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Interesting Anion-Inclusion Behavior of Cucurbit[5]uril and Its Lanthanide-Capped Molecular Capsule

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The selective encapsulation behavior of cucurbit [5]uril and its lanthanide-capped molecular capsule toward nitrate and chloride ions has been investigated. Using fluorescence spectroscopy, the metal-free host has been demonstrated to selectively include nitrate ion. In contrast, the lanthanide-capped molecular capsule showed preference toward the inclusion of chloride ion. Solid-state structures of the nitrate and chloride inclusion complexes with the La(III)-capped molecular capsule have been crystallographically determined.

Introduction

The recognition and sensing of anions by judiciously chosen host molecules has been one of the most active areas of host−guest chemistry in the recent past.[1−6] The interest is both fundamental and practical. Fundamentally, the complexation of anionic species is inherently more difficult than that of cations as anions are generally bulkier, with a much greater variety of geometries, and more heavily solvated and hence provide a weaker interaction with a host.[4] Furthermore, the speciation of certain anions depends highly on the pH condition of the system studied, and so does the specific form of the hosts.[4] These factors contribute to the difficulties in host design as well as less effective anion−host interaction, thus presenting many intellectual challenges. From a more practical standpoint, anions play important roles in chemical[7] and biological[8] as well as environmental processes,[9] for example, for catalyst design, sensor development, and ion transport for biological functions. A large

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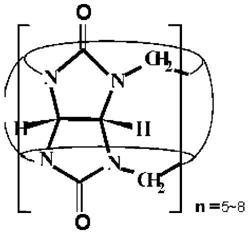

Figure 1. Molecular structure of cucurbit[n]urils.

number of host molecules, both naturally occurring and synthetic, have been utilized for the study of anion complexation.[10,11] A great variety of anion−host complexes with aesthetically pleasing structures have been realized, and in some cases intriguing anion template effects have been discovered.[10] Sensory platforms with high sensitivity and selectivity have also been developed.[11]

Our efforts in this vein has been focused on the use of cucurbit[*n*]uril ($n = 5-8$, Q[*n*]), a class of organic macrocyclic cavitands resembling in shape a barrel with its two identical openings or portals fringed by carbonyl groups (Figure 1).[12] The carbonyl groups are capable of metal coordination and hydrogen bonding, especially due to the convergent arrangement in close proximity, while the large void of the macrocycle is ideal for the formation of inclusion complexes with a variety of guest species.[13,14] Much work has been done on the use of cucurbit[*n*]urils for the formation of metal complexes and hydrogen-bonded supramolecular assemblies by making use of the polar carbonyl groups.[15] They have also been extensively utilized as selective hosts for cationic and neutral guest species.[16] Anion inclusion has also been demonstrated for these unique macrocyclic hosts,[17] but the work in this direction is much less as compared with the large body of research for cation and neutral inclusion.

We have recently reported a number of chloride/Q[5] complexes.[17d] In each case, crystallographic structural determination reveals that a chloride ion is situated in the internal cavity of the macrocycle. At least one of the carbonyl-fringed portals participates in metal coordination, forming a complete or an “open-lid” capsule. These findings made with chloride ion prompted us to look at the possibility of nitrate encapsulation, as nitrate ion is of essentially the same van der Waals radius as chloride but with a different geometry. Questions we wished to address include (1) whether nitrate encapsulation is possible, (2) can any selective complexation of the anions be demonstrated, and (3) if selective encapsulation is observed, what may the responsible factors be. Herein we report our results along these lines of research.

Experimental Section

Materials and Methods. Hydrochloric acid, nitric acid, sulfuric acid, and lanthanide nitrate were of commercial origin and used without further purification. Q[5] was synthesized by following published procedures.[18] The elemental analyses (CHN) were carried out using a CE EA 1110 elemental analyzer. The FT-IR spectra were recorded in the range 400−4000 cm^{-1} with a Nicolet Avatar

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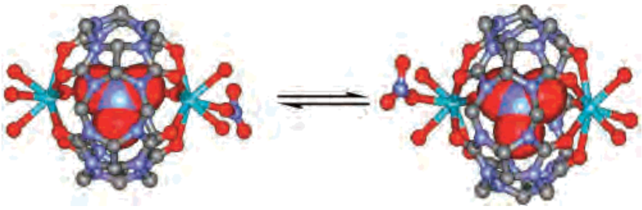

Figure 2. Ball and stick plot showing the coordination environment of La(III) center in **1**, in which when one La(III) center in the molecular capsule is coordinated by five terminal oxygen atoms of Q[5] three water molecules, the other La(III) center would be coordinated by five terminal oxygen atoms of Q[5], two water molecules, and one monodentate nitrate anion (La, cyan; O, red; C, gray; N, blue).

