Kinetics of Aquation and Base Hydrolysis of some *trans*-$[Co(tn)_2(B)Cl]^{n+}$ (tn = 1,3-diaminopropane; B = OH, NCS, N_3, NO_2, NH_3, or CN) Complexes. The Effect of Ring Size on Reactivity

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The rate constants for the displacement of Cl^- from *trans*-$[Co(tn)_2(B)Cl]^{n+}$ (tn = 1,3-diaminopropane; B = OH, NCS, N_3, NO_2, NH_3, or CN) have been measured in water over a range of temperature and pH and the behaviour is compared to that of the analogous 1,2-diaminoethane complexes. For B = NCS, OH (and Cl), where substitution is accompanied by stereochemical change and a large positive $\Delta S^\ddagger$, the rate of uncatalysed aquation is very much enhanced. For B = CN, NO_2, NH_3 (and SO_3), where the entropies of activation for uncatalysed aquation are smaller (even negative) and where substitution occurs with retention of configuration, the increase in reactivity is not much more than ten-fold. In the case of B = N_3, where the diaminoethane complex aquates with steric change but with a negative $\Delta S^\ddagger$ value, the reactivity increase is between the two limits and $\Delta S^\ddagger = +39$ J K^{-1} mol^{-1}. The base hydrolysis of all complexes studied is only increased by a factor of 10—20 in spite of the common occurrence of stereochemical change.

The great enhancement of solvolytic lability on going from *trans*-$[Co(en)_2Cl_2]^+$ (en = 1,2-diaminoethane) to the corresponding six-membered ring complex, *trans*-$[Co(tn)_2Cl_2]^+$ (tn = 1,3-diaminopropane) was first observed qualitatively by Werner [1] and further remarked upon by Bailar and Work [2] and by Pearson *et al.*[3] The kinetics of the reaction were first examined by Stranks and co-workers [4] and have since been examined by others.[5,6] The reactivity difference, encompassed by a factor of 1 600, was shown not to be present in the corresponding chromium(III) complexes,[7] nor if only one of the two five-membered rings was replaced, as for example in *trans*-$[Co(en)(tn)Cl_2]^+$.[7] House and co-workers [7] proposed that the extra strain generated by the two six-membered rings was released on going to the trigonal bipyramidal five-co-ordinate intermediate. It therefore seemed of interest to extend these studies to a much wider range of complexes of the type *trans*-$[Co(AA)_2(B)Cl]^{n+}$ (AA is a chelating diamine) to see whether this reactivity-enhancing effect was restricted to those substrates associated with stereochemical change and, by implication, the formation of a trigonal bipyramidal intermediate, or whether it was a general feature of the behaviour of all the complexes in the series.

Experimental

Preparations.—The complex *trans*-$[Co(tn)_2Cl_2]Cl$ was prepared by the method of Bailar and Work,[2] *trans*-$[Co(tn)_2(NO_2)_2]NO_2$ by the method of Werner.[1]

trans-*Chlorobis*(1,3-*diaminopropane*)(*nitro*)*cobalt*(III) *perchlorate*. The complex *trans*-$[Co(tn)_2(NO_2)_2]NO_2$ (10 g) was ground to a powder and added to concentrated hydrochloric acid (30 cm^3) in an evaporating basin. There was a brisk effervescence and the colour changed to pink-red. The mixture was cooled in ice and the pink solid filtered off, washed with ethanol and diethyl ether, and air dried. The crude chloride was dissolved in water, treated with an aqueous solution of sodium perchlorate, and cooled in ice. Red crystals of the perchlorate separated and were filtered off, washed with ethanol and ether, and air dried. Yield, 6 g (Found: C, 18.5; H, 5.20; Cl, 18.3; N, 17.9. $C_6H_{20}Cl_2CoN_5O_6$ requires C, 18.6; H, 5.20; Cl, 18.3; N, 18.0%).

