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Synthesis and characterization of cyclam complexes of rhodium(III)

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A series of complexes of the type Rh(cyclam)X_2^+ and Rh(cyclam)XY^{n+} have been prepared and characterized, where cyclam represents 1,4,8,11-tetraazacyclotetradecane and X and Y represent OH^-, H_2O, Cl^-, Br^-, I^-, N_3^-, NCS^-, and NO_2^-. The infrared and electronic spectra are discussed with respect to assignment of the *cis* and *trans* isomers, the linkage isomers, and the Rh–ligand stretching frequencies above 250 cm^{-1}. The thermodynamic *trans* effect is related to shifts in the Rh–ligand stretching frequencies. The intensities of the d–d transitions are related to distortion of the octahedral field to support the *cis* and *trans* assignments, and compared to show the decrease in bond constraint for propylene linkages in place of ethylene. Steric constraint accounts for the single case of stereoisomerization by *cis*-Rh(cyclam)I_2^+.

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Introduction

Macrocyclic quadridentate ligands such as 1,4,8,11-tetraazacyclotetradecane (cyclam) and 1,4,7,10-tetraazacyclododecane (cyclen) have become important since they provide a substrate for octahedral substitution mechanistic studies with some advantages over the more commonly studied bis(ethylenediamine) systems, and they are also much simpler than naturally occurring cyclic ligands such as the porphyrins. Several *trans*-Co(cyclam)X_2^+ complexes (1) and a few Ni(cyclam)X_2 complexes (2) were prepared by Tobe and co-workers. Collman and Schneider (3) prepared some *cis*-Co(cyclen)X_2^+ complexes and *cis*-Rh(cyclen)Cl_2^+. *cis*-Cr(cyclam)Cl_2^+, as well as the cyclam complexes of several other metals, Cu(II), Zn(II), Cd(II), and Pd(II) have been prepared by Allen and Pedwell (4). Poon and Tobe (5) have recently prepared more *cis*- and *trans*-Co(cyclam)X_2^+ and some Co(cyclam)-XY^+ complexes and have used them to study the mechanism and steric course of octahedral acid hydrolysis. The linear quadridentate analogs of cyclam have also received recent study. The triethylenetetramine (trien) complexes of Co(III) and Rh(III) were reported by Gillard and Wilkinson (6) and also by Sargeson and co-workers (7). 1,4,8,11-Tetraazaundecane (2,3,2-tet), an even more similar analog of cyclam, was studied by Hamilton and Alexander (8) and Gillard and co-workers (9). Gillard and co-workers termed these open-chain ligands as facultative, based on their ability to assume different configurations. The two possible *cis* configurations, as opposed to one for cyclam, make these systems more complicated and less desirable as a simple substrate for mechanistic studies.

The rigidity of the quadridentate cyclic structure is a barrier to isomerization, and for Rh(III) only the *cis*-diiodo complex isomerizes at reflux temperatures. This is due to the steric preference of the large iodo ligands for the *trans* configuration.

The greater number of different Rh(III) complexes of cyclam compared to the bis(ethylenediamine), $(en)_2$, analogs enlarges the scope for *trans* effect and mechanistic studies which will be reported in a later paper. The cyclam complexes are more inert than the bis(ethylenediamine) analogs and the substitution reactions can be measured by conventional spectrometric techniques. The larger enthalpies of activation for cyclam complexes support the prediction that their increased rigidity resists stereochemical rearrangement in the transition state, relative to

$(en)_2$. Another factor causing the destabilization of the transition state is the decrease in solvation with increasing chelation (10).

Results and Discussion

Stereoisomers

The *cis* and *trans* isomers of the Rh(cyclam)-XY^{n+} series were assigned on the basis of a comparison of the wavelengths and extinction coefficients of the absorption maxima of their electronic spectra (Tables 1 and 2). It is readily apparent that the *trans* isomers exhibit electronic transitions of lesser energy and lesser intensity than those for the *cis* compounds. This observation was used to assign the cyclam complexes for which there is no $(en)_2$ analog.

The *cis*-Rh(cyclam)Cl_2^+ isomer was confirmed by the resolution of the racemic mixture with *d*-α-bromocamphor-π-sulfonate. An optical rotary dispersion (o.r.d.) spectrum showed a very small specific rotation (cf. resolution of *cis*-[Rh(cyclam)Cl_2]Cl, below). Racemic *cis*-[Rh-$(en)_2Cl_2$]Cl has been successfully resolved (11) and the optical rotation of the *l-cis* isomer was measured ($[\alpha]_{535m\mu} = -58°$). The relatively small rotation of the cyclam optical isomer could have been the result of poor separation of the diastereoisomers or the increased symmetry of the cyclam *cis* isomer over the corresponding *cis*-$(en)_2$.

The relative extinction coefficients of the stereoisomers provide further evidence for the assignments. Distortion of the octahedral field around the central metal ion tends to remove the center of symmetry with respect to vibrations and the d^6 states lose some of their *g* character through vibronic coupling (12). This provides a mechanism for increasing the intensity of the d–d

TABLE 1

Electronic spectra of Rh(cyclam)XY^{n+} (absorption maxima)