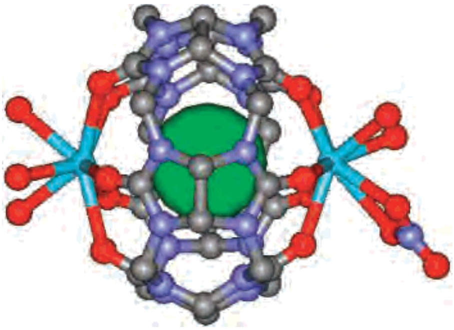

Figure 3. Ball and stick plot showing the coordination environment of La(III) centers in **2** (La, cyan; Cl, green; O, red; C, gray; N, blue).

FT-IR360 spectrometer using KBr pellets. All fluorescence measurements were performed on an F-4500 fluorescence spectrophotometer in aqueous solutions using 1.0-cm quartz cuvettes at 22 ± 1 °C. The experiments were carried out with excitation and emission monochromator band passes set at 10.0 nm and an excitation wavelength of 240 nm.

Preparation of Compounds. $\{[La(H_2O)_3][(NO_3{\subset}C_{30}H_{30}N_{20}O_{10})][La(\eta^1\text{-}NO_3)(H_2O)_2]\}(NO_3)_4{\cdot}2H_2O$ (1). An aqueous solution of $La(NO_3)_3$ (1.0 mL, 0.5 M) was mixed with a solution of Q[5] (5.0 mL, 0.02 M in 3.0 M HNO_3) in an open beaker. The mixture was allowed to evaporate at room temperature. Colorless crystals of **1** were obtained in 50% yield after 2 days. Anal. Calcd for **1** ($C_{30}H_{43}La_2N_{26}O_{35}$): C, 22.41; H, 2.74; N, 22.65. Found: C, 22.37; H, 2.62; N, 22.68. IR spectra (cm^{-1}): 3369 s, 1737 s, 1701 s, 1674 m, 1513 s, 1417 s, 1383 s, 1331 s, 1289 m, 1264 m, 1242 s, 1195 s, 1144 m, 958 s, 812 s, 797 s, 763 s, 685 m, 635 m.

$\{[La(H_2O)_3][(Cl{\subset}C_{30}H_{30}N_{20}O_{10})][La(\eta^2\text{-}NO_3)(H_2O)_2]\}(NO_3)_2Cl_2{\cdot}6H_2O$ (2). A solution of Q[5] (2.5 mL, 0.02 M in 3.0 M HCl) was mixed with another solution of Q[5] (2.5 mL, 0.02 M in 3.0 M HNO_3). Subsequent to the addition of a solution of $La(NO_3)_3$ (aqueous 0.4 mL, 0.5 M), the resulting mixture was left in an open beaker under ambient conditions. Colorless crystals of **2** were obtained in 76% yield after 2 days. Anal. Calcd for **2** ($C_{30}H_{52}Cl_3La_2N_{23}O_{30}$): C, 22.53; H, 3.28; N, 20.15. Found: C, 22.35; H, 3.15; N, 20.26. IR spectra (cm^{-1}): 3385 s, 1730 s, 1704 s, 1674 m, 1507 s, 1417 s, 1384 s, 1331 s, 1289 m, 1264 m, 1241 s, 1196 s, 1143 m, 978 w, 958 m, 812 s, 798 s, 763 s, 685 m, 635 m.

X-ray Crystallography. Data were collected on a Bruker Apex-2000 diffractometer. Absorption corrections were applied by using the multiscan program SADABS.[19a] The structures were solved by direct methods, and non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL program.[19b] The hydrogen atoms of organic molecules were generated geometrically (C−H, 0.96 Å). Crystal data for **1**: monoclinic, space group $C2/c$; $a = 21.657(3)$, $b = 16.618(2)$, $c = 14.120(2)$ Å; $\beta = 98.679(3)°$; $V = 5023.5(12)$ Å^3; $Z = 4$; $\rho_{calcd} = 2.124$ g·cm^{-3}; $M = 1606.73$; μ(Mo Kα) = 1.817 mm^{-1}; $R_1 = 0.0393$, wR_2(all data) = 0.1007. Crystal data for **2**: monoclinic, space group $P2_1/c$; $a = 14.777(5)$, $b = 17.190(5)$, $c = 22.242(7)$ Å; $\beta = 107.018(9)°$; $V = 5403(3)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.966$ g·cm^{-3}; $M = 1599.12$; μ(Mo Kα) = 1.824 mm^{-1}; $R_1 = 0.0967$, wR_2(all data) = 0.2495.

