MCD Spectra for Metal-Centered Transitions in the $Hg_3(dppm)_3^{4+}$ Cluster Complex

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The magnetic circular dichroism (MCD) spectrum for $Hg_3(dppm)_3(SO_4)_2$, dppm = bis(diphenylphosphino)methane, in 5:3:2 v/v ethanol−methanol−ether solvent in the range 2.5−3.7 μm^{-1} (1 $\mu m^{-1} = 10^4$ cm^{-1}) at 295 K (solution) shows two minima at 2.99 and 3.41 μm^{-1}, which resolve into a positive *A* term at 3.12 μm^{-1} and a negative *B* term at 3.40 μm^{-1} at 80 K (rigid glass). The absorption spectrum shows an intense band at 3.05 μm^{-1} at 295 K which sharpens and shifts slightly to 3.09 μm^{-1} at 80 K. The 80 K spectrum also reveals a lower intensity band maximum clearly resolved at 3.40 μm^{-1}. The MCD and absorption spectra are interpreted in terms of 6s 6s $\sigma \rightarrow \sigma^*$ and 6s 6p $\sigma \rightarrow \pi$ metal-centered transitions. The *A* term in the region of the lowest energy band is ascribed to the $\sigma \rightarrow \pi$ transition to the spin−orbit E′ state of $^3A_2''$ origin.

Introduction

The structure for $Hg_3(dppm)_3(SO_4)_2$, dppm = bis(diphenylphosphino)methane, which is sketched in Figure 1, contains the planar triangular Hg_3^{4+} cluster with bridging dppm ligands.[1] In the solid, the sulfate ions are positioned above and below the triangular plane, and the Hg−Hg distance was found to be 2.76−2.80 Å. The compound was reported[2] recently to exhibit an intense, lowest energy absorption band at 332 nm (3.01 μm^{-1}; 1 $\mu m^{-1} = 10^4$ cm^{-1}) in ethanol at 300 K and an intense luminescence at 658 nm (1.52 μm^{-1}) in an ethanol glass at 77 K. The absorption and emission were interpreted as metal-centered transitions associated with the triangular Hg_3^{4+} cluster. A simple orbital diagram based on D_{3h} symmetry was proposed in which the highest occupied molecular orbital (HOMO) of a_1' symmetry and the lowest unoccupied orbital (LUMO) of e′ symmetry were postulated as σ bonding and antibonding combinations of Hg 6s valence orbitals, respectively. The $(a_1')^2$ ground configuration and a $^1A_1'$ ground state were assumed. The absorption at 3.01 μm^{-1} was assigned to $^1A_1' \rightarrow {}^1E'$ ($a_1' \rightarrow e'$), a metal-centered $\sigma \rightarrow \sigma^*$ transition. The emission was then described as a phosphorescence from an associated triplet state → $^1A_1'$ ($e' \rightarrow a_1'$). A large Stokes shift was observed (estimated to be 1.19 μm^{-1}), and was taken as evidence for a Jahn−Teller type distortion of the emitting state.

Metal-centered electronic transitions in polynuclear metal complexes are of general interest and have been the focus of several previous studies in this laboratory.[3] This interest has prompted a closer look at the Hg_3^{4+} cluster, particularly in view of the supposed utilization of Hg 6s valence orbitals in metal−metal bonding interaction. The metal−metal bonding in a number of cluster complexes of gold of the type $Au(AuPPh_3)_n^{m+}$ (n = 6−12) has also been attributed to 6s orbital overlap.[4] In the present study, absorption and magnetic circular dichroism (MCD) spectra are reported for $Hg_3(dppm)_3(SO_4)_2$ in a 5:3:2 v/v ethanol−methanol−ether solvent mixture at 295 K (solution) and at 80 K (rigid glass). MCD has proven to be a useful spectroscopic tool for investigating degenerate excited states.[5]

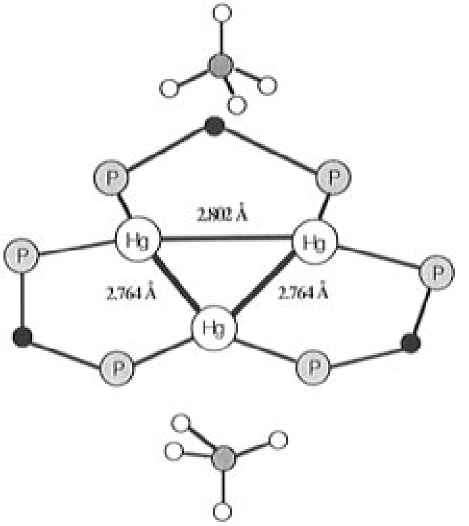

Figure 1. Structure of solid $Hg_3(dppm)_3(SO_4)_2$ with Hg−Hg distances indicated (phenyl substituents on the P atoms and hydrogens on the C atoms omitted for clarity).