Complex	λ (mμ)*	ε ($l\ cm^{-1}\ mole^{-1}$)
cis-Cl_2^+	354, 299, 207	223, 308, 33900
trans-Cl_2^+	406, 310sh, 242sh, 204	78, 80, 3300, 37100
cis-Br_2^+	367, 309	243, 871
trans-Br_2^+	429, 285, 235	97.3, 2520, 34600
cis-I_2^+	407, 295sh, 260sh, 228	1210, 5300, 17500, 38400
trans-I_2^+	515sh, 466, 353, 275, 226	64, 204, 13100, 34500, 22800
cis-$(N_3)_2^+$	339sh, 262	1250, 11800
trans-$(N_3)_2^+$	377, 286, 208	892, 12700, 27100
cis-$(NO_2)_2^+$	293sh	1030
trans-$(NO_2)_2^+$	320sh, 260sh, 213	535, 2100, 30800
cis-$(NCS)_2^+$	322, 244	1110, 3630
trans-$(NCS)_2^+$	377, 258	882, 3330
trans-$Cl(OH)^+$	363, 276	101, 180
trans-$Cl(H_2O)^{2+}$	385, 296sh, 224sh	55, 101, 4420
trans-$Br(OH)^+$	373, 277sh	113, 384
trans-$Br(H_2O)^{2+}$	468, 403, 310sh, 204	37, 63, 106, 25600
trans-$I(OH)^+$	443, 393, 275, 230	153, 158, 5330, 26300
trans-$I(H_2O)^{2+}$	494, 341sh, 301sh, 271, 230	222, 763, 1290, 2240, 24400
trans-$N_3(OH)^+$	357, 256	525, 6320
trans-$N_3(H_2O)^{2+}$	420sh, 363, 261	79, 715, 5640
cis-$(OH)(H_2O)^{2+}$	328, 291	251, 192
trans-$(OH)(H_2O)^{2+}$	342, 274	118, 222
trans-$ClBr^+$	418, 312sh, 260sh, 221	89, 95, 1950, 32700
trans-ClI^+	493, 445sh, 308, 245	230, 138, 3620, 31300
trans-$Cl(N_3)^+$	382, 270, 207	697, 9390, 23000
trans-$Cl(NCS)^+$	368, 252	340, 8080
trans-BrI^+	497, 459, 321, 256	151, 152, 6200, 33900
trans-$Br(N_3)^+$	393, 281, 214	698, 11900, 21400
trans-$Br(NCS)^+$	368, 262	355, 8980
trans-$I(N_3)^+$	465sh, 417, 300, 280sh, 225	283, 654, 10100, 8970, 20900
trans-$I(NCS)^+$	434, 412, 296, 274, 224	393, 413, 4220, 5660, 30600
trans-$(N_3)(NCS)^+$	352, 270	861, 7330
trans-$(OH)_2^+$	341, 277	101, 163
trans-$(H_2O)_2^{3+}$	352	65
cis-$(OH)_2^+$	331, 278	226, 202
cis-$(H_2O)_2^{3+}$	296, 251	249, 230

*sh = shoulder.

TABLE 2

Electronic spectra of $[Rh(en)_2XY]^+$ (absorption maxima)

Complex	λ (mμ)*	ε (l cm^{-1} $mole^{-1}$)	Reference
cis-Cl_2	352, 295	155, 180	11
trans-Cl_2	406, 286	75, 130	11
cis-Br_2	362, 276	210, 900	11
trans-Br_2	425, 276, 231	100, 2300, 30800	13
cis-I_2	375	1200	11
trans-I_2	462, 340, 269, 222	260, 14300, 31000, 20000	13
trans-$(N_3)_2$	375, 282	740, 13000	13
cis-$(NO_2)_2$	290, 245sh	660, 3500	11
trans-$(NO_2)_2$	300sh, 255sh	590, 2400	11
trans-ClI	440, 300, 242	154, 4350, 38500	13
trans-Cl(N_3)	377, 263	560, 9600	14
trans-Cl(NCS)	363	340	11
trans-BrI	455, 311, 253	260, 7500, 41500	13
trans-Br(N_3)	388, 272	580, 15100	14

*sh = shoulder.

TABLE 3

Electronic spectra (maxima) of some $[Rh(amine)Cl_2]^+$ complexes

Complex	λ (mμ)	ε (l cm^{-1} $mole^{-1}$)	Reference
trans-$[Rh(NH_3)_4Cl_2]^+$	412	66	11
trans-$[Rh(en)_2Cl_2]^+$	406	75	11
trans-$[Rh(cyclam)Cl_2]^+$	406	78	This work
cis-$[Rh(en)_2Cl_2]^+$	352	155	11
cis-$[Rh(cyclam)Cl_2]^+$	354	223	This work
cis-$[Rh(trien)Cl_2]^+$	352	250	11
cis-$[Rh(trien)Cl_2]^+$	370	300	3
cis-$[Rh(cyclen)Cl_2]^+$	365	535	3

transitions. The two spin-allowed bands ($^1T_{1g} \leftarrow {}^1A_{1g}$, $^1T_{2g} \leftarrow {}^1A_{1g}$) are easily observed and are obscured by charge-transfer bands only for nitro complexes with their large ligand field strengths. An increase in steric constraint would be expected to cause greater distortions and thereby greater intensities in the visible absorption of the complexes. Collman and Schneider (3) discuss this principle with respect to a *cis*-Rh(amine)X_2^+ series. The center of symmetry is removed in a *cis* isomer relative to a *trans*, considering the primary effects of the N donors and ignoring the secondary effects of the ethylene and propylene linkages. As a result, larger extinction coefficients for the d–d transitions are predicted for the *cis* isomers. Table 1 shows that this prediction is consistent with the assignment of stereoisomers. It is especially clear in the case of *cis*-[Rh(cyclam)I_2]I, which has the additional distortion resulting from the size of the iodo ligands. The lower energy d–d transition is about 20 times as intense for the *cis* isomer. In addition, as noted, the steric effect of the iodo ligands make this the only complex in the series which undergoes stereoisomerization at reflux temperature.

A comparison of some of the Rh(amine)Cl_2^+ complexes shows this trend very clearly (Table 3). This effect is more pronounced in the *cis* series than the *trans*. The table also shows that the larger size and greater flexibility of the cyclam ring relative to the cyclen ring results in less distortion of the octahedral field. The d–d transition intensity is less than that of complexes with only ethylene linkages. Therefore, the presence of the two propylene bridges in cyclam removes some of the steric constraint in the *cis* series of isomers.

The infrared (i.r.) spectra also provide evidence for the increased distortion of the octrahedral field in the *cis* series. The lower symmetry of the *cis* complexes results in greater detail in the spectrum (Table 4). The ν(N—H) and ν(Rh—N) modes and the CH_2 rocking modes appear as single bands in the *trans* and double bands in the *cis* series. In addition, the bands due to ν(NO_2) and ν(NCS) are resolved in the *cis* complexes.

