Kinetic Studies of the Base Hydrolysis of Cobalt(III) Chloropentamine Complexes containing (Triamine)(Diamine) Chromophores

Beth R. Cameron,[a] **Donald A. House**[b] **and Alexander McAuley**[a]
[a] *Chemistry Department, University of Victoria, PO Box 3055, Victoria, B.C., V8W 3P6, Canada*
[b] *Chemistry Department, University of Canterbury, Christchurch, New Zealand*

The rates of base hydrolysis of a series of $[CoCl(triamine)(diamine)]^{2+}$ complexes have been measured using stopped-flow techniques. The triamines used were tacn (1,4,7-triazacyclononane) or dien (3-azapentane-1,5-diamine) and the diamines were en (1,2-diaminoethane), tn (1,3-diaminopropane) or amp (2-aminomethylpyridine). Studies have also been carried out on a corresponding macrobicyclic pentamine 1,5,8,12,15-pentaazabicyclo[10.5.2]nonadecane (L^1) where the geometry of the ion is square pyramidal around the cobalt centre. Kinetic parameters [k_{OH}/dm^3 mol^{-1} s^{-1} at 25 °C (I/mol dm^{-3}), $\Delta H^‡$/kJ mol^{-1}, $\Delta S^‡$/J K^{-1} mol^{-1}] in the ligand order (triamine)(diamine) are: (tacn)(en), 9.66 (0.1), 3.66 (1.0), 96.6, 90; (tacn)(tn), 40.6 (0.1), 15.8 (1.0), 94.4, 94; (tacn)(amp), 154 (0.1), 66.7 (1.0), 83.3, 69; *ufac*-I-(dien)(amp), 334 (0.1), 183 (1.0), 79.6, 66; *ufac*-II-(dien)(amp), 762 (0.1), 359 (1.0), 73.3, 50; L^1, 3 × 10^3 (1.0). Many of the complex ions conform in some measure to the requirements for ready hydrolysis. However, in the last case identified as a result of the initial geometry of the ion, the rate is somewhat lower than anticipated possibly owing to the increased strain involved in the attainment of the trigonal-bipyramidal five-co-ordinate intermediate.

Although a mechanism for the base hydrolysis of cobalt(III) ammine complexes was presented over fifty years ago,[1] and the π-donor behaviour of the amido group responsible for its lability established some twenty years later,[2] there is still considerable interest in such reactions.[3] Following work by Tobe and co-workers[4-6] and others[7-11] on the base hydrolysis kinetics of $[CoCl(N_5)]^{2+}$ complexes, it is considered that the incorporation of a 'flat' secondary nitrogen[4] (*i.e.* the central atom in a group of three linked donors occupying meridional sites in a co-ordinated polyamine skeleton) *cis* to the co-ordinated chloro ligand induces a marked labilization of the leaving group. The incorporation of pyridine directly co-ordinated to the cobalt(III) centre also causes an increase in the rate of base hydrolysis when compared with an aliphatic monoamine.[8] The combination of both effects results in an extraordinary lability, and base hydrolysis rate constants of ≈ 10^7 dm^3 mol^{-1} s^{-1} (25 °C) have been recorded.[6]

In order to provide further insight into the geometrical influences on these effects we have measured the base hydrolysis rate constants for a series of $[CoCl(triamine)(diamine)]^{2+}$ complexes where the triamines are tacn or dien and the diamines are en, tn, or amp.* The first triamine co-ordinates exclusively facially and the last diamine allows the incorporation of a co-ordinated pyridine ligand in a diamine chelate (Fig. 1).

Although much attention has been paid to the substitution and anation reactions of these inert metal complexes,[12-14] controversy over the mechanism, be it dissociative (D) or interchange dissociative (I_D), still remains. Elegant mixed-anion competition studies of Jackson *et al.*[15] on the reaction of $[Co(NH_3)_5X]^{n+}$ have emphasized the existence of the five-co-ordinate intermediate $[Co(NH_3)_5]^{3+}$ in these substitution reactions. Clearly any ligand structures which may influence the attainment of the intermediate species are of interest.

