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Contribution from the Departments of Chemistry, University of Geneva, 1211 Geneva 4, Switzerland,
and University of Manchester, Manchester M13 9PL, United Kingdom

Ground-State Electronic Structure and the Nature of Excited States of Oxotetrahalo Complexes of Chromium(V) and Molybdenum(V): A Self-Consistent Field Multiple Scattering Xα Study

JACQUES WEBER*[1a] and C. DAVID GARNER[1b]

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Molecular orbital calculations using the all-electron self-consistent field multiple scattering Xα method have been carried out for the complexes $[CrOCl_4]^-$, $[MoOCl_4]^-$, and $[MoOBr_4]^-$. In the ground-state electronic structure of each system, the ordering of predominantly metal d orbitals is found to be $d_{xy} < d_{xz,yz} < d_{x^2-y^2} < d_{z^2}$, in agreement with previous predictions for CrO^{3+} and MoO^{3+} complexes. The main features of the chemical bonding in the complexes are discussed by using an analysis of the charge distribution of the valence levels. Calculations have been performed on the excited states of the complexes in an attempt to clarify the interpretation of their electronic absorption spectra. The results are very similar for the three systems and suggest that the lowest energy absorption is due mainly to the $d_{xy} \rightarrow d_{xz,yz}$ transition with some possible additional features due to halogen to metal charge-transfer excitations. The second absorption and the two higher energy bands are all predicted to arise from halogen to metal charge-transfer transitions which obscure the symmetry-forbidden d–d excitations.

The electronic structure of the d^1 monooxo chromophores CrO^{3+} and MoO^{3+} has attracted considerable interest.[2-12] Particular emphasis has been placed upon the interpretation of electron spin resonance and electronic absorption spectral data obtained for a wide range of complexes of these cations. The complexes $[CrOCl_4]^-$ and $[MoOX_4]^-$ (X = Cl or Br) and their substituted derivatives have been widely used in these studies but ambiguities still exist in the understanding of the chemical bonding and the electronic and electron spin resonance spectra of these systems. Reliable molecular orbital (MO) calculations could assist in solving these problems, but, to date, such results have been restricted to $[CrOCl_4]^-$,[10] partly because of the well-known difficulties of using standard MO methods for 4d transition-metal complexes.

The self-consistent field multiple scattering Xα (SCF MS Xα) method[13,14] has been shown to be well suited to MO calculations of the electronic structure and related properties of certain heavy-metal compounds.[15-18] This model is therefore most useful for theoretical comparisons between the electronic structure of oxotetrahalo complexes of chromium(V) and molybdenum(V). We report herein the results of such an investigation for the complexes $[CrOCl_4]^-$, $[MoOCl_4]^-$, and $[MoOBr_4]^-$; the nature of the bonding within the complex is discussed, and an assignment of the electronic spectral data is presented in each case.

Calculations

Table I. Calculation Parameters

	$[CrOCl_4]^-$	$[MoOCl_4]^-$	$[MoOBr_4]^-$
	α Values		
metal	0.713 52	0.703 41	0.703 41
oxygen	0.744 47	0.744 47	0.744 47
halogen	0.723 25	0.723 25	0.706 06
outer sphere + intersphere	0.725 17	0.723 48	0.712 02
	Sphere Radii (Atomic Units)		
metal	2.057 64	2.184 09	2.184 09
oxygen	1.721 88	1.619 04	1.619 04
halogen	2.194 30	2.224 70	2.615 88
outer sphere	6.424 47	6.479 26	7.273 27

The standard version of the SCF MS Xα method[14] was used. This model has been described in detail several times[14,19,20] and needs no further discussion here. However, some computational details, as well as the choice of the calculation parameters, deserve comment since they have been shown to have a nonnegligible influence on the results.[16,21,22]

Each complex was taken to have C_{4v} symmetry. To allow for the most meaningful comparisons between these and the ab initio results,[10] we assumed the same geometry for $[CrOCl_4]^-$ as in the earlier study: Cr–O = 1.60 Å, Cr–Cl = 2.25 Å, Cl–Cr–O = 95.8°. The geometries of $[MoOCl_4]^-$ and $[MoOBr_4]^-$ were taken from recent crystallographic[11,12] studies: Mo–O = 1.61 Å, Mo–Cl = 2.33 Å, Cl–Mo–O = 105.2° and Mo–O = 1.61 Å, Mo–Br = 2.54 Å, Br–Mo–O = 104°, respectively.