TABLE 4

Some details of the infrared spectra of diacidocyclamrhodium(III) complexes*

Complex	Frequency, cm^{-1}				
	ν(NH), s	r(CH_2), m	ν(CN or CC), s	ν(Rh—N), m	Other
cis-Cl_2	3060 3175	840 855	1053 1017 1001	505 459	
trans-Cl_2	3105	875	1020	493	
cis-Br_2	3065 3160	840 855	1052 1019 1001	477 450	
trans-Br_2	3135	890	1020	487	
cis-I_2	3065 3140	840 855	1052 1019 1000	470 423	
trans-I_2	3100	865	1018	482	
cis-$(N_3)_2$	3080 3180	845 860	1053 1029 1005	490 459	351 (Rh—N_3)
trans-$(N_3)_2$	3110	875	1048 1025	501	370 (Rh—N_3)
cis-$(NO_2)_2$	3050 3215	840 855	1055 1027 1002	479 412	815, 830 (NO_2^-)
trans-$(NO_2)_2$	3180	880	1055 1030	499	825 (NO_2^-)
cis-$(NCS)_2$	3125 3210	845 860	1056 1034 1010	533 480	2100, 2080; 835, 820 (NCS^-)
trans-$(NCS)_2$	3105	875	1045 1035	500	2090; 830 (NCS^-)
cis-(OH)(H_2O)	3090 3220	830 850	1040 1028	500 450	546 (Rh—OH)
trans-(OH)(H_2O)	3220	870	1040 1025	493	
trans-Cl(OH)	3225	880	1047 1018	501	523, 487 (Rh—OH)
trans-Cl(H_2O)	3225	875	1040	499	
trans-Br(OH)	3220	875	1050 1017	500	521, 482 (Rh—OH)
trans-Br(H_2O)	3225	875	1034	496	
trans-I(OH)	3220	875	1050 1020	501	516, 484 (Rh—OH)
trans-I(H_2O)	3220	870	1035	497	
trans-(N_3)(OH)	3230	880	1028 1010	502	533, 487 (Rh—OH); 343 (Rh—N_3)
trans-(N_3)(H_2O)	3230	875	1050 1030	499	370 (Rh—N_3)
trans-ClBr	3215	875	1040 1018	497	
trans-ClI	3180	875	1022	496	
trans-Cl(N_3)	3200	875	1021	499	362 (Rh—N_3)
trans-Cl(NCS)	3200	875	1047 1020	499	2090; 835 (NCS^-)
trans-BrI	3180	870	1040 1017	490	
trans-Br(N_3)	3190	875	1045	497	352 (Rh—N_3)
trans-Br(NCS)	3200	875	1040 1024	498	2090; 835 (NCS^-)
trans-I(N_3)	3200	870	1040 1021	491	347 (Rh—N_3)
trans-I(NCS)	3200	870	1045	493	835 (NCS^-)
trans-(N_3)(NCS)	3215	870	1040	499	2090; 833 (NCS^-); 357 (Rh—N_3)

*r = rocking vibration, s = strong, m = medium, assigned according to ref. 15.

Linkage Isomers

The thiocyanate ion was bonded in the isothiocyanato form (N-bonded) as determined from its spectra. A medium band near 835 cm^{-1} was observed for each thiocyanate complex (Table 4). Turco and Pecile (16) reported the range 780–860 cm^{-1} for the C—S stretching frequency in isothiocyanato complexes, as opposed to 690–720 cm^{-1} in thiocyanato complexes. In this work, no i.r. bands were observed in the 690–720 cm^{-1} range. A more reliable assignment can be made on the basis of the δ(NCS) fundamental mode, which occurs in the 460–490 cm^{-1} range for M—NCS, while the corresponding band for M—SCN occurs from 410 to 440 cm^{-1} (16). In this work, a single weak band was present near 460 cm^{-1}, which supports the isothiocyanato assignment. This is a necessary confirmation, since the first overtone of the δ(NCS) fundamental, which would occur for both M—SCN and M—NCS, is a band between 800 and 880 cm^{-1} with an intensity comparable to the ν(C—S) mode, and therefore may be mistaken as diagnostic of isothiocyanato. The most reliable criterion for M—NCS bonding is a broad band in the vicinity of 2000 cm^{-1}, while M—SCN gives a very sharp band in the same region in the spectrum of the solid (17). Again, the isothiocyanato assignment for all the complexes prepared, involving the thiocyanato ion, was indicated by a characteristically broad band in the range 2080–2100 cm^{-1}.

The electronic spectrum was in agreement with this assignment. According to Schaffer (18) and Jorgensen (19), thiocyanato should fit close to chloro and bromo in the spectrochemical series, while isothiocyanato should fit along with stronger ligands, such as azido, at lower wavelengths. Comparing the lower energy d–d transition of the thiocyanato, azido, and halo complexes (Table 1), it is evident that thiocyanato has a ligand field strength very close to that of azido.

The ultraviolet (u.v.) spectra of the dinitro complexes show that the linkage isomers contain nitro rather than nitrito ligands. Nitrito has a ligand field strength near that of hydroxo, whereas nitro is close to the strongest ligands in the spectrochemical series. The absorption maxima for the nitro complexes are the farthest in the u.v. and are observed as shoulders, due to the proximity of the charge transfer peaks. All the comparable hydroxo maxima are further in the visible region.

The sharp infrared band near 820 cm^{-1} is diagnostic of a nitro isomer (20). It should not be confused with a broad peak near 860 cm^{-1} found in both nitro and nitrito isomers.

The greater stability of the isothiocyanato and the nitro isomers over the thiocyanato and nitrito isomers tends to indicate the hardness (21) or "class *a*" character (22) of the Rh(cyclam) substrate. This principle is clearly illustrated by the triad Zn(II), Cd(II), and Hg(II): class *a* Zn(II) bonds with N, borderline Cd(II) bonds with N or S, and class *b* Hg(II) bonds with S (ref. 10, p. 297).

Trans Bond Weakening

The σ-inductive theory of the *trans* effect accounts for *trans* activation through competition for the σ_x molecular orbital (ref. 10, p. 372), or repulsion of electrons in the metal p_x orbital. Therefore, the theory predicts that *trans* destablization is related to *trans* labilization, provided π effects are not important. The assumption that the changes in ν(Rh—X) can be correlated with changes in bond strength is probably safe for a series of related compounds. Although there is no necessity that this assumption be so, due to the more complex bond strength relationships of coupled modes, the decrease in ν(Pt—X) in *trans*-$Pt(PEt_3)_2LCl$ (23) was found to be related to the increasing *trans* effect of L, provided that π bonding is not a complicating factor. In addition, a similar correlation has been found for ν(Pt—N) in *cis*-$PtX_2(NH_3)_2$ (24) and in *trans*-$Pt(NH_3)LCl_2$ (25); and for ν(Pt—H) in *trans*-PtA_2LH, where A is $As(Et)_3$ and a series of substituted phosphines (26). Similarly, the *trans* destabilization effect can be inferred from the shifts in the ν(Rh—X) frequencies. In each of the *cis* complexes, a different group is *trans* to a cyclam nitrogen. Therefore, shifts in the ν(Rh—N) frequencies provide a basis for ordering the *trans* ligands according to their bond weakening influence. From the data in Table 4, it is clear that the order of *trans* bond weakening ability is

$$NO_2^- > I^- > Br^- > Cl^- \sim N_3^- > N(cyclam) > NCS^-$$

N(cyclam) was positioned on the basis of the *trans* complexes in which N(cyclam) is *trans* to each Rh—N bond. The order is expected on comparison with the *trans*-effect orders of other octahedral systems, except for azido. However, azido is a good π donor, and as such has an

additional mechanism for *trans* activation, which is related more to the transition state than the ground state (27). The same relative order of *trans* bond weakening is observed for $\nu(Rh—N_3)$ in *trans*-$Rh(cyclam)L(N_3)^+$ and for $\nu(Rh—OH)$ in *trans*-$Rh(cyclam)L(OH)^+$, where L is a halo or azido ligand.

