

# Variable temperature and pressure study of the aquation reactions of cobalt(III) and chromium(III) penta- and tetra-amines †

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Preparation of a series of specific penta- and tetra-amine derivatives of Co<sup>III</sup> and Cr<sup>III</sup> with a neutral leaving ligand has been carried out in order to accomplish a fine tuning of the associativeness/dissociativeness of their substitution reactions. Spontaneous aquation reactions of the neutral ligands have been studied at variable temperature and pressure. Although rate constants and thermal activation parameters show an important degree of scatter, the values determined for the activation volumes of the substitution process illustrate the mechanistic fine tuning that may be achieved for these reactions. In all cases, in the absence of important steric constraints in the molecule, electronic inductive effects seem to be the most important factor accounting for the dissociative shifts observed both for pentaamine (*i.e.*  $\Delta V^\ddagger = +4.0$  or  $+14.0$  cm<sup>3</sup> mol<sup>-1</sup> and  $+5.2$  or  $+16.5$  cm<sup>3</sup> mol<sup>-1</sup> for the aquation of *cis*- or *trans*-[Co(MeNH<sub>2</sub>)(NH<sub>3</sub>)<sub>4</sub>(DMF)]<sup>3+</sup> and *cis*- or *trans*-[CoL<sub>15</sub>(DMF)]<sup>3+</sup> respectively, where L<sub>15</sub> represents a pentaamine macrocyclic ligand), and tetraamine systems (*i.e.*  $\Delta V^\ddagger = +4.1$  or  $+8.4$  cm<sup>3</sup> mol<sup>-1</sup> and  $-10.8$  or  $-7.4$  cm<sup>3</sup> mol<sup>-1</sup> for the aquation of *cis*-[Co(NH<sub>3</sub>)<sub>4</sub>Cl(DMAC)]<sup>2+</sup> (DMAC = dimethylacetamide) or *cis*-[Co(en)<sub>2</sub>Cl(DMAC)]<sup>2+</sup> and *cis*-[Cr(NH<sub>3</sub>)<sub>4</sub>Cl(DMF)]<sup>2+</sup> or *cis*-[Cr(en)<sub>2</sub>Cl(DMF)]<sup>2+</sup>). From the results, clear evidence is obtained which indicates that, only when the situation is borderline I<sub>a</sub>/I<sub>d</sub>, or the steric demands are increased dramatically, dissociative shifts are observed; in all other cases electronic inductive effects seem to be dominant for such a tuning of the substitution process.

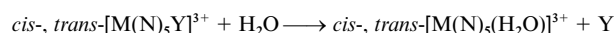
## Introduction

Differences in the mechanistic behaviour of substitution reactions on pentaam(m)inometal(III) complexes of cobalt, chromium and rhodium have attracted the interest of many groups in the past.<sup>1</sup> More recently the debate has been reopened, and the measurement of  $\Delta V^\ddagger$  for the water exchange in [M(MeNH<sub>2</sub>)<sub>5</sub>(H<sub>2</sub><sup>17</sup>O)]<sup>3+</sup> and for the aquation of neutral ligands (DMSO; dimethylacetamide, DMAC; DMF) in [M(NH<sub>3</sub>)<sub>5</sub>L]<sup>3+</sup> and [M(MeNH<sub>2</sub>)<sub>5</sub>L]<sup>3+</sup> (M = Co, Cr or Rh) has shown that a mechanistic differentiation does exist for the pentaam(m)ine complexes of these metal ions.<sup>2</sup> It is in general assumed that an increase in the steric demands of the non-participating ligands produces a dissociative shift of the intimate mechanism through which these reactions take place. In some cases even a definite I<sub>a</sub> to I<sub>d</sub> displacement has been observed.<sup>2b</sup>

Nevertheless, very little has been done to study the effects of chelation or *cis* and *trans* effects on the same mechanism. On the one hand, base-hydrolysis reactions have been studied for a number of chelate and macrocyclic complexes, but studies on the spontaneous reactions have not been pursued.<sup>3</sup> The obvious advantage of spontaneous hydrolysis studies lies in the possibility to choose neutral leaving ligands (DMF, DMSO or DMAC); by doing so, all possible electrostriction effects are eliminated, *i.e.* activation parameters related to volume and organization are 'true'.<sup>4</sup> On the other hand, although the spontaneous aquation mechanism on cobalt(III) pentaamine

complexes is assumed to be dissociatively activated, the reaction of *trans*-[Co(NH<sub>3</sub>)<sub>4</sub>(MeNH<sub>2</sub>)(X)]<sup>2+</sup> (X = Cl<sup>-</sup>, Br<sup>-</sup> or NO<sub>3</sub><sup>-</sup>) with H<sub>2</sub>O in 0.1 mol dm<sup>-3</sup> HClO<sub>4</sub> produces negative values of the  $\Delta V^\ddagger$  and  $\Delta S^\ddagger$  parameters;<sup>5</sup> electrostriction factors have been held responsible for this observed fact.

In this paper we present a study at variable temperature and pressure of the series of spontaneous aquation reactions run at [H<sup>+</sup>] = 0.1–0.2 mol dm<sup>-3</sup> (HClO<sub>4</sub>) and I = 1.0 mol dm<sup>-3</sup> (LiClO<sub>4</sub>) indicated in Scheme 1.



Scheme 1

With this study we explore the electronic and steric effects of chelation in addition to the influence of *cis* and *trans* isomerism of the substituted amine groups on the spontaneous aquation reactions. The aim is to be able to tune the substitution mechanisms in order to compare the possible shifts when going to more complicated ligand systems, such as those found in biologically relevant processes.

