

# Crown Thioether Complexes of Iron(II). Crystal Structures of *meso*-Bis(1,4,7-trithiacyclodecane)iron(II) Perchlorate and (1,4,7,11,14,17-Hexathiacycloicosane)iron(II) Perchlorate<sup>1</sup>

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The structure of the *meso* stereoisomer of bis(1,4,7-trithiacyclodecane)iron(II) perchlorate, [Fe(10S3)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, has been determined by single-crystal X-ray diffraction. Crystal data for *meso*-[Fe(10S3)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>: C<sub>14</sub>H<sub>28</sub>FeS<sub>6</sub>Cl<sub>2</sub>O<sub>8</sub>; monoclinic, space group *P*2<sub>1</sub>/*c*; *a* = 7.373(4) Å, *b* = 9.482(4) Å, *c* = 17.205(6) Å; β = 97.81(4)°, *V* = 1191.66 Å<sup>3</sup>; *Z* = 2. Carbon-13 NMR spectroscopy reveals that the predominant stereoisomer in solution is the *gauche* stereoisomer whose X-ray crystal structure was previously reported by us. These two stereoisomers are readily separated using fractional crystallization from water. The structure of the iron(II) complex of the twenty-membered macrocyclic hexathioether, 20S6, 1,4,7,11,14,7-hexathiacycloicosane, has also been determined by single-crystal X-ray diffraction. This is the first reported X-ray structure of a homoleptic complex of this ligand. The stereoisomer obtained in our case is a racemic one in which the two trimethylene bridges are *cis* to each other and the two diethylene units lie in a facial relationship to each other. Crystal data for [Fe(20S6)](ClO<sub>4</sub>)<sub>2</sub>: C<sub>14</sub>H<sub>28</sub>FeS<sub>6</sub>Cl<sub>2</sub>O<sub>8</sub>; orthorhombic, space group *Pna*2<sub>1</sub>; *a* = 13.200(3) Å, *b* = 16.653(3) Å, *c* = 11.128(1) Å; *V* = 2446.15 Å<sup>3</sup>; *Z* = 4. Ultraviolet–visible absorption spectroscopy, carbon-13 NMR spectroscopy, and magnetic studies of the [Fe(20S6)]<sup>2+</sup> complex are presented. In addition, the synthesis and characterization of a third iron(II)–crown thioether complex with the ligand 18S6 (1,4,7,10,13,16-hexathiacyclooctadecane) are reported. Carbon-13 NMR spectroscopy shows that the only observed stereoisomer is the *meso* stereoisomer in which all carbons are equivalent. All of the iron(II)–crown thioether complexes are low-spin, and the electrochemical behavior of the three complexes is described.

## Introduction

Research involving the coordination chemistry of thioether ligands is currently very active, with several research groups examining the complexation behavior of thioether ligands such as 1,4,7-trithiacyclononane (9S3).<sup>3–6</sup> This versatile ligand has now been complexed to over 30 different transition metal and p-block metal ions, and the list continues to expand at a rapid pace. Several excellent reviews dealing with the coordination chemistry of 9S3 as well as other crown thioethers have recently appeared.<sup>3–6</sup> Our research interests have focused on studying the effects that structural alterations on mesocyclic trithioether ligands might have on the ease of complex formation, complex stability, and complex structure.<sup>7–9</sup> We recently reported the synthesis of the ten-membered mesocyclic (medium-sized ring) thioether 1,4,7-

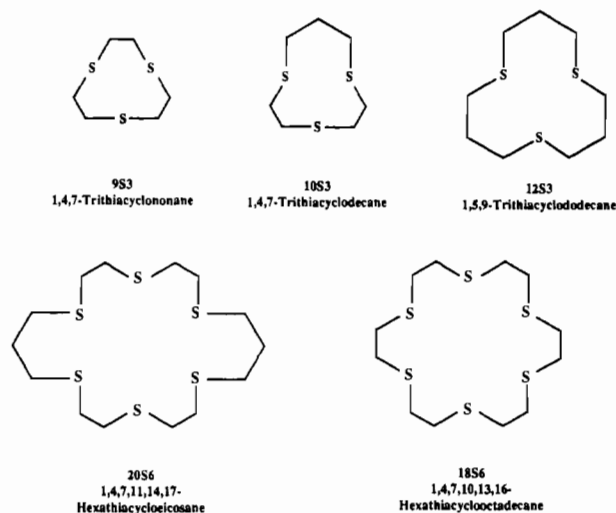


Figure 1. Crown thioether ligands discussed in this paper.

trithiacyclodecane (10S3) and presented some complexation studies with divalent first-row transition metals, heavy metal ions, and zerovalent metals.<sup>1,7,8</sup> This ligand typically complexes in a bis fashion, forming octahedral complexes in which all six sulfur atoms are coordinated. One important distinction in its coordination behavior compared to more symmetrical thioethers such as 9S3 is that 10S3 can complex to form three different stereoisomers. Note that bis octahedral complexes of the previously studied mesocyclic thioethers 9S3 and 12S3 (1,5,9-trithiacyclododecane) cannot exhibit this type of stereoisomerism due to the fact that they contain exclusively ethylene or trimethylene bridges between the sulfur atoms.

Figure 1 shows the crown thioether ligands presented in this work. The three possible stereoisomers for the facial octahedral coordination of 1,4,7-trithiacyclodecane are illustrated in Figure

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- (1) Synthesis and Complexation Studies of Mesocyclic and Macrocyclic Polythioethers. 11. Part 10: Setzer, W. N.; Tang, Y.; Grant, G. J.; VanDerveer, D. G. *Inorg. Chem.* **1992**, *31*, 1116. Part 9: Grant, G. J.; Sanders, K. A.; Setzer, W. N.; VanDerveer, D. G. *Inorg. Chem.* **1991**, *30*, 4053. This work was presented in part at the joint 42nd Southeastern Regional Meeting/46th Southwestern Regional Meeting of the American Chemical Society, New Orleans, LA, Dec 5–7, 1990 (Paper INOR 295), and the 201st National Meeting of the American Chemical Society, Atlanta, GA, April 14–19, 1991 (Paper INOR 140).
- (2) Undergraduate Research Scholar supported by the Petroleum Research Fund, The University of Tennessee at Chattanooga.
- (3) Schroder, M. *Pure Appl. Chem.* **1988**, *60*, 517.
- (4) Blake, A. J.; Schroder, M. In *Advances in Inorganic Chemistry*; Sykes, A. G., Ed.; Academic Press, Inc.: New York, 1990; No. 35, p 2.
- (5) Cooper, S. R.; Rawle, S. C. *Struct. Bonding* **1990**, *72*, 1.
- (6) Cooper, S. R. *Acc. Chem. Res.* **1988**, *21*, 141.
- (7) Grant, G. J.; Carpenter, J. P.; Setzer, W. N.; VanDerveer, D. G. *Inorg. Chem.* **1989**, *28*, 4128.
- (8) Setzer, W. N.; Cacioppo, E. L.; Guo, Q.; Grant, G. J.; Kim, D. D.; Hubbard, J. L.; VanDerveer, D. G. *Inorg. Chem.* **1990**, *29*, 2672.
- (9) Setzer, W. N.; Guo, Q.; Meehan, E. J., Jr.; Grant, G. J. *Heteroatom Chem.* **1990**, *1*, 425.

