

Aftereffects in zeolite-encapsulated ^{57}Co -complexes

Z. Homonnay^a, Gy. Vankó^a, A. Vértes^a, A. Nath^b, H. Spiering^c and P. Gütlich^c

^aDepartment of Nuclear Chemistry, Eötvös Loránd University, P.O. Box 32, H-1518 Budapest, Hungary

^bDepartment of Chemistry, Drexel University, Philadelphia, PA 19104, USA

^cInstitut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität, Staudinger Weg 9, D-55099 Mainz, Germany

Tris(2,2'-bipyridyl)- $^{57}\text{Co}^{\text{II}}$ and bis(2,2':6',2''-terpyridine)- $^{57}\text{Co}^{\text{II}}$ complexes were synthesised in the supercages of zeolite-Y in order to study the effect of molecular isolation on the aftereffects of the $^{57}\text{Co}(\text{EC})^{57}\text{Fe}$ decay. As compared to the regular crystalline salts of the complex ions where, according to the emission Mössbauer spectra, the most abundant species is low-spin Fe^{II} , the molecular isolation in the zeolite resulted in a larger fraction of low-spin Fe^{III} and a varying amount of high-spin Fe^{2+} species. In the investigated temperature range, 20 K to 295 K, the majority of the changes was observed above 80 K. In the case of tris(2,2'-bipyridyl)- $^{57}\text{Co}^{\text{II}}\text{-Y}$, the most characteristic change occurred in valence states, while for bis(2,2':6',2''-terpyridine)- $^{57}\text{Co}^{\text{II}}\text{-Y}$, the temperature dependence of the spin states was more prominent. The change in the low spin valence states is explained partly by donor-acceptor properties of the zeolite lattice. The variation in the high spin fraction is explained by radiation damage of the ligand sphere and/or fragmentation of the complex ion followed by incomplete recombination in the supercage. Molecular isolation itself did not seem to increase the chance of fragmentation (as a consequence of charge neutralization following Auger ionization) of these highly conjugated complex molecules.

1. Introduction

Mössbauer spectroscopy provides a unique tool to hot atom chemists to study hot atom processes [1]. The $^{57}\text{Co}(\text{EC})^{57}\text{Fe}$ decay is one example. In this case, the radiochemical consequences of an electron capture may be witnessed in the closest vicinity of the daughter nuclide in a well defined time interval by the help of the Mössbauer effect of ^{57}Fe . As part of the decay, a neutrino with 0.7 MeV maximum energy is emitted, but the 4.6 eV recoil energy associated with this emission is not enough to cause rupture of chemical bonds. The electron capture of ^{57}Co is followed by an Auger cascade which was first studied theoretically by Pollak [2], and found that iron can be ionized up to 7 or 8 fold positive charge depending on the initial valence state. This process is known to be completed in less than 10^{-15} s. As the 14.4 keV level of the ^{57}Fe nucleus is populated only 1.3×10^{-8} s after the electron capture of ^{57}Co , this is the time when one may start to track the events by recording Mössbauer spectra. In order to explain the aftereffect peaks appearing in the Mössbauer spectra one has to find either an appropriately slow relaxation process associated somehow

with the Auger cascade, or a possible output of the events that yields a stable or metastable species within about 10^{-8} s.

