cis isomer (2037 (m) and 1982 (s) cm^{-1}) and trans isomer (1960 (s) cm^{-1}). The frequencies of these bands are similar to those in the literature for related *cis*- and *trans*-bis(dinitrogen) complexes of molybdenum.[31] The assignment of the 1960-cm^{-1} band rather than the 1982-cm^{-1} band to the trans isomer is confirmed by the observation that the 1960-cm^{-1} band increased in intensity relative to the other bands in later crops isolated during recrystallization.

The formation of $[Mo(dmpe)_2(N_2)_2]$ as a mixture of cis and trans isomers was confirmed by the ^{31}P NMR spectrum of a freshly prepared THF solution of the complex. This contained a singlet, which could be assigned to the equivalent P nuclei of the trans isomer, together with two triplets assigned to the two sets of equivalent P nuclei of the cis isomer, which form an A_2B_2 coupling system.

Bis(dinitrogen) complexes of Mo(0) of the type $[MoL_4(N_2)_2]$, where L is a phosphane ligand, have been prepared previously with a range of phosphanes[31] including L = PMe_2Ph, PPh_2Me, or PEt_2Ph and $L_2 = Ph_2P(CH_2)_nPPh_2$ (n = 2 or 3) or $Ph_2PCH{=}CHPPh_2$, but most of the complexes have trans orientations of the N_2 ligands. The only exceptions to this are $[Mo(PMe_2Ph)_4(N_2)_2]$, formed as the cis isomer,[32] and $[Mo(Ph_2PCH{=}CHPPh_2)_2(N_2)_2]$, which has been reported to form initially as an unstable cis isomer that isomerizes to the characterized trans isomer.[1] $[Mo(dmpe)_2(N_2)_2]$ is unique in being formed as a relatively stable mixture of cis and trans isomers, but this probably does not indicate that the isomers have similar thermodynamic stability. It is more probable that trapping of the low-valent molybdenum species formed in the reduction is rapid and indiscriminate. This is suggested by comparison with the reduction of $[Mo(dmpe)_2Cl_2]$ under CO, which results in formation of an approximately 1.6:1 mixture of cis and trans isomers of $[Mo(dmpe)_2(CO)_2]$. Pure cis isomer could be isolated from this in 25% yield, and the trans isomer, contaminated with ca 11% cis, could be isolated in 19% yield. Since it is well established that the cis isomer is more stable than the trans,[33] we know that the ratio of the dicarbonyl isomers is kinetically controlled, and it is reasonable to infer that the ratio of bis(dinitrogen) isomers is also kinetically controlled.

Conclusion

Reaction of amorphous molybdenum dichloride with dmpe affords a convenient route to $[Mo(dmpe)_2Cl_2]$, establishing that this form of the dichloride behaves chemically as if it contains monomeric $MoCl_2$ and suggesting that it may be a convenient starting material for the preparation of other mononuclear Mo(II) complexes. The d^4 complex $[Mo(dmpe)_2Cl_2]$ is surprisingly inert to alkylation, but is readily oxidized to the cationic d^3 complex $[Mo(dmpe)_2Cl_2]^+$.

Acknowledgment. We thank the National Science Foundation for generous financial support of our research program.

Registry No. $[Mo(dmpe)_2Cl_2]$, 58904-16-8; $[Mo(dmpe)_2Cl_2]PF_6$, 101403-79-6; $[Mo(dmpe)_2Cl_2][SnCl_3]$, 101470-33-1; $[Mo(CO)_4Cl_2]$, 15712-13-7; $[Mo(dmpe)_2(CO)_2Cl]PF_6$, 101470-31-9; *cis*-$[Mo(dmpe)_2(CO)_2]$, 51005-80-2; *trans*-$[Mo(dmpe)_2(CO)_2]$, 63814-04-0; $[MoO(dmpe)_2Cl]Cl$, 101470-34-2; *cis*-$[Mo(dmpe)_2(N_2)_2]$, 101403-80-9; *trans*-$[Mo(dmpe)_2(N_2)_2]$, 101540-28-7; $SnCl_2$, 7772-99-8; $AgPF_6$, 26042-63-7; sodium amalgam, 11110-52-4.

Supplementary Material Available: Tables of anisotropic temperature factors, calculated hydrogen parameters, and bond lengths and angles for $[Mo(dmpe)_2Cl_2]$, $[Mo(dmpe)_2Cl_2][SnCl_3]$, and $[Mo(dmpe)_2(CO)_2Cl]PF_6$, and thermal ellipsoid plots for the independent molecules in all three structures (14 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (27 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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Oxygenated Titanium Sulfide Clusters. Synthesis and Structures of $(CH_3C_5H_4)_4Ti_4S_8O_x$ (x = 1, 2)

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The reaction of Li_2S_2 with $(CH_3C_5H_4)TiCl_3$ followed by exposure to oxygen gives both $(CH_3C_5H_4)_4Ti_4S_8O$ (**1**) and $(CH_3C_5H_4)_4Ti_4S_8O_2$ (**2**). Also isolated was the mixed-ligand complex $(C_5H_5)(CH_3C_5H_4)_3Ti_4S_8O_2$ (**2″**), which arises from an impurity in the starting material. Compound **1** can be converted to **2** by using $(NBu_4)IO_4$, *m*-chloroperoxybenzoic acid, and *tert*-butyl hydroperoxide. Experiments with **1** and its (C_5H_5) analogue indicate that this transformation occurs without cluster fragmentation. The compounds were purified chromatographically and were characterized by spectroscopic and, for **2**, crystallographic methods. ^1H NMR studies over the temperature range −70 to +90 °C show that **1** is dynamic, as the methyl groups give rise to four resonances at low temperatures that merge into three resonances at higher temperatures. The ^1H NMR spectrum of **2**, which does not vary over the temperature range of +80 to −70 °C, shows two methyl resonances and eight cyclopentadienyl ring proton resonances, two of which are coincident. Relative to **2**, the ^1H NMR spectrum of **2″** shows the following differences: (i) one of the two methyl resonances is halved in intensity and is shifted upfield, (ii) three of the eight ring proton resonances are halved in intensity, and (iii) one of the eight ring proton resonances overlaps with the single C_5H_5 peak. Complex **2** crystallizes in the trigonal space group $P3_121$ with a = 10.700 (2) Å, c = 22.530 (6) Å, V = 2233.9 (9) $Å^3$, and ρ_{obsd} = 1.75 g/cm^3 (ρ_{calcd} = 1.77 g/cm^3 for Z = 3). The structure was solved by direct methods leading to a final R = 0.0234 (R_w = 0.0246) with all non-hydrogen atoms anisotropic. The molecule possesses crystallographic C_2 symmetry and consists of a $Ti_4(\mu_4\text{-}O)$ core with two Ti atoms further bridged by an oxo ligand. Each of the four faces of the tetrahedral Ti_4O core is capped by a $\mu_3\text{-}S_2$ ligand.

