Electronic Absorption and MCD Spectra for $BiX_6{}^{3-}$, X = Cl^-, Br^-, and I^-, in Acetonitrile Solution: Metal-Centered vs Ligand-to-Metal Charge-Transfer Assignments

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Electronic absorption and 8.0 T magnetic circular dichroism (MCD) spectra at room temperature have been carefully measured for $BiX_6{}^{3-}$ complexes in acetonitrile solutions containing excess halide ligand. In each case the spectra exhibit a prominent low-energy band that is accompanied by a strong positive *A* term and is assigned to a metal-centered (MC) 6s to 6p transition to a formally triplet state which correlates with the $^3P_1$ atomic state (A band). At higher energy intense bands are observed with accompanying MCD spectra that resemble somewhat weaker negative *A* terms, though the MCD is rather broad and consists of overlapping features. These bands are ascribed to ligand-to-metal charge-transfer (LMCT) transitions from nonbonding or weakly π bonding halide np orbitals to the metal 6p orbital. Previous assignment of these higher energy bands to the MC 6s to 6p transition to the predominantly singlet state which correlates with the $^1P_1$ atomic state (C band) is shown to be inconsistent with the observed MCD.

Introduction

Halo complexes of Bi(III) and other ns² metal ions Pb(II), Tl(I), Hg(0), Sb(III), and Sn(II), for example, exhibit two intense electronic absorption band systems in the UV−vis region which have been assigned as metal-centered (MC) ns to np transitions.[1−7] In several cases magnetic circular dichroism (MCD) spectra[8] for solutions or solid halide matrices have been used to interpret the lowest energy bands as transitions to formally triplet states which correlate with the $^3P_1$ nsnp atomic state (A band).[9−17] The higher energy bands in these complexes were also assumed to be MC ns to np transitions to the predominantly singlet state which correlates with the $^1P_1$ atomic state (C band). However, recently there has been a growing recognition that both band systems possess varying degrees of ligand-to-metal charge-transfer (LMCT) character based on the typical observation of substantial red shifts in the spectra with the energy order I^- < Br^- < Cl^-.

The present report describes a study of the electronic absorption and MCD spectra of $BiCl_6{}^{3-}$, $BiBr_6{}^{3-}$, and $BiI_6{}^{3-}$ in acetonitrile solutions, which contain excess halide. These new spectral measurements provide a basis for discussion of MC 6s to 6p and LMCT halide to 6p transitions in six coordinated Bi(III) halo complexes. These transitions are of interest because of the very strong spin−orbit coupling from the Bi(III) and also from the iodo ligand in $BiI_6{}^{3-}$.

Experimental Section

The $BiX_6{}^{3-}$ ions were produced in acetonitrile solution by dissolving solid n-$Bu_4N[BiX_4]$ compounds in solutions containing 40−50:1 excess halide. The solid n-$Bu_4N[BiX_4]$ compounds were prepared by precipitation from aqueous solutions of BiX_3 dissolved in concentrated HX (aq) by adding concentrated aqueous solutions of n-Bu_4NX. The solid

compounds (Cl^-, white; Br^-, pale yellow; and I^-, bright orange) were collected by filtration and then washed with water, a small amount of cold ethanol, and finally diethyl ether. They were dried under vacuum overnight and analyzed; they gave satisfactory elemental analyses. When the solid n-$Bu_4N[BiX_4]$ complexes were dissolved in acetonitrile solution, Beer's law did not hold. However, in the presence of excess halide (ca. 40−50:1) the absorption bands shifted slightly to the red, and Beer's law was found to hold to within experimental error in the range 10^{-4}−10^{-5} M in Bi(III). An earlier study[4] showed that the emission spectrum for $Et_4N[BiCl_4]$ in acetonitrile changes markedly on the addition of excess Cl^- (ca. 83:1). This change was interpreted as formation of $BiCl_6{}^{3-}$ from $BiCl_4{}^-$ in the presence of excess Cl^-. Furthermore, a study here of the spectra for $BiI_4{}^-$ as a function of added I^- showed an isosbestic point at 2.248 μm⁻¹ (1 μm⁻¹ = 10^4 cm⁻¹) when the I^-:Bi(III) ratio was greater than 2.5, and the spectra showed very little change when the ratio was more than 20. For the measurements reported here, the excess halide:Bi(III) ratio was maintained between 40:1 and 50:1, and under these conditions, it was assumed that the Bi(III) solution species in each case is $BiX_6{}^{3-}$.

