the short-lived MLCT emission. Similar results were obtained for the other two complexes.

Figure 5 further supports this picture. The $\langle\tau_M\rangle$'s increase monotonically with increasing acidity and on going from bpy to phen to Me$_2$phen. In addition, the $\langle\tau_M\rangle$'s increase when the monitoring wavelength is changed from the peak of the MLCT emission to the wavelength of the ligand emission. The purest ligand emission is from (Me$_2$phen)Re(CO)$_3$CN where the 800-μs lifetime approaches that of organic phosphorescences. The shorter $\langle\tau_M\rangle$'s for (bpy)Re(CO)$_3$CN and (phen)Re(CO)$_3$CN arise from the greater MLCT emission contribution to the total emission.

Site Heterogeneity. Our lifetime results clearly show that the simple two-component model of Scheme I is an over simplification at 77 K. Such a model requires only two lifetimes; however, at least three and sometimes four components are required to provide satisfactory fits. Even the single component systems of (phen)Re(CO)$_3$CN and (Me$_2$phen)Re(CO)$_3$CN in methanol–water glasses require two lifetimes for the fit. Further, the $R(\lambda)$'s for all complexes are not flat at 0 N acid, indicating ground-state heterogeneity.

The most probable explanation is environmental site heterogeneity. In the rigid glasses, the polar molecules examined here can probably exist in different environments; due to the sensitivity of MLCT emissions to environmental effects, several lifetimes or a range of lifetimes can exist. This gives rise to our complex decay kinetics. For this reason, one should not make too much of our lifetimes and preexponential factors. Our fitting procedure represents this range or distribution of lifetimes as a discrete three-component fit. While the long and short lifetime contributions probably give reasonable estimates of the wings or limit contributions, the intermediate lifetime is probably an adjustable parameter that gives some average over the range and amplitude of lifetimes actually present.

Low-energy excitation favors MLCT emission regardless of ligand or acidity. In Figure 6, the increase in $R(\lambda)$ at long excitation wavelengths demonstrates increased CT emission. We attribute this to photoselection of sites that have the lowest MLCT states in the molecule, which then give predominantly, or exclusively, MLCT emissions.

Conclusion

As with previously studied Re(I) sensitizers, complexes of the form LRe(CO)$_3$CN [L = Me$_2$phen, phen, bpy] investigated in this study were found to exhibit MLCT and π–π* transitions in their absorption and emission spectra. Excited-state acid–base studies of these compounds in highly acidic methanol/sulfuric acid media indicate that protonation of the cyanide ligand is taking place. Further, our results indicate that spectra and lifetime changes are principally due to protonation of the CN and that ordinary solvatochromism plays at best a minor role. At room temperature, emissions from only MLCT transitions (associated with the unprotonated species of each complex) were observed except under the most acidic conditions; this indicates that the complexes are stronger acids in the excited state than in the ground state. At low temperature (77 K), emissions from both the unprotonated and protonated species were observed, as indicated by $^3(\pi-\pi^*)$ vibrational structure in the emission spectra and multicomponent fits of the luminescence decay curves. The low-temperature emission data also suggest that the degree of protonation is increasingly advanced on going from (bpy)Re(CO)$_3$CN to (phen)Re(CO)$_3$CN to (Me$_2$phen)Re(CO)$_3$CN.

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Hexanuclear Homo- and Heterobridged Ruthenium(II) Polypyridine Complexes: Syntheses, Absorption Spectra, Luminescence Properties, and Electrochemical Behavior

