

# Cobalt(II) and rhodium(III) complexes of 1,5-dithiacyclooctane (1,5-DTCO) and 1,5,9,13-tetrathiacyclohexadecane (TTH)

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## Abstract

Complexes of 1,5-dithiacyclooctane (1,5-DTCO) and 1,5,9,13-tetrathiacyclohexadecane (TTH) with cobalt(II) and rhodium(III) are reported.  $\text{Co}(\text{BF}_4)_2$  reacts with either 1,5-DTCO or TTH to form square pyramidal complexes  $[\text{Co}(1,5\text{-DTCO})_2\text{CH}_3\text{CN}]^{2+}$  and  $[\text{Co}(\text{TTH})\text{CH}_3\text{CN}]^{2+}$ . The  $\text{CH}_3\text{CN}$  cannot be removed from the 1,5-DTCO complex.  $\text{CoCl}_2$  reacts with TTH to form tetrahedral  $[\text{Co}(\text{TTH})]^{2+}$  and  $[\text{CoCl}_4]^{2-}$  ions.  $\text{CoCl}_2$  reacts with 1,5-DTCO to form a solid with an empirical formula of  $\text{Co}(1,5\text{-DTCO})_2\text{Cl}_2$ , which, when dissolved in nitromethane, dissociates to form tetrahedral  $[\text{Co}(1,5\text{-DTCO})\text{Cl}_2]$ .  $\text{RhCl}_3$  reacts with 1,5-DTCO and TTH to form *trans*-octahedral complexes of the form, *trans*- $[\text{RhS}_4\text{Cl}_2]^+$ .

## Introduction

As part of a continuing study of the coordination chemistry of mesocyclic dithioethers, complexes of 1,5-dithiacyclooctane (1,5-DTCO) with cobalt(II) and rhodium(III) were prepared [1, 2]. For comparison, cobalt(II) and rhodium(III) complexes of the macrocyclic tetrathioether, 1,5,9,13-tetrathiacyclohexadecane (TTH) were also prepared and characterized. We have already reported the properties of the copper(I) and nickel(II) complexes of 1,5-DTCO [3] and copper(I) and (II) complexes of TTH to show how the anion influences the structure of the complexes [4]. Copper(II) reduces 1,5-DTCO so readily that no stable complexes can be formed. Stein and Taube reported an unusually facile electron transfer reaction between ruthenium(II) and (III) via 1,5-DTCO as a bridging ligand [5].

In previous work on thioether complexes of cobalt(II), Morgan and Ledbury [6] noted a variation in the stoichiometry of metal complexes of the acyclic dithioether, 2,5-dithiahexane (2,5-DTH), with different anions and Carlin and Weissberger [7] showed that  $\text{Co}(2,5\text{-DTH})_2(\text{ClO}_4)_2$  is not isomorphous with the halide salt. Later, Cotton and Weaver [8] proved that  $\text{Co}(2,5\text{-DTH})_2(\text{ClO}_4)_2$  had a distorted octahedral structure with the perchlorate ions occupying *trans* positions. Flint and Goodgame [9] showed that when chloride was present, the spectrum of the complex is consistent with a polymeric structure having  $\text{Co}(2,5\text{-DTH})_2^{2+}$  cations and tetrahedral  $\text{CoCl}_4^{2-}$  anions.

Rhodium(III) chloride forms two different 2,5-DTH complexes [10].  $\text{Rh}(2,5\text{-DTH})_2\text{Cl}_3$  has a *trans*-octahedral structure whereas  $[\text{Rh}(2,5\text{-DTH})\text{Cl}_3]_2$  is dimeric with bridging halide.