trans-*Chlorobis*(1,3-*diaminopropane*)(*isothiocyanato*)-*cobalt*(III) *thiocyanate*. The complex *trans*-$[Co(tn)_2Cl_2]Cl$ (7.2 g) was dissolved in the minimum amount of ice-cold water and a solution of KCNS (2.4 g) in water (5 cm^3) was added. The green *trans*-$[Co(tn)_2Cl_2]NCS$, which is more soluble than the diaminoethane analogue, crystallised out and the mixture was warmed to nearly 50 °C until nearly all had dissolved. The filtrate was cooled in ice and treated with a second portion of KCNS (2.4 g). The thiocyanate salt crystallised out and was filtered off, washed with ethanol and ether, and air dried. In an alternative method, the precipitate of *trans*-$[Co(tn)_2Cl_2]NCS$ was filtered off, heated with water (10 cm^3) until all had dissolved, and the solution filtered and cooled. Addition of sodium perchlorate gave the *trans*-chloro(isothiocyanato) perchlorate contaminated with some bis(isothiocyanato) perchlorate. The required complex could be purified by extraction with hot methanol but the process is tedious and the yields are fairly low (Found: C, 26.7; H, 5.55; Cl, 10.0; N, 23.5; S, 17.9. $C_8H_{20}ClCoN_6S_2$ requires C, 26.8; H, 5.60; Cl, 9.90; N, 23.4; S, 17.9%).

trans-*Chloro*(*cyano*)*bis*(1,3-*diaminopropane*)*cobalt*(III) *perchlorate*. The complex *trans*-$[Co(tn)_2(SO_3)(CN)]$ (1.8 g), prepared by the method of Kawaguchi and Kawaguchi [8] was added to concentrated hydrochloric acid (3 cm^3) and stirred until it had dissolved. On standing, orange crystals of the chlorocyano chloride separated and were filtered off, washed with ethanol and ether, and air dried. The filtrate was treated with aqueous sodium perchlorate and the crystalline perchlorate which separated was filtered off, washed with ethanol and ether, and air dried. The chloride was dissolved in water (15 cm^3) and the filtered solution treated dropwise with aqueous sodium perchlorate. The crystalline perchlorate was filtered off, washed with ethanol and ether, and air dried. Both crops of perchlorate were dissolved in the minimum amount of water at 40 °C and the filtered solution was cooled as rapidly as possible and treated with aqueous sodium perchlorate. The perchlorate crystallised in well formed needles and was filtered off, washed with ethanol and ether, and dried under vacuum. Yield 1.8 g (Found: C, 22.8; H, 5.50; Cl, 19.5; N, 19.1. $C_7H_{20}Cl_2CoN_5O_4$ requires C, 22.8; H, 5.50; Cl, 19.3; N, 19.0%).

trans-*Amminebis*(1,3-*diaminopropane*)*sulphitocobalt*(III) *chloride*. This complex was prepared by treating *trans*-[$Co(tn)_2(SO_3)Cl$] (6.0 g), prepared by the method of Kawaguchi and Kawaguchi,[8] with aqueous ammonia (36 cm^3, 2 mol dm^{-3}), and warming the solution and precipitate to 50 °C until all the solid had dissolved. Methanol (*ca.* 20 cm^3) was added until the first sign of cloudiness and the solution set aside in the refrigerator to crystallise. Well formed brown crystals separated and were filtered off and washed with ethanol and ether. Yield of dull brown solid (4.8 g) (Found: C, 19.8; H, 6.75; Cl, 9.55; N, 18.9. $C_7H_{23}ClCoN_5O_3S \cdot 1.5H_2O$ requires C, 19.7; H, 7.15; Cl, 9.65; N, 19.1%).

Attempts to make the analogous methylamine and isopropylamine complexes led to the formation of *trans*-[$Co(tn)_2(SO_3)(OH)$].

