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Decomposition of a Mixed-Valence [2Fe-2S] Cluster to Linear Tetra-Ferric and Ferrous Clusters

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Abstract

Despite the ease of preparing di-ferric [2Fe-2S] clusters, preparing stable mixed-valence analogues remains a challenge, as these clusters have limited thermal stability. Herein we identify two decomposition products of the mixed-valence thiosalicylate-ligated [2Fe-2S] cluster, $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{3-}$ ((SArCOO)²⁻ = thiosalicylate).

Keywords

iron; sulfur; clusters

1. Introduction

Iron-sulfur ([Fe-S]) clusters are ubiquitous electron-transfer (ET) co-factors, and are essential components of several metalloenzymes that facilitate multi- e^- /multi- H^+ transformations [1, 2]. Over the years, many synthetic analogues have been prepared that mimic the rich cluster composition and redox-states that are found in their natural counterparts [3]. For example, thiolate ligated synthetic clusters of the type $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-/3-}$ (R = alkyl or aryl) that mimic the $[\text{Fe}_4\text{S}_4(\text{Cys})_4]^{2-/3-}$ redox states found in ferredoxins can be readily prepared. Use of bulky thiolate ligands allows for the isolation of synthetic analogues that mimic the $[\text{Fe}_4\text{S}_4(\text{Cys})_4]^{-2-}$ redox states of high-potential proteins, as first shown by Michelle Millar in the $[\text{Fe}_4\text{S}_4(\text{S}-2,4,6\text{-}i\text{Pr}_3\text{C}_6\text{H}_2)_4]^{-2-}$ cluster system [4]. In the absence of steric bulk, the oxidized clusters undergo solvent-mediated degradation [5].

The smaller [2Fe-2S] cluster is also biologically relevant, cycling between the di-ferric and $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ mixed-valence states [1, 3]. These enzymatic clusters range in composition from all Cys-ligated ferredoxins [1], to 3 Cys/1 His-ligated mitoNEET clusters [6], to 2 Cys/2 His-ligated Rieske clusters [1]. Stable synthetic [2Fe-2S] clusters can be accessed with a variety of auxiliary ligands in the di-ferric state [3, 7–15], but the mixed-valence analogues

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[†]Dedicated to the memory of Dr. Michelle Millar, a friend, an inspiration, and a positive force for inorganic chemistry and beyond.

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have limited stabilities. For instance, mixed-valence $[\text{Fe}_2\text{S}_2\text{X}_4]^{3-}$ clusters (X = anionic ligand) readily re-arrange to the more thermodynamically stable $[\text{Fe}_4\text{S}_4\text{X}_4]^{2-}$ clusters [3]. The use of chelating ligands hinders this decomposition pathway, but clusters of the type $[\text{Fe}_2\text{S}_2(\text{XX})_2]^{3-}$ (XX = dianionic chelating ligand) also prove to be unstable [7, 9, 12]. In some instances, the redox potentials of the di-ferric/mixed-valence and mixed-valence/di-ferrous couples are close, introducing the possibility of redox disproportionation [12]. In one case, attempts to crystallize a mixed-valence cluster resulted in isolation of the di-ferric species [15]. An exception to the observed instability of mixed-valence [2Fe-2S] clusters is bis-benzimidazolate ligated clusters, which are stable both in solution and as solids [8, 12–14].

As part of our studies on proton-coupled electron transfer reactions at [Fe-S] clusters [14], we have examined Gibson's thiosalicylate-ligated [2Fe-2S] cluster system [7]. The mixed-valence congener of this system is amongst the most stable for non bis-benzimidazolate ligated [2Fe-2S] clusters. In his original report, the di-ferric cluster was characterized by optical, IR, and NMR spectroscopy, and the presence of the mixed-valence congener was indicated by electrochemistry and EPR spectroscopy. Herein we identify by X-ray crystallography (XRD) two of the decomposition products of the mixed-valence cluster. We also present additional characterization of both the di-ferric (XRD and NMR) and mixed-valence (NMR) clusters.

