

succinimide, and indoline should in fact favor the low-spin state.³⁰ This corresponds to form **4b** which we have proposed. Unfortunately, to date only the indoline derivative has been reported³¹ and it was shown by Mössbauer isomer shift to be low spin.

Acknowledgment. We would like to thank Professor D. Chasteen of the University of New Hampshire for allowing us use of the Q-band ESR spectrometer and also Professor H. L. Ammon of the University of Maryland for use of computer programs used in the NMR spectral analysis. R.D.B. gratefully acknowledges a Camille and Henry Dreyfus Foundation Fellowship.

Registry No. K(pdte), 62641-74-1; Pd(pdte)₂, 63765-42-4; Pt(pdte)₂, 63765-41-3; Cd(pdte)₂, 52676-51-4; Fe(pdte)₃, 63765-40-2; Co(pdte)₂, 63765-39-9; Cu(pdte)₂, 61155-98-4; PtCl₂(pdte)₂, 63765-38-8; pyrrole, 109-97-7; CS₂, 75-15-0.

Supplementary Material Available: Tables of analytical results and IR and UV-visible data (4 pages). Ordering information is given on any current masthead page.

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Transition Metal Ions in High Formal Oxidation States. Synthesis and Structural Characterization of the Six-Coordinate Iron(IV) Complex of the 1,1-Dicarboethoxy-2,2-ethylenedithiolate Chelating Ligand

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Received March 25, 1977

AIC702213

The synthesis and structural characterization of bis(benzyltriphenylphosphonium) tris(1,1-dicarboethoxyethylene-2,2-dithiolato)ferrate(IV), [C₇H₇(C₆H₅)₃P]₂[(S₂CC(COOC₂H₅)₂)₃Fe] (I), are described. Complex I crystallizes in the monoclinic space group C2/c with four molecules per unit cell. The cell dimensions are $a = 19.114$ (6) Å, $b = 15.424$ (5) Å, $c = 24.308$ (8) Å, and $\beta = 97.50$ (2)°. Intensity data were collected with a four-circle computer-controlled diffractometer using the $\theta-2\theta$ scan technique. All of the atoms in the complex anion and the phosphorus atom in the cation were refined anisotropically. The carbon atoms in the cation were refined isotropically. The hydrogen atoms were included in their predicted positions but were not refined. Refinement by full-matrix least squares on 2350 data for 305 parameters gave a final R value of 0.042. The geometry of the MS₆ moiety in the structure can be described as originating from a trigonal prism which suffers individual rotations of the chelating ligands around the C₂ axes. One of these rotations is more severe than the other two causing a lowering of the overall symmetry to C₂. Values of selected bond distances and bond angles are as follows: Fe-S, 2.289 (2), 2.305 (2), and 2.301 (2) Å; S-S (intraligand), 2.737 (3), and 2.786 (2) Å; S-Fe-S (trans), 159.52 (8) and 158.75 (5)°; S-Fe-S (bite), 74.66 (6) and 72.97 (5)°. A description of the bonding is presented that attributes the stability of the complex to Fe(IV)-S bonding with considerable covalent character.

Introduction

The stability of complexes with metal ions in unusually high formal oxidation states depends to a great extent on the σ -bonding and π -back-bonding properties of the ligands. With sulfur ligands, the ability of the sulfur atoms to participate in π bonding in addition to σ donation allows for the formation of oxidized complexes in which the oxidation state of the metal ion, at least formally, can be described as unusually high. The concept of the "formal" oxidation-state description for the metal ions in oxidized sulfur chelate complexes is an attempt to by-pass the ambiguity concerning the site of oxidation in these complexes, since very often the possibility of ligand

centered oxidations or interligand oxidative interactions does not allow for an unambiguous description of the nature of the oxidation.

Among the 1,1-dithio chelates, the dithiocarbamate ligand seems to stabilize high formal oxidation states of transition metal ions in a variety of complexes.² The ambiguity described previously also is applicable to oxidized dithiocarbamate complexes where interligand oxidative interactions possibly could account for the stability of the oxidized chelates.³ A description which is more in agreement with experimental facts, however, is one that attributes the stability of highly oxidized metal ions in dithiocarbamate complexes to a π -

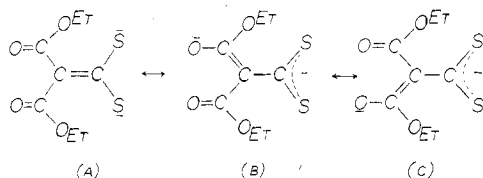


Figure 1. Resonance forms in the 1,1-dithio-2,2-dicarboethoxy-ethylenedithiolate (DED) ligand.

electron flow from the nitrogen atom of the ligand to the sulfur donor atoms.² A ligand which appears to be as effective as the dithiocarbamate ligand in stabilizing metal ions in high formal oxidation states and is characterized by a conjugated π system is the 1,1-dicarboethoxy-2,2-ethylenedithiolate dianion, (DED)²⁻ (Figure 1). Recently we reported on the structures of the Ni(DED)₂²⁻ and the "Cu(III)", Cu(DED)₂⁻ complexes.⁴ On the basis of our results, we suggested that oxidation, of at least the DED complexes, could best be described as loss of electrons from antibonding molecular orbitals composed primarily of metal and sulfur atomic functions.

