Base-catalysed Aquation of αβ-*syn*- and αβ-*anti*-Chloro- and Bromo-[1,9-bis(2′-pyridyl)-2,5,8-triazanonane]- and -[1,11-bis(2′-pyridyl)-2,6,10-triazaundecane]-cobalt(III) Cations. An Unusually Base-sensitive Halogenopentamine Cobalt(III) System

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Complexes of the type $[Co(picdien)X][ClO_4]_2$ and $[Co(picditn)X][ClO_4]_2$ [picdien = 1,9-bis-(2′-pyridyl)-2,5,8-triazanonane, picditn = 1,11-bis(2′-pyridyl)-2,6,10-triazaundecane; X = Cl, Br, NO_2, NCS, N_3, $MeCO_2$, or H_2O] have been prepared. All complexes have the αβ configuration, those of picdien existing in either or both *syn* and *anti* forms, while only the *anti* forms of the picditn complexes have been isolated. Structures have been established by single-crystal *X*-ray diffraction and ^1H n.m.r. spectroscopy in dimethyl sulphoxide and D_2O. All complexes are unusually sensitive to base-catalysed hydrolysis over very wide ranges of pH. The pH-independent contribution to the solvolysis of the chloro- and bromo-picdien complexes is observed only at high temperatures and at high $[H^+]$ but there is a very important pH-independent contribution to the solvolysis of the corresponding picditn species, which are also somewhat more sensitive to base catalysis. Proton-exchange studies show that proton transfer is faster than substitution in even the most labile systems. The mechanism is discussed.

In 1956, Basolo *et al.*[1] showed that, while the rates of acid hydrolysis of pentamine complexes of the type *cis*-$[Co(en)_2(am)Cl]^{2+}$ (en = 1,2-diaminoethane; am = NH_3, primary amines, or heterocyclic nitrogen bases) did not depend greatly upon the nature of the ligand am, the rate constants for base hydrolysis of the pyridine (py) and substituted pyridine complexes were some 10^3 times greater than those for the other members of the series. Subsequent work[2] has shown that the rate constants for the base hydrolysis of *cis*-$[Co(en)_2(py)Cl]^{2+}$ may not be as high as originally thought but a reactivity difference of two orders of magnitude was still indicated. This same enhancement of reactivity is to be found in a whole range of complexes where a pyridine or a pyridyl substituent in a multidentate or macrocyclic ligand replaces a NH_3, $-NH_2$, or $-NH-$ substituent.[3,4] It was suggested,[5] without any supporting evidence, that the labilising power of the pyridine might arise from 'covalent hydration',[6] where hydroxide effectively adds to the 2- or 4-carbon of the pyridine ring, destroying the aromaticity of the donor nitrogen and converting it into a secondary amine of relatively high acidity. However, House *et al.*[7] showed that the rate constants for the base hydrolysis of *cis*-$[Co(en)_2([^2H_5]py)Cl]^{2+}$ and *cis*-$[Co(en)_2([^1H_5]py)Cl]^{2+}$, were very similar whereas the 'covalent hydration' mechanism would require a significant isotope effect.

In our attempts to identify the cause of the labilising effect of pyridine we have synthesised a number of ligands and their complexes with the intention of forcing the pyridyl group to take specific positions with respect to the leaving group in the substrate and specific orientations in the intermediate formed by the dissociation of the conjugate base. One key target in this work was to synthesise a complex in which the pyridine was *trans* to the leaving group. This we have failed to do in spite of much effort and House and Blunt[8] have reported a similar failure to prepare the pyridine analogue of *trans*-$[CoL(am)Cl]^{2+}$ (L = 1,10-diamino-4,7-diazadecane) where the quadridentate ligand favours the *trans* isomer and other amines form the required complex without difficulty. Two of the ligands studied were 1,9-bis(2′-pyridyl)-2,5,8-triazanonane (picdien) and 1,11-bis(2′-pyridyl)-2,6,10-triazaundecane (picditn) which are linear quinquedentate nitrogen donor ligands with terminal pyridyl groups. The complexes obtained all adopt the αβ geometry, Figure 1, and the $[Co(picdien)X]^{2+}$ complexes exist in the *syn* and *anti* forms, the terms being used because the proton H^{17} on

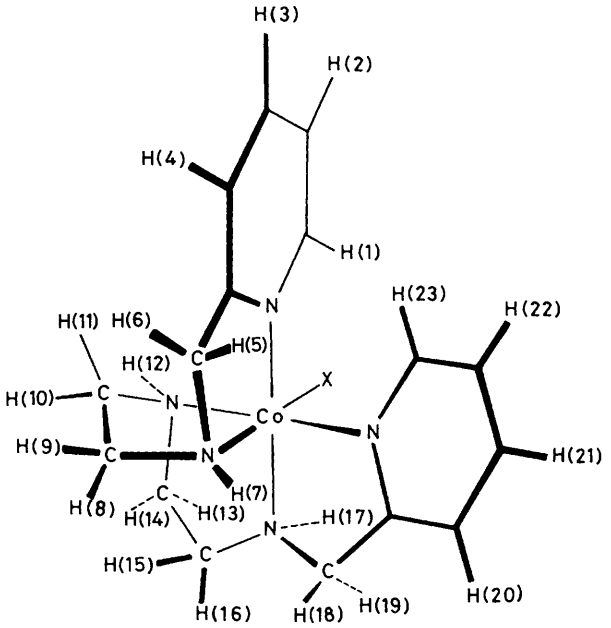


Figure 1. The structure of *syn*-αβ-$[Co(picdien)X]^{2+}$ showing the numbering system used to identify the individual protons. The *anti*-αβ form has the configuration of the nitrogen bearing H^{17} inverted so that this proton faces in the opposite direction to that in the *syn* isomer. The picditn complexes have an extra CH_2 group between the carbons bearing H^{10},H^{11}, and H^{12},H^{13} and another between those bearing H^{13},H^{14} and H^{15},H^{16}. All possess the *anti*-αβ configuration

the secondary amine, which is the source of the isomerism, points in the same direction as (*syn*) or in the opposite direction from (*anti*) the acido group. Only the *anti* isomer of the αβ-[Co(picditn)X]$^{2+}$ complexes has so far been characterised. The geometries of many of these complexes in the solid state have been established by single-crystal *X*-ray diffraction,[9–13] and this paper reports the preparations of the complexes, their characterisation by ^{1}H n.m.r. spectroscopy, and a detailed study of the acid- and base-dependent solvolyses of the *syn* and *anti* chloro and bromo complexes in aqueous solution.

Experimental

Preparations.—1,9-*Bis*(2′-*pyridyl*)-2,5,8-*triazanonane* (*picdien*). A mixture of 1,5-diamino-3-azapentane (12.4 g, 0.12 mol), ethanoic acid (50 cm^3), and zinc powder (50 g) in methanol (200 cm^3) was stirred strongly under reflux at 70—80 °C in a three-necked flask and a solution of pyridine-2-carbaldehyde (26.8 g, 0.25 mol) in methanol (150 cm^3) was added slowly over a period of 90 min. Further portions of powdered zinc (totalling 100 g) and ethanoic acid (totalling 100 cm^3) were added from time to time during the addition and the reaction mixture was kept for a further 4 h at 70—80 °C. After standing overnight at room temperature the pale yellow liquid was filtered from the solid Zn and $Zn(O_2CMe)_2$ and evaporated on a rotary evaporator. The syrup was diluted with propanone and filtered. The propanone was distilled off and the syrup neutralised by allowing it to stand overnight in contact with sodium hydroxide pellets. The crude ligand was washed with diethyl ether and, since distillation even under reduced pressure led to extensive decomposition. it was used as it was for the preparation of the complexes, through which the purification and characterisation was achieved.