Experimental Section

The compound $Hg_3(dppm)_3(SO_4)_2$ was prepared by the published procedure[1] and gave satisfactory elemental analysis. A preliminary absorption spectrum at room temperature in absolute ethanol solution was the same shape as that reported earlier,[2] but the absorptivity for the the intense band I observed at 3.04 μm^{-1} ($\epsilon = 3.97 \times 10^4$ M^{-1} cm^{-1}) was found to be approximately twice the value reported (2.04×10^4 M^{-1} cm^{-1}).[2] The absorptivity was carefully checked, and the origin of this discrepancy is not known. The 295 K solution spectra for 5:3:2 v/v ethanol−methanol−ether and for ethanol were very similar. Beer's law was found to hold for both solvents to within experimental error in the range of $(1-5 \times 10^{-5}$ M. No changes in the spectra were observed within the time required for the measurements (typically 1 h). Absorption spectra for $EtOH-MeOH-Et_2O$ solutions were determined initially by using a Cary 5e spectrophotometer.

[⊗] Abstract published in *Advance ACS Abstracts*, February 15, 1997.

(1) Hämmerle, B.; Müller, E. P.; Wilkinson, D. L.; Müller, G.; Peringer, P. *J. Chem. Soc., Chem. Commun.* **1989,** 1527.

(2) Kunkley, H.; Vogler, A. *Chem. Phys. Lett.* **1993,** *206*, 467.

(3) See for example Mason, W. R. *Inorg. Chem.* **1983,** *22*, 147. Isci, H.; Mason, W. R. *Inorg. Chem.* **1985**, *24*, 1761. Jaw, H.-R. C.; Savas, M. M.; Rogers, R. D.; Mason, W. R. *Inorg. Chem.* **1989**, *28*, 1028 and 4366. Smith, D. C.; Miskowski, V. M.; Mason, W. R.; Gray, H. B. *J. Am. Chem. Soc.* **1990,** *112*, 3759. Jaw, H.-R. C.; Mason, W. R. *Inorg. Chem.* **1990,** *29*, 3452; **1991,** *30*, 275 and 3552.

(4) Mingos, D. M. P. *J. Chem. Soc. Dalton Trans.* **1976,** 1163. Hall, K. P.; Mingos, D. M. P. *Prog. Inorg. Chem.* **1984**, *32*, 237.

(5) For a review of MCD spectroscopy together with the standard (Stephens) conventions adopted here, see: Piepho, S. B; Schatz, P. N. *Group Theory in Spectroscopy with Applications to Magnetic Circular Dichroism*; Wiley-Interscience: New York, 1983.

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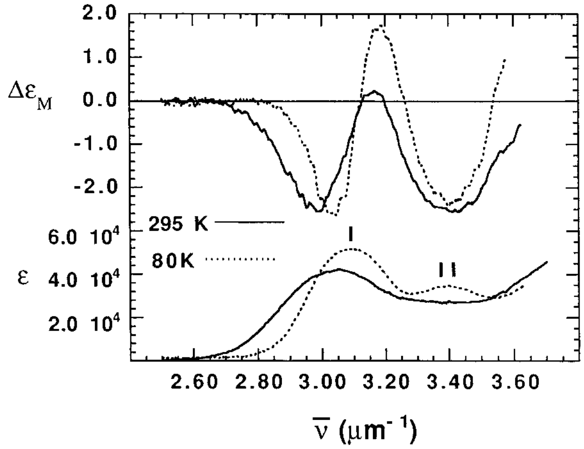

Figure 2. Magnetic circular dichroism (upper curves) and electronic absorption (lower curves) spectra for $Hg_3(dppm)_3(SO_4)_2$ in 5:3:2 v/v ethanol−methanol−ether solvent at 295 K (solid curves) and 80K (dotted curves). The units of ϵ and ϵ_M are M^{-1} cm^{-1} and M^{-1} cm^{-1} T^{-1} respectively and 1 $\mu m^{-1} = 10^4$ cm^{-1}.

