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Classic coordination complexes: The kinetics and stereochemistry of acid hydrolysis of *cis*- and *trans*-$[Co(NH_3)_4Cl_2]^+$

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Abstract

The kinetics and stereochemistry of acid hydrolysis of the classic complexes *cis*- and *trans*-$[Co(NH_3)_4Cl_2]^+$ have been determined. They hydrolyse at virtually the same rate, 2.4×10^{-3} s^{-1} and 2.2×10^{-3} s^{-1} for the *cis* and *trans* ions, respectively, (0.02 M $HClO_4$, 25 °C). The 'immeasurably fast' hydrolysis of the *cis* isomer has been dismissed as a myth. The *trans*-$[Co(NH_3)_4(OH_2)Cl]^{2+}$ isomer has been isolated for the first time, and the *trans*/*cis* isomerisation equilibration rate measured, again remarkably at virtually the same rate, 2.3×10^{-3} s^{-1}. The *cis* isomer is the more stable at equilibrium, 88%. The steric course of substitution has been determined as 55% *cis* product for the *cis*-dichloro reactant and 35% *cis* for the *trans* reactant. The kinetic and equilibrium data are compared to that for the well-studied $[Co(en)_2Cl_2]^+$ system, and the synthetic chemistry for the simpler tetraammine systems is elaborated.

Keywords: Werner complexes; Aquation kinetics; Stereochemistry; Cobalt(III); Inorganic synthesis

1. Introduction

Alfred Werner reported the synthesis and characterisation of *cis*-$[Co(NH_3)_4Cl_2]^+$ in 1907 to complete the *cis* and *trans* isomeric pair [1]. This historic achievement and others to follow precipitated his award of the Nobel Prize in chemistry in 1913, for reasons well-documented [2]. Werner also synthesised salts of a much wider range of the structurally related *cis*- and *trans*-$[Co(en)_2AX]^{n+}$ ions, described in a massive 272 page paper in 1912 [3], and it is these complexes that have been the focus of detailed investigations of the kinetics and stereochemistry of ligand substitution over many years [4–7]. In contrast, the synthesis and kinetics of substitution for the simpler tetraammine complexes have been virtually ignored.

The rate of hydrolysis for *cis*-$[Co(NH_3)_4Cl_2]^+$ has been described as 'very fast' [1,3,8], while that for the *trans* isomer has been quantified as 2.2×10^{-3} s^{-1}, in five independent studies (25 °C, $I = 1$ M) [8–12]. The stereochemistry of substitution has not been directly determined for either isomer, since *trans*-$[Co(NH_3)_4(OH_2)Cl]^{2+}$ was unknown. Linck has estimated it for the *trans*-$[Co(NH_3)_4Cl_2]^+$ substrate (45 ± 10% *trans* product) by an indirect method [10,13].

Herein we report the direct determination of the steric course of hydrolysis of both *cis*- and *trans*-$[Co(NH_3)_4Cl_2]^+$. Also determined or redetermined are the rates of hydrolysis, and the $[Co(NH_3)_4(OH_2)Cl]^{2+}$ isomerisation rates and equilibrium position.

2. Experimental

All chemicals were AnalaR or an equivalent grade. Proton NMR spectra were recorded on a Varian Unity Plus 400 MHz instrument at 20 °C. Solvents used were D_2O (pD ca. 3, DCl) with dioxane as the internal reference (δ 3.75 relative to DSS), and DMF-d_7 with the central peak

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of the higher field CD_2H quintet as the internal reference (δ 2.74 ppm, relative to $SiMe_4$). Time dependent visible (340–800 nm) and UV (220–320 nm) spectra and absorbance-time data generated from such data were recorded on a HP8453A diode array Vis/UV spectrophotometer thermostated to 25.0 ± 0.1 °C with use of a Lauda RM6 circulating water bath. Reported Vis/UV spectra for all compounds have been extrapolated to zero reaction time. Kinetic data were analysed by weighted non-linear regression on a Macintosh with the usual packages, or by importing the HP .kd files into Specfit® and carrying out Global Spectral Analysis (SVD data reduction) and subsequent fitting to either a single or double exponential integrated rate expression [14]. Carbon dioxide free Milli-Q® water was used for all physical measurements.

2.1. Synthesis and characterisation

$[Co(NH_3)_4(OCO_2)]NO_3 \cdot 0.5H_2O$ and $[Co(NH_3)_4(OCO_2)]Cl$ were prepared by two standard methods, the faster H_2O_2 oxidation procedure [15,16] being preferred over the aerial oxidation route [15,17]. $[Co(NH_3)_4(OCO_2)]_2SO_4 \cdot 3H_2O$ was made by the published procedure [10,18], as were *cis*-$[Co(NH_3)_4(OH_2)Cl]SO_4$ and *cis*-$[Co(NH_3)_4(OH_2)_2]_2(SO_4)_3 \cdot 3H_2O$ derived from it [15,18,19]. The carbonato sulfate was converted to the chloride by metathesis using the stoichiometric amount of $BaCl_2 \cdot 2H_2O$ to remove the sulfate and then crystallised by precipitation with methanol. *cis*-Diaqua sulfate was generated in situ from the carbonato sulfate with the required amount of H_2SO_4, and then treated with pyridine and $Na_2S_2O_6 \cdot 2H_2O$ to afford *cis*-$[Co(NH_3)_4(OH_2)OH]$ S_2O_6 [20]. Much less pyridine (30 g) is required than that reported (85 g) for the synthesis on the same scale [20]. Dehydration of the latter product (130 °C, 3 h) yielded the *cis*-diol quantitatively [20]; the observed weight loss on dehydration was precisely that calculated. The resultant *cis–cis*-$[(NH_3)_4Co(OH)_2Co(NH_3)_4](S_2O_6)_2$ was converted to the chloride salt by trituration of a thin aqueous slurry with excess NH_4Cl, analogous to that described for the Cr(III) analogue [20]. The product was recrystallised from a saturated aqueous by addition of a fifth volume of saturated NH_4Cl and careful dilution with methanol. The product was collected, and washed with methanol and ether, and air dried.

2.1.1. cis-$[Co(NH_3)_4(OH_2)Cl]SO_4$

The crude material was recrystallised by adding sufficient conc. H_2SO_4 to a thick aqueous suspension of the crude sulfate salt to dissolve much of it, filtering rapidly, and then collecting the resultant crystals on cooling. The process was repeated to afford the pure sulfate. *Anal.* Calc. for $CoN_4H_{14}ClSO_5$: H, 5.30; N, 19.66; Cl, 12.27; S, 11.22. Found: H, 5.05; N, 19.99; Cl, 12.63; S, 11.29%.

2.1.2. cis-$[Co(NH_3)_4(OH_2)Cl]Cl_2$

cis-$[Co(NH_3)_4(OH_2)Cl]SO_4$ (10 g) was treated with conc. HCl (50 mL) at ambient temperature, and after stirring for 5 min was filtered, washed with ethanol and ether, and air dried. Two recrystallisations from a saturated aqueous solution by adding a third volume of conc. HCl and cooling yielded the pure chloride salt. *Anal.* Calc. for $CoN_4H_{14}Cl_3O$: H, 5.61; N, 22.29; Cl, 42.30. Found: H, 5.39; N, 22.04; Cl, 42.05%. Vis/UV spectrum (0.02 M $HClO_4$): 531 nm, ε(max) 57.5; 372 nm, ε(max) 49.0 $M^{-1}\,cm^{-1}$. ^1H NMR spectrum (D_2O, DCl): δ 4.30 (6H, *cis*-Cl, OH_2); δ 3.63 (3H, *trans*-OH_2); δ 3.20 ppm (3H, *trans*-Cl).

cis-$[Co(NH_3)_4(OH_2)Cl]S_2O_6 \cdot H_2O$ was obtained by adding aqueous $Na_2S_2O_6$ to a solution of the complex chloride. Crystals which formed on cooling overnight were washed with ice water, methanol and then ether and air dried. *Anal.* Calc. for $CoN_4H_{16}ClS_2O_8$: H, 4.50; N, 15.62; Cl, 9.88; S, 17.88. Found: H, 4.24; N, 15.63; Cl, 9.91; S, 17.50%.

2.1.3. trans-$[Co(NH_3)_5(OH_2)Cl]Cl_2$

trans-$[Co(NH_3)_5Cl_2]Cl_2 \cdot H_2O$ [18,21] (12.7 g, 50.5 mmol) was partly suspended/dissolved in a mixture of ice (150 g) and water (150 mL) acidified with a few drops of neat CF_3SO_3H or CF_3CO_2H while well-stirred in an ice bath. To this was added dropwise over 4–5 min an ice-cold suspension (yellow) of HgO (red; 10.9 g, 50.3 mmol, 1.0 equiv.) which had been well-stirred and cooled in ice (25 g)/water (10 mL) containing neat CF_3SO_3H (16 g, 107 mmol). The green salt gradually dissolved to yield a violet solution. Some unreacted green complex remained. The addition of a mixture of ice (25 g) and $HClO_4$ (70%; 25 mL) was added to ensure complete precipitation of the unreacted green substrate. The mixture was then filtered, and the residual green solid (<0.2 g) was washed with one bed volume of acetone (50 mL). The filtrate and washing was treated with ice (30 g)/conc. H_2SO_4 (20 mL), and acetone (75 mL) was added to the point of cloudiness. After further stirring on ice (ca. 3 min), the mixture was filtered to remove the precipitate of *cis*-$[Co(NH_3)_4(OH_2)Cl]SO_4$ (ca. 6 g) and washed with acetone (50 mL). The now lavender-grey filtrate was carefully diluted with acetone (ca. 125 mL) just to the point of permanent cloudiness. After 5 min stirring on ice and a then further addition of acetone (100 mL), the crystallisation of *trans*-$[Co(NH_3)_4(OH_2)Cl]SO_4$ was complete. It was removed by filtration, washed with acetone and ether, and air dried (5.1 g). A second crop (1.4 g) was obtained from the filtrate by diluting further with acetone (to 1 L total volume) and allowing to crystallise for 5 min.

