

on the basis of a simple perturbation of the T_d model are of only limited usefulness.

Another feature of the spectrum for Ni(II) which is sensitive to changes in symmetry is the intensity of the ν_2 band. In the strong-field limit of T_d symmetry this becomes a two-electron transition and is therefore expected to be rather weak. In reflectance spectra it is observed to have an optical density less than, or about equal to, that of the ν_1 band. In C_{3v} and C_{2v} symmetries, however, a component of the ν_3 band becomes the two-electron transition, and the ν_2 band may increase in intensity relative to the other bands. This has been previously observed³ for the complexes of triphenylphosphine, and it has been noted¹⁴ that when solvolysis of the tetrahalonickelate ions occurs, the solvated species absorb more strongly in the ν_2 region than do the unperturbed anions. However, in view of the contributions to the intensity of these bands

which may be made by mixing with charge-transfer transitions,¹⁵ observation of these effects must be interpreted with caution.

For the nickel(II) complexes of C_{2v} symmetry, a reasonable indication of the extent of distortion from T_d symmetry may be obtained by considering the splitting and position of ν_1 and also the magnitude of the magnetic moment. However, with compounds of C_{3v} symmetry the spectrum may well be more informative than the magnetic measurements, unless these are very detailed, since large distortions may occur, as in the phosphine complexes, while the nickel ion retains considerable orbital contribution, if the 3E level lies lowest.

Acknowledgment.—We thank Dr. D. Rogers for the use of X-ray cameras.

(15) H. A. Weakliem, *J. Chem. Phys.*, **36**, 2117 (1962).

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Deprotonation Reactions of Bis(diethylenetriamine)rhodium(III) and -iridium(III) Halides^{1,2}

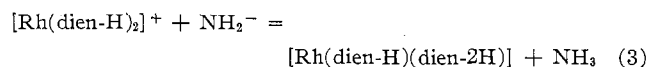
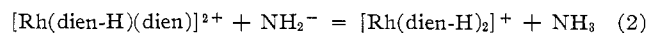
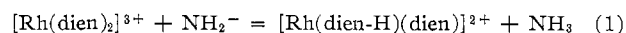
By GEORGE W. WATT AND B. JACK McCORMICK

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Treatment of bis(diethylenetriamine)rhodium(III) and -iridium(III) halides with potassium amide in liquid ammonia at -33.5° has led to the isolation and characterization of $[\text{Rh}(\text{dien-H})_2]\text{I}$, $[\text{Rh}(\text{dien-H})(\text{dien-2H})]$, and $[\text{Ir}(\text{dien-H})(\text{dien-2H})]$ and to evidence for related species not isolated. The effect of deprotonation upon the infrared spectra and possible implications relative to the origin of the protons abstracted are discussed.

Deprotonation of ethylenediamine complexes of transitional metals, M, of charge $n+$ to provide species of the general type $[\text{M}^{n+}(\text{en-xH})_y]^{(n-yx)+}$ has been observed in aqueous solution with gold,³ in anhydrous ethylenediamine with osmium,⁴ and in anhydrous liquid ammonia with platinum,^{5,6} palladium,⁷ iridium,⁸ and rhodium.⁹ While the extension of these studies to polyfunctional ligands such as diethylenetriamine and triethylenetetramine was in progress, Baddley, *et al.*,¹⁰ reported the synthesis of $[\text{Au}(\text{dien-H})\text{X}]\text{X}$ and some of its properties, but the question of whether the primary or secondary nitrogen is deprotonated was not unequivocally resolved.

The experiments described below show that protons on the nitrogen atoms in $[\text{Rh}(\text{dien})_2]^{3+}$ and $[\text{Ir}(\text{dien})_2]^{3+}$ are sufficiently acidic in liquid ammonia at -33.5° to permit their removal by reaction with amide ion, at least to a limited extent, *i.e.*



Although effects to demonstrate this reaction sequence by following the reactions potentiometrically were not successful, isolation and characterization of the products of (2) and (3) incontrovertibly establish that such acid-base reactions do occur. Even though the product of (1) was not isolated, it seems reasonable to postulate this reaction as the first of the series.

Apparently, a similar series of reactions occurs in the case of $[\text{Ir}(\text{dien})_2]^{3+}$; however, the evidence here is considerably less substantial than in the rhodium case since only $[\text{Ir}(\text{dien-H})(\text{dien-2H})]$ was isolated and partially characterized. In contrast to the reactions of $[\text{Ir}(\text{en})_3]^{3+}$ and $[\text{Rh}(\text{en})_3]^{3+}$ with amide ion,^{8,9} the

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

(2) dien denotes the tridentate diethylenetriamine ligand; (dien-nH) indicates the same ligand from which n protons have been removed.

