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Complexation and conformational analysis studies of 11-membered ring crown trithioethers

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Abstract

We wish to report the synthesis of a series of transition metal complexes with two isomeric 11-membered ring trithioethers, 1,4,7-trithiacycloundecane (11S3-147) and 1,4,8-trithiacycloundecane (11S3-148). With respect to Ni(II), Fe(II), Co(II), Co(III), and Ru(II), the two function as relatively strong field ligands, but their ligand field strengths fall between the stronger field and smaller ring trithioether ligands such as 1,4,7-trithiacyclononane(9S3) and the larger ring and weaker field ligand, 1,5,9-trithiacyclododecane(12S3). Complexes of both ligands with first row transition metals are much more sensitive to solvolysis reactions than the analogous 9S3 complexes. ¹³C NMR spectroscopy shows that there is little stereoisomer selectivity between the *cis* and *trans* diastereoisomers for the bis complexes of 11S3-147. The complex [Pd(11S3-147)₂]²⁺ does not display the unusual spectroscopic and electrochemical properties observed in smaller ring Pd(II) complexes. Its absorption spectrum does not show any d–d transitions and an irreversible ligand-centered oxidation is observed. A conformational analysis study for both macrocycles showed that neither has a lowest energy conformation suitable for tridentate coordination. The effects of the lack of pre-organization dominate the complexation behavior of the two macrocyclic ligands. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Transition metal complexes; Macrocyclic complexes; Trithioether complexes; Conformational analysis

1. Introduction

The coordination chemistry of crown thioethers has received a great deal of attention during the past few years [1–4], and much of this focus has centered on the nine-membered ring trithioether 1,4,7-trithiacyclononane (9S3) because of the many unusual properties displayed in its complexes. The surprising behavior of transition metal complexes of 9S3 is due to the ligand's unique all *endodentate* conformation of the three sulfur atoms. This effect highlights the importance of pre-organization in determining the complexation mode of 9S3 and other macrocyclic thioether ligands [5] (for a discussion of the conformations of medium-sized sulfur-containing heterocycles see Ref. [6]). Other re-

search groups including ours have examined the coordination chemistry of the ten-membered ring trithioether, 1,4,7-trithiacyclononane (10S3) [7–10], and the 12-membered ring trithioether, 1,5,9-trithiacyclododecane (12S3) [11,12]. An elegant catalytic synthesis of 12S3 has recently been reported by Adams [13]. However, 11-membered ring trithioethers have received scant attention to date. This observation is true for other 11-membered ring macrocycles and is not limited to crown thioethers. The benzene-fused trithioether, 2,5,8-trithia-[9]-*o*-benzenophane, forms an 11-membered ring upon complexation, and there have been several publications examining the coordination chemistry of this and related ligands, principally by the Loeb group [14,15]. There have also been a few reports examining the complexes formed by the related 11-membered ring triaza macrocycle, 1,4,8-triazacycloundecane [16].

For several years, our group has been interested in studying the effects structural alterations on mesocyclic

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or medium-sized ring trithioether ligands have on the ease of complex formation, complex stability, and complex structure. In the initial stages of the examination of the coordination chemistry of 10S3 we undertook a conformational analysis of this ligand [7a]. Several years ago we reported the synthesis for two structural isomers which are 11-membered ring trithioethers, 1,4,7-trithiacycloundecane (11S3-147) and 1,4,8-trithiacycloundecane (11S3-148) (see structures below) [17]. Upon coordination via all three-sulfur donors, the macrocycle 11S3-147 will form one seven-membered and two five-membered chelate rings while 11S3-148 forms one five-membered and two six-membered chelate rings. We subsequently synthesized highly functionalized 11-membered ring systems, which have high water solubility — an important property for biological and industrial applications [18]. Also, a report of the Ag(I) complex of an 11-membered ring bearing a ketone functionality has appeared in the literature [19]. In this account, we explore the coordination chemistry of both 11S3 macrocycles with a wide variety of transition metal ions, and examine the conformational preferences of the two systems. This study completes a research into the complexation behavior of a series of crown trithioethers ranging from nine- to 12-membered rings.

2. Experimental section

2.1. Materials

The isomeric 11S3 trithioethers were prepared by the published procedures [17]. All transition metal reagent salts were used as received without additional purification. Nitromethane and acetic anhydride were dried using common methods [20].

2.2. Measurements

Analyses were performed by Atlantic Microlab, Inc., of Atlanta, GA. Fourier transform infrared spectra were obtained using a Beckman FT 1100 infrared spectrophotometer. Solution UV–Vis spectra were obtained on a Varian DMS 200 UV–Vis spectrophotometer. Magnetic susceptibility measurements on solid samples were obtained using a Johnson-Matthey magnetic susceptibility balance at ambient temperatures, and standard diamagnetic correction factors were employed. Proton and ^{13}C NMR spectra were obtained on a Varian Gemini 300 MHz NMR spectrometer using CD_3NO_2 for both the deuterium lock and reference. The electrochemistry of $[\text{Pd}(11\text{S3-147})_2](\text{PF}_6)_2$ was studied using a Princeton Applied Research Versastat Polarographic Analyzer with sample concentrations of 2 mM in CH_3NO_2 and a scan rate of 100 mV s^{-1} . The supporting electrolyte was 0.1 M Bu_4NBF_4 , and the

ferrocene/ferrocenium couple was used as an internal reference. The standard three-electrode configuration was as follows: Pt working electrode, Pt-wire auxiliary electrode, and Ag/AgCl reference electrode.

2.3. Preparation of metal complexes of 1,4,7-trithiacycloundecane (11S3-1,4,7)

2.3.1. Preparation of $[\text{Ni}(11\text{S3})_2](\text{BF}_4)_2$

A mass of 1,4,7-trithiacycloundecane (11S3-247) (100 mg, 0.480 mmol) was dissolved in 5 ml of anhydrous nitromethane. To this solution a green solution of $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.082 g, 0.240 mmol) in 5 ml of nitromethane with acetic anhydride (147 mg, 1.44 mmol, 0.136 ml) was added. A purple color immediately appeared. Addition of 5 ml of diethyl ether to the ice cold stirred solution precipitated the complex as purple crystals. The crystals were collected by vacuum filtration under nitrogen and washed with ethyl ether ($2 \times 10 \text{ ml}$) giving a 78% yield (122 mg) of $[\text{Ni}(11\text{S3})_2](\text{BF}_4)_2$. The complex is stable in solution or under nitrogen, but the solid readily hydrolyzes upon contact with moist air. FT-IR (KBr, cm^{-1}) 2993, 2948, 1446, 1412, 1150–1036 (s, BF_4^-), 932, 913, 845, 792, 520. The electronic absorption spectrum measured in nitromethane showed two λ_{max} values at 866 nm ($\epsilon = 33$) and 564 nm ($\epsilon = 38$). The effective magnetic moment of the solid (μ_{eff}) was measured as 3.22 BM. *Anal.* Found: C, 29.75; H, 4.75; S, 29.87. Calc. for $\text{C}_{16}\text{H}_{32}\text{S}_6\text{B}_2\text{F}_8\text{Ni}$: C, 29.61; H, 4.97; S, 29.63%.

