Identification of iron cyclam complexes encapsulated inside zeolite Y

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Publication dedicated to my teacher, Professor Karl Wieghardt, on the occasion of his 60th birthday.

Abstract

The combination of EPR and Mössbauer spectroscopy along with IR, Diffuse Reflectance UV–Vis, and XRD techniques has proven to be a powerful tool for identifying and characterizing the molecular and electronic structure of various iron complexes formed inside the supercages of zeolite-Y. Especially interesting is the identification of encapsulated *trans*-[(cyclam)Fe(N$_3$)$_2$]$^+$@NaY, as a potent precursor for the synthesis of catalytically active Fe(V) nitrido species.
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1. Introduction

High-valent transition-metal complexes stabilized by a terminal chalcogenide or pnictogenide ligand have been recognized as highly reactive intermediates in atom transfer reactions. Oxidations mediated by ferryl and manganyl complexes are fundamental to biological hydrocarbon oxidation [1] and the species also find application in organic synthesis as epoxidation catalysts [2]. It was previously shown that the oxidation state +V can be stabilized for iron cyclam complexes (cyclam = 1,4,8,11-tetraazacyclotetradecane) with a terminal nitrido ligand and spectroscopically analyzed in frozen matrices at liquid nitrogen temperature [3]. However, these conditions do not allow for structural studies and investigations of catalytic reactivity. In liquid solution only dinuclear decomposition products, namely μ-nitrido bridged iron(III/IV) species, were observed [3].

To prevent these binuclear degradation reactions, we sought to encapsulate the highly reactive nitrido species within the supercages of zeolites. At a simplistic level, these immobilized complexes may be considered inorganic analogues of natural enzymes with the robustness of a zeolite framework representing the peptide scaffold of a protein [4]. Nitridoiron(V) cyclam species can be obtained by photolysis of the corresponding azidoiron(III) cyclam complexes. Herein, we report the synthesis and characterization of an azidoiron(III) cyclam complex encapsulated in zeolite-Y. Special efforts were made to identify the structural and electronic properties of the various iron species present in the zeolite-Y environment.

The macrocyclic ligand cyclam was chosen for several reasons. First, it has been shown that cyclam behaves as an 'innocent' supporting ligand on highly charged metal centers [3,5,6]. Second, the preparation of transition metal cyclam complexes encapsulated in zeolite cavities takes advantage of the so-called 'flexible ligand' synthesis [7]. The 14-membered ring of the cyclam ligand is flexible enough to infiltrate the channels, enter the cavities, and finally form the complex. In contrast, usage of non-innocent porphyrin, salen and phthalocyanine ligands must be template-driven (ship-in-the-bottle-synthesis) [4] and may yield incompletely formed metal complexes. This makes the detailed study of the entrapped species' electronic structure difficult, if not impossible. In addition, the cyclam ligand melts at the temperature employed for the synthesis of the iron complex, which obviates need for solvents.

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2. Experimental

2.1. Materials

1,4,8,11-Tetraazacyclotetradecane (cyclam), and tri-methylsilyl azide were purchased from Sigma-Aldrich, Inc.; ferric chloride ($FeCl_3 \cdot 6H_2O$) and hydrochloric acid were acquired from Fisher Scientific International and used without further purification. NaY zeolite was purchased from Sigma-Aldrich, Inc. and calcinated at 500 °C under reduced pressure before use. ^{57}Fe-enriched iron foil (95.85% enrichment) was purchased from Advanced Materials Technologies Ltd. (Israel). $^{57/56}FeCl_3$ was prepared as follows: metallic ^{57}Fe (51 mg) and ^{56}Fe foil (50 mg) was dissolved in 30 ml concentrated HCl with heating. The resulting solution was evaporated under reduced pressure and the solid residue washed three times with methanol. The synthesized $FeCl_3$ contains about 50% ^{57}Fe.

2.2. Preparations of compounds

2.2.1. Fe@NaY (1)

To a suspension of 25 g of NaY zeolite in water, 7 g of $FeCl_3 \cdot 6H_2O$ were added. The solution was stirred at pH 5 for 2 days and then filtered. The solid was collected, washed with deionized water, and dried in air. ICP measurements show 50% exchange of the sodium ions to give a 4.1 wt.% iron-exchanged zeolite (Scheme 1).