Results and Discussion

Crystal Structure Descriptions. The structure of **1**, shown in Figure 2, may be viewed as a molecular capsule formed by closure of the two carbonyl-fringed portals of Q[5] via carbonyl−La(III) coordination, one on each side of the barrellike host. The most salient feature is one nitrate ion being encapsulated in the cavity of the capsule. The La(III) ions are octacoordinate. One of the La(III) ions features coordination by five carbonyl groups, two water molecules, and one monodentate nitrato ligand. The coordination sphere of the other La(III) ion consists of the five terminal carbonyl groups on the other side and three water molecules. The bond lengths of La−$O_{Q[5]}$, La−O_{water}, and La−$O_{nitrate}$ are 2.531(3)−2.625(3), 2.408(14)−2.512(3), and 2.571(12)−2.579(5) Å, respectively. The La−$O_{Q[5]}$ and La−O_{water} distances are comparable to their counterparts in the previously reported, "open-lid" nonacoordinate La(III)/Q[5] complex.[17d]

Compound **2** is structurally very similar to **1** except that the encapsulated guest is a chloride ion and one of the La(III) ions is nonacoordinate featuring one bidentate nitrato ligand (Figure 3). The La−$O_{Q[5]}$, La−O_{water}, and La−$O_{nitrate}$ distances are 2.502(7)−2.733(8), 2.505(9)−2.583(10), and 2.574(9)−2.896(10) Å, respectively. These values are slightly different from those of their counterparts in **1** but still comparable to those reported for similar La(III)/Q[5] complex.[17d] Of particular relevance is the chloride-encapsulating Q[5] complex formulated as $\{[La(H_2O)_3][Cl{\subset}C_{30}H_{30}N_{20}O_{10}][LaCl(H_2O)_6]\}^{4+}$. In the crystal structure, one of the two portals is closed by lanthanide coordination while the other is only partially closed using only two of its five carbonyls for coordination to a second La(III) ion. This "half-open lid" structure represents an interesting intermediate toward the formation of the capsules as presented in this work. It also suggests that guest encapsulation may be achieved in a stepwise fashion with inclusion of the guest species followed by portal closure.

Anion-Encapsulation Studied by Fluorescence Spectroscopy. The observation of the encapsulation of both chloride and nitrate ions by the La(III)-capped Q[5] raised the question of binding selectivity in La(III)-capped Q[5] molecular capsule for nitrate and chloride anions and whether similar behaviors can be demonstrated with the metal-free host molecule. Unfortunately, trying to determine binding selectivity for nitrate and chloride anions was a failure, due to Q[5] only dissolving in the solution with high acidity that leads to difficulty of Q[5] binding to lanthanide ion. However, the interaction of these anions with Q[5] can be

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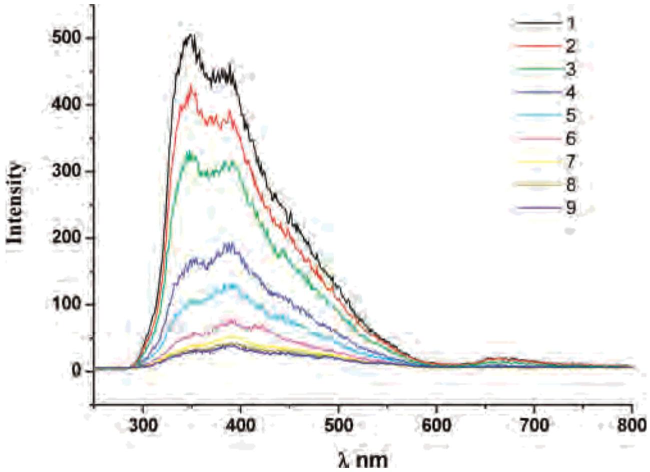

