Ammineruthenium Complexes of Hydrogen Sulfide and Related Sulfur Ligands

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Abstract: The ion $[Ru(NH_3)_5H_2S]^{2+}$ has been characterized, and salts containing it have been prepared. The value of pK_1 for the species is 4.0, and the equilibrium constant for the reaction of H_2S with $[Ru(NH_3)_5H_2O)]^{2+}$ is 1.5×10^3 M^{-1}, both at 25°. The complex is easily oxidized, and even in the solid, decomposes to liberate H_2. Thiophene has a much lower affinity for Ru(II) than has H_2S, while C_2H_5SH and $(CH_3)_2S$ have greater affinities. The *trans*-$[Ru(NH_3)_4(isn)H_2S](BF_4)_2$ complex was prepared in a pure crystalline form. When isonicotinamide (isn) is trans to H_2S, the complex becomes less stable to replacement of H_2S by H_2O, but more stable to oxidation. These effects are attributed to back-bonding, as is the increase in acidity of coordinated H_2S when isonicotinamide replaces NH_3 in the coordination sphere of Ru(II). The formal potential for the couple $e^- + H^+ + [Ru(NH_3)_5SH]^{2+} = [Ru(NH_3)_5H_2S]^{2+}$ in 1 M H^+ is −0.05 V vs. NHE, while for the couple $e^- + [Ru(NH_3)_5SH]^{2+} = [Ru(NH_3)_5SH]^{+}$ in 1 M NaOAc it is −0.29 V vs. NHE, both at 25°. The pentaammineruthenium(III) complexes of H_2S and C_2H_5SH have pK_1 values of approximately −10 and −7, respectively. Thus decreases in pK_1 of 14 and 16 units, respectively, are registered when the Ru(II) complexes of H_2S and C_2H_5SH are oxidized to the corresponding Ru(III) species.

Despite the growing interest in sulfur-containing ligands, and the obvious analogy between H_2O and H_2S, little has been done toward a systematic development of the coordination chemistry of H_2S and of related sulfur-containing ligands. This situation is in marked contrast to the vast amount of work which has been devoted to the coordination chemistry of the aquo complexes. To point up the difference in the state of development of the H_2S compared to the H_2O system, it should be recognized that prior to the work described in the Ph.D. Thesis of C.G.K.,[1] which is in large part reported here, no compounds containing H_2S as a lignad had been characterized.[2] Furthermore, virtually nothing has been published on the fundamental issue of the affinity of H_2S or related ligands for metal ions. However, it should be noted that two papers[3,6] do deal systematically with the important problem of the propensity which S-donor ligands have for back-bonding interactions with metal ions.

There are understandable reasons for the primitive development of H_2S ligand chemistry, many of which we encountered in the course of the work to be described. Among them are these: H_2S is not nearly as potent, as agreeable, or as tractable a solvent as is H_2O; equilibrium with respect to the formation of solid sulfides is established much more rapidly than it is for the corresponding reactions in the aquo system (which most often produce hydrous oxides or hydroxides); the species S^{2-}, HS^-, or H_2S and homologues are much more readily oxidized than are their oxo analogues. These properties tend to render complexes with sulfur donor ligands unstable, particularly when a proton is attached to the sulfur.

It was the goal of the research to be described to make a beginning in the systematic development of the basic chemistry of sulfur compounds as ligands. In line with this goal we selected H_2S and closely related molecules as the ligands of first choice, regarding them as the simplest to understand though not necessarily the simplest to deal with experimentally. Our choice of ruthenium as the metal center was of course governed by the accumulated experience we have had in the chemistry of ruthenium ammines, and it was encouraged by the conviction that the propensity which Ru(II) in combination with saturated ligands has for a π acid heteroligand would be of service in meeting our goal. The properties of the ruthenium ammines which were most important for the success of our program are the substitution inertia of both the Ru(II) and Ru(III) states and the fact that the Ru(III)-Ru(II) couple is only weakly oxidizing. It should be noted that though Ru(II), by virtue of its lower charge, loses ground relative to Ru(III) in substitution inertia for σ donor ligands, it can more than compensate for its reduced charge when π donor ligands are in question. The kinetic stability of the Ru(II)-π acid ligand combination of course borrows heavily on the thermodynamic stability which is conferred by back-donation.[7]

Experimental Section

1. Preparations. (a) General. The preparation of water of high purity, of O_2 free gases, and of reducing agents such as Eu^{2+} and Cr^{2+} have been dealt with in other reports from this laboratory.[8] Solutions of HBF_4 and HTFA (trifluoroacetic acid)[9] were prepared by dilution from high quality commercial products, J. T. Baker Purified Grade and Matheson Coleman Bell, respectively. Standard HCl, NaOH, and $Na_2S_2O_3$ solutions were prepared by diluting Titrisol (E. Merck Co.) samples. Other analytical reagents such as Fe(III) in HTFA or HBF_4 and I_2 in KI were prepared by standard procedures, using whatever slight modifications were necessary for present purposes. For some of our work it was necessary to transfer H_2S solutions quantitatively. Procedures for dealing with solutions of volatile solutes are not in common use so our approach to the problem is described in some detail.

Saturated H_2S solutions were prepared by bubbling the gas through the oxygen-free liquid (50 ml or less) for about 1 h. Experiments to determine the time needed for saturation indicated substantially full saturation in less than 0.5 h. Dilute H_2S solutions were obtained by purging an oxygen-free solution with a gas mixture of hydrogen sulfide and argon for about 1 h. Gas mixtures were produced using acrylic, purge flowmeters, purchased from Matheson Gas Products. Flowmeters with the flow ranges 0.01–0.08 and 0.10–2.00 standard cubic feet of air per hour were used for hydrogen sulfide and argon, respectively. The hydrogen sulfide solutions were standardized following the general iodometric titration procedure described by Skoog.[10]

Two procedures for transferring hydrogen sulfide solutions quantitatively from the preparation flask to the titration vessel were tried. (a) The solution (usually 0.1 M acid) was purged with argon and then saturated with hydrogen sulfide in a buret equipped with a three-way stopcock. A measured volume of the saturated solution was added directly to the iodine solution. (b) The second technique, which proved to be more convenient, was to transfer hydrogen sulfide solutions using a gas-tight syringe with a Pt needle. Before use, the syringe and needle were degassed with the hydrogen sulfide gas mixture being used, then the solution was transferred into the I_2 solution by placing the Pt needle below the surface during injection. In all cases the concentration of hydrogen sulfide was determined under the conditions used in the kinetic experiments, and at least duplicate titrations were performed for each experiment.

Isonicotinamide was recrystallized from hot water; 4-cyanopyridine was recrystallized from ethanol. Dimethyl sulfide, 98% minimum purity, and ethanethiol, 97% minimum purity, were supplied by Aldrich Chemical Co. Both required frequent distillation, because gas chromatographic analysis showed that one or more impurities developed on standing. Freshly distilled $(CH_3)_2S$ was shown to be sufficiently pure by gas chromatograph analysis, but distilled C_2H_5SH still showed about 1% impurity, and it was further purified by degassing over zinc amalgam for 15 min before use. Hydrogen sulfide, 99.6% minimum purity, was used as supplied in lecture bottles from Liquid Carbonic or Matheson Gas Products. According to the specifications, typical impurities were CS_2 (0.09%), CO_2 (0.13%), SO_2 (0.05%), and CH_3SH (0.02%). Deuterium sulfide was used as supplied in 1-l. lecture bottles from Matheson Gas Products. Thiophene, purchased from Aldrich Chemical Co., was distilled before use. Sulfur dioxide, 99.9% minimum purity, was used as purchased from Matheson Gas Products without further purification. Tetrahydrothiophene (Aldrich), L-cysteine ethyl ester hydrochloride (Aldrich), and DL-methionine methyl ester hydrochloride (Sigma Chemical) were used as supplied.

(b) Ruthenium Compounds. Standard Preparations. Chloropentaammineruthenium(III) chloride was prepared by refluxing hexaammineruthenium(III) chloride in 6 *M* HCl for 4 h and recrystallizing the solid from 0.1 M HCl.[11] *trans*-$[Ru(NH_3)_4SO_2Cl]Cl$ was prepared as described by Gleu et al.[12]

The preparations of salts containing $[Ru(NH_3)_5H_2O]^{2+}$, though not novel, are not yet common practice. An outline of our procedure follows. A hot solution of silver trifluoroacetate, made by dissolving 0.079 g of Ag_2O in 4 ml of 2 M HTFA, was added to 0.1 g of $[Ru(NH_3)_5Cl]Cl_2$. The AgCl precipitate was digested by heating and stirring for several minutes. The solution was filtered and allowed to cool to room temperature. The acidity was adjusted to about pH 3 by dropwise addition of 3 M NaOH. This solution was reduced over zinc amalgam in an inert atmosphere for 15–20 min. Solid NH_4PF_6 (about 0.5 g) was added to the reduced solution. The pale yellow solid, $[Ru(NH_3)_5H_2O](PF_6)_2$, which precipitated was filtered quickly and washed with ethanol and ether. The yield was about 89%. In a similar way $[Ru(NH_3)_5H_2O](BF_4)_2$ could be precipitated in high yield by adding 2 ml of saturated $NaBF_4$ solution, instead of solid NH_4PF_6.

The preparation of $[Ru(NH_3)_5(CH_3)_2SO](PF_6)_2$ has been described by Senoff et al.[13] However, an alternative method starting from $[(Ru(NH_3)_5Cl]Cl_2$ was found to be more convenient and is herewith described. A hot solution of 0.079 g of Ag_2O dissolved in 2 ml of 2 M HTFA was added to 0.10 g of $[Ru(NH_3)_5Cl]Cl_2$ to precipitate the ionic chloride. The AgCl precipitate was digested by heating and stirring the solution for several minutes. The solution was filtered hot and, after cooling, the pH of the solution was adjusted to 3 by dropwise addition of 1 M NaOH. The solution was reduced over fresh zinc amalgam for 15 min and transferred under argon to a flask which had been rinsed with $(CH_3)_2SO$. Reaction was allowed to proceed for 15 min, whereupon 1 g of $NaBF_4$ was added and the solution cooled at −5° for 1.5 h. The precipitate was filtered and washed with small amounts of water, ethanol, and acetone. The yield was about 51%, but after recrystallization from water, the yield was reduced to less than 25%.

$[Ru(NH_3)_5(CH_3)_2SO](BF_4)_2$	C	H	N
Calcd	5.50	4.83	16.00
Obsd	5.49	4.65	16.76

(c) Preparations of New Ruthenium Ammines with Sulfur Ligands. (i) (Dimethyl sulfide)pentaammineruthenium(II) Hexafluorophosphate or Tetrafluoroborate Salts. One-tenth gram of $[Ru(NH_3)_5Cl]Cl_2$ was dissolved in a minimum amount (20–25 ml) of 0.05 M *p*-toluenesulfonic acid solution. This solution was reduced with zinc amalgam for 15 min and was then transferred by means of a syringe into 5 ml of neat, degassed $(CH_3)_2S$ and was allowed to react 0.5 h with continued argon bubbling. During the reaction the solution changed from a golden yellow to pale yellow color. A pale yellow solid, $[Ru(NH_3)_5S(CH_3)_2](PF_6)_2$, precipitated immediately upon adding 0.5 g of solid NH_4PF_6.

To obtain the tetrafluoroborate salt, solution prepared as described was transferred under argon to about 10 ml of well-degassed, concentrated HBF_4 (48%) and refrigerated for 1–2 h in a sealed flask, whereupon the pale yellow solid $[Ru(NH_3)_5S(CH_3)_2](BF_4)_2$ precipitated.

Both solids were filtered in a glove bag and washed with ethanol and ether. The yield was about 70% in each case. After recrystallization from water the final yield was about 40%.

Perchlorate (caution!) and chloride salts were prepared similarly by using saturated $NaClO_4$ or concentrated HCl to precipitate the complex.

Attempts to prepare salts containing $[Ru(NH_3)_5S(CH_3)_2]^{3+}$ led to impure solids with low carbon analysis, indicating partial loss of the ligand. Subsequent work[14] has shown that $(CH_3)_2S$ is not readily lost from the Ru(III) complex and our failure may be ascribable to the fact that we were trying to produce the perchlorate salt.

(ii) (Ethanethiol)pentaammineruthenium(III) Hexafluorophosphate. A stoichiometric amount of Ag_2O (0.11 g, 1.0 mmol of Ag), dissolved in about 3 ml of 2 M HTFA, was added to 0.15 g of $[Ru(NH_3)_5Cl]Cl_2$ (0.51 mmol). The resulting AgCl precipitate was coagulated by heating and stirring for several minutes. The hot solution was filtered to remove AgCl and, after cooling to room temperature, its acidity was adjusted to pH 3. The solution was reduced over zinc amalgam for 15 min, and 2 ml of freshly distilled C_2H_5SH, separately degassed over zinc amalgam for 15 min, was then added. The solution was degassed with argon until C_2H_5SH as a separate phase had disappeared (ca. 0.5 h). The color of the solution was pale yellow—or pink, if a small amount of O_2 was present. Since the Ru(II) complex is extremely air-sensitive, it was usually oxidized and the air stable Ru(III) salt was precipitated. The oxidation was accomplished by adding 0.118 g of Ag_2O (1.0 mmol), dissolved in a minimum amount of 2 M HTFA (about 2 ml), i.e., just enough Ag^+ to precipitate one chloride and to oxidize the complex to Ru(III). The solids were filtered from the solution under an argon atmosphere and about 0.5 g of solid NH_4PF_6 was added to the resulting deep red solution to precipitate $[Ru(NH_3)_5(SC_2H_5)](PF_6)_2$. This was filtered and washed with ethanol and ether. The yield was about 18%. The resulting crude solid was about 90% pure at best, and all attempts to purify the solid (ion exchange, recrystallization, reprecipitation) failed. (This complex appeared to react with the cation exchange resin Bio Rad AG 50 W X2.) The coprecipitated impurity was not identified. Many variations of the above method of synthesis were tried, but they all yielded varying amounts of impurities.