II. Materials and Methods

II.1. General Considerations

Unless noted, all manipulations were carried out using standard Schlenk or glove-box techniques under a dinitrogen atmosphere. Glassware was oven-dried for 24 h prior to use. Celite and molecular sieves were dried by heating to 300 °C under vacuum for 24 h. Unless otherwise noted, solvents were deoxygenated and dried by sparging with Ar followed by passage through Grubbs-style columns filled with activated alumina. Acetonitrile was purchased from Burdick and Jackson® (< 5ppm low-water brand) and stored in an Ar pressurized stainless steel drum plumbed directly into a glove-box. Dimethylformamide was degassed and dried over activated 3 Å molecular sieves. Nonhalogenated solvents were tested with a standard purple solution of benzophenone ketyl in THF to confirm effective oxygen and moisture removal, and all glove-box solvents were stored over activated 3 Å molecular sieves. Deuterated solvents were purchased from Cambridge Isotopes Laboratories, Inc. and were degassed and stored over activated 3 Å molecular sieves prior to use. d_3 -MeCN was dried over CaH_2 and vac-transferred prior to storage over sieves. NMR spectra were collected on Bruker 500 MHz spectrometers and MestReNova (6.2.1) was used for NMR data workup. The ^1H chemical shifts are from the peak fitting, and are referenced to residual solvent.

II.2. Synthesis and characterization of clusters

Reagents, including thiosalicylic acid, were purchased from Aldrich and used without further purification. Sodium thiosalicylate was prepared by treatment of thiosalicylic acid with 2 equiv of sodium hydride, as described by Gibson [7]. $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2](\text{Et}_4\text{N})_2$ was prepared as described by Gibson, and $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2](\text{PPN})_2$ was prepared analogously, by treatment of 2 equiv Na_2SArCOO (generated *in situ* from thiosalicylic acid and 2 equiv sodium hydride) with $[\text{Fe}_2\text{S}_2\text{Cl}_4](\text{PPN})_2$ [7].

NMR characterization of $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2](\text{PPN})_2$ — ^1H NMR (d_3 -MeCN, 500 MHz, 25 °C): δ 10.51 (s, ArH, 1H), 10.44 (s, ArH, 1H), 9.97 (s, ArH, 1H), 9.95 (s, ArH, 1H), 7.42

– 7.71 (m, PPN⁺, 60H), 4.68 (s, ArH, 1H), 4.58 (s, ArH, 1H), 4.01 (s, ArH, 1H), 4.04 (s, ArH, 1H).

Reduction of [Fe₂S₂(SArCOO)₂](Et₄N)₂—A solution of CoCp^{*}₂ (6.7 mg, 0.020 mmol) in 3 mL MeCN was added dropwise to a stirring solution of [Fe₂S₂(SArCOO)₂](PPN)₂ (15.0 mg, 0.020 mmol) in 3 mL acetone. The solution immediately changed color from purple to red. The volatiles were removed after stirring for 2.5 h, and the resulting dark solids were triturated with pentane and Et₂O. The solids were then taken up in minimal acetonitrile and filtered through glass fibers. Slow vapor diffusion of Et₂O into this solution afforded yellow and dark orange crystals over the course of several days, as well as insoluble black solids. The crystals were then selectively removed with a spatula and suspended in Paratone oil prior to mounting onto the diffractometer. NMR studies of the mixed-valence species were performed by *in situ* reduction of [Fe₂S₂(SArCOO)₂](PPN)₂ or [Fe₂S₂(SArCOO)₂](Et₄N)₂ with CoCp^{*}₂ in *d*₃-MeCN. ¹H NMR data for [Fe₂S₂(SArCOO)₂][CoCp^{*}₂](PPN)₂ (*d*₃-MeCN, 500 MHz, 25 °C): δ 11.08 (s, ArH, 2H), 10.94 (s, ArH, 2H), 7.42 – 7.71 (m, PPN⁺, 60H), 4.87 (s, ArH, 2H), 3.08 (s, ArH, 2H), 1.66 (s, Cp^{*}H, 30H). Over the course of days, these resonances decay and the following grow in (*d*₃-MeCN, 500 MHz, 25 °C, integrals are relative to one another at *t* ≈ 98 h): δ 41.6 (s, 1H), 25.5 (s, 1H), 14.0 (bs, 0.2H), 13.7 (bs, 0.2H), –0.8 (bs, 0.2H), –11.2 (s, 1H), –13.0 (s, 1H).

