not a minimum in the energy-geometry surface but is on a decomposition channel toward $S^{2-} + N_2$. We could locate a minimum for a singlet bent form of NNS^{2-} with an NNS angle of 120° and NN and NS distances of 1.17 and 1.72 Å, respectively. This bent NNS^{2-} conformation is some 150 kcal/mol below the symmetric bent NSN^{2-} anion described in the previous section. Nevertheless, an HFS analysis of the bonding in this bent NNS^{2-} singlet indicates an unstable species. Indeed, the atom–atom overlap populations show a strong NS antibonding interaction and little NN bonding. Further this state is crossed by the triplet decomposition channel leading to S^{2-} and N_2 mentioned above. Thus the NNS^{2-} bent form would be unstable through intersystem crossing to the unbound triplet state.

V. Conclusions

The stability of the symmetric N_2S^{2-} species relative to that of the apparently elusive symmetric N_2S reaction fragment is not too surprising. Both the NS bond and the barrier to decomposition are considerably stronger in the dianion. We find $p_{NS}(2-) = 0.47$ vs. $p_{NS} = 0.41$ and $\Delta H_{dec}(2-) = 25–30$ kcal/mol vs. $\Delta H_{dec} = 9–15$ kcal/mol. Not surprisingly, the dianion can be considered as the reduction product of N_2S. The changes in structure, such as angle opening, and orbital energies are primarily those expected on addition of two electrons to N_2S. As in the case of the isoelectronic species, ozone, the UV band at 253 nm likely corresponds to a more complex transition than just a single excitation $4a_1 \rightarrow 2b_1$.

Contrary to the case of the neutral N_2S species, which has an asymmetric linear ground state, the asymmetric form of the dianion, according to our results, is unstable toward decomposition into $S^{2-} + N_2$.

Acknowledgment. This work was supported by NSERC/Canada and CNPq/Brazil grants. M.C. is grateful for a CNPq Fellowship. We thank T. Chivers for bringing this problem to our attention.

Registry No. N_2S^{2-}, 79796-15-9.

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

Excited-State Properties of Ruthenium(II) Tris Chelate Complexes Containing the Ligands 2,2′-Bipyridine (bpy) and Dipyrido[3,2-*c*:2′,3′-*e*]pyridazine (taphen)

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The complexes $Ru(bpy)_{3-n}(taphen)_n^{2+}$ (n = 0–3, bpy = 2,2′-bipyridine, taphen = dipyrido[3,2-*c*:2′,3′-*e*]pyridazine) have been prepared, and their absorption spectra, emission spectra, emission lifetimes, luminescence quantum yields, and redox potentials have been measured. The first reduction potential of the three taphen-containing complexes is almost the same as (~ −0.72 V vs. SCE) and much less negative than that of $Ru(bpy)_3^{2+}$ (−1.35 V). The first oxidation potential increases by 0.11 V as each bpy of $Ru(bpy)_3^{2+}$ is replaced by taphen. The maximum of the metal-to-ligand charge-transfer (MLCT) absorption band of the taphen-containing complexes lies at slightly higher energy than that of $Ru(bpy)_3^{2+}$, while the emission maximum lies at lower energy. The lifetime of the emitting excited state is in the 1-μs range at 77 K and in the 0.1-μs range at room temperature, as expected for formally triplet MLCT excited states. $Ru(taphen)_3^{2+}$ does not follow the correlation observed by other RuL_3^{2+} complexes between energy of the absorption maximum and $[E_{1/2}(RuL_3^{3+/2+}) - E_{1/2}(RuL_3^{2+/+})]$, showing that different π^*(taphen) orbitals are involved in the two processes. Examination of the analogous correlation involving the emission maxima shows that the π^*(taphen) orbital involved in reduction is presumably the same as that involved in the luminescence emission. A possible explanation for this behavior lies on the inverted energy ordering of the π^* ψ and χ orbitals in taphen compared with that found for α,α'-diimines. At 77 K the excited-state lifetime of $Ru(bpy)_{3-n}(taphen)_n^{2+}$ seems to be governed by the energy gap law. The shorter lifetimes of the complexes containing taphen at room temperature should not result from deactivation via ^{3}MC since the energy gap between the luminescent ^{3}MLCT levels and the upper lying ^{3}MC level is expected to be larger than in $Ru(bpy)_3^{2+}$.

