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ELECTROCHEMISTRY OF THE IRON—SULFUR CLUSTER COMPOUND $[(\eta\text{-}C_5H_5)_2Fe_2S_2(SC_2H_5)_2]$. SYNTHESIS AND PROPERTIES OF THE OXIDATION PRODUCTS *

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Summary

In order to gain some insight into the stability of configuration and the bonding in the novel disulfide-containing complex $[(\eta\text{-}C_5H_5)_2Fe_2S_2(SC_2H_5)_2]$, electrochemical properties of this compound and its SCH_3 and $SCH_2C_6H_5$ analogues were studied in various solvents and the magnetic properties of a subsequently isolated paramagnetic monocation were investigated. The cyclic voltammogram of $[(\eta\text{-}C_5H_5)_2Fe_2S_2(SC_2H_5)_2]$ shows a reversible one-electron oxidation at $E_{1/2}$ = +0.21 V and a quasi-reversible one-electron oxidation at $E_{1/2}$ = +0.90 V (vs. saturated calomel electrode). The stable monocation has been electrochemically synthesized and the magnetic susceptibility shows a simple paramagnetic behavior with one unpaired electron per dimeric unit. Frozen solutions of this species at 103K yielded anisotropic ESR spectra with $g_1 = 2.135$, $g_2 = 1.976$, and $g_3 = 1.934$. Labeling the complex with ^{33}S in the disulfide bridge resulted in no observable hyperfine splitting or line broadening in the ESR. The dicationic species is unstable with respect to loss of the S_2 bridge and formation of a solvent-ligated dication, $[(\eta\text{-}C_5H_5)Fe(NCCH_3)(SC_2H_5)]_2^{2+}$, isolated by electrolysis of the monocation at +1.2 V in CH_3CN.

Introduction

The structure [1,2] of the novel dinuclear iron—sulfur cluster compound, $[Cp_2Fe_2S_2(SC_2H_5)_2]$ (I) (Cp = $\eta\text{-}C_5H_5$), revealed an unprecedented feature with

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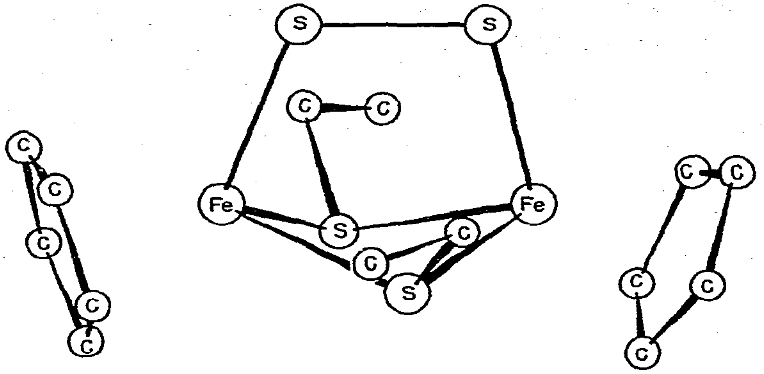

Fig. 1. Perspective view of $[(\eta\text{-}C_5H_5)_2Fe_2S_2(SC_2H_5)_2]^n$ (n = 0, +1).

regard to its stereochemical configuration. The S_2 ligand is bound to the two metals in a bridging manner, such that the metal and disulfide atoms are coplanar (Fig. 1). The non-bonding separation between the iron atoms (3.307 Å) brought up a question regarding the mode of bonding in the complex. The absence of a metal—metal bond in this complex is intriguing for several reasons: (1) On the basis of accepted bonding models for the ligands involved (e.g., S_2^{2-} as a four-electron donor, each SR^- as a four-electron donor, and each $C_5H_5^-$ as a six-electron donor), each metal would not attain a rare gas configuration without the formation of a direct metal—metal bond. (2) An odd electron on each iron would result in a strong paramagnetism, but this is not observed. (3) The unique stereochemical planarity of the metals and disulfide group could lend credence to a proposed coupling of odd electron spins on iron atoms via a super-exchange mechanism.

