

Ruthenium Ammine/Crown Ether Interactions in Solution: Effects of Modification of both Guest and Host on the Strength of Second-Sphere Complexation

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Charge-transfer absorption, electrochemical, and NMR-NOE studies of monomeric and dimeric (ligand-bridged) ruthenium ammine guest interactions with several crown ether hosts show that second-sphere complexation is prevalent in nitromethane as solvent and that complexation or binding constants can be varied by ca. 10^8 -fold by modifying both guest and host properties. For hosts, larger binding constants are obtained with larger macrocycles and with more flexible macrocycles (i.e. dicyclohexano vs dibenzo crowns). For guests, larger binding constants are observed in higher oxidation states and in the presence of strongly electron-withdrawing ancillary ligands. In all cases, binding appears to be driven primarily by ammine hydrogen/ether oxygen (Lewis acid/base) interactions. Evidence is also found, however, for contributions from favorable benzene(crown)/pyridine(complex) interactions and (apparently) benzene(crown) \rightarrow Ru(III) charge-transfer (donor/acceptor) interactions.

Introduction

Crown ethers and related macrocycles are capable of functioning not only as primary ligands for simple metal ions¹ but also as second-sphere ligands² for metal complexes, especially metal ammine complexes.^{2–7} We have been interested in exploiting the second-sphere ligating properties in our ongoing studies of metal-complex-based electron-transfer reactivity. With redox systems, we find that crowns can be used as (1) orientationally constrained, “local” solvents for potentially detailed molecular studies of solvent reorganizational energetics,⁶ (2) thermodynamic triggers for intramolecular electron-transfer events within asymmetric ligand-bridged binuclear metal complexes (based on the ability of crowns to shift redox potentials selectively),⁷ (3) trapping elements for partial localization of valencies in otherwise delocalized mixed-valence complexes,⁸ and (4) spacers or bridges, as well as hosts for molecular guests, in covalently-linked donor–crown–acceptor

complexes.⁹ For many of these last studies the desired guests are transition-metal ammine complexes.

With these applications in mind, we felt it desirable to examine in a more systematic fashion the dependence of binding strength upon both host and guest properties. We report here specifically on the effects of (1) host (crown) size and structure and (2) guest (ruthenium complex) oxidation state and primary ligand environment. We find generally that binding increases with increased size and flexibility of the crown ether. It also increases with increased availability of ammine ligands, higher oxidation state, and (related to both of the previous characteristics) increased Lewis acidity of the guest species. Furthermore, we find (consistent with previous studies^{4,5,6,7}) that relatively small amounts of crown ether can have substantial effects upon metal-based redox potentials, as well as metal–ligand and metal–metal charge-transfer absorption energies.

Experimental Section

Materials. All materials were used as received, except where noted. Dibenzo-18-crown-6, dibenzo-24-crown-8, dibenzo-30-crown-10, dicyclohexano-18-crown-6, and dicyclohexano-24-crown-8 were purchased from the Aldrich Chemical Co. Dibenzo-18-crown-6 was twice recrystallized from toluene. Dibenzo-36-crown-12 was prepared according to a literature procedure.¹⁰ Dibenzo-42-crown-14 was prepared by the same methodology, except that hexaethylene glycol bistosylate was used in place of pentaethylene glycol bistosylate as a synthetic intermediate. For dibenzo-42-C-14: ¹H NMR (CDCl₃, 300 MHz) δ 6.91–6.90 (m, 8H), 4.176–4.139 (m, 8H), 3.890–3.853 (m, 8H), 3.760–3.743 (m, 8H), 3.688–3.650 (m, 24H); ¹³C{¹H} NMR (CDCl₃, 300 MHz) δ 148.940, 121.520, and 114.612 (aromatic carbons), 70.839, 70.606, 69.760, and 68.749 (aliphatic carbons). On the basis of its intensity, the resonance at δ 70.606 appears to be the unresolved sum of three expected resonances. FAB-MS (*m*-NBA): *m/e* 735 ([M + Na]⁺, 100), 713 ([M + H]⁺, 41). Anal. Calcd for C₃₆H₅₆O₁₄·2H₂O: C, 57.74; H, 8.08. Found: C, 57.39; H, 7.64.

