

Evidence for Distortion of $[\text{FeL}_3]^{2+}$ ($\text{L} = \text{en}, \text{amp}, \text{bpy}, \text{phen}$) in a Y-type Zeolite†

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Mössbauer spectra of $[\text{Fe}(\text{bpy})_3]^{2+}$ and $[\text{Fe}(\text{phen})_3]^{2+}$ formed in the supercage of a Y-zeolite revealed structural distortions due to steric interactions of the complex ions with the internal surface of the zeolite, suggesting that the threefold axis of the complex ions may be parallel to the axis of the supercage.

Although it is important to obtain information as to the degree of steric distortion of materials in zeolites in order to understand the chemistry of intra-zeolite compounds in catalysis¹ and in gas separation-purification,² there are no reports presenting clear evidence for the distortion of intra-zeolite compounds. This communication, reporting distortion of $[\text{FeL}_3]^{2+}$ ions ($\text{L} = \text{en}, \text{amp}, \text{bpy}$ and phen) in a Y-zeolite supercage, is the first to give experimental evidence for distortion of coordination compounds formed in a zeolite.

$[\text{FeL}_3]^{2+}$ complex ions ($\text{L} = \text{amp}, \text{bpy}, \text{phen}$) located in a zeolite supercage were prepared *via* normal intra-zeolite synthesis procedures. Fe^{II} Y zeolite was prepared by suspending NaY zeolite in aqueous FeSO_4 (0.02 mol l^{-1}) containing hydrochloric acid for a day. The pH during the ion exchange was controlled in the range 1–2 to minimize formation of Fe^{3+} and hydronium exchange since oxidation of Fe^{2+} and hydronium exchange could be substantial at $\text{pH} > 2$ and $\text{pH} < 1$, respectively. Each complex ion was formed in the zeolite supercage by suspending Fe^{II} Y zeolite in aqueous solution containing the corresponding liquid. After filtration and washing with water, the zeolite sample was dispersed in aqueous NaCl to replace free Fe^{II} ions in the zeolite with Na^+ ions. The zeolite sample was filtered off, and washed with water until the filtrate became colourless. All the samples

were dried *in vacuo*. In the synthesis of $[\text{Fe}(\text{en})_3]^{2+}$ in the zeolite, dry methanol was used as solvent instead of water and treatment with aqueous NaCl was omitted to minimize oxidation of the Fe^{II} complex ion in the zeolite since Fe^{II} is oxidized easily by 1,2-diaminoethane in the presence of water. All manipulations were carried out under nitrogen.

Formation of the complexes in the zeolite supercage was characterized by UV-VIS spectroscopy and X-ray powder diffraction (XRD). Fig. 1 shows that the absorption spectrum of methanolic $[\text{Fe}(\text{phen})_3]\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ and the reflectance spectrum of $[\text{Fe}(\text{phen})_3]^{2+}$ in the zeolite are identical, verifying the formation of $[\text{Fe}(\text{phen})_3]^{2+}$ in the zeolite. In the XRD pattern for $[\text{Fe}(\text{phen})_3]^{2+}$ in the zeolite, the relative intensities of the [220] and [311] peaks changed from those for NaY and Fe^{II} Y zeolite. As reported,³ such changes may indicate complex formation in supercage. Formation of the other $[\text{FeL}_3]^{2+}$ complexes in the zeolite was also confirmed by UV-VIS spectroscopy and the XRD patterns. On the other hand, the formation of iron complexes with 4,4'-dimethyl-2,2'-bipyridine and 5,6-dimethyl-1,10-phenanthroline, which are somewhat larger than phenanthroline, was not detected in the UV-VIS spectra and XRD patterns.

The average number of iron atoms per supercage was determined by elemental analysis as 1.2, 1.9, 0.46 and 0.47 for $[\text{Fe}(\text{en})_3]^{2+}$, $[\text{Fe}(\text{amp})_3]^{2+}$, $[\text{Fe}(\text{bpy})_3]^{2+}$ and $[\text{Fe}(\text{phen})_3]^{2+}$, respectively. These values are an overestimate of the number coordinated iron atoms, because some of the iron atoms are ligand-free as shown later in the discussion on Mössbauer results.

