

Nickel(II) and Cobalt(II) Complexes of a New Sexadentate Macrocycle

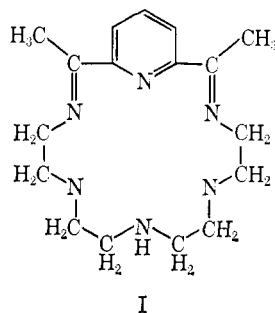
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Abstract: Nickel(II) and cobalt(II) complexes of the new macrocyclic sexadentate ligand, 12,13,26,27-tetrahydrotetrabenzo[*e,i,o,s*][1,4,11,14,7,18]tetrathiadiazacycloicosine (MAC) of the types $[M(\text{MAC})]X_2$ ($M = \text{Ni}$, $X = \text{ClO}_4, \text{I}$; $M = \text{Co}$, $X = \text{ClO}_4$) have been prepared. The complexes were initially prepared by reaction *in situ* of a solution of the appropriate metal salt with solutions of 1,2-bis(2-aminophenylthio)ethane and 1,4-bis(2-formylphenyl)-1,4-dithiabutane. Both nickel complexes are high spin, whereas the cobalt complex is low spin. For comparison, the high-spin nickel perchlorate complex of the related open-chain sexadentate, N,N' -[ethylenebis(thio-*o*-phenylenemethylidene)]bis[2-(methylthio)aniline], has also been prepared. Physical measurements indicate that in all the complexes the ligands are acting as sexadentate chelating agents.

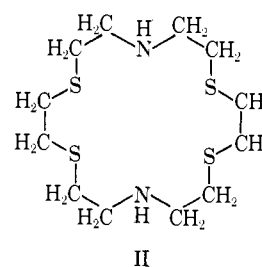
The metal complexes of a large number of quadridentate macrocycles have been synthesized, and most of these complexes have been investigated in considerable detail. In contrast, only a few complexes of macrocycles containing more than four donor atoms have been reported, and these have received less attention.^{1,2}

Condensation of 2,6-diacetylpyridine with tetraethylenepentamine in the presence of iron(II) yields an iron(III) complex of I.³ In this reaction the metal ion acts as a template for the condensation and thus discriminates against the formation of polymeric products. The ligand in this iron complex is probably

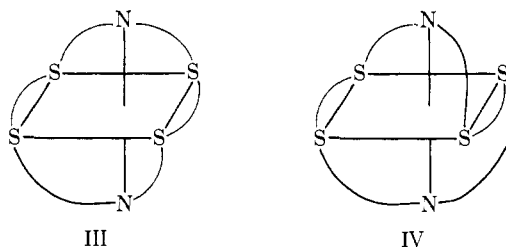


sexadentate; nevertheless, a molecular model indicates that such a six-coordinate structure is considerably strained unless the coordination polyhedron is an unusual one. In view of later studies on the iron(II) complex of a related pentadentate macrocycle,^{4,5} the disposition of donor atoms in the complex of I is probably not octahedral.

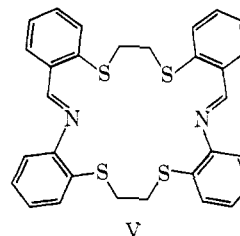
In a recent report,⁶ details of the preparation of nickel(II) and cobalt(II) complexes of II are given. If II coordinates simultaneously to all octahedral metal sites, then its flexibility permits two possible ligand configurations (III and IV). Although molecular models suggest that configuration IV allows the donor



atoms to position themselves more perfectly at the apices of an octahedron, less crowding of the ligand occurs in III. Thus no absolute assignments of the configurations of these chelates have yet been made.



We report here the syntheses of complexes of the macrocycle V (MAC) which, because of the planarity of each S-N-S section, can only coordinate about an octahedral metal ion in the configuration shown in IV. A molecular model confirms that the ligand can adopt this configuration without inducing undue strain into the



chelate rings. Thus in the complexes of V, the metal ion is surrounded in its equatorial plane by four thioether sulfur donors. In this respect the complexes of V are related to those of 1,4,8,11-tetrathiacyclotetradecane which have recently been prepared in these laboratories.⁷

(1) D. H. Busch, *Helv. Chim. Acta, Fasciculus Extraordinarius Alfred Werner*, 174 (1967), and references therein.

