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The synthesis, X-ray structure and hydrolysis kinetics of chloro(2-aminomethylpyridine)(triamine)chromium(III) salts

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Abstract

The chloro(diamine)(triamine)chromium(III) complexes, [CrCl(ampy)(dpt)]$(ClO_4)_2$ (**1**) and [CrCl(ampy)(2,3-tri)]$ZnCl_4 \cdot H_2O$ (**2**) were prepared from [$CrCl_3$(tri)] and 2-aminomethylpyridine (ampy) (tri = dpt = 1,5,9-triazanonane or 2,3-tri = 1,4,8-triazaoctane) and the isomeric configurations were established by single crystal X-ray structural analysis. **1**: orthorhombic, $P2_12_12_1$, $a = 8.281(1)$, $b = 13.390(1)$, $c = 19.091(2)$ Å, $V = 2116.73(30)$ Å^3, $Z = 4$. **2**: orthorhombic, $P2_12_12_1$, $a = 8.515(1)$, $b = 9.636(1)$, $c = 26.542(1)$ Å, $V = 2177.79(26)$ Å^3, $Z = 4$. In both complexes the tridentate polyamine adopts the *mer* configuration with the *sec*-N proton remote (*exo*) from the coordinated chloro ligand. For the dpt system the pyridine end of the ampy ligand is *trans* to the chloro ligand, but in the 2,3-tri system the pyridine end of the ampy ligand is *trans* to the *sec*-NH group of the tridentate. Thus the cations are formulated as *exo-trans*(py)-*mer*-[CrCl(ampy)(dpt)]$^{2+}$ (**1**) and *exo-cis*(py)-*mer*-[CrCl(ampy)(2,3-tri)]$^{2+}$ (**2**). The rates of thermal acid hydrolysis (k_H), Hg^{2+}-assisted acid hydrolysis (k_{Hg}) and base hydrolysis (k_{OH}) have been measured for **1** and **2**. Kinetic parameters (k_x (25 °C), $\Delta H^{\neq}$ (kJ mol^{-1}), $\Delta S^{\neq}$ (J K^{-1} mol^{-1})) for **1** are $10^7\ k_H = 3.16$ s^{-1}, 101, -32; $10^6\ k_{Hg} = 57.2$ M^{-1} s^{-1}, 102, $+16$; $k_{OH} = 2.17$ M^{-1} s^{-1}, 113, $+140$ and for **2** are $10^7\ k_H = 0.21$ s^{-1}, 109, -25; $10^6\ k_{Hg} = 4.4$ M^{-1} s^{-1}, 106, $+9$; $k_{OH} = 0.355$ M^{-1} s^{-1}, 108, $+110$. The incorporation of a coordinated pyridine ligand *cis* to the leaving group in **2** does not appear to have a significant acceleratory role in the base hydrolysis, with respect to the analogous *exo-mer*-[CrCl(en)(2,3-tri)]$^{2+}$ cation.

Keywords: Crystal structures; Kinetics and mechanism; Hydrolysis; Chromium complexes; Amine complexes

1. Introduction

Extensive kinetic studies on substitution reactions for Co(III) amine complexes have led to some predictable structure–reactivity patterns, where the nature of the non-replaced ligand is changed. Among these are acceleratory effects in base hydrolysis when an alkylamine is replaced by pyridine [1–3] or when a 'flat secondary nitrogen donor site' is introduced into the coordination sphere [4–8].

In acid hydrolysis (spontaneous thermal solvolytic substitution), acceleratory effects are observed when a five-membered diamine ring, e.g. en, is replaced by a six-membered analog, e.g. tn [4,9–13], or when C-alkyl substituents are added to five-membered chelate rings [14,15].

The sensitivity of Co(III) systems to such non-replaced ligand effects is in general agreement with the normally accepted dissociative interchange mechanism proposed for this metal center.

We have, for some time, been interested in the substitution process for Cr(III) amine complexes where (but with some exceptions [16–18]) a more associative interchange mechanism is proposed [19,20]. Co(III)/Cr(III) comparisons are often frustrated by lack of suitable starting materials, but when comparisons can be made, the acceleratory influences described for Co(III) are not generally observed in Cr(III) chemistry [10,11,21–23].