2.3.2. Preparation of $[\text{Ru}(11\text{S3})_2](\text{PF}_6)_2$

A mixture of $[\text{Ru}(\text{DMSO})_4]\text{Cl}_2$ (100 mg, 0.206 mmol) and 1,4,7-trithiacycloundecane (11S3-147) (89 mg, 0.412 mmol) was refluxed in 10 ml of methanol under nitrogen for 1.5 h. The color of the solution changed from an orange to a golden yellow, and a yellow precipitate, presumably the chloride salt was formed. A volume of 10 ml of water was added, and the solution was reheated to redissolve the solid. The hot solution was filtered and concentrated to one-half of its original volume. Next, a mass of NH_4PF_6 (155 mg, 0.960 mmol) was added, and a yellow precipitate immediately formed. After cooling, the solution was filtered, and the product was recrystallized from nitromethane–ether to yield 62 mg (37%) of $[\text{Ru}(11\text{S3})_2](\text{PF}_6)_2$ as yellow crystals. IR (KBr, cm^{-1}) 2999, 2933, 2860, 1450, 1420, 1315, 1244, 1178, 1032, 845(s, PF_6^-), 557. *Anal.* Found: C, 23.89; H, 3.99; S, 23.73. Calc. for $\text{C}_{16}\text{H}_{32}\text{S}_6\text{P}_2\text{F}_{12}\text{Ru}$: C, 23.79; H, 4.06; S, 23.82%. The electronic absorption spectrum measured in acetonitrile showed two λ_{max} values at 383 nm ($\epsilon = 299$) and 322 nm ($\epsilon = 423$). ^1H NMR ($\text{CH}_3\text{NO}_2\text{-d}_3$): broad, poorly resolved resonances between 3.5 and 2.2 ppm. ^{13}C NMR ($\text{CH}_3\text{NO}_2\text{-d}_3$): 10 resonances at δ 37.77, 37.59, 37.21, 36.77, 36.23, 34.29, 34.18, 26.26, 25.40, 25.25 ppm. These are all confirmed to be methylene resonances by a DEPT experiment.

2.3.3. Preparation of $[Pd(11S3)_2](PF_6)_2$

A mixture containing $K_2[PdCl_4]$ (80.0 mg, 0.245 mmol) and 11S3-147 (100.0 mg, 0.480 mmol) was refluxed in 40 ml of water–methanol (50:50) for 30 min. A yellow solution resulted. Addition of NH_4PF_6 (80.0 mg, 0.491 mmol) and heating for a second 30 min., followed by cooling yielded yellow–brown crystals of $[Pd(11S3)_2](PF_6)_2$. The crystals were washed with 3×10 ml of EtOH, 3×10 ml of ether and air dried to yield 98 mg (49%) of bis(1,4,7-trithiacycloundecane)palladium(II) hexafluorophosphate. IR (KBr, cm^{-1}) 2982, 2912, 1455, 1418, 1295, 942, 888–815 (s, PF_6^-), 668. The visible electronic spectrum measured in acetonitrile showed no visible absorption bands but one ultraviolet absorption with λ_{max} at 279 nm ($\epsilon = 12\,800$). *Anal.* Found: C, 23.50; H, 4.00; S, 23.66. Calc. for $C_{16}H_{32}PdS_6P_2F_{12}$: C, 23.63; H, 3.97; S, 23.66%. 1H NMR ($CH_3NO_2-d_3$): broad, poorly resolved resonances between 3.6 and 2.0 ppm. ^{13}C NMR ($CH_3NO_2-d_3$): four resonances at δ 39.97, 37.48, 36.71, 28.59 ppm. These are all confirmed to be methylene resonances by a DEPT experiment. Cyclic voltammetry measured in nitromethane showed a single, irreversible oxidation wave at +1.207 V vs. Fc/Fc^+ .

2.3.4. Preparation of $[Fe(11S3)_2](ClO_4)_2$

Under nitrogen, a solution of $Fe(ClO_4)_2 \cdot 6H_2O$ (55 mg, 0.151 mmol), acetic anhydride (92.4 mg, 0.906 mmol, 0.886 ml), and 3 ml of CH_3NO_2 was added dropwise with stirring to a solution of 1,4,7-trithiacycloundecane (63.0 mg, 0.302 mmol) in 3 ml of nitromethane. A dark purple solution formed immediately. The mixture was stirred for 1 h at room temperature and any insoluble materials 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 and washed with 20 ml of ether. A mass of 63 mg (62%) of bis(1,4,7-trithiacycloundecane)iron(II) perchlorate was obtained as purple crystals. The solid complex is stable under nitrogen, but readily hydrolyzes upon contact with moist air and at a moderate rate in nitromethane solution. IR (KBr, cm^{-1}) 2982, 2947, 2937, 2914, 1419, 1143–1087(s, ClO_4^-), 829, 621. The electronic absorption spectrum measured in nitromethane showed two λ_{max} values at 571 nm ($\epsilon = 105$) and 423 nm ($\epsilon = 115$). Room temperature magnetic susceptibility measurements showed that the complex was diamagnetic. *Anal.* Found: C, 28.75; H, 4.75; Cl, 10.55; S, 28.75. Calc. for $C_{16}H_{32}Cl_2FeO_8S_6$: C, 28.62; H, 4.80; Cl, 10.56; S, 28.64%.

2.3.5. Preparation of $[Co(11S3)_2](BF_4)_2$

A mass of $Co(BF_4)_2 \cdot 6H_2O$ (123 mg, 0.362 mmol) in nitromethane (3.97 ml) and acetic anhydride (0.21 ml, 2.2 mmol) was added dropwise with stirring to a solu-

tion of 11S3-147 (153 mg, 0.734 mmol) in nitromethane (1.07 ml). The color changed immediately from violet to deep brownish-pink. Dropwise addition of 20 ml of ether gave 86 mg (37%) of bis(1,4,7-trithiacycloundecane)cobalt(II) tetrafluoroborate as a brownish-red crystalline solid. IR (KBr, cm^{-1}) 2960, 2910, 1445, 1411, 1100–1010(s, BF_4^-), 1029, 626. The electronic spectrum measured in nitromethane shows one absorbance maximum at 887 nm ($\epsilon = 127$) and one absorbance shoulder at 517 nm ($\epsilon = 241$). The effective magnetic moment of the solid (μ_{eff}) was measured as 1.75 BM. *Anal.* Found: C, 30.00; H, 3.33; S, 30.30. Calc. for $C_{16}H_{32}B_2F_8CoS_6$: C, 30.11; H, 3.32; S, 30.14%.

