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Dimeric Complexes Containing the $[Fe_2S_2]^{2+}$ Cores Coordinated by Non-Sulfur Containing Terminal Ligands. The Crystal and Molecular Structures of the Et_4N^+ Salts of the $[Fe_2S_2(o,o'\text{-}C_{12}H_8O_2)_2]^{2-}$ and $[Fe_2S_2(C_4H_4N)_4]^{2-}$ Anions

D. Coucouvanis,* A. Salifoglou, M. G. Kanatzidis,
A. Simopoulos,† and V. Papaefthymiou†

Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48109

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The general spectroscopic properties of the structurally characterized bis(μ-sulfido) $[L_2FeS_2FeL_2]^{2-}$ complexes (L_2 = *o*-xylenedithiolate,[1] L = *p*-toluenethiolate,[1] $L_2 = S_5^{2-}$[2]) are very similar to those of the Fe/S centers in most of the plant type 2Fe-2S ferredoxins. Detailed comparative studies of the Mössbauer, EPR, and electronic spectra of the dimeric analogue complexes[3] and of representative 2Fe-2S ferredoxins[4] led to the realization that the Fe/S cores in the latter were structurally identical with the rhombic Fe_2S_2 units in the former. The validity of this structural assignment was confirmed by the X-ray crystal structure determination of the 2Fe-2S ferredoxin from *Spirulina platensis*,[5] which contains the Fe_2S_2 rhombic unit coordinated by four cysteinyl residues.

An unusual 2Fe-2S ferredoxin with unique spectroscopic properties coexists with cytochromes *b* and *c* in certain proteolipid complexes essential for respiratory electron transport in mitochondria,[6] chloroplasts,[7] and certain bacteria.[8] Some of the unique features of these "Rieske[9] proteins", as outlined in a recent detailed study of one such 2Fe-2S ferredoxin from *Thermus thermophilus*,[11] are (a) high redox potentials (E_m) in the range from +150 to +330 mV, (b) unusually low (~1.90) g_{av} values in the EPR spectra of the reduced 2Fe-2S clusters, (c) bathochromically shifted electronic spectra by comparison to the plant-type ferredoxins, and (d) unique Mössbauer spectra indicative of two iron sites for both the oxidized and the reduced forms of the protein. On the basis of detailed spectroscopic studies and analytical data it has been suggested[11] that ligands such as imidazole, phenolate, hydroxylate, or carboxylate may complete the coordination sphere of the Fe atoms in the Rieske proteins.

In this communication we report on the synthesis and structural characterization of two dimeric 2Fe-2S complexes with a full complement of oxygen and nitrogen donor terminal ligands.

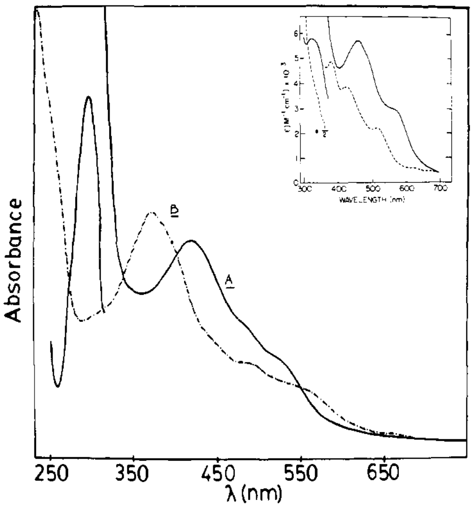

Figure 1. The electronic spectra in CH_3CN solution of A, $[Fe_2S_2(o,o'\text{-biphenolate})_2]^{2-}$, and B, $[Fe_2S_2(\text{pyrrolate})_4]^{2-}$. The electronic spectrum of the Rieske protein (oxidized form, solid line; reduced form, dotted line) from *Thermus thermophilus* is inserted (by permission from ref 11).

