Synthesis and base hydrolysis kinetics of the nitrile complexes $[Co(tetren)NCR]^{3+}$ (R = Me, Ph and *p*-$MeOC_6H_4$) and the synthesis and kinetics of formation of the tetrazolato complexes $[Co(tetren)N_4R]^{2+}$ (R = Me and Ph; tetren = 1,11-diamino-3,6,9-triazaundecane) by reaction with azide ion

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Summary

The N-bonded nitrile complexes αα-$[Co(tetren)NCR]^{3+}$ (R = Me, Ph, *p*-$MeOC_6H_4$) have been prepared by the reaction of αα-$[Co(tetren)OH_2]^{3+}$ with the corresponding nitrile. The kinetics of base hydrolysis have been studied by pH-stat methods. The reactions involve an S_N1CB displacement of the nitrile to give the hydroxopentamine; nucleophilic attack at the nitrile carbon to give the corresponding carboxamido complex does not occur. NaN_3 reacts with the nitrile complexes in slightly acidic solution (pH *ca.* 5.7) to give the tetrazolato complexes $[Co(tetren)N_4R]^{2+}$ (R = Me, Ph) which have been characterised. The reaction of azide ion with αα-$[Co(tetren)NCMe]^{3+}$ has been studied kinetically. The reaction is biphasic involving the initial rapid formation of the N_1-bonded (5-methyltetrazolato) pentaminecobalt(III) complex with $k = 2 \times 10^{-2}$ dm^3 mol^{-1} s^{-1} at 25 °C followed by the slow isomerisation to the N_2-bonded complex with $k = 3.5 \times 10^{-5}$ s^{-1} at pH 5.7.

Introduction

The pentadentate ligand 1,11-diamino-3,6,9-triazundecane (tetren) forms complexes with cobalt (III) of the type $[Co(tetren)X]^{n+}$, which can exist in four topological forms *(1)–(4)* (1,2), Figure 1. The αα-isomer *(1)* has a plane of symmetry and occurs as one diastereoisomer. The αβ-isomer *(2)* is asymmetric and can exist as two diastereoisomers resulting from the alternative configurations arising from the single chiral nitrogen centre present in the *mer* ring of the tetren ligand. The two diastereoisomers are designated αβ(R)- and αβ(S)-$[Co(tetren)X]^{n+}$. The ββ -isomer *(3)* is asymmetric and exists as one diastereoisomer. The β -*trans* isomer *(4)* is asymmetric and four diastereoisomers can arise due to the two chiral *sec*-NH centres which fuse the coplanar chelate rings.

Coordination of organonitriles to cobalt (III) pentammines gives complexes of the type $[(NH_3)_5CoNCR]^{3+}$ in which the nitrile is bonded end on by sigma donation *via* nitrogen to cobalt(III). There is neglible back pi-bonding from cobalt(III) into the pi* orbitals of the nitrile and, as a result, the nitrile carbon atom becomes susceptible to nucleophilic attack. Base hydrolysis of $[(NH_3)_5CoNCR]^{3+}$ can take place by hydroxide ion attack on the coordinated nitrile to give the coordinated carboxamido complex $[(NH_3)_5CoNHCOR]^{2+}$ or by an S_N1CB displacement of the nitrile by OH^- to give $[Co(NH_3)_5OH]^{2+}$. Base hydrolysis of the coordinated nitrile is normally several orders of magnitude faster than for the free nitrile(3–7). Thus the rate enhancement, in the case of benzonitrile, is some 10^6-fold(5).

The present paper deals with the preparation of a variety of nitrile complexes of the $[Co(tetren)]^{3+}$ moiety and studies of the base hydrolysis rates. The reaction of azide ion with $[Co(tetren)NCMe]^{3+}$ to give the 5-methyltetrazolato complex has also been studied in detail.

Experimental

Synthesis

Tetren·5HCl, αα-$[Co(tetren)Cl](ClO_4)Cl$ and αα-$[Co(tetren)OH_2](ClO_4)_3$ were prepared as previously described(2).

