

## Mechanistic Information from the Effect of Pressure on the Linkage Isomerization Reactions of *Cis*- and *Trans*-dinitritobis(ethylenediamine)cobalt(III) in Aqueous Acidic Solution

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The linkage isomerization mechanism of *cis*- $\text{Co}(\text{en})_2(\text{ONO})_2^+$  consists of two reactions: a fast step ( $k = (3.6 \pm 0.3) \times 10^{-3} \text{ sec}^{-1}$  at  $35^\circ\text{C}$ ,  $\Delta H^\ddagger = 15.5 \pm 0.5 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -19.1 \pm 1.7 \text{ cal K}^{-1} \text{ mol}^{-1}$ ) during which *cis*- $\text{Co}(\text{en})_2(\text{NO}_2)\text{ONO}^+$  is produced, followed by a slower step ( $k = (7.1 \pm 0.1) \times 10^{-4} \text{ sec}^{-1}$  at  $35^\circ\text{C}$ ,  $\Delta H^\ddagger = 19.5 \pm 0.2 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -9.4 \pm 0.6 \text{ cal K}^{-1} \text{ mol}^{-1}$ ) to produce *cis*- $\text{Co}(\text{en})_2(\text{NO}_2)_2^+$ . The *trans*- $\text{Co}(\text{en})_2(\text{ONO})_2^+$  species undergoes a slow isomerization reaction ( $k = (8.4 \pm 0.3) \times 10^{-4} \text{ sec}^{-1}$  at  $35^\circ\text{C}$ ) to form *trans*- $\text{Co}(\text{en})_2(\text{NO}_2)\text{ONO}^+$ , which is followed by a rapid reaction to produce *trans*- $\text{Co}(\text{en})_2(\text{NO}_2)_2^+$ . The volumes of activation for the various linkage isomerization reactions are between  $-3.4$  and  $-6.9 \text{ cm}^3 \text{ mol}^{-1}$ , and are interpreted in terms of intramolecular isomerization processes.

### Introduction

Linkage isomerization reactions of complexes of the type  $\text{M}(\text{NH}_3)_5\text{ONO}^{2+}$  to produce  $\text{M}(\text{NH}_3)_5\text{NO}_2^{2+}$  ( $\text{M} = \text{Co}(\text{III}), \text{Rh}(\text{III})$  and  $\text{Ir}(\text{III})$ ) have been demonstrated [1, 2] to proceed via intramolecular rearrangement mechanisms. An earlier study from this laboratory [3] reported volumes of activation of  $-6.7 \pm 0.4$ ,  $-7.4 \pm 0.4$  and  $-5.9 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$  for the mentioned isomerization reactions, respectively. Volume profile measurements showed that the volume of the transition state of such an isomerization reaction lies approximately halfway between the partial molar volumes of the nitroto and the nitro complex ions. A recent paper [4] reported that the base-catalyzed linkage isomerization reactions of the mentioned complexes also follow an intramolecular process. The volume of activation for the base-catalyzed isomerization of  $\text{Co}(\text{NH}_3)_5\text{ONO}^{2+}$  was

found [4] to be  $+27 \pm 1.4 \text{ cm}^3 \text{ mol}^{-1}$ , and was ascribed to a conjugate base pre-equilibrium mechanism.

Seel and Meyer [5, 6] reported the preparation, spectra and linkage isomerization kinetics of *cis*- and *trans*- $\text{Co}(\text{en})_2(\text{ONO})_2^+$ . They observed deviations in the initial part of the first-order plots for the isomerization of the *cis*-dinitrito complex and ascribed this to a mechanism consisting of two consecutive isomerization reactions during which a nitro-nitrito intermediate is formed. No such deviations were observed in the case of the *trans*-dinitrito species. In addition, it was demonstrated [4] that these isomerization reactions proceed with retention of configuration.

We have investigated the kinetics and mechanisms of the linkage isomerization reactions of *cis*- and *trans*- $\text{Co}(\text{en})_2(\text{ONO})_2^+$  in more detail, and report our findings, including those of the pressure dependencies of the various reaction steps, in the following sections.