Table I presents the SCF MS Xα calculation parameters used. The atomic exchange parameters α are taken from the calculations of Schwarz,[23,24] whereas a weighted average (based on the number of atoms) of the atomic values was chosen for the α value in the interatomic (intersphere) and extramolecular (outer sphere) regions. As reported in previous papers,[15,16] the choice of appropriate values for the radii of atomic spheres is a delicate problem. In this instance, some test calculations performed for $[CrOCl_4]^-$ showed that a reasonable choice of sphere radii could be done as follows: in a first step, the radii of overlapping spheres for metal and oxygen (25% overlap) are determined by using the procedure described by Norman;[25] the

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halogen sphere was then chosen so as to be tangential to the metal sphere. (The use of overlapping spheres is inadequate in this case since it leads to a much too large sphere for halogen and therefore to an unrealistic charge distribution within the cluster.) This procedure was used for the calculations on $[CrOCl_4]^-$ and $[MoOCl_4]^-$. For $[MoOBr_4]^-$, since the metal–oxygen distance is the same as in $[MoOCl_4]^-$, the same radii of metal and oxygen spheres were used, and the radius of the bromine sphere was determined by the "touching" spheres requirement. In each case, the extramolecular region was delimited by an externally tangential outer sphere centered at the origin.

In all of the calculations, partial waves up to $l = 3$ were included in the multiple scattering expansions in the metal sphere and extramolecular region, and up to $l = 1$ in oxygen and halogen spheres.[26] A Watson sphere of the same radius as the outer sphere and bearing a charge of +1 was used in the calculations to simulate the effect of an external stabilizing electrostatic field. Since SCF MS Xα is an all-electron MO model, the inner-shell electrons are also allowed to adjust their one-electron energies during the SCF procedure, but they are constrained to conserve their atomic character and to be entirely localized within the atomic spheres ("thawed" core approximation). The transition-state method[27] was used for the determination of excitation energies. All the calculations were performed by using the standard nonspin-polarized version of the SCF MS Xα computer programs. Therefore, when considering an electronic excitation, we calculated an average over multiplet states arising from the given electronic configuration, since in this model the determination of the energy differences between multiplet states of the same multiplicity requires additional spin-polarized calculations. Experience from previous calculations[16,28] shows that typical values of these splittings are 0.1–0.4 eV; therefore it is anticipated that they would have only a small quantitative effect and no qualitative effect upon the interpretation of the electronic absorption spectra.

Results and Discussion

Ground-State Electronic Structures. The ground-state electronic structures of $[CrOCl_4]^-$, $[MoOCl_4]^-$, and $[MoOBr_4]^-$ are represented in Tables II–IV.[29] For all the clusters, the electronic ground state is calculated to be $^2B_2$, with the unpaired electron in the predominantly metal $3d_{xy}$ MO $2b_2$.[30] This result is in agreement with the ab initio calculation[10] performed on $[CrOCl_4]^-$ and with semiempirical predictions[3-5,31] for CrO^{3+}, VO^{2+}, and MoO^{3+} complexes. Furthermore, the same sequence of predominantly metal d orbitals is predicted for the three complexes: d_{xy} ($2b_2$) < $d_{xz,yz}$ (7e) < $d_{x^2-y^2}$ ($4b_1$) < d_{z^2} ($8a_1$). This result is identical with that previously obtained in the semiempirical calculations,[3-5,31] but it is at variance with the ab initio result[10] $d_{xy} < d_{x^2-y^2} < d_{z^2} < d_{xz,yz}$. This is not surprising since it is known[32] that the Xα virtual orbital energies do not have the same physical significance as in the Hartree–Fock model. It is interesting to compare for the three complexes the calculated energy difference between the $8a_1$ and $2b_2$ MO's, this quantity representing the ligand field splitting of the metal d orbitals. These values are 26.2, 33.9, and 35.9 × 10^3 cm^{-1} for $[CrOCl_4]^-$, $[MoOCl_4]^-$, and $[MoOBr_4]^-$, respectively, in agreement with the well-known fact that the ligand field splitting increases when going from the first to the second transition period metal complexes.[33]

