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Cobalt(III) and Rhodium(III) Complexes of Cyclic Tetradentate Thioethers

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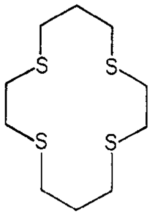
Received February 26, 1974 AIC40125R

A series of cobalt(III) complexes of the macrocyclic tetrathioether ligands 1,4,8,11-tetrathiacyclotetradecane (TTP) and 13,14-benzo-1,4,8,11-tetrathiacyclopentadecane (TTX) have been prepared and characterized. These are the first cobalt(III) species having four thioethers as donors and the first cobalt chelates having a macrocyclic tetradentate ligand with thioethers as the exclusive donors. The 14-membered ring, TTP, coordinates to cobalt(III) in a folded manner to give *cis*-$[Co(TTP)X_2]Y$ when X = Cl, Br, NCS, NO_2, and $^1/_2C_2O_4$ and is forced to coordinate with a planar array of the cyclic donor atoms when X = I to give *trans*-$[Co(TTP)I_2]B(C_6H_5)_4$. The 15-membered ring, TTX, coordinates to give *trans*-$[Co(TTX)X_2]Y$ when X = Cl and Br. The visible absorption spectra have been recorded and compared to the spectra of cobalt(III) tetraamine complexes. A few rhodium(III) complexes have also been prepared, notably $[Rh(TTP)X_2]X$, where X = Cl, Br, and I, $[Rh(TTP)Cl_2]Y$, where Y = BF_4 and $B(C_6H_5)_4$, $[Rh(TTX)Cl_2]Cl$, and a polymeric possibly dimeric complex $[Rh(TTP)Cl]_xCl_{2x}$. The macrocyclic ligands appear to coordinate to Rh(III) in a folded configuration. The ligand field strength of the thioether donors toward Rh(III) is comparable to that of secondary amines.

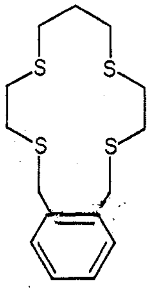
Introduction

Complexes of transition metals with several different types of synthetic macrocyclic tetradentate ligands have been described; however, metal chelates of macrocyclic ligands containing only thioethers as the exclusive donors have received attention only recently. Parallel to the initial studies of the new synthetic tetradentate nitrogen macrocycles which were dominated by nickel(II) derivatives, only the nickel(II) chelates of the macrocyclic tetradentate thioether ligands have thus far been reported.[1,2]

In this work a series of cobalt(III) derivatives of the ligands 1,4,8,11-tetrathiacyclotetradecane (TTP) and 13,14-benzo-1,4,8,11-tetrathiacyclopentadecane (TTX) have been prepared and characterized. Although examples of cobalt(II) complexes having four thioethers as donors have been reported,[3,4] these derivatives of TTP and TTX are the first cobalt(III) species having four thioethers as donors and the first cobalt chelates having a macrocyclic tetradentate ligand with thioethers as the exclusive donors.



TTP



TTX

Studies on metal chelates of several cyclic tetradentate ligands reported within the last decade have revealed the stereochemical consequences introduced by the size of the ring and the donor atom type in six-coordinate complexes. Macrocyclic ligands that are quite flexible coordinate in a folded manner when the metal ion is too large to be encompassed by them. This critical ring size occurs at different values for different sets of donor atoms and metal ions. In the case of four nitrogen donors in a fully saturated ring, House and Curtis[5] have shown that a 13-membered ring is capable of surrounding a first-row transition-metal ion while it has been shown by Collman and Schneider[6] that a 12-membered ring must fold. However, in the tetradentate macrocyclic ligands with the larger sulfur donors, it has been shown by Rosen and Busch[2] that the 13-membered ring, 1,4,7,10-tetrathiacyclotridecane, coordinates to nickel(II) in a folded manner, and the 14-membered ring, TTP, is required to encompass the metal ion.[1]

The results obtained in this work indicate that even the 14-membered ring of TTP is marginal in size for encompassing the first-row transition metals. The cobalt(III) complexes of the formula $[Co(TTP)X_2]^+$ contain folded TTP with the X groups mutually cis. The only cobalt(III) complex in which the ligand TTP encompasses the metal ion is the diiodo derivative. This indicates that the ring size of the ligand TTP is marginal for cobalt(III) and that the ligand is folded in all cases except when the X groups, such as the iodide ions, are too large to occupy the cis positions.

With the larger 15-membered tetradentate macrocyclic thioether ligand, TTX, only the trans cobalt(III) complexes have been characterized.

Rhodium(III) resembles cobalt(III) in its tendency to form numerous amine complexes, and the complexes of rhodium(III) with cyclic tetradentate nitrogen ligands such as 1,4,8,11-tetraazacyclotetradecane, cyclam,[7] and 1,4,7,10-tetraazacyclododecane, cyclen,[8] have been reported. Although there are many examples of rhodium complexes with ligands containing thioether donors reported in the literature, the new complexes described herein are believed to be the first rhodium complexes containing cyclic tetradentate thioether ligands. The rhodium(III) complexes of TTP all appear to contain the macrocyclic ligand coordinated in a folded manner giving rise to the *cis*-$[Rh(TTP)X_2]^+$ cationic species. It is interesting that without the restrictions which are imposed by the cyclic structure of TTP, only the trans complexes are obtained, *e.g.*, *trans*-$[Rh(DTH)_2X_2]^+$, where DTH is 2,5-dithiahexane.[9]

Results and Discussion

Syntheses of the Ligands. The tetradentate ligands were

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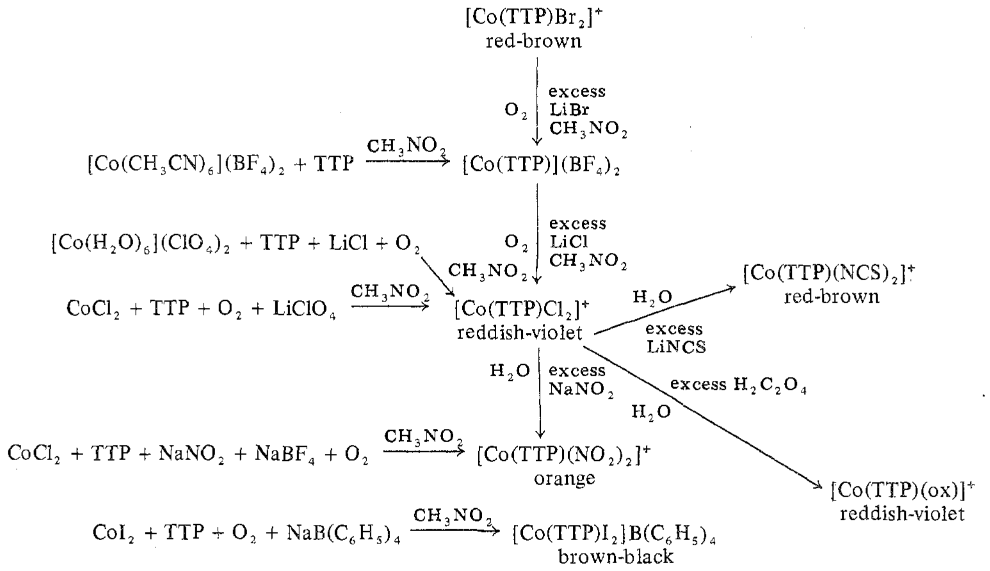

Figure 1. Preparation of cobalt(III) complexes of TTP.

synthesized according to published methods[1] with certain modifications to improve yield. Both ligands were made from the same precursor 1,4,8,11-tetrathiaundecane, TTU. Reaction of the dianion of TTU with the difunctional alkylhalides, 1,3-dibromopropane and α,α'-dibromo-*o*-xylene, yields the cyclic tetrafunctional ligands TTP and TTX, respectively. According to the original procedure for the preparation of TTP, the final ring-closing step gave a yield of 7.5%, and it was suggested that this low yield resulted from the competitive formation of polymeric materials. It has been shown in this investigation that the yield of the cyclic tetradentate ligands can be increased to 55% by performing the reactions at a much greater dilution of reactants.

