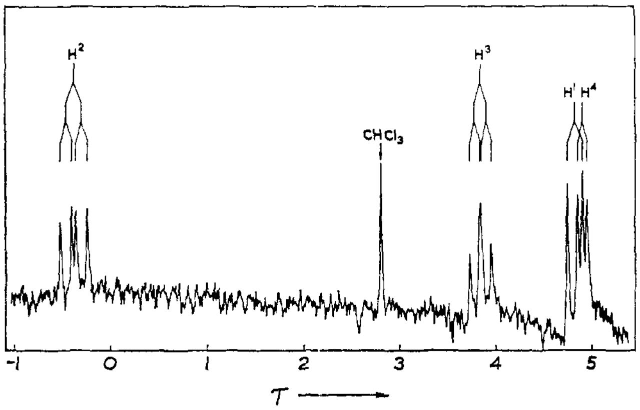

Figure 1. Nmr spectrum at 35° of 2,8,10,16-tetradehydro[17]-annulenone (**5**), measured in deuteriochloroform at 100 MHz.

(ϵ 48,000), 461 (710), *ca.* 500 sh (640), and *ca.* 550 sh (250):[11] $\nu_{\max}^{\mathrm{CHCl_3}}$ (cm^{-1}) 2190 (s) (C≡C), 1628 (s) (C=O), 1585 (m) (C=C), and 980 (m) (*trans* C=C); mass spectrum, molecular ion *m/e* 228, base peak *m/e* 200 (M − CO). Catalytic hydrogenation of **5** in ethanol over 10% palladium–charcoal led to cycloheptadecanone (identified by mass spectral comparison with an authentic sample), showing the compound to be monocyclic.

The nmr spectrum of **5** at 35°[12] (Figure 1) confirms the structure. The 2H double doublet at τ −0.31 is assigned to the inner H^2 protons ($J_{2,1}$ = 16 Hz, $J_{2,3}$ = 12 Hz), the 2H incompletely resolved double doublet at τ 3.88 to the outer H^3 protons ($J_{3,2}$ = 12 Hz, $J_{3,4}$ = 10 Hz), the 2H doublet at τ 4.87 to the outer H^1 protons ($J_{1,2}$ = 16 Hz), and the 2H doublet at τ 4.95 to the outer H^4 protons ($J_{4,3}$ = 10 Hz). The assignments were confirmed by frequency-swept double-irradiation experiments. The low-field position of the inner protons and the high-field position of the outer protons resemble those of the similarly placed protons in 1,9-bisdehydro-[16]annulene (**7**) at −80° (inner protons, τ 0.2; outer protons, τ 3.92–4.55)[13] and clearly indicate the existence of a magnetically induced paramagnetic ring current in the annulenone **5**.

Dehydroannulenes have been prepared previously by isomerization of certain cyclic polyacetylenes with potassium *t*-butoxide in *t*-butyl alcohol, and this procedure usually yielded small amounts of dehydroannulenes containing two fewer protons than the precursors as by-products.[14] By comparison, the presently observed formation of **5** (containing four fewer protons than the precursor **4**) as sole product is unusual. However, treatment of **4** in freshly distilled tetrahydrofuran with potassium *t*-butoxide in *t*-butyl alcohol at −70 to −20° yielded two new unstable red substances (probably also dehydro[17]annulenones), and no **5**. Unfortunately, these compounds decomposed on attempted determination of the mass spectra, and the structures are still unknown.

Acknowledgments. We are indebted to the Science Research Council for financial support and to Dr. R. H. Mitchell for determining the mass spectrum of **5**.

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[11] The ϵ values are approximate and represent minimum values.

[12] The spectrum at − 60° was essentially unchanged.

[13] I. C. Calder, Y. Gaoni, P. J. Garratt, and F. Sondheimer, *J. Amer. Chem. Soc.*, **90**, 4954 (1968).

[14] F. Sondheimer, Y. Gaoni, L. M. Jackman, N. A. Bailey, and R. Mason, *ibid.*, **84**, 4595 (1962); R. Wolovsky, *ibid.*, **87**, 3638 (1965); F. Sondheimer, R. Wolovsky, P. J. Garratt, and I. C. Calder, *ibid.*, **88**, 2610 (1966); I. C. Calder, Y. Gaoni, and F. Sondheimer, *ibid.*, **90**, 4946 (1968).