The redox properties of organometallic complexes can give good indications of the stability and potential accessibility of such compounds in various molecular oxidation states [3,4]. This has been found to be especially useful in the study of dimeric [5,6] or more highly clustered species [7—10]. The unique iron—sulfur core configuration in I has also been suggested as a potential model of some non-heme iron—sulfur proteins [11,12]; knowledge of the redox properties of I could give some indication of its acceptability in this regard. Therefore, in order to gain some insight into the stability of the configuration as well as the bonding in this novel disulfide-containing complex, its electrochemical properties were studied and the magnetic properties of a subsequently-isolated paramagnetic monocation were investigated.

Results and discussion

The cyclic voltammograms of I in CH_3CN (Fig. 2) show a reversible one-electron oxidation at $E_{1/2}$ = + 0.21 V and a quasi-reversible one-electron oxidation at +0.90 V (vs. saturated calomel electrode, SCE, as reference); at higher scan rates (500 mV sec^{-1}) the second oxidation appears reversible. Thus, the second oxidation product is less stable than the first and undergoes chemical reaction soon after its production. Voltammogram 2B shows a third, irreversible oxidation at +1.60 V. The species undergoing oxidation at this potential was identi-

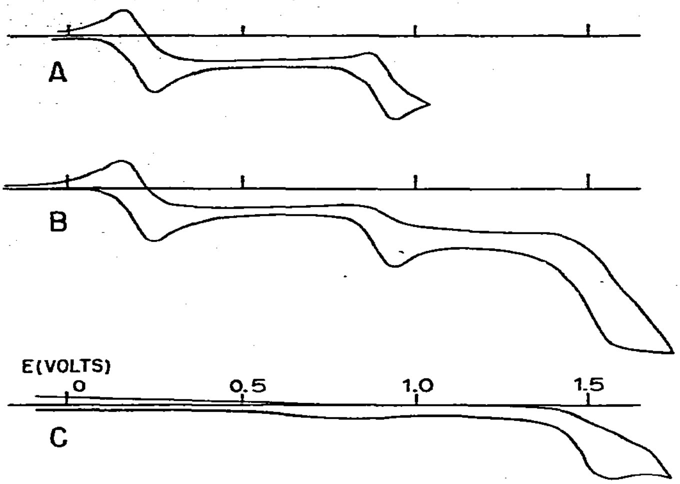

Fig. 2. Cyclic voltammograms of I and III in CH_3CN [0.1 *M* $(C_2H_5)_4NClO_4$ supporting electrolyte]. A and B: 8×10^{-4} *M* I. C: 5×10^{-4} *M* III. Reference electrode: saturated calomel. Scan rate: 38 mV sec^{-1}.

fied to be $[CpFe(NCCH_3)(SC_2H_5)]_2^{2+}$, (III), from the following observations: (a) III is a known product [13] * of chemical oxidation of I by $NOPF_6$; (b) Comparison of the cyclic voltammogram of the isolated PF_6^- salt of III (Fig. 2C) with voltammogram 2B shows the oxidation peak due to III to be identical to that of the third oxidation process for I; (c) III was found to be the product of the bulk electrolysis of I at a potential intermediate between that of the second and third oxidation waves. Thus it is reasonable to assume that III originates from the decomposition of an as yet unisolated dication of I and that the latter is unstable with respect to replacement of the bridging S_2 unit by solvent molecules. No reversible reduction of I was observed, but an irreversible process at −1.2 V did occur. The overall scheme may be summarized as follows:

$$\text{Irrev. red. prod.} \xleftarrow{-1.2\text{ V}} \underset{\text{(I)}}{[Cp_2Fe_2S_2(SC_2H_5)_2]} \overset{+0.21\text{ V}}{\rightleftharpoons} \underset{\text{(II)}}{[Cp_2Fe_2S_2(SC_2H_5)_2]^+}$$

$$\overset{+0.90\text{ V}}{\rightleftharpoons} [Cp_2Fe_2S_2(SC_2H_5)_2]^{2+} \xrightarrow[-S_2\text{ (or 2S)}]{CH_3CN} \underset{\text{(III)}}{[CpFe(NCCH_3)(SC_2H_5)]_2^{2+}}$$

$$\xrightarrow{+1.6\text{ V}} \text{Irrev. oxid. prod.}$$

Voltammograms displaying the first two oxidation waves were also obtained for I in CH_2Cl_2 (0.1 *M* $(n\text{-}C_4H_9)_4NClO_4$ supporting electrolyte) and in dimethylformamide.

