Inorganica Chimica Acta, *157* (1989) 175–185

Cluster Ions in the Electron and Chemical Ionization Mass Spectra of Magnesium, Mercury and Lead Acetates

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(Received July 4, 1988)

Abstract

This study documents the positive ion electron and chemical ionization mass spectra of magnesium, mercury and lead acetates. Of these three compounds, only magnesium acetate has been previously studied by electron ionization mass spectrometry. A characteristic feature in the electron ionization mass spectra of these compounds is the presence of cluster ions (ions with masses greater than that of the molecular ion) formed by reaction of stable ions with gas-phase, neutral molecules. The chemical ionization mass spectra of these compounds are reported here for the first time. In general, the chemical ionization mass spectra of these compounds contain cluster ions with relative abundances greater than observed in the electron ionization mass spectra, presumably as a result of collisional stabilization processes.

Introduction

Analytical mass spectrometrists have at their disposal a number of new ionization methods for the analysis of organometallic and coordination compounds. Desorption ionization methods such as fast atom bombardment (FAB) and secondary ion mass spectrometry (SIMS) have proved successful in the characterization of non-volatile and thermally fragile compounds [1–3]. In many such analyses, use of classical ionization methods, such as electron or chemical ionization, both of which require evaporation of the sample prior to ionization, are not successful. However, such classical methods have long been used in the study of a few classes of relatively volatile organometallic and coordination compounds [4–6]. In particular, much early work focused on the mass spectrometric analysis of the transition metal acetates. This work has been comprehensively reviewed by Westmore *et al.* [7]. The ability of transition metals to assume any of several oxidation states results in particularly complex mass spectra. Further, the demonstrated reactivity of bare metal ions, and of small metal-organic ions [8–10], makes the occurrence of ion/molecule reactions likely, and spectral complexity the rule rather than the exception.

A review of the mass spectral literature of transition metal acetates reveals inconsistencies, including the proposition of completely different formulae for ions at the same nominal mass. Some researchers note hydrogen incorporation into various ions in the mass spectra, presaging important catalytic chemistry, but the details of such chemistry is not presented. The appearance of doubly-charged ions has been noted, and in some cases the doubly-charged ions were significantly more abundant than the singly-charged analogs. In other cases, such doubly-charged ions are of very low abundance and are not apparent in low resolution, low sensitivity mass spectra. The presence of cluster ions, that is, ions of mass greater than that of the sample molecule under investigation, has been noted by several workers, but the origins of such ions have not been pursued. Lacking foreknowledge of such cluster ions, many workers simply did not scan the mass range above the molecular ion of the sample.

One aspect of our work over the past several years has been the use of a modern, high-resolution mass spectrometer to study the gas-phase ion chemistry of transition metal compounds. These studies have included the electron and chemical ionization mass spectral analysis of metal acetylacetonates and acetates [11–14]. In particular, the extent of cluster ion formation was studied, as well as the effect of the use of Bronstead acids as chemical ionization reagent ions on the nature and abundance of those cluster ions. Concomitantly, the accurate assignment of ion formula was pursued, backed by both exact mass measurements, and by the deconvolution of complex isotopic envelopes through comparison with calculated values. For example, DiDonato and Busch [11] have corrected a number of discrepancies in the reported mass spectra of copper acetate. One such discrepancy included the previous assignment of two

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0020-1693/89/$3.50

or more possible structures to the same nominal mass (due to the lack of high resolution information). Our recent work [11] also documented the extent of cluster ions in the mass range above the molecular ion, the measurement of additional doubly-charged ions, and the delineation of several metal-containing ions that incorporate additional hydrogen into their structure. A study of zinc and cobalt acetates provided a similar expansion of the known gas-phase chemistry of those systems [12].

The work for this study involved the study of a number of metal acetates including lead, lithium, magnesium, manganese, mercury, nickel and silver acetates. Of these compounds, lithium [13, 14], magnesium [15], manganese [15] and silver [16–18] acetates have previously been studied by electron ionization mass spectrometry. The absence of cluster ion formation in the electron ionization mass spectra measured in this study of manganese, nickel and silver acetates mirrors previously reported results. Discussion is therefore limited to the acetates of magnesium, mercury, and lead; the mass spectra of each of these compounds contained cluster ions formed in the electron ionization source. Electron ionization mass spectra of the latter two acetates have not been previously reported. The chemical ionization mass spectra of these transition metal acetates are reported here for the first time.

Experimental

Electron ionization (EI) and chemical ionization (CI) mass spectra were obtained on a Kratos MS80RFAQQ mass spectrometer of EBQ geometry. Electron energy was 70 eV, and an electron current of 100 microamps was maintained. Methane and ammonia, at a measured source pressure of 1 torr, were used as chemical ionization reagent gases. Usual mass resolution was 1000, and was increased to 7500 for exact mass measurements. Mass calibration was done using perfluorokerosene (PFK). The scan rate was 3 s/decade for low resolution and 10 s/decade for high resolution mass spectral measurements. The source temperature was held constant at 250 ℃ for all measurements. Samples (10 μg) were introduced via the direct insertion probe. The sample loading was deliberately high to encourage cluster ion formation. The mass spectra were measured at a probe temperature at which the total ion current trace reached a maximum value, at a temperature of 300–320 ℃ depending on the volatility of the sample. The temperature of the direct insertion probe was programmed from 35–400 ℃ at a rate of 20°/min. Higher probe temperatures correlate with elevated source pressures that suppress the signal from the mass calibrant (PFK), and direct high-resolution measurements under these conditions could not always be completed.

Mercuric acetate was purchased from Aldrich, magnesium acetate was purchased from Alfa, and lead acetate from Fischer.

Results and Discussion

Magnesium Acetate Tetrahydrate

Electron ionization

The low resolution electron ionization mass spectrum of magnesium acetate tetrahydrate recorded at an indicated probe temperature of 320 ℃ is summarized in Table 1, and displayed in Fig. 1. Both presentations are required due to the complexity of the spectrum. Reported relative ion abundances in Table 1 are those for a summation over the entire isotopic envelope. At higher masses, such a method reflects the true relative abundances of these particular ions, rather than the value for each mass within the isotopic envelope. Table 2 compares the ions and their relative abundances in the electron ionization mass spectrum reported by Marshall [15] to the present results. The assignments and the relative abundances of most ions are in close agreement. The base peak in both mass spectra is at *m/z* 407, assigned to $Mg_4(OAc)_5O^+$ where (OAc) is the acetate ligand. Marshall's reported mass spectrum [15] contains only two other species, *m/z* 265 and 174.5 (a doubly-charged ion) with relative abundances greater than 10%. Present work indicates that those at *m/z* 265, 174.5 and 83 have relative abundances greater than 10%. The issue of relative abundance can easily be over-emphasized. Relative abundance is an explicit function of the source pressure [19], which depends on the source temperature, direct insertion probe temperature, sample size, and the sample volatility. The mass spectrometer used in the present study did not have a means to measure directly the pressure within the source. Comparisons based on relative abundances are therefore not as meaningful as those based on the presence or absence of an ion, or on its identity based on exact mass measurements.