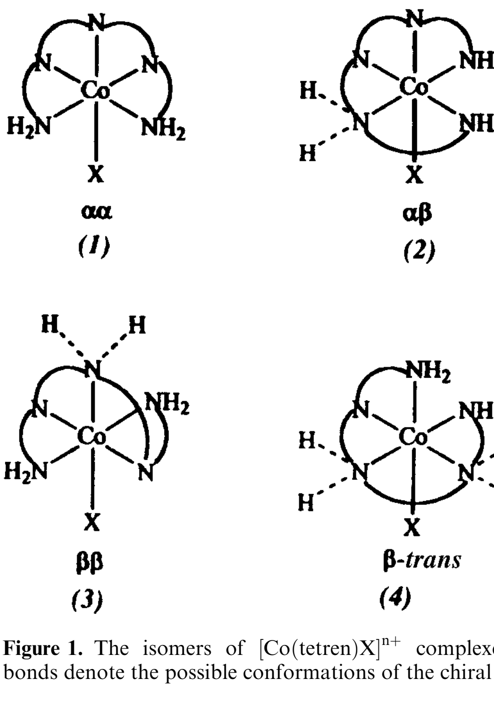

Figure 1. The isomers of $[Co(tetren)X]^{n+}$ complexes. The dashed bonds denote the possible conformations of the chiral *sec*-NH centres.

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αα-[Co(tetren)NCMe]$(ClO_4)_3$

A solution of αα-[Co(tetren)OH_2]$(ClO_4)_3$ (0.5 g, 0.88 mmol) in MeCN (20 cm^3) was heated at 60 °C for 30 min. During this time the solution changed from orange to yellow and yellow crystals deposited. The complex was filtered off, washed with EtOH, then Et_2O and dried in *vacuo*. (Found: C, 20.0; H, 4.25; N, 14.2. $C_{10}H_{26}N_6Cl_3O_{12}Co$ calcd.: C, 20.4; H, 4.45; N, 14.3%). The i.r. spectrum (KBr) has sharp NH bands at 2865 and 3180 cm^{-1} with a broad NH band in the 3000 to 3150 cm^{-1} range. The band due to coordinated MeCN occurs at 2320 cm^{-1} (*c.f.* free MeCN at 2250 cm^{-1}). The visible spectrum measured in 0.1 mol dm^{-3} $HClO_4$ has band maxima at 335 nm ($\varepsilon = 72$) and 464 nm ($\varepsilon = 88$ dm^3 mol^{-1} cm^{-1}).

αα-[Co(tetren)NCPh]$(ClO_4)_3$

This complex was prepared essentially as described above, replacing MeCN with PhCN. The yellow complex was filtered off, washed with EtOH, then Et_2O and dried in *vacuo* (Found: C, 26.0; H, 4.0; N, 12.9. $C_{15}H_{28}N_6Cl_3O_{12}Co$ calcd.: C, 26.7; H, 4.3; N, 12.9%). The i.r. spectrum (KBr) has sharp NH bands at 2870 and 3240 cm^{-1}. The ν(C≡N) band occurs at 2280 cm^{-1} (*cf.* free PhCN at 2230 cm^{-1}). The visible spectrum measured in 0.1 mol dm^{-3} $HClO_4$ has band maxima at 330 nm ($\varepsilon = 150$) and 465 nm ($\varepsilon = 145$ dm^3 mol^{-1} cm^{-1}).

αα-[Co(tetren)NCC_6H_4OMe]$(ClO_4)_3$

p-$MeOC_6H_4CN$ (0.17 g, 1.30 mmol) dissolved in the minimum vol of EtOH was added to a solution of αα-[Co(tetren)OH_2]$(ClO_4)_3$ (0.5 g, 0.88 mmol) in $HClO_4$ (15 cm^3; 0.1 mol dm−3) and the mixture stirred at 60 °C for 3 h. At the end of this time the EtOH was removed on a rotary evaporator. The aqueous solution was cooled leading to the precipitation of the required complex and unreacted *p*-$MeOC_6H_4CN$. The solids were filtered off then stirred with Et_2O to dissolve the organic nitrile. The complex was filtered of, washed with EtOH, then Et_2O and dried *in vacuo*. (Found: C, 28.2; H, 3.9; N, 12.25. $C_{16}H_{30}N_6CoCl_3O_{12}$ calcd.: C, 28.3; H, 4.45; N, 12.4%). The i.r. spectrum (KBr) of the complex has a sharp ν(NH) band at 2875 cm^{-1} and ν(C≡N) at 2275 cm^{-1} (*cf.* free *p*-$MeOC_6H_4CN$ at 2220 cm^{-1}. The visible spectrum of the complex in 0.1 mol dm^{-3} $HClO_4$ has a band maximum at 466 nm.

