

# Electrospray Mass Spectrometric Study of $[M_3O(RCOO)_6L_3]^+$ Cations ( $M = Cr, Fe; L = H_2O, MeOH, py$ )

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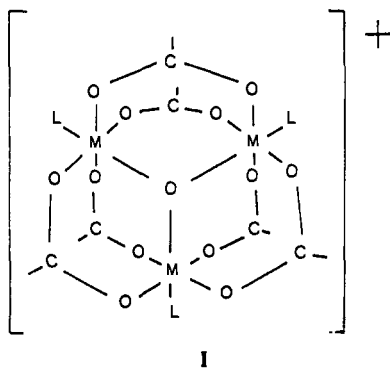
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Electrospray mass spectrometric (ESMS) studies have been made on some representative examples of the trinuclear complexes  $[M_3O(RCOO)_6(H_2O)_3]^+$  ( $M = Cr, Fe; R = H, CH_3, CH_3CH_2, (CH_3)_3C$ ) in methanol and pyridine/methanol solutions. The nonbridging water ligands in the Cr(III) complexes partially exchange with the solvent molecules and ions containing the central  $Cr_3O(RCOO)_6$  core, and various combinations of terminal ligand are observed. At low first skimmer voltages, intact ions with three terminal ligands are detected, but as the skimmer voltage is increased, interaction with solvent molecules within the ion source causes collisionally activated decompositions to occur, leading to progressive loss of the labile terminal groups. The ES mass spectra of  $[Fe_3O(CH_3COO)_6(H_2O)_3]^+$  in MeOH or pyridine/MeOH show that the water molecules exchange completely with the solvent, and for other iron derivatives the core carboxylate ligands exchange completely with the acetate in the mobile phase used in the spectrometer. Collisionally activated decomposition (CAD) mass spectra (argon, 200 V) have been observed for some of the core ions  $[M_3O(CH_3COO)_6]^+$ .

## Introduction

Complexes of the type  $[M_3O(CH_3COO)_6(H_2O)_3]^+$ , the so called basic acetates, are formed by a number of trivalent transition metals, but the best known examples are those of chromium(III)<sup>3</sup> and iron(III).<sup>4</sup> The structures of several of these compounds have been determined<sup>4a,b,5</sup> and the important features are shown in structure I. Examples of this type of complex with other



carboxylate groups have been prepared,<sup>6</sup> and it is also known that the water molecules which complete the octahedral coordination about each metal atom are relatively labile and can be exchanged with other ligands, such as the lower alcohols and pyridine.<sup>7</sup>

Mass spectrometry of inorganic and organometallic compounds has often involved volatilizing the species prior to forming ions

in the gas phase, and most early studies were therefore performed on neutral compounds. The original ionization technique of electron impact (EI) frequently led to extensive fragmentation, although the molecular ion was sometimes observed as a low intensity peak.<sup>8</sup> Consequently, considerable efforts have been made to devise softer ionization techniques, and fast atom bombardment mass spectrometry (FAB/MS) has been one of the more successful. In the study of neutral species, it often generates the molecular ion,<sup>9</sup> and in the case of ionic compounds, there have been numerous cases in which the intact ion has been observed.<sup>10</sup>

Electrospray mass spectrometry (ESMS) provides a new method of transferring preexisting ions from solution to the gas phase. The transfer is very soft and causes minimal fragmentation. The ES technique has been developed mainly by Fenn and his co-workers<sup>11</sup> and its most spectacular successes have been in the area of mass spectrometry of large biomolecules<sup>12</sup> where its use is expanding exponentially,<sup>13</sup> but to date there are few applications of the technique to inorganic chemistry.

We have begun investigating the application of ESMS to inorganic and organometallic systems. In the cases of nonlabile cations and anions, such as phosphonium salts and cations such as  $[(P-P)Pt(R_2dtc)]^+$  ( $P-P =$  diphosphine;  $R_2dtc =$  dithiocarbamate  $S_2CNR_2$ ), the intact ions are usually observed without difficulty.<sup>14</sup> However with labile complexes, product ions formed by loss of one or more ligands may be observed together with the