The major discrepancy between the present results and those of Marshall arises in the formula assignment of the ions at *m/z* 263 and 153. Marshall reports that the ion with a mass-to-charge value of 263 is $Mg_4(OAc)_2(OH)O_2^+$, whereas present work indicates that it is $Mg_3(OAc)_3CH_2^+$. This reassignment was based on two criteria. The first criterion is that the exact measured mass-to-charge value must be equal to the calculated mass-to-charge value. The second criterion is that the experimental isotopic envelope must match (within 10%) that predicted by calculation. In the case of $Mg_3(OAc)_3CH_2^+$, the measured mass-to-charge ratio is 263.0116, and the calculated value for an ion of this formula is 263.0107; the calculated mass-to-charge value for $Mg_4(OAc)_2$-

TABLE 1. Comparison of Electron Ionization, Ammonia Chemical Ionization, and Methane Chemical Ionization Mass Spectra of Magnesium Acetate Tetrahydrate[a]

Ion	*m/z*	Relative abundance		
		EI	NH_3-CI	CH_4-CI
$Mg_7(OAc)_9O_2^+$	731		0.2	0.8
$Mg_5(OAc)_7O^+$	549		0.1*	
$Mg_4(OAc)_7O^+$	525		0.1*	
$Mg_4(OAc)_7CH_3^+$	523		0.2*	
$Mg_4(OAc)_7^+$	509		19.7	0.3*
$Mg_5(OAc)_6OCH_3^+$	505			0.5*
$Mg_4(OAc)_6OH^+$	467	0.6	100.0	13.9
$Mg_4(OAc)_6O^+$	466		0.7	0.6
$Mg_4(OAc)_6CH_3^+$	465		0.5	5.4
$Mg_3(OAc)_6O^+$	442		0.2	
$Mg_4(OAc)_5(OH)_2^+$	425		6.4	
$Mg_4(OAc)_5(OH)O^+$	424		0.7	
$Mg_4(OAc)_5O_2^+$	423		0.2	
$Mg_4(OAc)_5O^+$	407	100.0	34.0	100.0
$Mg_4(OAc)_5CH_3^+$	406	3.0	1.4	2.0
$Mg_4(OAc)_5H_2^+$	393	0.7		
$Mg_4(OAc)_4(OH)O^+$	365	1.2	2.4	1.3
$Mg_4(OAc)_4O_2^+$	364	2.9	1.0	1.6
$Mg_4(OAc)_4OCH_3^+$	363			0.6
$Mg_4(OAc)_4(OH)H^+$	350	0.2		
$Mg_4(OAc)_4OH^+$	349	0.3	0.1*	0.2
$Mg_4(OAc)_4O^+$	348	1.9	0.2*	0.9
$Mg_3(OAc)_4OH^+$	325		1.7	0.6
$Mg_3(OAc)_4O^+$	324		0.3	0.2
$Mg_3(OAc)_4CH_3^+$	323		1.2	0.3
$Mg_3(OAc)_4CH_2^+$	322		0.2	0.1
$Mg_3(OAc)_4CH^+$	321			0.1
$Mg_4(OAc)_3O_2^+$	305	1.1		0.6
$Mg_3(OAc)_3(OH)_2^+$	283		2.5	
$Mg_3(OAc)_3O_2^+$	281		1.2	
$Mg_3(OAc)_3O^+$	265	21.4	0.2	14.3
$Mg_3(OAc)_3CH_3^+$	264	1.6	0.6	1.4
$Mg_3(OAc)_3CH_2^+$	263	1.8	7.6	1.1
$Mg_2(OAc)_3(OH)H^+$	243		0.2	
$Mg_2(OAc)_3OH^+$	242		0.4	
$Mg_2(OAc)_3O^+$	241		1.2	
$Mg_2(OAc)_3CH_3^+$	240		0.3	
$Mg_2(OAc)_3CH_2^+$	239		1.5	
$Mg_2(OAc)_3CH^+$	238		0.2	
$Mg_2(OAc)_3^+$	225		0.7	0.5
$Mg_3(OAc)_2(OH)O^+$	223	2.6	3.2	3.0
$Mg_3(OAc)_2O_2^+$	222		0.2	0.7
$Mg_3(OAc)_2OC_2H_2^+$	221	4.8	0.7	3.5
$Mg_3(OAc)_2OC_2H^+$	220			0.2
$Mg_3(OAc)_2OH^+$	207	1.5	0.2	
$Mg_3(OAc)_2O^+$	206	1.0	0.4	
$Mg_3(OAc)_2CH_3^+$	205	0.8	0.1	
$Mg_4(OAc)_5OH_2^{2+}$	204.5		0.1	
$Mg_3(OAc)_2CH_2^+$	204		0.3	
$Mg_4(OAc)_5O^{2+}$	203.5			1.0*
$Mg_3(OAc)_2CH^+$	203		0.5	3.1*
$Mg(OAc)_3H^+$	202		0.2	
$Mg(OAc)_3^+$	201		0.1	
$Mg_2(OAc)_2(OH)_2^+$	200		0.5	
$Mg_2(OAc)_2(OH)O^+$	199		1.3	
$Mg_2(OAc)_2O_2^+$	198		0.3	
$Mg_2(OAc)_2OCH_3^+$	197		1.6	
$Mg_2(OAc)_2OCH_2^+$	196		0.2	
$Mg_3(OAc)_5O^{2+}$	191.5		0.1*	
$Mg_3(OAc)_5^{2+}$	183.5		0.5	
$Mg_2(OAc)_2OH^+$	183		0.1	
$Mg_4(OAc)_4(OH)O^{2+}$	182.5		2.5	
$Mg_2(OAc)_2O^+$	182		0.4	
$Mg_2(OAc)_2CH_3^+$	181	1.5*	2.9	1.1*
$Mg_2(OAc)_2CH^+$	179	1.4*	0.6	
$Mg_4(OAc)_4OH^{2+}$	174.5	28.4*	0.5*	2.6*
$Mg(OAc)_2O_2^+$	174	17.4*	1.0*	5.2*
$Mg_4(OAc)_4CH_3^{2+}$	173.5			0.8*
$Mg_3(OAc)O_2^+$	163			0.8*
$Mg_4(OAc)_3(OH)_2^{2+}$	153.5	1.1		0.7*
$Mg_2(OAc)CO_2H_2^+$	153	2.4		1.6*
$Mg(OAc)_2C_2O_2H_2^+$	141		0.1*	
$Mg_2(OAc)O_2^+$	139			5.7*
$Mg_2(OAc)OCH_3^+$	138			4.4*
$Mg_3(OAc)_3O^{2+}$	132.5		0.1*	1.5*
$Mg_3(OAc)H^+$	132		0.4*	
$Mg(OAc)OC_2H_2^+$	125		0.3*	
$Mg_3(OAc)_2C_2O_2H^{2+}$	123.5	5.3	0.1*	1.7
$Mg_2(OAc)O^+$	123	0.4		9.1
$Mg_2(OAc)CH_3^+$	122	1.1		
$Mg_2C_2O_2H^+$	105	3.6		
$Mg(OAc)(OH)H^+$	101			2.9*
$Mg(OAc)O^+$	99		10.3*	3.0*
$Mg(OAc)CH_3^+$	98	18.6	1.3*	2.3*
$Mg(OAc)CH^+$	96	1.1		
$Mg_2CO_2H_2^+$	95	2.9		
$Mg_2CO_2H^+$	94	1.0		
$Mg_2OC_2H_3^+$	91	2.3		
$Mg(OAc)^+$	83	44.2	4.1*	0.3*
$MgC_2O_2H_2^+$	82	16.5	0.6*	
$MgC_2O_2H^+$	81	1.9	0.4*	
$Mg_2COH_3^+$	79	2.4	0.1*	
Mg_2OCH^+	77	2.8		

[a] The symbol * denotes that the experimental isotopic envelope does not match that of the theoretical.