Abbreviations used: en = $NH_2(CH_2)_2NH_2$, tn = $NH_2(CH_2)_3NH_2$, ibn = $NH_2C(CH_3)_2CH_2NH_2$, Me$_2$tn = $NH_2CH_2C(CH_3)_2CH_2NH_2$, ampy = 2-aminomethylpyridine, dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$, 2,3-tri = $NH_2(CH_2)_2NH(CH_2)_3NH_2$, dpt = $NH_2(CH_2)_3NH(CH_2)_3NH_2$, bn = $NH_2(CH_2)_4NH_2$.

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Recently we have described the synthesis of a series of eight [CrCl(bidentate)(tridentate)]$^{2+}$ complexes [20,24] with aliphatic polyamine ligands and have now extended this series to include salts of [CrCl(ampy)(dpt)]$^{2+}$ (**1**) and [CrCl(ampy)(2,3-tri)]$^{2+}$ (**2**).

Complexes **1** and **2** have the potential to adopt a variety of geometric configurations and the structures (Fig. 1) have been determined by single crystal X-ray analysis. The incorporation of the ampy ligand into the Cr(III) coordination sphere allows, for the first time, a determination of the influence of a coordinated pyridine moiety on the rate of base hydrolysis of [CrCl(diamine)(triamine)]$^{2+}$ complexes.

2. Experimental

2.1. Syntheses

Chloro(2-aminomethylpyridine)(triamine)chromium (III) tetrachlorozincate(II) salts. These complexes (Fig. 1) were prepared in good yield from [Cr(Cl$_3$(dpt)] [24] or [CrCl$_3$(2,3-tri)] [26] and ampy (Aldrich) using previously published procedures [20,24], and the tetrachlorozincate salts were recrystallized from warm 0.1 M HCl by the addition of 3 M HCl and solid ZnCl$_2$. *Anal.* molar mass (M_r) calculated for [CrCl(ampy)(dpt)]ZnCl$_4\cdot 2\frac{1}{2}$H$_2$O: 579. Found (by Cl$^-$ titration): 579. M_r calculated for [CrCl(ampy)(2,3-tri)]ZnCl$_4\cdot$H$_2$O: 538. Found: 540.

Visible absorption spectra (0.1 M HClO$_4$), nm (ϵ, M^{-1} cm^{-1}): [CrCl(ampy)(dpt)]$^{2+}$: λ_{max} 540 (49.8), $\lambda_{sh}\sim$470 ($\sim$26), λ_{min} 439 (21.4), λ_{max} 380 (84.8), λ_{min} 337 (22.9); [CrCl(ampy)(2,3-tri)]$^{2+}$: λ_{max} 508 (58.5), $\lambda_{sh}\sim$480 ($\sim$56), λ_{min} 422 (24.9), λ_{max} 373 (89.3), λ_{min} 337 (37.5).

[CrCl(ampy)(dpt)](ClO$_4$)$_2$ was prepared from the ZnCl$_4$$^{2-}$ salt by metathesis with NaClO$_4\cdot$H$_2$O and crystals suitable for X-ray structural analysis were obtained by spontaneous evaporation of an aqueous solution at room temperature. **Caution**: all perchlorate salts are potentially explosive.

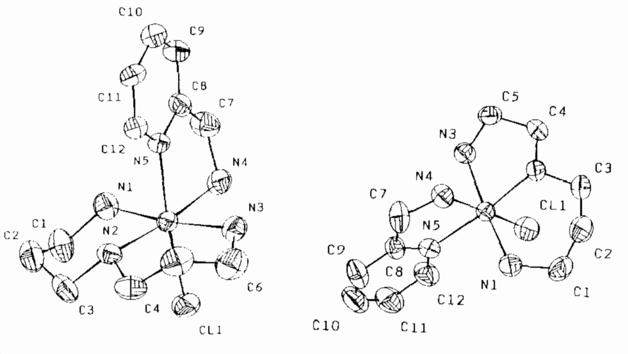

Fig. 1. SNOOPI [25] drawings of the cations in [CrCl(ampy)(dpt)](ClO$_4$)$_2$ (**1**) and [CrCl(ampy)(2,3-tri)]ZnCl$_4\cdot$H$_2$O (**2**) showing the numbering schemes adopted.

