

Gregory J. Grant*[#], Christopher G. Brandow[#], Chrystal Williams Bruce[#],
Mark A. Bryant[#], Rebecca M. Kirk[#], Sabrina D. Lee[#], Kerry R. Rickerd[#] and Larry F. Mehne[§]

Contribution from the Department of Chemistry, The University of Tennessee at Chattanooga, Chattanooga,

TN 37403, the Department of Chemistry, Covenant College, Lookout Mountain, GA

[#] Department of Chemistry, The University of Tennessee at Chattanooga

[§] Department of Chemistry, Covenant College

Received May 15, 2001

Dedication: This paper is dedicated to Professor Jerald S. Bradshaw upon his retirement, in recognition of the pioneering contributions by him and his BYU colleagues for the advancement of macrocyclic chemistry, and in particular, for their establishment and development of the International Symposium of Macrocyclic Chemistry.

The two macrocyclic hexathioethers, 1,4,7,12,15,18-hexathiacyclodocosane (22S6) and 1,4,7,11,14,17-hexathiacycloeicosane (20S6) have been examined with respect to their complexation behavior towards a variety of transition metals ions. In all of these complexes, the two ligands generate relatively strong ligand field, but their field strengths fall between the smaller ring and stronger field hexathioether ligands (such as 18S6) and larger ring and weaker field ligands, such as 24S6. The stability of the complexes towards hydrolysis parallels their reduced field strengths with first row transition metal complexes of both ligands showing enhanced sensitivity to solvolysis reactions compared to the analogous 18S6 complexes. In general, the electrochemical behavior of the hexathioether complexes shows metal centered oxidations which occur at higher potentials than those complexes involving trithioethers. We suggest that the hexathioether ligand is less able to expand and contract during the reduction and oxidation of the metal center. The complex $[\text{Pd}(22\text{S6})]^{2+}$ does not display the unusual spectroscopic and electrochemical properties observed in the analogous 18S6 complex.

J. Heterocyclic Chem., **38**, 1281 (2001).

1. Introduction.

The design and synthesis of new macrocycles which will selectively bind specific metal cations has been an important goal of this research community for a number of years [1]. Variations in the structure of the macrocycle ligand have included changing the size of the macrocyclic cavity, the number of sulfur donors, the size of the chelate rings, the conformational flexibility of the ring, and incorporation of mixed donor atoms into the ring [2-4]. Much of the research in this field has focused on crown ethers, but macrocyclic polythioethers have also been found to be effective polydentate ligands for complexing a variety of transition metals [5-9]. The coordination

chemistry of crown thioethers has received a marked increase in activity during the 1990's due in part to dramatic improvement in the yields of these macrocyclic materials. The unusual complexation behavior of the tridentate macrocycle 1,4,7-trithiacyclononane (9S3) and related crown thioethers has also been an impetus for this development, and some specific examples of these unexpected properties include their large ligand field strengths [10,11], their ability to reduce electron-electron repulsions and thereby form low spin complexes [12-19], their ability to stabilize unusual oxidation states and coordination geometries [20-28] and a rapidly emerging organometallic chemistry [29-34]. Several of these thioether macrocycles including 20S6 (1,4,7,11,14,17-

Table 1
Ligand Field Parameters and Electrochemical Data for Octahedral Ni(II) Complexes with Macrocyclic Hexathioether Ligands

Complex [a]	Dq, cm ⁻¹	f_{comp} [b]	B, cm ⁻¹	β [c]	2 ⁺ /3 ⁺ [d]	2 ⁺ / ⁺ [d]	REF
[Ni(22S6)] ²⁺	1138	1.31	737	0.71	+1.140, I	-0.040, I	PW
[Ni(20S6)] ²⁺	1201	1.38	640	0.61	+1.094, I	ES	PW
[Ni(18S6)] ²⁺	1227	1.41	863	0.83	+1.322, I [e]	ES	PW
[Ni(24S6)] ²⁺	1105	1.27	689	0.66	NM	NM	[61]
[Ni(bzo ₂ -18S6)] ²⁺	1277	1.47	844	0.81	ES	ES	[62]

PW = present work; NM = Not measured; ES = electrochemically silent; I = irreversible; [a] Ligand Abbreviations: 18S6=1,4,7,10,13,16-hexathiacyclooctadecane; 24S6=1,5,9,13,17,21-hexathiacyclotetracosane; bzo₂-18S6 = 2,3,11,12-dibenzo-1,4,7,10,13,16-hexathiacyclooctadeca-2,11-diene; [b] C.K. Jorgensen, Oxidation Numbers and Oxidation States; Springer: New York, 1969. pp. 84-85; [c] Ratio of $B_{\text{complex}}/B_{\text{free ion}}$ where $B_{\text{free ion}}$ for Ni(II) = 1041 cm⁻¹; [d] E°, Measured in V vs. Fc / Fc⁺; [e] Measured in acetonitrile as the picrate salt.

Table 2
Ligand Field Parameters and Electrochemical Data for Octahedral Ru(II) Hexakis(thioether) Complexes

Complex [a]	Dq, cm ⁻¹	f_{comp} [b]	B, cm ⁻¹	2 ⁺ /3 ⁺ [c]	REF
[Ru(22S6)] ²⁺	2810	1.41	237	NM	PW
[Ru(20S6)] ²⁺	2849	1.49	213	NM	PW
[Ru(18S6)] ²⁺	2959	1.48	488	NM	[39]
[Ru(9S3) ₂] ²⁺	3055	1.53	308	+1.41, quasi-rev.	[25]
[Ru(10S3) ₂] ²⁺	2987	1.49	315	+1.37, quasi-rev	[67]
[Ru(11S3) ₂] ²⁺	2707	1.35	323	+1.33, quasi-rev	[68]
[Ru(12S3) ₂] ²⁺	2946	1.47	216	+1.08, quasi-rev	[25]

PW = present work; NM = Not measured; ES = electrochemically silent; [a] Abbreviations for Ligands Not Previously Used: 10S3=1,4,7-Trithiacyclodecane, 11S3=1,4,7-Trithiacycloundecane, 12S3=1,5,9-Trithiacyclododecane; [b] C. K. Jorgensen, Oxidation Numbers and Oxidation States; Springer: New York, 1969. pp. 84-85; [c] E°, Measured in V vs. Fc / Fc⁺.

Table 3
Ligand Field Parameters and Electrochemical Data for Octahedral Hexakis(thioether) Fe(II) Complexes

Complex	Dq, cm ⁻¹	f_{comp} [a]	B, cm ⁻¹	β [b]	2 ⁺ /3 ⁺ [c]	REF
[Fe(22S6)] ²⁺	1850	1.85	418	0.40	-0.142, irreversible	PW
[Fe(20S6)] ²⁺	1913	1.91	412	0.39	+0.69, irreversible	[52]
[Fe(18S6)] ²⁺	1940	1.94	506	0.48	+1.08, irreversible	[52]
[Fe(9S3) ₂] ²⁺	2005	2.10	437	0.41	+0.98, reversible	[10]
[Fe(10S3) ₂] ²⁺	1943	1.94	490	0.46	+0.91, reversible	[10]
[Fe(bzo ₂ -18S6)] ²⁺	1982	1.98	477	0.45	ES	[62]

PW = present work; ES = electrochemically silent; [a] B.N. Figgis, Introduction to Ligand Fields; Interscience Publishers: New York, N.Y., 1966. p. 244 g value for Fe(II) = 10.0; [b] Ratio of $B_{\text{complex}}/B_{\text{free ion}}$ where $B_{\text{free ion}}$ for Fe(II) = 1058 cm⁻¹; [c] E°, Measured in V vs. Fc / Fc⁺.