$(OH)O_2^+$ (Marshall's assignment) was 262.9594. Exact mass measurements provide evidence for the present assignment of empirical formula rather than that of Marshall. A third possibility $Mg_3(OAc)_2$-$OCHCOO^+$ (*i.e.* loss of H_2 from $Mg_3(OAc)_3O^+$) is further removed in mass from the measured exact mass.

Additional evidence for ion formula assignment is derived from a comparison of the measured and the calculated isotopic envelope distribution. In this particular instance, the distribution of isotopes from $Mg_3(OAc)_3CH_2^+$ will overlap that of the ion of higher abundance at *m/z* 265, assigned both by Marshall and

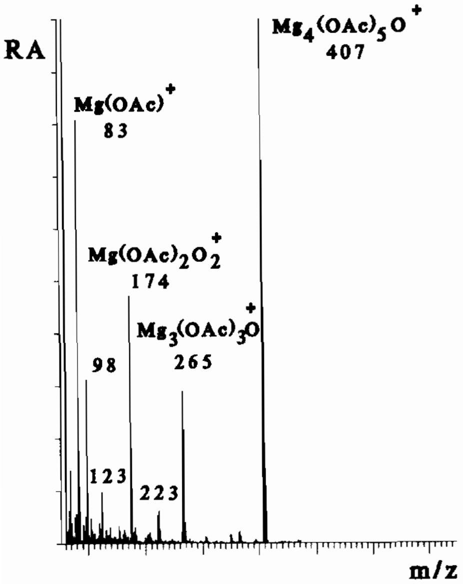

Fig. 1. Electron ionization mass spectrum of magnesium acetate tetrahydrate. Identities of non-labelled peaks are listed in Table 1.

TABLE 2. Comparison of the Electron Ionization Mass Spectra of Magnesium Acetate Tetrahydrate Obtained by Marshall [15] and Those from Present Work

Ion	*m/z*	Present (RA)	Marshall (RA)
$Mg_4(OAc)_5O^+$	407	100.0	100.0
$Mg_4(OAc)_4(OH)O^+$	365	1.2	2.5
$Mg_4(OAc)_4O_2^+$	364	2.9	2.0
$Mg_3(OAc)_3O^+$	265	21.4	20.3
$Mg_4(OAc)_2(OH)O_2^+$	263		3.1
$Mg_3(OAc)_3CH_2^+$	263	1.8	
$Mg_3(OAc)_2(OH)O^+$	223	2.6	4.3
$Mg_3(OAc)_2O^+$	206	0.8	1.0
$Mg_4(OAc)_4OH^{2+}$	174.5	28.4	12.0
$Mg_4(OAc)_3O_2^{2+}$	153		2.4
$Mg_2(OAc)CO_2H_2^+$	153	2.4	
$Mg_2(OAc)O^+$	123	0.4	1.9
$Mg(OAc)^+$	83	44.2	2.0

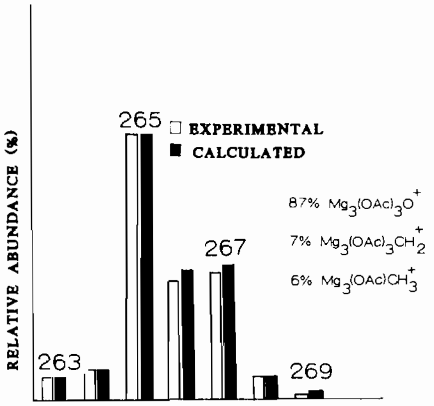

Fig. 2. Experimental and theoretical isotopic distributions for the cluster ion at *m/z* 265: 87% $Mg_3(OAc)_3O^+$, 7% $Mg_3(OAc)_3CH_2^+$, and 6% $Mg_3(OAc)_3CH_3^+$.

the present work as $Mg_3(OAc)_3O^+$. Further, initial calculation of the isotopic envelope of $Mg_3(OAc)_3CH_2^+$ provided an abundance of the ion at *m/z* 264 less than that actually observed in the mass spectrum, indicating that the additional presence of an ion of formula $Mg_3(OAc)_3CH_3^+$. An unambiguous confirmation of ion formula cannot therefore be provided solely by a comparison of the measured and calculated isotopic envelopes. Given the three ions that exact mass measurements indicate at *m/z* 263, 264, and 265, and the calculated isotopic envelopes for each, a match between the calculated and the measured envelopes can be generated, as shown in Fig. 2. The overlap between isotopic variants is evident at *m/z* 265, which consists of 87% $Mg_3(OAc)_3O^+$, 7% $Mg(OAc)_3CH_2^+$ and 6% $Mg_3(OAc)_3CH_3^+$, assuming contribution from the isotopic forms of magnesium only (^{24}Mg, ^{25}Mg, and ^{26}Mg). The exact masses of such ions ($^{24}Mg_3(OAc)_3O^+$, $^{24}Mg_2{}^{25}Mg(OAc)_3CH_3^+$ and $^{24}Mg_2{}^{26}Mg(OAc)_3CH_2^+$) would be 264.9899628, 265.0082486 and 265.0193175, respectively. Resolution ($M/\Delta M$) of 9000 is required to separate the lowest and highest mass ions, and resolution of 24000 is necessary to separate the two ions closest in mass. Although such resolution is attainable with modern mass spectrometers, there is insufficient ion signal for the latter two ion compositions at *m/z* 265 to complete the experiment.

The second disagreement between present and previous results occurs at *m/z* 153. Marshall assigns the ion at this mass-to-charge value to the doubly-charged ion $Mg_4(OAc)_3O_2^{2+}$, while present work indicates that it is $Mg_2(OAc)(CH_2O_2)^+$. The measured mass-to-charge value for this ion was 152.9889. The calculated value for Marshall's doubly-charged ion is 152.485 (cited by Marshall as questionable). The original tabulated mass value of 153 is at odds with the half-mass value. Since other half-mass values were identified, it is unclear as to why this particular ion was difficult to identify.