(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.*, **76**, 1008 (1953).

(5) G. W. Watt, R. E. McCarty, and J. W. Dawes, *ibid.*, **79**, 5163 (1957).

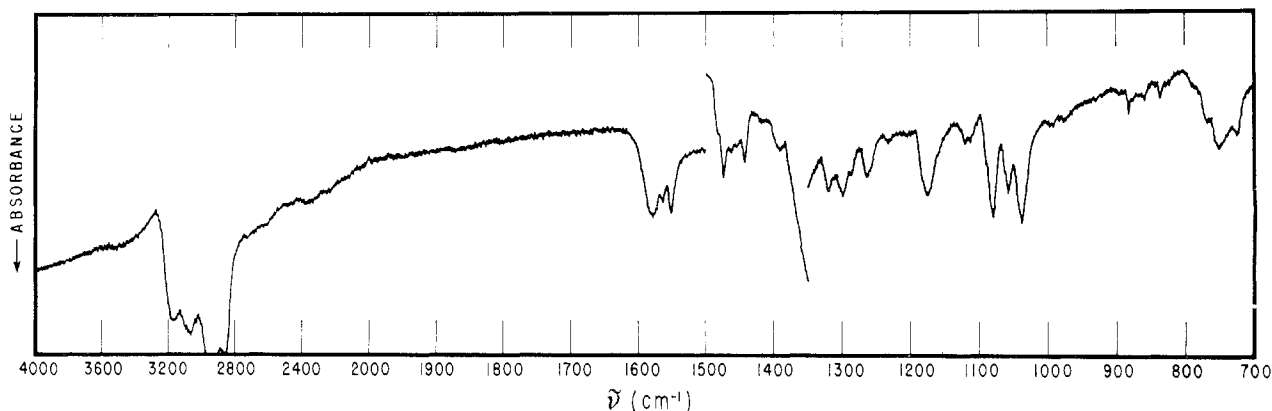
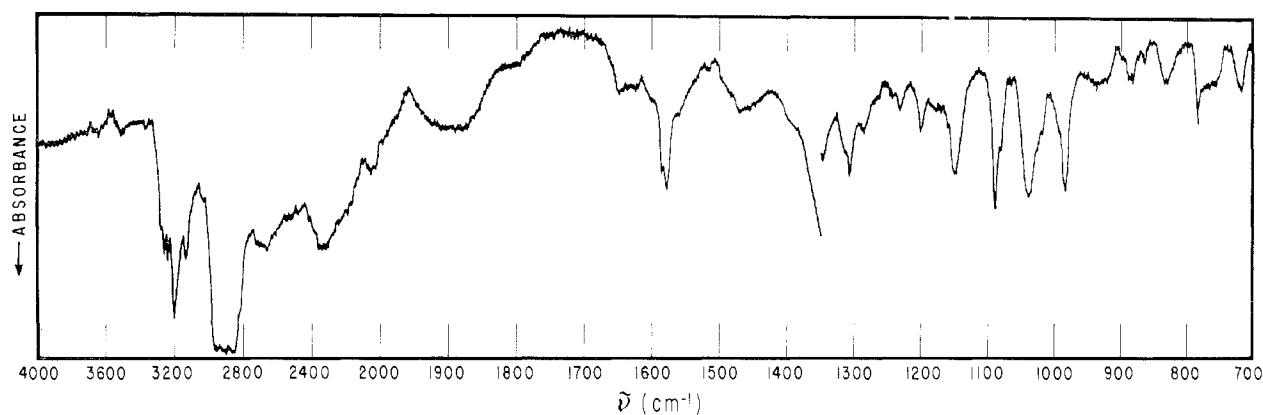
(6) G. W. Watt and J. W. Dawes, *ibid.*, **81**, 8 (1959).

(7) G. W. Watt and R. Layton, *ibid.*, **82**, 4465 (1960).

(8) G. W. Watt, L. E. Sharif, and E. P. Heivenston, *Inorg. Chem.*, **1**, 6 (1962).

(9) G. W. Watt and J. K. Crum, forthcoming publication.

(10) W. H. Baddley, F. Basolo, H. B. Gray, C. Nölting, and A. J. Poe, *Inorg. Chem.*, **2**, 921 (1963).

