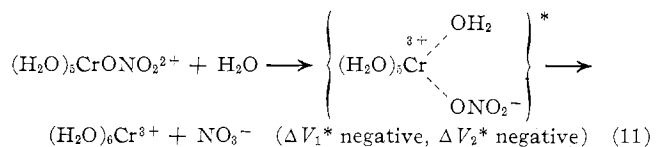
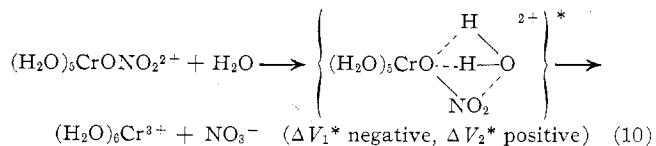
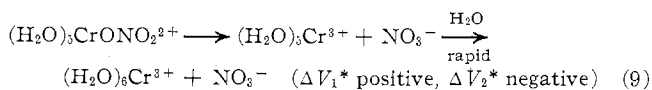
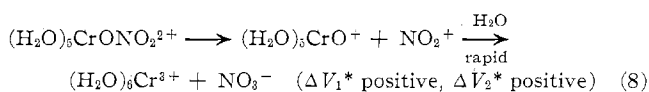


with HF separation<sup>8</sup>) and in the exchange of  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  with oxygen-18-labeled solvent,<sup>24</sup> in solutions containing about 0.1 *M* acid.

In the above discussion it has been assumed that the mechanism of aquation of  $\text{Cr}(\text{H}_2\text{O})_5\text{NO}_3^{2+}$  is the same as for the other  $\text{Cr}(\text{H}_2\text{O})_5\text{X}^{2+}$ , but the possibility of O-N rather than Cr-O bond breaking must be considered.<sup>3</sup> The measured volume of activation  $\Delta V^*$  for the aquation of  $\text{Cr}(\text{H}_2\text{O})_5\text{NO}_3^{2+}$  can be expressed as the sum of an intrinsic part  $\Delta V_1^*$  which will be positive if bond-breaking predominates and negative if bond making is the more important and an "electrostrictive" part  $\Delta V_2^*$  which will be positive if desolvation occurs in the transition state through dissipation of charge density and negative if extra charge is developed in going to the transition state. Four schematic mechanisms can be considered (eq 8-11), representing, respectively,  $\text{S}_{\text{N}}1$  at N,  $\text{I}_{\text{d}}$  ( $\text{S}_{\text{N}}1$ ) at Cr,  $\text{S}_{\text{N}}2$  at N, and  $\text{I}_{\text{a}}$  ( $\text{S}_{\text{N}}2$ ) at Cr.



The observed value of  $\Delta V^*$  is approximately  $-13 \text{ cm}^3 \text{ mol}^{-1}$  (Table III), and hence mechanism 8 is

(24) J. P. Hunt and R. A. Plane, *J. Amer. Chem. Soc.*, **76**, 5960 (1954).

obviously eliminated.  $|\Delta V_1^*|$  is of the order of  $2 \text{ cm}^3 \text{ mol}^{-1}$  in  $\text{Co}(\text{NH}_3)_5\text{X}^{n+}$  aquations<sup>18</sup> but  $|\Delta V_2^*|$  is much larger. Also the activation volume found<sup>18</sup> for the aquation of  $\text{Co}(\text{NH}_3)_5\text{NO}_3^{2+}$ , which proceeds by an extreme  $\text{I}_{\text{d}}$  mechanism with Co-O bond fission,<sup>25</sup> is about  $7 \text{ cm}^3 \text{ mol}^{-1}$  less negative (*i.e.*,  $-6 \text{ cm}^3 \text{ mol}^{-1}$ ) than for  $\text{Cr}(\text{H}_2\text{O})_5\text{NO}_3^{2+}$ . Hence mechanism 11 is to be preferred over 9 or 10, *i.e.*, it is the Co-O bond which is broken, and associative activation by the incoming water molecule is probably important.

The possibility remains that the nitratochromium(II) complex contains bidentate  $\text{NO}_3^-$  and that reversible ring opening precedes the rate-determining step in aquation. This could explain the deviations of this complex in linear free energy relationships<sup>3</sup> and perhaps account for the chloride-incorporation phenomenon described above. However, such ring-opening and -closing processes have not been investigated but they would have to be very rapid (half-periods of the order of 1 min or less), since they have not been detected by conventional kinetic methods,<sup>10,12</sup> and such rapid reactions are not characteristic of Cr(III) complexes. Anomalies in supposed linear free energy relationships can be ascribed to differences in the relative importance of bond making *vis à vis* bond breaking; there seems to be no reason why these factors should be exactly the same throughout a given series of reactions, and indeed it is probably unreasonable to expect linear free energy relationships to be strictly valid except when their slopes are near unity, *i.e.*, for  $\text{I}_{\text{d}}$  mechanisms.

**Acknowledgments.**—We thank the International Nickel Co. of Canada for a fellowship (to W. E. J.), the National Research Council of Canada for further financial support, Dr. H. W. Baldwin for permission to refer to his results in advance of publication, Dr. C. H. Langford for stimulating discussions, and Mr. B. D. Gaudette for conducting some preliminary experiments.

(25) W. E. Jones, R. B. Jordan, and T. W. Swaddle, *Inorg. Chem.*, **8**, 2504 (1969).