(iii) (Ethanethiol)pentaammineruthenium(II) Tetrafluoroborate. The complex $[Ru(NH_3)_5(HSC_2H_5)](BF_4)_2$ was isolated for use in aquation studies. Ionic chloride was removed from 0.10 g of $[Ru(NH_3)_5Cl]Cl_2$ by precipitation with 0.079 g of Ag_2O, dissolved in 3 ml of 2 M HTFA. After filtration, this solution was reduced over zinc amalgam in the presence of 2 ml of C_2H_5SH and 1 ml of 0.02 M Eu(II) solution in a Zwickel flask[15] (Figure 1) attached to a second flask containing 4 ml of concentrated HBF_4. The reaction was continued for 0.5 h with continued argon bubbling, after which the solution was transferred to the second flask. The resulting solution was cooled to precipitate $[Ru(NH_3)_5HSC_2H_5](BF_4)_2$. The solid was filtered in the glove box and washed with ethanol and water.

(iv) (Hydrogen sulfide)pentaammineruthenium(II) Tetrafluoroborate. The apparatus used is shown in Figure 1. Freshly prepared $[Ru(NH_3)_5H_2O](BF_4)_2$ (200 mg) was dissolved in 8 ml of degassed 0.1 M HCl solution in a Zwickel flask,[15] and 2 ml of a freshly reduced solution of 0.05 M Eu^{2+} ion in 0.1 M HCl was added using a syringe. The flask was attached to a smaller one containing 10 ml of 46% HBF_4. To ensure an inert, oxygen-free atmosphere, argon was passed through the apparatus and solutions for 20 min. Then hydrogen sulfide was bubbled through the ruthenium solution for 10–15 min, during which the original bright yellow solution turned pale yellow. By turning the four-way stopcock on the Zwickel flask, the reaction mixture was transferred to the smaller flask containing degassed HBF_4 solution. Within 5 min, the pale yellow solid $[Ru(NH_3)_5H_2S](BF_4)_2$ precipitated. The second flask was closed to air by means of stopcocks and detached. The reaction solution was frozen using liquid N_2 to keep the reaction mixture cold for the 25 min required to transfer the solution into the glove box for filtering. The solution was filtered in the glove box directly into a filter flask containing solid NaOH. The solid NaOH was used to prevent free H_2S from reaching the glove box catalyst. The pale yellow solid $[Ru(NH_3)_5H_2S](BF_4)_2$ was washed with ethanol and ether and stored in the glove box. The solid was used within several hours of preparation, since it undergoes decomposition. This is evidenced by color changes (pale yellow to red-brown to black) even in an inert atmosphere. Preparations following this procedure were analyzed to be about 90% pure. Further recrystallization or purification was impossible due to the instability of the complex.

A successful method for preparing a compound containing $[Ru(NH_3)_5H_2S]^{2+}$ was developed only after repeated failures. Some of the failures seem to merit at least brief mention. Unless excess reducing agent is present, even when the prescribed procedure is followed, the solutions rapidly turn orange (probably formation of $[Ru(NH_3)_5SH]^{2+}$). At high acid concentration, the orange color develops rapidly and the mixture soon turns black. In the solvents acetone, triethyl phosphate and methanol, the reaction of $[Ru(NH_3)_5H_2O]^{2+}$ with H_2S after evaporation of the solvent produced black precipitates; the solid left behind when glacial acetic acid was used, though pale in color, was found to contain little sulfur. No apparent reaction took place when $[Ru(NH_3)_5H_2O](PF_6)_2$ was dissolved in liquid H_2S and kept at −78° for 1 h.

(v) (Deuterium sulfide)pentaammineruthenium(II) Tetrafluoroborate. This was made by the procedure described for the hydrogen sulfide complex. Freshly prepared $[Ru(NH_3)_5H_2O](BF_4)_2$ (100 mg) was dissolved in 4 ml of degassed 0.1 M DCl, 0.05 M Eu^{2+} solution in D_2O in a Zwickel flask. Deuterium sulfide was bubbled through the ruthenium solution for 10 min. The complex was precipitated by the addition of 4 ml of saturated $NaBF_4$-D_2O solution. The complex was filtered in the glove box as described above and washed with ether.

(vi) *trans*-(Hydrogen sulfide)(isonicotinamide)tetraammineruthenium(*II*) Tetrafluoroborate. Samples of *trans*-$[Ru(NH_3)_4SO_4(isn)]Cl$[9] were prepared according to the method of Isied.[16]

To prepare the hydrogen sulfide complex, usually 80 mg of *trans*-$[Ru(NH_3)_4SO_4(isn)]Cl$ (0.163 mmol) was dissolved in 2 ml of 0.01 M *p*-toluenesulfonic acid. This solution was reduced for 10–15 min over zinc amalgam and then transferred to a degassed Zwickel flask using a gas-tight syringe. This solution was allowed to react with hydrogen sulfide by slowly bubbling the gas through the solution for 2 h. At the end of this time, the reaction solution was transferred to 2 ml of H_2S-saturated concentrated HBF_4 solution contained in a vessel attached to the Zwickel flask. This section was detached after the stopcocks were closed and the solution was refrigerated at −5° for 45 min to precipitate *trans*-$[Ru(NH_3)_4H_2S(isn)](BF_4)_2$. The solution was then frozen using liquid N_2 and transferred as before into the glove box for filtering. The yield was about 53 mg (65%) of crystalline brown *trans*-$[Ru(NH_3)_4H_2S(isn)](BF_4)_2$. Sometimes two modifications resulted from this procedure—one crystalline brown and one powder brown. Both gave the same spectra, although the crystalline form gave slightly better analysis. This solid appeared to be indefinitely stable when stored in a vacuum desiccator.

(vii) *trans*-$[Ru(NH_3)_4(isn)L](BF_4)_2$ where L = $(CH_3)_2S$ and C_2H_5SH. In analogy to the synthesis of the hydrogen sulfide complex, 40 mg of *trans*-$[Ru(NH_3)_4SO_4(isn)]Cl{\cdot}H_2O$ was dissolved in 0.5 ml of 0.05 *M* *p*-toluenesulfonic acid. This solution was reduced with zinc amalgam and 5–7 ml of degassed $(CH_3)_2S$ or C_2H_5SH was added by syringe. This solution was allowed to react for 1.5–2 h with slow argon bubbling. Three milliliters of concentrated HBF_4 (48–50%) was added and the entire solution was added to 100 ml of ethanol and refrigerated at −5° for 1–2 h. After cooling, the solution was filtered and 15–20 mg of solid was collected and washed with ethanol and ether. The yield varied from 33 to 45%. The *trans*-$[Ru(NH_3)_4(isn)C_2H_5SH](BF_4)_2$ is a red-brown solid and *trans*-$[Ru(NH_3)_4S(CH_3)_2(isn)](BF_4)_2$ is an orange solid.

(viii) $[Ru(NH_3)_5L]^{2+}$ where L = Thiophene, Tetrahydrothiophene, Methionine Methyl Ester, and Cysteine Ethyl Ester. The ionic chlorides were removed from 100 mg of $[Ru(NH_3)_5Cl]Cl_2$ by quantitative precipitation with 79 mg of Ag_2O in 4 ml of 2 M HTFA solution. Sodium hydroxide solution (3 M) was added dropwise to adjust the acidity to pH 1–2. This ruthenium solution was reduced over zinc amalgam in a Zwickel flask for 20–30 min. A more than fivefold excess of ligand was added. Thiophene and tetrahydrothiophene are not miscible with water. The substitution reaction was allowed to continue for 20–30 min with argon bubbling through the solution, whereupon the solution was transferred under argon from the Zwickel flask to a second flask containing 3–4 ml of concentrated HBF_4 solution.

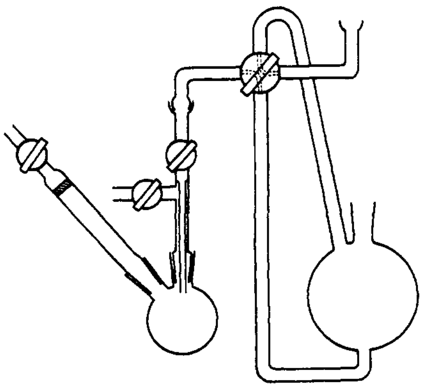

Figure 1. Diagram of Zwickel flask. The lower port on the right is used to introduce solutions and is then stoppered. The upper port is used for degassing.

The thiophene and tetrahydrothiophene complexes precipitated directly, but 15 ml of degassed ethanol was added to precipitate the methionine and cysteine ester complexes. The cysteine complex was filtered under an inert atmosphere, while the others were filtered in air. The Ru(II) forms of these complexes were varying shades of yellow. To purify the methionine and cysteine complexes reprecipitation from 0.1 M HCl was necessary. Yields varied from 50 to 80%.

(ix) $[(NH_3)_5RuSSRu(NH_3)_5]X_4$ where $X^- = Cl^-, Br^-, PF_6^-$. The preparation of salts containing $[(NH_3)_5RuSSRu(NH_3)_5]^{4+}$ has been described[17,16] and the only claim to novelty we make is that the method[18] we outline is the most convenient of those so far used.

About 140 mg of $[Ru(NH_3)_5SO_2]Cl_2$ was dissolved in 6–8 ml of 0.01 M HCl. Hydrogen sulfide was bubbled through the solution for about 2 min during which a very rapid and dramatic color change from red to green took place. After elemental sulfur was filtered off, a spectrum of the solution showed it to be pure $[(NH_3)_5RuSSRu(NH_3)_5]^{4+}$. The dimer could be precipitated by addition of concentrated HBF_4, HCl, HBr, or solid NH_4PF_6. Usually the solids were analytically pure without any further purification.

2. Apparatus and Methods. Many of the techniques are specific to the compounds studied, and in such cases any elaboration of procedure is left for the section on Results.

Ultraviolet and visible spectra were recorded on either a Cary 15 or 14 recording spectrophotometer.

Infrared spectra were recorded on a Perkin-Elmer 621 grating spectrophotometer in the region 4000–250 cm^{-1}. Samples were usually run as CsI pellets. To make a pellet, approximately 2 mg of sample and 200 mg of CsI were used. Air-sensitive samples such as $[Ru(NH_3)_5H_2S](BF_4)_2$ were mixed with CsI in the glove box (vide infra) and were pressed in the absence of air.

The Varian T-60 and XL-100 instruments were used to obtain proton NMR spectra. Complexes were dissolved in 1 ml of deuterated solvent. Trimethylsilyl propionate (TSP) was used as an internal standard for D_2O-DCl solutions. Tetramethylsilane (Me_4Si) was used as a standard in organic solvents.

Raman spectra were recorded on a SPEX Model 1401 instrument, calibrated using CCl_4 solution. The red 6471 Å exciting line was used. The assistance of Mr. K. Czworniak in running the Raman spectra is gratefully acknowledged.

Low resolution mass spectra were recorded on the MAT Atlas CH 4 mass spectrophotometer.

For kinetic experiments and whenever otherwise necessary a constant temperature was maintained using a constant temperature water bath (Forma-Temp Model 2073 A Scientific Inc., Ohio) to equilibrate solutions. Water from this bath was circulated through the cell compartment of the Cary 15 using insulated Tygon tubing. Whenever possible solutions were equilibrated in the constant temperature bath, and then the reaction was followed spectrophotometrically in the thermostated cell compartment. The temperature in the cell compartment was measured with a preci-

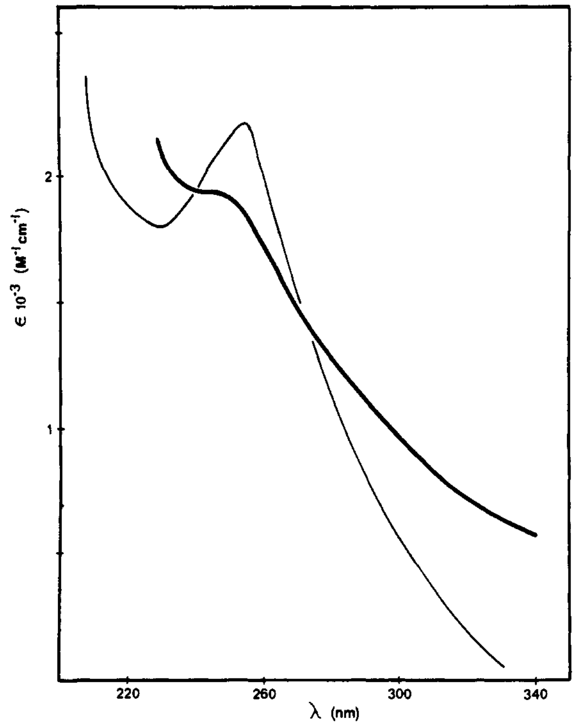

Figure 2. Ultraviolet spectra of $[Ru(NH_3)_5H_2S](BF_4)_2$ in 0.1 M Cl (light line) and in 0.1 M acetate buffer (heavy line).

sion thermometer (Scientific Glass Co.), calibrated to ±0.05°.

Magnetic susceptibility measurements were made on a Model 7600 Cahn Faraday magnetic susceptibility apparatus at room temperature. Diamagnetic corrections for the ligands and counterions were taken from tables in "Introduction to Magnetochemistry" by Earnshaw.[19] The sample weights varied from 20 to 40 mg. $Hg[Co(NCS)_4]$ was used as a standard.

A Metrohm combination microglass electrode (purchased from Brinkmann Instruments) and a Beckman Expandomatic or Metrohm 101 pH meter (Brinkmann) were used to make pH measurements. NBS buffers purchased from Beckman were used to standardize the pH meter.

An electrochemical circuit, designed and constructed by G. Tom, was used for making measurements by cyclic voltammetry, polarography, and potentiometric titrations. The output, scans of potential vs. current or potential vs. time, was recorded on an Omnigraphic 2000 X-Y recorder with type 5 and 6 precision attenuators (purchased from Houston Instruments, Texas). For conventional cyclic voltammetry, sweep rates of 100-200 mV/sec and for polarography sweep rates of 5 mV/sec were used. For fast scan cyclic voltammetry the sweep rate was 10-100 V/sec and the output was recorded on an oscilloscope (HP Model 130 Br) and photographed using 146-L Polaroid film.

Formal potentials, E_f, were measured at half the distance between the anodic and cathodic peaks. Formal potentials are defined in terms of concentrations, in contrast to standard potentials, which are defined in terms of activities of the products and reactants.

A Pt button electrode (Beckman Instruments) or a hanging Hg drop electrode (Brinkmann) was used as the indicator electrode for measuring positive or negative potentials, respectively. Potentials were measured with respect to a standard calomel electrode as a reference and were converted to the normal hydrogen electrode reference by adding 242 mV. Experiments were done in an H-shaped cell, holding the indicator and the reference electrodes, with a fine glass frit dividing the two sides of the cell. At least 0.1 M supporting electrolyte solution was added to each side of the H cell. The solution was carefully deaerated with argon for 10 min prior to measurement, and enough solid to make a 2-5 mM sample solution was added to one side of the cell.