The crude *trans* isomer was stirred in aqueous HCl (5 M) whence it transformed from a lavender grey to a fine grey-green Cl^- salt. It was filtered to remove the *cis* isomer which had selectively extracted. The extraction was repeated until the washings were virtually colorless and the residual solid had become a dull green. The purified *trans*-$[Co(NH_3)_4(OH_2)Cl]Cl_2$ was finally recrystallised from a minimum volume of ice water by filtering and quickly adding cold 5 M HCl. Shiny green-grey needles resulted, which were quickly collected, washed with methanol and ether and air dried. *cis* Isomer is introduced if crystallisation is delayed. *Anal.* Calc. for $CoN_4H_{14}Cl_3O$: H, 5.65; N, 22.42; Cl, 42.55. Found: H, 5.64; N, 22.05; Cl, 41.68%. Vis/UV spectrum (0.02 M $HClO_4$): 593 nm, ε(max) 30.7; 470 nm, ε(max) 24.1; 367 nm, ε(max) 50.0; 530 nm, ε 20.4 $M^{-1}\,cm^{-1}$. ^1H NMR spectrum (D_2O, DCl): δ 4.36 ppm (6H, *cis*-Cl, OH_2).

An aqueous solution of the Cl^- salt yielded crystals of the SO_4^{2-} or $S_2O_6^{2-}$ using the appropriate precipitant (5 M H_2SO_4 or 5 M aqueous $Li_2S_2O_6$).

An alternative synthesis of the *trans*-aquachloro complex is via reaction of *trans*-$[Co(NH_3)_4Cl_2]Cl \cdot H_2O$ in neat triflic acid, as described for the bis(ethylenediamine) analogue [22]. The product mixture required fractionation of the sulfate salts, as described above.

2.1.4. *trans-$[Co(NH_3)_4Cl_2]Cl \cdot H_2O$*

This followed that described by Jørgensen, reaction of *cis*-$[Co(NH_3)_4(OH_2)_2]_2(SO_4)_3 \cdot 3H_2O$ in conc. H_2SO_4, followed by reaction with 37% HCl, all at ambient temperature [18,21]. By warming to 50–60 °C, the time scale of the synthesis can be reduced from 48 h to 30 min, and reduced further by using $[Co(NH_3)_4(OCO_2)]_2SO_4 \cdot 3H_2O$ directly rather than first converting it to the *cis*-diaqua complex using aqueous H_2SO_4. The grass-green product is reported to be the chloride salt, but it contains free sulfate and requires recrystallisation from H_2O/HCl to yield pure *trans*-$[Co(NH_3)_4Cl_2]Cl \cdot H_2O$. The perchlorate salt was obtained by metathesis in water using 5 M $HClO_4$ as precipitant. *Anal.* Calc. for $CoN_4H_{14}Cl_3O$: H, 5.61; N, 22.29; Cl, 42.30. Found: H, 5.38; N, 22.11; Cl, 42.13%. Vis/UV spectrum (0.02 M $HClO_4$): 634 nm, ε(max) 42.1; 538 nm, ε(min) 4.7; 467 nm, ε(max) 21.5; 377 nm, ε(max) 36.8; 370 nm, ε(max) 46.4 $M^{-1}\,cm^{-1}$. ^1H NMR spectra: DMF-d_7: δ 4.20 (12H, *cis*-Cl); D_2O, DCl: δ 4.06 ppm (12H, *cis*-Cl).

2.2. *cis-$[Co(NH_3)_4Cl_2]ClO_4$*

The following is a modification of Werner's procedure [1]. Concentrated HCl which had been saturated with HCl (g) at 0 °C was allowed to warm to ca. 15 °C and then 30 mL was added to *cis–cis*-$[(NH_3)_4Co(OH)_2Co(NH_3)_4]Cl_4$ (5.0 g) in a mortar and ground rapidly for ca. 40 s. The crystals that had quickly changed consistency and colour were filtered and the then chilled filtrate and ethanol washings (2 × 10 mL) were treated with cold $HClO_4$ (5 M; 1:1 70% mixed with ice). On scratching blue crystals deposited which were collected, washed with ethanol and ether and air dried. The original solid was extracted with small portions of ice water to give a red solution of the diaqua complex which contained a little of the *cis*-dichloro complex; this was again crystallised using 5 M $HClO_4$. The solid residue was crude blue *cis*-dichloro chloride which was extracted with sufficient ice water to dissolve it all, filtered, and treated with a fifth volume of cold $HClO_4$ (5 M). The three fractions of *cis*-$[Co(NH_3)_4Cl_2]ClO_4$ were combined and quickly recrystallised from water/$HClO_4$. Yield: 1.6 g (46%, based on diol). *Anal.* Calc. for $CoH_{12}N_4Cl_3O_4$: H, 4.07; N, 18.84; Cl, 35.76. Found: H, 4.34; N, 18.51; Cl, 35.32%. Vis/UV spectrum (0.02 M $HClO_4$): 594 nm, ε(sh) 54.2; 563 nm, ε(max) 57.1; 456 nm, ε(min) 9.5; 390 nm, ε(sh) 61.0 $M^{-1}\,cm^{-1}$. ^1H NMR spectrum: DMF-d_7: δ 4.25 (6H, *cis*-Cl); δ 2.74 (6H, *trans*-Cl); D_2O, DCl: δ 4.10 (6H, *cis*-Cl); δ 3.35 ppm (6H, *trans*-Cl).

trans-$[Co(NH_3)_4(NO_2)_2]Cl$ was synthesised as described [23]. It was recrystallised from a saturated aqueous solution by addition of a fifth volume of saturated NH_4Cl and careful dilution with methanol. The perchlorate salt was obtained by metathesis in water using $HClO_4$ as precipitant. Vis/UV spectrum (H_2O): λ(max) 441 and 347 nm. ^1H NMR spectrum (DMF-d_7): δ 3.82 (12H, *cis*-NO_2).

cis-$[Co(NH_3)_4(NO_2)_2]Cl$ was initially prepared as reported by aerial oxidation of Co(II) in the presence of excess NH_3 and NO_2^- [18]; the yield of pure material is poor. The high yield synthesis of *cis*-$[Co(NH_3)_4(NO_2)_2]NO_3$ has been reported [23]. We have made the Cl^- salt by warming *cis*-$[Co(NH_3)_4(OH_2)Cl]Cl_2$ with excess $NaNO_2$ (5 equiv.) after the addition of HCl to first generate the nitritochloro complex. The yellow product was reprecipitated from water with HCl, and then freed of a little *trans* isomer by extracting about 90% of the product with water and crystallising using HCl. This process was repeated to afford yellow needles of the pure *cis* salt. The perchlorate was obtained as described for the *trans* isomer. Vis/UV spectrum (H_2O): λ(max) 441 and 324 nm. ^1H NMR spectrum (DMF-d_7): δ 3.86 (6H, *cis*-NO_2); δ 3.60 ppm (6H, *trans*-NO_2).

An alternative synthesis, and one that gives cis isomer cleanly, is as follows. $[Co(NH_3)_4(OCO_2)]Cl$ in water was treated with sufficient H_2SO_4 to generate the *cis*-$[Co(NH_3)_4(OH_2)_2]^{3+}$ species, as described [20]. Addition of excess $NaNO_2$ (5 equiv.) was added, and the stirred mixture was allowed to stand 48 h to allow the nitrito species to isomerise to the nitro complex. Ethanol was added to precipitate the product, and the filtered material was recrystallised from hot water by addition of a fifth volume of saturated NH_4Cl and dilution with methanol. Fine yellow-orange crystals slowly deposited on cooling. Curiously, this material was much less soluble than the *cis*-dinitro chloride obtained as above, and proved to contain no chloride but rather anionic sulfate which had carried through from the H_2SO_4 plus carbonato chloride initial step.

cis-$[Co(NH_3)_4(NO_2)Cl]Cl$ was obtained by allowing a stirred, thin slurry of *cis*-$[Co(NH_3)_4(NO_2)_2]Cl$ in conc. HCl (1 g in 5 mL) to react for 18 h. The crude product was collected by filtration, washed with ethanol and ether, and air dried. This was extracted carefully with water to yield a claret solution and a green residue of the less soluble *trans*-$[Co(NH_3)_4Cl_2]Cl$. Addition of HCl precipitated the red-claret chloride salt which was recrystallised from water using HCl as precipitant to afford the Cl^- salt. Trituration of the Cl^- salt in a thin slurry with 70% $HClO_4$ removed Cl^- as HCl, and the filtered product was recrystallised from water/$HClO_4$. ^1H NMR spectrum (DMF-d_7): δ 4.54 (6H, *cis*-NO_2, *cis*-Cl); δ 4.04 (3H, *cis*-Cl, *trans*-NO_2); δ 3.48 ppm (3H, *trans*-Cl).

trans-$[Co(NH_3)_4(NO_2)Cl]Cl$ was synthesised from *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$ as described for the *cis* isomer above but allowing a 27 h reaction time. The *trans*-dinitro complex is not very soluble in HCl but cleanly transforms to the *trans*-nitrochloro product quantitatively, whereas the *cis* isomer partly dissolves in HCl and some loss of the second NO_2^- ligand occurs. The salmon pink *trans*-nitrochloro product was obtained as Cl^- and ClO_4^- salts. ^1H NMR spectrum (DMF-d_7): δ 3.70 ppm (12H, *cis*-NO_2, *cis*-Cl).