## Experimental

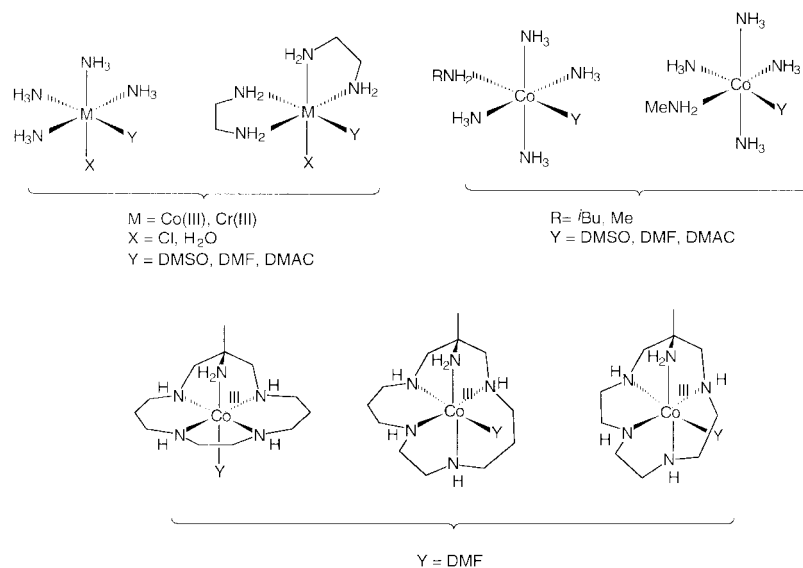
### Compounds ‡

The macrocyclic ligands L<sub>n</sub>·5HCl (n = 13- or 15-membered macrocyclic ring, see Scheme 1) and the complex [CoL<sub>13</sub>Cl]<sup>2+</sup> was prepared as previously described.<sup>6a</sup> The acyclic *cis*- and

† Supplementary data available: rotatable 3-D crystal structure diagram in CHIME format. See <http://www.rsc.org/suppdata/dt/1999/3973/>

Also available: elemental analyses, spectra and observed and calculated rate constants. For direct electronic access see <http://www.rsc.org/suppdata/dt/1999/3973/>, otherwise available from BLDSC (No. SUP 57661, 16 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (<http://www.rsc.org/dalton>).

‡ CAUTION: special care must be taken in handling perchlorate salts of compounds containing organic ligands or triflate anions. There is a high risk of explosion.



*trans*-[Co(N)<sub>5</sub>Cl]<sup>2+</sup>, *cis*-[M(N)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup> and *cis*-[M(N)<sub>4</sub>(H<sub>2</sub>O)Cl]<sup>2+</sup> species have been prepared also by published procedures.<sup>5,6b-e</sup>

***cis*- and *trans*-[CoL<sub>15</sub>Cl]<sup>2+</sup>.** To a solution of L<sub>15</sub>·5HCl (5 g) and CoCl<sub>2</sub>·6H<sub>2</sub>O (2.80 g) in water (500 cm<sup>3</sup>), 2 mol dm<sup>-3</sup> NaOH solution was added to pH 7 and the mixture aerated during 2 h at room temperature. Concentrated HCl (75 cm<sup>3</sup>) was added followed by activated charcoal (ca. 1 g), and aeration was continued for 12 h. The solution was filtered and the filtrate charged onto a Dowex 50W × 2 cation exchange column (60 × 5 cm, H<sup>+</sup> form). A minor green band eluted first with 2 mol dm<sup>-3</sup> HCl solution, and was discarded. The *cis*-[CoL<sub>15</sub>Cl]<sup>2+</sup> ion eluted soon after as a red band, well before the major band of *trans*-[CoL<sub>15</sub>Cl]<sup>2+</sup> which eluted as a broad red band. Concentration of the two separate red bands to ca. 50 cm<sup>3</sup> followed by addition of concentrated HClO<sub>4</sub> (ca. 5 cm<sup>3</sup>) gave lustrous dark red crystals of *cis*-[CoL<sub>15</sub>Cl][ClO<sub>4</sub>]<sub>2</sub> and *trans*-[CoL<sub>15</sub>Cl]Cl[ClO<sub>4</sub>]. Crystallographic and spectroscopic characterization of the *cis* isomer has been described.<sup>6a</sup> For *trans*-[CoL<sub>15</sub>Cl]Cl[ClO<sub>4</sub>]: <sup>13</sup>C NMR (D<sub>2</sub>O) δ 20.8, 21.5, 26.0, 47.2, 47.9, 49.1, 51.1, 54.5, 56.1, 58.4, 61.5 and 67.1; UV-Vis (water) λ<sub>max</sub> 542 nm (ε 94.3 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>), 460 (55) and 369 (128).

The [Co(N)<sub>5</sub>Y]<sup>3+</sup> and [M(N)<sub>4</sub>X(Y)]<sup>m+</sup> (Y = DMF, DMSO or DMAC) complexes were prepared by solvolysis and stoichiometric addition of AgClO<sub>4</sub> as Cl<sup>-</sup> abstractor, as published,<sup>6b-e</sup> the chloro complexes were dissolved in slightly acidified ligand (one drop of concentrated HClO<sub>4</sub>) and a stoichiometric amount of AgClO<sub>4</sub> was added. After AgCl precipitation was complete, addition of ethanol and diethyl ether produced the desired compounds. All complexes have been characterized by their elemental analyses, IR, NMR and UV-Vis spectra (SUP 57661).

### Kinetics

The reactions at atmospheric pressure were followed by UV-Vis spectroscopy in the full 750–300 nm range on a HP8542A instrument equipped with a multicell transport, thermostatted (±0.1 °C) with a circulation bath. Observed rate constants were derived from the absorbance *versus* time traces at the wavelengths where a maximum increase and/or decrease of absorbance was observed; all the obtained *k*<sub>obs</sub> values for all the complexes studied as a function of the leaving ligand, temperature and pressure are given in SUP 57661. No dependence of the values on the selected wavelengths was detected, as expected for reactions where a good retention of isosbestic points is observed. The general kinetic technique is that previously described.<sup>7</sup> Solutions for the kinetic runs were prepared by

dissolving the calculated amounts of the compounds, [M] = (1–5) × 10<sup>-3</sup> mol dm<sup>-3</sup>, in stock I = 1.0 mol dm<sup>-3</sup> (LiClO<sub>4</sub>), 0.1–0.2 mol dm<sup>-3</sup> HClO<sub>4</sub> solutions. In all cases no dependence on the concentration of complex and acid was detected.

For runs at elevated pressure a previously described pressurizing system and cylindrical or pillbox cells were used.<sup>8</sup> The solutions were made directly in the pressure cell by mixing the necessary amounts of solid product and stock solution medium. In these cases the absorbance *versus* time traces were recorded at a fixed wavelength on a Shimadzu UV1230 instrument fitted with fibre optics; alternatively a TIDAS instrument measuring the full spectrum was used. Rate constants were derived from exponential least squares fitting by the standard routines at a fixed wavelength or by evaluating all the spectral changes.<sup>9</sup> Although, in general, the value of the extrapolated rate constants at 1 atm is within the range measured for runs at ambient pressure, the differences in techniques and instrumentation does not allow for a usage of mixed data. Systematic errors in the temperature determination in different vessels and measuring systems translate into a uncertainty in activation entropy values. Activation enthalpies and volumes are much more reliable than entropies, since individual rate constant values are less reliable than their variation with either temperature or pressure.

