

Contribution from the Department of Chemistry,
Princeton University, Princeton, New Jersey 08544

Convenient Synthetic Route to $[\text{Fe}_2\text{S}_2(\text{SR})_4]^{2-}$ via Reaction of $[\text{Fe}(\text{SR})_4]^-$ with Sulfur

Sanghwa Han, Roman S. Czernuszewicz, and Thomas G. Spiro*

Received August 28, 1985

Iron-sulfur proteins containing $[2\text{Fe}-2\text{S}]$ clusters in their active sites are known to participate in many biological redox reactions such as photosynthesis (ferredoxin),¹ steroid hydroxylation (adrenodoxin),² and camphor hydroxylation (putidaredoxin).³ Various spectroscopic techniques have been applied to characterize the Fe-S centers.⁴ Although X-ray crystal structures are available for two proteins⁵ of this class, more information about the detailed structure of the cluster has emerged from the parallel studies on synthetic analogues.⁶

The first analogue, with *o*-xylene- α,α' -dithiolate as a bidentate terminal ligand, was prepared by Holm and co-workers.⁷ Since then, much effort has been devoted to improving synthetic methodology and extending it to other ligands.⁸ Two types of reactions utilizing monomeric clusters as starting materials have so far been developed. One of them,^{8d} the reaction of $[\text{Fe}^{\text{II}}(\text{SR})_4]^{2-}$ with elemental sulfur, gave a series of new Fe-S clusters, among which $[\text{Fe}_2\text{S}_2(\text{SC}_2\text{H}_4)_4]^{2-}$ was the first dimer with a monodentate alkanethiolate ligand. The other^{8a} involves oxidized monomers, $[\text{Fe}^{\text{III}}(\text{SR})_4]^-$, and HS^- as a source of inorganic sulfur.

During the course of synthetic work⁶ it has frequently been observed that thiolates are easily oxidized to disulfides, providing Fe(III) with reducing electrons. On the basis of this fact we have devised a convenient synthetic route to dimeric Fe-S clusters employing oxidized monomers and elemental sulfur as the starting materials. The simplest alkanethiolate derivative $[\text{Fe}_2\text{S}_2(\text{SCH}_3)_4]^{2-}$ has been prepared for the first time. The method is particularly convenient for the introduction of isotopes.

Syntheses

All the reactions and manipulations were routinely performed under a dinitrogen atmosphere by using a drybox and Schlenk techniques. $(\text{SH})_2\text{-}o\text{-xyl}^9$ was prepared by a published method¹⁰ and sublimed before use. The other chemicals were purchased from commercial sources and used without further purification. Solvents were purged with nitrogen for 20 min.

$[\text{Fe}(\text{SR})_4]^-$ ($\text{R} = \text{CH}_3$, Et; $\text{R}_2 = o\text{-xyl}$). Oxidized monomers were conveniently obtained in high yields by the method of Koch et al.¹¹ $[\text{Fe}(2,6\text{-dimethylphenolate})_4]^-$ was prepared under aerobic conditions and dissolved in DMF. Excess thiol was added¹² to the purged DMF solution and was followed by precipitation with excess ether. The dried monomers were employed directly in the reactions without recrystallization.

$(\text{Et}_4\text{N})_2[\text{Fe}_2\text{S}_2(\text{SCH}_3)_4]$. To a stirred solution of 1.13 g (3.0 mmol) $\text{Et}_4\text{N}[\text{Fe}(\text{SCH}_3)_4]^-$ in 25 mL of acetonitrile¹³ was added 100 mg (3.1 mmol) of elemental sulfur. The solution became reddish brown within several minutes, indicating the formation of dimeric cluster. Excess ether was added to the reaction mixture after 2 h of stirring, and the mixture was cooled to -20°C for 3 h. The product was filtered, washed with ether, and dried in vacuo; 0.79 g (84%) of black crystals was obtained. Anal. Calcd for $\text{C}_{20}\text{H}_{32}\text{N}_2\text{Fe}_2\text{S}_6$: C, 38.45; H, 8.39; N, 4.48. Found: C, 38.13; H, 8.47; N, 4.57. UV-vis (CH_3CN , 0.5 mM): λ 332 nm (ϵ 16500 $\text{cm}^{-1}\text{M}^{-1}$), 422 (11000), 455 (10000), \sim 545 (sh, 5000).

