comparison to simple amino acids (which only bind in a monodentate fashion), it was possible to prove that the ASP ligand must bind to the Tb(III) ion in a bidentate manner.[12] However, the ASP chelate ring contains seven members, while the LAC, MAN, and PLA chelate rings are five membered. A five-membered ring would have a different conformation than a seven-membered one (thus accounting for the difference in CPL line shape) and should also bring the asymmetric atom of the ligand closer to the metal (thus increasing the degree of CPL intensity).

It is our belief, therefore, that the mode of bonding (at low pH) existing at low pH is the same for MAL, LAC, MAN, and PLA complexes and involves bidentate attachment of the ligand to the metal via an ionized carboxyl and an unionized hydroxy group. In the case of the MAL complexes, a new terdentate mode of bonding becomes available once the solution pH exceeds 7.5, and one would assume that this mode would involve the other carboxyl group. Salama and Richardson[20] have demonstrated that MAL binds to Tb(III) in a bidentate fashion at low pH and in a terdentate fashion at high pH (this was done by examining solvent quenching of the Tb(III) ion and "counting" the number of coordinated water molecules) but had no evidence to suggest that the bidentate mode involved anything other than the two ionized carboxyl groups.

Conclusions

The studies reported in the present work clearly show the power of CPL spectroscopy when applied to studies of lanthanide complex stereochemistry. A careful analysis of line shape and dissymmetry factors may be used to assign the major contribution to the overall complex chirality and may also be used to deduce modes of ligand bonding. More detailed analysis must await further developments in theory and might be difficult to apply even after it is in place: the large number of crystal field components produced when the $^5D_4 \rightarrow {}^7F_5$ Tb(III) transition is placed in a low-symmetry crystal field makes resolution (in fluid solution at room temperature) of each component impossible. Nevertheless, CPL spectroscopy will remain a powerful tool to probe lanthanide ion stereochemistries. It shall be most powerful in the study of Tb(III)-substituted proteins, now that theoretically is possible to deduce the major contribution to the metal ion chirality from an examination of the CPL spectra.

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Registry No. Tb(DPA)$_2$(LAC), 76282-20-7; Tb(DPA)$_2$(MAN), 76282-21-8; Tb(DPA)$_2$(PLA), 76282-22-9; Tb(DPA)(LAC)$_2$, 76282-23-0; Tb(DPA)(MAN)$_2$, 76319-71-6; Tb(DPA)(PLA)$_2$, 76282-24-1; Tb(LAC)$_3$, 19042-17-2; Tb(MAN)$_3$, 37740-78-6; Tb(PLA)$_3$, 76282-25-2.

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Magnetic Circular Dichroism of Cyclic π-Electron Systems. 21.[1] The Trisulfur Trinitride Anion

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Magnetic circular dichroism of the $S_3N_3^-$ anion shows a negative *A* term for the transition at 27 800 cm^{-1} and confirms the assignment to a 2e″ → 2a″ (HOMO–LUMO) excitation of the $\pi^* \rightarrow \pi^*$ type. Both the sign and the magnitude (0.98 β_e) of the excited-state magnetic moment are in perfect agreement with expectations based on the perimeter model. The general applicability of the model to inorganic ring systems derived from $(4N + 2)$-electron delocalized perimeters is pointed out.

Introduction

Magnetic circular dichroism (MCD) of molecules derived from $(4N + 2)$-electron cyclic conjugated perimeters with n identical atoms in a ring can be understood simply in terms of the perimeter model.[2-4] The highly symmetrical parent $(4N + 2)$-electron perimeters can be divided into three classes (Figure 1). The first comprises systems with only two π-electrons ($N = 0$), in which the highest occupied MO of π symmetry (HOMO) is not degenerate while the lowest unoccupied MO of π symmetry (LUMO) is degenerate. The second contains perimeters with only two π holes [$N = (n/2) - 1$], and is possible only for cycles with an even number of vertices. In this case, HOMO is degenerate while LUMO is not. In these two types of parent perimeters, the low-energy HOMO → LUMO transition is doubly degenerate and the excited state will be referred to as the B state. The MCD *A* term of the transition into this state is positive if $N = 0$ and negative if $N = (n/2) - 1$. Symmetry-lowering perturbations which cause the n centers to differ in electronegativity or substitution, which introduce cross-links, bridges, etc., may remove this degeneracy. If so, they lead to two nondegenerate transitions labeled B_1 and B_2 in the order of increasing energy. These are polarized in mutually perpendicular directions in the perimeter model approximation. If $N = 0$, the B_1 transition has a positive and the B_2 transition a negative *B* term. If $N = (n/2) - 1$, the signs are just the opposite.

