Articles

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Luminescent Supramolecular Architectures: A Cyclodextrin Modified with a Europium(III) Crown Swing

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A new photoactive supramolecular assembly featuring a cyclodextrin modified with a $Eu^{3+}\subset$aza crown ether has been prepared. We report the complete characterization of the crown-modified cyclodextrin as well as the synthesis and photophysical properties when Eu^{3+} occupies the aza receptor site. The luminescence properties of the cyclodextrin appended with $Eu^{3+}\subset$aza mimic that of the simple $Eu^{3+}\subset$aza complex. However, enhanced europium emission is observed upon the introduction of benzene to solutions of the supramolecular assembly. We attribute this enhancement to an absorption–energy-transfer–emission process from benzene in the cavity of cyclodextrin to Eu^{3+} ion residing in the appended aza macrocycle.

Introduction

Molecular architectures composed of macropolycyclic structures with more than one recognition site for multiple substrate binding provide the underpinning of supramolecular chemistry.[1-4] When one or more of the guests residing in the binding sites of the supramolecular structure are photoactive, a variety of processes may take place that are modulated by the organization of the receptor and photoactive subunits. Such supramolecular architectures provide the opportunity to study fundamental photochemical processes such as photoinduced energy migration,[5,6] charge separation by electron transfer,[7,8] or selective photochemical reactions.[9]

One approach to introducing photoactive function to supramolecular assemblies is the incorporation of lanthanide ions as guests in the receptor sites of the structure.[6] These ions have found particular utility as photoactive centers in macrocyclic cryptand ligands, which are structural precursors to supramolecular assemblies.[10] Encapsulation of lanthanide ions in the cryptand cage shields the ion from water molecules, thereby increasing its luminescence.[2c,11] When the arm of the cryptand bears a light-harvesting unit such as bipyridine or phenanthroline, intense luminescence is observed owing to the efficient intramolecular transfer of energy from the light-harvesting subunit to the luminescent lanthanide ion.[12,13] Such light conversion processes, which have been described as absorption–energy transfer–emission (AETE), are not confined to intramolecular energy flows. For the case in which an exogenous light-harvesting center is capable of coordinating the caged lanthanide ion, intermolecular energy migration may be elaborated.[14] Fundamentally, the study of the AETE phenomenon of these lanthanide polycyclic complexes can provide an understanding of energy transduction in sophisticated multicomponent biological and chemical systems. Practically such assemblies provide the framework for the design of light conversion schemes for the development of luminescent materials and sensors.[15,16]

Because energy transfer exhibits a $1/r^6$ (Förster) or $e^{-\alpha r}$ (Dexter) distance dependence,[17] efficient transfer demands that the light-harvesting subunit be juxtaposed to the luminescent center. In most complexes to date, close distances have been ensured by incorporating light-harvesting centers in the primary ligating sphere of the lanthanide ion. For both fundamental and practical studies, this approach can place severe restrictions on the design of the assembly because only light-harvesting centers that coordinate the lanthanide ion can be considered. This limitation may be overcome by substituting one arm of a cryptand by a secondary receptor site to form a supramolecular assembly.

A properly functionalized cyclodextrin can ideally play the role of the receptor in such a supramolecular approach. Cyclodextrins (CDs) are cyclic oligosaccharide molecules consisting of six, seven, or eight $\alpha(1-4)$-linked D-glucose units (α-, β-, and γ-CD, respectively) that are arranged in a torus to give a rigid conical structure with a hydrophobic cavity.[18-20] Modification schemes

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of the CDs[21-25] primarily rely on the difference in chemical reactivity between the primary and secondary hydroxyl groups on the glucose subunits, with the former exhibiting greater reactivity than the latter. This feature provides the foundation on which to build cyclodextrins functionalized with a juxtaposed recognition site external to the CD cup. To this end, we were intrigued by Willner's monosubstitution of a primary alcohol of β-CD with a tosyl group and its subsequent replacement by the macropolycyclic ligand 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (aza)[26] to afford an aza-modified cyclodextrin, which we designate β-CD∪[1]aza.[27] In this structure, the conical cavity of the β-CD provides an ordered medium capable of molecular recognition to form inclusion complexes with a variety of molecules,[28,29] whereas the catenation of the aza ligand to a carbon of a primary alcohol functionality of the β-CD (i.e. attachment at the bottom of the CD cup) provides a receptor site for lanthanide ion binding. Supramolecular assemblies of this type are capable of juxtaposing a variety of energy donors to an acceptor without requiring donors to be directly bound to the photoactive lanthanide center.

