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Encapsulation of Cobalt Phthalocyanine in Zeolite-Y: Evidence for Nonplanar Geometry

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Cobalt (II) phthalocyanine (CoPc) molecules have been encapsulated within the supercage of zeolite-Y. The square-planar complex, being larger than the almost spherical cage, is forced to adopt a distorted geometry on encapsulation. A comparative spectroscopic and magnetic investigation of CoPc encapsulated in zeolite-Y and in the unencapsulated state is reported. These results supported by molecular modeling have been used to understand the nature and extent of the loss of planarity of CoPc on encapsulation. The encapsulated molecule is shown to be the trans-diprotonated species in which the center of inversion is lost due to distortions required to accommodate the square complex within the zeolite. Encapsulation also leads to an enhancement of the magnetic moment of the CoPc. This is shown to be a consequence of the nonplanar geometry of the encapsulated molecule resulting in an excited high-spin state being thermally accessible.

Introduction

The encapsulation of transition metal coordination complexes and organometallics within the voids of microporous zeolite has attracted attention since it provides a simple way of coupling the reactivity of the metal complex with the robustness and stereochemistry of the host zeolite.[1] Encapsulation provides a convenient route for the heterogenization of homogeneous catalytic processes, and indeed, these compounds have found application in catalysis and gas purification.[2,3] These hybrid catalysts offer the advantage of shape selectivity and site isolation, as provided by the zeolite matrix, while retaining the solution reactivity of the metal complex. The “ship-in-a-bottle” complexes, which for steric reasons have to be assembled in situ by bringing the metal and ligand species within the voids of the zeolite, are a fascinating class of encapsulated compounds.[4] Once assembled these complexes cannot be removed without destroying the lattice. It has been widely recognized that space constraints imposed by the zeolite as well as specific interactions with the zeolite framework can induce structural and functional modifications of the complex as compared to its solution or solid-state properties, the most visible manifestation of which are changes in the reactivity and catalytic properties. There are number of well-documented examples in which the catalytic activity of the encapsulated complex is either enhanced or more selective as compared to the same complex in solution.[5,6]

A less widely studied aspect of these materials is the fact that the topology of the void could have a profound influence on the geometry that the encapsulated complex adopts, which in turn could lead to appreciable changes in the electronic and magnetic properties of the complex. One of the earliest, and perhaps most dramatic, of such changes was reported by Mizuno and Lunsford.[7] Their electron paramagnetic

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resonance measurements indicated that the ship-in-a-bottle complex cobalt(II) tris(bipyridyl) complex ion, $[Co(bpy)_3]^{2+}$, encapsulated in the supercage of zeolite-Y, exhibits a temperature driven interconversion between a low-spin state and a high-spin state. The observation is interesting because normally the $[Co(bpy)_3]^{2+}$ complex ion retains a high-spin ground state, both in solution and in the solid state, irrespective of the temperature or the nature of the counterion.[8] From a comparative study of the magnetism and optical spectroscopy of the encapsulated and unencapsulated $[Co(bpy)_3]^{2+}$ complex ion, it was shown that such spin behavior was intramolecular in origin.[9] The topology of the supercage forces the $[Co(bpy)_3]^{2+}$ complex ion to adopt an octahedral geometry less distorted than in the unencapsulated state. The change in geometry, in turn, leads to a change in the spin state of the cobalt ion.[9] In this paper, we report the changes in the optical and magnetic properties of square-planar cobalt phthalocyanine (CoPc) on encapsulation within the supercages of zeolite-Y.

The encapsulation of transition metal phthalocyanine (MPc) complexes inside the faujasitic X and Y type zeolites as well as molecular sieves has been well established.[6,10−14] These ship-in-a-bottle complexes are formed by allowing the building blocks of the phthalocyanine ring, dicyanobenzene, to diffuse through the windows of the zeolite cages and condense around a metal ion previously introduced by ion exchange. The MPc complex so formed is trapped within the zeolite and not a surface-bound species.[12] The catalytic activity of the encapsulated MPc complexes has been reported in the literature; they are found to be the one of the more efficient heterogeneous mimics of the oxidation activity of the enzyme P-450 cytochrome.[15] The inclusion of FePc in zeolite-Y, for example, results in a catalyst which is at least 10^3 times more active for the oxidation of alkanes as compared to the homogeneous catalyst in solution.[14]

A less well-explored aspect of the encapsulated MPc is how the encapsulated square-planar complex is accommodated within the almost spherical supercages of the faujasitic zeolite. This problem is highlighted in the molecular graphics representation shown in Figure 1 of an undistorted square-planar CoPc inside the supercage of zeolite-Y (the view is of an orientation in which steric interactions with the walls have been minimized). The dimension of square-planar CoPc as found in the unencapsulated or “free” state from X-ray crystallographic studies[16] is 15 Å (end-to-end diagonal) while the diameter of the almost spherical supercage of zeolite-Y is 12.7 Å. The problem is, therefore, literally (rather than metaphorically) on how to fit “a square peg in a round hole”. It is evident from the molecular graphics representation of Figure 1 that the MPc molecule would have to distort and adopt a nonplanar geometry if it has to be accommodated within the supercage. We have carried out a spectroscopic and magnetic investigation of CoPc encapsulated in zeolite-Y and in its unencapsulated or free state. These results supported by molecular modeling have been used to understand the nature and the extent of distortion of the square-planar CoPc molecule on encapsulation in zeolite-Y.

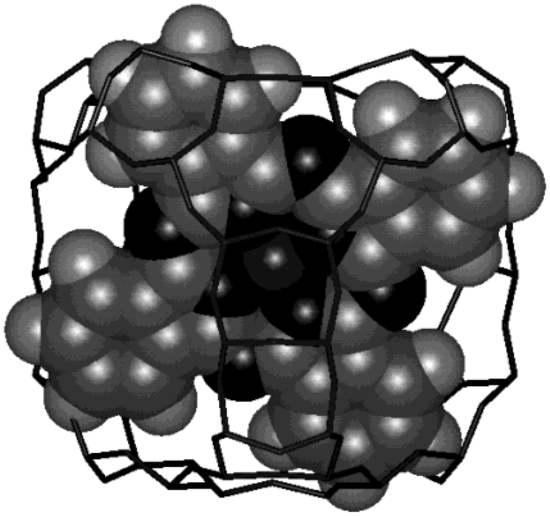

Figure 1. Molecular graphics representation of a square-planar Co phthalocyanine molecule encapsulated within the supercage of zeolite-Y.

