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Linkage Isomerization of (Urea)pentaammineruthenium(III) and Inter- vs. Intramolecular Substitution on Ruthenium(III)

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The selective syntheses, characterization, and reactivities of pentaammineruthenium(III) complexes of N- and O-bound urea are described. Under conditions where the coordinated urea ligand is not deprotonated (pH <2), the N-bonded isomer rearranges intramolecularly to the thermodynamically more stable O-bonded isomer ($k_{obsd} = 9.1 \times 10^{-3}\ s^{-1}$, 1.0 M CF_3SO_3H, 25.0 °C) without detectable parallel reactions. The N-bound form is much more acidic than the O-bound form ($pK_a = 1.80 \pm 0.05$, 25 °C, μ = 1.0 M (KCl); vs. $pK_a > 10$), and the ratio of the former to the latter increases with pH according to the relation $(K_a + [H^+])/[H^+]$. In aqueous media when pH > pK_a, a facile intramolecular O- to N-linkage isomerization occurs ($k_{obsd} = 1.3 \times 10^{-3}\ s^{-1}$, pH 6.2, 0.1 M NaMes, μ = 1.0 M ($NaCF_3SO_3$), 25.0 °C) together with some parallel aquation of the O-bonded isomer (15%). The equilibrium governing the distribution of linkage isomers ($K_{eq} = k^{NO}/k_s^{ON} \sim 9$) hence favors O-coordination of the neutral urea molecule to Ru(III), but this preference is much less, as observed for Rh(III) ($K_{eq} \sim 1$), than that for the smaller first-row transition metals, Co(III) (~240) and Cr(III) (>10^5). In aqueous acid, $[(NH_3)_5RuOC(NH_2)_2]^{3+}$ aquates to give $[(NH_3)_5RuOH_2]^{3+}$ and urea. The rate ($k_s^{obsd} = 2.1 \times 10^{-4}\ s^{-1}$, 1.0 M CF_3SO_3H, 25.0 °C) for this intermolecular substitution is compared with corresponding data for other new $[(NH_3)_5Ru(O\text{-ligand})]^{3+}$ ions (O-ligand = $OCHNH_2$, $OCHN(CH_3)_2$, $OC(CH_3)N(CH_3)_2$, $OP(OCH_3)_3$, $OP(OC_2H_5)_3$) prepared in this work as well as their Co(III) analogues. Activation parameters for the acid hydrolysis and O- to N- and N- to O-linkage isomerizations of (urea)pentaammineruthenium(III) are also reported, and mechanistic details of the reactions are discussed.

Introduction

There is emerging a consistent trend in the substitution reactions of pentaamminemetal ions, $[(NH_3)_5M(L\text{-}L')]^{n+}$, where L-L′ is an ambidentate ligand.[1,2] Accompanying net M–L bond cleavage there is appreciable capture of the formerly uncoordinated terminus of the ambidentate ligand leading to $[(NH_3)_5M(L'\text{-}L)]^{n+}$. These linkage isomerization processes are invariably intramolecular in solution since L-L′ never leaves the metal ion, as adduced from either isotopic labeling experiments or the rate of rearrangement. The latter is often too large to be accounted for by solvolysis followed by recapture of L′-L. Further, there is increasing evidence for substantial bond making by the incoming nucleophile in the transition state.[1,2]

There are several examples of facile linkage isomerization on pentaammineruthenium involving ambidentate ligands such as imidazole,[3] N_2,[4] and $OS(CH_3)_2$[5] (on Ru(II)) and $OS(CH_3)_2$,[5] $NH_2CH_2CO_2^-$,[6] NH_2CH_2COR (R = NH_2,[7] OC_2H_5[8]), and $HCONH_2$[9] (on Ru(III)). Where comparisons can be made with Ru(III), linkage isomerizations of the respective Co(III) analogues either are very slow (formamide)[10] or are unknown (i.e. glycinate).[11] These apparent kinetic differences between Ru(III) and Co(III), and the recent observations[12,13] of facile linkage isomerization for N-coordinated ureas in $[(NH_3)_5CoNH_2CONRR']^{3+}$ ions, prompted the following work. It was anticipated that if isomerization ensued for $[(NH_3)_5RuNH_2CONH_2]^{3+}$, it would be orders of magnitude faster than for $[(NH_3)_5CoNH_2CONH_2]^{3+}$, an expectation not realized. The kinetic data presented herein also distinguish between intramolecular (linkage isomerization) and intermolecular (acid hydrolysis) ligand substitution on Ru(III) and contribute to ongoing studies[14] concerning the mechanism of such substitution.

In another context the reactivity of the metal-bound urea complexes is of interest since the Ni(II) enzyme[15] jack bean urease is believed to catalyze the hydrolysis of urea to NH_3 and CO_2 by direct coordination of urea to Ni(II). Other urea complexes of Co(III),[13] Rh(III),[16] and Cr(III)[17] have failed to model such catalysis, but the greater electron-withdrawing property of Ru(III), relative to that of these metal ions, might have been expected to enhance the prospect for metal-promoted hydrolysis of urea. This expectation has not been realized.

Experimental Section

Equipment and Materials. Microanalyses were performed by the Stanford and Berkeley Microanalytical Laboratories. UV and visible spectra were recorded for solutions in a 1.0-cm cell on a Beckman Acta MVII 5270 spectrophotometer, and infrared spectra were obtained on a Perkin-Elmer 621 instrument for samples pressed as KBr disks. Measurements of pH were made at 25 °C with a Brinkman Instruments 101 digital pH meter and a Metrohm AG9100 combination glass electrode, standardized with buffer solutions (phthalate buffer (VWR), pH 4.00; 0.1 N HCl, pH 1.08; 0.1 *m* $KH_3(C_2O_4)_2 \cdot 2H_2O$; pH 1.48) as described.[18] Formal reduction potentials were determined from cyclic voltammograms, recorded with a PAR Model 173 potentiostat, PAR Model 175 universal programmer and a Hewlett-Packard 7045A X-Y recorder in combination with a Tektronix 5103N oscilloscope, as reported previously.[9,19] Prior to use, Biogel-P2 (Bio-Rad) was cleaned with 0.05 M sodium phosphate buffer (pH 6.88) followed by water. SP-Sephadex-C25 (Pharmacia) cation-exchange resin was washed with dilute aqueous Br_2 or H_2O_2 and copious quantities of water.

Tetramethylene sulfone (sulfolane, Aldrich) was vacuum distilled from KOH. Trifluoromethanesulfonic acid (triflic acid, 3M Co.) and trifluoromethanesulfonic anhydride (Aldrich) were also vacuum distilled prior to use. Acetone was used as supplied (Baker Chemicals), but if it had been subjected to prolonged exposure to air, it was converted to the NaI adduct[20] and freshly distilled. All other solvents and ligands were

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reagent grade. $[Ru(NH_3)_6]Cl_3$ was purchased from Matthey-Bishop, converted to $[Ru(NH_3)_5Cl]Cl_2$ as described elsewhere,[21] recrystallized from 0.1 N HCl and transformed to $[Ru(NH_3)_5O_3SCF_3](CF_3SO_3)_2$ by some slight modifications of the reported synthesis.[22] Tris is tris(hydroxymethyl)aminomethane; Mes is 2-morpholinoethanesulfonic acid.

Syntheses. $[Ru(NH_3)_5O_3SCF_3](CF_3SO_3)_2$.[22] $[Ru(NH_3)_5Cl]Cl_2$ (0.6 g) was slowly added to stirring CF_3SO_3H (15 mL) in a 25-mL beaker. The yellow solution was heated (110 °C, 2.5 h) to effect substitution of chloride and its removal as HCl. The solution did not discolor during this time, and it was found unnecessary[22] to bubble N_2 through the solution, either to drive off HCl or to prevent formation of $[Ru(NH_3)_5OH_2]^{3+}$ through absorption of atmospheric moisture. The hot reaction mixture was cautiously poured into cold (<0 °C) diethyl ether (50 mL), yielding a white precipitate. The supernatant was decanted, but retained for recovery of the anion as $NaCF_3SO_3$,[23] and the product was stirred with more diethyl ether. This washing process was repeated (5×) to ensure complete removal of traces of CF_3SO_3H, and the product was briefly air-dried before storing in vacuo over P_2O_5. Yield: 1.25 g (96%).

$[Ru(NH_3)_5NHCONH_2](PF_6)_2$. $[Ru(NH_3)_5O_3SCF_3](CF_3SO_3)_2$ (0.5 g) was added to a stirred suspension of urea (1 g) in acetone (10 mL). After 20 min at 20 °C, absolute ethanol (1 mL) and diethyl ether (50 mL) were added to the olive green solution to produce a pale yellow-green oily precipitate. The product was dissolved in ice-cold water and filtered through a glass frit, and, after 20 min, solid NH_4PF_6 (~1 g) was added to the filtrate. Three crops of crystals were collected by vacuum filtration, fractionally recrystallized several times from H_2O/NH_4PF_6 solution containing Tris (pH 8.0), washed with absolute ethanol and diethyl ether, and air-dried. Yield: 72%. Anal. Calcd for $[Ru(NH_3)_5NHCONH_2](PF_6)_2\cdot H_2O$: C, 2.17; H, 3.62; N, 17.72; P, 11.21. Found: C, 2.28; H, 3.86; N, 17.40; P, 10.96. Alternatively, the reaction can be performed in sulfolane, in which urea is more soluble, and purification of $[Ru(NH_3)_5NHCONH_2]^{2+}$ can also be achieved by using a 30-cm column of Biogel P2 with water as eluent (the major impurity, $[Ru(NH_3)_5OH]^{2+}$, elutes marginally behind the N-bonded isomer).