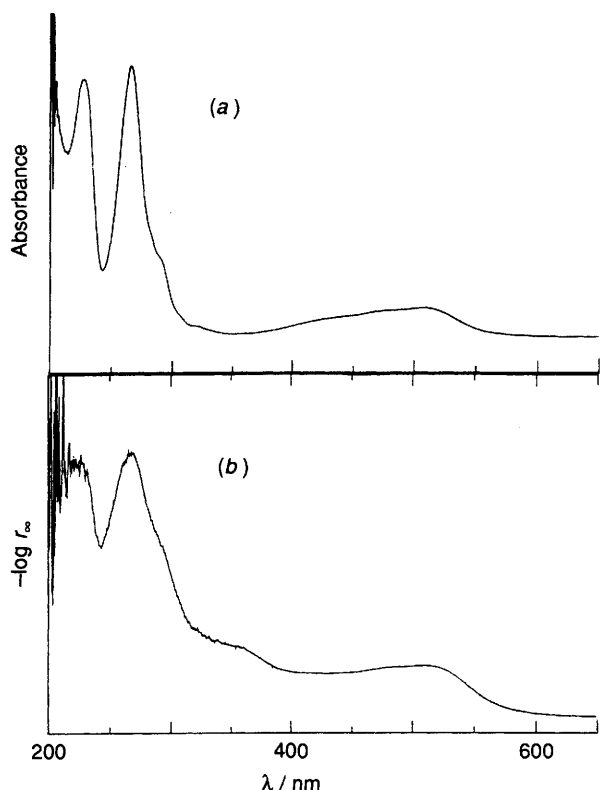


Fig. 1 (a) Absorption spectrum of methanolic $[\text{Fe}(\text{phen})_3]\text{Cl}_2$ and (b) reflectance spectrum of $[\text{Fe}(\text{phen})_3]^{2+}$ in the Y-zeolite

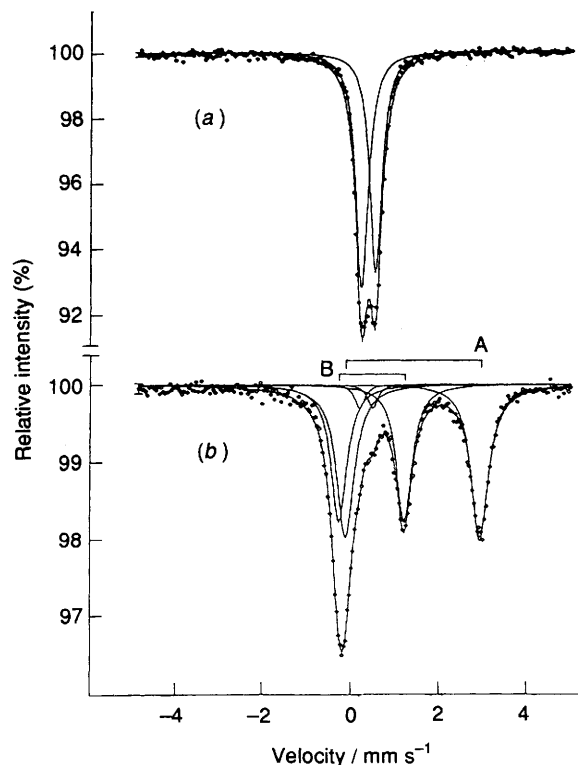


Fig. 2 Mössbauer spectra at 78 K of (a) $[\text{Fe}(\text{bpy})_3](\text{ClO}_4)_2$ and (b) $[\text{Fe}(\text{bpy})_3]^{2+}$ in the Y-zeolite

† en = ethane-1,2-diamine; amp = 2-(aminomethyl)pyridine; bpy = 2,2'-bipyridine; phen = 1,10-phenanthroline.

Table 1 Mossbauer parameters at 78 K of $[\text{FeL}_3]^{2+}$ salts and $[\text{FeL}_3]^{2+}$ ions in the Y-zeolite

	I.S./mm s ^{-1a}	Q.S./mm s ⁻¹
$[\text{Fe}(\text{en})_3](\text{ClO}_4)_2$	1.09(0) ^b	1.73(0)
$[\text{Fe}(\text{en})_3]^{2+}$ in zeolite	1.05(2)	1.89(3)
$[\text{Fe}(\text{amp})_3](\text{ClO}_4)_2$	0.52(0)	—
$[\text{Fe}(\text{amp})_3]^{2+}$ in zeolite	0.59(1)	—
$[\text{Fe}(\text{bpy})_3]\text{Cl}_2 \cdot 7\text{H}_2\text{O}$	0.39(0)	0.32(0)
$[\text{Fe}(\text{bpy})_3]^{2+}$ in zeolite	0.47(1)	1.48(1)
$[\text{Fe}(\text{phen})_3]\text{Cl}_2 \cdot 7\text{H}_2\text{O}$	0.40(1)	0.26(2)
$[\text{Fe}(\text{phen})_3]^{2+}$ in zeolite	0.54(1)	1.41(1)

^a Relative to α -iron. ^b Standard deviations in parentheses.

Mössbauer spectra (Table 1) of polycrystalline $[\text{Fe}(\text{en})_3](\text{ClO}_4)_2$ powder and $[\text{Fe}(\text{en})_3]^{2+}$ in the zeolite at 78 K showed a doublet ascribed to high-spin Fe^{II} (I.S. = 1.09 mm s⁻¹, Q.S. = 1.73 mm s⁻¹) in the former, and two pairs of doublets (I.S. = 0.53 mm s⁻¹, Q.S. = 0.53 mm s⁻¹ and I.S. = 1.05 mm s⁻¹, Q.S. = 1.89 mm s⁻¹) in the latter. The doublet with I.S. 0.53 mm s⁻¹ was assigned to high-spin Fe^{III} ions at ion-exchange sites in the zeolite,⁴ and that with I.S. 1.05 mm s⁻¹ to high-spin Fe^{II} ions of $[\text{Fe}(\text{en})_3]^{2+}$ in the zeolite. The I.S. and Q.S. values for the latter doublet were similar to those for polycrystalline $[\text{Fe}(\text{en})_3](\text{ClO}_4)_2$, suggesting that the electronic and coordination states of the Fe^{II} ion of the complex in the zeolite are similar to those in $[\text{Fe}(\text{en})_3](\text{ClO}_4)_2$, and that the $[\text{Fe}(\text{en})_3]^{2+}$ ion may not suffer any distortion.

