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Electron-Ionization Mass Spectra of Fluorinated β-Diketonate Complexes of Cerium(IV)[†]

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Electron-ionization mass spectra are reported for the first time for β-diketonate chelates of Ce(IV). The ligands are the conjugate bases of 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione, 4,4,4-trifluoro-1-phenyl-1,3-butanedione, and 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione. Spectra show the tendency of Ce to exhibit the Ce(IV) state by which these complexes resemble those of the group 4 early (hard) transition metals. The spectra show also a tendency of cerium to be reduced by a ligand, especially if aromatic, to Ce(III), after which the ion fragmentation resembles that of the complexes of trivalent lanthanides, with domination by fluorine rearrangement from ligand to metal. In this respect, there is less similarity to the behavior of the chelates of the later trivalent transition metals or of the main group 13 metals. New mechanisms are suggested for loss of CO and alkyl or aryl fluoride by the present complexes.

Introduction

Since the thorough study of the mass spectra of acetylacetonate complexes of various metals by Macdonald and Shannon[1] nearly 20 years ago, there has been continuing interest in the mass spectra of β-diketonate complexes. This is shown in several reviews.[2-4]

Although cerium is the most abundant of the lanthanide metals, its β-diketonate complexes seem to have been overlooked in previous mass spectrometric investigations. It is of interest in that it is one of the few metals and the only lanthanide with a readily available +4 oxidation state in its complexes. The neutral tetrakis chelates with the bidentate diketonate ligands show eight-coordination through oxygen about the cerium atom.[5] Partially fluorinated acetylacetonate derivatives have been used as ligands because their metal complexes are especially stable and volatile with solubility properties useful for analytical purposes.

The present work was undertaken to obtain electron-ionization mass spectra of three cerium(IV) chelates with the conjugate bases of 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione (commonly abbreviated tba⁻), 4,4,4-trifluoro-1-phenyl-1,3-butanedione (tpa⁻), and 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (tta⁻), respectively, to rationalize the positive-ion spectra in terms of unimolecular ion fragmentation mechanisms, and to compare these spectra and mechanisms with those previously given for analogous complexes, especially of other lanthanides and of other tetravalent metals.

Experimental Section

The complexes were prepared by a method previously given for Ce(tta)₄.[6] Ce(tba)₄ is dark orange with mp 128-130 °C, Ce(tpa)₄ is dark brown with mp 146 °C, and Ce(tta)₄ is brown with mp 199-202 °C (lit.[6] mp 190 ± 10 °C).

Samples were held under vacuum several hours in the mass spectrometer's (CEC Model 21-491) direct-probe inlet system before introduction to the ion-source region. Mass spectra were obtained with an ionizing energy of 70 eV unless otherwise noted and with an ion-repeller potential of 2.2 V. The ion-source temperature was typically 60-90 °C above the probe temperature, which was 70-85, 145-180, and 140-190 °C for the respective complexes. The mass range from approximately *m/z* 50 to 1100 was scanned.

Results

Low-mass peaks from ions without Ce varied in relative intensity with time and with sample temperature. They are attributed to interference from the free diketones[7] especially for Ce(tpa)₄ and Ce(tta)₄, which left dark residues in the sample holder after evaporation. In the latter case thermolysis to thiophene[8] seems to occur at the higher temperatures. Ions containing Ce are readily identifiable by the two isotopes ¹⁴⁰Ce and ¹⁴²Ce in an 8:1 ratio. Only Ce-containing ions, which gave consistent relative abundances

Table I. Mass Spectra at 70 eV for CeL₄ Complexes[a]

	L					
	tba		tpa		tta	
ion[b]	*m/z*[c]	RA[d]	*m/z*	RA	*m/z*	RA
[CeL₄]⁺	920	8.7	1000	11.4		
[CeL₄ − F]⁺	901	1.7	981	3.7		
[CeL₃]⁺	725	(100)	785	(100)	803	(100)
[CeL₂F]⁺	549	2.5	589	13.4	601	23.1
[CeL₂]⁺	530	29.4	570	21.5	582	55.7
[CeL₂ − CO]⁺	502	5.0	542	6.4	554	14.8
[CeL₂F − CF₃]⁺	480	7.2	520	13.4	532	26.2
[CeL₂ − CO − RF]⁺	426	4.6	446	15.4	452	28.0
[CeLF]⁺	354	20.3	374	41.3	380	84.2
[CeLF − CO]⁺	326	6.4	346	14.1	352	26.7
[CeLF₂ − CF₃]⁺	304	18.6	324	37.9	330	50.7
[CeF₂]⁺	178	7.9	178	31.5	178	70.0

[a] L is CF₃COCHCOR where R is (CH₃)₃C for tba, C₆H₅ for tpa, or C₄H₃S for tta. [b] Only ions containing Ce are shown. [c] Nominal value for an ion containing ¹⁴⁰Ce. [d] Abundance of ion relative to [CeL₃]⁺ = 100. Relative standard deviation is from10% for stronger peaks to 20% for weaker ones.

for at least five spectra per compound, are shown in Table I.

