We can consider two CT transitions:

$$\mathrm{Co(III)} + \mathrm{P}^{\bullet+} \rightarrow \mathrm{Co(II)} + \mathrm{P}^{2+} \quad (\mathrm{Co}:\ \mathrm{d}^6 \rightarrow \mathrm{d}^7) \qquad \text{(i)}$$

$$\mathrm{Co(III)} + \mathrm{P}^{\bullet+} \rightarrow \mathrm{Co(IV)} + \mathrm{P}^{0} \quad (\mathrm{Co}:\ \mathrm{d}^6 \rightarrow \mathrm{d}^5) \qquad \text{(ii)}$$

For the Co(II)/Co(III) couple, the redox potential is about +0.3 V, while for the $\mathrm{P}^0/\mathrm{P}^{\bullet+}$ and $\mathrm{P}^{\bullet+}/\mathrm{P}^{2+}$ couples, the $E_{1/2}$ values are about +1.0 and +1.2 V, respectively.[1] The transition (ii) can be excluded due to the unlikely oxidation process of Co(III) to Co(IV). The resulting CT states from (i) can be written as $S = {}^1/_2$, ${}^2\mathrm{B}_{2u}$ ($\pi \rightarrow \mathrm{d}$), with orbital contributions ($\mathrm{a}_{1u}{}^0$, $\mathrm{a}_{2u}{}^2$, $\mathrm{b}_{2g}{}^1$) for a transition from the ${}^2\mathrm{A}_{1u}$ ground state (a similar CT state is formed for the ${}^2\mathrm{A}_{2u}$ species).

Low-lying (d–d) states of Co(III) may also couple with the ground state of $\mathrm{P}^{\bullet+}$. Antipas and Gouterman[28] have reported that emission intensity is quenched in both Co(II) and Co(III) neutral porphyrins and have suggested that low-lying CT or ^{3}(d–d) states may be coupling to the ground state, such that this route offers an efficient nonradiative deactivation pathway. We do not believe that this mechanism would generate the MCD intensity growth in the C terms in the manner that we have observed.

In summary, we suggest that the most reasonable interpretation of the temperature dependence in the MCD spectra of both $\mathrm{Co^{III}OEP^{\bullet 2+}}$ species is that spin–orbit coupling in the porphyrin excited states due to the overlap of an LMCT band modifies the energies of the pure $L{\cdot}S$ π^* states such that the individual $L{\cdot}S$ components are no longer equally separated by the magnetic field. The temperature-dependent intensity can be described in terms of spin-dependent C terms that result from transitions out of the lower spin component of the ${}^2\mathrm{A}_{1u}$ or ${}^2\mathrm{A}_{2u}$ ground state. The low-temperature MCD spectrum of $[\mathrm{Co^{III}OEP}]^{\bullet 2+}(\mathrm{Br^-})_2$ is the first to exhibit features characteristic of the presence of degenerate excited states.

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Registry No. $\mathrm{Co^{II}OEP}$, 17632-19-8; $[\mathrm{Co^{III}OEP}]^{\bullet 2+}(\mathrm{Br^-})_2$, 32880-79-8; $[\mathrm{Co^{III}OEP}]^{\bullet 2+}(\mathrm{ClO_4^-})_2$, 33058-44-5.

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Cluster Ions in the Electron and Chemical Ionization Mass Spectra of Transition-Metal Acetylacetonates

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The electron ionization mass spectra of transition-metal acetylacetonates have been recorded under conditions that maximize the abundance of cluster ions (those ions containing two or more metal atoms). Present electron ionization results obtained for copper(II), iron(III), and vanadium(III) acetylacetonates are similar to previously reported results for ions smaller than the molecular ion, but several new cluster ions of higher mass are observed. Cluster ions for zirconium(IV) and palladium(II) acetylacetonates under electron ionization conditions are reported here for the first time. The methane and ammonia chemical ionization mass spectra of transition-metal acetylacetonates are also included in this report; this represents the first application of chemical ionization mass spectrometry to this class of compounds.

Introduction

Transition-metal acetylacetonates were among the first transition-metal complexes to be studied by electron ionization mass spectrometry due to their high volatility, thermal stability, and ease of preparation.[1] Interpretation of their mass spectra has allowed a comparison of the effect of different metals, and different metal oxidation states, on the pattern of fragmentation observed in the mass spectra. The importance of changes in metal valency during fragmentation, first noted in the mass spectra of metal chlorides by Shannon and Swan,[2] was further studied and confirmed in the investigation of these compounds. Perhaps no other class of coordination compounds has been so thoroughly studied by mass spectrometry. The mass spectra of metal acetylacetonates obtained by various investigators are reasonably similar with respect to the nature and relative abundances of the ions formed.[1,3–7] Fragmentation pathways have been extensively studied. Further, high-resolution mass spectrometry has been used to confirm empirical formulas, and isotopic labeling has been used to elucidate rearrangement reactions, especially those involving hydrogen.[5,6]

The most striking feature of the electron ionization mass spectra of transition-metal acetylacetonates is the presence of cluster ions (those ions containing two or more metal atoms) at masses above that of the molecular ion. MacDonald and Shannon, who carried out the first comprehensive study of these compounds,[1] noted several cluster ion species, with some ions including three metal atoms. The origin of these ions, whether derived from dissociations of still larger gas-phase cluster species or resulting from ion/molecule reactions, was not established in these initial investigations. In addition to the formation of cluster ions, complex atom transfer reactions have been reported both for the metal acetylacetonates[1] and for complexes of metals with fluorinated β-diketonates.[8]

The question of cluster ion formation in the gas phase was later addressed thoroughly by Schildcrout.[9] The dependence of the cluster ion abundances on sample pressure, temperature, repeller potential, and ionizing energy in an electron ionization source indicated that the cluster ions are products of reactions between metal-containing fragment ions and neutral monomers of the

