$$\mathrm{RMgX\cdot}n\ \mathrm{ether} + \mathrm{THF} \rightleftharpoons \mathrm{RMgX\cdot}(n - r)\mathrm{ether\cdot THF} + r\ \mathrm{ether}$$

However, there is no cogent reason for believing that $n \neq r \neq 1$.

Acknowledgment.—Partial support of this work by the U. S. Army Research Office (Durham) is gratefully acknowledged. We also wish to thank the Burrell Corporation for the gas chromatograph used in this work.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY,
EVANSTON, ILLINOIS

Synthesis and Characterization of Some Diacidotetraamminerhodium(III) Compounds[1]

BY SUSAN A. JOHNSON[2] AND FRED BASOLO

Received February 23, 1962

The syntheses of salts of the complex cations $[\mathrm{RhA}_m\mathrm{Cl}_2]^+$, where A = $\mathrm{NH_3}$, en, *m*-bn, *d,l*-bn, tetrameen, tren, or trien,[3] are described. Similarly, preparations are given for salts of the type $[\mathrm{Rh(en)_2X_2}]^+$, where X = $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{I^-}$, $\mathrm{NO_2^-}$, or $\mathrm{N_3^-}$, and for those of the type $[\mathrm{Rh(en)_2XCl}]^{+n}$ where X = $\mathrm{SCN^-}$, $\mathrm{NO_2^-}$, or $\mathrm{NH_3}$. In most cases it was possible to isolate both the *cis* and *trans* isomers. Proof of structure for the isomers of $[\mathrm{Rh(en)_2Cl_2}]^+$ was obtained by resolution of the *cis* form. In all other cases structural assignment was based on measurements of absorption spectra. For the $[\mathrm{RhA}_m\mathrm{Cl}_2]^+$ systems there was the supporting evidence that the rates of hydrolysis of the *trans* isomers are not base-catalyzed, whereas the *cis* isomers hydrolyze more rapidly in alkaline solution.

Introduction

Although extensive investigations have been carried out on the synthesis, properties, and reactive behavior of the diacidotetraamminecobalt(III) complex cations (*i.e.*, species of the type $[\mathrm{CoA}_m\mathrm{X}_2]^+$, where A_m signifies coördination of four of the six octahedral positions by amine nitrogens and may be comprised of four unidentate, two bidentate, or one quadridentate ligand, and X is a univalent anion such as $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{I^-}$, $\mathrm{SCN^-}$, $\mathrm{NO_2^-}$, $\mathrm{N_3^-}$, $\mathrm{OH^-}$, etc.), very little work has appeared in reference to analogous complexes of the congener Rh(III). The available information on diacidotetraamminerhodium(III) cations consists of reports of synthesis of half a dozen such complexes, some of which the present authors have found to be of questionable accuracy. In every case only one of the two possible geometric isomers was reported and its structure was never established. References to the previous work were given in a preliminary communication.[4]

The successful synthesis of the diacidotetraamminerhodium(III) salts reported here will enable us to draw quantitative behaviorial comparisons between the corresponding cobalt(III) and rhodium(III) complexes in regard to the kinetics and mechanisms of hydrolysis, isomerization, and racemization. Results of these comparisons will be reported later. This paper is intended to describe methods of synthesis and characterization of a variety of previously unknown diacidotetraamminerhodium(III) compounds.

Experimental and Results

Hydrated rhodium chloride ($\mathrm{RhCl_3\cdot 3H_2O}$) was generally used as the starting material for the preparation of dichlorotetraamminerhodium(III) complexes. Details of its preparation starting with Rh metal have been described elsewhere.[5]

***trans*-Dichlorotetraamminerhodium(III) Salts.**—The method reported by Lebedinski[6] for the synthesis of $[\mathrm{Rh(NH_3)_4Cl_2}]\mathrm{NO_3}$ was tried several times without success, the only isolable product of the reaction being $[\mathrm{Rh(NH_3)_3Cl_3}]$. The desired complex was isolated as a by-product

---

[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. AF 49(638)315. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] National Institutes of Health Fellow, 1960–1961.

[3] The symbols used are en = ethylenediamine, *m*-bn = *meso*-butylenediamine, *d,l*-bn = *d,l*-butylenediamine, tetrameen = C-tetramethylethylenediamine, tren = β,β′,β″-triaminoethylamine, and trien = triethylenetetramine.

[4] S. Anderson and F. Basolo, *J. Am. Chem. Soc.*, **82**, 4423 (1960).

[5] S. N. Anderson and F. Basolo, *Inorg. Syn.*, **7**, in press.

[6] W. W. Lebedinski, *Izv. Inst. Izučeniju Platiny*, **12**, 67 (1935).

of the reaction used by Lebedinski[7] to prepare $[Rh(NH_3)_5Cl]Cl_2$. Three g. of $RhCl_3\cdot3H_2O$ was dissolved in 40 ml. of H_2O. To this were added 10 g. of NH_4Cl and 7.5 g. of finely powdered $(NH_4)_2CO_3$. The mixture was heated on a steam bath for 3 hr., then cooled and allowed to crystallize. The golden yellow product was collected on a filter and extracted with about 100 ml. of boiling 2:1 hydrochloric acid:water. Lebedinski purified crude $[Rh(NH_3)_5Cl]Cl_2$ by recrystallization from this medium; however, $[Rh(NH_3)_5Cl]Cl_2$ prepared in this Laboratory was essentially insoluble in the hot acid while $[Rh(NH_3)_4Cl_2]Cl$ dissolved readily, allowing an effective separation of a mixture of the two complexes. The extract was filtered to remove $[Rh(NH_3)_5Cl]Cl_2$ and allowed to cool to room temperature whereupon $[Rh(NH_3)_4Cl_2]Cl$ precipitated. Lebedinski's earlier allegation that $[Rh(NH_3)_4Cl_2]Cl$ was too unstable with respect to disproportionation to $[Rh(NH_3)_3Cl_3]$ and $[Rh(NH_3)_5Cl]Cl_2$ to be isolated is not correct. The tetraammine was purified by conversion to the sparingly soluble nitrate, $[Rh(NH_3)_4Cl_2]NO_3\cdot H_2O$; the chloride was dissolved in a minimum amount of H_2O and filtered into a small amount of ice-cold concentrated HNO_3. The golden yellow complex was collected on a filter, washed with separate small portions of dilute HNO_3, ethanol, and ether, and then air-dried; yield, 0.5 g. (13%).