Introduction

After the discovery[2,3] of the extremely interesting photochemical and photophysical properties of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine),[4-8] a number of analogous Ru complexes have been prepared to obtain a better understanding of the metal–ligand and ligand–ligand interactions and to tune the excited-state properties in a controlled manner.[9-18] Continuing our studies in this field, we have synthetised a new family of Ru(II) complexes that contain the quite interesting taphen ligand (taphen = dipyrido[3,2-*c*:2′,3′-*e*]pyridazine, Figure 1). We report here results concerning a spectroscopic, photophysical, and electrochemical investigation of the $Ru(bpy)_{3-n}(taphen)_n^{2+}$ complexes (n = 0–3) and a comparative discussion of the observed properties.

Experimental Section

$Ru(bpy)_3^{2+}$, $Ru(bpy)_2(taphen)^{2+}$, $Ru(bpy)(taphen)_2^{2+}$, and $Ru(taphen)_3^{2+}$ as PF_6^- salts were prepared and purified by following a procedure previously described.[19] The synthesis of taphen will be reported elsewhere.[20] The solvents used were acetonitrile or ethanol–methanol

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(1) (a) Istituto Chimico "G. Ciamician". (b) Istituto FRAE-CNR. (c) University of Fribourg.

(2) Gafney, D. H.; Adamson, A. W. *J. Am. Chem. Soc.* **1972**, *94*, 8238.

(3) Crosby, G. A. *Acc. Chem. Res.* **1975**, *8*, 231.

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

(5) DeArmond, M. K.; Carlin, C. M. *Coord. Chem. Rev.* **1981**, *36*, 325.

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

(7) Balzani, V.; Bolletta, F.; Ciano, M.; Maestri, M. *J. Chem. Educ.* **1983**, *60*, 447.

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

(9) The literature in this field is very rich. Most of the previous papers are quoted in the recent references 10–18.

(10) Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1617.

(11) Crutchley, R. J.; Kress, N.; Lever, A. B. P. *J. Am. Chem. Soc.* **1983**, *105*, 1170.

(12) Kitamura, N.; Kawanishi, Y.; Tazuke, S. *Chem. Phys. Lett.* **1983**, *97*, 103.

(13) Allen, G. H.; White, R. P.; Rillema, D. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2613.

(14) Cherry, W. R.; Henderson, L. J. Jr. *Inorg. Chem.* **1984**, *23*, 983.

(15) Morris, D. E.; Ohsawa, Y.; Segers, D. P.; DeArmond, M. K.; Hanck, K. W. *Inorg. Chem.* **1984**, *23*, 3010.

(16) Ackermann, M. N.; Interrante, L. V. *Inorg. Chem.* **1984**, *23*, 3904.

(17) Juris, A.; Barigelletti, F.; Balzani, V.; Belser, P.; von Zelewsky, A. *Inorg. Chem.* **1985**, *24*, 202.

(18) Balzani, V.; Juris, A.; Barigelletti, F.; Belser, P.; von Zelewsky, A. *Riken Q.* **1984**, *78*, 78.

(19) Belser, P.; von Zelewsky, A. *Helv. Chim. Acta* **1980**, *63*, 1675.

(20) Belser, P., submitted for publication.

Table I. Spectroscopic and Electrochemical Properties of $Ru(bpy)_{3-n}(taphen)_n^{2+}$ Complexes

	absorption[a] at 293 K	emission[b] at 77 K		emission[a] at 293 K			electrochemistry[c] at 293 K	
	λ_{max} (ϵ, M^{-1} cm^{-1}), nm	λ_{max}, nm	τ,[d] μs	λ_{max}, nm	τ,[d] μs	Φ[d]	E(oxidn), V	E(redcn), V
$Ru(bpy)_3^{2+}$	452 (13 000) 290 (69 000)	582	5.0	622[e]	1.10	0.075[f]	1.26	−1.35
$Ru(bpy)_2(taphen)^{2+}$	440 (14 000) 334 (9960) 284 (60 400)	660	1.8	788[e]	0.05	0.004	1.37	−0.72
$Ru(bpy)(taphen)_2^{2+}$	438 (13 200) 334 (14 000) 276 (40 400)	650	2.0	750[e]	0.13	0.012	1.48	−0.74[g]
$Ru(taphen)_3^{2+}$	436 (15 700) 332 (20 800)	630	3.1	705[e]	0.33	0.034	1.60	−0.70[h]
bpy	284 (16 300)[i]	433[i]	10^6 [i]				...	−2.22[j]
taphen[k]	418 (195) 342 (2290) 327 (2700)	500[l]	0.023[l]	512[l]	0.017[l]		...	−1.26