Introduction

Oxidation is a fundamental reaction type and is of current interest in metal sulfide chemistry.[1-5] The oxidation of certain μ_3-S-containing cluster compounds has been shown to give μ_3-SO compounds whereas the μ-S ligand in an A-frame complex proceeds to the $\mu\text{-}SO_2$ derivative.[2] Disulfur ligands can be oxidized

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to S_2O and S_2O_2 moieties.[1,3,4] Less well-defined reactions of certain molybdenum and cobalt sulfides have provided examples of thiosulfito ($S_2O_2^{2-}$)[5] and dithiosulfato (S_3O_2)[5] complexes. In this paper we describe the novel process whereby monooxygenation of a metal sulfide occurs at the metal and not at the sulfur.

The present study evolved from our recent work on the $(CH_3C_5H_4)_2V_2S_4$ system.[6] The latter is a synthetically versatile compound that provides access to a range of vanadium sulfido clusters. Our early attempts to prepare analogous titanium complexes were directed toward $(CH_3C_5H_4)_2Ti_2(\mu\text{-}S_2)_3$ whose core structure was expected to resemble that of 2,2,2-bicyclooctane.[7] Such a compound would be of interest for the synthesis of titanium sulfide clusters.[8] Molecular sulfide clusters of the titanium and vanadium triads remain rare[9] in contrast to the extensive work that has been described for the polymeric binary sulfides of these elements.[10]

As described in the following section, our initial attempts to prepare $(CH_3C_5H_4)_2Ti_2S_6$ resulted in the isolation of a Ti_4S_8O species, the oxygen atom arising from adventitious contamination or abstraction from the solvent. Subsequent work showed that this Ti_4S_8O cluster could be prepared in good yields simply by oxygenation of $(CH_3C_5H_4)TiS_x$ solutions and that, under these conditions, a $Ti_4S_8O_2$ cluster was formed as well. These compounds appear to arise from the oxygenation and subsequent aggregation of species of the type $(CH_3C_5H_4)_2Ti_2S_4$. Furthermore, the oxygenation of the Ti_4S_8O cluster has been found to result in the coupling of two sulfide ligands.[11]

Results and Discussion

Syntheses of $(RC_5H_5)_4Ti_4S_8O_x$. The reaction of $(CH_3C_5H_4)TiCl_3$ with 1.5 equiv of Li_2S_2 was found to give dark brown solutions from which we have been unable to isolate simple sulfido clusters. The workup of one such reaction afforded small quantities of a species formulated as $(CH_3C_5H_4)_4Ti_4S_8O$ on the basis of field-desorption mass spectrometric data and microanalysis. This compound is readily soluble in polar organic solvents, giving moderately air-sensitive brown solutions. Subsequent studies revealed that this compound forms in good yield when the THF solutions prepared from $(CH_3C_5H_4)TiCl_3$ and Li_2S_2 were intentionally treated with molecular oxygen. These oxygenations also provided small quantities of a green dioxo cluster $(CH_3C_5H_4)_4Ti_4S_8O_2$ (**2**) (eq 1). In view of the rarity of titanium sulfido cluster

$$(CH_3C_5H_4)TiCl_3 \xrightarrow[(2)\ O_2]{(1)\ Li_2S_2} (CH_3C_5H_4)_4Ti_4S_8O + (CH_3C_5H_4)_4Ti_4S_8O_2 \quad (1)$$

compounds and the interesting stoichiometric relationship between **1** and **2**, we chose to study this system further.

Compound **1** was obtained in good yields according to eq 1, but only small amounts (~15%) of **2** were realized in this way.

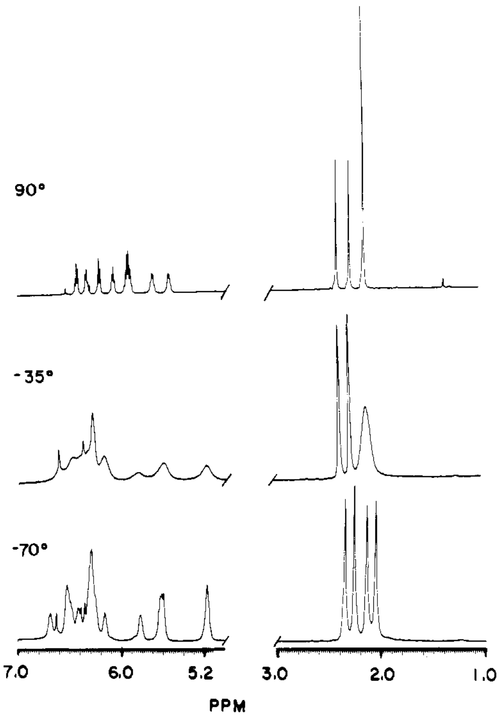

Figure 1. 200-MHz ^1H NMR spectra of $CDCl_3$ solutions of $(CH_3C_5H_4)_4Ti_4S_8O$ (**1**) at +90, −35, and −70 °C.

An improved route to **2** involves the oxidation of **1** with *tert*-butyl hydroperoxide, *m*-chloroperoxybenzoic acid (mCPBA), or tetrabutylammonium periodate (eq 2).

$$\underset{\mathbf{1}}{(CH_3C_5H_4)_4Ti_4S_8O} \xrightarrow{[O]} \underset{\mathbf{2}}{(CH_3C_5H_4)_4Ti_4S_8O_2} \quad (2)$$

In our initial studies it became obvious that our samples of dioxo **2** were contaminated with substantial amounts of $(CH_3C_5H_4)_3(C_5H_5)Ti_4S_8O_2$ (**2″**). The presence of **2″** was traced to an impurity of cyclopentadiene in our methylcyclopentadiene stock. We were surprised that we were able to obtain pure samples of **2″** using flash chromatography. We also prepared $(C_5H_5)_4Ti_4S_8O$ (**1′**) although the dioxo species $(C_5H_5)_4Ti_4S_8O_2$ was not observed, possibly due to its sensitivity to the silica gel chromatography employed in our workups. The mCPBA oxidation of a 1:1 mixture of pure **1** and **1′** gave **2** but no trace of **2″**. This result indicates that the conversion of the monoxo clusters to their dioxo derivatives occurs without cluster fragmentation.