Anal. Calcd. for $[Rh(NH_3)_4Cl_2]NO_3\cdot H_2O$: N, 21.69; H, 4.37; Cl, 22.0. Found: N, 21.88; H, 4.14; Cl, 21.9.

cis- **and** *trans-***Dichlorobis-(ethylenediamine)-rhodium-(III) Salts.**—Several unsuccessful attempts were made to repeat the synthesis of $[Rh(en)_2Cl_2]Cl\cdot2H_2O$ reported by Meyer and Kienitz.[8] *cis-* and *trans-*$[Rh(en)_2Cl_2]NO_3$ were prepared by the slow addition of aqueous KOH to a refluxing water solution of $RhCl_3\cdot3H_2O$ and en·2HCl. A mixture of 1.00 g. of $RhCl_3\cdot3H_2O$ and 1.01 g. of en·2HCl in 50 ml. of H_2O containing 0.426 g. of KOH (one-half enough for complete neutralization of the hydrochloride) was refluxed until the solution cleared. To the refluxing solution was added, through the top of the water-cooled condenser, another 0.426 g. of KOH in 50 ml. of H_2O in 5 ml. increments at 1–2 min. intervals. The resulting golden yellow solution was evaporated on a steam bath to about one-half its original volume, and to it was added 20 ml. of concentrated HNO_3. The mixture was allowed to stand with occasional stirring for about 2 hr., during which time the less soluble *trans-*$[Rh(en)_2Cl_2]NO_3$ was almost quantitatively precipitated as a golden yellow crystalline substance. The product was removed by filtration and recrystallized by dissolving in a minimum amount of H_2O and filtering into ice-cold concentrated HNO_3. It then was collected on a filter, washed with separate small portions of cold dilute HNO_3, ethanol, and ether, and air-dried; yield, 0.45 g. (33%).

Anal. Calcd. for $[Rh(en)_2Cl_2]NO_3$: C, 13.49; H, 4.53; Cl, 19.9. Found: C, 13.87; H, 4.63; Cl, 19.9.

Bright yellow *cis-*$[Rh(en)_2Cl_2]NO_3$ separated when the filtrate was allowed to stand and evaporate at room temperature for 24–48 hr. It was purified exactly as was the *trans* isomer; yield, 0.15 g. (11%).

Anal. Calcd. for $[Rh(en)_2Cl_2]NO_3$: C, 13.49; H, 4.53; Cl, 19.9. Found: C, 13.98; H, 4.31; Cl, 19.9.

It subsequently was found that the yield of *cis* isomer was substantially increased by the addition of 20% excess KOH to the reaction mixture. After following the preparative procedure described above for *cis-* and *trans-*$[Rh(en)_2Cl_2]^+$, 2 pellets (~0.2 g.) of solid KOH were dropped into the refluxing reaction solution. At this point there was evidence of some decomposition—a finely divided brownish black substance appeared. The solution was allowed to reflux for about 5 min. and then filtered to remove the decomposition product; the reaction mixture was concentrated and treated with nitric acid as described previously. The immediate voluminous precipitate was quickly removed by filtration and found to be about 0.5 g. of a mixture of approximately 85% *cis-* and 15% *trans-*$[Rh(en)_2Cl_2]NO_3$. The filtrate was allowed to stand for about 1 hr., during which time a small amount of (~0.1 g.) of *trans-*$[Rh(en)_2Cl_2]NO_3$ precipitated. During the next several days the filtrate yielded another 0.5 g. of pure *cis-*$[Rh(en)_2Cl_2]NO_3$. The total yield of *cis-*$[Rh(en)_2Cl_2]NO_3$ was 70%. Pure *cis* isomer may be obtained from a mixture of the two isomers by careful recrystallization, although removing a small amount of *trans* complex from a large amount of *cis* is more difficult than the reverse because of the lesser solubility of the former.

The composition of a mixture of *cis-* and *trans-*$[Rh(en)_2Cl_2]^+$ may be readily determined by heating a solution of the complexes ($\sim2.5 \times 10^{-3}$ *M*) in 0.1 *M* KOH at 80° for 5 min. Under these conditions *cis-*$[Rh(en)_2Cl_2]^+$ releases all of its chloride while *trans-*$[Rh(en)_2Cl_2]^+$ does not react; a titration for chloride in the resulting solutions allows a calculation of the per cent *cis* present originally.

Although it is possible through repeated recrystallizations to isolate *cis-* and *trans-*$[Rh(en)_2Cl_2]Cl$ directly from the original reaction mixture, in practice the rather soluble chloride salts are more readily obtained free from contamination by each other and by KCl by passing an aqueous solution of the appropriate nitrate salt over an anion exchange resin (as Dowex 1-X4) in the chloride form. The solution containing the complex chloride then is concentrated on a steam bath to the point of crystallization and cooled to room temperature. The product may be recrystallized by dissolving it in the least possible amount of H_2O at room temperature and filtering into about 1 ml. of ice-cold concentrated hydrochloric acid.

When the reaction between $RhCl_3\cdot3H_2O$ and en·2HCl was carried out without the addition of KOH, the product was a golden brown crystalline substance, $enH_2[Rh(en)Cl_4]_2$.

Anal. Calcd. for $enH_2[Rh(en)Cl_4]_2$: C, 10.7; H, 3.91; Rh, 30.7; Cl, 42.3. Found: C, 10.75; H, 4.07; Rh, 31.2; Cl, 42.0.

Salts of all dichlorobis-(substituted ethylenediamine)-rhodium(III) complexes were prepared by methods essentially identical with that used for $[Rh(en)_2Cl_2]^+$. Therefore, only slight variations in detail unique to the particular system are described. The substituted ethylenediamines used were obtained from materials previously prepared in this Laboratory.[9] All other amines are commercially available.

---

[7] W. W. Lebedinski, *Izv. Inst. Izučeniju Platiny*, **13**, 9 (1936).

[8] J. Meyer and H. Kienitz, *Z. anorg. allgem. Chem.*, **242**, 281 (1939).

[9] F. Basolo, Y. T. Chen, and R. K. Murmann, *J. Am. Chem. Soc.*, **76**, 956 (1954).

***trans*-Dichlorobis-(*meso*-butylenediamine)-rhodium-(III) Nitrate.**—The golden yellow solution resulting from the reaction of 1.00 g. of $RhCl_3 \cdot 3H_2O$, 1.22 g. of *m*-bn·2HCl, and 0.852 g. of KOH in 100 ml. of H_2O was evaporated on a steam bath to a volume of 10–15 ml., cooled to room temperature, and filtered into a few ml. of ice-cold concentrated HNO_3. Upon cooling the mixture in an ice–salt bath, *trans*-$[Rh(m\text{-bn})_2Cl_2]NO_3$ precipitated as a fluffy golden yellow powder in 38% yield.

