

# Limits of the *in Situ* Synthesis of Tris(2,2'-bipyridine)ruthenium(II) in the Supercages of Zeolite Y

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A systematic survey of zeolites Y containing tris(2,2'-bipyridine)ruthenium(II) with various levels of loading was undertaken. Almost pure Ru(bpy)<sub>3</sub><sup>2+</sup> was obtained whenever the loading was less than approximately one complex per two supercages. At higher loading an increasing amount of byproducts corresponding formally to Ru(bpy)<sub>n</sub>(NH<sub>3</sub>)<sub>6-2n</sub><sup>2+</sup>, *n* < 3, was found. This dependence of the yield of the “ship-in-a-bottle” synthesis of Ru(bpy)<sub>3</sub><sup>2+</sup> in zeolite Y on the ruthenium exchange degree was interpreted in terms of transport problems and in terms of sterical fitting between host zeolite Y supercages and guest Ru(bpy)<sub>3</sub><sup>2+</sup>. For high loadings, we observed a tendency of Ru(bpy)<sub>3</sub><sup>2+</sup> to accumulate toward the surface of the zeolite microcrystals instead of a random distribution in the bulk. The consequence of this was to slow down the bpy diffusion during the *in situ* complexation process and finally to prevent the reaction from being completed at high loading levels.

## Introduction

The pioneering work of Lunsford *et al.*<sup>1</sup> in the early 80's, dealing with the spectroscopic properties of *in situ* synthesized tris(2,2'-bipyridine)ruthenium(II), Ru(bpy)<sub>3</sub><sup>2+</sup>, in zeolite Y supercages, the so-called “ship-in-a-bottle” complexes, initiated many studies<sup>2</sup> in this attractive field. In the course of our research on artificial antenna systems<sup>3</sup> as components of solar energy conversion devices, we have paid special attention to highly loaded but pure materials. Most contributions concerning Ru(bpy)<sub>3</sub><sup>2+</sup> in zeolite Y are dealing with low-loaded materials. Dutta and co-workers,<sup>4</sup> however, focused on Ru(bpy)<sub>3</sub><sup>2+</sup>-modified zeolite Y up to nearly one complex per supercage, and they tried to understand the observed photophysical behavior of these materials by assuming a Perrin type quenching mechanism caused by relatively strong Ru(bpy)<sub>3</sub><sup>2+</sup>...Ru(bpy)<sub>3</sub><sup>2+</sup> interactions. Interestingly, the identity of the complexes in the supercages at high loading has not been seriously questioned up to now. We have for this reason performed a systematic survey of the *real* content of these Ru/bpy loaded zeolite Y microcrystals. A set of zeolite Y samples containing 1 ruthenium complex per 20.8, 8.4, 4.4, 3.0, 1.9, 1.5, 1.3, 1.15, and 1.02 supercages was prepared and analyzed chemically and spectrophotometrically, and we now report the results of these experiments.

## Experimental Section

**Physical Measurements.** UV-visible spectra were recorded using a Perkin-Elmer Lambda 14 spectrophotometer. For the solid-state diffuse reflectance measurements, the spectrophotometer was equipped

with an integrating sphere (Labsphere RSA-PE-20) and the data collected were subsequently transformed by applying the Kubelka–Munk formula before graphical representation. Routine luminescence checking for qualitative purposes was run with a standard laboratory UV lamp irradiating at  $\lambda = 350$  nm. For quantitative measurements, emission spectra were recorded with a Perkin-Elmer LS 50 B spectrofluorometer on  $\sim 10^{-5}$  M aqueous solutions. The crystallinity and the morphology of the samples were investigated by X-ray powder diffraction and SEM, respectively. No structural degradation was observed. The Si/Al ratio for all loaded samples was measured by energy dispersive X-ray spectroscopy. In no case was dealumination caused by the pretreatment of the zeolite detected.

**Materials.** Solvents (Fluka, pa) and reagents [Ru(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> (Johnson Matthey & Brandenberger AG), 2,2'-bipyridine (Fluka, puriss pa >99%) and NH<sub>4</sub>PF<sub>6</sub> (Fluka, purum) were used as received. Na<sup>+</sup>-Y zeolite was supplied by Union Carbide (LZY-52). The hydrofluoric acid (HF, *handle with care, highly corrosive!*) was purchased from Aldrich as a 48% aqueous solution and was subsequently diluted to 10% with bidistilled water before use.

**Preparation of Ruthenium/Bpy Loaded Zeolite Y. 1. Direct *In Situ* Synthesis.** Ru(bpy)<sub>3</sub><sup>2+</sup>-Y zeolite was prepared by the following procedure: 30 g of Na<sup>+</sup>-Y zeolite was suspended in water (1 L), and the pH was adjusted to 3.8 with 0.1 M HCl while stirring overnight. The zeolite was separated from the solution by filtration and washed with bidistilled water until no chloride could be detected in the filtrate using AgNO<sub>3</sub>. The acidified (Na<sup>+</sup>,H<sup>+</sup>)-Y zeolite was dried at 80 °C for 10 h and preconditioned at room temperature for 2 days before use. A 1 g amount of (Na<sup>+</sup>,H<sup>+</sup>)-Y zeolite was dispersed in water (100 mL) in a three-necked flask and stirred under Ar bubbling for 0.5 h, after which [Ru(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> was added (see Table 1) and ion-exchange was carried out under Ar bubbling for 24 h. The Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>-Y zeolite was filtered under inert Ar atmosphere and washed with deaerated water (100 mL) and then dried at 40 °C under vacuum for 2 h. The samples were ground and mixed thoroughly with 2,2'-bipyridine (bpy) in a mortar (mole ratio bpy/[Ru(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> = 4; see Table 1), added to a steel-made cylindrical vessel (7 mm × 70 mm), pressed by a stainless steel bar, and dried under vacuum overnight. The lid was screwed on tightly and the vessel heated at 215 °C for 24 h. The resulting reddish powder was dispersed in ethanol (100 mL), stirred for 1 h, filtered out, and subsequently washed thoroughly with ethanol and diethyl ether, to remove any remaining unreacted bpy. Superficially adsorbed Ru(bpy)<sub>3</sub><sup>2+</sup> was removed by stirring the loaded zeolite in 1 M NaCl aqueous solution (100 mL) for 0.5 h. The product was filtered out, washed with 1 M NaCl until the filtrate was colorless, and then washed with bidistilled water until no Cl<sup>-</sup> could be detected in the filtrate. The Ru(bpy)<sub>3</sub><sup>2+</sup>-Y zeolite was dried under vacuum overnight and preconditioned in atmosphere at room temperature before use.