(2) N. F. Curtis, *Coord. Chem. Rev.*, 3, 3 (1968), and references therein.

(3) J. D. Curry and D. H. Busch, *J. Am. Chem. Soc.*, 86, 592 (1964).

(4) S. M. Nelson, P. Bryan, and D. H. Busch, *Chem. Commun.*, 641 (1966).

(5) E. Fleischer and S. Hawkinson, *J. Am. Chem. Soc.*, 89, 720 (1967).

(6) D. St. C. Black and I. A. McLean, *Chem. Commun.*, 1004 (1968).

(7) W. Rosen and D. H. Busch, *Chem. Commun.*, 148 (1969).

Table I. Colors, Infrared Data, Molar Conductances, and Magnetic Moments of the Compounds

Compound	Color	Infrared data, ^a cm ⁻¹		Molar conductances, ^b ohm ⁻¹ cm ² mole ⁻¹	Magnetic data		
		$\nu_{C=N}$ and aromatic ring vibrations	(ClO ₄)		$10^6 \chi_M'$	μ , BM	T , °K
[Ni(MAC)](ClO ₄) ₂	Brown	1600 s, 1585 m, 1575 m, 1560 s	1095 s, 625 s	182	4110	3.12	296
[Ni(MAC)]I ₂	Brown	1595 sh, 1590 s, 1575 m, 1560 w, 1550 m	...	166	3980	3.07	296
[Co(MAC)](ClO ₄) ₂	Dark brown	1590 m, 1580 s, 1575 m, 1560 w, 1550 s	1090 s, 620 s	178	1500	1.86	295
MAC	Yellow	1625 s, 1575 w, 1560 vw, 1550 w
[Ni(LS)](ClO ₄) ₂	Yellow-brown	1600 s, 1585 m, 1575 m, 1565 m	1095 s, 625 s	175	3970	3.08	298
LS	Yellow	1620 s, 1585 w, 1570 m

^a s, strong; m, medium; w, weak; sh, shoulder. ^b In CH₃NO₂ at 23°.

Results and Discussion

Complexes of I of the type [M(MAC)]X₂ (M = Ni, X = ClO₄, I; M = Co, X = ClO₄) have been prepared by reaction of solutions of 1,2-bis(2-aminophenylthio)ethane⁸ and 1,4-bis(2-formylphenyl)-1,4-dithiabutane with a solution of the appropriate metal salt.

The infrared spectra of the metal complexes show the absence of strong bands found at 3440, 3350 (ν_{N-H}),⁸ and 1675 cm⁻¹ ($\nu_{C=O}$) in the respective spectra of the amine and aldehyde reactants. In addition, the complexes have new bands in the region 1600–1550 cm⁻¹ which are due to $\nu_{N=C}$ of the Schiff base linkages (Table I). Each of the perchlorate complexes exhibits the ν_3 and ν_4 modes of the perchlorate group as single strong absorptions which are typical of complexes containing ionic perchlorates.⁹ The molar conductivities in nitromethane (Table I) of all the complexes indicate that they are 2:1 electrolytes.

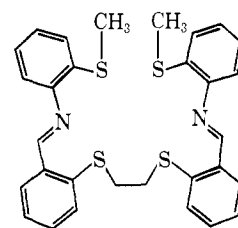
If [Ni(MAC)](ClO₄)₂ is heated in dimethylformamide, ligand displacement occurs and the free ligand precipitates from the solution as a highly crystalline yellow solid. The mass spectrum of this compound shows a peak at *m/e* 543 which corresponds to the monomeric parent ion for the macrocyclic ligand. Total elemental analyses confirm its composition, and its infrared spectrum is in accord with the proposed structure.

Reaction of the free macrocycle with nickel perchlorate in acetone leads to resynthesis of [Ni(MAC)](ClO₄)₂. The infrared spectrum of the complex prepared in this manner is identical with that of the product from the original preparation.