2.2.2. $[(Cyclam)Fe(H_2O)_2]^{3+}$@NaY (2)

A 250 ml round bottom flask was charged with 14.5 g of 1 (dehydrated at 250 °C) and 2 g of cyclam. The mixture was heated for 4 h at 220 °C under a dry nitrogen atmosphere. The color of the zeolite changed from white to brown during the course of the reaction. Excess ligand was removed by extracting the crude product with dichloromethane in a Soxhlet apparatus for 4 days. The product was collected by filtration and dried in air. Compound 2 cannot be obtained by refluxing a methanol suspension of 1 and cyclam.

2.2.3. $[(Cyclam)Fe(N_3)_2]^+$@NaY (3)

A 50 ml round bottom flask was charged with 2.4 g of 2, 10 ml of trimethylsilyl azide was added and the reaction mixture was stirred overnight at room temperature (r.t.). The product was isolated by filtration and the reddish powder washed with dichloromethane and dried in vacuum.

Synthesis of ^{57}Fe-enriched samples of 1–3 was achieved by using $^{57/56}FeCl_3$ for the preparation of the iron-exchanged precursor zeolite 1.
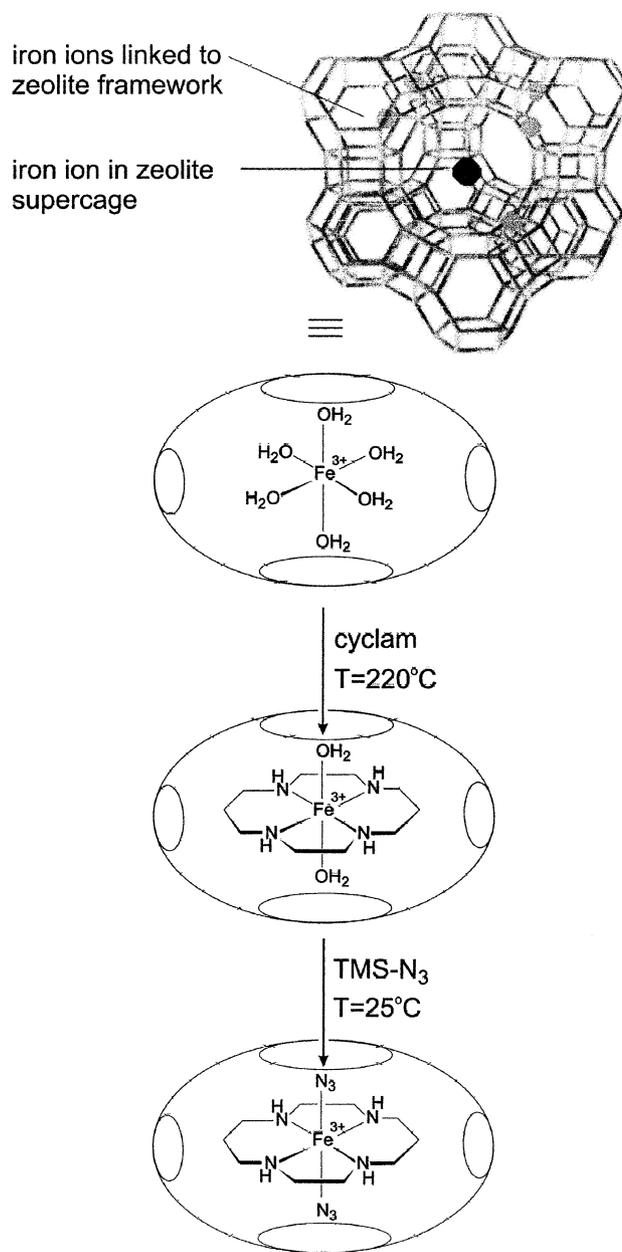
Scheme 1. Simplified diagram of Fe-exchanged zeolite-Y (Fe@Ze-Y) with position of the iron sites and the synthesis of iron containing cage complexes.

2.3. Physical measurement

ICP measurements were carried out at Scripps Institution of Oceanography, UCSD. X-ray powder diffraction (XRD) patterns were recorded on a Rigaku Geigerflex diffractometer using Cu Kα1 radiation. The DR UV–Vis spectra of the samples were recorded on a Shimadzu uv2401pc spectrometer with an ISR-240A integrating sphere assembly with $BaSO_4$ as a reference. Infrared spectra of solid samples (KBr pellets) were recorded on a JASCO IR-810 spectrophotometer. X-band EPR spectra were recorded on a Bruker Elexsys

E500 spectrometer equipped with a helium flow cryostat (Oxford 900). The zero-field Mössbauer data were recorded on an alternating constant-acceleration spectrometer. The minimum experimental line width was 0.24 mm s^{-1} (full-width-at-half-height). The sample temperature was maintained constant in an Oxford Instruments Variox cryostat.