Fig. 2 shows the Mössbauer spectra of polycrystalline $[\text{Fe}(\text{bpy})_3]\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ and $[\text{Fe}(\text{bpy})_3]^{2+}$ in the zeolite. The former consisted of a doublet with a very small Q.S. for low-spin Fe^{II} (I.S. = 0.39 mm s⁻¹, Q.S. = 0.32 mm s⁻¹). The spectrum of $[\text{Fe}(\text{bpy})_3]^{2+}$ in the zeolite showed two pairs of doublets: A (I.S. = 1.42 mm s⁻¹, Q.S. = 3.08 mm s⁻¹) and B (I.S. = 0.47 mm s⁻¹, Q.S. = 1.48 mm s⁻¹), together with some peaks from impurities. Doublet A was ascribed to ligand-free high-spin Fe^{II} ion at ion-exchange sites,⁴ and B to the low-spin Fe^{II} centre of $[\text{Fe}(\text{bpy})_3]^{2+}$ in the zeolite, since the doublet was not observed when treatment with bipyridine solution was omitted. It is clear that the doublet due to the Fe^{II} complex in the zeolite has a much larger Q.S. than the corresponding doublet of polycrystalline $[\text{Fe}(\text{bpy})_3](\text{ClO}_4)_2$. Since the quadrupole splitting depends on the electric field gradient at the iron centre, lowering of the symmetry of a complex results in an increase in the Q.S. value. The observed Q.S. values for $[\text{Fe}(\text{bpy})_3]^{2+}$ ions imply a greater distortion of $[\text{Fe}(\text{bpy})_3]^{2+}$ in

the zeolite than in the polycrystalline salt.⁵ We obtained similar results for $[\text{Fe}(\text{phen})_3]^{2+}$ in the zeolite.⁶

The I.S. and Q.S. values for $[\text{Fe}(\text{en})_3]^{2+}$ and $[\text{Fe}(\text{amp})_3]^{2+}$ in the zeolite are thus nearly identical to those for the polycrystalline complexes, but for $[\text{Fe}(\text{bpy})_3]^{2+}$ and $[\text{Fe}(\text{phen})_3]^{2+}$ in the zeolite the I.S. and Q.S. values are quite different from those of the corresponding polycrystalline salts (Table 1). It is known that the diameter of the supercage of the Y-zeolite is about 13 Å, *i.e.* comparable to the sizes of $[\text{Fe}(\text{bpy})_3]^{2+}$ and $[\text{Fe}(\text{phen})_3]^{2+}$. Complexes larger than $[\text{Fe}(\text{amp})_3]^{2+}$ may be strongly distorted in the zeolite by steric interactions with the internal surface of the supercage. Also, the Q.S. values for $[\text{Fe}(\text{bpy})_3]^{2+}$ and $[\text{Fe}(\text{phen})_3]^{2+}$ in the zeolite are similar even though $[\text{Fe}(\text{phen})_3]^{2+}$ is larger than $[\text{Fe}(\text{bpy})_3]^{2+}$. The agreement in Q.S. values implies that the degree of distortion of $[\text{Fe}(\text{phen})_3]^{2+}$ in the zeolite is similar to that of $[\text{Fe}(\text{bpy})_3]^{2+}$. From $[\text{Fe}(\text{phen})_3]^{2+}$ in the zeolite supercage may protrude three ligand 'projections' into the large pore channels between supercages. Elemental analysis and Mössbauer spectra indicated that one $[\text{Fe}(\text{phen})_3]^{2+}$ ion in the zeolite occupied 3.2 supercages, assuming an equal recoilless fraction of ⁵⁷Fe in the complex and the ligand-free ion. One $[\text{Fe}(\text{phen})_3]^{2+}$ ion can occupy 4 supercages if the carbon atoms at the 5- and 6-positions of the phenanthroline ligands protrude into the neighbouring three supercages. Thus the observed number of supercages occupied by the complex ion agrees with the estimated number of supercages. Such an orientation of $[\text{Fe}(\text{bpy})_3]^{2+}$ and $[\text{Fe}(\text{phen})_3]^{2+}$ with respect to the supercage is only attainable when the threefold axis of the complexes is parallel to the axis of the supercage.

Further details will be reported elsewhere, including calculations of the Mössbauer parameters from the degree of distortion of the complexes.

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