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Synthesis and Complexation Studies of Ten-Membered-Ring Trithioethers[1]

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The medium-sized (mesocyclic) ring thioethers 1,4,7-trithiacyclodecane (10S3), 1,4,7-trithiacyclodecan-9-one (keto-10S3), and 1,4,7-trithiacyclodecan-9-ol (hydroxy-10S3) have been synthesized and studied as potential ligands for the complexation of transition-metal and heavy-metal ions. Stable, isolable complexes of the thioether keto-10S3 with Fe(II), Co(II), Ni(II), Hg(II), and Pb(II) have been prepared and analyzed. All of these complexes involve two ligand molecules per metal cation. An X-ray crystal structure of the Ni(II) complex indicates that the two facially coordinating tridentate ligands form a distorted octahedral array of sulfur atoms about the nickel center. The meso stereoisomer is the one that is obtained in this case. Crystal data for [Ni(keto-10S3)$_2$](BF$_4$)$_2$: C$_{14}$H$_{24}$NiS$_6$O$_2$B$_2$F$_8$; triclinic, space group P$\bar{1}$; a = 8.401 (4), b = 10.039 (5), c = 10.463 (4) Å; α = 65.97 (3), β = 80.52 (3), γ = 68.92 (3)°; V = 751.8 (5) Å^3; Z = 1. The ligand also reacts with Cu(II) to give a complex that is unstable with respect to hydrolysis. Reaction of the thioether ligand with Fe(III) results in the reduction of iron from Fe(III) to Fe(II), giving finally the Fe(II) complex. 1,4,7-Trithiacyclodecane (10S3) has also been complexed to several transition-metal ions. Complexes of 10S3 with Ni(II), Co(II), and Fe(II) have been synthesized and analyzed. The reaction with Cu(II) produced a product that was again unstable with respect to hydrolysis. All of these complexes involve two ligand molecules per metal cation. An X-ray crystal structure of the Fe(II) complex of 10S3 has been solved, and surprisingly, the lower symmetry stereoisomer is obtained in this case. Even more surprisingly, the complex does not crystallize as a racemic mixture, but instead crystallizes in the optically active space group P2$_1$, an interesting case of spontaneous resolution and a unique example of an optically active octahedral thioether complex. Crystal data for [Fe(10S3)$_2$](ClO$_4$)$_2$: C$_{14}$H$_{28}$FeS$_6$Cl$_2$O$_8$; monoclinic, space group P2$_1$; a = 12.036 (4), b = 11.824 (4), c = 9.178 (2) Å; β = 110.51 (2)°; V = 1223.36 (20) Å^3; Z = 2. Reaction of 10S3 with Zn(II), Cd(II), or Hg(II) produces the anticipated 2:1 (ligand:metal) complexes. On the other hand, reaction of 10S3 with Pb(II) gives a 1:1 complex. The alcohol trithioether ligand 1,4,7-trithiacyclodecan-9-ol reacts with Fe(II), Co(II), Ni(II), Cu(II), Hg(II), Cd(II), and Pb(II). Although crystalline products were not isolated in the case of hydroxy-10S3, octahedral complexation does apparently take place, as indicated from solution ultraviolet–visible spectrophotometry. The three ten-membered crown trithioethers discussed in this work represent an important extension of the coordination chemistry of thioether ligands. In terms of their ligand field characteristics and metal–sulfur bond distances, they function as intermediate cases between the previously studied nine-membered and twelve-membered ring trithioether systems. The preferred conformation of the ligands and the presence of additional functional groups are critical factors in their complexation behavior. Also, these ligands offer novel stereochemical possibilities that are not present with their more symmetrical analogues.

Introduction

Research involving the coordination chemistry of thioether ligands, although not as extensive as that of amine, phosphine, and crown ether ligands, is currently very active. Two review articles on the coordination chemistry of thioethers have recently appeared.[3,4] Mesocyclic (medium-sized ring) and macrocyclic polythioethers have been found to be effective polydentate ligands for complexing a variety of transition metals. The mesocyclic thioether 1,4,7-trithiacyclononane (9S3) has been found to form particularly stable bis octahedral complexes with a number of transition metals including nickel(II),[5,6] cobalt(II),[5,7] cobalt(III),[8] copper(II),[5] iron(II),[9] iron(III),[10] ruthenium(II),[11–13] palladium-

(II),[14,15] palladium(III),[16] platinum(II),[17] rhodium(III),[18] silver(I),[19,20] and gold(III), for which a very recent publication reported a (9S3)$_2$ complex that has a distorted octahedral structure.[21] An octahedral complex between 9S3 and zinc(II) has recently been prepared, and the ligand forms stable complexes with the heavy metals cadmium(II), mercury(II), and lead(II) as well.[22] The unusual stability of these octahedral complexes can be attributed to the preferred endodentate conformation of the free ligand[23] and to the geometrical constrictions that this conformation imposes on the metal ion upon complexation.[5]

We are interested in studying the effects that structural alterations on mesocyclic trithioether ligands might have on the ease

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of complex formation, complex stability, and complex structure. We have recently reported the synthesis of the ten-membered mesocyclic thioether 1,4,7-trithiacyclodecane and presented some initial aspects of its coordination behavior.[1,24] We also wish to compare and contrast the complexation characteristics of these three thioether ring systems. In order to examine the complexation behavior of mesocyclic trithioether ligands other than the nine-membered ring, as well as to examine the effects of other functional groups on the ligand molecules, we have prepared and studied the ten-membered rings 1,4,7-trithiacyclodecane (10S3), 1,4,7-trithiacyclodecan-9-one (keto-10S3), and 1,4,7-trithiacyclodecan-9-ol (hydroxy-10S3).

10S3   keto-10S3   hydroxy-10S3
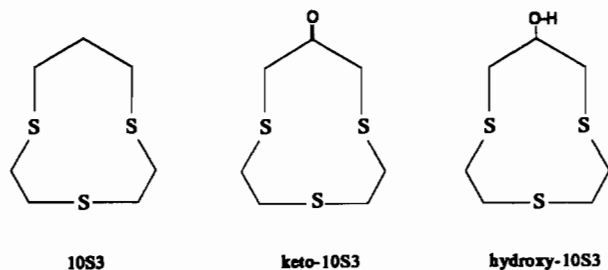
Experimental Section

Materials. Nitromethane, dimethylformamide, and acetic anhydride were dried by using common methods.[25] All transition-metal salts (Alfa) were used as received without additional purification. Cesium carbonate was purchased from Aldrich Chemical Co. The organic reagents bis(2-mercaptoethyl) sulfide and 1,3-dichloro-2-propanol were purchased from Aldrich Chemical Co. and distilled prior to use.

Measurements. Analyses were performed by Atlantic Microlab, inc., Atlanta, GA, or by Galbraith Laboratories, Inc., Knoxville, TN. Fourier transform infrared spectra were obtained with a Beckman FT 1100 infrared spectrophotometer, and infrared spectra were obtained with a Perkin-Elmer 1330 infrared spectrophotometer. Ultraviolet-visible spectra were obtained on a Varian DMS 200 UV–visible spectrophotometer. Magnetic susceptibility measurements on solid complexes were obtained by using a Johnson-Matthey magnetic susceptibility balance or by the Faraday method, and diamagnetism correction factors were included.

Preparation of 1,4,7-Trithiacyclodecane and 1,4,7-Trithiacyclodecan-9-one. The syntheses of the two ligands have been reported elsewhere.[1] The keto-10S3 is formed in 17.8% yield as a second product in the preparation of the twenty-membered-ring system 1,4,7,11,14,17-hexathiacycloeicosan-9,19-dione.

Preparation of 1,4,7-Trithiacyclodecan-9-ol. A 1-L three-necked round-bottom flask, equipped with matching calibrated 200-mL addition funnels, magnetic stir bar, heating mantle, and a nitrogen inlet-outlet, was charged with freshly distilled dimethylformamide (DMF, 300 mL) and cesium carbonate (32.6 g, 100 mmol). Into one funnel were added bis(2-mercaptoethyl)sulfide (13.7 mL, 16.2 g, 100 mmol) and sufficient anhydrous DMF to dilute to 200 mL. Into the other funnel were added 1,3-dichloro-2-propanol (9.5 mL, 12.9 g, 100 mmol) and sufficient anhydrous DMF to dilute to 200 mL. The two solutions were added simultaneously to the rapidly stirred, heated (held at 65 °C) DMF/Cs$_2$CO$_3$ mixture at the rate of about 15 drops/min. Upon completion of the addition (5 h), the reaction mixture was heated and stirred for an additional 12 h, cooled, and allowed to stir for another 24 h. The reaction mixture was vacuum filtered and the DMF removed by rotary evaporation to give 34.29 g of a light brown solid residue. A 15.89-g sample of the crude product was recrystallized three times from ethanol to give 2.260 g (23.2%) of hydroxy-10S3 as a colorless, microcrystalline solid: mp 74–79 °C; IR (KBr) 3600–3100 (s, b, O–H), 2950, 1800–1780, 1418, 1190, 1133, 1060, 1032, 992, 716, 677 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.81 (m, 4 H, –SCH$_2$ CH(OH)–), 2.93 (m, 8 H, –SCH$_2$CH$_2$S–), 4.47 (m, 1 H, –SCH$_2$CH(OH)–); mass spectrum (CI, methane) *m/e* (relative intensity) 210 (1%, M$^+$), 209 (1%), 149 (12%), 121 (14%), 117 (15%). 105 (32%), 87 (37%), 73 (42%), 61 (100%). Anal. Calcd for C$_7$H$_{14}$OS$_3$: C, 39.96; H, 6.71; S, 45.72. Found: C, 39.87; H, 6.71; S, 45.65.

General Synthesis of Metal Complexes. Metal ion complexes were prepared by using the procedure of Rosen and Busch.[26] A solution of

2 equiv of thioether ligand in anhydrous nitromethane was added to an anhydrous nitromethane solution of the hydrated metal salt (either tetrafluoroborate or perchlorate) containing 6 equiv of acetic anhydride. *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.

Preparation of Ni(keto-10S3)$_2$(BF$_4$)$_2$. A solution of 1,4,7-trithiacyclodecan-9-one (55.0 mg, 0.264 mmol) in 5 mL of anhydrous nitromethane was added to a solution of Ni(BF$_4$)$_2$·6H$_2$O (44.8 mg, 0.132 mmol) in 5 mL of anhydrous nitromethane and 5 drops of acetic anhydride. The color changed immediately from green to purple. Purple crystals were grown from the reaction mixture by solvent diffusion with anhydrous diethyl ether to give 60.1 mg (70.1% yield) of bis(1,4,7-trithiacyclodecan-9-one)nickel(II) tetrafluoroborate as a purple crystalline solid: IR (KBr, cm^{-1}) 3000–2820, 1685 (s, C=O), 1545, 1412, 1380, 1285, 1260, 1174, 1110–990 (s, BF$_4^-$), 910, 860, 826, 654, 514. The electronic spectrum measured in nitromethane shows two absorbances with λ$_{max}$'s at 833 nm (ε = 11) and 541 nm (ε = 16). The effective magnetic moment of the solid was found to be 3.07 μ$_B$. Anal. Calcd for C$_{14}$H$_{24}$B$_2$F$_8$NiO$_2$S$_6$: C, 25.91; H, 3.73; S, 29.64. Found: C, 25.81; H, 3.69; S, 29.44.