Table 4
Ligand Field Parameters and Electrochemical Data for Octahedral Cobalt(III) Complexes with Macrocyclic Hexathioether Ligands.

Complex	Dq, cm ⁻¹	f_{comp} [a]	B, cm ⁻¹	β [b]	2 ⁺ /3 ⁺ [c]	2 ⁺ / ⁺ [c]	REF
[Co(22S6)] ²⁺	1938	1.06	775	0.57	+195, Q	-752, I	PW
[Co(20S6)] ²⁺	2044	1.12	511	0.38	+257, R	-971, R	[54]
[Co(18S6)] ²⁺	2300	1.26	582	0.41	+257, R	-703, I	[14]
[Co(24S6)] ²⁺	NM	NM	NM	NM	+307, Q	NM	[7]
[Co(bzo ₂ -18S6)] ²⁺	2802	1.59	335	0.25	+193, R	-737, R	[62]

PW= present work; NM= Not measured; I = irreversible; R = reversible; Q= quasi-reversible; [a] C. K. Jorgensen, Oxidation Numbers and Oxidation States; Springer: New York, 1969. pp. 84-85; [b] Ratio of $B_{\text{complex}}/B_{\text{free ion}}$ where $B_{\text{free ion}}$ for Ni(II) = 1041 cm⁻¹; [c] E°, Measured in V vs. Fc/Fc⁺.

hexathiacycloicosane, see structure below) have been linked to polymer backbones for application as heavy metal absorbents [35]. The surprising behavior of

transition metal complexes of 9S3 is due to the ligand's unique all *endodentate* conformation of the three sulfur atoms which contrasts the structures of other thia

macrocycles where the *exodentate* conformation predominates [36-38]. The effect highlights the importance of pre-organization in determining the complexation mode of 9S3 and other macrocyclic thioether ligands.

Initial reports on larger and potentially hexadentate macrocycles have focused predominately on the eighteen-membered ring 18S6 (1,4,7,10,13,16-hexathiacyclooctadecane, see structure below). This compound is the all-sulfur analog of 18-crown-6, and many complexation studies involving the ligand have been reported including several crystal structures of mononuclear and polynuclear complexes [39-50]. However, only a limited number of complexation studies involving larger ring size hexathioethers have appeared. These include six reported crystal structures involving complexes of 20S6 [51-55] (principally by our group and the Lucas group), one crystal structure of a 24S6 complex [56], one Ag(I) complex of a hydroxylated hexathioether [57], and a few involving even larger macrocycles [58]. For several years, we have been interested in studying the effects that structural alterations on macrocyclic thioether ligands have on the ease of complex formation, complex stability, and complex structure. We have previously reported the crystal structures for two macrocyclic hexathioether ligands, 1,4,7,12,15,18-hexathiacyclodocosane (22S6, see structure below) and 20S6 [37,38]. Upon coordination *via* all six sulfur donors, the macrocycle 22S6 will form two seven-membered and four five-membered chelate rings

while 20S6 forms two six-membered and four five-membered chelates. For comparison purposes, we have also attempted to prepare the isomeric 22S6 ligand, 1,4,8,12,15,19-hexathiacyclodocosane, which would form two five-membered and four six-membered chelate rings. However, we have not observed the formation of this hexathioether, either by direct synthesis or as a dimeric by-product in the formation of the eleven-membered ring trithioether [38]. In this account, we explore the coordination chemistry of both hexathia macrocycles with a wide variety of transition metal ions and examine the complexation behavior of the two systems. The sulfur atoms for crown thioether ligands such as 22S6 typically adopt an exclusive *exodentate* orientation. However, the crystal structures of 18S6 and 20S6 show different behavior [36-38]. In the 18S6 structure, two sulfur atoms of the macrocycles are *anti endodentate* while 20S6 has two *syn endodentate* sulfur atoms. These conformational distinctions will have important consequences for chelation of metal ions. Our study completes research into the coordination chemistry of a series of crown hexathioethers ranging from eighteen to twenty-four-membered rings.

2. EXPERIMENTAL

2.1 Materials.

All transition metal reagent salts were used as received without additional purification. The ligands 22S6 [38] and 20S6 [37] and the complex $[\text{Ni}(18\text{S6})](\text{picrate})_2$ [43] were prepared by the reported methods. Nitromethane and acetic anhydride were dried using common methods [59].

General Synthesis of Metal Complexes.

All of the first row transition metal complexes as well as the cadmium(II) complexes were prepared using the procedure of Rosen and Busch [60]. A solution of two equivalents of thioether ligand in anhydrous nitromethane was added to an anhydrous nitromethane solution of the hydrated metal salt (either tetrafluoroborate or perchlorate) containing six equivalents of acetic anhydride. *Caution!!!* Although the perchlorate and picrate salts prepared in this report do not appear to be shock-sensitive, they should be handled with caution and only in very small quantities. Both ruthenium complexes were prepared by the previously reported method [67].

2.2 Measurements.

Analyses were performed by Atlantic Microlab, Inc. of Atlanta, Georgia. Fourier transform infrared spectra were obtained using a Beckman FT 1100 infrared spectrophotometer. Solution ultraviolet-visible spectra were obtained on a Varian DMS 200 UV-visible 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 carbon-13 NMR spectra were obtained either on a Varian Gemini 300 MHz NMR spectrometer using

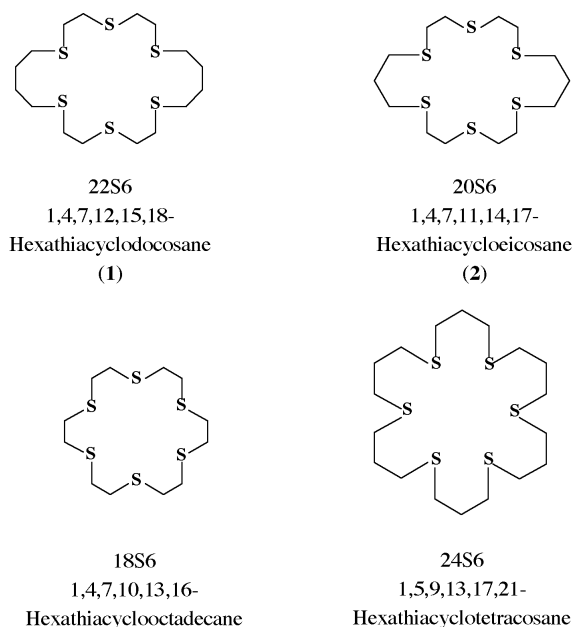


Figure 1

CD₃NO₂ for both the deuterium lock and reference or on a Bruker AF 200 MHz NMR spectrometer using D₂O or CD₃NO₂ as a solvent and TMS as an external reference. The electrochemistry of the complexes was studied using a Princeton Applied Research Versastat Polarographic Analyzer interfaced with an IBM/PC or a Bioanalytical Systems, Inc. CV-50W Potentiostat. Sample concentrations were 2 mM in CH₃NO₂ and a scan rate of 100 mV/sec was used except where noted. The supporting electrolyte was 0.1 M Bu₄NBF₄, 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/0.01 M Ag(I) non-aqueous pseudo-reference electrode.

