Optically Active Tris-Ethylenediamine Complexes of Ruthenium

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The resolution of the enantiomers of tris(ethylenediamine)ruthenium(III) iodide has been effected through fractional precipitation with optically active tris(oxalato)rhodate(III). Reduction of $(-)_{350}$-Ru(en)$_3^{3+}$ by zinc amalgam in an inert atmosphere yields $(-)_{375}$-Ru(en)$_3^{2+}$ with complete retention of optical activity. Absorption, optical rotatory dispersion, and circular dichroism data for both complexes are reported. The absolute configuration of $(-)_{350}$-Ru(en)$_3^{3+}$ was inferred by comparison with the tris(ethylenediamine)cobalt(III) enantiomers through the least soluble isomer method and the formation of active racemates; that of $(-)_{375}$-Ru(en)$_3^{2+}$ was inferred from the band assignments of the circular dichroism spectrum. Both $(-)_{350}$-Ru(en)$_3^{3+}$ and $(-)_{375}$-Ru(en)$_3^{2+}$ were found to have the D configuration. An external criterion for the completeness of resolution was obtained through the formation of active racemates.

Introduction

Optical isomers of tris-ethylenediamine complexes of transition metal ions have been known since the early days of coordination chemistry. Werner synthesized the complexes M(en)$_3^{n+}$, where M is Cr(III), Co(III), Rh(III), Ir(III), or Pt(IV), and he resolved their enantiomorphs through fractional precipitation with optically active anions.[2-6] More recently, the corresponding complexes of Cd(II),[7] Zn(II),[8] and possibly Cu(II)[9] have also been resolved.

The relative configurations of the tris-ethylenediamine complexes have been studied by various methods, such as the formation of the less soluble salt of an optically active counterion,[3,4] the formation of active racemates,[10] and a comparison of the general form of the Cotton-effect curves.[11] In addition, the absolute configuration of $(+)_{589}$-Co(en)$_3^{3+}$ has been determined by X-ray diffraction to be that which is conventionally termed as D-Co(en)$_3^{3+}$.[12] From the knowledge of the absolute configuration of this one complex, the absolute configurations of other dissymmetric trigonal complexes of metal ions with d^3 and d^6 configurations, including the tris-ethylenediamine complexes, have been inferred by relative configuration studies and, in particular, by applying the principle that two related optically active complexes have the same absolute configuration if they give a Cotton effect of the same sign in the absorption wavelength region of an electronic transition common to both complexes.[13]

The tris-ethylenediamine complex of Ru(III) has now been resolved by fractional precipitation with optically active tris(oxalato)rhodate(III). It has been found that Ru(en)$_3^{3+}$ in solution can be reduced to Ru(en)$_3^{2+}$ with complete retention of optical activity. Since Ru(II) is a d^6 metal ion, the stereochemical configuration of the enantiomers of Ru(en)$_3^{2+}$ can be related to that of $(+)_{589}$-Co(en)$_3^{3+}$ spectroscopically. Furthermore, because Ru(en)$_3^{3+}$ and Ru(en)$_3^{2+}$ are related chemically, the assignment of configuration can be extended to a d^5 dissymmetric trigonal complex.

Experimental Section

Methods.—All solutions of Ru(en)$_3^{3+}$ and Ru(en)$_3^{2+}$ were prepared in deoxygenated 0.01 *M* HTFA[14] under a nitrogen atmosphere in order to reduce the facile air oxidation of the complexes when in solution.

In denoting an enantiomer, the rotation refers to the sodium D line unless otherwise stated.

Materials.—[Ni(phen)$_3$]I$_2$ · 3H$_2$O was prepared and resolved by the method of Dwyer and Gyarfas.[15] K$_3$[Co(ox)$_3$] · 3H$_2$O was prepared and resolved by methods described in the literature.[16,17] [Co(en)$_3$]Cl$_3$ was prepared by a known procedure[18] and resolved through formation of chloride *d*-tartrate diastereoisomers.[3] The enantiomers and the racemic complex were isolated as iodide salts.[19]

K$_3$[Rh(ox)$_3$] · 4.5H$_2$O, prepared by Werner's method,[20] was dried *in vacuo* over P$_2$O$_5$ to yield the orange monohydrate. K$_3$[Rh(ox)$_3$] · H$_2$O was resolved by fractional precipitation with active [Ni(phen)$_3$]I$_2$ according to the method of Dwyer and Sargeson.[17] Since the specific rotations are small, $[\alpha]^{20}$D ± 85°,[17] more satisfactory evidence of the optical purity was found to be the value of $\epsilon_L - \epsilon_R$ at 400 nm in the CD spectrum. The literature value of $\epsilon_L - \epsilon_R = +2.85$[13] for $(+) - $Rh(ox)$_3^{3-}$ was obtained.

Preparation of Tris(ethylenediamine)ruthenium(II) Tetrachlorozincate, [Ru(en)$_3$]ZnCl$_4$.—The method of Meyer[21] was

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(12) Y. Saito, K. Nakatsu, M. Shiro, and H. Kuroya, *Bull. Chem. Soc. Japan*, **30**, 795 (1957).
(13) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965).

