Solvent Effects on the Efficacy of Recognition of Amminemetal Complexes by Macrocyclic Ethers: *In Situ* Probes of Extent of Encapsulation

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The solvent dependence of $-Ru^{III}(NH_3)$ association with macrocyclic ether species has been assessed by following intervalence charge-transfer absorbance energy changes in $(bpy)_2ClRu^{II}-pz-Ru^{III}(NH_3)_5^{4+}$. Depending on the identity of the solvent, $-Ru^{III}(NH_3)_5$·dicyclohexano-24-crown-8 association constants can vary by as much as 4 orders of magnitude, with the largest constants found in the solvents of lowest Lewis basicity. The solvent modulation effects are interpreted in terms of a second-sphere substitution process where association necessarily involves both an energy gain (ether oxygen/ligated ammonia hydrogen-bond formation) and an energy loss (molecular solvent/ligated ammonia hydrogen-bond destruction). The magnitude of the energy loss term is expected to increase as the Lewis basicity of the solvent increases, resulting in decreased crown association strength, as observed experimentally. In low-basicity solvents, crown association with $-Ru^{III}(NH_3)_5$ is strongly favored over association with $-Ru^{II}(NH_3)_5$—consistent with the known enhanced Lewis acidity for the ammine hydrogens in the higher metal oxidation state. A quasi-thermodynamic analysis of crown-induced intervalence energy shifts indicates that the preference for the higher oxidation state diminishes as the solvent basicity increases and is apparently lost when the solvent and the macrocycle have equivalent basicities. Careful consideration of solvatochromic effects associated with intervalence absorption offers a means for evaluating the extent of encapsulation of $-Ru^{III}(NH_3)_5$ by macrocyclic species in solution. The pentaammine guest is roughly one-third encapsulated by dicyclohexano-24-crown-8 and two-thirds encapsulated by dibenzo-42-crown-14, with intermediate degrees of encapsulation by dibenzo-30-crown-10 and dibenzo-36-crown-12. Finally, under some circumstances (high concentrations of dicyclohexano-24-crown-8 in low-basicity solvents) we observe 2:1 crown:metal-complex association stoichiometries.

Introduction

Macrocyclic ethers ("crowns") are capable of recognizing a(m)mine metal complexes, on the basis of primitive hydrogen-bonding interactions (a(m)mine proton/ether oxygen interactions)[1–7]—where a multiplicity of such interactions can lead to very large association or binding constants.[2,3] In prior studies, the recognition effect has been exploited to (a) alter charge-transfer excited-state properties,[4] (b) trigger intramolecular electron-transfer processes,[5] (c) evaluate medium reorganizational effects in localized mixed-valence systems,[6] and (d) induce valence localization (or partial localization) in otherwise delocalized mixed-valence systems.[7] In these studies, control of binding strength, or efficacy of recognition, has been achieved by varying the crown size and flexibility,[1j,3] by adjusting the number of ammine ligands,[3,7] by changing the identities of ancillary ligands,[3] and by changing the oxidation state of the metal center.[3,5,6]

We reasoned that an additional level of control could be achieved by changing the identity of the solvent (since recognition and binding inherently involve solvent displacement). We describe here the results of experiments designed to test the idea. The specific system examined was $(bpy)_2ClRu^{II}-pz-Ru^{III}(NH_3)_5^{4+}$ with each of several dibenzo crowns and with one dicyclohexano crown. This system was chosen because of (1) the presence of a $-Ru^{III}(NH_3)_5$ center, known to engage in strong crown-binding interactions (especially in comparison to analogous Ru^{II} species), and (2) the existence of an ancillary (and non-crown-interacting) electron donor ($(bpy)_2ClRu^{II}-$). The donor provides an electronic spectral handle (based on metal-

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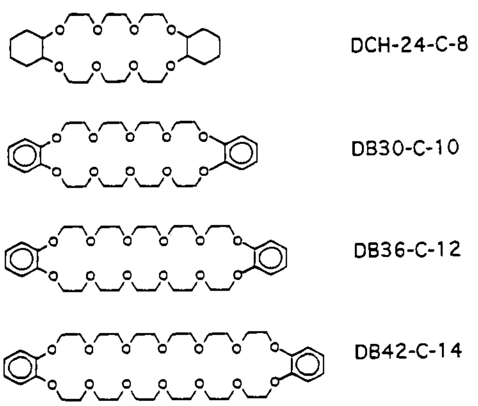

Figure 1. Structures of macrocyclic ethers used in association studies.