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## Conversion of Hexaammineruthenium(III) to Sulfamatopentaammineruthenium(III) by Attack on Coordinated Ammonia

By J. N. ARMOR AND H. TAUBE\*

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When oxygen is passed through a solution containing  $\text{Ru}(\text{NH}_3)_6^{3+}$  and  $\text{S}_2\text{O}_8^{2-}$  or  $\text{SPO}_3^{3-}$ ,  $\text{Ru}(\text{NH}_3)_5\text{NH}_2\text{SO}_3^+$  is produced in good yield. Comparison of the infrared spectra of salts containing this ion or its protonated form with sulfamate complexes of cobalt(III) amines which are known to be N bonded confirms that the new species are N bonded as well. The value of  $\text{p}K_{\text{a}}$  for  $\text{Ru}(\text{NH}_3)_5\text{NH}_2\text{SO}_3^+$  at  $25^\circ$  and  $\mu = 0.10$  was measured as 2.6. It is believed that the sulfamate is produced by the transfer of sulfur to coordinated amide, with subsequent oxidation by  $\text{O}_2$ .

### Introduction

Sulfamato complexes have been prepared by the direct reaction of sulfamate with a metal ion.<sup>1-3</sup>

(1) L. L. Po and R. B. Jordan, *Inorg. Chem.*, **7**, 526 (1968).

(2) R. J. Balahura and R. B. Jordan, *J. Amer. Chem. Soc.*, **92**, 1533 (1970). (Both N- and O-linked isomers of formamidopentaamminecobalt(III) are described.)

While pursuing our interest in the interaction of sulfur ligands with ruthenium amines, we observed the formation of a sulfamate complex by a novel route. Thiosulfate or thiophosphate in the presence of  $\text{O}_2$  and  $\text{Ru}(\text{NH}_3)_6^{3+}$  converts the latter in good yield to

(3) A. J. Saraceno, Ph.D. Thesis, University of Notre Dame, 1958.

$\text{Ru}(\text{NH}_3)_5\text{NHSO}_3^+$ . The method of preparation of this species, its characterization, and results on the acid dissociation constant are described in this paper.

### Experimental Section

**[Ru(NH<sub>3</sub>)<sub>5</sub>S<sub>2</sub>O<sub>3</sub>]Cl.**—As a step in characterizing the sulfamato complex, it was necessary to prepare and characterize  $\text{Ru}(\text{NH}_3)_5\text{S}_2\text{O}_3^+$ . In following the original procedure of Lever and Powell<sup>4</sup> the thiosulfate complex was produced in only low yield, but much higher yields were obtained by the direct reaction of  $\text{S}_2\text{O}_3^{2-}$  with  $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{3+}$  in an argon atmosphere.<sup>5</sup> A solution containing  $\text{S}_2\text{O}_3^{2-}$  (0.21 M) and  $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{3+}$  ( $2.5 \times 10^{-2}$  M) was prepared and deaerated using Ar. The solution, initially yellow, became deep red in a few minutes. Ion-exchange separation performed after 20 min indicated that conversion to  $\text{Ru}(\text{NH}_3)_5\text{S}_2\text{O}_3^+$  was 85% complete in that time. (After longer periods of time the thiosulfate complex decomposes, and a green, highly charged species is among the products formed.)

The thiosulfate complex was isolated on a cation-exchange resin and eluted with 0.5 M LiCl or NaI. Solid formed on concentrating the eluent by rotary evaporation. The solid was freed from alkali salt impurity using absolute ethanol which dissolves alkali halide but not the ruthenium salt. *Anal.* Calcd for  $[\text{Ru}(\text{NH}_3)_5\text{S}_2\text{O}_3]\text{Cl}$ : Ru, 30.3; N, 21.0; H, 4.5; Cl, 10.6; S, 19.2. Found: Ru, 30.4; N, 19.2; H, 4.2; Cl, 10.8; S, 19.6.

**[Ru(NH<sub>3</sub>)<sub>5</sub>NHSO<sub>3</sub>]X (Where X<sup>-</sup> = Cl<sup>-</sup> or I<sup>-</sup>).**—A solution (20 ml) 0.015 M in  $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$  and 0.12 M in  $\text{Na}_2\text{S}_2\text{O}_3$  was prepared and oxygen was passed through for 26 hr in the dark. At this point the reaction mixture was diluted to 100 ml and charged onto a cation-exchange column (Li<sup>+</sup> form for the chloride salt). On washing with water a violet band was removed, and the material desired which comprised a yellow band was eluted with 0.5 M LiCl. Using rotary evaporation, a dry solid was obtained. This was suspended in absolute ethanol to dissolve the LiCl present, and the yellow solid material was collected by filtration; yield >60%. *Anal.* Calcd for  $[\text{Ru}(\text{NH}_3)_5\text{NHSO}_3]\text{Cl}$ : Ru, 31.9; N, 26.5; H, 5.09; Cl, 11.2; S, 10.1. Found: Ru, 32.5; N, 26.5; H, 4.81; Cl, 12.0; S, 9.9.