[a] Acetonitrile solution. [b] In methanol–ethanol 4:1 v/v. [c] Conditions: redox potentials in acetonitrile solution vs. SCE, estimated error ±0.02 V; reversible or nearly reversible ($\Delta i_p < 80$ mV), except as otherwise noted. [d] Estimated error <10%. [e] Corrected emission spectrum. [f] Wallace, W. L., Bard, A. J. *J. Phys. Chem.* **1979**, *83*, 1350. [g] $\Delta i_p = 120$ mV. [h] $\Delta i_p = 135$ mV. [i] DeArmond, M. K.; Hillis, J. E. *J. Chem. Phys.* **1971**, *54*, 2247. [j] Reference 19. [k] The lowest energy absorption and the emission of the taphen molecule are of n → π^* origin. [l] In propionitrile–butyronitrile 4:5 v/v.

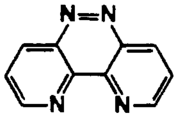

Figure 1. Structural formula of the dipyrido[3,2-*c*:2′,3′-*e*]pyridazine (taphen) ligand.

(1:4 v/v) of the best commercial grade. Absorption spectra were recorded with a Perkin-Elmer 323 spectrophotometer. The (uncorrected) emission spectra were obtained with a Perkin-Elmer 650-40 spectrofluorimeter equipped with a R928 tube. Emission lifetime measurements were carried out with a JK System 2000 neodymium YAG DLPY 4 laser or with a single photon-counting apparatus previously described.[17]

Emission quantum yields and corrected emission spectra were measured at room temperature (20 C) with the optically dilute method[21] by using a homemade spectrofluorimeter employing a S-1 response detector, which was calibrated with a standard lamp. $Ru(bpy)_3^{2+}$ in aerated aqueous solution was used as a quantum yield standard, assuming a value of 0.028.[22] The solutions of each complex were sealed under vacuum in 1-cm quartz cells after repeated freeze–pump–thaw cycles.

Electrochemical measurements were carried out by using a Metrohm E/506 Polarecord, a Metrohm E/612 VA scanner, and a Hewlett-Packard 7044A X-Y recorder. Cyclic voltammograms were obtained in acetonitrile solution 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. Scanning speed was 200 mV s^{-1}.

Results

The absorption spectra of the $Ru(bpy)_{3-n}(taphen)_n^{2+}$ complexes in acetonitrile solution at room temperature are shown in Figure 2. Figure 3 shows the emission spectra in acetonitrile at 293 K. A summary of the data concerning absorption spectra (at 293 K), emission spectra (at 77 and 293 K), emission lifetimes (at 77 and 293 K), and luminescence quantum yields (at 293 K) is given in Table I. Some relevant data concerning the free bpy and taphen ligands have also been reported in Table I for comparison purposes.

Discussion

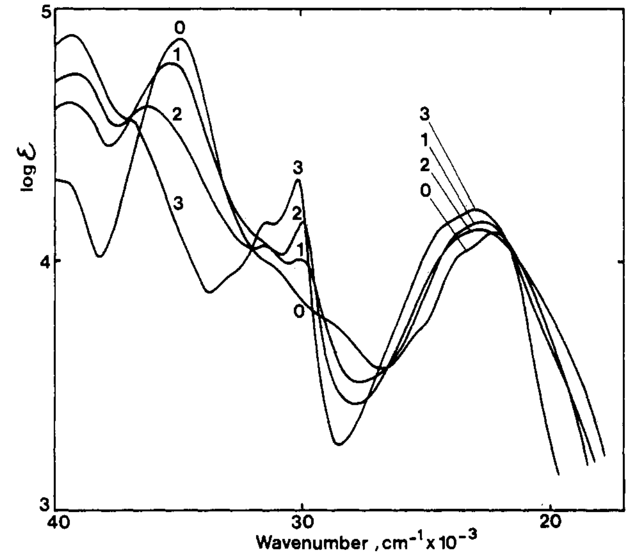

Figure 2. Absorption spectra in acetonitrile solution at room temperature. Each spectrum is identified by the *n* number of the general formula $Ru(bpy)_{3-n}(taphen)_n^{2+}$.

