Our conclusion suggests that hydroxide ion plays a crucial role in outer-sphere redox reactions of conjugate-base forms of aquo ions. At least in these Ti(III)–Ru(III) cases, hydroxide ion functions as an outer-sphere electron mediator, a kind of "bridging ligand". Since electronic reorganizations are rapid with respect to vibration times, such an interaction is quite possible even in a short-lived "encounter complex".[20] The requirement of hydroxide mediation of electrons does imply that the hydroxo ligand is physically located near the line joining the centers of the Ru and Ti atoms. This geometric requirement indicates that electron transfer could occur in only a small fraction (e.g., 0.1%) of collisions between reacting cations. The reactions of present interest are sufficiently slow as to be consistent with a factor of that magnitude.

Registry No. Ru, 7440-18-8; $Ru(acac)_3$, 14284-93-6; $Ru_2(OAc)_4$, 30553-94-7; Ti, 7440-32-6.

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Effect of the Nature of Other Ligands on the Rate of Nitrito-to-Nitro Linkage Isomerization of Octahedral Cobalt(III)–Amine Complexes in Aqueous Solution

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The spontaneous nitrito-to-nitro linkage isomerziation was followed spectrophotometrically for a variety of octahedral (nitrito)(amine)cobalt(III) complexes in aqueous solution to examine the effect of ligands other than the reacting nitrito group on the isomerization rate. The following characteristics were found: (i) The isomerization is retarded relative to that of $[Co(NH_3)_5(ONO)]^{2+}$ for the complexes with chelate rings trans to each other, but it is accelerated for those with chelate rings in other forms. (ii) An increase in the chelate ring size has little effect on the rate constant. (iii) The isomerization rate of *cis*-$[Co(en)_2(X)(ONO)]^{n+}$ is relatively insensitive to the nature of X ligands, while that of *trans*-$[Co(en)_2(X)(ONO)]^{n+}$ differs greatly for different X ligands trans to the ONO group. (iv) A change in net charge on the complex has no appreciable effect on the rate constant. These findings were discussed in the light of the reaction mechanisms proposed so far.

Introduction

It is well-known[1] that the nitrite ion NO_2^- is coordinated through either its O or N atom in Co(III) complexes and that the O-bound nitrito complexes isomerize spontaneously and stereoretentively[2] to the more stable N-bound nitro complexes both in the solid state and in solution. Furthermore, this reaction (called a nitrito-to-nitro linkage isomerization[3]) is confirmed to be an intramolecular process[4,5] for which a seven-coordinated[1,5-7] or six-coordinate π-bonded species[8] has been proposed as a reaction intermediate. However, little attention has been paid to the kinetic aspects of this reaction in solution. In fact, only a limited number of nitrito Co(III) complexes have been subjected to kinetic measurements: $[Co(NH_3)_5(ONO)]^{2+}$,[7-10] *trans*-$[Co(NH_3)_2(py)_2(ONO)_2]^+$,[11] *cis*- and *trans*-$[Co(en)_2(ONO)_2]^+$,[12-14] *cis*-$[Co(en)_2(NO_2)(ONO)]^+$,[10] *cis*-$[Co(NH_3)_4(ONO)_2]^+$,[15] and *cis*-$[Co(NH_3)_4(OH_2)(ONO)]^{2+}$[15] in aqueous solution.

By contrast, acid hydrolysis reactions, for example, have been extensively studied for a huge number of chloro(amine)cobalt(III) complexes to elucidate the factors determining the rate of chloride ion release, the factors examined so far being net charge of the complex, the number, size, and conformation of chelate ligands including various types of macrocyclic amines (and imines), and the electronic nature of the ligands cis and trans to the leaving Cl^- ion.[16-26] Furthermore, optically active complexes have been successfully utilized to obtain the information on the steric course of the reaction.[27,28] These elaborate studies have made signifciant

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contributions to the understanding of kinetic and mechanistic aspects of acid hydrolysis in Co(III) complexes. In the present study, the spontaneous nitrito-to-nitro linkage isomerization reaction was followed for several octahedral Co(III)–amine complexes in aqueous solution, and an attempt was made to examine the effect of varying the nature and position of ligands other than the reacting ONO group on this isomerization rate.

