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New Complexes of Ruthenium(II) with a Tetrapyrazolic Macrocycle

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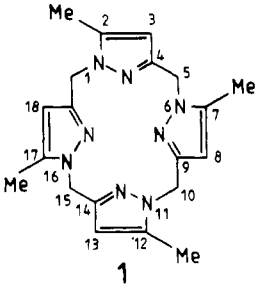
Received October 16, 1985

The preparation and properties of Ru(II) complexes $Ru(TZ)XY(PF_6)_2$ are described (TZ = 2,7,12,17-tetramethyl-1,6,11,16-tetraazaporphyrinogen; X = Me_2SO, Y = Me_2SO or pyridine; X = CH_3CN, Y = CH_3CN or pyridine; X = Y = pyridine or 4,4′-bipyridine). Thermal and photochemical labilizations of the axial ligands X and Y are studied. ^1H NMR spectroscopy allows easy complex structural characterization. Electronic spectral data and redox potential measurements are discussed.

Introduction

Ruthenium(II) complexes, mainly those with polypyridine, have been recently the subject of extensive studies due to their potential utilization as photosensitizers in energy conversion processes.[1] Comparatively, Ru(II) complexation of macrocycles has not been widely investigated with the exception of porphyrin[2-16] and phthalocyanine[9,17-20] complexes. This interest comes from the greater stability of ruthenium complexes compared to iron ones, making them easier to use in the study of hemoprotein models. Characteristics of this kind of complex are that the transition metal is inside the porphyrin or phthalocyanine cavity and that the axial ligands are thermally and photochemically labile except in the case of a carbonyl ligand. Most of the studies concern porphyrin complexes containing at least one axial carbonyl ligand mainly because they are easier to prepare, but some authors developed the synthesis of complexes with different axial ligands such as pyridine,[2,4,14,17,20] imidazole,[9] phosphine,[8,13,16,19] dimethyl sulfoxide,[17,18] and acetonitrile.[17] The other macrocyclic complex studies concern saturated tetraaza macrocycles of the cyclam family[21-23] for which stable Ru(II) complexes are rather difficult to obtain.

It seems to us of great interest to extend these investigations to other macrocycles having such properties that the Ru(II) complexes obtained would be stable and that the axial ligands would be less labile than in porphyrin ones; as a first example we chose a macrocycle with pyrazole units, the tetraazaporphyrinogen **1**[24] in which the four sp^2 nitrogen atoms and the aromatic nature



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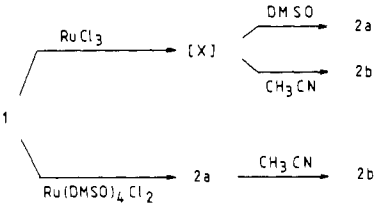
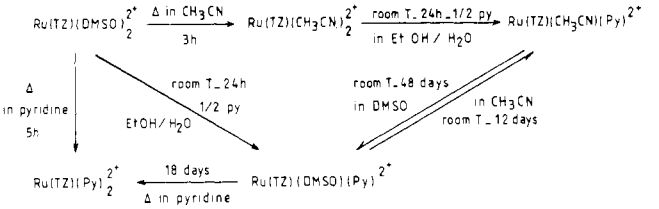
of pyrazole should stabilize Ru(II) complexes over Ru(III) ones by the occurrence of back-bonding. The cavity size of **1** is about the same as that of a porphyrin but they differ from each other by their electronic structure: **1** contains four isolated aromatic heterocycles whereas a porphyrin is an aromatic macrocycle; furthermore, macrocycle **1** must give charged Ru(II) complexes compared to the neutral porphyrin complexes described. These distinct properties should give to these two types of macrocycles different π-acceptor and σ-donor capacities, which greatly influence the axial ligand lability,[25] leading, we hoped, to a better stability of the axial ligands in the tetraazaporphyrinogen **1**.