In a previous communication we reported on the synthesis and characterization of the Fe(DED)₃²⁻ complex anion.⁵ The magnetic properties and Mössbauer spectra of this molecule⁶ were similar to those reported for the iron(IV) dithiocarbamate complexes and indicative of an octahedrally coordinated iron in a d⁴ configuration and a ³T₁ ground state.^{7,8} The crystal structure of the Fe(DED)₃²⁻ complex anion was found to be similar to the one reported for the Fe(pyrr(dtc))₃⁺ cation.⁹

In this paper we report in detail the structure of the Fe(DED)₃²⁻ complex and discuss the nature of the Fe-S bonding. The implication of Fe(IV) in the action of certain peroxidases^{10,11} and the similarity of the Mössbauer spectra of the Fe(DED)₃²⁻ complex⁵ to that of cytochrome *c* peroxidase¹² suggest that the ground-state description of the iron in peroxidase may be similar to that of the iron in the Fe(DED)₃²⁻ complex.

Experimental Section

The chemicals in this research were used as purchased. The synthesis used to obtain potassium 1,1-dicarboethoxy-2,2-ethylenedithiolate has been reported previously.¹³ Analyses were performed by the analytical services laboratory of the Chemistry Department of the University of Iowa.

Synthesis of Bis(benzyltriphenylphosphonium) Tris(1,1-dicarboethoxyethylene-2,2-dithiolato)ferrate(IV), [C₇H₇(C₆H₅)₃P]₂[(S₂CC(COOC₂H₅)₂)₃Fe]. A solution containing 1.10 g (0.041 mol) of FeCl₃·6H₂O in 100 mL of water was added to 4.00 g (0.013 mol) of K₂DED in 500 mL of water. The dark brown complex anion precipitated upon addition of 4.20 g (0.103 mol) of benzyltriphenylphosphonium chloride dissolved in water. The precipitate was washed with water, air-dried, and recrystallized from acetone-pentane mixture, black crystals.

X-Ray Diffraction Measurements. Crystals of benzyltriphenylphosphonium tris(1,1-dicarboethoxy-2,2-ethylenedithiolato)ferrate(IV) suitable for crystallographic studies were obtained by diffusion of *n*-pentane in acetone solutions of the compound. The crystals were needlelike and portions cut from the center of the needles were used for both preliminary work and data collection. Preliminary oscillation and Weissenberg photographs indicated a monoclinic cell, and systematic absences for *hkl*, *h* + *k* ≠ 2*n*, and for *h0l*, *l* ≠ 2*n*, indicated either space group *Cc* or *C2/c*. The latter was confirmed by analysis of the Patterson map and by the successful refinement of the structure.

A fresh crystal of approximate dimensions 0.16 × 0.24 × 0.35 mm was mounted on a glass fiber in air and used for cell dimension determination and data collection. It was mounted on a Picker-Nuclear four-circle diffractometer equipped with a Mo target x-ray tube, graphite monochromator ($2\theta_m = 12.20^\circ$), scintillation counter, and pulse-height analyzer and automated by a DEC PDP-1 computer and disk and FACS-I DOS software.

The preliminary cell dimensions were refined on the setting angles of 12 reflections between 25 and 31° 2θ (Mo K α λ 0.7107 Å), carefully centered in the receiving aperture. The refined dimensions and their

standard deviations are $a = 19.114 \pm 0.006$ Å, $b = 15.424 \pm 0.005$ Å, $c = 24.308 \pm 0.008$ Å, $\beta = 97.50 \pm 0.02^\circ$, $V = 7105$ Å³, d_{calcd} ($Z = 4$) = 1.37 g cm⁻³, and $\rho = 5.0$ cm⁻³. The observed density, measured pycnometrically, was 1.33 ± 0.03 g cm⁻³.

Data were collected using a θ - 2θ scan technique with a base width of 1.0° in 2θ centered on the predicted position for the Mo K α_1 peak (λ 0.709 26 Å) and expanded at the high 2θ end to allow for α_1 - α_2 dispersion. The peak was scanned at a rate of 1.0°/min in 2θ , and 10-s counts were taken with stationary crystal and counter at each end of the scan range to determine background. If the peak height exceeded 10 000 counts/s zirconium attenuation foils were inserted in the diffracted beam and the peak and backgrounds were remeasured with the attenuators in place. Three "standard" reflections ((680), (2,0,14), (930)) were measured after every 100 data points to monitor crystal and instrumental stability. Their intensities showed no systematic variation over the data collection period, and random variations were well within that range predicted by counting statistics.

Data were collected in the hemisphere of reciprocal space $+h + k + l$ to a 2θ value of 40° ($(\sin \theta)/\lambda \leq 0.48$). The 6670 raw data were reduced to net intensities corrected for attenuator factors, converted to F^2 values and equivalent reflections averaged as previously described.¹⁴ Of the 3335 unique reflections 2350 had $F^2 > 3\sigma(F^2)$ and were regarded as "observed" (the "ignorance factor", p , used throughout was 0.04).¹⁴

The least-squares routine used minimizes the function $\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2$, where $w = 0.0$ for those reflections with $F^2 \leq 3\sigma(F^2)$, and $w = 1/\sigma^2(F)$ for all others. All the atomic scattering factors of the neutral nonhydrogen atoms¹⁵ were corrected for both real and imaginary components of dispersion.¹⁶ The scattering factor for hydrogen was taken for the best-fit spherical case of Stewart, Davidson, and Simpson.¹⁷

