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Do Solid State Co-Cl Bond Lengths in $[CoCl(N)_5]^{2}$ Complexes Relate to Substitution Lability?-Experience Suggests Not

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Do Solid State Co–Cl Bond Lengths in $[CoCl(N)_5]^{2+}$ Complexes Relate to Substitution Lability?— Experience Suggests Not

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There is no apparent correlation between ground state Co–Cl bond length in $[CoCl(N)_5]^{2+}$ complexes and the solvolysis reaction rate.

Key Words: *octahedral substitution, Co–Cl bond length, chloroam(m)ine complexes, reaction rates*

Abbreviations: en = $NH_2(CH_2)_2NH_2$; pnol = $CH_3CH(OH)CH_2NH_2$; py = pyridine; imid = imidazole; benzimid = benzimidazole; 4-NO_2-imid = 4-nitro-imidazole; 4-Cl-imid = 4-chloro-imidazole; $theo^-$ = theophylline anion; ad^- = adenine anion; dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$; bn = $NH_2(CH_2)_4NH_2$; ampy = 2-aminomethyl-pyridine; dpt = $NH_2(CH_2)_3NH(CH_2)_3NH_2$; pn = $NH_2CH_2CH(CH_3)NH_2$; NMetn = $CH_3NH(CH_2)_3NH_2$; tacn = 1,4,7-triazacyclononane; 2,2,3-tet = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_3NH_2$; trien = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$; tren = $N(CH_2CH_2NH_2)_3$; bipy = 2,2′-bipyridine; phen = 1,10-phenanthroline; tetraen = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH(NH_2)_2NH_2$; Metetraen = $NH_2CH_2CH(CH_3)NH(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$; trenenol = $NH_2CH_2CH(OH)N[(CH_2)_2NH_2](CH_2)_2NH(CH_2)_2NH_2$

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1. ACID HYDROLYSIS (AQUATION)

Aqueous acidic solutions of $[CoCl(N)_5]^{2+}$ [$(N)_5$ = any combination of five nitrogen-donor ligands] undergo spontaneous thermal solvolysis (aquation) according to Eq. (1):

$$[CoCl(N)_5]^{2+} + H_2O \xrightarrow{k_H} [Co(N)_5(OH_2)]^{3+} + Cl^- \qquad (1)$$

In the absence of added chloride ion, this process generally proceeds to completion, but the reverse reaction (anation)[1] takes place at high chloride ion concentration, and, at intermediate chloride ion concentrations, an equilibrium is established.

The rate of reaction is usually measured in acidic aqueous media (pH 1–3) to avoid any possible contribution from base hydrolysis (OH^- as the reactant, see later) as there are some $[CoCl(N_5)]^{2+}$ systems that are so sensitive to base hydrolysis that even at pH = 3, the major solvolysis path is via this process.[2] Perchloric, trifluoroacetic, triflic and toluenesulfonic are the acids of choice, as these anions are generally regarded as weak ion-pairing and non-coordinating and will not compete in the reverse of (1).[3] The reaction rate is generally independent of $[H^+]$ and ionic strength in the range pH = 1–3 and $I < 0.1$ *M*.

The extent of reaction vs. time can be monitored either spectrophotometrically or by chloride release titration. The process is generally slow at room temperature (e.g., $t_{1/2}$ = 4.5 days, $(N)_5 = NH_3$), and most reaction rate studies have been made at elevated temperatures (50–80°C) and the data extrapolated to 25°C using conventional activation parameters ($\Delta H^{\#}$ and $\Delta S^{\#}$). In many cases, only a narrow temperature range has been employed (15–20°C), and an accuracy of better than ±2 kJ mol^{-1} in $\Delta H^{\#}$ and ±8 JK^{-1} mol^{-1} in $\Delta S^{\#}$ is not justified.[4]

2. HG^{2+}-ASSISTED AQUATION

The rate of aquation can be increased by addition of a chloride ion abstracting agent, e.g., Hg(II), to give the so-called Hg^{2+}-assisted aquation reaction [Eq.(2)][5].

$$[CoCl(N)_5]^{2+} + Hg^{2+} + H_2O \rightarrow [Co(N)_5(OH_2)]^{3+} + HgCl^+ \qquad (2)$$

Here, the reaction scheme for the process is usually described by the sequence

$$[CoCl(N)_5]^{2+} + Hg^{2+} \overset{K}{\rightleftharpoons} [(N)_5CoClHg]^{4+} \quad (3)$$

$$[(N)_5CoClHg]^{4+} + H_2O \xrightarrow{k} \text{products} \quad (4)$$

Thus k_{obs} for the reaction will be a composite quantity with contributions from K and k. If K can be regarded as constant for all $[CoCl(N)_5]^{2+}$ species, then k_H [Eq. (1)] should parallel k [Eq. (4)] provided both solvolysis processes proceed via a similar mechanism.

Using the spectrophotometric technique, isosbestic points in the visible absorption spectrum for reactions (**1**) and (**2**) should be identical if a common aqua ion is formed, as both Hg(II) species are colourless. Although the $HgCl^+$ product may also assist in the chloride release process,[5,6] the overall reaction rate can be expressed as

$$-d[CoCl(N)_5^{2+}]/dt = k_{Hg}[CoCl(N)_5^{2+}][Hg(II)] \quad (5)$$

For all $[CoCl(N)_5]^{2+}$ systems studied,[7] plots of k_{obs} (pseudo-first-order) vs. [Hg(II)] are linear, with a slope (through zero) of k_{Hg}. The use of the Hg^{2+}-assisted process allows a greater temperature range to be employed (40°C in favourable cases), as the reaction rate can be controlled by [Hg(II)] as well as temperature.