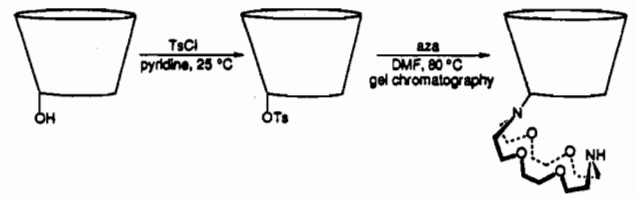
We now present a high-purity synthesis of the cyclodextrin functionalized with 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane containing the luminescent Eu^{3+} ion (β-CD∪[1]aza⊃Eu^{3+}). We also establish AETE photophysics for this supramolecular assembly with the demonstration of energy transfer from benzene residing in the cup of the CD to the Eu^{3+} ion encapsulated in the aza macrocycle.

Experimental Section

General Procedures. All solvents were deoxygenated, dried, and freshly distilled prior to use according to standard methods.[30] The synthesis of the modified β-CD required especially dry pyridine, *N*,*N*-dimethylformamide, and acetonitrile. All starting materials were purchased from Aldrich and were of reagent grade: β-CD was recrystallized from water and dried at 100 °C under a high-vacuum manifold (10^{-6} Torr); 1,4,10,13 tetraoxa-7,16-diazacyclooctadecane was dried prior to use; *p*-toluenesulfonyl chloride was used as received. Spectroscopic grade acetonitrile (Burdick & Jackson) was used for excitation spectroscopy, and the D_2O used for steady-state emission experiments was obtained from Cambridge Isotope Labs (99.9%). Deuterated dimethyl sulfoxide (99.9%), which was employed as a solvent for NMR spectroscopy, was purchased from Isotech and was used after drying over molecular sieves.

Syntheses of Modified β-CDs. Monotosylation at the primary face of β-CD to yield mono(6-*O*-*p*-tosyl)β-CD (β-CD–Ts) employed the methodologies elaborated by Matsui.[31] The product, which was recrystallized from water and dried, was characterized by ^1H and ^{13}C NMR, FTIR, positive ion FABMS and UV–vis spectroscopy. These spectra are available as supplementary material. The synthesis of β-CD∪[1]aza from β-CD–Ts was accomplished by employing the procedures of Willner.[26] Careful separation of the crude product by flash or gel permeation chromatography, over silica gel and Sephadex LH-20 respectively, leads to pure compound. The following solvent systems were used as eluants: AcOEt:*i*-PrOH:H_2O = 10:13:7 or DMF:H_2O = 1:1. The fragments were collected and identified by TLC, with a detection solvent system of AcOH:anisaldehyde:H_2SO_4:MeOH = 45:2:22:430, and by ^1H NMR spectroscopy. As described in the Results section, β-CD∪[1]aza was further characterized by ^{13}C NMR, FABMS, and ^1H NMR COSY spectra, which are available as supplementary material.

Scheme I



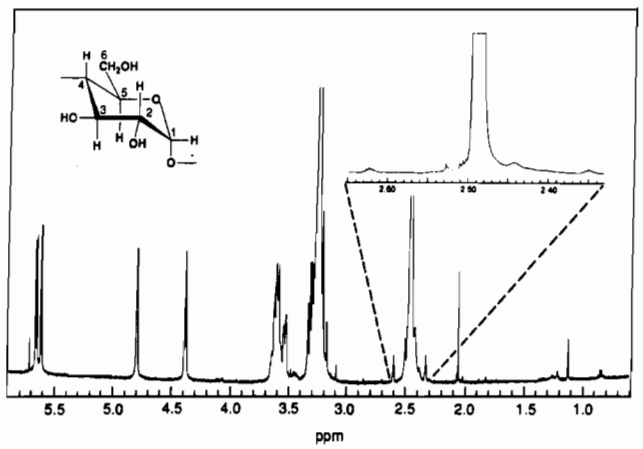


Figure 1. 500-MHz ^1H NMR spectrum of β-CD∪[1]aza. The inset spectrum displays an expanded region showing the triplet peak at 2.51 ppm flanking the DMSO solvent resonance; the numbering of the carbons of the glucose subunit is also depicted in an inset. See text for assignments.

