Oxygen versus Nitrogen Bonding of Carboxamides to Pentaammineruthenium(II/III)

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Reversible linkage isomerizations are identified for monodentate carboxamides on pentaammineruthenium(II) and -(III). The equilibrium between O-bonded and N-bonded amides is pH and oxidation-state dependent. When both O- and N-bound amides are neutral uncharged ligands (pH < 7, Ru(II); pH < 2, Ru(III)), the O-bonded isomers are thermodynamically more stable for both oxidation states. They are, however, inherently unstable, solvolyzing in coordinating solvents with loss of amide ligand (Ru(II), $t_{1/2}$ < 1 s; Ru(III), $t_{1/2}$ < 2 h; 25 °C, H_2O) or isomerizing to deprotonated N-bonded isomers in nonacidic solutions. Cyclovoltammetry in base produces reversible $Ru^{III/II}$ couples for the substitution-inert deprotonated form, $[(NH_3)_5RuNHCOR]^{2+/+}$, which protonates for Ru(II) in acidic and neutral solutions ($pK_a \sim 7$) and isomerizes to the O-bonded amide. Following oxidation to Ru(III), isomerization of the O-bonded amides ($pK_a \geq 10$) back to the N-bonded amides ($pK_a \leq 2$) is driven by selective deprotonation to $[(NH_3)_5Ru^{III}NHCOR]^{2+}$. In water (pH 6.2, 25 °C) the O-bonded amides on Ru(III) isomerize (∼50%) in parallel with aquation (R = H, $k_{obs} = k_{ON} + k_{aq} = 8.1 \times 10^{-4}$ s^{-1}), and both processes are catalyzed by base and Ru(II). In strong acid, Ru(III) complexes of uncharged N-bound amides are thermodynamically unstable but kinetically robust ($t_{1/2}$ > 6 days, 18 °C, H_2O) as the stable iminol tautomer, $[(NH_3)_5RuNH{=}C(OH)R]^{3+}$. This has to tautomerize to $[(NH_3)_5RuNH_2COR]^{3+}$ before N- to O-isomerization which is much slower than subsequent solvolysis of the O-bonded isomer and hence undetectable in coordinating solvents. The substitution lability of O-bonded amides in coordinating solvents, tautomerization of N-bonded amides on Ru^{III}, and catalysis by Ru^{II} and base complicate measurements of the rates for linkage isomerizations.

Introduction

Studies of linkage isomers[1] can provide important information about metal-ligand interactions, relative ligand affinities, the "hard" or "soft" character of metals in different oxidation states, and "intramolecular" or "inner sphere" reaction mechanisms. Carboxylic acid amides coordinate metals through oxygen[2,3] or nitrogen,[3−5] but there are few examples where pairs of linkage isomers have been found. Both linkage isomers are characterized for N- or O-bonded monodentate amides on $(NH_3)_5Co^{III}$ [6,7] and $dienPt^{II}$,[8] glycinamide chelated to $(NH_3)_4M$ (M = Co(III),[9] Ru(III)[10]) or monodentate on $(NH_3)_5Co(III)$,[11] and *N*′-ethylglycinamide and GlyGly on $(NH_3)_4Ru^{III}$.[10] Although few linkage isomers have been reversibly interconverted,[7b,8,12] factors that control their isomerizations are becoming better understood.

Facile linkage isomerizations have been observed on substitution-inert pentaammineruthenium(III) for glycinate[13] and ethylglycinate[14] (N- to O-); Me_2SO (S- to O-);[15] adenine (ring nitrogen to exocyclic carbon);[16] 7-methylhypoxanthine (N- to N-);[17] urea (N- to O-, O- to N-);[12] and acrylamide (alkene to N-).[18] By contrast, direct isomerization was not observed for $(NH_3)_4Ru^{III}$ chelates of glycinamide or derivatives. However N- to O-rearrangements were catalyzed by Ru(II), enabling determination of relative stabilities of chelated (N,O)- and (N,N′)- bonded forms on Ru(III).[10] The (N,O)-bonded form was always favored when the ligand was neutral.

On the other hand there is no evidence for N- to O-isomerizations of monodentate amides on Ru(III),[4] even though such (albeit slow) rearrangements are known for $(NH_3)_5Co^{III}$.[6b−d]

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To date, all isolated (amide)pentaammineruthenium(III) complexes have been (deprotonated) N-bonded amides.[4] However, the solid state structure[19] of an acidified complex (R = Me) has now been established as $[(NH_3)_5RuNH{=}C(OH)Me]^{2+}$. The failure to detect its rearrangement in acidic water may be either (i) that the N-isomer containing the neutral amide ligand is thermodynamically more stable, but this is contrary to findings[10] for chelating amides on $(NH_3)_4Ru$(III) and no special (N,O) stabilization has been found for chelation on for example Co(III); or (ii) that the O-bonded form of the neutral amide is thermodynamically stable as in the chelates, but N- to O-isomerization is extremely slow and possibly undetectable because the O-isomer may aquate faster than it is formed. The following work identifies properties of ruthenium-bonded amides, clarifies issues of isomer stability and reactivity, and demonstrates that (ii) is indeed the case.

Experimental Section

Chemicals and Reagents. $[(NH_3)_5RuOC(R)NMe_2]_2(S_2O_6)_3$ (R = H, Me),[12] $[(NH_3)_5RuNHCONH_2](PF_6)_2$,[12] $[(NH_3)_5RuOC(NH_2)_2](PF_6)_3$,[12] $[(NH_3)_5RuCl]Cl_2$,[20] and $[(NH_3)_5RuOSO_2CF_3](CF_3SO_3)_2$,[11,21] were prepared as described.

(a) $[(NH_3)_5RuNHCOMe](CF_3SO_3)_2$ was synthesized by dissolving $[(NH_3)_5Ru\ OSO_2CF_3](CF_3SO_3)_2$ (100 mg) in melted acetamide (5 mL, 90−95 °C). No base was needed to deprotonate acetamide, as it decomposes slightly on melting (pH > 8; $NH_{3(g)}$ was detected). After 10 min, the solution was poured into diethyl ether or $CHCl_3$ (250 mL) and washed by decantation (ether) and the yellow residue was dried *in vacuo* over P_2O_5 (Anal. Calcd: C, 8.86; H, 3.51; N, 15.50. Found: C, 8.96; H, 3.33; N, 14.74), recrystallized from warm water/NH_4PF_6 (Anal. Calcd for PF_6^- salt: C, 4.49; H, 3.56; N, 15.73; P, 11.61. Found: C, 4.38; H, 3.32; N, 15.50; P, 11.57), and gave reported spectral features (1.0 M $LiClO_4$,1.0 M $HClO_4$).[4a]

(b) $[(NH_3)_5RuNH{=}C(OH)Me(CF_3SO_3)_3{\cdot}H_2O$ was obtained as colorless crystals by evaporating a solution of $[(NH_3)_5RuNHCOMe](PF_6)_2$ in aqueous CF_3SO_3H. Crystals were washed with diethyl ether alone; alcohol deprotonates this acidic complex ($pK_a \approx 2.0$).[4a] Anal. Calcd: C, 8.45; H, 3.10; N, 11.83; S, 13.52; P, nil. Found: C, 8.20; H, 3.03; N, 11.39; S, 13.59; P, <0.02. Electronic spectrum (1.0 M CF_3SO_3H; λ, nm (ϵ, $M^{-1}\ cm^{-1}$)): 217 (2.36×10^3), 238 (2.43×10^3), 322 (1.55×10^3), ≈375 (0.38×10^3).

(c) $[(NH_3)_5RuNHCOCONH_2]^{2+}$ was prepared in situ by overnight aerial oxidation of the Ru(II) nitrile, $[(NH_3)_5RuNCCONH_2](PF_6)_2$, in aqueous 0.1 M CF_3SO_3H at 20 °C. Nitriles bound to Ru(III) hydrate to the corresponding amide complexes, a rapid process when the nitrile is activated by an adjacent electron-withdrawing group,[4bc,22] the carbonyl group in this case. The hydrolyzed solution gave a similar spectrum, two broad peaks ($\lambda = 385$ nm, $\epsilon = 1.5 \times 10^3\ M^{-1}\ cm^{-1}$; $\lambda = 313$ nm, $\epsilon = 2.1 \times 10^3\ M^{-1}\ cm^{-1}$) and a shoulder at 260 nm, to that[4b] for $[(NH_3)_5RuNHCOCOOC_2H_5]^{2+}$.