Electrochemical oxidation-reduction potentials for ruthenium complexes with sulfur ligands containing a dissociable proton were determined by potentiometric titration. Conventional or even fast scan cyclic voltammetry could not be used due to a large amount of chemisorption on the Pt or Hg electrode surfaces. Chemisorption was significant even when a fresh Hg drop was used for each scan. As a result, with cyclic voltammetry usually multiple, irreversible, and time-dependent waves were observed, apparently due to various ligand and metal oxidations involving adsorbed rather than bulk species.

An inert atmosphere glove box, complete with antechamber, pedatrol, and inert gas purifier (MO-40), purchased from Vacuum Atmospheres Co., Hawthorne, Calif., was used for many air-sensitive operations. An argon atmosphere was recycled through the glove box at a speed of 40 ft^3/min. The glove box was fitted with four *tert*-butyl gloves (0.30 cm). The atmosphere of the box was checked by the length of time that a broken 25-W light bulb could burn when plugged in. A bottle of diethyl zinc in heptane was used as a qualitative test for oxygen and water. The absence of fumes from the diethyl zinc indicated less than 5 ppm oxygen. The glove box catalyst and molecular sieve train were regenerated with a 5% H_2-N_2 mixture once a month, since both sulfur ligands and water were used in the glove box.

Microanalyses for carbon, nitrogen, hydrogen, sulfur, ruthenium, and halide were performed by the staff of the Stanford Microanalytical Laboratory.

Results

1. (Hydrogen sulfide)pentaammineruthenium(II). (a) Microanalysis of $[Ru(NH_3)_5H_2S](BF_4)_2$. Results of the microanalyses of $[Ru(NH_3)_5H_2S](BF_4)_2$ showed that the method of preparation yielded a solid which consistently analyzed to be about 94% pure. The sulfur, carbon, hydrogen, and nitrogen analyses were performed on the day of preparation of the sample. The results of a typical analysis for $[Ru(NH_3)_5H_2S](BF_4)_2$ are given below. The ratios observed were as expected for $[Ru(NH_3)_5H_2S](BF_4)_2$: C:H:N:Ru:S, 0:17:5:1:1. The persistent impurity which failed to respond to the analytical method may be a europium salt.

$[Ru(NH_3)_5H_2S](BF_4)_2$	C	H	N	Ru	S
% calcd	0	4.35	17.78	25.67	8.14
% obsd	0	4.06	16.54	23.5	7.48

(b) Ultraviolet-Visible Spectra. The ultraviolet spectra of a freshly prepared $[Ru(NH_3)_5H_2S](BF_4)_2$ sample in 0.1 M HCl and in 0.1 M HOAc-NaOAc buffer are shown in Figure 2 (λ_{max} 255 nm, $\epsilon \sim (2.2 \pm 0.2) \times 10^3\ M^{-1}\ cm^{-1}$ and λ_{max}(sh) 248 nm, $\epsilon \sim (1.9 \pm 0.2) \times 10^3\ M^{-1}\ cm^{-1}$). The $[Ru(NH_3)_5H_2S](BF_4)_2$ solutions were prepared and filled into spectrophotometric cells in the glove box. The capped spectrophotometric cells were removed from the glove box and the spectra were measured within 5 min.

Even in the absence of air, in 0.1 M H^+ the band at 255 nm for $[Ru(NH_3)_5H_2S]^{2+}$ decreased with time (about 10% within 1 h) while a visible band, λ_{max} 470 nm, gradually appeared. This change was found to be much more rapid at lower acid concentrations. The orange species is unstable and forms a black precipitate within a period of a few hours.

When exposed to air, $[Ru(NH_3)_5H_2S]^{2+}$ in 0.1 M HCl is oxidized to an orange species with a band at 470 nm and then to a green species. From spectral analysis and ion exchange behavior (AGW 50 X2 cation exchange resin, H^+ form), the main species in the green solution was shown to be $[(NH_3)_5RuSSRu(NH_3)_5]^{4+}$.[17] The orange intermediate oxidation product could not be further identified. In solutions of acidity much different from 0.1 M, $[Ru(NH_3)_5H_2S]^{2+}$ oxidized to give solutions containing many other species, in addition to varying amounts of $[(NH_3)_5RuSSRu(NH_3)_5]^{4+}$. The disulfide dimer does not seem to be the major oxidation product in the pH range above 1.

(c) Infrared, Raman, and NMR Spectra of $[Ru(NH_3)_5H_2S](BF_4)_2$. Little that was significant was learned from the infrared spectra of the salt (CsI pellet). A small band observed in the region of 2500-2700 cm^{-1} was also found in the spectrum of $[Ru(NH_3)_5Cl]Cl_2$, and thus cannot be assigned to the H-S stretching frequencies. The failure to observe the H-S infrared bands in the complex is not surprising in view of the fact that the infrared bands for H_2S (gas) at 2632, 2615, and 1236 cm^{-1} are weak.[20] A weak band at 285 cm^{-1} is tentatively assigned to the Ru-S stretching frequency.

We had greater hope for the Raman spectrum because the S-H bands are rather intense in the Raman. Laser Raman spectra were obtained using the 6471 Å line for excitation. A saturated H_2S solution (0.2 M) in 0.1 M HCl was measured as a reference, and two very weak bands at 2600 and 1300 cm^{-1} were observed. For $[Ru(NH_3)_5H_2S](BF_4)_2$, solutions of concentration $<10^{-2}$ M in 0.1 M HCl were prepared (concentration limited by the solubility of the salt) and no S-H bands were observed above the noise level. The Raman spectrum of the pale yellow solid $[Ru(NH_3)_5H_2S](BF_4)_2$ (freshly prepared) shows bands at 2523 and 2547 cm^{-1}. However, it was found that $[Ru(NH_3)_5Cl]Cl_2$ run under the same conditions had bands in the same positions with that at 2547 cm^{-1} being less intense. The overlap of N-H overtones with the S-H frequencies complicates the assignment of the S-H stretching frequency. In an attempt to resolve this, $[Ru(NH_3)_5D_2S](BF_4)_2$ was prepared and its Raman spectrum was compared to those of $[(Ru(NH_3)_5H_2S](BF_4)_2$ and $[Ru(NH_3)_5Cl]Cl_2$. For $[Ru(NH_3)_5Cl]Cl_2$ and $[Ru(NH_3)_5D_2S](BF_4)_2$, the two bands at 2547 and 2523 cm^{-1} were found to be of equal intensity, while for $[Ru(NH_3)_5H_2S](BF_4)_2$ the band at 2547 cm^{-1} was twice the intensity of the band at 2523 cm^{-1}. However, the S-D stretching frequency calculated to lie between 1700 and 1870 cm^{-1} (corresponding to 2500-2700 cm^{-1} for S-H) was not observed above the noise level. From these experiments it was concluded that the S-H stretching frequency in $[Ru(NH_3)_5H_2S](BF_4)_2$ is weak, and, although tentatively assigned at 2547 cm^{-1}, is complicated by the presence of N-H overtones in the same region.

Attempts to locate the Ru-S stretching frequency in the Raman spectra were hampered by the high noise-to-signal ratio in the region 350-100 cm^{-1}.

The attempts to obtain an NMR signal for the protons of coordinated H_2S ended in failure. After solvents with exchangeable protons are eliminated, only a few choices remain among those likely to provide adequate solubility. Deuterated DMSO was found to oxidize the complex to the orange form. The compound was found to be somewhat soluble in CD_3CN and CD_2Cl_2 but not sufficiently to yield NMR lines for either coordinated NH_3 or H_2S.

(d) Decomposition of Solid $[Ru(NH_3)_5H_2S](BF_4)_2$. The compound $[Ru(NH_3)_5H_2S](BF_4)_2$, a pale yellow solid when freshly prepared, decomposes in the solid state even with rigorous exclusion of O_2 and H_2O in the glove box. This behavior was evidenced by a series of color changes from pale yellow to red-brown to black within several days. A possible mode for decomposition of this complex is represented by the equation

$$2[Ru^{II}(NH_3)_5H_2S](BF_4)_2 = 2[Ru^{III}(NH_3)_5HS](BF_4)_2 + H_2 \quad (1)$$

To determine if and how much H_2 gas was evolved by decomposition, quantitative noncondensable gas analysis was performed on an analyzed sample which had been sealed in a vacuum tube, carefully evacuated immediately after preparation to $<10^{-5}$ Torr, and allowed to decompose for 1 month. The H_2 gas evolved was determined to be 25 ± 2% of the theoretical amount, using a Toepler pump to transfer the gas into a calibrated gas buret. Low resolution mass spectral analysis showed the gas to be H_2. Microanalysis of the decomposed sample showed its composition to be close to that of the starting compound; in particular, analysis showed no loss of sulfur.

(e) Rate of Substitution on $[Ru(NH_3)_5H_2O]^{2+}$. The procedure used to measure the rate of reaction 2:

$$[Ru(NH_3)_5H_2O]^{2+} + H_2S = [Ru(NH_3)_5H_2S]^{2+} + H_2O \quad (2)$$

was as follows. A stock solution of 2×10^{-2} M $[Ru(NH_3)_5Cl]Cl_2$ in 0.1 M HBF_4 was prepared. Either 10 or 25 ml of 0.1 M HBF_4 solution was saturated with H_2S or a H_2S-argon mixture by bubbling the gas mixture through the solution for 1 h. At the start of the reaction 0.25 or 0.50 ml of $[Ru(NH_3)_5H_2O]^{2+}$ was injected into the H_2S saturated solution. The 1-cm spectrophotometric cell was filled and placed in a thermostated Cary 15 cell compartment. The temperature was 25.0°. The reaction was monitored by the increase in absorbance at 255 nm to a constant value. Typical reaction times were 5 min. The H_2S concentration was varied from 0.2 to 0.09 M and was determined by duplicate iodometric titrations.

The results of the experiments are presented in Table I. The specific rate k_1 is defined as

$$\frac{d(\text{product})}{dt} = k_1[Ru(NH_3)_5H_2O^{2+}][H_2S]$$

From the data in Table I, the value of k_1 is 0.10 ± 0.004 $M^{-1}\,sec^{-1}$ ($H^+ = 0.10$ M, $I = 0.1$ M, 25.0°C).

Under the pseudo-first-order conditions chosen, the forward rate of reaction 2 is fast compared to the reverse and to decomposition reactions. The value of the absorbance at λ 255 nm measured after 5 min (ca. five half-lives) was in good agreement with that calculated using the measured extinction coefficient (λ 255 nm) as determined starting with solid $[Ru(NH_3)_5H_2S](BF_4)_2$. After 10 min there were slower increases in the absorbance which were attributed to side reactions similar to those observed in solutions of the solid $[Ru(NH_3)_5H_2S](BF_4)_2$. The data were plotted as log $(A_\infty - A)$ vs. time and were linear for 2.5 half-lives. The value of k_{obsd} ($\equiv k_1[H_2S]$) was calculated from the slope.

(f) Rate of Loss of H_2S from $[Ru(NH_3)_5H_2S]^{2+}$. The rate of loss of H_2S from $[Ru(NH_3)_5H_2S]^{2+}$ was determined by generating $[Ru(NH_3)_5H_2S]^{2+}$ in 0.1 M H^+, 0.02 M Eu^{2+} solution, degassing the excess hydrogen sulfide, and then adding an aliquot of $[Ru(NH_3)_5H_2S]^{2+}$ solution to excess 4-cyanopyridinium ion (4-cpyH^+).[9] The formation of $[Ru(NH_3)_5(4\text{-cpyH})]^{3+}$ was monitored by the increase in absorbance at λ 530 nm, near the maximum for the species $[Ru(NH_3)_5(4\text{-cpyH})]^{3+}$ (532 nm).[21] The reaction sequence is

$$[Ru(NH_3)_5H_2S]^{2+} \xrightarrow[\text{slow}]{k_{-1}} [Ru(NH_3)_5H_2O]^{2+} + H_2S \quad (3)$$

$$[Ru(NH_3)_5H_2O]^{2+} + 4\text{-cpyH}^+ \overset{\text{fast}}{=} [Ru(NH_3)_5(4\text{-cpyH})]^{3+} + H_2O \quad (4)$$

In 0.1 M H^+ 4-cyanopyridine is protonated at the pyridine nitrogen ($pK_a = 2.72$)[22] and substitution is possible only at the nitrile site. Moreover, in 0.1 M 4-cpyH^+ solution the rate of loss of H_2S from $[Ru(NH_3)_5H_2S]^{2+}$ is the rate determining step, since the specific rate of substitution of 4-cpyH^+ ion on $[Ru(NH_3)_5H_2O]^{2+}$ is 0.24 $M^{-1}\,s^{-1}$ [22] corresponding to a rate orders of magnitude faster than the aquation rate under the conditions used. An initial fast in-

Table I. Rate of Substitution of H_2S in $[Ru(NH_3)_5H_2O]^{2+}$ [a]

$10^4[Ru(NH_3)_5H_2O]^{2+}$, M	$[H_2S]$, M	k_1, $M^{-1}\ s^{-1}$
3.9	0.129	0.103
3.9	0.098	0.101
4.9	0.094	0.093
4.9	0.201	0.094

[a] Conditions: 0.1 M HBF_4, 25.0°, λ 255 nm, $I = 0.1$ M, average $k_1 = 0.10 \pm 0.004\ M^{-1}\ s^{-1}$.