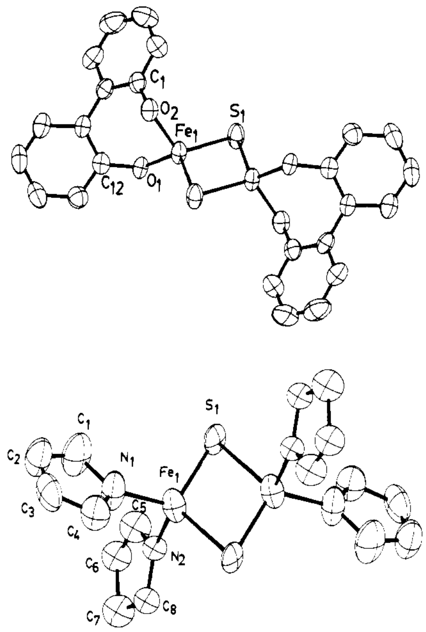

Figure 2. Structure and labeling of the anions in I and II. Thermal ellipsoids as drawn by ORTEP (Johnson, C. K. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965) represent the 50% probability surfaces. Due to a positional disorder the $C_5C_6C_7C_8N_2$ ligand was refined with isotropic temperature factors. Only one of the components is shown in the figure.

The metathetical reactions between $(Et_4N)_2[Cl_2FeS_2FeCl_2]$[12] and alkali metal salts of the *o,o'*-biphenolate ($C_{12}H_8O_2^{2-}$), the pyrrolate ($C_4H_4N^-$) anions, and the *p*-cresolate ($C_7H_7O^-$) anions at ambient temperature in dry CH_3CN are rapid, and the crystalline $(Et_4N)_2[L_2FeS_2FeL_2]$ complexes can be isolated[13] for $L_2 = C_{12}H_8O_2^{2-}$ (I, 79% yield), $L = C_4H_4N^-$ (II, 71% yield), and $L = C_7H_7O^-$ (III, 55% yield).

The electronic spectra of I (522 sh, 484 sh, 416 (ϵ 9260), 295 nm (ϵ 21 600)), II (550 sh, 490 sh, 370 nm (ϵ 8300)), and III (494 sh, 414 (ϵ 12 060), 280 nm (ϵ 26 100)) are similar to those reported[11] for the oxidized Rieske protein from *Thermus thermophilus* (560 sh, 458 nm (ϵ 6000), 325 nm (ϵ 11 500)) and bathochromically shifted (Figure 1) by comparison to typical spectra of Fe_2S_2 complexes with sulfur donor terminal ligands.[3] The magnetic moments[14] (μ_{eff}^{corr}, 298 K) of 2.06 and 2.16 μ_B for I and

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† Nuclear Research Center, "Demokritos" Aghia Paraskevi, Attiki, Greece.

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[13] Satisfactory elemental analyses have been obtained for I, II, and III.

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Table I. Selected Structural Parameters in A, $[Fe_2S_2(o,o'\text{-biphenolate})_2]^{2-}$ (I), B, $[Fe_2S_2(\text{pyrrolate})_4]^{2-}$ (II), C, $[Fe_2S_2(S_2\text{-}o\text{-xylyl})_2]^{2-}$, D, $[Fe_2S_2S(p\text{-tolyl})_4]^{2-}$, and E, $Fe_2S_{12}{}^{2-}$

	A[a]	B[a]	C[b]	D[b]	E[c]
Fe–Fe	2.699 (1)	2.677 (3)	2.698 (1)	2.691 (1)	2.701 (3)
$\overline{\text{Fe–S}_b}$	2.215	2.18	2.21	2.201	2.192
Fe–O_1(N_1)	1.895 (2)	1.96 (1)			
Fe–O_2(N_2)	1.892 (2)	2.09 (3)			
S_b–S_b	3.512 (2)	3.57 (5)	3.498 (3)	3.483 (3)	3.453 (5)
S_b–Fe–S_b	104.9 (1)[d]	104.3 (4)[e]	104.73 (4)	104.51 (4)	104.0 (2)
O(N)–Fe–(N)O	96.1 (1)	110.6 (6)			
Fe–S_b–Fe	74.1 (1)	75.7 (2)	75.27 (5)	75.39 (4)	76.1 (1)

[a] This work. [b] From ref 1. [c] From ref 2. [d] The other L–Fe–L angles vary from 96.1 (1)° for the O_1–Fe–O_2 angle to 117.8 (1)° for the O_2–Fe–S_1 angle. [e] The other L–Fe–L angles vary from 105.4 (9)° for the N_2–Fe–S_1 angle to 112.4 (6)° for the N_1–Fe–S_1 angle.

