Os^{2+} complexes, are available, it should be possible to estimate the role of delocalization of excitation energy in determining the level structure of the charge-transfer states.

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The Electronic Spectrum of $Fe(bpy)_3{}^{2+}$ and $Os(bpy)_3{}^{2+}$

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Abstract: The electronic absorption spectra of $Fe(bpy)_3{}^{2+}$ and $Os(bpy)_3{}^{2+}$ have been determined in single crystals of $Zn(bpy)_3SO_4{\cdot}7H_2O$ and $Zn(bpy)_3Br_2{\cdot}6H_2O$ at various temperatures down to 8 K. The main absorption intensity in the visible is assigned to two different charge-transfer transitions polarized perpendicular to the C_3 axis of the complex, consistent with the direction of charge transfer from metal to ligand. The lowest energy spin-forbidden charge-transfer bands of $Fe(bpy)_3{}^{2+}$ appear in σ and π polarization. Other π-polarized absorption, near 23 000 cm^{-1}, is assigned to perturbed singlet to triplet transitions of the bpy ligand. Owing to the much greater influence of spin-orbit coupling, the spin-forbidden transitions of $Os(bpy)_3{}^{2+}$ show significantly higher intensities and predominant σ polarization. A spin-forbidden transition to another triplet state appears in π polarization, its origin lying 75 cm^{-1} higher than the lowest σ-polarized triplet state. The mechanism for the π-polarized intensity is assumed to involve electron exchange between metal ion and ligands.

Introduction

The visible absorption spectrum of $Fe(bpy)_3{}^{2+}$ (bpy is 2,2′-bipyridine) was assigned by Williams[2] to a charge-transfer (t_2-π^*) electronic transition. The assignment was based on the interpretation of spectral band shifts observed with a number of π-bonding ligands. The majority of the absorption intensity associated with this type of transition should be polarized along the direction of metal to ligand, as shown by Day and Sanders.[3] The early work of Palmer and Piper,[4] using polarized single crystal spectra, was consistent with this expectation. The overall assignment to charge transfer is therefore firmly established. However, there are questions of detail which remain unanswered. Important among these are the number of spin-allowed transitions, the assignment of spin-forbidden transitions, and the contributions from different mechanisms to the overall absorption intensity.

The electronic spectrum of $Os(bpy)_3{}^{2+}$ appears to have been studied first by Crosby et al.,[5] at least so far as spectral assignments of both absorption and fluorescence properties are concerned. The strong absorption band system in the visible was attributed to charge transfer while the luminescence and its associated weak absorption were assigned to d-d transitions. Zuloaga and Kasha[6] argued in favor of spin-allowed charge transfer fluorescence. Demas and Crosby[7] then reached the conclusion that the luminescence bands were best ascribed to spin-forbidden charge-transfer transitions. This assignment was also made by Fujita and Kobayashi.[8]

Recently we gave a preliminary account of the polarized crystal spectra of $M(bpy)_3{}^{2+}$ (M = Fe, Ru, Os) in single crystals of $Zn(bpy)_3Br_2{\cdot}6H_2O$.[9] It was shown that answers to the questions raised above can be reached through the measurement of linearly and circularly polarized spectra of these complex ions. A previous paper dealt specifically and in detail with $Ru(bpy)_3{}^{2+}$.[10]

Experimental Section

Experimental details of sample preparation and the measurement of polarized single crystal spectra have been given previously.[4,9,10] We note again that considerable care has to be taken with the orientation of the M^{2+} doped $Zn(bpy)_3SO_4{\cdot}7H_2O$ crystal to obtain pure σ and π spectra.

