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Angular Geometry and the Electronic Spectrum of *cis*- and *trans*-Diammine(1,4,8,11-tetraazacyclotetradecane)chromium(III)

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Introduction

Several workers have noted that the first electronic absorption band maximum in ammine–cyclam complexes of chromium(III) occurs at about the same position as in $[Cr(NH_3)_6]^{3+}$ (21 550 cm^{-1})[1] and that the band position for the cis isomer is at a slightly lower energy than for the trans.[2–4] The conclusions drawn were that the effective ligand field strength of the cyclam nitrogens is nearly the same as that of ammonia, though lower in the cis complex because of greater steric strain. The unspecified strain might be the result of a longer bond length or an angular distortion away from the position of greatest overlap with the metal σ-bonding d orbitals. Comparisons involving Cr(III) complexes are quite useful, because in the first approximation the energy of the first band of an octahedral CrL_6 complex is equal to the ligand field strength of the ligand L, Δ_L. By means of a slightly looser approximation, the first band energy is often taken to be equal to the average ligand field strength when more than one different ligand is involved and no distinct band splitting is visible.

A Δ value for cyclam equal to that of ammonia appears to be at odds with the expectation that the more basic secondary amine should also have a higher ligand field strength. The angular overlap model (AOM) provides a particularly apt view of this situation.[5] A coordinating group is presumed to have the same ligand field properties in a variety of complexes, and geometrical differences are accounted for by angular factors.

When Cr(III) electronic spectra, including the sharp spin-forbidden transitions, have been treated in this manner, primary and secondary amines have indeed been found to have ligand field strengths higher than that of NH_3.[6,7] As part of a chelate ring, however, the primary or secondary amine nitrogen is often found to be considerably displaced from the Cartesian axes. The smaller overlap with the $d_{x^2-y^2}$ or d_{z^2} orbital then lowers the energy of the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition, giving the impression that the inherent ligand field strength of the amine is smaller than it actually is.

Given the electronic spectra of *cis*- and *trans*-$[Cr(NH_3)_2\text{cyclam}]^{3+}$ referred to above, we wish to test the hypothesis that angular distortions from octahedral geometry are responsible for the spectral properties noted. By means of ligand field calculations described in detail earlier,[8] we used values of e_σ for NH_3 and secondary amines found in previous AOM analyses,[7] together with known geometries of related complexes, to model the *cis*- and *trans*-diammine–cyclam complexes (whose structures are not yet known) to predict the transition energies. The specific questions of interest are as follows: (1) Are the predicted first band maxima in reasonable agreement with experiment? (2) Can the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition energy be represented as described in the model above, that is, in terms of a geometrically-determined attenuation of the nitrogen ligand field strengths? (3) Does the difference in the angular geometries of the cis and trans isomers account for the higher energy first band maximum for the trans complex? (4) Does the geometry account for the magnitude of the ^2E_g splitting in these complexes and for the difference in splitting between the cis and trans isomers?

The last question is especially interesting because the ^2E_g splittings can be determined very accurately (±1 or 2 cm^{-1} typically) and because they are only slightly affected by the ligand e_σ values. This is because when the ligands are exactly 90° apart there is no σ-interaction with the d_{xy}, d_{xz}, and d_{yz} orbitals, and because the ligands are amines, no π-interaction either. Displacement from the axes leads to different t_{2g} orbital energies, and splittings of the doublet states derived from them, but the extent of the displacement usually influences the splitting much more than does the magnitude of e_σ.[8] Thus geometry is the primary determinant of the splittings of the $(t_{2g})^3$ doublets. The diammine–cyclam complexes are particularly good test cases for this assertion, because the N–Cr–N angles differ significantly from 90°, and the distortions are not C_3-preserving. Angular distortions that preserve C_3 symmetry generally lead to small doublet splittings.[6]