Bulk electrolyses of I in CH_3CN or DMF at a potential 0.3 V more positive than that of the reversible oxidation wave yielded deep emerald-green solutions of $[Cp_2Fe_2S_2(SC_2H_5)_2]^+$ (II). This process was shown to be a one-electron oxidation by controlled-potential coulometry. The use of 0.1 *M* NH_4PF_6 or 0.1 *M*

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* The X-ray structure [16] of the PF_6^- salt of III shows one acetonitrile ligated to each iron in place of the disulfide bridge. The Fe—Fe separation (2.65 Å) is bonding.

$NaSbF_6$ in CH_3CN as supporting electrolyte allowed isolation of $[Cp_2Fe_2S_2(SC_2H_5)_2]X$ ($X = PF_6$ or SbF_6) upon partial solvent removal and crystallization under inert-atmosphere conditions. Recrystallization of the salts from CH_3CN/toluene yielded air-stable, deep-green microcrystalline solids. Solutions of these salts in CH_3CN containing excess counter-anion are oxidized by air to give $[CpFe(NCCH_3)(SC_2H_5)]_2(X)_2$ ($X = PF_6$ or SbF_6).

The fate of the S_2 group upon formation of $[CpFe(NCCH_3)(SC_2H_5)]_2^{2+}$ from the electrochemically-generated dication $[Cp_2Fe_2S_2(SC_2H_5)_2]^{2+}$, was not definitely determined by examination of reaction side products. Small amounts of ethyl polysulfide and iron-containing materials were found among the reaction products but the presence of elemental sulfur was not definitely established. Apparently some of the displaced S_2 sulfur became incorporated into polysulfide groups, possibly as a result of a side reaction in which complete cleavage of the dimer occurred.

Table I compares the oxidation potentials of $[Cp_2Fe_2S_2(SR)_2]$ for various R groups. The overall nature of the oxidations with respect to reversibility did not vary with R, but potential shifts did occur. The R group is an important factor in the oxidation potential position, since the half wave potentials were observed to increase with bulkiness of the group. Although the separations between peak anodic and peak cathodic current represented in the table for the first oxidation potential of each compound is larger than the 59 mV theoretical value expected for a reversible one-electron process, the values shown corresponded exactly to the values observed for a 1 m*M* Cp_2Fe wave observed immediately preceding the complex of interest. Electrode configuration and uncompensated internal resistance could possibly cause this. Other criteria for reversibility of an electrode process were also employed. The ratio of peak anodic and peak cathodic current was observed for the complex over a wide range of scan rates. Controlled potential coulometry was also utilized in studying the forward and reverse reactions for chemical reversibility.

Magnetic properties

The magnetic susceptibility of the neutral dimer was studied in the solid state over the temperature range $4 < T < 300K$. The compound is diamagnetic but the presence of a slight residual temperature independent paramagnetism was observed. No evidence for anti-ferromagnetic behavior was found. The monocationic species, however, is paramagnetic. A sample of the SbF_6^- salt demonstrates a simple Curie—Weiss behavior over the temperature range $4 < T < 190K$ with

TABLE 1

OXIDATION POTENTIALS FOR $[Cp_2Fe_2S_2(SR)_2]$ [a]

R	$E_{1/2}$ (V) [b]	Δ (mV) [c]	$E_{1/2}$ (V)	Δ (mV)	Scan rate
CH_3	0.19	74	0.79	173	200 mV sec^{-1}
C_2H_5	0.21	74	0.90	92	100 mV sec^{-1}
$C_6H_5CH_2$	0.28	89	0.99	139	100 mV sec^{-1}

[a] For 1 m*M* solutions in CH_3CN containing 0.1 *M* NH_4PF_6. [b] All potentials are vs. the saturated calomel electrode. [c] Peak separation.

no apparent anomalies. A linear regression analysis of the susceptibility data over this temperature range demonstrated a magnetic moment of 1.70 ± 0.05 BM, corresponding to one unpaired electron per dimeric unit. The intercept value (T when $1/\chi_M = 0$) was found to be —0.6 ± 1.8K.