Preparations

The preparation of cyclam was carried out according to the method of Tobe and co-workers (1) with two modifications which simplified the procedure and improved the yield. The product was precipitated directly from the reaction solution rather than being sublimed along with an added amount of 1,9-diamino-3,7-diazanonane. Secondly, the crude product was purified by vacuum sublimation rather than recrystallization from dioxane. The method of Stetter and Mayer (28) is more elegant but was not used because of its length and similar yield. However, the m.p. of 186–188 °C (sealed tube) was closer to that reported by Stetter and Mayer (185 °C) than that by Tobe and co-workers (173 °C). Recrystallization from dioxane was also used by Stetter and Mayer for purification.

Cyclam was observed to be very stable in air. It was quite soluble in water, in contradiction to the observation of Stetter and Mayer. However, the infrared spectrum corresponded exactly with their spectrum.

The preparation of the 1,5,9,13-tetraazacyclohexadecane analog of cyclam was attempted, since it is a more symmetric ring with four propylene linkages. While a crude product was isolated, it was not stable in air, turning brown, and it was quite viscous. Apparently the stability and high m.p. of cyclam are not shared by this analog. Other close analogs also have low melting points (1,3,7,10-tetraazacyclododecane, 35 °C; 1,4,8,11-tetraazacyclotridecane, 41 °C).

The stability of cyclam is explained by Tobe as the result of diagonal hydrogen bridging by two of the amine hydrogens. This structure leaves two lone pairs available for direct protonation, which agrees with the two pairs of steps involved in the protonation according to Curtis (29). In comparison, the protonation of the open chain follows a regular four-step sequence.

The preparation of the dichloro complex from $RhCl_3 \cdot 3H_2O$ and cyclam in water gave almost entirely the *cis* isomer. On the other hand, if the same preparation was carried out in methanol, the *trans* isomer predominated (60% *trans*, 30% *cis* isolated). When the reaction was carried out in a NaBr solution, sufficient *trans* isomer was produced to be separated, but the impure yield (17%) was much lower than the reaction of the dichloro complex with Br^- reported below. A NaI solution gave an even greater percentage of *trans* isomer, however, it could not be separated from the *cis*.

All the *cis*- and *trans*-$Rh(cyclam)X_2^+$ complexes were prepared from the respective *cis* or *trans* dichloro complex by heating at reflux temperature in an aqueous solution of the desired anion for extended periods of time. This was possible since only the *cis*-diiodo complex showed any tendency to isomerize. However, even the *cis*-diiodo complex could be prepared by carefully limiting the reflux period.

Since these preparations were time consuming, a catalytic approach was attempted. Gillard *et al.* (30) have suggested several catalysts for Rh(III) reactions. $NaBH_4$ was found to be ineffective. The solutions of $NaBH_4$ were basic, causing interference by the predominating base hydrolysis reaction. No further work was done with catalysis since base hydrolysis itself was found to be a convenient pathway for the desired mixed complexes.

The cyclam complexes of Rh(III) were very sensitive to base hydrolysis and gave complete dihydroxo formation in less than 1 h in approximately 0.1 *M* NaOH, with indications of the usual second-order rate dependence. The bis-(ethylenediamine) analogs, on the other hand, were not as susceptible to base hydrolysis and formed the dihydroxo complex at rates slower than the usual substitution rates, which are limited by the acid hydrolysis rate. The rapid formation of hydroxo complexes provided an excellent pathway for the preparation of $Rh(cyclam)XY^{n+}$. By carefully limiting the reflux period from 3 to 10 min, it was found that the solution contained only the mono- and dihydroxo products, and the monohydroxo product could be precipitated in very pure form (yields: approximately 50%) since the dihydroxo could not be precipitated with perchlorate. The monohydroxo complex was acidified to give the monoaquo, which was readily anated with several different anions to give the desired mixed XY complexes.

Experimental

$RhCl_3 \cdot 3H_2O$ from J. Bishop and Co. Platinum Works was used without further purification. Pure methanol (99.9 mole %) and ion-exchanged distilled water were used as solvents. Reagent grade sodium salts were used as a source of the anions for substitution and precipitation.

Electronic spectra were recorded on a Bausch and Lomb Spectronic 505, using water as the solvent for all samples except those with a hydroxo ligand. Hydroxo complexes were recorded in 0.1 *M* NaOH. Infrared spectra were recorded on a Beckman IR 10 using approximately 1% KBr pellets. The o.r.d. spectra were recorded on a Cary 60 instrument.

1,4,8,11-Tetraazacyclotetradecane (Cyclam)

The open-chain intermediate, 1,9-diamino-3,7-diazanonane, was prepared according to the method of Van Alphen (31). 1,3-Dibromopropane (250 g, 1.2 moles, 126 ml) was added dropwise to ethylenediamine (360 g, 6.0 moles, 400 ml) in 300 ml ethanol. The yellow solution was heated under reflux for 1 h. KOH (300 g, 5.3 moles) was added and the reaction mixture was stirred for 30 min. The KBr and excess KOH were removed by filtration. The ethanol and excess ethylenediamine were removed by distillation (116–117 °C). The 1,9-diamino-3,7-diazanonane was separated by vacuum distillation (138 °C, 4 mm Hg) as a clear viscous liquid (90 g, 0.56 mole, 47% yield).

