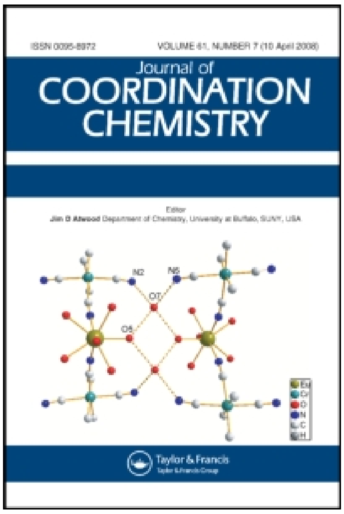

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KINETICS AND MECHANISM OF ANATION OF *β-cis*-(DIAQUO)-(TRIEN)COBALT(III) BY OXALATE

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The anation of *β-cis*-$[Co(trien)(OH_2)_2]^{3+}$ ion by oxalic acid, bioxalate anion and oxalate dianion has been studied at 30–45°C and I = 1.0 M (KNO_3). The common anation rate constant, k_0, of {*β-cis*-$[Co(trien)(OH_2)_2]^{3+}$, $H_2C_2O_4$} and {*β-cis*-$[Co(trien)(OH_2)_2]^{3+}$, $HC_2O_4^-$} ion-pairs is found to be 6.7×10^{-5} sec^{-1} at 40°C. The observed anation rate constant levels off to a limiting value ($7.0\ (\pm 0.8) \times 10^{-3}$, sec^{-1}) at 40°C, pH = 4.00 (±0.05) and $[C_2O_4^{2-}] \geqslant 0.15$ M, which is characteristic of the anation rate constant (k_1) of the oxalate dianion ion-pair. Activation enthalpy and entropy for the k_0 and k_1 paths are 24.5 K.cal $mole^{-1}$, 0.8 cal. deg^{-1} $mole^{-1}$ and 28.9 K.cal $mole^{-1}$, 24.0 cal. deg^{-1} $mole^{-1}$, respectively. The temperature independent ion-pair equilibrium constant for $H_2C_2O_4$ ion-pair was found to be 6.8 (±1.2) M^{-1}. The anation of {*β-cis*-$[Co(trien)(OH_2)_2]^{3+}$-X} ion pairs (X = $H_2C_2O_4$, $HC_2O_4^-$ or $C_2O_4^{2-}$) is believed to involve an 'Id' mechanism.

INTRODUCTION

The anation of aquopentaammine cobalt(III) by carboxylic acids and their anions has been reported.[1–13] It has been suggested that the anation reaction proceeds through the formation of an ion-pair between the cobalt(III) substrate and the anating anion in a rapid pre-equilibrium step followed by rate-determining expulsion of a ligand water molecule from the cobalt(III) centre by a dissociative interchange mechanism, I_d. However, when the carboxylic acids are the anating species, the reaction follows second order kinetics and the existence of the carboxylic acid-aquo cation ion-pairs as the reactive intermediates are not often observed. The anation of *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ (en = ethylenediamine) by oxalate species in acidic medium has been studied by Harris and coworkers[14,15] and Stranks and Vanderhoek.[16] The kinetic data was interpreted in terms of the rate-determining exchange of one of the ligand water molecules either by oxalic acid or by bioxalate anion preceeded by an ion-association equilibrium. The exchange reaction takes place by I_d mechanism and the subsequent chelation to generate $[Co(en)_2C_2O_4]^+$ was assumed to be very fast. The association of oxalic acid with diaquo *bis*(ethylenediamine) cobalt(III) cation has been attributed to the hydrogen bonding effects. The addition of oxalic acid to aquopentaammine cobalt(III) cation is believed to take place by OH bond cleavage.[4] From the activation parameter data,[14–16] however, the addition of oxalic acid to $[Co(en)_2(OH_2)_2]^{3+}$ cation was inferred to take place by Co—O bond cleavage. In this paper the results of the anation of *β-cis*-$[Co(trien)(OH_2)_2]^{3+}$ by oxalate under different conditions of pH and temperature are reported with a view to understand the mechanism of anation of this complex by a dicarboxylic acid and its anions.