(NH₃)₅Ru^{II}(4,4'-bpy)Ru^{III}(NH₃)₅⁵⁺ (4,4'-bpy is 4,4'-bipyridine) was prepared in situ from the 4+ (II,II) form as noted elsewhere.¹¹ [(NH₃)₅-Ru^{II}(py-x)](PF₆)₂ (py is pyridine; x is H, 3-Cl, 3,5-Cl₂, and 4-CH₃), [Ru(NH₃)₄(bpy)](PF₆)₂ (bpy is 2,2'-bipyridine), and [Ru(NH₃)₂(bpy)₂](PF₆)₂ were prepared by literature methods.¹² [Ru(bpy)₃](PF₆)₂ was

- (1) For comprehensive data compilations see: Izatt, R. M.; Pawlak, K.; Bradshaw, J. S. *Chem. Rev.* **1991**, *91*, 1721 and reviews referenced therein.
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obtained from $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (Aldrich) by metathesis in water with NH_4PF_6 . Except as noted, nitromethane (Aldrich, 98%) was used as solvent for all binding constant measurements. It was purified by distillation from P_2O_5 under an N_2 atmosphere.¹³

Measurements. An OLIS-modified Cary 14 spectrophotometer was used for visible and near-infrared absorption spectral measurements. A Bruker 600-MHz NMR spectrometer was used for 1-D NOE experiments. Electrochemical measurements (two-compartment cell; SCE reference with platinum counter and working electrodes) were made by using an EG & G Princeton Applied Research Model 174A polarographic analyzer connected to a Houston Instruments Omnigraphic 2000 recorder. The supporting electrolyte was generally 0.02 M tetrabutylammonium hexafluorophosphate. All measurements were made at ambient temperature, without additional thermostatic control.

Evaluation of Binding Constants. As noted previously,^{4,6} binding to Ru(II) complexes can be readily monitored on the basis of shifts in metal-to-(bi)pyridyl ligand charge-transfer energies (E^{MLCT}). If absorption spectra with and without crown are similar in shape and intensity, if the total shift in energy with crown binding (ΔE^{MLCT}) is small in comparison to the width of any individual absorption bands, and if the concentration of added crown is always severalfold greater than that of the metal complex, it can be shown that

$$E^{\text{MLCT}} = E_i^{\text{MLCT}} + \frac{\Delta E^{\text{MLCT}} K_{\text{II}} C}{1 + K_{\text{II}} C} \quad (1)$$

where E_i^{MLCT} is the MLCT absorption energy prior to crown addition, K_{II} is the crown-Ru(II) binding constant, and C is the crown concentration. Alternatively, if the band shape and/or energy requirements are not met, K_{II} can be extracted from absorbance measurements (A) at a single wavelength (λ) via

$$A_\lambda = A_{\lambda,i} + \frac{\Delta A_\lambda K_{\text{II}} C}{1 + K_{\text{II}} C} \quad (2)$$

While eq 2 is in principle more general than eq 1, its use (eq 2) is often less convenient, since it requires much closer attention to spurious sources of absorbance loss (e.g. photolability, thermally-induced solvolysis, oxidation by trace impurities, etc.). Consequently, energy measurements (eq 1) were used for most studies involving Ru(II) complexes. (Identical binding constants were obtained when both analyses were used.)

Binding to Ru(III) was examined by monitoring the absorption energy maximum (E^{MMCT}) for metal-to-metal charge-transfer in the mixed-valence complex $(\text{NH}_3)_5\text{Ru}^{\text{II}}(4,4'\text{-bpy})\text{Ru}^{\text{III}}(\text{NH}_3)_5^{5+}$. As shown previously,⁶ E^{MMCT} responds to binding at both redox sites. For stepwise binding (Ru(III) followed by Ru(II)) the MMCT energy is given by⁶

$$E^{\text{MMCT}} = E_i^{\text{MMCT}} + \frac{\Delta E_{\text{III}} K_{\text{III}} C}{1 + K_{\text{III}} C} + \frac{\Delta E_{\text{II}} K_{\text{II}} C}{1 + K_{\text{II}} C} \quad (3)$$