Figure 4. Fluorescence spectrum of Q[5] (0.02 M) in H_2SO_4 (4.0 M) solution in the absence (1) and presence (2−9) of NO_3^-. Concentration of NO_3^-: (2) 0.0016 M; (3) 0.004 M; (4) 0.012 M; (5) 0.020 M; (6) 0.040 M; (7) 0.060 M; (8) 0.080 M; (9) 0.100 M.

readily studied by fluorescence spectroscopy. Specifically, the change of fluorescence originated from the host molecule upon guest addition was monitored. Figure 4 shows the fluorescence spectra of Q[5] recorded at an excitation wavelength of 240 nm in the absence and presence of nitrate. It is clear that addition of NO_3^- causes reduction of the fluorescence intensity (Figure 4). The experimental data are fitted by using the following equation,[20] where F, F_0, and F_∞ are the fluorescence intensities with the addition of a certain amount of NO_3^-, with no NO_3^-, and with excess NO_3^- (i.e., 100% NO_3^- anion was encapsulated in the host molecules of Q[5]), respectively. [A] is the concentration of the guest, NO_3^- in the present case. K is the formation constant for the 1:1 inclusion product of anion⊂Q[5]).

$$F/F_0 = 1 + (F_\infty/F_0 - 1)\,\frac{[\mathrm{A}]K}{(1 + [\mathrm{A}]K)}$$

The plot of F/F_0, the percentage of remaining fluorescence, as a function of added nitrate anion was obtained (Figure 5). The sharp decrease at the initial stage of guest addition and the leveling-off upon further increase of guest concentration is indicative of the formation of a 1:1 host−guest complex.[21] Further analysis using the double reciprocal plot of $1/(F/F_0 - 1)$ versus $1/[\mathrm{A}]$ (Figure 5, inset) yields a linear relationship ($r = 0.997$), which confirms the formation of a 1:1 complex; if any higher-order complexes are formed, such a linearity will not be observed.[21] The conclusion is also consistent with the crystal structure of $Me_{10}Q[5]\cdot 3HNO_3\cdot 6H_2O$, a Q[5] fully substituted with methyl groups encapsulating one NO_3^- in the interior of the macrocycle.[17a] A $K = 170 \pm 14.7$ M^{-1} and $F_\infty/F_0 = 0.042$ are obtained by the fitting, and these values point to a moderately stable inclusion complex and rather efficient quenching of the host fluorescence upon complex formation.

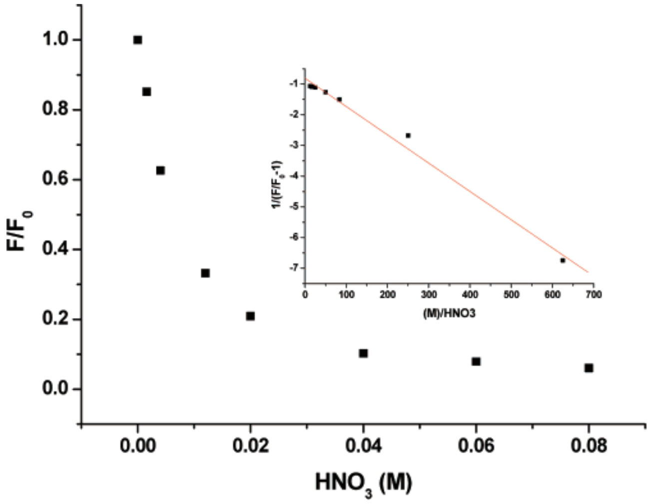

Figure 5. Fluorescence suppression of Q[5] (in H_2SO_4 solution) fluorescence as a function of added HNO_3. The solid line shows the best fit of the data to eq 1: $K = 170 \pm 14.7$ M^{-1}; $F_\infty/F_0 = 0.042$. The inset shows the linear double reciprocal plot.

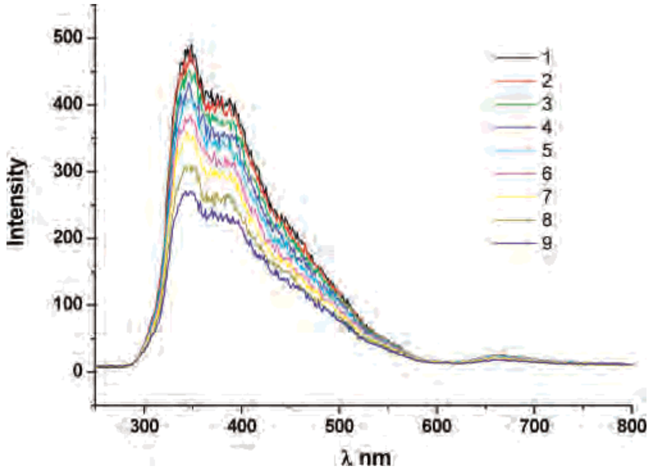

Figure 6. Fluorescence spectrum of Q[5] (0.02 M) in H_2SO_4 solution (4.0 M) in the absence (1) and presence (2−9) of HCl: (2) 0.004 M; (3) 0.024 M; (4) 0.064 M; (5) 0.139 M; (6) 0.283 M; (7) 0.599 M; (8) 1.093 M; (9) 1.748 M.

