

that suggested by Kray and Castro<sup>4</sup> for the analogous reactions of chromium(II) with vicinal dihalides. The higher rates observed for the vicinal dibromides com-

pared with monobromosuccinate are in line with similar differences found in the corresponding reactions of chromium(II).<sup>4</sup> No explanation is available for the markedly higher reactivity of *meso*- $\alpha,\beta$ -dibromosuccinate compared to the *dl* isomer, reflected in a difference of about 1.2 kcal./mole in  $\Delta H^*$ .

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## Deprotonation of Tris(ethylenediamine)rhodium(III) Iodide with Potassium Amide in Liquid Ammonia<sup>1,2</sup>

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*The interaction of tris(ethylenediamine)rhodium(III) iodide and potassium amide in liquid ammonia provides products in which protons are sequentially removed from the ligands. Of these, [Rh(en-H)(en)<sub>2</sub>]I<sub>2</sub> was isolated at -70°, and [Rh(en-H)<sub>2</sub>(en)]I and [Rh(en-H)<sub>3</sub>] were isolated at -33.5°. The infrared spectra of these and the parent complex were studied to examine the effect of deprotonation upon the nature of the metal ion-ligand bond.*

It is well established that ligands such as ethylenediamine and diethylenetriamine are sufficiently acidic to permit deprotonation in appreciably basic media.<sup>3-5</sup> Only little information, however, is thus far available as to the effect of deprotonation upon the nature of the interaction between the central metal ion and the ligand nitrogen atoms. It may be postulated that deprotonation should result in a drift of charge from the nitrogen atom toward the metal ion, thus increasing the bond order.

A comparison of the reactions of ethylenediamine complexes of Pt<sup>2+</sup>, Pd<sup>2+</sup>, Ir<sup>3+</sup>, and Os<sup>3+</sup> with solutions of potassium amide in liquid ammonia indicates that the acidic properties of the ethylenediamine ligands are enhanced by a high charge and small size of the central metal ion. The Rh<sup>3+</sup> cation affords a case in which the acidity of the ethylenediamine ligand is greater than in most of the other cases heretofore studied. Ac-

cordingly, a greater number of protons should be removable from the ethylenediamine ligands associated with Rh<sup>3+</sup>.

Since studies of the ultraviolet and visible spectra of complexes of this type have been impeded by the lack of a solvent, it was decided to investigate the infrared spectra of the solids isolated as described herein for clues to the nature of the bonding involved. Specifically, shifts in positions of infrared absorption bands should indicate changes in energy for significant atomic vibrational motions.

### Experimental Section

The equipment and procedures for reactions in liquid ammonia were the same as described elsewhere.<sup>6</sup>

Rhodium was determined by reduction to the metal in a hydrogen atmosphere at 750°. Iodine was determined by the method of Kolthoff and Stenger.<sup>7</sup> Carbon and hydrogen determinations were performed with a Coleman Model 33 carbon-hydrogen analyzer; and nitrogen was determined with a Coleman Model 29 nitrogen analyzer.

Infrared spectra were obtained with a Beckman IR-7 with CsI interchange optics. Spectra in the region from 700 to 4000 cm.<sup>-1</sup> were taken as mulls in Nujol or perfluorokerosene on NaCl plates. Spectra in the 200- to 700-cm.<sup>-1</sup> region were taken as Nujol mulls on either CsBr plates or strips of Handi-Wrap.

*Tris(ethylenediamine)rhodium(III) Iodide.* The methods for preparation of [Rh(en)<sub>3</sub>]<sup>3+</sup> salts reported by Werner<sup>8</sup> and Jaeger<sup>9</sup> gave products that were of low

(1) This work was supported by the Robert A. Welch Foundation and the U. S. Atomic Energy Commission.

(2) The notation (en-H) indicates an ethylenediamine ligand from which a proton has been abstracted.

(3) B. P. Block and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **73**, 4722 (1951).

(4) F. P. Dwyer and J. W. Hogarth, *ibid.*, **75**, 1008 (1953).

(5) G. W. Watt, *et al.*, *ibid.*, **79**, 5163 (1957); **81**, 8 (1959); **82**, 4465 (1960); *Inorg. Chem.*, **1**, 6 (1962); **4**, 143 (1965).

