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A three-coordinate Fe(μ) center within a [3Fe-(μ_3 -S)] cluster that provides an accessible coordination site[†]

Yousoon Lee,^a Khalil A. Abboud,^a Ricardo García-Serres^b and Leslie J. Murray*^a

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A μ_3 -sulfide bridged triiron cluster(II,II,III) supported by a cyclophane ligand undergoes metal-based reduction to yield an all-ferrous species. The latter complex incorporates a three-coordinate iron center that provides an accessible coordination site to a solvent molecule.

Iron-sulfur clusters are ubiquitous in biological systems and are integral components in electron transfer pathways and as reaction centers.¹ As reaction centers, iron-sulfur clusters typically employ a sub-site differentiated [4Fe-4S] cluster, in which a unique Fe atom is ligated by three S^{2-} donors with a fourth accessible site for substrate binding. In the broader context, other sulfide-bridged iron clusters have been identified as reaction centers, such as HvdG which assembles an $Fe(CO)_2(CN)$ fragment that is bridged by a sulfide to a proximal 4Fe-4S cluster.² The iron-molybdenum cofactor (FeMoco) - the reaction center for dinitrogen reduction in the molybdenum-dependent nitrogenases - is proposed to bind N₂ at one or more coordinatively unsaturated Fe atoms, which are each held within a pseudo-trigonal pyramidal geometry arising from a $(\mu_3-S)_2(\mu_2-S)(\mu_6-C)$ donor set.³ Synthetic sub-site differentiated 4Fe-4S clusters have been reported by Holm (Scheme 1A) and Tatsumi.^{4,5} However, most of these systems serve as structural models for substrate-bound forms of FeS active sites and only a few demonstrate reactivity. Noticeably, the cuboidal arrangement remains the predominant form for clusters with three or more Fe atoms. Previously, we reported a planar 3Fe-3S cluster (Fe₃S₃L) in which the cyclophane ligand likely enforces the planar and alternating arrangement of the iron and sulfur atoms (Scheme 1B).⁶ This cluster, however, lacked accessible coordination sites for substrate binding. Herein, we report a (μ_3 -sulfido)triiron(π,π,π) complex, Fe₃Br₂SL (2),‡

^b Univ. Grenoble Alpes, LCBM/PMB and CEA, IRTSV/CBM/PMB and CNRS,





Scheme 2 Synthesis of 2 and 3.

which can be chemically reduced to the all-ferrous complex $Fe_3(\mu$ -Br)(μ_3 -S)L, 3 (Scheme 2).

Addition of one equivalent of NaSCPh₃ to Fe₃Br₃L (1)⁷ in THF at -34 °C results in an immediate color change from red to dark green to afford Fe₃Br₂SL (2) in a reasonable yield (47%, Scheme 2). In the single-crystal structure of 2 (Fig. 1), a sulfide ligand occupies the central void of the cyclophane and bridges the three iron ions. Each iron center is held in a pseudo-trigonal pyramidal geometry (τ_4 values = 0.80–0.93⁸) by an N₂BrS donor set. To our knowledge and from a search of the Cambridge Structure Database (according to CSD V5.36), 2 represented a

^a University of Florida, Department of Chemistry, Center for Catalysis, Gainesville, FL 32611-7200, USA. E-mail: murray@chem.ufl.edu; Tel: +1-352-392-0564

LCBM UMR 5249, PMB, 38000 Grenoble, France. E-mail: ricardo.garcia@cea.fr † Electronic supplementary information (ESI) available: Full experimental procedures, spectroscopic data, cyclic voltammetry, differential pulse voltammetry, and crystallographic data. CCDC 1483321 and 1483322. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc04671a



Fig. 1 Single crystal structure of **2** (left) and **3** (right) at 65% thermal ellipsoids with co-crystallized THF molecules and hydrogen atoms omitted for clarity. C, N, S, Br and Fe atoms are depicted as grey, blue, yellow, pink and orange ellipsoids. The occupancy ratio of disordered Fe3: Fe3' is 1:1, and the coordinated THF solvent molecule is present with 50% occupancy.

unique polyiron complex featuring a μ_3 -S²⁻ in a planar 3Fe–S cluster. We have previously published a similar tricopper complex, Cu₃(μ_3 -S)L,⁹ and examples of self-assembled Ru, Y, and Yb tri- or tetramers have also been reported.¹⁰ All of the reported synthetic or biological polynuclear iron clusters containing a μ_3 -sulfide donor are either cuboidal or cubane-type with the sulfide situated out-of-plane of the three iron centers. These clusters typically have longer Fe–(μ_3 -S) distances than 2; the representative examples are Fe^{II}–(μ_3 -S) bonds of 2.291(1)–2.370(1) Å from all-ferrous synthetic [3Fe–4S] or [4Fe–4S] clusters¹¹ and Fe^{III}–(μ_3 -S) bonds of 2.254(2)–2.32(4) Å from all-ferric [4Fe–4S] clusters including an oxidized *Desulfovibrio gigas* ferredoxin II.¹² The differences are expected given the distinct donor set for this complex as compared to the [4Fe–4S] and [3Fe–4S] clusters.