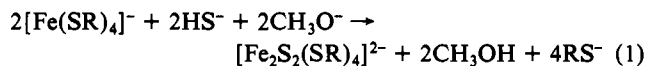
$(\text{Pr}_4\text{N})_2[\text{Fe}_2\text{S}_2(\text{SEt})_4]$. The preceding method and the same amounts of reagents were employed except that 1.46 (3.0 mmol) of $\text{Pr}_4\text{N}[\text{Fe}(\text{SEt})_4]^-$ was used. The yield was 0.85 g (71%). Anal. Calcd for $\text{C}_{32}\text{H}_{76}\text{N}_2\text{Fe}_2\text{S}_6$: C, 48.47; H, 9.66; N, 3.53. Found: C, 48.20; H, 9.76; N, 3.54. The UV-vis spectrum was identical with the published one.^{8d}

$(\text{Et}_4\text{N})_2[\text{Fe}_2\text{S}_2(\text{S}_2\text{-}o\text{-xyl})_2]$. Sulfur, 64 mg (2.0 mmol), was added to a stirred solution of 1.04 g (2.0 mmol) of $\text{Et}_4\text{N}[\text{Fe}(\text{S}_2\text{-}o\text{-xyl})_2]^-$ in 30 mL acetone. Conversion of monomer to dimer occurred slowly, yielding black microcrystals and a clear supernatant solution. After 3 h of stirring, mixture was filtered and the crystals were washed repeatedly with acetone and ether; 0.71 g (93%) of dried product was obtained. Anal. Calcd for $\text{C}_{32}\text{H}_{36}\text{N}_2\text{Fe}_2\text{S}_6$: C, 49.73; H, 7.30; N, 3.62. Found: C, 49.83; H, 7.21; N, 3.71. The product was also identified by its UV-vis spectrum.⁷

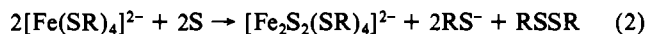
* To whom correspondence should be addressed.

Discussion

The original synthesis of a Fe_2S_2 species⁷ involved direct assembly of all constituents at their final oxidation level:



This route, however, was limited by the tendency for further reaction to tetrameric clusters. Only the bidentate ligand *o*-xylene- α,α' -dithiolate can be used successfully in reaction 1, since it is incapable of bridging the Fe coordination positions of Fe_4S_4 . It was subsequently found^{8d} that the redox reaction



provided a more versatile and general route to dimeric species. Instead of S_8 , one can use $(\text{PhCH}_2\text{S})_2\text{S}$ as a source of zerovalent sulfur.^{8b} The $[\text{Fe}^{\text{II}}(\text{SR})_4]^{2-}$ species are extremely air-sensitive, however. We were interested in preparing $^{54}\text{Fe}_2\text{S}_2$ isotope species and found daunting the prospect of preparing $^{54}\text{Fe}(\text{SR})_4]^{2-}$ from small amounts of difficult to purify $^{54}\text{FeCl}_4]^{2-}$.

We then discovered that Fe_2S_2 species formed cleanly when sulfur was allowed to react with $[\text{Fe}^{\text{III}}(\text{SR})_4]^-$. Presumably the reaction is



As pointed out by a reviewer, it is possible that the reaction of reduced monomers actually goes by reaction 3, since $[\text{Fe}(\text{SR})_4]^{2-}$ ($E_{1/2} \sim -0.6$ to -1.2 V) should readily be oxidized to $[\text{Fe}(\text{SR})_4]^-$ by elemental sulfur. $[\text{Fe}(\text{SR})_4]^-$ complexes can conveniently be prepared directly by the method recently introduced by Koch and co-workers,¹¹ using the sterically hindered phenolate complex $[\text{Fe}(2,6\text{-dimethylphenolate})_4]^-$, which is readily prepared from FeCl_3 . It is easy to prepare pure $^{54}\text{FeCl}_3$ by reacting commercially available $^{54}\text{Fe}_2\text{O}_3$ with thionyl chloride.¹⁴ Since elemental sulfur is also available in isotopically enriched form, its reaction with $[\text{Fe}(\text{SR})_4]^-$ is a convenient method of introducing Fe or S isotopes into Fe_2S_2 complexes.

While $[\text{Fe}(\text{SR})_4]^-$ are themselves unstable in air, their sensitivity

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to oxygen is much less than that of $[\text{Fe}(\text{SR})_4]^{2-}$. Probably the CH_3S^- complexes are the least stable examples in both oxidation states, and this may be why $[\text{Fe}_2\text{S}_2(\text{SCH}_3)_4]^{2-}$ has not previously been reported. Being the simplest member of the series, this complex is of interest for spectroscopic studies¹⁵ and for comparison with theoretical calculations.¹⁶

Acknowledgment. This work was supported by NIH Grant GM13498.