There are, however, inherent disadvantages in the Hg^{2+}-assisted process, as, under pseudo-first-order conditions, high ionic strengths are employed (1–2 *M*) and specific salt effects have been observed.[6] The solubility of $[CoCl(N)_5]^{2+}$ salts at high electrolyte concentration can also be a limiting factor. Nevertheless, with k_{Hg} data measured in, or extrapolated to, $I = 1.0$ *M* $HClO_4$, there is a good correlation between k_{Hg} and k_H [Eq. (6)] at 25°C[6,7]:

$$\log k_{Hg} - \log k_H = 4.5 \quad (6)$$

This free energy relationship between rate constants implies a constant $\Delta(\Delta G)$ for the two processes.

The mechanism of the thermal and Hg^{2+}-assisted aquation processes has been the subject of considerable speculation.[8–14] Obviously, both processes are related, as a water molecule is replacing either Cl^- or

$ClHg^+$ bound to the Co(III), center and it has been shown that the non-replaced ligands can exert a considerable influence on reactivity.

Most notable acceleratory influences are an increase in diamine ring size (en < $(NH_3)_2$ < tn < bn) in *unsym-fac*-$[CoCl(dien)(diamine)]^{2+}$ (**3**) systems or in steric bulk (NH_3 < NH_2CH_3) for $[CoCl(N)_5]^{2+}$ where $[CoCl(NH_2CH_3)_5]^{2+}$ aquates 20× faster than $[CoCl(NH_3)_5]^{2+}$ at 25°C. The latter observation has been taken as indicating an I_d mechanism for the process,[15] where the steric bulk of the NH_2CH_3 ligands would assist in the repulsion of the leaving group. More difficult to explain on this basis is the 7-fold increase in aquation rate[16] of *trans*-$[CoCl(en)_2(NH_2CH_3)]^{2+}$ relative to *trans*-$[CoCl(en)_2(NH_3)]^{2+}$ (at 25°C), as the en rings should shield the chloro ligand from the steric influences of the alkylamine. We note, in passing, that this rate ratio would decrease to 4-fold if 80°C was chosen as the comparative temperature, changing an apparently significant observation into one of perhaps lesser importance.

This highlights the problem of extrapolating mechanistic information from a direct comparison of rate constants,[17] and there has been some suggestion that this practise may lead to more confusion than enlightenment.

3. BASE HYDROLYSIS

If the pH of solutions containing $[CoCl(N)_5]^{2+}$ complexes is raised, a base hydrolysis reaction [Eq.(7)] occurs:

$$[CoCl(N)_5]^{2+} + OH^- \rightarrow [Co(OH)(N)_5]^{2+} + Cl^- \quad (7)$$

The rate law for such a reaction is

$$-d[Co(III)]/dt = k_{OH}[Co(III)][OH^-] \quad (8)$$

and an SN_1CB mechanism [Eqs.(9)–(11)] is widely accepted [18,19]:

$$[CoCl(NH_3)_5]^{2+} + OH^- \rightleftarrows [CoCl(NH_2)(NH_3)_4]^{3+} + H_2O \quad (9)$$

$$[CoCl(NH_2)(NH_3)_4]^{3+} \xrightarrow[\text{determining}]{\text{rate}} [Co(NH_2)(NH_3)_4]^{2+} + Cl^- \quad (10)$$

$$[Co(NH_2)(NH_3)_4]^{2+} + H_2O \xrightarrow{\text{fast}} [Co(OH)(NH_3)_5]^{2+} \quad (11)$$

The essential requirement for such a mechanism is that at least one NH proton be available for conjugate base formation in (9). This is not usually a limiting factor, and for many $[CoCl(N)_5]^{2+}$ systems there is the question of which NH proton is involved in the formation of the most labile conjugate base (e.g., *cis-* or *trans-* to the leaving group). Some quite labile deprotonation sites may be "dead end" sinks if the resulting conjugate base is relatively unreactive.

$[CoCl(N)_5]^{2+}$ complexes are now being designed with either one, site specific or zero NH protons (**49**). Despite having zero NH protons, the R = Me complex reacts with base at a rate proportional to the OH^- concentration. Proton exchange at the–CH_2–position in the pyridyl arm was observed, and amido activation through the pyridine ring is believed to be responsible for the OH^- dependent rate law.[20]

Base hydrolysis rates in $[CoCl(N)_5]^{2+}$ complexes are quite sensitive to changes in the structure of the non-replaced $(N)_5$ ligands. Acceleratory effects are observed when NH_3 is replaced by NH_2CH_3,[21] when NH_3 is replaced by py,[21] and when the *sec*-NH proton in a polyamine ligand is in a "flat" (meridonal) configuration (e.g., **1** or **2**).[18,19,21,22]

4. CO–CL BOND LENGTHS

From time to time in the literature there is the suggestion that the ground state M–Cl bond length may be correlated with M–Cl lability.[9,10,12]

While it has never been seriously suggested that base hydrolysis rates should correlate with Co–Cl bond lengths, indeed the contrary has been remarked upon,[23] and it has been noted that there is a linear free energy relationship between k_{OH} and k_H for $[CoX(NH_3)_5]^{n+}$ complexes.[18,21] This is not unreasonable, as a water molecule must approach the Co center in both cases [Eqs. (1) and (2)] to form the Co–OH_2 (aquation) or Co–OH (base hydrolysis) bond, and a constant set of non-replaced ligands $[(NH_3)_5]$ is involved.

The question of a correlation between Co–Cl bond lengths and solvolysis rate is addressed here by a survey of about 70 $[CoCl(N)_5]^{2+}$ complexes $[(N)_5$ = ammine, amine, polyamine, or heterocyclic amine] where single crystal X-ray structures are available, together with their measured or calculated [Eq. (6)] k_H (25°C) or k_{Hg} (25°C) values (Table I). Sketches of the structures of the $[CoCl(N)_5]^{2+}$ systems are shown in structures (**1**)–(**50**) at the end of this article.