Some macrocyclic tetrathioethers have been shown to form stable complexes with cobalt(III) and rhodium(III) but the sixteen-membered ring homolog of 1,5-DTCO was not studied. The fourteen-membered ring tetrathioether, 1,4,8,11-tetrathiatetradecane (TTP), and a benzene-fused fifteen-membered ring, 13,14-benzo-1,4,8,11-tetrathiacyclopentadecane (TTX) form a variety of complexes with rhodium(III) and cobalt(III) [11]. TTP normally coordinates to cobalt(III) in a folded manner. However, when the anions are large (e.g.  $\text{I}^-$ ) the four sulfurs are arranged in a plane. With TTX, complexes of cobalt(III) are *trans*-octahedral even when the anions are small (e.g.  $\text{Cl}^-$ ). No complexes with cobalt(II) have been reported.

## Experimental

### Electronic absorption spectra

Near infrared, visible and ultraviolet spectra were measured with Cary 14 and 17 recording spectrophotometers. Solution spectra were run in 1 cm and 1 mm matched quartz cells purchased from Helma Optics. For solid state spectra, Nujol mulls of complexes were soaked into Whatman No. 1 filter paper and Nujol soaked filter paper was used as the ref-

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erence. If the sample was not stable in the presence of air, the Nujol mull was placed between two quartz plates.

#### *Infrared absorption spectra*

Infrared spectra were measured with either a Perkin-Elmer 237B or a Beckman IR-12 grating spectrophotometer. Nujol mulls on potassium bromide were used in the 400–4000  $\text{cm}^{-1}$  region, and the Nujol mulls in polyethylene envelopes or on cesium iodide were used in the 250–650  $\text{cm}^{-1}$  region.

#### *Magnetic susceptibility measurements*

The magnetic moments of the solid complexes were determined by the Gouy method at room temperature. A double-ended Gouy tube was calibrated using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as the standard. The apparatus constant was checked by measuring the magnetic susceptibility of  $[\text{Co}(\text{en})_3]\text{S}_2\text{O}_3$ .

#### *Electrolytic conductivity measurements*

Electrolytic conductance measurements were made at 50–60 c.p.s. using a conductivity bridge, model RC 16B2, manufactured by Industrial Instruments, Inc., Cedar Grove, NJ. The conductivity cell was a model 3403 cell purchased from Yellow Springs Instrument Company, Inc. (cell constant =  $1.00 \pm 0.001$ ).

#### *Materials*

Cobalt(II) chloride (Mallinckrodt Chemical Works) hexahydrate was dehydrated by passing a stream of anhydrous hydrogen chloride across the solid while heating at 350 °C in a tube furnace. Hexaacetonitrile cobalt(II) tetrafluoroborate was prepared by the method of Hathaway *et al.* [12]. Rhodium(III) chloride (Engelhard, Lot No. 235) was used without further purification. Rhodium(III) bromide was prepared by slowly evaporating a solution of rhodium(III) chloride in excess hydrobromic acid several times.

#### *Ligands*

##### *1,5-Dithiacyclooctane*

1,5-DTCO was prepared using a method similar to the procedure of Meadow and Reid [13] and Leonard *et al.* [14].

##### *1,5,9,13-Tetrathiacyclohexadecane*

TTH was isolated as a by-product of the synthesis of 1,5-DTCO. The method of isolation was similar to the procedure of Ochrymowycz *et al.* [15].

#### *Complexes*

##### *1,5,9,13-Tetrathiacyclohexadecane(acetonitrile)-cobalt(II) tetrafluoroborate, $[\text{Co}(\text{TTH})(\text{CH}_3\text{CN})](\text{BF}_4)_2$*