II.3. X-ray Crystallography

Low-temperature diffraction data were collected on a Bruker APEXII single crystal diffractometer coupled to a Bruker APEXII CCD detector with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å), performing ϕ - and ω -scans. The structures were solved by direct or Patterson methods using SHELXS [16] and refined against *F*² on all data by full-matrix least squares with SHELXL-97 [17]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). The structures were refined using established methods [18].

No disorder was present in the crystals of [Fe₂S₂(SArCOO)₂](PPN)₂, allowing for refinement of the solution with no restraints.

Crystals of [Fe₄S₆(SArCOO)₂](Et₄N)₄ suffered from disorder in both the (Et₄N)⁺ cations and the (SArCOO)^{2–} ligands. One of the (Et₄N)⁺ of the asymmetric unit is disordered over two positions, and was refined with the use of a free variable (61:39 major:minor). The asymmetric unit also contains two disordered half molecules of (Et₄N)⁺. This disorder was treated by using the “PART -1” command. Additionally, the SAME restraint was employed to render the (Et₄N)⁺ cations equivalent. In some instances, restraints on the anisotropic thermal parameters were used on the disordered cations. The carboxylate and thiolate of the (SArCOO)^{2–} were compositionally disordered, which was treated with the use of another free variable. This treatment would suggest that only the *trans* isomer is present in the crystalline lattice. The crystal was not of sufficient quality to determine if both the *cis* and *trans* isomers are present by further modeling of the disorder.

Crystals of [Fe(SArCOO)₂][CoCp^{*}₂]₂ suffered from two-site disorder in one of the [CoCp^{*}₂]⁺ cations. It was found that each site was equally populated, so no free variables were required to refine the disorder. The disorder required extensive positional and thermal restraints within the cation to ensure refinement convergence.

III. Results and Discussion

III.1 Additional Characterization of $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{2-}$

Salt metathesis of 2 equiv sodium thiosalicylate with either $[\text{Fe}_2\text{S}_2\text{Cl}_4](\text{Et}_4\text{N})_2$ or $[\text{Fe}_2\text{S}_2\text{Cl}_4](\text{PPN})_2$ readily affords the di-ferric cluster, $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{2-}$ ($(\text{SArCOO})^{2-} =$ thiosalicylate) [7]. This cluster was originally reported by Gibson, as both tetraethylammonium and tetraphenylarsonium salts, though no solid-state structure was obtained. In our hands, attempts to grow crystals of $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2](\text{Et}_4\text{N})_2$ from DMF/ Et_2O or MeCN/ Et_2O mixtures resulted in microcrystalline solids. As a means to enhance crystallinity, we prepared the bis(triphenylphosphine)iminium (PPN) salt of $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{2-}$. Upon layering of Et_2O onto a saturated DMF solution of the PPN salt, large purple crystals suitable for XRD can be grown. The solid-state structure of $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2](\text{PPN})_2$ has been determined, and a thermal-ellipsoid rendition of the anion is shown in Figure 1. A crystallographic inversion center renders the two iron atoms equivalent. The metrical parameters about the Fe_2S_2 core are as expected (Table 1), based on structures of other di-ferric $[2\text{Fe}-2\text{S}]$ clusters [3, 9, 13–15][19][20]. For instance, the Fe–Fe distance is 2.665(1) Å, and the average Fe– $\text{S}_{\text{sulfide}}$ is 2.196(2) Å. The cluster has inversion symmetry, which requires that the thiosalicylate ligands be oriented *trans* to one another. The Fe– S_{SArCOO} distance of 2.278(1) Å is short relative to other Fe– $\text{S}_{\text{thiolate}}$ bond distances in thiolate-ligated $[2\text{Fe}-2\text{S}]$ clusters [20][21]. Of the 18 structures for thiolate-ligated $[2\text{Fe}-2\text{S}]$ structures in the Cambridge Structural Database [20][22], only $\{\text{Fe}(\text{ox-phS})\}_2(\mu\text{-S})_2$ ($(\text{ox-phS})^- = 2\text{-(4',4'-dimethyloxazolin-2'-yl)thiophenolate}$) has a shorter Fe–S distance, being 2.2611(9) Å [23]. The Fe– O_{SArCOO} distance of 1.956(2) Å is longer than that of other O-ligated $[2\text{Fe}-2\text{S}]$ clusters; the latter clusters are coordinated by phenoxide ligands, and hence this is anticipated [24, 25].