(d) $[(NH_3)_5RuNCCONH_2](PF_6)_2$ was obtained from $[(NH_3)_5RuNH_2CH_2CONH_2]\ (PF_6)_2$[23] by electrochemical oxidation (4 equiv, 0.05 M $NaHCO_3$ buffer, pH 9.3, +0.17V vs SCE) under Ar using a Pt basket working electrode. The nitrile complex was precipitated by adding NH_4PF_6 or $NaPF_6$. The product spectrum ($\lambda = 381$ nm, $\epsilon = 5.7 \times 10^3\ M^{-1}\ cm^{-1}$; $\lambda = 250$ nm, $\epsilon = 1.5 \times 10^4\ M^{-1}\ cm^{-1}$) was similar to that[4b] for $[(NH_3)_5)RuNCCO_2Et]^{2+}$. Anal. Calcd for $[(NH_3)_5RuNCCONH_2](PF_6)_2{\cdot}{}^1/_2NH_4PF_6$: C, 3.82; H, 3.03; N, 16.73. Found: C, 3.82; H, 2.97; N, 16.82. Calcd for $[(NH_3)_5RuNCCONH_2](PF_6)_2{\cdot}{}^1/_2NaPF_6$: C, 3.81; H, 2.70; N, 15.56. Found: C, 3.72; H, 2.65; N, 15.76. Cyclovoltammetry (0.1 M CF_3CO_2H, scan rate 10 V s^{-1}) gave only one reversible couple ($E_{1/2} \sim 0.05$ V vs NHE), a broad peak superimposing reduction peaks for $[(NH_3)_5RuNHCO\ CONH_2]^{2+}$ and the product, $[(NH_3)_5RuOH_2]^{3+}$, of aquation on Ru(II) (vide infra).

(e) $[(NH_3)_5RuOCHNH_2](BF_4)_3$ was obtained by stirring (20 min, 20 °C) a solution of $[(NH_3)_5RuOSO_2CF_3](CF_3SO_3)_2$ (0.5 g) in formamide (10 mL) with CF_3SO_3H (0.5 mL). The mixture was diluted with absolute ethanol (10 mL) and diethyl ether (200 mL), the supernatant was decanted, and the residue was washed several times with ether, dissolved in ice water, and rapidly filtered into ice-cold aqueous 40% HBF_4. Crystals were collected, washed copiously (diethyl ether), and recrystallized (ice-cold aqueous HBF_4). While stable in the solid state for several months, it eventually turns red. Isolated yield = 71%. Anal. Calcd: C, 2.44; H, 3.66; N, 17.09. Found: C, 2.38; H, 3.56; N, 16.60. The filtrate showed absorption maxima (222, 292, 340 (sh) nm) for the O-isomer.

(f) $[(NH_3)_5RuOC(Me)NH_2](BF_4)_3$ was similarly obtained from $[(NH_3)_5RuOSO_2CF_3]\ (CF_3SO_3)_2$ (0.5 g) and acetamide (1.0 g) in acetone (10 mL). Workup required only addition of diethyl ether, dissolution of the residue in strongly acidified ice-water, and rapid filtration into and recrystallization from cold (<0 °C) aqueous HBF_4. Yield = 60%. Elemental and spectrophotometric analyses indicated that $[(NH_3)_5RuOH_2]^{3+}$ (5−40%) was also present. Attempts to remove this by fractional crystallization (PF_6^-, $S_2O_6^{2-}$, NO_3^-, ClO_4^-, or $CF_3SO_3^-$ salts) were not successful.

Acetamide, formamide (Fluka, A. G., >99%), dimethylformamide (DMF) (Baker, 99.9%), dimethylacetamide (DMA) (Aldrich), acetone (Baker), and propylenecarbonate (Aldrich; over 3 Å molecular sieves) were used as received. Sulfolane (Aldrich) was distilled from KOH. KPF_6 (Alfa) was recrystallized from acetone. Deionized water was purified by a Barnstead Nanopure ultrafiltraion system. Visible/UV spectra were measured on a Beckman Acta MVII spectrophotometer, pH was measured with a calibrated[12] Brinkman Instruments pH-101 Metrohm digital pH meter, infrared spectra were recorded (KBr disks) on a Perkin-Elmer 621 instrument, and microanalyses were conducted by Stanford Microanalytical Laboratory.

Electrochemical Measurements. Cyclic voltammetry and electrolysis were performed with a PAR Model 173 potentiostat, Model 175 Universal Programmer System, Hewlett-Packard 7045A *X*−*Y* recorder, and Tektronix 5103N oscilloscope. In these experiments [Ru] ≈ 10^{-3} M, so dissociation of the acidic N-isomer was favorable except in strong acid. Also since acid/base proton exchange is much faster than the time scale of cyclic voltammetry (≈$10^3\ s^{-1}$), a single averaged Ru(III)/Ru(II) redox couple is observed for each acid/base pair of Ru(III) complexes, $[(NH_3)_5RuNHCOR]^{2+}/[(NH_3)_5RuNH{=}C(OH)R]^{3+}$, $[(NH_3)_5RuOC(NH_2)R]^{3+}/[(NH_3)_5RuOC(NH^-)R]^{2+}$, or $[(NH_3)_5RuOH_2]^{3+}/[(NH_3)_5RuOH]^{2+}$. Ar-saturated solutions (20 ± 1 °C) were used and [complexes] were 1−2 mM. For aqueous solutions a conventional two-compartment electrochemical cell was used with a saturated calomel reference electrode, isolated from the test solution by a glass frit, carbon paste working electrode, and Pt wire auxiliary electrode. Ionic strength was maintained at 0.1−0.2 M (CF_3CO_2H/CF_3CO_2Na or $HClO_4/LiClO_4$). Potentials were converted to the NHE scale by adding 0.24 V. For nonaqueous solutions, the electrochemical cell had one compartment with (Corning) Pt inlay (for $HCONH_2$, DMF), or hanging drop Hg, and Pt wire auxiliary electrodes. The reference electrode (for Pt, Ag//0.1 M $AgNO_3/CH_3CN$ (PAR); for Hg, SCE in acetone/0.1M KPF_6) was separated from the test solution by a Teflon tube containing electrolyte ($I = 0.1$ M (KPF_6)) and a Vycor tip. The $FeCp_2^{0/+}$ couple was used as a reference.

Kinetic Measurements. Rates were obtained by cyclic voltammetry and stopped-flow or conventional spectrophotometry. The stopped-flow system (Aminco-Morrow flow) was adapted to a Beckman DU spectrophotometer; absorbance was monitored on an oscilloscope (Tektronix D11). Rate constants (±3%) obtained from *A*, *t* data were evaluated by least-squares analyses and Guggenheim plots and checked graphically for linearity.

Results

Synthesis of N-Isomers. The N-bonded amide complexes of pentaammineruthenium(III) can be conveniently synthesized by the base-catalyzed hydration of the corresponding nitrile:[4a]

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$$[(NH_3)_5RuN{\equiv}CMe]^{3+} + OH^- \rightarrow [(NH_3)_5RuNHCOMe]^{2+}$$

Alternatively, the deprotonated amide complex $[(NH_3)_5Ru^{III}$-$NHCOMe]^{2+}$ ($\lambda_{max} = 383$ nm, $\epsilon = 3.46 \times 10^3$ M^{-1} cm^{-1}; 1.0 M $NaClO_4$)[4a] can be formed almost quantitatively in molten acetamide or in non-coordinating solvents containing acetamide and a non-coordinating base. In aqueous acid ($\geq$1 M CF_3SO_3H or $HClO_4$), $[(NH_3)_5RuNHCOMe]^{2+}$ undergoes protonation of acetamide, producing an absorption spectrum within 1 min that agrees with that reported ($\lambda_{max} = 322$ nm, $\epsilon = 1.55 \times 10^3$ M^{-1} cm^{-1}).[4a] This spectrum remained constant for 6 days (18 °C) and is attributed to $[(NH_3)_5RuNH{=}C(OH)Me]^{3+}$, which was isolated *vide infra* and characterized by elemental analyses and X-ray crystallography.[19]

The characteristic $\lambda_{max} = 322$ nM, attributed to charge transfer from a filled amide π orbital to a vacancy in a d_π orbital of Ru(III), is consistent with the *iminol* tautomer, rather than the *amide* form $[(NH_3)_5RuNH_2C(=O)Me]^{3+}$. A LMCT band for the latter requires a bonding electron to be excited, giving an absorption at higher energy as observed for $[Ru(NH_3)_6]^{3+}$ ($\lambda_{max} = 275$ nm, $\epsilon = 4.7 \times 10^2$ M^{-1} cm^{-1})[24] and $[(NH_3)_5RuNH_2$-$CH_2CO_2Et]^{3+}$ ($\lambda_{max} = 275$ nm, $\epsilon = 5.3 \times 10^2$ M^{-1} cm^{-1}).[14] The iminol tautomer has also been identified by NMR spectroscopy for N-bonded acetamide on Co(III)[6b-d] and Pt(II).[8a,c]

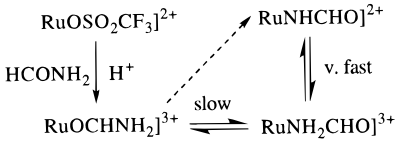
When colorless $[(NH_3)_5RuOSO_2CF_3](CF_3SO_3)_2$ was dissolved in formamide, the absorption maximum ($\lambda = 383$ nm, $\epsilon = (3.8 \pm 0.2) \times 10^3$ M^{-1} cm^{-1}) of the yellow solution was like those of other $[(NH_3)_5RuNHCOR]^{2+}$ ions[4,10,12] in water and markedly shifted (315 nm) upon acidifying. We conclude that in dilute formamide solutions the acidic Ru(III) complex had dissociated to $[(NH_3)_5RuNHCHO]^{2+}$. Its rate of formation (3.0×10^{-2} s^{-1}, 25 °C) was similar to the rate of aquation (9.3×10^{-2} s^{-1})[21] of the triflato precursor.