### Experimental

Some details concerning the synthesis of the complexes used in this study have been reported in a preliminary communication [7]. In addition, the following complexes were prepared as reported in the literature: *cis*- $[\text{Co}(\text{en})_2(\text{ONO})_2]\text{ClO}_4$  [5]; *trans*- $[\text{Co}(\text{en})_2(\text{ONO})_2]\text{ClO}_4$  [5]; *cis*- $[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{ClO}_4$  [8, 9]; and *trans*- $[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{ClO}_4$  [10]. In the case of the *cis*-dinitrito species, we found a considerable amount of the nitro-nitrito species in the raw product. Rapid dissolution of the raw product in cold water (2 g/250 ml), followed by the addition of  $\text{NaClO}_4$ , resulted in a 50% yield of the pure dinitrito species. Since both dinitrito complexes undergo linkage isomerization at room temperature in the solid phase, these substances were stored in liquid nitrogen. The results for the analyses [11]

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of the *cis*- and *trans*-dinitrito complexes, respectively, are (theoretically expected values quoted in brackets): % C: 13.25, 12.95 (12.95); % H: 4.25, 4.15 (4.32); % N: 22.7, 22.7 (22.7); % Cl: 9.65, 9.25 (9.58). U.V.-visible absorption spectra of the dinitrito and dinitro complexes are reported and compared to literature data in Table I. Chemicals of analytical reagent grade and doubly distilled water were used throughout this study.  $\text{NaClO}_4$  was used to adjust the ionic strength of the test solutions.

U.V.-visible absorption spectra were recorded on a Perkin Elmer 555 and a Zeiss DMR 10 spectrophotometer. pH measurements were made with a Radiometer PHM 64 instrument. Kinetic measurements at normal pressure were performed in the thermostatted cell compartment ( $\pm 0.1^\circ\text{C}$ ) of the Zeiss DMR 10 spectrophotometer, whereas those at elevated pressures on a Zeiss PMQ II spectrophotometer equipped with a thermostatted ( $\pm 0.1^\circ\text{C}$ ) high pressure cell [12]. Quartz 'pill-box' cuvettes [13] were used in the latter set-up. The kinetics were studied at wavelengths corresponding to the maximum absorbance changes. The observed first-order rate constants,  $k_{\text{obs}}$ , were calculated from plots of  $\ln(A_\infty - A_t)$  versus  $t$  where  $A_\infty$  and  $A_t$  are the absorbances at infinity and time  $t$  respectively. In some cases  $A_\infty$  was calculated (using a standard computer programme [14]), due to the interference of secondary reactions with the experimentally observed  $A_\infty$ . The first-order plots proved to be linear for at least 3 half-lives.

## Results and Discussion

Some preliminary experiments were designed to investigate possible secondary processes that could interfere with the reactions to be studied. In one of these the *cis* to *trans* isomerization of  $\text{Co}(\text{en})_2(\text{NO}_2)_2^+$  was investigated. Werner [15] and others [10] have reported the synthesis of the *trans*-dinitro complex *via* isomerization of the *cis*-species. A  $2 \times 10^{-4} \text{ M}$  solution of the *cis* complex was heated at *ca.*  $90^\circ\text{C}$  under reflux for several days, during which time samples were analysed spectrophotometrically. We were unable to confirm the isomerization process observed earlier. The observed spectral changes rather indicated decomposition of the complex, accompanied by the possible formation of  $\text{Co}(\text{II})$  species. We are at present further investigating the suggested isomerization process in detail, in order to clarify the apparent discrepancy. However, whatever the real nature of the observed process may be, it is indeed very slow [16] (half-life of *ca.* one day at  $90^\circ\text{C}$ ) and cannot interfere with the studied linkage

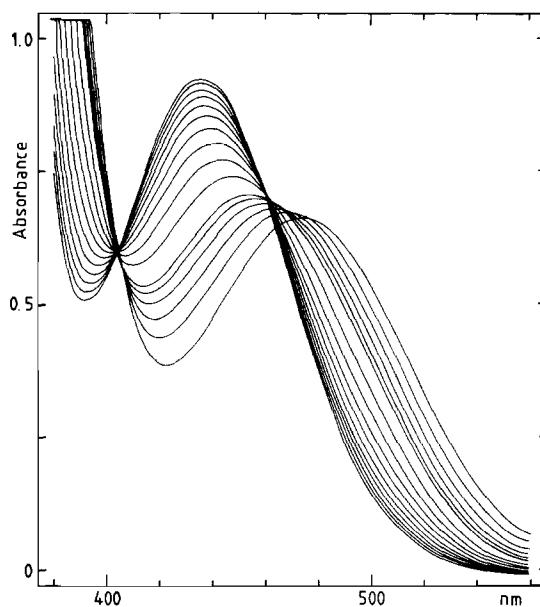


Fig. 1. Repetitive scan spectra for the process  $\text{cis-Co}(\text{en})_2(\text{ONO})_2^+ \rightarrow \text{cis-Co}(\text{en})_2(\text{NO}_2)_2^+$ .  $[\text{Co}(\text{III})] = 4.7 \times 10^{-3} \text{ M}$ ;  $\text{pH} \sim 4$ ;  $\text{temp.} = 25^\circ\text{C}$ ;  $\Delta t = 5$  and  $15$  min, optical path-length =  $1 \text{ cm}$ ;

isomerization reactions under the experimental conditions employed.

