dimer $[(bpy)_2Ru(pz)_2Ru(bpy)_2]^{3+}$. The unsymmetrical bridge-splitting reaction (eq 8) then follows because of the greater strength of the Ru(III)–pz bonds in an unsymmetrical dimer.

Our hope in preparing the pyrazolyl dimer was that the π-donor properties of the pyrazolyl ligand could be exploited to gain a strong Ru–Ru electronic interaction. In complexes like $[(bpy)_2ClRu(pyr)RuCl(bpy)_2]^{3+}$ (pyr is pyrazine), the orbital mechanism for Ru–Ru interaction appears to be $d\pi$(Ru(II))–π^*(pyr) mixing which carries the Ru(II) wave functions to the Ru(III) site and leads to electron delocalization from Ru(II) to Ru(III).[18] Given the extremely high π–π^* separation in pyrazole compared to that in pyrazine, the importance of Ru–Ru interactions by $d\pi$(Ru(II)) $\rightarrow$ π^*(pz) mixing is probably small, but, in principle, π(pz)–$d\pi$(Ru(III)) mixing could lead to Ru–Ru interactions by electron-hole donation from Ru(III) to Ru(II). If such an effect is important, the electronic resonance energy involved is apparently insufficiently strong to overcome the vibrational trapping energy and the result is a localized mixed-valence case.

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Registry No. $[(bpy)_2Ru(pzH)_2][PF_6]_2$, 71230-43-8; $(bpy)_2Ru(pz)_2$, 71230-42-7; $[(bpy)_2Ru(pz)(pzH)][PF_6]$, 71230-41-6; $[(bpy)_2Ru(pz)_2Ru(bpy)_2][ClO_4]_2$, 71230-40-5; $[(bpy)_2Ru(pz)(pzH)][ClO_4]$, 71230-39-2; $[(bpy)_2Ru(pzH)_2][ClO_4]_2$, 71230-37-0; $[(bpy)_2Ru(py)_2][PF_6]_2$, 71230-35-8; $[(bpy)_2Ru(py)Cl][PF_6]$, 36413-31-7; *cis*-$(bpy)_2RuCl_2$, 19542-80-4; $[(bpy)_2Ru(pz)]_2[PF_6]_2$, 71230-34-7; $[(bpy)_2Ru(pzH)_2]^{3+}$, 71230-32-5; $[(bpy)_2Ru(pz)(pzH)]^{2+}$, 71230-31-4; $[(bpy)_2Ru(pz)(pzH)]^{3+}$, 71230-30-3; $[(bpy)_2Ru(pz)_2]^{+}$, 71230-29-0; $[(bpy)_2RuCl_2]^{+}$, 47514-47-6; $[(bpy)_2RuCl_2]^{2+}$, 71230-28-9; $[(bpy)_2Ru(pz)]_2^{3+}$, 71249-99-5; $[(bpy)_2Ru(pz)]_2^{4+}$, 71230-27-8.

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Electron-Transfer Reactions of Some Derivatives of Pentaammine(pyridine)ruthenium(II) and -ruthenium(III)

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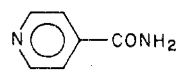
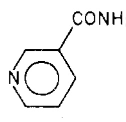
The pseudo exchange rate for the pentaammine(pyridine)ruthenium(II)–(III) couple has been determined by studying the rates of the reaction of $Ru(NH_3)_5isn^{3+}$ with $Ru(NH_3)_5nic^{2+}$ and the reverse. The rate constant is 4.7×10^5 M^{-1} s^{-1} at 25 °C in 1.0 M CF_3SO_3H, and the equilibrium quotient is 2.1, the latter to be compared with 2.5 ± 0.5 as determined from electrochemical measurements. The enthalpy and entropy of activation are 2.9 kcal mol^{-1} and −23 cal deg^{-1} mol^{-1}, respectively. Examination of the data on the rates of cross reactions in light of the Marcus correlation reveals no anomalies for reactions among the (pyridine)pentaammineruthenium reactions or for the reactions of the ruthenium complexes with V(II), but, as noted earlier by others, for the $Fe^{3+/2+}$ couple, the observed rate constants tend to be lower than those calculated. The discrepancy appears to be largely an entropic effect, suggesting the operation of a significant nonadiabatic factor in the $Fe^{3+/2+}$ couple.

The reactions of ammine complexes of ruthenium(III) have played an important role in demonstrating the effects of electronic structure of the participating metal ions on the mechanism of inner-sphere electron-transfer reactions.[1] The discovery of intervalence transfer transitions in ligand-bridged mixed-valence ruthenium ammine complexes[2,3] has stimulated a great deal of interest in this area.[4-8] The reactions of ligand-bridged precursor complexes of ruthenium(II) and cobalt(III) are being systematically investigated in a search for evidence of nonadiabatic effects.[9-11] The systems which have been mentioned so far involve intramolecular electron transfer. Evidence for nonadiabatic effects may also be found in bimolecular electron-transfer reactions.

