Electron Induced Dissociation: A Mass Spectrometry Technique for the Structural Analysis of Trinuclear Oxo-Centred Carboxylate-Bridged Iron Complexes

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We report electron induced dissociation (EID) Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry of the singly-charged cations $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6]^+$ and $[\text{Fe}_3\text{O}(\text{HCOO})_6 + \text{H}_2\text{O}]^+$. Trinuclear oxo-centred carboxylate-bridged iron complexes of this type are of interest due to their electronic and magnetic properties, and because of their role as synthetic precursors of single molecule magnets. EID of these complexes is particularly efficient and provides detailed information about the triangular core, and the nature and number of ligands. EID behavior is in marked contrast to the collision induced dissociation (CID) of these species. Whereas EID allows virtually complete structural characterization, the structural information provided by CID is very limited. The results suggest that EID is particularly suitable for the structural analysis of singly-charged polynuclear metal complexes. (J Am Soc Mass Spectrom 2010, 21, 1398–1403) © 2010 American Society for Mass Spectrometry

Trinuclear oxo-centred carboxylate-bridged metal complexes, of the form $[\text{M}_3\text{O}(\text{O}_2\text{CR})_6\text{L}_3]^+$ (where R is an alkyl or aryl group, L is a terminal ligand such as water, methanol, or pyridine), see [Scheme 1](#), have been of sustained scientific interest for many years [1–4]. The complexes comprise an oxo-centred triangular array of metal ions, with pairs of metal ions bridged by carboxylate ligands. Three terminal ligands complete the octahedral coordination of each metal ion. These polynuclear compounds are widely used as models for studying electronic and magnetic metal-metal interactions in clusters [5–7]. They are also precursors for clusters of higher nuclearity, e.g.; dodecanuclear manganese (Mn_{12}) complexes [8]—the classic single molecule magnets (SMMs) [9]. SMMs are currently the subject of intense scrutiny due to their potential applications in quantum computing, high-density information storage, and biomedicine [10–15].

Of the transition-metal trinuclear oxo-centred complexes, iron, chromium, and manganese complexes are those that have been studied most extensively. For example, the magnetic and spectroscopic properties of mixed-valence $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$ complexes have been reported by Brown and coworkers [16]. Hendrickson and coworkers studied the role of electron-transfer in mixed valence iron complexes [17]. Baranwal and coworkers

synthesized mixed-ligand mixed-valence iron complexes containing carboxylates and mercaptocarboxylate ligands [2]. Several oxo-centred, trinuclear, mixed-ligand complexes of chromium(III) have been synthesized and characterized by Baranwal and coworkers [3, 7, 18]. The magnetic properties of various trinuclear oxo-centred manganese complexes have been studied by An and coworkers [19]. Thornton and coworkers examined the magnetic properties of mixed-valence manganese carboxylates [20] and the crystal structures and magnetic properties of trinuclear homo- and mixed-valence manganese pivalate complexes were studied by Decurtins and coworkers [21].

The majority of information about the structure and properties of trinuclear oxo-centred complexes has been obtained on the basis of elemental analysis, X-ray studies, and magnetic susceptibility measurements (electronic and Mossbauer spectral data) [2, 16]. The electrospray mass spectrometry and collision-induced dissociation (CID) of a number of different iron and chromium trinuclear oxo-centred complexes was first studied by van den Bergen et al. [22]. They found that CID of these species was somewhat limited as a tool for structural characterization as it results in loss of up to only three carboxylate ligands followed by disintegration of the oxo-bridged trinuclear core. Palić and coworkers [23] applied electrospray ionization Fourier transform-ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) to study the exchange/substitution reactions of terminal ligands (L in [Scheme 1](#)) of mixed-terminal

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Scheme 1. Structure of the trinuclear oxo-centred carboxylate-bridged metal complex, $[M_3O(RCOO)_6L_3]^+$.

ligand oxo-centred carboxylate-bridged trinuclear complexes. As Palii noted, “mass spectrometry is far from being exploited to its full potential for the investigation of this class of compounds” [23]. That point is particularly pertinent given the current focus of the chemistry community on synthesis of single molecule magnets based on these structures.