### Linkage Isomerization of $\text{cis-Co}(\text{en})_2(\text{ONO})_2^+$

The repetitive scan spectra of a freshly prepared sample of  $\text{cis-}[\text{Co}(\text{en})_2(\text{ONO})_2]\text{ClO}_4$  in aqueous solution is illustrated in Fig. 1. It can be seen that the first few recorded spectra do not pass through the isosbestic points at 405 and 460 nm. This is typical for a two-stage process and may be considered as evidence for an initial fast linkage isomerization step to produce  $\text{cis-Co}(\text{en})_2(\text{NO}_2)\text{ONO}^+$ , followed by a second slower isomerization reaction to form  $\text{cis-Co}(\text{en})_2(\text{NO}_2)_2^+$ . This is in agreement with earlier observations by Seel and Meyer [6] and accounts for the difference in the absorption spectra recorded for the  $\text{cis-Co}(\text{en})_2(\text{ONO})_2^+$  species in Table I. If one allows the solid complex to stand at room temperature, distinct colour changes can be observed within a few hours, and repetitive scan spectra of such a sample no longer exhibit the initial deviations shown in Fig. 1. The isosbestic points in Fig. 1 can therefore be assigned to the second, slower isomerization reaction. The kinetics of the first isomerization process was followed at 460 nm, the isosbestic point of the second process, in order to eliminate the influence of the secondary reaction. On the Zeiss DMR 10 spectrophotometer we found an isosbestic point at 462.6 nm, which differs up to 3 nm from what we measured on other spectrophotometers. This wavelength proved to be very critical,

TABLE I. Absorption Spectra of Some Co(III) Nitro and Nitrito Complexes.

Complex	$\lambda_{\max}$ , nm	$\epsilon_{\max}$ , $M^{-1} \text{ cm}^{-1}$	Reference
<i>cis</i> -[Co(en) <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub> ]NO <sub>3</sub>	438, 325, 240	218.8, 5012, 16600	19
<i>cis</i> -[Co(en) <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub> ]ClO <sub>4</sub>	437, 322, 240	177.8, 3802, 22400	5
	436, 322	196.7, 3803	This work
<i>trans</i> -[Co(en) <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub> ]NO <sub>3</sub>	433, 250	199.5, 12300	19
<i>trans</i> -[Co(en) <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub> ]ClO <sub>4</sub>	430, 339, 250	199.5, 3467, 20400	5
	430, 335, 248	192.8, 3400, 21000	This work
<i>cis</i> -[Co(en) <sub>2</sub> (ONO) <sub>2</sub> ]ClO <sub>4</sub>	480, 330, 228	123.0, 933, 24550	5
	475, 328	140.4, 1443	This work
<i>trans</i> -[Co(en) <sub>2</sub> (ONO) <sub>2</sub> ]ClO <sub>4</sub>	513, 233	61.7, 29500	5
	515(sh), 233	66.8, 25600	This work

TABLE II.  $k_{\text{obs}}$  as a Function of Temperature and Pressure for the Reaction<sup>a</sup>: *cis*-Co(en)<sub>2</sub>(ONO)<sub>2</sub><sup>+</sup> → *cis*-Co(en)<sub>2</sub>(NO<sub>2</sub>)ONO<sup>+</sup>.

Temp. °C	Pressure bar	$k_{\text{obs}} \times 10^3 \text{ sec}^{-1}$	Activation Parameter
25.0	50	1.50, 1.57, 1.56, 1.51	$\Delta \bar{V}^\ddagger = -5.6 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$
	200	1.51, 1.48	
	400	1.71, 1.65, 1.60	
	600	1.72, 1.65, 1.68	
	800	1.78, 1.98, 1.73	
	1000	1.94, 1.89, 1.86	
18.2	1	0.772, 0.873, 0.815	$\Delta H^\ddagger = 15.5 \pm 0.5 \text{ kcal mol}^{-1}$
25.0		1.57, 1.67, 1.59, 1.54, 1.52	$\Delta S^\ddagger = -19.1 \pm 1.7 \text{ cal K}^{-1} \text{ mol}^{-1}$
30.0		2.71, 2.48, 2.63, 2.62	
35.0		3.35, 3.92, 3.65	

<sup>a</sup>[Co(III)] = 0.5–1.0 × 10<sup>-2</sup> M, ionic strength = 0.5 M, pH ~ 4, wavelength = 460 nm.

and changes in room and cell temperature influenced the optics of the spectrophotometer to such an extent that drifts (either up or down) occurred in the experimental  $A_\infty$  values.