A related linear sexadentate ligand (VI; LS) was also prepared for comparison with V. Reaction of 2-methylthioaniline with an alcohol solution of 1,4-bis(2-formylphenyl)-1,4-dithiabutane yields VI as yellow crystals. The infrared spectrum of VI is quite similar to the spectrum of V and contains no bands which can be assigned to free amine or aldehyde. This ligand, which will also adopt configuration IV around an octahedral metal ion, is a new member of the family of linear sulfur-containing sexadentate ligands previously reported.^{8,10–16} However, it is

(8) R. D. Cannon, B. Chiswell, and L. M. Venanzi, *J. Chem. Soc., A*, 1277 (1967).

(9) B. J. Hathaway and A. E. Underhill, *ibid.*, 3091 (1961).



VI

the first example of such a ligand in which four of the six donor atoms are sulfur. Reaction of VI with nickel perchlorate in alcohol yields [Ni(LS)](ClO₄)₂ which is a 2:1 electrolyte in nitromethane. The infrared spectrum of this compound is very similar to that of the analogous compound of V.

All the nickel complexes are high spin (Table I) and have magnetic moments which are typical of pseudo-octahedral nickel with a ³A_{2g} ground state. The visible electronic spectra of the complexes [Ni(MAC)]X₂ (X = ClO₄, I) in nitromethane are virtually identical (Table II), which again indicates that the respective

Table II. Electronic Spectral Bands

Compound	Medium	Absorptions ^a
[Ni(MAC)](ClO ₄) ₂	CH ₃ NO ₂ Solid	12,700 (66) 13,200
[Ni(MAC)]I ₂	CH ₃ NO ₂ Solid	12,700 (69) 13,200
[Ni(LS)](ClO ₄) ₂	CH ₃ NO ₂ Solid	12,100 (76), 9400 sh br (10) 12,100, 9400 sh br
[Co(MAC)](ClO ₄) ₂	CH ₃ NO ₂ Solid	13,900 (258) 13,900

^a Sh, shoulder; br, broad. Molar extinction coefficients in parentheses. In addition to the bands listed here, all complexes exhibit strong absorptions above ~17,000 cm⁻¹ which extend well into the ultraviolet region.

(10) F. P. Dwyer and F. Lions, *J. Am. Chem. Soc.*, **69**, 2917 (1947); **72**, 1545 (1950).

(11) F. P. Dwyer, F. Lions, and D. P. Mellor, *ibid.*, **72**, 5037 (1950).

(12) F. P. Dwyer, N. S. Gill, E. C. Gyarfas, and F. Lions, *ibid.*, **74**, 4188 (1952); **76**, 383 (1954); **79**, 1269 (1957).

(13) F. Lions and K. V. Martin, *ibid.*, **80**, 3858 (1958).

(14) E. Suenaga, *J. Chem. Soc. Japan*, **80**, 500 (1959).

(15) F. Lions, *Record Chem. Progr.*, **22**, 69 (1961).

(16) L. F. Lindoy, S. E. Livingstone, T. N. Lockyer, and N. C. Stephenson, *Australian J. Chem.*, **19**, 1165 (1966).

anions are not involved in coordination. The solution spectrum of $[\text{Ni}(\text{MAC})]^{2+}$ shows the lowest energy absorption (ν_1) as a single broad band. The symmetrical nature of this band suggests that the spectrum is best interpreted on the basis of an O_h model. Although V contains heterodonor atoms, the electron delocalization associated with the conjugation in this ligand together with its steric properties apparently results in a ligand field which approximates O_h symmetry. The position of ν_1 (${}^3T_{2g} \leftarrow {}^3A_{2g}$) in the solution spectrum gives a $10Dq$ value for this ligand of $12,700 \text{ cm}^{-1}$. The positions of the ligand field bands ν_2 and ν_3 normally observed for nickel in an O_h field could not be determined for the present complexes owing to masking by intense absorptions which are present above *ca.* $17,000 \text{ cm}^{-1}$ in the spectra. The solid-state spectra are similar to the solution spectra, but the positions of the peak maxima are shifted slightly ($10Dq$ for $[\text{Ni}(\text{MAC})]^{2+}$ in the solid state is $13,200 \text{ cm}^{-1}$). Such shifts have been observed in many other systems and are very likely the result of crystal lattice effects. The value of $10Dq$ for $[\text{Ni}(\text{MAC})]^{2+}$ compared to that for $[\text{Ni}(2,2'\text{-dipyridyl})_3]^{2+}$ ($12,650 \text{ cm}^{-1}$)¹⁷ and $[\text{Ni}(\text{NO}_2)_6]^{4-}$ ($13,590 \text{ cm}^{-1}$)¹⁸ indicates that MAC falls between 2,2'-dipyridyl and NO_2^- in the spectrochemical series, and thus MAC must be considered to be a fairly strong field ligand.

