

A Reinvestigation of the Mass Spectra of Zinc Acetate and Cobalt Acetate

G. C. DiDonato and K. L. Busch*

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Study of the electron ionization mass spectra of cobalt acetate and zinc acetate corrects previous misinterpretations of the spectra and establishes a very complex gas-phase chemistry that includes the formation of high-mass cluster ions under high-pressure conditions in the ionization source. High-resolution mass spectrometry establishes numerous new ions, including many at masses lower than that of the molecular ion, especially for cobalt acetate. The ability of cobalt to assume various oxidation states leads to an especially diverse set of cluster ions. Chemical ionization mass spectrometry is applied to the analysis of these compounds for the first time. Although some protonation is observed, most spectral changes relative to the electron ionization spectrum can be attributed to collisional stabilization at higher source pressures. Mixtures of zinc acetate and cobalt acetate produce a number of mixed-metal cluster ions in the electron ionization mass spectrum. Examination of the daughter ion MS/MS spectra establishes the differing reactivity of the Co-O and Zn-O bonds in collision-induced dissociation.

Introduction

Acetates of cobalt and zinc have been previously studied by electron ionization mass spectrometry,¹⁻⁵ both in their monomeric forms (with acetate ligands and waters of hydration in octahedral coordination about a central metal atom) and in their basic forms (with four metals in tetrahedral coordination about a central oxygen and six bridging carboxylate ligands). The electron ionization mass spectra of the monomeric species are similar to the mass spectra of the basic forms, suggesting that the basic structure is the more stable form in the gas phase, in contrast to their relative stability in the condensed phase.⁶ However, formulas proposed for certain ions in the mass spectra obtained by different investigators are not in agreement. Some differences are more serious than those that could be attributed to a change in source conditions or in the instruments employed in the various studies.

A reinvestigation of the mass spectra of these compounds was undertaken to resolve inconsistent spectral data that have complicated the interpretation of the electron ionization spectra in terms of structures in both the gaseous and solid phases. The mass spectra previously reported were obtained with relatively low-performance instrumentation of only moderate resolution. With modern equipment, the mass range investigated could be extended by a factor of 2, with greater sensitivity at the high-mass end, and high-resolution mass measurements could be used to establish the nature of some of the cluster ions expected. Several new experiments were also used in the analysis of these compounds. Deuterium labeling helped to establish the structures of higher mass ions when high-resolution measurements could not be completed. Mass spectrometry/mass spectrometry (MS/MS)⁷ was used to study the collision-induced dissociation of mixed-metal cluster ions formed by volatilizing a simple admixture of two acetates. In MS/MS, a particular ion is selected by the first mass analyzer and collided with a neutral target atom, and the daughter fragment ions are examined with the second mass analyzer. This experiment provides qualitative information about metal-ligand bond strengths. Finally, chemical ionization⁸ had never been used for the analysis of these samples, inviting a comparison with the usual electron ionization mass spectra. Before the results of the present investigation are discussed, a brief review of the pertinent literature is in order.

Several basic zinc carboxylates were studied by Mead, Reid, and Silver,¹ including 2-ethylhexanoates and acetates, using electron ionization mass spectrometry. In all instances, the base peak was $Zn_4O(RCO_2)_5^+$ with the molecular ion $Zn_4O(RCO_2)_6^{*+}$ noted to be extremely weak or, in the case of the acetate, completely absent. These workers were the first to report the observation of the relatively abundant doubly charged ions in the spectra. They reported metastable peaks, corresponding to fragmentation of the ions while in transit through the mass spectrometer, including dissociation of both singly and doubly charged ions.

Charalambous and co-workers² presented the most comprehensive mass spectral data on zinc acetate and cobalt acetate analyzed in the basic form and recognized the effect of the various oxidation states of cobalt on the fragmentations and stabilities of particular ions, most notably those of the molecular ion, $M_4O(OAc)_6^{*+}$ (M is either cobalt or zinc metal; OAc is the acetate ligand). Under their conditions of analysis, zinc acetate gave a weak molecular ion, whereas the corresponding cobalt molecular ion was very abundant. This was related to π -electron donation from the ligand into the empty d orbitals of the cobalt atom, making the molecular ion even-electron, and more stable than the corresponding odd-electron species.⁹ Such electron donation could not occur for zinc with a filled d orbital. The change in odd- or even-electron character can be related to oxidation states of the metals in the condensed phase. States of I, II, and III are fairly common for cobalt complexes, whereas the chemistry of zinc almost exclusively involves state II.¹⁰ The effect of oxidation state on the mass spectra of compounds containing metals was first noted by Shannon and Swan.¹¹ Charalambous provided accurate mass measurements for selected ions in the mass spectra, confirming the formulas of cluster ions such as $Zn_4O_2(OAc)_3^+$ and $Zn_3O(CH_3)(OAc)_2^+$, the latter being formed via the loss of CO_2 from $Zn_3O(OAc)_3^+$. Loss of the odd-electron acetate ligand from the even-electron $M_4O(OAc)_5^+$ occurred for both the cobalt and zinc species, but the corresponding doubly charged ions were observed to be much more intense, and this was also related to their even-electron character. Finally, Charalambous reported both doubly and singly charged ions for the species $M_4O_2(OAc)_3$ and $M_4O_2(OAc)_3H$, where M = Co or Zn. The data for the doubly charged ions were, however, reported as the combined abundance of both the protonated and unprotonated species.

The compositions of two fragment ions indicated by Sipachev and co-workers³ in their study of zinc acetate are in direct contradiction to formulas proposed for ions at isobaric masses by Charalambous. Sipachev proposed $Zn_3O_2OAc(CH_2CO_2)^+$ for the ion at m/z 341, formed by the loss of acetaldehyde CH_3CHO (44 daltons) from $Zn_3O(OAc)_3^+$. Charalambous proposed the loss of CO_2 (44 daltons) from $Zn_3O(OAc)_3^+$ to form Zn_3O -

* To whom correspondence should be addressed.