where E_i^{MMCT} is the value of E^{MMCT} in the absence of added crown, ΔE_{III} is the shift in MMCT absorption energy between the half-encapsulated (i.e. Ru(III)-encapsulated) species and the initial species, ΔE_{II} is the absorption energy difference between the half-encapsulated and fully encapsulated species, and K_{III} and K_{II} are the (stepwise) binding constants for the crown with $(\text{NH}_3)_5\text{Ru}^{\text{III}}$ - and $(\text{NH}_3)_5\text{Ru}^{\text{II}}$ -, respectively. Similar assumptions apply to eq 3 as to eq 1. In addition, for eq 3 we assume that the concentration (and therefore the absorbance contribution) of the species with the crown bound *only* to the Ru(II) site can be neglected. For all three equations, data fits and error analyses were carried out by using a nonlinear least-squares routine (Kaleida Graph software package, version 2.1, from Synergy Software, Reading, PA).

Metal complex concentrations for spectral measurements typically ranged from ca. 0.01 to 0.05 mM. Crown concentrations always exceeded metal complex concentrations by at least 5-fold. Upper limits (solubility limited) were ca. 50 mM for the dicyclohexano crowns and ca. 120 mM for dibenzo-18-C-6 and dibenzo-24-C-6. For the larger crowns, binding was sufficiently strong that upper limits ranging from ca. 6 to 25 mM could be employed (see figures). Typically, absorption data were collected at 15–20 crown concentrations (more for eq 3) and the results from three or four separate experiments were combined. The pooled (not averaged) data sets were then analyzed to extract binding constants and standard errors.

(13) In an earlier report⁶ activated alumina was used both as a drying agent for CH_3NO_2 and as a material for removal of aza impurities. We discontinued its use because of the likelihood of introduction of cationic impurities, which might compete for crown species.

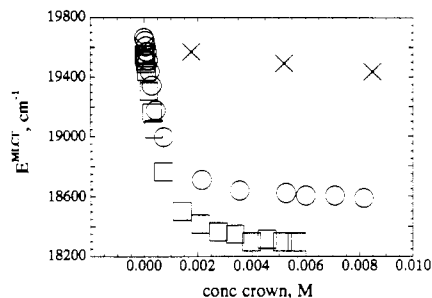


Figure 1. E^{MLCT} vs crown concentration for $(\text{NH}_3)_5\text{Ru}^{\text{II}}(4,4'\text{-bpy})\text{Ru}^{\text{III}}(\text{NH}_3)_5^{5+}$ (ca. 0.01–0.04 mM) with: (X) dibenzo-24-C-8 (additional data were obtained at higher concentrations), (O) dibenzo-30-C-10, and (□) dibenzo-36-C-12.

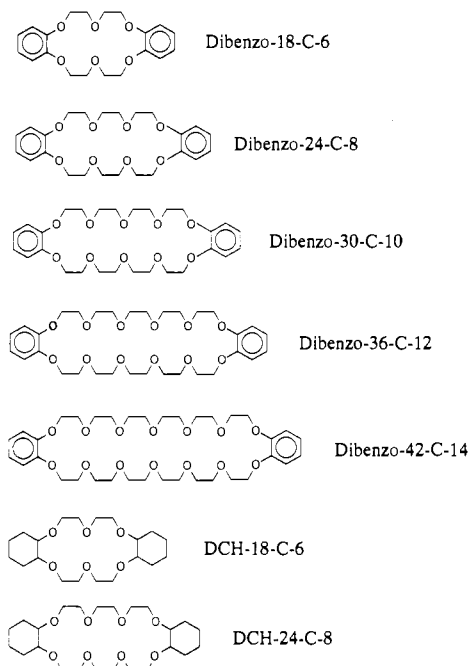


Figure 2. Crown ethers employed for binding studies.

Finally, for monomeric species, K_{III} values were obtained from *limiting* shifts in Ru(III/II) formal potentials (ΔE_f) with increasing crown concentration, by application of the following:

$$K_{\text{II}}/K_{\text{III}} = \exp(F\Delta E_f/RT) \quad (4)$$

In the equation, F is the Faraday constant, R is the gas law constant, and K_{II} is measured independently.