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- (1) DeWilde, W.; Peeters, G.; Lunsford, J. H. *J. Phys. Chem.* **1980**, *84*, 2306.
- (2) (a) Quayle, W. H.; Lunsford, J. H. *Inorg. Chem.* **1982**, *21*, 97. (b) Dutta, P. K.; Incavo, J. A. *J. Phys. Chem.* **1987**, *91*, 4443. (c) Incavo, J. A.; Dutta, P. K. *J. Phys. Chem.* **1990**, *94*, 3075. (d) Maruszewski, K.; Strommen, D. P.; Handrich, K.; Kincaid, J. R. *Inorg. Chem.* **1991**, *30*, 4579. (e) Dutta, P. K.; Turbeville, W. J. *J. Phys. Chem.* **1992**, *96*, 9410. (f) Borja, M.; Dutta, P. K. *Nature* **1993**, *362*, 43. (g) Maruszewski, K.; Strommen, D. P.; Kincaid, J. R. *J. Am. Chem. Soc.* **1993**, *115*, 8345. (h) Maruszewski, K.; Kincaid, J. R. *Inorg. Chem.* **1995**, *34*, 2002. (i) Ledney, M.; Dutta, P. K. *J. Am. Chem. Soc.* **1995**, *117*, 7687.
- (3) Binder, F.; Calzaferri, G.; Gfeller, N. *Sol. Energy Mater. Sol. Cells* **1995**, *38*, 175.
- (4) Turbeville, W.; Robins, D. S.; Dutta, P. K. *J. Phys. Chem.* **1992**, *96*, 5024.

**Table 1.** [Ru(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> and 2,2'-Bipyridine Used/g of (Na<sup>+</sup>,H<sup>+</sup>)-Y Zeolite for the Direct "Ship-in-a-Bottle" Syntheses

[Ru(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>3</sub> (g)	2,2'-bipyridine (g)	measd loading of Ru <sup>2+</sup> /supercage (%)
0.009	0.014	4.8
0.02	0.034	11.9
0.034	0.069	22.5
0.05	0.103	33.6
0.084	0.171	53.5
0.121	0.24	67.3
0.155	0.307	78.2
0.269	0.549	86.8
0.336	0.686	98.3

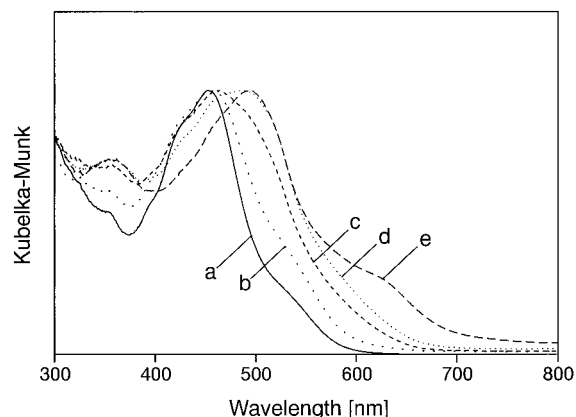
**2. 1st and 2nd "Iterative" Syntheses.** To get higher Ru(bpy)<sub>3</sub><sup>2+</sup> yields, the highly loaded zeolites from the previous batch were reacted with bpy a second and, in some cases, a third time. Typically, 0.5 g of the modified zeolite was ground and mixed with 1.0 g of bpy in a mortar after drying at 60 °C for 1 h. The mixture was filled into the steel vessel, pressed with a steel bar, and dried under vacuum for 1 h. The lid was screwed on tightly and the vessel heated at 205 °C for 20 h. The resulting product was suspended in ethanol (100 mL) and stirred for 1 h. The suspension was then suction filtered and washed with 50 mL 1 M NaCl aqueous solution, bidistilled water, ethanol, and diethyl ether. The zeolite powder was dried at 60 °C for 0.5 h.

**Determination of Modified Zeolites Contents. Qualitative Analyses.** Diffuse reflectance solid-state spectra were recorded on samples of modified zeolite diluted with a 2- to 10-fold excess of Na<sup>+</sup>-Y zeolite depending on the loading of the modified zeolite to prevent saturation of the absorption. Electronic absorption spectra of the samples were recorded in solution (transmission mode) after the following treatment: a few milligrams of the loaded zeolite were dissolved in 200 μL of 10% hydrofluoric acid (HF) aqueous solution and subsequently diluted with water to 50 mL.

