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Preparation, Properties, and Electronic Spectra of Coordination Compounds of Rhodium with Ethylenimine¹

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Twelve rhodium(III) complexes with ethylenimine of the types $[\text{RhAz}_3\text{X}_3]$, $[\text{RhAz}_4\text{X}_2]^+$, $[\text{RhAz}_5\text{X}]^{2+}$, $[\text{RhAz}_6]^{3+}$, $[\text{RhAz}_3(\text{H}_2\text{O})_2(\text{OH})]^{2+}$, and $[\text{Rh}(\text{NH}_3)_5\text{Az}]^{3+}$ (where X = halide and Az = ethylenimine) have been synthesized and isolated. Their general properties have been determined. The electronic spectra have been studied and term assignments have been made of the absorption bands. An unusual rhodium(I) compound $[\text{RhAz}_3\text{I}]$ was isolated and identified.

Coordination compounds of ethylenimine (aziridine) with uranium salts have been reported by Jones and co-workers.² More recently Jackson and Edwards³ reported inert complexes with Co(III), Cr(III), Pt(II), Pt(IV), and Pd(II). Labile complexes have also been prepared.⁴ Kiser and Lapp⁵ investigated the absorption spectra of nickel and cobalt complexes of ethylenimine.

We are reporting the preparation of a variety of rhodium complexes of ethylenimine and a tentative interpretation of their electronic spectra.

Experimental Section^{6,7}

Starting Materials.—Ethylenimine was obtained from the Chemirad Corp. It was stored over solid potassium hydroxide in a refrigerator and freshly distilled from sodium hydroxide previous to use; bp 55.5°.

Rhodium(III) chloride and bromide were obtained from the Fisher Scientific Co. or Johnson and Matthey. Chloropentamminerhodium(III) chloride and an aqueous solution (10%) of rhodium(III) nitrate were obtained from Engelhard Industries, Inc. Rhodium(III) iodide was prepared *via* the method described by Pascal.⁸

Trichlorotris(ethylenimine)rhodium(III), $[\text{RhAz}_3\text{Cl}_3]$, I.—An ice-cold solution of 2.0 g of rhodium(III) chloride trihydrate in 10 ml of anhydrous methanol was added dropwise with stirring to a cold solution of 3.7 g of ethylenimine in 6 ml of the same solvent. A tan precipitate which formed rapidly changed to bright yellow after a few minutes. After standing 5 hr in the refrigerator (with occasional shaking), the precipitate was removed by filtration, washed three times with 1 ml of cold methanol, once with 2 ml of anhydrous ether, and dried in a vacuum desiccator over potassium hydroxide pellets. The bright yellow product (0.5 g) was recrystallized from warm water for the analytical sample. The trichlorotris(ethylenimine)rhodium(III) is slightly soluble in cold water, moderately soluble in warm

water, dimethylformamide, and dimethyl sulfoxide, and insoluble in methanol, ethanol, acetone, ether, and tetrahydrofuran. *Anal.* Calcd for $\text{Rh}(\text{C}_2\text{H}_5\text{N})_3\text{Cl}_3$: C, 21.29; H, 4.48; N, 12.44. Found: C, 21.49; H, 4.70; N, 12.18.

Dichlorotetrakis(ethylenimine)rhodium(III) Chloride, $[\text{RhAz}_4\text{Cl}_2\text{Cl}]$, II, and Chloropentakis(ethylenimine)rhodium(III) Chloride, $[\text{RhAz}_5\text{Cl}]\text{Cl}_2$, III.—The filtrate from the preparation of I (above) was treated with anhydrous ether until the solution became hazy. After standing overnight in the refrigerator, the precipitate was separated by filtration and washed with three portions of 1 ml of ether. The precipitate was redissolved in 10 ml of methanol and fractionally crystallized by adding 10-ml portions of ether and allowing the solution to stand at 10° for 5 hr. The first fraction contained about 0.15 g of the tetraimine II and the third fraction contained about 0.05 g of the pentaamine III.

An alternate procedure to separate II and III was to evaporate the methanolic solution to dryness *in vacuo*, redissolve the solid mixture in a minimum of methanol, and remove the solvent slowly *in vacuo* at room temperature. The solid substance crystallizing during the evaporation was filtered from time to time, yielding several fractions. The first fraction contained tetraimine and the last one the pentaamine. Both compounds are bright yellow and are easily soluble in water, dimethyl sulfoxide, ethanol, and methanol but insoluble in ether.

