Inorg. Chem. **1994,** *33,* 67–72

Zeolite Encapsulated Cobalt(II) and Copper(II) Perfluorophthalocyanines. Synthesis and Characterization

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Received August 4, 1993[•]

Synthetic faujasite type zeolites have been modified with cobalt(II) and copper(II) hexadecafluorophthalocyanines ($MF_{16}Pc$) by synthesizing zeolite NaX around the $MF_{16}Pc$ complexes and by the template synthesis of the complexes inside NaY zeolites ion exchanged with Co^{2+} and Cu^{2+}. Mid FT-IR and UV–vis spectroscopy as well as X-ray powder diffraction and elemental analysis provide evidence for the encapsulation of the $MF_{16}Pc$ complexes inside the zeolites. The redox properties of the intrazeolite metal complexes were investigated by cyclic voltammetry. Site isolation of these complexes inside the zeolite has resulted in electrochemical data for Co(II)/Co(I) and Cu(II)/Cu(I) redox processes not observed in solution.

Introduction

The encapsulation of transition metal phthalocyanine complexes (MPc's) inside X and Y type zeolites as well as the molecular sieve VPI-5 has been well established.[2] Such intrazeolite complexes are physically trapped in the zeolite pores and are not necessarily bound to the surface. These encapsulated species have been termed ship-in-a-bottle complexes and could potentially provide new types of reactivity. Hybrid catalysts of this type might be viewed as heterogeneous but with retention of some of the solution properties of the metal complexes. The advantages of shape selectivity and site isolation inside the zeolite might also be realized. For example, the iron phthalocyanine catalyzed oxidation of alkanes suffers from low turnover numbers, which is due in part to irreversible dimerization or oxidative degradation of the macrocycle. The inclusion of FePc in Y-type zeolites results in a catalyst $>10^3$ times more active than the homogeneous catalyst.[2i] We recently prepared iron(II) perfluorophthalocyanine in both NaX and NaY zeolites.[3] Our goal was to enhance the oxidative stability as well as improve the catalytic activity of the intrazeolite MPc complexes by removing extractable hydrogens from the ligand while rendering the metal easier to reduce. This follows previous work on solution metal porphyrin and phthalocyanine complexes where electron withdrawing halogen substituents of the ligands was shown to dramatically improve the catalytic activity and stability.[4]

Although synthetic details associated with perhalogenated metal phthalocyanines are limited,[5,6] the electrochemical and electrocatalytic properties of these complexes have been the subject of recent interest.[7,8] The electrochemical behavior in aqueous solution of iron(II), cobalt(II) and zinc(II) hexadecachlorophthalocyanines ($MCl_{16}Pc$) adsorbed on graphite electrodes[7] as well as the electrocatalytic reduction of dioxygen in aqueous solution by $CoF_{16}Pc$ adsorbed on graphite electrodes has been reported.[8] The results from these studies clearly show that perhalogenation of the phthalocyanine ring leads to unusual redox properties. For example, the $[M(II)X_{16}Pc(-2)]/[M(I)X_{16}Pc(-2)]^-$ (M = Co, Fe) redox process was not observed in aqueous or organic solutions for the adsorbed and dissolved complexes. Lever et al.[7] proposed that the lack of an observable M(II)/M(I) redox process was a result of slow electron transfer kinetics due to chlorine substitution, which encourages the well-known spontaneous aggregation of the complexes in solution.

In this paper we report the synthesis of Co^{II}- and $Cu^{II}F_{16}Pc$ inside NaY as well as the synthesis of NaX around $Cu^{II}F_{16}Pc$ complexes. Spectroscopic (FT-IR, UV–vis) and electrochemical characterization of the fluorine-substituted phthalocyanines provides evidence for entrapment in the zeolite supercages. Since the intrazeolite complexes are site isolated, we were able to examine the M(II)/M(I) redox processes for the perfluorinated complexes that are not observed in solution. These results have also furthered our understanding of intrazeolite electrochemistry.[9–11]

[•] Abstract published in *Advance ACS Abstracts,* December 15, 1993.

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Experimental Section

Preparation of Co and Cu Perfluorophthalocyanines in NaY. The free $CoF_{16}Pc$ and $CuF_{16}Pc$ complexes were synthesized using a procedure similar to that previously reported.[5] A 1.4-mmol sample of metal(II) acetate obtained from Aldrich (0.28 g $Cu(CH_3CO_2)_2$ or 0.35 g $Co(CH_3CO_2)_2{\cdot}4H_2O$) was mixed with 1.4 g (7.0 mmol, 25% excess) of tetrafluorophthalonitrile in 20 mL of 1-chloronapthalene (Eastman) under nitrogen. The mixture was refluxed for 24 h, cooled to room temperature, and suction filtered. Then 100 mL of petroleum ether was added to the blue filtrate that was then submerged in an ice bath. A dark blue precipitate formed and was suction filtered through a fine Teflon filter. The $MF_{16}Pc$ complex was recrystallized from sulfuric acid[5] and isolated in 54–65% yield.