Preparation of the Co(III) Complexes. Three general methods have been used in the preparation of the cobalt(III) compounds (Figure 1): (1) preparation and isolation of the cobalt(II) derivative of TTP with noncoordinating anions, reaction of this complex with coordinating anions, and then air oxidation; (2) reaction of a cobalt(II) salt, macrocyclic ligand, coordinating and/or noncoordinating anions, and air oxidation all in a one-step procedure; (3) exchange of acido groups of a previously isolated cobalt(III) complex for those of a more strongly coordinating anion by metathetical procedures.

Experience gained in the preparation of the nickel(II) derivatives of the cyclic thioether ligands[1,2] led to the selection of the complex $[Co(CH_3CN)_6](BF_4)_2$[3] as a starting material for the preparation of the cobalt complexes. This complex was prepared by the procedure of Hathaway, Holah, and Underhill,[10] and the coordinated acetonitrile molecules were found to be easily replaced by the thioether donors of the macrocyclic ligand when acetonitrile or nitromethane was used as the solvent, yielding the cobalt(II) complex $[Co(TTP)](BF_4)_2$. This cobalt(II) complex, like the nickel(II) derivatives, is very unstable toward dissociation to the free ligand and solvated metal ion in solvents with good class "a" donor properties, such as water and ethanol. Thus, any procedure in which cobalt(II) complexes are involved must be carried out in nitromethane, acetonitrile, or a similar solvent. In nitromethane, the complex is quite stable toward oxidation until coordinating anions are introduced into the system.

When lithium chloride was added to the red-brown nitromethane solution of $[Co(TTP)](BF_4)_2$ a very intense purple color developed almost immediately. After a few minutes of stirring while open to the air, the intense purple coloration gave way to a less intensely colored reddish violet. The cobalt(III) complex *cis*-$[Co(TTP)Cl_2]BF_4$ was precipitated from this solution by the addition of anhydrous ether. The bromide derivative, *cis*-$[Co(TTP)Br_2]BF_4$, was prepared in a similar manner. The hydrated cobalt(II) salts, $Co(BF_4)_2 \cdot 6H_2O$ and $Co(ClO_4)_2 \cdot 6H_2O$, can be used in the preparation of the cobalt(III) complexes of the tetradentate sulfur macrocycles if there is no need to isolate the $[Co(TTP)]^{2+}$ intermediate. In the preparation of complexes according to method 2, it was necessary to use the anhydrous cobalt(II) halides. The macrocyclic thioether ligand did not seem to be able to displace the water molecules from the coordination sphere of the cobalt(II) ion in the presence of halides, even though it could replace water from the hydrated cobalt(II) salts of such noncoordinating anions as ClO_4^- and BF_4^-.

Attempts to prepare the thiocyanato or isothiocyanato derivative by methods 1 and 2 failed to give the desired product. The thiocyanato ion readily displaced the macrocyclic ligand from the cobalt(II) complex to give insoluble materials containing the $Co(NCS)_4^{2-}$ species. The isothiocyanato derivative of TTP–cobalt(III) was isolated, however, by method 3. The thiocyanate ion did not displace the macrocyclic ligand from cobalt(III).

The cobalt(III) complexes of TTP, unlike those of cobalt(II), are stable against dissociation by all common solvents. The success of preparations using method 3 was dependent on the stability of the $[Co(TTP)X_2]^+$ species in water. There was no evidence of dissociation of the complexes to give free macrocyclic ligand even in boiling water. By dissolving either *cis*-$[Co(TTP)Cl_2]BF_4$ or *cis*-$[Co(TTP)Cl_2]ClO_4$ in boiling water and adding the appropriate anions for the desired metathesis, Br, NCS, NO_2, C_2O_4, etc., the various cobalt(III) derivatives could easily be prepared. The complexes were readily isolated by precipitating them from the aqueous solutions as their tetraphenylborate salts and recrystallization of these precipitated complexes from hot acetonitrile to give analytically pure crystalline products.

The complexes, *trans*-$[Co(TTX)Cl_2]ClO_4$ and *trans*-$[Co(TTX)Br_2]ClO_4$, were prepared, using method 1, by reacting $[Co(TTX)](ClO_4)_2$ with the respective lithium halides in

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nitromethane. Reaction of [Co(TTX)](ClO_4)$_2$ with lithium iodide led to the immediate precipitation of the cobalt(II) complex [Co(TTX)I_2]. Attempts to prepare other TTX cobalt(III) derivatives by method 3 failed, because the *trans*-[Co(TTX)Cl_2]$^+$ species was unstable in hot water and readily decomposed to the hydrated cobalt(II) salt and free macrocycle ligand, TTX.

Infrared Spectra of the Co(III) Complexes. The infrared spectra of the transition-metal complexes derived from the ligand TTP all have certain features in common that enable one to distinguish between the coordinated and free ligand. The most useful change is in the C-S-C stretching modes which occur in the cyclic sulfides in the 600-700-cm^{-1} region.[11] Coordination of the sulfur to a metal atom causes both a decrease in the frequency and a marked lowering of the intensity of these modes. These effects have been utilized to illustrate sulfur bonding in complexes containing thioxane[12] and pentamethylene sulfide.[13] The C-S-C stretching modes which appear as a very strong split band in the 675-689-cm^{-1} region of the infrared spectrum of the free ligand, TTP, have disappeared completely in the spectra of its metal ion derivatives.

The far infrared spectral region 600-250 cm^{-1} is useful in distinguishing between cis and trans isomers of complexes of the general formula MA_4Cl_2. For a cis octahedral structure, there should be two infrared active metal-chlorine stretching frequencies, while for a trans structure, only one frequency would be expected. Lewis, Nyholm, and Rodley[14] claim to have observed two metal-chloride frequencies for the complex *cis*-[Co(diarsine)$_2Cl_2$]ClO_4 but fail to report where these frequencies appear. For *trans*-[Co(diarsine)$_2$-Cl_2]ClO_4 these same authors report one absorption due to the metal-chlorine stretching frequency at 384 cm^{-1}.

The infrared spectra of *cis*-[Co(TTP)Br_2]BF_4 and *cis*-[Co(TTP)Cl_2]BF_4 in the far infrared region are shown in Figure 2. The spectrum of the chloro derivative contains two bands, 260 and 336 cm^{-1}, which are not present in that of the bromo derivative. The positions of these two bands compare well with the Co-Cl stretching frequencies found for a known sample of the complex *cis*-[Co(en)$_2Cl_2$]Cl (260 and 320 cm^{-1}) and this indicates that [Co(TTP)Cl_2]$^+$ has the cis structure. In both the TTP and ethylenediamine complexes there is an absorption located between the two frequencies given above. This can be assumed to involve the cobalt-sulfur and cobalt-nitrogen stretching frequencies, respectively.

The spectra of *trans*-[Co(TTX)Cl_2]ClO_4 and *trans*-[Co(TTX)Br_2]ClO_4 are also shown in Figure 2. The spectrum of the chloro derivative has a strong absorption at 383 cm^{-1} which is absent from the spectrum of the bromo derivative. This corresponds reasonably well to the absorption at 360 cm^{-1} in the case of *trans*-[Co(en)$_2Cl_2$]Cl and even more closely to the absorption at 384 cm^{-1} reported for *trans*-[Co(diarsine)$_2Cl_2$]Cl.[14] No band of so great an intensity is found for *cis*-[Co(TTP)Cl_2]BF_4.

