Contribution from the Department of Chemistry, Purdue University,
West Lafayette, Indiana 47907

Desorption Ionization Mass Spectrometry: Secondary Ion and Laser Desorption Mass Spectra of Transition-Metal Complexes of β-Diketones

JANELLE L. PIERCE, KENNETH L. BUSCH, R. GRAHAM COOKS,* and RICHARD A. WALTON*

Received August 14, 1981

Studies on the secondary ion mass spectra (SIMS) of β-diketonate complexes of the transition metals have been carried out with NH_4Cl and NaCl as room-temperature matrices. Those systems studied included the acetylacetonate derivatives $M(acac)_3$ (M = Fe, Cr, Mn, or Co), $M(acac)_2$ (M = Ni or Cu), $VO(acac)_2$, and $MoO_2(acac)_2$ as well as $Cr(tfac)_3$ and $Cr(btac)_3$, which contain the unsymmetric $CF_3COCHCOCH_3^-$ (tfac) and $PhCOCHCOCF_3^-$ (btac) ligands. Of particular interest has been the production of bimetallic ions, including cationization, in a formal sense, of $M(acac)_3$ to produce the structurally informative secondary ions $[C + M(acac)_3]^+$ (C represents the "cationizing agent"). In addition to cationization by sodium (from the NaCl matrix) and silver (from the silver support), self-cationization and cationization by another first-row transition metal have also been observed. Mixtures of tris(acetylacetonates) were found to give $[C + M(acac)_3]^+$ ions in low abundances in all cases except $Cr(acac)_3 + Mn(acac)_3$. In addition, both mixtures of different β-diketonate complexes and mixtures containing a β-diketonate complex with a metal chloride were found to give rise to metal-ligand exchange during the course of the SIMS experiment. The implications of these latter findings for the use of SIMS in characterizing metal complexes of importance in heterogeneous catalysis are discussed. Laser desorption, like SIMS, was observed to give rise to bimetallic ions, including silver ion cationization of the neutral β-diketonate complex. Some of these species were characterized by mass spectrometry/mass spectrometry (MS/MS) through collision-induced dissociation at 7 keV. Consideration is given to the relationship between the mechanisms of SIMS and laser desorption mass spectrometry (LDMS) as applied to the characterization of coordination complexes.

Introduction

Desorption ionization (DI) mass spectrometry includes those techniques like secondary ion mass spectrometry (SIMS) and laser desorption (LD), which create ions directly from a condensed phase. Following a previous SIMS analysis of surfaces containing different classes of preformed coordination compounds and organometallics,[1] attention is now being focused upon individual groups of complexes with a view to probing the significance of SIMS as a means of eliciting information of structural importance. Not only do these SIMS measurements relate to the characterization of molecular complexes but this work is of potential importance in the structure determination of surfaces of significance in heterogeneous catalysis.

In the earlier SIMS study,[1] the tris(acetylacetonato) complex of iron, $Fe(acac)_3$, was found to exhibit a strikingly simple spectrum, with $Fe(acac)_2^+$ as the base peak and $Fe(acac)^+$ as the only other species of comparable abundance. The intact molecular ion $Fe(acac)_3^+$ is not observed, but under appropriate conditions, ions corresponding to the cationization of the molecule can be detected. The three cationized species observed were $[Na + Fe(acac)_3]^+$, $Fe_2(acac)_3^+$, and $[Ag + Fe(acac)_3]^+$; these arise from the cationization by Na^+ from the sodium chloride matrix, Fe^+ from $Fe(acac)_3$ itself, and Ag^+ from the silver support.[1] Since that report, the species $[K + Fe(acac)_3]^+$ has also been observed. The presence of such species can be extremely important in the identification of the molecular and surface structure.

The formation of cluster ions is a well-documented phenomenon in SIMS, both for metals and for molecular substrates.[2-7] Metal ion adducts of a wide variety of molecules have been encountered, and the cationized molecules have particular value in characterization of the surface under examination. Neither cluster ion formation nor cationization is expected in electron impact mass spectrometry, but bimetallic species have nevertheless been observed for β-diketonate complexes.[8,9] This has led to an intense interest in the electron impact mass spectrometry of these compounds, as summarized by Westmore.[10] Ligand exchange has been documented, and bimetallic species have been observed bearing little obvious structural relationship to the β-diketonate complexes themselves.[8,9,11,12] At source pressures of less than or equal to 0.01 torr, these bimetallic ions are reported to be the result of ion/molecule reactions in the gas phase, although surface reactions cannot be excluded.[9]

It is of obvious interest to determine whether the complex processes of electron impact mass spectrometry also occur in alternative methods of ionization. In the present study of a wide range of β-diketonate complexes of the transition metals, the SIMS technique (argon ion bombardment of a solid surface) has been shown to yield some of these same bimetallic species. Furthermore, the possibility of using laser desorption mass spectrometry (LDMS)[13] to generate bimetallic species and the use of mass spectrometry/mass spectrometry (MS/MS)[14] to characterize these ions have been explored.