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$(\text{CH}_3)(\text{OAc})_2^+$, citing high-resolution data as evidence. Sipachev suggested the loss of ketene from the ion at m/z 341 to form $\text{Zn}_3\text{O}_3(\text{OAc})^+$ at m/z 299. Charalambous proposed $\text{Zn}_3\text{O}(\text{CH}_3)(\text{OH})(\text{OAc})^+$, formed by a similar loss of ketene from $\text{Zn}_3\text{O}(\text{CH}_3)(\text{OAc})_2^+$. One goal of the present work is to resolve such discrepancies.

Filament-heated in-beam electron ionization⁴ has been used by Matsumoto and Kosugi to study the more common form of the acetate, the zinc(II) acetate dihydrate, with chelating carboxylate ligands and two waters of hydration. The only ions reported corresponded to ions found also in the mass spectra of the basic form, $\text{Zn}_4\text{O}(\text{OAc})_5^+$ and $\text{Zn}_3\text{O}(\text{OAc})_3^+$. These workers were the first to characterize the extensive formation of cluster ions in the electron ionization mass spectra of the metal acetates.

Similar transformations were noted in the electron ionization mass spectrum as reported by Marshall,⁵ who also examined the acetates of magnesium and manganese in addition to those of cobalt and zinc. The mass spectra were, in general, similar to those reported by Charalambous with two exceptions. For zinc, Marshall reported *only* the protonated doubly charged ion $\text{Zn}_4\text{O}_2(\text{OAc})_3\text{H}^{2+}$ and not the singly charged analogue reported by Charalambous. For cobalt, Marshall reported the ion $\text{Co}_4\text{O}_2(\text{OH})(\text{OAc})_2^+$, not observed at all by Charalambous. He also reported several novel mixed-metal species formed by magnesium and cobalt of the general form $\text{Mg}_n\text{Co}_{4-n}\text{O}(\text{OAc})_6^+$. This was achieved by preparing an equimolar solution of cobalt and magnesium acetate, evaporating to dryness, and analyzing the resulting solid by direct-probe mass spectrometry.

Experimental Section

Spectra were obtained on a Kratos MS80RFAQ mass spectrometer of EBQ geometry with a full mass range of 2400 daltons. Normal resolution was set to 1500. Exact mass measurements were obtained at a resolution of 7500. Electron ionization and chemical ionization spectra were recorded by using an off-line electron multiplier located after the magnetic sector but before the quadrupoles, coupled to a Kratos DS-55 data system. Daughter ion MS/MS spectra were recorded by using a conversion dynode electron multiplier located after the quadrupoles. The experiment involves use of the sector analyzer to select the parent ions, dissociation by collision with a neutral target gas, and analysis of the daughter ions formed with the analytical quadrupole. Argon was used as the collision gas at a pressure sufficient to reduce the intensity of the parent ion beam by 50%; collision energy was 12 eV. The calibration range for the low-resolution data presented was m/z 50–1505; the range under high-resolution conditions was m/z 50–650. Daughter ion MS/MS spectra were obtained at unit resolution. Low-resolution, high-pressure spectra were taken with a direct-probe temperature range of 280–350 °C, with the probe temperature increased by 50 °C/min from a starting temperature of 40 °C. Mixed-metal spectra were obtained in the temperature range 280–350 °C. Under these conditions, the acetates were rapidly volatilized and a significant increase in source pressure was noted; the occurrence of ion/molecule and molecule/molecule reactions was thus significantly increased. Such rapid heating precludes the use of high-resolution mass analysis, as the signal for the internal calibrant necessary for such measurements is suppressed. Therefore, high-resolution spectra were carried out in the temperature range 200–250 °C with slow heating of the direct-insertion probe. For electron ionization, 50-eV electrons (100 μA) were used. For chemical ionization, methane was used as the reagent gas, with the source pressure increased to about 1 Torr. Zinc(II) acetate dihydrate and cobalt(II) acetate tetrahydrate were used as received from Aldrich Chemical Co. Cobalt(II) acetate-*d*₃ was synthesized by metathesis of cobalt(II) carbonate hydrate in a concentrated aqueous solution of perdeuterated acetic acid (Aldrich Gold Label). Mixed-metal samples were prepared by mixing stoichiometric equivalents of the two metal acetates.

Results and Discussion

Zinc Acetate: Electron Ionization Mass Spectrum. The present electron ionization mass spectrum of the zinc acetate (Figure 1) is in general agreement with previous mass spectral analyses with respect to the nature and relative abundances of the ions observed. The base peak in the spectrum is $\text{Zn}_4\text{O}(\text{OAc})_5^+$ at m/z 571 formed by loss of ligand radical from the molecular ion, itself observed with very low relative abundance. Further fragmentations of $\text{Zn}_4\text{O}(\text{OAc})_5^+$ include loss of $\text{Zn}(\text{OAc})_2$ to form $\text{Zn}_3\text{O}(\text{OAc})_3^+$, loss of the radical CH_3CO , and losses of the even-electron species

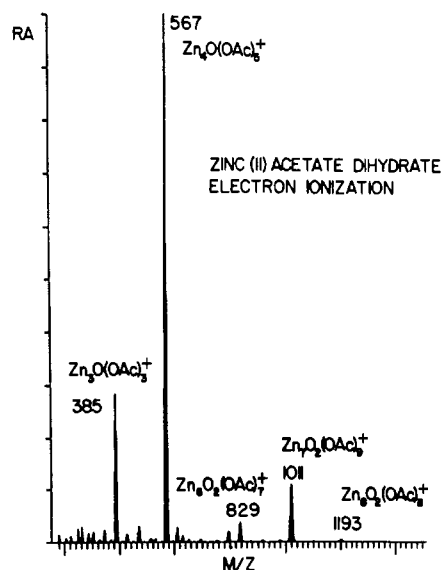


Figure 1. Electron ionization mass spectrum of zinc(II) acetate dihydrate (high-pressure, low-resolution conditions).