to-metal charge-transfer (MMCT) absorption) for detection of environmental changes at the otherwise transparent pentaammineruthenium(III) center:[8]

$$(bpy)_2ClRu^{II}-pz-Ru^{III}(NH_3)_5{}^{4+} \xrightarrow{h\nu} (bpy)_2ClRu^{III}-pz-Ru^{II}(NH_3)_5{}^{4+} \quad (1)$$

From measurements of the transition energy for eq 1 and from related electrochemical measurements, we find that the solvent alteration strategy can indeed be used to adjust binding free energies by up to a few 10's of kilojoules and to modulate binding constants by as much as 4 orders of magnitude. Furthermore, the observed modulation can be rationalized on the basis of known binding characteristics.[1-7] In addition, from the extent of attenuation of known MMCT "solvatochromism" effects[8] following crown binding, useful semiquantitative *in situ* assessments of the absolute extent of guest/host encapsulation can be obtained. Finally, the study reveals that pentaammine complexes can, under certain circumstances, bind more than one crown ether per complex.

Experimental Section

Materials. $[(bpy)_2ClRu-pz-Ru(NH_3)_5](PF_6)_3$ was synthesized and purified by a literature method.[8] The 4+ (mixed-valence) form was prepared *in situ* from the 3+ form by using $[Fe(bpy)_3](PF_6)_3$ as an oxidant. Dicyclohexano-24-crown-8 (DCH-24-C-8; mixture of isomers) and dibenzo-30-crown-10 (DB-30-C-10) were purchased from Aldrich and used as recieved. (Dibenzo-24-crown-8 is available, but the dicyclohexano analogue was chosen because of anticipated problems due to insufficient association strength for the former,[3] particularly in solvents of intermediate Lewis basicity.) Dibenzo-36-crown-12 (DB-36-C-12) and dibenzo-42-crown-14 (DB-42-C-14) were kindly provided by Dr. Dong Yoon; their syntheses have previously been described.[3,9] The structures of the crowns are shown in Figure 1. Tetraethylammonium perchlorate (TEAP) was purchased from GFS Chemicals.

Solvents. Benzonitrile (Aldrich) was distilled from P_2O_5.[10] (In the absence of distillation, previously reported MMCT energies[8] could not be reproduced.) Nitromethane (Aldrich) also was distilled just prior to use. Reagent grade (Aldrich) acetonitrile, nitrobenzene, propylene carbonate, and acetone were used as received.

Measurements. Visible and near-infrared (near-IR) absorption measurements were made with matched 1 cm path length cuvettes by using a Cary 14 spectrophotometer that had been rebuilt and computerized by OLIS. Electrochemical measurements were made in a two-compartment cell by using a PAR 273 potentiostat and a conventional three-electrode configuration (glassy carbon working electrode, platinum counter electrode, saturated (NaCl) calomel electrode (SSCE)).

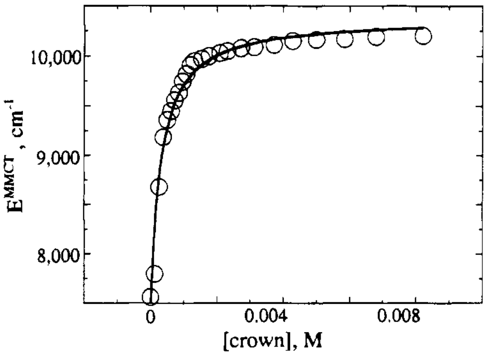

Figure 2. Intervalence absorption energy for 1^{4+} (eq 1) as a function of added dicyclohexano-24-crown-8 concentration in nitromethane as solvent.

Analysis. Association constants (*K*) were generally assessed by measuring MMCT absorption energies (E^{MMCT}; eq 1) as a function of crown concentration (*C*) and fitting the data to the following expression:[3]

$$E^{MMCT} = E_i^{MMCT} + (\Delta E^{MMCT} KC)/(1 + KC) \quad (2)$$

In eq 2, E_i^{MMCT} is the absorption energy prior to crown addition and ΔE^{MMCT} is the difference between E_i^{MMCT} and E^{MMCT} when association is complete. (In a few instances, where energy shifts were particularly small, we additionally (or alternatively) employed an expression with constant-wavelength absorption intensities in place of energies.) A nonlinear least-squares routine (Kaleida Graph, from Synergy Software, Reading, PA) was used to extract *K* and ΔE^{MMCT} values, as well as standard errors, from data fit to the energy expression or its absorbance analog.