Synthesis of O-Bonded Isomers. After solvation (40 °C) of $[(NH_3)_5RuOSO_2CF_3](CF_3SO_3)_2$ in formamide, the solution was acidified with CF_3SO_3H (to 1 M) until no $\lambda_{max} = 383$ nm remained. The new spectrum, containing a prominent shoulder at 315 nm and a weak shoulder at $\approx$375 nm, is attributed to $[(NH_3)_5RuNHC(OH)H]^{3+}$. Over several hours (40 °C) the absorbance grew below, and diminished above, 300 nm until a new absorption maximum appeared as a shoulder at $\sim$292 nm. This process, N- to O-linkage isomerization, followed first-order kinetics ($k_{NO} = 3.98 \times 10^{-5}$ s^{-1}, 40 °C; $k_{NO} = 1.79 \times 10^{-4}$ s^{-1}, 60 °C). The isolated complex was identical to that obtained below.

By contrast when formamide was acidified (to >1 M CF_3-SO_3H) prior to dissolving $[(NH_3)_5RuOSO_2CF_3](CF_3SO_3)_2$, the resulting spectra showed relatively fast formation of an absorption maximum at $\sim$292 nm by a first-order reaction ($k_{obs} \sim 3.5 \times 10^{-4}$ s^{-1},$\sim$18 °C). This maximum is characteristic of $[(NH_3)_5RuOCHNH_2]^{3+}$, which was isolated. No maxima characteristic of acid (315 nm) or base (383 nm) forms of the N-bonded formamide isomer were detected. Also when this acidic solution was basified (NEt_3 or Tris), the 292 nm peak shifted to a more intense $\lambda_{max} = 383$ nm at a rate ($t_{1/2} \sim$ min) that was distinctly slower than diffusion controlled deprotonation. Acidification instantly shifted the LMCT band to 315 nm, but realkalinization restored the λ_{max} at 383 nm.

The results are consistent with formation of $[(NH_3)_5$-$RuOCHNH_2]^{3+}$ in acidic formamide and isomerization to the deprotonated N-bonded formamide complex, $[(NH_3)_5RuNH$-$CHO]^{2+}$, in basic solutions (Scheme 1).

Scheme 1



The absorption spectrum attributed to $[(NH_3)_5RuOCHNH_2]^{3+}$ was similar for complexes isolated from reactions of $[(NH_3)_5$-$RuOSO_2CF_3](CF_3SO_3)_2$ with dimethylformamide and dimethylacetamide.[12] Those products $[(NH_3)_5RuOCRN(CH_3)_2]^{3+}$ (R = H, Me)[12] were formed without acid, there being no competition from the sterically hindered amide nitrogen for coordination to Ru(III). They also did not isomerize at pH 6. Formamide itself protonates on the carbonyl oxygen,[26] not the nitrogen atom, but this did not restrict O-bonding to the metal. Therefore the role of acid, in changing the course of reaction between formamide and the triflato complex, was to prevent dissociation and stabilization of any produced N-isomer. The significant resonance stabilization in the deprotonated N-bonded amide ($[Ru^{III}NH{=}CRO^-]^{2+} \leftrightarrow [Ru^{III}NHCR{=}O]^{2+}$) is reflected in the high acidity ($pK_a = 2.1$)[4a] of the conjugate acid $[Ru^{III}NH{=}C$-$(OH)R]^{3+}$.

We deduce that (i) the O-bonded isomer is formed first in acidic formamide; (ii) the isomer equilibrium is pH dependent owing to the high acidity of the N-isomer relative to O-isomer, favoring the inert (deprotonated) N-bonded form in weakly acidic to basic media but the O-bonded form in strong acid where the amide ligand is uncharged (pH $\leq$ 2); and (iii) for the neutral formamide ligand the N-bonded isomer is kinetically robust but thermodynamically the less stable isomer.

Spectrophotometric Studies of O-Bonded Amides on Ru-(III). The electronic absorption spectra of $[(NH_3)_5Ru$-$(OCRNH_2)]^{3+}$ (R = H; $\lambda = 292$ nm, $\epsilon = 1.2 \times 10^3$ M^{-1} cm^{-1}, and $\lambda = 222$ nm, $\epsilon = 2.1 \times 10^3$ M^{-1} cm^{-1}; R = CH_3; λ_{max} = 280, 340, and 212 nm) in aqueous 1.0 M CF_3SO_3H change slowly with time, producing the spectrum for $[(NH_3)_5RuOH_2]^{3+}$. No N-isomers were formed in the reaction since alkalinizing product solutions gave only the spectrum of $[(NH_3)_5RuOH]^{2+}$. No LMCT bands of ca. 380 nm characteristic of $[(NH_3)_5$-$RuNHCOR]^{2+}$ were present. The aquation reaction obeys first-order kinetics with rate constants (R = H, $k_{obs} = 3.8 \times 10^{-4}$ s^{-1}; R = CH_3, $k_{obs} = 8.2 \times 10^{-4}$ s^{-1} ($k_{obs} = 10.81 \times 10^{-4}$ s^{-1}, 0.1 M CF_3SO_3H); 25.0 °C) similar to those for aquation of $[(NH_3)_5RuOCRNMe_2]^{3+}$ (R = H, Me) (Table 1).[12] Temperature dependence and activation entropies and enthalpies for aquation of O-bonded amide complexes are reported in Table 1.

When isolated $[(NH_3)_5RuOCHNH_2](BF_4)_3$ was dissolved in aqueous 0.1 M Tris, the solution turned yellow within seconds (λ_{max} = 379, 298, and 252 nm; ratios, 1.22:1.09:1.00). The absorption at 298 nm is assigned to $[(NH_3)_5RuOH]^{2+}$ since it shifted to 265 nm upon titration with H^+. Consistent with its higher basicity relative to $[(NH_3)_5RuNHCHO]^{2+}$, the other absorptions were unaltered and the yellow color persisted. More acid instantly bleached the solution, producing a new spectrum (λ_{max} = 235, $\approx$265, 315, and $\approx$375 (sh nm; ratio, 1.0:4.3:6.8:10.2). Adding base restored the former spectrum, showing that the less basic ion was $[(NH_3)_5RuNHCHO]^{2+}$ (protonating < pH 2 forming $[(NH_3)_5RuNH{=}C(OH)H]^{3+}$) and verifying observations on $[(NH_3)_5RuOSO_2CF_3]^{2+}$ in acidic formamide.

(24) Krentzien, H. J. *Ph.D. dissertation*, Stanford University, **1976**.
(25) Eliades, T.; Harris, R. O.; Reinsalu, P. *Can. J. Chem.* **1969**, *47*, 3823.
(26) Zabicky, J., Ed. *The Chemistry of Amides*; Wiley Interscience: New York, 1970; Chapter 1, p 1.
(27) The redox potential for the protonated (N,N′) chelate can be estimated as $\approx$+0.05V vs NHE by using Figure 3 of ref 10 and the estimate of −1 for the pK_a of the (N,N′) chelate of Ru(III).[10]

Table 1. Temperature Dependence of Observed First-Order Rate Constants ($\times 10^4$ s^{-1}) for Aquation of $[(NH_3)_5Ru(O\text{-Amide})]^{3+}$ in Aqueous 1.0 M CF_3SO_3H

	temp (°C)	amide			
		$OCHNH_2$	$OC(Me)NH_2$	DMF[d]	DMA[d]
	25.0	3.8	8.1	0.99	1.51
	30.0	6.4	14.3	1.75	2.45
	35.0	11.4	23.3	2.96	4.61
	40.0	18.3	49.1	5.29	8.63
	45.0			9.43	14.60
$\Delta H^{\ddagger}$ [a]		82.2 ± 1.7	88.9 ± 5.3[c]	85.8 ± 1.5	88.8 ± 2.4
$\Delta S^{\ddagger}$ [b]		-35.1 ± 5.4	-6.4 ± 17.2[c]	-33.9 ± 4.8	-20.6 ± 7.9

[a] kJ mol^{-1}, derived from least squares fit of Eyring plot ($\ln(k_{obs}/T)$ vs $1/T$). [b] J mol^{-1} deg^{-1}, refer to *a*. [c] High uncertainties due to large standard deviations in 40 °C data (four runs, $k = (49 \pm 4) \times 10^{-4}$ s^{-1}). [d] DMF = *N*,*N*-dimethylformamide. DMA = *N*,*N*-dimethylacetamide.

More evidence for O- to N-linkage isomerization was provided in water by $[(NH_3)_5RuOCHNH_2]^{3+}$ at pH 6.2 (0.1 M NaMes; $\mu = 1.0$ M, $NaCF_3SO_3$). The final absorptions were as observed in aqueous Tris, except that they were produced more slowly (Table 2) and consistent with a rate law: $k_{obs} = k_s + k_{OH}[OH^-]$, where k_s is tabulated in Table 2. No attempt was made to determine k_{OH}.