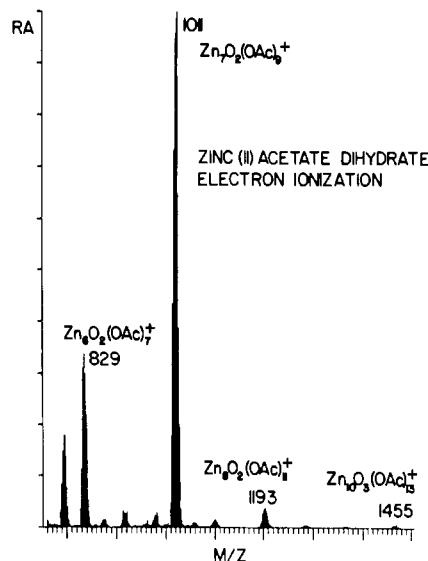


Figure 2. Expanded electron ionization mass spectrum of zinc(II) acetate dihydrate in the mass range above m/z 750.

acetic anhydride and ketene. The spectral evidence suggests that the starting material, zinc(II) acetate dihydrate, assumes the basic structure in the gas phase.

At higher pressures created in the source as the zinc acetate volatilizes, the electron ionization mass spectrum contains abundant species above the molecular ion, none of which have been previously reported. Figure 2 is an expanded mass spectrum of zinc(II) acetate dihydrate in the region above m/z 750, illustrating the shapes of the isotopic envelopes observed in the high-mass region (vide infra). The spectrum in Figure 2 is normalized to the ion at m/z 1011, $\text{Zn}_7\text{O}_2(\text{OAc})_9^+$, which is itself 17% of the base peak at m/z 571. The cluster ions observed include $\text{Zn}_{10}\text{O}_3(\text{OAc})_{13}^+$ at m/z 1455, $\text{Zn}_{10}\text{O}_4(\text{OAc})_{11}^+$ at m/z 1353, and $\text{Zn}_8\text{O}_2(\text{OAc})_{11}^+$ at m/z 1193. The $\text{Zn}_7\text{O}_2(\text{OAc})_9^+$ cluster ion contains fully 10% of the metal-containing ion current in the entire mass spectrum, and the isotopic envelope is spread over some 35 daltons. Fully 18% of metal-containing ions lie above the molecular ion, $\text{Zn}_4\text{O}(\text{OAc})_6^+$. Since zinc possesses five isotopes, combinations of zinc atoms and organic ligands in these cluster ions result in distinctive isotopic envelopes. A correspondence between experimental and calculated isotopic distributions can be used to unambiguously identify novel cluster ions. Figure 3 shows the experimental and calculated isotope pattern for the cluster $\text{Zn}_7\text{O}_2(\text{OAc})_9^+$ over the mass range 1011–1031

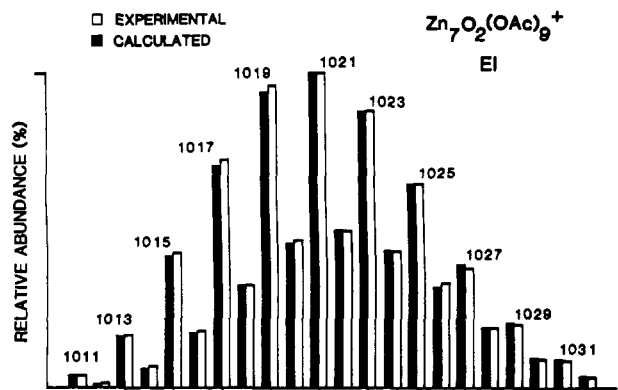


Figure 3. Comparison of experimental and calculated isotopic envelope distribution for the cluster ion $\text{Zn}_7\text{O}_2(\text{OAc})_9^+$.

daltons. The excellent agreement supports the formula assignment. Exact mass measurements used to unambiguously assign the formula are not possible under the high-pressure conditions necessary for formation of these ions. Not only are signals from the gas-phase calibrant suppressed, but the ions are transient in their appearance in the spectrum. A similar isotopic cluster agreement is found between the calculated and experimental distribution for $\text{Zn}_8\text{O}_2(\text{OAc})_{11}^+$. Less accurate agreements were found for other high molecular weight ions of lower abundance, but the data were sufficient for reasonable assignment of formulas.

These cluster ions are assumed to be formed at high source pressures as the products of gas-phase ion/molecule reactions. For instance, $\text{Zn}_7\text{O}_2(\text{OAc})_9^+$ could be formed by a condensation reaction between the $\text{Zn}_4\text{O}(\text{OAc})_6$ and the abundant ion $\text{Zn}_3\text{O}(\text{OAc})_3^+$. Loss of $\text{Zn}(\text{OAc})_2$ from $\text{Zn}_7\text{O}_2(\text{OAc})_9^+$ would then produce the ion at m/z 829, $\text{Zn}_6\text{O}_2(\text{OAc})_7^+$. In a similar manner, $\text{Zn}_8\text{O}_2(\text{OAc})_{11}^+$ might be formed by reaction between neutral $\text{Zn}_4\text{O}(\text{OAc})_6$ and the most abundant ion in the spectrum, $\text{Zn}_4\text{O}(\text{OAc})_5^+$. The formula of the cluster ion $\text{Zn}_{10}\text{O}_3(\text{OAc})_{13}^+$ suggests a trimeric species, which could arise similarly via a condensation reaction between the ion $\text{Zn}_6\text{O}_2(\text{OAc})_7^+$ and neutral $\text{Zn}_4\text{O}(\text{OAc})_6$.

The molecular ion $\text{Zn}_4\text{O}(\text{OAc})_6^+$ is present in very low abundance in the electron ionization mass spectrum. Interestingly, the protonated form is present with greater abundance, representing some process of proton transfer to the molecular ion. The proton source may be acetic acid molecules or ions present in the source. Protonation of $\text{Zn}_4\text{O}_2(\text{OAc})_4$ also occurs under high-pressure electron ionization conditions, suggesting that $\text{Zn}_4\text{O}_2(\text{OAc})_4$ exists as an abundant neutral species as well as an ion.

