For the two Cr(III) dimers, the remaining two sites are occupied by a chloro ligand and a bridging alkoxo oxygen from the second apdol ligand, while in the Co trimer, the remaining two sites are occupied by nitro-*O* and acetato-*O* oxygen donors. Perhaps these are not quite as spectacular as Geldman's example[29] [Pt(py)-(NH₃)(NO₂)(Cl)(Br)(I)], but they are certainly members of this rather rare situation.

Supplementary Material Available: Listings of atomic parameters for non-hydrogen atoms, bond lengths, bond angles, anisotropic thermal parameters for non-hydrogen atoms, and hydrogen atom parameters for the Cr(III) dimer and Co trimer (10 pages); listings of structure factors for both compounds (42 pages). Ordering information is given on any current masthead page.

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(30) The nomenclature adopted here is that the free ligand will be given an abbreviation, followed by the number of H atoms attached to oxygen in the alcohol form. On successive deprotonation, these will be reduced from the ligand abbreviation to give the number of H atoms remaining. The number and type of coordinated donor atoms will be indicated in the formula of the complex, after the ligand abbreviation. We use the following: NH₂(CH₂)₂OH, enol-H; NH₂(CH₂)₃OH, tnol-H; NH₂(CH₂)₂NH(CH₂)₂OH, 2-((2-aminoethyl)amino)ethanol, aeol-H; NH₂(CH₂)₃NH(CH₂)₂OH, 2-((3-aminopropyl)amino)ethanol, apol-H; NH₂-(CH₂)₃N(CH₂CH₂OH)₂, *N*-(3-aminopropyl)diethanolamine; apdol-H₂; NH₂(CH₂)₂NH₂, en; NH₂(CH₂)₃NH₂, tn; NH₂(CH₂)₂NH(CH₂)₂NH₂, diethylenetriamine, dien (2,2-tri); NH₂(CH₂)₂NH(CH₂)₃NH₂, *N*-(2-aminoethyl)-1,3-diaminopropane (2,3-tri). Thus, the completely chelated *N*-(3-aminopropyl)diethanolamine with all H atoms present will be represented as (apdol-H₂-*N,N',O,O'*).

(31) Further support for this arrangement is provided by the X-ray bonding geometry in which the Co–O bond lengths to the central cobalt are significantly longer than those to the terminal cobalt atoms, consistent with the greater ionic radius of Co(II) relative to Co(III). We thank a reviewer for this observation.

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Synthesis and Cluster Interconversion Chemistry of a Linear Trinuclear Hexakis(μ-benzenethiolato)triiron(II) Hexacarbonyl Compound

M. Anton Walters* and John C. Dewan

The neutral compound Fe₃(SPh)₆(CO)₆ (**1**) assembles in a solution containing NaSPh and FeCl₂ in a 2:1 ratio in ethanol under an atmosphere of carbon monoxide at room temperature. It also forms in the reaction of the Fe₄(SPh)₁₀²⁻ ion with CO and FeBr₂ and by the oxidative addition of PhSSPh to an Fe(0) carbonyl species with UV irradiation in an inert atmosphere under ambient conditions. Product **1** was characterized by X-ray diffraction and found to be a linear trinuclear complex in which the benzenethiolate ligands occupy bridging positions and the carbonyl ligands are exclusively terminally bonded. Crystal data are space group *P*2₁/*n* with *a* = 11.077 (1) Å, *b* = 10.488 (1) Å, *c* = 19.052 (2) Å, *β* = 95.41 (6)°, *V* = 2203.52 Å³, and *Z* = 2. On the basis of the observed octahedral coordination of each of the iron atoms in **1**, it is suggested that octahedral coordination may occur in the limit of unrestricted CO binding in the CO-inhibited states of iron–sulfur enzymes. Compound **1** converts to Fe(SPh)₄²⁻ (**2**) in neat Me₂SO solution where the counterion is probably Fe(Me₂SO)₆²⁺. The compound [Fe(Me₂SO)₆][Fe₄(SPh)₁₀] (**3**) is formed in a mixed solution of Me₂SO/THF (1:25, v/v) and can be isolated as brown crystals. The self-assembly of these clusters in lieu of others that could form with the same Fe:thiolate ratio suggests that those which are obtained represent clusters with particularly stable structures. The formation of clusters in such "stoichiometrically free" environments suggests new approaches to the study of cluster formation.