Experimental Section

Preparation and Characterization. Cobalt phthalocyanine encapsulated within zeolite-Y was prepared by following the procedure reported in the literature.[11,12] Co^{2+}-exchanged zeolite-Y was heated with excess amount of 1,2-dicyanobenzene (DCB). The dicyanobenzene molecule is small enough (∼6.5 Å) to diffuse through the 7.4 Å windows of the supercage of the zeolite and condense around the metal ion to form cobalt phthalocyanine. Co^{2+}-exchanged zeolite was prepared by ion-exchanging zeolite-Y $[Na_{56}Al_{56}Si_{136}O_{384}(H_2O)_y]$ with cobalt acetate solution of known concentration followed by filtration and calcination in air at 200 °C. The desired loading level was obtained by varying the concentration (0.005−0.02 M) of the cobalt acetate solution. The loading levels were determined by atomic absorption spectroscopy (Perkin-Elmer 2380 atomic absorption spectrometer) after dissolving the Co-exchanged zeolite in HF. The Co-exchanged zeolite-Y samples had loading levels typically ranging from $x = 2$ to 4 in the general formula $Co_xNa_{56-2x}Al_{56}Si_{136}O_{384}\cdot yH_2O$. Most studies reported here, unless otherwise stated, are for Co^{2+}-exchanged zeolite with $x = 4$.

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The encapsulated Co phthalocyanine (CoPc) was prepared by mixing dry Co^{2+}-exchanged zeolite-Y with a stoichiometric excess of 1,2-dicyanobenzene. The mixture was heated at 100 °C for 2 h under vacuum (10^{-2} Torr), sealed, and heated for a further 24 h at 250−270 °C. This temperature range was chosen so as to coincide with the temperature of the exotherm reported in a DSC study of the preparation of CoPc in zeolite-Y.[13] On heating, the solid mass changed in color from pink to blue. The product was crushed and purified by Soxhlet extraction using the sequence of solvents acetone, methanol, pyridine, acetone, and finally with diethyl ether to remove any unreacted species or species adsorbed on the surface of the zeolite crystallites and finally dried under vacuum. The encapsulated complex is not air sensitive and could therefore be handled under ambient conditions.

The powder X-ray diffraction patterns of the zeolite with encapsulated CoPc complex is similar to that of the Co^{2+}-exchanged zeolite-Y and the parent Na-zeolite-Y indicating that the integrity of zeolite structure is preserved. There are, however, differences in the relative peak intensities of the 220 and 311 reflections appearing at $2\theta = 10$ and 12°, respectively. For pure zeolite-Y and for Co-exchanged zeolite-Y $I_{220} > I_{311}$, but for the encapsulated complex $I_{311} > I_{220}$. This reversal in intensities has been observed in encapsulated complexes and has been empirically correlated with the presence of a large complex within the zeolite-Y supercage.[17] The above observation may therefore be construed as evidence for the successful encapsulation of Co phthalocyanine complex within the supercage.

CoPc was also encapsulated in the mesoporous molecular sieve MCM-41. MCM-41 with a Si/Al ratio of 20 was prepared by following the procedure reported in the literature.[18] The calcined MCM-41 was ion-exchanged with 0.025 M cobalt acetate aqueous solution, washed, and dried. CoPc was incorporated within the Co^{2+}-exchanged MCM-41 by following an identical procedure as used for the encapsulation of CoPc within zeolite-Y. “Free” or “unencapsulated” CoPc was prepared by heating 1,2-dicyanobenzene with anhydrous cobalt chloride.[19]

Instrumentation and Procedures. Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XD-D1 powder X-ray diffractometer using Cu Kα radiation ($\lambda = 1.542$ Å). XRD patterns were recorded in the 2θ range of 5−70° at a scanning rate of 2°/min. Optical absorption spectra were recorded using a Hitachi U-3000 spectrophotometer. The samples were finely dispersed in high-purity liquid paraffin and then smeared onto an optically polished quartz plate. The infrared spectra in the range of 750−4000 cm^{-1} were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer using a DRIFT accessory. The spectra of the zeolite-encapsulated complexes were recorded against a zeolite background, which was recorded at 100 °C after 1 h of evacuation at 10^{-2} Torr. The spectra of the free CoPc were recorded as KBr pellets. The Raman spectra (4000−100 cm^{-1}) of the free and zeolite-encapsulated complexes were recorded in the solid state using a Bruker RFS 100/S FT-Raman spectrometer. The Raman spectrum of free CoPc was recorded after dilution with spectral grade of KBr. Magnetic measurements in the temperature range 40−300 K were carried out on a Faraday magnetic balance calibrated using $HgCo(NCS)_4$. Low temperatures were obtained using a closed cycle cryostat (Air Product). The diamagnetic contribution of the zeolite was measured at room temperature and subtracted from the susceptibility of the encapsulated complex.

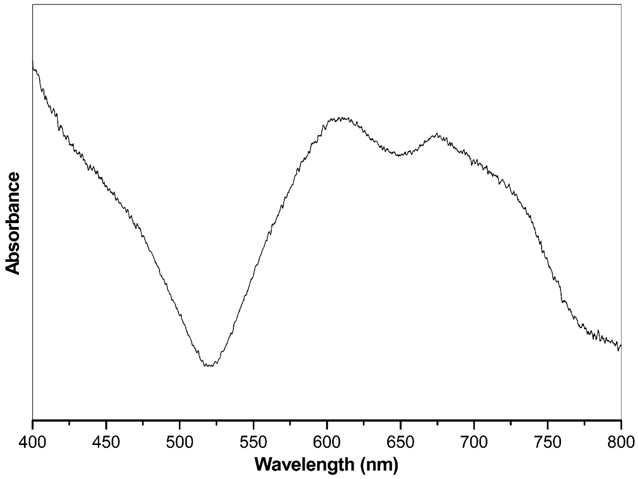

Figure 2. Absorption spectrum of CoPc encapsulated in zeolite-Y.

