

Addition of Activated Acetylenes to Coordinated Polysulfide Ligands. 2.¹ Synthesis of the $\text{Fe}_2[\text{S}_2\text{C}_2(\text{COOCH}_3)_2]_4^{2-}$ Dithiolene Complex by the Addition of $\text{CH}_3\text{OCC}\equiv\text{CCOOCH}_3$ to the $(\text{Fe}_2\text{S}_{12})^{2-}$ Anion. Crystal and Molecular Structure of $(\text{Ph}_4\text{P})_2\text{Fe}_2[\text{S}_2\text{C}_2(\text{COOCH}_3)_2]_4$

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The reaction of $(\text{Ph}_4\text{P})_2\text{Fe}_2\text{S}_{12}$ and $\text{CH}_3\text{OCC}\equiv\text{CCOOCH}_3$ in dimethylformamide (DMF) in a 1:2 molar ratio proceeds readily to afford the new $(\text{Ph}_4\text{P})_2\text{Fe}_2[\text{S}_2\text{C}_2(\text{COOCH}_3)_2]_4 \cdot 2\text{DMF}$ complex in 69% yield. The complex crystallizes in the triclinic space group $P\bar{1}$ ($Z = 2$) with one molecule per unit cell. The cell dimensions are $a = 12.343$ (4) Å, $b = 13.710$ (5) Å, $c = 14.787$ (8) Å, $\alpha = 63.79$ (4)°, $\beta = 68.23$ (4)°, and $\gamma = 85.32$ (3)°. Intensity data were collected with a P3F Nicolet automated diffractometer using the θ - 2θ scan mode. All the non-hydrogen atoms were refined anisotropically. Full-matrix least-squares refinement of 351 parameters on 2886 data gave final $R_w = 7.03\%$ and $R = 5.15\%$. The hydrogen atoms were included in their calculated positions but were not refined. The anion is located on the crystallographic center of symmetry with the $[\text{Fe}(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)_2]^-$ fragment as the asymmetric unit. The Fe(III) atoms are found in a tetragonal-pyramidal coordination environment with one basal sulfur S(3) on one Fe atom serving as the axial ligand for the other centrosymmetrically related Fe atom. The Fe-S(1) and Fe-S(2) basal bond lengths of the terminal ligand are 2.230 (2) Å. The other two basal Fe-S(3) and Fe-S(4) bonds of the bridging ligand are 2.256 (2) and 2.243 (2) Å, respectively. The axial bridging Fe-S(3') bond length is 2.466 (2) Å. Solution electronic spectral, electrochemical, ¹H NMR spectroscopic, and magnetic studies show that the dimeric structure is preserved in weakly dielectric media while in highly polar coordinating media the axial bridging interactions within the dimer are replaced by solvent coordination and the monomeric structure prevails with the system in a paramagnetic $S = 3/2$ state. The magnetic moments range from 3.78 to 1.87 μ_B in different solutions in the order $\text{Me}_2\text{SO} \sim \text{DMF} > \text{CH}_3\text{CN} > \text{CH}_2\text{Cl}_2$. EPR spectra at 93 K in DMF and Me_2SO show absorptions characteristic of a $S = 3/2$ spin ground state.

Introduction

Recently we have initiated studies on the reactivity of specific Mo-S complexes toward carbon disulfide and activated acetylenes¹ and have considered a possible relevance to the problem of understanding the heterogeneous hydrodesulfurization reaction.^{1,3} As an extension of our interest toward the chemical behavior of other binary M-S complexes with activated acetylenes, we report herein on the reaction of the $(\text{Ph}_4\text{P})_2\text{Fe}_2\text{S}_{12}$ complex⁴ with 2-butynedioic acid dimethyl ester (DMA) in dimethylformamide (DMF) in a 1:2 molar ratio and on the crystal and molecular structure of the resulting product $(\text{Ph}_4\text{P})_2\text{Fe}_2[\text{S}_2\text{C}_2(\text{COOCH}_3)_2]_4 \cdot 2\text{DMF}$ (I). The anion in this new complex contains the 1,2-bis(methoxycarbonyl)-dithiolene ligand and is analogous to the $\text{Fe}_2(\text{S}_2\text{C}_2(\text{CN})_2)_4^{2-}$ anion, a fully structurally characterized, Fe(III) dithiolene dimer.^{5,6} The $\text{M}_2(\text{dithiolene})_4^n$ complexes have been investigated previously and shown to exist as dimeric units.^{5,7}

The reactions between the organometallic polysulfide complexes of the type $(\text{Cp})_2\text{MX}_5$ ($X = \text{S}, \text{Se}; \text{M} = \text{Ti}, \text{V}$) and activated acetylenes such as DMA and diphenylacetylene have been reported by Rauchfuss and co-workers.⁸ In all cases the 1,2-dithiolene metal complexes also were formed. In this work we describe some of the chemical spectroscopic and electrochemical properties of I.

Experimental Section

Synthesis. The chemicals in this research were used as purchased. Dimethylformamide (DMF) was stored over 4-Å Linde molecular sieves for 24 h and then distilled under reduced pressure at $\sim 30^\circ\text{C}$. Acetonitrile (CH_3CN) and dichloromethane (CH_2Cl_2) were distilled from calcium hydride before use. Elemental analysis on samples dried under vacuum for 6-12 h were performed by Galbraith Analytical Laboratories, Knoxville, TN. Dimethyl acetylenedicarboxylate (DMA) was purchased from Aldrich Chemical Co. All solvents used in the electrochemical measurements were properly dried and distilled, and tetra-*n*-butylammonium perchlorate ($n\text{-Bu}_4\text{NClO}_4$) was used as the supporting electrolyte. Usual concentration of supporting electrolyte was 0.1 M. Purified argon was used to purge the solutions prior to the electrochemical measurements. The solutions for EPR spectra were prepared under a dinitrogen atmosphere in ~ 1 mM sample concentrations and were rapidly frozen in liquid nitrogen.

Physical Measurements. A three-electrode potentiostat (Princeton Applied Research Model 173 potentiostat/galvanostat with a Model 175 universal programmer) was used for the cyclic voltametric experiments. Cyclic voltammograms were recorded on a Hewlett-Packard X-Y recorder. The scans were initiated at the rest potential of each solution. The working electrode and counterelectrode were a platinum bead and coil, respectively. The reference electrode was the SCE.

Proton NMR spectra were recorded on a JEOL FX-90Q Fourier transform instrument irradiating at 89.56 MHz. This instrument was used to obtain the μ_{eff} values with the Evans NMR method.⁹ Measurements were carried out in deuterated solutions with use of 2% $(\text{CH}_3)_4\text{Si}$ as an internal reference.

Visible-UV spectra were recorded on a Varian Cary Model 219 spectrophotometer. EPR spectra were recorded on a Varian E-104A X-band spectrometer.