(6) G. W. Watt, *et al.*, *J. Inorg. Nucl. Chem.*, **9**, 311 (1959); *J. Electrochem. Soc.*, **98**, 1 (1951); **102**, 46, 454 (1955).

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

(8) A. Werner, *Ber.*, **45**, 1228 (1912).

(9) F. M. Jaeger, *Proc. Acad. Sci. Amsterdam*, **20**, 244 (1917).

yield and purity. Hence, the following method, which has given consistently good results, was devised for the synthesis of  $[\text{Rh}(\text{en})_3]\text{I}_3$ .

A 10-ml. portion of 98% ethylenediamine was slowly added at 25° to 3.03 g. of  $\text{RhCl}_3$  contained in a 250-ml. flask. The mixture was heated over a steam bath with constant stirring, and two more 10-ml. portions of 98% ethylenediamine were added slowly. When white crystals began to form in the flask, the flask and contents were allowed to cool, and an excess of isopropyl alcohol was added; the white solid was filtered under reduced pressure, washed with ten 10-ml. portions of isopropyl alcohol, and dried in air at 100°. The dry solid was dissolved in 25 ml. of water, and 20 g. of finely ground KI was added. The mixture was allowed to stand overnight, 95% ethyl alcohol was added, and this product was filtered and recrystallized from water containing excess KI. The crystals were filtered off, washed with ten 20-ml. portions of ethyl alcohol, and dried *in vacuo* at 110° for 24 hr.

*Anal.* Calcd. for  $[\text{Rh}(\text{en})_3]\text{I}_3$ : Rh, 15.5; I, 57.3; C, 10.8; H, 3.6. Found: Rh, 15.5; I, 57.6; C, 10.8; H, 3.6.

The yield was 48% based on  $\text{RhCl}_3$ . The X-ray *d* spacings and infrared spectrum are given in Table I and Figure 1, respectively. The iodide was found to be diamagnetic.

**Table I.** X-Ray Diffraction Data for  $[\text{Rh}(\text{en})_3]\text{I}_3$  and the Ammonia-Insoluble Products of Reactions of  $[\text{Rh}(\text{en})_3]\text{I}_3$  with  $\text{KNH}_2^a$

$[\text{Rh}(\text{en})_3]\text{I}_3$		$[\text{Rh}(\text{en-H})(\text{en})_2]\text{I}_2$	
<i>d</i> , Å.	<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> , Å.	<i>I</i> / <i>I</i> <sub>0</sub>
7.08	0.7	7.07	0.2
5.18	0.8	4.50	0.2
4.39	1.0	4.27	1.0
4.11	0.9	3.45	0.5
3.89	0.5 <sup>b</sup>	3.12	0.2 <sup>b</sup>
3.64	0.8		
3.53	1.0		
$[\text{Rh}(\text{en-H})_2(\text{en})]\text{I}$		$[\text{Rh}(\text{en-H})_3]$	
<i>d</i> , Å.	<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> , Å.	<i>I</i> / <i>I</i> <sub>0</sub>
6.28	1.0	8.97	0.8
5.15	0.8	7.61	0.9
4.84	0.8	6.10	1.0
4.50	0.8	4.17	0.5
3.72	1.0	3.31	0.4 <sup>b</sup>
2.97	0.9	2.93	0.5
2.78	0.8		
2.23	0.8 <sup>b</sup>		

<sup>a</sup> All X-ray diffraction data were obtained using Cu K $\alpha$  radiation (Ni filter), 35-kv. tube voltage, 15-ma. filament current, and 10–18-hr. exposure times. Relative intensities were estimated visually.

<sup>b</sup> Less intense lines not included here.

