

The fact that the rare earth complexes of 2-picolyl-iminodiacetic acid are nearly as stable as the HIMDA chelates despite the decreased basicity of the ligand is very interesting. A semiquantitative estimate of this enhancement of stability could be obtained if there were a relationship between the $\log K_1$ values of rare earth chelates and the pK values of the ligands. Although such a relationship is not available at present, it can still be concluded that the pyridine ring in this chemical environment is at least as effective in coordinating to the rare earths as the hydroxyl group of HIMDA, and in view of the basicity difference, probably slightly more so.

From this conclusion it is quite reasonable to expect that in the rare earth-dipicolinic acid chelates mentioned at the beginning of this paper, in which the pyridine ring is sterically required to be juxtaposed to the metal ion, there is an interaction (bonding) between the heterocyclic nitrogen atom and the rare earth ion. That this is not an isolated example is shown by the fact that picolinic acid itself forms rather strong chelates with rare earth ions.¹⁶ The stability of the rare earth complexes of 8-hydroxyquinoline and its derivatives¹⁷ should also be recalled.

(16) L. C. Thompson, *Inorg. Chem.*, submitted for publication.

(17) B. F. Freasier, A. G. Oberg, and W. W. Wendlandt, *J. Phys. Chem.*, **62**, 700 (1958).

An explanation for this effect is not forthcoming, since the factor which should stabilize pyridine complexes, suitably oriented d-orbitals for π -bonding, is missing in these ions. It has recently been shown that the alkaline earths behave in much the same way and no explanation could be offered.⁵ For both of these groups of metals, however, the effect of the pyridine ring is much less than for the other metals which have been studied. This is probably due to the fact that the alkaline earths and rare earths are bonded to the pyridine ring using only the σ -bonding character. Since the structure of the ligand is such that the nitrogen atom of the pyridine ring can approach a bonding position which is occupied by a water molecule, it is possible that the combination of the larger dipole moment of pyridine, compared with that of water, and the extra stability conferred on the structure by the additional chelated group are sufficiently large to displace the coordinated water molecule. Whatever the explanation, it is apparent that the rare earths coordinate to the pyridine ring in suitable environments more readily than had been expected.

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CONTRIBUTION FROM E. I. DU PONT DE NEMOURS AND CO.,
SAVANNAH RIVER LABORATORY, AIKEN, SOUTH CAROLINA

Chloro Complexes of Nitrosylruthenium^{1a}

By E. E. MERCER, W. M. CAMPBELL, JR., AND R. M. WALLACE^{1b}

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An investigation of the nitrosylruthenium chloro complexes formed in hydrochloric acid solutions has shown the existence of five monomeric complexes. The mono-, di-, tri-, tetra-, and pentachloro complexes were isolated by ion exchange and were shown to have the formulas $\text{RuNOCl}(\text{H}_2\text{O})_4^{+2}$, $\text{RuNOCl}_2(\text{H}_2\text{O})_3^+$, $\text{RuNOCl}_3(\text{H}_2\text{O})_2$, $\text{RuNOCl}_4(\text{H}_2\text{O})^-$, and RuNOCl_5^{-2} in acid media. The complex $\text{RuNOCl}_4(\text{H}_2\text{O})^-$ is a weak acid that dissociates to produce $\text{RuNOCl}_4(\text{OH})^{-2}$ with a dissociation constant of 9.5×10^{-7} . $\text{RuNOCl}_3(\text{H}_2\text{O})_2$ is a weak dibasic acid that dissociates to produce $\text{RuNOCl}_3(\text{H}_2\text{O})(\text{OH})^-$ and $\text{RuNOCl}_3(\text{OH})_2^{-2}$ with successive dissociation constants of 1.1×10^{-5} and 3.4×10^{-8} . One other chloro complex was detected but was not characterized.

Introduction

Solid crystalline chloro compounds of nitrosylruthenium such as $\text{RuNOCl}_3 \cdot 5\text{H}_2\text{O}$ and $\text{K}_2\text{RuNOCl}_5$ have been known for years. More recently amorphous $\text{H}_2\text{RuNOCl}_4\text{OH} \cdot 2\text{H}_2\text{O}$ and crystalline $(\text{NH}_4)_2[\text{RuNOCl}_4\text{OH}]$ have been studied,² but no chloro nitrosylruthenium complexes have been identified in solution. A study of the hydrolysis of $\text{RuNOCl}_3(\text{H}_2\text{O})_2 \cdot 3\text{H}_2\text{O}$ by Thomas and Mucci³ was interpreted as supporting

only $\text{RuNO}(\text{H}_2\text{O})_5^{+3}$ and $\text{RuNO}(\text{H}_2\text{O})_4(\text{OH})^{+2}$ in solution.

The present investigation deals with the isolation from aqueous solutions and characterization of chloro complexes of nitrosylruthenium. $[\text{RuNOCl}_5]^{-2}$, $[\text{RuNOCl}_4\text{H}_2\text{O}]^-$, $\text{RuNOCl}_3(\text{H}_2\text{O})_2$, $[\text{RuNOCl}_2(\text{H}_2\text{O})_3]^+$, and $[\text{RuNOCl}(\text{H}_2\text{O})_4]^{+2}$ present in mixtures of aqueous hydrochloric acid and $\text{RuNOCl}_3(\text{H}_2\text{O})_2 \cdot 3\text{H}_2\text{O}$ were separated by ion-exchange resins and their formulas were established.

Experimental

Preparation of Solid Compounds. $\text{RuNOCl}_3(\text{H}_2\text{O})_2 \cdot 3\text{H}_2\text{O}$.—A mixture of chloro complexes of nitrosylruthenium was prepared by dissolving nitrosylruthenium hydroxide, prepared by the

(1) (a) The information contained in this article was developed during the course of work under contract AT(07-2)-1 with the U. S. Atomic Energy Commission; (b) inquiries relating to this paper should be directed to this author.

(2) (a) J. M. Fletcher, *et al.*, *J. Inorg. Nucl. Chem.*, **1**, 378 (1955); (b) N. A. Parpiev and M. A. Porai-Kashits, *Kristallografiya*, **4**, 30 (1959).

