of the cations Fe^+, Co^+, and Ni^+ with ethylene oxide.[16,17] Previous matrix isolation studies on the chemistry of Fe/CH_3OH have shown that photoactivation of the $Fe(CH_3OH)$ adduct in the violet and ultraviolet regions led to the metal atom insertion into the O–H and C–O bonds of methanol, respectively. Photofragmentation of methanol occurred via UV excitation of its O–H insertion reaction intermediate, namely methoxyiron hydride, CH_3OFeH.[11] Peaks associated with CO, FeCO, and FeH_2 were observed, which suggested the photofragmentation of methanol to carbon monoxide and hydrogen.

V. Concluding Remarks

1. The infrared spectrum of the first and one of the simplest oxametallacycles, ferraoxetane, was obtained from the spontaneous insertion of an iron atom into the C–O bond of ethylene oxide in solid argon at 12.5–15 K.

2. Upon broad band irradiation with visible light, a metathesis reaction was observed with simultaneous cleavage of the C–O and Fe–C bonds of the oxametallacycle. The photoproduct was an iron monoxide molecule interacting with an ethylene molecule through the π-system. The FTIR spectrum of this π-complex was measured and compared to similar π-complexes.

3. The C–H activation of one of the inert C–H bonds of ethylene was achieved by UV photolysis of $FeO(C_2H_4)$. The FTIR spectrum of vinyliron hydroxide was thus identified for the first time.

4. Diiron seemed to have undergone similar photochemistry although a more detailed study is needed to confirm the reaction mechanism.

5. Evidence from the observation of an FeOFe stretching frequency suggests the formation of a double insertion product, a five-membered ring where the two iron atoms are bridging the oxygen atom, at one end and bonded to ethylene at the other end.

6. A secondary reaction for the metal atom appeared to have taken place leading to the photofragmentation of ethylene oxide into methane and carbon monoxide. More work is needed to delineate the mechanism of this reaction. A similar reaction was also observed for diiron where the final product was identified as a perturbed diiron monocarbonyl.

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Circular Dichroism Studies of the Solution Structure of Chiral Pyridine Substituted Crowns and Their Complexes

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Abstract: The solution structures of a series of chiral pyridino-18-crown-6 macrocycles and their alkali and alkaline earth complexes have been studied with circular dichroism (CD) spectroscopy. The crowns (4*S*,14*S*)-4,14-dimethyl-2,16-dithioxopyridino-18-crown-6, its 2,16-dioxo analogue, its 2,16-tetrahydro analogue, and (5*S*,13*S*)-5,13-diphenyl-2,16-dioxopyridino-18-crown-6 contain pyridine chromophores that have been used as direct structural probes. The induced CD in the lowest energy $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of pyridine has been interpreted in terms of the one-electron theory of optical activity. Sector rules have been derived for each of these transitions and used to predict the structures of these crowns and their complexes. These predictions are consistent with the results obtained from ^1H NMR spectroscopy.

The structures of crystalline macrocyclic polyethers and their complexes have been widely studied by means of X-ray diffraction.[1] In the solid state, lattice forces, including the accommodation of the anion, may significantly influence the crown complex structure. On the other hand, in dilute solution, solvation of the anion and the crown complex, as well as ion pairing, is the important structural influence. Since the ionophoric properties of crown ethers in solution are of such significance, it is important to study their solution structures directly. However, only a limited number of studies have addressed the question of crown conformation and anion coordination in solution. These include the use of IR,[2] NMR,[3] and UV[4] spectroscopies to determine the conformations of free and complexed crowns[2,3] and to measure complex formation.[4] UV spectra have also been used to probe the structure of crown complexed fluorenyl ion pairs in solution.[5]

The introduction of a chiral center (or centers) into the crown macrocycle opens the possibility of using circular dichroism (CD) spectroscopy as an additional structural probe. The well-established sensitivity of CD to conformational changes can provide more information than simple absorption spectra. CD has been used, for example, to study the solution structures of chiral dimethyl substituted benzo-15-crown-5 ethers and their complexes[6] and of chiral methyl substituted 18-crown-6 ether complexes of alkali and alkaline earth nitrate ion pairs.[7] In the work reported

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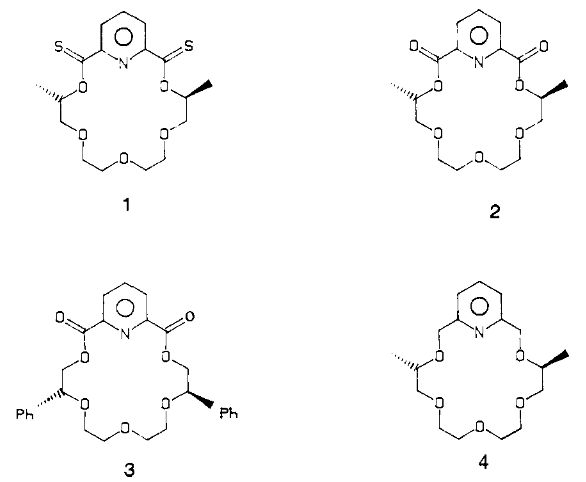

Figure 1. The four chiral pyridino substituted crowns used in this work.

here, the structures of the alkali and alkaline earth perchlorate complexes of a series of four chiral, pyridino-18-crown-6 ethers (Figure 1) have been studied in acetonitrile, using CD and ^{1}H NMR.[8]

The general phenomenon of induced CD in host-guest systems has been widely used in structural studies, particularly for the inclusion complexes of achiral aromatic chromophores with cyclodextrins.[9] Despite the utility of this technique and the increasing availability of chiral crown ethers,[10] few reports of the CD of these compounds and their complexes have been published. Since our original communications,[6a] three additional reports of crown ether CD have appeared. In two cases, the chiral centers were not part of the macroring,[11] but in the third Nakazaki and co-workers[12] investigated several isomeric crowns incorporating chiral tetrahydrofuran units in the crown ring itself. Significant changes in the CD spectra of these compounds were observed upon complexation, but little interpretation of these results was offered. In contrast, we have shown that the induced CD in chiral crown complexes can yield significant structural information.[6,7] In the present study, the one-electron mechanism of optical activity has been used to develop sector rules, which relate the structures and conformations of the pyridine substituted crowns and their complexes to the induced CD in the pyridine chromophores.