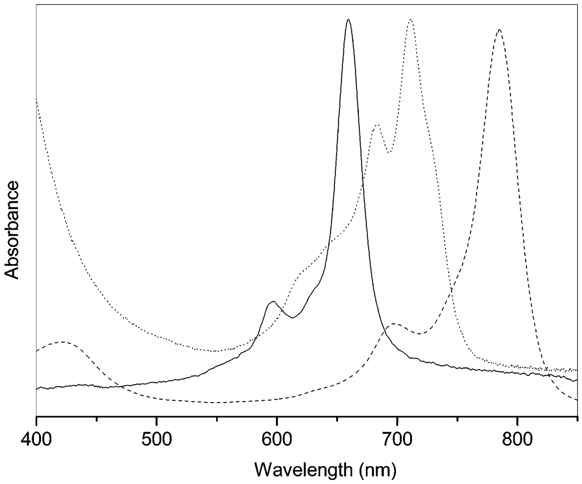

Figure 3. Absorption spectra of CoPc in methanol (solid line), in trifluoroacetic acid (dotted line), and in sulfuric acid (dashed line).

Results and Discussions

UV−Vis Spectra. The UV−vis absorption spectrum of CoPc encapsulated in zeolite-Y is shown in Figure 2. The spectrum shows two broad bands centered at 610 and 675 nm with a shoulder at around 730 nm. A broad band of medium intensity is also seen at around 470 nm. The UV−vis spectrum of free Co phthalocyanine in solution was also recorded. Figure 3 shows the spectrum of Co phthalocyanine dissolved in methanol (solid curve). The bands at 348 and 660 nm are the Soret or B band and the Q band, respectively.[20] The band appearing at 596 nm is a vibrational component of the Q band. For metallophthalocyanine complexes of D_{4h} symmetry, the HOMO orbitals are of a_{1u} and a_{2u} symmetry, whereas the vacant LUMO orbitals are degenerate and of e_g symmetry. The Q band consists of a $\pi \rightarrow \pi^*$ transition from the HOMO of a_{1u} symmetry to the

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LUMO of e_g symmetry, while the B band is due to the transition from the molecular orbital of a_{2u} symmetry to the LUMO.[21,22]

A comparison of the UV−vis spectra of the encapsulated CoPc complex with that of the free or unencapsulated complex in methanol solution (Figure 3) shows a number of noticeable differences.

Chief among them is the fact that the 660 nm band of the free complex appears to have split into two bands of nearly equal intensity at 675 and 610 nm. A broad band is also observed at around 725 nm.

For the zeolite-encapsulated CoPc, the Soret or B band is not seen because of a rising background due to scattering from the zeolite. The origin of the band appearing at 610 nm in the encapsulated complex cannot be due to a red shift of the 596 nm band of the free complex because the later is only a vibrational component of the Q band and is therefore not expected to have intensity comparable to that of the main Q band. The appearance of bands at 675 and 610 nm clearly suggests a lowering in symmetry from D_{4h}. A lowered symmetry, for example to D_{2h} as in the case of metal-free phthalocyanine, is known to split the Q bands into two components, Q_x and Q_y.[23] A possible origin of the spectral differences on encapsulation is that the CoPc encapsulated in zeolite-Y is forced to adopt a nonplanar geometry with a resultant lowering of symmetry. The effect of nonplanarity of the phthalocyanine molecules has been studied in the literature[24] by comparing the solution spectra of metal-free phthalocyanine with that in the solid state, recorded as evaporated films. Packing consideration in the solid-state forces the phthalocyanine molecule to adopt a nonplanar geometry with a reduction in molecular symmetry from D_{2h} to C_i.[25] The loss of planarity leads to an increased separation of the Q_x and Q_y components ($\Delta\lambda_{\text{solid}} = 60.5$ nm) as compared to the planar structure in solution ($\Delta\lambda_{\text{solution}} = 34.5$ nm). Molecular distortion of the metal-free phthalocyanine in the solid state enhances the band splitting in such a way that longer wavelength band is displaced further toward longer wavelengths while the shorter wavelength band to still shorter wavelengths.[25] There is also a broadening of the bands.

Another possible reason for the difference in the spectra of CoPc in zeolite-Y and the methanolic solution is that the encapsulated CoPc in addition to being nonplanar is protonated. It is well-known that phthalocyanine forms protonated species in acidic media.[21,26] Successive protonation of the *meso* bridging nitrogens of the phthalocyanine causes stepwise red shifts in the B and Q bands. The effect of protonation on the UV−vis spectrum of free CoPc is shown in Figure 3. The dotted line is the spectrum of the diprotonated $CoPc{\cdot}2H^+$, formed by dissolving CoPc in trifluoroacetic acid (TFAA), while the dashed line is the spectrum of the tetraprotonated $CoPc{\cdot}4H^+$, formed by dissolving CoPc in concentrated H_2SO_4. It may be seen that, in addition to the red shift of the Q band on protonation, the Q band is also split in the diprotonated $CoPc{\cdot}2H^+$ system.

The splitting of the Q band on protonation is indicative of a lowering of the symmetry of the molecule and is dependent on the number of protons attached. The addition of one, two, or three protons to CoPc yields derivatives of C_{2v} or D_{2h} symmetry. For these point groups, the e_g orbital splits and the number of possible absorption bands doubles. Upon the addition of a fourth proton, the D_{4h} symmetry is recovered and only one principle Q band is predicted and observed in the electronic spectrum.[21] This may clearly be seen in Figure 3. The spectrum of $CoPc{\cdot}2H^+$ (dotted line in Figure 3) shows intense bands at 683 and 711 nm due to the splitting of the Q band as a consequence of the lowered symmetry on diprotonation. In the fully protonated species (dashed line in Figure 3), however, the Q band appears as a single component.