(3) H. Thomas and J. F. Mucci, Ph.D. Thesis, Yale University, 1959.

method of Fletcher, *et al.*,^{2a} in 6 *M* HCl and heating until the solution turned purple. The solution was evaporated to dryness and heated to expel the excess water and hydrochloric acid. The resulting brick red powder was dissolved in hot water, and the trichloro compound crystallized from solution as the water evaporated at room temperature. The crystalline compound is difficult to prepare because of its high solubility in water and because it crystallizes from solution very slowly even when seeded.

Anal. Calcd. for $\text{RuNOCl}_3(\text{H}_2\text{O})_2 \cdot 3\text{H}_2\text{O}$: Ru, 30.99; N, 4.27; Cl, 32.5; mol. wt. in water, 328. Found: Ru, 30.3; N, 4.34; Cl, 31.6; mol. wt. in water, 298.

$(\text{NH}_4)_2\text{RuNOCl}_5$ and $\text{K}_2\text{RuNOCl}_5$.—A mixture of chloro complexes was prepared by heating a solution of nitrosylruthenium hydroxide in 6 *M* HCl until a purple color formed. From this solution the compounds $(\text{NH}_4)_2\text{RuNOCl}_5$ and $\text{K}_2\text{RuNOCl}_5$ were prepared by adding NH_4Cl or KCl and allowing the appropriate complex salt to crystallize. Each of the salts was recrystallized from water.

Anal. Calcd. for $(\text{NH}_4)_2\text{RuNOCl}_5$: Ru, 29.46; N (due to NH_4^+), 8.11; N (total), 12.17; Cl, 51.5. Found: Ru, 29.5; N (due to NH_4^+), 7.98; N (total), 12.18; Cl, 51.6. Calcd. for $\text{K}_2\text{RuNOCl}_5$: Ru, 26.1; N, 3.62; Cl, 45.88, K, 20.2. Found: Ru, 25.9; N, 3.56; Cl, 45.86; K, 21.2.

$\text{Ag}_2\text{RuNOCl}_4\text{OH}$.—The tetrachloro complex was isolated from a mixture of chloro complexes by elution from an anion-exchange column with nitric or perchloric acids. The eluate from the ion-exchange column was added to a 0.1 *M* solution of silver nitrate, and a pink precipitate of the desired compound was formed immediately. The precipitate was filtered, washed several times with water, and dried in a vacuum desiccator. An X-ray diffraction pattern of the precipitate indicated the absence of AgCl in the precipitate.

Anal. Calcd. for $\text{Ag}_2\text{RuNOCl}_4\text{OH}$: Ag, 42.7; Ru, 20.0; N, 2.77; Cl, 28.07. Found: Ag, 41.8; Ru, 20.2; N, 2.77; Cl, 28.09.

Preparation of the Acids $\text{H}_2\text{RuNOCl}_5$ and $\text{HRuNOCl}_4(\text{H}_2\text{O})$.—A solution of $\text{H}_2\text{RuNOCl}_5$ was prepared by dissolving 1 g. of $(\text{NH}_4)_2\text{RuNOCl}_5$ in 100 ml. of water and agitating the solution with 4.5 g. of Dowex 50W-X8 ion-exchange resin in the hydrogen form for 15 min. The solution was then passed through a column of the same type resin to ensure the complete removal of ammonium ion.

To prepare a solution of pure $\text{HRuNOCl}_4(\text{H}_2\text{O})$, a sample of the insoluble $\text{Ag}_2\text{RuNOCl}_4\text{OH}$ was placed in water and stirred with an excess of cation-exchange resin in the hydrogen form. The great affinity of silver ions for the resin caused an exchange reaction to occur, and the water gradually became colored by the soluble tetrachloro acid. When sufficient amounts of the acid were in solution the excess silver salt and resin were removed by filtration.

Isolation of Complexes from Solution by Ion-Exchange Resins.

—The penta-, tetra-, and trichloro complexes were isolated from solutions of $\text{RuNOCl}_3(\text{H}_2\text{O}) \cdot 3\text{H}_2\text{O}$ in 6 *M* HCl that had been held at 95° for 30 min. to 4 hr. The tetra-, tri-, di-, and monochloro complexes were isolated from solutions of $\text{RuNOCl}_3(\text{H}_2\text{O})_2 \cdot 3\text{H}_2\text{O}$ in water that had been held at 99° for 30 min. to 6 hr.; the same group of complexes was also obtained by heating aqueous solutions of $\text{K}_2\text{RuNOCl}_5$ or $(\text{NH}_4)_2\text{RuNOCl}_5$. The longer heating periods were required to obtain sufficient quantities of the monochloro complex for further studies. Prolonged heating of aqueous solutions also produced species other than those described in this paper, but insufficient quantities were obtained for complete characterization.

The two anionic complexes together with the neutral trichloro complex were isolated by absorption on an anion-exchange column and elution with nitric, hydrochloric, or perchloric acid of successively higher concentrations. The order of elution was always $\text{RuNOCl}_3(\text{H}_2\text{O})_2$, $\text{RuNOCl}_4(\text{H}_2\text{O})^-$, and RuNOCl_5^{-2} . The mechanism of the absorption and elution of the trichloro complex is somewhat obscure, since it is eluted with water or 2 *M* acid at about the same rate. It was possible, however, to elute all of

this complex with dilute acid without disturbing the other two complexes. The tetrachloro complex was eluted rapidly with 3–5 *M* HNO_3 or HCl and was completely separated from the pentachloro complex, which did not elute rapidly at HNO_3 or HCl concentrations below 7 *M*. The anionic complexes were eluted much more readily with perchloric acid than with either nitric or hydrochloric acid because of the greater affinity of perchlorate ions for the ion-exchange resin. The tetrachloro complex, for example, was eluted rapidly with 0.5 *M* HClO_4 .

The anionic complexes were isolated on columns of Dowex 1-X4 (100–200 mesh) anion-exchange resin initially in the chloride form. When elutions were to be made with either nitrate or perchlorate ion the column was converted to the appropriate form prior to absorption. In such cases it was possible to elute the excess chloride ion with dilute nitric or perchloric acid before eluting the complexes.