Preparation of Co(keto-10S3)$_2$(BF$_4$)$_2$. A solution of 1,4,7-trithiacyclodecan-9-one (50.5 mg, 0.242 mmol) in 5 mL of anhydrous nitromethane was added to a solution of Co(BF$_4$)$_2$·6H$_2$O (41.2 mg, 0.121 mmol) in 5 mL of anhydrous nitromethane and 5 drops of acetic anhydride. The color changed immediately from violet to deep brownish red. Brownish red crystals were grown from the reaction mixture by solvent diffusion with anhydrous diethyl ether to give 80 mg (100% yield) of bis(1,4,7-trithiacyclodecan-9-one)cobalt(II) tetrafluoroborate as a brownish red crystalline solid: IR (KBr, cm^{-1}) 2940, 1680 (s, C=O), 1542, 1406, 1256, 1150–930 (s, BF$_4^-$), 857, 826, 653, 513. The electronic spectrum measured in nitromethane shows one absorbance shoulder at 470 nm (ε = 64). The effective magnetic moment of the solid was found to be 1.82 μ$_B$. Anal. Calcd for C$_{14}$H$_{24}$B$_2$F$_8$CoO$_2$S$_6$: C, 25.90; H, 3.73; S, 29.63. Found: C, 25.76; H, 3.73; S, 29.52.

Preparation of Fe(keto-10S3)$_2$(ClO$_4$)$_2$. A solution of 1,4,7-trithiacyclodecan-9-one (50.0 mg, 0.240 mmol) in 5 mL of anhydrous nitromethane was added to a solution of Fe(ClO$_4$)$_2$·6H$_2$O (43.9 mg, 0.121 mmol) in 5 mL of anhydrous nitromethane and 5 drops of acetic anhydride. The color changed immediately to purple. Purple crystals were grown from the reaction mixture by solvent diffusion with anhydrous diethyl ether to give 60.1 mg (73.9% yield) of bis(1,4,7-trithiacyclodecan-9-one)iron(II) perchlorate as a purple crystalline solid: IR (KBr, cm^{-1}) 2940, 1780–1630 (s, C=O), 1400, 1250, 1100–1040 (s, ClO$_4^-$), 923, 850, 822, 617 (s, ClO$_4^-$), 497, 405, 356. The electronic spectrum measured in nitromethane shows a single absorption with λ$_{max}$ at 542 nm (ε = 67). Magnetic susceptibility measurements on the complex showed that it was diamagnetic. Anal. Calcd for C$_{14}$H$_{24}$Cl$_2$FeO$_{10}$S$_6$: C, 25.04; H, 3.60; S, 28.65. Found: C, 25.13; H, 3.61; S, 28.69.

Preparation of Hg(keto-10S3)$_2$(ClO$_4$)$_2$. A solution of 1,4,7-trithiacyclodecan-9-one (50.0 mg, 0.240 mmol) in 5 mL of anhydrous nitromethane was added to a solution of Hg(ClO$_4$)$_2$·3H$_2$O (54.4 mg, 0.120 mmol) in 5 mL of anhydrous nitromethane and 5 drops of acetic anhydride. Colorless crystals were grown from the reaction mixture by solvent diffusion with anhydrous diethyl ether to give 49.9 mg (50.9% yield) of bis(1,4,7-trithiacyclodecan-9-one)mercury(II) perchlorate as a colorless crystalline solid: IR (KBr, cm^{-1}) 2960, 2920, 2900, 1700 (s, C=O), 1645, 1618, 1552, 1400, 1376, 1275, 1146, 1106, 1087 (s, ClO$_4^-$), 658, 639, 628 (s, ClO$_4^-$). Anal. Calcd for C$_{14}$H$_{24}$Cl$_2$HgO$_{10}$S$_6$: C, 20.60; H, 2.96; S, 23.57. Found: C, 20.44; H, 3.05; S, 23.42.

Preparation of Pb(keto-10S3)$_2$(ClO$_4$)$_2$. A solution of 1,4,7-trithiacyclodecan-9-one (50.1 mg, 0.240 mmol) in 5 mL of anhydrous nitromethane was added to a solution of Pb(ClO$_4$)$_2$·3H$_2$O (55.3 mg, 0.120 mmol) in 5 mL of anhydrous nitromethane and 5 drops of acetic anhydride. Colorless crystals were grown from the reaction mixture by solvent diffusion with anhydrous diethyl ether to give 51.9 mg (52.6% yield) of bis(1,4,7-trithiacyclodecan-9-one)lead(II) perchlorate as a colorless crystalline solid: IR (KBr, cm^{-1}) 2880, 1670–1620 (s, C=O), 1435, 1412, 1397, 1372, 1290, 1265, 1203, 1184, 1150–980 (s, ClO$_4^-$), 930, 915, 888, 868, 848, 816, 700, 674, 617 (s, ClO$_4^-$), 560, 460, 389. Anal. Calcd for C$_{14}$H$_{24}$Cl$_2$PbO$_{10}$S$_6$: C, 20.44; H, 2.94; S, 23.38. Found: C, 20.48; H, 2.96; S, 23.33.

Reaction of keto-10S3 with Cu(BF$_4$)$_2$·xH$_2$O. A solution of 1,4,7-trithiacyclodecan-9-one (50.4 mg, 18.2% Cu by weight, 0.242 mmol) in 5 mL of anhydrous nitromethane was added to a solution of Cu(BF$_4$)$_2$·xH$_2$O (41.7 mg, 0.120 mmol) in 5 mL of anhydrous nitromethane and 5 drops of acetic anhydride. The color changed immediately to dark

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brown. The ultraviolet–visible spectrum of the dark brown solution showed no observable band maximum. Attempts to isolate the crystalline product resulted in hydrolysis of the complex; the brown solution slowly reverts back to green.

Reaction of keto-10S3 with Fe(ClO₄)₃·6H₂O. A solution of 1,4,7-trithiacyclodecan-9-one (50.0 mg, 0.240 mmol) in 5 mL of anhydrous nitromethane was added to a solution of Fe(ClO₄)₃·6H₂O (55.4 mg, 0.120 mmol) in 5 mL of anhydrous nitromethane and 5 drops of acetic anhydride. After several minutes the color of the solution changed from yellow to purple. Purple crystals were grown from the reaction mixture by solvent diffusion of anhydrous diethyl ether to give 30.2 mg (37.0% yield) of bis(1,4,7-trithiacyclodecan-9-one)iron(II) perchlorate as a purple crystalline solid. The spectroscopic data obtained for the purple solid were identical with the data previously obtained for bis(1,4,7-trithiacyclodecan-9-one)iron(II) perchlorate.

Preparation of Ni(10S3)₂(BF₄)₂. A solution of 1,4,7-trithiacyclodecane (100 mg, 0.514 mmol) in 5 mL of anhydrous nitromethane was added to a solution of Ni(BF₄)₂·6H₂O (87.5 mg, 0.257 mmol) and acetic anhydride (157.4 mg, 1.542 mmol, 0.146 mL) in 5 mL of anhydrous nitromethane. The color changed immediately from green to purple-red. Addition of 5 mL of diethyl ether to the solution precipitated the complex. The precipitate was washed with 5 mL of ether and air-dried to give 249 mg (78% yield) of bis(1,4,7-trithiacyclodecane)nickel(II) tetrafluoroborate as a purple-red crystalline solid: FT-IR (KBr, cm⁻¹) 2993, 2948, 1446, 1412, 1150–1036 (s, BF₄⁻), 932, 913, 845, 792, 520. The electronic spectrum measured in nitromethane shows two absorbances with λ_{max}'s at 807 nm (ϵ = 33) and 544 nm (ϵ = 54). The effective magnetic moment of the solid was found to be 3.00 μ_B. The equivalent conductivity in nitromethane measured by using a 0.0010 M solution is 167 Ω^{-1} cm² mol⁻¹. Anal. Calcd for C₁₄H₂₈B₂F₈NiS₆: C, 27.08; H, 4.54; S, 30.97. Found: C, 26.80; H, 4.60; S, 31.16.

Preparation of Co(10S3)₂(BF₄)₂. A solution of 1,4,7-trithiacyclodecane (250.0 mg, 1.290 mmol) in 3 mL of anhydrous nitromethane was added to a solution of Co(BF₄)₂·6H₂O (214 mg, 0.643 mmol) and acetic anhydride (405 mg, 3.97 mmol, 0.38 mL) in 5 mL of anhydrous nitromethane. The color changed immediately from violet to deep brownish purple. Dark purple-brown crystals were grown from the reaction mixture by solvent diffusion with diethyl ether to give bis(1,4,7-trithiacyclodecane)cobalt(II) tetrafluoroborate as a brownish red crystalline solid: IR (KBr, cm⁻¹) 2963.9, 2905.3, 1446.3, 1410.8, 1140–1087 (s, BF₄⁻), 1029.1, 626.2. The electronic spectrum measured in nitromethane shows one absorbance shoulder at 510 nm (ϵ = 370) and one absorbance maximum at 290 nm (ϵ = 11 800). The effective magnetic moment of the solid was measured as 1.78 μ_B. The equivalent conductivity in water measured by using a 0.0010 M solution is 239 Ω^{-1} cm² mol⁻¹. Anal. Calcd for C₁₄H₂₈B₂F₈CoS₆: C, 27.07; H, 4.54; S, 30.96. Found: C, 27.00; H, 4.66; S, 30.80.

Preparation of Fe(10S3)₂(ClO₄)₂. Under nitrogen, a solution of Fe(ClO₄)₂·6H₂O (58.8 mg, 0.162 mmol) in 5 mL CH₃NO₂ was added dropwise to a solution of 1,4,7-trithiacyclodecane (63.0 mg, 0.324 mmol) in 3 mL of nitromethane. A dark violet complex immediately formed. The product was filtered out and washed with 20 mL of anhydrous ether. The product was further purified by recrystallization from a water/ethanol mixture. A yield of 63.7 mg (61.6%) of product was obtained. A crystal suitable for X-ray diffraction studies was obtained by dissolving the complex in hot water and slowly allowing it to crystallize over a 3-day period: IR (KBr, cm⁻¹) 2982.0, 2947.3, 2936.8, 2913.8, 1419.3, 1079.3, 1023.3, 1002.8, 829.5, 621.4. The electronic spectrum shows two absorbances with λ_{max}'s at 540 nm (ϵ = 78) and 395 nm (ϵ = 103). Magnetic susceptibility measurements showed that the complex was diamagnetic. Anal. Calcd for C₁₄H₂₈Cl₂FeO₈S₆: C, 26.13; H, 4.39; S, 29.90. Found: C, 26.27; H, 4.41; S, 29.80.