trans-*Amminechlorobis*(1,3-*diaminopropane*)*cobalt*(III) *chloride hydrate*. The complex *trans*-[$Co(tn)_2(SO_3)(NH_3)$]Cl (4.8 g) was ground to a powder and then triturated with ice-cold concentrated hydrochloric acid, saturated with lithium chloride. The solid dissolved and the solution was allowed to warm up slowly, first to room temperature and then to 40 °C. A copious precipitate of *trans*-[$Co(tn)_2Cl_2$]$Cl \cdot HCl \cdot 2H_2O$ separated and the mixture was allowed to stand for a further 30 min at room temperature before the solid was filtered off. As much of the mother-liquor as possible was squeezed out of the precipitate which was then washed with a little more ice-cold concentrated HCl. The combined washings and filtrate were diluted with methanol (100 cm^3) and then ether until just before there was a permanent cloudiness. The purple solution was set aside undisturbed for 48 h to crystallise. (Fast precipitation leads to the formation of a hygroscopic powder that is not easy to remove completely from the filter.) Well formed long, thin plates separated and were filtered off, washed with ethanol and ether, and air dried. Yield 0.31 g. The compound was recrystallised by dissolving it in water (4 cm^3), adding concentrated HCl (2.5 cm^3), methanol (20 cm^3), and ether (30 cm^3) and setting the solution aside in a refrigerator for 48 h. Long, well formed needle crystals of the chloride hemihydrate separated from an almost colourless mother-liquor and were filtered off, washed with ethanol and then ether, and air-dried (Found: C, 21.2; H, 7.10; Cl, 31.1; N, 20.4. $C_6H_{23}Cl_3CoN_5 \cdot 0.5H_2O$ requires C, 21.2; H, 7.00; Cl, 31.3; N, 20.6%).

The *perchlorate* can be obtained as a purple-red crystalline powder by adding concentrated aqueous $LiClO_4$ solution to a concentrated solution of the chloride.

trans-*Diazidobis*(1,3-*diaminopropane*)*cobalt*(III) *perchlorate*. This complex was prepared by a modification of the method used by Buckingham *et al.*[9] for the preparation of the corresponding diaminoethane complex. Cobalt(II) carbonate (20 g) was suspended in water (400 cm^3), concentrated perchloric acid (60%, 50 cm^3) was added, and the mixture stirred and heated to 70 °C for 20 min before it was filtered through paper. A solution of 1,3-diaminopropane (24 cm^3) in water (50 cm^3) was added to the cooled, stirred solution, followed by one of sodium azide (24 g) in water (100 cm^3). Air was bubbled rapidly through the gelatinous blue suspension until the colour was chocolate. The product was filtered off through paper and washed with cold water, allowed to dry overnight, and then dissolved in dimethyl sulphoxide (dmso) (250 cm^3). The solution was filtered from the large amount of dark brown gelatinous material and poured into a solution of $NaClO_4$ (100 g) in water (500 cm^3). Dark green-grey (purplish in artificial light) well formed crystals separated and were filtered off, washed in turn with cold dilute aqueous $NaClO_4$, ethanol, and ether, and air dried. Yield 12.4 g (Found: C, 18.5; H, 5.25; Cl, 9.20; N, 35.2. $C_6H_{20}ClCoN_{10}O_4$ requires C, 18.4; H, 5.15; Cl, 9.10; N, 35.9%).

The complex is sparingly soluble in water to give a blue solution with peaks at 592 ($\varepsilon = 355$) and 325 nm ($\varepsilon = 10\,400$ cm^2 $mmol^{-1}$). The 400-MHz ^1H n.m.r. spectrum of a $(CD_3)_2SO$ solution, Table 1, has the typical three broad-peak ^1H n.m.r. spectrum with no detectable signal for the *cis* isomer.

trans-*Azidochlorobis*(1,3-*diaminopropane*)*cobalt*(III) *perchlorate*. This complex was prepared by a modification of the method of Jackson and Begbie.[10] The complex *trans*-[$Co(tn)_2(N_3)_2$]ClO_4 (4.2 g) was added to a stirred solution of concentrated HCl (36 cm^3) and water (12 cm^3) that had been cooled in an ice-salt freezing mixture. Stirring was continued for no more than 30 s and the solution was rapidly filtered into a cold (0 °C) solution of $NaClO_4$ (15 g) in water (30 cm^3). After standing for no more than 3 min the green crystalline product was filtered off and washed with ethanol and ether. **CAUTION**: owing to the toxic nature of HN_3 this preparation must be carried out in a good fume cupboard. The ^1H n.m.r. spectrum of a dmso solution indicated that this is a 3:2 mixture of *trans*-dichloro- and *trans*-chloro-azido(1,3-diaminopropane)-cobalt(III) perchlorates. The crude material (3.3 g) was dissolved in dimethylformamide (10 cm^3) and the solution was filtered, cooled in an ice–salt mixture, treated with aqueous sodium bicarbonate–carbonate buffer (0.20 mol dm^{-3}, 50 cm^3), and stirred for 10 s before pouring it on to perchloric acid (60%, 12 cm^3) and ice (10 g). The crystalline product was filtered off, washed with ethanol and ether, and air dried. The ^1H n.m.r. spectrum showed this to contain 75% of the required complex together with 21% *trans*-[$Co(tn)_2Cl_2$]ClO_4 and 4% of the *trans*-diazido perchlorate. The treatment could be repeated to remove much of the remaining dichloro complex but the yields were drastically reduced.

