Inorg. Chem. **1984**, *23*, 2997-3001

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Enthalpies of Reaction of Pentaammineruthenium(II) Complexes

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Received January 18, 1984

Enthalpies have been obtained for substitution in aquopentaammineruthenium(II) by acetonitrile, imidazole, pyridine, thiodiethanol, pentaammine(pyrazine)ruthenium(II) ion, isonicotinamide, pyrazine, *N*-methylpyrazinium ion, dimethyl sulfoxide, and carbon monoxide, by using a batch microcalorimeter. The values are −9.2, −9.3, −12.7, −13.7, −13.8, −15.3, −16.8, −18.0, −19.2, and −38.3 kcal mol^{-1}, respectively. Enthalpies also were obtained for the protonation of pentaammine(pyrazine)ruthenium(II) ion (−4.9 kcal mol^{-1}) and for the comproportionation of $[((NH_3)_5Ru)_2pyr]^{5+}$ (−3.9 kcal mol^{-1}). The enthalpies for the association of pentaammine(pyrazine)ruthenium(II) ion with H$^+$ and aquopentaammineruthenium(II) are compared with published values for $Ni^{2+}(aq)$, $Cu^{2+}(aq)$, and $Zn^{2+}(aq)$.

Introduction

The remarkable interactions of pentaammineruthenium(II) with π-acid ligands have led to a large number of studies. Of particular interest to us is the effect of π interactions on the stability of ruthenium–ligand bonds. In a few instances, association constants have been determined[1-5] indirectly from the ratio of the forward and reverse rate constants. Unfortunately, this method fails for some of the most interesting systems where the affinities are very high or when other reactions take place more rapidly than ligand loss. By contrast, there is no such limitation on the enthalpies of ligand substitution determined by the direct calorimetric method. Farquhar et al.[6] have reported ΔH for the ligand substitution reaction

$$2[(NH_3)_5RuOH_2]^{2+} + N_2(aq) = [((NH_3)_5Ru)_2N_2]^{4+} + 2H_2O(l) \quad (1)$$

as −22 ± 2 kcal mol^{-1} at 25 °C. Armor and Taube[2] obtained a value of −21.6 ± 3 kcal mol^{-1} from the temperature dependence of the association quotient. Using flow calorimetry, Watt measured a value of −22.4 ± 1.5 kcal mol^{-1} for reaction 1,[7] which agrees well with the earlier two determinations. However, some of Watt's calorimetric results on other ligands may be in error. Specifically, Watt reports values of −1.2 and −3.86 kcal mol^{-1} for the complexation enthalpies of aquopentaammineruthenium(II) with $NH_3(aq)$ and py(aq), respectively. When these enthalpy data are combined with reported[4] stability constants ($K = 3.5 \times 10^4$, 2.4×10^7), we calculate entropy changes that are unusually high[8] ($\Delta S = +17$, $+21$ cal deg^{-1} mol^{-1}). The small values of $-\Delta H$ obtained by Watt for these ligands and for acetonitrile ($-\Delta H = 4.8$ kcal mol^{-1}) may be the result of oxidation of $[(NH_3)_5RuOH_2]^{2+}$ during the procedure used for the removal of zinc ions from solution. By contrast, his enthalpy value for the μ-dinitrogen complex is not subject to this error, because it was obtained from a cycle involving oxidation of the complex.

The results reported here are part of a continuing program to obtain enthalpy values for the reactions of Ru(II) species with a variety of ligands.

Abbreviations: py, pyridine; pyz, pyrazine; isn, isonicotinamide; tos, *p*-toluenesulfonate; TFMS, trifluoromethanesulfonate.

Experimental Section

Reagents. Thiodiethanol, pyrazine, and acetonitrile were obtained from Aldrich and used without purification. Isonicotinamide was recrystallized from hot water. *N*-Methylpyrazinium *p*-toluenesulfonate, $[(NH_3)_5RuCl]Cl_2$, $[((NH_3)_5Ru)_2pyz](tos)_4 \cdot H_2O$, $[((NH_3)_5Ru)_2pyz](ClO_4)_6$, and $[(NH_3)_5Ru(pyz)](CF_3SO_3)_2$ were prepared by reported procedures,[9] except in the case of the last compound when sodium trifluoromethanesulfonate was used instead of sodium perchlorate. $[(NH_3)_5Ru(CF_3SO_3)](CF_3SO_3)_2$ was prepared according to the procedure of Dixon et al.[10]

In our initial experiments involving pyrazine, thiodiethanol, acetonitrile, Me_2SO, and $[(NH_3)_5Ru(pyz)]^{2+}$, solutions containing $[(NH_3)_5RuOH_2]^{2+}$ (0.005–0.02 M, except 0.12 M in the case of the last ligand) were prepared by reducing $[(NH_3)_5RuCl]^{2+}$ with Zn/Hg. This procedure might introduce a complication in interpreting the results because of effects arising from the ligand interactions with $Zn^{2+}(aq)$. However, due to their low affinity for Zn^{2+}, no appreciable effect is expected from these particular ligands at the reagent concentrations employed.