The role of carbon monoxide as a potent dead end inhibitor of the iron–sulfur enzyme hydrogenase[1,2] and the molybdenum–iron–sulfur enzyme nitrogenase[3] has stimulated our interest in synthetic iron–sulfur carbonyl complexes. In tandem with our study of CO binding to preformed iron–sulfur clusters in proteins and model compounds, we have attempted syntheses of iron–sulfur carbonyl compounds from simple precursors. This report delineates syntheses of a series of iron–sulfur (Fe–S) compounds, beginning with the neutral carbonyl cluster Fe₃(SPh)₆(CO)₆ (**1**) (Ph = C₆H₅), which forms under carbon monoxide in a solution containing sodium benzenethiolate and ferrous chloride in a 2:1 ratio. This complex provides insight into the preferred stereochemistry of Fe(II)–sulfur carbonyl complexes and is relevant to the interaction of CO and Fe–S enzyme active sites. In the coordinating solvent Me₂SO, CO is displaced as a terminal ligand in complex **1** followed by cluster rearrangement, leading to the formation of Fe(SPh)₄²⁻ (**2**) with solvated Fe(II) as a counterion in solution, and [Fe(Me₂SO)₆][Fe₄(SPh)₁₀] (**3**), which is isolated as a crystalline solid.

In the area of iron–sulfur carbonyl chemistry there has traditionally been an emphasis on compounds derived from the oxidative addition reactions of iron carbonyl compounds with alkyl or phenyl disulfides, resulting in Fe(I) compounds with bridging mercaptides or disulfides.[4-11] Recently, studies have appeared which focus on iron(II)–sulfur carbonyl compounds whose ster-

*To whom correspondence should be addressed at the Department of Chemistry, New York University, New York, NY 10003.

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Table I. Final Positional Parameters for the Atoms of Fe₃(SPh)₆(CO)₆ (1)[a]

atom	x	y	z
Fe(1)	0.0000	0.0000	0.0000
Fe(2)	0.25941 (5)	-0.13064 (5)	0.03089 (3)
S(1)	0.06794 (8)	-0.22603 (9)	0.00427 (5)
S(2)	0.15766 (8)	0.00164 (10)	0.10448 (5)
S(3)	0.19291 (8)	0.01302 (9)	-0.05823 (5)
O(1)	0.3685 (3)	-0.2710 (3)	-0.08082 (18)
O(2)	0.3036 (3)	-0.3340 (4)	0.13579 (19)
O(3)	0.4737 (3)	0.0196 (3)	0.08153 (16)
C(1)	0.3276 (4)	-0.2180 (4)	-0.0371 (2)
C(2)	0.2864 (4)	-0.2548 (4)	0.0959 (2)
C(3)	0.3922 (4)	-0.0398 (4)	0.0605 (2)
C(11)	0.0643 (3)	-0.3107 (4)	-0.0773 (2)
C(12)	0.0445 (4)	-0.2521 (4)	-0.1424 (2)
C(13)	0.0396 (5)	-0.3237 (5)	-0.2029 (3)
C(14)	0.0556 (5)	-0.4535 (5)	-0.1994 (3)
C(15)	0.0749 (5)	-0.5119 (5)	-0.1356 (3)
C(16)	0.0794 (4)	-0.4410 (4)	-0.0748 (3)
C(21)	0.1315 (3)	-0.0810 (4)	0.18356 (18)
C(22)	0.0245 (4)	-0.1422 (4)	0.1920 (2)
C(23)	0.0078 (5)	-0.2017 (5)	0.2548 (2)
C(24)	0.0978 (5)	-0.2043 (5)	0.3085 (2)
C(25)	0.2050 (5)	-0.1431 (6)	0.3004 (2)
C(26)	0.2217 (4)	-0.0803 (5)	0.2382 (2)
C(31)	0.2690 (3)	0.1640 (4)	-0.0556 (2)
C(32)	0.2744 (4)	0.2449 (4)	0.0013 (2)
C(33)	0.3329 (4)	0.3612 (4)	-0.0013 (3)
C(34)	0.3832 (4)	0.3970 (5)	-0.0608 (3)
C(35)	0.3756 (4)	0.3193 (5)	-0.1180 (3)
C(36)	0.3192 (4)	0.2009 (4)	-0.1164 (2)
H(12)	0.0344 (4)	-0.1622 (4)	-0.1447 (2)
H(13)	0.0256 (5)	-0.2831 (5)	-0.2475 (3)
H(14)	0.0532 (5)	-0.5026 (5)	-0.2414 (3)
H(15)	0.0846 (5)	-0.6018 (5)	-0.1332 (3)
H(16)	0.0938 (4)	-0.4819 (4)	-0.0302 (3)
H(22)	-0.0375 (4)	-0.1437 (4)	0.1540 (2)
H(23)	-0.0678 (5)	-0.2412 (5)	0.2607 (2)
H(24)	0.0873 (5)	-0.2484 (5)	0.3510 (2)
H(25)	0.2681 (5)	-0.1442 (6)	0.3378 (2)
H(26)	0.2952 (4)	-0.0360 (5)	0.2334 (2)
H(32)	0.2377 (4)	0.2205 (4)	0.0424 (2)
H(33)	0.3377 (4)	0.4166 (4)	0.0383 (3)
H(34)	0.4242 (4)	0.4763 (5)	-0.0623 (3)
H(35)	0.4092 (4)	0.3459 (5)	-0.1597 (3)
H(36)	0.3147 (4)	0.1456 (4)	-0.1561 (2)

[a] Numbers in parentheses are errors in the last significant digit(s).