EXPERIMENTAL

Materials and Methods

β-$[Co(trien)CO_3]\cdot ClO_4\cdot H_2O$ was prepared by the method reported in the literature.[17] The purity of the sample was checked by estimating its cobalt content (Calcd. Co, 15.41%, Found: Co, 15.1%). The extinction coefficient of this complex agreed well with the reported value {λ, nm(ε, M^{-1} cm^{-1})$_{(max)}$: 507 (174), 358 (138) 507 (178), 358 (140);[17]}. For the kinetic runs the *β-cis*-$[Co(trien)(OH_2)_2]^{3+}$ cation was generated by adding calculated amount of standard nitric acid to a weighed amount of $[Co(trien)CO_3]ClO_4\cdot H_2O$ and expelling CO_2 from the solution by bubbling CO_2 free air through it. The diaquo solution thus prepared was preserved as the stock solution, which contained 0.01 M free nitric acid. This solution was used for kinetic runs as such. The extinction coefficient of the diaquo cation at λ_{max} = 487 nm was found to be 122.0 M^{-1} cm^{-1} which agreed well with the reported value {λ_{max}, nm (ε M^{-1} cm^{-1}); 487 (121)}.[17] All other chemicals were of

'AnalaR' or extrapure grade. Potassium oxalate was prepared by neutralising a weighed amount of oxalic acid by calculated amount of standard potassium hydroxide solution. pH measurements were made with a digital pH meter, model 5651 (ECIL).

Kinetics

The reaction mixture of desired composition (without the aquo complex) was equilibrated in 50 ml volumetric flasks in a water thermostat. After thermal equilibrium was attained a definite volume of the stock aquo complex solution at the reaction temperature was transferred into the reaction flask and the volume was made up to the mark with distilled water previously equilibrated at the same temperature. The reaction flask was immediately replaced in the thermostat after thorough shaking. The progress of the reaction was followed by withdrawing aliquots (5 ml) at definite time intervals, cooling to room temperature by ice-cold water and measuring the absorbance of the solution at 510 nm (ε = 108, and 190 M^{-1} cm^{-1} for β-*cis*-$[Co(trien)(OH_2)_2]^{3+}$ and β-*cis*-$[Co(trien)C_2O_4]^+$ respectively). The relatively fast anation of the diaquo complex by oxalate at pH $\simeq$ 4.0 was, however, followed in the thermostatted cell compartment of the Beckman DU_2 spectrophotometer. The observed pseudofirst order rate constant was calculated from the slope of the plot of log $(A_\infty - A_t)$ *vs* t (sec) where 'A_∞' and 'A_t' stand for the absorbance at the completion of the reaction and at any time 't' respectively. The 'A_∞' values agreed satisfactorily (~7%) with the value calculated from the known extinction coefficient of β-*cis*-$[Co(trien)C_2O_4]^+$. The 'k_{obs}' values reported are average of at least duplicate runs which agreed within ±5%.

RESULTS AND DISCUSSION

The observed pseudo-first order rate constants, k_{obs}, for the anation of β-*cis*$[Co(trien)(OH_2)_2]^{3+}$ by oxalic acid at $[H_2C_2O_4]$ = 0.05 – 0.3 M, $[HNO_3]$ = 0.101 – 0.701 M and I = 1.0 M (KNO_3) have been collected in Table I. The 'k_{obs}' values, when oxalate was the anating species {pH $\simeq$ 4.0, I = 1.0 M (KNO_3)}, have been collected in Table II. Our attempts to study the anation of the diaquo cation with oxalate species in perchlorate medium proved unsuccessful due to poor solubility of the reactant

TABLE I

Observed pseudo first order rate constants for the anation of β-*cis*-$[Co(trien)(OH_2)_2]^{3+}$ by oxalic acid.
[Diaquo complex] = 3.0 × 10^{-3} M, I = 1.0 M (KNO_3)
λ = 510 nm.

	$[HNO_3]$(M)			
	$10^5 \times k_{obs}$, sec^{-1}			
$[H_2C_2O_4]$ (M)	0.701	0.501	0.301	0.101
35°C				
0.05	1.33	1.45	1.64	2.17
0.10	2.05	2.22	2.38	2.78
0.15	2.38	2.56	2.78	3.23
0.20	2.71	2.86	3.08	
0.30	3.14	3.23		
k_0 = 4.2 × 10^{-5} sec^{-1}, K_2 = 0.59(±0.03) M, Q_1 = 6.8(±1.2) M^{-1}				
40°C				
0.05		2.60	3.03	3.64
0.10		3.70	4.00	5.00
0.15		4.37	4.65	5.13
0.20		4.82	5.26	
0.30		5.32		
k_0 = 6.7 × 10^{-5} sec^{-1} K_2 = 0.59(±0.03) M, Q_1 = 6.8(±1.2) M^{-1}				
45°C				
0.05		6.08	6.76	8.47
0.10		9.10	9.61	10.99
0.15		10.13	10.87	11.90
0.20		11.63	11.90	
0.30		12.19		
k_0 = 15.2 × 10^{-5} sec^{-1}, K_2 = 0.59(±0.03) M, Q_1 = 6.8(±1.2) M^{-1}				