For the other studies, $[(NH_3)_5RuTFMS](TFMS)_2$ was added to 0.10 M *p*-toluenesulfonic acid solution or 0.10 M sodium *p*-toluenesulfonate solution that had been acidified with a few drops of the acid solution (1.0 M Na(tos) was used for the *N*-methylpyrazinium experiment). The Ru(III) solution was placed in a Zwickel flask[3] that was modified by the addition of two side arms separated from the main flask by fine sintered glass frits. The counterelectrode, a coil of fine Pt wire, was placed in one side arm with an Htos or Na(tos) electrolyte solution. The other side arm contained the saturated calomel reference electrode, which was connected to the electrolyte solution by a 1.0 M NaCl solution and a Vycor frit. The working electrode was a coil of Pt ribbon. The ruthenium solution was electrolyzed until the cell potential was −0.50 V vs. SCE, or lower if the pH was high. The pH was adjusted to the desired value with $NaHCO_3$ and/or Na_2CO_3 toward the end of the electrolysis so as to minimize disproportionation of $[(NH_3)_5RuOH_2]^{3+}$. After electrolysis was complete, the solution was transferred into an argon-flushed bubbler flask.

There are several advantages to the second technique. First, $[(NH_3)_5RuTFMS](TFMS)_2$, which reacts rapidly with water to give $[(NH_3)_5RuOH_2]^{3+}$ below pH 4.5, is more readily soluble and easier to reduce than salts of $[(NH_3)_5RuCl]^{2+}$. Second, avoiding chloride prevents the formation of $[(NH_3)_5Ru(Cl)_3Ru(NH_3)_3]^{2+}$ and thus reduces the risk of producing ruthenium metal, increasing the useful

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[†] Stanford University.
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(1) Armor, J. N.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 6874 (data for N_2O).
(2) Armor, J. N.; Taube, H. *J. Am. Chem. Soc.* **1970**, *92*, 6170 (data for N_2).
(3) Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689 (data for H_2S).
(4) Shepherd, R. E.; Taube, H. *Inorg. Chem.* **1973**, *12*, 1392 (data for NH_3 and pyridine).
(5) Sundberg, R. J.; Bryan, R. F.; Taylor, I. F., Jr.; Taube, H. *J. Am. Chem. Soc.* **1974**, *96*, 381 (association quotient for imidazole).
(6) Farquhar, E. L.; Rusnock, L.; Gill, S. J. *J. Am. Chem. Soc.* **1970**, *92*, 416.
(7) Watt, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 7351.
(8) The entropy changes mentioned here can be compared with those for the association of ammonia[18] with $Ni^{2+}(aq)$, which range from +0.9 to −14.2 cal deg^{-1} mol^{-1} for each step from the first to sixth association (based on average enthalpy), $Cu^{2+}(aq)$, +2.1 to −7.9 cal deg^{-1} mol^{-1} for the first to fourth steps (average enthalpy), and $Zn^{2+}(aq)$, +2.1 to −7.5 cal deg^{-1} mol^{-1} for the first to fourth steps (using individual enthalpies). For pyridine, entropy[18] changes based on average enthalpies for the first to fourth associations range between +0.8 and −5.9 cal deg^{-1} mol^{-1} for $Ni^{2+}(aq)$, +1.3 and −10.6 cal deg^{-1} mol^{-1} for $Cu^{2+}(aq)$, and +0.9 and −5.7 cal deg^{-1} mol^{-1} for $Zn^{2+}(aq)$.
(9) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086.
(10) Dixon, N. E.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 846.

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lifetime of the solution. Last, this method avoids Zn^{2+} entirely and permits complete reduction at any pH. One drawback is that diffusion through the fine frits of the side arms creates a concentration uncertainty which can be minimized but not eliminated. In practice, it was found that the slight positive pressure of Ar in the sample compartment pushed some of the Ru solution into the side arms, effectively preventing dilution in the sample compartment.

Due to the sensitivity of $[(NH_3)_5RuOH_2]^{2+}$ to oxidation, the concentration could not be adequately fixed by the amount of starting material employed. Therefore, the amount of product formed during each measurement for each ligand was determined spectrophotometrically and was used to normalize the calorimetric results. This protocol was followed for all ligands with the exception of thiodiethanol, Me_2SO, and formic acid (CO) for which the concentration of $[(NH_3)_5RuOH_2]^{2+}$ was determined spectrophotometrically by using isonicotinamide.

Ligand concentrations were chosen so that the reaction was complete in 10 min or less (0.2–0.5 M, except 5.0 M for HCOOH). Except for the early studies where no electrolyte was used, ligand solutions were also 0.10 M in Htos or Na(tos) and, except for the runs with HCOOH, were adjusted to the same pH as the corresponding Ru(II) solution.

