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Base-Catalyzed Nitrito to Nitro Linkage Isomerization of Cobalt(III), Rhodium(III), and Iridium(III) Pentaammine Complexes

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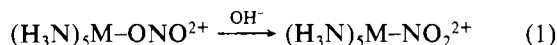
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The nitrito ions $[\text{M}(\text{NH}_3)_5(\text{ONO})]^{2+}$ ($\text{M} = \text{Co(III)}, \text{Rh(III)}, \text{or Ir(III)}$) rearrange to their nitro forms $[\text{M}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ in aqueous base according to the rate law $k_{\text{obsd}} = k_s + k_{\text{OH}}[\text{OH}^-]$ where at $\mu = 1.0 \text{ M}$, 25.0°C : $k_s = 6.9 (\pm 0.2) \times 10^{-5} \text{ s}^{-1}$, $\Delta H_s^\ddagger = 95 \pm 4 \text{ kJ mol}^{-1}$, $\Delta S_s^\ddagger = -4 \pm 12 \text{ J K}^{-1} \text{ mol}^{-1}$, $k_{\text{OH}} = 5.9 (\pm 0.2) \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $\Delta H_{\text{OH}}^\ddagger = 110 \pm 1 \text{ kJ mol}^{-1}$, $\Delta S_{\text{OH}}^\ddagger = +82 \pm 4 \text{ J K}^{-1} \text{ mol}^{-1}$, $\text{M} = \text{Co}$; $k_s = 9.6 (\pm 0.2) \times 10^{-4} \text{ s}^{-1}$, $\Delta H_s^\ddagger = 85 \pm 2.5 \text{ kJ mol}^{-1}$, $\Delta S_s^\ddagger = -18 \pm 9 \text{ J K}^{-1} \text{ mol}^{-1}$, $k_{\text{OH}} = 7.6 (\pm 0.2) \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $\Delta H_{\text{OH}}^\ddagger = 96 \pm 2 \text{ kJ mol}^{-1}$, $\Delta S_{\text{OH}}^\ddagger = +38 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1}$, $\text{M} = \text{Rh}$; $k_s = 3.0 (\pm 0.1) \times 10^{-5} \text{ s}^{-1}$, $\Delta H_s^\ddagger = 94 \pm 2 \text{ kJ mol}^{-1}$, $\Delta S_s^\ddagger = 16 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$, $k_{\text{OH}} = 2.7 (\pm 0.1) \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $\Delta H_{\text{OH}}^\ddagger = 109 \pm 2 \text{ kJ mol}^{-1}$, $\Delta S_{\text{OH}}^\ddagger = 34 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1}$, $\text{M} = \text{Ir}$. For the cobalt complex the pressure dependence of k_{OH} ($\Delta V^\ddagger = +27 (\pm 1.4) \text{ cm}^3 \text{ mol}^{-1}$, $\Delta \beta^\ddagger = 5 (\pm 2) \text{ cm}^3 \text{ kbar}^{-1} \text{ mol}^{-1}$) points to a conjugate base preequilibrium for the base-catalyzed path. The metal ion dependence of k_{OH}/k_s (95:9:1 for Co:Rh:Ir) is also consistent with a conjugate base process. $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ rearranges to $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ without exchange of oxygen with H_2^{18}O , $^{18}\text{OH}^-$, or free $\text{N}^{18}\text{O}_2^-$ (1 M); both the k_s and k_{OH} paths are intramolecular. Up to 1 M OH there is <1% competitive hydrolysis to $[\text{M}(\text{NH}_3)_5(\text{OH})]^{2+}$. Both rate constants k_s and k_{OH} for $\text{M} = \text{Co}$ decrease with increasing ionic strength (25°C, $10^5 k_s = 6.9, 7.4, 10^3 k_{\text{OH}} = 5.9, 14.5; \mu = 1.0, 0.1$, respectively). *cis*- and *trans*- $[\text{Co}(\text{en})_2(\text{ONO})_2]^+$ and $[\text{Co}(\text{en})_2(\text{ONO})(\text{NO}_2)]^+$ rearrange by both pathways to the dinitro complexes without change in configuration, and (+)*cis*- $[\text{Co}(\text{en})_2(\text{ONO})(\text{NO}_2)]^+$ rearranges without loss of chirality. For the k_{OH} reaction these results also differ from the normal substitution chemistry where there is some steric change. In addition to the O to N rearrangement, a much faster O to O scrambling process has been identified for the cobalt complex using ^{18}O tracers.

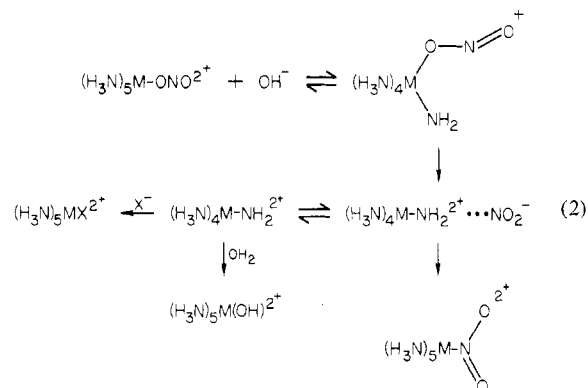
Introduction

The linkage isomerization of NO_2^- bound to metal amine complexes has been extensively studied and reviewed.²⁻⁹ O-Bound nitrito compounds of Co(III), Rh(III), Ir(III), and Pt(IV) isomerize thermally to the N-bound nitro complexes in the solid state and in solution.⁵ These were postulated to be intramolecular reactions, the rates of the solution reactions being independent of added nitrite concentration. Subsequently, the spontaneous isomerizations of $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ and *cis*- $[\text{Co}(\text{en})_2(\text{NO}_2)(\text{ONO})]^+$ ions were proved to be intramolecular by using ^{18}O tracer techniques.^{7,8} Neither the inner (Co-O) or outer (N-O) oxygen of the nitrito complexes exchanged with solvent or added nitrite ion during the isomerization. Furthermore, activation volumes for isomerization of $[\text{M}(\text{NH}_3)_5(\text{ONO})]^{2+}$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}$) are consistent with an intramolecular mechanism.⁹

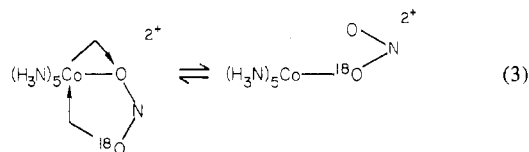
It seems remarkable that, despite the extensive investigations to date, a base-catalyzed path (eq 1) for the rearrangement



has not been revealed previously. Such a path has now been identified for $\text{M} = \text{Co}, \text{Rh}$, and Ir , and the results are presented in this paper. The immediate presumption was that the base-dependent process could be ascribed to the conjugate base dissociative mechanism typical of acidocobalt(III) amine complexes (eq 2). The prospect of a tight ion pair leading to rearrangement and dissociation was envisaged. The latter path could give hydroxo and other competition products. This proposal needed testing, and a detailed kinetic and competition study along with the pressure, ionic strength (Co(III)), complex concentration, and metal ion (Co(III), Rh(III), Ir(III)) dependence has been undertaken. An analogous reaction is the base-catalyzed isomerization and hydrolysis of the $[\text{Co}(\text{NH}_3)_5\text{SCN}]^{2+}$ and *trans*- $[\text{Co}(\text{en})_2(\text{NH}_3)(\text{SCN})]^{2+}$ ions.^{10,11} In line with this work we describe ^{18}O tracer studies and product analyses for the reaction of $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ in



base, as well as the stereochemistry for related *cis*- and *trans*- $\text{Co}(\text{en})_2$ nitrito complexes, to probe the detailed mechanism. For example the possibility of O to O scrambling (eq 3) was also explored by using ^{18}O labeling techniques.