Anal. Calcd. for $[Rh(m\text{-bn})_2Cl_2]NO_3$: C, 23.3; H, 5.87; Cl, 17.2. Found: C, 22.53; H, 5.83; Cl, 16.7.

***trans*-Dichlorobis-(*d,l*-butylenediamine)-rhodium(III) Nitrate.**—This complex was prepared exactly as was *trans*-$[Rh(m\text{-bn})_2Cl_2]NO_3$. A yield of 0.5 g. (32%) of the pale yellow powder was obtained.

Anal. Calcd. for $[Rh(d,l\text{-bn})_2Cl_2]NO_3$: C, 23.3; H, 5.87; Cl, 17.2. Found: C, 22.69; H, 5.69; Cl, 17.0.

The solubility of the chlorides of both butylenediamine complexes again made isolation in this form impractical. In each case evidence was found for only one geometric isomer which probably, as will be shown later, has the *trans* configuration.

***cis*- and *trans*-Dichlorobis-(tetramethylethylenediamine)-rhodium(III) Chloride.**—A solution containing 1.00 g. of $RhCl_3 \cdot 3H_2O$, 1.44 g. of tetrameen·2HCl, and 0.426 g. of KOH in 50 ml. of H_2O was refluxed, whereupon the color became bright orange. Slow addition of another 0.426 g. of KOH in 50 ml. of H_2O resulted in the rapid precipitation of a bright golden powder. This substance was too insoluble and too deeply colored to be the desired $[Rh(tetrameen)_2Cl_2]Cl$. Results of analysis point to the formulation $[Rh(tetrameen)Cl_3]$; the compound may be a dimer having a symmetrical dichloro-bridged structure. A molecular weight determination was not possible because the compound was insufficiently soluble in all available solvents.

Anal. Calcd. for $[Rh(tetrameen)Cl_3]$: C, 21.7; H, 4.96; Rh, 31.6. Found: C, 22.0; H, 4.98; Rh, 31.2.

After removal by filtration of the supposed dimer, a bright yellow solution remained. This was concentrated on a steam bath to the start of crystallization and from it separated a moderately soluble yellow crystalline substance, *trans*-$[Rh(tetrameen)_2Cl_2]Cl$. The product was collected on a filter, washed with separate small portions of cold water, ethanol, and ether, and then air-dried. The yield was 0.40 g. (24%).

Anal. Calcd. for $[Rh(tetrameen)_2Cl_2]Cl$: C, 32.63; H, 7.32; Rh, 23.3; Cl, 24.1. Found: C, 32.81; H, 7.10; Rh, 23.1; Cl, 23.9.

On one occasion the original reaction mixture was refluxed for a period of 10 hr. (in contrast to the 15–20 min. allowed above) in an unsuccessful attempt to cause further reaction of the insoluble material formed initially. The product of this reaction, isolated as described above, was *cis*-$[Rh(tetrameen)_2Cl_2]Cl$; yield, 0.33 g. (20%).

Anal. Calcd. for $[Rh(tetrameen)_2Cl_2]Cl$: C, 32.63; H, 7.32; Rh, 23.3; Cl, 24.1. Found: C, 32.54; H, 6.98; Rh, 22.8; Cl, 23.8.

The methods used to prepare complexes of the quadridentates β,β',β''-triaminoethylamine and triethylenetetramine were again essentially the same as those used for the ethylenediamine series. For this reason only variations in details or observations are given.

***cis*-Dichloro-(β,β',β''-triaminoethylamine)-rhodium-(III) Chloride.**—During the reaction of 1.00 g. of $RhCl_3 \cdot 3H_2O$, 0.99 g. of tren·3HCl, and 0.64 g. of KOH in 100 ml. of H_2O, the color change to bright yellow was rapid but accompanied by considerable decomposition to metallic rhodium, part of which was colloidal and removed with difficulty. After evaporation of the solution to 10–15 ml. on a steam bath, *cis*-$[Rh(tren)Cl_2]Cl$, a bright yellow rather soluble salt, crystallized in 35% yield.

Anal. Calcd. for $[Rh(tren)Cl_2]Cl$: Rh, 28.6; Cl (ionic), 9.9; Cl (total), 29.6. Found: Rh, 28.7; Cl (ionic), 10.2; Cl (total), 29.6.

Neutralization of two thirds of the hydrochloride (*i.e.*, addition of 0.43 g. of KOH rather than 0.64 g.) in the above reaction led to the isolation of a soluble orange-yellow crystalline compound, presumably $[Rh(trenH)Cl_3]Cl$.

Anal. Calcd. for $[Rh(trenH)Cl_3]Cl$: C, 18.38; H, 4.89; Rh, 26.0; Cl, 35.8. Found: C, 17.76; H, 5.20; Rh, 26.2; Cl, 35.0.

***cis*-Dichlorotriethylenetetraminerhodium(III) Chloride.**—The solution resulting from the reaction of 1.00 g. of $RhCl_3 \cdot 3H_2O$, 1.10 g. of trien·4HCl, and 0.852 g. of KOH in 100 ml. of H_2O was evaporated on a steam bath to a volume of 20–25 ml. and cooled in an ice–salt bath. Beautiful shiny bright yellow crystals or a fluffy yellow powder of $[Rh(trien)Cl_2]Cl \cdot H_2O$ resulted. The yield of complex, after recrystallization from water–ethanol, was 0.3 g. (21%).

Anal. Calcd. for $[Rh(trien)Cl_2]Cl \cdot H_2O$: C, 19.3; H, 5.4; Cl, 28.5; H_2O, 4.83. Found: C, 19.06; H, 5.49; Cl, 28.8; H_2O, 4.78.

The reaction of $RhCl_3 \cdot 3H_2O$ with trien·4HCl in the absence of KOH gave a soluble brown crystalline product which may be $[Rh(trienH_2)Cl_4]Cl$.

Anal. Calcd. for $[Rh(trienH_2)Cl_4]Cl$: C, 16.8; H, 4.72; Rh, 24.0. Found: C, 16.63; H, 4.69; Rh, 23.9.

cis- or *trans*-dichlorobis-(ethylenediamine)-rhodium(III) nitrate was used as the starting material in the preparation of all diacidobis-(ethylenediamine)-rhodium(III) salts to be described here. Without exception, these reactions appeared to proceed with complete retention of geometric configuration, *i.e.*, *cis*-$[Rh(en)_2Cl_2]^+$ gave rise to *cis* products and *trans*-$[Rh(en)_2Cl_2]^+$ to *trans* products.