Experimental Section

SIMS spectra were obtained on a Riber Instrument (Model SQ 156L) in the positive ion mode using an energy selector, a quadrupole mass filter, a Channeltron electron multiplier, and pulse-counting electronics. An argon ion beam was used at 5 keV with a primary ion current typically 10^{-10} A or less and was focused to a beam size of 0.1 cm². This fulfills the static SIMS requirement,[15] ensuring that individual surface molecules are not subject to multiple primary ion impacts. Main chamber pressure during analysis was 1×10^{-8} torr or less. Samples were admixed with an excess of ammonium chloride[16]

---

(1) Pierce, J.; Busch, K. L.; Walton, R. A.; Cooks, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 2583.
(2) Day, R. J.; Unger, S. E.; Cooks, R. G. *Anal. Chem.* **1980**, *52*, 557A.
(3) Honda, F.; Lancaster, G. M.; Fukuda, Y.; Rabalais, J. W. *J. Chem. Phys.* **1978**, *69*, 4931.
(4) Honda, F.; Fukuda, Y.; Rabalais, J. W. *J. Chem. Phys.* **1979**, *70*, 4834.
(5) Lancaster, G. M.; Honda, F.; Fukuda, Y.; Rabalais, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 1951.
(6) Jonkman, H. T.; Michl, J. *J. Am. Chem. Soc.* **1981**, *103*, 733.
(7) Orth, R. G.; Jonkman, H. T.; Michl, J. *J. Am. Chem. Soc.* **1981**, *103*, 1564.
(8) MacDonald, C. G.; Shannon, J. S. *Aust. J. Chem.* **1966**, *19*, 1545.
(9) Schildcrout, S. M. *J. Phys. Chem.* **1976**, *80*, 2834.
(10) Westmore, J. B. *Chem. Rev.* **1976**, *76*, 695.
(11) Majer, J. R.; Perry, R. *J. Chem. Soc., Chem. Commun.* **1969**, 271.
(12) Holtzclaw, H. F., Jr.; Lintvedt, R. L.; Baumgarten, H. E.; Parker, R. G.; Bursey, M. M.; Rogerson, P. F. *J. Am. Chem. Soc.* **1969**, *91*, 3774.
(13) Conzemius, R. J.; Capellen, J. M. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *34*, 197.
(14) McLafferty, F. W. *Acc. Chem. Res.* **1980**, *13*, 33.
(15) Benninghoven, A. *Surf. Sci.* **1973**, *35*, 427.

0020-1669/82/1321-2597$01.25/0 © 1982 American Chemical Society

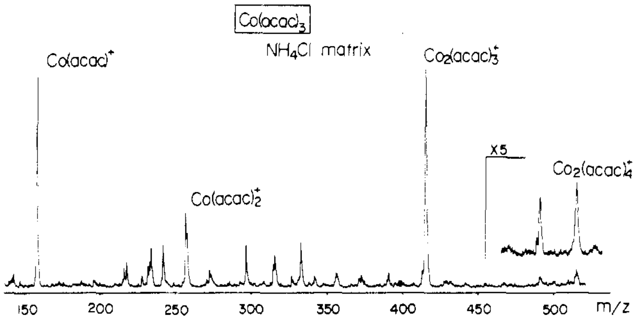

Figure 1. SIMS spectrum of $Co(acac)_3$ in an ammonium chloride matrix showing bimetallic species.

and were burnished directly onto an abrasively cleaned 1-cm^2 silver foil (0.0125 mm thick). Alternative methods of sample preparation employed a sodium chloride matrix, a slurry with polyphenyl ether,[17] or no matrix at all. When a matrix was used, samples were physically mixed with the matrix in a mortar and pestle before deposition on the silver planchette. No charge compensation was necessary in any of the experiments; both sample and the subjacent metal were exposed to the primary beam.

Laser desorption (LD) mass spectra were obtained either on the SIMS spectrometer, by replacing the primary ion gun with the laser, or on a reverse-geometry sector mass spectrometer. Details of both instrumental configurations are given elsewhere.[18,19] In all experiments a pulsed Nd:YAG laser was employed, with use of 1.06-μ radiation with 10-ns pulses, a 20-Hz repetition rate, and an instantaneous power density of about 10^7 W/cm^2. The MS/MS spectra were obtained by electric sector scans on the reverse-geometry instrument using published procedures.[14,19] Individual mass-analyzed ion beams were characterized by collision-induced dissociation at 7 keV using N_2 target gas at a nominal pressure of 10^{-3} torr.

The acetylacetonates of Mo(VI), V(IV), Cr(III), Mn(III), Co(III), Ni(II), and Cu(II), i.e., $MoO_2(acac)_2$, $VO(acac)_2$, $Cr(acac)_3$, $Mn(acac)_3$, $Co(acac)_3$, $Ni(acac)_2$, and $Cu(acac)_2$, were prepared by standard literature methods. Samples of Cr(III) complexes of the unsymmetrical β-diketone ligands $CF_3COCHCOCH_3^-$ and $PhCOCHCOCF_3^-$, abbreviated tfac and btac, respectively, were kindly provided by Professor D. R. McMillin. These complexes will be abbreviated $Cr(tfac)_3$ and $Cr(btac)_3$ in all subsequent discussions.

Results and Discussion

(a) SIMS Spectra of Individual β-Diketonate Complexes. The spectrum of $Co(acac)_3$ in an ammonium chloride matrix is shown in Figure 1. Abundant high-mass fragment ions include $Co(acac)_2^+$, $HCo(acac)_2^+$, and $Co(acac)^+$; the ion $Co_2(acac)_3^+$ is the base peak. The bimetallic $Co_2(acac)_4^+$ is also observed but in lower abundance. The effects of sample preparation and experimental variables have been investigated by using this complex as the substrate. No significant changes in relative abundances were discovered for any of these ions between neat samples, samples in NaCl or NH_4Cl solid matrices, a sample in polyphenyl ether solution, and samples to which other metal complexes and salts had been added. The possible effects of surface inhomogeneity were investigated by using a standard 1:1 mixture of $Co(acac)_3$ and $Fe(acac)_3$. The ratio of ion abundances $Co(acac)^+$:$Fe(acac)^+$ was measured at various positions on the sample and for different preparations of the same mixture and was always in the range of 1.1 ± 0.3, indicating that inhomogeneity in the matrix mixtures was not a problem.