As discussed previously,[3] eq 2 is applicable when extinction coefficients for associated and unassociated chromophores are similar, when crown-induced energy shifts are small in comparison to absorption bandwidths, when only two forms of the chromophore (i.e., associated and unassociated) are present, and when chromophore concentrations (ca. 0.1−1 mM) are small in comparison to 1/*K*. In a few cases, *K* was sufficiently large that the last condition could not be satisfied. Its value was then assessed by an alternative electrochemical and spectral strategy described below.

Results

Energy Effects. In solution, the association of a crown with a metal complex can equivalently be viewed as a second-sphere substitution process where one or more solvent molecules are necessarily displaced:

$$(bpy)_2ClRu-pz-Ru(NH_3)_5{}^{4+}\cdot n(\text{solvent}) + \text{crown} \rightarrow (bpy)_2ClRu-pz-Ru(NH_3)_5{}^{4+}\cdot\text{crown} + n\ \text{solvent} \quad (3)$$

As illustrated by the plot in Figure 2 (and observed more generally; see below), the association or substitution process is marked by shifts in the intervalence absorption maximum (eq 1) toward higher energy. Further experiments (Figure 3) show that the *limiting* energy shift (ΔE^{MMCT}) is sensitive to both the crown identity and the solvent identity: The shift clearly is larger for larger crowns and larger in solvents of lower Lewis base strength (where Gutmann's "donor number"[11] has been taken as an empirical measure of Lewis basicity).

While the majority of the intervalence absorption experiments yielded simple isosbestic behavior—implying the existence of only two chromophoric forms and the applicability of eq 3—a few experiments were characterized by more complicated behavior. In particular, for DCH-24-C-8 in nitromethane or

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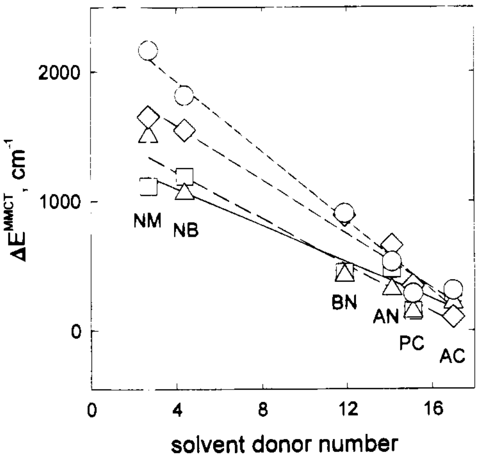

Figure 3. Limiting intervalence absorption energy shifts (ΔE^{MMCT}) for $\mathbf{1}^{4+}$•crown association (eq 3) versus solvent donor number. Key to crowns: (□) DCH-24-C-8; (△) DB-30-C-10; (◇) DB-36-C-12; (○) DB-42-C-14. Key to solvents: NM = nitromethane; NB = nitrobenzene; BN = benzonitrile; AN = acetonitrile; PC = propylene carbonate; AC = acetone.

nitrobenzene as solvent, two isosbestic points were found: The first was observed with 0 to approximately 1 equiv of added crown, while the second appeared for approximately 1 equiv up to many (with no apparent overlap between the two crown concentration regimes). In light of the exceptionally simple behavior found under other conditions, we view the more complicated behavior as compelling evidence for stepwise binding of a *pair* of crowns (i.e., eqs 3 and 4).[12]

$$(\mathrm{bpy})_2\mathrm{ClRu{-}pz{-}Ru(NH_3)_5}^{4+}\text{•crown} + \text{crown} \rightarrow (\mathrm{bpy})_2\mathrm{Ru{-}pz{-}Ru(NH_3)_5}^{4+}\text{•2(crown)} \quad (4)$$

Association Constants. Quantitative evaluation of the shapes of E^{MMCT}/crown concentration curves (eq 2; cf. Figure 2) has yielded K values for a representative macrocycle (DCH-24-C-8) in benzonitrile, acetonitrile, propylene carbonate, and acetone (first association step, eq 3) as well as nitromethane and nitrobenzene (second association step, eq 4) (see Table 1). Values for K(eq 3) in the latter solvents, however, proved too large to measure in this fashion. Instead, they were determined electrochemically, by employing the Nernst equation in the following form:

$$E = E_\mathrm{f} + (RT/F) \times \ln\{([\mathbf{1}^{4+}\text{•crown}]/[\text{crown}]K_{\mathrm{III}})/([\mathbf{1}^{3+}\text{•crown}]/[\text{crown}]K_{\mathrm{II}})\} = E_\mathrm{f} + (RT/F)\ln([\mathbf{1}^{4+}\text{•crown}]K_{\mathrm{II}}/[\mathbf{1}^{3+}\text{•crown}]K_{\mathrm{III}}) \quad (5)$$

