

Chromium(III) Complexes with 1,5,9-Triazanonane (3,3-tri) – $\text{CrX}_3(3,3\text{-tri})^{n+}$ and $\text{CrCl}(\text{diamine})(3,3\text{-tri})^{2+}$

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Abstract

The reaction of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (dehydrated in DMSO) with 1,5,9-triazanonane (3,3-tri) gives *mer*- $\text{CrCl}_3(3,3\text{-tri})$, the configuration being established by isomorphism with the corresponding Co(III) complex. This non-electrolyte is hydrolyzed in aqueous acidic solution and *mer*- $[\text{CrCl}_2(3,3\text{-tri})(\text{OH}_2)]\text{ClO}_4$ can be isolated by anation with HCl in the presence of HClO_4 . Reaction of *mer*- $\text{CrCl}_3(3,3\text{-tri})$ in DMF with diamines produces complexes of the type $[\text{CrCl}(\text{diamine})(3,3\text{-tri})]\text{Cl}_2$ [diamine = 1,2-diaminoethane (en), 1,2-diaminopropane (pn), 1,3-diaminopropane (tn), 2,2-dimethyl-1,3-diaminopropane (Me_2tn) and cyclohexanediamine (chxn, *cis* plus *trans* mixture; two isomers A and B)] and these have been characterized as the ZnCl_4^{2-} salts. The configuration of the triamine ligand in these complexes has been established as *mer*-(H \downarrow) by a single crystal X-ray analysis of $[\text{CrCl}(\text{en})(3,3\text{-tri})]\text{ZnCl}_4$, monoclinic, $P2_1$, $a = 7.932$, $b = 14.711$, $c = 8.312$ Å, $\beta = 104.6^\circ$ and $Z = 2$, refined to a conventional R factor of 0.034. The kinetics of the Hg^{2+} -assisted chloride release from $[\text{CrCl}(\text{diamine})(3,3\text{-tri})]\text{ZnCl}_4$ salts were measured spectrophotometrically ($\mu = 1.0$ M HClO_4 or HNO_3) over 15 K temperature ranges to give, in order, $10^4 k_{\text{Hg}}$ (298.2 K) ($\text{M}^{-1} \text{s}^{-1}$), E_a (kJ mol^{-1}), ΔS^\ddagger (J $\text{K}^{-1} \text{mol}^{-1}$): en(HClO_4): 5.95, 78.1, -53; pn(HClO_4): 5.24, 81.2, -44; tn(HClO_4): 26.7, 85.6, -15; $\text{Me}_2\text{tn}(\text{HClO}_4$): 21.8, 78.6, -40; A-chxn(HNO_3): 7.60, 81.0, -41; B-chxn(HNO_3): 18.3, 56.8, -115. A 'non-replaced ligand effect' on the rate is observed for the first time in this series of homologous Cr(III) complexes. The kinetics of the thermal aquation (k_{H} , 0.1 M HClO_4) were measured titrimetrically for $\text{CrCl}(\text{diamine})(3,3\text{-tri})^{2+}$ to give the following kinetic parameters: diamine = en: $10^7 k_{\text{H}}$ (298.2) = 5.34 s^{-1} , $E_a = 99.2$ kJ mol^{-1} , $\Delta S^\ddagger = -40$ J $\text{K}^{-1} \text{mol}^{-1}$; diamine = tn: $10^7 k_{\text{H}}$ (298.2) = 5.04 s^{-1} , $E_a = 82.8$, $\Delta S^\ddagger = -96$.

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Introduction

The availability of a wide range of chloropentaminecobalt(III) complexes ($\text{CoCl}(\text{N}_5)^{2+}$ systems) has allowed the accumulation of considerable kinetic and structural information for this class of compound [1]. The number of analogous Cr(III) complexes is, however, restricted to $\text{CrCl}(\text{NH}_3)_5^{2+}$ [1], $\text{CrCl}(\text{RNH}_2)_5^{2+}$ [1], $\text{CrCl}(\text{tetren})^{2+}$ [2]**, *s-fac*- $\text{CrCl}(\text{diamine})(\text{dien})^{2+}$ [3], (diamine = en, pn, tn) and *u-fac*- $\text{CrCl}(\text{N-Metn})(\text{dien})^{2+}$ [4]. In order to establish structure-reactivity patterns for this type of Cr(III) complex it is desirable to extend the series of compounds available.