One factor which can have a substantial effect on a SIMS spectrum is the primary ion current density.[20] For $Co(acac)_3$, $Co_2(acac)_3^+$ is the base peak at very low ion currents, but the fragment ion $Co(acac)^+$ increases in abundance at the expense of the bimetallic ion as the current is raised. This effect is demonstrated in Table I. Although primary ion currents less than 1×10^{-9} A/cm^2 correspond nominally to static SIMS conditions, a substantial difference in the spectra obtained by employing 1×10^{-10} A/cm^2 vs. 1×10^{-9} A/cm^2 implies dynamic SIMS conditions. If $Co_2(acac)_3^+$ and $Co_2(acac)_4^+$ were produced via a gas-phase bimolecular reaction, an increase in the primary ion current should produce the reverse effect. The decrease in abundance of $Co_2(acac)_3^+$ with subsequent increase in the fragment $Co(acac)^+$ as the primary ion current is increased therefore implies that these bimetallic ions $Co_2(acac)_3^+$ and $Co_2(acac)_4^+$ are derived directly from the substrate rather than produced from reactions such as cationization. This is consistent with the absence of matrix effects, for example, the failure of added salts to affect the bimetallic ion yields. For other ions such as $Co(acac)_2^+$, it is not possible to distinguish between (i) ejection directly from the solid and (ii) formation by fragmentation of a higher mass cluster ion. Although $Co(acac)_3$ exists in a monomeric state in the solid,[21] these results indicate that this complex belongs to the set of molecules in which intermolecular forces are not weak relative to intramolecular bond strengths. Consequently, the SIMS spectra do not yield simple molecular ions.[22]

Table I. Effect of Primary Current Density on Spectrum of $Co(acac)_3$[a]

current density, A/cm^2	rel abund			
	$Co(acac)^+$	$Co(acac)_2^+$	$HCo(acac)_2^+$	$Co_2(acac)_3^+$
1×10^{-10}	56	32	16	100
ca. 5×10^{-10}	96	33	26	100
1×10^{-9}	100	30	20	42

[a] Neat compound supported on a silver foil.

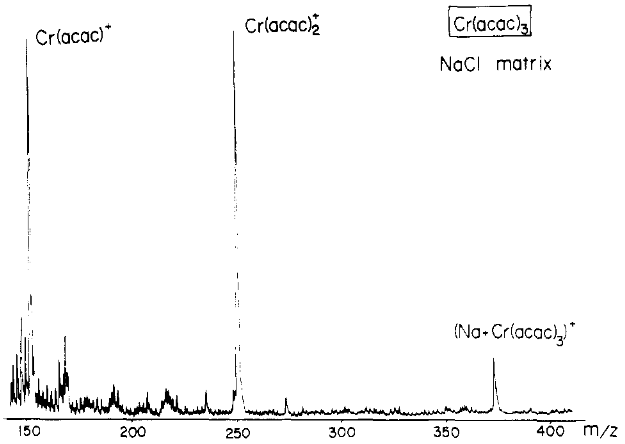

Figure 2. SIMS spectrum of $Cr(acac)_3$ in a sodium chloride matrix showing $[Na + Cr(acac)_3]^+$.

The tris(acetylacetonato) complexes $Cr(acac)_3$ and $Mn(acac)_3$ exhibit the same dominant fragmentation as their Fe(III) analogue,[1] namely, the loss of a single ligand yielding the base peak $M(acac)_2^+$. Lower abundance ions corresponding to the loss of two ligands to give $M(acac)^+$ and the loss of $CH_3\cdot$ from $M(acac)_2^+$ and $M(acac)^+$ constitute the remaining ions of signficance with *m/z* values less than those of the molecular ions. Unlike the EI mass spectra, which reveal molecular cation radicals, $M(acac)_3^{+\cdot}$ (usually of low abundance),[8,9] the SIMS spectra do not contain this form of molecular ion, a situation which is characteristic of this ion-

---

(16) Liu, L. K.; Busch, K. L.; Cooks, R. G. *Anal. Chem.* **1981**, *53*, 109.

(17) Busch, K. L.; Cooks, R. G., unpublished experiments.

(18) Busch, K. L.; Unger, S. E.; Vincze, A.; Cooks, R. G., submitted for publication.

(19) Zakett, D.; Schoen, A. E.; Cooks, R. G.; Hemberger, P. H. *J. Am. Chem. Soc.* **1981**, *103*, 1295.

(20) Unger, S. E.; Ryan, T. M.; Cooks, R. G. *Anal. Chim. Acta* **1980**, *118*, 169.

(21) Mehrotra, R. C.; Bohra, R.; Gaur, D. P. "Metal β-Diketonates and Allied Derivatives"; Academic Press: London, 1978.

(22) Murray, P. T.; Rabalais, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 1007.

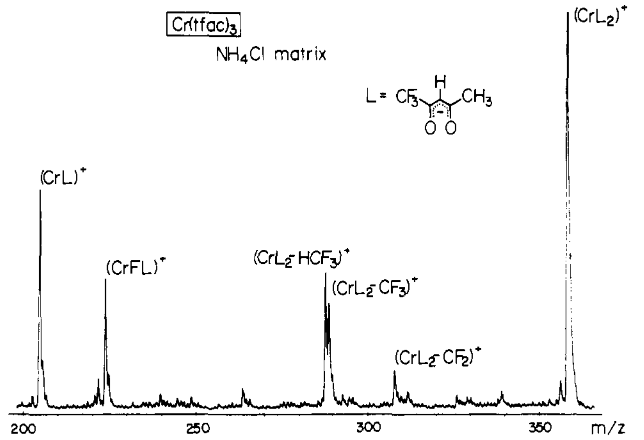

Figure 3. SIMS spectrum of $Cr(tfac)_3$ in an ammonium chloride matrix.

ization technique. This cannot be construed to mean that thermal decomposition has occurred, since cationization experiments (vide infra) permit the observation of the intact molecules in the SIMS experiment. The formation of $M(acac)_2^+$ as an abundant secondary ion in SIMS presumably arises by facile fragmentation of these higher mass cationized species.