Absorption bands at 1698, 1669, 1425, 1264, 787, and 543 cm^{-1} in the complex [Co(TTX)(ox)]ClO_4 have been assigned to the coordinated oxalate ion.[15] This indicates bidentate coordination of the oxalate anion and gives further proof that the macrocyclic ligand TTP coordinates in a folded manner in these cobalt(III) derivatives.

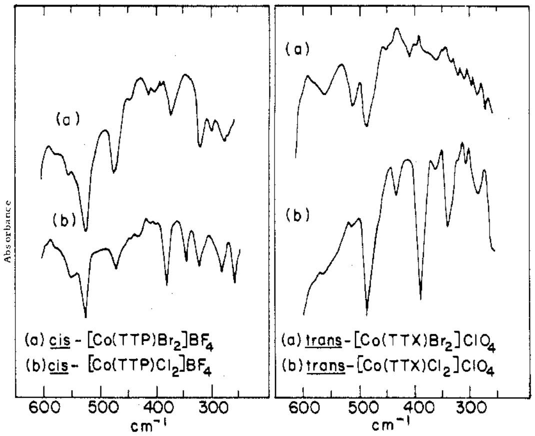

Figure 2. Far infrared spectra of Co(III) complexes of TTP and TTX.

Molar Conductances of the Co(III) Complexes. The molar conductance of the cobalt(III) complexes of TTP and TTX in nitromethane indicate that they are typical 1:1 electrolytes.[16] This is the behavior expected for a cobalt(III) complex which contains the four neutral donor atoms of the cyclic tetradentate ligand and two anionic donors filling the six coordination sites of the octahedrally coordinated cobalt(III) ion.

Magnetic Moments of the Co(III) Complexes. The magnetic moments calculated from the measured susceptibilities of the cobalt(III) complexes of TTP and TTX show that all the complexes are spin paired and exhibit only a small paramagnetism of the temperature-independent type. This supports the conclusion that the compounds contain cobalt in the 3$^+$ oxidation state.

Visible Absorption Spectra of the Co(III) Complexes. Many investigators have made use of visible and ultraviolet absorption spectra to compare the strengths of ligands and to establish the configurations of different isomers of pseudooctahedral tervalent cobalt complexes. The visible spectra of the cobalt(III) complexes of the cyclic tetradentate thioether ligands have been recorded and in the discussion which follows, these spectra are compared with the spectra of diacido tetraamine cobalt(III) complexes as reported in the literature. For an octahedral complex of cobalt(III), two bands, with maximum molar extinction coefficients of about 100 l. mol^{-1} cm^{-1}, are usually observed. These have been assigned to the spin-allowed transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ in the visible region and $^1A_{1g} \rightarrow {}^1T_{2g}$ in the near ultraviolet. For complexes of the type *trans*-[CoA_4X_2]$^{n+}$, with D_{4h} symmetry, the lower energy band splits into two components. For cis isomers of $CoA_4X_2{}^{n+}$ the overall splitting of the first band is always smaller than that for the corresponding band of the trans complex and it is often so small that only one band is observed experimentally.

Some of the spectra of the diacido-TTP-cobalt(III) are reproduced in Figure 3 and given in Table I. The spectra of these complexes can be divided into three groups according to the observed pattern of the bands. The complexes, [Co(TTP)X_2]$^+$ where X = Cl, Br, NCS, and $^1/_2C_2O_4$, all exhibit similar spectra with the first d-d band occurring at approximately 18,500 cm^{-1}. The second band can just barely be seen at approximately 24,000 cm^{-1} as a shoulder on an intense charge-transfer absorption that is centered at approximately 26,000-28,000 cm^{-1}.

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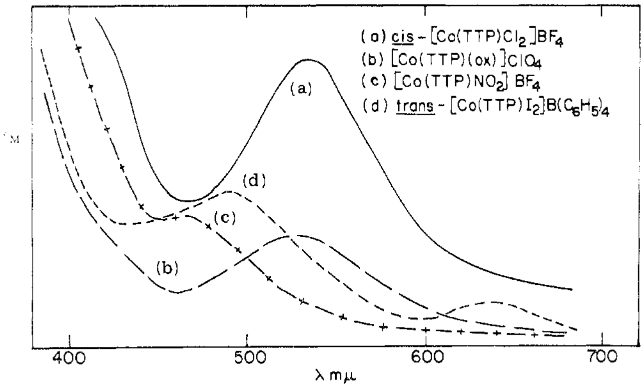

Figure 3. Visible spectra of (a) *cis*-$[Co(TTP)Cl_2]BF_4$, (b) $[Co(TTP)\cdot(ox)]ClO_4$, (c) $[Co(TTP)(NO_2)_2]BF_4$, and (d) *trans*-$[Co(TTP)I_2]B(C_6H_5)_4$.

Table I. Molar Conductances and Electronic Spectra[a] of Cobalt(III) TTP Complexes

Complex	λ_M[b]	Absorption bands (ν, cm^{-1})[c] CH$_3$OH	CH$_3$NO$_2$	Solid
cis-$[Co(TTP)Cl_2]BF_4$	95	18,690	18,760	18,520
		~23,800	~23,800	~23,300
		29,410		28,570
cis-$[Co(TTP)Br_2]BF_4$	92	18,180	18,180	18,180
				~21,700
		32,260		25,640
cis-$[Co(TTP)(NCS)_2]B(C_6H_5)_4$	69	18,520	18,520	18,520
		~23,800	~23,800	~22,700
		33,560		~33,300
cis-$[Co(TTP)(NO_2)_2]BF_4$	98	21,280	21,280	~20,800
				25,640
				29.850
trans-$[Co(TTP)I_2]B(C_6H_5)_4$	54	15,630	15,630	15,630
		20,410	20,410	~20,000
		30,490		

[a] The electronic spectra of other new cobalt complexes are given in Tables II and III. [b] All solutions about 10^{-3} *M* in nitromethane; in ohm^{-1} cm^2 mol^{-1}. [c] The extinction coefficient of the first absorption band in each of these complexes is given in Tables II and III.

The band maxima and extinction coefficients for the first transition are given in Table II. The new complexes are compared in this table with a series of *cis*-tetraamine complexes of cobalt(III). The positions of the band maxima for these tetrathioether complexes are close to those found for *cis*-tetraamine complexes[17-22] with the same respective acido ligands and differ greatly from those of the *trans*-tetraamine complexes[21,23,24] of cobalt(III) (Table III). This confirms the assignment of the cis structure to these complexes. A cis configuration must be assumed for $[Co(TTP)(ox)]ClO_4$ because of the bidentate nature of the oxalato ligand. The similarity of the visible absorption spectra of the other complexes to that of this complex further confirms the cis configuration.

The second spectral pattern is shown by the dinitro complexes. The spectral differences between *cis*- and *trans*-dinitro complexes of cobalt(III) is less clear-cut; however, the dinitro complexes prepared by metathesis on *cis*-$[Co(TTP)Cl_2]^+$ and by the other two methods all gave identical visible absorption spectra and all are assumed to be cis.