1,11-Bis(2′-pyridyl)-2,6,10-triazaundecane (picditn) was prepared in a similar way using 1,7-diamino-4-azaheptane (15.9 g, 0.12 mol) and was stored and used as the undistilled syrup.

syn-αβ-[1,9-*Bis*(2′-*pyridyl*)-2,5,8-*triazanonane*]*chlorocobalt*(III) *perchlorate*. A solution of $CoCl_2 \cdot 6H_2O$ (9.52 g, 40 mmol) in water (100 cm^3) was added to a solution of picdien (13.0 g, 46 mmol) in water (250 cm^3) and the mixture was oxidised by bubbling air through it for 6 h. The dark brown solution was acidified with concentrated hydrochloric acid (6 cm^3) and perchloric acid (60%; 10 cm^3) while thoroughly stirred and evaporated to a volume of 50 cm^3 on a steam-bath. **CAUTION**: Although we have carried out these preparations many times without any problems, it should be remembered that perchloric acid solutions of metal–amine complexes and their perchlorate salts have been known to detonate violently and great care should be taken when they are handled. On leaving overnight at room temperature, red crystals separated and were filtered off and recrystallised from dilute hydrochloric acid (6 mol dm^{-3}). The crystals were washed with ethanol and diethyl ether, dissolved in the minimum amount of dimethyl sulphoxide, and the solution cooled and treated with an equal volume of dilute perchloric acid (0.1 mol dm^{-3}). On leaving overnight in a refrigerator, crystals of the pure *syn* complex separated and were filtered off, washed with ethanol and ether, and air dried.

syn-αβ-[1,9-*Bis*(2′-*pyridyl*)-2,5,8-*triazanonane*]*bromocobalt*(III) *perchlorate* was prepared in an analogous manner using $CoBr_2 \cdot 6H_2O$ (10.0 g, 30 mmol) and picdien (17.0 g, 60 mmol). The air oxidation was continued for 7 h and the oxidised mixture was treated with hydrobromic acid (60%, 4 cm^3) and perchloric acid (60%, 10 cm^3). The solution was evaporated on a steam-bath while a current of air was passed over it until the volume was reduced to 50 cm^3. The crystals that separated were filtered off and recrystallised from dilute hydrobromic acid (6 mol dm^{-3}) and, after washing with ethanol and ether, recrystallised from dimethyl sulphoxide in the way already described.

anti-αβ-[1,9-*Bis*(2′-*pyridyl*)-2,5,8-*triazanonane*]*isothiocyanatocobalt*(III) *perchlorate*. Equimolar amounts of *syn*-αβ-[Co(picdien)Cl][ClO_4]$_2$ and sodium thiocyanate were separately dissolved in the minimum amount of water and the two solutions mixed and heated on a steam-bath for 15 min. On cooling in ice, vermilion crystals separated and were filtered off and washed several times with ethanol, then dry ether, and air dried. They were dissolved in the minimum amount of dimethyl sulphoxide and the solution placed in ice. A volume of dilute aqueous perchloric acid (0.1 mol dm^{-3}) twice that of the dimethyl sulphoxide was added slowly and the solution was left overnight in a refrigerator. The crystals were filtered off, washed, and dried in the usual way.

The same isomer is also obtained when the *anti*-αβ-aquo perchlorate is treated with LiSCN in dimethyl sulphoxide.

anti-αβ-*Azido*[1,9-*bis*(2′-*pyridyl*)-2,5,8-*triazanonane*]*cobalt*(III) *perchlorate* was prepared by reacting *syn*-αβ-[Co(picdien)Cl][ClO_4]$_2$ (0.59 g) and NaN_3 (0.080 g) in hot aqueous solution and recrystallised by adding dilute perchloric acid to a filtered solution in dimethyl sulphoxide.

syn-αβ-[1,9-*Bis*(2′-*pyridyl*)-2,5,8-*triazanonane*]*nitrocobalt*(III) *perchlorate* was prepared in a similar way from equimolar quantities of the chloro perchlorate and $NaNO_2$.

anti-αβ-*Aqua*[1,9-*bis*(2′-*pyridyl*)-2,5,8-*triazanonane*]*cobalt*(III) *perchlorate*. A solution of *syn*-αβ-[Co(picdien)Cl][ClO_4]$_2$ in the minimum amount of water was treated with the stoicheiometric amount of freshly prepared silver oxide. The mixture was stirred and heated to 80 °C for 5 min and then filtered. More silver oxide was added and the process repeated but the second filtration was carried out at room temperature. The filtrate was acidified to pH 2 with concentrated perchloric acid and kept in a thermostat at 25 °C for 2 d, during which time yellow crystals separated. These were filtered off, washed with ethanol and ether, and air dried. Because of the reaction with the solvent it was not possible to measure the ^{1}H n.m.r. spectrum in $(CD_3)_2SO$ but a recent single-crystal *X*-ray diffraction study[13] shows this to be the *anti*-αβ isomer in the crystalline solid.

anti-αβ-[1,9-*Bis*(2′-*pyridyl*)-2,5,8-*triazanonane*]*chlorocobalt*(III) *perchlorate*. The complex anti-αβ-[Co(picdien)(H_2O)][ClO_4]$_3$ (2.2 g) was dissolved in dimethyl sulphoxide (5 cm^3) and treated with a warm solution of anhydrous LiCl (1.5 g) in dimethyl sulphoxide (15 cm^3) and then heated for 15—20 min on a steam-bath. The solution was filtered, cooled in ice, and treated with perchloric acid (0.5 mol dm^{-3}, 34 cm^3). Concentrated perchloric acid (20 drops) was then added to the gently stirred solution which was set aside in a refrigerator for 24 h before the crystals were filtered off, washed with ethanol and ether, and air dried.

anti-αβ[1,9-*Bis*(2′-*pyridyl*)-2,5,8-*triazanonane*]*bromocobalt*(III) *perchlorate* was prepared in a similar way by reacting αβ-*anti*-[Co(picdien)(H_2O)][ClO_4]$_3$ (1 g) in dimethyl sulphoxide (4 cm^3) with a solution of anhydrous LiBr (1.5 g) in dimethyl sulphoxide (18 cm^3) for 10—15 min on a steam-bath. Perchloric acid (0.5 mol dm^{-3}, 65 cm^3) was added to the cooled solution and, after 24 h in a refrigerator, $NaClO_4$ (4.5 g) followed by concentrated perchloric acid (10 drops) were added and the crystals that separated after standing for a further 24 h in the refrigerator were filtered off, washed with ethanol and ether, and air dried.

anti-αβ-[1,11-*Bis*(2′-*pyridyl*)-2,6,10-*triazaundecane*]*chlorocobalt*(III) *perchlorate*. A solution of picditn (13 g, 40 mmol) in water (250 cm^3) was added to one of $CoCl_2 \cdot 6H_2O$ (9.52 g, 40 mmol) in water (250 cm^3) and a stream of air bubbled through the mixture for 7 h. The solution was transferred to an evaporating basin and heated on a steam-bath. Concentrated hydrochloric acid (6 cm^3) and perchloric acid (60%, 10 cm^3) were added and the solution allowed to cool slowly and left to

Table 1. Analytical data for the complexes with calculated values in parentheses

Complex	Colour	Analysis/% C	H	N	Cl
syn-αβ-[Co(picdien)Cl][ClO_4]$_2$	Orange-red	33.0 (33.2)	4.10 (4.00)	11.9 (12.1)	18.3 (18.4)
anti-αβ-[Co(picdien)Cl][ClO_4]$_2$·0.5H_2O	Orange-red	32.6 (32.7)	4.10 (4.10)	11.8 (11.9)	18.2 (18.1)
syn-αβ-[Co(picdien)Br][ClO_4]$_2$	Purple-violet	30.8 (30.8)	3.70 (3.70)	11.2 (11.2)	
anti-αβ-[Co(picdien)Br][ClO_4]$_2$	Purple-violet	30.9 (30.8)	3.85 (3.70)	10.9 (11.2)	
anti-αβ-[Co(picdien)(N_3)][ClO_4]$_2$	Carmine	32.8 (32.8)	4.00 (3.95)	19.3 (19.1)	12.0 (12.1)
anti-αβ-[Co(picdien)(NCS)][ClO_4]$_2$·2H_2O	Vermilion	32.0 (32.0)	3.75 (4.25)	12.9 (13.2)	11.0 (11.1)
syn-αβ-[Co(picdien)(NO_2)][ClO_4]$_2$	Yellow	32.6 (32.6)	4.00 (3.95)	14.3 (14.3)	12.1 (12.0)
anti-αβ-[Co(picdien)(H_2O)][ClO_4]$_3$	Orange	29.0 (29.1)	3.85 (3.80)	10.7 (10.6)	16.1 (16.1)
anti-αβ-[Co(picditn)Cl][ClO_4]$_2$	Dark red	35.5 (35.6)	4.55 (4.50)	11.7 (11.5)	17.4 (17.5)
anti-αβ-[Co(picditn)Br][ClO_4]$_2$	Violet	33.3 (33.2)	4.50 (4.20)	10.7 (10.8)	
anti-αβ-[Co(picditn)(N_3)][ClO_4]$_2$	Dark vermilion	35.5 (35.3)	4.60 (4.45)	18.3 (18.3)	11.6 (11.6)
anti-αβ-[Co(picditn)(NO_2)][ClO_4]$_2$	Dark brown	34.3 (35.0)	4.55 (4.40)	13.8 (13.6)	11.8 (11.5)
anti-αβ-[Co(picditn)(NO_3)][ClO_4]$_2$	Rose	34.5 (34.1)	4.05 (4.30)	13.3 (13.3)	10.9 (11.2)
anti-αβ-[Co(picditn)(NCS)][ClO_4]$_2$	Vermilion	35.7 (36.3)	4.55 (4.30)	13.3 (13.4)	11.4 (11.3)
anti-αβ-[Co(picditn)($MeCO_2$)][ClO_4]$_2$	Orange	37.7 (38.1)	5.05 (4.80)	11.2 (11.1)	11.4 (11.3)

stand overnight. The crystals were filtered off, washed with ethanol and ether, and recrystallised from dilute perchloric acid (3 mol dm^{-3}).