*Preliminary Experiments.* To determine whether  $[\text{Rh}(\text{en})_3]\text{I}_3$  undergoes reaction with liquid ammonia, ca. 0.1 g. of the salt was placed in a small reaction vessel<sup>10</sup> and ca. 40 ml. of ammonia was condensed on the solid. The  $[\text{Rh}(\text{en})_3]\text{I}_3$  was suspended in ammonia by continuous stirring for 6 hr. The ammonia was evaporated and the residual solid was dried *in vacuo* for 24

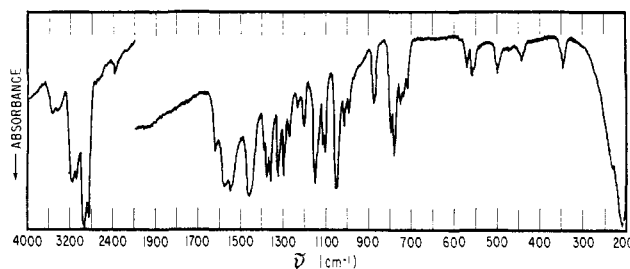


Figure 1. The infrared spectrum of  $[\text{Rh}(\text{en})_3]\text{I}_3$ .

hr. An X-ray diffraction pattern of the solid remaining after these operations led to data identical with those reported for  $[\text{Rh}(\text{en})_3]\text{I}_3$  in Table I.

*Potentiometric Titration of  $[\text{Rh}(\text{en})_3]\text{I}_3$  with  $\text{KNH}_2$ .* To investigate the effect of  $\text{KNH}_2$  on ammonia solutions of  $[\text{Rh}(\text{en})_3]\text{I}_3$ , 0.0634 g. of the salt was suspended in 50 ml. of ammonia and titrated with the  $\text{KNH}_2$  equivalent to 0.0191 g. of K dissolved in 18.2 ml. of ammonia. Potential measurements were made after the addition of each 0.2-ml. portion of the amide solution until all of the titrant had been consumed. The initial solution had a cloudy white appearance but cleared to a pale green after the addition of approximately 1 molar equiv. of  $\text{KNH}_2$ . When more than 1 equiv. had been added, the solution assumed a cloudy yellow color and a precipitate began to form; after approximately 5 equiv. of  $\text{KNH}_2$  had been added, a localized orange color appeared upon addition of each increment of titrant.

The calculated amounts of  $\text{KNH}_2$  are 4.1, 8.2, 12.3, and 16.4 ml. for 1, 2, 3, and 4 equiv., respectively. Inflections were observed in the curve drawn from the data at approximately 4.5, 9.2, 12.3, and 14.8 ml. of titrant.

Subsequently a titration was performed in which 0.7859 g. of  $[\text{Rh}(\text{en})_3]\text{I}_3$  was treated with 7 equiv. of  $\text{KNH}_2$  prepared from 0.3191 g. of K in 12.6 ml. of liquid ammonia. The same changes were observed up to 5 equiv. as described above. At 5 equiv. of  $\text{KNH}_2$  a localized orange color began to develop, but the quantity of precipitate decreased. With the addition of more  $\text{KNH}_2$  the precipitate redissolved completely and the solution became clear bright orange in color. At 7 equiv. of  $\text{KNH}_2$  the solution became dark red-brown and viscous. The viscous solution was cooled to  $-70^\circ$  by removal of the ammonia refrigerant bath and replacement with a bath of Dry Ice and isopropyl alcohol. After 10 hr. of stirring, the reaction product was still viscous and red-brown; there was no evidence of further reaction or precipitation.

*Reaction of  $[\text{Rh}(\text{en})_3]\text{I}_3$  with  $\text{KNH}_2$  (1:1) at  $-33.5^\circ$ .* This reaction was carried out by treating 1.5430 g. of  $[\text{Rh}(\text{en})_3]\text{I}_3$  (2.32 mmoles) dissolved and suspended in 50 ml. of liquid ammonia with 12.0 ml. of a 0.194 M  $\text{KNH}_2$  solution (2.33 mmoles). A clear, pale green solution resulted.

*Reaction of  $[\text{Rh}(\text{en})_3]\text{I}_3$  with  $\text{KNH}_2$  (1:1) at  $-70^\circ$ .* Since the product of the (1:1) reaction was found to be soluble at  $-33.5^\circ$ , the reaction was carried out at  $-70^\circ$ . Accordingly, 0.9846 g. of  $[\text{Rh}(\text{en})_3]\text{I}_3$  (1.48 mmoles) in ammonia was treated with 10 ml. of a 0.148 M  $\text{KNH}_2$  solution (1.48 mmoles). A white precipitate

(10) W. C. McMordie, Dissertation, The University of Texas, 1963.