The sequence of all the occupied levels is calculated to be the same in all three complexes. Immediately below the $2b_2$ MO, one finds several levels ($1a_2$, 6e, $3b_1$, 5e, $7a_1$) which are essentially nonbonding since they are localized only in halogen spheres and, to a lesser extent, in the interatomic region. The analysis of their charge distribution reveals that they are predominantly halogen p in character. The major contributions to metal–halogen bonding arise from the lower energy valence MO's 4e, $6a_1$, $1b_2$, and $2b_1$. These orbitals are essentially halogen p in character, but they exhibit a significant metal d component which increases along the series 4e–$2b_1$. Thus, the metal d character of $2b_1$ is 42%, 32%, and 37% in $[CrOCl_4]^-$, $[MoOCl_4]^-$, and $[MoOBr_4]^-$, respectively. At energies lower than these four levels are the 3e and $5a_1$ MO's which are responsible for π and σ metal–oxygen bonding, respectively. Finally, the low-lying valence levels have the following respective characters: chlorine 3s or bromine 4s ($1b_1$, 2e, $4a_1$), oxygen 2s ($3a_1$), chromium 3p or molybdenum 4p (1e, $2a_1$).

Table V. Comparison between Electronic Excitation Energies (10^3 cm^{-1}) Calculated for $[CrOCl_4]^-$ and Experimental Values

transition[a]				
orbitals	excited state	type of transition[b]	calcd value	exptl value[c]
$2b_2 \rightarrow 7e$	^2E	d → d	8.3	13.0
$6e \rightarrow 2b_2$	^2E	CT(Cl → Cr)	10.7	17.8
$5e \rightarrow 2b_2$	^2E	CT(Cl → Cr)	12.9	20.3
$1a_2 \rightarrow 7e$	^2E	CT(Cl → Cr)	17.8	~22.5
$4e \rightarrow 2b_2$	^4E	CT(Cl → Cr)	18.4	
$6e \rightarrow 7e$	$^2B_2$	CT(Cl → Cr)	19.2	~23
$2b_2 \rightarrow 4b_1$ (F)	$^2B_1$	d → d	19.4	
$5e \rightarrow 7e$	$^2B_2$	CT(Cl → Cr)	20.9	~25
$3b_1 \rightarrow 7e$	^2E	CT(Cl → Cr)	21.6	(~24)
$1b_2 \rightarrow 2b_2$	$^2B_2$	CT(Cl → Cr)	23.7	
$7a_1 \rightarrow 7e$	^2E	CT(Cl → Cr)	26.2	
$2b_2 \rightarrow 8a_1$ (F)	$^2A_1$	d → d	26.6	
$4e \rightarrow 7e$	$^2B_2$	CT(Cl → Cr)	26.9	
$6e \rightarrow 4b_1$	^2E	CT(Cl → Cr)	28.2	
$3b_1 \rightarrow 4b_1$	$^2B_2$	CT(Cl → Cr)	30.5	
$5e \rightarrow 4b_1$	^2E	CT(Cl → Cr)	30.6	
$6a_1 \rightarrow 7e$	^2E	CT(Cl → Cr)	32.0	
$1b_2 \rightarrow 7e$	^2E	CT(Cl → Cr)	32.0	
$2b_1 \rightarrow 7e$	^2E	CT(Cl → Cr)	32.3	
$3e \rightarrow 2b_2$	^2E	CT(O → Cr)	34.5	
$4e \rightarrow 4b_1$	^2E	CT(Cl → Cr)	36.0	
$6e \rightarrow 8a_1$	^2E	CT(Cl → Cr)	36.5	
$5e \rightarrow 8a_1$	^2E	CT(Cl → Cr)	38.4	
$3e \rightarrow 7e$	$^2B_2$	CT(O → Cr)	40.6	

[a] F = symmetry forbidden. [b] CT = charge transfer. [c] Reference 10. The values quoted correspond to polarized low-temperature measurements performed on single crystals of $[(C_6H_5)_4As]$-$[CrOCl_4]$.