**[Ru(NH<sub>3</sub>)<sub>5</sub>NH<sub>2</sub>SO<sub>3</sub>]Br<sub>2</sub>.**— $[\text{Ru}(\text{NH}_3)_5\text{NHSO}_3]\text{Cl}$  (0.16 mmol) was dissolved in a minimum amount of water (~3 ml). The solution was acidified with 1 M HBr, and then concentrated HBr was added to precipitate the bromide salt. *Anal.* Calcd for  $[\text{Ru}(\text{NH}_3)_5\text{NH}_2\text{SO}_3]\text{Br}_2$ : Ru, 23.0; N, 19.0; H, 3.88; Br, 36.2; S, 7.25. Found: Ru, 23.0; N, 19.5; H, 4.25; Br, 36.3; S, 7.34.

**[Co(NH<sub>3</sub>)<sub>5</sub>NHSO<sub>3</sub>]Cl.**—One-tenth gram of  $[\text{Co}(\text{NH}_3)_5\text{NH}_2\text{SO}_3]\text{Cl}_2$ <sup>6</sup> (0.37 mmol) was dissolved in 10 ml of aqueous ammonia. The solution was saturated with solid  $\text{NH}_4\text{Cl}$  and allowed to cool overnight. Violet crystals of  $[\text{Co}(\text{NH}_3)_5\text{NHSO}_3]\text{Cl}$  formed which were collected by filtration and were washed with methanol and ether. The shifts in the absorbance maxima for the uv-visible spectrum of the product as compared with those of the protonated form agreed with those reported by Po and Jordan.<sup>1</sup> The unprotonated form behaved as a 1+ ion on charging it onto a cation-exchange column. (The eluent, 0.5 M NaCl, was made slightly alkaline with  $\text{Na}_2\text{CO}_3$ .)

**Other Materials.**— $\text{Na}_3\text{SPO}_3$  was obtained from Alfa Inorganics. Sulfur S<sub>8</sub> was prepared according to the method described in ref 7. Oxygen enriched in <sup>18</sup>O (92.6 at. %) was purchased from Miles Laboratories, Elkhart, Ind.

**Ion Exchange.**—Bio-Rad AG 50W-X2, 200–400 mesh in the acid form, was cleaned<sup>8</sup> prior to converting it to the lithium or sodium form. After preparing the column, the product solution was charged onto it, and the components were eluted with either NaCl or LiCl stock solutions.

### Results

**Spectra.**—Visible and uv spectra were recorded on a Cary 15 recording spectrophotometer. Infrared spectra in the 4000–650-cm<sup>-1</sup> region were recorded on a

Perkin-Elmer 237-B infrared spectrometer. A Perkin-Elmer 421 grating spectrometer was used for the region 2000–416 cm<sup>-1</sup>. Spectra were calibrated with respect to polystyrene bands at 2850, 1601, 1585, 1181, and 901 cm<sup>-1</sup>. Below 650 cm<sup>-1</sup> the bands for water vapor at 526.0, 506.9, 502.3, and 492 cm<sup>-1</sup> were used.

**Infrared Spectra.**—The infrared spectra of  $[\text{Ru}(\text{NH}_3)_5\text{S}_2\text{O}_3]\text{Cl}$  (I),  $[\text{Ru}(\text{NH}_3)_5\text{NHSO}_3]\text{Cl}$  (II),  $[\text{Co}(\text{NH}_3)_5\text{NHSO}_3]\text{Cl}$  (III),  $[\text{Ru}(\text{NH}_3)_5\text{NH}_2\text{SO}_3]\text{Cl}_2$  (IV), and  $[\text{Co}(\text{NH}_3)_5\text{NH}_2\text{SO}_3]\text{Cl}_2$  (V) are shown in Figures 1–5. Frequency assignments where offered are in

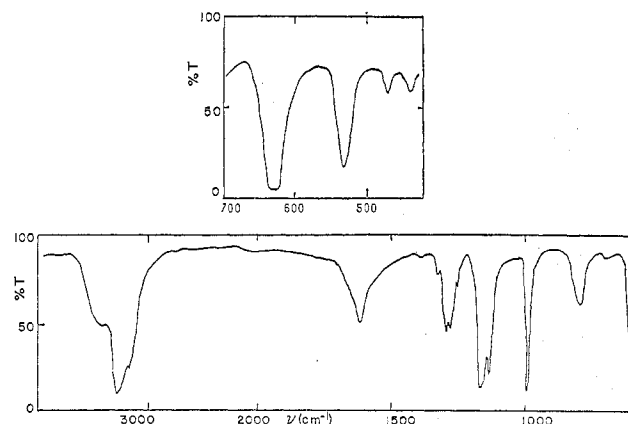


Figure 1.—Infrared spectrum of  $[\text{Ru}(\text{NH}_3)_5\text{S}_2\text{O}_3]\text{Cl}$ ,  $\nu$  (cm<sup>-1</sup>): 3420, 3285 ( $\nu_{\text{N-H}}$ ), 3160, 1620 ( $\delta_{\text{NH}_3}$  deg), 1330, 1303, 1288, 1268, 1168 ( $\nu_{\text{S-O}}$ ), 1145 ( $\nu_{\text{S-O}}$ ), 998, ( $\nu_{\text{S-O}}$ ), 810 ( $\rho_{\text{NH}_2}$ ), 630, 536, 472, 443.

analogy to those made by Saraceno.<sup>3</sup> It is clear that there are irreconcilable differences between the spectrum of the thiosulfato complex and those of the new ruthenium compounds, but that of the presumed  $[\text{Ru}(\text{NH}_3)_5\text{NHSO}_3]\text{Cl}$  (II) agrees with that of III, that of IV agrees with that of V.