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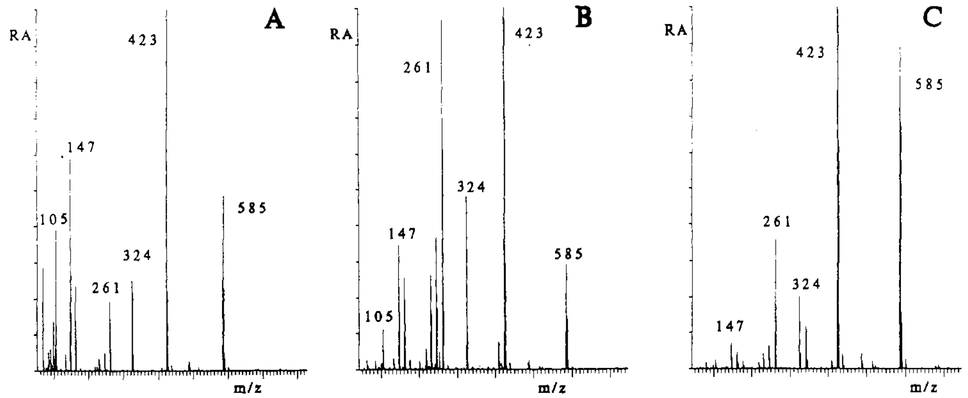

Figure 1. Mass spectra of copper(II) acetylacetonate: (A) electron ionization; (B) methane chemical ionization; (C) ammonia chemical ionization. Labeled peaks include $Cu_3(acac)_4^+$ at *m/z* 585, $Cu_2(acac)_3^+$ at *m/z* 423, $Cu(acac)_2^+$ at *m/z* 261, and $Cu(acac) - CH_3^+$ at *m/z* 147. Identities of the remaining peaks are listed in Table I.

coordination compound. By scanning the mass spectrometer up to *m/z* 900, Schildcrout discovered a number of cluster ions in the mass spectra beyond the masses of those initially observed by MacDonald and Shannon.

This paper describes the use of a high-resolution and high-sensitivity mass spectrometer to further characterize the mass spectra of these compounds. The instrument was operated under conditions purposefully chosen to maximize the abundances of the cluster ions. There are specific questions we sought to answer. To what masses do cluster ions extend? Do ion/molecule reactions occur only between coordinately unsaturated ions and neutrals, or are molecular ions involved? What, if any, is the effect on the use of chemical ionization as compared to that of electron ionization? Specifically, will chemical ionization using Brønsted acid reagent ions (such as CH_5^+ or NH_4^+) increase the abundances of ions, either cluster ions or fragmentations, that incorporate additional hydrogen into an otherwise simple structure? Although the electron ionization mass spectra of transition-metal acetylacetonates have been well-studied, there has been no report of the chemical ionization mass spectra of these compounds. We now report new cluster ions formed by electron ionization and also a comparison of the electron ionization mass spectra with those obtained under chemical ionization conditions.

Experimental Section

Electron and chemical ionization spectra were obtained on a Kratos MS80RFAQQ mass spectrometer of EBQ geometry, that is, a double-focusing instrument with an electric sector followed by a magnetic sector, followed then by deceleration optics and a quadrupole mass filter. Mass spectra were recorded with the intermediate detector, and so ions did not pass through the final quadrupole of the instrument. Normal resolution was set to 1000 and was increased to 7500 for exact mass measurements. Electron and chemical ionization spectra were recorded with the use of an off-line electron multiplier located after the magnetic sector but before the quadrupoles, coupled to a Kratos DS-55 data system. Calibration was accomplished with perfluorokerosene (PFK). The scan rate was set to 3 s/decade for low resolution and increased to 10 s/decade for exact mass measurements. Electron energy was 70 eV with an electron current of 100 μA for electron ionization. Methane and ammonia were used as chemical ionization reagent gases at an estimated source pressure of 1 Torr, as measured by an ionization gauge mounted on the source flange. Electron energy was 125 eV with an electron current of 500 μA for chemical ionization. Samples for both electron and chemical ionization were introduced into the source with the use of a direct-insertion probe that was heated from 40 to 300 °C at a rate of 25 °C/min. Total sample loading was 100 μg, an overload chosen specifically to increase the partial pressure of the sample molecules in the source. Spectra were recorded when the probe temperature was in the range of 170–220 °C. The ion source temperature was held constant at 200 °C. All metal acetylacetonates were obtained from Aldrich Chemical Co. (Milwaukee, WI). Predicted isotopic ratios for transition-metal-containing ions were calculated with an in-house computer program using standard procedures. Ion relative abundances listed in the tables are summed across the isotopic envelope for each ion reported. Since the appearance of the mass spectrum can therefore be noticeably different, figures are also given for each case to illustrate both the diversity of the cluster ions formed and the relative widths of their isotopic envelopes.

Results and Discussion

Copper(II) Acetylacetonate. Electron Ionization. The electron ionization mass spectrum of copper(II) acetylacetonate recorded in this investigation is in general agreement with previously recorded mass spectra with respect to both the nature and the relative abundances of the ions observed.[1] As the pressure in the souce increased due to increasing volatilization of the copper complex, a number of cluster ions were recorded, none of which have previously been reported (Table I, Figure 1). These ions include $Cu_3(acac)_4CH_2^+$ at *m/z* 599, $Cu_4(acac)_4C_2H_5^+$ at *m/z* 677, $Cu_3(acac)_5^+$ at *m/z* 684, and $Cu_4(acac)_5^+$ at *m/z* 747 (acac = acetylacetonate). Although these ions are present in low relative abundance, there is good agreement between the experimental and theoretical isotopic envelopes so that the assignments can be made with certainty. The presence of species such as $Cu_3(acac)_4^+$ with a low metal:ligand ratio is suggestive of the presence of Cu(I), formed by reduction of Cu(II) from the original molecule. Similar reduction of Cu(II) to Cu(I) was postulated to explain low metal:ligand ratios for many of the ions observed in the electron ionization mass spectra of copper(II) acetate.[10]

Chemical Ionization. The appearance of higher mass cluster ions and an increased degree of hydrogen incorporation in many of the fragment and cluster ions is apparent in the chemical ionization mass spectra of copper(II) acetylacetonate in comparison to the electron ionization mass spectrum. A similar result was reported for the analysis of copper(II) acetate.[10] The primary mechanism of chemical ionization for organic compounds is the transfer of a proton from a reagent gas ion (CH_5^+ or NH_4^+) to the neutral molecule. In this study, two reagent gases of different Brønsted acidities were used to assess the facility of the proton-transfer reaction. Ammonia should provide an $(M + H)^+$ ion of lower energy relative to that formed with methane as the reagent gas.