Electronic absorption spectral measurements were made by means of a Cary 5E spectrophotometer, and then simultaneous electronic absorption and MCD spectra along the same light path were measured by means of a computer-controlled spectrometer and an 8.0 T superconducting magnet system (Oxford Instruments Spectromag 4000) as described previously.[18] The solutions used for the measurements were

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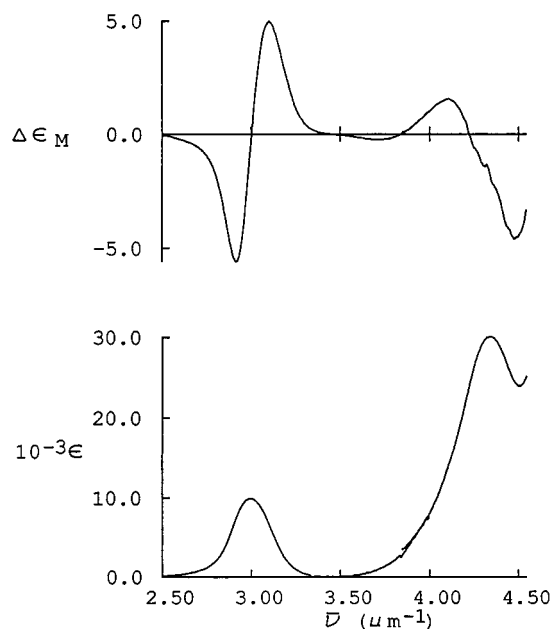(17) Tsuboi, T. *Physica* **1981**, *106B*, 97.

Figure 1. . Electronic absorption (lower curve) and MCD (upper curve) spectra for $BiCl_6^{3-}$ in acetonitrile solution containing a 50-fold excess of Et_4NCl. Units for the x-axis are $\mu m^{-1} = 10^4$ cm^{-1}; for the y-axis ϵ is in units of (M cm)$^{-1}$ and $\Delta\epsilon_M$ is in units of (M cm T)$^{-1}$.
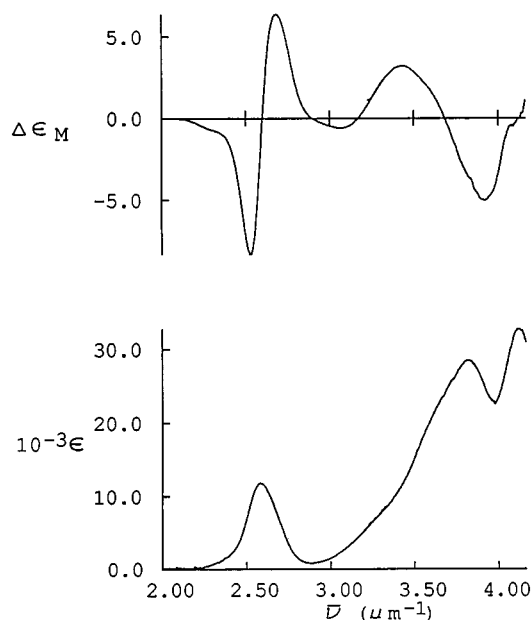

Figure 2. Electronic absorption (lower curve) and MCD (upper curve) spectra for $BiBr_6^{3-}$ in acetonitrile solution containing a 50-fold excess of n-Bu$_4$NBr. Units are as in Figure 1.

freshly prepared, were stored in the dark prior to use, and did not exhibit any change during the time required to obtain the spectra (typically 0.5–1 h). All spectra were corrected for the halide-containing blank.

Results and Discussion

Electronic Absorption and MCD Spectra for BiX_6^{3-}. Figures 1–3 present the absorption and MCD spectra for the BiX_6^{3-} complexes in acetonitrile solution containing excess X$^-$, while Table 1 summarizes quantitative spectral data. The absorption spectra for $BiCl_6^{3-}$ and $BiBr_6^{3-}$ compare favorably with earlier measurements[4,7] where acetonitrile solutions contained excess Cl$^-$ and Br$^-$, respectively. Figures 1–3 show that