Comparative studies using chloride as the guest were also carried out under otherwise identical conditions. In comparison with the observations in the nitrate inclusion, the decrease in fluorescence intensity is much more sluggish, and the remaining fluorescence is much higher when excess chloride was added (Figure 6). Similar data fitting using the equation yields the double reciprocal plot of $1/(F/F_0 - 1)$ versus $1/[Cl^-]$ (Figure 7). The nonlinear relationship means that formation of a stable 1:1 inclusion complex in solution between a chloride ion and Q[5] can be excluded. Please note that, however, chloride inclusion complexes have been crystallized and structurally characterized.[17c−e] With no exception, the carbonyl-fringed portals are at least partially blocked, either via metal coordination or hydrogen bonding involving the polar carbonyl groups.[17c−e] This kind of portal capping is probably why the inclusion complexes can be stabilized and crystallized out.

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(21) Wagner, B. D.; Boland, P. G.; Lagona, J.; Isaacs, L. *J. Phys. Chem. B* **2005**, *109*, 7686.

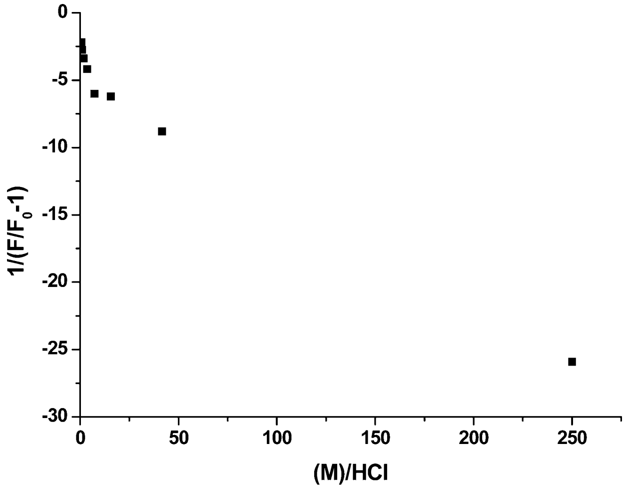

Figure 7. Nonlinear relationship for the double reciprocal plot of $1/(F/F_0 - 1)$ versus $1/[Cl^-]$.

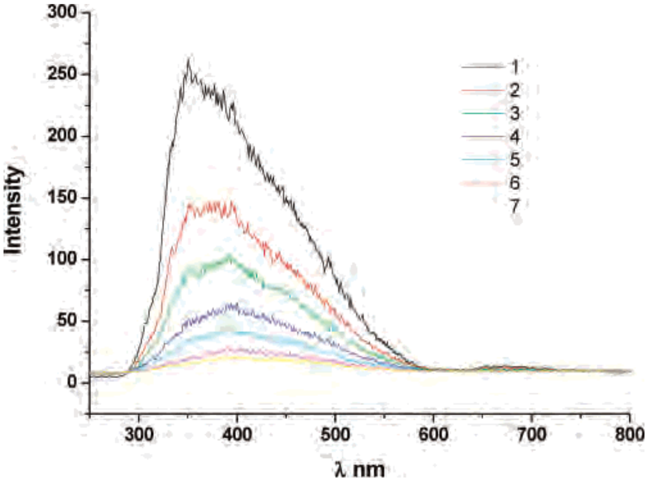

Figure 8. Fluorescence spectrum of Q[5] (0.02 M) in HCl solution (4.0 M) in the absence (1) and presence (2−9) of HNO_3: (2) 0.004 M; (3) 0.008 M; (4) 0.016 M; (5) 0.024 M; (6) 0.040 M; (7) 0.056 M.