In the equation, E_f is the formal potential for the $-\mathrm{Ru^{III/II}(NH_3)_5}$ couple in the absence of crown, E is its potential in the presence of crown, F is the Faraday constant, R is the gas law constant, T is the absolute temperature, and the subscripts denote the oxidation state of the $-\mathrm{Ru(NH_3)_5}$ site. Equation 5 is applicable when [crown] $\leq$ [**1**], i.e. under stoichiometrically starved conditions, where reaction 4 can reasonably be neglected.[13] In implementing the analysis, we noted that at E the total concentration of $\mathbf{1}^{4+}$ in the immediate vicinity of the electrode necessarily equals the total concentration of $\mathbf{1}^{3+}$ in the same region and that the concentrations of **1** in all other oxidation states can be neglected. In light of the anticipated large value for K_{III},[3] we further noted that the 4+ species should exist almost entirely in the $\mathbf{1}^{4+}$•crown form (which therefore must be present at approximately half the total **1** concentration). The required concentration of $\mathbf{1}^{3+}$•crown was calculated from K_{II} (where K_{II} was independently obtained by evaluating the crown concentration dependence of a pentaammineruthenium(II)-to-pyrazine transition). On this basis, the values obtained for K_{III}(first association) in nitromethane and nitrobenzene were 2.2×10^6 and 1.3×10^6 M^{-1}, respectively.[14]

Table 1. Association Constants for Dicyclohexano-24-crown-8 and $(\mathrm{bpy})_2\mathrm{ClRu^{II}{-}pz{-}Ru^{III}(NH_3)_5}^{4+}$ in Various Solvents

solvent	assn const (M^{-1})^{a,b}	solvent	assn const (M^{-1})^{a,b}
nitromethane	2.2 (±0.4) × 10$^{6\,c}$	benzonitrile	4300 ± 600
	(2900 ± 210)^d	acetonitrile	1750 ± 150
nitrobenzene	1.3 (±0.2) × 10$^{6\,c}$	propylene carbonate	900 ± 160
	(730 ± 40)^d	acetone	640 ± 190

[a] Indicated uncertainties are standard errors from nonlinear least-squares fits. Standard deviations from multiple fits are of similar magnitude. [b] Except as indicated, reported values are K_{III} values for the first crown association reaction (eq 3). [c] Indicated uncertainties also include uncertainties associated with electrochemical measurements. [d] K_{III} for second crown association reaction (eq 4).

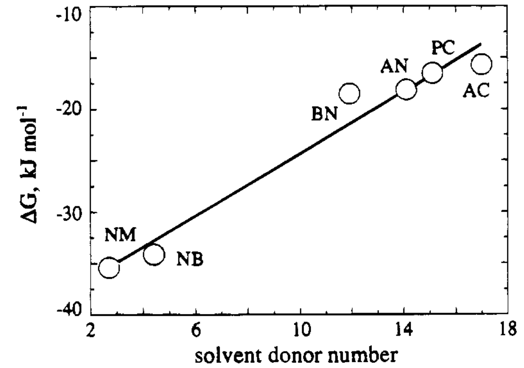

Figure 4. Free energy of association for DCH-24-C-8 with $\mathbf{1}^{4+}$ (eqs 3 and 6) versus solvent donor number.

Finally, with association constants (K_{III}) in hand for six solvents, we used eq 6 to evaluate the solvent dependence of

$$\Delta G = -RT \ln K \quad (6)$$

the corresponding free energies of association. Figure 4 shows that ΔG_{III}, like ΔE^{MMCT}, correlates reasonably well with solvent Lewis basicity—such that the largest (most negative) free energies are found in the solvents of weakest basicity.[15]

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(12) For simplicity, solvent displacement has been omitted from the second crown association reaction.

(13) In employing eq 5, we have neglected the following equilibrium: $\mathbf{1}^{4+}$•crown + $\mathbf{1}^{3+}$•crown ⇀ $\mathbf{1}^{4+}$•2(crown) + $\mathbf{1}^{3+}$. Consideration of the equilibrium would become most important when K_{III}(second association) greatly exceeds K_{II}(first association).

(14) In an earlier study with a related system,[3] we failed to recognize the (partial) occurrence of the second crown association reaction. Consequently, electrochemical measurements made with the macrocycle in large excess yielded a larger formal potential shift than required by the thermodynamics of the first association step in isolation. The larger shift was then incorrectly ascribed to an extremely large $K_{\mathrm{III}}/K_{\mathrm{II}}$ ratio and, therefore, a very large absolute K_{III} (2×10^8 M^{-1}). In the earlier study, measurements were made for several crowns; however, only the K_{III} value for dicyclohexano-24-crown-8 (in nitromethane) appears to require revision.