(14) The following abbreviations are used in this paper: HTFA, trifluoroacetic acid; en, ethylenediamine; ox, oxalate; phen, 1,10-phenanthroline.
(15) F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. N. S. Wales*, **83**, 232 (1949).
(16) J. C. Bailar, Jr., and E. M. Jones, *Inorg. Syn.*, **1**, 35 (1939).
(17) F. P. Dwyer and A. M. Sargeson, *J. Phys. Chem.*, **60**, 1331 (1956).
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(19) J. A. Broomhead, F. P. Dwyer, and J. W. Hogarth, *ibid.*, **6**, 183 (1960).
(20) A. Werner and J. Poupardin, *Ber.*, **47**, 1954 (1914).
(21) T. J. Meyer, Ph.D. Thesis, Stanford University, 1967.

used to synthesize $[Ru(en)_3]ZnCl_4$. In a typical synthesis 1.94 g of $RuCl_3 \cdot 3H_2O$ was refluxed about 50 min in a 100-ml three-neck flask with 30 ml of 25% ethylenediamine solution, the system having been purged with nitrogen prior to heating. About 1.0 g of powdered zinc was added in small amounts throughout the refluxing period. After the reflux mixture became bright orange-brown, it was refluxed 30 min more. The reflux mixture was filtered under nitrogen while still hot. It was cooled in ice and approximately 18 ml of concentrated ice-cold HCl was slowly added *via* a syringe until a pH of 2 was obtained. The collected product, which was yellow-brown, was washed with ethanol and ether. The yield of crude product was 2.94 g, 81%. The product was recrystallized under nitrogen from hot 0.01 M HTFA. The product collected was washed with ethanol and ether and dried *in vacuo* over P_2O_5. *Anal.* Calcd for $C_6H_{24}Cl_4N_6RuZn$: C, 14.75; H, 4.95; Cl, 29.03; N, 17.20; Zn, 13.38. Found: C, 14.96; H, 4.82; Cl, 29.02; N, 17.49; Zn, 13.35.

Preparation and Resolution of Tris(ethylenediamine)-ruthenium(III) Iodide, $[Ru(en)_3]I_3$.—$[Ru(en)_3]ZnCl_4$ dissolved in a minimal amount of 0.01 M HTFA was oxidized by the dropwise addition of iodine in a sodium iodide solution.[22] The complete oxidation of $Ru(en)_3^{2+}$ can be determined by a spot test with silver nitrate: if the oxidation is incomplete, a dark gray precipitate due to metallic silver forms immediately; if complete, only the cream-colored precipitate of silver chloride and silver iodide is formed. When the oxidation was complete, the complex was isolated and purified as described elsewhere.[22] *Anal.* Calcd for $C_6H_{24}I_3N_6Ru$: C, 10.89; H, 3.65; I, 57.50; N, 12.69. Found: C, 10.94; H, 3.66; I, 56.42; N, 12.36.

$[Ru(en)_3]I_3$ was successfully resolved by fractional precipitation with optically active $K_3[Rh(ox)_3]$. In a typical resolution, 0.52 g of $(\pm)-[Ru(en)_3]I_3$ was dissolved in 15 ml of warm, deoxygenated HTFA under nitrogen. To this solution, 0.22 g of $(-)-K_3[Rh(ox)_3]$ in 1 ml of deoxygenated HTFA was added with a syringe. After cooling in ice 15 min, the mixture was filtered under nitrogen into about 2 ml of concentrated sodium iodide solution.

The filtrate solution was cooled on a salt–ice bath and more sodium iodide solution was added as needed until crystallization of $[Ru(en)_3]I_3$ appeared to be complete. The dark purple crystals were collected on a filter, washed with ethanol and ether, and dried *in vacuo* over P_2O_5. The yield was 0.10 g, 19% of total $[Ru(en)_3]I_3$ used. The enantiomer which is obtained from the filtrate when $(-)-Rh(ox)_3^{3-}$ is the resolving agent has $\Delta\epsilon = +2.12$ at 284 nm and $\Delta\epsilon = -0.87$ at 328 nm when optically pure. This enantiomer will hereafter be designated as $(-)_{350}-Ru(en)_3^{3+}$ since in the rotatory dispersion curve the band at longer wavelengths is negative, with a minimum at 350 nm.

The yellow diastereoisomer, $[(+)_{350}-Ru(en)_3][(-)-Rh(ox)_3]$, collected on the filter was washed first with cold water and then with ethanol and ether and dried *in vacuo* over P_2O_5. The yield was 0.25 g, 86% based on $K_3[Rh(ox)_3]$ added. *Anal.* Calcd for $C_{12}H_{24}N_6O_{12}RhRu$: C, 22.23; H, 3.73; N, 12.96. Found: C, 22.18; H, 3.72; N, 13.06. This diastereoisomer was too insoluble in water to obtain any spectral information for it.

The $(+)_{350}-Ru(en)_3^{3+}$ isomer was obtained from the diastereoisomer by adding 3 ml of concentrated HI to about 0.2 g of the diastereoisomer in a deoxygenated serum bottle containing a magnetic stirring bar. The mixture was stirred at room temperature for 1 hr, cooled in a salt–ice bath for 30 min, and filtered. The product was washed with ethanol. The crude product was purified by dissolving as much as possible in about 4 ml of hot HTFA under nitrogen. The solution was filtered into concentrated sodium iodide solution. The mixture was cooled in a salt–ice bath and the dark purple crystals were collected on a filter, washed with ethanol and ether, and dried *in vacuo*. The product is $(+)_{350}-[Ru(en)_3]I_3$ with $\Delta\epsilon = -2.12$ at 284 nm and $\Delta\epsilon = +0.87$ at 328 nm when optically pure.

Fractional precipitation of $[Ru(en)_3]I_3$ with $(-)-K_3[Co(ox)_3]$ was carried out in a procedure identical with that for $(-)-K_3[Rh(ox)_3]$. The isomer obtained from the filtrate was $(+)_{350}-[Ru(en)_3]I_3$, but it was only 60% optically pure. The $(-)_{350}-Ru(en)_3^{3+}$ isomer could not be obtained from the diastereoisomer with HI as before.

The resolution of $[Ru(en)_3]I_3$ was attempted using various other resolving agents. A solution of the resolving agent in deoxygenated HTFA was added to a solution of $[Ru(en)_3]I_3$ in HTFA under nitrogen. The solution was evaporated under high vacuum until a considerable amount of precipitate had formed. The precipitate was removed and analyzed by passing a solution of it through a Dowex 50W-X8 cation-exchange column in hydrogen ion form. The eluent was titrated with a base and then, after acidifying, with silver nitrate. When the resolving agent was tartaric acid, *d*-camphorsulfonic acid, or the ammonium salt of *d*-α-bromocamphorsulfonic acid, the equivalents of iodide ion equaled the equivalents of hydrogen ion present, indicating the precipitate was $[Ru(en)_3]I_3$ and did not contain the resolving agent. Removal of the iodide with silver ion prior to adding a resolving agent was not feasible because the silver ion oxidizes $Ru(en)_3^{3+}$. Owing to its low solubility in an acidic medium, the sodium salt of *d*-α-nitrocamphor was unsuitable. A slight partial resolution was obtained with antimonyl tartrate.