TABLE I

Kinetic parameters (25°C) and Co–Cl bond lengths for $[CoCl(N)_5]^{2+}$ complexes.

$(N)_5$	Co–Cl (Å)	$10^7 k_H$[a] (s^{-1})	$10^3 k_{Hg}$[b] (M^{-1} s^{-1})	k_{OH}[c] (M^{-1} s^{-1})	Ref.
$(NH_3)_5$	2.303(6)[e]	17.7(94.2, –39, –5.1)[f]	137(64.8, –47, +1.7)[f]	1.58(116, +140, +33.0)[f]	24, 21, 21, 21
	2.286(2)[g]				25, -, -, -
	2.83(3)[h]				26, -, -, -
$(NH_2CH_3)_5$	2.283(1)[i]	367(89.3, –30, –2.3)	500(70.4, +5)	8×10^2(77.7, +72, +32.8)	27, 21, 28, 21
c-$(en)_2(NH_3)$	2.27(1)[j]	4.2(97.5, –39)	14.5(79.5, –21)	8.08(-, -, +31.8)	29, 21, 21, 30
	2.268(9)[g]				23, -, -, -
c-$(en)_2(NH_2CH_3)$	2.255(3)[g]	3.5(100, –33)	24.2(76.5, –25)	12.7(96, +100)	16, 31, 6, 30
t-$(en)_2(NH_2CH_3)$	2.291(1)[k]	24.0(92, –44)	[76][l]		16, 16, -, -
c-$(en)_2$(pnol*N*)	2.255(13)[m]	10.0(101, –24)	29.2	19.1(92.8, +123)	32, 32, 32, 33
c-$(en)_2$(py)	2.255(1)[g]	2.6(103, –50)	18.0(74.3, –29)	3.32×10^2(86.1, +84)	23, 21, 7, 21
	2.252(1)[n]				34, -, -, -
c-$(en)_2$(imid)	2.258(3)[g]	5.7(98.5, –32)	50.9(68.4, –48)	3.5(96.9, +90)	35, 36, 6, 37
c-$(en)_2$(benzimid)	2.270(2)[o]	9.67(109, +7)	[31][l]	27.0(90.6, +86)	35, 36, -, 37
	2.273[g]				38, -, -, -
c-$(en)_2$(4-NO_2-imid)	2.253(1)[g]				34, -, -, -
c-$(en)_2$(4-Cl-imid)	2.248(1)[g]				34, -, -, -
c-$(en)_2$(aniline)	2.259(1)[g]	3.6(130, +70)	[11.4][l]	2.6×10^4(100, +167)	38, 21, -, 21
c-$(en)_2$($theo^-$)	2.225(3)[p]	[50][i]	160(75.7, –14)		39, -, 40, -
c-$(en)_2$(ad^-)	2.259(1)[q]	[4.4][l]	13.9(56.3, –100)		41, -, 40, -
exo-mer-cis-(dien)$(NH_3)_2$	2.280(4)[m]	[6.8][l]	21.4	2.75×10^5	42, -, 43, 44

exo-mer-(dien)(en) (**2**)	2.268(4)[m]	1.78(101, –31)	5.17(77.3, –29, +4.2)	1.87×10^4(90.7, +150)	45, 46, 7, 47
unsym-fac-(dien)(en) (**3**)	2.249(3)[m]	2.56(107, –8, –4.6)	15.8(73.7, –32, +0.5)	23.9(83.8, +62)	45, 46, 7, 47
sym-fac-(dien)(en) (**4**)	2.27[s]	0.94(110, –7)	4.95(72.7, –45, +3.0)	4.71(84.5, +72)	48, 46, 7, 47
	2.260(1)[s]				49, -, -, -
unsym-fac-(dien)(bn)	2.2535(13)[m]	637(92.5, –15)	2170(63.5, –26)		50, 51, 51, -
unsym-fac-(dien)(ampy)-I (**5**)	2.261()[m]	8.82(98.0, –32)	35.5(75.5, –20)	3.34×10^2(79.6, +67)	52, 53, 53, 54
mer-(bamp)(ampy)-I (**6**)	2.25	[0.21][l]	0.675(98.9, +26)		55, 46, -, -
mer-(bamp)(ampy)-II	2.25	[4.2][l]	13.3(70.5, –33)		55, 46, -, -
exo-mer-(dpt)(en)-β	2.259(9)[m]	213(92.5, –25)	[673][l]	2.2×10^3	56, 46, -, 21
endo-mer-(dpt)(en)-α	2.21(2)[r]	116(102, –10)	[367][l]	8.6×10^3	57, 46, -, 21
unsym-fac-(NMetn)(dien)-V (**8**)	2.251(3)[m]	30.7(104, +3)	[97.1][l]	7.57(81, +82)	58, 59, -, 21
unsym-fac-(bipy)(dien)	2.263(2)[s]	[5.2][t]	16.2(70.1, –44)	1.92×10^3(89.9, +120)	60, -, 61, 61
exo-mer-(pn)(dien)-B (**7**)	2.252(2)[m]			3.39×10^4(68.8, +72)	62, -, -, 44
sym-fac-(en)(tri-1) (**9**)	2.239(2)[s]	30.6(103, –12)	317	2.43	63, 64, 65, 65
mer-(en)(tri-1) (**10**)	2.274(5)[m]	220		26.7	63, 63, -, 63
mer-(en)(dienim) (**50**)	2.2762(7)[m]		24.3		40, -, 67, -
mer-(ibn)(tri-2) (**11**)	2.259(2)[m]	[0.42][l]	1.33(71.3, – 61)		66, -, 67, -
mer-(tn)(tri-3) (**12**)	2.280(4)[m]	1040			68, 68, -, -
(tacn)(en)	2.2569(6)[m]	16.3(93, – 44, –3.6)	11.0(74.7, –32, +1.44)	97(96.6, +90)	50, 53, 53, 54
(tacn)(ampy)	2.237(1)[m]	3.43(103, –22)	10.2(75.6, –30, +0.9)	154(83.3, +69)	50, 53, 53, 54