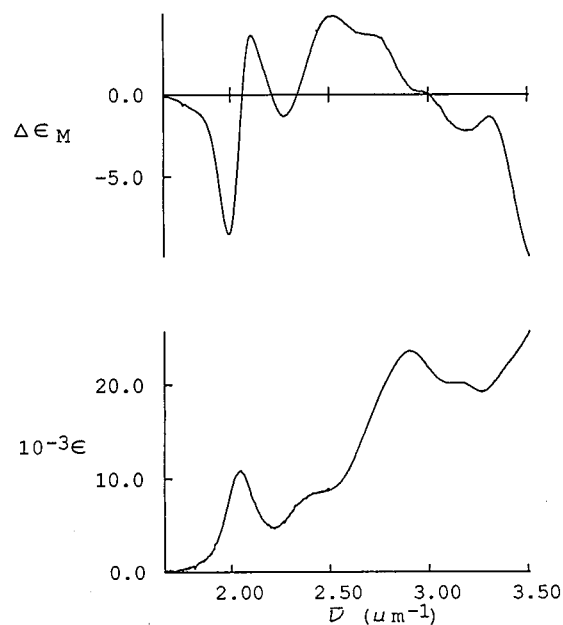(18) Mason, W. R. *Anal. Chem.* **1982**, *54*, 646.

Figure 3. Electronic absorption (lower curve) and MCD (upper curve) spectra for BiI_6^{3-} in acetonitrile solution containing a 50-fold excess of n-Bu$_4$NI. Units are as in Figure 1.

Table 1. Spectral Data for Acetonitrile Solution

	absorption			MCD	
band no.	$\bar{\nu}, \mu m^{-1}$ [a]	λ, nm	ϵ, (M cm)$^{-1}$	$\bar{\nu}, \mu m^{-1}$ [a]	$\Delta\epsilon_M$, (M cm T)$^{-1}$
		$BiCl_6^{3-}$ [b]			
				2.91	−5.58
I	2.99	334	9 520	3.00	0
				3.10	+5.02
				3.71	−0.23
				4.11	+1.55
II	4.34	231	28 600	4.22	0
				4.48	−4.55
		$BiBr_6^{3-}$ [c]			
				2.53	−8.33
I	2.59	387	11 700	2.60	0
				2.68	+6.39
II	3.24	308	5 300[d]	3.07	−0.59
				3.44	+3.18
III	3.82	262	27 200	3.68	0
				3.91	−4.99
IV	4.12	243	31 500		
		BiI_6^{3-} [e]			
				1.99	−8.49
I	2.04	490	10 800	2.06	0
				2.11	+3.65
				2.27	−1.31
II	2.43	412	8 460[d]		
				2.52	+4.84
				2.72	+3.67[d]
III	2.90	345	23 500		
				2.95	+0.18[d]
IV	3.16	317	20 000[d]	3.20	−2.23

[a] 1 $\mu m^{-1} = 10^4$ cm^{-1}. [b] [Et$_4$NCl] $= 4.98 \times 10^{-3}$ M. [c] [n-Bu$_4$NBr] $= 4.98 \times 10^{-3}$ M. [d] Shoulder. [e] [n-Bu$_4$NI] $= 5.21 \times 10^{-3}$ M.

in each case a prominent positive A term for the lowest energy band (band I) is observed in the MCD spectra. The higher energy band system in both absorption and MCD becomes progressively more complicated from $BiCl_6^{3-}$ to $BiBr_6^{3-}$ to BiI_6^{3-}, but overall the MCD resembles a negative A term through the system. Both band systems exhibit a pronounced systematic red shift from
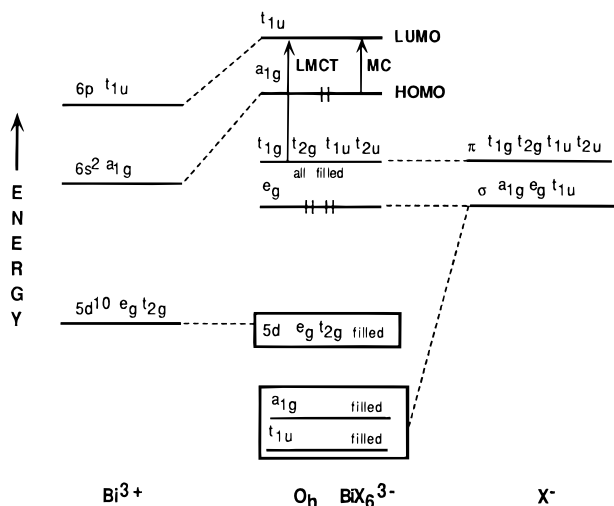
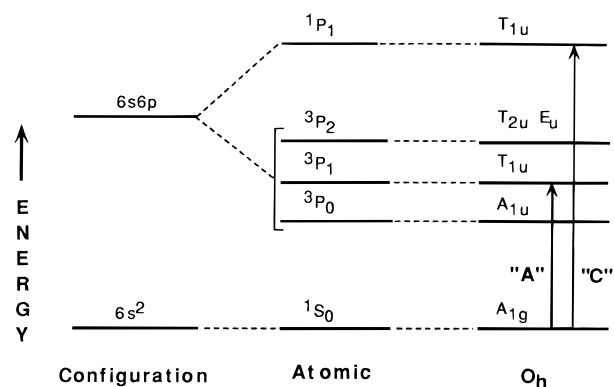**Figure 4.** Schematic molecular orbital energy level diagram for the BiX_6^{3-} ions assuming O_h symmetry.