A comparison of the UV−vis spectra of the encapsulated CoPc with those of the protonated free CoPc species suggests that the features of the UV−vis spectrum of the encapsulated complex may be explained by considering the encapsulated species to be the trans-diprotonated species $CoPc{\cdot}2H^+$. Trans protonation causes the e_g level to split into b_{2g} and b_{3g}. The band at 610 nm may therefore be assigned as the $a_u \rightarrow b_{3g}$ transition while the band at 675 nm is assigned to the $a_u \rightarrow b_{2g}$ transition. The formation of a cis-diprotonated species can be ruled out since cis protonation, apart from being electrostatically unfavorable, does not lift the degeneracy of the e_g orbital. On single protonation too, the geometry of $CoPc{\cdot}H^+$ is lowered from D_{4h} to C_{2v} and the degeneracy of the e_g level is lifted but the splitting is considerably less than that observed for the diprotonated species, and in fact, the two components of the Q band are usually not observed as two separate absorption bands.[21]

The formation of an encapsulated diprotonated $CoPc{\cdot}2H^+$ would also help to account for charge balance required to compensate for the negative charge of the zeolite framework. In fact, one of the proposed mechanisms for the formation of the encapsulated CoPc had suggested that charge compensation is probably by protons, the source of protons being water molecules from the hydration shell of the Co^{2+} ion.[11] The role of water is crucial. It has been reported that the encapsulation of metallophthalocyanine within zeolite-Y requires the presence of water for reaction with DCB to occur.[11] The mechanism (as modified from ref 27) for the formation of CoPc is shown in Scheme 1. Dissociation of water leads to the release of protons and the two electrons required in the first step. On the basis of the UV−vis spectra, we propose that a proton released in the first step leads to

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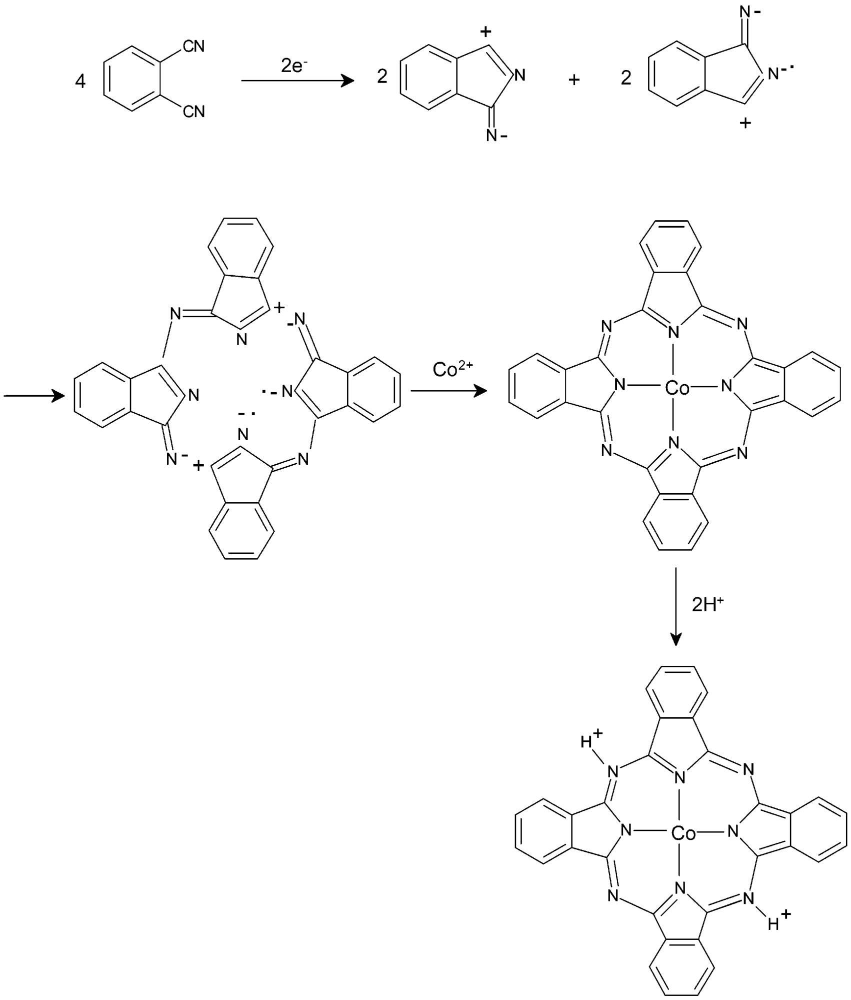
Scheme 1



the formation of the trans-protonated, CoPc·2H$^+$, encapsulated species.

While protonation of the encapsulated CoPc can explain the features of the UV−vis spectra, it is not, however, the whole story. As mentioned in the Introduction, the CoPc molecule would have to adopt a nonplanar geometry if it has to be accommodated within the supercage. To understand changes in geometry on encapsulation we have looked at the vibrational spectra of CoPc encapsulated in zeolite-Y.

Vibrational Spectra. The Raman spectra (1650−100) cm^{-1} of CoPc encapsulated in zeolite-Y and of the free CoPc in the solid state are shown in Figure 4. The spectral range of the corresponding IR spectra is limited to between 1600 and 1300 cm^{-1}; bands below 1300 cm^{-1} are obscured by intense zeolite bands. The Raman spectra, however, does not suffer from this drawback, but for the free CoPc the deep-blue color caused problems and the Raman spectra could be recorded only after dilution with KBr. The quality of the spectra of the free CoPc, as may be seen in Figure 4, was slightly inferior to that of the encapsulated CoPc complex. It is, unfortunately, not possible to record the vibrational spectra, either Raman or IR, of the diprotonated CoPc species since they exist only in aqueous acidic media.