3. Results and discussion

The zeolite-based iron cyclam complex [(cyclam)Fe(H$_2$O)$_2$]$^{3+}$@NaY (**2**) is prepared by reacting iron-exchanged zeolite-Y Fe@NaY (**1**) (4.1 wt.%, dehydrated at 250 °C) with cyclam for 4 h under a dry nitrogen atmosphere at 220 °C. Removal of excess and superficially adhered ligand was achieved by Soxhlet extraction with dichloromethane. Treatment of **2** with neat trimethylsilyl azide (TMSN$_3$) at room temperature results in formation of [(cyclam)Fe(N$_3$)$_2$]$^+$@NaY (**3**) an azido iron(III) complex of cyclam immobilized inside zeolite-Y (see Scheme 1). Although the formation of a mono-azido complex with the remaining coordination site occupied by framework oxygen is theoretically possible, the use of excess TMSN$_3$ in this reaction likely favors the formation of a bis-azido iron(III) complex as the main product of the reaction.

The zeolite crystallinity remains intact during the preparative procedure, as evidenced by the XRD patterns of samples of **1**–**3** (see Fig. 4, Section 5). The formation of iron cyclam complexes inside the zeolite supercages is confirmed by the change in the relative peak intensities of the 331, 220, and 311 reflections in the XRD patterns [8].

The diffuse-reflectance UV–Vis spectrum (DR–UV–Vis) of **2** (Fig. 1) exhibits a new broad absorption band at 614 nm, indicating the change of coordination sphere at the iron center upon reaction with the macrocyclic amine ligand. In the spectrum of **3**, additional absorption bands at 440 and 297 nm are observed that are readily assigned to the azide-to-iron LMCT and azide $\pi \rightarrow \pi^*$ transition, respectively, thereby confirming coordination of azide to the iron metal center. The formation of metal-coordinated azide ligands is confirmed by the intense azide v_{as}(N$_3$) IR stretching absorption present in the region of 2000–2200 cm^{-1}. In the IR spectrum of **3** (Fig. 5, Section 5) an intense absorption peak is observed at 2076 cm^{-1}, which is 74 cm^{-1} lower than in free TMSN$_3$, and 32 cm^{-1} higher in energy than in the spectrum of free *trans*-[(cyclam)Fe(N$_3$)$_2$]ClO$_4$ reported in the literature [3]. The latter hypsochromic shift can be associated with the distortion of the encapsulated complex inside the zeolite supercages and/or azide-framework hydrogen interactions.

Octahedral iron(III) cyclam complexes generally form *cis* and *trans* isomers with d^5 high-spin and low-spin configurations, respectively [3,9]. The reactivities of the *cis* and *trans* isomers differ significantly and it is known that only the low-spin *trans* isomer can be photolyzed to yield the desired nitrido iron(V) species [3].

EPR and Mössbauer measurements were carried out in order to elucidate the molecular and electronic structure of the zeolite-immobilized iron complexes in samples of **1**–**3**. The EPR spectrum of parent iron-exchanged zeolite **1** (Fig. 2, upper trace) shows a signal at $g = 4.25$ with a shoulder at $g \approx 9.0$ and a separate weak signal at $g = 2.00$. As suggested by Serwicka et al. [10], the first signal corresponds to a high-spin Fe(III) complex, [Fe(H$_2$O)$_{6-n}$O$_n$]$^{(3-2n)+}$, in a distorted octahedral environment and/or [Fe(H$_2$O)$_{4-n}$O$_n$]$^{(n-5)+}$ in a distorted tetrahedral environment with the Fe ions linked to the zeolite framework through lattice oxygen. The signal at $g = 2.00$ is associated with an octahedrally coordinated, high-spin hexaaqua–Fe(III) complex [10].
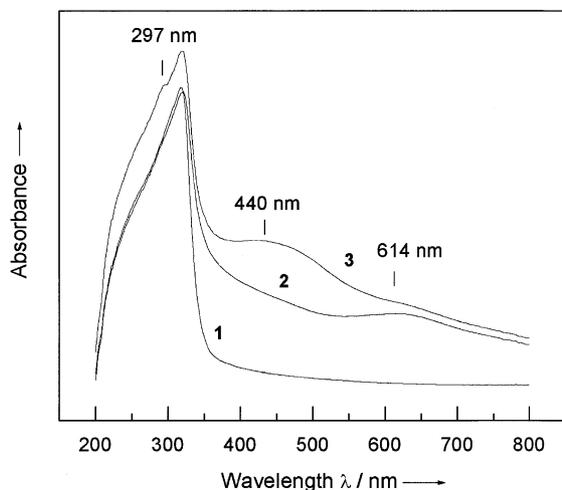