CD Spectra. Poly(vinyl alcohol) (PVA) foils containing (+)-$Fe(bpy)_3{}^{2+}$ were used for the CD measurements. Since complete racemization was observed during the evaporation of a PVA solution of the resolved complex, a blanc foil was sprayed with a methanol

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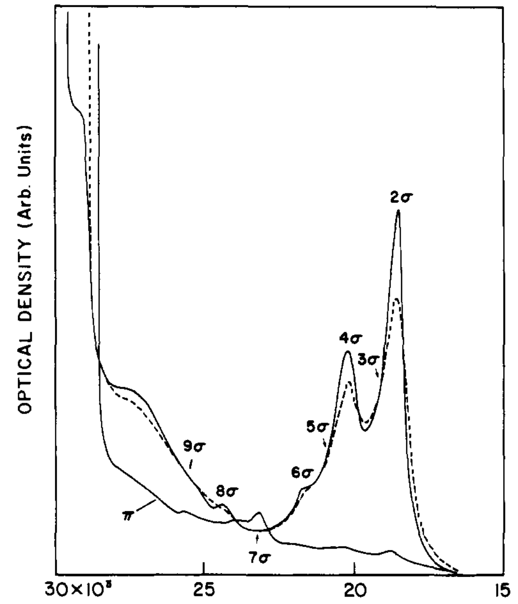

Figure 1. Absorption spectrum of $Fe(bpy)_3^{2+}$ at 8 (full curves) and 300 K (broken curve) in $Zn(bpy)_3SO_4{\cdot}7H_2O$. For σ and π see text.

Table I. Band Maxima in the Absorption Spectrum of $Fe(bpy)_3^{2+}$ in $Zn(bpy)_3SO_4{\cdot}7H_2O$ at 8 K

band	position, cm⁻¹	band	position, cm⁻¹
1π	17 120 ± 30	1σ	16 700 ± 100
2π	17 950 ± 50	2σ	18 620 ± 20
3π	18 860 ± 50	3σ (sh)	19 300 ± 100
4π	19 750 ± 100	4σ	20 280 ± 40
5π	20 250 ± 100	5σ (sh)	21 000 ± 100
6π	21 800 ± 100	6σ	21 740 ± 50
7π	23 220 ± 30	7σ	23 200 ± 50
8π	23 960 ± 40	8σ	24 400 ± 50
9π	25 700 ± 100	9σ	25 500 ± 100

solution of the antimonyl tartrate salt of (+)-$Fe(bpy)_3^{2+}$. CD spectra of these foils did not change significantly during a few weeks.

Room temperature CD spectra were recorded on a Roussel-Jouan dichrograph II. An instrument for measuring low-temperature CD spectra using a modulation technique was built in this laboratory.[1a] The light source was a high-pressure Xe arc lamp. A ¾-m Spex monochromator was used for the dispersion of the light. A photoelastic modulator, constructed according to literature procedures,[11] was used in conjunction with a Rochon prism to produce a modulated light beam with alternatively left and right circularly polarized components. An end window photomultiplier tube with an extended S20 response was used for detection. Phase-sensitive detection was achieved by means of a PAR Model 128A lock-in amplifier. The high voltage of the PM tube was regulated by a feedback system so as to keep a constant photocurrent.[12] The sample was placed in a liquid-nitrogen or liquid-helium Dewar. An aqueous solution of (+)-$Co(en)_3I_3{\cdot}H_2O$ was used to calibrate the signals.

Results

Figure 1 shows the 8 K absorption spectrum of Fe^{2+} in $Zn(bpy)_3SO_4{\cdot}7H_2O$ (σ and π) as well as the room-temperature spectrum (σ). The temperature behavior of the π spectrum is displayed separately in Figure 2, which also shows the 8 K absorption edge of the σ spectrum. The band positions are given in Table I. Figure 3 shows the visible region of the 77 K absorption and CD spectra of (+)-$Fe(bpy)_3^{2+}$ in a PVA foil.