TABLE II

Observed pseudo first order rate constants for the anation of β-*cis*-$[Co(trien)(OH_2)_2]^{3+}$ by oxalate.
[Diaquo complex] = 5.0 × 10^{-3} M, I = 1.0 M (KNO_3)
λ = 530 nm

$[H_2C_2O_4]$ (M)	$[K_2C_2O_4]$ (M)	pH[a]	$10^3 \times k_{obs}$, sec^{-1}		
			30°C	35°C	40°C
0.01	0.15	4.0	1.36	3.2	6.4
0.01	0.20	3.9	1.48	3.7	6.3
0.01	0.25	4.1	1.54	3.9	7.5
0.01	0.30	4.05	1.45	3.5	7.7
$10^3 \times k_1$, sec^{-1}			1.45(±0.10)	3.6(±0.3)	7.0(±0.8)

[a] measured pH values.

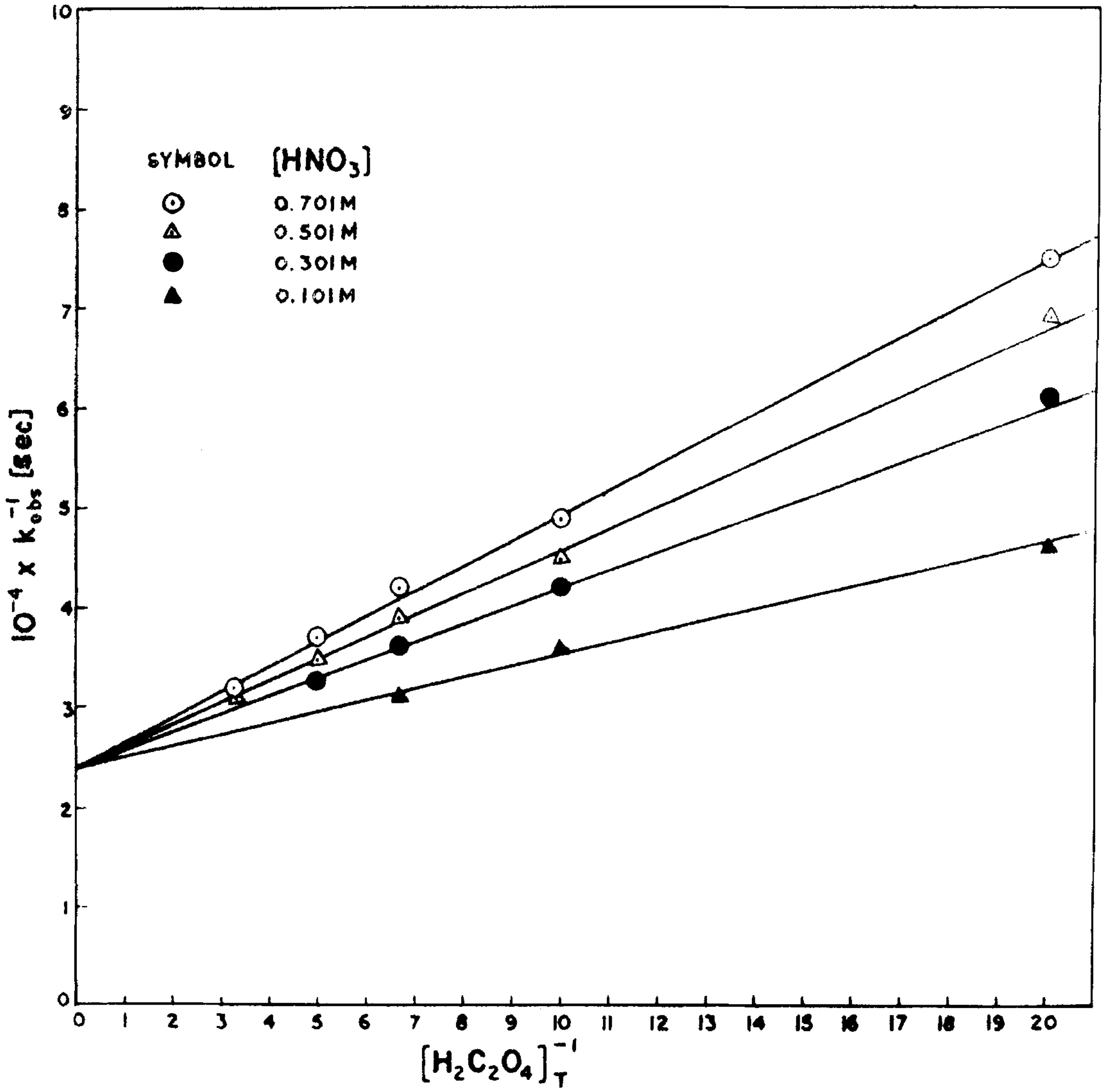


FIGURE 1 Plot of k_{obs}^{-1} *vs.* $[H_2C_2O_4]_T^{-1}$ at 35°C and different acidities.

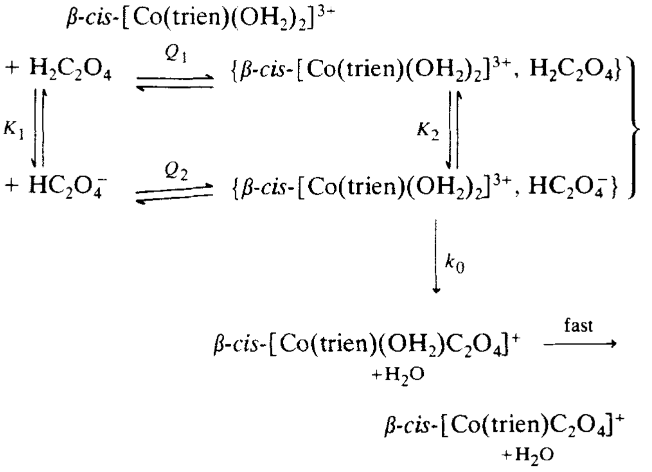
and the product oxalato complex. Our results, however, show (as reflected by the insensitivity of the rate constant to $[C_2O_4^{2-}]$ in the $NO_3^-/C_2O_4^{2-}$ mixture, see Table II that the nitrate effect observed by Eldik and Harris on the oxalate anation of *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ [15] is not of much significance in the present study.

Plots of k_{obs}^{-1} *vs* $[H_2C_2O_4]_T^{-1}$ at $[H^+]_T = 0.101–0.701$ M yielded straight lines with a common intercept and varying slopes, the latter increasing with $[H^+]$, (Figure 1). The double reciprocal plot is consistent with the following facts:

i) the aquocation and the oxalate species, $H_2C_2O_4$ and $HC_2O_4^-$ associate to form ion-pairs and

ii) both the ion-pairs, $\{Co(trien)(OH_2)_2, X\}^{n+}$ ($X = H_2C_2O_4$ and $HC_2O_4^-$) are transformed to the chelated oxalato complex virtually at the same rate.

The dependence of the slope of such plot on $[H^+]$ is, however, attributed to different associative propensity of $H_2C_2O_4$ and $HC_2O_4^-$ towards the diaquo cation. Similar observations have been made by Harris *et al.*[14] and Stranks and Vanderhoek[16] in the oxalate anation of *cis*-$[Co(en)_2(OH_2)_2]^{3+}$. The data can be best fitted to the following reaction scheme,



(SCHEME 1)

where 'k_0' is the common anation rate constant for oxalic acid and bioxalate ion pairs; K_1, K_2, Q_1, Q_2 are primary dissociation constant of free oxalic acid, primary dissociation constant of associated oxalic acid, ion pair association constants for oxalic acid and bioxalate anion respectively. For such a scheme the rate expression is given by:[14]

$$\frac{-d\ln[\mathrm{Co(III)}]_T}{dt} = k_{\mathrm{obs}} = \frac{k_0 Q_1 (K_2 + [H^+])[H_2C_2O_4]_T}{Q_1(K_2 + [H^+])[H_2C_2O_4]_T + K_1 + [H^+]} \qquad (1)$$

which can be rearranged to:

$$\frac{1}{k_{\mathrm{obs}}} = \frac{K_1 + [H^+]}{k_0 Q_1 (K_2 + [H^+])} \cdot \frac{1}{[H_2C_2O_4]_T} + \frac{1}{k_0} \qquad (2)$$