The Raman spectra of the encapsulated CoPc and free CoPc have many features in common. Although the relative intensities are different, the positions of most of the bands are identical and their assignments similar.[28,29] Attention is drawn to the peak at 232 cm^{-1} in the spectra of the

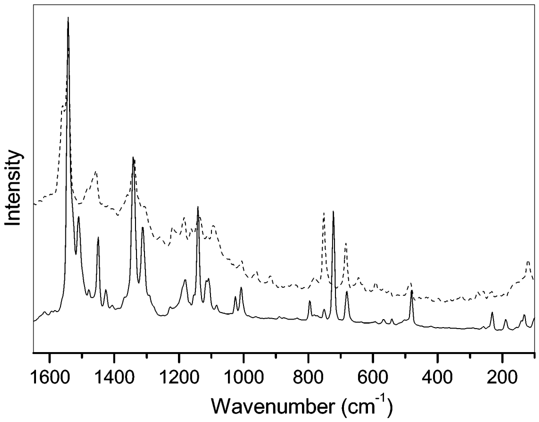


Figure 4. Raman spectra of CoPc encapsulated in zeolite-Y (solid line) and free CoPc (dashed line).

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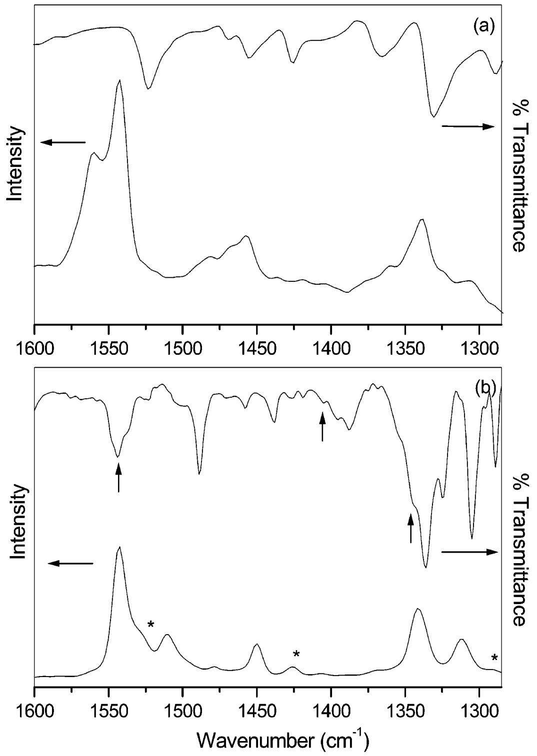

Figure 5. IR and Raman spectra of (a) CoPc and (b) CoPc encapsulated in zeolite-Y. The extra features observed in the IR spectrum of the encapsulated CoPc are marked with arrows, and those in the Raman spectrum, by asterisks.

encapsulated complex, which appears at the same frequency as in the free CoPc. The band has been assigned in the metallophthalocyanines to an M−N out-of-plane deformation mode.[29] The appearance of this band, therefore, provides conclusive evidence for the formation of a Co−N bond in the encapsulated CoPc complex.

The Raman spectra of the encapsulated complex show a number of additional features not seen in the spectrum of free CoPc. These are the bands at 1528, 1426, 1290, and 723 cm^{-1}. Without our going into a detailed assignment of these bands, it can be shown that the clue to the understanding of the origin of these features may be obtained from a comparison with the corresponding IR spectrum, in the 1600−1300 cm^{-1} spectral region. Figure 5 shows a comparison of the IR and Raman spectra in the 1600−1300 cm^{-1} region for CoPc encapsulated in zeolite-Y and the crystalline free CoPc. Free CoPc possesses a center of inversion (D_{4h}); the mutual exclusion principle would be valid, and consequently the IR-active vibrational modes are absent in the Raman spectra and vice-versa (Figure 5a). For the encapsulated CoPc complex, on the other hand, it may be seen from Figure 5b that the additional features in the Raman spectra (marked by asterisks) have corresponding features in the IR spectra. Similarly additional features are seen in the IR spectra of the encapsulated complex (marked by arrows) for which corresponding peaks are present in the Raman spectra. The presence of Raman-active modes in the IR spectra and vice-versa implies a loss of the center of inversion of the CoPc molecule on encapsulation. This would be the consequence of the fact that the CoPc molecule would have to distort from planar geometry if it has to be accommodated within the ~12.7 Å diameter supercage of zeolite-Y. Protonation of the CoPc molecule could also lead to a loss of the center of inversion, but as pointed out in the previous section, the encapsulated species is probably the trans-diprotonated $CoPc{\cdot}2H^{+}$ for which the center of inversion is preserved for planar geometry.

Molecular Modeling. The vibrational spectra clearly indicate a loss of center of inversion of the CoPc complex encapsulated in zeolite-Y, probably due to loss of planarity. The fact that it would be difficult to accommodate a CoPc molecule having the same geometry as in the free state within the zeolite-Y supercage is obvious from the dimension of the molecule (end to end distance 15 Å) as compared to the diameter of the supercage (12.7 Å) (Figure 1). The CoPc molecule has no choice but to adopt a nonplanar geometry on encapsulation. Molecular mechanics was used to explore the extent and nature of distortion of the encapsulated CoPc molecule and to determine the minimum energy geometry.

The potential energy of the CoPc molecule having different geometries within the supercage of zeolite-Y was calculated. For these calculations, we ignore the fact that encapsulated complex is protonated and consider only steric interactions. The total potential energy of the encapsulated complex is a sum of two parts:

(i) There is an internal energy, which is dependent on the geometry of the encapsulated CoPc. This for CoPc is defined as the extent of distortion from planar geometry, measured as the average root-mean-square (rms) displacement of the atoms of the phthalocyanine ring, except for the H atoms, from their positions in the planar structure of the free CoPc molecule.

(ii) Also there is the energy of interaction of the encapsulated CoPc molecule with the walls of the zeolite host, which depends on the position and orientation of the molecule inside the host.