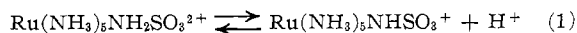
**Uv-Visible Spectra.**—The data on the complexes of present interest and on some related ones are shown in Table I.

TABLE I  
SUMMARY OF ABSORPTION CHARACTERISTICS  
FOR SOME RUTHENIUM(III) AMMINES

Compd	$\lambda_{\text{max}}$ , nm	$\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup>
$[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$	274	$473 \pm 6$
$[\text{Ru}(\text{NH}_3)_5\text{S}_2\text{O}_3]\text{Cl}$	487	$3.3 \times 10^3$
$[\text{Ru}(\text{NH}_3)_5\text{NHSO}_3]\text{Cl}$	398	$4.15 \times 10^3$
$\text{Ru}(\text{NH}_3)_5\text{NH}_2\text{SO}_3^{2+}$	280	$5.1 \times 10^2$
$\text{Ru}(\text{NH}_3)_5\text{OH}_2^{3+}$	268	752
$\text{Ru}(\text{NH}_3)_5\text{OH}^{2+}$	295	$1.5 \times 10^3$ <sup>a</sup>

<sup>a</sup> J. Stritar, Ph.D. Thesis, Stanford University, 1967.

**Determination of pK<sub>a</sub>.**—The disappearance of the intense band at 398 nm on acidifying a solution of  $\text{Ru}(\text{NH}_3)_5\text{NHSO}_3^+$  (cf. Table I) provides a method for determining pK<sub>a</sub> for the reaction



In a series of experiments at  $\mu = 0.10$  and 25° using NaCl to adjust the acidity, the pK<sub>a</sub> for reaction 1 was determined as 2.6.

**Observations on Rates.**—Semiquantitative observations were made on the rate of reaction of  $\text{Ru}(\text{NH}_3)_6^{3+}$  with  $\text{S}_2\text{O}_3^{2-}$  in the absence of O<sub>2</sub>—here the product of interest is  $\text{Ru}(\text{NH}_3)_5\text{S}_2\text{O}_3^+$ —and with O<sub>2</sub> present—the

(4) F. M. Lever and A. R. Powell, *Chem. Soc., Spec. Publ.*, No. 13, 135 (1959).

(5) Since we began our work, Lever and Powell have published their work on a new preparation similar to ours: F. M. Lever and A. R. Powell, *J. Chem. Soc. A*, 1477 (1969).

(6) This salt was kindly supplied by R. B. Jordan.

(7) P. D. Bartlett and W. Roderick, *Inorg. Syn.*, 8, 100 (1966).

(8) J. N. Armor, Ph.D. Thesis, Stanford University, May 1970.

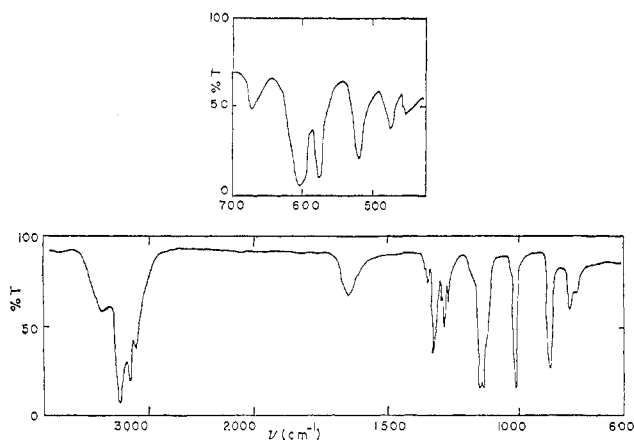


Figure 2.—Infrared spectrum of  $[\text{Ru}(\text{NH}_3)_5\text{NH}_2\text{SO}_3]\text{Cl}$ ,  $\nu$  ( $\text{cm}^{-1}$ ): 3430, 3285, 3200, 3145, 1645, 1343, 1320, 1293, 1283, 1263, 1140, 1130, 1010, 874, 800, 778, 642, 604, 576, 521, 475, 452.

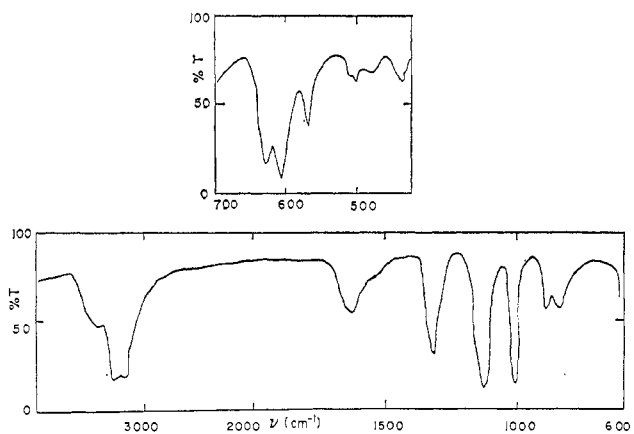


Figure 3.—Infrared spectrum of  $[\text{Co}(\text{NH}_3)_5\text{NH}_2\text{SO}_3]\text{Cl}$ ,  $\nu$  ( $\text{cm}^{-1}$ ): 3430, 3380, 3170, 1620, 1320, 1130, 1025, 885, 843, 628, 630, 608, 573, 510, 502, 482, 440.