Preparation of Bis(tetraphenylphosphonium) μ -Tetrakis(bis(methoxycarbonyl)ethylene-1,2-dithiolato-S,S')diferrate(III), $(\text{Ph}_4\text{P})_2\text{Fe}_2(\text{DMA})_4 \cdot 2\text{DMF}$. To a solution of 2.60 g (2.21 mmol) of $(\text{Ph}_4\text{P})_2\text{Fe}_2\text{S}_{12}$ in 60 mL of DMF was added 1.26 mL of $\text{MeOCC}\equiv\text{CCOOMe}$ (4.42 mmol), and the mixture was stirred for ca. 20 min until its color became deep brown-red. The solution was filtered, and to the filtrate was added 200 mL of diethyl ether until incipient crystallization. When the mixture was allowed to stand

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- (2) Present permanent address: Department of Chemistry, University of Michigan, Ann Arbor, MI 48109.
- (3) Coucouvanis, D.; Draganjac, M. *J. Am. Chem. Soc.* **1982**, *104*, 6820.
- (4) Coucouvanis, D.; Swenson, D.; Stremple, P.; Baenziger, N. C. *J. Am. Chem. Soc.* **1979**, *101*, 3392.
- (5) (a) Hamilton, W. C.; Bernal, I. *Inorg. Chem.* **1967**, *6*, 2003. (b) MNT^{2-} = sulfidomaleonitrile.
- (6) The crystal structure of the analogous $(n\text{-Bu}_4\text{N})_2\text{Fe}_2(\text{tdf})_4$ ($\text{tdf} = \text{S}_2\text{C}_2(\text{CF}_3)_2^{2-}$) compound was only briefly reported as an abstract: Epstein, E. F.; Bernal, I. Abstracts, American Crystallographic Association Meeting, University of South Carolina, Jan 1971; No. 14.
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Table I. Summary of Crystal, Intensity Collection, and Structure Refinement Data for $(\text{Ph}_4\text{P})_2\text{Fe}_2[\text{S}_2\text{C}_2(\text{COOCH}_3)_2]_2 \cdot 2\text{DMF}$

formula	$\text{C}_{78}\text{H}_{78}\text{N}_2\text{O}_{18}\text{P}_2\text{Fe}_2\text{S}_8$
mol wt	1760
<i>a</i> , Å	12.343 (4)
<i>b</i> , Å	13.710 (5)
<i>c</i> , Å	14.787 (8)
α , deg	63.79 (4)
β , deg	68.23 (4)
γ , deg	85.32 (3)
<i>V</i> , Å ³ ; <i>Z</i>	2074.7; 2
<i>d</i> _{calcd} , g/cm ³	1.41
<i>d</i> _{obsd} , g/cm ³ ^a	1.43
space group	<i>P</i> $\bar{1}$
cryst dimens, mm	0.70 × 0.19 × 0.04
abs coeff (μ), cm ⁻¹	6.6
radiation	Mo K α_1 ($\lambda = 0.70926$)
data colld ^b	<i>h, ±k, ±l</i> , $2\theta = 41^\circ$
no. of unique data	4124
data used in refinement, $F_o^2 > 3\sigma(F_o^2)$	2886
no. of atoms in asym unit	94
no. of variables	351
error in observn of unit wt	1.324
<i>R</i> , %	5.15
<i>R</i> _w , %	7.03

^a By flotation in $\text{CCl}_4/\text{pentane}$. ^b At ambient temperature.

^c $R = \sum(F_o - |F_c|)/\sum F_o$; $R_w = (\sum w(F_o - |F_c|)^2/\sum wF_o^2)^{1/2}$.

overnight, nice dark green crystals were deposited and collected by filtration leaving a reddish filtrate; yield 2.70 g (69%). The product can be recrystallized from DMF/diethyl ether mixtures. Anal. Calcd for $\text{C}_{78}\text{H}_{78}\text{N}_2\text{O}_{18}\text{P}_2\text{Fe}_2\text{S}_8$ (mol wt 1760): C, 53.18; H, 4.43; Fe, 6.36; S, 14.54; N, 1.59. Found: C, 52.82; H, 4.61; Fe, 6.65; S, 14.60; N, 1.65.

X-ray Diffraction Measurements. Collection and Reduction¹⁰ of Data. A small crystal of prismatic shape was chosen for data collection. It was sealed inside a 5-mm diameter capillary tube and transferred to a P3/F Nicolet automated four-circle diffractometer equipped with a Nova 3 Data General computer and a 10-megabyte disk drive. Unit cell dimensions were determined, and an orientation matrix was obtained from coordinates of 12 carefully centered reflections. The crystal data and details of the data collection and structure refinement are summarized in Table I.

The intensities of the entire reflection sphere ($\pm h, \pm k, \pm l$) were collected by using Mo K α radiation, monochromatized with a graphite crystal ($2\theta_m = 12.1^\circ$). The intensities of three check reflections were monitored every 100 reflections and did not show any significant loss of intensity over the data collection period. The data were subsequently corrected for Lorentz and polarization effects, and equivalent reflections were averaged. The least-squares program minimizes the function $\sum w(\Delta|F|)^2$. Accurate cell dimensions were obtained from the least-squares refinement of 2θ , ω , ϕ , and χ values of 25 carefully centered reflections with 2θ between 26 and 35° .

Determination of the Structure of $(\text{Ph}_4\text{P})_2\text{Fe}_2[\text{S}_2\text{C}_2(\text{COOCH}_3)_2]_2 \cdot 2\text{DMF}$. The crystal structure was solved by direct methods using the program MULTAN.¹¹ The iron, sulfur, and phosphorus atoms were located in the first list of atom coordinates. The phases from reflections with high $|E|$ values arising from the known positions of the heavy atoms (Fe, S, and P) were used to reveal the positions of 25 additional carbon atoms. Subsequent Fourier synthesis electron density maps revealed the rest of the cation and anion atoms. A full-matrix least-squares isotropic refinement of the model indicated agreement factors $R_w = 0.157$ and $R = 0.115$. At this stage a difference Fourier synthesis map revealed the presence of the DMF solvent molecule. Further isotropic refinement including the DMF atoms converged after four cycles to $R_w = 0.1225$ and $R = 0.0917$. Anisotropic temperature factors were assigned to all atoms, and further refinement converged to an *R* value of 0.0643. In the final refinement,

Table II. Positional Parameters^a of the Non-Hydrogen Atoms of I and Their Standard Deviations

