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Fragmentation of the (Cyclam-acetato)iron Azide Cation in the Gas Phase

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Mass spectrometry is used to investigate the fragmentation of the ligated azidoiron cation [(cyclam-acetato)Fe(N_3)]$^+$, which is accessible in the gas phase by electrospray ionization of a solution of its hexafluorophosphate salt in methanol/water. Upon collisional activation, mass-selected [(cyclam-acetato)Fe(N_3)]$^+$ undergoes competing loss of dinitrogen or HN_3 as the prevailing fragmentations. The former dissociation pathway is investigated in detail in order to determine whether or not the free, high-valent iron nitride [(cyclam-acetato)FeN]$^+$ is formed. The evidence obtained indeed supports the formation of the iron nitride species as an intermediate, although the long-lived ion sampled after mass selection may also have undergone further rearrangements.

Introduction

High-valent iron species are of long-standing interest in coordination chemistry due to their occurrence as reaction intermediates in metalloenzyme reactions.[1] The field has gained significant momentum since the discovery of the first proven Fe^{IV} intermediate in mononuclear nonheme iron enzymes[2] and the first crystal structure of an elusive Fe^{IV}-oxo species by Rohde et al.[3] More recently, it has proven possible to proceed beyond the oxidation state Fe^{IV} and to obtain definitive spectroscopic evidence for genuine Fe^{V}[4,5] and even Fe^{VI} species.[6,7] The high-valent iron sites in these compounds are stabilized in a distorted octahedral environment by an innocent framework provided by ligands designed on the basis of the cyclam motif together with an extremely basic axial nitrido ligand, which is generated in situ by photolysis of the corresponding iron azide precursors. For the time being these species can only be generated in an immobilized state in solids or frozen solutions, therefore their chemistry cannot yet be explored in detail. In this work we take a first step towards studying the reactivity of these elusive species by generating them in the gas phase. In addition to the interest from biological chemists, the chemistry of transition-metal nitride compounds is attracting ongoing attention due to their potential in organic synthesis, with the formation of C–N bonds being particularly important.[8–10] The evidence for metal nitride species is, however, often only circumstantial because of the intrinsically high reactivity of these species. Recently, the photolysis of solid [(cyclam-acetato)Fe(N_3)][PF_6] ([**1**][PF_6]), was described to yield the [(cyclam-acetato)FeN]$^+$ cation **2**$^+$ according to Equation (1).[5]

$$[(\text{cyclam-acetato})\text{Fe}(\text{N}_3)][\text{PF}_6] \rightarrow [(\text{cyclam-acetato})\text{FeN}][\text{PF}_6] + \text{N}_2 \qquad (1)$$

Cation **2**$^+$ can be viewed as an example of a genuine and isolated nitridoiron cation and hence offers a possibility for the investigation of the gas-phase reactivity of these compounds. In this context, it has been demonstrated previously[11,12] that the bare imidoiron cation $FeNH^+$ provides an excellent model system for the examination of transition-metal-mediated imine transfer in the gas phase. The chemical behavior of $FeNH^+$ towards oxygen, water, hydrogen, various aliphatic hydrocarbons (including methane), benzene, and toluene reveals an intrinsically high reactivity of $FeNH^+$, even under thermal conditions. Thus, reactions are brought about which are otherwise difficult to realize, such as the direct amination of organic substrates (RH) according to Equation (2).

$$\text{RH} + \langle\text{NH}\rangle \rightarrow \text{RNH}_2 \qquad (2)$$

Compared to $FeNH^+$, much less is known about the gas-phase chemistry of the diatomic iron nitride FeN.[13] Given the availability of the precursor salt [**1**][PF_6], electrospray ionization (ESI) appeared to be a promising method to probe the occurrence of reaction (1) in the gas phase and to subsequently investigate the gas-phase reactivity of such a rare transition-metal nitrido complex.