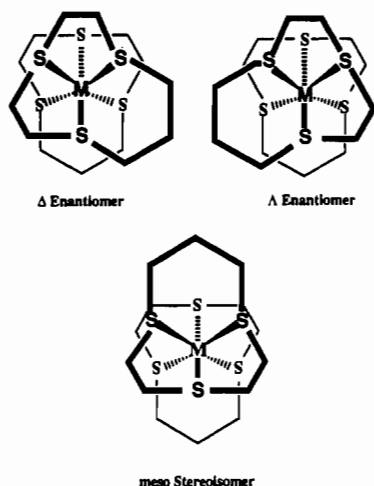


Figure 2. Stereoisomers of bis(10S3) complexes.

2. The first two stereoisomers have an enantiomeric relationship, and the third stereoisomer is a meso compound and thus is a diastereoisomer of the first two. We have used the designations  $\Delta$  and  $\Lambda$  to indicate the two possible orientations of the two six-membered chelate rings (trimethylene bridges between sulfur atoms). Note that in the meso stereoisomer the two six-membered chelate rings form an anti or a trans arrangement in the two trigonal faces whereas they have a gauche or cis arrangement in the pair of enantiomers. Similar designations have been used previously in work on bis(10N3) (10N3 = 1,4,7-triazacyclodecane) complexes of cobalt(III).<sup>10</sup> In the  $\Delta$  case, the two six-membered chelate rings form a right-handed helix. Carbon-13 NMR spectroscopy has been used to differentiate the diastereoisomers in solution.<sup>10</sup> We recently reported the crystal structure of the gauche form of the perchlorate salt of  $[\text{Fe}(\text{10S3})_2]^{2+}$ .<sup>8</sup> The compound surprisingly crystallized into optically active conglomerates (space group  $P2_1$ ), a rare example of the spontaneous resolution of a coordination complex.<sup>11,12</sup> Furthermore, this was the first example of the formation of an optically active hexakis(thioether) transition metal complex. Note that the origin of the optical activity in the complex arises from a configurational source—the relative arrangement of the chelate rings around the metal center—and is not due to conformational effects of the ligand. The iron(II) complexes are low-spin, which is typical of hexakis(thioether) complexes in general since thioethers strongly favor low-spin states.<sup>3-6,8</sup> We wish to report the isolation of the related meso stereoisomer of  $[\text{Fe}(\text{10S3})_2](\text{ClO}_4)_2$  and the determination of its structure by single-crystal X-ray diffraction.

In addition to the complexation properties of trithioethers, we recently reported the synthesis of several novel hexathioethers as well.<sup>13</sup> We have been interested in the complexation properties of the potentially hexadentate ligand 20S6, 1,4,7,11,14,17-hexathiacycloicosane. The ligand is formed as a secondary product in the synthesis of 10S3 and is its cyclic dimer.<sup>13</sup> In view of the intense research activity associated with the hexathioether 18S6, 1,4,7,10,13,16-hexathiacyclooctadecane, the related ligand 20S6 has received surprisingly little attention.<sup>3-6</sup> The only reported X-ray crystal structure involving 20S6 was a nonhomoleptic complex in which the 20S6 ligand bridged two Rh(I) centers in the complex  $[\{\text{Rh}(1,5\text{-cyclooctadiene})\}_2(20\text{S6})](\text{PF}_6)_2$ .<sup>14</sup> Also, an octahedral complex of 20S6 with Ru(II) was reported

but no structural information was given.<sup>15</sup> We undertook an initial complexation study of this ligand with Fe(II), since a good deal of structural information concerning complexes of thioether ligands with iron(II) exists in the literature and the absorption spectra of octahedral low-spin iron(II) complexes are readily interpretable by ligand field theory.

The third novel complex described in the present study is an octahedral homoleptic complex of the hexathioether 18S6, 1,4,7,10,13,16-hexathiacyclooctadecane. A number of homoleptic complexes of this ligand with first- and second-row transition metals have been reported, but none with iron(II).<sup>3-6</sup> In addition, numerous nonhomoleptic complexes of 18S6 with transition metals, p-block metals, and lanthanides have been reported as well.<sup>3-6</sup>

## Experimental Section

**Materials.** The ligands 10S3, 18S6, and 20S6 and the complex  $[\text{Fe}(\text{10S3})_2](\text{ClO}_4)_2$  were prepared by the reported methods.<sup>7,8,13,16</sup> Iron(II) perchlorate was purchased from Alfa Inorganics and used without additional purification. Nitromethane and acetic anhydride were dried by common methods.<sup>17</sup> *Caution!* Although the perchlorate salts described in this report do not appear to be sensitive to shock or heat, these materials, like all perchlorates, should be prepared only in small quantities.

**Measurements.** Cyclic voltammograms were recorded using a Princeton Applied Research Model 384B polarographic analyzer. The supporting electrolyte was 0.1 M  $\text{Bu}_4\text{NBF}_4$  in  $\text{CH}_3\text{CN}$  or 0.1 M  $\text{Bu}_4\text{N}(\text{triflate})$  in  $\text{CH}_3\text{NO}_2$ , and sample concentrations were approximately 1 mM. All voltammograms were recorded at a scan rate of 100 mV/s. The standard three-electrode configuration was as follows: glassy carbon working electrode, Pt-wire auxiliary electrode, and Ag/AgCl reference electrode. Carbon-13 NMR spectra were recorded at 50.324 MHz on a Bruker AF 200-MHz NMR spectrometer using  $\text{D}_2\text{O}$  or  $\text{CD}_3\text{NO}_2$  as a solvent and TMS as an external reference. Magnetic susceptibility measurements on solid samples were obtained using a Johnson-Matthey magnetic susceptibility balance, and diamagnetism correction factors were included. Ultraviolet-visible absorption spectra were obtained on a Varian DMS 200 UV-visible spectrophotometer. Fourier transform infrared spectra were obtained on a Beckman FT 1100 infrared spectrophotometer. Analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

### Separation of Gauche and Meso Stereoisomers of $[\text{Fe}(\text{10S3})_2](\text{ClO}_4)_2$

The separation of the two stereoisomers of  $[\text{Fe}(\text{10S3})_2](\text{ClO}_4)_2$  is readily accomplished using fractional crystallization from water. The preparation of this complex has been previously described.<sup>8</sup> The meso stereoisomer is virtually insoluble in room-temperature water but readily dissolves in nitromethane. In a typical separation, 248 mg of the unseparated complex was titrated with 25 mL of water at 25 °C. An insoluble purple powder was removed by filtration, and the aqueous solution was allowed to slowly evaporate to yield 175 mg (70% of original complex) of beautiful, purple crystals of the gauche stereoisomer. The insoluble meso isomer, weighing 65 mg (26% of original complex), was dissolved in 10 mL of nitromethane and allowed to slowly evaporate to yield clear, purple crystals. The electronic absorption spectrum of gauche- $[\text{Fe}(\text{10S3})_2](\text{ClO}_4)_2$  recorded in nitromethane showed two  $\lambda_{\text{max}}$ 's at 547 nm ( $\epsilon = 62$ ) and 409 nm ( $\epsilon = 75$ ). The electronic absorption spectrum of meso- $[\text{Fe}(\text{10S3})_2](\text{ClO}_4)_2$  recorded in nitromethane showed two  $\lambda_{\text{max}}$ 's at 550 nm ( $\epsilon = 62$ ) and 399 nm ( $\epsilon = 61$ ). <sup>13</sup>C NMR ( $\text{CD}_3\text{NO}_2$ ) for gauche- $[\text{Fe}(\text{10S3})_2](\text{ClO}_4)_2$ :  $\delta$  37.8, 36.5, 36.2, 36.0, 28.8, 25.7, 18.7 ppm. <sup>13</sup>C NMR ( $\text{CD}_3\text{NO}_2$ ) for meso- $[\text{Fe}(\text{10S3})_2](\text{ClO}_4)_2$ :  $\delta$  38.3, 35.5, 28.8, 19.6 ppm.