2.3. Kinetics of acid hydrolysis

Reactions were followed spectrophotometrically using a 8-cell compartment housed in an HP8453A diode array Vis/UV spectrophotometer and the in situ method described previously [24]. The solvent was 1.0, 0.1 or more usually 0.02 M $HClO_4$.

3. Results and discussion

3.1. Syntheses

trans-$[Co(NH_3)_4Cl_2]Cl \cdot H_2O$ was obtained by a modification of a published method [21]. It is much less soluble in water than the bis(ethylenediamine) analogue, and this is also true of methanol as solvent in which it is virtually insoluble. For the perchlorate salts, the water solubilities are reversed. The perchlorate counter ion does not precipitate the chloroaqua ions, and thus both *cis*- and *trans*-$[Co(NH_3)_4Cl_2]ClO_4$ are obtained free of the chloroaqua species which otherwise readily crystallise when Cl^-, SO_4^{2-} or $S_2O_6^{2-}$ are used as counterions.

Werner's classic *cis*-$[Co(NH_3)_4Cl_2]Cl$ complex was first synthesised by HCl cleavage of the *cis*-diol $[(NH_3)_4Co(\mu\text{-}OH)_2Co(NH_3)_4]Cl_4$ [1]. A 1:1 mixture of *cis*-$[Co(NH_3)_4Cl_2]Cl$ and *cis*-$[Co(NH_3)_4(OH_2)_2]Cl_3$ results. The HCl needs to be above the standard concentrated grade (11.7 M) or the yield of the dichloro complex from the bridge cleavage process is reduced. Treatment of *cis*-$[Co(NH_3)_4(NO_2)_2]Cl$ with concentrated HCl has been reported [18,25] as (rapidly) producing *cis*-$[Co(NH_3)_4Cl_2]Cl$, but in our hands it yielded (slowly) *cis*-$[Co(NH_3)_4(NO_2)Cl]Cl$, and on prolonged standing, *trans*-$[Co(NH_3)_4Cl_2]Cl$. Similarly, the *trans*-dinitro complex yielded *trans*-$[Co(NH_3)_4(NO_2)Cl]Cl$; these syntheses parallel the bis(ethylenediamine) chemistry [3]. Werner's alternative syntheses [3] of *cis*-$[Co(NH_3)_4Cl_2]Cl$ via reaction of $[Co(NH_3)_4\text{-}(OCO_2)]Cl$ in aqueous or ethanolic HCl yielded only *cis*-$[Co(NH_3)_4(OH_2)Cl]Cl_2$ in our hands. Also, we found that the latter gives *trans*-$[Co(NH_3)_4Cl_2]Cl$ on prolonged reaction in HCl.

In hindsight, it is surprising that any of these syntheses for the *cis*-dichloro complex work, even the successful diol cleavage reaction! Werner envisaged the reaction as a simple *cis*-Co–O cleavage reaction, with such bond rupture occurring on the same Co centre. However, acid cleavage of the diol might have proceeded either way, as shown in Scheme 1.

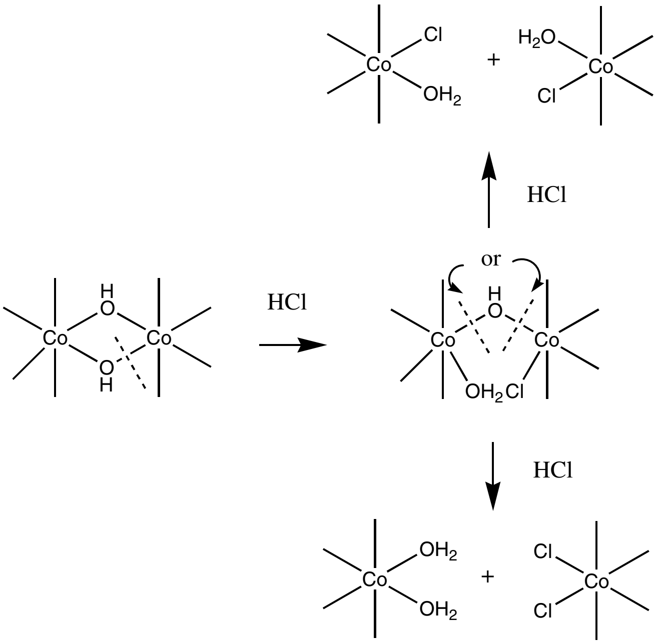
However, we can confirm that no observable *cis*-$[Co(NH_3)_4(OH_2)Cl]Cl_2$ is produced in the diol cleavage reaction. Similarly, the acid cleavage reactions of the carbonato and dinitro complexes, each reported to yield the *cis*-$[Co(NH_3)_4Cl_2]Cl$ complex, might have expected to yield aqua complexes, given the known modes of bond cleavage revealed through tracer studies [4,26], Scheme 2.

In our hands, no *cis*-dichloro complex was formed.

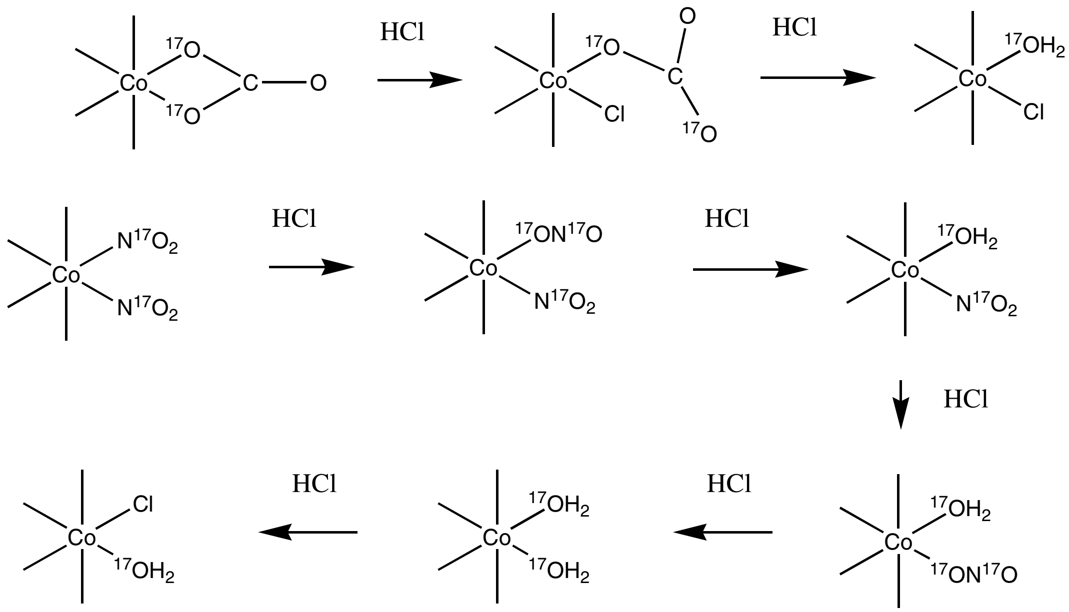
We have found that neither *cis*- nor *trans*-$[Co(NH_3)_4(OH_2)Cl]^{2+}$ yield *cis*-$[Co(NH_3)_4Cl_2]^+$ on reaction with HCl under a variety of conditions, nor does evaporation of an aqueous solution of the *trans*-dichloro chloride, a strategy successful in the bis(ethylenediamine) system.

Finally, the anation of either *cis*-$[Co(NH_3)_4(OSMe_2)_2](ClO_4)_3$ using Et_4Cl in either DMSO or DMF failed to yield appreciable *cis*-dichloro isomer, yet in the corresponding bis(ethylenediamine) systems [27] the *cis*-dichloro complex is formed and is strongly stabilised by ion-pairing in such dipolar aprotic media.

cis-$[Co(NH_3)_4(OH_2)Cl]SO_4$ and *cis*-$[Co(NH_3)_4(OH_2)Cl]S_2O_6 \cdot H_2O$ were too insoluble to be generally useful, while the more soluble *cis*-$[Co(NH_3)_4(OH_2)Cl]Cl_2$ as prepared by various published routes was not pure (^1H NMR). Conversion to the sulfate and back to the chloride removed these impurities. The chloride and sulfate salts were anhydrous; hydrates have been reported [13].