We have determined the rate constants and activation parameters for the bimolecular electron-exchange reaction of the pentaammine(pyridine)ruthenium(II)–(III) couple. This exchange reaction was studied by making use of the spectral differences in the ruthenium complexes of two pyridine derivatives, namely, isonicotinamide and nicotinamide. A comparison of the free energy of activation for this electron-ex-



isonicotinamide (isn)



nicotinamide (nic)

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Table I. Formal Potentials of $M^{3+/2+}$ Couples and Thermodynamic Parameters for the Reaction $M^{3+} + {}^1/_2H_2 = M^{2+} + H^+$

couple	E_f (25 °C), V	ΔH_f, kcal mol^{-1}	ΔS_f, cal deg^{-1} mol^{-1}	medium
$Ru(NH_3)_5isn^{3+/2+}$ [a]	+0.384	−12.3	−12	1.0 M CF_3SO_3H
$Ru(NH_3)_5nic^{3+/2+}$ [a]	+0.363	−10.9	−9	1.0 M CF_3SO_3H
$Ru(NH_3)_5py^{3+/2+}$ [a]	+0.299	−10.4	−12	1.0 M CF_3SO_3H
$Fe(H_2O)_6{}^{3+/2+}$ [b]	0.739	−9.8	+24	1.0 M $HClO_4$
$V(H_2O)_6{}^{3+/2+}$ [c]	−0.282	9.8	+11	0.2–1.0 M H_2SO_4
$Co(phen)_3{}^{3+/2+}$ [d,e]	+0.37	−10.3	−3.6	unknown
	+0.38	−7.8	+4	0.05 M KCl
$Ru(bpy)(NH_3)_4{}^{3+/2+}$ [f]	+0.52	−14	−7	0.1 M CF_3SO_3H
$Ru(NH_3)_6{}^{3+/2+}$ [g]	+0.067	−5.7	−14	1.0 M CF_3SO_3H
$Ru(NH_3)_5(H_2O)^{3+/2+}$ [g,e]	+0.084	−3.0 ± 0.3	−3.6 ± 1.1	1.0 M CF_3SO_3H
	+0.082	−0.7	+4	0.2 M CF_3COOH

[a] This work. [b] Reference 22. [c] Reference 23. [d] Unpublished work; quoted in ref 14. [e] Reference 35. [f] G. M. Brown, unpublished work. [g] Reference 16.

change reaction will be made with the energy of the intervalence transfer transition of related ligand-bridged ruthenium ammine complexes, leading to the conclusion that this exchange reaction is adiabatic.

Marcus and Sutin[12] have extended the cross-reaction relations[13] to include the enthalpy and entropy of activation, and Chou et al.[14] have recently examined in detail the assumptions of the Marcus equation in order to determine if any systematic deviations occur between observed and calculated results. In this paper a comparison is made between the observed and calculated rate constants and activation parameters of the electron-transfer reactions of pentaammine(pyridine)ruthenium with a series of reactants.

Experimental Section

Chemicals and Solutions. Pentaammine(pyridine)ruthenium(II) hexafluorophosphate was prepared essentially by the procedure described by Gaunder[15] for the perchlorate salt except that NH_4PF_6 was used to precipitate the complex from solution. The pentaammineruthenium(II) and -ruthenium(III) complexes of isonicotinamide and nicotinamide as perchlorates were prepared by the literature procedure.[15] The purity of the ruthenium(II) complexes was determined from their absorption spectra and elemental analysis and of the ruthenium(III) complexes by reducing them to ruthenium(II) with a slight excess of Eu(II) followed by spectrophotometric analysis as before.

Trifluoromethanesulfonic acid (3M Co.) was purified by reduced-pressure distillation. The concentrations of dilute solutions of CF_3SO_3H were determined by titrations with standard base. A solution of Fe(III) in CF_3SO_3H was prepared by dissolving iron wire in the acid followed by oxidizing Fe(II) to Fe(III) with excess H_2O_2 (Malinckrodt, 30%). The solution of Fe(III) was heated to 50 °C to decompose the excess H_2O_2 and its strength was determined by a standard procedure.

Electrochemical Measurements. The potentials of the Ru(III)/Ru(II) couples of the pentaamminepyridine complex and the other pyridine derivatives were measured by cyclic voltammetry in 1.0 M CF_3SO_3H. The $Ru(NH_3)_5(H_2O)^{3+/2+}$ couple was used as an internal reference. Thermodynamic parameters for the reaction

$$Ru(NH_3)_5(H_2O)^{3+} + {}^1/_2H_2 = Ru(NH_3)_5(H_2O)^{2+} + H^+$$

have been measured[16] in 1.0 M CF_3SO_3H and provide a convenient means of correcting for the reference electrode–solution junction potential in this medium. These potentials are uncorrected for the diffusion coefficient term $E_f = E_{1/2} + 0.059/n[\log (D_{Red}/D_{Ox})]$. We have assumed that the term $\log (D_{Red}/D_{Ox})$ for the $Ru(NH_3)_5(H_2O)^{3+/2+}$ couple is approximately equal to the same term for the pyridine complex and its derivatives. The instrumentation for cyclic voltammetry consisted of a Princeton Applied Research Model 173 potentiostat and a Model 175 universal programmer with a Houston Instruments Model 2000 XY recorder for data presentation. The potential of the Fe(III)/Fe(II) couple was determined by potentiometric titration of a solution of Fe(II) with Ce(IV).