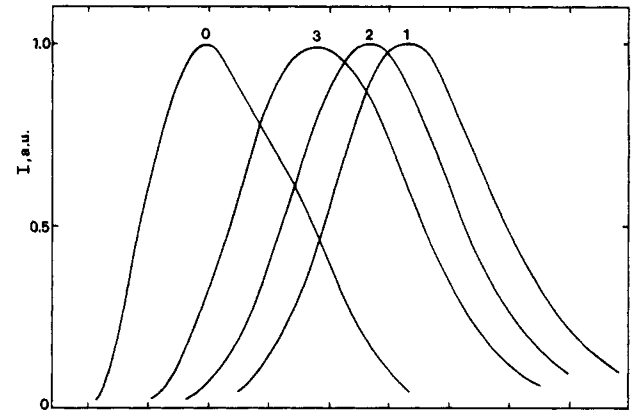

Figure 3. Corrected emission spectra in acetonitrile at 293 K. Each spectrum is identified by the *n* number of the general formula $Ru(bpy)_{3-n}(taphen)_n^{2+}$.

Electrochemical Properties. As one can see from Table I, the reduction potential of the free taphen ligand is much less negative than that of the free bpy ligand. Since the reduction of Ru(II)-polypyridine complexes involves a π^* orbital of a single aromatic ligand,[5,23–25] it is expected that the reduction potential of the complexes containing taphen is much less negative than that of $Ru(bpy)_3^{2+}$. The reduction potentials reported in Table I show that this expectation is fulfilled and that the value of the first reduction potential is almost the same for the three complexes containing taphen. This demonstrates that in the mixed-ligand

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(21) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.
(22) Nakamaru, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697.
(23) Vlcek, A. A. *Coord. Chem. Rev.* **1982**, *43*, 39.
(24) Saji, T.; Aoyagui, S. *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *58*, 401.
(25) Heath, G. A.; Yellowlees, L. J.; Braterman, P. S. *Chem. Phys. Lett.* **1982**, *92*, 646.

complexes the first reduction process involves taphen and that ligand–ligand interactions do not play an important role.

Oxidation of Ru(II)–polypyridine complexes is known to involve the $\pi(t_{2g})$ metal orbitals.[26] The values reported in Table I show that the sequential replacement of the bpy ligands of Ru(bpy)$_3^{2+}$ with taphen increases the first oxidation potential by 0.11 V. This shows that, compared to bpy, taphen lowers the energy of the $\pi(t_{2g})$ metal orbitals. Since bpy and taphen have the same pK_a value,[20] the results concerning the oxidation potentials indicate that there is a larger interaction (i.e., back-donation) between the $\pi(t_{2g})$ metal orbitals and the π^* taphen orbitals.

Absorption and Emission Spectra. The ultraviolet region of the absorption spectra (Figure 2) shows intense bands, which can be readily attributed to $\pi \rightarrow \pi^*$ ligand-localized transitions of bpy or taphen (Table I). In the visible region all the complexes exhibit a rather intense absorption, which, in the case of Ru(bpy)$_3^{2+}$, is well-known to correspond to metal-to-ligand $\pi(t_{2g}) \rightarrow \pi(\psi)$ charge transfer (MLCT) transitions.[3-6,8] Although there is no doubt that the visible absorption of the Ru(taphen)$_3^{2+}$ complex can also be attributed to MLCT transitions, we will see later that there is some problem concerning the specific assignment of the ligand orbital involved. For the mixed-ligand complexes, the visible absorption most likely results from the overlap between Ru → taphen and Ru → bpy CT transitions.

It is also well-known that the Ru(bpy)$_3^{2+}$ luminescence has MLCT orbital origin and, formally, triplet multiplicity.[3-6,8] The same assignment can be proposed for the luminescence emission of the complexes containing taphen on the following bases: (i) emission occurs at lower energy than that of Ru(bpy)$_3^{2+}$, as expected because of the less negative reduction potential of taphen; (ii) the emission lifetime and the half-width of the emission band are comparable with those of Ru(bpy)$_3^{2+}$; (iii) the LC emission of taphen occurs at much higher energy and exhibits very different lifetimes (Table I); (iv) luminescence from MC excited states would be characterized by a broader emission band and a much shorter lifetime at room temperature; (v) the energy of the emission maximum roughly parallels the oxidation potential, as expected for a MLCT emission.