Table II. Rate of Aquation of $[Ru(NH_3)_5H_2S]^{2+}$ [a]

$10^5[Ru(NH_3)_5H_2S^{2+}]$, M	[4-cpy H+], M	10^5k_{-1}, s^{-1}
9.63	0.100	5.94
23.8	0.100	7.68
17.5	0.100	6.91
8.70	0.200	6.13*
8.70	0.100	7.01
8.70	0.100	6.48

[a] Conditions: 25.0°, 0.11 M HCl, λ 530 nm, $I = 0.21$ M, except for (*) where $I = 0.31$ M, average $k_{-1} = (6.7 \pm 0.5) \times 10^{-5}\ s^{-1}$.

crease in absorbance (λ 530 nm) observed was attributed to the reaction of residual $[Ru(NH_3)_5H_2O]^{2+}$ with 4-cpyH$^+$. Following this a slower increase in absorbance, taking place at a rate independent of the concentration of 4-cpyH$^+$, occurred due to the loss of H_2S from $[Ru(NH_3)_5H_2S]^{2+}$ and subsequent fast substitution by 4-cpyH$^+$ ion on the aquated Ru(II) species. The reaction to form $[Ru(NH_3)_5(4\text{-}cpyH)]^{3+}$ did not go to completion, and side reactions such as oxidation and loss of ammonia interfered. Thus A_∞ could not be measured directly and was determined by measuring the absorbance of the desired product $[Ru(NH_3)_5(4\text{-}cpyH)]^{3+}$ under identical conditions but in the absence of H_2S. The value of A_∞ was based on ϵ $1.625 \times 10^4\ M^{-1}\ cm^{-1}$ at 530 nm, determined under these conditions, a factor of two different from the value reported by Ford and Clarke[21] (ϵ $8.3 \times 10^3\ M^{-1}\ cm^{-1}$ at 532 nm). Because of the complications mentioned, collection of data was limited to the early phase of the reaction. Beyond 30% reaction, significant contributions from side reactions were observed. It should be noted that though the side reactions precluded the direct determination of A_∞ and introduce other complications, they are slow compared to the reaction we were interested in, and thus the method of initial rates is applicable.

The results for the specific rate of loss of H_2S (k_{-1}) from $[Ru(NH_3)_5H_2S]^{2+}$ in 0.1 M H$^+$ ($I = 0.21$ M) at 25.0° are shown in Table II. The specific rate k_{-1} defined by the equation

$$\frac{d[Ru(NH_3)_5H_2O^{2+}]}{dt} = k_{-1}[Ru(NH_3)_5H_2S^{2+}]$$

is independent of the concentration of $[Ru(NH_3)_5H_2S]^{2+}$ ($(8.7\text{-}23.8) \times 10^{-5}$ M) and independent of the 4-cpyH$^+$ concentration (0.1-0.2 M). The average value of k_{-1} is $(6.7 \pm 0.5) \times 10^{-5}\ sec^{-1}$.

Several experiments to determine the rate of aquation of $[Ru(NH_3)_5H_2S]^{2+}$ in 0.1 M H$^+$ by degassing the free hydrogen sulfide gas into a standard Fe(III) solution and determining the amount of Fe(II) produced with time were also done. The reaction $H_2S + 2\ Fe^{3+} = 2\ Fe^{2+} + S(0)$ is known to be quantitative,[23] but to ensure complete absorption of H_2S it was necessary to disperse the gas thoroughly through the Fe(III) solution. Aliquots of oxidizing solution were removed periodically, and the amount of Fe(II) was determined spectrophotometrically by reaction with *o*-phenanthroline in acetate buffer. The specific rate k_{-1} by this method was found to be approximately the same as that determined in the experiments with 4-cpyH$^+$. This method is more tedious and is less accurate than the method using 4-cpyH$^+$ as a competing nucleophile.

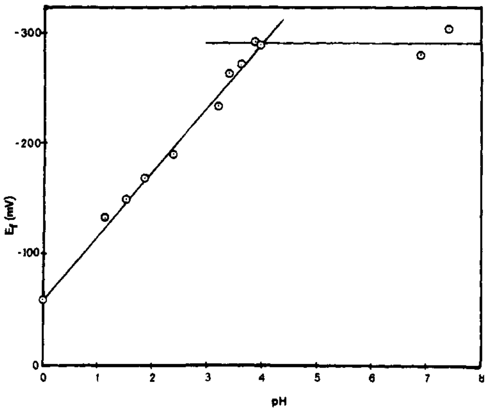

Figure 3. Formal reduction potentials (E_f) vs. pH for $[Ru(NH_3)_5(HS)]^{2+}$-$[Ru(NH_3)_5(H_2S)]^{2+}$ at 25° (tetrafluoroborate salt).

(g) The Affinity of H_2S for Ru(II) in Aqueous Solution. Using the specific rates for the forward and reverse reactions, the equilibrium constant for the reaction

$$[Ru(NH_3)_5H_2O]^{2+} + H_2S = [Ru(NH_3)_5H_2S]^{2+} + H_2O \qquad (5)$$

at 25° is calculated to be $(1.50 \pm 0.11) \times 10^3\ M^{-1}$.

(h) Electrochemistry of Solutions of $[Ru(NH_3)_5H_2S]^{2+}$. The electrochemical studies yielded values of E_f for the Ru(III)-Ru(II) couple with sulfide as a ligand. These values are of interest in their own right and as a function of [H$^+$] they led to a value of pK_a for $[Ru(NH_3)_5H_2S]^{2+}$ and to the related conclusion that the corresponding Ru(III) complex is completely dissociated to $[Ru(NH_3)_5HS]^{2+}$ + H$^+$ over the whole range of acidity covered in our studies.

To obtain the value of pK_a for $[Ru(NH_3)_5H_2S]^{2+}$ (more objectively, the variation of E_f with pH) the following procedure was adopted. A solution of ca. 11 mg of $[Ru(NH_3)_5H_2S](BF_4)_2$ in 2 ml of 0.05 M Eu^{2+} ion (0.075 M H$^+$, 0.175 M Cl$^-$) was titrated with the addition of a deaerated solution of 0.1 M Fe(III) (0.1 M H$^+$, 0.075 M Cl$^-$, 0.1 M TFA$^-$) until the concentrations of Ru(II) and Ru(III) were equal. At this point the addition of Fe(III) solution was stopped, and small increments of 2 M NaOAc solution were added using a 0.2-ml Gilmont micrometer syringe. The pH and the potential (as measured using the calomel and dropping mercury electrode) were recorded after each addition. To obtain the pH vs. potential values for the region pH 4-7.5, the titration was continued with 1 M NaOH instead of sodium acetate solution. Between readings the solution was abundantly purged with argon. The pK_a was determined from the break in a graph of E_f vs. pH.

The ionic strength was not kept constant but was about 0.25 at the critical point. In any case, it did not vary markedly during the titration. The results of a typical experiment are shown in Figure 3. Below pH ca. 4, E_f varies with [H$^+$] as expected for a reaction in which one proton is consumed for each electron absorbed by the oxidizing agent (slope 60.5 mV/pH unit compared to 59.5 theoretical). At pH 4.0, E_f becomes independent of pH. Thus below pH 4, the half-reaction can be taken to be:

$$e^- + H^+ + [Ru(NH_3)_5HS]^{2+} = [Ru(NH_3)_5H_2S]^{2+} \qquad (6)$$

This and related experiments show pK_a for H_2S coordinated to Ru(II) to be 4.0.

The potentiometric titration of $[Ru(NH_3)_5H_2S]^{2+}$ by an oxidizing agent covering the complete range of Ru(II)-Ru(III) concentrations is difficult, particularly when Ru(II) becomes largely converted to Ru(III), because $[Ru(NH_3)_5HS]^{2+}$ is unstable. However, a good titration profile was obtained in 1 M HCl, with two different oxidizing agents, which led to a value of E_f for half-reaction (eq 7) of −0.05 V (vs. NHE). This is in reasonable agreement with the extrapolated value of −0.06 V shown in Figure 3 for lower ionic strength. E_f for half-reaction

$$e^- + [Ru(NH_3)_5HS]^{2+} = [Ru(NH_3)_5H_2S]^+ \qquad (7)$$

is −0.29 V.

2. $[Ru(NH_3)_5S(CH_3)_2]^{2+}$, $[Ru(NH_3)_5SC_2H_5]^{2+}$, and Related Complexes. (a) Microanalyses. $[Ru(NH_3)_5S(CH_3)_2](BF_4)_2$, $[Ru(NH_3)_5S(CH_3)_2](PF_6)_2$, and $[Ru(NH_3)_5SC_2H_5](PF_6)_2$ were analyzed as follows:

$[Ru(NH_3)_5S(CH_3)_2](BF_4)_2$	C	H	N	Ru	S
% calcd	5.69	4.78	16.60	24.00	7.60
% obsd	5.65	4.78	16.77	24.3	7.81
$[Ru(NH_3)_5S(CH_3)_2](PF_6)_2$					
% calcd	4.46	3.93	13.01	18.77	5.96
% obsd	4.38	3.77	13.50	18.50	6.29
$[Ru(NH_3)_5SC_2H_5](PF_6)_2$					
% calcd	4.47	3.72	13.03		5.97
% obsd	4.65	3.50	12.89		5.84
% obsd	4.28	3.48	12.94		5.99

(b) Ultraviolet–Visible Spectra. The ultraviolet spectrum of $[Ru(NH_3)_5S(CH_3)_2](BF_4)_2$ in 0.1 M HCl shows two peaks: λ 258 nm, (ϵ 2.14 × 10^3 M^{-1} cm^{-1}), and λ 235 nm (ϵ 2.05 × 10^3 M^{-1} cm^{-1}) but no visible absorption bands. The ultraviolet peaks decrease slowly with time (ca. 5% within 1 h). The complex *cis*-$[Ru(NH_3)_4S(CH_3)_2(H_2O)](PF_6)_2$, isolated as a solid and found to be ~90% pure, has a peak at 255 nm (ϵ ~1.6 × 10^3 M^{-1} cm^{-1}) and a shoulder at 225 nm (ϵ ~1.8 × 10^3 M^{-1} cm^{-1}). The ion $[Ru(NH_3)_5S(CH_3)_2]^{3+}$, generated in solution by oxidation with Ag_2O-$HClO_4$ solution, has a shoulder at λ 258 nm (ϵ ~1.5 × 10^3). No solid of $[Ru^{III}(NH_3)_5S(CH_3)_2]^{3+}$ could be isolated.

The complex $[Ru(NH_3)_5SC_2H_5](PF_6)_2$ has a maximum at 508 nm (ϵ 1.9 × 10^3 M^{-1} cm^{-1}) in 0.1 M HCl and its spectrum is the same in 0.1 M NaOH and in 6 M HCl, indicating that the thiol is always unprotonated on Ru(III). The solid was difficult to obtain pure and often unidentified impurities introduced bands at 330 or 390 nm. The reduced species, $[Ru(NH_3)_5HSC_2H_5]^{2+}$, has a maximum at 255 nm (ϵ 1.9 × 10^3 M^{-1} cm^{-1}) in degassed 0.1 M HCl.

(c) Infrared Spectra of $[Ru(NH_3)_5S(CH_3)_2]^{2+}$ Salts. The infrared spectra of $[Ru(NH_3)_5S(CH_3)_2](BF_4)_2$ (CsI pellet), and of the corresponding perchlorate, hexafluorophosphate, and bromide salts, were obtained. Two especially meaningful frequencies, C-S stretch (weak) and S-CH_2 wag (medium) are listed below and compared to the corresponding ones in $S(CH_3)_2$ and $S(CH_3)_3^+$.

	C–S stretch (cm^{-1})	$-S-CH_2$ wag (cm^{-1})
$[Ru(NH_3)_5S(CH_3)_2]X_2$ where $X^- = BF_4^-, Br^-, PF_6^-$	675	1250
$[Ru(NH_3)_5S(CH_3)_2](ClO_4)_2$	680	1260
$S(CH_3)_2$	685	1300
$S(CH_3)_3^+PF_6^-$	654	1350

(d) NMR Spectrum of $[Ru(NH_3)_5S(CH_3)_2](ClO_4)_2$. An NMR spectrum of $[Ru(NH_3)_5S(CH_3)_2](ClO_4)_2$ in DMSO-*d* with 1% TMS[9] showed the methyl peak at 2.06 ppm, which is unshifted from the methyl peak in the spectrum of $(CH_3)_2S$ in DMSO-*d*. In comparison, the methyl peak in $S(CH_3)_3^+$ is at 2.84 ppm. The cis and trans NH_3 peaks in $[Ru(NH_3)_5S(CH_3)_2](ClO_4)_2$ are at 2.2 and 3.0 ppm, respectively.

Table III. Rate of Substitution of $S(CH_3)_2$ on $[Ru(NH_3)_5H_2O]^{2+a}$

$10^4[Ru(NH_3)_5H_2O^{2+}]$, M	$[H^+]$, M	$10^2 \times [(CH_3)_2S]$, M	$10^3 \times k_{obsd}$, s^{-1}	10^2k_1, s^{-1} M^{-1}
9.6	0.1 HBF_4	6.4	4.9	7.7
9.6	0.1 HBF_4	6.4	4.8	7.5
9.4	0.1 TFA	6.4	4.9	7.7
9.0	0.1 TFA	12.2	9.2	7.5
9.6	0.1 TFA	3.3	3.2	9.6
16.3	0.1 TFA	6.4	5.5	8.6

[a] Conditions: 25.0° λ 256 nm, I = 0.1 M, average k_1 = (8.0 ± 0.6) × 10^{-2} s^{-1} M^{-1}.

Table IV. Rate of Substitution of C_2H_5SH on $[Ru(NH_3)_5H_2O]^{2+a}$

$10^4 \times [Ru(NH_3)_5H_2O^{2+}]$, M	$10^2[C_2H_5SH]$, M	10^2k_1, M^{-1} s^{-1}
9.45	5.9	8.0
9.45	5.9	7.9
9.04	11.3	7.3
4.7	5.9	7.5

[a] Conditions: 25°, 0.1 M HTFA, λ 255 nm, I = 0.1 M, average k_1 = (7.7 ± 0.3) × 10^{-2} M^{-2} s^{-1}.

An NMR spectrum of $[Ru(NH_3)_5S(CH_3)_2](ClO_4)_2$ in 0.1 M DCl-D_2O showed only two peaks, the trans NH_3 peak at 2.94 ppm and a peak at 2.1 ppm which was the superposition of the methyl peak and the cis NH_3 peak. By adding a weighed amount of TSP,[9] the peaks could be integrated and all protons accounted for.

(e) Rate of Substitution of $S(CH_3)_2$ and C_2H_5SH in $[Ru(NH_3)_5H_2O]^{2+}$. The rate of complex formation was measured by the direct spectrophotometric method, following the increase in absorbance at or near the band maximum in the uv spectrum.

