Preparation, Crystal Structure and Kinetics of Acid Hydrolysis of an Isomer of $[Cr(picdien)Cl][ZnCl_4]$ [picdien = 1,9-bis(2′-pyridyl)-2,5,8-triazanonane]

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The complex $[Cr(picdien)Cl][ZnCl_4]$ [picdien = 1,9-bis(2′-pyridyl)-2,5,8-triazanonane] has been prepared and its structure determined by a single-crystal *X*-ray diffraction study of the triclinic crystals: $a = 9.118(3)$, $b = 9.581(5)$, $c = 14.042(5)$ Å, $\alpha = 78.04(3)$, $\beta = 86.37(3)°$, and $\gamma = 76.56(3)°$. The complex cation has the *anti*-αβ configuration. The kinetics of aquation of the perchlorate salt has been studied in dilute aqueous nitric acid solution, [complex] = 5×10^{-3} mol dm^{-3}. The rate constants are independent of $[H^+]$ over the range $0.10 < [H^+] < 0.001$ mol dm^{-3}: $k_{25 °C} = 6.0 \times 10^{-6}$ s^{-1}, $\Delta H^{\ddagger} = 93.1 \pm 2.2$ kJ mol^{-1}, $\Delta S^{\ddagger} = -32.9 \pm 6.9$ J K^{-1} mol^{-1}.

In comparison to the amount of work done on analogous cobalt(III) species, complexes of Cr^{III} containing linear pentadentate ligands have received relatively little attention. Octahedral complexes containing such ligands provide a rich field of isomerism, both geometrical and conformational, and much recent work has focused on Co^{III} as the central metal atom[1-5] and on its picdien [1,9-bis(2′-pyridyl)-2,5,8-triazanonane] complexes.[6-10] These systems are of considerable importance in the study of the factors that determine the sensitivity of the metal amine complex towards hydrolysis and, in particular, the extent to which such processes are sensitive to base catalysis.

Although the first studies of the aquation of the *cis*- and *trans*-$[Cr(en)_2Cl_2]^+$ (en = 1,2-diaminoethane) cations suggested that Cr^{III} was similar in its kinetic behaviour to Co^{III} it was soon shown that this was not typical and that even the apparently simple displacement of Cl^- could be complicated by parallel ring opening and even loss of the diamine.[11-14] The effects of changing the nature of the amine ligands are quite considerable but Cr^{III} and Co^{III} do not follow the same patterns. In general, the labilities of the cobalt(III) dichloro complexes seem to relate to the ability of the spectator ligands to facilitate a trigonal-bipyramidal geometry in the five-coordinate intermediate, whereas the chromium(III) system can be rationalised in terms of the accommodation of the water molecule in an I_a transition state.[15] Some chromium(III) dichlorotetra-amine complexes are exceptionally labile, for example the β-*cis*-$[Cr(trien)Cl_2]^+$ cation[16] (trien = 1,8-diamino-3,6-diazaoctane), the $[Cr(tren)Cl_2]^+$ cation[17] [tren = tris(2-aminoethyl)amine], and especially the $[Cr(cyclen)Cl_2]^+$ cation[18] (cyclen = 1,4,7,10-tetra-azacyclododecane) which aquates with a rate constant of 7.6×10^{-2} s^{-1} at 25 °C. In general, the sensitivity of such chromium(III) complexes towards base-catalysed solvolysis is very much less than that observed for the analogous cobalt(III) species.[15]

As part of a study of the synthesis and reactivity of metal complexes with potentially pentadentate ligands we have prepared a chromium(III) complex containing picdien and examined the kinetics of its aquation. Because the paramagnetism of the metal ion prevents the use of high-resolution ^1H n.m.r. spectroscopy to assign the structure, we have had to use single-crystal *X*-ray diffraction. The results are reported in this paper.