Solution and Refinement of the Structure. With $Z = 4$ and three ligands around the iron atom, the anion was limited to the special position on the twofold axis in the centric space group. A three-dimensional Patterson map was interpreted to locate the iron atom and the three independent sulfur atoms of the ligands. Successive cycles of least squares followed by electron density maps unequivocally revealed the positions of all nonhydrogen atoms in the cell with the exception of the ethyl carbons of the ligand which was constrained to lie on the twofold axis. Isotropic refinement of these atoms gave a conventional R value of 0.11. On a difference Fourier map from these results the major peaks were near the heavy atoms, due to anisotropic thermal motion, and two very broad peaks of low-electron density near the positions where the ethyl carbons were expected, suggesting either some form of disorder or very large thermal motion. These two additional atoms were added to the refinement and the R value dropped to 0.085 in two cycles. Inclusion of the hydrogen atoms in their predicted positions reduced the R value to 0.073. In all further cycles of least squares they were not refined but predicted after each cycle and given an isotropic thermal parameter equal to that of the carbon to which they were attached or equivalent to the average root mean square thermal motion of the carbon if it was being refined with anisotropic thermal parameters.

All of the atoms of the anion and the phosphorus atom in the cation were then allowed to refine with anisotropic thermal parameters, including the two ethyl carbon atoms of the twofold restricted ligand, C(12) and C(13). (Space limitations on the computer prevented the anisotropic refinement of the entire structure.) Both C(12) and C(13) refined to highly anisotropic parameters for their temperature factors, and in order to recheck the possibilities of disorder they and the hydrogen atoms attached to them were removed from the structure-factor calculations and a difference Fourier was calculated. The peaks on the phased map showed no indication of double maxima, which would suggest disorder, and so it was decided to accept the large thermal motion as "real". After detection and correction of two data collection errors caused by misspunched paper tape, refinement continued for three more cycles of full-matrix least squares to converge at a conventional R value of 0.042 for 305 parameters on 2350 data with $F^2 > 3\sigma(F^2)$, and the R value on all data was 0.062. The weighted R value, R_w ,¹⁸ was 0.051 and the standard deviation of an observation of unit weight was 1.50.¹⁸ All parameter shifts in the last cycle were less than 0.1 times their esd's except those of C(12) and C(13), which were less than 0.3 times their esd's. Inspection of F_o and F_c for high-intensity reflections revealed no indication of secondary extinction. The final difference Fourier map showed no peaks greater than 0.5 e/Å³, and these were near the carbon atoms of the phenyl rings in

Table I. Positional^a and Thermal^b Parameters and Their Standard Deviations^c in Fe(DED)₃(BzlPPH₃)₂