(continued)

TABLE I *(Continued)*

$(N)_5$	Co–Cl (Å)	$10^7 k_H$[a] (s^{-1})	$10^3 k_{Hg}$[b] ($M^{-1} s^{-1}$)	k_{OH}[c] ($M^{-1} s^{-1}$)	Ref.
t-(2.2.3-tet)(NH_3)	2.254(2)[m]	10.0(119, +40)	[31.6][l]		50, 40, -, -
cis-α-(trien)(NH_3) (**13**)	2.271(2)[i]			10.6	69, -, -, 21
(tame)(tameH) (**48**)	2.274(1)[u]			1.68×10^3 (20°C)	70, -, -, 70
exo-cis-β-(trien)(py) (**14**)	2.261[k]				71, -, -, -
p(tren)(py) (**15**)	2.276(3)[k]				72, -, -, -
(bisdap-tacn) (**16**)	2.246(3)[o]				73, -, -, -
endo-mer-(bipy)(dpt)	2.260(2)[o]				74, -, -, -
endo-mer-(phen)(dpt)	2.268(2)[o]				74, -, -, -
αα-tetraen (**19**)	2.263(3)[k]	[7.1][l]		22.6(69.9, –42)	75, -, 7, -
endo-T-αα-				18.7	-, -, 76, -
Metetraen (**21**)	2.257(2)[e]				77, -, -, -
exo-N-αα–Metetraen (**22**)	2.265(3)[e]				77, -, -, -
endo-αβ–tetraen(S) (**18**)	2.271(5)[o]	0.36(110, –17, –3.6)	1.34(77.0, –41)	3.5×10^4(98, +171)	78, 79, 7, 79
exo-αβ–tetraen(R) (**17**)	2.215(9)[o]	0.97(120, –28, –1.7)	2.20(86.8, –5)	1×10^4	78, 79, 7, 79
	2.26[m]				80, -, -, -
exo-αβ–bispicdien (**23**)	2.242(8)[m]	[0.97][l]	3.07(73.3, –47)	7.4×10^6(57, +76)	81, -, 7, 2
exo-αβ–bispicditn (**20**)	2.237(4)[s]	8870(98.0, +25)		2.4×10^7(38, +23)	82, 7, -, 2
		1820 (99.0, +14)			-, 2, -, -
s-trenen (**25**)	2.2670(9)[k]	[4.7][l]	14.8(77.4, –20)	518	83, -, 7, 84
t-trenenol (**27**)	2.273(3)[n]				85, -, -, -
unsym-NMetrenen (**26**)	2.248(5)[e]			29	84, -, -, 84

Mepictren (**28**)	2.289(2)[o]	[1.2][l]	3.81(87, +1)		86, -, 40, -
	2.267(2)[o]				86, -, -, -
anti-p-NMetren(NH_3)(RS) (**30**)	2.301(2)[m]	19.5	22	5×10^4	87, 87, 87, 87
anti-p-NMetren(NH_3)(S)	2.288(2)[m]				87, -, -, -
s-NMetren(NH_3)(RS) (**32**)	2.291(4)[m]	110	340	4.5×10^3	87, 87, 87, 87
syn-p-NMetren(NH_3)(RS) (**29**)		295	1840	1.9×10^3	-, 87, 87, 87
2,3,2,2,3-pent *anti-meso* (**33**)	2.249(1)[k]	[2300][l]	7200		88, -, 76, -
2,2,2,2,3-pent *syn-meso* (**34**)	2.242(9)[k]				89, -, -, -
2,2,2,3,3-pent	2.258(2)[t]				90, -, -, -
trans-III-cyclam 2,5,10, 12-tetramethyl-5 -aminomethyl (**35**)	2.264(1)[k]	350		2.23×10^4	91, 91, -, 91
2,3,2-tet-3-Me-3NH_2-	2.261(1)[k]			2.4	100,-,-,100
				1.1(131, +177)	-,-,-,93
trans-2,3,2-tet-bis-cyclohexyl-- 3-Me-3-NH_2 (**37**)	2.241(1)[k]			22.6(109, +128) 1.47(105, +93)	92,-,-,92
pyane-N_5 (**39**)	2.173(5)[o]				93,-,-,-
macro-N_5 (**38**)	2.26(1)[s]				94,-,-,-
3,2,2,-tet-	2.244(2)[s]			4.3×10^3 (67, +47)	95, -, -, 95
3-Me-3-NH_2-*cis* (**40**)	2.246(2)[s]				
3,2,3,2-tet- 3-Me-3-NH_2-*cis* (**41**)	2.236(2)[o]			76(75, +42)	96,-,-,96

(continued)

TABLE I *(Continued)*

$(N)_5$	Co–Cl (Å)	$10^7 k_H{}^a$ (s^{-1})	$10^3 k_{Hg}{}^b$ (M^{-1} s^{-1})	$k_{OH}{}^c$ (M^{-1} s^{-1})	Ref.
3,2,3,2-tet-3-Me-3-NH_2-*trans*	2.244(2)[o]			9.1×10^3(61, +33)	96,-,-,96
3,3,2,3,-tet-3-Me-3-NH_2-*cis* (**42**)	2.273(2)[o]			6.7×10^3(58, +30)	95,-,-,95
3,3,3,3-tet-3-Me-3-NH_2-*trans* (**43**)	2.222(3)[k]			1.1×10^4(34, +31)	96,-,-,96
3,3,2,2,-tet-3-Me-3-NH_2-*cis* (**44**)	2.252(1)[o]			9.1×10^3(60, +35)	97,-,-,97
3,2,3,2-tet-3-Me-3-NH_2-10-CO_2H-*cis* (**45**)	2.266(2)[o]				98,-,-,-
3,2,3,2,-tet-3-Me-3-NH_3^+-10-Me-10-NH_2-*trans* (**46**)					
α(+,+,+,+)	2.237/(8)[v]				99,-,-,-
γ(+,+,+,–)	2.264(8)[u]				99,-,-,-
β(+,+,–,–)	2.243(2)[v]				99,-,-,-
3,2,3,2-tet-3-Me-3-NH_2-10-Me-10-NH_2-*trans* (**47**)					
α(+,+,+,+)	2.247(4)[o]				99,-,-,-

[a]Rate constant for the reaction: $[CoCl(N)_5]^{2+} + H_2O \rightarrow [Co(N)_5(OH_2)]^{3+} + Cl^-$. k_H is virtually independent of $[H^+]$ (at pH < 3) and I.