Experimental Section

Preparation of Complexes. $[Co(NH_3)_5(ONO)]Cl_2$,[9] *cis*-$[Co(NH_3)_4(ONO)_2]NO_3$,[15] *trans*-$[Co(en)_2(ONO)_2]NO_3$,[29,30] *trans*-$[Co(en)_2(NCS)(ONO)]NO_3$,[9b] *cis*-$[Co(en)_2(NO_2)(ONO)]NO_3$,[10] and *cis*-$[Co(en)_2(ONO)_2]NO_3$[30,31] were prepared according to the methods described in the literature. In addition to these six complexes, the following nitrito complexes were obtained in a usual way[10] in which aqua complexes directly prepared or derived from the chloro complexes were allowed to react with $NaNO_2$ at pH 4 (adjusted with acetic acid) in ice-cold water, followed by the addition of $NaClO_4$ or $NaNO_3$: *cis*- and *trans*-$[Co(en)_2(NH_3)(ONO)](NO_3)_2$ (from the corresponding aqua complexes[32]), π- and ω-$[Co(en)(dien)(ONO)](NO_3)_2$ (Ag^+-induced aquation of the corresponding chloro complexes[33]), *trans*-$[Co(R,S,S,R\text{-cyclam})(NH_3)(ONO)](ClO_4)_2$ (base hydrolysis of the chloro complex[34]), *cis*-$[Co(en)_2(NCS)(ONO)]NO_3$ (spontaneous aquation of the chloro complex[35]), *cis*-$[Co(en)_2(CN)(ONO)]NO_3$ (from the aqua complex[22,36]), and *cis*-$[Co(tn)_2(NH_3)(ONO)](ClO_4)_2$ (Ag^+-induced aquation of the chloro complex[37]). Since the charge of the nitrito complex formed is lower by one than that of the corresponding aqua complex used as a starting material, the formation of the nitrito complex was easily and effectively monitored by ion-exchange chromatography in the preparation procedure. For *cis*-$[Co(en)_2(NCS)(ONO)]^+$ and *cis*-$[Co(en)_2(NO_2)(ONO)]^+$, optically active species were also prepared by the reaction with $NaNO_2$ of the Λ-cis isomers of the corresponding aqua complexes, which were obtained by aquation of the respective chloro complexes resolved with ammonium *d*-3-bromocamphor-9-sulfonate.[38]

The attempt to isolate *trans*-$[Co(en)_2(NO_2)(ONO)]^+$ starting with *trans*-$[Co(en)_2(NO_2)(OH_2)]^{2+}$ in a usual way[10] resulted in the formation of *trans*-$[Co(en)_2(NO_2)_2]^+$ only, as already reported by Pearson et al.[10] This fact was attributed to extremely rapid isomerization of the *trans*-nitronitrito complex to the dinitro complex as shown later but not to the low solubility of *trans*-$[Co(en)_2(NO_2)_2]NO_3$ as supposed by Pearson et al.[10] Similarly, the reaction of *trans*-$[Co(en)_2(CN)(OH_2)]^{2+}$[36,39] with aqueous $NaNO_2$ gave *trans*-$[Co(en)_2(CN)(NO_2)]^+$ but not the nitrito complex even at a considerably low temperature.

The purity of the nitrito complexes thus obtained was found satisfactory by checking them with ion-exchange chromatography and absorption spectra of aqueous nitro complexes derived from them in warm water in the dark. In addition, the nitro complexes thus derived were also subjected to ion-exchange chromatography to confirm that no detectable impurities were present either in the nitrito or in the nitro complexes.

Kinetic Measurements. The isomerization was followed by detecting the change in the optical density of an aqueous nitrito complex at an appropriate wavelength in the d–d transition region with a Shimadzu UV-200 double-beam spectrophotometer, the cell compartment of which was thermostated within at least ±0.1 °C. The concentrations of the nitrito complexes were in the range of 5 mM, and no diverse electrolyte was added to adjust the ionic strength, though a slight dependence of the rate constant on the ionic strength was recognized.[7,8a,8c,10] Freshly prepared nitrito complexes were used for the kinetic runs, since they isomerized even in the solid state.[1,5,14] After the final absorption spectrum of the sample solution, which had been kept standing over 1–3 days in the dark, was recorded and proved to be identical with that of the authentic nitro complex,[40] the solution was subjected to ion-exchange chromatography to further confirm that the isomerization went to completion and no side reactions like aquation or cis–trans isomerization took place.