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Table I. Base-Catalyzed Linkage Isomerization Rates for $\text{Co}(\text{NH}_3)_5(\text{ONO})^{2+}$ at Various Temperatures^{a, b}

$[\text{OH}^-], \text{M}$	$10^4 k_{\text{obsd}}, \text{s}^{-1}$	$[\text{OH}^-], \text{M}$	$10^4 k_{\text{obsd}}, \text{s}^{-1}$
Temperature = 8.7 °C			
0.01	0.093 ($\pm 0.00_6$)	0.40	1.71 (± 0.02)
0.05	0.26 ($\pm 0.00_3$)	0.60	2.61 (± 0.03)
0.10	0.48 (± 0.02)	0.80	3.50 (± 0.05)
0.20	0.89 ($\pm 0.01_3$)	1.00	4.11 (± 0.08)
Temperature = 16.1 °C			
0.01	0.37 (± 0.02)	0.40	6.27 (± 0.04)
0.05	0.98 (± 0.02)	0.60	8.91 (± 0.19)
0.10	1.75 (± 0.04)	0.80	12.06 (± 0.14)
0.20	3.10 (± 0.02)	1.00	15.03 (± 0.36)
$[\text{OH}^-], \text{M}$	$10^3 k_{\text{obsd}}, \text{s}^{-1}$	$[\text{OH}^-], \text{M}$	$10^3 k_{\text{obsd}}, \text{s}^{-1}$
Temperature = 24.4 °C			
0.01	0.11 ($\pm 0.00_3$)	0.40	2.25 (± 0.02)
0.05	0.34 (± 0.01)	0.60	3.44 (± 0.05)
0.10	0.60 ($\pm 0.01_5$)	0.80	4.50 (± 0.08)
0.20	1.18 (± 0.02)	1.00	5.58 (± 0.16)
Temperature = 30.7 °C			
0.01	0.27 (± 0.01)	0.40	5.50 (± 0.11)
0.05	0.87 (± 0.03)	0.60	8.08 (± 0.19)
0.10	1.57 (± 0.05)	0.80	10.8 (± 0.3)
0.20	2.65 (± 0.12)	1.00	13.4 (± 0.4)

^a Ionic strength = 1.0 M (NaClO_4). ^b Average of three independent runs; standard errors in parentheses.

Table II. Base-Catalyzed Linkage Isomerization Rates for $\text{Ir}(\text{NH}_3)_5(\text{ONO})^{2+}$ at Various Temperatures^{a, b}

$[\text{OH}^-], \text{M}$	$10^5 k_{\text{obsd}}, \text{s}^{-1}$	$[\text{OH}^-], \text{M}$	$10^5 k_{\text{obsd}}, \text{s}^{-1}$
Temperature = 24.5 °C			
0.01	2.90 (± 0.04)	0.40	3.79 (± 0.07)
0.05	2.99 (± 0.03)	0.60	4.34 (± 0.04)
0.10	3.17 (± 0.06)	0.80	4.78 (± 0.04)
0.20	3.28 (± 0.03)	1.00	5.32 (± 0.07)
$[\text{OH}^-], \text{M}$	$10^4 k_{\text{obsd}}, \text{s}^{-1}$	$[\text{OH}^-], \text{M}$	$10^4 k_{\text{obsd}}, \text{s}^{-1}$
Temperature = 34.2 °C			
0.01	0.93 (± 0.01)	0.40	1.34 (± 0.02)
0.05	1.00 (± 0.01)	0.60	1.60 (± 0.01)
0.10	1.06 (± 0.02)	0.80	1.82 (± 0.01)
0.20	1.14 (± 0.01)	1.00	2.01 (± 0.02)
Temperature = 41.0 °C			
0.01	2.28 (± 0.01)	0.40	3.35 (± 0.03)
0.05	2.39 (± 0.01)	0.60	3.93 (± 0.02)
0.10	2.53 (± 0.01)	0.80	4.29 (± 0.02)
0.20	2.82 (± 0.02)	1.00	4.86 (± 0.03)
Temperature = 46.6 °C			
0.01	4.13 (± 0.02)	0.40	6.29 (± 0.09)
0.05	4.39 (± 0.09)	0.60	7.30 (± 0.09)
0.10	4.82 (± 0.06)	0.80	8.54 (± 0.10)
0.20	5.36 (± 0.08)	1.00	9.92 (± 0.13)

^a Ionic strength = 1.0 M (NaClO_4). ^b Average of three independent runs; standard errors in parentheses.

Results and Discussion

The O to N Rearrangement: Kinetic and ¹⁸O Tracer Studies. The base-catalyzed linkage isomerization of each of the (nitro)pentaamminemetal complexes was studied at eight different base strengths between 0.01 and 0.1M, each over a temperature range of about 20 °C. The data obtained are presented in Tables I–III. Each set of data at a given ionic strength and temperature obeys the relationship

$$k_{\text{obsd}} = k_s + k_{\text{OH}}[\text{OH}^-] \quad (4)$$

and least-squares analysis yielded the two independent rate constants k_s (spontaneous) and k_{OH} (base catalyzed), for each metal ion system. These results are presented in Tables IV–VI.

Table III. Base-Catalyzed Linkage Isomerization Rates for $\text{Rh}(\text{NH}_3)_5(\text{ONO})^{2+}$ at Various Temperatures^{a, b}

$[\text{OH}^-], \text{M}$	$10^3 k_{\text{obsd}}, \text{s}^{-1}$	$[\text{OH}^-], \text{M}$	$10^3 k_{\text{obsd}}, \text{s}^{-1}$
Temperature = 6.7 °C			
0.01	0.11 ($\pm 0.00_3$)	0.40	0.28 ($\pm 0.01_5$)
0.05	0.13 ($\pm 0.00_3$)	0.60	0.40 (± 0.01)
0.10	0.16 ($\pm 0.00_6$)	0.80	0.53 ($\pm 0.01_3$)
0.20	0.20 (± 0.01)	1.00	0.67 ($\pm 0.02_3$)
Temperature = 14.1 °C			
0.01	0.29 ($\pm 0.00_3$)	0.40	0.94 (± 0.01)
0.5	0.35 (± 0.01)	0.60	1.34 (± 0.03)
0.10	0.44 (± 0.01)	0.80	1.70 (± 0.02)
0.20	0.55 ($\pm 0.01_3$)	1.00	2.04 (± 0.04)
Temperature = 19.2 °C			
0.01	0.43 (± 0.01)	0.40	1.85 (± 0.04)
0.05	0.65 (± 0.02)	0.60	2.68 (± 0.06)
0.10	0.84 (± 0.03)	0.80	3.26 (± 0.15)
0.20	1.13 (± 0.02)	1.00	3.94 (± 0.18)
Temperature = 24.7 °C			
0.01	0.93 (± 0.03)	0.40	3.76 (± 0.12)
0.05	1.26 (± 0.03)	0.60	5.26 (± 0.05)
0.10	1.67 (± 0.02)	0.80	6.67 (± 0.11)
0.20	2.41 (± 0.08)	1.00	8.20 (± 0.22)

^a Ionic strength = 1.0 M (NaClO_4). ^b Average of three independent runs; standard errors in parentheses.

Table IV. Spontaneous and Base-Catalyzed Rate Constants for Isomerization of $\text{Co}(\text{NH}_3)_5(\text{ONO})^{2+}$ at Various Temperatures, $\mu = 1.0 \text{ M } (\text{NaClO}_4)$

temp, °C	spontaneous path $10^5 k_s, \text{s}^{-1}$	base-catalyzed path $10^3 k_{\text{OH}}, \text{M}^{-1} \text{s}^{-1}$
8.7	0.68	0.41 (± 0.06)
16.1	2.3	1.48 (± 0.02)
24.4	6.1	5.55 (± 0.03)
30.7	14.9	13.30 (± 0.02)
25.0	6.9 ^b	5.9 ^b
	7.4 ^c	14.5 ^c

^a Calculated from least-squares analysis of data in Table I. ^b Calculated using the activation parameters of Table VII. ^c $I = 0.1 \text{ M}$.

Table V. Spontaneous and Base-Catalyzed Rate Constants for Isomerization of $\text{Rh}(\text{NH}_3)_5(\text{ONO})^{2+}$ at Various Temperatures, $\mu = 1.0 \text{ M } (\text{NaClO}_4)$

temp, °C	spontaneous path $10^3 k_s, \text{s}^{-1}$	base-catalyzed path $10^3 k_{\text{OH}}, \text{M}^{-1} \text{s}^{-1}$
6.7	0.09	0.56 (± 0.02)
14.1	0.24 _s	1.79 (± 0.03)
19.2	0.44	3.52 (± 0.04)
24.7	0.93	7.30 (± 0.05)
25.0	0.96 ^b	7.6 ^b

^a Calculated from least-squares analysis of data in Table III. ^b Extrapolated from above data.