Peaks are assigned by comparing observed and calculated patterns for isotopic multiplets arising from the minor isotopes of C, S, and Ce and by comparison with previously reported spectra for analogous compounds. Table I shows the relative abundance for the predominant isotopic species for each chemically different ion.
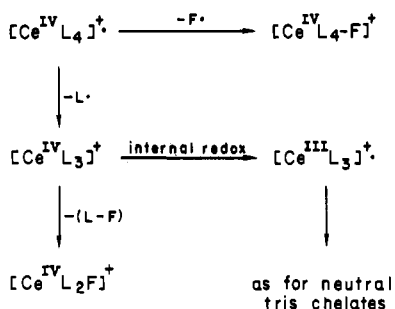
Spectra of Ce(tba)₄ nominally at 20 eV showed [Ce(tba)₄]⁺ at nearly the same relative abundance as at 70 eV, [Ce(tba)₂]⁺ close to half its relative abundance for 70 eV, and all other fragments at less than 1% of the base-ion abundance.

Discussion

The formulations for the observed ions are consistent with those made for analogous complexes of other metals by previous workers,

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[†] In this paper the periodic group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18.

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Scheme I. Mechanism for Early Fragmentation of CeL$_4$ Including Reduction of Metal

$$[Ce^{IV}L_4]^+ \xrightarrow{\ -F\cdot\ } [Ce^{IV}L_4-F]^+$$

$$\downarrow -L\cdot$$

$$[Ce^{IV}L_3]^+ \xrightarrow{\text{internal redox}} [Ce^{III}L_3]^+$$

$$\downarrow -(L-F) \qquad\qquad \downarrow$$

$$[Ce^{IV}L_2F]^+ \qquad\qquad \text{as for neutral tris chelates}$$

who have suggested fragmentation mechanisms based in many cases on observation of metastable ions. The appropriateness of these mechanisms for the present complexes will be considered. Differences in relative abundances and whether an ion is observed at all will be rationalized by an ion-fragmentation scheme that considers cerium and the other metals, according to their available oxidation states and hardness or softness as acids, as well as the ligands.

The low or undetectable abundance of the odd-electron molecular ion [CeL$_4$]$^+\cdot$ is explained by rapid loss of neutral L$\cdot$ to give the abundant even-electron [CeL$_3$]$^+$, which is responsible for the base peak for each complex and whose Ce maintains its +4 state (Scheme I). The constancy of the relative abundances of these two ions from Ce(tba)$_4$ between 70 eV and 20 eV indicates that they have similar appearance energies and that [CeL$_4$]$^+\cdot$ → [CeL$_3$]$^+$ + L$\cdot$ has a low energy barrier. This facile loss of neutral ligand from the molecular ion is similarly evidenced in the mass spectra of β-diketonates of tetravalent Ti, Zr, Hf, and Th.[1,9-12] Trivalent-metal β-diketonates similarly and typically show [ML$_2$]$^+$ (M is metal) more abundant than [ML$_3$]$^+$ with the former often giving the base peak whether M is a lanthanide,[13,14] a main-group metal,[15] or a transition metal.[1,11,16] Alternatively [CeL$_4$]$^+\cdot$ can lose neutral F$\cdot$, also leaving an even-electron ion. Such a process was not reported for M(tpa)$_4$ where M = Ti, Zr, or Hf[12] although it was reported for M(hfa)$_4$ where M = Zr or Hf and hfa$^-$ is hexafluoroacetylacetonate ion.[10]

Because Ce has available the +3 oxidation state, as do the other lanthanides, the similarity between the further fragmentation of CeL$_4$ and that of the tris chelates of the lanthanides[13,14] is understandable. Thus the even-electron [Ce^{IV}L$_3$]$^+$ undergoes a formal ligand-to-metal electron transfer to give [Ce^{III}L$_3$]$^+\cdot$ with a radical site on a ligand. Further fragmentation should then resemble that of the lanthanide ML$_3$ complexes, which show abundant [ML$_2$]$^+$ and other ions involving M(III).