The ^1H NMR spectrum of a single crystal of $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2](\text{PPN})_2$ dissolved in d_3 -MeCN is shown in Figure 2. The spectrum shows four pairs of contact-shifted resonances for the aryl protons, which are centered at 10.48, 9.96, 4.63, and 4.03 ppm. The presence of a pair of peaks for each aryl resonance suggests the presence of both *cis* and *trans* isomers in solution. Spectral fitting of the pairs of peaks indicates that the two components are of approximate equal intensity, and hence that the two isomers are *ca.* equimolar in solution. Though Gibson did not observe pairs of peaks for each aryl resonance, the chemical shifts reported for $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2](\text{Et}_4\text{N})_2$ in d_6 -DMSO are similar to those noted above [7]. Given that the resonances are broad and that the splitting in the pairs of peaks is small, it is likely that the two isomers are only resolved with high-field spectrometers. As noted by Gibson, the isotropic shifts for the aryl protons are dominated by contact interactions through the thiolate. Thus, the relatively broad resonances centered at 4.63 and 10.48 ppm correspond to the protons *ortho* to the thiolate and carboxylate, respectively, and the resonances at 9.96 and 4.03 ppm correspond to the protons *meta* to the thiolate and carboxylate, respectively [7]. The difference in chemical shifts between the *cis* and *trans* isomers is larger for the aryl protons that are *ortho* to the thiolate and carboxylate (0.10 and 0.07 ppm, respectively) than the aryl protons that are *meta* to the thiolate and carboxylate (0.03 and 0.02 ppm, respectively). The breadth of the contact-shifted aryl proton resonances (16 – 15.4 Hz) does not allow for any H,H coupling to be observed.

III.2 Characterization and Decomposition of $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{3-}$

Chemical reduction of $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{2-}$ with 1 equiv CoCp^*_2 results in a rapid color change from purple to red and formation of the mixed-valence congener, $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{3-}$. The use of decamethylcobaltocene as a chemical reductant ensures that over-reduction to the di-ferrous cluster does not occur [7, 26]. Despite being $S = 1/2$, the ^1H NMR spectrum (d_3 -MeCN) of this species shows four relatively sharp resonances

between 3 and 11.1 ppm (Figure 2), which correspond to the four aryl protons. Integration of these resonances to that of $[\text{CoCp}^*_2]^+$ indicates two ligands per equivalent of decamethylcobaltocenium. Unlike the spectrum of di-ferric $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{2-}$, each resonance appears to be a single peak. This indicates that either only one isomer is present in solution or that isomerization between the *cis* and *trans* isomers is fast on the NMR time-scale.