Table II. Bond Distances (Å) and Angles (deg) for Fe₃(SPh)₆(CO)₆ (1)

Bond Distances			
Fe(1)···Fe(2)	3.188 (1)	Fe(2)–C(2)	1.803 (4)
Fe(1)–S(1)	2.486 (1)	Fe(2)–C(3)	1.798 (5)
Fe(1)–S(2)	2.521 (1)	S(1)–C(11)	1.786 (4)
Fe(1)–S(3)	2.506 (1)	S(2)–C(21)	1.785 (4)
Fe(2)–S(1)	2.357 (1)	S(3)–C(31)	1.792 (4)
Fe(2)–S(2)	2.336 (1)	C(1)–O(1)	1.130 (5)
Fe(2)–S(3)	2.341 (1)	C(2)–O(2)	1.130 (5)
Fe(2)–C(1)	1.810 (4)	C(3)–O(3)	1.139 (5)

Bond Angles			
S(1)–Fe(1)–S(2)	78.2 (1)	S(2)–Fe(2)–C(3)	85.6 (1)
S(1)–Fe(1)–S(3)	78.4 (1)	S(3)–Fe(2)–C(1)	85.9 (1)
S(1)–Fe(1)–S(1')	180.00	S(3)–Fe(2)–C(2)	170.2 (1)
S(1)–Fe(1)–S(2')	101.8 (1)	S(3)–Fe(2)–C(3)	94.6 (1)
S(1)–Fe(1)–S(3')	101.6 (1)	C(1)–Fe(2)–C(2)	94.2 (2)
S(2)–Fe(1)–S(3)	78.2 (1)	C(1)–Fe(2)–C(3)	96.2 (2)
S(2)–Fe(1)–S(1')	101.8 (1)	C(2)–Fe(2)–C(3)	95.1 (2)
S(2)–Fe(1)–S(2')	180.00	Fe(1)–S(1)–Fe(2)	82.3 (1)
S(2)–Fe(1)–S(3')	101.8 (1)	Fe(1)–S(1)–C(11)	117.6 (1)
S(3)–Fe(1)–S(1')	101.6 (1)	Fe(2)–S(1)–C(11)	110.1 (1)
S(3)–Fe(1)–S(2')	101.8 (1)	Fe(1)–S(2)–Fe(2)	81.9 (1)
S(3)–Fe(1)–S(3')	180.00	Fe(1)–S(2)–C(21)	120.5 (1)
S(1)–Fe(2)–S(2)	84.6 (1)	Fe(2)–S(2)–C(21)	110.1 (1)
S(1)–Fe(2)–S(3)	84.4 (1)	Fe(1)–S(3)–Fe(2)	82.2 (1)
S(1)–Fe(2)–C(1)	93.4 (1)	Fe(1)–S(3)–C(31)	116.9 (1)
S(1)–Fe(2)–C(2)	85.9 (1)	Fe(2)–S(3)–C(31)	115.5 (1)
S(1)–Fe(2)–C(3)	170.2 (1)	Fe(2)–C(1)–O(1)	178.4 (4)
S(2)–Fe(2)–S(3)	85.3 (1)	Fe(2)–C(2)–O(2)	178.9 (4)
S(2)–Fe(2)–C(1)	171.1 (1)	Fe(2)–C(3)–O(3)	177.1 (4)
S(2)–Fe(2)–C(2)	94.3 (1)	Fe(2')···F(1)···Fe(2)	180.00

[a] Primed atoms are related to those unprimed by a center of symmetry at Fe(1). See Figure 1.

eochemistry is in part determined by polydentate ligands.[12-15] Compound **1** is a useful addition to this body of work in that it is derived from simple cluster self-assembly and incorporates iron in an oxidation state found in physiologically relevant cluster complexes.