Frozen solutions containing the monocation yielded anisotropic ESR spectra at 103K, with $g_1 = 2.135$, $g_2 = 1.976$, and $g_3 = 1.934$. Figure 3 shows the spectrum obtained from a sample prepared by electrochemical generation of II in DMF; similar spectra resulted from CH_3CN solutions. Frozen solutions of the isolated salt, $[Cp_2Fe_2S_2(SC_2H_5)_2]PF_6$, gave ESR spectra identical to those of the samples electrochemically-generated in situ. The observed g values are similar to those reported for other low-spin iron cluster compounds which contain one unpaired electron per cluster, [14].

The assumption of a superexchange mechanism between iron centers via the bridging S_2 group might be expected to manifest itself in an observable hyperfine splitting (or at least a line broadening from unresolved hyperfine splitting) in the ESR spectrum of the monocation if the disulfide bridge were labeled with the nuclear-spin containing isotope, ^{33}S. In order to test this hypothesis, synthesis of the monocation labeled with ^{33}S in the S_2 bridge (~50% overall substitution) was carried out [13]. An ESR spectrum of this spin-labeled species exhibited no observable ^{33}S hyperfine splitting and, in fact, displayed no measurable line broadening [15].

This observation indicates that the unpaired electron in the monocation is found in a molecular orbital which has negligible contribution from sulfur s orbitals and which leads to negligible spin polarization of the sulfur atoms. The above is consistent with the idea that the unpaired electron is in a molecular orbital which is essentially metal in character.

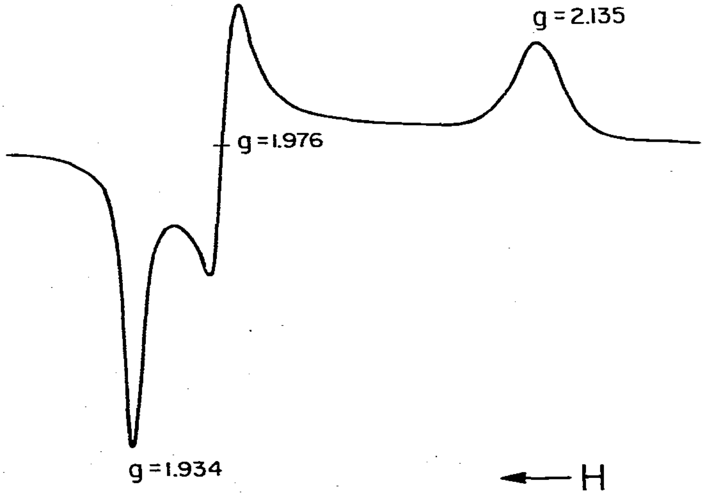
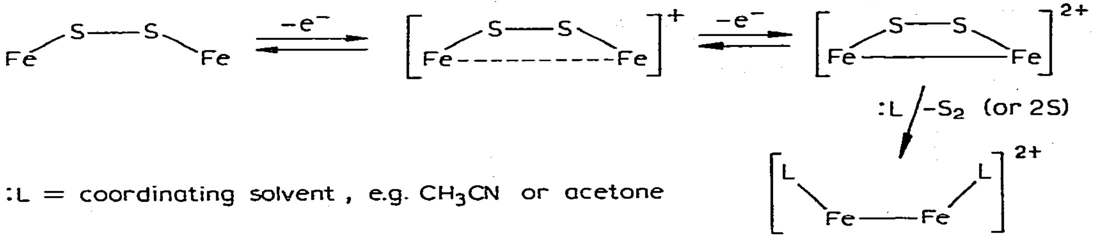


Fig. 3. X-band ESR spectrum of II in frozen DMF at −170°C.