The cationic complexes were separated by absorption and elution from cation-exchange columns of Dowex 50W-X8 (50–100 mesh) resin in the hydrogen form. These complexes were absorbed from dilute aqueous solutions and were eluted with nitric, hydrochloric, or perchloric acid solutions of successively higher concentrations. The dichloro complex was eluted rapidly with 1 *M* acid and was completely separated from the monochloro complex, which was not eluted rapidly with acid concentrations below 3 *M*. Both complexes were eluted in discrete bands that were readily detected by their intense color; this type of elution was also characteristic of the anionic complexes described above. In solutions that had been heated for prolonged periods two other cationic species were observed, one that was eluted rapidly with 0.5 *M* acid, and one that could not be eluted with 7 *M* HNO_3 or 4 *M* HClO_4 . The latter species was removed from the column after it had remained in contact with 2 *M* H_2SO_4 for 24 hr.

Both the anionic and cationic species were eluted with nitric acid when a determination of the chloride–ruthenium ratio was desired, and with perchloric acid to obtain solutions of the complexes for determinations of the charge per species and charge per Ru atom. Each of the species was also isolated by elution with hydrochloric acid, and the visible absorption spectrum of each was compared with that of the corresponding complex isolated by elution with the other acids.

Analysis for Ruthenium.—Ruthenium was determined spectrophotometrically by the method of Gortsema.⁴ Ruthenium in acid solution was oxidized to RuO_4 with an excess of periodic acid, and the concentration of ruthenium was calculated from the absorbance at 385 *mμ*; a molar extinction coefficient of 930, determined by Connick and Hurley,⁵ was used for RuO_4 at this wave length. Interference from chloride was eliminated by heating samples for 30 min. in concentrated HNO_3 before ruthenium analysis.

Analysis for Chloride–Ruthenium Ratio.—The ratio of chloride to ruthenium was determined by X-ray fluorescence; the ratio of intensities of the Cl $K\alpha$ and the Ru $L\alpha$ lines was measured directly on solutions. A calibration curve was prepared by the analysis of known samples of different ratios and concentrations; the coefficient of variation ranged from 6.2% at 10^{-2} *M* Ru to 2% at 1 *M*.

Analysis for Chloride.—In general, chloride was determined from the Cl:Ru ratio and the ruthenium analysis. On several samples, the chloride content was verified by titration of chloride with mercuric ion, with diphenylcarbazide as an indicator.^{6,7} Interference from ruthenium was avoided by reduction of ruthenium to the metal with magnesium in dilute sulfuric acid before titration.

Absorption Spectra.—Absorption spectra were obtained on a Cary Model 11 recording spectrophotometer with 1-cm. quartz cells.

(4) F. P. Gortsema, Ph.D. Thesis, Purdue University, 1959.

(5) R. E. Connick and C. R. Hurley, *J. Am. Chem. Soc.*, **74**, 5012 (1952).

(6) I. Roberts, *Ind. Eng. Chem., Anal. Ed.*, **8**, 365 (1936).

(7) F. E. Clarke, *Anal. Chem.*, **22**, 553 (1950).

Determination of Molecular Weights.—The molecular weight of $\text{RuNOCl}_3(\text{H}_2\text{O})_2 \cdot 3\text{H}_2\text{O}$ was determined by the freezing point depression in water. Freezing point measurements were made with a Fenwal G465 thermistor in conjunction with a five-place Wheatstone bridge and a sensitive galvanometer. The thermistor was calibrated by determining its resistance at the freezing points of water and of sucrose solutions of known concentrations. All other procedures were standard.

Titration Curves.—Ten-ml. samples of solutions of $\text{RuNOCl}_3(\text{H}_2\text{O})_2$, $\text{HRuNOCl}_4(\text{H}_2\text{O})$, and $\text{H}_2\text{RuNOCl}_5$ whose initial concentrations were 5.86×10^{-3} , 3.72×10^{-3} , and $6.65 \times 10^{-3} M$, respectively, were titrated with $0.1 M \text{ NaOH}$ and the usual titration curves plotted (Fig. 2). Titrations were performed with a Gilmont buret in conjunction with a Beckman Model G pH meter and miniature glass and saturated calomel electrodes. The titrations were performed at about 5° and were run as rapidly as possible to minimize hydrolysis of the complexes when the solutions became basic. Acid dissociation constants were calculated when possible from points lying between one-fourth and three-fourths of the distance between inflections in the titration curve; appropriate corrections were made for dilution of the solutions by the titrant.

Measurement of Charge per Ru Atom.—The measurement of charge per Ru atom was made by two different methods described by Connick and Cady.⁸

The first method consisted of the absorption of a known amount of the species in question on an ion-exchange column and measurement of the amount of the ion originally present on the resin that was liberated. Cation resins initially in the acid form were used with cationic species, and anion resins initially in the chloride form were used with anions. The charge per atom was calculated from the formula

$$\text{charge per atom} = \frac{(\text{charge of ion liberated})(\text{moles of ion liberated})}{(\text{g.-atoms of Ru absorbed})}$$

The number of moles of ion liberated was determined by titration of the hydrogen or chloride ion.

When the charge per atom was determined for the cationic species (obtainable only in acidic media), corrections were made for the amount of acid originally in the sample. In all experiments the ruthenium species were absorbed so strongly that none was found in the effluent from the column.

The second method consisted of absorbing the species of a cation-exchange column initially in the hydrogen form and eluting with a solution of lanthanum perchlorate in dilute perchloric acid, whose concentration with respect to each component was known. Since the lanthanum ion was absorbed much more strongly than the ruthenium complex, which in turn was absorbed much more strongly than hydrogen ion, the complex moved as a discrete band ahead of the lanthanum and essentially saturated the resin in the region of the band. When the band was finally eluted from the column, the ruthenium and hydrogen ion concentrations were measured (lanthanum was shown to be absent) and the charge per ruthenium atom was determined from the formula

$$\text{charge per atom} = \frac{3(\text{La moles/l. in elutriant})}{(\text{g.-atoms of Ru/l. in eluate})}$$

No correction was made for hydrogen ion since its concentration was the same in both the elutriant and eluate.