Kinetics.—The reagent solution containing all components except the complex was brought to the reaction temperature in the thermostatted cell of a spectrophotometer. The reaction was initiated either by adding a known amount of the appropriate complex that had been taken into an open glass capillary tube, or by adding a freshly made, concentrated solution (*ca.* 0.050 cm^3) of the complex in dimethylformamide. The reactions were followed by the change in absorbance at a suitable wavelength, chosen after making preliminary multiple scan runs. The slower reactions were followed by the multiple scan technique only. The base-catalysed hydrolysis reactions of the solvolytically labile species were also followed in this way, care being taken to ensure that the concentration of the hydroxide was at least 100 times that of the complex. Under these circumstances the reactions were followed in the charge-transfer region of the spectrum in the ultra-violet at concentrations of complex of the order of 10^{-4} mol dm^{-3}. The base-catalysed hydrolysis of the less solvolytically labile species was studied by the stopped-flow technique using a Hi-Tec stopped-flow spectrophotometer and the data were collected and processed with an Apple IIe computer.

Results

The complexes of the type *trans*-[$Co(tn)_2(B)Cl$]$^{n+}$ have been prepared by modifications of the methods used to obtain the analogous diaminoethane complexes. Those with B = NO_2[11] and NCS[11] have already been described and had been prepared by the reaction of *trans*-[$Co(tn)_2Cl_2$]Cl with the appropriate salt in methanol. The *trans*-chloroammine complex was made by a modification of the method used to place a ^{15}N-labelled ammonia *trans* to chlorine in the penta-amminechlorocobalt(III) complex[12] rather than by the more tedious oxidation of the *trans*-[$Co(AA)_2(NCS)Cl$]$^+$ salt as used in the diaminoethane case.[1,13] Attempts to isolate solid salts of the *trans*-chloro-(hydroxo) complex by methods that worked for the corresponding diaminoethane complex[14] were unsuccessful. How-

Table 1. Characteristic features of the ^1H n.m.r. spectra of the *trans*-$[Co(tn)_2(B)Cl]^{n+}$ complexes in $[^2H_6]$dimethyl sulphoxide

Complex	Chemical shift	Assignment
trans-$[Co(tn)_2Cl_2]ClO_4$	1.7 m 4 H	C–CH–C
	2.35 m 4 H	N–CH–C
	2.42 m 4 H	N–CH–C
	4.54 t 4 H	Co–NH–C
	4.855 d 4 H	Co–NH–C
trans-$[Co(tn)_2(N_3)_2]ClO_4$	1.72 m 4 H	C–CH–C
	2.39 m 8 H	N–CH–C
	4.37 m 8 H	Co–NH–C
trans-$[Co(tn)_2(NO_2)Cl]ClO_4$	1.59 m 4 H	C–CH–C
	2.13 m 4 H	N–CH–C
	2.59 m 4 H	N–CH–C
	4.41 m 4 H	Co–NH–C
	4.53 m 4 H	Co–NH–C
trans-$[Co(tn)_2(NCS)Cl]ClO_4$	1.63 m 2 H	C–CH–C
	1.86 d 2 H	C–CH–C
	2.34 m 4 H	N–CH–C
	2.49 m 4 H	N–CH–C
	4.64 t 4 H	Co–NH–C
	5.30 d 4 H	Co–NH–C
trans-$[Co(tn)_2(CN)Cl]ClO_4$	1.41 m 2 H	C–CH–C
	1.79 d 2 H	C–CH–C
	2.52 m 8 H	N–CH–C
	3.85 q 4 H	Co–NH–C
	4.47 d 4 H	Co–NH–C
trans-$[Co(tn)_2(NH_3)Cl][ClO_4]_2$	1.595 m 2 H	C–CH–C
	1.767 m 2 H	C–CH–C
	2.330 m 4 H	N–CH–C
	2.62 m 4 H	N–CH–C
	2.750 m 3 H	Co–NH
	4.599 m 4 H	Co–NH–C
	4.685 m 4 H	Co–NH–C