The results expected include an increase in the extent of hydrogen incorporation into the ions observed in the mass spectrum, such as observed previously,[10] and an increase in the relative abundances of high-mass cluster ions due to collisional stabilization at increased pressure.[11] As seen in Table I, there are a number of high-mass cluster ions observed in the ammonia chemical ionization mass spectrum that are not present in the electron ionization mass spectrum. Examination of the relative abundances indicates that those cluster ions with a mass-to-charge ratio greater than that of the base peak, $Cu_2(acac)_3^+$ at *m/z* 423, exhibit an increased abundance. Ammonia chemical ionization also produces a higher abundance of ions that incorporate additional hydrogen than does electron ionization. For example, $Cu_3(acac)_4H^+$ (*m/z* 586) exhibits a relative abundance of 26.7% under ammonia chemical ionization and is not observed at all under electron ionization conditions. Additionally, the use of ammonia chemical

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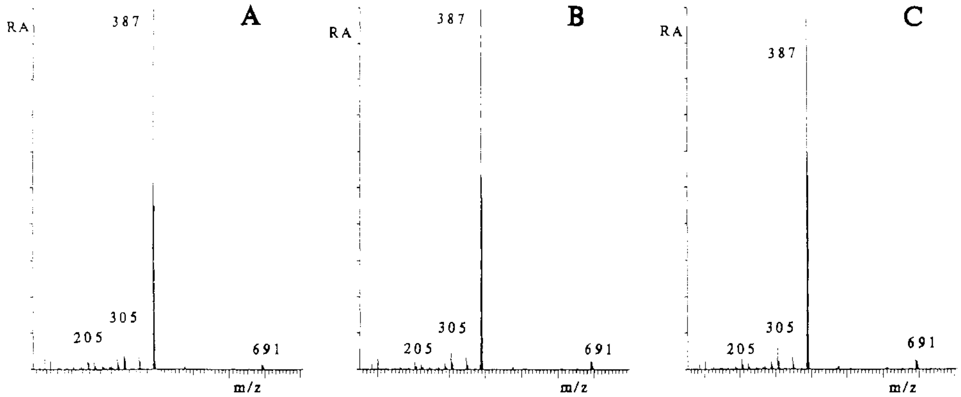

Figure 2. Mass spectra of zirconium(IV) acetylacetonate: (A) electron ionization; (B) methane chemical ionization; (C) ammonia chemical ionization. Labeled peaks include $Zr_2O(acac)_5^+$ at *m/z* 691, $Zr(acac)_3^+$ at *m/z* 387, and $Zr(acac)_2OH^+$ at *m/z* 305. Identities of the remaining peaks are listed in Table II.

Table I. Electron Ionization (EI), Methane Chemical Ionization (CI), and Ammonia CI Mass Spectra of Copper(II) Acetylacetonate[a]

ion	*m/z*	rel abund, %		
		EI	CI (CH_4)	CI (NH_3)
$Cu_4(acac)_5^+$	747	0.7		
$Cu_3(acac)_5^+$	684	0.7		1.2
$Cu_4(acac)_4C_2H_5^+$	677	0.6		0.7
$Cu_3(acac)_4CH_2^+$	599	1.2	0.7	0.5
$Cu_3(acac)_4H^+$	586			26.7
$Cu_3(acac)_4^+$	585	59.1	35.8	91.0
$Cu_3(acac)_4 - H^+$	584			0.5
$Cu_2(acac)_4^+$	522			1.1
$Cu(acac)_4C_2O_2^+$	515	0.8*	0.6*	1.3*
$Cu_3(acac)_3^+$	486	2.7	2.6	4.1
$Cu_2(acac)_3CH_3^+$	438		0.4	
$Cu_2(acac)_3CH_2^+$	437	1.7	2.0	3.5
$Cu_2(acac)_3H^+$	424	13.5	6.2	33.2
$Cu_2(acac)_3^+$	423	100.0	100.0	100.0
$Cu_2(acac)_3 - H^+$	422	0.6	0.9	1.3
$Cu(acac)_3C_2O_2^+$	416		1.3	
$Cu_2(acac)_3 - CH_3^+$	408	0.9	8.3	2.0
$Cu_2(acac)_3 - C_2H_5^+$	394	w	0.5	
$Cu_2(acac)_2C_2O_2^+$	380	0.1*	0.8*	0.4*
$Cu_2(acac)_2OH^+$	341			9.8
$Cu_2(acac)_2CH_3^+$	339	0.1	0.3	0.1
$Cu_2(acac)_2CH_2^+$	338	0.2	0.7	w
$Cu_2(acac)_2H^+$	325		0.6	
$Cu_2(acac)_2^+$	324	25.2	49.5	16.7
$Cu_2(acac)_2 - H^+$	323		0.4	w
$Cu_2(acac)_2 - CH_3^+$	309	0.3	0.1	0.3
$Cu_2(acac)_2 - C_2H_5^+$	295	0.3	0.8	
$Cu(acac)_2CH_2^+$	275		1.0*	
$Cu(acac)_2CH$	274	0.4*		
$Cu(acac)_2H^+$	262	2.5	24.0	5.6
$Cu(acac)_2^+$	261	11.0	69.8	21.0
$Cu(acac)_2 - CH_3^+$	246	4.1	27.0	3.7
$Cu(acac)_2 - H_2O^+$	243	0.3	1.1	0.2
$Cu(acac)_2 - (CH_3)_2^+$	231	3.0	21.5	2.7
$Cu_2(acac)^+$	225	1.1	1.0	0.2
$Cu(acac)C_2HO_2^+$	219	0.9	4.1	1.0
$Cu_2O_2C_3H_7^+$	201	0.6*	2.2*	0.4*
$Cu(acac)C_2H_3^+$	189	0.4*		
$Cu_2(OH)_2CH_3^+$	175	0.7*		
$Cu(acac)H^+$	163	6.9	12.0	2.4
$Cu(acac)^+$	162	15.2	14.6	3.0
$Cu(acac) - H^+$	161	0.2	1.0	0.2
$Cu(acac) - CH_3^+$	147	39.5	23.4	4.0
$Cu(acac) - C_2H_5^+$	133	3.2	2.2	0.4
$CuC_2OH_2^+$	105	26.9	7.7	1.4
$CuOH^+$	80			0.8