Experimental

Preparations.—The ligand 1,9-bis(2′-pyridyl)-2,5,8-triazanonane, was prepared as described in the literature.[10]

Chloro[1,9-*bis*(2′-*pyridyl*)-2,5,8-*triazanonane*]*chromium*(III) *tetrachlorozincate*(II). This was prepared by a modification of the method used for the synthesis of *trans*-$[Cr(cyclam)Cl_2]Cl$ (cyclam = 1,4,8,11-tetra-azacyclotetradecane).[19] Anhydrous $CrCl_3$ (0.56 g) was placed in the filter thimble of a Soxhlet extractor together with Zn–Hg amalgam (1 cm^3) and a solution of picdien (1.0 g) in dry ethanol (75 cm^3) was added to the reservoir flask. Oxygen-free dried nitrogen was bubbled through the ethanol for 10 min before heating and the chromium chloride was then extracted as a deep green solution and reacted slowly with the picdien to produce a very dark solution. When all the $CrCl_3$ had been extracted (after *ca.* 1 h) the apparatus was opened to the air and a salmon-pink precipitate formed. This powder was filtered off, washed with dry ethanol, and air-dried. Yield (27%) (Found: C, 32.40; H, 4.00; Cr, 8.35; N, 11.45; Zn, 11.30. $C_{16}H_{23}Cl_5CrN_5Zn$ requires C, 33.10; H, 4.00; Cr, 8.95; N, 12.10; Zn, 11.25%).

The perchlorate salt was obtained by adding dilute perchloric acid to a filtered aqueous solution of the tetrachlorozincate. The crystals that formed were filtered off, washed with ice-cold dilute perchloric acid (0.1 mol dm^{-3}), cold water, ethanol, and diethyl ether and air dried [Found: C, 33.20; H, 3.95; ionic Cl, 6.50; N, 11.85%. $C_{16}H_{23}Cl_3N_5O_8$ requires C, 33.60; H, 4.05; ionic Cl (= $\frac{1}{3}$ of total), 6.20; N, 12.25%].

Crystallography.—Crystals of $[Cr(picdien)Cl][ZnCl_4]$ were prepared by the slow evaporation of an aqueous solution of the compound and mounted on glass fibres. The cell dimensions

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† [1,9-Bis(2′-pyridyl-κ*N*)-2,5,8-triazanonane-κ^3*N*^{2},*N*^{5},*N*^{8}]chlorochromium(III) tetrachlorozincate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Some crystallographic data for [Cr(picdien)Cl][ZnCl$_4$]

Formula	$C_{16}H_{23}Cl_5CrN_5Zn$
Crystal system	Triclinic
Space group	$P\bar{1}$
Crystal size (mm)	0.18 × 0.2 × 0.44
a/Å	9.118(3)
b/Å	9.581(5)
c/Å	14.042(5)
α/°	78.04(3)
β/°	86.37(3)
γ/°	76.56(3)
U/Å^3	1 167.1
D_c/g cm^{-3}	1.66
λ/Å	0.7093
μ/cm^{-1}	20.92
F(000)	586
2θ range/°	3—50

Table 2. Important peaks (cm^{-1}) in the i.r. spectra of [Cr(picdien)Cl][ZnCl$_4$] (**1**) and [Cr(picdien)Cl][ClO$_4$]$_2$ (**2**) in KBr discs except where otherwise indicated

Compound				
(**1**)	3 100s (br)	1 610s	1 480m	900w
		1 565w	1 450s	850w
			1 430 (sh)	820w
	3 120m (br)*			
(**2**)	3 200s (br)	1 610s	1 480m	900 (sh)
	3 020s	1 565w	1 450br	850w
				820w
	3 200s (br)*			

Estimated relative intensities: s = strong, m = medium, w = weak, br = broad, and sh = shoulder.

* Hexachlorobutadiene mull.

were obtained by the angular measurement of 25 strong reflections in the range $5 < 2\theta < 20°$. Some crystallographic data are given in Table 1.

Data were collected at room temperature on a Nicolet R3m four-circle diffractometer using graphite-monochromatised Mo-K_α radiation. ω—2θ Scans with variable scan rate from 4 to 30° min^{-1} and a scan width of 1° were used. 3 559 Reflections were measured of which 3 002 had $|F_o > 3\sigma F_o|$.