d = Doublet, q = quartet, and m = unresolved multiplet.

Table 2. First-order rate constants for the aquation of *trans*-$[Co(tn)_2(B)Cl]^{n+}$ in aqueous solution in the presence of 0.010 mol dm^{-3} $HClO_4$

B	Temperature/ °C	10^4 $k_{obs.}$/ s^{-1}	B	Temperature/ °C	10^4 $k_{obs.}$/ s^{-1}
NCS	25.0	0.62	CN	33.2	16.8
	39.6	5.74		40.1	33.3
	49.3	21.4			
			N_3	10.1	40.0
NO_2	10.0	27		15.0	83.4
	14.1	48		20.1	162
	20.3	108		25.2	324
	30.1	333		30.1	652
	39.5	910		34.6	1 051
CN	15.0	1.79	NH_3	39.9	0.446
	20.0	3.02		49.9	1.64
	23.2	4.8		59.9	4.95
	25.0	5.9			
	30.5	11.2			

ever, it was observed that, as in the case of the diaminoethane species,[15] the major (if not the only) product of the first stage of the base hydrolysis of the *trans*-dichlorobis(1,3-diaminopropane) complex was the *trans*-chloro(hydroxo) species. Consequently, the rate constants for the second stage of the base-catalysed hydrolysis of the dichloro species were determined in the presence of sufficient sodium hydroxide to replace the first chloride and to ensure that the solution remained basic. The absorbance change at 300 nm was first order and values of $k_{obs.}$ were essentially independent of $[OH^-]$ over the concentration range $0.0010 \leqslant [OH^-] \leqslant 0.010$ mol dm^{-3}. At higher $[OH^-]$ there is a significant increase in rate constant and an approximate value can be obtained for the rate constant for base hydrolysis. When the reaction mixture was acidified as soon as possible after the first stage of the base hydrolysis was complete a greenish yellow solution was formed and its colour rapidly changed to pink. This change is almost certainly due to the isomerisation of the *trans*-$[Co(tn)_2(H_2O)Cl]^{2+}$ formed initially but the rate ($t_{\frac{1}{2}}$ at 0 °C is estimated to be $\simeq 1$ s) is too fast to measure spectrophotometrically with the available equipment.

The visible–u.v. spectra of these complexes have the same form as those of the diaminoethane species but the lower-energy peaks are shifted to longer wavelengths. This has already been discussed in terms of the weaker ligand field of the 1,3-diaminopropane ligand.[8,11]

The *trans* configuration of all of these complexes has been confirmed by n.m.r. spectroscopy. The ^1H n.m.r. spectra of solutions of the perchlorate salts in $(CD_3)_2SO$ indicate a wide range of behaviour patterns. The dichloro, dinitro, and diazido complexes have three broad peaks, in the ratio 1:2:2, assigned to the protons on carbons adjacent to C, carbons adjacent to N, and the amine protons, respectively. The spectra of the *trans*-$[Co(tn)_2(B)Cl]^{n+}$ complexes have the extra complexity expected from the reduction in the symmetry and the N–*H*, N–C*H*–C, and C–C*H*–C peaks are split and show the structures due to coupling. The extent to which these peaks are split depends upon the nature of B. The general details of the spectra are summarised in Table 1, but a proper discussion of the resolved spectra in terms of ring conformation will be presented separately.