***trans*-Dibromobis-(ethylenediamine)-rhodium(III) Nitrate.**—One half g. of *trans*-$[Rh(en)_2Cl_2]NO_3$ and 1.45 g. of NaBr (a 5-fold excess) in 30 ml. of H_2O were refluxed for about 30 min., the color turning from yellow to orange during the reaction. The solution was filtered and cooled to room temperature, and to it was added a few ml. of concentrated HNO_3, whereupon an orange product crystallized. An analysis for coördinated bromide showed substitution of chloride by bromide to have been incomplete and the product again was refluxed for about 15 min. with a 5-fold excess of NaBr and precipitated as the nitrate. The complex was recrystallized from H_2O–HNO_3, washed with separate small portions of cold dilute HNO_3, ethanol, and ether, and then air-dried at room temperature; yield, 0.35 g. (56%).

Anal. Calcd. for $[Rh(en)_2Br_2]NO_3$: C, 10.8; H, 3.63; Br, 36.0. Found: C, 11.03; H, 3.60; Br, 36.0.

Roberts[10] recently has succeeded in preparing and

---

(10) J. Roberts, Ph.D. Thesis, Northwestern University, 1961.

separating *cis*- and *trans*-$[Rh(en)_2Br_2]Br$ by a reaction of $RhBr_3 \cdot 3H_2O$ with en·2HBr which is analogous to that reported here for *cis*- and *trans*-$[Rh(en)_2Cl_2]^+$.

***trans*-Diiodobis-(ethylenediamine)-rhodium(III) Iodide.**—One half g. of *trans*-$[Rh(en)_2Cl_2]NO_3$ and 2.1 g. of NaI (a 5-fold excess) in 30 ml. of H_2O were refluxed for about 10 min., during which time the solution rapidly turned brown. The reaction mixture was filtered quickly as it immediately began to deposit rust-brown crystals of *trans*-$[Rh(en)_2I_2]I$. The sparingly soluble complex was recrystallized by dissolving it in the minimum amount of warm water and filtering into a small amount of concentrated NaI solution. When collected on a filter, washed with separate small portions of ice-cold H_2O, ethanol, and ether, and air-dried, the product weighed 0.5 g. (59% yield).

Anal. Calcd. for $[Rh(en)_2I_2]I$: C, 7.96; H, 2.67; Rh, 17.0; I (ionic), 21.0. Found: C, 7.92; H, 3.08; Rh, 17.0; I (ionic), 21.3.

***cis*-Diiodobis-(ethylenediamine)-rhodium(III) Iodide.**—Under the identical conditions used to prepare *trans*-$[Rh(en)_2I_2]I$, a mixture of *cis*- and *trans*-$[Rh(en)_2I_2]I$ was obtained when *cis*-$[Rh(en)_2Cl_2]NO_3$ was the starting material. However, the reaction is believed to proceed with retention of configuration, the presence of the *trans* isomer being due to the subsequent isomerization of the *cis* product. What is presumably pure *cis*-$[Rh(en)_2I_2]I$ (*i.e.*, no change in visible spectrum occurred upon further recrystallization) was obtained by quickly dissolving the mixture in warm water (~40°) and isolating the immediate product upon filtering into a few ml. of a concentrated solution of NaI. *trans*-$[Rh(en)_2I_2]I$ appeared in later fractions. The brick-red powder, after having been washed with ethanol and ether and air-dried, weighed 0.3 g. (35% yield).

Anal. Calcd. for $[Rh(en)_2I_2]I$: C, 7.96; H, 2.67; I (ionic), 21.0. Found: C, 7.85; H, 2.90; I (ionic), 21.0.

***trans*-Dinitrobis-(ethylenediamine)-rhodium(III) Nitrate.**—One half g. of *trans*-$[Rh(en)_2Cl_2]NO_3$ and 1.0 g. of $NaNO_2$ (a 5-fold excess) in 30 ml. of H_2O were refluxed until the solution became colorless (about 1 hr.). After filtering and cooling, a few ml. of concentrated HNO_3 was added to the solution (destroying the excess ionic nitrite), which then was cooled in an ice–salt bath. The white crystalline product was collected by filtration, washed with separate small portions of cold dilute HNO_3, ethanol, and ether, and then air-dried. It weighed 0.3 g. (57% yield).

Anal. Calcd. for $[Rh(en)_2(NO_2)_2]NO_3$: C, 12.7; H, 4.28; Cl, none. Found: C, 12.7; H, 4.20; Cl, none.

***cis*-Dinitrobis-(ethylenediamine)-rhodium(III) Nitrate.**—Under conditions identical to those described above for the *trans* isomer, *cis*-$[Rh(en)_2Cl_2]NO_3$ gave *cis*-$[Rh(en)_2(NO_2)_2]NO_3$ as beautiful white needle-like crystals in 50% yield.

Anal. Calcd. for $[Rh(en)_2(NO_2)_2]NO_3$: C, 12.7; H, 4.28; Cl, none. Found: C, 12.88; H, 4.07; Cl, none.

***trans*-Chloronitrobis-(ethylenediamine)-rhodium(III) Nitrate.**—When the mole ratio of $NaNO_2$ to *trans*-$[Rh(en)_2Cl_2]NO_3$ in the preparation of *trans*-$[Rh(en)_2(NO_2)_2]NO_3$ outlined above was reduced by a factor of 2 (*i.e.*, to a 2.5-fold excess), the final solution was pale yellow rather than colorless and yielded only a small amount of the dinitro complex upon treatment with HNO_3. This was removed on a filter and the resulting filtrate was allowed to stand and evaporate at room temperature for 24–48 hr. During this time large pale yellow crystals of *trans*-$[Rh(en)_2NO_2Cl]NO_3$ formed. The product was recrystallized by dissolving the powdered complex in a minimum amount of water and filtering into a small amount of ice-cold concentrated HNO_3. It was washed with separate small portions of cold dilute HNO_3, ethanol, and ether, and then air-dried, whereupon it weighed 0.1 g. (20% yield).

Anal. Calcd. for $[Rh(en)_2NO_2Cl]NO_3$: N, 22.93; Cl, 9.7. Found: N, 23.23; Cl, 10.4.