Measurements of the charge per atom were made on the dichloro, trichloro, and tetrachloro complexes by the first method. With the trichloro and tetrachloro complexes, solutions of pure $\text{RuNOCl}_3(\text{H}_2\text{O})_2$ and $\text{HRuNOCl}_4(\text{H}_2\text{O})$ were analyzed for ruthenium, and known volumes of these solutions were passed through columns of Dowex 1-X4 (40–100 mesh) initially in the chloride form. The columns were washed with water, and the amount of chloride ion was determined in the eluate from the column. $\text{RuNOCl}_3(\text{H}_2\text{O})_2$: mg.-atoms of Ru absorbed, 0.0328; mg.-atoms of Cl^- liberated, 0.0457; charge per atom, -1.39 .

$[\text{RuNOCl}_4\text{OH}]^{-2}$: mg.-atoms of Ru absorbed, 0.0226; mg.-atoms of Cl^- liberated, 0.0435; charge per atom, -1.93 .

Since the dichloro complex could only be obtained in acid solutions, a modified procedure was used. A solution of $\text{RuNOCl}_3(\text{H}_2\text{O})_2$ obtained by elution of the complex from a cation-exchange column with $1 M \text{ HClO}_4$ was stirred with Dowex 1-X4 anion resin in the hydroxide form until the pH of the solution rose to 2.63. The solution was filtered to remove the resin and analyzed for ruthenium, and a 10-ml. portion was passed through a column of Dowex 50-X8 in the hydrogen form. The column was washed with water, and the acid in the eluate was determined. A solution of perchloric acid was adjusted to pH 2.63 and a 10-ml. volume was titrated; the number of equivalents found was subtracted from the total acid in the eluate from the column to obtain the amount of acid liberated by the complex. $\text{RuNOCl}_3(\text{H}_2\text{O})_2$: mg.-atoms of Ru absorbed, 0.0833; mg.-atoms of H^+ in eluate, 0.1122; mg.-atoms of H^+ in original solution, 0.0228; charge per atom, $+1.07$.

The charge per atom of the monochloro complex $\text{RuNOCl}(\text{H}_2\text{O})_4^{+2}$ was determined by the second method. The complex was isolated as described previously and then reabsorbed on a column of Dowex 50-X8 (200–400 mesh) in the hydrogen form. The column was eluted with a solution which was $0.0357 M$ in lanthanum perchlorate and $0.0582 M$ in perchloric acid. Three fractions of the ruthenium band were collected. Each was analyzed for ruthenium, and the visible spectrum examined. Lanthanum was shown to be absent in each solution by failure to obtain a precipitate with oxalic acid. The hydrogen ion concentration of each solution was assumed to be the same as that of the elutriant, since the pH was the same. The concentrations of Ru in the eluates were 0.0576, 0.0524, and 0.0495 mg.-atom/l. in fractions 1–3, respectively, which corresponds to charges per atom of 1.86, 2.04, and 2.16, respectively.

Measurement of Charge Per Species.—The charge per species was measured by a modification of the method of Connick and Cady.⁸ The method consists of measuring the distribution of the species in question between an ion-exchange resin and an aqueous phase as a function of the concentration of some other ion of known charge in the aqueous phase. The distribution of the cationic species was measured between Dowex 50-X8 and an aqueous phase containing varying hydrogen ion concentrations. The distribution of the anionic complexes was measured between Dowex 1-X8 and the solution as a function of perchlorate ion concentration.

Each of the species isolated from ion-exchange columns by elution with perchloric acid was absorbed on a batch of ion-exchange resin of a type appropriate to the charge on the ion. Each batch of resin was then equilibrated with successively higher concentrations of perchloric acid, and the concentrations of ruthenium in the aqueous and resin phase were determined after each equilibration. The usual precautions were taken to establish that sufficient time was allowed for equilibrium to be attained.

The charge per species was then determined by fitting the equation $\log D = \log K - Z \log X$ to the data; where D is the relative distribution ratio of the ruthenium species, K is a constant, Z is the charge per species, and X represents the hydrogen ion concentration in measurements with cations and the perchlorate ion in measurements with anions. The above equation is derivable from conditions for equilibrium in ion-exchange reactions where activity coefficients are assumed to be unity. The quantity D is the ratio of g.-atoms of ruthenium in the total resin phase to g.-atoms of ruthenium per l. of solution. Accurate knowledge of the weight of dry resin necessary for calculation of the distribution ratio as usually expressed was not needed in the present work since the same batch of resin was used throughout a given sequence of measurements. Failure to include the weight of the resin in the calculations will only affect K but not Z .

In distribution measurements with the cationic species the ruthenium and acid concentrations of the aqueous phases were determined after each equilibration while the amount of ruthenium in the resin phase was found by difference. Ruthenium

(8) H. H. Cady and R. E. Connick, *J. Am. Chem. Soc.*, **80**, 2646 (1958).

concentrations in these solutions were measured spectrophotometrically as RuO_4 .

Measurements with the anionic species were made with complexes labeled with Ru^{106} . Equilibrations of the resin and solutions were made in a small fritted tube which permitted both the solution and the resin phase to be counted for Ru^{106} γ activity after each equilibration. The phases were mixed by a slow stream of nitrogen passed through the frit and separated by vacuum filtration. The resin phase was counted by placing the entire tube in a well-type γ scintillation counter; aliquots of solution were counted in the same counter.

Attempts made to study the distribution of the anionic complexes between the resin phase and hydrochloric acid were abandoned because the complexes were absorbed so strongly by the resin that reliable measurements could be made only at very high chloride concentrations. Reliable measurements were made with perchlorate concentrations between 0.05 and 1 M with the tetrachloro complex and between 0.2 and 1 M with the pentachloro complex.

Distribution studies were also made with the trichloro complex between the anion-exchange resins and solutions of different concentration of hydrogen, chloride, and nitrate ions in an attempt to discover the mechanism by which this apparently neutral species is absorbed by the resin.