Experimental

Infrared spectra were recorded as KBr discs using a Bruker IFS25 spectrometer, ^{13}C NMR spectra in D_2O (relative to $SiMe_4$) using a Bruker AMX 360 MHz or a WM 250 MHz spectrometer, and the visible absorption spectra on either a Phillips PU8740 or a Cary 5 recording spectrophotometer, using, in general, reagent solutions in 10^{-2} mol dm^{-3} $HClO_4$. Base hydrolysis rates were determined using an Applied Photophysics stopped-flow apparatus with the temperature controlled to ± 0.1 °C. One syringe was charged with a solution of the complex (≈ 10^{-4} mol dm^{-3}) dissolved in aqueous $NaClO_4$ (1.0 mol dm^{-3}) solution, while the other contained the appropriate $NaOH-NaClO_4$ (I = 1.0 mol dm^{-3}) mixture.

Synthesis of $[CoCl(tacn)(diamine)][ZnCl_4]$ *Complexes* (*diamine = en, tn or amp*).—The salt $Na_3[Co(CO_3)_3]\cdot 3H_2O$ was prepared using the method of Bauer and Drinkard,[16] stored at 0 °C and discarded after 2 weeks. The compound tacn·3HCl was synthesised according to literature procedures,[17] and en, tn, amp and dien (Aldrich) were used without further purification.

One mole equivalent of tacn·3HCl (0.5 g in 15 dm^3 water) was treated at room temperature with an aqueous slurry (15 dm^3) of $Na_3[Co(CO_3)_3]\cdot 3H_2O$ (0.76 g) to give a clear red solution. One mole equivalent of the diamine was then added dropwise and the solution warmed to 40 °C. Upon slow addition of 3 mol dm^{-3} HCl (effervescence) a clear orange acidic solution was obtained. Solid $ZnCl_2$ (5 g) was added and heating at 80 °C was continued (1–2 h) to give a crystalline deposit of red $[CoCl(tacn)(diamine)][ZnCl_4]$. Yields were about 50% based on tacn·3HCl. The salts were recrystallized quantitatively from 0.1 mol dm^{-3} HCl by the addition of 3 mol dm^{-3} HCl and solid $ZnCl_2$.

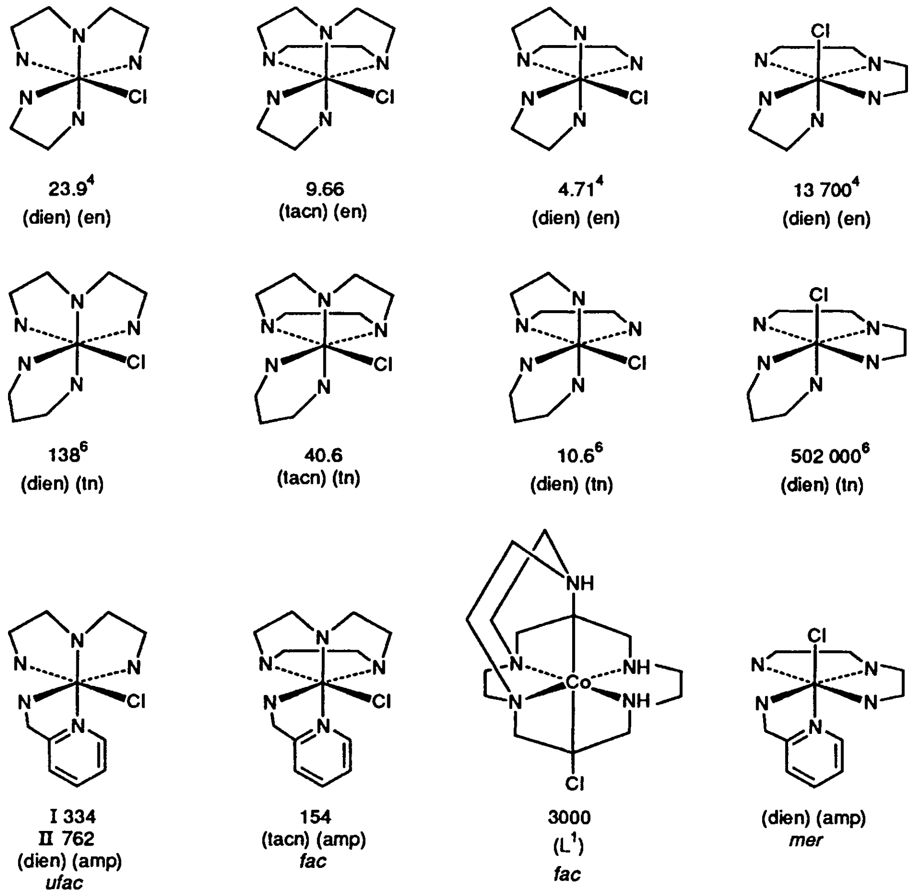
$[CoCl(tacn)(en)][ZnCl_4]$: λ_{max} = 523 (ε 79.7), 362 (77.7 dm^3 mol^{-1} cm^{-1}) and weak shoulder at 480 nm; ^{13}C NMR (D_2O), δ 51.59, 51.47, 51.14, 51.05, 44.52 and 44.40.