Absorption and MCD spectra were then determined simultaneously and synchronously along the same light path by means of a spectrometer described earlier.[6] A magnetic field of 8.0 T was provided by a superconducting magnet system (Oxford Instruments Spectromag 4000, fitted with a variable-temperature insert). The spectra at 80 K were corrected for solvent contraction on glass formation (22 ± 1%). All spectra were corrected for solvent blank.

Results and Discussion

Figure 2 presents the absorption and MCD spectra for $Hg_3(dppm)_3(SO_4)_2$ in EtOH−MeOH−Et_2O solvent in the region 2.5−3.7 μm^{-1} (1 $\mu m^{-1} = 10^4$ cm^{-1}). The dppm ligand and SO_4^{2-} counter ions are transparent in this region, and the spectral features in Figure 2 are attributed to transitions within the Hg_3^{4+} cluster framework. The onset of strong absorption by the phenyl substituents on the dppm ligand at 3.7 μm^{-1} precluded the investigation of the spectra to higher energy. The MCD spectrum at 295 K shows two minima at 2.99 and 3.41 μm^{-1} which correspond to the intense band I at 3.05 μm^{-1} nm and a weaker unresolved band II near 3.40 μm^{-1}. At 80 K the MCD feature in the region of band I is resolved into a positive *A* term,[5] and the weaker absorption band II is resolved into a maximum at 3.40 μm^{-1}, so that the MCD minimum at 3.40 μm^{-1} is easily interpreted as a negative *B* term.[5] A moment analysis[7] of the 80 K spectra gave the following results: band I, $\bar{A}_1/\bar{D}_0 = +0.11 \pm 0.01$, $\bar{B}_0/\bar{D}_0 = (-8 \pm 1) \times 10^{-5}$ cm^{-1}, $\bar{\nu}_0 = 3.06$ μm^{-1}, $\bar{D}_0 = 6.9 \pm 0.3$; band II, $\bar{A}_1/\bar{D}_0 = 0.00$, $\bar{B}_0/\bar{D}_0 = (-1.0 \pm 0.3) \times 10^{-3}$ cm^{-1}, $\bar{\nu}_0 = 3.40$ μm^{-1}, $\bar{D}_0 = 0.40 \pm 0.05$. The bands in both the absorption and the MCD spectra decrease in band width at 80 K compared to 295 K, but the intensity does not decrease on cooling, which provides evidence for allowed electronic transitions. Band I is shifted slightly from 3.05 μm^{-1} at 295 K to 3.09 μm^{-1} at 80 K. Quantitative spectral data are collected in Table 1.

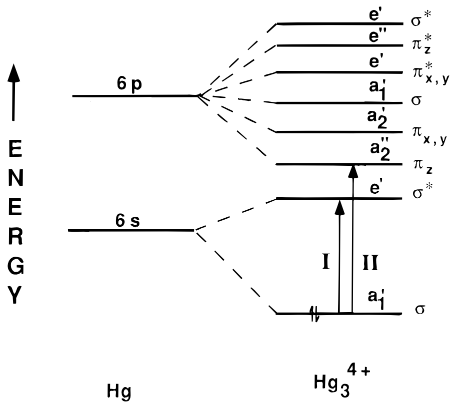

Figure 3. Metal-centered molecular orbital energy levels for Hg_3^{4+} in D_{3h} symmetry.

Table 1. Spectral Data for 5:3:2 v/v Ethanol−Methanol−Ether Solvent

	absorption			MCD	
band no.	$\bar{\nu}$, μm^{-1}	λ, nm	ϵ, (M cm)$^{-1}$	$\bar{\nu}$, μm^{-1}	$\Delta\epsilon_M$, (M cm T)$^{-1}$
			295 K Solution		
				2.99	−2.54
I	3.05	327	42 100	3.13	0.0
				3.16	+0.19
II	3.40	294	30 000[a]	3.41	−2.55
			80 K Glass		
				3.04	−2.53
I	3.09	323	51 400	3.12	0.0
				3.18	+1.63
II	3.40	294	35 000	3.40	−2.31

[a] Unresolved shoulder.