The structure was solved by the Patterson heavy-atom method and subsequent electron difference syntheses. The structure was refined by full-matrix least-squares treatment and anisotropic thermal parameters were assigned to all non-hydrogen atoms. Methylene and pyridyl hydrogens were placed in idealised positions. Amine protons were located from the Fourier difference map and included in the refinement. The weighting scheme used was $[\sigma^2(F_o) + g(F_o)^2]^{-1}$, where σ is the estimated standard deviation based on counting statistics and g an adjustable variable, its final value being 0.000 32. A final difference map indicated maximum residuals of 0.5 e Å^{-3}. The refinement (3 002 data, 263 variables) converged at $R = 0.0354$, $R' = 0.0349$. Complex neutral scattering factors[20] were used throughout the structure solution and refinement. All calculations were carried out using SHELXTXL[21] on a Nova 4S computer.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Kinetics.—The reactions were followed spectrophotometrically using a Perkin-Elmer 553 fast scanning u.v.–visible spectrophotometer, and carried out in a 1-cm cell. The temperature was held constant (±0.2 °C) by circulating water from a Haake thermostat water-bath through the cell housing. The appropriate solutions (3 cm^3) of nitric acid together with $NaNO_3$ to maintain constant ionic strength (0.5 mol dm^{-3}) were brought to the reaction temperature and a small quantity of [Cr(picdien)Cl][ClO$_4$]$_2$ was added to start the reaction, the solution, being shaken to ensure that all was dissolved before the cell was replaced in the spectrophotometer. The spectrum over the range 750—320 nm was scanned from time to time and the rate constants determined from the change of absorbance with time at 381 nm. Plots of $\ln|A_t - A_\infty|$ (A_t and A_∞ being the absorbances at time t and at the end of the reaction respectively) against time were linear, A_∞ being determined after 10 half-lives by Swinbourne's method,[22] with slope = $k_{obs.}$. The temperature was determined by inserting a thermocouple into the cell at the end of the reaction.

The concentration of ionic chloride at the end of the reaction was determined by potentiometric titration with standard $AgNO_3$ solution using a Sargent-Welch LS pH meter with silver electrodes and a Cu^0–$Cu(NO_3)_2$ (0.05 mol dm^{-3}) reference electrode in a separate quantitative experiment.

The acid solutions were prepared by diluting stock nitric acid (0.47 mol dm^{-3}) and brought to constant ionic strength with $NaNO_3$.

Analyses.—Elemental analyses were carried out on a Perkin-Elmer 240B microanalyser at University College London. The contents of Cr and Zn of suitably decomposed samples of the complex were determined by atomic absorption spectrometry using a Varian 475 instrument.

Infra-red spectra of KBr pellets or hexachlorobutadiene suspensions of the complexes, in the range 4 000—200 cm^{-1}, were recorded on a Perkin-Elmer 599B spectrometer.

Results

Synthesis.—The initial attempts to prepare the complex met with variable success until it was realised that the presence of zinc as an impurity remaining from an earlier stage of the preparation facilitated the precipitation of the desired product as the salmon-pink tetrachlorozincate. Once obtained this could be easily converted into the perchlorate by adding perchloric acid to a slightly acidified aqueous solution. Important peaks in the i.r. spectra of these species are reported in Table 2 and features of the u.v.–visible spectra in Table 3.

Structure.—The final positional parameters for *anti*-$\alpha\beta$-[Cr(picdien)Cl][ZnCl$_4$] are reported in Table 4 and bond lengths and angles in Tables 5 and 6. The molecular structure is shown in the Figure together with the atom numbering scheme adopted.

The structure consists of discrete [Cr(picdien)Cl]$^{2+}$ cations and ZnCl$_4$ anions. The co-ordination geometry of the cation is that of an almost regular octahedron with the ligand in the $\alpha\beta$ configuration.[5] Two secondary nitrogens [N(3) and N(4)] and two (*cis*) pyridine nitrogens [N(1) and N(5)] are essentially coplanar and the third secondary nitrogen [N(2)] and the chloride ligand occupy the remaining *trans* positions. Atom N(4) is termed a 'flat' nitrogen, being the central donor of a meridional sequence of three, while the other two secondary nitrogens are 'angular', being the central donors of facial sequences; N(2) and N(4) are chiral having *S* and *R* configurations in the enantiomer drawn in the Figure.