Experimental Section

All syntheses were carried out anaerobically by using standard Schlenck line techniques. All solvents and reagents were used as received. (Me₄N)₂Fe₄(SPh)₁₀ was synthesized by the method of Hagen et al.[16]

Syntheses. Fe₃(SPh)₆(CO)₆ (1). **Method A.** NaSPh was prepared by adding Na (0.97 g, 42 mmol) to PhSH (4.2 mL, 42 mmol) in 30 mL of ethanol under an atmosphere of argon. This solution was transferred in a Vacuum Atmospheres glovebox under a helium atmosphere to a Parr bomb with a glass insert containing FeCl₂·4H₂O (4.2 g, 21 mmol). The bomb was pressurized to 350 psi of carbon monoxide, and the solution was stirred at room temperature for 3 days. CO was vented and replaced by 1 atm of argon and the crude product transferred to Schlenck ware

as an EtOH slurry. The crude product was washed with heptane followed by repeated extraction under CO using a total of 50 mL of chloroform. Heptane (50 mL) was added to the solution which was then allowed to stand overnight. Product **1** was obtained as small black crystals which were collected by filtration, washed with heptane, and vacuum dried; yield 2.9 g (41%). Compound **1** can also be prepared in somewhat lower yield when the reaction is carried out under 1 atm of CO.

Method B. (Et₄N)₂Fe₄(SPh)₁₀ (1.0 g, 0.68 mmol) was combined with excess FeBr₂ (0.18 g, 0.83 mmol) in 50 mL of THF under 1 atm of CO for 24 h. The resulting green solution was filtered and concentrated under vacuum to a volume of 20 mL. Product **1** was obtained as microcrystals upon the slow addition of 40 mL of heptane to this solution. The product was collected by filtration washed with acetonitrile and vacuum dried; yield 0.85 g (76%).

X-ray diffraction data were acquired by using crystals isolated directly from the reaction of NaSPh and FeCl₂ in ethanol under 1 atm of CO. In the solid state product **1** is relatively air stable, undergoing no apparent decomposition for several days. It is readily soluble and is air sensitive in CHCl₃, THF, and CCl₄.

Anal.[17] Calcd for Fe₃S₆C₄₂.₃H₃₀.₃O₆Cl: Fe, 16.27; C, 50.15; H, 3.03; S, 18.68. Found: Fe, 16.50; C, 50.23; H, 2.97; S, 18.82.

[Fe(Me₂SO)₆][Fe₄(SPh)₁₀] (3). Product **1** (0.25 g, 0.25 mmol) was dissolved in 15 mL of THF to which 0.71 g of Me₂SO (9.1 mmol) was added. The solution was stirred with several cycles of evacuation and flushing with argon to remove carbon monoxide. Small brown crystals of **3** began to form within an hour. After the reaction mixture was cooled to -20 °C overnight, the product was collected by filtration, washed with ether, and dried under a stream of argon gas; yield 0.28 g (89%).

Anal. Calcd for Fe₅S₁₆C₇₂H₈₆O₆: C, 47.0; H, 4.71; S, 27.88. Found: C, 46.98; H, 4.48; S, 27.73.

Electrochemistry. Cyclic voltammetry experiments were carried out by using a platinum working electrode and a Ag⁺/AgCl reference electrode in a 0.5 mM solution of **1** in methylene chloride with 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte.

Crystallography. X-ray data for **1** were collected at -20 °C on an Enraf-Nonius CAD4F-11 κ geometry diffractometer equipped with a

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(17) Product used in the acquisition of X-ray crystallographic data was isolated from ethanol without recrystallization. After recrystallization, as detailed in the Experimental Section, CHCl₃ is observed to be included in product **1** to the extent of 0.33 of an equivalent by proton NMR of **1** in THF-d₈.
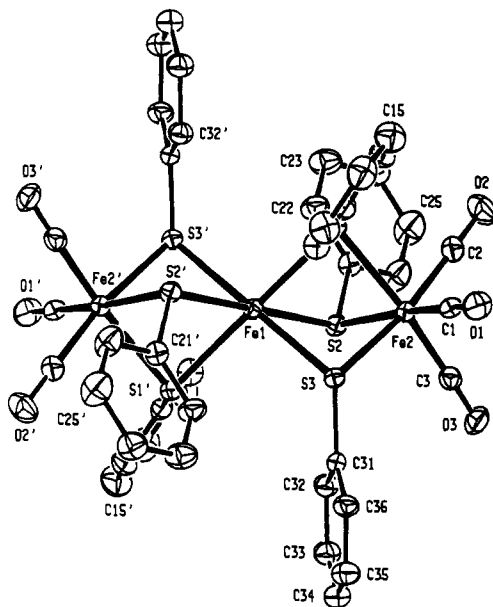
Figure 1. Structure of Fe₃(SPh)₆(CO)₆ (1) showing the atom labeling scheme and 30% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Primed atoms are related to those unprimed by a center of symmetry at the position of Fe(1). Phenyl ring carbon atoms are labeled as C(n1)–C(n6), n = 1–3.