A stock solution of 1 × 10^{-3} M $[Ru(NH_3)_5Cl]Cl_2$ in 0.1 M HBF_4 or HTFA with 10% ethanol-water mixture was prepared. Twenty milliliters was reduced over zinc amalgam by bubbling argon through the solution in a Zwickel flask for at least 0.5 h. With C_2H_5SH as ligand, 1 ml of 0.02 M Eu^{3+} in 0.1 M HCl was added to the ruthenium solution and reduced as well. A stock solution of $(CH_3)_2S$ or C_2H_5SH was prepared by pipetting 10 ml of freshly distilled $(CH_3)_2S$ or C_2H_5SH into 50 ml of ethanol and diluting to 100 ml with water. The concentration of the $(CH_3)_2S$ solution was 1.34 ± 0.03 M, as calculated from the known density of $(CH_3)_2S$ and as determined by the microanalytical laboratory. The concentration of the C_2H_5SH solution was calculated to be 1.35 ± 0.03 M. Because $(CH_3)_2S$ and C_2H_5SH are extremely volatile (bp ~36°), the solutions were not degassed but instead 0.5-2 ml of the $(CH_3)_2S$ or C_2H_5SH stock, depending on the desired concentration, was transferred by means of a syringe directly into the ruthenium solution. The liquid was quickly filled into a 1-cm spectrophotometric cell using a Zwickel flask and placed into a thermostated cell compartment in the Cary 15 spectrophotometer. The results at 25.0°, H^+ = 0.1 M, in 12-13% ethanol-water mixtures, are presented in Tables III and IV. The specific rate k_{obsd} is defined as

$$\frac{d[\text{product}]}{dt} = k_{obsd}[Ru(NH_3)_5H_2O^{2+}]$$

where $k_{obsd} = k_1[L]$, L = $S(CH_3)_2$ or C_2H_5SH.

Because the solutions containing the sulfur ligands were

Table V. Rate of Aquation of $[Ru(NH_3)_5S(CH_3)_2]^{2+a}$

$10^5[Ru(NH_3)_5S(CH_3)_2{}^{2+}]$, M	$[H^+]$, M	$[4\text{-cpyH}^+]$, M	10^6k_{-1}, s^{-1}
9.6	0.10	0.10	4.8
28.9	0.10	0.10	4.1
52.6	0.10	0.10	4.3
19.4	0.10	0.20*	3.7

[a] Conditions: 25.0°, λ 490 nm, $I = 0.2$ M, except for (*) $I = 0.3$ M, average $k_{-1} = (4.2 \pm 0.3) \times 10^{-6}$ s^{-1}.

not degassed, some oxidation producing $[Ru(NH_3)_5Cl]Cl_2$ was observed, but this inert species did not affect the rate of substitution on Ru(II). Experiments were done under pseudo-first-order conditions with sulfur ligand in high excess concentrations, and the reverse specific rate k_{-1} was negligible. Plots of log $(A_\infty - A)$ vs. time were linear for 3-3.5 half-lives. The specific rates for the substitution of $S(CH_3)_2$ and C_2H_5SH on $[Ru(NH_3)_5H_2O]^{2+}$ are $(8.0 \pm 0.6) \times 10^{-2}$ and $(7.7 \pm 0.3) \times 10^{-2}$ M^{-1} sec^{-1}, respectively.

Earlier work by Allen and Ford[22] on the substitution of pyridines in $[Ru(NH_3)_5H_2O]^{2+}$ showed that rates in 12% ethanol-water mixtures are not significantly different from rates in water.

(f) The Aquation of $[Ru(NH_3)_5S(CH_3)_2]^{2+}$ and $[Ru(NH_3)_5HSC_2H_5]^{2+}$. The aquation of the sulfur ligands on $[Ru(NH_3)_5S(CH_3)_2]^{2+}$ and $[Ru(NH_3)_5HSC_2H_5]^{2+}$ proved to be relatively slow reactions ($t_{1/2} > 10$ h) even in 0.1 M H^+ solution. We attempted to follow the progress of the aquation reaction by the 4-cpyH^+ scavenging method described for the aquation of the H_2S complex.

In the case of $[Ru(NH_3)_5S(CH_3)_2](BF_4)_2$ aquation, studies were done in the presence of 0.1 M H^+ and 0.1 M 4-cpyH^+ in glass-sealed 1-cm spectrophotometric cells. A band gradually appeared ($t_{1/2} \sim 50$ hr) at 490 nm, instead of at 532 nm for $[Ru(NH_3)_5(4\text{-cpyH})]^{3+}$, and did not shift wavelength for long periods of time (~1 week), indicating that NH_3 was being lost rather than $S(CH_3)_2$. The reaction scheme is

$$[Ru(NH_3)_5S(CH_3)_2]^{2+} \xrightarrow[k_{-1}]{\text{slow}} [Ru(NH_3)_4(H_2O)S(CH_3)_2]^{2+} + NH_3 \quad (8)$$

$$[Ru(NH_3)_4(H_2O)S(CH_3)_2]^{2+} + 4\text{-cpyH}^+ = [Ru(NH_3)_4S(CH_3)_2(4\text{-cpyH})]^{3+} \quad (9)$$

The system reached a reaction plateau at the stage represented by eq 9, but further reactions resulted in continued increase in absorbance and a shift of the wavelength of the maximum. The data were plotted as log $(A_\infty - A)$ vs. time by estimating A_∞, using an extinction coefficient for $[Ru(NH_3)_4S(CH_3)_2(4\text{-cpyH})]^{3+} = 1.2 \times 10^4$ M^{-1} cm^{-1}. This extinction coefficient was close to that measured for *cis*-$[Ru(NH_3)_4S(CH_3)_2(4\text{-cpyH})]^{3+}$, generated in solution by allowing *cis*-$[Ru(NH_3)_4S(CH_3)_2H_2O](PF_6)_2$ to react for 2 h with 0.1 M 4-cpyH^+ in 0.1 M HCl. Though the spectrum of the product of reaction 9 corresponded to that of the synthetic cis product, we cannot be certain that the trans product was absent (the trans 4-cpyH^+ product was not characterized). Plots of log $(A_\infty - A)$ vs. time for one half-life (~50 h) were fairly linear. The results are presented in Table V. The specific rate for the loss of NH_3 from $[Ru(NH_3)_5S(CH_3)_2]^{2+}$ is 4.2×10^{-6} s^{-1}.

For the aquation studies on $[Ru(NH_3)_5HSC_2H_5](BF_4)_2$ in the presence of 0.1 M 4-cpyH^+, 0.1 M H^+, the situation was even more complicated. A band appeared at λ 525 nm (note that $[Ru(NH_3)_5(4\text{-cpyH})]^{3+}$ has a band maximum at 532 nm) and gradually increased in intensity while the wavelength maximum shifted to about 500 nm within 2 days. The continuous shifting of the wavelength of the band maximum from a position close to that for $[Ru(NH_3)_5(4\text{-cpyH})]^{3+}$ (532 nm) to lower wavelengths suggests that loss of NH_3 and loss of C_2H_5SH are concurrent.

From the absorbance change described, an estimate for the upper limit of the rate of aquation of C_2H_5SH was obtained. The A_∞ for the reaction was estimated from the curvature of a plot of absorbance vs. time. From plots of log $(A_\infty - A)$ vs. time, linear for 12 h, a limit for the rate of aquation of C_2H_5SH was determined to be $\leq 3 \times 10^{-5}$ s^{-1}.

(g) Estimated Stabilities for $[Ru(NH_3)_5S(CH_3)_2]^{2+}$ and $[Ru(NH_3)_5HSC_2H_5]^{2+}$. Using the forward specific rate for the substitution of $S(CH_3)_2$ on $[Ru(NH_3)_5H_2O]^{2+}$, k_1, and the reverse specific rate for the loss of NH_3, k_{-1}, a lower limit for the equilibrium constant for the reaction

$$[Ru(NH_3)_5H_2O]^{2+} + S(CH_3)_2 = [Ru(NH_3)_5S(CH_3)_2]^{2+} + H_2O$$

can be calculated. Therefore

$$K_{eq} \geq \frac{5k_1}{k_{-1}} \geq \frac{5(8.0 \times 10^{-2})}{4.2 \times 10^{-6}} \geq 9.5 \times 10^4 \ M^{-1}$$

In applying the correction for the statistical factor of 5, it is assumed that NH_3 can be lost from cis, as well as trans positions.

Similarly, using the forward specific rate for substitution of C_2H_5SH on $[Ru(NH_3)_5H_2O]^{2+}$, k_1, and the upper limit for the reverse rate, K_{eq} for the reaction

$$[Ru(NH_3)_5H_2O]^{2+} + C_2H_5SH = [Ru(NH_3)_5C_2H_5SH]^{2+} + H_2O$$

is $\geq 3 \times 10^3$ M^{-1}.

(h) Electrochemistry of $[Ru(NH_3)_5S(CH_3)_2]^{2+}$ and $[Ru(NH_3)_5HSC_2H_5]^{2+}$. Cyclic voltammetry of $[Ru(NH_3)_5S(CH_3)_2]^{2+}$ in 0.1 M HCl showed a well-behaved reversible wave, with $E_f = 0.504$ V. The presence of even one dissociable proton on the sulfur ligand invalidated cyclic voltammetry as a means to determine reduction potentials for the complex $[Ru(NH_3)_5HSC_2H_5]^{2+}$. Therefore the reduction potential of the $[Ru^{III}(NH_3)_5SC_2H_5]^{2+}$-$[Ru^{II}(NH_3)_5HSC_2H_5]^{2+}$ couple was determined by a potentiometric titration with standard Fe(III) solution in 0.1 M H^+, similar to that carried out for the Ru(III)-Ru(II) sulfide couple. The potential was recorded after each addition of the standard Fe(III) solution (0.1 M). The value of E_f for $[Ru^{III}(NH_3)_5SC_2H_5]^{2+}$-$[Ru^{II}(NH_3)_5HSC_2H_5]^{2+}$ in 0.1 M HCl was estimated to be +0.04 V from the graph of EMF plotted against volume of oxidant solution. As expected, the solution changed from colorless $[Ru(NH_3)_5HSC_2H_5]^{2+}$ to red $[Ru(NH_3)_5SC_2H_5]^{2+}$ during titration. The alkyl group in place of hydrogen on the sulfur ligand stabilizes the Ru(III) state against the formation of the $[S_2{}^{2-}]$ bridged dimer.

(i) Determination of the pK_a of $[Ru(NH_3)_5HSC_2H_5]^{2+}$. The ionization constant of the coordinated C_2H_5SH was determined by the method used for the $[Ru(NH_3)_5H_2S]^{2+}$ complex. In a titration half of the $[Ru(NH_3)_5HSC_2H_5]^{2+}$ in 0.1 M HCl was quantitatively oxidized with 1 equiv of standard Fe(III) solution to the equivalence potential, +0.04 V, determined for this pH. At this point the solution was titrated with 1 *N* Na_3PO_4 solution, and the pH and the potential were recorded after each addition. The potentials measured were taken to be the formal potentials for the Ru(III)-Ru(II)-ethanethiol couple at different pH values. A plot of these formal potentials vs. pH showed the potential to vary with pH below 9.2 (slope 60 mV/pH) and to be independent of pH above this value. We conclude that the ligand is completely deprotonated on Ru(III) over the whole pH range 1-11, and that pK_a for reaction 10 is 9.2 ± 0.2

$$[Ru(NH_3)_5HSC_2H_5]^{2+} = [Ru(NH_3)_5SC_2H_5]^{+} + H^{+} \quad (10)$$

3. Characterization of $[Ru(NH_3)_5L]^{2+}$ (L = Thiophene and Tetrahydrothiophene) and $[Ru(NH_3)_4L]^{2+}$ (L = Methionine Methyl Ester and Cysteine Ethyl Ester). (a) Elemental analyses of the tetrahydrothiophene (THT) and thiophene complexes were as follows:

$[Ru(NH_3)_5THT](BF_4)_2$	C	H	N
% calcd	10.72	5.17	15.63
% obsd	10.51	5.04	15.40

$[Ru(NH_3)_5thiophene](PF_6)_2$	C	H	N
% calcd	8.5	3.4	12.5
% obsd	7.0	3.3	13.0

Analysis of the thiophene complex indicated that the solid was probably only 80% $[Ru(NH_3)_5(thiophene)](PF_6)_2$ (and 20% $[Ru(NH_3)_5H_2O](PF_6)_2$). In view of the lability of the thiophene complex, to be discussed presently, contamination as suggested is not surprising.

The methionine ester and cysteine ester complexes were prepared independently also by Diamond[14] and the properties as measured by him agree with those described herein.

The ultraviolet spectrum of $[Ru(NH_3)_5THT](BF_4)_2$ in 0.1 M HCl showed two peaks: λ 235 nm, ε 1.9 × 10^3 M^{-1} cm^{-1}, and λ 262 nm, ε 1.9 × 10^3 M^{-1} cm^{-1}. The spectrum was stable with time, there being only about 5% change (increase in the peak at λ 235 and decrease in the peak at λ 262 nm) in 1 h.

The spectrum of $[Ru(NH_3)_5(thiophene)](BF_4)_2$ in 0.1 M HCl showed a small peak at λ 450 nm (ε ~200 M^{-1} cm^{-1}) and a shoulder at λ 260 nm (ε ~2 × 10^3 M^{-1} cm^{-1}). Within minutes of dissolution of the solid, the peaks at 450 and 260 nm disappeared with corresponding growth of a new peak at 327 nm.

The methionine methyl ester complex has an ultraviolet spectrum with two peaks at λ 234 and 255 nm with extinction coefficients of the order of 10^3 M^{-1} cm^{-1}. The spectrum is stable for a period of 0.5 h.

(b) Electrochemistry of Ruthenium Complexes of Thiophene, Tetrahydrothiophene, Methionine Methyl Ester, and Cysteine Ethyl Ester. Cyclic voltammograms of $[Ru(NH_3)_5THT]^{2+}$,[9] $[Ru(NH_3)_5(thiophene)]^{2+}$, and the methionine methyl ester complex all showed reversible redox couples in 0.1 M HCl with that of $[Ru(NH_3)_5(thiophene)]^{2+}$ disappearing completely within minutes. These reduction potentials are given in Table X.

The cysteine ethyl ester complex, in 0.1 M HCl, gave a very irreversible wave (245 mV separation), similar to that for the ethanethiol complex, and no formal potential could be obtained from cyclic voltammetry.

Table VI. Rate of Aquation of $[Ru(NH_3)_5(thiophene)]^{2+}$

$10^4[Ru(NH_3)_5$-(thiophene)$]^{2+}$, M	10^3k_{-1}, s^{-1}
1.3	7.2[a]
0.9	7.5[a]
1.1	8.5[a]
11	9.9[b]
11	7.7[b]

[a] Conditions: 0.1 M 4-cpyH^+, 0.1 M HCl, 25°, λ 530 nm, I = 0.1 M. [b] Conditions: 0.1 M HTFA, 25°, λ 450 nm, I = 0.1 M, average $k_{-1} = (8.2 \pm 0.8) \times 10^{-3}\ s^{-1}$.