Scheme 1. Alternative modes of acid catalysed OH– bridge cleavage in the diol.



Scheme 2. Acid induced bond cleavage and rearrangement modes for carbonate and nitrite complexes of cobalt(III).

The *trans*-$[Co(NH_3)_4(OH_2)Cl]Cl_2$ complex is new. It was synthesised by Hg(II) induced aquation of *trans*-$[Co(NH_3)_4Cl_2]^+$, a method similar to that described for the bis(ethylenediamine) analogue [28]. It was also obtained [22] by reacting *trans*-$[Co(NH_3)_4Cl_2]Cl \cdot H_2O$ with triflic acid to yield $[Co(NH_3)_4(O_3SCF_3)Cl]CF_3SO_3$, which rapidly formed a *cis*-/*trans*-$[Co(NH_3)_4(OH_2)Cl]^{2+}$ mixture on hydrolysis, and this could be separated using the sulfate counter-ion. *cis*/*trans* Mixtures of salts of $[Co(NH_3)_4(OH_2)Cl]^{2+}$ proved virtually impossible to separate completely as the Cl^-, SO_4^{2-} or $S_2O_6^{2-}$ salts, due to the relatively rapid rate of trans to cis isomerisation and because, for SO_4^{2-} and $S_2O_6^{2-}$, the *trans* isomer is more soluble; the *cis* form then tends to co-crystallise. As the Cl^- salt, even small amounts of the *cis* form rendered the crystals grey, although they appeared homogeneous under the microscope. It could, however, be rendered completely free of it by successive extractions with small amounts of 1 M HCl until the extracts were a consistent pale violet colour. The residue was a dull green salt.

The four nitro complexes, of which *cis*- and *trans*-$[Co(NH_3)_4(NO_2)Cl]^+$ appear to be new, were reactants or products of the synthetic reactions described, and which did not proceed as reported. They are analogous to their bis(ethylenediamine) counterparts, and were characterised by their Vis/UV and ^1H NMR spectra; the characteristic difference between *cis* and *trans*-nitro species in the UV is noted.

3.2. Isomerisation of $[Co(NH_3)_4(OH_2)Cl]^{2+}$

The isomerisation of *trans*-$[Co(NH_3)_4(OH_2)Cl]^{2+}$ in dilute $HClO_4$ at 25 °C was followed in both the visible (340–700 nm) and UV (220–320, 270–300 nm) regions. In the visible region, two sharp isosbestic points were observed (589 nm, ε 30.7 $M^{-1}\,cm^{-1}$; and 473 nm, ε 23.8 $M^{-1}\,cm^{-1}$) and the absorbance changes were large (Fig. 1). Absorbance changes in the UV were much smaller (Figure 1S) because *cis*- and *trans*-$[Co(NH_3)_4(OH_2)Cl]^{2+}$ have very similar spectra throughout this region. Nonetheless, by working on the tail of the UV where the absorbance is low yet proportional absorbance changes are appreciable, and through raising the [Co] to take advantage of this, a sharp isosbestic point was observed at 284 nm (Figure 2S), and the absorbance-time data accurately fitted a single exponential ($k_{obsd} = 2.31 \times 10^{-3}\ s^{-1}$). The rate data obtained from the three spectral regions were in good agreement (Table 1), and k_{obsd} is not appreciably medium dependent (1.0, 0.1, 0.02 M $HClO_4$).

The *trans*/*cis* equilibrium, while it favours the *cis* side (88%), is not so far to that side that the rate could not be measured starting with the *cis* isomer. The spectral changes commencing with *cis* are small (Figure 3S) but sufficient to define the rate well (Table 1), and even the two isosbestic points (473 and 590 nm). The measured k_{obsd} should be the same since the sum of the forward and reverse rates are measured commencing with either isomer, and indeed this is born out by the results (Table 1).

Equilibrium $[Co(NH_3)_4(OH_2)Cl]^{2+}$ data are given in Table 2 and results are internally consistent for the four different starting materials. This result, 88 ± 1% *cis*, is not too different to that estimated by Linck's indirect method [10,13] (90.5 ± 1.0% *cis*).

The ^1H NMR spectrum (Fig. 2) show the single line spectrum for the trans isomer in D_2O/DCl change into the 2:1:1 pattern expected for *cis*-$[Co(NH_3)_4(OH_2)Cl]^{2+}$, and confirm its presence at equilibrium to the extent of ca. 10%.

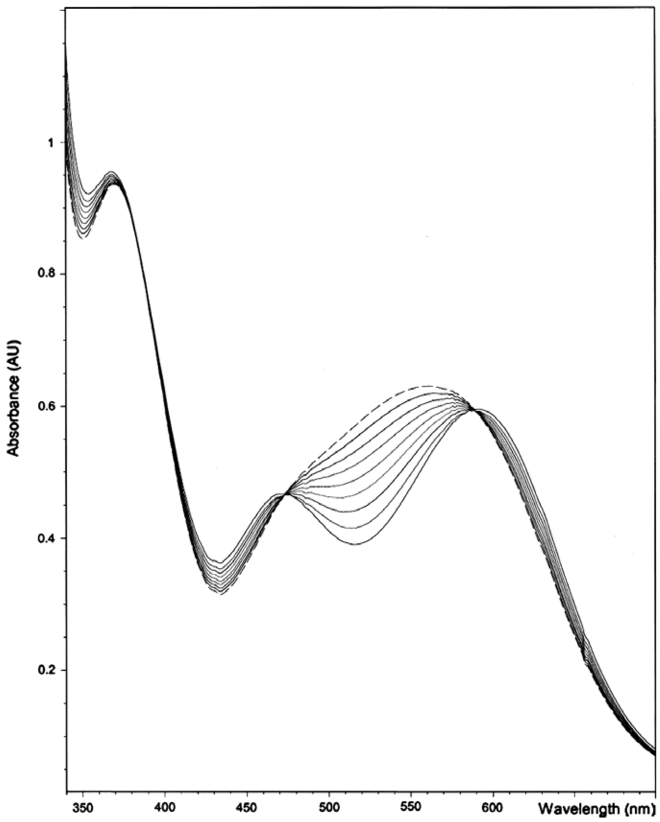


Fig. 1. Visible spectral changes for the isomerization of *trans*-$[Co(NH_3)_4(OH_2)Cl]^{2+}$ in H_2O/H^+, 25 °C.

Table 1
Rate data for the reversible isomerisation of *trans*-$[Co(NH_3)_4(OH_2)Cl]^{2+}$ in dilute $HClO_4$ at 25 °C

$[HClO_4]$ (M)	Region[c]	10^3k_2 (s^{-1})[a]
0.020	vis	2.31 (10)
	vis	2.32 (3)[b]
	UV	2.17 (6)
0.10	vis	2.36 (3)
1.0	vis	2.62 (9)

[a] $k_2 = k_{tc} + k_{ct}$; $k_{tc}/k_{ct} = 88/12$ (Table 2). The number of determinations is given in parenthesis.

[b] Reactant was *cis*-$[Co(NH_3)_4(OH_2)Cl]Cl_2$.

[c] Global analysis fits (refer text).

Table 2
Equilibrium data for the reversible isomerisation of *trans*-$[Co(NH_3)_4(OH_2)Cl]^{2+}$ in 0.020 M $HClO_4$ at 25 °C

Reactant	ε (530 nm) (M^{-1} cm^{-1})	%*cis*(equil)[a]
cis-$[(OH_2)Cl]SO_4$	53.0 (2)	88
cis-$[(OH_2)Cl]S_2O_6 \cdot H_2O$	52.8 (3)	87
cis-$[(OH_2)Cl]Cl_2$	53.7 (2)	90
trans-$[(OH_2)Cl]Cl_2$	53.5 (2)	89
trans-$[Cl_2]Cl \cdot H_2O$	53.0 (2)	88
cis-$[Cl_2]ClO_4$	52.6 (2)	87
Ave:	53.0 (13)	88 (13)

[a] Number of determination in parenthesis; results calculated from ε(530) for the *cis* isomer, 57.5, and ε(530) for the *trans* form, 20.4 M^{-1} cm^{-1}.