Results and Discussion

Host Modifications. Shown in Figure 1 are representative data (E^{MLCT} vs crown concentration) for binding of three different crown species (Figure 2) to the Ru^{II} end of $(\text{NH}_3)_5\text{Ru}^{\text{II}}(4,4'\text{-bpy})\text{Ru}^{\text{III}}(\text{NH}_3)_5^{5+}$. The data are suggestive of an increase in binding strength with increasing crown size—a suggestion borne out by the quantitative data in Table I. In the table, K_{II} values vary as in the order dibenzo-18-C-6 < dibenzo-24-C-8 < dibenzo-30-C-10 \approx dibenzo-36-C-12 < dibenzo-42-C-14, with an overall variation of ca. 1000-fold. A similar trend is evident for binding to Ru^{III}, except that the total range is larger and binding by dibenzo-36-C-12 is now clearly stronger than binding by dibenzo-30-C-10.

From several previous studies,⁷ the second-sphere complexation effects are known to arise primarily from favorable ether oxygen/amine hydrogen interactions. The macrocyclic size effects almost certainly reflect, therefore, the ability of the larger crowns to establish larger numbers of oxygen/amine contacts. Obviously more contacts are possible when more ether oxygens

Table I. Crown Ether Binding to $(\text{NH}_3)_5\text{Ru}^{\text{II}}(4,4'\text{-bpy})\text{Ru}^{\text{III}}(\text{NH}_3)_5^{5+}$ in Nitromethane Solvent

crown ^a	$K_{\text{II}}, \text{M}^{-1}$ ^b	$K_{\text{III}}, \text{M}^{-1}$ ^b	$\Delta E^{\text{MLCT}}, \text{cm}^{-1}$ ^c	$\Delta E_{\text{f}} \text{mV}^d$
dibenzo-24-C-8	23 ± 7^e	1600 ± 400^e	-1300	$> -67^f$
dibenzo-30-C-10	1670 ± 150^g	$5 (\pm 2) \times 10^6$ ^h	-1260	-210 ± 10
dibenzo-36-C-12	1630 ± 150^g	$2.3 (\pm 1.1) \times 10^8$ ^h	-1440	-310 ± 10
dibenzo-42-C-14	4300 ± 400^g	$2.1 (\pm 0.6) \times 10^9$ ^h	-1560	-338 ± 6
dicyclohexano-18-C-6	250 ± 20^g		-1080	
dicyclohexano-24-C-8	364 ± 13^g	$1.9 (\pm 0.5) \times 10^8$ ^h	-1540	-336 ± 6

^a K_{II} for dibenzo-18-C-6 is estimated as 4 M^{-1} on the basis of a fit of E^{MLCT} data with an assumed ΔE^{MLCT} of -1080 cm^{-1} , i.e. the value measured for dicyclohexano-18-C-6. If the true ΔE^{MLCT} value is smaller, then K_{II} will be larger. ^b Reported errors are standard errors from nonlinear least-squares fits (and, if applicable, propagated uncertainties from electrochemical measurements). ^c Limiting shifts in MLCT energies based on best fits of E^{MLCT} vs crown concn. ^d Data obtained with the model compound $\text{Ru}(\text{NH}_3)_5(\text{py})^{3+/2+}$. ^e Obtained from MMCT data by using eq 3; previously reported in ref 6. ^f Lower limit estimate; see ref 6. ^g Obtained from MLCT data. ^h Estimated via eq 4 by using K_{II} data for the dimer and ΔE_{f} data for the model compound $\text{Ru}(\text{NH}_3)_5(\text{py})^{3+/2+}$.

comprise the crown; however, the size advantage might also partially reflect a flexibility advantage in creating maximal host-guest contact.