Figure 5. Energy level correlation between atomic states and MC 6s to 6p transitions for the O_h BiX_6^{3-} ions.

$BiCl_6^{3-}$ to $BiBr_6^{3-}$ to BiI_6^{3-}, but the higher energy more intense system seems to shift more strongly ($5000-9000$ cm^{-1}) compared to the weaker lower energy system ($4000-5500$ cm^{-1}).

The positive A term observed for band I for each of the complexes is sufficiently separated from the higher energy bands that a moment analysis[19] was deemed feasible. The moment analysis of the experimental spectra provides a measure of the sign and magnitude of an A term in terms of the parameter ratio A_1/D_0. The results of this analysis showed that the A_1/D_0 values (calculated about $\bar{\nu}_0$) were $BiCl_6^{3-}$, $+1.6$ (3.01 μm^{-1}), $BiBr_6^{3-}$, $+1.7$ (2.60 μm^{-1}), and BiI_6^{3-}, $+1.8$ (2.04 μm^{-1}), respectively. A moment analysis of the higher energy band systems was not attempted because of the overlapping features observed.

Electronic States and MCD Terms for BiX_6^{3-}. Figure 4 shows a schematic molecular orbital energy level diagram for the $6s^2$ BiX_6^{3-} ions. The highest occupied orbital (HOMO) is the a_{1g} MO, which is predominantly 6s on Bi(III), and the lowest empty orbital (LUMO) is the t_{1u} MO, predominantly Bi(III) 6p. Both 6s6p MC and halide np Bi(III) LMCT transitions are noted by the arrows in Figure 4. Figure 5 illustrates the correlation between Bi(III) atomic states and the 6s6p MC states for the

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(19) See ref 8, 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 0. The zeroth moment about this $\bar{\nu}_0$ gives 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 B_0 (the MCD B term), and the first MCD moment is proportional to A_1.

Table 2. Low-Energy Electronic States[a] for BiX_6^{3-}

MC 6s6p Excited States			
$^1T_{1u}$		T_{1u}	
$^3T_{1u}$		(A_{1u}) (E_u) T_{1u} (T_{2u})	

LMCT $t_{2g}t_{1u}$ Excited States		LMCT $t_{1g}t_{1u}$ Excited States	
$^1A_{2u}$	(A_{2u})	$^1A_{1u}$	(A_{1u})
$^3A_{2u}$	(T_{2u})	$^3A_{1u}$	T_{1u}
^1E_u	(E_u)	^1E_u	(E_u)
^3E_u	T_{1u} (T_{2u})	^3E_u	T_{1u} (T_{2u})
$^1T_{1u}$	T_{1u}	$^1T_{1u}$	T_{1u}
$^3T_{1u}$	(A_{1u}) (E_u) T_{1u} (T_{2u})	$^3T_{1u}$	(A_{1u}) (E_u) T_{1u} (T_{2u})
$^1T_{2u}$	(T_{2u})	$^1T_{2u}$	(T_{2u})
$^3T_{2u}$	(A_{2u}) (E_u) T_{1u} (T_{2u})	$^3T_{2u}$	(A_{2u}) (E_u) T_{1u} (T_{2u})

[a] Forbidden states in parentheses.