2.2. Kinetics

The rates of loss of the chloro ligand in aqueous acidic solution (0.1 M HClO$_4$) were measured either spectrophotometrically ($\leqslant$60 °C) or by chloride ion titration [24] (>60 °C). Hg^{2+}-assisted chloride release rates (I=1.0 M) were measured spectrophotometrically [24] and base hydrolysis rates (I=0.1 or 1.0 M) were measured using an Applied Photophysics stopped flow apparatus [27]. For the latter two systems, pseudo-first-order procedures were adopted ([OH$^-$] or [Hg^{2+}]>10 times [Cr(III)]), and, where possible, a range of Hg^{2+} or OH$^-$ concentrations was employed, to check the validity of the rate relationship $k_{obs}=k_R[R]$ (R=Hg^{2+} or OH$^-$). Activation parameters were computer-calculated (least-squares method) from the variation of k_R versus T data (Tables 1 and 2).

Isosbestic points observed in the absorption spectral changes (361, 440, 509 nm for **1**; 358, 422, 504 nm for **2**) during the spontaneous thermal and Hg^{2+}-assisted reactions were identical, indicating that the general stoichiometry

$$\mathrm{CrCl(N_5)^{2+} + H_2O \longrightarrow Cr(N_5)(OH_2)^{3+} + X}$$

X=Cl$^-$ or HgCl$^+$, was followed for both types of reaction.

2.3. Crystallographic data

X-ray diffraction data were collected with a CAD-4 automated four-circle diffractometer and the structures were solved by direct methods using SHELX-86 [32] and refined using CRYSTALS [33] (Table 3). Non-hydrogen atom coordinates for the cations are listed in Table 4 and important bond lengths, bond angles and dihedral angles are given in Table 5.

3. Results and discussion

3.1. Synthesis and structure

The preparation of two new pentaamminechlorochromium(III) complexes is described in Section 2. These are of the [CrCl(diamine)(triamine)]$^{2+}$ type and thus have the potential for exhibiting geometrical isomerism [28]. Single crystal X-ray structural analysis of [CrCl(ampy)dpt)](ClO$_4$)$_2$ (**1**) [CrCl(ampy)(2,3-tri)]-ZnCl$_4\cdot$H$_2$O (**2**) show these to have the configurations presented in Fig. 1.

Both complexes have the tridentate ligand in the *mer* arrangement with the *sec*-N proton remote (*exo*) from the coordinated chloro ligand, but the dpt and 2,3-tri

Table 1
Observed and calculated rate constants for the thermal acid hydrolysis, Hg^{2+}-assisted chloride release and base hydrolysis of $[CrCl(ampy)(triamine)]^{2+}$

T (°C)	$[OH^-]$ (M)	k_{obs}[b] (s^{-1})	k_{OH}[c] ($M^{-1}\ s^{-1}$)	k_{OH}(calc.)[d] ($M^{-1}\ s^{-1}$)
Triamine = dpt (**1**)				
Base hydrolysis[a]				
39.0	0.25	4.53 ± 0.3	17.4 ± 1.2	17.4
	0.15	2.60 ± 0.1	17.3 ± 0.6	
31.9	0.15	0.973 ± 0.04	6.48 ± 0.3	6.21
25.0	0.25	0.555 ± 0.02	2.22 ± 0.08	2.17
	0.15	0.296 ± 0.01	1.97 ± 0.06	
	0.10	0.224 ± 0.01	2.24 ± 0.1	
	0.05[e]	0.259 ± 0.01	5.18 ± 0.2	
11.2	0.25	0.0572 ± 0.002	0.229 ± 0.008	0.227
Triamine = 2,3-tri (**2**)				
39.0	0.25	0.728 ± 0.03	2.91 ± 0.12	2.62
	0.15	0.399 ± 0.008	2.66 ± 0.05	
	0.10	0.259 ± 0.008	2.59 ± 0.08	
	0.04	0.100 ± 0.004	2.50 ± 0.10	
25.0	0.25	0.098 ± 0.001	0.392 ± 0.002	0.355
	0.15	0.056 ± 0.008	0.373 ± 0.05	
	0.10	0.037 ± 0.003	0.370 ± 0.03	
	0.05	0.0192 ± 0.003	0.384 ± 0.04	
	0.05[e]	0.0357 ± 0.002	0.714 ± 0.04	
11.3	0.25	0.0109 ± 0.0001	0.0436 ± 0.003	0.0415