Experimental Section

Preparation of Complexes. The crowns used in this work were prepared as previously reported.[13] The perchlorate salts were completely dehydrated at 101 °C under high vacuum (0.05–0.001 Torr) in an Abderhalden drying tube (with $Mg(ClO_4)_2$ as desiccant) until the infrared spectrum indicated that the salts were anhydrous. All perchlorate salts and their complexes were handled with great caution. Anhydrous alkali and alkaline earth perchlorate salts themselves are not particularly shock- or heat-sensitive; nevertheless, perchlorate is a strong oxidant and it is well-documented that when perchlorate is in the presence of oxidizable species, the potential exists for violent explosive reaction.[14] Because of the hazardous nature of perchlorate salts, only small amounts (less than 0.1 g) were handled at one time. Acetonitrile (Fisher spectrograde) was purified by distillation from CaH_2 under dry N_2. The fraction having a UV cutoff of at least 210 nm was used to prepare the CD solutions. Solutions of metal perchlorate crown complexes were prepared in a glovebox under dry N_2 (exclusion of water is *essential*) by stirring a tenfold excess of the anhydrous metal salt with a solution of crown in acetonitrile until the salt was dissolved. Care was taken to avoid isolation of *any* solid complexes of the metal perchlorates.

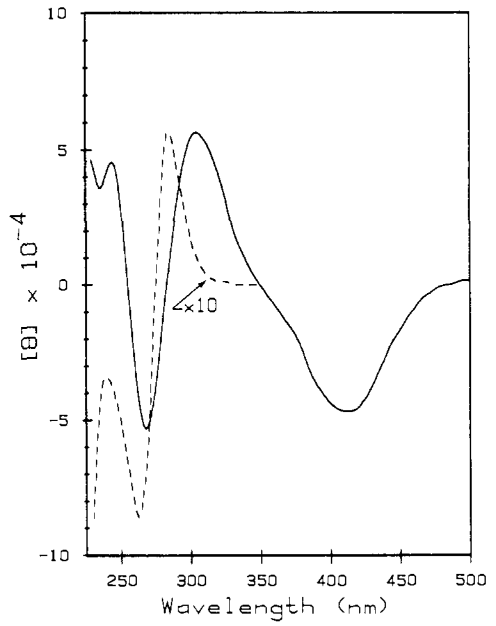

Figure 2. Circular dichroism spectra of the uncomplexed (4*S*,14*S*)-4,14-dimethyl-2,16-dithioxopyridino-18-crown-6 (**1**) (—) and (4*S*,14*S*)-4,14-dimethyl-2,16-dioxopyridino-18-crown-6 (**2**) (---) in MeCN. The spectra of the alkali cation complexes are indistinguishable from those of the complexed crowns.

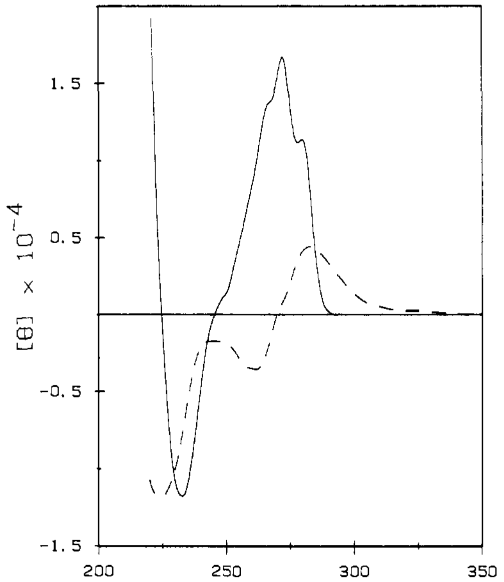

Figure 3. Circular dichroism spectrum of the uncomplexed 5,13-diphenyl-2,16-dioxopyridino-18-crown-6 (**3**) in MeCN (---) and the Na^+ complex in MeCN (—).

Circular Dichroism Measurements. CD spectra were recorded on either a JASCO Model ORD-CD-5 with SS-20 modification or a Jobin-Yvon Circular Dichrographe 111. The instruments were calibrated in the region of the pyridine absorptions with a solution of the tris(hy-

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(8) The common names for these crowns are more practical than the cumbersome formal nomenclature (for example, the complete IUPAC designation of **1** is (4*S*,14*S*)-4,14-dimethyl-13,6,9,12,15-pentaoxa-21-azabicyclo[15.3.1]heneicosa-1(21),17,19,triene-2,16-dithione). In the context of a discussion of crown ethers the following common names—(4*S*,14*S*)-4,14-dimethyl-2,16-dithioxopyridino-18-crown-6 (**1**), (4*S*,14*S*)-4,14-dimethyl-12,16-dioxopyridino-18-crown-6 (**2**), (5*S*,13*S*)-5,13-diphenyl-12,16-dioxopyridino-18-crown-6 (**3**), and (4*S*,14*S*)-4,14-dimethylpyridino-18-crown-6 (**4**)—may be used without confusion.

