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Wheel-Shaped Lanthanide Iron Sulfide Clusters

Sergey N. Konchenko,*[a] Tanja Sanden,[b] Nikolay A. Pushkarevsky,[a] Ralf Köppe,[b] and Peter W. Roesky*[b]

Sulfur-bridged iron sulfide clusters are the active sites of several non-heme iron ferredoxins and enzymes such as hydrogenases. The development of model compounds for these kinds of compounds has attracted chemists for several decades now.[1] More recently, mixed-metal sulfur–iron carbonyl cores, such as [MoFe] and [NiFe] were discovered as active sites within some hydrogenases.[2–4] A number of model complexes, which structurally mimic the dithiolate-bridged iron or mixed-metal iron centers were reported.[5] Particular attention was focused on inorganic Fe_4S_4 clusters containing halide and thiolate ligands. On the other hand, the chemistry of "abiological" organometallic iron chalcogenide clusters primarily with carbonyl and cyclopentadienyl ligands[6,7] had attracted less interest. However, in the meanwhile the former species have been found to exhibit interesting redox transformations giving rise to fascinating catalytic activity, for example, in the processes of photochemical hydrogen production.[8,9]

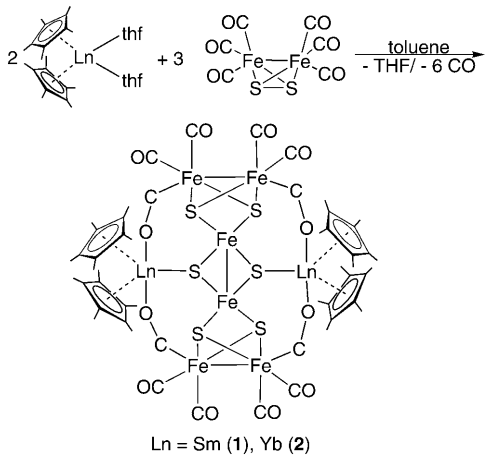
During the catalytic hydrogen production, which is assumed to be a $2e^-$ process, one or several reduction steps within the iron—carbonyl–sulfur core take place.[1,10] The reduction chemistry has been studied by electrochemical and theoretical methods.[11] In this context we aimed to study the chemical reduction of an iron–carbonyl–sulfur cluster with divalent lanthanide compounds as the reducing agent. Divalent inorganic and organometallic lanthanide reagents are well-established reducing agents.[12,13] Thus, we expected to isolate a reduction intermediate. Since the number of sulfur-bridged lanthanide–transition-metal compounds is very limited and no lanthanide–sulfide–iron cluster is known, we were also interested in synthesizing this kind of compounds. To the best of our knowledge only six structurally characterized sulfur-bridged lanthanide–transition-metal complexes have been reported to date. These are three Eu/M^{II} (M = Zn, Cd, Hg) benzenethiolate clusters,[14] $[(\eta^5\text{-}C_5Me_5)_2Sm(\mu\text{-}S)_2WS_2](PPh_4)$, $[\{(\eta^5\text{-}C_5Me_5)_2Sm\}_2Mo(\mu\text{-}S)_4](PPh_4)$,[15] and $[(\eta^5\text{-}C_5H_5)_2MoS_2GdBr_4(THF)]_2$.[16] Within this series no lanthanide–iron complex and no lanthanide–carbonyl–sulfur cluster was to the best of our knowledge synthesized. Herein we report on the reaction of the binuclear iron–sulfur–carbonyl $[Fe_2(\mu\text{-}S_2)(CO)_6]$ with divalent lanthanide compounds. $[Fe_2(\mu\text{-}S_2)(CO)_6]$ is a well-known starting reagent for a great number of heterometallic clusters and organometallic derivatives.[7,17,18] It undergoes two-electron reduction causing the cleavage of the S–S bond, giving rise to the formation of the $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$ dianion.[17] The latter can be used as a versatile nucleophilic synthon, which is to a certain degree analogous to organic thiolates.[18]