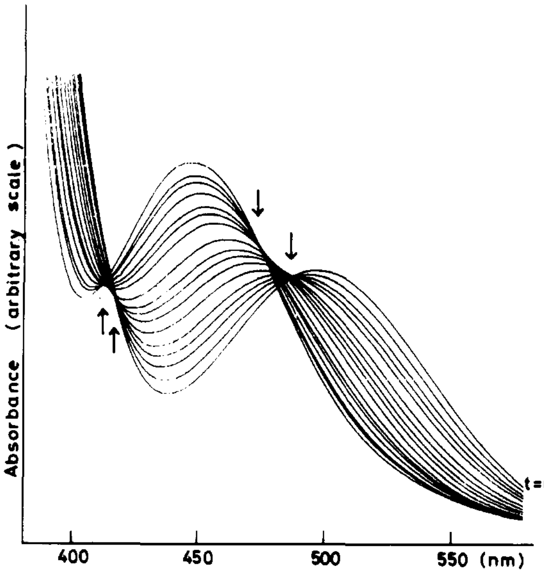

Figure 1. Change in the absorption spectrum of aqueous *cis*-$[Co(NH_3)_4(ONO)_2]^+$ accompanied by its isomerization to the nitro complex.

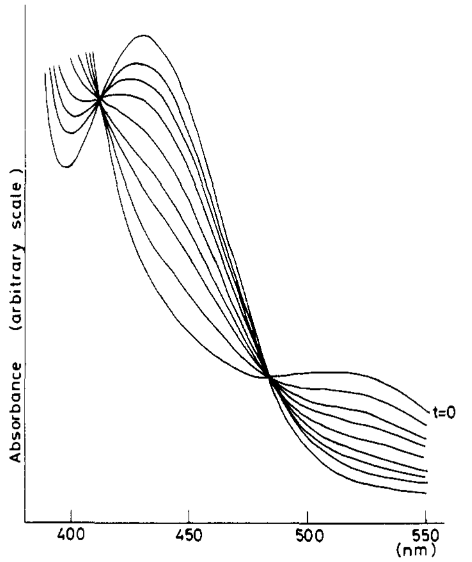

Figure 2. Change in the absorption spectrum of aqueous *trans*-$[Co(en)_2(ONO)_2]^+$ accompanied by its isomerization to the nitro complex.

The CD spectra of Λ-*cis*-$[Co(en)_2(NO_2)(ONO)]^+$ and Λ-*cis*-$[Co(en)_2(NCS)(ONO)]^+$ were also recorded at appropriate time intervals with a Jasco J-40CS spectropolarimeter.

Results

Figure 1 shows the change in the absorption spectrum with time of aqueous *cis*-$[Co(NH_3)_4(ONO)_2]^+$. Two sets of isos-

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(40) The λ_{max} of *cis*-$[Co(en)_2(CN)(NO_2)]^+$ is reported to be 437 nm in ref 36, but our authentic sample exhibits an absorption maximum at 423–424 nm. Judging from the λ_{max} values of the *cis*-dinitro (439 nm) and -dicyano (400 nm) complexes, we think the value of 437 nm reported earlier is probably in error.

bestic points observed (indicated by arrows) demonstrate that this complex isomerizes in two successive steps, as expected, from the dinitrito through the nitronitrito to the dinitro complex, though Yalman and Kuwana[15] reported almost 30 years ago that this complex isomerized in a single step. A similar two-step reaction was found in *cis*-$[Co(en)_2(ONO)_2]^+$, again though Adell[12a] regarded its isomerization as an apparent single-step reaction. Recent experimental data reported by Seel and Meyer[13] and by Rindermann et al.[14] are in complete agreement with out observation. Thus, the rate constants k_1 and k_2 referring to the first and second steps had to be determined graphically[41] for these two *cis*-dinitrito complexes. Nevertheless, the k_2 value thus derived for *cis*-$[Co(en)_2(ONO)_2]^+$ agreed well with the rate constant obtained when *cis*-$[Co(en)_2(NO_2)(ONO)]^+$ was used as a reactant.