High-resolution data confirm the formulas of many previously unreported ions and clarify the discrepancies discussed in the Introduction. When resolution was not sufficient to separately measure the ion containing solely ^{64}Zn , exact mass measurements were completed for ^{66}Zn - and ^{68}Zn -containing ions. For example, the exact mass of $^{64}(\text{ZnO})_4\text{H}^+$ could not be measured directly, but exact mass measurements were available for $^{64}\text{Zn}_2^{66}\text{Zn}_2\text{O}_4\text{H}^+$, $^{64}\text{Zn}_2^{66}\text{Zn}^{68}\text{ZnO}_4\text{H}^+$, and $^{66}\text{Zn}_2^{68}\text{Zn}_2\text{O}_4\text{H}^+$ to confirm this formula assignment. $\text{Zn}_3\text{O}(\text{OAc})_2^{2+}$, though not previously reported, does indeed exist, despite its odd-electron character. The doubly charged ion $\text{Zn}_4\text{O}_2(\text{OAc})_3\text{H}^{2+}$ exists *only* in the protonated form; the corresponding $\text{Zn}_4\text{O}_2(\text{OAc})_3^{2+}$ described by Charalambous is not observed. The present high-resolution data confirm that the ions at m/z 341 and 299 are $\text{Zn}_3\text{O}(\text{CH}_3)(\text{OAc})_2^+$ and $\text{Zn}_3\text{O}(\text{CH}_3)(\text{OH})(\text{OAc})^+$ respectively, as shown by Charalambous, and *not* $\text{Zn}_3\text{O}_2(\text{CH}_2\text{CO}_2)^+$ and $\text{Zn}_3\text{O}_3(\text{OAc})^+$, as claimed by Sipachev³.

Zinc Acetate: Chemical Ionization Mass Spectrum. The observation of protonated ions in the high-pressure electron ionization mass spectra prompted an investigation of the chemical ionization mass spectra of zinc acetate for the first time. Since the primary mechanism of chemical ionization for organic compounds is the transfer of hydrogen from the reagent gas to the neutral molecule, an increase in the relative abundances of the protonated ions in the spectrum was expected. The higher source pressures were also

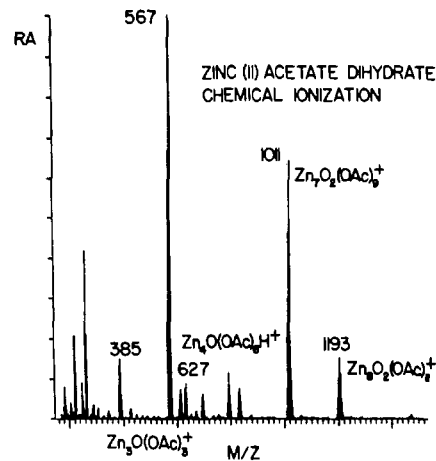


Figure 4. Chemical ionization mass spectrum of zinc(II) acetate dihydrate.

expected to increase the relative abundances of some of the higher mass cluster ions by collisional stabilization. The chemical ionization mass spectrum of zinc(II) acetate is illustrated in Figure 4. Under chemical ionization, increased relative abundances of the higher molecular weight cluster ions were observed. In this spectrum, the ion at m/z 1011 is of 68% abundance relative to the base peak at m/z 571, as compared to only 17% in the electron ionization spectrum. In addition, the relative abundances of both $\text{Zn}_6\text{O}_2(\text{OAc})_7^+$ and $\text{Zn}_6\text{O}_2(\text{OAc})_6\text{OH}^+$ are increased with respect to those observed in the electron ionization spectrum. The increased abundances of the high-mass ions have been attributed to collisional stabilization, in which excess internal energy, which would normally produce fragmentation, is dissipated by collision with the high-pressure gas.

The total number of high molecular weight cluster ions is significantly decreased to only 12 in chemical ionization from 22 identifiable species above m/z 567 in EI. This may also be due to collisional stabilization, as the probability of decomposition to fragment ions is decreased. The use of chemical ionization does not provide an increased relative abundance of the protonated molecular ion, $\text{Zn}_4\text{O}(\text{OAc})_6\text{H}^+$. However, no signal for the unprotonated molecular ion is observed in the chemical ionization spectrum. In contrast to previous results with copper acetate,¹² there are no new species formed, nor are the relative abundances of protonated ions increased. Changes in relative abundances of the higher mass cluster ions can be attributed solely to the generation of a higher source pressure and the processes of collisional stabilization that result.

Cobalt Acetate: Electron Ionization Mass Spectrum. The mass spectral results for cobalt acetate are similar to those for zinc acetate, in terms of both a general agreement with previous reports and the formation of several novel cluster ions under the high-pressure conditions used in this study. However, high-resolution mass spectrometry has also confirmed several ions of mass *less* than that of the molecular ion, $\text{Co}_4\text{O}(\text{OAc})_6^+$ at m/z 606. Discussion turns first to the mass spectrum recorded under low-resolution, high-pressure source conditions.

The EI mass spectrum is presented in Figure 5. The molecular ion is observed with a relative abundance of 65%; the base peak is $\text{Co}_3\text{O}(\text{OAc})_3^+$. As in the case of zinc acetate, novel cluster ions are observed, such as $\text{Co}_8\text{O}_2(\text{OAc})_{11}^+$ at m/z 1153, $\text{Co}_7\text{O}_2(\text{OAc})_{10}^+$ at m/z 1035, and $\text{Co}_7\text{O}_2(\text{OAc})_9^+$ at m/z 976. These are produced via ion/molecule or molecule/molecule reactions in a manner analogous to that for the zinc acetate clusters.