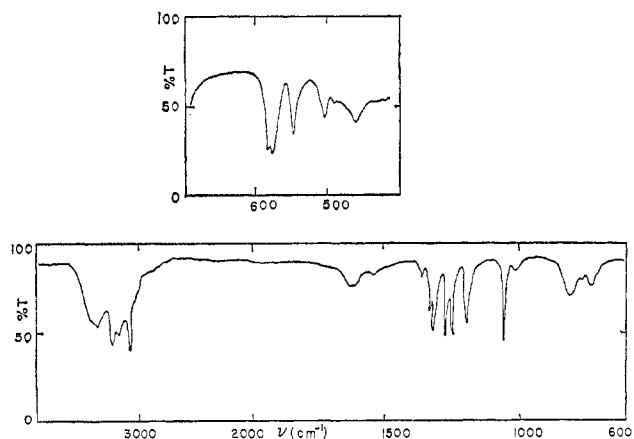


Figure 4.—Infrared spectrum of  $[\text{Ru}(\text{NH}_3)_5\text{NH}_2\text{SO}_3]\text{Br}_2$ ,  $\nu$  ( $\text{cm}^{-1}$ ): 3490, 3420, 3285, 3240, 3125, 1625, 1538, 1360, 1330, 1318, 1268, 1245, 1190, 1053, 805, 770, 725, 584, 578, 549, 505, 460.

product of interest now being the sulfamato complex. In the  $\text{O}_2$ -free systems, Ar was used as blanketing gas. The results in the  $\text{O}_2$ -free systems will be described first.

In an unbuffered system with  $\text{Ru}(\text{NH}_3)_6^{3+}$  initially at 0.029  $M$  and  $\text{Na}_2\text{S}_2\text{O}_3$  at 0.23  $M$ , after 3 days, a 12% yield of  $\text{Ru}(\text{NH}_3)_5\text{S}_2\text{O}_2^+$  was obtained with 83%

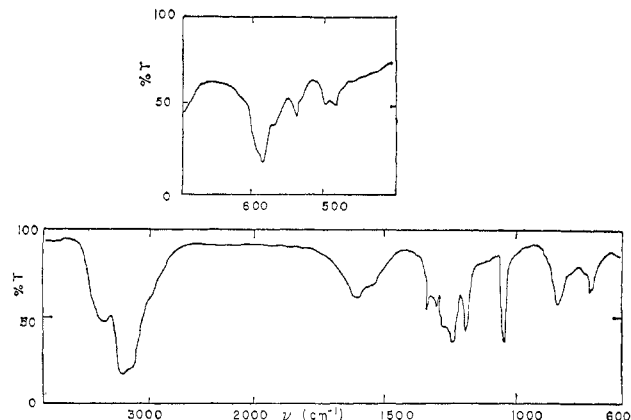


Figure 5.—Infrared spectrum of  $[\text{Co}(\text{NH}_3)_5\text{NH}_2\text{SO}_3]\text{Cl}_2$ ,  $\nu$  ( $\text{cm}^{-1}$ ): 3430, 3250, 1615, 1540, 1345, 1305, 1270, 1248, 1198, 1049, 840, 720, 585, 570, 538, 497, 483, 457 (sh).

$\text{Ru}(\text{NH}_3)_6^{3+}$  remaining unreacted.<sup>9</sup> In a buffer medium at pH 9.7 (0.025  $M$   $\text{CO}_3^{2-}$ –0.017  $M$   $\text{HCO}_3^-$ ) and with  $\text{S}_2\text{O}_3^{2-}$  and  $\text{Ru}(\text{NH}_3)_6^{3+}$  initially at 0.78 and 0.032  $M$ , after 21 hr, 54% of the  $\text{Ru}(\text{NH}_3)_6^{3+}$  was consumed, but only 15% of the total ruthenium was accounted for as the thiosulfato complex. At pH 10.2 (glycine–NaOH buffer) and with  $\text{S}_2\text{O}_3^{2-}$  and  $\text{Ru}(\text{NH}_3)_6^{3+}$  initially at 0.45 and 0.012  $M$ , the ruthenium ammine disappeared virtually completely in 10 hr (the yield of the thiosulfato complex not determined in this experiment).

The results just described show that the rate of deterioration of  $\text{Ru}(\text{NH}_3)_6^{3+}$  increases with pH in  $\text{O}_2$ -free solutions containing  $\text{S}_2\text{O}_3^{2-}$ ; the results to be described show that the rate of formation of the sulfamato complex ( $\text{O}_2$  present) also increases with pH. At pH 7.0 (0.05  $M$   $\text{HPO}_4^{2-}$ –0.1  $M$   $\text{H}_2\text{PO}_4^-$ ) and with  $\text{S}_2\text{O}_3^{2-}$  and  $\text{Ru}(\text{NH}_3)_6^{3+}$  at 0.25 and 0.035  $M$ , respectively, the latter reagent was virtually unaffected after 24 hr. In a buffer at higher pH (borax, 8.8) 7, 24, 51, and 87% of the ruthenium appeared as the sulfamato complex after 6.5, 15, 24, and 48 hr, respectively, while 94, 75, 51, and <1%  $\text{Ru}(\text{NH}_3)_6^{3+}$  remained unreacted. When  $\text{Na}_2\text{S}_2\text{O}_3$  was omitted, after 24 hr 92% of the  $\text{Ru}(\text{NH}_3)_6^{3+}$  was recovered intact. In a reaction medium using 0.78  $M$   $\text{S}_2\text{O}_3^{2-}$ , 0.032  $M$   $\text{Ru}(\text{NH}_3)_6^{3+}$  at pH 9.7 (0.025  $M$   $\text{CO}_3^{2-}$ –0.017  $M$   $\text{HCO}_3^-$ ), 11, 25, 42, and 81% of the ruthenium appeared as the sulfamato complex after 1.5, 3.5, 6.5, and 24 hr, respectively, while 85, 73, 58, and 4%  $\text{Ru}(\text{NH}_3)_6^{3+}$  remained.