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By use of the "complexes as ligands" strategy, the trinuclear complexes {Ru[(BL$_a$)Ru(bpy)$_2$]$_2$Cl$_2$}(PF$_6$)$_4$ (**5**, BL$_a$ = 2,3-dpp; **6**, BL$_a$ = 2,5-dpp) have been synthesized from the reaction of RuCl$_3$·3H$_2$O with [Ru(bpy)$_2$(2,3-dpp)](PF$_6$)$_2$ and [Ru(bpy)$_2$(2,5-dpp)](PF$_6$)$_2$, respectively (bpy = 2,2'-bipyridine; dpp = bis(2-pyridyl)pyrazine). Reaction of two units of **5** or **6** with the 2,3-dpp or 2,5-dpp bridging ligands has led to the formation of four hexanuclear complexes (**1**–**4**) of general formula {[(bpy)$_2$Ru(BL$_a$)]$_2$Ru(BL$_b$)Ru[(BL$_a$)Ru(bpy)$_2$]$_2$}(PF$_6$)$_{12}$, where BL$_a$ = BL$_b$ = 2,3-dpp (**1**), BL$_a$ = BL$_b$ = 2,5-dpp (**2**), BL$_a$ = 2,3-dpp and BL$_b$ = 2,5-dpp (**3**), and BL$_a$ = 2,5-dpp and BL$_b$ = 2,3-dpp (**4**). Such hexanuclear compounds exhibit extremely intense absorption bands in the UV region (λ_{max} = 283 nm, ϵ_{max} of the order of 2 × 10^5 M^{-1} cm^{-1}), which can be assigned to ligand-centered transitions, and intense bands in the visible region (λ_{max} between 540 and 582 nm, ϵ_{max} of the order of 5 × 10^4 M^{-1} cm^{-1}), which can be assigned to metal-to-ligand charge-transfer transitions. Complexes **1**–**4** are luminescent both in rigid matrix at 77 K and in fluid solution at 298 K. Luminescence originates from the lowest (formally triplet) metal-to-ligand charge-transfer excited state. The emission spectra and lifetimes are approximately the same for **1** and **3** and for **2** and **4**. For **1** and **3** emission occurs at higher energies and exhibits a longer lifetime compared to **2** and **4** (770 vs 810 nm and 54 vs 42 ns, in acetonitrile solution at 298 K). These results, as well as a comparison with the behavior of analogous di- and trinuclear compounds, indicate that in all cases luminescence takes place from the peripheral (bpy)$_2$Ru(BL$_a$)$^{2+}$ chromophoric units. Corrected excitation spectra have shown that energy transfer from the central chromophoric units to the peripheral ones takes place with ~100% efficiency. In electrochemical experiments, the four peripheral metal ions are oxidized at about the same potential (~+1.4 V, vs SCE), whereas oxidation of the two inner metal ions cannot be observed in the potential window examined (<+2.0 V). Several reduction overlapping waves are present beginning at about −0.5 V.

Introduction

There is an increasing interest in luminescent and redox-reactive polynuclear metal complexes[2-4] because of their relevance for the design of photochemical molecular devices.[4-7] In several cases polynuclear complexes may be considered as supramolecular

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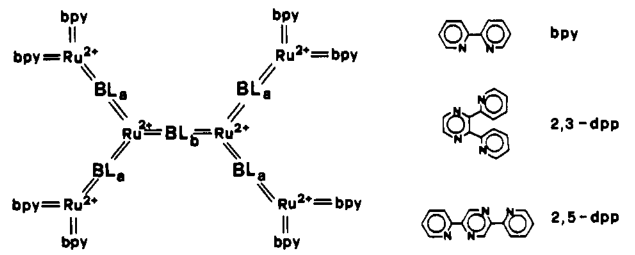

1 $BL_a = BL_b = 2,3\text{-dpp}$
2 $BL_a = BL_b = 2,5\text{-dpp}$
3 $BL_a = 2,3\text{-dpp}; BL_b = 2,5\text{-dpp}$
4 $BL_a = 2,5\text{-dpp}; BL_b = 2,3\text{-dpp}$

Figure 1. Structures of 2,2′-bipyridine (bpy) and of the bridging ligands (BL) 2,3-bis(2-pyridyl)pyrazine (2,3-dpp) and 2,5-bis(2-pyridyl)pyrazine (2,5-dpp) and schematic representation of the hexanuclear complexes **1**–**4**.

species made of metal-containing units.[4] An important family of such complexes is that based on the Ru^{2+} and Os^{2+} metal ions, the 2,3- and 2,5-isomers of bis(2-pyridyl)pyrazine (2,3-dpp and 2,5-dpp, Figure 1) as bridging ligands (BL), and bipyridine-type compounds (e.g., 2,2′-bipyridine, bpy, Figure 1) as terminal ligands.[8-20] A number of dinuclear complexes have been prepared in the past few years by using such metals and ligands.[3] More recently, much effort has been devoted to the synthesis of complexes of higher nuclearity. Several trinuclear[15,19,20] and tetranuclear[11,14,19-21] luminescent complexes have been prepared, and a heptanuclear[18] luminescent complex has also been obtained.