$[CoCl(tacn)(tn)][ZnCl_4]$: λ_{max} = 537, 371 and moderate shoulder at 480 nm; ^{13}C NMR (D_2O), δ 53.84, 53.55, 52.70, 40.69, 40.53, 40.42 and 27.85.

$[CoCl(tacn)(amp)][ZnCl_4]$: λ_{max} = 521, 361 and weak

---

* Abbreviations used: tacn = 1,4,7-triazacyclononane, dien = 3-azapentane-1,5-diamine, en = 1,2-diaminoethane, tn = 1,3-diaminopropane, and amp = 2-aminomethylpyridine.



23.9[4] (dien) (en)

9.66 (tacn) (en)

4.71[4] (dien) (en)

13 700[4] (dien) (en)

138[6] (dien) (tn)

40.6 (tacn) (tn)

10.6[6] (dien) (tn)

502 000[6] (dien) (tn)

I 334
II 762
(dien) (amp)
ufac

154
(tacn) (amp)
fac

3000
(L^1)
fac

(dien) (amp)
mer

Fig. 1 Values of k_{OH}/dm^3 mol^{-1} s^{-1} for various [chloro(pentaammine)cobalt(III)] complexes, I = 0.1 mol dm^{-3}

shoulder at 470 nm; ^{13}C NMR (D_2O), δ 165.19, 151.39, 140.99, 126.40, 122.86, 53.52, 53.33, 53.17, 49.99, 49.92, 49.33 and 49.08.

Isomers of [CoCl(dien)(amp)][$ZnCl_4$].—An aqueous mixture (50 dm^3) of $Co(NO_3)_2 \cdot 6H_2O$ (3.0 g), dien (1.0 dm^3) and amp (1.0 dm^3) was oxygenated with dioxygen gas at room temperature for 30 min to give a chocolate-brown solution. Ice cooling yielded a sticky brown-black solid. Further attempts to isolate the μ-peroxo intermediate were discontinued. However, upon addition of hydrochloric acid (50 cm^3, 6 mol dm^{-3}) and $ZnCl_2$ (5 g), and heating to 60 °C until effervescence was complete, a pink solution formed. This was left for about 2 weeks at room temperature, and the crystalline material which deposited was removed periodically. As each crop was isolated it was recrystallized as the [$ZnCl_4$]$^{2-}$ salt by dissolving in warm 0.1 mol dm^{-3} HCl and adding 3 mol dm^{-3} HCl and solid $ZnCl_2$. The yield and IR spectrum of the recrystallized material were recorded.