$[Ru(NH_3)_5OC(NH_2)_2](PF_6)_3$. Urea (1 g) was dissolved in degassed (N_2) sulfolane (20 mL; 30 °C) containing triflic acid anhydride (0.1 mL), and N_2 was bubbled through the solution for 20 min. $[Ru(NH_3)_5O_3SCF_3](CF_3SO_3)_2$ (1 g) was then added, and the reaction mixture was stirred (15 min). The resultant deep green solution became lighter upon subsequent addition of CF_3SO_3H (0.3 mL), and the solution was stirred for 20 min (40 °C) more. An equal volume of acetone and excess diethyl ether caused deposition of an oily green residue. The clear supernatant was decanted, and the residue was saturated with ice-cold water containing CF_3SO_3H, filtered, and crystallized by addition of solid NH_4PF_6. The white crystalline product was twice recrystallized from ice-cold aqueous CF_3SO_3H containing a large excess of NH_4PF_6; two fractions were collected, washed with cold absolute ethanol and diethyl ether, and air-dried. Yield: ~62%. Anal. Calcd for $[Ru(NH_3)_5OC(NH_2)_2](PF_6)_3\cdot H_2O$: C, 1.72; H, 3.00; N, 14.02; P, 13.30. Found: C, 2.01; H, 3.16; N, 13.95; P, 13.04.

It was noted that in certain preparations in which the heating temperatures or times were increased, some $[Ru(NH_3)_5NCO](PF_6)_2$ (characterized by infrared spectroscopy)[25] was obtained in the more water-soluble crystalline fractions. It most likely arises through a thermally induced elimination of NH_3 from $[Ru(NH_3)_5NH_2CONH_2]^{3+}$ (or perhaps the deprotonated form) as suspected for other $[M(NH_3)_5NHCONH_2]^{2+}$ ions (M = Co(III),[24] Rh(III)[25]).

$[Ru(NH_3)_5OC(NH_2)_2](BF_4)_3$ was also obtained by filtering a cold aqueous solution of $[Ru(NH_3)_5NHCONH_2]^{2+}$ into cold (−10 °C) aqueous 30% HBF_4, and the product was purified by recrystallization from dilute ice-cold aqueous HBF_4. Crystals were washed copiously with diethyl ether and dried in vacuo over P_2O_5. Anal. Calcd: C, 2.37; H, 3.75; N, 19.34. Found: C, 2.22; H, 3.33; N, 18.99.

$[Ru(NH_3)_5OCHNH_2](PF_6)_3$. A solution of $(CF_3SO_2)_2O$ in sulfolane (0.1 mL in 25 mL) was stirred under N_2 for 10 min (30 °C) whereupon formamide (10 mL; Fluka) was added. After 5 min, finely ground $[Ru(NH_3)_5O_3SCF_3](CF_3SO_3)_2$ (1 g) was added to the mixture, which turned yellow-green. After a further 30 min, the mixture was acidified with CF_3SO_3H (0.5 mL), which caused some discoloration. The reaction was continued for 2 h at 60 °C during which time the mixture became slightly orange. Workup with ether or acetone/ether followed by acidic ice-cold water/NH_4PF_6, as described above, led to a white crystalline product in 60% yield. Three fractional recrystallizations from ice-cold water (pH <1)/NH_4PF_6 produced the title complex. Anal. Calcd for $[Ru(NH_3)_5OCHNH_2](PF_6)_3\cdot H_2O$: C, 1.75; H, 2.92; N, 12.28; P, 13.59. Found: C, 1.97; H, 3.16; N, 12.42; P, 13.18. In some preparations using 2–5 times the quantity of both $(CF_3SO_2)_2O$ and CF_3SO_3H, the crude aqueous product analyzed as follows: C, 9.58; H, 3.18; N, 10.51; S, 6.68; F, 33.92; P, 9.26. This product showed properties similar to those of the authentic title complex, and the analyses are consistent with the sulfolane adduct, $[Ru(NH_3)_5OCHNH_2](PF_6)_{1.75}(CF_3SO_3)_{1.25}\cdot C_4H_8S_1O_2$: C, 9.48; H, 3.29; N, 10.62; S, 6.86; F, 34.22; P, 9.10.

$[Ru(NH_3)_5OCHN(CH_3)_2]_2(S_2O_6)_3$. $[Ru(NH_3)_5O_3SCF_3](CF_3SO_3)_2$ (0.1 g) was dissolved in *N,N*-dimethylformamide (15 mL) and stirred for 80 min (20 °C). Dropwise addition to diethyl ether (80 mL) yielded a yellow-brown oily solid. The supernatant was decanted and the residual ether evaporated, the oily residue was dissolved in ice-cold water, and filtered, and saturated aqueous $Na_2S_2O_6$ was added to the filtrate. After cooling (0 °C; 20 min), off-white needles, which had precipitated, were recrystallized from a minimum volume of ice-cold water by addition of ice-cold acetone (~2 L). Yield: 83%. Anal. Calcd for $[Ru(NH_3)_5OCHN(CH_3)_2]_2(S_2O_6)_3\cdot 3H_2O$: C, 6.84; H, 4.75; N, 15.97; S, 18.25. Found: C, 6.74; H, 4.62; N, 15.90; S, 18.10.

$[Ru(NH_3)_5OC(CH_3)N(CH_3)_2]_2(S_2O_6)_3$. $[Ru(NH_3)_5O_3SCF_3](CF_3SO_3)_2$ (0.1 g) was stirred in $OC(CH_3)N(CH_3)_2$ (10 mL) for 60 min (20 °C). Dropwise addition to diethyl ether (100 mL) produced a yellow oil. Decantation of the ether and crystallization from ice-cold water/$Na_2S_2O_6$, as described above, resulted in lemon-colored crystals, which were washed with ethanol and ether and air-dried. Yield: ~85%. Anal. Calcd for $[Ru(NH_3)_5OC(CH_3)N(CH_3)_2]_2(S_2O_6)_3\cdot 3H_2O$: C, 8.89; H, 5.00; N, 15.55; S, 17.77. Found: C, 8.65; H, 4.62; N, 15.82; S, 17.40.

$[Ru(NH_3)_5OP(OR)_3]_2(S_2O_6)_3$ (R = CH_3, C_2H_5). $[Ru(NH_3)_5O_3SCF_3](CF_3SO_3)_2$ (50 mg) was dissolved in $OP(OR)_3$ (5 mL) and, after 1 h (20 °C), was added slowly to diethyl ether (50 mL). After a further 1 h, the resulting fine white precipitate was collected by vacuum filtration. Anal. Calcd for $[Ru(NH_3)_5OP(OC_2H_5)_3](CF_3SO_3)_3$: C, 13.25; H, 3.68; N, 8.59; P, 11.41; S, 11.78. Found: C, 12.87; H, 3.68; N, 8.17; P, 11.40; S, 11.49. The triflato salt could be recrystallized by redissolving it in a minimum volume of ice-cold water and filtering into a one-third volume of saturated aqueous $Na_2S_2O_6$. Cooling (0 °C; 60 min) caused precipitation, and the solid product was washed (ethanol, ether) and air-dried. Yield: ~42%. Anal. Calcd for $[Ru(NH_3)_5OP(OCH_3)_3]_2(S_2O_6)_3\cdot 3H_2O$: C, 6.07; H, 4.55; N, 11.80; S, 16.19; P, 15.68. Found: C, 6.21; H, 4.40; N, 11.32; S, 16.56; P, 16.05.

Kinetic Measurements. Buffers were prepared from reagent grade materials and 5.00, 1.00, and 0.10 M HCl ("Dilut-it" analytical concentrate, Baker) or freshly prepared and standardized CF_3SO_3H solutions, and ionic strength was maintained at 1.0 M with KCl or $NaCF_3SO_3\cdot 3H_2O$. All reactions were initiated by rapidly but completely dissolving solid ruthenium complexes in preequilibrated solutions contained in a thermostated cell. The concentration of the complex was typically $<10^{-4}$ M. The cell temperature, which was regulated to better than ±0.1 °C at 20–40 °C by water circulated from a Haake thermostat bath, was monitored before and after each run by using a United Systems Corporation 702A thermistor miniprobe linked to a properly calibrated Digitec HT5810 thermistor thermometer. Each reaction was followed by repeated scans of absorbance in the 450–200-nm range and/or continuously at selected wavelengths reported ahead. All kinetic data fitted strictly first-order rate laws over $>3t_{1/2}$, as assessed initially by graphical means and later also by programmable-calculator-fitted standard least-squares analyses, with standard deviations from linearity of $<\pm 2\%$. Reported rate constants are mean values for three replicate kinetic runs reproducible to within ±2%.