On the other hand, only one set of isosbestic points is observed throughout the isomerization of *trans*-$[Co(en)_2(ONO)_2]^+$, as shown in Figure 2, though it has two reacting ONO groups. This means that the *trans*-dinitrito complex isomerizes apparently in a single step.[13,14] Adell has already found an apparent first-order kinetics for this complex[12a] as well as for *trans*-$[Co(NH_3)_2(py)_2(ONO)_2]^+$.[11] He rationalized this seemingly anomalous behavior by assuming $k_1 = 2k_2$. However, his assumption is in conflict with out observation shown in Figure 2. Since the final product is proved to be the dinitro complex, either k_1 or k_2 must be too great to be determined in order to meet our observation. The fact that the reaction of *trans*-$[Co(en)_2(NO_2)(OH_2)]^{2+}$ with $NaNO_2$ gives *trans*-$[Co(en)_2(NO_2)_2]^+$ but not *trans*-$[Co(en)_2(NO_2)(ONO)]^+$[42] (see Experimental Section and ref 10) leads us to conclude that the second step is too rapid to be followed by the usual techniques. The same conclusion has been recently drawn by Rindermann et al.[14] The first-order kinetics found by Adell for *trans*-$[Co(NH_3)(py)_2(ONO)_2]^+$ should be, therefore, interpreted in the same way. In fact, he isolated *trans*-$[Co(NH_3)_2(py)_2(NO_2)_2]^+$ but not *trans*-$[Co(NH_3)_2(py)_2(NO_2)(ONO)]^+$ by treating *trans*-$[Co(NH_3)_2(py)_2(NO_2)(Cl)]^+$ successively with aqueous $AgNO_3$ and $NaNO_2$.[12b] Similarly, the isomerization of *trans*-$[Co(en)_2(CN)(ONO)]^+$ may be too fast to be measured, since the corresponding cyanoaqua complex gives the cyanonitro complex only. Details of the kinetics of *trans*-$[Co(NH_3)_2(py)_2(ONO)_2]^+$ and its related complexes will be reported elsewhere.

Since each of the dinitrito complexes examined here has two equivalent ONO groups, their rate constants k_1 summarized in the following tables are half the rate constants obtained by the usual analysis. For mononitrito complexes, only one set of isosbestic points was observed in the absorption spectra and thus the rate constants were directly determined by the clean first-order kinetics observed.

Figure 3 shows the change in the CD spectrum of aqueous Λ-*cis*-$[Co(en)_2(NO_2)(ONO)]^+$ with reaction time. It is seen that two isodichroic points are observed throughout the reaction and the final CD pattern agrees with that of Λ-*cis*-$[Co(en)_2(NO_2)_2]^+$.[35] Furthermore, since the reaction product is proved to be pure *cis*-$[Co(en)_2(NO_2)_2]^+$ by its absorption spectrum and ion-exchange chromatography, it is evident that its cis configuration is fully retained in the isomerization process. Similarly, a sharp isodichroic point is displayed at 509 nm when Λ-*cis*-$[Co(en)_2(NCS)(ONO)]^+$ undergoes a rearrangement to the nitro complex,[38] and the final CD and absorption spectral patterns are identical with those of Λ-*cis*-$[Co(en)_2(NCS)(NO_2)]^+$.[35] In addition, the rate constants estimated for the two complexes by following the CD changes agree well with those derived from the optical density changes.

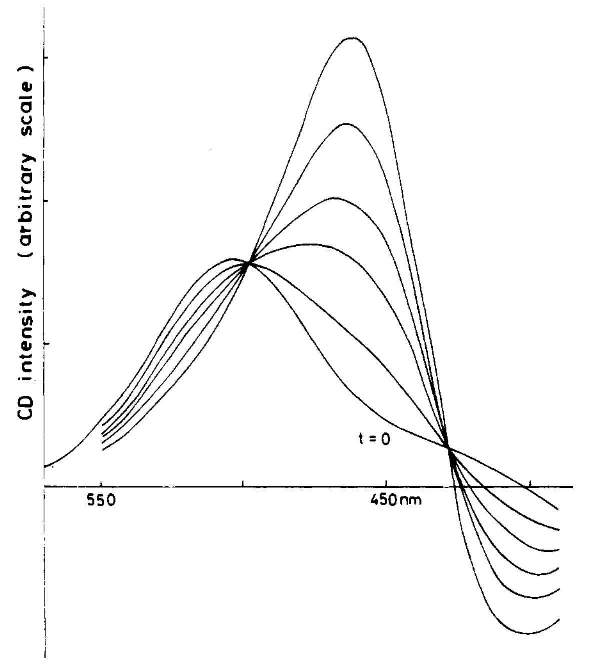
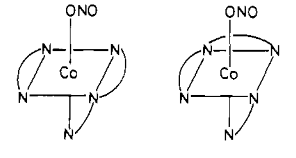


Figure 3. Change in the CD spectrum of aqueous Λ-*cis*-$[Co(en)_2(NO_2)(ONO)]^+$ accompanied by its isomerization to the dinitro complex.