2.3 Preparation of Metal Complexes of 1,4,7,12,15,18-Hexathiacyclodocosane (I).

1,4,7,12,15,18-Hexathiacyclodocosanenickel(II) Tetrafluoroborate (1a).

A solution of 1,4,7,12,15,18-hexathiacyclodocosane (I) (100 mg, 0.240 mmol) in 5 mL of nitromethane was prepared. To this was added with stirring a solution of Ni(BF₄)₂•6 H₂O (81.0 mg, 0.238 mmol) and acetic anhydride (147 mg, 1.44 mol, 0.14 mL) in 5 mL of anhydrous nitromethane. The color of the mixture changed immediately from green to purple. Addition of 5 mL of diethyl ether to the solution precipitated the complex. Under nitrogen, the precipitate was filtered and washed with 5 mL of ether and air-dried to give 68.3 mg (44.1 % yield) of (1,4,7,12,15,18-hexathiacyclodocosane)nickel(II) tetrafluoroborate as a blue-violet crystalline solid. Although solutions of the complex appear moderately stable to hydrolysis, the solid complex will immediately hydrolyze in air, yielding the free ligand. ir (KBr, cm⁻¹) 2993, 2948, 1446, 1412, 1150-1036 (s, BF₄⁻), 932, 913, 845, 792, 520. uv-vis (CH₃NO₂): λ_{max} 879 nm (ε=38 M⁻¹ cm⁻¹), 569 nm (ε= 37 M⁻¹ cm⁻¹). The effective magnetic moment was found to be 3.05 B.M. An irreversible oxidation wave is observed at an E_{1/2} value of +1140 mV vs. Fc/Fc⁺, and an irreversible reduction wave is observed at an E_{1/2} value of -40 mV vs. Fc/Fc⁺.

Anal. Calcd. for C₁₆H₃₂B₂F₈NiS₆: C, 29.61; H, 4.97; S, 29.63. Found: C, 29.48; H, 4.80; S, 29.50.

1,4,7,12,15,18-Hexathiacyclodocosaneruthenium(II) Perchlorate (1b).

The reagent μ-dichloro-bis(benzenechlororuthenium(II)) (60.0 mg, 0.120 mmol) was dissolved in 24 mL of methanol. Next, a 100 mg mass (0.240 mmol) of 1,4,7,12,15,18-hexathiacyclodocosane (I) was added, and the solutions were stirred for 24 hours. The reaction solution was then filtered to remove unreacted ligand. Sodium perchlorate (58.8 mg, 0.359 mmol) was then added to the reaction mixture, and a yellow precipitate formed immediately. The yellow solid was filtered, washed with 3 x 5 mL of ether to yield 54.1 mg (31.8 %) of 1,4,7,12,15,18-hexathiacyclodocosaneruthenium(II) perchlorate. ir (KBr, cm⁻¹): 2963, 2926, 1437, 1416, 1090 (s, b, ClO₄⁻), 928, 878, 850, 835, 804, 758, 731, 717, 676, 660, 622 (C-S), 563, 543, 512, 480, 446. Magnetic susceptibility measurements showed that the complex was diamagnetic. uv-vis (H₂O): λ_{max} 366 nm (ε = 737 M⁻¹ cm⁻¹), 322 nm (ε = 1190 M⁻¹ cm⁻¹).

Anal. Calcd. for C₁₆H₃₂Cl₂O₈RuS₆: C, 26.68; H, 4.50; S, 26.84; Cl, 9.89. Found: C, 26.51; H, 4.47; S, 26.90, Cl, 9.90.

1,4,7,12,15,18-Hexathiacyclodocosaneiron(II) Perchlorate (1c).

All manipulations were carried out under a nitrogen atmosphere. Under nitrogen, a mass of 1,4,7,12,15,18-hexathiacyclodocosane (I) (100 mg, 0.240 mmol) in 5 mL of CH₃NO₂ was added to a mass of Fe(ClO₄)₂•6H₂O (82.9 mg, 0.228 mmol) dissolved in 3 mL of CH₃NO₂ and 0.14 mL (1.37 mmol, 139 mg) acetic anhydride. Upon mixing the ligand dissolved, and the solution turned lavender. Crystals were obtained by the slow addition of ether (20 ml) to the solution. These were filtered and washed with 2 x 15 ml of ether and dried to give 35 mg (23 % yield) of (1,4,7,12,15,18-hexathiacyclodocosane)iron(II) perchlorate as a lavender crystalline solid. The solid is very sensitive to hydrolysis in the air and moderately sensitive in solution. The complex is diamagnetic. uv-vis (CH₃NO₂): λ_{max} 567 nm (ε=103 M⁻¹ cm⁻¹), 431 nm (ε= 107 M⁻¹ cm⁻¹). An irreversible oxidation wave is observed at an E_{1/2} value of -142 mV vs. Fc/Fc⁺.

Anal. Calcd. for C₁₆H₃₂Cl₂O₈FeS₆: C, 28.62; H, 4.80; S, 28.64; Cl 10.56. Found: C, 28.58; H, 4.97; S, 28.75; Cl, 10.77.

1,4,7,12,15,18-Hexathiacyclodocosanecobalt(II) Tetrafluoroborate (1d).

Under nitrogen, a mass of 1,4,7,12,15,18-hexathiacyclodocosane (I) (100 mg, 0.234 mmol) in 5 mL of CH₃NO₂ was added to a mass of Co(BF₄)₂•6H₂O (79.8 mg, 0.234 mmol) dissolved in 3 mL of CH₃NO₂ and 0.14 mL (1.37 mmol, 139 mg) acetic anhydride. Upon mixing the ligand dissolved, and the solution became purple. Purple crystals were obtained by slow diffusion of ether into the reaction solution. These were filtered and washed with 3 x 10 mL of ether to give 28 mg (18 % yield) of (1,4,7,12,15,18-hexathiacyclodocosane)cobalt(II) tetrafluoroborate a purple crystalline solid. However, the crystals are highly sensitive to hydrolysis to air and in solution. uv-vis (CH₃NO₂): λ_{max} 887 nm (ε = 127 M⁻¹ cm⁻¹), 514 nm (sh, ε = 241 M⁻¹ cm⁻¹). The effective magnetic moment was measured as 1.77 B.M. A quasi-reversible oxidation wave is observed at an E_{1/2} value of +195 mV vs. Fc/Fc⁺ while an irreversible reduction wave is observed at -752 mV vs. Fc/Fc⁺.

Anal. Calcd. for C₁₆H₃₂B₂F₈CoS₆: C, 30.11; H 3.32; S, 30.14. Found: C, 30.00; H, 3.33; S, 30.30.

1,4,7,12,15,18-Hexathiacyclodocosanecobalt(III) Perchlorate (1e).