Integral heats of dilution were determined for all of the ligand solutions by using the same electrolyte solutions but without the Ru(II) ion. In the case of *N*-methylpyrazinium ion, isonicotinamide, and formic acid, experimentally determined dilution corrections to the observed exothermic reaction heats were −10%, +15%, and +9%, respectively. In all other cases, the heat of dilution was less than the mechanical mixing heat.

Instruments. Batch Experiments. A differential-heat-conduction calorimeter built according to ref 11 was used for these experiments. Modifications were made to the thermochemical cells to adapt them to inert-atmosphere work. Each cell (as pictured in Figure 2b of ref 11) was machined out of Lucite as one piece from the side (as opposed to two pieces from the top). A flat sheet of the same material was sealed on with adhesive to form the other side of the cell. The Teflon stoppers were replaced by plugs cut from GC septa and held in by O-rings. These plugs permit argon flushing of the cells and transfers with gastight syringes. Solution volumes of 200 μL were used for each reagent. Care was taken to ensure complete mixing of the reactant solutions.

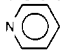
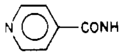
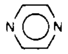
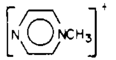
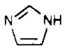
Titration Experiment. A Tronac Model 1250 isoperibol titration calorimeter, equipped with a 4-mL Dewar flask, was used to determined the enthalpy of substitution of pyridine onto $[(NH_3)_2RuOH_2]^{2+}$.

A motor-driven 2.5-mL Gilmont micrometer syringe was used to deliver the ruthenium solution to the reaction vessel through narrow PVC tubing. The syringe end of the tubing was drawn over the end of a no. 3 point 22-gauge platinum needle (Hamilton) that was fitted to the Luer tip of the syringe. PVC tubing was used instead of Teflon tubing in this application because it was found that significant oxidation of reagent occurred during the residence time of the solution when a Teflon titrant line was used. A survey of various tubing materials using methylene blue as an oxidation indicator led to the choice of PVC. It is also sufficiently chemically inert for our purposes.

A 2.5-mL sample of an Ar-bubbled solution 1 M in pyridine, 0.075 M in Na(tos), and 0.025 M in $NaHCO_3$ was placed in the Dewar, and Ar was bubbled into the vessel through another tube for 1 h. A solution, nominally 0.2 M in $[(NH_3)_5RuOH_2]^{2+}$, 0.075 M in Na(tos), and 0.025 M in $NaHCO_3$, was generated electrochemically as described above and placed in the syringe. Argon was bubbled through the vessel intermittently during the experiment between measurements. The total volume of titrant added was 1.0 mL. After the experiment, the absorbance of an aliquot of the solution of the reaction vessel was used to determine the actual concentration of $[(NH_3)_5RuOH_2]^{2+}$ in the titrant solution as 0.194 M. This calculation was based on the absorbance of $[(NH_3)_5Ru(py)]^{2+}$ (λ_{max} = 407 nm, $\epsilon = 7.77 \times 10^3$).[4]

Kinetic Measurement. A solution 1.22×10^{-3} M in $[(NH_3)_5RuNCCH_3](BF_4)_2$ and 0.10 M in LiCl was degassed over Zn/Hg with argon in an ordinary Zwickel flask[3] for 20 min and transferred under Ar to a 1.0-cm spectrophotometric cell fitted with a stopcock. The pH of the solution was 7.3. The cell and stem were completely filled with solution and then the stopcock was closed. The solution was kept away from light in a water bath at 25 °C. Spectra were recorded at intervals of several hours for the first week and at longer intervals thereafter. After 4 months, the cell was opened and the products were analyzed by cyclic voltammetry and spectrophotometry using the UV–vis region of the spectrum.

Table I. Enthalpies of Substitution on $[(NH_3)_5RuOH_2]^{2+}$ at 25 °C

entry	L(aq)	$-\Delta H^\circ$, kcal mol^{-1}	[Ru(II)], M	[L], M
1		12.7 ± 1.0	0.194[a]	1.0[a]
2		15.3 ± 0.4	0.008	0.20
3		16.8 ± 0.1	0.0093	0.20
4		18.0 ± 0.3	0.014	0.50
5		13.8 ± 0.8	0.12	0.012
6	CH_3CN	9.2 ± 0.2	0.013	0.10
7	$S(CH_2CH_2OH)_2$[b]	13.7 ± 0.1	0.018	0.30
8	$(CH_3)_2SO$	19.2 ± 0.8	0.011	0.2
9	CO	38.2 ± 1.4	0.0057	5.0[c]
10		9.3 ± 0.5	0.01	0.2

[a] As mentioned in the text, a titration calorimeter was employed to obtain the enthalpy for pyridine. [b] In this case, the volume of the Ru(II) solution compared to that of the ligand was 0.75, instead of 1.0. [c] As HCOOH.