Anal. Calcd for II, $\text{Rh}(\text{C}_2\text{H}_5\text{N})_4\text{Cl}_3$: C, 25.18; H, 5.28; N, 14.68; Cl, 27.89. Found: C, 25.11; H, 5.22; N, 14.46; Cl, 27.84.

Anal. Calcd for III, $\text{Rh}(\text{C}_2\text{H}_5\text{N})_5\text{Cl}_3$: C, 28.28; H, 5.95; N, 16.49. Found: C, 27.98; H, 6.22; N, 16.26.

Hexakis(ethylenimine)rhodium(III) Chloride, $[\text{RhAz}_6]\text{Cl}_3$, IV.—During the 1-week period that 0.5 g of I was allowed to stand in the refrigerator in an excess (2.0 g) of ethylenimine, the trimine dissolved and yellowish white crystals of the hexamine appeared on the bottom of the flask. Trituration with methanol removed excess ethylenimine plus some II and III which are by-products. The remaining impure hexamine was dissolved in water and reprecipitated with ethanol and ether. The final product was white, but the analysis suggests that some impurities contaminated IV. The yield was low (about 0.01 g). This preparation was difficult to reproduce. *Anal.* Calcd for $\text{Rh}(\text{C}_2\text{H}_5\text{N})_6\text{Cl}_3$: C, 30.81; H, 6.48; N, 17.97; Cl, 22.74. Found: C, 31.60; H, 7.23; N, 17.81; Cl, 22.45.

Dichlorotetrakis(ethylenimine)rhodium(III) Bromide, $[\text{RhAz}_4\text{Cl}_2\text{Br}]$, V.—A solution of 0.05 g of II in 2 ml of water was rubbed with 0.15 g of finely powdered potassium bromide. A yellow precipitate was separated after 1 hr, redissolved in water, and reprecipitated with ethanol and ether. The yellow analytical sample was washed with a few drops of ice-cold ethanol and ether, in turn, and dried *in vacuo* over potassium hydroxide. Yield: 0.04 g. *Anal.* Calcd for $\text{Rh}(\text{C}_2\text{H}_5\text{N})_4\text{Cl}_2\text{Br}$: C, 22.55; H, 4.73; N, 13.15; Cl, 16.63; Br, 18.75. Found: C, 22.55; H, 4.69; N, 13.07; Cl, 16.50; Br, 18.59.

In a similar manner, the iodide, $[\text{Rh}(\text{Az})_5\text{Cl}_2\text{I}]$, VI, was pre-

(1) Supported in part by Grants CA-07521 and CY-4813 from the U. S. Public Health Service.

(2) R. G. Jones, E. Bindschadler, D. Blume, G. Karmas, G. A. Martin, Jr., J. R. Thirtle, and H. Gilman, *J. Am. Chem. Soc.*, **78**, 6027 (1956).

(3) T. B. Jackson and J. O. Edwards, *Inorg. Chem.*, **1**, 398 (1962).

(4) T. B. Jackson and J. O. Edwards, *J. Am. Chem. Soc.*, **83**, 355 (1961).

(5) R. W. Kiser and T. W. Lapp, *Inorg. Chem.*, **1**, 401 (1962).

(6) Analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., or Alfred Bernhard Mikroanalytisches Laboratorium, Mülheim, Germany.

(7) Infrared spectra of solid mulls in Nujol were taken on a Perkin-Elmer grating spectrophotometer, Model 337, with sodium chloride plates. Electronic spectral data in the 200–800-m μ range were taken on a Bausch and Lomb Spectronic 505 using 1-cm quartz cells or on a Cary 14 recording spectrophotometer. The reflectance spectra were recorded on the reflectance attachment for the Cary, MgCO₃ being the standard.

(8) P. Pascal, "Nouveau Traité de Chimie Minérale," Vol. 19, Masson et Cie, Paris, 1958, p 330.

pared from the corresponding chloride, II. *Anal.* Calcd for $\text{Rh}(\text{C}_2\text{H}_5\text{N})_4\text{Cl}_2\text{I}$: C, 20.30; H, 4.26; N, 11.83. Found: C, 20.16; H, 4.26; N, 11.50.