Acid hydrolysis rates of the coordinated chloro ligand in Cr(III) complexes containing five-membered polyamine chelate rings are often complicated by concurrent Cr–N bond rupture during the course of hydrolysis [5–7]. Such effects are rarely observed in analogous Cr(III) complexes containing six-membered chelate rings [8–10].

We have been able to exploit this observation to prepare a series of $\text{CrCl}(\text{diamine})(\text{triamine})^{2+}$ complexes, where the triamine is 1,5,9-triazanonane ($\text{NH}_2(\text{CH}_2)_3\text{NH}(\text{CH}_2)_3\text{NH}_2 = 3,3\text{-tri}$), a tridentate polyamine which forms two fused six-membered chelate rings on coordination [11–13]. The key starting material, *mer*- $\text{CrCl}_3(3,3\text{-tri})$, is easily prepared and this reacts smoothly with diamines to give $\text{CrCl}(\text{diamine})(3,3\text{-tri})^{2+}$ salts in good yield.

Whilst the *mer*-configuration of the triamine was expected to be retained during this reaction, this could not be taken for granted (see 'discussion') and the configuration of the tridentate ligand in $[\text{CrCl}(\text{en})(3,3\text{-tri})]\text{ZnCl}_4$ was established as *mer*-

**Abbreviations used: en = $\text{NH}_2(\text{CH}_2)_2\text{NH}_2$; pn = *R,S*- $\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}_2$; tn = $\text{NH}_2(\text{CH}_2)_3\text{NH}_2$; $\text{Me}_2\text{tn} = \text{NH}_2\text{CH}_2\text{C}(\text{Me})_2\text{CH}_2\text{NH}_2$; chxn = *meso* + *racemic* $\text{C}_6\text{H}_{10}(\text{NH}_2)_2$, 1,2-diaminocyclohexane; dien = 2,2-tri = $\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$; 2,3-tri = $\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{NH}_2$; 3,3-tri = $\text{NH}_2(\text{CH}_2)_3\text{NH}(\text{CH}_2)_3\text{NH}_2$; tetren = $\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$; *N*-Me-tn = $\text{CH}_3\text{NH}(\text{CH}_2)_3\text{NH}_2$; DMSO = $(\text{CH}_3)_2\text{SO}$; DMF = $(\text{CH}_3)_2\text{NCHO}$.

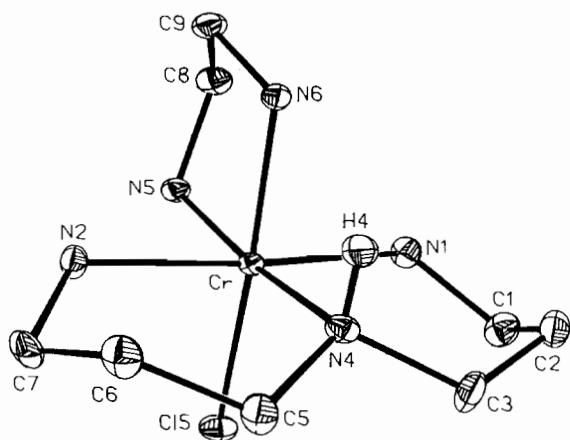


Fig. 1. A perspective view of the *mer*-(H₄)-CrCl(en)(3,3-tri)²⁺ cation. This is very similar to the molecular mechanics calculated view of the analogous Co(III) complex presented in Fig. 7 of ref. 13.

H₄)* by a single crystal structure determination (Fig. 1).

The coordinated chloro ligands in this series are very inert (in contrast to the Co(III) analogs [14]) but both thermal and Hg²⁺-assisted chloride kinetics

*Current nomenclature rules are unable to distinguish between the two potential isomers of *mer*-[CrCl(AA)-(ABA)]²⁺ (AA = diamine, ABA = symmetrical triamine). The nomenclature adopted here is that the (H₄)-isomer has the *sec*-NH proton remote from the coordinated chloro ligand (Fig. 1).

have been measured to establish the influence of the non-replaced ligands on reaction rate. It is found that in this series, and for the first time in an homologous series of Cr(III) complexes, that the non-replaced ligands do influence the rate of Hg²⁺-assisted chloride release.