A Dimeric Iron(III) Complex Containing Two Ethyl Mercaptide and Two Ethyl Thioxanthate Groups as Bridging Ligands

Sir:

Recently we have been investigating the coordination chemistry of iron–sulfur complexes of possible relevance to certain nonheme iron protein (NHIP) systems.[1,2] Since sulfur-bridged iron(III) dimers and higher oligomers have been postulated for the NHIP,[3,4] one objective of our research has been to prepare and characterize inorganic analogs of similar structure. The reaction shown in eq 1 (R = $\mathrm{C_6H_5CH_2}$) was discovered

$$\mathrm{Fe(S_2CSR)_3} \xrightarrow[\mathrm{C_2H_5OH}]{\mathrm{THF}} [\mathrm{Fe(S_2CSR)_2(SR)}]_2 + 2\mathrm{CS_2} \qquad (1)$$

by one of us[5] during the course of a systematic investigation of trithiocarbonate ester complexes of nickel.[6] The product was originally formulated as a μ-benzylthio-bis(benzyltrithiocarbonato)iron(III) dimer (isomer II below) by analogy to the nickel complexes, although no physical measurements were reported at that time.[5] Since the reaction shown in eq 1 provides an interesting route to possible NHIP analogs, we decided to study it and the products more carefully. The present communication reports the solid-state and solution structural characterization of the compound, $[\mathrm{Fe(S_2CSC_2H_5)_2(SC_2H_5)}]_2$.

The ethyl complex was prepared according to eq 1[7] and recrystallized from carbon disulfide–pentane. *Anal.* Calcd for $\mathrm{C_8H_{15}S_7Fe}$: C, 24.5; H, 3.86. Found: C, 24.4; H, 3.91. Dark red-brown prisms suitable for X-ray diffraction studies were obtained. Preliminary Weissenberg and precession photographs revealed the Laue symmetry, 2/m, with lattice constants a = 12.19 ± 0.01 Å, b = 8.47 + 0.01 Å, c = 19.82 ± 0.01 Å, β = 130.1 ± 0.1°, and space group $P2_1/c$. The measured density, ρ = 1.64 g/cc, is in good agreement with the value calculated for four formula units of $\mathrm{C_8H_{15}S_7Fe}$ per unit cell, 1.66 g/cc. Intensity data were collected on a Picker full-circle automated diffractom-

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[1] D. Coucouvanis and S. J. Lippard, *J. Am. Chem. Soc.*, **90**, 3281 (1968).

[2] D. Coucouvanis and S. J. Lippard, *ibid.*, **91**, 307 (1969).

[3] A. San Pietro, Ed., "Non-Heme Iron Proteins: Role in Energy Conversion," Antioch Press, Yellow Springs, Ohio, 1965.

[4] R. Malkin and J. C. Rabinowitz, *Ann. Rev. Biochem.*, **36**, 113 (1967).

[5] D. Coucouvanis, Ph.D. Thesis, Case Institute of Technology, 1967.

[6] Work on the nickel complexes is actively being pursued in Professor J. P. Fackler's laboratory, Case-Western Reserve University.

[7] The complex $[\mathrm{Fe(S_2CSC_2H_5)_3}]$ has been previously reported by Ewald and Sinn.[8]

[8] A. H. Ewald and E. Sinn, *Austral. J. Chem.*, **21**, 927 (1968).

eter, corrected for absorption and Lp effects, placed on a common scale by Wilson's method, and used to compute a three-dimensional Patterson map. Solution of the Patterson revealed the location of the iron and two sulfur atoms, which enabled the complete structure to be determined in subsequent Fourier and least-squares refinement calculations.[9] At present the conventional R^{10} factor for isotropic refinement of all nonhydrogen atoms is 0.086 for 1465 independent nonzero reflections.

The molecular structure is shown in Figure 1. Selected bond distances and angles are summarized in Table I. The complex is a centrosymmetric dimer with ethyl mercaptide bridges. In addition, two thioxanthate ligands function as bridging groups, a mode of ligation commonly found among the complexes of simple carboxylic acids.[11] The remaining two ethyl thioxanthate groups are terminal and complete the distorted octahedral coordination spheres of the two iron atoms. Thus, ignoring the ethyl groups, the approximate symmetry is D_{2h}. If each iron atom is assumed to accept six electron pairs from six sulfur atoms in d^2sp^3 hybrid orbitals, a total of six metal d orbitals remain to accommodate the ten electrons of two Fe(III) atoms. Taking the x and y axes on each iron atom to lie nearly along the metal–sulfur bonds, a set of molecular orbitals may be constructed for metal–metal bonding in which the two iron d_{xy} orbitals overlap to form $\sigma(xy)$ and $\sigma^*(xy)$ MO's, and the remaining d_{xz}, d_{yz} orbitals on each atom are approximately degenerate and nonbonding.[12] In terms of this scheme, ten electrons populate the $\sigma(xy)$ and four nonbonding MO's, accounting for the observed diamagnetism (*vide infra*) of the complex and requiring a Fe–Fe σ-bond order of one. The observed Fe–Fe bond distance of 2.61 Å is comparable to similar distances found in other dimeric iron complexes for which metal–metal bonding has been postulated.[13,14] Other geometric features of the molecule, summarized in Table I, are reasonable,[2] and will be discussed in detail in a future publication.