Kinetic Measurements. A thermostated Aminco-Morrow stopped-flow mixing apparatus adapted to fit on a Beckman DU monochromator was used for all rate measurements. This system as previously described[17] was modified in the following manner. An amplifier was added to the circuitry to boost the output from the current-to-voltage converter to 1 V. A General Data Corp. Nova I computer was used for data acquisition and analysis. This computer system uses a 12-bit analog-to-digital converter (±1-V window) and was programmed to take 200 data points at integral multiples of 0.1 ms followed by a variable wait period before an average value of I_∞ was recorded. Transmittance data were converted to absorbance by standard techniques, and rate constants were calculated by fitting the data, using linear least-squares methods, to the integrated first-order rate expression. Temperature measurements were made with a thermocouple, referenced to the ice point of water, attached to the mixing chamber of the stopped-flow apparatus. All values of ΔH^* and ΔS^* reported in this work were calculated from a linear least-squares fit of the data to the Eyring absolute rate expression

$$\ln (k/T) = -\Delta H^*/RT + \Delta S^*/R + \ln (k_B/h)$$

$Ru(NH_3)_5isn^{3+/2+}$–$Ru(NH_3)_5nic^{3+/2+}$ Exchange Reactions. The rate of approach to equilibrium in this system was measured in both the forward and reverse directions. In each case a sufficient excess of the Ru(III) complex was used to drive the reaction to greater than 95% completion so that k_f and k_r could be determined independently. Under these conditions the rate law reduces to simple first-order behavior with

$$k_{obsd} = k[Ru(III)]$$

All measurements were made at 480 nm.

Fe(III) Oxidation Reactions. Rate constants were measured under first-order conditions with an excess of $Fe(H_2O)_6{}^{3+}$. The progress of the reactions was followed by monitoring the disappearance of the Ru(II) pyridine complexes at the maxima of the MLCT transition: 480 nm for isonicotinamide, 427 nm for nicotinamide, and 407 nm for pyridine.

Results

Electrode Potentials. The formal potentials of the Ru(III)/Ru(II) couple for the pentaamminepyridine complex and its derivatives are included in Table I. The measurement technique used in this work should allow the reference electrode–solution junction potential and other medium effects to be accounted for. An accurate accounting of these factors has frequently not been made in the reported values of E_f for the Ru(III)/Ru(II) couple of ruthenium ammine complexes. For instance, some of the reported values of the $Ru(NH_3)_5py^{3+/2+}$ couple, in volts vs. NHE, are as follows: 0.42,[15] 0.305,[18] 0.298,[19] 0.273,[20] and 0.253.[21]

Values of E_f, ΔH_f, and ΔS_f for other redox couples of interest to this work are also included in Table I. The potential of the $Fe(H_2O)_6{}^{3+/2+}$ couple was remeasured at 25 °C in 1.0 M CF_3SO_3H. The measured value after correction for the junction potential is +0.74 V, in excellent agreement with that reported[22] for the medium 1.0 M $HClO_4$. The values of ΔH_f and ΔS_f for this couple will be taken as applicable in CF_3SO_3H media.

Thermodynamic parameters for the $V(H_2O)_6{}^{3+/2+}$ couple have been measured in sulfuric acid solution.[23] The formal potential (Table I) for this couple is an average value in the range 0.2–1.0 M H_2SO_4. It should be noted that the value

Table II. Rate Constants for the $Ru(NH_3)_5isn^{3+/2+}$-$Ru(NH_3)_5nic^{3+/2+}$ Electron-Exchange Reaction in 1.0 M CF_3SO_3H

T, °C	$10^5 \times$ [Ru(II)], M	$10^4 \times$ [Ru(III)], M	k_{obsd},[a] s^{-1}	$10^{-5}k_{obsd}$/[Ru(III)], $M^{-1}\ s^{-1}$
Reaction: $Ru(NH_3)_5nic^{2+} + Ru(NH_3)_5isn^{3+}$				
14.0	2.32	3.57	213 ± 11	5.97
15.0	1.02	2.89	173 ± 8	5.98
25.0	2.02	2.00	135 ± 1	6.75
25.0	0.99	1.40	97 ± 9	6.93
33.4	0.99	1.40	106 ± 8	7.57
Reaction: $Ru(NH_3)_5isn^{2+} + Ru(NH_3)_5nic^{3+}$				
10.8	1.05	5.32	121 ± 6	2.28
16.5	0.98	5.13	129 ± 9	2.52
16.5	0.98	6.18	159 ± 10	2.57
25.0	1.70	5.72	199 ± 1	3.48
26.6	0.97	5.97	212 ± 30	3.55
36.1	0.99	5.14	217 ± 41	4.23
36.1	0.99	2.66	120 ± 10	4.51

[a] The observed rate constants are the average of 5–11 runs. The error limits are average deviations.

of $S_{V(II)} - S_{V(III)}$ calculated from Jones and Colvin's data (32 cal deg^{-1} mol^{-1}) is in mild disagreement with the value calculated from Newton's estimate of $S_{V(II)}$[24b] and $S_{V(III)}$[24a] (−23 (±3) + 65) based on the Powell–Latimer equation.[25]

Rates and Equilibria in the $Ru(NH_3)_5isn^{3+/2+}$-$Ru(NH_3)_5nic^{3+/2+}$ Exchange Reaction. The rate constants for the electron-transfer reaction represented in eq 1 were measured in both the forward and reverse directions. Rate constants as a function of temperature are given in Table II. The best fit values of k_1 and k_{-1} at 25 °C are 6.8×10^5 $M^{-1}\ s^{-1}$ and 3.3×10^5 $M^{-1}\ s^{-1}$, respectively. The equilibrium quotient K_1 for reaction 1 is 2.1 as calculated from the ratio of the rate constants, and this is in satisfactory agreement with the value of 2.5 ± 0.5 as calculated from the electrode potential data in Table I.