Chloropentakis(ethylenimine)rhodium(III) Tetraiodomercurate(II), $[\text{RhAz}_5\text{Cl}][\text{HgI}_4]$, VII.—A solution of 0.03 g of III in 3 ml of water was treated with a solution of 0.06 g of potassium tetraiodomercurate in 2 ml of water. Immediately, a heavy, yellow precipitate formed. After 1 hr the colorless solution was filtered, and the precipitate was washed with water, ethanol, and ether, in turn, and dried *in vacuo*. Yield: 0.05 g. The compound is insoluble in water, methanol, ethanol, and acetone but is easily soluble in warm hydrochloric acid. *Anal.* Calcd for $\text{Rh}(\text{C}_2\text{H}_5\text{N})_5\text{ClHgI}_4$: C, 11.30; H, 2.35; N, 6.58. Found: C, 11.22; H, 2.20; N, 6.22.

Tribromotris(ethylenimine)rhodium(III), $[\text{RhAz}_3\text{Br}_3]$, VIII.—A solution of 0.15 g of I in 30 ml of water was heated on the steam bath for 6 hr with 10 ml of constant-boiling (48%) hydrobromic acid. Small additions of the acid finally put all of the original chloro compound into solution. The solution was concentrated to about 15 ml by evaporation on the steam bath. After cooling the reddish brown solution, red-orange crystals precipitated; these were filtered, washed with water, ethanol, and ether, in turn, and dried *in vacuo*. Yield: 0.14 g. VIII has a low solubility in water, methanol, ethanol, and acetone. *Anal.* Calcd for $\text{Rh}(\text{C}_2\text{H}_5\text{N})_3\text{Br}_3$: C, 15.28; H, 3.18; N, 8.92; Br, 50.82. Found: C, 15.36; H, 3.40; N, 8.82; Br, 51.03.

Dibromotetrakis(ethylenimine)rhodium(III) Bromide, $[\text{RhAz}_4\text{Br}_2]\text{Br}$, IX.—A cold solution of 0.5 g of rhodium(III) bromide in 3 ml of water was added dropwise to a cold solution of 0.37 g of ethylenimine in 2 ml of water. A dark brown precipitate formed at once; the reaction mixture was allowed to stand overnight in the refrigerator. The brown product was filtered, washed with ice water, and dried. Yield: 0.15 g. The analytical sample was prepared by recrystallizing from ethanol. *Anal.* Calcd for $\text{Rh}(\text{C}_2\text{H}_5\text{N})_4\text{Br}_3$: C, 18.67; H, 3.92; Br, 46.56. Found: C, 18.52; H, 3.89; Br, 46.67.

Diiodotetrakis(ethylenimine)rhodium(III) Iodide, $[\text{RhAz}_4\text{I}_2]\text{I}$, X.—Rhodium(III) iodide (0.8 g) was introduced into a solution of 1.6 g of ethylenimine in 10 ml of ethanol. The solution was heated at reflux for 1 hr at 60–70°. During the heating the solution became reddish brown, and a yellow-brown substance began to precipitate. The reaction mixture was left overnight at room temperature, then filtered, and the precipitate was washed with ethanol and ether, in turn, and dried *in vacuo*. X is slightly soluble in warm water, insoluble in methanol, ethanol, and ether. *Anal.* Calcd for $\text{Rh}(\text{C}_2\text{H}_5\text{N})_4\text{I}_3$: C, 14.65; H, 3.06; N, 8.55. Found: C, 14.92; H, 2.88; N, 8.54.

Hydroxodiaquotris(ethylenimine)rhodium(III) Tetraiodomercurate(II), $[\text{RhAz}_3(\text{H}_2\text{O})_2\text{OH}][\text{HgI}_4]$, XI.—I (0.3 g) was heated slowly in 20 ml of water to the boiling point in the presence of 1.0 g of silver oxide until the yellow salt was completely dissolved and then boiled 15 min longer. The greenish yellow filtrate after cooling was treated dropwise (with stirring) with aqueous potassium tetraiodomercurate(II). A greenish yellow precipitate was filtered, washed with water, methanol, and ether, and dried *in vacuo*. *Anal.* Calcd for $\text{Rh}(\text{C}_2\text{H}_5\text{N})_3\text{O}_3\text{H}_5\text{HgI}_4$: C, 7.25; H, 2.04; N, 4.22. Found: C, 7.80; H, 1.92; N, 4.05.