In 75 ml of  $\text{CH}_2\text{Cl}_2$ , 0.22 g ( $7.4 \times 10^{-4}$  mol) of TTH was dissolved and heated gently on a hot plate. To this solution, 0.29 g ( $6.1 \times 10^{-4}$  mol) of freshly prepared  $[\text{Co}(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$  was added by placing the  $[\text{Co}(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$  in a paper filter funnel and washing with  $\text{CH}_2\text{Cl}_2$ . Upon the addition of  $\text{Co}(\text{BF}_4)_2$ , a red solution formed with immediate precipitation of a maroon crystalline product (0.120 g, 35% yield). The complex  $[\text{Co}(\text{TTH})(\text{CH}_3\text{CN})](\text{BF}_4)_2$  was recrystallized from  $\text{CH}_2\text{Cl}_2$  using a Soxhlet extractor. The same complex could also be prepared by placing  $[\text{Co}(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$  in a Soxhlet and extracting with  $\text{CH}_2\text{Cl}_2$  into a solution containing excess ligand. *Anal.* Calc. for  $[\text{Co}(\text{C}_{12}\text{H}_{24}\text{S}_4)\text{CH}_3\text{CN}](\text{BF}_4)_2$ : C, 29.48; H, 4.78; S, 22.49. Found: C, 29.64; H, 4.74; S, 22.26%.

##### *1,5,9,13-Tetrathiacyclohexadecane cobalt(II) tetrafluoroborate, $[\text{Co}(\text{TTH})](\text{BF}_4)_2$*

This complex was prepared by drying  $[\text{Co}(\text{TTH})(\text{CH}_3\text{CN})](\text{BF}_4)_2$  in vacuum at 80 °C for 24 h. *Anal.* Calc. for  $[\text{Co}(\text{C}_{12}\text{H}_{24}\text{S}_4)](\text{BF}_4)_2$ : C, 27.28; H, 4.59. Found: C, 26.94; H, 4.66%.

##### *Bis(1,5-dithiacyclooctane)acetonitrilecobalt(II) tetrafluoroborate, $[\text{Co}(1,5\text{-DTCO})_2\text{CH}_3\text{CN}](\text{BF}_4)_2$*

This complex was prepared by a procedure analogous to  $[\text{Co}(\text{TTH})(\text{CH}_3\text{CH})](\text{BF}_4)_2$  using 1,5-DTCO with a mole ratio of cobalt to 1,5-DTCO of two (81% yield). The complex is stable in the solid state but it is only stable for short periods of time in dry  $\text{CH}_3\text{NO}_2$  or  $\text{CH}_2\text{Cl}_2$  in the absence of air. *Anal.* Calc. for  $[\text{Co}(\text{C}_6\text{H}_{12}\text{S}_2)_2\text{CH}_3\text{CN}](\text{BF}_4)_2$ : C, 29.48; H, 4.78. Found: C, 29.60; H, 4.68%.

##### *Bis(1,5-dithiacyclooctane)cobalt(II) chloride, $\text{Co}(\text{DTCO})_2\text{Cl}_2$*

Anhydrous cobalt(II) chloride ( $0.088$  g,  $6.8 \times 10^{-4}$  mol) was dissolved in a minimum amount of hot  $\text{CH}_3\text{CN}$  and slowly added to a solution of  $0.209$  g ( $1.4 \times 10^{-3}$  mol) of 1,5-DTCO in 50 ml of  $\text{CH}_2\text{Cl}_2$ . After the addition of  $\text{CoCl}_2$ , the volume was reduced until an oil remained. The oil crystallized on cooling. The crystals were filtered, washed with 5 ml of  $\text{CH}_2\text{Cl}_2$  and copious amounts of anhydrous ether, and vacuum dried. The product was recrystallized from nitromethane. *Anal.* Calc. for  $\text{Co}(\text{C}_6\text{H}_{12}\text{S}_2)_2\text{Cl}_2$ : C, 33.79; H, 5.68. Found: C, 34.00; H, 5.52%.

*1,5,9,13-Tetrathiacyclohexadecanecobalt(II) tetrachlorocobaltate(II), [Co(TTH)]CoCl<sub>4</sub>*

This complex was prepared by a similar procedure to Co(1,5-DTCO)<sub>2</sub>Cl<sub>2</sub>. Although the mole ratio of Co:TTH was one to two, the product isolated had a mole ratio of cobalt to TTH of two to one. The product was recrystallized from CH<sub>3</sub>NO<sub>2</sub>. *Anal. Calc.* for [Co(TTH)]CoCl<sub>4</sub>: C, 25.91; H, 4.36. Found: C, 25.14; H, 4.61%.