**Preparation of  $[\text{Fe}(\text{20S6})](\text{ClO}_4)_2$ .** Under nitrogen, a solution of  $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (234 mg, 0.644 mmol), acetic anhydride (395 mg, 3.87 mmol, 0.387 mL), and 5 mL of  $\text{CH}_3\text{NO}_2$  was added dropwise to a solid sample of 20S6 (436 mg, 0.676 mol). There was an immediate color change from golden yellow to dark purple. The mixture was stirred for 1 h at room temperature, and any insolubles were removed by filtration. The solution was cooled in an ice bath for 30 min, and then 10 mL of ether was added dropwise to precipitate the iron complex. The product was filtered off and washed with 20 mL of anhydrous ether. A yield of

- (10) Searle, G. H.; Angley, M. E. *Inorg. Chim. Acta* **1981**, *49*, 185.  
 (11) Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates, and Resolutions*; John Wiley and Sons, Inc.: New York, 1981; p 79.  
 (12) Bernal, I.; Cetrullo, J. *Inorg. Chim. Acta* **1988**, *144*, 227-232 and references cited therein.  
 (13) Setzer, W. N.; Afshar, S.; Burns, N. L.; Ferrante, L. A.; Hester, A. M.; Meehan, E. J.; Grant, G. J.; Isaac, S. M.; Laudeman, C. P.; Lewis, C. M.; VanDerveer, D. G. *Heteroatom Chem.* **1990**, *1*, 375.  
 (14) Riley, D. P.; Oliver, J. D. *Inorg. Chem.* **1983**, *22*, 3361.

- (15) Rawle, S. C.; Sewell, T. J.; Cooper, S. R. *Inorg. Chem.* **1987**, *26*, 3769.  
 (16) Ochrymowycz, L. A.; Mak, C.-P.; Michna, J. D. *J. Org. Chem.* **1974**, *39*, 2079. Black, D. StC.; McLean, I. A. *Aust. J. Chem.* **1971**, *24*, 1401.  
 (17) Jolly, W. L. *The Synthesis and Characterization of Inorganic Compounds*; Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1970; pp 116-121.

**Table I.** Crystallographic Data and Details of Refinement for *meso*-[Fe(10S3)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (I) and [Fe(20S6)](ClO<sub>4</sub>)<sub>2</sub> (II)

	I	II
formula	C <sub>14</sub> H <sub>28</sub> Cl <sub>2</sub> FeO <sub>8</sub> S <sub>6</sub>	C <sub>14</sub> H <sub>28</sub> Cl <sub>2</sub> FeO <sub>8</sub> S <sub>6</sub>
fw	643.26	643.26
cryst size, mm	0.31 × 0.27 × 0.12	0.41 × 0.37 × 0.31
cryst syst	monoclinic	orthorhombic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> na2 <sub>1</sub>
<i>a</i> , Å	7.373(4)	13.200(2)
<i>b</i> , Å	9.482(8)	16.653(3)
<i>c</i> , Å	17.205(6)	11.128(1)
<i>V</i> , Å <sup>3</sup>	1191.66	2446.15
β, deg	97.81(4)	
<i>D</i> (calcd), g cm <sup>-3</sup>	1.793	1.747
<i>Z</i>	2	4
μ, mm <sup>-1</sup>	1.40	1.37
quadrant collected	± <i>h</i> , + <i>k</i> , + <i>l</i>	- <i>h</i> , + <i>k</i> , ± <i>l</i>
no. of rflns measd	2177	4550
no. of unique rflns measd	2101	4306
no. of indep rflns with <i>I</i> ≥ 2.5σ( <i>I</i> )	1566	3723
<i>F</i> (000)	664.00	1328.00
<i>R</i> <sup>a</sup>	0.039	0.038
<i>R</i> <sub>w</sub> <sup>b</sup>	0.046	0.046
<i>w</i>	1.0/[(σ( <i>F</i> <sub>o</sub> )) <sup>2</sup> + 0.005 <i>F</i> <sub>o</sub> <sup>2</sup> ]	1.0/[(σ( <i>F</i> <sub>o</sub> )) <sup>2</sup> + 0.005 <i>F</i> <sub>o</sub> <sup>2</sup> ]

$${}^a R = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad {}^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$$

372 mg (90% yield) of product was isolated. IR (KBr, cm<sup>-1</sup>): 2951, 2925, 1419, 1143–1087 (s, ClO<sub>4</sub><sup>-</sup>), 944, 940, 919, 835, 825, 693, 681, 627. The electronic absorption spectrum recorded in nitromethane showed two λ<sub>max</sub>'s at 548 nm (ε = 103) and 415 nm (ε = 114). Room-temperature magnetic susceptibility measurements showed that the complex was diamagnetic. Anal. Calcd for C<sub>14</sub>H<sub>28</sub>Cl<sub>2</sub>FeO<sub>8</sub>S<sub>6</sub>: C, 26.13; H, 4.39; S, 29.90. Found: C, 26.00; H, 4.35; S, 29.80. <sup>1</sup>H NMR (CD<sub>3</sub>NO<sub>2</sub>): broad, poorly resolved resonances between 2.0 and 4.0 ppm. The <sup>1</sup>H DEPT NMR spectrum showed that only methylene protons were present. <sup>13</sup>C NMR (CD<sub>3</sub>NO<sub>2</sub>): δ 40.0, 38.8, 37.6, 35.2, 32.7, 28.7, 24.8 ppm.

**Preparation of [Fe(18S6)](ClO<sub>4</sub>)<sub>2</sub>.** A solution containing iron(II) perchlorate hexahydrate, Fe(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, (230 mg, 0.634 mmol) in 20 mL of ethanol was added dropwise with stirring to a slurry of 18S6 (249 mg, 0.690 mmol) in 20 mL of refluxing ethanol under a nitrogen atmosphere. The color changed from greenish-yellow to purple after the addition of the first few drops. The mixture was then refluxed an additional 1 h and cooled. A lavender precipitate was filtered off and washed with four 20-mL portions of chloroform and four 20-mL portions of anhydrous ether. A mass of 335 mg (0.544 mmol, 85.8%) of (1,4,7,10,13,16-hexathiacyclooctadecane)iron(II) perchlorate was obtained. The sample decomposed upon heating at 180 °C, and the product was insoluble in most common solvents. Room-temperature magnetic susceptibility measurements showed that the complex was diamagnetic. IR (KBr, cm<sup>-1</sup>): 2902, 2900, 1440, 1370, 1280, 1240, 1150–1080 (s, ClO<sub>4</sub><sup>-</sup>), 920, 820, 790, 590. Anal. Calcd for C<sub>12</sub>H<sub>24</sub>Cl<sub>2</sub>FeO<sub>8</sub>S<sub>6</sub>: C, 23.42; H, 3.93; S, 31.26. Found: C, 23.67; H, 3.99; S, 31.43. The sulfate, tetrafluoroborate, and trifluoromethanesulfonate (triflate) salts of the complex can be prepared by a similar procedure starting with the appropriate Fe(II) salt. Of all of the [Fe(18S6)]<sup>2+</sup> salts which were prepared, only the triflate salt was soluble in common solvents. The electronic absorption spectrum of [Fe(18S6)](triflate)<sub>2</sub> recorded in nitromethane showed two λ<sub>max</sub>'s at 540 nm (ε = 25) and 392 nm (ε = 41). <sup>13</sup>C NMR (CD<sub>3</sub>NO<sub>2</sub>): δ 33.4 ppm.