Tetrazolato complexes

[Co(tetren)N_4CMe]$(ClO_4)_2$

The [Co(tetren)NCMe] $(ClO_4)_3$ complex (1.0 g, 1.7 mmol) was dissolved in dilute $HClO_4$ and NaN_3 (0.22 g, 3.4 mmol) was added in small amounts to the solution (fume cupboard). Throughout the addition the solution was kept at or below pH 5 by dropwise addition of $HClO_4$. The mixture was then heated at 60 °C for 2 h resulting in a change from yellow to orange. Upon cooling, yellow crystals were obtained which were filtered off, washed with EtOH, then Et_2O and dried in air. The crude product was recrystallised from 0.1 mol dm^{-3} $HClO_4$ to remove unreacted NaN_3. (Found: C, 22.3; H, 4.8; N, 23.7. $C_{10}H_{26}N_9CoCl_2O_8$ calcd.: 22.7; H, 4.9; N, 23.8%). The i.r. spectrum (KBr) has a sharp ν(NH) band at 2860 cm^{-1} and the visible spectrum in 0.1 mol dm^{-3} $HClO_4$ has a broad maximum at 456 nm.

A second crop of crystals obtained from the mother liquor of this preparation was identified as [Co(tetren) N_3]$(ClO_4)_2$ with i.r. and visible spectral parameters agreeing with literature values(7).

[Co(tetren)N_4CPh]$(ClO_4)_2$

This complex was prepared essentially as described above. The solution vol was reduced on a rotary evaporator and EtOH added to precipitate yellow crystals of the product. The complex was recrystallised from 0.1 mol dm^{-3} $HClO_4$. (Found: C, 29.9; H, 4.7; N, 21.5. $C_{15}H_{28}N_9CoCl_2O_8$ calcd.: C, 30.4; H, 4.8; N, 21.9%). The i.r. spectrum (KBr) of the complex has a sharp NH band at 2880 cm^{-1}. The visible spectrum determined using 0.1 mol dm^{-3} $HClO_4$ as solvent has a band maximum at 468 nm.

Kinetics

The kinetics of base hydrolysis of the nitrile complexes [Co(tetren)NCR]$(ClO_4)_3$ (R = Me, Ph and *p*-MeO-C_6H_4) were studied by pH-stat methods at 25 °C and I = 0.1 mol dm^{-3} over the pH range 7.0–8.5. The reaction product, [Co(tetren)OH]$^{2+}$, reacts very rapidly with CO_2 to give the monodentate carbonato complex and for this reason spectrophotometric monitoring was not employed. The pH-stat measurements were made with a Radiometer TTT1 automatic titrator in the pH-stat mode. A high alkalinity glass electrode type G202B was employed as the indicator electrode and a calomel K401 electrode as the reference. The electrode system was standardised before each run with NBS borate buffer (pH 9.18 at 25 °C) and phthalate buffer (pH 4.01 at 25 °C). The runs were carried out in a double-walled beaker capable of holding 50 cm^3 of the requisite solution. The temperature was controlled to 25 + 0.2 °C by circulating water from a thermostat. Pre-saturated nitrogen was passed through the solution for 5 min prior to the start of the measurements and was continued throughout the run. The ionic strength was maintained at 0.1 mol dm^{-3} using KNO_3. Kinetic runs were initiated by adding a known weight of the requisite complex to 50 cm^3 of 0.1 mol dm^{-3} KNO_3 in the titration cell. The complexes rapidly dissolved on continuous magnetic stirring. Hydroxide ion concentrations were calculated from the pH using an activity coefficient of 0.772 estimated from the Davies' equation(8) and $pK_w = 13.9965$(9). Plots of $\ln(V_\infty - V_t)$ *versus* time where V_∞ is the final volume of base consumed and V_t is the volume consumed at time t were linear for several half lives. Interval scan spectra for the base hydrolysis reactions were obtained using freshly prepared buffer solutions to avoid carbon dioxide contamination.

