

# After-effects of the $^{57}\text{Co}(\text{EC})^{57}\text{Fe}$ nuclear decay in tris(2,2'-bipyridyl)cobalt(II) encapsulated in the supercage of zeolite Y

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$^{57}\text{Fe}$  emission Mössbauer spectroscopy was used to study the after-effects of the  $^{57}\text{Co}(\text{EC})^{57}\text{Fe}$  decay in tris(bipy)cobalt(II) (bipy=2,2'-bipyridyl) encapsulated in the supercage of zeolite Y. The spectra revealed two low-spin species,  $[\text{}^{57}\text{Fe}(\text{bipy})_3]^{2+}$  and  $[\text{}^{57}\text{Fe}(\text{bipy})_3]^{3+}$ , as well as a high-spin species of  $[\text{}^{57}\text{Fe}(\text{bipy})_3]^{2+}$ . An anomalously high spectral contribution of  $\text{Fe}^{\text{III}}$  was found with an anomalous temperature dependence, i.e., the amount of  $\text{Fe}^{\text{III}}$  diminished with the temperature elevation. A time-delayed Mössbauer experiment was performed to determine the time scale of this phenomenon, which indicated that the processes responsible for the  $\text{Fe}^{\text{III}}$  to  $\text{Fe}^{\text{II}}$  transition was completed in the first nanoseconds after the nuclear decay. Another effect of the zeolite encapsulation was the absence of a second high-spin  $[\text{}^{57}\text{Fe}(\text{bipy})_3]^{2+}$  species identified in pristine crystalline compounds as an excited ligand field state of  $\text{Fe}^{2+}$ . This observation is attributed to the spatial restriction implied by the supercage. The possible fragmentation origin of the first high-spin  $[\text{}^{57}\text{Fe}(\text{bipy})_3]^{2+}$  species, the complex ion with a damaged ligand, is also discussed. © 1998 American Institute of Physics. [S0021-9606(98)03620-4]

## INTRODUCTION

Among the different systems comprising zeolites, the so-called “ship in a bottle complexes,” where coordination compounds are built up in the cavities of zeolites, are of particular interest, mostly because of their potential application as catalysts or main components of light-storage devices.<sup>1</sup> The rigid and stable zeolite framework with its interconnected cavities makes it possible to set up experiments where the nature of the environment of the entrapped complex can be varied in a more controlled way than in the pristine crystalline compound or in a solution. In addition, one can produce such systems for the purpose of the spatial separation of the complex molecules. This allows special spectroscopic investigations with no intermolecular interactions between the complexes, so the effects caused by the neighboring molecules in the bulk phase of the pristine crystalline compound can at least partially be excluded.

In the present work,  $[\text{}^{57}\text{Co}(\text{bipy})_3]^{2+}$  was synthesized in the supercages of specially pretreated zeolite Y in order to study the role of the microenvironment of the decaying  $^{57}\text{Co}$  (from the point of view of after-effects) by Mössbauer emission spectroscopy. The electron capture of  $^{57}\text{Co}$  generally triggers an Auger cascade, which is followed by a rapid neutralization process. These processes may lead to after-effects, i.e., changes in the valence state, bond rupture, and other

physicochemical effects.<sup>2–4</sup> The bipy ligand is known to be stable against self-radiolysis. Also, the nucleogenic  $[\text{}^{57}\text{Fe}(\text{bipy})_3]^{2+}$  ion has an  $^1A_1$  (low-spin) ground state, so its Mössbauer parameters make it easy to distinguish from any other species (i.e., the after-effect products), which differ in either valence or spin state. Moreover,  $[\text{}^{57}\text{Co}(\text{bipy})_3]^{2+}$  as well as  $[\text{}^{57}\text{Co}(\text{phen})_3]^{2+}$ , the latter having very similar properties, have been studied extensively, thus many aspects of the after-effects regarding these compounds have become clear by now.<sup>2–10</sup>

Zeolite Y<sup>11</sup> is an ideal matrix to separate Co-chelate molecules from each other, as it contains cavities with a size comparable to that of the chelates. The framework of the zeolite is built up from  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra forming smaller cavities (sodalite cages, hexagonal prisms) and larger ones (supercages), the latter with a diameter of 1.3 nm. Due to the tetrahedral arrangement, each supercage has four openings to neighboring supercages with a diameter of 0.75 nm. The negative charge of the  $\text{AlO}_4$  units of the lattice should be compensated by cations, which can be easily exchanged with other cations. However, if a cation, like  $[\text{}^{57}\text{Co}(\text{bipy})_3]^{2+}$ , is too large due to its coordinated ligands, the zeolite framework may be impenetrable for it. On the other hand, if a cation is exchanged into the zeolite in the form of a free ion, i.e., an aquacomplex, and then a ligand that forms a strong complex with the cation is added to the

system, the stable complex may form in the cavities and is trapped right away.<sup>12</sup> We shall refer to this system as  $[^{57}\text{Co}(\text{bipy})_3]^{2+} @ \text{Y}$  to emphasize entrapment.