As demonstrated previously in the case of $Fe(acac)_3$,[1] addition of the cationizing agent NaCl and exposure of the silver support to the primary ion beam can be an effective means of producing $[Na + M(acac)_3]^+$ and $[Ag + M(acac)_3]^+$. This is illustrated in Figure 2 for the case of $Cr(acac)_3$ where $[Na + Cr(acac)_3]^+$ is shown, but analogous results could not be obtained for the Co and Mn complexes. The spectra of both these latter complexes contain $M_2(acac)_3^+$ ions, formally the result of self-cationization but possibly originating from even higher mass polymetallic ions. The $M_2(acac)_3^+$ ion was observed for all four complexes (Fe, Co, Cr, and Mn), and $M_2(acac)_4^+$ ions were also apparent for Co and Cr. Cationization with silver or sodium ions may compete with the formation of bimetallic cluster ions. Large differences in the ease of cationization suggest that the use of this procedure for the SIMS analysis of metal acetylacetonates may necessitate experimenting with several cationizing reagents in order to ensure that optimum conditions have been achieved for the formation of structurally diagnostic ions, e.g., adduct ions $[C + M(acac)_3]^+$ in the case of the tris(acetylacetonates) of Cr, Mn, Fe, and Co. There may, of course, exist even more reactive metal cationizing agents that those demonstrated here. Different populations and energies of high-mass cluster ions such as $Co_2(acac)_3^+$ may also be the reason for differences in fragment ion abundances, explaining why $Co(acac)^+$, for example, is more abundant than $Co(acac)_2^+$, a situation the reverse of that found in the SIMS spectra of $Cr(acac)_3$, $Mn(acac)_3$, and $Fe(acac)_3$. No obvious electronic or structural difference can be correlated with this result.

In the extension of this work to include other β-diketone ligands, $Cr(tfac)_3$ and $Cr(btac)_3$, which contain $CF_3COCHCOCH_3^-$ (tfac) and $PhCOCHCOCF_3^-$ (btac), were chosen. The resulting SIMS spectra, recorded with an NH_4Cl matrix, characteristically identify each complex through the $M(tfac)_2^+$ or $M(btac)_2^+$ ion. Both derivatives exhibit a more complex spectrum than $Cr(acac)_3$ but share the lack of a radical molecular ion. The fragmentation pattern (Figure 3) is in close agreement with the fragmentation scheme proposed for the EI mass spectrum, except for the appearance of a molecular ion in EI,[23] suggesting that many of the observed ions are derived directly from $M(tfac)_2^+$ or $M(btac)_2^+$. No higher mass cluster ions were observed in the SIMS spectra or reported in the EI results.

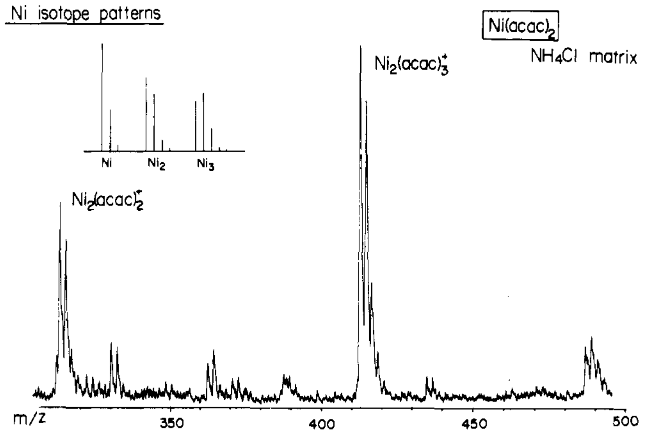

Figure 4. SIMS spectrum of $Ni(acac)_2$ in an ammonium chloride matrix showing clusters containing up to three Ni atoms. The inset shows the calculated isotopic patterns for n = 1, 2, and 3.

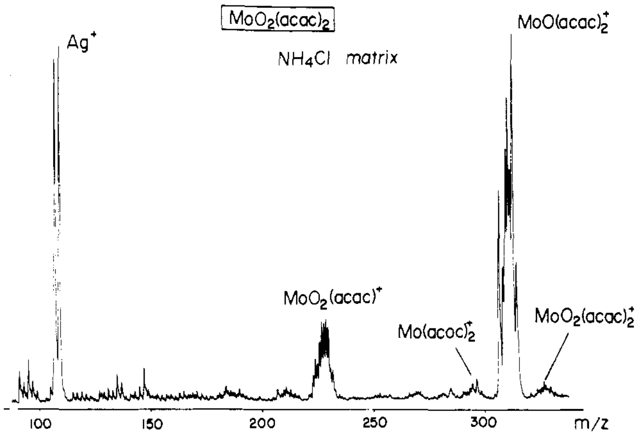

Figure 5. SIMS spectrum of $MoO_2(acac)_2$ in an ammonium chloride matrix.

In the case of β-diketonate complexes of divalent metal ions of the first transition series, and in contrast to the tris(β-diketonate) complexes, the solid-state species exhibit different degrees of oligomerization;[21] $Cu(acac)_2$ is a monomer and $Ni(acac)_2$ is trimeric. So that it could be ascertained whether such structural differences are reflected by differences in SIMS spectra, comparative studies were conducted on $Cu(acac)_2$ and $Ni(acac)_2$. When sputtering was done from NH_4Cl matrices with dilution ratios of approximately 1:5, SIMS spectra of both complexes display metal cluster ions $[M_n(acac)_m]^+$ up to n = 3. For copper, $Cu_3(acac)_m^+$ (m = 3 or 2), $Cu_2(acac)_m^+$ (m = 2 or 1), and $Cu(acac)^+$ are quite abundant, with the base peak being $Cu_2(acac)_2^+$, i.e., the formally self-cationized secondary ion of $Cu(acac)_2$. Similar results were obtained for $Ni(acac)_2$, with $Ni_2(acac)_3^+$ as the base peak and $Ni_2(acac)_2^+$ (m/z 314, 70% relative abundance), $Ni_2(acac)^+$ (m/z 215, 25%), and $Ni(acac)^+$ (m/z 157, 90%) as additional abundant ions. As shown in Figure 4, there is an additional cluster centered at m/z 490 which corresponds to an ion containing three nickel atoms that is formally "$[Ni_3(acac)_3 + 17]^{+}$". Comparison of SIMS spectra revealed no correlation between the observation of stable gas-phase cluster ions and the degree of oligomerization in the solid state. This situation is reminiscent of that which pertains for frozen molecules such as N_2O[7] or benzene;[5] here clustering obscures the relationship between structure and spectra. Such is not the case for most organic molecules examined at room temperature.[2]