An attempt to isolate *cis*-$[Rh(en)_2NO_2Cl]NO_3$ from a similar reaction with *cis*-$[Rh(en)_2Cl_2]NO_3$ was unsuccessful.

Chlorothiocyanatobis-(ethylenediamine)-rhodium(III) Thiocyanate.—One half g. of *trans*-$[Rh(en)_2Cl_2]NO_3$ and 1.14 g. of NaSCN (a 5-fold excess) in 30 ml. of H_2O were refluxed for about 1 hr., during which time the yellow color intensified somewhat. The solution was filtered and cooled in an ice–salt bath, whereupon a bright yellow substance precipitated. The complex was collected on a filter, washed with ethanol and ether, and air-dried; yield, 0.3 g. (54%).

Anal. Calcd. for $[Rh(en)_2(NCS)Cl]SCN$: C, 19.2; H, 4.31; Rh, 27.5. Found: C, 18.98; H, 4.17; Rh, 27.6.

No evidence for a dithiocyanato complex was found. Refluxing *trans*-$[Rh(en)_2(NCS)Cl]SCN$ with a further 5-fold excess of NaSCN for 30 min. produced no apparent change. The product, isolated as before, had a visible spectrum and analyses which were essentially identical with those of the original material. The isolation of $[Rh(en)_2(NCS)Cl]SCN$ rather than $[Rh(en)_2(NCS)_2]SCN$ is not surprising if one looks at the analogous cobalt compounds. The acid hydrolysis[11] of *trans*-$[Co(en)_2(NCS)Cl]^+$, which probably must occur in order to form *trans*-$[Co(en)_2(NCS)_2]^+$, is only 1/320 as fast as that of *trans*-$[Co(en)_2Cl_2]^+$. *trans*-$[Rh(en)_2(NCS)Cl]^+$ also appears to hold its chloride with great tenacity.

Under similar reaction conditions *cis*-$[Rh(en)_2Cl_2]NO_3$ gave a compound of questionable formulation. The complex, which appeared as bright yellow rosette-shaped crystals upon slow cooling of the reaction solution to room temperature, is very sparingly water soluble. Carbon and hydrogen analyses suggest the formulation $[Rh(en)_2(SCN)_2]SCN$, but addition of ferric ion to a solution of the complex indicates the presence of very little ionic thiocyanate.

Anal. Calcd. for $[Rh(en)_2(SCN)_2]SCN$: C, 21.2; H, 4.1. Found: C, 21.4; H, 4.43.

***trans*-Diazidobis-(ethylenediamine)-rhodium(III) Chloride.**—One half g. of *trans*-$[Rh(en)_2Cl_2]NO_3$ and 0.91 g. of NaN_3 (a 5-fold excess) in 30 ml. of H_2O were refluxed for about 1 hr.; at this point the solution was bright orange. It then was concentrated to a volume of 10–15 ml. on a steam bath and cooled in an ice–salt bath. The resultant precipitate of *trans*-$[Rh(en)_2(N_3)_2]N_3$, a deep golden crystalline substance, was light-sensitive and turned brown upon exposure to daylight for several hours.

---

[11] C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1961 (1956).

A sample of 0.5 g. of *trans*-$[Rh(en)_2(N_3)_2]N_3$ was dissolved immediately upon isolation in 20 ml. of H_2O and shaken for a few minutes with 5 g. of Dowex 1-X4 in the chloride form. The resin was removed by filtration and the resulting solution evaporated to about 5 ml. on a steam bath. After cooling in an ice bath, an equal volume of 1:1 ethanol:ether was added and golden yellow *trans*-$[Rh(en)_2(N_3)_2]Cl$ precipitated. This complex is only slightly light-sensitive and does not decompose nearly as rapidly as the azide salt. A sample of *trans*-$[Rh(en)_2(N_3)_2]Cl$ in an aluminum foil-wrapped vial showed no evidence of decomposition after several months; yield, 0.3 g. (48%).

Anal. Calcd. for $[Rh(en)_2(N_3)_2]Cl$: Cl, 10.3. Found: Cl, 10.2.

***trans*-Chloroamminebis-(ethylenediamine)-rhodium (III) Nitrate.**—One half g. of *trans*-$[Rh(en)_2Cl_2]NO_3$ in 30 ml. of NH_4OH was refluxed until no further color change was observable (about 10 min. after the complex had dissolved completely). The pale yellow solution was evaporated on a steam bath to a volume of about 10 ml. and N_2 was bubbled through it for 5–10 min. to ensure complete removal of ammonia. The solution then was evaporated to dryness on a steam bath. The residue was dissolved in a minimum amount of H_2O (about 2 ml.) and the solution filtered into an equal volume of cold concentrated HNO_3. Ethanol (95%) was added to the mixture until cloudiness just disappeared on stirring. Slow cooling in an ice bath resulted in the precipitation of *trans*-$[Rh(en)_2NH_3Cl](NO_3)_2$, a pale yellow powdery substance. An oil was formed if the mixture was cooled too rapidly. After crystallization had begun another 25 ml. of ethanol was added to complete precipitation. The product was removed by filtration and recrystallized from 6 *N* HNO_3–ethanol, after which it was washed with ethanol and ether and air-dried; yield, 0.25 g. (45%).

Anal. Calcd. for $[Rh(en)_2NH_3Cl](NO_3)_2$: N, 24.5; Cl, 8.9. Found: N, 24.7; Cl, 9.0.

***cis*-Chloroamminebis-(ethylenediamine)-rhodium(III) Nitrate.**—In a reaction sequence identical with that used to prepare the *trans* isomer, *cis*-$[Rh(en)_2Cl_2]NO_3$ gave pale yellow *cis*-$[Rh(en)_2NH_3Cl](NO_3)_2$ in 40% yield.

Anal. Calcd. for $[Rh(en)_2NH_3Cl](NO_3)_2$: N, 24.5; Cl, 8.9. Found: N, 24.78; Cl, 9.3.