One can take advantage of this situation to encapsulate  $[^{57}\text{Co}(\text{bipy})_3]^{2+}$  in the large cavities of zeolite Y.  $\text{Co}^{2+}$  ions can be exchanged at any cation site in the zeolite, but after reacting  $\text{Co}^{\text{II}}\text{-Y}$  with 2,2'-bipyridyl (which easily penetrates into the structure),  $[^{57}\text{Co}(\text{bipy})_3]^{2+}$  can form only in the supercages. It is vital to prevent  $\text{Co}^{2+}$  from migrating into the sodalite cage, where, for steric reasons, complex formation is impossible,<sup>6</sup> otherwise the appearance of extra lines would cause difficulties in the interpretation of the emission Mössbauer spectra. To avoid this problem, we exploited the properties of the Na-Y(La) system described in Ref. 13 to block sodalite cages from cobalt by filling them up with lanthanum.

## EXPERIMENTAL SECTION

### A. Preparation of zeolite-encapsulated complexes

*Na-Y(La).* The Na-exchanged zeolite Y was ion exchanged with  $\text{La}^{3+}$ . Then Na,L a-Y was heated at 450 °C for several hours in air, which resulted in a strong bonding of lanthanum with the cationic sites of the sodalite cages, making it incapable of further cationic exchange.<sup>13</sup> Na-Y(La) prepared in this way was used for all Mössbauer experiments as a starting material.

$[\text{Fe}(\text{bipy})_3]^{2+} @ \text{Y(La)}$  and  $[\text{Fe}(\text{bipy})_3]^{3+} @ \text{Y(La)}$ . Preparation of  $[\text{Fe}(\text{bipy})_3]^{2+} @ \text{Y(La)}$  is described in Ref. 14. For the oxidation of the encapsulated complex, the sample was first evacuated at  $10^{-5}$  Torr for several hours then treated with chlorine gas at 50 °C for 20 h. In accordance with the remarkable stability of the  $[\text{Fe}(\text{bipy})_3]^{2+}$  state ( $\epsilon^0 = 0.96$  V), only 15% of the total iron content could be oxidized.

$[^{57}\text{Co}(\text{bipy})_3]^{2+} @ \text{Y(La)}$ . For the synthesis of zeolite-encapsulated tris(2,2'-bipyridyl)- $^{57}\text{Co}^{2+}$ , 200 mg Na-Y(La) was reacted with an aqueous solution of 2.7 mg  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  doped with 1 mCi  $^{57}\text{Co}$  at pH 5. The mixture was stirred for a day and then centrifuged in order to separate the light pink colored zeolite from the liquid phase. Removing the solution, Co-Y(La) was then washed with 20 cm<sup>3</sup> of distilled water four times. The activity of the removed liquid portions was about 1.4% of the total activity, indicating that the ion exchange was practically quantitative. This amount of  $\text{Co}^{2+}$  results in ion exchange in one supercage out of 9, i.e., nearly one  $\text{Co}^{2+}$  per unit cell. After removing the last portion of distilled water from the centrifuge tube Co-Y(La) was reacted with 15 cm<sup>3</sup> ethanol containing 23 mg 2,2'-bipyridyl (three-fold excess). This mixture was stirred overnight in a closed centrifuge tube at room temperature. Finally, the light beige colored zeolite was washed with 20 cm<sup>3</sup> ethanol five times. The ethanol showed no activity after washing, indicating that all  $^{57}\text{Co}^{2+}$  was trapped effectively in the supercages in the form of tris(2,2'-bipyridyl)- $^{57}\text{Co}^{2+}$  complex. The sample was then dried at 80 °C overnight. For Mössbauer measurements, the dry powder was put into a sample holder and sealed. The sample holder was then mounted on a cryotip.

$[\text{Co}(\text{bipy})_3]^{2+} @ \text{Y(La)}$  and  $[\text{Co}(\text{bipy})_3]^{3+} @ \text{Y(La)}$ . For electronic absorption measurements inactive samples were prepared in the same way as described above. The aqueous suspension of the inactive sample was exposed to oxygen bubbling through it overnight to obtain the oxidized form of the entrapped complex.

### B. Characterization of zeolite-encapsulated tris(2,2'-bipyridyl)- $\text{Co}^{11}$

*X-ray diffractometry.* X-ray diffractograms were taken by a Phillips PW 1830 diffractometer using Ni-filtered  $\text{Cu K}_\alpha$  radiation in the range of  $2\theta = 4^\circ - 50^\circ$ .

*Electronic absorption spectra.* Spectra were obtained with a MR 3000 spectrometer in the 200–900 nm range. The zeolite samples were dispersed in mineral oil to help the recording of transmission spectra.

### C. Mössbauer spectroscopic measurements

*Mössbauer absorption spectra (MAS).* Spectra were obtained with a Wissel spectrometer operated in a constant acceleration mode. All the isomer shift values in this paper are given with respect to an  $\alpha$  iron at room temperature.

*Time-integral Mössbauer emission spectra (TIMES).* Spectra were obtained with a Wissel spectrometer operated in constant acceleration mode. The data were collected for 5 to 12 days over the temperature range 30–250 K using a moving standard PFC absorber. The sample was kept in a vacuum ( $10^{-4}$  Torr). The velocity scale of every emission spectrum has been reversed for better comparison with Mössbauer absorption spectra.

*Time-delayed Mössbauer emission spectrum (TDMES).* The spectrum was obtained with a coincidence Mössbauer spectrometer described in Ref. 15. The measuring time was two months. TDMES was recorded at 222 K with only one time window of 80 ns to 400 ns for technical reasons.