The N(4)–H(4) bond and the Cr–Cl(1) bond lie on opposite sides of the Cr, N(1), N(3), N(4), and N(5) plane and the isomer is therefore designated '*anti*'. The complex is therefore comparable in structure with the corresponding cobalt(III) species, whose ZnCl$_4$ salt has been examined.[6] It is of interest

Table 3. Electronic spectra of the cations [Cr(picdien)X]$^{n+}$ [a]

Compound	$\lambda_{max.}$	ε	$\lambda_{min.}$	ε	$\lambda_{max.}$	ε	$\lambda_{min.}$	ε
[Cr(picdien)Cl][ZnCl$_4$] [b]	487	140	420	71	381	129	350	76
[Cr(picdien)Cl][ClO$_4$]$_2$ [b]	487	140	420	69	381	132	350	76
[Cr(picdien)(H$_2$O)]$^{3+}$ [c]	480	144	410	68	370(sh)	90		

[a] λ/nm, ε/cm^2 mmol^{-1}. [b] In water at 25 °C. [c] In aqueous HNO$_3$ (0.010 mol dm^{-3}) at 67.5 °C.

Table 4. Atom co-ordinates (× 10^4) for [Cr(picdien)Cl][ZnCl$_4$]

Atom	*x*	*y*	*z*
Cr	7 371(1)	2 566(1)	2 099(1)
Zn	4 370(1)	8 226(1)	3 092(1)
Cl(1)	7 726(1)	4 062(1)	638(1)
Cl(2)	2 741(1)	6 938(1)	3 892(1)
Cl(3)	6 614(1)	8 000(1)	3 789(1)
Cl(4)	4 932(1)	7 627(1)	1 607(1)
Cl(5)	3 063(1)	10 608(1)	2 961(1)
N(1)	8 966(3)	3 187(2)	2 812(3)
C(1)	9 504(4)	4 414(3)	2 510(4)
C(2)	10 383(4)	4 857(3)	3 091(4)
C(3)	10 733(4)	4 051(3)	4 004(4)
C(4)	10 190(4)	2 810(3)	4 328(4)
C(5)	9 295(3)	2 411(2)	3 721(4)
C(6)	8 631(4)	1 096(2)	4 006(4)
N(2)	7 189(3)	1 347(2)	3 497(3)
C(7)	5 868(4)	2 121(4)	4 014(4)
C(8)	5 639(4)	3 747(3)	3 672(5)
N(3)	5 639(3)	4 094(3)	2 578(3)
C(9)	4 162(4)	4 072(3)	2 172(4)
C(10)	4 406(4)	3 287(3)	1 328(4)
N(4)	5 616(3)	1 957(2)	1 603(3)
C(11)	6 137(4)	1 095(3)	837(4)
C(12)	7 702(4)	183(2)	1 058(4)
C(13)	8 281(5)	−1 067(3)	703(5)
C(14)	9 756(5)	−1 787(3)	881(5)
C(15)	10 614(5)	−1 245(3)	1 428(5)
C(16)	9 974(4)	−12(3)	1 781(4)
N(5)	8 533(3)	709(2)	1 600(3)

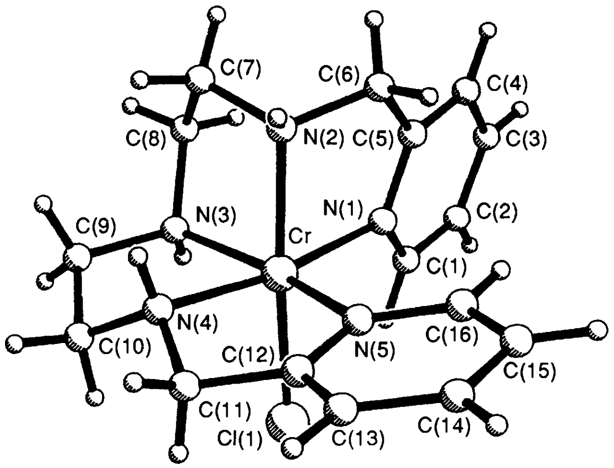

Figure. Perspective view of the complex cation

Table 5. Bond lengths (Å) and angles (°)