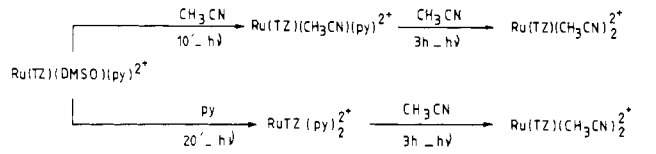
Scheme I



Scheme II



Scheme III



In the present contribution we report on the synthesis and physicochemical and photochemical studies of some Ru(II) com-

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Table I. ^{1}H NMR Data for Noncomplexed Ligands and Complexed[a] Macrocycles in CD_3CN[b]

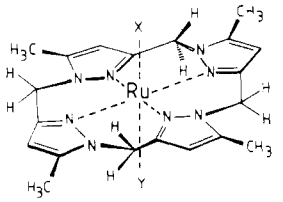
compd	δ(H) H(pyr)	CH_3(pyr)	CH_2(mac)	X[c]	Y[c]
TZ (**1**)	5.83	2.16	4.85		
py					8.50 (α), 7.06 (β), 7.48 (γ)
4,4′-bpy					8.63 (α), 7.58 (β)
$Ru(TZ)(Me_2SO)_2^{2+}$ (**2a**)	6.49 (+0.66)	2.52 (+0.36)	5.45 (+0.60)		2.42, 2.47
$Ru(TZ)(CH_3CN)_2^{2+}$ (**2b**)	6.48 (+0.65)	2.53 (+0.37)	5.34 (+0.49)		2.49
$Ru(TZ)(py)_2^{2+}$ (**2c**)	6.44 (+0.61)	2.46 (+0.30)	4.75 (−0.10)	7.45 (α) (−1.05),	6.98 (β) (−0.08), 7.60 (γ) (+0.1
$Ru(TZ)(Me_2SO)(py)^{2+}$ (**2d**)	6.49 (+0.66)	2.47 (+0.31)	4.95 (+0.10)	2.47	7.28 (α) (−1.22)
			5.50 (+0.65)[e]		7.09 (β) (+0.03)
					7.74 (γ) (+0.26)
$Ru(TZ)(CH_3CN)(py)^{2+}$ (**2e**)	6.48 (+0.65)	2.45 (+0.29)	4.81 (−0.04)	2.45	7.33 (α) (−1.17)
			5.32 (+0.47)[e]		6.95 (β) (−0.11)
					7.61 (γ) (+0.13)
$Ru(TZ)(4,4'\text{-bpy})^{2+}$ (**2f**)	6.48 (+0.65)	2.51 (+0.35)	4.85 (0.00)		7.65 (α) (−0.98)
					7.37 (β) (−0.21)
					8.72 (α′) (+0.09)[d]
					7.59 (β′) (+0.01)[d]

[a] In all cases the anion is PF_6^-. [b] Values in parentheses are the chemical shift differences between the complexed and noncomplexed ligand. [c] α, β, and γ refer to positions relative to the complexed pyridinic nitrogen atom. [d] α′ and β′ refer to positions relative to the noncomplexed nitrogen atoms. [e] J = 17.2 Hz.

plexes of the tetrapyrazolic macrocycle **1**.

Results and Discussion

Compounds Obtained. The complexes obtained are such that the Ru atom is inside the polypyrazolic macrocycle with two axial ligands on each side of the macrocyclic plane as in porphyrin complexes. Complex **2a** has been synthesized by two ways (see Scheme I): the use of $RuCl_3 \cdot 3H_2O$ leads to very impure materials **2a** or **2b**, whereas starting with $Ru(Me_2SO)_4Cl_2$ gives these two compounds very cleanly so that the first method was abandoned later on. CH_3CN and pyridine ligands have been introduced by using the Me_2SO lability in presence of these coordinating molecules (see Scheme II). If for **2a** it is easy to substitute both Me_2SO groups with pyridine molecules at the same time, it is relatively difficult to introduce the second pyridine in **2d** where one is already present.



2a, X = Y = Me_2 = SO
b, X = Y = CH_3CN
c, X = Y = py
d, X = Me_2SO, Y = py
e, X = CH_3CN, Y = py
f, X = Y = 4,4′-bpy

Photochemical Behavior. Exposure to sunlight of **2c–e** in CH_3CN shows the great photoinstability of the axial ligands: these three compounds are transformed within 3 h into complex **2b**, **2e** being an intermediate in the case of **2c** and **2d** (see Scheme III). These transformations have been followed by absorption spectroscopy (see Table II). What is remarkable is that it is easy to photosubstitute the Me_2SO ligand of **2d** by a molecule of pyridine within 20 min compared to the 18 days required at 100 °C thermally. One may notice that pyrazoles within the macrocycle encapsulating the Ru atom are photostable which is not the case in complexes as $Ru(L\text{–}L')_3^{2+}$ where L or L′ is a pyrazolic ring:[26] in that case the ligand L–L′ is photosubstituted by two molecules of solvent.