The kinetic results are summarized as a function of temperature and pressure in Table II. The activation parameters were calculated in the usual way, and the plot of  $\ln k_{\text{obs}}$  versus pressure was linear within the experimental error limits concerned. The second isomerization process could be followed without any complications, and the values of  $k_{\text{obs}}$  as a function of pressure are summarized in Table III.  $\Delta \bar{V}^\ddagger$  was calculated from the linear dependence of  $\ln k_{\text{obs}}$  on pressure. No temperature-dependence study of this reaction was performed, since such data have been reported in the literature [6].

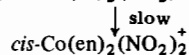
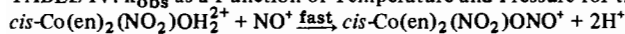
In addition, kinetic data for the second isomerization step was obtained in a completely different way

TABLE III.  $k_{\text{obs}}$  as a Function of Pressure for the Reaction<sup>a</sup>: *cis*-Co(en)<sub>2</sub>(NO<sub>2</sub>)ONO<sup>+</sup> → *cis*-Co(en)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub><sup>+</sup>

Pressure bar	$k_{\text{obs}} \times 10^4 \text{ sec}^{-1}$	$\Delta \bar{V}^\ddagger \text{ cm}^3 \text{ mol}^{-1}$
50	7.88, 7.94, 8.59, 8.09	$-6.9 \pm 0.7$
	8.35, 7.59, 8.25	
500	9.53, 9.35, 9.01, 9.00	
1000	10.6, 11.2, 10.2	
1500	12.7, 13.5, 12.8, 13.1	
	10.6, 9.8	

<sup>a</sup>[Co(III)] = 4–6 × 10<sup>-4</sup> M, ionic strength = 0.5 M, pH ~ 4, wavelength = 322 nm, temp. = 35.0 °C.

by starting with *cis*-Co(en)<sub>2</sub>(NO<sub>2</sub>)OH<sub>2</sub><sup>2+</sup> in solution [7]. Such species are capable of reacting quite rapidly with NO<sup>+</sup> (produced by NO<sub>2</sub><sup>-</sup> at pH 3 to 5) [17, 18]

TABLE IV.  $k_{\text{obs}}$  as a Function of Temperature and Pressure for the Reaction<sup>a</sup>:

Temp. °C	Pressure bar	$k_{\text{obs}} \times 10^4 \text{ sec}^{-1}$	Activation Parameter
35.0	50	7.09, 7.10, 7.15, 7.01, 7.01, 7.11	$\Delta\bar{V}^\ddagger = -3.4 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$
	500	7.83, 7.67, 7.62	
	1000	8.21, 8.16, 8.12, 8.08, 8.04	
	1500	8.63, 8.56, 8.27, 9.00	
22.0	50	1.71, 1.61, 1.46, 1.61	$\Delta H^\ddagger = 19.5 \pm 0.2 \text{ kcal mol}^{-1}$
35.0		7.09, 7.10, 7.15, 7.01	
		7.01, 7.11	
47.0		24.6, 25.1, 24.3	$\Delta S^\ddagger = -9.4 \pm 0.6 \text{ cal K}^{-1} \text{ mol}^{-1}$
53.0	44.3, 41.1, 40.0, 42.2		

<sup>a</sup>[Co(III)] =  $1-2 \times 10^{-2} \text{ M}$ , ionic strength = 0.5 M,  $[\text{NO}_2^-]_{\text{T}} = 0.2 \text{ M}$ , pH = 3.6, wavelength = 438 nm.