**X-ray Crystal Structures of *meso*-Fe(10S3)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> and Fe(20S6)-(ClO<sub>4</sub>)<sub>2</sub>.** A clear red crystal of *meso*-[Fe(10S3)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> suitable for X-ray diffraction was grown by ether diffusion into a nitromethane solution. The crystal, having approximate dimensions 0.31 × 0.27 × 0.12 mm, was mounted on a Syntex P2<sub>1</sub> diffractometer equipped with a scintillation counter, Mo Kα radiation (λ = 0.710 73 Å), and a graphite monochromator. The automatic centering, indexing, and least-squares routines were carried out on 15 independent reflections in the range 13.75° < 2θ < 24.40° to obtain the unit cell dimensions which are given in Table I. The ω-scan technique over the range 4° ≤ 2θ ≤ 50° was used to collect the data of which those with *I* ≥ 2.5σ(*I*) were considered observed. No correction was made for absorption. The structure was solved by the heavy-atom method. The position of the iron atom was located from a three-dimensional Patterson map and placed at 0, 0, 0, and the remaining atoms were located by subsequent structure factor calculations and

difference electron density maps.<sup>18</sup> The structure was refined by full-matrix least-squares techniques. The hydrogen atoms were located by difference maps and were isotropically refined (positional parameters were not refined). All non-hydrogen atoms were refined anisotropically converging at

$$R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.039$$

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.046$$

$$\text{GoF} = [\sum w(|F_o| - |F_c|)^2 / (\text{no. of rflns} - \text{no. of params})]^{1/2} = 1.262$$

A clear purple crystal of [Fe(20S6)](ClO<sub>4</sub>)<sub>2</sub> suitable for X-ray diffraction was grown by ether diffusion into a nitromethane solution. The crystal, having approximate dimensions 0.31 × 0.27 × 0.12 mm, was mounted on a Syntex P2<sub>1</sub> diffractometer equipped with a scintillation counter, Mo Kα radiation (λ = 0.710 73 Å), and a graphite monochromator. The automatic centering, indexing, and least-squares routines were carried out on 15 independent reflections in the range 12.55° < 2θ < 22.15° to obtain the unit cell dimensions which are given in Table I. The solution of the structure was performed as described above for *meso*-[Fe(10S3)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>. All non-hydrogen atoms were refined anisotropically converging at

$$R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.038$$

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.046$$

$$\text{GoF} = [\sum w(|F_o| - |F_c|)^2 / (\text{no. of rflns} - \text{no. of params})]^{1/2} = 1.338$$

The final atomic parameters for *meso*-[Fe(10S3)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> and [Fe(20S6)](ClO<sub>4</sub>)<sub>2</sub> with their standard deviations are given in Table II. Selected bond distances and bond angles are given in Table III.

## Results

Structural studies were undertaken for the complexes *meso*-[Fe(10S3)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> and [Fe(20S6)](ClO<sub>4</sub>)<sub>2</sub>. These results are presented in Tables I–IV. Also, these two complexes and the complex [Fe(18S6)](triflate)<sub>2</sub> were studied using electronic spectroscopy, electrochemistry, and <sup>13</sup>C NMR spectroscopy. These results are presented in Tables V and VI and will be described in detail along with the structural results at the appropriate places in the sections that follow.

## Discussion

**Structural Studies.** (a) *meso*-[Fe(10S3)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>. The *meso* 10S3 complex crystallizes in the space group *P*2<sub>1</sub>/*c* and is isostructural with the related bis Fe(II) complex 9S3.<sup>19</sup> A structural perspective of the complex cation is shown in Figure 3. As expected, the thioether ligand coordinates facially in a tridentate fashion and the complex involves a distorted octahedral environment of sulfur atoms about the iron. The iron ion is located at a crystallographic inversion center. As mentioned previously, the two six-membered chelate rings (trimethylene bridges) are in an anti or a trans relationship, not a gauche relationship as in our previously reported stereoisomer. The *meso* stereoisomer is the same one that we previously obtained for the nickel(II) complex of the functionalized ten-membered-ring trithioether keto-10S3 (1,4,7-trithiacyclodecan-9-one) and also the one that Zompa and co-workers obtained for the bis Ni(II) complex of 10N3 (1,4,7-triazacyclodecane), the analogous ten-membered-ring triamine ligand.<sup>8,20</sup> To our knowledge, the pair of diastereoisomers of

(18) The programs used for the solution and refinement of this structure were those in NRCVAX from the National Resource Council, Ottawa, Canada.

(19) Wiegardt, K.; Kuppers, H.-J.; Weiss, J. *Inorg. Chem.* **1985**, *24*, 3067.

(20) Zompa, L. J.; Margulis, T. N. *Inorg. Chim. Acta* **1980**, *45*, L263.

**Table II.** Atomic Positional and Thermal Parameters for Non-Hydrogen Atoms (Esd's in Parentheses)

atom	x	y	z	$B_{iso}, \text{\AA}^2$
<i>meso</i> -[Fe(10S3) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>				
Fe	0	0	0	2.01(4)
S1	0.11266(19)	0.12542(14)	0.10639(8)	3.00(5)
C2	0.3477(7)	0.0624(6)	0.1293(3)	3.26(23)
C3	0.3681(7)	-0.0925(6)	0.1143(3)	3.18(24)
S4	0.25804(17)	-0.13262(14)	0.01591(8)	2.72(5)
C5	0.2145(8)	-0.3204(6)	0.0225(3)	3.5(3)
C6	0.0984(9)	-0.3663(6)	0.0838(4)	4.0(3)
C7	-0.0987(9)	-0.3255(6)	0.0703(4)	4.2(3)
S8	-0.14900(18)	-0.13959(15)	0.07676(8)	2.98(5)
C9	-0.0574(8)	-0.0976(7)	0.1787(3)	4.0(3)
C10	-0.0044(9)	0.0581(7)	0.1864(3)	4.1(3)
Cl	0.53179(19)	0.42363(15)	0.16071(8)	3.25(6)
O1	0.5647(8)	0.5706(5)	0.1677(3)	6.4(3)
O2	0.4554(6)	0.3893(4)	0.08246(23)	4.47(21)
O3	0.6994(7)	0.3533(6)	0.1810(3)	7.7(3)
O4	0.4080(7)	0.3844(6)	0.2134(3)	6.6(3)
[Fe(20S6)](ClO <sub>4</sub> ) <sub>2</sub>				
Fe	0.77877(5)	0.87011(4)	0.00000	2.311(23)
S1	0.90133(10)	0.94768(8)	0.08104(15)	2.98(5)
C2	0.9819(4)	0.8816(4)	0.1702(6)	4.3(3)
C3	0.9699(5)	0.7954(4)	0.1379(6)	4.3(3)
S4	0.84049(12)	0.76508(8)	0.10433(15)	3.60(6)
C5	0.7778(5)	0.7701(4)	0.2504(5)	4.6(3)
C6	0.7410(5)	0.8518(5)	0.2832(5)	4.4(3)
S7	0.67299(10)	0.89191(9)	0.15513(15)	3.63(6)
C8	0.6662(6)	0.9975(5)	0.1941(8)	6.3(4)
C9	0.6161(7)	1.0438(6)	0.0922(12)	8.5(6)
C10	0.6823(5)	1.0599(4)	-0.0144(10)	6.1(4)
S11	0.7182(11)	0.97395(10)	-0.10784(17)	4.14(6)
C12	0.5961(6)	0.9398(5)	-0.1707(11)	7.7(5)
C13	0.5619(5)	0.8636(4)	-0.1295(8)	6.0(4)
S14	0.65530(11)	0.79219(9)	-0.07952(15)	3.73(6)
C15	0.7075(5)	0.7516(4)	-0.2168(6)	4.0(3)
C16	0.7885(5)	0.8041(4)	-0.2714(5)	4.1(3)
S17	0.87801(10)	0.82673(9)	-0.15295(14)	3.08(5)
C18	0.9518(5)	0.9067(4)	-0.2190(5)	4.1(3)
C19	1.0292(4)	0.9356(4)	-0.1257(6)	3.86(25)
C20	0.9876(4)	0.9898(4)	-0.0288(6)	4.3(3)
Cl1	0.02296(11)	0.75987(9)	0.48892(14)	3.99(6)
O1	0.0073(4)	0.7273(3)	0.6062(4)	6.5(3)
O2	0.1146(5)	0.7972(5)	0.4490(10)	11.0(5)
O3	0.0123(5)	0.6965(3)	0.4044(5)	6.9(3)
O4	-0.0575(5)	0.8176(3)	0.4676(5)	7.4(3)
Cl2	0.70704(12)	1.04976(10)	0.54690(16)	4.42(6)
O5	0.6988(7)	1.0877(5)	0.4378(6)	10.8(5)
O6	0.6185(4)	1.0618(5)	0.6126(8)	10.5(5)
O7	0.7827(4)	1.0894(5)	0.6111(9)	10.4(5)
O8	0.7385(9)	0.9709(4)	0.5343(10)	13.4(67)

