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Symmetry Aspects of the Electronic Spectra of Binuclear Complexes with D_{3h} Symmetry

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The definition of σ, π, and δ bonds refers to the angular momentum properties of the corresponding orbitals. By resorting to real expressions for the d orbitals, one can define percent π and δ character of metal–metal bonding orbitals in D_{3h} symmetry. The MO level scheme is a_1 (σ), e′ $({}^{2}/_{3}\delta + {}^{1}/_{3}\pi)$, e″ $({}^{2}/_{3}\delta^* + {}^{1}/_{3}\pi^*)$, e″ $({}^{2}/_{3}\pi^* + {}^{1}/_{3}\delta^*)$, and a_2'' (σ^*). This serves as a starting point for an analysis of the "anomalous" optical bands in the $Mo_2X_9^{n-}$ and $W_2X_9^{n-}$ (X = Cl, Br; $n = 2, 3$) ions. In so doing one must recall that weak orbital overlap produces large singlet–triplet separations. Two moderately intense bands at approximately 13 300 and 15 500 cm^{-1} in the electronic absorption spectra of $M_2X_9^{3-}$ complexes are attributed to e′ $({}^{2}/_{3}\delta + {}^{1}/_{3}\pi) \rightarrow$ e′ $({}^{2}/_{3}\pi + {}^{1}/_{3}\delta)$ and a_1' (σ) $\rightarrow$ e′ $({}^{2}/_{3}\pi + {}^{1}/_{3}\delta)$ transitions. The e′ $({}^{2}/_{3}\pi + {}^{1}/_{3}\delta)$ orbital is primarily of metal–ligand σ-antibonding character. An intense absorption at ca. 21 000 cm^{-1} in the electronic absorption spectra of $W_2X_9^{3-}$ (X = Cl, Br) complexes is assigned to the $a_1' \rightarrow a_2''$ ($\sigma \rightarrow \sigma^*$) one-electron excitation. Analogous transitions are present in the $M_2X_9^{2-}$ (M = Mo, W) complexes.

Introduction

Metal d orbital σ, π, and δ bonds have been the subject of intense experimental and theoretical study.[1] Although covalent metal–ligand interactions can spoil the simple conceptual picture, the utility of classifying metal–metal overlap according to σ, π, and δ character remains useful. In compounds such as $Mo_2Cl_8^{4-}$, $Re_2Cl_8^{2-}$, and other d^4–d^4 dimers, the metal–metal interaction picture remarkably well approximates the bonding situation.[1] Even in more sophisticated theoretical treatments a model finds application as a means of describing complex wave functions.

Real representations of atomic d orbitals $|z^2\rangle$, $|xy\rangle$, $|xz\rangle$, $|yz\rangle$, and $|x^2 - y^2\rangle$ are well suited for discussing metal–metal interactions when a fourfold symmetry axis coincides with the metal–metal bond. However, the extension of the discussion to complexes with a confacial bioctahedral (D_{3h}) structure,[2] Figure 1 (e.g., $M_2X_9^{n-}$ (M = Cr, Mo, W; X = Cl, Br; n = 2, 3)), requires some modifications.

Most of our discussion will be an application of theory, which was originally derived by Abragram, Pryce, and Runciman;[3] however, the essential features of trigonal symmetry were recognized by Van Vleck[4] as early as 1938. Mixing of π and δ character was recently employed by Hoffmann et al.[5] to analyze rotational barriers in ML$_3$(olefin) complexes as well as metal–ligand and metal–metal bonding in M_2L_9 compounds. In this paper we consider the types of expected optical transitions from a valence bond viewpoint.