Table 2. Low-Energy Excited Configurations and States

confgn[a]	zero-order states	spin−orbit states[b]	$\bar{A}_1/\bar{D}_0$[c]
$(a_1')(e',\sigma^*)$	$^1E'$	$1E'$	neg
	$^3E'$	$2E'$	neg
		$1A_2''$	
		$(1A_1''$ $1E'')$	
$(a_1')(a_2'',\pi_z)$	$^1A_2''$	$2A_2''$	
	$^3A_2''$	$3E'$	pos
		$(2A_1'')$	
$(a_1')(a_2',\pi_{x,y})$	$^1A_2'$	$(1A_2')$	
	$^3A_2'$	$(1A_1', 2E'')$	
$(a_1')(a_1',\sigma_{6p})$	$^1A_1'$	$(2A_1')$	
	$^3A_1'$	$(2A_2', 3E'')$	

[a] Notation as in Figure 3. [b] Electric dipole forbidden states in parentheses. [c] Determined from eq 1 (see text).

In order to interpret the spectra, Figure 3 presents a schematic energy level diagram for the metal-centered MO's of the Hg_3^{4+} cluster. The Hg_3P_6 core of the complex is assumed to have D_{3h} local symmetry in solution, and the highest energy occupied orbital is a σ bonding a_1' MO composed of predominantly Hg 6s orbitals. The diamagnetic ground state is totally symmetric $^1A_1'$ $(a_1')^2$. Low energy excited configurations and states are given in Table 2. There the zero-order singlet and triplet states in the absence of spin−orbit coupling are listed together with the spin−orbit states in the presence of strong coupling. These latter states should be used for the Hg_3^{4+} cluster complex because of the strong heavy atom spin−orbit interaction (for example $\zeta_{6p} \cong 0.46$ μm^{-1} for a free Hg atom[8]). The lowest energy empty orbital was proposed[2] earlier to be the antibonding

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(6) Mason, W. R. *Anal. Chem.* **1982,** *54*, 646. The spectrometer has been upgraded by replacing the analog lock-in amplifier with a newer DSP lock-in (Stanford Research Systems SR850) and by replacing the PDP 11/03 computer by a faster PDP 11/73 computer. The optical components and measurement methodology remain essentially the same.

(7) See ref 5, chapter 7 for details concerning MCD parameters from moment analyses. The value of $\bar{\nu}_0$ is first found by setting the first absorption moment to zero. The zeroth moment about this $\bar{\nu}_0$ gives $\bar{D}_0$, which is proportional to the dipole strength of the transition. The MCD moments are then determined about $\bar{\nu}_0$. The zeroth MCD moment is proportional to $\bar{B}_0$ and the first MCD moment is proportional to $\bar{A}_1$.

(8) Moore, C. E. *Natl. Bur. Stand. Circ. (U. S.) No. 467*, **1958**, Vol III.

σ^* e′ MO, also composed of Hg 6s orbitals. In D_{3h} symmetry, electric dipole transitions are allowed to E′ (*xy*-polarized) and A_2'' (*z*-polarized) excited states. Formally spin-forbidden singlet → triplet transitions can gain intensity due to the effect of strong spin−orbit-coupling intermixing singlet and triplet excited states. The intensity of such transitions would be in proportion to the singlet character in the resulting spin−orbit excited state. A transition to a degenerate E′ spin−orbit state may exhibit an *A* term in the MCD spectrum due to Zeeman splitting in the magnetic field; transitions to both E′ and A_2'' states can exhibit B terms due to field induced mixing; but *C* terms will be absent because of the diamagnetic ground state.[5]

The assignment proposed[2] for band I is a $\sigma \rightarrow \sigma^*$ transition localized on the Hg_3^{4+} cluster (see Figure 3), which consists of the predominantly singlet-singlet $a_1' \rightarrow e'$ excitation and thus gives the 1E′ spin−orbit excited state (see Table 2 for notation). It is tempting to ascribe the positive *A* term observed in the region of band I to the transition to this state. However in order to provide a satisfactory assignment, the sign and approximate magnitude of the *A* term must be consistent with the nature of the electronic state. The space averaged MCD *A* term expected for an E′ state in solution is given by eq 1,[5] where $\bar{D}_0$ =

$$\bar{A}_1/\bar{D}_0 = -(2)^{-1/2}\mu_B^{-1}\langle E'||\mu||E'\rangle \qquad (1)$$