$Zn(bpy)_3Br_2{\cdot}6H_2O$ was also used as a host crystal, but, as noted previously,[9,10] the Fe^{2+}, Ru^{2+}, and Os^{2+} complexes are distorted as shown by an anisotropy for light propagating along the c axis of the crystal. Linearly polarized light was therefore used to determine the axial spectrum. Absorption spectra (8 and 300 K) of Os^{2+} in $Zn(bpy)_3Br_2{\cdot}6H_2O$ are given in Figures 4 and 5. The spectra labeled σ^x and σ^y refer to polarization directions defined earlier.[9,10] The corresponding band positions are listed in Table II. Crystal spectra of Fe^{2+} in this host material have been given earlier.[9]

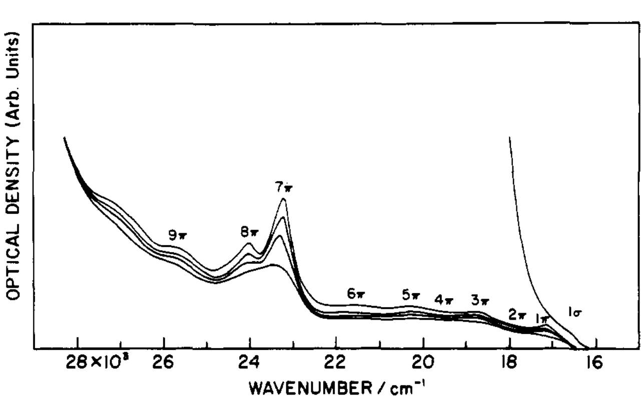

Figure 2. Temperature dependence of the π spectrum (see text) of $Fe(bpy)_3^{2+}$ in $Zn(bpy)_3SO_4{\cdot}7H_2O$.

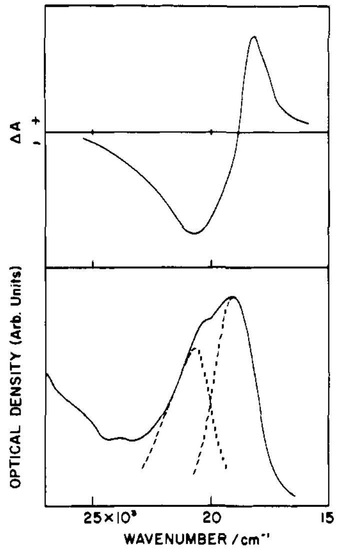

Figure 3. Lower: absorption spectrum of $Fe(bpy)_3^{2+}$ at 77 K in a PVA foil. Upper: CD of (+)-$Fe(bpy)_3^{2+}$ in PVA foil at 77 K.

Table II. Band Maxima in the Absorption Spectrum of $Os(bpy)_3^{2+}$ in $Zn(bpy)_3Br_2{\cdot}6H_2O$ at 8 K

band[a]	position, cm⁻¹	band[a]	position, cm⁻¹
1π	14 890 ± 5	$1\sigma^x$, $1\sigma^y$	14 815 ± 5
2π	15 106 ± 20	$2\sigma^x$,$2\sigma^y$	15 385 ± 10
3π	15 284 ± 10	$3\sigma^x$,$3\sigma^y$	15 924 ± 20
4π	15 535 ± 10	$4\sigma^x$,$4\sigma^y$	16 340 ± 20
5π	16 064 ± 30	$5\sigma^y$	17 018 ± 20
		$5\sigma^x$	17 100 ± 20
6π	16 435 ± 5	$6\sigma^{x,y}$ (sh)	19 400 ± 100
7π	16 980 ± 20	$7\sigma^x$,$7\sigma^y$	19 910 ± 20
8π	17 960 ± 20	$8\sigma^{x,y}$	20 600 ± 50
9π	18 500 ± 50	$9\sigma^{x,y}$	21 420 ± 50
10π	19 160 ± 30	$10\sigma^y$	22 570 ± 20
11π	20 700 ± 50	$10\sigma^x$	22 650 ± 20
12π	21 330 ± 30		
13π	22 100 ± 50		
14π	22 480 ± 50		

[a] See Figures 1 and 2.

