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Received October 15, 2004

Using potentially bidentate ligands (−SC₂H₅NH₂), we produced [2Fe–2S]⁺ species of different coordination geometries by fission of [4Fe–4S]²⁻ complexes. Even though the ligands are monodentate in the cubane complexes, both monod- and bidentate complexes were observed in the [2Fe] fission products through self-assembly because of the high reactivity of the tricoordinate iron sites. The electronic structure of the [2Fe] species was probed using photoelectron spectroscopy and density functional calculations. It was found that tetracoordination significantly decreases the electron binding energies of the [2Fe] complexes, thus increasing the reducing capability of the [2Fe–2S]⁺ clusters.

The iron–molybdenum cofactor (FeMoco) is the site where nitrogenase reduces N₂ to NH₃.¹ The originally determined structure² of FeMoco consisted of a Mo₇Fe₇S₉ cluster in which six of the seven iron atoms in the cluster core exhibited the rare distorted trigonal geometry. The existence of an internal ligand atom X (X = C, N, or O) in the center of FeMoco was recently discovered.³ This revision has been an incentive for chemists to synthesize structural models with the unusual three-coordinate, unsaturated iron sites.⁴ However, these iron atoms are highly distorted in symmetry, and their interaction with the hypervalent ligand X bonds are most likely because of the high reactivity of the tricoordinate iron sites. The Fe−X bonds are most likely to substitute the original monodentate ligand, aminoethylethiol (−SC₂H₅NH₂), to replace the original monodentate ligand −SEt (Et = C₂H₅) in [Fe₆S₆(SEt)₆]²⁻ to form the precursor cubane complexes [Fe₅S₅(SEt)₅−L₉]²⁻ (L = −SC₂H₅NH₃, n = 0−4). We envisioned that self-assembly caused by the tricoordinate iron site might occur following the CID to generate [Fe₂S₅(SEt)₅−Lₓ]²⁻ (x = 0−2) complexes with different geometries (Figure 1a).


The experiments were carried out using a PES apparatus equipped with an electrospray source and a magnetic-bottle TOF photoelectron analyzer.\(^{(9,10)}\) CID experiments on [Fe\(_4\)S\(_4\) (SEt)\(_4\)\]\(^{2-}\) were carried out by applying a voltage of 2.5–6 V to the first skimmer of the instrument.\(^{(8,9)}\) Complete CID of the [4Fe–4S] cubanes could be obtained when the mass peaks of the two species with \(n\) = 1 and 3 disappeared from the mass spectrum (Figure S1).\(^{(11)}\) In the PES experiment, two detachment photon energies were used: 266 nm (4.661 eV) from a Nd:YAG laser and 193 nm (6.424 eV) from an ArF eximer laser.

The PES spectra at the two photon energies for the ligand-substituted [Fe\(_2\)S\(_2\)(SEt)\(_2\)]\(^{2-}\) complexes (Figure 2) are very similar to that of [Fe\(_4\)S\(_4\)(SEt)\(_4\)]\(^{2-}\).\(^{(10)}\) Significant spectral cutoffs were observed in the higher-binding-energy side in each spectrum, typical of PES spectra for multiply charged species.\(^{(12)}\) The adiabatic binding energy (ADE) increases sequentially from 0.29 to 0.66 eV with ligand substitution number \(n\) from 0 to 4 (Table S1).

The key results of this study are shown in Figure 3. The apparent difference in the PES spectra between [Fe\(_2\)S\(_2\)(SEt)\(_2\)]\(^{2-}\) and their [4Fe–4S] cubane parents is the significant increase in binding energy and the lack of spectral cutoffs, because of the absence of intramolecular Coulomb repulsion and RCB in the singly charged [2Fe–2S] products.\(^{(13)}\) The species for \(x = 0\) and 1 showed spectral patterns similar to those of their corresponding [4Fe–4S] parents, exhibiting two features in the low electron binding energy range (X, A).\(^{(8,12)}\) However, in contrast to the binding energy increase for the [4Fe–4S] clusters as a function of \(L'\) substitution (Figure 2), a dramatic decrease in the electron binding energy was observed for [Fe\(_2\)S\(_2\)(SEt)\(_2\)]\(^{2-}\) from 3.14 eV at \(x = 0\) to 2.79 eV at \(x = 1\). More surprisingly, an additional feature was observed in the spectra of [Fe\(_2\)S\(_2\)L\(_x\)]\(^{2-}\) (X’ in Figure 3). The ADE measured from the threshold peak (X) is 2.24 eV, a 0.55-eV decrease from that of 1. The second peak (X’) at 3.10 eV (VDE) is much stronger, and its relative intensity is very similar to the threshold feature of species 1.

**Figure 1.** (a) Schematic structures of the [2Fe–2S] clusters with different coordination geometries. (b) Schematic molecular orbital energy diagram of \(2'\) showing the difference between tri- and tetracordinate iron sites. The large arrows represent the \(d^5\) majority-spin electrons on each Fe, and the small arrows represent the minority-spin electron.

**Figure 2.** Photoelectron spectra of [Fe\(_2\)S\(_2\)(SEt)\(_2\)]\(^{2-}\) (\(n = 0–4\)) at (a) 266 and (b) 193 nm.

**Figure 3.** Photoelectron spectra of [Fe\(_2\)S\(_2\)(SEt)\(_2\)]\(^{2-}\) (\(x = 0–2\)) at (a) 266 and (b) 193 nm.
The DFT results are in good agreement with the experimental observation (Figure 3). The decrease of electron binding energies in 1 relative to 0 is a strong indication of the bidentate coordination of L’ to the ferrocene center. The observed decrease of 0.35 eV (Table S1) is consistent with the DFT result of ~0.5 eV. If L’ in 1 were monodentate, we would expect an increase of electron binding energies due to the electrostatic interactions of the polar −NH₂ group, as observed for the cubane complexes (Figure 2).¹⁷ For [Fe₂S₃L₂]⁺, two isomers (2 and 2’) are possible. 2 would result in a further decrease of the electron binding energies relative to 1 because of the electrostatic interaction of the uncoordinated −NH₂ group. In fact, both 2 and 2’ were observed in the PES experiment (Figure 3). The weak feature X is readily assigned to 2: its binding energy is lower than that of 0 by 0.9 eV, in very good agreement with the DFT value of 0.8 eV. The stronger feature X’ is assigned to 2’: its electron binding energy is increased by 0.23 eV relative to that of 1, consistent with the expected electrostatic effect of the −NH₂ group. We note that the 0.64-eV difference in the electron binding energies between 2 and 2’ represents a pure structural effects on the electron binding energy of the [2Fe–2S] center. The intensity ratio for the peaks X and X’ (~0.11) suggested that, in our experiment, ~10% of the fission product was isomer 2 and ~90% was isomer 2’. Our DFT results suggested that 2 is slightly more stable than 2’ by ~1.2 kcal/mol. This observation apparently indicated that the formation of 2 and 2’ was kinetically controlled.

In summary, both PES experiments and DFT calculations suggest that the bidentate coordination of the [2Fe–2S] cluster results in significantly lower electron binding energies, thus increasing its reducing power as a redox center. This observation might be relevant to understanding the electronic structure of FeMoco and might suggest further insight into the role of the central atom X.

Acknowledgment. This work was funded by the National Institutes of Health (GM-63555 to L.S.W. and GM-45303 to T.I.). The experimental work was performed at the EMSL, a national user facility sponsored by the U.S. DOE’s Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, operated for the DOE by Battelle.

Supporting Information Available: Electrospray mass spectra, table of electron binding energies. These materials are available free of charge via the Internet at http://pubs.acs.org.