The appropriate metal cation (Cu^{2+} or Co^{2+}) was incorporated into the NaY zeolite (CBV-100, Si/Al = 2.5) through ion exchange using standard procedures.[13] Approximately 1 g of CuNaY or CoNaY was heated in a Pyrex ampule at 350 °C under vacuum ($<10^{-3}$ Torr) for 2 h and then cooled to room temperature. Then 1 g of tetrafluorophthalonitrile (Aldrich) was introduced and the ampule was again evacuated for 2 h before sealing. The finely powdered mixture was placed horizontally in a tube furnace and heated at 300 °C for 24 h. The reactor was cooled to room temperature then the contents removed and transferred to a Sohxlet extractor. The zeolites were extracted for 72 h with acetone, pyridine, and acetonitrile and again with acetone. The $MF_{16}Pc$-modified zeolites were dried at 90 °C in vacuo (<1 Torr) for 15 h.

NaX Zeolite Synthesis in the Presence of Copper Perfluorophthalocyanine. The synthesis of zeolite NaX incorporating $CuF_{16}Pc$ was similar to that previously described.[21] Aluminum isopropoxide, silica, and sodium hydroxide obtained from Aldrich were used without purification. The silicate gel was prepared from 2.0 g of silica, 1.6 g of NaOH, 0.15 g of $CuF_{16}Pc$ and 4.0 mL of H_2O. Addition of the aluminate solution (4.5 g of $Al(i\text{-}OPr)_3$, 1.6 g of NaOH, 6.0 mL of H_2O) resulted in a sticky gel with an intense blue color. An additional 18.0 mL of deionized water was added, and then the gel was transferred to a polypropylene bottle. The mixture having a molar ratio of $SiO_2{:}Al_2O_3{:}Na_2O{:}H_2O{:}CuF_{16}Pc$ = 3.0:1.0:3.6:141:0.015 was aged at room temperature with magnetic stirring for 24 h and then heated at 90 °C for 15 hours. The crystallization mixture was allowed to cool to room temperature, diluted with copious amounts of deionized water, and then isolated by centrifugation. The light blue solid that was separated was dried at 90 °C for 24 h and was labeled CuF_{16}–NaX–A. The mother liquid obtained after centrifugation was filtered through a fine Teflon filter. A solid was separated, washed with deionized water and dried at 90 °C for 24 h. This dark-blue sample was labeled $CuF_{16}Pc$–NaX–B. The samples were Sohxlet extracted with acetone and pyridine and then with acetone again for 72 h and then dried at 90 °C in vacuo (<1 Torr) for 15 h.

Electronic spectra of the zeolites were obtained from the samples prepared as Nujol mulls between quartz plates using a Hitachi U-2000 UV–vis spectrophotometer. Mid-IR spectra were obtained from KBr pellets using a Mattson 2025 FT–IR spectrophotometer. X-ray powder diffraction patterns were recorded on a Scintag XDS 2000 diffractometer using CaF_2 as an internal standard. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

The modified pressed powder electrodes containing the $MF_{16}Pc$–NaY were prepared according to our previously reported method.[9,10,11] A 30-mg sample of $MF_{16}Pc$–NaY was added to 30 mg of high purity (99.999+%) powdered graphite (Koch Light), mixed thoroughly, and then pressed onto a 13-mm-diameter platinum gauze disk. The modified electrodes obtained by such a way are noted as graphite–Y/complex.

The electrochemical behavior of the electrodes was studied by cyclic voltammetry in 0.1M DMSO solutions of tetrabutylammonium tetrafluoroborate ($(TBA)BF_4$) as supporting electrolyte. These solutions were routinely deoxygenated with high-purity argon for 20 min prior the analysis. The potential values are quoted with reference to a Tacussel XR 110 aqueous saturated calomel electrode (SCE). The specific instrumentation utilized was a Tacussel potentiostat-galvanostat, Model PJT 24-1, and a Tacussel waveform generator, Model GST-4.