In the $[CrOCl_4]^-$ case, the predicted ordering and charge distribution of the occupied valence levels are very similar to those obtained from the ab initio calculation:[10] the sequence of the levels is the same, with the exception of an inversion of the $1b_2$ and $6a_1$ MO's whose energies are very close to one another anyway. In spite of a significant amount of intersphere contributions in the SCF MS Xα results, the charge distributions of the levels show the same trends in both calculations. The good overall agreement between the results of these two calculations is encouraging and gives further confidence in the model used here.

Electronic Absorption Spectra. The electronic excitation energies of $[CrOCl_4]^-$, $[MoOCl_4]^-$, and $[MoOBr_4]^-$, calculated by using the transition-state method[27] (i.e., by taking into account of the major orbital relaxation effects), are compared with the experimental peak positions of the corresponding absorption spectrum[10,11,34] in Tables V–VII, respectively. These

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(26) In the case of $[MoOBr_4]^-$, the 3d electrons of the bromine atoms are treated as inner-shell electrons. Thus, partial waves up to $l = 1$ are adequate for the valence shell only.

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Table VI. Comparison between Electronic Excitation Energies (10^3 cm^{-1}) Calculated for $[MoOCl_4]^-$ and Experimental Values

transition^a				
orbitals	excited state	type of transition^b	calcd value	exptl value^c
$2b_2 \rightarrow 7e$	^2E	d → d	15.6	15.0
$6e \rightarrow 2b_2$	^2E	CT(Cl → Mo)	18.7	21.6
$5e \rightarrow 2b_2$	^2E	CT(Cl → Mo)	23.0	26.4
$2b_2 \rightarrow 4b_1$(F)	$^2B_1$	d → d	23.3	
$4e \rightarrow 2b_2$	^2E	CT(Cl → Mo)	25.7	
$1b_2 \rightarrow 2b_2$	$^2B_2$	CT(Cl → Mo)	32.0	
$1a_2 \rightarrow 7e$	^2E	CT(Cl → Mo)	33.0	
$6e \rightarrow 7e$	$^2B_2$	CT(Cl → Mo)	33.9	
$2b_2 \rightarrow 8a_1$	$^2A_1$	d → d	37.0	

[a] F = symmetry forbidden. [b] CT = charge transfer. [c] Reference 11. The values quoted correspond to polarized low-temperature measurements performed on single crystals of $[(C_6H_5)_4As][MoOCl_4]$.

Table VII. Comparison between Electronic Excitation Energies (10^3 cm^{-1}) Calculated for $[MoOBr_4]^-$ and Experimental Values

transition^a				
orbitals	excited state	type of transition^b	calcd value	exptl value^c
$6e \rightarrow 2b_2$	^2E	CT(Br → Mo)	12.0	21
$2b_2 \rightarrow 7e$	^2E	d → d	15.0	~12
$5e \rightarrow 2b_2$	^2E	CT(Br → Mo)	16.1	~23
$4e \rightarrow 2b_2$	^2E	CT(Br → Mo)	19.0	
$2b_2 \rightarrow 4b_1$(F)	$^2B_1$	d → d	19.5	
$1b_2 \rightarrow 2b_2$	$^2B_2$	CT(Br → Mo)	23.9	25
$1a_2 \rightarrow 7e$	^2E	CT(Br → Mo)	25.7	26
$6e \rightarrow 7e$	$^2B_2$	CT(Br → Mo)	27.0	

[a] F = symmetry forbidden. [b] CT = charge transfer. [c] Reference 34. The values quoted correspond to polarized low-temperature measurements on single crystals of $[(C_6H_5)_4As][MoOBr_4(H_2O)]$.