Furthermore, an alternative ion formula $Mg_4(OAc)_3O_2H^{2+}$ would provide a mass-to-charge ratio of 152.9889, which is the exact measured mass of the proposed ion $Mg_2(OAc)(CH_2O_2)^+$ of 152.9889. Both predicted values therefore agree with the measured value. The burden of proof for the identity of this ion therefore falls on a comparison of the measured and calculated isotopic envelopes for these two ion formulas. A doubly-charged ion was observed at *m/z* 153.5, which could be due to the ^{26}Mg isotope of $Mg_4(OAc)_3O_2H^{2+}$, or to a separate ion $Mg_4(OAc)_3(OH)_2^{2+}$. The origin of this particular ion was pursued because of Marshall's original assignment. However, no combination of ions matches the observed isotopic distribution. The ion abundance is too low to afford further study. Simplicity leads us to assign the singly-charged formula in Table 2. Differentiation of the singly- from the doubly-charged ion is difficult in this case because of the identity of the masses of the two ions, and the overlap in the isotope envelope. Procedures for using MS/MS to differentiate singly- from doubly-charged ions have been described [20]. In a triple quadrupole mass spectrometer, the experiment uses a collision gas that promotes reduction of the doubly-charged ion, and scans the third quadrupole towards increasing mass at a rate twice the scan rate of the first quadrupole. An equivalent scan function for a hybrid geometry mass has not yet been incorporated into our instrument.

As seen in Fig. 1 and Table 1, the ions at *m/z* 83, 98, 123, 174, 223, 265 and 407 are all present with greater than 5% relative abundance in the electron ionization mass spectrum of magnesium acetate tetrahydrate. The ion at *m/z* 83 corresponds to $Mg(OAc)^+$, and the calculated mass of 82.9983 agrees with the exact mass measurement. However, since the experimental isotopic distribution does not match that of the theoretical, the presence of additional ions is suggested. An ion at *m/z* 82 $(MgCH_2COO)^+$ is present, as is an ion at *m/z* 81 $(MgCHCOO)^+$. However, the ion $Mg(OAc)^+$ accounts for 75% of the signal at *m/z* 83; all other possible contributors are not identified due to both the large number of possibilities and the higher spectral background at lower mass values. The ion at *m/z* 98 corresponds to $Mg(OAc)CH_3^+$, which has a calculated exact mass of 98.0218. The isotopic envelope distribution again shows that there are other species present, but their relative abundances are very low. The ion at *m/z* 123 corresponds to $Mg_2(OAc)O^+$, which has an exact mass of 122.9783. Deconvolution of this isotopic envelope suggested the presence of a doubly-charged ion $Mg_4(OAc)_2O_2H^{2+}$ as well as several other singly-charged ions. Exact relative contributions could not be assessed due to the presence of a more abundant ion at *m/z* 123.5 corresponding to $Mg_3(OAc)_2C_2O_2H^{2+}$. The ion at *m/z* 174 corresponds primarily to $Mg(OAc)_2O_2^+$, which has an exact mass of 174.0015. The isotopic envelope for this cluster is very complex. There are at least two doubly-charged ions and two singly-charged ions. This envelope was not fully deconvoluted, so the precise identity of all of these ions was not determined. The ion at *m/z* 223 corresponds to $Mg_3(OAc)_2(OH)O^+$, which has an exact mass of 222.9784. In this case, the isotopic envelope was easily deconvoluted, and 65% of the ion current at *m/z* 223 was assigned to $Mg_5(OAc)C_2H_2O^+$ and 35% was assigned to $Mg_3(OAc)_2(OH)O^+$. The ion at *m/z* 265 corresponds primarily to $Mg_3(OAc)_3O^+$, which has an exact mass of 264.9899. The contributions of several ions to this isotopic envelope have already been discussed. The final ion is the base peak at *m/z* 407, $Mg_4(OAc)_5O^+$, with an exact mass of 407.0016. No other contributions to this ion were apparent, with the exception of a small isotopic contribution from the ion at *m/z* 406. Many other cluster ions become apparent when the tabulated data is reviewed (see Table 1); a full deconvolution of each isotopic envelope has not been attempted due to the expanding time required for the calculation effort.

Chemical ionization

Ammonia reagent gas. Both ammonia and methane were used as reagent gases for the chemical ionization studies. Ammonia provides a less exothermic protonation reaction, and might be expected to induce less fragmentation from the molecular ions formed in a proton transfer reaction. Other work has suggested that reactant ions from ammonia and methane can protonate different sites in organic molecules [21], prompting the inclusion of both reagent gases in this study. Table 1 contains the tabulated positive ion ammonia and methane chemical ionization mass spectra of magnesium acetate tetrahydrate. Figure 3 compares the mass spectra for ammonia (a) and methane (b) chemical ionization. The most striking feature of the ammonia CI mass spectrum, compared to both the EI and methane CI data, is the increased abundance of the ion at *m/z* 467 relative to the ion at *m/z* 407. As can be seen in Table 1, both ammonia and methane chemical ionization, but especially the former, extend the mass range of the higher mass cluster ions that are formed. This same trend has been noted previously [11, 12]. In addition, chemical ionization provides a greater variety of fragment ions in the lower mass region of the spectrum. The large number of ions resulted in the overlap of many of the isotopic envelopes, and deconvolution of the signals became even more difficult than in the electron ionization mass spectrum. The identities of the principal ions in the spectra are given in Fig. 3 and Table 1.

The ion at *m/z* 407 corresponds to $Mg_4(OAc)_5O^+$, as in the electron ionization spectrum. No incorporation of hydrogen from the reagent gas is noted. The ion at *m/z* 467 corresponds to $Mg_4(OAc)_6OH^+$; this same ion was observed in EI, but with a much lower abundance. The high pressures in the chemical ionization source may serve to collisionally stabilize higher mass cluster ions; the same ions may be formed in EI, but with internal energies sufficient to cause almost complete dissociation. In this particular example, neither the CH_5^+ from methane nor the NH_4^+ from ammonia seems to react to create new protonated species in the mass spectrum. The peak at *m/z* 509 corresponds to $Mg_4(OAc)_7^+$ with an exact mass of 509.0333. The theoretical isotopic distribution matches that of the experimental. Several high mass cluster ions were observed. As can be seen from Table 1, ions with mass-to-charge values as large as

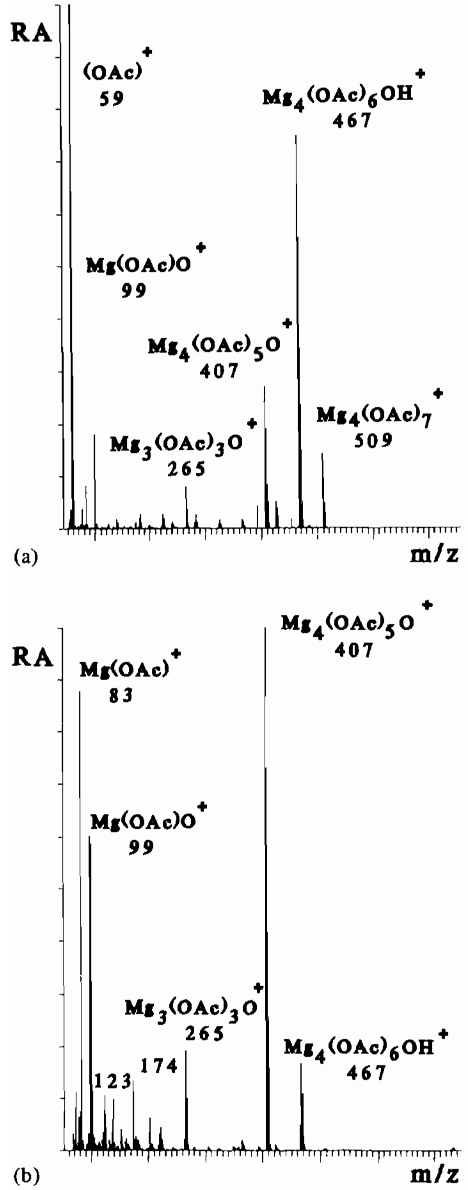

Fig. 3. Mass spectra of magnesium acetate tetrahydrate: (a) ammonia chemical ionization; (b) methane chemical ionization. Identities of non-labelled peaks are listed in Table 1.