Fig. 1. Diffuse reflectance UV–Vis spectra of **1**–**3**.
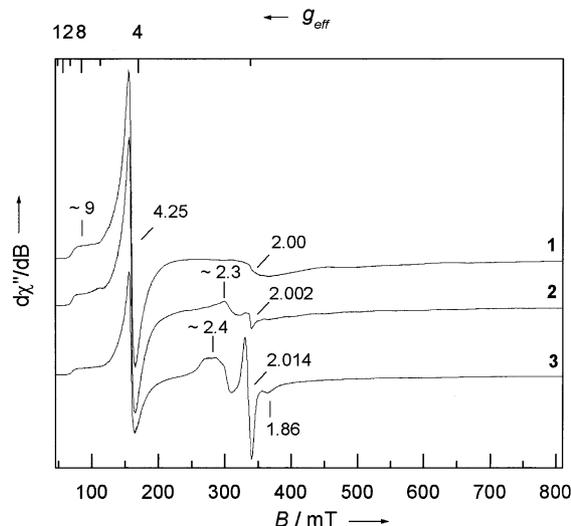

Fig. 2. X-band EPR spectra of **1**–**3** recorded at 9.47 GHz and 6 K.

It should be noted that the signal at $g = 4.25$ and $g \approx 9.0$ remains virtually unchanged in samples of **1–3**, which shows the corresponding iron species' inertness towards ligand exchange. This is consistent with their reportedly high resistance to back-exchange with sodium ions [10]. However, upon treatment of **1** with cyclam, the $g = 2.00$ signal of **1** is replaced by a signal centered at $g = 2.002$ with a broad shoulder at $g \approx 2.3$ (Fig. 2, center trace). This signal suggests the existence of an iron(III) complex with a low-spin ($S = 1/2$) iron center in **2**. We, therefore, associate this signal with an iron cyclam complex, *trans*-[(cyclam)Fe(H$_2$O)$_2$]$^{3+}$. Evidence for the coordination of water instead of lattice oxygen comes from the accessibility of the iron center for azide ligand substitution, as probed by IR spectroscopy. The formation of an azide iron cyclam complex **3** upon treatment of **2** with TMSN$_3$ is also reflected in the EPR spectrum (Fig. 2, lower trace). This species exhibits an intense rhombic signal centered at $g = 2.014$ with a broad shoulder at $g \approx 2.4$ and a characteristic resonance at $g = 1.86$. We assign this signal to the *trans*-[(cyclam)Fe(N$_3$)$_2$]$^+$ species with a low-spin Fe(III) center. The *trans* conformation is further evidenced by comparison of the IR spectrum of **3** (Fig. 5) with those of free *cis* and *trans*-[(cyclam)Fe(N$_3$)$_2$]X (X = ClO$_4^-$, PF$_6^-$) [3]. The free *cis* isomer exhibits two ν_{as}(N$_3$) stretching frequencies at around 2050 cm^{-1}, whereas the *trans* isomer shows only one absorption band in this region. Since only a single band at 2076 cm^{-1} is observed in the IR spectrum, the co-existence of *cis* and *trans* conformation in **3** is excluded.