Correlation between Electrochemical and Spectroscopic Quantities. DeArmond and co-workers[5,15] and others[23] have repeatedly emphasized that in the Ru(II)–polypyridine complexes the π^* ligand orbital involved in the first electrochemical reduction (redox orbital) is the same as that involved in the MLCT absorption and emission processes (spectroscopic orbital). In Ru(bpy)$_3^{2+}$ as well in most of the Ru(II)–polypyridine complexes this LUMO orbital is an antisymmetric (in C_{2v} symmetry) $\pi^*(\psi)$ orbital, as discussed by Ceulemans and Vanquickenborne[27] (vide infra). When the redox and spectroscopic orbitals are the same, a linear correlation can be expected[28-30] between the maximum of the MLCT absorption and the quantity $\Delta E_{1/2} = [E_{1/2}(\mathrm{RuL_3}^{3+/2+}) - E_{1/2}(\mathrm{RuL_3}^{2+/+})]$, which is a measure of the energy difference between the HOMO ($\pi(t_{2g})$) and LUMO (π_L^*) orbitals. As one can see from Figure 4a, such a correlation is indeed followed by several RuL$_3^{2+}$ complexes,[31] but Ru(taphen)$_3^{2+}$ is clearly an exception.[33] A similar linear correlation is also expected[10,34] between the maximum of the MLCT emission and $\Delta E_{1/2}$. Figure 4b shows that such a correlation is less strictly obeyed in general and that the point corresponding to Ru(taphen)$_3^{2+}$ is not far from the least-squares line obtained from the other available data. From the plots of Figure 4 we may thus conclude that the MLCT transition responsible for the absorption maximum of Ru(taphen)$_3^{2+}$ does *not* involve the same π^*(taphen) orbital that is responsible for the reduction process. However, the π^*(taphen) orbital involved in the MLCT emission is likely the same as that responsible for the reduction process. This anomalous behavior of Ru(taphen)$_3^{2+}$ is also reflected in the shift between absorption (at 293 K) and emission (at 77 K) maximum (~6800 cm^{-1}), which is considerably larger than that observed for Ru(bpy)$_3^{2+}$ (~5000 cm^{-1}) and other RuL$_3^{2+}$ complexes.[18] A larger shift (~7000 cm^{-1}) was previously observed for Ru(Azpy)$_3^{2+}$[35] (Azpy = 2-(phenylazo)pyridine) and attributed to the less rigid nature of the Azpy ligand compared with bpy and to a more localized nature of the π^* ligand orbital, which would cause a greater distortion along some vibrational coordinate in the excited state. However, taphen is expected to be more rigid than bpy, so that the larger shift has more likely an electronic rather than a nuclear origin.

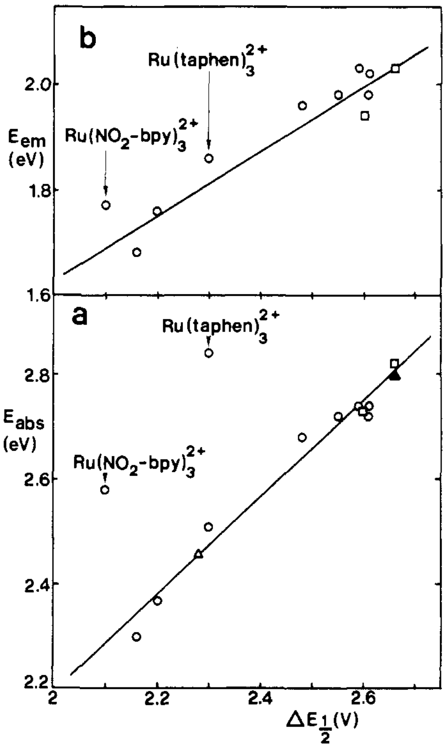

Figure 4. Correlations between the maxima of MLCT absorption (a) or emission (b) and $\Delta E_{1/2}$ for ruthenium(II) tris(polypyridine) complexes (see text). Data for acetonitrile solutions at room temperature: □, ref 10; ○, ref 18; ▲, ref 28; △, ref 32. For absorption, leaving aside Ru(taphen)$_3^{2+}$ and Ru(NO$_2$-bpy)$_3^{2+}$, the best-fitting line has a correlation coefficient of 0.99 and a slope of 0.93. For emission, the best-fitting line has a correlation coefficient of 0.90 and a slope of 0.61.