It is important to note that molecular oxygen does not induce the conversion of **1** to **2**. The fact that substantial amounts of **2** are formed along with ca. 60% yield of **1** in the oxygenation of the $[(CH_3C_5H_4)TiS_x]_n$ solutions suggests to us that **1** and **2** arise via the coupling of species of type $(CH_3C_5H_4)_2Ti_2S_4O$ with itself (to give **2**) or with $(CH_3C_5H_4)_2Ti_2S_4$ (to give **1**).

^1H NMR Properties of $Ti_4S_8O_x$ Clusters. The compound $(CH_3C_5H_4)_4Ti_4S_8O$ (**1**) exhibited a temperature-dependent ^1H NMR spectrum. At elevated temperatures three methyl resonances, in the relative ratio of 1:1:2, are observed (Figure 1). Upon cooling, the high-field singlet broadens and then splits, giving a total of four resonances of equal intensity at −70 °C. Using the methods of calculation described in the Experimental Section, we found the rate constant for this process to be 32 s^{-1} at the coalescence temperature, which indicates a $\Delta G^{\ddagger}$ of 50.9 kJ/mol. To our knowledge, this represents the first observation of a structurally dynamic core in a metal sulfide cluster.

When the ring proton ($CH_3C_5\mathit{H}_4$) portions of the ^1H NMR spectra for **1** are examined, only the high-temperature data are easily interpretable (Figure 1). At 90 °C (200 MHz) seven multiplets are observed in the relative intensities 1:1:1:1:2:1:1. Below 20 °C a very complex pattern is observed, although the intensity-weighted average of the resonances remains unchanged. This complexity is however consistent with 16 diastereotopic ring

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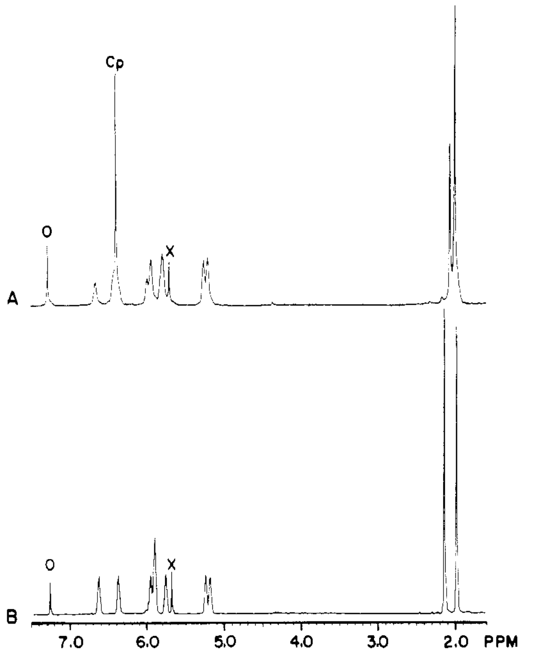

Figure 2. 200-MHz ^{1}H NMR spectra for $(CH_3C_5H_4)_3(C_5H_5)Ti_4S_8O_2$ ($2''$) (spectrum A) and $(CH_3C_5H_4)_4Ti_4S_8O_2$ (**2**) (spectrum B) in $CDCl_3$ (O). An impurity is indicated by (×).

protons associated with the four diastereotopic methyl resonances also observed at low temperature. The more intense ring proton signal can be attributed to the accidental degeneracy of two ring proton resonances; consistent with this view, this more intense multiplet occurs over a relatively broad frequency range.

The ^{1}H NMR spectrum of the dioxide complex $(CH_3C_5H_4)_4Ti_4S_8O_2$ (**2**) did not vary over the temperature range +80 to −70 °C, but it did afford some structural information. The fact that two methyl resonances along with seven (of the possible eight) low-field resonances for the cyclopentadienyl ring protons were observed is indicative that the molecule contains a C_2 axis of symmetry (Figure 2).

The ^{1}H NMR spectrum of **2** could be partially assigned to comparison with that of $2''$ (Figure 2). The ^{1}H NMR spectrum of $(CH_3C_5H_4)_3(C_5H_5)Ti_4S_8O_2$ ($2''$) was unexpectedly simple, indicating the presence of only one isomer where two were possible by virtue of the two inequivalent sites for cyclopentadienyl groups in this cluster (vide infra). The most obvious features of this spectrum are the methyl singlets of unequal intensity and the C_5H_5 singlet. The lower field methyl resonance in $2''$ has shifted nearly 0.1 ppm upfield from that of **2** while the higher field methyl singlet occurs at the same frequency in both compounds. The chemical shift change of one methyl resonance upon substituton of a C_5H_5 for a $CH_3C_5H_4$ group is quite large and may indicate some steric compression in the $(CH_3C_5H_4)_4$ complex. The ^{1}H NMR spectrum of $2''$ could be partially assigned since four ring proton resonances are expected to be halved in intensity relative to those of **2**, (because of the C_5H_5 substitution). A slight complication arises because the C_5H_5 absorption nearly overlaps with one $CH_3C_5\mathit{H}_4$ peak, and one $CH_3C_5\mathit{H}_4$ resonance shifts (as one methyl resonance has) to higher field. The resulting assignments (Figure 2) are in accord with those arrived at by chemical shift correlated 2-D NMR spectroscopy.[12]

Molecular Structure of $(CH_3C_5H_4)_4Ti_4S_8O_2$. An ORTEP drawing of the molecule with labeling scheme employed is shown in Figure 3, while a drawing of the $Ti_4S_8O_2$ core is shown in Figure 4. Selected bond distances and angles are presented in Table I.