The reaction of NaN_3 with [Co(tetren)NCMe]-$(ClO_4)_3$ was studied kinetically at 25 °C using spectrophotometric monitoring. The concentration of NaN_3 was in at least a ten-fold excess over the concentration of the cobalt(III) complex so that first order kinetics were observed. Sodium azide solutions were made up in aqueous perchloric acid so that the final solution pH was *ca.* 5.7. Below pH 5.7 the NaN_3 solutions rapidly discoloured presumably due to the formation of HN_3 which has a pk = 4.7.

Results and discussion

The nitrile complexes $[Co(tetren)NCR](ClO_4)_3$ were readily prepared by reaction of the aquapentamine with the appropriate nitrile. All of the complexes have a band at *ca.* 460 nm in the visible region which is characteristic of a CoN_6 chromophore. Two bonding modes are possible for Co-NCR; (a) end-on bonding *via* the nitrogen atom and (b) side-on bonding *via* C≡N. The i.r. spectra of many metal-nitrile complexes have been studied and the stretching frequency of the C═N bond has been found to be characteristic of the type of bonding involved(10). When the RCN group coordinates to the metal ion by side-on pi-bonding the C═N stretching frequency tends to be lower than that of the uncomplexed nitrile. When the nitrile is bonded end on to the metal ion the C═N stretching frequency is dependent on the electronic nature of the metal ion. Sigma donation occurs from the nitrogen but when the metal ion has strong pi donating ability then back pi bonding into the pi* orbitals of the nitrile can occur and the C═N stretching frequency is shifted to a lower frequency than that of the free nitrile. For metal ions with little or no back donation ability the (C═N) stretching frequency is shifted to a frequency higher than that of the free nitrile. A good example of these effects is observed with the ruthenium(III) and ruthenium(II) pentammine complexes with PhCN. The C≡N stretching vibration of benzonitrile (2231 cm^{-1}) shifts to a higher frequency (2267 cm^{-1}) when coordinated to pentammineruthenium(III) but to a lower frequency (2188 cm^{-1}) when coordinated to pentammineruthenium(II) which is a strong pi-donor metal centre. The i.r. data for the $[Co(tetren)NCR]^{2+}$ complexes are summarised in Table 1. The shift of the C═N band to higher frequencies is consistent with end on bonding through the nitrogen atom with little back bonding from cobalt(III) to the nitrile taking place.

It was found that reaction of the nitriles with isomerically pure $\alpha\alpha$-$[Co(tetren)OH_2]^{3+}$ gave the pure $\alpha\alpha$-$[Co(tetren)NCR]^{3+}$ complexes; this result was confirmed by the kinetic studies as only a single kinetic process was observed.

Table 1. The C═N stretching frequencies (cm^{-1}) in free and complexed nitriles RCN

R	$[Co(tetren)NCR]^{3+}$	$[Co(NH_3)_5NCR]^{3+}$	Free RCN
Me	2320	2320	2250
Ph	2280	2270	2230
p-MeO-C_6H_4	2275	–	2220

Values for the $[Co(NH_3)_5NCR]^{3+}$ complexes are from ref. 5.

