TABLE IV
UV ABSORPTION BANDS FOR SOME LANTHANIDE ISOPROPOXIDES

COMPOUND*	λ_{max} (mμ)									
$Y(OC_3H_7)_3$	270	260	255	249	243	238	234			
$Sm(OC_3H_7)_3$	262	258	252	245	240					
$Eu(OC_3H_7)_2$	265	259	253	246	232					
$Gd(OC_3H_7)_3$	297	278	276	243						
$Tb(OC_3H_7)_3$	302	264	257							
$Dy(OC_3H_7)_3$	296	260	254	248	240					
$Ho(OC_3H_7)_3$	338	292	289	281	260	254	249	242		
$Er(OC_3H_7)_3$	268	261	254	249	244	239	234	230		
$Tm(OC_3H_7)_3$	289	287	284	274	268	265	260	254	249	243
$Lu(OC_3H_7)_3$	260	255	249	243						

* Cyclohexane solution.

TABLE V
VISIBLE REGION ABSORPTION BANDS FOR COLORED LANTHANIDE ISOPROPOXIDES

COMPOUND*	λ_{max} (mμ)													
$Pr(OC_3H_7)_3$	494	484	475	458										
$Nd(OC_3H_7)_3$	601	598	594	590	584	582	579	536	532	528	434	432	361	354
$Sm(OC_3H_7)_3$	408	404	478	372										
$Ho(OC_3H_7)_3$	631	462	460	452	447	416	366	362						
$Er(OC_3H_7)_3$	545	531	525	522	521	520	385	382	381	379	366			

*Cyclohexane solution.

the bands observed for the different alkoxides are unique and characteristic of each highly colored species.

Nmr Spectra.—Although nmr spectroscopy has been used for structure analysis of metal isopropoxides,[9,10] most of the lanthanide ions are paramagnetic and their isopropoxides cannot be analyzed by this method. However, the trivalent ions of Y, La, and Lu are diamagnetic and nmr spectra were obtained for these isopropoxides. The characteristic spectrum of a monomeric isopropoxide consists of a doublet in the τ 7–9 region resulting from the resonance of the CH_3 protons and a septet in the τ 5–7 region due to the CH proton. Polymeric species give spectra with overlapping doublets and septets. Bradley[10] has indicated that this overlapping is due to the chemical shifts of two or more differently situated alkoxy groups, such as terminal or bridging sites. Bridging tends to deshield the protons causing the resonance signals to occur at lower field.

The three nmr spectra obtained for the lanthanide isopropoxides were characteristic of polymeric isopropoxides although some of the peaks were somewhat broadened due to the inherent poor nmr resolution generally observed in rare earth metal complexes. The spectrum of $La(OC_3H_7)_3$ in benzene consisted of two doublets at 91.3 and 112.3 Hz and a broad septet around 272 Hz. Only one broad doublet was observed at 83 Hz for the $Y(OC_3H_7)_3$–benzene solution with the septet at 264 Hz. The $Lu(OC_3H_7)_3$ spectrum exhibited three overlapping doublets at 42.4, 49.0, and 69.5 Hz and the broad septet at about 230 Hz. The progressive lower field chemical shifts from Lu to La may be attributed to the combination of the deshielding of the CH_3 protons, the nature of covalency of the metal ions, and/or an increase in the degree of polymerization. It should be noted, however, that there is no definite correlation of the mass of the metal atom with the observed degree of lower field chemical shift.

Mass Spectrometry.—Mass spectra of some of the isopropoxides were recorded to obtain molecular weight measurements since the extreme moisture sensitivity of these alkoxides limits molecular weight determinations by the conventional method of vapor pressure osmometry. Previously Mazdiyasni, *et al.*,[5] had proposed the dimeric structure similar to that of the smallest tris(aluminum alkoxide) involving a four-covalent metal with the tetrahedral configuration for aluminum.[3] Misra and coworkers,[11] however, found the isopropoxides of La, Pr, and Nd to be monomeric in benzene.

Preliminary mass spectra recorded of the isopropoxides of Nd, Er, Tb, and Lu have shown peaks at low mass numbers corresponding to the isopropoxy group and its fragmentation and the next significant peaks in the mass number ranges for dimeric and tetrameric species. The tetrameric structure is postulated to be quite similar to the aluminum tris(isopropoxide) structure reported by Brown and Mazdiyasni.[9] This part of the investigation is continuing with high-resolution mass spectrometric measurements of the molecular ion peaks and construction of the possible empirical formula by computer calculation.