[a] In this table, *m/z* values are reported for the ^{63}Cu isotope. The symbol w denotes that the ion is present with less than 0.1% relative abundance. The symbol * indicates that the cluster was not fully deconvoluted.

Table II. EI, Methane CI, and Ammonia CI Mass Spectra of Zirconium(IV) Acetylacetonate[a]

ion	*m/z*	rel abund, %			HR
		EI	CI (CH_4)	CI (NH_3)	
$Zr_2(acac)_7^+$	873	w			×
$Zr_2O(acac)_5^+$	691	2.7	3.9	4.4	×
$Zr_2O_2(acac)_4H^+$	609	0.6	0.6	0.8	×
$Zr_2O_2(acac)_3^+$	509	0.5	0.4	0.5	×
$Zr(acac)_3^+$	387	100.0	100.0	100.0	×
$Zr(acac)_3 - H^+$	386	1.6	1.3	1.7	
$Zr(acac)_3 - CH_2^+$	373	0.2	w	0.1	
$Zr(acac)_3 - H_2O^+$	369	0.1	w	0.1	
$Zr(acac)_2C_2H_3O_2^+$	347	5.3	2.8	2.5	
$Zr(acac)_2C_3H_5O^+$	345	0.4	0.2	0.2	
$Zr(acac)_2OH^+$	305	7.6	3.9	4.4	×
$Zr(acac)_2^+$	288	1.4	1.4	1.5	×
$Zr(acac)_2 - H^+$	287	2.2	0.4	0.6	×
$Zr(acac)_2 - H_3O^+$	269	1.6	0.8	0.8	
$Zr(acac)C_3H_4O^+$	245	0.8	0.7	1.4	
$Zr(OH)_2(acac)^+$	223	2.3	1.2	1.4	
$ZrO(acac)^+$	205	4.2	2.2	2.3	×
$Zr(acac) - H_2^+$	187	1.0	0.6	0.6	
$ZrC_3H_5O_2^+$	163	1.2	0.5	0.5	

[a] In this table, *m/z* values are reported for the ^{90}Zr isotope. The symbol w denotes that the ion is present with less than 0.1% relative abundance. HR indicates confirmation of formula by exact mass measurement.

ionization produces a greater abundance of the ion $Cu_2(acac)_3H^+$ than does electron ionization, although this ion is formed in both ionization modes. Consistently, ions with additional hydrogen are formed under chemical ionization conditions with the generic formula $Cu_x(acac)_{x+1}H^+$ (e.g., $Cu(acac)_2H^+$, $Cu_2(acac)_3H^+$, and $Cu_3(acac)_4H^+$). If these ions are the result of protonation of a neutral molecule, reduction of Cu(II) to Cu(I) would have to occur in each of the two higher mass examples.

The mass spectrum measured with methane chemical ionization is more directly similar to the electron ionization mass spectrum. As seen in Table I, no new cluster ions are observed and the higher mass clusters ($m/z > 677$) are absent. The degree of hydrogen incorporation in all cluster ions is similar to that obtained under electron ionization conditions for species with a mass-to-charge ratio greater than that of the base peak ($Cu_2(acac)_3^+$). As mass-to-charge values below that of the base peak, the relative degree of hydrogen incorporation increases. A first explanation is that initial protonation of a neutral molecule occurs but that the protonated molecule is a relatively unstable species that dissociates to lower mass fragment ions.

Zirconium(IV) Acetylacetonate. Electron Ionization. Cluster ions are reported here for the first time for zirconium(IV) acetylacetonate as shown in Table II and Figure 2. Previous reports[1] indicated ions in the mass spectrum only up to (but not including) the mass of the parent ion $Zr(acac)_4^+$, which itself is also not observed in any of the mass spectra recorded in the present study. The base peak in our electron ionization mass spectrum is $Zr(acac)_3^+$ at *m/z* 387, representing a loss of one ligand from the