Hg^{2+}-assisted aquation[f]

T (°C)	$[H^+]$ (M)	$[Hg^{2+}]$ (mM)	$10^4\ k_{obs}$ (s^{-1})	$10^4\ k_{Hg}$[g] ($M^{-1}\ s^{-1}$)	$10^4\ k_{Hg}$(calc.)[h] ($M^{-1}\ s^{-1}$)
Triamine = dpt (**1**)					
70.0	0.88	38.7	5.63 ± 0.2	145 ± 5	145
60.0	0.76	77.2	3.70 ± 0.09	47.9 ± 1.2	48.1
50.0	0.76	77.2	1.16 ± 0.01	15.0 ± 0.1	14.9
Triamine = 2,3-tri (**2**)					
80.0	0.76	77.2	3.19 ± 0.3	41.3 ± 4	41.1
70.0	0.76	77.2	1.07 ± 0.09	13.8 ± 1.2	13.9
60.0	0.76	77.2	0.345 ± 0.01	4.46 ± 0.1	4.43
Acid hydrolysis[i] *($10^5\ k_H$ (s^{-1}))*					
dpt	(obs.)	20.6 (T)[j] (80.0)[k]	12.3 (T) (75.0)	7.62 (T) (70.0)	2.49 (S) (60.0)
	(calc.)[h]	20.6	12.5	7.43	2.51
2,3-tri	(obs.)	18.7 (T,S) (100.0)	2.51 (T) (80.0)	0.697 (T) (70.0)	
	(calc.)[h]	19.2	2.32	0.743	

[a] As $ZnCl_4^{2-}$ salts with $I = 1.0$ M ($NaClO_4$), using stopped flow spectrophotometry at 375 nm.

[b] Mean of ten or more observations.

[c] $k_{OH} = k_{obs}[OH^-]^{-1}$.

[d] Calculated from the activation parameters. $\Delta H^{\neq} = 113 \pm 2$, $\Delta S^{\neq} = +140 \pm 6$ for **1** and $\Delta H^{\neq} = 108 \pm 3$ kJ mol^{-1}, $\Delta S^{\neq} = +110 \pm 7$ J K^{-1} mol^{-1} for **2**.

[e] $I = 0.1$ M ($NaClO_4$).

[f] $I = 1.0$ M ($HClO_4$, $Hg(NO_3)_2$).

[g] $k_{Hg} = k_{obs}[Hg^{2+}]^{-1}$.

[h] Calculated from the activation parameters cited in Table 2.

[i] Reproducibility in k_H is ±5%.

[j] T = titrimetric, S = spectrophotometric ($\lambda = 380$ or 535 nm).

[k] Temperature (°C) of measurement.

systems differ in an end-for-end isomerization of the ampy coordination. In the dpt complex the py end of the unsymmetrical diamine is *trans* to the coordinated chloro ligand but in the 2,3-tri complex the diamine ligand arrangement is reversed (Fig. 1). Dihedral angles for the tridentate ligands in *mer*-$[CrCl(ampy)(dpt)](ClO_4)_2$ and *mer*-$[CrCl(en)(dpt)]ZnCl_4$ [24] are very similar (within ±5°) (Table 5), but the λ-ampy ring

Table 2
Kinetic parameters for the rate of thermal acid hydrolysis (k_H) and Hg^{2+}-assisted acid hydrolysis (k_{Hg}) for some $CrCl(N_5)^{2+}$ complexes ($I = 1.0$ M, 25 °C)