On the time-scale of minutes, the one electron reduction of $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{2-}$ to $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{3-}$ is reversible. Thus, addition of 1 equiv of ferrocenium to $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{3-}$ (generated *in situ* from $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{2-}$ and CoCp^*_2), causes a color change from red to purple and the cluster is quantitatively oxidized to its di-ferric form, as ascertained by ^1H NMR spectroscopy. However, solutions of $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{3-}$ gradually decompose: red solutions of $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{3-}$ darken and black solids precipitate. Whereas Gibson reports a $t_{1/2}$ of 30 min in DMF [7], 3 mM d_3 -MeCN solutions of $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{3-}$ (prepared *in situ* from $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{2-}$ and CoCp^*_2), decay with a crude $t_{1/2}$ of 24 h, with *ca.* 15 % $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{3-}$ remaining after 98 h (from the integration of aryl proton resonances relative to residual solvent peaks in ^1H NMR spectra). Concomitant with this decay is the growth of two sets of paramagnetically shifted resonances in the ^1H NMR spectrum. The new species are present in a ratio of *ca.* 5 to 1 at both $t = 24$ and 98 h. The major species has relatively sharp resonances of equal intensity at 41.6, 25.5, -11.2, and -13.0 ppm. Broad peaks that integrate 1:1:1 centered at 14.0, 13.7, and -0.8 ppm are associated with the minor species. Of note, during the course of decomposition, resonances associated with mixed-valence $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{3-}$ do not shift, nor do peaks that correspond to $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{2-}$ grow in, implying that the di-ferric congener does not form. At $t = 24$ and 98 h, no other resonances are observed.

Attempts to grow crystals of $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2][\text{CoCp}^*_2](\text{Et}_4\text{N})_2$ by layering Et_2O onto a saturated MeCN solution containing the mixed-valence cluster did not give the desired crystals. Rather, over the course of several days, yellow and dark orange crystals were obtained, in addition to dark, non-crystalline solids. ^1H NMR analysis (d_3 -MeCN) of the bulk solids indicates that the only soluble species present are the two decomposition products identified above. The pale yellow mother liquor of crystallization contains the major decomposition product identified above, as well as one or more diamagnetic products; in the ^1H NMR spectrum of the mother liquor, the region between 6.7 and 8.1 ppm is comprised of at least eight ill-defined multiplets.

The two types of crystal present were of sufficient quality for diffraction, and the solid-state structures of these two decomposition products have been obtained. Thermal ellipsoid renditions of the iron-containing anions are shown in Figure 3.

XRD analysis of the dark orange crystals revealed a tetrahedral bis-thiosalicylate ligated iron(II) complex, $[\text{Fe}(\text{SArCOO})_2][\text{CoCp}^*_2]_2$ (Figure 3 and Table 2). Though this species is not known in the literature, the related 5-coordinate ferric $[\text{Fe}(\text{SArCOO})_2(2\text{-Me-Im})](\text{Et}_3\text{NH})$ has been reported [27].

The second decomposition product is a linear tetra-ferric cluster, $[\text{Fe}_4\text{S}_6(\text{SArCOO})_2](\text{Et}_4\text{N})_4$ (Figure 3 and Table 3). This species crystallizes in the $P2(1)/n$ monoclinic space group, with half of the tetramer present in the asymmetric unit; a crystallographic inversion center relates the two halves of the tetramer. The carboxylate and thiolate of the $(\text{SArCOO})^{2-}$ ligand are compositionally disordered, modeled as a 56/44 ratio of the carboxylate lying on the same side of the Fe1-S2-Fe2 plane as S4 or S4'.

Tetra-ferric $[\text{Fe}_4\text{S}_6(\text{SArCOO})_2](\text{Et}_4\text{N})_4$ is a rare example of a linear $[4\text{Fe-6S}]$ cluster. To our knowledge, there is only one other linear cluster of this type that has been

crystallographically characterized: the thiolate ligated $[\text{Fe}_4\text{S}_6(\text{SEt})_4]^{4-}$, reported by Coucouvanis twenty years ago [28]. Clusters of this type can be regarded as a central $[\text{Fe}_2\text{S}_6]^{6-}$ that is capped by two $[\text{FeX}_2]^+$ subunits. As for $[\text{Fe}_4\text{S}_6(\text{SEt})_4]^{4-}$, the bonding within the terminal Fe_2S_2 core of $[\text{Fe}_4\text{S}_6(\text{SArCOO})_2]^{4-}$ is asymmetric, with the Fe1-S2/S3 distances (2.167(2)/2.168(2) Å) being shorter than the Fe2-S2/S3 distances (2.243(2)/2.246(2) Å). The central Fe_2S_2 core is more symmetric, with the Fe2-S4 and Fe2-S4' distances being 2.226(2) and 2.205(2) Å, respectively. The longer Fe-S bonds in the central Fe_2S_2 unit results in an Fe2-Fe2' distance of 2.723(2) Å that is slightly longer than the Fe1-Fe2 distance of 2.719(1) Å. Overall, the metrical parameters are similar for $[\text{Fe}_4\text{S}_6(\text{SArCOO})_2]^{4-}$ and $[\text{Fe}_4\text{S}_6(\text{SEt})_4]^{4-}$, though the Fe-Fe and Fe-S distances are ca. 0.01 – 0.02 shorter in $[\text{Fe}_4\text{S}_6(\text{SArCOO})_2]^{4-}$.