(c) Dynamics of $[Ru(NH_3)_5(thiophene)]^{2+}$ in water. The aquation of thiophene from $[Ru(NH_3)_5(thiophene)]^{2+}$ proved to be quite rapid ($t_{1/2}$ ~ 85 sec). Preliminary work on the rate of aquation, using the complex approximately 80% pure, was followed by two methods. In one, the rate of loss of thiophene was directly determined by monitoring the decrease in the peak at 450 nm. In the second method, the aquation of thiophene was determined in the presence of 0.1 M 4-cpyH^+, 0.1 M H^+, by monitoring the increase in a peak at 530 nm, near the maximum for $[Ru(NH_3)_5$4-cpy$H]^{3+}$ (532 nm). The results for both methods are presented in Table VI. Based on these preliminary data the average specific rate, k_{-1}, for the reaction

$$H_2O + [Ru(NH_3)_5(thiophene)]^{2+} \xrightarrow{k_{-1}} [Ru(NH_3)_5H_2O]^{2+} + \text{thiophene}$$

is (8.2 ± 0.8) × 10^{-3} s^{-1} at 25°, 0.1 M H^+.

The specific rate of substitution of C_2H_5SH and $(CH_3)_2S$ on $[Ru(NH_3)_5H_2O]^{2+}$ has been determined to be 8 × 10^{-2} M^{-1} s^{-1}, and in other studies on the specific rate for substitution on $[Ru(NH_3)_5H_2O]^{2+}$ has been found to be almost independent of the nature of the incoming ligand for a variety of neutral molecules.[7] Therefore k_1 = 8 × 10^{-2} M^{-1} s^{-1} was taken as an estimate for the reaction

$$[Ru(NH_3)_5H_2O]^{2+} + \text{thiophene} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ru(NH_3)_5(thiophene)]^{2+} + H_2O$$

The value of the equilibrium constant for the association of thiophene with $[Ru(NH_3)_5H_2O]^{2+}$ can therefore be estimated from the forward and reverse specific rates

$$K_{eq} = \frac{k_1}{k_{-1}} \sim \frac{8 \times 10^{-2}\ M^{-1}\ s^{-1}}{8 \times 10^{-3}\ s^{-1}} \sim 10\ M^{-1}$$

4. *trans*-$[Ru(NH_3)_4(isn)(H_2S)](BF_4)_2$ and Its $(CH_3)_2S$ and C_2H_5SH Analogues. (a) Microanalyses. Solids of *trans*-$[Ru(NH_3)_4(isn)(H_2S)](BF_4)_2$ consistently analyzed in good agreement with that formula:

	C	H	N	Ru	S
% calcd	14.43	4.04	16.84	20.2	6.42
% obsd	14.32	4.02	16.95	19.9	6.2

The preparation of *trans*-$[Ru(NH_3)_4(isn)(S(CH_3)_2)](BF_4)_2$ and *trans*-$[Ru(NH_3)_4(isn)(C_2H_5SH)](BF_4)_2$ was also carried out for comparative studies. The elemental analyses of these indicated some impurity, but no further purification of the samples was attempted.

		C	H	N
	% calcd	18.26	4.60	15.97
trans-$[Ru(NH_3)_4(isn)(S(CH_3)_2)](BF_4)_2$	% obsd	17.35	4.54	15.33
trans-$[Ru(NH_3)_4(isn)$-$(C_2H_5SH)](BF_4)_2$	% obsd	18.82	4.74	14.08

(b) Ultraviolet–Visible Spectra. Figure 4 shows the spectra of *trans*-$[Ru(NH_3)_4(isn)(H_2S)](BF_4)_2$ in degassed, 1 M HCl, saturated hydrogen sulfide solution at 5° and in degassed, phosphate buffer (pH 7)–KCl solution (I = 1), at 25°. The values of λ_{max} are 430 nm, ε 1.10 × 10^4 M^{-1} cm^{-1}, (slight shoulder), ε 0.75 × 10^4 M^{-1} cm^{-1} for the H_2S form, and 511 nm, ε 1.0 × 10^4 M^{-1} cm^{-1}, and 255 nm (shoulder), ε 0.45 × 10^4 M^{-1} cm^{-1} for the HS^- form. The reported extinction coefficients for the protonated form are accurate to within 5%. Fairly rapid aquation occurred in acidic media as evidenced by the shift of λ_{max} from 430 to 480 nm (λ_{max} for *trans*-$[Ru(NH_3)_4(isn)H_2O]^{2+}$ 480 nm), while at neutral pH the spectrum did not change for a period of 1 h. Therefore to minimize the aquation while taking

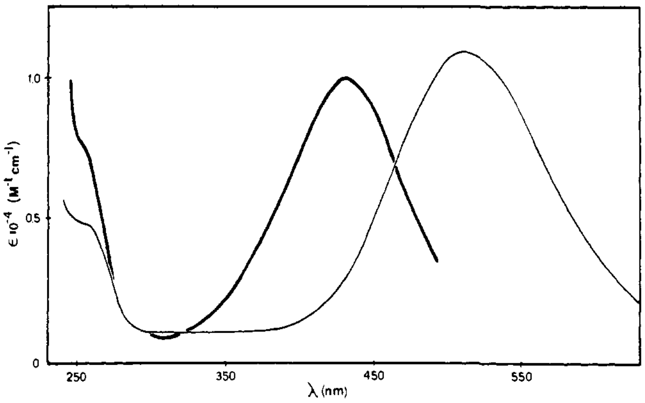

Figure 4. Ultraviolet-visible spectra of *trans*-[Ru(N-$H_3)_4$(isn)$H_2S](BF_4)_2$ in H_2S-saturated, 1 M HCl at 5° (heavy line) and in phosphate buffer (pH 7)–KCl solution (I = 1) at 25° (light line).

the spectrum of *trans*-[Ru$(NH_3)_4$(isn)$(H_2S)]^{2+}$ in 1 M HCl, the solution was saturated with H_2S at 5° and the solid was dissolved in the solution immediately before determining the spectrum. The strong absorption in the visible region proved a great convenience in studying the complex.

The complex *trans*-[Ru$(NH_3)_4$(isn)$(S(CH_3)_2)](BF_4)_2$ in water showed a spectrum with λ_{max} 430 nm, ϵ 8.6 × 10^3 M^{-1} cm^{-1}, and λ_{max} 251 nm (shoulder), ϵ 6.8 × 10^3 M^{-1} cm^{-1}, similar in shape to that of *trans*-[Ru(N-$H_3)_4$(isn)$(H_2S)]^{2+}$. The complex *trans*-[Ru(N-$H_3)_4$(isn)$(C_2H_5SH)](BF_4)_2$ has two bands with maxima at 373 nm (ϵ 2.6 × 10^3 M^{-1} cm^{-1}) and 252 nm (ϵ 3.9 × 10^3 M^{-1} cm^{-1}) in 0.1 M HCl, which are unstable with time. Within minutes the band at 373 nm disappeared and the band at 252 nm shifted to 258 nm. The band at 373 nm does not appear to be consistent with the more dependable observations made for the H_2S and $(CH_3)_2S$ complexes, and we have no confidence that we have described the spectrum of the C_2H_5SH complex correctly.

(c) **Infrared and Raman Spectra.** The infrared spectrum of *trans*-[Ru$(NH_3)_4$(isn)$(H_2S)](BF_4)_2$ (CsI pellet) was taken but as with $[Ru(NH_3)_5H_2S](BF_4)_2$ no S-H stretching frequency could be distinguished in the N-H overtone region, 2500-2700 cm^{-1}. A band at 280 cm^{-1} is tentatively assigned to a Ru-S stretching frequency. Raman spectra of the *trans*-[Ru$(NH_3)_4$(isn)$(H_2S)](BF_4)_2$ solid were difficult to obtain because of its dark brown color. Solution spectra were not measured due to complications arising from aquation of the complex. In the solid samples no S-H stretch could be observed, using the 6471 Å laser line for excitation, nor was a Ru-S stretch found in the Raman.

Infrared spectra of *trans*-[Ru$(NH_3)_4$(isn)L]$(BF_4)_2$, where L = $S(CH_3)_2$ and C_2H_5SH, showed the typical N-H and ligand bands expected.

(d) **Rate of Substitution of H_2S on *trans*-[Ru(N-$H_3)_4$(isn)$H_2O]^{2+}$.** The specific rate of reaction 11 was determined spectrophotometrically

$$trans\text{-}[Ru(NH_3)_4(isn)H_2O]^{2+} + H_2S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[Ru(NH_3)_4(isn)(H_2S)]^{2+} + H_2O \quad (11)$$

Under the conditions studied, the contributions by the k_1 and k_{-1} paths are comparable, and, for the results presented in Table VII, k_{obsd} is defined as $k_{obsd} = k_1[H_2S] + k_{-1}$

$$d(product) = k_{obsd}[Ru(II)]$$

Table VII. Rate of Approach to Equilibrium in the Reaction of H_2O with *trans*-[Ru$(NH_3)_4$(isn)$H_2O]^{2+a}$

10^4 (*trans*-[Ru$(NH_3)_4$(isn)H_2O^{2+}]), M	$[H_2S]$, M	10^3k_{obsd}, s^{-1}
3.33	0.18	2.22
3.33	0.18	2.13
3.33	0.18	2.24
3.33	0.18	2.14
3.33	0.18	2.09

[a] Conditions: 25.0°, 0.50 M HTFA, λ 520 nm, I = 0.5 M, $k_{obsd} = k_1[H_2S] + k_{-1}$; average k_{obsd} = (2.16 ± 0.5) × 10^{-3} s^{-1}.

Table VIII. Rate of Aquation of *trans*-[Ru$(NH_3)_4$(isn)$H_2S]^{2+a}$

10^4(*trans*-[Ru-$(NH_3)_4$(isn)H_2S^{2+}]), M	10^3k_{-1}, s^{-1}
2.20	1.00
2.20	0.873
2.20	0.974
1.10	0.914
22.2	0.938

[a] Conditions: 25.0°, 0.50 M HTFA, λ 470 nm, I = 0.50 M, average k_{-1} = (0.94 ± 0.04) × 10^{-3} s^{-1}.

The complex *trans*-[Ru$(NH_3)_4$(isn)$H_2O]^{2+}$ has a maximum at 478 nm (ϵ ~10^4 M^{-1} cm^{-1}) and the substitution of H_2S could be conveniently monitored by the decrease in absorbance. Light at 520 nm proved to be convenient for monitoring the reaction since no contribution from the product was observed at this wavelength.

At 25° and 0.5 M HTFA the concentration of H_2S in saturated solution was determined to be 0.18 M by iodometric titration. The average k_{obsd} (Table VII) was (2.16 ± 0.05) × 10^3 s^{-1} for the conditions studied.

Since the concentration of H_2S was not varied, the forward specific rate k_1 could be calculated from k_{obsd} (forward) only after k_{-1} had been independently determined.

(e) **Aquation Studies on *trans*-[Ru$(NH_3)_4$(isn)L]$^{2+}$, where L = H_2S, $S(CH_3)_2$, and C_2H_5SH.** The rate of loss of H_2S from *trans*-[Ru$(NH_3)_4$(isn)$H_2S]^{2+}$ was studied independently by dissolving the complex in 0.5 M HTFA and following the increase in absorbance at 470 nm resulting from the formation of *trans*-[Ru$(NH_3)_4$(isn)$H_2O]^{2+}$.

The specific rates k_{-1} measured for the reaction 12

$$H_2O + trans\text{-}[Ru(NH_3)_4(isn)H_2S]^{2+} \xrightarrow{k_{-1}} trans\text{-}[Ru(NH_3)_4(isn)H_2O]^{2+} + H_2S \quad (12)$$

are summarized in Table VIII. The value of k_{-1} is found to be (0.94 ± 0.04) × 10^{-3} s^{-1} at 25° and 0.50 M HTFA. The forward rate was insignificant at the level of H_2S concentration (10^{-4} M) present during the aquation reaction. Thus these experiments measure the specific rate k_{-1} independently.

Using the values for k_{-1} = 0.94 × 10^{-3} s^{-1}, k_{obsd} = 2.16 × 10^{-3} s^{-1}, and $[H_2S]$ = 0.18 M in the expression

$$k_{obsd} = k_1[H_2S] + k_{-1}$$

the forward specific rate k_1 was calculated to be 6.78 × 10^{-3} s^{-1} M^{-1}.

Preliminary studies on the aquation of *trans*-[Ru(N-$H_3)_4$(isn)$(S(CH_3)_2)]^{2+}$ and *trans*-[Ru$(NH_3)_4$(isn)-$(C_2H_5SH)]^{2+}$ in 0.5 M HTFA at 25° were done in glass-sealed spectrophotometric cells. The presence of a visible band, attributed to a πd-π^* charge transfer for Ru(II)-isn, provided a convenient means of studying the aquation of these complexes spectrophotometrically.

For *trans*-[Ru$(NH_3)_4$(isn)$(S(CH_3)_2)]^{2+}$ it appeared that isn was lost prior to $S(CH_3)_2$. This conclusion is based on the observation that the band at 430 nm disappears at an estimated specific rate of about $9 \times 10^{-6}\ s^{-1}$ and a colorless solution is formed. Note, that Ru(II)-$S(CH_3)_2$ has no visible absorption band while both *cis*- and *trans*-$[Ru(NH_3)_4(isn)H_2O]^{2+}$ have a visible band near 480 nm.[16] Discharge of color by air oxidation was eliminated as a possibility since the experiment was done in a spectrophotometric cell which was carefully degassed and glass-sealed. The same results were observed for duplicate experiments.

Similar observations on the aquation of *trans*-$[Ru(NH_3)_4(isn)(C_2H_5SH)]^{2+}$ in 0.5 M HTFA at 25° showed that C_2H_5SH was lost rather than isn, and at a rate comparable to the loss of H_2S from the analogous complex, *trans*-$[Ru(NH_3)_4(isn)(H_2S)](BF_4)_2$. This statement is based on the disappearance of a band at 370 nm and the simultaneous growth of a peak at 475 nm within about 1 h. The estimated specific rate is $1 \times 10^{-3}\ s^{-1}$. The visible absorption in the final solution corresponded to that of *trans*-$[Ru(NH_3)_4(isn)H_2O]^{2+}$.