**Table II.** Infrared Spectra of  $[\text{Rh}(\text{en})_3]\text{I}_3$  and Products of Its Reactions with  $\text{KNH}_2$ 

$[\text{Rh}(\text{en})_3]\text{I}_3$	$[\text{Rh}(\text{en}-\text{H})-(\text{en})_2]\text{I}_2$	$[\text{Rh}(\text{en}-\text{H})_2-(\text{en})]\text{I}$	$[\text{Rh}(\text{en}-\text{H})_3]$	N-H/N-D <sup>a</sup>	Tentative assignments
3190 (s)	3150 (w)	3200 (s)	3150 (vw)	1.39	N-H stretch
3080 (s)	3150 (w)				
2950 (w, sh)	b	2950 (w, sh)	2950 (w, sh)	...	C-H stretch
1620 (m)	...	...	...	1.38	Water
1580 (s)	1565 (s)	1587 (s)	1590 (s)	1.38	NH <sub>2</sub> bend
1550 (s)	...	...	...	...	NH <sub>2</sub> bend
1458 (s)	b	1460 (w)	1458 (m)	...	CH <sub>2</sub> bend
1362 (m)	1367 (w, sh)	...	...	...	CH <sub>2</sub> wag
1328 (m)	1324 (w)	1320 (vw)	...	1.40	NH <sub>2</sub> wag
1300 (m)	1295 (w)	1300 (w)	1300 (w)	...	CH <sub>2</sub> twist
1275 (w)	1275 (w)	1260 (m)	1260 (m)	...	CH <sub>2</sub> twist
1208 (w)	1208 (vw)	...	...	1.39	NH <sub>2</sub> wag
1152 (s)	1141 (s)	1158 (m)	1160-90 (w)	1.40	NH <sub>2</sub> twist or wag
1119 (s)	1112 (w)			1.39	NH <sub>2</sub> twist
1110					
1058 (s)		1058 (s)	1055 (s)	...	C-N stretch
1051	1051 (s)				
1021 (vw)	1020 (vw)	1018 (vw)	1019 (vw)	...	C-C stretch
999 (vw)	997 (vw)	...	...	...	NH <sub>2</sub> twist
879 (m)	878 (w)	880 (w)	880 (w)	...	CH <sub>2</sub> rock
800 (s)	800 (w)	...	...	1.23	NH <sub>2</sub> rock
780 (s)	780 (w)	...	...	1.24	NH <sub>2</sub> rock
750 (w)	...	...	...	1.25	?
740 (w)	...	...	...	...	?
570 (w)	572 (w)	582 (w)	585 (w)	...	Rh-N stretch
558 (w)	...	...	...	...	Rh-N stretch
499 (w)	500 (w)	510 (w)	511 (w)	...	Skeletal vib.
444 (w)	450 (w)	455 (w)	455 (w)	...	Skeletal vib.
348 (w)	359 (w)	375 (w)	385 (vw)	...	Skeletal vib.
	352 (w)				
...	...	275 (w, sh)	310 (w)	...	Skeletal vib.

<sup>a</sup>  $[\text{Rh}(\text{en})_3]\text{I}_3$  was deuterated by heating it with excess 99.7%  $\text{D}_2\text{O}$  on a steam bath for 2 hr., followed by drying over  $\text{Mg}(\text{ClO}_4)_2$  *in vacuo*.

<sup>b</sup> Bands for C-H motions at *ca.* 2950 and 1460  $\text{cm}^{-1}$  were observed in perfluorokerosene mulls; the spectra for the 1-equiv. product was not observed in perfluorokerosene, but the bands in these regions were assumed to be present.

formed almost immediately; it was washed four times with 40-ml. portions of ammonia and transferred to the drybox after drying *in vacuo* for 12 hr. X-Ray diffraction data and infrared data for this product are shown in Tables I and II, respectively. This product was diamagnetic at 25°.