Table VI. Spontaneous and Base-Catalyzed Rate Constants for Isomerization of $\text{Ir}(\text{NH}_3)_5(\text{ONO})^{2+}$ at Various Temperatures, $\mu = 1.0 \text{ M } (\text{NaClO}_4)$

temp, °C	spontaneous path $10^4 k_s, \text{s}^{-1}$	base-catalyzed path $10^4 k_{\text{OH}}, \text{M}^{-1} \text{s}^{-1}$
24.5	0.29	0.24 (± 0.01)
34.2	0.93	1.09 (± 0.06)
41.0	2.29	2.60 (± 0.08)
46.6	4.15	5.57 (± 0.18)
25.0	0.30 ^b	0.27 ^b

^a Calculated from least-squares analysis of data in Table II. ^b Extrapolated from above data.

Activation enthalpies and entropies calculated from the temperature dependences of k_s and k_{OH} are presented in Tables VII and VIII. The activation volume and compressibility

Table VII. Activation Parameters for Linkage Isomerization of $\text{Co}(\text{NH}_3)_5(\text{ONO})^{2+}$

process	ΔH^\ddagger , kJ mol ⁻¹	ΔS^\ddagger , J K ⁻¹ mol ⁻¹	ΔV^\ddagger , cm ³ mol ⁻¹	$\Delta\beta^\ddagger$, cm ³ kbar ⁻¹ mol ⁻¹	ref
base-catalyzed	110 (±1)	+82 (±4)	+27 (±1.4)	5 (±2)	a
spontaneous	95 (±4)	4 (±12)			a
	92 (±1)	-17 (±3)	-6.7 (±0.4)	0	9
	92	-21			5

^a This work.

Table VIII. Activation Parameters for Linkage Isomerization of $\text{Rh}(\text{NH}_3)_5(\text{ONO})^{2+}$ and $\text{Ir}(\text{NH}_3)_5(\text{ONO})^{2+}$

process	ΔH^\ddagger , kJ mol ⁻¹	ΔS^\ddagger , J K ⁻¹ mol ⁻¹	ΔV^\ddagger , cm ³ mol ⁻¹	ref
Rhodium				
base catalyzed	96 (±2)	+38 (±6)		a
spontaneous	85 (±2.5)	-18 (±9)		a
	80 (±2)	-33 (±7)	-7.4 (±0.4)	9
	76	-50		5
Iridium				
base catalyzed	109 (±2)	+34 (±6)		a
spontaneous	94 (±2)	-16 (±5)		a
	95 (±1)	-11 (±4)	-5.9 (±0.6)	9
	80	-59		5

^a This work.

Table IX. Pressure Dependence of Linkage Isomerization of $\text{Co}(\text{NH}_3)_5(\text{ONO})^{2+}$

pressure, bar	$10^4 k_{\text{obsd}}$, s ⁻¹	$10^4 k_s$, ^b s ⁻¹	$10^3 k_{\text{OH}}$, ^c M ⁻¹ s ⁻¹
1	7.28 ± 0.06 (4) ^d	0.37	6.91
170	5.80 ± 0.15 (2)	0.39	5.41
345	4.81 ± 0.06 (3)	0.41	4.40
690	3.57 ± 0.12 (3)	0.44	3.13
1035	2.80 ± 0.10 (3)	0.49	2.31
1380	2.23 ± 0.07 (3)	0.54	1.69
1725	1.86 ± 0.05 (2)	0.59	1.27

^a Measured in 0.1 M NaOH at 20.5 °C; $\mu = 0.1$ M. ^b Calculated from data in ref 9. ^c $k_{\text{OH}} = (k_{\text{obsd}} - k_s)/[\text{OH}^-]$. ^d Number of independent runs in parentheses.

coefficient of activation for the cobalt complex obtained from the pressure dependence of k_{OH} (Table IX) are also given (Table VII).

For both the spontaneous and base-catalyzed paths, the rates of isomerization for the three metal complexes follow the order $\text{Co} < \text{Rh} > \text{Ir}$. At 25 °C and 1.0 M ionic strength, the rate constants for the spontaneous path are 6.9×10^{-5} , 9.6×10^{-4} , and 3.0×10^{-5} s⁻¹ for the Co, Rh, and Ir complexes, respectively; the rate constants for the base-catalyzed path are 5.9×10^{-3} , 7.6×10^{-3} , and 2.7×10^{-5} M⁻¹ s⁻¹, respectively. The observed reactivity order $\text{Rh} > \text{Co} > \text{Ir}$ differs from the general pattern for substitution chemistry for both acid and base hydrolysis where $\text{Co} > \text{Rh} \gg \text{Ir}$ for the trivalent oxidation state.¹² The greater reactivity of the Rh complex lies largely in the lower ΔH^\ddagger for both the spontaneous and base-catalyzed routes. Note that the apparent anomaly does not lie in photocatalysis since the rates are unaltered when a nitrito sample is either continuously or intermittently irradiated in the spectrophotometer.

Differences to normal substitution chemistry are also apparent in the stereochemistry of the linkage isomerization reaction. The hydrolysis of suitable A_5MX^{n+} complexes, which

yield $\text{A}_5\text{M}(\text{OH}_2)^{m+}$, often proceeds with stereochemical change for $\text{M} = \text{Co}(\text{III})$.³³ This is particularly true of base-catalyzed hydrolysis. However, the Rh(III) and Ir(III) systems are generally retentive and there are a few authenticated examples otherwise. The spontaneous linkage isomerization of (+)_D*cis*-[Co(en)₂(ONO)(NO₂)⁺] has been reported to give (+)_D*cis*-[Co(en)₂(NO₂)₂]⁺ with full retention of the *cis* configuration and of chirality.⁸ However, this observation is not mechanistically revealing, since the induced and spontaneous hydrolysis of X from chiral *cis*-[Co(en)₂(NO₂)X]ⁿ⁺ ions follows the same pattern.¹⁴ In base, however, chiral *cis*-[Co(en)₂(NO₂)₂]⁺ ions hydrolyze with appreciable *cis* to *trans* rearrangement (34%) and loss of chirality (74%).¹⁵ It is therefore important to note that (+)_D*cis*-[Co(en)₂(ONO)(NO₂)⁺] rearranges to (+)_D*cis*-[Co(en)₂(NO₂)₂]⁺ in base also without significant loss of chirality (6%). Stereoretention was also observed for the linkage isomerizations of *cis*- and *trans*-[Co(en)₂(ONO)(NO₂)⁺] ions. The results are consistent with synchronous bond breaking (Co-O) and bond making (Co-N) (at least by the base-catalyzed route) and with nitrite ion remaining bonded to cobalt throughout the rearrangement.

It is noted also that the ionic strength dependence of the linkage isomerization rates (Table IV) is consistent with the usual dependences for the substitution chemistry; i.e., the rates decrease slightly with increasing ionic strength.¹²

It has been estimated that hydrolysis of $[\text{M}(\text{NH}_3)_5\text{Br}]^{2+}$ for $\text{M} = \text{Co}(\text{III})$, Rh(III), and Ir(III) should proceed at rates of the order of 4000:1000:1 for Co:Rh:Ir, and the general expectation for the rate behavior for an analogous series of the different metal complexes is $\text{Co} > \text{Rh} \gg \text{Ir}$.¹⁵ Acid hydrolysis of (carboxylato)pentaamminemetal(III) complexes proceeds at rates of 50:50:1 for Co:Rh:Ir.¹⁶ Also, water exchange in the aquopentaamminemetal(III) complexes have rates of 90:170:1 for Co:Rh:Ir.¹⁷ However, the rates of linkage isomerization of $[(\text{H}_3\text{N})_5\text{M}-\text{ONO}]^{2+}$ are 23:320:1 for Co:Rh:Ir for the spontaneous path and 220:280:1 for the base-catalyzed path. For these isomerization reactions, some enhancement of the rate expected for both the Rh and Ir complexes occurs, and this is more obvious in the spontaneous path. These facts highlight the mechanistic differences to normal substitution chemistry. The result is not so surprising if nitrite leaves the metal ion during the rearrangement.

