Mercury(II)- and Nitrosyl-induced Aquation of Anionopenta-aminecobalt(III) Species. Reactions of the *t*-$[Co\{N(CH_2CH_2NH_2)_3\}(NH_3)X]^{2+}$ † Ions ($X = Cl^-$ or N_3^-) and the Importance of Ion Pairs

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Evidence is presented which demonstrates that the Hg^{2+}- and NO^+-induced aquations of *t*-$[Co(tren)(NH_3)Cl]^{2+}$, (1), and *t*-$[Co(tren)(NH_3)(N_3)]^{2+}$, (2), respectively, follow different paths; *i.e.* that a common intermediate of the type $[Co(tren)(NH_3)]^{3+}$ is not involved [tren = 2,2′,2″-triaminotriethylamine, $N(CH_2CH_2NH_2)_3$]. Saturation entry of NO_3^- to form *t*-$[Co(tren)(NH_3)(NO_3)]^{2+}$ (3) occurs as $[NO_3^-]$ is raised to 1 mol dm^{-3} [48% for (1); 35% for (2)] and this limiting condition is interpreted in terms of pre-formed ion pairs (K_{ip} *ca.* 5 dm^3 mol^{-1}). Second-order rate constants for the Hg^{2+}-induced reaction of *p*-$[Co(tren)(NH_3)Cl]^{2+}$ and *t*-$[Co(tren)(NH_3)Cl]^{2+}$ are 5.6 ± 0.2 and 9.7 ± 0.1 dm^3 mol^{-1} s^{-1} respectively.

THE recent demonstration of the equivalence in the steric course of the spontaneous (H_2O) and the induced (Hg^{2+}, NO^+, and Cl_2) aquations of various *cis*-(+)-$[Co(en)_2AX]^{+,2+}$ [1] and $[Co(NH_3)_5X]^{2+}$ [2] ions (en = ethylenediamine, A = amine, X = anion) has placed a large burden of proof for any mechanistic difference on the results of competition experiments. Whereas competition between H_2O and NO_3^- (or HSO_4^-) during the Hg^{2+}-induced hydrolysis of $[Co(NH_3)_5X]^{2+}$ has been shown to be independent of the leaving group ($X = Cl^-$, Br^-, or I^-),[3,4] similarly for the NO^+-induced reactions of $[Co(NH_3)_5(N_3)]^{2+}$ [4,5] and $[Co(NH_3)_5(OCONH_2)]^{2+}$,[4] the competition numbers appear to differ for the two processes. Also, studies in CH_3OH–H_2O and dmso–H_2O (dmso = dimethyl sulphoxide) mixtures give different values for the entry of these neutral species.[6] The two results suggest that ionic atmosphere or ion-pairing effects may play significant roles in these classic [7] dissociative processes.

It is the purpose of this paper to demonstrate that different transition states are indeed required for entry of a competing anion (NO_3^-) in the Hg^{2+}- and NO^+-induced reaction of, respectively, *t*-$[Co(tren)(NH_3)Cl]^{2+}$ (1) and *t*-$[Co(tren)(NH_3)(N_3)]^{2+}$ (2) (tren = 2,2′,2″-triaminotriethylamine), and that saturation entry of NO_3^- is observed suggesting entry from within a pre-formed ion pair.

EXPERIMENTAL

The various *t*-$[Co(tren)(NH_3)X]^{2+,3+}$ complexes ($X = Cl^-$, N_3^-, NO_3^-, or H_2O) were prepared and characterised as described previously.[8,9]

Rate data for the Hg^{2+}-induced reaction was obtained spectrophotometrically on a Cary 219 instrument. Solutions were mixed by shaking and the optical density (o.d.) decrease at 540 nm followed. Plots of ln(o.d.$_t$ − o.d.$_\infty$) against time were linear for at least four half-lives.