Table 3. A_1/D_0 Values for T_{1u} Excited States[a]

MC 6s6p			
$T_{1u}(^1T_{1u})$	$+2.00$	$T_{1u}(^3T_{1u})$	$+3.00$
LMCT $t_{2g}^5t_{1u}$		LMCT $t_{1g}^5t_{1u}$	
$T_{1u}(^3E_u)$	-2.00	$T_{1u}(^3A_{1u})$	$+4.00$
$T_{1u}(^1T_{1u})$	-0.50	$T_{1u}(^3E_u)$	-2.00
$T_{1u}(^3T_{1u})$	$+1.75$	$T_{1u}(^1T_{1u})$	$+1.50$
$T_{1u}(^3T_{2u})$	-2.25	$T_{1u}(^3T_{1u})$	$+2.75$
		$T_{1u}(^3T_{2u})$	-1.25

[a] By approximating t_{1u} as Bi^{3+} 6p and t_{2g} or t_{1g} as np on X^- (see Chapter 8 of ref 8 for detailed procedure for determining A_1/D_0).

BiX_6^{3-} ions in O_h symmetry. The excited spin−orbit states from the 6s6p MC configuration and also the $t_{2g}^5t_{1u}$ and $t_{1g}^5t_{1u}$ LMCT configurations are collected in Table 2. Transitions from the diamagnetic, totally symmetric ground state $^1A_{1g}$ are fully allowed only to T_{1u} excited states in the O_h symmetry assumed for the complex ions. The transitions to the various T_{1u} states are expected to show A terms in the MCD, the sign and magnitude of which are dependent upon the spin and orbital composition of the state. The A term ratio A_1/D_0 for an isotropic O_h complex is given by eq 1,[8] where D_0, the dipole strength of

$$A_1/D_0 = 2/(6^{1/2}\mu_B) \langle T_{1u}||\mu^T_1||T_{1u}\rangle \tag{1}$$

the transition, is given by $D_0 = (1/3)|\langle^1A_{1g}||\mathbf{m}^T_{1u}||^1T_{1u}\rangle|^2$, in which $\mathbf{m} = e\mathbf{r}$; μ_B is the Bohr magneton; and the reduced matrix element (RME) in eq 1 is of the magnetic moment operator $\mu = -\mu_B(\mathbf{L} + 2\mathbf{S})$ where $\mathbf{L}$ and $\mathbf{S}$ are the orbital and spin angular momentum. The A term sign and relative magnitude may be determined from A_1/D_0 ratios for the T_{1u} states of Table 2 by approximating the one-electron MOs as 6p Bi(III) atomic orbitals for t_{1u} MO or np halide atomic orbitals for t_{2g} and t_{1g} MOs. Using a standard basis and the usual conventions[8] for evaluating the RME in eq 1 in a one-center approximation, the A_1/D_0 values were determined for the T_{1u} states of Table 2 and are given in Table 3 (Chapter 18 of ref 8 should be consulted for the detailed procedure).

Band Assignments. The strong positive A term observed for the lowest energy band, band I in each case, is consistent with the 6s6p MC transition to the $T_{1u}(^3T_{1u})$ state, as assigned previously. The magnitudes of the A terms from the moment analysis ($+1.6-1.8$, see above) are somewhat lower than predicted ($+3.00$) from the simple approximations and the use of eq 1, but this can be rationalized by (1) a quenching of the orbital contribution to the excited state magnetic moment due to covalent bonding of the t_{1u} metal 6p orbital (a complete orbital quenching would predict a value of $+2.00$) and (2) some reduction of the spin moment contribution due to spin−orbit coupling with the MC $T_{1u}(^1T_{1u})$ state at higher energy. Lower moments were also found from the MCD for Bi(III), Pb(II),

and Tl(I) in aqueous acid solution.[10] The red shift observed as Cl^- is replaced by Br^- and then by I^- is also consistent with covalent halide contribution to both the a_{1g} HOMO and the t_{1u} LUMO, which would make the energies of these orbitals sensitive to the halide ligand.