$$Ru(NH_3)_5isn^{3+} + Ru(NH_3)_5nic^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru(NH_3)_5isn^{2+} + Ru(NH_3)_5nic^{3+} \quad (1)$$

A troubling feature of the data is the apparent large difference in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for electron transfer in reaction 1 when measured in the forward and reverse directions. The linear least-squares best fit values of $\Delta H^\ddagger_1$, $\Delta S^\ddagger_1$, $\Delta H^\ddagger_{-1}$, and $\Delta S^\ddagger_{-1}$ are 1.6 ± 0.3 kcal mol^{-1}, −26 ± 2 cal deg^{-1} mol^{-1}, 4.1 ± 0.3 kcal mol^{-1}, and −19 ± 2 cal deg^{-1} mol^{-1}, respectively. Although the data set is somewhat limited, the differences appear to be statistically significant. As a further check, values of ΔH_f and ΔS_f were computed from both the kinetic data and the electrode potential data. From the kinetic data as given above, the values are −2.5 kcal mol^{-1} and −7 cal deg^{-1} mol^{-1}, respectively, to be compared to −1.5 kcal mol^{-1} and −3 cal deg^{-1} mol^{-1} as calculated from the electrode potential data. In principle, a determination of the equilibrium parameters for reaction 1 from the electrode potential data should be the more accurate. The discrepancies between the two data sets may indicate failure to separate k_{-1} from k_1 in the kinetic measurement. The signs of ΔH_f and ΔS_f in reaction 1 can be rationalized on the basis that there is a greater back-bonding interaction between Ru(II) and isonicotinamide relative to nicotinamide.[26]

It is reasonable to assume that the exchange rates of the three pentaammine(pyridine)ruthenium derivatives are approximately the same (this assumption will be justified in a later section). The exchange rate constant for the complexes can be calculated from k_1 by taking K_1 into account.

$$k_{exch} = k_1/(K_1)^{1/2} = 4.7 \times 10^5\ M^{-1}\ s^{-1}$$

Table III. Rate Constants for the Oxidation of Pentaammine(pyridine)ruthenium(II) Derivatives by Fe(III) in 1.0 M CF_3SO_3H

complex	T, °C	$10^4 \times$ [Fe(III)], M	k_{obsd},[a] s^{-1}	$10^{-4}k_{obsd}$/[Fe(III)], $M^{-1}\ s^{-1}$
$Ru(NH_3)_5isn^{2+}$	14.0	19.3	28.7 ± 0.3	1.49
	14.2	7.72	11.7 ± 0.1	1.52
	25.0	4.83	13.2 ± 0.2	2.53
	25.0	9.65	25.1 ± 0.3	2.60
	34.7	3.86	14.6 ± 0.2	3.78
	34.7	5.79	22.4 ± 0.3	3.87
$Ru(NH_3)_5nic^{2+}$	14.8	7.72	16.9 ± 0.2	2.19
	25.0	3.86	11.3 ± 0.4	2.93
	34.7	3.86	19.4 ± 0.2	5.03
$Ru(NH_3)_5py^{2+}$	25.0	3.86	22.4 ± 0.4	5.80

[a] The observed rate constants are the average of 4–7 runs. The error limits are average deviations.

Table IV. Rate Constants and Activation Parameters for Electron-Exchange Reactions

redox couple	k (25 °C), $M^{-1}\ s^{-1}$	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, cal deg^{-1} mol^{-1}	medium
$Ru(NH_3)_5py^{3+/2+}$ [a]	4.7×10^5	2.9	−22	1.0 M CF_3SO_3H
$Fe(H_2O)_6^{3+/2+}$ [b]	4.0	9.3	−25	0.55 M $HClO_4$
$V(H_2O)_6^{3+/2+}$ [c]	1×10^{-2}	12.6	−25	2.0 M ClO_4^-
$Co(phen)_3^{3+/2+}$ [d]	4×10^1	9	−21	0.05 M ClO_4^- and 0.1 M KNO_3
$Ru(NH_3)_6^{3+/2+}$ [e]	4×10^3			0.1 M $HClO_4$
$Ru(NH_3)_4bpy^{3+/2+}$ [f]	1.2×10^7	1.2	−22	1.0 M $HClO_4$

[a] This work; the rate constant and activation parameters for this reaction also apply to the nicotinamide and isonicotinamide derivatives. [b] Reference 28. [c] Reference 29. [d] See text. [e] T. J. Meyer and H. Taube, *Inorg. Chem.*, 7, 2369 (1968). [f] Reference 36.

Similarly $\Delta H^\ddagger_{exch}$ and $\Delta S^\ddagger_{exch}$ can be calculated from the equations

$$\Delta H^\ddagger_{exch} = \Delta H^\ddagger_1 - \Delta H_1/2 = 2.9\ kcal\ mol^{-1}$$

$$\Delta S^\ddagger_{exch} = \Delta S^\ddagger_1 - \Delta S_1/2 = -23\ cal\ deg^{-1}\ mol^{-1}$$

These equations follow from an application of Marcus theory (see eq 8–14). The values of ΔH_f and ΔS_f used in the above calculations were those derived from the kinetic data. Their use is justified because it will compensate for any error introduced by a failure to separate k_1 from k_{-1}.