In principle, a second component of binding could be a benzene/(bi)pyridine π -stacking (or dispersive) interaction. This type of binding is clearly important, for example, in the second-sphere complexation of $\text{Pt}(\text{NH}_3)_2(\text{bpy})^{2+}$ by dibenzo crowns,^{5c,d} as well as in the encapsulation of diquat (6,7-dihydrodipyrido[1,2-*a*:2',1'-*c*]pyrazinediium) by the same species.¹⁰ Conceivably, these interactions could contribute also to the macrocycle size dependence (based on the presumable ability of the largest macrocycles to place both benzene functionalities in close proximity to the 4,4'-bpy bridging ligand). To evaluate these possibilities, a 1-D NOE NMR experiment was performed in CD_3NO_2 with dibenzo-36-C-12 and an equimolar amount of a simpler guest, $(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{py}-\text{CH}_3)^{2+}$. It was assumed that two limiting complexation conformations might exist: (1) a benzene/pyridine stacking conformation as described above or (2) a conformation in which the benzenes themselves stack, but are pointed away from the methylpyridine ligand. Upon selective excitation of the methyl (pyridine) protons (2.32 ppm) in the NOE experiment, a cross-coupling response was seen from the benzene protons of the crown (6.90 ppm, α and β resonances unresolved), implying a separation distance of ca. 5 Å or less and, therefore, supporting conformation 1 (or some variant) as the solution-phase binding configuration.

We reasoned that a more quantitative measure of the importance of π interactions could be obtained by comparing the dibenzo crown results with ones obtained from hosts lacking planar aromatic substituents. In order to mimic (at least in part) the likely steric features of the dibenzo crowns, we chose for comparison a pair of dicyclohexano (DCH) crowns: DCH-18-C-6 and DCH-24-C-8. Remarkably, as shown in Table I, these two proved superior to their dibenzo congeners in their ability to bind both the Ru(II) and Ru(III) ends of $(\text{NH}_3)_5\text{Ru}^{\text{II}}(4,4'\text{-bpy})\text{Ru}^{\text{III}}(\text{NH}_3)_5^{5+}$. A tentative interpretation is that modest differences in crown flexibility significantly affect the strength of binding. Alternatively, binding by the dibenzo host might entail disruption of benzene/benzene interactions perhaps present in the free crown. If the presumed disruption were not fully compensated by a gain in stability from benzene/bipyridine interactions, then a net decrease in binding strength in comparison to the dicyclohexano crowns would result.

Guest Modifications. Studies of the dimeric ruthenium mixed-

Table II. Dibenzo-30-crown-10 Binding to $\text{Ru}(\text{NH}_3)_x((\text{bpy})_y)^{2+}$ Species in Nitromethane Solvent

complex	$K_{\text{II}}, \text{M}^{-1}$ ^a	$\Delta E^{\text{MLCT}}, \text{cm}^{-1}$ ^b	complex	$K_{\text{II}}, \text{M}^{-1}$ ^a	$\Delta E^{\text{MLCT}}, \text{cm}^{-1}$ ^b
$\text{Ru}(\text{NH}_3)_5(\text{py})^{2+}$	650 ± 30	-1070	$\text{Ru}(\text{NH}_3)_2(\text{bpy})_2^{2+}$	350 ± 50	-1100
$\text{Ru}(\text{NH}_3)_4(\text{bpy})^{2+}$	800 ± 100	-1070	$\text{Ru}(\text{bpy})_3^{2+}$	<i>c</i>	<i>d</i>

^a Reported errors are standard errors from nonlinear least-squares fits. ^b Limiting shifts in E^{MLCT} following crown binding. ^c No binding detected. ^d No shift detected.

valance ion were complemented with measurements on monomeric $\text{Ru}(\text{NH}_3)_5(\text{py})^{2+}$, $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{2+}$, $\text{Ru}(\text{NH}_3)_2(\text{bpy})_2^{2+}$, and $\text{Ru}(\text{bpy})_3^{2+}$, with the explicit aim of assessing quantitatively the role of ammine ligand content. Data for complexation by dibenzo-30-C-10 are summarized in Table II. As expected, binding is completely absent for the ammine-free tris(bipyridine)ruthenium ion. Surprisingly, however, for the other three, no clear dependence of binding strength on the number of available ammine ligands was discerned. Similarly, no (significant) dependence of the crown-induced MLCT energy shift (ΔE^{MLCT}) on the number of available NH_3 ligands was found. These latter findings may be contrasted with purely solvent-based studies of MLCT energy shifts, where shifts in E^{MLCT} correlate linearly with the number of ammine ligands for a large number of solvent pairs or overall solvent series.¹²