π-(en)(dien)(ONO) ω-(en)(dien)(ONO)

Figure 4. π- and ω-isomers of $[Co(en)(dien)(ONO)]^{2+}$.

These observations do not necessarily afford decisive evidence for complete retention of chirality in the isomerization of the two cis complexes. However, when *cis*-$[Co(en)_2(NO_2)(Cl)]^+$ and *cis*-$[Co(en)_2(NCS)(Cl)]^+$ undergo acid hydrolysis involving a five-coordinated species as an intermediate, their chirality is known to be fully retained.[27,28] Since the present linkage isomerization is an intramolecular process in which no Co(III)–ligand bonds are ruptured,[4] it is fairly likely that chirality[2] as well as configuration is retained for the two nitrito complexes during the isomerization. The same will probably hold for other nitrito complexes. In this way, we suppose that all the nitrito complexes examined in the present study isomerize without any net stereochemical change, though α-$[Co(tetren)(ONO)]^{2+}$ has been reported to isomerize with a geometrical change to form β-$[Co(tetren)(NO_2)]^{2+}$[43] (tetren = tetraethylenepentamine).

Discussion

The isomerization rate constants thus obtained at a temperature range of 15–50 °C are now discussed in relation to steric and electronic effects of the ligands other than the reacting ONO group.

Number and Size of Chelate Rings. In Table I summarized the rate constants k at 25 °C and the activation parameters for $[Co(N)_5(ONO)]^{2+}$ type complexes with different numbers of chelate rings. These data clearly show that replacement of four NH_3 ligands in $[Co(NH_3)_5(ONO)]^{2+}$ by two en or tn (=trimethylenediamine) chelate ligands accelerates the isomerization in cis complexes by a factor of ca. 2, but additional chelation as in ω-$[Co(en)(dien)(ONO)]^{2+}$ (dien = diethylenetriamine; see Figure 4), having one more in-plane

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[41] Wilkins, R. W. "The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes", Allyn and Bacon: Boston, 1974.

[42] Rindermann, W.; van Eldik, R. *Inorg. Chim. Acta* **1982**, *64*, L203.

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Table I. Isomerization Rate Constants at 25 °C and Activation Parameters for $[Co(N)_5(ONO)]^{2+}$ Complexes

$[Co(NO)_5(ONO)]^{2+}$	10^5k, s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	ref	10^7k_H,[a] s^{-1} (ref)
$[Co(NH_3)_5(ONO)]^{2+}$	7.6	90.8	−20.1	*b*	17.7 (23a)
	3.2	92	−21	9, *c*	
	7.7			10	
	7.4	91.6	−17	7	
	6.9	95	+4	8a	
	7.8	93	−10	8c	
cis-$[Co(en)_2(NH_3)(ONO)]^{2+}$	16.8	90.8	−12.6	*b*	5.0 (22)
trans-$[Co(en)_2(NH_3)(ONO)]^{2+}$	4.22	94.1	−13.4	*b*	3.4 (21a, 22)
ω-$[Co(en)(dien)(ONO)]^{2+}$	18.5	91.2	−10.5	*b*	0.94 (23a).
π-$[Co(en)(dien)(ONO)]^{2+}$	4.02	95.8	−7.4	*b*	2.56 (23a)
trans-$[Co(cyclam)(NH_3)(ONO)]^{2+}$	0.6	114.6	+40.2	*d*	0.73 (21a)
cis-$[Co(tn)_2(NH_3)(ONO)]^{2+}$	14			*b*	65 (37)

[a] Acid hydrolysis rate constants of the corresponding chloro complexes at 25 °C. [b] This work. [c] Also quoted in ref 3 and 6. [d] Extrapolated from the data obtained in this work at 40, 45, and 50 °C.