Results and Discussion

Under mild ionization conditions, ESI of [(cyclam-acetato)Fe(N_3)][PF_6] dissolved in methanol/water provides an intense signal for the molecular cation [(cyclam-acetato)-Fe(N_3)]$^+$ (**1**$^+$) at *m*/*z* 355 for the most abundant ^{56}Fe isotope

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with the expected isotope pattern.[14,15] Under increasingly harsher ionization conditions, $\mathbf{1}^+$ undergoes consecutive dissociations, and ESI under enforced conditions can hence be used to generate these fragment ions (see below).[16,17] CID of mass-selected $[(\text{cyclam-acetato})\text{Fe}(\text{N}_3)]^+$ shows mass differences, Δm, of –28 and –43 as the major fragmentation pathway in the CID spectra over the whole range of collision energies studied (Figure 1). Phenomenological analysis of the energy behavior reveals an appearance energy of 1.0 ± 0.2 eV for the Δm = –28 fragmentation and 1.9 ± 0.4 eV for the Δm = –43 fragmentation. Accordingly, the fragmentation with Δm = –28 is the lowest-energy dissociation pathway of $\mathbf{1}^+$.

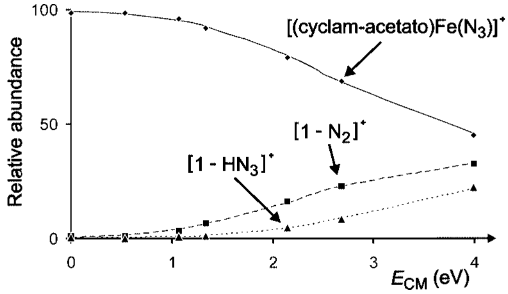


Figure 1. Collision-induced fragmentation of mass-selected $[(\text{cyclam-acetato})\text{Fe}(\text{N}_3)]^+$ ($\mathbf{1}^+$) as a function of collision energy (center-of-mass frame). The lines connecting the experimental data points show the result of the fits using sigmoid functions (see Experimental Section).

Given the elemental composition of $\mathbf{1}^+$ ($\text{C}_{12}\text{H}_{25}\text{N}_7\text{O}_2\text{Fe}$), the mass difference of –43 can be associated with various combinations of neutral molecules lost. However, the presence of an azido group very much implies the expulsion of HN_3 according to reaction (3).

$$\underset{m/z\ 355}{[(\text{cyclam-acetato})\text{Fe}(\text{N}_3)]^{+}} \rightarrow \underset{m/z\ 312}{[(\text{cyclam-acetato} - \text{H})\text{Fe}]^{+}} + \text{HN}_3 \qquad (3)$$

$$\rightarrow \underset{m/z\ 327}{[(\text{cyclam-acetato})\text{FeN}]^{+}} + \text{N}_2 \qquad (4)$$

The additional proton required for the formation of neutral HN_3 must come from the ligand backbone, most probably from one of the three NH groups. This view is supported by an analogous and moreover exclusive loss of CH_3OH from the related species $[(\text{cyclam-acetato})\text{Fe}(\text{OCH}_3)]^+$, which is formed upon slow solvolysis of $[\mathbf{1}][\text{PF}_6]$ in methanol/water solution (half-life of about 5 days at ambient temperature). If the Δm = –43 fragmentation were instead due to a facile degradation of the cyclam ligand itself (e.g. a loss of vinylamine), the same mass difference would also be expected for $[(\text{cyclam-acetato})\text{Fe}(\text{OCH}_3)]^+$; however, such a fragmentation is not observed even in traces. By the same line of reasoning, the Δm = –28 fragmentation is attributed to the expulsion of a nitrogen molecule from the azido group, see reaction (4), which is in perfect analogy to the occurrence of reaction (1) in the condensed phase.[5] If this mass loss were instead due to a fragmentation of the cyclic ligand, it would also be expected to occur for the methoxido complex, for which it is not observed experimentally.

The key question which we will pursue in the following is the nature of the ionic fragment $[\mathbf{1} - \text{N}_2]^+$ formed in reaction (4) because it could either correspond to the elusive nitridoiron cation $\mathbf{2}^+$ or an isomeric product of a subsequent rearrangement (see below). While mass spectrometry alone cannot provide an unambiguous answer in this respect, analysis of the fragmentation pattern might provide insight into the isomeric structures conceivable from an experimental point of view.[18] Hence, the fragment ion $[\mathbf{1} - \text{N}_2]^+$ (*m*/*z* 327) formed in the ESI source under slightly enforced ESI conditions was mass-selected and subjected to CID.