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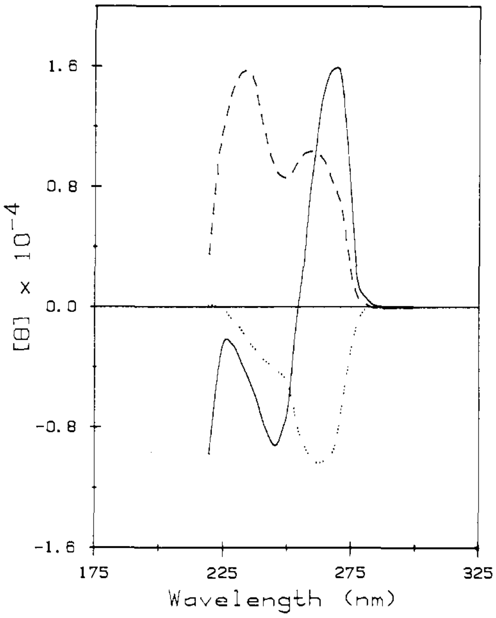

Figure 4. Circular dichroism spectra of the alkali perchlorate complexes of 4,14-dimethylpyridino-18-crown-6 (**4**) in MeCN (5 × 10^{-5}M): Li^+ (- - -), Na^+ (—) and K^+ (···).

droxymethyl)aminomethane salt of (+)-*d*-camphorsulfonic acid (TRIS-CSA) according to the method of Pearson et al.[15] The instrument sensitivity was typically adjusted on scale 20 (20 mdeg per cm) such that a 1.04 × 10^{-3} g/cm^3 aqueous solution of TRIS-CSA gave a pen deflection of 11.9 cm at 290 nm, corresponding to a molecular ellipticity of +7260 deg^2 $dmol^{-1}$. Cylindrical sample cells were used and were determined to be strain free by examination between crossed polarizers.

NMR Measurements. ^1H NMR spectra were obtained on a Bruker 250-MHz or Bruker 300-MHz instrument. Solutions of the crowns and their complexes were prepared in $CDCl_3$ as described above. Only a slight excess of the perchlorate salts was used, however, because of the low solubility of these salts in $CDCl_3$.

Results

CD of the Thioxo– and Oxo–Pyridine Substituted Crowns. The uncomplexed thioxo- (**1**) and oxo- (**2** and **3**) substituted pyridino-18-crown-6 macrocycles exhibit relatively intense CD bands in the near-UV in MeCN solution. The spectra of free crowns **1** and **2** are plotted in Figure 2 and the spectrum of free crown **3** in Figure 3 in units of the molecular ellipticity [θ]. The transitions associated with these Cotton effects are the lowest energy pyridine $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. With one exception (see below) the CD bands of these three crowns are not very sensitive to complexation. For example, addition of a tenfold excess of the perchlorate salt of Li^+, Na^+, or K^+ to MeCN solutions of **1** and **2** causes *no* detectable changes in the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ CD bands of these crowns. Among the complexes of **1**, **2**, and **3** only the Na^+ complex of the diphenyl substituted crown **3** has a significantly different CD spectrum from the uncomplexed crown. The addition of $NaClO_4$ to an MeCN solution of **3** causes the CD bands to shift in energy and increase in intensity (Figure 3).

CD of the Reduced Pyridine Substituted Crown. In marked contrast to the other crowns, the CD of crown **4** is extremely sensitive to complexation. In fact, *no CD is detectable for this crown in the absence of metal salts.* However, when an excess of the perchlorate salt of Li^+, Na^+, or K^+ is added, a relatively intense CD spectrum is observed (Figure 4). The absorption spectra corresponding to these CD spectra are shown in Figure 5. The absorption spectra show only subtle difference among the different alkali complexes and the free crown, compared to the dramatic changes observed in the CD spectra. The addition of the perchlorate salt of Mg^{2+}, Ca^{2+}, or Ba^{2+} results in the appearance of CD bands (Figure 6) which are similar in sign and intensity to the bands observed for the alkali complexes. The absorption spectra of these complexes are also very similar to those of the corresponding alkali complexes. This similarity of spectra of alkali and alkaline earth complexes is very different from the behavior of the chiral methyl substituted 18-crown-6 ethers studied previously.[7]

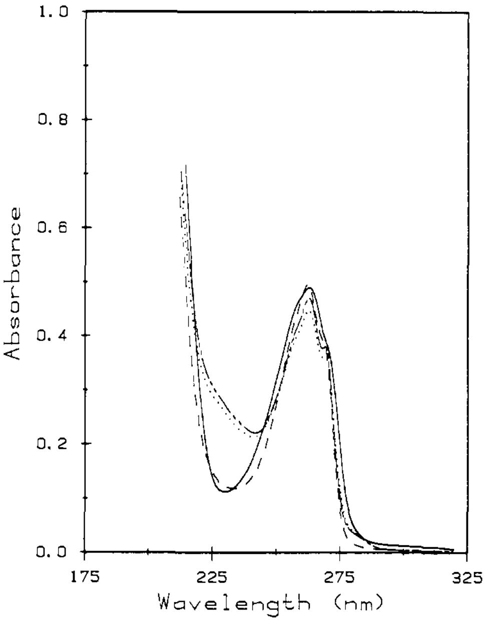

Figure 5. Absorption spectra of the alkali perchlorate complexes of 4,14-dimethylpyridino-18-crown-6 (**4**) in MeCN (5 × 10^{-5}M): free crown (—), K^+ (···), Na^+ (- - -), and Li^+ (- - -).