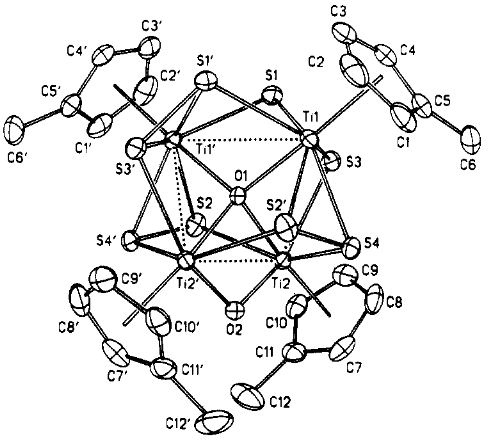

Figure 3. Molecular structure and labeling scheme for $(CH_3C_5H_4)_4Ti_4S_8O_2$ (**2**). Thermal ellipsoids are depicted at the 40% probability level.

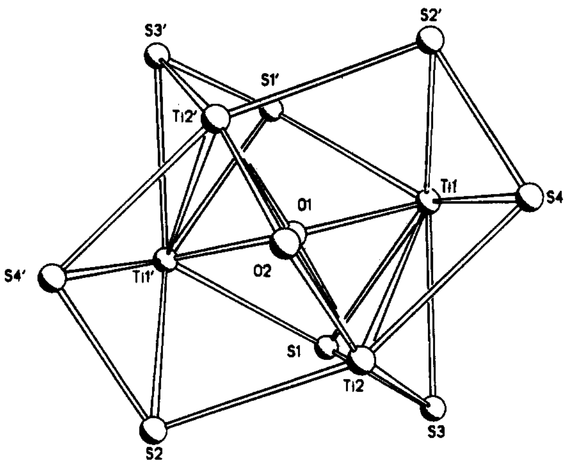

Figure 4. Cluster framework for **2** as viewed along the crystallographic 2-fold axis (the *a* axis of the unit cell).

Table I. Selected Bond Distances and Angles for $(CH_3C_5H_4)_4Ti_4S_8O_2$ (**2**)

	(a) Bond Distances (Å)		
Ti(1)···Ti(2)	3.202 (1)	Ti(2)–S(2)	2.593 (1)
Ti(1)···Ti(1′)	3.329 (1)	Ti(2)–S(3)	2.588 (1)
Ti(2)···Ti(2′)	2.985 (1)	Ti(2)–S(4)	2.531 (1)
Ti(1)–S(1)	2.540 (1)	Ti(1)–O(1)	2.063 (1)
Ti(1)–S(2′)	2.599 (1)	Ti(2)–O(1)	2.045 (2)
Ti(1)–S(3)	2.503 (1)	Ti(2)–O(2)	1.843 (1)
Ti(1)–S(4)	2.472 (1)	S(1)–S(3)	2.043 (1)
Ti(1)–S(1′)	2.561 (1)	S(2)–S(4′)	2.057 (1)
	(b) Bond Angles (deg)		
S(1)–Ti(1)–S(3)	47.6 (0)	O(1)–Ti(2)–O(2)	79.0 (1)
S(1)–Ti(1)–S(4)	128.4 (0)	Ti(1)–S(1)–Ti(1′)	81.5 (0)
S(3)–Ti(1)–S(4)	84.3 (0)	S(3)–S(1)–Ti(1′)	108.8 (0)
S(1)–Ti(1)–O(1)	74.6 (0)	Ti(2)–S(2)–Ti(1′)	89.8 (0)
S(1)–Ti(1)–S(1′)	76.8 (0)	Ti(2)–S(2)–S(4′)	96.7 (0)
S(3)–Ti(1)–S(1′)	122.2 (0)	Ti(1′)–S(2)–S(4′)	62.9 (0)
S(4)–Ti(1)–S(1′)	133.5 (0)	Ti(1)–S(3)–Ti(2)	77.9 (0)
O(1)–Ti(1)–S(1′)	74.1 (0)	Ti(1)–S(3)–S(1)	67.2 (0)
S(1)–Ti(1)–S(2′)	144.9 (0)	Ti(2)–S(3)–S(1)	108.1 (0)
S(3)–Ti(1)–S(2′)	126.1 (0)	Ti(1)–S(4)–Ti(2)	79.6 (0)
S(4)–Ti(1)–S(2′)	47.8 (0)	O(1)–Ti(1)–S(2′)	70.8 (0)
S(1′)–Ti(1)–S(2′)	88.2 (0)	Ti(2)–S(4)–S(2′)	103.0 (0)
S(2)–Ti(2)–S(3)	86.9 (0)	Ti(1)–S(4)–S(2′)	69.3 (0)
S(2)–Ti(2)–S(4)	147.0 (0)	Ti(1)–O(1)–Ti(2)	102.4 (0)
S(3)–Ti(2)–S(4)	81.4 (0)	Ti(1)–O(1)–Ti(1′)	107.6 (1)
S(2)–Ti(2)–O(2)	91.7 (0)	Ti(2)–O(1)–Ti(1′)	126.3 (0)
S(3)–Ti(2)–O(2)	152.4 (1)	Ti(2)–O(1)–Ti(2′)	93.8 (1)
S(4)–Ti(2)–O(2)	85.1 (0)	Ti(2)–O(2)–Ti(2′)	108.2 (1)

As was predicted from the NMR results, **2** possesses a 2-fold (crystallographic) axis through the two oxygen atoms, affording equivalent pairs of methylcyclopentadienyl groups. The relatively complicated core structure of **2** can be built up beginning with a pseudotetrahedral Ti_4O array followed by the attachment of a γ-S_2 unit to each of the four faces of the tetrahedron. Finally, one edge of the tetrahedron is spanned by a μ-oxo group. The

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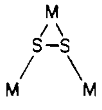
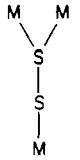
(12) Zank, G. A. Ph.D. Thesis, University of Illinois, 1985.