The base hydrolysis of $\alpha\alpha$-$[Co(tetren)NCMe](ClO_4)_3$ was studied by pH-stat and the kinetic results obtained are summarised in Table 2. The value of the second order rate constant $k_{OH} = k_{obs}/[OH^-] = 6.2 + 0.1 \times 10^2$ dm^3 mol^{-1} s^{-1} at 25 °C and I = 0.1 mol dm^{-3}. The plot of log $(V - V_t)$ *versus* time is linear for several half lives, Figure 2, and one mole of base is consumed per mole of complex. Spectrophotometric monitoring of the reaction established that isosbestic points occurred at 412 and 465 nm. The visible spectrum of the product is identical to that of an authentic sample of $[Co(tetren)OH]^{2+}$ with band maxima of equal intensity at 350 and 490 nm. The reaction involves SN_1CB displacement of the nitrile ligand to give the hydroxopentamine complex. The pH-stat results also confirm that the sample of $\alpha\alpha$-$[Co(tetren)NCMe]^{3+}$ used in the study was isomerically pure. For the reaction of hydroxide ion with $[Co(NH_3)_5NCMe]^{3+}$ both SN_1CB displacement of the ligand and base hydrolysis of the coordinated nitrile to give the carboxamido complex $[Co(NH_3)_5NHCOMe]^{2+}$ occurs. For the latter reaction $k_{OH} = 3.5$ dm^3 mol^{-1} s^{-1} at 25 °C(6). A rate constant of a similar order of magnitude would be predicted for the base hydrolysis of the nitrile in the tetren complex and since k_{OH} for the SN_1CB displacement is 6.2×10^2 dm^3 mol^{-1} s^{-1} it can readily be shown

Table 2. Kinetics of base hydrolysis of $\alpha\alpha$-$[Co(tetren)NCCH_3](ClO_4)_3$ monitored by pH-stat at I = 0.1 mol dm^{-3} (KNO_3)

pH	10^6 $[OH^-]$ (mol dm^{-3})	10^3 k_{obs} (s^{-1})	10^{-2} $k_{obs}/[OH^-]$ (dm^3 mol^{-1} s^{-1})
8.00	1.30	0.78	6.0
8.20	2.07	1.28	6.2
8.35	2.92	1.85	6.3
8.39	3.20	2.00	6.25

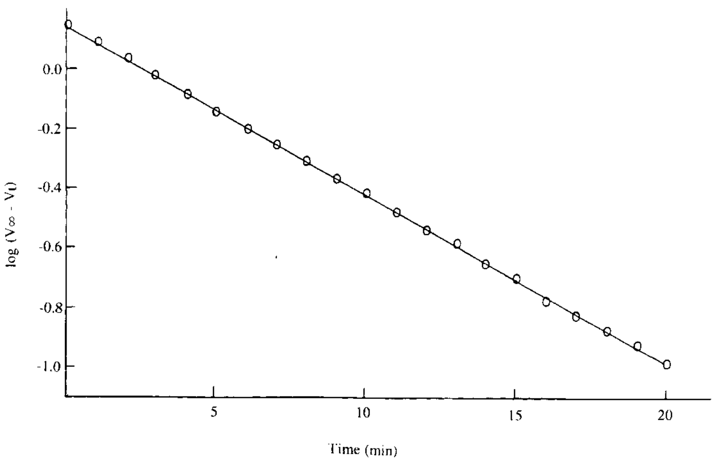


Figure 2. Plot of $\log(V_\infty - V_t)$ *versus* time for the base hydrolysis of α-$[Co(tetren)\ NCCH_3]^{3+}$ at 25 °C and I = 0.1 mol dm^{-3} (KNO_3) at pH 8.39. The half life of the reaction is 5.75 min.