<sup>a</sup>  $B_{iso}$  is the mean of the principal axes of the thermal ellipsoid.

[Fe(10S3)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> represents the first example of two different diastereoisomers of the same crown thioether complex to be structurally characterized.

The structural features of the complex seem to be regular and comparable to those of the reported hexakis(thioether) complexes of iron(II).<sup>8,19,21</sup> Structural information regarding the five known crown hexakis(thioether) complexes of iron(II) is presented and compared in Table IV. All of the reported Fe–S bonds are compressed relative to the sum of the covalent radii for low-spin iron(II) and sulfur (2.31 Å). As was obtained for the gauche stereoisomer of the 10S3 ligand, there is a tetragonal distortion about the iron center due to the lengthening of two of the Fe–S bonds which are trans to each other. One of the Fe–S bonds (Fe–S4) in each of the two six-membered chelate rings is long, with a bond length of 2.266 Å. However, this tetragonal distortion is not as great as in the gauche structure but is greater than observed for the 9S3 complex.<sup>8,19</sup> Interestingly, the reported 10N3 complex exhibits trigonal distortion around the octahedral

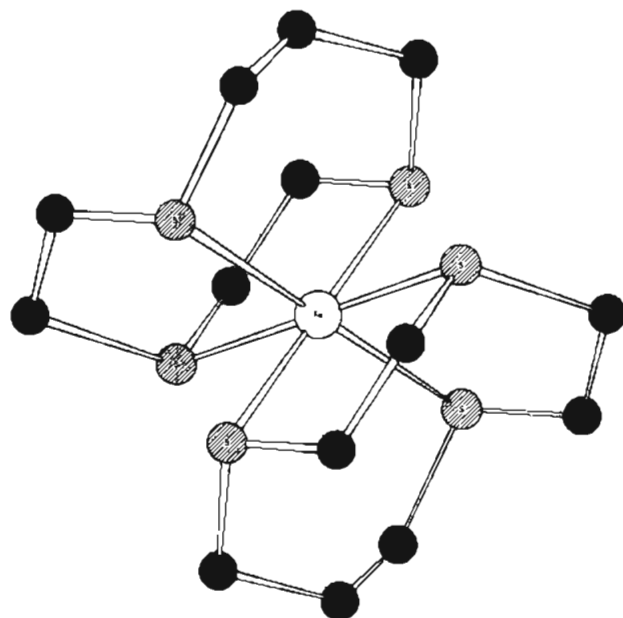


Figure 3. Structure of *meso*-[Fe(10S3)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>.

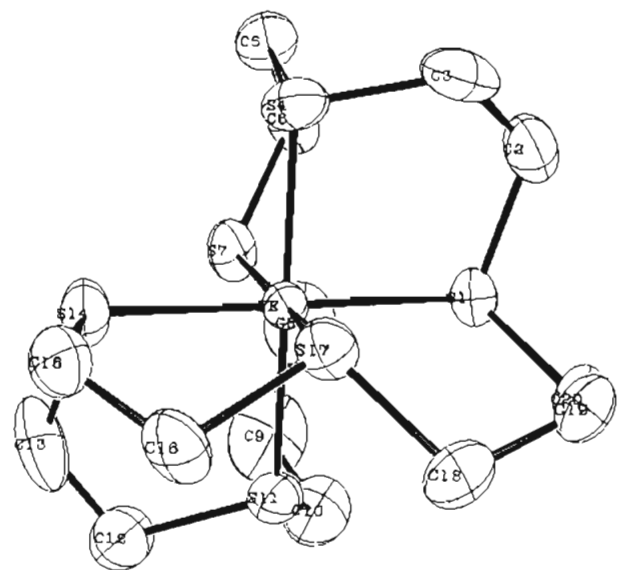


Figure 4. ORTEP perspective of [Fe(20S6)](ClO<sub>4</sub>).

nickel(II) center and not the tetragonal distortion observed for the 10S3 structures.<sup>20</sup> There is an interesting difference between the internal S–Fe–S angles of the five-membered and six-membered chelate rings. The five-membered chelate rings are constricted (average S–Fe–S: 89.23°), while the more flexible six-membered chelate rings have opened up (average S–Fe–S: 94.09°).

We recently reported a conformational analysis of two ten-membered-ring trithioethers, 10S3 and keto-10S3.<sup>9</sup> The conformation adopted by the 10S3 ligand in this structure is a [2323] conformation, the same conformation adopted by the ligand in the gauche stereoisomer of the complex. In this conformation the six-membered chelate ring is in the chair form.

While this report was being prepared, a paper describing the X-ray crystal structures of the *meso* bis(10S3) complexes of Ni(II) and Co(II) was published.<sup>22</sup> Both of those complexes crystallized in the same space group as the *meso* Fe(II) complex,  $P2_1/c$ .

(b) [Fe(20S6)](ClO<sub>4</sub>)<sub>2</sub>. The 20S6 complex crystallizes in the noncentrosymmetric space group  $Pna2_1$ , and an ORTEP per-

(21) Kuppers, H.-J.; Wiegardt, K.; Nuber, B.; Weiss, J.; Bill, E.; Trautwein, A. X. *Inorg. Chem.* 1987, 26, 3762.

(22) Chandrasekhar, S.; McAulley, A. *Inorg. Chem.* 1992, 31, 480.

(23) Margulis, T. N.; Zompa, L. J. *J. Chem. Soc., Chem. Commun.* 1978, 430.