Activation parameters were derived from standard Eyring or linear ln *k* *versus* *P* plots. All the values for *k*<sub>obs</sub> were the averages of 2–4 runs and the errors from the calculated values from the Eyring or ln *k* *versus* *P* plots are collected in SUP 57661; in any case they were, in general, within the 10% margin. Table 2 collects all the activation parameters derived for these reactions under the conditions used.

### Crystallography

Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections measured on an Enraf-Nonius CAD4 four circle diffractometer employing graphite monochromated Mo-Kα radiation (0.71073 Å) and operating in the ω–2θ scan mode. Data reduction and empirical absorption corrections (ψ scans) were performed with the XTAL package.<sup>10</sup> Structures were solved by heavy atom methods with SHELXS 86<sup>11</sup> and refined by full-matrix least-squares analysis with SHELXL 97.<sup>12</sup> All non-H atoms were refined with anisotropic thermal parameters except minor contributors to perchlorate O-atom disorder. Alkyl H atoms were included at estimated positions. Selected bond lengths and angles are presented in Table 1, and the atomic nomenclature is defined in Figs. 1 and 2 drawn with PLATON.<sup>13</sup>

**Table 1** Relevant bond distances (Å) for the complexes *cis*-[CoL<sub>15</sub>Cl][ClO<sub>4</sub>]<sub>2</sub>, *trans*-[CoL<sub>15</sub>Cl]Cl[ClO<sub>4</sub>], *trans*-[CoL<sub>15</sub>(H<sub>2</sub>O)][ClO<sub>4</sub>]<sub>3</sub> and *cis*-[CoL<sub>13</sub>Cl][CoCl<sub>4</sub>]<sup>a</sup>

	<i>cis</i> -[CoL <sub>15</sub> Cl][ClO <sub>4</sub> ] <sub>2</sub> <sup>a</sup>	<i>trans</i> -[CoL <sub>15</sub> Cl]Cl[ClO <sub>4</sub> ]	<i>trans</i> -[CoL <sub>15</sub> (H <sub>2</sub> O)][ClO <sub>4</sub> ] <sub>3</sub>	<i>cis</i> -[CoL <sub>13</sub> Cl][CoCl <sub>4</sub> ] <sup>a</sup>
Co–NH <sub>2</sub> R	1.962(5)	1.964(6)	1.936(4)	1.963(6)
Co–NHR'R''	1.982(5)	1.984(6)	1.962(4)	1.974(6)
	1.982(6)	1.984(6)	1.963(4)	1.930(6)
	2.005(7)	1.955(6)	1.981(4)	1.953(6)
	1.974(6)	1.959(6)	1.981(4)	1.922(6)
Co–Cl/OH <sub>2</sub>	2.273(2)	2.228(2)	1.928(3)	2.245(2)

<sup>a</sup> Ref. 6(a).**Table 2** Kinetic and activation parameters for the spontaneous aquation reactions of the *cis*- and *trans*-[Co(N)<sub>5</sub>Y]<sup>3+</sup> complexes as a function of the (N)<sub>5</sub> ligands, *cis/trans* geometry and Y ([H<sup>+</sup>] = 0.1–0.2 mol dm<sup>-3</sup> (HClO<sub>4</sub>), I = 1.0 mol dm<sup>-3</sup> (LiClO<sub>4</sub>))

(N) <sub>5</sub>	<i>cis/trans</i>	Y	10 <sup>5</sup> k <sup>298</sup> <sub>extrapolated</sub> /s <sup>-1</sup>	ΔH <sup>‡</sup> /kJ mol <sup>-1</sup>	ΔS <sup>‡</sup> /J K <sup>-1</sup> mol <sup>-1</sup>	ΔV <sup>‡</sup> /cm <sup>3</sup> mol <sup>-1</sup>
(NH <sub>2</sub> Me)(NH <sub>3</sub> ) <sub>4</sub>	<i>trans</i>	DMSO	10	89(4)	-20(11)	+10.8(6)
		DMF	0.8	108(3)	+21(8)	+14.0(20)
		DMAC	0.8	91(2)	-36(7)	+12.6(4)
(NH <sub>2</sub> Bu <sup>t</sup> )(NH <sub>3</sub> ) <sub>4</sub>	<i>trans</i>	DMF	0.8	104(2)	+5(5)	+12.0(5)
		(NH <sub>2</sub> Me)(NH <sub>3</sub> ) <sub>4</sub>	<i>cis</i>	DMF	0.3	103(2)
L <sub>15</sub>	<i>trans</i>	DMF	0.3	105(3)	+3(8) <sup>a</sup>	+16.5(9)
		DMF	1	106(2)	+17(5)	+5.2(1)
L <sub>13</sub>	<i>cis</i>	DMF	0.05	116(6)	+20(16)	+4.9(2)
		(NH <sub>3</sub> ) <sub>5</sub> <sup>b</sup>	—	DMSO	2	103(3)
(NH <sub>2</sub> Me) <sub>5</sub> <sup>c</sup>	—	DMF	0.2	111(4)	+16(8)	+2.6(4)
		DMSO	300	103(1)	+53(3)	+5.9(2)
		DMF	10	109(1)	+44(3)	+6.3(3)

<sup>a</sup> There might be a systematic uncertainty in the activation entropy reading, which produces a significant difference in the absolute values of the rate constants determined in different conditions (see SUP 57661). <sup>b</sup> Ref. 16. <sup>c</sup> Ref. 17.

**Crystal data.** *trans*-[CoL<sub>15</sub>Cl]Cl[ClO<sub>4</sub>], C<sub>12</sub>H<sub>29</sub>Cl<sub>3</sub>CoN<sub>5</sub>O<sub>4</sub>, *M* = 615.7, monoclinic, space group *C*2, *a* = 16.783(7), *b* = 7.454(2), *c* = 16.124(7) Å, β = 114.664(8)°, *U* = 2337(1) Å<sup>3</sup>, *D*<sub>c</sub> (*Z* = 4) = 1.605 g cm<sup>-3</sup>, μ(Mo-Kα) = 13.15 cm<sup>-1</sup>, *F*(000) = 984, *T* = 296 K, *N* = 1860, *N*<sub>o</sub> = 1677 [|*F*<sub>o</sub>| > 2σ(|*F*<sub>o</sub>|)], 2.2 < θ < 25°, *R*1 = 0.0466, *wR*2 = 0.1254.