Experimental

The commercially available ligands were used without further purification. The cyclohexane diamine used (EGA-Chemie, 97%) is a mixture of *trans* (*racemic*) and *cis* (*meso*) isomers; ¹³C NMR spectroscopy shows an approximately 60/40 *trans/cis* ratio, with a background (<10%) of other C-containing materials.

Unless otherwise stated, the complexes prepared here were washed successively with isopropanol and ether and air dried.

Caution: Although we have experienced no difficulty with the perchlorate salts described here, these should be regarded as potentially explosive and handled accordingly.

Analytical data for the isolated salts are presented in Table I and visible absorption spectral parameters in Tables II and III.

mer-Trichloro(1,5,9-triazanonane)chromium(III), CrCl₃(3,3-tri)

Hydrated chromium(III) chloride, CrCl₃·6H₂O (10 g) was dehydrated by boiling (190 °C) in a well

TABLE I. Analytical Data

| Complex | Calc. (%) | | | Found (%) | | |
|---|-----------|------|-------|-----------|------|-------|
| | C | H | N | C | H | N |
| CrCl ₃ (3,3-tri) | | | | | | |
| C ₆ H ₁₇ N ₃ Cl ₃ Cr | 24.89 | 5.92 | 14.51 | 24.77 | 6.03 | 14.41 |
| [CrCl ₂ (3,3-tri)(OH ₂)]ClO ₄ | | | | | | |
| C ₆ H ₁₉ N ₃ Cl ₃ O ₅ Cr | 19.39 | 5.15 | 11.31 | 19.32 | 5.06 | 11.37 |
| [CrCl(3,3-tri)(en)]ZnCl ₄ | | | | | | |
| C ₈ H ₂₅ N ₅ Cl ₅ ZnCr | 19.77 | 5.18 | 14.41 | 19.38 | 5.12 | 14.30 |
| [CrCl(3,3-tri)(tn)]ZnCl ₄ ·2H ₂ O | | | | | | |
| C ₉ H ₃₁ N ₅ Cl ₅ O ₂ ZnCr | 20.16 | 5.83 | 13.07 | 20.20 | 5.78 | 13.27 |
| [CrCl(3,3-tri)(Me ₂ tn)]ZnCl ₄ ·H ₂ O | | | | | | |
| C ₁₁ H ₃₃ N ₅ Cl ₅ OZnCr | 24.19 | 6.09 | 12.83 | 24.13 | 6.33 | 12.88 |
| A-[CrCl(3,3-tri)(chxn)]ZnCl ₄ | | | | | | |
| C ₁₂ H ₃₁ N ₅ Cl ₅ ZnCr | 26.69 | 5.79 | 12.97 | 26.54 | 5.97 | 12.91 |
| B-[CrCl(3,3-tri)(chxn)]ZnCl ₄ ·H ₂ O | | | | | | |
| C ₁₂ H ₃₃ N ₅ Cl ₅ OZnCr | 25.83 | 5.96 | 12.55 | 25.85 | 6.10 | 12.57 |
| [CrCl(3,3-tri)(pn)]ZnCl ₄ | | | | | | |
| C ₉ H ₂₇ N ₅ Cl ₅ ZnCr | 21.62 | 5.44 | 14.01 | 21.81 | 5.65 | 14.02 |
| [CrCl(2,3-tri)(en)]ZnCl ₄ | | | | | | |
| C ₇ H ₂₃ N ₅ Cl ₅ ZnCr | 17.82 | 4.89 | 14.84 | 18.11 | 4.82 | 14.94 |
| [CrCl(3,3-tri)(en)]ClO ₄ ·NO ₃ | | | | | | |
| C ₈ H ₂₅ N ₆ Cl ₂ O ₇ Cr | 21.92 | 5.75 | 19.17 | 22.18 | 5.99 | 19.46 |

TABLE II. Visible Absorption Maxima and Minima (350–600 nm) of some *trans*-Dichloro(aqua)(triamine)- and *mer*-Triaqua(triamine)chromium(III) Complexes^a