## RESULTS

The quality of the samples was checked by XRD using nonradioactive materials. The clear XRD patterns showed that the zeolite framework was intact in each sample. For the determination of the location of the complex we have adapted the method used by Quayle *et al.*,<sup>12</sup> which is based on the comparison of the intensity of the [220], [311], and [331] reflections of zeolite Y. If the cationic sites of the supercages are not occupied by large transition metal complexes, then the small cations are randomly distributed, and the [220] reflection is more intense than that of [311]. This is the case in the Na-Y and Co-Y samples, and even in  $\text{Co}(\text{bipy})_3/\text{Na-Y}$ , where Na-Y is impregnated with the preprepared  $[\text{Co}(\text{bipy})_3]^{2+}$  complex, that is, the complex ions are not intercalated. After synthesis of the complex in the supercage, the relative intensity of the [220] and [311] reflections is reversed [Fig. 1(a)]. The introduction of lanthanum into the smaller cavities changes the XRD patterns, mostly by reducing the intensities, but its effects upon the tendency described above have not been analyzed in the literature. In the diffractogram of Na-Y(La), the [220] reflection practically disappears, [311] has very small intensity,

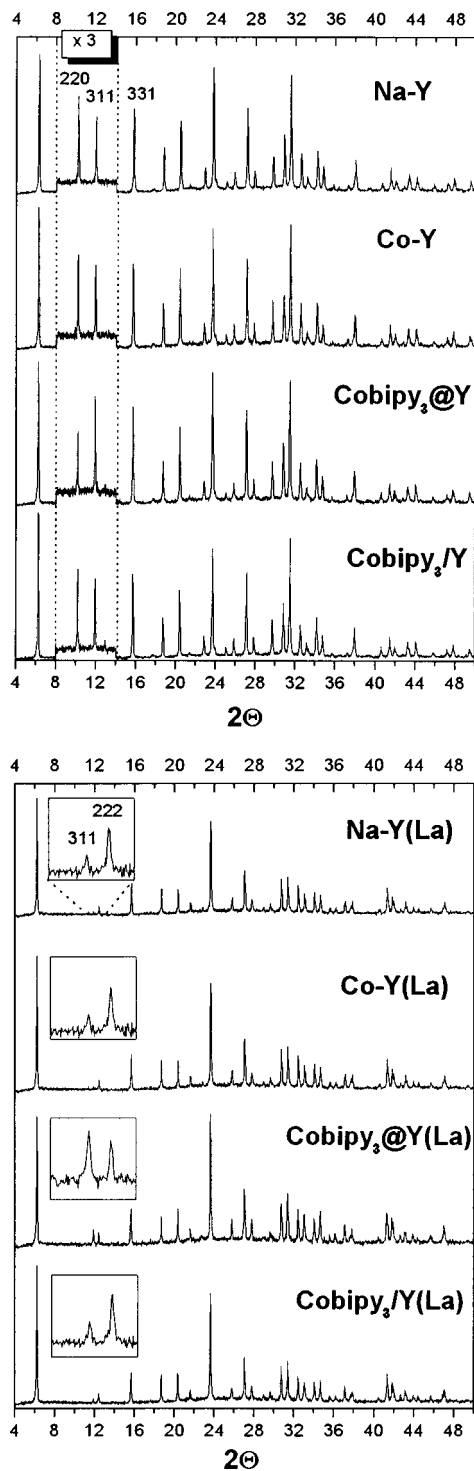


FIG. 1. Effects of formation of the  $[\text{Co}(\text{bipy})_3]^{2+}$  complex on the XRD patterns of (a) Na-Y and (b) Na-Y(La). Note that the intensity values for the  $2\theta = 8^\circ - 12^\circ$  interval are three-fold enlarged in (a). Also, the relevant region for each diffractogram can be seen magnified in the corresponding inserts in (b).

and the [222] reflection shows up with a considerable intensity. This is valid for Na-Y(La), Co-Y(La), and  $\text{Co}(\text{bipy})_3/\text{Na-Y}(\text{La})$ . However, the relative intensity of [311] exceeds that of [222] when the supercages are filled with the chelated  $\text{Co}^{2+}$  [Fig. 1(b)]. This increase of the  $I_{311}$  upon complex formation in the supercages of Y(La) is in accordance with the intensity variations described above for

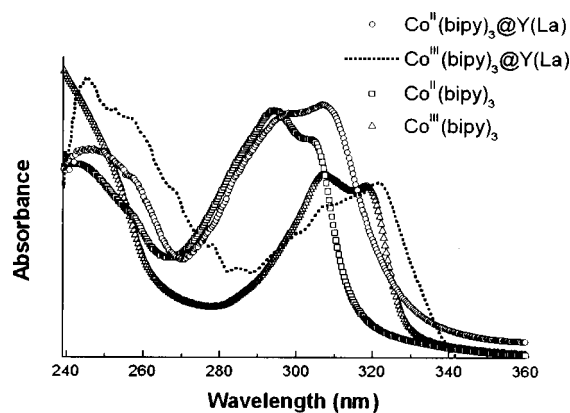


FIG. 2. Electronic absorption spectra of the divalent and trivalent tris(bipyridyl)cobalt complex in solution and in the zeolite cavities.

the Na-Y system. Moreover, our preliminary investigations on other complexes [e.g.,  $\text{Fe}(\text{bipy})_3$ ,  $\text{Co}(\text{terpy})_2$ ] synthesized in Y(La) gave similar XRD behavior, which also confirms that the encapsulation of complexes in the supercages of Y(La) can be followed by the relative intensity increase of the [311] reflection.