Iodotris(ethylenimine)rhodium(I), $[\text{RhAz}_3\text{I}]$, XII.—I (0.3 g) was treated with 1 g of silver oxide as previously described. To the greenish yellow solution obtained after filtration an excess of potassium iodide (nearly 5.0 g) was added. After warming on the steam bath, a dark brown substance precipitated; the length of time necessary to achieve precipitation depends on the amount of potassium iodide present and the concentration of the solution. This precipitation was filtered, washed with water by suction, and dried *in vacuo*. XII is insoluble in water but soluble in methanol and ethanol. *Anal.* Calcd for $\text{Rh}(\text{C}_2\text{H}_5\text{N})_3\text{I}$: C, 20.10; H, 4.19; N, 11.73. Found: C, 19.75; H, 3.97; N, 11.42.

Pentaamminoethyleniminerhodium(III) Chloride, $[\text{Rh}(\text{NH}_3)_5\text{-}$

Az]Cl₃, XIII.—One gram of chloropentaamminerhodium(III) chloride was dissolved in 25 ml of water at the boiling point. The filtered solution was refluxed with 8 ml of ethylenimine for 1 hr. The solution was cooled and diluted with methanol and ether to a volume of 200 ml. Upon standing at refrigerator temperature overnight, a white precipitate formed. This salt was dissolved in a minimum of warm water and reprecipitated with an excess of methanol and ether. The product was dried *in vacuo* for an analytical sample. In repeating the synthesis of XIII, in some cases the first precipitated product was yellowish due to the presence of some unreacted $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$; this impurity was eliminated by recrystallization. *Anal.* Calcd for $\text{RhC}_2\text{H}_{30}\text{N}_6\text{Cl}_3$: C, 7.12; H, 5.97; N, 24.90. Found: C, 6.27; H, 5.70; N, 24.40.

Many of the compounds described above tend to form oily products whose handling and purification are difficult. In order to avoid such products, freshly distilled ethylenimine was always used, and the amount of added precipitating agent—usually ether—was carefully measured. In most of the experiments the separation of oily substances could be avoided by adding the precipitating solvent at room temperature until the solution became hazy and then by placing the solution in the refrigerator for several hours or overnight. Under these conditions, the substances precipitated slowly, usually in filterable, nonoily form.

Results and Discussion

General Properties of Complexes.—The variety of coordination compounds formed by rhodium and other metals with ethylenimine exemplify the tendency of this imine to act as a typical monodentate ligand, resulting in compounds similar to the well-known ammine complexes.

By reaction of solutions of rhodium(III) chloride with an excess of ethylenimine, three products can be isolated; these are the triimine I, the tetraimine II, and the pentaamine III complexes. Working with ice-cold solutions of rhodium(III) chloride and ethylenimine, there resulted first a tan precipitate which was unstable and which changed after a short time to the yellow triimine. The analysis of the tan product indicated a composition intermediate between a triimine and a diimine. Presumably, it is a mixture of I and $[\text{RhAz}_2(\text{H}_2\text{O})\text{Cl}_3]$; the aquo complex is unstable and in the presence of free ethylenimine forms the less soluble triimine.

By reaction of a solution of $[\text{RhAz}_4\text{Cl}_2]\text{Cl}$ with an excess of potassium bromide or potassium iodide at room temperature, the ionic chloride is replaced by bromide or iodide whereas the coordinated chloride ions remain unaffected.

In the reaction between rhodium(III) chloride and ethylenimine in aqueous solution, the insoluble rhodium hydroxide does not form; the rhodium-chlorine bond must be quite inert and may also be strong, for only the coordinated water molecules are easily replaced by ethylenimine. The formation of complexes with greater imine content, which require displacement of chloride ions from the coordination sphere, takes place only slowly and in the presence of an excess of ethylenimine. On the other hand, treating an aqueous solution of rhodium(III) nitrate with ethylenimine results in immediate precipitation of the hydroxide.

Replacement of coordinated chloride by bromide ions takes place at higher temperature and with excess

bromide; the reaction is slow and requires several hours. In this way, $[\text{RhAz}_3\text{Br}_3]$ was prepared from I. The dibromotetraimine, $[\text{RhAz}_4\text{Br}_2]\text{Br}$, was obtained by direct reaction between rhodium(III) bromide and ethylenimine in alcoholic solution. In contrast to the chloro compound, the bromo compound is only slightly soluble in water. The iodo complex, $[\text{RhAz}_4\text{I}_2]\text{I}$, was prepared by the reaction of rhodium(III) iodide and ethylenimine.