2.3.6. Preparation of $[Co(11S3)_2](PF_6)_3$

A mass of $[Co(11S3-147)_2](BF_4)_2$ (160 mg, 0.250 mmol) was added to a solution of 60 mg (0.250 mmol) of sodium peroxydisulfate and 163 mg (1.00 mmol) of ammonium hexafluorophosphate in 5.0 ml of water. Upon swirling, the color changed immediately to orange. Slow evaporation of the aqueous solution yield 45 mg (20%) of bis(1,4,7-trithiacycloundecane)cobalt(III) hexafluorophosphate as a orange crystalline solid. IR (KBr, cm^{-1}) 2960, 2910, 1445, 1411, 830(s, PF_6^-), 645. The electronic spectrum measured in water shows one absorbance shoulder at 525 nm ($\epsilon = 470$), a second at 340 nm ($\epsilon = 478$), and a charge transfer absorption at 324 nm ($\epsilon = 11,800$). Room temperature magnetic susceptibility measurements showed that the complex was diamagnetic. *Anal.* Found: C, 21.40; H, 2.35; S, 21.40. Calc. for $C_{16}H_{32}P_2F_{18}CoS_6$: C, 21.36; H, 2.35; S, 21.38%. 1H NMR ($CH_3NO_2-d_3$): broad, poorly resolved resonances between 3.8 and 2.0 ppm. ^{13}C NMR ($CH_3NO_2-d_3$): 10 resonances at δ 41.0, 40.8, 40.5, 39.9, 39.3, 38.7, 38.4, 26.1, 25.9, 25.5 ppm. These are all confirmed to be methylene resonances by a DEPT experiment.

2.3.7. Preparation of $[Pt(11S3)Cl_2]$

A mixture of $K_2[PtCl_4]$ (50.0, 0.120 mmol) and 1,4,7-trithiacycloundecane (50.0 mg, 0.240 mmol) was refluxed in 15 ml of a 2:1 methanol–distilled water solution for 2 h. During reflux, the formation of an insoluble, yellow solid was observed. After reflux, the solution was allowed to cool slightly and then filtered to remove any insoluble solids. There was no bis product detected in the filtrate. The yellow product, $[Pt(11S3)Cl_2]$, was washed with 3×20 ml of ether to yield 29.0 mg of product (50.0%). *Anal.* Found: C, 20.30; H, 3.51; Cl, 15.05; S, 20.30. Calc. for $C_8H_{11}PtS_3Cl_2$: C, 20.26; H, 3.40; Cl, 14.95; S, 20.27%. FT-IR (KBr, cm^{-1}): 2999, 2955, 2930, 1438, 1406, 1293, 1249, 1186, 1148, 1010, 941, 897, 815, 695, 594, 563.

2.4. Preparation of metal complexes of 1,4,8-trithiacycloundecane (11S3-148)

2.4.1. Preparation of $[\text{Ni}(11\text{S}3)_2](\text{BF}_4)_2$

Under nitrogen, a mass of 1,4,8-trithiacycloundecane (11S3-148) (22.5 mg, 0.108 mmol) was dissolved in 5 ml of anhydrous nitromethane. To this solution a green solution of $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (18.4 mg, 0.054 mmol) in 5 ml of nitromethane with six drops of acetic anhydride was added. A blue color appeared immediately. Addition of 5 ml of diethyl ether to the ice-cold stirred solution precipitated the complex as blue crystals. The crystals were collected by vacuum filtration under nitrogen and washed with ethyl ether (2×10 ml) giving a 35% yield (12.2 mg) of $[\text{Ni}(11\text{S}3)_2](\text{BF}_4)_2$. The complex readily hydrolyzes upon contact with moist air and gradually undergoes solvolysis in solution. Solutions of the complex also are very susceptible to hydrolysis and must be prepared in anhydrous solvents. IR (KBr, cm^{-1}) FT-IR (KBr, cm^{-1}) 2994, 2947, 1450, 1412, 1140–1035 (s, BF_4^-), 932, 915, 850, 793, 540. The electronic absorption spectrum measured in nitromethane showed two λ_{max} values at 890 nm ($\epsilon = 50$) and 576 nm ($\epsilon = 60$). The effective magnetic moment of the solid (μ_{eff}) was measured as 3.19 BM. *Anal.* Found: C, 29.67; H, 4.75; S, 29.87. Calc. for $\text{C}_{16}\text{H}_{32}\text{S}_6\text{B}_2\text{F}_8\text{Ni}$: C, 29.61; H, 4.97; S, 29.63%.

2.4.2. Preparation of $[\text{Fe}(11\text{S}3)_2](\text{ClO}_4)_2$

Under nitrogen, a solution of $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (18.3 mg, 0.0504 mmol), acetic anhydride (6 drops), and 5 ml of CH_3NO_2 was added dropwise with stirring to a solution of 1,4,8-trithiacycloundecane (21.0 mg, 0.101 mmol) in 5 ml of nitromethane. A blue–green solution formed immediately. Addition of 5 ml of diethyl ether to the ice cold stirred solution precipitated the complex as bluish-green crystals. A mass of 21 mg (62%) of bis(1,4,8-trithiacycloundecane)iron(II) perchlorate was obtained. The solid complex is stable under nitrogen, but readily hydrolyzes upon contact with moist air and slowly decomposes in nitromethane solution. IR (KBr, cm^{-1}) 2985, 2945, 1419, 1145–1088 (s, ClO_4^-), 830, 666. The electronic absorption spectrum measured in nitromethane showed two λ_{max} values at 584 nm ($\epsilon = 180$) and 474 nm ($\epsilon = 154$). Room temperature magnetic susceptibility measurements showed that the complex was diamagnetic. *Anal.* Found: C, 28.85; H, 4.63; Cl, 10.55; S, 28.75. Calc. for $\text{C}_{16}\text{H}_{32}\text{Cl}_2\text{FeO}_8\text{S}_6$: C, 28.62; H, 4.80; Cl, 10.56; S, 28.64%.

2.4.3. Preparation of $[\text{Co}(11\text{S}3)_2](\text{BF}_4)_2$

A mass of $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (21.9 mg, 0.064 mmol) in nitromethane (5.00 ml) and acetic anhydride (six drops) was added dropwise with stirring to a solution of 1,4,8-trithiacycloundecane (26.7 mg, 0.128 mmol) in nitromethane (5.00 ml). The color changed immediately

from maroon to reddish violet. Dropwise addition of 10 ml of ether gave 15.4 mg (37.0%) of bis(1,4,7-trithiacycloundecane)cobalt(II) tetrafluoroborate as a brownish-red crystalline solid. IR (KBr, cm^{-1}) 2960, 2910, 1445, 1411, 1100–1010 (s, BF_4^-), 929, and 626. The electronic spectrum measured in nitromethane shows one peak at 879 ($\epsilon = 88$) and one absorbance shoulder at 510 nm ($\epsilon = 310$). The effective magnetic moment of the solid (μ_{eff}) was measured as 1.88 BM. *Anal.* Found: C, 29.99; H, 4.84; S, 29.96. Calc. for $\text{C}_{16}\text{H}_{32}\text{B}_2\text{F}_8\text{CoS}_6$: C, 29.60; H, 4.97; S, 29.62%.