Values of 'k_0' obtained from the intercepts of the plots of $1/k_{\mathrm{obs}}$ *vs*. $1/[H_2C_2O_4]_T$ are collected in Table I. It is, however, easy to note that Eq. (3) is obtained from the slope (S) and intercept (I) of such plots.

$$(I/S)(K_1 + [H^+]) = Q_1 K_2 + Q_1[H^+] \qquad (3)$$

Since K_1 (0.0933 M at 30–45°C)[18] is known, a linear plot of $(I/S)(K_1 + [H^+])$ *vs* $[H^+]$ could be made to obtain Q_1 and K_2. Activation enthalpys and entropys ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) have been calculated from the relationship:

$$\ln k_0/T = -\frac{\Delta H^{\neq}}{R} \cdot \frac{1}{T} + \left(\frac{\Delta S^{\neq}}{R} + \ln k/h\right)$$

The data are collected in Table III.

The dissociation constant of the oxalic acid ion-pair, $\{Co(trien)(OH_2)_2, H_2C_2O_4\}^{3+}$, is found to be ~7 times higher than that of free oxalic acid. This is not unusual as the bioxalate ion-pair is expected to be thermodynamically more stable than its oxalic acid analogue on electrostatic grounds and hydrogen bonding effects. Q_1 is found to be virtually temperature independent in the range studied. The water exchange rate constant for the free ion *β-cis*-$[Co(trien)(OH_2)_2]^{3+}$ is not presently available. However, it is not likely to be widely different from that for the *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ ($k_{\mathrm{ex}} = 7.7 \times 10^{-5}\ \mathrm{s}^{-1}$ at 40°C).[19] The anation rate constant for the oxalic acid and bioxalate ion pairs of *β-cis*-$[Co(trien)(OH_2)_2]^{3+}$ is close to this value (see Table III). Comparing the activation parameter data for the anation of *β-cis*-diaquo(trien)Co(III) with those of aquopentamine and *cis*-diaquo *bis*(ethylenediamine)Co(III) (see Table III) it can be concluded that the

TABLE III

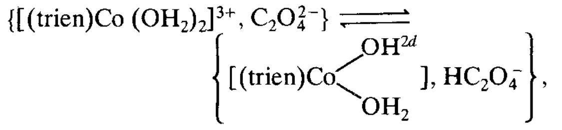
Comparative listing of the rate and activation parameters for the anation of aquoammine cobalt(III) cations by oxalate species.

Complex	Anating species	10^5 k (40°C) s^{-1}	$\Delta H^{\neq}$ Kcal mol^{-1}	$\Delta S^{\neq}$ caldeg^{-1} mol^{-1}	Ref.
cis-$[Co(en)_2(OH_2)_2]^{3+}$	$H_2C_2O_4$	4.1	24.8 ± 0.5	+1.5 ± 1.5	(14)
		1.6[a]	27.4 ± 1.3[a]	+6.7 ± 3.8[a]	(15)
	$HC_2O_4^-$	1.4[b]	27.0 ± 0.8[b]	+5.5 ± 2.5[b]	(15)
cis-$[Co(trien)(OH_2)_2]^{3+}$	$H_2C_2O_4$ $HC_2O_4^-$	6.7	24.5	+0.8	this work
	$C_2O_4^{2-}$	700	28.9	+24	this work
cis-$[Co(en)_2(NH_3)(OH_2)]^{3+}$	$H_2C_2O_4$	0.54[c]	22.9 ± 3.3	−9 ± 10	(13)
	$HC_2O_4^-$	1.76	26.0 ± 0.5	+3 ± 2	(13)
	$C_2O_4^{2-}$	1.53	25.8 ± 0.7	+2 ± 3	(13)
$[(NH_3)_5Co(OH_2)]^{3+}$	$H_2C_2O_4$	2.03[c]	13.7 ± 0.2	−36 ± 1	(9)
	$HC_2O_4^-$	1.94	22.4 ± 2.2	−9 ± 7	(4)
	$C_2O_4^{2-}$	1.01	25.0 ± 1.7	−2 ± 5	(4)

[a] data for oxalic acid; [b] data for bioxalate anion [c] unit: $s^{-1}\ M^{-1}$.

anation of β-*cis*-$[Co(trien)(OH_2)_2]^{3+}$ by oxalic acid and bioxalate anion proceeds through the Id mechanism i.e. by cleavage of Co—O bond.