Cr–Cl(1)	2.298(1)	Cr–N(1)	2.075(3)
Cr–N(2)	2.084(3)	Cr–N(3)	2.071(3)
Cr–N(4)	2.032(3)	Cr–N(5)	2.079(3)
Zn–Cl(2)	2.249(1)	Zn–Cl(3)	2.270(1)
Zn–Cl(4)	2.273(1)	Zn–Cl(5)	2.291(1)
N(1)–C(1)	1.356(5)	N(1)–C(5)	1.350(4)
C(1)–C(2)	1.369(6)	C(2)–C(3)	1.367(5)
C(3)–C(4)	1.374(6)	C(4)–C(5)	1.381(5)
C(5)–C(6)	1.493(5)	C(6)–N(2)	1.483(5)
N(2)–C(7)	1.492(4)	C(7)–C(8)	1.501(6)
C(8)–N(3)	1.502(5)	N(3)–C(9)	1.502(5)
C(9)–C(10)	1.510(7)	C(10)–N(4)	1.478(4)
N(4)–C(11)	1.479(5)	C(11)–C(12)	1.503(5)
C(12)–C(13)	1.372(6)	C(12)–N(5)	1.348(5)
C(13)–C(14)	1.373(6)	C(14)–C(15)	1.379(7)
C(15)–C(16)	1.366(6)	C(16)–N(5)	1.347(4)
Cl(1)–Cr–N(1)	93.9(1)	Cl(1)–Cr–N(2)	173.3(1)
N(1)–Cr–N(2)	79.6(1)	Cl(1)–Cr–N(3)	95.0(1)
N(1)–Cr–N(3)	91.7(1)	N(2)–Cr–N(3)	83.7(1)
Cl(1)–Cr–N(4)	93.3(1)	N(1)–Cr–N(4)	170.8(1)
N(2)–Cr–N(4)	93.0(1)	N(3)–Cr–N(4)	82.1(1)
Cl(1)–Cr–N(5)	91.9(1)	N(1)–Cr–N(5)	105.2(1)
N(2)–Cr–N(5)	91.4(1)	N(3)–Cr–N(5)	161.4(1)
N(4)–Cr–N(5)	80.3(1)	Cl(2)–Zn–Cl(3)	118.4
Cl(2)–Zn–Cl(4)	109.6	Cl(3)–Zn–Cl(4)	106.1
Cl(2)–Zn–Cl(5)	103.3	Cl(3)–Zn–Cl(5)	107.8
Cl(4)–Zn–Cl(5)	111.6	Cr–N(1)–C(1)	125.6(2)
Cr–N(1)–C(5)	115.4(2)	C(1)–N(1)–C(5)	118.2(3)
N(1)–C(1)–C(2)	121.9(3)	C(1)–C(2)–C(3)	119.7(4)
C(2)–C(3)–C(4)	119.4(4)	C(3)–C(4)–C(5)	119.0(3)
N(1)–C(5)–C(4)	121.9(3)	N(1)–C(5)–C(6)	114.9(3)
C(4)–C(5)–C(6)	123.2(3)	C(5)–C(6)–N(2)	110.0(3)
Cr–N(2)–C(6)	109.0(2)	Cr–N(2)–C(7)	109.3(2)
C(6)–N(2)–C(7)	113.1(3)	N(2)–C(7)–C(8)	110.2(3)
C(7)–C(8)–N(3)	108.9(4)	Cr–N(3)–C(8)	107.5(2)
Cr–N(3)–C(9)	110.4(3)	C(8)–N(3)–C(9)	112.5(3)
N(3)–C(9)–C(10)	111.1(3)	C(9)–C(10)–N(4)	107.3(3)
Cr–N(4)–C(10)	107.8(3)	Cr–N(4)–C(11)	110.5(2)
C(10)–N(4)–C(11)	116.1(3)	N(4)–C(11)–C(12)	109.7(3)
C(11)–C(12)–C(13)	122.8(4)	C(11)–C(12)–N(5)	115.4(3)
C(13)–C(12)–N(5)	121.7(3)	C(12)–C(13)–C(14)	119.5(4)
C(13)–C(14)–C(15)	119.0(4)	C(14)–C(15)–C(16)	119.2(4)
C(15)–C(16)–N(5)	122.1(4)	Cr–N(5)–C(12)	114.3(2)
Cr–N(5)–C(16)	127.2(3)	C(12)–N(5)–C(16)	118.5(3)

that the two substances are not isomorphous, crystallising in triclinic ($P\bar{1}$) and orthorhombic (*Pbca*) forms respectively.

