rationale to offer for this at the moment, and more experimental data are needed before any conclusion can be reached.

The present results show that the manganese–radical chains are well suited for yielding bulk magnetic materials, because, even if the interchain interactions are weak and mainly dipolar in nature, the strong intrachain coupling gives a high correlation at low temperature enhancing the interchain interaction. In order to reach the goal to increase the transition temperature, it will be necessary to pass from one dimension to two or three dimensions involving directly the metal ions and the radicals or to create interchain exchange pathways either by using appropriate coligands or by introducing suitable substituents on the radicals.

Registry No. Mn(hfac)$_2$NIT-*i*-Pr, 113547-95-8.

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Kinetics and Mechanism of the Ligand Substitution Reactions of *N*-(Hydroxyethyl)ethylenediaminetriacetate Complexes of Ruthenium(III) in Aqueous Solution

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The kinetics of the substitution reactions of Ru(hedtra)H$_2$O (hedtra = *N*-(hydroxyethyl)ethylenediaminetriacetate) with SCN$^-$, N$_3^-$, thiourea, and substituted thiourea were studied as a function of pH (2–8), temperature (20–45 °C), and pressure (0.1–100 MPa). The observed rate constants exhibit a characteristic decrease with increasing pH in the range 3.5–6 but remain constant in the ranges 2–3.5 and 6–8.5. The activation parameters measured in the pH-independent regions fall in the ranges $34 \le \Delta H^* < 40$ kJ mol^{-1}, $-108 \le \Delta S^* \le -92$ J K^{-1} mol^{-1}, and $-14 \le \Delta V^* \le -4$ cm^3 mol^{-1} and support the operation of an associatively activated ligand substitution process. The results are discussed in reference to data for the corresponding ethylenediaminetetraacetate complexes and in terms of the labilization effect of such chelate ligands.

Introduction

We recently reported a detailed kinetic and mechanistic study of the substitution behavior of ethylenediaminetetraacetate complexes of Ru(III) with a series of anionic and neutral ligands in aqueous solution.[2] In general, these complexes exhibit a remarkable lability in comparison to other nonchelated complexes of Ru(III).[3,4] A maximum reactivity is reached at 4 < pH < 6, which is ascribed to the participation of the very labile Ru(edta)H$_2$O$^-$ species, although the reason for this effect remains unresolved.[2,5–7] We concluded[2] that hydrogen bonding between the free carboxylate oxygen and the coordinated water molecule must account for the high lability of the water molecule. This can either result in the creation of an open area and accessible site for associative substitution or labilize the water molecule directly by affecting the metal–oxygen bond strength.[5]

In an effort to gain more insight into the intimate nature of this catalytic effect, we are presently investigating the influence of the nature of the pendant group in a series of Ru^{III}(L)H$_2$O complexes, where L denotes N-substituted ethylenediaminetriacetate. Ogino and co-workers demonstrated that the transient coordination of the pendant group plays an important role in the unexpected rapid substitution reactions of the corresponding Cr(III) complexes.[7–9] In this paper we report our results for the substitution of Ru(hedtra)H$_2$O by SCN$^-$, N$_3^-$, SC(NH$_2$)$_2$, SC(NHMe)$_2$, and SC(NMe$_2$)$_2$, where hedtra = *N*-(hydroxyethyl)ethylenediaminetriacetate. This complex is substantially less labile than the Ru(edta)H$_2$O$^-$ complex and demonstrates the important effect of the pendant carboxylate group in the latter case.

Experimental Section

Materials. K[Ru(hedtra)Cl] was prepared from K$_2$[RuCl$_5$(H$_2$O)] in the following way: To 0.5 g (1.33 mmol) of K$_2$[RuCl$_5$(H$_2$O)] in 10 mL of 0.001 M HClO$_4$ was added 0.506 g (1.33 mmol) of Na$_3$hedtra in 15 mL of 0.001 M HClO$_4$. The solution was refluxed for ca. 2 h, followed by evaporation on a water bath to a small volume and addition of ethanol, which produced a greenish yellow precipitate. The latter was filtered off, washed with a cold water–ethanol (1:9) mixture, and dried in a desiccator. Anal.[10] Found (calcd): C, 26.6 (26.6); H, 4.3 (3.4); N, 6.5 (6.2). All other chemicals used were of analytical reagent grade, and deionized water was used to prepare all solutions. Acetate–acetic acid, borate, and phosphate buffers were used to maintain a constant pH. The ionic strength of the solutions was adjusted with Na$_2$SO$_4$.