Preparation of Tris(ethylenediamine)ruthenium(II) Solutions.—Solutions of $[Ru(en)_3]I_3$ of known concentration were added with a syringe to excess zinc amalgam in deoxygenated serum bottles. The solutions were allowed to stand over the zinc 1–2 hr before using them. Completion of reduction was demonstrated by analysis of the $Ru(en)_3^{2+}$ by the reduction of iodine. When reduced, $(+)_{350}-Ru(en)_3^{3+}$ yielded the optical isomer with $\Delta\epsilon = +2.32$ at 284 nm and which will hereafter be designated as $(+)_{375}-Ru(en)_3^{2+}$ from the sign of the maximum rotation at longer wavelengths as seen in the rotatory dispersion curve.

Partial Resolution of Tris(ethylenediamine)cobalt(III) Iodide Monohydrate, $[Co(en)_3]I_3 \cdot H_2O$.—In a procedure identical with that of the resolution of $[Ru(en)_3]I_3$ with $(-)-K_3[Rh(ox)_3]$, a partial resolution of $(\pm)-[Co(en)_3]I_3 \cdot H_2O$ was obtained by fractional precipitation with $(-)-K_3[Rh(ox)_3]$. The isomer obtained from the filtrate was $(+)-Co(en)_3^{3+}$, and $\Delta\epsilon$ obtained at 493 nm was +0.30, considerably less than the literature value of $\Delta\epsilon = +1.89$.[23]

Cocrystallization Experiments.—(1) In 18 ml of deoxygenated HTFA 0.210 g of $(+)_{350}-[Ru(en)_3]I_3$ and 0.374 g of $(\pm)-[Co(en)_3]-I_3 \cdot H_2O$ were dissolved under a nitrogen atmosphere. The solution was evaporated under high vacuum to about one-third the original volume. The dark purple, needle-shaped crystals that were formed were collected on a filter and washed with ethanol. The circular dichroism of the crystals exhibited a negative displacement at 284 nm and positive displacements at 328 and 493 nm, which is indicative of $(+)_{350}-Ru(en)_3^{3+}$ and $(+)-Co(en)_3^{3+}$. The filtrate showed a negative displacement at 493 nm in the circular dichroism spectrum, indicating the filtrate contained an excess of $(-)-Co(en)_3^{3+}$. Decreasing the ratio of $(+)_{350}-Ru(en)_3^{3+}$ to $(\pm)-Co(en)_3^{3+}$ from 1:2 as above to 1:8 yielded similar results.

(2) A solution of 0.205 g of racemic $[Ru(en)_3]I_3$ and 0.085 g of $(-)-[Co(en)_3]I_3 \cdot H_2O$ dissolved in 8 ml of HTFA was subjected to the above procedure. The circular dichroism spectrum of the filtrate contained negative displacements at 284 and 493 nm; for the crystals, a positive displacement at 284 nm and a negative displacement at 493 nm. Hence, the predominant isomers in the crystals are $(-)_{350}-Ru(en)_3^{3+}$ and $(-)-Co(en)_3^{3+}$, and in the filtrate, $(+)_{350}-Ru(en)_3^{3+}$ and $(-)-Co(en)_3^{3+}$. The mixed crystals were recrystallized from HTFA by adding sodium iodide solution.

(3) Using saturated solutions at room temperature and under identical conditions, 1.05 ml of $(-)-[Co(cn)_3]I_3$ was added to 1.05 ml of $(-)_{350}-[Ru(en)_3]I_3$ and to 1.05 ml of $(+)_{350}-[Ru(en)_3]-$

(22) T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968).

(23) A. J. McCaffery and S. F. Mason, *Mol. Phys.*, **6**, 359 (1963).

I_3. A precipitate formed in the solution mixture containing $(-)_{350}$-Ru(en)$_3$$^{3+}$ and $(-)$-Co(en)$_3$$^{3+}$, but no precipitate appeared in the solution of $(+)_{350}$-Ru(en)$_3$$^{3+}$ and $(-)$-Co(en)$_3$$^{3+}$. Upon cooling the solutions the amount of precipitate in the former noticeably increased, while a small amount also formed in the latter.

Analyses.—The amount of Ru(en)$_3$$^{2+}$ in a reduced solution of Ru(en)$_3$$^{3+}$ was determined by adding an aliquot of the Ru(en)$_3$$^{2+}$ solution with a constant-volume pipet to a deoxygenated solution of iodine. The latter had been produced by adding an excess of potassium iodide to an acidic, oxygen-free solution of a known amount of potassium iodate. The excess iodine was titrated with a standard thiosulfate solution. A blank solution of Ru(en)$_3$$^{3+}$ indicated that that complex was not oxidized by iodine under the conditions present.

The concentrations of the Ru(en)$_3$$^{3+}$ solutions were known from the volumetric preparations. This was checked by the absorption spectrum and occasionally by the analysis of the iodide ion in solution. Since silver ion oxidizes Ru(en)$_3$$^{3+}$ in solution, the iodide ion concentration was determined by titration with silver nitrate after first passing the aliquot through a Dowex 50W-X8 cation-exchange column.

The solubility of the iodide salt of a given tris-ethylenediamine complex was determined by analysis of the iodide ion concentration in the saturated solution in equilibrium with excess solid complex at a given temperature. As above, the iodide ion analysis consisted of removing the Ru(en)$_3$$^{3+}$ complex, if present, by ion exchange and titration with silver nitrate.

All elemental analyses of the complexes were performed in the Microanalytical Laboratory of the University of Illinois.