The activation parameters for the k_s and k_{OH} pathways differ substantially, indicating obvious mechanistic differences. However, irrespective of the actual mechanisms for the two pathways, a clue to the origin of the base catalysis comes from the relative dominance of the base-catalyzed path in 1.0 M base which falls off dramatically from Co to Rh to Ir. If the base-catalyzed path involves a conjugate base deprotonation preequilibrium, this behavior might be expected to parallel the variation in the amine proton exchange rates for these complexes. Indeed for the related $[\text{M}(\text{NH}_3)_6]^{3+}$ ions, proton exchange rates at 24.5 °C are 110:14:1 for Co:Rh:Ir.¹⁸ Thus the similar trend for k_{OH}/k_s observed here of 95:9:1 for Co:Rh:Ir provides good evidence for a general conjugate base mechanism.

Support for the conjugate base path at least for the Co complex also derives from the pressure dependence of k_{OH} . A large positive ΔV^\ddagger is observed (27 ± 1.4 cm³ mol⁻¹), and $\Delta\beta^\ddagger = 5 (\pm 2)$ cm³ kbar⁻¹ mol⁻¹. These values are consistent with the release of electrostricted water in a conjugate base preequilibrium, eq 5, such that $\Delta V_{\text{exptl}}^\ddagger = \Delta V_{\text{cb}}^\circ + \Delta V_2^\ddagger$.¹⁹

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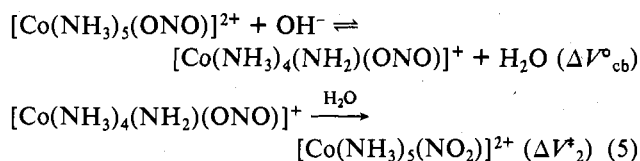
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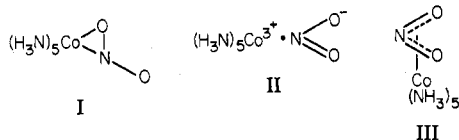
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The hydroxide ion has an unusually large volume of electrostriction ($\bar{V}_{\text{el}} \approx 22 \text{ cm}^3 \text{ mol}^{-1}$),¹⁹ and since ions such as $[\text{Co}(\text{NH}_3)(\text{OH})]^{2+}$ and $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$ have similar partial molar volumes, there are good grounds^{20,21} for assigning $\Delta V_{\text{cb}}^\ddagger$ in the range $+18$ – $22 \text{ cm}^3 \text{ mol}^{-1}$. Hence a value of at least $+5 \text{ cm}^3 \text{ mol}^{-1}$ can be assigned to ΔV_2^\ddagger . Since the partial molar volumes of $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ and $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ are 82.3 and $69.4 \text{ cm}^3 \text{ mol}^{-1}$, respectively, the overall volume change for the reaction is $\Delta V^\circ = \bar{V}_{\text{CoNO}_2} - \bar{V}_{\text{CoONO}} = -12.9 \text{ cm}^3 \text{ mol}^{-1}$.⁹ The small positive value of ΔV_2^\ddagger indicates a transition state for the complex ion of similar volume to the deprotonated precursor, i.e., $[\text{Co}(\text{NH}_3)_4(\text{NH}_2)(\text{ONO})]^+$. This analysis is therefore in keeping with that for the spontaneous nitrito to nitro isomerization process.⁹ Furthermore the large positive activation volume ($\Delta V^\ddagger = 27 \text{ cm}^3 \text{ mol}^{-1}$) and nonzero activation compressibility coefficient ($\Delta\beta^\ddagger = 5 \text{ cm}^3 \text{ kbar}^{-1} \text{ mol}^{-1}$) are similar to the values of these parameters obtained for base hydrolysis of $[\text{Co}(\text{NH}_3)_5(\text{OSO})_3]^+$ ($\Delta V^\ddagger = 19.5 \text{ cm}^3 \text{ mol}^{-1}$, $\Delta\beta^\ddagger = 9.5 \text{ cm}^3 \text{ kbar}^{-1} \text{ mol}^{-1}$) and $[\text{Co}(\text{NH}_3)_5(\text{OPO}_3)]$ ($\Delta V^\ddagger = 28.9 \text{ cm}^3 \text{ mol}^{-1}$, $\Delta\beta^\ddagger = 7.7 \text{ cm}^3 \text{ kbar}^{-1} \text{ mol}^{-1}$), where a conjugate base mechanism is favored also.¹⁹ We conclude that the k_s and k_{OH} isomerization processes are mechanistically similar after account is taken of the conjugate base preequilibrium step.

The base-catalyzed rearrangement of $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ in labeled $^{18}\text{OH}_2$ with or without added $\text{N}^{18}\text{O}_2^-$ (up to 1 M) yields unlabeled $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$. It was therefore not surprising that OH^- or N_3^- (up to 1 M) did not compete with the linkage isomerization reaction (see Experimental Section). Conceivably the base catalysis could arise by the reversible addition of OH^- to the $[\text{Co}-\text{ONO}]^{2+}$ moiety, but the present results exclude this possibility and support the earlier analysis in terms of a conjugate base process involving coordinated NH_3 . The ^{18}O results clearly establish that the NO_2^- ion never leaves the influence of the coordination sphere and that the base-catalyzed linkage isomerization is intramolecular; the same result has been demonstrated previously for the spontaneous isomerization. Note that nitrite ion bridging two metal centers is known²² but it is not difficult to see that the ^{18}O data and the rates which are independent of complex concentration exclude this alternative route to the isomerization.

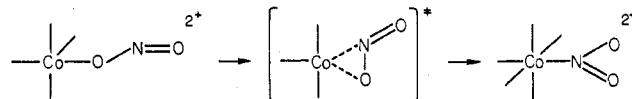
There appear to be three feasible activated complexes or intermediates consistent with the intramolecularity: a heptacoordinate state (I), a pentacoordinate tight ion pair (II), or a six-coordinate π -bonded species such as III. The ion-pair



formulation II appears to fit the experimental observations least. The reaction is carried out in a solvent which readily dissociates ion pairs yet no exchange is detected. Neither are the ionic strength effects consistent with a dissociation mechanism for an ion pair. However, such an intermediate could be appropriate should the lifetime of the ion pair be very

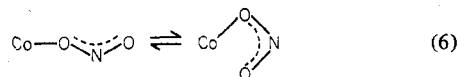
short, less than a collision to collision lifetime ($\sim 10^{-10} \text{ s}$), and should the capture of N be very efficient.

On the basis of a negative $\Delta V^\ddagger = (-6.7 \text{ cm}^3 \text{ mol}^{-1})$ for the spontaneous isomerization of $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$, a transition-state volume virtually intermediate between the volumes of the precursor and product complexes is indicated.⁹ This observation is entirely consistent with the type intermediate (I) envisaged by Basolo and Pearson,¹⁵ formed via the rearrangement



There is no such compelling case for the base-catalyzed path, where it seems that the volume of the conjugated-base transition state is close to or slightly larger than that of the deprotonated nitrito complex ($\Delta V_2^\ddagger \sim 5 \text{ cm}^3 \text{ mol}^{-1}$).