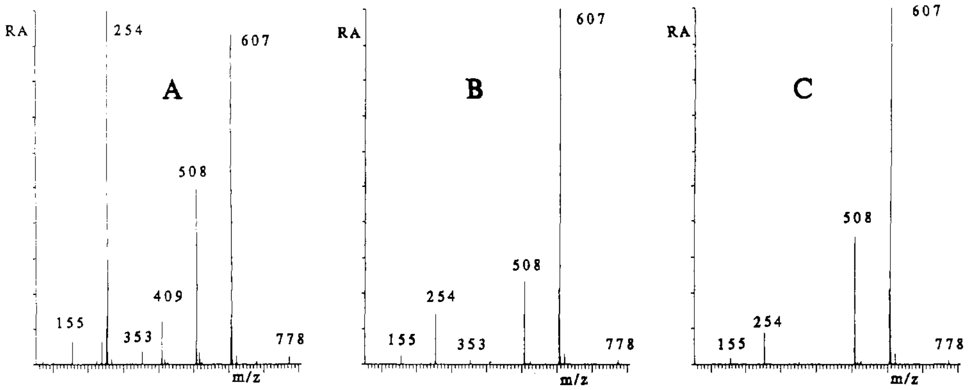

Figure 3. Mass spectra of iron(III) acetylacetonate: (A) electron ionization; (B) methane chemical ionization; (C) ammonia chemical ionization. Labeled peaks include $Fe_3O(acac)_6^+$ at *m/z* 778, $Fe_2(acac)_5^+$ at *m/z* 607, $Fe_2(acac)_4^+$ at *m/z* 508, and $Fe(acac)_2^+$ at *m/z* 254. Identities of the remaining peaks are listed in Table III.

molecular ion. Three of the four ions with masses above that of the molecular ion contain additional oxygen atoms (i.e., oxygen atoms not included within the structure of the acetylacetonate ligand itself), reflecting the susceptibility of zirconium(IV) to oxidation to form ZrO^{2+}.[12] The ion $Zr_2(acac)_7^+$ at *m/z* 873 is the only ion of stoichiometry $M_2(acac)_7^+$ (where M is the metal) to be reported for any transition-metal acetylacetonate in this study and reflects the retention of a highly oxidized form of zirconium(IV). Since the absence of a partially filled d shell provides no stereochemical requirements for ligand binding, zirconium(IV) can exhibit unusually high coordination.[13] A condensation reaction between ionic and neutral species in the ion source is suggested to form this unusual high-mass ion, viz, $Zr(acac)_3^+ + Zr(acac)_4^0 \rightarrow Zr_2(acac)_7^+$. Other cluster ions observed in the electron ionization mass spectrum may form via dissociation of $Zr_2(acac)_7^+$, or even larger unstable cluster ions, or might arise through condensation reactions similar to the one shown above. Such reactions have been specifically noted in the electron ionization mass spectrum of molybdenyl acetylacetonate.[14]

Chemical Ionization. The mass spectra recorded under both methane and ammonia chemical ionization conditions are very similar to that obtained under electron ionization conditions (Table II). The base peak, $Zr(acac)_3^+$ at *m/z* 387, is again 10 times more abundant than any of the other species in the spectra. In contrast to the results discussed above for copper(II) acetylacetonate, neither of the chemical ionization spectra exhibited an increase in the relative abundances of ions that incorporate additional hydrogen over the abundances measured in the electron ionization mass spectrum. In fact, the *only* ion in which additional hydrogen incorporation can be discerned is that at *m/z* 609, $Zr_2O_2(acac)_4H^+$, but the relative abundance of this ion is low in all ionization methods.

Iron(III) Acetylacetonate. Electron Ionization. The measured electron ionization mass spectrum of iron(III) acetylacetonate shown in Table III and Figure 3 is in generally good agreement with previous results.[1] However, several new cluster ions are observed, including $Fe_3O(acac)_6^+$ at *m/z* 778, $Fe_2(acac)_5CH_2^+$ at *m/z* 621, and $Fe_2(acac)_4OH^+$ at *m/z* 525. As in the mass spectra of the previous two examples, cleavage of the C–O bond appears to favor formation of a metal–oxygen bond, such as RFeO.

Chemical Ionization. The results obtained for methane and ammonia chemical ionization are summarized in Table III. The use of neither methane nor ammonia in a chemical ionization process caused an increase in the number of cluster ions observed at mass-to-charge values greater than that of the base peak. However, there is an increase in the number of different ion species in the region *m/z* 509–580 under chemical ionization conditions. The most striking difference between the chemical and electron ionization data is the ion at *m/z* 608, $Fe_2(acac)_5H^+$, which has a 20% relative abundance under methane chemical ionization, has a 12% relative abundance under ammonia chemical ionization, and is not observed in the electron ionization mass spectra. These data suggest that $Fe_2(acac)_5$ is a neutral species that is more readily protonated by the stronger acid CH_5^+. As before, the relative abundances of ions at mass-to-charge values lower than that of the base peak are larger under electron ionization conditions than under chemical ionization conditions, suggesting the collisional stabilization of the higher mass ions with the higher source pressure used in the chemical ionization source.

Table III. EI, Methane CI, and Ammonia CI Mass Spectra of Iron(III) Acetylacetonate[a]

		rel abund, %			
ion	*m/z*	EI	CI (CH_4)	CI (NH_3)	HR
$Fe_3O(acac)_6^+$	778	1.6	1.1	1.1	
$Fe_3O(acac)_5^+$	679	1.0	0.1		
$Fe_2(acac)_5CH_2^+$	621	2.4	3.0	2.9	
$Fe_2(acac)_5H^+$	608		20.0	12.2	×
$Fe_2(acac)_5^+$	607	100.0	100.0	100.0	×
$Fe_2(acac)_5 - H^+$	606			1.0	
$Fe_3O(acac)_4^+$	580	w	0.4	0.4	
$Fe_2(acac)_4C_2H_3O_2^+$	567		0.4	0.4	
$Fe_2(acac)_4OH^+$	525	1.0	0.9	1.0	
$Fe_2(acac)_4CH_2^+$	522	0.9	0.5	0.6	
$Fe_2(acac)_4^+$	508	50.1	21.5	33.6	×
$Fe(acac)_4^+$	452	0.3	w	w	
$Fe_2(acac)_3OH^+$	426	0.1	0.1	w	
$Fe_2(acac)_3O^+$	425	0.4	0.6	w	
$Fe_2(acac)_3^+$	409	11.3	0.7	0.3	×
$Fe(acac)_3^+$	353	3.0	0.9	0.5	×
$Fe(acac)_3 - H_2O^+$	335			w	
$Fe(acac)_2C_3H_5O^+$	311	w		w	
$Fe(acac)_2C_3H_4O^+$	310	0.1		w	
$Fe(acac)_2OH^+$	271			0.1	
$Fe(acac)_2CH_2^+$	268	1.4	0.1	w	×
$Fe(acac)_2^+$	254	84.5	10.6	6.9	×
$Fe(acac)_2 - CH_3^+$	239	3.3	0.4	0.2	×
$Fe(acac)_2 - OH^+$	237	0.3			
$Fe(acac)_2 - H_2O^+$	236		0.4		
$Fe(acac)_2 - C_2H_5^+$	225	0.3			
$Fe(acac)OH^+$	172	0.3	0.1	0.2	×
$Fe(acac)^+$	155	5.9	1.7	1.3	×
$Fe(acac) - CH_2^+$	139	1.0	0.2	0.1	×
Fe_2^+	112	0.5	w	w	×