The Auger ionization of the nucleogenic ^{57}Fe atom is followed by a rapid neutralization process which is accompanied by deposition of a large amount of excitation energy on the parent molecule. Nath et al. proposed that this is the key process for the fate of the molecule containing ^{57}Co , and in many cases one can expect fragmentation of the molecule [3,4]. It was observed by the authors that the higher the degree of conjugation of the ligand sphere of the nucleogenic ^{57}Fe , the less is the chance for fragmentation. Even if one disregards the possible role of the energy build-up during charge neutralization, it became clear that the imminent surroundings of the ^{57}Co atom is crucial to the fate of the nucleogenic ^{57}Fe ion. The ligands may show different resistance against Auger electrons and X-rays, thereby affecting the charge redistribution process and the spin state after the Auger event. Irradiation experiments performed by Baggio-Saitovitch et al. on various iron complexes supported this idea [5]. Afanasov et al. studied variously substituted $^{57}\text{Co}^{\text{III}}-\beta$ -diketonates, and found [6] that the ratio of the nucleogenic Fe^{II} and Fe^{III} depended on the substituent on the central carbon atom of the diketonate ligand. A sensitive dependence of the observed $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ ratio on the donor-acceptor properties of the matrix was also reported in frozen solutions of the strong field complex tris(2,2'-bipyridyl)cobalt(III)-perchlorate [7,8]. This indicates that beyond the first ligand sphere, also the next neighbour molecules play an important role in the relaxation process.

In highly conjugated Co/Fe-chelates, there is a big chance that the multi-ionized ^{57}Fe shares its positive charge with its ligands. This involves also sharing of excitation energy during charge neutralization that may then be transferred to neighbouring alike molecules (ligands) very effectively by a resonance mechanism (plasmon or exciton migration). If the neighbouring molecules are different ones, i.e., the molecule incorporating ^{57}Co is isolated, one should expect larger fraction of either fragmentation events or slower relaxation process, unless there exists another mechanism [9] which helps the molecule get rid of its excitation energy very rapidly.

For aqua complexes, i.e., when the ligands are water molecules, chemical reaction between its radiolysis products and the central metal ion can also be responsible for aftereffect peaks reflecting aliovalent charge states of iron. In $[^{57}\text{Co}(\text{H}_2\text{O})_6]^{2+}$, the nucleogenic Fe^{2+} can react with the radiolysis product OH radical (autoradiolysis due to Auger electrons) and yield Fe^{3+} that can be observed in the Mössbauer spectrum [10,11]. If such a straightforward radiolysis process is not known, the formation of aliovalent charge states can be explained by the competing acceptors model. This assumes that in systems where competitors for electron capture stronger than $^{57}\text{Fe}^{3+}$ (nucleogenic) exist, the neutralization process may be terminated at the Fe^{3+} state while the stronger electron acceptor is reduced by the missing electron.

In order to study the role of the microenvironment of the decaying ^{57}Co from the point of view of aftereffects, we have selected the tris(2,2'-bipyridyl)cobalt and the bis(2,2':6',2''-terpyridine)cobalt system. The difference between the two systems is the structure of the ligand sphere of cobalt: 6 pyridine rings linked at the α position carbon

atoms to form 3 bipyridyl or 2 terpyridine molecules. Encapsulation into the zeolite was designed to isolate the complex molecules and thus to hamper fast energy transfer ($< 10^{-14}$ s) to neighboring alike molecules after charge neutralization following the Auger cascade. Molecular isolation also eliminates the possibility of exchange of a highly excited free $^{57}\text{Fe}^{2+}$ (or $^{57}\text{Fe}^{3+}$) with a neighboring cobalt ion in an undisturbed coordination environment. This latter could mask fragmentation events.

2. Experimental

Zeolite-Y is an ideal matrix to separate Co-chelate molecules from each other as it contains cavities with a diameter of 1.3 nm (supercage), slightly higher than that of many Co-chelates.

In zeolite Y, Co^{2+} ions can enter six different cationic sites, and only three of them are located in the supercage. As the formation of the chelated complex ions is possible only in the supercage, it was necessary to block other cationic exchange sites, otherwise, any residual quantity of unchelated Co^{2+} causes, possibly, appearance of high-spin Fe^{2+} and Fe^{3+} signals in the emission spectra, which could be erroneously regarded as aftereffect peaks of the complex. To avoid this problem, we used lanthanum treated zeolite-Y where the cationic sites outside the supercages are made incapable for ion exchange [12].