Cyclam was prepared according to Tobe and coworkers (1) with some modifications. 1,3-Dibromopropane (50 g, 0.25 mole) and 1,9-diamino-3,7-diazanonane (40 g, 0.25 mole) were added to 4 l ethanol and heated under reflux for 24 h, during which the solution turned yellow. Three liters of ethanol were removed by distillation. KOH (35 g, 0.62 moles) was added and the volume was reduced to about 500 ml by distillation. The solution was cooled and the KBr was removed by filtration. The volume was reduced to 150 ml, during which the excess KOH was removed by decantation. The viscous yellow solution was cooled overnight to precipitate the white product (3.0 g, 6%), which was filtered, washed with acetone, and purified by vacuum sublimation (120 °C, 2 mm Hg). The melting point in a sealed tube was 186 °C.

Anal. Calcd. for $C_{10}H_{24}N_4$: C, 59.95; H, 12.08; N, 27.97. Found: C, 59.93; H, 12.24; N, 27.93.

cis-[Rh(cyclam)Cl_2]Cl

$RhCl_3 \cdot 3H_2O$ (7.5 g, 28 mmoles) and cyclam (7.5 g, 37 mmoles) were dissolved in 300 ml methanol and heated under reflux for 5 min, during which the red mixture turned to a yellow solution with a yellow precipitate. The reaction mixture was cooled and filtered. The yellow product (3.1 g, 27%) was washed with ethanol and ether and dried under vacuum for 2 h.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)Cl_2]Cl$: C, 29.32; H, 5.91; N, 13.68; Cl, 25.97. Found: C, 29.26; H, 5.99; N, 14.02; Cl, 25.80.

trans-[Rh(cyclam)Cl_2]Cl

The filtrate from the preparation of *cis*-[Rh(cyclam)Cl_2]Cl in methanol was treated with 25 ml concentrated HCl to precipitate the excess cyclam as the tetrahydrochloride (analyzed as 3.5 HCl), and any *cis* isomer left in the solution. After filtration, the yellow solution was evaporated to dryness. The yellow residue was recrystallized from 75 ml water and 25 ml concentrated HCl, washed with acetone and ether and dried under vacuum for 2 h (5.8 g, 50%).

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)Cl_2]Cl$: C, 29.32; H, 5.91; N, 13.68; Cl, 25.97. Found: C, 29.38; H, 5.89; N, 13.68; Cl, 26.17.

cis-[Rh(cyclam)Cl_2]ClO_4

$RhCl_3 \cdot 3H_2O$ (2.0 g, 7.6 mmoles), cyclam (1.5 g, 7.6 mmoles), and NaCl (2.0 g, 34 mmoles) were added to 50 ml water and heated under reflux for 30 min, during which the red mixture changed to a yellow solution. $HClO_4$ (5 ml, 70%) was added to precipitate the product. The yellow product (2.4 g, 70%) was recrystallized by repeating the procedure.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)Cl_2]ClO_4$: C, 25.36; H, 5.11; N, 11.83; Cl, 22.46. Found: C, 25.57; H, 5.29; N, 11.91; Cl, 22.47.

cis-[Rh(cyclam)Br_2]Br

cis-[Rh(cyclam)Cl_2] (500 mg, 1.22 mmoles) and NaBr (2.5 g, 24 mmoles) were dissolved in 50 ml water and heated under reflux for 3 h. The solution turned from yellow to orange, with the formation of an orange precipitate. The reaction mixture was cooled to precipitate the orange product, which was recrystallized by repeating the procedure (450 mg, 68%), washed with ethanol and ether and dried under vacuum for 2 h.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)Br_2]$: C, 22.12; H, 4.46; N, 10.32; Br, 44.15. Found: C, 22.26; H, 4.47; N, 10.34; Br, 43.86.

trans-[Rh(cyclam)Br_2]Br

Using the *trans*-dichloro compound, the procedure was the same as for the *cis* isomer with a 5 h reflux period and NaBr (4.6 g, 44 mmoles) in 50 ml water. The *trans* isomer (240 mg, 41%) was also orange.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)Br_2]Br$: C, 22.12; H, 4.46; N, 10.32; Br, 44.15. Found: C, 22.28; H, 4.43; N, 10.50; Br, 43.92.

cis-[Rh(cyclam)I_2]I

cis-[Rh(cyclam)Cl_2]Cl (500 mg, 1.22 mmoles) was dissolved in 0.33 *M* NaI and heated under reflux for 30 min. The solution turned from yellow to orange. It was cooled to precipitate the orange product, which was recrystallized by repeating the procedure twice. The orange product (370 mg, 45%) was washed with ethanol and ether and dried under vacuum for 2 h.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)I_2]I$: C, 17.56; H, 3.54; N, 8.19; I, 55.66. Found: C, 18.07; H, 3.77; N, 8.43; I, 55.66.

trans-[Rh(cyclam)I_2]I

trans-[Rh(cyclam)Cl_2]ClO_4 (504 mg, 1.06 mmoles) and NaI (3.2 g, 21 mmoles) were added to 150 ml water and heated under reflux for 3 h, during which a brown precipitate was formed. The solution was cooled and the brown product was recrystallized by heating in 2 l water and NaI (3.2 g, 21 mmoles) for 3 days, followed by slow evaporation to 200 ml. The product (610 mg, 84%) was washed with ethanol and ether and dried under vacuum for 2 h.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)I_2]I$: C, 17.56; H, 3.54; N, 8.19; I, 55.66. Found: C, 17.38; H, 3.54; N, 8.20; I, 55.74.

cis-[Rh(cyclam)(N$_3$)$_2$]ClO$_4$

cis-[Rh(cyclam)Cl_2]Cl (500 mg, 1.22 mmoles) and NaN_3 (1.0 g, 15 mmoles) were dissolved in 25 ml water and heated under reflux for 3 h. The yellow solution became golden. $HClO_4$ (5 ml, 70%) was added to precipitate the yellow product, which was recrystallized by repeating the procedure. The product (460 mg, 78%) was washed with ethanol and ether and dried under vacuum for 2 h. The product was protected from light to prevent decomposition to a brown compound.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)(N_3)_2]ClO_4$: C, 24.68; H, 4.97; N, 28.78; Cl, 7.28. Found: C, 24.70; H, 5.12; N, 29.02; Cl, 7.40.

trans-[Rh(cyclam)(N$_3$)$_2$]ClO$_4$

The *trans* isomer was prepared using the same procedure as for the *cis* compound. The yellow product (390 mg, 73%) was protected from light.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)(N_3)_2]ClO_4$: C, 24.68; H, 4.97; N, 28.78. Found: C, 24.88; H, 4.96; N, 28.73.