The geometry adopted by the CoPc molecule on encapsulation was obtained by minimizing the total potential energy with respect to the geometrical parameters of the complex as well as its position and orientation within the supercage. The internal energy of the CoPc molecule was calculated as a function of the deviation from planar geometry using the extensive systematic force field (ESFF).[30] The parameters were chosen such that the planar geometry of the free CoPc molecule was predicted to be the minimum energy geometry.

For planar structures such as phthalocyanines and porphyrins two types of distortion from planarity have usually been considered, the ruffled and saddle-type distortions. In the ruffled geometry, opposite isoindole rings are counter-rotated so that the N_{β} atoms between the two isoindole rings are alternatively displaced above or below the molecular plane (the labeling of the atoms of the phthalocyanine rings is indicated in the inset of Figure 6). The rotation leaves the carbon atoms of the isoindole ring either above or below

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(30) *Discover User Guide, Part 1*, version 2.9.5; Biosym Technologies: San Diego, CA, 1994.

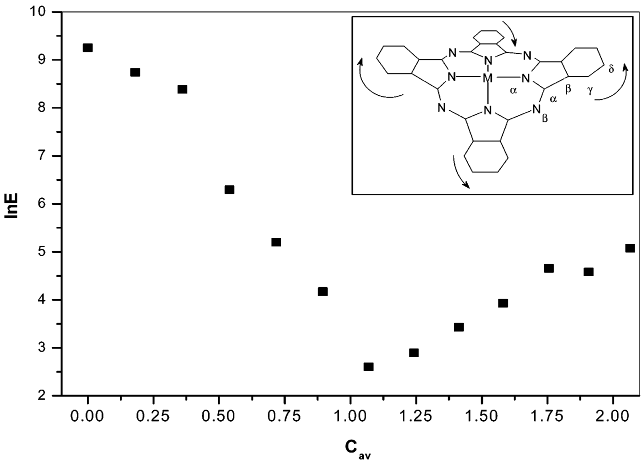

Figure 6. Total potential energy for CoPc encapsulated in zeolite-Y as a function of the average rms displacement of the atoms of the Pc ring from planar geometry (C_{av}). The saddle-type distortion is shown in the inset.

the molecular plane. In the saddle-type distortion each of the pairs of C_β carbon atoms of the isoindole rings are alternatively displaced above and below the molecular plane along with the axis joining the C_α atoms of each pyrrole ring (see inset of Figure 6). The saddle distortion leaves the central CoN_8 ring essentially planar. In this study the ruffled geometry was not considered since for this distortion, unlike the saddle distortion, the center of inversion of the CoPc molecule is preserved. Additionally, for the saddle distortion only symmetric distortions were considered in which the displacements of the isoindole rings either above or below the molecular plane are equal. The Co−N distances, too, were kept fixed at their value in the unencapsulated molecule, 1.91 Å.

The energy of interaction of the CoPc molecule with the walls of the supercage of zeolite-Y was calculated using the Lennard-Jones 6−12 potential for van der Waals interactions. Electrostatic interactions were ignored. The interaction energy was minimized as a function of the orientations and positions of the center of gravity of CoPc using the Monte Carlo energy minimization scheme of the Biosym Catalysis-Solid Docking software package.[31]

The total potential energy of the encapsulated CoPc molecule as function of the extent of deviation from planarity for a saddle-type distortion is shown in Figure 6. In this figure, for each geometry, characterized by the average rms displacement of the atoms (except H atoms) of the phthalocyanine ring from planarity, the interaction energy of the CoPc molecule with the walls of the supercage has been minimized. It may be seen that introduction of nonplanarity causes the host−guest interaction to decrease dramatically, easily compensating for the associated increase in the internal energy of the molecule. The total potential energy shows a minimum for a saddle distortion with an average rms displacement of 1 Å from planar geometry. The molecular graphics representation of this geometry with the interaction energy minimized is shown in Figure 7.

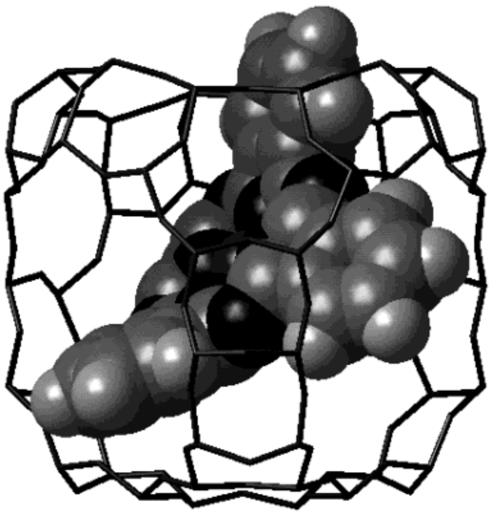

Figure 7. Molecular graphics representation of Co phthalocyanine within the supercage of zeolite-Y having the minimum energy geometry with saddle-type distortion. The figure is of the orientation with minimum interaction energy with the walls of the supercage.

The accuracy of the energy values as well as the minimum energy geometry predicted from a molecular mechanics calculations obviously depends on the quality of the force field used. In the present exercise no such claim is made on the absolute values of the energies considering the approximate nature of the force field as well the calculations. The calculations are, however, representative. It may be seen from the molecular graphics representation (Figure 7) that for the minimum energy, saddle-deformed geometry, it is possible to orient and position the CoPc molecule in such a way that large sections of the isoindole ring can be accommodated within the windows of the supercage which are tetrahedrally disposed, resulting in a lowering of the interaction energy. As mentioned earlier, this geometry does not possess a center of inversion in agreement with the vibrational spectroscopic results.

Magnetic Measurements. The vibrational spectroscopy as well as molecular modeling indicates a nonplanar geometry for the phthalocyanine ring characterized by a loss of the center of inversion. The spectral regions studied in both the vibrational as well as electronic spectra, however, are not diagnostic of the geometry of the Co atom. We have used magnetic measurements to investigate the effect of encapsulation on the geometry of the Co atom in Co phthalocyanine.