There are only two reports in the literature for the electron ionization mass spectrum of cobalt acetate.^{2,5} In both of the reported spectra, no ions above the molecular ion $\text{Co}_4\text{O}(\text{OAc})^+$ at m/z 606 were reported. The ions shown in Figure 5 above m/z 606 are here reported for the first time. While the relative

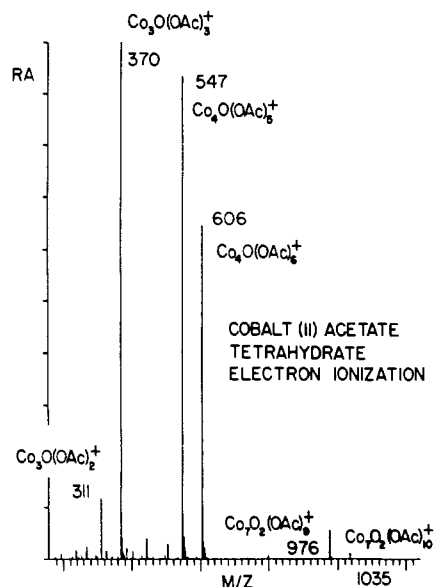


Figure 5. Electron ionization mass spectrum of cobalt acetate tetrahydrate.

abundances of major ions as reported by Charalambous² and Marshall⁵ and this spectrum are similar, there are significant differences in the distribution and abundances of other ions. In resolving differences between the two previous reports in terms of the actual ions observed, this report confirms Marshall's observation of $\text{Co}_4\text{O}_2(\text{OH})(\text{OAc})_2^+$, not observed by Charalambous. Further, ions reported exclusively by Charalambous [$(\text{Co}_4\text{O}(\text{OAc})_5 - \text{CH}_2^+)$, $\text{Co}_4\text{O}(\text{OAc})_4^+$, $\text{Co}_3\text{O}_2(\text{OAc})_3^+$, $\text{Co}_3\text{O}_2(\text{OAc})_2^+$, and $\text{Co}_2(\text{OAc})_2^+$] are all confirmed by the present results.

Equally significant, the electron ionization mass spectrum contains large numbers of lower mass ions that have not previously been reported. The exact mass measurement is especially valuable in confirming the existence of hydrogen-containing ions such as $\text{Co}_4\text{O}_2(\text{OH})(\text{OAc})_2^+$, $\text{Co}_4\text{OH}(\text{OAc})_2^+$, and $(\text{CoO})_4\text{H}_2^+$, formed under electron ionization conditions.

Among new ions revealed by the high-resolution data are $\text{Co}_3\text{O}(\text{OAc})_4^+$ at m/z 428.8522 and $\text{Co}_4\text{O}(\text{OAc})_3^+$ at m/z 428.7616. The ion currents from these two species are combined in the low-resolution mass measurement, and the total ion current is too low to permit a deconvolution of the isotopic envelope. High-resolution data are essential in confirming the presence of both these species. The required resolution to unambiguously identify these ions is $M/\Delta M = 4700$. The high-resolution data also support the assignment of $\text{Co}_3\text{O}_2(\text{OAc})_2^+$ and $\text{Co}_3\text{O}(\text{OH})(\text{OAc})_2^+$ at m/z 326.8143 and 327.8229, respectively, differentiating these ions from their isobaric partners $\text{Co}_4\text{O}_2(\text{OAc})^+$ and $\text{Co}_4\text{O}(\text{OH})(\text{OAc})^+$ at m/z 326.7340 and 327.7423, respectively. $\text{Co}_3\text{O}(\text{OAc})_2^+$ and $\text{Co}_4\text{O}(\text{OAc})^+$ are also observed as a doublet separated by high resolution, with masses of 310.8233 and 310.7440 daltons, respectively. The former ion has been reported before in the literature; the latter has not. The presence of these and several other diverse clusters defined in the high-resolution spectrum may be related to the ability of the cobalt to change oxidation state. A monocation with four cobalt atoms, one acetate ligand, and two oxygen atoms [$\text{Co}_4\text{O}_2(\text{OAc})^+$] would formally require two cobalt atoms in the +2 oxidation state and two cobalt atoms in a +1 state. As mentioned in the Introduction, cobalt readily assumes these various oxidation states in the condensed phase. A similar analysis of $\text{Co}_4\text{O}(\text{OAc})^+$ showed that all four cobalt atoms would be in a +1 oxidation state. With the low number of ligands present in this latter ion, it would not be unreasonable to invoke metal-metal bonding as contributing to the stability of these ions. Such metal-metal bonding for cobalt is known, especially when the metal is in a low oxidation state, e.g. Co_2CO_8 .¹³ Further direct evidence for metal-metal cobalt

bonding is provided by the presence of Co_2^+ in the spectrum.

Cobalt oxide clusters are also present in the electron ionization mass spectrum, including Co_4O_4^+ at m/z 299.7121, as well as $\text{Co}_4\text{O}_4\text{H}^+$, $\text{Co}_4\text{O}_4\text{H}_2^+$, Co_3O_3^+ , $\text{Co}_3\text{O}_3\text{H}^+$, and $\text{Co}_3\text{O}_3\text{H}_2^+$. The hydrogen- and dihydrogen-containing ions were assigned on the basis of the fact that the relative abundances at those masses were greater than that expected from ^{17}O and ^{18}O abundances of the oxides. The measured exact mass is consistent with either these ions or the oxygen isotopic peaks from the non-hydrogen-containing oxide. The resolution required to separate $\text{Co}_4^{18}\text{O}_4^+$ from $\text{Co}_4^{16}\text{O}_4\text{H}_2^+$ is in excess of 80 000, a resolution unattainable with the instrument employed in this study.

Cobalt Acetate: Chemical Ionization Mass Spectrum. The chemical ionization mass spectrum of cobalt acetate has not been previously reported. Of particular interest was the question of whether a protonated molecular ion could be created. For zinc acetate, such an ion was observed in the electron and chemical ionization mass spectra. The molecular ion, $\text{Co}_4\text{O}(\text{OAc})_6^{++}$ at m/z 606, is still observed but is now only 37% of the base peak, $\text{Co}_4\text{O}(\text{OAc})_5^+$. The protonated molecular ion is observed with 14% relative abundance; this does not appear in the electron ionization mass spectrum.