Not unexpectedly, the fragmentation pattern of $[\mathbf{1} - \text{N}_2]^+$ is rather rich, and the most significant dissociation pathways are associated with mass differences of –16, –17, –30, –44, –61, –99, and –142. Most of these routes cannot be explained in a straightforward manner, although this is to be expected if $\mathbf{2}^+$ were indeed formed. Thus, Δm = –16, for example, can correspond to either losses of neutral CH_4, NH_2, or O. Likewise, Δm = –17 may account for expulsion of NH_3 or OH, and for Δm = –30 neutral fragments like C_2H_6, CH_2NH_2, CH_2O, or even NO are conceivable. In the case of the larger mass differences, the options become increasingly more complex. Due to the manifold of fragments, the collision-energy dependence of the fragmentation behavior is also not analyzed in detail. Qualitatively, however, it can be noted that the fragments associated with Δm = –17, –30, –44, and –99 already appear at lower collision energies (Figure 2, a), whereas those with Δm = –16, –61, and –142 are more pronounced at elevated collision energies (Figure 2, b); the comparison indicates that the latter are either due to consecutive fragmentations or correspond to entropically favored, but energy-demanding, direct bond cleavages.[19]

In general, isotopic labeling would appear to be an ideal strategy for the identification of the various neutral losses. Selective isotope labeling of the ligand is, however, not easily applicable here because the precursor synthesis is not trivial and our major interest concerns the nature of the putative nitridoiron species rather than the degradation of the ligand backbone. Therefore, only three isotopic ions were considered. At first, the ion with *m*/*z* 325 was mass-selected as this can be attributed exclusively to the ^{54}Fe isotope of $[\mathbf{1} - \text{N}_2]^+$ and shows the same mass differences as listed above. Accordingly, none of the neutrals lost upon CID contain the iron atom of $[\mathbf{1} - \text{N}_2]^+$. Next, the precursor $[\mathbf{1}][\text{PF}_6]$ was dissolved in D_2O and the solution was stored for 2 h at room temperature. In the resulting mass spectrum, the signal due to $\mathbf{1}^+$ is cleanly shifted three mass units higher, which is attributed to the exchange of all amino hydrogen atoms by deuterium, i.e. $[N,N,N\text{-D}_3]\text{-}\mathbf{1}^+$ (*m*/*z* 358). CID of mass-selected $[N,N,N\text{-D}_3]\text{-}\mathbf{1}^+$ yields the loss of N_2 (Δm = –28) and DN_3 (Δm = –44), as expected from the occurrence of reactions (3) and (4) for the unlabeled ion.

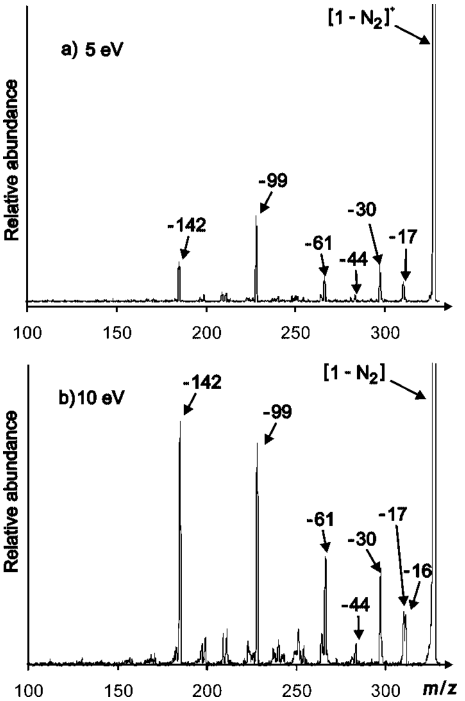


Figure 2. CID spectra of mass-selected $[\mathbf{1} – N_2]^+$ at a collision energy of a) 5 and b) 10 eV. In both spectra, the parent ion is 20-fold off-scale.