The temperature variation of the magnetic susceptibility of CoPc encapsulated in zeolite-Y is shown in Figure 8. The susceptibility does not obey Curie−Weiss law, and the moment changes continuously with temperature varying from 3.29 μ_B at 300 K to 3.18 μ_B at 70 K. (At the loading levels studied, exchange coupling between encapsulated CoPc units may be ruled out.) For comparison the magnetic susceptibility of free CoPc is also shown in Figure 8. The susceptibility of the free CoPc, too, does not follow Curie−Weiss law; the magnetic moment varies from 2.8 μ_B at 300 K to 1.8 μ_B

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(31) *Catalysis User Guide*, version R-40; Biosym Technologies: San Diego, CA, 1993.

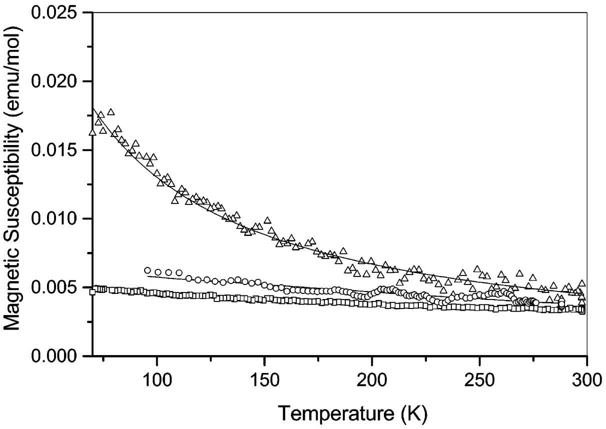

Figure 8. Temperature variation of magnetic susceptibilities of CoPc in free state (△), CoPc encapsulated in zeolite-Y (□), and CoPc encapsulated in MCM-41 (○). The solid lines are the best fits of eq 1 to the experimental susceptibilities.

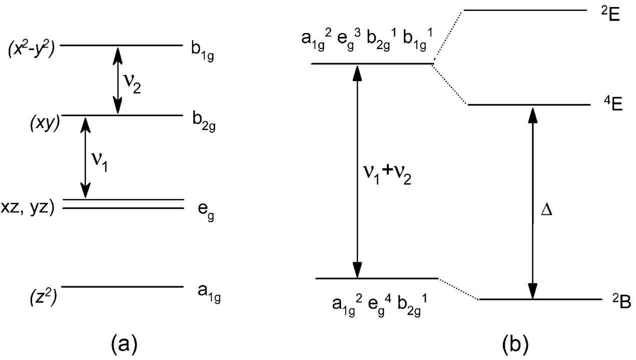

Figure 9. Splitting of d orbitals for a square-planar Co(II) and the corresponding term energy levels. △ is the energy difference between the low-spin ground state and the first high-spin state.

at 60 K. The room-temperature value of the moment of free CoPc is similar to that reported in the literature,[32] 2.72 μ_B at 300 K.

It is obvious from Figure 8 that encapsulation causes a significant change in both the magnetic moment and its temperature dependence of the CoPc molecules. To understand these changes it is important to first understand the magnetism of free CoPc. The room-temperature moment of 2.8 μ_B for free CoPc is typical of many Co(II) d^7 square planar complexes. For a Co(II) d^7 ion in square planar crystal fields the degeneracy of the d-electron manifold is lifted as shown in Figure 9, giving rise to an orbitally singlet ground state $^2B_2$ ($a_{1g}^2e_g^4b_{2g}^1$). (The ordering of orbitals in Figure 9 is not unique. An alternate scheme in which the relative ordering of the e_g and a_{1g} levels is reversed has also been suggested,[33] but this in no way affects the subsequent arguments.) The magnetic moment associated with this ground state is expected to be close to 1.73 μ_B, the spin-only value for a single unpaired spin, since spin−orbit coupling is absent for the orbital singlet $^2B_2$ state. The unusually high moment of CoPc and other Co(II) square planar complexes has been qualitatively explained by Lever[34] by suggesting that an orbital contribution could arise through mixing-in of orbitally degenerate excited states such as the ^2E ($b_{2g}^2e_g^3a_{1g}^2$). Such a model, however, predicts a temperature-independent moment contrary to the experimental observation. It would also not be able to explain the higher moment observed for the encapsulated CoPc complex.

We consider an alternative scenario in which a higher lying high-spin state is thermally accessible. It may be seen from Figure 9 that if the energy separations of the one-electron states, ν_1 and ν_2, are comparable to the electron−electron repulsion, then the high-spin ^4E ($a_{2g}^2e_g^3b_{2g}^1b_{1g}^1$) could be thermally accessible.

The Van Vleck magnetic susceptibility of a d^7 ion in a square planar field having a doublet ground state ($^2B_2$) and a higher lying quartet (^4E) can be derived from the Van Vleck expression.[35] The molar susceptibility for such a system is

$$\chi_M = \frac{Ng^2\beta^2}{2kT}\frac{[1/2 + 5\exp(-\Delta/kT)]}{[1 + 2\exp(-\Delta/kT)]} + N\alpha \qquad (1)$$

where g is the Landé factor, N the Avogadro's number, k the Boltzmann constant, β the Bohr magneton, $N\alpha$ the temperature-independent part of the susceptibility, and Δ the energy separation of the low-spin paramagnetic $^2B_2$ state and high-spin ^4E paramagnetic state. (In the above expression the orbital contribution of the higher lying ^4E state has been ignored.)

The above expression was fitted to the experimental susceptibility of the free CoPc. A reasonably good fit is obtained for a value of $\Delta/K = 351$ K (solid line in Figure 8). The model clearly explains the origin of the temperature dependence of the moment of free CoPc. At low temperature only the ground-state $^2B_2$ spin-doublet is populated and consequently the observed moment (1.8 μ_B) is close to the expected value for a single unpaired spin (1.73 μ_B). At higher temperature the higher lying high-spin-quartet state becomes thermally accessible and the moment increases with increasing temperature. This model was also used for analyzing the susceptibility of the encapsulated CoPc. The solid line in Figure 9 is the best fit of eq 1 to the experimental susceptibility of the encapsulated CoPc (the Landé "g" value was kept fixed at 2). The fit shown was obtained for $\Delta/K = 22$ K, which is considerably lower than that of the free CoPc. The effect of encapsulation is, therefore, a lowering of the energy difference Δ between the higher lying high-spin-quartet state and the low-spin-doublet ground state.