There are again significant shifts in the relative abundances of the cluster ions observed in the mass spectrum. In the EI spectrum, $\text{Co}_3\text{O}(\text{OAc})^+$ and $\text{Co}_4\text{O}(\text{OAc})_5^+$ are of nearly equal abundance; in the CI spectrum, this has been shifted in favor of the higher mass cluster ion. Several new ions appear in the chemical ionization mass spectrum that contain additional hydrogen beyond that in the acetate ligand. These include protonated species at m/z 430, $\text{Co}_3\text{O}(\text{OAc})_4\text{H}^+$, as well as ions at m/z 296 and 297, $\text{Co}_2(\text{OAc})_3\text{H}^+$ and $\text{Co}_2(\text{OAc})_3\text{H}_2^+$, respectively. Protonated ions are observed for those neutral molecules which are thought to be abundant in the gas phase. Thus, the protonation of the molecular ion is straightforward. $\text{Co}_3\text{O}(\text{OAc})_4$ as a neutral molecule contains three Co(II) metal atoms countering the formal six negative charges from the oxygen and four acetate ligands. The neutral molecule of $\text{Co}_2(\text{OAc})_3$ may form $\text{Co}_2(\text{OAc})_3\text{H}^+$ by protonation of $\text{Co}^{\text{I}}\text{Co}^{\text{II}}(\text{OAc})_3$. $\text{Co}_2(\text{OAc})_3\text{H}$ could also exist as the neutral molecule if both cobalt atoms were present as Co(I), and then protonation of this neutral would yield $\text{Co}_2(\text{OAc})_3\text{H}_2^+$. The protonation of analogous copper species has been recently reported.¹²

A novel ion appears at m/z 1212, which is assigned the formula $\text{Co}_8\text{O}_2(\text{OAc})_{12}^+$, a dimer of the molecular ion $\text{Co}_4\text{O}(\text{OAc})_6^+$. The presence of a dimer of the stoichiometry $\text{M}_8\text{O}_2(\text{OAc})_{12}^+$ (where M is cobalt or zinc) in the case of cobalt (but not zinc) supports the formation of this cluster ion via a condensation reaction involving a neutral and ionic species. The relative stability of the ion $\text{Co}_4\text{O}(\text{OAc})_6^+$ is evidenced by its high relative abundance in the spectrum. The neutral species is undoubtedly present in high abundance as well. The relatively low abundance of the analogous zinc ion, $\text{Zn}_4\text{O}(\text{OAc})_6^+$, precludes the formation of the dimeric $\text{Zn}_8\text{O}_2(\text{OAc})_{12}^+$ and explains its absence in the zinc acetate spectrum. However, $\text{Zn}_4\text{O}(\text{OAc})_5^+$ is an abundant ionic species. Its reaction with neutral $\text{Zn}_4\text{O}(\text{OAc})_6$ is feasible, and the resulting high-mass ion $\text{Zn}_8\text{O}_2(\text{OAc})_{11}^+$ is observed in the zinc acetate spectrum.

As previously mentioned, the high-pressure mass spectra are necessarily of low resolution, as exact mass measurements are precluded because of suppression of signal from the mass calibrant. In the case of the zinc clusters, formulas could be confidently assigned on the basis of agreement between calculated and experimental isotopic distributions. In addition, the metal and the ligand are of different nominal mass, which also facilitates formula assignment. Neither option was available for the assignments made with cobalt, which is monoisotopic and has the same nominal mass as the ligand, 59 daltons. Another means was necessary to confirm the low-resolution assignments of formulas, involving use of an isotopic label on the ligand. The perdeuterated cobalt acetate was synthesized and analyzed by both EI and CI methods. The molecular ion is shifted to m/z 624, representing $\text{Co}_4\text{O}(\text{OAc})_6^+$. Several formulas from the low-resolution mass spectrum of the

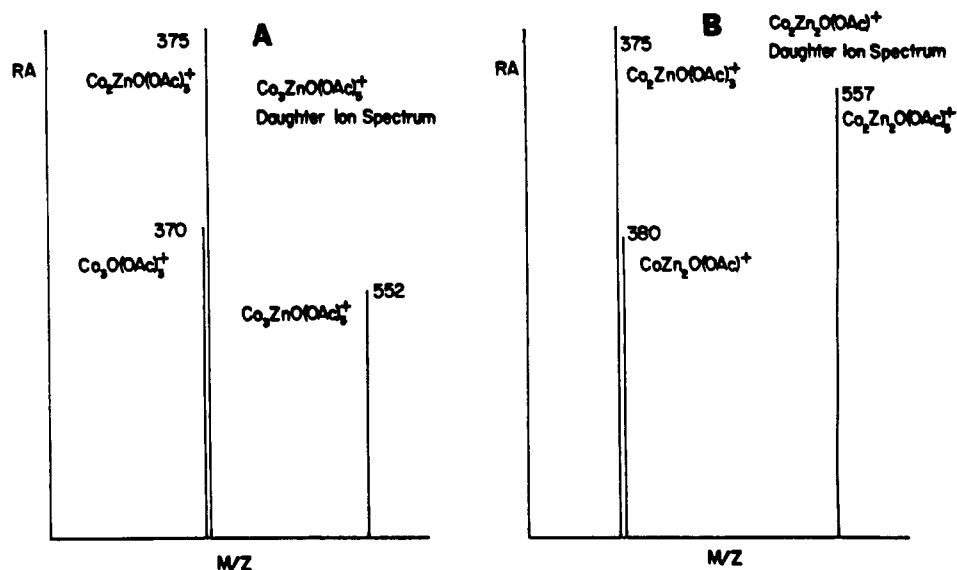


Figure 6. Daughter ion MS/MS spectra of (A) $\text{Co}_3\text{ZnO}(\text{OAc})_5^+$ and (B) $\text{Co}_2\text{Zn}_2\text{O}(\text{OAc})_5^+$.

undeuterated cobalt acetate are confirmed by mass shifts. For instance, $\text{Co}_3\text{O}_2(\text{OAc})_{11}^+$, is now shifted to m/z 1186, up 33 daltons from the undeuterated ion at m/z 1153.