Results and Interpretation

Syntheses. The labile $[Ru(NH_3)_5O_3SCF_3]^{2+}$ ion mixed with urea in weakly coordinating solvents (acetone, sulfolane) yields a mixture of (urea-*O*)- and (urea-*N*)pentaammineruthenium(III). This was indicated initially by an infrared spectrum of the solid product, obtained following addition of diethyl ether to the acetone or sulfolane solutions, which showed stretching frequencies characteristic of both authentic isomers isolated later. It was further supported by rapidly scanning the UV–vis spectrum of an aqueous solution of this product, since intense LMCT absorptions characteristic of $[(NH_3)_5RuNHCONH_2]^{2+}$ (383, 215 nm (sh)) and $[(NH_3)_5RuOC(NH_2)_2]^{3+}$ (287 nm) were observed in ratios typically 0.5:0.65:0.8, respectively, within 1–2 min (25 °C) of dissolution. These ratios changed rapidly, and within 10 min the 383- and 215-nm absorption maxima were dominant,

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Table I. Molar Absorptivities for $[(NH_3)_5RuL]^{n+}$ Ions

L	λ, nm (ε, M^{-1} cm^{-1})	medium
OH_2	320 (100), 268 (748), 210 (910)	0.01 M CF_3SO_3H[a]
$OC(NH_2)_2$	287 (2.10×10^3), 248 sh (895)	0.1 M CF_3SO_3H[b]
$OCHNH_2$	294 (1.02×10^3), 224 (1.83×10^3)	1.0 M HCl
$OCHN(CH_3)_2$	335 (1.43×10^3), 280 sh (939), 240 sh (2.47×10^3)	1.0 M CF_3SO_3H
$OC(CH_3)N(CH_3)_2$	348 (1.59×10^3), 293 (1.76×10^3), 205 sh (1.07×10^3)	1.0 M CF_3SO_3H
$NHCONH_2$	383 (3.2×10^3)	0.1 M NaO_2CCH_3, pH 8.5[c]
	358 (2.8×10^3), 226 (1.6×10^3)	0.1 M CF_3SO_3H[d]
NHCHO	383 (3.8×10^3)	$HCONH_2$[e]
$NHCOCH_3$	383 (3.46×10^3), 249 (2.31×10^3)	1.0 M $NaClO_4$[f]
	322 (1.55×10^3)	1.0 M $HClO_4$[f]
$NHCOC_6H_5$	393 (4.08×10^3), 314 (3.68×10^3) 270 sh (2.68×10^3), 219 (9.45×10^3)	HCO_3^-, pH 8[f]
	385 (1.47×10^3), 320 (3.45×10^3) 270 sh (3.78×10^3), 228 (9.40×10^3)	2 M $HClO_4$[f]

[a] Reference 26. [b] From extrapolating spectra at 15.0 and 25.0 °C to zero time. [c] in H_2Of; 383 (3.22×10^3), 215 (1.95×10^3) nm. [d] Extrapolated to zero time from 12 and 15 °C scans. [e] Reference 9. [f] Reference 27.

while the intensity of the 287-nm maximum had diminished substantially and the band had shifted to 295 nm.

These spectral changes are interpreted as facile O-bonding to N-bonding rearrangement of the bound urea in $[(NH_3)_5RuOC(NH_2]^{3+}$, since $[(NH_3)_5RuNHCONH_2]^{2+}$ was isolated in 70% yield from such aqueous solutions (pH >4). There is some competing aquation of the O-bonded isomer as indicated by the absorbance at 295 nm ($[Ru(NH_3)_5OH]^{2+}$) which promptly moved to 268 nm ($[Ru(NH_3)_5OH_2]^{3+}$) upon acidification of the solution. By extrapolation of the aqueous spectra to zero time, it was calculated that the acetone reaction produces ca. 80% $[(NH_3)_5RuOC(NH_2)_2]^{3+}$. When the total acetone or sulfolane reaction product was dissolved, either directly in cold aqueous acid or in water which was later acidified, the 287-nm absorption maximum grew with time and $[(NH_3)_5RuOC(NH_2)_2]^{3+}$ was isolated in 60% yield.

These selective synthetic routes to the respective linkage isomers can be attributed to the striking difference in acidity of the urea ligand in $[(NH_3)_5RuOC(NH_2)_2]^{3+}$ ($pK_a > 10$) and $[(NH_3)_5RuNH_2CONH_2]^{3+}$ ($pK_a < 2$) and the consequent dependence upon pH of the direction of, and facility for, linkage isomerization. The O-bonding to N-bonding rearrangement is driven by deprotonation of the acidic $[(NH_3)_5RuNH_2CONH_2]^{3+}$ ion, and the deprotonated form is inert except in strongly acidic media where it protonates and isomerizes quickly to $[(NH_3)_5RuOC(NH_2)_2]^{3+}$. Salts of both $[(NH_3)_5RuOC(NH_2)_2]^{3+}$ and $[(NH_3)_5RuNHCONH_2]^{2+}$ have been obtained in crystalline form; salts of $[(NH_3)_5RuNH_2CONH_2]^{3+}$ can also be isolated, but the cation appears to isomerize rapidly even in the solid state.

Characterization. The stoichiometries of the complexes were established principally by elemental analyses, but their cation-exchange properties are also consistent with given assignments. The color and electronic absorption spectra allow ready distinction between the coordination modes of urea (Table I). The yellow ion $[(NH_3)_5RuNHCONH_2]^{2+}$ exhibits a characteristic low-energy LMCT band (383 nm, $\epsilon \sim 10^3$ M^{-1} cm^{-1}; pH 4–7), which has also been observed for analogous $[(NH_3)_5RuNHCOR]^{2+}$ ions (R = H,[9] alkyl, aryl[27]) and is attributed to transfer of charge from a filled π orbital on urea to a vacancy in a dπ orbital of Ru(III).

Consistent with protonation of the bound urea, acidified solutions of $[(NH_3)_5RuNHCONH_2]^{2+}$ are bleached, the LMCT absorption shifting to higher energy (358 nm; 1 M HCl). This energy is significantly less than that associated with LMCT absorptions of analogous complexes of NH_2COCH_3 (322 nm),[27] $NH_2SO_3^-$ (280 nm),[28] $NH_2CH_2CO_2C_2H_5$ (275 nm),[8] NH_3 (276 nm), and OH_2 (268 nm)[26] but greater than that for $NH_2COC_6H_5$ (385 nm).[27] The colorless $[(NH_3)_5RuOC(NH_2)_2]^{3+}$ ion gives rise to a LMCT band at a much shorter wavelength (287 nm, $\epsilon \sim 10^3$ M^{-1} cm^{-1}) as observed for other pentaammineruthenium(III) complexes with neutral O-bound ligands ($O_2CCH_2NH_3$, 288 nm;[6] OH_2, 268 nm;[26] $OCHNH_2$, 294 nm; Table I). Transitions associated with absorption maxima at 280–295 nm for $[(NH_3)_5RuOCHN(CH_3)_2]^{3+}$ and $[(NH_3)_5RuOC(CH_3)N(CH_3)_2]^{3+}$ (Table I) are also likely LMCT in nature, while the shorter wavelength absorptions are typical of MLCT. The origin of the absorption maxima above 300 nm is less certain. The *N*-dimethyl complexes were synthesized in order not only to establish characteristics of $[(NH_3)_5Ru[O\text{-ligand})]^{3+}$ ions but also to measure rates for their aquation since there is a paucity of such data for substitution on Ru(III).

Infrared spectroscopy is of little help in structure elucidation for these complexes, but it is of value as a fingerprinting tool to distinguish between isomers. For $[(NH_3)_5RuNHCONH_2](PF_6)_2$, distinctive stretching frequencies at 3360, 3293 (strong, sharp), 1585 (m), and 1455 (br, strong) cm^{-1} distinguish it from $[(NH_3)_5RuOC(NH_2)_2](PF_6)_3$, which has unique absorptions at 3383, 3283 (strong, sharp), and 1526 (br, strong) cm^{-1}. Both complexes display a band at ca. 1635 (m) cm^{-1} attributable to the delocalized carbonyl group. A strong absorption was also observed at 1640–45 cm^{-1} for $[(NH_3)_5RuOCHN(CH_3)_2]_2(S_2O_6)_3\cdot 3H_2O$ and $[(NH_3)_5RuOC(CH_3)N(CH_3)_2]_2(S_2O_6)_3\cdot 3H_2O$, and this supports the proposed O-bonding mode of these amides since the sterically hindered N-bound mode requires a band at ≥1700 cm^{-1} characteristic of a localized C=O group.