Figure 1.—The infrared spectrum of $[\text{Rh}(\text{dien})_2]\text{I}_3$.Figure 2.—The infrared spectrum of $[\text{Rh}(\text{dien-H})_2]\text{I}$.

abstraction of protons from the diethylenetriamine complexes apparently involves unfavorable equilibria, as evidenced by the fact that 3.5 molar equivalents of NH_2^- is required to effect complete conversion of the parent compounds to $[\text{Rh}(\text{dien-H})(\text{dien-2H})]$ and $[\text{Ir}(\text{dien-H})(\text{dien-2H})]$, respectively. It is tempting to rationalize this difference between diethylenetriamine and ethylenediamine complexes by assuming that the former are weaker acids than the latter. However, this argument is subject to question since certain ethylenediamine complexes also have required amide ion in excess of the stoichiometric amounts to effect deprotonation,⁵ and Baddley and co-workers have shown that $[\text{Au}(\text{dien-X})\text{X}_2]$ is a stronger acid in water than is $[\text{Au}(\text{en})_2]\text{X}_3$.

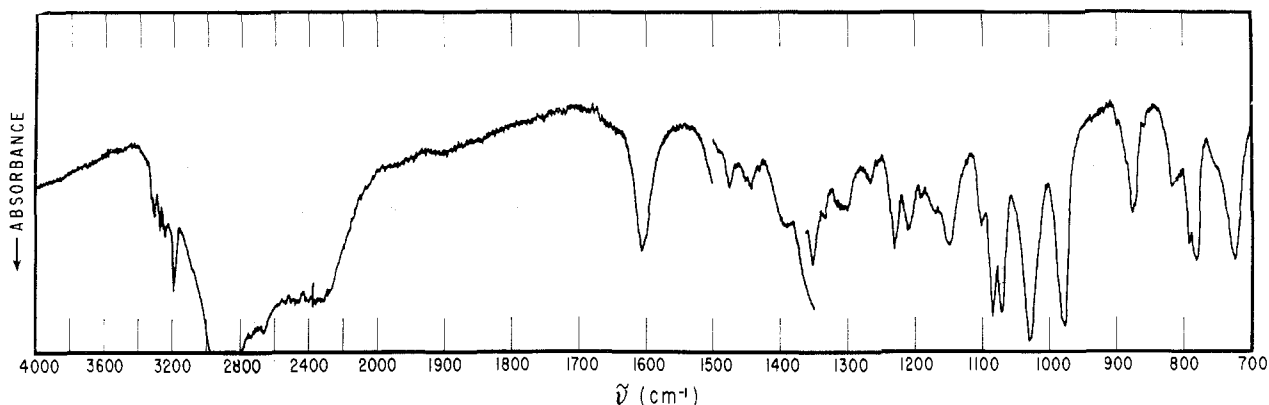
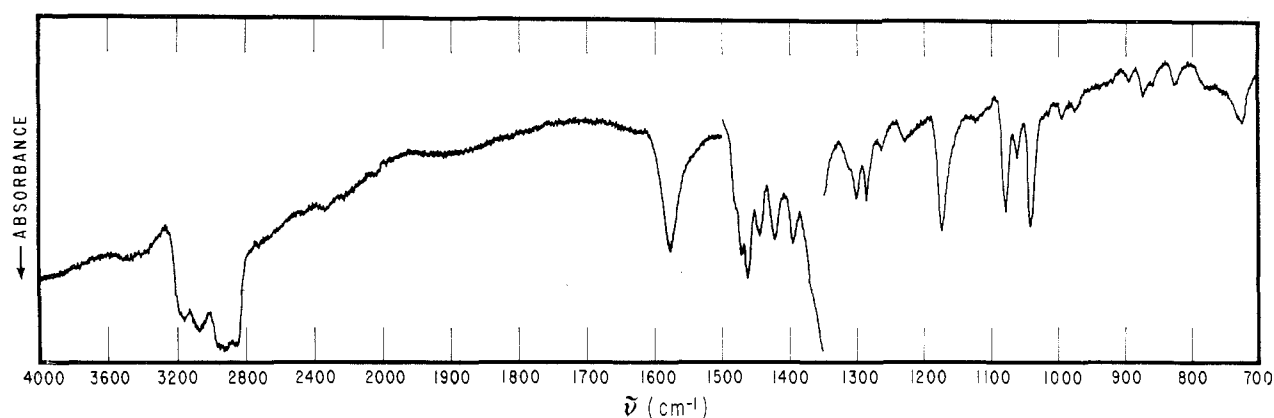
There is no *a priori* way to determine the site of proton abstraction in the reaction of $[\text{Rh}(\text{dien})_2]^{3+}$ with NH_2^- . Initially it was hoped that infrared spectral data for the product complexes would reveal whether protons are removed from primary or secondary nitrogen atoms. However, the infrared data are of somewhat limited utility owing to the fact that $[\text{Rh}(\text{dien})_2]^{3+}$ may or may not be a mixture of the three possible geometrical isomers that might be expected to have somewhat different spectra. Nevertheless, it is felt that the infrared spectra do permit some tentative conclusions concerning the points of abstraction of protons. The spectrum of $[\text{Rh}(\text{dien})_2]\text{I}_3$ in the region 700–4000 cm^{-1} is shown in Figure 1.