anti-αβ-[1,11-*Bis*(2′-*pyridyl*)-2,6,10-*triazaundecane*]*bromocobalt*(III) *perchlorate* was prepared in a similar way by the air oxidation (8 h) of a solution of $CoBr_2$·6H_2O (10 g, 30 mmol) in water (11 cm^3) containing a solution of picditn (13.5 g, 41 mmol) in water (250 cm^3). Concentrated HBr (4 cm^3) and perchloric acid (60%, 10 cm^3) were added and the solution evaporated to one third of its volume on a steam-bath. Violet crystals were deposited when the solution was allowed to cool slowly to room temperature. These were filtered off, washed with ethanol and ether, and air dried.

anti-αβ-[1,11-*Bis*(2′-*pyridyl*)-2,6,10-*triazaundecane*]*nitrocobalt*(III) *perchlorate*. The complex *anti*-αβ-[Co(picditn)Cl][ClO_4]$_2$ (0.42 g) was dissolved in the minimum amount of water and an equivalent amount of sodium nitrite (0.048 g) was added. The solution was heated on a water-bath at 50—60 °C for 30 min and then set aside to crystallise overnight at room temperature. The brown crystals were filtered off, washed with ethanol and ether, and air dried.

anti-αβ-[1,11-*Bis*(2′-*pyridyl*)-2,6,10-*triazaundecane*]*isothiocyanatocobalt*(III) *perchlorate* was prepared in a similar way using equimolar amounts of sodium thiocyanate.

anti-αβ-*Azido*[1,11-*bis*(2′-*pyridyl*)-2,6,10-*triazaundecane*]-*cobalt*(III) *perchlorate* was prepared in a similar way using sodium azide.

anti-αβ-*Acetato*[1,11-*bis*(2′-*pyridyl*)-2,6,10-*triazaundecane*]-*cobalt*(III) *perchlorate* was prepared by the air oxidation (8 h) of a solution of cobalt(II) acetate (9.0 g) in water (100 cm^3) that had been mixed with one of picditn (13 g) in water (250 cm^3). The solution was then treated with acetic acid (3.5 cm^3) and perchloric acid (60%, 10 cm^3) and evaporated on a steam-bath until the volume was reduced to 50 cm^3. The solution was allowed to cool slowly to room temperature. After 1 d crystals separated and were filtered off, washed with ethanol and ether, and air dried.

anti-αβ-[1,11-*Bis*(2′-*pyridyl*)-2,6,10-*triazaundecane*]*nitratocobalt*(III) *perchlorate* was prepared by the air oxidation (6 h) of an aqueous solution of $Co(NO_3)_2$·6H_2O (100 cm^3, 11.6 g) and picditn (250 cm^3, 13 g). The oxidised solution was treated with nitric acid (3 cm^3) and perchloric acid (60%, 10 cm^3) and left to evaporate at room temperature until its volume was halved. Ethanol (100 cm^3) was added and the solution set aside to crystallise. A rose microcrystalline solid slowly separated and was filtered off, washed with ethanol and ether, and air dried.

Analytical data for all the complexes reported are collected in Table 1.

All other reagents were AR grade or else the best quality available.

Kinetics.—The slower reactions were followed in the thermostatted cell compartment of a Unicam SP 1750 spectrophotometer. Solutions of all the reagents, except the complex, were brought to the reaction temperature and the reaction was initiated by adding a known amount of the finely powdered complex. The spectra were scanned from time to time to establish suitable wavelengths for the kinetic analysis and subsequent reactions were followed at a single wavelength.

Faster reactions were followed with a HiTec stopped-flow spectrometer in which the heat exchanger, mixing chamber, and cuvette were all immersed in a thermostat. The light from the monochromator was led in through optical fibres and the photon multiplier, outside the bath, was optically connected to the cuvette by a silvered silica rod. Solutions of the complex, acidified where necessary to pH ≈ 3 to prevent premature solvolysis, and the appropriate buffer were made up to the same ionic strength using $NaClO_4$ and mixed to start the reaction. The pH of the reaction solution was determined by mixing the reagents at the same temperature as that used to study the reaction and measuring the pH with an accurate calibrated pH meter. For the slower reactions it could be shown that the pH did not change significantly in the course of the reaction and it was assumed that the same was true for the faster ones. Rate constants were determined by linear least-squares analysis of the plots of $\ln|A - A_\infty|$ *versus* t or, in the stopped-flow experiments, by a curve-fitting program that optimised the values of A_∞ and $k_{obs.}$ in the relationship $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs.}t)$, where A_0, A_t, and A_∞ are the absorbances of the reaction solution on mixing, at time t, and at the end of the reaction respectively. Hydroxide concentrations were calculated from the pH using values of the ionic product of water at the relevant ionic strength and temperature taken from the literature.[14]

N.m.r. spectra were measured on a Varian 200 MHz FT spectrometer.

Results

Air oxidation of a solution of CoX_2·6H_2O (X = Cl or Br) and picdien followed by reaction with HX leads to the formation of

complexes of the type $[Co(picdien)X]^{2+}$. The ^1H n.m.r. spectra of the perchlorate salts in $(CD_3)_2SO$ indicated the presence of at least two isomeric forms which could not be separated conveniently by fractional crystallisation of the aqueous solution. The first of the two isomers, which was the major component of the mixture, could be obtained pure by selective precipitation from a solution of the mixture in Me_2SO by adding dilute perchloric acid. Single-crystal *X*-ray diffraction analysis of the chloro and bromo complexes prepared in this way show that they are the *syn*-αβ isomers.[10,11] Reactions of the chloro complex with NaY (Y = NO_2, NCS, or N_3) converted these into the corresponding $[Co(picdien)Y]^{2+}$ complexes. A single-crystal *X*-ray diffraction study has shown the nitro complex to have the same *syn* form[11] but the azido and isothiocyanato complexes consist mainly of the *anti* isomer and it has not yet been possible to isolate samples of the *syn* form. The *anti*-αβ-chloro and bromo isomers were obtained by the action of LiX on a solution of *anti*-αβ-$[Co(picdien)(H_2O)][ClO_4]_3$ in Me_2SO and the configuration confirmed by single-crystal *X*-ray diffraction studies.[12] The *anti*-αβ-isothiocyanato complex can also be prepared in this way. Only one isomeric form of the corresponding $[Co(picditn)X]^{2+}$ complexes (X = Cl, Br, NO_2, NO_3, NCS, N_3, or $MeCO_2$) has been isolated until now and a single-crystal *X*-ray diffraction study of the tetrachlorocobaltate(II) salt of the chloro complex shows it to be the *anti*-αβ isomer.[9]

Unlike the brown-red and purple-red α and β isomers of the corresponding $[Co(tetren)Cl]^{2+}$ complex (tetren = 1,11-diamino-3,6,9-triazaundecane), which have the same *syn*-αβ and *anti*-αβ configurations,[15] the isomers of the chloro and bromo picdien complexes have identical colours, very similar visible and u.v. absorption spectra, and differ only slightly in the appearance of their crystalline forms. The only way in which they can be characterised unambiguously and their purity assessed is by n.m.r. spectroscopy.