Similar properties were observed for the O-bonded acetamide complex. In aqueous 0.1 M Tris, absorption maxima were detected within seconds at 381, 295, and 248 nm and no further changes occurred over 30 min. The process was slower ($t_{1/2} \sim$ 10 min) at pH 6.2 (0.1 M NaMes). Acidifying to pH $\approx$ 0 bleached the solution, producing new maxima of $\approx$375 (sh), 322, $\approx$265 (sh), 239, and 216 nm characteristic of $[(NH_3)_5RuNH{=}C(OH)CH_3]^{3+}$ except for that at ca. 265 nm, assigned to $[(NH_3)_5RuOH_2]^{3+}$. Adding base regenerated the yellow color and absorption spectrum observed in aqueous Tris.

Table 2 reports first-order rate constants for the reactions of $[(NH_3)_5RuOCHNH_2]^{3+}$ in aqueous 0.1 M NaMes buffer (pH = 6.2, $\mu = 1.0$ M ($NaCF_3SO_3$)) and in nonaqueous solvents. The data are sums of O- to N-linkage isomerization and solvolysis of O-bonded isomer, and approximate product distributions assessed from composite visible spectra are recorded in Table 2. Both O- to N-isomerization and solvolysis were base-catalyzed. In all of these coordinating solvents detectable linkage isomerization ensued (10−90%), so the observed rate constants are upper limits for linkage isomerization. Assuming that there was no catalysis in these solvents, we conclude from Table 2 that O- to N-isomerization competed less effectively with solvolysis in dipolar aprotic coordinating solvents (DMF, 10%; dimethyl sulfoxide (DMSO), 12%; DMA, 24%) than in water (59%). There was not a strong solvent dependence for the rate of isomerization, k_{ON} (Table 2).

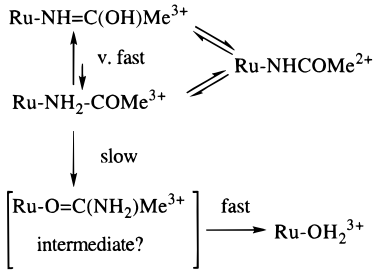
The O-bonded formamide complex evidently decomposes via two parallel processes, hydrolysis and linkage isomerization, and is governed by the equation

$$k_{obs} = k_1 + k_2[OH^-]; \quad k_1 = k_s + k_{ON} \text{ and } k_2 = k_{OH} + k_{ON'}$$

where k_s and k_{OH} are the spontaneous and base-catalyzed rates for aquation of the O-bonded isomer, while k_{ON} and $k_{ON'}$ are the spontaneous and base-catalyzed rates for O- to N-linkage isomerization. We have not attempted to determine the base-catalyzed rate constants (k_{OH}, $k_{ON'}$).

The effect of pH on k_{obs} was briefly monitored in water to better characterize the role of the acid/base equilibrium on O- to N-linkage isomerization. The following rate law was obtained below pH 7:

Scheme 2



$$k_{ON}(obs) = k_{ON}.\{(K_a + [H^+])/[H^+]\}$$

This is consistent with a pH-dependent equilibrium constant as observed previously for analogous cobalt systems:[7b]

$$K_{NO}(obs) = [\text{O-bonded isomer}]/[\text{N-isomer}] = K_{NO}.[H^+]/(K_a + [H^+])$$

For formamide, K_{NO} is estimated at $\geq 10^2$ since no N-isomer is detected in highly acidic formamide solutions. An estimate for K_a is 10^{-1} for the N-bonded formamide isomer (*vide infra*). Thus, the observed equilibrium varies with pH such that at pH 1, $K_{NO}(obs) = 50$; at pH 4, $K_{NO}(obs) = 10^{-1}$; at pH 6, $K_{NO}(obs) = 10^{-3}$; and at pH 10, $K_{NO}(obs) = 10^{-7}$. This is consistent with qualitative observations that only O-bonded isomer is observed at pH 0 and only deprotonated N-isomer is detected at pH 6.

Spectrophotometric Studies of N-Bonded Amides on Ru(III). Acidic aqueous solutions of $[(NH_3)_5RuNHCOMe]^{2+}$ were also examined for evidence of N- to O-isomerization. The absorption spectrum of $[(NH_3)_5RuNHCOMe]^{2+}$ in 1 M CF_3SO_3H was unchanged from 1 min to 6 days (18 °C) after dissolution. After 15 days some aquation had occurred, the $\lambda_{max} \sim 322$ nm decreasing with a shoulder ~ 268 nm corresponding to λ_{max} for $[(NH_3)_5RuOH_2]^{3+}$.[25] On raising the pH (>7, Tris), the spectrum consisted of absorptions expected for a mixture of $[(NH_3)_5RuOH]^{2+}$ ($\lambda_{max} = 295$ nm) and $[(NH_3)_5RuNHCOMe]^{2+}$ ($\lambda = 381$ and 248 nm). Using extinction coefficients for acid and base forms of the N-bonded acetamide complex, as well as $[(NH_3)_5RuOH]^{2+}$, we calculated that 20% conversion to $[(NH_3)_5RuOH_2]^{3+}$ had occurred after 11 days ($\approx$18 °C; Scheme 2).

Aquation rates for O-bonded amide complexes of Ru(III) (Table 1) suggest that if N- to O-isomerization was occurring in water, the O-bonded isomers would be undetectable because of ensuing rapid aquation. An upper limit on the rate of N- to O-linkage isomerization in water, if it occurred, was obtained from the rate of absorbance decrease at 257 nm for $[(NH_3)_5RuNH{=}C(OH)CH_3]^{3+}$ at 60 °C. This wavelength was identified as an *isosbestic* wavelength for aquation of the O-bonded isomer. The data obeyed first-order kinetics, yielding $k_{obs} = 7.06 \times 10^{-5}$ s^{-1} ($t_{1/2} \approx 3$ h, 60 °C; 1.0 M CF_3SO_3H). This may comprise contributions from solvolysis of the N-isomer, parallel N- to O-linkage isomerization, and hydrolysis of free amide released from the metal. The final spectrum was that expected for 100% $[(NH_3)_5RuOH_2]^{3+}$. We conclude that N- to O-isomerization did not occur or was undetectable (Scheme 2). To avoid the complication of aquation in water, we monitored absorbance changes for the N-bonded isomers in nonaqueous solvents.

In sulfolane, a poor coordinating solvent, similar reactivity was sought for the acetamide analogue. At 60 °C with introduced CF_3SO_3H (1 M), $[(NH_3)_5RuNH{=}C(OH)Me]^{3+}$ was consumed in a first-order reaction at a rate ($k_{obs} = 4.12 \times 10^{-4}$ s^{-1}) comparable in magnitude to the analogous formamide-N complex in acidified formamide at 60 °C; *vide supra*. It was

Table 2. First-Order Rate Constants[a] and Product Distributions[b] for the Reaction of $[(NH_3)_5RuOCHNH_2]^{3+}$

temp (°C)	solvent	10^5k_{obs} (s^{-1})	$[Ru(solvent)]^{3+}$ [b] (%)	$[RuNHCHO]^{2+}$ [b] (%)	10^5k_{ON} [b] (s^{-1})
25	$OS(CH_3)_2$	6.4	88	12	0.77
	$OP(OCH_3)_3$	29	58	42	12.2
	H_2O, pH 6.2	81	41	59	47.8
	$OCHN(CH_3)_2$	87	90	10	8.7
	$OC(CH_3)N(CH_3)_2$	8.8	76	24	2.1
40	sulfolane	3.5	0	100	3.5
30	H_2O, pH 6.2	205			
35	H_2O, pH 6.2	387			
40	H_2O, pH 6.2	683			

[a] Measured for absorbance increases at 383 nm. [b] Percentages determined from composite absorption spectra of products and known concentration of reactant. $k_{ON} = k_{obs} \times$ (% N-bonded isomer).

Table 3. Redox Potentials of Carboxamide Complexes of Ruthenium(III/II) Ammines[a]

couple	$E_{1/2}$ (V)	solvent
$[(NH_3)_5RuNHCOCH_3]^{2+/+}$	−0.305	H_2O (pH 10.5)
	−1.13	DMF
	−1.17[b]	propylenecarbonate
	−1.09[b]	acetone
	−0.99[b]	sulfolane
$[(NH_3)_5RuNH{=}C(OH)CH_3]^{3+/2+}$	+0.02	H_2O (pH 1)
	−0.80	DMF
	−0.32[b]	sulfolane/H^+
$[(NH_3)_5RuOC(CH_3)NH_2]^{3+/2+}$	−0.77[b]	acetone
	−0.45[b]	sulfolane/H^+
$[(NH_3)_5RuNHCHO]^{2+/+}$	−0.94	$HCONH_2/N(CH_3)_3$
	−1.13[b]	acetone−0.96[b] sulfolane
$[(NH_3)_5RuNH{=}C(OH)H]^{3+/2+}$	−0.33[b]	sulfolane/H^+
$[(NH_3)_5RuOCHNH_2]^{3+/2+}$	−0.54	$HCONH_2$
	−0.75[b]	acetone
	−0.45[b]	sulfolane
$[(NH_3)_5RuNHCONH_2]^{2+/+}$	−0.98[b]	sulfolane
$[(NH_3)_5RuNHC(OH)NH_2]^{3+/2+}$	−0.33[b]	sulfolane/H^+
$[(NH_3)_5RuOC(NH_2)_2]^{3+/2+}$	−0.45[b]	sulfolane/H^+
$[(NH_3)_4Ru(NH{=}COCH_2NH_2)]^{2+/+}$	−0.265[c]	H_2O (pH 6.8)
$[(NH_3)_4Ru(NH{=}C(OH)CH_2NH_2)]^{3+/2+}$	+0.05[d]	H_2O
$[(NH_3)_4Ru(OC(NH_2)CH_2NH_2)]^{3+/2+}$	+0.14[c]	H_2O (pH 1)
$[(NH_3)_5RuOC(NH_2)CONH_2]^{3+/2+}$	+0.19	H_2O (pH 1)
$[(NH_3)_5RuOCHN(CH_3)_2]^{3+/2+}$	−0.60	DMF
$[(NH_3)_5RuOCOCH_2CH(CH_3)O]^{3+/2+}$	−0.78[b]	propylenecarbonate
$[(NH_3)_5RuOC(CH_3)N(CH_3)_2]^{3+/2+}$	−0.15[b]	DMA