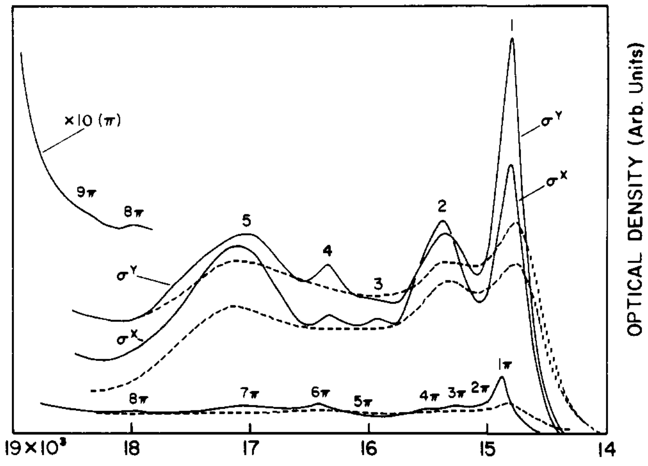

Figure 4. Absorption spectrum of $Os(bpy)_3{}^{2+}$ at 8 (full curves) and 300 K (broken curves) in $Zn(bpy)_3Br_2{\cdot}6H_2O$. σ^x and σ^y refer to the (axial) polarization directions defined in ref 9 and 10. The π spectrum is for light propagating perpendicular to the *c* axis, polarized parallel to this axis.

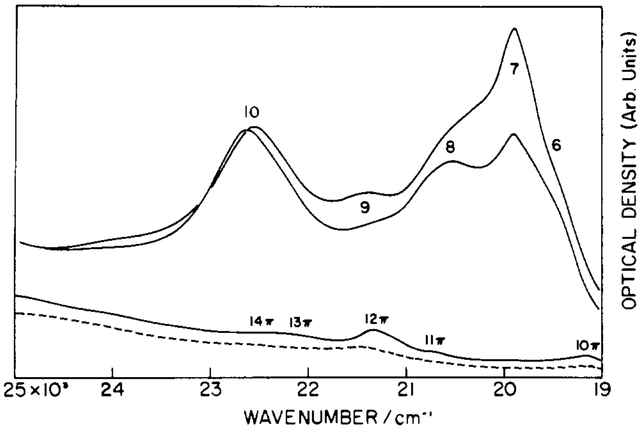

Figure 5. Same as for Figure 4 except that the ordinate scale is twice that in Figure 4.

Discussion

$Fe(bpy)_3{}^{2+}$. We deal with the σ-polarized spectrum first (Figure 1), recalling that it is in this polarization that we find the predominant part of the intensity associated with the charge-transfer terms.[3,9,10] The most intense band (2σ) is asymmetric and has a shoulder about 700 cm^{-1} to the higher energy side (3σ). Band 4σ carries the second highest intensity and it is separated by 1660 cm^{-1} from 2σ. It has been assumed by others[13] that 4σ is a vibrational satellite of 2σ. However, we have shown recently[9] that this cannot be the correct interpretation. The interval is probably too large to be a vibrational frequency of the ligand, judged from the absorption and fluorescence spectra of $Zn(bpy)_3{}^{2+}$,[14] and the separations between the analogous bands in the corresponding Ru^{2+} and Os^{2+} spectra are even larger.[9,10]

There is an interval of 1460 cm^{-1} between bands 4σ and 6σ which is probably a vibrational frequency. Here, the major fraction of the intensity lies in the (pure electronic) band 4σ, which is more reasonable than for the assignment of band 4σ to a satellite of 2σ. This is because the transferred electron is spread over three ligands so that the net increase of the bpy molecular framework is relatively small and only minor nuclear adjustments accompany the transferred electron. The majority of the absorption intensity will therefore appear in the pure electronic transition.