The present results may be contrasted with the (thiocyanato/isothiocyanato)pentaamminecobalt(III) system where in base some exchange of bound and free SCN^- occurs, where there is appreciable competitive hydrolysis, and where some steric change about cobalt accompanies the CoSCN to CoNCS rearrangement for the reaction $\text{trans-}[\text{Co}(\text{en})_2(\text{NH}_3)(\text{SCN})]^{2+} \xrightarrow{\text{OH}^-} \text{cis-} + \text{trans-}[\text{Co}(\text{en})_2(\text{NH}_3)(\text{NCS})]^{2+}$. The formal analogy between the spontaneous and base-catalyzed S to N thiocyanato rearrangements and O to N nitrite rearrangements brings to mind the revised anion competition results for the $[\text{Co}(\text{NH}_3)_5\text{X}]^{n+}$ ions, hydrolyzed in basic NCS^- media. The reexamination¹⁰ showed that both N- and S-bound thiocyanato complexes were formed initially but the S-bonded isomer rearranged subsequently and rapidly to the N-bound form; only the N-bound product was observed in the original study.²³ Similarly, anion competition for the base hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{X}]^{n+}$ in NO_2^- media was reported to yield just the N-bonded nitro isomer,²³ but a careful reexamination has shown now, as anticipated, the appreciable amounts of the O-bound form are produced initially.²⁴ The latter isomer was not detected in the original study, not only because the acid quenching employed converts $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ to $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$ but also because, as the present work has shown, the nitrito isomer rearranges rapidly in base to the nitro form. A detailed reinvestigation will be reported elsewhere, but the salient point here is that the oxygen of the nitrite ion competes effectively with nitrogen in trapping the presumed $[\text{Co}(\text{NH}_3)_4(\text{NH}_2)]^{2+}$ intermediate in the base hydrolysis reaction. It therefore seemed reasonable to inquire if O competed effectively with N in the linkage isomerization reaction, particularly as one of the two nitrito complex conformers seems well disposed toward such a O to O rearrangement:



Moreover, this information bears on the nature of the intermediate or transition state since, for example, only intermediate III permits competitive O and N capture. Implicit is the assumption that they arise via a common route although competitive paths cannot be excluded yet. These questions were examined by using the (presumably) specifically ^{18}O -labeled complex, $[\text{Co}(\text{NH}_3)_5(\text{ON}^{18}\text{O})]^{2+}$ or $[\text{Co}(\text{NH}_3)_5(^{18}\text{ONO})]^{2+}$, as now described.

O to O Rearrangement: ^{18}O Tracer Studies of $[\text{Co}(\text{NH}_3)_5(\text{ON}^{18}\text{O})]^{2+} \rightleftharpoons [\text{Co}(\text{NH}_3)_5(^{18}\text{ONO})]^{2+}$. Using the ^{18}O labeling technique, Murmann and Taube showed that $[\text{Co}$

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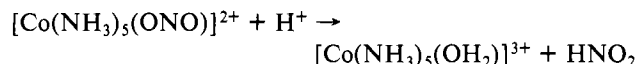
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$(\text{NH}_3)_5(\text{OH}_2)^{3+}$ when reacted with HNO_2 forms $[\text{Co}(\text{NH}_3)_5(\text{ONO})^{2+}]$ containing one labeled ^{18}O atom.⁷ Our results confirm this; $[\text{Co}(\text{NH}_3)_5(^{18}\text{ONO})]\text{Cl}_2$ prepared from $[\text{Co}(\text{NH}_3)_5(^{18}\text{OH}_2)]^{3+}$ and excess HNO_2 forms $[\text{Co}(\text{NH}_3)_5(\text{ONO})^{2+}]$ with just 50% of the oxygen atoms enriched in ^{18}O to the same extent as the starting aqua complex, similarly for the labeled nitrito complex prepared from $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$ and excess HN^{18}O_2 . These results were universally interpreted as retention of the Co–O bond. It follows that the reverse reaction, namely



must occur without Co–O cleavage, at least under the same conditions for the nitrosation reaction (pH \sim 5, which is optimum for the fastest rate of nitrosation). It has been implicitly assumed, but to date not proven, that the labeled nitrito complexes prepared by the two routes are distinct, one giving adjacent labeled oxygen and the other terminally labeled oxygen, i.e., $[\text{Co}(\text{NH}_3)_5(^{18}\text{ONO})]^{2+}$ and $[\text{Co}(\text{NH}_3)_5(\text{ON}^{18}\text{O})]^{2+}$. This could be tested by acid decomposition; the former should yield ^{18}O enriched aqua complex and the latter aqua complex of normal oxygen isotopic composition. This experiment does not seem to have been performed previously and Murmann and Taube measured the total oxygen enrichment in the O-bound nitrite (by completely removing NO_2^- from the Co complex).⁷ Interestingly, this was done in base, and the present work shows that the reaction first proceeds to $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ in which ion the oxygens are indistinguishable.

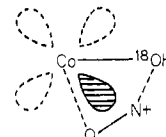
Assuming the inner and outer ^{18}O -labeled nitrito complexes to be distinguishable, we performed a base-catalyzed reaction to see if, in addition to the O to N rearrangement, an ^{18}O to ^{16}O (or vice versa) rearrangement was occurring. The reaction was quenched at $\sim 1t_{1/2}$ for the O \rightarrow N isomerization and the unreacted nitrito complex recovered as aquapentaammine after treatment with acid decomposition. The tracer results implied that, in base, ^{18}O scrambling had indeed occurred. Recovered $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$ showed only 50% of the expected enrichment rather than 100%, commencing with $[\text{Co}(\text{NH}_3)_5(^{18}\text{ONO})]^{2+}$; the same 50% enrichment was observed commencing with $[\text{Co}(\text{NH}_3)_5(\text{ON}^{18}\text{O})]^{2+}$ (rather than 0%). Furthermore, an identical result was obtained by using a significantly milder acid decomposition process for the nitrito complex (pH \sim 5, HN_3/N_3^- buffer in lieu of 1 M HCl or HBr²⁵). This result effectively eliminates acid-catalyzed ^{18}O – ^{16}O scrambling. It is clear therefore that either OH^- leads to ^{18}O – ^{16}O scrambling or that the oxygens of the $[\text{CoN}_5^{18}\text{ONO}]^{2+}$ or $[\text{CoN}_5\text{ON}^{18}\text{O}]^{2+}$ salts are already scrambled in solution and/or in the solid state.

Further experiments showed that ^{18}O scrambling had actually occurred during the synthesis of the two distinct ^{18}O labeled complexes. Attempts were made to avoid or at least reduce the ^{18}O scrambling through the use of lower temperatures and by rapid isolation of the solid products (see Experimental Section). Regardless of how the experiments were done, identical results were obtained, clearly showing that the oxygen scrambling is quite rapid ($t_{1/2} \lesssim 60$ s at 10 °C) either in solution or in the solid state. This was an unexpected and interesting result and merits some comment.

If the exchange takes place by O to O interconversion, then analogous chemistry could be expected for monodentate carbonate, carboxylate, and phosphate complexes for example. There is evidence that the rates of O to O interchange in these systems are not fast.²⁶ The oxygen atoms in carbonate complex formed from $\text{Co}(\text{NH}_3)_5(^{18}\text{OH})^{2+}$ in aqueous $\text{HC}^{16}\text{O}_3^-$

solution remains unscrambled for at least 20 exchanges of C^{16}O_2 (see Experimental Section).²⁷ Further it has been shown that for some cobalt(III) pentaamminecarboxylato complexes the exchange between the oxygen in water and the carboxylato oxygen atoms is different.^{26,28} One exchanges much more slowly than the others, which implies that the carbonyl and bound oxygens do not interchange rapidly. It should be pointed out however, that rapid oxygen scrambling has been observed for CO_2 addition to $\text{Cr}(\text{NH}_3)_5(^{18}\text{OH})^{2+}$.²⁹

There is no expectation therefore that spontaneous O to O interconversion for the nitrito complex should be rapid and other explanations for the scrambling in the synthesis need to be entertained. An alternate possibility for scrambling arises if NO^+ attaches to the filled nonbonding d orbitals of the metal ions as depicted below.



Provided proton loss is rapid and N attaches to the bound oxygen atoms to give a symmetrically bound seven-coordinate nitrito complex, either the labeled or unlabeled oxygen can leave rapidly to yield the six-coordinate complex with 50% bound ^{18}O and 50% unbound ^{18}O . Electrophilic reactions of this type have rarely been observed with first-row transition-metal complexes despite the fact that they are mostly electron-rich systems and hence, superficially at least, candidates for such processes. Also N bound nitrite could be expected as a direct consequence of such a mechanism. It is clear that these scrambling processes merit investigation for a variety of other coordinated oxanions, e.g., $[\text{Co}(\text{NH}_3)_5(\text{ONO}_2)]^{2+}$, $[\text{Co}(\text{NH}_3)_5(\text{OPO}_3)]$, and $[\text{Co}(\text{NH}_3)_5(\text{OSO}_3)]^+$ as well as a more detailed examination of the current system by ^{17}O NMR spectroscopy.

