Chiral Metal Complexes. Part 16.* The Λ-α- to Δ-β-[Co(trien)CO_3]$^+$ Inversion

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Our discovery of a number of new inversions of octahedral coordination compounds [1, 2] has led us to conclude that such rearrangements are not as uncommon as previously thought. Accordingly, we have been prompted to reexamine several previous reports of reactions which may involve such a process. The isomerization (1), which was carried out using racemic

$$\alpha\text{-}[Co(trien)CO_3]^+_{(aq)} \longrightarrow \beta\text{-}[Co(trien)CO_3]^+_{(aq)} \quad (1)$$

α-[Co(trien)CO_3]$^+$, [3], attracted our attention on the basis that it could proceed with inversion or racemization at the metal centre. The results of our study of this reaction, reported below, have shown that it does indeed involve inversion followed by racemization of the β-isomer.

Experimental

Λ-α-[Co(trien)CO_3]ClO_4·H_2O

The carbonato-complex was prepared from Λ-α-[Co(trien)Cl_2]Cl [4]. This dichloro-species was resolved using optically active [Co(en)$(ox)_2$]$^-$, [5, 6], which was itself resolved using optically active [Co-$(en)_2(NO_2)_2$]$^+$, [7, 8]. The carbonato-complex had $\Delta\epsilon_{522}$ = +4.33 dm^2 mol^{-1} in aqueous solution (Lit.: +4.35 dm^2 mol from the figure in ref. [9]). *Anal.*: Found: C, 21.8; H, 5.4; N, 14.4%. Calc. for C_7H_{20}-N_4O_8ClCo: C, 22.0; H, 5.3; N, 14.6%.

Solutions of the complex at the required pH using borate buffer [10] in a fashion analogous to that of Dasgupta and Harris [3] or in aqueous $NaHCO_3$ solutions of known formality were kept in a thermostatted water bath at 55 °C. The pH of the reaction solutions at 55 °C was measured using a Corning digital instrument. Preliminary experiments indicated that the rates of isomerization, monitored by observing the change in absorbance of cooled reaction mixtures, at 503 nm using a Pye-Unicam SP8000 spectrophotometer, or the rates of racemization, measured by observing the change of CD signal at 520 nm using a Jobin Yvon CNRS Dichrographe III, in bicarbonate solution were not much affected by additions of Na-ClO_4 to maintain ionic strength. Thus, no supporting electrolyte was added to these solutions.

Results and Discussion

While optically pure Λ-α-[Co(trien)CO_3]$^+$ is quite stable in aqueous solution at room temperature, it isomerizes in basic solution at elevated temperatures to give the β-isomer [3]. Furthermore, the product of the reaction is predominantly Δ-β-[Co(trien)-CO_3]$^+$ and thus the initial reaction observed involves inversion of configuration at the metal centre. The change in circular dichroism during a typical run is shown in Fig. 1. Results from a number of experiments concerning the maximum yield of inverted product with varying reaction conditions are given in Table I. The variation of the rate of isomerization with varying pH is known to be complex [3], but in basic solution, irrespective of reaction conditions, the ratio of Δ-β to Λ-β isomers is found to have a maximum of about 70:30. In all cases, electronic spectral measurements reveal that the products of reaction are solely Δ- (and/or Λ-) -β-[Co(trien)CO_3]$^+$, and with time the optical activity of the reaction mixture falls to zero. Hence the reaction can be represented as shown in (1), with inversion followed

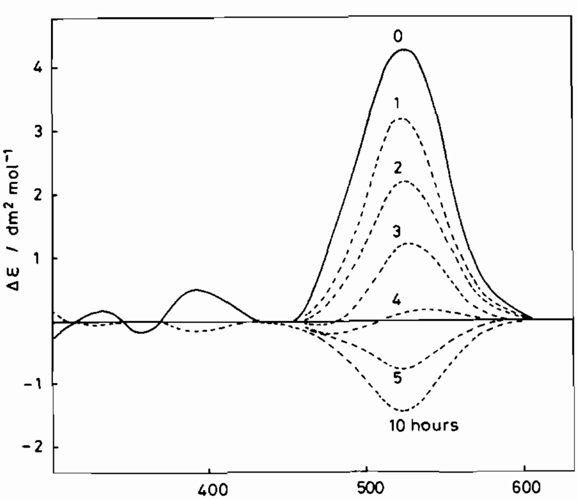

Fig. 1. CD spectra recorded during the course of the isomerization of Λ-α-[Co(trien)CO_3]$^+_{(aq)}$ at 55 °C in pH 8.6 borax buffer. The time (in hours) is shown on each trace of the main visible transition.