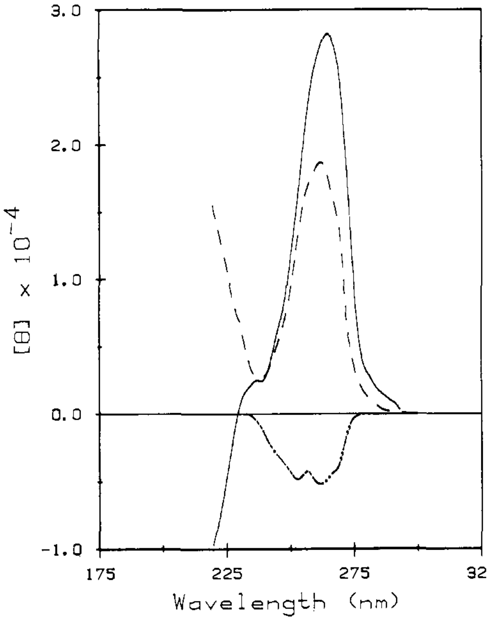

Figure 6. Circular dichroism spectra of the alkaline earth perchlorate complexes of 4,14-dimethylpyridino-18-crown-6 (**4**) in MeCN (5 × 10^{-5}M): Mg^{2+} (- - -), Ca^{2+} (—), and Ba^{2+}(- - -).

^1H NMR of Pyridine Substituted Crown Complexes. The 250-MHz ^1H NMR spectrum (expanded in the region between 3.40 and 4.20 ppm) of the uncomplexed oxo-substituted pyridino-18-crown-6 (**2**) and the spectra of the Li^+, Na^+, and K^+ complexes are shown in Figure 7. The assignments of the free crown peaks based on their coupling patterns and chemical shifts are as follows: methyl protons, d, 1.43 ppm; methylene protons, m, 3.45–4.15 ppm; methine protons, m, 5.30 ppm; meta pyridine protons, d, 8.25 ppm; and para pyridine proton, d of d, 7.94 ppm. The assignments for the complexed crown are the same, although the chemical shifts and appearance of the peaks are considerably different, particularly in the methylene region, which is expanded

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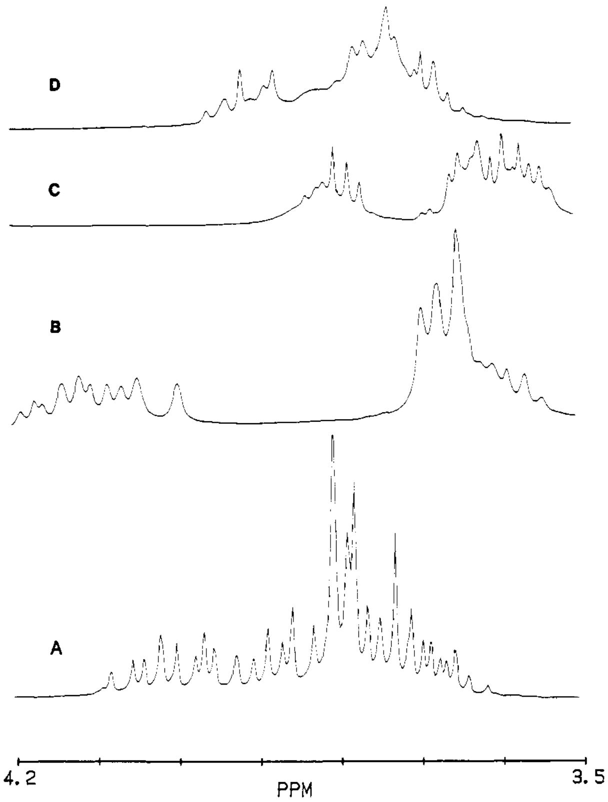

Figure 7. ^{1}H NMR spectra (250 MHz) for the alkali perchlorate complexes of 4,14-dimethyl-2,16-dioxopyridino-18-crown-6 (**2**) in $CDCl_3$ (expanded in the region between 3.50 and 4.20 ppm): free crown (A), Li^+ (B), Na^+ (C), and K^+ (D).

in Figure 7. The 300-MHz ^{1}H NMR spectrum of the uncomplexed, reduced crown **4** and the spectra of its Li^+ and Na^+ complexes are shown in Figure 8. The assignments based on the splitting and chemical shifts are as follows: methyl protons, d, 1.32 ppm; methylene protons (α to the pyridine ring), s, 4.86 ppm; other methylene protons, m, 3.47–3.81 ppm. Upon complexation, the most significant changes in this spectrum occur in the methylene resonances, particularly for the α protons. These are split into an AB doublet pattern in the alkali complexes.

Discussion

Complex Formation in MeCN. The alkali and alkaline earth complexes of **1–4** were formed by addition of a tenfold excess of the metal perchlorate to a solution of each crown in MeCN. Direct evidence of complex formation was obtained from the absorption, CD, and NMR spectra of these complexes (vide supra). Izatt and Christensen have also determined that the achiral parent compounds of **1–4** form stable complexes with alkali and alkaline earth cations in MeOH.[16] The formation constants of these complexes are only slightly lower than those of 18-crown-6 itself. For example, log K_f for both the K^+ and Na^+ complexes of 2,16-dioxopyridino-18-crown-6 is greater than 4.[16] The analogous complexes of **1–4** in the less polar, aprotic solvent MeCN should be even more stable. In any case, an excess of each cation was used to assure complete complexation.

Crown Host Chromophores. The structures of crowns **1–4** and their complexes can be probed directly by using circular dichroism because of the presence of the pyridine chromophore. The absorption spectrum of pyridine contains two prominent bands that are remarkably similar to the π-isoelectronic benzene chromophore. The lowest energy transition in benzene is a $\pi\rightarrow\pi^*$ transition ($^1A_{1g} \rightarrow {}^1B_{2u}$, or ^1L_b in Platt's notation), which is both electric- and magnetic-dipole forbidden. The weak absorption band corresponding to this transition is characterized by prominent vibronic structure, revealing the mechanism by which it gains intensity.