ATCM FE	X	Y	Z	B11	B22	B33	B12	B13	B23
	0	0.18624(7)	0.250	3.11(5)	2.97(6)	3.48(6)	0	0.01(4)	0
S(1)	0.01961(7)	0.1009(1)	0.32749(6)	2.79(6)	3.77(7)	4.12(8)	0.14(6)	0.43(6)	0.70(6)
S(2)	0.11956(7)	0.1587(1)	0.26213(6)	3.19(6)	4.03(8)	3.68(8)	-0.28(6)	0.41(6)	0.67(6)
S(3)	-0.00169(8)	0.3062(1)	0.30610(7)	4.69(8)	3.49(7)	3.90(8)	-0.26(6)	0.06(6)	-0.63(6)
P	0.15178(7)	0.0675(1)	0.60384(6)	3.03(7)	3.13(7)	3.79(8)	-0.50(6)	0.07(6)	0.06(6)
O(1)	0.0935(2)	-0.0107(3)	0.4167(2)	3.3(2)	4.5(2)	5.9(2)	0.2(2)	1.6(2)	1.6(2)
O(2)	0.2063(2)	-0.0511(3)	0.4156(2)	3.3(2)	4.6(2)	4.0(2)	0.8(2)	0.4(2)	1.5(2)
O(3)	0.2762(2)	0.1036(3)	0.3459(2)	3.9(2)	6.0(3)	8.4(3)	-1.3(2)	1.8(2)	-1.3(2)
O(4)	0.2435(2)	-0.0188(3)	0.3036(2)	3.0(2)	6.1(3)	5.5(2)	-0.3(2)	1.2(2)	-2.0(2)
C(1)	0.1478(3)	-0.0059(4)	0.3960(2)	3.1(3)	3.1(3)	3.7(3)	-0.1(2)	0.0(3)	0.2(3)
C(2)	0.1607(3)	0.0493(4)	0.3501(2)	2.2(3)	3.2(3)	3.2(3)	0.1(2)	0.4(2)	0.2(2)
C(3)	0.2327(3)	0.0496(4)	0.3331(2)	2.8(3)	3.7(3)	3.8(3)	-0.5(3)	-0.3(2)	0.2(3)
C(4)	0.1086(3)	0.0965(3)	0.3199(2)	3.2(3)	2.8(3)	3.1(3)	-0.6(2)	0.4(2)	-0.4(2)
C(5)	0.2014(3)	-0.1100(4)	0.4608(3)	5.1(4)	5.0(4)	5.5(4)	1.5(3)	0.7(3)	1.5(3)
C(6)	0.2736(4)	-0.1299(5)	0.4867(3)	6.8(4)	5.5(4)	6.3(4)	1.8(3)	-0.4(3)	1.3(3)
C(7)	0.3123(3)	-0.0295(5)	0.2847(3)	3.8(3)	8.4(5)	5.4(4)	-0.4(3)	1.5(3)	-1.6(4)
C(8)	0.3124(3)	-0.1119(5)	0.2554(3)	4.1(3)	7.0(4)	7.2(4)	0.8(3)	1.4(3)	-0.6(4)
O(5)	0.0376(3)	0.5854(4)	0.3068(3)	10.1(4)	5.0(3)	14.2(5)	-3.0(3)	-0.6(3)	-1.4(3)
O(6)	-0.0170(3)	0.4792(4)	0.3427(3)	10.4(4)	7.5(3)	10.2(4)	-4.1(3)	4.4(4)	-5.1(3)
C(9)	0.0095(4)	0.5160(5)	0.3019(4)	4.3(4)	3.3(4)	10.5(7)	-0.5(3)	0.7(4)	-1.4(4)
C(10)	0	0.4642(6)	0.250	2.7(4)	2.9(5)	7.9(7)	0	1.1(4)	0
C(11)	0	0.3758(6)	0.250	2.6(4)	3.6(5)	5.8(5)	0	0.7(3)	0
C(12)	0.0012(7)	0.5165(9)	0.3988(6)	15.2(10)	16.0(10)	16.8(12)	-7.9(8)	9.8(9)	-13.0(10)
C(13)	-0.0579(9)	0.5220(10)	0.4219(5)	17.4(11)	18.1(13)	8.3(8)	-0.3(10)	-2.7(7)	-4.5(8)
C(14)	0.0685(3)	0.0529(4)	0.5589(2)	3.4(1)					
C(15)	0.0310(3)	0.1361(4)	0.5392(2)	3.2(1)					
C(16)	0.0256(3)	0.1634(4)	0.4855(2)	4.1(1)					
C(17)	-0.0074(3)	0.2376(5)	0.4669(3)	5.2(1)					
C(18)	-0.0408(4)	0.2837(5)	0.5039(3)	5.8(2)					
C(19)	-0.0416(3)	0.2581(5)	0.5561(3)	5.7(2)					
C(20)	-0.0052(3)	0.1816(4)	0.5750(2)	4.3(1)					
C(21)	0.2164(3)	0.1228(4)	0.5701(2)	3.3(1)					
C(22)	0.2185(3)	0.1077(4)	0.5144(2)	3.7(1)					
C(23)	0.2748(3)	0.1364(4)	0.4885(3)	4.7(1)					
C(24)	0.3300(3)	0.1788(4)	0.5193(3)	4.8(1)					
C(25)	0.3281(3)	0.1959(4)	0.5743(3)	5.0(1)					
C(26)	0.2715(3)	0.1681(4)	0.6003(3)	4.6(1)					
C(27)	0.1346(3)	0.1251(4)	0.6645(2)	3.4(1)					
C(28)	0.1360(3)	0.2155(4)	0.6658(3)	4.4(1)					
C(29)	0.1147(3)	0.2576(5)	0.7107(3)	5.1(1)					
C(30)	0.0919(3)	0.2128(4)	0.7534(3)	4.9(1)					
C(31)	0.0921(3)	0.1237(4)	0.7526(3)	4.5(1)					
C(32)	0.1127(3)	0.0799(4)	0.7085(2)	3.7(1)					
C(33)	0.1866(3)	-0.0390(4)	0.6208(2)	3.3(1)					
C(34)	0.1444(3)	-0.1126(4)	0.6165(2)	3.6(1)					
C(35)	0.1736(3)	-0.1928(4)	0.6292(3)	4.3(1)					
C(36)	0.2432(3)	-0.2015(4)	0.6467(3)	4.8(1)					
C(37)	0.2860(3)	-0.1301(4)	0.6514(3)	5.2(1)					
C(38)	0.2581(3)	-0.0490(4)	0.6379(3)	5.1(1)					

^a In this and the following tables the estimated standard deviation of the least significant digit(s) is given in parentheses. ^b The form of the temperature factor (B 's in units of \AA^2) is $T = \exp(-0.25(B_{11}h^2a^{*2} + 2B_{12}hka^*b^* + \dots))$ for anisotropic and $T = \exp(-B(\sin^2 \theta)/\theta^2)$ for isotropic thermal parameters. ^c An appendix to Table I will appear as supplementary material. Predicted 1 hydrogen atom positions are listed in this appendix. The hydrogen atoms were included in the structure factor calculations but were not refined.

the cation and probably due to anisotropic thermal motion not included in the model.

The final refined parameters and their esd's are given in Table I together with the predicted positions of the hydrogen atoms. A table of the observed F values, their esd's and the differences $|F_o| - |F_c|$ has been deposited as supplementary material (see paragraph at the end of the paper).

Results

Atomic positional parameters with standard deviations derived from the inverse matrix of the least-squares refinement are compiled in Table I. Predicted positional parameters for the hydrogen atoms are compiled as an appendix to Table I (supplementary material).

Intramolecular bond distances and angles are given in Tables II and III for the complex anion and in Table IV for the cation. The atom numbering scheme is illustrated in Figure 2.