Table II. Comparison of the Electronic Spectra of a Series of *cis*-Tetraamine Complexes of Cobalt(III) with the *cis*-Tetrathioether Complexes of Cobalt(III)

Complex	Solvent	ν_1, cm^{-1} (ϵ)[a]	ν_2, cm^{-1} (ϵ)[a]	Ref
cis-$[Co(en)_2Cl_2]^+$	H_2O	18,870 (78)	26,320 (69)	17
cis-$[Co(trien)Cl_2]^+$	Dil $HClO_4$	18,550 (130)	26,250 (135)	18
cis-$[Co(cyclen)Cl_2]^+$	30% HCl	17,860 (185)	25,640 (165)	6
cis-$[Co(cyclam)Cl_2]^+$		17,920 (105)		19
cis-$[Co(TTP)Cl_2]^+$	CH_3NO_2	18,760 (654)	23,800 (?)	*b*
cis-$[Co(en)_2Br_2]^+$	H_2O	17,860 (110)		20
cis-$[Co(cyclen)Br_2]^+$	Concd HBr	17,540 (180)	25,640 (170)	6
cis-$[Co(TTP)Br_2]^+$	CH_3NO_2	18,180 (640)		*b*
$[Co(en)_2(C_2O_4)]^+$		20,000 (113)	28,170 (144)	21
$[Co(cyclen)(C_2O_4)]^+$	H_2O	19,230 (245)	27,400 (205)	6
$[Co(TTP)(C_2O_4)]^+$	CH_3NO_2	18,940 (579)		*b*
cis-$[Co(en)_2(NO_2)_2]^+$	H_2O	22,990 (182)		22
cis-$[Co(cyclen)(NO_2)_2]^+$	H_2O	22,470 (355)	31,250 (4460)	6
cis-$[Co(cyclam)(NO_2)_2]^+$		21,510 (279)		19
cis-$[Co(TTP)(NO_2)_2]^+$	CH_3NO_2	21,280 (814)		*b*
cis-$[Co(cyclam)(NCS)_2]^+$		19,610 (392)		19
cis-$[Co(TTP)(NCS)_2]^+$	CH_3NO_2	18,520 (840)	23,800 (?)	*b*

[a] 1. mol^{-1} cm^{-1}. [b] This work.

Table III. Comparison of the Electronic Spectra of a Series of *trans*-Tetraamine Complexes of Cobalt(III) with the *trans*-Tetrathioether Complexes of Cobalt(III)

Complex	ν_1, cm^{-1} (ϵ)[a]	ν_2, cm^{-1} (ϵ)[a]	Ref
trans-$[Co(en)_2Cl_2]^+$	16,200 (34)	25,800 (36)	21
trans-$[Co(cyclam)Cl_2]^+$	15,700 (31)	23,200 (41)	23
trans-$[Co(TTP)I_2]^+$	15,630 (820)	21,280 (3420)	*b*
trans-$[Co(TTX)Cl_2]^+$	15,870 (69)		*b*
trans-$[Co(TTX)Br_2]^+$	15,150 (80)		*b*

[a] 1. mol^{-1} cm^{-1}. [b] This work.

The third spectral pattern is shown by the complex $Co(TTP)I_2B(C_6H_5)_4$. This complex shows its first absorption maximum at 15,600 cm^{-1}. The position of this band is close to those found for the *trans*-tetraamine complexes of cobalt(III) (Table III) and corresponds to the lower energy component of the first spin-allowed ligand field band. The second component of this split band appears at 21,280 cm^{-1}. Using the crystal field model of Wentworth and Piper,[24] values of the spectral parameters are calculated: $Dq^{xy} = 2420$ cm^{-1}, $Dt = 545$ cm^{-1}, $Dq^z = 1465$ cm^{-1}. Comparison of the ligand field parameter Dq^{xy} for TTP with those for the *trans*-tetraamine complexes $[Co(NH_3)_4Cl_2]^+$,[24] $[Co(en)_2Cl_2]^+$,[25] $[Co(en)_2Br_2]^+$,[25] $[Co(1,4\text{-}CT)Cl_2]^+$,[26] and $[Co(1,7\text{-}CT)Br_2]^+$,[26] whose values are 2278, 2530, 2530, 2640, and

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2620 cm^{-1}, respectively, indicates that the thioether donor ligand can exert an in-plane ligand field strength similar to those of the nitrogen donor ligands.

The cobalt(III) derivatives of TTX, [Co(TTX)Cl$_2$]ClO$_4$, and [Co(TTX)Br$_2$]ClO$_4$, exhibit spectra similar to that found for *trans*-[Co(TTP)I$_2$]B(C$_6$H$_5$)$_4$, with the first component of the split band at 15,870 and 15,150 cm^{-1}, respectively. Unfortunately, the position of the second component of this spin-allowed transition is obscured by an intense charge-transfer transition and the calculation of ligand field parameters is not warranted. This problem is often encountered in the interpretation of the spectra of cobalt(III) complexes. It occurs, for example, among the diacidobis(diarsine)cobalt(III) complexes first studied by Dunn, Nyholm, and Yamada[27] and more recently by Feltham and Silverthorn.[28]

Comparison of the extinction coefficients for the series of cis complexes (Table II) shows that those of the cyclic thioether ligand are several times larger than those of the *cis*-tetraamines. This presumably reflects an increase in the covalent nature of the metal–ligand bond. Also, larger extinction coefficients for d–d transitions are predicted for cis isomers and this is borne out in the case of the TTP and TTX complexes: $\epsilon = 500$ to 800 l. mol^{-1} cm^{-1} for cis isomers and $\epsilon = 69$ amd 80 l. mol^{-1} cm^{-1} for trans isomers.

The molar extinction coefficients for the two bands of the complex *trans*-[Co(TTP)I$_2$]B(C$_6$H$_5$)$_4$ ($\epsilon = 820$ and 3420) are unusually high. This seems to be generally true among the Co(III) complexes that contain iodide ligands,[29] *e.g.*, [Co(diarsine)$_2$I$_2$]I[30] (ν_2, 20,830 cm^{-1}; $\epsilon = 4664$), and [Co(dmg)$_2$I$_2$][31] ($\nu_2 = 21{,}930$ cm^{-1}; $\epsilon = 7614$).

Synthesis of the Rh(III) Complexes. In contrast to the preparation of the TTP complexes of the first-row transition metals,[1,2] the rhodium(III) complexes of TTP can be prepared in almost any solvent in which the rhodium salt and the macrocyclic ligand are both soluble. However, the procedure used by Walton[9] in the preparation of the DTH complexes, employing boiling ethanol as the solvent, was found to be most satisfactory. [Rh(TTP)Cl$_2$]Cl and [Rh(TTP)Br$_2$]Br were prepared by adding the respective rhodium trihalides, dissolved in a minimum amount of hot water, to a boiling ethanol solution containing excess of the dissolved ligand. Complexation was fast as evidenced by the rapid disappearance of the deep red-brown color of the rhodium trihalide to give a clear yellow solution.

The complexes [Rh(TTP)I$_2$]I and [Rh(TTP)(NO$_2$)$_2$]B(C$_6$H$_5$)$_4$ were prepared by treating the rhodium trichloride solutions with excess lithium iodide or lithium nitrite, respectively, before complexation with the ligand TTP. All of the above complexes were readily obtained as crystalline products by reducing the volume of the solution in which they were formed and adding ether. [Rh(TTP)Cl$_2$]BF$_4$ was readily precipitated when tetrafluoroboric acid was added to an ethanol solution of [Rh(TTP)Cl$_2$]Cl.