Computations

The ligand field calculations[8] were based on the 120 × 120 secular determinant from the d^3 configuration. Values for the interelectronic repulsion and spin–orbit coupling parameters were taken from analyses of the spectra of ethylenediamine (en) and triazacyclononane (tacn) complexes:[6,7] $B = 700$, $C = 2800$, α_T (Trees correction) $= 170$, and $\zeta = 250$ cm^{-1}. Note that B and C were both determined by spectral fitting in the works referenced. That the C/B ratio corresponds to a common approximation is accidental. Neither the first spin-allowed band maximum nor the ^2E_g splitting is very sensitive to these values, but one would expect them to need some revision in order to fit the actual $^4A_{2g} \rightarrow {}^2E_g$ energies or the $^4A_{2g} \rightarrow {}^4T_{1g}$ band maximum.

AOM analyses of spectra of en and tacn complexes of Cr(III) suggest that e_σ is about 7500 cm^{-1} for a primary amine[6] and about 7700 cm^{-1} for a secondary amine,[7] which value was initially used for all the cyclam nitrogens in both isomers. For NH_3, e_σ is about 7000 cm^{-1}.[9]

For the trans complex, the CrL_6 skeletal geometry of $[CrBr_2\text{cyclam}]^+$ was used,[10] and for the cis complex, $[CrCl_2\text{cyclam}]^+$, replacing the halogens with nitrogens.[10,11] The model took into account only the angular geometry. Other factors can influence the ^2E_g splitting besides the skeletal geometry, including the positions of the carbon atoms in the chelate rings[6] and the anions,[12] but these have been neglected here, in part because we are using geometries from model complexes in which the anions may be disposed differently. The field from the nearest counterions may cause splittings as high as 50 cm^{-1} when their orientation is far from cubic with respect to the natural axis system of the complex.[12] Some exploratory calculations on the model complexes led to ^2E_g splittings that were affected by less than 5 cm^{-1} by the nearest anions. The large distance of the nearest anions from the metal (>5 Å), and the expected R^{-3} or R^{-5} dependence for the ligand field from them,[12] makes it improbable that a different anion geometry from the model complexes would have a large influence on the ^2E_g splitting.

Results and Discussion

With the common approximations of no spin–orbit coupling and maximum symmetry, the $^4A_{2g} \rightarrow {}^4T_{2g}$ bands for *cis*- and

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Table I. Calculated and Experimental Electronic Spectral Features for *cis*- and *trans*-$[Cr(NH_3)_2cyclam]^{3+}$ (Values in cm^{-1})

	$^4A_{2g} \rightarrow {}^4T_{2g}$ energy			
	^4E	^4B	$^4A_{2g} \rightarrow {}^2E_g$ splitting	ref
calcd^a				
cis	22.6×10^3		71	
trans	22.5×10^3	24.0×10^3	56	
exptl				
cis	21.5×10^3		64	4
trans	21.6×10^3 (sh)	24.0×10^3	49	4
	22.5×10^3 (sh)	23.8×10^3		2

^{a} Parameter values: $e_{\sigma N}$(ammonia) = 7000, $e_{\sigma N}$(cyclam) = 8100, B = 700, C = 2800, α_T = 170, ζ = 250.

trans-CrA_2B_4 complexes are each split into two components. The trans splitting is $^1/_2|\Delta_A - \Delta_B|$, while the cis splitting is $^1/_4|\Delta_A - \Delta_B|$.[13] Since we can assume no π-interaction, these become $3(e_{\sigma A} - e_{\sigma B})/2$ and $3(e_{\sigma A} - e_{\sigma B})/4$, respectively. Splitting is observable in the experimental solution absorption spectrum of *trans*-$[Cr(NH_3)_2cyclam]^{3+}$, but not for the cis isomer. For the trans isomer we therefore calculated (without these approximations) separate energies for the $^4B_{2g} \rightarrow {}^4E_g$ and $^4B_{2g} \rightarrow {}^4B_{1g}$ transitions (in D_{4h} notation), by averaging the corresponding component energies, four for ^4E_g and two for $^4B_{1g}$. For the cis isomer all six component energies were averaged. In neither case is the procedure entirely satisfactory, because it ignores differences among the extinction coefficients for the individual components that can cause the actual position of the peak maximum to deviate considerably from the average positions of the contributing components. Only the $^4B_{1g}$ peak for the trans isomer is immune to this, because the two components are usually closely spaced. The spread of component energies calculated was 600 cm^{-1} for the cis complex, and for the trans complex it was 170 cm^{-1} for the ^4E_g state and 5 cm^{-1} for the $^4B_{1g}$.