*Dichloro(1,5,9,13-tetrathiacyclohexadecane)-rhodium(III) chloride, [Rh(TTH)Cl<sub>2</sub>]Cl*

Rhodium trichloride, 0.04 g ( $1.8 \times 10^{-4}$  mol) was dissolved in 150 ml of boiling ethanol. To this solution was slowly added 0.080 g ( $2.6 \times 10^{-4}$  mol) of TTH dissolved in 5 ml of CH<sub>2</sub>Cl<sub>2</sub>. The reaction mixture was filtered while hot and the yellow filtrate was evaporated to approximately 8 ml. The complex was precipitated by the addition of ether to give 0.031 g (34%) of [Rh(TTH)Cl<sub>2</sub>]Cl. The yellow precipitate was recrystallized from ethanol. *Anal. Calc.* for [Rh(C<sub>12</sub>H<sub>24</sub>S<sub>4</sub>)Cl<sub>2</sub>]Cl: C, 28.49; H, 4.79; Cl, 21.02. Found: C, 28.74; H, 4.90; Cl, 20.87%.

*Dichlorobis(1,5-dithiacyclooctane)rhodium(III) chloride, [Rh(1,5-DTCO)<sub>2</sub>Cl<sub>2</sub>]Cl*

To 100 ml of ethanol in a 250 ml round bottom flask, 0.25 g ( $10^{-3}$  mol) of RhCl<sub>3</sub> was added. This solution was heated to reflux and 0.595 g ( $4 \times 10^{-3}$  mol) of 1,5-DTCO in 100 ml of ethanol was added dropwise. After the addition of 1,5-DTCO, the reaction mixture was refluxed overnight, filtered to remove any insoluble materials, and concentrated to 15 ml. Upon the addition of anhydrous ether, a yellow precipitate formed, which was recrystallized from ethanol to give 0.34 g (71%) of pure [Rh(1,5-DTCO)<sub>2</sub>Cl<sub>2</sub>]Cl. *Anal. Calc.* for [Rh(C<sub>8</sub>H<sub>12</sub>S<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]: C, 28.49; H, 4.79; Cl, 21.02. Found: C, 28.76; H, 4.95; Cl, 20.52%.

*Dibromobis-(1,5-dithiacyclooctane)rhodium(III) bromide, [Rh(1,5-DTCO)<sub>2</sub>Br<sub>2</sub>]Br*

This complex was prepared by a procedure analogous to [Rh(1,5-DTCO)<sub>2</sub>Cl<sub>2</sub>]Cl using RhBr<sub>3</sub>. *Anal. Calc.* for [Rh(C<sub>8</sub>H<sub>12</sub>S<sub>2</sub>)<sub>2</sub>Br<sub>2</sub>]Br: C, 22.55; H, 3.79; Br, 37.50. Found: C, 22.17; H, 3.90; Br, 37.17%.

## Results and discussion

### Cobalt complexes

In Table 1, the physical properties of the cobalt(II) and rhodium(III) complexes are tabulated. When Co(CH<sub>3</sub>CN)<sub>6</sub>(BF<sub>4</sub>)<sub>2</sub> is added to a warm CH<sub>2</sub>Cl<sub>2</sub> solution containing excess 1,5-DTCO, an orange colored