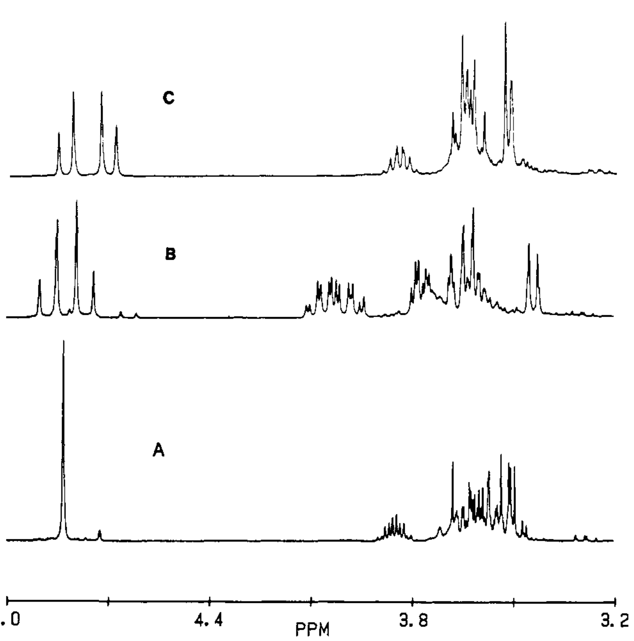

Figure 8. ^{1}H NMR Spectra (300 MHz) for the alkali perchlorate complexes of 4,14-dimethylpyridino-18-crown-6 (**4**) in $CDCl_3$: free crown (A), Li^+ (B), and Na^+ (C).

This transition becomes electric- and magnetic-dipole allowed in pyridine ($^1A_1 \rightarrow {}^1B_2$) as a result of the reduction in symmetry to C_{2v}.[17] However, the transition is still relatively weak ($\epsilon \simeq$ 2000), suggesting that the π electronic system is not significantly distorted from D_{6h} symmetry. The high-energy transition of pyridine (corresponding to the ^1L_a benzene transition) is not accessible in MeCN because it occurs at higher energy than the solvent cutoff.

Compared to benzene, the near-UV spectrum of pyridine contains a new feature, owing to the presence of the nitrogen lone pair. The excitation of one of the lone pair electrons to a π^* orbital is electric- and magnetic-dipole allowed in C_{2v} ($^1A_1 \rightarrow {}^1B_1$), and in nonpolar solvents such as hexane it is observed as a weak shoulder on the long-wavelength side of the π–π^* transition.[18] However, in protic solvents such as MeOH, this shoulder is shifted to higher energy, consistent with the assignment of this transition as $n\rightarrow\pi^*$.

The absorption spectra of crowns **1–4** closely resemble the spectrum of pyridine in protic solvents. The $n\rightarrow\pi^*$ shoulder is not visible in any of the spectra and must be buried under the more intense $\pi\rightarrow\pi^*$ transition at higher energy. The spectrum of the reduced crown **4** has a band maximum at 262 nm, which matches the band maximum of 2-methylpyridine in water.[19] The energy of the $\pi\rightarrow\pi^*$ transition is relatively insensitive to solvent effects; thus it is not surprising that little change is observed for this band upon complexation of the crowns by alkali metals (Figure 5). The interaction of the nitrogen lone pair with a metal cation should have little effect on the energy of the $\pi\rightarrow\pi^*$ transition. A bathochromic shift of the band maximum is observed for the oxo- (λ_m = 278 nm) and the thioxo- (λ_m = 285 nm) substituted crowns due to hyperconjugation effects.

Although the $n\rightarrow\pi^*$ transition is buried under the more intense $\pi\rightarrow\pi^*$ transition in the absorption spectra of **1–4**, both transitions are visible in the CD spectra. The $n\rightarrow\pi^*$ transition is resolved in the CD spectra because it has the opposite sign to that of the $\pi\rightarrow\pi^*$ transition. In addition, since it is magnetic-dipole allowed, its CD intensity is enhanced relative to that of the $\pi\rightarrow\pi^*$ tran-

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sition. Resolution of the n→π* transition has been previously observed in the dispersion induced circular dichroism spectrum of pyridine in (+)-diethyl tartrate solution.[20] In the dispersion-induced CD spectrum, only the n→π* transition is detected. As expected, it occurs on the low-energy side of the unresolved absorption band, between 260 and 270 nm. The low-energy CD band in the spectra of **1**–**4** is therefore assigned to the n→π* transition.

Proposed Model for Induced CD in Pyridine Transitions. The One-Electron Model. The planar pyridine molecule is, of course, inherently achiral. The mechanisms by which a planar chromophore in an asymmetric environment can gain rotational strength have been described by using first-order perturbation theory.[21] Because the pyridine transitions under consideration are relatively weak and magnetic dipole allowed, the μ–μ (coupled oscillator) mechanism should contribute little to the rotational strength. Instead, transitions of this type are usually treated with use of the one-electron model of Condon, Altar, and Eyring.[22] In this model, the rotational strength induced in a transition α, through mixing with a transition β on the *same* chromophore, is given by

$$R_\alpha = \frac{-V_{\alpha\beta}}{\epsilon_\beta - \epsilon_\alpha}[\mu_\beta m_\alpha]$$

where μ_β and m_α are the electric- and magnetic-dipole moments of the respective transitions and $v_{\alpha\beta}$ is the interaction potential that produces mixing between the transitions.[23] According to this model, the pyridine n→π* and π→π* transitions gain rotational strength through mixing with other transitions at higher energy. The asymmetric environment of the rest of the crown acts as a perturbing field which mixes the transitions.