For the fragment ion $[\{N,N,N\text{-}D_3\}\text{-}\mathbf{1}^+ – N_2]^+$, mass differences of –17, –19, –30, –31, –32, –44, –63, –99, –100, –142, and –143 are observed (Table 1). Likewise, a sample of the precursor was investigated in which the azido ligand is $^{15}N_1$-labeled – terminally $^{15}N_1$-labeled azide was used in the preparative synthesis to afford a 1:1 mixture of $[(\text{cyclam-acetato})\text{Fe}(^{15}N^{14}N^{14}N)]^+$ and $[(\text{cyclam-acetato})\text{Fe}(^{14}N^{14}N^{15}N)]^+$. CID of the mass selected ion $[^{15}N_1]\text{-}\mathbf{1}^+$ (*m*/*z* 356) shows a 1:1 ratio of $^{14}N_2$ and $^{14}N^{15}N$ losses (Δm = –28 and – 29) as well as an expulsion of neutral $[^{15}N_1]\text{-}HN_3$ (Δm = –44). Hence, the fragmentations of $\mathbf{1}^+$ exclusively involve the azido group, as already concluded above from the behavior of the methoxido complex $[(\text{cyclam-acetato})\text{Fe}(OCH_3)]^+$. Mass selection of $[\{^{15}N_1\}\text{-}\mathbf{1} – N_2]^+$ and subsequent CID lead to mass differences of –17, –18, –30, –44, –62, –100, and –143, thus indicating the participation of the labeled nitrogen atom in most of the neutral losses.

The following conclusions can be drawn from the mass shifts observed for the ions compared to the unlabeled species (Table 1): (i) The mass differences Δm = –16 and –17 are most likely associated with loss of an amino radical and ammonia, respectively, with exclusive participation of the azido N-atom and incorporation of one H-atom from the hydrocarbon linkers while the other hydrogen(s) stem(s) from the amino groups; (ii) with the given elemental composition of $[\mathbf{1} – N_2]^+$, the mass difference Δm = –30 can correspond to the formation of either C_2H_6, $[CH_4N]$, CH_2O, or NO. Based on the results for the deuterated compound, participation of the amino groups is obvious and hence implies loss of $[CH_4N]$ (e.g. an aminomethyl radical CH_2NH_2 or CH_3NH),[20] although a definitive assignment of the neutral fragment cannot be made; (iii) even though other options cannot be rigorously excluded, the labeling patterns as well as the known structure of $[\mathbf{1}][PF_6]$ imply that Δm = –44 corresponds to decarboxylation, which is further supported by the fragment with Δm = –61, whose genesis can be explained by combined losses of CO_2 and ammonia; (iv) Δm = –99 and Δm = –142 are assigned to fragmentations of the ligand backbone after initial decarboxylation, with only limited participation of the amino protons. It is noteworthy that the azido N-atom is incorporated in the neutral fragment lost; (v) investigation of the ^{54}Fe isotope demonstrates that iron is not contained in any of the neutral fragments lost.