atom	<i>x</i>	<i>y</i>	<i>z</i>
Fe	-0.00389 (8)	0.60214 (7)	0.52146 (9)
S(1)	0.1126 (2)	0.5616 (1)	0.6153 (2)
S(2)	-0.1084 (2)	0.6871 (2)	0.6193 (2)
S(3)	0.1365 (1)	0.5655 (1)	0.3938 (2)
S(4)	-0.0681 (2)	0.7168 (2)	0.3919 (2)
O(1)	0.0668 (6)	0.8829 (5)	0.1134 (6)
O(2)	0.9214 (5)	0.7653 (4)	0.1588 (5)
O(3)	0.2882 (5)	0.5959 (4)	0.1752 (5)
O(4)	0.1744 (5)	0.6909 (5)	0.0847 (5)
O(5)	0.0556 (5)	0.6259 (5)	0.8629 (5)
O(6)	0.1996 (7)	0.5534 (7)	0.7826 (7)
O(7)	-0.0936 (6)	0.8021 (5)	0.7759 (6)
O(8)	0.8036 (6)	0.6374 (6)	0.8816 (6)
P	-0.4823 (2)	0.8276 (1)	0.4369 (2)
CA(1)	0.0480 (6)	0.6091 (5)	0.7152 (6)
CA(2)	0.0494 (6)	0.3393 (5)	0.2829 (6)
CA(3)	0.8883 (7)	0.7094 (7)	0.7930 (8)
CA(4)	0.1087 (7)	0.5911 (6)	0.7895 (7)
CA(5)	0.1095 (9)	0.6182 (8)	0.9368 (8)
CA(6)	0.739 (1)	0.676 (1)	0.963 (1)
CA(7)	0.0263 (6)	0.7117 (5)	0.2758 (6)
CA(8)	0.1148 (6)	0.6483 (5)	0.2714 (6)
CA(9)	0.1928 (7)	0.6473 (6)	0.1690 (7)
CA(10)	1.0094 (7)	0.7966 (7)	0.1730 (7)
CA(11)	0.8965 (8)	0.8424 (9)	0.0646 (8)
CA(12)	0.3679 (9)	0.5937 (7)	0.0750 (8)
C(1)	0.5375 (6)	0.7259 (5)	0.3877 (6)
C(2)	0.6486 (6)	0.7039 (6)	0.3376 (7)
C(3)	0.6655 (6)	0.6205 (6)	0.3087 (7)
C(4)	0.5706 (7)	0.5605 (6)	0.3247 (7)
C(5)	0.4587 (7)	0.5805 (6)	0.3729 (8)
C(6)	0.4399 (6)	0.6623 (6)	0.4058 (7)
C(7)	0.6480 (6)	0.9236 (5)	0.3567 (6)
C(8)	0.7198 (6)	0.9364 (6)	0.4047 (7)
C(9)	0.8225 (7)	1.0067 (6)	0.3391 (7)
C(10)	0.8498 (7)	1.0633 (7)	0.2326 (8)
C(11)	0.7813 (8)	1.0521 (7)	0.1821 (8)
C(12)	0.6775 (7)	0.9798 (6)	0.2463 (7)
C(13)	0.5075 (6)	0.7636 (5)	0.5756 (6)
C(14)	0.5860 (6)	0.6878 (6)	0.6008 (7)
C(15)	0.5858 (6)	0.6410 (6)	0.7059 (7)
C(16)	0.5102 (7)	0.6703 (6)	0.7830 (8)
C(17)	0.4313 (7)	0.7442 (6)	0.7577 (8)
C(18)	0.4299 (6)	0.7929 (6)	0.6539 (7)
C(19)	0.3891 (6)	0.8945 (5)	0.4273 (6)
C(20)	0.3962 (6)	1.0021 (6)	0.3506 (7)
C(21)	0.2946 (7)	1.0498 (6)	0.3414 (7)
C(22)	0.1880 (7)	0.9912 (6)	0.4038 (8)
C(23)	0.1769 (7)	0.8817 (7)	0.4812 (8)
C(24)	0.2788 (6)	0.8362 (6)	0.4913 (7)
CS(1) ^b	0.325 (1)	0.877 (1)	1.180 (1)
CS(2)	0.516 (1)	0.827 (1)	1.095 (1)
CS(3)	0.3944 (9)	0.8934 (9)	0.998 (1)
NS	0.4085 (7)	0.8647 (7)	1.0929 (8)
OS	0.4569 (8)	0.8810 (7)	0.9242 (9)

^a The thermal parameters have been deposited as supplementary material. ^b The last five atoms belong to the DMF solvate molecule.

the 78 hydrogen atoms were included in the structure factor calculation at their calculated positions (0.95 Å from the C atoms) but were not refined. The final *R*_w and *R* values were 0.0703 and 0.0515, respectively. The final parameters of the structure with their esd's as calculated from the inverse least-squares matrix are given in Table II.

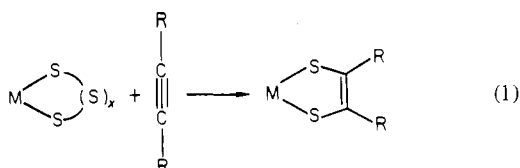
Results and Discussion

Synthesis of $(\text{Ph}_4\text{P})_2\text{Fe}_2(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)_4$. The reaction of the $\text{Fe}_2\text{S}_{12}^{2-}$ anion⁴ with dimethyl acetylenedicarboxylate (DMA) proceeds readily at ambient temperature to afford the new 1,2-dithiolate complex $\text{Fe}_2(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)_4^{2-}$. Dimeric Fe(III) 1,2-dithiolene complexes have been investigated previously in considerable detail. Interest in I derives primarily from the reaction by which it is obtained. This type of reaction

(10) The protocol used in the reduction of data and refinement has been described in detail previously: Coucouvanis, D.; Stremple, P.; Simhon, E. D.; Swenson, D.; Baenziger, N. C.; Draganjac, M.; Chan, L. T.; Simopoulos, A.; Papaefthymion, V.; Kostikas, A.; Petrouleas, V. *Inorg. Chem.* **1983**, *22*, 293.

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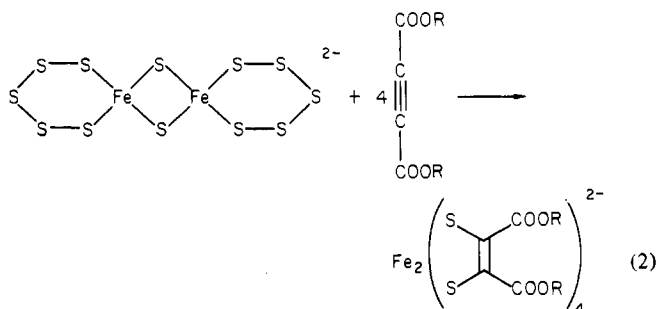
(eq 1) appears to be a general one, and thus far it has been



observed with metal polysulfide complexes of Ti,⁸ V,¹² Mo,¹ and Pt.¹³

The mechanism by which this reaction occurs at present is not understood. In a recent kinetic study, Rauchfuss and co-workers have suggested⁶ that the first step in the reaction between (Cp)₂TiS₅ and DMA might be the formation of a bipolar intermediate. The presence of a carboxylic group on the acetylene molecule enhances the rate of the reaction considerably.¹⁴ The electron-withdrawing COOCH₃ substituents render the acetylenic carbon atoms susceptible to nucleophilic attack by the sulfur lone pairs of the S₅²⁻ ligands. Apparently two sulfur atoms from the S₅²⁻ ligand become available for the formation of the 1,2-dithiolate moiety. The fate of the remaining sulfur atoms in the S₅²⁻ ligand remains to be established; however, it is quite likely that they eventually form elemental sulfur.

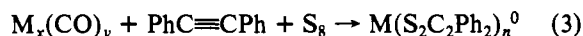
In the reaction of Fe₂S₁₂²⁻ and DMA (eq 2), the possibility



exists that the μ-sulfido ligands in the Fe₂S₂²⁺ core are incorporated into the dithiolene ligand. Whether this indeed occurs is at present a subject open to speculation.

Rakowski et al.¹⁵ have studied the reactions of several organometallic dimeric complexes of molybdenum containing bridging sulfur ligands with alkynes. In these cases the formation of the corresponding 1,2-dithiolate also was observed.