Significantly, when NO_3^- was added to the above mixture containing both Q[5] and Cl^-, sharp reduction in the host fluorescence intensity was again observed, similar to the situation when only NO_3^- was present (Figure 8). This observation suggests selective inclusion of NO_3^- over Cl^-. Data fitting produced the linear relationship of $1/(F/F_0 - 1)$ versus $1/[A]$ ($r = 0.997$, Figure 9), suggesting the formation of a 1:1 complex, putatively that of Q[5] with the inclusion of one NO_3^- ion. $K = 272 \pm 27.6\ M^{-1}$ and $F_\infty/F_0 = 0.022$ were obtained. If experimental errors are taken into consideration, these values agree well with those obtained in the NO_3^--only case, further confirming the nature of the complex and the selective encapsulation of NO_3^-.

The observed discrepancy in the host inclusion of two anions with essentially the same van der Waals radius warrants further discussion. However, in aqueous solutions, NO_3^- is probably more heavily solvated than Cl^-, leading effectively to a larger volume of the NO_3^- and a better physical fit with the host. Moreover, NO_3^- is more charge diffused, which is preferred by the hydrophobic interior of the host. The heavier salvation of NO_3^- is also expected to further reduce its charge density, favoring its inclusion into the host. Nevertheless, inclusion of anionic guests by cucurbiturils is probably not as facile as cations or neutral aromatic organic molecules. This may be understood in terms of the kinetic barrier that needs to be overcome when a negative charged species approaches the polar carbonyl aligned portals. "Neutralizing" the negative charge density by hydrogen bonding or metal coordination is expected to facilitate the inclusion of anions. However, the association of metal ions or hydrogen-bonding capable species with the host is expected to lead to the blocking of the portals. As a result, the smaller Cl^- is more favored to be encapsulated than a NO_3^- ion, leading to the observed reversed preference for Cl^- in the La(III)-capped capsules. In addition, the strong association of NO_3^- with highly oxophilic lanthanide ions may have also contributed to the high-yield production of **2**. Further studies using other anionic guests are underway to verify these hypotheses.

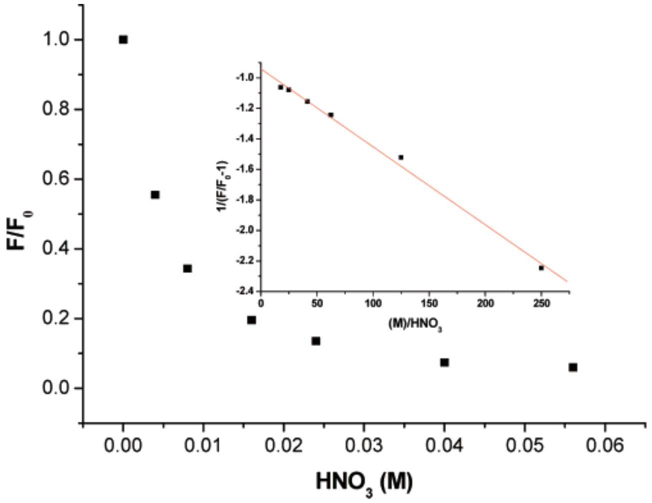

Figure 9. Fluorescence suppression of Q[5] (in HCl solution) as a function of added HNO_3. The solid line shows the best fit of the data to eq 1: $K = 272 \pm 27.6\ M^{-1}$; $F_\infty/F_0 = 0.022$. The inset shows the linear double reciprocal plot.

Summary

Anion-encapsulation behaviors of cucurbit[5]uril toward NO_3^- and Cl^- have been studied. In the absence of any metal ions, the host has been shown to selectively include the more heavily solvated and charge diffused NO_3^- with the formation of a 1:1 complex in solution. Formation of a stable 1:1 inclusion complex with Cl^- was not observed, possibly due to its smaller size and, therefore, a poorer fit with the host, as well as its higher negative charge density, which is not favored by the electron-rich and hydrophobic interior of the host. Upon La(III) coordination to the portal carbonyl groups of the host, reversed preference for Cl^- was observed. Although inclusion complex of NO_3^- by the La(III)-capped host capsule can be crystallized out and structurally characterized, in the presence of competitive Cl^-, only Cl^- inclusion complex was isolated in high yield. This discrepancy in anion-encapsulation behavior between the host and its metal-complex capsule may be understood in terms of the effective size and charge density of the guest, the effect of metal coordination on the binding ability of the host, and the kinetic processes of the host−guest interaction.

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Supporting Information Available: X-ray crystallographic files in CIF format for complexes **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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