[a] Reference electrodes: NHE for aqueous solutions; Ag//0.1 M $AgNO_3/CH_3CN$ for $HCONH_2$ and $OCHN(CH_3)_2$; SCE (0.1 M KPF_6 in acetone) for acetone, sulfolane, propylenecarbonate and DMA. [b] Relative to $FeCp_2/FeCp_2+$ couple assigned 0.0 V. [c] See ref 10. [d] Calculated from ref 10.

not clear whether the O-bonded isomer was formed because of solvent absorption, but since sulfolane is a notably poor coordinating ligand (*e.g.*, $[(NH_3)_5CoNH{=}C(OH)CH_3]^{3+}$ and $[(NH_3)_5CoOC(CH_3)NH_2]^{3+}$ do not solvolyze in this solvent),[6b] it seems reasonable to attribute the absorbance changes to N- to O-linkage isomerization of the bound acetamide, particularly as the spectrum for $[(NH_3)_5RuNHCOCH_3]^{2+}$ was regenerated on slightly alkalinizing but only after several minutes, consistent with the measurable rate of O- to N-isomerization.

We did not pursue more detailed kinetics in these unusual highly acidic solvent mixtures, resorting instead to electrochemistry for more evidence of isomerizations. We could not equilibrate N- and O-isomers of Ru(III) in water using a catalyst (*e.g.*, Ru(II)[10]) because this leads to loss of the monodentate amide ligand.[4b,c,23]

Cyclovoltammetry in Coordinating Solvents. Table 3 summarizes formal reduction potentials for complexes measured in this study.

(a) Water. At pH 10.5 (0.1 M $LiClO_4$ + NaOH), $[(NH_3)_5RuNHCOMe]^{2+}$ showed a reversible cyclovoltammogram ($E_{1/2} = -0.305$ V vs NHE). However, cyclic voltammetry in aqueous 0.1 M CF_3CO_2H at 0.5 V s^{-1} was irreversible. Appearing on the first scan was the reduction wave of the N-isomer, but only oxidation of $[(NH_3)_5RuOH_2]^{2+}$ appeared in the oxidation phase. On repetitive scans, only waves of the aqua species were observed. At scan rate 20 V s^{-1}, the oxidation wave was a superposition of peaks for the aqua and *N*-acetamide complexes. The reduction potential was estimated as +0.02 V vs NHE. which is closer to that of the protonated glycinamide-*N*,*N*′ (+0.05 V vs NHE)[22] than N,O- (+0.14 V) chelate[10] and is therefore consistent with the proposed N-coordination of neutral acetamide on pentaammineruthenium-(III). Using the potential of $[(NH_3)_5RuNH{=}C(OH)Me]^{3+}$ and known pK_a (2.0),[4a] an estimate was made for the pK_a (~7.4) of the Ru(II) analogue. This is 3 orders of magnitude less acidic than the glycinamide-*N*,*N*′ chelate on $(NH_3)_4Ru^{II}$, a difference also observed for the Ru(III) analogues.[10] Thus, no N- to O-isomerization was detected in acidic water.

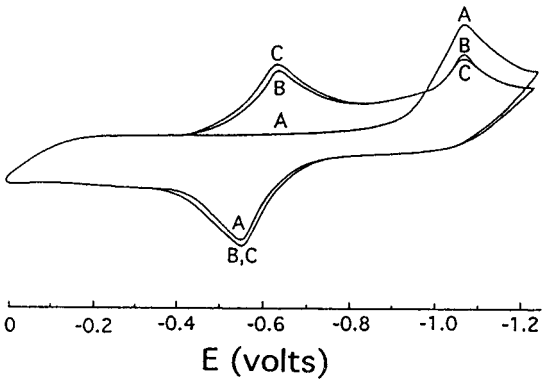


Figure 1. Cyclic voltammograms of $[(NH_3)_5RuNHCOMe]^{2+}$ in 0.1 M KPF_6 in DMF (0.027 M CF_3SO_3H neutralized by NMe_3; scan rate = 0.1 V s^{-1}, potential in volts vs Ag//0.1 M $AgNO_3$/MeCN): A, first scan; B, second scan; C, fifth scan.

(b) Dimethylformamide. $[(NH_3)_5RuNHCOCH_3](CF_3SO_3)_2$ showed a reversible couple (−1.13 V vs Ag//0.1 M $AgNO_3/CH_3CN$) with 80 mV separation between peaks. Thus, the deprotonated N-bound form persists for both Ru^{II} and Ru^{III} without substitution by DMF. Upon adding CF_3SO_3H (3−27 mM), cyclovoltammograms showed two very broad widely-separated peaks centered at −0.8 V. The separation was strongly dependent on $[H^+]$ (270 mV, 3 mM $[H^+]$; 625 mV, 27 mM $[H^+]$). When NEt_3 was added to neutralize the acid, peaks appeared in the first reduction wave at −1.075 V and the oxidation wave at −0.56 V (Figure 1A). On repetitive scans another reduction peak appeared at −0.64 V (Figure 1B, C). For a fresh solution, reversing at −0.8 V showed no peaks from 0 to −0.8 V.

These results indicate that, for the neutral ligand, the N-isomer of Ru(II) transforms to the O-bonded isomer or $[Ru(NH_3)_5$-

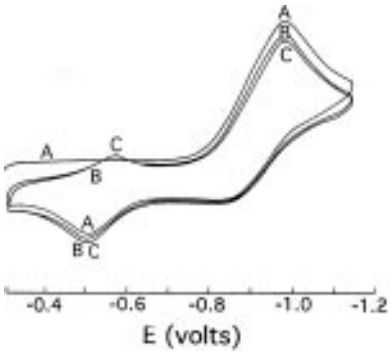


Figure 2. Cyclic voltammograms of $[(NH_3)_5RuNHCHO]^{2+}$ in 0.1 M KPF_6 in $HCONH_2$ (scan rate = 0.5 V s^{-1}; potential in volts vs Ag//0.1 M $AgNO_3$/MeCN): A, first scan; B, second scan; C, third scan.

(solvent)]$^{2+}$. The former is true for the chelated form of the neutral glycinamide ligand.[10] For acetamide, although the N-isomer of Ru(III) ($pK_a = 2.1$) is deprotonated, the more basic Ru(II) analogue can adopt protons from solution ($pK_a = 7$, protonated form). Following protonation of the *N*-amide on Ru(II), rearrangement to the O-bonded isomer and/or substitution of acetamide by DMF could ensue. On the basis of the substitution lability of Ru(II) and the statistical factor ([DMF] versus [acetamide]), the ultimate formation of the (dimethylformamide-*O*) complex, rather than (acetamide-*O*) complex, of $(NH_3)_5Ru^{III}$ is favored. This was supported by dissolving $[(NH_3)_5RuOSO_2CF_3](CF_3SO_3)_2$ in DMF and finding reversible cyclovoltammetry with $E_{1/2}$ (−0.60 V) identical to that observed for the acetamide complex on repetitive scanning.

(c) Propylenecarbonate. $[(NH_3)_5RuNHCOMe]^{2+}$ showed initially a reversible ($\Delta E = 80$ mV) couple ($E_{1/2} = -1.06$ V vs −0.11 V for $FeCp_2^{0/+}$; scan rate = 500 mV s^{-1}). However, the oxidation peak was only half the intensity of the reduction peak, and a second oxidation peak was observed at −0.64 V. On successive scans another reduction peak appeared at −0.72 V at the expense of the peak at −1.10 V, which shifted to −1.05 V. When $[(NH_3)_5RuOSO_2CF_3](CF_3SO_3)_2$ was dissolved in propylenecarbonate, reduction peaks appeared at −0.41 V (transient) and −0.675 V and oxidation peaks at −0.12 V and −0.61 V. The dominant reversible couple near −0.65 V is attributed to $[(NH_3)_5Ru(propylenecarbonate)]^{3+/2+}$, suggesting that reduction of $[(NH_3)_5RuNHCOMe]^{2+}$ leads to solvolysis presumably after proton abstraction from solution, giving $[(NH_3)_5Ru^{II}NH_2COMe]^{2+}$. Similarly, $[(NH_3)_5RuNH{=}C(OH)Me]^{3+}$ showed a reduction peak at −1.05 V due to acid dissociation, but produced a reversible couple at −0.67 V for $[(NH_3)_5Ru(propylenecarbonate)]^{3+/2+}$.