tables contain all the electronic transitions allowed in C_{4v} symmetry, together with the symmetry-forbidden transitions of the d–d type, which are calculated to occur below ca. 40 × 10^3 cm^{-1} for the chloro complexes and ca. 30 × 10^3 cm^{-1} for $[MoOBr_4]^-$. The differences between the relative orbital energy separations for the ground state of these compounds are carried over to the relative energies of the transition energies. In each case the order of the d–d transitions is $2b_2 \rightarrow 7e$; $\rightarrow 4b_1$; $\rightarrow 8a_1$ ($d_{xy} \rightarrow d_{xz,yz}$; $\rightarrow d_{x^2-y^2}$; $\rightarrow d_{z^2}$), as predicted in the first theoretical considerations of these complexes[3-5] and the ab initio calculation for $[CrOCl_4]^-$.[10] The d–d transitions are at a higher energy for the MoO^{3+} complexes than for $[CrOCl_4]^-$ and the 10*D*q value for the "in-plane" ligands is in the expected order $[MoOCl_4]^- > [MoOBr_4]^- > [CrOCl_4]^-$, although the variation 23.3, 19.5, and 19.4 × 10^3 cm^{-1} is smaller than might have been anticipated. For $[CrOCl_4]^-$ or $[MoOBr_4]^-$ vs. $[MoOCl_4]^-$, the smaller energy difference between the metal $(n-1)$d and the halide *n*p orbital separation is manifest in a lower set of ligand → metal charge-transfer transitions. An examination of the charge-transfer spectra of a large number of halide complexes[35] shows that bromine → metal transitions occur some 5 to 8 × 10^3 cm^{-1} lower in energy than the corresponding chlorine → metal ones. Consequently, it is not surprising to find that the charge-transfer transitions for $[MoOBr_4]^-$ are calculated to be 6–7 × 10^3 cm^{-1} lower in energy than those for $[MoOCl_4]^-$. A similar ordering of these transitions is obtained for every complex; the lowest energy charge-transfer transitions involve promotion into the $2b_2$ (d_{xy}) MO and, at slightly higher energy, the 7e ($d_{xz,yz}$) MO. These results for $[CrOCl_4]^-$ disagree with those obtained from the ab initio treatment,[10] where the lowest energy "charge-transfer" transitions were calculated to involve electronic redistribution within the Cr–O group, from the π- or σ-bonding orbitals into the σ^* or π^* orbitals, respectively. This disagreement is apparently surprising in view of the very similar electronic structures predicted by both methods for the ground state of $[CrOCl_4]^-$, but one has to keep in mind that the calculations on the excited states are performed in a completely different way in each model. For example, the "unfavorable Coulombic repulsions" predicted by the ab initio model for transitions from the predominantly Cl 3p MO's to the $2b_2$ level are practically absent in the SCF MS Xα results; consequently these transitions are found at a much lower energy in the present calculations. Both calculations agree that the energies of the electronically forbidden $d_{xy} \rightarrow d_{x^2-y^2}$ and d_{z^2} transitions are superior to those of a number of electronically allowed charge-transfer transitions for $[CrOCl_4]^-$, and the present study suggests that this also occurs for $[MoOBr_4]^-$ and, to a lesser extent, for $[MoOCl_4]^-$. The assignment of the electronic transitions for $[CrOCl_4]^-$, $[MoOCl_4]^-$, and $[MoOBr_4]^-$ follows from the data presented in Tables V–VII. However, the difficulty of calculating the energy of electronic transitions, particularly when they involve a significant charge redistribution, by a basically one-electron method should be remembered in any comparison of the theoretical and experimental values.

The results presented in Table V suggest that the first band of the spectrum of $[CrOCl_4]^-$ originates simultaneously from the d–d orbital excitation $2b_2 \rightarrow 7e$ *and* from the chlorine to metal charge-transfer excitations $6e \rightarrow 2b_2$ and $5e \rightarrow 2b_2$. The first part of this interpretation is in agreement with the earlier ab initio predictions and the spectral characteristics of this band. There seems to be no doubt that the $2b_2 \rightarrow 7e$ d–d transition is indeed responsible for the origin of this first band, which suggests that the present calculations underestimate by 4–5 × 10^3 cm^{-1} this transition energy. However, the second part of the interpretation is more dubious since it is surprising to find charge-transfer excitations at so low an energy. Furthermore, the low value of the oscillator strength of the first band (1.8 × 10^{-4})[10] seems to exclude the possibility of a charge-transfer transition.