Under nitrogen, a mass of 1,4,7,12,15,18-hexathiacyclodocosane (I) (100 mg, 0.240 mmol) in 5 mL of CH₃NO₂ was added to a mass of Co(BF₄)₂•6(H₂O) (78.0 mg, 0.229 mmol) dissolved in 3 mL of CH₃NO₂ and 0.14 mL (1.37 mmol, 139 mg) acetic anhydride. Upon mixing, the ligand dissolved and the solution became purple indicating formation of the above Co(II) complex. To this solution a mass of NOBF₄ (28 mg, 0.240 mmol) followed by tetrabutylammonium perchlorate (472 mg, 1.38 mmol) was added yielding a deep red solution. Crystals were obtained by the slow diffusion of ether into the reaction solution. These were filtered and washed with 3 x 15 mL of ether to give 51 mg (29 % yield) of (1,4,7,12,15,18-hexathiacyclodocosane)cobalt(III) perchlorate as red crystals. The crystals show moderate sensitivity to hydrolysis by air or in solution. ir (KBr) 2929, 2822, 1441, 1412, 1300, 1110-1075 (s, perchlorate), 624 cm⁻¹. uv-vis (CH₃CN): λ_{max} 528 nm (ε = 77 M⁻¹ cm⁻¹), 348 nm (ε = 137 M⁻¹ cm⁻¹), 249 nm (sh, ε = 1400 M⁻¹ cm⁻¹). The solid is diamagnetic. ¹H nmr (CD₃NO₂): δ 1.92 - 2.36

(br, 8 H), 3.13 - 3.26 (br, 8 H), and 3.49 - 3.99 (br, 16 H) ppm. $^{13}\text{C}\{^1\text{H}\}$ nmr (CD_3NO_2): δ 23.9 (s), 27.8 (s), 38.9 (s), 40.3 (s), 41.2 (s), 44.1(s), 45.4 (s) ppm.

Anal. Calcd. for $\text{C}_{16}\text{H}_{32}\text{Cl}_3\text{CoO}_{12}\text{S}_6$: C 24.83; H 4.17; S 24.85, Cl 13.77. Found: C, 25.00; H, 4.19; S, 25.00; Cl 13.88.

1,4,7,12,15,18-Hexathiacyclodocosanepalladium(II) Hexafluorophosphate (**1f**).

A mass of 1,4,7,12,15,18-hexathiacyclodocosane (**1**) (25.1 mg, 0.0602 mmol) was added to a solution of H_2O (2 mL) and methanol (2 mL). A mass of potassium tetrachloropalladate (19.6 mg, 0.0601 mmol) was added, and the solution was refluxed for 30 minutes. A yellow solution resulted which was filtered to remove a small amount of insoluble material, presumably unreacted ligand. A mass of ammonium hexafluorophosphate (19.6 mg, 0.120 mmol) was added to the yellow filtrate, which was then chilled overnight at 0 °C. A yellow precipitate formed which was filtered and then washed with methanol (2 x 10 mL) and ether (2 x 10 mL). Yellow crystals of 1,4,7,12,15,18-hexathiacyclodocosanepalladium(II) hexafluorophosphate (21 mg, 43.0 %) were obtained. The crystals had good stability in both solution and in the air. ir (KBr) 2991, 2979, 2993, 2881, 2852, 1452, 1415, 1291, 1349, 1216, 1113, 1016, 836 (s, PF_6^-), 739, 558 cm^{-1} . ^1H nmr (CD_3NO_2): δ 2.33 - 3.66 (br) ppm. $^{13}\text{C}\{^1\text{H}\}$ nmr (CD_3NO_2): δ 27.9 - 41.9 (br, m) ppm. uv-vis (CH_3CN): λ_{max} 371 nm ($\epsilon = 2810 \text{ M}^{-1} \text{ cm}^{-1}$), 269 nm ($\epsilon = 14,000 \text{ M}^{-1} \text{ cm}^{-1}$). In acetonitrile, the complex shows two irreversible reduction waves at -1408 mV vs. Fc/Fc^+ , and at -2106 mV vs. Fc/Fc^+ .

Anal. Calcd. for $\text{C}_{16}\text{H}_{32}\text{S}_6\text{PdP}_2\text{F}_{12}$: C, 23.62; H, 3.94; S, 23.67. Found: C, 23.54; H, 3.71; S, 23.51.

1,4,7,12,15,18-Hexathiacyclodocosanecadmium(II) Perchlorate (**1g**).

A mass of 1,4,7,12,15,18-hexathiacyclodocosane (**1**) (100.0 mg, 0.2399 mmol) was dissolved in 5 mL of CH_3NO_2 . A mass of $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (100.0 mg, 0.2384 mmol) was dissolved in 3 mL of CH_3NO_2 and 0.14 mL (0.137 mmol, 13.9 mg) acetic anhydride. Upon mixing the ligand completely dissolved indicating complexation. Colorless crystals were obtained by the slow diffusion of ether into the reaction solution. The crystals were filtered and washed with ether (3 x 15 mL) to give 1,4,7,12,15,18-hexathiacyclodocosanecadmium(II) perchlorate monohydrate in a 52.3 % yield (92.9 mg). The sample is quite stable in air or in solution. ir (KBr) 3557-3437 (broad, OH), 2924, 1429, 1417, 1215, 1124-1029 (s, perchlorate), 918, 627 (C-S) cm^{-1} . ^1H nmr (CD_3NO_2): δ 2.50 - 3.50 (br) ppm; $^{13}\text{C}\{^1\text{H}\}$ nmr (CD_3NO_2): δ 28.7(s), 30.2(s), 33.1(s), 33.8(s) ppm.

Anal. Calcd. for $\text{C}_{16}\text{H}_{34}\text{S}_6\text{CdCl}_2\text{O}_9$: C, 25.76; H, 4.59; S, 25.78, Cl, 9.50. Found: C, 25.81; H, 4.57; S, 25.69, Cl, 9.43.

2.4. Preparation of Metal Complexes of 1,4,7,11,14,17-Hexathiacycloeicosane (**2**).

1,4,7,11,14,17-Hexathiacycloeicosanenickel(II) Tetrafluoroborate (**2a**).

The perchlorate salt of the complex has been reported [21]. A mass of 1,4,7,11,14,17-hexathiacycloeicosane (**2**) (75.0 mg, 0.193 mmol) was added to a solution of $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (66.0 mg, 0.194 mmol) and acetic anhydride (119 mg, 1.16 mmol, 0.11 mL) in 5 mL of anhydrous nitromethane. The color of the mixture changed immediately from green to purple.

The reaction was stirred for one hour at which time all of (**2**) had reacted. The addition of 5 mL of diethyl ether precipitated the complex as a purple crystalline solid. The precipitate was washed with 3x 5 mL of ether and air-dried to give 104 mg (86.5 % yield) of (1,4,7,11,14,17-hexathiacycloeicosane)nickel(II) tetrafluoroborate as a purple crystalline solid. ir (KBr) 2993, 2948, 1446, 1412, 1150-1036 (s, BF_4^-), 932, 913, 845, 792, 520 cm^{-1} . uv-vis (CH_3NO_2): λ_{max} 833 ($\epsilon = 96 \text{ M}^{-1} \text{ cm}^{-1}$), 560 nm ($\epsilon = 72 \text{ M}^{-1} \text{ cm}^{-1}$). The equivalent conductivity in nitromethane measured using a 0.0010 M solution is $173 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. The effective magnetic moment was found to be 2.95 B.M. In nitromethane, the complex shows an irreversible oxidation wave at +1094 mV vs. Fc/Fc^+ , but no reduction waves are present.