The present complexes of Ce, as well as those of the other lanthanide[13,14] and of the early transition metals,[12] show very extensive fluorine atom migration to the metal, especially to give [MLF]$^+$. Such a migration occurs in the loss of CF$_2$, which is considered to result from cleavage of the C–CF$_3$ bond accompanied by migration of F to the metal.[16,17] Thus the structure of the ion formed by loss of 50 u from [CeL$_2$]$^+$ is formulated (Table I) as [CeL$_2$F – CF$_3$]$^+$ rather than [CeL$_2$ – CF$_2$]$^+$, and [CeLF$_2$ – CF$_3$]$^+$ is shown rather than [CeLF – CF$_2$]$^+$. Facile fluorine

Scheme II. Mechanism for CO Elimination from [CeL$_2$]$^+$ or [CeLF]$^+$
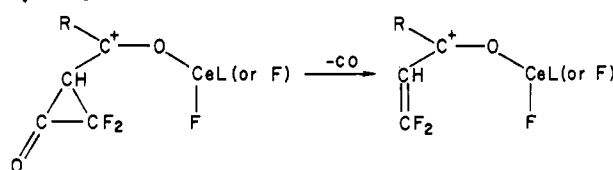
Scheme III. Mechanism for RF Elimination from [CeL$_2$ – CO]$^+$
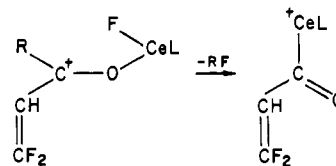
migration in these cases is rationalized by hard–soft acid–base theory[18] as a favorable hard acid–base interaction because the complexes of the less ionic, softer metals, Ga and In[15] and the later transition metals,[19] show much less F migration. Trichloroacetylacetonate complexes accordingly show ready migration of Cl$^-$ (a softer base than F$^-$) to softer transition metals.[20] The availability of the Ce(IV) state permits the present complexes to undergo F migration, yielding [ML$_2$F]$^+$ (Scheme I), which is not reported for the trivalent lanthanides.[13,14]

The present complexes rearrange to eliminate CO from [ML$_2$]$^+$ and [MLF]$^+$. The other lanthanide complexes show such a process,[13,14] but it is not reported for complexes of transition metals[12,16] and main group 13 metals[15] or for HL.[7] A mechanism for CO loss involving an intraligand migration of CF$_3$ has been proposed,[13] but since this would be little affected by the metal, it does not seem as satisfactory as Morris and Koob's suggestion for the chlorinated ligands with transition metals that CO elimination occurs only after Cl migrates to the metal.[20] Adapting this for the present complexes gives Scheme II. The ease of the migration of F to Ce and to other lanthanides, as already discussed, accounts also for this CO elimination.

The complexes of Ce, as well as those of the trivalent lanthanides,[13,14] show loss of the elements of RCOF from [ML$_2$]$^+$. As with CO loss, this is not reported for the complexes of the transition metals,[12,16] main group 13 metals,[15] or the proton.[7] Das and Livingstone report the metastable transition and postulate a mechanism involving loss of RCO$\cdot$ followed by loss of F$\cdot$ although loss of only RCO$\cdot$ is not reported[13] and is not seen in the present case. To account for the dependence upon the metal of the loss of RCOF from ML$_2$$^+$, it is now suggested that the process occurs first by loss of CO as already discussed for the chelates of Ce and the other lanthanides. An internal rotation about the C–O bond of the product in Scheme II should permit rearrangement with elimination of RF to give an ion with conjugated double bonds and a formal charge on the metal as in Scheme III. This mechanism has the thermodynamic advantages that the product ion should have a higher entropy, if not a lower energy, than that associated with the constrained four-membered-ring structure previously suggested[13] and that the neutral products CO + RF should be about 400 kJ mol^{-1} more stable than RCO$\cdot$ + F$\cdot$. It also explains why the process is seen only in those cases where [ML$_2$]$^+$ can eliminate CO. The inhibition of the process in Ce(tba)$_4$ compared to the other CeL$_4$ complexes (Table I) is understandable since the rearrangement to form the R–F bond should be sterically hindered by the bulky *tert*-butyl group.

The present complexes and those of the other lanthanides[13,14] and the early transition metals[12] show no migration of R to the metal, although such processes are reported for tris complexes of Ga and especially In[15] and for those of Cr, Fe, and Co but not

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Al.[16] This also is rationalized by hard–soft acid–base theory whereby the soft base R will migrate more readily to the softer metals than to the harder ones. The tendency is now opposite to that shown in F migration.