In the preparations of the complexes described above, the necessity of using boiling alcohol cannot be overemphasized for the use of cold or even very warm solutions results in the formation of an insoluble precipitate which cannot be redissolved when the solution reaches the boiling point. In some preparations employing boiling ethanol, these precipitates were initially formed; however, their existence was only temporary, and they always redissolved in a short time and were converted to the desired complexes. Similar behavior was observed by Walton with the rhodium–DTH systems.[9]

Table IV. Physical Data for the New Rhodium(III) Complexes

Complex	Λ_M[a] (CH$_3$NO$_2$)	μ, BM	λ_{max}, nm (ϵ) (H$_2$O)
[Rh(TTP)Cl$_2$]Cl	74	0.34	350 (2,270) 320 sh (1,900) 252 (26,950)
[Rh(TTX)Cl$_2$]Cl	78		350 (1,935) 255 (20,300)
[Rh(TTP)Br$_2$]Br	78	0	370 (2,180) 245 (24,150)
[Rh(TTP)I$_2$]I	76	0.27	405 (2,460) 320 (8,550) 245 (22,550)
[Rh(TTP)(NO$_2$)$_2$]B(C$_6$H$_5$)$_4$	69	0.69	
[Rh(TTP)Cl$_2$]BF$_4$	79		
[Rh(TTP)Cl$_2$]B(C$_6$H$_5$)$_4$	65		

[a] Standard values for 1:1 and 2:1 electrolytes in nitromethane are approximately 80–95 and 160–190, respectively: T. D. Dubois and D. W. Meek, *Inorg. Chem.*, 8, 146 (1969).

Elemental analysis has shown that the insoluble precipitates have the same composition as the [Rh(TTP)X$_2$]X complexes. Since the infrared spectra of the chloro derivatives exhibit bands which have been assigned to the vibrations of bridging rhodium–chlorine–rhodium bonds, these precipitates can best be formulated as polymeric or dimeric products, [Rh(TTP)X]$_x$X$_{2x}$, with the rhodium–TTP species being held together with halogen bridges.

The molar conductances of the rhodium complexes of TTP are given in Table IV. Although the values are a little low, it is concluded that the complexes of rhodium(III) behave as 1:1 electrolytes. This is consistent with the tetradentate ligand occupying four of the six sites of the octahedral coordination sphere of rhodium(III). The magnetic moments for the rhodium(III) complexes of TTP given in Table I are consistent with the spin-paired d^6 electronic configuration of the metal ion.

Infrared Spectra of Rh(III) Complexes. The infrared spectra of the complexes [Rh(TTP)Cl$_2$]Cl, [Rh(TTP)Br$_2$]Br, and [Rh(TTP)I$_2$]I are identical in the region 4000 to 400 cm^{-1}. The spectrum of the so-called polymer [Rh(TTP)Cl]$_x$Cl$_{2x}$ is similar in this region but less sharp. The spectra of all these compounds show bands due to the coordinated ligand which are very similar to those seen for the cobalt(III) complexes of TTP.

Evidence for the cis structure of these rhodium(III) complexes derives from an examination of the rhodium–chlorine stretching frequencies in the far infrared region of the spectrum (600–250 cm^{-1}). Walton[9] examined the infrared spectra for the 2,5-dithiahexane complexes of rhodium(III) in this region and reported that the complex *trans*-[Rh(DTH)$_2$Cl$_2$]Cl displayed a sharp band at 362 cm^{-1} due to the *trans*-Cl–Rh–Cl stretching vibration.

The far infrared spectra of some of the rhodium complexes of TTP and TTX are shown in Figure 4. The absorptions due to the Rh–Cl stretching vibrations were assigned on the bases of a comparison of the spectra of the complexes [Rh(TTP)Cl$_2$]Cl, [Rh(TTP)Cl$_2$]BF$_4$, [Rh(TTP)Cl]$_x$Cl$_{2x}$, and [Rh(TTX)Cl$_2$]Cl with that of [Rh(TTP)Br$_2$]Br and those of the cobalt complexes discussed earlier.

All of the complexes show weak but sharp bands at approximately 362 cm^{-1}, at which position Walton had observed the strong absorption due to the rhodium–chlorine

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(27) T. M. Dunn, R. S. Nyholm, and S. Yamada, *J. Chem. Soc.*, 1564 (1962).

(28) R. D. Feltham and W. Silverthorn, *Inorg. Chem.*, 7, 1154 (1968).

(29) K. M. Long and D. H. Busch, in press.

(30) R. S. Nyholm, *J. Chem. Soc.*, 2071 (1950).

(31) A. V. Ablov, *Bull. Soc. Chim. Fr.*, 7, 151 (1940).

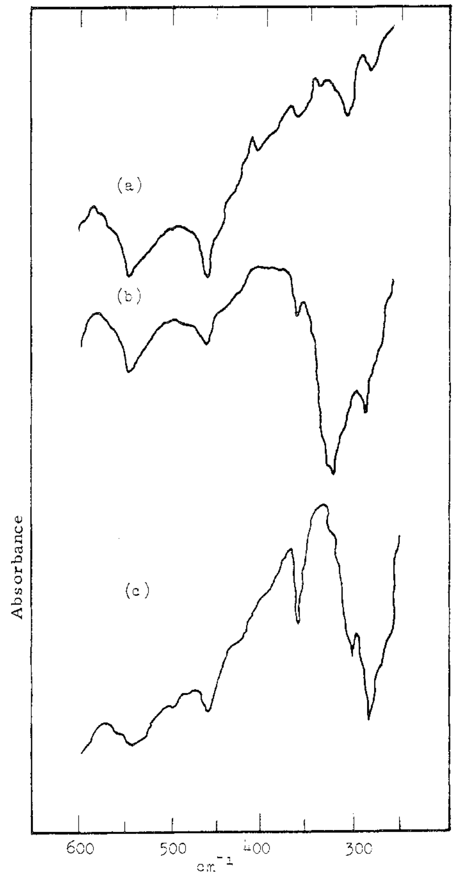
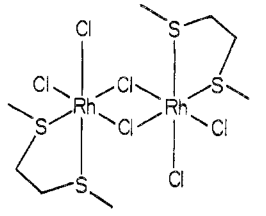


Figure 4. Far infrared spectra of (a) *cis*-[Rh(TTP)Br_2]Br, (b) [Rh(TTP)Cl]$_x$$Cl_{2x}$, and (c) *cis*-[Rh(TTP)$Cl_2$]Cl.

bond in *trans*-[Rh$(DTH)_2Cl_2$]Cl. However, since this band also appears in the spectrum of the bromide derivative of rhodium(III) (Figure 4a) and more clearly among the cobalt(III) complexes of TTP (Figure 2, especially 2a), the possibility that it is involved with a rhodium–chlorine stretch in the TTP complexes seems unlikely.

The complexes [Rh(TTP)Cl_2]Cl, [Rh(TTP)Cl_2]BF_4, and [Rh(TTX)Cl_2]Cl show strong absorption bands at 304 sh, 288 s; 308, 288; and 290, 280 cm^{-1}, respectively (see Figure 4c). From symmetry considerations two infrared active bands are expected for the *cis*-diacido configuration of an octahedral MY_4X_2 system, whereas, only one is expected for the trans complex. Thus, the appearance of two bands associated with the Rh–Cl_2 grouping in the infrared spectra of the above complexes is consistent with the presence of the cis isomer. It should be noted that a close correspondence exists between the bands assigned for the cis and trans isomers of the cobalt and rhodium complexes (trans: Co, 383 cm^{-1}; Rh, 362 cm^{-1}. cis: Co, 336 and 260 cm^{-1}; Rh, ~300 and 288 cm^{-1}).

The polymeric (or dimeric) complex of rhodium with TTP [Rh(TTP)Cl]$_x$$Cl_{2x}$, exhibits a strong band at 326 cm^{-1} with a weak band appearing on the low-energy side at 288 cm^{-1} (Figure 4b). Walton observed a similar pattern for the polymeric material [Rh(THD)Cl_3]$_n$ for which he assigned structure I. Though any structural assignment made for this complex must be viewed as speculative, structure II seems most reasonable and is consistent with the data cited.