731 are observed. This ion corresponds to an empirical formula of $Mg_7(OAc)_9O_2^+$.

Methane reagent gas. The methane chemical ionization mass spectrum (Table 1) tends to resemble the electron ionization spectrum more so than it does the ammonia CI mass spectrum. The base peak is at *m/z* 407 as in the electron ionization spectrum. The ions at *m/z* 83, 123, 174 and 265 are also present as in the electron ionization mass spectrum (and absent in the ammonia CI mass spectrum), but they differ in relative abundance.

A striking difference is in the composition of the ion at *m/z* 99. The isotopic envelope of the ion at *m/z* 99 is much broader than any of the others in the spectrum, indicating that there are a number of different ions contributing to the signal. Deconvolution of the isotopic envelope was not possible due to the inordinately large number of possibilities arising from multiple fragmentation routes.

Doubly-charged ions

One striking feature in all three of the mass spectra acquired for magnesium acetate is the appearance of doubly-charged ions. Table 3 contains a listing of these ions and the mode of ionization in which they were formed. It is possible that other doubly-charged ions are formed, but are less obvious since the predominant isotopic form appears at an integral mass value. All doubly-charged ions that were observed contained at least three magnesium atoms, and at least two acetate ligands. Chemical ionization with methane or ammonia as reagent gas produces a greater variety of doubly-charged ions than does electron ionization mass spectrometry, especially at the higher mass values. This may result from the mechanism of collisional stabilization discussed earlier.

TABLE 3. A Listing of the Doubly-charged Ions Formed under the Conditions of Electron Ionization, Ammonia Chemical Ionization and Methane Chemical Ionization

Ion	*m/z*	Mode of ionization
$Mg_4(OAc)_5(OH)H^{2+}$	204.5	NH_3-CI
$Mg_4(OAc)_5O^{2+}$	203.5	CH_4-CI
$Mg_3(OAc)_5O^{2+}$	191.5	NH_3-CI
$Mg_3(OAc)_5^{2+}$	183.5	NH_3-CI
$Mg_4(OAc)_4(OH)O^{2+}$	182.5	NH_3-CI
$Mg_4(OAc)_4OH^{2+}$	174.5	EI, NH_3-CI, CH_4-CI
$Mg_4(OAc)_4CH_3^{2+}$	173.5	EI
$Mg_4(OAc)_3(OH)_2^{2+}$	153.5	EI, CH_4-CI
$Mg_3(OAc)_3O^{2+}$	132.5	NH_3-CI, CH_4-CI
$Mg_3(OAc)_2C_2O_2H^{2+}$	123.5	EI, NH_3-CI, CH_4-CI

In summary, the mass spectra recorded in this study are in general agreement with the results obtained by Marshall. However, several discrepancies in mass or formula assignment have been noted, assuming that the ions formed do not change with source conditions. In addition many of the ions that were previously assigned as one formula have been shown to contain contributions from a number of ions. In the first application of chemical ionization to the analysis of these compounds, it was shown that CI produces cluster ions of higher mass than does electron ionization, but that these ions do not necessarily incorporate hydrogen from the chemical ionization reagent ions. Further, doubly-charged ions are observed in both electron ionization and chemical ionization mass spectra.

Mercuric Acetate

There have been no reports in the literature of either the electron or chemical ionization mass spectra of mercuric acetate. It is unclear why this should be so, since the compound is readily available and as volatile as any of the other acetates studied. The complexity of the isotope pattern of mercury (^{196}Hg 0.144% abundance, ^{198}Hg 10.02% abundance, ^{199}Hg 16.84% abundance, ^{200}Hg 23.13% abundance, ^{201}Hg 13.22% abundance, ^{202}Hg 29.80% abundance, ^{204}Hg 6.85% abundance) would suggest that the mass spectrum would be difficult to interpret in the case of overlapping ions. As the following discussion will show, however, the mass spectra for both EI and CI are simple and only in a few cases are overlapping ion signals evident.

Electron ionization

The low resolution electron ionization mass spectrum of mercuric acetate at a probe temperature of 300 °C is summarized in Table 4, and displayed in Fig. 4. Reported ion abundances in Table 4 are again those summed over the entire isotopic envelope, and the mass values are given for ^{202}Hg. The most abundant ions in the electron ionization mass spectrum generally correspond to simple combinations of mercury atoms and acetate ligands.

The ion at *m*/*z* 202 is Hg^+; the exact mass (201.9706) and the isotopic envelope distribution match predicted values. Matches are also obtained for the ion at *m*/*z* 218 (HgO^+), *m*/*z* 261 [$Hg(OAc)^+$], *m*/*z* 305 [$Hg(OAc)CO_2^+$], and the ion at *m*/*z* 581 [$Hg_2(OAc)_3^+$]. The electron ionization mass spectrum of mercuric acetate is remarkably uncluttered relative to that of the magnesium acetate tetrahydrate previously discussed.

Chemical ionization

Ammonia reagent gas. Table 4 contains the tabulated results and Fig. 5a contains the ammonia chemical ionization mass spectrum of mercuric acetate. There are a number of differences between the electron ionization mass spectrum and the ammonia chemical ionization mass spectrum. A notable difference is the shift in base peak in ammonia CI to *m*/*z* 278 as compared to *m*/*z* 261 observed in EI mass spectrum. This is a relatively modest shift in the position of the base peak. Inspection of Table 4 also reveals that ammonia chemical ionization produces a wider variety of ions than seen in the electron ionization mass spectrum. As for magnesium acetate tetrahydrate, ammonia CI produces higher mass cluster ions, presumably through a mechanism of collisional stabilization. A question underlying this study is

TABLE 4. Comparison of Electron Ionization, Ammonia Chemical Ionization and Methane Chemical Ionization Mass Spectra of Mercuric Acetate[a]