The mechanism for the decomposition of $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{3-}$ is not evident from the data available. As noted in the introduction, mixed-valence clusters of the type $[\text{Fe}_2\text{S}_2\text{X}_4]^{3-}$ readily re-arrange to the more thermodynamically stable $[\text{Fe}_4\text{S}_4\text{X}_4]^{2-}$ clusters [3]. This degradation is impeded by use of chelating ligands, but clusters of the type $[\text{Fe}_2\text{S}_2(\text{XX})_2]^{3-}$ are also thermally unstable. Gibson noted that the stability of $[\text{Fe}_2\text{S}_2(\text{XX})_2]^{3-}$ crudely tracks with the separation between the di-ferric/mixed-valence and mixed-valence/di-ferrous couples [12]. He suggested that mixed-valence clusters may decompose via disproportionation, with the instability of the di-ferrous cluster driving the disproportionation and hence decomposition [12]. Indeed, in an attempt to crystallize a bis-thiolate ligated mixed-valence $[2\text{Fe}-2\text{S}]$ cluster, Meyer and coworkers accidentally isolated the di-ferric cluster [15]. It is therefore unusual that di-ferric $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{2-}$ is not present in any detectable amounts during the decomposition of the mixed-valence species. This suggests that if the decomposition of $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{3-}$ is initiated by disproportionation, the resulting di-ferric cluster is not stable in the presence of the more reduced clusters or their degradation products. Of note, no intermediates to the formation of $[\text{Fe}_4\text{S}_6(\text{SArCOO})_2]^{4-}$ and $[\text{Fe}(\text{SArCOO})_2]^{2-}$ are observed by ^1H NMR spectroscopy.

The mechanism for the formation of $[\text{Fe}_4\text{S}_6(\text{SArCOO})_2]^{4-}$ is likely complex. The related thiolate cluster $[\text{Fe}_4\text{S}_6(\text{SEt})_4]^{4-}$ can be prepared in 30 % yield by treatment of $[\text{Fe}(\text{SEt})_4]^{2-}$ with elemental sulfur (4:6) [28]. However, the solutions of $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{3-}$ are strongly reducing, making it unlikely that there is an oxidizing sulfur atom source to react with $[\text{Fe}(\text{SArCOO})_2]^{2-}$. This is especially unlikely since similar relative amounts of $[\text{Fe}_4\text{S}_6(\text{SArCOO})_2]^{4-}$ and $[\text{Fe}(\text{SArCOO})_2]^{2-}$ are present during the decomposition of $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{3-}$. Similar issues argue against the alternative suggestion that the tetra-ferric clusters result from oxidative coupling of two di-ferric clusters with elemental sulfur [28]. Such a mechanism would require disproportionation of $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{3-}$ to provide low concentrations of the di-ferric cluster.

IV. Conclusions

The di-ferric $[2\text{Fe}-2\text{S}]$ thiosalicylate cluster $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{2-}$ is indicated by NMR spectroscopy to exist in solution as a mixture of the *cis* and *trans* isomers. The solid-state structure of di-ferric $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{2-}$, however, has a *trans* (centrosymmetric) structure. The mixed-valence species decomposes at room temperature, as previously reported [7]. Two products of the decomposition have been crystallographically characterized: ferrous $[\text{Fe}(\text{SArCOO})_2]^{2-}$ and tetra-ferric $[\text{Fe}_4\text{S}_6(\text{SArCOO})_2]^{4-}$. To our knowledge, this is the first report identifying the decomposition products of a mixed-valence $[2\text{Fe}-2\text{S}]$ clusters that are ligated by chelating ligands.