Oxidation of Ru(II) Pyridine Derivatives by Fe(III). Rate constants for the oxidation of the pentaammine(pyridine)ruthenium(II) complex and the complexes of the pyridine derivatives by $Fe(H_2O)_6^{3+}$ in 1.0 M CF_3SO_3H are listed in Table III. The reaction rates were measured as a function of temperature and from these data activation parameters were calculated. These values are listed in Table IV along with rate constants and activation parameters of other cross reactions of interest. A plot of the logarithm of the rate constant for oxidation of these ruthenium complexes by Fe(III) vs. the logarithm of the equilibrium quotient yields a slope which is in reasonable agreement with the Marcus cross-reaction equation (see below). This justifies the use of a single exchange rate constant for the pyridine derivatives of pentaammineruthenium.

Other Exchange Reactions. The reported exchange rates for $V(H_2O)_6^{3+/2+}$[28] and $Fe(H_2O)_6^{3+/2+}$[29] are based on careful measurements. The latter exchange reaction in particular has been extensively dealt with[30] and is without doubt accurate. The $Co(phen)_3^{3+/2+}$ exchange constant was determined by Baker, Basolo, and Neumann.[31] Their results suggest the exchange rate constant is anion dependent. More recently,

Table V. Observed and Calculated Rate Constants and Activation Parameters for the Net Electron-Transfer Reactions

reaction	k, M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}	k_{calcd}, M^{-1} s^{-1}	$\Delta H^{\ddagger}$(calcd), kcal mol^{-1}	$\Delta S^{\ddagger}$(calcd), cal deg^{-1} mol^{-1}
(A) $Ru(NH_3)_5py^{2+}$ + Fe(III)[a]	7.76×10^4	4.7 ± 0.5[e]	−20 ± 2[e]	2.5×10^6	6.4	−10
(B) $Ru(NH_3)_5nic^{2+}$ + Fe(III)[a]	2.9×10^4	6.7 ± 1.5	−15 ± 5	9.5×10^5	7.0	−10
(C) $Ru(NH_3)_5isn^{2+}$ + Fe(III)[a]	2.57×10^4	7.4 ± 0.2	−14 ± 1	6.9×10^5	7.2	−9
(D) $Ru(NH_3)_5py^{3+}$ + V(II)[b]	3.0×10^5	0.0	−33	1.2×10^6	0.2	−31
(E) $Ru(NH_3)_5isn^{3+}$ + V(II)[c]	1.3×10^6	−0.3 ± 0.5	−32 ± 4	3.8×10^6	0.1	−30
(F) $Ru(NH_3)_5py^{2+}$ + $Co(phen)_3{}^{3+}$ [b,d]	2.0×10^3	8.6	−15	$(1.5\text{–}2.1) \times 10^4$	6–7.2	−14 to −18
(G) $Ru(NH_3)_5py^{3+}$ + $Ru(NH_3)_6{}^{2+}$ [b]	1.4×10^6			5.0×10^6		
(H) $Ru(NH_3)_5py^{2+}$ + $Ru(NH_3)_4bpy^{3+}$ [b]	1.1×10^8			1.1×10^8		

[a] This work. [b] Reference 14. [c] Reference 15. [d] The rate constant and activation parameters for this reaction have been reported elsewhere.[34] Although the rate constant at 25 °C is in good agreement with the value in ref 14, the activation parameters reported do not calculate to the value of $\Delta G^{\ddagger}$ at 25 °C. In addition an anomalous two-term rate law was reported for the reaction. [e] J. N. Braddock, Ph.D. Thesis, The University of North Carolina, 1973. These activation parameters were measured in 1.0 M $HClO_4$.

Neumann[32] has reinvestigated the reaction by monitoring the loss in optical activity of a resolved sample of $Co(phen)_3{}^{3+}$ in the presence of the Co(II) complex. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ observed for the reaction were 5.1 kcal mol^{-1} and −34 cal deg^{-1} mol^{-1}, respectively, in 0.1 M KNO_3. Farina and Wilkins[33] have studied the reactions

$$Co(terpy)_2{}^{3+} + Co(bpy)_3{}^{2+} \xrightleftharpoons[k_{-2}]{k_2} Co(terpy)_2{}^{2+} + Co(bpy)_3{}^{3+} \quad (2)$$

$$Co(terpy)_2{}^{3+} + Co(phen)_3{}^{2+} \xrightarrow{k_3} Co(terpy)_2{}^{2+} + Co(phen)_3{}^{3+} \quad (3)$$

in 0.05 M $ClO_4{}^-$ medium. The entropies of activation for k_2, k_{-2}, and k_3 are all in the range −19 to −21 cal deg^{-1} mol^{-1}. Reaction 3 has also been studied[34] in 0.5 M NaCl, and $\Delta S^{\ddagger}$ as reported for this medium is in good agreement with the previously noted values. Weaver and co-workers[35] have measured $S_{M(II)} - S_{M(III)}$ for the couples $Co(phen)_3{}^{3+/2+}$, $Co(bpy)_3{}^{3+/2+}$, and $Co(terpy)_2{}^{3+/2+}$. The respective values, determined from electrode potential data, are 22 ± 3, 22 ± 3, and 17 ± 2 cal deg^{-1} mol^{-1}. These experimental data show that ΔS_f for reactions 2 and 3 is small (≤5 cal deg^{-1} mol^{-1}). The activation entropies and ΔS_f for these reactions form the basis of a strong argument for assuming similar exchange activation entropies for the three polypyridyl cobalt complexes. An application of Marcus theory (eq 13) suggests $\Delta S^{\ddagger}$ for the $Co(phen)_3{}^{3+/2+}$ exchange reaction is approximately −21 cal deg^{-1} mol^{-1}. From an analysis of the available data, the parameters for this reaction are consonant with those listed in Table IV.