*trans*-[CoL<sub>15</sub>(H<sub>2</sub>O)][ClO<sub>4</sub>]<sub>3</sub>·3H<sub>2</sub>O, C<sub>12</sub>H<sub>35</sub>Cl<sub>3</sub>CoN<sub>5</sub>O<sub>15</sub>, *M* = 654.73, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 9.599(6), *b* = 16.335(2), *c* = 16.653(9) Å, β = 100.62(3)°, *U* = 2567(2) Å<sup>3</sup>, *D*<sub>c</sub> (*Z* = 4) = 1.694 g cm<sup>-3</sup>, μ(Mo-Kα) = 10.58 cm<sup>-1</sup>, *F*(000) = 1360, *T* = 296 K, *N* = 4581, *N*<sub>o</sub> = 3916 [|*F*<sub>o</sub>| > 2σ(|*F*<sub>o</sub>|)], 2.2 < θ < 25°, *R*1 = 0.0669, *wR*2 = 0.1927.

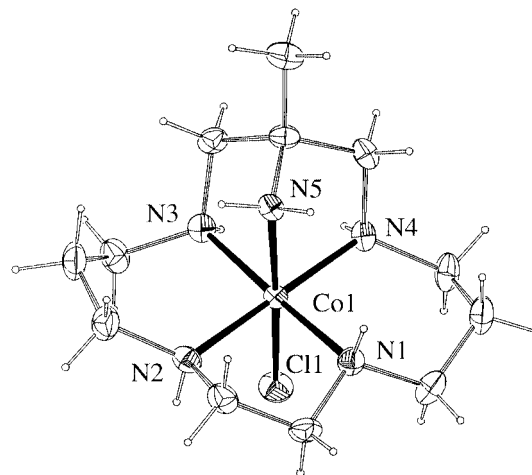
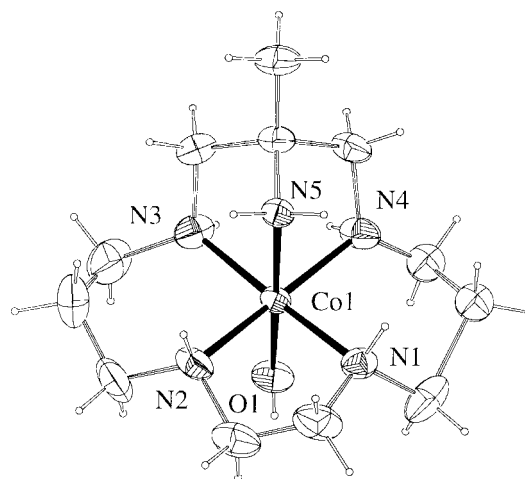
CCDC reference number 186/1680.

See <http://www.rsc.org/suppdata/dt/1999/3973/> for crystallographic files in .cif format.

## Results and discussion

In the crystal structure of *trans*-[CoL<sub>15</sub>Cl]Cl[ClO<sub>4</sub>] the complex cation and Cl<sup>-</sup> anion are on general sites while there are two independent ClO<sub>4</sub><sup>-</sup> anions both disordered about a twofold axis. The co-ordination geometry is defined in Fig. 1, where the unusual asymmetric *trans-II* configuration of the four secondary N-donors is revealed. This asymmetry was also apparent in the <sup>13</sup>C NMR spectrum of the complex, which revealed all twelve C atoms to be magnetically inequivalent. The coordinate bond lengths (Table 1) are comparable with those of the corresponding *cis* isomer.<sup>6a</sup> In the crystal structure of the aqua derivative *trans*-[CoL<sub>15</sub>(H<sub>2</sub>O)][ClO<sub>4</sub>]<sub>3</sub> (Fig. 2) the macrocycle adopts the more symmetrical *trans-III* configuration. Disorder in the six-membered chelate ring containing N(1) and N(4) was refined as a mixture of a chair and twisted-boat conformations.

Tables 2, 3 and 4 collect all the relevant kinetic and activation parameters for all the reactions of the (N)<sub>5</sub> and (N)<sub>4</sub> systems presented in this paper. For all the spontaneous aquation reactions of the O-bonded DMF, DMAC and DMSO ligands the values of the rate constants and thermal and pressure activation parameters are within the expected range for this type of reaction.<sup>14</sup> For the Co<sup>III</sup>(N)<sub>5</sub> systems all the values found

**Fig. 1** A PLATON drawing of the cation *trans*-[CoL<sub>15</sub>Cl]Cl<sup>2+</sup>.**Fig. 2** A PLATON drawing of the cation *trans*-[CoL<sub>15</sub>(H<sub>2</sub>O)]<sup>3+</sup>.

**Table 3** Kinetic and activation parameters for the spontaneous reactions of the *cis*-[Co(N)<sub>4</sub>X(Y)]<sup>2,3+</sup> complexes as a function of (N)<sub>4</sub>, X and Y ([H<sup>+</sup>] = 0.1–0.2 mol dm<sup>-3</sup> (HClO<sub>4</sub>), I = 1.0 mol dm<sup>-3</sup> (LiClO<sub>4</sub>))

(N) <sub>4</sub>	X	Y	10 <sup>5</sup> k <sup>298</sup> <sub>extrapolated</sub> /s <sup>-1</sup>	ΔH <sup>‡</sup> /kJ mol <sup>-1</sup>	ΔS <sup>‡</sup> /J K <sup>-1</sup> mol <sup>-1</sup>	ΔV <sup>‡</sup> /cm <sup>3</sup> mol <sup>-1</sup>
(NH <sub>3</sub> ) <sub>4</sub>	Cl	DMSO	1	112(1)	+38(10) <sup>a</sup>	+3.7(1)
		DMF	1	111(5)	+34(16) <sup>a</sup>	+4.9(3)
		DMAC	3	99(6)	+3(17) <sup>a</sup>	+4.1(1)
	H <sub>2</sub> O	DMSO	1	101(2)	+1(5) <sup>a</sup>	+8.3(4)
		DMF	0.1	120(1)	+42(3) <sup>a</sup>	+8.7(4)
		DMAC	9	97(1)	2(3) <sup>a</sup>	+8.3(6)
(en) <sub>2</sub>	Cl	DMSO	2	106(6)	+19(17) <sup>a</sup>	+6.6(3)
		DMF	0.4	114(2)	+35(6)	+6.0(3)
		DMAC	0.1	123(3)	+47(15) <sup>a</sup>	+8.4(6)
	H <sub>2</sub> O	DMSO	0.2	115(5)	+33(13) <sup>a</sup>	+10.1(4)
		DMF	0.08	127(1)	+64(3) <sup>a</sup>	+11.1(2)
		DMAC	2	103(2)	-10(7) <sup>a</sup>	+11.3(3)

<sup>a</sup> There might be a systematic uncertainty in the activation entropy reading, which produces a significant difference in the absolute values of the rate constants determined in different conditions (see SUP 57661).