[b]Rate constant for the reaction: $[CoCl(N)_5]^{2+} + Hg^{2+} + H_2O \rightarrow [Co(N)_5(OH_2)]^{3+} + HgCl^+$. k_{Hg} is dependent on I with specific salt effects. Data have been normalised to I = 1.0 M, $HClO_4$.[6]

[c]Rate constant for the reaction: $[CoCl(N)_5]^{2+} + OH^- \rightarrow [Co(OH)(N)_5]^{2+} + Cl^-$. k_{OH} is dependent on I. The specific reference should be consulted to establish the ionic strength used.

[d]The reference sequence is: Co–Cl bond length, k_H, k_{Hg}, k_{OH}.

[e]As the SiF_6^{2-} salt.

[f]Numbers in parentheses are: activation enthalpy ($\Delta H^{\#}$, kJ mol^{-1}); activation entropy ($\Delta S^{\#}$, J K^{-1} mol^{-1}); activation volume ($\Delta V^{\#}$, cm^3 mol^{-1}). The original literature should be cited for error estimates. Activation volume data are from Refs. 101–103.

[g]As the dichloride salt.

[h]As the $HgCl_4^{2-}$ salt.

[i]As the dinitrate salt.

[j]As the bis(bromocamphorsulfonate) salt.

[k]As the chloride perchlorate salt.

[l]Calculated from k_H or k_{Hg} using Eq. (6).

[m]As the $ZnCl_4^{2-}$ salt.

[n]As the bromide perchlorate salt.

[o]As the diperchlorate salt.

[p]As the monoperchlorate salt.

[q]As the monobromide salt

[r]As the diiodide salt

[s]As the $CoCl_4^{2-}$ salt.

[t]As the chloride bromide salt.

[u]As the trichloride salt.

[v]As the chloride, $ZnCl_4^{2-}$ salt.

The mean Co–Cl distance is 2.26(2) Å (n = 83) with a range from 2.303(6) to 2.173(5), and the aquation rate varies from (0.4 to 2000) × 10^{-7} s^{-1} (25°C), i.e., over almost 4 orders of magnitude. Figure 1 shows a frequency plot for the Co–Cl data exhibiting the expected "normal" distribution about the mean of 2.26 Å. The aquation rates have been divided into two groups–slow (10^7 k_H = 0.21 to 40) and fast (10^7 k_H = 40 to 2000). The average Co–Cl distance for the "slow" group is 2.262(20) Å and for the "fast" group 2.254(30). Figure 2 shows a plot of Co–Cl vs. k_H (both experimental and calculated), and the slope of the least squares best fit line is zero within experimental error.

On an individual basis, the Co–Cl distances in *cis*-$[CoCl(en)_2(py)]Cl_2$, *cis*-$[CoCl(en)_2(NH_2Et)]Cl_2$, $[CoCl(tacn)(en)]ZnCl_4$ and *unsym-fac-*

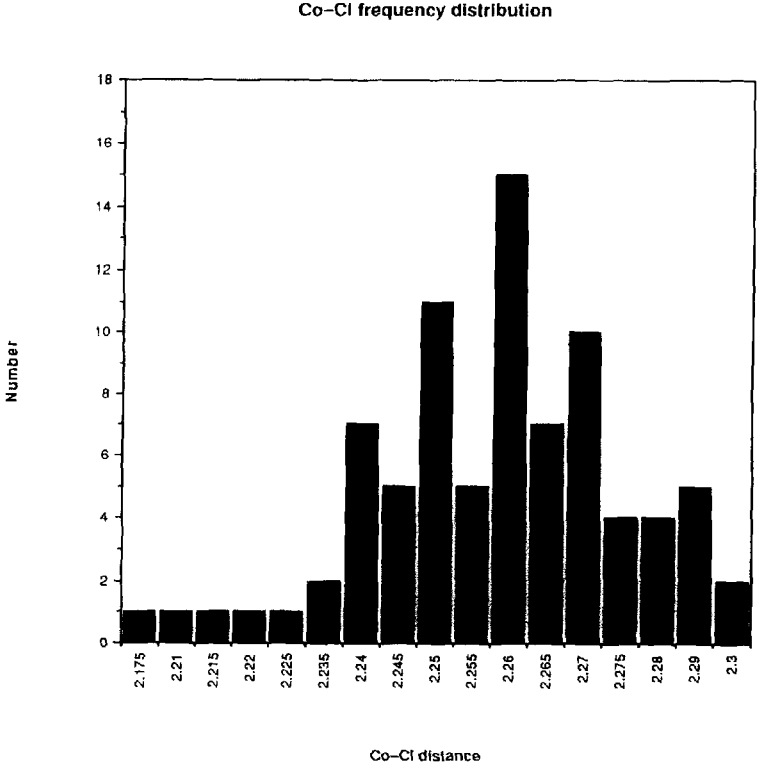


FIGURE 1 A frequency plot for Co–Cl bond distances in $[CoCl(N)_5]^{2+}$ complexes.