Ion	*m*/*z*	Relative abundance		
		EI	NH_3-CI	CH_4-CI
$Hg_3(OAc)_2OCH^+$	753		0.1*	
$Hg_3(OAc)_2CH_2^+$	738			1.9
$Hg_3(OAc)CO_2H_3^+$	712			0.8
$Hg_2(OAc)_3OH^+$	598		3.9	
$Hg_2(OAc)_3CH_2^+$	595			0.5
$Hg_2(OAc)_3CH^+$	594			0.5
$Hg_2(OAc)_3^+$	581	10.9	1.5	100.0
$Hg_2(OAc)_2C_2OH^+$	563			2.0
$Hg_2(OAc)_2OH^+$	539	4.5		
$Hg_2(OAc)_2CH_3^+$	537		9.0*	17.1
$Hg_2(OAc)_2OH^+$	522	0.9		
$Hg_2(OAc)_2^+$	521	0.3		
$Hg_2(OAc)C_2O_2H^+$	520		1.5*	
$Hg_2(OAc)(CO)_2^+$	519			1.1
$Hg(OAc)_4(CO)_2^+$	494			10.5
$Hg_2(OAc)OCH_2^+$	493		3.4*	
$Hg_2(OAc)CH_3^+$	478		1.3*	
$Hg_2(OAc)^+$	463	4.6	0.2	1.1
$Hg(OAc)_4C^+$	450			0.6
$Hg(OAc)_3(CO)_2^+$	435			0.2*
$Hg_2CH_3^+$	419		0.1*	
Hg_2^+	404	1.5	1.5	0.2
$Hg(OAc)_3H_2^+$	381		0.1	
$Hg(OAc)_3H^+$	380		0.2	
$Hg(OAc)_3^+$	379		0.1	
$Hg(OAc)_2C_2OH_3^+$	363		0.5	0.2
$Hg_2(OAc)_2C_2OH_2^+$	362		0.1	
$Hg(OAc)_2C_2H_3^+$	346		0.2*	
$Hg(OAc)_2(OH)H^+$	338		7.8	
$Hg(OAc)_2OH^+$	337		0.5	
$Hg(OAc)_2CH_3^+$	335	0.2*		0.4
$Hg(OAc)_2H^+$	321		14.4	5.9
$Hg(OAc)_2^+$	320	8.2*	3.0	
$Hg(OAc)CO_2^+$	305	50.0		
$Hg(OAc)C_2OH_3^+$	304		4.2	0.5
$Hg(OAc)C_2OH_2^+$	303		1.5	3.5
$Hg(OAc)O_2^+$	293	1.3		0.7
$Hg(OAc)OCH_3^+$	292			0.1
$Hg(OAc)OCH_2^+$	291	1.9		0.2
$Hg(OAc)OH_2^+$	279	1.2		0.5
$Hg(OAc)OH^+$	278		100.0	0.7
$Hg(OAc)O^+$	277		7.0	1.8
$Hg(OAc)CH_3^+$	276	1.0		
$Hg(OAc)CH_2^+$	275	2.2		
$Hg(OAc)H^+$	262		8.9	
$Hg(OAc)^+$	261	100.0	5.3	
$HgC_2O_2H_2^+$	260		5.3	
$HgC_2O_2H^+$	259		0.4	
$HgCO_2^+$	246	5.8*		
$HgC_2OH_3^+$	245		1.1	0.1*
$HgC_2OH_2^+$	244	1.1*	7.4	0.5*
HgC_2OH^+	243	2.0*		0.1*
$Hg(OH)O^+$	235		14.9	
HgO_2^+	234	0.2*	24.2	0.2*

(continued)

TABLE 4. *(continued)*

Ion	m/z	Relative abundance		
		EI	NH_3-CI	CH_4-CI
$HgOCH_3^+$	233	0.7*		
$HgOCH_2^+$	232	0.8*		
$HgCO^+$	230	0.4*		
$HgOH^+$	219		25.8	
HgO^+	218	44.6		0.1
$HgCH_3^+$	217			1.9
Hg^+	202	53.0	3.9	2.1

[a]All assignments were based on the 202 isotope of mercury. The symbol * denotes that the experimental isotopic envelope does not match that of the theoretical values.

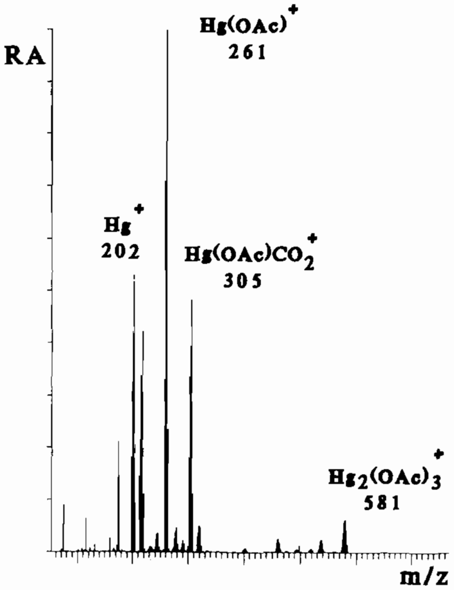

Fig. 4. Electron ionization mass spectrum of mercuric acetate. Identities of non-labelled peaks are listed in Table 4.

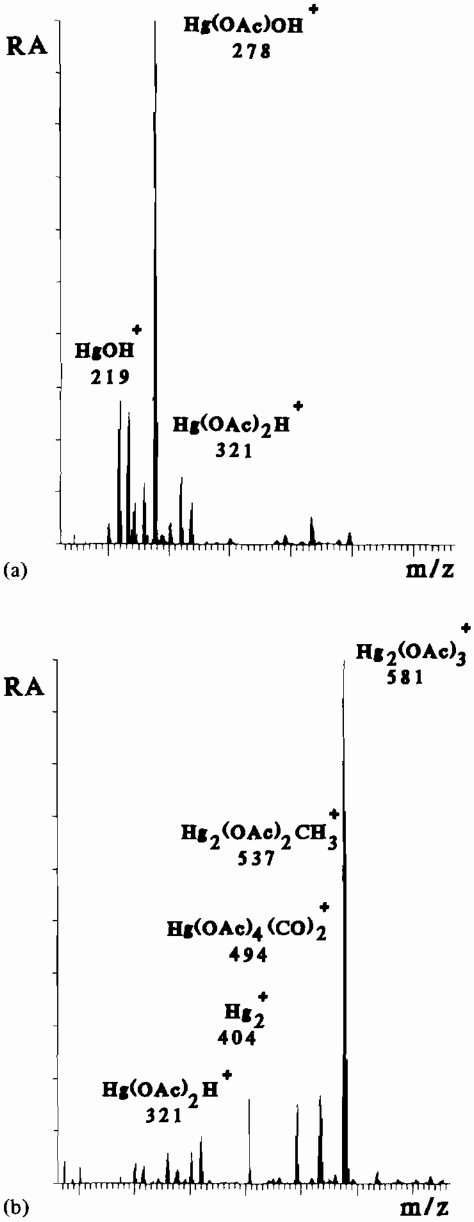

Fig. 5. Mass spectra of mercuric acetate: (a) ammonia chemical ionization; (b) methane chemical ionization. Identities of non-labelled peaks are listed in Table 4.

whether the proton-donating reactions of NH_4^+ (or CH_5^+) with neutral sample molecules result in the appearance of ions with additional protons. For magnesium acetate, no such ions were observed. Such is not the case with mercuric acetate, as several new ions are observed in the ammonia chemical ionization mass spectrum. In particular, ions $Hg(OAc)_2H^+$, $Hg(OAc)H^+$, HgO_2H^+ and $HgOH^+$ are found in the ammonia chemical ionization mass spectrum and not in the electron ionization mass spectrum. The first two ions in this series are of relatively high abundance, and indicate that proton transfer from NH_4^+ to neutral sample molecules may occur. The existence of these protonated ion forms was established by examination of exact mass values and a comparison of measured and predicted isotopic envelopes. For instance, the ion at m/z 234 corresponds to HgO_2^+, with an exact mass of 233.9635. Deconvolution of this isotopic envelope revealed the presence of a second ion, and the total signal at this mass was shown to consist of 62% HgO_2^+ and 38% HgO_2H^+. The ion at m/z 278 corresponds to $Hg(OAc)OH^+$ (exact mass of 277.9867); deconvolution of the isotopic cluster again revealed the presence of a second ion, $Hg(OAc)O^+$. An assignment of 93% $Hg(OAc)OH^+$ and 7% $Hg(OAc)O^+$ produced a theoretical isotopic envelope to match that experimentally measured. The ion at m/z 321 corresponds to $Hg(OAc)_2H^+$ (exact mass of 321.0051); deconvolution of this cluster assigned 18% to $Hg(OAc)_2^+$ and 82% to $Hg(OAc)_2H^+$.