Table 1. Elemental Analyses for Zeolites Modified with $MF_{16}Pc$

sample	% M by wt	% F by wt	[M]/[F] ratio	no. of $MF_{16}Pc$/100 α cages
$CoF_{16}Pc$–NaY	3.00	6.88	0.13	61[a]
$CuF_{16}Pc$–NaY	4.17	6.31	0.20	55[a]
$CuF_{16}Pc$–NaX–A	0.09	0.35	0.076	3.3
$CuF_{16}Pc$–NaX–B	0.16	0.69	0.069	5.8
$MF_{16}Pc$ (theory)			0.063	

[a] Calculation is based on fluorine content.

Results and Discussion

Metal phthalocyanines have been incorporated into zeolite molecular sieves by two methods. The *template synthesis* approach involves the condensation of four phthalonitrile molecules inside a zeolite modified with the metal ion to be complexed. The target metal ion may be introduced by ion exchange or by adsorption of a precursor metal complex. Zeolite X and Y encapsulated MPc complexes, where M = Cu, Ni, Co, Fe, Mn, Ru, Os, and Rh, have been prepared.[2] The template synthesis of intrazeolite phthalocyanine derivatives by the reaction of substituted phthalonitriles in the zeolite should be feasible. Therefore, we reacted tetrafluorophthalonitrile (TFP) with Cu(II) and Co(II) exchanged NaY zeolites to prepare the entrapped $MF_{16}Pc$ complexes. We have previously reported[3] the preparation of zeolite-encapsulated $FeF_{16}Pc$ by the reaction of TFP with NaY impregnated with $Fe(CO)_5$.

We have also prepared zeolite-encapsulated $CuF_{16}Pc$ by the second of these encapsulation methods, which involves synthesis of a zeolite such as NaX around the metal complex. We had previously discovered that the introduction of MPc complexes during zeolite crystallization results in significant amounts of the metal complex being encapsulated.[21] The *zeolite synthesis* approach provides many advantages over the *template synthesis* method where the nature of the resulting intrazeolite complex may be poorly defined. Synthesizing the zeolite around the metal complex ensures that there is no free metal ion or ligand present in the zeolite that could complicate characterization or reactivity.[21,3] Zeolite NaX was crystallized around $CuF_{16}Pc$ using this strategy. The zeolite phase purity and crystallinity were confirmed by X-ray powder diffraction. The NaX sample modified with $CuF_{16}Pc$ was divided into two fractions labeled A and B, where fraction A represents the bulk of the crystals found at the bottom of the reactor and while fraction B was collected at the top. This separation of crystals was also observed for NaX synthesized with $FeF_{16}Pc$.[3] We suspect that portions of the gel with higher concentrations of metal complex become more hydrophobic and float to the top of the reaction mixture. The zeolites modified with $MF_{16}Pc$ complexes were purified by a series of solvent extractions to remove surface species. The intrazeolite $MF_{16}Pc$ complexes do not appear to be as stable as the MPc complexes to sublimation, so this was not employed as a purification technique.

The elemental analyses for the NaY and NaX zeolites modified with the $MF_{16}Pc$ complexes are listed in Table 1. In the case of the complexes prepared in the NaY zeolites the [M]/[F] ratios clearly indicate that not all of the metal ions react with TFP to form a complex. In contrast, Table 1 indicates that the [M]/[F] ratios for the NaX samples crystallized around $MF_{16}Pc$'s are quite close to the theoretical value. This highlights an advantage of the *zeolite synthesis* method, namely the nature of the intrazeolite species is well-defined. This further confirms our observations that $CuF_{16}Pc$ is stable under zeolite synthesis conditions. The loading of $CuF_{16}Pc$ in NaX is slightly greater in fraction B (top) than in fraction A, which indicates there is a heterogeneous distribution of $MF_{16}Pc$ in the precursor gel.

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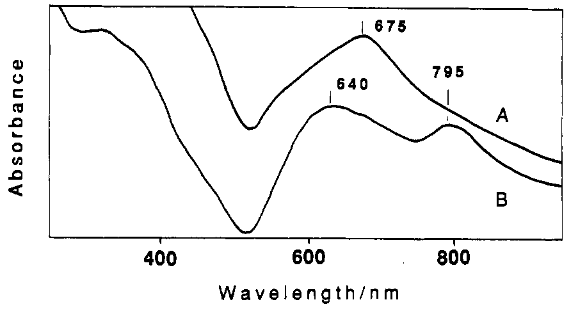

Figure 1. Electronic spectra of (A) a sample of $CuF_{16}Pc$–NaX–B and (B) a mixture of NaX and $CuF_{16}Pc$ complex prepared as Nujol mulls.