Instrumentation. Substitution reactions were followed spectrophotometrically by using a Shimadzu UV 250 spectrophotometer and a Durrum D110 stopped-flow instrument. Kinetic measurements at elevated pressure (up to 100 MPa) were performed on a homemade high-pressure stopped-flow unit.[11] All the instruments used for the kinetic measurements were thermostated to ±0.1 °C. The absorbance–time plots were analyzed with the aid of a data acquisition system,[12] and the corresponding first-order plots were linear for at least 2–3 half-lives of the reaction. pH measurements were carried out with a Radiometer PHM 64 instrument.

Results and Discussion

The K[Ru(hedtra)Cl] complex was characterized by elemental analyses and IR data. It exhibits a characteristic band at 1632 cm^{-1} due to the coordination of carboxylate to the Ru center. This complex hydrolyzes rapidly on dissolution to produce the Ru(hedtra)H$_2$O species, which exhibits a maximum absorbance at 285 nm. This peak shifts to 330 nm on increasing the pH (see Figure 1) with an isosbestic point at 312 nm due to the formation of the Ru(hedtra)OH$^-$ species. Similar spectral changes have also been reported for the deprotonation of Cr(hedtra)H$_2$O and Cr-

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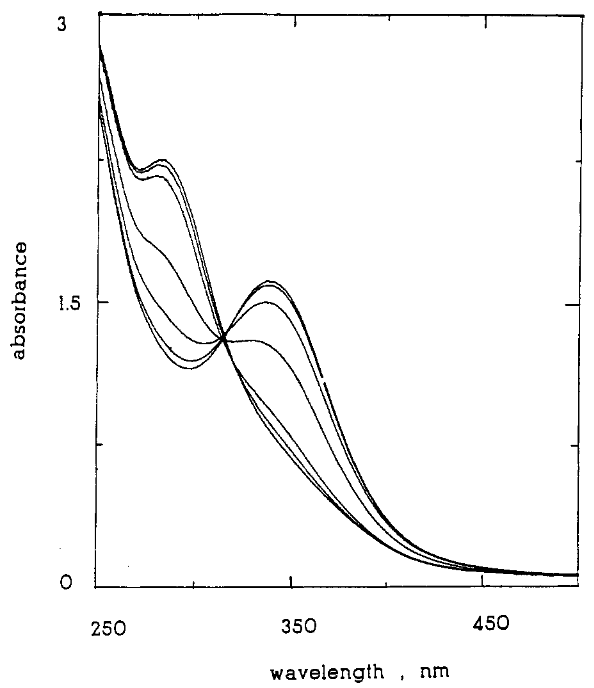

Figure 1. UV–vis spectra of $Ru^{III}(hedtra)H_2O$ as a function of pH. $[Ru^{III}(hedtra)H_2O] = 1.0 \times 10^{-3}$ M; ionic strength = 0.2 M (Na_2SO_4). pH = 3.0, 3.4, 3.9, 4.9, 5.7, 6.4, and 7.7 (top to bottom at 285 nm).

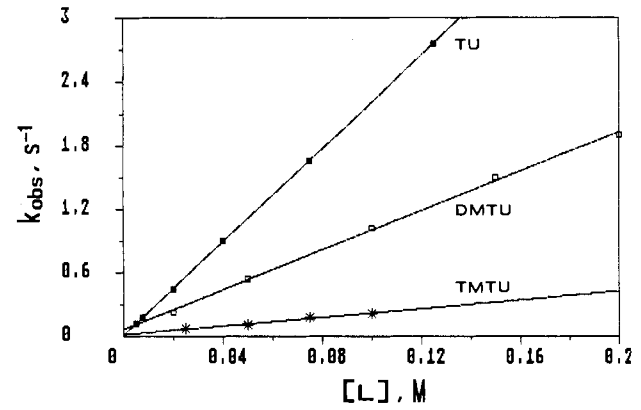

Figure 2. Dependence of k_{obsd} on [L] for the reaction of $Ru(hedtra)H_2O$ with a series of ligands. $[Ru(III)] = 5.0 \times 10^{-4}$ M; pH = 3.0 (acetate buffer, 0.1 M); ionic strength = 0.2 M (Na_2SO_4); temp = 25 °C; TU = thiourea; DMTU = dimethylthiourea; TMTU = tetramethylthiourea.