| Complex | λ_{\max} | λ_{\min} | λ_{\max} | λ_{\min} | λ_{\max} | Reference |
|---|------------------|------------------|------------------|------------------|------------------|-----------|
| <i>trans</i> -dichloro(aqua) complexes | | | | | | |
| CrCl ₂ (NH ₃) ₃ (OH ₂) ⁺ | 595sh (46) | | 512 (63.6) | 472 (53.3) | 428 (80.0) | b |
| CrCl ₂ (dien)(OH ₂) ⁺ | 595 (23.5) | | 525sh (14.5) | 469 (9.4) | 410 (25.2) | c |
| CrCl ₂ (3,3-tri)(OH ₂) ⁺ | 594 (21.5) | 537 (11.8) | 501 (14.3) | 465 (11.1) | 408 (37.7) | d |
| CrCl ₂ (2,3-tri)(OH ₂) ⁺ | 583 (22.3) | 563 (20.6) | 498 (38.2) | 459 (30.1) | 419 (38.1) | e |
| <i>mer</i> -triaqua complexes | | | | | | |
| Cr(NH ₃) ₃ (OH ₂) ₃ ³⁺ | | | 503 (26.3) | 432 (9.1) | 376 (26) | b |
| Cr(dien)(OH ₂) ₃ ³⁺ | | | 495 (67.0) | 430 (13.3) | 375 (32.2) | c |
| Cr(3,3-tri)(OH ₂) ₃ ³⁺ | | | 493 (25.9) | | 375 (39.2) | d |
| Cr(2,3-tri)(OH ₂) ₃ ³⁺ | | | 481 (46.7) | 425 (21.0) | 376 (37.6) | e |

^aValues in parenthesis are the molar absorptivity coefficients (ϵ (M⁻¹ cm⁻¹)). ^bRef. 37. ^cRef. 38. ^dThis research. ^eRef. 22.

TABLE III. Absorption Maxima and Minima (350–600 nm) of some Aqua and Chloropentaaminechromium(III) Complexes at 18–23 °C^a

| | λ_{\max} | λ_{sh} | λ_{\min} | λ_{\max} | Reference |
|--|------------------|----------------|------------------|------------------|-----------|
| CrCl(NH ₃) ₅ ²⁺ | 512 (36) | | 429 (13.3) | 375 (39) | c |
| <i>s-fac</i> -CrCl(en)(dien) ²⁺ | 514 (79.3) | | 428 (24.5) | 373 (9.14) | d |
| <i>s-fac</i> -CrCl(pn)(dien) ²⁺ ^e | 514 (74.5) | | 417 (22.9) | 372 (85.7) | d |
| <i>s-fac</i> -CrCl(tn)(dien) ²⁺ | 526 (71.5) | | 432 (21.3) | 375 (87.6) | d |
| <i>u-fac</i> -CrCl(N-Me-tn)(dien) ²⁺ ^f | 521 (66.6) | 480 (50) | 436 (25.8) | 380 (85.9) | g |
| <i>mer</i> -CrCl(en)(3,3-tri) ²⁺ | 526 (53.0) | 475 (32) | 434 (16.8) | 381 (75.5) | h |
| <i>mer</i> -CrCl(pn)(3,3-tri) ²⁺ ^e | 527 (54.1) | 477 (34) | 435 (20.8) | 381 (78.5) | h |
| <i>mer</i> -A-CrCl(chxn)(3,3-tri) ²⁺ | 531 (50.8) | 475 (31) | 435 (16.6) | 381 (73.7) | h |
| <i>mer</i> -B-CrCl(chxn)(3,3-tri) ²⁺ | 528 (51.2) | 477 (32) | 435 (19.6) | 381 (74.7) | h |
| <i>mer</i> -CrCl(tn)(3,3-tri) ²⁺ | 519 (40.7) | 474 (31) | 431 (12.6) | 381 (53.4) | h |
| <i>mer</i> -CrCl(Me ₂ tn)(3,3-tri) ²⁺ | 521 (41.4) | 475 (30) | 433 (11.6) | 381 (50.8) | h |
| Aqua Complexes ⁱ | | | | | |
| Cr(NH ₃) ₅ (OH ₂) ³⁺ | 484 (35) | | 410 (9.4) | 360 (29) | j |

(continued)