Kinetics.—The spectrum of a solution of *anti*-αβ-[Cr(picdien)Cl][ClO$_4$]$_2$ in 0.001 mol dm^{-3} nitric acid changes with time and isosbestic points are maintained at 360, 425, and 495 nm throughout the reaction. No slower subsequent changes are observed at this pH. Spectral features of the product are reported in Table 3. Potentiometric analysis of the chloride-ion concentration shows that this spectral change corresponds to release of the co-ordinated chloride and the final spectrum is therefore assigned to the [Cr(picdien)(H$_2$O)]$^{3+}$ cation.

The kinetics of aquation were studied over a range of acid concentrations and temperatures. The reactions were first order, plots of $\ln|A_\infty - A_t|$ against time being linear for more than three half-lives. The values of the rate constants, $k_{obs.}$ are collected in Table 7.

Discussion

One of the problems associated with the study of chromium(III)

Table 6. Selected torsion angles (°)

N(1)–C(5)–C(6)–N(2)	−30.1(0.4)
N(2)–C(7)–C(8)–N(3)	49.8(0.4)
N(3)–C(9)–C(10)–N(4)	−43.0(0.4)
N(4)–C(11)–C(12)–N(5)	−26.0(0.4)
C(5)–C(6)–N(2)–C(7)	−85.5(0.3)
C(6)–N(2)–C(7)–C(8)	90.0(0.4)
C(7)–C(8)–N(3)–C(9)	78.9(0.4)
C(8)–N(3)–C(9)–C(10)	−136.2(0.3)
C(9)–C(10)–N(4)–C(11)	−174.3(0.3)
C(10)–N(4)–C(11)–C(12)	157.5(0.3)

Table 7. Rate constants for the acid hydrolysis of the αβ-*anti*-$[Cr(picdien)Cl]^{2+}$ cation

T/K	$[HNO_3]$/mol dm^{-3}	$10^4\, k_{aq}$/s^{-1}
340.7	0.100	8.2
	0.010	7.2
	0.0010	8.2
320.7	0.010	0.88
313.7	0.010	0.43
304.2	0.010	0.12

Using data for 0.010 mol dm^{-3} HNO_3, $\Delta H^{\ddagger} = 93.1 \pm 2.2$ kJ mol^{-1}, $\Delta S^{\ddagger} = -32.9 \pm 6.9$ J K^{-1} mol^{-1}.

complexes with multidentate ligands is the paramagnetism of the d^3 central ion which prevents the use of high-resolution n.m.r. spectroscopy in the assignment of the isomeric form and also in the detection of small amounts of isomeric impurities that might be subsequently extracted and purified. The main, and the only reliable, way to assign a detailed configuration to the complex is by means of single-crystal *X*-ray diffraction, it being assumed that no rapid stereochemical change accompanies the dissolution of the complex in the reaction medium.

The electronic spectra of the tetrachlorozincate and perchlorate salts of the chloro cation are virtually identical; the small difference in the molar absorption coefficients of the peak at 381 nm might indicate the presence of a small amount of a second isomer in the sample of the tetrachlorozincate salt. There is a significant difference between the i.r. spectra of the two salts in that part of the spectrum associated with ν(N–H). A single peak is seen at 3 200 cm^{-1} in a hexachlorobutadiene mull of the perchlorate but, in a KBr disc, a second peak appears at 3 020 cm^{-1}. The analogous vibration of the tetrachlorozincate is hardly affected by the means whereby the sample is dispersed. It is probable that the hydrogen-bonding interactions involving the amine protons are different in the two salts and may be affected by interaction with the mulling agent.