dihedral angle between the Ti(2,2′)–μ_4-O and Ti(1,1′)–μ_4-O planes is 108.7°, giving rise to a chiral Ti_4O core. The Ti(2,2′)–μ-O distances of 1.84 Å may be indicative of some π-donation from the oxygen to the titanium centers while the Ti–μ_4-O distances are much longer at 2.06 and 2.05 Å.[13] The sulfur–sulfur distances of 2.03 and 2.06 Å are normal.[11] The titanium–sulfur distances range from 2.47 to 2.59 Å, even though the titanium centers are formally electron-deficient.[8,14] With respect to the Ti–Ti contacts, four are 3.20 Å and one is 3.329 (1) Å. The pair of titanium atoms that are bridged by two oxo groups are separated by only 2.985 (1) Å. For comparison the average Ti–Ti distance in $(C_5H_5)_6Ti_6O_8$ is 2.891 (1) Å while for $(C_5H_5)_5Ti_5S_6$ the Ti–Ti distances fall in the range 3.076 (5)–3.214 (5) Å.[8]

One pair of titanium atoms in **2** is bound to three sulfur atoms as well as the μ- and μ_4-oxo atoms, while the other ("bottom") pair of titanium atoms are bound to five sulfur atoms and the μ_4-oxide. The coordination environment of the bottom pair of titanium atoms resembles that found in $(C_5H_5)Ti(S_2CNMe_2)_3$.[15] The coordination about the S_2 group is similar to that found in $Mn_4(CO)_{15}S_4$[16] and $[(C_5H_5)_4Fe_4S_5]^+$[17] (A-type); the alternative (Y-type) geometry is found in $(C_5H_5)_4Fe_4(S_2)_2S_2$.[18]



A-type



Y-type

The μ_4-oxo ligand present in **2** adds to a growing list of such ligands found in both inorganic and organometallic compounds. A series of $(base)_4Cu_4Cl_6O$ (base = pyridine, Ph_3PO, or Me_4N) complexes have been shown to consist of an adamantane arrangement of Cu and Cl atoms, with the four Cu centers equidistant from the μ_4-oxide.[19a] A second class of compounds featuring a tetrahedral array of metals and a μ_4-oxide are the carboxylates of the formula $M_4O(O_2CR)_6$, where M = Zn(II), Co(IV) and Fe(III).[19b] Recently the unsymmetrical $ZnV_3(\mu_4\text{-}O)$ subunit was found in $[VZnO(O_2CC_6H_5)_3THF]_4{\cdot}2THF$.[20] There have been two complexes reported that contain both μ_4-oxide- and sulfur-based ligand sets. One is a zinc complex with dithiophosphate ligands, $Zn_4[S_2P(OR)_2]_6O$,[21] while the other is an anionic molybdenum nitrosyl sulfide $[Mo_4(NO)_4(S_2)_6O]^{2-}$.[22]

Structure of $(CH_3C_5H_4)_4Ti_4S_8O$. X-ray quality single crystals of the monooxide compound were not obtained despite numerous efforts. In constructing candidate structures for **1**, we relied on the following constraints and hypotheses.

(i) $(CH_3C_5H_4)_4Ti_4S_8O$, like the dioxide **2**, probably contains a μ_4-oxo ligand.

(ii) As in $(CH_3C_5H_4)_4Ti_4S_8O_2$, the titanium centers in **1** assume a formal oxidation state of IV, thereby requiring the sulfur donor set of $(S^{2-})_2(S_2^{2-})_3$ (for a total of 10 e). This does not exclude less conventional (unlikely) donor sets such as $(S^{2-})_3(S_3^{2-})(S_2^{2-})$ and $(S^{2-})_4(S_4^{2-})$. The assignment of the titanium(IV) oxidation state rests on its diamagnetism, the similarity of the ^1H NMR chemical shifts for **1** and **2**, and the *complete* absence of any electrochemical activity in the range +2.0 to −1.5 V (vs. Ag/AgCl).

(iii) The ground state structure of **1** contains four diastereotopic $(CH_3C_5H_4)$ groups as seen in its low-temperature ^1H NMR spectrum.

(iv) A low-energy process ($\Delta G^{\ddagger}$ = 50.9 kJ/mol) induces a time-averaged plane of symmetry into the Ti_4S_8O cluster, giving at higher temperatures a 1:1:2 set of methyl singlets and a 1:1:1:1:2:1:1 set of signals for the ring protons.

(v) On the basis of the intramolecularity of the conversion of **1** and **2**, this oxidation proceeds with a minimum of overall rearrangement of the cluster itself (see point i).

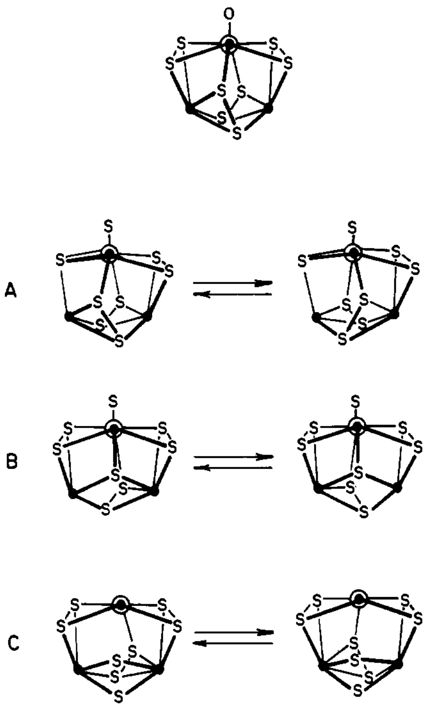


Figure 5. Structure for $(CH_3C_5H_4)_4Ti_4S_8O_2$, and three possibilities for **1** (A–C). The μ_4-O and $CH_3C_5H_4$ ligands are omitted for clarity. Three titanium atoms are represented by filled-in circles, while the eclipsed one is indicated by a large open circle.

On the basis of the above considerations the three structures represented in Figure 5 are viable candidates.

In reviewing these possibilities, structure C is seen to possess two very electron-deficient titanium centers, which have essentially "lost" an oxygen atom from **2** and have "gained" nothing in return. This structure is inconsistent with this compound's considerable chemical stability. Structure B involves the migration of one of the sulfur atoms from a "bottom" disulfide to replace the μ-oxide of **2**, leaving a μ_3-sulfide on a basal face. Structure A simply involves the migration of a sulfur atom from a "top" disulfide to replace the missing μ-O, again leaving a μ_3-sulfide. With either structure, A or B, the time-averaged symmetry plane (cf. variable-temperature NMR results) would be introduced by the reversible breaking of one Ti–S bond.