The first three crops (1.19 g total) had identical IR spectra and were combined and further recrystallized. The ^{13}C NMR spectrum of the dien region (δ 54.34, 53.37, 49.79, 44.36 and 43.16) is consistent with unsym-*fac* co-ordination[18] (isomer **I**). Based upon IR information, crop 4 (1.04 g) contained a new isomer and the dien-fragment ^{13}C NMR spectrum (δ 54.74, 54.28, 49.77, 43.07 and 42.78) again indicates unsym-*fac* co-ordination[18] (isomer **II**). Likewise, crop 5 (0.21 g), a third isomer, had a visible absorption spectrum indicating *mer*-dien co-ordination [λ_{max} = 360, 483 and 525 nm (sh)]. This isomer was not used in the kinetic studies.

Synthesis of [CoCl(L^1)][$ZnCl_4$].—The synthesis of the free ligand, 1,5,8,12,15-pentaazabicyclo[10.5.2]nonadecane (L^1) has been described earlier.[19] An aqueous solution (≈10 dm^3) of $Co(ClO_4)_2 \cdot 6H_2O$ (105 mg) was added to a refluxing solution of L^1 (77 mg) in ethanol–water (80:20) (total 50 dm^3). The reaction mixture turned green almost immediately, and the addition of a catalytic amount of activated charcoal yielded a pink solution. This was refluxed for 2 h and air bubbled through it. After cooling to room temperature the charcoal was filtered off and one drop of 9 mol dm^{-3} $HClO_4$ added to the filtrate. Following purification by Sephadex gel filtration, the [$ZnCl_4$]$^{2-}$ salt was prepared in the manner described above: λ_{max} = 553 (ε 80), 377 (106 dm^3 mol^{-1} cm^{-1}), moderate shoulder at 484 nm; ^{13}C NMR (D_2O), δ 61.65, 58.95, 57.95, 52.99, 51.85, 48.04 and 23.97 (Fig. 3).

Results and Discussion

Stereochemical Assignments.—Only one isomer is expected (and found) for each of [CoCl(tacn)(diamine)]$^{2+}$ (diamine = en, tn or amp). Although amp is an unsymmetrical bidentate ligand, the symmetry of the facially co-ordinated tacn requires that the end-for-end isomers are equivalent (Fig. 1).

This is not the case for [CoCl(dien)(amp)]$^{2+}$ since there are three topological forms for the (dien)(bidentate ligand) combination, *sfac*, *ufac*, and *mer*, and non-equivalent, end-for-end isomers of amp in the *ufac* and *mer* situations. Within the two *mer* combinations, the secondary NH proton can be either adjacent to or remote from the co-ordinated chloro ligand (Fig. 2). In the present study two isomeric forms have been isolated where the dien is in the *ufac* configuration, but we are unable to make an absolute assignment. Similarly, in the *mer* series the isomers with the secondary NH proton remote from the co-ordinated chloro ligand are most likely, but we are unable to make a more definite assignment. The *mer* isomer shown in Fig. 1 would be of considerable interest since cobalt(III) complexes with pyridine co-ordinated *trans* to a chloro leaving group are rare.[14]