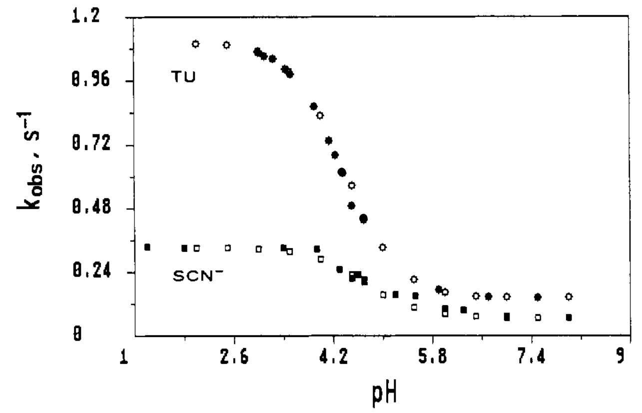

Figure 3. Variation of k_{obsd} with pH for the reaction of $Ru(hedtra)H_2O$ with L. $[Ru(III)] = 5.0 \times 10^{-4}$ M; [L] = 0.05 M; ionic strength = 0.2 M (Na_2SO_4); temp = 25 °C; TU = thiourea. Open points are calculated by using resolved rate constants; closed points are observed rate constants.

$(medtra)H_2O$,[8,9] where medtra = *N*-methylethylenediaminetriacetate. From the spectral changes in Figure 1, a plot of the absorbance at 285 nm versus pH for a 1 mM complex solution at an ionic strength of 0.2 M results in a pK_a value for the $Ru(hedtra)H_2O$ complex of 4.95 at 25 °C. A potentiometric titration of the complex resulted in a value of 4.90 under similar experimental conditions. The assignment of the 285-nm band to the aqua complex was further underlined by treating solutions of $Ru(hedtra)Cl^-$ with $AgClO_4$ to remove the free chloride in solution. Addition of excess chloride to the aqua complex results in almost no spectral changes for $[Cl^-] \leq 0.1$ M and a broadening of the band at 285 nm and shift toward longer wavelength at $[Cl^-] > 0.1$ M. This can be ascribed to the partial formation of the chloro complex, and a formation constant of 0.14 M^{-1} for this species was estimated from the observed spectral changes. This means that, at complex concentrations in the range of 1 mM, as used in this investigation, and in the absence of added chloride, the chloro complex is completely converted to the aqua complex. In addition, these observations stress the lability of the chloride ligand in this complex. The pK_a value of 4.9 for the $Ru(hedtra)H_2O$ complex is significantly lower than the value of 7.6 for the $Ru(edta)H_2O^-$ complex.[2] This can partly be ascribed to the effect of the negative charge on the edta complex, which will make it more difficult to deprotonate the complex, and partly to the higher stability of the $Ru-H_2O$ bond in the case of the hedtra complex (see further discussion), which should be accompanied by a weaking of the O–H bond, i.e. a lower pK_a value. A similar difference in pK_a was reported for $Fe^{III}(edta)H_2O^-$ and $Fe^{III}(hedtra)H_2O$, viz. 7.6 and 4.1, respectively.[13,14] In the case of the corresponding Cr(III) complexes the difference is significantly smaller, viz. 7.4 and 6.1, respectively,[8] indicating that the $Cr-H_2O$ bond strength does not change drastically on replacing edta by hedtra.