An attempt to prepare an iodo derivative in the same manner as the bromo derivative, by reaction of I with hydriodic acid, resulted in a maroon, impure ethyleniminerhodium(I) complex. Presumably, the hydriodic acid is acting as a reducing agent. The pure complex $[\text{RhAz}_3\text{I}]$, XII, was obtained by the reaction of the hydroxyaquotris(ethylenimine)rhodium(III) complex with potassium iodide in aqueous solution on the steam bath. It is evident that the ethylenimine molecules remain coordinated to the rhodium atom during the reduction process. The unusual dark color of this compound is in keeping with the uncommon oxidation state of the rhodium atom. The ease of reduction of the ethyleniminerhodium(III) complexes to rhodium(I) complexes by iodide ions indicates that the oxidation-reduction potential of the Rh(I)-Rh(III) couple is close to the I^- - I_2 couple in this type of complex; this is surprising in view of the fact that ethylenimine would not be expected to act as a π -bonding ligand such as carbon monoxide or a phosphine which stabilizes rhodium(I).

The low solubility of the nonelectrolytes $[\text{RhAz}_3\text{Cl}_3]$ and $[\text{RhAz}_3\text{Br}_3]$ suggests a high lattice energy in the solid compounds. On the other hand, the relatively high solubility of the electrolytes, *e.g.*, II and III, in methanol and ethanol is noteworthy. For both the electrolyte and nonelectrolytes, the solubilities decrease with increasing mass of the halide. The anion HgI_4^{2-} also forms salts of low solubility.

In dilute aqueous solutions of halorhodium(III) compounds, aquation of the complex occurs on standing. The coordinated halide ions are slowly replaced by water molecules, presumably resulting in aquoimine complexes. These changes are reflected, among others, in the electronic spectra of the aqueous solutions (*vide infra*).

The replacement of coordinated halide ions by water molecules can be accelerated by warming the solution of the haloimine complex with silver oxide. Applying this well-known procedure to $[\text{RhAz}_3\text{Cl}_3]$ resulted in a mixture of aquoimine and hydroxyaquoimine complexes in solution, from which the salt $[\text{RhAz}_3(\text{H}_2\text{O})_2\text{OH}][\text{HgI}_4]$ could be isolated. The coordinated halide can be replaced also by other nucleophiles, *e.g.*, ammonia, upon warming a complex under reflux with aqueous ammonia solution. Analysis indicates that some of the coordinated ethylenimine is also replaced by ammonia. The data obtained here, along with previous studies,^{3,4} suggest that the order of bond strength to rhodium(III) is $\text{NH}_3 > \text{C}_2\text{H}_5\text{N} > \text{Cl}^- > \text{H}_2\text{O}$; for

example, ammonia can replace ethylenimine, but we have been unable to accomplish the reverse process.

Coordinated Ligand Reactions.—The compounds with a higher number (five or six) of coordinated ethylenimines were more difficult to isolate than are the corresponding ammine complexes, possibly as a result of the steric hindrance arising from the bulk of the ethylenimine molecule. Such an effect has also been observed in other ethylenimine complexes.³

On the other hand, the coordinated ethylenimine molecule exhibits a much higher ring stability than the free molecule toward acids and nucleophiles. Treating I (which is, of course, inert to ligand replacement) with a solution of hydrochloric acid does not result in ring opening of the coordinated ethylenimine. Similarly, treatment with hydriodic acid reduces the metal without concomitant ring opening. The retention of the ring structure is shown by the presence of the characteristic symmetric ring deformation band in the infrared spectra of the acid-treated compounds. In ethylenimine itself, the ring is easily broken by mineral acids,⁹ by weak organic acids,¹⁰ and particularly by acids in the presence of strong nucleophiles.¹¹ The stabilization of the ethylenimine ring in the complexes toward acids is presumably due to the coordinate saturation of the nitrogen atom; this precludes the addition of a proton to this imino nitrogen, a prelude to the ring-opening process. It is also evident that a metal ion when attached to the imino nitrogen does not exert a labilizing effect on ring opening to any extent comparable to an attached hydrogen ion.