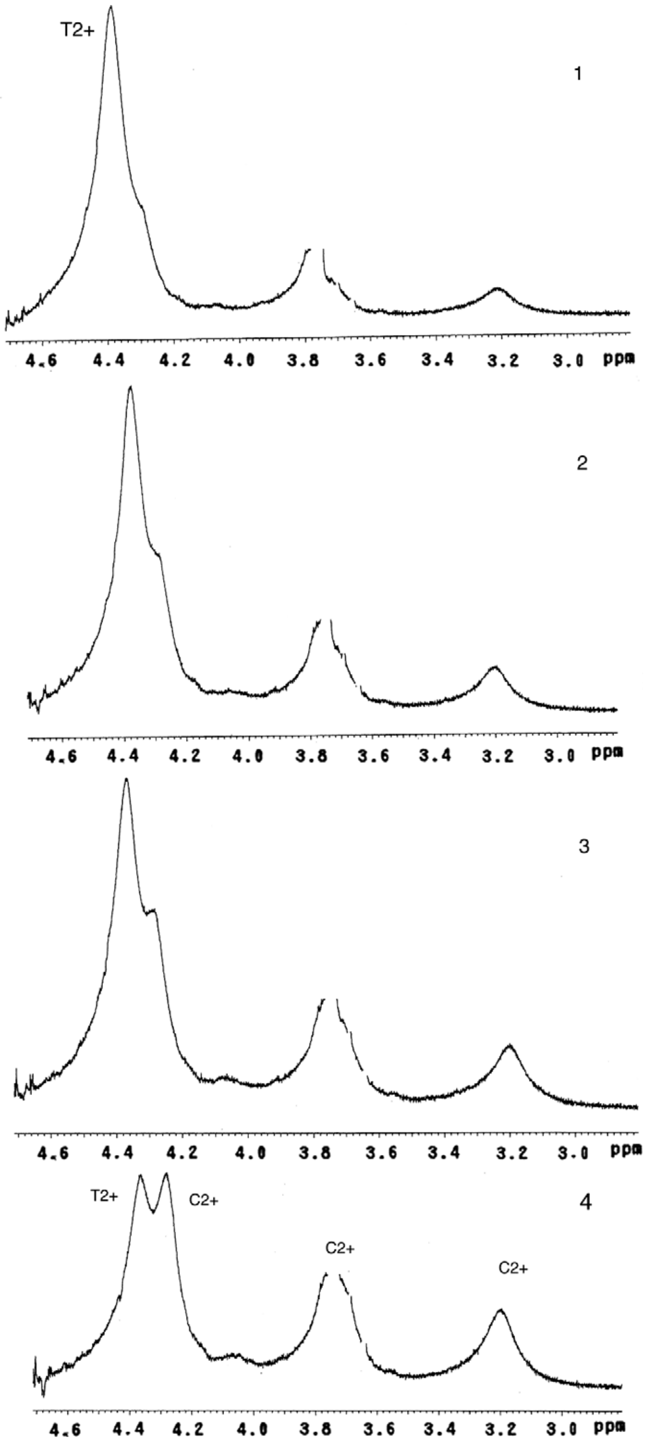


Fig. 2. ^1H NMR spectra (NH region) for the isomerization of *trans*- (T2+) to cis- (C2+) $[Co(NH_3)_4(OH_2)Cl]^{2+}$ in D_2O/D^+ at ca. 21 °C; times increase from 1 to 4.

3.3. Aquation of *cis*-$[Co(NH_3)_4Cl_2]^+$

The hydrolysis rate for the *cis* isomer has never been measured. It has been described as 'very fast' by Pearson et al. [8], and that the aquation was very rapid was implied by Werner [1,3] in his experimental descriptions of poor recovery through rapid recrystallisation from water. It is a myth. It hydrolyses at about the same rate as the *trans*

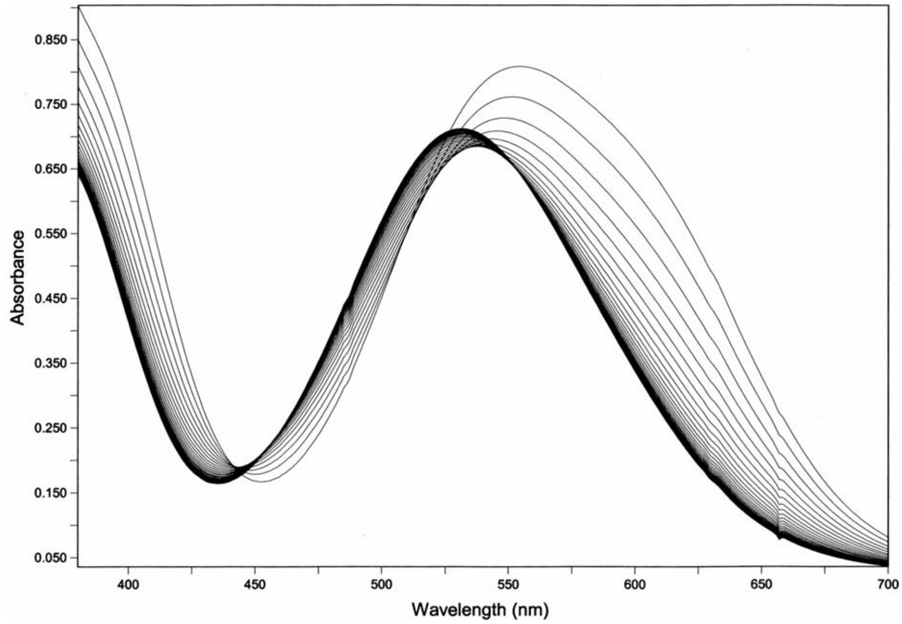


Fig. 3. Visible spectral changes for the hydrolysis of *cis*-$[Co(NH_3)_4Cl_2]^+$ in H_2O/H^+, 25 °C. The absorbance decreases with time at 600 nm.

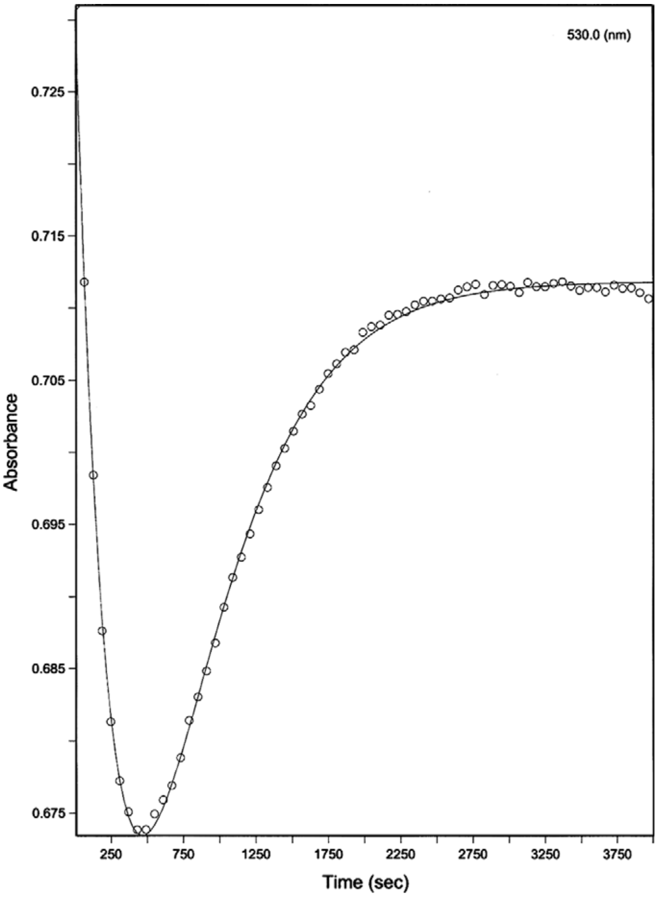


Fig. 4. Absorbance–time trace at 530 nm for the hydrolysis of *cis*-$[Co(NH_3)_4Cl_2]^{2+}$ in H_2O/H^+, 25 °C, illustrating the biphasic nature of the reaction.

isomer. The changes in visible spectra (340–700 nm; Fig. 3) with time hide the fact that there are two early sharp isosbestic points, one of which changes quickly with time (Fig. 4S. 440 nm, ε 13.0; 514 nm, ε 39.0 $M^{-1}\,cm^{-1}$). The first phase is loss of one Cl^- and the second is *cis-/trans-*$[Co(NH_3)_4(OH_2)Cl]^{2+}$ isomerisation. The final spectrum corresponds to a 88% *cis*/22% *trans* distribution (Table 2). The absorbance–time trace at 530 nm (Fig. 4) clearly indicates the biphasic behaviour, and in particular it shows that the second phase corresponds to *trans–cis* rather than *cis–trans* isomerisation, i.e., the initial hydrolysis reaction leads to not only both *cis*- and *trans*-$[Co(NH_3)_4(OH_2)Cl]^{2+}$ but an isomeric mixture which contains more *trans* isomer than does the equilibrium distribution.

The changes in the UV absorption spectra accompanying the hydrolysis of the *cis*-dichloro complex are relatively small (Figure 5S), but nonetheless sufficient to determine a rate constant for the hydrolysis. The data fitted a single exponential because in the region examined (280–320 nm) the absorbance changes for the secondary isomerisation process are much smaller, and negligible. The results (see below) bear this out – the visible and UV rate data agree.

The primary hydrolysis rate constant was determined by fitting the 589 nm data to a single exponential. The fits were good, since this wavelength is an isosbestic point for the secondary *trans*/*cis* isomerisation reaction. The 530 nm data (Fig. 4) were then fitted to two exponentials with the first exponential (k_1) fixed at the value determined from the 589 nm data. This yielded k_2 which is the aquachloro isomerisation rate, and the check on the correctness of the analysis is the reasonable agreement of this value and that determined independently for this reaction (Table 3; cf. Table 1).