[a] In this table, *m/z* values are reported for the ^{56}Fe isotope. The symbol w denotes that the ion is present with less than 0.1% relative abundance. HR indicates confirmation of formula by exact mass measurement.

Vanadium(III) Acetylacetonate. Electron Ionization. The electron ionization mass spectrum of vanadium(III) acetylacetonate is much more complex than indicated in a preliminary study.[14] Unlike the other transition metals in this study, the isotopic distribution of vanadium is very simple and consists of one major isotope (^{51}V) of 99.76% abundance and one minor

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(13) Shibata, S.; Onuma, S.; Inoue, H. *Inorg. Chem.* **1985**, *24*, 1723.
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Table IV. EI, Methane CI, and Ammonia CI Mass Spectra of Vanadium(III) Acetylacetonate^a

ion	m/z	rel abund, % EI	CI (CH_4)	CI (NH_3)	HR
$V_3O_2(acac)_6^+$	779		0.2	0.2	
$V_3O(acac)_6^+$	763	4.8	1.8	2.0	
$V_3(acac)_6^+$	747	w			
$V_2(acac)_6C_2O^+$	736	0.5	0.4	0.4	
$V_3O_3(acac)_5^+$	696	0.2		0.7	
$V_3O_2(acac)_5CH_3^+$	695		0.9		
$V_3O_2(acac)_5CH_2^+$	694		w		
$V_3O_2(acac)_5^+$	680	7.0	6.3	4.4	
$V_3O(acac)_5^+$	664	0.3		w	
$V_3(acac)_5 - OH^+$	631	0.3*			
$V_2(acac)_5CH_2^+$	611	1.4	0.7	0.5	×
$V_2(acac)_5^+$	597	81.4	47.5	49.2	×
$V_2(acac)_5 - H^+$	596	0.3	0.4	0.6	
$V_2(acac)_5 - H_2O^+$	579	0.4*	0.2	0.2	
$V_2(acac)_5 - C_2H_2^+$	571	0.3*	0.3*	0.4*	
$V_2(acac)_4C_2H_3O_2^+$	557	0.5	0.3*	0.3	
$V_2O(acac)_4CH_2^+$	528	0.7	0.7	0.3	
$V_2O(acac)_4H^+$	515		6.9	2.5	
$V_2O(acac)_4^+$	514	62.6	70.5	51.9	×
$V_2O(acac)_4 - H^+$	513	0.3	0.4	0.7	
$V(acac)_4C_2O_2^+$	503	1.4	1.8	0.7	
$V_2(acac)_4^+$	498	2.6	1.3	1.7	
$V_2(acac)_4 - H_2^+$	496	0.4*	0.5*	0.3*	
$V(acac)_4C_2OH^+$	488	0.7	2.2	1.0	
$V_2(acac)_4 - CH_2^+$	484	0.3	0.5	0.4	
$V_2(acac)_4 - C_2H_3^+$	471	0.8	0.8	1.2	
$V_2O_2(acac)_3CH_2^+$	445		0.5	0.2	×
$V_2O_2(acac)_3^+$	431	30.6	78.3	40.1	×
$V_2O(acac)_3CH_3^+$	430	0.3	1.1	0.6	
$V_2O(acac)_3CH_2^+$	429	w	w	w	
$V_2O(acac)_3^+$	415	10.8	6.0	7.6	
$V_2(acac)_3CH_2^+$	413	0.6	0.9	0.7	
$V(acac)_3OC_3H_2^+$	402	0.2*			
$V_2(acac)_3$	399	0.2	w	0.2	
$V(acac)_3C_3H_7^+$	391	0.3	0.6	0.5	
$V(acac)_3(OH)_2^+$	382	0.1*	0.4*	0.1*	
$V(acac)_3CH_2^+$	362	2.5	2.9	1.7	×
$V(acac)_3H^+$	349	15.4	51.2	63.8	×
$V(acac)_3^{\bullet+}$	348	100.0	100.0	100.0	×
$V(acac)_3 - H^+$	347	1.2	1.3	1.3	
$V_2O_2(acac)_2^+$	332	2.1	6.7	4.9	×
$V_2O(acac)_2CH_3^+$	331		0.3	0.2	
$V_2O(acac)_2CH_2^+$	330			0.3	
$VO(acac)_2C_2H_5^+$	294		5.5		
$VO(acac)_2CH_3^+$	280		2.4		
$VOH(acac)_2^+$	266		45.4	36.2	×
$VO(acac)_2^+$	265	16.1	76.5	55.8	×
$V(acac)_2CH_3^+$	264		0.7	0.3	×
$V(acac)_2CH_2^+$	263	0.3	0.3	0.4	
$V(acac)_2H^+$	250	5.5	7.4	12.0	×
$V(acac)_2^+$	249	47.8	63.8	78.3	×
$V(acac)_2 - H^+$	248	0.8	1.2	3.0	
$V(acac)O_2C_3H_5^+$	223	0.2*	4.0*	0.5*	
$V(acac)O_2C_2H_3^+$	209	0.1	0.8	0.9	
$VO(acac)OH^+$	183	2.6	9.8	16.9	×
$VO(acac)H^+$	167	2.5	6.0	9.4	
$VO(acac)^+$	166	7.7	19.1	0.2	
$V(acac)CH_3^+$	165	2.6	3.0	27.8	
$V(acac)H^+$	151	0.6	1.7	1.6	
$V(acac)^+$	150	1.3	2.8	3.2	×
$V(acac) - H^+$	149	0.6	1.1	1.3	
$V(acac) - H_2^+$	148	0.8	1.7	2.2	
$VC_3H_5O_2^+$	124	2.8*	9.8*	5.4*	
VOH^+	68	3.3	0.7	3.8	×