The position of ν_1 in the solid and solution spectra of $[\text{Ni}(\text{LS})](\text{ClO}_4)_2$ gives a $10Dq$ value of $12,050 \text{ cm}^{-1}$ for this complex. Even though the compounds of V and VI have similar stereochemistries and the same types of donor functions, the ligand field exerted by the acyclic sexadentate ligand (VI) is slightly lower than that exerted by V. The greater field strength in the complexes of V most probably reflects the additional constraint imposed by this cyclic ligand on the positions of its donor atoms. Conceivably this restraint may result in a shortening of some or all of the metal-donor bond distances with a concomitant increase in the overall ligand field strength. Both in the solution and solid-state spectra of $[\text{Ni}(\text{LS})](\text{ClO}_4)_2$, ν_1 is less symmetrical and shows a distinct shoulder of low intensity at about 9400 cm^{-1} . This lower symmetry of ν_1 is consistent with a greater deviation from regular O_h symmetry in $[\text{Ni}(\text{LS})]^{2+}$ compared to $[\text{Ni}(\text{MAC})]^{2+}$. The positions of ν_2 and ν_3 in the solution and solid-state spectra again are masked by strong absorptions which occur above approximately $17,000 \text{ cm}^{-1}$ in both spectra.

The magnetic moment of the cobalt complex (Table I) is in the range 1.7–2.0 BM expected for spin-paired cobalt(II) in an octahedral field.¹⁹ Although the spin-free configuration is most common for octahedral cobalt(II) complexes, there are several complexes which appear to be completely spin paired at room temperature.²⁰ In addition, a large group of complexes have intermediate moments at room temperature; these moments have been rationalized in terms of thermal equilibria between the high- and low-spin states.^{21, 22}

(17) C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p 297.

(18) H. Elliott, B. J. Hathaway, and R. C. Slade, *Inorg. Chem.*, **5**, 669 (1966).

(19) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 12 (1954).

(20) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 192 (1964); R. L. Carlin, *Transition Metal Chem.*, **1**, 1 (1965).

(21) D. H. Busch in "Cobalt," R. S. Young, Ed., A.C.S. Mono-

graph Series, Reinhold Publishing Corp., New York, N. Y., 1960, Chapter 6.

The visible spectra of spin-paired cobalt(II) complexes have received little attention in the past.^{18, 23} Inspection of the Tanabe-Sugano diagram indicates that such a d^7 complex has a 2E_g (2G) ground state and in a regular octahedral field would be expected to give a single absorption (${}^2T_{2g}, {}^2T_{1g} \leftarrow {}^2E_g$) at an energy of the approximate value of $10Dq$ for the octahedral nickel(II) complex.^{18, 24} This absorption may or may not be split owing to spin-orbit coupling.²⁵ The spectrum of $[\text{Co}(\text{MAC})](\text{ClO}_4)_2$ is dominated both in solution and the solid state by a single absorption at $13,900 \text{ cm}^{-1}$ which is thus in the region expected for the ${}^2T_{2g}, {}^2T_{1g} \leftarrow {}^2E_g$ transition. However, apart from absorptions at higher energies which are assigned to charge-transfer transitions, the spectrum also has a very broad absorption of low intensity below $10,000 \text{ cm}^{-1}$ which extends well into the near-infrared region. Thus the spectrum cannot be satisfactorily interpreted on the basis of a simple octahedral model, and the lack of spectral assignments on other similar d^7 complexes makes further speculation about the band assignments for this complex inappropriate.