The third class of $(4N + 2)$-electron [n]-center perimeters contains all other cases [$N \neq 0$, $N \neq (n/2) - 1$]. In this instance, both HOMO and LUMO are degenerate, and there are four possible single-electron promotions of the HOMO → LUMO type. In charged perimeters ($n \neq 4N + 2$), they give rise to two doubly degenerate excited states, L at lower energies and B at higher energies. In uncharged perimeters ($n = 4N + 2$), they lead to two nondegenerate excited states, L_b and L_a in the order of increasing energy, followed by a high-energy degenerate B state. Transitions into the states of the L type are forbidden by symmetry and appear in the experimental spectra only due to vibronic mixing. Transitions into the B state are allowed and have a small *A* term, whose sign and size are given by simple formulas given in ref 2. The MCD effect of both L and B transitions is usually complicated by

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[1] Part 20: S. L. Wallace and J. Michl, *Tetrahedron*, **36**, 1531 (1980).
[2] J. Michl, *J. Am. Chem. Soc.*, **100**, 6801 (1978).
[3] J. Michl, *J. Am. Chem. Soc.*, **100**, 6812 (1978).
[4] J. Michl, *J. Am. Chem. Soc.*, **100**, 6819 (1978).

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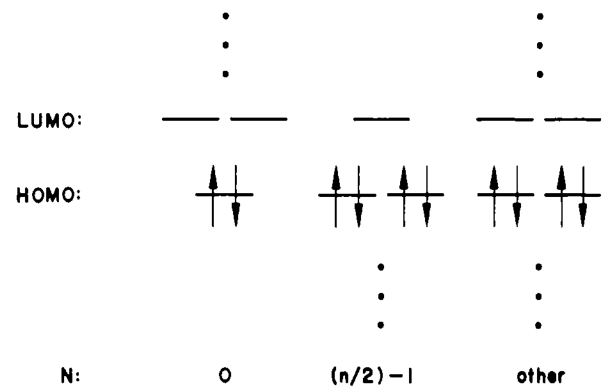

Figure 1. Possible arrangements of HOMO's and LUMO's of a ($4N + 2$)-electron [n]-center π-electron ring system: left, a "two-π-electron" case; center, a "two-π-hole" case (n even); right, a general case.

vibronic interactions. If symmetry is lowered in such a way that a threefold or higher axis of symmetry remains, the L transition may become allowed. Simple symmetry considerations[2] show whether it does and what sign its A term will have. Further removal of symmetry leads to four nondegenerate transitions whose polarizations, intensities, and MCD signs are related to the nature of the perturbation in a relatively simple structure-sensitive way described in detail in ref 2–4.

While the perimeter model has already been applied successfully to numerous carbon-based ($4N + 2$)-electron ring systems in the preceding papers of this series,[1,5,6] none of these were of the two-π-electron ($N = 0$) or two-π-hole [$N = (n/2) - 1$] types. This is understandable in that the required charge states of the parent [n]annulene perimeter, $C_nH_n^{(n-2)+}$ ($N = 0$) and $C_nH_n^{(2-n)+}$ [$N = (n/2) - 1$], are unknown with the exception of $C_3H_3^+$, and even suitable derivatives are very scarce. Recently, we have applied the model to a series of oxocarbon dianions $C_nO_n^-$ (n = 4–6), formally derived from the highly positively charged two-π-electron perimeters $C_nH_n^{(n-2)+}$ by substitution with a O^- group at each carbon.[7]