The structural features of the cation in the tetrachlorozincate salt closely resemble those of other chromium(III) multidentate amine complexes and other picdien-containing species. The Cr–Cl(1) bond length (2.298 Å) is in the same range as those reported for other chromium(III) complexes and is significantly longer than that reported for the analogous cobalt(III) species (2.242 Å).[6] With the exception of Cr–N(4), all Cr–N distances are similar with a mean value of 2.077 Å; this value is similar to those observed in the *cis*-$[Cr(cyclam)Cl_2]^+$ ion[23] and in the $[Cr(Me_6\text{-cyclam})(H_2O)Cl]^{2+}$ ion (Me$_6$-cyclam = 5,5,7*e*,12,12,14*e*-hexamethyl-1,4,8,11-tetra-azacyclotetradecane).[24] The Cr–N(4) distance is shorter, 2.032(3) Å. A similar shortening of the bond between the 'flat' nitrogen and the metal can be seen in the cobalt(III) complex (1.96 and 1.92 Å, respectively), but the overall metal–nitrogen bond length is increased by an amount that is twice as great as that observed for the metal–chlorine bond. The distortions of the angles about the octahedron are within 4° of the regular angle of 90° with the exception of N(1)–Cr–N(2) and N(5)–Cr–N(6) which are approximately 80° and reflect the lower flexibility of this part of the ligand. The effect is less marked in the cobalt(III) complex. Bond angles within the ligand are close to the trigonal-planar angles within the pyridyl groups and the tetrahedral angles elsewhere with the exception of C(10)–N(4)–C(11) 116.1(3)° which reflects the strain at the 'flat' nitrogen. This is also observed in the cobalt(III) complex. All the chelate rings adopt envelope conformations with δ and λ helicities. Some torsion angles are given in Table 6. No short inter- or intra-molecular contacts are observed involving the co-ordinated chloride ion but there is an extensive hydrogen-bonded network connecting the anion and the cation through N(2)–H(200) ··· Cl(3), N(3)–H(300) ··· Cl(4), and N(4)–H(400) ··· Cl(5), with H ··· Cl distances of 2.57, 2.54, and 2.51 Å respectively. The cations and anions in the analogous cobalt(III) complex are also held together by hydrogen bonding, with both H(200) and H(300) close to Cl(3), H ··· Cl 2.35 and 2.50 Å respectively, and N(4)–H(400) ··· Cl(2), with H ··· Cl 2.18 Å (the labelling has been changed to conform with that used in the Figure; it should also be pointed out that the *a* and *b* parameters appear to have been inadvertently exchanged in ref. 6). There is an unusually close approach between one of the pyridine protons, H(4), and Cl(5) (2.039 Å) in the cobalt(III) complex which is not found in the chromium(III) analogue.

The $[ZnCl_4]^{2-}$ anion shows a tetrahedral arrangement of chloride ions around the central zinc atom with a mean Zn–Cl bond distance of 2.270 Å.

The spectrophotometric changes on heating an acidified aqueous solution indicate that only one reaction takes place within 120 min at 67.5 °C. In 0.0010 mol dm^{-3} HNO_3 analysis of the ionic chloride in the solution after this time indicated that the process being studied was the loss of the co-ordinated chloride and that no further changes were observed even over much longer periods. However, at higher acid concentrations there is a subsequent change in the u.v.–visible spectrum which is acid catalysed and which has tentatively been assigned to the rupture of a Cr–N bond. Such reactions are well known complications to the study of the aquation of acido-amine complexes of Cr^{III}.[11–14] No attempt was made to study these subsequent processes. At higher pH, in acetate buffer, the complex undergoes spectrophotometric changes that differ from those observed for acid hydrolysis, Cr–N bond rupture, or even base hydrolysis; it is possible that acetate is replacing chloride in the complex.

The rate constants for the acid hydrolysis of the analogous picdien complexes of Cr^{III} and Co^{III} are compared in Table 8 where it will be seen that the reactivity of the chromium(III) complex is two orders of magnitude greater than that of the cobalt(III) species.

The effect upon the lability of the chromium(III) complex of introducing a pyridyl group into the pentadentate ligand cannot be assessed in the absence of data for the analogous chromium(III) tetren complex (tetren = 1,11-diamino-3,6,9-triazaundecane) but an examination of the data for the $[M(L\text{–}L\text{–}L)(L\text{–}L)Cl]^{2+}$ (M = Co or Cr; L–L–L = terdentate triamine, L–L = a bidentate diamine) complexes, extensively studied and reviewed by House,[25,26] allows some tentative conclusions to be drawn. He has shown quite clearly that, while the rate constants for acid hydrolysis are sensitive to the steric and geometric properties of the spectator ligands, the cobalt(III) complexes tend to become more labile as the steric congestion increases, whereas the chromium(III) complexes seem to be subject to steric retardation. As a result, there are examples where the chromium(III) species is much more reactive than its cobalt(III) analogue and others where the latter is the more reactive. A selection is collected in Table 8.