Methane reagent gas. Table 4 contains the tabular results and Fig. 5b presents the methane CI mass spectrum of mercuric acetate. The mass spectrum obtained under methane chemical ionization is dramatically different from both the electron ionization and the ammonia chemical ionization mass spectra. The most noticeable change is the general shift in relative abundances from ions with one mercury atom to ions with two mercury atoms. Significantly, the ion $Hg_2(OAc)_3^+$ is now recorded as the base peak in the spectrum. Paradoxically, the amount of fragmentation seems greater in the ammonia CI mass spectrum than in the methane CI mass spectrum. However, the major ions in the mass spectra are the same, and the exact masses and measured isotopic envelopes for each of the ions indicated in the figure matches the expected values.

Lead Acetate

Electron ionization

The electron ionization mass spectrum of lead acetate has not been previously reported. The low resolution electron ionization mass spectrum of lead acetate at a probe temperature of 320 °C is summarized in Table 5 and displayed in Fig. 6. The results in Table 5 are reported with ion abundances summed over the isotopic envelope, and masses reported to ^{208}Pb. The EI mass spectrum is very simple, containing not even the molecular ion $Pb(OAc)_2^+$, but only fragment ions $Pb(OAc)C_2O^+$, $Pb(OAc)^+$, $Pb(OH)^+$ and Pb^+. Doubly-charged ions observed in the mass spectrum are of low relative abundance. All measured masses and isotopic envelopes agree with those predicted based on a single ionic composition for each peak.

Chemical ionization

Ammonia reagent gas. The change to ammonia chemical ionization results in significant changes in the mass spectrum of lead acetate (Fig. 7a). The base peak in the mass spectrum is at *m/z* 267 [$Pb(OAc)^+$], and the relative abundances of Pb^+, $PbOH^+$ and $Pb(OAc)C_2O^+$ are remarkably similar to those observed in the EI mass spectrum. With the higher pressures of the chemical ionization source, collisional stabilization again seems to lead to higher mass cluster ions such as $Pb(OAc)_2H^+$, $Pb_2(OAc)O^+$, $Pb_2(OAc)_2^+$, $Pb_2(OAc)_3^+$ and $Pb_2(OAc)_3C_2O^+$. Proton transfer from the reagent ion is evident in the enhanced abundance of the ion $Pb(OAc)_2H^+$, seen only with a low relative abundance in the electron ionization mass spectrum.

TABLE 5. Comparison of Electron Ionization, Ammonia Chemical Ionization and Methane Chemical Ionization Mass Spectra of Lead Acetate[a]

Ion	*m/z*	Relative Abundance		
		EI	NH_3-CI	CH_4-CI
$Pb_2(OAc)_3C_2O^+$	633		2.7	
$Pb_2(OAc)_3^+$	593		37.2	26.1
$Pb_2(OAc)_2^+$	534		4.8	3.8
$Pb_2(OAc)O^+$	491		6.5	7.1
$Pb(OAc)_2C_2O^+$	366	0.4*		
$Pb(OAc)_2C_2O^+$-H	365		0.1*	
$Pb(OAc)_2H^+$	327	0.1	8.9	1.8
$Pb(OAc)_2^+$	236		0.1	
$Pb(OAc)_2^+$-H	325	0.1	5.5	
$Pb(OAc)CO_2^+$	311	2.2	0.8	1.7
$Pb(OAc)C_2O^+$	307	5.2	11.7	0.1
$Pb(OAc)OH_2^+$	285			0.1*
$Pb(OAc)OH^+$	284		1.1*	
$Pb(OAc)CH_2^+$	281			0.1*
$Pb(OAc)^+$	267	100.0	100.0	100.0
$PbCO_2^+$	252	0.1*	0.3	0.3
PbC_2OH^+	249	0.1*	0.1	0.1
$PbCOH_2^+$	238		0.2*	0.2
$PbOH^+$	225	23.9	13.0	12.9
PbO^+	224	4.0	2.0	1.4
$PbCH_3^+$	223	2.0	0.5	1.2
Pb^+	208	58.7	31.6	31.9
$Pb(OAc)C_2O^{2+}$	152.5	0.2		
$Pb(OAc)COH^{2+}$	148	0.4		0.2
$Pb(OAc)^{2+}$	133.5	0.2	0.1	0.1
$PbCO_2^{2+}$	126			0.6
$PbCOH_2^{2+}$	119	0.3		0.1
Pb^{2+}	104	0.4	0.1	

[a] All assignments were based on the 208 isotope of lead. The symbol * denotes that the experimental isotopic envelope does not match that of the theoretical.

Interesting ions in the ammonia chemical ionization mass spectrum of lead acetate are $Pb(OAc)C_2O^+$ and $Pb_2(OAc)_3C_2O^+$. In many ions previously observed, the remaining moiety can be thought of as familiar –CO, $-CO_2$, –OH or OCH_3 groups. The composition of a $-C_2O$ grouping is unknown, and further, is unique to the mass spectra of lead acetate.

Methane reagent gas. Again, the relative abundances of the lower mass ions in the methane chemical ionization mass spectrum of lead acetate (Fig. 7b) are similar to the ammonia CI and EI mass spectra. Cluster ions observed in the methane CI mass spectrum are the same as noted above. Criteria of exact mass and isotopic envelope matches confirm the presence of a single ion in each envelope. The protonated molecule $Pb(OAc)_2H^+$ is again observed, and corresponds to proton transfer to the neutral monomeric molecule.

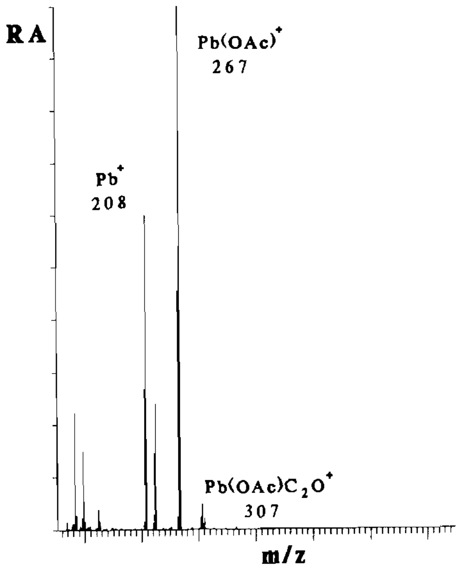

Fig. 6. Electron ionization mass spectrum of lead acetate. Identities of non-labelled peaks are listed in Table 5.