The aquation and base-hydrolysis reactions were followed spectrophotometrically. In the more labile systems, preliminary multiple scan experiments were used to establish the best wavelengths for following the reaction. In some cases the aqua product underwent further isomerisation, frequently with a rate constant that was large compared to that of the aquation process. Where possible, the spectrophotometric analysis was made at a wavelength at or close to the isosbestic point for the product isomerisation but even in an unfavourable system, *e.g.* the aquation of the *trans*-dichloro complex where at 530 nm there is a noticeable induction period before the first-order change gets under way, the interference is minimal. The aquation of the chloroazido complex was studied using a sample contaminated with some 20% of the *trans*-dichloro and 4% of *trans*-diazido species. The absorbance change was studied at 600 nm where there is an isosbestic point for the aquation of the dichloro complex in order to eliminate interference from this source. Rate constants obtained in the same way from solutions of the samples containing 70% of the *trans*-dichloro species agree reasonably well with these indicating that this treatment of the data is acceptable. The great lability of the dichloro complex towards base-catalysed hydrolysis meant that this part of the reaction was complete before the first data were recorded.

The first-order rate constants, determined from the slope of the plot of $\ln(A_t - A_\infty)$ against time (A_t and A_∞ are the absorbances at time t and at the end of the reaction) are collected in Table 2, each entry being the average from at least three concordant runs. The rate constants for the base-catalysed aquations of the solvolytically labile complexes were determined in a similar way, care being taken to ensure that the concentration of complex was sufficiently small compared to that of

Table 3. First-order rate constants for the base hydrolysis of *trans*-$[Co(tn)_2(B)Cl]^{n+}$ [a]

B	Temperature/ °C	10^3 $[OH^-]$/ mol dm^{-3}	$k_{obs.}$/s^{-1}	k_{OH} [b]/ dm^3 mol^{-1} s^{-1}
NCS	0.0	12.5	0.0541	4.33
		25.0	0.108	4.31
		37.5	0.180	4.79
		50.0	0.234	4.68
	5.0	50.0	0.528	10.5
	10.0	50.0	1.16	23.2
	15.0	50.0	2.43	48.6
	20.0	50.0	4.82	96.4
	25.0	50.0	9.22	184
NO_2	10.0	0.00	0.0027	
		2.50	0.0161	5.4
		5.0	0.0323	5.9
		12.5	0.074	5.7
N_3	10.0	0.00	0.003 95	
		1.00	0.0237	20
		2.00	0.049	22
		4.00	0.092	22
		10.0	0.205	20
NH_3	0.0	12.5	0.178	14.2
		25.0	0.376	15.0
		37.5	0.554	14.8
		50.0	0.766	15.2
	5.0	50.0	1.75	35.0
	10.0	50.0	3.02	60.4
	15.0	50.0	7.13	142
	20.0	50.0	13.7	274
CN	0.0	12.5	0.0749	6.0
		25.0	0.139	5.6
		37.5	0.232	6.2
		50.0	0.352	7.0
	5.0	50.0	0.604	12.1
	8.0	50.0	0.994	19.9
	10.0	50.0	1.31	26.2
	15.0	25.0	1.15	46
		37.5	1.88	50
		50.0	2.60	52
	20.0	50.0	5.16	103
	25.0	50.0	9.8	196
OH	10.0	4.00	0.13 [c]	
		10.0	0.12	
		40	0.13	
		100	0.18	0.7

[a] $I = 0.10$ mol dm^{-3} ($NaClO_4$). [b] $k_{OH} = (k_{obs.} - k_{aq.})/[OH^-]$. [c] Rate constant for the second stage of the base hydrolysis of *trans*-$[Co(tn)_2Cl_2]ClO_4$.

the sodium hydroxide to ensure pseudo-first-order conditions. The solvolytic labilities of the chloroisothiocyanato and chloroammine complexes were low enough for the stopped-flow method to be used. Fresh solutions of the complex were prepared for each set of runs and mixed with a sufficient excess of sodium hydroxide to ensure pseudo-first-order conditions. For the chlorocyano complex, whose half-life for aquation was about 30—40 min at room temperature, the stock solution was kept in a refrigerator and the reservoir frequently replenished with fresh samples of the cold solution of the complex. The first-order rate constants were obtained from a least-squares curve-fitting program using the relationship $A_t = A_\infty - (A_\infty - A_0)$ exp $(-k_{obs.}t)$. Plots of $k_{obs.}$ against $[OH^-]$ were linear and the values of the slopes (k_{OH}) are collected in Table 3.