For the synthesis of zeolite-encapsulated tris(2,2'-bipyridyl)- $^{57}\text{Co}^{\text{II}}$ and bis(2,2':6',2''-terpyridine)- $^{57}\text{Co}^{\text{II}}$, 200 mg Na-Y(La) made from Linde's zeolite-Y was reacted with the neutral aqueous solution of 2.7 mg $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ doped with 1 mCi ^{57}Co . The mixture was stirred for 25 hours and then centrifuged in order to separate the exchanged zeolite from the liquid phase. After removing the solution, Co-Y(La) was washed with 20 cm³ of distilled water twice. This amount of Co^{2+} results in ion-exchange in every 8th supercage, i.e., one Co^{2+} per unit cell.

Co-Y(La) was then reacted with 15 cm³ ethanol containing 23 mg 2,2'-bipyridyl or 2,2':6':2''-terpyridine (5-fold excess). This mixture was stirred overnight in a closed centrifuge tube at room temperature. Finally, the zeolite was washed with 3×20 cm³ ethanol. The samples were then dried at 80°C overnight.

Quality of the samples was also checked by X-ray diffractograms using non-radioactive materials. We have adapted the method used by Quayle et al. [13] which is based on comparison of the intensity of the [2 2 0], [3 1 1] and [3 3 1] reflections of zeolite Y. Our XRD spectra confirmed that encapsulation of $[\text{Co}(\text{bpy})_3]^{2+}$ and $[\text{Co}(\text{terpy})_2]^{2+}$ in the supercages of Y(La) was successful.

For the interpretation of the Mössbauer spectra, it is crucial to have information about the initial oxidation state of cobalt in the encapsulated molecule. One may note that Co^{II} in low spin state is rather sensitive to aerial oxidation during the preparation. We have checked our samples by recording UV-VIS spectra in the 200–900 nm range. The zeolite samples were dispersed in Nujol to help record the transmission spectra. The spectra revealed that the zeolite encapsulated samples contained both forms in

comparable amounts. More quantitative information about the $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$ ratio could not be obtained.

3. Results and discussion

Mössbauer spectra of $[\text{}^{57}\text{Co}^{\text{II}}(\text{bpy})_3]\text{-Y(La)}$ recorded from 30 K to 250 K indicated at least three different species with variable amounts (figure 1). The majority of the spectra consisted of two characteristic doublets with isomer shifts (δ) 0.35 and 0.10 mm/s and quadrupole splittings (Δ) 0.31 and 1.9 mm/s (at room temperature, isomer shifts relative to $\alpha\text{-Fe}$), respectively. These parameters perfectly match those of the corresponding low-spin (LS) Fe^{II} and LS Fe^{III} bipyridyl chelates. The third component with $\delta = 1.1$ mm/s and $\Delta = 2.5$ mm/s is a high-spin (HS) Fe^{2+} species. These species did show a remarkable temperature variation (figure 2). The amount of the high-spin species decreased from 25% to about 8–10% as the temperature was