2.4.4. Preparation of $[\text{Hg}(11\text{S}3)_2](\text{ClO}_4)_2$

A solution of 1,4,8-trithiacycloundecane (41.0 mg, 0.197 mmol) in 3 ml of anhydrous nitromethane was added to a solution containing $\text{Hg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (44.0 mg, 0.0970 mmol) and 5 drops of acetic anhydride in 3 ml of anhydrous nitromethane. Colorless crystals were grown from the reaction mixture by solvent diffusion with diethyl ether to give 62.4 mg (78.8% yield) of $[\text{Hg}(11\text{S}3)_2](\text{ClO}_4)_2$ as a colorless crystalline solid. IR: (KBr, cm^{-1}) 2910, 1540, 1435, 1344, 1290, 1250, 1150–1060 (s, ClO_4^-), 940, 900, 850, 720, 700, 630. *Anal.* Found: C, 23.59; H, 3.96; S, 23.47. Calc. for $\text{C}_{16}\text{H}_{32}\text{S}_6\text{Cl}_2\text{O}_8\text{Hg}$: C, 23.54; H, 3.95; S, 23.57%.

2.4.5. Preparation of $\text{Hg}(11\text{S}3)\text{Cl}_2$

A hot solution of 1,4,8-trithiacycloundecane (44.0 mg, 0.210 mmol) in 3 ml of anhydrous nitromethane was added to a hot solution containing HgCl_2 (28.5 mg, 0.105 mmol) and in 3 ml of anhydrous nitromethane. A colorless precipitate formed immediately which was filtered, washed with 3×10 ml of ether, and dried in vacuo to give 42.4 mg (84.1% yield) of $[\text{Hg}(11\text{S}3)\text{Cl}_2]$ as a colorless crystalline solid. IR: (KBr, cm^{-1}) 2903, 1435, 1400, 130, 1290, 1270, 1250, 1140, 900, 850, 840, 750, 710, 630, 385, 350 cm^{-1} . *Anal.* Found: C, 20.04; H, 3.38; Cl, 14.77; S, 19.93. Calc. for $\text{C}_8\text{H}_{16}\text{S}_3\text{Cl}_2\text{Hg}$: C, 20.02; H, 3.36; Cl, 14.78; S, 20.04%.

3. Results and discussion

Homoleptic complexes for both 11S3 macrocycles with Ni(II), Fe(II), and Co(II) have been synthesized and characterized by several methods including microanalysis. Both Ni(II) complexes have magnetic moments typical of two unpaired electrons, and their values are consistent with previous observations of similar complexes for these two ions [3,7a,21,22]. Both Fe(II) complexes are diamagnetic complexes, and this magnetic behavior and their absorption spectra (see below) are consistent with a low-spin d^6 system [23]. Both of the 11S3 complexes of Co(II) have magnetic moments consistent with one unpaired electron, a low-spin d^7 system. Hexakis(thioether) cobalt(II) complexes

are invariably low-spin, but these low-spin configurations are unusual for octahedral Co(II) complexes [2,24]. All of the complexes with these ions are extremely sensitive towards solvolysis with anhydrous nitromethane being the solvent of choice for stability.

In contrast to its behavior with Period 4 divalent transition metal ions, the ligand 11S3-147 forms a stable bis homoleptic complex with Ru(II), which like Fe(II) is a low-spin d^6 system. The ion Ru(II) has been noted as the ideal metal ion to stabilize thioether complexes for the formation of hexakis(thioether) octahedral structures [11b,25]. The isoelectronic Co(III) also forms a homoleptic complex with this ligand, and the complex is prepared by oxidation of the related Co(II) complex.

For several years our group and others have been interested in the complexation behavior of crown thioethers towards Pd(II) and Pt(II) [26,27] and the unusual structural, spectroscopic, and electrochemical properties seen in these complexes. Our group is especially interested as to how these unusual properties may be influenced and controlled by the ligand structure and conformation. The complex $[\text{Pd}(\text{11S3-147})_2](\text{PF}_6)_2$ is readily prepared by the reaction of a tetrachloropalladate anion with 2 equiv. of 11S3. In the reaction, the 11S3 ligand displaces the chloride ions from the palladium center, yielding the desired bis(11S3) homoleptic complex. However, using the same procedure with tetrachloroplatinate, we were not able to prepare a bis homoleptic complex, instead isolating a complex of the formula $[\text{Pt}(\text{11S3})\text{Cl}_2]$. This was the only observed product even with a large excess of 11S3 ligand present. The reactivity difference between Pd(II) and Pt(II) towards 11S3 may reflect the difference in ligand substitution rates between the two ions. In contrast, the homoleptic complexes of both 9S3 and 10S3 with Pt(II) and Pd(II) are readily prepared. We would like to note, however, that the large 12S3 ligand does complex Pd(II) and Pt(II) in bis fashion only with some difficulty [28]. These observations may reflect steric interactions or conformational factors involving the larger ring trithioethers.

The isomeric ligand 11S3-148 readily forms complexes with mercury(II). With mercury(II) perchlorate, a bis homoleptic complex was obtained, presumably with an octahedral-like similar to its 9S3 complex [29]. However, with mercury(II) chloride only a mono 11S3-148 complex (1:1 11S3-148/Hg) was obtained. This result is similar to our observations for the reactions between platinum(II) and 11S3-147. In contrast to its behavior towards mercury(II), we were not able to synthesize any Cd(II) complexes of 11S3-148 using similar synthetic procedures.

3.1. Electronic spectroscopy

3.1.1. Ni(II) complexes

Nickel(II) serves as an excellent spectroscopic probe for electronic interactions in coordination complexes. An octahedral complex of Ni(II) would be expected to exhibit three spin-allowed $d-d$ transitions corresponding to the transitions: ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$; ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$; ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$. However, the latter of these transitions is usually obscured in the thioether complexes due to an intense sulfur-metal charge-transfer band, and indeed, only the two low energy $d-d$ transitions are observed for the two 11S3 complexes of Ni(II). Ligand field parameters have been calculated for both complexes, and these results are presented in Table 1. Since the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ transition is obscured, the value of B , the interelectronic repulsion parameter, is calculated from the two observed transitions (ν_1 is the longer wavelength transition, ν_2 the shorter) using the following equation [30].

$$B = \frac{(2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2)}{(15\nu_2 - 25\nu_1)}$$

As one might anticipate, the two 11-membered ring systems have D_q values which fall intermediate between the ten-membered ring system, 10S3, and the weaker field thioether ligand 12S3 (1,5,9-trithiacyclododecane) [7a,22]. The ordering of the ligand field strengths follows the trend: 9S3 > 10S3 > both 11S3 ligands > 12S3.

Table 1
Ligand field parameters for bis octahedral Ni(II) complexes with trithioether ligands ^a

Complex	D_q (cm^{-1})	f_{comp} ^b	B (cm^{-1})	β ^c	References
$[\text{Ni}(\text{11S3-147})_2]^{2+}$	1155	1.33	724	0.70	PW
$[\text{Ni}(\text{11S3-148})_2]^{2+}$	1139	1.31	687	0.66	PW
$[\text{Ni}(\text{9S3})_2]^{2+}$	1271	1.46	665	0.64	[22]
$[\text{Ni}(\text{10S3})_2]^{2+}$	1239	1.42	652	0.63	[7a]
$[\text{Ni}(\text{12S3})_2]^{2+}$	1112	1.29	778	0.75	[22]
$[\text{Ni}(\text{BTS})_2]^{2+}$	1302	1.50	689	0.66	[31]
$[\text{Ni}(\text{ttn})_2]^{2+}$	1134	1.30	821	0.79	[22]

^a PW = present work; ligand abbreviations: BTS = benzene trisulfide, ttn = 2,5,8-trithianonane

^b A value of 870 cm^{-1} was used for the Jorgensen constant, g , for Ni(II) [42].