Discussion

The rate constants and activation parameters for the aquation and base hydrolysis of the complexes are collected in Table 4 where they are compared with the literature values for the corresponding bis(1,2-diaminoethane) complexes. In general, all the $(tn)_2$ complexes are more labile than their $(en)_2$ analogues but the extent to which the lability is increased depends upon the nature of ligand B. The chloroisothiocyanato and chlorohydroxo complexes behave like the dichloro complexes and are some three orders of magnitude more labile, while the chloronitro, chlorocyano, and chloroammine complexes, like the previously reported acidosulphito species, are only about one order of magnitude more reactive. As it has not yet been possible to isolate and characterise the isomeric forms of the corresponding $[Co(tn)_2(B)(H_2O)]^{n+}$ complexes, nor indeed to measure the rate of isomerisation, it is not possible to give any indication of the steric course of substitution in the 1,3-diaminopropane system. However, if one falls back on the observation that, in the $(en)_2$ series and many other cases,[16] the systems that aquate with stereochemical change have a much greater entropy of activation than those that aquate with retention, the pattern emerges that the systems with the much enhanced reactivity are those that aquate in both the en and tn systems with a large positive entropy of activation and presumably with stereochemical change. The systems that have the small increase are those that aquate with negative or only small positive entropies of activation and, in the $(en)_2$ case, with retention of configuration. The case where $B = N_3$ stands out as an exception to this rule and is of some interest. The increase in reactivity lies between that found for the positive and negative $\Delta S^‡$ systems and there is a remarkable change in the sign and magnitude of $\Delta S^‡$ on going from the $(en)_2$ to the $(tn)_2$ system, which is not observed in the other cases. The *trans*-$[Co(en)_2(N_3)Cl]^+$ cation presents one of the few cases that does not obey the rule that when aquation of a chloroamine complex takes place with stereochemical change, the entropy of activation is large and positive.[10] One possible explanation could be that, in this case and over the temperature range studied, the two reaction pathways have comparable free energies of activation and run in parallel. If the stereochemical change pathway makes only a relatively small contribution to account for the 10% or so *trans*-to-*cis* rearrangement, the activation parameters would be dominated by the retention pathway. Changing from en to tn would increase the rate of the stereochemical change pathway much more than the retentive pathway and the former would dominate. The entropy of activation would be expected to be more positive and the enthalpy of activation larger. This is what is observed. However, it also follows that the Eyring plot ($\ln k/T$ *vs.* T^{-1}) for the aquation of *trans*-$[Co(en)_2(N_3)Cl]^+$ should be curved as the low activation enthalpy reaction will be replaced by the one with the higher enthalpy of activation as the temperature increases. The rate constants for the aquation of the $(en)_2$ complex have been measured over a 60 °C range of temperature[17] and there was no sign of any significant increase in the slope of the Eyring plot at higher temperatures. This system must therefore be a prime candidate for a further revisitation.[10]

The behaviour pattern is therefore consistent with the original idea that the labilising effect of the 1,3-diaminopropane is steric in origin and is only apparent when the substrate changes to an incipient trigonal bipyramidal transition state and thereby releases some of the strain that was present in the octahedral substrate. The incipient square pyramidal transition state, formed simply by the lengthening of the Co–Cl bond, retains the strain.

The rate constants and activation parameters for the base-catalysed aquations are collected in Table 5 and compared with

Table 4. A comparison of the rate constants, $k_{aq.}/s^{-1}$, at 25.0 °C, and the activation parameters, $\Delta H^{\ddagger}$/kJ mol^{-1} and $\Delta S^{\ddagger}$/J K^{-1} mol^{-1}, for the aquation of *trans*-$[Co(AA)_2(B)Cl]^{n+}$