The optical spectra of the $M_2X_9^{3-}$ compounds have remained an unexplained puzzle. Saillant and Wentworth,[6] and at about the same time Smith and Wedd,[7] noted that the visible absorption spectrum of $Cr_2Cl_9^{3-}$ resembles that of $CrCl_6^{3-}$. This implies essentially no metal–metal interaction in the dimer excited states, and magnetic[6] as well as crystallographic[8] data support a similar conclusion for the ground states. Analogous molybdenum(III) compounds $Mo_2X_9^{3-}$ (X = Cl, Br) show magnetic[9] and crystallographic[8] evidence for weak metal–metal bonding. Interestingly enough, two moderately intense ($\epsilon \sim 75$) and perpendicularly polarized optical absorption bands appear at 13 350 and 15 150 cm^{-1} (X = Cl).[9] These features could not be attributed to transitions present in $MoCl_6^{3-}$. The complexes $W_2X_9^{3-}$ (X = Cl, Br) are diamagnetic.[6] Both X-ray crystallography[7,10] and the vibrational studies of Ziegler and Risen[11] indicate strong metal–metal bonding. Again, two "anomalous", moderately intense absorptions are present in the electronic spectrum, now at 13 200 and 15 900 (X = Cl).[9] Furthermore, an intense electronic absorption band appears[9] at 21 900 cm^{-1}. Assignment of these transitions and also the spectra of $M_2X_9^{2-}$ compounds will be discussed.

Results and Discussion

Consider the D_{3h} confacial bioctahedral arrangement[2] (Figure 1) and the nature of the metal-localized d orbitals. When confronted with two octahedra joined along a C_3 axis, it is natural to begin the analysis with d-orbital wave functions which are quantized along the C_3 axis[2,3] (assumed to be the z direction of the metal-centered coordinate system). Recasting the C_3-quantized d orbitals in real form[12] and imposing local O_h symmetry[13] yield

$$t_{2g}{}^{0} = |z^2\rangle$$

$$t_{2g}{}^{+} = \sqrt{2/3}|x^2 - y^2\rangle - \sqrt{1/3}|xz\rangle = \sqrt{2/3}\delta - \sqrt{1/3}\pi$$

$$t_{2g}{}^{-} = \sqrt{2/3}|xy\rangle + \sqrt{1/3}|yz\rangle = \sqrt{2/3}\delta + \sqrt{1/3}\pi$$

$$e_{g}{}^{+} = \sqrt{1/3}|x^2 - y^2\rangle + \sqrt{2/3}|xz\rangle = \sqrt{1/3}\delta + \sqrt{2/3}\pi$$

$$e_{g}{}^{-} = \sqrt{1/3}|xy\rangle - \sqrt{2/3}|yz\rangle = \sqrt{1/3}\delta - \sqrt{2/3}\pi$$

The δ and π designations follow by analogy to the fourfold

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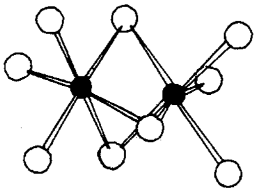

Figure 1. The D_{3h} M_2X_9 structure.

case. An assumption of local O_h symmetry, for each metal ion in the confacial bioctahedral structure, should be reasonable for the $M_2X_9{}^{n-}$ complexes. When both metal wave functions are coupled, the normalized D_{3h} dimer molecular orbitals (MO's) are

$$a_1' = (t_{2g}{}^0(a) + t_{2g}{}^0(b))/\sqrt{2(1 + S(\sigma))} = \sigma$$

$$a_2'' = (t_{2g}{}^0(a) - t_{2g}{}^0(b))/\sqrt{2(1 - S(\sigma))} = \sigma^*$$

$$e' = (t_{2g}{}^+(a) + t_{2g}{}^+(b))/\sqrt{2(1 + {}^2\!/_3S(\delta) + {}^1\!/_3S(\pi))} = {}^2\!/_3\delta + {}^1\!/_3\pi$$

$$e' = (t_{2g}{}^-(a) + t_{2g}{}^-(b))/\sqrt{2(1 + {}^2\!/_3S(\delta) + {}^1\!/_3S(\pi))} = {}^2\!/_3\delta + {}^1\!/_3\pi$$

$$e'' = (t_{2g}{}^+(a) - t_{2g}{}^+(b))/\sqrt{2(1 - {}^2\!/_3S(\delta) - {}^1\!/_3S(\pi))} = {}^2\!/_3\delta^* + {}^1\!/_3\pi^*$$