For the product determinations *ca.* 70 mg of (*i*) *t*-$[Co(tren)(NH_3)Cl][ClO_4]Cl$ and (*ii*) *t*-$[Co(tren)(NH_3)(N_3)][ClO_4][NO_3]$ were accurately weighed out and dissolved in 20 cm^3 of the following solutions: for (*i*) (*a*) mixtures of Hg^{2+} (0.4 mol dm^{-3}), H^+ (0.2 mol dm^{-3}), and NO_3^- or ClO_4^- (1.0 mol dm^{-3}) or (*b*) water, Hg^{2+} (0.4 mol dm^{-3}), H^+ (0.2 mol dm^{-3}), and NO_3^- (1.0 mol dm^{-3}); for (*ii*) water, HNO_3 (0.33 mol dm^{-3}), and $Na[NO_3]$ (1.0 mol dm^{-3}). After reaction was complete (10 $t_{\frac{1}{2}}$), the solution was diluted to *ca.* 100 cm^3 and the products adsorbed onto, and eluted (1—3 mol dm^{-3} HCl) from, Dowex 50W × 2 cation-exchange resin (1 × 10 cm). Spectral estimations were made within 15 min of recovery using the following ε values (dm^3 mol^{-1} cm^{-1}): *t*-$[Co(tren)(NH_3)(OH_2)]^{3+}$ 102 (498 nm) and *t*-$[Co(tren)(NH_3)(NO_3)]^{2+}$ 134 (503 nm).[9]

RESULTS

The formation of unusually large amounts of *t*-$[Co(tren)(NH_3)(NO_3)]^{2+}$ (3) at relatively low NO_3^- concentrations was first noticed during preparation of the *t*-$[Co(tren)(NH_3)(OH_2)]^{3+}$ ion.[9] When *t*-$[Co(tren)(NH_3)Cl][ClO_4]Cl$ was treated with 0.05 mol dm^{-3} $Ag[NO_3]$ or $Hg[NO_3]_2$ solutions (0.1 mol dm^{-3} in $HClO_4$) the resulting reddish solution was shown by ion-exchange chromatography to contain surprisingly large amounts (*ca.* 20%) of *t*-$[Co(tren)(NH_3)(NO_3)]^{2+}$ (3); when excess of $Na[NO_3]$ was added the sparingly soluble salt *t*-$[Co(tren)(NH_3)(NO_3)][NO_3]_2$ precipitated. When higher concentrations of $Hg[NO_3]_2$ or $Ag[NO_3]$ were used more (3) formed, but qualitatively this seemed to maximize at *ca.* 50% with little increase above 0.25 mol dm^{-3} $Hg[NO_3]_2$. These observations led to the following quantitative experiments.

$$t\text{-}[Co(tren)(NH_3)Cl]^{2+} + Hg^{2+} + NO_3^- \longrightarrow t\text{-}[Co(tren)(NH_3)(OH_2)]^{3+} + t\text{-}[Co(tren)(NH_3)(NO_3)]^{2+} + HgCl^+ \quad (1)$$

Two sets of experiments were carried out, the first at constant ionic strength (1.0 mol dm^{-3}) using $Na[NO_3]$–$Na[ClO_4]$ mixtures, and the second with only $Na[NO_3]$ present, Table 1. The products were separated by ion exchange and the 2+ (*t*-NO_3) and 3+ (*t*-OH_2) ions estimated spectrally; good recoveries (98—100%) were achieved (90 min—2 h), and the reproducibility was excellent (Table 1). The two sets of results differ, with those in the absence of ClO_4^- giving substantially more *t*-NO_3, especially at low $[NO_3^-]$. Also, Figure 1 shows that in the absence of ClO_4^- the amount of *t*-NO_3 approaches a limiting value as $[NO_3^-]$ approaches 1.0 mol dm^{-3}. In the presence of ClO_4^- (constant ionic strength) the same limiting distribution is approached, but

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† The letters *t* and *p* denote the isomers with the tertiary and primary amine centre, respectively, *trans* to the electronegative group X.

more gradually. The data at $[NO_3^-] = 1$ mol dm^{-3}, Table 1(*a*), shows that the product distribution is independent of H^+ and Hg^{2+} concentrations.

Qualitatively similar, but quantitatively different, data are obtained for the nitrosation of *t*-$[Co(tren)(NH_3)(N_3)]^{2+}$ (2). In this reaction co-ordinated N_3^- is removed rapidly by attack of NO^+ or $H_2NO_2^+$,[5] and NO_3^- again competes effectively with H_2O for the vacated site (Table 2, Figure 1).