**Quantitative Analyses.** The total amount of loaded ruthenium in each sample was determined spectrophotometrically by using the hydrolyzed modified zeolites as starting material for the synthesis of the well-known Ru(bpy)<sub>3</sub><sup>2+</sup> chromophore. In a typical dosage, 15 mg of the loaded zeolite was dissolved in 500 μL of 10% HF aqueous solution and diluted with bidistilled water (10 mL). The solution was neutralized with 500 μL of 4 M NaOH; a large excess of bpy (300 mg) dissolved in ethylene glycol (30 mL) was added to the previously prepared aqueous solution, and the mixture was stirred and heated to 120 °C for 48 h. The initially red-brown solution (for highly loaded zeolites) turned to a light red-orange colored and strongly luminescent solution, featuring the Ru(bpy)<sub>3</sub><sup>2+</sup> complex. The mixture was cooled to room temperature and diluted with water (40 mL). The excess of bpy was washed out with diethyl ether (4 × 100 mL). The aqueous solution of Ru(bpy)<sub>3</sub><sup>2+</sup> was filtered, and the volume of the filtrate was then adjusted to exactly 100 mL with bidistilled water. The Ru(bpy)<sub>3</sub><sup>2+</sup> concentration of this solution was determined spectrophotometrically afterward.

The effective amount of "ship-in-a-bottle" Ru(bpy)<sub>3</sub><sup>2+</sup> synthesized in each sample was also determined by spectrophotometrical analysis after selective extraction of the concerned chromophore, by proceeding as follows. A 25 mg amount of the probe was dissolved in 10% HF aqueous solution (1 mL), and then bidistilled water (20 mL) and 4 M NaOH aqueous solution (1 mL) were added for neutralization. The aqueous phase was adjusted to 100 mL precisely, and dichloromethane (100 mL) was added. A 65 mg amount of NH<sub>4</sub>PF<sub>6</sub> was added to this mixture, which was then stirred for 0.5 h in the dark. After extraction, it was verified that no residual luminescence originating from the Ru(bpy)<sub>3</sub><sup>2+</sup> chromophore remained in the aqueous phase. Finally, UV-visible spectra of the organic phase, which contains the pure [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> complex, and of the aqueous phase, which contains other ruthenium derivatives and byproducts, were recorded. For some samples, a complementary and quantitative analysis was made on the starting dissolved material by preparative thin-layer chromatography on aluminum oxide plates with a mixture of dichloromethane and acetone (2:1) as eluent; results were found to be the same as with the extraction method.

**Location of Ru(bpy)<sub>3</sub><sup>2+</sup>.** A 15 mg amount of Ru/bpy-loaded zeolite Y was suspended in 1 M NH<sub>4</sub>PF<sub>6</sub> aqueous solution (10 mL); then

**Figure 1.** Diffuse reflectance spectra of Ru(bpy)<sub>n</sub>(NH<sub>3</sub>)<sub>6-2n</sub><sup>2+</sup>-Y zeolites at different loadings. The spectra are normalized to the same peak height. [Ru<sup>2+</sup>]<sub>T</sub> of the different samples is 22.5% (a), 53.5% (b), 78.2% (c), 86.8% (d), and 98.3% (e).

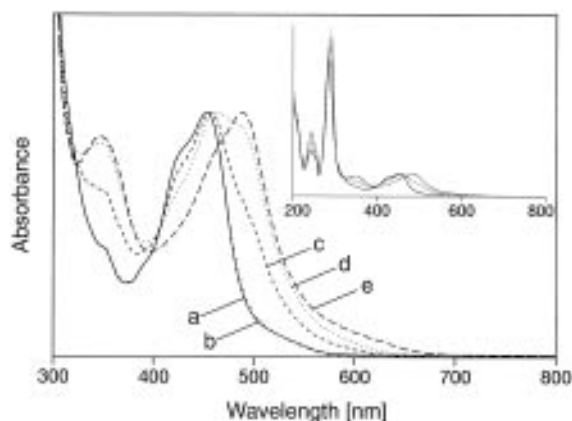
dichloromethane (20 mL) was added, and the mixture was stirred vigorously for 48 h at room temperature and in the dark. The organic phase containing [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> and byproducts was subsequently separated from the aqueous solution, and the volume was precisely adjusted to 50 mL with dichloromethane. To this solution transferred to a round bottom flask was added bidistilled water (50 mL), and the mixture was stirred vigorously for 5 min. A 35 mg amount of NH<sub>4</sub>PF<sub>6</sub> was then added, and the biphasic solution was stirred for another 25 min. The electronic absorption spectra of the organic phase, containing the pure [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>, and of the aqueous phase, containing side products, were then recorded.

This treatment can be adapted for a supplementary washing applied after the conventional cleaning procedure of the Ru/bpy-loaded zeolite Y with EtOH and an aqueous solution of NaCl; the removal of Ru(bpy)<sub>3</sub><sup>2+</sup> residue adsorbed on the surface of the zeolite grains is thus warranted. Typically, 100 mg of Ru/bpy-loaded material was suspended in 1 M NH<sub>4</sub>PF<sub>6</sub> aqueous solution (50 mL); then dichloromethane (150 mL) was added, and the mixture was heated under reflux while being stirred vigorously for 48 h. The organic phase mainly containing [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> was extracted, and the aqueous phase was filtered off. The solid was then successively washed with bidistilled water, ethanol, and diethyl ether and dried at 60 °C.