$$e'' = (t_{2g}{}^-(a) - t_{2g}{}^-(b))/\sqrt{2(1 - {}^2\!/_3S(\delta) - {}^1\!/_3S(\pi))} = {}^2\!/_3\delta^* + {}^1\!/_3\pi^*$$

$$e' = (e_g{}^+(a) + e_g{}^+(b))/\sqrt{2(1 + {}^2\!/_3S(\pi) + {}^1\!/_3S(\delta))} = {}^2\!/_3\pi + {}^1\!/_3\delta$$

$$e' = (e_g{}^-(a) + e_g{}^-(b))/\sqrt{2(1 + {}^2\!/_3S(\pi) + {}^1\!/_3S(\delta))} = {}^2\!/_3\pi + {}^1\!/_3\delta$$

$$e'' = (e_g{}^+(a) - e_g{}^+(b))/\sqrt{2(1 - {}^2\!/_3S(\pi) - {}^1\!/_3S(\delta))} = {}^2\!/_3\pi^* + {}^1\!/_3\delta^*$$

$$e'' = (e_g{}^-(a) - e_g{}^-(b))/\sqrt{2(1 - {}^2\!/_3S(\pi) - {}^1\!/_3S(\delta))} = {}^2\!/_3\pi^* + {}^1\!/_3\delta^*$$

where $S(\sigma)$, $S(\pi)$, and $S(\delta)$ denote σ, π, and δ orbital overlaps and the metal-centered z axes are taken to lie along the intermolecular axis. A standard MO diagram is presented in Figure 2. To derive the preceding wave functions, we assumed idealized metal d orbitals and local O_h symmetry. Consequently σ, δ, and π orthogonality hold. The quantities above such as ${}^2/_3\pi + {}^1/_3\delta$ describe the relative fractions of π and δ bonding (irrespective of phases). We caution the reader that the metal–ligand potential will destroy δ–π orthogonality and the above treatment must be viewed as a semiquantitative origin for discussion. Additional complications can be expected if mixing of the metal p orbitals with the e′ orbitals is significant. One feature does stand out. The lowest metal–metal bonding orbitals are σ (a_1') followed by (${}^1/_3\pi + {}^2/_3\delta$) (e′). Metal–metal π bonding is mainly between the e_g single-site orbitals, which are removed from the lower energy region due to their metal–ligand σ-antibonding character. This situation contrasts with that of D_{4h} complexes[1] (like $Re_2Cl_8{}^{2-}$) where only the metal–metal δ interactions are sacrificed for metal–ligand σ bonding. It is apparent that D_{3h} geometry does not optimize metal–metal bonding as well as the D_{4h} structure. An MO ordering of Figure 2 was earlier employed by Saillant and Wentworth[6,8,9] and later by McCarley and co-workers[14] in pioneering studies of $M_2X_9{}^{n-}$ compounds.

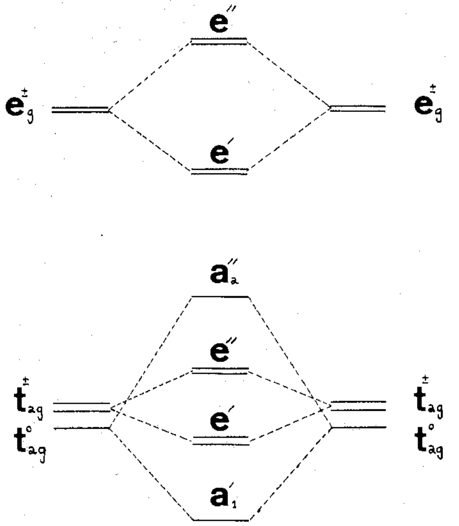

Figure 2. Molecular orbital diagram for metal–metal interactions in dimeric complexes with D_{3h} symmetry.