Table 2. UV–Vis Band Positions (nm) for Solution Complexes

sample	pyridine	sulfuric acid (18 M)
$CoF_{16}Pc$–NaY		300, 708, 760 sh, 796 s
$CoF_{16}Pc$	600, 661 s	300, 710, 760 sh, 796 s
$CoCl_{16}Pc$[a]		832[a,b]
CoPc		786[a,b]
$CuF_{16}Pc$–NaY[d]		442, 756 s, 774 sh, 817 s
$CuF_{16}Pc$	615, 645, 677 s	442, 756 sh, 774 s, 817 s
$CuF_{16}Pc$[c]		446, 779, 821

[a] Reference 7. [b] Only Q band reported. [c] Reference 5. [d] Spectra of the H_2SO_4 extractions for $CuF_{16}Pc$–NaX–A,B samples are analogous.

However, we expect the complexes to be evenly distributed within the NaX crystals. The loadings in the NaY zeolites are quite high, but the distribution of complexes probably decreases toward the centers of the crystals. This is because TFP must diffuse into the crystal to react, and the $MF_{16}Pc$ complexes formed in the outer portions of the crystals then begin to block diffusion pathways.

Zeolites modified with phthalocyanine complexes are generally deep blue or green in color. This intense color, which arises from ligand $\pi \rightarrow \pi^*$ transitions, is characteristic of both free and encapsulated complexes. This provides a unique spectroscopic handle for characterizing intrazeolite complexes and differentiating surface species. The UV–vis spectrum for the zeolite sample $CuF_{16}Pc$–NaX–B is shown in Figure 1a. A comparison with the spectrum of $CuF_{16}Pc$ adsorbed on the zeolite outer surface (Figure 1b) illustrates the differences between the encapsulated and free complex. The Q band for the $CuF_{16}Pc$–NaX–B sample (675 nm) is red shifted from the outer surface physisorbed complex (640 nm). The adsorbed complex has an additional band at 795 nm which is, probably, associated with the formation of surface aggregates.[2f] The size of the planar Pc ligand (~13 Å) exceeds the effective dimensions of the zeolite supercage (12 Å). We and others have calculated the lowest energy configuration for these complexes inside the zeolite which results in a distortion of the macrocycle from planarity.[2d,h,l,3,14] Recent Raman and NMR data do not agree with this result;[2r] however, the shift to lower energy for these ligand based electronic transitions inside the zeolite is consistent with distortion of the ligand. This could be considered partial evidence for inclusion of $MF_{16}Pc$ complexes.

The only way to remove the $MF_{16}Pc$ complexes from the zeolite is to destroy the molecular sieve lattice. Partial digestion of the zeolites in concentrated H_2SO_4 results in release of the $MF_{16}Pc$ complexes into solution. The band positions from the electronic spectra for these samples are listed in Table 2. A comparison of free $MF_{16}Pc$ complexes dissolved in H_2SO_4 with the complexes recovered from the zeolites indicates they are the same with no evidence of free ligand. The formation of free ligand in intrazeolite MPc template syntheses is a problem.[2h,i,r] The lack of free ligand in our case may reflect the lower reactivity of TFP. The band positions in concentrated H_2SO_4 are red shifted because of protonation of the peripheral nitrogens on the ligand. As was the case with $FeF_{16}Pc$, the Q band of $CoF_{16}Pc$ at 796 nm in sulfuric acid is red shifted relative to CoPc but not as much as for $CoCl_{16}Pc$. This shift is consistent with the electron-withdrawing effects of fluorine substituents.