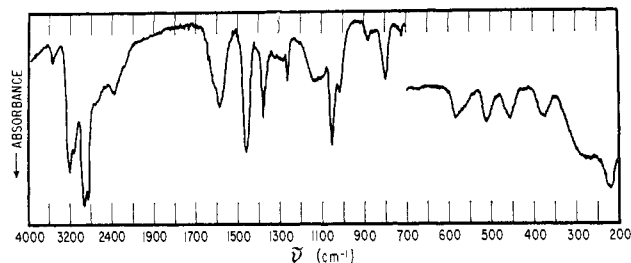


Figure 2. The infrared spectrum of  $[\text{Rh}(\text{en}-\text{H})_2(\text{en})]\text{I}$ .

*Anal.* Calcd. for  $[\text{Rh}(\text{en}-\text{H})(\text{en})_2]\text{I}_2$ : Rh, 19.2; I, 47.4; H, 4.3. Found: Rh, 18.3; I, 48.2; H, 4.1.

*Reaction of  $[\text{Rh}(\text{en})_3]\text{I}_3$  with  $\text{KNH}_2$  (1:2) at -33.5°.* This reaction was carried out with 1.8085 g. of  $[\text{Rh}(\text{en})_3]\text{I}_3$  (2.72 mmoles) in 50 ml. of liquid ammonia, by titrating dropwise with 5.4 ml. of a 1.01 M solution of  $\text{KNH}_2$  (5.45 mmoles). The supernatant solution was transferred to a trap and the pale yellow, insoluble product was washed with five 50-ml. portions of am-

monia and dried *in vacuo* for 6 hr. The reactor was transferred to the drybox for sampling. The bulk of the product was stored in an air-tight desiccator, in which it appeared to be stable indefinitely.

*Anal.* Calcd. for  $[\text{Rh}(\text{en}-\text{H})_2(\text{en})]\text{I}$ : Rh, 25.2; H, 5.4. Found: Rh, 25.6; H, 5.3.

The product was found to be diamagnetic at 25°. X-Ray diffraction data are given in Table I, and the infrared data are given in Table II and Figure 2.

In an identical experiment, a 1.4381-g. sample of  $[\text{Rh}(\text{en})_3]\text{I}_3$  (2.17 mmoles) in ammonia was titrated with 5.2 ml. of 0.828 M  $\text{KNH}_2$  solution (4.30 mmoles). The combined filtrate and washings were found to contain 0.548 g. of iodine, or 100% of that which should be recovered as KI in the trap if  $[\text{Rh}(\text{en}-\text{H})_2(\text{en})]\text{I}$  is a product of the reaction.

Because of the similarity of elemental compositions of the compounds  $[\text{Rh}(\text{en}-\text{H})_2(\text{en})]\text{I}$  and  $[\text{Rh}(\text{en})_2(\text{NH}_2)_2]\text{I}$ , further experiments were conducted to establish that the latter was not formed as a product of the reaction. A run similar to those just described was performed and the filtrate and washings were carefully collected to preserve any free ethylenediamine which would result from ligand substitution. The ammonia-soluble products of the reaction were transferred to the trap, and the solvent ammonia was removed under reduced pressure. The ammonia-soluble material was dissolved in anhydrous ether and treated with a saturated alcoholic solution of picric acid. The solution was concentrated on a steam bath for 30 min., but a precipitate of ethylenediamine picrate was not obtained.

The deprotonated product,  $[\text{Rh}(\text{en-H})_2(\text{en})]\text{I}$ , dissolved in water to form a clear, light yellow basic solution.

To establish regeneration of the starting material *via* an acid-base reaction, a 0.2594-g. sample was suspended in ammonia and titrated with a solution of 0.1845 g. of  $\text{NH}_4\text{I}$  in 8.2 ml. of ammonia (mole ratio 1:2). The pale yellow solid product was separated by filtration, washed with four 30-ml. portions of liquid ammonia, and dried *in vacuo* for 12 hr. The X-ray data showed that this product was identical with  $[\text{Rh}(\text{en})_3]\text{I}_3$ .

*Anal.* Calcd. for  $[\text{Rh}(\text{en})_3]\text{I}_3$ : Rh, 15.5; I, 57.3. Found: Rh, 15.1; I, 57.8.