Table II. UV–Visible Absorption Spectral Data and Cyclic Voltammetry Data in CH_3CN

compd	γ_{max}, nm	ε, M^{-1} cm^{-1}	$E°$(oxidn), V vs. SCE	$E°$(redn), V vs. SCE
$Ru(TZ)(Me_2SO)_2^{2+}$ (**2a**)	196	14320	1.36	
	277.5	4680		
$Ru(TZ)(CH_3CN)_2^{2+}$ (**2b**)	197	17700	1.05	
	289.5	5140		
$Ru(TZ)(py)_2^{2+}$ (**2c**)	250.4	4230	0.81	
	314[a]	5275		
	387	4140		
$Ru(TZ)(Me_2SO)(py)^{2+}$ (**2d**)	280	5200	1.26	
$Ru(TZ)(CH_3CN)(py)^{2+}$ (**2e**)	302	3030	0.92	
	376	1060		
$Ru(TZ)(4,4'\text{-bpy})_2^{2+}$ (**2f**)	311	7380	0.84	−1.62[c]
	458[b]	8180		−1.91

[a] Solvent sensitive: $\epsilon_{387}/\epsilon_{314}$ = 0.78 in CH_3CN. In pyridine, bands are shifted to 330 and 393 nm with $\epsilon_{393}/\epsilon_{314}$ = 0.83. [b] Asymmetric absorption band. Inflection at ~515 nm. [c] Peak to peak separation 130 (first wave) and 180 mV (second wave) at 0.1 V s^{-1} scan rate.

^{1}H NMR Spectroscopy. The ^{1}H NMR data are reported in Table I. This method has been highly useful as it allowed us to identify all the complexes. Observation of the macrocyclic CH_2 protons gives the best information: In the noncomplexed macrocycle, they appear as four identical A_2 systems. When complexation with Ru(II) occurs, they are shifted strongly downfield, the shift magnitude depending on the axial ligand nature. The signal multiplicity depends on the symmetry: if the axial ligands are the same (**2a–c**, **2f**), the macrocyclic CH_2 protons give rise to four identical A_2 systems whereas in the case of different axial ligands they appear as four identical AB systems. The chemical shift of each type of proton is typical of the nature of the axial ligand placed on the same side of the macrocycle: if a methylenic proton faces a Me_2SO group, its signal is shifted downfield by +0.50 ppm compared to the free ligand; in the case of a CH_3CN ligand it is shifted by about +0.60 ppm, but if the axial ligand is a pyridine, it is displaced by −0.10 to +0.10 ppm. This last shift shows that a through-space effect occurs, due to the anisotropy of the opposite axial ligand. That the shifts observed for the

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methylenic protons are not due to electronic through-bond effects is shown by the weak effects occurring on the pyrazolic protons.

One interesting point is the spectrum observed for complex **2a** in CD_3CN: in the methyl region, besides the methyl pyrazolic protons, two other peaks are observed. It is known from several studies on $Ru(Me_2SO)_nX_{6-n}^{(n-4)+}$ that the Me_2SO ligands can be O- or S-bonded.[27] When two Me_2SO molecules are trans, one is O-bonded, the other being S-bonded. This occurs because of the different nature of O (strong σ-donor) and S (π-acceptor). In these complexes the methyl Me_2SO groups are much more shifted toward the downfield region (about 1 ppm) in the case of a S-ligation because of the proximity to the Ru complexation site. In the case of a bis(dimethyl sulfoxide)phthalocyanine complex,[17] the authors are in favor of the two Me_2SO axial ligands being S-bonded: in fact what is sure from their IR and potential measurements is that they have at least one S-bonded Me_2SO. In our case, the presence of several signals in the methyl Me_2SO region shows that we may have O- and S-bonded Me_2SO. Attempts to distinguish the two Me_2SO signals by using the faster solvent exchange rate of the possible O-bonded Me_2SO[27] were not conclusive. The upfield shift of the complexed Me_2SO methyl groups compared to that for the $Ru(DMSO)_nX_{6-n}^{(n-4)+}$ compounds may be explained by the anisotropic influence of the macrocyclic pyrazole rings (one may notice that the acetonitrile methyl groups in **2b** or **2e** are shifted downfield as they do not undergo any pyrazole effect due to their linear position with the nitrile complexing part).