Table 8. Comparison of rate constants for acid hydrolysis of analogous complexes of Co^{III} and Cr^{III} of the type $[M(L_5)Cl]^{2+}$ [a]

L_5	Isomer	M	$10^7\ k_{aq}/s^{-1}$	$k_{aq}(Cr)/k_{aq}(Co)$	Ref.
picdien	αβ-*anti*	Cr	60	100	This work
picdien	αβ-*anti*	Co	0.6 [b]		10
tetren	αβ-*anti*	Co	1.0 [b]		*c*
dien, en	*sym-fac*	Cr	224	238	*d*
dien, en	*sym-fac*	Co	0.94		*e*
L^1, en	*mer-anti*	Cr	2.9	0.076	26
L^1, en	*mer-anti*	Co	38 [f]		26
L^2, en	*mer-anti*	Cr	5.3	0.025	26
L^2, en	*mer-anti*	Co	213		26

L^1 = 1,6-Diamino-3-azahexane, L^2 = 1,7-diamino-4-azaheptane.

[a] At 25.0 °C. [b] Extrapolated from data at 70 °C using $\Delta H^{\ddagger} = 100$ kJ mol^{-1}. [c] T. L. Ni and C. S. Garner, *Inorg. Chem.*, 1967, **6**, 1071. [d] B. Dawson and D. A. House, *Inorg. Chem.*, 1977, **16**, 1354. [e] T. K. Huan, J. N. Mulvihill, A. R. Gainsford, and D. A. House, *Inorg. Chem.*, 1973, **12**, 1517. [f] Calculated from the empirical relationship between the rate constant for the mercury-catalysed aquation, k_{Hg}, and that for aquation, k_{aq}: $\log k_{Hg} = 0.96 \log k_{aq} + 4.36$.

The complexes can exist in four diastereomeric forms (more when the ligands are unsymmetrical), *sym-fac*, *unsym-fac*, *syn-mer*, and *anti-mer*. The *sym-fac* chromium(III) complex is considerably more labile than the cobalt(III) analogue when all chelate rings are five membered, but on changing to the *mer-anti* isomer the reactivity sequence is reversed as a result of a decrease in the reactivity of Cr^{III} and an increase in the reactivity of Co^{III}. However, in order to have a pair of *mer-anti* isomers it seems to be necessary to increase the ring size and the comparison is made with 1,7-diamino-4-azaheptane which contains two linked six-membered rings. A decrease in the size of one of the linked chelate rings (1,6-diamino-3-azahexane) reduces the reactivity of the cobalt(III) complex much more than that of the chromium(III) species. This reactivity increase associated with increased ring size is a common feature of cobalt(III) amine complex reactivity and is seen in the change from αβ-$[Co(picdien)Cl]^{2+}$ to αβ-$[Co(picditn)Cl]^{2+}$ [picditn = 1,11-bis(2′-pyridyl)-2,6,10-triazaundecane].[10] The chromium(III) species with the *sym-fac* (Cl is *trans* to the secondary nitrogen) ligand arrangement is some 200 times more reactive than its cobalt(III) analogue even though the chelate rings are five membered. The 100-fold increase in reactivity on going from the cobalt(III) to the chromium(III) species of *anti*-αβ-$[M(picdien)Cl]^{2+}$ is by no means the highest recorded. The pentadentate ligand has a *mer* fragment and a *fac* fragment and it is more likely that the accessibility of the metal to associative attack behind the occupied face is responsible for the enhanced lability of the chromium(III) *sym-fac* and αβ complexes and we predict that the αβ-$[Cr(tetren)Cl]^{2+}$ will be much more labile than the analogous cobalt(III) species. It does not appear to be necessary to invoke any labilising effect from the pyridyl groups in either Co^{III} or Cr^{III} in the acid-hydrolysis reaction.

A major difference between the cobalt(III) and chromium(III) picdien complexes is the sensitivity towards base-catalysed hydrolysis. Over the range of acid concentrations used to study the reactions of the chromium(III) complex the rate constant for the cobalt(III) species is inversely proportional to $[H^+]$ and it is necessary to work at concentrations of acid in the region of 1.0 mol dm^{-3} in order to measure the $[H^+]$-independent component. The rate constant for the reaction of the chromium(III) species is independent of $[H^+]$ over the whole range studied. The sensitivity towards base catalysis is therefore much less than that found for analogous cobalt complexes, an observation that holds for the large range of complexes so far examined.[5,27] The base-catalysed reactions of the chromium(III) complex are currently under investigation and the results will be published elsewhere.

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