Anal. Calcd. for $\text{C}_{14}\text{H}_{28}\text{B}_2\text{F}_8\text{NiS}_6$: C, 27.08; H, 4.54; S, 30.97. Found: C, 26.90; H, 4.55; S, 30.80.

1,4,7,11,14,17-Hexathiacycloeicosaneruthenium(II) Perchlorate (**2b**).

The reagent μ -dichloro-bis(benzenechlororuthenium(II)) (129 mg, 0.323 mmol) was dissolved in 6 mL of methanol, and the ligand 1,4,7,11,14,17-hexathiacycloeicosane (**2**) (250 mg, 0.643 mmol) was dissolved in 10 mL of methanol. The two solutions were mixed and allowed to react for one week at room temperature. Sodium perchlorate (157 mg, 1.28 mmol) was added to the filtrate which immediately formed a yellow precipitate. The yellow solid was filtered and washed with 3 x 5 mL of ether. The mass of the resulting bright yellow crystals of 1,4,7,11,14,17-hexathiacycloeicosaneruthenium(II) perchlorate was 239 mg (54.0 % mmol). The complex is very stable in air or in water. uv-vis (H_2O): λ_{max} 360 nm ($\epsilon = 725$), 322 nm ($\epsilon = 1435 \text{ M}^{-1} \text{ cm}^{-1}$), 233 nm ($\epsilon = 17,073 \text{ M}^{-1} \text{ cm}^{-1}$). ir (KBr, cm^{-1}) 2925, 1467, 1437, 1091(s, b, ClO_4^-), 930, 837, 758, 728, 716, 656, 622 (C-S), 559, 503. Magnetic susceptibility measurements showed that the complex was diamagnetic.

Anal. Calcd. For $\text{C}_{14}\text{H}_{28}\text{Cl}_2\text{O}_8\text{RuS}_6$: C, 24.41; H, 4.1; S, 27.92. Found: C, 24.31; H, 4.07; S, 27.79.

1,4,7,11,14,17-Hexathiacycloeicosanecadmium(II) Perchlorate Dihydrate (**2c**).

A mass of 1,4,7,11,14,17-hexathiacycloeicosane (**2**) (100 mg, 0.257 mmol) was dissolved in 5 mL of CH_3NO_2 . To this a solution of $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (103 mg, 0.246 mmol), 3mL of CH_3NO_2 , and 0.14 mL (0.137 mmol, 13.9 mg) acetic anhydride was added. Upon mixing, the ligand completely dissolved indicating complexation. Colorless crystals were obtained by ether diffusion into the reaction solution. These were filtered and washed with 3 x 15 mL of ether to give 88.5 mg (47.1% yield) of 1,4,7,11,14,17-hexathiacycloeicosanecadmium(II) perchlorate dihydrate as a colorless air-stable solid. ir (KBr, cm^{-1}) 3600-3400 (broad, OH), 2948, 2925, 1420, 1112-1087, (s, b, ClO_4^-), 926, 625 (C-S), 491. ^1H nmr (CD_3NO_2): 2.50-3.50 (br) ppm. $^{13}\text{C}\{^1\text{H}\}$ nmr (CD_3NO_2): 26.68 (s), 27.42(s), 28.03 (s) ppm.

Anal. Calcd. for $\text{C}_{14}\text{H}_{32}\text{Cl}_2\text{O}_{10}\text{CdS}_6$: C, 22.84; H, 4.38; S, 26.13; Cl, 9.63. Found: C, 23.18; H, 4.26; S, 26.31; Cl, 9.67.

Reaction between Copper(II) and 1,4,7,11,14,17-Hexathiacycloeicosane.

Under nitrogen a solution of $\text{Cu}(\text{BF}_4)_2 \cdot \text{X H}_2\text{O}$ (47.4 mg, 19.6 % Cu by weight, 0.146 mmol), acetic anhydride (0.0137 mL, 14.8 mg, 0.145 mmol), and 5 mL of anhydrous CH_3NO_2 was added dropwise to a solution of

1,4,7,11,14,17-hexathiacycloicosane (20S6) (**2**) (56.8 mg, 0.146 mmol) in 5 mL of anhydrous nitromethane. The mixture immediately turned dark green. No precipitate was observed. Several variations of crystallization were attempted, but none resulted in isolable crystals due to the sensitivity of the complex to hydrolysis. uv-vis (CH_3NO_2): λ_{max} 669 nm ($\epsilon = 23 \text{ M}^{-1} \text{ cm}^{-1}$), 407 nm ($\epsilon = 5180 \text{ M}^{-1} \text{ cm}^{-1}$). The complex shows no significant electrochemistry.

Results and Discussion.

General Syntheses.

Homoleptic complexes for the macrocycle 22S6 (**1**) with Ni(II), Fe(II), Co(II), Co(III), Cd(II), Ru(II), and Pd(II) have been synthesized and characterized by several methods including microanalysis. Similarly, new complexes of 20S6 (**2**) with Ni(II), Cd(II), Ru(II), and Cu(II) are also presented in this report. The magnetic moments for the Ni(II) complexes were in the range of 2.95–3.05 B.M., similar to previously reported values of hexakis(thioether) nickel(II) complexes and consistent with two unpaired electrons per nickel [9,51,61,62]. Magnetic susceptibility measurements on the 22S6 complexes of Fe(II) and Co(II) complexes show that both are low-spin complexes, and their absorption spectra (see below) are also consistent with low-spin systems. This is typical of the general complexation behavior of crown thioethers towards the two divalent metal ions in which low-spin states in octahedral complexes are invariably generated [14,15,52]. The d^6 ion Co(III) also forms a homoleptic complex with the 22S6 ligand, and the complex is readily prepared by oxidation of the related Co(II) complex. All of the 22S6 complexes with these ions are extremely sensitive towards solvolysis with anhydrous nitromethane being the only solvent of choice for stability.

In contrast to its behavior with Period 4 transition metal ions, the ligand 22S6 forms quite stable homoleptic complexes with later transition metal ions such as Ru(II), Pd(II), and Cd(II). Ruthenium(II) has been noted as the ideal ion for stabilizing hexakis(thioether) octahedral complexes of thioethers [25,39]. For several years our group and others have studied the complexation behavior of crown thioethers towards Pd(II) and Pt(II) and the unusual structural, spectroscopic, and electrochemical properties observed in these complexes [22,40,53]. Of particular interest is the influence and control of these unusual properties by changes in the ligand structure and conformation. The complex $[\text{Pd}(22\text{S6})](\text{PF}_6)_2$ is readily prepared by reaction of a tetrachloropalladate anion with one equivalent of 22S6. In the reaction, the 22S6 ligand displaces the chloride ions from the palladium ion, yielding the desired homoleptic complex. However, using the same procedure with tetrachloroplatinate as the metal source, we were not able to prepare a homoleptic complex, instead isolating a yellow solid that does not conform to any stoichiometry, but does incorporate chlorine. We have previously noted the reactivity difference between Pd(II) and Pt(II) with other crown thioethers including the related two isomeric 11S3 systems [63]. Both Cd complexes of 20S6 and 22S6 are isolated as hydrates, and the same phenomena has been seen in other Cd(II) complexes of crown thioethers [64].