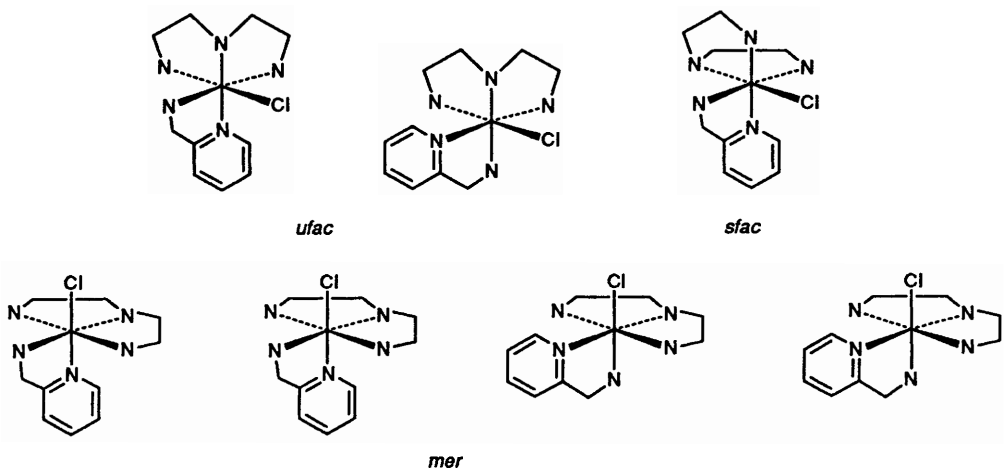


Fig. 2 Potential geometric isomers for the $[CoCl(dien)(amp)]^{2+}$ ion

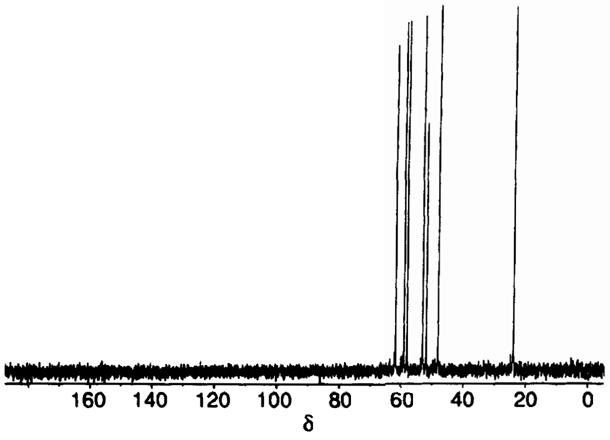


Fig. 3 The ^{13}C NMR spectrum for $[CoCl(L^1)][ZnCl_4]$ in D_2O

In the case of the cobalt(III) bicyclopentamine complex, while there is no crystallographic evidence for the structure, the ^{13}C NMR spectrum (Fig. 3) displaying seven lines is consistent with a single isomeric form of square-pyramidal conformation. This structure has been observed previously for the corresponding copper(II) complex.[19] In the present instance, the conformation of the cyclam ring is *trans* I (Fig. 1). Previous studies have shown a different geometry for the cobalt(III) complex of the precursor ligand to the macrobicycle,[20] but in this case there is a flexibility of the pendant arms to co-ordinate such that the chloro ligand is located *trans* to a tertiary amine. In the fully developed macrobicycle the geometry is consistent with the chloro ligand being adjacent to two secondary amines and *trans* to the third.

Base Hydrolysis Kinetics.—In order to avoid the problems of converting pH into $[OH^-]$ in high ionic strength media[21] which are inherent in the use of buffers or a pH-stat, we have measured the base hydrolysis rates using stopped-flow techniques in the range $[OH^-]$ 5–250 mmol dm^{-3} (I = 1.0 mol dm^{-3}, $NaClO_4$), $[Co^{III}] \approx 0.1$ mmol dm^{-3}. With the present apparatus, reactions with half-lives of < 5 ms may be measured easily, so that k_{OH} values of $> 1.4 \times 10^5$ dm^3 mol^{-1} s^{-1}, may be evaluated using the most dilute OH^- solution. Where possible, a range of $[OH^-]$ was used to check the linearity and zero intercept of the $[OH^-]$ *vs.* k_{obs} plot. These data are presented in Table 1. Activation parameters (Table 2) were evaluated from the temperature variation of k_{OH}.