cis-[Rh(cyclam)(NO$_2$)$_2$]ClO$_4$

cis-[Rh(cyclam)Cl_2]ClO_4 (500 mg, 1.05 mmoles) and $NaNO_2$ (1.7 g, 24 mmoles) were dissolved in 50 ml water and heated under reflux for 3 h. The solution turned paler yellow. $HClO_4$ (5 ml, 70%) was added to precipitate the product, which was recrystallized by repeating the procedure. The pale yellow product (400 mg, 76%) was washed with ethanol and ether and dried under vacuum.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)(NO_2)_2]ClO_4$: C, 24.28; H, 4.89; N, 16.99. Found: C, 24.44; H, 4.93; N, 16.64.

trans-[Rh(cyclam)(NO$_2$)$_2$]ClO$_4$

trans-[Rh(cyclam)Cl_2]Cl (719 mg, 1.75 mmoles) and $NaNO_2$ (3.5 g, 51 mmoles) were added to 50 ml water and heated under reflux for 20 h. $HClO_4$ (5 ml, 70%) was added to precipitate the product, which was recrystallized by repeating the procedure. The white powder (484 mg, 58%) was washed with ethanol and ether and dried under vacuum.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)(NO_2)_2]ClO_4$: C, 24.28; H, 4.89; N, 16.99; O, 25.87. Found: C, 24.56; H, 4.97; N, 17.00; O, 25.59.

cis-[Rh(cyclam)(NCS)$_2$]ClO$_4$

trans-[Rh(cyclam)(OH)(H_2O)]$(ClO_4)_2$ (375 mg, 0.697 mmole), NaSCN (2.0 g, 25 mmoles), and $NaClO_4 \cdot H_2O$ (10 g, 72 mmoles) were dissolved in 25 ml water and heated under reflux for 2 h during which the solution became darker yellow. The solution was cooled to precipitate the product. The yellow-white product (165 mg, 46%) was washed with ethanol and ether and dried under vacuum.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)(NCS)_2]ClO_4$: C, 27.78; H, 4.66; N, 16.20; S, 12.36. Found: C, 27.84; H, 4.57; N, 16.20; S, 12.29.

trans-[Rh(cyclam)(NCS)$_2$]ClO$_4$

trans-[Rh(cyclam)(OH)(H_2O)]$(ClO_4)_2$ (218 mg, 0.405 mmole) and NaSCN (1.0 g, 12 mmoles) were added to 25 ml water and 5 drops of dilute $HClO_4$. The yellow solution was heated under reflux for 50 h. $NaClO_4 \cdot H_2O$ (10 g, 72 mmoles) was added to precipitate the product. The pale yellow complex was added to 50 ml 1.0 *M* NaSCN, heated under reflux for 10 h, and precipitated with $NaClO_4$. The product (72 mg, 34%) was washed with ethanol and ether and dried under vacuum.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)(NCS)_2]ClO_4$: C, 27.78; H, 4.66; N, 16.20; S, 12.36. Found: C, 27.56; H, 4.57; N, 15.96; S, 12.44.

trans-[Rh(cyclam)Cl(OH)]ClO$_4$

trans-[Rh(cyclam)Cl_2]Cl (306 mg, 0.747 mmole) and NaOH (1 pellet, ~2.5 mmoles) were dissolved in 20 ml water and heated under reflux for 5 min. $NaClO_4 \cdot H_2O$ (5.0 g, 36 mmoles) was added to precipitate the white complex (153 mg, 45%), which was washed with ethanol and ether and dried under vacuum.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)Cl(OH)]ClO_4$: C, 26.39; H, 5.54; N, 12.31; Cl, 15.58. Found: C, 26.36; H, 5.48; N, 12.07; Cl, 15.71.

trans-[Rh(cyclam)Cl(H$_2$O)](ClO$_4$)$_2$

trans-[Rh(cyclam)Cl_2]Cl (510 mg, 1.24 mmoles) and NaOH (1 pellet, ~2.5 mmoles) were dissolved in 25 ml water and heated under reflux for 4 min. The pale yellow solution was cooled on ice and slightly acidified with dilute $HClO_4$. $NaClO_4 \cdot H_2O$ (10 g, 72 mmoles) was added to precipitate the yellow product (387 mg, 56%), which was washed with ethanol and ether and dried under vacuum for 2 h.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)Cl(H_2O)](ClO_4)_2$: C, 21.62; H, 4.72; N, 10.08; Cl, 19.14. Found: C, 21.46; H, 4.35; N, 10.07; Cl, 19.30.

trans-[Rh(cyclam)Br(OH)]ClO$_4$

trans-[Rh(cyclam)Br_2]Br (203 mg, 0.374 mmole) and NaOH (1 pellet, ~2.5 mmoles) were dissolved in 15 ml water and heated under reflux for 3 min, during which the solution turned paler yellow. $NaClO_4 \cdot H_2O$ (5.0 g, 36 mmoles) was added to precipitate the pale yellow complex (95 mg, 51%), which was washed with 1:1 ethanol and ether and dried under vacuum.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)Br(OH)]ClO_4$: C, 24.04; H, 5.04; N, 11.21; Br, 15.99; Cl, 7.10. Found: C, 24.23; H, 4.94; N, 11.12; Br, 16.04; Cl, 7.08.

trans-[Rh(cyclam)Br(H$_2$O)](ClO$_4$)$_2$

trans-[Rh(cyclam)Br_2]Br (214 mg, 0.394 mmole) and NaOH (1 pellet, ~2.5 mmoles) were dissolved in 15 ml water and heated under reflux for 3 min. The yellow solution was cooled and acidified with dilute $HClO_4$. $NaClO_4 \cdot H_2O$ (5.0 g, 36 mmoles) was added to precipitate the pale orange complex (127 mg, 54%), which was washed with 1:1 ethanol and ether and dried under vacuum.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)Br(H_2O)](ClO_4)_2$: C, 20.01; H, 4.37; N, 9.34; Br, 13.32; Cl, 11.82. Found: C, 20.42; H, 4.18; N, 9.49; Br, 12.94; Cl, 11.66.

trans-[Rh(cyclam)I(OH)]ClO$_4$

trans-[Rh(cyclam)I_2]I (268 mg, 0.392 mmole) and NaOH (1 pellet, ~2.5 mmoles) NaOH were added to 15 ml water and heated under reflux for an additional 5 min. $NaClO_4 \cdot H_2O$ (5.0 g, 36 mmoles) was added to precipitate the orange complex (51 mg, 24%), which was

washed with 1:1 ethanol and ether and dried under vacuum.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)I(OH)]ClO_4$: C, 21.97; H, 4.61; N, 10.25; I, 23.22; Cl, 6.49. Found: C, 22.12; H, 4.49; N, 10.10; I, 23.16; Cl, 6.39.