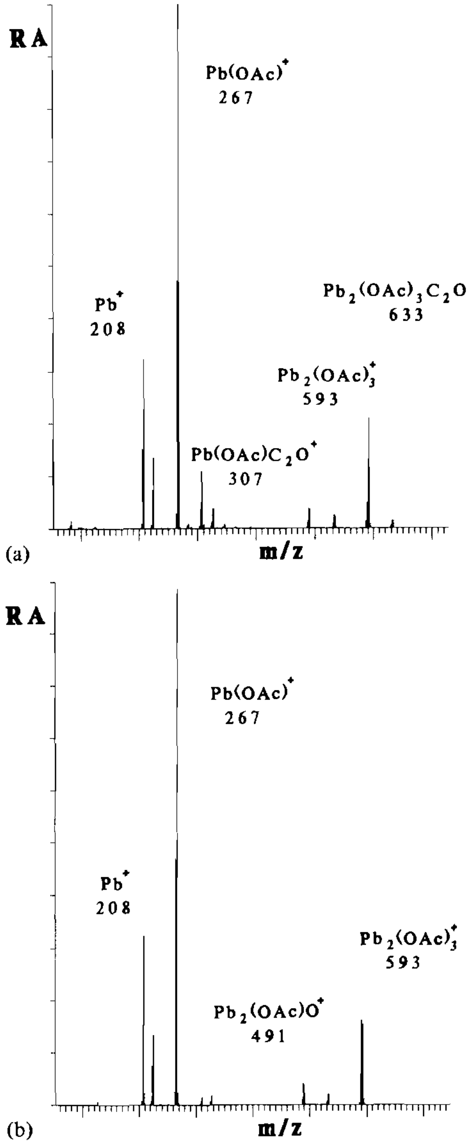

Fig. 7. Mass spectra of lead acetate: (a) ammonia chemical ionization; (b) methane chemical ionization. Identities of non-labelled peaks are listed in Table 5.

Conclusions

This study of magnesium acetate tetrahydrate is generally similar to earlier results reported by Marshall. The major discrepancies result from two sources: the identity of the ions at m/z 263 and 153, and the overall number of species observed. A comparison of the electron and chemical ionization mass spectra of this compound reveals an increase in the abundances of cluster ions formed under chemical ionization conditions. Many of the ions with relative abundances less than three percent were verified only by exact mass measurements due to clustered isotopic envelope distributions.

Neither the electron nor chemical ionization mass spectra of mercuric acetate has previously been reported. A comparison of the electron, methane chemical and ammonia chemical ionization reveals that methane chemical ionization caused the greatest increase in cluster ion formation. Ammonia chemical ionization also produced an increase in the cluster ion formation over that of electron ionization. It is of interest to note that the base peak in each of the spectra is at a different mass-to-charge value.

Lead acetate has also not been previously studied by electron or chemical ionization mass spectrometry. Unlike mercuric acetate, the electron ionization mass spectrum of lead acetate did not show any ions at mass-to-charge values equal to or greater than that of the molecular ion. The base peak in both the electron and chemical ionization mass spectra was $Pb(OAc)^+$ at m/z 267 (a loss of OAc from the molecular ion). Chemical ionization (both methane and ammonia reagent gases) provided an increase in the cluster ion abundances up to the ion $Pb_2(OAc)_3^+$ at m/z 593. The lead acetate study presented three unique ions with the C_2O group as the ligand. This particular ligand group has not been observed in any of the other acetate studies, and its presence here is not fully understood.

As in previous work, the role of chemical ionization in producing higher mass cluster ions is established. The reluctance of ions from magnesium and mercury acetates to add hydrogen from the reagent gas contrasts with the situation for mercuric acetate, which seems to readily participate in proton transfer reactions. The diversity of ion species, produced by dissociation and the propensity of metal acetates to form cluster ions is established.

These studies complement investigations of reactions of bare metal ions, or of simple metallo-organic ions with organic molecules documented in numerous studies with Fourier Transform mass spectrometry [22–24]. The complexity of ion/molecule reaction chemistry uncovered in those studies is reflected in the diversity of ions created in electron and chemical ionization of the transition metal acetates.

References

1 M. Barber, R. S. Bordoli, G. J. Elliott, R. D. Sedgwick and A. N. Tyler, *Anal. Chem., 54* (1982) A645.
2 J. M. Miller, *Adv. Inorg. Chem. Radiochem., 28* (1984) 1.
3 M. I. Bruce and M. J. Liddell, *Appl. Org. Chem., 1* (1987) 191.
4 R. A. W. Johnston (ed.), *A Specialist Periodical Report: Mass Spectrometry*, Vol. 7, Royal Society of Chemistry, London, 1984.
5 M. R. Litzow and T. R. Spalding, *Mass Spectrometry of Inorganic and Organometallic Compounds*, Elsevier, Amsterdam, 1973.
6 F. Adams, R. Gijbels and R. Van Grieken (eds.), *Inorganic Mass Spectrometry*, Wiley, New York, 1988.
7 C. Reichert, D. K. C. Fung, D. C. K. Lin and J. B. Westmore, *J. Chem. Soc., Chem. Commun.*, (1968) 1094.
8 D. A. Edwards and R. Richards, *Inorg. Nucl. Chem. Lett., 8* (1972) 783.
9 K. S. Khariton, A. V. Ablov and G. A. Popovich, *Dokl. Adad. Nauk. SSSR, 204* (1972) 547.
10 T. Ogura and Q. Fernando, *Inorg. Chem., 12* (1973) 261.
11 G. C. DiDonato and K. L. Busch, *Int. J. Mass Spectrom. Ion Proc., 69* (1986) 67.
12 G. C. DiDonato and K. L. Busch, *Inorg. Chem., 25* (1986) 1551.
13 E. White, *Org. Mass Spectrom., 13* (1978) 495.
14 K. Matsumoto, Y. Kosugi, M. Yanagisawa and I. Fujishima, *Org. Mass Spectrom., 15* (1980) 606.
15 G. L. Marshall, *Org. Mass Spectrom., 18* (1983) 168.
16 S. K. Adams, D. A. Edwards and R. Richards, *Inorg. Chim. Acta, 12* (1975) 163.
17 G. D. Roberts and E. White, *Org. Mass Spectrom., 16* (1981) 546.
18 K. L. Busch, R. G. Cooks, R. A. Walton and K. V. Wood, *Inorg. Chem., 23* (1984) 4093.
19 J. Charalambouš, *Mass Spectrometry of Metal Compounds*, Butterworths, Boston, 1975, p. 30.
20 H. I. Kenttamaa, K. V. Wood, K. L. Busch and R. G. Cooks, *Org. Mass Spectrom., 18* (1983) 561.
21 R. A. Flurer and K. L. Busch, *Org. Mass Spectrom., 23* (1988) 118.
22 B. S. Freiser, L. Sallans, K. R. Lane and R. R. Squires, *J. Chem. Soc., 107* (1985) 4379.
23 L. Sallans, K. Lane, R. R. Squires and B. S. Freiser, *J. Am. Chem. Soc., 105* (1983) 6352.
24 C. J. Cassady and B. S. Freiser, *J. Am. Chem. Soc., 106* (1984) 6176.