The vanadyl complex $VO(acac)_2$, the SIMS spectrum of which was reported in an earlier study,[1] was unique among

---

(23) Clobes, A. L.; Morris, M. L.; Koob, R. D. *Org. Mass. Spectrom.* **1971**, *5*, 633.

β-diketonate complexes in that the molecular ion (albeit of low intensity) was observed in its SIMS spectrum. Other abundant ions in this spectrum were $V(acac)_2^+$, the base peak, and $VO(acac)^+$; i.e., loss of only a single oxygen atom or a single acac ligand occurs. In the present investigation, the SIMS spectrum of $MoO_2(acac)_2$ (Figure 5) shows a remarkable resemblance to that of the vanadyl analogue. The base peak at *m/z* 312 is formed by loss of oxygen from the molecular ion, presumably to produce $MoO(acac)_2^+$. Loss of a single acac ligand to form $MoO_2(acac)^+$ also occurs, and the cluster of peaks centered at *m/z* 328 is most likely due to the molecular ion, present in low abundance. $Mo(acac)_2^+$ is observed in low abundance, in contrast to the higher abundance of $V(acac)_2^+$.[24]

The behavior of these complexes with terminal metal–oxygen bonds can be rationalized in terms of facile cationization at the nucleophilic oxygen atom to yield a species, not necessarily observed, which is the precursor to lower mass fragment ions. Thus loss of (cation + O) would occur more reasonably than cleavage of the strong M–O bond to form ions such as $MoO(acac)_2^+$. In addition, this electronegative oxygen atom confers a relatively low ionization energy to the complex, allowing observation of the radical molecular ion.

(b) Mixed-Metal Species from Mixtures of Complexes. It has been shown from this and previous work[1] that the sample matrix can influence the nature of the secondary ions produced in the SIMS experiment. Thus with sodium and silver ions available, cationized secondary ions in SIMS yield definitive information on the molecular weight, as is often the case in the analysis of organic compounds. The ability of the $M(acac)_3$ complexes (M = Cr, Mn, Fe, or Co) to form self-cationized species and successfully compete with cationization by silver or sodium suggests that adduct formation of $M(acac)_3$ with other transition metals may also occur. In other words, what is the propensity for the formation of analytically useful $[C + M(acac)_3]^+$ ions, where C and M represent different first-row transition metals? For a study of this phenomenon, mixtures of $M(acac)_3$ and the other transition metal (C) in the form of finely divided metal powder, a chloride salt, or as its own β-diketonate complex were utilized.

In the case of admixture with a metal powder or metal chloride in an approximate 1:1 ratio, there was no evidence under these experimental conditions for $[C + M(acac)_3]^+$. Only those ions which were characteristic of the $M(acac)_3$ complex itself were observed along with the ion corresponding to C^+. For example, $Fe(acac)_3$ showed an ion due to $Fe_2(acac)_3^+$, the abundance of which could not be enhanced by mixing the complex with either $FeCl_3$ or ferrous gluconate or by analyzing the sample from an exposed iron support. Formation of the $Fe_2(acac)_3^+$ ion would therefore seem to arise by fragmentation of a larger ion, rather than a cationization reaction, per se. The influence of the primary ion current on the SIMS spectrum of $Co(acac)_3$, which shows $Co_2(acac)_3^+$ enhanced in abundance relative to $Co(acac)^+$ at low primary ion current, lends support to this hypothesis.

In a few instances, mixtures of $M(acac)_3$ and a metal chloride gave SIMS spectra that were characteristic of both metals as β-diketonate complexes. For example, the $Fe(acac)_3/CrCl_3/NH_4Cl$ mixture gave ions corresponding to $Cr(acac)^+$ and $Cr(acac)_2^+$, as well as $Fe(acac)^+$ (base peak), $Fe(acac)_2^+$, $[Fe(acac) - CH_3]^+$, and $[Fe(acac)_2 - CH_3]^+$. In other words, $Cr(acac)_n^+$ ions are formed either by fragmentation of a mixed-metal cationized species (not itself detected) or by the reaction of the neutral ligand with Cr^+ in the plasma generated at the surface by primary ion beam impact. For this and other systems that gave similar results, the $C(acac)^+$:$M(acac)^+$ ratio (C represents the metal added in the form of its chloride salt) varied greatly, with no apparent preference for one metal over another, except that ions derived from the original metal acetylacetonate (i.e., $M(acac)_3$) were generally present in higher abundance. Conclusions concerning relative metal–acac bond strengths, therefore, cannot be drawn from the relative abundances of $C(acac)^+$ vs. $M(acac)^+$, but the presence of both series of ions indicates a considerable degree of metal–ligand mixing for these compounds.