The two broad bands in the 2900–3200 cm^{-1} region can be assigned unequivocally as NH_2 and NH stretching modes. The three bands in the 1550–1590 cm^{-1} region are assigned as NH_2 and NH bending modes. This assignment of the NH_2 bend would seem beyond question; however, the assignment of the NH bend is questionable since the NH bending frequency in $[\text{Pd}(\text{dien-X})\text{X}]$ has been tentatively assigned¹¹ at ca. 1450 cm^{-1} .

For $[\text{Rh}(\text{dien-H})_2]\text{I}$ the bands in the NH_2 and NH stretching region are shifted to higher frequencies and are greatly split, as compared with $[\text{Rh}(\text{dien})_2]\text{I}_3$ (Figure 2). In view of the high degree of splitting caused by deprotonation, it would seem reasonable to suggest that the protons are abstracted from NH_2 groups. If the two NH protons were abstracted to form $[\text{Rh}(\text{dien-H})_2]^+$ it is difficult to understand why the spectrum would change so drastically, since the remaining NH_2 groups should exhibit essentially "normal" stretching modes. This argument concerning the source of the protons is substantiated by the great similarity of the spectrum of $[\text{Rh}(\text{dien-H})_2]\text{I}$ to that of $[\text{Rh}(\text{dien-H})(\text{dien-2H})]$ (Figure 3), in which case at least one proton must be removed from an NH_2 group.

Treatment of $[\text{Rh}(\text{dien-H})_2]\text{I}$ and $[\text{Rh}(\text{dien-H})(\text{dien-2H})]$ with 2 and 3 equivalents, respectively, of NH_4I in liquid ammonia produced a compound

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

Figure 3.—The infrared spectrum of $[\text{Rh}(\text{dien-H})(\text{dien-2H})]$.Figure 4.—The infrared spectrum of the products from titration of deprotonated rhodium(III) species with NH_4I in ammonia.

having NH_2 and NH stretching frequencies that were identical with those for the starting material $[\text{Rh}(\text{dien})_2]\text{I}_3$.

The NH_2 and NH bending modes also are affected by deprotonation; the splittings are reduced and the frequencies are increased. However, it is difficult to understand the difference between the NH_2 and NH bending region in the parent $[\text{Rh}(\text{dien})_2]\text{I}_3$ and that obtained from titration of $[\text{Rh}(\text{dien-H})_2]^+$ and $[\text{Rh}(\text{dien-H})(\text{dien-2H})]$ with NH_4I (Figure 4). The only explanation that can be offered at present is that the compound obtained from the reactions with NH_4I may be an isomer or mixture of isomers different from the starting material; thus altered NH_2 and NH bending modes might be observed. This interpretation is supported by the observation that reprotonation of $[\text{Rh}(\text{dien-H})_2]\text{I}$ by treatment with NH_4I in ammonia results in pink $[\text{Rh}(\text{dien})_2]\text{I}_3$ in contrast to the colorless original complex. Also, $[\text{Rh}(\text{dien-H})_2]\text{I}$ dissolves in water to form a pink solution.

Equation 3 does not represent the maximum extent of reaction at -33.5° since an orange-colored homogeneous solution resulted from addition of 6 equivalents of amide ion to $[\text{Rh}(\text{dien})_2]^{3+}$ at -33.5° . Addition of 6 equivalents of NH_4I to this solution resulted in the formation of a pale pink solid for which X-ray diffraction and infrared data are given in Table I and Figure 4, respectively. Experiments designed to

TABLE I
X-RAY DIFFRACTION DATA FOR
BIS(DIETHYLENETRIAMINE)RHODIUM(III) IODIDE
AND BIS(DIETHYLENETRIAMINE)IRIDIUM(III) BROMIDE^a