TABLE 1

Products of the Hg^{2+}-induced hydrolysis of *t*-$[Co(tren)(NH_3)Cl]Cl_2$ in the presence of $Na[NO_3]$ [a]

$[Hg^{2+}]$	$[H^+]$	$[NO_3^-]$ [b]	$[ClO_4^-]$	*t*-$Co(NO_3)$ [c]	*t*-$Co(OH_2)$ [c]	*R* [d]
mol dm^{-3}				%		
(*a*) $Na[ClO_4]$ added ($I = 1.0$ mol dm^{-3})						
0.4	0.2	0(1)	1.0	0.0	100	
0.2	0.2	0.10(2)	0.9	9.8(4)	90.2(4)	1.09
0.4	0.2	0.20(2)	0.8	17.3(3)	82.7(3)	1.04
0.4	0.2	0.40(2)	0.6	28.5(5)	71.5(1.0)	1.00
0.4	0.2	0.60(2)	0.4	36.3(5)	63.7(1.0)	0.95
0.4	0.2	0.80(3)	0.2	33.2(5)	56.8(1.0)	0.95
0.4	0.2	1.0(3)	0	48.0(7)	52.0(1.0)	0.92
0.1	0.2	1.0(1)	0	47.6	52.4	
0.1	0.05	1.0(1)	0	47.5	52.5	
(*b*) $Na[ClO_4]$ absent (*I*, variable)						
0.02	0.01	0.05(3)	0	17.2(3)	82.8(5)	4.15
0.04	0.02	0.10(2)	0	23.6(4)	76.4(5)	3.09
0.06	0.02	0.15(2)	0	31.0(5)	69.0(7)	3.00
0.12	0.06	0.30(2)	0	37.5(5)	62.5(7)	2.00
0.20	0.10	0.50(2)	0	44.4(5)	55.6(5)	1.60
0.30	0.15	0.75(3)	0	46.7(5)	53.3(5)	1.17
0.40	0.20	1.00(3)	0	48.0(5)	52.0(5)	0.92
0.40	0.20	2.00(1)	0	49.4	50.6	

[a] [Co] *ca.* 1×10^{-2} mol dm^{-3}. [b] Number of experiments given in parentheses. [c] Maximum deviation of any one experiment from the mean given in parentheses. [d] See text.

The product composition was independent of H^+ and NO_2^- concentration.

$$t\text{-}[Co(tren)(NH_3)(N_3)]^{2+} + NO^+ + NO_3^- \longrightarrow t\text{-}[Co(tren)(NH_3)(OH_2)]^{3+} + t\text{-}[Co(tren)(NH_3)(NO_3)]^{2+} + N_2 + N_2O \quad (2)$$

In both reactions the aquo- and nitrato-products retain the *t*-configuration. This was established for the aquo-species by reanation with HCl when a quantitative yield of *t*-$[Co(tren)(NH_3)Cl]^{2+}$ [ε (530 nm) = 123 dm^3 mol^{-1} cm^{-1}] [9] was obtained; and by spectral [ε (530 nm) = 134 dm^3 mol^{-1} cm^{-1}] and ion-exchange identification of the nitrato-product.

TABLE 2

Products of the NO^+-induced hydrolysis of *t*-$[Co(tren)(NH_3)(N_3)][ClO_4][NO_3]$ in the presence of $Na[NO_3]$ [a] (no added $Na[ClO_4]$)

$[NO_3^-]$/ mol dm^{-3}	*t*-$Co(NO_3)$	*t*-$Co(OH_2)$	*R* [b]
	%		
0.0	0	100.0	
0.11	15.0	86.0	1.59
0.31	26.0	74.0	1.13
0.51	31.0	69.0	0.88
0.71	33.0	67.0	0.69
1.00	35.0	65.0	0.54

[a] [Co] = (0.69—1.10) $\times 10^{-2}$ mol dm^{-3}; $[H^+]$ = 0.033—0.33 mol dm^{-3}; $[NO_2^-]$ = variable, *ca.* 10^{-3} mol dm^{-3}. [b] See text.