The structure of 2 is consistent with a valence localized cluster. Specifically, the µ3-sulfide to Fe1 and Fe2 bonds are 2.2918(8) and 2.2915(8) Å, respectively, whereas the Fe3-S bond is shorter by ~ 0.1 Å (2.1722(8) Å). The Fe3-S bond in 2 is comparable in length to the Fe^{III}-S bonds of 2.1827(8), 2.1911(8) Å in Fe₃S₃L.⁶ Based on the difference in bond distances, we assign Fe3 as a ferric ion and Fe1 and Fe2 as ferrous (vide infra). The different oxidation states of metal centers also relate to $Fe-N_L$ distances (where N_L = nacnac N-donor atom) and bite angles (*i.e.*, $\angle N_L$ -Fe- N_L); higher oxidation states typically results in shorter Fe-N_L bonds and larger nacnac bite angles. Indeed, the Fe1/Fe2-N_L bonds are slightly longer than those of Fe3-N_L (2.001(2)-2.011(2) Å for Fe1, Fe2 $\nu s.$ 1.992(2), 1.994(2) for Fe3). The nacnac bite angles, however, do not correlate with this trend (*viz.*, $101.1(1)^{\circ}$, $96.1(1)^{\circ}$, and $96.8(1)^{\circ}$ for Fe1, Fe2, and Fe3, respectively), which we suggest arises from Fe3 lying out of the NCCCN plane of the nacnac backbone (Table S1, ESI[†]). We note that the cyclophane ligand appears to be more distorted in the 2 than in 1.⁷ This increased distortion is evidenced by the larger dihedral angle between the two arene rings in 2 (8.3°) than previously reported for 1 (5.4°) or for our prior complexes in which these arene rings preferentially adopt a coplanar arrangement.^{6,9,13} Although both 1 and 2 contain a comparable $[Fe_3(\mu_3-X)Y_2]^{3+}$ (X = Br or S, Y = Br) core, the higher oxidation state of one iron center and the smaller size of the



Fig. 2 80 K, zero-field Mössbauer spectra of **2** (top) and **3** (bottom). The black solid lines overlaid with the experimental points are theoretical simulations. The coloured lines are their component quadrupole doublets with the simulation parameters reported in Table 1.

Table 1 Simulations parameters for quadrupole doublets in the Mössbauer spectra of 2 and 3 recorded at 80 K. Negative values for Γ (FWHH) indicate a pseudo-Voigt shape

Complex	Doublet	$\delta \text{ (mm s}^{-1}\text{)}$	$\Delta E_{\rm Q} \ ({\rm mm} \ {\rm s}^{-1})$	$\Gamma \text{ (mm s}^{-1}\text{)}$	Ratio
2	2a (blue)	0.87	1.74	0.40	2
	2 b (red)	0.31	0.94	0.34	1
3	3a (blue)	0.81	2.45	-0.35/-0.25	1
	3b (green)	0.71	1.37	0.42/0.35	1
	3c (purple)	0.73	0.75	0.40/0.42	1

 μ_3 -sulfide in 2 (*cf.* bromide in 1) results in shorter metal–(μ_3 -X) distances, which consequently positions the two remaining bromides – especially the terminal one – in closer proximity to the methylene groups of the Et substituents on the ligand.⁷ We have previously proposed that such steric effects dominate the structural preferences in these compounds.

Mössbauer spectra collected on powder samples of 2 at 80 K confirm our valence-localized assignment. The spectra are well simulated using two symmetric quadrupole doublets in a 2:1 ratio (Fig. 2). The less intense doublet ($\delta = 0.31$ and $\Delta E_Q = 0.94$ mm s⁻¹) is assigned to an Fe(m), whereas the more intense doublet ($\delta = 0.87$ mm s⁻¹ and $\Delta E_Q = 1.74$ mm s⁻¹) is assigned to two equivalent Fe(n) centers. These data are consistent with the solid-state structure, as Fe1 and Fe2 are in similar environments and bond lengths indicate that these are iron(n) cations. The isomer shifts are also consistent with four-coordinate, high-spin iron(m,n) centers in mixed N₂S₂ environment.¹⁴