Complex	$10^7 k_H$ (s^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	Ref.	$10^4 k_{Hg}$ (M^{-1} s^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	Ref.
$(NH_3)_5$	95	86.9	−50	[28]	480[a]	60	−56	[29]
$(MeNH_2)_5$	2.48	111	−2	[28]	21.5	93.2 ± 0.6	+16.5 ± 1	[30]
mer-(en)(dpt)	5.34	96.8	−4	[24]	6.44	75.5 ± 3	−53 ± 6	[31]
mer-(tn)(dpt)	5.04	80.4	−96	[24]	29.1	87 ± 6	−1 ± 10	[31]
mer-(en)(2,3-tri)	2.87	88.5	−73	[24]	1.94	87 ± 8	−24 ± 16	[31]
mer-(ampy)(dpt)	3.16	101 ± 2.3	−32 ± 6	this work	0.572	102 ± 0.4	+16 ± 1	this work
mer-(ampy)(2,3-tri)	0.306	110 ± 4	−20 ± 8	this work	0.044	106 ± 1	+9 ± 3	this work

[a] Extrapolated from $I = 2.0$ M.

Table 3
Crystallographic data for $[CrCl(ampy)(dpt)](ClO_4)_2$ (**1**) and $[CrCl(ampy)(2,3\text{-tri})]ZnCl_4 \cdot H_2O$ (**2**)

Complex	**1**	**2**
Formula	$C_{12}H_{25}Cl_3CrN_5O_8$	$C_{11}H_{25}Cl_5CrN_5OZn$
M_r	525.7	538.0
Colour	red	orange
Size (mm)	0.45 × 0.3 × 0.25	0.27 × 0.29 × 0.34
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a (Å)	8.281(1)	8.515(1)
b (Å)	13.390(1)	9.636(1)
c (Å)	19.091(2)	26.542(1)
V (Å^3)	2116.73(30)	2177.79(26)
D_{calc} (g cm^{-3})	1.650	1.641
Z	4	4
T (K)	293	293
Radiation, λ (Å)	Mo Kα, 0.71069	Cu Kα, 1.54180
F(000)	1084	1080
Linear absorption coefficient (cm^{-1})	9.564	114.710
θ_{max}	30.44	77.50
Independent reflections	3605	2620
Reflections used ($F > 3\sigma$)	2708	2360
No. variables	262	225
Final R_w (R)	4.13(3.45)	5.06(4.34)
Weighting system, w	wght$[1 - (\delta(F)/6\sigma F)^2]^2$	
Weighting parameters	8.34, −3.16, 6.75	96.3, −130, 107, −40.4, 17

(−21.0°) is much flatter than the δ-en ring (+51.4°). The λ-ampy ring flattening (−6.6°) is even more marked in *mer*-$[CrCl(ampy)(2,3\text{-tri})]ZnCl_4 \cdot H_2O$. The end-for-end ampy isomerization results in considerable differences in color and visible absorption spectra for the two systems (although in the [CrCl(bidentate)(tridentate)]$^{2+}$ series the 2,3-tri complexes are often more orange), but little difference in Cr–Cl bond distance (2.2884(9) Å in **1** and 2.292(1) Å in **2**.

3.2. Acid hydrolysis

The chloro complexes [CrCl(ampy)(triamine)]$^{2+}$ are extremely inert (Table 1) and aqueous acidic solutions of [CrCl(ampy)(2,3-tri)]$^{2+}$ have a half-life of about one year in 0.1 M $HClO_4$ at 25 °C, with respect to chloride release. This inertness is also reflected in small values for the rate constants associated with the Hg^{2+}-assisted chloride release reaction (Table 1). Comparative data for other $[CrCl(N_5)]^{2+}$ systems are presented in Table 2. There is currently considerable controversy in the literature with regard to the mechanism of acid hydrolysis in Cr(III) systems [16–19,34] (associative [17–19] or dissociative [16,34]) and we are now measuring the Hg^{2+}-assisted chloride release kinetics for a series of *trans*-$[CrCl_2(N_4)]^+$ and $[CrCl(RNH_2)_5]^{2+}$ complexes in the hope that the combined kinetic data may provide some definitive mechanistic information.