A tentative explanation for the anomalous behavior of Ru(taphen)$_3^{2+}$ may be the following. As discussed by Orgel,[36] any π or π^* ligand orbital can be classified as χ or ψ with respect to a twofold rotation axis bisecting the chelate angle. The χ orbitals are symmetric (a_2 in C_{2v} symmetry) and the ψ orbitals antisymmetric (b_1), and their overlap with t_{2g} metal orbitals of appropriate symmetry results in the CT transition. According to EH type calculations, in typical α,α'-diimine ligands the LUMO is a $\pi^*(\psi)$ orbital, which in the free 2,2′-bipyridine, 1,10-phenanthroline, and 2,2′-biquinoline ligands lies about 1.0, 0.3, and 1.1 V lower than the lowest $\pi^*(\chi)$ orbital, respectively.[37] In the free taphen ligand, however, the LUMO is a $\pi^*(\chi)$ orbital,[37] which lies about 1 eV

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

(27) Ceulemans, A.; Vanquickenborne, L. G. *J. Am. Chem. Soc.* **1981**, *103*, 2238.

(28) Lever, A. B. P.; Pickens, S. R.; Minor, P. C.; Licoccia, S.; Ramaswamy, B. S.; Magnell, K. *J. Am. Chem. Soc.* **1981**, *103*, 6800. Crutchley, R. J.; Lever, A. B. P. *Inorg. Chem.* **1982**, *21*, 2276.

(29) Dodsworth, E. S.; Lever, A. B. P. *Chem. Phys. Lett.* **1984**, *112*, 567.

(30) Curtis, J. C.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 1562.

(31) Data taken from ref 10, 18, 28, and 32 (see caption of Figure 4).

(32) Monserrat, K.; Foreman, T. K.; Graetzel, M.; Whitten, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 6667.

(33) As it appears from Figure 4, there is another complex (Ru(NO$_2$–bpy)$_3^{2+}$) showing anomalous behavior.

(34) Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 2444.

(35) Krause, R. A.; Krause, K. *Inorg. Chem.* **1982**, *21*, 1714. Wolfgang, S.; Strekas, T. C.; Gafney, H. D.; Krause, R. A.; Krause, K. *Inorg. Chem.* **1984**, *23*, 2650.

(36) Orgel, L. E. *J. Chem. Soc.*, **1961**, 3683.

(37) Daul, C., semiempirical calculations. We thank Dr. C. Daul for making available these results.

Table II. Excited-State Properties of the $Ru(bpy)_{3-n}(taphen)_n^{2+}$ Complexes

	E^{0-0},[a] eV	$^*E$(oxidn),[b] V	$^*E$(reducn),[c] V
$Ru(bpy)_3^{2+}$ [d]	2.13	-0.87	0.78
$Ru(bpy)_2(taphen)^{2+}$	1.88	-0.51	1.16
$Ru(bpy)(taphen)_2^{2+}$	1.91	-0.43	1.17
$Ru(taphen)_3^{2+}$	1.97	-0.37	1.27

[a] Emission maximum, 77 K. [b] Reduction potential of the couple $Ru^{3+}/^*Ru^{2+}$ obtained from the reduction potential of the Ru^{3+}/Ru^{2+} couple and the excited-state energy. [c] Reduction potential of the couple $^*Ru^{2+}/Ru^{+}$ obtained from the reduction potential of the Ru^{2+}/Ru^{2+} couple and the excited-state energy. [d] Data from ref 18.

below a $\pi^*(\psi)$ orbital. The orbital involved in the electrochemical reduction of $Ru(taphen)_3^{2+}$ is thus a $\pi^*(\chi)$ orbital, while the MLCT absorption maximum, as suggested by the lack of relationship between redox and absorption energies (Figure 4a), could correspond to a $\pi(t_{2g}) \rightarrow \pi^*(\psi)$ transition. The overlap between the $\pi(t_{2g})$ and $\pi^*(\psi)$ orbitals is larger than that between the $\pi(t_{2g})$ and $\pi^*(\chi)$ orbitals. As a consequence, the states derived from the $\pi(t_{2g}) \rightarrow \pi^*(\psi)$ transition are expected to exhibit higher extinction coefficients. Luminescence emission, however, could involve a substantial participation of the χ orbital.

Luminescence Lifetimes and Quantum Yields. It is well-known that the MLCT luminescence emission of Ru(II) polypyridine complexes takes place from a cluster of more or less closely spaced thermally equilibrated levels.[3,5] A detailed description of these levels is a very difficult task that can only be attempted on the basis of accurate temperature-dependence studies. Waiting for the conclusion of such a study,[38] we would only like to make here some simple considerations.