The observed pseudo first order rate constant, k_{obs}, for the anation of β-*cis*-$[Co(trien)(OH_2)_2]^{3+}$ by oxalate dianion tends to level off under the experimental conditions (see Table II). This indicates that the diaquo cation is virtually completely associated with $C_2O_4^{2-}$ at $[C_2O_4^{2-}] \geq 0.15$ M. Activation parameter data for this reaction (Table II) are suggestive of Id mechanism. The first order anation rate constant for the oxalate dianion ion-pair is about 100 times higher than that for oxalic acid or bioxalate ion-pair. This is a rather surprising result in view of the fact that the oxalate and bioxalate ion-pairs of α-*cis*-ethylenediamine-*N*, *N*′-diacetato diaquo cobalt(III), α-*cis*-$[Co(EDDA)(OH_2)_2]^+$, are reported to be transformed to β-*cis*-$[Co(EDDA)C_2O_4]^-$ chelate at the same rate.[20] It may be assumed that the associated oxalate anion generates the aquohydroxo species in the ion-pair due to hydrogen bonding,



$$\{[(trien)Co\,(OH_2)_2]^{3+}, C_2O_4^{2-}\} \rightleftharpoons \left\{[(trien)Co\begin{matrix}OH^{2d}\\ \\ OH_2\end{matrix}], HC_2O_4^-\right\},$$

and small difference in pK between the diaquo species (pK = 5.3 at 20°C)[21] and $HC_2O_4^-$ (pK ≃ 3.7 at 50 to 80°C).[4] Such a species would undergo fast exchange with the associated anion due to the strong labilising action of the hydroxo ligand. However, further studies on related systems are needed to establish such a conclusion.

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REFERENCES

1. A. C. Dash and N. Ray, *Indian. J. Chem.*, **14A**, 78 (1976).
2. A. C. Dash and M. S. Dash, *J. Coord. Chem.*, **6**, 1 (1976).
3. A. C. Dash and M. S. Dash, *J. Coord. Chem.*, **10**, 79 (1980).
4. R. Van Eldik and G. M. Harris, *Inorg. Chem.*, **14**, 10 (1975).
5. P. R. Jubert and R. Van Eldik, *Inorg. Chim. Acta*, **14**, 259 (1975).
6. P. R. Jubert and R. Van Eldik, *Inorg. Chim. Acta*, **12**, 205 (1975).
7. P. R. Jubert and R. Van Eldik, *J. Inorg. Nucl. Chem.*, **37**, 1817 (1975).
8. P. R. Jubert and R. Van Eldik, *Int. J. Chem. Kinetics*, **8**, 411 (1976).
9. R. van Eldik, *J. Inorg. Nucl. Chem.*, **38**, 8846 (1976).
10. D. Banerjea and J. Roy, *Z. Anorg. Allg. Chem.*, **400**, 89 (1973).
11. A. C. Dash and B. Mohanty, *Indian J. Chem.*, **17**, 296 (1979).
12. A. C. Dash and B. Mohanty, *J. Inorg. Nucl. Chem.*, **41**, 1053 (1979).
13. A. C. Dash and B. Mohanty, *J. Inorg. Nucl. Chem.*, **42**, 1161 (1980).
14. P. M. Brown and G. M. Harris, *Inorg. Chem.*, **7**, 1872 (1968).
15. R. van Eldik and G. M. Harris, *Inorg. Chem.*, **18**, 1997 (1979).
16. D. R. Stranks and N. Vanderhoek, *Inorg. Chem.*, **15**, 2645 (1976).
17. A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 787 (1967).
18. T. W. Kallen, *Inorg. Chem.*, **15**, 440 (1976).
19. W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **83**, 1280 (1961).
20. J. A. Weyh, A. K. Newlun, T. J. Baker and T. K. Shioyama, *Inorg. Chem.*, **12**, 2374 (1973). The α-cis to β-cis geometry change is reported to occur at or after the rate determining step.
21. C. J. Hawkins, A. M. Sargeson and G. H. Searle, *Australian J. Chem.*, **17**, 598 (1964).