It is evident that k_1 and k_2 are very similar in magnitude. Because of this, the global analysis of the visible absorption spectral data (340–700 nm) involves a shallow minimum with considerable flexibility in the derived values for both k_1 and k_2 and the spectrum for the intermediate (kinetic)

Table 3
Rate data for the acid hydrolysis of *cis*-$[Co(NH_3)_4Cl_2]^+$ in 0.020 M $HClO_4$ at 25 °C

Region	10^3k_1 (s^{-1})	10^3k_1 (s^{-1}) (589 nm)[a]	10^3k_2 (s^{-1}) (530 nm)[b]
UV (260–300 nm)	2.12 (3)		
Vis		2.35 (9)[b]	2.47 (9)
		2.39[c]	2.46[c]
		2.33[c]	2.48[c]
		2.37[d]	2.31[d]

[a] Single exponential fit at one of the *cis-/trans*-$[Co(NH_3)_4(OH_2)Cl]^{2+}$ isomerisation isosbestic points.

[b] Double exponential fit, with k_1 fixed at the value determined at 589 nm for the same run.

[c] Global fit (340–700 nm) double exponential fit with no restriction on k_1 or k_2, for selected data sets (>95% reaction).

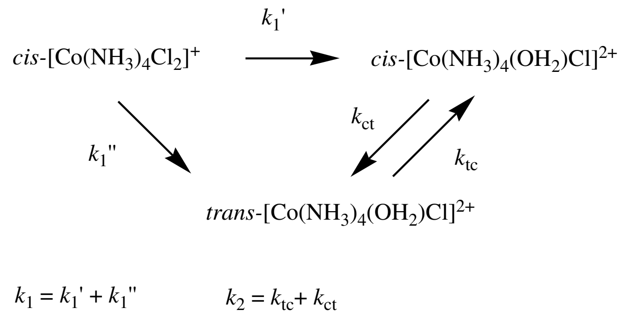
[d] Double exponential fit with k_2 fixed at the independently determined value.

$[Co(NH_3)_4(OH_2)Cl]^{2+}$ isomer distribution. This is a general problem when $k_1 \sim k_2$ [14]. However, fitting to a single wavelength data set such as the fall-rise seen at 530 nm gives much better defined parameters when the two rates are similar, provided the data cover a time period in excess of 95% reaction.

The steric course for the primary substitution reaction was determined as described previously [29] by fitting the ε, *t* data to Eq. (1) which applies to Scheme 3 as shown:

$$\begin{aligned}\varepsilon_{\text{obsd}} = \varepsilon_\infty &+ \{(\varepsilon_A - \varepsilon_C) + (k_1(\varepsilon_B - \varepsilon_C)/(k_2 - k_1))\} \\ &\times \exp(-k_1 t) - \{(k_1(\varepsilon_B - \varepsilon_C)/(k_2 - k_1))\} \\ &\times \exp(-k_2 t). \qquad (1)\end{aligned}$$

Here 'B' is the first formed *cis-/trans*-aquachloro mixture and 'C' is the equilibrium mixture. The initial *cis/trans* ratio is best defined from absorbance data at around 530 nm where the component spectra differ the most. We also carried out a multiwavelength version of this analysis by globally fitting (Specfit®) the 340–700 nm data to a A → B → C scheme fixing the values of k_1 (determined at 589 nm, Table 3) and k_2 (independently determined, Table 1), and determining the full spectrum of the intermediate isomer mixture (Fig. 5). Note that even though we are dealing with first order reactions, absolute times must be used to get the correct spectrum of the intermediate B. The intermediate spectrum was fitted to the spectra of its two components and yielded a 55% *cis*, 45% *trans* kinetic distribution; similarly, the final spectrum corresponded to 88% *cis*, 12% *trans*.



Scheme 3. The sequential hydrolysis reaction for *cis*-$[Co(NH_3)_4Cl_2]^+$.

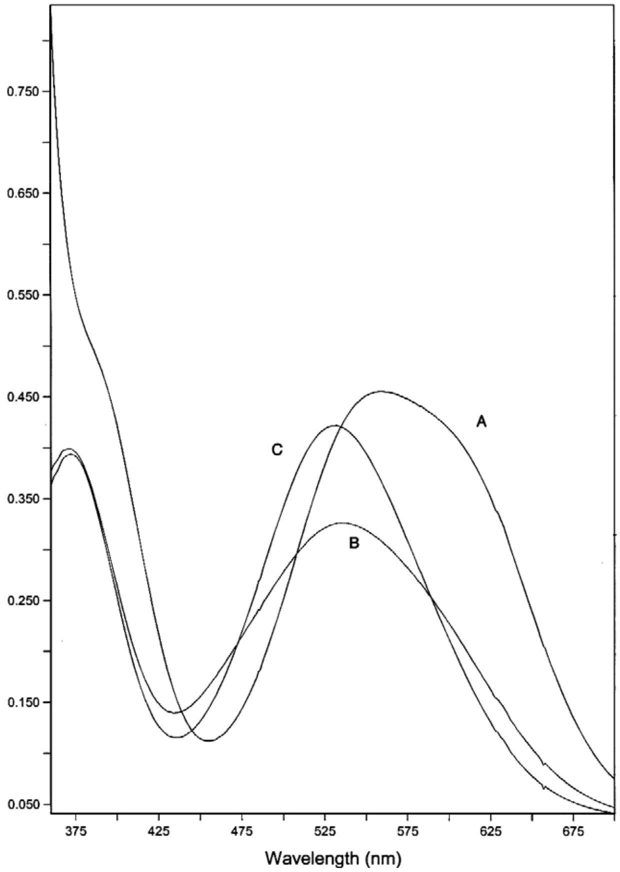


Fig. 5. Computed intermediate (B) and final (C) *cis-/trans*-$[Co(NH_3)_4(OH_2)Cl]^{2+}$ visible spectra, for the hydrolysis of *cis*-$[Co(NH_3)_4Cl_2]^+$ (A) in H_2O/H^+ at 25 °C. The vertical scale is absorbance, for an arbitrary [Co].

The 440 nm isosbestic point (ε 13.0; ε(*cis*) = 11.0, ε(*trans*) = 19.3 M^{-1} cm^{-1}) is not very sensitive to the *trans-/cis*- product ratio but the 514 nm isosbestic is. The initial product distribution calculated from this (ε 39.0; ε(*cis*) = 53.5 and ε(*trans*) = 19.7 M^{-1} cm^{-1}), while intrinsically less accurate, gives excellent agreement (57% *cis*). This shifts quite quickly with time, and it was important to define it using a number of scans collected within the first 40 s (10% reaction). After 2 min the isosbestic, still reasonably well defined, is at 516 nm (ε 40.5 M^{-1} cm^{-1}) and this corresponds to nearly 60% *cis* product. As the simulation shows (Table 4), for an initial 55% and final 88% *cis*, the 55% changes quickly in a system where k_1 and k_2 are very similar.

Fig. 6 shows the ^1H NMR spectra for the *cis*-dichloro complex hydrolysing in D_2O (pD 2, DCl) at ca. 21 °C. The *cis*- and *trans*-aquachloro ions grow in parallel, before ultimately the *trans* isomer decays back to the *cis*. The lowest field peak is *trans* (12H) and the next lowest is the major *cis* peak (6H), and from their areas the product distribution at 2–3 min reaction time is estimated as 60% *cis*, 40% *trans*, which is entirely in accord with the spectrophotometric determination.

Table 4
Changing product distribution with time for a consecutive reaction scheme for the *cis*-$[Co(NH_3)_4Cl_2]^+$ reactant and where $k_1 = 2.4 \times 10^{-3}\ s^{-1}$, $k_2 = 2.3 \times 10^{-3}\ s^{-1}$, and the initial and final *cis*-$[Co(NH_3)_4(OH_2)Cl]^{2+}$ product proportions are 55% and 88%

t	A	B	C	%*cis*
0	1.000	0.000	0.000	55.0
5	0.988	0.012	0.000	55.2
10	0.976	0.023	0.000	55.4
15	0.965	0.035	0.001	55.6
20	0.953	0.046	0.001	55.8
25	0.942	0.057	0.002	55.9
30	0.931	0.067	0.002	56.1
35	0.919	0.077	0.003	56.3
40	0.908	0.087	0.004	56.5
45	0.898	0.097	0.005	56.7
50	0.887	0.107	0.006	56.9
55	0.876	0.116	0.008	57.0
60	0.866	0.125	0.009	57.2
65	0.856	0.134	0.011	57.4
70	0.845	0.143	0.012	57.6
75	0.835	0.151	0.014	57.8
80	0.825	0.159	0.016	57.9
85	0.815	0.167	0.017	58.1
90	0.806	0.175	0.019	58.3
95	0.796	0.182	0.021	58.5
100	0.787	0.190	0.024	58.7
105	0.777	0.197	0.026	58.8
110	0.768	0.204	0.028	59.0
115	0.759	0.211	0.031	59.2
120	0.750	0.217	0.033	59.4
125	0.741	0.224	0.036	59.5
130	0.732	0.230	0.038	59.7
135	0.723	0.236	0.041	59.9
140	0.715	0.242	0.044	60.0
145	0.706	0.248	0.046	60.2
150	0.698	0.253	0.049	60.4
155	0.689	0.258	0.052	60.5
160	0.681	0.264	0.055	60.7
165	0.673	0.269	0.058	60.9
170	0.665	0.274	0.061	61.0
175	0.657	0.278	0.065	61.2
180	0.649	0.283	0.068	61.4

3.4. Aquation of *trans*-$[Co(NH_3)_4Cl_2]^+$

The UV absorption maximum at ca. 250 nm for the *trans*-dichloro ion [10] is associated with Co–Cl charge transfer absorption (ε ca. 15,000 $M^{-1}\ cm^{-1}$). It is roughly twice as intense and to lower energy than the corresponding absorption for the *trans*- and *cis*-monochloro ions (ca. 230 nm), and that, being associated with the Co–Cl charge transfer, is insensitive to the *cis* or *trans* stereochemistry. Thus the hydrolysis of the dichloro to monochloro ions involves a large absorption change in the UV region (Figure 6S) whereas the *trans*-/*cis*-isomerisation involves very little change. The latter change was sufficient, however, to easily determine the isomerisation rate spectrophotometrically (Table 1).