(d) Formamide. To avoid the ligand loss observed above in coordinating solvents (H_2O, DMF, propylenecarbonate), the amide ligand was used as solvent. In formamide, standard test compounds (ferrocene, $Ru(NH_3)_6^{3+}$) gave reversible cyclovoltammograms (ΔE = 60−80 mV). Following solvation of $[(NH_3)_5RuOSO_2CF_3](CF_3SO_3)_2$ in formamide containing NEt_3, a reversible couple ($E_{1/2} = -0.94$ V, scan rate = 0.1−1.0 V s^{-1}) was detected for $[(NH_3)_5RuNHCHO]^{2+/+}$. In the absence of base a peak was observed at −0.98 V for reduction of $[(NH_3)_5RuNHCHO]^{2+}$ (Figure 2, scan A), but no corresponding oxidation peak was observed. Instead a new pair of peaks (scans B, C) appeared at $E_{1/2} = -0.54$ V assigned to $[(NH_3)_5RuOCHNH_2]^{3+/2+}$. Thus, on Ru(II) the deprotonated N-bonded amide can protonate, but $[(NH_3)_5RuNH_2CHO]^{2+}$ is unstable, undergoing linkage isomerization to $[(NH_3)_5RuOCHNH_2]^{2+}$. At this potential the reduction peak is smaller than the oxidation peak at scan rate = 0.5 V s^{-1}, nearly disappears at 0.1 V s^{-1}, is almost as intense as the oxidation peak at 2 V s^{-1}, but is very broad at higher scan rates. It is significant that for DMF on Ru^{III} the amplitudes of oxidation and reduction waves were equal (Figure 1). The Ru^{III} ion undergoing reduction at −0.57 V is estimated to decay (O- to N-isomerization) at a much faster rate (≈1 s^{-1}) than that measured above from UV−vis spectra and indicates catalysis by Ru^{II}.

In Figure 2 the oxidation peak for $[(NH_3)_5Ru^{II}OCHNH_2]^{2+}$ is less prominent than the reduction peak of $[(NH_3)_5Ru^{III}NHCHO]^{2+}$. There were no other oxidation peaks, so the Ru(II) complex must rapidly form a species with a $Ru^{III/II}$ couple outside the potential range. This was confirmed by reducing $[(NH_3)_5RuNHCHO](CF_3SO_3)_2$ in formamide with Zn/Hg under Ar. After 1.5 h, 90% of the absorption characteristic of Ru(III) had disappeared and <10% was restored following aerial oxidation. The reduced solution gave an infrared stretching frequency (1929 cm^{-1}) characteristic[28] of a bound CO ligand in $[(NH_3)_5RuCO]^{2+}$.

As solutions in Figure 2 became very acidic (0.1−2 M H^+), the reduction peak for N-isomer shifted to more positive potential (consistent with partial protonation) and diminished in intensity. Commensurate with these changes, the redox couple for the O-bonded isomer (*ca.* −0.55 V) began to dominate the voltammogram and the reduction peak for $[(NH_3)_5RuOCHNH_2]^{3+}$ became more prominent. At ≈2 M $[H^+]$, the reduction peak for residual N-isomer merged with and broadened the latter peak. Similarly when $[(NH_3)_5RuOSO_2CF_3](CF_3SO_3)_2$ was dissolved directly in preacidified formamide (>1 M CF_3CO_2H), a single redox couple characteristic of the O-bonded isomer was observed on initial and repeated scans. Upon making the solution basic, a single couple at −0.92 V, identical to that for $[(NH_3)_5RuNHCHO]^{2+/+}$, was observed. Reacidification reproduced the results above. $[(NH_3)_5RuOCRNH_2]^{3+}$ (R = H, Me) were later isolated and gave the same electrochemical results.

Cyclovoltammetry in Weakly Coordinating Solvents. (a) Acetone. Reversible couples were observed in acetone, a poor ligand, at −0.89 V (R = Me) and −0.93 V (R = H) for $[(NH_3)_5RuNHCOR]^{2+/+}$ versus $FeCp_2^{0/+}$, +0.2 V. Solutions of $[(NH_3)_5RuNH{=}C(OH)Me](CF_3SO_3)_3$ in acetone quickly turned yellow (dissociation) and also showed a reversible couple at −0.89 V. Continuous scanning produced other small peaks at ≈ −0.6 V in the reduction wave and at −0.15 V in the oxidation wave, but no matching peaks were detected at scan rates of 10−500 mV s^{-1}. For $[(NH_3)_5RuOC(R)NH_2](BF_4)_3$ complexes, peaks were observed in the reduction wave (500 mV s^{-1}) at −0.58 and −0.83 V (R = H) and −0.60 V (R = Me) and in the oxidation wave at −0.10 and −0.78 V (R = H) and ≈−0.1 and −0.53 V (R = Me). Peaks near −0.5 to −0.6 V are assigned to the O-bonded isomers (Table 3). In both cases the solutions gradually turn yellow over a few minutes on standing, commensurate with formation of reversible couples at −0.81 (R = H) and −0.89 V (R = Me). This is consistent with O- to N-linkage isomerization on Ru(III). The species oxidizing ca. −0.1 V grows with time but was not identified. It did however also form for $[(NH_3)_5RuOSO_2CF_3](CF_3SO_3)_2$ alone in acetone.

(b) Sulfolane. $[(NH_3)_5RuNHCOR]^{2+}$ and $[(NH_3)_5RuNH{=}C(OH)R]^{3+}$ ions both showed reversible couples (40 °C; $FeCp_2^{0/+}$, +0.30 V) at −0.69 (R = Me) and −0.66 V (R = H), suggesting

(28) The intense infrared stretching frequency for coordinated CO in $[(NH_3)_5RuCO]^{2+}$ is anion dependent (Cl^-, 1925 cm^{-1}; Br^-, 1932 cm^{-1}; I^-, 1943 cm^{-1}); see Allen, A. D.; Eliades, T.; Harris, R. O.; Reinsalu, P. *Can. J. Chem.* **1969**, *47*, 1605.

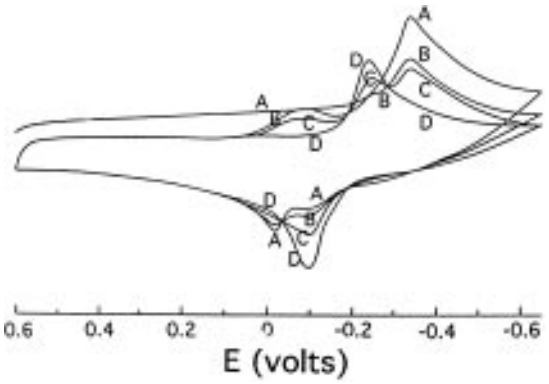


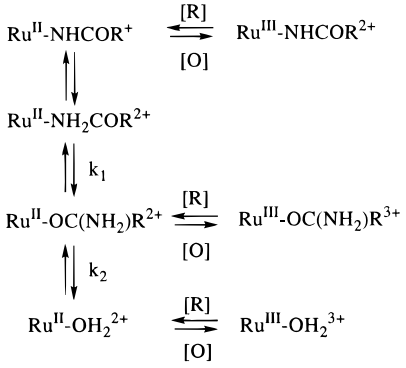
Figure 3. Cyclic voltammograms of $[(NH_3)_5RuNHCOCONH_2]^{2+}$ in aqueous 0.1 M CF_3CO_2H (scan rate = 20 V s^{-1}; potential in volts vs SCE): A, first scan; B, third scan; C, fifth scan; D, twentieth scan.

dissociation[29] of the acid form. Adding CF_3SO_3H produced a single reversible couple at ≈−0.02 V (500 mV s^{-1}) for $[(NH_3)_5RuNH{=}C(OH)R]^{3+/2+}$ but a different reduction peak (−0.18 V) at 10 mV s^{-1}. After aging this solution for ≈12 h (40 °C), the cyclovoltammogram showed a distinct peak at −0.20 V in the reduction wave and one at +0.03V in the oxidation wave. For $[(NH_3)_5RuOC(R)NH_2](BF_4)_3$ in acidic sulfolane (40 °C, 500 mV s^{-1}) reduction peaks were also seen at −0.18 (R = CH_3) and −0.19 V (R = H) and oxidation peaks at +0.03 V (R = Me, H). This reversible couple (60 mV separation at 200 mV s^{-1}) diminished when no acid was used after standing (40 °C, 1 h) and the solution developed a yellow color (O- to N-isomerization) with formation of a couple at −0.66 V. Reacidification regenerated the previous results. In contrast $[(NH_3)_5RuOSO_2CF_3]$ $(CF_3SO_3)_2$ shows a reversible couple (ΔE = 80 mV) at 0.0 V in sulfolane.

