follows in ppm (J_{BH}, Hz): 9.2 (147), −4.2 (153), −9.1 (152), −29.9 (149), −34.0 (126), −36.0 (147 Hz). The ^{11}B NMR spectrum of the major compound (CH_2Cl_2 solvent) contained five doublets with relative areas of 1:1:2:3:2, respectively, as follows in ppm (J_{BH}, Hz): 11.4 (144), −2.3 (172), −5.9 (155), −27.8 (134), −32.4 (148 Hz). The ^{11}B NMR spectrum of the major compound was different from but still quite similar to that of compound IX. An analysis of the ^{11}B NMR spectra of $B_9H_{11}E$·ligand (where E = S, Se, or Te) compounds has been reported previously.[16] Both the major and minor compounds have ^{11}B NMR spectra very similar to those of other known $B_9H_{11}S$·ligand derivatives. After stirring of the mixture at room temperature for 2 h, nearly complete conversion of this major compound to the thiacarborane I was observed. the quantity of IX did not change during this prolonged reaction at room temperature. Even an attempt to convert IX to I by reflux in toluene for 48 h was not successful.

We interpret this result to mean that there are two isomeric $B_9H_{11}S·CN(t\text{-}C_4H_9)$ adducts initially formed. One isomer, IX, is stable and cannot easily be converted to the thiacarborane, but the second adduct is more reactive and readily converts to I. The structures of these two adducts are of great interest and are presently under study. It is possible that IX has the structure given in Figure 1 and that the less stable isomer has the alkyl isocyanide ligand coordinated to the same boron atom but extending over the open face of the $B_9H_{11}S$ unit.

The presence of isomeric adducts of $B_9H_{11}S·NCCH_3$ was previously suggested by the observation in the ^1H NMR spectrum of two singlet resonances attributed to the methyl group.[14] A similar finding was observed for $B_9H_{11}E·NCCH_3$ (E = Se or Te) as well.[16]

There are a few previous reports of the synthesis of thia- and selenacarboranes. Reaction of $K[7,8\text{-}B_9C_2H_{12}]$ with $K_2S_2O_5$ at 100 °C formed *nido*-$SC_2B_8H_{10}$.[21,22] Treatment of $Na[C_2B_{10}H_{13}]$ with HCl and $KHSO_3$ formed *arachno*-$SCH_2B_7H_9$ (a $B_7C_2H_{13}$ analogue).[22] A low yield of $B_7C_2H_{11}Se$ was produced by reaction of $B_7C_2H_{13}$ with polyselenide ion in aqueous base and subsequent acidification of the mixture.[23] The nido derivative $B_9H_9SeCN(CH_3)_3$ was prepared by reaction of $B_9H_{11}CN(CH_3)_3$ with the polyselenide ion.[24] The thia- and selenacarboranes reported previously were each obtained in low yield. The synthetic route described in this paper gives for the first time thia- and selenacarboranes in sufficiently high yields so that futher chemical studies of this type of molecule can be made and such studies are under way at present.

Acknowledgment. This work was supported in part by a departmental instrument grant for the 360-MHz NMR instrument from the National Science Foundation.

Registry No. I, 87639-05-2; II, 87639-06-3; III, 87616-12-4; IV, 87616-13-5; V, 87639-07-4; VI, 87616-15-7; VII, 87639-08-5; VIII, 87616-16-8; IX, 87616-17-9; $B_9H_{11}S$, 12447-77-7; $CsB_9H_{12}S$, 11092-86-7; $B_9H_{11}Se$, 72985-65-0; $(CH_3)_4[B_9H_{12}Se]$, 73116-65-1; *tert*-butyl isocyanide, 7188-38-7; iodine, 7553-56-2; cyclohexyl isocyanide, 931-53-3; sodium cyanide, 143-33-9; trimethylsilyl bromide, 2857-97-8.