Conclusions

There is a rapidly increasing body of data on organometallic cluster compounds which demonstrate reversible redox potentials. In most cases the reversible potentials indicate that there are no stereochemical changes that alter the metal—ligand coordination. When there has been solid-state structural information of oxidized and reduced forms of a redox couple, the observations have been overwhelmingly in favor of the argument that the orbitals which the electrons are removed from by oxidation or added to by reduction are primarily metal in character [6,8,10,16]. Following this line of reasoning, the results of the electrochemical and magnetic studies presented here could be rationalized in the manner shown in the following scheme:



:L = coordinating solvent, e.g. CH_3CN or acetone

The formation of a one-electron metal—metal bond in going from the neutral dimer to the monocation has, in fact, been shown to be what occurs by structural characterization of the monocation [16]. Further oxidation to the S_2-bridged dication would be expected to decrease the Fe—Fe distance and place a great deal of strain on the bond angles about the S_2 ligand. Decomposition of this as yet unisolated disulfide-containing dication is rapid at room temperature; however, its stabilization and isolation may be possible under more favorable experimental conditions. An interesting feature of this reaction scheme is the possibility that the S_2 moiety is released as molecular S_2 or atomic sulfur, species not normally present at ambient temperatures and pressures. Thus, trapping of these species, either by chemical or physical means, could prove to be valuable for purposes of synthesis or for physical studies of the sulfur species themselves.

$[Cp_2Fe_2S_2(SC_2H_5)_2]$ and its monocation constitute the first example of an inorganic redox couple containing the S_2 unit. As previously suggested, configurations containing disulfide-bridged metal atoms should not be over-looked as possible structural models for some of the active sites of biological systems containing metal—sulfur clusters. These electrochemical studies demonstrate that such a configuration can be retained during a reversible redox reaction of the type necessary to the function of proteins such as the ferredoxins in electron-transport processes.

Experimental

Electrochemical experiments were carried out using a three-electrode cell system on both a Princeton Applied Research Model 170 Electrochemical Apparatus and an instrument utilizing a Wenking 66TS10 Potentiostat connected to a Hewlett—Packard 7004A X-Y recorder. Cyclic voltammograms were obtained at a stationary platinum bead electrode, using approximately one m*M* solutions of the complex of interest in dry, deoxygenated solvents (0.1 *M* in supporting electrolyte) at 25°C. Bulk electrolyses utilized a Pt screen working electrode, separated from the counter electrode by glass frits (Fig. 4). X-band ESR spectra were recorded on a Varian 4100, using frozen acetonitrile solutions, prepared under oxygen-free conditions at 77K. The magnetic susceptibility of the monocation was obtained on a Princeton Applied Research Model 150 Vibrating Reed Magnetometer.

All experiments were performed under nitrogen. The complexes $Cp_2Fe_2S_2(SR)_2$ ($R = CH_3$, C_2H_5, and $CH_2C_6H_5$) were prepared in low-yield (ca. 10%) by refluxing $[CpFe(CO)(SR)]_2$ [17] with excess sulfur in methylcyclohexane for 3 h (overnight for benzyl derivative) [13]. The crude products were purified by chromatography on alumina. This method of preparation was found to be preferable to the original synthesis [2] of $Cp_2Fe_2S_2(SC_2H_5)_2$ from $[CpFe(CO)_2]_2$ and $(C_2H_5)_2S_n$ ($n = 3, 4$). $NaSbF_6$ and NH_4PF_6 (99.5%) were obtained from Ozark-Mahoning and recrystallized from CH_3CN/ether (twice) and acetone/CH_2Cl_2, respectively. Eastman Spectrograde acetonitrile was used without further purification, except for recrystallization of $[Cp_2Fe_2(S_2)(SC_2H_5)_2]^+$ wherein it