In a glycine–NaOH buffer (1.67  $M$  glycine, 1.22  $M$  NaOH, pH 10.2), with  $\text{S}_2\text{O}_3^{2-}$  and  $\text{Ru}(\text{NH}_3)_6^{3+}$  at 0.45 and 0.012  $M$ , respectively, reaction was apparently complete within 10 hr, and the sulfamato complex was produced in yields in excess of 90%. The high yield of the desired product in the glycine buffer suggested this as the medium in which to attempt to determine the kinetics of the  $\text{Ru}(\text{NH}_3)_6^{3+}$ – $\text{S}_2\text{O}_3^{2-}$ – $\text{O}_2$  reaction. The formation of the sulfamato complex was followed at 390 nm as a function of time, the initial concentrations being fixed as above. Plots of  $\ln(A_\infty - A_t)$  vs. time, where  $A$  is the absorbance at 398 nm, began to exhibit some curvature after about 1 half-life (~6 hr). Using the initial slopes, the pseudo-first-

(9) In this and the other experiments,  $\text{Ru}(\text{NH}_3)_6^{3+}$  was identified by ion-exchange techniques which involved exposure of the solution to air. Thus, the possibility that an air-free sample of  $\text{Ru}(\text{NH}_3)_6^{3+}$  is reduced in whole or in part to  $\text{Ru}(\text{NH}_3)_5^{2+}$ , which is then reoxidized, is not covered by the work.

order rate constants were observed to decrease  $\sim 50\%$  when air was substituted for oxygen and to increase  $\sim 30\%$  on doubling the initial concentration of  $\text{Na}_2\text{S}_2\text{O}_3$ .

Substitution of  $\text{Na}_3\text{SPO}_3$  for  $\text{Na}_2\text{S}_2\text{O}_3$  in the unbuffered reaction medium still produced the sulfamate complex, as identified by its uv-visible spectrum, its ion-exchange behavior, and the effect of acid on the band at 398 nm. If the  $\text{SPO}_3^{3-}$  reaction was carried out in a borax buffer (pH 8.8), 10% of the ruthenium appeared as the  $\text{Ru}(\text{NH}_3)_5\text{NHSO}_3^+$  complex after 48 hr, while 71%  $\text{Ru}(\text{NH}_3)_6^{3+}$  remained. The interpretation of these results was complicated by a precipitate which formed in the reaction medium upon addition of the solid  $\text{Na}_3\text{SPO}_3$ . Using a  $\text{CO}_3^{2-}\text{-HCO}_3^-$  buffer (pH 9.6), all the  $\text{Na}_3\text{SPO}_3$  dissolved when it was added to the oxygen-saturated  $\text{Ru}(\text{NH}_3)_6^{3+}$  solution. After 24 hr, more than 60% of the ruthenium appeared as  $\text{Ru}(\text{NH}_3)_5\text{NHSO}_3^+$ . This increased yield of the sulfamate complex may be due in part to the enhanced stability of  $\text{SPO}_3^{3-}$  in carbonate solutions.<sup>10</sup>

The  $\text{SPO}_3^{3-}$  experiment suggested that the exo sulfur of  $\text{SSO}_3^{2-}$  appeared in the ruthenium sulfamate complex. Since the exo sulfur can be thought of as sulfur(0), an experiment substituting  $\text{S}_6$  for  $\text{S}_2\text{O}_3^{2-}$  was attempted. Using a borax buffer, the two-phase mixture of  $\text{Ru}(\text{NH}_3)_6^{3+}$  and  $\text{S}_6$  was saturated with oxygen. After allowing the reaction to proceed for 24 hr, ion exchange of the product solution indicated 95% of the ruthenium was still in the form of  $\text{Ru}(\text{NH}_3)_6^{3+}$ . Unfortunately, oxygen also enhances the conversion<sup>7</sup> of  $\text{S}_6$  to  $\text{S}_8$ , and thus the question of reactivity of  $\text{S}_6$  in the system is not really settled.