Preliminary kinetic experiments demonstrated that the employed buffer components, as well as the medium selected to control the ionic strength of the solutions, did not interfere with the investigated substitution reactions. The nucleophilicity of the selected ligands is so high that the other potential nucleophiles, when these are added to the ligand-containing solution prior to mixing with the aqua complex, have no significant effect. The substitution reactions of the type in eq 1 were studied under

$$Ru(hedtra)(H_2O/OH^-) + L \rightarrow Ru(hedtra)L + H_2O/OH^- \qquad (1)$$

pseudo-first-order conditions, and the observed rate constants increase linearly with increasing [L], as demonstrated for a few typical examples in Figure 2. The plots exhibit very minor intercepts, which are presumably due to a contribution from the reverse aquation reaction. Here it is important to note that the selected L are all strong nucleophiles in order to stabilize the Ru(hedtra)L species. Typical values for the observed rate constants for the reverse aquation reactions, i.e. the intercepts in Figure 2, are 0.03 (L = TU), 0.06 (L = DMTU) and 0.01 s^{-1} (L = TMTU). Combining these values with the forward rate constants (slopes of the lines in Figure 2) results in complex formation constants of 750, 160, and 210 M^{-1} for L = TU, DMTU, and TMTU, respectively. Similar values were found for the other investigated ligands. The substitution reactions exhibit a characteristic pH dependence (as shown in Figure 3), which can be interpreted in terms of the mechanism outlined in (2), for which the rate expression is given in (3).

$$Ru(hedtra)H_2O \overset{K_a}{\rightleftharpoons} Ru(hedtra)OH^- + H^+$$

$$Ru(hedtra)H_2O + L \xrightarrow{k_1} Ru(hedtra)L + H_2O \qquad (2)$$

$$Ru(hedtra)OH^- + L \xrightarrow{k_2} Ru(hedtra)L + OH^-$$

$$k_{obsd} = \left(\frac{k_1[H^+] + k_2K_a}{[H^+] + K_a}\right)[L] \qquad (3)$$

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Table I. Summary of k_{obsd} as a Function of Temperature and Pressure for the Reaction

$$Ru^{III}(hedtra)H_2O + L \rightarrow Ru^{III}(hedtra)L + H_2O$$

ligand	[ligand], M	temp, °C	press., MPa	k_{obsd}, s^{-1}
thiourea[a]	0.05	25	5	1.07 ± 0.03
			25	1.15 ± 0.04
			50	1.19 ± 0.04
			75	1.24 ± 0.02
			100	1.27 ± 0.04
	0.005	25	0.1	0.113 ± 0.010
		30		0.143 ± 0.005
		35		0.178 ± 0.002
		40		0.223 ± 0.004
		45		0.283 ± 0.005
dimethylthiourea[a]	0.05	25	5	0.525 ± 0.006
			25	0.558 ± 0.005
			50	0.609 ± 0.006
			75	0.627 ± 0.006
			100	0.671 ± 0.005
	0.02	25	0.1	0.204 ± 0.005
		28		0.272 ± 0.010
		34		0.341 ± 0.007
		41		0.476 ± 0.020
tetramethylthiourea[a]	0.075	25	5	0.173 ± 0.003
			25	0.204 ± 0.005
			50	0.227 ± 0.004
			75	0.242 ± 0.006
			100	0.255 ± 0.006
	0.025	25	0.1	0.062 ± 0.002
		30		0.081 ± 0.005
		35		0.100 ± 0.005
		40		0.130 ± 0.005
		45		0.182 ± 0.004
thiocyanate[a]	0.1	25	5	0.612 ± 0.020
			25	0.643 ± 0.011
			50	0.682 ± 0.016
			75	0.733 ± 0.023
			100	0.815 ± 0.015
	0.04	25	0.1	0.272 ± 0.003
		30		0.364 ± 0.005
		35		0.448 ± 0.006
		40		0.617 ± 0.007
thiourea[b]	0.05	25	5	0.217 ± 0.021
			25	0.232 ± 0.022
			50	0.247 ± 0.010
			75	0.272 ± 0.023
			100	0.297 ± 0.039
thiocyanate[b]	0.05	25	5	0.042 ± 0.003
			25	0.047 ± 0.003
			50	0.051 ± 0.002
			75	0.056 ± 0.004
			100	0.065 ± 0.003
	0.075	25	0.1	0.079 ± 0.006
		29.7		0.097 ± 0.005
		34		0.134 ± 0.004
		39		0.170 ± 0.007
		45.7		0.238 ± 0.010
azide[b]	0.1	25	5	0.21 ± 0.01
			25	0.26 ± 0.03
			50	0.29 ± 0.04
			75	0.34 ± 0.05
			100	0.37 ± 0.04
	0.05	25	0.1	0.133 ± 0.005
		30		0.179 ± 0.011
		35		0.240 ± 0.006
		39.5		0.328 ± 0.005
		44.7		0.434 ± 0.008