Tandem mass spectrometry (MS/MS), in which a precursor ion is characterized according to its fragments, is well-established as a method for structural elucidation. Perhaps the most widely used MS/MS technique is CID. However, as described above, CID is not ideal for the analysis of the oxo-centred trinuclear metal complexes. In recent years, a number of fragmentation methods have been developed, which involve the interaction of ions with electrons [24]. Electron capture dissociation (ECD) [25] entails irradiation of multiply-charged cations with very low-energy (<0.2 eV) electrons. Electron capture by the precursor ion occurs followed by decomposition of the charge-reduced species. If higher energy electrons are used (termed ‘hot’ (H)ECD) [26], electronic excitation accompanies electron capture. For anions, the technique of electron detachment dissociation (EDD) may be applied [27]. ECD cannot be applied to singly-charged precursor ions as the product is neutral and cannot be detected in the mass spectrometer. However, at higher electron energies further ionization and/or excitation followed by dissociation of the singly-charged ion may occur. These methods have been variously termed EIEIO (electron-induced excitation of ions from organics) [28], EED (electronic excitation dissociation) [29], and EID (electron ionization dissociation) [30]. O’Hair and coworkers suggested that a generic description of these methods is electron-induced dissociation (also EID) [31]. Here, we use EID (electron-induced dissociation) to describe the fragmentation observed following interaction of singly-charged ions with high-energy (>10 eV) electrons. EID has been applied to singly-charged peptide ions [30, 31], metabolites [32], betaine dimers [33], gold hydride dimers [34], and sodium chloride cluster cations [35].

We have applied EID to the structural analysis of the oxo-centred trinuclear carboxylate-bridged iron complexes $[Fe_3O(CH_3COO)_6]^+$ and $[Fe_3O(HCOO)_6 + H_2O]^+$. The results show that the EID fragmentation behavior of the oxo-centred trinuclear carboxylate-bridged iron com-

plexes is very different to that observed following CID, providing virtually complete structural characterization. EID mass spectrometry gives detailed information about the structure of the trinuclear oxo-centred Fe_3O core, and the nature and number of carboxylate and terminal ligands; loss of all six acetate/formate ligands is observed. In comparison, CID results in loss of only up to three acetate ligands from $[Fe_3O(CH_3COO)_6]^+$ and no loss of formate ligands from $[Fe_3O(HCOO)_6 + H_2O]^+$ ions. The EID technique promises to be a powerful tool for structural characterization of oxo-bridged trinuclear and other polynuclear metal complexes.

Experimental

Sample Preparation

$FeCl_3$ was purchased from BDH Ltd. (Poole, England) and used without further purification. $FeCl_3$ was dissolved in water (J. T. Baker, Deventer, Holland) and diluted to a concentration of 10 pmol/ μ L in methanol (Fisher Scientific, Loughborough, UK) and acetic acid (Fisher Scientific) (30:70:4, vol/vol), or methanol and formic acid (Fisons Scientific, Loughborough, UK) (30:70:4, vol/vol).