Additionally, the evidence from the CD favors the assignment of bands 2σ and 4σ to two different electronic transitions (Figure 3). The absorption band is not resolved into its two main components, but they are indicated by the broken curves. Comparison between the CD and the absorption spectrum shows that the negative CD at 20 600 cm^{-1} coincides with the higher energy absorption band. The lower energy absorption band, on the other hand, does not coincide with a maximum in the CD spectrum, similar to the case with $Ru(bpy)_3{}^{2+}$ considered earlier.[9]

The separation between the negative CD at 20 600 cm^{-1} and the positive CD at 18 100 cm^{-1} is 2500 cm^{-1}. As for the corresponding Ru^{2+} case[9] we look for a π-polarized band separated by about 2500 cm^{-1} from the σ-polarized band 4σ. There is a weak band 2π at 17 950 cm^{-1}, which is then assigned to the forbidden transition to the $^1A_2$ partner of ^1E (ψ^*). This assignment, standing alone, is not clear-cut. However, it is strongly supported from comparisons between the corresponding CD and polarized absorption spectra of the Fe^{2+}, Ru^{2+}, and Os^{2+} (cf. next section) complex ions.[9,10]

Next we consider the location of the triplet (spin-forbidden) transitions. Examination of the low-temperature crystal absorption spectra reveals a very weak σ-polarized band (1σ) at 16 700 cm^{-1} (Figure 2) and a π-polarized band (1π) of similar intensity at 17 120 cm^{-1}. We assign these bands to transitions to the lowest energy triplet charge transfer states. There are corresponding bands present in the spectra of the Ru^{2+} and Os^{2+} complex ions[9] which show regularities of intensity[10] which are consistent with spin-forbidden transitions, in support of this assignment.

The remaining π-polarized absorption bands include 3π, . . . , 6π in one group and 7π, 8π, 9π in another group. The first group most probably represents σ-polarized intensity which has "leaked" into the π-polarized absorption spectrum because of internal reflections in the crystal and other depolarizing factors. The second group has a different origin. As well as showing an increase of intensity on cooling the crsytal, there is a shift of the bands to lower wavenumber (see Figure 2). Again, there are analogous π-polarized bands in the spectra of the corresponding Ru^{2+} and Os^{2+} complex ions[9,10] and we assign them to singlet–triplet transitions localized in the bpy. The intensity of these bands very likely arises through an exchange mechanism involving the overlap of the electron orbitals of the metal ion and the ligands. The intensity can be stolen either from the ligand internal transitions or from transitions centered at the Fe^{2+}.

The effect of heavy atoms on the intensity of singlet–triplet transitions of N-heterocycles has been discussed by McGlynn et al.[15] A quantitative evaluation of the important exchange integrals involved is very difficult, but the involvement of overlap-dependent terms is demanded by the increase of absorption intensity on cooling of the crystal. From the absence of CD near 24 000 cm^{-1} (see Figure 3) it appears likely that the majority of the intensity of 7π, 8π, 9π is stolen from internal transitions of the Fe^{2+}

Two sets of semiempirical MO calculations exist in the literature. Hanazaki and Nagakura[16,17] used a "molecules-in-molecule" approach, treating the ligands by the Pariser-Parr-Pople method and then coupling the ligand systems to the low-spin Fe^{2+}. Excited-state energies and transition intensities were calculated by a configuration-interaction procedure including the ground-state configuration, 27 locally excited (at the ligands), and 36 charge-transfer configurations. Rotatory strengths were calculated using the above wave functions. The following three transitions were thus obtained in the visible region: $^1A_1 \rightarrow V_1(^1E)$, 18 820 cm^{-1}, $f = 0.005$, $R = 0.078 \times 10^{-3}$ Å^2; $^1A_1 \rightarrow V_2(^1A_2)$, 18 820 cm^{-1}, $f = 0.013$, $R = -0.087 \times 10^{-3}$ Å^2; $^1A_1 \rightarrow V_3(^1E)$, 19 040 cm^{-1}, $f = 0.306$, $R = 0.025 \times 10^{-3}$ Å^2. All these excited states derive from a transfer into the same π^* antibonding orbital of the bpy. The most intense visible absorption band (2σ) was assigned by these authors to $V_3(^1E)$, while the higher energy shoulder (4σ) was interpreted as a vibrational structure. This assignment is fundamentally different from ours in that the bulk of the visible absorption is assigned to only one electronic transition. Our experimental evidence as well as earlier MCD measurements on $Fe(phen)_3^{2+}$ [19] clearly point to the presence of two intense electronic transitions under the visible absorption band.