The 200-MHz ^1H n.m.r. spectra of the $[Co(picdien)X][ClO_4]_2$ complexes in $(CD_3)_2SO$ have been measured and mainly assigned. The numbering scheme for the protons discussed below is set out in Figure 1. The spectra consist of three parts, the upfield section, δ < 3.5, containing multiplets assigned to the methylene protons between the NH groups, the middle-field region, δ 3.5—5, assigned to the methylene protons on the carbons adjacent to the pyridine rings, and most deshielded, δ 5—9, the signals assigned to the pyridine protons which overlap with the characteristically broad NH proton signals.

The presence of two non-equivalent sets of peaks assigned to pyridine protons in both isomers is consistent with the αβ geometry. There is one doublet whose chemical shift is very dependent upon the nature of X and it has been assumed that this can be assigned to the proton that is closest to X (H^1). For the chloro, bromo, isothiocyanato, and azido complexes this is well separated from the other signals and allows a sensitive test for the presence of impurities (generally the other isomer). A series of decoupling experiments allow the other protons on that same pyridine to be identified (H^{2-4}). Protons H^2 and H^3 appear as triplets with resolvable further splitting due to non-adjacent proton coupling, H^4 as a doublet. The lowest-field doublet of the bis(pyridyl) set, which belongs to the second ring, is assigned to the proton that lies above the nitrogen on the first pyridyl ring and is strongly shielded by it (H^{23}). A similar effect has been observed in the ^1H n.m.r. spectrum of the *cis*-$[Co(picen)Cl_2]^+$ [picen = 1,6-bis(2′-pyridyl)-3,6-diazahexane] cation and has been assigned in a similar way.[16] The other protons in the second ring (H^{20-22}) have been assigned by successive decoupling experiments. The three NH protons can be observed as three characteristically broad peaks in this area, sometimes underneath some of the pyridyl multiplets, where they can be shown to be present by the integration of the area under the peaks. These areas are diminished by exchange with ^2H in D_2O solution and have been assigned in the way described below.

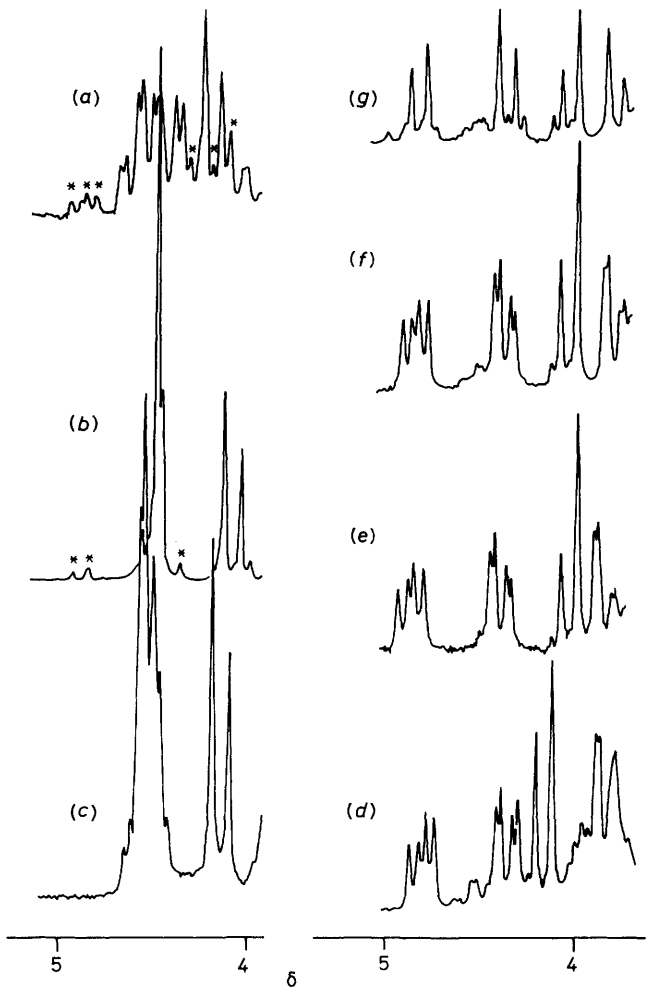


Figure 2. Proton n.m.r. spectra of the methylene protons adjacent to the pyridyl groups (protons 5, 6, 18, and 19) in: (*a*) *anti*-αβ-$[Co(picdien)(N_3)][ClO_4]_2$ (the peaks due to *syn* impurity are marked with asterisks); (*b*) *anti*-αβ-$[Co(picdien)Cl][ClO_4]_2$ (amine protons 7 and 17 replaced by D); (*c*) *anti*-αβ-$[Co(picdien)Br][ClO_4]_2$; (*d*) *syn*-αβ-$[Co(picdien)(NO_2)][ClO_4]_2$; (*e*) *syn*-αβ-$[Co(picdien)Cl][ClO_4]_2$; (*f*) *syn*-αβ-$[Co(picdien)Br][ClO_4]_2$; (*g*) the same with NH replaced by ND. Solutions in $(CD_3)_2SO$, $\delta(SiMe_4) = 0$

The CH_2 protons adjacent to the pyridyl rings give the signals that are diagnostic in distinguishing between the *syn* and *anti* isomers. The *syn* isomers all have two well resolved doublets of doublets whose chemical shifts and coupling constants are not sensitive to the nature of X. The second pair of methylene protons adjacent to pyridine also exhibit *gem* coupling (^2J = 17 Hz) but only the upfield one is coupled to the adjacent NH protons. It is this upfield methylene proton that is exceptionally sensitive to the isomeric forms of the substrate. In the spectra of the *anti* isomers the doublet of doublets assigned to this proton appears downfield of the doublet that has no H–C–N–H coupling. In the spectra of the *anti*-αβ-chloro and bromo complexes the chemical shifts of the other pair of methylene protons are virtually identical and there is only very small *gem* coupling. In the spectra of the *anti*-αβ-isothiocyanato and azido complexes the corresponding signals appear as well resolved doublets of doublets. The ^1H n.m.r. spectra in the region δ 3—5 are shown in Figure 2.

No attempt has been made to assign the multiplets arising from the methylene protons between the NH groups.

The assignment of the amine protons, which is of prime importance in the proton-exchange studies, and of the methylene protons adjacent to the pyridines was made by analysing the effects of proton decoupling and ion association on the ^{1}H n.m.r. spectra in $(CD_3)_2SO$. The reasoning will be described in detail for the *syn*-bromo and *anti*-bromo complexes, whose spectra closely resemble those of the corresponding chloro species. The assignments for the other complexes are based on similar arguments.

For the *syn*-bromo complex, irradiation of the amine proton signal at δ 8.40 changes the quartets based on δ 4.86 and 4.39, and assigned to the methylene protons adjacent to a pyridyl group, into a pair of doublets. The signal must be assigned either to H^{17} or H^7. A similar effect is achieved when the proton responsible for this coupling is replaced by deuterium. Addition of lithium bromide to the solution causes the NH proton signal at δ 6.84 to be shifted downfield. This is an indication of ion association and shows that the proton concerned must be remote from the co-ordinated bromide.[17] This signal is therefore assigned to H^7 and so H^{17} must appear at δ 8.40. Irradiation of the signal at δ 6.84 has no effect on the multiplet at about δ 4.05 but removes the coupling with the signal at δ 3.81. Examination of a Dreiding model shows that the N–H^7 and C–H^6 bonds have a dihedral angle of 90° while that for N–H^7 and C–H^5 is *ca.* 30° and so the signal at δ 4.05 is assigned to H^6 and that at δ 3.81 to H^5. The third amine proton signal at δ 7.68 is assigned to H^{12}. Decoupling leads to no observed change in the rest of the spectrum (possibly a little sharpening around δ 2).

The addition of lithium bromide also has a strong effect on the chemical shift of the quartet at δ 4.86, moving it eventually to δ 5.32 when $[Br^-] \approx 0.2$ mol dm^{-3}. This signal is therefore assigned to H^{18} and that at δ 4.39 is therefore due to H^{19}.

For the *anti*-bromo complex the three amine proton signals appear at δ 7.00, 7.55, and 7.85 (the last being concealed beneath a pyridine proton multiplet). Irradiation of the signal at δ 7.85 does not affect the spectrum in the δ 3—5 region. Addition of lithium bromide to a solution of *anti*-αβ-$[Co(picdien)Br][ClO_4]_2$ in $(CD_3)_2SO$ causes the amine proton signals at δ 7.00 and 7.55 to shift downfield. The third proton signal is hardly shifted. Using the arguments cited for the *syn* isomer, the signals are assigned as follows: δ 7.00, H^7; 7.55, H^{17}; 7.85, H^{12}. The doublet at δ 4.13, with *gem* coupling of 18 Hz, is coupled to a doublet of doublets centred on δ 4.44. The signal at δ 4.13, which is not coupled to an amine proton, is still assigned to H^6, and so that at δ 4.44 is assigned to H^5. The unresolved sharp multiplet at δ 4.48 contains signals for H^{18} and H^{19}.