Formal reduction potentials also distinguish between the bonding modes of the ambidentate ligand, although present indications[14] are that there is little variation between complexes with like chromophores (e.g. $[(NH_3)_5RuNHCOR]^{2+}$ (R = H, CH_3, NH_2), $E_f = -100$ to -130 mV (formal potentials vs. NHE; 0.1 M NaO_2CCH_3); $[(NH_3)_5Ru(O\text{-ligand})]^{3+}$ (ligand = $OCHNH_2$, $OCHN(CH_3)_2$, $OC(CH_3)N(CH_3)_2$, $OC(NH_2)_2$), $E_f = 60$–70 mV (0.1 M *p*-toluenesulfonic acid/0.1 M sodium *p*-toluenesulfonate)).[14]

Finally, the acidities and chemical reactivities to be described are consistent with the specific assignments of N- and O-bonding modes and closely resemble the properties of the more readily and completely characterized Co(III) analogues.[2,10,13]

Reactivity of $[(NH_3)_5RuNHCONH_2]^{2+}$. Like the cobalt(III) analogue,[13] $[(NH_3)_5RuNHCONH_2]^{2+}$ is fairly stable above pH 3, but quite reactive in more acidic media. Figure 1 shows the initial reaction of $[(NH_3)_5RuNHCONH_2]^{2+}$ in aqueous 1 M HCl. Protonation of the coordinated urea is signified by the instantaneous bleaching of the yellow-green color of the conjugate base, the LMCT absorption shifting to lower wavelength. The intensities of absorbances due to protonated N-bonded isomer (358, 226 nm) rapidly decrease concomitant with formation of an absorption maximum at 287 nm. The persistance of isosbestic wavelengths (254, 314 nm) during the first reaction stage suggests, but does not require, that a single reaction path is involved. The product at this stage is an intermediate and slowly undergoes subsequent decay (not shown). In 1.0 M CF_3SO_3H, this slow second or consecutive reaction is characterized by absorbance decrease over the whole 200–400-nm range, except at 220 nm, which is an isosbestic wavelength, and results, after several hours (25 °C), in a final absorption spectrum (210 nm (sh;$\epsilon = 940$ M^{-1} cm^{-1}),

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(28) Armor, J.; Taube, H. *Inorg. Chem.* **1971**, *10*, 1570.
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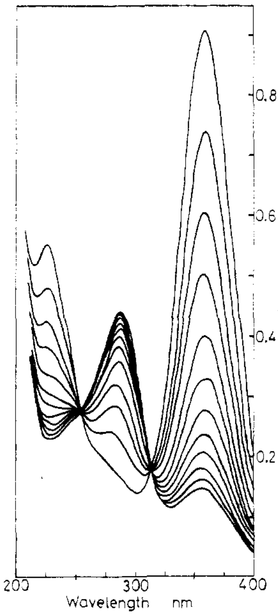

Figure 1. Spectra for the isomerization of $[(NH_3)_5RuNHCONH_2](PF_6)_2$ in 1.0 M HCl (12.0 °C) at 12, 88, 167, 245, 355, 450, 550, 650, 750, 870, 990, and 1110 s following dissolution.

268 nm (ϵ = 733), 325 nm (sh; ϵ = 105)) identical with that for $[Ru(NH_3)_5OH_2]^{3+}$ (Table I). In 1.0 M HCl the same absorbance decrease was observed as well as a third process, due to slower anation of $[Ru(NH_3)_5OH_2]^{3+}$, leading ultimately to a peak at 327 nm for $[Ru(NH_3)_5Cl]^{2+}$.

A kinetic study of these processes was undertaken by monitoring the rate of absorbance decrease at 220 and 383 nm. For absorbance changes at the former wavelength, an isosbestic point in the consecutive reaction, plots of ln ($A - A_\infty$) vs. time were strictly linear over $>4t_{1/2}$, yielding $k_{obsd} = 9.1 \times 10^{-3}$ s^{-1} (1.0 M CF_3SO_3H) and 7.3×10^{-3} s^{-1} (0.1 M CF_3SO_3H) for the initial step (25.0 °C). Since the product at this stage has an absorption spectrum very similar to that of $[(NH_3)_5RuOC(NH_2)_2]^{3+}$, isolated later in this work, the above kinetic data relate to N- to O-linkage isomerization. The succeeding process was studied by monitoring the absorbance decrease at 383 nm (and later at 314 nm). When early time data associated with the initial quick step were ignored, plots of ln ($A - A_\infty$) vs. time were also linear over $>5t_{1/2}$. The deduced first-order rate constant ($k_{obsd} = 1.9_6 \times 10^{-4}$ s^{-1}; 1.0 M CF_3SO_3H, 25.0 °C) agrees reasonably with the measured rate for acid hydrolysis (aquation) of the authentic O-bonded isomer under identical conditions ($k_{obsd} = 2.0_6 \times 10^{-4}$ s^{-1}).

We conclude that in aqueous acid the N-bonded isomer reacts predominantly according to

$$[(NH_3)_5RuNHCONH_2]^{2+} \overset{K}{\rightleftharpoons} [(NH_3)_5RuNH_2CONH_2]^{3+} \underset{k^{ON}}{\overset{k^{NO}}{\rightleftharpoons}} [(NH_3)_5RuOC(NH_2)_2]^{3+} \xrightarrow{k_s^{H_2O}} [(NH_3)_5RuOH_2]^{3+} + \text{urea}$$

No competing reactions of the N-bonded isomer in acidic solution have been identified. While k^{NO} and $k_s^{H_2O}$ have been measured, the possibility of some competing aquation of the N-bonded isomer cannot be entirely discounted. However, by analysis of the UV absorption spectra, a limit of <10% can be set from the lack of absorbance at 268 and 210 nm. The isosbestic wavelengths (Figure 1) are not likely to be sensitive to <10% competing aquation.

The infrared spectrum of $[Ru(NH_3)_5NHCONH_2](PF_6)_2$ in Me_2SO/CF_3SO_3H was monitored with time to check for formation of $[Ru(NH_3)_5NCO]^{2+}$ (2220 cm^{-1})[25] and CO_2 (2300 cm^{-1}), but neither was detected. $[Ru(NH_3)_5NCO]^{2+}$ (347 nm (ϵ = 3610 M^{-1} cm^{-1}), 265 nm (ϵ = 292); in H_2O)[25] and its hydrolysis products, $[Ru(NH_3)_5NH_2H]^{3+}$ (234 nm)[25] and $[Ru(NH_3)_6]^{3+}$ (276 nm), were also sought spectrophotometrically as reactive intermediates formed from $[(NH_3)_5RuNHCONH_2]^{2+}$ in aqueous acid, but they were not observed. There is evidence for related products being formed from $[(NH_3)_5RhNHCONH_2]^{2+}$ [16] and $[(NH_3)_5CoNHCONHC_6H_5]^{2+}$,[2] but not from $[(NH_3)_5CoNHCONH_2]^{2+}$,[13] in acidic media. Unfortunately, the normally definitive chromatographic product analysis experiments were not conclusive because, under conditions where $[Ru(NH_3)_5OH]^{2+}$ and $[(NH_3)_5RuOC(NH_2)_2]^{3+}$ are most readily separated (pH >4), there was substantial decomposition.

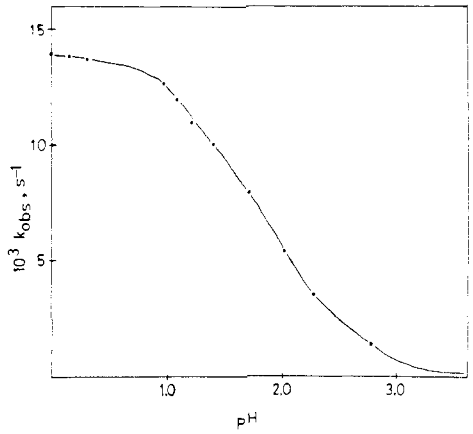

Figure 2. Dependence on pH of observed first-order rate constants for isomerization of $[(NH_3)_5RuNH_2CONH_2]^{3+}$ in aqueous HCl (μ = 1.0 M (KCl)) at 25.0 °C.

The acidity of the N-bonded isomer has been determined from kinetic data for its isomerization to $[(NH_3)_5RuOC(NH_2)_2]^{3+}$ at pH <3. First-order rate constants for this process (25.0 °C, μ = 1.0 M (KCl)) varied with pH (Table II, supplementary material) as a sigmoidal titration curve (Figure 2) typical[12] of a rate law: $-d[\text{complex}]/dt = k[H^+]/(K_a + [H^+])$. Graphical and least-squares analyses gave values for the acid dissociation constant, $K_a = 1.58 \times 10^{-2}$ (pK_a = 1.80 ± 0.05), and the limiting first-order rate constant, $k = 1.42\ (\pm 0.05) \times 10^{-2}$ s^{-1} (μ = 1.0 M (KCl)). Over the pH range studied absorbance changes were large, and complications associated with competing or successive reactions were negligible at the wavelength monitored (220 nm).

Acid Hydrolysis of $[(NH_3)_5Ru(O\text{-ligand})]^{3+}$. Rates for the spontaneous aquation of pentaammineruthenium(III) complexes containing O-bonded ligands (Table III, supplementary material) were measured in an attempt to compare intermolecular substitution on Ru(III) with that on Co(III), as well as with intramolecular substitution (linkage isomerization).

The purity of $[(NH_3)_5RuOC(NH_2)_2]^{3+}$, obtained in high yield from acidic solutions of $[(NH_3)_5RuNHCONH_2]^{2+}$ by N- to O-linkage isomerization, was assessed by electronic spectra and kinetic behavior in aqueous acid. The latter analysis is especially sensitive to traces of $[(NH_3)_5RuNH_2CONH_2]^{3+}$ or $[(NH_3)_5RuNCOH]^{3+}$, which react far more rapidly than $[(NH_3)_5RuOC(NH_2)_2]^{3+}$. For the latter ion, which aquates relatively slowly ($t_{1/2} \sim 1$ h) yielding entirely free urea and $[(NH_3)_5RuOH_2]^{3+}$, plots of ln ($A - A_\infty$) vs. time were strictly linear over $>5t_{1/2}$, consistent with the simple rate law $-d[\text{complex}]/dt = k_{obsd}[\text{complex}]$ and first-order rate constant $k_{obsd} = 2.06 \times 10^{-4}$ s^{-1} (1.0 M CF_3SO_3H, 25.0 °C).