Results

Ligand Substitution Enthalpies. The data obtained on the enthalpies of reaction of a number of ligands with $[(NH_3)_5RuOH_2]^{2+}$ are summarized in Table I. The net change in each case is

$$[(NH_3)_5RuOH_2]^{2+}(aq) + L(aq) = [(NH_3)_5RuL]^{2+}(aq) + H_2O(l) \quad (2)$$

Carbon Monoxide. In the case of CO the reaction measured is[12]

$$[(NH_3)_5RuOH_2]^{2+}(aq) + HCOOH\ (2.5\ M) \rightarrow [(NH_3)_5RuCO]^{2+}(aq) + 2H_2O(l) \quad (3)$$

The experimentally determined heat for this reaction is −34.8 ± 1.4 kcal mol^{-1}. To adjust this enthalpy value to reflect the reaction with CO(g), we must calculate ΔH for

$$CO(g) + H_2O(l) \rightarrow HCOOH\ (2.5\ M,\ 2.75\ m)$$

This is done as follows:

$$HCOOH\ (1\ m) \rightarrow HCOOH\ (2.75\ m) \quad +0.02\ kcal\ mol^{-1}\ {}^{13}$$

$$H_2O + Co(g) \rightarrow HCOOH\ (1\ m) \quad -6.95\ kcal\ mol^{-1}\ {}^{14}$$

$$\text{net:}\ H_2O + Co(g) \rightarrow HCOOH\ (2.75\ m) \quad -6.93\ kcal\ mol^{-1}$$

Therefore, the net enthalpy for CO(g) + $[(NH_3)_5RuOH_2]^{2+}$ is −41.7 ± 1.4 kcal mol^{-1} [−34.8 + (−6.9) kcal mol^{-1}]. Watt[7] obtained a value of −36.1 ± 1.6 kcal mol^{-1} by another indirect method in which 3 equiv of Ce^{IV} was used to oxidize

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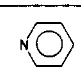
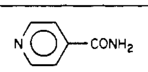
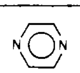
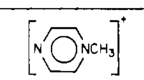
(11) Mudd, C.; Berger, R. L.; Hopkins, H. P.; Friauf, W. S.; Gibson, C. *J. Biochem. Biophys. Methods* **1982**, *6*, 179.

(12) P. A. Lay, using cyclic voltammetry, showed that the formation of the carbon monoxide complex from formic acid is rapid (to be submitted for publication). A specific rate of 4×10^{-3} M^{-1} s^{-1} is estimated by comparing chart output from the calorimeter with output from reactions of known rate.

(13) "CRC Handbook of Chemistry and Physics", 63rd ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1982; p D-126.

(14) Reference 13, pp D-60, D-71.

Table II. Spectroscopic Back-Bonding Stabilization Energies (E_π), Association Quotients (K_{II}, K_{III}) and pK_a's of Some N-Heterocycle Ligands

				
$E_\pi([(NH_3)_5Ru^{II}L]^{n+})$,[a] kcal mol^{-1}	3.1	6.0	6.6	21
$E_\pi([(NH_3)_5Os^{II}L]^{n+})$,[b] kcal mol^{-1}	15	19	24[d]	
$K_{II}([(NC)_5Fe^{II}L]^{n-})$,[c] M^{-1}	3.3×10^5	4.0×10^5	9.0×10^5	2.0×10^6
$K_{III}([(NC)_5Fe^{III}L]^{n-})$,[c] M^{-1}	9.4×10^3	5.2×10^3	1.7×10^3	4.7×10^{-1}
pK_a[c]	5.23	3.61	0.65	−5.8

[a] Reference 21. [b] Reference 22. [c] Reference 23. [d] $[(NH_3)_4ClOs(pyz)]^+$.

$[(NH_3)_5RuCO]^{2+}$ in sulfuric acid solution, producing $CO_2(g)$ and $[(NH_3)_5Ru(HSO_4)]^{2+}$.

To adjust our enthalpy value to dilute aqueous CO, we use

$$CO(aq) \rightarrow CO(g) \qquad \Delta H = 3.44 \text{ kcal mol}^{-1}\,{}^{15}$$

to obtain the value of −38.3 kcal mol^{-1} reported in Table I.

Acetonitrile. The relatively low exothermicity for the reaction of acetonitrile with $[(NH_3)_5RuOH_2]^{2+}$ (see Table I) suggested to us that the stability constant for the reaction might be small enough to allow the direct measurement of the rate of aquation of CH_3CN. Accordingly, we monitored the spectral changes that occurred when isn was added to a solution of the acetonitrile complex in 0.10 M LiCl. In the simplest case, when the aquopentaammineruthenium(II) ion is scavenged by isn, an absorption band at 478 nm would arise from the formation of $[(NH_3)_5Ru(isn)]^{2+}$. (The concentration level of isn was 0.10 M, which is high enough so that the released CH_3CN cannot compete for the aquo ion.) We observed an absorption maximum to develop at 440 nm; the growth of this band follows first-order kinetics with $k_{obsd} = 3 \times 10^{-7}$ s^{-1}. This absorption is ascribable to the formation of $[(NH_3)_4Ru(NCCH_3)isn]^{2+}$. Both cis and trans forms of this species were prepared and were found to have the following characteristics respectively in 0.10 M LiCl: $\lambda = 430$ nm, $E_{1/2} = 0.712$ V; $\lambda_{max} = 438$ nm, $E_{1/2} = 0.692$ V. A strong signal is observed in a cyclic voltammetry trace after 1 half-life at 0.696 V. Both the position of the band maxima and the values of $E_{1/2}$ suggest that the major side product is *trans*-$[(NH_3)_4Ru(NCCH_3)isn]^{2+}$.