chelate ring adjacent to another in-plane ring, leads to only a little change in the rate constant. On the other hand, the rate constant of *trans*-$[Co(en)_2(NH_3)(ONO)]^{2+}$, having two in-plane chelate rings trans to each other, is half that of the parent $[Co(NH_3)_5(ONO)]^{2+}$ at 25 °C, and π-[Co(en)(dien)(ONO)]$^{2+}$, having one out-plane chelate ring besides the two "trans" in-plane rings (Figure 4), isomerizes at a rate comparable with that of *trans*-$[Co(en)_2(NH_3)(ONO)]^{2+}$. A more retarded isomerization is exemplified by *trans*-[Co(cyclam)(NH$_3$)(ONO)]$^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane), which has two pairs of such "trans" in-plane chelate rings and which isomerizes ca. 13 times more slowly than $[Co(NH_3)_5(ONO)]^{2+}$ at 25 °C.

Acid hydrolysis reactions of $[Co(N)_5(Cl)]^{2+}$ type complexes have been extensively studied. A noteworthy finding is that the acid hydrolysis rate is progressively lowered with increase in chelation of the $(N)_5$ ligands. In Table I are also given acid hydrolysis rate constants k_H of the corresponding chloro complexes at 25 °C. It is seen that both *trans*- and *cis*-$[Co(en)_2(NH_3)(Cl)]^{2+}$ release Cl^- ion more slowly than $[Co(NH_3)_5(Cl)]^{2+}$ and that π- and ω-[Co(en)(dien)(Cl)]$^{2+}$ and *trans*-[Co(cyclam)(NH$_3$)(Cl)]$^{2+}$, having more chelate rings, are much less reactive to hydrolysis. The diminished reactivity of these chloro complexes by chelation has been attributed mainly to their increased stereorigidity leading to their decreased tendency to form five-coordinated (trigonal bipyramidal or tetragonal pyramidal) intermediates. That is, increased chelation resists the geometrical distortion of the complex accompanied by Cl^- ion release, as far as octahedral Co(III) complexes with five-membered chelate rings are concerned.

In the nitrito-to-nitro isomerization, on the other hand, chelation does no uniformly affect the rate constant. The isomerization is retarded by chelation for "trans" complexes, including π-[Co(en)(dien)(ONO)]$^{2+}$, but it is accelerated for "cis" complexes. These stereospecific chelation effects suggest that the geometrical distortion of the complex, if necessitated in going to the transition state, is localized within the plane defined in Figure 4. If the distortion of the complex as a whole were necessary for the isomerization, *cis*-$[Co(en)_2(NH_3)(ONO)]^{2+}$ and ω-[Co(en)(dien)(ONO)]$^{2+}$ would also isomerize more slowly than $[Co(NH_3)_5(ONO)]^{2+}$. Thus, species of drastically changed coordination number are not imagined as a reaction intermediate. An octahedral framework may be retained in the transition state even if the isomerization proceeds via a seven-coordinated intermediate.[1,5–7] If so, it is natural that the isomerization should proceed with complete stereoretention.

Though why "cis" chelate rings promote the isomerization reaction is not known at present, similar acceleration by chelation is observed in *cis*-$[Co(en)_2(ONO)_2]^+$. In Table II are listed its rate constants k_1 and k_2 at 25 °C as well as those of *cis*-$[Co(NH_3)_4(ONO)_2]^+$. It is evident that both k_1 and k_2 of the en complex are greater than the corresponding rate constants of the tetraammine complex.

Table II. Isomerization Rate Constants at 25 °C for *cis*-$[Co(N)_4(ONO)_2]^+$ Complexes

cis-$[Co(N)_4(ONO)_2]^+$	10^4k_1, s^{-1}	10^4k_2, s^{-1}	10^4k_2,[a] s^{-1}
cis-$[Co(NH_3)_4(ONO)_2]^+$	2.5	1.0	2.4 (25 °C)[b]
cis-$[Co(en)_2(ONO)_2]^+$	9.0	2.3	0.52 (20 °C)[c] 1.2 (20 °C)[d] 2.4 (25 °C)[e] 7.55 (35 °C)[f]

[a] Rate constants k_2 reported by earlier workers. [b] Interpolated from the data at 20 and 30 °C.[15] [c] Estimated on the assumption $k_1 = 2k_2$ in ref 12. [d] Recalculated in ref 13 from the data obtained by Adell.[12] [e] Reference 13. [f] Reference 10.