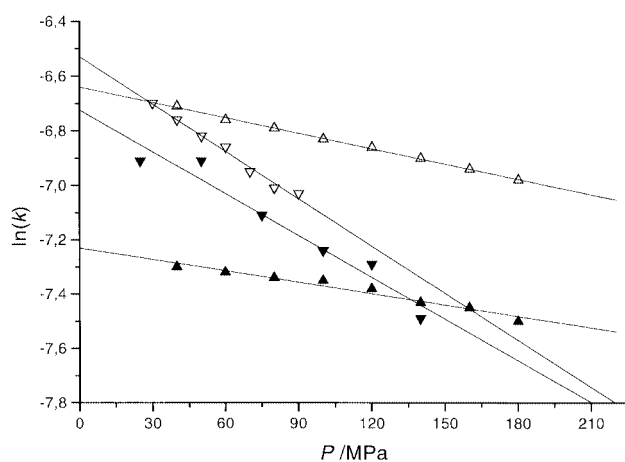
**Table 4** Kinetic and activation parameters for the spontaneous aquation reactions of the *cis* [Cr(N)<sub>4</sub>X(Y)]<sup>2,3+</sup> complexes as a function of (N)<sub>4</sub>, X and Y ([H<sup>+</sup>] = 0.1–0.2 mol dm<sup>-3</sup> (HClO<sub>4</sub>), I = 1.0 mol dm<sup>-3</sup> (LiClO<sub>4</sub>))

(N) <sub>4</sub>	X	Y	10 <sup>5</sup> k <sup>298</sup> <sub>extrapolated</sub> /s <sup>-1</sup>	ΔH <sup>‡</sup> /kJ mol <sup>-1</sup>	ΔS <sup>‡</sup> /J K <sup>-1</sup> mol <sup>-1</sup>	ΔV <sup>‡</sup> /cm <sup>3</sup> mol <sup>-1</sup>
(NH <sub>3</sub> ) <sub>4</sub>	Cl	DMSO	2	84(5)	-55(6) <sup>a</sup>	-6.3(4)
		DMF	2	73(3)	-86(8) <sup>a</sup>	-10.8(7)
		DMAC	4	77(3)	-71(6)	-10.1(4)
	H <sub>2</sub> O	DMSO	0.7	93(1)	-31(4)	-2.0(1)
		DMF	0.5	96(2)	-26(5)	-3.9(2)
		DMAC	0.6	97(2)	-19(5)	-4.0(2)
(en) <sub>2</sub>	Cl	DMSO	1	100(2)	2(7) <sup>a</sup>	-3.7(5)
		DMF	1	94(7)	-23(21) <sup>a</sup>	-7.4(12)
		DMAC	5	85(2)	-45(5)	-7.0(16)
	H <sub>2</sub> O	DMSO	10	78(1)	-59(2)	-2.3(1)
		DMF	8	80(1)	-55(5)	-2.5(1)
		DMAC	7	86(1)	-38(2)	-2.9(1)

<sup>a</sup> There might be a systematic uncertainty in the activation entropy reading, which produces a significant difference in the absolute values of the rate constants determined in different conditions (see SUP 57661).

for the activation parameters are as a whole, positive, as expected for reactions taking place *via* a dissociatively activated mechanism; nevertheless, the values found for ΔS<sup>‡</sup> are in the low limit of those determined for similar systems, as indicated in Table 2. With respect to the (N)<sub>4</sub> systems (Tables 3 and 4), the values found for ΔH<sup>‡</sup> for the reactions of the chromium(III) complexes are smaller than those for the corresponding cobalt(III) analogue as a whole, which is also in the line with that found for similar systems.<sup>2b</sup> As for the values determined for ΔS<sup>‡</sup> and ΔV<sup>‡</sup>, they are all clearly negative for the chromium(III) derivatives (associatively activated substitution reactions) in contrast to those for the corresponding cobalt(III) complexes. Taking into account all the mechanistic considerations about electrostriction and aquation of complexes bearing non-charged O-donor leaving ligands, the results as a whole are quite a good indicator of the mechanistic shifts that can be obtained for subtle changes in these systems.<sup>2</sup> The stereoretention of the *cis/trans* isomers for both (N)<sub>5</sub> and (N)<sub>4</sub> systems, during the timescale of the processes studied, has been checked by UV-Vis spectrophotometry by comparison with the known spectra of [Co(N)<sub>5</sub>(H<sub>2</sub>O)]<sup>3+</sup>, [M(N)<sub>4</sub>Cl(H<sub>2</sub>O)]<sup>2+</sup> and [M(N)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup> systems.<sup>6,15</sup>

For the Co(N)<sub>5</sub> systems indicated in Table 2 it is clear that dramatic differences occur according to the geometry and steric demands of the (N)<sub>5</sub> ligands when all the series of DMF complexes are considered. The differences between the *cis* and *trans* isomers of both the (NH<sub>2</sub>Me)(NH<sub>3</sub>)<sub>4</sub> and L<sub>15</sub> systems are dramatic. In both cases, taking into account the errors involved, the values determined for ΔH<sup>‡</sup> and ΔS<sup>‡</sup> are fairly similar (independent of spatial distribution of the ligands), but a drastic increase (Fig. 3) in the values of ΔV<sup>‡</sup> is found on going