(15) Similar trends have been observed for the interaction of amminemetal complexes with lasolocid A (Quian, Z.; Chen, Y.; Matamoros, R.; Mao, W.; Curtis, J. C. Unpublished studies at the University of San Francisco) and with poly(vinylpyrrolidone) (Cortese, S.; Coerper, E.; Zhu, L.; Curtis, J. C. Unpublished studies at the University of San Francisco).

Discussion

Spectral Energy Effects and Relative Association Strengths. Figures 3 and 4 show that the solvent exerts a substantial influence upon **1**·crown association or recognition efficacy and upon crown-induced perturbations of intervalence energetics. To understand the latter, it is useful to consider the underlying redox energetics. For electronically localized mixed-valence species such as **1**, E^{MMCT} can be written approximately as the sum of a Marcus-type reorganization energy (λ) and an initial-state/final-state separation energy, ΔG_{op} (see Figure 5).[8,16,17] The latter can be taken approximately as the difference in formal potentials for the donor ($(bpy)_2ClRu-$) and acceptor ($-Ru(NH_3)_5$) sites. Previous work from our laboratory has shown that λ for a related mixed-valence complex is relatively unperturbed by crown binding (at least with small crowns),[6] while Curtis and co-workers have shown that λ for intervalence transfer specifically within **1** is relatively unaffected by solvent variations.[18] Consequently, we ascribe the energy effects observed here exclusively (or nearly exclusively) to ΔG_{op} variations. Additional work has shown that ΔG_{op} variations in systems similar to **1** arise from E_f variations at the ammine–metal site only (as one would expect, on the basis of the site-selective nature of the crown-binding phenomenon).[8] In low- to moderate-basicity solvents, such as nitromethane or acetonitrile, crown association shifts E_f to more negative values (leading to larger (more positive) ΔG_{op} values and larger E^{MMCT} values; see Figures 2 and 3). The negative sign of the shift indicates that crown binding preferentially stabilizes $-Ru^{III}(NH_3)_5$ in comparison to $-Ru^{II}(NH_3)_5$, where the preference arises chemically from the enhancement of ligated ammine Lewis acidity following metal oxidation.[19]

Turning to the solvent dependence of the crown-induced energy shift phenomenon, we find (Figure 3) that it is progressively attenuated as the basicity of the medium increases. Expressed another way, the ability of each of the crowns to distinguish between binding to $-Ru^{III}(NH_3)_5$ vs $-Ru^{II}(NH_3)_5$ is progressively diminished as the solvent donor number or basicity increases. The observation can be made more quantitative by assuming (see above) that binding-induced shifts in E^{MMCT} arise entirely from $-Ru^{III/II}(NH_3)_5$ potential shifts. We then can write

$$\Delta E^{\mathrm{MMCT}} \approx RT\ln(K_{\mathrm{III}}/K_{\mathrm{II}}) \qquad (7)$$

From Figure 3 and eq 7, the estimated ratios of K_{III} to K_{II} for DCH-24-C-8 are 320 in nitrobenzene, 220 in nitromethane, 9 in benzonitrile, 10 in acetonitrile, and just 2 and 4, respectively, in propylene carbonate and acetone. Values for the first two solvents are in fair to good agreement with directly measured ratios of 510 and 2600. For the larger crowns, the solvent effects are even greater. For example, for DB-42-C-14, eq 7 yields a $K_{\mathrm{III}}/K_{\mathrm{II}}$ estimate of 3.5×10^4 in nitromethane as solvent, which decreases to 4 in propylene carbonate. (For a related pentaammineruthenium compound[3] the directly measured K_{III} to K_{II} ratio (in nitromethane) is 1.8×10^5, i.e. sufficiently close to support the approximate validity of eq 7.)