| $[\text{Rh}(\text{dien})_2]\text{I}_3$ | | $[\text{Rh}(\text{dien})_2]\text{I}_3$ after exposure to NH_3 | | $\text{Ir}(\text{dien})_2\text{Br}_3$ | |
|--|-------------------|--|-------------------|--|-------------------|
| $d, \text{Å}$ | I/I_0 | $d, \text{Å}$ | I/I_0 | $d, \text{Å}$ | I/I_0 |
| 7.48 | 0.50 | 7.48 | 0.50 | 7.31 | 1.00 |
| 5.74 | 0.25 | 5.80 | 0.25 | 6.55 | 1.00 |
| 4.44 | 1.00 | 4.44 | 1.00 | 5.21 | 0.50 |
| 3.93 | 0.20 | 3.94 | 0.30 | 4.31 | 0.50 |
| 3.67 | 0.10 ^b | 3.43 | 0.10 ^b | 3.81 | 0.50 ^b |
| 3.57 | 0.10 | 2.98 | 0.15 | | |
| 3.43 | 0.15 | | | | |
| 2.91 | 0.10 | | | | |
| [$\text{Rh}(\text{dien})_2]\text{I}_3$ from | | | | | |
| $[\text{Rh}(\text{dien-H})_2]\text{I} + 2\text{NH}_4\text{I}$ in NH_3 | | $[\text{Rh}(\text{dien-H})(\text{dien-2H})] + 3\text{NH}_4\text{I}$ in NH_3 | | $[\text{Rh}(\text{dien-2H})_2]^{3+}$ (?) + $6\text{NH}_4\text{I}$ in NH_3 | |
| $d, \text{Å}$ | I/I_0 | $d, \text{Å}$ | I/I_0 | $d, \text{Å}$ | I/I_0 |
| 7.49 | 0.40 | 7.51 | 0.75 | 7.44 | 0.50 |
| 5.76 | 0.20 | 5.76 | 0.15 | 5.71 | 0.20 |
| 4.39 | 1.00 | 4.44 | 1.00 | 4.37 | 1.00 |
| 3.90 | 0.30 | 3.92 | 0.30 | 3.89 | 0.30 |
| 2.98 | 0.15 ^b | 3.26 | 0.20 | 3.71 | 0.10 ^b |
| | | 2.97 | 0.15 ^b | 2.95 | 0.10 |

^a All X-ray diffraction data were obtained from patterns made using $\text{Cu K}\alpha$ radiation (Ni filter), 35-kv. tube voltage, 15-ma. filament current, and 10–18-hr. exposure times. Samples were diluted with 1–5 volumes of starch; relative intensities were estimated visually. ^b Less intense lines not included here.

precipitate the 6-equivalent species by dilution with toluene or ether did not lead to the expected products.

The strong base properties of $[\text{Rh}(\text{dien-H})_2]^+$ and $[\text{Rh}(\text{dien-H})(\text{dien-2H})]$ are evident from the facts that aqueous solutions of these complexes have a high pH (*ca.* 11) and that the compounds react with 2 and 3 equivalents, respectively, of NH_4I in liquid ammonia to regenerate the parent compound or an isomer thereof.

Experimental

Unless otherwise indicated, all procedures for carrying out reactions in ammonia and characterization of the resulting products were the same as those described previously.¹² Infrared spectra were measured with a Beckman Model IR-7 instrument; mulling agents were Nujol (700–1360, 1500–4000 cm^{-1}) and high-boiling perfluorokerosene (1360–1500 cm^{-1}). Ultraviolet and visible spectra were recorded with a Cary Model 14 spectrophotometer.

Rhodium and iridium analyses were carried out in this laboratory by hydrogen reduction at 900°; other analyses were performed by commercial analytical laboratories.

Bis(diethylenetriamine)rhodium(III) iodide was prepared by the dropwise treatment of 3.0 g. of finely divided $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ ($x = 2-3$) in 1 ml. of H_2O with 5.0 ml. of diethylenetriamine (distilled at 39–41° (3 mm.) before use). When the addition of diethylenetriamine was complete, the solution was heated over a steam cone for 2 hr.; then an additional 4 ml. of 75% dien was added and heating was continued for 3 hr. After standing for 24 hr., the mixture was treated with 15 ml. of H_2O and poured slowly and with stirring into 300 ml. of ethanol containing 5.0 g. of NaI . The resulting solution and gray precipitate were cooled for 2 hr. at 0°, after which the precipitate was filtered, washed with 100 ml. of 95% ethanol, air-dried, and redissolved in 50 ml. of hot water. After filtration and addition of 5 ml. of 0.7 *M* NaI , evaporation of this solution to incipient crystallization followed by cooling to 0° overnight produced $[\text{Rh}(\text{dien})_2]\text{I}_3$ which was slightly contaminated with NaI . Recrystallization from 50 ml. of H_2O gave 3.1 g. of pure $[\text{Rh}(\text{dien})_2]\text{I}_3$, which was dried *in vacuo* over $\text{Mg}(\text{ClO}_4)_2$ for 24 hr.