Registry No. $(\text{Et}_4\text{N})_2[\text{Fe}_2\text{S}_2(\text{SCH}_3)_4]$, 102261-05-2; $\text{Et}_4\text{N}[\text{Fe}(\text{SCH}_3)_4]$, 102261-06-3; $(\text{Pr}_4\text{N})_2[\text{Fe}_2\text{S}_2(\text{SEt})_4]$, 102261-07-4; S, 7704-34-9; $\text{Pr}_4\text{N}[\text{Fe}(\text{SEt})_4]$, 86689-79-4; $(\text{Et}_4\text{N})_2[\text{Fe}_2\text{S}_2(\text{S}_2\text{-}o\text{-}xy)_2]$, 56083-11-5; $\text{Et}_4\text{N}[\text{Fe}(\text{S}_2\text{-}o\text{-}xy)_2]$, 57456-65-2.

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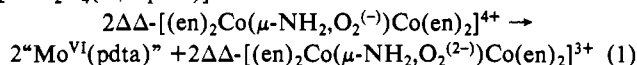
Contribution from the Department of Chemistry,
 Faculty of Science, Tohoku University,
 Aoba, Aramaki, Sendai 980, Japan

Stereoselectivity Induced by an Optically Active Cationic Cobalt(III) Complex Ion on the Outer-Sphere Redox Reaction between Racemic Binuclear Molybdenum(V) Anions and Hexachloroiridate(IV) in Water

Yoichi Sasaki,* Katsuhiko Meguro, and Kazuo Saito*¹

Received January 14, 1986

We have reported the existence of stereoselectivity on outer-sphere redox reaction 1.²⁻⁴ The selectivity was in favor of the $[\text{Mo}^{\text{V}}_2\text{O}_4(\text{R},\text{S-pdta})]^{2-} +$



S-pdta and the *R-pdta* complex at lower and higher ionic strengths, respectively. Kinetic analysis^{5,6} of the observed rate data suggested that the selectivity at the precursor formation (equilibrium constant K_{IP}) and the net electron-transfer step (rate constant k_e) operate in reversed directions, the ratio $K_{\text{IP}}(\text{R})/K_{\text{IP}}(\text{S})$ being >1.09 at $I = 0.5 \text{ M}$.²

In order to elucidate the mechanism of selectivity at the precursor formation step, we have used nonchiral hexachloroiridate(IV) as oxidant and examined the influence of optically active cations on the oxidation of the racemic $[\text{Mo}^{\text{V}}_2\text{O}_4(\text{R},\text{S-pdta})]^{2-}$ complex.

Experimental Section

Preparations of the Complexes. $\text{Na}_2[\text{Mo}_2\text{O}_2(\mu\text{-O})_2(\text{R},\text{S-pdta})]\cdot 3\text{H}_2\text{O}$,⁷ $\Delta\text{-}[\text{Co}(\text{en})_3]\text{Cl}_3$,⁸ and $\Delta\text{-}$ and $\Delta\text{-}[\text{Co}(\text{gly})(\text{en})_2]\text{Cl}_2$ ⁹ were prepared by the known methods. $\Delta\text{-}[\text{Co}(\text{etaH})(\text{R-chxn})_2](\text{ClO}_4)_3\cdot 5\text{H}_2\text{O}$ and $\Delta\text{-}[\text{Co}(\text{S-}$

Table I. Ratio of Rates of Oxidation of $[\text{Mo}^{\text{V}}_2\text{O}_4(\text{R-pdta})]^{2-}$ and $[\text{Mo}^{\text{V}}_2\text{O}_4(\text{S-pdta})]^{2-}$ with $[\text{IrCl}_6]^{2-}$ in the Presence of Optically Active Cobalt(III) Ions^a

Co ^{III} complex	enantiomeric excess (% ee) of unreacted Mo(V) dimer (isomer in excess)	ratio of oxidn rates (easily oxidized isomer)
$\Delta\text{-}[\text{Co}(\text{en})_3]^{3+}$	0.14 (<i>R-pdta</i>) 0.51 (<i>R-pdta</i>)	1.003 (<i>S-pdta</i>) ^b 1.010 (<i>S-pdta</i>) ^c
$\Delta\text{-}[\text{Co}(\text{S-praH})(\text{R-chxn})_2]^{3+}$	0.55 (<i>S-pdta</i>)	1.011 (<i>R-pdta</i>) ^b
$\Delta\text{-}[\text{Co}(\text{etaH})(\text{R-chxn})_2]^{3+}$	1.99 (<i>S-pdta</i>)	1.04 (<i>R-pdta</i>) ^c
$\Delta\text{-}[\text{Co}(\text{gly})(\text{en})_2]^{2+}$	0.15 (<i>S-pdta</i>)	1.003 (<i>R-pdta</i>) ^c
$\Delta\text{-}[\text{Co}(\text{gly})(\text{en})_2]^{2+}$	~ 0.07 (<i>S-pdta</i>)	~ 1.001 (<i>R-pdta</i>) ^c
$\Delta\text{-}[\text{Co}(\text{gly})(\text{en})_2]^{2+}$	~ 0.04 (<i>R-pdta</i>)	~ 1.001 (<i>S-pdta</i>) ^c