Acknowledgments.—The authors gratefully acknowledge the assistance of Barbara Schaper in the preparation of the alkoxides, Lee Smithson in obtaining the mass spectra, and Sally Allen in typing the manuscript.

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[9] L. M. Brown and K. S. Mazdiyasni, *Anal. Chem.*, **41**, 1243 (1969).

[10] D. C. Bradley and C. T. Holloway, *Offic. Dig. J. Paint Technol. Eng.*, **37**, 487 (1965).

[11] S. N. Misra, T. N. Misra, R. N. Kapoor, and R. C. Mehrotra, *Chem. Ind. (London)*, 120 (1963).

CONTRIBUTION FROM THE MICHAEL FARADAY LABORATORIES,
DEPARTMENT OF CHEMISTRY,
NORTHERN ILLINOIS UNIVERSITY, DEKALB, ILLINOIS 60115

The Synthesis, Characterization, and Some Reactions of *trans*-Diacetatobis(trimethylenediamine)chromium(III) Chloride Monohydrate

BY JOE W. VAUGHN,* GARY J. SEILER,[1]
M. WILLIAM JOHNSON,[2] AND GEORGE L. TRAISTER

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The reaction of an aqueous solution of hydrated chromium(III) chloride, hydrofluoric acid, and various diamines such as ethylenediamine (en) or trimethylene-

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* To whom correspondence should be addressed.

[1] National Science Foundation Undergraduate Research Participant, Summers, 1968–1969.

[2] Student Science Training Program Participant, Summer, 1969.

diamine (tn) has been utilized in the past to prepare complex cations of the type *trans*-$Cr(AA)_2F_2^+$.[3,4] The reaction goes readily to produce the trans cations as easily isolable solids.

The present research was initiated to determine what the effect would be on the nature of the products formed when the hydrofluoric acid was replaced by a weaker acid such as acetic and to compare the relative donor properties of the acetate and fluoride ions in this system. Chromium(III) is an avid water acceptor in aqueous solution, and the previous investigations with the fluoro complexes would suggest that this method might provide a suitable synthetic route to presently unknown acetate complexes of chromium(III), which in turn could be utilized as starting materials for the preparation of diacidobis(diamine) complexes.

Experimental Section

Synthesis of Diacetatobis(trimethylenediamine)chromium(III) Chloride Monohydrate.—A solution of 15 g (0.055 mol) of chromium(III) chloride hexahydrate in 50 ml of water was treated with 18 g (0.30 mol) of glacial acetic acid. The solution was cooled in ice and 55 g (0.75 mol) of trimethylenediamine was added dropwise over a period of 1 hr. The purple reaction mixture was heated on a steam bath until the color of the thick paste turned from purple to red-orange. The reaction mixture was cooled to room temperature, 10 ml of cold water was added, and the entire mixture was slurried for 10–15 min at room temperature. The insoluble orange crystals were collected by filtration, washed with 50 ml of acetone, and air dried. This method gave 11.4 g of bright orange product which was recrystallized from water at 45°. *Anal.* Calcd for $[Cr(tn)_2(C_2H_3O_2)_2]Cl \cdot H_2O$: C, 32.4; H, 7.6; N, 15.1; Cl, 9.6; H_2O, 4.85. Found: C, 32.4; H, 7.8; N, 15.1; Cl, 9.6; H_2O, 4.9. The mole of water of hydration per mole of complex was removed by heating the chloride for 24 hr at 120° and the loss in weight was accompanied by a very slight color change to a pale orange. The infrared spectrum in the 400–600-cm^{-1} region (CsI plates, Nujol mull) exhibited strong absorptions at 450, 505, and 535 cm^{-1}.

The resistance of a 1 mM aqueous solution of the complex at 25° indicated the molar conductance to be 107 ohm^{-1} which is well within the range for 1–1 electrolyte. The molar conductance increased to 126 ohm^{-1} after the solution had aged for 2 hr.

A 10 mM aqueous solution of the complex at room temperature had a pH of ~6 and the pH was ~8 after the solution was heated for 15 min on a steam bath.