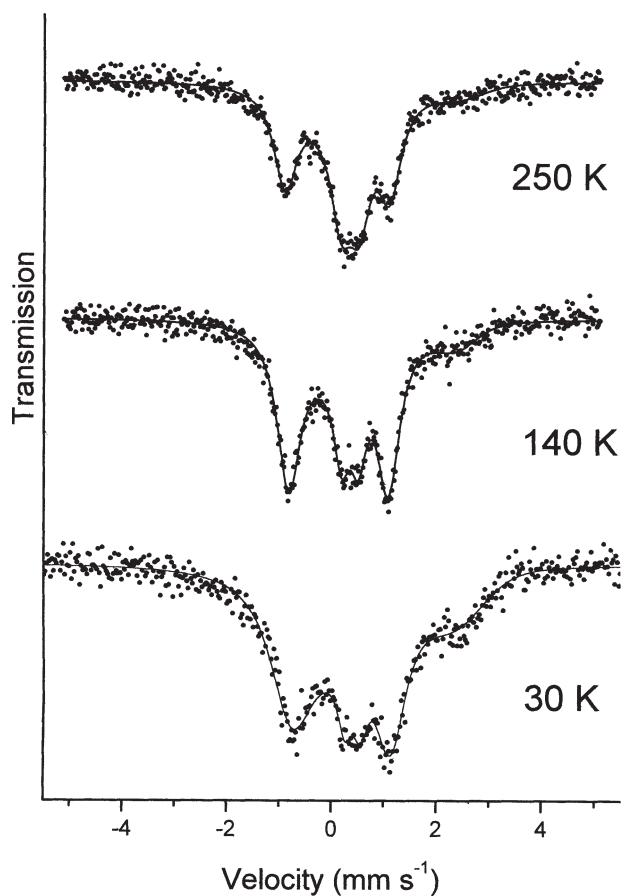


Figure 1. Mössbauer spectra of $[\text{}^{57}\text{Co}^{\text{II}}(\text{bpy})_3]\text{-Y(La)}$ recorded at three different temperatures. The velocity scale refers to $\alpha\text{-Fe}$; signs correspond to transmission experiments.

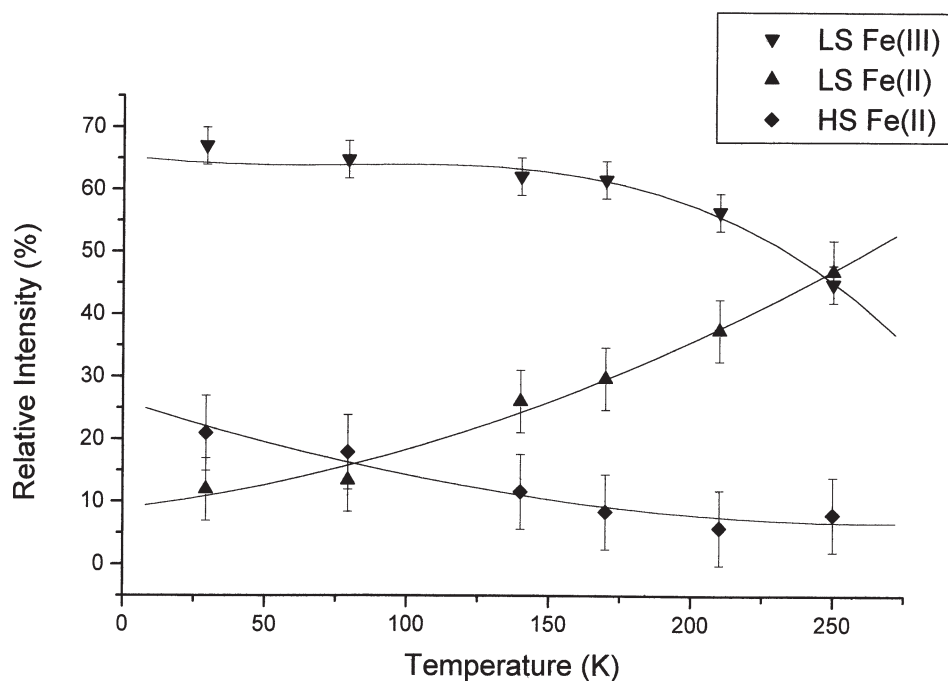


Figure 2. Temperature dependence of the relative areas of the doublets representing nucleogenic LS $^{57}\text{Fe}^{\text{II}}$, LS $^{57}\text{Fe}^{\text{III}}$ and HS $^{57}\text{Fe}^{2+}$ species in the emission Mössbauer spectra of $[\text{Co}^{\text{II}}(\text{bpy})_3]\text{-Y(La)}$.

raised from 30 K to 170 K. (We neglect possible differences in Mössbauer–Lamb factors.) Above this temperature, there was not any more significant change. The LS species showed a more pronounced variation: the amount of LS Fe^{III} decreased, and LS Fe^{II} increased with increasing temperature.