This value may be compared with aquation rates of similar Ru(III) complexes (Table III), as well as the corresponding Co(III) analogues. Generally the observed rates for the Ru(III) complexes correlate with the order of basicity of the O-coordinating ligands, an observation previously made for the Co(III) analogues[2] and other Co(III) complexes.[30] The effect of substituting Ru(III) for Co(III) in these complexes is a 2–5-fold increase in the rate of M–O bond cleavage. Exceptions to this trend are the O-bound formamides ($OCHNH_2$, $OCHN(CH_3)_2$), which undergo Co–O bond cleavage much more slowly than their Lewis basicities warrant.[2,10] On Ru(III), however, their rates of aquation, while 60–100 times faster than those of their Co(III) counterparts, are about as expected in view of the relative basicity of the formamide molecules.[31]

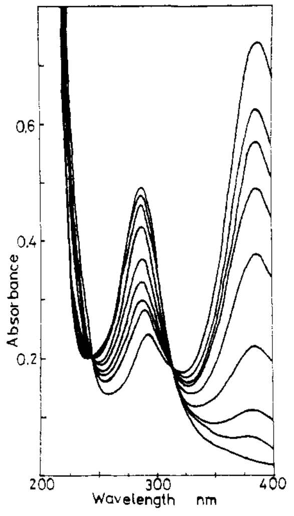

Figure 3. Absorption spectra of $[(NH_3)_5RuOC(NH_2)_2](BF_4)_3$ in aqueous 0.1 M NaMes buffer (pH 6.2; μ = 1.0 M ($NaCF_3SO_3$); 21.5 °C) after 1, 3, 6, 14, 29, 44, 59, 74 and 144 min.

It is perhaps worth noting that, in general, acid hydrolyses of pentaammineruthenium(III) complexes do proceed at greater rates than those for the corresponding pentaamminecobalt(III) complexes, contrary to the opposite conclusion,[30] which was based solely on the halopentaamminemetal(III) ions. This broad statement is founded upon available data for both neutral[32a] and anionic[32b] leaving groups and is consistent with lability predictions based upon the d-electron configuration of the central metal. Furthermore, the similarity in the rates of acid hydrolysis of the present set of ruthenium complexes and their cobalt analogues, together with data for their anation and competition between water and other ligands,[33] tentatively suggests that, while bond making is of greater importance for $Ru(NH_3)_5{}^{3+}$ than for $Co(NH_3)_5{}^{3+}$, cleavage of the bond between Ru(III) and the non-ammine ligand is still more important than, or at least as important as, bond making to the incoming water molecule.[32b,c]

Isomerization of $[(NH_3)_5RuOC(NH_2)_2]^{3+}$. It has been indicated, in relation to the syntheses of linkage isomeric urea complexes, that the acetone route leads to ~80% $[(NH_3)_5RuOC(NH_2)_2]^{3+}$ but that this product is unstable in water. Spectral changes associated with its reactivity are shown in Figure 3. Aqueous solutions (pH >2) of $[(NH_3)_5RuOC(NH_2)_2]^{3+}$ rapidly turn yellow-green, commensurate with an absorbance decrease at 287 nm and increases at 383 and 215 nm. Isosbestic wavelengths are observed at 244 and 319 nm in unbuffered water.

A kinetic study for this reaction was undertaken by measuring the rate of absorbance increase at 383 nm, which signals formation of $[(NH_3)_5RuNHCONH_2]^{2+}$, over the pH range 3.5–6.6. The absorption spectrum of the final reaction solution at pH 6 suggests a small but significant (15%) contribution from aquation of the complex, producing $[(NH_3)_5RuOH]^{2+}$. The major product however is the N-bound isomer. Since the observed first-order rate constants at pH 3.88 and 4.60 ($k_{obsd} = 1.99 \times 10^{-3}$ s^{-1} and 2.13×10^{-3} s^{-1}, respectively, 0.1 M sodium citrate buffer, 25.0 °C) and pH 6.2 ($k_{obsd} = 1.62 \times 10^{-3}$ s^{-1}, 0.1 M NaMes buffer, μ = 0.1 M; $k_{obsd} = 1.26 \times 10^{-3}$ s^{-1}, 0.1 M NaMes buffer, μ = 1.0 M ($NaCF_3SO_3$), 25 °C) do not differ substantially, we conclude that the rate of isomerization is independent of pH and not subject to specific-acid or -base catalysis in the range studied.

In Table IV (supplementary material), rate data for isomerization of the N-bonded isomer ($k_{obsd}{}^{NO}$, pH 0) and for the composite reaction of the O-bonded isomer ($k_{obsd}{}^{ON}$ pH 6.2) are recorded as a function of temperature. The latter data were also corrected ($k_s{}^{ON}$) for the contributions from aquation ($k_s{}^{H_2O}$), as these were determined in separate experiments at low pH, it being assumed that these rates of aquation are independent of pH between 0 and 6.5 and free of specific effects. This assumption is bolstered by the fact that the direct spectrophotometric determination of $[(NH_3)_5RuOH]^{2+}$ in a product solution at pH 6, though approximate, is in accord with it. It is further supported by the similarity in the rates of aquation of $[(NH_3)_5RuOCHN(CH_3)_2]^{3+}$, for which linkage isomerization does not occur, in 1.0M CF_3SO_3H $k_{obsd} = (1.40 \pm 0.04) \times 10^{-4}$ s^{-1} and at pH 6.2 $k_{obsd} = (1.34 \pm 0.5) \times 10^{-4}$ s^{-1} (0.1 M NaMes, μ = 1.0 M ($NaCF_3SO_3$)) at 25.0 °C, which implies negligible base catalysis for the aquation path below pH 6.5. It is further noted that the relative proportions of the two parallel reaction paths of the *O*-urea complex are virtually temperature independent between 20 and 40 °C.

Activation Parameters. The temperature dependence of the first-order rate constants for reactions of $[(NH_3)_5RuOC(NH_2)_2]^{3+}$ (pH 0 and 6.2) and $[(NH_3)_5RuNH_2CONH_2]^{3+}$ (pH 0) is summarized in Table IV. Eyring plots of ln (k_{obsd}/T) vs. $1/T$ (not shown) were strictly linear, and the activation parameters presented were determined by weighted least-squares analyses. Comparison of these data for the two reaction paths of the O-bonded isomer—acid hydrolysis ($k_s{}^{H_2O}$; pH 0) and linkage isomerization ($k_s{}^{ON}$, pH 6.2)—suggests that the difference in rates (6–7-fold) for these paths is primarily entropic in origin. The facility of the O to N rearrangement must be explained by the less negative activation entropy (activation enthalpies are virtually identical). This property is indicative of greater order in the transition state for the isomerization path and is akin to the entropy-based effect generally observed for chelation in metal complexes. Note that the analogous reactions of $[(NH_3)_5CoOC(NH_2)_2]^{3+}$ have been assigned as separate pathways not involving a common intermediate.[13] Interpretation of the activation parameters for the *N*- to *O*-urea isomerization is difficult at this time for the reasons discussed ahead.

One noteworthy comparison is the acid hydrolysis of $[(NH_3)_5RuOC(NH_2)_2]^{3+}$ (Table IV) vs. $[(NH_3)_5RuOC(CH_3)N(CH_3)_2]^{3+}$,[14] for which activation enthalpies and entropies are almost identical.[34] Moreover, $\Delta H^{\ddagger}$ is about 20 kJ mol^{-1} less and $\Delta S^{\ddagger}$ ca. 20–30 J mol^{-1} deg^{-1} more negative than for the corresponding reactions of the Co(III) analogues.[35] The significance of this finding is not known, although it can be said that this trend is expected for the larger cation (Ru(III)) and supports the contention that the acid hydrolysis of these Ru(III) complexes involves a larger fraction of associative character than for their Co(III) analogues.

Discussion

The notable enhancement in the acidity of urea (pK_a ~ 14) upon N-coordination to pentaammineruthenium(III) (pK_a = 1.8) has previously been observed for Co(III) (2–3)[12,13] and Rh(III) (3.9),[16] and it is much greater than that observed for O-coordination to these metals (Co, 13.2;[36] Rh, 13.7;[16] Cr, 13.5[17]). The acidity of $[(NH_3)_5RuOC(NH_2)_2]^{3+}$ has not been accurately determined in this work (qualitatively pK_a > 10) but a value of ca. 13 seems reasonable in relation to those recorded for other pentaamminemetal(3+) ions. This large difference among the acidities of coordinated urea, depending on the site of binding, has also been noted for pentaamminemetal(III) complexes of amides,[2,10,16,17,37,38] carbamates,[2,39] sulfinamides,[2] and sulfamates.[40,41]

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(31) Zabicky, J., Ed. "The Chemistry of Amides" Ed. J. Wiley-Interscience: New York, 1970; Chapter 1, p 1.

(32) (a) This work and unpublished results. (b) Poon, C. K.; Lau, T. C. *Inorg. Chem.* **1983**, *22*, 1664 and references therein. (c) For a counterconclusion see: Fairhurst, M. T.; Swaddle, T. W. *Inorg. Chem.* **1979**, *18*, 3241 and references contained therein.