## Results and Discussion

The first batch of Ru(bpy)<sub>3</sub><sup>2+</sup>-loaded zeolite Y samples was prepared according to the conventional method<sup>1,4</sup> by reacting Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>-exchanged zeolite Y with 2,2'-bipyridine (bpy) at 215 °C. Minor deviations from the original experimental procedure did not alter the nature of the final products, and we found that our spectroscopic results agreed with those published in the literature.<sup>4</sup> Additional chemical experiments were performed, however, the results of which are now reported. We verified that only the zeolite framework was destroyed by the treatments carried out in the aqueous hydrofluoric acid solutions<sup>2d</sup> but not the Ru(bpy)<sub>3</sub><sup>2+</sup> complex and related compounds. The loading of a species is defined as its number in the modified zeolite Y, *n*<sub>species</sub>, divided by the number of supercages, *n*<sub>sc</sub>. A 100% loading value refers to an occupancy of 1 species per supercage, which means that all supercages within the modified zeolite are filled.

**1. Qualitative Analyses.** We first investigated the electronic spectra of the powders and of the solutions obtained after destruction of the zeolite framework. The solid-state diffuse reflectance spectra for different cases are shown in Figure 1. Noticeable changes of the spectral features are present for highly Ru/bpy-loaded zeolites. The characteristic MLCT band with λ<sub>max</sub> = 453 nm decreases with increasing loading, and a new band with a maximum around λ<sub>max</sub> = 490 nm builds up.

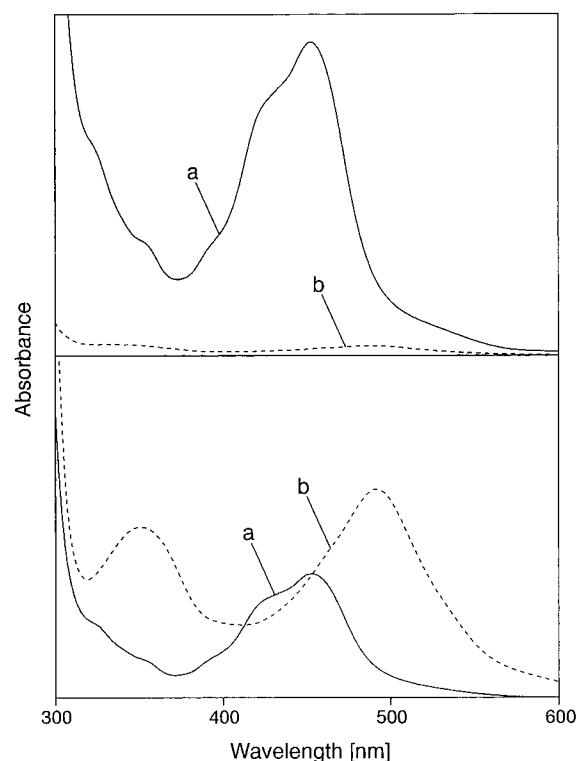


**Figure 2.** Solution absorption spectra after hydrofluoric acid dissolution of  $\text{Ru}(\text{bpy})_n(\text{NH}_3)_{6-2n}^{2+}-\text{Y}$  zeolites at different loadings. The spectra are normalized to the same peak height.  $[\text{Ru}^{2+}]_{\text{T}}$  of the different samples is 22.5% (a), 53.5% (b), 78.2% (c), 86.8% (d), and 98.3% (e). The inset shows an extended range (200–800 nm) of the spectra.

Simultaneously a new band appears at  $\sim 350$  nm. These observations are consistent with those reported in the literature.<sup>4</sup> The 350 nm band has, however, not yet been discussed. Figure 2 presents the electronic absorption spectra of the same samples as above but recorded after destruction of the host crystalline aluminosilicate structure in HF solution. It is remarkable that the spectra show qualitatively the same behavior as those in Figure 1. For low loading (spectra a, b), the maximum of the MLCT band is at 453 nm. At the highest loading, spectrum e, a new maximum at 489 nm appears. The spectra c and d show an intermediate behavior. Again we find the growth of the new band at  $\sim 350$  nm with increasing loadings. In the light of these observations, the assertion<sup>4</sup> that the MLCT band at 490 nm in highly Ru/bpy-loaded zeolite Y is the same as the one situated at 453 nm for low-loaded materials but shifted because of  $\text{Ru}(\text{bpy})_3^{2+} \cdots \text{Ru}(\text{bpy})_3^{2+}$  interactions due to intrazeolitic confinement must be questioned. The shoulder at  $\sim 550$  nm in spectrum b of Figure 1, which is not present in spectrum b of Figure 2, is probably caused by the significant change of refractive index of the microcrystals upon loading with  $\text{Ru}(\text{bpy})_3^{2+}$ . The band centered around 640 nm in spectrum e of Figure 1 can be ascribed to a minor blue byproduct bound to the aluminosilicate framework of the type  $(\text{Al})\text{Si}-\text{O}-\text{Ru}(\text{bpy})_2(\text{OH})_2^{2+}$ , identified by Kincaid *et al.*<sup>2d</sup> The destruction of the framework with acidic aqueous solution also hydrolyzed the blue species giving rise to the  $\text{Ru}(\text{bpy})_2(\text{OH})_2^{2+}$  species which shows spectral properties<sup>5</sup> similar to those of the  $\text{Ru}(\text{bpy})_2(\text{NH}_3)_2^{2+}$  chromophore.

**2. Quantitative Analyses.** At this stage of our study, a quantitative analysis of the actual content of the loaded materials was required. After it was established in which cases the “ship-in-a-bottle” synthesized ruthenium complexes were chemically pure and in which cases the reaction was incomplete, the aim was to find a selective procedure to evaluate the overall loading of ruthenium and the portion of  $\text{Ru}(\text{bpy})_3^{2+}$ .