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Appendix A. Supplementary Data

CCDC 889319 contains the supplementary crystallographic data for $[\text{Fe}_2\text{S}_2(\text{SARCOO})_2](\text{PPN})_2$, CCDC 889317 contains the supplementary crystallographic data for $[\text{Fe}(\text{SARCOO})_2][\text{CoCp}^*_2]_2$, and CCDC 889318 contains the supplementary crystallographic data for $[\text{Fe}_4\text{S}_6(\text{SARCOO})_2](\text{Et}_4\text{N})_4$. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Figure 1. Thermal ellipsoid rendition (50 %) of the dianion of $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2](\text{PPN})_2$. Hydrogen atoms have been removed for clarity.

Figure 2.

^1H NMR spectra (d_3 -MeCN) of (top): $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{2-}$ (experimental: black; fit: red) and (bottom): $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{3-}$. Chemical shifts for $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2]^{2-}$ (from peak fitting; all peaks of equal intensity): 10.51, 10.44, 9.97, 9.95, 4.68, 4.58, 4.01, 4.04.

Figure 3. Thermal ellipsoid renditions (50 %) of the dianion of $[\text{Fe}(\text{SArCOO})_2][\text{CoCp}^*_2]$ (top) and the tetranion of $[\text{Fe}_4\text{S}_6(\text{SArCOO})_2](\text{Et}_4\text{N})_4$ (bottom). Hydrogen atoms have been removed for clarity. Both components of the disordered $(\text{SArCOO})^{2-}$ ligand of $[\text{Fe}_4\text{S}_6(\text{SArCOO})_2]^{4-}$ are shown, with the bonds and ellipsoids of the minor component (45%) being more faint.

Table 1Select bond distances and angles for the dianion of $[\text{Fe}_2\text{S}_2(\text{SArCOO})_2](\text{PPN})_2$.

Distance / Å		Angle / °	
Fe1-Fe1'	2.6643(10)	Fe1-S1-Fe1'	52.73(3)
Fe1-S1	2.1937(10)	Fe1-S1'-Fe1'	52.58(3)
Fe1-S1'	2.1983(10)	S1-Fe1-S1	105.31(3)
Fe1-S2	2.2779(10)		
Fe1-O2	1.9558(24)		

Table 2Select bond distances and angles for the dianion of $[\text{Fe}(\text{SArCOO})_2][\text{CoCp}^*_2]$.

Distance / Å		Angle / °	
Fe1-O1	1.953(7)	O1-Fe1-O3	113.7(3)
Fe1-O3	1.951(7)	S1-Fe1-S2	111.3(1)
Fe1-S1	2.317(3)	O1-Fe1-S2	125.2(3)
Fe1-S2	2.311(3)	O3-Fe1-S1	124.7(3)
		O1-Fe1-S1	92.3(2)
		O3-Fe1-S2	92.8(2)

Table 3Select bond distances and angles for the tetraanion of $[\text{Fe}_4\text{S}_6(\text{SArCOO})_2](\text{Et}_4\text{N})_4$.

	Distance / Å		Angle / °
Fe1-O2	1.958(20)	Fe1-S2-Fe2	76.14(6)
Fe1-O4	1.966(15)	Fe1-S3-Fe2	76.05(5)
Fe1-S1	1.168(5)	S2-Fe1-S3	106.47(7)
Fe1-S5	2.26(1)	S2-Fe2-S3	101.34(6)
Fe1-S2	2.167(2)	Fe2-S4-Fe2'	75.85(5)
Fe1-S3	2.168(2)	S4-Fe2-S4'	104.15(5)
Fe2-S2	2.243(2)	Fe1-Fe2-Fe2'	178.73(5)
Fe2-S3	2.246(2)		
Fe2-S4	2.226(2)		
Fe2-S4'	2.205(2)		
Fe1-Fe2	2.719(1)		
Fe2-Fe2'	2.723(2)		