As far as pyridine axial ligands are concerned, one may observe a strong upfield shift of the protons α to the complexed nitrogen. In the case of the complexes $Ru(NH_3)_5py$[28] or $Ru(py)_6$,[29] pyridyl protons α to N are upfield shifted by −0.10 ppm and −0.45 ppm respectively, whereas in our case for **2c–e** these same protons are much more shifted toward the upfield region (−1.05 to −1.22 ppm). The same kind of shift is observed for the protons α to the complexed nitrogen of the 4,4′-bipyridine complex **2f**: this can be explained by the anisotropy effect due to the four macrocyclic pyrazoles. As for the two pyridine complexes described in the literature,[28,29] γ pyridyl protons are downfield shifted and the shift value depends on the nature of the trans ligand.

UV–Visible Absorption. In Table II are given values corresponding to absorption spectra of **2a–f**. The absorption coefficients of the transitions of lowest energy are in the range 1000–8000 M^{-1} cm^{-1}. This shows that these transitions are mostly of MLCT character. There is sometimes, as in **2e**, a second transition, which is probably of the same nature, whereas transitions in the 200-nm region are mostly $\pi^*-\pi$ in character. The MLCT character of the low-lying transitions can also be seen from their sensitivity to the nature of the solvent (see **2c** in Table II). It can be noticed that substitution of Me_2SO by one CH_3CN has almost the same effect as substitution by one pyridine, as far as wavelengths are concerned. No emission, whether at room temperature or liquid-nitrogen temperature could be detected for any of these compounds.

Electrochemistry. The results of the voltammetric experiments at moderate sweep rate (0.1–1 V s^{-1}) are summarized in Table II. Between 0.8 and 1.4 V each compound features a reversible wave corresponding to a one-electron oxidation of Ru(II). This wave is reversible and shows a peak to peak separation that does not exceed 70 mV at 0.1 V s^{-1} scan rate. For the symmetrical complexes the potentials are more positive with Me_2SO (**2a**) and CH_3CN (**2b**) than with pyridines (**2c**, **2f**) as axial ligands. This is explained by the fact that better σ-donor groups like pyridines stabilize Ru(III), thus giving rise to less positive potentials of the $Ru^{II/III}$ couple.[30–32] Ru(II) on the other hand is stabilized by π-back-bonding to π-acceptor ligands like CH_3CN;[30] for instance, substitution of one bipyridine by two CH_3CN in $Ru(bpy)_3^{2+}$ leads to an increase in potential from 1.27 to 1.44 V.[33] A similar difference is observed between **2c** and **2b** (Table II). For Me_2SO, which can act either as a σ-donor (coordinating via oxygen) or as a π-acceptor (via sulfur) (see discussion in the NMR spectroscopy part) the highest potential is found (Table II). This suggests that at least one of the axial Me_2SO ligand in **2a** is S-coordinated;[34] this conclusion is in agreement with the ^1H NMR results. With two different axial ligands (**2d**, **2e**) the potentials are intermediate of those of the corresponding symmetrical complexes. Similar results have been obtained in the Ru(II)–bipyridine system.[33] Interesting is the fact that upon substitution of one Me_2SO by a pyridine in **2a**, only a small decrease of the potential is observed. This suggests that only one Me_2SO is S-coordinated in **2a**, whereas the other is O-coordinated. Substituting the latter by the weakest π-acceptor pyridine leads to a decrease of the potential, accordingly. Since the oxidation potentials can be easily understood in terms of the σ-donor and π-acceptor properties of the ligands, additional minor waves could be identified; for example, with compound **2e**, we have measured the oxidation potential on a very impure sample, still containing a great amount of **2d**, and we have observed two unambiguously assigned waves at 0.92 V for **2e** and at 1.26 V for **2d**. In reduction no wave is observed above −2 V/SCE except for compound **2f**, which shows two rather broad waves (Table II); these can be assigned to stepwise one electron reductions of the 4,4′-bipyridine ligands. This is in accordance with the case of $Ru(2,2'\text{-bpy})_3^{2+}$, which shows these successive ligand waves.[30] Unlike 2,2′-bipyridine, 4,4′-bipyridine acts only as a monodentate ligand and its π-system is less influenced by Ru(II); this is reflected by the fact that **2f** is reduced at more negative potentials than $Ru(2,2'\text{-bpy})_3^{2+}$.