Table III. Selected Bond Lengths and Bond Angles

<i>meso</i> -[Fe(10S3) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>					
Bond Lengths (Å)					
Fe-S1	2.2453(16)	S1-C2	1.825(6)	C2-C3	1.501(8)
Fe-S4	2.2659(16)	S1-C10	1.835(6)	C3-S4	1.816(6)
Fe-S8	2.2576(16)	S4-C5	1.815(6)	C5-C6	1.511(8)
S8-C9	1.836(6)	C6-C7	1.491(9)	C7-S8	1.808(6)
C9-C10	1.531(10)				
Bond Angles (deg)					
S1-Fe-S4	89.08(7)	S1-Fe-S8	89.38(6)	S1-Fe-S1'	180.0
S1-Fe-S4'	90.92(7)	S1-Fe-S8'	90.62(6)	S4-Fe-S8	94.09(7)
S4-Fe-S8'	85.91(7)	Fe-S1-C2	103.75(19)	Fe-S1-C10	105.59(22)
Fe-S4-C3	104.93(18)	Fe-S4-C5	113.53(19)	Fe-S8-C7	114.57(21)
Fe-S8-C9	106.66(20)	S1-C2-C3	113.4(4)	S4-C5-C6	116.6(4)
C5-C6-C7	116.7(5)	C2-S1-C10	104.7(3)	C2-C3-C4	108.8(4)
C3-S4-C5	102.0(3)	C6-C7-S8	116.5(4)	C7-S8-C9	102.6(3)
S8-C9-C10	110.4(4)	S1-C10-C9	114.2(4)		
[Fe(20S6)](ClO <sub>4</sub> ) <sub>2</sub>					
Bond Lengths (Å)					
Fe-S1	2.2580(14)	S1-C2	1.812(6)	C2-C3	1.488(10)
Fe-S4	2.2519(16)	S1-C20	1.812(6)	C3-S4	1.820(7)
Fe-S7	2.2499(15)	S4-C5	1.826(6)	C5-C6	1.490(11)
Fe-S11	2.2515(16)	C6-S7	1.812(7)	C8-C9	1.521(15)
Fe-S14	2.2636(15)	S7-C8	1.814(8)	C9-C10	1.498(15)
Fe-S17	2.2659(15)	C10-S11	1.831(9)	C12-C13	1.423(11)
C13-S14	1.801(7)	S14-C15	1.807(6)	C15-C16	1.509(9)
C16-S17	1.810(6)	S17-C18	1.806(6)	C18-C19	1.534(9)
C19-C20	1.510(9)				
Bond Angles (deg)					
S1-Fe-S4	88.82(6)	S1-Fe-S11	91.60(6)	S1-Fe-S14	179.47(6)
S1-Fe-S7	92.63(5)	S1-Fe-S17	93.92(6)	S4-Fe-S7	87.38(6)
S4-Fe-S11	178.82(7)	S4-Fe-S17	86.02(6)	S7-Fe-S11	93.71(7)
S7-Fe-S14	86.88(6)	S7-Fe-S17	170.60(6)	S11-Fe-S14	88.64(6)
S11-Fe-S17	92.85(6)	S14-Fe-S17	86.55(6)	S4-Fe-S14	90.96(6)
Fe-S1-C2	106.84(21)	Fe-S1-C20	113.73(21)	C2-S1-C20	103.5(3)
S1-C2-C3	112.9(4)	C2-C3-S4	114.7(4)	Fe-S11-C12	105.96(24)
C10-S11-C12	103.3(5)	S11-C12-C13	115.4(5)	C12-C13-S14	118.1(5)
Fe-S14-C13	103.62(23)	Fe-S14-C15	105.68(21)	C13-S14-C15	104.3(4)
S14-C15-C16	113.2(4)				
C15-C16-S17	106.8(4)	Fe-S4-C3	103.27(19)	Fe-S4-C5	105.05(24)
C3-S4-C5	103.3(3)	S4-C5-C6	114.0(4)	C5-C6-S7	107.8(4)
Fe-S7-C6	103.69(21)	Fe-S7-C8	111.7(3)	C6-S7-C8	101.2(4)
S7-C8-C9	109.6(6)	C8-C9-C10	115.3(7)	Fe-S17-C16	103.66(20)
Fe-S17-C18	112.49(21)	C16-S17-C18	102.1(3)	S17-C18-C19	108.4(4)
C18-C19-C20	115.4(5)	S1-C20-C19	118.6(4)	C9-C10-S11	117.4(6)
Fe-S11-C10	112.9(3)				

Table IV. Comparison of Structural Features of Fe(II)-Crown Thioether Complexes

complex	Fe-S, Å			space group	ref
	av	min	max		
<i>meso</i> -[Fe(10S3) <sub>2</sub> ] <sup>2+</sup>	2.256	2.245	2.258	<i>P</i> <sub>2</sub> <sub>1</sub> / <i>c</i>	this work
<i>gauche</i> -[Fe(10S3) <sub>2</sub> ] <sup>2+</sup>	2.262	2.245	2.275	<i>P</i> <sub>2</sub> <sub>1</sub>	8
[Fe(20S6)] <sup>2+</sup>	2.257	2.250	2.266	<i>Pna</i> <sub>2</sub> <sub>1</sub>	this work
[Fe(9S3) <sub>2</sub> ] <sup>2+</sup>	2.250	2.241	2.259	<i>P</i> <sub>2</sub> <sub>1</sub> / <i>c</i>	19
[Fe(9S3)(9S3(O))] <sup>2+</sup>	2.257	2.250	2.263	<i>P</i> <sub>1</sub>	21 <sup>a</sup>

<sup>a</sup> 9S3(O) = 1,4,7-trithiacyclononane 1-oxide; only thioether Fe-S bonds are included.

spective of the complex is shown in Figure 4. The 20S6 ligand can wrap around a metal center in an octahedral fashion to potentially form three different diastereoisomers or geometric isomers which are shown in Figure 5. In the first case, isomer 1, the *meso* diastereoisomer, the two diethylene-three sulfur units form a facial arrangement, which necessarily forces the two six-membered chelate rings to span *trans* positions in order to maintain internal symmetry. For isomer 2, the two six-membered chelate rings again span *trans* positions, but the diethylene units lie in a meridional arrangement, necessitating an anti conformation around the C-S bonds in the diethylene units. Anti conformations are preferred around C-N and C-O bonds, but *gauche* conformations are preferred around C-S bonds.<sup>5</sup> For isomer 3, the two

Table V. Ligand Field Parameters for Hexakis(thioether)iron(II) Complexes

Fe(II) complex <sup>a</sup>	<i>Dq</i> , cm <sup>-1</sup>	<i>f</i> <sup>b</sup>	<i>B</i> , cm <sup>-1</sup>	<i>β</i> <sup>c</sup>	ref
[Fe(20S6)] <sup>2+</sup>	1913	1.91	412	0.39	<i>d</i>
[Fe(18S6)] <sup>2+</sup>	1940	1.94	506	0.48	<i>d</i>
<i>gauche</i> -[Fe(10S3) <sub>2</sub> ] <sup>2+</sup>	1920	1.92	438	0.42	<i>d</i>
<i>meso</i> -[Fe(10S3) <sub>2</sub> ] <sup>2+</sup>	1905	1.91	499	0.47	<i>d</i>
[Fe(9S3)(9S3(O))] <sup>2+</sup>	2244	2.24	357	0.34	21
[Fe(9S3) <sub>2</sub> ] <sup>2+</sup>	2005	2.00	437	0.41	19
[Fe(HO-10S3) <sub>2</sub> ] <sup>2+</sup>	1979	1.98	170	0.16	8
[Fe(ttn) <sub>2</sub> ] <sup>2+</sup>	1808	1.81	443	0.42	<i>e</i>

<sup>a</sup> Abbreviations: 9S3(O) = 1,4,7-trithiacyclononane 1-oxide; ttn = 2,5,8-trithianonane; HO-10S3 = 1,4,7-trithiacyclodecan-9-ol. <sup>b</sup> Figgis, B. N. *Introduction to Ligand Fields*; Interscience Publishers: New York, 1966; p 244. <sup>c</sup> *g* value for Fe(II) is 10.0. <sup>d</sup> Ratio of *B*(complex)/*B*(free ion) where *B*(free ion) for Fe(II) is 1058 cm<sup>-1</sup>. <sup>e</sup> This work. <sup>f</sup> Unpublished results from our laboratories.

six-membered chelate rings span *cis* positions, with the diethylene units facially coordinated. Isomer 3 is the one that is obtained in our case (point group symmetry *C*<sub>2</sub>). Also, the same diastereoisomer is observed in the octahedral nickel(II) complex of 1,4,7,11,14,17-hexaazacycloicosane (20N6) as well as the 20S6 complex of the isoelectronic Co(III) metal ion.<sup>22,24</sup> In a fourth case, <sup>13</sup>C NMR spectroscopy of the Co(III) complex of 20N6 showed that this same diastereoisomer was the only one