In 10 mM aqueous solution at room temperature the electronic spectrum exhibited absorption maxima at 508 and 370 nm with molar absorptivities of 39.5 and 38.5 M^{-1} cm^{-1}, respectively. The band at 508 nm was not symmetrical but exhibited a broadening of the band on the high-energy side. The spectrum was redetermined after 15 min of aging and the result was identical with the initial spectrum. Thus aquation of the complex was not appreciable during this time interval. The electronic spectrum of a sample of the complex which had been heated for 24 hr at 120° was determined and compared with that of the hydrated complex. These two spectra were identical. A cold freshly prepared solution of the complex was treated with silver nitrate, and the precipitate was collected and quickly added to a large volume of boiling water. The precipitate did not dissolve under these conditions, and, therefore, it could not be silver acetate.

Anion Replacement on Diacetatobis(trimethylenediamine)chromium(III) Chloride Monohydrate.—A 1.0-g (2.7-mmol) sample of diacetatobis(trimethylenediamine)chromium(III) chloride monohydrate was dissolved in the minimum amount of water at room temperature and the solution was filtered. The red-orange filtrate was treated with a saturated aqueous solution of potassium iodide to precipitate $[Cr(tn)_2(C_2H_3O_2)_2]I \cdot 1.5H_2O$ as a pale orange powder. The product was washed with acetone and allowed to air dry; yield 75%. *Anal.* Calcd for $[Cr(tn)_2(C_2H_3O_2)_2]I \cdot 1.5H_2O$: C, 25.4; H, 6.15; N, 11.9; I, 26.9; H_2O, 5.8. Found: C, 25.5; H, 6.45; N, 12.4; I, 26.9; H_2O, 5.3. The complex was dried for 12 hr at 110° to remove the water of hydration and the analysis was repeated. *Anal.* Calcd for $[Cr(tn)_2(C_2H_3O_2)_2]I$: C, 27.0; H, 5.85; N, 12.6; I, 28.6. Found: C, 26.9; H, 5.51; N, 12.6; I, 28.7.

A 1mM aqueous solution of the complex had a molar conductance of 113 ohm^{-1} at 25°.

A 1.5-g (3-mmol) sample of the iodide was dissolved in a minimum amount of water at room temperature and filtered, and the filtrate was treated with solid anhydrous sodium perchlorate. This method produced $[Cr(tn)_2(C_2H_3O_2)_2]ClO_4 \cdot H_2O$ in 66% yield. *Anal.* Calcd for $[Cr(tn)_2(C_2H_3O_2)_2]ClO_4 \cdot H_2O$: C, 27.6; H, 6.45; N, 12.9. Found: C, 27.6; H, 6.50; N, 12.8. A 1 mM aqueous solution of the complex had a molar conductance of 90 ohm^{-1} at 25°. The electronic spectrum of a 0.01 M solution of the complex in 0.1 M perchloric acid exhibited absorption maxima at 506 and 370 nm with molar absorptivities of 39.6 and 38.3 M^{-1} cm^{-1}, respectively.

Reaction of the Diacetatobis(trimethylenediamine)chromium(III) Ion with Hydrohalic Acids.—A 0.76-g (0.17-mmol) sample of the perchlorate salt was dissolved in an excess of 48% hydrofluoric acid and evaporated to dryness on a steam bath. The solid product was taken up in water, the solution was filtered, and the filtrate was treated with a concentrated aqueous solution of sodium iodide. The pink plates which had precipitated were collected, washed with acetone, and dried overnight at 110°. This method gave $[Cr(tn)_2F_2]I \cdot 0.5H_2O$ in 28% yield. *Anal.* Calcd for $[Cr(tn)_2F_2]I \cdot 0.5H_2O$: C, 19.2; H, 5.6 N, 14.9. Found: C, 19.3; H, 5.4; N, 14.8. The electronic spectrum of this complex in aqueous solution was identical with that of an authentic sample of the *trans*-$Cr(tn)_2F_2^+$ ion prepared by another method.[5] The complex appears to be rather hygroscopic and it was not possible to obtain a completely anhydrous product although a wide variety of drying conditions was utilized.