**Fig. 3** Plot of  $\ln k$  versus  $P$  for some of the Co<sup>III</sup>(N)<sub>5</sub> systems studied with Y = DMF.  $\Delta$ : (N)<sub>5</sub> = *cis*-L<sub>15</sub>, 61.7 °C.  $\nabla$ : (N)<sub>5</sub> = *trans*-L<sub>15</sub>, 70.8 °C;  $\blacktriangledown$ : (N)<sub>5</sub> = *cis*-(MeNH<sub>2</sub>)(NH<sub>3</sub>)<sub>4</sub>, 70.8 °C.  $\blacktriangle$ : (N)<sub>5</sub> = *trans*-(MeNH<sub>2</sub>)(NH<sub>3</sub>)<sub>4</sub>, 59.8 °C.

from a *cis* to a *trans* geometrical arrangement of the ligands (see Scheme 1). It seems that, although the enthalpic and entropic barrier is independent of the geometry of the inert skeleton of the complexes, the actual expansion of the molecule on going to the transition state is much larger for the *trans* complexes (+14.0 versus +4.0 and +16.5 versus +5.2 cm<sup>3</sup> mol<sup>-1</sup>). For processes taking place with the same free energy barrier, results for the non-macrocyclic complexes indicate that a smaller degree of expansion occurs on going to the transition

state with the more sterically (*trans* versus *cis*) demanding ligand systems. In addition, a greater  $\sigma$ -donor capacity ( $pK_b(\text{NH}_3) = 9.32$ ;  $pK_b(\text{MeNH}_2) = 10.72$ ) of the *trans* ligand results in a greater degree of expansion on going to the transition state. In each case the mechanism becomes more dissociative. The differences found for the *cis*-( $\text{NH}_2\text{Me}$ )( $\text{NH}_3$ )<sub>4</sub> and the published ( $\text{NH}_3$ )<sub>5</sub> systems<sup>16</sup> are very clarifying. In this case, apart from its steric effect, the presence of a *cis*-methylamine ligand instead of  $\text{NH}_3$  should only slightly increase the electron density on the cobalt(III) centre.<sup>4</sup> The results indicated in Table 2 agree quite well with the assumption that the  $\sigma$ -donor capability of the *trans* ligand is much more dominant. In this respect, the differences between the ( $\text{NH}_3$ )<sub>5</sub> and *cis*-( $\text{NH}_2\text{Me}$ )( $\text{NH}_3$ )<sub>4</sub> systems are very small when compared with those involving the *trans*-( $\text{NH}_2\text{Me}$ )( $\text{NH}_3$ )<sub>4</sub> system; in the latter case, only electronic inductive factors (*trans* influence/effect) can account for the differences. As for the results involving the ( $\text{NH}_2\text{Me}$ )<sub>5</sub>/Co<sup>III</sup> system published,<sup>17</sup> the values found for  $\Delta V^\ddagger$  are in the middle of those for the *cis*-( $\text{NH}_2\text{Me}$ )( $\text{NH}_3$ )<sub>4</sub> and *trans*-( $\text{NH}_2\text{Me}$ )( $\text{NH}_3$ )<sub>4</sub> systems. Only in this case, the much greater steric demands of the inert skeleton appear partially to counterbalance the above-mentioned *trans* effect. The Co–Cl bond length in the existing crystal structure data for the [ $\text{Co}(\text{NH}_3)_5\text{Cl}$ ]<sup>2+</sup>, [ $\text{Co}(\text{MeNH}_2)_5\text{Cl}$ ]<sup>2+</sup> and *trans*-[ $\text{Co}(\text{MeNH}_2)(\text{NH}_3)_4\text{Cl}$ ]<sup>2+</sup> cations<sup>14,18</sup> can be misleading given the fact that for the latter complex the Co–Cl distance is significantly shorter than expected while Co– $\text{NH}_2\text{Me}$  is longer. Packing forces derived from the different counter anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{ClO}_4^-$  respectively) can be held responsible for this fact, as found for similar systems ([ $\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})$ ]<sup>3+</sup>/ $\text{IO}_3^-/\text{S}_2\text{O}_6^{2-}$ ).<sup>19</sup> Electron spectroscopy for chemical analysis (ESCA) data available for the [ $\text{Co}(\text{NH}_3)_5\text{Cl}$ ]<sup>2+</sup>/*trans*-[ $\text{Co}(\text{MeNH}_2)(\text{NH}_3)_4\text{Cl}$ ]<sup>2+</sup>/ $[\text{Co}(\text{MeNH}_2)_5\text{Cl}]^{2+}$  systems clearly support the electronic inductive effect of the Me substituent on the amine on the *trans* Co–Cl bond.<sup>20</sup> In any case, as reported recently, any attempt to separate electronic effects from intramolecular strain in co-ordination compounds is bound to be fruitless.<sup>21</sup> Finally, as found in other similar studies carried out in this laboratory,<sup>2b</sup> no meaningful differences are found when DMSO, DMF and DMAC are compared for the same Co<sup>III</sup>(N)<sub>5</sub> system (*trans*-[ $\text{Co}(\text{NH}_2\text{Me})(\text{NH}_3)_4\text{Y}$ ]<sup>3+</sup>) indicating that no further changes are imposed by the leaving ligand in these cases.

Looking at the macrocyclic systems, large differences between the *trans* and *cis* isomers of Co<sup>III</sup>L<sub>15</sub> are observed. In this case the greater basicity of the secondary versus primary amine donors in the macrocycle does not seem to produce the expected *trans* labilizing effects. The data in Table 2 indicate a larger degree of dissociation for the *trans* isomer (see Scheme 1), whereas the anticipated lower basicity of the pendant primary amine should result in a diminished *trans* labilizing effect of the DMF leaving ligand. Nevertheless, the crystal structures of *cis*-[ $\text{CoL}_{15}\text{Cl}$ ]<sup>2+</sup>, *trans*-[ $\text{CoL}_{15}\text{Cl}$ ]<sup>2+</sup> and *trans*-[ $\text{CoL}_{15}(\text{H}_2\text{O})$ ]<sup>3+</sup> indicate that the Co– $\text{NH}_2\text{R}$  bond distances are shorter, in all cases, than the average for the Co–NHRR' bond (1.962 versus 1.986 Å, 1.964 versus 1.971 Å, and 1.936 versus 1.972 Å for the three complexes respectively). These results indicate, as pointed out above, that despite the electronic differences in the N-donors, the steric demands of the macrocyclic ligand are dominant; the Co– $\text{NH}_2\text{R}$  bond being shorter dominates the weakening of the Co–DMF bond.<sup>21</sup> When one compares the *cis* isomers of Co<sup>III</sup>L<sub>13</sub> and Co<sup>III</sup>L<sub>15</sub>, the data in Table 2 indicate that the expansion of the complex on going to the transition state for both systems is practically the same, which indicates that macrocyclic ring size effects are not as important as *trans/cis* isomerism.