We are thus faced with the following alternatives: either the present calculations significantly underestimate the energies of the Cl to Cr charge-transfer transitions and the $6e \rightarrow 2b_2$ and $5e \rightarrow 2b_2$ transitions are associated with higher energy bands or the $6e \rightarrow 2b_2$ and $5e \rightarrow 2b_2$ transitions have such a low intensity that they account for the additional features observed in the first band and previously interpreted as originating from vibronic coupling.[10] On the basis of the similar nature, i.e., the polarization and vibronic coupling profile, of the second band of the absorption spectrum of $[CrOCl_4]^-$ and $[MoOCl_4]^-$ and the assignment proposed for the latter (vide infra), the former alternative is favored. Specifically, on the basis of these calculations, it is suggested that the absorption with the origin at 17.8 × 10^3 cm^{-1} is due to the $6e \rightarrow 2b_2$ chlorine to chromium charge-transfer transition and that at ca. 20.3 × 10^3 cm^{-1} the absorption is due to the $5e \rightarrow 2b_2$ one. The absorptions to higher energy are also assigned to chlorine to chromium charge-transfer transitions: the broad feature at 22–25 × 10^3 cm^{-1} (in *xy* polarization) to the $1a_2 \rightarrow 7e$, $4e \rightarrow 2b_2$, and (perhaps) $3b_1 \rightarrow 7e$ ($^2B_2 \rightarrow {}^2E$) promotions; the shoulders at 23 and 25 × 10^3 cm^{-1} (*z* polarization) to the $6e \rightarrow 7e$ and $1b_2 \rightarrow 2b_2$ ($^2B_2 \rightarrow {}^2E$) promotions. Other charge-transfer transitions account for the intense absorptions above 20 × 10^{-3} cm^{-1}. The symmetry-forbidden $d_{xy} \rightarrow d_{x^2-y^2}$ and $\rightarrow d_{z^2}$ ($2b_2 \rightarrow 4b_1$ and $\rightarrow 8a_1$) transitions are predicted to occur in the same energy range as the symmetry-allowed chlorine to chromium charge-transfer transitions, and thus the

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former are probably obscured by the latter.

The lowest energy absorption of $[MoOCl_4]^-$ with an origin at ca. 15.0×10^3 cm^{-1} is assigned to the $d_{xy} \rightarrow d_{xz,yz}$ ($2b_2 \rightarrow 7e$) transition calculated to occur at 15.6×10^3 cm^{-1} (Table VI). The experimental information obtained for this transition[11] is fully consistent with this assignment. On the basis of these calculations, the second and third bands in the spectrum, with origins at ca. 21.6 and 26.4×10^3 cm^{-1} and intensities in xy polarization greater than z, are assigned to the chlorine to molybdenum charge-transfer ($^2B_2 \rightarrow {}^2E$) transitions $6e \rightarrow 2b_2$ and $5e \rightarrow 2b_2$, respectively. The intense absorptions to higher energy are also assigned to such transitions. The symmetry-forbidden $d_{xy} \rightarrow d_{x^2-y^2}$ and $\rightarrow d_{z^2}$ ($2b_2 \rightarrow 4b_1$ and $\rightarrow 8a_1$) transitions, calculated to occur in the same energy range as these symmetry-allowed chlorine to molybdenum charge-transfer transitions, are presumed to be obscured by them.

The situation for $[MoOBr_4]^-$ resembles that for $[CrOCl_4]^-$ and is further complicated by the rather poor spectral resolution so far achieved[34] for the former complex. The lowest energy band in the spectrum of $[MoOBr_4(H_2O)]^-$ is more intense in xy than in z polarization and shows some evidence for coupling with a vibrational mode of frequency ca. 900 cm^{-1}. Thus, in comparison to $[MoOCl_4]^-$, this band is assigned to the $d_{xy} \rightarrow d_{xz,yz}$ ($2b_2 \rightarrow 7e$) transition which is calculated to have an energy of 15.0×10^3 cm^{-1}. The lowest energy transition is calculated to be the $6e \rightarrow 2b_2$ bromine → molybdenum charge-transfer transition, and therefore the calculations are assumed to significantly underestimate the energies of these excitations. A series of reasonably intense bands dominate the visible and UV absorption spectrum of $[MoOBr_4(H_2O)]^-$ and are generally more intense in xy than in z polarization, and a tentative assignment of the lower energy transitions is included in Table VII. Once more, it is considered that the two symmetry-forbidden d → d transitions are not evident in the absorption spectrum.