In view of present work, rapid base catalysis of the scrambling process is an additional prospect. The experiments described in the previous paragraph on labeled $[(\text{NH}_3)_5\text{Co}(\text{ONO})]^{2+}$ in base do not, of course, indicate whether ^{18}O scrambling is base catalyzed since the ^{18}O – ^{16}O scrambling equilibrium was already attained before the addition of OH^- . However, since the O to N rearrangement is base catalyzed, it seems likely that this is true also for the O to O scrambling process.

The establishment of a base-catalyzed intramolecular path for linkage isomerization of nitritopentaamminecobalt(III) and analogous rhodium(III) and iridium(III) cations complements the previously established intramolecular spontaneous isomerization for these complexes. However, an unequivocal synthesis of a selectively labeled nitrito complex is required before the O to O base-catalyzed process can be established. We are currently working on these problems by using ^{17}O NMR spectroscopy. O and N capture of bound nitrite arising from the creation of a vacant coordination site cis to the nitrite ion is also being examined.³⁰

Experimental Section

Spectrophotometric measurements were made on Cary 118C and Gilford recording instruments and mass spectral measurements for CO_2 on a ratio recording GD-150 instrument.

Rhodium trichloride and chloroiridic acid were obtained from Johnson & Matthey. Enriched ^{18}O water (1.5 and 1.7 g-atom %) was purchased from Bio-Rad Laboratories. All other chemicals used

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were Analytical Grade. Cation-exchange experiments were conducted with Bio-Rad Analytical Grade Dowex 50WX2 (H⁺ form, 200–400 mesh) and Sephadex SP C25 (Na⁺ form) resins.

Compound Preparation. The nitrito complexes [Co(NH₃)₅(ONO)](ClO₄)₂, [Rh(NH₃)₅(ONO)](ClO₄)₂, and [Ir(NH₃)₅(ONO)]Cl₂ were prepared with minor modifications of methods described previously.⁵ Anal. Calcd for H₁₅N₆Cl₂CoO₁₀: Co, 15.2; H, 3.9; N, 21.6; Cl, 18.2. Found: Co, 15.3; H, 4.1; N, 21.8; Cl, 18.0. Calcd for H₁₅N₆C₂RhO₁₀: H, 3.5; N, 19.5. Found: H, 3.8; N, 20.0. Calcd for H₁₅N₆Cl₂IrO₂: H, 3.8; N, 21.3. Found: H, 4.2; N, 21.3. The nitrito complexes used were freshly prepared. This was particularly important for the Rh complex which isomerized rapidly to the nitrito form even in the solid state. The Co and Ir complexes could be stored satisfactorily at -15 °C for a limited period (≤14 days). The accumulation of any nitro isomer was monitored typically as follows. [Co(NH₃)₅(ONO)](ClO₄)₂ (0.2 g) was dissolved in water (20 mL) and treated with HBr (10 mL, 48%) or HCl (10 mL, 10 M). After 1 min, NaN₃ (0.05 g) was added to destroy liberated HNO₂, and the mixture was diluted with water (300 mL) and sorbed on Sephadex cation-exchange resin, washed, and then eluted with 1.0 M NaClO₄ (pH 3, HClO₄). Any [Co(NH₃)₅(NO₂)₂]²⁺ appeared as a yellow band well in front of [Co(NH₃)₅(OH₂)₂]³⁺. Samples indicating >1% nitro isomer (estimated spectrophotometrically, ε₄₆₇^{max} 95.9 M⁻¹ cm⁻¹, nitro complex, ε₄₉₂^{max} 47.7, aqua complex) were recrystallized to chromatographic purity from H₂O/NaClO₄ or discarded. The nitrito and nitro linkage isomers were not separated by chromatography on Sephadex (NaClO₄ or NaCl eluant). The nitro complexes [M(NH₃)₅(NO₂)](ClO₄)₂ were prepared by routine methods and also by isomerizing the above nitrito complexes by heating in aqueous solution (90 °C, 15 min). The samples prepared by both methods had identical absorption spectra and contained no nitrito isomer (acid quenching and chromatography). They analyzed satisfactorily. The cobalt complex crystallized from water (20 °C, NaClO₄) as the diperchlorate hemihydrate. Anal. Calcd for [Co(NH₃)₅(NO₂)](ClO₄)₂·H₂O: Co, 14.8; H, 4.0; N, 21.1; Cl, 17.8. Found: Co, 14.5; H, 4.2; N, 21.2; Cl, 17.7. The water was removed by vacuum drying (P₂O₅/24 h). Anal. Calcd for [Co(NH₃)₅(NO₂)](ClO₄)₂: Co, 15.2; H, 3.9; N, 21.6; Cl, 18.2. Found: Co, 15.3; H, 4.0; N, 21.7; Cl, 18.2.

The syntheses of *cis*- and *trans*-[Co(en)₂(ONO)]ClO₄ and [Co(en)₂(ONO)(NO₂)]ClO₄ will be reported elsewhere.³⁰ The resolution of *cis*-[Co(en)₂(ONO)(NO₂)]⁺ with α -bromo-*d*-(+)-camphor-*trans*- π -sulfonate as described⁸ is not reproducible in our hands. A sample of (+)_D*cis*-[Co(en)₂(ONO)(NO₂)]ClO₄ was prepared from (+)_D-[Co(en)₂(CO₃)]ClO₄·0.5H₂O³⁰ and recrystallized to constant rotation. [M]₅₈₉²⁰ +240° M⁻¹ m, [M]₄₃₆²⁰ 1430° (H₂O), literature value⁸ [M]₅₈₉²⁰ +230°. *cis*-³¹ and *trans*-[Co(en)₂(NO₂)₂]³² salts were prepared by established methods and the *cis* isomer was resolved as described³³ by using antimonyl (+)-tartarate: *l* form (Δ), [M]₄₃₆²⁰ +5380; *d* form (Δ), [M]₄₃₆²⁰ 5400° M⁻¹ m; Br⁻ salt, [α]₅₈₉²⁰ ±42.5° (H₂O, literature value³³ ±44°).

Reaction Stoichiometry and Product Analyses. The visible absorption spectrum of [Co(NH₃)₅(ONO)]²⁺ in water changed with time and displayed sharp isosbestic points at 484 nm (ε 69.5), 415 (ε 47.5), and 370 (ε 248). These agree closely with those expected for [Co(NH₃)₅(NO₂)₂]²⁺ as the only product (484 nm (ε 70.5), 415.5 (ε 47.4), and 370 (ε 255)). In aqueous NaOH identical but more rapid changes were observed (isosbestic points ε₄₈₄ = 70.5, ε₄₁₅ = 47.8, ε₃₆₉ = 253). The absence of any significant base hydrolysis of [Co(NH₃)₅(ONO)]²⁺ to give [Co(NH₃)₅(OH)]²⁺ was confirmed as follows. Samples of the nitrito complex (0.5 g) were dissolved in H₂O, 1 M NaClO₄, 0.1 M NaOH (μ = 0.1 M), or 0.1 M NaOH (μ = 1.0 M, NaClO₄), as appropriate, and allowed to react for 10t_{1/2} (26 h, 28 h, 80 min, and 196 min, respectively). The reactions were quenched to pH ~2 with HClO₄ and the Co solutions were sorbed on and eluted from Sephadex resin with 0.2 M NaClO₄. In no case was [Co(NH₃)₅(OH₂)₂]³⁺ detected. In otherwise identical experiments, the reactions were quenched with HBr (48%, 20 min) followed by NaN₃ (0.05 g) and the diluted (500 mL of H₂O) mixture was again chromatographed on Sephadex. Only a trace of Co(NH₃)₅(OH₂)₂³⁺ was detected, clearly arising from residual Co(NH₃)₅(ONO)²⁺. In another experiment [Co(NH₃)₅(NO₂)](ClO₄)₂ was treated as described for

the nitrito isomer and was recovered unchanged from the Sephadex column.