^c A value of 1041 cm^{-1} is used for the Racah parameter B , for the free ion value of Ni(II).

Table 2
Ligand field parameters for macrocyclic hexakis(thioether) iron(II) complexes ^a

Complex ^b	D_q (cm ⁻¹)	f^c	B (cm ⁻¹)	β^d	References
[Fe(11S3-147) ₂] ²⁺	1837	1.84	437	0.41	PW
[Fe(11S3-148) ₂] ²⁺	1790	1.79	518	0.49	PW
[Fe(9S3) ₂] ²⁺	2005	2.00	437	0.41	[40]
<i>cis</i> -[Fe(10S3) ₂] ²⁺	1920	1.92	438	0.42	[23]
<i>trans</i> -[Fe(10S3) ₂] ²⁺	1905	1.91	499	0.47	[23]
[Fe(18S6)] ²⁺	1940	1.94	506	0.48	[23]
[Fe(20S6)] ²⁺	1913	1.91	412	0.39	[23]
[Fe(9S3)(9S3O)] ²⁺	2244	2.24	357	0.34	[40]
[Fe(keto-10S3) ₂] ²⁺	1937	1.94	490	0.46	[7]
[Fe(dibenzo-18S6)] ²⁺	1982	1.98	477	0.45	[41]

^a PW = present work.

^b Ligand abbreviations: 9S3O = 1,4,7-trithiacyclononane-1-oxide; keto-10S3 = 1,4,7-trithiacyclodecan-9-one.

^c g value for Fe(II) = 10.0 [42].

^d Ratio of $B_{\text{complex}}/B_{\text{free ion}}$ where $B_{\text{free ion}}$ for Fe(II) = 1058 cm⁻¹.

That is, the larger and more flexible crown trithioethers generate progressively weaker ligand fields. The highly rigid macrocyclic trithioether BTS has a very large ligand field strength while the open trithioether (ttn) is much weaker [22,31]. This ordering of the ligand field strengths for the assortment of trithioether ligands underscores the importance of the preorganized conformation of the ligand, and the effects that these conformational constraints have on the complexation properties of the ligand.

The nephelauxetic ratio ($\beta = B_{\text{complex}}/B_{\text{free ion}}$) for two 11S3 ligands is approximately 0.7 which is in agreement with virtually all previously studied cases of Ni(II)–hexakis(thioether) complexes [22]. In contrast, this ratio in amine complexes of Ni(II) is around 0.9 [32]. A high degree of covalency between metal and thioether ligand orbitals is indicated by this relatively low value. The ordering of the field strengths with respect to Ni(II) for the triaza crowns follows the same general trend as we observe for trithioethers — larger macrocyclic rings generate weaker ligand fields [32]. It is interesting to note that both 11S3 ligands are stronger field ligands than the analogous triaza 11N3 macrocycle — a result that has been seen for other thia crowns. In general, the thioether macrocycle forms a stronger ligand field than its analogous amine macrocycle.

3.1.2. Fe(II), Ru(II), and Co(III) complexes

An octahedral complex containing a low-spin d⁶ metal ion such as Fe(II), Ru(II), or Co(III) would be expected to exhibit two spin-allowed d–d transitions corresponding to the transitions: ¹A_{1g} → ¹T_{1g} and ¹A_{1g} → ¹T_{2g}. Both transitions are observed in the two 11S3 complexes, and the ligand field parameters for these two and a series of homoleptic thioether iron(II) complexes are presented in Table 2. We have used a BASIC computer program that was used to obtain the values of D_q and B from the energies of the two

observed transitions for the two Fe(II) complexes as well as the isoelectronic Ru(II) and Co(III) complexes (see below) of 11S3-147 [33]. The following two equations were used in the calculation of the ligand field parameters:

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

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

Since only two spin-allowed transitions were observed, the assumption that $C = 4B$ was made for the calculation. As was true for the Ni(II) complexes, the D_q values for the 11-membered ring systems for all three low-spin d⁶ metal ions are weaker than the 9S3 and 10S3 complexes of the same metal ion.

For Fe(II) both 11S3 complexes have D_q values near 1800 cm⁻¹. As mentioned previously this value is lower than for the smaller trithioether macrocycles, but it is still larger than the bis(9N3) Fe(II) complex (1675 cm⁻¹) indicating the strong ligand fields generated by crown thioethers in general. The nephelauxetic ratio for both 11S3 complexes is about 0.45, typical for hexakis(thioether) complexes and indicating a relatively large degree of metal–ligand orbital mixing for the thioether ligands. The D_q values for the Fe(II) complexes are larger than those of the Ni(II) complexes with identical ligands.

In the complex [Ru(11S3-147)₂]²⁺ two d–d transitions are observed enabling ligand field calculations to be made as described above. These two transitions are typically observed near 360 and 310 nm in all hexakis(thioether) ruthenium(II) complexes, and the same is true for the 11S3 complex [11b,25]. We obtain a value of D_q equal to 2707 cm⁻¹ and a B value equal to 323 cm⁻¹. As expected the value of D_q has increased by about 900 cm⁻¹ while comparing the homoleptic Fe(II) complexes to the congeneric Ru(II) complex. Again, the 11S3 ligand functions as a weaker field ligand relative

to 9S3 and 10S3, but the decrease in strength is not as pronounced as in the Fe(II) and Ni(II) complexes.

Unless obscured by charge transfer bands, two transitions are typically observed near 500 and 360 nm in all hexakis(thioether) cobalt(III) complexes. Both transitions are seen in the complex $[\text{Co}(\text{11S3-147})_2]^{3+}$ resulting in a value of D_q equal to 1950 cm^{-1} and a value of B equal to 829 cm^{-1} . The 11S3 ligand functions as strong field ligands towards Co(III), but again is a weaker ligand compared to 9S3 and 10S3 [34,35]. The Co(III) 11S3-147 complex shows an increase in its ligand field splittings (by about 125 cm^{-1}) compared to the analogous Fe(II) complexes. This would be expected on the basis of the increased positive charge for Co(III) on the d^6 metal center. The spectrochemical series for the crown trithioethers generally follows what

has previously been observed for the other metal ions (Fig. 1). That is, there is a steady decrease in the ligand field strength as the ring size of the macrocycle increases.

3.1.3. Other complexes

The electronic spectra for both homoleptic 11S3 Co(II) complexes show two d–d bands with transitions near 880 and 515 nm. These two are assigned, respectively, as the ${}^2E_g \rightarrow {}^2T_{1g}$ and ${}^2E_g \rightarrow {}^2T_{2g}$ transitions. The spectra are consistent with other hexakis(thioether)-cobalt(II) complexes and support the presence of a low-spin Co(II) center [8a,36]. The calculated D_q values for the two complexes are 1127 cm^{-1} (11S3-147) and 1138 cm^{-1} (11S3-148). Both values represent weaker ligand fields than the analogous 9S3 and 10S3 complexes.