While complexes of high nuclearity are interesting per se, an important aim of our research is to obtain supramolecular species where photoinduced energy migration (or charge separation) takes place in the desired direction.[21,22] This requires (i) knowledge of the properties (absorption spectra, redox potentials, excited-state energy, etc.) of the various components (i.e., of each metal-containing unit $M(BL)_n(L)_{3-n}{}^{2+}$, $n = 1-3$, which is present in the supramolecular species), (ii) knowledge of the extent to which the properties of each component are affected by the order components, and (iii) the availability of synthetic strategies for the preparation of polynuclear compounds where different units (i.e., components that differ in M, BL, and/or L) can be located in specific sites of the supramolecular structure.[21,23] The properties of the various $M(BL)_n(L)_{3-n}{}^{2+}$ units are reasonably well-known,[19,24-26] and several pieces of information are now available concerning intercomponent interactions.[3,4,9-20] Much less is known concerning synthetic procedures to assemble a large number of components in ordered supramolecular arrays.

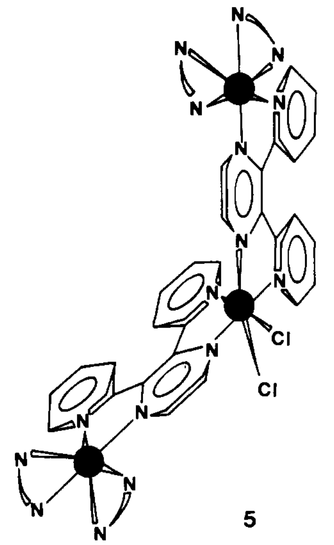

Figure 2. Schematic view of the trinuclear complex **5**.[27] N-N represents bpy.

In previous papers[15,18-21] we have shown that a quite useful approach to obtain polynuclear compounds of the above family is the so-called "complexes as ligands" strategy, which is also used in other fields of inorganic synthesis. According to this strategy, species of high nuclearity can be obtained from building blocks constituted of complexes of lower nuclearity that contain an unsaturated coordination site. For example, the tetranuclear complex $Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)(2,3\text{-dpp})]_3{}^{8+}$ was prepared by treating $RuCl_3$ with three $Ru(2,3\text{-dpp})_2(bpy)^{2+}$ "ligands",[18] and decanuclear complexes have also been obtained.[23] Another strategy involves the use of building blocks constituted by complexes that contain easily replaceable ligands.[18,23] The two strategies described above, in fact, are complementary and can be either coupled or used in subsequent steps to build up compounds of high nuclearity.

Following these guidelines, we have first used the complexes as ligands strategy to prepare the trinuclear compounds $\{Ru[(BL_a)Ru(bpy)_2]_2Cl_2\}(PF_6)_4$ (**5**, BL_a = 2,3-dpp, Figure 2; **6**, BL_a = 2,5-dpp) from the reaction of $RuCl_3{\cdot}3H_2O$ with $[Ru(bpy)_2(2,3\text{-dpp})](PF_6)_2$ and $[Ru(bpy)_2(2,5\text{-dpp})](PF_6)_2$, respectively. Then we have used **5** and **6**, which contain two labile Cl^- ligands, to obtain the hexanuclear complexes **1**–**4** (Figure 1) of general formula $\{[(bpy)_2Ru(BL_a)]_2Ru(BL_b)Ru[(BL_a)Ru(bpy)_2]_2\}(PF_6)_{12}$, where $BL_a = BL_b$ = 2,3-dpp (**1**), $BL_a = BL_b$ = 2,5-dpp (**2**), BL_a = 2,3-dpp and BL_b = 2,5-dpp (**3**) and BL_a = 2,5-dpp and BL_b

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Table I. Colors, Yields, Analytical Data, Selected IR Absorption Maxima, and Conductivity Values of the Novel Complexes

			elemental anal.,[b] %				
no.	color	yield[a]	C	H	N	IR data[c]	Λ[d]
1[e]	cyclamen	70	36.39 (36.54)	2.49 (2.66)	10.48 (10.22)	1601 (m), 1555 (w, br), 1467 (s), 1448 (s), 1416 (s), 1394 (s)	643.3
2[e]	deep green	70	36.37 (36.54)	2.44 (2.66)	10.44 (10.22)	1602 (m), 1555 (w, br), 1462 (s), 1448 (s), 1428 (m, sh)	649.7
3[f]	purple	70	36.80 (36.95)	2.58 (2.60)	10.43 (10.34)	1602 (m), 1555 (w, br), 1469 (s), 1449 (s), 1420 (s), 1397 (m)	658.2
4[e]	deep green	70	36.53 (36.54)	2.47 (2.66)	10.60 (10.22)	1602 (m), 1556 (w, br), 1462 (s), 1448 (s), 1424 (w), 1385 (w)	604.4
5[g]	green	80	38.86 (38.86)	2.71 (2.49)	10.56 (10.66)	1607 (m), 1559 (w, br), 1470 (s), 1450 (s), 1423 (s), 1393 (s)	316.4
6[g]	deep green	84	38.85 (38.86)	2.66 (2.49)	10.58 (10.66)	1603 (m), 1560 (w, br), 1460 (s), 1445 (s), 1425 (m), 1400 (w, br)	310.0