trans-[Rh(cyclam)I(H₂O)](ClO₄)₂

trans-[Rh(cyclam)I_2]I (292 mg, 0.427 mmole) and NaOH (1 pellet, ~2.5 mmoles) were added to 25 ml water and treated according to the *trans* iodohydroxo preparation. The yellow solution was cooled on ice and slightly acidified with dilute $HClO_4$, which made the solution red. $NaClO_4 \cdot H_2O$ (5.0 g, 36 mmoles) was added to precipitate the red complex (75 mg, 27%), which was washed with 1:1 ethanol and ether and dried under vacuum.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)I(H_2O)](ClO_4)_2$: C, 18.56; H, 4.05; N, 8.65; I, 19.61; Cl, 10.96. Found: C, 18.31; H, 4.11; N, 7.99; I, 19.55; Cl, 11.04.

trans-[Rh(cyclam)(N₃)(OH)]ClO₄

trans-[Rh(cyclam)$(N_3)_2$]ClO_4 (203 mg, 0.417 mmole) and NaOH (1 pellet, ~2.5 mmoles) were dissolved in 25 ml water and heated under reflux for 10 min, which made the solution paler yellow. $NaClO_4 \cdot H_2O$ (5.0 g, 36 mmoles) was added to precipitate the pale yellow complex (76 mg, 36%), which was washed with 1:1 ethanol and ether, dried under vacuum, and protected from light.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)(N_3)(OH)]ClO_4$: C, 26.01; H, 5.46; N, 21.24. Found: C, 26.17; H, 5.39; N, 20.96.

trans-[Rh(cyclam)(N₃)(H₂O)](ClO₄)₂

trans-[Rh(cyclam)$(N_3)_2$]ClO_4 (233 mg, 0.458 mmole) was treated with NaOH as described for the hydroxo preparation. The yellow solution was cooled on ice and slightly acidified with dilute $HClO_4$. $NaClO_4 \cdot H_2O$ (5.0 g, 36 mmoles) was added to precipitate the yellow complex (140 mg, 54%) which was washed with 1:1 ethanol and ether, dried under vacuum, and protected from light.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)(N_3)(H_2O)](ClO_4)_2$: C, 21.36; H, 4.66; N, 17.44. Found: C, 21.45; H, 4.42; N, 17.27.

cis-[Rh(cyclam)(OH)(H₂O)](ClO₄)₂

cis-[Rh(cyclam)Cl_2]Cl (496 mg, 1.21 mmoles) and NaOH (2 pellets, ~5 mmoles) were added to 25 ml water and heated under reflux for 5 min, during which the solution turned paler yellow. $NaClO_4 \cdot H_2O$ (10 g, 72 mmoles) was added and the solution was neutralized with dilute $HClO_4$ to precipitate the very pale yellow product (429 mg, 0.798 mmole, 66%), which was washed with ethanol and ether and dried under vacuum.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)(OH)(H_2O)](ClO_4)_2$: C, 22.32; H, 5.24; N, 10.41; Cl, 13.18. Found: C, 22.42; H, 5.15; N, 10.44; Cl, 13.20.

trans-[Rh(cyclam)(OH)(H₂O)](ClO₄)₂

trans-[Rh(cyclam)Cl_2]Cl (698 mg, 1.70 mmoles) and NaOH (5 pellets, ~12 mmoles) were dissolved in 20 ml water and heated under reflux for 100 min during which the solution became very pale yellow. $NaClO_4 \cdot H_2O$ (10 g, 72 mmoles) was added and the solution was neutralized with dilute $HClO_4$. The pale yellow precipitate (610 mg, 67%) was washed with ethanol and ether and dried under vacuum.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)(OH)(H_2O)](ClO_4)_2$: C, 22.32; H, 5.24; N, 10.41; Cl, 13.18. Found: C, 22.09; H, 5.19; N, 10.21; Cl, 13.10.

trans-[Rh(cyclam)ClBr]ClO₄

trans-[Rh(cyclam)Cl_2]Cl (218 mg, 0.531 mmole) and NaOH (1 pellet, ~2.5 mmoles) were dissolved in 25 ml water and heated under reflux for 5 min, during which the solution turned paler yellow. Concentrated HBr (10 ml, 87 mmoles) and 10 ml 70% $HClO_4$ were added and the solution was heated at 55 °C for 20 h, during which a yellow precipitate was formed. The product (118 mg, 43%) was recrystallized from water, washed with ethanol and ether, and dried under vacuum.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)ClBr]ClO_4$: C, 23.19; H, 4.67; Br, 15.42; Cl, 13.69. Found: C, 23.36; H, 4.70; Br, 15.35; Cl, 13.76.

trans-[Rh(cyclam)ClI]ClO₄

trans-[Rh(cyclam)I_2]I (200 mg, 0.292 mmole) was dissolved in 400 ml 0.1 *M* NaCl and heated at 60 °C in a constant-temperature bath for 2 days. $HClO_4$ (25 ml, 70%) was added to precipitate the complex, which was purified by repeating the procedure. The orange product was washed with ethanol and ether and dried under vacuum.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)ClI]ClO_4$: C, 21.26; H, 4.28; I, 22.46; Cl, 12.55. Found: C, 21.55; H, 4.60; I, 22.39; Cl, 12.84.

trans-[Rh(cyclam)Cl(N₃)]ClO₄

trans-[Rh(cyclam)$(N_3)_2$]ClO_4 (232 mg, 0.476 mmole) was added to 50 ml 1.0 *M* HCl and heated at 85 °C for 6 h. $HClO_4$ (5 ml, 70%) was added to precipitate the complex, which was recrystallized from 40 ml water and 2 ml 70% $HClO_4$. The yellow product (140 mg, 61%) was washed with ethanol and ether and dried under vacuum.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)Cl(N_3)]ClO_4$: C, 25.10; H, 5.16; N, 20.42; Cl, 14.76. Found: C, 25.15; H, 4.95; N, 20.29; Cl, 14.81.