Data from solution absorption spectra are listed in Table I. With the AOM and other parameters listed above, the peaks for the trans complex were calculated to lie at 21.9 (^4E) and 22.8 ($^4B_1$) × 10^3 cm^{-1}. For the cis complex, the peak would lie at 21.8 × 10^3 cm^{-1}, the average of the six component energies. Only the $^4B_1$ peak deviates substantially from the experimental values, yet that is the peak that should be most accurately modeled. This suggests that $e_{\sigma N}$ for the cyclam nitrogens is greater than it is for the tacn nitrogens. This behavior has been seen previously.[14,15] Data from nickel(II) tetraazo macrocycles demonstrates that the nitrogen ligand field strength decreases markedly and the Ni–N bond length increases with increasing ring size.[14,16] In fact, Dq fits a $1/R^5$ law quite well for these complexes, as is predicted by simple crystal field theory.[17] The tacn ligand fits into this series at approximately the same position, in both Dq and R(Ni–N), as [15]aneN$_4$.[14–16,18] We can safely conclude that one cannot expect to characterize secondary nitrogens by a single e_σ value, even approximately, at least when dealing with macrocyclic ligands.

Table I shows the results of the calculation described above, except that $e_{\sigma N}$ for the cyclam nitrogens was set at 8100 cm^{-1}, which brings the calculated $^4B_{1g}$ band from the trans isomer into agreement with experiment. The ^4E_g band appears as a shoulder and it is difficult to pinpoint the maximum, which is seen in the difference in the two experimental values in Table I.[2,4] We are thus unable to evaluate how good the calculated energy is. All else being equal, one would expect the ^4E_g transition to be more intense than the $^4B_{1g}$ because of its higher degeneracy. The latter transition corresponds to an orbital promotion from d_{xy} to $d_{x^2-y^2}$. The CrN_4 skeleton in the xy plane is further from centrosymmetric than the corresponding CrN_4 skeletons in the xz and yz planes, so the $xy \rightarrow x^2 - y^2$ transition is likely to be less forbidden than the corresponding transitions in the other two planes.

The calculations place the $^4A_{2g} \rightarrow {}^4T_{2g}$ energy for the cis complex too high. This might conceivably occur because the higher energy components have much higher extinction coefficients. Alternatively, the cyclam nitrogens may have a smaller ligand field strength in the cis complex than in the trans. In fact, Cr–N bond lengths are different in the two model complexes (2.055 Å in *trans*-$[CrBr_2cyclam]^+$ and an average of 2.100 Å in *cis*-$[CrCl_2cyclam]^+$).[10,11] With an R^{-5} dependence, this would reduce $e_{\sigma N}$ from 8100 cm^{-1} in the trans to 7300 cm^{-1} in the cis. With this value, the calculated $^4A_{2g} \rightarrow {}^4T_{2g}$ band maximum occurs at 20.6 × 10^3 cm^{-1}, thereby including the observed value in the predicted range.

Comparing calculated and experimental ^2E_g splittings is much more straightforward than comparing quartet band positions. Each peak represents a single component, uncomplicated by the assumptions normally applied to broad bands, such as the assumption that transitions are vertical.