Preparation of Zn(10S3)₂(BF₄)₂. A solution of 1,4,7-trithiacyclodecane (50.0 mg, 0.257 mmol) in 5 mL of anhydrous nitromethane was added to a solution of Zn(BF₄)₂·6H₂O (48.6 mg, 0.129 mmol) in 5 mL of anhydrous nitromethane and 5 drops of acetic anhydride. Colorless crystals were grown from the reaction mixture by solvent diffusion with ethyl acetate to give 46.8 mg (47.5% yield) of Zn(10S3)₂(BF₄)₂ as a hygroscopic, crystalline solid: IR (KBr, cm⁻¹) 3600–3300 (s, b, OH), 2900, 1605, 1432, 1404, 1294, 1270, 1258, 1120–1010 (s, b, BF₄⁻), 742, 513, 474. Anal. Calcd for C₁₄H₂₈S₆B₂F₈Zn: C, 26.79; H, 4.50; S, 30.64. Found: C, 26.11; H, 4.54; S, 29.60.

Preparation of Cd(10S3)₂(ClO₄)₂. A solution of 1,4,7-trithiacyclodecane (50.0 mg, 0.257 mmol) in 5 mL of anhydrous nitromethane was added to a solution of Cd(ClO₄)₂·6H₂O (54.1 mg, 0.129 mmol) in 5 mL of anhydrous nitromethane and 5 drops of acetic anhydride. Colorless crystals were grown from the reaction mixture by solvent diffusion with diethyl ether to give 96.3 mg (92.5% yield) of Cd(10S3)₂(ClO₄)₂ as a colorless crystalline solid: IR (KBr, cm⁻¹) 2900, 1538, 1430, 1395, 1266, 1132, 1107, 1076 (s, ClO₄⁻), 996, 824, 649, 628, 618 (s, ClO₄⁻). Anal.

Calcd for C₁₄H₂₈S₆Cl₂O₈Cd: C, 24.02; H, 4.03; S, 27.48. Found: C, 23.97; H, 3.91; S, 27.25.

Preparation of Hg(10S3)₂(ClO₄)₂. A solution of 1,4,7-trithiacyclodecane (50.0 mg, 0.257 mmol) in 5 mL of anhydrous nitromethane was added to a solution of Hg(ClO₄)₂·3H₂O (58.3 mg, 0.129 mmol) in 5 mL of anhydrous nitromethane and 5 drops of acetic anhydride. Colorless crystals were grown from the reaction mixture by solvent diffusion with diethyl ether to give 80.3 mg (74.2% yield) of Hg(10S3)₂(ClO₄)₂ as a colorless crystalline solid: IR (KBr, cm⁻¹) 2890, 1539, 1396, 1313, 1262, 1205, 1131, 1104, 1076 (s, ClO₄⁻), 908, 896, 809, 765, 679, 648, 627, 618 (s, ClO₄⁻). Anal. Calcd for C₁₄H₂₈S₆Cl₂O₈Hg: C, 21.33; H, 3.58; S, 24.40. Found: C, 20.88; H, 3.64; S, 24.36.

Preparation of Pb(10S3)(ClO₄)₂·H₂O. A solution of 1,4,7-trithiacyclodecane (50.0 mg, 0.257 mmol) in 5 mL of anhydrous nitromethane was added to a solution of Pb(ClO₄)₂·3H₂O (59.4 mg, 0.129 mmol) in 5 mL of anhydrous nitromethane and 5 drops of acetic anhydride. Colorless crystals were grown from the reaction mixture by solvent diffusion with diethyl ether to give 26.1 mg (32.7% yield) of Pb(10S3)-(ClO₄)₂·H₂O as a colorless crystalline solid: IR (KBr, cm⁻¹) 3600–3400 (b, OH⁻), 2905, 1593, 1531, 1445, 1412, 1138, 1110, 1085 (s, ClO₄⁻), 994, 623 (s, ClO₄⁻). Anal. Calcd for C₇H₁₆S₃Cl₂O₉Pb: C, 13.59; H, 2.61; S, 15.55. Found: C, 13.60; H, 2.58; S, 15.61.

Reaction of Cu(II) and 10S3. Under nitrogen a solution of Cu(BF₄)₂·xH₂O (47.4 mg, 19.6% Cu by weight, 0.146 mmol), acetic anhydride (0.0828 mL, 89.4 mg, 0.876 mmol), and 5 mL of anhydrous CH₃NO₂ was added dropwise to a solution of 1,4,7-trithiacyclodecane (56.8 mg, 0.292 mmol) in 5 mL of anhydrous nitromethane. The mixture immediately turned dark brown. No precipitate was observed. Several variations of recrystallization were attempted, but none resulted in isolable crystals due to the sensitivity of the complex to hydrolysis. The electronic spectrum of the brown solution shows a single intense absorption with λ_{max} at 483 nm (ϵ > 500).

Reaction of hydroxy-10S3 with Fe(ClO₄)₂·6H₂O. 1,4,7-Trithiacyclodecan-9-ol (50.0 mg, 0.238 mmol) was placed in the thimble of a Bantamware Soxhlet extractor, and a solution of Fe(ClO₄)₂·6H₂O (43.3 mg, 0.119 mmol) in 15 mL of anhydrous nitromethane and 5 drops of acetic anhydride was placed in the pot. The solution was refluxed until all of the ligand had dissolved into the reaction mixture, giving a dark red-orange solution. The reaction mixture was filtered while hot into a solvent diffusion chamber. Ether was allowed to diffuse into the nitromethane reaction mixture. The complex did not crystallize out of the reaction mixture but rather deposited as a brown oil. The supernatant was removed from the oil, and the oil was dried overnight under high vacuum, leaving an amorphous solid: IR (KBr, cm⁻¹) 3600–3100 (s, b, O–H), 2920, 1765, 1650–1524, 1390, 1150–980 (s, b, ClO₄⁻), 940, 762, 618 (s, ClO₄⁻); UV–vis (nitromethane) λ_{max}'s at 520 nm (ϵ = 131) and at 458 nm (ϵ = 171). Magnetic susceptibility measurements on the solid complex showed that it was diamagnetic.

Reaction of hydroxy-10S3 with Co(BF₄)₂·6H₂O. 1,4,7-Trithiacyclodecan-9-ol (55.5 mg, 0.264 mmol) was placed in the thimble of a Bantamware Soxhlet extractor, and a solution of Co(BF₄)₂·6H₂O (45.1 mg, 0.132 mmol) in 15 mL of anhydrous nitromethane and 5 drops of acetic anhydride was placed in the pot. The solution was refluxed until all of the ligand had dissolved into the reaction mixture, giving a red-brown solution. The reaction mixture was filtered while hot into a solvent diffusion chamber. Ether was allowed to diffuse into the nitromethane reaction mixture. The complex did not crystallize out of the reaction mixture but rather deposited as an orange-brown oil. The supernatant was removed from the oil, and the oil was dried overnight under high vacuum, leaving an amorphous solid: IR (KBr, cm⁻¹) 3560–3320 (s, b, O–H), 2990, 2935, 1790–1770, 1620, 1540, 1410, 1336, 1288, 1230, 1130–990 (s, b, BF₄⁻), 974, 955, 920, 831, 804, 761, 600, 515; UV–vis (nitromethane) λ_{max}'s at 487 nm (ϵ = 319) and at 447 nm (ϵ = 392). The effective magnetic moment of the solid was measured as 1.78 μ_B.

Reaction of hydroxy-10S3 with Ni(BF₄)₂·6H₂O. 1,4,7-Trithiacyclodecan-9-ol (53.9 mg, 0.256 mmol) was placed in the thimble of a Bantamware Soxhlet extractor, and a solution of Ni(BF₄)₂·6H₂O (43.7 mg, 0.128 mmol) in 15 mL of anhydrous nitromethane and 5 drops of acetic anhydride was placed in the pot. The solution was refluxed until all of the ligand had dissolved into the reaction mixture, giving a purple-blue solution. The reaction mixture was filtered while hot into a solvent diffusion chamber. Ether was allowed to diffuse into the nitromethane reaction mixture. The complex did not crystallize out of the reaction mixture but rather deposited as a purple-blue oil. The supernatant was removed from the oil, and the oil was dried overnight under high vacuum, leaving an amorphous solid: IR (KBr, cm⁻¹) 3580–3220 (s, b, O–H), 2962, 2920, 1775, 1625, 1544, 1405, 1280, 1255, 1168, 1122–1000 (s, b, BF₄⁻), 970, 855, 764, 703, 654, 519; UV–vis (nitromethane) λ_{max}'s at 877 nm (ϵ = 30) and at 562 nm (ϵ = 30). The effective magnetic moment of the solid was measured as 3.12 μ_B.

Reaction of hydroxy-10S3 with Cu(BF$_4$)$_2$·6H$_2$O. 1,4,7-Trithiacyclodecan-9-ol (54.4 mg, 0.258 mmol) was placed in the thimble of a Bantamware Soxhlet extractor, and a solution of Cu(BF$_4$)$_2$·6H$_2$O (44.7 mg, 0.129 mmol) in 15 mL of anhydrous nitromethane and 5 drops of acetic anhydride was placed in the pot. The solution was refluxed until all of the ligand had dissolved into the reaction mixture, giving a dark green-brown solution that gradually turned pale green. The reaction mixture was filtered while hot into a solvent diffusion chamber. Ether was allowed to diffuse into the nitromethane reaction mixture. The complex did not crystallize out of the reaction mixture but rather deposited as a pale green oil. The supernatant was removed from the oil, and the oil was dried overnight under high vacuum, leaving an amorphous solid: IR (KBr, cm^{-1}) 3600–3200 (s, b, O–H), 2975, 2910, 1780, 1615, 1538, 1400, 1280, 1250, 1168, 1125–980 (s, b, BF$_4^-$), 830, 763, 710, 650, 513; UV–vis (nitromethane) λ_{max} at 593 nm (ϵ = 232) of the brown solution before decomposition.

Reaction of hydroxy-10S3 with Cd(ClO$_4$)$_2$·6H$_2$O. 1,4,7-Trithiacyclodecan-9-ol (57.6 mg, 0.274 mmol) was placed in the thimble of a Bantamware Soxhlet extractor, and a solution of Cd(ClO$_4$)$_2$·6H$_2$O (57.5 mg, 0.137 mmol) in 15 mL of anhydrous nitromethane and 5 drops of acetic anhydride was placed in the pot. The solution was refluxed until all of the ligand had dissolved into the reaction mixture, giving a pale yellow solution. The reaction mixture was filtered while hot into a solvent diffusion chamber. Ether was allowed to diffuse into the nitromethane reaction mixture, and the complex precipitated out of the reaction mixture as a pale yellow powder. The supernatant liquid was removed, and the oil was dried overnight under high vacuum, leaving a pale yellow solid: IR (KBr, cm^{-1}) 3500–3240 (s, b, O–H), 2900, 1785, 1540, 1415, 1340, 1258, 1188, 1120–1030 (s, b, ClO$_4^-$), 970, 925, 915, 835, 767, 713, 675, 650, 620 (s, ClO$_4^-$), 545, 500, 455, 379, 303.