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Acid Hydrolysis of Organonitriles Coordinated to Ruthenium(III)

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Previous reports have demonstrated that the base hydrolysis of organonitriles is catalyzed by a factor of about 10^8 on coordination to pentaammineruthenium(III) and by about 10^6 on coordination to Co(III) and Rh(III). Although not previously reported, there is a base-independent hydrolysis path as well. The reported specific rates of base hydrolysis at 25 °C for acetonitrile and benzonitrile coordinated to Ru(III) are 2.2×10^2 and 2.0×10^3 M^{-1} s^{-1}, respectively. The rates of acid hydrolysis for acetonitrile, benzonitrile, and 1-adamantylcarbonitrile complexes at 25 °C are 1.2×10^{-5}, 3.4×10^{-5} and 7.2×10^{-6} s^{-1}, respectively. In acid aqueous solution, the hydrolysis reaction rate constant is independent of acid concentration and ionic strength, indicating that the attacking nucleophile is a water molecule. The activation parameters for the acid hydrolysis of pentaammineruthenium(III) complexes of acetonitrile, benzonitrile, and 1-adamantylcarbonitrile ($\Delta H^{\ddagger} = 20.0 \pm 0.2$ kcal mol^{-1}, $\Delta S^{\ddagger} = -13.9 \pm 0.5$ eu, $\Delta G^{\ddagger} = 24.1$ kcal mol^{-1}; $\Delta H^{\ddagger} = 19.0 \pm 0.2$ kcal/mol^{-1}, $\Delta S^{\ddagger} = -15.3 \pm 0.5$ eu, $\Delta G^{\ddagger} = 23.5$ kcal/mol^{-1}; $\Delta H^{\ddagger} = 21.2 \pm 0.3$ kcal/mol^{-1}, $\Delta S^{\ddagger} = -10.8 \pm 1.0$ eu, $\Delta G^{\ddagger} = 24.4$ kcal mol^{-1}, respectively) are very similar, which is consistent with postulation of a similar mechanism for each reaction.

Introduction

In 1973 Buckingham, Keene, and Sargeson reported that the hydrolysis of acetonitrile in basic aqueous solution is catalyzed by a factor of 2×10^6 on coordination to $Co(NH_3)_5^{3+}$.[1] More recently, Zanella and Ford reported that the effect of coordination to $Rh(NH_3)_5^{3+}$ was similar to that of $Co(NH_3)_5^{3+}$ and that $Ru(NH_3)_5^{3+}$ was an even more effective catalyst by 2 orders of magnitude.[2] In both cases, there was no evidence for a base-independent hydrolysis path. We have synthesized bimetallic complexes with Co(III) and Ru(III) ammines bound to nitrile groups for the study of intramolecular electron-transfer reactions.[3] When such complexes are dissolved in acidic aqueous solution, spectral changes consistent with hydrolysis of the nitrile group bound to Ru(III) occur slowly. To understand the nature of this reaction and to determine how well the reaction rate can be predicted for given conditions, we undertook the study of the acid hydrolysis of organonitriles bound to Ru(III) reported herein.

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Table I. Kinetic Results for the Acid Hydrolysis of Organonitrile Complexes of Ru(III) in 0.005 M Aqueous Trifluoromethanesulfonic Acid[a]

complex	temp, °C	rate const, s^{-1}
$Ru(NH_3)_5NCCH_3^{3+}$	25.0	$(1.24 \pm 0.02) \times 10^{-5}$
	37.0	$(4.85 \pm 0.22) \times 10^{-5}$
	50.0	$(1.83 \pm 0.13) \times 10^{-4}$
$Ru(NH_3)_5NCC_6H_5^{3+}$	25.0	$(3.39 \pm 0.05) \times 10^{-5}$
	37.0	$(1.24 \pm 0.01) \times 10^{-4}$
	50.0	$(4.39 \pm 0.08) \times 10^{-4}$
$Ru(NH_3)_5NC(adamantane)^{3+}$	25.0	$(7.20 \pm 0.15) \times 10^{-6}$
	37.0	$(2.90 \pm 0.02) \times 10^{-5}$
	50.0	$(1.25 \pm 0.03) \times 10^{-4}$

[a] The limits indicated are the average deviations for 2–10 individual runs. For each run, the correlation coefficient for the fit for first-order dependence was better than 0.99 and the variance for absorbance readings of individual points was 0.002 absorbance units or less.