The calculated and experimental ^2E_g splittings are in quite good agreement, considering the approximations made. As we mentioned earlier, the ^2E_g splitting can be a very sensitive indicator of the extent of the distortion from orthoaxiality, though some types of distortion produce greater splittings than others. In the *cis*-$[CrCl_2cyclam]^+$ geometry used, the average angular displacement of the coordinating atoms from Cartesian axes, chosen to minimize the squares of the displacements from the axes, is 3.1°, and the maximum is 6.8°. In the *trans*-$[CrBr_2cyclam]^+$ geometry, the average displacement is 2.4° and the maximum is 2.9°.

The calculated ^2E_g splitting can be quite sensitive to the differences in the nitrogen positions caused by changes in the conformation of the cyclam rings. Some alternative conformations were generated by means of molecular mechanics calculations.[19] For the trans isomer, the splitting did not vary greatly with conformation, but the cis isomer was remarkably sensitive. The calculated splittings varied from 20 to 95 cm^{-1} for the conformations we tested, even though the calculated strain energies were similar for all the conformations, and the average angular displacement of the nitrogen atoms from the axes was always near 3°. The calculated values in Table I, therefore, were obtained from the crystallographically observed atom positions in the model complexes.

Another factor that could in principle contribute to the ^2E_g splittings is off-axis bonding, which has been explored by Gerloch et al. in a series of papers.[21–23] The calculations discussed above assumed that each cyclam nitrogen lone pair orbital was directed along the Cr–N axis. If it is not, the σ-interaction will be smaller than supposed and there will be a nonzero π-interaction. These effects can be modeled quantitatively through an off-diagonal entry, $e_{\sigma\pi}$, in the AOM matrix,[21] though there is as yet no good way to estimate the magnitude of $e_{\sigma\pi}$ from the geometry. Because the hydrogen positions in cyclam complexes are usually fixed geometrically we have examined the geometry of an N-substituted tetramethylcyclam complex instead. In $[Co(N_3)Me_4cyclam]ClO_4$, there is a 7° difference between the Co–N bond axes and the pseudo-C_3 axes defined as the average of the three N–C

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vectors.[24] It is far from certain that this correctly defines the orientation of the lone pair, nor is it clear how large a perturbation would result. If we assume that $e_{\sigma\pi} = e_\sigma \sin \theta$, it would be approximately 1000 cm^{-1}. We inserted this value and recalculated the transition energies. The calculated ^2E_g splittings were reduced, by at most 6 cm^{-1}. While this in fact fit the experimental data even better, the effect was too small to evaluate its significance or validity.

Conclusions

AOM calculations provide some answers to the questions posed earlier.

1. Are the predicted first band maxima in reasonable agreement with experiment? Not if $e_{\sigma N}$ from $[Cr(tacn)_2]^{3+}$ is used. The nitrogen ligand field strength really does depend on the ring size. It is the metal–ligand bond distance that is responsible for this rather than the angular alignment.

2. Can the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition energy be represented in terms of a geometrically-determined attenuation of the nitrogen ligand field strengths? The deviations from orthoaxiality were not sufficient to judge this. If 90° angles were imposed, the largest increase in any of the calculated $^4A_2 \rightarrow {}^4T_2$ energies would be just 300 cm^{-1}.

3. Does the difference between the cis and trans angular geometries account for the higher energy first band maximum for the trans complex? No. Angular deviations from the Cartesian axes can explain a maximum shift of less than 300 cm^{-1}. More important is that for the trans complex the band maximum corresponds to the higher energy $^4B_{1g}$ state even though it has the lower degeneracy. It is also likely that $e_{\sigma N}$ for the cyclam nitrogens is higher in the trans orientation, based on bond lengths in the two complexes.

4. Does the angular geometry account for the measured ^2E_g splittings? Yes, and the difference between the cis and trans isomers is predicted quite well. Because of the high sensitivity to angular geometry and the low sensitivity to the ligand field strength, as well as the precision with which ^2E_g splittings can be measured, this is a much better probe of geometry than the broad band maxima.

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