[a] %, after purification. [b] Found (calcd). [c] cm^{-1} in KBr pellets. [d] Ω^{-1} cm^2 mol^{-1}. Approximately 5×10^{-3} M solutions in nitromethane. [e] Formulated with 9 mol of H_2O. [f] Formulated with 6 mol of H_2O. [g] Formulated with 3 mol of H_2O.

Table II. Absorption, Luminescence, and Electrochemical Data[a]

	absorption[b] 298 K		luminescence[c] 298 K		luminescence[c] 77 K		electrochemistry[d] 298 K	
complex	λ_{max}, nm	ϵ, 10^3 M^{-1} cm^{-1}	λ_{max}, nm	τ, ns	λ_{max}, nm	τ, μs	E_{ox}, V	E_{red}, V
1	540	59.0	770	53	716	1.33	+1.44	−0.55[e]
2	582	52.0	810	40	756	0.83	+1.38	−0.50[e]
3	540	62.2	768	55	716	1.30	+1.41	−0.50[e]
4	577	54.1	812	44	764	0.83	+1.36	−0.50[e]

[a] Acetonitrile solutions, unless otherwise noted. [b] Lowest energy band. [c] Uncorrected emission maxima and luminescence lifetimes in aerated acetonitrile solution (298 K) or 4:1 MeOH/EtOH matrix (77 K). [d] $E_{1/2}$ values vs SCE. [e] Overlapping waves; see text.

= 2,3-dpp (**4**).[27] We have also investigated the absorption spectra, luminescence properties, and electrochemical behavior of these complexes.

Experimental Section

Materials and Methods. The preparation of the bichelating ligands and of the precursor complexes $[Ru(bpy)_2(2,3\text{-dpp})](PF_6)_2$ and $[Ru(bpy)_2[2,5\text{-dpp})](PF_6)_2$, as well as the details and procedures for elemental analyses, IR spectra, conductivity measurements, absorption and luminescence spectra, luminescence lifetimes, and electrochemical measurements, have been previously reported.[19] All reactions were carried out under argon.

Luminescence spectra at room temperature were obtained with a Perkin-Elmer 650-40 spectrofluorometer, and those at 77 K, with a Perkin-Elmer LS-5 spectrofluorometer. Emission lifetimes were measured with Edinburgh single-photon-counting equipment. Electrochemical measurements were carried out at room temperature with PAR 273 multipurpose equipment interfaced to a PC. For reversible processes, half-wave potentials (vs SCE) were calculated as an average of the cathodic and anodic peaks. The criteria for reversibility were the separation between cathodic and anodic peaks, the close to unity ratio of the intensities of the cathodic and anodic currents, and the constancy of the peak potential on changing scan rate. The multielectron nature of some waves was inferred from comparison with the wave of $Os(phen)_3^{2+}$ oxidation as an internal standard (vide infra).

Experimental errors in the reported data are as follows: absorption maxima, 2 nm; emission maxima, 4 nm; emission lifetimes, 10%; redox potentials, 20 mV. As far as the extinction coefficients are concerned, the uncertainty in their absolute values is ~10% because of the highly diluted solutions used (10^{-5}–10^{-4} M).

Preparation of $\{Ru[(BL_a)Ru(bpy)_2]_2Cl_2\}(PF_6)_4$ (5, BL_a = 2,3-dpp; 6, BL_a = 2,5-dpp). In a typical preparation, a mixture of $RuCl_3 \cdot 3H_2O$ (0.011 g, 0.043 mmol), $[Ru(bpy)_2(BL_a)](PF_6)_2$ (0.080 g, 0.086 mmol), and LiCl (0.012 g, 0.280 mmol) in 95% ethanol (15 mL) was refluxed for 7 h. After 1 h the solution became green. The reaction mixture was then cooled to room temperature and an excess of solid NH_4PF_6 was added. The powder that formed was dissolved in acetonitrile, reprecipitated with 95% ethanol, washed with this solvent and then with diethyl ether, and eventually dried in vacuo (0.079 g, 84% yield).