Experimental Section

The pentaammineruthenium(III) complexes were synthesized by the method previously reported for the 1-adamantylcarbonitrile complex.[4] In this procedure, (trifluoromethanesulfonato)pentaammineruthenium(III) trifluoromethanesulfonate is combined with an excess of the ligand in sulfolane with $(CF_3SO_2)_2O$ added to remove trace amounts of water. The reaction mixture is heated for about 15 min at 60 °C and cooled to ambient temperature. The product is precipitated by adding an equal volume of acetone and diethyl ether in an amount about 20 times that of the original volume. The product is quickly dissolved in a minimum amount of water, the resultant solution is filtered, and the product is recovered by precipitation with 5 M $H_3O^+CF_3SO_3^-$. The acetonitrile and benzonitrile complexes made in this manner have the appropriate spectral properties.[2]

The $H_3O^+CF_3SO_3^-$ was obtained by careful addition of a stoichiometric amount of water to anhydrous HCF_3SO_3 (3M, "Fluorad") and vacuum distillation twice. The $LiCF_3SO_3$ was obtained by the addition of dilute $H_3O^+CF_3SO_3^-$ to recrystallized $LiCO_3$.

Data were obtained with a Beckman DU-8 spectrophotometer with a Peltier thermoregulated cuvette holder and were treated with statistics programs available on the PROPHET computing system.[5]

Results and Discussion

The results of the kinetics of acid-hydrolysis reactions of pentaammineruthenium(III) complexes of acetonitrile, benzonitrile, and 1-adamantylcarbonitrile are given in Table I. All of these reactions show excellent first-order behavior (typical correlation coefficients of 0.999 and standard deviations of individual data points of <0.002 absorbance units). From the data previously presented for the base-hydrolysis paths of the acetonitrile and benzonitrile complexes of 2.2×10^2 and 2.0×10^3 M^{-1} s^{-1} at 25 °C, respectively,[2] no competition from the base-hydrolysis path is expected at pH values below 4. Since the lowest concentration of $[OH^-]$ used in previous studies was 10^{-6} M, it is not unreasonable that the acid-hydrolysis path for Ru(III) organonitrile complexes was not previously detected. The rate law for the hydrolysis of the Ru(III) organonitrile complexes is therefore

$$-d \ln [Ru(NH_3)_5NCR^{3+}]/dt = k_0 + k_1[OH^-]$$

where k_0 is the rate constant for the acid-hydrolysis path and k_1 the specific rate constant for the base-hydrolysis path.

The product of the base-hydrolysis reaction for a Ru(III), Rh(III), and Co(III) organonitrile complex has been demonstrated to be the corresponding coordinated amide complex.[2,1] The spectral UV–visible changes are pronounced and are characteristic of the conversion of the nitrile to the amide.[1,2] We find the same spectral changes for the acetonitrile and benzonitrile complexes as previously reported,[2] and the changes for the 1-adamantylcarbonitrile complex are very similar to that for the acetonitrile complex (Table II). To demonstrate that the reaction in acidic solution does not involve hydroxide ion as the attacking nucleophile, the effect of changes in acid concentration and ionic strength were investigated, as shown in Table III. The independence of the rate constant on acid concentration and ionic strength indicate the attack of an uncharged nucleophile, the water molecule. In the experiment at an acid concentration of 0.100 M, the spectrum of the product indicates a substantial concentration of the protonated amide complex, consistent with the pK_a of 2.00 previously reported by Zanella and Ford.[2] The rate constant to produce this product is the same as that for the unprotonated coordinated amide (produced at 1.0×10^{-3} and 5.0×10^{-3} M acid) as expected for protonation as a rapid step subsequent to hydrolysis. The reaction sequence for organonitrile hydrolysis at pH >> pK_a is

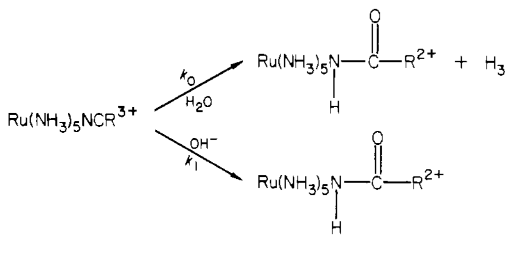

Table II. Absorption Maxima and Extinction Coefficients for Amido Complexes of Pentaammineruthenium(III)

complex	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
$Ru(NH_3)_5(CH_3CONH)^{2+}$	383	3.5×10^3 [a]
	249	2.3×10^3 [a]
$Ru(NH_3)_5(CH_3CONH_2)^{3+}$	322	1.6×10^3 [a]
$Ru(NH_3)_5(C_6H_5CONH)^{2+}$	393	4.0×10^3 [a]
	314	3.7×10^3 [a]
$Ru(NH_3)_5(C_{10}H_{15}CONH)^{2+}$	388	3.6×10^3
	276	2.4×10^3

[a] Reference 2.