TABLE III. (continued)

| | λ_{\max} | λ_{sh} | λ_{\min} | λ_{\max} | Reference |
|---|------------------|-----------------------|------------------|------------------|-----------|
| <i>s-fac</i> -Cr(en)(dien)(OH ₂) ³⁺ | 482 (69.4) | | 410 (21.7) | 360 (55.7) | d |
| <i>s-fac</i> -Cr(pn)(dien)(OH ₂) ^{3+ e} | 482 (65.3) | | 410 (19.5) | 362 (52.9) | d |
| <i>s-fac</i> -Cr(tn)(dien)(OH ₂) ³⁺ | 490 (58.9) | | 414 (19.4) | 362 (54.9) | d |
| <i>u-fac</i> -Cr(N-Me-tn)(dien)(OH ₂) ^{3+ f} | 481 (72.9) | | 415 (23.4) | 361 (67.7) | g |
| <i>mer</i> -Cr(en)(3,3-tri)(OH ₂) ³⁺ | 492 (34.4) | | | 373 (44.9) | h |
| <i>mer</i> -Cr(pn)(3,3-tri)(OH ₂) ^{3+ e} | 489 (35.8) | | | 372 (47.3) | h |
| <i>mer-A</i> -Cr(chxn)(3,3-tri)(OH ₂) ^{3+ k} | 491 (37.5) | | | 373 (48.1) | h |
| <i>mer</i> -Cr(tn)(3,3-tri)(OH ₂) ³⁺ | 479 (36.2) | | 419 | 365 (43.3) | h |
| <i>mer</i> -Cr(Me ₂ tn)(3,3-tri)(OH ₂) ³⁺ | 483 (35.0) | | 422 | 367 (39.9) | h |

^aValues in parenthesis are the molar absorptivity coefficients (ϵ (M⁻¹ cm⁻¹)). ^bIn 0.1 M HClO₄. ^cRef. 39. ^dRef. 40. ^e*R,S*-1,2-diaminopropane. ^fThis complex has the CH₃-NH- end of the diamine ligand *trans* to the *sec*-NH group of the tridentate [5]. ^gRef. 5. ^hThis research. ⁱIn 0.88 M HClO₄ containing 4.47×10^{-2} M Hg(NO₃)₂. ^jRef. 41. ^kIn 0.82 M HNO₃ containing 5.74×10^{-2} M Hg(NO₃)₂.

stirred solution of DMSO (40 ml). The now purple solution was allowed to cool to 170 °C and 3,3-tri (5 ml) was slowly added. Dark olive green crystals deposited (6 g, 55% yield), and these were collected by filtration from the cooled solution. The preparation was subsequently repeated on a 50 g scale (CrCl₃·6H₂O) giving 34 g (63%) of the trichloride. We were unable to find a suitable solvent for the recrystallization of this material, but satisfactory analytical data (Table I) were obtained using the directly isolated product.

mer-Aqua(dichloro)(1,5,9-triazanonane)chromium(III) Perchlorate, [CrCl₂(3,3-tri)(OH₂)]ClO₄

Trichloro(1,5,9-triazanonane)chromium(III) (1.5 g) was suspended in 0.1 M HCl (20 ml) and the solution was heated to 80 °C. The complex slowly dissolved to give a magenta coloured solution (10 min). After cooling to room temperature, HCl (20 ml, 12 M) and HClO₄ (5 ml, 60%) were added. Large green needles deposited over a period of 10 days at room temperature.

Chloro(diamine)(1,5,9-triazanonane)chromium(III) Tetrachlorozincate(II) Salts, [CrCl(AA)(3,3-tri)]ZnCl₄

The following general method was used for AA = en, pn, tn, Me₂tn and chxn.

Trichloro(1,5,9-triazanonane)chromium(III) (5 g) was suspended in DMF (40 ml) containing 1.5–2 fold excess of the diamine. The magnetically stirred

mixture was heated to 110–120 °C when an almost quantitative yield of a pink solid deposited (the yields were lower for tn and Me₂tn)

This product (presumably the chloride salt of CrCl(AA)(3,3-tri)²⁺) was collected by filtration from the cooled DMF solutions.

The isolated pink solids were dissolved in 100 ml of 0.1 M HCl at 50–60 °C, an equal volume of 12 M HCl was added, followed by 10 g of solid ZnCl₂.

Red crystals of the ZnCl₄²⁻ salts were obtained from the ice cooled solutions. In the case of AA = chxn, a chloride salt (isomer B) deposited on the addition of HCl. This was removed from the cooled solution and ZnCl₂ was added to the warmed mother liquor to give the ZnCl₄²⁻ salt (isomer A). The ZnCl₄²⁻ salt of isomer B was obtained by recrystallization of the chloride from dilute HCl by addition of ZnCl₂. The yields on recrystallization were again almost quantitative. In a typical synthesis, for example, 5 g of CrCl₃(3,3-tri) gave 7 g of crude [CrCl(en)(3,3-tri)]Cl₂, 2.5 g of which gave 3 g of [CrCl(en)(3,3-tri)]ZnCl₄.