Reaction of hydroxy-10S3 with Hg(ClO$_4$)$_2$·3H$_2$O. 1,4,7-Trithiacyclodecan-9-ol (52.6 mg, 0.250 mmol) was placed in the thimble of a Bantamware Soxhlet extractor, and a solution of Hg(ClO$_4$)$_2$·3H$_2$O (56.8 mg, 0.125 mmol) in 15 mL of anhydrous nitromethane and 5 drops of acetic anhydride was placed in the pot. The solution was refluxed until all of the liquid had dissolved into the reaction mixture, giving a pale yellow solution. The reaction mixture was filtered while hot into a solvent diffusion chamber. Ether was allowed to diffuse into the nitromethane reaction mixture, and the complex precipitated out of the reaction mixture as a pale yellow powder. The supernatant liquid was removed, and the oil was dried overnight under high vacuum, leaving a pale yellow solid: IR (KBr, cm^{-1}) 3520–3210 (s, b, O–H), 2980, 2917, 1772, 1540, 1400, 1355, 1150–1010 (s, b, ClO$_4^-$), 920, 830, 765, 654, 620 (s, ClO$_4^-$).

Reaction of hydroxy-10S3 with Pb(ClO$_4$)$_2$·3H$_2$O. 1,4,7-Trithiacyclodecan-9-ol (57.2 mg, 0.272 mmol) was placed in the thimble of a Bantamware Soxhlet extractor, and a solution of Pb(ClO$_4$)$_2$·3H$_2$O (62.4 mg, 0.136 mmol) in 15 mL of anhydrous nitromethane and 5 drops of acetic anhydride was placed in the pot. The solution was refluxed until all of the ligand had dissolved into the reaction mixture, giving a pale yellow solution. The reaction mixture was filtered while hot into a solvent diffusion chamber. Ether was allowed to diffuse into the nitromethane reaction mixture. The complex did not precipitate out of the reaction mixture but rather oiled out as a pale yellow oil. The supernatant liquid was removed, and the oil was dried overnight under high vacuum, leaving a pale yellow amorphous solid: IR (KBr, cm^{-1}) 3500–3300 (s, b, O–H), 2900, 1770, 1695, 1540, 1400, 1260, 1130, 1065 (s, b, ClO$_4^-$), 938, 765, 713, 623 (s, ClO$_4^-$).

X-ray Crystal Structure of Ni(keto-10S3)$_2$(BF$_4$)$_2$. A maroon crystal of the complex, suitable for X-ray diffraction and having approximate dimensions 0.21 × 0.24 × 0.30 mm, was sealed in a glass capillary with epoxy cement and mounted on a Nicolet R3m/V auto diffractometer equipped with a scintillation counter, Mo Kα radiation (λ = 0.71073 Å), and a graphite monochromator. The automatic centering, indexing, and least-squares routines were carried out on 15 independent reflections in order to obtain the unit cell dimensions that are given in Table I. The crystal data were collected and reduced, the structure was solved by direct methods, and the refinement was carried out as described by us for other crystal structures.[27] The values for the *hkl* data were as follows: *h*, 0 to +9; *k*, −9 to +10; *l*, −10 to +11. Final atomic parameters for Ni-(keto-10S3)$_2$(BF$_4$)$_2$ with their standard deviations are listed in Table II. Bond lengths and bond angles are compiled in Table III.

X-ray Crystal Structure of Fe(10S3)$_2$(ClO$_4$)$_2$. A clear red crystal suitable for X-ray diffraction and having approximate dimensions 0.48 × 0.24 × 0.20 mm was mounted on a Syntex P2$_1$ auto diffractometer equipped with a scintillation counter, Mo Kα radiation (λ = 0.71073 Å), and a graphite monochromator. The automatic centering, indexing, and least-squares routines were carried out on 15 independent reflections in

Table I. Crystallographic Data and Details of Refinement for [Ni(keto-10S3)$_2$](BF$_4$)$_2$ (I) and for [Fe(10S3)$_2$](ClO$_4$)$_2$ (II)

	I	II
formula	C$_{14}$H$_{24}$B$_2$F$_8$NiO$_2$S$_6$	C$_{14}$H$_{28}$Cl$_2$FeO$_8$S$_6$
fw	841.4	643.26
color, habit	maroon prisms	red prisms
cryst size, mm	0.21 × 0.24 × 0.30	0.48 × 0.24 × 0.20
cryst syst	triclinic	monoclinic
space group	P$\bar{1}$	P2$_1$
a, Å	8.401 (4)	12.036 (4)
b, Å	10.039 (5)	11.824 (4)
c, Å	10.463 (4)	9.178 (2)
V, Å^3	751.8 (5)	1223.4 (6)
α, deg	65.97 (3)	90
β, deg	80.52 (3)	110.51 (2)
γ, deg	68.92 (2)	90
D(calcd), g cm^{-3}	1.858	1.747
Z	1	2
μ, cm^{-1}	1.13	1.37
no. of rflns measd	1973	4433
no. of unique rflns measd	1973	4285
no. of indep rflns with $I \geq 2.5\sigma(I)$	1635	3826
F(000)	876	664
R	0.083	0.035
R$_w$	0.113	0.034
no. of params refined	207	307
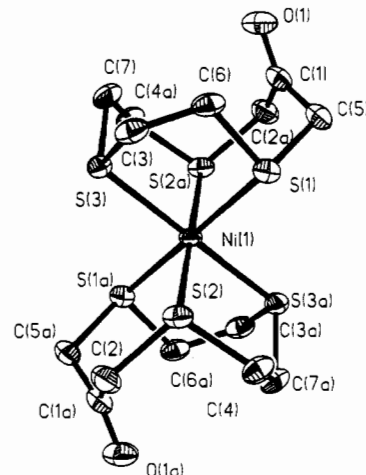
Figure 1. ORTEP perspective of [Ni(keto-10S3)$_2$](BF$_4$)$_2$.

the range of 15.63° < 2θ < 23.59° to obtain the unit cell dimensions that 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 $I \geq 2.5\sigma(I)$ were considered observed. No correction was made for absorption. The values for the *hkl* data were as follows: *h*, −14 to +13; *k*, −14 to +14; *l*, 0 to +10.

The structure was solved by the heavy-atom method. The position of the iron atom was located from a three-dimensional Patterson map, and the remaining atoms were located by subsequent structure factor calculations and difference electron density maps.[28] 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

$$R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.035$$

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.034$$

and

$$GoF = [\sum w(|F_o| - |F_c|)^2(\text{no. of rflns} - \text{no. of params})]^{1/2} = 1.753$$

The final atomic parameters for Fe(10S3)$_2$(ClO$_4$)$_2$ with their standard deviations are given in Table II. Selected bond distances and bond angles are given in Table III.

(27) Setzer, W. N.; Black, B. G.; Hubbard, J. L. *Phosphorus, Sulfur, Silicon Relat. Elem.*, in press.

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

Results and Discussion

Structural Studies. There are three possible stereoisomers for the facial octahedral coordination of 1,4,7-trithiacyclodecane and its derivatives, and these stereoisomers are illustrated as follows:

Δ Enantiomer   **Λ Enantiomer**
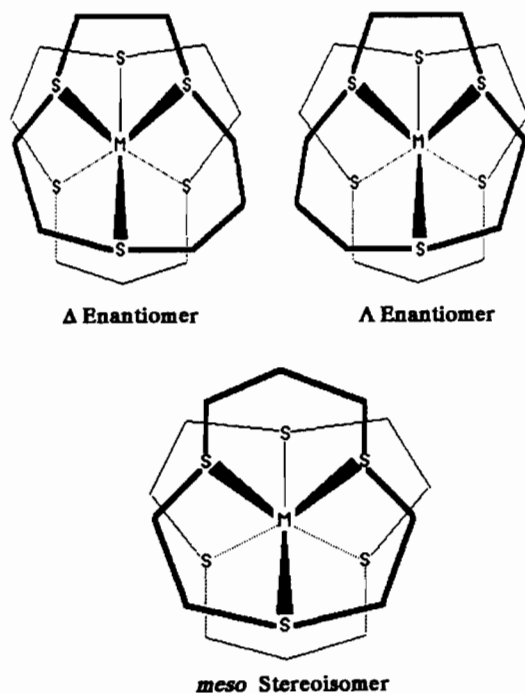
***meso* Stereoisomer**

The first two stereoisomers have an enantiomeric relationship, and the third stereoisomer is a meso compound. We have used the designations Δ and Λ 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 from an anti arrangement in the two trigonal faces whereas they have a gauche arrangement in the pair of enantiomers. Similar designations have been used previously in work on $(10N3)_2$ ($10N3 = 1,4,7$-triazacyclodecane) complexes of cobalt(III).[29] In the Δ case the two six-membered chelate rings form a right-handed helix. The bis octahedral complexes of the previously studied mesocyclic thioethers 9S3 and 12S3 (1,5,9-trithiacyclododecane) cannot exhibit this type of stereoisomerism due to their high symmetry.

X-ray Crystal Structure of [Ni(keto-10S3)₂](BF₄)₂. A side view of the structure of the molecule is shown in Figure 1. The complex involves a distorted octahedral environment of sulfur atoms about the nickel provided by the two facially coordinated tridentate keto-10S3 ligands. The nickel ion is located at a crystallographic inversion center (space group: triclinic, $P\bar{1}$). Thus, the two ligand molecules are bonded to give the meso stereoisomer in which the two ketone functionalities are anti with respect to each other rather than the d-l stereoisomers. The [2233] conformation is the one adopted by the complexed keto-10S3 ligand (see Figure 4). The disorder of the tetrafluoroborate anions and the fact that the crystal was mounted in a capillary account for the relatively high R value for this crystal structure.

The coordination sphere about the nickel center in [Ni(keto-10S3)₂](BF₄)₂ compares favorably with other octahedral nickel(II) thioether complexes, [Ni(9S3)₂](BF₄)₂[5] and Ni(1,5-DTCO)₂Cl₂ (1,5-DTCO = 1,5-dithiacyclooctane).[30] The complex contains both five-membered and six-membered chelate rings. The S–Ni–S bond angles for the five-membered rings average 88.3°, comparable to those for [Ni(9S3)₂](BF₄)₂ (88.5°), whereas the angle for the six-membered ring is significantly larger (96.9°), reflecting the larger "bite" of the 1,5-chelate compared to the 1,4-chelate. The Ni–S bond lengths also show differences. The Ni–S bond lengths for the six-membered chelate ring [i.e., Ni–S(1), Ni–S(2)]

(29) Searle, G. H.; Angley, M. E. *Inorg. Chim. Acta* **1981**, *49*, 185–192.
(30) Hill, N. L.; Hope, H. *Inorg. Chem.* **1974**, *13*, 2079–2081.