Discussion

There is good evidence that the $Ru(NH_3)_5py^{3+/2+}$ exchange reaction is adiabatic. The rate constant for electron exchange in a series of ruthenium–ammine–pyridine complexes correlates well with the theoretical predictions based on the equations suggested by Marcus[36]

$$k = Z \exp(-w_r/RT) \exp(-\Delta G_\lambda/RT) \quad (4)$$

In this equation, Z is the collision frequency of neutral molecules in solution, w_r is the work required to bring the reactants together, and ΔG_λ is the Franck–Condon activation energy to rearrange the inner and outer coordination spheres of the reactants. This equation can be rewritten in the form[36,37]

$$k = K_0 k_{et} \quad (5)$$

$$K_0 = Zh/k_BT \exp(-w_r/RT) \quad (6)$$

$$k_{et} = k_BT/h \exp(-\Delta G_\lambda/RT) \quad (7)$$

where K_0 is the equilibrium constant for precursor complex formation and k_{et} is the rate constant for electron transfer within the complex. An estimate for k_{et} can be obtained from the energy of the IT band for the mixed-valence complex $[(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5]^{5+}$ [3] and the relationship $E_{op} = 4\Delta G_\lambda$.[38] From the maximum at 1050 nm and eq 7, assuming $\Delta S^{\ddagger}$ to be zero, the calculated rate constant is 6.2×10^7 s^{-1}. From the rate constant for the bimolecular exchange reaction and from eq 6 for the equilibrium constant for precursor complex formation,[39] the value for k_{et} is estimated to be 1.6×10^8 s^{-1},[40] in good agreement with the value from spectroscopic data. An analogous approach has been taken by Meyer and coworkers[8,42] in correlating the rate constant for bimolecular electron exchange in mononuclear complexes with the energy of the IT band in ligand-bridged binuclear complexes.

Comparison of Observed and Calculated Rate Constants and Activation Parameters. Nonadiabaticity should manifest itself in the transmission coefficient for the electron-transfer process being small, i.e., $\langle\kappa\rangle < 1$ in the equation

$$k = \langle\kappa\rangle k_BT/h \exp(-\Delta G^{\ddagger}/RT)$$

If $\langle\kappa\rangle$ contains only electronic transmission information, then this low probability is expected to reflect itself as a more negative entropy of activation.[37,43]

The Marcus cross-reaction equation[13]

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \quad (8)$$

$$\log f = \frac{(\log K_{12})^2}{4 \log (k_{11}k_{22}/Z^2)}$$

will be used to calculate rate constants. In eq 8 the subscript 12 refers to the cross reaction and 11 (and 22) refers to the individual exchange reactions. Equation 8 can also be written in terms of free energies of activation.

$$\Delta G_{12}{}^* = (\Delta G_{11}{}^* + \Delta G_{22}{}^*)/2 + \Delta G_{12}{}^\circ\,(1+\alpha)/2 \quad (9)$$

$$\alpha = \Delta G_{12}{}^\circ/4(\Delta G_{11}{}^* + \Delta G_{22}{}^*)$$

Marcus and Sutin[12] derived equations for the enthalpy and entropy of activation by differentiating eq 9 with respect to temperature.

$$\Delta H_{12}{}^* = \left[\frac{\Delta H_{11}{}^* + \Delta H_{22}{}^*}{2}\right](1 - 4\alpha^2) + \frac{\Delta H_{12}{}^\circ}{2}(1 + 2\alpha) \quad (10)$$

$$\Delta S_{12}{}^* = \left[\frac{\Delta S_{11}{}^* + \Delta S_{22}{}^*}{2}\right](1 - 4\alpha^2) + \frac{\Delta S_{12}{}^\circ}{2}(1 + 2\alpha) \quad (11)$$

The relationships between ΔG^*, ΔH^*, and ΔS^* and the quantities derived from an application of absolute reaction rate theory are

$$\Delta G^{\ddagger} = \Delta G^* - RT \ln (hZ/kT) \quad (12)$$

$$\Delta S^{\ddagger} = \Delta S^* + R \ln (hZ/kT) - \tfrac{1}{2}R \quad (13)$$

$$\Delta H^{\ddagger} = \Delta H^* - \tfrac{1}{2}RT \quad (14)$$

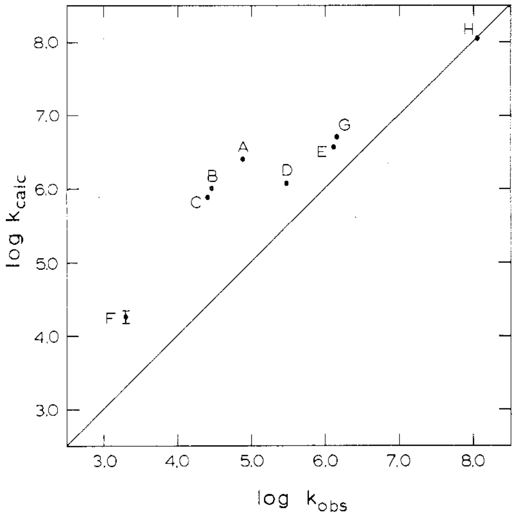

Figure 1. Plot of the logarithm of k_{calcd} (eq 8) vs. the logarithm of k_{obsd}. The data points are lettered as the reactions in Table V.