Kinetics

The rates of Hg²⁺-assisted chloride release were measured spectrophotometrically (Varian DMS-100 or Varian Superscan recording spectrophotometers).

Solutions of Hg(NO₃)₂ were prepared in HClO₄ or HNO₃ to give a final ionic strength of 1.0 M and Hg²⁺ concentrations were determined by titration with standard KCl solution using diphenylcarba-

TABLE IV. Observed and Calculated Rate Constants for the Hg²⁺-assisted Aquation of [CrCl(AA)(3,3-tri)]ZnCl₄ salts ($\mu = 1.0$ M)

| <i>T</i> (°C[K]) | [H ⁺] ^a (M) | [Hg ²⁺] _i ^b (mM) | 10 ⁴ <i>k</i> _{obs} ^c (s ⁻¹) | 10 ³ <i>k</i> _{Hg} ^d (M ⁻¹ s ⁻¹) | 10 ³ <i>k</i> _{Hg} (calc) ^e (M ⁻¹ s ⁻¹) |
|--|---------------------------------------|---|--|---|--|
| AA = en | | | | | |
| 25.0[298.2] | | | | | 0.595 |
| 45.3[318.5] | 0.76 | 93.4 | 4.16 ± 0.08 | 4.45 ± 0.09 | 4.43 |
| 53.2[326.4] | 0.76 | 93.4 | 8.32 ± 0.05 | 8.91 ± 0.05 | 9.06 |
| | 0.76 | 93.4 | 8.51 ± 0.07 | 9.11 ± 0.07 | |
| 58.8[332.0] | 0.82 | 64.5 | 9.63 ± 0.06 | 14.9 ± 0.09 | 14.7 |
| 63.1[336.3] | 0.88 | 35.2 | 7.39 ± 0.06 | 21.0 ± 0.17 | 21.1 |
| | 0.82 | 64.5 | 13.7 ± 0.1 | 21.2 ± 0.15 | |
| | 0.82 ^f | 57.4 ^f | 15.4 ± 0.2 ^f | 28.1 ± 0.4 ^{f,g} | |
| AA = pn | | | | | |
| 25.0[298.2] | | | | | 0.524 |
| 42.5[315.7] | 0.76 | 93.4 | 3.01 ± 0.05 | 3.22 ± 0.05 | 3.21 |
| 53.2[326.5] | 0.76 | 93.4 | 8.18 ± 0.23 | 8.76 ± 0.25 | 8.87 |
| 58.8[332.0] | 0.82 | 64.5 | 9.76 ± 0.14 | 15.1 ± 0.22 | 14.7 |
| 63.1[336.3] | 0.82 | 64.5 | 13.6 ± 0.16 | 21.1 ± 0.25 | 21.4 |
| AA = chxn, isomer A (HNO ₃) ^f | | | | | |
| 25.0[298.2] | | | | | 0.760 |
| 45.3[318.5] | 0.82 | 57.4 | 3.50 ± 0.05 | 6.09 ± 0.09 | 6.11 |
| 53.2[326.5] | 0.82 | 57.4 | 7.41 ± 0.05 | 12.9 ± 0.09 | 12.8 |
| 63.1[336.3] | 0.82 | 57.4 | 17.7 ± 0.35 | 30.8 ± 0.63 | 30.9 |
| AA = chxn, isomer B (HNO ₃) ^f | | | | | |
| 25.0[298.2] | | | | | 1.83 |
| 45.3[318.5] | 0.82 | 57.4 | 4.55 ± 0.14 | 7.93 ± 0.24 | 7.90 |
| 53.2[326.5] | 0.82 | 57.4 | 7.61 ± 0.15 | 13.2 ± 0.26 | 13.3 |
| 58.8[332.0] | 0.82 | 57.4 | 10.8 ± 0.12 | 18.9 ± 0.21 | 18.9 |
| 63.1[336.3] | 0.82 | 57.4 | 14.2 ± 0.21 | 24.7 ± 0.37 | 24.6 |
| AA = tn | | | | | |
| 25.9[298.2] | | | | | 2.67 |
| 30.4[303.6] | 0.76 | 93.4 | 4.61 ± 0.05 | 4.94 ± 0.05 | 4.94 |
| 36.1[309.3] | 0.76 | 93.4 | 8.63 ± 0.05 | 9.24 ± 0.05 | 9.24 |
| 40.2[313.4] | 0.76 | 93.4 | 13.4 ± 0.2 | 14.3 ± 0.2 | 14.3 |
| | 0.82 ^f | 57.4 ^f | 10.8 ± 0.3 ^f | 18.8 ± 0.5 ^{f,g} | |
| 45.3[318.5] | 0.82 | 64.5 | 15.6 ± 0.2 | 24.2 ± 0.3 | 24.2 |
| AA = Me ₂ tn | | | | | |
| 25.0[298.2] | | | | | 2.18 |
| 29.1[302.3] | 0.76 | 93.4 | 3.14 ± 0.04 | 3.36 ± 0.04 | 3.35 |
| 34.9[308.1] | 0.82 | 64.5 | 3.91 ± 0.09 | 6.06 ± 0.14 | 6.04 |
| 40.8[314.0] | 0.82 | 64.5 | 6.81 ± 0.14 | 10.6 ± 0.22 | 10.8 |
| | 0.82 | 64.5 | 6.95 ± 0.14 | 10.8 ± 0.22 | |
| 45.3[318.5] | 0.82 | 64.5 | 10.7 ± 0.18 | 16.6 ± 0.28 | 16.4 |