Discussion

Four complex dianions, $\text{Fe}(\text{DED})_3^{2-}$, and eight benzyltriphenylphosphonium cations, BzlPh_3P , occupy the unit cell. The cations are found in the general equivalent positions of the unit cell and each of the dianions on the four crystallographic twofold axes. The iron atom is located at, and one of the ligands (S(3), S(3'), C(11), ...) is bisected by, the twofold crystallographic axis. The exact point symmetry of the anion is C_2 . The structure of the complex dianion and atom labeling scheme are shown in Figure 1, with the approximate threefold

Table II. Distances (\AA) and Angles (deg) in the FeS_6 Coordination Sphere^a

Distances			
Fe-S(1)	2.289 (2)	S(1)-S'(2)	3.332 (2)
Fe-S(2)	2.305 (2)	S(1)-S(3)	3.226 (2)
Fe-S(3)	2.301 (2)	S(2)-S(3)	3.512 (2)
S(1)-S'(1)	3.744 (3)	S(2)-S'(3)	3.468 (2)
S(1)-S(2) ^b	2.786 (2)	S(3)-S'(3) ^b	2.737 (3)
Angles			
S(1)-Fe-S'(1)	109.77 (5)	S(2)-Fe-S(3)	99.37 (7)
S(1)-Fe-S(2) ^b	74.66 (6)	S(2)-Fe-S'(3)	97.68 (7)
S(1)-Fe-S'(2)	93.00 (7)	S(3)-Fe-S'(3) ^b	72.97 (5)
S(1)-Fe-S(3)	89.32 (7)	Fe-S(1)-C(4)	89.5 (2)
S(1)-Fe-S'(3)	159.52 (8)	Fe-S(2)-C(4)	89.0 (2)
S(2)-Fe-S'(2)	158.75 (5)	Fe-S(3)-C(11)	91.6 (2)

^a Primed atoms are related to unprimed atoms by the crystallographic twofold axis through the iron. See Figure 2.
^b Distances and angles involving the S,S "bite" of a ligand.

axis of the octahedron perpendicular to the plane of the paper. The structure of the $\text{C}_7\text{H}_7(\text{C}_6\text{H}_5)_3\text{P}^+$ cation is normal. The structure of the same cation was determined previously¹⁹ and will not be discussed any further.

The structural parameters of the DED ligands in the present structure are similar to those observed in the structures of the $\text{Ni}(\text{DED})_2^{2-}$ and $\text{Cu}(\text{DED})_2^-$ complexes⁴ (Table V). The major differences are associated with the twists of the car-

Table III. Distances (Å) and Angles (deg) in the DED Ligands

Distance	Ligand 1	Ligand 2 ^a	Angle	Ligand 1	Ligand 2 ^a
C(4)–S(1)	1.735 (5)		S(1)–C(4)–S(2)	106.8 (2)	
C(4)–S(2)	1.735 (6)		S(3)–C(11)–S'(3)		103.8 (2)
C(11)–S(3)		1.739 (6)	S(1)–C(4)–C(2)	128.2 (3)	
C(4)–C(2)	1.369 (7)		S(2)–C(4)–C(2)	124.9 (3)	
C(11)–C(10)		1.363 (12)	S(3)–C(11)–C(10)		128.1 (2)
C(2)–C(1)	1.450 (8)		C(4)–C(2)–C(1)	122.7 (6)	
C(2)–C(3)	1.487 (8)		C(4)–C(2)–C(3)	119.0 (5)	
C(10)–C(9)		1.485 (9)	C(11)–C(10)–C(9)		122.6 (8)
C(1)–O(1)	1.215 (6)		C(1)–C(2)–C(3)	118.2 (5)	
C(1)–O(2)	1.350 (7)		C(9)–C(10)–C'(9)		114.9 (4)
C(3)–O(3)	1.190 (7)		C(2)–C(1)–O(1)	126.6 (4)	
C(3)–O(4)	1.307 (7)		C(2)–C(1)–O(2)	111.0 (4)	
C(9)–O(5)		1.196 (8)	O(1)–C(1)–O(2)	122.4 (4)	
C(9)–O(6)		1.301 (9)	C(2)–C(3)–O(3)	124.7 (5)	
O(2)–C(5)	1.438 (7)		C(2)–C(3)–O(4)	111.6 (4)	
C(5)–C(6)	1.472 (9)		O(3)–C(3)–O(4)	123.7 (5)	
O(4)–C(7)	1.458 (7)		C(10)–C(9)–O(5)		124.7 (8)
C(7)–C(8)	1.457 (10)		C(10)–C(9)–O(6)		113.3 (6)
O(6)–C(12)		1.479 (13)	O(5)–C(9)–O(6)		121.9 (8)
C(12)–C(13)		1.328 (17)	C(1)–O(2)–C(5)	117.5 (5)	
S(1)···O(1)	2.977 (4)		O(2)–C(5)–C(6)	107.8 (4)	
S(2)···O(3)	3.499 (5)		C(3)–O(4)–C(7)	118.5 (6)	
S(2)···O(4)	3.675 (5)		O(4)–C(7)–C(8)	108.1 (4)	
			C(9)–O(6)–C(12)		117.7 (8)
			O(6)–C(12)–C(13)		107.8 (8)

^a Constrained by a crystallographic twofold axis through C(10) and C(11).