(33) Fairlie, D. P.; Taube, H., unpublished observations.

(34) For $[(NH_3)_5RuOC(CH_32)N(CH_3)_2]^{3+}$ in 1.0 M CF_3SO_3H (25.0–45.0 °C), $\Delta H^{\ddagger} = 88.8 \pm 2.4$ kJ mol^{-1} and $\Delta S^{\ddagger} = -20.6 \pm 7.9$ J mol^{-1} deg^{-1}.[14]

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It is clear in considering the conjugate bases, $[(NH_3)_5RuNHCOR]^{2+}$ and $[(NH_3)_5RuOC(NH^-)R]^{2+}$, that the metal withdraws far more electron density from the deprotonated urea in the former, much less basic, ion. Therefore it is this ion which is more effectively stabilized by resonance than $[(NH_3)_5RuOC(NH^-)R]^{2+}$:

$$[Ru{-}{}^-NH{-}C(R){=}O]^{2+} \leftrightarrow [Ru{-}NH{=}C(R){-}O^-]^{2+}$$

$$[Ru{-}O{=}C(R)NH^-]^{2+} \leftrightarrow [Ru{-}{}^-O{-}C(R){=}NH]^{2+}$$

It is also known for a range of metal ions (Co(III),[10] Rh(III),[16] Cr(III),[17] Ru(III)[14]) that $[(NH_3)_5MOC(NH_2)R]^{3+}$ is a few orders of magnitude more acidic for amides (p$K_a \sim 11$–12; R = H, alkyl, aryl) than ureas (p$K_a \sim 13$–14; R = NR′R″), and consequently $[(NH_3)_5MOC(NH^-)R]^{2+}$ must be less resonance stabilized for ureas than amides.

As a consequence of these resonance stabilizations, both linkage isomers of $[(NH_3)_5Ru(urea)]^{3+}$, in which the urea molecule is neutral, are observed only in strongly acidic media. Under these conditions, the N-bound urea in $[(NH_3)_5RuNH_2CONH_2]^{3+}$ is a feeble σ donor, with no π-donor/π-acceptor properties, and is readily substituted. However, instead of being directly substituted intermolecularly by solvent molecules, a faster intramolecular substitution by the formerly uncoordinated O-terminus of urea is observed prior to consecutive solvolysis of $[(NH_3)_5RuOC(NH_2)_2]^{3+}$. It is precisely the occurrence of the latter process that characterizes the intramolecular nature of the N- to O-linkage isomerization. In nonacidic or weakly acidic media the reverse O to N rearrangement proceeds, and, since this is almost 10 times faster than parallel aquation of the O-bonded isomer, it must likewise be intramolecular.

For the complexes reported herein, there is a small, but significant, rate distinction between inter- (spontaneous aquation) and intramolecular (linkage isomerization) substitution on Ru(III). The intermolecular substitution is 2–5-fold faster on Ru(III) than on Co(III) and is almost certainly predominantly dissociative in nature for both metals. However the intramolecular linkage isomerizations of (urea-*O*)-, (urea-*N*)-, and (formamide-*O*)-pentaammineruthenium(III)[14] are several times faster than the competing aquation and likely involve some bond making by the incoming donor atom to the metal ion in the transition state. From this study it is not clear whether the linkage isomerization is facilitated because the entering group, which is in the proximity of the metal, increases the coordination number of Ru(III), either via a π-bound urea or a discrete 7-coordinate intermediate,[1] or whether the process is concerted (dissociative/associative interchange mechanism).

In Table V (supplementary material) are summarized data on the specific rates of O- to N-linkage and N- to O-linkage isomerization for urea bound to several different metals and data on the equilibrium quotient [O bound]/[N bound] ($K_{N\to O}^{obsd}$). It should be noted that data for Cr(III) are estimates only, and even for Rh(III), there are a number of competing reactions that may compromise the accuracy of the rate data. Nevertheless it is certain that for both Co(III) and Cr(III) there is a marked preference for the → O-terminus of urea and that this preference, while maintained, is substantially less for Ru(III) and Rh(III). The rate functions for the O to N and N to O rearrangements are k_s^{ON}[M(urea-*O*)] and k^{NO}[M(urea-*N*)], so that the ratio k^{NO}/k_s^{ON} defines the equilibrium quotient for

$$[M(\text{urea-}N)]^{3+} \rightleftarrows [M(\text{urea-}O)]^{3+} \quad K_{N\to O}^{obsd}$$

The urea-*O* to urea-*N* isomerization is much more facile for Ru(III) than for other metal ions (Ru(III) $\gg$ Rh(III) > Co(III) > Cr(III); Table V), and this appears also to be true of $[(NH_3)_5MOCHNH_2]^{3+}$.[14] Since the rearrangements are not significantly base catalyzed in the pH region studied (0–7), they do not proceed by initial deprotonation of the O-bonded isomer and are hence not dependent upon concentrations of either $[(NH_3)_5RuOC(NH^-)R]^{2+}$ or $[(NH_3)_4(NH_2)RuOC(NH_2)R]^{2+}$ (R = NH$_2$, H).[14] The facility for O to N isomerization must be ascribed to an intrinsic property of Ru(III) related to bond making/breaking. It is tentatively suggested that the greater π-acceptor power of Ru(III) relative to that of the above metals may be important if the transition state does indeed involve a π-bonded urea ligand. Such a π-bonded intermediate has been proposed[1] for the rearrangement of $[(NH_3)_5CoONO]^{2+}$ and appears likely in the (urea)pentaamminecobalt(III) linkage isomerizations.[13]

The order of rates for (urea-*N*)- to (urea-*O*)-linkage isomerizations is Cr(III) $\gg$ Ru(III) > Co(III) $\gg$ Rh(III) (Table V). It was initially surprising that $[(NH_3)_5MNH_2CONH_2]^{3+}$ rearranged at similar rates for M = Co(III) and Ru(III), since $(NH_3)_5$Ru(III) complexes of (glycinato-*N*),[6] (ethyl glycinato-*N*),[8] and (glycinamide-*N*)[7] isomerize much more rapidly than their Co(III) counterparts. Moreover the ~3-fold isomerization rate increase upon substituting Ru(III) for Co(III) in $[(NH_3)_5MNH_2CONH_2]^{3+}$ is reminiscent of the factor observed on replacing Co(III) by Ru(III) in the acid hydrolysis of $[(NH_3)_5M(O\text{-ligand})]^{3+}$ ions (Table III) and might be taken to indicate a similar mechanism for isomerization on the two metal ions. However this latter comparison is likely to be fortuitous because the propensity for N- to O-linkage isomerization is more probably related to the site of protonation in $[(NH_3)_5MNH\mathrel{\substack{-\\ -\,-}}C(R)\mathrel{\substack{-\\ -\,-}}O]^{2+}$ and should be considered in the context of the tautomeric equilibria

$$[M{-}NH_2{-}C(R){=}O]^{3+} = [M{-}NH\mathrel{\substack{-\\ -\,-}}C(R)\mathrel{\substack{-\\ -\,-}}OH]^{3+} \quad K_T$$

This can affect the observed lability of the N-bonded isomer as well as other properties of the amide complexes. A remarkable result from the study of $[(NH_3)_5CoNH_2COR]^{3+}$ ions is that the value of K_T is very sensitive to the nature of R. The convincing evidence that $K_T \gg 1$ when R = CH$_3$, but $K_T \ll 1$ for R = NH$_2$, obtains from ^{1}H NMR measurements.[10,13] However, since Ru(III) is paramagnetic, the same experimental approach is less applicable in resolving the issue of which of the tautomeric forms of the urea-*N* complex of Ru(III) is dominant.

The possibility of the tautomeric equilibrium lends special interest to a consideration of the acidities of coordinated amides. On the basis of pK_a values given earlier for $[M(NH_3)_5]^{3+}$ complexes of O- and N-bonded amides and simple inductive effects, $K_{a,N}{}^N$ is expected to be greater than $K_{a,O}$ by a factor of approximately 10^{10}.

$$[M{-}NH_2{-}C(R){=}O]^{3+} = [M{-}NH\mathrel{\substack{-\\ -\,-}}C(R)\mathrel{\substack{-\\ -\,-}}O]^{2+} + H^+ \quad K_{a,N}{}^N$$

$$[M{-}O{=}C(R)NH_2]^{3+} = [M{-}O\mathrel{\substack{-\\ -\,-}}C(R)\mathrel{\substack{-\\ -\,-}}NH]^{2+} + H^+ \quad K_{a,O}$$

Because of the intervention of the tautomeric equilibrium, the dissociation reaction

$$[M{-}NH\mathrel{\substack{-\\ -\,-}}C(R)\mathrel{\substack{-\\ -\,-}}OH]^{3+} = [M{-}NH\mathrel{\substack{-\\ -\,-}}C(R)\mathrel{\substack{-\\ -\,-}}O]^{2+} + H^+ \quad K_{a,N}{}^O$$

must also be taken into account. When $K_T \gg 1$, the acidity quotient $K_{a,N}{}^O$ rather than $K_{a,N}{}^N$ will be measured for the N-bound form. In this event, the ratio of the acidity of the N-bound to the O-bound form will be diminished by the factor $1/K_T$ (note that $K_{a,N}{}^O = K_{a,N}{}^N/K_T$) from that which would be realized in the absence of tautomerism. Other things being equal, it is then expected that the contrast in measured acidity between the N- and O-bound forms will be greater when the dominant form of the N-bound isomer retains the proton on nitrogen (amide form).