Table VI. Electrochemical Data for Ligands and Fe(II) Complexes

species	$E^a$	comments	ref
10S3	+0.71	oxidn, irreversible	this work
10S3	-0.33	redn, quasi-reversible <sup>b</sup>	this work
20S6		no activity	this work
[Fe(10S3) <sub>2</sub> ] <sup>2+</sup>	+0.91	Fe <sup>2+</sup> /Fe <sup>3+</sup> oxidn, reversible	this work
[Fe(18S6)] <sup>2+</sup>	+1.08	Fe <sup>2+</sup> /Fe <sup>3+</sup> oxidn, irreversible	this work
[Fe(20S6)] <sup>2+</sup>	+0.69	Fe <sup>2+</sup> /Fe <sup>3+</sup> oxidn, reversible	this work
[Fe(9S3) <sub>2</sub> ] <sup>2+</sup>	+0.98	Fe <sup>2+</sup> /Fe <sup>3+</sup> oxidn, reversible	19
[Fe(9S3)(9S3(O))] <sup>2+</sup> <sup>c</sup>	+1.32	Fe <sup>2+</sup> /Fe <sup>3+</sup> oxidn, reversible	21

<sup>a</sup> Formal redox potentials in volts measured vs ferrocene/ferrocenium.

<sup>b</sup>  $i_{pa}/i_{pc} = 0.72$ . <sup>c</sup> 9S3(O) = 1,4,7-trithiazacyclononane 1-oxide.

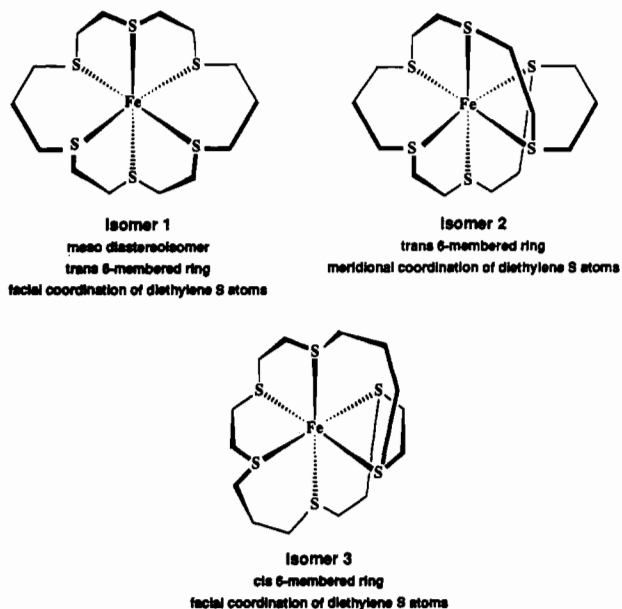


Figure 5. Stereoisomers of 20S6 complexes.

present in solution.<sup>10</sup> The observed preference for this particular diastereoisomer by twenty-membered-ring hexaheteromacrocycles with differing heteroatoms seems to be due to the relative ease with which the two six-membered chelate rings can adopt chair conformations rather than to the preferred conformations around individual carbon-heteroatom bonds. Thus, isomer 3 is the predominant one seen for the 20S6 complex, since not only can the six-membered chelate rings adopt a chair conformation but also the diethylene-three sulfur unit is facially coordinating, whereby the C-S bonds can obtain their preferred gauche conformation. As was observed for the other Fe complex, there is an interesting difference between the internal S-Fe-S angles of the five-membered and six-membered chelate rings. The five-membered chelate rings are constricted (average S-Fe-S: 87.88°), while the more flexible six-membered chelate rings have again opened up (average S-Fe-S: 93.82°). The six-membered chelate rings both adopt a chair conformation. One of the two five-membered rings in each of the S-CH<sub>2</sub>-CH<sub>2</sub>-S-CH<sub>2</sub>-CH<sub>2</sub>-S fragments is in the λ conformation, while the other is in the δ conformation.

**Electronic Spectra.** All of the reported iron(II) complexes with crown thioether ligands are low-spin. An octahedral complex containing a low-spin d<sup>6</sup> metal ion such as Fe(II) or Co(III) would be expected to exhibit two spin-allowed d-d transitions corresponding to the transitions <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1g</sub> and <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>2g</sub>. Both transitions are observed in the 20S6 and 18S6 complexes, allowing the ligand field parameters *Dq* and *B* to be readily calculated as previously described.<sup>8,25</sup> The ligand field parameters for seven iron(II)-crown thioether complexes are presented in

Table V. As anticipated, all of the thioether ligands function as strong-field ligands with *f* values much larger than 1.00. The relative ordering of the ligand field strength for the three crown thioethers presented in this work is 18S6 > gauche 10S3 > 20S6 ~ meso 10S3. The nephelauxetic ratio, β, for all three is relatively small, with an average value near 0.4, indicating a relatively large degree of metal-ligand orbital mixing for the thioether ligands. For example, the nephelauxetic ratio is about 0.55 for the iron(II) complexes with the amine ligands such as 1,4,7-triazacyclononane (9N3).<sup>19</sup> The relatively low value of the two extinction coefficients for the 18S6 complex is indicative of the highly symmetrical meso stereoisomer.

**<sup>13</sup>C NMR Spectra.** The gauche and meso stereoisomers of [Fe(10S3)<sub>2</sub>]<sup>2+</sup> can be identified using carbon-13 NMR spectroscopy. The stereoisomer with resonances at 38.3, 35.5, 28.8, and 19.6 ppm in approximately a 2:2:2:1 ratio is the meso stereoisomer. These peaks correspond to the carbons on the two ethylene bridges, the α-methylene carbons on the propylene bridge, and the β-methylene carbons on the propylene bridge, respectively. The gauche stereoisomer exhibits a seven-line spectrum with resonances of approximately equal intensity at 37.8, 36.5, 36.2, 36.0, 28.8, 25.7, and 18.7 ppm. The two stereoisomers of [Fe(10S3)<sub>2</sub>]<sup>2+</sup> are readily separated by fractional crystallization from water. Due to the much greater water solubility of the gauche isomer, a single crystallization gives a solid which is more than 90% pure in one isomer, as measured by carbon-13 NMR. The ratio of the gauche to the meso stereoisomer is approximately 2.7 to 1. Interestingly, the <sup>13</sup>C and <sup>59</sup>Co NMR spectra of [Co(10S3)<sub>2</sub>]<sup>3+</sup> were recently reported.<sup>22</sup> In that work, <sup>13</sup>C and <sup>59</sup>Co NMR demonstrate that the gauche stereoisomer predominates for Co(III), as we have observed for Fe(II). However, the crystal structures of [Co(10S3)<sub>2</sub>]<sup>2+</sup> and [Ni(10S3)<sub>2</sub>]<sup>2+</sup> reported in that work are of the meso stereoisomer. As we have noted in our study, the preferred crystallization of the meso stereoisomer seems to be based upon its lower solubility relative to the gauche stereoisomer and not upon its abundance in solution. Our initial crystallographic study of [Fe(10S3)<sub>2</sub>]<sup>2+</sup> yielded the gauche stereoisomer because the crystal was grown from water.<sup>8</sup> The chemical shifts of the carbon-13 resonances of the iron(II) complexes of 10S3 have been shifted downfield relative to the values obtained for the cobalt(III) complexes due to the decreased charge of the iron atom. Although carbon NMR spectra are useful in the identification of stereoisomers, proton NMR studies of the complexes have proven of limited value because of the broad, overlapping peaks that are obtained. Carbon-13 NMR studies have been done on the related bis(10N3) cobalt(III) system, and these show a meso:gauche ratio of 96:4 in solution, opposite of what is observed with the thioether ligands.<sup>26</sup> This is again a reflection of the preferred gauche conformation around the C-S bonds whereas the anti conformation is preferred around the C-N bonds.