[a] [Ru(III)] = 5.0×10^{-4} M; pH = 3.0; acetate–acetic acid buffer, 0.1 M; ionic strength = 0.2 M (Na_2SO_4). [b] [Ru(III)] = 5.0×10^{-4} M; pH = 8.3; HCl–borate buffer, 0.025 M; ionic strength = 0.2 M (Na_2SO_4).

Under limiting conditions eq 3 reduces to $k_{obsd} = k_1[L]$ and $k_{obsd} = k_2[L]$ at low and high pH, respectively. The sigmoid-shaped curves in Figure 3 underline the validity of eq 3, and an appropriate fit of the experimental data results in $k_1 = 6.8 \pm 0.3$, $k_2 = 1.1 \pm 0.2$ M^{-1} s^{-1}, and $pK_a = 4.7 \pm 0.3$ for the reaction with L = SCN^-. The data for the reaction with L = $SC(NH_2)_2$ results in $k_1 = 22.6 \pm 0.8$, $k_2 = 2.8 \pm 0.5$ M^{-1} s^{-1}, and $pK_a = 4.4 \pm 0.1$. These pK_a values are in fair agreement with those reported above as obtained from independent measurements. The significant difference between k_1 and k_2 once again demonstrates the higher lability of the aqua complex as compared to that of the hydroxo species, and a more detailed interpretation is presented along with the discussion of the activation parameters. However, it is important to note that the pH dependence observed for the substitution of Ru(hedtra)H_2O differs significantly from that reported for Ru(edta)H_2O^-.[2] In the latter case a decrease in rate constant occurs at pH < 4 due to the protonation of the uncoordinated acetate moiety of the edta ligand. In the present case such a protonation of the *N*-hydroxyethyl group is not possible and the observed rate constant remains constant at lower pH.

Table II. Summary of Rate Parameters for the Reaction[a]

$$Ru^{III}(hedtra)H_2O + L \rightarrow Ru^{III}(hedtra)L + H_2O$$

ligand	pH	k (25 °C), M^{-1} s^{-1}	ΔH^*, kJ mol^{-1}	ΔS^*, J K^{-1} mol^{-1}	ΔV^*, cm^3 mol^{-1}
thiourea	3.0	22.6 ± 1.0	34 ± 1	−105 ± 2	−4.1 ± 0.7
	8.3	2.8 ± 0.5			−7.1 ± 0.5
dimethylthiourea	3.0	9.4 ± 2.0	37 ± 4	−99 ± 13	−6.2 ± 0.5
tetramethylthiourea	3.0	2.05 ± 0.2	39 ± 2	−108 ± 5	−10.4 ± 1.0
thiocyanate	3.0	6.8 ± 0.3	39 ± 2	−100 ± 7	−7.3 ± 0.6
	8.3	1.1 ± 0.1	40 ± 2	−105 ± 5	−10.8 ± 0.7
azide	5.0	18.5 ± 2.6	38 ± 1	−92 ± 2	
	8.3	2.6 ± 0.1	45 ± 1	−86 ± 3	−14.1 ± 1.2

[a] Acetic acid–acetate buffer, 0.1 M, for pH = 3.0; HCl–borate buffer, 0.025 M, for pH = 8.3; ionic strength = 0.2 M (Na_2SO_4).

