On the synthesis and steric distortion of the tris(2,2′-bipyridine)iron(II) complex ion in zeolite-Y

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Mössbauer spectra and X-ray diffraction patterns of $[Fe(bpy)_3]^{2+}$ synthesized in supercages of zeolite Y reveal three interesting features of this system: first, the spectra show no evidence of steric distortion of the complex, secondly, special pretreatment of zeolite (ion exchange with La^{3+} and a subsequent heat treatment in order to block the small cavities) can stimulate the complex formation in the zeolite, and thirdly, despite the fact that the large complex cannot be introduced directly into the Y zeolite, it can be removed (at least partially) by cation exchange, by taking advantage of the dynamic feature of complex equilibrium in the presence of a ligand-eliminating process.

Metal ion-exchanged zeolites, which combine the advantages of the shape selectivity of zeolites with the extremely high dispersion of the metal ions, are of particular interest in catalysis studies. Identification and control of the distribution of the metal ions in these systems is crucial. It is also important to see whether large molecules formed in the intracrystalline spaces are under distortion or affected in any other way by the zeolite lattice, which may lead to unusual physical and chemical behaviour.

In this work we synthesized $[Fe(bpy)_3]^{2+}$ complexes in large cavities (supercages) of zeolite Y (NaY). Zeolite Y also has a number of cation sites in its smaller cavities (sodalite cages and hexagonal prisms),[1] where complex formation is impossible for steric reasons. Our objective was to work out the best strategy for building such a complex without leaving any iron uncoordinated, and to investigate if the complex has any peculiar property as a consequence of being encapsulated in the zeolite. Achieving these goals was vital to avoid extra patterns in the Mössbauer spectrum due to uncomplexed Co in the investigation of the after-effects of the $^{57}Co(EC)^{57}Fe$ decay in the analogous system containing cobalt.[2]

Three types of samples were prepared. S1: Fe^{2+}-exchanged zeolite Y ($Fe^{II}Y$) prepared by a conventional ion-exchange method was mixed and heated with 2,2′-bipyridine as described in ref. 3. S2: $Fe^{II}Y$ was suspended in an absolute ethanolic solution of 2,2′-bipyridine. After 24 hours, the sample was filtered and washed with ethanol, and dried at room temperature. S3: to prevent Fe^{2+} ions from exchanging to cation sites in the smaller cavities, we blocked these with La^{3+} ions introduced first by ion exchange into the supercages and then compelled by an appropriate heat treatment to occupy sites in the sodalite cages.[4] The LaY obtained by such a procedure was used instead of NaY; other steps of the preparation were the same as in S2. All samples were exposed to air after preparation. Crystallinity was checked by X-ray powder diffraction (XRD) using Fe-filtered Co radiation. The samples were deep red and contained approximately one Fe atom per unit cell of zeolite Y (*ca.* 0.3 mass% Fe).

Mössbauer spectra of S1 and S2 consist of two quadrupole doublets each, DA with isomer shift $\delta = 0.32$ mm s^{-1} and quadrupole splitting $\Delta = 0.32$ mm s^{-1}, and DB with $\delta = 0.5$ mm s^{-1} and $\Delta = 1.3$–1.5 mm s^{-1}. These spectra differ only in the relative intensities of the doublets; the intensity of DA varies between 38 and 56% of the total spectral area. A typical spectrum is shown in Fig. 1(*a*). Parameters of DA are characteristic of low-spin Fe^{2+} in an octahedral environment and are very close to those parameters that were found in crystalline compounds ($\delta = 0.39$ mm s^{-1}, $\Delta = 0.32$ mm s^{-1}) and frozen aqueous solutions ($\delta = 0.40$ mm s^{-1}, $\Delta = 0.32$ mm s^{-1}) of $[Fe(bpy)_3]^{2+}$, and thus DA can be assigned to $[Fe(bpy)_3]^{2+}$ in the supercage. DB represents high-spin Fe^{3+} with a very asymmetric environment. However, the spectrum of S3 [Fig. 1(*b*)] shows only the DA doublet with a narrow linewidth of 0.25 mm s^{-1}. This indicates that lanthanum effectively blocked the small cages from Fe^{2+} ions, and in the supercages all of the iron could become coordinated. Thus we achieved our goal in having a uniform distribution of iron in the form of $[Fe(bpy)_3]^{2+}$ complex ions in the supercages. This result may open up new possibilities for catalysis design.