While negatively charged two-π-hole carbon-based perimeters $C_nH_n^{(2-n)+}$ and molecules derived from them are very hard to find, their inorganic isoelectronic analogues are known. It has already been noted[2] that the MCD signs of the first transitions in the two-π-hole dications S_4^{2+}, Se_4^{2+}, and Te_4^{2+} reported some time ago[8] are in agreement with the simple model. In the present paper, we report the MCD spectrum of the recently characterized[9,10] two-π-hole anion $S_3N_3^-$ which contains a six-membered ring with 10 π electrons ($n = 6$, $N = 2$). Our purpose is threefold. First, we wish to draw attention to the fact that absolute MCD signs of cyclic π systems derived from ($4N + 2$)-electron perimeters are now readily interpretable. While the applications have been limited to organic molecules so far, the principles should be equally valid in the inorganic realm and are likely to be helpful in the spectroscopy of S–N heterocycles, B–N heterocycles, etc. Second, we use the results to confirm the π^*–π^* spectroscopic assignment proposed for the first strong transition in $S_3N_3^-$ on basis of calculations.[10] Third, we use the measured magnitude of the excited-state magnetic moment to check the validity of a previously derived approximate formula[2] for magnetic moments of perimeter orbitals.

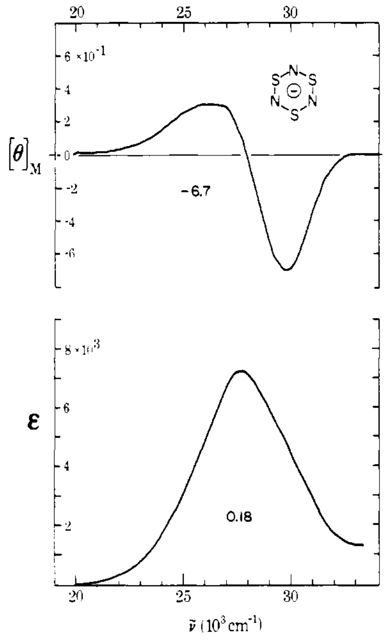

Figure 2. Spectra of $PPN^+S_3N_3^-$ in acetonitrile: top, MCD (A term in β_eD^2); bottom, absorption (oscillator strength given).

Experimental Section

A crystalline sample of $[(C_6H_5)_3P]_2N^+S_3N_3^-$ was obtained from Professor Chivers (Calgary). Its spectra were run in acetonitrile (distilled from CaH_2 and then P_2O_5). Solutions were prepared by standard vacuum-line techniques (10^{-6} torr). Absorption was measured on a Cary 17 spectrophotometer and magnetic circular dichroism on a Jasco 500C spectropolarimeter equipped with a 15-kG electromagnet and calibrated with the CD signal of *d*-camphorsulfonic acid and the MCD signal of naphthalene.

Oscillator strength f and the MCD terms were evaluated from the formulas $f = 4.319 \times 10^{-9} \int \epsilon \, d\tilde{\nu}$, $A = 33.53^{-1} \int (\tilde{\nu} - \tilde{\nu}_0)[\theta]_M/\tilde{\nu} \, d\tilde{\nu}$, and $B = -33.53^{-1} \int [\theta]_M/\tilde{\nu} \, d\tilde{\nu}$, where $\tilde{\nu}$ is the wavenumber, $\tilde{\nu}_0$ is the band center, ϵ is the decadic molar extinction coefficient, and $[\theta]_M$ is molar ellipticity per unit magnetic field in deg L m^{-1} mol^{-1} G^{-1}. The magnetic moment of the excited state μ was evaluated from $\mu = -2A/D$, where D is the dipole strength of the transition, obtained from the relation $D = 9.1834 \times 10^{-3} \int \epsilon/\tilde{\nu} \, d\tilde{\nu}$.

Results and Discussion

The absorption and MCD spectra of $S_3N_3^-$ up to 33 000 cm^{-1} are given in Figure 2. At higher energies, the spectrum is obscured by the absorption of the PPN^+ cation and is not shown. The absorption spectrum shows the previously reported[10] band at 27 800 cm^{-1} with oscillator strength $f = 0.18$. The MCD spectrum shows a negative A term (-6.7 β_eD^2) centered at this energy, thus yielding a value of $\mu = 0.98$ β_e for the magnetic moment of the excited state. The B term of the transition is 2.6×10^{-4} β_eD^2/cm^{-1}, but this value is probably rather inaccurate due to the overlap with a large A term. Both in absorption and in MCD, the band tails into the visible region, possibly due to the presence of a weak transition at lower energies.