A 1.0-g (2.1-mmol) sample of $[Cr(tn)_2(C_2H_3O_2)_2]I \cdot 1.5H_2O$ was dissolved in 5–6 ml of concentrated hydrobromic acid, the solution was filtered, and the filtrate was allowed to stand at room temperature overnight. Dark green crystals of $[Cr(tn)_2Br_2]Br \cdot 0.5H_2O$ were collected by filtration, washed with acetone, and air dried. This method produced the dibromo complex in 20% yield. *Anal.* Calcd for $[Cr(tn)_2Br_2]Br \cdot 0.5H_2O$: Br, 53.5. Found: Br, 53.4. The crude product was dissolved in water at room temperature and filtered, and the filtrate was treated with a concentrated solution of ammonium bromide. The product was collected, washed with acetone, and dried at 110° for 18 hr. *Anal.* Calcd for $[Cr(tn)_2Br_2]Br$: C, 16.3; H, 4.6; N, 12.8; Br, 54.5. Found: C, 16.3; H, 4.7; N, 12.4; Br, 54.5.

The above procedure was repeated in the same manner except concentrated hydrochloric acid was used in place of hydrobromic acid and a saturated solution of ammonium nitrate was used to precipitate the product. *Anal.* Calcd for $[Cr(tn)_2Cl_2](NO_3)$: C, 21.6; H, 6.0; N, 21.0. Found: C, 21.6; H, 6.4; N, 21.0.

The Ethylenediamine–Acetic Acid–Hydrated Cr(III) Ion Reaction.—A solution of 30 g (0.11 mol) of chromium(III) chloride hexahydrate in 100 ml of water was treated with 38 g (0.63 mol) of glacial acetic acid. This solution was cooled in an ice bath and 100 ml (1.5 mol) of commercial ethylenediamine was added in a dropwise fashion. The reaction mixture was transferred to a large evaporating dish and heated on a steam bath for 4 hr; at the end of the heating period the reaction mixture was removed from the steam bath and allowed to stand overnight at room temperature. During the time required for the concentration of the solution the reaction mixture underwent a color change from purple to red-orange. The red-orange solution (1 vol) was

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(3) J. W. Vaughn, O. J. Stvan, Jr., and V. E. Magnuson, *Inorg. Chem.*, **7**, 736 (1968).

(4) J. W. Vaughn, *Inorg. Nucl. Chem. Lett.*, **4**, 183 (1968).

(5) D. J. Wierschke, M.S. Thesis, Northern Illinois University, 1969.

added to a mixture of 3 vol of ethanol and 1 vol of acetone to precipitate a yellow solid. The solid was collected by filtration, washed with acetone, and air dried. This method produced 17.0 g (39%) of crude $[Cr(en)_3]Cl_3 \cdot 3.5H_2O$. The crude material was recrystallized from water at 60° (1 g of product/1 ml of water), washed with acetone, and air dried. *Anal.* Calcd for $[Cr(en)_3]Cl_3 \cdot 3.5H_2O$: C, 17.9; H, 7.7; N, 20.9; Cl, 26.5. Found: C, 17.5; H, 7.7; N, 20.7; Cl, 26.5. The electronic spectrum of this material was identical with that reported for the $Cr(en)_3{}^{3+}$ ion.

The Propanediamine–Acetic Acid–Hydrated Cr(III) Ion Reaction.—A solution of 15 g (0.055 mol) of chromium(III) chloride hexahydrate in 50 ml of water was treated with 18 g (0.30 mol) of glacial acetic acid. The solution was cooled in an ice bath and 65 g (0.79 mol) of propanediamine was added in a dropwise fashion over a period of 1 hr. The purple mixture was placed in a large evaporating dish and allowed to concentrate on a steam bath for 4 hr. At the end of the evaporation period the thick mixture was cooled to room temperature and 65 ml of the solution was placed in a beaker on a magnetic stirrer. This mixture was diluted with 100 ml of acetone followed by 150 ml of ethanol. The resulting solution was diluted again with three 100-ml portions of acetone to precipitate a very fine yellow solid. The precipitate was allowed to coagulate for 1–2 hr before it was collected in a sintered-glass filter. The product was stirred with 150 ml of fresh acetone, washed with ether, and air dried. The product may become sticky on drying and this can be avoided by quickly transferring the product to a clean dry filter to complete the drying. This method gave 5.7 g of crude $[Cr(pn)_3]Cl_3 \cdot 1.5H_2O$. The complex was recrystallized from a minimum amount of warm water and dried as described above. *Anal.* Calcd for $[Cr(pn)_3]Cl_3 \cdot 1.5H_2O$: C, 26.4; N, 20.6; H, 8.1; Cl, 26.2. Found: C, 26.3; N, 20.3; H, 7.7; Cl, 26.3.