The nitrito bis(ethylenediamine)cobalt complexes were reacted for 30 min in 0.1 M NaOH and then acid quenched (HBr), as described for the nitropentaammine cobalt ion. Sorption and elution from Sephadex revealed a single 1+ yellow band. In a separate experiment *cis*- and *trans*-[Co(en)₂(NO₂)₂]²⁺ were shown to separate cleanly on the column (0.05–0.1 M NaClO₄). The *trans* isomer eluted first.

(+)_D*cis*-[Co(en)₂(ONO)(NO₂)]ClO₄ was reacted similarly in 0.1 M NaOH for 30 min. The yellow product showed [M]₄₃₆²⁰ -5080 which did not change further with time (up to ~5 h). In a separate experiment, the same (+)_D*cis* nitronitrito sample was isomerized spontaneously in water (24 h, 25 °C), and it gave a slightly higher final [M]₄₃₆²⁰ value (-5410), identical with an authentic sample of (+)_D*cis*-[Co(en)₂(NO₂)₂]²⁺ ([M]₄₃₆²⁰ -5390). The loss in activity in 0.1 M NaOH (~6%) is small but real and is not accounted for by subsequent (+)*cis*-[Co(en)₂(NO₂)₂]²⁺ racemization (~30%, 2 days 25 °C).

Kinetic Studies. The linkage isomerization kinetics were followed by using a Gilford spectrophotometer fitted with a thermostated and cycling four-compartment sample holder. Temperature equilibrium was obtained by water circulation from a Haake refrigerating water bath. The large absorbance changes with time at 350 nm (Co), 300 nm (Rh), and 275 nm (Ir) were monitored. Rate constants were determined by the usual least-squares analysis of absorbance data collected for at least 4 half-lives. Base concentrations between 0.1 and 1.00 M were employed, generally at unit ionic strength adjusted with AnalaR sodium perchlorate. Complex concentrations were typically 1 × 10⁻³ M.

The rate of isomerization of Co(NH₃)₅(ONO)²⁺ was also measured in 0.1 M aqueous sodium hydroxide at various pressures up to 1725 bar at a single temperature (20.5 °C, μ = 0.1 M) by using a high-pressure spectrophotometer cell fitted into a Varian 635D spectrophotometer. Rate constants were calculated at each pressure via the Guggenheim method, and the activation volume (ΔV[‡]) and compressibility coefficient of activation (Δβ[‡]) were calculated by least-squares analysis of the relationship¹⁸ between k_{OH} and pressure:

$$\ln k_p = \ln k_0 + bP + cP^2 \quad (7)$$

whence ΔV[‡] = -bRT and Δβ[‡] = -2cRT. The pressure-dependent base-catalyzed rate (k_{OH}) was calculated at each pressure from k_{obsd} - k_s, using previously determined⁹ rates for the spontaneous isomerization (k_s) at each pressure.

¹⁸O Labeled Compounds. [Co(NH₃)₅(¹⁸OH₂)](ClO₄)₃ was prepared by dissolving unlabeled complex⁷ (2 g) in ¹⁸O-enriched water (20 mL) and heating at 45 °C for 48 h. The complex precipitated from the cooled product solution upon addition of a large excess of concentrated aqueous lithium perchlorate. It was separated by filtration, washed with methanol (30 cm³), and vacuum dried.

Presumed [Co(NH₃)₅(¹⁸ONO)](ClO₄)₂ was prepared from the labeled aqua complex as follows: A suspension of [Co(NH₃)₅(¹⁸OH₂)](ClO₄)₃ (2.0 g) in water (10 mL) was treated with a solution of NaNO₂ (2.0 g) in water (10 mL). The mixture was cooled to 5 °C and HClO₄ (0.50 mL, 70%) was added. It was shaken vigorously for 3–5 min and the precipitated orange-pink product was collected, washed with ice-cold water (5 mL) followed by methanol (30 mL), and then briefly (30 min) vacuum dried.

Presumed [Co(NH₃)₅(ON¹⁸O)](ClO₄)₂ was prepared essentially as described above by using unlabeled aqua complex and labeled nitrite. NaNO₂ (2 g) was dissolved in ¹⁸O water (10 mL), and HClO₄ (0.5 mL, 70%) was added. After complete ¹⁸O exchange (~2 h, 20 °C), a suspension of [Co(NH₃)₅(OH₂)](ClO₄)₃ (2.0 g) in H₂¹⁸O (10 mL) was added, and the mixture was shaken vigorously for 3–5 min. The precipitated product was immediately isolated as above, and chromatography revealed no 3+ aqua complex impurity.

The three complexes above were recrystallized from unlabeled water by using NaClO₄. An analysis for their total ¹⁸O content before and after recrystallization revealed no significant difference (e.g., 0.883 and 0.890 atom % for [Co(NH₃)₅(ON¹⁸O)]Cl₂ prepared from N¹⁸O₂⁻ 1.7 atom %).

Analytical Procedures for ¹⁸O. For labeled [Co(NH₃)₅(OH₂)₂]³⁺, the ¹⁸O content was determined as C¹⁸O₂ by driving H₂¹⁸O from the anhydrous [Co(NH₃)₅(¹⁸OH₂)]Br₃ salt (12 h, 80 °C)³⁴ and converting

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it to CO_2 by heating at 400°C with a $\text{HgCl}_2\text{-Hg}(\text{CN})_2$ mixture as described previously.³⁵ ^{18}O contents were determined for $\text{H}_2^{18}\text{O}/\text{H}^{18}\text{O}^-/\text{N}^{18}\text{O}_2^-$ solutions by distilling an aliquot of water under high vacuum after degassing (freeze-thaw method) and equilibrating with normal CO_2 as above. For ^{18}O -enriched $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ and $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$, the anhydrous chloride or bromide salts (~ 0.01 g) were pyrolyzed (12 h, 400°C) with $\text{HgCl}_2/\text{Hg}(\text{CN})_2$ (~ 0.1 g) to manufacture C^{18}O_2 . The label in $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ was also measured by converting the complex to $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]\text{Br}_3$ with aqueous HBr and determining the ^{18}O content of the aqua complex as above. This method measures the label in the inner (Co-O) oxygen (see Discussion). In all cases the ^{18}O in the CO_2 and hence the complex samples was measured as $m/e(46+45)/44 (=R)$ on a ratio recording mass spectrometer (Atlas GD 150) and calculated from the relation

$$\text{atom } \% \ ^{18}\text{O} = 10^2 R / (2 + R)$$

^{18}O Tracer Monitored Rearrangements. Labeled $[\text{Co}(\text{NH}_3)_5(\text{ONO})](\text{ClO}_4)_2$ (0.50 g) was dissolved in NaOH (1 M, 20 mL) and allowed to react for 5 min at 25°C ($\sim 5t_{1/2}$). The mixture was quickly cooled on ice and excess LiCl (5 g) was added to the solution. The precipitated nitro complex was collected, washed well with methanol (AR, 3×20 mL), and dried on a vacuum line. A portion (~ 0.1 g) was immediately analyzed for its ^{18}O content (0.883 atom %) together with the starting labeled nitrito complex as its chloride salt (0.889 atom %) obtained as follows. The nitrito perchlorate (0.2 g in a minimum volume water) was treated with concentrated aqueous LiCl , and the pink chloride salt precipitated immediately. It was collected, washed with methanol (2×20 mL), and dried under vacuum. Samples of both the labeled nitrito and nitro chlorides were recrystallized from normal water/ LiCl and the ^{18}O analyses repeated (0.89 atom % each). Each was shown to be pure by acid quenching of aqueous solutions and chromatography on Sephadex.