Reduction of $[Fe_2(\mu\text{-}S_2)(CO)_6]$ with the divalent metallocenes of the lanthanides $[(\eta^5\text{-}C_5Me_5)_2Ln(THF)_2]$ (Ln = Sm, Yb)[19–22] resulted in the octanuclear lanthanide iron clusters of composition $[Fe_6Ln_2(\mu_3\text{-}S)_6(\mu,\eta^2\text{-}CO)_4(CO)_8(\eta^5\text{-}C_5Me_5)_4]$ (Ln = Sm (**1**), Yb (**2**)) (Scheme 1). The redox reactions run smoothly for both compounds. In contrast, no reaction was observed by using the milder reducing agent $[(\eta^5\text{-}C_5Me_5)_2Eu(THF)_2]$. This is not very surprising as Eu has the lowest redox potential within this series. The new complexes have been characterized by standard analytical/spectroscopic techniques, and the solid-state structures were established by single-crystal X-ray diffraction. Compound **1** crystallized in the monoclinic space group $P2_1/c$ with two molecules in the unit cell (Figure 1) and compound **2** crystallized in the triclinic space group $P\bar{1}$ with one molecule in the unit cell (Figure 2).

Both compounds form a 14-membered ring. The clusters consist of a central $[Fe_6(\mu_3\text{-}S)_6(CO)_{12}]^{2-}$ unit, which binds to two $[(\eta^5\text{-}C_5Me_5)_2Ln]$ units. During the reduction step the lanthanide atoms were oxidized to the trivalent oxidation

[a] Prof. Dr. S. N. Konchenko, Dr. N. A. Pushkarevsky
Nikolaev Institute of Inorganic Chemistry SB RAS
Prosp. Lavrentieva 3, 630090 Novosibirsk (Russia)
E-mail: konch@niic.nsc.ru

[b] Dipl.-Chem. T. Sanden, Dr. R. Köppe, Prof. Dr. P. W. Roesky
Institut für Anorganische Chemie
Karlsruher Institut für Technologie (KIT)
Engesserstrasse 15, 76128 Karlsruhe (Germany)
Fax: (+49) 721-608-4854
E-mail: roesky@kit.edu



Scheme 1. Synthesis of compounds **1** and **2**.

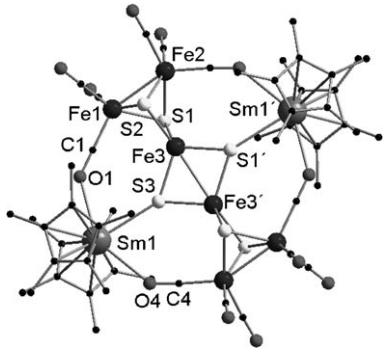


Figure 1. Solid-state structure of **1** (hydrogen atoms omitted for clarity). Selected bond lengths [Å] or angles [°]: Sm–O1 2.680(3), Sm–O4 2.721(4), Sm–S3 2.835(2), Fe1–C1 1.780(5), Fe1–S1 2.2950(15) Fe1–S2 2.3030(15), Fe1–Fe2 2.5267(11), Fe2–S2 2.2945(15), Fe2–S1 2.2966(15), Fe3–S3 2.2263(15), Fe3–S1 2.2680(15), Fe3–S2 2.2737(15), Fe3–Fe3' 2.7876(14), O1–C1 1.149(6); O1-Sm-O4 144.59(11), C1-Fe1-S1 104.56(16), C1-Fe1-S2 101.73(16), S1-Fe1-S2 85.89(5), C1-Fe1-Fe2 149.2(2), S1-Fe1-Fe2 56.64(4), S2-Fe1-Fe2 56.50(4), S2-Fe2-S1 86.05(5), S2-Fe2-Fe1 56.82(4), S1-Fe2-Fe1 56.58(4), S3'-Fe3-S3 102.50(5), S1-Fe3-S2 87.22(5), S3-Fe3-Fe3' 51.23(4), Fe1-S1-Fe2 66.77(4), Fe2-S2-Fe1 66.68(5), Fe3'-S3-Fe3 77.50(5), Fe3-S3-Sm 139.40(6), C1-O1-Sm 140.2(3), C4-O4-Sm 142.2(4), O1-C1-Fe1 177.7(5).