Over the $[Hg^{2+}]$ range 0.063—0.295 mol dm^{-3} removal of Cl^- obeys the rate law $k_{obs.} = k_{Hg^{2+}}[Hg^{2+}]$, Table 3, with $k_{Hg^{2+}} = 9.7 \pm 0.1$ dm^3 mol^{-1} s^{-1}. A similar value of 5.6 ± 0.2 dm^3 mol^{-1} s^{-1} was obtained for *p*-$[Co(tren)(NH_3)Cl]^{2+}$. The effect of $[NO_3^-]$ on the rate was not investigated since a more complete reinvestigation of the $[Co(NH_3)_5X]^{2+}$ (X = Cl^-, Br^-, I^-, N_3^-, or $OCONH_2^-$) system is being undertaken.[10]

DISCUSSION

Previously [3-5] the Hg^{2+}- and NO^+-induced reactions have been discussed in terms of the entering group (H_2O or Y^-) competing for a discrete CoA_5^{3+} intermediate generated by the rate-determining loss of HgX^+, or of $N_2 + N_2O$. Entry of Y^- *via* CoA_5^{3+} or ion-paired

$$CoA_5X^{2+} + Hg^{2+} \xrightarrow[\text{(X = Cl, Br, or I)}]{\text{slow}} CoA_5^{3+} + HgX^+$$

$$CoA_5X^{2+} + NO^+ \xrightarrow[\text{(X = N}_3\text{ or OCONH}_2\text{)}]{\text{slow}} CoA_5^{3+} + N_2 + N_2O \text{ (or } CO_2 + H_2O) \quad (3)$$

$CoA_5^{3+}{\cdot}Y^-$ intermediates (Scheme 1) leads to the competition ratio, *R*, as in equation (5).

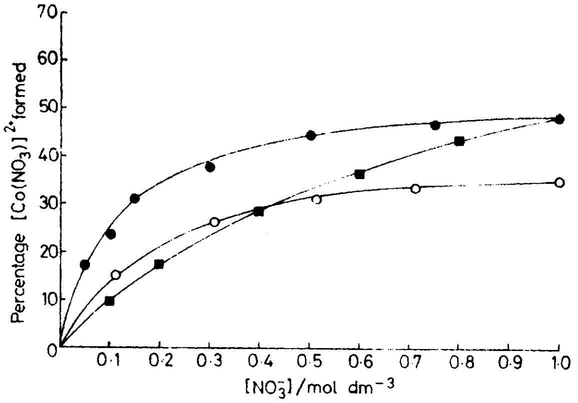
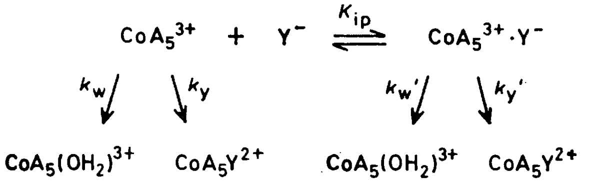


FIGURE 1 Plot of percentage *t*-$[Co(tren)(NH_3)(NO_3)]^{2+}$ formed against $[NO_3^-]$ for the Hg^{2+}-induced aquation of *t*-$[Co(tren)(NH_3)Cl]^{2+}$: NO_3^- only (●); $NO_3^- + ClO_4^- = 1.0$ mol dm^{-3} (■); and for the NO^+-induced aquation of *t*-$[Co(tren)(NH_3)(N_3)]^{2+}$ with NO_3^- only (○). 100% represents *t*-$[Co(tren)(NH_3)(OH_2)]^{3+}$

In previous work[4] R was said to be independent of the Y^- concentration ($Y = NO_3$) leading to the contention that ion pairing was unimportant, *i.e.* $R = k_y/k_w$. The present results do not agree with this analysis. R decreases gradually from 1.09 to 0.92 as $[NO_3^-]$ is increased from 0.1 to 1.0 mol dm^{-3} at constant ionic strength, and in the absence of supporting electrolyte a large change in R occurs, $R = 4.12$ ($[NO_3^-] = 0.05$) to $R = 0.5$ ($[NO_3^-] = 2.0$). Obviously ClO_4^- influences

$$R = \frac{[CoA_5Y^{2+}]}{[CoA_5(OH_2)^{3+}][Y^-]} = \frac{k_y + k_y'K_{ip}}{k_w + k_w'K_{ip}[Y^-]} \quad (5)$$

the products by reducing that part giving rise to $CoA_5(NO_3)^{2+}$.