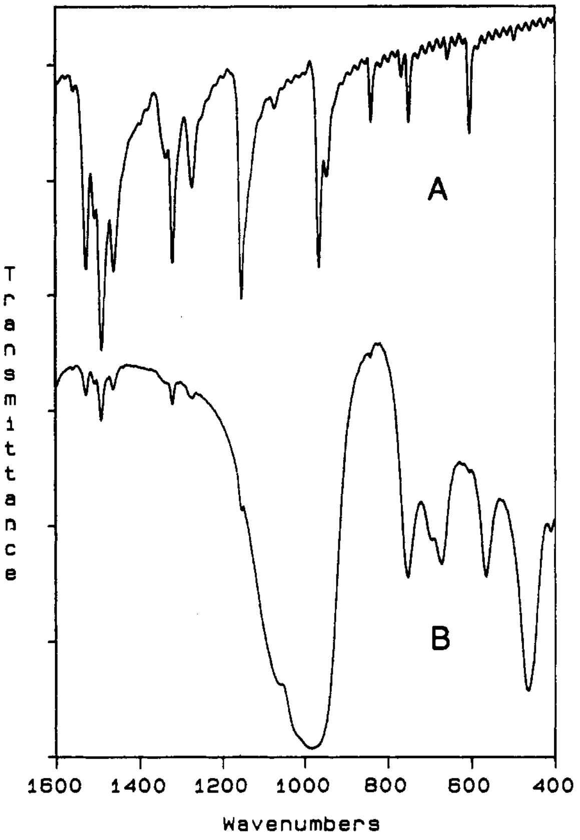

Figure 2. FT-IR spectra of (A) the free $CuF_{16}Pc$ complex and (B) a sample of $CuF_{16}Pc$–NaX–B recorded as KBr pellets.

The IR spectra can also provide information on encapsulation as well as crystallinity. The NaY samples modified with $MF_{16}Pc$ do not show significant band broadening or shifts that would result from dealumination. Figure 2 shows the IR spectra for the free $CuF_{16}Pc$ complex and for $CuF_{16}Pc$–NaX–B. The zeolite bands dominate this region of the spectrum; however, the presence of $CuF_{16}Pc$ is obvious. The observable IR bands are apparently not as sensitive to expected distortions of the encapsulated complexes as the UV–vis spectra. The bands at 1250–1550 cm^{-1} may be attributed to C–C stretch vibrations of the phenyl or isoindole rings, although they differ from those observed for non-halogenated phthalocyanine ligand.[2m,n,r] Even if the phthalocyanine ring system undergoes a saddle deformation, the four phenyl rings can penetrate the apertures of the zeolite supercages without considerable distortions.[2h,3,14] It becomes clear why a combination of analytical techniques is needed to confirm the intrazeolite location of the complexes.

We have previously shown that cyclic voltammetry can provide information on the nature of intrazeolite metal complexes that may not be readily apparent from spectroscopic studies.[3,9–12] Additionally, we have observed the electrocatalyzed reduction of alkyl halides as well as the activation of dioxygen by zeolite encapsulated complexes.[10,11] Electrochemical data for intrazeolite $MF_{16}Pc$ complexes were obtained from zeolite/graphite composite electrodes. The NaY-modified zeolites that were studied may contain uncomplexed M^{2+}; however, we have previously shown that redox processes associated with the ions might be distinguished from the complexes.[9,10] The NaX samples were not studied because of the low loadings of $CuF_{16}Pc$, but we expect the result would be similar to those for NaY samples. The results in Table 3 should reflect the redox activity of intrazeolite

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Table 3. Summary of E_{eq} (V/SCE) Potential Values of the Redox Processes[a] for the Encapsulated and Free $MF_{16}Pc$ Complexes in DMSO + 0.1 M $(TBA)BF_4$

	encapsulated complex			Free complex		
sample	I	II	III	I	II	III
$Co^{II}F_{16}Pc$						
E_{eq} in DMSO	−0.10	−1.21		−0.13	−1.07	
E_{eq} in ACN	−0.10	−1.29				
$Co^{II}Pc$						
E_{eq} in DMSO	−0.48	−1.41		−0.50	−1.43	
$Cu^{II}F_{16}Pc$						
E_{eq} in DMSO	−0.12	−0.67	−0.95		−0.88	−1.45
$Cu^{II}Pc$						
E_{eq} in DMSO				−0.73	−1.43	

[a] $[M^{II}F_{16}Pc(-2)]/[M^IF_{16}Pc(-2)]^-$, $[M^IF_{16}Pc(-2)]^-/[M^IF_{16}Pc(-3)]^{2-}$ and $[M^IF_{16}Pc(-3)]^{2-}/[M^IF_{16}Pc(-4)]^{3-}$ are the redox processes I, II, and III, respectively.

complexes located in the supercages and held in sufficient proximity to the electronic conductor. Since all the supercages are not occupied by metal complexes, we suggest that the extended electron-hopping process can occur between the encapsulated molecules located near the apertures of the outer cavities and the external graphitic species. Therefore, only a small fraction of the $MF_{16}Pc$ guests might be observed electrochemically.