It is useful first to compare observed and calculated rate constants (Table V). Figure 1 is a plot of log k_{obsd} vs. log k_{calcd}. The agreement is remarkably good for reactions D, E, G, and H. The latter two are expected to be in good agreement with theoretical predictions since these are reactions between ruthenium ammine complexes. Reactions G and H in particular serve to demonstrate that the use of eq 8 is warranted. Reactions of the V(II)/V(III) couple such as reactions D and E have been shown previously to yield good results with the Marcus equation. Chou et al.[14] have previously noted the failure of rate constants for the reaction of Fe(II) or Fe(III) to give good agreement with predictions. The general trend of the data is that calculated rate constants are larger than observed rate constants, again in accord with previous observations.[14]

The electrode potential data in Table I, the activation parameters for the individual exchange reactions in Table IV, and eq 10–14 were used to calculate $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for reactions A–F. These results are included in Table V. The calculated values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the reduction of the Ru(III) complexes by V(II) (reactions D and E) are in very good agreement with the observed values. As was the case in the Fe(II) reductions of tris(polypyridyl) complexes of iron(III)[44] and ruthenium(III),[45] Marcus theory accounts for[12] nearly zero enthalpy of activation. In both of these reactions a large and negative enthalpy change for the net reaction largely determines the enthalpy of activation. A comparison of observed and calculated values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the Fe(III) oxidation of the ruthenium(II) pyridine derivatives is quite revealing. The discrepancy between observed and calculated rate constants is primarily an entropic effect. A $\Delta S^{\ddagger}$ which is ~6 cal deg^{-1} mol^{-1} too negative can be taken as evidence for a $\langle\kappa\rangle$ of $\sim 5 \times 10^{-2}$.[46] The calculated activation parameters for the $Co(phen)_3^{3+}$ oxidation of $Ru(NH_3)_5py^{2+}$ show a deviation in $\Delta H^{\ddagger}$. There may be significant errors involved in our estimation of the thermodynamic and activation exchange parameters for these reactions. These errors arise from medium effects that cannot be taken into account, and more accurate data are required before conclusions can be drawn with complete confidence. A deviation from the Marcus correlation (eq 8) can indicate the presence of nonadiabaticity in outer-sphere electron transfer reactions. Nonetheless it should be noted that a good correlation of rate constants with the equilibrium driving force does not require the reaction to be adiabatic.[37,47]

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Registry No. $Ru(NH_3)_5isn^{3+}$, 46372-32-1; $Ru(NH_3)_5isn^{2+}$, 19471-53-5; $Ru(NH_3)_5nic^{3+}$, 50762-76-0; $Ru(NH_3)_5nic^{2+}$, 19471-62-6; $Ru(NH_3)_5py^{3+}$, 33291-25-7; $Ru(NH_3)_5py^{2+}$, 21360-09-8; $Ru(bpy)(NH_3)_4^{3+}$, 69799-61-7; $Ru(bpy)(NH_3)_4^{2+}$, 54194-87-5.

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$$w_r = \frac{z_1 z_2 e^2}{D_s r(1 + Kr)}$$

The value for r, the distance of closest approach of the Ru centers, was taken to be the mean value of 7.6 Å
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Synthesis and Structure of Salts of the Bicyclic Sulfur–Nitrogen Cation $S_4N_5^+$ and a Comparison of the Electronic Structures of the Tetrasulfur Pentanitride(1+) and -(1−) Ions

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The new sulfur–nitrogen halide S_4N_5Cl has been prepared in good yield from trithiazyl trichloride, $S_3N_3Cl_3$, and bis[(trimethylsilyl)imido]sulfur, $Me_3SiN{=}S{=}NSiMe_3$, in carbon tetrachloride. An X-ray structural determination of this compound shows it to have a polymeric, predominantly ionic, structure in which bicyclic $S_4N_5^+$ cations are symmetrically bridged by Cl^- ions. Crystals of S_4N_5Cl are orthorhombic and belong to the space group *Pnma* with a = 17.491 (17) Å, b = 7.819 (2) Å, and c = 4.838 (4) Å, V = 661.7 (5) Å^3, Z = 4, and D_c = 2.346 g cm^{-3}. The structure was solved by direct methods and Fourier techniques and refined to a conventional R factor of 0.066 for 1162 independent reflections with $I \geq 3\sigma(I)$. The reaction of S_4N_5Cl with silver(II) fluoride or antimony pentachloride gives S_4N_5F or $S_4N_5SbCl_6$, respectively. The vibrational spectra of these salts of the $S_4N_5^+$ cation are reported. Ab initio Hartree–Fock–Slater SCF calculations have been carried out for $S_4N_5^+$ and for the related anion $S_4N_5^-$ in order to compare their ground-state electronic structures with that of S_4N_4, and, in particular, to assess the importance of S--S interactions within these S–N cages. These calculations show that the introduction of a bridging N^- entity into the S_4N_4 framework destroys one of the transannular S--S bonds and weakens the S–N framework bonds. In $S_4N_5^+$ there are no S--S bonds, as expected for loss of 2 electrons from the $S_4N_5^-$ anion.