Spectra.—All spectra were recorded at room temperature using 1-cm cells and (1.0–2.0) $\times$ 10^{-3} M solutions. The ultraviolet and visible spectra were measured on a Cary Model 14 recording spectrophotometer and the CD curves were recorded with a Roussel-Jouan Dichrographe. The ORD curves were recorded with a JASCO ORD/UV-5 optical rotatory dispersion recorder.

Results

The absorption and circular dichroism spectra in the region 260–450 nm for a 2.0 $\times$ 10^{-3} M solution of $(-)_{350}$-[Ru(en)$_3$]I$_3$ in 0.01 M HTFA at room temperature are given in Figure 1. Dilute solutions exhibit only one absorption band in the ultraviolet region at 310 nm and do not absorb in the visible region, although at 450 nm there is an outer-sphere charge-transfer transition in concentrated solutions[24] as well as absorption due to a decomposition product if air oxidation has occurred. The absorption band at 310 nm consists of two transitions as indicated by the maxima at 284 and 328 nm in the CD curve. In the CD spectrum, the beginning of a strong negative band which extends further into the ultraviolet is observed. The $\Delta\epsilon$ value at 284 nm was used as a good criterion for optical purity throughout this study.

The rotatory dispersion curve for the same isomer, given in Figure 2, is a composite of the positive and negative Cotton-effect curves for the individual transitions. From the ORD curve it is obvious that no rotation can be observed at the sodium D line. Table I summarizes the absorption, CD, and ORD data for this complex ion.

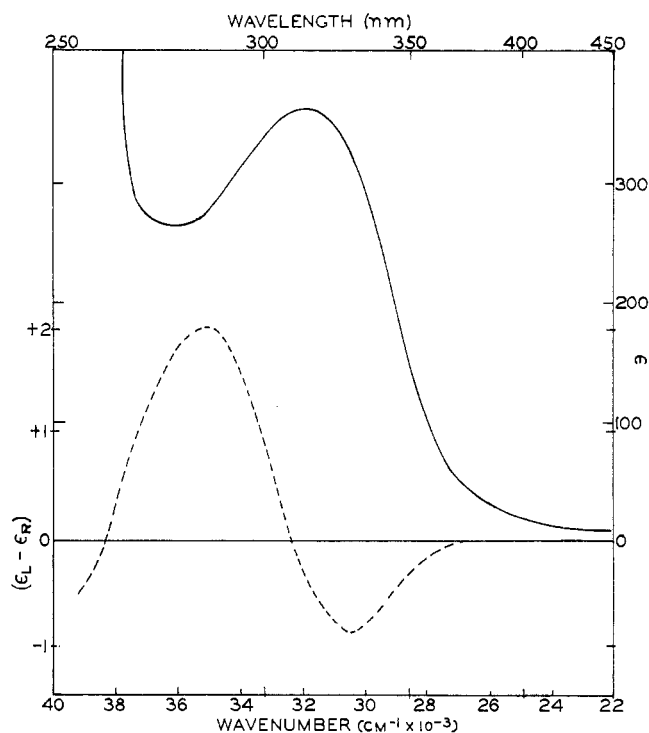The reduction of Ru(en)$_3$$^{3+}$ in HTFA medium and oxygen-free conditions over excess zinc amalgam was

(24) H. Elsbernd and J. K. Beattie, *Inorg. Chem.*, **7**, 2468 (1968).

Figure 1.—The absorption spectrum (————) and the circular dichroism curve (---------) for $(-)_{350}$-Ru(en)$_3$$^{3+}$.

Figure 2.—Optical rotatory dispersion curve for $(-)_{350}$-Ru(en)$_3$$^{3+}$ (————) and $(-)_{375}$-Ru(en)$_3$$^{2+}$ (---------).

complete after 1 hr as determined by analysis for Ru(en)$_3$$^{2+}$. Complete retention of configuration upon the formation of Ru(en)$_3$$^{2+}$ was demonstrated by reducing a solution of Ru(en)$_3$$^{3+}$ in the usual manner and then oxidizing the resulting Ru(en)$_3$$^{2+}$ solution
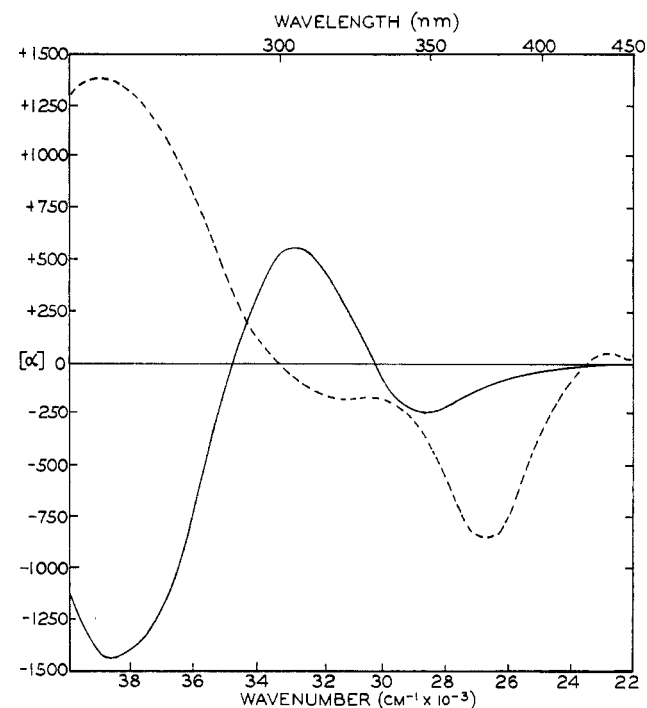
Absorption		Circular dichroism		Rotatory dispersion	
λ_{max}, nm (ϵ_{max})		λ_{max}, nm ($\epsilon_L - \epsilon_R)_{max}$		λ_{max}, nm	$[\alpha]_{max}$, deg
		$(-)_{350}$-Ru(en)$_3{}^{3+}$			
310 (360 ± 25)[a]	328	−0.87		350	−244
	284	+2.12		300	+564
				259	−1460
		$(-)_{375}$-Ru(en)$_3{}^{2+}$			
370 (120 ± 10)[a]	402	+0.93		375	−851
	348	−1.49		255	+1380
304 (1020 ± 60)[a]	284	−2.32			

[a] T. J. Meyer, Ph.D. Thesis, Stanford University, 1967.

with a solution of ferric ion. Although the absorption at wavelengths less than 300 nm was so great, owing to the effects of the excess ferric ion, as to prohibit the observation of the CD spectrum at higher energies, the CD curve in the 360–300-nm region was that of Ru(en)$_3{}^{3+}$. The original solution and the final solution exhibited values for $\Delta\epsilon$ at 328 nm that differed only within experimental error.