Results

The spectra of the complexes isolated by ion exchange are shown in Fig. 1, and data concerning the positions of the absorption maxima and the extinction coefficients at the maxima are given in Table I. The spectrum of each complex was independent of the acid used for elution, HCl , HNO_3 , or HClO_4 , which indicates the complexes were not altered during elution and that they were the same complexes that existed in the original HCl solutions. The spectrum of the pentachloro complex was also identical with the spectra of $\text{K}_2\text{RuNOCl}_5$ and $(\text{NH}_4)_2\text{RuNOCl}_5$ while the spectrum of the trichloro complex was identical with that of $\text{RuNOCl}_3(\text{H}_2\text{O})_2 \cdot 3\text{H}_2\text{O}$.

TABLE I
SPECTRAL CHARACTERISTICS OF RuNO CHLORO COMPLEXES

Complex	λ_{max} , $m\mu^a$	ϵ_{max}^b
RuNOCl_5^{-2}	519	50.4
$\text{RuNOCl}_4(\text{H}_2\text{O})^-$	500	50.2
$\text{RuNOCl}_3(\text{H}_2\text{O})_2$	480	49.0
$\text{RuNOCl}_2(\text{H}_2\text{O})_3^+$	448	47.9
$\text{RuNOCl}(\text{H}_2\text{O})_4^{+2}$	420 (sh)	...

^a Wave length of absorption maximum. ^b Molar extinction coefficient at the absorption maximum.

The titration curves for $\text{RuNOCl}_3(\text{H}_2\text{O})_2$, $\text{HRuNOCl}_4(\text{H}_2\text{O})$, and $\text{H}_2\text{RuNOCl}_5$ are shown in Fig. 2. The curve for the trichloro complex shows the presence of two dissociable hydrogen ions per molecule whose dissociation constants were calculated to be $1.12 \pm 0.12 \times 10^{-5}$ and $3.40 \pm 0.33 \times 10^{-8}$. The curve for the tetrachloro complex indicated the presence of one completely dissociated hydrogen ion and a second with a dissociation constant of $9.5 \pm 0.3 \times 10^{-7}$, while the pentachloro complex is seen to possess two strongly acidic protons.

Data concerning the chloride-to-ruthenium ratio, the charge per atom, and the charge per species of the

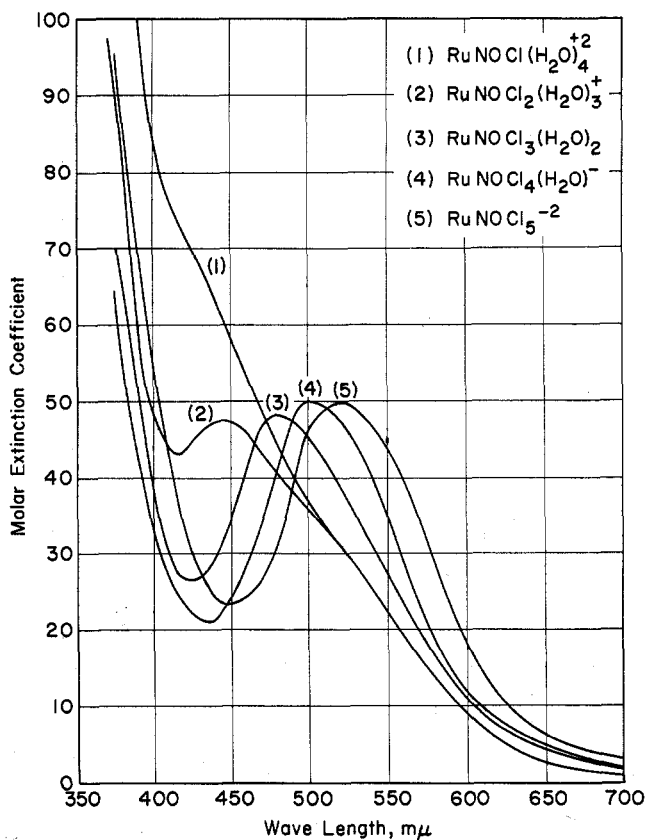


Fig. 1.—Spectra of nitrosylruthenium chloro complexes.

complexes are shown in Table II. The $\text{Cl}:\text{Ru}$ ratio and charge per species were determined directly with solutions isolated by ion-exchange elutions as were values of the charge per atom for the mono- and dichloro complexes. Values for the charge per atom of the tri- and tetrachloro complexes were determined with solutions of $\text{RuNOCl}_3(\text{H}_2\text{O})_2 \cdot 3\text{H}_2\text{O}$ and $\text{HRuNOCl}_4(\text{H}_2\text{O})$, respectively, while that of the pentachloro complex was inferred from the composition of its potassium and ammonium salts.

TABLE II

Complex	Mole ratio, $\text{Cl}:\text{Ru}$	Charge/ Ru atom	Charge/ species
RuNOCl_5^{-2}	5.00	-2.0	-1.72
$\text{RuNOCl}_4(\text{H}_2\text{O})^-$	4.03	-1.93	-0.88
$\text{RuNOCl}_3(\text{H}_2\text{O})_2$	3.00	-1.39	...
$\text{RuNOCl}_2(\text{H}_2\text{O})_3^+$	1.97	+1.07	+0.94
$\text{RuNOCl}(\text{H}_2\text{O})_4^{+2}$	1.03	+2.02	+1.71

Curves of the distribution ratios of the various complexes between ion-exchange resins and aqueous perchloric acid solutions, from which values of the charge per species were calculated, are shown in Fig. 3 and 4. All points were used in the calculations except in measurements with RuNOCl_5^{-2} where a definite curvature at the higher perchloric acid concentrations indicated a change in the ion to one of lower charge; the first three points were chosen as representative of the charge on the ion at lower acid concentrations.