Extrapolation of data in Figure 3 leads to ΔE^{MMCT} values of zero—and K_{III} to K_{II} ratios of unity—in (hypothetical) solvents of donor numbers 17.5–19.5. Further extrapolation leads to a sign change for the intervalence energy shift and a predicted reversal of binding preferences (eq 7); i.e., K_{II} should exceed K_{III} in solvents of high to very high basicity.[20] To understand both the observed and predicted behavior, we return to reaction 3, where crown association is represented as a second-sphere solvent substitution process. From eq 3, crown binding clearly involves both an energy gain (ether oxygen/ammine ligand hydrogen-bond formation) and an energy loss (solvent molecule/ammine ligand hydrogen-bond destruction). The absolute magnitude of the energy loss term should increase (a) as the solvent basicity, and therefore the H-bond strength, increases, (b) as the metal oxidation state, and therefore the ligated ammine acidity (and ligand/solvent H-bond strength), increases, and (c) as the macrocycle size (and therefore the number of ligand/solvent H-bonds to be disrupted) increases. Independent of metal oxidation state, a balance between *enthalpic* energy gained and *enthalpic* energy lost should ultimately be achieved when the basicity of the solvent (effectively, the H-bond accepting ability) equals that of the macrocycle (assuming that the absolute number of H-bonds gained equals the absolute number lost). If we accept the donor number parameter as an approximate measure of basicity and diethyl ether (DN = 19.7) as a model for the crown species, then ΔE^{MMCT} should equal zero (with K_{III} equal to K_{II}; eq 7) when the solvent donor number reaches 19.7. Comparison with experiment reveals very good agreement.

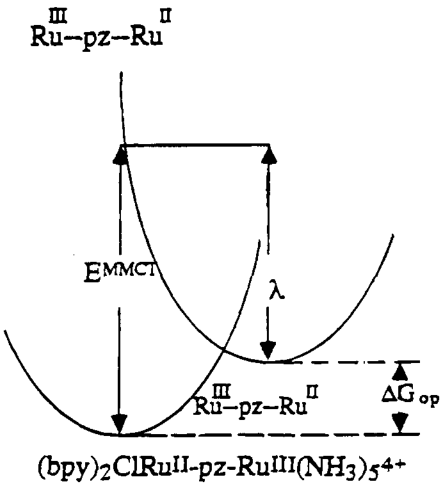

Figure 5. Schematic representation of intervalence charge-transfer absorption energetics.

Extending the argument to solvents of even higher basicity (i.e., DN > 19.7), enthalpy lost upon crown association should now exceed enthalpy gained—and more so, as the metal oxidation state increases. Consequently, K_{III} should become *smaller* than K_{II}—consistent with the extrapolation of ΔE^{MMCT} data discussed above. Conversely, for low- to moderate-basicity solvents, enthalpy lost should be less than enthalpy gained—with the difference again increasing as the oxidation state increases. Consequently, K_{III} should exceed K_{II}, ΔE^{MMCT} should be negative, and the absolute value of ΔE^{MMCT} should increase as the solvent donor number increases. Again, we find reasonable qualitative agreement with experiment.

Absolute Association Constants. In view of eq 3 and the preceding discussion of relative binding strengths, the observed trends in *absolute* crown-binding strength (Table 1 and Figure 4) can likewise be interpreted in terms of hydrogen-bond energy

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(16) (a) Marcus, R. A. *J. Chem. Phys.* **1965**, *45*, 679. (b) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.

(17) For a review of mixed-valence chemistry and energetics, see: Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

(18) Curtis and co-workers do report[8] a small residual dependence of λ on solvent basicity (i.e., small in comparison to the ΔE_{op} dependence).

(19) See, for example: Curtis, J. C.; Sullivan, B. P.; Meyer, T. *J. Inorg. Chem.* **1983**, *22*, 224.

(20) Unfortunately, attempts to detect binding in high-basicity solvents (such as dimethyl sulfoxide) were not successful.

gained (macrocycle/ammine) versus hydrogen-bond energy lost (solvent/ammine). Thus the systematic decrease in absolute association free energy with increasing solvent basicity is attributed directly to the increasing energetic expense of solvent/ligand H-bond destruction with increasing basicity. Extrapolation of the ΔG_{III} versus donor number (or basicity) plot in Figure 4 to DN = 19.6 (i.e., the donor number of the model solvent, diethyl ether) offers an opportunity for evaluation of the association free energy under conditions of approximately zero net enthalpic driving force. The value obtained for DCH-24-C-8 with $\mathbf{1}^{4+}$ is -10 kJ mol^{-1} (or ca. 50 M^{-1} for K_{III}). That the association energy differs substantially from zero is understandable for two reasons. First, crown association, in comparison to simple solvation, is obviously heavily favored entropically. Second, the absolute numerical value assigned to either ΔG_{III} or K_{III} depends, of course, upon the standard states chosen. In our analysis these are 1 M for the crown and pure liquid for the solvent (where we have neglected any dilution of the solvent). Representation of the association process as second-sphere substitution, however, suggests that a more "objective" evaluation could be made by choosing identical standard states for the crown and solvent (e.g., 1 M for both) and explicitly including the solvent in the association equilibrium expression. For a typical organic solvent of concentration 15 M (neat), the resulting K_{III} values (having dimensions of M^{n-1}) would exceed the corresponding K_{III} (M^{-1}) values by 15^n, where n is the number of solvent molecules displaced upon association.[21] Similarly, the association free energies obtained with the alternative standard state description would differ numerically from the values in Figure 4 by ca. $-7n$ kJ mol^{-1}. Thus, the "true" entropic component of crown·**1** association ($-T\Delta S$) is significantly greater than the -10 kJ mol^{-1} implied by the ΔG_{III} value estimated for zero enthalpic driving force conditions.