Table III. Isomerization Rate Constants at 25 °C and Activation Parameters for *cis*-$[Co(en)_2(X)(ONO)]^{n+}$ Complexes

X	10^4k, s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	10^6k_H,[a] s^{-1} (ref)
ONO^-	9.0[b]			
	(8.0)[b,c]	(64.8)[c]	(−85.6)[c]	
NCS^-	8.1	81.2	−31.4	11 (*e*)
NO_2^-	2.3	84.9	−30.1	110 (22)
	(2.4)[d]	(85.1)[d]	(−28.3)[d]	
	(2.8)[c]	(81.5)[c]	(−39.3)[c]	
CN^-	4.2	96.7	+15.1	0.62 (21)
NH_3	1.7	90.8	−12.6	0.50 (22)

[a] Acid hydrolysis rate constants of the corresponding chloro com complexes at 25 °C. [b] Half the rate constant obtained by a usual analysis. [c] Reference 14. [d] Reference 13. [e] Baldwin, E. A.; Tobe, M. L. *J. Chem. Soc.* **1960**, 4275.

It is well documented[16,23a,41] that acid hydrolysis of Co(III) complexes is greatly facilitated when the chelate ring size is increased. For example, *cis*-$[Co(tn)_2(NH_3)(Cl)]^{2+}$ aquates 13 times more readily than *cis*-$[Co(en)_2(NH_3)(Cl)]^{2+}$ at 25 °C (Table I). The greater lability of the tn complex has been ascribed to its easier distortion to a five-coordinated intermediate,[37] since the six-membered tn chelate is thought to be more flexible and less stable than the five-membered en chelate. In the isomerization reaction, however, an increase in the chelate ring size gives rise to little change in the rate constant, implying that the transition states are completely different between the two reactions. We suppose that nitrito complexes undergo a rearrangement to nitro compexes without a drastic geometrical change in the $(N)_5$ portion of the complexes, qualitatively in keeping with the mechanism involving a six-coordinate π-bonded intermediate proposed recently by Jackson et al.[8]

Effect of the Nature of Ligands Cis and Trans to the ONO Group. In Tables III and IV are summarized the isomerization rate constants k and activation parameters of *cis*- and

Table IV. Isomerization Rate Constants at 25 °C and Activation Parameters for *trans*-$[Co(en)_2(X)(ONO)]^{n+}$ Complexes

X	10^5k, s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	10^5k,[a] s^{-1}	10^6k_H,[b] s^{-1} (ref)
ONO^-	13[c]	94.3	−2.6	13.0[d]	
		97.5[e]	+8.5[e]	12.8[e]	
				2.2[f]	
NCS^-	0.42	103.3	−1.3	0.15[g]	0.046 (21a)
NO_2^-	very fast			1.1[f]	980 (21a)
CN^-	very fast				82 (21a, 22)
NH_3	4.2	94.1	−13.4		0.34 (21a, 22)

[a] Isomerization rate constants at 25 °C reported earlier. [b] Acid hydrolysis rate constants of the corresponding chloro complexes at 25 °C. [c] Half the rate constant obtained for the dinitrito complex. [d] Half the rate constant estimated in ref 13 from the data obtained by Adell.[12] [e] Activation parameters and half the rate constant reported in ref 13. [f] Estimated on the assumption $k_1 = 2k_2$ for the dinitrito complex in ref 12. [g] Reference 9b.

trans-$[Co(en)_2(X)(ONO)]^{n+}$ type complexes toghether with acid hydrolysis rate constants k_H of the corresponding chloro complexes at 25 °C. For cis complexes, k is relatively insensitive to the change in the X ligands. By contrast, acid hydrolysis rates of the corresponding chloro complexes differ greatly for different X ligands; *cis*-$[Co(en)_2(NO_2)(Cl)]^+$ releases Cl^- ion almost 180 times more easily than *cis*-$[Co(en)_2(CN)(Cl)]^+$ at 25 °C, as seen in Table III. A close inspection of Table III reveals that the isomerization rate increases in the order $NH_3 < NO_2^- < CN^- < NCS^- < ONO^-$, which is not in agreement either with the order of ligand field strength or with the order of acid hydrolysis rate of the chloro complexes ($NH_3 < CN^- << NCS^- << NO_2^-$). It is not possible at present to account for the order of the isomerization rate constants obtained for these cis complexes.