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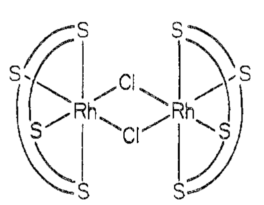

II

Electronic Spectra of Rhodium(III) Complexes of TTP and TTX. The two spin-allowed transitions, ${}^1T_{1g} \leftarrow {}^1A_{1g}$ and ${}^1T_{2g} \leftarrow {}^1A_{1g}$, are often observed in the spectra of pseudo-octahedral rhodium(III) complexes, but commonly the second band is obscured by charge-transfer absorptions.[32] In complexes where the second band is observed, its position is often shifted considerably by admixture with the charge-transfer transition.

By comparison of the wavelengths and molar extinction coefficients of the first absorption maxima of the electronic spectra of the complexes given in Table V, it becomes apparent that the trans isomers of rhodium tetraamines exhibit transitions of lesser energy and intensity than do those of the cis compounds. These two variations occur uniformly between the complexes TTP and DTH, thereby supporting the suggestion that Rh(DTH)X_2^+ are trans while Rh(TTP)X_2^+ are cis in configuration (compare data from Tables IV and V).

The spectra of the rhodium(III) complexes of TTP (Table IV) exhibit band maxima very similar to those of the cis rhodium tetraamine complexes which contain the same respective halides (Table V). The complexes *trans*-[Rh$(DTH)_2Cl_2$]$^+$ and *trans*-[Rh$(DTH)_2Br_2$]$^+$, on the other hand, exhibit band maxima (Table V) which are similar to those of the trans rhodium tetraamine complexes (Table V). It is remarkable that the tetradentate thioether and tetradentate nitrogen macrocyclic ligands result in crystal field splittings of almost equal energy.

Experimental Section

All the chemicals and solvents used were reagent grade except for the nitromethane (practical grade, Matheson Coleman and Bell) used when oxidizing the cobalt(II) solutions. Infrared spectra were recorded on Perkin-Elmer 337 and 457 recording infrared spectrophotometers. Visible and near infrared spectra were recorded on a Cary 14 spectrophotometer either on solutions or by diffuse transmittance on Nujol mulls. Chemical analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., or Alfred Bernhardt, Mikroanalytisches Laboratorium, 5251 Elbach uber Engelskirchen, West Germany. Conductivity measurements were obtained on ~10^{-3} *M* nitromethane or acetonitrile solutions at 25° in a standard 15 ml conductivity cell in conjunction with an Industrial Instruments conductivity bridge, Model RC 16B. Magnetic susceptibilities were measured by the Faraday method.[33]

Synthesis of Ligands. 1,11-Dioxa-4,8-dithiaundecane. Under an atmosphere of nitrogen, 11.5 g (0.5 g-atom) of sodium metal was dissolved in 500 ml of absolute ethanol. This mixture was heated gently and 27.0 g (0.25 mol) of 1,3-propanedithiol (Aldrich) was added slowly. To the resulting solution, 40.25 g (0.5 mol) of 2-chloroethanol (Eastman) was cautiously added, and the mixture was than refluxed for several hours. The mixture was cooled, and the sodium chloride which had formed during the reaction was removed by filtering. The ethanol was removed from the filtrate on a flash-evaporator leaving a thick colorless liquid which was then distilled at reduced pressure. After a small forerun, a thick viscous liquid was collected: bp 179–181° (0.5 mm), yield 45 g (92%).

1,4,8,11-Tetrathiaundecane (TTU). Into a 1-l. round-bottom flask were placed 39.0 g (0.2 mol) of 1,11-dioxa-4,8-dithiaundecane, 30.5 g (0.4 mol) of thiourea (Matheson), and 105 ml of concentrated hydrochloric acid, and the mixture was refluxed under nitrogen for 12 hr. The solution was then cooled, and 67 g (1.2 mol) of potassium hydroxide in 400 ml of water was added very cautiously. This mixture was refluxed and stirred for an additional 3 hr. The two-phase

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[32] S. A. Johnson and F. Basolo, *Inorg. Chem.*, 1, 925 (1962).

[33] L. F. Lindoy, V. Katovic, and D. H. Busch, *J. Chem. Educ.*, 49, 117 (1972).

Table V. Electronic Spectra of a Series of Cis and Trans Rhodium(III) Complexes

Complex	λ, nm	ε, l. cm^{-1} mol^{-1}	Ref
cis-[$Rh(cyclam)Cl_2$]$^+$	354, 299, 207	223, 308, 33,900	7
trans-[$Rh(cyclam)Cl_2$]$^+$	406, 310 sh, 242 sh, 204	78, 80, 3300, 37,100	7
cis-[$Rh(cyclam)Br_2$]$^+$	367, 309	243, 871	7
trans-[$Rh(cyclam)Br_2$]$^+$	429, 285, 235	97, 2520, 34,600	7
cis-[$Rh(cyclam)I_2$]$^+$	407, 295 sh, 260 sh, 228	1210, 5300, 17,500, 38,400	7
trans-[$Rh(cyclam)I_2$]$^+$	515 sh, 466, 353, 275, 266	64, 204, 13,100, 34,500, 22,800	7
cis-[$Rh(en)_2Cl_2$]$^+$	352, 295	155, 180	32
trans-[$Rh(en)_2Cl_2$]$^+$	406, 286	75, 130	32
cis-[$Rh(en)_2Br_2$]$^+$	362, 276	210, 900	32
trans-[$Rh(en)_2Br_2$]$^+$	425, 276, 231	100, 2300, 30,800	7
cis-[$Rh(en)_2I_2$]$^+$	375	1200	32
trans-[$Rh(en)_2I_2$]$^+$	462, 340, 269, 222	260, 14,300, 31,000, 20,000	32
cis-[$Rh(trien)Cl_2$]$^+$	352	250	32
cis-[$Rh(cyclen)Cl_2$]$^+$	365	535	8
trans-[$Rh(NH_3)_4Cl_2$]$^+$	412	66	8
trans-[$Rh(DTH)_2Cl_2$]$^+$	431, 354, 266, 219	190, 300	9
trans-[$Rh(DTH)_2Br_2$]$^+$	455, 366, 263, 227		9

system which resulted was cooled and separated, and the upper aqueous layer was acidified with dilute hydrochloric acid and extracted with 200 ml of chloroform. The chloroform layer was combined with the oily organic layer from the reaction mixture, and this solution was dried over anhydrous magnesium sulfate (Mallinckrodt). The dried chloroform was removed on the flash-evaporator leaving a thick liquid which was then distilled. The fraction boiling between 145 and 180° (0.5 mm) was collected and then redistilled to give the desired product: bp 159–161° (0.5 mm), yield 28 g (60%).

1,4,8,11-Tetrathiacyclotetradecane (TTP). In 1500 ml of absolute ethanol, under nitrogen, 2.02 g (0.088 g-atom) of sodium metal was dissolved. To this solution, 10 g (0.44 mol) of 1,4,8,11-tetrathiaundecane was slowly added, and the mixture was refluxed gently. To the resulting mixture, 8.88 g (0.044 mol) of 1,3-dibromopropane (Eastman) diluted to a total volume of 250 ml with absolute ethanol was added very slowly (3 hr) while continuing the gentle reflux. After the addition, the mixture was stirred under reflux for an additional hour. The mixture was then allowed to cool, and the ethanol was removed on a rotary evaporator. The residual solid was washed with water to remove the sodium bromide which had formed during the reaction and dried *in vacuo* to remove any remaining water. The desired product was then sublimed from the white materials at 0.5 mm and 110° to give a white solid, mp 119–120°. Recrystallization of this solid from ethanol gave beautiful white needles with the same melting point. The product was identified by its infrared spectrum and melting point which showed it to be identical with a previously prepared sample of known composition. Therefore elemental analysis was not performed. The yield under these conditions averaged about 55% for several runs.