The two homoleptic bis Pd(II) complexes of 9S3 and 10S3 show remarkable spectroscopic and electrochemical properties due to their surprising elongated octahedral structures [26,27,37]. The complexes are blue-green in color due to a d–d absorption near 600 nm. In contrast, however, the complex $[\text{Pd}(\text{11S3-147})_2]^{2+}$ is brown-yellow in color, not blue-green, and shows an electronic spectrum containing only charge transfer bands. Thus, due to differences in its structure and conformation, the 11-membered ring thioether displays very different coordination behavior towards palladium(II) than do 9S3 and 10S3.

3.2. NMR and electrochemical measurements

Two possible stereoisomers can arise in the case of bis complexes of either of the two 11S3 ligands, and these are shown for the 11S3-147 ligand in Fig. 2. The *meso* diastereoisomer has the two butylene bridges spanning *trans* positions around the octahedral center. For this diastereoisomer, the two 11S3 ligands are equivalent and a four-line C NMR spectrum with all lines of equal intensity would be observed. The other two diastereoisomers are enantiomers of each other and involve a *cis* positioning of the two butylene bridges. One would anticipate an eight-line C NMR spectrum for these diastereoisomers. Proton NMR spectra for these types of complexes are usually quite complex and have limited value for stereochemical assignments. The chemical shifts in the carbon spectra for all complexes are consistent with the presence of α -carbon and β -carbon methylene resonances, and the carbon connectivity in all cases is confirmed through a DEPT experiment.

In order to investigate stereoisomer selectivity and to minimize ligand substitution reactions, we prepared the stable complex, $[\text{Ru}(\text{11S3-147})_2]^{2+}$. We obtained a 10-line C NMR spectrum for the complex, suggesting that more than one diastereoisomer was indeed present.

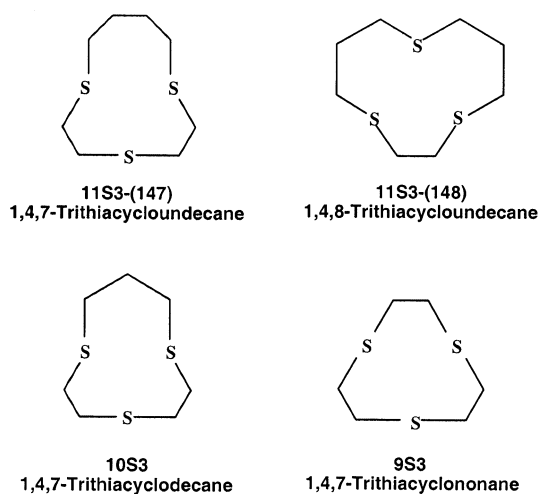


Fig. 1. Crown trithioethers.

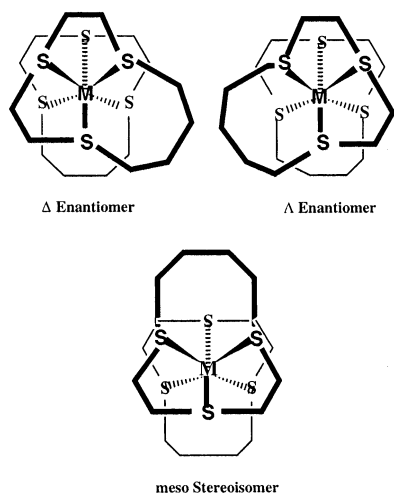


Fig. 2. Diastereoisomers of bis(1,4,7-trithiacycloundecane) octahedral complexes.

Similarly, the diamagnetic $[\text{Co}(\text{11S3-147})_2]^{3+}$ complex also shows a 10-line NMR spectrum, again consistent with the presence more than a single diastereomer. Thus, there appears to be little selectivity for the formation of one diastereomer over the other. We have observed similar behavior in bis 10S3 complexes of d^6 metal ions such as Ru(II), Fe(II), and Co(III) where little selectivity of diastereoisomers is also seen [8a,23,25]. As expected the methylene resonances in the more electropositive Co(III) are deshielded relative to the Ru(II) resonances. The complex $[\text{Pd}(\text{11S3-147})_2]^{2+}$ shows a four line spectrum which is consistent with the sole formation of the *meso* diastereomer or a fluxional process of the 11S3 ligand. Fluxional processes are very common for both Pt(II) and Pd(II) complexes of trithioethers and certainly cannot be eliminated here [8b,26].

The electrochemical properties of the complex $[\text{Pd}(\text{11S3-147})_2]^{2+}$ contrast those of the analogous 9S3 and 10S3 complexes. The latter two complexes show a reversible Pd(II)/Pd(II) oxidation wave near +0.60 V vs. Fc/Fc^+ . However, this behavior is not seen in the 11S3 complex. Instead, electrochemical behavior in nitromethane shows an irreversible oxidation wave at a much more positive potential, +1.204 V vs. Fc/Fc^+ . Based upon its irreversibility and voltage, we propose that the oxidation is ligand-centered, not palladium-centered since the 10S3 ligand itself has similar electrochemical characteristics [23]. The conformational distinctions between 11S3 and the two smaller trithioether rings are thus also seen in the electrochemical behavior of their Pd(II) complexes.

3.3. Conformational analysis of 11S3-147 and 11S3-148

The conformational analysis for both 11S3-147 and 11S3-148 have been carried out using the MM2 technique [38] and we have used the nomenclature for ligand conformations described originally by Dale [39]. The results of the calculations are presented in Fig. 3 for 11S3-147 and Fig. 4 for 11S3-148. The lowest energy conformation for 11S3-147 is [335]D. Note that this conformation is not suitable for chelation in that the two sulfurs are *exodentate*. There are two other conformations with relatively low strain energy; [12323]I and [12323]K. While the sulfur atoms in the former are *endodentate*, they are not on the same face of the ring. That is, they are *anti endodentate* rather than *syn endodentate* as required for tridentate complexation. Conformer [12323]K has two *anti endodentate* sulfur atoms and one *exodentate* sulfur, and, therefore, is also unsuitable for chelation Fig. 5.

There are seven possible conformations of 11S3-147 which have the requisite *syn endodentate* sulfur atoms

suitable for facial tridentate coordination. These are [335]B, [335]C, [344]C, [344]F, [12323]F, [2345]C, and [245]K. Of these, [335]C is relatively low in strain energy, only $1.02 \text{ kcal mol}^{-1}$ higher in energy than the lowest-energy conformer, [335]D. Thus, there is a small energy difference between the lowest energy conformation of 11S3-147 and one suitable for tridentate conformation. However, the lack of a suitable lower energy conformer appears to account for the complexation characteristics (weaker ligand field splitting, enhanced sensitivity to hydrolysis) of 11S3-147.