As a prelude to a discussion of the optical spectra of these complexes, we note that large differences could occur between triplet and singlet excitations. The MO approach emphasizes the symmetry aspects of metal–metal bonding; however, it can yield a physically unrealistic description of ground- and excited-state wave functions.[15] Recall that MO wave functions are notoriously bad for closed-shell diatomic molecules with long bond lengths or when orbital overlap is small.[16] This happens because simple MO theory assumes equal covalent and ionic character in both the bonding and antibonding states.[17] A more appropriate approximation in the regime of weak orbital overlap is the less familiar valence bond (VB) scheme. For simplicity of discussion, consider the VB description of metal–metal σ bonding in $M_2X_9{}^{3-}$ complexes. The extension to the ${}^1/_3\pi + {}^2/_3\delta$ bonds is straightforward.

All possible linear combinations of a nondegenerate orbital, Ψ, which can accommodate two d(σ) electrons are

$$[1] \quad [1/\sqrt{2(1 + S^2)}][(\Psi_a(1))(\Psi_b(2)) + (\Psi_a(2))(\Psi_b(1))]$$

$$[2] \quad [1/\sqrt{2(1 - S^2)}][(\Psi_a(1))(\Psi_b(2)) - (\Psi_a(2))(\Psi_b(1))]$$

$$[3] \quad [1/\sqrt{2(1 + S^2)}][(\Psi_a(1))(\Psi_a(2)) + (\Psi_b(1))(\Psi_b(2))]$$

$$[4] \quad [1/\sqrt{2(1 - S^2)}][(\Psi_a(1))(\Psi_a(2)) - (\Psi_b(1))(\Psi_b(2))]$$

Now the Pauli principal demands that the total orbital-spin wave function must be antisymmetric to exchange of electrons 1 and 2. Also, recall that singlet spin wave functions are antisymmetric and triplet are symmetric. Therefore, symmetric orbital functions 1 and 3 above must be spin singlets and function 2 the triplet. We discard solution 4 because it is impossible (Pauli restriction) to assign a triplet spin wave function when both electrons are placed in the same orbital, as in this ionic resonance structure. Of the two singlet states we assign [1] to the lowest energy spin-paired covalent-bonding state. Singlet function 3 represents an ionic resonance

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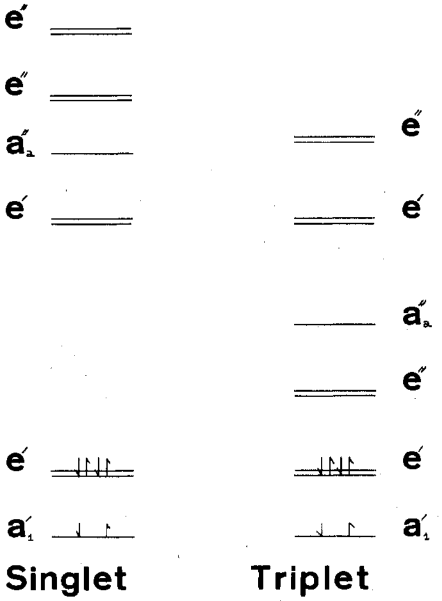

Figure 3. Schematic of the valence bond orbital-like diagrams for the relative energies in singlet and triplet excited states. The uppermost e″ level in the singlet diagram is meant to correspond to population of the ($^2/_3\pi^* + {}^1/_3\delta^*$) derived orbital. In the triplet manifold it should be understood that a spin flip occurs upon electron promotion. Orbital splittings within a specific one-electron configuration are neglected.