The relevant ^{1}H n.m.r. data are collected in Table 2. Recent two-dimensional 400 MHz n.m.r. studies confirm these assignments and detailed discussion of the n.m.r. spectra of these complexes and the structural implications will be published elsewhere.

In aqueous solution, the chloro and the bromo complexes are solvolytically labile, the spectra changing in a simple first-order fashion to that of the aqua complex. The first-order rate constants depend on the acid concentration and plots of $k_{obs.}$ *versus* $[H^+]^{-1}$ are linear. The slopes and intercepts are collected in Table 3. For the picdien complexes there is no detectable intercept at $[H^+]^{-1} = 0$ when the data collected at $I = 0.1$ mol

Table 2. Proton n.m.r. resonances (δ, with respect to $SiMe_4$, δ = 0) for some *syn*- and *anti*-αβ-$[Co(picdien)X][ClO_4]_2$ complexes in $[^2H_6]$dimethyl sulphoxide

Proton	*syn*-Cl	*syn*-Br	*syn*-NO_2	*syn*-NCS[a]	*syn*-N_3[b]	*syn*-$MeCO_2$
1	9.35 (d)	9.58 (d)	8.39 (d)	8.81 (d)	8.86 (d)	8.90 (d)
2	7.95 (t)	7.92 (t)	7.89 (t)		7.97 (t)	8.02 (t)
3	8.32 (t)	8.35 (t)	8.35 (t)		8.34 (t)	8.39 (t)
4	7.84 (d)	7.84 (d)	7.75 (d)		7.83 (d)	8.41 (d)
5	3.85 (d of d)	3.81 (d of d)	8.87 (d of d)	3.88 (d of d)	3.97 (d of d)	3.77 (d of d)
6	4.04 (d)	4.05 (d)	4.20 (d)	4.04 (d)	4.12 (d)	3.96 (d)
7	6.8 (br)	6.84 (br)	6.75 (br)	6.80 (br)	6.75 (br)	6.32 (br)
12	7.6 (br)	7.68 (br)	7.36 (br)		7.17 (br)	7.37 (br)
17	8.4 (br)	8.40 (br)	7.78 (br)	8.53 (br)	7.61 (br)	7.81 (br)
18	4.90 (d of d)	4.86 (d of d)	4.84 (d of d)	4.86 (d of d)	4.86 (d of d)	4.93 (d of d)
19	4.41 (d of d)	4.39 (d of d)	4.39 (d of d)	4.44 (d of d)	4.40 (d of d)	4.58 (d of d)
20	7.84 (d)	7.84 (d)	7.82 (d)	7.89 (d)	7.86 (d)	7.84 (d)
21	8.16 (t)	8.16 (t)	8.17 (t)	8.20 (t)	8.17 (d)	8.17 (t)
22	7.53 (t)	7.53 (t)	7.57 (t)	7.58 (t)	7.56 (t)	7.52 (t)
23	7.43 (d)	7.50 (d)	7.40 (d)	7.45 (d)	7.27 (d)	7.32 (d)
	anti-Cl	*anti*-Br		*anti*-NCS	*anti*-N_3	
1	9.36 (d)	9.67 (d)		8.78 (d)	8.76 (d)	
2	8.35 (t)	7.85 (t)		7.96 (t)	7.92 (t)	
3	8.10 (t)	8.35 (t)		8.43 (t)	8.34 (t)	
4	7.90 (d)	7.95 (d)		7.94 (d)	7.92 (d)	
5	4.50 (d of d)	4.44 (d of d)		4.54 (d of d)	4.52 (d of d)	
6	4.09 (d)	4.13 (d)		4.13 (d)	4.18 (d)	
7	6.97 (br)	7.00 (br)		7.14 (br)	6.87 (br)	
12	7.77 (br)	7.85 (br)		8.18 (br)	8.00 (br)	
17	7.77 (br)	7.55 (br)		7.75 (br)	7.34 (br)	
18	4.40 (s)	4.48 (s)		4.63 (d of d)	4.60 (d of d)	
19	4.40 (s)	4.48 (s)		4.32 (d of d)	4.32 (d of d)	
20	7.90 (d)	7.79 (d)		7.78 (d)	7.78 (d)	
21	7.44 (t)	8.10 (t)		8.15 (t)	8.11 (t)	
22	7.86 (t)	7.48 (t)		7.47 (t)	7.48 (t)	
23	7.30 (d)	7.66 (d)		7.26 (d)	7.29 (d)	

[a] Peaks detected in a sample containing 10% *syn* + 90% *anti*. [b] Peaks identified in a 1:4 *syn*:*anti* mixture.

Table 3. Slopes and intercepts for the plots of $k_{obs.}$ *versus* $[H^+]^{-1}$ for the solvolysis of αβ-*syn*- and αβ-*anti*-$[Co(L_5)X]^{2+}$ [a]

L_5	Form	X	Temperature/ °C	10^6 slope/mol dm^{-3} s^{-1}	10^5 Intercept/s^{-1}	10^{-7} k_{OH} [b]/dm^3 mol^{-1} s^{-1}
picdien	*syn*	Cl	25.0	0.34 ± 0.01	0.22 ± 0.33	2.0
			30.0	0.68 ± 0.03	1.4 ± 1.4	2.8
			35.0	1.27 ± 0.06	−0.8 ± 2.5	3.6
			40.0	2.27 ± 0.11	1.9 ± 4.1	4.6
			45.0	3.95 ± 0.07	1.3 ± 2.6	5.8
			50.0	6.44 ± 0.15	6.4 ± 5.7	6.9
	anti		25.0	0.123 ± 0.001	0.041 ± 0.019	0.74
			30.0	0.263 ± 0.004	0.11 ± 0.18	1.06
			35.0	0.58 ± 0.01	−0.21 ± 0.49	1.68
			40.0	1.01 ± 0.04	−1.3 ± 1.4	2.1
			45.0	2.39 ± 0.05	1.1 ± 2.1	3.5
			50.0	4.31 ± 0.04	−1.8 ± 1.5	4.6
			70.5	26.0 ± 0.4 [c]	1.35 ± 0.07 [c]	
	syn	Br	25.0	2.43 ± 0.14	0.8 ± 5.6	14.7
			30.0	4.61 ± 0.27	−10.1 ± 1.07	19.0
			35.0	9.4 ± 0.4	−10.7 ± 16.4	27
			40.0	16.0 ± 1.1	−28 ± 47	33
			45.0	29.2 ± 1.3	8 ± 51	43
			50.0	51.9 ± 0.7	27 ± 30	56
			70.5	204 ± 6	12.3 ± 1.3 [c]	
	anti		25.0	1.08 ± 0.02	−1.7 ± 0.9	6.5
			30.0	2.58 ± 0.13	11.2 ± 5.0	10.6
			35.0	4.96 ± 0.13	−4.4 ± 5.4	14.2
			40.0	9.4 ± 0.3	5.4 ± 13.5	19.1
			45.0	18.7 ± 0.6	−10 ± 25	28
			50.0	39.4 ± 0.6	−28 ± 23	40
picditn	*anti*	Cl	20.0	0.234 ± 0.019	9.2 ± 0.7	2.1
			25.0	0.401 ± 0.026	18.2 ± 1.0	2.4
			30.0	0.74 ± 0.03	38.1 ± 1.2	3.1
			35.0	1.50 ± 0.05	67 ± 2	4.3
			40.0	2.68 ± 0.06	130 ± 2	5.5
			45.0	4.81 ± 0.05	239 ± 2	7.1
			50.0	8.5 ± 0.1	438 ± 4	9.1
		Br	10.0	0.174 ± 0.062	42 ± 2	3.65
			15.0	0.388 ± 0.024	90 ± 0.1	5.3
			20.0	1.04 ± 0.09	175 ± 4	9.3
			25.0	1.94 ± 0.02	343 ± 1	11.7
			30.0	4.1 ± 0.04	650 ± 1	17.0
			35.0	7.7 ± 0.1	1 220 ± 5	22.0

[a] In water, I = 0.10 mol dm^{-3} ($NaClO_4$). Determined from the variation of $k_{obs.}$ over the range of $[H^+]$ from 0.001 00 to 0.0100 mol dm^{-3}. [b] Using values for K_w taken from ref. 14. [c] I = 1.0 mol dm^{-3}, determined from variation of $k_{obs.}$ with $[H^+]$ over the range 0.110 to 1.0 mol dm^{-3}.