3.2. Electronic Spectroscopy.

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: ${}^3A_{2g} \rightarrow {}^3T_{2g}$; ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$; ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$. However, the latter of these transitions is usually obscured in thioether complexes due to an intense sulfur-metal charge-transfer band. We observe the two low energy $d-d$ transitions for both Ni(II) complexes. Ligand field parameters have been calculated for the nickel(II) complexes, and these are shown in Table 1. Since the ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition is obscured, the value of B, the interelectronic repulsion parameter, is calculated as we have described in earlier reports [9].

Both 20S6 and 22S6 function as strong field ligands towards Ni(II). Among the five hexathioether macrocyclic complexes in Table 1, the value of Dq, the ligand field splitting, decreases with increasing ligand ring size; $\text{bzo}_2\text{-18S6} > 18\text{S6} > 20\text{S6} > 22\text{S6} > 24\text{S6}$. There is a successive 5–10 % drop in the ligand field strength as the macrocyclic ring gets progressively larger. These trends in field strength are related to the conformational preferences of the crown thioether, a relationship highlighted by other researchers and us [6,9,11]. In addition, the hexathioether complexes exhibit lower field strengths than the corresponding *bis* (trithioether) complexes (*i.e.*, $\text{bis}(11\text{S3}) > 22\text{S6}$), and the macrocyclic thioethers are stronger field ligands than their crown aza analogs. The nephelauxetic ratio, β , for the 20S6 and 22S6 complexes is consistent with other hexakis(thioether) complexes of Ni(II) and is relatively small with an average value near 0.7 indicating a large degree of metal-ligand orbital mixing. Interestingly, the stability towards hydrolysis for the hexathioether complexes parallels the observed ligand field strengths; the 18S6 complex being the most stable, the 20S6 complex being of moderate stability, and the 22S6 and 24S6 complexes are so sensitive to hydrolysis that they hydrolyze in moist air. To summarize, a larger macrocyclic ring exhibits a weaker ligand field strength and lower stability.

Low-spin d^6 Complexes Ru(II), Fe(II), and Co(III).

An octahedral complex containing a low-spin d^6 metal ion such as Ru(II), Fe(II), or Co(III) 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 three 22S6 complexes allowing the ligand field parameters, Dq and B, to be readily calculated as previously described [9]. The ligand field parameters for thioether complexes of the three metal ions are presented in Tables 2–4, respectively. As was observed for Ni(II), the 22S6 ligand functions as a strong field ligand towards all three ions, and the relative ordering of the ligand field strength for the hexathioethers remains the same. That is, one observed a weaker ligand field with increasing macrocycle size, $18\text{S6} > 20\text{S6} > 22\text{S6}$, and with a similar magnitude of decrease.

Two $d-d$ transitions are typically observed near 365 nm and 325 nm in all hexakis(thioether) ruthenium(II) complexes, and the new 22S6 and 20S6 complexes show similar behavior. With ruthenium, there is much less variation among the hexathioethers

with respect to their field strengths (only 5 % from highest to lowest). The relative ligand field strengths follow the noted trend, but the decrease is not as pronounced as with Fe(II) and Co(III). The relatively small value of B indicates a high degree of covalency between the ruthenium and sulfur bonds.

With respect to Fe(II) the 22S6 complex has a Dq value of 1850 cm^{-1} . Note that this value is lower than for the other hexathioether macrocycles, but it is still larger than for Fe(II) complexes of macrocyclic amines which indicates the strong ligand fields generated by crown thioethers in general [65]. The nephelauxetic ratio for the complex is approximately 0.40, consistent with other values for these types of complexes and again indicating a relatively large degree of metal-ligand orbital mixing for the thioether ligand [52]. Not surprisingly, the value of Dq has increased by about 1000 cm^{-1} when comparing the homoleptic Fe(II) complexes to the congeneric Ru(II) complex, but the value is still larger than those of the Ni(II) complex.

Unless obscured by charge transfer bands, two transitions are typically observed near 500 nm and 360 nm for all hexakis(thioether) cobalt(III) complexes, and these two are seen in the 22S6 complex. The 22S6 ligand functions as strong field ligands towards Co(III), but again is a weaker ligand compared to other hexathioether macrocycles. The Co(III) complex of 22S6 shows about a 1000 cm^{-1} increase in its ligand field, compared to the analogous Fe(II) complex, and 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. That is, there is a steady decrease in the ligand field strength as the ring size of the macrocycle increases. With respect to the four metal ions, the trend follows the order, Ru(II) > Co(III) > Fe(II) > Ni(II).

3.2.3. Other complexes.

The electronic spectra for the Co(II) complex of 22S6 shows two $d-d$ bands with transitions at 887 nm and 514 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 [14,54]. The calculated Dq value for the complexes is 1127 cm^{-1} , similar to the values reported for the *bis*(11S3) complexes, but less than for 20S6 and other trithioether ligands.

Due to their unusual elongated octahedral structure, homoleptic complexes of palladium(II) with the trithioethers 9S3 and 10S3 and the hexathioether 18S6 exhibit an unusual blue-green color. This color is due to a $d-d$ absorption near 600 nm. In contrast, the complex $[\text{Pd}(\text{22S6})]^{2+}$ is yellow in color, not blue-green, and shows an electronic spectrum containing only charge transfer bands. In this respect, the complex bears a strong resemblance to $[\text{Pd}(\text{20S6})]^{2+}$ which has been structurally characterized and shows no axial Pd-S interactions [53].

Electrochemical Studies.

The 22S6 ligand is electrochemically silent in the solvent nitromethane over the range of +1400 mV through -1000 mV. Likewise, the ligand 20S6 is also electrochemically silent in the same solvent over this range, but other workers have reported different behavior in acetonitrile [17]. The electrochemical data for the Ni(II) complexes with hexathioether macrocycles are summarized in Table 1. In each cyclic voltammogram, the three hexathioether Ni(II) complexes show a single irreversible

oxidation wave whose anodic half-wave potential varies somewhat with the identify of the ligand. These oxidation processes do appear to be metal based since the ligands do not exhibit electrochemical activity in this region. Therefore, this oxidation process is assigned to the oxidation of the Ni(II) center to Ni(III). There are several interesting differences in the electrochemical behavior of the Ni(II)-hexathioether complexes compared to those with the smaller trithioether complexes of 9S3 and 10S3 [10,13]. The oxidation to Ni(III) occurs less readily in the hexathioether complexes compared to trithioether complexes since the potentials are more positive. Also, all oxidations for the hexathioether complexes are irreversible while they are either reversible or quasi-reversible for the trithioether complexes. Furthermore, a reduction wave to Ni(I) is not usually observed for the hexathioether complexes in contrast to the 9S3 and 10S3 complexes which show this reduction. The electrochemical behavior of the hexathioether complexes can probably be explained by the fact that the hexathioether ligand is less able to expand and contract during the reduction and oxidation of the metal center and by the changes in bond distances that accompany these processes. The hexathioether ligand fully encapsulates the metal ion. In contrast, the two coordinated tridentate thioether ligands are better able to expand and contract around the metal and do not restrict the changes in bond length which accompany oxidation and reduction of the nickel(II) center.