In contrast to band I for the BiX_6^{3-} ions, the assignment of the higher energy more intense band (band II for $BiCl_6^{3-}$, and band III for $BiBr_6^{3-}$ and BiI_6^{3-}) to the 6s6p MC transition to $T_{1u}(^1T_{1u})$ is *not* consistent with the MCD spectra where in each case the observed feature resembles a negative *A* term. The transition to the MC $T_{1u}(^1T_{1u})$ state is expected to show a positive *A* term, though of smaller magnitude than the lower energy transition to $T_{1u}(^3T_{1u})$. Table 3, however, shows that a number of transitions to the LMCT states, especially from the $t_{2g}^5t_{1u}$ configuration, are expected to have negative *A* terms in the MCD. Thus a logical assignment for the higher energy band system would be to one or more of these LMCT transitions. In view of the high intensity of the absorption for band II for $BiCl_6^{3-}$, and band III for $BiBr_6^{3-}$ and BiI_6^{3-}, a reasonable assignment might be to a transition to a $T_{1u}(^1T_{1u})$ state with predominantly singlet character from either the $t_{2g}^5t_{1u}$ or $t_{1g}^5t_{1u}$ configuration. The $T_{1u}(^1T_{1u})$ state from the $t_{1g}^5t_{1u}$ configuration can be ruled out because it should have a strong positive *A* term, contrary to what is observed. The $T_{1u}(^1T_{1u})$ state from the $t_{2g}^5t_{1u}$ configuration, on the other hand, is expected to show a negative *A* term, weaker than for band I (see Table 3), and therefore would be consistent with experiment. If this assignment is made, then a transition to the corresponding $t_{2g}^5t_{1u}$ $T_{1u}(^3T_{1u})$ state of triplet parentage would be expected to lower energy and should have a positive *A* term, the magnitude of which should be in proportion to the singlet character in the $T_{1u}(^3T_{1u})$ spin−orbit state. A close examination of the MCD spectra shows a weak negative signal between band I and the higher energy band system for all three complexes, which together with the broadness on the lower energy (positive) side of the negative *A* term for the intense band system may signal the presence of the positive *A* term for this transition. The broadness on the low-energy side of the absorption band II for $BiCl_6^{3-}$ and the weak shoulders (bands II) observed in the absorption spectra for $BiBr_6^{3-}$ and BiI_6^{3-} are thus interpreted as the weak transition to the $T_{1u}(^3T_{1u})$ LMCT state. It is noteworthy that the higher band system becomes more complicated as the halide ligand becomes heavier. This behavior is consistent with the increased spin−orbit coupling from the halo ligand (ζ_{3p} = 587 cm^{-1} for Cl^-, ζ_{4p} = 2457 cm^{-1} for Br^-, and ζ_{5p} = 5069 cm^{-1} for I^-), which is a characteristic feature of LMCT from np orbitals in halo complexes.[20] Increased ligand spin−orbit coupling is expected to enhance the intermixing of the LMCT T_{1u} spin−

orbit states of different spin parentage, giving greater intensity to transitions that would be formally spin forbidden in the absence of strong spin−orbit coupling. The net effect would be to make the spectrum more complicated as the intensity is spread over several close-lying states.

In addition to the support given from the observed MCD discussed above, the assignment of the higher energy band system in BiX_6^{3-} as LMCT rather than MC 6s to 6p can be supported on energetic grounds. The energy separation of the 6s and 6p orbitals in the free Bi(III) ion can be estimated from atomic spectral data[21] to be 3.87 μm^{-1}, so that the transition to the state corresponding to $^1P_1$ in the free ion (the C band) should be at least 3−3.5 μm^{-1} higher in energy than the transition corresponding to the $^3P_1$ state in the free ion (the A band). If band I for the BiX_6^{3-} ions is reasonably associated with the A band of the free ion, then the C band should be found at energies more than 3 μm^{-1} higher. In contrast, the observed energy separations between band I and the higher energy band systems (taken to be the intense maximum in each case) are only 1.35, 1.23, and 0.84 μm^{-1}, respectively, for $BiCl_6^{3-}$, $BiBr_6^{3-}$, and BiI_6^{3-}. The C band in the complexes is thus expected to be at higher energy than the intense band systems observed here and in a region obscured by absorption due to the excess halide in acetonitrile solution. Thus LMCT from halide to Bi(III) seems completely plausible for the intense band systems in the BiX_6^{3-} ions.

Conclusions

The lowest energy band presented by the BiX_6^{3-} ions is easily ascribed to the 6s6p MC transition to the $T_{1u}(^3T_{1u})$ state which correlates with the $^3P_1$ atomic state and thus with the A band of the 6s^2 metal ion. The band energy is expected to depend upon the halide ligand due to ligand character in the HOMO and LUMO resulting from X^-−Bi(III) covalent bonding. In contrast, the higher energy band system observed for these ions is assigned here on the basis of the MCD spectral results as predominantly LMCT from halide np to Bi(III) 6p. Given the high positive charge on the Bi(III) and therefore stable 6p LUMO, LMCT transitions from the halide np orbitals are visualized as shifted into the region between the A band and the higher energy C band which correlates with the $^1P_1$ atomic state; this latter band is estimated to be at least 3−3.5 μm^{-1} higher in energy than the A band.

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