For the interpretation of the ME spectra, it is crucial to have information about the initial oxidation state of cobalt in the encapsulated molecule. Since in complexes with a strong ligand field one may expect  $\text{Co}^{\text{II}}$  to become sensitive to oxidation due to the stable  $t_{2g}^6$  valence shell configuration of low-spin  $\text{Co}^{\text{III}}$ , we have checked our samples by recording electronic absorption spectra. Figure 2 shows the relevant 240–350 nm region. A comparison with reference spectra of aqueous solutions of  $[\text{Co}(\text{bipy})_3]^{2+}$  and  $[\text{Co}(\text{bipy})_3]^{3+}$  revealed that the zeolite-encapsulated samples contained the  $\text{Co}^{\text{II}}$  form. The bathochromic shift caused by the zeolite on both oxidation states of the complex is worth noting.

Mössbauer absorption spectra of  $[\text{Fe}(\text{bipy})_3]^{2+}$  and  $[\text{Fe}(\text{bipy})_3]^{3+}$  synthesized in the supercage of zeolite Y are known from the literature.<sup>12</sup> However, inconsistency in the reported isomer shift values, reports<sup>16</sup> about the distortion of the encapsulated complex, as well as the somewhat different nature of our sample (namely, the presence of lanthanum, and the lower loading of the supercages), suggested that we should perform a reference measurement on  $[\text{Fe}(\text{bipy})_3]^{2+}@\text{Y}(\text{La})$ . In a recent publication<sup>14</sup> we showed that there was no sign of distortion of the tris(2,2'-bipyridyl)- $\text{Fe}^{2+}$  in the supercage present in the Mössbauer spectrum. In order to see the Mössbauer parameters of the  $\text{Fe}^{\text{III}}$  state in the supercage, the encapsulated complex was oxidized by a treatment with chlorine gas. Comparing the spectrum obtained on this sample with that of  $^{57}\text{Co}(\text{bipy})_3^2+@\text{Y}(\text{La})$ , the nucleogenic  $^{57}\text{Fe}(\text{bipy})_3^{2+}$  and  $^{57}\text{Fe}(\text{bipy})_3^{3+}$  forms could be convincingly identified [Fig. 3(a)].

Mössbauer emission spectra of  $[\text{Co}(\text{bipy})_3]^{2+}@\text{Y}(\text{La})$  recorded from 30 to 250 K indicated three different species with variable amounts (Fig. 4). The decomposition of the spectra is shown in Fig. 3(b); the relative intensities are tabulated in Table I. The major part of the spectra consisted of two characteristic doublets with isomer shifts ( $\delta$ ) 0.35–0.38

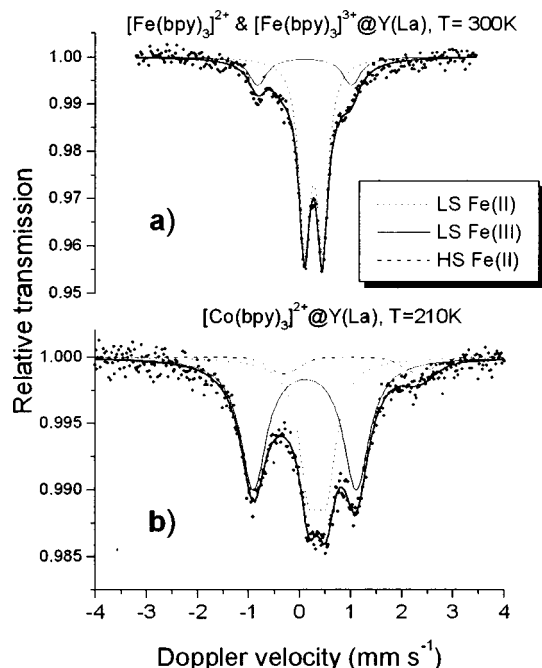


FIG. 3. (a) Mössbauer absorption spectrum of  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}(\text{bipy})_3@Y(\text{La})$ . (b) Decomposition of the Mössbauer emission spectrum of  $\text{Co}^{\text{II}}(\text{bipy})_3@Y(\text{La})$ .

and 0.10–0.17 mm/s and quadrupole splittings ( $\Delta$ ) 0.31–0.35 and 1.9–2.0 mm/s, respectively. These parameters perfectly match those of the corresponding low-spin (LS)  $\text{Fe}^{\text{II}}$  and LS  $\text{Fe}^{\text{III}}$  bipyridyl chelates. The third component with  $\delta = 1.0$ –1.2 mm/s and  $\Delta = 2.2$ –2.6 mm/s is a high-spin (HS)  $\text{Fe}^{\text{II}}$  species. The relative intensity of these species did show a remarkable temperature variation (Table I). The amount of the high-spin species decreased from 21% to about 8% as the temperature was raised from 30 to 170 K. Above this temperature, there was no more significant change. The LS spe-