structure where both electrons are found either on atom a or on atom b. For $Mo_2Cl_9^{3-}$ we might pictorially write Mo(IV)–Mo(II) ↔ Mo(II)–Mo(IV) to describe ionic resonance form 3. This corresponds to the singlet state derived from a_1' (σ) → a_2'' (σ^*) in the MO scheme presented earlier. Rather than a bonding to antibonding transition, it is more correct to describe the singlet excitation process as a transformation from covalent bonding to ionic resonance, if metal–metal overlap is small. It is possible for this kind of transition to occur at high energies, even though σ overlap is weak! Note that function 2, belonging to the triplet state, does correspond to a "covalent" σ-antibonding situation. If orbital overlap is weak, we do expect the covalent-antibonding triplet transition to lie at quite low energies. Therefore, we expect two qualitatively different orbital-like energy level schemes (Figure 3), depending on whether triplet or singlet excitations are being considered. It should be emphasized that Figure 3 is simply a descriptive way of representing the singlet and triplet *states* in terms of an *orbital-like* energy diagram (i.e., the orbital energies have been ordered so that transition energies directly correspond to orbital energy differences). This does not imply that actual one-electron orbital energies (as in a spin-unrestricted SCF calculation[17]) would appear this way. The conventional MO energy level diagram (Figure 2) will most closely represent the orbital energy diagram appropriate for triplet spectra since it assumes that both the singlet and triplet states have similar ionic and covalent character and differ in energy by only twice an exchange integral.[17] The distinction between VB and MO descriptions of excited states was elegantly discussed by Mulliken[16] some time ago. Further ramifications of the VB approach may be found therein. For spin doublet systems the VB and MO methods are equivalent and the simple MO wave functions are then useful for qualitatively analyzing electronic transitions (within the doublet manifold) for the unpaired electron.

Spectral Analysis of $Mo_2X_9^{n-}$ and $W_2X_9^{n-}$ Complexes

Perhaps the strongest metal–metal interactions are found in the $Mo_2Cl_8^{4-}$ and $Re_2Cl_8^{2-}$ type complexes;[1] however, δ overlap, as evidenced by the low energy of the triplet state,[18] must be small. Bond lengths of 2.139 (Mo–Mo)[19] and 2.241 Å (Re–Re)[20] have been measured in crystallographic studies. Comparison with the respective metal–metal bond lengths of 2.66[8] and 2.41 Å[10] in the $Mo_2Cl_9^{3-}$ and $W_2Cl_9^{3-}$ compounds leads us to expect that direct δ and even π overlap will be small in these later complexes. This agrees quite well with the conclusion of Ziegler and Risen[11] that the W–W bond order is only slightly greater than one in $W_2Cl_9^{3-}$. The present model would attribute the weak bonding character of the occupied e′ orbital to its large percent δ character. By comparing $W_2Br_9^{2-}$ with $W_2Cl_9^{3-}$, $Mo_2Br_9^{3-}$, and $Mo_2Cl_9^{3-}$, Templeton, Jacobson and McCarley[14] noted that a small (0.03 Å) lengthening of the W–W bond could be attributed to loss of the "bonding" electron in $W_2Br_9^{2-}$. Again, this agrees with the conclusion that the lowest e′ ($^1/_3\pi + {}^2/_3\delta$) orbital contributes little to the metal–metal bond strength.

Evidence for a small e′–e″ splitting in the triplet states (Figure 3) may be obtained by comparing $Mo_2Cl_9^{3-}$ (Mo–Mo = 2.66 Å)[8] with $Mo_2Br_9^{3-}$ (Mo–Mo = 2.82 Å).[8] The 0.16-Å increase in the Mo–Mo bond length is sufficient to render the latter compound paramagnetic.[9] From our previous discussion, it follows that the related singlet electronic transitions will be largely ionic in character and occur with weak intensity (proportional to the square of the overlap)[16] and at high energies (expected for the charge separated excited state). Increased metal–metal overlap would mix covalent character into the ionic state (and ionic character into the bound singlet and antibonding triplet) and at first lower the energy of this transition, as well as result in enhanced intensity for the absorption process.

In the D_{3h} point group, electric dipole transitions from a $^1A_1'$ ground state are allowed to $^1A_2''$ (z polarized) and $^1E'$ (xy polarized) excited states. Figure 3 then predicts the two lowest, allowed singlet transitions to be e′ → e′ ($^1E'$) and a_1' → e′ ($^1E'$) for $M_2X_9^{3-}$ complexes. This suggests respective e′ → e′ and a_1' → e′ assignments for the xy-polarized bands which occur at 13 350 and 15 150 cm^{-1} in $Mo_2Cl_9^{3-}$ [9] and for the similar absorptions at 13 200 and 15 900 cm^{-1} in $W_2Cl_9^{3-}$.[9]