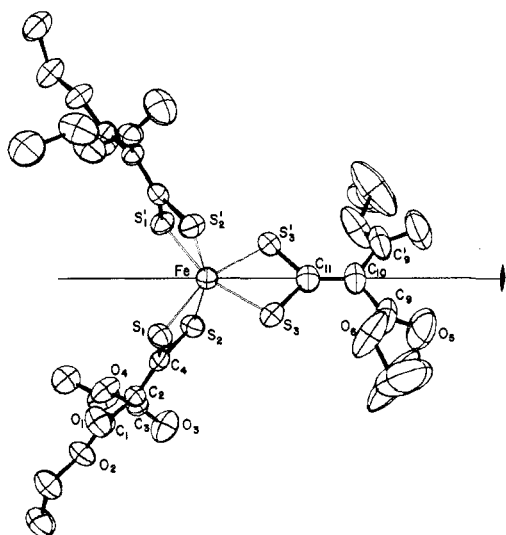


Figure 2. Molecular structure of $\text{Fe}[\text{S}_2\text{CC}(\text{COOC}_2\text{H}_5)_2]_3^{2-}$. Thermal ellipsoids as drawn by ORTEP³¹ represent the 50% probability surfaces.

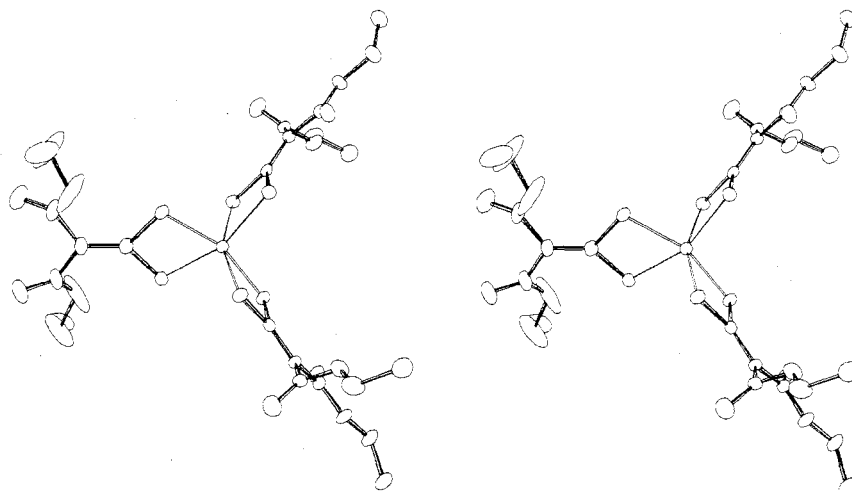


Figure 3. Stereoscopic view of the molecular structure of $\text{Fe}(\text{DED})_3^{2-}$ as drawn by ORTEP.³¹

boethoxy groups around the C—C single bonds. In the previous two structures one of the two carboethoxy groups was twisted only slightly out of the plane of the ligand backbone, $\text{S}_2\text{C}=\text{C}<$, while the second carboethoxy group was twisted considerably out of this plane. For this twisted type of ligand, dihedral angles of 77.7 and 136.1° were observed with the $\text{S}_2\text{C}=\text{C}<$ plane in the structures of $\text{Ni}(\text{DED})_2^{2-}$ and $\text{Cu}(\text{DED})_2^-$, respectively. In the structure of the $\text{Fe}(\text{DED})_3^{2-}$ complex the carboethoxy group of the ligand located on the twofold axis (and its symmetry-related counterpart) shows a smaller twist about the C—C single bond and the dihedral angle with the ligand backbone is only 27.2°.

In the other ligand (as well as that related by the C_2 axis) both of the carboethoxy groups are twisted out of the $\text{S}_2\text{C}=\text{C}$ plane. One of the carboethoxy groups forms a dihedral angle of only 5.8° while the other is nearly perpendicular with a dihedral angle of 81.9°.

In the $\text{Fe}(\text{DED})_3^{2-}$ dianion, the coordination around the iron is distorted octahedral. Two parameters that have been used²⁰ to describe the degree of distortion from either the trigonal-prismatic or trigonal-antiprismatic geometry are (a) the

Table IV. Distances (Å) and Angles (deg) in the Benzyltriphenylphosphonium Cation