Experimental Section

Measurements. The ^1H NMR spectra were obtained with a Varian EM 390 spectrometer using Me_4Si as internal reference; chemical shifts are given in ppm and coupling constants in Hz.

UV–visible absorption spectra were recorded on a Varian Superscan III or a SP8-400 Unicam spectrophotometer using standard 10-mm or 1-mm quartz cuvettes. The cell compartment temperature was kept at 22 °C.

Luminescence spectra were obtained on a spectrofluorimeter built in the laboratory around two Instrument SA John Yvon M25 monochromators and selected low-noise RCA IP21 or Hamamatsu R928 photomultipliers. This system uses a phase-sensitive detection in a ratio recording mode (for a full description see ref 26).

Cyclic voltammograms were recorded from 2 mM solutions of the complexes in acetonitrile (I = 0.1 M; Et_4NClO_4) at 18 °C under N_2 in the dark. Experimental details are given elsewhere.[35] A standard three-electrode setup was used; the working electrode was a glassy-carbon disk (o.d. = 3 mm) from IMC Industry Group, grade GCA Potentials are given relative to the saturated calomel electrode (SCE). Values of the standard potential (E_0) were obtained from the midpoint between anodic and cathodic peak potentials.

Photolysis procedures were as follows: For irradiations carried in the sunlight, a 2-cm water filter was used. For irradiations carried on the optical bench, a 250-W quartz–tungsten lamp built into a parabola was used. Aside from a collimating lens, a running water filter (4 cm thick) and cutoff filters (Corning glass) were inserted in the optical path.

Materials. The macrocycle **1** has been prepared as reported earlier.[24] $RuCl_3 \cdot 3H_2O$ was obtained from Aldrich or Strem Chemicals. $Ru(Me_2SO)_4Cl_2$ was used as purchased from Strem Chemicals or prepared

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(34) In both **2a** and **2d** an additional wave is observed if the potential is set at the position of the oxidation wave, at 0.14 (**2a**) and 0.63 V (**2d**), respectively. Most likely the Me_2SO ligands are oxidized to yield a ligand which—on the basis of $E_{1/2}$—is a strong σ-donor.
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by following the method of Evans and co-workers.[27a] All compounds have been characterized by analyses and NMR spectroscopy.

Ru(TZ)(Me$_2$SO)$_2$(PF$_6$)$_2$ (2a). Ru(Me$_2$SO)$_4$Cl$_2$ (10^{-3} mol, 485 mg) and the macrocycle TZ (**1**) (10^{-3} mol, 376 mg) are heated at reflux for 3 h in 100 mL of a mixture of EtOH/H$_2$O, 75/25. Most of the EtOH is evaporated; the complex is precipitated as the hexafluorophosphate by a dropwise addition of a concentrated NH_4PF_6 aqueous solution. The precipitate is filtered, washed, and dried to give a yellow powder. Yield: 90%.

Ru(TZ)(CH$_3$CN)$_2$(PF$_6$)$_2$ (2b). This complex is obtained by refluxing complex **2a** for 3 h in CH_3CN. Yield: 100%. Anal. ($C_{24}H_{30}N_{10}RuP_2F_{12}$) C, H, N.

Ru(TZ)(py)$_2$(PF$_6$)$_2$ (2c). This complex may be obtained by two methods, the first one being cleaner.[36]

$Ru(Me_2SO)_4Cl_2$ (145 mg) and the macrocycle TZ (**1**) (113 mg) are refluxed for 3 h in 12 mL of a mixture of EtOH/H$_2$O, 75/25. Part of the solvent is evaporated; then the residue is heated at reflux for 5 h with 0.1 mL of pyridine. The solvent is evaporated to dryness, the solution obtained by addition of 14 mL of H$_2$O is filtered, an aqueous concentrated NH_4PF_6 solution is added to the filtrate, and the precipitate formed is filtered and washed three times with H$_2$O, twice with EtOH, and once with ether. Yield: 83%. Anal. ($C_{30}H_{34}N_{10}RuP_2F_{12}$) C, H, N.

$RuCl_3 \cdot 3H_2O$ (157 mg) and the macrocycle TZ (226 mg) are refluxed in 24 mL of H$_2$O for 4 h. After the addition of 2.4 mL of an aqueous Na_3PO_2 solution, the mixture is heated again at reflux for another 2 h. The solution is filtered on Celite, then 0.1 mL of pyridine is added, and the mixture is refluxed for 5 h. After evaporation to dryness, 2.8 mL of H$_2$O are added and the solution filtered, a NH_4PF_6 solution is added to the filtrate, and the precipitate obtained is filtered, washed with H$_2$O, and dried. Yield: 70%.