The absorption spectrum of Ru(en)$_3{}^{2+}$, as given in Figure 3, contains two maxima—one at 370 nm and a more intense band at 304 nm. The CD spectrum of $(-)_{375}$-Ru(en)$_3{}^{2+}$, also shown in Figure 3, contains a positive band with maximum at 402 nm and two negative bands centered at 348 and 284 nm. As with Ru(en)$_3{}^{3+}$, the beginning of an intense band extending into the far-ultraviolet region is observed. The
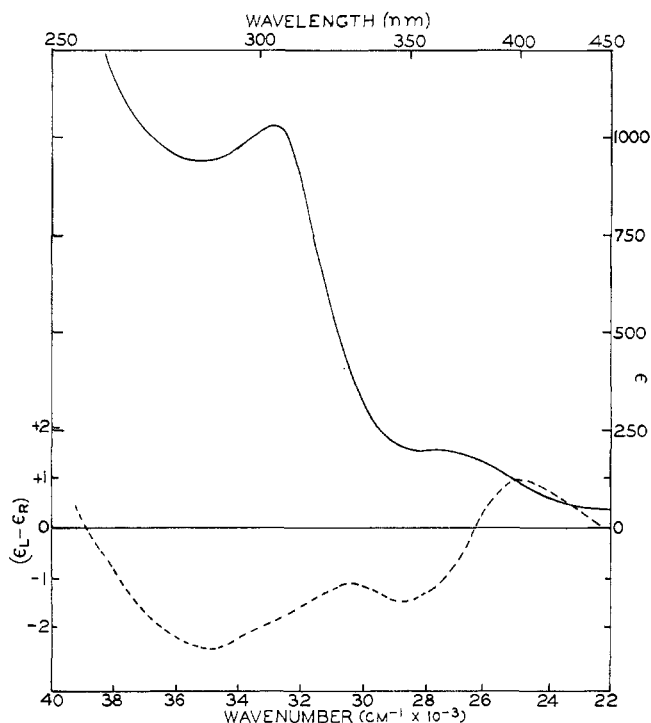

Figure 3.—The absorption spectrum (———) and the circular dichroism curve (- - - - - -) for $(-)_{375}$-Ru(en)$_3{}^{2+}$.

anomalous rotatory dispersion curve given in Figure 2 for $(-)_{375}$-Ru(en)$_3{}^{2+}$ is a complex composite of the Cotton-effect curves for the individual transitions. The rotation at the sodium D line is negligible for this complex. The data obtained from the absorption, CD, and ORD spectra of $(-)_{375}$-Ru(en)$_3{}^{2+}$ are summarized in Table I also.

Both Ru(en)$_3{}^{3+}$ and Ru(en)$_3{}^{2+}$ are rather stable to racemization. Solutions of Ru(en)$_3{}^{3+}$ maintained under nitrogen atmosphere at room temperature for 24 hr show no loss of optical activity. Solutions of Ru(en)$_3{}^{2+}$ kept over zinc amalgam and under nitrogen at room temperature have a decrease of 8.5% after 24 hr. The slight changes in the absorption spectra during this time indicate that this decrease may be due in part to decomposition of the complex. After 4 hr at 60°, the loss of optical activity for a solution of the divalent complex was about 12%; for the trivalent complex it was about 45%, but decomposition had occurred in both cases. However, even if air oxidation is rigorously excluded in the latter case, decomposition still occurs, as is evident by the purple coloration of the sample and the appearance of an absorption band at 568 nm, which may be due to an iodide-substituted complex. The same decomposition product was observed for solutions of active [Ru(en)$_3$]I$_3$ maintained at room temperature under nitrogen for 72 hr with a small loss of activity.

When saturated solutions of the sodium salts of phosphate, pyrophosphate, hydrogen arsenate, and arsenite were added to equal volumes of solutions of Ru(en)$_3{}^{2+}$, such that the final concentrations of Ru(en)$_3{}^{2+}$ were 1.5×10^{-3} and 3.1×10^{-3} M and those of the anions were 0.12–0.77 M, small but regular changes in the circular dichroism curve were observed. By comparison with the CD curve of solutions of Ru(en)$_3{}^{2+}$ at the same concentration in HTFA, solutions with added anions were found to exhibit a 2–12% increase in intensity at the band maximum at 348 nm, and a 1–4% decrease in band intensity at 402 nm. The small increase and decrease in band intensities at 348 and 402 nm, respectively, were observed for all solutions of added anions studied.