The β-CD∪[1]aza⊃Eu^{3+} complex was prepared by following a procedure similar to that described for the preparation of Eu^{3+}⊂aza.[32] Because aza is a strong base this procedure requires strictly anhydrous conditions to prevent hydrolysis of Eu^{3+}. The Eu^{3+}⊂aza complex was also synthesized for comparison of its photophysical properties with β-CD∪[1]aza⊃Eu^{3+}; both compounds were characterized by emission and excitation spectroscopy. For the energy-transfer studies, the β-CD∪[1]aza⊃Eu^{3+} complex was dissolved in acidified D_2O (pH = 5.5) solutions so that hydrolysis would be circumvented; its concentration was held constant, and benzene was added. There was no need for volume corrections to relative luminescence intensity measurements since benzene was added in microliter quantities.

Instrumentation and Methods. ^1H NMR spectra were recorded on VXR-500 and Gemini 300 instruments at 500 and 300 MHz, respectively, while the ^{13}C NMR spectra were recorded on a Gemini 300 spectrometer at 75 MHz. Positive ion fast atom bombardment mass spectroscopy (FABMS) was performed on a JEOL HX 110 double-focusing mass spectrometer housed at the National Institutes of Health/Michigan State University Mass Spectrometry Facility. Triethanolamine and glycerol were used as matrices. Electronic absorption spectra were recorded on a Varian 2300 UV–vis–near-IR spectrometer. The emission and excitation spectra were obtained by using a spectrometer designed and constructed at Michigan State University.[33] For excitation spectra, the source was a 150-W Xe lamp, and the $^5D_0 \rightarrow {}^7F_2$ emission was monitored at 616 nm; emission spectra were recorded by exciting at 313 and 394 nm with a Xe/Hg lamp. Both emission and excitation spectra were recorded at 23 ± 1 °C and were corrected for instrument response functions. The energy minimized conformation of the supramolecular assembly was determined on a Silicon Graphics IRIS 40-70GTX computer by using a DREIDING force field[34] as implemented by BioGraph software (BioDesign Inc) in the carbohydrate mode. Because lanthanide ions are not included in the software package, a hypothetical calcium cation with 3+ charge was selected for the minimization.

Results and Discussion

Synthesis and Characterization. The preparation of β-CD∪[1]aza is accomplished by the reaction sequence shown in Scheme I. We

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have found that proper function of the supramolecular assembly as a photophysical template requires the careful separation and isolation of each intermediate. Extremely dry β-CD, β-CD-Ts, and β-CD⋃[1]aza are established by the observation of a well-resolved triplet (δ = 4.42 ppm) and two doublets (δ = 5.64 and 5.68 ppm) for the primary and secondary hydroxyl proton resonances, respectively, in DMSO.[35] The presence of interfering trace solvents at the very least obscures these proton splittings and more often causes the complete disappearance of the hydroxyl resonances. Furthermore, in the case of β-CD-Ts, the high-purity synthesis of the monotosylated compound is confirmed by a 4:7 ratio of the aromatic protons of the tosylate to the anomeric H_1 signal of the cyclodextrin.[36]