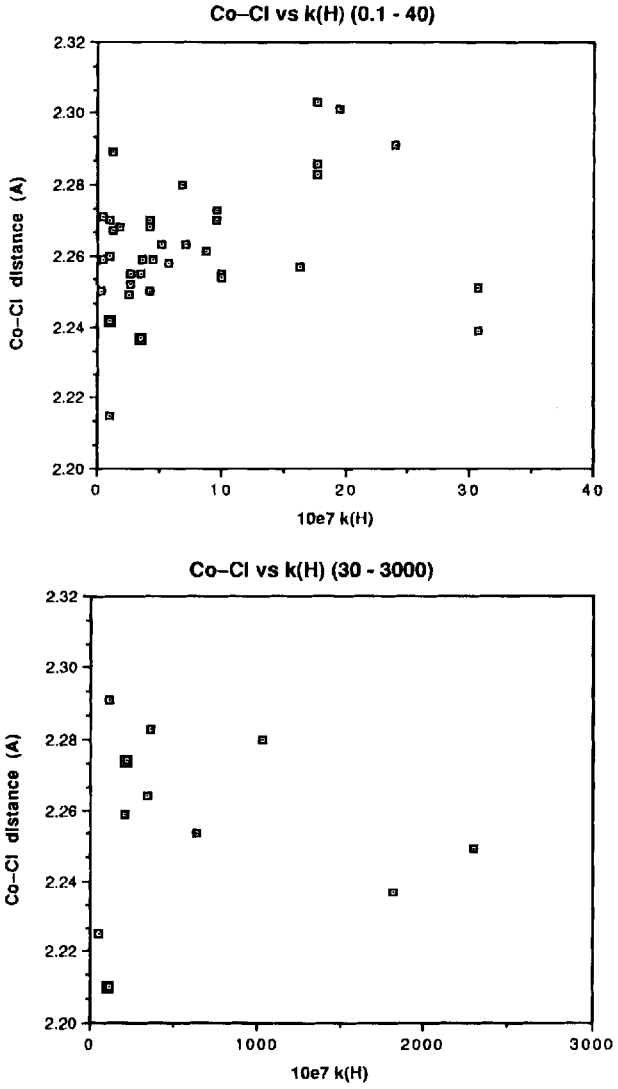


FIGURE 2 Plots of Co–Cl bond distance vs. k_H (see text).

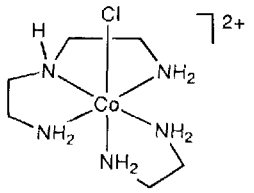
[CoCl(dien)(bn)]$ZnCl_4$ are all about 2.255(3) Å, but the 10^7 k_H values at 25°C are 2.6, 3.5, 16.3 and 637 s^{-1}, respectively.

Factors other than Co–Cl bond lengths, e.g., the approach trajectory of the incoming water molecule, are obviously more important in influencing the solvolysis rate, and these have been discussed elsewhere.[7,14] The correlation between k_H and k_{Hg}, mentioned earlier, implies that Hg^{2+}-assisted rates are also not correlated with Co–Cl bond lengths.

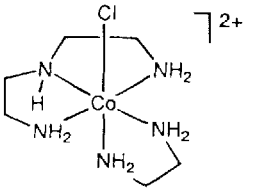
5. CONCLUSION

From an analysis of the published data on Co–Cl bond distances and solvolysis rates, there appears to be no justification for any proposed correlation between these parameters. This casts doubt on the suggestion that M–Cl distances, in general, are important in predicting kinetic behaviour in substitution processes.

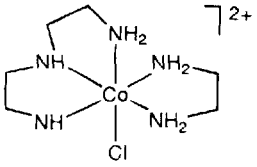
STRUCTURES



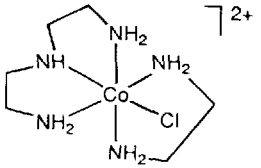
endo(syn)-(dien)(en)
(1)



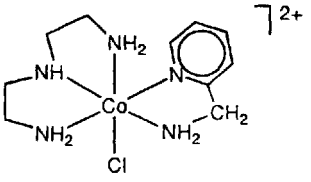
exo(anti)-(dien)(en)[45]
(2)



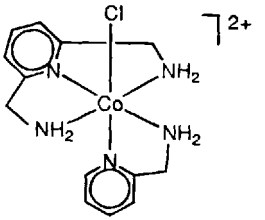
unsym-fac-(dien)(en)[45]
(3)



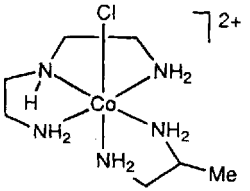
sym-fac-(dien)(en)[48,49]
(4)



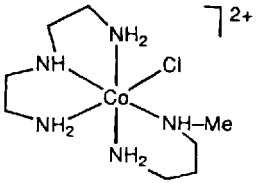
unsym-fac-(dien)(ampy)-l[52]
(**5**)



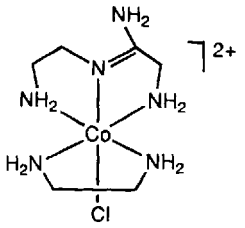
mer-(bamp)(ampy)-l[55]
(**6**)



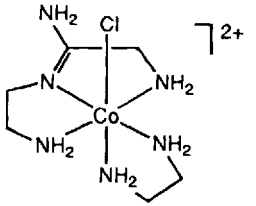
exo-mer-(dien)(pn)-B[62]
(**7**)



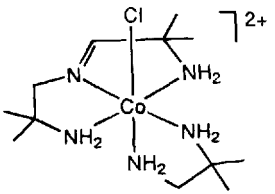
unsym-fac-(dien)(Metn)-V[58]
(**8**)