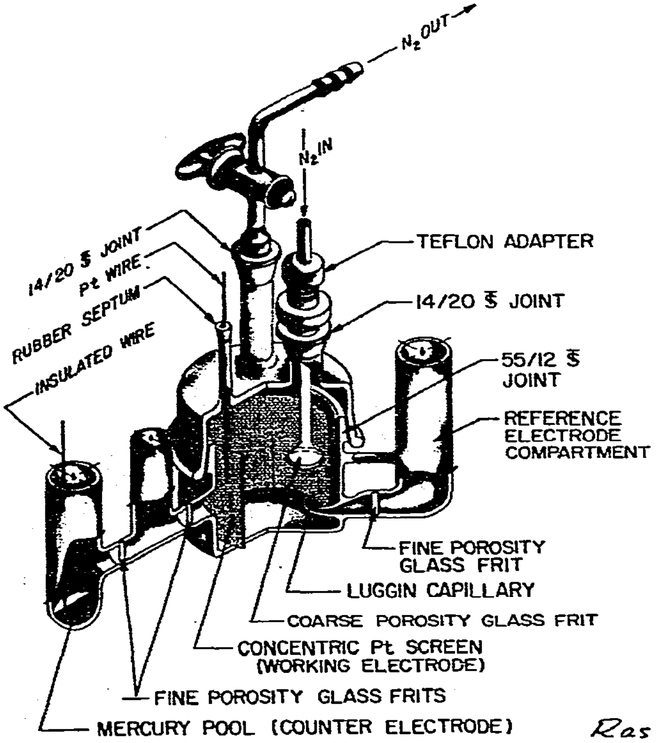


Fig. 4. Cell used for bulk electrolyses. A positive nitrogen pressure is maintained in the working electrode compartment, thus making it unnecessary to grease the joints. The Teflon adapter allows vertical movement of the course frit to provide nitrogen flow either above or below the electrolyte surface. The electrolyte level in the reference electrode compartment must be maintained above that in the working electrode compartment to prevent diffusion of electroactive species through the Luggin capillary. The solution was stirred magnetically.

was distilled from P_2O_5 prior to use. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee, U.S.A.

Preparation of $[Cp_2Fe_2S_2(SC_2H_5)_2]^+X^-$ ($X = PF_6$ *or* SbF_6) *by electrolysis of* $Cp_2Fe_2S_2(SC_2H_5)_2$

The supporting electrolyte (0.1 *M*) was prepared by dissolving 2.59 g of $NaSbF_6$ in 100 ml of CH_3CN. The electrolysis cell (Fig. 4) compartments were filled with electrolyte, and the solution in the working electrode compartment (~50 ml) degassed with nitrogen. One mmol (0.428 g) of $Cp_2Fe_2S_2(SC_2H_5)_2$ was added and electrolyzed, starting at +0.1 V vs. SCE. The voltage was slowly increased to keep pace with the drop-off of current caused by depletion of neutral species. The current was maintained at or below 200 mA to prevent overheating. The oxidation was complete at +0.4 V vs. SCE (the voltage was maintained at or below this value since further oxidation to $[CpFe(NCCH_3)(SC_2H_5)]_2^{2+}$ occurs above +0.6 V). The number of electrons per mole, *n*, was determined to be 1.0. The deep green solution was then transferred, with careful exclusion of air, to a flask, from which solvent was removed in vacuo. When ~15 ml of solution remained, crystallization of $[Cp_2Fe_2S_2(SC_2H_5)_2]SbF_6$ began, at which point solvent removal was stopped. The flask was cooled overnight in a refrigerator, and the microcrystalline, black product was collected on a frit, thoroughly washed first with water to remove $NaSbF_6$, then with ether, and dried. The yield was 0.355 g (54%). Recrystallization under nitrogen from dry CH_3CN/toluene gave 0.31 g of black microcrystals. The use of rigorously dried solvents was prompted by the observation that solutions of $Cp_2Fe_2S_2(SC_2H_5)_2^+$ in organic solvents containing significant amounts of water slowly change color to a different shade of green, even under nitrogen.