Although there is no isosbestic point for the isomerisation coincident with the isosbestic at 239 nm for the hydrolysis of *trans*-$[Co(NH_3)_4Cl_2]^+$ (the so-called triple isosbestic point), we have determined that the spectra for *cis*- and *trans*-$[Co(NH_3)_4(OH_2)Cl]^{2+}$ are indeed very similar to each other and to the *trans*-$[Co(NH_3)_4Cl_2]^+$ ion in this region, and it confirms Linck's surmise [10] on this point, i.e., the persistence of the sharp isosbestic point at 239 nm for 10 $t_{1/2}$ of the primary reaction, despite the second step having essentially the same rate as the first step, the

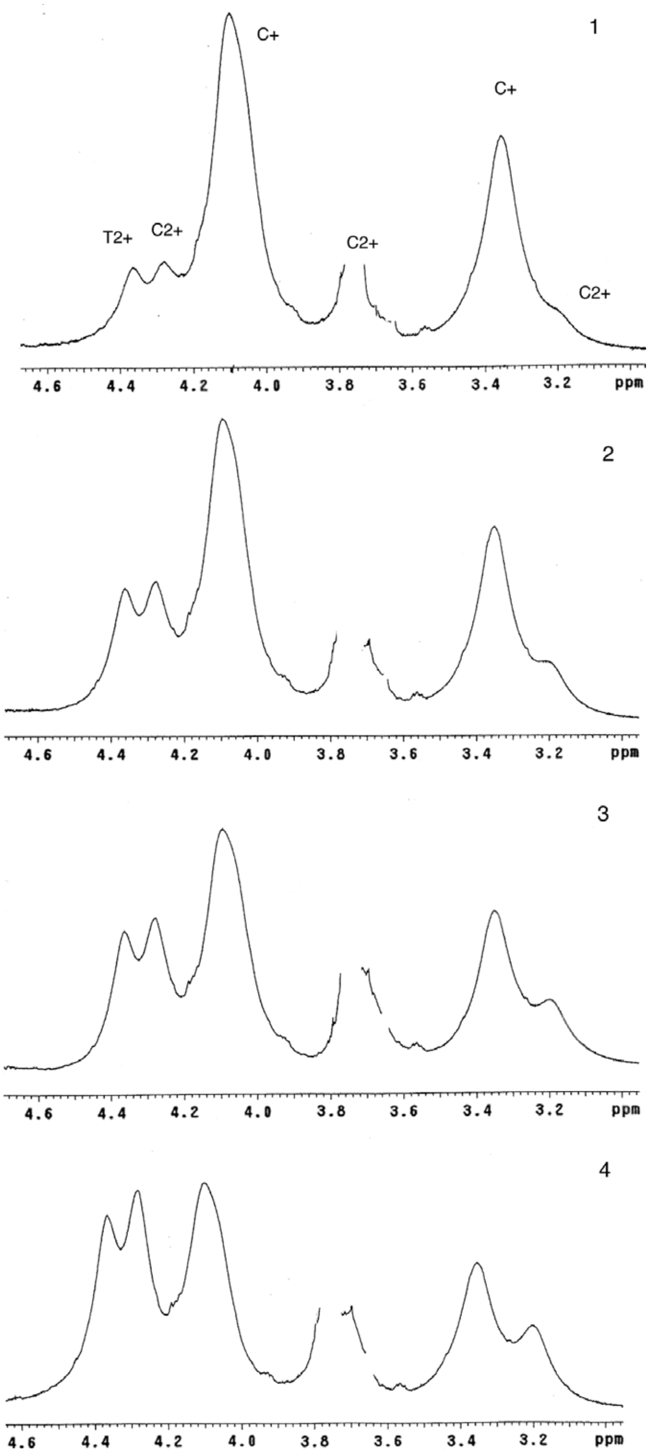


Fig. 6. ^1H NMR spectra (NH region) for the hydrolysis of *cis*-$[Co(NH_3)_4Cl_2]^+$ (C+) in D_2O/D^+ at ca. 21 °C; C2+ and T2+ denote the signals for *cis*- and *trans*-$[Co(NH_3)_4(OH_2)Cl]^{2+}$. Times increase, from 1 to 4.

primary aquation and secondary isomerisation reactions. Indeed, the small absorbance changes in the UV for the secondary reaction are the reason for the good single phase kinetics for the primary reaction as measured in the UV region at any wavelength. The rates obtained are all the same, and in particular the same as those determined from the UV data at 284 nm (Table 5), which is an isosbestic point for the *trans*-/*cis*-$[Co(NH_3)_4(OH_2)Cl]^{2+}$ isomerisation reaction (Figure 2S).

The reaction studied in the visible spectral region revealed four sharp isosbestic points: 353 nm, ε 43.4; 397 nm, ε 33.2; 467 nm, ε 21.5; 597 nm, ε 28.2 $M^{-1}\,cm^{-1}$ (Fig. 7). None were definitive of the steric course of substitution because the spectra of *cis*- and *trans*-$[Co(NH_3)_4(OH_2)Cl]^{2+}$ are very similar at each of these wavelengths (see Figs. 1 and 8).

Table 5
Rate data for the acid hydrolysis of *trans*-$[Co(NH_3)_4Cl_2]^+$ in 0.020 M $HClO_4$ at 25 °C

Region	10^3k_1 (s^{-1})
UV	2.22 (12)[a]
Vis	2.22 (22)[b]
UV	2.23 (4)[c]

[a] Global analysis (UV: 220–320 nm) single exponential fit.

[b] Global analysis (Vis: 340–700 nm) double exponential fit, with k_2 fixed at $2.31 \times 10^{-3}\,s^{-1}$.

[c] Single exponential fit, for data collected at 284 nm, an isosbestic point for $[Co(NH_3)_4(OH_2)Cl]^{2+}$ isomerisation.

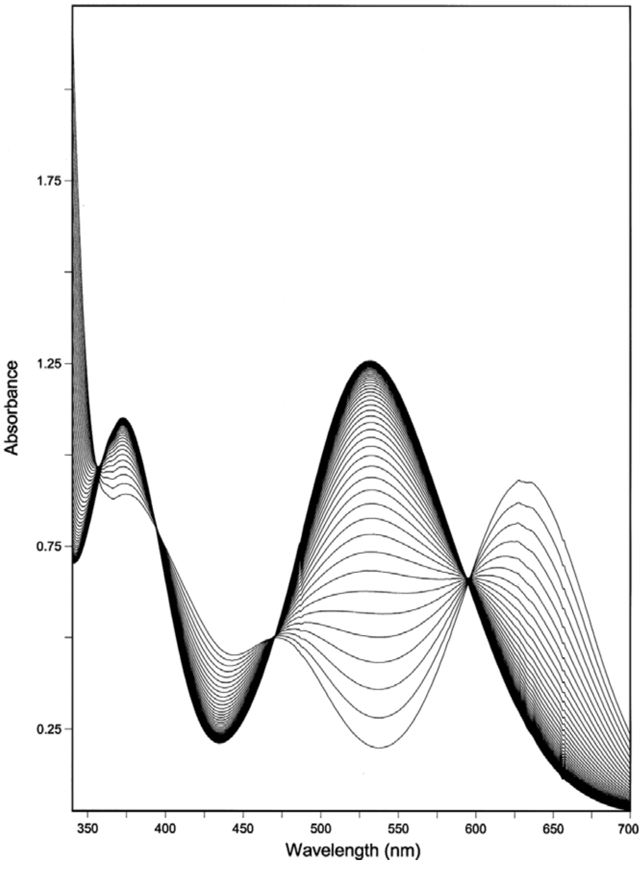


Fig. 7. Visible spectral changes for the hydrolysis of *trans*-$[Co(NH_3)_4Cl_2]^+$ in H_2O/H^+, 25 °C. The absorbance increases with time at 530 nm.

The data in the 340–700 nm visible range actually fit a single exponential quite well, but this is fortuitous, as discussed elsewhere [30]. The data were refitted to a double exponential, appropriate to a consecutive reaction scheme, with k_2 fixed at its known value $2.31 \times 10^{-3}\,s^{-1}$. The results for k_1 so obtained are presented in Table 5, and the value is in agreement with that determined in a more straightforward fashion from the UV data.

Quite remarkably, the hydrolysis rate for the *trans* isomer (k_1, $2.2 \times 10^{-3}\,s^{-1}$) is almost identical to that determined for the *cis* isomer ($2.4 \times 10^{-3}\,s^{-1}$), and also is essentially that for the subsequent isomerisation reaction ($2.3 \times 10^{-3}\,s^{-1}$).