As early as 20 years ago,¹⁶ Schrauzer et al. reported on the formation of 1,2-dithiolate ligands in the reaction of M_x(CO)_y (M = Mo, x = 1, y = 6; M = Fe, x = 3, y = 12) with diphenylacetylene and elemental sulfur (eq 3). More recently



the reaction of Fe₃(CO)₁₂ with S₈ and cyclohexene also was reported to produce Fe 1,2-dithiolate complexes.¹⁷ In view

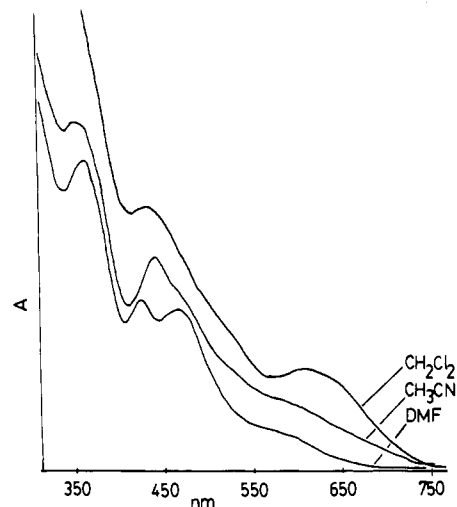


Figure 1. Visible spectra of equimolar solutions of (Ph₄P)₂Fe-[S₂C₂(COOCH₃)₂]₄ in CH₂Cl₂, CH₃CN, and DMF.

Table III. Isotropic Shifts^a of the Proton Resonances, Absorption Maxima, Magnetic Moments,^b and EPR Results^c for I in Various Solvents at 26 °C

solvent ^d	(ΔH/H ₀) _{iso} , ppm	μ _{eff} , μ _B	λ, nm	ε, M ⁻¹	(g _y)	(g _x)	(g _z)
CH ₂ Cl ₂	-0.44	1.87	429	9536	5.53	...	2.08
			608	4282			
			432	6266			
CH ₃ CN	-0.87	2.22	334	10533	4.66	~3.4 (2)	2.08
			432	1866			
			584	1866			
DMF	-0.90	3.66	358	9302	4.79	~3.3 (2)	2.08
			423	4844			
			468	4612			
Me ₂ SO	-0.91	3.78	580	1395	4.79	~3.3 (2)	2.08

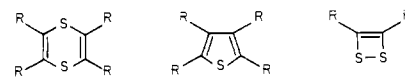
^a (ΔH/H₀)_{iso} = (ΔH/H₀)_{obsd} - (ΔH/H₀)_{dia}; for (ΔH/H₀)_{dia} see ref 25. ^b Diamagnetic correction has been applied to all values. ^c The EPR spectra were recorded as frozen solutions at 93 K. ^d For values concerning the NMR results, all the solvents were completely deuterated.

of the fact that metal carbonyls react with elemental sulfur to produce M-S_x complexes¹⁸ and that M-S_x systems react readily with acetylenes, it is reasonable to assume that these reactions (eq 3) may well involve M-S_x intermediates.^{19,20} A possible mechanistic pathway could be the formation²¹ and oxidative addition of a dithietene to the metal carbonyls (eq 4 and 5).

Not unlike other 1,2-dithiolene iron(III) complexes,²² I exists primarily in its dimeric form in noncoordinating solvents such as CH₂Cl₂ or CH₃NO₂, but it is dissociated into monomeric species in coordinating solvents such as DMF, CH₃CN, or

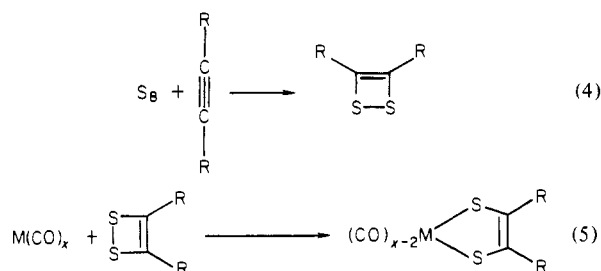
- (12) Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *Organometallics* **1982**, *1*, 1551.
 (13) Fackler, J. P., personal communication.
 (14) The reaction of Fe₂S₁₂²⁻ with PhC≡CH proceeds at a slower rate. If HC≡CH is used instead, no reaction is observed under the same conditions.
 (15) (a) Rakowski DuBois, M.; DuBois, D. L.; vanDerveer, M. C.; Haltiwagner, R. C. *Inorg. Chem.* **1981**, *20*, 3064. (b) DuBois, D. L.; Miller, W. K.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1981**, *103*, 3429.
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 (17) (a) Nametkin, N. S.; Tyurin, V. D.; Aleksandrov, G. G.; Petrosyan, I. V.; Kolobkov, B. I.; Krapivin, A. M.; Struchkov, Yu. T. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, *11*, 2572. (b) Nametkin, N. S.; Tyurin, V. D.; Nekhaev, A. I.; Kondratevai, M. G.; Sobolev, Yu. P. *Ibid.* **1982**, *1*, 217. (c) Nametkin, N. S.; Tyurin, V. D.; Nekhaev, A. I.; Kondratevai, M. G.; Sobolev, Yu. P. *Ibid.* **1982**, *1*, 218.

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 (19) We have oxidized Zn metal with S₈ in the presence of DMA in refluxing DMF solution to produce a new (Et₄N)₂Zn(S₂C₂(COOCH₃)₂)₂ compound, which at present is under characterization. Proof that this compound contains the 1,2-S₂C₂(COOCH₃)₂²⁻ ligand derives from the fact that it reacts with FeCl₃ to give (Et₄N)₂Fe₂(S₂C₂(COOCH₃)₂)₄. The above Zn compound can also be prepared by allowing the reaction product between Zn metal and S₈ in refluxing DMF to react with CH₃OOC≡COOCH₃.
 (20) Seyferth, D.; Henderson, R. S. *J. Organomet. Chem.* **1979**, *182*, C39.
 (21) The reaction between S₈ and CH₃COOC≡CCOOCH₃ proceeds readily in DMF to yield a mixture of products. Preliminary mass spectral evidence indicates that among the products are included



where R = COOCH₃.

- (22) Schultz, A. J.; Eisenberg, R. *Inorg. Chem.* **1973**, *12*, 518.



dimethyl sulfoxide (Me₂SO). Evidence for this behavior is derived from the electronic, ¹H NMR, and EPR spectra as well as electrochemical studies (vide infra) of this complex. Although the synthesis of I must be performed under inert atmosphere, solid samples of the compound are air stable for indefinite periods of time.

The IR spectrum (KBr pellet) of I shows bands primarily derived from cation and ligand transitions. The ν(C=O) and ν(C—O) stretching vibrations absorb at 1700 and 1240 cm⁻¹, respectively, while the ν(C=C) stretch is observed at 1520 cm⁻¹.