Concluding Remarks

The compounds described in this paper represent rare examples of titanium sulfide clusters. They probably owe much of their stability to the presence of a quadruply bridging oxide, which not only tethers the four titanium centers but also functions as a six-electron ligand.

Through the use of C_5H_5 and $CH_3C_5H_4$ as labels we were able to show that the conversion of **1** to **2** occurs without cluster fragmentation. The DNMR characteristics of **1** limit the number of structural possibilities (as does its facile conversion to **2**). We conclude that **1** is properly formulated as $(CH_3C_5H_4)_4Ti_4(O)(S_2)_3(S)_2$ and that the introduction of a second oxo ligand induces the coupling of the two sulfides. It is significant that

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molecular oxygen does not convert **1** to **2** since both are formed in the oxygenation of the $(CH_3C_5H_4)TiS_x$ solution. One rationale for this observation is provided by the sequence of reactions

$$2(CH_3C_5H_4)TiCl_3 \rightarrow (CH_3C_3H_4)_2Ti_2S_4$$

$$(CH_3C_5H_4)_2Ti_2S_4 + {}^1/_2O_2 \rightarrow (CH_3C_5H_4)_2Ti_2S_4O$$

$$(CH_3C_5H_4)_2Ti_2S_4O + (CH_3C_5H_4)_2Ti_2S_4 \rightarrow \mathbf{1}$$

$$2(CH_3C_5H_4)_2Ti_2S_4O \rightarrow \mathbf{2}$$

The oxidation of metal sulfido and disulfido complexes has been examined recently by ourselves and Herberhold et al. We have found that many compounds containing μ_3-S and terminal η^2-S_2 ligands could be converted smoothly to the respective μ_3-SO and η^2-S_2O_x (x = 1, 2) derivatives.[1] These transformations are most effectively conducted by using peroxy carboxylic acids. Herberhold has recently discovered that $(C_5Me_5)Mn(S_2)(CO)_2$ is converted to $(C_5Me_5)Mn(S_2O)(CO)_2$ even with molecular oxygen.[5] This prior work stands in contrast to the present results wherein *an oxygen is delivered to the metal concomitant with the coupling of two sulfido ligands*. It is conceivable that this reaction proceeds via the intermediacy of an S_2O complex. This pattern of oxidation of the metal centers concomitant with S–S coupling was proposed recently by us in the reaction of $(CH_3C_5H_4)_2V_2S_2$(PTD) with a second equivalent of PTD (PTD = 1-phenyl-1,3,5-triazolinedione).[23]

Experimental Section

Materials and Methods. All preparative reactions were performed under an atmosphere of purified nitrogen and workups were done aerobically. Tetrahydrofuran (THF) was redistilled from sodium–potassium alloy under nitrogen; 1 M solutions of $LiHBEt_3$ in THF were purchased from Aldrich Chemical Co. Methylcyclopentadiene (90% Aldrich) was cracked by using a 40-cm vacuum-jacketed Vigreux column collecting the 63–65 °C fraction. The $CH_3C_5H_5$ monomer was then purified by two distillations employing the column described above, giving material with less than 1% impurity of cyclopentadiene (C_5H_6).[24] $(C_5H_5)TiCl_3$ and $(CH_3C_5H_4)TiCl_3$ were prepared in sealed Carius tubes according to the method of Green.[25] Flash chromatography was performed with Woehm 32-63 silica gel in 2 × 18-in. columns.

All new compounds were isolated as crystalline solids that gave satisfactory analysis. These data were obtained by the University of Illinois Microanalytical Laboratory. Field desorption (FD) mass spectra were measured by Carter Cook on a Varian 731 spectrometer at the University of Illinois Mass Spectrometry Laboratory. ^1H NMR measurements were made on a Varian XL-200 instrument. The following abbreviations are used to describe the NMR data: s (singlet), pt (pseudo triplet), br (broad), m (multiplet).

$(CH_3C_5H_4)_4Ti_4S_8O$ (1) and $(CH_3C_5H_4)_4Ti_4S_8O_2$ (2). In a typical reaction $LiHBEt_3$ (60 mL, 60 mmol) was added to elemental sulfur (960 mg, 30 mmol) followed by the addition of sulfur (960 mg, 30 mmol) to the homogeneous pale yellow solution of Li_2S.[26] This solution was then transferred via a stainless-steel cannula into a THF (50 mL) solution of $(CH_3C_5H_4)TiCl_3$ (4.68 g, 20 mmol). The then dark purple-brown solution was stirred for 24 h under nitrogen and an equal amount of time in air. The products were purified by removal of the THF on a rotary evaporator followed by adsorbing the residue on silica gel and flash column chromatography eluting with 7/3 hexanes/dichloromethane. Collection of the green band followed by concentration of the eluent to a small volume gave $(CH_3C_5H_4)_4Ti_4S_8O_2$ (**2**) as green crystals in 15% yield (600 mg). Anal. Calcd for $C_{24}H_{28}Ti_4S_8O_2$: C, 36.18; H, 3.54; Ti, 24.05; S, 32.20. Found: C, 36.04; H, 3.62; Ti, 23.71; S, 30.66. FDMS (*m/e*): 796, M^+. ^1H NMR ($CDCl_3$): δ 6.63 (pt, 2 H), 6.38 (pt, 2 H), 5.96 (pt, 2 H), 5.91 (m, 4 H), 5.76 (pt, 2 H), 5.24 (pt, 2 H), 5.18 (pt, 2 H), 2.15 (s, 6 H), 1.99 (s, 6 H). The slower moving brown band was stripped to dryness. The residue was crystallized by dissolution in hot hexane followed by cooling to −30 °C (2.20 g, 56% yield). Anal. Calcd for $C_{24}H_{28}Ti_4S_8O$: C, 36.92; H, 3.62; Ti, 24.54; S, 32.86. Found: C, 36.03; H, 3.61; Ti, 24.39; S, 32.86. FDMS (*m/e*): 780, M^+. ^1H NMR ($CDCl_3$) at 90 °C: δ 6.44 (pt, 2 H), 6.33 (pt, 2 H), 6.21 (pt, 2 H), 6.08 (pt, 2 H), 5.93 (m, 4 H), 5.71 (pt, 2 H), 5.55 (pt, 2 H), 2.37 (s, 3 H), 2.24 (s, 3 H), 2.10 (s, 6 H).