liquid-nitrogen low-temperature device and using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The data collection, reduction, and refinement procedures used in this laboratory are described elsewhere.[18] A total of 3866 reflections (+h,+k,±l) were collected in the range 3° ≤ 2θ ≤ 50°. Of these, 2852 reflections with F_o > 4σ(F_o) were used in the structure refinement which was carried out by full-matrix least-squares techniques (274 variables) using SHELX-76. The structure was solved by direct methods using MULTAN-78. Final R_1 = 0.039 and R_2 = 0.040. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions (C–H = 0.95 Å) and constrained to "ride" on their respective carbon atoms. The largest peak on the final difference Fourier map was 0.35 e/Å³. Crystal data are a = 11.077 (1) Å, b = 10.488 (1) Å, c = 19.052 (2) Å, β = 95.41 (6)°, V = 2203.52 Å³, space group P2₁/n, Z = 2, mol wt = 990.60, ρ(calcd) = 1.493 g cm⁻³, and μ = 12.6 cm⁻¹. An absorption correction was not applied since an absorption curve measured on one reflection near χ = 90° was featureless. Table I lists final positional parameters for 1, and Table II lists bond distances and angles. Figure 1 displays the geometry of 1.

Results and Discussion

IR spectra of 1 were recorded in three different media for which the CO stretching frequencies are given: THF, 2081 and 2031 cm⁻¹ (br); CCl₄ 2080, and 2032 cm⁻¹ (br); and KBr, 2076, 2037, and 2014 cm⁻¹.

Proton NMR (250 MHz) of 1 in THF-d₈ reveals three shifts: −2.8 (meta-H), +12.2 (para-H), and +43.8 (ortho-H) ppm with an intensity ratio of 1.8:1.0:1.5, where (+) and (−) indicate resonances upfield and downfield, respectively, relative to Me₄Si. NMR assignments are based on comparisons with the NMR spectra of the p- and m-toluenethiolate analogues.

Mössbauer data on compound 1 recorded at 4.2 K reveals two doublets with a 2:1 intensity ratio. Their isomer shifts occur at 0.1 and 1.00 mm, respectively, with quadrupole splittings of 0.22 and 2.00 mm, respectively. This spectrum is consistent with the central metal as high-spin Fe(II) and the terminal metals as low-spin Fe(II).

A magnetic moment of 5.62 μ_B was recorded for 1 at 294 K by the Evans method. A ⁵T_{2g} ground term is predicted for 1 on the basis of the single high-spin octahedrally coordinated central iron atom. For this system an orbital angular momentum contribution is expected, which explains the occurrence of a magnetic

moment higher than the spin-only value of 4.9 μ_B.

The cyclic voltammogram of 1 exhibits an irreversible oxidation wave at +0.48 V vs. Ag⁺/AgCl.

Hieber and Kaiser[11] reported several years ago on a compound with the same composition as 1, obtained photochemically by the reaction of Fe(CO)₅ with PhSSPh in pentane. They formulated the product as a triangulo-Fe(0,I,I) complex containing two disulfide and two thiolate ligands. During the course of our work, Berger and Strahle[19] reported on the photochemical synthesis and structural characterization of this compound which they showed to have a benzenethiolate-bridged linear structure, with each iron in the 2+ oxidation state. Compound 1 was isolated independently in this laboratory by the routes shown in Scheme I and found to be spectroscopically identical with the compound reported by Hieber and Kaiser.[11] Our X-ray crystallographic results, in conjunction with those of Berger and Strahle,[19] show that product 1 is obtained via the conjugation of an Fe(II) thiolate species with carbon monoxide and by the photochemical oxidative addition of PhSSPh to a coordinatively unsaturated Fe(0) carbonyl species.[19,20] The two crystallographic studies give independent determinations of 1 since in the Berger and Strahle[19] work the compound crystallizes in space group P1̄ as the acetone solvate whereas the structure reported here belongs to space group P2₁/n and contains no solvent of crystallization. The structure of 1 and that reported by Berger and Strahle[19] are directly comparable. In 1, the central Fe atom lies on a point of 1̄ symmetry as is the case in ref 19 where there are two molecules per unit cell. However they both lie such that the central iron atom is at a site of T symmetry. In all cases, bond distances and angles observed for 1 in this work differ in no significant way from those reported in ref 19.