There are three low energy conformations of 11S3-148 which are virtually equal in energy. These are [335]C, [335]D, and [335]F. Again, none of these are suitable for complexing a metal ion in tridentate fashion. Both [335]C and [335]F have *anti endodentate* sulfur atoms while [335]D has one *exodentate* sulfur. There are only three conformations of 11S3-148 with *syn endodentate* sulfur atoms, namely [13223]D, [12323]A, and [12314]K. Of these three, [12323]A is $1.77 \text{ kcal mol}^{-1}$ higher in energy than the low energy [335] conformer while the former and latter are 2.72 and $3.32 \text{ kcal mol}^{-1}$, respectively, higher in energy. Although 11S3-148 is lower in total strain energy than 11S3-147, both for the lowest energy conformation as well as for the lowest energy *syn endodentate* conformation, the energy difference between the lowest energy conformation and the lowest energy *syn endodentate* conformation in 11S3-147 is less than the analogous energy difference in 11S3-148. Nevertheless, an energy difference of $1.77 \text{ kcal mol}^{-1}$ is not a larger energy difference for 11S3-148 ligand to overcome to function as a *facially* coordinating tridentate ligand. However, like 11S3-147 and unlike 9S3 and 10S3, the ligand does not have a preorganized conformation for complexation in this fashion and these conformational effects are seen in properties of its complexes.

4. Conclusions

We have prepared a series of complexes with a variety of transition metal ions involving the two isomeric 11-membered ring trithioethers, 1,4,7-trithiacycloundecane (11S3-147) and 1,4,8-trithiacycloundecane (11S3-148). The two function as relatively strong field ligands, but their ligand field strengths fall between the stronger field and smaller ring trithioether ligands such as 1,4,7-trithiacyclononane and 1,4,7-trithiacyclodecane and the larger ring and weaker field ligand, 1,5,9-trithiacyclododecane. Complexes of both ligands with first row transition metals are much more sensitive to solvolysis reactions than 9S3 complexes, but complexes with Ru(II) and Hg(II) are relatively stable. ^{13}C NMR

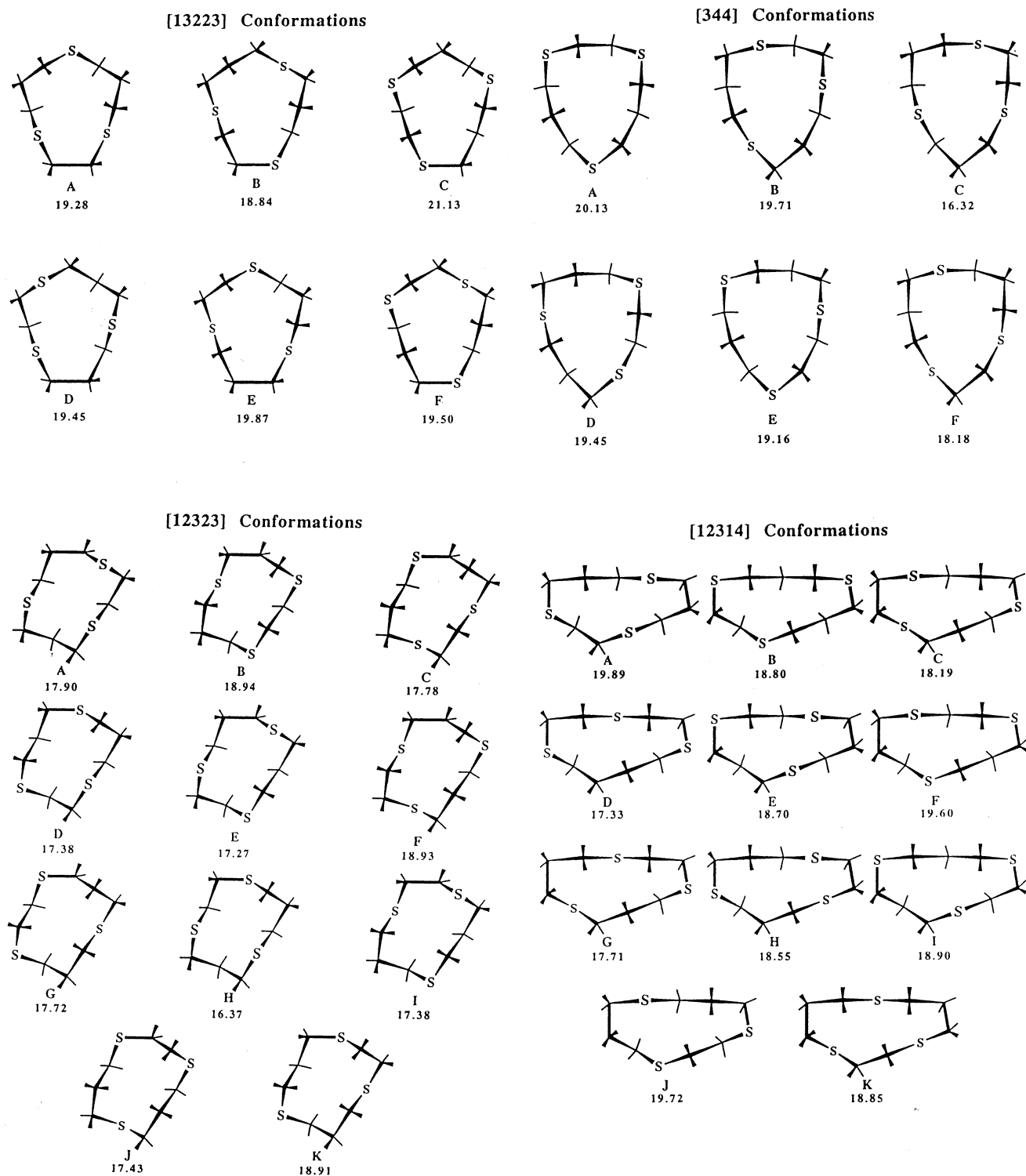


Fig. 3. Conformations of 11S3-148 [13223], [344], [12323], and [12314].

spectroscopy for the Ru(II) and Co(III) complexes of 11S3-147 shows that there is little stereoisomer selectivity between the *cis* and *trans* diastereoisomers with both isomers observed. The complex $[\text{Pd}(\text{11S3-147})_2]^{2+}$ does not display the unusual spectroscopic and electrochemi-

cal properties observed in smaller ring Pd(II) complexes. The complex is brown, not blue-green in color, and its electronic spectrum is dominated by the charge transfer bands. Furthermore, a Pd(II)/Pd(III) reversible couple is not observed electrochemically, but an irre-

versible ligand-centered oxidation is seen instead. A conformational analysis on both macrocycles showed that neither has a lowest energy conformation suitable

for tridentate coordination. The effects of the lack of ligand pre-organization dominate the complexation behavior of these two 11-membered ring trithioethers.