**Determination of the Loading of  $\text{Ru}(\text{bpy})_3^{2+}$ ,  $[\text{Ru}(\text{bpy})_3^{2+}]$ .** The first step of the characterization was to determine the effective loading of  $\text{Ru}(\text{bpy})_3^{2+}$  species contained in each sample of loaded zeolite Y. The aluminosilicate framework of zeolite Y can be dissolved in strong acidic media<sup>2d</sup> so that its overall content is released into solution and can be subsequently analyzed. We found that after destruction of the host with an aqueous solution of hydrofluoric acid and neutralization of the solution with sodium hydroxide, addition of the appropriate quantity of the phase-transfer agent hexafluorophosphate to a



**Figure 3.** Absorption spectra of the organic phase (a) and the aqueous phase (b) of an extraction of dissolved  $\text{Ru}(\text{bpy})_n(\text{NH}_3)_{6-2n}^{2+}-\text{Y}$  zeolite.  $[\text{Ru}^{2+}]_{\text{T}}$  is 53.5% for the sample in the upper figure and 86.8% for the sample in the lower figure. From the spectra of the organic phases, the  $\text{Ru}(\text{bpy})_3^{2+}$  loadings  $[\text{Ru}(\text{bpy})_3^{2+}]$  can be calculated as 51.7% (97% of  $[\text{Ru}^{2+}]_{\text{T}}$ ) for the upper and 23% (26% of  $[\text{Ru}^{2+}]_{\text{T}}$ ) for the lower case.

mixture of this solution with dichloromethane allowed separation of a yellow (and strongly luminescent) organic phase and an orange to violet nonluminescent aqueous phase in cases where the “ship-in-a-bottle” synthesis was not complete. From the electronic spectra of both phases up to three ruthenium coordination compounds could be identified, depending on the samples. Two examples of these extractions are given in Figure 3 for a 53.5- and a 86.8%-loaded zeolite Y. The organic phase contains pure  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ , and the aqueous phase contains a mixture of  $\text{Ru}(\text{bpy})_2(\text{NH}_3)_2^{2+}$  and  $\text{Ru}(\text{bpy})(\text{NH}_3)_4^{2+}$ . The two latter species are characterized by the shape and positions of two broad bands centered at 350 and 500 nm, which are in fact a combination of their MLCT electronic transitions<sup>6</sup> weighted by their relative abundance.

The effective amount of  $\text{Ru}(\text{bpy})_3^{2+}$  in the loaded zeolites was evaluated by performing these extractions in a quantitative way, i.e. by controlling all parameters such as the amount of starting material, the volumes of organic and aqueous phases, and others. The calculation of the loading of the zeolite Y supercages with  $\text{Ru}(\text{bpy})_3^{2+}$  was based on the known<sup>7</sup> molar extinction coefficient of  $14\,600\text{ M}^{-1}\text{ cm}^{-1}$  for the MLCT band at 453 nm for  $\text{Ru}(\text{bpy})_3^{2+}$ . In addition, the incorporation of a cationic  $\text{Ru}(\text{bpy})_3^{2+}$  ( $M_r = 569.6\text{ g mol}^{-1}$ ) into a zeolite Y supercage is associated to the release of two sodium cations

- (6)  $\text{Ru}(\text{bpy})_2(\text{NH}_3)_2^{2+}$  data were collected by: Bryant, G. M.; Fergusson, J. E.; Powell, H. K. *J. Aust. J. Chem.* **1971**, *24*, 257. Electronic spectra were recorded in MeOH giving the following values  $\lambda/\text{nm}$  ( $\epsilon/\text{M}^{-1}\text{ cm}^{-1}$ ) for MLCT bands: 350 (8020) for  $t_2 \rightarrow \pi^*(2)$  and 494.5 (9340) for  $t_2 \rightarrow \pi^*(1)$ .  $\text{Ru}(\text{bpy})(\text{NH}_3)_4^{2+}$  data were collected by: Alvarez, V. E.; Allen, R. J.; Matsubara, T.; Ford, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 7686. Values recorded in dilute aqueous solution are 367 (5700) for  $t_2 \rightarrow \pi^*(2)$  and 523 (3500) for  $t_2 \rightarrow \pi^*(1)$ .
- (7) Lin, C.-T.; Böttcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6536.

**Table 2.** Loading of Zeolite Y with  $\text{Ru}(\text{bpy})_n(\text{NH}_3)_{6-2n}^{2+}$ ,  $n = 0, 1, 2$ , and  $3^a$ 

direct <i>in situ</i> synth				1st iterative synth				2nd iterative synth			
tot. amt of $\text{Ru}^{2+}$		amt of $\text{Ru}(\text{bpy})_3^{2+}$		tot. amt of $\text{Ru}^{2+}$		amt of $\text{Ru}(\text{bpy})_3^{2+}$		tot. amt of $\text{Ru}^{2+}$		amt of $\text{Ru}(\text{bpy})_3^{2+}$	
$\mu\text{mol/g}$	loading (%)	$\mu\text{mol/g}$	loading (%)	$\mu\text{mol/g}$	loading (%)	$\mu\text{mol/g}$	loading (%)	$\mu\text{mol/g}$	loading (%)	$\mu\text{mol/g}$	loading (%)
22.1	4.8	15.3	3.3								
55.2	11.9	48.8	10.5								
104.2	22.5	100.7	21.7								
155.5	33.6	156.3	33.7								
247.7	53.5	239.7	51.7								
311.9	67.3	237	51.2	315.3	68	281.6	60.8	311.9	67.3	293.9	63.4
362.3	78.2	183.8	39.7	351.3	75.8	268.3	57.9	333	71.9	285	61.5
402.3	86.8	106.5	23	406.1	87.6	155.8	33.6	390.1	84.2	195.2	42.1
455.6	98.3	36.7	7.9	429.4	92.7	69.2	14.9				