Mass Spectrometry Experiments

All mass spectrometry experiments were conducted on a Thermo Finnigan LTQ FT mass spectrometer (Thermo Fisher Scientific, Bremen, Germany). Samples were introduced to the mass spectrometer using an Advion Biosciences Triversa Nanomate electrospray source (Advion Biosciences, Ithaca, NY, USA). Data acquisition and analysis was performed using the Xcalibur 2.0 software (Thermo Fisher Scientific). Mass spectra in all experiments (MS and MS/MS) were acquired at a resolution of 100,000 at m/z 400. All the MS and MS/MS spectra were averaged over 30 scans and analyzed manually. For all EID experiments, the ions of interest were first mass selected and isolated in the linear ion trap and then transmitted to the ICR cell for EID. Isolation width was 10 m/z . Automatic gain control (AGC) was used to accumulate sufficient precursor ions for EID (target value 1×10^6). Electrons were generated on the surface of an indirectly heated barium tungsten cylindrical dispenser cathode (Heat Wave Labs, Inc, Watsonville, CA, USA). Precursor ions were irradiated with high-energy electrons (>10 eV) for 70 ms at 25% energy (corresponding to a cathode potential of –23.79 V). All CID experiments were performed in the front-end linear ion trap and the fragments transferred to the ICR cell for detection. Isolation width was 10 m/z . AGC target value was 1×10^6 . Helium gas at normalized collision energy of 35% was used for all CID experiments.

Results and Discussion

Mass Spectrometry

The electrospray ionization Fourier transform ion cyclotron resonance (FT-ICR) mass spectrum of FeCl_3 in water/methanol/acetic acid solution, shown in Figure 1 (top), reveals the oxo-centered trinuclear carboxylate-bridged iron complexes: $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6]^+$ ($m/z_{\text{meas}} 537.8779$, $m/z_{\text{calc}} 537.8791$), $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6 + \text{H}_2\text{O}]^+$ ($m/z_{\text{meas}} 555.8878$, $m/z_{\text{calc}} 555.8896$), and $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6 + \text{CH}_3\text{OH}]^+$ ($m/z_{\text{meas}} 569.9052$, $m/z_{\text{calc}} 569.9053$). Each of these complexes contains an oxo-centered triangular array of iron ions, with every two iron ions bridged by two acetate groups. The complexes $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6 + \text{H}_2\text{O}]^+$ and $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6 + \text{CH}_3\text{OH}]^+$ each have one terminal ligand, water and methanol respectively. Van den Bergen et al. showed that external ligands in oxo-centered trinuclear carboxylate-bridged metal complexes are relatively labile, for example, ligands such as water or methanol can easily exchange with lower alcohols and pyridine [22]. Both van den Bergen et al. [22] and Palii et al. [23] showed that electrospray of these complexes results in peaks corresponding to $[\text{M}_3\text{O}(\text{RCOO})_6\text{L}_x]^+$, where $x = 0-3$. The isolation mass spectrum (isolation width 10 m/z centered on m/z 537.8779) for $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6]^+$ ions (Figure 1 (top), inset) shows a peak at $m/z_{\text{meas}} 555.8878$, corresponding to $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6 + \text{H}_2\text{O}]^+$. That result suggests that at least some of the species with terminal ligands observed in MS1 are being formed in the linear ion trap, i.e.; by reaction of $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6]^+$ with gaseous water and methanol. Such behavior has also been observed for metal cluster ions Ca_n^+ , Sr_n^+ and Ba_n^+ by Stace and coworkers [36]. Reducing the trapping time to 5 ms did not remove, or reduce, the peak corresponding to $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6 + \text{H}_2\text{O}]^+$.

Figure 1 (bottom) shows the electrospray FT-ICR mass spectrum of FeCl_3 dissolved in water/methanol and formic acid. The peaks at m/z 471.7944, m/z 489.8045, m/z 503.8201, and m/z 517.8362 can be assigned to following complexes: $[\text{Fe}_3\text{O}(\text{HCOO})_6 + \text{H}_2\text{O}]^+$ ($m/z_{\text{calc}} 471.7957$), $[\text{Fe}_3\text{O}(\text{HCOO})_6 + 2\text{H}_2\text{O}]^+$ ($m/z_{\text{calc}} 489.8063$), $[\text{Fe}_3\text{O}(\text{HCOO})_6 + \text{H}_2\text{O} + \text{CH}_3\text{OH}]^+$ ($m/z_{\text{calc}} 503.8219$), and $[\text{Fe}_3\text{O}(\text{HCOO})_6 + 2\text{CH}_3\text{OH}]^+$ ($m/z_{\text{calc}} 517.8376$). No species without terminal ligands were observed, even with increased ESI lens voltage. Figure 1 (bottom), inset, shows the isolation mass spectrum for the complex with one terminal water ligand (isolation width 10 m/z centered on m/z 471.7957). The presence of the complex with two terminal water ligands in the isolation mass spectrum of the complex with one terminal water ligand suggests that at least some of the $[\text{Fe}_3\text{O}(\text{HCOO})_6 + 2\text{H}_2\text{O}]^+$ ions are formed in the linear trap.