Although well over 35 previously unreported ions are indicated in the high-resolution spectrum of cobalt acetate, analysis of the deuterated cobalt acetate data reveals several additional ions by virtue of the mass shifts. The ion $\text{Co}_4\text{O}_2(\text{OAc})_6^+$ would appear at m/z 622 in its undeuterated form, overlapping with $\text{Co}_5\text{O}_2(\text{OAc})_5^+$. Since both are formed under high-pressure conditions, high resolution is not available for their differentiation, although the required $M/\Delta M$ separation is only 7750. Once the mass of each ion is shifted by the isotopic label in the acetate ligand, the former ion is shifted to m/z 640 and the latter to m/z 637, and the relative abundance of each species can be separately determined. In a similar manner, a new ion, $\text{Co}_3\text{O}_2(\text{OAc})_3^+$ (overlap at m/z 386 with $\text{Co}_4\text{O}_2(\text{OAc})_2^+$), is also established. The cobalt oxide clusters $\text{Co}_3\text{O}_3\text{H}^+$ and $\text{Co}_3\text{O}_3\text{H}_2^+$, which were previously assigned solely on the basis of isotopic abundance data, are confirmed by the shift in mass with replacement of the hydrogen by deuterium. For example, the cobalt oxide hydrogen and dihydrogen species, at m/z 301 and 302, respectively, are now shifted to m/z 302 and 304, while the Co_4O_4^+ remains at m/z 300.

Mixed-Metal Cluster Ions. Marshall⁵ reported that a mixture of metal acetates produced mixed-metal cluster ions, containing up to four metal ions with various proportions of each metal present. These are formed from ion/molecule reactions in the gas phase as the pressure in the electron ionization source is increased. With the demonstrated ability to produce higher source pressures and to examine the dissociations of ions by MS/MS, work turned toward the examination of these novel cluster ions.

Mixed-metal species observed in the electron ionization mass spectrum of a 1:1 stoichiometric mixture of zinc acetate and cobalt acetate are formed with great diversity, including six different ions containing seven metal atoms, such as $\text{Zn}_6\text{CoO}(\text{OAc})_9^+$ at m/z 1006, and a variety of nine different mixed-metal clusters with four metal atoms and a number of different acetate ligands, such as $\text{Zn}_2\text{Co}_2\text{O}_2(\text{OAc})_3^+$ at m/z 455. In general, the mixed-metal ions contain more zinc than cobalt, perhaps due to the greater volatility of the zinc acetate. The high-mass cluster ions with mixed metals are remarkably abundant, especially comparing the data to those generated for zinc acetate alone. The presence of cobalt atoms in the cluster ions seems to increase their stability, reflecting the ability of the cobalt to change oxidation state, making the molecular ion even- instead of odd-electron.

Cluster ions containing five metal atoms are observed in the mass spectrum of either zinc acetate or cobalt acetate alone with very low relative abundances. There are indeed *no* mixed-metal cluster ions containing five metal ions observed in the spectrum of the acetate mixture. This observation is consistent with the

tetrahedral arrangement of four metal atoms in the molecular structure and the disruption of that structure with the addition of a single metal atom. For still larger cluster ions, the structure presumably rearranges to a more open form to accommodate the additional metals and ligands.

As mentioned in the Introduction, MS/MS can be used to probe mixed-metal ion reactivity and to determine relative ligand-metal or, in the case of the acetate, metal-oxygen bond strengths. The daughter ion spectrum of $\text{Co}_3\text{ZnO}(\text{OAc})_5^+$ is shown in Figure 6A. The only two daughter ions formed by dissociation are $\text{Co}_3\text{O}(\text{OAc})_3^+$ at m/z 370 and $\text{Co}_2\text{ZnO}(\text{OAc})_3^+$ at m/z 375, representing the loss of $\text{Zn}(\text{OAc})_2$ and $\text{Co}(\text{OAc})_2$, respectively, from the parent ion. If such losses were to occur with equal statistical probability, the loss of $\text{Co}(\text{OAc})_2$ should occur 3 times as readily as the loss of $\text{Zn}(\text{OAc})_2$, and the relative abundances of the daughter ions $\text{Co}_3\text{O}(\text{OAc})_3^+$ and $\text{Co}_2\text{ZnO}(\text{OAc})_3^+$ should be 1:3. This is clearly not the case, and the daughter ion abundances indicate that $\text{Zn}(\text{OAc})_2$ is lost more readily from the parent ion $\text{Co}_3\text{ZnO}(\text{OAc})_5^+$.

The daughter ion MS/MS spectrum of $\text{Co}_2\text{Zn}_2\text{O}(\text{OAc})_5^+$ is shown in Figure 6B. As in the previous system, only two daughter ions are formed, $\text{Co}_2\text{ZnO}(\text{OAc})_3^+$ at m/z 375 and $\text{CoZn}_2\text{O}(\text{OAc})_3^+$ at m/z 380. With equal numbers of cobalt and zinc atoms in the parent ion, it could be expected that the loss of $\text{Co}(\text{OAc})_2$ and $\text{Zn}(\text{OAc})_2$ should occur with equal facility, and the two daughter ions should be of equal abundances. Once again, this is not the case. $\text{CoZn}_2\text{O}(\text{OAc})_3^+$ at m/z 380 is notably less abundant than $\text{Co}_2\text{ZnO}(\text{OAc})_3^+$, again indicating that $\text{Zn}(\text{OAc})_2$ is lost more readily than $\text{Co}(\text{OAc})_2$.

Since it is impossible to assign a specific gas-phase structure for the parent ions, conclusions regarding relative metal-oxygen bond strengths must be preliminary. However, the consistent deviation of the relative abundances of the daughter ions from the abundances expected from statistical evaluation suggests that the metal-oxygen bond strength is greater for cobalt than for zinc, reflecting the electron transfer from ligand to cobalt and not to zinc. The weaker Zn-O bond may be cleaved more readily, and the $\text{Zn}(\text{OAc})_2$ is more easily lost. This corresponds with condensed-phase metal-oxygen bond strengths, which increase from right to left on the periodic chart.¹⁰ These data represent the first application of MS/MS to the examination of dissociation products of mixed-metal chelates formed under high-pressure conditions. Smaller mixed-metal clusters have been formed under low-pressure conditions by a number of investigators using ion cyclotron resonance spectroscopy.¹⁴⁻¹⁶ The application of this experiment to

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other systems in which mixed-metal species are formed under high-pressure conditions, and for which structural assignment may be feasible, should prove a valuable means of assessing gas-phase thermochemical data.