<sup>a</sup> The total amount of  $\text{Ru}^{2+}$  and the amount of  $\text{Ru}(\text{bpy})_3^{2+}$  are each given in  $\mu\text{mol/g}$  of zeolite and as percentage values referring to the loading  $[\text{Ru}^{2+}]_{\text{T}}$  or  $[\text{Ru}(\text{bpy})_3^{2+}]$ , respectively.

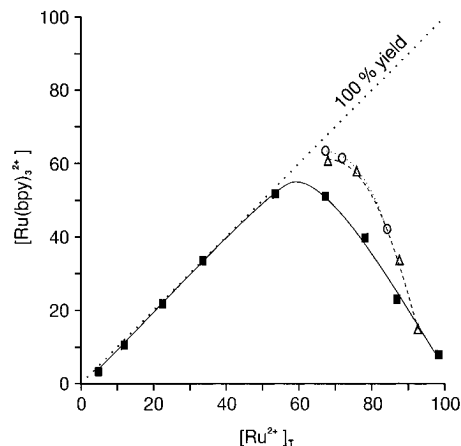
and most of the water molecules (see ref 4 and references cited therein). Thus, the gain in molecular weight due to  $\text{Ru}(\text{bpy})_3^{2+}$  insertion is assumed to be almost compensated by the loss in weight due to water and sodium release. Since no more precise data are available, all percentage values ( $[\text{Ru}(\text{bpy})_3^{2+}]$  and  $[\text{Ru}^{2+}]_{\text{T}}$ ) were therefore calculated with a unique molecular weight of  $17\,266\text{ g mol}^{-1}$  for the modified zeolites, independently of the loading. The results of these analyses are summarized in Table 2.

**Determination of the Overall Loading of Ruthenium,  $[\text{Ru}^{2+}]_{\text{T}}$ .** The second step of the characterization was to measure the *total* amount of ruthenium compounds  $[\text{Ru}^{2+}]_{\text{T}}$  contained in each sample of loaded zeolite Y, i.e. the rate of filling of zeolite Y supercages with ruthenium complexes, *whatever their chemical nature is*.  $[\text{Ru}^{2+}]_{\text{T}}$  is expressed as a percentage  $[\text{Ru}^{2+}]_{\text{T}} = n_{\text{Ru}}/n_{\text{sc}} \times 100\%$ , where  $n_{\text{Ru}}$  is the number of ruthenium compounds and  $n_{\text{sc}}$  the number of supercages contained in the loaded zeolite.  $[\text{Ru}(\text{bpy})_3^{2+}]$  and  $[\text{Ru}(\text{bpy})_n(\text{NH}_3)_{6-2n}^{2+}]_{n=0,1,2}$  are defined in the same way, so that eq 1 holds.

$$[\text{Ru}^{2+}]_{\text{T}} = [\text{Ru}(\text{bpy})_3^{2+}] + [\text{Ru}(\text{bpy})_n(\text{NH}_3)_{6-2n}^{2+}]_{n=0,1,2} \quad (1)$$

We found that addition of alcohol-based solutions containing a large excess of bpy to the aqueous solutions of dissolved highly Ru/bpy-loaded zeolite Y increased the amount of  $\text{Ru}(\text{bpy})_3^{2+}$  after sufficient heating in cases where incompletely reacted Ru species were present and led to orange solutions showing the same UV-visible spectroscopic and emission properties as *pure*  $\text{Ru}(\text{bpy})_3^{2+}$ . The ligand addition to the dissolved material drove to completion the complexation reaction. This method could therefore be used to determine the total amount of ruthenium encapsulated in zeolite Y. For this purpose a known amount of each sample of Ru/bpy-loaded zeolite Y was dissolved in an aqueous solution of hydrofluoric acid. The mixture was then neutralized and taken as starting material to complete the formation of  $\text{Ru}(\text{bpy})_3^{2+}$ . Full transformation was achieved by adding a large excess of bpy in ethylene glycol and by heating at  $120\text{ }^\circ\text{C}$  for 2 days. After purification and identification, the loading  $[\text{Ru}^{2+}]_{\text{T}}$  was calculated. The results of this analysis are summarized in Table 2 and in Figure 4, which illustrates the variation of the  $\text{Ru}(\text{bpy})_3^{2+}$  loading,  $[\text{Ru}(\text{bpy})_3^{2+}]$ , as a function of the total ruthenium loading,  $[\text{Ru}^{2+}]_{\text{T}}$ . The diagonal of the plot corresponds to pure  $\text{Ru}(\text{bpy})_3^{2+}$  in the zeolite Y supercages.