Further support for the "allowed" nature of these transitions derives from their pure[9] ⊥ polarization in $Cs_3Mo_2Cl_9$. Employing the standard group theoretical selection rules[21] for vibronic transitions, one can prove that all dipole-forbidden transitions, which are vibronically allowed, may be both parallel and perpendicularly polarized. An alternative assignment of the 13 350 and 15 150 cm^{-1} absorptions to vibronic transitions is therefore unlikely. As additional support for these assignments, consider the nature of the orbitals. Upper e′ and e″ orbitals are derived from the monomer metal–ligand σ-antibonding e_g levels and the lower a_1' and e′ orbitals from t_{2g}. The value of $10Dq$ for $MoCl_6^{3-}$ has been determined[22] at 19 400 cm^{-1}. Energetically, the assignments are reasonable because of the slightly weakened one-center metal–ligand bonding in the dimer and the fact that the e′ level is stabilized by metal–metal bonding. In $W_2Cl_9^{3-}$ metal σ overlap should increase and result in stabilization of the a_1' orbital. The blue shift of the a_1' → e′ transition, relative to $Mo_2Cl_9^{3-}$, is consistent with this expectation. A small red shift of the e′ → e′ transition agrees with the larger stabilization of the upper e′ level ($^2/_3\pi + {}^1/_3\delta$). An alternative assignment of these absorptions to simultaneous pair excitations[23] does not seem likely, as the energies do not correspond to a combination of $MoCl_6^{3-}$ transition energies. Also, the intensities appear too

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Table I. Spectral Data Comparing $M_2X_9^{2-}$ and $M_2X_9^{3-}$ Complexes

compd	transition energies, cm^{-1} (molar extinction coeff, M^{-1} cm^{-1})			
$Mo_2Cl_9^{3-}$ [a]	11 950 (13)	13 350 (78)	15 150 (100)	
$Mo_2Cl_9^{2-}$ [b]	10 250 (163)	12 800 (171)	15 280 (265)	
$W_2Cl_9^{3-}$ [a]		13 200	15 900	21 900
$W_2Cl_9^{2-}$ [c]		13 530 (1040)	17 200 (1700)	25 600 (618)
$W_2Br_9^{3-}$ [d]		12 400 (43)	15 300 (123)	20 300 (27 542)
$W_2Br_9^{2-}$ [e]		13000 (1100)	16 100 (1300)	18 200 (1100) 23 800 (5100) 27 000 (6600)

[a] Reference 9. [b] W. H. Delphin, R. A. D. Wentworth, and M. S. Matson, *Inorg. Chem.*, 13, 2552 (1974). [c] R. Saillant and R. A. D. Wentworth, *J. Am. Chem. Soc.*, 91, 2174 (1969). [d] Reference 25. [e] Reference 14.

large by comparison with well-characterized examples.[24] Stucky and co-workers[24] have observed weak ($\epsilon < 10$) bands attributable to these kinds of transitions in the structurally related $MCrX_3$ (M = a monopositive ion; X = halide) compounds.

The tungsten(III) dimers possess an additional intense absorption (ϵ_{max} 4700) at 21 900 cm^{-1} (X = Cl)[9] and 20 300 cm^{-1} (ϵ_{max} 27 500) (X = Br).[25] Assignment to a charge-transfer transition, which involves X, seems unlikely for two reasons. First, a red shift of the band by 4000–6000 cm^{-1} would be expected when changing from X = Cl to X = Br. Second, the nearly identical optical electronegativities of Mo and W in equivalent oxidation states[26] would predict that a similar transition should occur in the $Mo_2X_9^{3-}$ species. A possible explanation for the origin of this band acknowledges the increased metal–metal overlap in the tungsten complexes. This should lead to increased covalency in the $^1A_2''$ ($\sigma \rightarrow \sigma^*$) state. As was discussed earlier, this circumstance should yield a transition with metal $\sigma \rightarrow \sigma^*$ character. Spectral studies by Gray and co-workers[27] have shown that $\sigma \rightarrow \sigma^*$ type transitions are generally quite intense and occur in the visible and near-UV spectral region for metal–metal bond orders near 1. Significant ligand effects on the transition energy and intensity should be apparent. It is known[28] that mixing between the metal–metal σ-bonding orbital and those of the halide ligands occurs in other metal–halide dimers.