Product 1 features octahedral coordination about each of the three Fe(II) atoms in contrast to four- or five-coordination observed in most simple Fe(II,III)–sulfur compounds.[21] However, terminal iron tricarbonyl groups are well-known in Fe(0,I,II) carbonyl compounds. For example, 1 is structurally related to the Fe₄S₄(CO)₁₂ cubane-like compound[22] that exhibits octahedral coordination about each Fe(II), with three bridging sulfurs and three terminal carbonyls in the ligand set. It bears an even closer structural resemblance to the recently reported[23] Mn₂(μ-SPh)₃(CO)₆⁻ anion in which the Mnᴵ(CO)₃⁺ d⁶ fragment is isolobal with the Feᴵᴵ(CO)₃²⁺ fragment of product 1. The tendency for octahedral coordination in Fe(II) carbonyls is noted even in complexes where there are fewer than three carbonyls in the ligand set, as is the case when bidentate thiolates are employed for complex formation.[13,15]

Octahedral coordination about iron in protein-contained iron–sulfur clusters under carbon monoxide inhibition can be considered to be the limiting geometry. However, recent results on the hydrogenase enzymes from *Clostridium pasteurianum* show that only a single CO binds during inhibition, resulting in five-coordination about one iron atom.[24] It is likely in this case that carbon monoxide ligation is restricted by protein-imposed structural rigidity of the reactive Fe–S cluster(s) of hydrogenase. In nitrogenase, however, with its structurally undefined nitrogen binding site containing metal–sulfur clusters, the possibility of a dicarbonyl complex formation with six-coordination of one or more iron atoms

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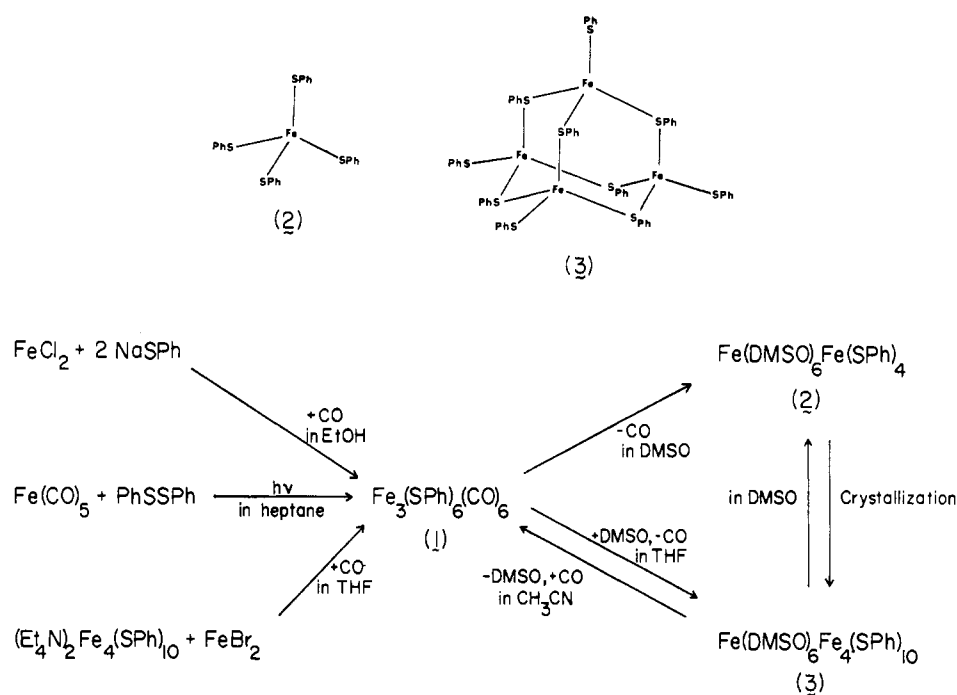(22) Nelson, L. L.; Lo, F. Y.-K.; Rae, A. D.; Dahl, L. F. *J. Organomet. Chem.* **1982**, *225*, 309.
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Scheme I

(2)

(3)

$FeCl_2 + 2 NaSPh$

$Fe(CO)_5 + PhSSPh \xrightarrow[\text{in heptane}]{hv} Fe_3(SPh)_6(CO)_6$ (1)

$(Et_4N)_2Fe_4(SPh)_{10} + FeBr_2$

$Fe(DMSO)_6Fe(SPh)_4$ (2)

$Fe(DMSO)_6Fe_4(SPh)_{10}$ (3)

+CO in EtOH

−CO in DMSO

+CO in THF

+DMSO,−CO in THF

−DMSO,+CO in CH$_3$CN

in DMSO   Crystallization

is worthy of consideration. It may, for example, explain the observed CO concentration dependence in the EPR signal of CO-inhibited nitrogenase.[3]