The prospect of inner (Co-O) and outer (N-O) oxygen scrambling of the $[\text{Co}(\text{NH}_3)_5(^{18}\text{ONO})]^{2+}$ complex in base was examined as follows. Labeled nitrito perchlorate (0.883 atom % for nitrito oxygen) (1.0 g) in 1 M NaOH (90 mL) at 25°C was reacted for 2 min ($\sim 1t_{1/2}$) and then immediately quenched with concentrated HCl (10 M, 10 mL). This selectively precipitated yellow $[\text{Co}(\text{NH}_3)_5(^{18}\text{O}^{16}\text{O})]\text{Cl}_2$ together with a little unreacted pink-orange ^{18}O - $[\text{Co}(\text{NH}_3)_5(\text{NH}_3)_2(\text{ONO})]\text{Cl}_2$. The orange filtrate containing $[\text{Co}(\text{NH}_3)_5(^{18}\text{OH}_2)]^{3+}$ derived from the remaining ^{18}O - $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ was quickly cooled to 0°C in an ice-salt bath, and ice-cold HBr (sp gr 1.78, 20 mL) was added. Approximately 15 min later and after a further addition of HBr (50 mL), the precipitated $[\text{Co}(\text{NH}_3)_5(^{18}\text{OH}_2)]\text{Br}_3$ was filtered, washed with ice water (1×5 mL) and then methanol (2×20 mL), and dried under high vacuum. A sample was analyzed for ^{18}O (0.856 atom %). The first precipitate, largely nitro complex, was dissolved in water (100 mL) and treated slowly with HCl (10 M, 10 mL). The pure yellow nitro complex precipitated leaving aquapentaammine derived from the nitrito complex impurity in solution. After 10 min at 5°C it was collected, washed, and analyzed for ^{18}O as before (0.886 atom %). A mixture of nitrito and nitro complexes can be separated by fractional crystallization from water (Cl^- salt, nitrito less soluble; ClO_4^- , nitro less soluble), but the method is not efficient.

The above experiment was repeated by using the presumed $[\text{Co}(\text{NH}_3)_5(\text{ON}^{18}\text{O})](\text{ClO}_4)_2$ in lieu of $[\text{Co}(\text{NH}_3)_5(^{18}\text{ONO})](\text{ClO}_4)_2$ with the same result.

To check whether ^{18}O scrambling was occurring spontaneously in aqueous solution or in the solid state, we dissolved $[\text{Co}(\text{NH}_3)_5(^{18}\text{ONO})](\text{ClO}_4)_2$ (1.0 g) in water (90 mL, 20°C) and added HCl (10

M, 10 mL) without delay with stirring. Some $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ survived acid decomposition by rapidly precipitating as its insoluble Cl^- salt; this was filtered off (0.883 atom %). $[\text{Co}(\text{NH}_3)_5(^{18}\text{OH}_2)]\text{Br}_3$ was quickly recovered from the filtrate, as described above and analyzed for ^{18}O (0.856 atom %). The experiment was repeated by using $[\text{Co}(\text{NH}_3)_5(\text{ON}^{18}\text{O})](\text{ClO}_4)_2$ and a lower temperature ($\sim 5^\circ\text{C}$) (product, 0.848 atom %).

Conceivably strong H^+ could affect ^{18}O scrambling in $[\text{Co}(\text{NH}_3)_5(^{18}\text{ONO})]^{2+}$ or $[\text{Co}(\text{NH}_3)_5(\text{ON}^{18}\text{O})]^{2+}$ prior to conversion to $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+} + \text{HNO}_2$, and so a milder N-O cleavage reaction was developed: ^{18}O -labeled (inner or outer) $[\text{Co}(\text{NH}_3)_5(\text{ONO})](\text{ClO}_4)_2$ (0.6 g) was dissolved in aqueous NaN_3 (26 g, 0.4 mol, in 1 L) and HCl (250 mL, 1 M, 0.25 mol) was added to give a HN_3/N_3^- buffer solution, pH 4.5 (*Caution: HN_3 is toxic*). After the mixture was stirred for 90 min at 25°C , cation-exchange resin (Dowex 50 WX_2 , Na^+ form; 2 g) was added and the mixture shaken to sorb the $[\text{Co}(\text{NH}_3)_5(^{18}\text{OH}_2)]^{3+}$ (0.773 atom %). On settlement and decantation, the resin was collected and washed (5×10 mL of H_2O). $[\text{Co}(\text{NH}_3)_5(^{18}\text{OH})]^{2+}$ was eluted quickly from a small column of this resin by using LiBr (1 M, pH 10, adjusted with LiOH). The eluate (~ 200 mL) was cooled to 5°C and cold HBr (30 mL, sp gr 1.78) added. After 30 min, the precipitated $[\text{Co}(\text{NH}_3)_5(^{18}\text{OH})]\text{Br}_3$ was collected, washed, and dried as earlier and analyzed for ^{18}O (0.768 atom %).

To check whether ^{18}O scrambling also occurred rapidly in the analogous $[\text{Co}(\text{NH}_3)_5(^{18}\text{OCO}_2\text{H})]^{2+}$ complex in solution, we added $[\text{Co}(\text{NH}_3)_5(^{18}\text{OH}_2)](\text{ClO}_4)_3$ (0.46 g) to a solution of sodium bicarbonate (0.5 g) in water (10 mL) where the pH had been adjusted to 7.80 with HClO_4 . The solution was allowed to stand for 5 min, quenched by the addition of ice-cold HBr (sp gr 1.78, 5 mL), and the precipitated $[\text{Co}(\text{NH}_3)_5(^{18}\text{OH}_2)]\text{Br}_3$ recovered and analyzed for ^{18}O as described above. The ^{18}O content of the recovered complex (1.415 atom %) was essentially identical with that of the initial sample (1.456 atom %), although at least 20 exchanges of C^{16}O_2 occur under the reaction conditions chosen.²⁷

Anion Competition. (a) **In 1 M $\text{N}^{18}\text{O}_2^-$.** A sample of unenriched $[\text{Co}(\text{NH}_3)_5(\text{ONO})](\text{ClO}_4)_2$ (0.2 g) was isomerized to $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ in 1 M Na^{18}OH containing $\text{NaN}^{18}\text{O}_2$ (1 M). The reaction medium was prepared by first exchanging NO_2^- (0.70 g, NaNO_2) in H_2^{18}O (1.7 atom %) for 3 h at pH ~ 5 , adjusted with HClO_4 (70%, 0.20 mL). NaOH (0.4 g) was then added to bring the pH up to ~ 14 . The nitro complex product was isolated as its chloride salt and analyzed for ^{18}O as described earlier (0.00 atom %).

(b) **In 1 M NaN_3 .** The above experiment was repeated on a 0.5-g scale by using 1.0 M NaOH , 1 M in NaN_3 in place of 1.0 M Na^{18}OH + 1.0 M $\text{NaN}^{18}\text{O}_2$. After 10 min, the mixture was diluted to 500 mL with water, sorbed, washed, and eluted (1 M NaClO_4 , pH 3) from Dowex resin. A single yellow band (2+ ion) was obtained, with a visible spectrum identical with that of $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ except that the extinction coefficients were $\sim 2\%$ lower (i.e., 98% recovery of Co from the resin). None of the intensely absorbing violet $[\text{Co}(\text{NH}_3)_5\text{N}_3]^{2+}$ ($\epsilon_{515}^{\text{max}} 272$) was detected.

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Registry No. $[\text{Co}(\text{NH}_3)_5(\text{ONO})](\text{ClO}_4)_2$, 14970-12-8; $[\text{Rh}(\text{NH}_3)_5(\text{ONO})](\text{ClO}_4)_2$, 72609-92-8; $[\text{Ir}(\text{NH}_3)_5(\text{ONO})](\text{ClO}_4)_2$, 72609-91-7; *cis*- $[\text{Co}(\text{en})_2(\text{ONO})_2]^{2+}$, 46361-12-0; *trans*- $[\text{Co}(\text{en})_2(\text{ONO})_2]^{2+}$, 53955-76-3; *cis*- $[\text{Co}(\text{en})_2(\text{ONO})(\text{NO}_2)]^{2+}$, 72746-29-3; *trans*- $[\text{Co}(\text{en})_2(\text{ONO})(\text{NO}_2)]^{2+}$, 72746-31-7; (+)-*cis*- $[\text{Co}(\text{en})_2(\text{ONO})(\text{NO}_2)]^{2+}$, 72746-30-6; $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)](\text{ClO}_4)_2$, 15040-54-7.