Sign Correlations. The sign of the induced CD in the pyridine transitions can be correlated to the geometric arrangement of the chiral portion of the crown ring with respect to the pyridine chromophore. Since the relative orientation of the transitions being mixed is determined only by the electronic structure of pyridine, the sign of the optical factor $[\mu_\beta m_\alpha]$ has no geometric dependence. Instead, the basis of sign correlations is the geometric dependence of the interaction potential, $v_{\alpha\beta}$. It has been demonstrated that $v_{\alpha\beta}$ depends on the symmetry of the chromophore itself.[23] The symmetry dependence of $v_{\alpha\beta}$ results in the following simple rule: if the natural planes of symmetry of the chromophore are used to divide the surrounding space into regions, or sectors, the contribution of a perturbing group to the rotational strength of a particular transition ("third sphere" contributions[24]) changes sign at each region boundary.[23] Furthermore, when the symmetries of the orbitals involved in the transition have a higher effective symmetry than the group, it is generally assumed that the third sphere contributions mirror the symmetry of the transition moment. The pyridine n→π* transition moment, for example, has three nodal planes perpendicular to the plane of the pyridine molecule, which pass between the ring atoms. These nodal planes must also be considered to divide the surrounding space into sectors. The sign of the contribution to the rotational strength of a perturbing group which lies in a particular sector can be established empirically or by explicit calculation. Once the sign of a particular sector is established, the others follow, since the sign must always change on passing through a nodal plane.

The Sector Rules for Pyridine Substituted Crowns. The sector rules proposed for the n→π* and π→π* transitions of pyridine are illustrated in Figure 9 for **4**. The same sector rules apply to any pyridine derivative. The pyridine chromophores each have two planes of symmetry, one that contains the pyridine ring and the other perpendicular to it, along the C_2 axis. The additional nodal planes due to the state symmetry of the n→π* ($^1A_1 \rightarrow {}^1B_1$) and the π→π* ($^1A_1 \rightarrow {}^1B_2$) transitions are shown in Figure 9. The signs of the contributions to R are shown for the sectors above the plane of the crown (the sectors below have the opposite signs). The assignment of the sector signs for the π→π* transition is based on the convention used by Snatzke for the analogous π→π* transition of benzene in derivatives having C_2 symmetry. Snatzke's treatment has been successfully applied to a variety of such compounds.[25]

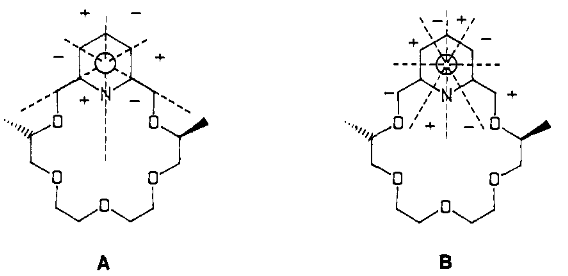

Figure 9. Proposed sector rules for the pyridine π→π* (A) and n→π* (B) transitions. The sector signs correspond to the sectors above the plane of the ring.

The assignment of the sector signs for the n→π* transition is not as straightforward since there is no analogous transition in benzene. Nevertheless, the ^1L_a transition of benzene has the same symmetry as the pyridine n→π* transition and is polarized in the same direction (out of plane). A tentative assignment is therefore made by analogy to Snatzke's assignment for the benzene ^1L_a transition. The predictive power of these sector rules can be tested by using CD data for chiral pyridine compounds of known structure. The CD spectra of a variety of optically active pyridine derivatives have been reported.[26–30] However, nearly all of these derivatives are conformationally labile, which causes ambiguity in relating the observed CD data to the molecular structure in solution. Many of these pyridine derivatives also have OH or NH_2 functional groups which can influence the energy, intensity, and even the sign of the CD bands through interaction with the pyridine nitrogen or with the solvent.[26] The only report of the CD of a rigid molecule containing pyridine and no labile protons of which we are aware is that of 5α-cholest-2-eno[3,2-*b*]pyridine.[27] Ring A (adjacent to pyridine) of the cholestane moiety adopts a tetralin-like half-chair conformation and the molecule is sufficiently rigid that no chair inversion of ring A occurs. In this conformation, the sector rules predict a negative n→π* and a positive π→π* transition, which is exactly what is observed.

Proposed Structures of the Pyridino Crowns and Their Complexes. Oxo and Thioxo Substituted Crowns. If we assume for crowns **1**–**3** that the macrocycle is approximately flat and that its mean plane is coincident with the plane of the pyridine ring, then the sector rule for the CD of the π→π* transition (the higher energy transition) predicts that its sign should be negative. In such a coplanar conformation most of the crown would lie close to the nodal plane of the pyridine ring and the net contribution to the rotational strength (R) would be minimal. However, the methyl substituents (or phenyl substituents in the case of **3**) would protrude well into negative sectors (one above and one below the plane of the ring) and, to the extent that rotomer interconversion was suppressed, would have a dominant influence on R. This sign prediction is consistent with the negative π→π* transitions observed for all three crowns (Figures 2 and 3). Furthermore, according to the sector rule for the n→π* transition, the planar conformation for these crowns would give rise to a *positive* n→π*

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CD band since the sectors containing the methyl (or phenyl) substituents would be positive in this case. A positive CD band is actually observed for the $n\rightarrow\pi^*$ transition for each of these crowns. (Figures 2 and 3).