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Table I. Electrospray Mass Spectrometric Data<sup>a</sup>

compd/solvent	ions obsd ( $m/z$ ) <sup>b</sup>
$[Cr_3O(HCOO)_6(H_2O)_3]^+$ in methanol	$[(core)]^+$ (442), $[(core)(H_2O)]^+$ (460), $[(core)(MeOH)]^+$ (474), $[(core)(H_2O)_2]^+$ (478), $[(core)(H_2O)(MeOH)]^+$ (492), $[(core)(H_2O)_3]^+$ (496), $[(core)(MeOH)_2]^+$ (506), $[(core)(H_2O)_2(MeOH)]^+$ (510), $[(core)(H_2O)(MeOH)_2]^+$ (524), $[(core)(MeOH)_3]^+$ (538) (576), $[(core)(MeOH)_2]^+$ (590), $[(core)(H_2O)(MeOH)_2]^+$ (608), $[(core)(MeOH)_3]^+$ (622)
$[Cr_3O(CH_3COO)_6(H_2O)_3]^+$	$[(core)]^+$ (526), $[(core)(H_2O)]^+$ (544), $[(core)(MeOH)]^+$ (558), $[(core)(H_2O)(MeOH)]^+$ (576), $[(core)(MeOH)_2]^+$ (590), $[(core)(H_2O)(MeOH)_2]^+$ (608), $[(core)(MeOH)_3]^+$ (622)
$[Cr_3O(CH_3CH_2COO)_6(H_2O)_3]^+$ in methanol	$[(core)]^+$ (610), $[(core)(H_2O)]^+$ (628), $[(core)(MeOH)]^+$ (642), $[(core)(H_2O)(MeOH)]^+$ (660), $[(core)(MeOH)_2]^+$ (674), $[(core)(H_2O)(MeOH)_2]^+$ (692), $[(core)(MeOH)_3]^+$ (706)
$[Cr_3O(CH_3)_3CCOO)_6(H_2O)_3]^+$ in methanol	$[(core)]^+$ (778), $[(core)(MeOH)]^+$ (810), $[(core)(H_2O)(MeOH)]^+$ (828), $[(core)(MeOH)_2]^+$ (842), $[(core)(H_2O)_2(MeOH)]^+$ (846), $[(core)(H_2O)(MeOH)_2]^+$ (860), $[(core)(MeOH)_3]^+$ (874)
$[Cr_3O(HCOO)_6(H_2O)_3]^+$ in pyridine	$[(core)]^+$ (442), $[(core)(H_2O)_3]^+$ (496), $[(core)py]^+$ (521), $[(core)(H_2O)py]^+$ (539), $[(core)(MeOH)py]^+$ (553), $[(core)(H_2O)_2py]^+$ (557), $[(core)(MeOH)_2py]^+$ (585), $[(core)py_2]^+$ (600), $[(core)(H_2O)py_2]^+$ (618), $[(core)(MeOH)py_2]^+$ (632), $[(core)py_3]^+$ (679)
$[Cr_3O(CH_3COO)_6(H_2O)_3]^+$ in pyridine	$[(core)]^+$ (526), $[(core)(H_2O)]^+$ (544); $[(core)(MeOH)]^+$ (558), $[(core)(H_2O)_2]^+$ (562), $[(core)(H_2O)(MeOH)]^+$ (576), $[(core)(H_2O)_3]^+$ (580), $[(core)(MeOH)_2]^+$ (590), $[(core)(H_2O)_2(MeOH)]^+$ (594), $[(core)py]^+$ (605), $[(core)(H_2O)(MeOH)_2]^+$ (608), $[(core)(MeOH)_3]^+$ (622), $[(core)(MeOH)py]^+$ (637), $[(core)(H_2O)(MeOH)py]^+$ (655), $[(core)(MeOH)_2py]^+$ (669), $[(core)py_2]^+$ (684), $[(core)(MeOH)py_2]^+$ (716), $[(core)py_3]^+$ (763)
$[Cr_3O(CH_3CH_2COO)_6(H_2O)_3]^+$ in pyridine	$[(core)]^+$ (610), $[(core)(H_2O)]^+$ (628), $[(core)(MeOH)]^+$ (642), $[(core)(H_2O)(MeOH)]^+$ (660), $[(core)(MeOH)_2]^+$ (674), $[(core)py]^+$ (689), $[(core)(H_2O)(MeOH)_2]^+$ (692), $[(core)(MeOH)_3]^+$ (706), $[(core)(MeOH)(py)]^+$ (721), $[(core)(H_2O)(MeOH)py]^+$ (739), $[(core)(MeOH)_2py]^+$ (753), $[(core)py_2]^+$ (768), $[(core)(MeOH)py_2]^+$ (800)
$[Cr_3O((CH_3)_3CCOO)_6(H_2O)_3]^+$ in pyridine	$[(core)]^+$ (778), $[(core)(MeOH)]^+$ (810), $[(core)(H_2O)(MeOH)]^+$ (828), $[(core)(MeOH)_2]^+$ (842), $[(core)(H_2O)(MeOH)_2]^+$ (860), $[(core)(MeOH)_3]^+$ (874), $[(core)(MeOH)(py)]^+$ (889), $[(core)(H_2O)(MeOH)(py)]^+$ (907), $[(core)(MeOH)_2(py)]^+$ (921), $[(core)(py)_2]^+$ (936), $[(core)(MeOH)(py)_2]^+$ (968), $[(core)(py)_3]^+$ (1015)
$[Fe_3O(CH_3COO)_6(H_2O)_3]^+$ in methanol	$[(core)]^+$ (538), $[(core)(MeOH)]^+$ (570), $[(core)(MeOH)_2]^+$ (602) $[(core)(MeOH)_3]^+$ (634)
$[Fe_3O(CH_3COO)_6(H_2O)_3]^+$ in pyridine	$[(core)]^+$ (538), $[(core)py]^+$ (617), $[(core)py_2]^+$ (696)