Anal. Calcd. for $[\text{Rh}(\text{dien})_2]\text{I}_3$: Rh, 14.8; I, 55.2. Found: Rh, 14.9; I, 55.1. X-Ray diffraction and infrared spectral data are included in Table I and Figure 1, respectively. The ultraviolet and visible absorption spectra of a solution of $[\text{Rh}(\text{dien})_2]\text{I}_3$ in water showed no change with time, and maxima were observed at 225 and 302 $\mu\mu$. This compound was diamagnetic, as expected.

Bis(diethylenetriamine)iridium(III) bromide was prepared by heating 4.09 g. of powdered $\text{IrBr}_3 \cdot x\text{H}_2\text{O}$ ($x \cong 3$) with 15 ml. of dien for 12 hr. at 100°. The reddish solution and cream-colored precipitate were added slowly and with stirring to 400 ml. of ethanol at 40°. The flocculent precipitate which formed was filtered, washed with ethanol, air-dried, and then redissolved in 50 ml. of H_2O ; this solution was filtered, evaporated on a steam cone to *ca.* 80 ml., and then added slowly to 400 ml. of ethanol. The white precipitate was filtered and washed with 100 ml. of ethanol, *without allowing the precipitate to become dry*. While still quite wet with ethanol the precipitate was transferred to a desiccator and dried *in vacuo* over $\text{Mg}(\text{ClO}_4)_2$; the yield was 3 g.

Anal. Calcd. for $[\text{Ir}(\text{dien})_2]\text{Br}_3$: Ir, 30.1; N, 13.2. Found: Ir, 30.0; N, 13.4. X-Ray diffraction data are included in Table I.

Experiments with $[\text{Ir}(\text{dien})_2]\text{Br}_3$.—To investigate the over-all reaction of bis(diethylenetriamine)iridium(III) bromide with amide ion, 0.1307 g. of $[\text{Ir}(\text{dien})_2]\text{Br}_3$ was titrated potentiometrically with 6 molar equivalents of KNH_2 in ammonia. Although changes were observed visually throughout the titration, a plot of potential *vs.* volume of amide solution failed to give meaningful results. Numerous attempts were made to isolate pure products from the reaction of $[\text{Ir}(\text{dien})_2]\text{Br}_3$ with 1.9–3.3 equivalents of amide. In all cases products were obtained which were mixtures. However, upon addition of 3.5 equiva-

lents of KNH_2 an apparently pure product was isolated. In a typical experiment a compound that is apparently $[\text{Ir}(\text{dien-H})(\text{dien-2H})]$ was obtained.

Anal. Calcd. for $[\text{Ir}(\text{dien-H})(\text{dien-2H})]$: Ir, 48.6. Found: Ir, 48.2. Analysis of the combined filtrate and washings accounted for 99.4% of the bromine added initially as the parent compound. This neutral complex was pyrophoric and unstable even in an atmosphere of dry He; hence, substantiating analytical data for C and H were not obtained. Because of the restrictive properties of this compound and the preparative difficulties encountered, further experiments were not performed with $[\text{Ir}(\text{dien})_2]\text{Br}_3$.

Preliminary Experiments with $[\text{Rh}(\text{dien})_2]\text{I}_3$.—In order to establish that $[\text{Rh}(\text{dien})_2]\text{I}_3$ is not solvolyzed by ammonia, a 0.10-g. sample of the iodide was treated with 5 ml. of liquid ammonia at the boiling point for 3 hr. The solvent was removed completely, and the residual white solid was shown to be identical with the starting material by X-ray diffraction data (Table I) and infrared spectra, which were identical with those for $[\text{Rh}(\text{dien})_2]\text{I}_3$.

The over-all reaction between $[\text{Rh}(\text{dien})_2]\text{I}_3$ and KNH_2 was examined by titrating 0.101 g. of the iodide dissolved and suspended in 100 ml. of ammonia with potassium amide formed from 34.3 mg. of potassium in 17.1 ml. of ammonia. The titration was not followed potentiometrically since, as discussed above, the analogous iridium complex did not afford meaningful potential data. Visual observations during the titration are as follows. Upon addition of 1 molar equivalent of amide a homogeneous solution was not obtained, in contrast to the case of $[\text{Ir}(\text{en})_3]\text{I}_3$; instead a turbid yellow solution and suspension resulted. The yellow color of the solution persisted and the appearance of a white solid was observed at 2 equivalents. Between 2 and 3 equivalents the yellow color diminished with the concomitant formation of a voluminous white solid. This condition persisted through the addition of 3.5 equivalents. At 4 equivalents the amount of precipitate decreased and the solution again assumed a distinct yellow color. Continued addition of KNH_2 to a total of 6 equivalents resulted in the formation, first, of a greenish solution and precipitate and finally a clear orange-colored solution. After evaporation of the solvent a red solid remained.