For trans complexes, on the other hand, the rate constant is greatly dependent on the kind of X ligands trans to the ONO group. When X = NO_2^- and CN^-, the isomerization is so fast that its rate constant cannot be determined by the usual techniques. This finding, which was not correctly recognized by Adell,[12] is ascribed to the so-called trans effect of NO_2^- and CN^-.[14,16,17,22,44] Actually, it is seen in Table IV that *trans*-$[Co(en)_2(X)(ONO)]^{n+}$ isomerizes faster if the corresponding chloro complex, *trans*-$[Co(en)_2(X)(Cl)]^{n+}$, releases Cl^- more easily and vice versa.

Finally, it is worthy of note that the isomerization of *trans*-$[Co(en)_2(NCS)(ONO)]^+$ is exceptionally slow. Even trans-$[Co(cyclam)(NH_3)(ONO)]^{2+}$ isomerizes faster than the NCS complex. In parallel with the extremely low reactivity of the NCS complex, acid hydrolysis of *trans*-$[Co(en)_2(NCS)(Cl)]^+$ is exceptionally slow among monovalent *trans*-$[Co(en)_2(X)(Cl)]^+$ type complexes.[23a,45] In the acid hydrolysis of chloro(amine)cobalt(III) complexes, the Co(III)–Cl^- bond strength is one of the dominant factors determining the rate constant, since the so-called I_d mechanism prevails for Co(III) complexes. Therefore, the low reactivity of the two NCS complexes leads us to suppose that the slower loosening of the Co(III)–ONO^- bond in *trans*-$[Co(en)_2(NCS)(ONO)]^+$ is responsible for its extremely slower isomerization. Much slower isomerization is thus expected for *trans*-$[Co(cyclam)(NCS)(ONO)]^+$. It is also informative to remember that *trans*-$[Co(en)_2(NCS)(ONO)]^+$ isomerizes in the solid state with a rate fairly slower than those of other nitrito complexes.[1,5,9b]

Effect of Net Charge on the Complexes. It is well-known[16,41] that the acid hydrolysis rate of chloro(amine)cobalt(III) complexes is greatly affected by the change in their net charge. This is because charge separation takes place when a five-coordinated intermediate is formed. A comparison of the isomerization rate constants listed in Tables I–IV establishes that the net charge on the complex has no practical effect on its isomerization rate. This observation is consistent with the assertion that the isomerization is an intramolecular process which involves no appreciable charge separation in the transition state, and a dissociative mechanism is ruled out completely.[4]

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Registry No. $[Co(NH_3)_5(ONO)]^{2+}$, 16633-04-8; *cis*-$[Co(en)_2(NH_3)(ONO)]^{2+}$, 85610-84-0; *trans*-$[Co(en)_2(NH_3)(ONO)]^{2+}$, 85610-85-1; ω-$[Co(en)(dien)(ONO)]^{2+}$, 85533-77-3; π-$[Co(en)(dien)(ONO)]^{2+}$, 85610-86-2; *trans*-$[Co(cyclam)(NH_3)(ONO)]^{2+}$, 85533-78-4; *cis*-$[Co(tn)_2(NH_3)(ONO)]^{2+}$, 85552-54-1.

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Correlation of Spectroscopic Parameters with Ligand Basicity for Uranyl Bis(hexafluoroacetylacetonate) Adducts

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The infrared transition frequencies (vapor and solution phases) of the uranyl and hexafluoroacetylacetonate (hfacac) moieties, as well as ^{13}C and ^1H NMR shifts, correlate linearly with the relative basicity of the neutral bases (B) for 15 $UO_2(hfacac)_2$ adducts. Solvation effects and relative entropy changes appear to be minimal for the base-exchange equilibrium, suggesting that the observed shifts in these easily measurable spectroscopic properties predominantly reflect the Lewis acid–base relative bond strengths. We interpret the observed shifts in terms of electronic structure perturbations of both the uranyl and hfacac moieties arising from changes in neutral base (L–M) bonding.

Introduction

The chelated uranyl ion, $UO_2(hfacac)_2$, recently has been shown to behave as a model hard Lewis acid to a variety of oxygen and nitrogen bases.[1] The free energies ($\Delta G°$) for the base-exchange reaction

$$UO_2(hfacac)_2THF + B \xrightleftharpoons{CDCl_3} UO_2(hfacac)_2B + THF \tag{1}$$