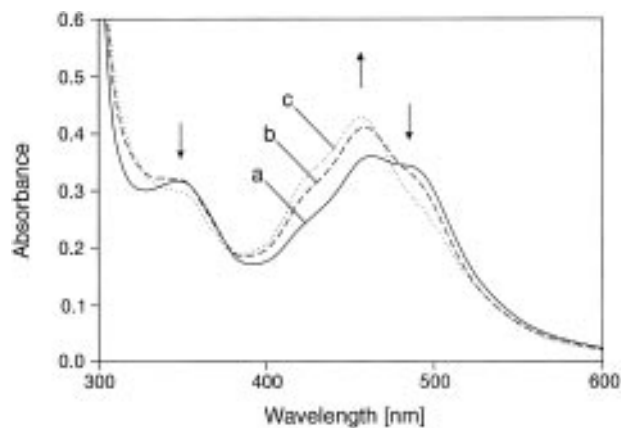
The experimental values first show a monotonic increase related to a  $\sim 100\%$  yield  $\text{Ru}(\text{bpy})_3^{2+}$  formation up to an overall loading  $[\text{Ru}^{2+}]_{\text{T}}$  of  $53.5\%$ . Strictly speaking, with respect to the four lower loaded zeolites (up to  $[\text{Ru}^{2+}]_{\text{T}} = 33.6\%$ ), no trace of other ruthenium compounds was detected. The deviations



**Figure 4.** Analysis data for  $\text{Ru}(\text{bpy})_n(\text{NH}_3)_{6-2n}^{2+}$ -Y zeolites at different loadings. The loading  $[\text{Ru}(\text{bpy})_3^{2+}]$  is drawn as a function of the loading  $[\text{Ru}^{2+}]_{\text{T}}$ . A 100% value corresponds to a loading of 1 ruthenium/bpy complex per supercage. The samples at high loadings were reacted with bpy a second time and, in some cases, a third time: ■, direct *in situ* synthesis; △, 1st iterative synthesis; ○, 2nd iterative synthesis.

between the numerical values of  $[\text{Ru}^{2+}]_{\text{T}}$  and  $[\text{Ru}(\text{bpy})_3^{2+}]$  reported in Table 2 are due to the experimental limits of the analytical procedures. Therefore, in the range of loading  $0\% < [\text{Ru}^{2+}]_{\text{T}} \leq 33.6\%$ , the yield of *in situ* synthesis of  $\text{Ru}(\text{bpy})_3^{2+}$  is quantitative. Regarding  $[\text{Ru}^{2+}]_{\text{T}} = 53.5\%$ , traces of ruthenium side products were detected in the aqueous phase, see also Figure 3, such that the yield of the “ship-in-a-bottle”  $\text{Ru}(\text{bpy})_3^{2+}$  synthesis was estimated to be about 97% in this case. A plateau is reached between roughly  $53.5\%$  and  $67.3\%$  loading. This means that the yield evaluated to 97% for  $[\text{Ru}^{2+}]_{\text{T}} = 53.5\%$  starts to decrease and corresponds to 76% only when  $[\text{Ru}^{2+}]_{\text{T}}$  is  $67.3\%$ . For higher  $[\text{Ru}^{2+}]_{\text{T}}$  values, the effective amount of “ship-in-a-bottle”  $\text{Ru}(\text{bpy})_3^{2+}$  decreases steadily to  $\sim 8\%$  when  $[\text{Ru}^{2+}]_{\text{T}}$  is  $\sim 98\%$ .

**3. Attempts To Diminish the Amount of Side Products at High Loading.** Bis-bpy complexes of ruthenium ( $n = 2$ ) located within the cavities of zeolite Y were synthesized and identified by Kincaid and co-workers,<sup>2d</sup> who used these compounds as precursors for the preparation of zeolite-entrapped bis-heteroleptic Ru(II) polypyridine complexes. We tried a similar procedure (the “iterative” synthesis) to enhance the amount of  $\text{Ru}(\text{bpy})_3^{2+}$  in the high-loaded samples. The method consists of grinding the samples of the first batch with an excess of 2,2'-bipyridine and subsequent heating. Appreciable increases of  $[\text{Ru}(\text{bpy})_3^{2+}]$  were observed. Figure 5 presents an overlay of the electronic spectra of the  $86.8\%$ -loaded sample after the direct *in situ* synthesis and the 1st iterative and the 2nd iterative syntheses, recorded in solution after destruction



**Figure 5.** Absorption spectra of  $\text{Ru}(\text{bpy})_n(\text{NH}_3)_{6-2n}^{2+}\text{-Y}$  zeolites dissolved in hydrofluoric acid for the  $[\text{Ru}^{2+}]_{\text{T}} = 86.8\%$  sample after the direct *in situ* synthesis (a) and the 1st (b) and 2nd (c) iterative syntheses steps. After the 2nd iterative step,  $[\text{Ru}^{2+}]_{\text{T}}$  decreases to 84.2%, but the  $\text{Ru}(\text{bpy})_3^{2+}$  loading,  $[\text{Ru}(\text{bpy})_3^{2+}]$ , increases significantly (see Table 2). All spectra are taken at a concentration of 0.115 mg/mL.

of the zeolite framework. The maximum at lower energy for the MLCT band, situated at  $\lambda_{\text{max}} = 490$  nm, progressively turns into a shoulder to the benefit of the intensity of the first maximum at  $\lambda_{\text{max}} = 453$  nm; at the same time, the band centered at  $\lambda_{\text{max}} = 350$  nm progressively vanishes. The spectral features of the 2nd iteration products are closer to that of pure  $\text{Ru}(\text{bpy})_3^{2+}$  than they were at the beginning. An overview of this “iterative” synthesis approach is reported in Figure 4 and in Table 2.