<sup>a</sup> Core =  $M_3O(RCOO)_6$ . <sup>b</sup> Most intense peak in the isotopic mass distribution.

intact ions. Interestingly, in cationic or anionic systems where ligands are exchanging rapidly on the NMR time scale at room temperature, the ESMS technique allows observation at room temperature of the individual species present in solution and it provides a viable alternative to low-temperature NMR studies for their characterization. Examples of rapidly exchanging labile systems to which this technique has already been applied include Cu(I) mixed phosphine cations,<sup>15</sup> mixed phosphine complexes of Hg(II)<sup>16</sup> and mixed tris(dithiophosphato)zinc(II) anions.<sup>17</sup>

In this paper we describe the application of the ESMS technique to polynuclear cationic systems for the first time by examining a number of the trinuclear  $[M_3O(RCOO)_6L_3]^+$  species which nicely combine some of the characteristics of both inert and labile complexes.

### Experimental Section

The cations  $[M_3O(RCOO)_6(H_2O)_3]^+$  ( $M = Cr(III), Fe(III); R = H, Me, Et, Me_3C$ ) were all prepared by the literature method.<sup>18</sup>

Electrospray mass spectra were recorded with a VG Bio-Q triple quadrupole mass spectrometer<sup>19</sup> with a water/methanol/acetic acid mobile phase. The compounds were dissolved in either methanol or pyridine (2 mM), and this solution was then diluted 1:10 with methanol. The diluted solution was injected directly into the spectrometer via a Rheodyne injector using a Phoenix 20 micro LC syringe pump to deliver the solution to the vaporization nozzle of the electrospray ion source at a flow rate of  $3 \mu L \text{ min}^{-1}$ . Voltages at the first skimmer electrode (B1) were varied between 100 V and the minimum possible consistent with retaining a stable ion jet. This varies from time to time but is usually in the range 30–35 V. Increasing the B1 voltage enhances the formation of product ions by collisions with solvent molecules within the ion source. In addition, ions of a particular  $m/z$  value (e.g. the peak maximum in an isotopic mass