The result of cocrystallizing $(+)_{350}$-[Ru(en)$_3$]I$_3$ with $(\pm)$-[Co(en)$_3$]I$_3$ is to effect a partial resolution of the enantiomers of Co(en)$_3{}^{3+}$. After a partial crystallization of the complexes from the solution, an excess of $(-)$-Co(en)$_3{}^{3+}$ was found in the remaining solution and an excess of $(+)$-Co(en)$_3{}^{3+}$ was in the crystals. Similarly, when $(-)$-[Co(en)$_3$]I$_3$ is crystallized with $(\pm)_{350}$-[Ru(en)$_3$]I$_3$, the CD spectrum at 284 nm shows an excess of $(+)_{350}$-Ru(en)$_3{}^{3+}$ in the filtrate and $(-)_{350}$-Ru(en)$_3{}^{3+}$ in the crystals. Fractionally recrystallizing the mixed crystals did not change the predominance of specific Ru(III) and Co(III) isomers in any fraction for any of the cocrystallizations. Furthermore, the ratio of the amounts of activity for the two complexes in the crystals was constant. The ratio of the maximum displacements, $\Delta(\text{mm})_{284}/\Delta(\text{mm})_{493}$, was -1.08 (± 0.05) for the various fractions. The only exception was a

more negative ratio obtained for the crystals resulting from a mixture of $(+)_{350}$-[Ru(en)$_3$]I$_3$ with $(\pm)$-[Co(en)$_3$]I$_3$ in a 1:2 mole ratio. The same ratio, $\Delta(\text{mm})_{284}/\Delta(\text{mm})_{493} = -1.09$, was found for the crystals obtained by mixing solutions of $(-)$-[Co(en)$_3$]I$_3$ and $(-)_{350}$-[Ru(en)$_3$]I$_3$.

A marked difference was observed between the solubility of a mixture of $(-)$-[Co(en)$_3$]I$_3$ and $(+)_{350}$-[Ru(en)$_3$]I$_3$ and that of a $(-)$-[Co(en)$_3$]I$_3$ and $(-)_{350}$-[Ru(en)$_3$]I$_3$ mixture. In the latter case, a mixture of the components is much less soluble at room temperature than is either of the components alone. From the CD spectra of the supernatant solutions, the concentrations of $(-)$-Co(en)$_3{}^{3+}$ in the two solutions at 0° were found to be 3.8×10^{-2} and 2.9×10^{-2} M, respectively, while the total concentrations of both complexes in the supernatant solutions at 0° was 5.0×10^{-2} and 3.2×10^{-2} M, respectively. For comparison, the concentrations of saturated solutions of the active and racemic complexes were determined and these are listed in Table II.

TABLE II

THE CONCENTRATIONS OF SATURATED SOLUTIONS OF ACTIVE AND RACEMIC COMPLEXES

Complex	Temp, °C	Concn × 10^{-2}, M
$(-)$-[Co(en)$_3$]I$_3$	0	7.7
$(\pm)$-[Co(en)$_3$]I$_3$	0	2.7
$(-)$-[Co(en)$_3$]I$_3$	25	14
$(\pm)$-[Co(en)$_3$]I$_3$	25	6.9
$(-)_{350}$-[Ru(en)$_3$]I$_3$	0	5.9
$(\pm)_{350}$-[Ru(en)$_3$]I$_3$	0	2.0
$(-)_{350}$-[Ru(en)$_3$]I$_3$	25	14
$(\pm)_{350}$-[Ru(en)$_3$]I$_3$	25	5.5

Discussion

The extent of resolution of [Ru(en)$_3$]I$_3$ varied considerably in successive experiments. By recrystallization of the enantiomers and by resolving partially resolved samples a second time, complete resolution of some samples has apparently been attained. The data reported here are believed to represent optically pure isomers. The completeness of resolution is further confirmed by the external criterion for $\Delta\epsilon$ at 284 nm for Ru(en)$_3{}^{3+}$ obtained from the cocrystallization experiments. If the crystals resulting when $(\pm)$-[Co(en)$_3$]I$_3$ and $(+)_{350}$-[Ru(en)$_3$]I$_3$ cocrystallize are completely racemic, that is, if the total concentration of D-M(en)$_3{}^{3+}$ cations equals that of the L-M(en)$_3{}^{3+}$ isomers, then the concentration of $(+)_{350}$-Ru(en)$_3{}^{3+}$ incorporated into the crystals must equal the concentration by which the one Co(en)$_3{}^{3+}$ isomer is in excess of the other. Hence, the ratio of the maximum displacements in the CD spectrum, $\Delta(\text{mm})_{284}/\Delta(\text{mm})_{493}$, should be that of the values of $\Delta\epsilon$ at those wavelengths for the Ru(en)$_3{}^{3+}$ and Co(en)$_3{}^{3+}$ isomers present. The fact that three different types of mixtures of the

active and racemic complexes yielded mixed crystals exhibiting the same value for $\Delta(\text{mm})_{284}/\Delta(\text{mm})_{493}$ seems to indicate that the crystals are completely racemic. Hence, $\Delta\epsilon = -2.14$ at 284 nm for $(+)_{350}$-Ru(en)$_3{}^{3+}$ is the value calculated from the ratio $\Delta(\text{mm})_{284}/\Delta(\text{mm})_{493} = -1.08$ for the mixed crystal and $\Delta\epsilon = +1.89$ at 493 nm for $(+)$-Co(en)$_3{}^{3+}$,[23] after adding a small correction term for the displacement of 284 nm due to active Co(en)$_3{}^{3+}$ present. A similar calculation gives the value $\Delta\epsilon = +0.87$ at 328 nm for $(+)_{350}$-Ru(en)$_3{}^{3+}$. Both of these values agree with those obtained from the direct resolution of [Ru(en)$_3$]I$_3$.

It is of interest to note that while the tris-ethylenediamine complexes of Co(III), Ir(III), and Rh(III) can be resolved with tartaric acid or nitrocamphorsulfonic acid,[3–5] attempts to resolve Ru(en)$_3{}^{3+}$ with any of the usual organic anionic resolving agents have been unsuccessful. The solubility of [Ru(en)$_3$]I$_3$ is less than that of any of the possible diastereoisomers and the removal of iodide ion from the solution by the usual procedure of precipitation with silver ion is not feasible, as already indicated. Although at least a partial resolution of [Ru(en)$_3$]I$_3$ can be obtained with active K$_3$[Co(ox)$_3$], the latter was found less suitable for use in these studies because of the difficulty in obtaining the Ru(en)$_3{}^{3+}$ isomer from the diastereoisomer. It appears that stirring the cobaltate diastereoisomer with concentrated HI, as is done with the analogous rhodate complex, results in oxidation of the Ru(III) complex by the Co(III) ion.