The emission Mössbauer spectra of $[\text{Co}^{\text{II}}(\text{terpy})_2]\text{-Y(La)}$ recorded in the 20 to 300 K temperature range showed a different behavior from those of $[\text{Co}^{\text{II}}(\text{bpy})_3]\text{-Y(La)}$ (figure 3). Above ~ 140 K, the spectra contained the two characteristic doublets of low spin $[\text{Fe}(\text{terpy})_2]^{2+}$ and low spin $[\text{Fe}(\text{terpy})_2]^{3+}$ with Mössbauer parameters matching literature values, and only a small amount ($\sim 15\%$) of a high spin Fe^{2+} species was present. Below 140 K, there was a substantial increase in the fraction of the high spin species. In contrast with the encapsulated bipyridyl chelate, there was no change in the amount of the low-spin Fe^{II} and low spin Fe^{III} species at the expense of each other in the whole investigated temperature range (their spectral intensity decreased parallel to the increase of the high spin species with decreasing temperature). This is illustrated in figure 4.

In order to explain the presence and the temperature dependence of the species observed by us in the zeolite encapsulated complexes, Mössbauer results on the normal, crystalline compounds may be quoted. Deisenroth et al. studied $[\text{Co/Mn}(\text{bpy})_3](\text{PF}_6)_2$ both in powdered [14] and single crystal [15] form. In the time integral emission spectrum, four species could be identified. Two LS species

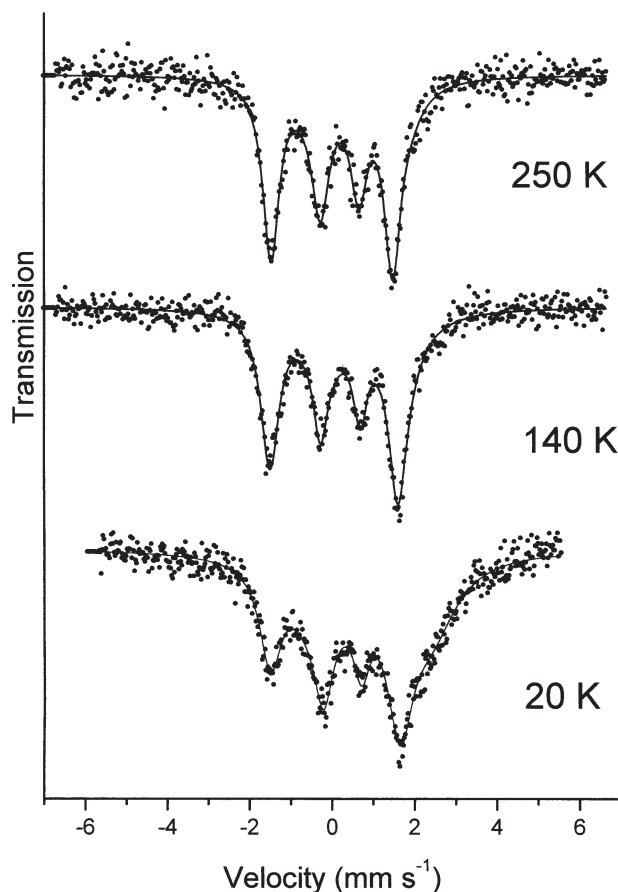


Figure 3. Mössbauer spectra of $[\text{}^{57}\text{Co}^{\text{II}}(\text{terpy})_2]\text{-Y(La)}$ recorded at three different temperatures. The velocity scale refers to $\alpha\text{-Fe}$; signs correspond to transmission experiments.

represented Fe^{II} and Fe^{III} , and two HS Fe^{2+} species were also found with a very remarkable temperature dependence at low temperatures ($T < 80$ K). One of the HS species, HS1, with approximate parameters $\delta = 1.3$ mm/s and $\Delta = 1.5$ mm/s was identified as an excited Fe^{2+} state by the help of comparison of laser excitation experiments on the iron analogue compound (LIESST) and TDMES measurements on $[\text{}^{57}\text{Co/Mn}(\text{bpy})_3](\text{PF}_6)_2$. The second HS component, HS2, did not show any time dependence by the TDMES spectra, and it was suggested, on the basis of the single crystal experiments, that this was a species with a damaged ligand.