When the MO's of a ($4N + 2$)-electron [$2(N + 1)$]-atom π perimeter possessing the symmetry of a regular polygon are chosen complex, the HOMO pair is ψ_N and ψ_{-N} ($=\psi_N^*$) and the LUMO is $\psi_{N+1} \equiv \psi_{-N-1}$, where $\psi_k = n^{-1/2} \sum_{\mu=0}^{n-1} \phi_\mu \exp(2\pi i\mu k/n)$ and ϕ_μ is the μth AO [$0 \leq \mu \leq n - 1$, $n = 2(N + 1)$]. Among excitations involving levels of π symmetry, only the members of the degenerate pair $\psi_N \rightarrow \psi_{N+1}$ and $\psi_{-N} \rightarrow \psi_{N+1}$ are electric dipole allowed. The excited state is of E_{1u} symmetry, and its label, "the B state",[2] was chosen in analogy

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(8) P. J. Stephens, *Symp. Faraday Soc.*, No. 3, 40 (1969); *J. Chem. Soc. D*, 1496 (1969).

(9) J. Bojes and T. Chivers, *J. Chem. Soc., Chem. Commun.*, 453 (1977); *Inorg. Chem.*, **17**, 318 (1978).

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to Platt's label for that transition in an uncharged perimeter which changes the "angular momentum quantum number" k by one.[11] The magnetic moment of the B state is given by $-2A/D = -\mu[2(N+1), N]$, where $\mu[2(N+1), N]$ is the out-of-plane component of the magnetic moment of an electron in the orbital ψ_N defined above for a $2(N+1)$-atom perimeter. In this orbital, net electron current runs in the counterclockwise sense and $\mu[2(N+1), N]$ must therefore be negative. It can be expressed more explicitly if a series of appromations[2] is adopted, i.e.

$$\mu(n,k) = -|\beta|(m\beta_e l_0^2/\hbar^2) \cot(\pi/n) \times [\sin(2\pi k/n) - 0.15 \sin(4\pi k/n)]$$

where $n > 3$, β is the resonance integral between neighbors, m is the electron mass, β_e is the Bohr magneton, l_0 is the bond length, and the constant 0.15 is appropriate for carbon perimeters and will have slightly different values for other types of perimeters (it reflects the magnitude of the resonance integral between Löwdin-orthogonalized AO's on next-nearest neighbors in units of β). Since $\mu[2(N+1), N]$ is negative, the transition into the B state must always have a negative A term, and this has been observed for the three representatives of this class of molecules whose MCD spectra have been easured so far:[8] S_4^{2+}, Se_4^{2+}, Te_4^{2+}. The physical origin of the negative sign is easily understood if the light and the magnetic field $\vec{B}$ are both directed along z, perpendicular to the molecular plane. A left-handed circular polarized photon (angular momentum $\hbar$) is needed to promote an electron from ψ_N (irreducible representation ϵ_N in the C_n group) to ψ_{N+1} ($\epsilon_{N+1} \equiv b$ in the C_n group). Before excitation, the out-of-plane component of the magnetic moment of the electron due to its orbital motion, $\mu[2(N+1), N]$, was negative; after excitation, it is zero since ψ_N is nondegenerate. The ground state had no magnetic moment since the effect of the angular motion of an electron in ψ_N compensated exactly that of an electron in ψ_{-N}. The excited state has an uncompensated electron in ψ_{-N} and therefore has a positive magnetic moment, $-\mu[2(N+1), N]$. In magnetic field, its energy will be lowered by the Zeeman term $\mu[2(N+1), N]B_z$. The right-handed circular polarized state $\psi_{-N} \rightarrow \psi_{N+1}$ will be raised by the same amount. The differential absorption $\epsilon_L - \epsilon_R$ will therefore be positive at lower energies and negative at higher energies, and the resulting shape is known as a negative A term.

A symmetry-lowering perturbation of a two-π-hole perimeter which preserves an at least threefold axis of rotation symmetry such as the one which produces $S_3N_3^-$ ($N = 2$) has no effect on the MCD spectrum if changes in MO coefficients and thus in the magnetic moment of HOMO are neglected,[2] so that a negative A term for the B transition is still expected. In the D_{3h} group of $S_3N_3^-$,[10] the B state is of symmetry E′ and is due to the excitation $2e'' \rightarrow 2a_2''$ (HOMO–LUMO), with a small admixture of the high-energy excitation $1e'' \rightarrow 2a''_2$, and this is the assignment proposed for the 27 800-cm^{-1} transition in $S_3N_3^-$ on the basis of calculation.[10]