The base hydrolysis reaction (1) involves two ions of different

$$[CoCl(N_5)]^{2+} + OH^- \longrightarrow [Co(OH)(N_5)]^{2+} + Cl^- \quad (1)$$

charges and is thus expected to exhibit a negative salt effect.[22] Since it is frequently useful to compare values of k_{OH} from one N_5 system to another[1] it is important to take this effect into consideration. Ionic strengths of 0.1 and 1.0 mol dm^{-3} ($NaClO_4$) are often used and for a number of the systems described here we have measured k_{OH} under both conditions. The relationship k_{OH} (I = 0.1 mol dm^{-3}) $\approx 2.2k_{OH}$ (I = 1.0 mol dm^{-3}) appears to hold quite well (Table 2). Although in complex ions such as $[CoCl(tacn)(en)]^{2+}$ or $[CoCl(tacn)(tn)]^{2+}$ the facial geometry of the macrocycle provides two secondary amine centres *cis* to the chloro group, a feature known to promote reaction, they cannot readily become 'flat' in the trigonal plane of the intermediate. For this reason these species display few of the accelatory influences outlined in the Introduction. The observed base hydrolysis rates of less than 50 cm^3 mol^{-1} s^{-1} (ref. 4) are consistent with this consideration. The tn complex reacts about four times faster than the en enalogue, a ratio similar to that found for other systems[5] where the replacement of a five- by a six-membered ring (*i.e.* tn for en) induced increases of about tenfold in base hydrolysis rates (Fig. 1). The incorporation of the pyridine ligand in the five-membered chelate ring does cause a 16-fold increase in rate relative to en in the $[CoCl(tacn)(diamine)]^{2+}$ pair, but this is not as great as found for *cis*-$[CoCl(en)_2(py)]^{2+}$ (py = pyridine) relative to *cis*-$[CoCl(en)_2(NMeH_2)]^{2+}$ (30-fold).[8] However, in the *ufac*-$[CoCl(dien)(diamine)]^{2+}$ (diamine = en or amp) pair (Fig. 1) the relative rate increase is again 30-fold. If folding to a five-co-ordinate intermediate is important in base hydrolysis, then tacn is less flexible than dien and consequently somewhat less reactive. Nevertheless, the nature of the diamine also contributes to the distortion since the (tacn)(diamine):(dien)(diamine) rate ratios increase in the order en, tn, amp (Fig. 1).

The two *ufac*-$[CoCl(dien)(amp)]^{2+}$ isomers undergo base hydrolysis relatively rapidly, one about twice as fast as the other (Table 2), and end-for-end interchange in this system (py *trans* to secondary NH/py *trans* to NH_2, Fig. 2) appears to have little influence.

The activation parameters obtained (Table 2) are normal for this type of reaction,[22] with $\Delta H^{\ddagger}$ in the range 70–90 kJ mol^{-1} and large positive entropies of activation ($\Delta S^{\ddagger}$ = 50–95 J K^{-1} mol^{-1}). This positive entropy change is in contrast to the large negative $\Delta S^{\ddagger}$ usually observed for acid hydrolysis,[22] and has been used as evidence to support the concept of a hydroxide-ion-dependent pre-equilibrium process in the mechanism.[23]

An interesting result is that obtained for the macrobicyclic complex which appears to conform to almost all the requirements for ready hydrolysis.[14] However, despite the presence of two secondary amines *cis* to the leaving chloro ligand with the ability to become planar, the rate is only about an order of

Table 1 Observed rate constants for the base hydrolysis of chloro(pentamine)cobalt(III) complexes at I = 1.0 mol dm^{-3} $NaClO_4$