The complex was converted to the corresponding iodide by dissolving the crude product in a minimum volume of water and adding solid potassium iodide to the solution. The product was collected, washed with acetone, and air dried. *Anal.* Calcd for $[Cr(pn)_3]I_3 \cdot 0.5H_2O$: C, 16.3; H, 4.7; N, 12.7; I, 57.4. Found: C, 16.3; H, 4.5; N, 12.9; I, 57.6.

Infrared spectra were determined on all complexes with a Beckman IR-12 spectrophotometer by using Nujol or hexachlorobutadiene mulls between cesium iodide plates. Electronic spectra were measured using a Cary 14 spectrophotometer equipped with matched 1.0-cm silica cells.

Discussion

The coordination of the acetato ligands in the complex $[Cr(tn)_2(C_2H_3O_2)_2]Cl$ was established in several ways. First, a series of compounds was prepared from $[Cr(tn)_2(C_2H_3O_2)_2]Cl$ in which the anion was exchanged for either iodide or perchlorate. In all cases the elemental analysis confirmed the presence of 2 mol of acetate ion/mol of complex. Second, the visible electronic spectra of the complexes prepared by the exchange of the anions were identical with that of the starting material, diacetatobis(trimethylenediamine)chromium(III) chloride monohydrate. Third, the initial pH of a 10 m*M* aqueous solution of the original complex was *ca.* 6 and the pH increased to 8 after the solution was heated for 15 min in a steam bath. The pH of an aqueous solution of green $[Cr(tn)_2Br_2]Br$ remained essentially constant before and after heating. Fourth, the molar conductances of the chloride, iodide, and perchlorate salts were in the range normally found for 1–1 electrolytes. Collectively the experimental observations are all in accord with the acetate ion being present in the complex as a monodentate ligand and not as a simple anion outside the coordination sphere.

The geometries of the complexes prepared in this investigation were assigned by means of electronic and infrared spectral studies. The number of bands in the diacetato, dichloro, and dibromo complexes as well as the magnitude of the molar absorptivities strongly suggests that all of these complexes involve a trans arrangement of the monodentate ligands.

TABLE I

ELECTRONIC SPECTRA OF SOME COMPLEXES OF THE TYPE $Cr(tn)_2X_2{}^+$ IN THE 700–350-NM RANGE

Complex	λ_{max}	ε, M^{-1} cm^{-1}	λ_{max}	ε, M^{-} cm^{-1}	λ_{max}	ε, M^{-} cm^{-1}	λ_{max}	ε, M^{-1} cm^{-1}
$Cr(tn)_2(C_2H_3O_2)_2{}^{+}$[a]	507	39.5			370	38.5		
$Cr(tn)_2(C_2H_3O_2)_2{}^{+}$[b]	507	39.6			370	38.3		
$Cr(tn)_2F_2{}^+$	537	16.4	465	20.7	398	16.5	356	16.5
$Cr(tn)_2Cl_2{}^+$	592	24.8	450[c]	24	392	38.2		
$Cr(tn)_2Br_2{}^+$	622	31.2	450[c]	26.7	388	37.0		

[a] In aqueous solution with no acid added. [b] In 0.1 *N* $HClO_4$. [c] Shoulder on the high-energy band.

The unsymmetrical nature of the low-energy band in the electronic spectrum of the diacetato complex is also consistent with a trans structure. In general trans complexes exhibit this type of behavior with the spectra being characterized by two rather well-defined bands and a rather ill-defined shoulder between the high- and low-energy bands. By comparison of the electronic spectrum of the difluoro complex prepared in this study with that of *trans*-$Cr(en)_2F_2{}^+$,[3] the trans structure can be reliably assigned to the trimethylenediamine complex.