state. Both lanthanide atoms are bound to one sulfur atom each (Ln–S3 2.835(2) Å (**1**) and 2.757(2) Å (**2**)) of the iron–sulfur unit. Moreover, two isocarbonyl bridges are formed, which close the outer ring (Ln–O1 2.680(3) Å (**1**), 2.753(6) Å (**2**) and Ln–O4 2.721(4) Å (**1**), 2.753(6) Å (**2**)). The isocarbonyl bridges form a bite angle of O1-Ln-O4 144.59(11)° (**1**) and 145.42(12)° (**2**). For both compounds a crystallographic inversion center is observed in the center of the wheel. The central $[Fe_6S_6(CO)_{12}]^{2-}$ core has been reported previously as ammonium or bis(triphenylphosphine)iminium salts, which were prepared in a much different way starting from the iron–sulfur–carbonyl dianions $[Fe_3S(CO)_9]^{2-}$,[23] $[Fe_5S_4(CO)_{12}]^{2-}$,[24] or K_2S_4.[25] A coordination of the $[Fe_6S_6(CO)_{12}]^{2-}$ core to another metal is so far not known. As a result of the isocarbonyl bridges the shape of the $[Fe_6S_6(CO)_{12}]^{2-}$ dianion in compounds **1** and **2** is slightly different from that in the ammonia salts. The bridging CO groups are bent towards the lanthanide atoms (C1-Fe1-Fe2 149.2(2)° (**1**) and 147.1(2)° (**2**); av 151.32° in $[N(PPh_3)_2]_2[Fe_6S_6(CO)_{12}]$).[23] The bond lengths of the central Fe_2S_6 unit are in agreement with those in the literature (e.g. Fe1–Fe2 2.5267(11) Å (**1**), 2.5254(13) (**2**) Å, and 2.506(1) Å in $[N(PPh_3)_2]_2[Fe_6S_6(CO)_{12}]$).[23] The Fe–Fe distance across the central rhombus is longer (Fe3–Fe3' 2.7876(14) Å (**1**), 2.765(2) (**2**) Å) than the Fe1–Fe2 bond lengths (Fe1–Fe2 2.5267(11) Å (**1**), 2.5254(13) (**2**) Å).

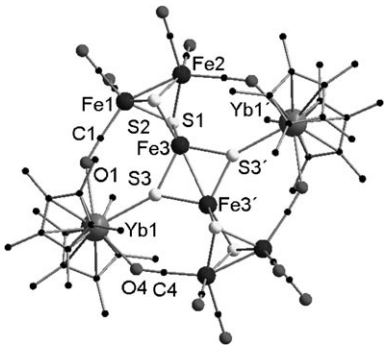


Figure 2. Solid-state structure of **2** (hydrogen atoms omitted for clarity). Selected bond lengths [Å] or angles [°]: Yb–O1 2.753(6), Yb–O4 2.511(4), Yb–S3 2.757(2), Fe1–C1 1.789(7), Fe1–S1 2.2934(15), Fe1–S2 2.293(2), Fe1–Fe2 2.5254(13), Fe2–S2 2.2977(18), Fe2–S1 2.297(2), Fe3–S3' 2.2247(17), Fe3–S3 2.2309(15), S3–Fe3' 2.2247(17), Fe3–S1 2.262(2), Fe3–S2 2.2675(17), Fe3–Fe3' 2.765(2), O1–C1 1.156(8); O1-Yb-O4 145.42(12), C1-Fe1-S1 101.5(2), C1-Fe1-S2 101.7(2), S2-Fe1-S1 86.31(6), C1-Fe1-Fe2 147.1(2), S1-Fe1-Fe2 56.69(4), S2-Fe1-Fe2 56.71(5), S1-Fe2-S2 86.13(6), S2-Fe2-Fe1 56.55(5), S1-Fe2-Fe1 56.55(4), S3'-Fe3-S3 103.28(6), S1-Fe3-S2 87.67(6), S3-Fe3-Fe3' 51.54(5), Fe1-S1-Fe2 66.75(5), Fe1-S2-Fe2 66.74(5), Fe3'-S3-Fe3 76.72(6), Fe3-S3-Yb 139.40(7), Fe3'-S3-Yb 143.82(6), C1-O1-Yb 141.4(4), C4-O4-Yb 142.9(4), O1-C1-Fe1 176.1(5).

In the IR spectra of compounds **1** and **2** the υCO stretching frequencies are observed as strong bands at 2054, 2014, 2004, and 1897 cm^{-1} for **1** and at 2055, 2015, 2004, and 1887 cm^{-1} for **2**. The bands close to 2000 cm^{-1} are attributed to the terminal CO groups. This is in line with the IR spectrum found for $[Et_4N]_2[Fe_6S_6(CO)_{12}]$[25] or $[Fe_2S_2(CO)_6]$.[26] The absorptions at 1897 cm^{-1} (**1**) and 1887 cm^{-1} (**2**) are typical for lanthanide isocarbonyl bridges.[27] The observed metal–carbonyl stretching frequencies at 602 cm^{-1} (**1**) and 601 cm^{-1} (**2**) are in line with the force field analysis on $[Fe_2S_2(CO)_6]$.[26]

In summary we have prepared the first lanthanide–carbonyl–sulfide–iron clusters by redox reactions of the metallocenes of the divalent lanthanides and $[Fe_2(\mu\text{-}S_2)(CO)_6]$. The resulting 14-membered wheels have $[Fe_6(\mu_3\text{-}S)_6(CO)_{12}]^{2-}$ units in the center.