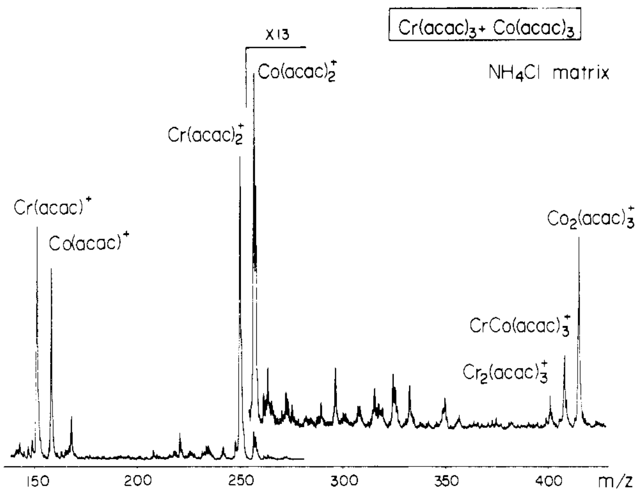

Figure 6. SIMS spectrum of an approximately 1:1 mixture of $Cr(acac)_3$ and $Co(acac)_3$ in an ammonium chloride matrix showing $Cr_2(acac)_3^+$ (*m/z* 401), $[Co + Cr(acac)_3]^+$ (*m/z* 408), and $Co_2(acac)_3^+$ (*m/z* 415).

Table II. Relative Intensities of Ions Observed in the SIMS Spectra of Mixtures of β-Diketonate Complexes[a]

$ML_3 + M'L_3$[b]	ML^+	$M'L^+$	ML_2^+	$M'L_2^+$	$M_2L_3^+$	$MM'L_3^+$	$M'_2L_3^+$
$CrL_3 + MnL_3$	100	93	90	16			3
$CrL_3 + FeL_3$	37	30	100	87	4	3	4
$CrL_3 + CoL_3$	77	63	100	9	1	2	5
$MnL_3 + FeL_3$	100	78	22	57	6	3	2
$MnL_3 + CoL_3$	83	100	36	11	1	2	9
$FeL_3 + CoL_3$	84	100	93	9	1	1	4

[a] All spectra were recorded by using an NH_4Cl matrix and a primary ion current of 1×10^{-9} A/cm². [b] M and M′ = metal; L = acac.

SIMS results for two-component mixtures of the $M(acac)_3$ complexes (M = Cr, Mn, Fe, or Co) in NH_4Cl matrices to enhance ion intensity demonstrate that in all instances, except for the mixture of $Cr(acac)_3$ with $Mn(acac)_3$, mixed-metal species are formed in low abundance. These spectra displayed the appropriate $M(acac)_n^+$ ions (*n* = 1 or 2) in addition to $[C + M(acac)_3]^+$ and the self-cationized $M_2(acac)_3^+$ (i.e., C = M) (an example is given in Figure 6). In the case of mixtures of $Cr(acac)_3$ and $Mn(acac)_3$, while no ions were observed which contained both Cr and Mn, the silver-cationized species $[Ag + Mn(acac)_3]^+$ (*m/z* 459 and 461), an ion not seen in the SIMS of $Mn(acac)_3$ alone, was detected. These results are summarized in Table II. Measurements of $Ni(acac)_2/Cu(acac)_2$ and $Fe(acac)_3/VO(acac)_2$ mixtures showed that the secondary ions observed were characteristic of the individual complexes, the only evidence for a mixed-metal species $[C + M(acac)_3]^+$ being the presence of a very low-abundance ion

---

[24] In the EI mass spectrum of $VO(acac)_2$, loss of oxygen is not observed; instead, loss of 15 amu from the ligand forms $(M - 15)^+$.[8] On the other hand, in the EI mass spectrum of $MoO_2(acac)_2$ (CEC21-110 mass spectrometer, probe temperature 140 °C), $MoO_2L_2^+$ (*m/z* 328, 66%), $(MoO_2L_2 - CH_2CO)^+$ (*m/z* 286, 72%), and MoO_2L^+ (*m/z* 229, 100%) are the most abundant ions; other less abundant but identifiable ions are $MoOL_2^+$ (*m/z* 312, 8%), $MoOL^+$ (*m/z* 213, 15%), $(MoO_2L - CH_2CO)^+$ (*m/z* 187, 17%), and MoO^+ (*m/z* 114, 4%). Note: *m/z* values are quoted relative to the ^{98}Mo isotope. While different base peaks are observed in the SIMS and EI mass spectra of $MoO_2(acac)_2$, the SIMS spectrum is simpler than the EI mass spectrum, and both show fragment ions corresponding to loss of an oxygen atom.

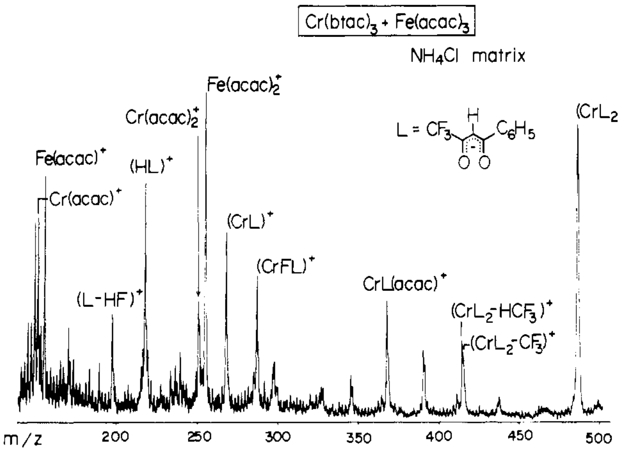

Figure 7. SIMS spectrum of a mixture of $Cr(btac)_3$ and $Fe(acac)_3$ in an ammonium chloride matrix.

at *m/z* 404, corresponding to $[V + Fe(acac)_3]^+$.