In a more recent theoretical publication[18] transition energies and intensities were obtained from semiempirical calculations on $Fe(bpy)_3^{2+}$, which are in no way compatible with our experimental assignments. Again, as in the previous calculations, there is only one dominating $^1A_1 \rightarrow {}^1E$ transition in the visible. More disturbing, the lowest lying triplet states $^3A_1$ and ^3E were found as low as 3300 and 6000 cm^{-1}, respectively. From the regularities observed in the spectra of the series $M(bpy)_3^{2+}$ (M = Fe^{2+}, Ru^{2+}, Os^{2+}) and from the known luminescence behavior of the Ru^{2+} and Os^{2+} complexes it is unlikely that the $Fe(bpy)_3^{2+}$ complex has any excited states below 15 000 cm^{-1}.

$Os(bpy)_3^{2+}$. The visible absorption spectrum of $Os(bpy)_3^{2+}$ falls naturally into two regions, a low-energy region between 14 000 and 19 000 cm^{-1} (Figure 4) and a high-energy region between 19 000 and 25 000 cm^{-1} (Figure 5). The first region has been assigned[9] to spin-forbidden charge-transfer transitions being the analogues of the spin-allowed transitions which comprise the second region. We consider first the spectra in Figure 5.

The majority of the absorption intensity appears in two groups of bands, one near 20 000 cm^{-1}, the other near 22 600 cm^{-1}. These two band groups are predominantly σ polarized. They are assigned to spin-allowed charge-transfer transitions to ^1E states. Bands $10\sigma^x$ and $10\sigma^y$ are assigned to slightly split components of one excited state, degenerate in D_3 symmetry. There is a larger splitting in the band group 6σ, 7σ, and 8σ, which is assigned to another spin-allowed transition, derived from transfer into a bpy π^* orbital which is symmetric (χ) under the C_2 symmetry operation retained in the complex ion. If we consider the three individual metal-ligand transition moments, they combine to give E and A_1 in the D_3 complex ion. The A_1 combination corresponds to an exact cancellation of the three individual moments and the transition to $^1A_1$ is forbidden. However, with a reduction of symmetry, e.g., from D_3 to C_2, the cancellation will no longer necessarily hold and the transition to the $^1A_1$ state can carry intensity. We assign the weak shoulder $6\sigma^{x,y}$ to the forbidden (in D_3) transition to $^1A_1$; 7σ and 8σ are the two orbitally split components of the degenerate (in D_3) transition to ^1E. Comparison with the corresponding Ru^{2+} spectrum[10] reveals a similar splitting into three components for the analogous band near 22 000 cm^{-1}. The distortion of the complex therefore has a considerably greater effect on the lower energy spin-allowed band than on the higher energy band. Band 10π has already been associated with the nominally π allowed charge transfer transition to $^1A_2$ (ψ^*).[9] It carries very little intensity, because the main charge-transfer mechanism provides σ intensity only.

Comparison between Figures 4 and 5 shows a striking similarity of the two sets of σ-polarized bands. We see the correlation between $5\sigma^x$, $5\sigma^y$ and $10\sigma^x$, $10\sigma^y$ and between $1\sigma^{x,y}$, $2\sigma^{x,y}$, $4\sigma^{x,y}$ and $7\sigma^{x,y}$, $8\sigma^{x,y}$, $9\sigma^{x,y}$. It is natural to assign the lower energy bands to the spin-forbidden analogues of the more intense higher energy system and the mechanism for the removal of the spin prohibition needs to be considered at this point.