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TABLE I. Optical Yields in the Reaction of Λ-α-[Co(trien)CO_3]$^+$ in Aqueous Solution[a] at 55 °C.

pH	$[HCO_3^-]$/F	$\Delta\epsilon^d$/dm^2 mol^{-1} (at 520 nm)	% (Δ-β-[Co(trien)CO_3]$^+$)
7.4[b]		−0.23	54.1
8.6[c]		−1.47	76.2
9.4[c]		−0.82	64.5
10.3[c]		−0.82	64.5
8.1	0.05	−1.60	78.5
8.6	0.10	−1.46	75.2
8.1	1.00	−1.21	71.5

[a][complex]$_{tot}$ = 1.7 × 10^{-3} mol dm^{-3}. [b]Complex dissolved in H_2O alone. [c]Borax buffer [10]. [d]Maximum negative CD measured. [e]Maximum percentage of Δ-β isomer calculated using $\Delta\epsilon_{520}$ = −2.81 dm^2 mol^{-1} for pure Δ-β-[Co(trien)CO_3]$^+$ [9].

by racemization of the inverted product at a slower rate (2). Total inversion is not observed under the

$$\Delta\text{-}\beta\text{-[Co(trien)CO}_3]^+_{(aq)} \rightleftharpoons \Lambda\text{-}\beta\text{-[Co(trien)CO}_3]^+_{(aq)} \quad (2)$$

reaction conditions employed because of this competing racemization.

Dasgupta and Harris [3] measured the rate of isomerization (1) over a wide range of pH values in borate buffer, and k_{obs} at 55 °C was found to be around 1.5 × 10^{-4} sec^{-1} in slightly alkaline solutions. We have repeated some of their measurements and our results agree with those reported within experimental error. Some values for k_{obs} for both the isomerization of the α-complex and the racemization of the β-species are collected together in Table II.

TABLE II. Effects of pH and Added Carbonate Ion on the Rates of Inversion of Λ-α- and Racemization of β-[Co(trien)CO_3]$^+$ at 55 °C.

pH	$[HCO_3^-]$/F	k_{obs}/sec^{-1} (isomerization)	k_{obs}/sec^{-1} (racemization)
8.2		1.2 × 10^{-4}[a]	
8.65		1.3 × 10^{-4}[a]	
8.6			1.5(1) × 10^{-6}
8.1	0.05	1.17(2) × 10^{-5}[b]	1.8(1) × 10^{-6}
8.6	0.10		1.0(1) × 10^{-6}
8.0	1.00	0.79(4) × 10^{-6}	0.4(1) × 10^{-6}

[a]From ref. [3]. [b]Standard deviation in parentheses from least-squares analyses of five runs.

The most striking result is that the rate of inversion of Λ-α-[Co(trien)CO_3]$^+$ is markedly dependent upon carbonate (or, of course, bicarbonate) concentration. This finding in turn indicates that the rate law for the reaction involves carbonate and is more complex than that derived earlier [3], and suggests that 'carbonate-free' complexes are directly responsible for the inversion. It is thus apparent that the processes (3) and (4) are involved in the overall reaction. These equilibria themselves are rather complex and have been studied in considerable detail by Lapidus and Harris [11].