With reference to the *cis*-[ $\text{Co}(\text{N})_4\text{X}(\text{Y})$ ]<sup>2,3+</sup> complexes the results collected in Table 3 are much more homogeneous, as expected when no drastic electronic changes are taking place within the inert co-ordination skeleton of the cobalt centre. All activation enthalpy values are of the same order as those found

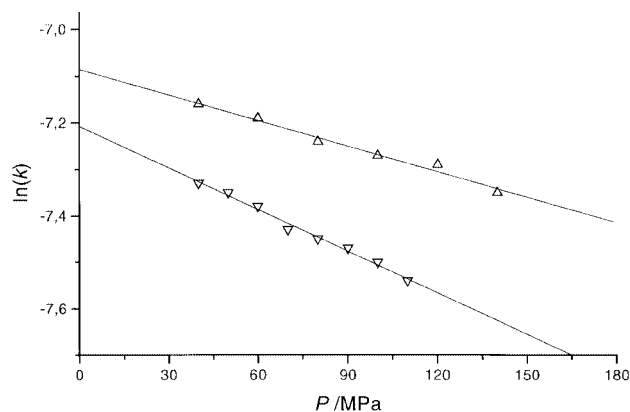


Fig. 4 Plot of  $\ln k$  versus  $P$  for some of the  $\text{Co}^{\text{III}}(\text{N})_4$  systems studied with  $\text{Y} = \text{DMF}$ .  $\Delta$ : ( $\text{N})_4\text{X} = \text{cis}-(\text{NH}_3)_4\text{Cl}$ , 52.4 °C.  $\nabla$ : ( $\text{N})_4\text{X} = \text{cis}-(\text{NH}_3)_4(\text{H}_2\text{O})$ , 70.8 °C.

for similar  $\text{Co}^{\text{III}}(\text{N})_5$  systems. The available data for substitution processes on  $\text{Co}^{\text{III}}(\text{N})_4$  systems are related to base hydrolysis or isomerization reactions occurring through a conjugate-base mechanism. Only spontaneous aquation of halide and pseudo-halide ligands has been studied;<sup>22</sup> differences of timescale and electrostriction makes any comparison very difficult. All the determined activation entropies are clearly positive although with an important scatter; activation volumes are much more reliable and clearly positive in all cases, indicating that the substitution process is activated dissociatively. The absence of important electrostriction factors within the reactions chosen makes both these two values much more indicative of the process taking place. As indicated before for the (N)<sub>5</sub> systems, no shift in the degree of dissociation is observed for a given *cis*-[ $\text{Co}(\text{N})_4\text{X}(\text{Y})$ ]<sup>2,3+</sup> complex on changing the leaving ligand (Y). It seems clear that these small variations only affect the degree of associativeness–dissociativeness when the system is very close to the I<sub>a</sub>/I<sub>4</sub> borderline classification, which is not the case for the *cis*-[ $\text{Co}(\text{N})_4\text{X}(\text{Y})$ ]<sup>2,3+</sup> system.<sup>2b</sup> In general the values determined for the volumes of activation in these substitution reactions follow two tendencies: (i) activation volumes for the aquation of ligands Y are more positive for X = H<sub>2</sub>O than for X = Cl<sup>−</sup> (Fig. 4); (ii) these values are also more positive for (N)<sub>4</sub> = (en)<sub>2</sub> than for (N)<sub>4</sub> = (NH<sub>3</sub>)<sub>4</sub>. Taking electronic and steric effects into account the results can easily be rationalized.

On the one hand, substitution of a chloro by an aqua ligand reduces steric hindrance in the co-ordination sphere; the Cl<sup>−</sup> ligand being larger and the strain reaching a maximum for a *cis* geometry, the immediate consequence is that steric factors cannot be held responsible for the trends observed. On the other hand, important electronic factors point to a much more favoured dissociation of the leaving ligand on *cis*-[ $\text{Co}(\text{N})_4\text{Cl}(\text{Y})$ ]<sup>2+</sup> when compared with the *cis*-[ $\text{Co}(\text{N})_4(\text{H}_2\text{O})\text{Y}$ ]<sup>3+</sup>, as detected *via* the determined  $\Delta V^\ddagger$  collected in Table 3. Although simple charge factors (+2 versus +3) could explain this fact, the trends observed for the chromium(III) complexes (see Table 4) studied do not agree with this; the absence of important electrostriction factors and outer-sphere complexation seems to reduce these charge factors to a minimum. A common explanation to the two (Co<sup>III</sup> and Cr<sup>III</sup>) systems comes from a possible necessary elongation of the Co<sup>III</sup>–Cl bond to go to the transition state, so increasing its dipole moment, in comparison with the Co<sup>III</sup>–OH<sub>2</sub> system; this fact has to produce an important increase in electrostriction and a more negative activation volume. Further explanation comes from considering inductive factors due to the poorer basicity of the Cl<sup>−</sup> ligand, and the small  $\pi$ -bonding capacity of a d<sup>6</sup> complex<sup>23</sup> which would produce a metal centre with better Lewis acid characteristics than for the aqua derivative. If the comparison is done between the tetraammine and the bis(ethylenediamine) derivatives, the more positive values found for the bis-chelate derivatives can be

related with the higher basicity of primary amines compared with that of ammonia. The N–Co–N angle of ethylenediamine complexes, being around 85.4;§ indicates that on dissociation of the leaving ligand no greater steric relief is produced with respect to the tetraammine complexes; no steric reasons can be held responsible for the larger degree of dissociation in *cis*-[Co(en)<sub>2</sub>X(Y)]<sup>2+3+</sup>. Finally, it is surprising that comparison of the *cis*-[Co(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)Y]<sup>3+</sup> aquation activation volume data (Table 3) with those for [Co(NH<sub>3</sub>)<sub>5</sub>Y]<sup>3+</sup> indicates that neither the stronger electron donation of the ammine ligand, compared with aqua, nor differences in size, can be held responsible for the enlarged degree of dissociation in the *cis*-[Co(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)Y]<sup>3+</sup> series.