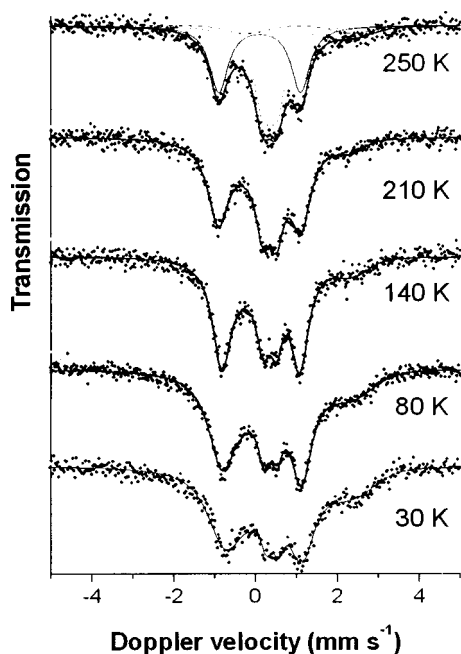


FIG. 4. The temperature dependence of the time-integral Mössbauer emission spectra of  $\text{Co}^{\text{II}}(\text{bipy})_3@Y(\text{La})$ .

TABLE I. Relative intensities in the TIMES of  $\text{Co}^{\text{II}}(\text{bipy})_3@Y(\text{La})$ .

T/K	Evacuated sample			Sample exposed to air		
	LS $\text{Fe}^{\text{III}}$	LS $\text{Fe}^{\text{II}}$	HS $\text{Fe}^{\text{II}}$	LS $\text{Fe}^{\text{III}}$	LS $\text{Fe}^{\text{II}}$	HS $\text{Fe}^{\text{II}}$
30	0.670	0.120	0.210	...	...	...
80	0.655	0.175	0.180	0.665	0.103	0.232
140	0.621	0.262	0.117	...	...	...
170	0.617	0.298	0.085	0.612	0.162	0.226
210	0.565	0.375	0.059	...	...	...
250	0.450	0.470	0.080	0.491	0.275	0.234

cies showed a more pronounced variation: the amount of LS  $\text{Fe}^{\text{III}}$  decreased, that of LS  $\text{Fe}^{\text{II}}$  increased with increasing temperature. At the same time, the total amount of  $\text{Fe}^{\text{II}}$  increased, and the isomer shifts varied similarly with the elevation of temperature. These findings indicate that the observed phenomenon is not an artefact of the different temperature behaviors of the Mössbauer–Lamb factors.

The time-delayed and the time-integral spectra recorded simultaneously are shown in Fig. 5. Apart from the expected decrease in the linewidths of the time-delayed spectra and different statistics, the two spectra are identical.

The zeolite cavities contain adsorbed molecules, even in a vacuum. Most of these molecules in our sample must have been ethanol due to the preparation procedure. The guest molecules can be mobile and thus take part in transfer processes or reactions after the electron capture. Changing these molecules, therefore, can affect the spectra, which allows more insight into the processes following the EC decay. To achieve this, the evacuated sample was exposed to air for several days, so oxygen, water, etc. could fill the cavities. Afterward we measured emission Mössbauer spectra at three different temperatures with a nonevacuated sample holder, where the adsorbed water (and oxygen) could remain in the zeolite. The results are shown in Table I. One significant difference was found as compared to the former series of

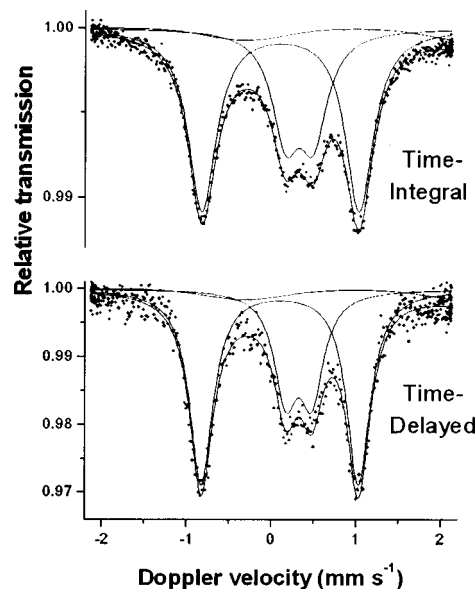


FIG. 5. The time-delayed and the simultaneously recorded time-integral Mössbauer emission spectrum of  $\text{Co}^{\text{II}}(\text{bipy})_3@Y(\text{La})$ .

measurements, namely, the relative amount of the HS Fe<sup>II</sup> species lost its temperature dependence, giving 23% of the total spectral area at all the measured temperatures. After washing the sample for a day with ethanol, the ME spectrum at 80 K became identical with that measured before the exposure to air.

## DISCUSSION

In order to explain the presence and the temperature dependence of the species observed by us in the zeolite-encapsulated [Co(bipy)<sub>3</sub>]<sup>2+</sup>, some recent Mössbauer spectroscopic results on the pristine compound might be usefully quoted. Note that these results are supported by analogous results obtained on systems containing [Co(phen)<sub>3</sub>]<sup>2+</sup> complexes.<sup>2,3</sup>

Deisenroth *et al.* studied [<sup>57</sup>Co/Mn(bipy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> both in powdered<sup>8</sup> and in single crystal<sup>9</sup> form. In the time-integral emission spectrum four species could be identified. Two LS species represented Fe<sup>II</sup> and Fe<sup>III</sup>, and two HS Fe<sup>II</sup> species were also found with a very remarkable temperature dependence. The relative intensity of the LS Fe<sup>III</sup> species (as well as that of the analogous component in the spectra of [Co(phen)<sub>3</sub>]<sup>2+</sup>) remained constant at all temperatures. One of the HS species, HS1 (with approximate parameters  $\delta = 1.1$  mm/s and  $\Delta = 1.2$  mm/s at 100 K) was identified as an excited ligand field state of Fe<sup>2+</sup> by comparison of lifetimes obtained from optical lifetime measurements on the analogous iron compound and from TDMES measurements on [<sup>57</sup>Co/Mn(bipy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>. The second HS component, HS2, did not decay up to room temperature, and it was attributed to a distorted environment (e.g., a species with a damaged ligand).