If one considers the two general mechanisms described by Shaw et al.[15] for the electrochemical process at zeolite modified electrodes

$$E^{m+}(z) + mC^+(s) \Leftrightarrow E^{m+}(s) + mC^+(z) \qquad (1)$$

$$E^{m+}(s) + ne^- \Leftrightarrow E^{(m+n)+}(s)$$

$$E^{m+}(z) + ne^- + nC^+(s) \Leftrightarrow E^{(m-n)+}(z) + nC^+(z) \qquad (2)$$

(where E^{m+} is the electroactive species, (z) indicates the zeolite matrix, (s) is the solution and C^+ is the electrolyte cation) we can see that mechanism 1 occurs only with small electroactive complexes fixed within the zeolite by ion exchange that can move freely through the pore system. Therefore, this mechanism can be rejected in the case of the ship-in-a-bottle complexes. In mechanism 2, the electroactive complex already encapsulated undergoes electron transfer within the zeolite cavities. This may occur according to the electron-hopping mechanistic picture now well accepted for polymers with discrete redox groups.[16] Li and Mallouk[17] have provided evidence of such an electron-hopping process between a redox species contained within the zeolite cavities and an external one. Recently, De Castro-Martins et al.[18] showed, in the case of titanium silicalite that the Ti(IV)/Ti(III) electrochemical process is not limited to the surface titanium ions at the zeolite–carbon boundaries but extends to the inner part of the zeolite crystallites. The mechanism for electron transfer in these materials is not known, although various observations corroborate the fact that electrochemical techniques such as cyclic voltammetry provide information that reflects the electroactivity of the intrazeolite species. Additionally, it is important to note that the role of the electrolyte cations in modulating zeolite activity is not fully understood and remains controversial since it has been studied by several researchers with somewhat conflicting results.[10,19,20] We suggest that the electrolyte does not have to diffuse very far inside the zeolite cavities, due to the ionic conductivity of the zeolites. This is because the charge balance may be achieved if the charge compensation sites are located close to the cavity apertures which would then not exclude electrolyte cations based on size.

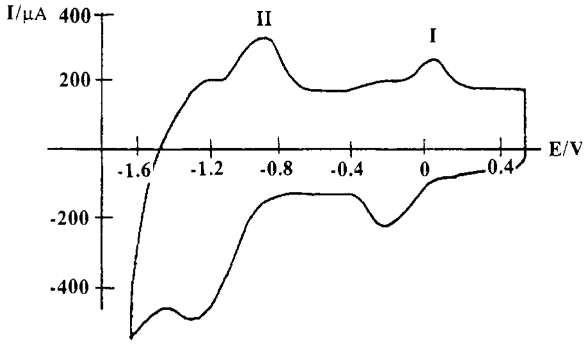

Figure 3. Cyclic voltammetry of a graphite–Y/$CoF_{16}Pc$ pressed powder electrode in DMSO + 0.1 M $(TBA)BF_4$ with a potential sweep rate of 20 mV/s.

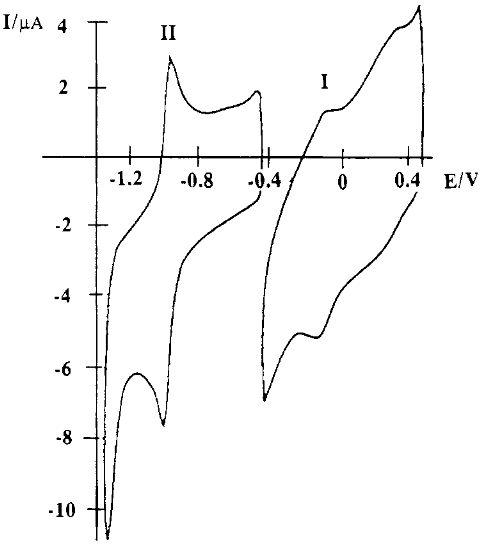

Figure 4. Cyclic voltammetry of $CoF_{16}Pc$ (5 mM) at a vitreous carbon disk electrode (A = 0.071 cm^2) in DMSO + 0.1 M $(TBA)BF_4$ with a potential sweep rate of 100 mV/s.

Figures 3 and 4 show the cyclic voltammograms of a graphite–Y/$CoF_{16}Pc$-modified electrode and $CoF_{16}Pc$ complex in DMSO + 0.1 M $(TBA)BF_4$ solution in the potential ranges +0.5 to −1.6 V and +0.5 to −1.3 V, respectively. These voltammograms exhibit two couples of peaks denoted as **I** and **II** and situated at E_{eq}(**I**) and E_{eq}(**II**) respectively, where $E_{eq} = (E_{pa} + E_{pc})/2$. E_{pa} is defined as the potential value of the anodic peak, and E_{pc} is the potential value of the corresponding cathodic peak. In comparing these results with some of the reported studies of cobalt phthalocyanine derivatives in organic solvents,[9,21-27,28] we find the redox process