Isolation of $[\text{Rh}(\text{dien-H})_2]\text{I}$.—A solution and suspension of 0.675 g. (0.976 mmole) of $[\text{Rh}(\text{dien})_2]\text{I}_3$ in *ca.* 75 ml. of ammonia at -33.5° was treated with a solution containing 2.05 molar equivalents of KNH_2 in 14 ml. of ammonia. After a digestion period of 1 hr., the resulting white precipitate was separated from the yellow solution by filtration and washed with five 25-ml. portions of ammonia. After complete removal of the solvent under reduced pressure, the solid residue was transferred to an inert atmosphere box for removal of samples.

Anal. Calcd. for $[\text{Rh}(\text{dien-H})_2]\text{I}$: Rh, 23.7; N, 19.4. Found: Rh, 23.2; N, 18.6. X-Ray diffraction data are given in Table II and the infrared spectrum is shown in Figure 2.

Properties and Reactions of $[\text{Rh}(\text{dien-H})_2]\text{I}$.—Diamagnetic (at 25°) $[\text{Rh}(\text{dien-H})_2]\text{I}$ is unstable in air, where it rapidly absorbs moisture and turns pink, but it appears to be stable indefinitely in a dry He atmosphere. The complex dissolves readily in water to give a basic solution which is very faintly pink when concentrated.

A 0.120-g. sample of this product was dissolved and suspended in *ca.* 50 ml. of ammonia and titrated with 0.0804 g. (2.00 molar equivalents) of NH_4I in 9.0 ml. of ammonia. The very faint pink solid product obtained was digested for 1 hr., separated by filtration, and washed with 30 ml. of ammonia. After removal of the solvent under reduced pressure, the product was removed from the reactor in a glove bag filled with dry N_2 .

Anal. Calcd. for $[\text{Rh}(\text{dien})_2]\text{I}_3$: Rh, 14.9. Found: Rh, 15.3. X-Ray diffraction data are given in Table I; the infrared spectrum was identical with that shown in Figure 4.

Isolation of $[\text{Rh}(\text{dien-H})(\text{dien-2H})]$.—To a solution and suspension of 1.408 g. of $[\text{Rh}(\text{dien})_2]\text{I}_3$ in *ca.* 50 ml. of ammonia was added slowly 11.0 ml. of ammonia containing KNH_2 prepared

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

TABLE II
X-RAY DIFFRACTION DATA FOR $[\text{Rh}(\text{dien-H})_2]\text{I}$
AND $[\text{Rh}(\text{dien-H})(\text{dien-2H})]^a$

| $[\text{Rh}(\text{dien-H})_2]\text{I}$ | | $[\text{Rh}(\text{dien-H})(\text{dien-2H})]$ | |
|--|----------------------------------|--|----------------------------------|
| <i>d</i> , Å. | <i>I</i> / <i>I</i> ₀ | <i>d</i> , Å. | <i>I</i> / <i>I</i> ₀ |
| 8.52 | 0.50 | 8.40 | 0.25 |
| 6.47 | 0.50 | 7.64 | 0.50 |
| 6.03 | 0.10 ^b | 6.22 | 1.00 |
| 5.63 | 0.50 | 5.79 | 0.20 |
| 4.37 | 1.00 | 5.01 | 0.20 |
| 3.46 | 0.20 | 4.54 | 0.10 ^b |
| 2.94 | 0.40 | 4.08 | 0.20 |
| 2.81 | 0.10 | 2.91 | 0.15 |
| 2.52 | 0.15 | 2.71 | 0.10 |
| 2.37 | 0.10 | 2.62 | 0.10 |
| 2.03 | 0.10 | 2.52 | 0.10 |

^a See footnote a, Table I. ^b Less intense lines not included here.

from 0.2795 g. of K (3.50 molar equivalents). After a digestion period of 1.5 hr. the tan product was separated by filtration and washed with six 30-ml. portions of ammonia. The product then was handled as described above. Analysis of the combined filtrate and washings accounted for 98.8% of the iodine added initially as $[\text{Rh}(\text{dien})_2]\text{I}_3$.

Anal. Calcd. for $[\text{Rh}(\text{dien-H})(\text{dien-2H})]$: Rh, 33.6; N, 27.4. Found: Rh, 34.0; N, 27.4. X-Ray diffraction data are given in Table II and the infrared spectrum is shown in Figure 3.