Returning to Figure 4, the observed correlation of the association free energy with the solvent donor number suggests that ΔG and K values can be reliably predicted for solvents not yet examined. While this may indeed be true to a degree, a modicum of caution is appropriate: Our interpretation of solvent effects considers two important factors but neglects a third associated with crown/solvent H-bond interactions. Presumably, for a given crown, the strength of such interactions will increase as the Lewis acidity of the solvent increases—and, in turn, the absolute free energies for crown/metal complex association will decrease as the acidity increases. The six solvents examined here are of comparatively low Lewis acidity—and, perhaps more importantly, relatively constant Lewis acidity. For better Lewis acids (for example, alcohols, amides, or water), we would predict considerably weaker crown association than suggested solely by donor number correlations. Conversely, for poorer Lewis acids (chloroalkanes?) we would predict greater crown association than expected from DN correlations.

Encapsulation. For certain applications—for example, studies of local medium reorganization in ET processes—it is desirable to obtain not only host/guest association constants but also absolute measures of the extent of guest encapsulation. In principle, encapsulation information can be derived from X-ray crystal structures.[1h,i,2] Unfortunately, we have not yet succeeded in growing suitable crystals. Even with crystal structure information, however, additional *in situ* characterization of encapsulation would be desirable. Multidimensional NMR studies offer one route to this information. While we are indeed pursuing these kinds of studies with other species, NMR investigations can be problematic with paramagnetic guests such as $\mathbf{1}^{4+}$. We find, however, that additional analysis of the solvent effects in Figure 3 can yield semiquantitative information concerning encapsulation specifically at the pentaammine–metal site.

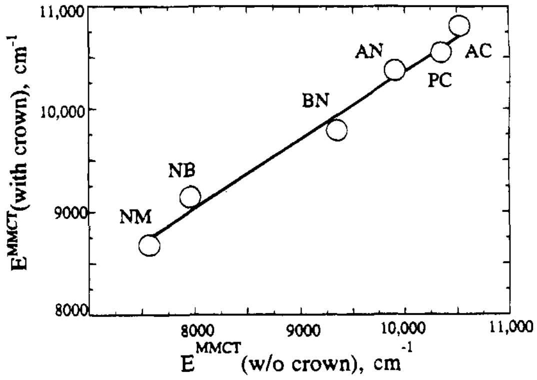

Figure 6. E^{MMCT} for $\mathbf{1}^{4+}$·DCH-24-C-8 versus E^{MMCT} for $\mathbf{1}^{4+}$ (alone) in several solvents. See caption to Figure 3 for solvent abbreviations.

To obtain encapsulation information, we note that the energetics of intervalence transfer within **1** (eq 1) are sensitive not only to crown association but also to variations in the identity of the pure solvent.[8] The known solvatochromism of eq 1 is derived from specific ammine ligand/solvent interactions. The oxidation-state dependence of the interactions (see above) leads to systematic ammine–ruthenium formal potential shifts and, therefore, shifts in intervalence energy.[8] Prior work has shown that (1) the solvatochromic effects correlate strongly with the Lewis basicity (or hydrogen-bond accepting ability) of the solvent[8] and (2) the interactions giving rise to the correlation are highly localized (as one would expect on the basis of a hydrogen-bonding interpretation).[22,23] Additional studies with related chromophores have shown that the magnitude of the solvatochromism scales with the number of ammine ligands.[19] We reasoned that if solvent molecules were blocked (by crown encapsulation) from interacting with ammine ligands, the solvatochromism of **1** would diminish. Furthermore, the extent of diminution should scale as the extent of encapsulation (such that complete encapsulation would lead to a complete loss of solvatochromism).

Figure 6 shows a solvatochromic comparison in the form of a plot of E^{MMCT} with added DCH-24-C-8 (in the limit of complete association; eq 3) vs E^{MMCT} without the crown, for each of the six available solvents. Significant solvent effects exist in both cases—but they are clearly diminished (as expected) when the crown is present. The extent of diminution is indicated by the slope of the plot (0.67). We suggest that the extent of *encapsulation* can be expressed as 1 minus the slope. (Thus, complete encapsulation would yield a slope of zero (no sensitivity to solvent) but a difference of 1. A complete absence of encapsulation would yield a slope of 1 (no diminution of solvent effects) but a difference of zero.)