precipitate with stoichiometry [Co(1,5-DTCO)<sub>2</sub>-CH<sub>3</sub>CN](BF<sub>4</sub>)<sub>2</sub> is formed. The CH<sub>3</sub>CN is bound so firmly that the complex can be dried at elevated temperatures under vacuum without loss of CH<sub>3</sub>CN. Although the complex is stable in the solid state, it is only stable for short periods of time in dry CH<sub>3</sub>NO<sub>2</sub> or CH<sub>2</sub>Cl<sub>2</sub> in the absence of air. The molar conductivity in CH<sub>3</sub>NO<sub>2</sub> was determined rapidly and gave a value of 155 mho cm<sup>2</sup> mol<sup>-1</sup>. This suggests a 1:2 electrolyte with ionic BF<sub>4</sub><sup>-</sup>. The infrared spectrum of the solid complex displays two sharp bands at 2295 and 2255 cm<sup>-1</sup>. The appearance of two bands in this region suggests either the presence of two CH<sub>3</sub>CN molecules per complex or two different environments for the same CH<sub>3</sub>CN. The stoichiometry rules out two CH<sub>3</sub>CN molecules per complex and it is difficult to formulate a complex having CH<sub>3</sub>CN in two appreciably different locations. An explanation of this observation may be found in a paper by Byler and Shriver [16] who report that the SbCl<sub>5</sub>·CH<sub>3</sub>CN complex also has two bands in the 2300 cm<sup>-1</sup> region. They assigned the higher energy band to  $\nu_1$  (the CN stretching frequency) and the lower energy band to a combination band ( $\nu_3 + \nu_4$ ) of the CH<sub>3</sub>CN group. Thus, the two bands in the cobalt complex can be assigned in the same manner – 2295 ( $\nu_1$ ) and 2255 ( $\nu_3 + \nu_4$ ) cm<sup>-1</sup>. Both absorptions are higher than that of uncoordinated CH<sub>3</sub>CN. The magnetic moment is 2.4 BM and the molecule has broad absorptions in the visible region of the spectrum at 494 and 405 nm and weak absorption at 1380 nm. All the data is consistent with the [Co(1,5-DTCO)<sub>2</sub>CH<sub>3</sub>CN](BF<sub>4</sub>)<sub>2</sub> complex having distorted low-spin square pyramidal cobalt(II). This complex would be similar to [Co(1,5-diazacyclooctane)<sub>2</sub>Cl]ClO<sub>4</sub> which was shown to have a square pyramidal geometry by an X-ray crystal structure determination [17]. An alternative structure having two bridging 1,5-DTCO molecules is also possible, but it appears that there would be steric crowding between the bridges so that this type of dimer formation would be minimized.

The TTH complex of Co(BF<sub>4</sub>)<sub>2</sub> is different. When the reaction is carried out in the usual way, [Co(TTH)CH<sub>3</sub>CN](BF<sub>4</sub>)<sub>2</sub> is formed. However, CH<sub>3</sub>CN is easily removed at room temperature under vacuum. [Co(TTH)CH<sub>3</sub>CN](BF<sub>4</sub>)<sub>2</sub> has a molar conductance of 150 mho cm<sup>2</sup> mol<sup>-1</sup> and also has two bands in the 2200–2300 cm<sup>-1</sup> region of the infrared (at 2303 and 2268 cm<sup>-1</sup>). Since the magnetic moment is 2.2 BM and the absorption spectrum exhibits three bands, all the physical properties are consistent with cobalt(II) having a square pyramidal geometry. Thus the major difference in the two complexes is the ease with which CH<sub>3</sub>CN is lost.