Ru(TZ)(Me$_2$SO)(py)(PF$_6$)$_2$ (2d). Ru(TZ)(Me$_2$SO)$_2$Cl$_2$ (352 mg) and pyridine (20 mg) are left at room temperature in 20 mL of a mixture of EtOH/H$_2$O, 75/25. The solvent is evaporated, 15 mL of H$_2$O are added, and the complex as the hexafluorophosphate is precipitated by an aqueous concentrated NH_4PF_6 solution. The precipitate is filtered and washed with H$_2$O. Yield: 90%. Anal. ($C_{27}H_{35}N_9OSRuP_2F_{12}$) C, H, N.

Ru(TZ)(CH$_3$CN)(py)(PF$_6$)$_2$ (2e). This complex is obtained by heating at reflux for 3 h the complex **2d** in CH_3CN. Yield: 100%. Anal. ($C_{27}H_{12}N_{10}RuP_2F_{12}$) C, H, N.

Ru(TZ)(4,4'-bpy)$_2$(PF$_6$)$_2$ (2f). Ru(Me$_2$SO)$_4$Cl$_2$ (145 mg) and the macrocycle TZ (113 mg) are heated at reflux for 3 h in a mixture of EtOH/H$_2$O, 75/25 (12 mL). Then a large excess of 4,4'-bipyridine (20 times) is added and the solution is refluxed for 6 h. The complex is precipitated as the hexafluorophosphate by a concentrated NH_4PF_6 aqueous solution. The precipitate dissolved in a minimum of DMF is loaded on a Sephadex LH 20 column and eluted with DMF. After evaporation of the solvent, the red complex **2f**[37] is obtained with a yield of 90%.

Registry No. **2a**, 101165-12-2; **2b**, 101165-14-4; **2c**, 101165-16-6; **2d**, 101165-18-8; **2e**, 101165-20-2; **2f**, 101165-22-4; Ru(Me$_2$SO)$_4$Cl$_2$, 89395-66-4.

(36) Complex **2c** may be also obtained directly from **2a** as PF_6^- salt by heating it in pyridine for 5 h.

(37) Complex **2f** has not been obtained analytically pure because of the presence of small quantities of polymeric impurities impossible to separate.

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New Ligand-Bridged Polyruthenium(II) Complexes with Cofacial Tetrapyrazolic Macrocycles

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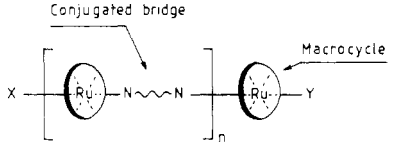
Received October 16, 1985

Three binuclear Ru(II) bimacrocyclic cofacial complexes X(TZ)Ru(bpy)Ru(TZ)X(PF$_6$)$_4$ (TZ = 2,7,12,17-tetramethyl-1,6,11,16-tetraazaporphyrinogen; X = Me$_2$SO, CH$_3$CN, or pyridine; bpy = 4,4'-bipyridine) and two tetranuclear tetramacrocyclic homologues have been prepared in order to study their capacities as electron carriers. ^{1}H NMR data and redox potential measurements show that no interaction occurs between the metal centers under these experimental conditions. The insertion in bilayer lipid membranes gives rise to stationary photocurrents of small amplitude.

Introduction

Lately the chemistry of biruthenium complexes has been widely investigated, especially with the aim to study the behavior of their mixed-valence species.[1-4] Most of the work has been based on complexes made of "Ru(NH$_3$)$_5^{2+}$" and "Ru(bpy)$_2^{2+}$" units linked by various bridging groups such as pyrazine, 4,4'-bipyridine, or cyano derivatives; the best example is the now well-known Creutz-Taube ion, the behavior of which is still the subject of controversy.[5-8] But few studies have been devoted to polymetallic complexes containing more than two ruthenium atoms.[9,10]

Our aim was to prepare a new series of polynuclear ruthenium(II) complexes such that one could expect an electron-transfer directionality through a known number of Ru atoms as represented in



Such an arrangement has been described in long polymeric phthalocyanine, porphyrin, and hemiporphyrazine systems with

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0020-1669/86/1325-1778$01.50/0