The visible electronic spectra of I in three different solvents are depicted in Figure 1. The apparent solvent dependence of the spectra is associated with solvolysis of the dimeric unit in coordinating solvents. The absorption maxima and extinction coefficients of the spectra in three different solvents are included in Table III. The UV-vis spectrum in CH₂Cl₂ represents the undissociated form, and it is identical with the spectrum of a suspension of I in CCl₄. The obvious spectral difference of the complex in CH₃CN and DMF could be attributed to the difference in axial ligation for the monomeric forms and/or differences in the dimer ⇌ monomer equilibrium constants. As indicated, the dimer is completely dissociated into monomers in DMF or Me₂SO solutions. In CH₃CN solution there appears to exist an equilibrium between the two forms with both species in considerable concentrations. Solvents such as DMF or Me₂SO apparently occupy the fifth axial position of a square-pyramidal Fe(III) atom. The five-coordinate adduct of I, [Fe(DMA)₂(SPh)]²⁻, can be isolated from CH₃CN or DMF solutions of I that contain PhS⁻. This adduct-forming behavior of I is consistent with the tendency of other 1,2-dithiolene dimers to form five-coordinate complexes with NO, PR₃, NR₃, and pyridine.²³ The details of the synthesis and structure of the SPh adduct will be reported in a subsequent publication.²⁴

Cyclic Voltammetry. Table IV summarizes all the electrochemical results obtained in three different solvent systems. The electrochemical behavior of I varies with solvent as might be expected, and it is represented by the cyclic voltammograms illustrated in Figures 2 and 3. In dichloromethane solution two reversible oxidation waves are observed at +0.350 and +0.813 V with *i*_{pa}/*v*^{1/2}*C* ratios corresponding to one electron.^{24,25} This uncomplicated electrochemical behavior can be rationalized in terms of the following reactions



and indicates that I in a noncoordinating medium such as dichloromethane is dimeric. The values of the potentials suggest that at least the monoanionic species should be accessible by chemical oxidation.

In DMF the electrochemical behavior changes dramatically. An examination of the range from +1.0 to -1.2 V in this

Table IV. Cyclic Voltammetric Results^a in Various Solvents of the [Ph₄P]₂Fe₂(S₂C₂(COOCH₃)₂)₄ Dimer

	<i>E</i> _{pa} ^b V	<i>E</i> _{pc} ^b - <i>E</i> _{pa} ^b mV	<i>i</i> _{pc} / <i>i</i> _{pa}	concn. mM	<i>i</i> _{pa} / <i>v</i> ^{1/2} <i>C</i>	<i>E</i> _{1/2} ^c V
CH ₂ Cl ₂	0.350	135 ^d	1.00	1.62	42.4	0.282
	0.813	123 ^d	1.00	1.62	41.3	0.751
CH ₃ CN	0.343	81	0.96	1.99	53.2	0.302
DMF ^e	0.467	169	0.38	0.91	115.0	0.382

^a Solutions were 0.1 M in *n*-Bu₄NClO₄. Potentials are reported vs. a saturated calomel electrode. In all parameters reported above the scan rate was 200 mV/s. ^b At Pt working electrode. ^c *E*_{1/2} values were taken as the average of *E*_{pa} and *E*_{pc} values. ^d The *iR* drop in CH₂Cl₂ was not compensated.

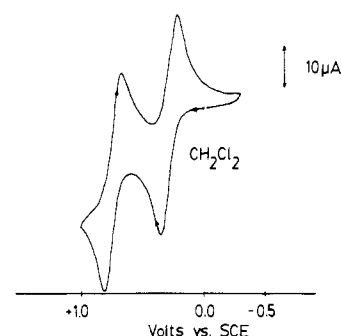


Figure 2. Cyclic voltammogram of 1.62 mM (Ph₄P)₂Fe₂[S₂C₂(COOCH₃)₂]₄ in CH₂Cl₂ (0.1 M *n*-Bu₄NClO₄) at *v* = 0.2 V/s.

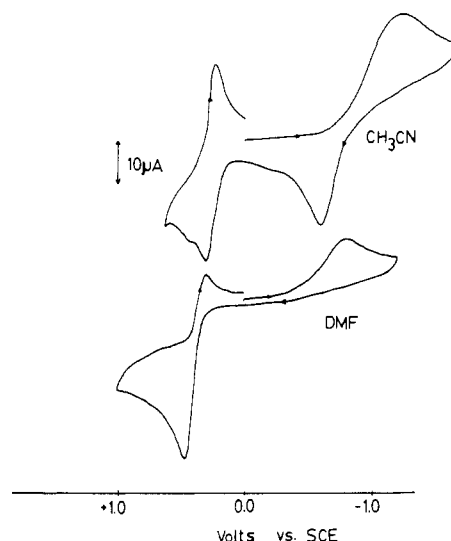


Figure 3. Cyclic voltammograms of (Ph₄P)₂Fe₂[S₂C₂(COOCH₃)₂]₄: (a) in CH₃CN (0.1 M *n*-Bu₄NClO₄); (b) in DMF (0.1 M *n*-Bu₄NClO₄). Concentrations were 1.99 and 0.91 mM, respectively. The scan rate was 0.2 V/s.

solvent shows one irreversible multielectron oxidation wave at 0.467 V. A similar behavior is observed in Me₂SO.

In CH₃CN one irreversible reduction at -1.183 V and an irreversible oxidation wave at -0.566 V appear in the range from 0.0 to -1.6 V. The latter is attributed to the reduction product obtained by the irreversible reduction in the forward process. In scanning the 0.0-+1.0 V range, we observe two oxidation waves at +0.343 and +0.813 V. The first wave indicates a one-electron²⁵ quasi-reversible oxidation and the second wave a multielectron irreversible process. When the switching potential is +0.5 V, the wave at +0.343 V becomes completely reversible (see Figure 3). This wave is attributed to the Fe₂(DMA)₄^{2-/1-} couple. Such behavior has been observed previously in the electrochemistry of the Fe₂(S₂C₂(CN)₂)₄²⁻ (II) and Fe₂(S₂C₂(CF₃)₂)₄²⁻ (III) anions by Balch, Dance, and Holm²⁶ and was explained in terms of monomer

(23) Eisenberg, R. *Prog. Inorg. Chem.* 1971, 12, 295.

(24) Kanatzidis, M. G.; Coucouvanis, D., to be submitted for publication.

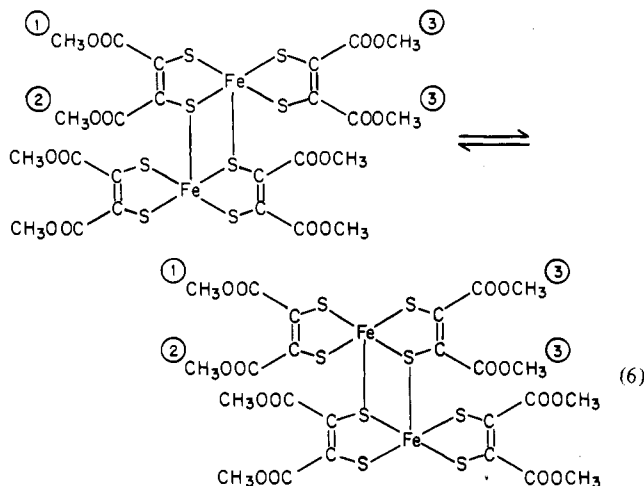
(25) The current function *i*_{pa}/*v*^{1/2}*C*^{*} was calculated on the assumption that the complex is in solution in its dimeric form. If the assumption is made that in solution the compound exists as a monomer, the current function value corresponds to a half electron.