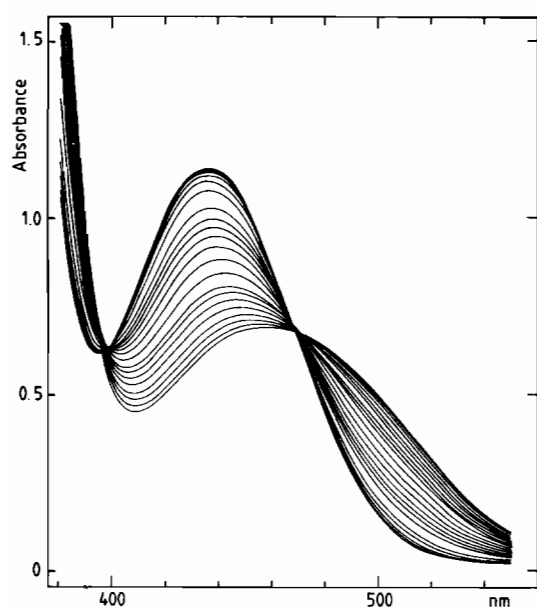


Fig. 2. Repetitive scan spectra for the process  $\text{cis-Co(en)}_2(\text{NO}_2)\text{OH}_2^{2+} + \text{NO}^+ \rightarrow \text{cis-Co(en)}_2(\text{NO}_2)_2^+ + 2\text{H}^+$ . [Co(III)] =  $5.6 \times 10^{-3} \text{ M}$ ;  $[\text{NO}_2^-]_{\text{T}} = 0.1 \text{ M}$ ; pH = 3.6; Temp. = 25 °C;  $\Delta t = 6, 30$  and 120 min, respectively; optical pathlength = 1 cm.

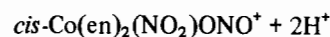
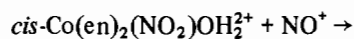
to form the corresponding nitrito complex, i.e.  $\text{cis-Co(en)}_2(\text{NO}_2)\text{ONO}^+$ , which undergoes subsequent linkage isomerization. Repetitive scan spectra (Fig. 2) indicate initial deviations from the isobestic points due to the interference of the  $\text{NO}^+$  uptake process. This situation can be improved substantially by lowering the pH, in order to increase the rate of the  $\text{NO}^+$  uptake process [18]. The isobestic points

TABLE V.  $k_{\text{obs}}$  as a Function of Pressure for the Reaction<sup>a</sup>:  $\text{trans-Co(en)}_2(\text{ONO})_2^+ \rightarrow \text{trans-Co(en)}_2(\text{NO}_2)_2^+$ 

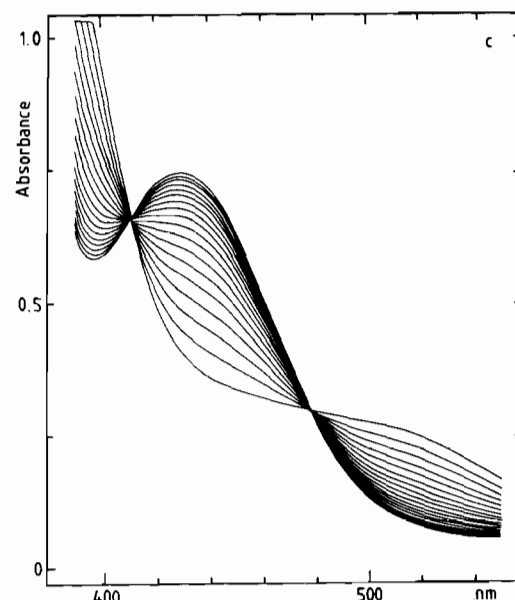
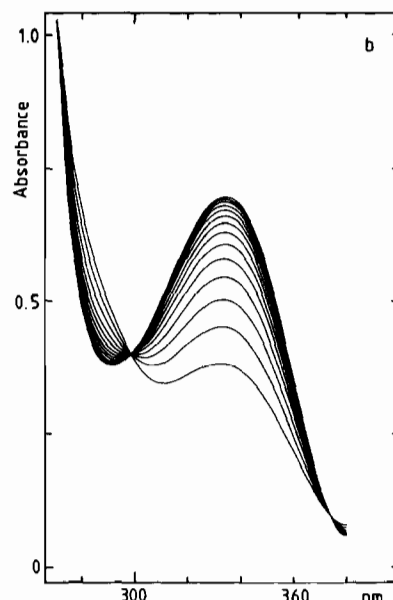
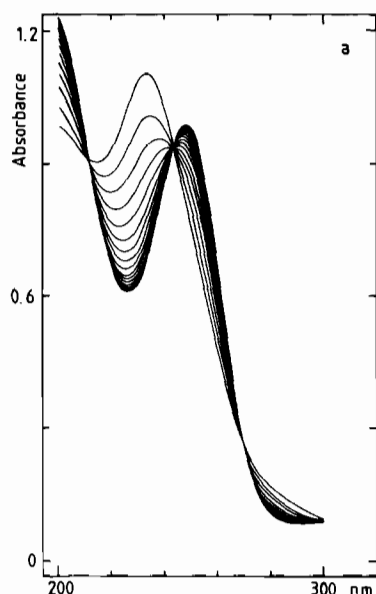
Pressure bar	$k_{\text{obs}} \times 10^3 \text{ sec}^{-1}$	$\Delta\bar{V}^\ddagger \text{ cm}^3 \text{ mol}^{-1}$
50	0.84, 0.88, 0.83, 0.82	$-3.6 \pm 0.4$
	0.88, 0.83, 0.83	
250	0.84, 0.95	
500	0.98, 0.97, 0.96, 0.95, 0.93	
750	0.92, 0.91, 0.91, 0.92	
1000	1.06, 1.00, 0.99, 0.99, 1.02	
1250	0.91, 1.07, 1.02	
1500	1.07, 1.05, 1.04	
1750	1.05, 1.11	

