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Electronic structure and fragmentation properties of $[Fe_4S_4(SEt)_{4-x}(SSEt)_x]^{2-}$

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Abstract

A limited exposure of $(n\text{-}Bu_4N)_2[Fe_4S_4(SEt)_4]$ solutions in acetonitrile to air was found to produce a new series of [4Fe–4S] cluster complexes, $[Fe_4S_4(SEt)_{4-x}(SSEt)_x]^{2-}$ ($x = 1$–4), with the original –SEt ligands substituted by –SSEt di-sulfide ligands, which were formed due to partial decomposition of the [4Fe–4S] core in parent $[Fe_4S_4(SEt)_4]^{2-}$. The products were first observed in the experiments with an ESI-ion Trap-TOF mass spectrometer and were further identified using high resolution Fourier transform ion cyclotron resonance (FTICR) mass spectrometer. Photoelectron spectra of the $[Fe_4S_4(SEt)_{4-x}(SSEt)_x]^{2-}$ dianions revealed that the –SSEt coordination induced little change in the electronic structure of the [4Fe–4S] cluster, but the electron binding energies of $[Fe_4S_4(SEt)_{4-x}(SSEt)_x]^{2-}$ increased from 0.52 to 0.73 eV with increase in x from 0 to 4, suggesting a greater electron withdrawing ability of –SSEt than –SEt. In high resolution MS/MS experiments on $[Fe_4S_4(SEt)_3(SSEt)]^{2-/1-}$, clusters with both charge states yielded fragment $[Fe_4S_4(SEt)_3]^-$, suggesting that –SSEt could be lost either as a negatively charged ion $SSEt^-$ from the doubly charged precursor, or as a radical $^{\bullet}SSEt$ from the singly charged species. The biological implication of the interaction between $[Fe_4S_4(SEt)_4]^{2-}$ and O_2 is discussed in comparison to the air exposure of [4Fe–4S] proteins to the air.

Keywords: FTMS; Electrospray ionization source; Tandem mass spectrometry; Photoelectron spectroctroscopy; Fe–S protein

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1. Introduction

Iron–sulfur proteins are involved in a wide range of vital biological processes, such as respiration, photosynthesis and nitrogen fixation [1–3]. The active sites of these proteins normally contain iron–sulfur clusters with one to four iron atoms coordinated by inorganic sulfur and incorporated into the protein structure through terminal coordination by cysteine side chains from the proteins. Fe–S proteins are an important class of electron transfer agents and they also have important functions as catalysts and gene transcription regulators [4]. The correlation between the electronic structure of the Fe–S clusters and the functionalities of the proteins has been extensively studied, and it can help the rational design of biomimic catalysts or drugs [5–7]. Experimental investigations have covered both protein samples and synthetic analogues using spectroscopic techniques, such as NMR, ESR, Mossbauer, Raman, etc. [8,9]. All these methods are performed in the condensed phases (solutions or solids).

On the other hand, rapid development of mass spectrometry, in particular, the soft-ionization technique of electrospray ionization (ESI) [10,11], has made it possible to transport intact solution species directly into the gas phase. Tandem mass spectrometry (MS/MS) has been used to analyze metal complex coordination structure in coordination chemistry through ion–molecule reactions [12–14]. Gas phase experiments provide an opportunity to study the intrinsic properties of the Fe–S core without interference resulting from solvent or lattice effects. The technique developed in our laboratory that combines ESI and photoelectron spectroscopy (PES) provides an excellent platform for investigation of the electronic structures of molecules in the gas phase [15]. Using this technique, we have been able to transport a variety of synthetic Fe–S analogue complexes from solution into the gas phase and systematically investigated their electronic properties [16–20]. The PES data provided intrinsic oxidation potentials of the complexes reveal-

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ing the electrostatic nature of the interactions between the cubane core [4Fe–4S] and the terminal ligands [16,17]. Furthermore, we used collision induced dissociation (CID) to probe the fragmentation properties of the [4Fe–4S] cubane core. We observed symmetric fission of the doubly charged cubane complexes [21–23], $[Fe_4S_4L_4]^{2-} \rightarrow 2[Fe_2S_2L_2]^-$, which provided direct experimental evidence for the two-layer spin-coupling model for the [4Fe–4S] cubane core [24–26]. Asymmetric fission channels were also observed for several mixed ligand clusters $[Fe_4S_4L_xL'_{4-x}]^{2-}$ [27]. Novel [2Fe–2S] clusters were created using the asymmetric fission method [28]. Cubane clusters with various oxidation states from $[4Fe–4S]^-$ to $[4Fe–4S]^{3+}$ were generated in the form of $[Fe_4S_4L_x]^-$ with variable ligand L [29]. In a recent high resolution Fourier transform ion cyclotron resonance (FTICR) mass spectrometric work, MS/MS experiments on mixed ligand complexes $[Fe_4S_4(SEt)_xCl_{4-x}]^{2-}$ ($x = 0–4$) proved that the coordination environment has a significant influence on the fragmentation properties of [4Fe–4S] clusters [30].