This point is illustrated for (acetamide)pentaamminecobalt(III). The measured pK_a values of the N-bound and O-bound forms are 3.0[38] and 11.6,[2] and the acidity ratio is 4×10^8. The ^{1}H NMR spectrum of the N-bonded isomer indicates that $[(NH_3)_5CoNH{=}C(OH)CH_3]^{3+}$ is predominant in solution,[10] and a value of $K_T \geqslant 100$ is predicted. This number could even be closer[10] to 10^3 as measured for $NH_2{=}C(OH)CH_3$.[42c] Thus an estimate of the pK_a for $[(NH_3)_5CoNH_2COCH_3]^{3+}$ would be $\leq$0–1 and the acidity ratio is $\geq 10^{10-11}$. Note that for $(NH_3)_5$Ru(III) complexes of *N*- and *O*-acetamide, the pK_a values are 2.0[27] and ~11 (estimate),[14] respectively, and the acidity ratio is ~10^9 in

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accord with the imide formulation, $[(NH_3)_5RuNH{=}C(OH)CH_3]^{3+}$.

The point is not so well illustrated for (urea)pentaamminecobalt(III).[13] The measured pK_a values of N- and O-bonded isomers are 2–3 and 13.2, and the acidity ratio is $\sim 10^{11}$. In this case $[(NH_3)_5CoNH_2CONH_2]^{3+}$ is predominant,[13] and if K_T were $\leq 10^{-2}$ as suggested by NMR data, the pK_a of the less abundant tautomer would be ≤ 0–1 and the acidity ratio for $[(NH_3)_5CoNH{=}C(OH)NH_2]^{3+}/[(NH_3)_5CoOC(NH_2)_2]^{3+}$ would be $\geqslant 10^{13}$. However for acetamide (R = CH_3), there is more delocalization in the $[M{-}NH \mathrel{\underset{\cdots}{-}} C(R) \mathrel{\underset{\cdots}{-}} OH]^{3+}$ form than in $[M{-}NH_2{-}C(R){=}O]^{3+}$, whereas for urea the exo substituent (R = NH_2) also shares in the delocalization and this detracts from the benefit of stability that accrued for amides from relocation of the proton. Note that for (urea)pentaammineruthenium(III) the acidity ratio is approximately $10^{(>13-1.8)} = 10^{>11.2}$, and this value lies between those ($\sim 10^{11}$, $\sim 10^{13}$) expected for $[(NH_3)_5RuNH_2CONH_2]^{3+}$ and $[(NH_3)_5RuNH{=}C(OH)NH_2]^{3+}$ were their acidities identical with those of their Co(III) counterparts and K_T the same. However, it cannot be taken for granted that, because $K_T < 1$ for the Co(III)–urea complex, the same will be true for the Ru(III) analogue. Ru(III) is intrinsically more acidic than Co(III)—note that the pK_a value of $[(NH_3)_5RuOH_2]^{3+}$ is ca. 2.4 units lower[29] than that of $[(NH_3)_5CoOH_2]^{3+}$. As the acidity of the metal ion increases, K_T is expected to increase as will the acidity ratio. This follows because as the acidity of the metal center increases, the basicity of nitrogen, being directly attached to the metal, will decrease much more sharply than that of the oxygen, which is two atoms removed.

A comparison of the acidities of the N-bound urea complexes of Co(III) and Ru(III) gives some support to the idea that for the latter species $K_T > 1$. Since the acidity of free urea is about the same as that of water, a similar *difference* would be expected for the acidities of the N-bound ureas as for the acidities of the aquo complexes. For the former, the difference lies between 0.2 and 1.2, significantly less than 2.4, as registered for the aquo complexes. The small difference in the case of the urea-*N* complexes is understood if for the Ru(III) complex the imide form of the N-bound complex predominates. When $K_T >> 1$, the observed value of K_a would be that appropriate to the $[M{-}NH_2{-}CO{-}NH_2]^{3+}$ form multiplied by $1/K_T$. The equilibrium

$$[M(\text{urea-}N)]^{3+} = [M(\text{urea-}O)]^{3+} \quad K_{N\rightarrow O}{}^{\text{obsd}}$$

will also be affected by the tautomeric change:

$$[M{-}NH_2{-}C(R){=}O]^{3+} = [M{-}O{=}C(R){-}NH_2]^{3+} \quad K_{NH_2\rightarrow O}$$

$$[M{-}NH_2{-}C(R){=}O]^{3+} = [M{-}NH \mathrel{\underset{\cdots}{-}} C(R) \mathrel{\underset{\cdots}{-}} OH]^{3+} \quad K_T$$

When the amide form is dominant, $K_{N\rightarrow O}{}^{\text{obsd}}$ is measured by $K_{NH2\rightarrow O}$, but when the imide form is dominant, the principal equilibrium is

$$[M{-}NH \mathrel{\underset{\cdots}{-}} C(R) \mathrel{\underset{\cdots}{-}} OH]^{3+} = [M{-}O{=}C(R){-}NH_2]^{3+} \quad K_{NH_2\rightarrow O}/K_T$$

and $K_{N\rightarrow O}{}^{\text{obsd}} = K_{NH_2\rightarrow O}/K_T$. In fact it appears that a lower limit of K_T for M = Ru(III) can be set by considering the results[13] for Co(III). For this case, $K_{NH_2\rightarrow O} = 2.4 \times 10^2$ and the carbonyl oxygen of urea is somewhat more basic toward $[(NH_3)_5Co]^{3+}$ than the urea nitrogen (NH_2). Because $[(NH_3)_5Ru]^{3+}$ is slightly more acidic than $[(NH_3)_5Co]^{3+}$, $K_{NH_2\rightarrow O}$ for it is expected to be somewhat greater than 2.4×10^2. The quotient K_T then will be $>2.4 \times 10^2/8.6$ or >28. Note also that from the pK_a of $NH{=}C(OH)CH_3$ (0.63),[42] $[(NH_3)_5RuNH{=}C(OH)CH_3]^{3+}$ (2.0),[27] and $NH{=}C(OH)NH_2$ (0.1),[42] the pK_a of $[(NH_3)_5RuNH{=}C(OH)NH_2]^{3+}$ might be predicted to be 1.47–2.0, consistent with the observed value of 1.80.

The observations on the relative facility of the Co(III) and Ru(III) urea complexes to undergo linkage isomerization also point to the same structural difference that is suggested by the evidence thus far outlined. Because the equilibrium constants are not the same for the two cases, it is difficult to discuss meaningfully the reaction rates as reported. A measure of lability, in which the effect of driving force will be very much moderated, is the comparison of the values of $(k_f k_r)^{1/2}$, where subscripts f and r represent forward and reverse reactions. When the structures of reactants and products are alike, and K_{eq} is not much different from 1, the specific forward rate can be expressed by the product $k_i K_{eq}{}^{1/2}$, where k_i is related to an intrinsic barrier and is the same for forward and reverse processes. The specific rate of the reverse reaction will be given by $k_i(1/K^{1/2})$ so that the equilibrium quotient cancels out in the product $k_f k_r$. This is an adaptation of the analysis by Marcus,[43] of how the rate of reaction depends on driving force.

On this basis the labilities of the Ru(III) and Co(III) urea systems are measured by the quantities 3×10^{-3} s^{-1} and 2×10^{-4} s^{-1}. Though by this comparison the Ru(III) system is shown to be inherently more labile than the Co(III) system, it is only so by a factor of about 15, much less than that observed in other cases of linkage isomerization that have been studied. At least for the case of the glycine complex it is unlikely that the enormous difference in intrinsic lability can be ascribed to a vastly different driving force for the Co(III) and Ru(III) complexes. The isomerization is expected to be far less rapid for the imido form than for the amido form because of the necessity in the former case of relocating the proton when isomerization occurs. This effect is clearly demonstrated by studies with $[(NH_3)_5Co]^{3+}$ complexes of $RCONH_2$, where it is found that (N → O) linkage isomerization is much more rapid for the amido (R = NH_2, NR′R″, OR′; $t_{1/2}$ = 40–400 s, 25 °C, H_2O)[2,13] than for the imido (R = H, alkyl, aryl; $t_{1/2}$ = 10–20 h, 25 °C, H_2O)[2,10] form. For the latter imido complexes it has been suggested that all of the isomerization occurs via the $[Co{-}NH_2{-}CO{-}R]^{3+}$ tautomer, its low standing concentration being responsible for the low rates observed.[10]

Consistent with these observations, it is notable that in acidic media there is also a clear distinction between the reactivities of the quite unstable protonated form of $[(NH_3)_5RuNHCONH_2]^{2+}$ and the far more robust $[(NH_3)_5RuNH{=}C(OH)R]^{3+}$ ions (R = H, CH_3, C_6H_5).[9,14] It seems likely that all of these results simply reflect the relative proportions (K_T) of the tautomer, $[(NH_3)_5MNH_2COR]^{3+}$, which is more reactive toward linkage isomerization. Thus while the observed N- to O-isomerization rates of urea complexes of $[Co(NH_3)_5]^{3+}$ and $[Ru(NH_3)_5]^{3+}$ are similar, $K_T \leqslant 0.01$ for the cobalt complex[13] and the presumed reactive form is present in high concentration (ca. 100%), but $K_T \geqslant 28$ for the ruthenium analogue and the reactive tautomer is only in minute concentration ($\leq 3\%$). It is also pertinent to note for the urea complexes that when the approach to isomer equilibrium for $[(NH_3)_5MNH_2CONH_2]^{3+}$ is much slower (M = Rh(III),[16] Os(III)[33]) than for Co(III) and Ru(III), elimination of the *exo*-NH_2 (leading to $[(NH_3)_5MNCO]^{2+}$) competes significantly with N- and O-linkage isomerization.