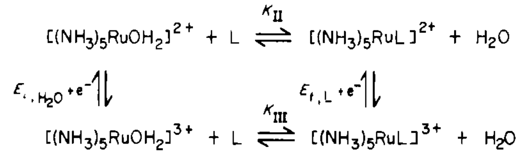
In the early reaction phases, the absorption that appears can be accounted for by two product species, but at longer times diffusion of O_2 through the stopcock grease complicated spectroscopic analysis. When the spectrum of the sample after 3×10^3 min (~5% conversion) was corrected for the absorption of *trans*-$[(NH_3)_4Ru(NCCH_3)isn]^{2+}$, the band at 478 nm was revealed. The rate of aquation of CH_3CN from $[(NH_3)_5RuNCCH_3]^{2+}$ was calculated as 1×10^{-7} s^{-1}.

Comproportionation of $[((NH_3)_5Ru)_2pyz]^{5+}$. We also have determined the enthalpy change for the reaction

$$[((NH_3)_5Ru)_2pyz]^{4+} + [((NH_3)_5Ru)_2pyz]^{6+} = 2[((NH_3)_5Ru)_2pyz]^{5+} \quad (4)$$

In the batch calorimeter, a solution of 1.0×10^{-2} M [4+] and 0.10 M HCl was mixed with an equal volume of a solution of 9.1×10^{-2} M [6+] and 0.10 M HCl. On the basis of four separate experiments, we calculated ΔH of reaction 4 as −7.7 ± 0.6 kcal mol^{-1}.

Scheme I



The Reference State: Gaseous vs. Aqueous. When discussing the enthalpy values obtained in terms of metal–ligand interactions, one must remember that solvation effects also contribute to the overall enthalpy change of reaction 2. To compare the strengths of metal–ligand interactions among a variety of ligands, the reaction of actual interest is

$$[(NH_3)_5RuOH_2]^{2+}(g) + L(g) \rightarrow [(NH_3)_5RuL]^{2+}(g) + OH_2(g) \quad (5)$$

Enthalpies of vaporization and solution can be obtained for most of the ligands studied here. However, the corresponding values for the ruthenium-containing species, which are at least as significant to the overall process, are not available. Hence, adjustment of the enthalpy values obtained for reaction 2 to standardize the ligands to the gaseous state[7] (reaction 5), does not fully correct for ligand solvation effects, since the ruthenium-bound ligands also interact with the solvent to varying degrees. Use of such adjusted enthalpy values, therefore, does not help to clarify the relative strengths of ruthenium–ligand interactions. In fact, using the aqueous ligand as the reference state for this series of reactions permits our enthalpy values to be used in conjunction with solution free energy data to calculate entropy values. For these reasons, only enthalpies corresponding to reaction 2 are reported in Table I.

Discussion

Thermodynamic Profiles of Pentaammineruthenium(II) Complexes of Some Azabenzenes. Reference to the data in Table I shows that the exothermicities for substitution of the four six-member heterocycles (entries 1–4) on $[(NH_3)_5RuOH_2]^{2+}$ increase with their potency as π-acceptors. This trend reflects the contribution of back-bonding to the metal–ligand interaction. This general trend also is found in spectroscopically inferred estimates of back-bonding stabilization in $[(NH_3)_5Ru^{II}L]^{n+}$ and $[(NH_3)_4ClOs^{II}L]^{n+}$ complexes[21,22] and is reflected in the stability constants of the $[(NC)_5Fe^{II}L]^{n-}$ series.[23] (See Table II.)

For the same series of ligands the order of stability constants is expected to be reversed for $[(NH_3)_5RuOH_2]^{3+}$ when account is taken of ligand pK_a's as it is in the $[(NC)_5Fe^{III}L]^{n-}$ series[23] (Table II).

These two trends can be used to set the upper and lower limits of K_{III} and K_{II} for isn and pyz as ligands by using Scheme I, which relates K_{II} and K_{III}.