Table 4. Hydrolysis of *anti*-αβ-$[Co(picdien)Cl]^{2+}$ in basic solution [a]

Temperature/ °C	pH	$10^7[OH^-]$/ mol dm^{-3}	$k_{obs.}/s^{-1}$	$10^{-7}k_{OH}$/ dm^3 mol^{-1} s^{-1}
5.0	6.400	0.0758 [b]	0.034	0.45
	8.489	9.31	5.5	0.60
	9.000	30.2	17.3	0.57
	9.740	166	53	0.32
25.0	5.353	0.0370 [c]	0.047	1.3
	6.406	0.418	0.47	1.1
	7.578	6.21	10.7	1.7
	8.499	51.7	55	1.1
	8.740	90.2	152.1	1.7
	8.860	119	203.3	1.7

[a] I = 0.10 mol dm^{-3} $NaClO_4$. [b] K_w at 5 °C and I = 0.10 mol dm^{-3} is 3.02×10^{-15} mol^2 dm^{-6}. [c] K_w at 25 °C and I = 0.10 mol dm^{-3} is 1.64×10^{-14} mol^2 dm^{-6}.

dm^{-3} are plotted. A series of studies of the kinetics of aquation of the *syn*-bromo and *anti*-chloro complexes at much higher acid concentrations (0.1—1.0 mol dm^{-3}) and with I = 1.0 mol dm^{-3} allowed the value of k_{aq} to be determined at 70.5 °C (Table 3).

On the other hand, the acid-independent pathway makes a major contribution to the reaction of the picdien complexes over the whole range of acid concentration examined. A series of stopped-flow studies of the reactions of the *anti*-αβ-$[Co(picdien)Cl]^{2+}$ cation with buffer solutions of increasing pH were carried out until the rate was too fast to measure. The rate constants are collected in Table 4. The kinetics of exchange of the amine protons with D_2O was followed by ^1H n.m.r. spectroscopy in acid solution by measuring the changing areas under the amine proton peaks as a function of time. The rate constants determined from the slope of a plot of ln I_t against time, where I_t is the integrated area under the assigned peak at time t, are collected in Table 5 and converted into k_1, the rate constant for deprotonation by dividing by $[OD^-]$, calculated from the known acid concentration and the appropriate values for the ionic product of D_2O at the reaction temperature and ionic strength. In the absence of data for D_2O systems, the activity coefficient quotient for the H_2O systems was used.

Discussion

The rate constants at 25 °C and activation parameters for the spontaneous and base-catalysed aquations of the chloro- and bromo-picdien- and picditn-cobalt(III) cations are collected in

Table 5. Proton-exchange rate constants for αβ-*syn*-[Co(picdien)X]$^{2+}$ in D_2O–$HClO_4$ [a]

X	δ	Proton	$[D^+]$/mol dm^{-3}	$10^{14}[OD^-]$ [b]/ mol dm^{-3}	$10^5 k_{obs.}$/s^{-1}	$10^{-8}k_1$/dm^3 mol^{-1} s^{-1}
Cl	6.74	7	0.019	8.2	66 ± 3	80
			0.029	5.4	51 ± 2	95
			0.043	3.6	40 ± 1	110
	7.60	12	0.029	5.4	0.45 ± 0.05	0.8
	8.34	17	0.019	8.2	5.9 ± 0.1	7.2
			0.029	5.4	4.6 ± 0.2	8.5
			0.043	3.6	3.9 ± 0.5	11
Br	6.84	7	0.019	8.2	67 ± 2	81
			0.029	5.4	46 ± 2	85
			0.043	3.6	32 ± 0.5	89
NO_2	6.74	7	0.019	8.2	28 ± 2	34
			0.043	3.6	7.2 ± 0.2	20

[a] At 22.5 °C; I = 0.43 mol dm^{-3} ($NaClO_4$). [b] Using the ionic product of D_2O at 22.5 °C and I = 0.043 mol dm^{-3} as 1.56 × 10^{-14} mol^2 dm^{-6}.[15]

Table 6. Rate constants at 25 °C ($10^5 k_{aq}$/s^{-1}, $10^{-7}k_{OH}$/dm^3 mol^{-1} s^{-1}), enthalpies of activation ($\Delta H^{\ddagger}$/kJ mol^{-1}), and entropies of activation ($\Delta S^{\ddagger}$/J K^{-1} mol^{-1}) for the reactions of $[Co(L_5)X]^{2+}$ in aqueous solution

L_5	Isomer	X	$10^5 k_{aq}$	$10^{-7}k_{OH}$	$\Delta H^{\ddagger}_{aq}$	$\Delta S^{\ddagger}_{aq}$	$\Delta H^{\ddagger}_{OH}$	$\Delta S^{\ddagger}_{OH}$	Ref.
picdien	αβ-*syn*	Cl	*a*	2.0			37 ± 1	+18 ± 4	This work
picdien	αβ-*anti*	Cl	0.006 [b]	0.74			57 ± 3	+76 ± 4	This work
picdien	αβ-*syn*	Br	0.05 [b]	14.7			40 ± 1	+46 ± 4	This work
picdien	αβ-*anti*	Br [a]		6.5			55 ± 2	+89 ± 8	This work
picditn	αβ-*anti*	Cl	18.2	2.4	99 ± 1	14 + 3	38 ± 2	+ 23 ± 6	This work
picditn	αβ-*anti*	Br	340	11.7	97 ± 2	33 ± 5	50 ± 3	+78 ± 10	This work
tetren	αβ-*syn*	Cl	0.04	0.0035	113	−29	100	+171	18
tetren	αβ-*anti*	Cl	0.01 [b]	0.0010 [b]	123	−28			18

[a] Too small to be detected (see text). [b] Extrapolated from data at 70 °C using an enthalpy of activation of 100 kJ mol^{-1}.

Table 6 where they are compared with data for the analogous tetren complexes[18] which have the same skeletal form but with a quinquedentate ligand that has NH_2 as the terminal substituent instead of pyridyl. These complexes also obey the rate equation $k_{obs.} = k_{aq} + k_H[H^+]^{-1}$ but on analysis it is clear that k_{OH} ($=k_H/K_w$) is increased by a factor of nearly three orders of magnitude when the NH_2 is replaced by a pyridyl group. The system therefore adopts the same behaviour as the *cis*-$[Co(en)_2(amine)Cl]^{2+}$ complexes. This is a frequent, but not necessarily universal, observation for a wide range of ligands whether they are bi-, quadri-, or quinque-dentate, linear or macrocyclic.[3] Although cobalt(III) complexes whose aquation has an inverse first-order dependence on $[H^+]$ are by no means uncommon,[19–21] the two isomeric forms of αβ-$[Co(picdien)X]^{2+}$ (X = Cl or Br) are extreme examples in the sense that the acid-independent contribution to the reactivity is too small to be measured, even in 0.10 mol dm^{-3} perchloric acid. It was possible to determine a rough value for k_{aq} at high temperature and at high acid concentration but the absence of reliable temperature-dependence data only allows an approximate extrapolation to 25 °C. Using an enthalpy of activation of 100 kJ mol^{-1}, k_{aq} for *anti*-αβ-$[Co(picdien)Cl]^{2+}$ is estimated to be 6 × 10^{-8} s^{-1} at 25 °C. While the pH-dependent pathway is expected to show primary salt effects, the uncatalysed aquation is not, so the effects of changing the ionic strength from 0.1 to 1.0 mol dm^{-3} are negligible when compared to the inaccuracies arising from the long extrapolation of the data for 70 °C. Thus there seems to be no great difference in the labilities of the analogous picdien and tetren complexes with respect to uncatalysed aquation. In the other examples it has been assumed that the inverse acid dependence was caused by a classical D_{cb} mechanism which requires the removal of an amine proton by hydroxide to generate a dissociatively labile amido conjugate base.