Table II. Atomic Positional Parameters (×10⁴ for Ni(II) Complex) for Non-Hydrogen Atoms with Esd's in Parentheses

[Ni(keto-10S3)₂](BF₄)₂ (I)

atom	x	y	z	10^3U, Å²
Ni	0	0	0	33 (1)
S(1)	−1386 (3)	1250 (3)	−2238 (2)	44 (1)
S(2)	−2840 (3)	1079 (3)	846 (3)	45 (1)
S(3)	−636 (3)	−2227 (3)	262 (3)	45 (1)
O(1)	1611 (6)	−837 (10)	−4030 (9)	71 (14)
C(7)	1164 (13)	−3199 (11)	−615 (11)	53 (4)
C(6)	−2017 (13)	−236 (12)	−2375 (12)	51 (5)
C(5)	190 (14)	1485 (12)	−3665 (10)	58 (5)
C(4)	−2865 (12)	3042 (11)	421 (12)	50 (4)
C(3)	−2325 (12)	−1389 (12)	−953 (11)	50 (5)
C(2)	−3189 (14)	302 (13)	2715 (10)	57 (5)
C(1)	1671 (14)	41 (13)	−3526 (10)	52 (4)
B(1)	−7293 (18)	3669 (15)	3225 (13)	60 (6)
F(1)	−6947 (14)	2348 (12)	4275 (11)	157 (5)
F(2)	−6595 (15)	3712 (12)	2069 (10)	138 (5)
F(3)	−8224 (20)	4906 (15)	3515 (17)	138 (7)
F(3A)	−6099 (42)	3972 (49)	3336 (48)	176 (10)
F(4)	−9044 (16)	3515 (17)	2859 (17)	180 (7)
B(2)	−6200 (13)	3771 (12)	7501 (11)	37 (4)
F(5)	−5786 (14)	2449 (13)	7593 (13)	136 (6)
F(6)	−7037 (26)	5053 (22)	6269 (19)	246 (5)
F(7)	−6151 (12)	4030 (11)	8512 (11)	118 (5)
F(8)	−4460 (44)	3864 (54)	6575 (44)	853 (1)

[Fe(10S3)₂](ClO₄)₂ (II)

atom	x	y	z	B,[a] Å²
Fe	0.21325 (5)	0.00000	0.03467 (7)	2.021 (23)
S(1)	0.22236 (11)	−0.02499 (12)	0.28253 (13)	2.72 (6)
C(2)	0.3546 (5)	−0.1104 (4)	0.3714 (6)	3.4 (3)
C(3)	0.4532 (4)	−0.0911 (4)	0.3107 (6)	3.36 (23)
S(4)	0.39299 (11)	−0.08329 (12)	0.09712 (15)	2.77 (6)
C(5)	0.5008 (4)	0.0080 (5)	0.0559 (6)	3.9 (3)
C(6)	0.5216 (5)	0.1238 (5)	0.1284 (7)	4.4 (3)
C(7)	0.4196 (5)	0.2072 (5)	0.0598 (7)	4.0 (3)
S(8)	0.284443 (11)	0.17788 (11)	0.10095 (15)	2.84 (6)
C(9)	0.3373 (5)	0.1829 (5)	0.3136 (6)	3.7 (3)
C(10)	0.2585 (5)	0.1141 (5)	0.3730 (6)	3.7 (3)
S(1′)	0.03078 (10)	0.07690 (12)	−0.02598 (15)	2.82 (5)
C(2′)	−0.0696 (4)	−0.0422 (5)	−0.0517 (7)	4.0 (3)
C(3′)	−0.0332 (4)	−0.1427 (4)	−0.1261 (6)	3.41 (23)
S(4′)	0.12368 (10)	−0.17222 (11)	−0.01672 (14)	2.45 (5)
C(5′)	0.1653 (5)	−0.2537 (5)	−0.1573 (6)	3.7 (3)
C(6′)	0.1503 (6)	−0.1967 (5)	−0.3089 (7)	4.7 (4)
C(7′)	0.2226 (6)	−0.0954 (6)	−0.3089 (7)	5.0 (3)
S(8′)	0.20629 (12)	0.03163 (12)	−0.20968 (15)	3.23 (6)
C(9′)	0.0525 (5)	0.0721 (6)	−0.3216 (7)	4.9 (3)
C(10′)	−0.0038 (5)	0.1355 (5)	−0.2209 (7)	4.2 (3)
Cl(1)	0.59573 (12)	0.06893 (13)	0.71029 (16)	3.88 (7)
O(1)	0.5992 (7)	−0.0460 (4)	0.7196 (7)	11.9 (6)
O(2)	0.4824 (5)	0.1061 (8)	0.6957 (7)	12.0 (5)
O(3)	0.6134 (5)	0.1075 (5)	0.5747 (6)	7.8 (3)
O(4)	0.6766 (4)	0.1171 (5)	0.8436 (5)	7.7 (3)
Cl(2)	0.16878 (14)	0.40307 (16)	0.65331 (17)	4.66 (7)
O(5)	0.0541 (5)	0.4178 (8)	0.6561 (7)	12.3 (6)
O(6)	0.2389 (7)	0.3457 (6)	0.7835 (8)	12.8 (5)
O(7)	0.2161 (6)	0.5090 (6)	0.6501 (7)	10.12 (4)
O(8)	0.1535 (6)	0.3478 (6)	0.5178 (7)	10.5 (4)

[a] B is the mean of the principal axes of the thermal ellipsoid.

average 2.423 Å, while the Ni–S(3) bond is 2.381 Å, comparable to those found in [Ni(9S3)₂](BF₄)₂ (Ni–S average = 2.386 Å). It is interesting to note that the Ni–S bond lengths in Ni(1,5-DTCO)₂Cl₂ average 2.49 Å.

X-ray Crystal Structure of [Fe(10S3)₂](ClO₄)₂. A view of the molecule projected down the pseudo-3-fold axis of the complex is shown in Figure 2, and a side view of the molecule is shown in Figure 3. As expected, the thioether ligand coordinates facially in tridentate fashion, and the complex involves a distorted octahedral environment of sulfur atoms about the iron. Two unusual results are found in the structure. Surprisingly, the crystal obtained is *not* the meso stereoisomer but rather the one of lower symmetry. Thus, the two six-membered chelate rings have a

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for Compounds I and II

[Ni(keto-10S3)$_2$](BF$_4$)$_2$ (1)

Bond Lengths

Ni–S(1)	2.422 (3)	S(1)–C(6)	1.814 (15)	O(1)–C(1)	1.215 (19)	Ni–S(3A)	2.381 (3)	S(3)–C(3)	1.790 (11)	C(2)–C(1A)	1.505 (18)
Ni–S(2)	2.424 (3)	S(1)–C(5)	1.824 (11)	C(7)–C(4A)	1.546 (18)	B(1)F(1)	1.324 (14)	B(1)–F(2)	1.348 (17)	C(1)–C(2A)	1.505 (18)
Ni–S(3)	2.381 (3)	S(2)–C(4)	1.828 (12)	C(6)–C(3)	1.519 (13)	B(1)–F(3)	1.302 (23)	B(1)–F(4)	1.413 (25)	B(2)–F(5)	1.212 (18)
Ni–S(1A)	2.422 (3)	S(2)–C(2)	1.804 (10)	C(5)–C(1)	1.504 (14)	B(2)–F(6)	1.452 (18)	B(2)–F(7)	1.198 (19)	B(2)–F(8)	1.626 (38)
Ni–S(2A)	2.424 (3)	S(3)–C(7)	1.815 (11)	C(4)–C(7A)	1.546 (18)	B(1)–F(3A)	1.425 (49)	F(2)–F(3A)	1.594 (59)	F(3)–F(3A)	1.7123 (69)

Bond Angles

S(1)–Ni–S(2)	83.1 (1)	S(1)–Ni–S(3)	87.1 (1)	S(2)–Ni–S(2)	90.6 (1)
S(1)–Ni–S(1A)	180.0 (0)	S(2)Ni–S(1A)	96.9 (1)	S(3)–Ni–S(1A)	92.9 (1)
S(1)–Ni–S(2A)	96.9 (1)	S(2)–Ni–S(2A)	180.0 (0)	S(3)Ni–S(2A)	89.4 (1)
S(1A)–Ni–S(2A)	83.1 (1)	S(1)–Ni–S(3A)	92.9 (1)	S(2)–Ni–S(3A)	89.4 (1)
S(3)–Ni–S(3A)	180.0 (0)	S(1A)–Ni–S(3A)	87.1 (1)	S(2A)–Ni–S(3A)	90.6 (1)
Ni–S(1)–C(6)	103.8 (3)	Ni–S(1)–C(5)	110.3 (4)	Ni–S(2)–S(4)	100.1 (3)
Ni–S(2)–C(2)	115.9 (3)	Ni–S(3)–C(7)	103.0 (4)	Ni–S(3)–C(3)	100.9 (4)
C(7)–S(3)–C(3)	103.4 (5)	C(4)–S(2)–C(2)	105.4 (6)	C(7)–S(3)–C(3)	103.4 (5)
S(3)–C(7)–C(4A)	113.1 (9)	S(1)–C(6)–C(3)	112.4 (9)	S(1)–C(5)–C(1)	114.2 (7)
S(2)–C(4)–C(7A)	115.8 (6)	S(3)–C(3)–C(6)	115.5 (8)	S(2)–C(2)–C(1A)	113.0 (8)
O(1)–C(1)–C(5)	120.2 (11)	O(1)–C(1)–C(2A)	121.5 (9)	C(5)–C(1)–C(2A)	118.2 (12)
F(1)–B(1)–F(2)	109.9 (11)	F(1)–B(1)–F(3)	117.0 (14)	F(7)–B(2)–F(8)	108.5 (23)
F(1)–B(1)–F(4)	103.7 (13)	F(1)–B(1)–F(3A)	84.6 (18)	F(2)–B(1)–F(3)	119.1 (13)
F(2)–B(1)–F(3A)	70.1 (22)	F(2)–B(1)–F(4)	101.2 (14)	F(3)–B(1)–F(3A)	77.6 (23)
F(3)–B(1)–F(4)	103.1 (14)	F(3A)–B(1)–F(4)	169.9 (21)	B(1)–F(2)–F(3A)	57.2 (16)
B(1)–F(3)–F(3A)	54.4 (21)	B(1)–F(3A)–F(2)	52.7 (20)	B(1)–F(3A)–F(3)	48.0 (14)
F(2)–F(3A)–F(3)	87.3 (22)	F(5)–B(2)–B(6)	121.4 (16)	F(5)–B(2)–F(7)	119.6 (10)
F(6)–B(2)–F(7)	118.1 (13)	F(5)–B(2)–F(8)	87.1 (21)	F(6)–B(2)–F(8)	84.2 (15)

[Fe(10S3)$_2$](ClO$_4$)$_2$ (II)