The zero-field Mössbauer spectra of **1–3** are shown in Fig. 3, and the data are summarized in Table 1. In the spectrum of **1**, a major doublet **I** with an isomer shift $\delta = 0.48$ mm s^{-1} and a quadrupole splitting $\Delta E_Q = 0.88$ mm s^{-1} is readily assigned to a high-spin Fe(III) ion in an octahedral ligand environment, namely the [Fe(H$_2$O)$_6$]$^{3+}$ species identified by EPR study. Doublet **II** with $\delta = 1.27$ mm s^{-1} and $\Delta E_Q = 3.14$ mm s^{-1} is assigned to a high-spin Fe(II) impurity, which is often observed in the Mössbauer spectra of samples of iron-exchanged zeolite-Y [11]. The zeolite framework coordinated high-spin iron(III) species observed in the EPR spectrum of **1**, are not present in sufficient concentrations to be detected by Mössbauer spectroscopy. In the Mössbauer spectrum of **2**, doublet **I** can also be observed, but with decreased intensities, and a new doublet **III** at $\delta = 0.12$ mm s^{-1} and $\Delta E_Q = 2.19$ mm s^{-1} can be identified. This doublet is assigned to the low-spin Fe(III) species, *trans*-[(cyclam)Fe(H$_2$O)$_2$]$^{3+}$. The isomer shift is small compared with other low-spin iron(III) cyclam complexes, which likely is due to the influence of the zeolite lattice acting as the counter anion. It should be noted that in the spectrum of **2** the intensity of doublet **II** has increased, indicating the formation of further iron(II) species. The formation of
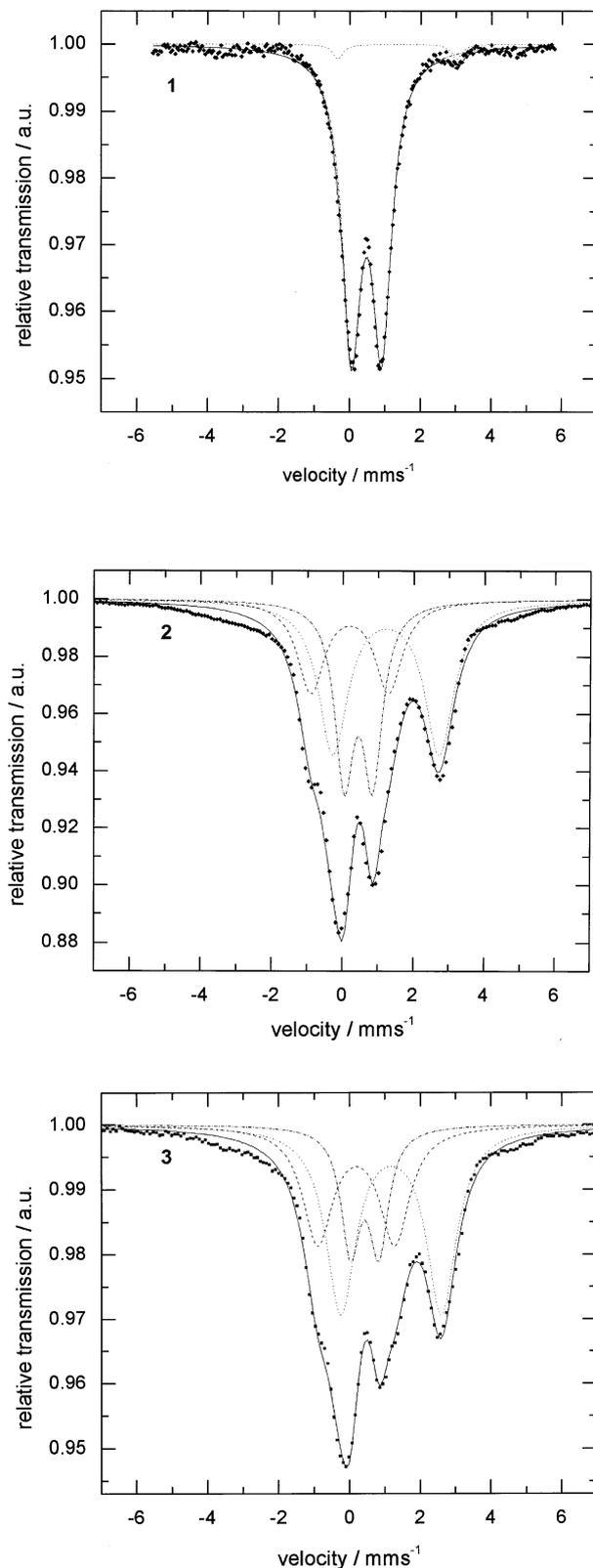

Fig. 3. Mössbauer spectra of a sample of **1** (–·–··–·– doublet **I**, ····· doublet **II**, — resulting fit), **2** (–·–··–·– doublet **I**, ····· doublet **II**, ----- doublet **III**, — resulting fit), and **3** (–·–··–·– doublet **I**, ····· doublet **II**, ----- doublet **IV**, — resulting fit) recorded at 80 K.