13,14-Benzo-1,4,8,11-tetrathiacyclopentadecane (TTX). A procedure similar to that given above for TTP was employed using the appropriate mole ratio of α,α'-dibromo-*o*-xylene (Eastman) in place of the 1,3-dibromopropane. Unlike TTP, this ligand was purified by repeated recrystallization from absolute ethanol. Its purity was checked by comparing its infrared spectrum and melting point with those of a known sample.

Preparation of Cobalt Derivatives. Hexaacetonitrilecobalt(II) Tetrafluoroborate. This starting material was prepared by stirring metallic cobalt pellets (excess) with nitrosyl tetrafluoroborate (2.0 g) in acetonitrile (50 ml) as reported by Hathaway, Holah, and Underhill.[10] The reaction system was kept free of the evolving nitric oxide by continuous evacuation. After all the nitrosyl tetrafluoroborate had reacted (approximately 2 hr), the solution was filtered to remove the excess cobalt. The orange filtrate was concentrated, and anhydrous ether was added. The orange crystalline product which separated was isolated by filtration and used in the preparation that follows.

1,4,8,11-Tetrathiacyclotetradecanecobalt(II) Tetrafluoroborate. $[Co(CH_3CN)_6](BF_4)_2$ was stirred with an excess of the ligand TTP in nitromethane. The red-brown solution was filtered, and ether was added. The red-brown microcrystalline product which separated was isolated by filtration, washed with ether, and dried.

Anal. Calcd for $[Co(C_{10}H_{20}S_4)](BF_4)_2$: C, 23.97; H, 4.02; S, 25.60. Found: C, 24.20; H, 4.13; S, 25.78.

***cis*-Dichloro(1,4,8,11-tetrathiacyclotetradecane)cobalt(III) Tetrafluoroborate.** A solution of $[Co(TTP)](BF_4)_2$ in nitromethane was stirred in an Erlenmeyer flask open to air with excess lithium chloride for 5 hr. During this time the color of the solution changed almost immediately from a red-brown to an intense purple and then more slowly to a reddish violet. The solution was filtered and concentrated, and ether was added. The product separated as red-violet microcrystals which were isolated by filtration, washed with ether, and recrystallized by redissolving in a minimum of hot nitromethane, cooling to approximately room temperature, adding a few milliliters of ether, and cooling in the refrigerator.

Anal. Calcd for $[Co(C_{10}H_{20}S_4)Cl_2]BF_4$: C, 24.75; H, 4.15; Cl, 14.61. Found: C, 24.72; H, 4.07; Cl, 14.29.

***cis*-Dibromo(1,4,8,11-tetrathiacyclotetradecane)cobalt(III) Tetrafluoroborate.** This complex was prepared by the same procedure as that used for the chloro derivative, substituting lithium bromide for lithium chloride. A dark red-brown microcrystalline product was isolated.

Anal. Calcd for $[Co(C_{10}H_{20}S_4)Br_2]BF_4$: C, 20.92; H, 3.51; Br, 27.83. Found: C, 21.16; H, 3.69; Br, 27.68.

***trans*-Diiodo(1,4,8,11-tetrathiacyclotetradecane)cobalt(III) Tetraphenylborate.** Anhydrous cobalt(II) iodide was stirred with an equimolar amount of the ligand TTP in nitromethane. The initially formed cobalt complex, containing the tetrahedral species CoI_4^{2-} as the anion, was precipitated from solution by addition of ether and isolated by filtration. The excess ligand remained in solution. The complex was then redissolved in nitromethane and allowed to stand exposed to the air for a few days. Sodium tetraphenylborate was added to the oxidized cobalt solution, and the product was precipitated by the addition of ether. The complex was recrystallized from hot acetonitrile to give glistening black needles.

Anal. Calcd for $[Co(C_{10}H_{20}S_4)I_2]B(C_6H_5)_4$: C, 45.35; H, 4.47; I, 28.18. Found: C, 45.42; H, 4.59; I, 28.40.

***cis*-Dichloro(1,4,8,11-tetrathiacyclotetradecane)cobalt(III) Perchlorate.** Either cobalt(III) perchlorate hexahydrate and excess lithium chloride or anhydrous cobalt(II) chloride and excess lithium perchlorate were stirred together with a slight molar excess of the ligand TTP in nitromethane for 5 hr. The resulting solution was filtered and ether was added to the filtrate. The reddish violet complex which separated was isolated by filtration, dried, and used to prepare other cobalt(III) derivatives as given below.

***cis*-Diisothiocyanato(1,4,8,11-tetrathiacyclotetradecane)cobalt(III) Tetraphenylborate.** A solution of *cis*-$[Co(TTP)Cl_2]ClO_4$ and excess sodium thiocyanate in water was stirred and refluxed for 2 hr. The mixture was filtered while hot, and sodium tetraphenylborate was added. The complex separated immediately and was isolated by filtration, washed with water, and air dried. Recrystallization from hot acetonitrile yielded red-brown needles.

Anal. Calcd for $[Co(C_{10}H_{20}S_4)(NCS)_2]B(C_6H_5)_4$: C, 56.67; H, 5.28; N, 3.67. Found: C, 56.61; H, 5.40; N, 3.50.

Oxalato(1,4,8,11-tetrathiacyclotetradecane)cobalt(III) Perchlorate. A solution of *cis*-$[Co(TTP)Cl_2]^+$ (0.001 mol) and sodium oxalate (0.001 mol) in 75 ml of water was stirred and refluxed for 2 hr during which time the color of the solution turned a brighter red. The mixture was filtered while hot, and the water was removed by evaporation. The complex was recrystallized by redissolving the solid in a minimum amount of cold nitromethane and adding ether. The reddish violet microcrystalline product was isolated by filtration, washed with ether, and dried.

Anal. Calcd for $[Co(C_{10}H_{20}S_4)C_2O_4]ClO_4$: C, 27.99; H, 3.91; S, 24.91. Found: C, 27.60; H, 3.87; S, 24.40.

***cis*-Dinitro(1,4,8,11-tetrathiacyclotetradecane)cobalt(III) Tetrafluoroborate. Method 1.** Anhydrous cobalt(II) chloride (0.001 mol), sodium nitrite (0.003 mol), sodium tetrafluoroborate (0.002 mol), and an excess of ligand TTP (0.3 g, 0.00112 mol) were stirred together in nitromethane (50 ml) for about 4 hr. The resulting mixture was filtered giving an orange filtrate which was concentrated to about 10 ml. Upon addition of ether, an orange microcrystalline product separated. The complex was purified by recrystallization from a minimum amount of hot acetonitrile.

Method 2. *cis*-$[Co(TTP)Cl_2]BF_4$ was dissolved with stirring in hot water, and an excess of sodium nitrite was added. The dark red-violet solution, which turned orange almost immediately, was allowed to boil for 30 min. The solution was then cooled and filtered, and the water was removed by evaporation. The orange microcrystalline product was purified by recrystallization from hot acetonitrile.

Anal. Calcd for $[Co(C_{10}H_{20}S_4)(NO_2)_2]BF_4$: C, 23.72; H, 3.98; N, 5.53. Found: C, 23.63; H, 4.07; N, 5.29.

***trans*-Dichloro(13,14-benzo-1,4,8,11-tetrathiacyclopentadecane)cobalt(III) Perchlorate.** Cobalt(II) perchlorate hexahydrate was stirred in nitromethane with an excess of the ligand TTX. The resulting red-brown solution was filtered, and ether was added to the filtrate. The red-brown microcrystalline product which separated, $[Co(TTX)](ClO_4)_2$, was isolated by filtration and redissolved in nitromethane. An excess of lithium chloride was added and the mixture was stirred for 10 min. The resulting green solution was filtered, and the filtrate was concentrated to a few milliliters. Addition of ether to this solution caused a green microcrystalline product to separate. The complex was collected and purified by recrystallization from nitromethane and washing with ether.