Introduction

The growing number of binary S–N cations which have been structurally characterized attests to the rich diversity of this area of nonmetal chemistry. This list now includes NS^+,[1] NS_2^+,[2] $S_3N_2^+$,[3] $S_4N_3^+$,[4] $S_4N_4^{2+}$,[5] $S_5N_5^+$,[6] and $S_6N_4^{2+}$.[7] In a preliminary communication we described the synthesis and structure of S_4N_5Cl,[8] which contains the first bicyclic S–N cation, $S_4N_5^+$. In this paper we report the full details of the synthesis and spectroscopic characterization of three salts of the $S_4N_5^+$ ion. In addition, we have carried out ab initio Hartree–Fock–Slater (HFS) SCF calculations of the ground-state electronic structures of $S_4N_5^+$ and the related anion $S_4N_5^-$,[9] in order to assess the effect of introducing an N^- or N^+ species into the S_4N_4 framework with particular reference to the importance of transannular S--S interactions in these S–N cages.

Experimental Section

General Procedures. All experiments were performed under dry nitrogen (Linde 99.998% passed through silica gel) in oven-dried glassware. Manipulations involving air-sensitive compounds were carried out in a Vacuum Atmospheres drybox. Carbon tetrachloride and methylene chloride were stored over P_2O_5 and distilled before use. $S_3N_3Cl_3$[10] and $Me_3SiNSNSiMe_3$[11] were prepared by standard literature procedures. Thionyl chloride, sulfuryl chloride, and antimony pentachloride were freshly distilled before use. All other chemicals were commercial samples used as received.

Infrared spectra (4000–250 cm^{-1}) were recorded as Nujol mulls on a Perkin-Elmer 467 spectrophotometer using CsI windows. Raman spectra were obtained on samples sealed in capillaries under nitrogen by using a He/Ne (6328 Å) laser and a Jarrell-Ash spectrophotometer and were calibrated against carbon tetrachloride. UV–visible spectra were recorded on a Cary 15 spectrometer. Mass spectra were recorded on a Varian CH5 spectrometer operating at 70 eV. Elemental analyses were performed by the Analytische Laboratorien, Engelskirchen, West Germany.

Preparation of S_4N_5Cl. $Me_3SiNSNSiMe_3$ (0.83 g, 4.03 mmol) was added to a stirred solution of $S_3N_3Cl_3$ (0.95 g, 3.88 mmol) in carbon tetrachloride (55 mL), which had been filtered through a fine glass frit. The solution was allowed to stand at 23 °C for 12 h, whereupon the supernatant liquid was decanted by pipet from the crystalline product. The golden green crystals were washed with carbon tetrachloride and dried in vacuo for 20 min to give tetrasulfur pentanitride chloride, mp 108 °C (0.56 g, 2.40 mmol, 62% yield). Anal. Calcd for S_4N_5Cl: S, 54.86; N, 29.97; Cl, 15.17. Found: S, 54.58; N, 29.97; Cl, 15.23.

Removal of solvent from the decanted solution produced a further 0.16 g of S_4N_5Cl as a yellow powder. The crystals obtained above were found to be suitable for the X-ray structural determination described below. In preparations in which the solution of reagents was stirred during the reaction, the product was obtained as a yellow powder.

Caution! Like all nitrogen-rich S–N species, S_4N_5Cl is potentially explosive and care should be exercised to avoid subjecting samples to friction or sudden heating.

Preparation of S_4N_5F. An excess of silver difluoride (1.57 g, 10.7 mmol) was stirred with a solution of S_4N_5Cl (0.26 g, 1.10 mmol) in methylene chloride (15 mL). The yellow solution turned green and effervesced for the first 10 min. After 13 h, the solution was decanted from the black residue (1.56 g) and solvent was removed by slow vacuum transfer at −78 °C. When the volume was ca. 4 mL, the supernatant liquid was decanted to give dark green crystals of S_4N_5F (0.15 g, 6.91 mmol, 63%), which were dried in vacuo for 15 min. Anal. Calcd for S_4N_5F: S, 59.02; N, 32.23; F, 8.74. Found: S, 58.70; N, 32.09; F, 8.59.

Removal of solvent from the decanted solution produced a further 0.05 g of S_4N_5F.

Preparation of $S_4N_5SbCl_6$. A solution of antimony pentachloride (0.50 g, 1.68 mmol) in methylene chloride (3.5 mL) was slowly added to a clear yellow solution of S_4N_5Cl (0.34 g, 1.48 mmol) in methylene chloride (25 mL). A yellowish precipitate, which formed immediately, was filtered off, washed with methylene chloride (20 mL), dried in vacuo for 30 min, and identified as $S_4N_5SbCl_6$ (0.56 g, 1.07 mmol, 73% yield). Anal. Calcd for $S_4N_5Cl_6$: S, 24.07; N, 13.15; Cl, 39.93. Found: S, 23.77; N, 13.28; Cl, 40.08.

Crystal Data for S_4N_5Cl. Golden prisms suitable for X-ray diffraction studies were obtained as described above. The dimensions of the crystal used in this study were 0.25 × 0.25 × 0.28 cm. All

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