Conclusions

The utilization of an array of mass spectrometric techniques, including high-pressure mass spectrometry, high-resolution mass spectrometry, deuterium labeling, and tandem mass spectrometry, has provided abundant new information concerning the behavior of cobalt and zinc acetates in the gas phase. Previously misidentified ions in the spectra were correctly established.

High-pressure-source conditions have led to the formation of novel cluster ions with molecular weights in excess of 1000 daltons for both cobalt acetate and zinc acetate. These are formed through ion/molecule reactions that occur between abundant fragment ions and abundant neutral species. Those cluster ions that are dimers and trimers of the monomer $M_4O(OAc)_6$ probably involve one or more bridging carboxylate ligands between monomeric units. Identification of many cluster ions is, in the case of zinc, facilitated by comparison of the calculated and the measured

isotope patterns. In the case of cobalt, the results of deuterium labeling aid in the identification of cluster ion formulas and provide a means of confirming hydrogen incorporation.

High-resolution mass spectrometry reveals a number of novel species of mass less than the molecular ion. Though only a few novel lower mass species were found for zinc acetate, a far greater number of ions were discovered for cobalt acetate. Novel mixed-metal cluster ions incorporating both zinc and cobalt were easily produced when a mixture of the two acetates was introduced. MS/MS experiments, which select by mass parent ions of a given metal content, indicate differing reactivity of metal-oxygen bonds toward collision-induced dissociation.

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Supplementary Material Available: Tabularized mass spectral data (13 pages). Ordering information is available on any current masthead page.

Contribution from the Intermediates Technology Division of Exxon Chemical Company and Exxon Research and Development Laboratories, Baton Rouge, Louisiana 70821

Synthesis and Structure of Three (Tricyclohexylphosphine)rhodium Complexes and Their Interconversion with Carbon Monoxide and Hydrogen

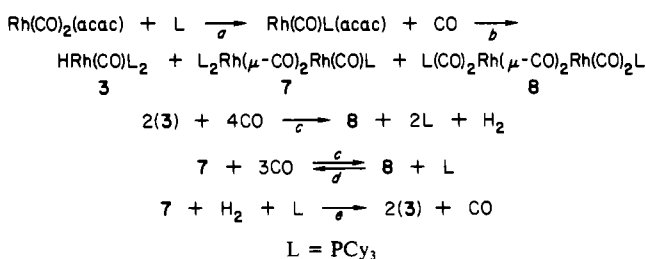
Michael A. Freeman^{1a} and David A. Young^{*1b}

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The reaction of $Rh(CO)_2(acac)$ with CO and H_2 in the presence of excess tricyclohexylphosphine (PCy_3) gave an easily separated mixture of $HRh(CO)(PCy_3)_2$ (**3**) and $(PCy_3)_2Rh(\mu-CO)_2Rh(CO)PCy_3$ (**7**). The structures of **3** and **7** were determined by X-ray crystallography and related to appropriate structures previously reported. Crystal data for **3**: monoclinic, $P2_1/c$ (C_{2h}^2 , No. 14), $a = 10.066$ (2) Å, $b = 15.910$ (4) Å, $c = 23.438$ (6) Å, $\alpha = 90.00^\circ$, $\beta = 94.13$ (2)°, $\gamma = 90.00^\circ$, $Z = 4$. Crystal data for **7**: triclinic, $P\bar{1}$ (C_1^1), $a = 13.681$ (3) Å, $b = 14.261$ (4) Å, $c = 19.235$ (5) Å, $\alpha = 104.15$ (2)°, $\beta = 99.70$ (2)°, $\gamma = 84.98$ (2)°, $Z = 2$. **3** has a trans square-planar configuration. **7** contains a square-planar $Rh(CO)PCy_3$ and a distorted-tetrahedral $Rh(PCy_3)_2$. The ^{31}P NMR spectra of **7** indicated an intramolecular geminal phosphine site exchange process on $Rh(PCy_3)_2$. **3** and **7** both react with CO, forming $PCy_3(CO)_2Rh(\mu-CO)_2Rh(CO)_2PCy_3$ (**8**), which was stable only in the presence of CO, reverting back to **7** in the absence of CO. **7** reacted with H_2 , re-forming **3**.

The structure and reactivity of rhodium(I) phosphine complexes are important to several areas of catalysis including α -olefin hydroformylation.² The mechanism of low-pressure hydroformylation, initially reported by Wilkinson and co-workers in the late 1960s, is still an area of active interest and controversy.³⁻⁵ Wilkinson found that $HRh(CO)L_3$ (**1**), ($L = PPh_3$) reacted with carbon monoxide forming $HRh(CO)_2L_2$ (**2**), ($L = PPh_3$) via the intermediate $HRh(CO)L_2$ (**3**), ($L = PPh_3$).^{3b} While neither complex could be isolated, **2** has recently been observed by NMR spectroscopy.^{5b,c} According to Wilkinson this complex loses hy-

Scheme I



^a 25 °C. ^b 80 °C, 8.3×10^3 kPa of CO + H_2 , 15 min, excess PCy_3 . ^c 25 °C, 1.0×10^2 kPa of CO, 5 min. ^d 25 °C, removal of CO. ^e 50 °C, 1.0×10^2 kPa H_2 , 15 min.

drogen in the presence of carbon monoxide, forming a yellow dimer, recently characterized by Chan and co-workers as $L_2-(CO)Rh(\mu-CO)_2Rh(CO)_2L$ (**4**) ($L = PPh_3$).⁶ Wilkinson found that **4** reacts with hydrogen, re-forming **3**, and that removal of

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