Preparation of $\{[(bpy)_2Ru(BL_a)]_2Ru(BL_b)Ru[(BL_a)Ru(bpy)_2]_2\}(PF_6)_{12}$ (1, BL_a = BL_b = 2,3-dpp; 2, BL_a = BL_b = 2,5-dpp; 3, BL_a = 2,3-dpp, BL_b = 2,5-dpp; 4, BL_a = 2,5-dpp, BL_b = 2,3-dpp). In a typical preparation, $\{Ru[(BL_a)Ru(bpy)_2]_2Cl_2\}(PF_6)_4$ (0.060 g, 0.028 mmol) dissolved in 95% ethanol (3 mL) was treated with a solution of $AgNO_3$ (0.010 g, 0.059 mmol) in 95% ethanol (3 mL) at room temperature. The reaction mixture turned blue, and a precipitate of AgCl appeared. After 3 h of stirring, the appropriate BL_b species (0.0034 g, 0.015 mmol) and ethylene glycol (3 mL) were added, and the mixture was refluxed for 48 h and then cooled to room temperature. AgCl was separated by repeated centrifugations, and to the mother liquor was added a saturated aqueous solution of NH_4PF_6. The crude product that formed was vacuum-dried over night and then dissolved in acetonitrile and precipitated with ethanol. The last operation was repeated, and the solid, after washings with ethanol and diethyl ether, was vacuum-dried (yield 0.049 g, 70%).

Results

The trinuclear compounds $\{Ru[(BL_a)Ru(bpy)_2]_2Cl_2\}(PF_6)_4$ (**5**, BL_a = 2,3-dpp, Figure 2; **6**, BL_a = 2,5-dpp) have been synthesized as shown in Scheme I, by using two $Ru(bpy)_2(BL_a)^{2+}$ complexes as entering ligands on $RuCl_3 \cdot 3H_2O$.

Scheme I

$$RuCl_3 \cdot 3H_2O + [Ru(bpy)_2(BL_a)](PF_6)_2 \xrightarrow[\text{LiCl excess}]{1:2} \xrightarrow[NH_4PF_6]{} \{Ru[(BL_a)Ru(bpy)_2]_2Cl_2\}(PF_6)_4$$

The hexanuclear complexes **1**–**4** have been obtained from the reaction of **5** or **6** with the appropriate BL_b ligand (Scheme II).

Scheme II

$$\{Ru[(BL_a)Ru(bpy)_2]_2Cl_2\}(PF_6)_4 \xrightarrow[AgNO_3]{1:2} \xrightarrow[BL_b]{2:1} \xrightarrow[NH_4PF_6]{} \{[Ru(bpy)_2(BL_a)]_2Ru(BL_b)Ru[(BL_a)Ru(bpy)_2]_2\}(PF_6)_{12}$$

To promote the aquation reaction, a usually somewhat difficult thermal process, the trinuclear complexes have been treated at room temperature with 2 equiv of Ag^+. For the following step a reaction temperature of 120–130 °C was adopted, so that reaction could be complete within 2 days.

For all new complexes, satisfactory elemental analyses and consistent conductivity values were obtained. IR spectra were in agreement with the presence of μ-dpp ligands, as already discussed for other oligonuclear species.[19] The characterization data and yields are reported in Table I. For the precursor complexes **5** and **6**, FAB mass spectra (presently under detailed interpretation) were also obtained that clearly show $(M - PF_6)^+$ parent ions with the appropriate isotopic patterns.

The absorption spectra of complexes **1**–**4** in acetonitrile solution at 298 K are displayed in Figures 3 and 4, where the luminescence bands are also shown. The wavelength and molar absorption coefficient of the lowest energy absorption bands, the luminescence data, and some electrochemical potentials are collected in Table II. In all cases corrected excitation spectra have shown that the

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(27) It must be pointed out that in principle complexes **5** and **6** can exist as three different geometrical isomers, depending on the arrangements of the ligands around the central atom. Consequently, the structural features of complexes **1**–**4** may be rather complicated. Furthermore all these compounds can be mixtures of several diastereoisomeric species, owing to the chiral nature of each metal center. For these reasons structural investigations on these species are presently prevented, as already discussed in ref 19.