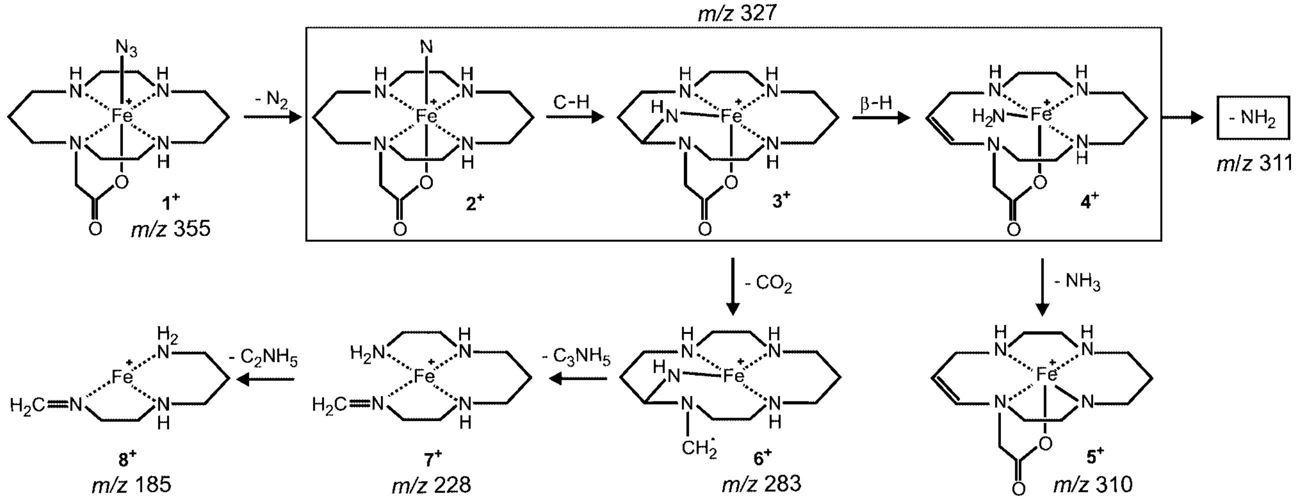
Some additional information can be derived by inspecting the CID spectra of some of the major fragment ions of $[\mathbf{1} – N_2]^+$ which are formed under more drastic ionization conditions. For example, the ion at *m*/*z* 310 formally corresponding to loss of ammonia from $[\mathbf{1} – N_2]^+$ shows a mass loss of –44 as the most abundant mass difference upon CID. Further, the relationship of Δm = –99 and –142 as consecutive processes is supported by the observation of Δm = –43 as a major fragmentation pathway in the CID spectrum of $[\mathbf{1} – N_2 – 99]^+$. Not all fragment ions of interest can be investigated by this approach, however, because of interfering isobaric ions formed in the course of ESI.

Combining the insights derived from the CID spectra together with the data of the isotopologs, a sequence for the successive fragmentation of $\mathbf{1}^+$ can be suggested (Scheme 1). While such a scenario is necessarily also based on several assumptions derived from chemical plausibility considerations, it can provide a consistent explanation for most of the fragmentations observed. Thus, in the first step, molecular nitrogen is lost from $\mathbf{1}^+$ to afford the elusive nitridoiron species $\mathbf{2}^+$. Next, this nitridoiron species is suggested to undergo an intramolecular insertion into one of the C–H bonds of the methylene groups in one of the C_3 bridges

Table 1. Mass differences[a] and relative abundances observed in the CID spectra of mass-selected $[\mathbf{1} – N_2]^+$ and some of its isotopologs at a collision energy of 10 eV.

Precursor ion	*m*/*z*	Mass difference (abundance)[b]
$[\mathbf{1} – N_2]^+$	327	–16 (20), –17 (25), –30 (40), –44 (8), –61 (45), –99 (90), –142 (100)
$[\{^{54}Fe\}\text{-}\mathbf{1} – N_2]^+$	325	–16 (20), –17 (30), –30 (40), –44 (10), –61 (55), –99 (100), –142 (90)
$[\{D_3\}\text{-}\mathbf{1} – N_2]^+$	330	–17 (45), –19 (25), –30 (10), –31 (25), –32 (35), –44 (12), –63 (30), –99 (100), –100 (35), –142 (70), –143 (30)
$[\{^{15}N\}\text{-}\mathbf{1} – N_2]^{+[c]}$	328	–17 (40), –18 (60), –30 (45), –44 (10), –61 (45), –100 (95), –143 (100)

[a] Only selected peaks are listed; the complete CID spectrum of the unlabeled ion $[\mathbf{1} – N_2]^+$ (*m*/*z* 327) is shown in Figure 2b. [b] Given relative to the base peak of the CID spectrum (100). [c] The CID spectrum is corrected for interfering isotopes of $[\mathbf{1} – N_2]^+$ which is also formed from $[^{15}N\text{-}\mathbf{1}]^+$ upon loss of $^{14}N^{15}N$.



Scheme 1.