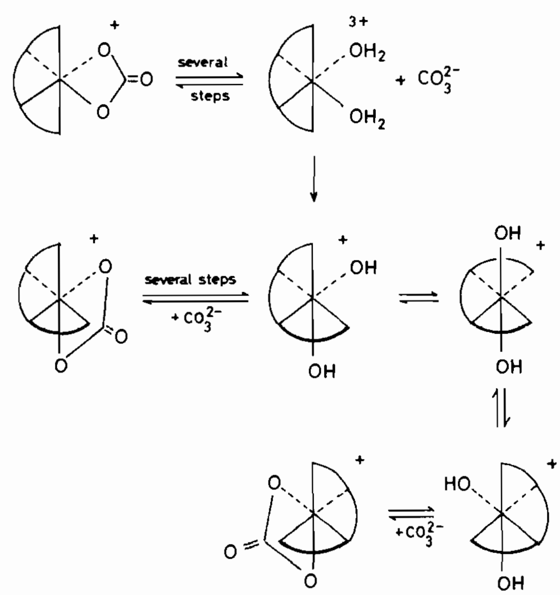
$$\Lambda\text{-}\alpha\text{-[Co(trien)CO}_3]^+ \xrightleftharpoons{H_2O} \Lambda\text{-}\alpha\text{-[Co(trien)(H}_2\text{O)}_2]^{3+} + CO_3^{2-} \quad (3)$$

$$\Delta\text{-}\beta\text{-[Co(trien)CO}_3]^+ \xrightleftharpoons{H_2O} \Delta\text{-}\beta\text{-[Co(trien)(H}_2\text{O)}_2]^{3+} + CO_3^{2-} \quad (4)$$

Given that bis aquo species are present during the reactions, together with the fact [4, 12] that CO_3^{2-} coordinates to α-[Co(trien)$(H_2O)_2$]$^{3+}$ and β-[Co(trien)$(H_2O)_2$]$^{3+}$ with retention of configuration, the processes observed are readily explained. The inversion (5) is a well known one, studied originally

$$\Lambda\text{-}\alpha\text{-[Co(trien)(H}_2\text{O)}_2]^+ \xrightarrow{OH^-} \Delta\text{-}\beta\text{-[Co(trien)(OH)}_2]^+ \quad (5)$$

by Bailar *et al.* [12]. Δ-β-[Co(trien)$(H_2O)_2$]$^{3+}$ does not invert to the Λ-α-species under the same conditons but Δ-β-[Co(trien)$(OH)_2$]$^+$ slowly racemizes in aqueous solution *via* a *trans* intermediate [13]. Thus a racemic product ultimately forms, and the inversion and racemization (less inhibited by added bicarbonate) are simply the result of the base hydrolyses of the various complexes shown in the Scheme.



Scheme.

Acknowledgements

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References

1 T. J. Goodwin, P. A. Williams and R. S. Vagg, *Inorg. Chim. Acta, 63*, 133 (1982).
2 J. A. Chambers, M. W. Mulqi, P. A. Williams and R. S. Vagg, *Inorg. Chim. Acta, 81*, 55 (1984).
3 T. P. Dasgupta and G. M. Harris, *Inorg. Chem., 12*, 488 (1973).
4 A. M. Sargeson and G. H. Searle, *Inorg. Chem., 6*, 787 (1967).
5 F. P. Dwyer, I. K. Reid and F. L. Garvan, *J. Am. Chem. Soc., 83*, 1285 (1961).
6 J. H. Worrell, *Inorg. Synth., 13*, 195 (1972).
7 H. F. Holtzclaw, D. P. Sheetz and B. D. McCarty, *Inorg. Synth., 4*, 176 (1953).
8 F. P. Dwyer and F. L. Garvan, *Inorg. Synth., 6*, 195 (1960).
9 A. M. Sargeson and G. H. Searle, *Inorg. Chem., 4*, 45 (1965).
10 R. G. Bates, 'Determination of pH', Wiley, New York, 1954, p. 160.
11 G. Lapidus and G. M. Harris, *J. Am. Chem. Soc., 85*, 1223 (1963) and refs. therein.
12 E. Kyuno, L. J. Boucher and J. C. Bailar Jr, *J. Am. Chem. Soc., 87*, 4488 (1965).
13 E. Kyuno and J. C. Bailar Jr, *J. Am. Chem. Soc., 88*, 1120 (1966).