The relatively simple absorption spectrum of Ru(en)$_3{}^{3+}$ is difficult to interpret. The single absorption band at 310 nm results from two transitions as observed in the CD curve. This band is probably due to d → d transitions, although it has been suggested on the basis of the relatively high molar absorptivity that the absorption band at 275 nm in the spectrum of the analogous Ru(NH$_3$)$_6{}^{3+}$ complex may be due to a charge-transfer transition.[25] If one assumes d → d transitions, assignment of these transitions is still impossible on the basis of this study since a d^5 metal ion in a strong field and octahedral environment has a $^2T_{2g}$ ground state and the first excited doublet states of $^2T_{1g}$ and $^2A_{2g}$.[26] In the D$_3$ symmetry of tris-ethylenediamine complexes, the degeneracy of the ^2T states can be removed, and ^2A and ^2E states result for each of them. In the spectrum of the comparable spin-paired d^5 system of Fe(en)$_3{}^{3+}$, numerous d → d bands are observed.[27] Undoubtedly, the strong charge-transfer absorption at wavelengths less than 250 nm masks some of the d → d transitions in the Ru(III) complex. Any suggestion as to which of the possible transitions occur at 284 and 328 nm would be a haphazard guess at this point.

The d^6 metal ions in a strong field and D$_3$ symmetry

(25) C. K. Jørgensen in "Halogen Chemistry," Vol. 1, V. Gutmann, Ed., Academic Press, New York, N. Y., 1967, p 348.

(26) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 275.

(27) G. A. Renovitch and W. A. Baker, Jr., *J. Am. Chem. Soc.*, **90**, 3585 (1968).

TABLE III

THE ABSORPTION AND CIRCULAR DICHROISM SPECTRA OF d^3 AND d^6 METAL
COMPLEXES OF ETHYLENEDIAMINE IN AQUEOUS SOLUTION

Complex	Absorption λ_{max}, nm (ϵ_{max})	Circular Dichroism λ_{max}, nm	$(\epsilon_L - \epsilon_R)_{max}$	Transition	Config	Ref
(+)-Co(en)$_3^{3+}$	469 (84)	493	+1.89	E_a	D	a
		428	−0.17	A_2		
	340 (74)	351	+0.25	E_b		
(+)-Cr(en)$_3^{3+}$	460 (74)	456	+1.36	E_a	D	b
	353 (65)	350	−0.05	E_b		
(−)-Rh(en)$_3^{3+}$	306 (251)	320	+2.0	E_a	D	b
		287	−0.1	A_2		
	257 (246)	258	+0.8	E_b		
(−)-Ir(en)$_3^{3+}$	310 (500)	315	+0.4	E_a	D	c
(−)$_{375}$-Ru(en)$_3^{2+}$	370 (120)	402	+0.93	E_a	D	d
		348	−1.49	A_2		
	304 (1020)	284	−2.32	CT		

^{a} A. J. McCaffery and S. F. Mason, *Mol. Phys.*, **6**, 359 (1963). ^{b} A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965). ^{c} J. P. Mathieu, *J. Chim. Phys.*, **33**, 78 (1936). ^{d} Present work.

have been characterized and studied more fully.[23,28-30] The ground state is $^1A_1$ and the singlet excited states of $^1T_{1g}$ and $^1T_{2g}$ in an octahedral environment are both split into E and A states in D_3 symmetry. Transitions to states arising from $^1T_{2g}$ are magnetically forbidden and will ordinarily not show any optical activity, although this is sometimes observed for $^1A_1 \rightarrow {}^1E_b$ transitions, resulting from a mixing of excited E states.[28] In general, these trigonal metal complexes in solution give two CD bands with opposed signs, due to the A_2 and the E_a transitions, and a single CD band, due to the E_b transition at shorter wavelengths.[13] This can be observed from the examples given in Table III. For Ru(en)$_3^{2+}$ three CD bands are observed. The intense one at highest energy, centered at 284 nm, is probably charge transfer in nature since the molar absorptivity in the order of 10^3 appears too great for a d → d transition. The absorption band at 370 nm consists of two d → d transitions, and the CD bands at 402 and 348 nm thus are undoubtedly due to ^1E_a and $^1A_2$ excitations. For trigonal complexes, the E_a transition usually occurs at lower energy and is more intense than the A_2 transition. Since some of the intensity of the 348-nm band in the Ru(en)$_3^{2+}$ CD spectrum probably arises from the more intense charge-transfer transition at 284 nm, we suggest that the E_a excitation occurs at 402 nm. Positive assignment of these transitions may be obtained directly from the measurement of the axial circular dichroism of the complex ion orientated in a uniaxial crystal,[23] a method that is of interest to pursue further with this complex.

The assignment of these transitions can also be inferred from the gegenion effect in solution. Since it has been observed that in the presence of tetrahedral or trigonal anions the areas of the A_2 and the E_a circular dichroism bands in the spectra of the tris-ethylenedi-

amine complexes of Co(III), Cr(III), or Rh(III) are enhanced and diminished, respectively,[31] this method was applied to help identify the circular dichroism bands in the spectrum of Ru(en)$_3^{2+}$. The slight decrease in band intensity at 402 nm and increase at 348 nm upon the addition of oxyanions to solutions of Ru(en)$_3^{2+}$ corroborates the assignments of the 402-nm band as due to an E_a transition and the 348-nm band as A_2. These changes in the circular dichroism spectrum are much smaller for Ru(en)$_3^{2+}$ than for Co(en)$_3^{3+}$.[31] While this weakens the evidence for band assignments, it is to be expected since the smaller charge on the metal ion will lessen the electrostatic interaction between the complex cation and the anions and thus decrease the ion association.