Table III. Kinetic Results for Acid Hydrolysis of $[Ru(NH_3)_5NCCH_3^{3+}]$ at Various Acid Concentrations and Ionic Strengths[a]

acid concn, M	rate const, s^{-1}	I, M	rate const, s^{-1}
1.0×10^{-3}	4.15×10^{-5}	0.0267	4.23×10^{-5}
5.0×10^{-3}	4.13×10^{-5}	0.0517	4.22×10^{-5}
100×10^{-3}	4.31×10^{-5}	0.103	4.22×10^{-5}

[a] At 37.0 °C. The ionic strength was varied with $LiCF_3SO_3$ and $[H^+] = 0.0050$ M with $H_3O^+CF_3SO_3^-$.

Table IV. Activation Parameters for the Acid Hydrolysis of Pentaammineruthenium(III) Organonitrile Complexes of Acetonitrile, Benzonitrile, and 1-Adamantylcarbonitrile[a]

complex	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, eu	$\Delta G^\ddagger$, kcal mol^{-1} (298 °C)
$Ru(NH_3)_5NCCH_3^{3+}$	20.0 ± 0.2	-13.9 ± 0.5	24.1
$Ru(NH_3)_5NCC_6H_5^{3+}$	19.0 ± 0.2	-15.3 ± 0.5	23.5
$Ru(NH_3)_5NCC_{10}H_{15}$	21.2 ± 0.3	-10.8 ± 1.0	24.4

[a] Activation parameters were obtained by the Eyring formalism using two values at each temperature. These points were obtained by addition and subtraction of average deviation of all values obtained at that temperature to the average value for all runs at that temperature.

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(5) The PROPHET computing system is a multisite network, the CBIS system of the NIH, which includes a wide array of statistics and structural simulation software. We are grateful to the NIH for the installation of the Hunter College Facility.

The activation parameters for the acid-hydrolysis path of the Ru(III) organonitrile complexes shown in Table IV are very similar to one another. There may be a compensation of more favorable ΔH^* values by less favorable ΔS^* values, as expected for reactions with the same mechanism, especially in cases where bond formation is important, but experiments over a larger temperature range would be necessary to substantiate this effect.

The relative rates for the benzonitrile, acetonitrile, and 1-adamantylcarbonitrile reactions (3.4×10^{-5}, 1.2×10^{-5} and 7.2×10^{-6} s^{-1}) are consistent with the ideas previously advanced for the base-hydrolysis reactions,[1,2] i.e., that the metal atom catalyzes hydrolysis by withdrawing electron density from the nitrile group when the nucleophile attacks and that substituents on the nitrile group can retard the reaction by donating electron density. As previously found for the base-hydrolysis reactions, the acid hydrolysis of organonitriles coordinated to Co(III) and Ru(II) appears to be much slower.

With regard to electron-transfer reactions of organonitrile complexes of Ru(III) and Co(III), the hydrolysis of the Ru(III) nitrile moiety can be predicted quite readily and the extent can be ascertained readily from the visible absorption spectrum of the complex. The half-lives of such reactions at 25 °C are sufficiently long to allow sample preparation without an unacceptable loss of concentration of the desired nitrile complex. Upon reduction of Ru(III) to Ru(II), hydrolysis is greatly for retarded (by a factor of at least 10^6 for the base-hydrolysis path and undetected for the acid-hydrolysis path), posing no significant limitation to the study of reactions of Ru(II)-Co(III) bimetallic complexes.

Acknowledgment. We gratefully acknowledge support by the National Institutes of Health (Grants GM 27179 and RR 08176), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the PSC-BHE Grants Program of the City University of New York.