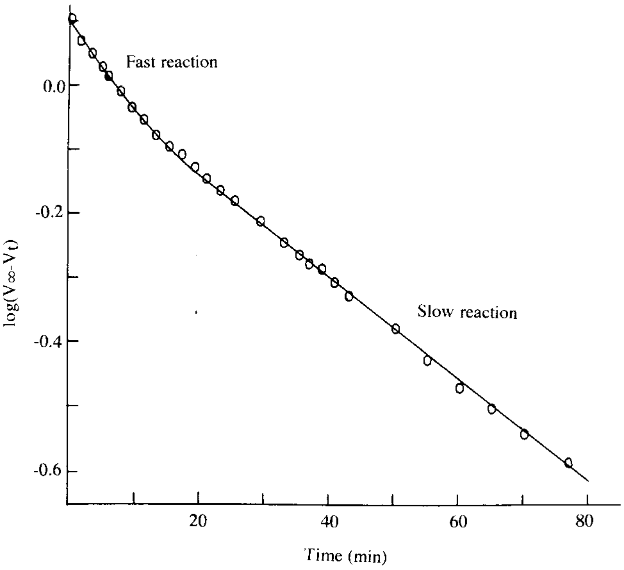


Figure 3. Plot of $\log(V_\infty - V_t)$ *versus* time for the base hydrolysis of an isomeric mixture of $[Co(tetren)NCMe]^{3+}$ at pH 7.57 and 25 °C and $I = 0.1$ mol dm^{-3}.

that the product ratio $[Co(tetren)OH]^{2+}/[Co(tetren)NHCOMe]^{2+} = 6.2 \times 10^2/3.5 = 1.77 \times 10^2$ so that effectively no formation of the carboxamido complex occurs. If $[Co(tetren)NCMe]^{2+}$ is prepared from isomerically impure $[Co(tetren)OH_2]^{3+}$ the pH-stat measurements indicate the presence of two isomeric nitrile complexes, Figure 3. There is an initial fast reaction which is followed by a slow reaction. Approximate values of k_1 and k_2 were estimated from the initial and final slopes of the plot and were refined using the ORIGIN program. The second order rate constant are $k_{OH} = 2 \times 10^4$ dm^3 mol^{-1} s^{-1} and $k_{OH} = 6.7 \times 10^2$ dm^3 mol^{-1} s^{-1}. The rate constant for the slow reaction is in reasonably good agreement with the rate constant $k_{OH} = 6.2 \times 10^2$ dm^3 mol^{-1} s^{-1} previously determined for the αα-isomer. The fast reaction can be assigned to base hydrolysis of αβ(R)- or αβ(S)-$[Co(tetren)NCMe]^{3+}$.

Table 3. Base hydrolysis of αα-$[CO(tetren)NCC_6H_5](ClO_4)_2$ by pH-stat at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3)

pH	10^7 [OH$^-$] (mol dm^{-3})	10^3 k_{obs} (s^{-1})	10^{-3} k_{obs}/[OH$^-$] (dm^3 mol^{-1} s^{-1})
7.35	2.92	0.66	2.3
7.56	4.50	1.04	2.3
7.70	6.54	1.53	2.3
7.80	8.24	1.86	2.25

Table 4. Base hydrolysis of αα-$[CO(tetren)NCC_6H_4OMe](ClO_4)_3$ by pH-stat at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3)

pH	10^7 [OH$^-$] (mol dm^{-3})	10^3 k_{obs} (s^{-1})	10^{-2} k_{obs}/[OH$^-$] (dm^3 mol^{-1} s^{-1})
7.30	2.60	0.17	6.5
7.51	4.22	0.27	6.4
8.07	15.61	1.01	6.5
8.20	20.69	1.33	6.4

Kinetic studies were made with the isomerically pure αα-$[Co(tetren)NCC_6H_5]^{3+}$ and αα-$[Co(tetren)NCC_6H_4OMe]^{3+}$ complexes and the results obtained are summarised in Tables 3 and 4. For the PhCN complex the average value of $k_{OH} = 2.3 \times 10^3$ dm^3 mol^{-1} s^{-1}. The reaction also displays three tight isosbestic points at 340, 412 and 476 nm, Figure 4. For the *p*-OMe derivative $k_{OH} = 6.45 \times 10^2$ dm^3 mol^{-1} s^{-1} at 25 °C and the various rate constants obtained are summarised in Table 5.