Bond Lengths

Fe–S(1)	2.2583 (14)	S(1)–C(2)	1.819 (5)	C(2)–C(3)	1.494 (8)	C(5')–C(6')	1.499 (8)	S(1')–C(2')	1.817 (6)	C(2')–C(3')	1.510 (8)
Fe–S(4)	2.2604 (15)	S(1)–C(10)	1.825 (5)	C(3)–S(4)	1.839 (5)	C(6')–C(7')	1.481 (9)	S(1')–C(10')	1.825 (6)	C(3')–S(4')	1.835 (5)
Fe–S(8)	2.2721 (15)	S(4)–C(5)	1.826 (5)	C(5)–C(6)	1.505 (9)	C(9')–C(10')	1.521 (9)	Cl(1)–O(2)	1.395 (5)	Cl(1)–O(3)	1.410 (5)
Fe–S(1')	2.2591 (15)	S(8)–C(9)	1.829 (5)	C(6)–C(7)	1.529 (8)	Cl(1)–O(4)	1.391 (5)	Cl(2)–O(5)	1.401 (6)	Cl(2)–O(7)	1.380 (6)
Fe–S(4')	2.2749 (14)	S(4')–C(5')	1.816 (5)	C(7)–S(8)	1.827 (5)	Cl(2)–O(8)	1.360 (6)	Cl(2)–O(6)	1.376 (6)	Cl(1)–O(1)	1.362 (5)
Fe–S(8')	2.2451 (15)	S(8')–C(9')	1.839 (6)	C(9)–C(10)	1.490 (8)			C(7')–S(8')	1.803 (6)		

Bond Angles

S(1)–Fe–S(4)	89.04 (5)	S(1)–Fe–S(8)	88.32 (5)	S(1)–Fe–S(1')	90.04 (5)
S(1)–Fe–S(4')	86.79 (5)	S(1)–Fe–S(8')	117.85 (5)	S(4)–Fe–S(8')	91.34 (6)
S(4)–Fe–S(4')	90.26 (5)	S(8)–Fe–(1')	172.30 (5)	S(4)–Fe–S(1')	177.81 (5)
S(1')–Fe–S(4')	87.71 (5)	S(4')–Fe–S(8')	95.33 (5)	S(1')–Fe–S(8')	89.65 (6)
S(8)–Fe–S(8')	89.53 (5)	S(8)–Fe–S(1')	86.34 (5)	S(4)–Fe–S(8)	95.61 (6)
Fe–S(1)–C(2)	104.50 (17)	Fe–S(1)–C(10)	105.07 (18)	C(2)–S(1)–C(10)	105.3 (3)
S(1)–C(2)–C(3)	115.6 (3)	S(1')–C(2')–C(3')	112.5 (4)	C(2')–C(3')–S(4')	108.0 (4)
Fe–S(4')–C(3')	105.36 (17)	Fe–S(4')–C(5')	113.18 (20)	C(3')–S(4')–C(5')	101.5 (3)
S(4')–C(5')–C(6')	116.6 (4)	C(2)–C(3)–S(4)	109.7 (3)	Fe–S(4)–C(3)	106.05 (17)
Fe–S(4)–C(5)	112.11 (19)	C(3)–S(4)–C(5)	101.98 (25)	S(4)–C(5)–C(6)	117.8 (4)
C(5)–C(6)–C(7)	114.8 (5)	C(5')–C(6')–C(7')	118.9 (5)	C(6')–C(7')–S(8')	120.4 (4)
Fe–S(8')–C(7')	113.17 (19)	Fe–S(8')–C(9')	106.25 (20)	C(7')–S(8')–C(9')	101.6 (3)
S(8')–C(9')–C(10')	1121.3 (4)	S(1')–C(10')–C(9')	114.3 (4)	C(6)–C(7)–S(8)	1165.9 (4)
Fe–S(8)–C(7)	113.56 (19)	Fe–S(8)–C(9)	105.85 (18)	C(7)–S(8)–C(9)	102.2 (3)
S(8)–C(9)–C(10)	110.2 (3)	S(1)–C(10)–C(9)	1134.0 (4)	Fe–S(1')–C(2')	105.36 (17)
Fe–S(1)–C(10')	105.21 (20)	C(2')–S(1')–C(10')	104.7 (3)	O(1)–Cl(1)–O(2)	109.1 (5)
O(1)–Cl–O(3)	111.5 (4)	O(1)–Cl–O(4)	110.9 (4)	O(2)–Cl(1)–O(3)	105.0 (4)
O(2)–Cl–O(4)	108.4 (4)	O(3)–Cl(1)–O(4)	111.6 (4)	O(5)–Cl(2)–O(6)	110.7 (5)
O(5)–Cl(2)–O(7)	107.7 (5)	O(5)–Cl(2)–O(8)	105.0 (4)	O(6)–Cl(2)–O(7)	109.5 (4)
O(6)–Cl(2)–O(8)	113.7 (4)	O(7)–Cl(2)–O(8)	109.9 (4)		

gauche relationship rather than a anti relationship as was obtained for the [Ni(keto-10S3)$_2$](BF$_4$)$_2$ complex. The two six-membered chelate rings adopt a Δ configurational relationship in our crystal structure, and the conformation adopted by the ten-membered-ring ligand in this iron(II) complex is the [2323] conformation (see Figure 4).

This gauche relationship is unusual. For example, the bis Ni(II) complex of the analogous ten-membered-ring triamine ligand, [Ni(10N3)$_2$]$^{2+}$, crystallizes as the meso stereoisomer.[31] Equilibration studies on the [Co^{III}(10N3)$_2$]$^{3+}$ system show a ratio of 96% anti/4% gauche distribution of stereoisomers in solution.[32]

Even more surprising than the stereoisomer result is the fact that the complex does not crystallize as the anticipated racemic mixture of a d-l pair but instead crystallizes with two identical enantiomers per unit cell. That is, the crystal itself is optically active (space group P2$_1$). The R_F and R_W values that were

calculated for the opposite enantiomer were 0.0362 and 0.0351, respectively. The R_F and R_W values in the reported structure were 0.0347 and 0.0336, respectively.

This observation represents a highly unusual case of the formation of a conglomerate due to a spontaneous resolution of two enantiomers. In their monograph Jacques, Collet, and Wilen define a conglomerate as "a mechanical mixture of crystals of the two pure enantiomers" that is "formed as a result of a spontaneous resolution."[33] At the time of publication of their monograph (1981), they had located in the chemical literature 248 examples of compounds that formed conglomerates.[34] Of these only about a dozen were either coordination or organometallic complexes. We have located several more recent examples of spontaneous resolution of conglomerates, but to the best of our knowledge, the number of Werner-type complexes that exhibit this phenomena remains under 25.[35] Bernal has published an elegant series of

(31) Zompa, L. J.; Margulis, T. N. *Inorg. Chim. Acta* **1980**, *45*, L263–L264.
(32) Angley, M. E.; Dwyer, M.; Lincoln, S. F.; Searle, G. H.; Geue, R. J.; Keene, F. R. *Inorg. Chim. Acta* **1980**, *45*, L91–L93.

(33) Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates, and Resolutions*: John Wiley and Sons, Inc.: New York, 1981; p 4.
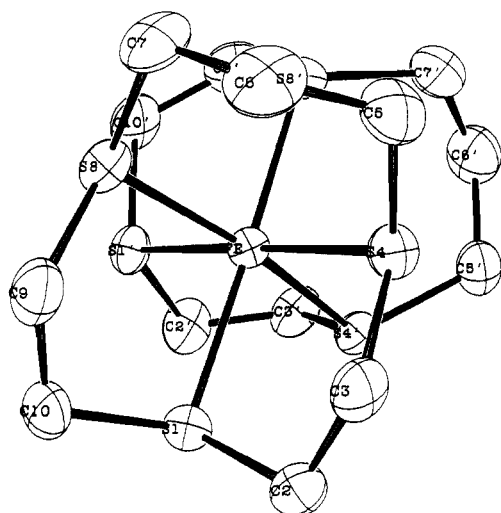(34) Reference 33, p 79 and references cited therein.

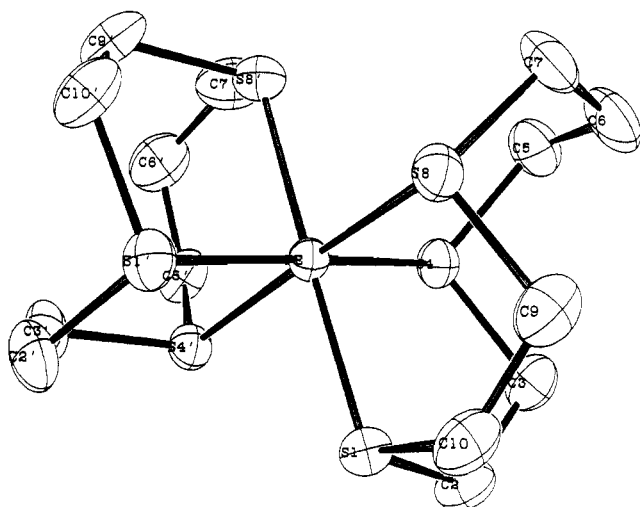**Figure 2.** ORTEP perspective of [Fe(10S3)$_2$](ClO$_4$)$_2$ viewed down the pseudo-3-fold axis of the molecule.

Figure 3. ORTEP perspective of [Fe(10S3)$_2$](ClO$_4$)$_2$.

papers examining the causes of conglomerate formation in complexes such as [Co(en)$_2$(NO$_2$)$_2$]$^+$.[36] He attributed the spontaneous resolution of these types of complexes to hydrogen bonding between oxygen atoms on the nitro groups and amino hydrogens on the amine ligands. However, the inability of thioether ligands to form hydrogen bonds suggests that a different mechanism must be operating in these complexes. Our crystal structure represents a rare case of an iron complex that forms conglomerates. In addition, this appears to be the first example of an optically active hexakis(thioether) complex.

(35) Multiple listings of these complexes are found in the following references: Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates, and Resolutions*; John Wiley and Sons, Inc.: New York, 1981; p 79. Bernal, I. *Inorg. Chim. Acta* **1988**, *142*, 21–22. Bernal, I.; Kaufmann, G. B. *J. Chem. Educ.* **1987**, *64*, p 608. In addition, single listings can be found in the following references: Dubicki, L.; Ferguson, J.; Geue, R. J.; Sargenson, A. M. *Chem. Phys. Lett.* **1980**, *74*, 393. Blank, L. F.; Huxtable, C.; O'Brien, P. *Inorg. Chim. Acta* **1982**, *65*, L159. Kojima, M.; Ishii, T. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 1095–1098. Bernal, I. *Inorg. Chim. Acta* **1985**, *96*, 99–110. Okamoto, K.; Konno, J.; Nomoto, M.; Einaga, H.; Hidaka, J. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1494–1498. We do not mean to suggest that these references are a complete listing of all coordination complexes that form conglomerates by spontaneous resolution. As noted by Jacques, Collet, and Wilen in ref 34, p 80, "The retrieval of new instances—or even of old cases—of spontaneous resolutions described in the literature, that is, conglomerates, is a hit-or-miss proposition. Such behavior is often described only in the experimental sections of articles, sometimes incidentally or imprecisely."