The most important path for removing the spin restriction involves spin-orbit coupling within the $t_2^5\pi^*$ electron configuration as we discussed earlier,[10] so that intensity can be stolen from the strong σ-polarized bands in Figure 5. This intensity must appear in σ polarization and it therefore accounts for the majority of the intensity observed for the spin-forbidden charge-transfer bands (Figure 4).

However, the observable triplet states are not the exact analogues of the singlet states which dominate the spin-allowed absorption spectrum. In addition to the analogue of the latter (transfer of an electron from $t_\pm$) there are ^3E states (one for χ^* and one for ψ^*), corresponding to the transfer of an electron from t_0, which can gain intensity in σ polarization via the metal-centered spin-orbit coupling mechanism. A detailed treatment of the band structure of the spin-forbidden bands must await further experimental studies which include the effect of external magnetic fields. Such experiments are planned. For the present we note that metal ion spin-orbit coupling between triplet and singlet states cannot lead to measurable π-polarized intensity. This is in good agreement with our earlier observation that the π-polarized spin-forbidden intensity in the series $Fe(bpy)_3^{2+}$, $Ru(bpy)_3^{2+}$, $Os(bpy)_3^{2+}$ is not proportional to the squares of the metal ion spin-orbit constants.[9]

Disregarding spin-orbit pathways it is posible to remove the spin prohibition through second-order terms which involve electron exchange between the metal ion and the ligands. Intensity stealing can then occur from either metal-centered or ligand-centered transitions. The problem of paramagnetic ion or molecule enhancement of singlet to triplet transitions in aromatic molecules was discussed first by Hoijtink[20] and Murrell,[21] while McGlynn et al.[15] have provided a review of the experimental and theoretical work up to about 1968. It is quite impossible at this stage to make a quantitative assessment of the role of electron exchange. Much more experimental results are required in order to delineate the important pathways from among a very large number of possibilities. We note, however, that the π-polarized intensity in the range 15 000–19 000 cm^{-1} increases on cooling of the crystal. This is consistent with the electron-exchange mechanism because it involves the fourth power of overlap between the interacting orbitals[15,20,21] and cooling of the crystal leads to an overall contraction.

The absorption bands 1π to 9π appear to form a progression. Band 1π is the origin while bands 6π and 8π represent one and two quanta, respectively, of a 1545-cm^{-1} vibrational mode. Bands 7π and 9π are likely to be another vibrational separation from 6π and 8π, respectively. This latter interval, 545 cm^{-1}, is close to the mean of the separations between 3π, 4π, and 1π, so that the same two (but broadened) vibrational modes might be involved. In any case the wavenumber intervals and the decreasing intensity distribution from 1π through 9π both suggest the involvement of only one electronic excited state, whose origin is 1π.

There is no reason to expect that the electron-exchange mechanism will provide intensity only in π polarization. Owing to the near coincidence of 1π and $1\sigma^{x,y}$ it is impossible, however, to determine the exchange-induced σ intensity. Measurements of transverse and longitudinal Zeeman effects, for example, are required before detailed assignments can be made. It is clear, however, that the most important triplet states which appear in σ polarization carry no π intensity.

Turning to Figure 5 we see that the intense σ-polarized bands have no associated π intensity in keeping with the charge-transfer character of the transitions; 10π has been assigned to the state $^1A_1$ and 11π is a 1540-cm^{-1} vibrational satellite, analogous to bands 6π and 8π (in relation to 1π). Bands 12π, 13π, and 14π represent a set of absorption bands which, unlike the other π-polarized bands, move to lower energy as the temperature is lowered. We have assigned them earlier[9,10] to triplet transitions of the bpy. Their intensity increases on cooling of the crystal so that an overlap dependent electron-exchange mechanism (as discussed above) must be involved.