Figure 1 (bottom), inset, shows the isolation mass spectrum for the complex with one terminal water ligand (isolation width 10 m/z centered on m/z 471.7957). The presence of the complex with two terminal water ligands in the isolation mass spectrum of the complex with one terminal water ligand suggests that at least some of the $[\text{Fe}_3\text{O}(\text{HCOO})_6 + 2\text{H}_2\text{O}]^+$ ions are formed in the linear trap.

Figure 1. (top) Electrospray FT-ICR mass spectrum of FeCl_3 in water/methanol/acetic acid solution. Inset: isolation mass spectrum (isolation width 10 m/z centered on m/z 537.8779) for $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6]^+$ ions. (bottom) Electrospray FT-ICR mass spectrum of FeCl_3 in water/methanol/formic acid solution. Inset: isolation mass spectrum for the complex with one terminal water ligand $[\text{Fe}_3\text{O}(\text{HCOO})_6 + \text{H}_2\text{O}]^+$ (isolation width 10 m/z centered on m/z 471.7957). Peaks selected for subsequent EID and CID experiments have been highlighted.

Electron Induced Dissociation Mass Spectrometry (EID-MS) of the $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6]^+$ and $[\text{Fe}_3\text{O}(\text{HCOO})_6 + \text{H}_2\text{O}]^+$ Complexes

The EID mass spectrum of the oxo-centered trinuclear acetate-bridged iron complex $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6]^+$ is shown in Figure 2a. The most abundant fragments are summarized in Table 1. The major fragmentation channel was loss of complete acetate ligands, accompanied by a decrease in iron oxidation state. As a result of the consecutive loss of up to six acetate ligands the following singly-charged ions were observed: $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_5]^+$, $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_4]^+$, $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_3]^+$, $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_2]^+$, $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})]^+$, and Fe_3O^+ (see Figure 2a, Table 1). A second dissociation channel involves loss of complete acetate ligand(s) combined with fragmentation within another acetate ligand. One oxygen atom from the “other” acetate ligand remains attached to the polynuclear complex, whereas the rest of the ligand (CH_3CO) is lost. Possibly, that dissociation channel is the result of secondary CID fragmentation of the EID products, i.e.; via collision with the helium in the ion trap. The following fragments were observed $[\text{Fe}_3\text{O}_2(\text{CH}_3\text{COO})_4]^+$, $[\text{Fe}_3\text{O}_2$

Figure 2. (a) Electron induced dissociation mass spectrum of $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6]^+$ ions. Double-headed arrows indicate loss of CH_3COO . Inset: Expanded m/z region showing peak corresponding to Fe_3O^+ . (b) Collision induced dissociation mass spectrum of $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6]^+$ ions. Double-headed arrows indicate loss of CH_3COO . * denotes noise peak. (c) Electron induced dissociation mass spectrum of $[\text{Fe}_3\text{O}(\text{HCOO})_6+\text{H}_2\text{O}]^+$ ions. Double headed arrows indicate loss of HCOO , except where indicated. (d) Collision induced dissociation mass spectrum of $[\text{Fe}_3\text{O}(\text{HCOO})_6+\text{H}_2\text{O}]^+$ ions. * denotes noise peak.