^{a}The symbol w denotes that the ion is present with less than 0.1% abundance. The symbol * indicates that the cluster was not fully deconvoluted. HR indicates confirmation of formula by exact mass measurement.

isotope (^{50}V) of 0.24% abundance. The diversity of cluster and fragment ions measured in this study are indicated in Table IV and Figure 4. Many of the ions are of relatively low abundance. The base peak in the spectrum is the molecular ion, $V(acac)_3^{\bullet+}$, at m/z 348. For the five transition-metal acetylacetonates examined in this study, $V(acac)_3$ and $Pd(acac)_2$ (vide infra) were the only compounds to produce the molecular ion as the base peak. An overall increase in the relative abundance of high-mass clusters in comparison to results obtained by Schildcrout[9] is seen in our study. Vanadium(III), like zirconium(IV), is readily oxidized, thus accounting for the stability of such odd-electron species as $V_3O(acac)_6^+$ at m/z 763, $V_3O(acac)_5^+$ at m/z 664, and $V_2O_2(acac)_3^+$ at m/z 431.

Table V. EI, Methane CI, and Ammonia CI Mass Spectra of Palladium(II) Acetylacetonate

ion	m/z range	rel abund, % EI	CI (CH_4)	CI (NH_3)
$Pd_3(acac)_4^+$	708–726	1.1	2.0	16.8
$Pd_3(acac)_3^+$	609–625	0.9	1.2	4.2
$Pd_2(acac)_3^+$	505–517	31.1	18.5	48.2
$Pd_2(acac)_2CH_3^+$	420–433	8.0	3.2	7.2
$Pd_2(acac)C_4H_6O^+$	376–389	3.4	2.2	1.9
$Pd(acac)_2H^+$	301–311	52.4	55.5	70.5
$Pd(acac)_2^{\bullet+}$	300–310	100.0	100.0	100.0
$Pd(acac)C_4H_4O_2^+$	285–294	7.2	9.8	0.9
$Pd(acac)H^+$	201–211	16.2	15.9	1.6
$Pd(acac)^+$	200–210	17.2	17.6	2.2
$PdC_3H_7^+$	143–153	19.6	14.4	
$PdC_3H_5^+$	142–152	2.9	2.3	
$PdC_3H_3^+$	141–151	0.4	0.2	

Chemical Ionization. Both methane and ammonia chemical ionization mass spectra of vanadium(III) acetylacetonate do show a tendency for increased hydrogen incorporation into both cluster and fragment ions, as seen in Table IV. For example, $V(acac)_3H^+$ at m/z 349 has the following relative abundances: 51.2% under methane chemical ionization, 63.8% under ammonia chemical ionization, and 15.4% under electron ionization conditions. Increased abundances of $V(acac)H^+$, $VO(acac)H^+$, $V(acac)_2H^+$, and $V_2O(acac)_4H^+$ are also apparent from the table. For vanadium(III) acetylacetonate, several entirely new ions were observed in the chemical ionization mass spectra. These species include $VOH(acac)_2^+$ at m/z 266, $V(acac)_2CH_3^+$ at m/z 264, and $V_2O_2(acac)_3CH_2^+$ at m/z 445; the formulas of these ions have been confirmed by high-resolution mass measurements.

Palladium(II) Acetylacetonate. Electron Ionization. Previous study of palladium(II) acetylacetonate yielded mass spectra that did not have any metal-containing ions.[3] The present electron ionization spectrum of palladium(II) acetylacetonate is presented in Table V and Figure 5; under our experimental conditions, metal-containing fragment and cluster ions were formed. A difficulty in the identification of these ions, and in the deconvolution of the palladium ion cluster ions, is that the isotopic distribution of palladium consists of an envelope that extends over several mass units: ^{102}Pd (0.8% abundance), ^{104}Pd (9.3% abundance), ^{105}Pd (22.6% abundance), ^{106}Pd (27.1% abundance), ^{108}Pd (26.7% abundance), and ^{110}Pd (13.5% abundance). This broad isotopic envelope, especially for ions containing more than one palladium atom, causes a good deal of overlap between cluster ions of slightly different masses. As a result, those cluster ions that are of low relative abundance cannot be fully deconvoluted even with the present high-resolution instrument. The base peak in the electron ionization spectrum is the molecular ion $Pd(acac)_2^{\bullet+}$ with an isotopic envelope encompassing m/z 300–310. A number of ions of higher mass are present, including $Pd_3(acac)_4^+$ with an envelope of m/z 708–726 and $Pd_2(acac)_3^+$ with an envelope of m/z 505–517. Reduction of Pd(II) to Pd(I) is readily accomplished, as evidenced by the number of ions observed in which the palladium is formally in the I oxidation state.