<sup>a</sup>[Co(III)] =  $2-6 \times 10^{-4} \text{ M}$ , ionic strength = 0.5 M, pH ~ 4, wavelength = 335 nm, temp. = 35 °C.

in Fig. 2 at 398 and 464 nm are in close agreement with those shown in Fig. 1. The differences are ascribed to the absorbance of nitrite at lower wavelengths in the former case (Fig. 2). Attempts to determine the isobestic points for the reaction



in a similar way as performed for the corresponding pentaammineaquo species [18] were unsuccessful. Some kinetic measurements demonstrated that  $k_{\text{obs}}$  for the linkage isomerization of  $\text{cis-Co(en)}_2(\text{NO}_2)\text{ONO}^+$  is independent of pH and  $[\text{NO}_2^-]$  in the ranges 2.5 to 5.3 and 0.1 to 0.3 M, respectively. The values of  $k_{\text{obs}}$  as a function of pressure (Table IV) and the corresponding volume of activation are lower than



those reported for the same reaction in Table III. This is most probably due to some minor influence of the nitrosation step.

#### Linkage Isomerization of $\text{trans-Co(en)}_2(\text{ONO})_2^+$

Repetitive scan spectra of a freshly prepared sample of the *trans*-dinitrito complex ion (Fig. 3) show clean isosbestic points at 212, 244, 270, 298, 374, 411 and 478 nm. No deviations are observed initially as in the case of the *cis*-species, and we conclude that only the rate-determining isomerization process is seen kinetically. The absorbance changes result in good first-order plots [6], and  $k_{\text{obs}}$  was shown to be independent of pH in the range 3 to 6. The data for  $k_{\text{obs}}$  as a function of pressure are summarized in Table V, and  $\Delta\bar{V}^\ddagger$  was calculated as before. A different experimental approach was adopted to clarify whether the first or the second isomerization step is rate-determining.

$\text{Trans-Co(en)}_2(\text{NO}_2)\text{OH}_2^{2+}$  was prepared in solution as described before [7], and treated with  $\text{NO}_2^-$  at pH 3.6 to produce the intermediate *trans*-nitro-nitrito species. Repetitive scan spectra of such a reaction mixture (Fig. 4) show a clean isosbestic point at 469 nm, which differs completely from those observed in Fig. 3, and which could possibly be considered as evidence for the occurrence of the second isomerization process. However, the data in Table VI clearly illustrate that the observed process strongly depends on pH and  $[\text{NO}_2^-]$ , and must therefore, be associated with the  $\text{NO}^+$  uptake process [18]. Furthermore, the temperature and pressure dependences of this process are in good agreement with those reported recently for the uptake of  $\text{NO}^+$  by  $\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$  [18]. The rather large error limits

Fig. 3. Repetitive scan spectra for the process  $\text{trans-Co(en)}_2(\text{ONO})_2^+ \rightarrow \text{trans-Co(en)}_2(\text{NO}_2)_2^+$ .  $[\text{Co(III)}] = 4.7 \times 10^{-5}$  (a),  $2 \times 10^{-4}$  (b),  $4 \times 10^{-3}$  (c) M; pH  $\sim$  4; temp. = 25 °C;  $\Delta t = 7$  min; optical pathlength = 1 cm.

on  $\Delta\bar{V}^\ddagger$  are due to the complexity of the system which consists of a series of reactions and equilibria [18]. The data, however, do illustrate that the minimum pressure of 50 bar applied during the temperature dependence study to eliminate the formation of gas bubbles should have no significant influence on the values of  $k_{\text{obs}}$ . The final spectrum in Fig. 4 is in excellent agreement with that for the *trans*-dinitro species, from which we derive that the