To understand the origin of the lower value of Δ on encapsulation of CoPc in zeolite-Y we have looked at the susceptibility of CoPc encapsulated in MCM-41. In MCM-41 the void space is much larger (39.2 Å) and consequently the CoPc molecule can be accommodated with considerable less distortion than in zeolite-Y. The magnetic susceptibility of CoPc encapsulated in MCM-41 is shown in open circles in Figure 8. It may be seen that the susceptibility values and

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(32) (a) Figgis, B. N.; Nyholm, R. S. *J. Chem. Soc.* **1959**, 338. (b) Klemm; Klemm. *J. Prakt. Chem.* **1935**, *143*, 82. (c) Figgis, B. N.; Nyholm, R. S. *J. Chem. Soc.* **1954**, 12.

(33) Ballhausen, C. J.; Liehr, A. D. *J. Am. Chem. Soc.* **1959**, *81*, 538.

(34) Lever, A. B. P. *J. Chem. Soc.* **1965**, 1821.

(35) Mabbs, F. E.; Machin, D. J. *Magnetism and Transition Metal Complexes*; Chapman and Hall: London, 1973.

its temperature dependence is close to that of the free CoPc. For CoPc encapsulated in MCM-41, the moment varies from 2.9 μ_B at 300 K to 2.1 μ_B at 80 K. The value of the energy separation Δ was obtained by fitting eq 1 to the experimental susceptibility of CoPc in MCM-41. The best fit (solid line in Figure 8) was obtained for a Δ/K value of 241 K which is much closer to the value for free CoPc than to that of the zeolite-Y encapsulated CoPc. The results suggest that the decrease in Δ, the energy separation between the quartet and doublet spin states, is related with the extent of distortion in the geometry around the Co(II) from that in the square planar free CoPc complex.

This decrease in Δ with "distortion" can be understood, for example, by considering the distortion to be such that the Co(II) is pushed out of the plane of the four N atoms of the phthalocyanine ring. This could be a consequence of the distortion required to accommodate the CoPc molecule in the supercage. The effect of this square pyramidal distortion would lower the symmetry around the Co(II) from D_{4h} to C_{4v}. This would stabilize the $d_{x^2-y^2}$ and d_{xy} while destabilizing the energies of the d_{z^2}, d_{xz}, and d_{yz} orbitals. The net result is a reduction in the single electron orbital separation energies i.e., ν_1 and ν_2, of the d-electron manifold. This in turn would lead to a reduction in the energy difference between the low-spin-doublet ground state and the higher lying quartet-spin state. The reduction in Δ for such distortion is clearly related to the extent of deviation from planar geometry around the Co atom.

The magnetic behavior of CoPc encapsulated in zeolite-Y is quite different from that of $[Co(bpy)_3]^{2+}$ encapsulated in zeolite-Y, where too a change in the moment on encapsulation is observed. The observed magnetic behavior in the encapsulated $[Co(bpy)_3]^{2+}$ is, however, a consequence of the temperature dependence of the thermal equilibrium between two spin isomers with a low-spin and high-spin ground state, respectively. In the case of CoPc encapsulated in zeolite-Y, on the other hand, the enhanced moment and non-Curie behavior is a consequence of thermally populating a higher lying high-spin state. The effect of encapsulation for CoPc is a lowering of the energy difference between the ground-state spin-doublet and higher lying spin-quartet state making the latter thermally more accessible.

Conclusion

We have carried out a comparative spectroscopic and magnetic study of the Co phthalocyanine complex encapsulated in zeolite-Y and in the unencapsulated state. This paper focuses on the effect of the size and topology of the host supercage on the geometry adopted by the square-planar complex on encapsulation. The electronic spectrum of CoPc encapsulated in zeolite-Y complex shows that the phthalocyanine Q band is split into bands of nearly equal intensity indicating a lowering of symmetry. This has been explained as due to the trans-diprotonation of the *meso* nitrogens of the encapsulated complex. The protonation of the CoPc formed in the zeolite supercage also satisfies the requirement of charge compensation of the framework negative charge. Vibrational spectroscopic studies indicate a breakdown of the mutual exclusion principle; on encapsulation of CoPc, IR modes of the complex become Raman active and vice-versa. This loss of center of inversion is a consequence of the nonplanar geometry that the CoPc is forced to adopt on encapsulation inside the 12.7 Å diameter supercage of zeolite-Y.

Molecular modeling studies show that a saddle-type distortion in which alternate isoindole rings of the phthalocyanine are lifted either above or below the plane of the molecule could dramatically lower the steric interaction energy of the encapsulated CoPc with the walls of the supercage. This changed geometry on encapsulation is also reflected in the magnetic behavior. There is an enhancement in the magnetic moment of CoPc complex on encapsulation from its value in the unencapsulated or free state. This enhancement is related to the extent of distortion of the CoPc from planar geometry since when the complex is encapsulated in the larger voids of mesoporous MCM-41, where it can be accommodated without significant loss of planarity, the moments are similar to that of the unencapsulated or free CoPc. The enhancement of the moment on encapsulation in zeolite-Y has been explained as resulting from a lowering of the energy difference between the low-spin-doublet ground state and a higher lying high-spin-quartet state making the latter thermally accessible. The lowering of the energy difference between the low-spin and high-spin states is a consequence of the distortion from planar geometry of the encapsulated CoPc.

Supporting Information Available: Powder X-ray diffraction patterns of zeolite-Y and CoPc encapsulated in zeolite-Y and a table giving the positions of the Raman bands and their assignments for CoPc and CoPc encapsulated in zeolite-Y. This material is available free of charge via the Internet at http://pubs.acs.org.

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