The analysis of our infrared data, which were employed to identify the ring in the complexes, was based on other data.¹²⁻¹⁴ The presence of a strong band between 850 and 890 cm^{-1} in the compounds served as evidence, along with the analytical data, for the integrity of the ethylenimine ring. A more detailed study of the infrared spectra of ethylenimine complexes is being made.

Electronic Spectra.—An increase in the number of coordinated ethylenimine molecules in the complex is marked by a hypsochromic effect. For instance, in the series $[\text{RhAz}_x\text{Cl}_{6-x}]$, the triimine is bright yellow, the tetra- and pentaamine are pale yellow, and the hexaamine (like the ammonia complex) is white. For compounds with the same number of ethylenimine ligands, replacement of chloride by a heavier halide results in an intensification of visible color and a bathochromic effect. Both of these changes in color are reflected in corresponding shifts of the absorption bands in the electronic spectra of the compounds although low solubilities and the replacement problems mentioned above make it difficult to give quantitative significance to the visible effects.

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TABLE I
 ELECTRONIC SPECTRA OF RHODIUM(III) COMPLEXES IN WATER

Compd	Concn, M	$\bar{\nu}_{\max}$, cm^{-1}	ϵ_{\max}	Tentative term assignment
[RhAz ₃ Cl ₃]	2×10^{-4}	44,800	9,800	...
	2×10^{-3}	30,700 25,400	115 180	¹ T _{2g} ¹ T _{1g}
[RhAz ₄ Cl ₂]Cl	2×10^{-4}	44,800	9,700	...
	10^{-3}	34,800 29,400	410 250	¹ T _{2g}
		24,000	250	¹ T _{1g}
[RhAz ₄ Cl ₂]Br	5×10^{-4}	44,400	3,900	...
		35,200 29,800	400 170	¹ T _{2g}
		24,100	170	¹ T _{1g}
[RhAz ₄ Cl ₂]I	1.2×10^{-4}	43,900	16,100	...
	6×10^{-4}	34,700 29,800	616 400	¹ T _{2g}
		24,000	400	¹ T _{1g}
[RhAz ₅ Cl]Cl ₂	3×10^{-4}	45,200	6,300	...
		34,600	460	¹ T _{2g}
		30,300	340	¹ T _{1g}
		24,400	230	¹ T _{1g}
[RhAz ₃ Br ₃]	$\sim 10^{-4}$	44,800
		35,300	...	¹ T _{2g}
		23,900	...	¹ T _{1g}
[RhAz ₄ Br ₂]Br	2×10^{-4}	44,400	9,800	...
		34,500	$\sim 2,100$	¹ T _{2g}
[RhAz ₄ I ₂]I	$\sim 10^{-4}$	43,900
		35,600	...	¹ T _{2g}
		27,900	...	¹ T _{1g}
		20,500	...	³ T _{1g}
[Rh(NH ₃) ₅ Az]Cl ₃	10^{-3}	45,700	940	...
		30,900	370	¹ T _{1g}

Most of the discussions and interpretations of the absorption spectra of complexes containing metals with partly filled d shells have been concerned with the first transition series. Less work has been done with complexes containing elements with 4d and 5d electrons. Spin-orbit coupling becomes larger in these complexes and cannot be treated as an unimportant perturbation. The interpretation of the experimental results is, therefore, more difficult. Electronic spectra of rhodium compounds have been recorded and discussed by Jørgensen,¹⁵ by König and Schläfer,¹⁶ and by Schmidtke.¹⁷

The results on the electronic spectra of aqueous solutions at room temperature of our complexes are presented in Table I. Because of the low solubility of some of the compounds, it was not always possible to establish ϵ_{\max} , and in some cases the given values are approximations due to partial solvolysis during the dissolution of the complexes. We found that Beer's law was not exactly obeyed for the intense absorptions near 220 m μ (45,500 cm^{-1}). The extinction coefficient increased on dilution for several complexes. This is not the direction that would be expected on the basis of ion pairing. At the present time, we do not understand the reason for this change in extinction coefficient

with concentration. The d-d transitions were evaluated with saturated solutions owing to the relative weakness of the adsorption and the low solubilities.

The assignment of electronic bands observed for the complexes has been carried out in accordance with standard ligand field theory procedures;¹⁸ we used symmetry class O_h in these assignments. Most of our complexes have more than one type of ligand, and we have no data on configuration (*cis* or *trans*, etc.). Therefore, the treatment of these complexes as having octahedral symmetry is only an approximate one.