Finally, on the issue of the solution structure of the N-bound form of the urea complex, we consider the electronic absorption spectra. The $[(NH_3)_5Ru(\text{urea-}N)]^{3+}$ ion, in which urea is a neutral N-bound ligand, shows an absorption at 358 nm ($\epsilon = 2 \times 10^3$ M^{-1} cm^{-1}). This is almost certainly LMCT, and a band at such low energies does not seem compatible with the amide form where LMCT would require a bonding electron to be excited. Hexaammineruthenium(III), it should be noted, shows LMCT at 275 nm ($\epsilon = 4.7 \times 10^2$ M^{-1} cm^{-1})[26] and $[(NH_3)_5RuNH_2CH_2CO_2C_2H_5]^{3+}$ at 275 nm ($\epsilon = 5.3 \times 10^2$ M^{-1} cm^{-1}).[8] The absorption shown by the N-bonded urea complex has characteristics similar to those of the N-bonded acetamide complex (λ_{max} = 322 nm; $\epsilon = 1.6 \times 10^3$ M^{-1} cm^{-1})[27] and the N-bonded glycine

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(42) pK_a values given in: West, R. C., Ed. "Handbook of Chemistry and Physics", 64th ed.; CRC Press: Boca Raton, FL, 1983; p D164. The carbonyl oxygen is the likely site of protonation for both acetamide ((a) See ref 31. (b) Gillespie, R. J.; Birchall, T. *Can. J. Chem.* **1963**, *41*, 148, 2642. (c) Benderley, H.; Rosenheck, K. *J. Chem. Soc., Chem. Commun.* **1972**, 179) and urea ((d) Olah, G. A.; White, A. M. *J. Am. Chem. Soc.* **1968**, *90*, 6087. (e) Worshaw, J. E., Jr.; Busing, W. R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1969**, *B25*, 572. (f) Bryden, J. H. *Acta Crystallogr.* **1957**, *10*, 714. (g) Redpath, C. R.; Smith, J. A. S. *Trans. Faraday Soc.* **1962**, *58*, 462).

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chelate (λ_{max} = 340 nm; ϵ not reported).[44] The shifts on deprotonation (in each case to lower energy) are rather similar in the three cases (25, 61, and 20 nm, respectively), a comparison that also suggests similar structures of the parent species.

Though the case we have made for oxygen protonation of the N-bound isomer of urea seems to us to be strong, the point cannot be taken as settled. When arguments of the type we have used are extended to the urea complex of $[(NH_3)_5Rh]^{3+}$, inconsistencies appear. Because Ru(III) is paramagnetic, the issue is not easily settled in solution by NMR evidence, nor, owing to rather rapid isomerization in the solid, does solid-state structure determination by X-ray diffraction seem feasible.

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Registry No. $[Ru(NH_3)_5OC(NH_2)_2]^{3+}$, 97352-84-6; $[Ru(NH_3)_5NH_2CONH_2]^{3+}$, 97352-85-7; $[Ru(NH_3)_5OP(OCH_3)_3]^{3+}$, 97352-86-8; $[Ru(NH_3)_5OP(OC_2H_5)_3]^{3+}$, 97352-87-9; $[Ru(NH_3)_5OC(CH_3)N(CH_3)_2]^{3+}$, 97352-88-0; $[Ru(NH_3)_5OCHNH_2]^{3+}$, 97352-94-8; $[Ru(NH_3)_5OCHN(CH_3)_2]^{3+}$, 97352-89-1; $[Ru(NH_3)_5NHCONH_2](PF_6)_2$, 97352-91-5; $[Ru(NH_3)_5O_3SCF_3](CF_3SO_3)_2$, 84278-98-8; $[Ru(NH_3)_5OC(NH_2)_2](PF_6)_3$, 97352-92-6; $[Ru(NH_3)_5OC(NH_2)_2](BF_4)_3$, 97352-93-7; $[Ru(NH_3)_5OCHNH_2](PF_6)_3$, 97352-95-9; $[Ru(NH_3)_5OCHN(CH_3)_2]_2(S_2O_6)_3$, 97352-96-0; $[Ru(NH_3)_5OC(CH_3)N(CH_3)_2]_2(S_2O_6)_3$, 97352-97-1; $[Ru(NH_3)_5OP(OCH_3)_3]_2(S_2O_6)_3$, 97414-11-4; $[Ru(NH_3)_5OP(OC_2H_5)_3]_2(S_2O_6)_3$, 97352-98-2.

Supplementary Material Available: Tables of rate constants for isomerization of $[(NH_3)_5RuNH_2CONH_2]^{3+}$ (Table II), acid hydrolysis of $[(NH_3)_5ML]^{n+}$ (Table III), and linkage isomerization and aquation of $[(NH_3)_5RuNH_2CONH_2]^{3+}$ (Table IV) and equilibrium and rate constants for linkage isomerism of $[(NH_3)_5ML]^{3+}$ (Table V) (4 pages). Ordering information is given on any current masthead page.

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N–O Bond Cleavage of Cluster-Coordinated Nitric Oxide Ligands Using Molecular Hydrogen

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The reaction of several clusters containing nitric oxide ligands with molecular hydrogen has been studied. For $HRu_3(CO)_{10}(NO)$ the products are $H_2Ru_3(NH)(CO)_9$, $HRu_3(NH_2)(CO)_{10}$, $H_4Ru_4(CO)_{12}$, trace amounts of $H_3Ru_4(NH_2)(CO)_{12}$, and a hexane-insoluble, THF-soluble precipitate. The compounds have been characterized by spectroscopy (including ^{15}N NMR) and for $HRu_3(NH_2)(CO)_{10}$ by a single-crystal X-ray crystallographic analysis (monoclinic crystal system, $P2_1/a$ space group, a = 11.778 (3) Å, b = 11.928 (3) Å, c = 12.010 (4) Å, β = 98.54 (2)°, Z = 4). A system was built that allowed the reactions to be followed directly by high-pressure liquid chromatography. A kinetic analysis of the disappearance of $HRu_3(CO)_{10}(NO)$ revealed that the reaction is first order in cluster concentration and is inhibited by CO. The rate also depends on the pressure of H_2, exhibiting a saturation effect above 1400 psig. The reduction of $Ru_3(NOCH_3)(CO)_{10}$ yields a product distribution similar to that found for $HRu_3(CO)_{10}(NO)$ with the important exception that no hexane-insoluble species is formed. Methanol is isolated from this reaction. The major product resulting from the reduction of $Ru_3(NOH)(CO)_{10}$ is the same hexane-insoluble product as found for $HRu_3(CO)_{10}(NO)$. A discussion of the mechanism of these reactions based upon the observations is presented.

Introduction

The need to remove toxic NO_x pollutants from the atmosphere has led to the development of several catalytic methods to reduce nitric oxide.[2,3] The reducing agent is either CO or H_2, and the products are shown in eq 1 and 2. The reduction of NO with

$$2NO + 2CO \rightleftharpoons N_2 + 2CO_2 \qquad (1)$$

$$2NO + 5H_2 \rightleftharpoons 2NH_3 + 2H_2O \qquad (2)$$

CO can be effected with use of either heterogeneous or homogeneous catalysts (the latter catalysts produce N_2O instead of N_2), while only the heterogeneous systems have been used for eq 2.

Recent interest in clusters containing the NO ligand has centered around the reduction of the N–O bond. In several examples cluster-coordinated NO has been reduced with CO to produce CO_2 and a nitrido cluster.[4,5] This reaction bears a striking similarity to eq 1 in which surface-absorbed nitrogen atoms have been postulated as intermediates. Alternatively, the triply bridging nitrosyl ligand in $(\eta^5\text{-}C_5H_4Me)_3Mn_3(NO)_4$ can be reduced to a μ_3-NH ligand with use of protons.[6] The electrons required for this conversion apparently are derived by sacrificially oxidizing some of the cluster species present. The use of protons and electrons to reduce a coordinated NO on the mononuclear complex $[Ru(trpy)(bpy)(NO)]^{3+}$ has been accomplished by electrochemical means.[7]

In a preliminary communication of this work we reported the first use of molecular hydrogen to reduce the coordinated NO of $HRu_3(CO)_{10}(NO)$.[8] Recently an independent study of this same reaction was also reported that involved the direct observation of the reaction solution by using a high-pressure infrared cell.[9] While the final products observed in both of these studies are similar, some differences in the proposed steps of the reaction exist. In this study we present the details of our work with $HRu_3(CO)_{10}(NO)$ and the closely related cluster $Ru_3(CO)_{10}(NOCH_3)$. The combination of these results has allowed us to address some

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