TABLE 1. Physical properties of Co(II) and Rh(III) complexes of 1,5-DTCO and TTH

Compound	Electronic absorption (nm) <sup>a</sup>	Molar conductivity (mho cm <sup>2</sup> mol <sup>-1</sup> ) <sup>b</sup>	Magnetic moment (BM)	Infrared absorption (cm <sup>-1</sup> )
[Co(1,5-DTCO) <sub>2</sub> CH <sub>3</sub> CN](BF <sub>4</sub> ) <sub>2</sub>	Nujol 1380 494 405	155	2.4	$\nu_1$ (CH <sub>3</sub> CN) 2295 $(\nu_3 + \nu_4)$ CH <sub>3</sub> CN 2255
[Co(TTH)CH <sub>3</sub> CN](BF <sub>4</sub> ) <sub>2</sub>	Nujol 1300 530 350	154	2.2	$\nu_1$ (CH <sub>3</sub> CN) 2303 $(\nu_3 + \nu_4)$ CH <sub>3</sub> CN 2268
Co(1,5-DTCO) <sub>2</sub> Cl <sub>2</sub>	Nujol 680sh 575 450sh 400	17		
Co <sub>2</sub> (TTH)Cl <sub>4</sub>	Nujol 1500vb 720 680 580 360vb CH <sub>3</sub> NO <sub>2</sub> 1350(23) 675(449) 650(436) 595(455)	58 38 <sup>c</sup>		$\nu$ Co-Cl 317 3.27/Co 4.8 <sup>d</sup>
[Rh(1,5-DTCO) <sub>2</sub> Cl <sub>2</sub> ]Cl	H <sub>2</sub> O 380sh (1600) 307 (19000) 228 (22700)	73		$\nu$ Rh-Cl 358
[Rh(1,5-DTCO) <sub>2</sub> Br <sub>2</sub> ]Br	H <sub>2</sub> O 350sh (2339) 306 (12525) 254 (11409)	72		$\nu$ Rh-Br 325
[Rh(TTH)Cl <sub>2</sub> ]Cl <sub>2</sub>	H <sub>2</sub> O 440 (226)	77		$\nu$ Rh-Br 364

<sup>a</sup>Extinction coefficients are in parentheses. <sup>b</sup>In 10<sup>-3</sup> M nitromethane. <sup>c</sup>In 10<sup>-3</sup> ethanol. <sup>d</sup>Magnetic moment for Co(TTH)<sup>2+</sup>.

Travis and Busch have shown that Co(BF<sub>4</sub>)<sub>2</sub> complexes of TTP and TTX are easily oxidized by air in CH<sub>3</sub>CN in the presence of excess halide to give Co(III) complexes [11]. We were unsuccessful in obtaining a cobalt(III) complex of TTH in this manner; only hydrated cobalt(III) complexes were obtained.

When CoCl<sub>2</sub> is treated with 1,5-DTCO in CH<sub>3</sub>CN, an amorphous dark green complex with stoichiometry Co(1,5-DTCO)<sub>2</sub>Cl<sub>2</sub> is obtained. This solid complex is air stable but dissociates in CH<sub>3</sub>NO<sub>2</sub> to give Co(1,5-DTCO)Cl<sub>2</sub>. Co(1,5-DTCO)Cl<sub>2</sub> exhibits highly structured absorptions in the 500 to 700 nm region which are characteristic of tetrahedral cobalt(II).

Treatment of CoCl<sub>2</sub> with TTH gives a dark green complex with stoichiometry Co<sub>2</sub>(TTH)Cl<sub>4</sub>. This complex is air-stable and soluble in solvents such as C<sub>2</sub>H<sub>5</sub>OH and CH<sub>3</sub>NO<sub>2</sub>. The molar conductivity of 58 mho cm<sup>2</sup> mol<sup>-1</sup> in CH<sub>3</sub>NO<sub>2</sub> and 38 mho cm<sup>2</sup> mol<sup>-1</sup> in C<sub>2</sub>H<sub>5</sub>OH is consistent with a typical 1:1

electrolyte. The far infrared spectrum exhibits a band at 317 cm<sup>-1</sup> which is near the value found for molecules containing the CoCl<sub>4</sub><sup>2-</sup> anion: [Co(*o*-C<sub>6</sub>H<sub>4</sub>(PO<sub>2</sub>)<sub>2</sub>)<sub>2</sub>]<sup>2+</sup>[CoCl<sub>4</sub><sup>2-</sup>], 320 cm<sup>-1</sup>; [Co(*o*-C<sub>6</sub>H<sub>4</sub>(PO<sub>2</sub>)(AsO<sub>2</sub>)<sub>2</sub>)<sub>2</sub>]<sup>2+</sup>[CoCl<sub>4</sub><sup>2-</sup>], 315 cm<sup>-1</sup> [18]. The electronic absorption spectrum in CH<sub>3</sub>NO<sub>2</sub> is also characteristic of the CoCl<sub>4</sub><sup>2-</sup> ion with peaks at 595 ( $\epsilon=455$ ), 650 ( $\epsilon=435$ ) and 675 ( $\epsilon=449$ ) nm. Although there is little spectral evidence to support the structure of the Co(TTH)<sup>2+</sup> cation, a planar structure is not present since the overall paramagnetism is too high. A distorted tetrahedral structure is not inconsistent with the data.