Resolution of *racemic-cis*-Dichlorobis-(ethylenediamine)-rhodium(III) Chloride.—*cis*-$[Rh(en)_2Cl_2]Cl$ was resolved into its optical isomers through the *d*-α-bromocamphor-π-sulfonate salt. A solution of 0.45 g. of *cis*-$[Rh(en)_2Cl_2]Cl$ and 0.9 g. of *d*-ammonium α-bromocamphor-π-sulfonate in 15 ml. of H_2O was frozen in an ice–salt bath. After melting, the *l*-*cis*-$[Rh(en)_2Cl_2][d\text{-}C_{10}H_{14}O_4SBr]$ was collected on a filter and washed with a few drops of ice-cold water. The diastereoisomer then was ground thoroughly with 2 ml. of a 1:1:1 mixture of ethanol: ether:concentrated HCl, and the *l*-*cis*-$[Rh(en)_2Cl_2]Cl$ removed by filtration; yield, 0.13 g. (59% of *l* salt). The specific optical rotation of a 0.4% aqueous solution of this isomer is $[\alpha]_{535\,m\mu} = -58°$. This wave length, obtained from a thallium lamp, was chosen in preference to the more often used sodium D line because it gave a significantly larger value for the angle of optical rotation.

Anal. Calcd. for $[Rh(en)_2Cl_2]Cl$: C, 14.58; H, 5.89. Found: C, 14.50; H, 5.08.

Isomerization of *cis*-Diiodobis-(ethylenediamine)-rhodium(III) Iodide.—The visible absorption spectrum of a dilute (2.56×10^{-4} *M*) solution of *cis*-$[Rh(en)_2I_2]I$ was recorded at intervals for a period of 5 days, during which time it approached that of *trans*-$[Rh(en)_2I_2]I$. Spectra obtained immediately upon dissolution of *cis*-$[Rh(en)_2I_2]I$, after 2 days, and after 5 days are shown in Fig. 1 along with that of *trans*-$[Rh(en)_2I_2]I$. This study was not intended to determine an accurate value for the rate of the process but merely to investigate the nature of the change. The amount of ionic iodide in the solution was checked periodically and found to remain constant; thus the possibility that the change in spectrum was due to hydrolysis rather than isomerization was excluded.

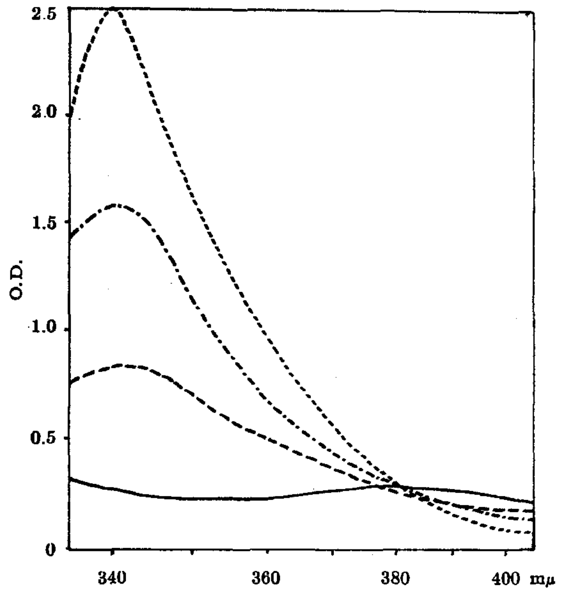

Fig. 1.—Absorption spectra: *cis*-$[Rh(en)_2I_2]I$, 2.56×10^{-4} *M* ——; after 2 days — —; after 5 days —·—; *trans*-$[Rh(en)_2I_2]I$, 2.56×10^{-4} *M* - - -.

Analyses.—Determinations of carbon, hydrogen, and nitrogen content were done using standard microanalytical combustion techniques. Rhodium was determined by heating a weighed sample of a compound in a porcelain microcrucible in the hottest flame obtainable with a Meker burner for 15–20 min. or until constant weight was achieved and weighing the metallic rhodium which remained as ash. Ionic nitrates could not be treated in this manner as they tended to explode with resultant loss of compound. Chloride and bromide were determined by titration with mercuric nitrate using sodium nitroprusside as the indicator.[12] Mercuric nitrate also was used to titrate iodide with diphenylcarbazide as the indicator and pyridine added to prevent coagulation of HgI_2.[13]

Absorption Spectra.—Measurements of absorption spectra in the visible and ultraviolet regions were made with a Beckman DK-2 ratio recording spectrophotometer using 1-cm. quartz cells. Tables I and II give the positions and intensities of the principal visible and ultraviolet

---

(12) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The MacMillan Co., New York, N. Y., 1953, pp. 460, 547–549.

(13) I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Interscience Publishers Inc., New York, N. Y., 1947, Vol. 2, p. 335.

absorption peaks of the various dichlorotetraamminerhodium(III) and diacidobis-(ethylenediamine)-rhodium(III) complexes, respectively.

Infrared spectra were measured in potassium bromide disks using a Baird AB-2 recording spectrophotometer. Some characteristic details of the infrared spectra of the various complexes are given in Table III.

TABLE I

THE VISIBLE AND ULTRAVIOLET ABSORPTION MAXIMA OF *cis*- AND *trans*-DICHLOROTETRAAMMINERHODIUM(III) COMPLEXES

Complex	λ(mμ)	ε(molar absorbance)
trans-$[Rh(en)_2Cl_2]^+$	406, 286	75, 130
trans-$[Rh(NH_3)_4Cl_2]^+$	412 *a*	66
trans-$[Rh(m\text{-}bn)_2Cl_2]^+$	409, 290 (sh)[b]	75, 120
trans-$[Rh(d,l\text{-}bn)_2Cl_2]^+$	405, 283	75, 120
trans-$[Rh(tetrameen)_2Cl_2]^+$	412 *a*	75
cis-$[Rh(en)_2Cl_2]^+$	352, 295	155, 180
cis-$[Rh(trien)Cl_2]^+$	352, 293	250, 200
cis-$[Rh(tetrameen)_2Cl_2]^+$	360, 294 (sh)[b]	160, 180

[a] Spectrum below 340 mμ not measured. [b] (sh), shoulder.

Discussion

The failure of previous attempts to prepare amine complexes of rhodium(III) may be ascribed to the sensitivity of the complex rhodium chlorides to substitution by hydroxide ion. All efforts to prepare dichlorotetraamminerhodium(III) complexes by direct reaction of $RhCl_3 \cdot 3H_2O$ or $K_2[Rh(H_2O)Cl_5]$ with a free amine led to immediate decolorization of the wine-red solution and precipitation of extremely insoluble, often semicolloidal, yellow substances. No amount of additional heating or prolonged standing seemed to induce further reaction.

The desirability of avoiding high concentrations of hydroxide ion led to an investigation of reactions using, instead of the free amines, the amine hydrochlorides. However, the reaction of one mole of rhodium(III) with one or two moles of amine hydrochloride invariably resulted in only partial substitution of amine for the four coördinated chloro ligands to be replaced. For example, such compounds as the previously mentioned $enH_2[Rh(en)Cl_4]_2$ and $[Rh(trienH_2)Cl_4]Cl$ were isolated.