$(\text{CH}_3\text{COO})_3]^+$, $[\text{Fe}_3\text{O}_2(\text{CH}_3\text{COO})_2]^+$, $[\text{Fe}_3\text{O}_2(\text{CH}_3\text{COO})]^+$, and Fe_3O_2^+ . The peaks corresponding to $[\text{Fe}_2\text{O}(\text{CH}_3\text{COO})_2]^+$, $[\text{Fe}_2\text{O}(\text{CH}_3\text{COO})]^+$, $[\text{Fe}_2\text{O}_2]^+$, and $[\text{Fe}_2\text{O}]^+$ result from disintegration of the oxo-bridged triangular core, either via loss of FeO from, for example, $[\text{Fe}_3\text{O}_2(\text{CH}_3\text{COO})_2]^+$ or via loss of Fe from, say, $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_2]^+$. We postulate that the fragment $[\text{Fe}_3\text{O}_3\text{H}]^+$ is the result of loss of CH_2CO from $[\text{Fe}_3\text{O}_2(\text{CH}_3\text{COO})]^+$ ion. A peak corresponding to loss of CO_2 from the oxo-centered trinuclear fragment with three acetate ligands was also observed; $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_3-\text{CO}_2]^+$.

As mentioned above, the loss of acetate ligands from $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6]^+$ ions is accompanied by the decrease in iron oxidation state. Formation of the naked core Fe_3O^+ , see Figure 2a, inset, demonstrates that EID has been accompanied by a change in oxidation state of Fe(III) to Fe(I) for each iron atom. Formation of gas-phase metal complexes with unusual metal oxidation states has been reported previously by Stace and co-workers [37–39]. Moreover, previous experiments in our laboratory showed that electron capture by gas-

phase metal complex cations may allow access to oxidation states that are not readily available in solution [40].

For comparison, the CID mass spectrum obtained for singly-charged $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6]^+$ ions is shown in Figure 2b. CID was performed in the ion trap and the fragments transferred to the ICR cell for detection. The fragments observed are summarized in Table 2. The extent of CID is much less than that observed for EID. Two major fragments, resulting from the loss of one and two complete acetate ligands, $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_5]^+$ and $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_4]^+$ are observed. A minor peak corresponding to loss of a third ligand was also observed. The CID parameters (activation energy, time) were varied and under no circumstances were peaks corresponding to complexes with less than three ligands detected. Some secondary fragmentation was observed in the form of $[\text{Fe}_3\text{O}_2(\text{CH}_3\text{COO})_4]^+$, which is the result of loss of one complete acetate ligand combined with loss of CH_3CO from a second acetate ligand. Two additional peaks are observed which correspond to $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_5+\text{H}_2\text{O}]^+$ and $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_4+\text{H}_2\text{O}]^+$. Note that the isolation mass spectrum, Figure 1 (top) inset,

Table 1. Fragment ions observed following EID of $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6]^+$ ions

<i>m/z</i> (Measured)	<i>m/z</i> (Calculated)	Assignment
555.8979	555.8896	$[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6]^+ + \text{H}_2\text{O}$
537.8844	537.8791	$[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6]^+$
478.8714	478.8657	$[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_5]^+$
435.8527	435.8474	$[\text{Fe}_3\text{O}_2(\text{CH}_3\text{COO})_4]^+$
419.8566	419.8525	$[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_4]^+$
376.8380	376.8341	$[\text{Fe}_3\text{O}_2(\text{CH}_3\text{COO})_3]^+$
360.8421	360.8391	$[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_3]^+$
317.8236	317.8207	$[\text{Fe}_3\text{O}_2(\text{CH}_3\text{COO})_2]^+$
316.8522	316.8493	$[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_3\text{-CO}_2]^+$
301.8283	301.8258	$[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_2]^+$
258.8093	258.8074	$[\text{Fe}_3\text{O}_2(\text{CH}_3\text{COO})]^+$
245.8927	245.8908	$[\text{Fe}_2\text{O}(\text{CH}_3\text{COO})_2]^+$
242.8143	242.8125	$[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})]^+$
216.7982	216.7968	$[\text{Fe}_3\text{O}_3\text{H}]^+$
199.7953	199.7941	$[\text{Fe}_3\text{O}_2]^+$
186.8786	186.8775	$[\text{Fe}_2\text{O}(\text{CH}_3\text{COO})]^+$
183.8003	183.7992	$[\text{Fe}_3\text{O}]^+$
143.8598	143.8592	$[\text{Fe}_2\text{O}_2]^+$
127.8648	127.8642	$[\text{Fe}_2\text{O}]^+$