The monotosylate is substituted by aza to yield β-CD⋃[1]aza, but pure compound was obtained only when chromatography was employed. Evidence of a pure product comes from the FABMS spectrum, which shows the molecular ion cluster at 1379.8 amu with a profile in accordance with a simulated isotope distribution. The loss of the aza–CH_2 in the FABMS is observed with a fragment centered at 1105 amu. Figure 1 shows the ^{1}H NMR spectrum of purified β-CD⋃[1]aza. The peaks at 4.8, 3.7–3.5, and 3.4–3.2 ppm have previously been assigned to the H_1, $H_{3,5,6,6'}$, and $H_{2,4}$ proton resonances, respectively, of the glucopyranose ring (see inset for numbering scheme).[36] A signature of the substitution is the appearance of aza ^{1}H resonances for methylene groups α to oxygen at 3.50 and 3.45 ppm (singlet and triplet), which can be observed only under the high-resolution conditions of a 500-MHz instrument; at lower fields these resonances are obscured by the strong $H_{3,5,6,6'}$ resonances of the glucose subunits of the cyclodextrin. The protons on methylene carbons attached to nitrogen are expected to shift upfield compared to their resonance in free aza (2.63 ppm) because of the change of the secondary amine to a tertiary amine upon reaction with the cyclodextrin. Consistent with this expectation is the appearance of a triplet at 2.51 ppm flanking the DMSO solvent peak (see inset of Figure 1). In addition, the $H_{6,6'}$ resonance of the CD is expected to shift upfield upon substitution of the primary hydroxyl of the glucopyranose with nitrogen of the aza macrocycle. Obscured by the DMSO solvent peak, a resonance at 2.50 ppm is observed for D_2O solutions of the modified CD, which we tentatively assign to the $H_{6,6'}$ resonance. These assignments are supported by the two-dimensional COSY contour plot of the ^{1}H NMR spectrum of β-CD and β-CD⋃[1]aza. The coupling between H_1–H_2, H_5–H_6, H_2–H_3, H_4–H_5, and H_3–H_4 connectivities are easily distinguished from the cross-peak correlations. In addition, the triplet peak at 2.51 ppm displays a cross peak with the 3.45 ppm diagonal peak, which is expected from the coupling between the protons of the aza ligand.

Further evidence for substitution at C_6 is supported by ^{13}C NMR. β-CD⋃[1]aza shows an upfield shift of one C_6 (substituted with the aza) from 60 ppm for β-CD to 55 ppm for the aza-substituted compound. This upfield shift is similar to that observed for primary hydroxyl substitution by alkylamines.[24,36]

Although the tosylate is readily substituted by aza, as described by Willner and co-workers, our chromatographic separation scheme is essential to obtaining compound free of tosylated impurities. In addition to pure β-CD⋃[1]aza, a substituted β-CD is isolated with a downfield shift of the aza methylene triplet resonance at 3.0 ppm. However this resonance is always accompanied by resonances from the phenyl ring of tosylate. In that the substitution of β-CD tosylate by aza produces *p*-toluenesulfonic acid, we believe that the fraction displaying the 2.8 ppm resonance is the tosylate salt of the protonated β-CD⋃[1]aza supramolecule. In support of this contention are the following two observations: a downfield shift of the aza methylene resonances (δ = 2.6 ppm to δ = 3.0 ppm) occurs with protonation of the native aza amine

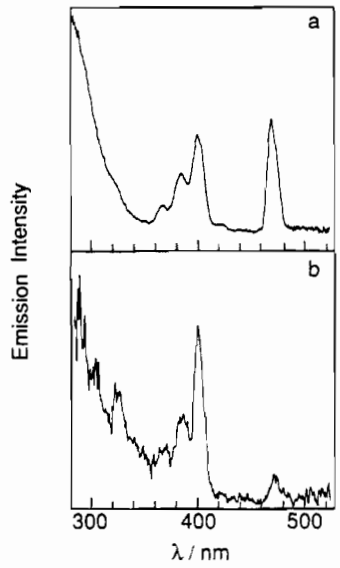

Figure 2. Excitation spectra of (a) Eu^{3+}⊂aza and (b) β-CD⋃[1]aza⊃Eu^{3+} in CH_3CN monitored at λ_{em} = 616 nm.

by *p*-toluenesulfonic acid, and pure β-CD⋃[1]aza can be recovered upon dissolution of the proposed β-CD⋃[1]aza tosylate salt in basic aqueous solution with subsequent precipitation by tetrachloroethylene.

The introduction of Eu^{3+} into the aza receptor site of β-CD proceeds with the methodologies established for the preparation of lanthanide ions encapsulated by crown and aza polycyclic ligands.[10,32] Although residency of the Eu^{3+} ion in the aza straps is established by the large and obvious paramagnetic shifts of the aza and β-CD proton resonances, the quantitative assignment of many of these resonances was frustrated by signal broadening coupled with the limited solubility of the compound such that only modest concentrations were attained for nmr characterization. To this end, luminescence spectroscopy provides sufficient spectral sensitivity to monitor the incorporation of Eu^{3+} into the aza crown ether strap of β-CD⋃[1]aza.