Properties and Reactions of $[\text{Rh}(\text{dien-H})(\text{dien-2H})]$.—This product dissolved readily in water to give a basic solution. The bulk material was somewhat pyrophoric in air; however, when powdered the complex did not burn in air but was very hygroscopic. In an atmosphere of dry He, $[\text{Rh}(\text{dien-H})(\text{dien-2H})]$ appeared to be somewhat unstable, as evidenced by a darkening in color over a period of 1–2 months. The complex was diamagnetic at 25°.

To a suspension of 0.208 g. of $[\text{Rh}(\text{dien-H})(\text{dien-2H})]$ in ca. 40 ml. of ammonia was added 0.295 g. of NH_4I (3.0 molar equivalents in 10.2 ml. of NH_3). The product was separated by filtration and washed once with 30 ml. of ammonia. After removal of the solvent, the X-ray diffraction data included in Table I were obtained. The infrared spectrum was identical with that shown in Figure 4.

A 37-mg. sample of $[\text{Rh}(\text{dien-H})(\text{dien-2H})]$ was pyrolyzed *in vacuo* to determine whether dien might be liberated. At 200° the complex darkened and a colorless liquid began to condense in the cooler (ambient temperature) portion of the pyrolysis tube. The liquid continued to distil as the temperature was raised slowly to 500°. The liquid that condensed in the trap was identified as dien both by mass spectrographic analysis and by the fact that the melting point of its picrate was identical with that of the picrate prepared from an authentic sample of dien. A black residue consisting mostly of Rh, as shown by an X-ray diffraction pattern, remained in that portion of the tube which was heated.

Reaction of $[\text{Rh}(\text{dien})_2]\text{I}_3$ with 6KNH₂.—To 0.5872 g. (8.5×10^{-4} mole) in 40 ml. of ammonia was added, slowly, 13.8 ml. of ammonia containing 6.0 molar equivalents of KNH₂. The orange solution was aged for 1 hr. with no change in appearance. To this solution was added 6.0 equivalents of NH_4I in 10 ml. of NH_3 . The pink product obtained was washed three times with 20-ml. portions of NH_3 . The pink product was stable indefinitely in an atmosphere of dry He and dissolved readily in H_2O to form a pink neutral solution which became colorless over a period of several hours.

Anal. Calcd. for $[\text{Rh}(\text{dien})_2]\text{I}_3$: Rh, 14.9. Found: Rh, 14.9. X-Ray diffraction data are given in Table I and the infrared spectrum is shown in Figure 4.

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Reflectance Spectra and the Coordination of Divalent Metal Ions in 5-Trifluoromethyltetrazole Complexes¹

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The nature of the coordination of Fe(II), Co(II), Ni(II), and Cu(II) with the 5-trifluoromethyltetrazolyl anion has been ascertained on the basis of a correlation of the reflectance spectra with previously reported observations.^{2,3} All of the complexes appear to be octahedral or distorted octahedral σ -bonded complexes involving coordination by tetrazolyl anion and water.

Introduction

Jonassen and co-workers^{2,3} have prepared complexes of several divalent transition metal ions with the 5-trifluoromethyltetrazolyl anion (Figure 1) and assigned a preliminary structure to the dihydrate of the iron(II) complex on the basis of the Mössbauer-effect study.³ A re-evaluation of the structure of this com-

pound and some understanding of the others is now possible by correlation of the reflectance spectra with previous measurements of other properties of the complexes. All of the experimental evidence correlates well for σ -bonded tetrazole complexes, in contrast to the π -bonded structure previously entertained for the iron complex.³

Experimental

Chemicals.—The chemicals used in this investigation were reagent grade. The tetrazole sample was prepared by Norris,^{4,5} whose generosity in supplying a large sample is gratefully acknowledged. The complexes $\text{Fe}(\text{C}_2\text{F}_3\text{N}_4)_2 \cdot 2\text{H}_2\text{O}$, $\text{Co}(\text{C}_2\text{F}_3\text{N}_4)_2 \cdot 6\text{H}_2\text{O}$

(1) Experimental results presented in part at the Southwest Regional Meeting of the American Chemical Society, Houston, Texas, Dec. 1963, and abstracted in part from a dissertation submitted by A. D. Harris in partial fulfillment of the requirements for the Ph.D., Tulane University, 1964.

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(3) A. D. Harris, R. H. Herber, H. B. Jonassen, and G. K. Wertheim, *J. Am. Chem. Soc.*, **85**, 2927 (1963).

(4) U. S. Naval Ordnance Test Station, China Lake, Calif.

(5) W. P. Norris, *J. Org. Chem.*, **27**, 3248 (1962).