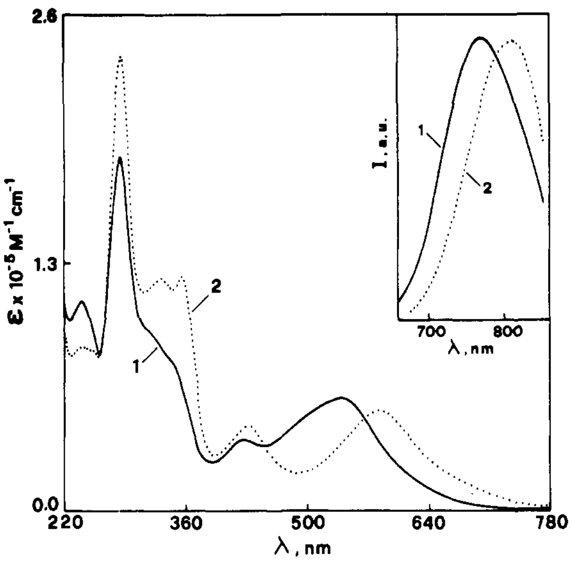

Figure 3. Absorption and (inset) emission spectra of **1** and **2** in acetonitrile solution at 298 K.

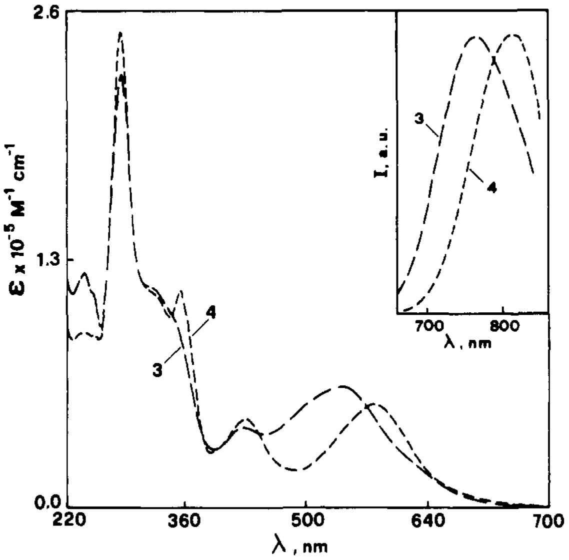

Figure 4. Absorption and (inset) emission spectra of **3** and **4** in acetonitrile solution at 298 K.

intensity of the luminescence band is independent of the excitation wavelength. Compounds **5** and **6** do not show any luminescence.

Cyclic voltammetry and differential pulse voltammetry experiments carried out on solution containing equal concentrations of **1**–**4** and $Os(phen)_3^{2+}$ showed that the intensity of the first oxidation wave of the hexanuclear compounds is about 3.2 times higher than that of the one-electron oxidation wave of the Os complex. If allowance is made for the larger size of the hexanuclear species, this result is consistent with the assignment of the first oxidation wave of **1**–**4** to a four-electron process. Further confirmation comes from the intensity ratio of the pulse-voltammetry waves of hexa- and decanuclear heterometallic Ru–Os complexes.[23]

Discussion

The synthetic work reported in this paper is of interest for two reasons:

(i) The trinuclear complexes **5** and **6** can be prepared in a relatively simple way, with satisfactory yields and purities. These complexes can be used to introduce a trinuclear fragment in species that have an unsaturated chelating site.[28] This is an important step toward the *design of complexes of higher nuclearity*. For example, by this strategy we have prepared[23] a decanuclear compound starting from a $Ru(2,3\text{-dpp})_3^{2+}$ core.

(ii) It has been possible for the first time to obtain heterobridged complexes (see also ref 28). More generally, the possibility to introduce a trinuclear fragment into a vacant chelating position of other complexes opens a way to *the design of species that possess specific components in specific sites of the supramolecular array*. By a suitable choice of such components it is then possible to channel the migration of electronic energy in the desired direction,[21] a requirement that may be necessary for several types of applications[22] (e.g., for spectral sensitization of semiconductor electrodes).

These synthetic strategies would receive a further impulse from the possibility of protecting by methylation (and then deprotecting) a chelating site of a bridging ligand. Investigations along this line are in progress in our laboratories.