3.3. Base hydrolysis

The S_N1 cb mechanism is generally accepted for the base hydrolysis of $[CoCl(N_5)]^{2+}$ complexes [8] but there are considerable difficulties in a direct application of

Table 4
Non-hydrogen atomic coordinates for the cations in $[CrCl(ampy)(dpt)](ClO_4)_2$ (**1**) and $[CrCl(ampy)(2,3\text{-}tri)]ZnCl_4 \cdot H_2O$ (**2**)[a]

Atom	*x/a*	*y/b*	*z/c*
$[CrCl(ampy)(dpt)]^{2+}$			
Cr(1)	0.07874(6)	0.97110(3)	0.87482(2)
Cl(1)	−0.0717(1)	0.82781(6)	0.87181(5)
N(1)	−0.1190(4)	1.0613(3)	0.8980(2)
C(1)	−0.2267(5)	1.0365(4)	0.9583(2)
C(2)	−0.1338(6)	1.0297(4)	1.0252(2)
C(3)	−0.0206(5)	0.9415(3)	1.0292(2)
N(2)	0.1251(4)	0.9520(2)	0.9829(1)
C(4)	0.2373(5)	0.8690(3)	1.0031(2)
C(5)	0.3903(5)	0.8642(3)	0.9605(3)
C(6)	0.3685(6)	0.8212(3)	0.8882(3)
N(3)	0.2813(4)	0.8900(2)	0.8405(2)
N(4)	0.0365(4)	1.0061(2)	0.7703(1)
C(7)	0.0627(5)	1.1144(3)	0.7566(2)
C(8)	0.1881(4)	1.1545(2)	0.8052(2)
C(9)	0.2706(5)	1.2426(3)	0.7927(2)
C(10)	0.3852(5)	1.2752(3)	0.8385(2)
C(11)	0.4144(5)	1.2208(2)	0.8985(2)
C(12)	0.3264(4)	1.1349(2)	0.9097(2)
N(5)	0.2148(3)	1.1015(2)	0.8645(1)
$[CrCl(ampy)(2,3\text{-}tri)]^{2+}$			
Cr(1)	0.80660(8)	0.01628(8)	0.12649(3)
Cl(1)	0.5687(1)	0.0152(2)	0.08612(5)
N(1)	0.8457(6)	0.2225(5)	0.1069(2)
Cl(1)	0.7230(9)	0.3268(6)	0.1223(3)
C(2)	0.693(1)	0.3273(7)	0.1774(3)
C(3)	0.6075(8)	0.1994(7)	0.1972(2)
N(2)	0.7044(5)	0.0731(5)	0.1949(2)
C(4)	0.6168(7)	−0.0496(6)	0.2143(2)
C(5)	0.7189(7)	−0.1757(6)	0.2073(2)
N(3)	0.7608(5)	−0.1853(4)	0.1531(2)
N(4)	1.0296(5)	0.0024(6)	0.1589(2)
C(7)	1.1505(7)	−0.0425(8)	0.1241(3)
C(8)	1.0914(6)	−0.0609(5)	0.0717(2)
C(9)	1.1934(8)	−0.0924(7)	0.0327(3)
C(10)	1.131(1)	−0.1142(9)	−0.0145(3)
C(11)	0.973(1)	−0.104(1)	−0.0222(2)
C(12)	0.8776(8)	−0.0708(8)	0.0179(2)
N(5)	0.9362(5)	−0.0482(5)	0.0647(1)

[a] See Fig. 1 for the atom numbering schemes adopted.