^a Reaction conditions: $[\text{Mo}^{\text{V}}_2] = [\text{Ir}^{\text{IV}}] = 1.0 \times 10^{-4} \text{ M}$; $[\text{Co}^{\text{III}}] = 1.0 \times 10^{-3} \text{ M}$; 60 °C. ^b $I = 0.2 \text{ M}$ (NaClO_4); pH 3.7 (acetate buffer). ^c pH ca. 5.5; NaClO_4 was not added.

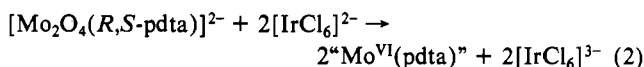
praH})(\text{R-pdta})_2](\text{ClO}_4)_3 were supplied by Dr. T. Nishide.¹⁰ Optical purity of the cobalt(III) complexes was checked by the intensity of circular dichroism (CD) spectra to be almost 100%. Commercial $\text{Na}_2[\text{IrCl}_6]\cdot 6\text{H}_2\text{O}$ was recrystallized once from water.

Measurements of Stereoselectivity. An aqueous solution (9 cm³) of $2.0 \times 10^{-3} \text{ M}$ $\text{Na}_2[\text{IrCl}_6]\cdot 6\text{H}_2\text{O}$ ($1 \text{ M} = 1 \text{ mol dm}^{-3}$) was added to a solution (171 cm³) containing $1.05 \times 10^{-4} \text{ M}$ $\text{Na}_2[\text{Mo}_2\text{O}_4(\text{R},\text{S-pdta})]\cdot 3\text{H}_2\text{O}$, $1.05 \times 10^{-3} \text{ M}$ optically active cobalt(III) complex, and appropriate amounts of NaClO_4 and buffer component at 60 °C. The mixture was kept at 60 °C for 1 h until the characteristic strong absorption bands of $[\text{IrCl}_6]^{2-}$ in the visible region¹¹ disappeared. The solution was diluted with water and treated with a cation-exchange column (SP Sephadex C-25 in Na^+ form) to remove the cationic cobalt(III) complex. The eluate was concentrated to less than 10 cm³ and made up to 10 cm³ with water for measuring the absorption and CD spectra in the region 340-440 nm. Since the stoichiometry of the redox reaction $[\text{Mo}_2] \text{ vs. } [\text{Ir}]$ is 1 to 2,^{12,13} half the molybdenum(V) dimer remains unreacted. The observed CD band around 385 nm should be due to the unreacted molybdenum(V) dimer, since neither $[\text{Ir}^{\text{III}}\text{Cl}_6]^{3-}$ nor the molybdenum(VI) complex has a CD band in this region.² From the $\Delta\epsilon$ value (-5.5 at 387 nm) of pure $[\text{Mo}_2\text{O}_4(\text{R-pdta})]^{2-}$ ¹⁴ was estimated the enantiomeric excess of the unreacted molybdenum(V) dimer.

The absorption and CD spectra were recorded with a Hitachi 330 spectrophotometer and a JASCO J-40A automatic recording spectropolarimeter, respectively. The pH of solution was measured by a Metrohm Herisau E300B pH meter.

Results and Discussion

The overall reaction is written as (2). Equimolar amounts of the reactants were used so that half of the molybdenum(V) dimer remained unchanged, which should give optical activity if the reaction proceeded stereoselectively. Thirteen optically active



cobalt(III) complex cations were used, but most of them gave precipitation with $[\text{IrCl}_6]^{2-}$ even in the presence of $\text{Na}_2\text{H}_2\text{edta}$.^{2,5} The data were obtained only for a limited number of systems, but significant selectivity was observed in the presence of optically active complex cations, which remained unchanged throughout the progress of the redox reaction (Table I).

Table I clearly indicates that the absolute configuration of the cobalt(III) ion rules the preference with which either the *R-pdta* or the *S-pdta* complex of $\text{Mo}^{\text{V}}_2\text{O}_4^{2+}$ is more rapidly oxidized: i.e. a Δ -cation favors more rapid oxidation of the *R-pdta* complex, and a Λ -cation favors that of the *S-pdta* complex. It is less likely that the rate of net electron transfer between nonchiral iridate(IV)

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