Reactions with azide ion

The reaction of azide ion with αα-$[Co(tetren)NCMe]^{3+}$ under conditions where displacement of the nitrile by OH^- was excluded (pH 5.7) was also studied kinetically. Interval scan spectra of the reaction using azide in large excess (> 0.068 mol dm^{-3} NaN_3) established that a biphasic reaction took place. The final spectrum has a band maximum at 465 nm consistent with the formation of a CoN_6 chromophore. The initial fast reaction was first order in the concentration of the complex and first order in the azide concentration with the rate = k_{azide} [Complex] [N_3^-] with $k_{azide} = 2 \times 10^{-2}$ dm^3 mol^{-1} s^{-1} at 25 °C. The second reaction was independent of the azide concentration with $k = 3.5 \times 10^{-5}$ s^{-1} at 25 °C. Interval scan spectra for the second reaction show an increase in absorbance at all visible wavelengths with little change in the position of the band maxima. These observations are consistent with the initial reaction

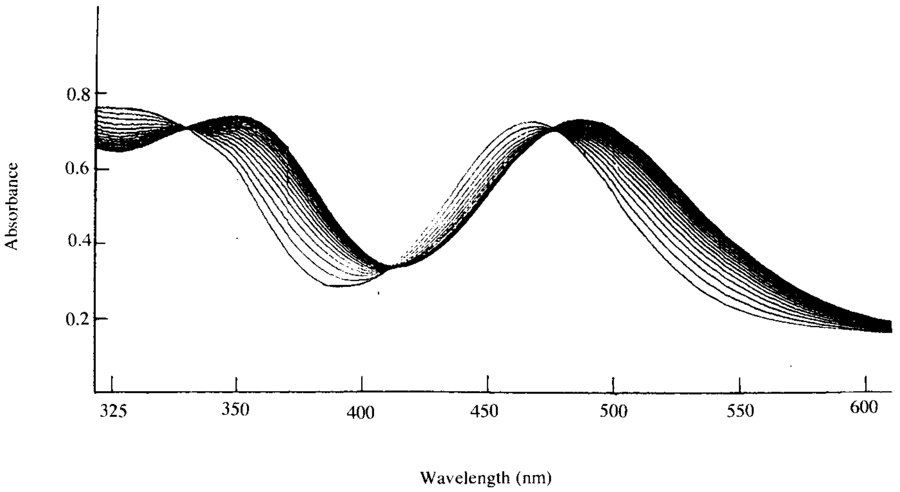
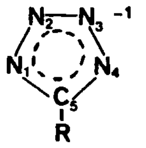


Figure 4. Absorbance changes at pH 7.40 for the base hydrolysis of αα-$[Co(tetren)NCC_6H_5]^{3+}$ at 25 °C and $I = 0.1$ mol dm^{-3}.

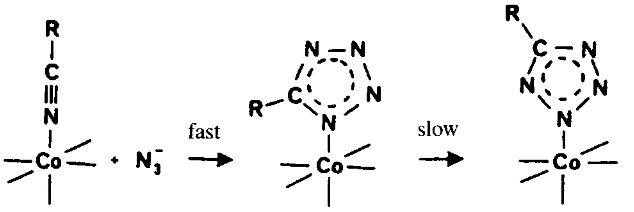
Table 5. Values of k_{OH} for the hydrolysis of the various nitrile complexes at 25 °C and $I = 0.1$ mol dm^{-3}

Complex	k_{OH} (mol dm^{-3})
$\alpha\alpha$-[Co(tetren)NCMe]$^{3+}$	6.2×10^2
$\alpha\beta$-[Co(tetren)NCMe]$^{3+}$	2×10^4
$\alpha\alpha$-[Co(tetren)NCC_6H_5]$^{3+}$	2.3×10^3
$\alpha\alpha$-[Co(tetren)NCC_6H_4OMe]$^{3+}$	6.5×10^2

being the attack of azide ion on the coordinated nitrile to give the tetrazolato complex which then undergoes slow linkage isomerisation as shown in Scheme 1.



tetrazolato ring and numbering scheme



Scheme 1.

Purcell(11,12) has shown that similar reactions occur on reacting azide ion with [Co$(NH_3)_5$NCMe]$^{3+}$. The rate of the N_1 to N_2 linkage isomerisation of the 5-methyltetrazolato-pentammine cobalt(III) is markedly pH dependent. The reaction is rapid at low pH and becomes much slower at pH values approaching neutrality. The pH dependence is attributed to the different rates of isomerisation of the protonated and deprotonated complex, with the deprotonated (2^+complex) undergoing slower isomerisation.

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