reveals the presence of $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6 + \text{H}_2\text{O}]^+$ formed in the ion trap via reaction of $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6]^+$ with gaseous water. The additional peaks are either the result of acetate ligand loss from the complex with a terminal water ligand, or are the result of reaction of the CID fragment $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_5]^+$ with water in the ion trap.

The EID mass spectrum of the singly-charged oxo-centered trinuclear formate complex, $[\text{Fe}_3\text{O}(\text{HCOO})_6 + \text{H}_2\text{O}]^+$, is shown in Figure 2c. The most abundant fragments observed are detailed in Table 3. The dominant fragmentation channels observed are: (1) loss of the terminal water ligand, (2) loss of complete formate ligands (up to six), and (3) loss of complete formate ligands combined with fragmentation within another formate ligand, which leads to loss of HCO from the “other” ligand and one oxygen atom from that ligand remaining attached to the polynuclear complex. As described above, possibly the third fragmentation channel is the result of secondary (CID) fragmentation of EID products. The loss of formate ligands from the $[\text{Fe}_3\text{O}(\text{HCOO})_6 + \text{H}_2\text{O}]^+$ complex is accompanied by a decrease in iron oxidation state (Fe(III) to Fe(I)), as was

Table 2. Fragment ions observed following CID of $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6]^+$ ions

<i>m/z</i> (Measured)	<i>m/z</i> (Calculated)	Assignment
537.8798	537.8791	$[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6]^+$
496.8768	496.8763	$[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_5 + \text{H}_2\text{O}]^+$
478.8864	478.8657	$[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_5]^+$
453.8583	453.8579	$[\text{Fe}_3\text{O}_2(\text{CH}_3\text{COO})_4 + \text{H}_2\text{O}]^+$
435.8478	435.8474	$[\text{Fe}_3\text{O}_2(\text{CH}_3\text{COO})_4]^+$
419.8522	419.8525	$[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_4]^+$
360.8396	360.8391	$[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_3]^+$
322.9151	322.9147	$[\text{Fe}_2\text{O}(\text{CH}_3\text{COO})_3 + \text{H}_2\text{O}]^+$
304.9045	304.9042	$[\text{Fe}_2\text{O}(\text{CH}_3\text{COO})_3]^+$

Table 3. Fragment ions observed following EID of $[\text{Fe}_3\text{O}(\text{HCOO})_6 + \text{H}_2\text{O}]^+$ ions

<i>m/z</i> (Measured)	<i>m/z</i> (Calculated)	Assignment
489.8104	489.8063	$[\text{Fe}_3\text{O}(\text{HCOO})_6 + 2\text{H}_2\text{O}]^+$
471.7993	471.7957	$[\text{Fe}_3\text{O}(\text{HCOO})_6 + \text{H}_2\text{O}]^+$
453.7887	453.7852	$[\text{Fe}_3\text{O}(\text{HCOO})_6]^+$
424.7855	724.7824	$[\text{Fe}_3\text{O}_2(\text{HCOO})_5]^+$
408.7903	408.7875	$[\text{Fe}_3\text{O}(\text{HCOO})_5]^+$
379.7873	379.7848	$[\text{Fe}_3\text{O}_2(\text{HCOO})_4]^+$
363.7921	363.7898	$[\text{Fe}_3\text{O}(\text{HCOO})_4]^+$
334.7890	334.7871	$[\text{Fe}_3\text{O}_2(\text{HCOO})_3]^+$
318.7938	318.7922	$[\text{Fe}_3\text{O}(\text{HCOO})_3]^+$
289.7909	289.7894	$[\text{Fe}_3\text{O}_2(\text{HCOO})_2]^+$
274.8036	274.8023	$[\text{Fe}_3\text{O}(\text{HCOO})_3\text{-CO}_2]^+$
244.7928	244.7918	$[\text{Fe}_3\text{O}_2(\text{HCOO})]^+$
228.7977	228.7968	$[\text{Fe}_3\text{O}(\text{HCOO})]^+$
199.7948	199.7941	$[\text{Fe}_3\text{O}_2]^+$
183.7992	183.7992	$[\text{Fe}_3\text{O}]^+$
172.8624	172.8619	$[\text{Fe}_2\text{O}(\text{HCOO})]^+$
143.8595	143.8592	$[\text{Fe}_2\text{O}_2]^+$
127.8645	127.8642	$[\text{Fe}_2\text{O}]^+$