Distances			
P-C(14)	1.823 (6)	C(27)-C(28)	1.396 (8)
P-C(21)	1.787 (5)	C(28)-C(29)	1.376 (8)
P-C(27)	1.787 (6)	C(29)-C(30)	1.365 (8)
P-C(33)	1.799 (6)	C(30)-C(31)	1.376 (9)
C(14)-C(15)	1.516 (8)	C(31)-C(32)	1.368 (8)
C(15)-C(16)	1.367 (8)	C(32)-C(27)	1.387 (7)
C(16)-C(17)	1.390 (9)	Av phenyl C-C	1.378 (5) ^a
C(17)-C(18)	1.369 (9)	C(33)-C(34)	1.388 (8)
C(18)-C(19)	1.329 (9)	C(34)-C(35)	1.376 (8)
C(19)-C(20)	1.416 (9)	C(35)-C(36)	1.350 (9)
C(20)-C(15)	1.375 (7)	C(36)-C(37)	1.366 (9)
Av phenyl C-C	1.374 (12) ^a	C(37)-C(38)	1.383 (9)
C(21)-C(22)	1.379 (8)	C(38)-C(33)	1.385 (8)
C(22)-C(23)	1.386 (7)	Av phenyl C-C	1.375 (6) ^a
C(23)-C(24)	1.375 (9)		
C(24)-C(25)	1.367 (8)		
C(25)-C(26)	1.390 (8)		
C(26)-C(21)	1.392 (8)		
Av phenyl C-C	1.382 (4) ^a		
Angles			
C(14)-P-C(21)	112.7 (4)	C(23)-C(24)-C(25)	120.5 (6)
C(14)-P-C(27)	108.4 (3)	C(24)-C(25)-C(26)	120.5 (6)
C(14)-P-C(33)	107.0 (3)	C(25)-C(26)-C(21)	119.6 (6)
C(21)-P-C(27)	110.7 (3)	P-C(27)-C(28)	120.7 (3)
C(21)-P-C(33)	106.5 (3)	P-C(27)-C(32)	119.5 (3)
C(27)-P-C(33)	111.6 (4)	C(28)-C(27)-C(32)	119.4 (6)
P-C(14)-C(15)	115.2 (3)	C(27)-C(28)-C(29)	118.9 (6)
C(14)-C(15)-C(16)	120.8 (5)	C(28)-C(29)-C(30)	121.5 (6)
C(14)-C(15)-C(20)	119.2 (5)	C(29)-C(30)-C(31)	119.5 (6)
C(16)-C(15)-C(20)	119.9 (5)	C(30)-C(31)-C(32)	120.4 (6)
C(15)-C(16)-C(17)	120.7 (5)	C(31)-C(32)-C(27)	120.3 (5)
C(16)-C(17)-C(18)	118.3 (6)	P-C(33)-C(34)	122.4 (3)
C(17)-C(18)-C(19)	122.5 (7)	P-C(33)-C(38)	119.4 (3)
C(18)-C(19)-C(20)	119.5 (7)	C(34)-C(33)-C(38)	118.2 (6)
C(19)-C(20)-C(15)	119.0 (5)	C(33)-C(34)-C(35)	120.3 (5)
P-C(21)-C(22)	118.8 (3)	C(34)-C(35)-C(36)	120.9 (6)
P-C(21)-C(26)	121.2 (3)	C(35)-C(36)-C(37)	120.0 (6)
C(22)-C(21)-C(26)	119.1 (5)	C(36)-C(37)-C(38)	120.2 (6)
C(21)-C(22)-C(23)	120.9 (5)	C(37)-C(38)-C(33)	120.4 (6)
C(22)-C(23)-C(24)	119.4 (6)		

^a Standard deviation of the average calculated from $(\sum_i(d_{av} - d_i)^2/n(n-1))^{1/2}$.

Table V. Selected Structural Parameters in the Ni(DED)₃²⁻ and Fe(DED)₃²⁻ Complexes^a (Distances in Å; Angle in deg)

	Ni(II)	Fe(IV) ^b
M-S ₁	2.196 (1)	2.289 (2), 2.301 (2)
-S ₂	2.193 (1)	2.305 (2)
S ₁ -S ₂ (bite)	2.789 (2)	2.786 (2), 2.737 (3)
S ₁ -C ₄ -S ₂	106.2 (2)	106.8 (2), 103.8 (2)
C ₄ -S ₁	1.738 (5)	1.735 (5), 1.739 (6)
-S ₂	1.749 (4)	1.735 (6)
-C ₂	1.367 (6)	1.369 (7), 1.363 (12)
C ₂ -C ₁	1.450 (7)	1.450 (8)
-C ₃	1.486 (7)	1.487 (8), 1.485 (9)
C ₁ =O ₁	1.208 (6)	1.215 (6)
C ₃ =O ₃	1.190 (6)	1.190 (7), 1.196 (8)

^a The atom numbering scheme is that of Figure 2. ^b Ligand constrained by crystallographic twofold symmetry.

S-M-S angles for sulfur atoms trans to each other and (b) the projection angle between the two triangular faces of the prism (trigonal twist angle).

The calculation of the twist angle ϕ in octahedral complexes has been described²¹ in terms of the nonbonded contacts (s), the ligand bite (b), the metal-ligand distances (a), and the distance between the two equivalent triangles (h). This calculation is valid only if the two threefold faces are parallel, the three ligand bites are equal, the nonbonded contacts are equal, and the metal atom lies on the line joining the centroids

of the two faces. This calculation on the present structure²² (which does not adhere to some of the above restrictions) yielded $\phi = 35.9^\circ$.

Dymock and Palenik²³ have concluded that in distorted octahedra, where the above conditions are not met, the twist angle ϕ is calculated best as the dihedral angle between the planes defined by L, C, C' and L', C, C' where C and C' are the centroids of the two triangular faces and L and L' donor atoms on the same bidentate chelate.²³

Calculation of individual twist angles by this method in the FeS₆ core of the Fe(DED)₃²⁻ dianion shows angles of 40.93° for the unique ligand (on the twofold axis) and 33.58 and 33.91° for the other two ligands. Although the variation in individual twist angles is significant, the average twist angle (36.1°) is comparable to the one calculated by the method of Stiefel and Brown²¹ (35.9°).