The equation which relates the equivalent conductivity (Λ_e) of a solution of an electrolyte to its equivalent concentration (C_{eq}) is

$$\Lambda_0 - \Lambda_e = B\sqrt{C_{eq}}$$

where Λ_0 is the equivalent conductivity at infinite dilution.²⁶ Both Λ_0 and B are characteristic of the particular type of electrolyte and both depend upon the charge on the respective ions in solution. In the case of $[\text{Co}(\text{MAC})](\text{ClO}_4)_2$ in acetonitrile, both the values of Λ_0 (184) and B (826) are typical of a 2:1 electrolyte in this solvent.^{27, 28} Some deviation from the usual linear relationship occurs at high dilutions. This may reflect an equilibrium involving the displacement of ligand by solvent.²⁷

In other *in situ* preparations of Schiff base metal chelates, the metal is known to act as a "template" for the condensation reaction.^{29, 30} Although it is possible that the metal ion undertakes a similar role in the present reaction, infrared evidence indicates that reaction of the two components of the macrocyclic ligand (V) in the absence of a metal ion apparently does lead to formation of V in appreciable amounts together with varying amounts of other products. Thus in the absence of kinetic studies, it is difficult to estimate the importance of the kinetic template effect in the promotion of this condensation reaction.

The complexes of V described here provide well-characterized examples of the rare class of macrocyclic complexes containing more than four donor atoms. In

graph Series, Reinhold Publishing Corp., New York, N. Y., 1960, Chapter 6.

(22) E. K. Barefield, S. M. Nelson, and D. H. Busch, *Quart. Rev.* (London), **22**, 457 (1968).

(23) K. G. Caulton and R. F. Fenske, *Inorg. Chem.*, **6**, 562 (1967).

(24) B. N. Figgis, "Introduction to Ligand Fields," Interscience Publishers, New York, N. Y., 1967, p 165.

(25) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., London, 1962, p 118.

(26) R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1967).

(27) A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, **6**, 458 (1967); F. A. Cotton, W. R. Robinson, R. A. Walton, and R. Whyman, *ibid.*, **6**, 929 (1967).

(28) A. L. Balch, I. G. Dance, and R. H. Holm, *J. Am. Chem. Soc.*, **90**, 1139 (1968).

(29) D. H. Busch, *Record Chem. Progr.*, **25**, 107 (1964).

(30) L. F. Lindoy, *Coord. Chem. Rev.*, **4**, 41 (1969).

addition, these complexes provide models in which some constraint is imposed on the positions of all six donor atoms about the metal ion. It is apparent that there is a need to synthesize similar complexes of other related macrocycles before useful generalizations can be made about the effects of this constraint on the physical properties of the resulting complexes. Further studies of this sort are at present being performed in these laboratories.

Experimental Section

Elemental analyses were determined by the Alfred Bernhardt Microanalytical Laboratory, West Germany. All chemicals were reagent grade. Conductivity measurements were obtained with an Industrial Instruments Inc. conductivity bridge using a cell with platinized electrodes. Electronic spectra were determined on a Cary Model 14 recording spectrometer. Infrared spectra were determined on a Perkin-Elmer Model 337 spectrometer using mineral oil or halocarbon oil mulls. Magnetic moments were determined by the Faraday method. Diamagnetic corrections were calculated from Pascal's constants. The mass spectrum was obtained using an MS-9 mass spectrometer.

Preparation of 1,4-Bis(2-formylphenyl)-1,4-dithiabutane. 1,4-Bis(2-carboxyphenyl)-1,4-dithiabutane (A) was prepared by the method of Livingstone,³¹ mp 299° (lit.³¹ 297°).