Next, we sought to investigate the redox properties and reactivity of **2**. Specifically, we were interested in accessing a compound with open coordination site on one or more Fe atoms upon loss of one or both halide donors. The redox behavior of **2** was assessed by cyclic voltammetry. The CV data displayed one reversible and one irreversible reductive wave at $E_{\frac{1}{2}(1)} = -0.42$ V and $E_{\frac{1}{2}(2)} =$ -0.98 V, respectively, referenced to Fc/Fc⁺ (Fig. S1, ESI⁺). The reversibility was validated using differential pulse voltammetry: a symmetric peak with FWHM ~97 mV at $E_{p(1)} = -0.41$ V followed by multiple asymmetric features (Fig. S2, ESI⁺). This first reversible event is assigned to iron-based reduction (*vide infra*). The redox behavior of 2 in electrochemistry contrasts the irreversible redox events in the CV of **1**.⁷ In particular, the second reductive event at -0.98 V correlates to the predicted reduction of the all-iron(n) congener of **2**. This result likely arises from the greater delocalization afforded by the more covalent Fe–S bonds in **2** as compared to the Fe–Br bonds in **1**.

Based on the reduction potentials observed in the electrochemical experiments, we then treated 2 with two equiv. of Na/Hg amalgam (0.5 wt% Na) in THF at -34 °C. Subsequently, diffusion of hexanes to a THF solution of the crude reduction product yielded red-brown crystals of 3 in 52% yield (Scheme 2). The single-crystal X-ray analysis revealed that only the terminal bromide ligand was absent upon reduction; the µ-bromide is retained and coordinated between Fe1 and Fe2 (Fig. 1). This result was initially unexpected insofar as Na/Hg should be sufficiently reducing to access the second redox event observed at -0.98 V vs. Fc/Fc⁺. Loss of the terminal bromide after the first reduction of 2 could result in structural changes that shift the second potential to more negative values. In contrast, a reaction of 2 with 1 equiv. of KC₈ under an N₂ atmosphere reproduced 3 but, unfortunately, the analogous reactions with 2 or 3 equiv. KC8 afforded neither single-crystals suitable for X-ray analysis nor products with new IR absorptions. The iron center that was coordinated to the terminal bromide in 2 is disordered over two sites in an approximately 1:1 ratio in the structure of 3; one site (Fe3) is four-coordinate with a THF solvent molecule, and the other (Fe3') is three-coordinate with an N₂S donor group. The product, therefore, was assigned the formula Fe₃BrSL·0.5THF (3), which agrees with combustion analysis data.

Each iron center in 3 (except for Fe3') has a pseudo-trigonal pyramidal geometry ($\tau_4 = 0.82-0.89$), which is analogous to the ferrous Fe1 and Fe2 centers ($\tau_4 = 0.80, 0.84$) in 2. The most noticeable structural variation in 3 as compared to 2 is that the bond between the four-coordinate Fe3 and the μ_3 -S is significantly elongated to 2.238(1) Å vs. 2.1722(8) Å for the analogous Fe3– $(\mu_3$ -S) in 2. Additionally, Fe3– N_L bonds became slightly longer than those in 2 (viz. 2.002(2), 2.012(2) Å for 3 vs. 1.992(2), 1.994(2) Å for 2) and comparable to those for the Fe1/Fe2- N_L bonds (2.002(2)-2.013(2) Å) in 3. The longer bonds around Fe3 support a decrease in the oxidation state of this iron center in 3, and agree with our earlier assignment of the first reduction of 2 as metal-based. The three-coordinate Fe3' adopts a trigonalplanar coordination geometry with sum of angles = 358.8° . Fe3' is coplanar with the NCCCN backbone of the nacnac arm to which it is coordinated in comparison with Fe3. The Fe3'-N_L bond distances (1.975(2), 1.979(2) Å), the large nacnac bite angle $(100.33(8)^{\circ})$, and shorter Fe3'-S bond (2.1148(9) Å) than Fe3-S are expected given the lower coordination number of Fe3'. However, the three coordinate Fe3' center bears strong

resemblance with the iron atoms in the reported (μ -sulfido)bis(β -diketiminatoiron(π)) complex;¹⁵ yet, the Fe–S distances we observe here are shorter, and the Fe \cdots Fe distances in 2 and 3 are longer than in that diiron compound. We surmise that the cyclophane ligand imposes steric constraints on the 3Fe–S cluster, which are relaxed in the self-assembled diiron system.