The electrochemistry of the complex $[\text{Co}(\text{22S6})]^{2+}$ shows only a single, quasi-reversible oxidation wave at +0.19 V vs. Fc/Fc^+ , and an irreversible reduction wave at -0.752 V vs. Fc/Fc^+ . These are assigned as a Co(II)/Co(III) and a Co(II)/Co(I) couple, respectively, and the potentials and behavior of the waves are similar to other hexathioether complexes as shown in Table 4. As was observed for Ni(II), the oxidation waves occur at more positive potentials including a greater difficulty in forming Co(III) for the larger rings. The electrochemistry of the complex $[\text{Fe}(\text{22S6})]^{2+}$ shows only a single, irreversible oxidation wave at -0.142 V, indicating that the oxidation to Fe(III) occurs more readily than with the other Fe(II) complexes [52]. However, the complex is highly sensitive to hydrolysis which could be responsible for this value. The Cu(II) complex of 20S6 is electrochemically silent over the range studied in nitromethane in contrast to its reported behavior in water/methanol [66].

The electrochemical properties of the complex $[\text{Pd}(\text{22S6})]^{2+}$ contrast those of the analogous 9S3, 10S3, and 18S6 complexes [6,8]. While the latter three complexes show a reversible Pd(II)/Pd(III) oxidation wave near +0.60 V vs. Fc/Fc^+ , the 22S6 complex shows no oxidative electrochemistry whatsoever. Two irreversible reduction waves are observed at -1408 mV and -2106 mV which are assigned as the Pd(II)/Pd(I) and Pd(I)/Pd(0) couples, respectively. As noted in the spectroscopic properties of this complex, we believe the lack of Pd-S axial interactions precludes the unusual oxidative electrochemistry observed for small ring macrocycles, and in this regard, the 22S6 complex parallels the behavior of the 20S6 Pd(II) complex [53].

NMR

Proton NMR spectra for these types of complexes are often quite complex and have limited value for stereochemical assignments. The chemical shifts in the carbon spectra for all complexes are consistent with the exclusive presence of α -carbon

and β -carbon methylene resonances which are confirmed through a DEPT experiment. The ^{13}C NMR spectrum for $[\text{Pd}(\text{22S6})]^{2+}$ is complicated with many broad resonances observed. This is consistent with the presence of multiple stereoisomers, an observation that we have also seen in the 20S6 complex [53].

Conclusions.

We have prepared a series of complexes with a variety of transition metal ions involving the two crown hexathioethers 1,4,7,12,15,18-hexathiacyclodocosane (22S6) and 1,4,7,11,14,17-hexathiacycloeicosane (20S6). Both function as relatively strong field ligands, but their ligand field strengths fall between the stronger field and smaller ring trithioether ligands such as 18S6 and the larger ring and weaker field ligand, 24S6. Complexes of both ligands with first row transition metals are much more sensitive to solvolysis reactions than the corresponding 18S6 complexes, but complexes with later transition metals are relatively stable. Oxidations from the divalent to the trivalent state occur less readily than with smaller ring macrocycles. The complex $[\text{Pd}(\text{22S6})]^{2+}$ does not display the unusual spectroscopic and electrochemical properties observed in smaller ring Pd(II) complexes. The complex is brown, not blue-green in color, and its electronic spectrum is dominated by charge transfer bands. Furthermore, a Pd(II)/Pd(III) reversible couple is not observed electrochemically, but two irreversible metal-centered reductions are seen instead.

Acknowledgements.

This research was generously supported by grants from the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, and the Grote Chemistry Fund (UTC). We appreciate the assistance of UTC students Bruce McCosar and Jacob Forster with some of the spectroscopic measurements.

REFERENCES AND NOTES

- [1] J. S. Bradshaw and R. M. Izatt, *Acc. Chem. Res.*, **30**, 338 (1997).
- [2] R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christensen, and D. Sen, *Chem. Rev.*, **85**, 271 (1985).
- [3] R. M. Izatt, K. Pawlak, J. S. Bradshaw, and R. L. Bruening, *Chem. Rev.*, **91**, 1721 (1991).
- [4] R. M. Izatt, K. Pawlak, J. S. Bradshaw, and R. L. Bruening, *Chem. Rev.*, **95**, 2529 (1995).
- [5] A. J. Blake and M. Schröder, *Adv. in Inorg. Chem.*, **35**, 2 (1990).
- [6] S. R. Cooper, *Acc. Chem. Res.*, **21**, 141 (1988).
- [7] S. R. Cooper and S. C. Rawle, *Structure and Bonding (Berlin)*, **72**, 1 (1990).
- [8] M. Schröder, *Pure and Appl. Chem.*, **60**, 517 (1988).
- [9] W. N. Setzer, E. L. Cacioppo, Q. Guo, G. J. Grant, D. D. Kim, J. L. Hubbard, and D. G. VanDerveer, *Inorg. Chem.*, **29**, 2672 (1990).
- [10] K. Wieghardt, H.-J. Küppers, and J. Weiss, *Inorg. Chem.*, **24**, 3067 (1985).
- [11] G. J. Grant, C. D. Grant, and W. N. Setzer, *Inorg. Chem.*, **30**, 252 (1991).
- [12] H.-J. Küppers, A. Neves, C. Pomp, D. Ventur, K. Wieghardt, B. Nuber, and J. Weiss, *Inorg. Chem.*, **25**, 2400 (1986).
- [13] S. Chandrasekhar, and A. McAuley, *Inorg. Chem.*, **31**, 480 (1992).
- [14] J. R. Hartman, E. J. Hints, and S. R. Cooper, *J. Amer. Chem. Soc.*, **108**, 1208 (1986).
- [15] J. R. Hartman, E. J. Hints, and S. R. Cooper, *J. Chem. Soc., Chem. Commun.*, 386 (1984).
- [16] G. S. Wilson, D. D. Swanson, and R. S. Glass, *Inorg. Chem.*, **25**, 3827 (1986).
- [17] C. R. Lucas, S. Liu, and J. N. Bridson, *Can. J. Chem.*, **73**, 1023 (1995).
- [18] H.-J. Küppers, K. Wieghardt, B. Nuber, J. Weiss, E. Bill, and A. X. Trautwein *Inorg. Chem.*, **26**, 3762 (1987).
- [19] D. Reinen, A. Ozarowski, B. Jakob, J. Pebler, H. Stratemeier, K. Wieghardt, and I. Tolksdorf, *Inorg. Chem.*, **26**, 4010 (1987).
- [20] A. J. Blake, A. J. Holder, T. I. Hyde, Y. V. Roberts, A. J. Lavery, and M. Schröder, *J. Organomet. Chem.*, **323**, 261 (1987).
- [21] A. J. Blake, R. O. Gould, A. J. Holder, T. I. Hyde, A. J. Lavery, M. O. Odulate, and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 118 (1987).
- [22] G. J. Grant, K. A. Sanders, W. N. Setzer, and D. G. VanDerveer, *Inorg. Chem.*, **30**, 4053 (1991).
- [23] S. Chandrasekhar, and A. McAuley, *Inorg. Chem.*, **31**, 480 (1992).
- [24] A. J. Blake, R. O. Gould, A. J. Holder, T. I. Hyde, and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1861 (1988).
- [25] S. C. Rawle, R. Yagbasan, K. Prout, and S. R. Cooper, *J. Am. Chem. Soc.*, **109**, 6186 (1987).
- [26] A. J. Blake, J. A. Greig, A. J. Holder, T. I. Hyde, A. Taylor, and M. Schröder, *Angew. Chem., Int. Ed. Engl.*, **29**, 197 (1990).
- [27] S. R. Cooper, S. C. Rawle, R. Yagbasan, and D. J. Watkin, *J. Am. Chem. Soc.*, **113**, 1600 (1991).
- [28] S. O. Matondo, P. Mountord, D. J. Watkin, W. B. Jones, and S. R. Cooper, *J. Chem. Soc., Chem. Commun.*, 161 (1995).
- [29] R. A. Adams, W. Huang, and J. A. Queisser, *J. Am. Chem. Soc.*, **118**, 9442 (1996).
- [30] M. A. Bennett, L. Y. Goh, and A. C. Willis, *J. Am. Chem. Soc.*, **118**, 4984 (1996).
- [31] A. J. Welch and A. S. Weller, *Inorg. Chem.*, **35**, 4548 (1996).
- [32] K. Brandt and W. S. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1237 (1996).
- [33] J. Cannadine, A. Hector and A. F. Hill, *Organometallics*, **11**, 2333 (1992).
- [34] A. J. Blake, M. A. Halcrow and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 253 (1991).
- [35] K. Yamashita, K. Kurita, K. Ohara, K. Tamura, M. Nanog, and K. Tsuda, *Reactive and Functional Polymers*, **31**, 47 (1996).
- [36] R. E. Wolf, Jr., J. R. Hartman, J. E. Storey, B. M. Foxman, and S. R. Cooper, *J. Am. Chem. Soc.*, **109**, 4328 (1987).
- [37] W. N. Setzer, G. J. Grant, E. J. Meehan, S. Ahsahr, E. L. Forsythe, S. D. Lee, R. M. Kirk, Y. Tang, S.-Y. Liou, C. R. Yang, and C. K. Wu, *J. of Mol. Recog. and Inc. Phen.*, **35**, 649 (1999).
- [38] W. N. Setzer, S. Afshar, N. L. Burns, L. A. Ferrante, A. M. Hester, E. J. Meehan, G. J. Grant, S. M. Isaac, C. P. Laudeman, C. M. Lewis, and D. G. VanDerveer, *Heteroatom Chem.*, **1**, 375 (1990).
- [39] M. N. Bell, A. J. Blake, A. J. Holder, T. I. Hyde, and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 3841 (1990).
- [40] A. J. Blake, R. O. Gould, A. J. Lavery, and M. Schröder, *Angew. Chem., Int. Ed. Engl.*, **25**, 274 (1986).
- [41] J. R. Hartman and S. R. Cooper, *J. Am. Chem. Soc.*, **108**, 1202 (1986).
- [42] A. J. Blake, R. O. Gould, A. J. Holder, T. I. Hyde, and M. Schröder, *Polyhedron*, **8**, 513 (1989).
- [43] E. J. Hints, J. R. Hartman, and S. R. Cooper, *J. Am. Chem. Soc.*, **105**, 3738 (1983).