The effect of temperature and pressure on k_{obsd} was studied under the limiting pH conditions, i.e. where a change in pH due to a chance in temperature or pressure should not affect the observed rate constant. The results are summarized as rate constants and activation parameters for various L in Tables I and II, respectively. Plots of ln k versus pressure were all linear within the experimental error limits over the pressure range studied, and ΔV^* was estimated from the slope ($=-\Delta V^*/RT$) of such plots. It follows from Table II that the studied reactions are all characterized by low values of ΔH^* and significantly negative values of ΔS^* and ΔV^*. An increase in steric hindrance on the entering ligand (introduction of methyl substituents on thiourea) results in a significant decrease in k_1 which is accompanied by an increase in ΔH^* and a constant ΔS^*. Similar trends were reported for the substitution behavior of the Ru(edta)H_2O^- complex.[2] In the case of the substitution by SCN^- and N_3^-, the activation parameters were determined at pH 3.0 and 8.3. ΔH^* and ΔS^* do not exhibit a significant dependence on pH for these reactions, which means that the substitution mechanisms of Ru(hedtra)H_2O and Ru(hedtra)OH^- are indeed similar.

The values of ΔV^* in Table II underline the operation of an associative mechanism. The more negative ΔV^* found for the reactions with substituted thiourea nicely demonstrates the dependence of the volume decrease during bond formation on the partial molar volume of the entering ligand. The observed ΔV^* for substitution by neutral ligands can mainly be ascribed to intrinsic volume changes. The more negative ΔV^* values observed for the reaction of Ru(hedtra)OH^- with SCN^- and N_3^- at pH 8.3 are ascribed to solvational changes resulting from charge concentration, which will be accompanied by an increase in electrostriction and a decrease in volume. These values are very similar to those found for the corresponding reactions of Ru(edta)H_2O^-. The reaction with N_3^- could not be measured at pH 3.0 due to the protonation of N_3^- under such conditions. The data at pH 5 do demonstrate the significantly higher lability of the aqua complex, but the activation parameters cannot be interpreted due to the influence of the acid dissociation equilibrium under such conditions. A systematic comparison will be made in a forthcoming paper following completion of a series of studies on the

Ru(medtra)H_2O system,[15] where medtra = *N*-methylethylenediaminetriacetate. The magnitude of ΔV^* suggests the operation of an I_a rather than a limiting A mechanism.[16]

A comparison of the substitution rate constants in Table II with those reported previously[2] for the substitution of Ru(Hedta)H_2O, Ru(edta)H_2O^- and Ru(edta)OH^{2-} clearly indicates that the edta complexes are at least 1 order of magnitude more reactive and in some cases more than 2 orders of magnitude for the Ru(edta)H_2O^- species. This must be due to the labilizing effect of the additional (uncoordinated) acetate ligand as compared to that of the *N*-hydroxyethyl group in the hedtra complexes, which reaches a maximum in the case of the Ru(edta)H_2O^- complex, i.e. where the acetate substituent is unprotonated and H_2O is the leaving group. Nevertheless, even for the protonated form of the ligand in Ru(Hedta)H_2O, the acetic acid moiety still has a substantially higher labilization effect than the *N*-hydroxyethyl group. This difference is presumably due to the large difference in basicity of these ligand moieties. The intimate nature of this labilization effect remains uncertain, and various studies are presently under way to clarify this aspect.

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Registry No. Ru^{III}(hedtra)H_2O, 118170-06-2; K[Ru(hedta)Cl], 57132-64-6; thiourea, 62-56-6; dimethylthiourea, 534-13-4; tetramethylthiourea, 2782-91-4; thiocyanate, 302-04-5; azide, 14343-69-2.

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Cobalt-Induced Facile Degradation of Phenylurea to Ammonia, Carbon Dioxide, and Anilinium Ion and Other Reactions of Linkage Isomeric Cobalt(III) Complexes of Phenylurea