II, respectively, are similar to those reported previously[1] for the sulfur terminal ligand analogues and very likely reflect antiferromagnetic coupling between the two high-spin Fe(III) ions in the dimers. As a result of these magnetic moments the NMR spectra of I and II display isotropically shifted proton resonances in CD_3CN solution. The ortho H, meta H, meta H, and para H resonances in I are observed at 2.85, 9.61, 9.31, and 2.69 ppm, and the ortho H and meta H resonances in II are observed at 10.30 and 8.95 ppm. For both I and II irreversible reduction is observed in cyclic voltammetric measurements[15] which show large negative potentials of −1.30 and −1.60 V, respectively. The Mössbauer spectra at 77 K consist of sharp doublets and show isomer shift (IS) values (vs. Fe) and quadrupole splittings (ΔE_Q) of 0.35 (2) and 1.02 (1) mm/s for I and 0.26 (1) and 0.49 (1) mm/s for II. These values are similar to those reported for the $[(PhS)_2Fe_2S_2(SPh)_2]^{2-}$ complex[16] (IS, 0.28 (1); ΔE_Q, 0.32 (2), 77 K) the $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-}$ complex,[9] and the oxidized Rieske protein from *Thermus thermophilus*[11] (IS_A, 0.32, IS_B, 0.24; ΔE_{QA}, 0.91, ΔE_{QB}, 0.52; 4.2 K). The Mössbauer data also demonstrate that the Fe(III) IS values in the $[Fe_2S_2L_4]^{2-}$ complexes are relatively insensitive to the nature of the terminal ligands (L) when tetrahedral coordination is maintained.

In the crystal structures[17] of both I and II the dianions are located on crystallographic centers of symmetry. Selected structural parameters for the anions in I and II (Figure 2) are shown in Table I and are compared to corresponding parameters in the structures of the $[Fe_2S_2(S_2\text{-}o\text{-xylyl})_2]^{2-}$, $[Fe_2S_2(S\text{-}p\text{-tolyl})_4]^{2-}$,[1] and $Fe_2S_{12}{}^{2-}$ [2] anions. The striking similarities in the Fe_2S_2 units are apparent.

The available spectroscopic data on I–III and particularly the Mössbauer and electronic spectral data are very similar to corresponding data for the Rieske proteins. These similarities, however, can only be of limited significance when the pronounced differences in the redox potentials are taken into consideration. In the $[L_2FeS_2FeL_2]^{2-}$ analogue complexes, substitution of the sulfur ligands by either oxygen or nitrogen ligands and maintenance of the tetrahedral coordination for the Fe(III) ions results in complexes with more *negative* redox potentials. A positive shift in the redox potentials of the $[Fe_4S_4(SR)_4]^{2-}$ clusters apparently occurs only when the thiolate ligands are displaced by carboxylate ligands.[18] The possibility that positive shifts in the redox potential of the $[L_2FeS_2FeL_2]^{2-}$ complexes are brought about by carboxylate terminal ligands (and changes in coordination number or geometry) at present is under investigation in our laboratory.

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Supplementary Material Available: Tables of structure factors, positional and thermal parameters, and data reduction and structure solution protocol (20 pages). Ordering information is given on any current masthead page.

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(15) Cyclic voltammetry in CH_3CN on a Pt electrode with Bu_4NClO_4 as supporting electrolyte. Potentials are reported with SCE as a reference electrode.

(16) Gillum, W. O.; Frankel, R. B.; Foner, S.; Holm, R. H. *Inorg. Chem.* **1976**, *15*, 1095.