	AA = en				AA = tn				
B	$10^4\ k_{aq.}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Ref.	$10^4\ k_{aq.}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Ref.	k_{tn}/k_{en}
OH	1.60[a]	107	+61	14	1 300[a]			This work	810
Cl	0.42	109	+36	*b*	680	92	+36	4	1 620
NCS	0.000 45	125	+30	*c*	0.62	114	+59	This work	1 380
N_3	2.5	87	−25	17	324	93	+39	This work	121
NH_3	0.034	97	−46	*d*	0.064	102	−4	This work	19
NO_2	9.8	87	−8	*e*	180	86	+9	This work	18
CN	0.82	94	−8	*f*	5.8	88	−10	This work	7
SO_3	5 560[g]			*h*	67 500			*h*	12
	821[i]			*h*	8 150			*h*	10
	400[j]			*h*	10 000			*h*	25

[a] At 10 °C. [b] S. C. Chan, *Aust. J. Chem.*, 1967, **20**, 595. [c] M. E. Baldwin and M. L. Tobe, *J. Chem. Soc.*, 1960, 4275. [d] M. L. Tobe, *J. Chem. Soc.*, 1959, 3776. [e] S. Asperger and C. K. Ingold, *J. Chem. Soc.*, 1956, 2862. [f] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 1963, 514. [g] Displacement of N_3^-. [h] Y. Ito, A. Terada, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2898. [i] Displacement of NO_2^-. [j] Displacement of NCS^-.

Table 5. A comparison of the rate constants, k_{OH}/dm^3 mol^{-1} s^{-1}, at 10 °C and the activation parameters, $\Delta H^{\ddagger}$/kJ mol^{-1} and $\Delta S^{\ddagger}$/J K^{-1} mol^{-1}, for the base hydrolysis of *trans*-$[Co(AA)_2(B)Cl]^{n+}$ [a]

	AA = en				AA = tn				
B	k_{OH}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Ref.	k_{OH}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Ref.	k_{tn}/k_{en}
OH	0.072	92	+71	15	0.7	—	—	This work	10
Cl	167	96	+146	6	2 670	—	—	6	16
NCS	1.47	96	+113	*b*	23	95.9	+120	This work	16
N_3	2.0[c]	—	—	*d*	21	—	—	This work	10
NH_3	6.1[c]	—	—	13	60.4	95.1	+126	This work	12
NO_2	0.39[c]	100	+100	*e*	5.7	—	—	This work	15
CN	0.63	95	+86	*f*	26	92.1	+108	This work	41

[a] $I = 0.10$ mol dm^{-3} ($NaClO_4$). [b] C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1956, 1691. [c] Extrapolated to 10.0 °C using $\Delta H = 100$ kJ mol^{-1}. [d] P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 1960, 4803. [e] S. Asperger and C. K. Ingold, *J. Chem. Soc.*, 1956, 2862. [f] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 1963, 514.

those for the corresponding diaminoethane complexes. The reactivity increase on going from the five- to the six-membered ring system is of the order of 10—30 fold. We had expected to find a much greater increase since it is generally thought that the base-catalysed solvolysis proceeds by way of the dissociation of the amido conjugate base[18] and we reasoned that the effect seen in the uncatalysed solvolyses of the dichloro, chlorohydroxo, and chloroisothiocyanato complexes would also be found here. It has previously been shown that the base hydrolysis of the *trans*-dichloro cation was only increased by a factor of 20 on going from the five- to the six-membered ring complex[6] but this was shown to be due to the fact that the diaminoethane system was near to the point where the deprotonation was rate limiting and the greater lability of the amido derivative of the 1,3-diaminopropane system simply pushed the balance to the point where the deprotonation was completely rate limiting. The rate constants for amine deprotonation are much less sensitive to ring-size effects. The same explanation cannot be used for the behaviour of the other complexes in this series. The diaminoethane complexes all fit into the category of reactions with rapid and reversible proton transfer and the rate constant for the dissociation of the conjugate base enters fully into the expression for k_{OH}. There is no indication from the activation parameters to suggest that there has been any change in the rate-limiting step on going from the $(en)_2$ to the $(tn)_2$ system. It must be inferred, therefore, that the requirements of the planar amido group to orient itself with respect to the trigonal plane of the cobalt in the five-co-ordinate intermediate[19] are of more importance than the relief of the strain due to the two six-membered rings.

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