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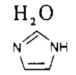
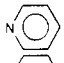
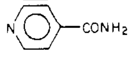
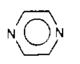
(15) "International Critical Tables"; National Research Council: Washington, DC, 1929; Vol. V, p 181.
(16) Pereira, M. S.; Malin, J. M. *Inorg. Chem.* **1974**, *13*, 386.
(17) Malin, J. M.; Shepherd, R. E. *J. Inorg. Nucl. Chem.* **1972**, *34*, 3203.
(18) Christensen, J. J.; Izatt, R. M.; "Handbook of Metal Ligand Heats"; Marcel Dekker: New York, 1970 (ammonia, pp 30, 31; pyridine, pp 152, 153; imidazole, pp 103, 104).
(19) Matsubara, T.; Ford, P. C. *Inorg. Chem.* **1976**, *15*, 1107.
(20) Lim, H. S.; Barclay, D. J.; Anson, F. C. *Inorg. Chem.* **1972**, *11*, 1460.
(21) Zwickel, A. M.; Creutz, C.; *Inorg. Chem.* **1971**, *10*, 2395.
(22) (a) Magnuson, R. H.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 5129. (b) Sen, J; Taube, H. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 125.
(23) (a) Toma, H. E.; Creutz, C. *Inorg. Chem.* **1977**, *6*, 545. (b) Coelho, A. L.; Toma, H. E.; Malin, J. M. *Ibid.* **1983**, *22*, 2703.

Table III. Formal Potentials, Association Quotients, and Thermodynamic Values for $[(NH_3)_5RuL]^{2+}$ Complexes[a]

L	E_f, V vs. NHE	K_{II}/K_{III}	K_{II}, M^{-1}	K_{III}, M^{-1}	ΔG_{II}, kcal mol^{-1}	ΔH_{II}, kcal mol^{-1}	ΔS_{II}, cal deg^{-1} mol^{-1}
H_2O	+0.067[b]	1	1	1	0	0	0
	+0.11[d]	5.3	2.8×10^6[d]	5×10^5	−8.8	−9.3[f]	−2 ± 2
CH_3CN	+0.426[b]	1.2×10^6	2.8×10^6[f]	2.5	−8.8	−9.2[f]	−1 ± 1
	+0.298[b]	8.1×10^3	2.4×10^7[e]	3×10^3	−10.1	−12.7[f]	−9 ± 3
	+0.375[b]	1.6×10^5	**1×10^8**[e]	*6×10^2*	*−10.9*	−15.4[f]	*−15*
			5×10^8	**3×10^3**	*−11.8*		*−12*
	+0.490[c]	1.4×10^7	**1×10^8**	*7*	*−10.9*	−16.8[f]	*−20*
			1×10^9	*8×10*	*−12.3*		**−15**
			5×10^9	*4×10^2*	*−13.2*		**−12**
			4×10^{10}	**3×10^3**	*−14.5*		*−8*

[a] Quantities set in normal type are experimentally determined. Quantities in boldface are based on the assumptions discussed in the text and are used to calculate the quantities set in italics in the same row. [b] Reference 19. [c] Reference 20. [d] Reference 5. [e] Reference 4. [f] This work.

The relation between K_{II} and K_{III} can be expressed by eq 6. Values are collected in Table III.

$$\frac{K_{II}}{K_{III}} = \exp\left[\frac{F}{RT}(E_{f,L} - E_{f,H_2O})\right] \qquad (6)$$

The association constant K_{II} for pyridine has been measured[4] as 2.4×10^7 M^{-1}, which corresponds to an association free energy of −10.1 kcal mol^{-1}. Using this $\Delta G°$ value in conjunction with our calorimetrically determined association enthalpy of −12.7 ± 1 kcal mol^{-1}, we calculate an association entropy of −9 ± 3 cal mol^{-1} deg^{-1}. On the basis of eq 6, we calculate $K_{III,py} = 3 \times 10^3$ M^{-1}. From the argument described above, we expect $K_{III,isn} < K_{III,py}$, so $K_{III,isn} < 3 \times 10^3$ M^{-1}. Using eq 6, we calculate an upper limit for $K_{II,isn}$ to be 5×10^8 M^{-1}. Shepherd and Taube[4] have reported a lower limit of $K_{II,isn}$ as 1×10^8 M^{-1}. Combining these limits with our experimental enthalpy of −15.4 kcal mol^{-1}, we calculate $\Delta G° = -11.8$ kcal mol^{-1} and $\Delta S° = -12$ cal deg^{-1} mol^{-1} for the upper limit and $\Delta G° = -10.9$ kcal mol^{-1} and $\Delta S° = -15$ cal deg^{-1} mol^{-1} for the lower limit. These quantities and the corresponding stability constants are shown in Table III.

In the case of pyrazine, the most conservative estimates must be based on the same limits as isonicotinamide; that is to say, $K_{II,pyz} > 1 \times 10^8$ M^{-1} and $K_{III,pyz} < 3 \times 10^3$ M^{-1} (see Table III). This leads to limits for $K_{II,pyz}$ which differ by a factor of 420. However, if $\Delta S°_{II,pyz}$ is the same as $\Delta S°_{II,isn}$, we calculate values for $K_{II,pyz}$, $K_{III,pyz}$, and $\Delta G°_{II,pyz}$, which fall in the center of the larger range. These values have also been included in Table III.