The infrared data presented in Table II are in accord with the assignment of a trans structure to the complexes studied. The small number of absorption bands in the 400–600-cm^{-1} region would strongly indicate a trans arrangement of the monodentate ligands. Cis complexes because of lower symmetry would be expected to show more bands and more splitting in this region. On the basis of the infrared data the green dichloro and dibromo complexes, the orange diacetato, and the pink difluoro complexes would appear to be pure trans isomers since no weak or split bands were found between 400 and 600 cm^{-1}. The CH rocking mode near 880 cm^{-1} was not split in any of the complexes studied. In the case of Co(III) complexes of the type $Co(AA)_2X_2{}^+$, where AA is ethylenediamine, the rocking mode is split into two bands for cis isomers but only a single band is found for trans complexes.[6] For Cr(III) complexes of the same type other workers have found some trans complexes to exhibit split bands in this region.[7] However, since the complexes studied in

TABLE II

INFRARED SPECTRAL DATA FOR SOME COMPLEXES OF THE TYPE $Cr(tn)_2X_2{}^+$ IN THE 400–600-CM^{-1} REGION

Complex	Absorption bands, cm^{-1}		
$Cr(tn)_2(C_2H_3O_2)_2{}^+$	445	505	545
$Cr(tn)_2F_2{}^+$	440	495	560
$Cr(tn)_2Br_2{}^+$	435	490	503
$Cr(tn)_2Cl_2{}^+$	440	490	505

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(6) M. E. Baldwin, *J. Chem. Soc.*, 4369 (1960).

(7) M. N. Hughes and W. R. McWhinnie, *ibid.*, *A*, 592 (1967).

this investigation exhibited only a single band in this region, this would strongly support the assignment of a trans geometry.

An independent synthesis and structure proof of *trans*-$Cr(tn)_2Cl_2^+$ has been developed by Professor House,[8] at the University of Canterbury.

If as in the case of the ethylenediamine complexes of the type *trans*-$Cr(en)_2X_2^+$ the bands near 500 and 440 cm^{-1} are essentially pure Cr–N stretching modes in the trimethylenediamine complexes, the complexes studied in this investigation may possibly represent two different cases.

The diacetato and difluoro complexes have similar infrared spectra in that they both have bands near 550 cm^{-1} and the dichloro and dibromo complexes are similar in that the band near 550 cm^{-1} is absent. However, the assignment of the 550-cm^{-1} band is in doubt and further speculation is not warranted at this time.

The products formed in the reaction of hydrated chromium(III) chloride, a diamine, and a weak acid in aqueous solution under a rather specific set of conditions appear to depend on the nature of the acid used in the synthesis.

[8] D. A. House, submitted for publication.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
BOSTON UNIVERSITY, BOSTON, MASSACHUSETTS 02215

Synthesis and Characterization of Oxalatobis(ethylenediamine)rhodium(III) Nitrate

BY TARA P. DASGUPTA, RONALD M. MILBURN,*
AND LENORE DAMRAUER

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Although various diacidotetraammine complexes of rhodium(III) have been synthesized and characterized,[1,2] there appear to be no reports of the preparation of oxalatotetraammine complexes of rhodium(III). In continuance of our investigations on oxalato complexes[3,4] it has become desirable to examine the reactivity of the oxalatobis(ethylenediamine) rhodium(III) ion. The preparation and characterization of this complex, which involve several interesting features, are described herein.

Experimental Section

cis-Dichlorobis(ethylenediamine)rhodium(III) nitrate was prepared as described by Johnson and Basolo[1] except for some modifications in the procedures of adding the potassium hydroxide. In one procedure, after adding to the refluxing solution[5] the second 0.426-g portion of potassium hydroxide (in 50 ml of water added in 5-ml increments at 1–2 min intervals) a further 0.5 g of potassium hydroxide in 10 ml of water was added at one time. Following the last addition of potassium hydroxide the solution was evaporated to half its original volume, after which 20 ml of concentrated nitric acid was added. On standing for 1.5–2 hr the trans isomer along with some cis isomer precipitated, as expected.[1] The solid was separated by filtration, and the filtrate was allowed to stand at room temperature for 2 days during which time the bright yellow *cis*-$[Rh(en)_2Cl_2]NO_3$ separated. This method resulted in a 0.30-g (22%) yield of cis isomer without any contamination from the trans isomer.

The yield of the *cis*- and *trans*-$[Rh(en)_2Cl_2]NO_3$ mixture, as described by Johnson and Basolo,[1] was certainly significantly increased by the addition of two to three pellets of solid potassium hydroxide to the refluxing reaction solution. However, we failed to notice a brownish black substance or other indications of decomposition following the addition of the potassium hydroxide pellets. Also, the predicted 70% yield of cis product has not been approached in spite of several attempts. Yields of up to ~40% have been obtained.