In compounds **3** and **4** the central bridging ligand BL_b is chemically different from the peripheral bridging ligands BL_a. In compounds **1** and **2** BL_a and BL_b are chemically identical; nevertheless, they are not equivalent because they bridge different metal-containing units. To a first approximation (i.e., neglecting differences arising from geometrical or optical isomers[27]), in each compound **1**–**4** the two inner metal ions, the four BL_a bridging ligands, the four peripheral metal ions, and the eight peripheral bpy ligands are equivalent (Figure 1).

Electrochemistry. Previous investigations on mono-, di-, tri-, and tetrametallic compounds of the same family[8-20] have shown that (i) oxidation is metal centered, (ii) reduction is ligand centered, (iii) the bridging ligands are reduced by two electrons before reduction of the terminal bpy ligands can take place, (iv) coordinated 2,5-dpp is slightly easier to reduce than 2,3-dpp, and (v) interaction between equivalent metals or equivalent ligands is noticeable for metals coordinated to the same bridging ligand and for ligands coordinated to the same metal, whereas it is small for metals or ligands that are sufficiently far apart. The electrochemical behavior of compounds **1**–**4** was expected to be very complicated because of the presence of six metal ions, five bridging ligands, and eight peripheral ligands. In acetonitrile solution at room temperature, each compound shows a multielectron reversible oxidation wave at about +1.4 V (Table II) that, by comparison with the oxidation wave of $Os(phen)_3^{2+}$, can be assigned to one-electron oxidation of the four peripheral, noninteracting Ru^{2+} ions.[29] The peripheral Ru^{2+} ions are easier to oxidize than the inner ones because of the stronger electron-donor power of the bpy ligands compared to the bridging ligands. Once the peripheral Ru^{2+} ions are oxidized, the oxidation potential of the two remaining metal ions is expected to be strongly displaced toward more positive potentials because of electrostatic repulsion and metal–metal interaction through the BL_a bridges. As a matter of fact, oxidation of the two inner ions could not be observed within the potential window examined (<+2.0 V). It should also be noted that the two inner ions are expected to be oxidized at different potentials because of the short separation distance and the interaction through BL_b. In an attempt to obtain a more complete picture of the oxidation behavior, we are planning to study the oxidation processes in liquid SO_2.[31,32] As far as reduction is concerned, the very complicated wave patterns (which are similar, but not identical, for the four compounds) begin with a broad, multielectronic wave around −0.50 V (Table II). A slightly more negative reduction potential for **1** compared to **2** was anticipated on the basis of the known properties of the two bridging ligands.[19] The first composite wave, which is thought to comprise the first one-electron reduction wave of the five bridging ligands, is followed in all cases by another broad wave around −1.1 V, which should

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[28] Complex **5** has also been used in the synthesis[21] of the tetranuclear "asymmetric" species.

[29] For a thorough discussion of the electrochemical behavior of noninteracting centers, see ref 30.

[30] Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248.

[31] SO_2 is an ideal solvent to study electrochemical oxidation processes of polypyridine metal complexes.[32]

[32] Garcia, E.; Kwak, J.; Bard, A. J. *Inorg. Chem.* **1988**, *27*, 4377.

comprise the second one-electron reduction wave of the bridging ligands, and by two narrower multielectronic waves at about −1.4 and −1.6 V, which should correspond to the reduction of the two sets of equivalent bpy ligands. In the attempt to arrive at a complete and detailed interpretation of the reduction processes, we are currently investigating these systems in DMF solution at 220 K.[33,34]