Recall that the oxidized complexes $M_2X_9^{2-}$ contain an unpaired electron (or hole) in the e′ $({}^2/_3\delta + {}^1/_3\pi)$ orbital. In binuclear Mo(II) and Re(III) complexes the $\delta \rightarrow \delta^*$ excitation is considerably red-shifted in the one-electron-oxidized products.[29] This results because the resonance complications[15,16] associated with singlet and triplet states are no longer present. By analogy to these other systems,[29] the allowed e′ $({}^2/_3\delta + {}^1/_3\pi) \rightarrow$ e″ $({}^2/_3\delta^* + {}^1/_3\pi^*)$ $({}^2E' \rightarrow {}^2E'')$ electronic transitions should occur in the near-IR region of the absorption spectrum. Furthermore, the oscillator strength of the transition should be weak. As yet, this spectral region has not been explored. An additional transition, which should be unique to the $M_2X_9^{2-}$ systems, is a_1' (σ) $\rightarrow$ e′ $({}^2/_3\delta + {}^1/_3\pi)$ $({}^2E' \rightarrow {}^2A_1')$. Although it is difficult to precisely estimate the energy of this transition, it would be expected to occur in the near-IR or visible spectral region.

The e′ $({}^2/_3\delta + {}^1/_3\pi) \rightarrow$ e′ $({}^2/_3\pi + {}^1/_3\delta)$, a_1' (σ) $\rightarrow$ e′ $({}^2/_3\pi + {}^1/_3\delta)$, and a_1' (σ) $\rightarrow$ a_2'' (σ^*) one-electron transitions are all allowed. These are expected to occur at approximately the same energies in $M_2X_9^{2-}$ compounds as in the corresponding $M_2X_9^{3-}$ complexes. From the data in Table I it appears that all $M_2X_9^{2-}$ and $M_2X_9^{3-}$ (M = Mo, W) compounds possess absorptions at ca. 13 000 and 16 000 cm^{-1} which may be attributed to the respective e′ → e′ and $a_1' \rightarrow$ e′ excitations. An interesting observation pertains to the increased intensities of these transitions in the $M_2X_9^{2-}$ complexes (Table I). Templeton, Jacobson, and McCarley[14] have provided evidence for a Jahn–Teller distortion in $W_2Br_9^{2-}$, as should occur for the orbitally degenerate $^2E'$ ground state. Because the e′ $({}^2/_3\delta + {}^1/_3\pi) \rightarrow$ e′ $({}^2/_3\pi + {}^1/_3\delta)$ and a_1' (σ) $\rightarrow$ e′ $({}^2/_3\pi + {}^1/_3\delta)$ transitions are derived from coupling of the $t_{2g} \rightarrow e_g$ single-site transitions, one would expect that perturbations which result in an increased departure of the one-center pseudosymmetry from O_h should increase the intensities of these transitions. The tungsten complexes also appear to exhibit an $a_1' \rightarrow a_2''$ transition in the 22 000–26 000-cm^{-1} spectral region; however, the picture is complicated by additional transitions when X = Br.

The near-infrared absorption spectra of these complexes should prove interesting. Further experimental studies will be necessary to locate the e′ $({}^2/_3\delta + {}^1/_3\pi) \rightarrow$ e′ $({}^2/_3\delta^* + {}^1/_3\pi^*)$ and a_1' (σ) $\rightarrow$ e′ $({}^2/_3\delta + {}^1/_3\pi)$ transitions. We note that a moderately intense transition has been reported at 10 250 cm^{-1} (Table I) in the spectrum of $Mo_2Cl_9^{2-}$.

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Registry No. $Mo_2Cl_9^{3-}$, 45835-69-6; $Mo_2Cl_9^{2-}$, 51059-87-1; $W_2Cl_9^{3-}$, 26443-76-5; $W_2Cl_9^{2-}$, 39448-64-1; $W_2Br_9^{3-}$, 72428-80-9; $W_2Br_9^{2-}$, 60267-85-8.

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