TABLE VI.  $k_{\text{obs}}$  as a Function of  $[\text{NO}_2^-]$ , pH, Temperature and Pressure for the Reaction<sup>a</sup>:  $\text{trans-Co(en)}_2(\text{NO}_2)\text{OH}_2^{2+} + \text{NO}_2^-/\text{H}^+ \rightarrow \text{trans-Co(en)}_2(\text{NO}_2)_2^+$ 

Temp. °C	Pressure bar	$[\text{NO}_2^-]_{\text{T}}$ M	pH	$k_{\text{obs}} \times 10^3 \text{ sec}^{-1}$
21.0	1	0.1	4.5	0.37, 0.39
		0.15		0.54
		0.2		0.85, 0.80
		0.25		1.16
		0.3		1.54, 1.28
20.0	1	0.2	3.5	1.49
			4.0	1.02
			4.3	0.85
			4.8	0.72
			5.6	0.53
19.8	50	0.2	3.6	0.94, 0.84, 1.01
25.0				1.25, 1.20, 1.57, 1.41
29.5				2.20, 2.47, 2.31, 2.04
				2.52, 2.15, 1.90, 1.99
35.0				4.04, 4.03, 3.68, 3.96
35.0	500	0.2	3.6	3.36, 3.18, 3.92, 3.86
	1000			3.34, 3.04, 2.62, 2.91, 2.92
				2.69, 2.78, 2.79, 2.87, 2.87
				3.89, 3.86, 3.10, 3.19
				3.02, 3.02
19.8–35.0	50	0.2	3.6	$\Delta H^\ddagger = 16.4 \pm 0.7 \text{ kcal mol}^{-1}$ $\Delta S^\ddagger = -16.3 \pm 2.5 \text{ cal K}^{-1} \text{ mol}^{-1}$
35.0	50–1000	0.2	3.6	$\Delta \bar{V}^\ddagger = 3.5 \pm 2.0 \text{ cm}^3 \text{ mol}^{-1}$

<sup>a</sup> $[\text{Co(III)}] = 1-2 \times 10^{-2} \text{ M}$ , ionic strength = 0.5 M, wavelength = 430 nm.

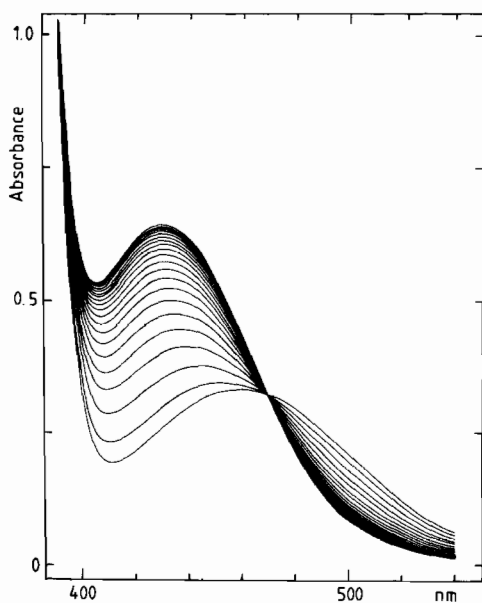
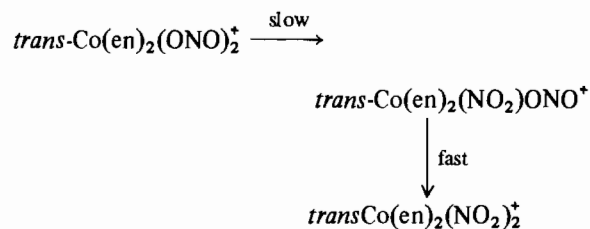


Fig. 4. Repetitive scan spectra for the process  $\text{trans-Co(en)}_2(\text{NO}_2)\text{OH}_2^{2+} + \text{NO}_2^- \rightarrow \text{trans-Co(en)}_2(\text{NO}_2)_2^+ + 2\text{H}^+$ .  $[\text{Co(III)}] = 3.3 \times 10^{-3} \text{ M}$ ;  $[\text{NO}_2^-]_{\text{T}} = 0.1 \text{ M}$ ; pH = 3.6; Temp. = 25 °C;  $\Delta t = 7 \text{ min}$ ; optical pathlength = 1 cm.

isomerization step following  $\text{NO}^+$  uptake is indeed very fast. This further allows us to conclude that the observed spectral changes in Fig. 3 can be ascribed to the first isomerization reaction being the rate-determining step, viz.



followed by the fast second isomerization process.