*Reaction of  $[\text{Rh}(\text{en})_3]\text{I}_3$  with  $\text{KNH}_2$  (1:3) at  $-33.5^\circ$ .* This reaction was carried out with 1.4012 g. of  $[\text{Rh}(\text{en})_3]\text{I}_3$  (2.11 mmoles) in 50 ml. of anhydrous ammonia, by titrating with 16.6 ml. of 0.395 M  $\text{KNH}_2$  solution (6.55 mmoles). The ammonia-soluble material from the reaction was transferred to the trap for further analysis. The yellow, insoluble material was washed five times with 40-ml. portions of ammonia, dried *in vacuo*, and transferred to the drybox. This material, unlike that prepared in the 1:2 titration, absorbed moisture immediately on exposure to air and began to turn black when exposed to air even for short periods of time. The product appeared to be stable in a helium atmosphere.

*Anal.* Calcd. for  $[\text{Rh}(\text{en-H})_3]$ : Rh, 36.7; N, 30.0; C, 25.7; H, 7.6. Found: Rh, 36.7; N, 29.8; C, 25.6; H, 7.7.

X-Ray and infrared data for this compound are given in Tables I and II, respectively. The product was found to be diamagnetic at  $25^\circ$ ; it dissolved rapidly in water to give a colorless basic solution.

To establish reversion to the starting material, a 0.0903-g. sample of  $[\text{Rh}(\text{en-H})_3]$  in 50 ml. of liquid ammonia was titrated with 0.1416 g. (slightly  $>3$  molar equiv.) of  $\text{NH}_4\text{I}$  dissolved in 10 ml. of liquid ammonia. A pale yellow solid remained after evaporation of the solvent.

*Anal.* Calcd. for  $[\text{Rh}(\text{en})_3]\text{I}_3$ : Rh, 15.5; I, 57.3. Found: Rh, 15.7; I, 58.1.

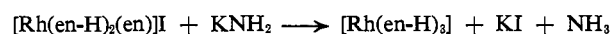
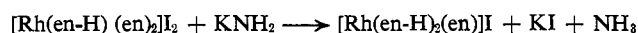
In a similar and closely related experiment, 0.352 g. of  $[\text{Rh}(\text{en})_3]\text{I}_3$  (0.53 mmole) in liquid ammonia was titrated with 10 ml. of 0.16 M  $\text{KNH}_2$  (1.60 mmoles); the usual color changes accompanying the addition of 1, 2, and 3 equiv. of  $\text{KNH}_2$  were observed. The yellow product formed with 3 equiv. of  $\text{KNH}_2$  was washed four times with 30-ml. portions of ammonia, then resuspended in 50 ml. of ammonia. A 0.258-g. sample of  $\text{NH}_4\text{I}$  was dissolved in 10 ml. of ammonia and slowly added to the suspended material. The expected color changes were observed corresponding to the formation of  $[\text{Rh}(\text{en-H})_2(\text{en})]\text{I}$  and  $[\text{Rh}(\text{en-H})(\text{en})_2]\text{I}_2$ , and a white solid product was obtained when 3 equiv. of  $\text{NH}_4\text{I}$  had been added. This solid was dried *in vacuo* and removed from the reactor. An X-ray diffraction pattern provided data identical with those reported for  $[\text{Rh}(\text{en})_3]\text{I}_3$  (Table I).

The solid residue remaining after evaporation of the solvent from the combined filtrate and washings from the foregoing reaction was dissolved in 500 ml. of water, and a 100-ml. aliquot was treated with 0.1 N  $\text{AgNO}_3$  to precipitate  $\text{AgI}$ . This yielded 0.153 g. of iodine, which is 100% of that introduced as  $[\text{Rh}(\text{en})_3]\text{I}_3$ .

*Reaction of  $[\text{Rh}(\text{en})_3]\text{I}_3$  with  $\text{KNH}_2$  (1:5) at  $-33.5^\circ$ .* A sample of 1.0489 g. of  $[\text{Rh}(\text{en})_3]\text{I}_3$  (1.58 mmoles) in 50 ml. of ammonia was treated with 12.0 ml. of 0.725 M  $\text{KNH}_2$  solution (8.7 mmoles). The ammonia-soluble portion of the reaction mixture was transferred to the trap under reduced pressure. The ammonia-insoluble product was washed five times with 30-ml. portions of ammonia and dried *in vacuo* for 24 hr. The reactor was placed in the drybox for sampling. An X-ray diffraction pattern of the yellow product established that it was identical with the material isolated after adding 3 equiv. of  $\text{KNH}_2$  in ammonia (Table I).