One possible interpretation of the current results is that dibenzo-30-C-10 is (perhaps) incapable sterically of interacting with the full complement of ammine ligands (at least in the pentaammine and tetraammine cases), despite the hypothetical availability of up to 10 ether oxygen binding sites. Modest supporting evidence for this interpretation may be derived from a more quantitative comparison with the solvatochromic studies of Curtis et al.¹² In those studies, an empirical correlation was developed between E^{MLCT} for ruthenium ammine complexes and Gutman's donor number,¹⁵ a purported measure of solvent Lewis basicity. For the complexes studied here, the shift in E^{MLCT} with solvent was found to be ca. 16–22 cm^{-1} per ammine ligand per donor number unit. If diethyl ether is used as a surrogate for the crown species, the difference in donor number between nitromethane and crown ethers as solvent is about 21.¹⁵ From the ΔE^{MLCT} values in Table II, one would then infer the participation of roughly 2.3–3.3 ammine ligands in crown binding for any of the three complexes. Nevertheless, in the absence of direct structural evidence, the interpretation must be viewed as speculative.

Somewhat simpler effects seem to occur when the ancillary ligand composition is varied. For the series $\text{Ru}(\text{NH}_3)_5(\text{py}-x)^{2+}$, where *x* is 4-methyl, hydrogen, 3-chloro, or 3,5-dichloro, K_{II} values for second-sphere complexation by dibenzo-30-C-10 vary between 640 and 2070 M^{-1} . Figure 3 shows that the binding constants can be correlated with the $\text{p}K_{\text{a}}$ of the free pyridyl ligand, where the $\text{p}K_{\text{a}}$ ¹⁶ is likely to provide a good measure of the comparative σ -electron-donating or -withdrawing characteristics of the ligand. One effect of pyridine substituent variation would be to vary the electron density at the ruthenium center and therefore indirectly perturb the electron density and Lewis acidity at the ammine ligand sites. Substituents with strong electron-withdrawing tendencies would be expected to increase Lewis acidity and therefore enhance ammine hydrogen/ether oxygen binding

(14) The dicyclohexano crowns were purchased as mixtures of isomers (cis-syn-cis, cis-anti-cis, trans-syn-trans, trans-anti-trans) and separation was not attempted. If ruthenium ammine binding constants for the various isomers differ (see, for example: Coxon, et al. *J. Am. Chem. Soc.* **1978**, *100*, 8260), then the observed binding constants would obviously represent only lower limit estimates for the most effective isomer.

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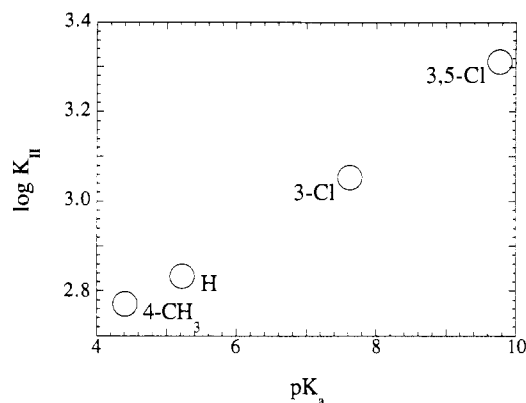


Figure 3. Dibenzo-30-C-10 complexation of $\text{Ru}(\text{NH}_3)_5(\text{py}-x)^{2+}$ species: $\log K_{\text{II}}$ vs free pyridyl ligand $\text{p}K_{\text{a}}$.^{16,22}

strengths, while those that are electron donating should exert the opposite effect. While the available data set is small, the results are consistent with this interpretation.¹⁷ We note that related effects have been reported by Smid and co-workers for the binding of Na^+ by benzo crowns, except that there the substituents were used instead to tune the Lewis basicity of the ether oxygens.¹⁸ Returning to the pentaammineruthenium experiments, a secondary effect conceivably could be the tuning of benzene/pyridine donor/acceptor (DA) interactions. From both electrochemical studies (ease of oxidation)¹⁹ and host/guest binding studies (DA charge-transfer bands),¹⁰ evidence exists to support the contention that crown-derivatized benzenes are effective π -electron donors. Pyridine, of course, is a fair electron acceptor when coordinated to a doubly charged metal center (as evidenced, for example, by the appearance of accessible MLCT transitions). Introduction of pyridyl substituents should lead to enhanced DA interactions (and greater binding strength) when the substituent withdraws electron density and diminished DA effects when electron density is donated, again consistent with the trend in Figure 3.