also observed for the acetate-bridged complex. The peaks corresponding to $[\text{Fe}_2\text{O}(\text{HCOO})]^+$ and $[\text{Fe}_2\text{O}]^+$ are the result of core disintegration either via loss of FeO from $[\text{Fe}_3\text{O}_2(\text{HCOO})]^+$ and Fe_3O_2^+ , respectively, or via loss of Fe from $[\text{Fe}_3\text{O}(\text{HCOO})]^+$ and Fe_3O^+ respectively. Peaks corresponding to loss of one iron atom from Fe_3O_2^+ and to loss of CO_2 from the complex containing three formate ligands were also noted; Fe_2O_2^+ and $[\text{Fe}_3\text{O}(\text{HCOO})_3\text{-CO}_2]^+$, respectively. Again for comparison, the CID mass spectrum obtained for the formate-bridged complex, $[\text{Fe}_3\text{O}(\text{HCOO})_6 + \text{H}_2\text{O}]^+$, is shown in Figure 2d. The only dissociation process observed was loss of the terminal ligand and formation of the ion: $[\text{Fe}_3\text{O}(\text{HCOO})_6]^+$ (m/z_{meas} 453.7831, m/z_{calc} 453.7852). The presence of $[\text{Fe}_3\text{O}(\text{HCOO})_6 + 2\text{H}_2\text{O}]^+$ ions are the result of gas-phase reactions within the linear ion trap.

Electron induced dissociation mass spectrometry gives very detailed information regarding the structure of both the $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6]^+$ and $[\text{Fe}_3\text{O}(\text{HCOO})_6 + \text{H}_2\text{O}]^+$ complexes. In marked contrast, the CID mass spectra were very limited in terms of useful structural information. EID resulted in sequential loss of all six acetate/formate ligands and formation, in both cases, of the singly charged Fe_3O^+ ion. Given the high mass accuracy of FT-ICR mass spectrometry, there can be no question as to the elemental composition or charge of the fragments. CID resulted in loss of up to only three acetate ligands and no formate ligands, regardless of the severity of CID conditions, i.e.; CID does not provide information about the oxo-centred core and the number of ligands. Given the current synthetic focus on these types of structure and concomitant requirement for suitable analytical techniques, our results suggest that EID may become a useful tool for structural characterization of oxo-bridged polynuclear complexes.

Conclusions

Our results show that the combination of high mass accuracy FT-ICR mass spectrometry and electron induced dissociation (EID) can be successfully used for the structural analysis of singly-charged oxo-centred trinuclear carboxylate-bridged metal complexes. EID mass spectrometry gives detailed information about the structure of the Fe_3O core, and the nature and number of carboxylate and terminal ligands. In general, the EID technique promises to be a powerful tool for structural characterization of various singly-charged polynuclear complexes which cannot be studied by other techniques, for example, magnetic resonance spectroscopy (because of paramagnetism), or other mass spectrometry methods such as electron capture dissociation (ECD), which can only be applied to multiply-charged ions.

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