Luminescence Spectroscopy of β-CD⋃[1]aza⊃Eu^{3+}. Generally, europium(III) complexes are signified by bright red luminescence, which originates from transitions between the lowest energy $^5D_0$ excited state to the ^7F_J spin orbit manifold of the ground state. Usually seven peaks are observed in Eu^{3+} luminescence spectra ($^5D_0 \rightarrow {}^7F_0$ (580 nm), $^7F_1$ (592 nm), $^7F_2$ (616 nm), $^7F_3$ (650 nm), $^7F_4$ (700 nm), $^7F_5$ (750 nm), and $^7F_6$ (810 nm)),[37,38] with the $^5D_0 \rightarrow {}^7F_1$, $^7F_2$, and $^7F_4$ transitions accounting for over 95% of the emission intensity.

The spectroscopic properties of Eu^{3+}⊂aza provide the benchmark for the interpretation of the excitation spectrum of a β-CD⋃[1]aza⊃Eu^{3+} supramolecular assembly. Figure 2a displays the excitation spectrum of Eu^{3+}⊂aza obtained by monitoring the $^5D_0 \rightarrow {}^7F_2$ transition at 616 nm. The dominant $^5L_6 \leftarrow {}^7F_0$ and $^5D_2 \leftarrow {}^7F_0$ transitions, which also can be easily observed in the absorption spectra of solutions of the Eu^{3+}⊂aza at modest concentrations, are in evidence at 394 and at 470 nm, respectively. Moreover the ultraviolet spectral region displays a broad and rising profile with increasing energy that is also observed in the absorption spectrum of this compound. A similar ultraviolet profile observed in the absorption and excitation spectra of Eu^{3+}⊂2.2.1 has been assigned to a ligand-to-metal charge-transfer transition from the nitrogens of the aza ligand to the Eu^{3+} center.[10a] Our observation of a parallel transition in Eu^{3+}⊂aza is satisfying inasmuch as the skeleton of the aza and 2.2.1 ligands are com-

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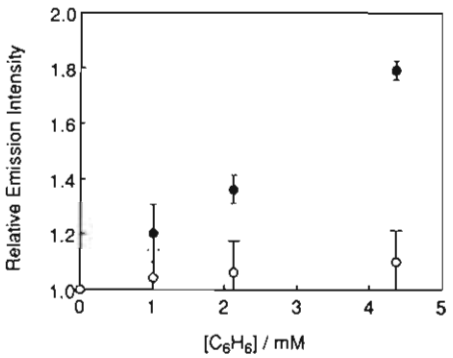

Figure 3. Dependence of the emission intensity (λ_{exc} = 254 nm) from D_2O solutions of $Eu^{3+}\subset$aza (○) and β-CD$\cup$^{1}aza$\supset Eu^{3+}$ (●) upon addition of benzene. Concentrations of the lumophore are 2.5×10^{-4} M.

parable, with the former differing from the latter by only the absence of a diethyl ether strap. These unique spectral features in the $Eu^{3+}\subset$aza excitation spectra are preserved in the spectrum of the product obtained from the reaction of Eu^{3+} with β-CD$\cup$ ^{1}aza. As shown in Figure 2b, the $^5L_6 \leftarrow {}^7F_0$ and $^5D_2 \leftarrow {}^7F_0$ transitions of the Eu^{3+} ion and the LMCT excitation profile in the ultraviolet are both clearly apparent.

Red luminescence is observed from acetonitrile solutions of $Eu^{3+}\subset$aza and β-CD$\cup$^{1}aza$\supset Eu^{3+}$ when excited at wavelengths coincident with the $^5L_6 \leftarrow {}^7F_0$ transition (λ_{exc} = 394 nm). Steady-state luminescence spectra reveal the characteristic $^5D_0 \rightarrow {}^7F_J$ pattern of Eu^{3+} compounds. Excitation into the LMCT transition at 313 nm shows the same emission pattern for both the model $Eu^{3+}\subset$aza compound and the supramolecular assembly.