Registry No. $Ru(NH_3)_5NCCH_3^{3+}$, 44819-54-7; $Ru(NH_3)_5NCC_6H_5^{3+}$, 46343-59-3; $Ru(NH_3)_5NCR^{3+}$ (R = adamantane), 87518-03-4; $Ru(NH_3)_5(C_{10}H_{15}CONH)^{2+}$, 87518-04-5; Ru, 7440-18-8; acetonitrile, 75-05-8; benzonitrile, 100-47-0; 1-adamantylcarbonitrile, 23074-42-2.

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Proton-Promoted Chelate-Ring Opening in Copper(II) Polyamine Complexes

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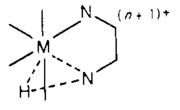
Kinetic studies of the acid aquation of Cu(II) complexes of a structurally related series of polyamines have been made as a function of $[H_3O^+]$, temperature, and presence of a general acid for catalysis of the chelate-ring opening reaction. The polyamines studied include en, dien, trien, tren, dach, and [9]aneN$_3$. Activation parameters are reported for a rate-limiting reorganization step; the rates of all ligands in the series for the dissociation of the CuL^{2+} complex saturate in $[H_3O^+]$ except the strained ligand dach. $Cu(dach)(H_2O)_4^{2+}$ dissociates with a strictly first-order law in $[H_3O^+]$. The mechanism for chelate-ring opening via a distorted intermediate, CuL^{*2+}, for ligands of this series is compared to the reported ligand dissociation reactions for analogous Ni(II) complexes where comparable data exist. It is concluded that the more rapidly dissociating Cu(II) complexes proceed to products predominantly via intermediates in which protonation of a partially ruptured Cu-N bond is assisted by H_3O^+ as an ion pair with an electrolyte anion. However with $Cu(tren)(H_2O)^{2+}$, two different intermediates are required to explain two different kinetically active paths that saturate in $[H_3O^+]$ at 3 s^{-1} (pH 3.0-5.0) and 500 s^{-1} ($[H_3O^+] > 0.050$ M). The path saturating at 3 s^{-1} has activation parameters like those of other straight-chain polyamines. This path is independent of counteranion, ClO_4^- or Cl^-. The one at 500 s^{-1} has an 8.3 kcal/mol lower activation enthalpy in Cl^- solution than for $Cu(en)(H_2O)_4^{2+}$ at 12.0 ± 1.8 kcal/mol (NO_3^- medium). The more rapidly dissociating intermediate is described as one in which an H_3O^+,X^- pair intercepts a partially ruptured Cu-N bond of $Cu(tren)(H_2O)^{2+}$ prior to the time for the rupturing ring to rotate out of the first coordination sphere of Cu(II). The rate of this path is counteranion dependent. Cl^- provides an additional lowering of the barrier by ca. 2.0 kcal/mol vs. ClO_4^-. The $Cu(tren)(H_2O)^{2+}$ dissociation in acetate buffers (pH 3.0-5.0) exhibits approximately the same general-acid acceleration as recently reported for $Ni(en)(H_2O)_4^{2+}$. The influence of increasing chain length or a modification of the CuL^{2+} structure that increases strain for the dissociation step is discussed for complexes of the above series.

Introduction

Dissociation of a chelate ligand, such as ethylenediamine, is much slower than the analogous loss of monodentate ligands of the same donor type (NH_3 for en) from a metal ion center. Acid can accelerate the dissociation of chelate rings by several orders of magnitude. Wilkins and co-workers observed the acid acceleration in their early mechanistic studies of the dissociation of $Ni(en)(H_2O)_4^{2+}$ and $Cu(en)(H_2O)_4^{2+}$.[1-6] Their conclusions have largely held up to the test of time for most of the labile-ion transition-metal systems that have been examined mechanistically.[7] Most of the mechanistic conclusions have been drawn from studies of Ni(II) complexes because the rates with Ni(II) are slower (albeit kinetically rapid) than with most other ions of interest of the first-row transition metal ions. The Ni(II) cases are therefore more amenable to kinetic methods.

Ahmed and Wilkins suggested in their earliest studies of chelate-ring openings with Ni(II) and Cu(II) complexes that H^+ might be involved in the direct attack of the shared electron pair between ligand and metal ion center.[6]



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