(triamine)-(diamine)	T/ °C	[NaOH]/ mol dm^{-3}	k_{obs}/s^{-1}	k_{OH}/ dm^3 mol^{-1} s^{-1}
(tacn)(en)	39.0	0.25	5.93 ± 0.3	23.7 ± 1.2
		0.15	3.40 ± 0.07	22.6 ± 0.4
		0.10	2.24 ± 0.1	22.4 ± 1.0
			Mean	22.9 ± 1.0
	25.0	0.05*	0.483 ± 0.013	9.66 ± 0.26
	24.6	0.25	0.874 ± 0.02	3.50 ± 0.08
		0.15	0.497 ± 0.012	3.31 ± 0.08
		0.10	0.361 ± 0.013	3.61 ± 0.13
			Mean	3.47 ± 0.1
	11.4	0.25	0.142 ± 0.006	0.568 ± 0.02
		0.15	0.0841 ± 0.006	0.561 ± 0.04
		0.10	0.0565 ± 0.003	0.565 ± 0.03
			Mean	0.564 ± 0.03
(tacn)(tn)	39.0	0.25	20.5 ± 0.5	82.0 + 2
		0.15	14.7 ± 0.8	98.0 ± 5
		0.10	9.70 ± 0.2	97.0 ± 2
		0.05	4.16 ± 0.2	83.2 ± 4
			Mean	90.0 ± 5
	25.0	0.05*	2.03 ± 0.12	40.6 ± 2.4
	24.7	0.15	2.23 ± 0.08	14.8 ± 0.5
		0.10	1.57 ± 0.07	15.7 ± 0.7
			Mean	15.2 ± 0.4
	11.4	0.25	0.595 ± 0.01	2.38 ± 0.04
		0.15	0.360 ± 0.01	2.40 ± 0.07
		0.10	0.240 ± 0.01	2.40 ± 0.10
		0.04	0.0970 ± 0.005	2.42 ± 0.12
			Mean	2.40 ± 0.01
(tacn)(amp)	39.0	0.15	45.5 ± 1.0	303 ± 7
		0.10	31.4 ± 1.0	314 ± 10
			Mean	308 ± 5
	25.0	0.05*	7.69 ± 0.26	154 ± 5
		0.10	6.33 ± 0.31	63.3 ± 3
		0.05	3.54 ± 0.07	70.8 ± 1
			Mean	66.7 ± 2
	11.2	0.15	1.85 ± 0.09	12.3 ± 0.6
		0.10	1.21 ± 0.04	12.1 ± 0.4
			Mean	12.2 ± 0.4
I (dien)(amp)	38.6	0.15	129 ± 8	860 ± 53
	25.0	0.05*	16.7 ± 0.54	334 ± 11
		0.15	27.7 ± 1.2	184 ± 8
		0.10	18.1 ± 1.2	181 ± 12
			Mean	183 ± 3
	11.2	0.25	9.26 ± 0.7	37.0 ± 3
		0.15	6.09 ± 0.6	40.6 ± 4
		0.10	4.02 ± 0.3	40.2 ± 3
			Mean	39.3 ± 1
II (dien)(amp)	38.6	0.15	196 ± 14	1310 ± 93
	25.0	0.05*	38.1 ± 0.75	762 ± 15
		0.15	53.8 ± 1.2	359 ± 8
	11.2	0.15	11.4 ± 0.3	76.0 ± 2
		0.10	8.18 ± 0.2	81.8 ± 2
			Mean	78.9 ± 1
L^1	25.0	0.005	15.0	3000

* I = 0.1 mol dm^{-3} ($NaClO_4$).

Table 2 Second-order rate constants for the base hydrolysis of some chloro(pentamine)cobalt(III) complexes at 25.0 °C

(triamine)-(diamine)	I^a/mol dm^{-3}	k_{OH}/dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	Ref.
sfac-(dien)(en)	0.1	4.71	87.0	72	4
ufac-(dien)(en)	0.1	23.9	86.3	62	4
mer-(dien)(en)	0.1	18 700	93.2	149	4
(tacn)(en)	0.1	9.66			
	1.0	3.66	96.6 ± 0.8	90 ± 2.4	*b*
(tacn)(tn)	0.1	40.6			
	1.0	15.8	94.4 ± 1.2	94 ± 4	*b*
(tacn)(amp)	0.1	154			
	1.0	66.7	83.3 ± 1.2	69 ± 4	*b*
ufac-**I**-(dien)-(amp)	0.1	334			
	1.0	183	79.6 ± 1.7	66.6 ± 6	*b*
ufac-**II**-(dien)-(amp)	0.1	762			
	1.0	359	73.3 ± 1.3	50 ± 5	*b*
L^1	1.0	3000			*b*

[a] Using $NaClO_4$. [b] Present study.

magnitude greater than for the *ufac*-(dien)(amp) isomers. This may be the result of failure to achieve the optimum geometry with respect to the five-co-ordinate intermediate. In the most favourable circumstances, second-order rate constants ranging from 3 × 10^4 to 5 × 10^5 dm^3 mol^{-1} s^{-1} have been determined.[4] The rearrangement from a square-pyramidal configuration is accompanied by some steric strain which is exhibited in the lower rate observed in the present study. Although it is possible to construct a model of a trigonal-bipyramidal intermediate, there is strong evidence for hydrogen–hydrogen interactions and overall strain especially around the Co–N amido linkage which is somewhat shorter than other metal–nitrogen bonds.[24,25] Further examples of such effects may be available through the use of other macrobicycles now being synthesised in this laboratory and elsewhere.