Comparing the Mössbauer spectra of crystalline $[\text{}^{57}\text{Co/Mn}(\text{bpy})_3](\text{PF}_6)_2$ and zeolite encapsulated $[\text{Co}(\text{bpy})_3]^{2+}$ it was found that the relative amount of the Fe^{II} species is much lower in the zeolite encapsulated compound than in the normal one. It is clear from the work of Srivastava et al. [7] and also from a later work of Afanasov et al. [8] that the amount of LS Fe^{II} very sensitively depends on the matrix in which the complex is embedded. These authors performed experiments systematically on

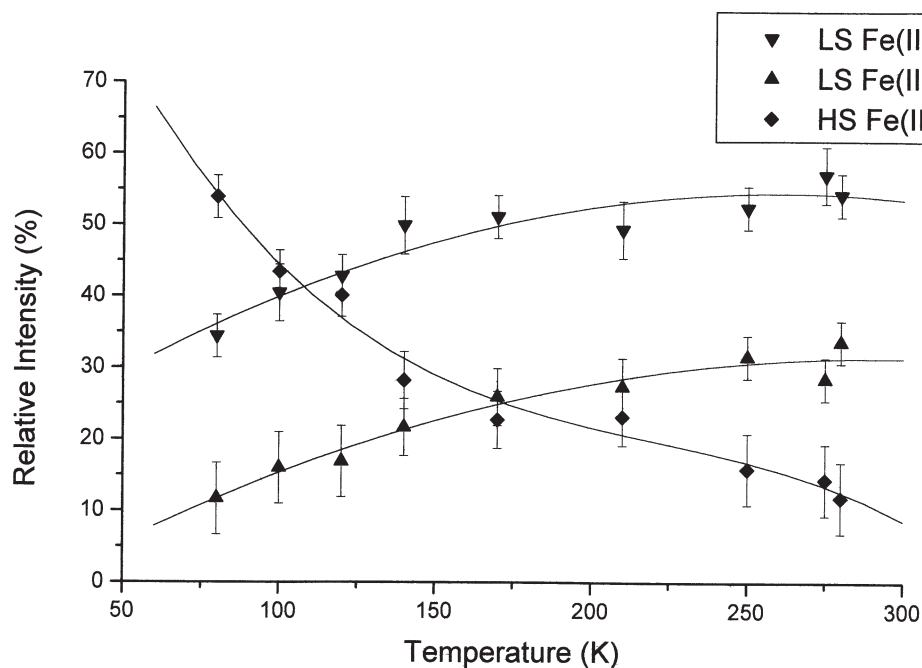


Figure 4. Temperature dependence of the relative areas of the doublets representing nucleogenic LS $^{57}\text{Fe}^{\text{II}}$, LS $^{57}\text{Fe}^{\text{III}}$ and HS $^{57}\text{Fe}^{2+}$ species in the emission Mössbauer spectra of $[\text{}^{57}\text{Co}^{\text{II}}(\text{terpy})_2]\text{-Y(La)}$.

the trivalent $\text{Co}(\text{bpy})_3$ complex dispersed in various matrices, and found a LS Fe^{II} fraction as high as 60% in the spectra (at 80 K). In our experiments, the LS Fe^{II} fraction varies from 10 to 45% as a function of the temperature, and most importantly, this variation proved to be reversible in several temperature cycles. The reversibility proves that a substantial fraction of one of the LS valence states of the nucleogenic $\text{Fe}(\text{bpy})_3$ complex is a consequence of the effect of the immediate environment on the neutralization process following the Auger events. In other words, the final valence state of the $\text{Fe}(\text{bpy})_3$ complex is determined by the donor–acceptor properties of the matrix. With this model, also the increase of the fraction of LS Fe^{II} with temperature can be explained, as the donation of an electron to a Fe^{III} species must be a thermally activated process, thus at higher temperature one expects more Fe^{II} .