All of these results indicate the thermodynamic stability of the O-bonded isomer of Ru(III) when complexes contain the neutral or uncharged amide ligand (strongly acidic media), but the N-isomer becomes thermodynamically more stable in weakly acidic to basic media by virtue of its greater acidity (≥7 orders of magnitude over O-bonded isomer). Selective deprotonation drives the equilibrium toward the substitution inert ion, $[(NH_3)_5RuNHCOR]^{2+}$, a conclusion similar to that drawn for urea complexes of penatammineruthenium(III).[12] Coordinating solvents (water, DMF, propylenecarbonate) complicate the observations because the O-bonded isomer is solvolyzed too fast to be detected, but in noncoordinated solvents (acetone, sulfolane, formamide) the isomer equilibria could be ascertained without this complication. Both base and Ru(II) catalyze O- to N-isomerization.

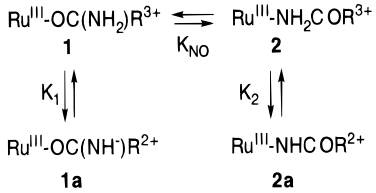
N- to O-Isomerization of $[(NH_3)_5Ru^{II}NH_2COCONH_2]^{2+}$. Figure 3 shows the cyclovoltammogram of $[(NH_3)_5RuNHCOCONH_2]^{2+}$ in 0.1 M aqueous CF_3CO_2H. The first scan (A, Figure 3) at 20 V s^{-1} shows one reduction peak and two peaks in the oxidation wave. In the second scan (B, Figure 3), the original peak in the reduction wave is diminished and two new peaks appear at more positive potentials. There are still two peaks in the oxidation wave. After many more repetitive scans, one peak is left in the reduction wave and one in the oxidation wave centered at a potential of +0.07 V vs NHE. This potential corresponds to the $[(NH_3)_5RuOH_2]^{3+/2+}$ couple.[30,31] We infer that the transient pair of peaks centered at +0.19 V vs NHE belong to the $[(NH_3)_5RuOC(NH_2)CONH_2]^{3+/2+}$ couple. The single most negative peak, which was the only peak in the first oxidation wave, is for reduction of $[(NH_3)_5RuNHCOCONH_2]^{2+}$. There is no matching peak in the oxidation wave because the N-bonded form of Ru(II) protonates and rearranges rapidly to the O-bonded isomer which then aquates (Scheme 3). The rate of linkage isomerization to the O-bonded isomer after reduction was too great to measure under the conditions ($k_1 > 1 \times 10^2$ s^{-1}). The rate of aquation (k_2) of this O-bonded isomer can, however, be estimated at ∼2 s^{-1}.

Scheme 3



Discussion

Both O- and N-bonded amide complexes of pentaammineruthenium(III) have been isolated and characterized. The O-bonded amide complexes have not previously been observed in studies of N-bonded amide complexes of pentaammineruthenium(III). The reason for this is that they are unstable. The amide is readily substituted by coordinating solvents (*e.g.*, H_2O, DMF, and DMSO) in acidic media ($t_{1/2}$ < 2 h, 25 °C) and rearranges to the deprotonated N-bonded form in basic or neutral solutions. Paradoxically the O-bonded amides are thermodynamically more stable than their N-bonded amide linkage isomers, as indicated in formamide, acetone, and sulfolane. This comparison can, however, only fairly be made when the amide is being considered as a neutral or uncharged ligand. This is only true in strongly acidic solutions because the N-bonded form is very acidic (pK_a < 2.5),[4a] much more so than the O-bonded form (pK_a(estd) ≥ 10).[12] Reasons for the differing acidities of the linkage isomers ($[(NH_3)_5RuNH{=}C(OH)R]^{3+}$, R = Me, pK_a = 2.0;[4a] R = H, $pK_{a(estd)} \approx 1$; $[(NH_3)_5RuOCRNH_2]^{3+}$, $pK_{a(estd)}$ > 9) have been discussed before.[12]



The different products from $[(NH_3)_5RuOSO_2CF_3]^{2+}$ in $HCONH_2$ vs $HCONH_2/H^+$ reflect the driving force for O- to N-linkage isomerization, namely deprotonation of the much more acidic N-isomer.

This driving force (**2** → **2a**) for O- to N-isomerization (**1** → **2**) is greatly reduced in acidic formamide, where dissociation of the much more acidic N-isomer (**2**) to the relatively inert deprotonated N-isomer (**2a**) is minimized and

(29) The p*K* of $HClO_4$, a strong acid in H_2O, is 2.7 in sulfolane (Benoit, R. L.; Buisson, C.; Choux, G. *Can. J. Chem.* **1970**, *48*, 2353); so the less acidic $[(NH_3)_5RuNH{=}C(OH)R]^{3+}$ ions should also be undissociated in sulfolane.

(30) Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689.

(31) Lim, H. S.; Barclay, D. J.; Anson, F. C. *Inorg. Chem.* **1972**, *11*, 1460.

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O- to N-rearrangement was consequently not observed. Consistent with this result, we were able to obtain $[(NH_3)_5Ru(OCRNH_2)]^{3+}$ in good yield from the triflato precursor in preacidified solutions of monodentate amides. These were free of N-isomer, since treatment with aqueous 1 M CF_3SO_3H gave 100% $[Ru(NH_3)_5(OH_2)]^{3+}$ within a few hours at 25 °C and subsequent alkalinization gave only $[Ru(NH_3)_5OH]^{2+}$. Neither $[(NH_3)_5RuNH{=}C(OH)R]^{3+}$ nor $[(NH_3)_5RuNHCOR]^{2+}$, both stable to aquation under these conditions and easily detected by their intense LMCT absorptions, were observed.

The O- to N-isomerization of amides on Ru(III) is faster than on Co(III); for the latter it has not been observed to compete with solvolysis in H_2O (pH 0−14) or nonaqueous solvents (except under basic conditions).[6] Conversely N- to O-rearrangement is faster for Co(III) and extraordinarily slow on Ru(III). Superficially these results seem to suggest that K_{eq} ($=k_{NO}/k_{ON}$), which is >100 for Co(III),[6c] is <1, and is perhaps <0.01 for Ru(III) with the N-isomer being thermodynamically more stable. However, the O- to N-rearrangement on Ru(III) has only been observed under conditions where the N-isomer can dissociate (pH ≥ 2). No such rearrangement was detected below pH 2, where formamide is a neutral ligand, yet in this circumstance decomposition of the N-isomer, albeit slow, has been witnessed. Therefore, on Ru(III), as on Co(III), the O-bonded amide complex is the thermodynamically more stable linkage isomer except under conditions where the acidic N-isomer deprotonates.

Data presented in Table 1 for aquation of Ru(III) complexes of O-bound amides indicate that the order of amides as leaving groups is $OC(CH_3)NH_2 > OCHNH_2 > OC(CH_3)N(CH_3)_2 > OCHN(CH_3)_2$. This greater tendency for the acetamides to be displaced during spontaneous aquation has also been noted on Co(III).[6b] Specific rates of aquation are virtually independent of $[H^+]$ in the range pH 0−6, although O- to N-isomerization contributes to observed (composite) rates at a pH above the pK_a (1−2) of the product N-isomer. The tabulated activation enthalpies and entropies are similar in magnitude to those observed for the analogous O-urea complex of $(NH_3)_5Ru(III)$[12] and are respectively *ca*. 20 kJ mol^{-1} less and 20−30 J mol^{-1} deg^{-1} more negative than for aquation of corresponding $(NH_3)_5Co^{III}$ complexes.[34] As on Co(III), the dimethylamide-*O* complexes of ruthenium(III) complexes have higher activation enthalpies than the unsubstituted (amide-*O*) congeners.

N- to O-linkage isomerization could not be detected for acetamide on $(NH_3)_5Ru(III)$ in aqueous acid. The problem is similar to that seen previously for Co(III).[6c] It may occur in water but is far slower than subsequent aquation of the intermediate O-bonded isomer and consequently cannot be observed. This is lent credence by the detection of very slow N- to O-rearrangement in the absence of competing solvolysis such as in weakly coordinating nonaqueous solvents (and for $[(NH_3)_5RuNH{=}C(OH)H]^{3+}$ in acidic formamide), as evidenced by monitoring aging acetone and sulfolane solutions using UV−vis absorption spectroscopy and cyclovoltammetry. In these cases no distinction could be made between inter- and intramolecular linkage isomerization because of possible dissociation and reassociation of the amide. However, if isomerization also occurs in the more strongly coordinating solvents, as it does for $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$ (R = H, alkyl, aryl, NH_2)[6b−d,7b] and $[(NH_3)_5RuNH{=}C(OH)NH_2]^{3+}$,[12] then it is clearly intramolecular since the ultimate product is solventopentaammineruthenium(III).