Rhodium(III) has an electronic configuration [Kr]-(4d⁶) where [Kr] represents the krypton kernel. The ground state of most octahedral rhodium(III) complexes is ¹A_{1g} from the closed subshell configuration (t_{2g})⁶; the next electron distribution, belonging to the configuration (t_{2g})⁵(e_g)¹, has four levels ³T_{1g}, ³T_{2g}, ¹T_{1g}, and ¹T_{2g}. Consequently, by electronic transitions from the ground state to the nearest excited states, there can result four bands. The transitions to the triplet levels are spin-forbidden and can generate only weak bands, though the spin-orbit interaction at transition elements with 4d electrons is approximately twice the interaction at elements with 3d electrons and the transitions become less improbable. The spin-forbidden transition ¹A_{1g} → ³T_{1g} has been reported by Jørgensen¹⁸ in the absorption spectra of [RhCl₆]³⁻, [Rh(C₂O₄)₃]³⁻, and [Rh(NH₃)₅Br]²⁺ in aqueous solutions. We find a similar transition in the spectra of [RhAz₃Cl₃] and [RhAz₄I₂]I. The other bands occurring in the region of 20,000–33,000 cm^{-1} with low molar extinction coefficients ($\epsilon_{\max} \sim 10^2$) are considered to be due to ¹A_{1g} → ¹T_{1g} and ¹A_{1g} → ¹T_{2g} transitions.

Besides the bands resulting from d-electron transitions, the electronic spectra of all ethylenimine rhodium(III) complexes present strong absorptions in the region 45,700 to 43,900 cm^{-1} (see Table I). In this spectral region, there is an ethylenimine absorption. Also, the extinction coefficients suggest that there are charge-transfer transitions from halide ligands to the rhodium. In some cases, e.g., for compounds containing unbound iodide ion, the absorption band for the hydrated anion should appear in the same region. In aqueous solutions of halo complexes, the value of ϵ_{\max} of this band slowly decreases with time, and λ_{\max} slowly shifts toward shorter wavelength. These changes are connected with the progressive aquation of the complex (replacement of coordinated halide with water) similar to that observed in the spectrum of [RhCl₆]³⁻ solutions;¹⁵ the kinetics of this process has recently been investigated.¹⁹

The results obtained for the reflectance spectrum and the absorption spectra in different solvents of [RhAz₃Cl₃] are given in Table II; the spectral data for aqueous solutions of this solute were given in Table I. Typical spectra are shown in Figure 1. The two bands assigned to singlet-singlet transitions are observed even in the spectra of dilute ($\sim 10^{-4} M$) solutions of [RhAz₃Cl₃]. A

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TABLE II
REFLECTANCE AND SOLUTION ABSORPTION SPECTRA OF $[\text{RhAz}_3\text{Cl}_3]$

Spectral source	Concn, M	$\bar{\nu}_{\text{max}}$, cm^{-1}	ϵ_{max}	Tentative assignment
Reflectance		30,100	...	${}^1\text{T}_{2g}$
		25,300	...	${}^1\text{T}_{1g}$
		19,600	...	${}^3\text{T}_{1g}$
Soln in DMF- CH_3OH (1:9)	2×10^{-4}	31,100	140	${}^1\text{T}_{2g}$
		25,800	240	${}^1\text{T}_{1g}$
Soln in DMF- CH_3OH (4:1)	2×10^{-3}	31,300	~ 200	${}^1\text{T}_{2g}$
		25,800	194	${}^1\text{T}_{1g}$

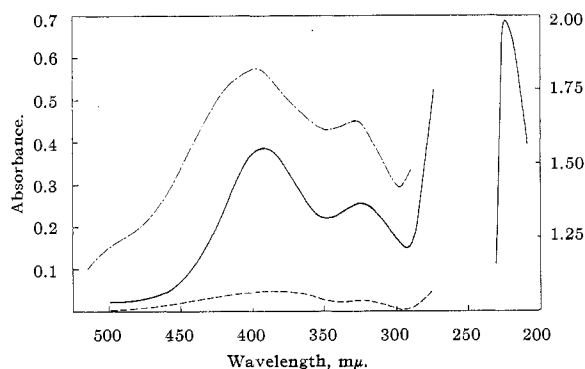


Figure 1.—Electronic absorption spectra of $[\text{RhAz}_3\text{Cl}_3]$: ····, reflectance spectrum; —, in H_2O ; ----, in DMF + CH_3OH (1:9).