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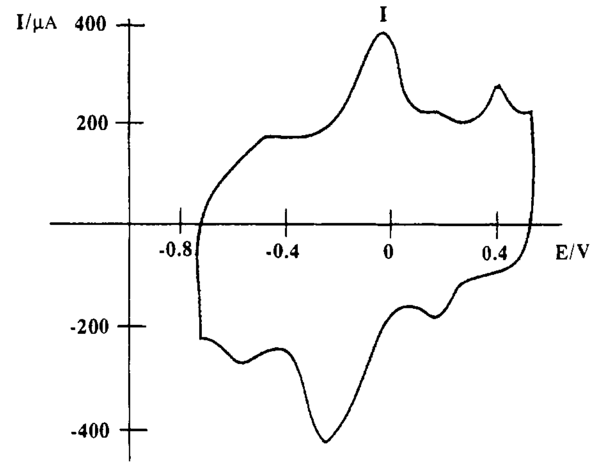

Figure 5. Cyclic voltammetry of a graphite–Y/$CuF_{16}Pc$ pressed powder electrode in DMSO + 0.1 M $(TBA)BF_4$ with a potential sweep rate of 20 mV/s.

for the $CoF_{16}Pc$ and encapsulated complex are indeed occurring at more positive potential than the unsubstituted CoPc due to the presence of the highly electron withdrawing fluorine substituents[7,8,29] (see Table 3). These two pairs of peaks can be attributed to the well-known monoelectronic redox process involving, at E_{eq}(I), a metal-based electron transfer, namely the $[Co^{II}F_{16}Pc(-2)]/[Co^{I}F_{16}Pc(-2)]^-$ redox process, followed by the phthalocyanine ring reduction process $[Co^{I}F_{16}Pc(-2)]^-/[Co^{I}F_{16}Pc(-3)]^{2-}$ at E_{eq}(II). It should also be noted that there is an additional ill defined voltammetric peak in Figure 4 near 0.4 V which may reflect the $Co(II)F_{16}Pc$ oxidation process that is expected in this potential range.

It is important to note that the couple of peaks (I) related to the Co(II)/Co(I) redox process is clearly more well-defined for the encapsulated complex than for the solution one. This observation can be interpreted as a consequence of site isolation of the complexes within the zeolite and corroborates the results reported by Lever and co-workers[7] for the dissolved chloro-substituted Co(II) phthalocyanine in DMF where the aggregation of the dissolved complexes leads to an associated slow kinetics pathway for electron transfer to the aggregates, that prevents the clear observation of the Co(II)/Co(I) redox process. This may not be the only explanation for our observations but is certainly plausible.

Our potential measurements for both dissolved and zeolite encapsulated complexes were very similar at E_{eq}(I) but at E_{eq}(II) the $[Co(I)F_{16}Pc(-2)]^-/[Co(I)F_{16}Pc(-3)]^{2-}$ couple was approximately 100 mV more negative for the encapsulated complex than the dissolved one. We presume that the metal-based electron transfer of the first reduction is less susceptible to the protic nature of the organic solvent unlike the ligand base reaction of the second couple. Indeed, in experiments using ACN, DMSO and DMF + 0.1 M $(TBA)BF_4$ solutions, the position of the Co(II)/Co(I) couple remains approximately constant regardless of solvent, whether in solution or within the zeolite matrix. A combination of solvent effects, the charged environment of the zeolite structure itself, and/or the variable amount of water molecules present within the cages account for the variation in potential found in the ligand-based couple. Further support for this argument is the previously noted pH dependence of the potential values for $Co^{II}Cl_{16}Pc$, $Fe^{II}Cl_{16}Pc$, and $CoF_{16}Pc$ complexes in aqueous solutions.[7,8]