Elimination of neutral HF is not detected for the present complexes or for the analogous complexes of the other lanthanides[13,14] although it is reported as low-abundance [ML$_2$F − CF$_3$ − HF]$^+$ from tpa complexes of Al, Cr, and Fe[16] and tpa and tta complexes of In.[15] The suggested mechanism involves transfer of F$^-$ from the metal to the γ-hydrogen of the ligand,[16] which should be difficult with the strong M–F bond that the hard metals provide.[19]

Comparing the ligands for the CeL$_4$ complexes, one sees that for most fragments the relative abundance is greatest when L = tta and least when it is tba. As discussed above, fragmentation to [CeL$_2$]$^+$ and beyond is believed to proceed from the odd-electron [Ce^{III}L$_3$]$^+$· ion. Formation of this from the even-electron [Ce^{IV}L$_3$]$^+$ requires the ligand to reduce the metal. This ability should be in the order tta > tpa > tba since the aromatic ring in tta and tpa, especially with the sulfur atom in tta, should favor oxidation of the ligand to a radical.

Other mass spectrometric studies involving chelates with some of the present ligands confirm the trends already mentioned. These chelates are of the type EuL$_3$,[21,22] PdL$_2$, and UO$_2$L$_2$.[23]

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Conclusions

The mass spectra of the present CeL$_4$ complexes are understandable in terms of an ion-fragmentation scheme dominated first by Ce(IV) and then by Ce(III) with extensive rearrangement.

Facile loss of L· from the molecular ion to form [CeL$_3$]$^+$ gives the base peak. In that the Ce(IV) state is maintained in this ion and in others such as [CeL$_2$F]$^+$, these complexes resemble the analogous complexes of the group 4 transition metals.

The availability of the Ce(III) state and the ability of these ligands, especially those with aromatic substituents, to provide a radical site permit reduction of Ce(IV) by the ligand. This is followed by expulsion of L· to give [CeL$_2$]$^+$.

Fragmentation beyond [CeL$_2$]$^+$ resembles that of the tris complexes of the other lanthanides. Nearly every step involves rearrangement, especially fluorine migration from ligand to metal, which is favored by the hard-acid character of the metal. This involves an even-electron ion losing an even-electron neutral such as CF$_2$, CO, or RF. For loss of the latter two species, new mechanisms are proposed.

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Ab Initio Study of Additivity. 2

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The addition of energy changes when correlation or polarization effects are included in a starting basis set is compared with the results when both effects are included, starting from several different basis sets. If the starting basis is STO-3G for a selected set of molecules, additivity holds quite well, but the relative total energies of these molecules are not accurate. This accuracy is improved if polarization corrections (STO-3G to STO-3G*) and correlation corrections (STO-3G to MP2/STO-3G), obtained at a single-ζ basis set level, are applied to the relative energies obtained at a double-ζ basis set level, 6-31G. This procedure allows tolerably good energies in moderately large molecular systems.

Method

In studies of molecular orbital energetics of complex molecules it is often impractical to include both polarization (d orbitals on first-row atoms, p orbitals on H) and correlation. Hence, some approximate methods must be employed. One such method is to obtain energies for a reaction or isomerization, a → b, at an appropriate starting level such a 6-31G (double-ζ) basis, to extend that basis with either polarization or correlation (double excitations CID, or MP2, or MP3), and then to add these two energy increments in order to approximate the much larger calculation in which both effects are included. In several studies[1-16] the errors of this "additivity" are usually small (a few kcal/mol) when the results are compared to the full calculation for the process a → b. In our systematic study[1] the reference wave function was CID/6-31G**, while the starting set for extension was 6-31G. Here, we examine the results for several processes a → b of basis set extension and correlation (CID, MP2, MP3) starting from either STO-3G or 6-31G basis sets (eq 1-6). Equation 7 is the additivity approximation.

$$(CID/6\text{-}31G^{**} - 6\text{-}31G)_b - (CID/6\text{-}31G^{**} - 6\text{-}31G)_a =$$
$$\Delta_{pol-cor} \quad (1)$$

$$(6\text{-}31G^{**} - 6\text{-}31G)_b - (6\text{-}31G^{**} - 6\text{-}31G)_a = \Delta_{pol} \quad (2)$$

$$(CID/6\text{-}31G - 6\text{-}31G)_b - (CID/6\text{-}31G - 6\text{-}31G)_a = \Delta_{cor} \quad (3)$$

$$(CID/STO\text{-}3G^* - STO\text{-}3G)_b -$$
$$(CID/STO\text{-}3G^* - STO\text{-}3G)_a = \Delta_{pol-cor} \quad (4)$$

$$(STO\text{-}3G^* - STO\text{-}3G)_b - (STO\text{-}3G^* - STO\text{-}3G)_a = \Delta_{pol} \quad (5)$$

$$(CID/STO\text{-}3G - STO\text{-}3G)_b -$$
$$(CID/STO\text{-}3G - STO\text{-}3G)_a = \Delta_{cor} \quad (6)$$

$$\Delta_{pol} + \Delta_{cor} \approx \Delta_{pol-cor} \quad (7)$$

In Table I we compare, for the reaction a → b, the energy increment from the STO-3G or 6-31G basis to a basis that includes

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