The distribution ratio of $\text{RuNOCl}_3(\text{H}_2\text{O})_2$ between

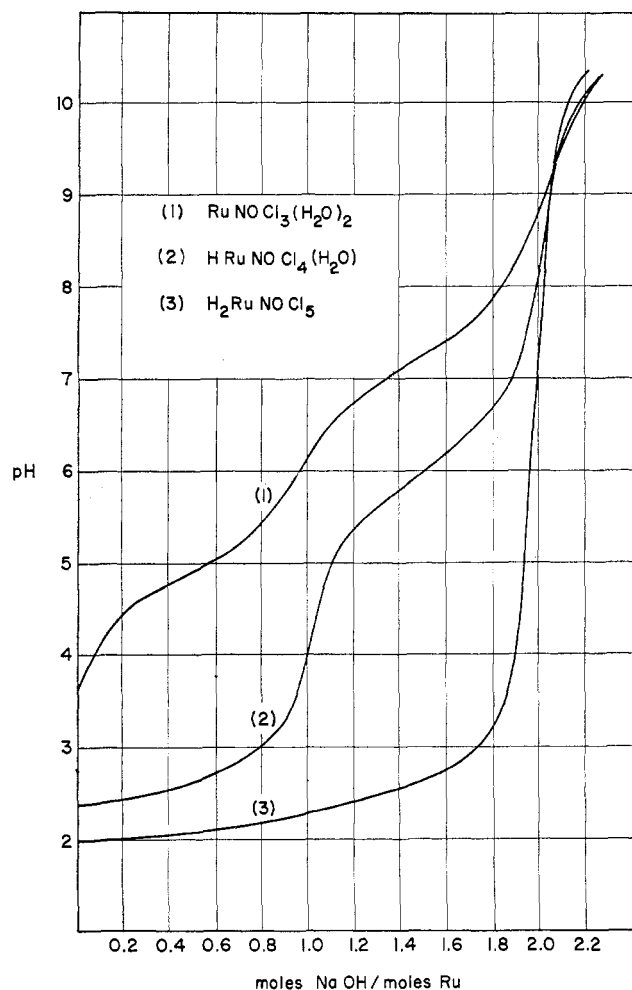
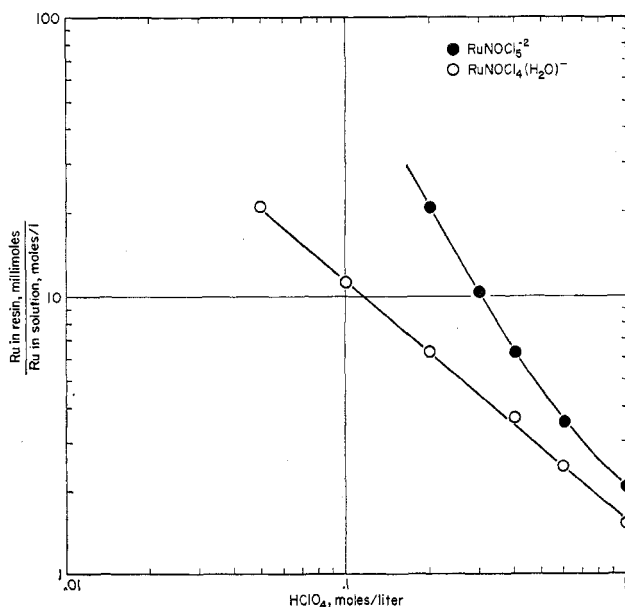
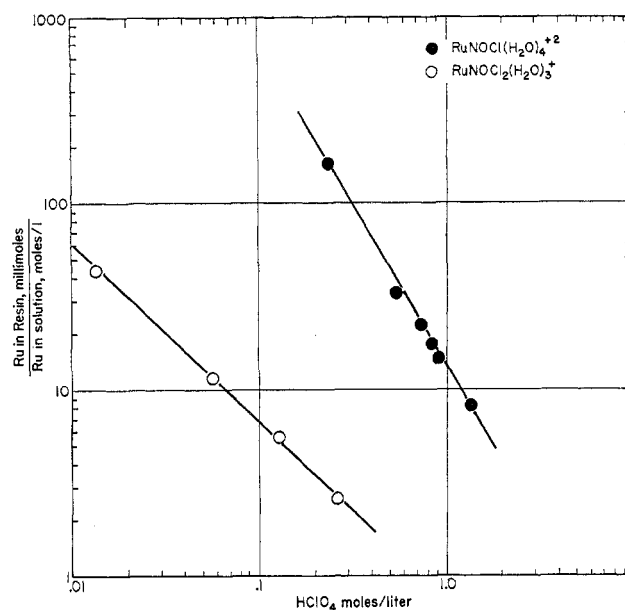


Fig. 2.—Titration curves of nitrosylruthenium chloro complexes.

Fig. 3.—Relative distribution ratios of anionic complexes between Dowex 1-X8 and HClO_4 .

anion-exchange resins and solutions of nitrate and chloride ions was virtually independent of the anion and the hydrogen ion concentrations. The distribution ratio varied only from 9.00 to 9.75 when the hy-

Fig. 4.—Relative distribution ratios of cationic complexes between Dowex 50-X8 and HClO_4 .

drogen ion concentration was varied from 0.04 to 0.01 M in solutions containing HCl and NaCl with a total chloride concentration of 0.1 M . Variations of the concentration of HCl , in salt-free solutions, from 0.04 to 0.10 M caused the distribution ratio to vary from 8.05 to 7.90. Similar results were obtained with solutions containing nitrate ions.

Characterization of Complexes.—The common characteristics of nitrosylruthenium complexes reported previously are the presence of an extremely stable Ru-NO group which bears a charge of $+3$ and that ruthenium in these complexes has a coordination number of six.^{2a,9} The principal chemistry of nitrosylruthenium involves the exchange of ligand groups on five of the six possible coordination positions, the Ru-NO bond being so stable that it survives treatment with boiling solutions of 8 M nitric acid or concentrated base.^{2a} It is not surprising that the Ru-NO group was not destroyed by the comparatively mild conditions employed in the present work.