$^1/_3|\langle A_1'||\mathbf{m}||E'\rangle|^2$ is related to the dipole strength of the transition to the E′ state, μ_B = Bohr magneton, $\mu = -\mu_B(\mathbf{L} + 2\mathbf{S})$ and $\mathbf{m} = e\mathbf{r}$ are the magnetic and electric moment operators, respectively, in the reduced matrix elements. The reduced matrix element in eq 1 can be calculated for the transition to the predominantly singlet 1E′ spin−orbit state in terms of the one-electron e′ ± 1 MO's in a standard basis,[5] eq 2. Since the e′

$$\bar{A}_1/\bar{D}_0 = \pm\langle e' \pm 1|l_0|e' \pm 1\rangle \qquad (2)$$

orbitals are assumed to becomposed of Hg 6s atomic orbitals, the origin of the *A* term must arise from two-centered integrals because one-centered terms would lack any orbital angular momentum. In order to test this hypothesis, the two-centered terms necessary to determine the matrix element of eq 2 were approximated (in units of $\hbar$) by terms as in eq 3,[9] where ϕ_i and

$$\langle\phi_i|l_z|\phi_j\rangle = iR_{0j}\cos 60\,\langle\phi_i|\partial/\partial x_j|\phi_j\rangle \qquad (3)$$

ϕ_j (i, j = 1, 2, 3) represent the 6s atomic orbitals on the three Hg atoms, $i = \sqrt{-1}$, and R_{0j} is the distance from the origin to Hg atom *j*. If the 6s functions are approximated by Slater type orbitals, the right side of eq 3 can be reduced to overlap integrals and therefore can be evaluated for the average Hg−Hg distance in the Hg_3^{4+} cluster. When substitutions were made into eq 3, the $\langle\phi_i|l_z|\phi_j\rangle$ matrix elements were found to be positive and of small magnitude, proportional to the overlap.[10] When these results are then substituted into the right side of eq 2, using the standard basis e′ orbital functions[5], the $\bar{A}_1/\bar{D}_0$ ratio is found to be *negative* (≈−0.5 or smaller). Therefore the prediction for the $\sigma \rightarrow \sigma^*$ transition to the 1E′ state is for $\bar{A}_1/\bar{D}_0$ to be *negative* and have a small value, determined by the magnitude of the overlap integrals. Thus the observed positive *A* term in the region of band I is not consistent with the $\sigma \rightarrow \sigma^*$ assignment in this approximation. The involvement of the higher energy Hg 6p orbitals in the σ bonding in the triangular plane (as some type of sp hybrid) might also be visualized. This possibility was also considered. When the e′ orbitals were assumed to be linear combinations of both 6s and in-plane 6p orbitals, $\sigma_{6s} + \lambda\sigma_{6p}$, for example, several one-centered terms were found to contribute to $\bar{A}_1/\bar{D}_0$ in eq 1. These terms also result in *negative* values for $\bar{A}_1/\bar{D}_0$, but they are larger than those for 6s alone because of the orbital angular momentum of the 6p orbitals. A third possible explanation of the observed *A* term is that it could result from a weak unresolved transition to the 2E′ state of triplet parentage from the $a_1'e'$ excited configuration. However straightforward reasoning shows that the *A* term for a transition to this state depends only on orbital angular momentum and therefore is predicted to have the same sign (negative) as the *A* term for the 1E′ state of the same excited configuration and thus can not explain the observed MCD. Therefore, either the assignment of band I is not correct, or the assignment is correct, but the *A* term is too weak to be detected, and there are other transitions in the same region that can account for the observed MCD spectrum. This latter possibility is considered the most reasonable.