AETE of the Benzene Inclusion Complex of β-CD$\cup$^{1}aza$\supset Eu^{3+}$. The property of CDs to form inclusion compounds permits luminescence from the β-CD$\cup$^{1}aza$\supset Eu^{3+}$ supramolecular assembly to be observed not only by direct excitation but also by AETE. Figure 3 displays the dependence of the integrated emission intensity from D_2O solutions of $Eu^{3+}\subset$aza and β-CD$\cup$^{1}aza$\supset Eu^{3+}$ compounds on the concentration of added benzene. In the case of the former compound, the relative luminescence intensity increases marginally for concentrations of benzene as high as 5×10^{-3} M. Insofar as benzene can not ligate the $Eu^{3+}\subset$aza ion, energy transfer is restricted to an inefficient bimolecular process owing to the short lifetime of benzene. In comparison the relative luminescence intensity of the β-CD$\cup$^{1}aza$\supset Eu^{3+}$ supramolecule increases markedly over this same concentration range. The intensity change does not arise from a perturbation of the electronic structure of the Eu^{3+} ion by benzene as evidenced by the insensitivity of the energy and lifetime (τ_0 = 1.3 ms for $[C_6H_6] = 0$ to 10^{-3} M) of Eu^{3+} luminescence over this concentration range. In light of the affinity of benzene for the hydrophobic cavity of β-CD (K_{assoc} = 200 M^{-1}),[39] we attribute this enhancement of the emission intensity to the unimolecular AETE process involving benzene as the energy donor and the Eu^{3+} ion as the energy acceptor. A noteworthy observation is that H_2O effectively quenches the luminescence of the benzene-associated supramolecular assembly. A similar result is observed for the $Eu^{3+}\subset$aza complex, which displays an emission quantum yield in D_2O that is attenuated by 75% when dissolved in H_2O. These results are not surprising because the high-frequency O–H vibrations of coordinated water molecules result in efficient nonradiative decay of lanthanide emission. Conversely, $Eu^{3+}\subset$2.2.1 is less susceptible to quenching by H_2O ($\phi_e(H_2O)$ is 25% that of $\phi_e(D_2O)$ for $^5D_0$ luminescence upon $^5L_6$ excitation). Presumably the additional diethyl ether arm of the 2.2.1 cage as compared to aza effectively shields the ion from H_2O. For the case of the β-CD$\cup$^{1}aza$\supset Eu^{3+}$ assembly, if the aza ligand was cradled below the cup, then its conformation would be akin to the $Eu^{3+}\subset$2.2.1 complex inasmuch as the CD cup will cover the open face of the Eu^{3+} ion in place of the diethyl ether arm of 2.2.1. Thus we believe that the β-CD$\cup$^{1}aza$\supset Eu^{3+}$ compound would be only marginally affected by H_2O in a conformation with the aza cradled below the cup. However, this is not the case and indeed the H_2O quenching effect of β-CD$\cup$^{1}aza$\supset Eu^{3+}$ parallels that of $Eu^{3+}\subset$aza. These results suggest that the aza ligand is swung away from the base of the CD cup. In such a swing conformation, the Eu^{3+} ion is accessible to coordination by H_2O, and therefore its emission will be quenched.