(4)

Scheme 1

Table 3

Rate constants for the Hg^{2+}-induced aquation of the *p*- and *t*-$[Co(tren)(NH_3)Cl]^{2+}$ ions * $\{I = 1.0$ mol dm^{-3} $(Na[ClO_4])$; 25.0 °C$\}$

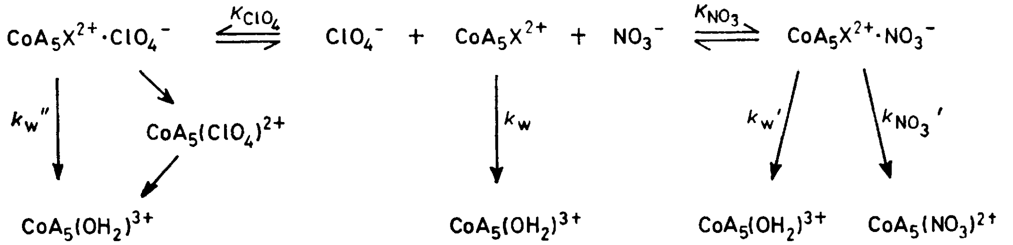
(*a*) *p*-isomer

$[Hg^{2+}]$/mol dm^{-3}	0.063			0.125			0.295	
$[H^+]$/mol dm^{-3}	0.10	0.05	0.10	0.10	0.10	0.05	0.10	0.10
$k_{obs.}/10^{-3}$ s^{-1}	6.06	6.06	6.78	5.89	12.14	12.11	28.5	28.5
$k_{Hg^{2+}}/10^{-2}$ dm^3 mol^{-1} s^{-1}	9.7	9.7	10.8	9.4	9.7	9.7	9.7	9.7

(*b*) *t*-isomer

$[Hg^{2+}]$/mol dm^{-3}	0.063	0.077	0.125		0.295	
$[H^+]$/mol dm^{-3}	0.10	0.10	0.10	0.05	0.10	0.05
$k_{obs.}/10^{-3}$ s^{-1}	3.20	4.32	6.55	7.55	16.6	16.6
$k_{Hg^{2+}}/10^{-2}$ dm^3 mol^{-1} s^{-1}	5.1	5.6	5.2	6.0	5.6	5.6

* $k_{Hg^{2+}} = k_{obs.}/[Hg^{2+}]$.



Scheme 2

The curved plots of R against $[NO_3^-]$, Figure 1, with a limiting composition of *ca.* 48% $CoA_5(NO_3)^{2+}$ for the Hg^{2+} reaction and 35% for the NO^+ reaction, suggests ion pairs as the major path for anion entry. Also, the different limits for the two reactions requires entry of NO_3^- to be influenced by the reactant or by leaving group; *i.e.* that a discrete five-co-ordinate ion pair $CoA_5^{3+}\cdot NO_3^-$ is not of major importance. What is not clear at this stage is whether the entering anion is associated with the reactant [as $HgNO_3^+$ or $NONO_3$ (or $H_2NO_2NO_3$)],[5] or with the cobalt complex as a true ion pair [$CoA_5Cl^{2+}\cdot NO_3^-$ or $CoA_5(N_3)^{2+}\cdot NO_3^-$] since both would account for the present observations. Studies in progress should resolve this problem.[10]

Scheme 2, with X = $HgCl^+$ or NON_3, accounts for the results in terms of ion pairs,* and leads to the competition ratio (6) if k_w'' is interpreted as including aquation of $CoA_5(ClO_4)^{2+}$. Provided scavenging for nearest

$$R = \frac{k_{NO_3}'K_{NO_3}}{k_w + k_w'K_{NO_3}[NO_3^-] + k_w''K_{ClO_4}[ClO_4^-]} \quad (6)$$

neighbours is the route for anion or water entry[11] then this latter species will undoubtedly be formed, but experiments with $Co(NH_3)_5(ClO_4)^{2+}$[12] demonstrate that its subsequent aquation (which is very fast) leads to only very small amounts (*ca.* ⩽5% for Cl^-) of incorporated ionic species.