The steric course of hydrolysis was determined as described above for the *cis* isomer – globally fitting the visible spectral data (340–700 nm) to a consecutive reaction scheme with the derived values for k_1 and k_2. The results are shown in Fig. 8. The average 530 nm result is $\varepsilon_B = 32.7\,M^{-1}\,cm^{-1}$ (22 determinations), which corresponds to 65% *trans* and 35% *cis* product. The error here is likely ±5%. Linck had estimated 45 ± 10% *trans* product by an indirect method [10,13].

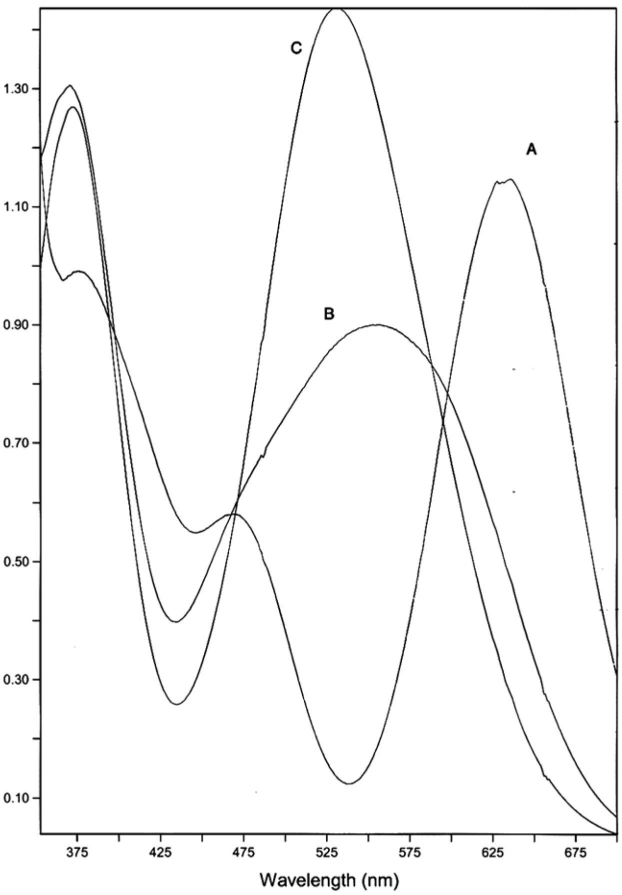


Fig. 8. Computed intermediate (B) and final (C) *cis*-/*trans*-$[Co(NH_3)_4(OH_2)Cl]^{2+}$ visible spectra, for the hydrolysis of *trans*-$[Co(NH_3)_4Cl_2]^+$ (A) in H_2O/H^+ at 25 °C. The vertical scale is absorbance, for an arbitrary [Co].

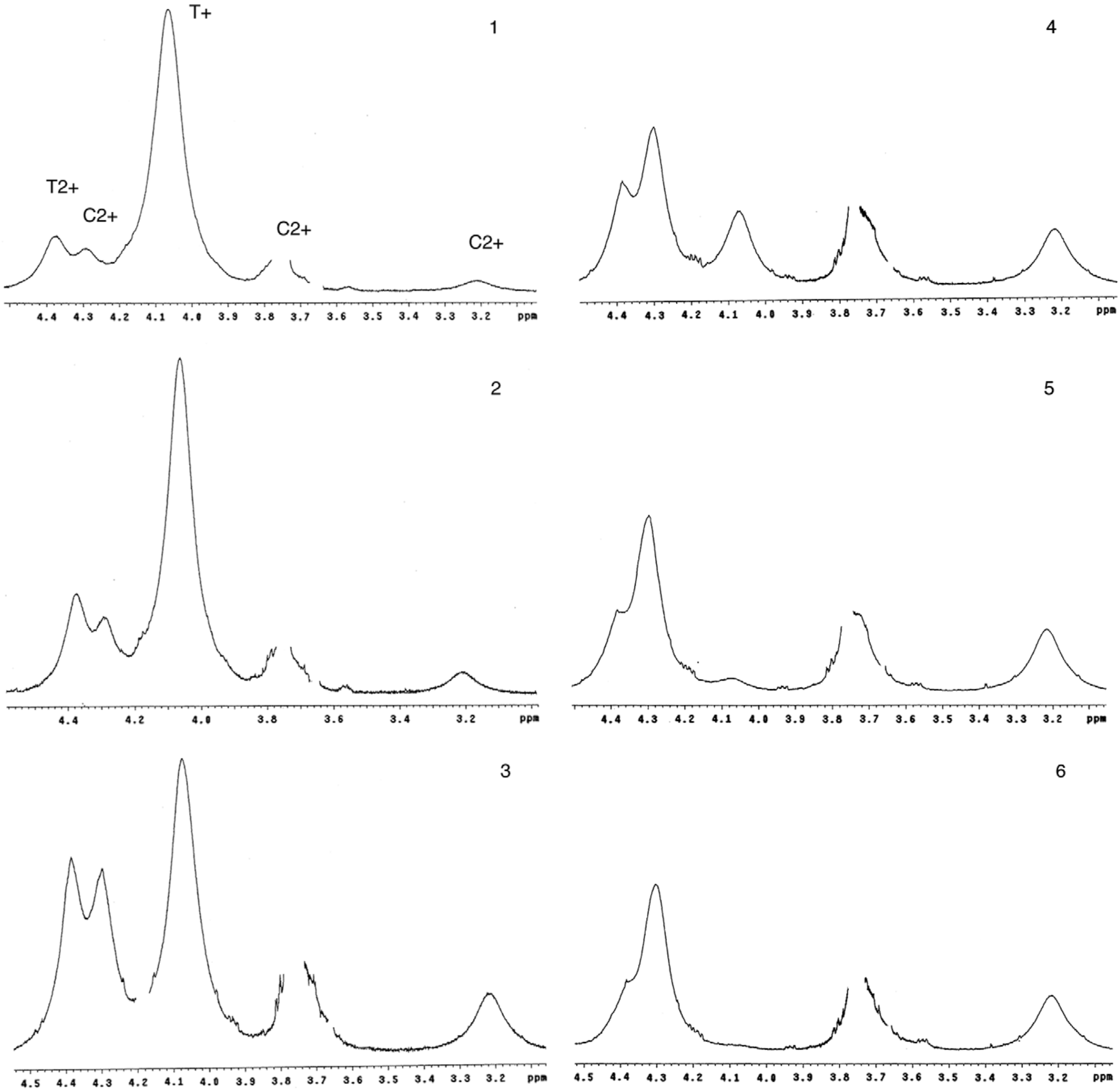


Fig. 9. ^{1}H NMR spectra (NH region) for the hydrolysis of *trans*-(T+) $[Co(NH_3)_4Cl_2]^+$ in D_2O/D^+ at ca. 21 °C; times increase from 1 to 6. C2+ and T2+ are *cis*- and *trans*-$[Co(NH_3)_4(OH_2)Cl]^{2+}$, respectively.

The ^{1}H NMR spectra for *trans*-$[Co(NH_3)_4Cl_2]^+$ reacting in D_2O/DCl are shown in Fig. 9. Compared to the corresponding changes for the *cis* isomer (Fig. 6), there is a little more *trans* product formed initially, estimated as 60% which is in good agreement with that determined spectrophotometrically.

4. Summary and conclusions

The *cis*- and *trans*-dichloro complexes hydrolyse at coincidentally the same rate. For the bis(ethylenediamine) analogues [7], the *cis* isomer is about sixfold more reactive than the *trans*, and both rates are between 10- and 50-fold smaller than the corresponding tetraammine rates; for the latter the *cis* isomer is about 10-fold more reactive than the *trans* isomer. The previous notion [8] that *cis*-$[Co(NH_3)_4Cl_2]^+$ hydrolyses extraordinarily rapidly is unfounded. Both isomers yield *cis*- and *trans*-$[Co(NH_3)_4(OH_2)Cl]^{2+}$ products directly, in different proportions, with the *trans* isomer showing more rearrangement (35% *cis* product; 65% rearrangement) than the *cis* form (55% *cis* product, 45% rearrangement). This also parallels the bis(ethylenediamine) chemistry, but there the extents of rearrangement are less (the *trans* reactant gives 74% *trans* product, the *cis* reactant gives 76% *cis* product; these numbers correspond to 26% and 24% rearrangement, respectively) [7]. The aquachloro equilibrium isomer distributions in the two systems are also similar (en, 79% *cis*; NH_3, 88% *cis*).

The new stereochemical data for the tetraammine system again show that *cis* isomers are not universally retentive. It was once believed [4] the norm for the bis(ethylenediamine) complexes, but shown otherwise [6,29]. It thus seems unlikely that a study of the kinetics and stereochemistry of other $[Co(NH_3)_4AX]^{n+}$ complexes will uncover anything beyond what is described herein, notwithstanding the fact that the synthetic chemistry is not yet developed.

Acknowledgement

The author is grateful to Professor Hans Riesen for an accurate translation of sections of Werner's original Berichte paper.

Appendix A. Supplementary data

Figures 1S–6S, visible/UV spectral data. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2005.12.015.

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