A labeling experiment using  $^{18}\text{O}$  was carried out on the reaction of  $\text{Ru}(\text{NH}_3)_6^{3+}$  with  $\text{S}_2\text{O}_3^{2-}$  in the presence of  $\text{O}_2$ . A 10-ml solution of  $\text{Ru}(\text{NH}_3)_6^{3+}$  (0.32 mmol) contained in a round-bottom flask was taken through several cycles of the freeze, pump, and thaw cycle. Solid  $\text{Na}_2\text{S}_2\text{O}_3$  (0.89 mmol) was added to the frozen mass, and the flask was then evacuated. The dissolved gases were again removed by successive cycles of the freeze, pump, and thaw cycle. Oxygen-18 (92 at. %) was admitted into the 25-ml evacuated volume above the frozen ruthenium(III) solution. The vessel was then covered with a black cloth, and its contents were allowed to react for 45 hr. The results obtained were compared to those obtained from a blank experiment using  $^{16}\text{O}$ . Using the expanded wavelength scale (2000–416  $\text{cm}^{-1}$ ) of the Perkin-Elmer 421 ( $\pm 1$  cm), the infrared spectrum of the  $^{18}\text{O}$  product was identical with that for the  $^{16}\text{O}$  product. Though the experiment is conclusive on the net isotopic change, it is not conclusive on the mechanism. (Exchange of oxygen on the sulfur may be quite rapid in the lower oxidation states of sulfur.)

It also seemed of interest to investigate the formation of the sulfamate complex with sulfite as the source of sulfur. Oxygen saturation of a borax buffer containing  $\text{Ru}(\text{NH}_3)_6^{3+}$  (0.033 M) and  $\text{HSO}_3^-$  (0.195 M) also produced the sulfamate complex; however, the yield was not as high as that obtained using  $\text{S}_2\text{O}_3^{2-}$  instead of  $\text{SO}_3^{2-}$  as the source of sulfur. After 8 and 24 hr, 5 and 12%, respectively, of the ruthenium appeared as the  $\text{Ru}(\text{NH}_3)_5\text{NHSO}_3^+$  complex. After 24 hr, the pH of the solution had risen to 9.8, and a blue residue

had formed on the sides of the flask. At this point,  $\text{Ru}(\text{NH}_3)_6^{3+}$  was no longer a major component of the mixture. If  $\text{Na}_2\text{SO}_4$  (1.77 mmol) was substituted for the  $\text{SO}_3^{2-}$  solution, no sulfamate complex formed over a 24-hr period, and the major ruthenium component was still  $\text{Ru}(\text{NH}_3)_6^{3+}$ .

### Discussion

Po and Jordan<sup>1</sup> advanced three arguments in support of the conclusion that the sulfamate in V is N bound rather than O bound. They are as follows. (a) The acidity of the coordinated sulfamate ( $\text{p}K = 5.38$ ) is too high compared to that of free sulfamate ion (this species is too weakly acidic to make  $\text{p}K$  measurable in water) to be accounted for by the O-bound structure. (b) The position of the maximum of the long-wavelength band in the visible region corresponds to an N-bound and not an O-bound species. (c) The sensitivity of the absorption spectrum at shorter wavelengths to removal of the proton is better understood on the basis of an N-bound species. The first two arguments especially are convincing. In view of the similarities in the infrared spectra between II and III and between IV and V, the compounds we have prepared can also be taken to be N bound. Argument (a), it should be noted, applies with even greater force to the ruthenium complex,  $\text{p}K$  for it being even lower than for the Co(III) complex.

This assignment of structure finds support in the analysis by Saraceno<sup>3</sup> of the infrared spectrum of *trans*- $\text{K}_2[\text{Pt}(\text{NH}_2\text{SO}_3)_2\text{Cl}_2]$ . He noted a large shift for the N-H frequencies from  $\geq 3277$   $\text{cm}^{-1}$  in  $\text{KNH}_2\text{-SO}_3$  to 3070  $\text{cm}^{-1}$  in the complex and cited this as evidence that Pt(II) is coordinated to  $\text{NH}_2$  rather than to O. The spectrum of IV, it should be noted, shows a sharp strong band at 3125  $\text{cm}^{-1}$  which can reasonably be attributed to  $\text{NH}_2$  bound to the metal ion. In our system the situation is complicated by the fact that other N-H frequencies contribute in a nearby wavelength region. The assignment made by Saraceno is supported by the fact that the N-S frequency of sulfamate ion is strongly shifted on coordination, while the symmetric stretch of  $\text{SO}_3$  and the degenerate stretching frequencies of the  $\text{SO}_3$  group are only slightly affected.

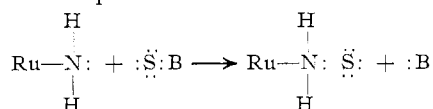
Ruthenium(III) having a vacancy in a nonbonding, low-lying orbital tends to show a ligand-to-metal charge-transfer transition at longer wavelengths than does Co(III) or Ru(II), for example, both of which are low-spin  $d^6$  species. The strong absorption at 487 nm noted for the thiosulfate complex can reasonably be attributed to ligand-to-metal ion charge transfer, and a similar assignment seems in order for the absorption recorded for  $\text{Ru}(\text{NH}_3)_5\text{NHSO}_3^+$  at 398 nm. When a proton is added, the electron pair on the nitrogen atom of sulfamate is occupied, and the charge-transfer absorption is expected to shift to much shorter wavelengths. The longest wavelength absorption recorded for the protonated species is at 280 nm, close to that shown by other Ru(III) species which do not have readily ionizable atoms in contact with the metal ion.

Much less straightforward than the issues considered thus far are those concerned with the mechanism by which coordinated  $\text{NH}_3$  is converted to sulfamate.

(10) S. K. Yasuda and J. L. Lambert, *Inorg. Syn.*, **5**, 102 (1957).