Finally, a substantial dependence of binding strength on metal

oxidation state was observed. In all cases, binding is enhanced in the higher oxidation state. Furthermore, the advantage of Ru(III) over Ru(II) increases as the crown size increases. The oxidation-state dependence clearly must be related to enhancement of ammine ligand acidity in the Ru(III) form.²⁰ A contributing factor, however, appears to be benzene-to-ruthenium(III) charge transfer. Addition of dibenzo-30-C-10 to $\text{Ru}(\text{NH}_3)_5(3,5\text{-Cl-py})^{3+}$ in CH_3NO_2 leads to the appearance of an absorption feature (a well-defined shoulder) near 470 nm which is tentatively assigned to charge transfer.²¹

Summary

Crown interactions with simple ruthenium ammine complexes are observable over a range of 10^8 in binding constant. In all cases, binding appears to be driven by favorable ether oxygen/ammine hydrogen interactions. Binding or second-sphere complex formation is enhanced by increasing the macrocyclic host size and, therefore, the number of ether oxygen donor atoms. It is also enhanced by replacing benzene functionalities with cyclohexanes in the macrocycle framework. Guests are complexed most successfully in high oxidation states or in the presence of strongly electron-withdrawing ancillary ligands, which enhance the Lewis acidity of ligated ammonias. Somewhat surprisingly, however, binding strength is not especially sensitive to the total number of ammine ligands present (although at least some must be present). The insensitivity to ligand count may possibly be indicative of effective involvement (at least for medium-sized crowns) of only two or three of the total available NH_3 sites, regardless of the overall primary ligand-sphere composition.

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- (17) Comparison of K_{II} values in Figure 3 with the K_{II} value for $(\text{NH}_3)_5\text{-Ru}^{\text{II}}(4,4'\text{-bpy})\text{Ru}^{\text{III}}(\text{NH}_3)_5^{3+}$ (Table I) suggests an increase in pyridine $\text{p}K_{\text{a}}$ of ca. 3.3 upon modification of py by $(\text{py})\text{Ru}^{\text{III}}(\text{NH}_3)_5^{3+}$ as a substituent, a finding which seems plausible on the basis of qualitative electrostatic considerations. Presumably, much larger, pendent metal–ammine binding and $\text{p}K_{\text{a}}$ effects would be observed with shorter bridges such as cyanopyridine.
- (18) Ungaro, R.; El Haj, B.; Smid, J. *J. Am. Chem. Soc.* **1976**, *98*, 5198. See also: Gustowski, D. A.; Gatto, V. J.; Mallen, J.; Eschegoyen, L.; Gokel, G. W. *J. Org. Chem.* **1987**, *52*, 5172.
- (19) Angely, L.; Questaigne, V.; Rault-Berthelot, J.; Simonet, J. *New J. Chem.* **1990**, *14*, 841.

(20) See also refs 4, 6, and 7.

(21) Note the precedent in ref 10, based on dibenzo-30-C-10 as a donor and diquat as an acceptor.

(22) Detailed binding data: $K_{\text{II}}(4\text{-CH}_3) = 640 \pm 40 \text{ M}^{-1}$; $\Delta E^{\text{MLCT}} = 1180 \text{ cm}^{-1}$, [crown] = 0–27 mM.; $K_{\text{II}}(3\text{-Cl}) = 1160 \pm 70 \text{ M}^{-1}$, $\Delta E^{\text{MLCT}} = 1100 \text{ cm}^{-1}$, [crown] = 0–23 mM.; $K_{\text{II}}(3,5\text{-Cl}) = 2070 \pm 120 \text{ M}^{-1}$, $\Delta E^{\text{MLCT}} = 1100 \text{ cm}^{-1}$, [crown] = 0–21 mM.