\rightleftharpoons dimer equilibria, with the dimeric forms being electroactive at those potentials. According to these authors, the dimeric forms are consumed at the electrode and therefore drive the equilibria in favor of the dimeric forms. This notion is also supported by the similarity of the first oxidation potential of I in CH_2Cl_2 and CH_3CN , respectively. The reason that the second oxidation wave attributed to the $\text{Fe}_2(\text{DMA})_4^{-/0}$ couple is not observed in CH_3CN at potential greater than 0.700 V is probably because the CH_3CN molecule reacts irreversibly with the neutral species at that potential.²⁷

NMR Spectroscopy and Solution Magnetic Studies. The NMR spectroscopy results are summarized in Table III. The protons of the CH_3 group of the COOCH_3 functional group of the 1,2-dithiolene ligand are observed in the ^1H NMR spectrum as a sharp peak at 4.20 pp isotropically shifted downfield from the diamagnetic value.²⁸ The same signal appears as a broader peak in CH_3CN , DMF, and Me_2SO at 4.62, 4.66, and 4.67 ppm, respectively. This trend reflects the dissociated nature of the dimer in coordinating solvents where the five-coordinate^{26,29} Fe^{III} paramagnetic centers exist.

In CH_2Cl_2 the dimeric form persists giving rise to a sharp slightly shifted signal. In this solvent the two Fe^{III} atoms are believed to be antiferromagnetically coupled. An analogous diamagnetic behavior is found in II and III.²⁹

The NMR spectra at temperatures as low as -40°C show that the two potentially different methyl groups in the monomer as well as the methyl groups in the dimer are equivalent. This equivalency probably arises as a result of rapid rotation around the $-\text{C}-\text{CO}$ bond. In the dimer where there can be three different types of CH_3 groups (even with rapid rotation of the COOMe group around the $=\text{C}-\text{COOMe}$ bond), the presence of only one CH_3 signal in CH_2Cl_2 is interesting. It could be explained in terms of either insufficient instrumental resolution or a dynamic equilibrium that averages out the environment around the CH_3 groups (eq 6).



(26) Balch, A. L.; Dance, I. G.; Holm, R. H. *J. Am. Chem. Soc.* **1968**, *90*, 1139.

(27) Very similar cyclic voltametric behavior is observed in another relatively noncoordinating solvent, CH_3NO_2 . The oxidation waves in this solvent are observed at +0.271 and +0.740 V, respectively, on a Pt electrode using 0.1 M *n*- Bu_4NClO_4 supporting electrolyte. In CH_3NO_2 solution, the second wave appears to be quasi-reversible in nature and tends to become completely reversible at rate $V > 1000$ mV/s. At the lowest scan rate studied, 50 mV/s, the i_{pc}/i_{pa} ratio was 0.70 while at 1000 mV/s it was 0.96. It appears that there exists a chemical reaction following the second electron transfer. The rate of this reaction, which most likely may involve the CH_3NO_2 molecule, is slow enough to compete against the reverse wave at higher scan rates as follows:



(28) This value was taken as 3.76 ppm from the diamagnetic $(\text{Cp})_2\text{Ti}(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)$ from ref 7.

(29) Davidson, A.; Edelstein, N.; Holm, R. H.; Maki, A. H. *Inorg. Chem.* **1964**, *3*, 814.

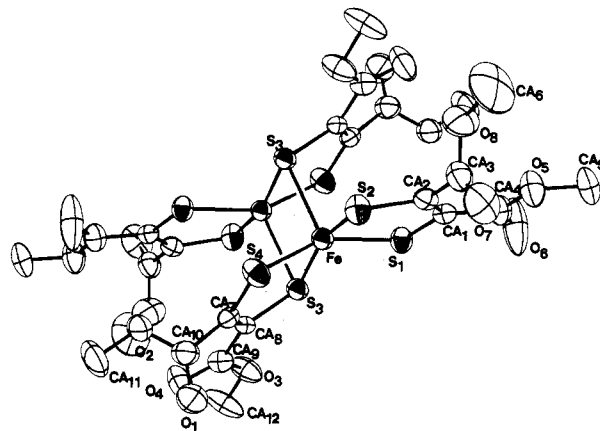


Figure 4. Structure and labeling of the $\text{Fe}_2[\text{S}_2\text{C}_2(\text{COOCH}_3)_2]_4^{2-}$ anion. Thermal motion is represented by 50% probability ellipsoids as drawn by ORTEP.⁴⁰

The foregoing evidence for dimer–monomer dissociation is complemented by the solution magnetic studies. The μ_{eff} (spin-only) value increases in the order $\text{Me}_2\text{SO} \sim \text{DMF} > \text{CH}_3\text{CN} > \text{CH}_2\text{Cl}_2$. The magnetic moments in these solvents are shown in Table III. The intermediate μ_{eff} value in CH_3CN supports the postulation of the dimer \rightleftharpoons monomer equilibrium in this solvent. The μ_{eff} values in Me_2SO and DMF are representative of $S = 3/2$ spin systems. Analogous behavior has been encountered in the solution studies of II and III.²⁹ The small magnetic moment exhibited in CH_2Cl_2 could be due to Boltzmann population of higher lying magnetic states at room temperature.

EPR Spectra. EPR spectra of I at $\sim 93^\circ\text{K}$ in DMF and Me_2SO glasses were recorded and indicate $S = 3/2$ spin systems possessing rhombic symmetry. The observed g values are listed in Table III and are assigned from theory³⁰ to transitions within the $|\pm 1/2\rangle$ Kramers doublet. A weak absorption at $g = 5.9$ also appears as a shoulder to the $g \sim 4.6$ in DMF and Me_2SO . According to the theory,³¹ this signal may be assigned to the g_z component of the $|\pm 3/2\rangle$ Kramers doublet. The g_x and g_y components occur at a magnetic field too high to be accessible by normal EPR spectroscopy. For $g_x \sim 3.3$ in DMF and 3.1 in Me_2SO , the spectra are consistent with $|E/D| \sim 0.11$ and 0.14, respectively.³⁰ These values compare favorably with the g values ($g_x = 3.74$, $g_x = 4.21$, $g_z = 2.03$) reported for the structurally and electronically analogous³¹ $\text{FeCl}(\text{S}_2\text{CN}(i\text{-C}_3\text{H}_7)_2)_2$. The latter is a member of a general series of compounds with the formula $\text{FeX}(\text{S}_2\text{CNR}_2)_2$ ($X = \text{Cl}, \text{Br}, \text{I}$) with established nondegenerate $^4\text{A}_2$ ground states. To date, to the best of our knowledge, solution EPR spectra of dimeric $\text{Fe}_2(\text{dithiolene})_4^{2-}$ compounds have not been studied or reported. The EPR results support the hypothesis that five-coordinate species with quartet ground states exist in coordinating solvents. A quartet ground state for four- and six-coordinate Fe^{3+} atoms is highly unlikely.³²

The EPR spectrum of I in a solvent such as CH_3CN is quite different from that in DMF or Me_2SO . In CH_3CN the dimer appears to be in equilibrium with the monomer, and apparently the monomeric species gives rise to the EPR signals at $g_1 = 5.53$ and $g_2 = 2.08$. The g_2 component shows hyperfine structure with three individual lines with a splitting of 110 G. The pronounced difference of the EPR spectrum in CH_3CN reflects possible structural or electronic differences of the

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(31) Wickman, H. H.; Merrit, R. F. *Chem. Phys. Lett.* **1967**, *1*, 117.