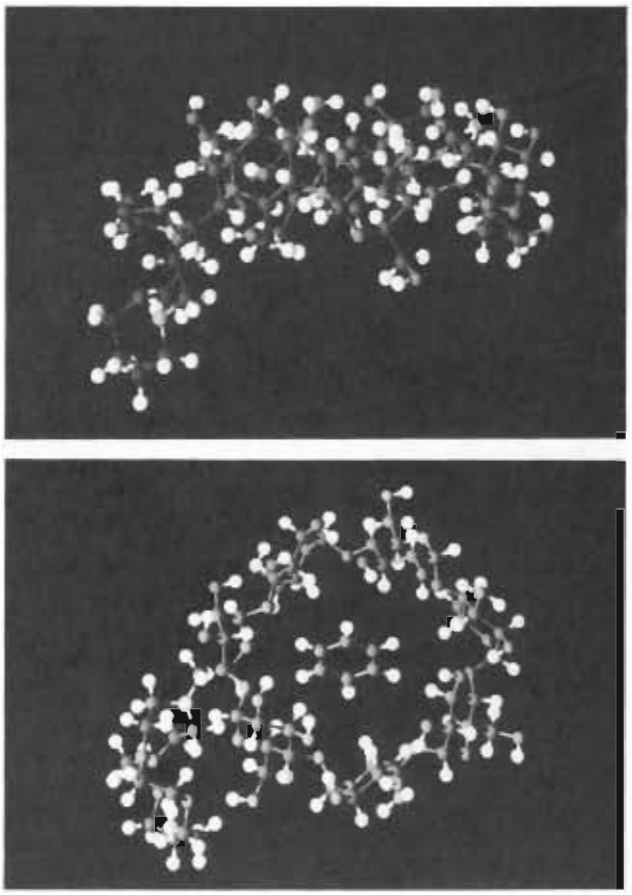

Figure 4. Energy minimized conformation of β-CD$\cup$^{1}aza$\supset Eu^{3+}$ with benzene included in the CD cup: viewed from the side with the appended aza swung away from the base of the CD cup (top); viewed from the top of the CD cup (bottom). For clarity, the cation is not shown residing in the aza macrocycle.

In support of this contention are molecular mechanics calculations of β-CD$\cup$^{1}aza$\supset Eu^{3+}$, which show the aza to be tethered to the β-CD cup in the conformation illustrated in Figure 4. Such a conformation is undesirable to our supramolecular design not only because the Eu^{3+} ion residing in the aza macrocycle is exposed to quenchers in the solution environment (including solvent itself) but also because the distance for energy transfer from the benzene in the β-CD cup to the Eu^{3+} center is not optimally short. To this end a cradle geometry in which both nitrogens of the aza ligand are tethered to the primary alcohols at the base of the β-CD cup is ideal. Experiments are currently underway to prepare the supramolecule with aza capped at the (A, D) primary alcohols of the β-CD and to compare its AETE photophysics to the assembly described herein.

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Registry No. β-CD, 7585-39-9; β-CD-Ts, 67217-55-4; β-CD∪^{1}aza, 89359-18-2; β-CD∪^{1}aza⊃Eu^{3+}, 138259-95-7; Eu^{3+}⊂aza, 128703-72-0; β-CD∪·TsOH, 138259-94-6.

Supplementary Material Available: Figures showing the ^{1}H and ^{13}C NMR, IR, positive ion FABMS, and UV-vis spectra of β-CD-Ts and ^{13}C NMR, FABMS, and ^{1}H NMR COSY spectra of β-CD∪^{1}aza (9 pages). Ordering information is given on any current masthead page.

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Variable-Temperature and -Pressure Multinuclear Magnetic Resonance Study of Solvent Exchange at the Tris(ethylenediamine)nickel(II) Ion in Ethylenediamine

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The solvent exchange between ethylenediamine molecules in the bulk solvent and ethylenediamine molecules coordinated to the nickel(II) ion in neat ethylenediamine and mixtures involving *N,N*-dimethylformamide as a diluent has been studied by the ^{1}H, ^{13}C, and ^{14}N NMR line-broadening technique. The exchange rate constant at 298 K and activation parameters are as follows: $k = 19.6\ s^{-1}$, $\Delta H^{\ddagger} = 69 \pm 3\ kJ\ mol^{-1}$, $\Delta S^{\ddagger} = 10 \pm 11\ J\ mol^{-1}\ K^{-1}$, $\Delta V^{\ddagger} = 11.4 \pm 2.0\ cm^3\ mol^{-1}$ (383 K). The exchange rate is independent of the concentration of ethylenediamine in solvent. It has been proposed that the exchange reaction proceeds via a dissociative mechanism and that it involves a hexacoordinated intermediate with two equivalent monodentate ethylenediamine molecules.

Introduction

Solvent-exchange processes at solvated metal ions are fundamental phenomena of metal ions in solution and are important for elucidating the reaction mechanisms of metal complex formation.[1,2] In most cases, the rate-determining step for metal complex formation with multidentate ligands is the substitution of the coordinated solvent molecule by one of the donor atoms of the entering ligand and the subsequent chelate-ring closure is not rate limiting.[1,2] The solvent-exchange reaction has not been studied in a solvent which acts as a multidentate ligand. Saito's group has published a series of papers dealing with the exchange of acetylacetonate on a variety of metal ions in neat acetylacetone and acetonitrile.[3] The exchange of acetylacetonate is not a simple exchange reaction, and it necessarily involves proton dissociation. In this work, ethylenediamine was selected as a solvent which acts as a bidentate ligand. The exchange of ethylenediamine does not involve proton dissociation, and it can be compared with other solvent-exchange reactions on a common basis.