Table 5
Selected bond lengths and angles in $[CrCl(ampy)(dpt)](ClO_4)_2$ (**1**), $[CrCl(ampy)(2,3\text{-}tri)]ZnCl_4 \cdot H_2O$ (**2**) and $[CrCl(en)(dpt)]ZnCl_4$ (**3**)[a]

	1	2	3 [24]
Bond length (Å)			
Cr–Cl	2.2884(9)	2.292(1)	2.287(3)
Cr–N(1)	2.082(3)	2.081(5)	2.095(5)
Cr–N(2)	2.114(3)	2.086(4)	2.097(4)
Cr–N(3)	2.103(3)	2.103(3)	2.089(5)
Cr–N(4)	2.080(3)	2.089(4)	2.093(4)
Cr–N(5)	2.087(3)	2.072(4)	2.104(4)
Bond angle (°)			
Cl–Cr–N	173.1(7) N(5)	174.7(1)	174.0(1)
N(1)–Cr–N(3)	173.2(1)	174.5(2)	173.3(2)
N(2)–Cr–N	173.9(1) N(4)	171.7(2) N(5)	172.3(2)
Torsion angle (°C)			
N(1)–C(1)–C(2)–C(3)	−68.7	−70.6	−70.3
C(1)–C(2)–C(3)–N(2)	72.1	68.9	73.8
C(2)–C(3)–N(2)–C(4)	169.7		171.6
C(3)–N(2)–C(4)–C(5)	178.0		178.8
N(2)–C(4)–C(5)–C(6)	−76.3		−69.7
C(4)–C(5)–C(6)–N(3)	71.9		75.4
N(4)–C(7)–C(8)–N(5)	−21.0	−6.58	51.4 (δ-en)
N(2)–C(4)–C(5)–N(3)		−56.4 (λ-en)	

[a] The numbering systems used are shown in Fig. 1.

this mechanism to Cr(III) analogs and a more associative interchange modification has recently been proposed [20]. A number of structure–reactive correlations has been made with regard to the S_N1 cb mechanism in Co(III) systems, among these being a modest (×30) labilizing effect when coordinated pyridine is substituted for an alkylamine *cis* to the leaving group and a more dramatic ($\times 10^3$) accelatory influence on the incorporation of a 'flat' secondary nitrogen [5,34] in a similar environment. We have recently shown [35] that the 'flat' secondary nitrogen effect is not greatly marked in the base hydrolysis of appropriate Cr(III) systems, and here we explore the so called 'pyridine' effect.

A pyridine group has been incorporated into the Cr(III) coordination sphere using the ampy ligand and the end-for-end isomerization puts the py *trans* to the leaving group in $[CrCl(ampy)(dpt)]^{2+}$ and *cis* in $[CrCl(ampy)(2,3\text{-}tri)]^{2+}$ (Fig. 1).

Base hydrolysis rates were measured using stopped flow techniques ($I = 1.0$ and 0.1 M) over a range of $[OH^-]$ and temperature (Table 1) and the observed pseudo-first-order rate constants were converted into second-order k_{OH} values using the expression $k_{OH} = k_{obs}[OH^-]^{-1}$ (Table 1).

The incorporation of py in a position *trans* to the leaving group causes a modest (×20) rate increase ($[CrCl(en)(dpt)]^{2+}$ versus $[CrCl(ampy)(dpt)]^{2+}$), but with py in the *cis* position the reaction rate is hardly changed ($[CrCl(en)(2,3\text{-}tri)]^{2+}$ versus $[CrCl(ampy)(2,3\text{-}tri)]^{2+}$). This is not what would be expected for Co(III) systems with py in the *cis* position, but the effect of a *trans*-py on the base hydrolysis of Co(III) complexes has yet to be investigated. It thus appears that the acceleratory effects caused by changes in the non-replaced ligands in Co(III) chemistry are not manifest in analogous Cr(III) systems. There are, however, some N_5-macrocyclic ligand systems that can induce extreme lability in the base hydrolysis of $[CrCl(N_5)]^{2+}$ systems, to such an extent that the rates are 10^6 times *faster* than their Co(III) analogs [36].

4. Supplementary material

A complete listing of all atom coordinates, e.s.d.s and isotropic *U* values; anisotropic displacement parameters; bond lengths and angles; and possible H bonds for both $[CrCl(ampy)(dpt)](ClO_4)_2$ (**1**) and $[CrCl(ampy)(2,3\text{-tri})]ZnCl_4 \cdot H_2O$ (**2**) (8 pp) are available from author D.A.H.

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