Support for the assumption of the "coplanar" conformation of crowns **1**–**3** and their complexes is found in several crystal structures. The most pertinent of these is that of the (*S*)-α-(1-naphthyl)ethylammonium complex of **2**, which does, in fact, show virtual coincidence of the pyridine and mean macrocycle planes, with the macrocycle in a pseudo-D_{3d} conformation and the methyl groups axial, as predicted.[31] Although the coplanarity of the macrocycle and pyridine rings in this structure may also be influenced to some extent by interaction between the pyridine and naphthyl rings, a similar coplanarity is also observed in the H_2O complex of the parent compound of **2** (without methyl substituents),[32] suggesting that the presence of the oxo and thioxo groups is in fact the dominant factor in maintaining the approximately coplanar conformation. The fact that the CD of these crowns shows no change on formation of complexes with alkali cations (or in the case of **3**, at least no change in sign) for the $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions (Figures 2 and 3) is consistent with the prediction that the steric constraints imposed by the oxo or thioxo groups should maintain the open "planar" macrocycle conformation even in the absence of a guest. Thus the positive $n\rightarrow\pi^*$ and negative $\pi\rightarrow\pi^*$ CD pattern can be reasonably proposed as characteristics of this (coplanar) conformation.

According to this model the greater sensitivity of the CD of **3** to complexation (relative to **1** and **2**) is due to the difference between 5,13 and 4,14 substitution. In the free crown the 5,13 phenyl substituents of **3** have more conformational freedom than the 4,14 methyls of **1** and **2**. The axiality of the methyl groups would be little affected by complexation. However, the added rigidity imposed by complexation to a central cation would tend to lock the phenyls in place and furthermore to enhance their axiality. This would explain the increase in CD intensity with retention of sign for the complexes of **3** relative to the free crown (Figure 3).

The intensity of the CD for the $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions of **1** is an order of magnitude greater than for those of **2**. The most likely cause of this difference is the greater steric bulk of the sulfur. Since the van der Waals radius of S (1.85 Å) is much larger than that of O (1.40 Å), the methyl groups of **1** should be displaced farther from the ring plane (i.e., farther from the S), deeper into their respective sectors than those of **2**. Consequently, their contributions to the rotational strength of the transitions of **1** should be greater. The intensity of the CD observed for **3** and its complexes (Figure 3) is of the same order of magnitude as that observed for **2**. This seems surprising at first glance since the phenyl substituents might be expected to contribute to the CD to a greater extent than the smaller methyl substituents. However, the influence of each perturbing group should show an r^{-3} dependence on its distance from the chromophore. The data are qualitatively consistent with this prediction.

Reduced Crown **4**. In this group of four pyridino crowns, the reduced crown **4** is unique in that no CD is observed for the pyridine transitions of the uncomplexed molecule. The lack of the CD bands in this case must be related to the increased flexibility of crown **4** compared to **1**–**3**. Apparently the flexibility of **4** in the uncomplexed form allows it to adopt an average conformation, which induces undetectably small rotational strength in the pyridine transitions. This flexibility is likely to be similar to that observed for uncomplexed dibenzo-18-crown-6 and dibenzo-30-crown-10, in which the ether fragments are observed to undergo rapid interconversion between the syn- and anti-gauche rotamers.[34] Since the sector rules for **4** have a nodal plane that contains the pyridine ring, rotamer interconversion in the macrocycle ring would tend to move substituents from positive to negative sectors, or vice versa, effectively nullifying the net rotational strength in the pyridine transitions. Furthermore, as observed in the crystal structure of the non-methyl-substituted analogue of **4**,[33] in the absence of a guest, conformations involving at least partial collapse of the macrocycle ring are likely.

In the presence of an alkali or alkaline earth cation, CD bands are observed for both the $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions of the reduced crown **4** (Figures 4 and 6). The appearance of CD bands for the complexed crown suggests that it is more rigid in this form and, in fact, the presence of a metal cation in the crown cavity is known to strongly inhibit rotamer interconversion (see below).[34] The interaction of the cation with the crown oxygens must be sufficiently strong to lock the crown into one conformation (or at least a limited number of conformations), which induces a net optical activity in the pyridine transitions.

In contrast to the CD observed for the complexes of **1**–**3**, both signs and intensities of the $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ bands of **4** depend on which alkali cation is complexed. The positive $n\rightarrow\pi^*$, negative $\pi\rightarrow\pi^*$ pattern found for all the complexes of **1**–**3** (as well as for the free crowns) is observed only for the Na^+ complex of **4**. This, coupled with the prediction that the effective cavity size of **4** will be slightly smaller than that of 18-crown-6 owing to the presence of the pyridine subunit and the methyl substituents, suggests that the best fit cation is Na^+ and that its complex with **4** has a "coplanar" conformation similar to the complexes of **1**–**3**.[35]

In contrast, for both the Li^+ and K^+ complexes, the signs of the $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions are the same. The sector rules indicate that this must be due to a significant distortion from a coplanar conformation. We propose that Li^+ and K^+ cause a buckling of the bicyclic host in the absence of the rigidity imposed by the oxo and thioxo groups. For Li^+ this buckling is most likely the result of a "wrapping around" that enables the ether oxygens to coordinate the smaller cation more effectively, such that the cation is held on the *concave* side of the buckled host. Similar "wrap around" effects have been observed for other crown complexes of cations smaller than the optimum crown cavity. Conversely, K^+, being somewhat too large for the cavity of **4**, can be predicted to buckle the crown in the opposite sense, such that the ether dipoles are directed out of the mean plane toward the cation on the *convex* side of the buckled bicycle. In either case, the buckling thrusts a major portion of the macrocyclic ring out of the extended plane of the pyridine ring. The CD sign would therefore be dominated by the position of the methylene portion of the ring relative to the chromophore. This portion of the crown lies in sectors that have the same signs for both the $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions and thus they should have the same sign for a buckled conformation. Although these observations do not lead to a priori prediction of the absolute signs of the CD bands for the Li^+ and K^+ complexes, the fact that both bands are positive for Li^+ and both are negative for K^+ suggests that the proposed buckled conformations are reasonable ones.