Anal. Calcd for $[Co(C_{15}H_{22}S_4)Cl_2]ClO_4$: C, 32.18; H, 3.95; Cl, 18.99. Found: C, 32.18; H, 3.86; Cl, 18.83.

***trans*-Dibromo(13,14-benzo-1,4,8,11-tetrathiacyclopentadecane)cobalt(III) Perchlorate.** When the red-brown complex $[Co(TTX)](ClO_4)_2$ was stirred with an excess of lithium bromide in nitromethane for 30 min, a green-brown complex could be isolated in a manner similar to that given for the chloro complex.

Anal. Calcd for $[Co(C_{15}H_{22}S_4)Br_2]ClO_4$: C, 27.77; H, 3.41; Br, 24.63; Cl, 5.46. Found: C, 27.64; H, 3.44; Br, 24.50; Cl, 5.33.

Preparation of Rhodium Complexes. *cis*-Dichloro(1,4,8,11-tetrathiacyclotetradecane)rhodium(III) Chloride. Rhodium(III) chloride (K + K) was dissolved in a minimum amount of water and filtered into a boiling ethanol solution containing an excess of the ligand TTP. The resulting clear yellow solution was filtered, and most of the solvent was removed. Upon addition of ether a bright yellow microcrystalline product separated. The complex was filtered and washed with acetone and ether before drying.

Anal. Calcd for $[Rh(C_{10}H_{20}S_4)Cl_2]Cl$: C, 25.13; H, 4.21; Cl, 22.25. Found: C, 25.34; H, 4.38; Cl, 21.95.

***cis*-Dichloro(13,14-benzo-1,4,8,11-tetrathiacyclopentadecane)rhodium(III) Chloride.** The procedure given above for cis-$[Rh(TTP)Cl_2]Cl$ was used substituting the ligand TTX.

Anal. Calcd for $[Rh(C_{15}H_{22}S_4)Cl_2]Cl$: C, 33.37; H, 4.10; Cl, 19.70. Found: C, 33.22; H, 4.27; Cl, 19.53.

***cis*-Dibromo(1,4,8,11-tetrathiacyclotetradecane)rhodium(III) Bromide.** The procedure above was repeated using rhodium(III) bromide. The complex isolated is a bright yellow crystalline product.

Anal. Calcd for $[Rh(C_{10}H_{20}S_4)Br_2]Br$: C, 19.65; H, 3.29; Br, 39.22. Found: C, 19.50; H, 3.40; Br, 38.98.

***cis*-Diiodo(1,4,8,11-tetrathiacyclotetradecane)rhodium(III) Iodide.** Rhodium(III) chloride was dissolved in a minimum amount of water and treated with an excess of lithium iodide. This solution was then filtered into a boiling ethanol solution containing an excess of the ligand TTP. The volume of the resulting red-brown solution was reduced. The red-brown crystals which formed were collected and recrystallized from ethanol to which lithium iodide had been added.

Anal. Calcd for $[Rh(C_{10}H_{20}S_4)I_2]I$: C, 15.96; H, 2.68; I, 50.37. Found: C, 16.51; H, 2,87; I, 47.37.

***cis*-Dichloro(1,4,8,11-tetrathiacyclotetradecane)rhodium(III) Tetrafluoroborate.** A few drops of 48% tetrafluoroboric acid was added to an ethanol solution of $[Rh(TTP)Cl_2]Cl$. There was an immediate separation of a light yellow complex. This complex was insoluble in ethanol but could be successfully recrystallized from acetonitrile.

Anal. Calcd for $[Rh(C_{10}H_{20}S_4)Cl_2]BF_4$: C, 22.69; H, 3.81; Cl, 13.39. Found: C, 22.80; H, 3.87; Cl, 13.68.

Dimer of 1,4,8,11-Tetrathiacyclotetradecanerhodium(III) Trichloride. Rhodium(III) chloride was dissolved in a minimum amount of water and filtered into a cold ethanol solution of the ligand TTP. There was an immediate separation of a tan colored solid which was insoluble in hot water, ethanol, and other common organic solvents.

Anal. Calcd for $[Rh_2(C_{10}H_{20}S_4)_2Cl_6]$: C, 25.13; H, 4.21; Cl, 22.35. Found: C, 25.21; H, 4.55; Cl, 23.19.

Acknowledgment. The financial support of the National Science Foundation is gratefully acknowledged.

Registry No. 1,11-Dioxa-4,8-dithiaundecane, 16260-48-3; TTU, 25676-62-4; $[Co(TTP)](BF_4)_2$, 52392-77-5; $[Co(CH_3CN)_6](BF_4)_2$, 15170-09-9; *cis*-$[Co(TTP)Cl_2]BF_4$, 52392-93-5; *cis*-$[Co(TTP)Br_2]BF_4$, 52392-90-2; *trans*-$[Co(TTP)I_2]B(C_6H_5)_4$, 52392-92-4; *cis*-$[Co(TTP)Cl_2]ClO_4$, 52392-82-2; *cis*-$[Co(TTP)(NCS)_2]B(C_6H_5)_4$, 52392-84-4; $[Co(TTP)C_2O_4]ClO_4$, 52392-88-8; *cis*-$[Co(TTP)(NO_2)_2]BF_4$, 52392-86-6; *trans*-$[Co(TTX)Cl_2]ClO_4$, 52392-95-7; *trans*-$[Co(TTX)Br_2]ClO_4$, 52392-97-9; *cis*-$[Rh(TTP)Cl_2]Cl$, 52393-01-8; *cis*-$[Rh(TTX)Cl_2]Cl$, 52392-75-3; *cis*-$[Rh(TTP)Br_2]Br$, 52393-02-9; *cis*-$[Rh(TTP)I_2]I$, 52392-98-0; *cis*-$[Rh(TTP)Cl_2]BF_4$, 52393-00-7; $[Rh(TTP)Cl]_xCl_{2x}$, 52392-80-0.

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Dissymmetric Arsine Complexes. Preparation, Properties, and Electronic Structures of Cobalt-Arsine Complexes Containing Co-Co Bonds

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Received March 14, 1974 AIC401845

Cobalt(III)-diaquo complexes of the type *cis*-$[Co(As)_4(OH_2)_2]^{3+}$ are reduced in primary alcohols and give Co-Co dimers *trans,trans*-$[H_2O(As)_4Co\text{-}Co(As)_4OH_2]^{4+}$. Three arsines were used, namely, the quadridentate ligands *R,R*:*S,S*-tetars (and *R,R*-tetars) and *R,S*-tetars and the bidentate chelate diars. The tetars complexes form stable acetonitrile adducts whereas the diars dimer appears to contain quasi-five-coordinate Co atoms. These diamagnetic complexes are stable in solution in the absence of catalysis, but their stability seems to be kinetically controlled because spontaneous dimerization of the monomeric cobalt(II) arsines does not occur. Evidence is presented which suggests that the alcohol reductions involve a hydrido intermediate. A number of observations support a quasi crystal field interpretation of the visible absorption spectra of the dimers; in essence it is assumed that the "d-d" transitions are localized on each Co atom except for the levels derived from the Co-Co bond. The consequences of this scheme in relation to the bonding in these complexes is briefly discussed.

Of all the transition elements which might be expected to form stable metal-metal bonds, those of Co(II) appear to be the least studied. There are a variety of reasons for this but probably the main inconvenience is associated with the well