#### Rhodium complexes

Rhodium(III) forms complexes with 1,5-DTCO having the stoichiometry [Rh(1,5-DTCO)<sub>2</sub>X<sub>2</sub>]X, where X = Cl<sup>-</sup> and Br<sup>-</sup>. These complexes are stable in air and in a variety of solvents. The molar conductivities are consistent with a 1:1 electrolyte and

an inspection of the infrared spectra can be used to determine whether the halides are *cis* or *trans* in an octahedral complex. The chloride exhibits a strong absorption at  $358\text{ cm}^{-1}$  and weaker absorptions at  $304$  and  $293\text{ cm}^{-1}$ . The bromide has no absorption at  $358\text{ cm}^{-1}$  but a new absorption appears at  $325\text{ cm}^{-1}$ . The assignment of the *trans* geometry to the 1,5-DTCO complexes can be made based on the data obtained from the TTH complexes of rhodium(III).

Yellow  $[\text{Rh}(\text{TTH})\text{Cl}_2]\text{Cl}$  is prepared by adding TTH (in  $\text{CH}_3\text{CN}$ ) to a boiling ethanolic solution of  $\text{RhCl}_3$ . A tan precipitate (polymer) and a yellow solution are formed. The yellow monomeric complex is isolated by adding ether to the cooled solution. The molar conductivity is consistent with a 1:1 electrolyte and the infrared spectrum suggests an octahedral geometry of the complex with the halides in *trans* positions. According to a simple crystal field model, the *cis* isomer should absorb at higher energy ( $\sim 350\text{ nm}$ ) and have a high molar extinction coefficient ( $\sim 2000$ ); the *trans* isomer should absorb at lower energy ( $\sim 400\text{ nm}$ ) and have a lower molar extinction coefficient ( $\sim 200$ ) [11]. By comparison with a series of known thioether complexes of rhodium(III) [11] it can be seen that, since  $[\text{Rh}(\text{TTH})\text{Cl}_2]\text{Cl}$  absorbs at  $440\text{ nm}$  ( $\epsilon=226$ ), its structure should be *trans*. The far infrared spectrum also supports a *trans* structure of the complex. The *trans* isomer, having  $D_4$  symmetry should give a single Rh-Cl stretching frequency whereas the *cis* isomer with  $C_{2v}$  symmetry, should give two bands. The single strong absorption band at  $364\text{ cm}^{-1}$  in the chloride complex strongly supports the *trans* structure. The spectrum is very similar to *trans*- $[\text{Rh}(2,5\text{-DTH})_2\text{Cl}_2]\text{Cl}$  [19] where the Rh-Cl stretch is at  $362\text{ cm}^{-1}$ . The planar conformation of TTH with rhodium(III) to give *trans*-octahedral complexes may be compared with the results of the fifteen-membered ring tetra-thioether, TTX [11]. TTX coordinates to rhodium(III) in a folded manner to give *cis* complexes

whereas TTH gives *trans* complexes. This suggests that the smallest sized ring able to give a planar array of four thioether groups about rhodium(III) is sixteen. Thus, based on a comparison of the 1,5-DTCO complex with the TTH complex,  $[\text{Rh}(1,5\text{-DTCO})_2\text{Cl}_2]\text{Cl}$  is also *trans*-octahedral.

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