Identification of the circular dichroism band due to the A_2 or the E_a transition makes possible the assignment of the absolute configuration of a complex since the stereochemical configuration of a trigonal metal complex is related to the signs of the rotational strengths of the A_2 and E_a transitions.[32] If the E_a circular dichroism band is positive, the enantiomer has the absolute configuration conventionally termed D. If the circular dichroism band at 402 nm for the enantiomers of Ru(en)$_3^{2+}$ is due to the E_a transition, then (−)$_{375}$-Ru(en)$_3^{2+}$ has the absolute configuration of D-Ru(en)$_3^{2+}$. A more complete stereochemical specification of this configuration is P(C$_2$) or M(C$_3$); P(plus) and M(minus) designating a right-handed helical segment I and a left-handed helical form II, respectively, about the indicated symmetry axis.[13]

Credibility in this assignment is gained from the solubility studies with Ru(en)$_3^{3+}$. With potassium antimonyl tartrate, the (+)-Co(en)$_3^{3+}$ isomer[33] and the (−)$_{350}$-Ru(en)$_3^{3+}$ isomer form the less soluble diastereoisomers, while with (−)-Rh(ox$_3$)$^{3+}$ these same

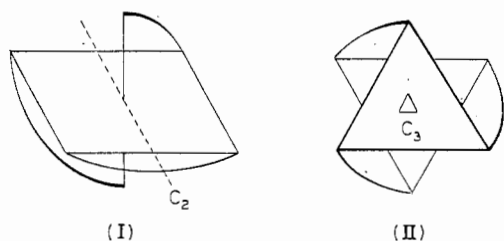(28) S. F. Mason, *Quart. Rev.* (London), **17**, 20 (1963).
(29) W. Moffitt, *J. Chem. Phys.*, **25**, 1189 (1956).
(30) S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, **33**, 98 (1960).

(31) S. F. Mason and B. J. Norman, *J. Chem. Soc.*, A, 307 (1966).
(32) R. E. Ballard, A. J. McCaffery, and S. F. Mason, *Proc. Chem. Soc.*, 331 (1962).
(33) K. Garbett and R. D. Gillard, *Coord. Chem. Rev.*, **1**, 179 (1966).

(I)   (II)

two enantiomers were found to be the more soluble isomers. This indicates that $(+)$-$Co(en)_3^{3+}$ and $(-)_{350}$-$Ru(en)_3^{3+}$ probably have the same absolute configuration.

In the crystallization of $(+)_{350}$-$[Ru(en)_3]I_3$ in $(\pm)$-$[Co(en)_3]I_3$, $(+)_{350}$-$Ru(en)_3^{3+}$ displaces $(-)$-$Co(en)_3^{3+}$ in the crystal. Similarly, $(-)$-$Co(en)_3^{3+}$ displaces $(+)_{350}$-$Ru(en)_3^{3+}$ in a crystal of $(\pm)_{350}$-$[Ru(en)_3]I_3$. These crystallization products appear to be true racemic compounds containing equal amounts of D and L isomers in one crystal, rather than racemic mixtures or racemic solid solutions,[34] from the constant ratio obtained for the maximum displacements in the circular dichroism spectrum, as described above. If there is a difference in the amount of water of hydration for the iodide salts of active and racemic $Co(en)_3^{3+}$ and $Ru(en)_3^{3+}$—those of $Co(en)_3^{3+}$ are monohydrates[19] while those of $Ru(en)_3^{3+}$ have not been carefully determined—it apparently does not prevent the formation of active racemates. Thus in the above co-crystallizations, the chirality of the displaced isomer is the same as that of the enantiomer replacing it and one can conclude that $(-)_{350}$-$Ru(en)_3^{3+}$ has the same enantiomorphic form as $(+)$-$Co(en)_3^{3+}$.

(34) A. M. Sargeson in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, p 215.

Also in accord with Delépine's method of active racemates[35] is the observation that the solubility of a mixture of $(-)$-$[Co(en)_3]I_3$ and $(-)_{350}$-$[Ru(en)_3]I_3$ is considerably less than that of a mixture of $(-)$-$[Co(en)_3]I_3$ and $(+)_{350}$-$[Ru(en)_3]I_3$. Since the iodide salt of the racemic complex is less soluble at room temperature than that of the active complex for both $Co(en)_3^{3+}$ and $Ru(en)_3^{3+}$, as can be seen from the data in Table II, one can infer that the solubility will be less for that mixture which contains both D and L metal complex ions, that is, one in which the $Ru(en)_3^{3+}$ isomer has the absolute configuration opposite that of $(-)$-$Co(en)_3^{3+}$. Thus, $(-)$-$Co(en)_3^{3+}$ and $(-)_{350}$-$Ru(en)_3^{3+}$ must have opposite configurations.

The absolute configuration of $(+)$-$Co(en)_3^{3+}$ is known to be the D configuration.[12] Since all of the above evidence indicates that $(+)$-$Co(en)_3^{3+}$ and $(-)_{350}$-$Ru(en)_3^{3+}$ have the same absolute configuration, $(-)_{350}$-$Ru(en)_3^{3+}$ must be L-$Ru(en)_3^{3+}$. Since $(-)_{375}$-$Ru(en)_3^{2+}$ and $(-)_{350}$-$Ru(en)_3^{3+}$ are related by electron-transfer reactions which are almost certainly outer sphere, they will have the same absolute configuration. Hence, $(-)_{375}$-$Ru(en)_3^{2+}$ also has the D configuration. This conclusion agrees with the assignment made above on the basis of the circular dichroism spectrum of $Ru(en)_3^{2+}$.

The resolution of $[Ru(en)_3]I_3$ permits further study of the d^5 trigonal complexes since the interconversion reactions between two dissymmetric tris(ethylenediamine)ruthenium complexes makes possible the assignment of the absolute configuration to a d^5 dissymmetric trigonal complex. We are presently studying the electron-transfer reaction between $Ru(en)_3^{3+}$ and $Ru(en)_3^{2+}$, using optical activity to follow the course of the reaction.

(35) M. Delépine, *Bull. Soc. Franc. Mineral.*, **53**, 73 (1930).