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A search for metal ion promoted hydrolysis of urea and the factors influencing linkage isomerization on a metal has led us to prepare and examine reactivities of N- and O-bound phenylurea complexes of pentaamminecobalt(III). The N-bonded isomer reacts in aqueous acid to yield principally $[Co(NH_3)_6]^{3+}$, CO_2, and anilinium ion (ca. 70%) but also via parallel paths leading to $[(NH_3)_5CoOC(NH_2)NHC_6H_5]^{3+}$ (linkage isomerization) and $[(NH_3)_5CoOH_2]^{3+}$ (aquation). The major path involves an elimination reaction of $[(NH_3)_5CoNH_2CONHC_6H_5]^{3+}$ to give anilinium ion and $[(NH_3)_5CoNCO]^{2+}$. The latter complex, which has been isolated and characterized, is known to undergo rapid hydration (pH < 2) to $[(NH_3)_5CoNH_2CO_2H]^{3+}$, which subsequently decomposes along three parallel paths to $[Co(NH_3)_6]^{3+}$ and traces of $[(NH_3)_5CoOH_2]^{3+}$ and $[(NH_3)_5CoOCONH_2]^{3+}$. Kinetic data for the three parallel reactions of $[(NH_3)_5CoNH_2CONHC_6H_5]^{3+}$ in aqueous $HClO_4$ (1.0 M, 25.0 °C) are $k_{elim} = 1.04 \times 10^{-2}\ s^{-1}$ (elimination), $k_{NO} = 2.39 \times 10^{-3}\ s^{-1}$ (isomerization), and $k_{aq} = 1.13 \times 10^{-3}\ s^{-1}$ (aquation). A single-crystal structure reveals that the urea exo C–N bond is 0.11 Å longer than the endo C–N bond and, as in uncoordinated phenylurea, the electron-withdrawing phenyl ring is neither planar with nor conjugated to the urea moiety. These features are likely retained in the protonated form and account for the facility of the elimination path. By contrast, neither elimination nor hydrolysis of the O-bonded phenylurea complex was detected; instead it slowly undergoes parallel aquation and O- to N-linkage isomerization. Both processes are base-catalyzed, and each obeys a rate law of the form $k(\text{obsd}) = k_s + k_{OH}[OH^-]$. The equilibrium constant ($K'_{NO} = k_{NO}/k_{ON} = 166$) reflects the strong thermodynamic preference for the O rather than the N terminus of the neutral phenylurea molecule. However, the observed equilibrium is pH-dependent ($K'(\text{obsd}) = K'_{NO}[H^+]/(K_a + [H^+])$); for pH > 3, the N-bonded isomer is more stable due to its selective deprotonation ($K'_{NO}(\text{obsd}) \approx 10^{-5}$, pH 6.2). The single-crystal structure determination of $[(NH_3)_5CoNHCONHC_6H_5](ClO_4)_2\cdot H_2O$ shows the cobalt in an approximately octahedral environment with phenylurea bonded as its anion through the indicated nitrogen center. As observed for the free ligand, the phenyl substituent is twisted (37°) with respect to the approximately planar urea moiety. The compound crystallizes in the monoclinic system ($\beta = 91.64°$), with $V = 1887.0$ Å^3, space group $C2/c$, $Z = 8$, $a = 15.751$ (6) Å, $b = 12.277$ (5) Å, $c = 9.762$ Å, and $R = 0.046$ and $R_w = 0.043$ for 1381 diffractometer data (244 variables) with $I \geq 3\sigma(I)$, $\mu = 105.47\ cm^{-1}$, and $F(000) = 1023.96$.

Introduction

The Ni(II)-containing enzyme[2] jack bean urease catalyzes the degradation of urea to ammonia and carbon dioxide by a factor of 10^{14} (pH 7.0, 38 °C).[3] Since it is believed that specific coordination of urea to Ni(II) is intrinsic to the mechanism of catalysis,[3] there is special interest in synthesizing metal complexes of urea that might model urease by undergoing facile decomposition to NH_3 and CO_2. The enzymic degradation of urea is currently believed to be a hydrolysis[4] (eq 1) rather than the elimination reaction (eq 2) that is known[5] for nonenzymic degradation of urea in aqueous media at pH 7–14.

$$H_2NCONH_2 + H_2O \rightarrow H_2NCO_2H + NH_3 \quad (1)$$

$$H_2NCONH_2 + H_2O \rightarrow HNCO + NH_3 + H_2O \quad (2)$$

The latter process is independent of pH between 2 and 12.[6] Sumner and co-workers first demonstrated that the urease reaction yielded ammonium carbamate rather than free cyanate[7] but

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