For the Cr<sup>III</sup>(N)<sub>4</sub> systems studied, whose kinetic and activation data are collected in Table 4, results are completely in line with the expected associativeness generally established for pentaam(m)ine chromium(III) complexes.<sup>1,14b</sup> In all cases entropies and volumes of activation are negative indicating both contraction and ordering on going to the transition state; enthalpies of activation are much more scattered than for the analogous cobalt(III) compounds as expected for an associatively activated mechanism.<sup>2b</sup> At first glance it is clear from the results obtained that the drastic dissociative shift observed for the transition from Cr<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub> to Cr<sup>III</sup>(MeNH<sub>2</sub>)<sub>5</sub> systems is not taking place with our complexes,<sup>2b</sup> even the observed small I<sub>a</sub> shift observed for the latter systems on changing the leaving ligand does not take place in the present study. For the series of complexes studied all the chloro derivatives, *cis*-[Cr(N)<sub>4</sub>Cl(Y)]<sup>2+</sup>, show a greater degree of association as seen from the ΔV<sup>‡</sup> values collected (the large error and scatter found for the ΔS<sup>‡</sup> values makes them less reliable, as usual) in Table 4. In the first place, this fact is in good agreement with what has been observed for the analogous cobalt(III) derivatives; the larger size of the chloro ligand does not induce a lower degree of association. Only its worse Lewis base characteristics, when compared with the aqua ligand, explain the more associative character of the transition state for the substitution on *cis*-[Cr(N)<sub>4</sub>Cl(Y)]<sup>2+</sup> than that on *cis*-[Cr(N)<sub>4</sub>(H<sub>2</sub>O)Y]<sup>3+</sup>. Nevertheless, in this case, the established much more important degree of Cr–Cl π bonding in chromium(III) complexes (d<sup>3</sup>) compared with their cobalt(III) analogues can also explain this fact; the Cr–Cl bond distance has to be much shorter for its greater double bond character and steric hindrance is severely diminished. In fact, it has been claimed that for aquation reactions of [Cr(N)<sub>5</sub>Cl]<sup>2+</sup> complexes this degree of π bonding plays a key role in a certain dissociative character of the mechanism in pentaam(m)ine complexes.<sup>23</sup>

As for changes from (NH<sub>3</sub>)<sub>4</sub> to (en)<sub>2</sub> ligands in the inert coordination sphere, the results collected in Table 4 indicate that for the chelating ligand the degree of associativeness is less. Again, as for the analogous cobalt(III) derivatives, no steric reasons can be held responsible for this fact (N–Cr–N angle of ethylenediamine complexes being around 82.5°); only the greater basicity of the N donors can be held responsible for a greater electron density on the chromium(III) centre that hinders partial association of the entering ligand. In this respect, the differences in the Y hydrolysis reactions of the chloro or aqua (X) complexes on going from (NH<sub>3</sub>)<sub>4</sub> to (en)<sub>2</sub> are very indicative. While the rate constants and enthalpies of activation are, as a whole, more favourable for substitution on *cis*-[Cr(NH<sub>3</sub>)<sub>4</sub>Cl(Y)]<sup>2+</sup> when compared to *cis*-[Cr(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)Y]<sup>3+</sup>, the trend is reversed on going to the ethylenediamine derivatives. That is, substitution is more favourable on *cis*-[Cr(en)<sub>2</sub>(H<sub>2</sub>O)Y]<sup>3+</sup> than on *cis*-[Cr(en)<sub>2</sub>Cl(Y)]<sup>2+</sup>. In the

latter, electronic donation from both the en nitrogens and the π bond from the chloro ligand to the chromium(III) centre is bound to produce a certain degree of retardation of the reaction rate for association of the entering ligand, if the degree of association of the transition state is considered independently. As for the dissociative shift found in the spontaneous aquation reactions (Table 4) of *cis*-[Cr(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)Y]<sup>3+</sup> with respect to [Cr(NH<sub>3</sub>)<sub>5</sub>Y]<sup>3+</sup> (DMSO, –3.2 cm<sup>3</sup> mol<sup>-1</sup>; DMF, –7.4 cm<sup>3</sup> mol<sup>-1</sup>; DMAC, –6.2 cm<sup>3</sup> mol<sup>-1</sup>),<sup>21</sup> similarly to that found for the cobalt(III) systems, neither the stronger donor characteristics of the NH<sub>3</sub> ligand with respect to H<sub>2</sub>O nor differences in size can be held responsible.

Another factor that becomes apparent in Table 4 data is the less negative values found for the activation volume for hydrolysis of DMSO in all the complexes. Given all the above-mentioned considerations, the different basicity of the O donor group for these complexes when compared with the analogous DMF and DMAC derivatives can not explain the observations. The only plausible interpretation we can postulate is related with the charge separation taking place on slight dissociation of the DMF and DMAC ligands on association of the entering water ligand (I<sub>a</sub>); this effect will bring electrostriction factors into play and a greater contraction would occur during the process. This fact should be observed more clearly for the cobalt(III) analogues given their dissociative activation; data in Table 3 unambiguously indicate that this is not the case as well as for the Cr<sup>III</sup>(N<sub>5</sub>) and Co<sup>III</sup>(N<sub>5</sub>) systems in the literature.<sup>14</sup>

## Conclusions

The spontaneous aquation reactions of *cis/trans*-[Co(N)<sub>5</sub>Y]<sup>3+</sup> and *cis*-[Co(N)<sub>4</sub>X(Y)]<sup>2+3+</sup> studied have indicated that electronic factors, such as an increase in the basicity of the ligands, play a key role in the fine tuning of the degree of associativeness or dissociativeness of the reaction mechanism. Comparison with systems where the steric demands are much larger indicates that only when steric hindrance is dramatically increased, or on the I<sub>a</sub>/I<sub>a</sub> borderline, a sterically driven dissociative shift takes place. The importance of such an inductive dissociative effect is made more evident when a *trans* effect/influence is possible given the stereoisomerism of the ligands in the inert skeleton. As a whole, this work produces a new insight on the fine tuning of substitution reactions; it is the result of a balance between the steric and electronic changes in the system. The effect these changes produce depends not only on the modifications themselves, but on *where* the system is on the mechanistic continuum, and *how* it is being modified.

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Paper 9/07895I