Table I. Average Dimensions in the Molecule[a,b]

Bond	Distance, Å	Interbond angle, deg	
	Iron–Terminal Thioxanthate		
Fe–S	2.34	S–Fe–S	73.4
S–C	1.69	Fe–S–C	87.3
C–S(ethyl)	1.71	S–C–S	112.1
S–C(ethyl)	1.84	S–C–S(ethyl)	123.9
S···S(bite)	2.80	C–S–C(ethyl)	102.7
	Iron–Bridging Thioxanthate		
Fe–Fe	2.61	Fe–S–C	111.8
Fe–S	2.28	S–C–S	126.3
S–C	1.68	S–C–S(ethyl)	116.8
C–S(ethyl)	1.73	C–S–C(ethyl)	107.8
S–C(ethyl)	1.79		
S···S(bite)	3.00		
	Iron–Ethyl Mercaptide		
Fe–S	2.22	S–Fe–S	107.7
S–C(ethyl)	1.85	Fe–S–Fe	72.3
		Fe–S–C(ethyl)	113.2

[a] Values reported are averages of all crystallographically independent dimensions of a given type. [b] Bond distances have individual estimated standard deviations of ±0.01 Å and interbond angles, ±0.7° or less.

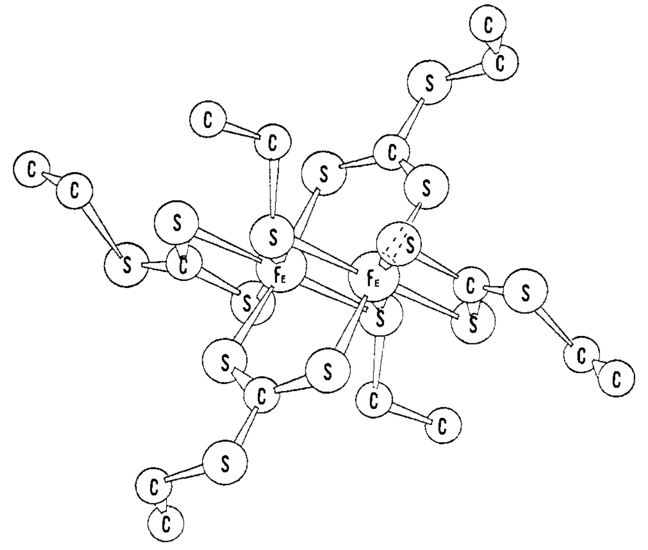
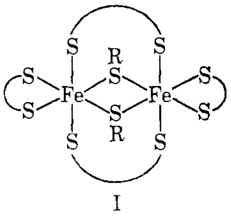


Figure 1. Molecular structure of $[Fe(S_2CSC_2H_5)_2(SC_2H_5)]_2$. The dimer has a crystallograpically required center of symmetry.

In order to investigate the molecular structure in solution, and as a check on the diamagnetism of the complex, 100-MHz proton nmr spectra of CS_2 solutions of $[Fe(S_2CSC_2H_5)_2(SC_2H_5)]_2$ were recorded. From the presence of three equally intense methyl triplets ($J \sim 8$ Hz) at τ 7.95, 8.33, and 9.09 ppm and three methylene quartets ($J \sim 8$ Hz) at 6.25, 7.43, and 7.46 ppm, we conclude that the dimeric structure I, found in the solid state, persists in solution. Isomer II is apparently less stable as in any monomeric form of the complex, at least for the case where R is ethyl. Further studies of this and related molecules (R = benzyl, propyl, butyl) are in progress.



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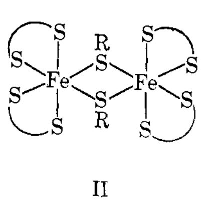

II

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(9) All calculations were performed on the IBM 360-75 computer using modified programs described elsewhere.[2]

(10) Defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$.

(11) C. Oldham, *Progr. Inorg. Chem.*, 10, 223 (1968).

(12) Iron–sulfur π bonding could alter the energies of these remaining orbitals.

(13) L. F. Dahl and C. H. Wei, *Inorg. Chem.*, 2, 328 (1963).

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(15) Fellow of the Alfred P. Sloan Foundation, and author to whom correspondence should be addressed.

(16) Woodrow Wilson Fellow, 1966–1967; National Institutes of Health Predoctoral Fellow, 1967–present.

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