In order to interpret the positive *A* term found in the region of band I, the assignment of band II must be considered in detail. The presence of band II as a poorly defined shoulder was noted earlier,[2] but it was neither assigned nor discussed further. The negative MCD feature at 3.40 μm^{-1} and the 80 K absorption maximum at 3.40 μm^{-1} (Figure 2) clearly establish the presence of an electronic transition of lower intensity and about 0.3 μm^{-1} higher in energy than band I. Therefore on the basis of its energy and lower absorption intensity, a logical assignment of band II would be to the $\sigma \rightarrow \pi$ transition from $a_1' \rightarrow a_2''$ (see Figure 3). The predominantly singlet excited state would be non degenerate $2A_2''$ and would be expected to exhibit a *B* term in the MCD spectrum. The sign of the *B* term would depend upon the state(s) with which the $2A_2''$ state is magnetically coupled. The a_2'' orbital is an out-of-plane π orbital composed of $6p_z$ orbitals on the Hg atoms. To a first approximation the 6s σ^* e′ orbital and the out-of-plane 6p π a_2'' orbital will have zero coupling matrix elements of the type $\langle e' \pm 1|l_0|a_2''\rangle$ and therefore no mutual *B* term contributions are expected for the 1E′ and $2A_2''$ states. The negative *B* term for band II must arise from magnetic interaction with a state or states to higher energy, beyond the range of the present study (for example from E′ states resulting from transitions to the 6p MO's e′ $\pi^*_{x,y}$ or e′ σ^*—see Figure 3). The present results do not provide any experimental basis for making a *B* term sign prediction, but the observation of a *B* term for band II seems consistent with the $2A_2''$ assignment. Furthermore, if the $2A_2''$ state assignment for band II is accepted, then a possible source for the positive *A* term in the region of band I can be envisioned. The spin−orbit state 3E′ is predicted to be lower in energy than the $2A_2''$ state, and the $\bar{A}_1/\bar{D}_0$ ratio calculated for this state, which depends on spin angular momentum, is *positive*. Therefore the *A* term associated with a weak unresolved transition to the 3E′ state would be expected to be *positive* and to lower energy than band II, just where the intense band I is found. Band I would certainly obscure the associated absorption for the transition to the 3E′ state. The small experimental $\bar{A}_1/\bar{D}_0$ value of +0.11 is probably reasonable in view of the large $\bar{D}_0$ value for band I due primarily to the transition to 1E′. This interpretation of the positive A term in the region of band I leads to the conclusion that if the $\sigma \rightarrow \sigma^*$ 1E′ state is responsible for the

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[9] Stephens, P. J.; Suetaak, W.; Schatz, P. N. *J. Chem. Phys.* **1966**, *44*, 4592. Equation 2 results when $l_0 = l_z$ is translated from the origin to Hg atom *j* with the integral $\langle\phi_i|l_{zj}|\phi_j\rangle = 0$.

[10] The integrals consist of terms of opposite sign, which give a small (positive) difference. The difference was found to be approximately +0.61 for Hg−Hg of 2.80 Å. Slater exponents for Hg given by Underwood et al. (Underwood, D. J.; Hoffman, R.; Tatsumi, K.; Nakamura, A.; Yamamoto, Y. *J. Am. Chem. Soc.* **1985**, *107*, 5968) were used for the calculation. Because of the approximations involved, the quantitative values are not deemed precise, but the sign and small magnitude are considered reliable.

intensity of band I as proposed,[2] the (negative) *A* term for the 1E′ state must be quite small and obscured by the positive *A* term for the 3E′ $\sigma \rightarrow \pi$ state. Thus a small and essentially undetected *A* term for the $\sigma \rightarrow \sigma^*$ transition to the 1E′ state provides a measure of indirect support for the 6s atomic orbital description of the $Hg_3{}^{4+}$ σ and σ^* MO's because if 6p orbitals were involved to any significant extent, a negative *A* term should be observed.

The large Stokes shift suggested from the emission study[2] was used as a basis for postulating a Jahn−Teller distortion in the emitting state. The possibility that the two MCD features and band I and II could be due to Jahn−Teller components from a single distorted excited E′ state was considered. If an E′ state is distorted, its degeneracy will be lifted and two non degenerate states will be produced. To a first approximation these two components will transform like the two partners of the degenerate E′ state. If there is a nonzero *A* term for the E′ state, then it can be shown that as the degeneracy is lifted there will be two *B* terms of opposite sign (pseudo-*A* term) associated with the two nondegenerate states.[5] Furthermore, the transition intensity to the two nondegenerate states should be approximately the same. Thus it seems unlikely that the observed spectra, where the MCD features are different and where the intensity of the two transitions is significantly different, can be interpreted in terms of an excited state Jahn−Teller splitting of an E′ state. The distorted emitting state, which was presumed to be a triplet state lower in energy than the 1E′ state,[2] is simply not detected by the absorption or MCD spectra.

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