Acknowledgements

We thank the Natural Sciences and Engineering Council (NSERC, Canada) for operating and equipment (Cary 5 spectrometer) support. B. R. C. acknowledges the award of a NSERC Postgraduate Scholarship.

References

1 F. J. Garrick, *Nature (London)*, 1937, **109**, 507.
2 R. G. Pearson and F. Basolo, *J. Am. Chem. Soc.*, 1956, **78**, 4878.
3 M. L. Tobe, *Advances in Inorganic and Bioinorganic Mechanisms*, ed. A. G. Sykes, Academic Press, London, 1983, vol. 2, p. 1.
4 R. A. Henderson and M. L. Tobe, *Inorg. Chem.*, 1977, **16**, 2576.
5 D. A. House and M. L. Tobe, *J. Chem. Soc., Dalton Trans.*, 1989, 853.
6 E. Ahmed, C. Chatterjee, C. J. Cooksey, M. L. Tobe, G. Williams and M. Humanes, *J. Chem. Soc., Dalton Trans.*, 1989, 645.
7 D. A. House, P. R. Norman and R. W. Hay, *Inorg. Chim. Acta*, 1980, **45**, L117.
8 J. McKenzie and D. A. House, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1843.
9 A. A. Watson, M. Prinsep and D. A. House, *Inorg. Chim. Acta*, 1986, **115**, 95.
10 P. D. Ford, K. B. Nolan and D. C. Povey, *Inorg. Chim. Acta*, 1982, **61**, 189.
11 Lim Say Dong and D. A. House, *Inorg. Chim. Acta*, 1976, **19**, 23.
12 M. C. Ghosh, P. Bhattacharya and P. Banerjee, *Coord. Chem. Rev.*, 1988, **91**, 1.
13 P. A. Lay, *Comments Inorg. Chem.*, 1991, **11**, 235.
14 M. L. Tobe, *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. McCleverty, Pergamon Press, Oxford, 1986, vol. 1, p. 281.
15 W. G. Jackson, B. C. McGregor and S. S. Jurrison, *Inorg. Chem.*, 1990, **29**, 4677.
16 H. F. Bauer and W. C. Drinkard, *J. Am. Chem. Soc.*, 1960, **82**, 5031.
17 G. H. Searle and R. J. Geue, *Aust. J. Chem.*, 1984, **37**, 959.
18 J. W. Blunt, Foo Chuk Ha and D. A. House, *Inorg. Chim. Acta*, 1979, **32**, L5.
19 D. G. Fortier and A. McAuley, *J. Am. Chem. Soc.*, 1990, **112**, 2640.
20 D. G. Fortier and A. McAuley, *J. Chem. Soc., Dalton Trans.*, 1991, 101.
21 D. A. House, *Coord. Chem. Rev.*, 1992, **114**, 249.
22 D. A. House, *Coord. Chem. Rev.*, 1977, **23**, 223.
23 J. O. Edwards, F. Monacelli and G. Ortaggi, *Inorg. Chim. Acta*, 1974, **11**, 47 (section 8).
24 R. J. Geue, T. W. Hambley, J. McB. Harrowfield, A. M. Sargeson and M. R. Snow, *J. Am. Chem. Soc.*, 1984, **106**, 5478.
25 H. B. Bürgi, in *Perspectives in Coordination Chemistry*, eds. A. F. Williams, C. Floriani and A. Merbach, Verlag Helvetica Chimica Acta, Basel, 1992, pp. 1–31.

Received 15*th September* 1992; *Paper* 2/04952J