## Discussion

It has been established that  $[\text{Rh}(\text{en})_3]\text{I}_3$  reacts with amide ion in liquid ammonia as shown in the following series of reactions. The deprotonated products have



been isolated and characterized, and it has been demonstrated that each of these basic species can be reconverted to  $[\text{Rh}(\text{en})_3]\text{I}_3$  by treatment with ammonium iodide (an acid in liquid ammonia). Thus, for the first time, all products of successive deprotonation reactions have been isolated and this permits study of the effect of gradual changes in properties. Accordingly, a study was made of the infrared spectra of the sequence  $[\text{Rh}(\text{en})_3]\text{I}_3$ ,  $[\text{Rh}(\text{en-H})(\text{en})_2]\text{I}_2$ ,  $[\text{Rh}(\text{en-H})_2(\text{en})]\text{I}$ , and  $[\text{Rh}(\text{en-H})_3]$ .

To understand better the effects of deprotonation on the infrared spectrum of  $[\text{Rh}(\text{en})_3]\text{I}_3$ , it was necessary to make partial assignments of absorption bands for the various motions of the molecule. In the absence of theoretical calculations, this has been done by: (1) study of the infrared spectrum of deuterated  $[\text{Rh}(\text{en})_3]\text{I}_3$ , and (2) comparison with the assignments for motions in similar compounds.

The  $\text{NH}_2$  stretching region in ammine complexes has been well characterized.<sup>11-13</sup> For  $[\text{Rh}(\text{en})_3]\text{I}_3$  the broad band centered at *ca.* 3190  $\text{cm}^{-1}$  shifted on deuteration to 2300  $\text{cm}^{-1}$  ( $\text{N-H/N-D} = 1.39$ ). The same shift was observed for  $\text{NH}_2$  stretching vibrations in the analogous  $[\text{Co}(\text{en})_3]\text{I}_3$  ( $\text{N-H/N-D} = 1.35$ ).<sup>13</sup> Therefore, the absorption in the infrared spectrum of  $[\text{Rh}(\text{en})_3]\text{I}_3$  at *ca.* 3200  $\text{cm}^{-1}$  can be assigned with confidence to the  $\text{NH}_2$  stretching vibrations.

The  $\text{NH}_2$  bending modes have been assigned at *ca.* 1600  $\text{cm}^{-1}$  for most metal amines.<sup>12-15</sup> In this study,  $[\text{Rh}(\text{en})_3]\text{I}_3$  exhibited absorption at 1500 and 1580  $\text{cm}^{-1}$  which shifted on deuteration to 1145 and 1172  $\text{cm}^{-1}$ , respectively ( $\text{N-H/N-D} = 1.35$ ). The absorptions at 1550 and 1580  $\text{cm}^{-1}$  are therefore attributed to  $\text{NH}_2$  bending modes.

In the spectrum of  $[\text{Rh}(\text{en})_3]\text{I}_3$  absorption bands occur at 1328, 1208, and 1152, and a doublet at 1119-1110

(11) A. Sabatini and S. Califano, *Spectrochim. Acta*, **16**, 677 (1960).

(12) L. Sacconi and A. Sabatini, *J. Inorg. Nucl. Chem.*, **25**, 1389 (1963).

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

cm.<sup>-1</sup>. All of these bands shift to lower frequencies on deuteration by a factor of *ca.* 1.39. From assignments that have been made for other ammine complexes, it appears fairly certain that all of these correspond to NH<sub>2</sub> wagging or twisting motions. In the absence of calculations on the number of each type of motion that is allowed by selection rules, it is difficult to distinguish between the wagging and twisting motions in this region. In studies on hydrazine complexes<sup>12</sup> and bis(ethylenediamine) complexes,<sup>14,15</sup> the wagging motions were assigned at higher frequencies than the twisting motions, so we might assume the same order prevails here. A true distinction between wagging and twisting motions is not germane to this study, so we arbitrarily assign the wagging motions at the higher frequencies.