In a complex with a unique amine proton, the base-catalysed hydrolysis can be represented as in equations (1) and (2). In the

$$[Co(L_4)(R_2NH)X]^{n+} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Co(L_4)(\dot{R}_2N)X]^{(n-1)+} + H_2O \quad (1)$$

$$[Co(L_4)(R_2N)X]^{(n-1)+} \underset{}{\overset{k_2}{\rightleftharpoons}} [Co(L_4)(R_2N)]^{n+} + X^- \quad (2)$$

picdien and picditn complexes there are three non-equivalent protons, each capable of being exchanged by reaction (1) and, although it is probable that one of the amido conjugate bases is very much more labile than the other two,[3] the general expression for the base-hydrolysis rate constant would be given by $-d[complex]/dt = k_{OH}[complex][OH^-]$, with $k_{OH} = \Sigma k_1{}^i k_2{}^i/(k_{-1}{}^i + k_2{}^i)$. If $k_{-1}{}^i \gg k_2{}^i$ (*i.e.* rapid pre-equilibrium proton transfer), the contribution from that deprotonation to k_{OH} would simplify to $k_{OH} = k_1{}^i k_2{}^i/k_{-1}{}^i$, while if $k_2{}^i \gg k_{-1}{}^i$ (*i.e.* rate-limiting deprotonation) the contribution simplifies to $k_{OH} = k_1{}^i$.

In acid solution the inverse acid-dependent rate constant, k_H, is related to the base-hydrolysis rate constant, k_{OH}, by the relationship $k_{OH} = k_H/K_w$, where K_w is the ionic product of water at the temperature and ionic strength at which the experiments are carried out.

The change from picdien to picditn does not change the skeletal form adopted by the linear quinquedentate ligand but the solvolytic lability of the complexes is much increased, so much so that, at pH < 3, the solvolytic process is dominated by the uncatalysed aquation that is not observed for the picdien analogues. Using a rough extrapolation of the data from 70 °C for the picdien species it would seem that there is a 3 × 10^3-fold

increase in reactivity of the *anti*-chloro complex. No data are available for complexes of the skeletally equivalent quinquedentate amine, 1,13-diamino-3,7,11-triazatridecane, but a similar large increase of solvolytic lability as a result of increasing ring size has been observed before in the *trans*-$[Co(LL)_2(A)Cl]^{n+}$ systems where the lability is enhanced by more than three orders of magnitude when LL is changed from 1,2-diaminoethane to 1,3-diaminopropane provided A is one of the ligands that induces stereochemical change in the solvolyses of the $(en)_2$ species (*e.g.*, NCS or Cl).[22] However, the features of the two systems are so different that it would be rash to offer the same explanation. The reactions take place with complete retention of skeletal configuration (all the isolated species having the αβ geometry) but this may reflect only the high stability of this form. No figures are available for the entropies of activation of the uncatalysed aquation of the chloro picdien species and those for the picditn analogues do not give a clear indication of the shape of the five-co-ordinate intermediate.[23] The base-catalysed solvolyses of the $[Co(picdien)X]^{2+}$ and $[Co(picditn)X]^{2+}$ complexes, on the other hand, are far less sensitive to the increase in ring size; this too is true for the *trans*-$[Co(LL)_2(A)X]^{n+}$ systems.[22]

The values of k_{OH}, calculated in this way, are unusually large, possibly among the largest observed for cobalt(III) amine complexes and, in the case of the bromo complexes, within a couple of orders of magnitude of a diffusion-controlled process. The activation energies are low (between 35 and 50 kJ mol^{-1}) and there is apparently a large difference between the values observed for the *syn* and *anti* isomers, even though their rate constants do not differ by more than a factor of 3 or so. Although it has often been suggested that such low enthalpies of activation are characteristic of rate-limiting deprotonations,[24,25] there are well established cases where they are not.[26] Studies of the proton exchange of the *syn*-αβ-$[Co(picdien)X]^{2+}$ cations (X = Cl, Br, or NO_2) carried out in acidified D_2O indicate that all three amine protons of the nitro complex are completely exchanged long before there is any solvolysis and those in the chloro and bromo complexes are substantially exchanged in recovered unreacted material.

The kinetics of exchange of each of the three secondary amine protons in the chloro complex can be studied without drastic interference from solvolysis, while in the bromo complex, which is the most solvolytically labile, only the fastest exchange can be studied without undue interference. Nevertheless, non-quantitative studies of the ^1H n.m.r. spectra of *syn*-αβ-$[Co(picdien)Br][ClO_4]_2$ precipitated at various times from acidified D_2O solution show that H^7 is about 100 times more labile than H^{17} which, in turn, is somewhat more labile than H^{12}.

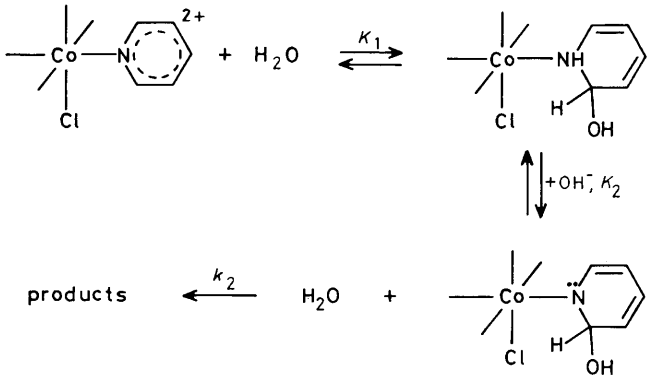
It therefore appears that, in all three *syn* complexes examined, the protons *trans* to the acido ligand, H^7, are the most labile, indeed, they are among the most labile reported in cobalt(III) acido-amine complexes and compare to the similarly sited proton in *sym*-$[Co(trenen)Cl]^{2+}$ [trenen = 1,8-diamino-3-(2-aminoethyl)-3,6-diazaoctane] where k_1 measured under similar conditions, but at 25 °C, is 5×10^9 dm^{-3} mol^{-1} s^{-1}.[27]

It is worth noting that the most labile proton in the picdien complex is bound to a 'bent' secondary nitrogen atom (the term 'bent' refers to central atom of a set of three facial donors in a multidentate ligand, while 'flat' describes the central atom in a set of three meridional donors), while that in the trenen complex is bound to a 'flat' nitrogen. It seems that the much higher lability of a complex where the appropriately sited nitrogen is 'flat' is, as has been previously stated,[5] due to the dissociative lability of the conjugate base (k_2) rather than any enhanced lability of the proton (k_1).

The nitro complex is clearly a case where $k_{-1} \gg k_2$ but, for the chloro complex, the magnitudes of the rate constants k_{-1} and k_2 are closer. Evidence collected from a wide range of studies suggests that the 'flat' nitrogen, *cis* to the leaving group, will be the most potent labilising amido group,[4] so that the rate constant for the exchange of H^7 is the one that must be considered. Bearing in mind that the isotope effect arising from the difference between the removal of H^+ by OH^- in H_2O and the removal of H^+ by OD^- in D_2O is probably a reduction of no more than 50%, even with a pessimistically wide range of uncertainty, the rate constant k, lies between 2×10^8 and 8×10^8 dm^3 mol^{-1} s^{-1}, and is still nearly 10 times greater than k_{OH}. The bromo complex is too solvolytically labile for the exchange kinetics of the relevant proton to be studied by this simple *in situ* method, but the absence of a satisfactory separation technique, similar to that used elswhere,[26,28,29] prevented a more elaborate investigation. It is likely that the most important change on going from the chloro to the bromo complex is the increase in k_2 so that the ratio k_{-1}/k_2 will be smaller. It is unlikely that the limit where $k_2 \gg k_{-1}$ is reached. The chloro and bromo substrates are therefore in the region where $k_{-1} \approx k_2$. We might expect to observe, as in other such cases,[26,30] that the Eyring plots [$\ln(k_{OH}/T)$ *versus* T^{-1}] are curved but the range of temperature covered is not large enough and the scatter of the data points is too much for this to be established with certainty. The quoted activation parameters are obtained from best least-squares fits to the experimental data, and it is not unreasonable to suggest that the large variation in the enthalpies of activation of the different substrates is a consequence of a difference in the temperatures at which $k_{-1} = k_2$, the smaller enthalpies of activation being associated with smaller values of the ratio k_{-1}/k_2.