Thus it appeared necessary either to attempt the reactions in appropriately buffered media or to neutralize the hydrochloride gradually, releasing all of the amine for eventual reaction but obviating the presence of excess hydroxide ion in the solution at any time. The latter approach was chosen to minimize the concentration of extraneous salts which might later cause difficulty in the isolation of products. This general method, involving the slow addition of the stoichiometric amount of potassium hydroxide to the refluxing reaction mixture, was used successfully in the preparation of all dichlorotetraamminerhodium(III) salts reported here with the exception of $[Rh(NH_3)_4Cl_2]Cl$.

The reason for the dependence of the ratio of *cis*- and *trans*-$[Rh(en)_2Cl_2]^+$ obtained upon the amount of potassium hydroxide added to the $RhCl_3 \cdot 3H_2O$–en·2HCl reaction mixture is not clear. The only other dichlorotetraamminerhodium(III) complex of which both *cis* and *trans* isomers were isolated is $[Rh(tetrameen)_2Cl_2]Cl$. In this case the *cis* compound resulted from rather extreme conditions involving extended refluxing of the reaction solution. The dichloro-(β,β',β''-triaminoethylamine)-rhodium(III) complex must, by the nature of the ligand, have the *cis* configura-

TABLE II

THE VISIBLE AND ULTRAVIOLET ABSORPTION MAXIMA OF *cis*- AND *trans*-DIACIDOBIS-(ETHYLENEDIAMINE)-RHODIUM(III) COMPLEXES

Complex	λ(mμ)[a]	ε (molar absorbance)
trans-$[Rh(en)_2Cl_2]^+$	406, 286	75, 130
cis-$[Rh(en)_2Cl_2]^+$	352, 295	155, 180
trans-$[Rh(en)_2Br_2]^+$	425, 276	100, 1800
cis-$[Rh(en)_2Br_2]^+$	362, 276 (sh)	210, 900
trans-$[Rh(en)_2I_2]^+$	462, 341, 269, 222	260, 10,000, 30,000, 20,000
cis-$[Rh(en)_2I_2]^+$	375	1200
trans-$[Rh(en)_2(NO_2)_2]^+$	300 (sh), 255 (sh)	590, 2400
cis-$[Rh(en)_2(NO_2)_2]^+$	290, 245 (sh)	660, 3500
trans-$[Rh(en)_2NH_3Cl]^{2+}$	342, 275	95, 120
cis-$[Rh(en)_2NH_3Cl]^{2+}$	342, 276	150, 195
trans-$[Rh(en)_2(NCS)Cl]^+$	363	340
trans-$[Rh(en)_2(N_3)_2]^+$	375, 282	780, 12,000
trans-$[Rh(en)_2NO_2Cl]^+$	310 (sh), 255–265 (sh)	310, 860

[a] (sh), shoulder.

TABLE III

SOME DETAILS OF THE INFRARED SPECTRA OF *cis*- AND *trans*-DIACIDOTETRAAMMINERHODIUM(III) COMPLEXES

Complex	NH_3 asym. def. (cm.$^{-1}$)	Other characteristic absorptions (cm.$^{-1}$)
trans-$[Rh(en)_2Cl_2]Cl$	1600	1110, 1125
cis-$[Rh(en)_2Cl_2]Cl$	1570, 1625	3200,[a] 3400, 1105, 1120, 1140
trans-$[Rh(m\text{-bn})_2Cl_2]NO_3$	1605	
trans-$[Rh(d,l\text{-bn})_2Cl_2]NO_3$	1600	
trans-$[Rh(tetrameen)_2Cl_2]Cl$	1595	
cis-$[Rh(tetrameen)_2Cl_2]Cl$	1550, 1620	
cis-$[Rh(trien)Cl_2]Cl$	1580, 1640	
trans-$[Rh(en)_2Br_2]NO_3$	1610	3220
trans-$[Rh(en)_2I_2]I$	1600	3200
cis-$[Rh(en)_2I_2]I$	1575, 1605	3200, 3460
trans-$[Rh(en)_2(NO_2)_2]NO_3$	1600	825 (NO_2^-)
cis-$[Rh(en)_2(NO_2)_2]NO_3$	1580, 1605	830, 840 (NO_2^-)
trans-$[Rh(en)_2NO_2Cl]NO_3$	1600	830 (NO_2^-)
trans-$[Rh(en)_2NH_3Cl](NO_3)_2$	1600	
cis-$[Rh(en)_2NH_3Cl](NO_3)_2$	1590, 1615[b]	
trans-$[Rh(en)_2(NCS)Cl]SCN$	1600	735, 835 2060, 2150 (SCN^-)
trans-$[Rh(en)_2(N_3)_2]Cl$	1610	2060 (N_3^-)

[a] The value quoted in the 3200 cm.$^{-1}$ region is, in each case, the high frequency side of a complex absorption band containing 3 or 4 sharp, but incompletely resolved, peaks. [b] Not well resolved.

tion. *cis*-$[Rh(trien)Cl_2]Cl$, again due to the nature of the ligand, is expected to be more stable than the corresponding *trans* isomer. *cis*- and *trans*-$[Co(trien)Br_2]Br$ both have been prepared[14]; the lesser tendency of bromides to occupy neighboring *cis* positions presumably causes the amine to assume the *trans* configuration. No evidence was found for *cis*-$[Rh(NH_3)_4Cl_2]^+$, *cis*-$[Rh(m\text{-bn})_2Cl_2]^+$, or *cis*-$[Rh(d,l\text{-bn})_2Cl_2]^+$.

Most of the diacidobis-(ethylenediamine)-rhodium(III) salts were prepared as both geometric isomers. Among the pairs of *cis–trans* isomers which were investigated, the only evidence for interconversion between the two forms was obtained for *cis*- and *trans*-$[Rh(en)_2I_2]^+$. In dilute aqueous solution the former isomerizes to the latter at room temperature; the half-life of the reaction is roughly 3 days (Fig. 1). From steric considerations the stability of the *cis* form relative to that of the *trans* in the series $[Rh(en)_2X_2]^+$, $X = Cl, Br, I$, might be expected to decrease in the order $Cl > Br > I$; the bulky iodide groups should have the least tendency to assume a *cis* configuration. That the lone example of *cis*→*trans* isomerization among the dihalo complexes occurs for $[Rh(en)_2I_2]^+$ while the yield of *cis*-$[Rh(en_2)_2Cl_2]^+$ relative to that of *trans*-$[Rh(en)_2Cl_2]^+$ may be increased by suitable modification of the reaction conditions appears to substantiate the expected trend.