Product **1** forms a green solution in noncoordinating solvents such as tetrahydrofuran, chloroform, and ether. In Me_2SO, a coordinating solvent, it forms a bright orange solution which slowly changes to brown over several hours. The proton NMR spectrum of compound **1** dissolved in perdeuteriated Me_2SO revealed the quantitative formation of $Fe(SPh)_4^{2-}$ (**2**). The proton resonances observed for this ion at −21.7 (meta-H), 18.0 (ortho-H), and 24.5 (para-H) ppm are identical with those of the compound $(Et_4N)_2Fe(SPh)_4$ in acetonitrile as reported by Hagen et al.[16] This result indicates the disproportionation of **1** to $Fe(Me_2SO)_nFe$-$(SPh)_4$ with loss of CO (reaction 1). By analogy with product

$$Fe_3(SPh)_6(CO)_6 \xrightarrow{Me_2SO} {}^3/_2Fe(Me_2SO)_6Fe(SPh)_4 + 6CO \quad (1)$$
$$\mathbf{1} \qquad\qquad\qquad \mathbf{2}$$
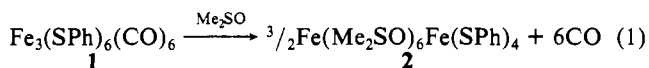
3 whose composition is discussed below, it is suggested that $n = 6$ for the counterion of **2**, octahedral coordination of transition metals by Me_2SO being of common occurrence.[25] A crystalline product is isolated either from THF, as detailed in the Experimental Section, or from a solution consisting initially of **1** in neat Me_2SO (reaction 2). By the latter method, the Me_2SO solution

$$Fe(Me_2SO)_nFe(SPh)_4 \rightarrow$$
$$\mathbf{2}$$
$${}^2/_5Fe(Me_2SO)_6Fe_4(SPh)_{10} + ((5n-12)/5)Me_2SO \quad (2)$$
$$\mathbf{3}$$
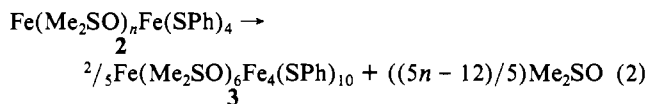
is concentrated by vacuum distillation followed by the slow addition of a minimum amount of cold acetonitrile to product **1** on an ice bath to promote crystallization. Proton NMR spectra of the crystalline product dissolved in CD_3CN revealed the $Fe_4(SPh)_{10}^{2-}$ ion, with proton resonances at −16.2, −5.4 ($Fe(Me_2SO)_6^{2+}$), 3.4, 9.3, and 12.2 ppm relative to Me_4Si, congruent with the proton NMR spectrum of $(Et_4N)_2Fe_4(SPh)_{10}$.[26] The broad resonance at −5.4 ppm was assigned to the methyl protons of $Fe(Me_2SO)_6^{2+}$ as determined by its absence in the spectrum of the $Fe(Me_2SO$-$d_6)_6^{2+}$-containing analogue. This counterion has been observed

in at least one other Fe–S-containing complex, $[Fe(Me_2SO)_6]$-$[(Cl_2Fe)MoS_4]$, obtained by the reaction of $FeCl_2 \cdot 4H_2O$ with $(NH_4)_2MoS_4$ in Me_2SO reported by Müller and co-workers.[27]

The formation of products **2** and **3** represented in Scheme I underscores the stabilities of the $Fe(SPh)_4^{2-}$ and $Fe_4(SPh)_{10}^{2-}$ anions mentioned in an earlier study of cluster self-assembly.[16] With $Fe(Me_2SO)_6^{2+}$ serving as the counterion in complex **3** and as the likely counterion in **2** it is possible to observe cluster rearrangements of a type which are not restricted by the initial number of thiolate ligands per iron. The greater stability of **3** than **2** in the solid state is evidenced by the nearly quantitative isolation of **3** as a crystalline material. Product **3** is converted quantitatively to **2** when dissolved in Me_2SO but undergoes no structural rearrangement in CH_3CN. However, when dissolved in CH_3CN in the presence of CO, product **3** reacts over several hours to form a black crystalline product identified as **1** on the basis of ^{1}H NMR and IR spectra. Under similar conditions, $(Et_4N)_2Fe_4(SPh)_{10}$ with added $FeBr_2$ was also converted to **1**. These interconversions are summed up in Scheme I.

In the chemical system discussed here the interconversions that do not occur are as noteworthy as those that do. Products **2** and **3** are observed but not $Fe(Me_2SO)_6Fe_2(SPh)_6$ or Fe-$(Me_2SO)_6Fe_3(SPh)_8$, for example, although their occurrence is restricted by neither valence nor stoichiometry. Indeed the $Fe_2(SPh)_6^{2-}$ cluster is known to form a stable tetraethylammonium salt.[28] The ready formation of complexes **2** and **3** and the equilibrium established between them in the presence of Me_2SO suggest avenues for detailed examinations of iron thiolate cluster formation. Recent work by Holm[29] and co-workers and Averill[30] and co-workers using $Fe_2S_2(CO)_6$ as a reagent in the synthesis of new iron–sulfur clusters suggests a similar application for complex **1**.