The isostructural [16] PF_6^- salt can be prepared by substituting NH_4PF_6 for $NaSbF_6$ in the electrolyte solution. It is somewhat more soluble than the SbF_6^- salt. Both salts are air-stable in the solid state but are readily air-oxidized when dissolved in polar solvents. Anal. Found: C, 29.3; H, 3.5; S, 22.4; P, 5.4; F, 19.9. $Fe_2C_{14}H_{20}S_4PF_6$ calcd.: C, 29.5; H, 3.5; S, 21.7; P, 5.4; F, 19.8%.

Synthesis of $[CpFe(NCCH_3)(SC_2H_5)]_2(PF_6)_2$ *by electrolysis of* $Cp_2Fe_2S_2(SC_2H_5)_2^+$

One mmol (428 mg) of $Cp_2Fe_2S_2(SC_2H_5)_2$ was electrochemically oxidized to its monocation as in the above-described manner, using NH_4PF_6 as supporting electrolyte. The monocation was then further oxidized at 1.2 V vs. SCE. The *n* value for this process was slightly greater than 1. The solvent was removed by evaporation and the remaining NH_4PF_6 was washed from the residue with water. The residue was dried and extracted with CS_2 to remove any traces of non-ionic organic and organometallic components as well as sulfur or sulfur-containing products of the oxidation. Finally, the $[CpFe(NCCH_3)(SC_2H_5)]_2(PF_6)_2$ was isolated by extracting the washed residue with CH_3CN (ca. 50 ml) and allowing the resulting deep-red solution to evaporate to dryness. The black, crystalline product weighed 625 mg (85% yield). It was easily identified by comparison with previously-characterized samples [13] of $[CpFe(NCCH_3)(SC_2H_5)]_2(PF_6)_2$ prepared by oxidation of $Cp_2Fe_2S_2(SC_2H_5)_2$ with $NOPF_6$ or air.

Evaporation of the CS_2 extract yielded a glassy, viscous yellow residue (ca. 50 mg) which did not solidify even upon prolonged vacuum drying at 60°C. Infrared spectra indicated that it contained ethyl polysulfide species by comparison with an authentic sample of $(C_2H_5)_2S_4$.

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References

1 G.J. Kubas, T.G. Spiro and A. Terzis, J. Amer. Chem. Soc., 95 (1973) 273.
2 A. Terzis and R. Rivest, Inorg. Chem., 12 (1973) 2132.
3 R.E. Dessy and L.A. Bares, Acc. Chem. Res., 5 (1972) 415, and references cited therein.
4 J.B. Headridge, Electrochemical Techniques for Inorganic Chemists, Academic Press, New York, NY., 1969.
5 P.D. Frisch, M.K. Lloyd, J.A. McCleverty and D. Seddon, J. Chem. Soc., Dalton Trans., (1973) 2268.
6 N.G. Connelly and L.F. Dahl, J. Amer. Chem. Soc., 92 (1970) 7472.
7 P.J. Vergamini, H. Vahrenkamp and L.F. Dahl, J. Amer. Chem. Soc., 93 (1971) 6327.
8 G.L. Simon and L.F. Dahl, J. Amer. Chem. Soc., 95 (1973) 2164.
9 T. Toan, W.P. Fehlhammer and L.F. Dahl, J. Amer. Chem. Soc., 94 (1972) 3389.
10 P.J. Vergamini, R.R. Ryan and G.J. Kubas, to be published.
11 E. Bayer, H. Eckstein, H. Hagenmaier, D. Josef, J. Koch, P. Krauss, A. Röder and P. Schretzmann, European J. Biochem., 8 (1969) 33.
12 W.H. Orme-Johnson, Ann. Rev. Biochem., (1973) 159.
13 G.J. Kubas and P.J. Vergamini, to be published.
14 M. Clare, H.A.O. Hill, C.E. Johnson and R. Richard, Chem. Commun., (1970) 1376.
15 R. Mathews, S. Charlton, R.H. Sands and G. Palmer, J. Biol. Chem., 249 (1974) 4326.
16 P.J. Vergamini, R.R. Ryan and G.J. Kubas, J. Amer. Chem. Soc., 89 (1976) 1980.
17 R.B. King and M.B. Bisnette, Inorg. Chem., 4 (1965) 482.