Confirmation of the presence of the nitrosyl group in the penta-, tetra-, and trichloro complexes was obtained by elemental analysis of the salts $\text{K}_2\text{RuNOCl}_5$, $(\text{NH}_4)_2\text{RuNOCl}_6$, $\text{Ag}_2\text{RuNOCl}_4\text{OH}$, and $\text{RuNOCl}_3(\text{H}_2\text{O})_2 \cdot 3\text{H}_2\text{O}$ (see Experimental section). The infrared spectrum of each of these compounds showed an intense band between 1800 and 1920 cm^{-1} that is characteristic of the NO group. The presence of the NO group in the mono- and dichloro complexes was inferred from the fact that these complexes were converted into the higher chloro complexes simply by heating in a 6 M HCl solution, a condition that could not introduce the NO group.

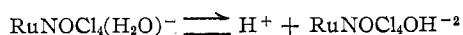
Specific Complexes. RuNOCl_5^{2-} .—The mole ratio of chloride to ruthenium determined on the complex shows that the species is the pentachloro complex.

The charge per species of -1.72 is sufficiently close to assume the actual value to be -2 . The agreement between the charge per atom and the charge per species shows that the complex is monomeric, since a polymeric complex would have a larger charge per species than charge per atom.

Further evidence for the above formulation was given by the titration curve (Fig. 2) of the acid $\text{H}_2\text{RuNOCl}_3$, which showed the presence of two highly dissociated hydrogen ions per ruthenium atom.

$\text{RuNOCl}_4(\text{H}_2\text{O})^-$.—The mole ratio of chloride to ruthenium found in the complex and the composition of the silver salt $\text{Ag}_2\text{RuNOCl}_4(\text{OH})$ shows that this is a tetrachloro complex.

The charge per Ru atom determined by ion-exchange methods and the composition of the silver salt both indicated that the actual charge per atom was -2 . The charge per species, obtained by ion-exchange methods, indicated the actual charge per species to be -1 . This apparent anomaly was clarified by titration of the acid $\text{HRuNOCl}_4(\text{H}_2\text{O})$, which showed the presence of two dissociable hydrogen ions per ruthenium atom, one characteristic of a nearly completely dissociated hydrogen ion, while the dissociation constant for the second was 9.5×10^{-7} . The dissociation of the second hydrogen ion can be represented by the equation



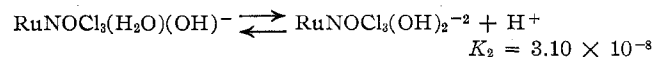
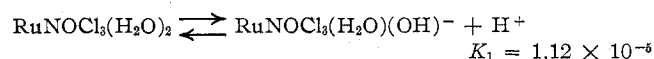
The aquo form of the complex is therefore stable in acid media, while the hydroxo form is the predominant species in neutral or basic solutions. Since the charge per Ru atom was determined by absorption on an ion-exchange resin from a neutral solution, the charge per atom should be -2 . The charge per species was determined in acidic solutions where the charge per species should be -1 .

Although the silver salt of this complex was precipitated from acidic solution, the salt of the hydroxo form was obtained; this can be explained by the greater insolubility of the salt of the hydroxo form than that of the salt of the aquo form. The infrared spectrum of $\text{Ag}_2\text{RuNOCl}_4\text{OH}$ exhibited bands at 1880 and 3400 cm^{-1} due to the NO and OH groups, respectively.

$\text{RuNOCl}_3(\text{H}_2\text{O})_2$.—The mole ratio of chloride to ruthenium in the complex isolated by ion exchange and the composition of the compound $\text{RuNOCl}_3(\text{H}_2\text{O})_2 \cdot 3\text{H}_2\text{O}$ show that the complex contains three chloride ions per ruthenium atom. The molecular weight, 298 , determined from the freezing point depression is sufficiently close to the calculated value of 328 to demonstrate the complex to be monomeric in aqueous solutions. The low result obtained for the molecular weight may be due in part to the dissociation of the complex and in part to difficulty in purifying the compound by crystallization because of its high solubility in water.

The charge per atom of -1.39 , obtained by absorbing the complex on an anion-exchange column from a neutral solution and measuring the chloride liberated,

indicates that the complex can behave as an anion and that more than one anionic species is absorbed. The titration curve, which showed the presence of two weakly acidic protons per ruthenium atom, suggests that the following reactions are involved.



The evidence above indicates two water molecules are firmly coordinated to the ruthenium in this complex and that the solid compound which has been frequently formulated as $\text{RuNOCl}_3 \cdot 5\text{H}_2\text{O}$ should more properly be written $\text{RuNOCl}_3(\text{H}_2\text{O})_2 \cdot 3\text{H}_2\text{O}$. Further evidence for this view was obtained from the infrared spectrum of this compound which exhibited, in addition to the sharp NO band at 1920 cm^{-1} , sharp bands at 1600 and 3400 cm^{-1} characteristic of waters of hydration and a broad band centered at 2900 cm^{-1} characteristic of hydrogen-bonded substances such as carboxylic acids, indicating the presence of two different kinds of water in the compound.

The absorption of the trichloro complex by anion-exchange resins would appear to be due to the absorption of the anionic hydroxo complexes. This is undoubtedly true when the complex is absorbed from neutral solutions, since it displaces chloride ion from the resin. However, in acid solutions the distribution coefficients of the trichloro complexes are virtually independent of both the hydrogen ion and nitrate or chloride concentrations, a result completely at variance with the absorption of these anionic species. It is possible that the trichloro complex is absorbed by anion resins from acidic media by forming an outer-sphere complex with anions in the resin phase.

$\text{RuNOCl}_2(\text{H}_2\text{O})_3^+$.—The mole ratio of Cl to Ru, the charge per Ru atom, and the charge per species are all in agreement with the proposed formula of a monomeric complex containing two chloride ions per ruthenium and bearing a charge of $+1$. The three aquo groups associated with the complex are assumed on the basis of a coordination number of six for ruthenium in its nitrosyl complexes, a fact borne out by our study of the three higher chloro complexes. A further indication of the validity of this formulation is the regular manner in which the visible absorption spectra of this series of complexes change upon the replacement of a chloride ion by an aquo group in the coordination sphere (Fig. 1). Since the dichloro complex continues the trend established by the three higher complexes, it is reasonable to assume the same process to be involved.