The alkaline earth complexes of **4** also display a dependence of the sign and intensity of the CD on the cation. The Mg^{2+} bands are positive, the Ba^{2+} bands are negative, and the intermediately sized Ca^{2+} bands are positive and negative. This is the same pattern observed for the alkali cations of similar size. The close correspondence of the signs and intensities of these bands is in contrast to the differences observed between the alkali and alkaline earth complexes of chiral, methyl substituted 18-crown-6 macrocycles.[7] For those compounds, ion pairing was found to cause significant differences in the structures of the alkali and alkaline earth nitrate complexes.[7] In the current study the very weakly coordinating perchlorate anion has been used, and in addition, conditions for which ion pairing is negligible have been maintained. In the absence of ion pairing, the structure of the complex must

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primarily depend on the cation size. For example, the reduced crown **4** is free to wrap around the small Mg^{2+} cation (r = 0.66 Å) in the same manner as for the Li^+ (r = 0.68 Å) complex. The two coordinated (ion-paired) nitrate anions prevent such a conformational change in the $Mg(NO_3)_2$ complexes of the aliphatic crowns,[7] which illustrates the significant influence ion pairing can have on the structure of the macrocycle–cation complex.

NMR Spectra of Complexes of 2 and 4. Although the CD spectrum of **2** is unaffected by addition of metal cations, the ^1H NMR spectrum of this crown indicates that the methylene portion of the ring undergoes conformational changes upon complexation. There are two distinct groups of methylene protons which exhibit overlapping resonances in the spectra of both free and complexed **2**. The methylene protons α to the methyl substituents constitute one group and form an ABX spin system with the chiral proton H_x. The ether units (OCH_2CH_2O) comprise the second group and form a four-spin AA′BB′ coupled system. Because of extreme overlap between the AA′BB′ and ABX methylene resonances even at 300 MHz, these spectra could not be analyzed by using the pertinent relationships[36] nor could they be fit in a unique manner by using the iterative program PANIC.[37] Nevertheless, although a complete analysis of the methylene resonances is not possible with use of these spectra alone, the following qualitative observations can be made. The AA′ portion of the spectrum is partially resolved in the spectrum of uncomplexed **2** and appears to be the typical pattern observed when the methylene units are undergoing rapid interconversion between the syn- and anti-gauche rotamers.[34] In the presence of a cation this pattern collapses and broadens, suggesting that rotamer interconversion is slower.

The overlap of the AA′BB′ and ABX patterns is even more severe in the case of **4** (Figure 8). However, the peak(s) due to the methylene protons α to the pyridine ring are clearly resolved. These protons form an AB spin system since they are magnetically inequivalent. Despite being inequivalent, they appear as a singlet in uncomplexed **4**, meaning that the chemical shifts of H_a and H_b are nearly equal. This observation is consistent with rapid rotamer interconversion, which would average the chemical shifts. Complexed **4** exhibits an AB doublet pattern (Li^+, J = 15.3 Hz, $\delta\nu$ = 29.1 Hz; Na^+, J = 13.0 Hz, $\delta\nu$ = 35.6 Hz). As noted previously, complexation is known to slow rotamer interconversion, due to the cation–oxygen interaction. These results are also consistent with the observation of CD only for the *complexes* of **4**, particularly since the CD is most sensitive to the conformation of this portion of the crown.

Conclusion

It is clear that the sector rules provide a simple yet adequate framework for the interpretation of induced CD in the near-UV pyridine transitions. The structures these rules predict are reasonable and in accord with the NMR data. This last conclusion may seem unwarranted at first since the NMR spectra of complexes of **2** indicate that the methylene portion of the ring changes with complexation, while the CD of **2** is unaffected by the presence of cations. However, the sector rules predict that the sign and intensity of the CD for **2** in the coplanar conformation are determined by the positions of the methyl groups. Since these are located on the rigid portion of the macrocyclic ring, their positions, and thus the CD, are insensitive to complexation. In contrast, the chiral centers of both **3** and **4** are located on the more flexible methylene portion of the ring and consequently the CD is much more sensitive to conformational changes due to complexation than for **1** and **2**. Thus, both the CD and NMR data are consistent with the increased rigidity of these crowns in the presence of a central cation.

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NMR Spectra of Porphyrins. 31.[1] Ring Currents in Hydroporphyrins

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Abstract: The dipole–dipole network model of the porphyrin macrocyclic ring current is used to investigate the ring currents in reduced (hydro)porphyrins derived from phylloerythrin methyl ester. Reduction of ring D to afford the corresponding chlorin results in a decrease of the inner loop and pyrrole subunit ring currents by about 10%. Further reduction of another pyrrole ring gives very different results depending upon the pyrrole ring reduced. In bacteriochlorophyll *a*, in which the opposite pyrrole subunits (B and D) are reduced, there is a further 10% reduction in the pyrrole ring current and a 20% reduction of the inner loop ring current. In the isobacteriochlorin system (rings A and D reduced) there is a much larger decrease in the inner loop ring current, to about 45% of the chlorin value. In the pyrrocorphin (hexahydroporphyrin) system (rings A, B, and D reduced) there is a further 10% decrease in the pyrrole ring current and the inner loop ring current is only 25% of the chlorin value. These results are discussed in terms of steric effects in the macrocycle. The ring current models thus obtained are used to investigate structural and conformational differences in the various isobacteriochlorin isomers.

Recently, there has been an upsurge of interest in the highly reduced porphyrin systems,[4a] catalyzed by the discovery of the isobacteriochlorin prosthetic group in the nitrite and sulfite reductases[4b] and heme d_1[4c] and the structure of the nickel containing

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