Several methods were used successfully to distinguish between *cis*- and *trans*-dichlorotetraamminerhodium(III) complexes, principally visible–ultraviolet spectra, infrared spectra, and hydrolytic behavior. The structure of *cis*-$[Rh(en)_2Cl_2]^+$ was proved unequivocally by resolution into its optical isomers; no attempt was made to resolve any of the other *cis* complexes.

It may be seen from Table I that the visible absorption maxima of the complexes to which the *trans* configuration has been assigned occur within the range 405–412 mμ; that of the known *trans* complex, *trans*-$[Rh(en)_2Cl_2]^+$, is at 406 mμ. The isomers believed to have a *cis* configuration absorb in the region 352–360 mμ; the known *cis* complex, *cis*-$[Rh(en)_2Cl_2]^+$, has its maximum at 352 mμ. The trend for *cis* isomers to absorb at somewhat shorter wave lengths than the corresponding *trans* complexes continues among the various *cis*- and *trans*-diacidobis-(ethylenediamine)-rhodium(III) salts (see Table II). In view of the close relationship of ammonia and ethylenediamine as ligands it is not surprising that the d–d absorption maxima of *cis*- and *trans*-$[Rh(en)_2NH_3Cl]^{2+}$ appear at essentially the same wave length. It has been shown theoretically and experimentally[15] for the *cis* and *trans* isomers of diacidotetraamminecobalt(III) complexes that the *cis* isomer exhibits the more intense

---

(14) J. Selbin and J. C. Bailar, *J. Am. Chem. Soc.*, **82**, 1524 (1960).

(15) F. Basolo, C. J. Ballhausen, and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).

absorption. Such is also the case for all pairs of *cis*- and *trans*-diacidotetraamminerhodium(III) isomers described here.

cis- and *trans*-$[Rh(en)_2Cl_2]^+$ exhibit distinctive differences in three areas of their infrared spectra, near 3200, 1600, and 1100 cm.$^{-1}$ (see Table III). In each case a greater degree of splitting occurs in the absorption of the *cis* isomer. The shape of the NH_2 asymmetric deformation frequency near 1600 cm.$^{-1}$ was found to be characteristic for nearly all *cis*- and *trans*-diacidobis-(ethylenediamine or substituted ethylenediamine)-rhodium(III) complexes. Almost without exception the spectrum of a *trans* isomer contains a single sharp peak while that of a *cis* isomer shows a nicely resolved doublet in this area. Similar results have been reported for some *cis*- and *trans*-diacidobis-(ethylenediamine)-cobalt(III) complexes.[16] A significant difference often is observable between *cis* and *trans* isomers in the N–H stretching region near 3200 cm.$^{-1}$; the area around 1100 cm.$^{-1}$ is generally too complex to be useful as a means of identification of geometric structure.

From studies of the acid and base hydrolyses of *cis*- and *trans*-dichlorotetraamminerhodium(III) complexes, the quantitative aspects of which will be discussed in a forthcoming paper, came a qualitative observation which could be used in establishing the geometric structure of the reaction complex. It was found that the rates of base

$$[RhA_mCl_2]^+ + 2OH^- \longrightarrow [RhA_m(OH)_2]^+ + 2Cl^-$$

hydrolysis of *trans*-dichlorotetraamminerhodium(III) complexes are independent of the concentration of hydroxide ion up to pH values as high as 13; each of the corresponding *cis* complexes exhibits a transition from zero to first order dependence upon hydroxide ion within the pH range 9–11.

An interesting point of discussion is the bonding of the SCN^- group in *trans*-$[Rh(en)_2(NCS)Cl]$-SCN. Such amminecobalt(III) complexes[17] are assigned a cobalt–nitrogen bond, Co–NCS. However, in certain rhodium compounds containing thiocyanate, such as $K_3[Rh(SCN)_6]$, the bond has been found to be rhodium to sulfur.[18] When an attempt was made to titrate the ionic thiocyanate of *trans*-$[Rh(en)_2(NCS)Cl]SCN$ with mercuric nitrate, approximately twice the calculated amount of mercuric ion was required to reach the end point. However, reasonably good results were obtained using the Volhard method, which involves addition of excess silver nitrate and back titration with sodium thiocyanate. These results suggest that the mode of bonding is Rh–NCS and that mercuric ion is able to attach itself to the free sulfur end of the group, Rh–NCS–Hg; thus both ionic and coördinated thiocyanate are titrated. Silver ion certainly does this also, but thiocyanate added to back titrate excess silver ion may remove the silver which had become attached to the coördinated thiocyanate, Rh–NCS–Ag.

Schäffer[19] has suggested that due to the different crystal field splittings induced by $-SCN^-$ and $-NCS^-$, the d–d transition bands in the visible absorption spectra of complexes containing M–SCN should appear near those of the corresponding M–Cl and M–Br complexes, whereas the visible absorption of compounds bonded M–NCS should occur at somewhat lower wave lengths than those of either M–Cl or M–Br. The spectra of *trans*-$[Rh(en)_2Cl_2]^+$, *trans*-$[Rh(en)_2Br_2]^+$, and *trans*-$[Rh(en)_2(NCS)Cl]^+$ suggest the presence of a Rh–NCS bond; the d–d transition bands for these complexes (see Table I) appear at 406, 425, and 363 mμ, respectively.

The following ranges for C–S stretching frequencies in N– and S– coördinated thiocyanato complexes[20] have been reported: M–NCS, 780–860 cm.$^{-1}$; M–SCN, 690–720 cm.$^{-1}$. The coördinated thiocyanate C–S stretching frequency of *trans*-$[Rh(en)_2(NCS)Cl]SCN$ at 835 cm.$^{-1}$ further substantiates the assignment of a Rh–NCS bond to the complex.

---

(16) M. L. Morris and D. H. Busch, *J. Am. Chem. Soc.*, **82**, 1521 (1960).

(17) M. M. Chamberlain and J. C. Bailar, *ibid.*, **81**, 6412 (1959).

(18) Z. V. Zvonkova, *Zh. Fiz. Khim.*, **27**, 100 (1953).

(19) C. E. Schäffer, Abstracts of Papers submitted to International Conference on Coördination Chemistry, London, 1959, Special Publication No. 13, The Chemical Society, p. 153.

(20) A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).