Conversion of A to 1,4-Bis(2-chlorocarboxylphenyl)-1,4-dithiabutane (B). A (54 g) was dried at 100°, powdered, and then treated with thionyl chloride (110 g). The resultant slurry was heated (under nitrogen) at the reflux temperature for 4 hr, and the HCl evolved was removed from the top of the condenser. Excess thionyl chloride was removed by vacuum distillation to yield crude B as a yellow solid.

Conversion of B to Its Bis-N-methylanilide Derivative (C). The entire yield from the above preparation was added to hot dioxane (500 ml, dried over molecular sieves), and the resulting suspension was slowly added to a stirred suspension of N-methylaniline (31 g) in 5% caustic soda solution (400 ml). After the addition of water (2 l.), the suspension was stirred for a further 12-hr period. The crude product was isolated by filtering, recrystallized from acetone, washed with ether, and dried *in vacuo* over P₄O₁₀; yield 35 g. A small amount of this product was further purified by recrystallization from acetone, mp 143°. *Anal.* Calcd for C₃₀H₂₈S₂O₂N₂: C, 70.3; H, 5.5; N, 5.5. Found: C, 70.3; H, 5.6; N, 5.6.

Conversion of C to 1,4-Bis(2-formylphenyl)-1,4-dithiabutane. To C (30 g) in tetrahydrofuran (500 ml, dried by refluxing over LiAlH₄) at 0° was added LiAlH₄ (3.2 g). The resulting suspension was contained in a flask fitted with a CaCl₂ outlet and allowed to stir at 0° for 17 hr. The solution was then hydrolyzed slowly with ice and poured into 6 l. of water. After acidification with hydrochloric acid, the solution and solid were stirred for 4 hr before isolation of the crude product which was purified by dissolving in acetone, adding a small amount of alcohol, and concentrating the solution; yield of white product, 6.0 g (34% based on C), mp 137°. *Anal.* Calcd for C₁₆H₁₄S₂O₂: C, 63.5; H, 4.7. Found: C, 63.5; H, 4.7.

12,13,26,27-Tetrahydrotrabenz[e,i,o,s][1,4,11,14,7,18]tetrathiadiazacycloeicosinenickel(II) Perchlorate. 1,2-Bis(2-aminophenylthio)ethane (1.06 g) and 1,4-bis(2-formylphenyl)-1,4-dithiabutane (1.16 g) were added to nickel perchlorate hexahydrate (1.4 g) in hot acetone (125 ml). The resulting solution was allowed to evaporate over several days during which time the crude product deposited as brown crystals, yield 2.7 g. A small amount was recrystallized

from nitromethane then dried *in vacuo* over P₄O₁₀. *Anal.* Calcd for NiC₃₀H₂₆N₂S₄(ClO₄)₂: Ni, 7.3; C, 45.0; H, 3.3; N, 3.5. Found: Ni, 7.5; C, 45.0; H, 3.5; N, 3.6.

12,13,26,27-Tetrahydrotrabenz[e,i,o,s][1,4,11,14,7,18]tetrathiadiazacycloeicosine. Some of the product (0.8 g) from the above preparation was heated in dimethylformamide (10 ml) on a steam bath for 1 hr. A color change from brown to green was observed and lustrous yellow crystals of the free macrocycle deposited. These were isolated by filtration, washed with alcohol and then ether, and dried *in vacuo* over P₄O₁₀, yield 0.5 g, mp >225°. *Anal.* Calcd for C₃₀H₂₆N₂S₄: C, 66.4; H, 4.8; N, 5.2; S, 23.6. Found: C, 66.2; H, 4.9; N, 5.3; S, 23.5.

Resynthesis of 12,13,26,27-Tetrahydrotrabenz[e,i,o,s][1,4,11,14,7,18]tetrathiadiazacycloeicosinenickel(II) Perchlorate from the Free Macrocylic Ligand. 12,13,26,27-Tetrahydrotrabenz[e,i,o,s][1,4,11,14,7,18]tetrathiadiazacycloeicosine (0.80 g) was added to nickel perchlorate hexahydrate (0.54 g) in hot acetone (500 ml). The solution was heated for 1.5 hr during which time the volume was reduced to 100 ml and brown crystals of the product formed. These were isolated by filtration, washed with acetone, and dried *in vacuo* over P₄O₁₀, yield 1.1 g. *Anal.* Calcd for NiC₃₀H₂₆N₂S₄(ClO₄)₂: Ni, 7.3; C, 45.0; H, 3.3; S, 16.0. Found: Ni, 7.2; C, 45.2; H, 3.5; S, 16.0.