The <sup>13</sup>C NMR spectrum of the complex [Fe(20S6)]<sup>2+</sup> shows seven intense resonances at 40.0, 38.8, 37.6, 35.2, 32.7, 28.7, and 24.8 ppm. This seven-line spectrum observed for the complex would be expected for isomer 3, the same isomer on which the single-crystal X-ray diffraction study was performed. Thus, <sup>13</sup>C NMR spectroscopy reveals the cis facial isomer is the predominant one in solution, the same stereoisomer observed in the solid state. No evidence is seen in the <sup>13</sup>C NMR spectrum of either of the other two stereoisomers.

The 18S6 ligand can coordinate in a hexadentate fashion to yield two potential stereoisomers, as shown in Figure 6. Due to the lack of solubility of most common salts and the instability of the triflate salt with respect to hydrolysis, single crystals suitable for X-ray diffraction could not be obtained. However, the presence of a single resonance in the carbon-13 NMR spectrum demon-

(24) Grant, G. J.; Setzer, W. N.; Stoddard, S. L.; VanDerveer, D. G. Manuscript in preparation.

(25) Nathan, L. C. *A Laboratory Project in Coordination Chemistry*; Brooks/Cole Publishing Co.: Monterey, CA, 1981.

(26) Angley, M. E.; Dwyer, M.; Lincoln, S. F.; Searle, G. H.; Geue, R. J.; Keene, F. R. *Inorg. Chim. Acta* 1980, 45, L9.

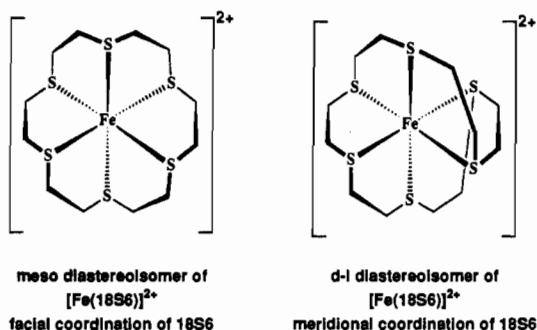


Figure 6. Stereoisomers of 18S6 complexes.

strates that the meso stereoisomer is the only one present. This observation is in agreement with all other 18S6 complexes which have been structurally characterized, whereby only the meso stereoisomer is obtained.<sup>5</sup> The reason behind this exclusive formation of the meso stereoisomer has been attributed to the preference of the gauche conformation around the C–S bonds in the 18S6 ligand.<sup>27</sup>

**Electrochemical Studies.** The electrochemical data for the ligands and complexes are summarized in Table VI. Cyclic voltammetry of the [Fe(10S3)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> complex in acetonitrile or nitromethane shows a single oxidation wave with a cathodic half-wave potential at +0.87 V vs Fc/Fc<sup>+</sup> and an anodic peak potential at +0.95 V vs Fc/Fc<sup>+</sup>. Square-wave voltammetry of the complex in acetonitrile shows a single peak at +0.92 V vs Fc/Fc<sup>+</sup>, which corresponds to  $E_{1/2}$  at +0.91 V. The peak-to-peak separation is 80 mV. The process is chemically reversible with  $i_{pa}/i_{pc}$  equal to 1.02. A single reversible oxidation process is noted, which is assigned to the oxidation of the Fe(II) center to Fe(III). The oxidation process does appear to be metal based since the 10S3 ligand in acetonitrile or nitromethane shows only an irreversible oxidation wave at +0.71 V vs Fc/Fc<sup>+</sup>. Also, Wieghardt and co-workers have reported very similar electrochemical behavior for the bis(9S3) complex of iron(II).<sup>19</sup> Cyclic and square-wave voltammetry of the [Fe(20S6)](ClO<sub>4</sub>)<sub>2</sub> complex in nitromethane shows similar electrochemical behavior. Cyclic voltammetry of the [Fe(20S6)](ClO<sub>4</sub>)<sub>2</sub> complex in nitromethane shows a single oxidation wave with a cathodic half-wave potential at +0.65 V vs Fc/Fc<sup>+</sup> and an anodic peak potential at +0.72 V vs Fc/Fc<sup>+</sup>. Square-wave voltammetry of the complex in acetonitrile shows a single peak at +0.70 V vs Fc/Fc<sup>+</sup>, which corresponds to  $E_{1/2}$  at +0.69 V. The peak-to-peak separation is 70 mV. This oxidation is also chemically reversible with  $i_{pa}/i_{pc}$  equal to 1.00. This oxidation is again assigned to the oxidation of the Fe(II) center to Fe(III) since the 20S6 ligand shows no electrochemical activity between +2.0 and –2.0 V. Cyclic voltammetry of the [Fe(18S6)](triflate)<sub>2</sub> complex in nitromethane

using tetrabutylammonium triflate as the electrolyte shows a single irreversible oxidation wave at +1.08 V vs Fc/Fc<sup>+</sup>. Schroder and co-workers recently published the synthesis of the bis iron(III) complex of 9S3 via the oxidation of the iron(II) complex to yield an unusual low-spin Fe(III) center.<sup>28</sup> Our data suggest that the oxidation to Fe(III) for the complexes [Fe(10S3)<sub>2</sub>]<sup>2+</sup> and particularly [Fe(20S6)]<sup>2+</sup> should occur more readily since these oxidations occur at less positive potentials than for the related 9S3 complex. The same electrochemical behavior is observed for 20S6 in its Co and Ni complexes.<sup>24</sup> However, the more positive potential for the 18S6 complex indicates that the divalent state is favored for this particular ligand. This is also seen in the irreversible nature of the oxidation wave.

## Conclusions

This work extends the study of the coordination chemistry of crown thioether ligands to three octahedral iron(II) complexes. The complexes are all low-spin, and the three ligands function as strong-field ligands. The gauche stereoisomer of the 10S3 complex is the predominant one formed in solution and can readily be separated from the meso stereoisomer by fractional crystallization from water. The X-ray crystal structure of the meso isomer is presented and complements our previously reported structure of the gauche stereoisomer. The 20S6 ligand complexes with iron(II) to form exclusively the cis facial diastereoisomer which is characterized in the solid state by single-crystal X-ray diffraction and in solution by carbon-13 NMR spectroscopy. A strong preference for this particular stereoisomer is seen among twenty-membered-ring hexadentate macrocyclic ligands. The 18S6 ligand complexes with Fe(II) to form exclusively the meso stereoisomer, as anticipated from the previous coordination behavior of this ligand. The spectroscopic and electrochemical properties of the hexakis(thioether)–Fe(II) complexes are dependent upon the nature of the coordinated crown thioether ligand.

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**Supplementary Material Available:** Listings of complete bond lengths and bond angles, complete atomic positional parameters, and anisotropic thermal parameters for *meso*-[Fe(10S3)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> and [Fe(20S6)](ClO<sub>4</sub>)<sub>2</sub> (16 pages). Ordering information is given on any current masthead page.

(27) Wolf, R. E., Jr.; Hartman, J. R.; Storey, J. M. E.; Foxman, B. M.; Cooper, S. R. *J. Am. Chem. Soc.* **1987**, *109*, 4328.

(28) Blake, A. J.; Holder, A. J.; Hyde, T. I.; Schroder, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1433.