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Contribution from the Institute for Physical Chemistry, University of Frankfurt, 6000 Frankfurt/Main, FRG, and Department of Chemistry and Quantum Institute, University of California, Santa Barbara, California 93106

Pressure Effects on the Excited-State Reaction Dynamics of *cis*-Bis(bipyridine)dichlororhodium(III), *cis*-Rh(bpy)₂Cl₂⁺

S. Wieland,[1] J. DiBenedetto,[2] R. van Eldik,*[1] and P. C. Ford*[2]

Pressure effects on the photosubstitution quantum yields and luminescence lifetimes of the *cis*-Rh(bpy)₂Cl₂⁺ ion (bpy = 2,2′-bipyridine) were studied over the range 0–200 MPa in aqueous solution. The combined results of these measurements lead to a calculated activation volume of –9.7 ± 0.8 cm³ mol⁻¹ for chloride aquation from the ligand field excited state. The principal photoproduct is the *cis*-Rh(bpy)₂(H₂O)Cl²⁺ ion, but spectroscopic data are described that support partial isomerization to give *trans*-Rh(bpy)₂(H₂O)Cl²⁺ as a minor photoproduct as well. These and related data are discussed in terms of possible excited-state mechanisms.

Introduction

Our interest in the photophysical and photochemical properties of d⁶ metal complexes has led to a series of detailed investigations of the mechanisms of the excited-state reactions of rhodium(III) ammine ions using high-pressure techniques.[3–6] In these studies, rate constants and volumes of activation (ΔV^*) for the different physical and chemical decays from the lowest energy excited states (ligand field triplet states, ³LF) were determined from photoreaction quantum yields (ϕ_p) and luminescence lifetimes (τ) measured as functions of pressure. The resulting data were compared with reaction profiles drawn from partial molar volumes obtained by density measurements, and mechanistic conclusions concerning the nature of the excited-state processes were drawn and were correlated with earlier assignments.[7–15] In general, the observations concerning photosubstitution and photoisomerization reactions of such rhodium(III) ammine complexes could be interpreted in terms of a limiting dissociative ligand labilization from the ³LF state.

The present study deals with the pressure effects on the photochemistry and photophysics of the *cis*-Rh(bpy)₂Cl₂⁺ ion, which has previously been reported to undergo photoaquation to the monoaquo complex *cis*-Rh(bpy)₂(H₂O)Cl²⁺ in acidic aqueous solution[16] and to show a weak emission from the lowest energy

Table I. UV/Vis Data for the Synthesized Compounds

complex[a]	λ_{max}, nm	ϵ, M⁻¹ cm⁻¹ × 10⁻⁴
cis-[Rh(bpy)₂Cl₂]⁺	384 (sh)	1.04 × 10⁻²
	311	2.73
	302 (sh)	2.35
	252	2.32
cis-[Rh(bpy)₂(H₂O)Cl]²⁺	316 (sh)	2.12
	307	2.58
	248	2.44
cis-[Rh(bpy)₂(H₂O)₂]³⁺	319	2.68
	306	2.75
	299 (sh)	1.99
	243	2.77

[a] Spectra obtained as perchlorate salts in dilute aqueous solution, at pH 2 and 25 °C.

³LF state under such conditions.[17] Determination of reaction quantum yields, emission lifetimes, and the pressure dependencies of these parameters under the same conditions enable calculation of rate constants (k_i) and activation volumes (ΔV_i^*) for ligand substitution and nonradiative deactivation. Density measurements were also carried out to determine partial molar volumes of the reactant and of the major product *cis*-Rh(bpy)₂(H₂O)Cl²⁺. In addition, NMR analyses of the photochemical reaction solutions revealed evidence for the formation of a minor photoproduct concluded to be the *trans*-Rh(bpy)₂(H₂O)Cl²⁺ isomer.[18]

Experimental Section

Materials. The complexes *cis*-[Rh(bpy)₂Cl₂]Cl·2H₂O, *cis*-[Rh(bpy)₂Cl(H₂O)](ClO₄)₂·H₂O, and *cis*-[Rh(bpy)₂(H₂O)₂](ClO₄)₃·H₂O were prepared and recrystallized according to published procedures[19,20] with the modifications noted below for the aqua chloro complex. The salt *cis*-[Rh(bpy)₂Cl₂](ClO₄)·2H₂O was prepared from an aqueous so-

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