Figures 5 and 6 show the cyclic voltammograms of a graphite–Y/$CuF_{16}Pc$ modified electrode and free $CuF_{16}Pc$ complex dissolved in DMSO + 0.1 M $(TBA)BF_4$ solution over the potential ranges +0.5 to −0.8 V and −0.5 to −0.8 V, respectively. The narrow potential range selected for the measurement of the dissolved complex was chosen to reduce interference due to the potential-dependent adsorption of the phthalocyanine on the graphite electrode, leading to unreproducible results. The voltammogram of the encapsulated complex shown in Figure 5 exhibits, in the restricted potential range [+0.5 to −0.7 V], a well-defined pair of peaks at −0.12 V, which can be attributed to the $[Cu^{II}F_{16}Pc(-2)]/[Cu^{I}F_{16}Pc(-2)]^-$ redox process **I**. The exact nature and the origin of the small additional waves observed in this voltammogram are uncertain. Two additional processes have been recorded at −0.67 and at −0.95 V, which can be attributed to the $[Cu^{I}F_{16}Pc(-2)]^-/[Cu^{I}F_{16}Pc(-3)]^{2-}$ and $[CuF_{16}Pc(-3)]^{2-}/[CuF_{16}Pc(-4)]^{3-}$ reactions for the encapsulated complex. Figure 6 shows the well-defined cyclic voltammogram of these two redox processes, **II** and **III**, for the free $CuF_{16}Pc$ complex. By analogy with the reported results for CuPc complexes in DMSO,[21] it can be clearly seen that the redox processes for both free $CuF_{16}Pc$ and the encapsulated complex are indeed occurring at the more positive potentials due to their highly electron-withdrawing substituents (see Table 3). This result corroborates that for $CoF_{16}Pc$ described above. In addition, the Cu(II)/Cu(I) redox process appears to be clearly well-defined when the complexes are entrapped within the zeolite cavities, likely as a consequence of their site isolation, while the same process for the dissolved molecules is extremely ill-defined and the electrochemical response is not very reproducible because of aggregation.

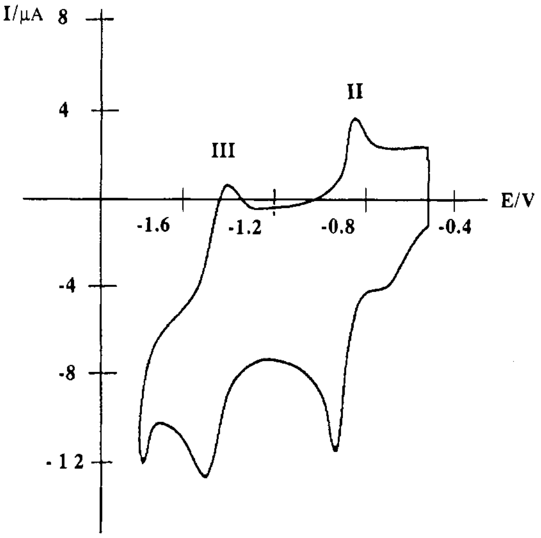

Figure 6. Cyclic voltammetry of $CuF_{16}Pc$ (5 mM) at a vitreous carbon disk electrode (A = 0.071 cm^2) in DMSO + 0.1 M $(TBA)BF_4$ with a potential sweep rate of 100 mV/s.

Taking into account the quantities of charge passed in the reduction or oxidation voltammetric peaks (Figures 3 and 5), we can estimate the amount of accessible intrazeolite metal complexes (note that the charges under the voltammograms are independent of the potential scan rate for rates slower than 20 mV/s). A comparison between the calculated quantities of charge (2 and 3 mC in the case of Y/$CoF_{16}Pc$ and $CuF_{16}Pc$, respectively) and the total $MF_{16}Pc$ loading in the zeolites (Table 1) suggests that only 0.5% of the encapsulated metal complexes are electroactive. From these data, it is clear that the bulk of the intrazeolite complexes cannot be reached. However, this is consistent with the proposed electron-transfer mechanism and corroborates the fact that only the complexes in supercages near the surface of the crystal are electroactive.[12] The presence of empty supercages inhibits the electron-hopping process between complexes trapped deep in the crystal. We are currently developing strategies for mediating the communication between guest molecules in the bulk of the zeolite. Finally, we have noted that the voltammetric peak amplitudes show a slight decrease after several successive potential scans. This may be related to the motion of the electrolyte within the congested zeolite pore system.[11,12]

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Conclusions

We have shown that Cobalt(II) and Copper(II) perfluorophthalocyanine complexes can be encapsulated in both NaX and NaY zeolites by either the *zeolite synthesis* or the *template synthesis* method. Cyclic voltammetry reveals reversible pairs of peaks assigned to the M(II)/M(I) redox processes that are difficult to observe in solution. The redox behavior of the inclusion compounds seems to be a consequence of their site isolation within the zeolite matrix while the simple adsorption of the molecules on electrode surface or on any other mineral support does not prevent aggregate formation. Additional support for these results as well as further evidence for the accessibility of the intrazeolite complexes by solution species[10,11] (pyridine or molecular oxygen) will be provided by continuing electrochemical studies in alkaline solutions.[12]

Acknowledgment. We would like to thank NATO (Grant CRG 920275) for financial support. We are also grateful to Robert A. Welch Foundation for a graduate student fellowship (S.L.B.).