Proton exchange with the *anti* complexes was not studied quantitatively but examination of the ^1H n.m.r. spectra in acidified D_2O shows that H^7 exchanges the fastest and is completely exchanged without any observable change in the pyridine proton peaks; H^{17} exchanges more slowly but also without any sign of solvolysis (or isomerisation); and H^{12} remained unexchanged throughout the experiment.

When this work was commenced, many years ago, we thought that the high lability of these complexes and the other pyridine-containing species might be the result of covalent hydration, represented by the Scheme, which would give rise to



Scheme.

the same rate law as the usual conjugate base mechanism but, if the first two stages were fast and reversible, $k_{OH} = K_1K_2k_2$. There is no indication in the ^1H n.m.r. spectrum in acidified D_2O of any significant covalent hydration, the spectrum due to the pyridine protons being fully consistent with the structure found in the solid state. It may be possible that while K_1 is very small, K_2 is large, but it can be argued that an unusually low pK_a, which would be the result of extensive delocalisation of the lone pair of the nitrogen around the part of the ring that retains its conjugation, as shown in the Scheme, would reduce the

availability of the same lone pair to facilitate the dissociation of the conjugate base and thereby cause a relatively small value of k_2. Nevertheless, a significant departure from the linearity of $k_{obs.}$ *vs.* [OH$^-$] might be deemed to be supporting evidence for covalent hydration.

An analogous case is found in the base hydrolysis of *cis*-$[Co(en)_2(im)Cl]^{2+}$ (im = imidazole), where the co-ordinated imidazole possesses an acidic proton.[31] There, the plot of log $k_{obs.}$ *vs.* [OH$^-$] has two linear regions of unit slope separated by a region where the slope is less. It was suggested that the first linear region (at lower pH) arose from dissociation of the conjugate base formed by deprotonation of the imidazole, while the other region was due to the removal of a second proton, this time from the diaminoethane. (It should be pointed out that the rate law does not allow one to distinguish this mechanism from one in which both regions with slope = 1 arise from conjugate bases produced by the deprotonation of the diaminoethane. In the first, it is the imidazole complex that is undergoing dissociation, while in the second the imidazolate complex is dissociating and has to be much less reactive.[3])

The dependence of $k_{obs.}$ for the hydrolysis of *anti*-αβ-$[Co(picdien)Cl]^{2+}$ has been studied over as wide a range of pH as possible. Until the point is reached where the reaction is too fast for the stopped-flow technique (*ca.* 200 s^{-1}), a plot of log $k_{obs.}$ *vs.* pH is linear with slope = 1.03 ± 0.03 at 25 °C and 0.981 ± 0.057 at 5.0 °C. The second-order rate constant at 25.0 °C, k_{OH} = (1.4 ± 0.3) × 10^7 dm^3 mol^{-1} s^{-1}, is reasonably close to that determined in acid solution.

The absence of departure from linearity indicates that $k_2 \geqslant 2 \times 10^3$ s^{-1} at 5.0 °C and since the value of k_{aq} at 5 °C is approximately 3 × 10^{-9} s^{-1} (extrapolated from the value determined at 70 °C assuming an enthalpy of activation of 100 kJ mol^{-1}) the rate enhancements resulting from the removal of a proton from one of the secondary amine nitrogens or the addition of hydroxide to one of the pyridine rings is probably greater than 10^{12}. Since Cl$^-$ is too labile to allow the reaction to be probed at high enough pH, we have studied the reactions of *syn*-αβ-$[Co(picdien)X]^{2+}$ (X = NCS^-, N_3^-, on NO_2^-) and do indeed observe departures from the first-order dependence on [OH$^-$] at concentrations above 10^{-2} mol dm^{-3}. The results will be discussed elsewhere.

The lability of the intermediate seems to be too large for the unusual sensitivity of these pyridyl-containing complexes to be due to covalent hydration. A further unfavourable argument can be produced by noting the similarity of the reactivities of the *syn* and *anti* isomers. The covalent hydration mechanism would

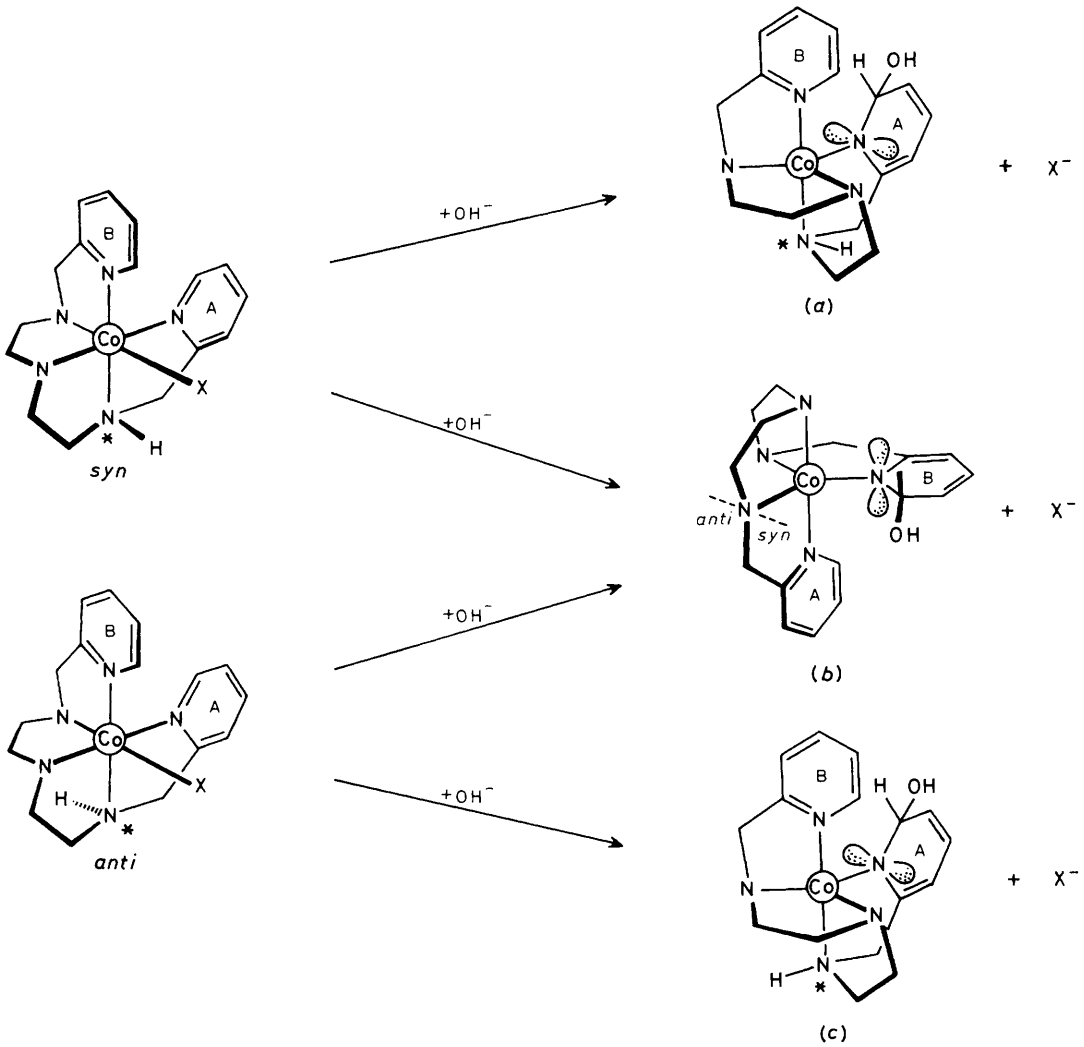


Figure 3. Possible trigonal-bipyramidal five-co-ordinate intermediates derived from *syn*- and *anti*-αβ-$[Co(picdien)X]^{2+}$ showing how an intermediate making use of covalent hydration of pyridyl group A would lead to considerable strain when derived from the *anti* isomer. The inability of pyridyl group B to orient its plane perpendicular to the trigonal plane of cobalt is also indicated

require that the pyridine ring that functions as the π donor would lie with its nitrogen in the trigonal plane of a trigonal bipyramid and its plane at right angles to it. The *anti* isomer would allow such an intermediate to form with no strain but the *syn* isomer would either be highly strained or else would have to use the other pyridyl group (Figure 3).

The evidence, taken together, indicates that the 'covalent hydration mechanism' is an unlikely cause of the reactivity enhancement of the pyridyl group. The real cause remains concealed but the final answer must account for both an enhanced deprotonation lability (k_1) as well as an enhanced dissociative lability (k_2).

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