- [44] A. J. Blake, R. O. Gould, W.-S. Li, V. Lippolis, S. Parson, C. Radek, and M. Schröder, *Inorg Chem.*, **37**, 5070 (1998).
- [45] A. J. Blake, V. Lippolis, S. Parson, and M. Schröder, *Crystal Structure Commun.*, **57**, 36 (2001).
- [46] R. O. Gould, A. J. Lavery, and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1492 (1985).
- [47] A. J. Blake, R. O. Gould, A. J. Holder, A. J. Lavery, and M. Schröder, *Polyhedron*, **9**, 2919 (1990).
- [48] N. Galesic, M. Herceg, and D. Sedvic, *Acta Cryst.*, **C44**, 1405 (1988).
- [49] M. N. Bell, A. J. Blake, M. Schröder, and T. A. Stephenson, *J. Chem. Soc., Chem. Commun.*, 471 (1986).
- [50] A. J. Blake, R. O. Gould, S. Parson, C. Radek, and M. Schröder, *Angew. Chem, Int. Ed. Engl.*, **34**, 2374 (1995).
- [51] C. R. Lucas, S. Liu, and J. N. Bridson, *Can. J. Chem.*, **73**, 1023 (1995).
- [52] G. J. Grant, S. M. Isaac, W. N. Setzer, and D. G. VanDerveer, *Inorg. Chem.*, **32**, 4294 (1993).
- [53] G. J. Grant, N. J. Spangler, W. N. Setzer, and D. G. VanDerveer, L. F. Mehne, *Inorg. Chim. Acta*, **246**, 31(1996).
- [54] G. J. Grant, S. S. Shoup, C. E. Hadden, and D. G. VanDerveer, *Inorg. Chim. Acta*, **274**, 192 (1998).
- [55] D. P. Riley, and J. D. Oliver, *Inorg. Chem.*, **22**, 3361 (1983).
- [56] S. C. Rawle, J. R. Hartman, D. J. Watkin, and S. R. Cooper, *J. Chem. Soc., Chem. Commun.*, 1083 (1986).
- [57] R. Alberto, W. Nef, A. Smith, T. A. Kaden, M. Neuberter, M. Zehnder, A. Frey, U. Abram, and P. A. Schubiger, *Inorg. Chem.*, **35**, 3420 (1996).
- [58] A. J. Blake, W.-S. Li, V. Lippolis, A. Taylor, M. Schröder, *J. Chem. Soc., Dalton Trans.*, 2931 (1998).
- [59] W. L. Jolly, *The Synthesis and Characterization of Inorganic Compounds*; Prentice-Hall, Inc.: Englewood Cliffs: NJ, 1970; pp 116-121.
- [60] W. Rosen and D. H. Busch, *Inorg. Chem.*, **9**, 262 (1970).
- [61] S. R. Cooper, S. C. Rawle, J. R. Hartman, E. J. Hints, and G. A. Admans, *Inorg. Chem.*, **27**, 1209 (1988).
- [62] D. Sellman, H.-P. Neuner, and F. Knoch, *Inorg. Chim. Acta*, **190**, 61 (1991).
- [63] G. J. Grant, S. S. Shoup, C. L. Baucom, and W. N. Setzer, *Inorg. Chim. Acta*, **317**, 91 (2001).
- [64] W. N. Setzer, Y. Tang, G. J. Grant and D. G. VanDerveer, *Inorg. Chem.*, **30**, 3652 (1991); W. N. Setzer, Y. Tang, G. J. Grant and D. G. VanDerveer, *Inorg. Chem.*, **31**, 1116 (1992).
- [65] From Reference 10: The Dq value of $[\text{Fe}(\text{9N3})_2]^{2+}$ is 1675 cm^{-1} .
- [66] T. E. Jones, D. B. Rorabacher and L. A. Ochrymowycz, *J. Am. Chem. Soc.*, **97**, 7485 (1975).
- [67] G. J. Grant, B. M. McCosar, W. N. Setzer, J. D. Zubkowski and E. J. Valente, *Inorg. Chim. Acta.*, **244**, 73 (1996).
- [68] Unpublished results from our laboratories.