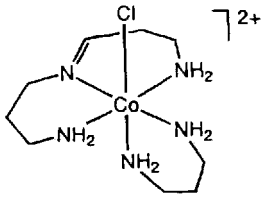
sym-fac-(en)(tri-1)[63]
(**9**)



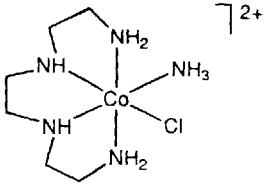
mer-(en)(tri-1)[63]
(**10**)



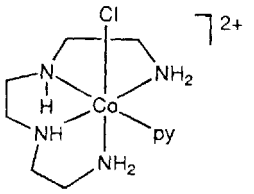
mer-(ibn)(tri-2)[66]
(**11**)



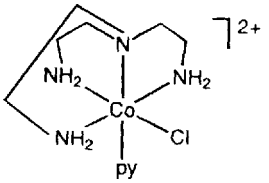
mer-(tn)(tri-3)[68]
(**12**)



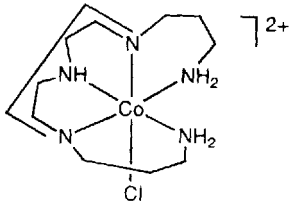
cis-α-(trien)$(NH_3)^{69}$
(**13**)



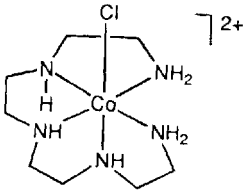
exo-cis-β-(trien)$(py)^{71}$
(**14**)



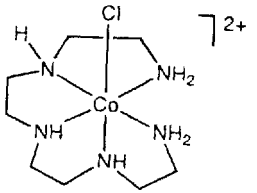
p-(tren)$(py)^{72}$
(**15**)



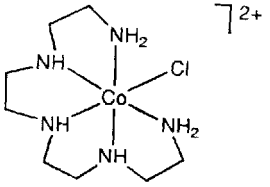
(bisdap-tacn)^{73}
(**16**)



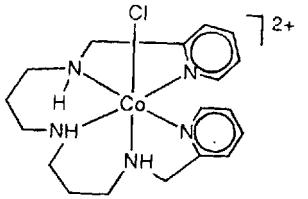
exo-αβ-(tetraen)$(R)^{78,80}$
(**17**)



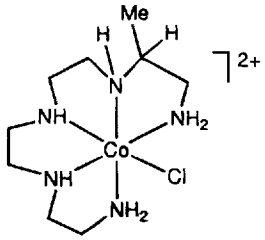
endo-αβ-(tetraen)$(S)^{78}$
(**18**)



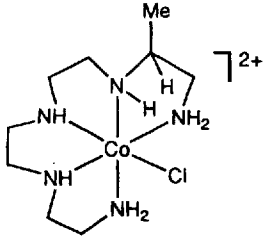
αα-(tetraen)^{75}
(**19**)



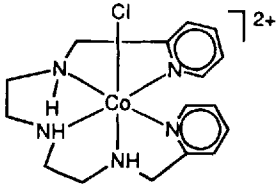
exo-αβ-bispicditn^{82}
(**20**)



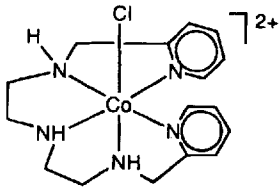
exo-N-αα-Metetraen[77]
(21)



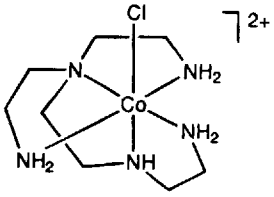
endo-T-αα-Metetraen[77]
(22)



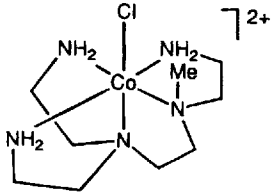
exo-αβ-bispicdien[81]
(23)



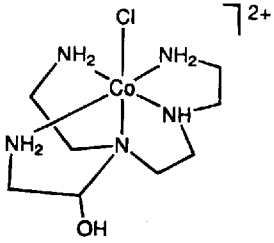
endo-αβ-bispicdien
(24)



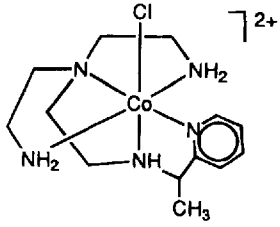
s-(trenen)[83]
(25)



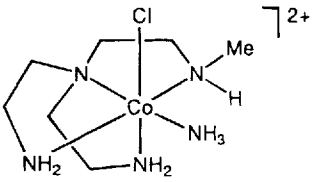
unsym-NMetrenen[84]
(26)



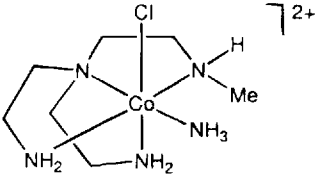
t-(trenenol)[85]
(27)



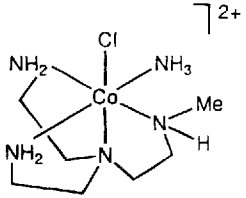
Mepictren[86]
(28)



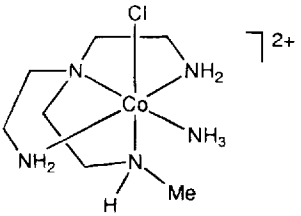
syn-p-Metren(NH_3)
(**29**)



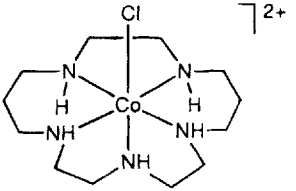
anti-p-Metren(NH_3)
(**30**)



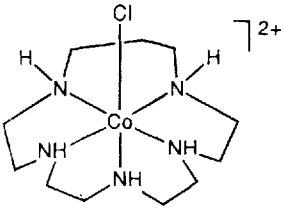
t-NMetren(NH_3)
(**31**)