Pure *trans*-$[Rh(en)_2Cl_2]NO_3$ was obtained easily following the method of Johnson and Basolo.[1]

The purity of the above cis and trans complexes was confirmed by comparing uv, visible, and ir spectra with those reported in the literature.[1]

Oxalatobis(ethylenediamine)rhodium(III) Nitrate. (a) **Preparation from *cis*-Dichlorobis(ethylenediamine)rhodium(III) Nitrate.**[6]—A mixture consisting of 0.460 g (1.29×10^{-3} mol) of *cis*-$[Rh(en)_2Cl_2]NO_3$, 0.447 g (3.34×10^{-3} mol) of $Na_2C_2O_4$, and 35 ml of water was refluxed for about 2 hr, during which time the solution changed from a deep yellow to a pale yellow. The hot solution was filtered twice and then cooled in an ice bath. Between 3 and 4 ml of saturated sodium nitrate solution was then added and the solution was placed in a refrigerator. After about 3 hr a very pale yellow crystalline solid precipitated. The yield was increased by adding a further 1 ml of saturated sodium nitrate solution and leaving in the refrigerator overnight. The pale yellow crystalline solid was collected by suction filtration, washed with cold dilute nitric acid, cold 95% ethanol, and cold ether, sucked dry, and stored in a vacuum desiccator; yield 0.34 g. The product was recrystallized by dissolving in 10 ml of water at 80°, filtering while hot, cooling slowly, and washing and drying as before; overall yield, 0.20 g (40%). *Anal.* Calcd for $[Rh(N_2C_2H_8)_2C_2O_4]NO_3 \cdot H_2O$: C, 18.4; H, 4.64; N, 17.9; Rh, 26.3. Found: C, 18.4; H, 4.37; N, 18.1; Rh, 26.2.[7,8]

(b) **Preparation from *trans*-Dichlorobis(ethylenediamine)rhodium(III) Nitrate.**—The complex can be prepared in poor yield from *trans*-$[Rh(en)_2Cl_2]NO_3$; therefore it may also be obtained from trans–cis mixtures of the dichloro complexes. For these purposes the same procedure as under (a) has been followed, except that considerably longer times are needed before the refluxing solution changes from bright to pale yellow. Typically, in preparations from *trans*-$[Rh(en)_2Cl_2]NO_3$, 12–16 hr was used. In such preparations from the *trans*-dichloro complex, which had been carefully purified by repeated recrystallization,[1] yields of ~6% were obtained following two or three recrystallizations of the oxalato product. Although the yields were very low, they were significantly greater than those which could be attributed to any *cis*-$Rh(en)_2Cl_2^+$ impurity in the *trans*-$Rh(en)_2Cl_2^+$ starting material. From ir and visible–uv spectra we estimate the maximum amount of any such *cis*-dichloro impurity to

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* To whom correspondence should be addressed.

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

[2] S. N. Anderson and F. Basolo, *Inorg. Syn.*, **7**, 214 (1963).

[3] (a) L. Damrauer and R. M. Milburn, *J. Amer. Chem. Soc.*, **90**, 3884 (1968); (b) L. Damrauer and R. M. Milburn, Proceedings of the XIIth International Conference on Coordination Chemistry, Sydney, Australia, 1969, p 38.

[4] M. W. Hsu, H. G. Kruszyna, and R. M. Milburn, *Inorg. Chem.*, **8**, 2201 (1969).

[5] Containing 1.00 g of $RhCl_3 \cdot 3H_2O$, 1.00 g of en·2HCl, 50 ml of water, and 0.426 g of potassium hydroxide.

[6] L. Damrauer, Ph.D. Dissertation, Boston University, 1969.

[7] C, H, and N analysis by Galbraith Laboratories, Inc., Knoxville, Tenn.

[8] Rhodium analysis in this laboratory by the stannous chloride method: (a) E. B. Sandell, "Colorimetric Determination of Trace Metals," Interscience, New York, N. Y., 1959, p 769; (b) I. M. Kolthoff and P. J. Elving, Ed., "Treatise on Analytical Chemistry," Part II, Vol. 8, Interscience, New York, N. Y., 1963, p 468.