The fragment ion $PdC_3H_7^+$ (isotopic envelope spanning m/z 143–453) is unique in the mass spectra to all the metal acetylacetonates presently studied. This ion is thought to be formed by expulsion of one or two carbon monoxide molecules from the acetylacetonate ligand in $Pd(acac)^+$. Subsequent H_2 losses from $PdC_3H_7^+$ yield the ions $PdC_3H_5^+$ and $PdC_3H_3^+$. Also noteworthy is the relatively high abundance of the $(M + H)^+$ ion even under electron ionization conditions, perhaps reflecting the catalytic properties of palladium. Palladium has been shown to be an

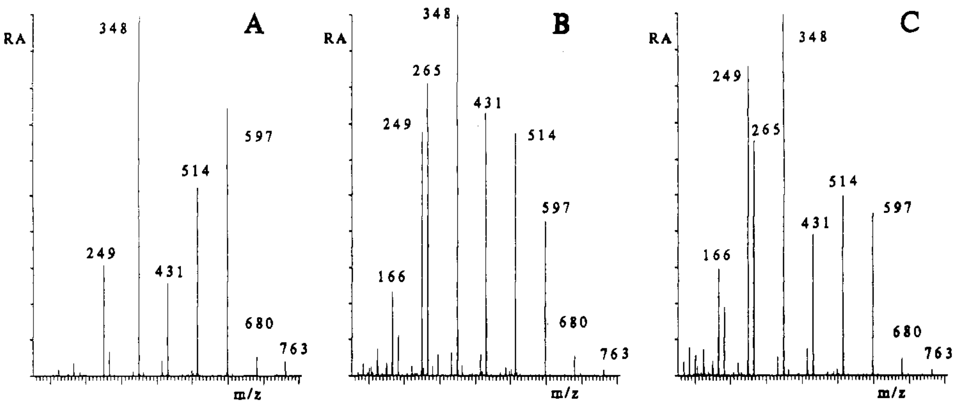

Figure 4. Mass spectra of vanadium(III) acetylacetonate: (A) electron ionization; (B) methane chemical ionization; (C) ammonia chemical ionization. Labeled peaks include $V_3O(acac)_6^+$ at *m/z* 763, $V_2(acac)_5^+$ at *m/z* 597, $V_2O(acac)_4^+$ at *m/z* 514, and $V(acac)_3^+$ at *m/z* 348. Identities of the remaining peaks are listed in Table IV.

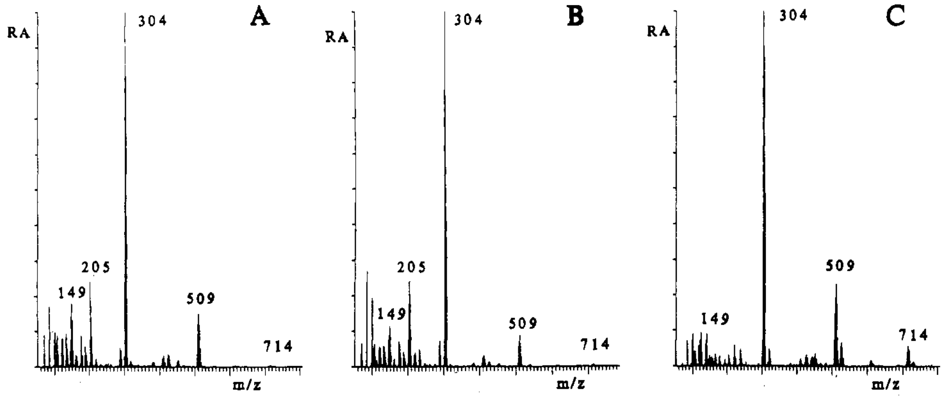

Figure 5. Mass spectra of palladium(II) acetylacetonate: (A) electron ionization; (B) methane chemical ionization; (C) ammonia chemical ionization. Labeled peaks include $Pd_3(acac)_4^+$ at *m/z* 714, $Pd_2(acac)_3^+$ at *m/z* 509, $Pd(acac)_2^+$ at *m/z* 304, and $Pd(acac)^+$ at *m/z* 205. Identities of the remaining peaks are listed in Table V.

extremely active catalyst for the hydrogenation of olefins,[16] with hydrogen transfer thought to occur in a Pd–H complex.

Chemical Ionization. Having established that palladium-containing ions tend to incorporate additional hydrogen into their structures, it was expected that the use of chemical ionization mass spectrometry would increase the abundances of such ions significantly. However, the chemical ionization spectra of palladium(II) acetylacetonate is similar to that obtained by electron ionization conditions, as seen in Table V. Neither methane nor ammonia chemical ionization conditions produced increases in the relative abundances of hydrogen-rich ions. In each case (EI, CH_4-CI, NH_3-CI), the base peak in the mass spectrum is $Pd(acac)_2^{\bullet +}$. Ammonia chemical ionization causes a decrease in the relative abundances of ions with mass-to-charge values less than that of the base peak and an increase in the relative abundances of ions with mass-to-charge values greater than that of the base peak, consistent with a collisional stabilization rather than a chemical ionization process. Like copper(II) acetylacetonate, the mass spectrum obtained for methane chemical ionization is very similar to that obtained under electron ionization conditions.

Conclusions

The present study has established the presence of new higher mass cluster ions that had not previously been reported for transition-metal complexes. These new ions can be observed because of both better instrumental transmission at higher masses and higher sample loading in the source. The methane and ammonia chemical ionization mass spectra for five transition metals are reported here for the first time. Unlike the metal carboxylates,[15] the metal acetylacetonates did not in general show a great increase in abundance of cluster ion formation under chemical ionization conditions. There are some differences from the electron ionization mass spectra in the relative abundances of reported ions, and in some cases there is an increase in the abundance of hydrogen-rich ions measured under chemical ionization conditions. The relative insensitivity of these spectra to drastic changes in source conditions suggests that evaporation of polymeric species from the direct-insertion probe and subsequent ion/molecule reactions in the gas phase are the primary determinants for the final appearance of the mass spectrum.

Registry No. $Cu(acac)_2$, 13395-16-9; $Zr(acac)_4$, 17501-44-9; $Fe(acac)_3$, 14024-18-1; $V(acac)_3$, 13476-99-8; $Pd(acac)_2$, 14024-61-4.

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[16] Pines, H. *The Chemistry of Catalytic Hydrocarbon Conversions*; Academic: New York, 1981.