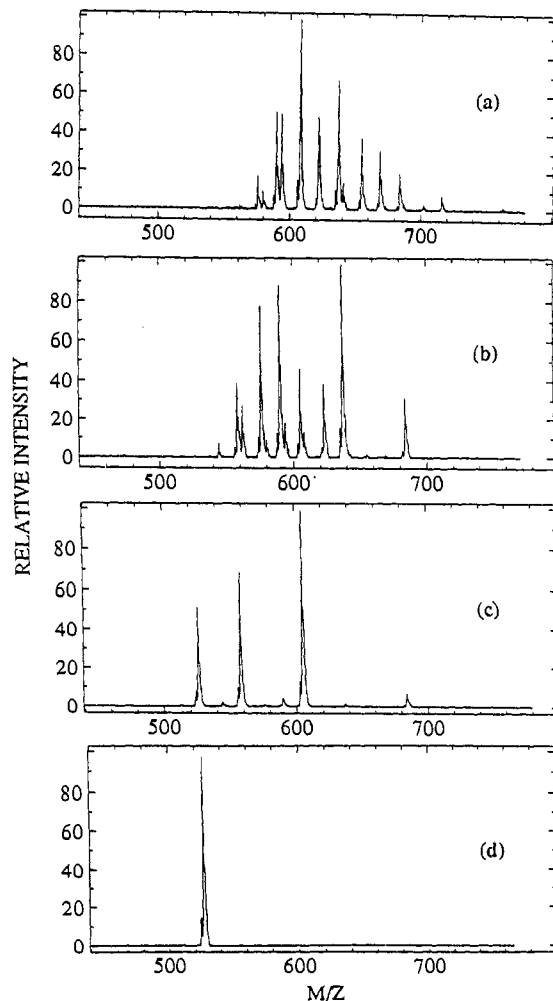


Figure 1. ES mass spectrum at different ion source (B1) voltages of  $[Cr_3O(CH_3COO)_6(H_2O)_3]^+$  dissolved in pyridine (2 mM) and diluted (1:10) with methanol: (a) 30 V; (b) 40 V; (c) 60 V; (d) 100 V.

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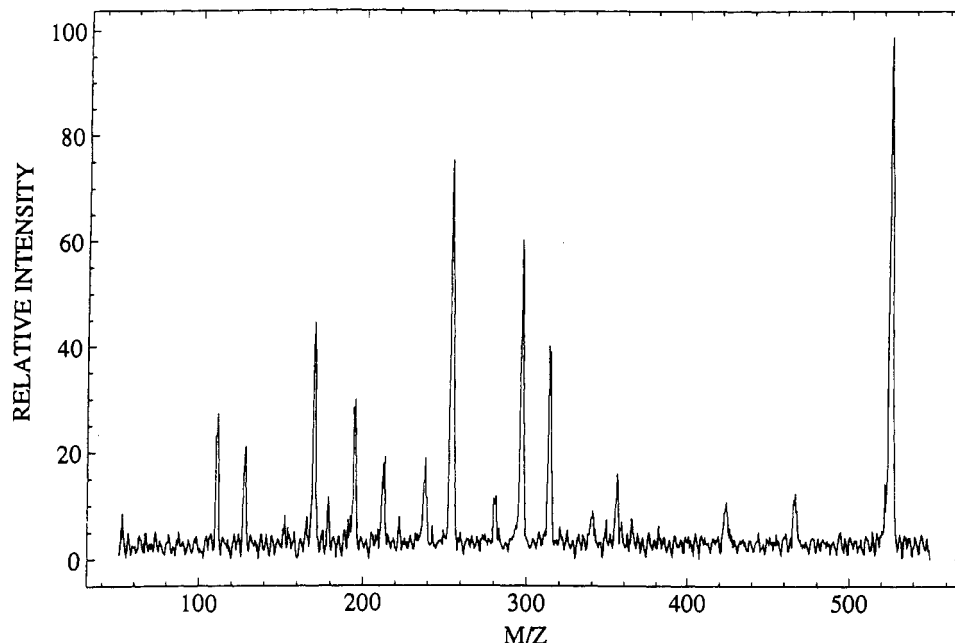


Figure 2. CADMS of  $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6]^+$  (argon) at 200 V.

distribution) can be selected and passed through a collision cell into a second mass analyzer. In the absence of gas in the collision cell the stabilities of the selected ions can be investigated. Collision-activated decomposition (CAD) mass spectra of the selected ions were obtained by admitting argon to the collision cell to a pressure that gave an approximately 50% reduction in the parent ion abundance, usually with an accelerating voltage of 200 V.

### Results and Discussion

Throughout this paper the term "core" will be used to represent the central  $\text{M}_3\text{O}(\text{RCOO})_6$  unit in the cations  $[\text{M}_3\text{O}(\text{RCOO})_6\text{L}_3]^+$ . The  $m/z$  values are given for the most intense peak in the isotopic mass distribution, and in all cases the experimental distribution agreed well with the calculated one.