**4. Location of the  $\text{Ru}(\text{bpy})_3^{2+}$  Chromophores.** The distribution of the  $\text{Ru}(\text{bpy})_3^{2+}$  complexes in the bulk material can be estimated by applying a slightly destructive procedure for the zeolite framework which causes *superficial damage only*. This treatment, performed with concentrated aqueous solutions of  $\text{NH}_4\text{PF}_6$  on samples of the direct *in situ* synthesis, allowed us to analyze the ruthenium compounds entrapped in a spatially restricted region close to the surface of the loaded zeolite Y microcrystals. We define the loading parameters  $[\text{Ru}(\text{bpy})_3^{2+}]_{\text{S}}$  and  $[\text{Ru}(\text{bpy})_3^{2+}]_{\text{Core}}$  as the number of  $\text{Ru}(\text{bpy})_3^{2+}$  extracted and that remaining, respectively, divided by the number of supercages  $n_{\text{sc}}$ , so that eq 2 holds.

$$[\text{Ru}(\text{bpy})_3^{2+}] = [\text{Ru}(\text{bpy})_3^{2+}]_{\text{S}} + [\text{Ru}(\text{bpy})_3^{2+}]_{\text{Core}} \quad (2)$$

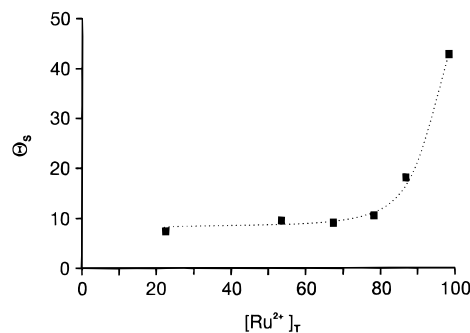
On the basis of this, we define the distribution parameter  $\Theta_{\text{S}}$  as follows:

$$\Theta_{\text{S}} = \frac{[\text{Ru}(\text{bpy})_3^{2+}]_{\text{S}}}{[\text{Ru}(\text{bpy})_3^{2+}]} \times 100 \quad (3)$$

If the guest  $\text{Ru}(\text{bpy})_3^{2+}$  complexes are randomly distributed in the host zeolite Y, the ratio  $\Theta_{\text{S}}$  will stay constant wherever it is measured in the bulk of each probe and also *whatever the loading is*. The data reported in Table 3 and illustrated in Figure 6 show that  $\Theta_{\text{S}}$  remains constant at low and intermediate loadings up to  $[\text{Ru}^{2+}]_{\text{T}} \approx 65\%$ . This behavior is expected for a homogeneous distribution of the chromophore in the zeolite Y microcrystals. For  $[\text{Ru}^{2+}]_{\text{T}} > 65\%$ , where the yield of formation of  $\text{Ru}(\text{bpy})_3^{2+}$  decreases,  $\Theta_{\text{S}}$  increases strongly with increasing  $[\text{Ru}^{2+}]_{\text{T}}$ , which corresponds to a nonhomogeneous filling. At  $[\text{Ru}^{2+}]_{\text{T}} = 98.3\%$ , almost half of the total amount of the  $\text{Ru}(\text{bpy})_3^{2+}$  loaded in the zeolite is concentrated toward

**Table 3.** Loading and Distribution Parameters Describing the Homogeneity of the Samples

$[\text{Ru}^{2+}]_{\text{T}}$ (%)	$[\text{Ru}(\text{bpy})_3^{2+}]$ (%)	$[\text{Ru}(\text{bpy})_3^{2+}]_{\text{S}}$		$\Theta_{\text{S}}$
		$\mu\text{mol/g}$	%	
22.5	21.7	7.4	1.6	7.4
53.5	51.7	22.8	4.92	9.5
67.3	51.2	21.5	4.65	9.1
78.2	39.7	19.3	4.17	10.5
86.8	23	19.3	4.16	18.1
98.3	7.9	15.7	3.39	42.8



**Figure 6.** Distribution parameter  $\Theta_{\text{S}}$ , as a function of the total ruthenium loading,  $[\text{Ru}^{2+}]_{\text{T}}$ .

the surface. Thus, the distribution of  $\text{Ru}(\text{bpy})_3^{2+}$  in the zeolite grains is space-dependent in highly loaded zeolite Y, and  $\text{Ru}(\text{bpy})_3^{2+}$  chromophores tend to accumulate on a superficial location.

## Conclusions

We have shown that the “ship-in-a-bottle” synthesis leads to almost pure  $\text{Ru}(\text{bpy})_3^{2+}$  up to a loading of about 50%. At higher loading the reaction is incomplete. Reacting the highly loaded samples a second and a third time with bpy leads to nearly pure  $\text{Ru}(\text{bpy})_3^{2+}$  in the zeolite Y supercages up to about 65% loading. However, attempts to fill nearly all supercages with one  $\text{Ru}(\text{bpy})_3^{2+}$  failed. Analysis of the homogeneity showed that at a loading up to about 65% a homogeneous distribution of the complexes is realized, but above 65% the complexes are first formed at sites close to the surface so that probably all or at least most of the outer supercages are occupied with a  $\text{Ru}(\text{bpy})_3^{2+}$ . Since one guest  $\text{Ru}(\text{bpy})_3^{2+}$  (diameter 12.1 Å) fills a host supercage (diameter 13 Å) of zeolite Y almost completely, these occupied supercages act as obstacles and they prevent the bpy from entering and finally reaching the inner part of the microcrystals. The critical occupation was found to be about 2 complexes per 3 supercages. We conclude that it is important to verify the identity of the complexes obtained by the “ship-in-a-bottle” procedure as a function of the loading by chemical means more carefully than it was done up to now. We suspect that some of the interpretations of photophysical and spectroscopic data reported in the literature should be reinvestigated.

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