(a) At 77 K the emission lifetimes of the complexes containing taphen lie in the usual range of the MLCT luminescence of Ru(II) polypyridine complexes. It can be noted that in the $Ru(bpy)_{3-n}(taphen)_n^{2+}$ series there is a clear decrease of the emission lifetime with decreasing excited-state energy (Table I). Since the emission lifetimes in a rigid matrix at 77 K are governed by radiationless transitions[39] occurring via a weak coupling mechanism,[40] the observed trend is likely the result of the energy gap law.[41]

(b) At room temperature the lifetime of the luminescence emission of Ru(II)–polypyridine complexes is usually controlled by the upper lying ^3MC excited state, which provides the most efficient deactivation channel to the emitting ^3MLCT levels.[42] Since taphen and bpy have a similar σ-donor strength,[20] the stronger π-acceptor properties of taphen should increase the ligand field strength and thus move the ^3MC excited state toward higher energies. Coupled with the lower energy of the Ru → taphen emitting excited state, this would predict a much larger ^3MLCT–^3MC energy gap for the taphen-containing complexes compared with $Ru(bpy)_3^{2+}$. One could thus expect that at room temperature the complexes containing taphen should live longer than $Ru(bpy)_3^{2+}$. This expectation, however, is in disagreement with the observed results. An explanation for the observed behavior will be searched for in the temperature-dependence studies, which are now in progress.[38]

$Ru(bpy)_{3-n}(taphen)_n^{2+}$ Complexes as Excited-State Reactants. Recent trends in chemical research have shown that there is a growing interest in processes involving photoinduced electron- and energy-transfer processes.[6,7,43-47] Such processes are extremely important for theoretical reasons (i.e., for a development of the theory of electron-transfer reactions[48]) as well for practical applications (e.g., photochemical conversion of solar energy,[49-51] photochemical synthesis,[52] etc.). To perform systematic experiments in these fields and to optimize practical devices, one needs a series of compounds covering a broad range of excited state energies and redox potentials. From this point of view the Ru(II) complexes containing the taphen ligand are quite interesting because their excited-state properties (Table II) nicely fill some holes in the list of the previously available excited-state energies, excited-state oxidation potentials, and particularly excited-state reduction potentials.[18]

Acknowledgment. This work was supported by the Italian National Research Council, Ministero della Pubblica Istruzione, and by the Swiss National Science Foundation.

Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; $Ru(bpy)_2(taphen)^{2+}$, 98914-20-6; $Ru(bpy)(taphen)_2^{2+}$, 98914-21-7; $Ru(taphen)_3^{2+}$, 98914-22-8; $Ru(bpy)_2(taphen)^{3+}$, 98914-37-5; $Ru(bpy)_2(taphen)^{+}$, 98933-30-3; $Ru(bpy)(taphen)_2^{3+}$, 98914-38-6; $Ru(bpy)(taphen)_2^{+}$, 98933-31-4; $Ru(taphen)_3^{3+}$, 98914-39-7; $Ru(taphen)_3^{+}$, 98933-32-5.

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(38) Work in progress in our laboratories.

(39) As one can see from Table I, $k_{nr} \gg k_r$.

(40) Englman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145.

(41) Kober, E. M.; Sullivan, B. P.; Dressick, W. J.; Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 1383. Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630. Caspar, J. V.; Sullivan, B. P.; Kober, E. M.; Meyer, T. J. *Chem. Phys. Lett.* **1982**, *91*, 91.

(42) Kemp, T. J. *Prog. React. Kinet.* **1980**, *10*, 301.

(43) Balzani, V.; Scandola, F. In "Energy Resources by Photochemistry and Catalysis"; Graetzel, M., Ed.; Academic Press: London, 1983.

(44) Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275.

(45) Meyer, T. J. *Prog. Inorg. Chem.* **1983**, *11*, 94.

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

(47) Whitten, D. G. *Acc. Chem. Res.* **1980**, *13*, 83.

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

(49) Connoly, J. S., Ed. "Photochemical Conversion and Storage of Solar Energy"; Academic Press: New York, 1981.

(50) Rabani, J., Ed. "Photochemical Conversion and Storage of Solar Energy"; Weizmann Science Press of Israel: Jerusalem, Israel, 1982.

(51) Graetzel, M., Ed. "Energy Resources by Photochemistry and Catalysis"; Academic Press: London, 1983.

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