12,13,26,27-Tetrahydrotrabenz[e,i,o,s][1,4,11,14,7,18]tetrathiadiazacycloeicosinenickel(II) Iodide. 1,2-Bis(2-aminophenylthio)ethane (1.38 g) and 1,4-bis(2-formylphenyl)-1,4-dithiabutane (1.50 g) were added to nickel iodide (1.55 g) in hot alcohol (400 ml). The solution was heated at reflux for 40 min and then cooled. The brown crystalline product was isolated by filtration, recrystallized twice from minimum amounts of boiling methanol, and dried *in vacuo* over P₄O₁₀, yield 1.7 g. *Anal.* Calcd for NiC₃₀H₂₆N₂S₄I₂: Ni, 6.9; C, 42.2; H, 2.8; N, 3.3. Found: Ni, 7.1; C, 42.1; H, 3.0; N, 3.2.

12,13,26,27-Tetrahydrotrabenz[e,i,o,s][1,4,11,14,7,18]tetrathiadiazacycloeicosinecobalt(II) Perchlorate. 1,4-Bis(2-formylphenyl)-1,4-dithiabutane (1.50 g) was added to cobalt perchlorate hexahydrate (1.83 g) in hot alcohol (200 ml). To this suspension was added 1,2-bis(2-aminophenylthio)ethane (1.38 g) in hot alcohol (100 ml). As the dialdehyde dissolved, the product formed as a dark brown crystalline solid. The resulting suspension was stirred vigorously and heated on the steam bath until the volume had been reduced to 200 ml. The product was isolated by filtration, washed with alcohol, and dried *in vacuo* over P₄O₁₀, yield 3.2 g. *Anal.* Calcd for CoC₃₀H₂₆N₂S₄(ClO₄)₂: Co, 7.4; C, 45.0; H, 3.3; N, 3.5. Found: Co, 7.2; C, 45.0; H, 3.5; N, 3.7.

N,N'-[Ethylenebis(thio-o-phenylenemethylene)]bis[2-(methylthio)aniline]. o-Methylthioaniline (1.11 g) was added to 1,4-bis(2-formylphenyl)-1,4-dithiabutane (1.11 g) in hot alcohol (170 ml). The resulting yellow solution was concentrated to 15 ml and let stand at 0°. The yellow product that formed was recrystallized from alcohol and dried *in vacuo* over P₄O₁₀, yield 1.2 g, mp 136°. *Anal.* Calcd for C₃₀H₂₈N₂S₄: C, 66.1; H, 5.2; N, 5.1. Found: C, 66.0; H, 5.0; N, 5.3.

N,N'-[Ethylenebis(thio-o-phenylenemethylene)]bis[2-(methylthio)aniline]nickel(II) Perchlorate. N,N'-[Ethylenebis(thio-o-phenylenemethylene)]bis[2-(methylthio)aniline] (0.81 g) in hot alcohol (20 ml) was added to nickel perchlorate hexahydrate (0.55 g) in hot alcohol (70 ml). The brown solution was concentrated to 20 ml and allowed to then stand. The yellow-brown crystals that formed were washed with alcohol and dried *in vacuo* over P₄O₁₀, yield 0.4 g. *Anal.* Calcd for NiC₃₀H₂₈N₂S₄(ClO₄)₂: C, 44.9; H, 3.5; N, 3.5; S, 16.0. Found: C, 44.8; H, 3.7; N, 3.5; S, 15.8.

Acknowledgment. This investigation was supported by U. S. Public Health Service Grant GM-10040 from the National Institute of General Medical Sciences.

(31) S. E. Livingstone, *J. Chem. Soc.*, 437 (1956).