The SIMS spectrum of a 1:1 mixture of $Co(acac)_3$ and $Cr(acac)_3$ (Figure 6) is particularly interesting. Neither radical molecular ion, $M(acac)_3^{+\cdot}$, is observed, as expected. The abundances of $M(acac)^+$ ions are approximately equal, but the abundances of $M(acac)_2^+$ are strikingly different. The energetics of the ionization and fragmentation of these compounds are well-known.[10] The ionization potentials for $Co(acac)_3$ and $Cr(acac)_3$ are 7.8 and 8.1 eV, respectively. Appearance potentials for the $M(acac)_2^+$ ions are 10.7 eV (Co) and 11.3 eV (Cr). If $M(acac)_2^+$ was formed from $M(acac)_3^+$ in each case, the $Co(acac)_2^+$ ion should be of higher abundance than $Cr(acac)_2^+$. Exactly the opposite is observed, suggesting that these fragment ions form from the higher bimetallic species shown. Furthermore, note that the abundances of these species are not equal; $Co_2(acac)_3^+$ is of greater abundance than $Cr_2(acac)_3^+$, suggesting a greater stability and hence less fragmentation to $Co(acac)_2^+$.

The preceding results demonstrate that, of the metal acetylacetonates studied, $Fe(acac)_3$ shows the largest variety of bimetallic cluster ions yet observed (adducts with K, Na, Ag, V, Cr, Mn, Co, and Fe). For this reason the investigation of the SIMS of mixtures of $Fe(acac)_3$ (and for comparison $Mn(acac)_3$ and $Co(acac)_3$) with the chromium complexes $Cr(tfac)_3$ and $Cr(btac)_3$, which contain β-diketonate ligands different from acac, was undertaken. This was an opportunity to study metal–ligand exchange using "labeled" β-diketone ligands. With the mixtures $Mn(acac)_3/Cr(tfac)_3$ and $Co(acac)_3/Cr(tfac)_3$, there was little evidence for other ions than those which characterize the SIMS of the individual complexes. On the other hand, a mixture of $Fe(acac)_3$ and $Cr(tfac)_3$ was found to exhibit a SIMS spectrum with ions at *m/z* 182 and 304; these were not present in the SIMS of the separate components. The ion at *m/z* 304 is the base peak in the spectrum and most probably corresponds to the mixed-ligand species $Cr(acac)(tfac)^+$; *m/z* 182 remains unidentified. For the $Fe(acac)_3/Cr(btac)_3/NH_4Cl$ mixture (Figure 7) ions at *m/z* 250 and 254 due to $Cr(acac)_2^+$ and $Fe(acac)_2^+$, respectively, were observed and the formation of the mixed-ligand ion $Cr(acac)(btac)^+$ was indicated by the peak at *m/z* 366. These results demonstrate that metal–ligand exchange reactions can occur during the SIMS experiment.

(c) Laser Desorption Mass Spectrometry and Mass Spectrometry/Mass Spectrometry. Although few studies have been reported in which laser-induced ionization techniques have been used for the detection of transition metal compounds in mass spectrometry,[25-27] the available data reveal interesting similarities with SIMS results. Thus the laser desorption mass spectra of $VO(bzac)_2$ (bzac = benzoylacetone) and other vanadyl species, obtained with a laser microprobe (LAMMA),[26,27] show that, as in SIMS (as revealed by studies on $VO(acac)_2$), the loss of oxygen to form stable $V(acac)_2^+$ is observed along with fragments due to loss of β-diketone ligands. Encouraged by these results, we have obtained the LD spectra of $Co(acac)_3$ and $Fe(acac)_3$ supported on Ag foils. Both spectra contain bimetallic ions, including those which incorporate silver from the foil (See Table III). In LD, as in SIMS, no intact molecular ions are observed; however, many of the same bimetallic cluster ions are formed.

Table III. LD Mass Spectra of $Co(acac)_3$ and $Fe(acac)_3$ Obtained on a Reverse-Geometry MS/MS Instrument[a]

$Co(acac)_3$	$Fe(acac)_3$
$AgCo(acac)_2^{+}$ [b]	$AgFe(acac)_2^{+}$ [b]
$Co_2(acac)_3^{+}$ [b]	$Fe(acac)_2^+$
$HCo(acac)_2^+$	$AgFe(acac)_3^+$
$Co(acac)_2^+$	$Fe_2(acac)_3^+$
$Co(acac)^+$	$Fe(acac)^+$
	$Fe_2(acac)_4^+$

[a] Ions are listed in order of decreasing abundance. [b] MS/MS spectra obtained.

Table IV. MS/MS Spectra of Silver Containing Cluster Ions for Metal Acetylacetonates[a]

	main beam	
	$AgFeL_2^+$	$AgCoL_2^+$
fragments	$AgFeLO^+$	$AgCoLC_3H_6O^+$
	FeL_2^+	$AgCoLO^+$
	$(FeL_2 - CH_3)^+$	CoL_2^+
	$(FeL_2 - 2CH_3)^+$	$(CoL_2 - CH_3)^+$
	FeL^+	CoL^+
	Ag^+	Ag^+

[a] L = acetylacetonate. The six most abundant fragment ions are listed in order of decreasing mass.

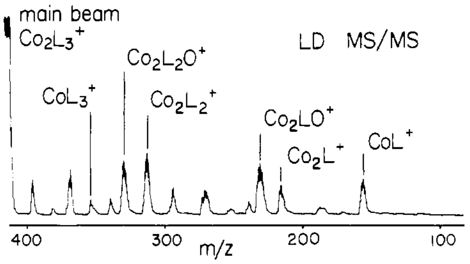

Figure 8. LD MS/MS spectrum of $Co(acac)_3$. The primary ion $Co_2(acac)_3^+$ is mass selected, excited by collision with nitrogen target gas and the fragment ions recorded.