A comparison of the rate and activation parameters for the different isomerization processes is given in Table VII. From this and the earlier presented information it follows that the linkage isomerization reactions of *cis*- and *trans*- $\text{Co(en)}_2(\text{ONO})_2^+$  differ significantly. In the case of the *cis* system the dinitrito species isomerizes rapidly to the nitro-nitrito intermediate, followed by a slower process during which the dinitro species is produced. The *trans* dinitrito complex on the other hand

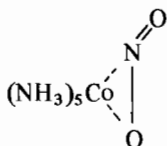
TABLE VI. Summary of Rate and Activation Parameters for the Linkage Isomerization Reactions of  $\text{cis-}$  and  $\text{trans-Co(en)}_2(\text{ONO})_2^+$ .

Reaction	$k_{\text{obs}} \times 10^4$ at 35 °C, $\text{sec}^{-1}$	$\Delta\bar{V}^\ddagger$ $\text{cm}^3 \text{mol}^{-1}$	$\Delta H^\ddagger$ $\text{kcal mol}^{-1}$	$\Delta S^\ddagger$ $\text{cal K}^{-1} \text{mol}^{-1}$	Reference
$\text{cis-Co(en)}_2(\text{ONO})_2^+ \rightarrow \text{cis-Co(en)}_2(\text{NO}_2)\text{ONO}^+$	$36.4 \pm 2.8$	$-5.6 \pm 0.6^{\text{a}}$	$15.5 \pm 0.5$	$-19.1 \pm 1.7$	Table II
$\text{cis-Co(en)}_2(\text{NO}_2)\text{ONO}^+ \rightarrow \text{cis-Co(en)}_2(\text{NO}_2)_2^+$	$7.68 \pm 0.03$	—	$20.6 \pm 0.7$	$-5.9 \pm 2.5$	6
	7.55				20
	$8.10 \pm 0.33$	$-6.9 \pm 0.7^{\text{b}}$	—	—	Table III
	$7.08 \pm 0.06$	$-3.4 \pm 0.2^{\text{b}}$	$19.5 \pm 0.2$	$-9.4 \pm 0.6$	Table IV
$\text{trans-Co(en)}_2(\text{ONO})_2^+ \rightarrow \text{trans-Co(en)}_2(\text{NO}_2)\text{ONO}^+$	$10.2 \pm 0.1$	—	$23.0 \pm 0.5$	$+2.6 \pm 1.5$	6
	$8.44 \pm 0.25$	$-3.6 \pm 0.4^{\text{b}}$	—	—	Table V

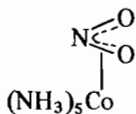
<sup>a</sup>Temp. = 25 °C. <sup>b</sup>Temp. = 35 °C.

undergoes rate-determining isomerization to produce the nitro–nitrito intermediate, followed by a fast consecutive step to produce the dinitro species.  $k_{\text{obs}}$  for the first isomerization step of the  $\text{cis}$ -dinitrito complex is approx. three times the value for the  $\text{trans}$  species. This is also reflected in significantly lower  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values. This may be due to some interaction between the two nitrito ligands  $\text{cis}$  to each other, which may assist the isomerization process. The significantly faster second isomerization step of the  $\text{trans}$  complex compared to that of the  $\text{cis}$  species is ascribed to the strong  $\text{trans}$  labilizing effect of the nitro ligand, which will weaken the Co–ONO bond and thus promote the isomerization process. The values of  $k_{\text{obs}}$  and its activation parameters are in good agreement with the available literature data [6, 20].

The magnitudes of the volumes of activation for the various reactions quoted in Table VII are in good agreement with those reported before [3] for similar isomerization processes. Two alternative explanations can account for a decrease in volume during the isomerization reactions of the pentamine-nitrito complexes. Basolo and Pearson [17] suggested a reaction sequence that involves a heptacoordinate transition state of the type



Alternatively, Sargeson and co-workers [4] considered the possibility of a six-coordinate  $\pi$ -bonded intermediate species of the type



Both intermediates will give rise to a decrease in volume during the formation of the transition state and so account for the fact that the transition state volume lies between the volume of the precursor and product complexes [3]. We therefore suggest that a similar situation accounts for the volumes of activation reported in this study. The actual geometry of the transition state may differ significantly for the  $\text{cis-}$  and  $\text{trans-}$  isomers, since an interaction with the adjacent nitrito/nitro ligand is bound to occur in the case of the  $\text{cis}$  species.

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