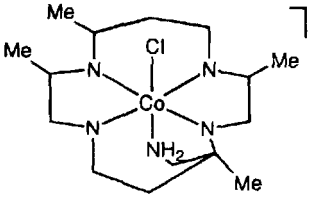
s–NMetren(NH_3)[87]
(**32**)



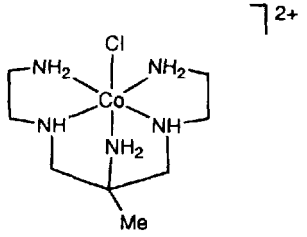
2,3,2,2,3-pent-
anti-meso[88]
(**33**)



2,2,2,2,3-pent-
syn-meso[89]
(**34**)

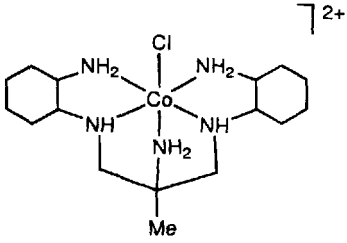


trans-(III)-(+,+,-,-)-
2,5,10,12-tetramethyl
-5-aminomethylcyclam[91]
(35)



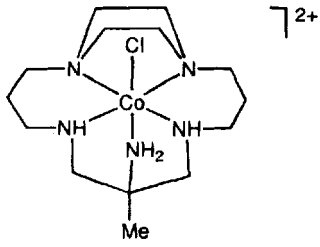
2,3,2-tet-
3-Me-3-NH_2-[100]

(36)



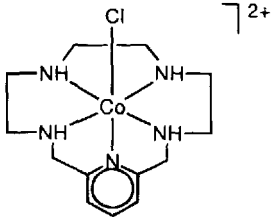
trans-2,3,2-tet-
biscyclohexyl-
3-Me-3-NH_2[92]

(37)



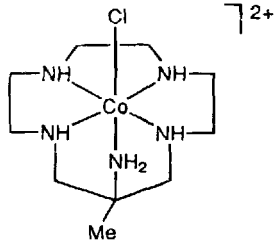
macro-N_5[94]

(38)



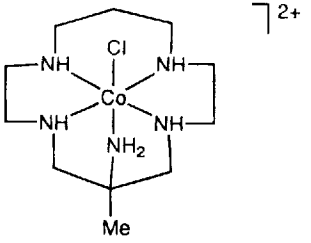
payne-N_5[93]

(39)

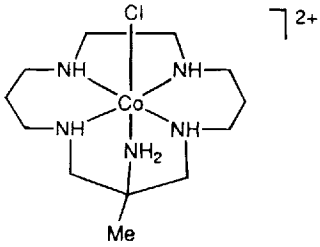


3,2,2,2-tet-
3-Me-3-NH_2-*cis*[95]

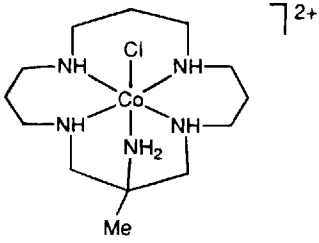
(40)



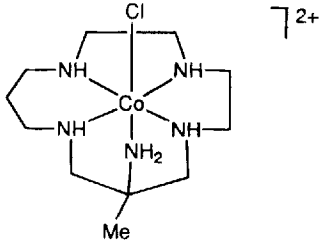
3,2,3,2-tet-
3-Me-3-NH_2-*cis*[96]
(**41**)



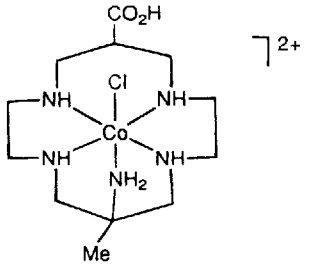
3,3,2,3-tet-
3-Me-3-NH_2-*cis*[95]
(**42**)



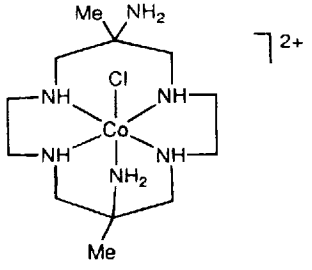
3,3,3,3-tet-
3-Me-3-NH_2-*trans*[96]
(**43**)



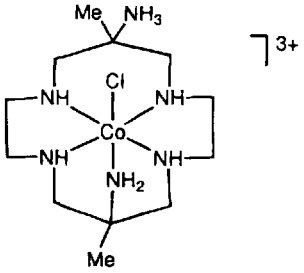
3,3,2,2-tet-
3-Me-3-NH_2-*cis*[97]
(**44**)



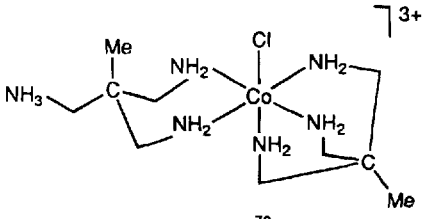
3,2,3,2-tet-
3-Me-3-NH_2-10-
CO_2H-*cis*[98]
(**45**)



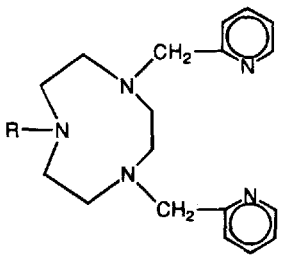
3,2,3,2-tet-
3-Me-3-NH_2-10-Me-
10-NH_2-*trans*[99]
(**46**)



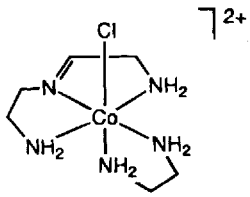
3,2,3,2-tet-
3-Me-3-NH_3^+-10-
Me-10-NH_2-*trans*[99]
(47)



(tame)(tameH)[70]
(48)



R = H, R = Me
(49)



(50)

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