(f) Equilibrium Constant of *trans*-$[Ru(NH_3)_4(isn)(H_2S)](BF_4)_2$. The equilibrium constant for the reaction

$$trans\text{-}[Ru(NH_3)_4(isn)H_2O]^{2+} + H_2S = trans\text{-}[Ru(NH_3)_4(isn)(H_2S)]^{2+} + H_2O$$

at 25° was calculated from the ratio of the forward and reverse specific rates to be

$$K_{eq} = \frac{k_f}{k_r} = \frac{6.78 \times 10^{-3}}{0.94 \times 10^{-3}} = 7.2\ M^{-1}$$

(g) Electrochemistry of *trans*-$[Ru(NH_3)_4(isn)L]^{2+}$ where L = H_2S, $S(CH_3)_2$, and C_2H_5SH. All attempts to determine the oxidation potentials of *trans*-$[Ru(NH_3)_4(isn)(H_2S)]^{2+}$ were unsuccessful. Because of its fairly rapid aquation rate ($t_{1/2} \sim 10$ min), potentiometric titration could not be used. Fast scan cyclic voltammetry scans over the entire pH range did not yield meaningful results, presumably because of complicated electrode surface reactions, as was observed with other sulfur ligands having a dissociable proton. Cyclic voltammetry results for *trans*-$[Ru(NH_3)_4(isn)(C_2H_5SH)]^{2+}$ in the region pH 1-10 also could not be interpreted. On the other hand, cyclic voltammetry of *trans*-$[Ru(NH_3)_4(isn)S(CH_3)_2]^{2+}$ in 0.1 M HBF_4 gave a reversible wave at +0.705 vs. NHE.

(h) Determination of pK_a for *trans*-$[Ru(NH_3)_4(isn)(H_2S)]^{2+}$. The large spectral change associated with deprotonation of *trans*-$[Ru(NH_3)_4(isn)(H_2S)]^{2+}$ was used to determine the pK_a using a spectrophotometric pH titration method. To minimize the degree of aquation of *trans*-$[Ru(NH_3)_4(isn)(H_2S)]^{2+}$ the titration was done at 5° as quickly as possible. The results of a typical titration of *trans*-$[Ru(NH_3)_4(isn)(H_2S)]^{2+}$ with 1.00 M HCl (1×10^{-4} M complex, $I = 0.5$ M with 0.475 M NaTos, 0.025 M KHP, and the initial pH adjusted to 6.3, 5°), plotted as absorbance (λ 530 nm) vs. pH are shown in Figure 5.

Three separate titrations were done including titrations from acidic to basic and basic to acidic solutions. Besides the above mentioned experiment, a solution $\sim 1 \times 10^{-4}$ M complex in 0.05 M HCl, 0.45 M NaTos, was titrated initially with 1 M NaOAc and later with 1 M NaOH. Also a solution $\sim 1.6 \times 10^{-4}$ M complex in 0.025 M KPH, 0.475 M NaTos, with the initial pH adjusted to pH 1.5, was titrated with 1.00 M NaOH.

From these experiments the pK_1 corresponding to the reaction

$$trans\text{-}[Ru(NH_3)_4(isn)(H_2S)]^{2+} = trans\text{-}[Ru(NH_3)_4(isn)(HS)]^{+} + H^{+}$$

was determined as 3.25 ± 0.2 at 5°. We concluded that the value of pK_2 is greater than 14 since the spectrum of *trans*-$[Ru(NH_3)_4(isn)(H_2S)](BF_4)_2$ at pH 7 is almost identical with its spectrum in 1 M NaOH (λ_{max} 515 nm, ϵ 1×10^4 $M^{-1}\ cm^{-1}$).

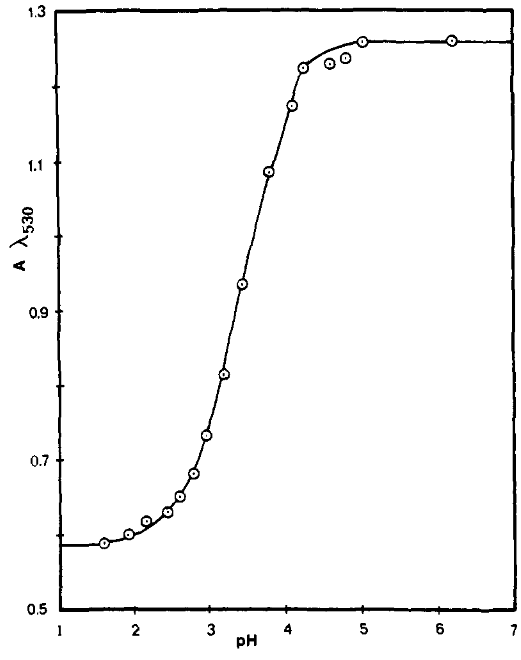

Figure 5. Spectrophotometric determination of pK_a for *trans*-$[Ru(NH_3)_4(isn)H_2S](BF_4)_2$ at 5° (pK_a = 3.25 ± 0.2).

5. Determination of the Values of pK_a for Some Aquo Ions. (a) *trans*-$[Ru(NH_3)_5(isn)H_2O]^{2+}$. As in the case of the analogous H_2S complex, there is a marked change in spectrum when the aquo ion loses a proton, and again the value of the pK_a could conveniently be determined spectrophotometrically. The aquo ion shows a band maximum at 478 nm while in the hydroxo complex this has shifted to 520 nm. The extinction coefficients at the maximum for both ions are $10^4\ M^{-1}\ cm^{-1}$.

In a typical titration the trans complex at 1×10^{-4} M concentration in 0.475 M NaTos, 0.025 M $NaHCO_3$, was titrated with 1 M NaOH, and the absorbance was registered as a function of pH. From those titrations the value of pK_a for reaction 13,

$$trans\text{-}[Ru(NH_3)_4(isn)H_2O]^{2+} = trans\text{-}[Ru(NH_3)_4OH]^{+} + H^{+} \quad (13)$$

was determined as 11.7 ± 0.1 at 25°.

(b) $[Ru(NH_3)_5H_2O]^{2+}$. A tentative value of 10.7 was reported[24] as pK_a for the species $[Ru(NH_3)_5H_2O]^{2+}$ but later work[25] using cyclic voltammetry cast doubt on the earlier result and showed the value of pK to be considerably higher. Since the measurement is of interest in making comparisons to the H_2S complex, we considered it worthwhile to reexamine the matter.

The pK_a of $[Ru(NH_3)_5H_2O]^{2+}$ was redetermined[26] by measuring the formal potentials of $[Ru(NH_3)_5H_2O]^{2+}$ using cyclic voltammetry for a series of solutions varying from pH 1 to 14. All attempts to determine the pK_a of $[Ru(NH_3)_5H_2O]^{2+}$ by either spectrophotometric or direct pH titration methods proved unsuccessful. Two series of cyclic voltammetry experiments were done, using KCl to maintain constant ionic strength $I = 0.45$ M, and using $NaClO_4$ to maintain constant ionic strength, $I = 1.0$ M. The potentials were not a sensitive function of ionic strength and all the points are plotted in Figure 6, as indicated. The slope of the line between pH 4 and 13 was equal

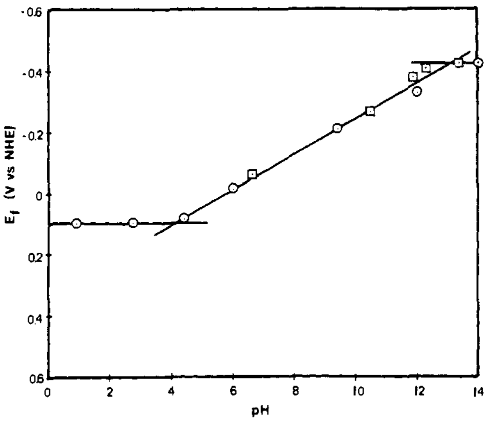

Figure 6. Formal reduction potentials vs. pH for $[Ru(NH_3)_5H_2O]^{3+/2+}$.

to 57.9 mV/pH compared to a theoretical value of 59 mV/pH. From the inflection points, the pK_a of reactions 14 and 15 could be determined to be 4.1 and 13.1 ± 0.1 pK, respectively.

$$[Ru(NH_3)_5H_2O]^{3+} = [Ru(NH_3)_5OH]^{2+} + H^+ \quad (14)$$

$$[Ru(NH_3)_5H_2O]^{2+} = [Ru(NH_3)_5OH]^{+} + H^+ \quad (15)$$

The pK_a of $[Ru(NH_3)_5H_2O]^{3+} = 4.1 \pm 0.1$ agrees well with the previously reported value, 4.2, determined by direct acid-base titration. Our value of pK_a for reaction 15 agrees reasonably well with the value 12.3 reported by Lim et al.,[25] considering the difference in ionic strength (up to 1 M in our case).

6. Summary of Some Properties of Ru-S Complexes. Spectrophotometric Properties. The characteristics of the uv-visible absorption spectra are summarized in Table IX. The uv band maxima are subject to ±3 nm error.

Reduction Potentials. The reduction potentials for the ruthenium-sulfur complexes are listed in Table X, as are some couples which are of interest for comparisons. The values of E_f are defined as the potential vs. NHE when the concentration of the oxidizing and of the reducing agent are equal. When the net half-reaction involves H^+, the values of E_f are $[H^+]$ dependent (i.e., the standard state of 1 M H^+ is not specified in our use of E_f).

Magnetic Susceptibilities. The values of magnetic susceptibility have not been referred to in the foregoing, because they proved to be of limited usefulness. The compound $[Ru(NH_3)_5(SC_2H_5)](PF_6)_2$ proved to be paramagnetic (1.83 μ_B for Ru) as did $[Ru(NH_3)_5Cl]Cl_2$ (2.13 μ_B for Ru). A large number of Ru(II) complexes ($S(CH_3)_2$, DMSO, H_2S, isn + H_2S, isn + SO_2, SO_2 + Cl^-) after correction for diamagnetism showed residual paramagnetism, ranging from 0.2 to 0.6 μ_B for Ru (calculated from single temperature measurements at 25°) which is undoubtedly attributable to temperature independent paramagnetism.

Discussion

Even with the advantages which the $Ru(NH_3)_5^{2+}$ center offers, it is clear that the preparation of its H_2S complex is barely possible, and in fact the solid salts which were prepared were not quite pure. It was unexpected that the principal spoiling reaction proved to be oxidation of the Ru(II) complex, rather than its degradation to the solid sulfide. The reactivity of the Ru(II)-H_2S combination as a reducing system is quite remarkable. Thus it should be noted that although $[Ru(NH_3)_5OH]^+$ is a stronger reducing agent than is $[Ru(NH_3)_5SH]^+$ (Table X) its deterioration to form Ru(III) + H_2 seems to be less rapid.

Table IX. Band Maxima and Extinction Coefficients for Ruthenium–Sulfur Complexes

Complex[d]	λ, nm (ε, M^{-1} cm^{-1})
$[Ru(NH_3)_5S(CH_3)_2]^{2+}$	258 (2.1 × 10^3), 235 (2. × 10^3)
$[Ru(NH_3)_5THT]^{2+}$	262 (1.9 × 10^3), 235 (1.9 × 10^3)
$[Ru(NH_3)_5$(methionine methyl ester)$]^{2+}$	255 (~10^3), 234 (~10^3)
$[Ru^{II}(NH_3)_5(HSC_2H_5)]^{2+}$	255 (1.9 × 10^3)
$[Ru(NH_3)_5$(thiophene)$]^{2+}$	260 sh (~2 × 10^3), 450 (~200)
$[Ru(NH_3)_5H_2S]^{2+}$	255 (~2.2 × 10^3)
$[Ru(NH_3)HS]^{+}$[a]	248 sh (~1.9 × 10^3)
trans-$[Ru(NH_3)_4$(isn)-$H_2S]^{2+}$[b]	430 (1.0 × 10^4), 255 sh (7.5 × 10^3)
trans-$[Ru(NH_3)_4$(isn)(HS)$]^{+}$[c]	511 (1.0 × 10^4), 255 sh (4.5 × 10^3)
trans-$[Ru(NH_3)_4$(isn)S-$(CH_3)_2]^{2+}$	430 (~9 × 10^3), 251 sh (~7 × 10^3)
$[Ru(NH_3)_5DMSO]^{2+}$	313 (240), 210 (2.6 × 10^3)
$[Ru^{III}(NH_3)_5$(Cyst-et)$]^{2+}$	500
$[Ru^{III}(NH_3)_5(SC_2H_5)]^{2+}$	508 (1.9 × 10^3)
$[Ru(NH_3)_5SH]^{2+}$	470
$[Ru(NH_3)_5S(CH_3)_2]^{3+}$	258 sh (~1.5 × 10^3)

[a] In 0.1 M acetate buffer. [b] In H_2S saturated, 1 M HCl, 5°. [c] In phosphate buffer (pH 7)–KCl solution (I = 1). [d] 25° in 0.1 M HCl, except where otherwise noted.

Other spoiling reactions also take place in the mixtures which are used to prepare the hydrogen sulfide complex. Among them are the reaction of $[Ru(NH_3)_5H_2O]^{2+}$ with the H_2S complex which appears to lead to singly bridged binuclear species. This is also some loss of NH_3, which in the limit will lead to a solid sulfide being formed. It should be noted, however, that the coordination sphere is not particularly labilized by H_2S.

Though the Ru(III)-SH^- species was not fully characterized, the absorption spectrum suggests that $[Ru(NH_3)_5SH]^{2+}$ is the immediate oxidation product of $[Ru(NH_3)_5H_2S]^{2+}$. The species is unstable, and either by disproportionation

$$4[Ru(NH_3)_5SH]^{2+} = [(NH_3)RuSSRu(NH_3)_5]^{4+} + 2[Ru(NH_3)_5H_2S]^{2+}$$

or by further oxidation produces the disulfide bridged dimer. Preliminary experiments which we have done suggest that the reactions referred to can be controlled, and further investigation is certain to lead to the characterization of new sulfur containing species.