(here it is shown in the vicinity of the carboxymethyl substituent). The thus-formed insertion intermediate **3**$^+$ can subsequently undergo β-hydrogen transfer to afford structure **4**$^+$, from which either an NH_2 group can be lost directly at higher collision energies (Δm = –16) or ammonia is released (**4**$^+$→**5**$^+$; Δm = –17). As an alternative, decarboxylation of intermediate **3**$^+$ is suggested to afford the aminoalkyl radical **6**$^+$ (Δm = –44), which then loses a $[C_3H_5N]$ unit in a rapid consecutive reaction to afford **7**$^+$ (Δm = –99); note that the latter process already has a related precedent in the mass spectra of CH^+ adducts of the cyclam ligand.[21] Eventual degradation of the neighboring C_2 bridge can then lead to **8**$^+$ (Δm = –142). Note, however, that we have deliberately not included the loss of CH_2NH_2 because the labeling patterns (particularly the lack of a mass shift upon ^{15}N-labeling) preclude us from even proposing a speculative pathway.

The entire fragmentation sequence is thus fully in accordance with the formation of the genuine nitridoiron cation **2**$^+$. Specifically, the suggested C–H bond insertions and the formations of NH_2 and NH_3 are indicative of the presence of a highly reactive intermediate which is capable of bond-activation processes such as the bare iron oxide cation FeO^+[22,23] or the iminoiron cation $FeNH^+$.[11,12] It is of crucial importance to note, however, that this chemical evidence very much supports the presence of structure **2**$^+$ as an intermediate but does not prove that the long-lived [**1** – N_2]$^+$ ion sampled in the MS/MS experiments described here still exhibits this particular structure. In fact, the experimental data reported so far are consistent with all isomeric structures **2**$^+$–**4**$^+$ suggested in Scheme 1 in that the reactions considered to be characteristic for the nitridoiron cation will also occur for the products of consecutive rearrangements.

In light of this, we finally attempted to probe the structure of [**1** – N_2]$^+$ by investigating its ion/molecule reactions at thermal energy. To this end, mass-selected [**1** – N_2]$^+$ was allowed to interact with butane, 1-butene, as well as deuterated methanol, where the order of the neutral reagents parallels the ease of bond-activation processes.[24,25] No reactions were observed at all with the two hydrocarbons, however, and with CD_3OD only a very slow formation of the formal adduct [**1** – N_2 + CD_3OD]$^+$ was observed. While again not providing unambiguous evidence, these preliminary reactivity studies suggest that long-lived [**1** – N_2]$^+$ may indeed exist in an already rearranged structure such as **3**$^+$ or **4**$^+$. We would like to point out that this conclusion is all but trivial because it is quite often simply assumed that well-known reactions, such as the decomposition of an azide, lead to the species anticipated by analogies from other media. However, it needs to be tested in every instance that the particular structures are also maintained on a unimolecular level and are not altered by subsequent rearrangements. In the present case, for example, we do not have any reasonable doubt that the nitrido species **2**$^+$ is formed as an intermediate – in fact it has been observed in frozen matrices[5] – but the experimental evidence obtained for the gaseous ion at least indicates that the long-lived ions bears a different connectivity.

Conclusions

Electrospray mass spectrometry has been used to show that the decomposition of gaseous [(cyclam-acetato)Fe(N_3)]$^+$ leads to the bare, high-valent Fe^V nitride cation [(cyclam-acetato)FeN]$^+$, as already suggested for the condensed phase. Analysis of the fragmentation pattern implies, however, that this iron nitride species undergoes further rearrangements which mean that the long-lived ion might have a different structure. This question cannot be solved unambiguously with the mass spectrometric methods used here, and further studies of mass-selected [(cyclam-acetato)-FeN]$^+$ would hence be desirable in order to investigate whether or not the cyclam-acetato ligand has indeed lost his "innocence", i.e. has undergone degradation processes due to the close vicinity of the free iron nitride unit. In this respect, the CID experiments reported here are not ideal for a distinction of isomeric structures,[18] and this question is perhaps best addressed by the appropriate spectroscopic experiments in the gas phase coupled with quantum chemical calculations; work along these lines is in progress in our laboratories.[26]