$\text{RuNOCl}_4(\text{H}_2\text{O})_4^{2+}$.—The mole ratio of chloride to ruthenium, the charge per ruthenium atom, and the charge per species are all consistent with a monomeric complex containing one chloride ion per ruthenium atom and bearing a charge of $+2$. The four aquo groups associated with the complex were assumed for the same reasons discussed under the dichloro complex.

Other Complexes.—Four of the five monomeric complexes isolated in the present work are capable of exhibiting geometric isomerism, but no evidence for such isomerism was found. Changes were sought in the visible absorption spectra of complexes as they were eluted from ion-exchange columns; failure to find such changes does not rule out the existence of isomers, but may be due to the insensitivity of the spectra to variations in structure.

Two other cationic species were observed during the study. One of these was absorbed by cation-exchange resins so tenaciously that it could only be removed by drastic conditions, while the other was eluted with very dilute acid. The former was probably $\text{RuNO}(\text{H}_2\text{O})_5^+$,³

since its behavior was similar to that observed for the pentaquo complex in a study of the nitrato complexes of nitrosylruthenium.⁹ The second species had an apparent chloride to ruthenium mole ratio of 1.64 and a spectrum different from either the dichloro or the monochloro complex. This species may be a polymeric complex, but we were not able to obtain sufficient quantities for a complete characterization.

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CONTRIBUTION FROM THE EVANS LABORATORY OF CHEMISTRY,
THE OHIO STATE UNIVERSITY, COLUMBUS 10, OHIO

Boron Heterocycles. II. Reactions of Diborane with Ethanedithiol; Preparation and Properties of 1,3,2-Dithiaborolane¹

By B. Z. EGAN, S. G. SHORE, AND J. E. BONNELL

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Depending upon the mole ratio of reactants, $\text{H}_2\text{BSCH}_2\text{CH}_2\text{SBH}_2$, $(\text{CH}_2\text{S})_2\text{BH}$, and $(\text{CH}_2\text{S})_2\text{BSCH}_2\text{CH}_2\text{SB}(\text{SCH}_2)_2$ are prepared through the reaction of B_2H_6 with $\text{HSCH}_2\text{CH}_2\text{SH}$ in ether. Infrared spectra indicate that $\text{H}_2\text{BSCH}_2\text{CH}_2\text{SBH}_2$ and $(\text{CH}_2\text{S})_2\text{BH}$ are not simple, molecular species in the condensed state, but are associated through intermolecular boron-sulfur coordinate bonds. No evidence is observed for hydrogen bridges between boron atoms. In the vapor phase $(\text{CH}_2\text{S})_2\text{BH}$ is a monomer which does not disproportionate at elevated temperatures (90°). The addition compounds $(\text{CH}_3)_3\text{NBH}_2\text{SCH}_2\text{CH}_2\text{SBH}_2\text{N}(\text{CH}_3)_3$, $(\text{CH}_2\text{S})_2\text{HBN}(\text{CH}_3)_3$, and $(\text{CH}_2\text{S})_2\text{HBP}(\text{CH}_3)_3$ are stable *in vacuo* at room temperature. Oxygen bases such as ether do not cause significant dissociation of boron-sulfur coordinate bonds in $[\text{H}_2\text{BSCH}_2\text{CH}_2\text{SBH}_2]_x$ and $[(\text{CH}_2\text{S})_2\text{BH}]_x$.

Introduction

The present investigation is part of a systematic program to study the preparation and properties of selected boron heterocycles. Of particular interest is the effect of substituent ring atoms on the apparent stability of the heterocycle and the nature of the boron as an electron pair acceptor. A previous investigation¹ showed that the heterocycle 1,3,2-dioxaborolane, $(\text{CH}_2\text{O})_2\text{BH}$, is a monomer in the vapor phase. It is a weak Lewis acid which disproportionates readily into more symmetrical species. Although a variety of alkylthioboranes have been reported,²⁻⁵ the effect of sulfur on boron as a Lewis acid and the ability of boron to participate in hydrogen bridge bonds had not been established. In view of these considerations, we have prepared and examined some sulfur-substituted boron compounds which are derived from the reaction of diborane with ethanedithiol.

Experimental

(A) **Materials.**— B_2H_6 was obtained from the Callery Chemical Co.; it was purified by trap-to-trap distillation at -120° . $\text{HSCH}_2\text{CH}_2\text{SH}$ was obtained from the Aldrich Chemical Co.; it was distilled at room temperature *in vacuo*. Commercial $\text{N}(\text{CH}_3)_3$ was dried over CaH_2 and distilled *in vacuo*. $\text{P}(\text{CH}_3)_3$ was prepared by treating CH_3MgI in ether with PCl_3 .⁶ It was isolated as the solid $((\text{CH}_3)_3\text{PAgI})_4$ complex. Gaseous $\text{P}(\text{CH}_3)_3$ was obtained by heating the solid, anhydrous complex to 100° *in vacuo*. $(\text{C}_2\text{H}_5)_2\text{O}$ and tetrahydrofuran were distilled from LiAlH_4 *in vacuo*.

(B) **Apparatus.**—Standard high vacuum techniques were used for handling air-sensitive materials.⁷ Outside of the vacuum line, these materials were handled in a drybox under a dry nitrogen atmosphere. The reaction system depicted in Fig. 1 was used for preparing large quantities (30–50 mmoles) of $\text{H}_2\text{BSCH}_2\text{CH}_2\text{SBH}_2$, $(\text{CH}_2\text{S})_2\text{BH}$, and $(\text{CH}_2\text{S})_2\text{BSCH}_2\text{CH}_2\text{SB}(\text{SCH}_2)_2$. The 2-l. metal bulb was of sufficient volume to accommodate gaseous reactants and products; the system could be closed off at the valve and removed from the vacuum line to a safety area where the reaction was allowed to take place. Perkin-Elmer Models 21, 221-g, and 337 recording spectrophotometers were used to obtain infrared spectra. The instruments were calibrated with polystyrene. Mass spectra were obtained on a Consolidated Engineering Model 21-32 mass spectrometer.

(C) **Ethylenedithiobisborane.** (1) **Synthesis.**— H_2BSCH_2 —

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