The anomalously slow isomerization of the N-bound amides on Ru(III), compared to other rearrangements of this kind which are orders of magnitude faster on Ru(III) and usually faster than on Co(III),[31] is consistent with the tautomeric equilibrium:

$$\underset{\text{amide}}{RuNH_2COR^{3+}} \rightleftarrows \underset{\text{iminol}}{RuNH{=}C(OH)R^{3+}} \qquad K_T$$

We have described this before for urea.[12] The iminol tautomer is predicted to be the less reactive tautomer, having to relocate a proton and rearrange via the amide tautomer to the O-bonded isomer. Results above suggest that K_T ([iminol]/[amide]) for $Ru^{III} \gg Co^{III}$, K_T having been estimated for Co(III) as ≥100.[6c] This is also true for urea (R = NH_2) except that K_T is much smaller for both metals ($K_T \approx 30$, Ru; $K_T < 0.01$, Co).[12] Based on these differences ($>100 \times >30/0.01 = >3 \times 10^5$), K_T can be estimated at $>10^5$ for amides on Ru(III). ^{1}H-NMR measurements previously established the site of protonation in $[(NH_3)_5MNHCOR]^{2+}$ (M = Co(III),[6,7] Rh(III)[8c]) as the carbonyl oxygen in the case of amides (R = H, alkyl, aryl) but the coordinated nitrogen for ureas (R = NH_2, $NHCH_3$). On the paramagnetic Ru(III), evidence for protonation of the carbonyl oxygen comes from the position of the LMCT absorption ($\lambda > 300$ nm)[12] and the X-ray crystal structure for $[(NH_3)_5RuNH{=}C(OH)Me]^{3+}$.[19]

Consistent with the three important equilibria

$$[(NH_3)_5RuOCHNH_2]^{2+} \rightleftarrows [(NH_3)_5RuNH{=}C(OH)H]^{3+} \qquad K_{ON}$$

$$[(NH_3)_5RuNH{=}C(OH)H]^{3+} \rightleftarrows [(NH_3)_5RuNH_2CONH_2]^{3+} \qquad K_T$$

$$[(NH_3)_5RuNH_2CONH_2]^{3+} \rightleftarrows [(NH_3)_5RuNHCHO]^{2+} + H^+ \qquad K_a$$

the isomer equilibrium K_{ON}(obs) was affected by the acid/base equilibrium of the N-isomer:

$$K_{ON}(\text{obs}) = [\text{N-isomer}]/[\text{O-bonded isomer}] = K_{ON}\cdot\{(K_a + [H^+])/[H^+]\}$$

In the Discussion and elsewhere we estimated that $K_{ON} \le 10^{-2}$. So using $K_a \sim 10^{-1}$ for $[(NH_3)_5RuNH{=}C(OH)H]^{3+}$, we calculate that K_{ON}(obs) would be $\sim 10^{-2}$ (favoring the O-bonded isomer) at pH 1 but $\sim 10^3$ (favoring N-isomer) at pH 6. This is consistent with what has been observed.

Electrochemical experiments on $[(NH_3)_5RuOSO_2CF_3](CF_3SO_3)_2$ and $[(NH_3)_5RuOCHNH_2]^{3+}$ in formamide confirmed rearrangement on Ru(III) of the O-bonded amide to $[(NH_3)_5RuNHCHO]^{2+}$. The isomerization likely goes via the protonated N-isomer followed by dissociation to the relatively inert deprotonated form. Similarly, when the O-bonded isomer was dissolved in other solvents, absorption increased in the 380 nm region, indicating formation of $[(NH_3)_5RuNHCHO]^{2+}$, by pseudo-first-order kinetics (Table 2, $k_{obs} = 10^{-6}-10^{-3}$ s^{-1}, 25 °C) and final spectra indicated mixtures of $[(NH_3)_5Ru(solvent)]^{3+}$ and $[(NH_3)_5RuNHCHO]^{2+}$ (Table 2). Therefore specific rates for O- to N-linkage isomerization are slightly lower than these observed rate constants (*e.g.*, $\le 10^{-4}$ s^{-1}). The disparity in rates between the electrochemical ($k \sim 1$ s^{-1}) and the spectrophotometric measurements ($k \sim 10^{-4}$ s^{-1}) can be explained by catalysis with Ru(II)[4c,23] generated during the electrochemistry. This is highlighted by experiments in which solutions of the O-bonded isomer in nonaqueous solvents were aged in the electrochemical cell. Periodic monitoring by cyclovoltammetry showed the *slow* emergence of the charac-

(34) Lawrance, G. A. *Inorg. Chem*. **1982**, *21*, 3687.

teristic reduction potential of $[(NH_3)_5RuNHCHO]^{2+/+}$ at rates consistent with those measured spectrophotometrically for O- to N-rearrangement of formamide on Ru(III) in the same solvents. The O- to N-linkage isomerization of acetamide on Ru(III) was also established by spectral and electrochemical experiments and occurred at a rate $<10^{-3}$ s^{-1} in all solvents.

O- to N-linkage isomerization on Ru(III) is slightly faster than competing spontaneous aquation and, as reported for the urea analogue,[12] must consequently be intramolecular in coordinating solvents—once displaced the amide does not reenter the first coordination sphere of Ru(III). On the otherhand N- to O-isomerization may be intermolecular on Ru(II). The O- to N-rearrangement on Ru(III) is many orders of magnitude faster than on Co(III).[7b] This difference is not due to base catalysis at pH 6 for Ru(III), although the process is certainly base-catalyzed on both metals at higher pH.

We have not measured the pK_a of $[(NH_3)_5RuOC(NH_2)R]^{3+}$ but, on the basis of our qualitative observations on base catalysis of the rate of O- to N-linkage isomerization, it is likely >9. For example $[(NH_3)_5RuOH_2]^{3+}$ and $[Ru(NH_3)_6]^{3+}$ are about 2 orders of magnitude more acidic than their Co(III) analogues (pK_a = 4.1[30] and 13.2,[32] vs 6.2,[31] and >15, respectively), so a p$K_a \geq 9$ might be expected for formamide-*O* on $(NH_3)_5Ru^{III}$. As O- to N-rearrangement on Ru(III) is not base-catalyzed at pH 6, another explanation is required for the facility of this isomerization. It may lie in the potential π-accepting πd^5 Ru(III) center having high affinity for a π-bound or anionic (π-donor ?) amide.

This has been sugested[12] for O- to N-isomerization of urea in $[(NH_3)_5RuOC(NH_2)_2]^{3+}$. For the latter ion the pK_a is predicted to be $\geq$11, and, since the O- to N-rearrangement was essentially independent of pH in the range 4−6, the influence of some unique property of Ru(III) on the rate of isomerization seems warranted. It is notable that neither spontaneous nor base-catalyzed O- to N-linkage isomerization of amides or urea on Ru(III) or Co(III) is more than a few times faster than the competing aquation. This may be merely a neighbouring effect, resulting from the proximity of the incoming and anchored donor atom, the amide N-terminus having a higher effective concentration relative to solvent at the metal and thus a higher probability of bonding to it.

The redox potentials of some of the complexes studied are compared in Table 3 with values for the tetraammineglycinamide chelates. In water, reduction potentials for acetamide complexes are only 0.03−0.04 V more negative than for tetraammine chelates with corresponding coordination of the amide, and thus support their asssignments. The value for the oxamide-*O* complex (0.05 V more positive than glycinamide-(*N*,*O*) chelate) is attributed to conjugation of the two carbonyls which stabilizes Ru(II) by facilitating MLCT.[35] In nonaqueous solvents isostructural complexes have similar potentials which serve to distinguish linkage isomers and acid/base forms.

Ru^{II} complexes of monodentate amides are quite labile, rapidly solvolyzing in H_2O, DMF, formamide, and propylenecarbonate. Analogous chelates of the bidentate amide, in which the ligand is anchored to Ru^{II} by the amine function, exist predominantly in the closed chelate form though ring opening is involved in their rapid linkage isomerizations.[10] As for tetraammine chelates of glycinamide and derivatives[10] selective deprotonation of the monodentate amide-*N* ligand, which is much less acidic on Ru^{II} than on Ru^{III} but still more acidic than the amide-*O* ligand on Ru(II/III), stabilizes $[(NH_3)_5Ru^{II}NHCOR]^+$ at pH > 7. In Ru^{II} complexes of monodentate or chelating amides the lability is high enough that isomer equilibria are established rapidly, the thermodynamically more stable O-bonded isomer prevailing in nonbasic media, prior to solvolysis. The thermodynamic stability of the O-bonded isomer is clearly evidenced in formamide (Figure 2), although solvolysis and isomerization were indistinguishable, and for oxamide even in water where the O-bonded isomer was detected because its solvolysis was slow (Figure 3).

The proposed decomposition to $[(NH_3)_5RuCO]^{2+}$ following reduction of (formamide)pentaammineruthenium(III) in formamide is analogous to reduction of $[(NH_3)_5OsOSO_2CF_3](CF_3SO_3)_2$ in formamides where both the infrared spectrum and oxidation potential characteristic of $[(NH_3)_5OsCO]^{2+}$ have been observed.[36] These processes were too fast to measure by our cyclic voltammetry but clearly require O- to C-migration, perhaps via a η^2-amide intermediate. Free amides cannot be decomposing, they are thermodynamically favored over CO and amine.

In conclusion we have identified facile O- to N- and N- to O-isomerization of monodentate amides on Ru(II) and Ru(III). The N- to O-rearrangement demonstrated on Ru(III) was very slow in acidic formamide and sulfolane and undetectable in coordinating solvents. The N-isomer is kinetically more labile than the O-bonded isomer of Ru(II), but the reverse is true on the "harder" Ru(III) because of proton migration from the *N*-amide yielding the kinetically more stable *N*-iminol tautomer.

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