Another important aspect of this work is that Mössbauer parameters of the $[Fe(bpy)_3]^{2+}$ complex encapsulated in zeolite Y do not show distortion of the molecule. Comparing the size of the complex to that of the supercage, one might find this unsurprising, but we think this point should be emphasized since recent papers[5,6] claim to have evidence for steric distortions of complexes of such size. Those accounts are based

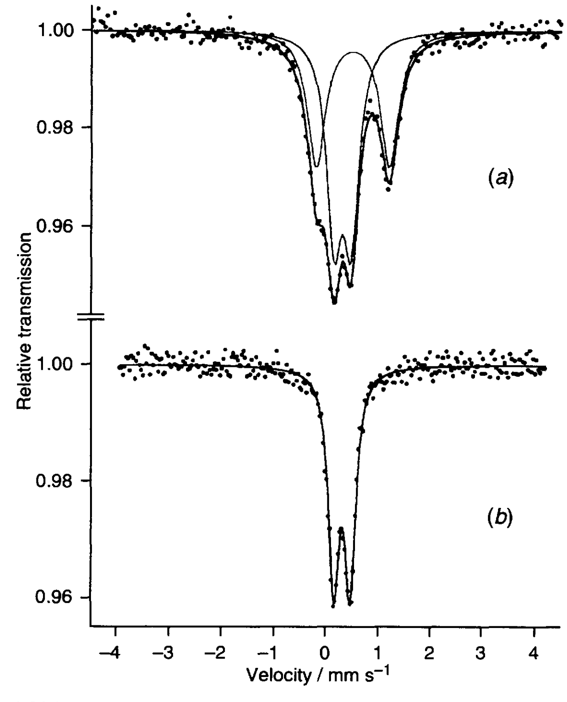

Fig. 1 80 K Mössbauer spectra of samples S2 (*a*) and S3 (*b*); zero velocity corresponds to α-iron at room temperature

on a faulty assignment of an δ = 0.47 mm s^{-1}, Δ = 1.48 mm s^{-1} doublet, to [Fe(bpy)$_3$]$^{2+}$. Such changes in quadrupole splitting (from 0.32 to 1.48 mm s^{-1}) would indeed indicate huge distortion. We, however, claim that it is DA that belongs to the complex inside the supercage as the following arguments should clarify. Since it is clear from the foregoing that DA represents [Fe(bpy)$_3$]$^{2+}$, here we wish to show that the complex was located *inside* the supercage. Under the conditions of the preparations, where no free cations are present in the ligand solution, the Fe^{2+} ions cannot migrate out of the exchange sites of Fe^{II}Y. This is especially true in the case of S1 where no solvent is used for the synthesis of the complex, which, therefore, should take place inside the zeolite. In the XRD patterns the relative intensities of the [220] and [311] peaks showed significant changes after complex formation: the intensity of [311] increased pronouncedly while the intensity of [220] diminished (see Table 1). Such changes indicate complex formation in the supercages.[3] With LaY, the La treatment reduces the intensity of these peaks; however, one can also observe a large increase in the intensity of the [311] peak in the case of S3. XRD of LaY and NaY impregnated with the complex did not show these changes, therefore, it is clear that the complexes bound to the external surface do not contribute to the intensity change. In the literature, one can also find EPR investigations[7] of similar systems which show that complex formation primarily takes place inside the zeolite.

Table 1 Relative intensities of the relevant [220], [311] and [331] XRD peaks with their sum normalized to unity

	[220]	[311]	[331]
NaY	0.26	0.18	0.56
S2	0.09	0.30	0.61
LaY	0.14	0.14	0.72
S3	0.10	0.43	0.47
S2/NaCl	0.20	0.20	0.60

Finally, we stirred S2 in a concentrated aqueous solution of NaCl for several days and washed it with water, in order to remove uncomplexed Fe^{3+} ions *via* ion exchange. To our surprise the sample (S2/NaCl) lost [Fe(bpy)$_3$]$^{2+}$: the colour of the sample faded, the Mössbauer absorption decreased and the XRD patterns showed a reverse change in the peak intensities. This shows that the complex was detached from the exchange sites by sodium cation exchange and so could leave the crystal. Since the free apertures of the supercages are smaller than the diameter of [Fe(bpy)$_3$]$^{2+}$, this could only happen if the complex decomposed and was rebuilt outside. (In refs. 5 and 6 similar washing procedures were pefomed as final steps of the preparation; therefore, it seems the materials studied there were not what those authors expected). This finding also draws attention to the dynamic nature of complex equilibria: no matter how high the stability constant is, complex decomposition can be caught in the act provided that a suitable mechanism exists for eliminating the products of decomposition. In the present case the cage openings act as sinks for such a draining system.

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