Absorption Spectra. The absorption spectra of compounds **1–4** in acetonitrile solution (Figures 3 and 4) show extremely intense (ϵ_{max} (1–2) × 10^5 M^{-1} cm^{-1}) bands in the UV region and broad intense (ϵ_{max} ~5 × 10^4 M^{-1} cm^{-1}) bands in the visible region. The highest intensity band (λ_{max} 283 nm for **1** and **3**, 284 nm for **2** and **4**) can be assigned to bpy-centered $\pi \rightarrow \pi^*$ transitions. The two absorption maxima of **2** at 329 and 353 nm can be assigned to $\pi \rightarrow \pi^*$ transitions localized on the 2,5-dpp ligand, while from the spectrum of **1** it is clear that also the 2,3-dpp ligand exhibits a broad absorption in the same spectral region. The highest energy band in the visible region is almost unaffected by the nature of the bridging ligand (λ_{max} 425 nm (**1**), 431 nm (**2**), 426 nm (**3**), and 430 nm (**4**)) and can thus be assigned to a Ru → bpy charge-transfer (CT) transition. By contrast, the position of the lowest energy maximum is clearly dependent on the nature of the bridging ligands (λ_{max} 540 nm (**1**), 582 nm (**2**), 540 nm (**3**), and 577 (**4**)) and can thus be assigned to Ru → BL_a CT transitions. These assignments are in complete agreement with those previously discussed for analogous complexes of lower nuclearity.[19] It can be noted that the Ru → BL CT bands are much broader than the Ru → bpy CT bands even in the cases of compounds **1** and **2**, where BL_a = BL_b. This can be easily understood, since the eight Ru–bpy units of the supramolecular array are all equivalent whereas there are three different types of Ru–BL units even when BL_a is chemically identical with BL_b: (i) peripheral Ru–BL_a; (ii) inner Ru–BL_a; (iii) inner Ru–BL_b. As we have seen above, in the homobridged compounds the peripheral Ru^{2+} ions are easier to oxidize than the inner Ru^{2+} ions, and BL_b is easier to reduce than BL_a. Therefore, it can be expected that the CT transitions in units i and iii are lower in energy than those in unit ii. As we will see later, the luminescence spectra show that the lowest energy CT level belongs to unit i in *both* the heterobridged compounds **3** and **4**, which indicates that the difference between the oxidation potentials of peripheral and inner Ru^{2+} ions overcomes the difference between the reduction potentials of the two types (2,3-dpp and 2,5-dpp) of ligands.

Luminescence Spectra and Decays. Compounds **1–4** are luminescent in rigid matrix at 77 K and in fluid solution at room temperature (Figures 3 and 4, Table II). As it usually happens for ruthenium(II) polypyridine complexes,[35] emission originates from the lowest energy excited state, which is a formally spin-forbidden metal-to-ligand CT level. As expected on the basis of the electrochemical results and of the behavior of parent compounds of lower nuclearity,[19,20] **1** emits at slightly higher energy than **2**. The mixed-bridge compounds **3** and **4** clearly emit at the same wavelength (Figures 3 and 4) and exhibit luminescence lifetimes (Table II) similar to those of **1** and **2**, respectively. These results indicate that the luminescent excited state does not concern the central bridging ligand even in the case of compound **3** where BL_b is 2,5-dpp, which is easier to reduce than 2,3-dpp. Thus, as anticipated in the previous section, the lowest excited state in each complex involves the Ru → BL_a CT transitions of the peripheral $(bpy)_2Ru(BL_a)$ units. Energy transfer from the inner to the peripheral units takes place with ~100% efficiency, as shown by the corrected excitation spectra. The values found for the luminescence lifetimes are in the usual range of "triplet" metal-to-ligand CT levels of ruthenium(II) polypyridine complexes[35] and are lower for the lower energy levels, as expected on the basis of the energy-gap rule.[36,37] The lack of luminescence from the trinuclear $Ru[(BL_a)Ru(bpy)_2]_2Cl_2^{4+}$ species is likely due to the presence of distorted metal-centered excited states at low energies.[35]

Conclusions

The trinuclear compounds $\{Ru[(BL_a)Ru(bpy)_2]_2Cl_2\}(PF_6)_4$, where BL_a is 2,3-dpp (Figure 2) or 2,5-dpp, have been obtained by using the "complexes as ligands" strategy and have then been used to synthesize the first hexanuclear (**1–4**) and heterobridged (**3** and **4**) ruthenium(II) polypyridine complexes (Figure 1). Such hexanuclear compounds (i) exhibit quite intense absorption bands in the UV (ϵ_{max} of the order of 2 × 10^5 M^{-1} cm^{-1}) and visible (ϵ_{max} ~5 × 10^4 M^{-1} cm^{-1}) spectral regions, (ii) are luminescent both in rigid matrix at 77 K and in fluid solution at room temperature, and (iii) can undergo a great number of oxidation and reduction processes. In all cases, the luminescent level is populated with ~100% efficiency regardless of the absorbing chromophoric unit. The trinuclear complexes **5** and **6**, as well as other analogous compounds that can now be obtained by the same procedure, are important building blocks to prepare complexes of high nuclearity, since they can be used to introduce a trinuclear fragment in species that have an unsaturated chelating site. Furthermore, this strategy allows the design of luminescent polynuclear complexes with specific components in specific sites of the supramolecular array, which allows migration of electronic energy in the desired direction.[21,23]

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[33] Roffia, S.; et al. Work in progress. For a recent investigation on the electrochemical behavior of oligometallic complexes in DMF at 220 K, see ref 34.

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