Despite the simplistic approach adopted in these calculations, for example the neglect of spin–orbit coupling, multiplet structure and many-electron effects, they have provided a reasonable basis for the interpretation of the electronic spectra of $[CrOCl_4]^-$, $[MoOCl_4]^-$, and $[MoOBr_4]^-$. The principal debate concerning the assignments of these spectra is the location of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition and/or the origin of the second absorption band. The theoretical results described here clearly suggest that this band is due to a halogen → metal charge-transfer transition, in contrast to the oxygen → metal transition suggested by the ab initio calculation for $[CrOCl_4]^-$. The majority of the arguments advanced[10,11] in favor of the latter assignment vs. the $d_{xy} \rightarrow d_{x^2-y^2}$ promotion for the second band in the absorption spectra of $[CrOCl_4]^-$ and $[MoOCl_4]^-$ are equally applicable to the halogen → metal transition. However, it is recognized that more experimental and theoretical work is needed before the interpretation of the electronic spectrum of the oxotetrahalometalates of Cr(V) and Mo(V) can be regarded as settled.

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Supplementary Material Available: Tables II–IV (ground-state electronic structures of the complexes) (3 pages). Ordering information is given on any current masthead page.

Contribution from the Transuranium Research Laboratory, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830,
and Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916

Chemical Consequences of Radioactive Decay. 1. Study of ^{249}Cf Ingrowth into Crystalline $^{249}BkBr_3$: A New Crystalline Phase of $CfBr_3$[1]

J. P. YOUNG,*[2a] R. G. HAIRE,[2b] J. R. PETERSON,[2c] D. D. ENSOR,[2c] and R. L. FELLOWS[2c]

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Spectrophotometric and X-ray powder diffraction methods have been applied to a study of the ingrowth of californium-249 by β^- decay of berkelium-249 in crystalline $^{249}BkBr_3$. It was found that the Cf daughter grows in with the same oxidation state and crystal structure as the parent. Thus, six-coordinate $BkBr_3$ ($AlCl_3$-type monoclinic structure) generates six-coordinate $CfBr_3$, and eight-coordinate $BkBr_3$ ($PuBr_3$-type orthorhombic structure) generates eight-coordinate $CfBr_3$, a previously unknown form of $CfBr_3$. It was also found that the daughter Cf(III) in the $BkBr_3$ parent compound can be reduced to Cf(II) by treatment with H_2, as it can in pure $CfBr_3$.

Introduction

The solid-state compounds of elements in the decay chain

$$^{253}\mathrm{Es} \xrightarrow[\text{20.5 days}]{\alpha} {}^{249}\mathrm{Bk} \xrightarrow[\text{314 days}]{\beta^-} {}^{249}\mathrm{Cf} \left(\xrightarrow[\text{352 years}]{\alpha} {}^{245}\mathrm{Cm} \right)$$

provide a unique sample system in which a number of interesting and basic phenomena of nature can be examined. Transformation in the Es, Bk, Cf portion of this series occurs in a reasonable length of time, and studies of compounds of these elements are presently under way, utilizing both spectrophotometric and X-ray powder diffraction techniques to gain insight into the chemical consequences of α and β decay as these processes pertain to the generation of progeny compounds in the solid state. As an introduction to this broad area of study, we focus attention, first, on the consequences of β^- decay by a study of the behavior of Cf as it grows into a Bk compound.

Although other investigations have addressed the general area of chemical consequences of radioactive decay, such

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[2] (a) Analytical Chemistry Division, Oak Ridge National Laboratory. (b) Transuranium Research Laboratory, Oak Ridge National Laboratory. (c) University of Tennessee and Transuranium Research Laboratory, Oak Ridge National Laboratory.

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