Experimental Section

The experiments were performed using a VG BIO-Q mass spectrometer as described in detail elsewhere.[27] Briefly, the VG BIO-Q is a commercial instrument which consists of an electrospray ionization source combined with a tandem mass spectrometer of QHQ configuration (Q stands for quadrupole and H for hexapole). In the present experiments, millimolar solutions of [(cyclam-acetato)Fe(N_3)][PF_6] in methanol/water (4:1) were introduced through a fused-silica capillary to the ESI source with a syringe pump (ca. $5\,\mu\mathrm{L\,min^{-1}}$). Nitrogen was used as nebulizing and drying gas at a source temperature of about 80 °C. Maximal yields of the desired ions **1**$^+$ and **2**$^+$ (see below) were achieved by adjusting the cone voltage to about 30 and 60 V, respectively. For collision-induced dissociation (CID) at low collision energies, the ions of interest were mass-selected using Q1, interacted with xenon as a collision gas in the hexapole H under single-collision conditions (typically 2×10^{-4} mbar) at variable collision energies (E_lab = 0–20 eV), while scanning Q2 to monitor the ionic products. At E_lab = 0 eV, no significant fragmentations of either mass-selected **1**$^+$ or **2**$^+$ were observed under these conditions. We note in passing that the sample examined contains some traces of potassium, which lowers the yield of Fe-containing cations in the ESI spectra somewhat but does not hinder the experiments.

As pointed out previously, the VG Bio-Q does not allow the direct extraction of quantitative threshold information from CID experiments due to several limitations of the commercial instrument.[27] For weakly bound ions,[28] for example, a non-negligible amount of ion decay is observed even at E_lab = 0 eV, which is in part attributed to the presence of collision gas not only in the hexapole but also in the focusing regions between the mass analyzers. Note that this dissociation does not correspond to metastable ions because it does not occur in the absence of collision gas. To a first approximation, however, the energy dependence of the product distributions in the CID spectra can be modeled by a sigmoid function,[29] which allows the extraction of some semi-quantitative information about the energetics of the ions examined.[30] Nevertheless, the energy dependence of the CID fragments can be approximated by sigmoid functions of the type $I_\mathrm{i}(E_\mathrm{CM}) = \{BR_\mathrm{i}/[1 + \mathrm{e}^{(E_{1/2} - E_\mathrm{CM})b}]\}$ using a least-squares criterion; for the parent ion M, the relation is $I_\mathrm{M}(E_\mathrm{CM}) = \{1 - \Sigma(BR_\mathrm{i}/[1 + \mathrm{e}^{(E_{1/2,\mathrm{i}} - E_\mathrm{CM})b}{}_\mathrm{i}]\}$, where BR_i is the branching ratio of a particular product ion ($\Sigma BR_\mathrm{i} = 1$), $E_{1/2}$ is the energy at which the sigmoid function of ion intensities has reached half of its maximum, E_CM is the collision energy in the center-of-mass frame [$E_\mathrm{CM} = m_\mathrm{T}/(m_\mathrm{T} + m_\mathrm{I})\times E_\mathrm{lab}$, where m_T and m_I stand for the masses of the collision gas and the ion, respectively], and b describes the rise of the sigmoid curve. In consecutive dissociations, all secondary product ions were added to the intensity of the primary fragment. Further, non-negligible ion decay at E_lab = 0 eV as well as some fraction of nonfragmenting parent ions at large collision energies were acknowledged by means of appropriate scaling and normalization procedures. This empirical, yet physically reasonable, approach is able to reproduce the measured ion yields quite well; note, however, that this simplified formalism does not explicitly include a treatment of competitive branching ratios at elevated energies. It is obvious, however, that the term $E_{1/2}$ used in the exponent corresponds neither to the intrinsic appearance energy of the fragmentation of interest nor to the thermochemical thresholds at 0 K. The phenomenological threshold energies given below were derived from linear extrapolations of the rise of the sigmoid curves at $E_{1/2}$ to the base line.

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