Table II. Atom Coordinates (×10^4) and Temperature Factors (10^3 Å^2) for **2**

atom	x	y	z	U^a
Ti(1)	7180 (1)	1784 (1)	3248 (1)	25 (1)
Ti(2)	4187 (1)	689 (1)	3932 (1)	23 (1)
S(1)	7430 (1)	215 (1)	4031 (1)	34 (1)
S(2)	3587 (1)	−1901 (1)	4217 (1)	34 (1)
S(3)	6749 (1)	1557 (1)	4344 (1)	32 (1)
S(4)	5587 (1)	2841 (1)	3257 (1)	30 (1)
O(1)	5149 (2)	0	3333	21 (1)
O(2)	2833 (2)	0	3333	29 (1)
C(1)	8736 (3)	4185 (3)	2872 (2)	49 (1)
C(2)	9080 (4)	3243 (4)	2588 (2)	56 (1)
C(3)	9651 (3)	2717 (4)	3001 (2)	49 (1)
C(4)	9667 (3)	3343 (3)	3549 (2)	42 (1)
C(5)	9104 (3)	4268 (3)	3474 (2)	43 (1)
C(6)	8975 (5)	5195 (4)	3932 (2)	66 (2)
C(7)	3044 (4)	2042 (4)	4236 (1)	49 (2)
C(8)	4368 (4)	2632 (3)	4528 (2)	51 (2)
C(9)	4313 (4)	1615 (4)	4922 (1)	45 (2)
C(10)	2963 (3)	373 (3)	4861 (1)	40 (1)
C(11)	2161 (3)	655 (4)	4445 (1)	41 (1)
C(12)	646 (5)	−414 (7)	4268 (3)	86 (3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

$(C_5H_5)_4Ti_4S_8O$ (1′). A solution of Li_2S_2 (1170 mg, 15 mmol) prepared as described above was added as a THF (50 mL) solution to a 50-mL THF solution of $(C_5H_5)TiCl_3$ (2200 mg, 10 mmol). After the resulting brown solution was stirred under nitrogen for 24 h and an equal amount of time in air, the solvent was removed in vacuo. The product was extracted from the residue with CH_2Cl_2 (70 mL) and obtained as black crystals by adding of toluene (30 mL), concentrating to 20 mL, and cooling to −30 °C (800 mg, 44.4%). Anal. Calcd for $C_{20}H_{20}Ti_4S_8O$: C, 33.15; H, 2.76; Ti, 26.50; S, 35.36. Found: C, 33.44; H, 2.88; Ti, 26.64; S, 35.81. FDMS (*m/e*): 740, $(C_5H_5)_4Ti_4S_8O_2$; 724, M^+. ^1H NMR ($CDCl_3$): δ 6.55 (s, 5 H), 6.40 (s, 5 H), 5.92 (br, s, 10 H).

$(CH_3C_5H_4)_3(C_5H_5)Ti_4S_8O_2$ (2″). This synthesis was conducted in a manner identical with that described for **1** and **2** above except that $(CH_3C_5H_4)TiCl_3$ impure with $(C_5H_5)TiCl_3$ was used. In the chromatography step, a green band slower than that for $(CH_3C_5H_4)_4Ti_4S_8O_2$ was observed. Collection of this band followed by concentrating to 5 mL and cooling to −30 °C gave 31 mg (<1% yield) of $(CH_3C_5H_4)_3(C_5H_5)Ti_4S_8O_2$ (**2″**). Anal. Calcd for $C_{23}H_{26}Ti_4S_8O_2$: C, 35.30; H, 3.34; Ti, 24.48; S, 32.77. Found: C, 34.66; H, 3.20; Ti, 23.82; S, 31.79. FDMS (*m/e*): 782, M^+. ^1H NMR ($CDCl_3$): δ 6.62 (pt, 1 H), 6.40 (pt, 1 H), 6.39 (s, 5 H), 6.02 (pt, 1 H), 5.92 (pt, 2 H), 5.80 (m, 3 H), 5.27 (pt, 2 H), 5.20 (pt, 2 H), 2.07 (s, 3 H), 2.01 (s, 6 H). We were unable to isolate pure samples of $(CH_3C_5H_4)_3(C_5H_5)Ti_4S_8O$.

Oxidation of $(CH_3C_5H_4)_4Ti_4S_8O$. In a typical reaction $(CH_3C_5H_4)_4Ti_4S_8O$ (50 mg, 0.064 mmol) was stirred with *m*-chloroperbenzoic acid (55 mg, 0.32 mmol) in CH_2Cl_2 (10 mL) for 24 h. At this time all of **1** had been consumed, and the reaction mixture was purified by chromatography through 10 cm of silica gel. The yield of the recrystallized $(CH_3C_5H_4)_4Ti_4S_8O_2$ (**2**) was 12 mg (26%). Similar yields were obtained by using tetrabutylammonium periodate and *tert*-butyl hydroperoxide. Oxygen or propylene oxide resulted in decomposition.

Oxidation of $(CH_3C_5H_4)_4Ti_4S_8O$ in the Presence of $(C_5H_5)_4Ti_4S_8O$. To a CH_2Cl_2 (50 mL) solution of $(CH_3C_5H_4)_4Ti_4S_8O$ (98 mg, 0.125 mmol) and $(C_5H_5)_4Ti_4S_8O$ (90 mg, 0.125 mmol) was added *tert*-butyl hydroperoxide (170 mL, 2.5 mmol). After 24 h, chromatographic workup (as described above) gave $(CH_3C_5H_4)_4Ti_4S_8O_2$ (by NMR) but no $(CH_3C_5H_4)_3(C_5H_5)Ti_4S_8O_2$.

Dynamic NMR Calculations.[27] The rate constant was determined from

$$k = \pi(\delta\nu)^2/2(W^* - W_0)$$

where k = rate constant (s^{-1}), $\delta\nu$ = peak separation at slow exchange (17 Hz), W^* = line width at half-height at coalescence (18 Hz), and W_0 = line width at slow exchange (4 Hz). The activation free energy was calculated from

$$\Delta G^* = aT(10.319k + \log T)$$

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where $a = 4.575 \times 10^{-3}$ kcal/mol, T = coalescence temperature (K), and k = rate constant (s^{-1}).