A summation of ligand-ligand repulsion energies for complexes of the type M(bidentate)₃^{x-} shows that there exists a continuous change from regular octahedral stereochemistry to trigonal-prismatic stereochemistry as the "bite" of the bidentate ligand is progressively decreased.²⁴ The minimum energy corresponding to the most stable stereochemistry occurs for the regular octahedron at $\phi = 60^\circ$ only when the bite distance to the metal-ligand bond length ratio is $= 2^{1/2} = 1.414$. This ratio in the present structure is ~ 1.29 and for this value the energetically most stable configuration occurs²⁴ for a distorted octahedron with $\phi \approx 49^\circ$. The deviation of this value from the observed value of $\sim 36^\circ$ is significant and reflects the tendency of the present structure toward the trigonal-prismatic coordination. This tendency also becomes apparent by an examination of the "trans" S-Fe-S angles. The average intraligand S-Fe-S angle of $\sim 74^\circ$ observed in the present structure dictates a "trans" S-Fe-S angle of 164° for the corrected octahedral limit.²⁰ The values observed for the Fe(DED)₃²⁻ complex are 152.52 (8) and 158.75 (5)°. These values, however, are still much higher than the trigonal-prismatic limit ($\sim 136^\circ$).

The nonequivalence of the "trans" S-Fe-S angles can be traced to the nonequivalence of the individual ligand twist angles which indicate that one of the ligands (S(3)-S(3')) is rotated less toward the trigonal-prismatic structure than the other two ligands. The geometry of the FeS₆ core in the present structure is very similar to those observed in the M(S)₆ cores of the tris(dithiocarbamato)iron(IV) complex,⁹ the tris(benzenedithiolato)tantalum(V) monoanion,²⁵ the In-(S₂C₂Ph₂)₃²⁶ complex, and the tris(dimethyldithiocarbamato)tantalum(III) complex,²⁷ Tl(Me₂dtc)₃.

For the tris(benzenedithiolato)tantalum(V) complex, the symmetry at the tantalum atom has been described as originating from a trigonal prism, which suffers individual rotations of the chelating ligands around the C₂ axes. One of these rotations is more severe than the other two causing a lowering of the overall symmetry to C₂. The same type of distortion also has been discussed for the Tl(Me₂dtc)₃ complex²⁷ in terms of the average propeller pitch angle Ψ .

This description is supported by the fact that a detailed ligand field analysis of the Mössbauer spectra of Fe(DED)₃²⁻ has shown⁶ that the temperature variation of the quadrupole splitting is well accounted for by ascribing to this complex a geometry close to a trigonal prism with an exact C₂ point symmetry.²⁸

An examination of the structural parameters of the crystallographically unconstrained, complexed DED ligand shows no significant differences when compared to corresponding values in the structure of the Ni(DED)₂²⁻ complex⁴ (Table V). In a similar fashion the infrared spectra of these two complexes are nearly identical. These results suggest that delocalization of charge in the ligand is virtually independent of the formal

oxidation state of the central metal ion. It appears therefore that *inter- or intraligand oxidation cannot adequately explain the apparent stability of the Fe(DED)₃²⁻ complex*. This contention is supported further by the fact that the infrared spectrum of the (BzIPh₃P)₂Sn(DED)₃ complex is virtually identical with that of the iron analogue. The two complexes are x-ray isomorphous and most likely isostructural. The lack of evidence for intra- or interligand interaction differences between complexes of ions with considerable difference in oxidizing potential is striking and demonstrates that the site of oxidation in the Fe(DED)₃²⁻ complex is centered in the FeS₆ core. The Fe-S bond lengths in the present structure are significantly shorter than those in the high-spin iron(III) tris(dithiocarbamate) chelates such as the Fe(pyrrDtc)₃²⁹ and Fe(Et₂Dtc)₃²⁸ at 297 K (2.41 (1) and 2.357 (5) Å, respectively). However, they are similar to those found in the structures of the low-spin Fe(MePhDtc)₃²⁷ and Fe(Et₂Dtc)₃³⁰ at 79 K complexes (2.31 (1) and 2.306 (2) Å, respectively) and very similar to those found in the only other iron-sulfur complex which formally contains iron in the +4 oxidation state. Thus in the structure of the tris(pyrrolidylthiocarbamate)iron(IV) cation, Fe-S bond lengths of 2.300 (2) Å have been observed.⁹

The successful interpretation of the Mössbauer data⁶ by a method based on ligand field theory is an additional indication that in the FeS₆ core of the Fe(DED)₃²⁻ complex anion the iron exists in the +4 oxidation state. A decrease in the spin-orbit coupling parameter by about 30% from the free ion value (~500 cm⁻¹), as derived from the Mössbauer data analysis, is attributed to either a radial expansion or to overlap with sulfur orbitals. Appreciable covalency in the M-S bond was considered as the most likely interpretation for the nearly identical M-S bond lengths in the structures of the Ni^{II}(DED)₂²⁻ and Cu^{III}(DED)₂⁻ complexes.⁴

The structural and spectral data on the Fe^{IV}(DED)₃²⁻ complex as well are consistent with Fe(IV)-S bonding with considerable covalent character.

Acknowledgment. The authors are grateful for a Grant (IROLGM18144-O1A1) from the National Institutes of Health for financial support of this research. D.C. also is grateful to the Alfred P. Sloan Foundation for a Fellowship (1972-1974).

Registry No. I, 53259-89-5.

Supplementary Material Available: Listings of hydrogen positional and thermal parameters and of observed structure factor amplitudes,

their estimated standard deviations, and the difference $|F_o| - |F_c|$ (14 pages). Ordering information is given on any current masthead page.

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