trans-[Rh(cyclam)Cl(NCS)]ClO₄

trans-[Rh(cyclam)$Cl(H_2O)](ClO_4)_2$ (134 mg, 0.242 mmole) and NaSCN (1.0 g, 12 mmoles) were dissolved in 15 ml water and heated under reflux for 15 min. $NaClO_4 \cdot H_2O$ (5.0 g, 36 mmoles) was added to precipitate the yellow complex (73 mg, 61%), which was washed with ethanol and ether and dried under vacuum.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)Cl(NCS)]ClO_4$: C, 26.62; H, 4.88; N, 14.11; Cl, 14.29; S, 6.46. Found: C, 26.56; H, 4.81; N, 13.84; Cl, 14.33; S, 6.46.

trans-[Rh(cyclam)BrI]ClO₄

trans-[Rh(cyclam)I_2]I (280 mg, 0.410 mmole) and NaOH (1 pellet, ~2.5 mmoles) were added to 50 ml water and heated under reflux for 15 min. The yellow solution was filtered, concentrated HBr (4.0 ml, 35 mmoles) was added, and the solution was heated at 70 °C for 5 min. The volume was increased to 500 ml to dissolve the bromide. $HClO_4$ (50 ml, 70%) was added to precipitate the perchlorate. The orange crystals (158 mg, 63%) were

washed with ethanol and ether and dried under vacuum.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)BrI]ClO_4$: C, 19.71; H, 3.97; N, 9.19; Br, 13.11; I, 20.82. Found: C, 19.70; H, 3.80; N, 9.01; Br, 12.90; I, 20.92.

trans-[Rh(cyclam)Br(N_3)]ClO_4

trans-[Rh(cyclam)$(N_3)_2$]ClO_4 (149 mg, 0.306 mmole) was added to 25 ml 1.0 *M* $HClO_4$ and heated under reflux for 5 h. NaBr (2.6 g, 25 mmoles) was added and the yellow solution was heated at 70 °C for 1 h. $HClO_4$ (5 ml, 70%) was added to precipitate the product, which was recrystallized from 25 ml water and 2 ml 70% $HClO_4$. The orange crystals (110 mg, 69%) were washed with ethanol and ether, dried under vacuum, and protected from light.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)Br(N_3)]ClO_4$: C, 22.90; H, 4.61; N, 18.69; Br, 15.23; Cl, 6.76. Found: C, 22.76; H, 4.74; N, 18.55; Br, 15.08; Cl, 6.78.

trans-[Rh(cyclam)Br(NCS)]ClO_4

trans-[Rh(cyclam)Br(H_2O)]$(ClO_4)_2$ (214 mg, 0.340 mmole) and NaSCN (1.0 g, 12 mmoles) were dissolved in 15 ml water and heated under reflux for 10 min, which made the solution turn from orange to yellow. $NaClO_4 \cdot H_2O$ (10 g, 72 mmoles) was added to precipitate the yellow complex (144 mg, 78%), which was washed with ethanol and ether and dried under vacuum.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)Br(NCS)]ClO_4$: C, 24.64; H, 4.47; N, 12.95; Br, 14.78; Cl, 6.56. Found: C, 24.82; H, 4.39; N, 12.97; Br, 14.59; Cl, 6.70.

trans-[Rh(cyclam)I(N_3)]ClO_4

trans-[Rh(cyclam)I_2]I (306 mg, 0.447 mmole) and NaOH (1 pellet, ~2.5 mmoles) were added to 200 ml water and heated under reflux for 5 min. The yellow solution was filtered and NaN_3 (20 g, 310 mmoles) was added. Then the solution was neutralized with dilute $HClO_4$, during which it turned orange. $HClO_4$ (50 ml, 70%) was added to precipitate the orange product (81 mg, 32%), which was washed with ethanol and ether and dried under vacuum.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)I(N_3)]ClO_4$: C, 21.01; H, 4.23; N, 17.15; I, 22.20. Found: C, 21.26; H, 4.21; N, 17.09; I, 22.31.

trans-[Rh(cyclam)I(NCS)]ClO_4

trans-[Rh(cyclam)I(H_2O)]$(ClO_4)_2$ (289 mg, 0.466 mmole) and NaSCN (1.0 g, 12 mmoles) were dissolved in 25 ml water and heated under reflux for 15 min, which made the solution turn from red to orange. $NaClO_4 \cdot H_2O$ (10 g, 72 mmoles) was added to precipitate the pale orange complex (227 mg, 87%), which was washed with ethanol and ether and dried under vacuum.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)I(NCS)]ClO_4$: C, 22.48; H, 4.12; N, 11.92; I, 21.59; Cl, 6.03. Found: C, 22.60; H, 4.03; N, 11.95; I, 21.74; Cl, 5.94.

trans-[Rh(cyclam)(N_3)(NCS)]ClO_4

trans-[Rh(cyclam)$(N_3)(H_2O)$]$(ClO_4)_2$ (243 mg, 0.432 mmole) and NaSCN (1.0 g, 12 mmoles) were dissolved in 20 ml water and heated at 70 °C for 75 min, during which the solution remained yellow. $NaClO_4 \cdot H_2O$ (10 g, 72 mmoles) was added to precipitate the yellow complex (142 mg, 64%), which was washed with ethanol and ether and dried under vacuum.

Anal. Calcd. for $[Rh(C_{10}H_{24}N_4)(N_3)(NCS)]ClO_4$: C, 25.77; H, 4.72; N, 21.85; S, 6.25. Found: C, 25.97; H, 4.72; N, 21.97; S, 6.27.

Resolution of cis-[Rh(cyclam)Cl_2]Cl

cis-[Rh(cyclam)Cl_2]Cl (500 mg, 1.22 mmoles) and *d*-ammonium α-bromocamphor-π-sulfonate (0.90 g, 2.7 mmoles) were dissolved in 15 ml water and frozen for 1 week. The mixture was melted and filtered. The pale yellow precipitate was washed with a few drops of ice cold water and ground thoroughly with 2 ml of 1:1:1 ethanol, concentrated HCl, and ether. The *l-cis*-[Rh(cyclam)Cl_2]Cl was filtered (149 mg, 60%).

Using a mercury and sodium lamp, the rotation of a 0.58% solution was too small to measure on a Rudolph polarimeter.

The o.r.d. spectrum of a 1.13% solution was recorded and exhibited zero rotation at 353 and 300 mμ, which corresponds to the absorption maxima of the *cis* isomer. There was a positive rotation (0.0007°) at 325 mμ and a negative rotation (0.0007°) at 370 mμ.

$$[\alpha]_{325\ m\mu} = +6°$$
$$[\alpha]_{370\ m\mu} = -6°$$

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