(32) Carlin, R. L.; van Duynveldt, A. J. In "Magnetic Properties of Transition Metal Compounds"; Springer-Verlag: New York, 1977; p 226.

Table V. Selected Structural Parameters of Some 1,2-Dithiolene Fe(III) Dimeric Compounds (Distances in Å and Angles in deg)

	Fe ₂ (MNT) ₄ ²⁻ ^a	Fe ₂ (EDT) ₄ ²⁻ ^b	Fe ₂ (DMA) ₄ ²⁻ ^c	Fe ₂ (TFD) ₄ ²⁻ ^d
Fe-Fe	3.083 (5)	3.410 (3)	3.120 (2)	2.767 (4)
Fe-S(1)	2.200 (7)	2.220 (3)	2.230 (2)	2.177 (4)
Fe-S(2)	2.200 (7)	2.247 (3)	2.230 (2)	2.173 (4)
Fe-S(3)	2.280 (7)	2.265 (3)	2.256 (2)	2.204 (4)
Fe-S(4)	2.250 (7)	2.236 (3)	2.243 (2)	2.205 (4)
Fe-S(3)'	2.460 (7)	2.503 (3)	2.466 (2)	2.311 (5)
S(1)-Fe-S(3)	99.00 (30)	111.20 (10)	105.02 (10)	106.7 (1)
S(1)-Fe-S(2)	90.00 (30)	89.50 (10)	88.08 (10)	88.6 (1)
S(1)-Fe-S(3)	88.00 (30)	88.00 (10)	89.38 (9)	86.0 (1)
S(1)-Fe-S(4)		142.10 (10)	152.76 (11)	155.5 (1)
S(2)-Fe-S(3)		98.9 (10)	100.12 (10)	100.7 (1)
S(2)-Fe-S(3)			162.36 (11)	154.4 (1)
S(2)-Fe-S(4)	88.00 (30)	87.60 (10)	85.97 (9)	87.7 (1)
S(3)-Fe-S(3)	99.00 (30)	88.80 (10)	97.40 (11)	104.9 (1)
S(3)-Fe-S(4)	90.00 (30)	89.70 (10)	88.35 (10)	88.6 (1)
S(4)-Fe-S(3)		106.6 (10)	102.12 (10)	96.4 (1)
Fe-S(3)-Fe	81.00 (30)	91.20 (10)	82.60 (8)	75.1 (1)
S(1)-CA(1)	1.73		1.770 (7)	1.703 (9)
S(2)-CA(2)	...		1.740 (8)	1.687 (9)
S(5)-CA(8)	...		1.769 (7)	1.763 (9)
S(4)-CA(7)	...		1.708 (8)	1.701 (9)
CA(1)-CA(2)	1.39		1.343 (9)	1.33 (1)
CA(7)-CA(8)	1.39		1.340 (9)	1.33 (1)

^a MNT = 1,2-dicyanoethylenedithiolate; ref 5 and 6. ^b EDT = 1,2-ethanedithiolate; ref 34. ^c DMA = 1,2-bis(methoxycarbonyl)-ethylenedithiolate; this work. ^d TFD = 1,2-bis(trifluoromethyl)ethylenedithiolate; ref 22.

Table VI. Selected Interatomic Distances (Å) and Angles (deg) Other Than Those Listed in Table V in the Fe₂[S₂C₂(COOCH₃)₂]₄²⁻ Anion

Distances			
S(1)-S(2)	3.100 (3)	CA(4)-O(6)	1.204 (9)
S(1)-S(3)	3.155 (3)	CA(4)-O(5)	1.309 (9)
S(2)-S(4)	3.050 (3)	CA(3)-O(7)	1.185 (9)
S(3)-S(4)	3.135 (3)	CA(3)-O(8)	1.339 (11)
S(3)-S(3)	3.550 (4)	CA(9)-O(3)	1.334 (9)
CA(1)-CA(4)	1.472 (10)	CA(9)-O(4)	1.222 (10)
CA(2)-CA(3)	1.495 (11)	CA(10)-O(1)	1.196 (9)
CA(7)-CA(10)	1.530 (11)	CA(10)-O(2)	1.318 (9)
CA(8)-CA(9)	1.468 (11)		
Angles			
Fe-S(2)-CA(2)	105.72 (23)	S(1)-CA(1)-CA(4)	116.44 (40)
Fe-S(1)-CA(1)	105.70 (22)	S(2)-CA(2)-CA(3)	113.17 (38)
Fe-S(3)-CA(8)	104.99 (25)	S(3)-CA(8)-CA(7)	117.80 (43)
Fe-S(4)-CA(7)	104.41 (24)	S(4)-CA(7)-CA(8)	124.42 (42)
S(1)-CA(1)-CA(2)	119.04 (40)	S(3)-CA(8)-CA(9)	120.35 (41)
S(2)-CA(2)-CA(1)	121.02 (41)	S(4)-CA(7)-CA(10)	113.40 (40)

CH₃CN solvated monomeric forms. The absence of absorption at $g \sim 5.9$ in CH₃CN suggests that in this solvent the monomeric form either contains a six-coordinate Fe³⁺ center that has a $S = 5/2$ ground state or exists in an unusual but not unprecedented³³ spin-admixed state of $S = 5/2$ and $S = 3/2$ character.

Description of the Structure. The crystal consists of discrete, well-separated cations and anions. There are no abnormally short interionic contacts. Figure 4 shows the anion with the atomic numbering scheme and Figure 5 (supplementary material) gives a stereoscopic view of the molecular packing in the unit cell. Interatomic distances and angles of the anion are listed in Tables V and VI. The final atomic positional parameters with their standard deviations are compiled in Table II.

The anionic dimeric unit Fe₂[S₂C₂(COOCH₃)₂]₄²⁻ and the center of the Fe₂S₂ rhombus is located on a crystallographic center of symmetry. Each of the iron atoms has a tetragonal-pyramidal coordination geometry. The two 1,2-bis(methoxycarbonyl)dithiolene ligands occupy the basal sites [Fe-S(1) = 2.230 (2) Å, Fe-S(2) = 2.230 (2) Å, Fe-S(3) =

2.256 (2) Å, Fe-S(4) = 2.243 (2) Å]. The axial site is occupied by the sulfur atom S(3)' of another dithiolene ligand that serves as a basal ligand for the centrosymmetrically related Fe atom. The axial Fe-S(3)' distance is the longest iron sulfur distance in the molecule at 2.466 (2) Å. The Fe atom lies 0.434 (1) Å above the nearly perfect plane defined by S(1), S(2), S(3), and S(4) atoms. The S-Fe-S angles in the tetragonal pyramid between the axial Fe-S(3)' bond and the basal Fe-S bonds vary from 97.40 (11) to 105.02 (10)° with a mean value of 101 (3)°. A difference in the average Fe-S distance within the half-dimer between terminal and bridging DMA ligands [2.230 (2) and 2.250 (2) Å, respectively] is apparent.