Back-Bonding Effects in Complexes of Pentaammineruthenium(II) and Pyrazine. To quantify the contribution of back-bonding to the first and second association of $[(NH_3)_5RuOH_2]^{2+}$ to pyrazine, we will compare our results with the interactions of first-row divalent metal ions and pyrazine. The assumption here is that the first-row metals demonstrate the same σ acid–base interaction, solvent, and electrostatic effects but lack the back-bonding contribution.

The reaction for the first association is

$$\begin{gathered}[ML_5(OH_2)]^{2+} + pyz \rightarrow [ML_5(pyz)]^{2+} + H_2O \\ ML_5 = (NH_3)_5Ru \text{ or } (H_2O)_5Ni\end{gathered} \qquad (7)$$

For $[(NH_3)_5RuOH_2]^{2+}$, we measure the enthalpy for reaction 7 to be −16.8 kcal mol^{-1}. By contrast, the enthalpy[17] for $Ni(aq)^{2+}$ is −3.2 kcal mol^{-1}. This leads to an estimated stabilization of 13.6 kcal mol^{-1} in $[(NH_3)_5Ru(pyz)]^{2+}$ due to back-bonding. A spectroscopically determined estimate of stabilization based on the analysis detailed by Zwickel and Creutz[21] would be $2E_{\pi,pyz} = 13.2$ kcal mol^{-1}. The good agreement of these two estimates is fortuitous, since our estimate is based on enthalpy data that also include contributions from solvent effects and differences in ligand field stabilization between Ni(II) and Ru(II) in the absence of back-bonding.

Table IV. Reactions of Lewis Acids with $[(NH_3)_5Ru(pyz)]^{2+}$ at 25 °C

Lewis acid	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, cal mol^{-1} deg^{-1}	$\Delta G°$, kcal mol^{-1}	ref
$H^+(aq)$	−4.9 ± 0.1[a]	−5.1 ± 0.3	−3.4[c]	this work
$Ni^{2+}(aq)$	−6.0 ± 0.8[b]	−15 ± 3	−1.5	16
$Cu^{2+}(aq)$	−4.3 ± 0.5[b]	−7 ± 2	−2.2	16
$Zn^{2+}(aq)$	−4.3 ± 0.5[b]	−12 ± 3	−0.7	16
$[(NH_3)_5RuOH_2]^{2+}$	−13.8 ± 0.8[a]			this work

[a] Calorimetric determination. [b] van't Hoff treatment. [c] Reference 10.

The exothermicity of substitution of pyrazine on $[(NH_3)_5RuOH_2]^{2+}$ is decreased by 3 kcal mol^{-1} when a second $(NH_3)_5Ru^{II}$ is coordinated to the pyrazine (Table I, entry 5). We would expect the additional positive charge to make a purely electrostatic contribution to $\Delta H°$, which most likely would be both small and exothermic. In this connection, it should be noted that $\Delta H°$ for the association of SO_4^{2-} with $[Co(NH_3)_6]^{2+}$ is reported$_{24}$ as 0.4 kcal mol^{-1}. Here, the magnitude of the product of the charges is greater than in our case, and the charge centers are closer together. The reduced exothermicity we observe for the addition of the second Ru(II) more likely reflects the fact that the same π-acceptor orbital is being donated to by both Ru(II) centers.

In Table IV, the data for the interaction of $[(NH_3)_5Ru(pyz)]^{2+}$ with $H^+(aq)$, $Ni^{2+}(aq)$, $Cu^{2+}(aq)$, $Zn^{2+}(aq)$, and $[(NH_3)_5RuOH_2]^{2+}$ are summarized. The relevant reaction is

$$[(NH_3)_5Ru(pyz)]^{2+} + M^{n+} \rightarrow [(NH_3)_5Ru(pyz)M]^{(n+2)+} \qquad (8)$$

Again, if the enthalpies obtained for the first-row ions are taken to account for all effects except back-bonding, stabilization by back-bonding in the case of $(NH_3)_5Ru^{II}$ still amounts to 8 or 9 kcal mol^{-1}.

Other Ligands. For imidazole, we measure a substitution enthalpy of −9.3 ± 0.5 kcal mol^{-1} (Table I). In conjunction with the $\Delta G°$ value of −8.8 kcal mol^{-1} reported by Sundberg et al.,[5] we calculate an entropy value of −2 ± 2 cal deg^{-1} mol^{-1}. By comparison, $\Delta H° = -5.2$ kcal mol^{-1} and $\Delta S° = -2.9$ cal deg^{-1} mol^{-1} for the first association of imidazole with $Ni^{2+}(aq)$.[18]

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(24) Posey, F. A.; Taube, H. *J. Am. Chem. Soc.* **1956**, *78*, 15.