(17) Crystal and refinement data for $(Et_4N)_2[Fe_2S_2(o,o'\text{-}C_{12}H_8O_2)_2]$ (I): $a = 11.500$ (2) Å, $b = 13.541$ (3) Å, $c = 26.612$ (5) Å, $\beta = 92.25$ (1)°; space group $C2/c$ (No. 15); $Z = 4$; $d_{calcd} = 1.29$ g/cm^3, $d_{obsd} = 1.30$ (2) g/cm^3; $\mu = 8.07$ cm^{-1}; $2\theta_{max}$ 45° (Mo/Kα,λ 0.710 69 Å). Reflections collected 6603; unique reflections used in refinement $F_o{}^2 > 3\sigma(F_o{}^2)$, 2108; parameters 310; final $R = 0.032$. Crystal and refinement data for $(Et_4N)_2[Fe_2S_2(C_4H_4N)_4]$ (II): $a = 9.689$ (3) Å, $b = 16.362$ (2) Å, $c = 11.910$ (5) Å, $\beta = 97.74$ (3)°; space group $P2_1/n$; $Z = 2$; $d_{calcd} = 1.24$ g/cm^3; $d_{obsd} = 1.32$ g/cm^3; $\mu = 8.84$ cm^{-1}; $2\theta_{max}$ 40° (Mo Kα,λ 0.710 69 Å). Reflections collected 2328; unique reflections used in refinement $F_o{}^2 > 3\sigma(F_o{}^2)$, 1197; parameters 173; final $R = 0.069$.

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Hypervalent Iodine. Mixed Iodonium Ylides

Robert M. Moriarty,* Indra Prakash, Om Prakash, and Wade A. Freeman

Department of Chemistry
University of Illinois at Chicago
Chicago, Illinois 60680

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The relatively unfamiliar aryliodonium ylides owe their stability to delocalization of the carbanionic charge adjacent the onium center in the zwitterionic form:[1]

$$\text{ArI}{=}\text{CR}_2 \leftrightarrow \text{ArI}^+{-}{}^-\text{CR}_2$$

The first stable iodonium ylide, discovered by Neilands et. al., in 1957, possessed a β-dicarbonyl system ($^-CR_2$ equals $^-C(COR)_2$ in the above expression) and was synthesized via reaction of dimedone with (difluoroiodo)benzene $C_6H_5IF_2$.[2] Most stable iodonium ylides subsequently reported incorporate a β-dicarbonyl carbanionic group,[3a,b] although other stable anionic systems also occur.[4]

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(3) (a) For example, the carbanionic part may be derived from 1,3-indanedione (Neilands O.; Vanag, G. *Dokl. Chem.* (*Engl. Transl.*) **1961**, *141*, 1232), dibenzoylmethane (Neilands, O. *J. Org. Chem. USSR* (*Engl. Transl.*) **1965**, *1*, 1888, 5-phenyl-1,3-cyclohexanedione and benzoylacetone (Neilands, O.; Vanag, G. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1961**, *31*, 137. Neilands, O.; Karele, B. *J. Org. Chem. USSR* (*Engl. Transl.*) **1966**, *2*, 49, ethyl acetoacetate and dimethyl and diethyl malonate (Neilands, O.; Karele, B. *J. Org. Chem. USSR* (*Engl. Transl.*) **1965**, *1*, 1884), Meldrum's ester and isopropylidene malonate (Neilands, O.; Karele, B. *J. Org. Chem. USSR* (*Engl. Transl.*) **1971**, *7*, 1674), and barbituric acid and *N*,*N*-dimethylbarbituric acid (Neilands, O.; Neiman, D. E. *J. Org. Chem. USSR*. (*Engl. Transl.*) **1970**, *6*, 2522). (b) Monocarbonyl ylides of the type ArI=CHCOR have not been isolated presumably due to the lack of sufficient stabilization of the carbanionic system (the present authors have proposed the intermediacy of ArI(OH)CH_2COAr in the reaction of ArI=O with $ArCOCH_3$). The final product in this reaction results from I^{III}–C cleavage rather than loss of H_2O (to form the ylide).

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