As shown in Figure 7, the extent of encapsulation defined in this way varies from ca. 0.33 to 0.63—with encapsulation increasing as the crown size increases. The analysis is predicated, of course, upon constancy in the degree of encapsulation as the solvent changes. It also assumes that only species in direct contact with the NH_3 ligands can affect the intervalence energetics and that a direct proportionality exists between changes in slope and changes in the fraction of ligand species

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(21) For any equilibrium constant having dimensions, of course, the numerical value of K (as well as those of ΔG and ΔS) will reflect the (arbitrary) choice made for the standard state.

(22) Ennix, K. S.; McMahon, P. T.; de la Rosa, R.; Curtis, J. C. *Inorg. Chem.* **1987**, *26*, 2660.

(23) See also: Hupp, J. T.; Weydert, J. *Inorg. Chem.* **1987**, *26*, 2657.

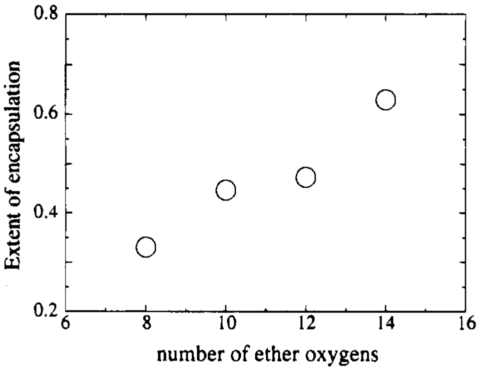

Figure 7. Extent of encapsulation of **1**$^{4+}$ (see text) as a function of encapsulating crown size.

interacting with the solvent. From prior studies, both of the latter assumptions appear to be justified.[19,22,23] In any case, the degree of encapsulation clearly increases essentially as expected from increases in association free energy.[24] Also, the analysis reveals that the extent of encapsulation by the smallest crown is sufficiently small to accommodate our observation (above) of double association at the highest DCH-24-C-8 concentrations. Additionally, the relatively modest degree of encapsulation by either DB-30-C-10 or DB-36-C-12 seems to offer at least a partial explanation for the inability of these species to perturb solvent reorganization energies in an earlier study of a decaamminediruthenium system.[6] Finally, the modest value found for DB-30-C-10 is also qualitatively consistent with an earlier observation that this particular crown is largely ineffective in distinguishing between guests containing two vs four vs five NH_3 ligands.[3] While no doubt an oversimplification, the product of the degree of encapsulation (0.45) and the number of ammine ligands available on **1** (5) suggests that two ligands would be approximately sufficient to satisfy fully the binding propensity of DB-30-C-10.

Conclusions

Changes in solvent can change crown$\cdot$**1**$^{4+}$ association constants by up to 4 orders of magnitude and *ratios* of association constants for $-Ru^{III}(NH_3)_5$ versus $-Ru^{II}(NH_3)_5$ by comparable amounts (where binding to the former is favored). The solvent effects can be correlated empirically with the so-called solvent donor number, where association is weakest in solvents of highest donor number. The effects can be rationalized by recognizing that association necessarily involves solvent displacement and ligated ammine/solvent hydrogen-bond destruction. Energy lost due to H-bond destruction is likely to be greatest in solvents of high donor number (or high Lewis basicity). In (hypothetical) solvents of DN $\approx$ 20, enthalpy lost due to solvent displacement is approximately balanced by enthalpy gained due to crown association (ether oxygen/ammine hydrogen interactions). Under these conditions, association apparently still can be driven (i.e., extrapolated association free energies are still negative), because of the tremendous entropic advantage held by the macrocycles. In solvents of even higher basicity, an inversion of the metal−ammine oxidation-state dependence of association strengths is predicted by the solvent displacement model.

Further analysis of the intervalence solvatochromic effects used to detect association provides a means for estimating the absolute degree of encapsulation (albeit, not the geometry of encapsulation) of $-Ru(NH_3)_5$ by crown species in solution. Encapsulation varies from roughly one-third to roughly two-thirds complete for the available crowns—where the variations scale with the size of the macrocycle. Finally, in a few instances 2:1 crown:metal complex association is detected. The observation is consistent with the analysis of the extent of encapsulation by a single macrocyclic entity.

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(24) Previous studies involved $Ru(NH_3)_5(pyridine)^{2+}$ as the guest.