weak band at about $19,600 \text{ cm}^{-1}$ which was assigned to a singlet-triplet transition could be observed only in the reflectance spectrum. The flat minimum (of $\epsilon \sim 100$) between the two singlet bands may indicate a slight splitting by asymmetric field effects or the existence of isomeric impurities. The absorption of DMF in the ultraviolet region makes difficult the detection of solute absorption bands in that region. Dilution of the DMF with methanol moved the solvent absorption to shorter wavelength and permitted spectral measurements on the solute complex in the visible and near-ultraviolet regions. Changes in the solvent nature (Tables I and II) influence the intensity but not the general position of the ligand-field bands.

Using the assignments for $[\text{RhAz}_3\text{Cl}_3]$ from reflectance data in Table II, it is possible to calculate the crystal-field-splitting parameter $10Dq$, the Racah electronic interaction parameter B , and the nephelauxetic ratio β (defined as $\beta = B_{\text{complex}}/B_{\text{Rh}^{3+}}$). Using the treatment for a low-spin octahedral d^6 complex,¹⁸ we find $10Dq$ equal to $28,100 \text{ cm}^{-1}$ and B equal to 300 cm^{-1} ; taking into account the subshell configuration interaction,²⁰ the corrected value of B is 296 cm^{-1} . The

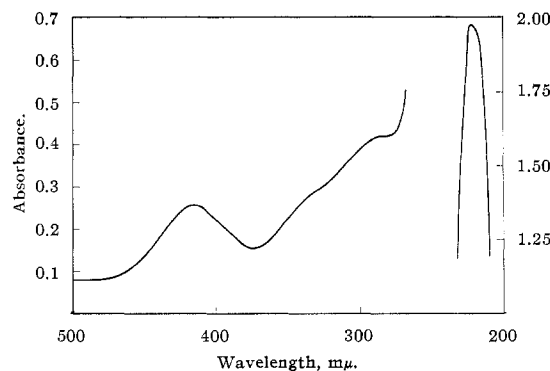


Figure 2.—Electronic absorption spectrum of $[\text{RhAz}_4\text{Cl}_2]\text{Cl}$ in aqueous solution at room temperature.

value of B for Rh^{3+} is 720 cm^{-1} ,²⁰ and consequently β is equal to 0.41.

The spectrum of an aqueous solution of $[\text{RhAz}_3\text{Br}_3]$ is similar to that of the corresponding chloride, but the larger energy difference between the two singlet transitions in the bromo complex indicates a higher value of B and a stronger electronic interaction of the central atom with the more polarizable bromine atom.

The spectra of dilute solutions of II (Figure 2) and III present many similarities to each other. Besides the strong band at $44,800 \text{ cm}^{-1}$, they show three ligand-field bands whose intensities suggest that they arise from singlet-singlet transitions. The presence of three peaks instead of two is possibly the result of splittings due to the difference of the two ligands in the same complex. It is not clear why the first transition (assigned ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$) which occurs in the region of $410 \text{ m}\mu$ has a lower energy than the corresponding transition in $[\text{RhAz}_3\text{Cl}_3]$.

In the spectrum of a dilute ($\sim 10^{-4} M$) aqueous solution of $[\text{RhAz}_4\text{Br}_2]\text{Br}$, only two absorption bands could be observed. The spectrum of $[\text{RhAz}_4\text{I}_2]\text{I}$ showed three bands aside from the intense high-energy band at $43,900 \text{ cm}^{-1}$; using the values of λ_{max} and the assignments given in Table I, we calculate that $10Dq$ equals $31,600 \text{ cm}^{-1}$, B equals 478 cm^{-1} (corrected B equals 474 cm^{-1}), and β equals 0.66 for this complex.

The relatively low value of ϵ_{max} for the high-energy band in the spectrum of $[\text{RhAz}(\text{NH}_3)_5]\text{Cl}_3$ is consistent with the absence of an intramolecular charge-transfer band (there being no halide ion in the coordination sphere). The breadth of this band at $45,700 \text{ cm}^{-1}$ suggests an intermixing of the ethylenimine absorption characteristic of this region with a d-d transition; the band at $30,900 \text{ cm}^{-1}$ is similar to the ligand-field bands observed with the other complexes.

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