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Molecular Complexes of Cyclic Polyethers. 6. Structure of and Binding Interactions in a Host–Guest Complex of a Macrocyclic Hexaether with *tert*-Butylammonium Perchlorate. Survey of Crystallographic Data

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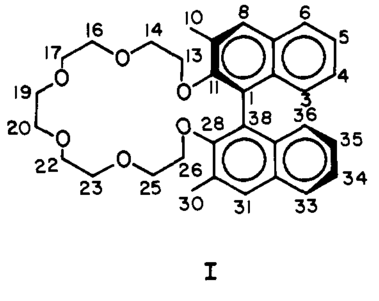
Abstract: This paper reports the crystal and molecular structures of a macrocyclic polyether ligand, 2,3:4,5-bis[1,2-(3-methylnaphtho)]-1,6,9,12,15,18-hexaoxacycloeicosa-2,4-diene ($C_{32}H_{36}O_6$, I), and of its 1:1 complex with *tert*-butylammonium perchlorate (II), as determined by X-ray diffraction methods. The inclusion complex crystallizes with 1 mol of benzene in the triclinic space group $P\bar{1}$ with a = 8.902 (5) Å, b = 11.117 (5) Å, c = 20.885 (12) Å, α = 91.69 (4)°, β = 91.07 (5)°, γ = 96.30 (4)°, and Z = 2. Crystal data of the uncomplexed hexaether: a = 8.738 (3) Å, b = 12.037 (5) Å, c = 13.771 (4) Å, α = 104.11 (3)°, β = 84.57 (3)°, γ = 96.46°, Z = 2, space group $P\bar{1}$. The host molecules are conformationally disordered in the crystal when uncomplexed, but have an ordered structure in the complex they form with $(CH_3)_3CNH_3^+ClO_4^-$. The observed geometry of the intermolecular host–guest type association is correlated with that found in previous studies of related compounds. Structural data confirm that two types of interactions binding an ammonium guest to a macrocyclic polyether host are important: (a) $^+NH \cdots O$ hydrogen bonds and (b) direct $N^+ \cdots O$ pole–dipole attractions where one of the lone-pair orbitals of a donor oxygen is directed at the electrophilic N. Inspection of the molecular structures reveals that the preferred overall conformation of this ligand is asymmetric, the mean plane of the macroring forming an angle of about 40° with the 1,1′-dinaphthyl bond and approaching one of the methyl substituents. As a result, the two faces of the macrocyclic cavity are equivalent with respect to the complexation of an ammonium guest only by virtue of rapidly established equilibria in solution between conformers.

The occurrence of intermolecular complexes of macrocyclic polyether hosts with organic guests, and in particular with alkylammonium ions, is well documented in the literature on host–guest chemistry.[1-4] In their extensive chemical studies in solution, Cram and his co-workers have shown that the affinity of polyether ligands for ammonium substrates is largely dependent on the topological features of the interacting species.[2,3] They have also described relationships between the relative size and shape of optically pure components and the degree of stereoselectivity obtained in the complex-formation process.[5] In the course of our investigations into the structural chemistry of crown ether complexes, we have recently characterized by low-temperature X-ray analyses the geometry of interaction between polyether hosts and alkylammonium guests in several model compounds. Previous reports dealt with the complexes of 2,6-dimethylylbenzoic acid 18-crown-5,[6a] bis(2,3-naphtho-18-crown-6),[6b] and a hexaether host containing two 2,2′-substituted 1,1′-dinaphthyl units[6c] (formulas V, VI, and VII in Figure 2), and it has been established that lipophilization of RNH_3^+ salts by crown ethers is principally due to complexation through a tripod arrangement of $^+NH \cdots O$ hydrogen bonds. The latter complex provided also an illustration of the kinds of steric forces that affect chiral recognition among optically pure species, involving the *R* isomer of a primary amine salt $C_6H_5CH(CO_2CH_3)NH_3^+PF_6^-$ and the *S,S* isomer of host VII.

The present study is concerned with the hexaether host I, which contains a 3,3′-dimethyl-1,1′-dinaphthyl unit bound to oxygen in the 2,2′ positions (systematic name: 2,3:4,5-



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