When the rate constant for aquation of $[(NH_3)_5RuNCH_3]^{2+}$ is combined with that for complex formation, K_{eq} for complex formation is calculated as 3×10^6 and $\Delta G°$ as -8.8 kcal mol^{-1}. This leads to a value for the entropy change on complex formation of -1 ± 1 cal deg^{-1} mol^{-1}. A survey[8] of the entropies of formation of 1:1 complexes of dipositive ions with neutral ligands shows them to be in the range of 0 to -15 cal deg^{-1} mol^{-1}. Thus, the entropy we obtain, based on our value of $\Delta H°$, falls in the normal range. If the value of $\Delta H°$ reported by Watt is used, $\Delta S°$ is calculated as $+13$ cal deg^{-1} mol^{-1} which, as is true of two other examples cited in the Introduction, seems outside the usual range.

By application of eq 6, we calculate the equilibrium quotient for the formation of the nitrile complex from $[(NH_3)_5RuOH_2]^{3+}$ to be 2.5. To our knowledge, this is the only determination that has been made of the affinity of a nitrile for a tripositive ion.

If the entropy of substitution for thiodiethanol is close to that of other ligands, then our calorimetrically measured substitution enthalpy corresponds to an affinity or ruthenium(II) for thioethers that is perhaps as high as that of isonicotinamide. This result is in agreement with the lower limit set by Kuehn[3] (isonicotinamide, not $(CH_3)_2S$, is lost from *cis*-$[(NH_3)_4Ru(isn)((CH_3)_2S)]^{2+}$). Due to the biological significance of sulfur-containing ligands, further investigation of the thermochemistry of ruthenium(II) with such ligands is warranted.

Comproportionation of the Creutz–Taube Ion. Comproportionation (reaction 9) can be represented as the sum of two half-reactions. We measured the enthalpy of reaction 9 by

$$[((NH_3)_5Ru)_2pyz]^{4+} \rightarrow [((NH_3)_5Ru)_2pyz]^{5+} + e^- \quad nE_f = -0.375 \text{ V} \quad (9a)$$

$$[((NH_3)_5Ru)_2pyz]^{6+} + e^- \rightarrow [((NH_3)_5Ru)_2pyz]^{5+} \quad nE_f = +0.772 \text{ V} \quad (9b)$$

$$\text{net: } [((NH_3)_5Ru)_2pyz]^{4+} + [((NH_3)_5Ru)_2pyz]^{6+} \rightarrow 2[((NH_3)_5Ru)_2pyz]^{5+} \quad nE_f = +0.397 \text{ V (or } -9.15 \text{ kcal mol}^{-1})$$

using the 4+ ion as the limiting reagent so that the amount of 5+ ion produced could be determined spectrophotometrically at 565 nm. Reduction potentials for the 5+/4+ couple and the 6+/5+ couple, obtained by cyclic voltammetry in 0.10 M HCl, lead to a free energy of comproportionation of -9.15 ± 0.1 kcal mol^{-1}. On taking this in conjunction with our calorimetrically measured enthalpy of -7.7 ± 0.6 kcal mol^{-1}, we calculate an entropy of $+5.0 \pm 2.0$ cal mol^{-1} deg^{-1}. The statistical contribution to the entropy is $R \ln 4 = 2.75$ cal mol^{-1} deg^{-1}. The remaining entropy of $+2.2$ cal mol^{-1} deg^{-1} can be attributed to electrostriction of the solvent. This depends on the squares of the ionic charges; hence, comproportionation represents an overall increase in disorder of the solution. The entropy change above the statistical, however, is quite small. In fact, if the distances between the metal ions in the binuclear complexes were large enough, the nonstatistical entropy would be zero.

Due to the design of the bicompartment calorimetric cells employed, ligands with appreciable vapor pressures above their aqueous solutions may diffuse into the ruthenium solution and react before the two solutions are mixed. For this reason, ligands such as hydrogen sulfide and ammonia could not be investigated with the present cell design. To circumvent this problem, we are beginning a program in which the enthalpies for these ligands will be determined by using titration and/or flow calorimetry. Since the corresponding affinities already are known for these ligands, our calorimetric data will allow us to calculate complete thermodynamic profiles for the binding processes.

Acknowledgment. Support of this work by National Institutes of Health Grants GM13638-17 (H.T.) and GM23509-5 (K.J.B.) and a National Science Foundation Graduate Fellowship for J.F.W. are gratefully acknowledged. J.F.W. also thanks Jan Van Gastel for his work on the electrolytic Zwickel flask.

Registry No. py, 110-86-1; isn, 1453-82-3; pyr, 290-37-9; $[(NH_3)_5RuOH_2]^{2+}$, 21393-88-4; $[(NH_3)_5Ru(pyz)]^{2+}$, 19471-65-9; CH_3CN, 75-05-8; $S(CH_2CH_2OH)_2$, 111-48-8; Me_2SO, 67-68-5; CO, 630-08-0; Ru, 7440-18-8; *N*-methylpyrazinium, 17066-96-5; imidazole, 288-32-4.