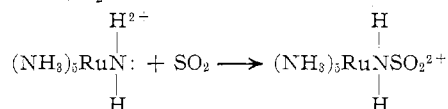
(11) A. M. Vuagnat and E. L. Wagner, *J. Chem. Phys.*, **26**, 77 (1957).

The most significant observation made in this connection is that thiophosphate as well as thiosulfate produces the complex in good yield. The high pH may be necessary if for no other reason than that a proton needs to be dissociated from coordinated ammonia so that displacement on S can occur



the sulfur then being oxidized by O<sub>2</sub>. It is possible that proton dissociation is promoted by a valence change on Ru. Ru(IV) is expected to be very acidic; it can arise by disproportionation of Ru(III)<sup>12</sup> enhanced by O<sub>2</sub> oxidation of Ru(II). The oxidation of the coordinated S may also be assisted by the Ru center.

The fact that SO<sub>3</sub><sup>2-</sup> also leads to the sulfamate complex, though slowly, is compatible with the ideas advanced. Sulfur dioxide can be expected to add to coordinated NH<sub>2</sub><sup>-</sup>



(12) D. P. Rudd has shown that Ru(NH<sub>3</sub>)<sub>5</sub>py<sup>3+</sup> in mildly alkaline solutions rapidly forms Ru(II) and Ru(IV).

The slowness of the reaction with sulfite as source of sulfur can be attributed to the fact that amide, a strongly basic species, and SO<sub>2</sub> cannot coexist at high concentrations. Thus, when the solutions are alkaline enough to produce amide, SO<sub>3</sub><sup>2-</sup> rather than SO<sub>2</sub> is present and SO<sub>3</sub><sup>2-</sup> is a very poor SO<sub>2</sub> donor.

The observations made on the direct replacement of NH<sub>3</sub> from Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> by S<sub>2</sub>O<sub>3</sub><sup>2-</sup> deserve further attention. In other work<sup>13</sup> it has been shown that *t*<sub>1/2</sub> at 25° for the spontaneous loss of NH<sub>3</sub> from Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> in slightly acidic solution is about 3 years. The formation of the Ru(III)-S<sub>2</sub>O<sub>3</sub><sup>2-</sup> bond takes place much more rapidly than this. The higher rate, in the absence of a detailed kinetic study, can be attributed to (a) an OH<sup>-</sup>-promoted path for release of NH<sub>3</sub>, (b) an SN2 process for entry of S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, or (c) formation of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> which is known to be more labile than Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>. It is clearly of interest to resolve the questions of mechanism raised.

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(13) Continuation of experiments described in footnote 4 of J. N. Armor, H. Scheidegger, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 5928 (1968).

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## The Synthesis and Properties of Diamminedinitratocobalt(II) and Related Diammine Complexes<sup>1</sup>

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Thermal decomposition of both hexaamminecobalt(II) dinitrate and  $\mu$ -peroxy-bis[pentaamminecobalt(III)] tetranitrate under vacuum leads to formation of diamminedinitratocobalt(II). Similarly, the complex diamminedinitratocobalt(II) was prepared from the tetraamminezinc(II) salt. Magnetic susceptibility and infrared and electronic spectral measurements suggest that the cobalt ion in the diamminecobalt complex is hexacoordinated, with two bidentate nitrate groups. This complex in organic solvents reacts with iodide ion to give first diammine(iodo)(nitrate)cobalt(II) and eventually diammine(diiodo)cobalt(II). Both complexes were isolated. Infrared and optical spectra suggest that the nitrate ions in the former are bound in bidentate fashion; the latter is known to be a tetrahedral complex.

### Introduction

As part of a study of oxygen-bridged binuclear complexes,  $\mu$ -peroxy-bis[pentaamminecobalt(III)] tetranitrate was found to yield an intensely rose-violet solid when heated under vacuum. This material was shown to be diamminedinitratocobalt(II) by chemical analysis. This paper describes the preparation and characterization of this and other related diammine complexes.

### Experimental Section

#### Preparation and Purification of Diamminedinitratocobalt(II).

—The  $\mu$ -peroxy-bis[pentaamminecobalt(III)] tetranitrate was prepared as described elsewhere.<sup>2</sup> This material is easily synthe-

sized but difficult to purify; it was used immediately without attempts at recrystallization. Approximately 3 g of the tetranitrate salt was heated to ca. 85° under vacuum for 36 hr. During this time, the color of the material changes from greenish brown to rose-violet. Because of the product's extreme sensitivity to moisture, it was transferred to a nitrogen-flushed drybag without exposure to the atmosphere. Reagent grade acetonitrile and benzene were dried by distillation from calcium hydride under a flow of dry nitrogen. The compound was stirred with 20 ml of acetonitrile and allowed to stand for a few minutes. The resulting solution was then carefully filtered off. This extraction process was repeated with additional solvent until it seemed that most of the rose-violet material had been separated from the remaining insoluble solid. Benzene was added slowly to the acetonitrile solution until the volume was approximately doubled. The solution was allowed to stand quietly for several hours. During this time, a rose-violet solid crystallized out of solution. This material was recrystallized by dissolving it in dry acetonitrile, filtering, and adding benzene; it was then washed several times with benzene and dried under vacuum. The material

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) M. Mori, J. A. Weil, and M. Ishiguro, *J. Amer. Chem. Soc.*, **90**, 615 (1968).