There are two major differences between the Mössbauer spectra of crystalline [<sup>57</sup>Co/Mn(bipy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> and zeolite-encapsulated [Co(bipy)<sub>3</sub>]<sup>2+</sup>.

First, the relative amount of the LS Fe<sup>II</sup> species is much lower and the amount of the LS Fe<sup>III</sup> species is much higher in the zeolite-encapsulated compound than in the pristine one at comparable temperatures. Moreover, the relative amount of the LS Fe<sup>III</sup> species, unlike in the other analogous compounds investigated so far, where this fraction was constant at all temperatures,<sup>3,10</sup> diminished with the increase in the temperature. It is clear from the work of Srivastava *et al.*<sup>7</sup> and also from a later work of Afanasov *et al.*<sup>6</sup> that the amount of LS Fe<sup>II</sup> very sensitively depends on the matrix in which the complex is embedded. These authors performed experiments systematically on the trivalent Co(bipy)<sub>3</sub> complex dispersed in various matrices, and found a LS Fe<sup>II</sup> fraction as much as 60% in the spectra (at 80 K). In our experiments, the LS Fe<sup>II</sup> fraction varies from 10% to 45% as a function of the temperature and, most importantly, this variation shows temperature reversibility. This proves that (a substantial fraction of) the LS Fe<sup>III</sup> state of the nucleogenic Fe(bipy)<sub>3</sub> complex is a consequence of the effect of the closest environment on the neutralization process following the Auger events. In other words, the final valence state of the Fe(bipy)<sub>3</sub> complex is determined by the donor/acceptor properties of the matrix. With this model, the decrease of the

TABLE II. Fitting parameters for the relative intensity data of the Fe<sup>III</sup> fraction in the time-integral spectra.

	$p_A(\infty) = 0$	$p_A(\infty) = 0.45$
A	$3.06(3.87) \times 10^8$	$2.94(1.31) \times 10^{11}$
$E^*$	$9.6(2.6)$ kJ/mol	$19.6(8.3)$ kJ/mol
$p_A(0)$	$0.652(12)$	$0.644(13)$

fraction of LS Fe<sup>III</sup> with increasing temperature can also be explained: as the donation of an electron to an Fe<sup>3+</sup> species must be a thermally activated process, at a higher temperature more Fe<sup>II</sup> is to be expected.

Since irradiated zeolites are known to behave as electron acceptors and to stabilize the ionized forms of intercalated molecules,<sup>17</sup> the relatively large Fe<sup>III</sup>/Fe<sup>II</sup> ratio makes good sense. The LS Fe<sup>III</sup> species represents a ground state, so its decrease is probably due to an Fe<sup>III</sup> + e<sup>-</sup> → Fe<sup>II</sup> reaction with Arrhenius-type temperature dependence (which may take place in the Mössbauer time window), rather than the result of the relaxation of an excited state.

The observation of such reactions via Mössbauer spectroscopy is very rare, because of the strict time requirements concerning the rate of the reaction to appear in the Mössbauer time window. However, we can examine theoretically what effects would be imposed on the Mössbauer spectra in this situation, and check their presence experimentally.

For simplicity, let us denote the Fe<sup>III</sup> species as A. The spectral intensity of A in the time-integral Mössbauer emission spectrum (TIMES) is

$$P_A = \frac{1}{\tau_M} \int_0^\infty p_A(t) e^{-t/\tau_M} dt, \quad (1)$$

where  $\tau_M = 141$  ns and  $p_A(t)$  is the amount of A at time  $t$ . With Fe<sup>III</sup> one can expect a pseudo-first-order reaction, therefore,  $p_A(t)$  takes the form  $p_A(t) = [p_A(0) - p_A(\infty)]e^{-kt} + p_A(\infty)$ , in which  $k$  can be expressed in the well-known form of the Arrhenius equation:

$$k = A e^{-E^*/RT}.$$

The above argument suggests that the temperature dependence of  $P_A$  arises from the temperature dependence of  $k$ . One can fit the  $P_A(T)$  data with Eq. (1). Since  $p_A(\infty)$  is not known, for the fitting we used both possible extremes, 0 and 0.45, the latter representing  $P_A$  at 250 K (cf. Table I). The fitting parameters are shown in Table II, and the fitted data and the fitting functions are shown in Fig. 6. The significance of the results of the fitting should not be overestimated, but they are very suitable for predicting the spectral intensities for different temperatures and different time windows of TDMES.

One should keep in mind that the  $t=0$  event for the Mössbauer spectra occurs, on average, 12 ns after the EC. Therefore, if the reduction of Fe<sup>III</sup> takes place within the first 12 ns, the temperature dependence of the spectral intensity will show the temperature dependence of  $p_A(0)$ . A decision between the two possible situations requires a TDMES measurement, where the time evaluation of the Mössbauer spectra can be followed.