Mössbauer spectra of 3 support our assignment of the reduction as metal centered. The 80 K Mössbauer spectrum of 3 reveals multiple doublets, consistent with the X-ray structure, which contains six different Fe crystallographic sites in similar relative proportions. However, the environments of crystallographic sites Fe1 and Fe2 are very similar, both with each other, and between the two complexes (with or without a THF molecule). This similarity in their coordination spheres is expected to result in overlapping absorptions with comparable parameters for these spectral components. In order to avoid over-parameterization, the number of doublets used in the simulation was reduced to only three asymmetric, nested doublets in equal proportions, which afforded a good fit to the data. The pairing of the peaks was determined by monitoring the Mössbauer parameters at various temperatures, ranging from 4.2 K to 200 K. The fitted isomer shift values range from 0.71 to 0.81 mm s⁻¹, consistent with our previously reported Fe(n) complexes with the same ligand. It is noteworthy that the four spectral components attributable to Fe1 and Fe2 in the two forms of 3 (i.e., Fe1 and Fe2 in the structures with or without THF), which account for 2/3 of the total iron in the sample, cannot be simulated with a single quadrupole doublet. Unlike the equivalent Fe1 and Fe2 ferrous sites observed in Mössbauer spectra of 2, Fe1 and Fe2 in 3 display distinct Mössbauer parameters. This correlates with the different Fe–N and Fe–S distances for Fe1 and Fe2 in 3, where in 2 those distances are almost identical. Distinct Fe(II) sites had already been observed for the all-ferrous Fe₃(NH₂)₃L.^{13a}

The three-coordinate Fe3' in 3 provides a vacant site for coordination of a THF molecule, which readily alters the geometry from trigonal planar to pseudo-trigonal pyramidal. Three-coordinate irons in a nacnac-supported, self-assembled dimeric [2Fe^{II}-(µ-S)] complex have been observed to form a trigonal pyramidal geometry as they bind N-donor substrates (e.g., hydrazine derivatives and ammonia).^{15,16} In that system, the geometric distortion towards trigonal pyramidal was proposed to be electronically controlled as there was no correlation with donor size or strength of the incoming ligands (e.g., hydrazine).¹⁵ The variation in coordination number and geometry for the iron centers is reminiscent of those for Fe2 and Fe6 in FeMoco, especially in the CO-inhibited structure where one μ_2 -S²⁻ is replaced by CO.¹⁷ The central μ_6 -carbide ligand in the cofactor was suggested to structurally support the transient three-coordinate Fe2 and Fe6 prior to bonding with CO.17 In a similar vein, we propose that the strongly π -donating μ_3 -sulfide ligand stabilizes the low coordinate iron centers within the cluster, leading to open coordination sites that may allow for coordination of substrates in a similar fashion as for the THF in 3. The stabilizing effect of the μ_3 -sulfide can also explain the reversible redox event (albeit only the first is reversible) in the CV of 2 and the modest geometrical variations between 2 and 3. We also note that reversible redox events were not observed in Fe_3S_3L , implying that sulfide bridges alone are not sufficient for this electrochemical behavior.

To conclude, we report two (μ_3 -sulfide)-bridged triiron clusters supported by a trinucleating cyclophane ligand. Chemical reduction of Fe₃Br₂SL (2) yields Fe₃BrSL·0.5THF (3) incorporating a threecoordinate iron center that binds a solvent molecule. The combination of Fe centers with accessible coordination sites and an interstitial sulfide donor within one cluster bear similarities to the proposed reaction site of FeMoco. Ongoing work focuses on accessing iron(1) centers in this structure type, and the downstream reactivity of such species with small molecule substrates, as well as substituting the bromide donors with reactive ligands.

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Notes and references

[‡] (2): C₄₉H₇₁N₆O₁Br₂S₁Fe₃, *M*_r = 1119.54, triclinic, *P*Ī, *a* = 11.9958(6), *b* = 12.5852(7), *c* = 17.0913(9) Å, *α* = 104.697(1)°, *β* = 102.692(1)°, *γ* = 91.246(1)°, *V* = 2426.6(2) Å³, *Z* = 2, *ρ*_{calcd} = 1.532 M g m⁻³, *μ* = 2.618 mm⁻¹, *R*₁ = 0.0368, w*R*₂ = 0.0840, GOF = 0.958. (3): C_{50.88}H_{74.76}N₆O_{1.47}Br_{1.03}S₁Fe₃, *M*_r = 1075.92, triclinic, *P*Ī, *a* = 11.6510(3), *b* = 12.6465(4), *c* = 17.0493(5) Å, *α* = 94.401(1)°, *β* = 95.909(1)°, *γ* = 96.266(1)°, *V* = 2474.0(1) Å³, *Z* = 2, *ρ*_{calcd} = 1.444 M g m⁻³, *μ* = 1.787 mm⁻¹, *R*I = 0.0294, w*R*₂ = 0.0796, GOF = 1.077.

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