Absorption bands in the spectrum of [Rh(en)<sub>3</sub>]I<sub>3</sub> at 800, 780, and 750 cm.<sup>-1</sup> in the NaCl region shift on deuteration to 652, 631, and 597 cm.<sup>-1</sup> in the CsI region. Other workers have assigned motions in this region to NH<sub>2</sub> rocking modes. Studies on Rh<sup>3+</sup> ethylenediamine complexes with (PtCl<sub>4</sub>)<sup>2-</sup> as the anion have shown NH<sub>2</sub> rocking modes at 783 and 773 cm.<sup>-1</sup>.<sup>16</sup> It seems reasonable, therefore, to assign the two bands at 800 and 780 cm.<sup>-1</sup> to NH<sub>2</sub> rocking motions, and the band at 750 cm.<sup>-1</sup> to a NH<sub>2</sub> motion of unknown origin (perhaps also a rocking motion).

Certain vibrational motions were unaffected or changed only slightly on deprotonation; the C-C, C-N, and C-H stretching motions and the CH<sub>2</sub> bending, twisting, and rocking motions are cases in point. This is not surprising since the bonds to the carbon atoms should be less affected by deprotonation than the bonds to nitrogen atoms. Accordingly the former are not discussed here except for the assignments included in Table II, from which several shifts attributable to coupling with NH<sub>2</sub> vibrations are evident. For example, the CH<sub>2</sub> wagging motion (at 1362 cm.<sup>-1</sup> in [Rh(en)<sub>3</sub>]I<sub>3</sub>)

(14) D. S. Klett, Dissertation, The University of Texas, 1963.

(15) G. W. Watt and D. S. Klett, *Spectrochim. Acta*, **20**, 1053 (1964).

(16) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 1112 (1961).

shifted *ca.* 14 cm.<sup>-1</sup> on deuteration and was not observed in the spectra of the deprotonated complexes.

The region of the metal-nitrogen stretching mode has been fairly well established by prior work. Powell and Sheppard<sup>16</sup> assigned the Rh-N stretching frequency in Rh<sup>3+</sup> ethylenediamine complexes at 580 cm.<sup>-1</sup>. Klett<sup>14</sup> assigned M-N stretching modes at 571 and 508 cm.<sup>-1</sup> for [Pd(en)<sub>2</sub>]I<sub>2</sub> and at 579 and 537 cm.<sup>-1</sup> for [Pt(en)<sub>2</sub>]I<sub>2</sub>. It is therefore reasonable to assign the two bands at 570 and 558 cm.<sup>-1</sup> as Rh-N stretching motions for [Rh(en)<sub>2</sub>]I<sub>2</sub>. All of the deprotonated species show medium absorptions in the 570-585-cm.<sup>-1</sup> region.

Of particular interest in the spectra of compounds isolated from the reactions of [Rh(en)<sub>3</sub>]I<sub>3</sub> with 1, 2, and 3 molar equiv. of KNH<sub>2</sub> is the effect of deprotonation on the metal-nitrogen stretching frequency. As expected, a more energetic vibrational motion was detected with successive deprotonation. This indicates a transfer, in the direction of the metal, of charge remaining on the coordinated amino nitrogen of the ethylenediamine ligand after removal of the proton. The larger increment of change for the Rh-H stretching motions between the singly and doubly deprotonated species could indicate removal of both protons from the same ligand.

It seems remarkable that most of the nitrogen-hydrogen vibrational motions gradually disappear from the spectrum as deprotonation proceeds. This is true of most of the NH<sub>2</sub> wagging, bending, twisting, and rocking motions. The bands for one NH<sub>2</sub> bending and one NH<sub>2</sub> twisting motion moved to higher energies on deprotonation, but the bands steadily decreased in intensity. These observations indicate a decreased effect of NH<sub>2</sub> vibrations in the complex as deprotonation proceeds. The NH<sub>2</sub> stretching modes are not discussed here because of the poor resolution of these bands.

Finally, we wish to report that diamagnetic Rh(en-H)<sub>3</sub> can be further deprotonated to provide a product that is paramagnetic.<sup>17</sup>

(17) G. W. Watt, J. K. Crum, and J. T. Summers, *J. Am. Chem. Soc.* **87**, 4641 (1965).