Plots of $1/R$ against $[NO_3^-]$, Figure 2, show excellent linearity both in the presence and absence of ClO_4^- with intercepts for $[ClO_4^-] = 0$ ($k_w/k_{NO_3}'K_{NO_3}$) of 0.22 (Hg^{2+}) and 0.47 (NO^+) mol dm^{-3} and slopes (k_w'/k_{NO_3}') of 0.85 (Hg^{2+}) and 1.36 (NO^+). In the presence of ClO_4^- (constant ionic strength) the small positive slope requires $k_w'K_{NO_3}/k_w''K_{ClO_4}$ to be slightly greater than unity; if it equalled 1.0 then R would show no NO_3^- dependence as was suggested previously.[4] The larger intercept for the

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* It must be stressed that although we have interpreted the experimental constant as a concentration constant, K_{ip}^c, its value would not be expected to be independent of ionic strength. Apparently, within the accuracy of the experiments described, effects arising from changes in activity coefficients are minimal or effectively cancel.

NO^+ reaction requires $k_{NO_3}'K_{NO_3}$ (Hg^{2+} reaction) $\simeq 2k_{NO_3}'$-K_{NO_3} (NO^+ reaction). Assuming a K_{NO_3} value of 5 dm^3 mol^{-1} for the 2+ complex * this leads to k_w' and k_{NO_3}' values of 0.77, 0.91 (Hg^{2+}) and 0.58, 0.43 (NO^+) relative to 1.0 for k_w. Obviously orientation effects within the ion pair will decide whether H_2O or NO_3^- enters, but the chosen value of K_{NO_3} does require the ion-paired species to be more reactive than the non ion-paired species, $k_w' + K_{NO_3}' > k_w$. The important point is that the present scheme differs from that given before[4] in that NO_3 can only enter from a preformed reactant ion pair containing the leaving group; no path is available *via* a discrete CoA_5^{3+} intermediate. This description is in keeping with recent stereochemically based experiments on the analogous *p*-isomers which also argued against the possibility of common intermediates for different leaving groups.[11] However a clear distinction between a $D_{int.}$ (dissociative interchange) mechanism (capture of the nearest neighbour) and an I_d process with some degree of bond making in the rate-determining transition state is still open to experimental test.

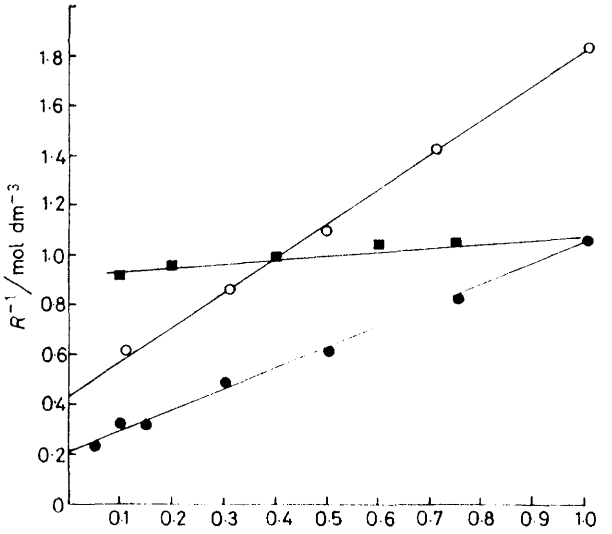

FIGURE 2 Plot of $1/R$ (see text) against $[NO_3^-]$ for the Hg^{2+}- and NO^+-induced reactions: *t*-$[Co(tren)(NH_3)Cl]^{2+}$ + Hg^{2+} with NO_3^- only (●); with NO_3^- + ClO_4^- = 1 mol dm^{-3} (■); and *t*-$[Co(tren)(NH_3)(N_3)]^{2+}$ + NO^+ with NO_3^- only (○)

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* The Fuoss equation (R. M. Fuoss, *J. Amer. Chem. Soc.*, 1958, **80**, 5059) predicts K_{ip} = 5 dm^3 mol^{-1} for a 2+, 1− ion pair and recent measurements (M. J. Pavelich, S. M. Maxey, and R. C. Pfaff, *Inorg. Chem.*, 1978, **3**, 564) lend experimental support.

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