These structural characteristics are very similar to those reported for the structures of other dimeric complexes with a localized square-pyramidal sulfur environment about an iron atom such as the Fe₂(S₂C₂(CF₃)₂)₄¹⁻ monoanion²² and the Fe₂(S₂C₂(CN)₂)₄²⁻ dianion.⁵ Other complexes that are crystallographically characterized with an iron atom in a total five-coordinate sulfur environment include the Fe₂(S₂C₂H₄)₄²⁻ dianion,³⁴ Fe₂(S₂CNET₂)₄,³⁵ the Fe₄S₄(S₂C₂(CF₃)₂)₄²⁻ dianion,³⁶ and the recently prepared Fe₄S₄(SPh)₂(S₂CNET₂)₂²⁻ mixed-ligand iron sulfur cubane.³⁷ The coordination geometry around the iron atom in the above complexes is square pyramidal with the exception of Fe₂(S₂C₂H₄)₄²⁻ where it is trigonal bipyramidal.

Important structural parameters of some structurally related dimers as well as of I are shown in Table V.

A closer look at the Fe₂(S₂C₂(COOCH₃)₂)₄²⁻ dianion reveals that the bridging S(3)-CA(8)-CA(7)-S(4) ligand fragments are planar with the Fe atom as well as CA(9), CA(10), O(3), and O(4) atoms lying in the plane. This is not true for the terminal S(1)-CA(1)-CA(2)-S(2) fragment that does not define a good plane and shows the S(1) and CA(2) atoms deviating by 0.22 Å above and below the plane, respectively. The Fe atom lies 0.410 (1) Å above the S(1)-CA(1)-CA(2)-S(2) plane. One interesting feature of the S₂C₂-

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(COOCH₃)₂²⁻ ligand, present in both the bridging and terminal modes of binding, is that one carboxylate function is essentially coplanar with the SC=CS frame while the other is approximately perpendicular to it. This structural feature is also observed in the structure of the Mo(S₂C₂(COOCH₃)₂)₃²⁻ anion¹ and in the structures of complexes with the S₂C=C-(COOEt)₂²⁻ (DED) ligand.³⁸

The intermetallic Fe-Fe distance in I is 3.120 (2) Å, considerably shorter than the corresponding distance in Fe₂(EDT)₄²⁻ (II)³⁹ (3.410 (3) Å) but longer than its closer electronic and structural analogue Fe₂(MNT)₄²⁻ (III) (3.083 (5) Å), Table V. Originally the difference between the Fe-Fe distances in II and III was interpreted²² in terms of the considerable electron-withdrawing ability, or π-acidity differences

between the MNT and EDT ligand, with the former being a much stronger π acid. The obvious difference of the same distances in I and III could very well reflect analogous π-acidity differences between the DMA and MNT ligands. This observation is consistent with the greater electron-withdrawing ability of CN vs. COOCH₃.

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Registry No. I, 88358-02-5; (Ph₄P)₂Fe₂S₁₂, 71072-87-2; DMA, 762-42-5; Zn, 7440-66-6; S₈, 10544-50-0.

Supplementary Material Available: Listings of thermal parameters of non-hydrogen atoms, least-squares planes, positional and thermal parameters, and observed and calculated structure factors, and a stereoscopic view of the unit cell (Figure 5) (21 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of a Dinuclear Chromium(III) Complex with a Linear Oxygen Bridge

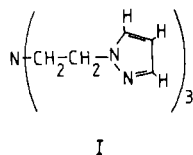
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The dinuclear oxo-bridged chromium(III) complex $[\{\text{Cr}(\text{NCS})(\text{TPyEA})\}_2\text{O}](\text{BPh}_4)_2$, where TPyEA is the tetradentate ligand tris(2-pyrazol-1-ylethyl)amine, is formed by oxidation in CH₃CN or (CH₃)₂CO solution of the chromium(II) complex $[\text{Cr}(\text{NCS})(\text{TPyEA})]\text{BPh}_4$. Crystal data for $[\{\text{Cr}(\text{NCS})(\text{TPyEA})\}_2\text{O}](\text{BPh}_4)_2$: triclinic, $P\bar{1}$, $Z = 2$, $a = 19.098$ (7) Å, $b = 14.688$ (5) Å, $c = 13.826$ (5) Å, $\alpha = 105.83$ (6)°, $\beta = 86.85$ (5)°, $\gamma = 101.78$ (6)°; $R = 0.077$ for 3361 reflections. Each of the metal atoms in the compound is in a distorted-octahedral environment formed by four nitrogen atoms of a TPyEA ligand, by the NCS nitrogen atom, and by the bridging oxygen atom. The Cr-O-Cr bridge is almost linear (Cr-O-Cr = 176.5 (6)°) and symmetrical with a 1.815 (6) Å mean value of the Cr-O distances. The value of μ_{eff} per Cr atom is 1.63 μ_{B} at 300 K and 0.98 μ_{B} at 86 K.

Although transition-metal systems containing two metal atoms linked by one bridging atom have been extensively investigated, only one μ -oxo complex of chromium(III) has been characterized so far in the solid state, namely the (μ -oxo)bis(pentaamminechromium(III)) chloride monohydrate, also known as the "basic rhodo" complex.^{1,2}

We have found that the chromium(II) complex $[\text{Cr}(\text{NCS})(\text{TPyEA})]\text{BPh}_4$ formed by the tetradentate ligand tris(2-pyrazol-1-ylethyl)amine, TPyEA (I), undergoes rapid



oxidation in solution, yielding the (μ -oxo)dichromium(III) complex with the formula $[\{\text{Cr}(\text{NCS})(\text{TPyEA})\}_2\text{O}](\text{BPh}_4)_2$, which has been isolated in the solid state. The structure of the latter complex, determined by X-ray diffraction methods, is reported here, and the spectral and magnetic properties of the compound are briefly discussed.

Experimental Section

Materials. All reagents and solvents used were of reagent grade purity. All operations on both the chromium(II) and the ¹⁸O-labeled (μ -oxo)dichromium(III) complex were carried out in a nitrogen atmosphere with solvents deaerated before their use. Oxygen-18 was purchased from Prochem (London); a sample containing 70% ¹⁸O₂ was employed. The syntheses of the ligand TPyEA and of the anhydrous chromium(II) halides have been reported in previous papers.^{3,4}

Synthesis of $[\{\text{Cr}(\text{NCS})(\text{TPyEA})\}_2\text{O}](\text{BPh}_4)_2$. The ligand (10^{-3} mol) dissolved in 15 mL of ethanol was added to a warm solution of Cr(NCS)₂ (10^{-3} mol) in ethanol (25 mL), prepared in situ by the metathetic reaction of CrBr₂(C₂H₅OH)_n and KNCS dissolved in ethanol. An excess of NaBPh₄ dissolved in 10 mL of boiling ethanol was added to the reactant solution. Crystallization of a blue compound occurred in a short time. The mother liquor was then eliminated by decantation, and the crystalline compound was washed several times by decantation with ethanol and diethyl ether. Finally, the compound was filtered off and dried in a stream of dry nitrogen at 80 °C. Anal. Calcd for C₄₀H₄₁N₈CrBS: C, 65.93; H, 5.67; N, 15.38. Found: C, 65.4; H, 5.55; N, 15.5.

Synthesis of $[\{\text{Cr}(\text{NCS})(\text{TPyEA})\}_2\text{O}](\text{BPh}_4)_2$. The blue $[\text{Cr}(\text{NCS})(\text{TPyEA})]\text{BPh}_4$ complex dissolved in acetone or acetonitrile is oxidized almost instantaneously by atmospheric O₂, giving a green solution from which a crystalline green compound with formula

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