When isn is also contained in the coordination sphere, the H_2S complex is much more tractable. This undoubtedly arises from the fact that $Ru(NH_3)_4isn^{2+}$ is much less strongly reducing than is $Ru(NH_3)_5^{2+}$. Salts containing $[Ru(NH_3)_4isn(H_2S)]^{2+}$ can in fact be handled in air with little deterioration. Though the isn-containing complex is more stable to oxidation than is the pentaammine, it is less stable to H_2S loss. The decrease in the affinity of H_2S for $[Ru(NH_3)_5H_2O]^{2+}$ compared to $[Ru(NH_3)_4(isn)H_2O]^{2+}$ (from 1.5 × 10^3 to 7.2) is in line with expectation if it is assumed that the affinity of H_2S and related molecules owes something to back-donation. When both isn and H_2S compete for πd electron density, there is a decrease in the strength of the Ru(II) interaction with each of the ligands. In this connection, it should be noted that the affinity of $(CH_3)_2S$ for Ru(II) is so much greater than that of H_2S, that when both $(CH_3)_2S$ and isn are bound to Ru(II), aquation of isn occurs in preference to $(CH_3)_2S$.

Apart from the fact that a number of new species con-

Table X. Formal Reduction Potentials (E_f)[a]

Complex	V vs. NHE	Conditions
$[Ru(NH_3)_5SH]^{2+} + H^+ - [Ru(NH_3)_5H_2S]^{2+}$*	−0.12	0.1 M HCl
$[Ru(NH_3)_5SH]^{2+/+}$*	−0.29	1 M NaOAc + NaOH (pH 7)
$[Ru(NH_3)_5(SC_2H_5)]^{2+} + H^+ - [Ru(NH_3)_5(HSC_2H_5]^{2+}$*	+0.05	0.1 M HCl
$[Ru(NH_3)_5(SC_2H_5]^{2+/+}$*	−0.43	1 N Na_3PO_4 (pH 11)
$[Ru(NH_3)_5S(CH_3)_2]^{3+/2+}$	+0.50	0.1 M HCl
$[Ru(NH_3)_5THT]^{3+/2+}$	+0.47	0.1 M HCl
$[Ru(NH_3)_5$(thiophene)$]^{3+/2+}$	+0.61	0.1 M HCl
$[Ru(NH_3)_5$(methionine methyl ester)$]^{3+/2+}$	+0.53	0.1 M HCl
$[Ru(NH_3)_5DMSO]^{3+/2+}$	+1.0	0.1 M HCl
cis-$[Ru(NH_3)_4(H_2O)S(CH_3)_2]^{3+/2+}$	+0.48	0.1 M HCl
trans-$[Ru(NH_3)_4$(isn)$S(CH_3)_2]^{3+/2+}$	+0.71	0.1 M HCl
$[Ru(NH_3)_5H_2O]^{3+/2+}$	+0.10	0.1 M HCl
$[Ru(NH_3)_5OH]^{2+/+}$	−0.42	0.1 M NaOH
$[Ru(NH_3)_5N_2]^{3+/2+}$	+1.10[25]	1 M $HClO_4$
$[Ru(NH_3)_5$(pyr)$]^{3+/2+}$	+0.49[25]	1 M NaCl
$[Ru(NH_3)_6]^{3+/2+}$	+0.06	0.1 M HCl
$[Ru(NH_3)_5Imz]^{3+/2+}$	+0.11[28]	0.1 M HCl

[a] All potentials were determined by cyclic voltammetry, except those designated (*) which were determined by potentiometric redox titration; ±0.010 V.

taining simple sulfur ligands has been prepared, the most significant results of this work have been the measurement of the affinities of Ru(II) and Ru(III) for a number of the ligands. We will turn now to a detailed examination of the equilibrium data, considering first some of the observations made on the values of pK_a for coordinated ligands which have dissociable protons.

At the outset it should be noted that the equilibrium constant for the dissociation of a proton from RSH is more sensitive to a change in the identity of R than is the case for the same change in ROH. Thus the pK_a values of C_2H_5SH[29] and HSH[30] are 12 and 7, respectively, while those for C_2H_5OH[31] and HOH are 18 and 15.7 (the latter value has been corrected for the molal factor of 55.5 for liquid water). The qualitative difference is expected because SH^- is more polarizable than OH.

In Table XI, the data on the values of pK_a for coordinated H_2O, H_2S, and C_2H_5SH are summarized. Those pertaining to Ru(II) were measured directly by spectrophotometric or electrochemical means as outlined in the Results Section. Since H_2S and C_2H_5SH when coordinated to Ru(III) are dissociated over the whole pH range investigated, the values entered for them cannot be gotten directly from the data. They were obtained by assuming that E_f for

$$e^- + RuH_2S^{3+} \text{ (or } C_2H_5SH) = RuH_2S^{2+} \text{ (or } C_2H_5SH)$$

is the same as it is when $(CH_3)_2S$ is the ligand. Some error is involved in this assumption, but it likely does not exceed one or at most two units in pK. Though Ru(II) is stabilized more by $(CH_3)_2S$ than it is by H_2S, the same is probably true of Ru(III) ($(CH_3)_2S$ is expected to be a better σ base than H_2S) and thus some cancellation of effects occurs.

Two features are noteworthy in the comparisons that can be made using the data in Table XI: the enhancement in the acidity of coordinated H_2O or H_2S when isn replaces NH_3—this is an expected result if isn is acknowledged to be acting as a π acid—and the increase in acidity of the ligands H_2S or C_2H_5SH which attends the oxidation of Ru(II) to Ru(III). For C_2H_5SH the assumption made in calculating pK_a for the Ru(III) state is likely to be little in error and in this case 16 powers of 10 are registered as the increase in acidity when the 2+ state is oxidized to the 3+. For H_2O as a ligand, the ratio is only 10^9, in harmony with the observation made earlier that the SH dissociation is more sensitive than is that of OH to a given change in the nature of the other groups coordinated to the acid bearing function. Keeping this in mind, it is significant that the increase in acidity when H_2S (or C_2H_5SH) in the free state is transferred to the coordination sphere of Ru(II) is only slightly greater than it is for H_2O undergoing the same transfer. This reflects the effect of back-bonding, which is expected to be greater for H_2S than it is for HS^-, thus decreasing the tendency of the proton to dissociate from coordinated H_2S.

Table XI. Comparison of pK_a Values

	$-OH_2$	$-SH_2$	$-C_2H_5SH$
$[(NH_3)_5Ru]^{2+}$	13.1	4.0	9.2
trans-$[(NH_3)_4$(isn)$Ru]^{2+}$	11.7	<3.2[a]	–
$[(NH_3)_5Ru]^{3+}$	4.2	−10[b]	−7[b]

[a] Measured at 5° as 3.2. [b] Estimated values.

Table XII. Comparison of the Affinities of Ligands for $[Ru(NH_3)_5H_2O]^{2+}$ and $[Ru(NH_3)_5H_2O]^{3+}$

	$[Ru(NH_3)_5H_2O]^{2+}$	$[Ru(NH_3)_5H_2O]^{3+}$	Ratio	Ref
N_2	3.3×10^4	4×10^{-13}	8×10^{16}	32
Thiophene	~10	$\sim 2.5 \times 10^{-8}$	4×10^8	
H_2S	1.5×10^3	2.4×10^{-4}	6×10^6	
$(CH_3)_2S$	$\geqslant 10^5$	$\geqslant 1.6 \times 10^{-2}$	$\sim 6 \times 10^6$	
Pyridine	2.4×10^7	6×10^3	4×10^3	7
Imidazole	2.8×10^6	1.9×10^6	1.5	28
H_2O	1	1	1	
NH_3	3.5×10^4	1.6×10^5	2×10^{-1}	
Cl^-	0.4	1.1×10^2	4×10^{-1}	25, 33
HS^-	1.5×10^6	2.4×10^{13}	6×10^{-8}	
HO^-	6×10^2	6×10^{11}	1×10^{-9}	

In Table XII, the affinities of Ru(II) and Ru(III) for a variety of ligands are summarized. These include most of the values determined in the course of the present work as well as some from the literature which are useful for comparisons. The ligands are arranged in decreasing order of affinity for Ru(II) compared to Ru(III).

The data which form the basis for the compilation are measured values of affinity for ruthenium(II) combined with pK_a values and with electrochemical data. In all cases, when electrochemical data were used, E_f for the couple $[Ru(NH)_3)_5H_2O]^{3+}$-$[Ru(NH_3)_5H_2O]^{2+}$ was taken to be 0.10. The assumptions made in getting an entry for H_2S on Ru(III) have already been mentioned. Ionic strength is not necessarily constant and thus, particularly when charged ligands are in question, some variation with ionic strength must be allowed for, but the range covered, both with respect to absolute values of affinities, ca. 10^9 for Ru(II), ca. 10^{26} for Ru(III), and the ratios, ca. 10^{26}, is so great that any corrections would not seriously change the pattern.

Two properties of the ligands which affect the affinity are the capacity to form a σ bond (both charge density and polarizability contribute to this) and the capacity to accept π electrons from the metal ion. Ruthenium(III) is a stronger σ acid than is Ru(II), but in contrast to Ru(II), it is a very weak base. The difference in the properties of the two metal ions is most strikingly illustrated by the entries for N_2 as ligand. This ligand is a very weak σ base, hence the complex with Ru(III) is very unstable, but by virtue of its capacity to act as a π acid, it makes a rather stable complex with Ru(II). A third factor probably plays a role in the interaction of Ru(II) with N_2, namely the mutual strengthening of the σ and π components to the bond.

The π^* orbital for thiophene undoubtedly lies lower than does that of N_2, and thiophene is a better σ base than N_2—thus note that the affinity of Ru(III) for thiophene is ca. 10^5 greater than it is for N_2—yet the affinity of Ru(II) for thiophene is less than it is for N_2. The reason in part may be that owing to the fact that few atoms are involved in the π system of N_2, the interaction between the σ and π components of the bond made to the ligand is greater. If this explanation is valid, it shows that the so-called synergistic effect, far from being a minor refinement in our ideas of back-donation, is a major effect. Contributing also to the difference is the fact that for N_2 two π orbitals are implicated in back-donation, while with thiophene, likely only one contributes.

The affinity of H_2S for Ru(III) is less than that of H_2O, as expected because H_2O is a better σ base than is H_2S, but for Ru(II), the relative affinities are reversed. Hydrogen sulfide undoubtedly owes its high affinity for Ru(II) to back-bonding. What is somewhat surprising is that the affinity of $(CH_3)_2S$ is even greater than that of H_2S, by a factor of perhaps 100. It is unlikely that this difference is ascribable to the σ bond. The π^* orbital may be sensitive to the nuclear separation in the R_2S molecule—the proton can more completely be buried in the electron cloud of S^{2-} than can the positive center CH_3^+.

The effect of back-bonding in affecting affinities can also be traced in the HO^-, HS^- comparison. The affinity of HS^- for Ru(III) is 40 times greater than that of HO^-, but for Ru(II), which certainly has a lower capacity than Ru(III) to polarize HS^-, the ratio favoring the attachment of HS^- is ca. 2500. It was not possible to get an estimate of the affinity of S^{2-} for Ru(II), but a lower limit can be set based on the observation that the spectrum of *trans*-$[Ru(NH_3)_4(isn)HS]^+$ is not substantially altered in 1 *M* NaOH. This indicates that the dissociation constant for HS^- coordinated to Ru(II) is less than 10^{-15}, even when an acidity enhancing ligand such as isn is present in the coordination sphere of Ru(II). The value of 10^{-15} can be used as a conservative lower limit for the dissociation constant of $[Ru(NH_3)_5HS]^+$. In fact, in view of the observation made for isn affecting the acidity of H_2O also coordinated to Ru(II), it seems likely that pK_a for $[Ru(NH_3)_5HS]^+$ is less than 10^{-17}, but even using the conservative value of 10^{-15}, and as pK_2 for H_2S the value of 17.1,[34] the association constant for S^{2-} reacting with $[Ru(NH_3)_5H_2O]^{2+}$ is calculated at less than 10^8. Thus, the association constant of S^{2-} is less than a factor of 100 greater than that of HS^-. This is a very modest change, considering the increase in charge. It is reasonable to suppose that owing to the large negative charge residing on S^{2-} there is very little back-bonding, and that the loss in back-bonding in changing from HS^- to S^{2-} almost compensates for the increase in charge.

Some comments on the spectra of the sulfur containing ligands seem in order. The orange color of $[Ru(NH_3)_5SC_2H_5]^{2+}$ or of $[Ru(NH_3)_5SH]^{2+}$ arises from a band with maxima at 508 (ϵ 1.9×10^3) and 470 nm, respectively. This absorption can reasonably be attributed to ligand to metal charge transfer. The increase in the energy of the absorption when $SC_2H_5^-$ is replaced by SH^- shows that the ionizing potential of the former ion is lower than the latter.

All of the pentaammineruthenium(II) complexes with neutral sulfur(−II) have a rather strong absorption at about 260 nm. This is not shown by the ligands themselves, and it probably represents metal to ligand charge transfer. In line with this assignment is the fact that the band shifts to higher energies when coordinated H_2S loses a proton. In the case of $S(CH_3)_2$ and THT, there are clearly two bands in the uv region. The splitting may be a consequence of the low symmetry imposed by the carbon radicals on sulfur (two πd orbitals on ruthenium can interact with π orbitals on sulfur).

Acknowledgment. Financial support of this research by the National Institutes of Health under Grant No. GM13638 is gratefully acknowledged. This work has benefited from the synthetic skills of Dr. Stephan Isied and the electrochemical expertise of Glenn Tom; their help is greatly appreciated.

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(2) Strohmeier et al.[3] reported the infrared spectrum in benzene solution of the product of the reaction of H_2S with $[CpMn(CO)_2THF]$ at −80°. In analogy with the reactions of other more tractable ligands, it is rather certain that the compound $CpMn(CO)_2$ was being dealt with. Vaska[4a] has reported the formation of the H_2S adduct of $[IrY(CO)(Ph_3P)_2]$ ($Y^- = Cl^-, Br^-$) but this reaction may involve oxidative rather than simple addition of H_2S to the Ir(I) complex; Flynn and Vaska have reported $Rh(CO)(Ph_3P)_2SH$.[4b] Ardon and Taube[5] described a species which they formulated as $[(H_2O)_5CrSH]^{2+}$ in aqueous solution, but concluded that the thiol ligand is not protonated even in strong acid.

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(9) Glossary of abbreviations: HTFA, trifluoroacetic acid; isn, isonicotinamide; TSP, trimethylsilyl propionate; TMS, tetramethylsilane; DMSO, dimethyl sulfoxide; 4-cpyH, 4-cyanopyridine.

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