Table 1
Mössbauer data of samples of **1**–**3** recorded at 80 K

Sample	Doublet	δ [a] (mm s^{-1})	ΔE_Q [b] (mm s^{-1})	%
1 [c]	**I**	0.48	0.85	97
	II	1.34	3.37	3
2	**I**	0.45	0.80	45
	II	1.23	3.00	38
	III	0.20	2.19	17
3	**I**	0.43	0.80	21
	II	1.18	2.85	50
	IV	0.19	2.17	29

[a] Isomer shift, δ, referring to α-Fe.
[b] Quadrupole splitting, ΔE_Q.
[c] An unidentified background signal ($\delta = 0.44$, $\Delta E_Q = 0$, $W_{fwhm} = 14.75$ mm s^{-1}) was subtracted for the determination of relative intensities of **I** and **II**.

Fe(II) species under dehydrating conditions in vacuum was first observed by Rees et al. and here can be explained by the dehydration of **1** in vacuum prior to treatment with cyclam [11]. The spectra of samples of **3** are very similar to those of **2** with three sets of observed doublets. Doublets **I** and **II** are assigned as in **1** and **2** while a new feature, doublet **IV**, with $\delta = 0.19$ mm s^{-1} and $\Delta E_Q = 2.17$ mm s^{-1} was assigned to the azido iron(III) complex cation, *trans*-[(cyclam)Fe(N$_3$)$_2$]$^+$. Although the isomer shift and quadrupole splitting of this doublet is similar to that of *trans*-[(cyclam)Fe(H$_2$O)$_2$]$^{3+}$ in **2**, the changes in the DR–UV–Vis, IR, and EPR spectra of **2** and **3** support this assignment.

4. Conclusion

In summary, the combination of EPR and Mössbauer spectroscopy and IR, DR, and XRD techniques proves to be a powerful tool for identifying and characterizing in the iron species formed inside the supercages of zeolite-Y. Especially interesting is the identification of encapsulated *trans*-[(cyclam)Fe(N$_3$)$_2$]$^+$@NaY, a potent precursor for the synthesis of an Fe(V) nitrido species. The decomposition pathway to form dinuclear μ-nitrido bridged species likely is effectively quenched and the activation of each isolated and immobilized azide complex should yield persistent iron(V) species. Attempts to photolyze the encapsulated *trans*-[(cyclam)Fe(N$_3$)$_2$]$^+$ to yield a catalytically active iron(V) nitrido species are underway.

5. Supplementary material

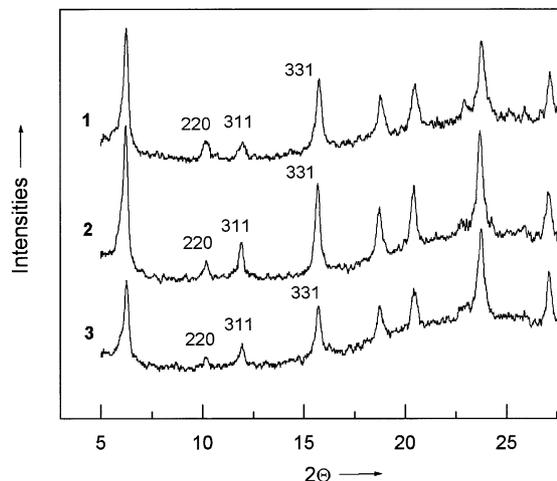XRD traces and IR spectra of samples of **1**–**3** are included as supplemental materials (Figs. 4 and 5).

Fig. 4. XRD patterns of samples of **1**–**3**. The relative intensities of the [220], [311], and [331] peaks change significantly for **1**–**3**. This indicates the formation of a large transition metal complex inside the supercages of zeolite-Y (see ref. [8]).
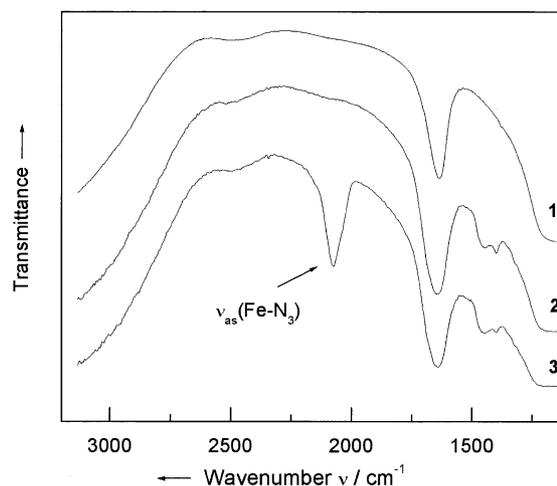

Fig. 5. IR spectra of samples of **1**–**3**.

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