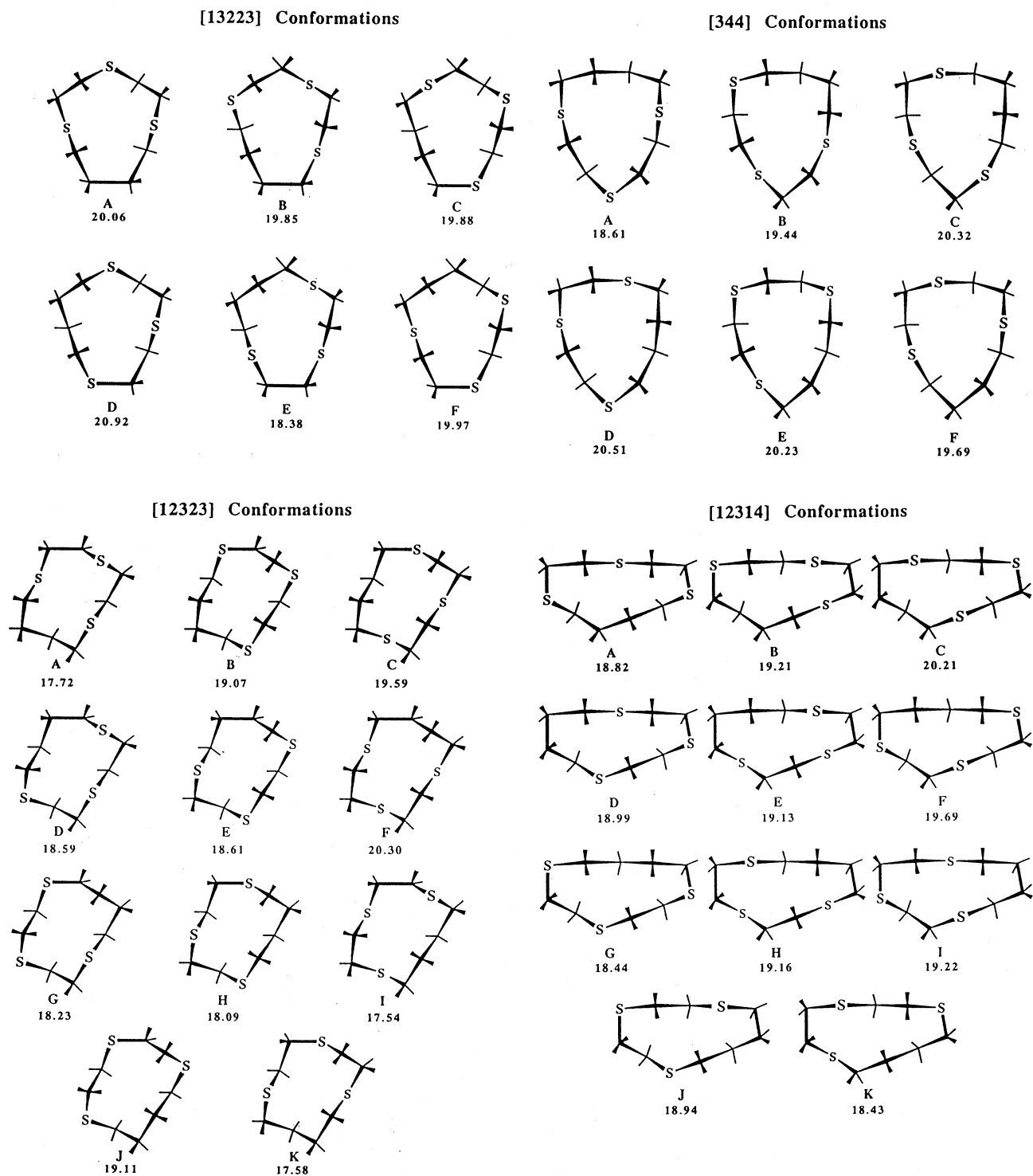


Fig. 4. Conformations of 11S3-147 [13223], [344], [12323], and [12314].

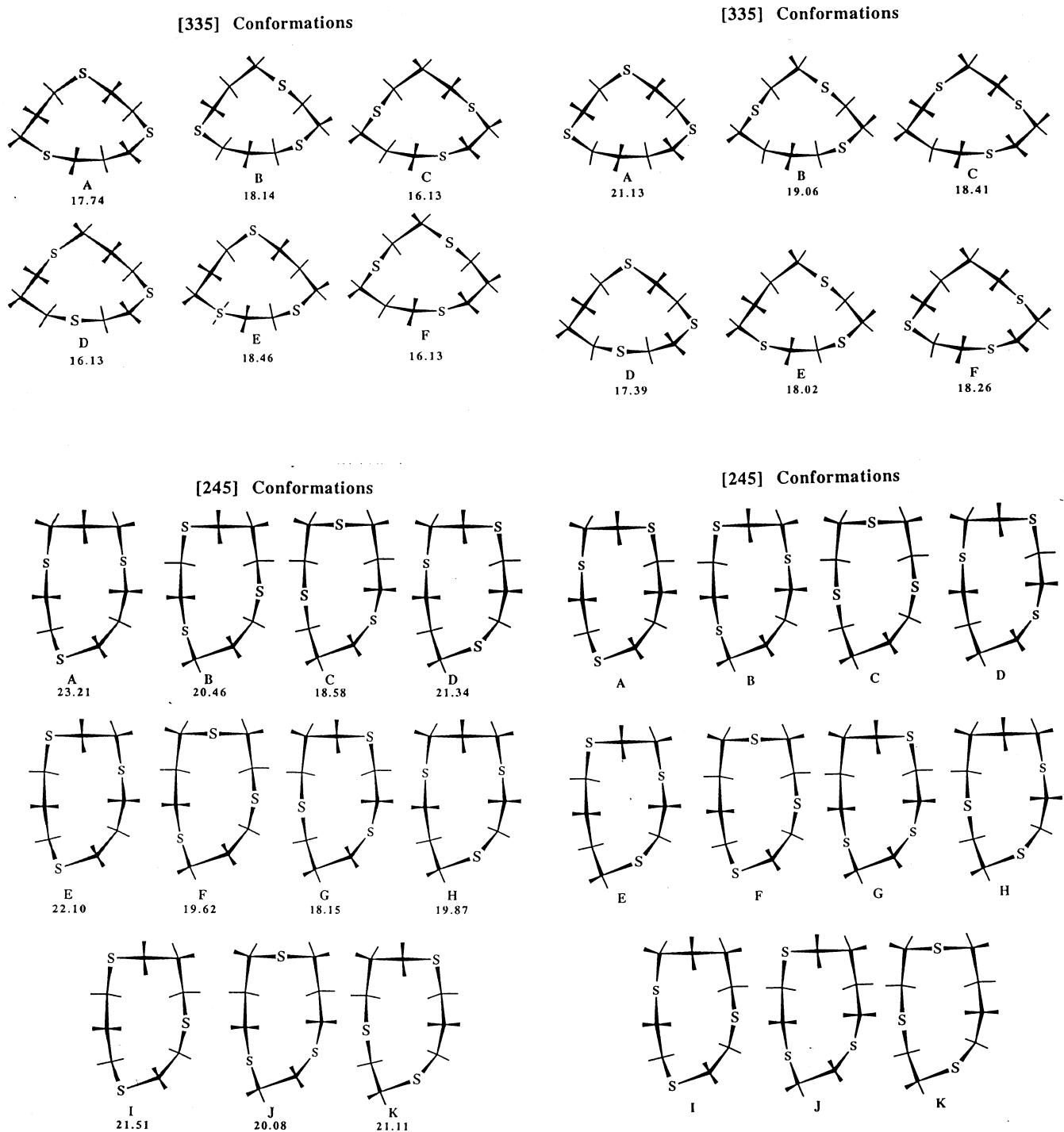


Fig. 5. [335] and [245]. Conformations of 11S8-148 (left) and 11S3-147 (right).

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