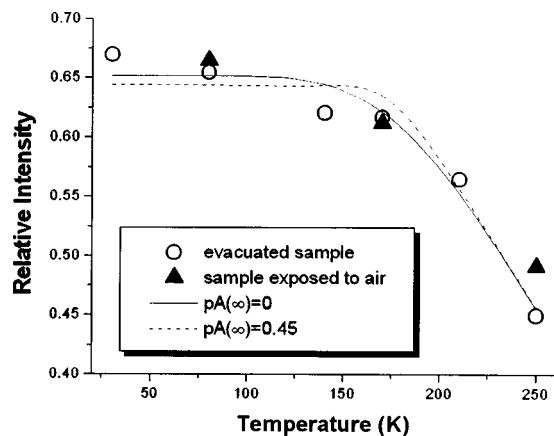


FIG. 6. Relative intensity of the  $\text{Fe}^{\text{III}}$  fraction in the time-integral spectra, with two fitting curves (cf. the description in the text).

The time-delayed spectrum was recorded at 222 K (where the temperature behavior suggests a rapid reaction), with only one time window of 80–400 ns after the population of the 14.4 keV energy level of the  $^{57}\text{Fe}$  nucleus. In this case, the modifications needed on Eq. (1) are changing its integration limits and the normalization ( $N$ ):

$$P_{\text{A}}^{\text{DEL}} = \frac{1}{N} \int_{8 \times 10^{-8}}^{4 \times 10^{-7}} p_{\text{A}}(t) e^{-t/\tau_{\text{M}}} dt.$$

The measured time-integral and time-delayed spectra are shown in Fig. 5. To test whether the charge relaxation occurs in the Mössbauer time window, one has to compare the calculated and measured  $P_{\text{A}}/P_{\text{A}}^{\text{DEL}}$  ratios. The calculated ratios are 1.15 and 1.08 for  $p_{\text{A}}(\infty)=0$  and  $p_{\text{A}}(\infty)=0.45$ , respectively. The measured ratio falls out of this region: it is 0.98(4), which undoubtedly indicates the absence of time dependence in the time interval available for Mössbauer spectroscopy, that is,  $p_{\text{A}}(t)=p_{\text{A}}(0)$ . The temperature dependence of the  $\text{Fe}^{\text{III}}$  species observed in the TIMES, therefore, is due to some processes taking place in the first 12 ns following the electron capture. The lack of time dependence in the Mössbauer time window rules out the probability of temperature having a direct effect on the observed  $\text{Fe}^{\text{III}} + e^- \rightarrow \text{Fe}^{\text{II}}$  reaction. Therefore, the observed temperature-dependent behavior must be due to an effect on the availability of the charge carriers responsible for the reaction. The number of electron–hole pairs (i.e., charge carriers) created in the track of Auger electrons are independent of temperature, but their mobility, and also the donor/acceptor properties of the matrix depend on the ambient temperature. It is plausible that the observed variation simply reflects this dependence. However, it is still puzzling why the LS  $\text{Fe}^{\text{III}}$  fraction is constant at all temperatures in other samples of  $[\text{Co}(\text{bipy})_3]^{2+}$  and  $[\text{Co}(\text{phen})_3]^{2+}$  that have been studied on various occasions. We expect that our ongoing systematic studies, when we modify the donor/acceptor properties of the matrix by filling up the cavities around the encapsulated complexes with different substances, will shed some light on this problem.

The second main difference between the zeolite-encapsulated  $[\text{Co}(\text{bipy})_3]^{2+}$  and  $^{57}\text{Co}/\text{Mn}(\text{bipy})_3(\text{PF}_6)_2$  is

that only one HS  $\text{Fe}^{\text{II}}$  species could be found in the former case in the investigated temperature range. The “missing” HS species is the one that was identified<sup>8</sup> as an excited ligand field state of  $\text{Fe}^{2+}$  and designated by HS1. This state is analogous to the HS state found in spin-crossover compounds, as became clear after the discovery of the effect called light-induced excited spin state trapping (LIESST).<sup>18</sup> In the ME spectra of spin-crossover systems this component is predominant, and these spectra do not comprise the LS  $\text{Fe}^{\text{II}}$  lines at any temperature. Even in the case of low-spin compounds, like  $[\text{Fe}(\text{bipy})_3]^{2+}$  and  $[\text{Fe}(\text{phen})_3]^{2+}$ , a HS→LS relaxation can be observed in the time-differential ME spectra, where the ratio of the initial population of LS  $\text{Fe}^{\text{II}}$  to that of HS1 has been determined to be very close to zero;<sup>10</sup> this suggests that the LS  $\text{Fe}^{\text{II}}$  species forms via the decay of the HS states. In the light of these facts, our observation is rather interesting, and shows that the effect of the zeolite on the nucleogenic complex is enormous. With iron(II) complexes having  $\text{FeN}_6$  cores, the metal–ligand bond lengths belonging to this HS  $^5T_2$  state are known to be some 20 pm longer than those of the LS  $^1A_1$  ground state.<sup>19</sup> Transition to the  $^5T_2$  state, therefore, involves a relatively large expansion of the molecule, which in our case is hampered by the zeolite. Since it is well established that the rate of the HS→LS relaxation can be increased if one applies pressure on the system,<sup>19</sup> in our case, the steric effect of the zeolite leads to a situation when the energy of the  $^5T_2$  state is much higher, and so the relaxation of this excited ligand field species to the ground state becomes so fast that it cannot be seen in the Mössbauer time window.