**Chromium(III) Complexes.** At a B1 voltage of 40 V the ES mass spectrum of  $[\text{Cr}_3\text{O}(\text{HCOO})_6(\text{H}_2\text{O})_3]^+$  (0.2 mM) dissolved in methanol shows a series of peaks which correspond to ions containing the core and up to three terminal ligands with various combinations of water and methanol being observed, as detailed in Table I. The compound was dissolved in the methanol only about 5 min before the data were acquired, so exchange of the terminal ligands is quite rapid. This is the first time that ligand exchange reactions on a polynuclear cation have been observed by ESMS. As the B1 voltage is increased, collisionally activated decompositions occur more readily in the ion source and peaks due to ions deficient in terminal ligands become relatively more intense. At B1 = 70 V only the ion [core] $^+$  has significant intensity. Similar ES mass spectra were obtained for  $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]^+$ ,  $[\text{Cr}_3\text{O}(\text{CH}_3\text{CH}_2\text{COO})_6(\text{H}_2\text{O})_3]^+$ , and  $[\text{Cr}_3\text{O}\{(\text{CH}_3)_3\text{CCOO}\}_6(\text{H}_2\text{O})_3]^+$  in methanol, except that for the pivalate a much higher B1 voltage ( $\sim 120$  V) is required to produce an ES mass spectrum showing only the core ion. This suggests that the terminal ligands are more strongly bound to chromium in the pivalate complex. All data are summarized in Table I.

When  $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]^+$  is dissolved in pyridine, exchange occurs with the water ligands, but because the solution was subsequently diluted with methanol, (so that a stable ion beam could be maintained), the ES mass spectrum shows a series of ions containing the core and combinations of water, methanol and pyridine terminal ligands. These species would be extremely difficult to detect and identify in solution by any other technique. Figure 1 shows the ES mass spectra observed at several B1 voltages, and as before, the ions with three terminal ligands are observed at low voltage. Increasing the voltage causes collisionally activated decompositions to occur more readily until at 100 V

only the core ion is observed (Figure 1d). Similar spectra are observed when  $[\text{Cr}_3\text{O}(\text{HCOO})_6(\text{H}_2\text{O})_3]^+$ ,  $[\text{Cr}_3\text{O}(\text{CH}_3\text{CH}_2\text{COO})_6(\text{H}_2\text{O})_3]^+$ , and  $[\text{Cr}_3\text{O}\{(\text{CH}_3)_3\text{CCOO}\}_6(\text{H}_2\text{O})_3]^+$  are dissolved in pyridine, and data are given in Table I. When the solutions of the compounds in pyridine are allowed to stand for some time (20–30 min) before dilution and data acquisition, the intensities of those peaks due to ions containing two and three pyridine ligands are enhanced relative to those containing water and methanol, showing that exchange of pyridine is relatively slow on chromium. Thus ESMS can be used to study relatively slow exchange reactions, at least in a qualitative manner.

**Iron(III) Complexes.** When  $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]^+$  is dissolved in methanol and the ESMS data acquired about 5 min later, the resulting spectra are much simpler than for the chromium case. As the B1 voltage is varied only the species  $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6(\text{MeOH})_x]^+$  ( $x = 0-3$ ) are observed (Table I) indicating that complete exchange between the water ligands and the solvent methanol occurs. This is consistent with the greater lability of Fe(III) complexes compared with chromium(III). However, when  $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]^+$  is dissolved in pyridine (0.2 mM) and the solution then diluted 1:10 with methanol, only ions containing pyridine are observed (Table I). This indicates that the trinuclear cation prefers to bond to pyridine rather than methanol. This is somewhat surprising since it is usually acknowledged that Fe(III) has a lower affinity for monodentate nitrogen donor ligands than oxygen ones.<sup>20</sup>

When a solution of  $[\text{Fe}_3\text{O}(\text{C}_6\text{H}_5\text{CO}_2)_6(\text{H}_2\text{O})_3]^+$  is dissolved in methanol and a sample injected into the spectrometer, no peaks are observed corresponding to any cation containing the benzoate ligand. Instead, at higher B1 voltage the only significant peak is at  $m/z$  538 corresponding to  $[\text{Fe}_3\text{O}(\text{CH}_3\text{CO}_2)_6]^+$ , and at lower voltages ions with additional water and methanol ligands are observed. Thus this iron complex completely exchanges its core carboxylate ligands with the acetate in the mobile phase very quickly, and this is consistent with the lability of Fe(III). As a consequence of this result, no other iron complexes were examined as they would also exchange their carboxylate ligands. Thus ESMS readily demonstrates that the global ligand exchange reactions on the Fe(III) trimers are much faster than the corresponding reactions on the Cr(III) trimers.