In the current work, we will demonstrate that limited exposure of $[Fe_4S_4(SEt)_4]^{2-}$ solutions to the air results in formation of $[Fe_4S_4(SEt)_{4-x}(SSEt)_x]^{2-}$ species. Photoelectron spectroscopy was used to probe the electronic structure of these novel complexes with disulfide ligands. Fragmentation behavior and stabilities of $[Fe_4S_4(SEt)_3(SSEt)]^{2-/1-}$ were probed using MS/MS experiments in a high resolution FTICR mass spectrometer.

2. Experimental methods

2.1. Sample preparation

All sample preparations were carried out in a dry N_2 glove box. Stock solutions of anions $[Fe_4S_4(SEt)_4]^{2-}$ were prepared by dissolving solid samples of $(n\text{-}Bu_4N)_2[Fe_4S_4(SEt)_4]$ in O_2-free acetonitrile (1×10^{-4} mol/L). Air exposure was carried out in a syringe by letting in an air bubble from the needle and shaking for different periods of time to give a crude control of the degree of air exposure. These solutions were used directly for electrospray in TOF, PES and FTICR experiments.

2.2. TOF-MS and PES spectra

The PES experiments were carried out with a magnetic-bottle PES apparatus equipped with an ESI source, a quadruple ion trap (QIT) and a time-of-flight (TOF) mass spectrometer. Details of the experimental method have been given elsewhere [15–17]. Briefly, solution samples were sprayed from a syringe and the produced anions were guided into the QIT, where they were accumulated for 0.1 s before being extracted into the TOF tube for mass analyses. In the PES spectra, the species of interest were selected and decelerated before being crossed by a laser beam (193 nm) for photodetachment.

2.3. FTICR spectra

The FTICR experiments were performed on a specially designed 6 T instrument at the Pacific Northwest National Laboratory [31]. Ions were generated in a high-transmission external ESI source equipped with an electrodynamic ion funnel, a collision quadrupole, a mass resolving quadrupole and an accumulation quadrupole. The collision quadrupole was operated in the RF only mode for ion focusing.

For surface-induced dissociation (SID) experiments, the resolving quadrupole was operated in its mass-resolving mode with a typical dc offset in the range of 5–10 V. The isotopic envelope of the precursor ion was selected in the resolving quadrupole, and stored in the accumulation quadrupole for 0.5–10 s. Ions were extracted into the electrostatic ion guide, transferred through the ICR cell, and collided with a fluorinated self-assembled monolayer (FSAM) surface at normal incidence [31–34]. The collision energy was calculated from the potential difference between the offset of the accumulation quadrupole and the surface.

In CID experiments, the resolving quadruple was operated in an RF only mode. All ions generated in the ESI source were transferred into the ICR cell and captured using gated trapping. In MS/MS experiments, all unwanted ions were ejected by applying a stored waveform inverse Fourier transform (SWIFT) excitation [35,36]. Sustained off-resonance irradiation (SORI)-CID experiments [37] were performed on the isolated single isotope peak or an isotopic envelope of the ion of interest. Collision gas (Ar or O_2) was introduced into the cell using a pulsed valve. The isolated precursor ions were radially excited slightly off resonance for 40 ms with maximum collision energies in the range of 0.5–1.7 eV by changing the peak-to-peak voltage applied to the excitation plates. After 10 s pumping delay, ions in the cell were excited for detection by broadband chirp excitation. The maximum kinetic energy (peak–peak) achieved in SORI-CID was calculated as previously reported [31–35].

2.4. UV–vis absorption spectra

Solutions with different degree of air-exposure prepared in a syringe, as described above, were diluted directly into a well-sealed quartz cuvette to about 10^{-5} to 10^{-6} mol/L using O_2-free solvent in a glove box. The UV–vis absorption spectra were measured using a commercial UV–vis spectrophotometer (Varian Analytical Instruments).

3. Results

3.1. ESI-TOF mass spectra

Fe–S cluster complexes are known to be extremely air-sensitive. All relevant experiments are usually carried out under inert gas atmosphere with purged solvent to remove the residual air. A typical TOF mass spectrum for a clean acetonitrile solution of $(Bu_4N)_2[Fe_4S_4(SEt)_4]$ is shown in Fig. 1a with only one peak at m/z 298, corresponding to the parent cubane core. However, when an unpurged acetonitrile solvent was accidentally used to dissolve $(Bu_4N)_2[Fe_4S_4(SEt)_4]$, a series of unexpected peaks was observed in addition to the precursor ion peak. Shown in Fig. 1b is a spectrum taken using a sample prepared by controlled air-exposure. Exposure of $(Bu_4N)_2[Fe_4S_4(SEt)_4]$ to the laboratory air yields four new peaks at m/z 314, 330, 346 and 362 with