(36) Bernal, I.; Cetrullo, J. *Inorg. Chim. Acta* **1988**, *144*, 227–232 and references cited therein.

complex	λ, mm (ε, L mol^{-1} cm^{-1})	μ_{eff}, μ_B
[Ni(10S3)$_2$]$^{2+}$	807 (33), 544 (54)	3.00
[Ni(keto-10S3)$_2$]$^{2+}$	833 (11), 541 (16)	3.07
[Ni(hydroxy-10S3)$_2$]$^{2+}$	877 (30), 562 (30)	3.12
[Co(10S3)$_2$]$^{2+}$	510 (sh, 370), 290 (11 800)	1.78
[Co(keto-10S3)$_2$]$^{2+}$	470 (sh, 64)	1.82
[Co(hydroxy-10S3)$_2$]$^{2+}$	487 (319), 447 (392)	1.78
[Fe(10S3)$_2$]$^{2+}$	540 (78), 395 (103)	diamagnetic
[Fe(keto-10S3)$_2$]$^{2+}$	542 (67)	diamagnetic
[Fe(hydroxy-10S3)$_2$]$^{2+}$	520 (131), 458 (171)	diamagnetic

^{a} Measured in nitromethane or aqueous solution. ^{b} 298 K.

The structural features of the complex seem to be regular and comparable to the analogous [Fe(9S3)$_2$](PF$_6$)$_2$[9] and [Ni(keto-10S3)$_2$](BF$_4$)$_2$ (vide supra). There is an interesting bond length difference in the Fe(II) structure, however. One of the Fe–S bonds for each of the two six-membered chelate rings is long (i.e., Fe–S(8) and Fe–S(4') average 2.274 Å), while the other four Fe–S bonds are comparable in length (range 2.246–2.261 Å). Note, then, that the coordination sphere about the Fe(II) center exhibits tetragonal distortion about the Fe(II) center involving *lengthening* of the two trans Fe–S bonds whereas the coordination sphere about the Ni(II) center show the tetragonal distortion with a *shortening* of the two trans Ni–S bonds relative to the other four bonds.

Conformational Analysis. There are four conformational possibilities for the tridentate facial coordination of 1,4,7-trithiacyclodecane and its derivatives. They are [2323], [2233], [1333], and [1324]. The fifth conformational possibility, the [1414] case, cannot complex in a tridentate facial fashion. Note that in order to achieve tridentate facial coordination the sulfur atoms of these ten-membered-ring trithioethers must all be endodentate, limiting the number of conformations available (see Figure 4).

The conformation adopted by the 1,4,7-trithiacyclodecane ligand in [Fe(10S3)$_2$](ClO$_4$)$_2$ is the [2323] or boat–chair–boat conformation. In contrast, the conformation adopted by the 1,4,7-trithiacyclodecan-9-one ligand in [Ni(keto-10S3)$_2$](BF$_4$)$_2$ is the [2233] conformation. A consequence of both of these conformations is that the six-membered chelate ring is a chair. Curiously, the conformation adopted by 10S3 in [(10S3)(CO)$_3$Mo^0] is the [1333] conformation.[37] This conformation of the ten-membered-ring ligand results in a boat conformation of the six-membered chelate ring. Note that complexation of 10S3 or a derivative thereof involving a [1234] conformation would also result in a boat conformation of the six-membered chelate ring.

The [2323] conformation is the preferred conformation for cyclodecane and is found in a number of its derivatives including 1,6-dithiacyclodecane and 1,2,6,7-tetrathiacyclodecane.[38] One would expect the [2323] conformation to be preferred in this heterocycle as well.

In order to provide some conformational insight into these ten-membered-ring trithioethers, we have carried out a molecular mechanics conformational analysis of 1,4,7-trithiacyclodecane using MM2.[39] The results of these calculations are summarized in Figure 4. Interestingly, the most stable conformation according to the MM2 calculations is a [1333] conformation and not a [2323] conformation.

Neither of the low-energy conformations of 1,4,7-trithiacyclodecane are suitable for complexation of metal ions in tridentate fashion. Facial tridentate complexation requires a conformation

(37) Grant, G. J.; Carpenter, J. P.; Setzer, W. N.; VanDerveer, D. V. *Inorg. Chem.* **1989**, *28*, 4128–4132.

(38) For a discussion of the conformations of medium-sized sulfur-containing heterocycles, see: Setzer, W. N.; Glass, R. S. In *Conformational Analysis of Medium-Sized Heterocycles*; Glass, R. S., Ed.; VCH: Deerfield Beach, FL, 1988; Chapter 4.

(39) We used the program Chem Cad, suitable for IBM PC, available from C Graph Software, Inc., Austin, TX.
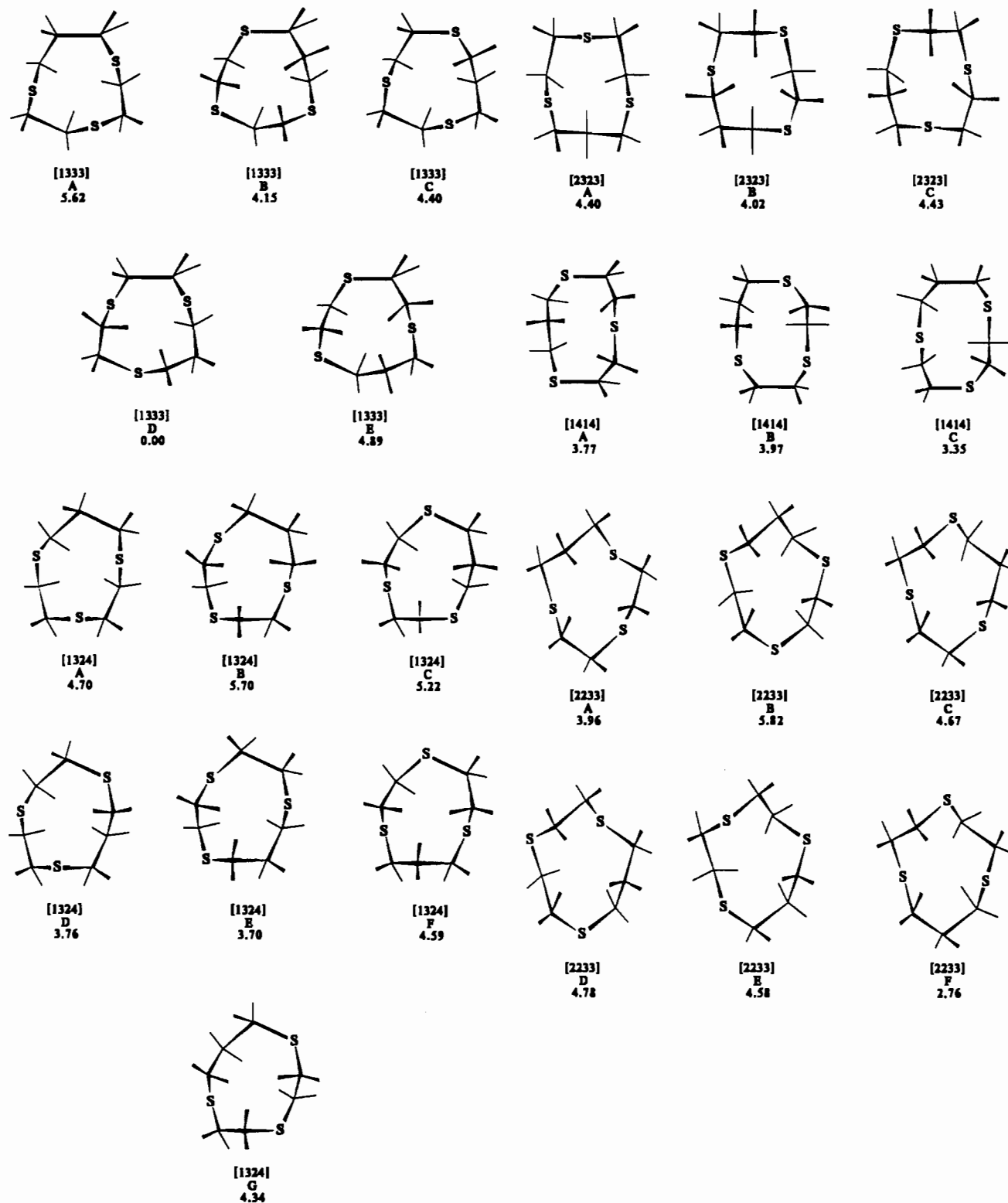
Figure 4. Conformations of 10S3.

in which all of the sulfur atoms are syn endodentate. The conformations that meet this requirement, [2323] A, [2233] A, [1333] A, and [1324] A, are all relatively high in energy (>4 kcal/mol higher in energy than [1333] D).[40] Apparently, a conformational change must take place in these ligands in order for tridentate complexation to occur. Although studies of the conformational

effects of crown thioethers have been published, the principal focus of previous research has been on crown thioethers that exclusively contain ethyl bridges between the sulfur atoms (18S6, 15S5, 12S4, 9S3).[23,41] Our work extends the conformational analysis of this class of ligands to include crown thioethers that contain propyl bridges between sulfur atoms and other functional groups as well.

Electronic Spectroscopy. Ni(II) Complexes. An octahedral complex of Ni(II) would be expected to exhibit three spin-allowed

(40) It is not certain at this point what is the preferred conformation of any of these ligands. 1,4,7-Trithiacyclodecane is a viscous liquid at room temperature. Both keto-10S3 and hydroxy-10S3 are crystalline solids, but we have thus far been unsuccessful in growing X-ray-quality crystals of these materials.

(41) Wolf, R. E.; Hartman, J. R.; Storey, J. M. E.; Foxman, B. M.; Cooper, S. R. *J. Am. Chem. Soc.* **1987**, *109*, 4328–4335.