The temperature variation of the ratio of the LS Fe^{II} and LS Fe^{III} species fed the expectation that the processes responsible for the formation of these species may proceed in the Mössbauer time window. In order to check it, we have performed a time delayed experiment at 222 K. The spectrum recorded in the time interval $t > 80$ ns ($t = 0$ marks the emission of the 122 keV gamma quanta) disproved this idea because it was practically identical with the time integral emission spectrum.

In contrast to the observation of Deisenroth et al. [14], only one HS Fe^{2+} species could be found in the zeolite encapsulated complex in the investigated temperature range. The “missing” HS species is the one designated by HS1 in the $[\text{}^{57}\text{Co}/\text{Mn}(\text{bpy})_3](\text{PF}_6)_2$ system, namely the one that was identified as an excited Fe^{2+}

state (NIESST). A reasonable explanation of this finding is that excitation from $^1\text{A}_1$ state to $^5\text{T}_2$ state involves expansion of the molecule which is hampered in the supercage of the zeolite. As a result, the excited species may either not form at all, or its relaxation to the ground state becomes so fast that it cannot be seen in the Mössbauer time window.

HS2 was considered to be a $[\text{Fe}(\text{bpy})_3]^{2+}$ species with a damaged bipyridyl ligand [15]. The formation of a damaged ligand may be explained in several ways. As proposed in [15], one of the bipyridyl ligands may have a positive charge, and this can be enough to reduce the ligand field strength and convert the complex into the high spin state. If the complex ion fragments [3,4] and recombination is not completed within the Mössbauer time window, then high spin states can be expected. This idea is supported by the rather broad lines of this doublet. Damage of the ligand sphere can also mean change of the conformation of the bipyridyl ligands, also resulting in diminished ligand field.

The “normal” $^{57}\text{Co}(\text{terpy})_2(\text{NO}_3)_2$ system was measured by us and found that the spectra consisted mostly of LS $^{57}\text{Fe}(\text{terpy})_3^{2+}$ in the whole temperature range. LS Fe^{III} state was absent. The fraction of the high spin states increased somewhat at lower temperatures, and at 20 K, two high spin species could be seen.

In the zeolite encapsulated complex, the major change is the appearance of a large fraction of LS Fe^{III} , just as in the case of the bipyridyl complex, and a remarkable increase of the high spin species with decreasing temperature. As far as the valence states (LS) are concerned, the same comments apply as for the bipyridyl containing system. It is noteworthy, however, that the LS Fe^{II} to LS Fe^{III} ratio does not show the temperature dependence observed in the zeolite encapsulated bipyridyl complex. If we accept that this ratio is basically determined by the donor–acceptor properties of the immediate environment (in our case mostly the zeolite lattice), we can draw the reasonable conclusion that the coordinated bipyridyl and terpyridine molecules act differently as bridging species for electron transfer from the zeolite lattice to the central Fe^{III} species.

The increase of the high spin species in $^{57}\text{Co}^{\text{II}}(\text{terpy})_2\text{-Y(La)}$ at low temperature may be attributed to the appearance of a second high spin species, however, evaluations with Lorentzian line shapes did not make it convincingly clear. If we do not consider a NIESST state due to the spatial restriction in the supercage, a similar reasoning may be applied as for the HS species in the bipyridyl system. As compared to bipyridyl, the terpyridine molecule has a more extended conjugated system and therefore a lower first ionization energy. This results in more stable terpy^+ ion than bipy^+ , and a higher chance to observe a high spin state in the emission spectrum. Terpyridine has much more different conformations, thus more chance to form a distorted complex with diminished ligand field strength. Also, recombination with the central iron ion after a possible fragmentation is more difficult for a larger ligand in a small cavity. All the three processes can sensitively depend on temperature.

Our experiments did not clearly indicate a higher fraction of fragmentation events in the encapsulated complexes. This suggests a mechanism of energy dissipation from

the molecule after charge neutralization, in which neighboring alike molecules do not play a key role [9].

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