Experimental Section

Reagents. Ethylenediamine (en) was purified by the following procedure. Under dry nitrogen gas, reagent grade en (200 cm^3) was shaken with activated 4A molecular sieves (18 g) for ca. 3 days; the supernatant liquid was decanted and then agitated for ca. 30 h in the presence of both calcium oxide (11 g) and potassium hydroxide (3 g). The supernatant liquid was distilled under vacuum in the presence of freshly activated 4A molecular sieves (20 g). The obtained en was again distilled under vacuum over sodium metal (3 g), and the purified en was stored over 4A molecular sieves (20 g). Just before use, it was transferred by distillation on a standard vacuum line.

Reagent grade *N,N*-dimethylformamide (DMF) agitated with barium oxide (20 g) for 3 days was distilled twice under vacuum. The purified DMF stored over 4A molecular sieves (10 g) was transferred by distillation for sample preparation. Tris(ethylenediamine)nickel(II) perchlorate was obtained by the addition of ca. 0.5 mol dm^{-3} sodium perchlorate solution (100 g) to a solution containing 40 g of ethylenediamine and 50 g of nickel(II) nitrate. The purple precipitate was recrystallized from water, and the crystals were dried at 373 K in vacuum. The composition was confirmed as $[Ni(C_2H_8N_2)_3](ClO_4)_2$ by C, H, N, and Ni elemental analyses. The electronic absorption spectrum of the solution of $[Ni(en)_3](ClO_4)_2$ was recorded on a Shimazu UV-265FW spectrophotometer (Figure S1 in the supplementary material).

Sample Preparation. Ten solutions for NMR measurements were prepared in a glovebox by dissolving weighed quantities of the perchlorate of $Ni(en)_3^{2+}$ in suitable amounts of freshly distilled en and DMF. The compositions of the solutions are given in Table SI (supplementary material). Samples for variable-temperature NMR measurements were introduced into 5 mm o.d. NMR glass tubes that were then flame-sealed after degassing. The variable-pressure sample was contained in a 7 mm o.d. thin glass tube capped with a flexible Teflon tube, as previously described.[4,5]

NMR Measurements. Variable-temperature ^{1}H, ^{13}C, and ^{14}N NMR measurements were performed on a JEOL JNM-GX270 FT-NMR spectrometer operating at 270, 67.89, and 19.52 MHz, respectively. Some ^{14}N NMR spectra were also measured with a JEOL JNM FX100 instrument. The ^{1}H NMR spectra were measured using a 5 mm o.d. NMR sample tube. A 5 mm o.d. NMR sample tube for ^{13}C and ^{14}N NMR measurements was placed into a 10 mm o.d. NMR tube containing a lock solvent (D_2O and/or deuterated ethylene glycol) and nitromethane as a chemical shift standard. The temperature was measured by a substitution technique with a thermistor (D111-1031 or D641, Takara Thermistor Co.). About 20 min was required for the temperature equilibration of the NMR sample solution, and the temperature stability was ±0.2 K.

The variable-pressure NMR experiment was carried out using a high-pressure NMR probe constructed for the wide-bore superconducting magnet (6.34 T) of a JEOL JNM-GX270 FT-NMR spectrometer.[5] A 7 mm o.d. glass tube with a flexible Teflon cap was used. The pressure generated by a pressure-generating pump (KBP56, Hikarikouatsu Co., Hiroshima) was measured with a Heise Bourdon gauge. Daifloil No. 1 (poly(chlorotrifluoroethylene), Daikin-Kogyo Co.) was used as a pressure-transmitting liquid. The temperature of the sample was measured by a substitution technique with a thermistor before applying high pressure and then monitored with a thermocouple in the pressure vessel during the high-pressure experiment. The temperature was kept to within ±0.2 K. *Caution!* Concentrated solutions of nickel(II) perchlorate in en or en/DMF at high temperature constitute a potential explosion hazard.

Results and Discussion

Variable-Temperature Study. Immediately before or after each NMR measurement of a sample solution at a given temperature,

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