X-ray Crystallography. Dark green crystals of $(CH_3C_5H_4)_4Ti_4S_8O_2$ were grown from CH_2Cl_2 solutions layered with hexanes. A crystal with dimensions 0.22 × 0.30 × 0.38 mm was found to be trigonal with cell dimensions a = 10.700 (2) Å, c = 22.530 (6) Å, and V = 2233.9 (9) Å^3. The measured density of 1.75 g/cm^3 was in good agreement with the calculated density of 1.77 g/cm^3 for Z = 3. The data were collected on a Nicolet R3 automated diffractometer by using the ω-scan technique ($4° \leq 2\theta \leq 50°$) at ambient temperature with monochromatized Mo Kα (λ = 0.71069 Å) radiation, μ = 16.3 cm^{-1}. Of the 4271 reflections collected, 2633 were unique and 2619 were observed at the $(F_o) > 2.5\sigma(F_o)$ level of confidence. The structure was solved by direct methods in $P3_1$; after the presence of a 2-fold rotational symmetry became apparent, the coordinates were transformed to those for $P3_121$ (in $P3_221$, R = 0.0259). All non-hydrogen atoms were refined with anisotropic temperature factors; all methyl group hydrogen atoms were located and refined isotropically with ring hydrogen atoms placed in idealized positions. At convergence R = 0.0234, R_w = 0.0246, GOF = 0.935, mean Δ/σ = 0.09, and the highest residual peak = 0.34 e/Å^3. Atomic coordinates and anisotropic thermal parameters are presented in Table II.

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Registry No. **2**, 101224-50-4; **2″**, 101224-51-5; $(CH_3C_5H_4)TiCl_3$, 1282-31-1; $LiHBEt_3$, 22560-16-3; Li_2S_2, 51148-09-5; $(C_5H_5)TiCl_3$, 1270-98-0.

Supplementary Material Available: Listings of complete bond lengths and angles, anisotropic thermal parameters, all hydrogen atom parameters, and structure factors (21 pages). Ordering information is given on any current masthead page.

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Synthesis of an Iron(III) Porphyrin Dimer with a *trans*-Dicyanoethylenedithiolate Bridging Ligand: Structural and Magnetic Studies on (μ-FNT-*S*,*S*′)$[Fe(TPP)]_2 \cdot 2C_6H_6$

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An iron(III) porphyrin dimer containing a novel bridge involving the FNT^{2-} ligand (FNT^{2-} = *trans*-1,2-dicyanoethylenedithiolate) has been synthesized. A single-crystal X-ray diffraction study (monoclinic, $P2_1/n$, a = 14.263 (3) Å, b = 15.184 (4) Å, c = 19.172 (4) Å, β = 93.92 (2)°, Z = 2) of **1** ((μ-FNT-*S*,*S*′)$[Fe(TPP)]_2 \cdot 2C_6H_6$) shows that the iron(III) atoms of the centrosymmetric dimer are axially bonded to the trans sulfur atoms of the planar FNT^{2-} bridging ligand (Fe–S = 2.324 (2) Å). The plane of the bridging ligand is nearly parallel to the porphyrin plane, implying that the iron atoms interact with π electrons of the FNT^{2-} bridge. The metric parameters for the $[Fe(TPP)]^+$ unit indicate high-spin character for the iron atoms. The magnetic susceptibility of **1** is matched well between 1.8 K and room temperature by susceptibilities calculated from a theoretical model that includes antiferromagnetic coupling between two such high-spin iron(III) atoms; the best values of J and $|D|$ are −8.5 and 9.6 cm^{-1}, respectively. Mössbauer and EPR spectroscopic results for **1** support the high-spin assignment and antiferromagnetic coupling scheme.

Introduction

Bonds between the iron atom of an iron(III) porphyrin unit and axial thiolate ligands occur in a number of heme protein systems.[2] The ability of sulfur-containing ligands to mediate the electronic coupling between metal centers and to affect the spin state of individual iron(III) atoms is of considerable importance in understanding the biological role of these sulfur-ligated heme units. However, only a small number of systems containing an iron(III) porphyrin with axial sulfur ligands have been prepared and structurally characterized,[3] in part because of the facile oxidation–reduction reaction that occurs between iron(III) and many sulfur-containing ligands of interest.

We have prepared a dimer of ferric porphyrins, in which bridging between the two iron(III) atoms is accomplished by binding of the iron atoms to the trans sulfur atoms of FNT^{2-} (FNT^{2-} = *trans*-1,2-dicyanoethylenedithiolate, or fumaronitriledithiolate). The structure and physical properties of this system ((μ-FNT-*S*,*S*′)$[Fe(TPP)]_2 \cdot 2C_6H_6$, hereafter **1**) constitute the subject of this report.

Experimental Section

Synthesis of (μ-*trans*-1,2-Dicyanoethylenedithiolato-*S*,*S*′)bis((tetraphenylporphinato)iron(III))–2-Benzene, (μ-FNT-*S*,*S*′)$[Fe(TPP)]_2 \cdot 2C_6H_6$ (1). $[Fe(TPP)(ClO_4)] \cdot 0.5C_6H_5CH_3$[4] and sodium *trans*-1,2-dicyanoethylenedithiolate (Na_2FNT)[5,6] were prepared by literature methods. A mixture of $[Fe(TPP)(ClO_4)] \cdot 0.5C_6H_5CH_3$ (0.2056 g, 2.53×10^{-4} mol) and Na_2FNT (0.0958 g, 5.15×10^{-4} mol) in benzene (130 mL) was stirred at reflux temperature for 6 h, cooled to room temperature, and passed through a medium frit to separate excess solid Na_2FNT. *n*-Heptane (50 mL) was added to the filtrate slowly, with constant stirring. After reduction of solvent volume (to ca. 30 mL), fine purple-black crystals of **1** were collected on a medium frit, washed with *n*-heptane, weighed (0.1833 g, 89% yield), and analyzed. (Anal. Calcd for $C_{104}H_{68}N_{10}S_2Fe_2$: C, 76.47; H, 4.20; N, 8.57. Found: C, 76.66; H, 4.44; N, 8.83.) The solution spectrum in benzene is shown in Figure 1.

Single crystals of **1** of suitable size and quality for X-ray diffraction studies were grown by vapor diffusion of *n*-heptane into a solution of **1**

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