Table V. Ligand Field Parameters for Octahedral Bis(tridentate thioether)nickel(II) Complexes

Ni(II) complex[a]	10Dq, cm^{-1}	f[b]	β[c]	ref
[Ni(10S3)$_2$]$^{2+}$	1239	1.42	0.63	d
[Ni(keto-10S3)$_2$]$^{2+}$	1200	1.38	0.73	d
[Ni(hydroxy-10S3)$_2$]$^{2+}$	1140	1.31	0.75	d
[Ni(9S3)$_2$]$^{2+}$	1271	1.46	0.64	5, 9
[Ni(ttn)$_2$]$^{2+}$	1134	1.30	0.79	e, 4
[Ni(12S3)$_2$]$^{2+}$	1120	1.29	0.75	4, 26

[a] Abbreviations: ttn = 2,5,8-trithianonane; 9S3 = 1,4,7-trithiacyclononane; 12S3 = 1,5,9-trithiacyclododecane. [b] Jørgensen, C. K. *Oxidation Numbers and Oxidation States* Springer: New York, 1969; pp 84–85. [c] Ratio of B(complex)/B(free ion), where B(free ion) for Ni(II) = 1041 cm^{-1}. [d] This work. [e] Unpublished results from our laboratories.

d–d transitions corresponding to the transitions $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$. However, the last of these transitions is usually obscured in thioether complexes due to an intense sulfur–metal charge-transfer band. The electronic spectra for the three nickel(II) complexes are presented in Table IV. Note that the two low-energy d–d transitions are observed for all three complexes. Ligand field parameters have been calculated for the nickel(II) complexes, and these are shown in Table V. Since the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition is obscured, the value of B, the interelectronic repulsion parameter, is calculated by using the following equation:

$$B = \frac{2\nu_1{}^2 + \nu_2{}^2 - 3\nu_1\nu_2}{15\nu_2 - 27\nu_1}$$

The three ten-membered-ring systems have Dq values that fall between the nine-membered-ring system 9S3 and the two weaker field thioether ligands ttn (2,5,8-trithianonane) and 12S3 (1,5,9-trithiacyclododecane).[6] This ordering of the ligand field strengths for the various thioether ligands underscores the importance of the preferred conformation of the ligand and the effects that these conformational constraints have on the complexation properties of the ligand. The three ten-membered-ring systems presented in our work form an important series of ligands that are intermediate cases between the previously studied nine-membered- and twelve-membered-ring systems.[5,6,26] It is important to note that although the 9S3 ligand adopts an endodentate conformation, the 12S3 ligand adopts an exodentate conformation.[42] This conformational change has a critical effect upon the complexation characteristics of the two ligands.

The nephelauxetic ratio (β = B(complex)/B(free ion)) for all three of the novel ligands is approximately 0.7, which is in agreement with previously studied cases of Ni(II)–thioether complexes.[6] In contrast, this ratio in amine complexes of Ni(II) is around 0.9.[6] A high degree of covalency between metal and thioether ligand orbitals is indicated by this relatively low value.

The replacement of the ethyl bridges in the mesocyclic thioether 9S3 with propyl bridges in 12S3 greatly reduces the ligand field strength of the latter.[6] There is a corresponding increase of about 0.04 Å in the Ni–S bond distances with an average Ni–S bond length of 2.386 Å for [Ni(9S3)$_2$]$^{2+}$ and 2.422 Å for [Ni(12S3)$_2$]$^{2+}$.[5,6] On the basis of its intermediate Dq value, one would anticipate a Ni–S bond length for a ten-membered-ring thioether to lie between the values of the 9S3 and 12S3 complexes. This is, in fact, observed with an average Ni–S bond length of 2.409 Å in the complex [Ni[(keto-10S3)$_2$]$^{2+}$. The effect of the compression of the metal–sulfur bonds on the electronic properties of the complex is underscored by this correlation between bond length and field strength. The Dq values of all three ten-membered crown thioethers fall intermediate between those of the ethyl-bridged and propyl-bridged crown thioethers, and the Ni–S bond lengths in the complexes should show a commensurate relationship. Our observations support and extend the conclusions regarding ring size effects and the compression of metal ions by crown ligands

Table VI. Ligand Field Parameters for Selected Octahedral Low-Spin Iron(II) Complexes

Fe(II) complex[a]	10Dq, cm^{-1} [45]	f[b]	B, cm^{-1} [45]	β[c]	ref
[Fe(10S3)$_2$]$^{2+}$	1943	1.94	490	0.46	d
[Fe(hydroxy-10S3)$_2$]$^{2+}$	1979	1.98	170	0.16	d
[Fe(9S3)$_2$]$^{2+}$	2005	2.00	437	0.41	9
[Fe(9S3)(9S3(O))]$^{2+}$	2244	2.24	357	0.34	10
[Fe(ttn)$_2$]$^{2+}$	1808	1.81	443	0.42	e
[Fe(9N3)$_2$]$^{2+}$	1894	1.89	575	0.54	9
[Fe(phen)$_3$]$^{2+}$	1310	1.31	602	0.57	f
[Fe(CN)$_6$]$^{4-}$	3220	3.22	490	0.46	f
[Fe(OCN)$_6$]$^{4-}$	2770	2.77	410	0.39	f

[a] Abbreviations: 9S3(O) = 1,4,7-trithiacyclononane-1-oxide; ttn = 2,5,8-trithianonane; 9N3 = 1,4,7-triazacyclononane; phen = 1,10-phenanthroline; CN$^-$ = cyano; OCN$^-$ = cyanato. [b] Figgis, B. N. *Introduction to Ligand Fields*; Interscience Publishers: New York, 1966; p 244. g value for Fe(II) = 10.0. [c] Ratio of B(complex)/B(free ion), where B(free ion) for Fe(II) = 1058 cm^{-1}. [d] This work. [e] Unpublished results from our laboratories. [f] Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1968; p 302.

noted by previous researchers.[6,43,44]

Fe(II) Complexes. An octahedral complex of Fe(II) would be expected to exhibit two spin-allowed d–d transitions corresponding to the transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$. Both transitions are observed in the 10S3 and hydroxy-10S3 complexes, but the high-energy transition is obscured in the case of the keto-10S3 complex. The electronic spectra for the iron(II) complexes are presented in Table IV. Ligand field parameters have been calculated for the iron(II) complexes, and these are shown in Table VI. The first five complexes listed in Table VI have FeS6 coordination spheres. A BASIC computer program was used to obtain the values of Dq and B from the energies of the two observed transitions.[45] The following two equations were used in the calculation of the ligand field parameters:

$$E[^1A_{1g} \rightarrow {}^1T_{1g}] = 10Dq - C + 86B^2/10Dq$$

$$E[^1A_{1g} \rightarrow {}^1T_{2g}] = 10Dq + 16B - C + 2B^2/10Dq$$

Since only two spin-allowed transitions were observed, the assumption that C = 4B was made for the calculation. The $^1A_{1g} \rightarrow {}^1T_{2g}$ transition for the keto-10S3 complex was obscured by an intense charge-transfer transition, making the calculation of ligand field parameters for the complex impossible. However, the proximity of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition for both the 10S3 and keto-10S3 iron(II) complexes (near 540 nm) indicates that the two ligands are generating approximately the same ligand field. As was true for the Ni(II) complexes, the Dq values for the ten-membered-ring systems lie intermediate between those of the thioether ligands 9S3 and ttn. The nephelauxetic ratio is again depressed relative to the amine ligands 9N3 (1,4,7-triazacyclononane) and phen, indicating a relatively large degree of metal–ligand orbital mixing for the thioether ligands. The thioether ligands have an average value of β near 0.4. Note that this high degree of covalency is also true for the cyano and the cyanato complexes as well as for the thioether ones. The small β value for the hydroxy-10S3 complex is due to the relatively high wavelength of absorbance for the second transition. The values of the extinction coefficients for the two transitions in [Fe(10S3)$_2$]$^{2+}$ are rougly double those values obtained for the [Fe(9S3)$_2$]$^{2+}$ complex.[9] The increase is due to the reduction of symmetry from the approximately octahedral FeS6 coordination sphere in the 9S3 complex to the less symmetrical one in the 10S3 complex.. The Dq values for the Fe(II) complexes are larger than

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those of the Ni(II) complexes with identical ligands, and this observation has been noted by Figgis in the spectra of other complexes containing the two divalent transition-metal ions.[46] As previously noted for the Ni(II) complexes, one would predict on the basis of the Dq values that the Fe–S bond lengths in the 10S3 complex would be elongated relative to the Fe–S bond lengths in the 9S3 complex, and this elongation is again observed (average Fe–S = 2.250 Å for $[Fe(9S3)_2]^{2+}$ and 2.262 Å for $[Fe(10S3)_2]^{2+}$).[9]

Other Complexes. The spectra of the Co(II) complexes for the three ligands are presented in Table IV. Ligand field assignments for one thioether–Co(II) complex on the basis of a high-spin complex have been attempted,[9] but the complex proved to be low-spin.[7] The presence of charge-transfer transitions in the spectrum, poorly resolved absorbance shoulders, and the splitting of low-spin d^7 complexes by Jahn–Teller distortions make the band assignments in Co(II)–thioether complexes difficult.[47] The copper(II) complexes of most thioether ligands show intense charge-transfer transitions in the visible region, which accounts for their characteristic brown color in solution or in the solid state.[44] The reported absorption spectra of the copper(II) and cobalt(II) complexes are similar to those spectra previously obtained for the $(9S3)_2$ complexes of copper(II) and cobalt(II).[5] An analysis of the bis complexes of 9S3 with Co(II) and Cu(II) based upon the angular-overlap model has appeared recently in the literature.[48]

Other Properties. The values for the magnetic moments for the three nickel(II) complexes are typical for complexes with two unpaired electrons. As expected, all three of the cobalt(II) complexes are low-spin. This is in agreement with observations on virtually every other hexakis(thioether)cobalt(II) complex, which are all invariably low-spin.[4,7,9] Surprisingly, these are among the few low-spin cobalt(II) complexes known. All three iron(II) complexes are low-spin and diamagnetic, as is the case for previously reported hexakis(thioether) complexes of iron(II).[9,10] The solution conductivity measurements of the 10S3 complexes of Ni(II) and Co(II) demonstrate that these complexes do indeed form 2:1 electrolytes in nitromethane and water, respectively. Although stability constants have not yet been quantitatively determined for the complexes, a high stability for the Fe(II) complexes and a low stability for the Co(II) complexes with respect to hydrolysis have been observed. This is in contrast to the typical Irving–Williams stability series.[49] We attribute the high stability of the Fe(II) complexes to the iron ion's low-spin d^6 configuration, and we suggest that the instability of the copper(II) complexes is due to the facial steric requirements for coordination of these ligands and the preferred meridional coordination for copper(II). Similar observations have been noted by Zompa, who measured

the equilibrium constants for the formation of the $(10N3)_2$ complex of copper(II).[50] In the reaction between $Fe(ClO_4)_3$ and keto-10S3, the thioether ligand has apparently reduced the Fe(III) to Fe(II), since the visible absorption spectrum of the product is similar to the (keto-10S3)$_2$ complex of Fe(II). Identical observations were obtained by Wieghardt et al. for the reaction between $Fe(ClO_4)_3$ and 9S3.[9]

Conclusions

The three ten-membered crown trithioethers discussed in this work represent a very important extension of the coordination chemistry of thioether ligands. These ligands contain both ethyl bridges and propyl bridges between sulfur atoms and thus serve to supplement previous work done on exclusively ethyl- or propyl-bridged ligand systems. In terms of their ligand field strengths and metal–sulfur bond distances, they function as intermediate cases between the previously studied nine-membered- and twelve-membered-ring trithioether systems. The importance of conformational factors and the influence of additional functional groups are critical factors in determining the complexation behavior of this class of ligands. In addition, the lower symmetry of these ten-membered-ring ligands offers novel stereochemical possibilities that are not present in their more symmetrical analogues. This distinction is realized with the spontaneous resolution of $[Fe(10S3)_2]^{2+}$ into conglomerates—the first example of an optically active hexakis(thioether) complex.

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