Experimental Section

All manipulations were carried out under strictly anaerobic and anhydrous conditions.

$[Fe_6Ln_2(\mu_3\text{-}S)_6(\mu,\eta^2\text{-}CO)_4(CO)_8(\eta^5\text{-}C_5Me_5)_4]$ (Ln = Sm (1), Yb (2)): For the synthesis a two-section ampoule was used. $[(\eta^5\text{-}C_5Me_5)_2Ln(THF)_2]$ (0.1 mmol) and $[Fe_2(\mu\text{-}S_2)(CO)_6]$ (0.15 mmol) were placed into different sections of the ampoule and toluene (10 mL) was added to each section. The ampoule was cooled to −35 °C and the solutions were mixed. The mixture was left at this temperature for several days. Then, the reaction solution was heated to room temperature for 24 h. An amorphous precipitate was separated by decantation of the solution to the other section of the ampoule. Black crystals of $[Fe_6Ln_2(\mu_3\text{-}S)_6(\mu,\eta^2\text{-}CO)_4(CO)_8(\eta^5\text{-}C_5Me_5)_4]$ were obtained by slow evaporation of the solution to the other section of the ampoule after two weeks (**1**, Ln = Sm; **2**, Ln = Yb). **1**: Yield: 0.006 g, 3.5 %. IR (KBr): $\tilde{\nu}$ = 2962 (w), 2917 (m), 2852 (w), 2054 (vs), 2014 (vs), 2004 (vs), 1897 (vs), 1444 (w), 1389 (w), 1378 (w), 1019 (w), 602 (m) cm^{-1}; elemental analysis calcd (%) for ($[Fe_6Sm_2(\mu_3\text{-}S)_6(\mu,\eta^2\text{-}CO)_4(CO)_8(\eta^5\text{-}C_5Me_5)_4]$ toluene): C 39.43, H 3.81, S 10.70; found: C 39.60, H 3.57, S 11.94. (As a result of the high sensitivity of the sample the results of the measurements vary even for the same crop of crystals). **2**: Yield: 0.006 g, 3.4 %. IR (KBr): $\tilde{\nu}$ = 2965 (w), 2910 (w), 2856 (w), 2055 (vs), 2015 (vs), 2004 (vs), 1887 (vs), 1446 (w), 1379 (w), 1022 (w), 601 (m) cm^{-1}; elemental analysis calcd (%) for ($[Fe_6Yb_2(\mu_3\text{-}S)_6(\mu,\eta^2\text{-}CO)_4(CO)_8(\eta^5\text{-}C_5Me_5)_4]$THF): C 36.90; H 3.76; S 10.56; found: C 36.87, H 3.51, S 9.96.

Crystal data for **1**: $C_{52}H_{60}Fe_6O_{12}S_6Sm_2$, M = 1705.16, monoclinic, a = 14.607(3), b = 10.669(2), c = 20.604(4) Å, β = 106.43(3)°, V = 3079.9(11) $Å^3$, T = 200(2) K, space group $P2_1/c$, Z = 2, $\mu(Mo_{K\alpha})$ = 3.504 mm^{-1}, 27938 reflections measured, 8305 independent reflections (R_{int} = 0.0692). The final R_1 values were 0.0461 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0911 (all data). The goodness of fit on F^2 was 1.057.

Crystal data for **2**: $C_{52}H_{60}Fe_6O_{12}S_6Yb_2{\cdot}2(C_4H_8O)$, M = 1894.75, triclinic, a = 9.5592(19), b = 13.303(3), c = 14.950(3) Å, α = 86.83(3), β = 86.12(3), γ = 80.68(3)°, V = 1869.8(7) $Å^3$, T = 200(2) K, space group $P\bar{1}$, Z = 1, $\mu(Mo_{K\alpha})$ = 3.825 mm^{-1}, 18225 reflections measured, 9283 independent reflections (R_{int} = 0.0520). The final R_1 values were 0.0439 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1156 (all data). The goodness of fit on F^2 was 0.966.

CCDC-781536 (**1**) and CCDC-781537 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: clusters · iron · rare earths · samarium · sulfur

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