These LD spectra were obtained on a reverse sector mass spectrometer, which can be used to obtain MS/MS spectra of ions created by laser irradiation. Ions for which these spectra were obtained are so indicated in Table III. An example of such a spectrum is given in Figure 8 for $Co_2(acac)_3^+$. These spectra suggest that these cluster ions cannot be considered simply as metal cations loosely complexed with neutral sample molecules; dominant losses of either metal are not observed. Rather, a stable structure incorporating two metal atoms is indicated perhaps most strongly by the presence in these spectra of such fragments as Co_2^+ or $AgFe^+$ although in low abundance. Collision-induced fragmentation from these cluster ions to form $M(acac)_2^+$ or $M(acac)^+$ provides evidence that such processes also occur in the SIMS and LD mass spectra. A summary of the MS/MS results for the indicated

---

(25) Muller, J. F.; Magar, J. M.; Cagniant, D.; Grimblot, J.; Bonnelle, J. P. *J. Organomet. Chem.* **1980**, *186*, 389.

(26) Muller, J. F.; Magar, J. M.; Cagniant, D.; Mouchot, J. M.; Grimblot, J.; Bonnelle, J. P. *J. Organomet. Chem.* **1981**, *205*, 329.

(27) Heinen, H. J. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *38*, 309.

cluster ions is given in Table IV.

It is observed that the laser desorption mass spectrum of $Cu(phen)Cl_2$ (phen = 1,10-phenanthroline) on a silver support contains ions similar to those in the SIMS spectrum,[1] with $Cu(phen)^+$ as the base peak. Further, the SIMS spectrum of $[RhCl_2(dth)_2]PF_6$ (dth is the 2,5-dithiahexane ligand)[1] contains the intact cation as does the LAMMA spectrum of salts of $[RhCl_2(S_4)]^+$, where S_4 represents the thioether ligand 1,4,8,11-tetrathiacyclotetradecane.[26] One difference between the latter pair of complexes is that fragment ions of $[RhCl_2(S_4)]^+$ corresponding to loss of one and two chlorines are seen in the LAMMA[26] but not in the SIMS spectrum. Even at this early stage of comparison between SIMS and LD mass spectra of metal complexes, there are strong indications of similarities in the mechanisms of ion formation; thus LD MS/MS studies can be used to interpret SIMS results, as also shown in other studies.[19] Further comparisons along these lines clearly merit much more attention in the future.

(d) Conclusions. The SIMS spectra of molecules containing strong intramolecular and weak intermolecular attractive forces, e.g., most organic molecules, contain abundant ions corresponding to cationized molecular species such as (Na + molecule)$^+$ and (Ag + molecule)$^+$ and fragment ions that appear to arise by unimolecular fragmentations from these and other stable species.[28,29] Samples which exhibit strong intermolecular attractions, e.g., simple inorganic salts and some small frozen molecules such as water and benzene, on the other hand, tend to exhibit abundant cluster ions in which distinctive structural information may be obscured.[3,5,30] It is apparent from results of the present study that the β-diketonate complexes exhibit intermediate behavior; i.e., significant cationization is observed and higher mass cluster ions are also formed. Conditions that favor the formation of simple cationized molecular species are preferable for obtaining information such as the molecular weight of the sample. Although such species have been observed for the compounds studied here, the facile formation of mixed-metal and mixed-ligand species occurs even when an isolation matrix of ammonium chloride is used. It has been shown that these ions do not reflect the degree of oligomerization in the undisturbed condensed phase and do not reflect relative metal–ligand bond strengths. The study does show that these species are formed in a variety of processes that include sample–sample, sample–support, and sample–matrix interactions and that fragment ions in the spectra can originate from these cluster ions, many of which may not be observed.

The generation of mixed-metal species is of particular significance in light of interest in such compounds as probes into electronic and geometric factors that influence the catalytic properties of alloys and dinuclear and cluster compounds of the transition metals.[31,32] These studies on mixtures of different β-diketonate complexes, and mixtures containing a β-diketonate complex with a metal chloride, also provide evidence for metal–ligand exchange, i.e., the formation of new metal–ligand bonds during the course of the SIMS experiment. This observation is most important in view of the potential of SIMS as a means of characterizing catalytically significant surface species. However, it must be emphasized that the SIMS behavior of β-diketonate complexes of transition metals is intermediate between that of organic compounds and that of salts. The unique characteristics of these compounds are evident even in their electron impact mass spectra. The complexity of the spectra makes it possible to discern a variety of secondary ion formation processes and also points to the need for a careful interpretation of SIMS or LD results on systems where different metals in different ligand environments are present in close proximity. The present study also points to deep-seated similarities between LD and SIMS, which include the generation of cationized ions and similarities in cluster ion formation processes occurring at the surface. For both techniques, metal-containing fragment ions may originate from multimetal cluster ions, as indicated by the MS/MS results, the mixed-complex studies, and the primary current density observations. The LD MS/MS spectra of transition metal complexes give information on the structure of bimetallic ions, specifically that strong metal–metal interactions are present.

Acknowledgment. This work was supported by a grant from the National Science Foundation through the NSF-MRL program (Grant DMR77-23798 and DMR80-20249). We thank Rick Korzeniowski for assistance with the laser desorption experiments.

Registry No. $Co(acac)_3$, 21679-46-9; $Cr(acac)_3$, 21679-31-2; $Mn(acac)_3$, 14284-89-0; $Fe(acac)_3$, 14024-18-1; $Cr(tfac)_3$, 14592-89-3; $Ni(acac)_2$, 3264-82-2; $MoO_2(acac)_2$, 17524-05-9; $Cr(btac)_3$, 28096-65-3; $Cu(acac)_2$, 13395-16-9.

---

(28) Grade, H.; Cooks, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 5615.

(29) Day, R. J.; Unger, S. E.; Cooks, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 499.

(30) Compana, J. E.; Barlak, T. M.; Colton, R. J.; DeCorpo, J. J.; Wyatt, J. R.; Dunlap, B. I. *Phys. Rev. Lett.* **1981**, *47*, 1046.

(31) Sinfelt, J. H. *Acc. Chem. Res.* **1977**, *10*, 15 and references therein.

(32) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1975**, *84*, 959.