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**Table II.** Collisionally Activated Decomposition Mass Spectrometric Data<sup>a</sup>

$[Cr_3O(CH_3COO)_6]^+$	$[Cr_3O\{(CH_3)_3CCOO\}]_6^+$	$[Fe_3O(CH_3COO)_6]^+$
$[Cr_3O(CH_3COO)_6]^+$ (526)	$[Cr_3O\{(CH_3)_3CCOO\}]_6^+$ (778)	$[Fe_3O(CH_3COO)_6]^+$ (538)
$[Cr_3O(CH_3COO)_5]^+$ (467)	$[Cr_3O\{(CH_3)_3CCOO\}]_5^+$ (677)	$[Fe_3O(CH_3COO)_5]^+$ (479)
	$[Cr_3O\{(CH_3)_3CCOO\}]_4^+$ (576)	$[Fe_3O(CH_3COO)_4]^+$ (419)
$[Cr_3O_2(CH_3COO)_4]^+$ (424)		
	$[Cr_3O\{(CH_3)_3CCOO\}]_3^+$ (475)	$[Fe_3O(CH_3COO)_3]^+$ (360)
$[Cr_2O(CH_3COO)_4]^+$ (356)		
$[Cr_2O_2(CH_3COO)_3]^+$ (313)		
$[Cr_2O(CH_3COO)_3]^+$ (297)	$[Cr_2O\{(CH_3)_3CCOO\}]_3^+$ (423)	$[Fe_2O(CH_3COO)_3]^+$ (305)
$[Cr_2O_2(CH_3COO)_2]^+$ (254)		
$[Cr_2O(CH_3COO)_2]^+$ (238)	$[Cr_2O\{(CH_3)_3CCOO\}]_2^+$ (322)	$[Fe_2O(CH_3COO)_2]^+$ (246)
$[Cr_2O_3(CH_3COO)]^+$ (212)		
		$[Fe_2O(CH_3COO)]^+$ (187)
$[CrO_2(CH_3COO)_2]^+$ (196)		
$[CrO(CH_3COO)_2]^+$ (170)		
$[CrO(CH_3COO)]^+$ (127)		
$[Cr(CH_3COO)]^+$ (111)		

<sup>a</sup> *m/z* given in parentheses.

**Tandem Mass Spectrometry—CADMS.** Ions  $[Cr_3O(CH_3COO)_6]^+$  (*m/z* 526) were selected and passed through the collision cell and into the second mass analyzer. In the absence of gas in the collision cell only one peak, due to the parent ion, appeared in the second detector, so the cation is stable in the gas phase on the timescale of this experiment ( $\sim 100 \mu s$ ). However, with argon in the cell and an accelerating voltage of 200 V, a rich collisionally activated decomposition (CAD) mass spectrum is obtained as shown in Figure 2 and the peaks are identified in Table II. Although many of the product ions result from loss of complete acetate ligands, several examples of acetate ligand fragmentation are observed with an oxygen atom remaining attached to the polynuclear metal ion as the rest of the acetate is lost (e.g.  $[Cr_3O_2(CH_3COO)_4]^+$  and  $[Cr_2O_2(CH_3COO)_2]^+$ ) and in each case the ion corresponding to further loss of CrO is also observed. The CAD mass spectrum at 200 V of the chromium pivalate complex  $[Cr_3O\{(CH_3)_3CCOO\}]_6^+$  is much simpler as detailed in Table II and suggests that the pivalate ligand is more tightly bound to chromium than is the acetate.

For  $[Fe_3O(CH_3COO)_6]^+$  the fragmentation pattern is also simpler than that of  $[Cr_3O(CH_3COO)_6]^+$ , showing loss of successive acetate groups until  $[Fe_3O(CH_3COO)_3]^+$  is formed. An iron atom is then lost, followed by further acetate ligands. Presumably these differences are related to the general lability of Fe(III) complexes compared with those of Cr(III).

### Conclusions

The most important conclusion to be drawn from this work is that it shows that ESMS is a powerful technique with which to investigate polynuclear cations in solution. Many inorganic systems contain polynuclear or metal-metal-bonded clusters in solution, but they are often not amenable to study by other techniques such as multinuclear magnetic resonance spectroscopy because of paramagnetism or lack of a suitable NMR nucleus, and structures of species in solution are often inferred from those of the solids isolated from the solutions. In the present case, because there was never any doubt that the species in solution and those in the solid are the same, this is a good system with which to evaluate the utility of ESMS for the study of both kinetically labile and inert polynuclear ionic compounds for the first time.

The chromium compounds studied here have an inert core unit and labile peripheral ligands, so they show ES mass spectral behavior that shows aspects of both inert and labile compound behavior. There are some differences in the fragmentation patterns in CAD mass spectra of the core ions of various compounds which can be related to the strengths of the metal carboxylate bonds.

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