The identification of the high-spin species as an analog to HS2 in  $^{57}\text{Co}/\text{Mn}(\text{bipy})_3(\text{PF}_6)_2$  is based on the Mössbauer parameters as well as on its long lifetime. As mentioned before, HS2 was considered to be a  $[\text{Fe}(\text{bipy})_3]^{2+}$  species, either with a distorted environment or a damaged bipyridyl ligand.<sup>8</sup> It is improbable that this defect in the ligand would be simply (due to) a missing electron, since the necessary  $[\text{Fe}^{\text{II}}(\text{phen})^+(\text{phen})_2]^{3+}$  LMCT state in the analogous  $[\text{Fe}(\text{phen})_3]^{3+}$  complex was found to be very short lived (ca. 10 ps).<sup>2</sup>

The formation of a damaged ligand may be explained by the fragmentation of the complex molecule. As proposed earlier<sup>5</sup> by Nath *et al.*, coordination compounds of nucleogenic  $^{57}\text{Fe}$  may not survive the neutralization process, in which several tens of electron-volts are deposited on the molecule that may lead to fragmentation of the molecule. In some cases, however, fragmentation is not observed, and it was concluded that the higher the conjugation of the ligands is, the lower the chance of fragmentation becomes. In what follows, we discuss the behavior of the HS  $\text{Fe}^{\text{II}}$  (HS2) component through this fragmentation model.

In the highly conjugated  $[\text{Co}(\text{bipy})_3]^{2+/3+}$ , the extent of fragmentation is expected to be low, in agreement with the low intensity of HS2. It is also logical to assume that the recombination of the fragmented molecule is faster at a higher temperature, thus the intensity of HS2 is expected to decrease, and this is precisely what was observed. If the fragmented species have to compete for the metal ion with other molecules like water, this would also result in the higher

intensity of the HS2 doublet in the emission spectra. And indeed, this was observed in our experiments on the sample exposed to air (Table I).

With these spectra, rather surprisingly, the relative amount and temperature behavior of LS Fe<sup>III</sup> did not show any significant difference from those observed in the evacuated sample. This means that the highly reactive oxygen and water molecules did not influence the formation and reduction of the aliovalent LS Fe<sup>III</sup> species. However, the HS Fe<sup>II</sup> fraction was the same for all three temperatures. This indicates that the HS component is completely different in nature from the HS1 component, an excited electronic state often found in such systems. The relaxation of the HS Fe<sup>II</sup> component found in our system can be hampered by introducing water and oxygen, which means that these molecules either have a direct effect on the ligands that makes them incapable of relaxing to the LS Fe<sup>II</sup> ground state, or they influence the environment (i.e., the zeolite framework) not to participate in a process that could help in some form the mentioned relaxation.

The very broad lines of the HS2 doublet, and the fact that this doublet did not show any asymmetry at any angle in the single crystal experiment of Deisenroth *et al.*, are also consistent with the fragmentation origin. For a closer identification of the damaged ligand, one may take into account that a rupture of the relatively strong C–C or C–N bonds as a consequence of charge neutralization following the Auger ionization is not likely. What can occur is the rupture of the metal–ligand bonds, and perhaps a change in the conformation of the bipyridyl molecule. If, during recombination, the equilibrium conformation is not attained, and this can occur especially at low temperatures, the resultant species will have a diminished ligand field strength and, consequently, a high-spin state.

Comparing the fraction of the HS2 species in the zeolite-encapsulated [Co(bipy)<sub>3</sub>]<sup>2+</sup> and [<sup>57</sup>Co/Mn(bipy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>, one can conclude that they are roughly equal. If we now assume that this is the species that exclusively represents the fragmentation events, then it seems to be clear that the neighboring molecules of the same type (in pristine compounds) have no substantial influence on the probability of fragmentation. This supports the existence of the mechanism of rapid energy dissipation from the molecule suggested by Nath *et al.*,<sup>20</sup> namely, that the collectively excited conjugated system (plasmon state), formed as a consequence of charge neutralization, can get rid of its excitation energy by ejecting one single high-energy electron. A recent investigation into C<sub>60</sub> revealed a plasmon state decaying via this type of relaxation, that is, an emission of an electron.<sup>21</sup> This mechanism is rapid enough to save the molecule from fragmentation. The non-fragmented part can be observed in the spectra as a ground state, low-energy excited state (like HS1) or an aliovalent charge state.

## CONCLUSIONS

The zeolite encapsulated has several effects on the fate of the nucleogenic [<sup>57</sup>Fe(bipy)<sub>3</sub>]<sup>2+/3+</sup>. The Fe<sup>III</sup> fraction is

unexpectedly large, and shows an unusual temperature dependence. These facts can be explained by the donor/acceptor properties of the zeolite host. The steric hindrance of the supercage elevates the energy level of the <sup>5</sup>T<sub>2</sub> state of the [Fe(bipy)<sub>3</sub>]<sup>2+</sup>, thus substantially shortening its lifetime. The behavior of the other high-spin Fe<sup>II</sup> species can be seen as a result of its possible fragmentation origin.

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