In a better approximation, it is recognized that the perturbation will alter the form of the MO's. The HOMO, 2e″, is then no longer given by the ψ_2, ψ_{-2} pair defined above, but contains an admixture of the orbitals ψ_1, ψ_{-1}: $2e_\pm'' = c_2\psi_{\pm 2} + c_1\psi_{\pm 1}$. Its magnetic moment is no longer equal to $\mu(6, 2)$ but contains contributions from both $\psi_{\pm 2}$ and $\psi_{\pm 1}$: $\mu(2e'') = c_2^2[\mu(6, 2)] + c_1^2[\mu(6, 1)]$, where $c_2^2 > c_1^2$. The magnitudes of c_1^2 and c_2^2 are determined by the difference between the electronegativities of nitrogen and sulfur. However, since $\mu(6, 2)$ and $\mu(6, 1)$ are both negative, this cannot affect the expected negative sign of the A term of the B state in $S_3N_3^-$ but can affect only its magnitude. We conclude that the observed negative A term provides support for the proposed[10] assignment of the 27 800-cm^{-1} band of $S_3N_3^-$ to the B transition ($\pi^* \rightarrow \pi^*$).

The observed magnitude of the magnetic moment of the excited state, 0.98 β_e, can be used to check the validity of the approximate formula for the magnetic moments of perimeter orbitals given above. A two-π-electron or a two-π-hole system is best for this purpose: first, the excited-state magnetic moment only reflects a magnetic moment of one perimeter orbital, LUMO or HOMO, respectively, rather than a difference or sum of two such orbitals, and second, complications due to vibronic mixing of L and B states are avoided. The main difficulty with using our result for $S_3N_3^-$ for this purpose is the uncertainty about the actual values of the mixing coefficients c_1^2 and c_2^2. The limits on these are $c_1^2 = 0$ and $c_2^2 = 1$ if sulfur and nitrogen had identical electronegativities and $c_1^2 = c_2^2 = {}^1/_2$ if their electronegativities were infinitely different. In order to apply the formula for $\mu(n, k)$ to the S–N perimeter, we use $l_0 = 1.6$ Å[10] and ignore the small possible change of the factor 0.15 in front of the correction term in the formula. A value for β_{NS} can be taken from published π-electron calculations for S–N rings which produced reasonable agreement with experimental excitation energies. We take the value −1.854 eV utilized in the PPP calculation on $S_5N_5^+$ in ref 12 (bond lengths 1.465–1.59 Å) as typical. The resulting magnetic moments of the S–N perimeter HOMO orbital then are −1.06 β_e in the first limit ($c_2^2 = 1$) and −0.92 β_e in the second limit ($c_2^2 = 0.5$). These values bracket the observed value −0.98 β_e, and one could not ask for a better agreement. Although some of this agreement could well be fortuitous, the result certainly suggests that the above formula for $\mu(n, k)$ provides reasonable estimates of orbital magnetic moments and that the table of the calculated magnetic moments $\mu(n, k)$ given in ref 2 provides a useful guide to the interpretation of experimental data.

It should be noted that the calculated effects of the decreased absolute value of the resonance integral and of the increased bond length for the S–N bond relative to the C–C bond on the value of $\mu(n, k)$ almost exactly cancel: $\mu(6, 2) = -1.05\ \beta_e$ for C–C, $\mu(6, 2) = -1.06\ \beta_e$ for N–S. The same appears to be true in the comparison of C–C with Se–Se and Te–Te bonds: the expected magnetic moment for the B state of $C_4H_4^-$ is 0.61 β_e, the observed[8] moments for the B states of isoelectronic species are 0.66 β_e for Se_4^{2+} and 0.50 β_e for Te_4^{2+}.

In conclusion, we believe that the perimeter model will be useful for the interpretation of MCD spectra of many inorganic ring systems. Clearly, there can be little doubt about the correctness of the assignment of the 27 800-cm^{-1} transition in $S_3N_3^-$ as due to the $2e'' \rightarrow 2a_2''$ excitation. Finally, we find that the formula for perimeter orbital magnetic moments given in ref 2 provides satisfactory agreement with experiment.

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Registry No. $PPN^+S_3N_3^-$, 72884-86-7.

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