^aHClO₄ unless otherwise stated. ^bInitial Hg²⁺ concentration as Hg(NO₃)₂. Initial [Cr(III)] ~ 2 mM. ^cObserved pseudo-first-order rate constant measured spectrophotometrically at 380 nm. ^d*k*_{Hg} = *k*_{obs}[Hg²⁺]_i⁻¹. ^eCalculated from the activation parameters cited in Table V. ^f $\mu = 1.0$ M HNO₃. ^gNot included in *E*_a calculations.

zone indicator [15]. The reaction solution was allowed to reach thermal equilibrium in a jacketed 1.00 cm spectrophotometer cell and small quantities of [CrCl(AA)(3,3-tri)]ZnCl₄ were added, such that

the initial Hg(II) concentration was ≥ 8 times the initial Cr(III) concentration. Solution was generally rapid, but the AA = chxn salts (isomers A and B) were not soluble in HClO₄ media, and HNO₃ was used

TABLE V. Activation Parameters for the Hg^{2+} -assisted Chloride Release from some $\text{CrCl}(\text{N}_5)^{2+}$ complexes^a ($\mu = 1.0 \text{ M}$, HClO_4) at 298.2 K

| N_5 | Config. | $10^4 k_{\text{Hg}}$ ($\text{M}^{-1} \text{s}^{-1}$) | E_a (kJ mol^{-1}) | $\Delta S_{298.2}^\ddagger$ ($\text{J K}^{-1} \text{mol}^{-1}$) | Reference |
|--------------------------------|------------------------|---|-----------------------------------|--|-----------|
| $(\text{NH}_3)_5^b$ | | 873 ^c (480) ^l | 62 | -56 | d |
| (en)(dien) | <i>sf</i> | 236 | | | e |
| (pn)(dien) | <i>sf</i> | 226 | | | e |
| (tn)(dien) | <i>sf</i> | 216 | | | e |
| (N-Me-tn)(dien) | <i>uf</i> ^f | 20.1 | 64.2 | -89 | g |
| (en)(3,3-tri) | <i>mer</i> | 5.95 | 78.1 ± 0.7 | -53.0 ± 1.4 | h |
| (pn)(3,3-tri) | <i>mer</i> | 5.24 | 81.2 ± 1.3 | -44 ± 3 | h |
| A-(chxn)(3,3-tri) ⁱ | <i>mer</i> | $7.60(5.85)^j$ | 81.0 ± 0.6 | -41 ± 1.2 | h |
| B-(chxn)(3,3-tri) ⁱ | <i>mer</i> | $18.3(14.1)^j$ | 56.8 ± 0.4 | -115 ± 0.8 | h |
| (tn)(3,3-tri) | <i>mer</i> | 26.7 | 85.7 ± 0.1 | -15.0 ± 0.2 | h |
| (Me ₂ tn)(3,3-tri) | <i>mer</i> | 21.8 | 78.6 ± 0.6 | -40.5 ± 1.2 | h |
| (en)(2,3-tri) | <i>mer</i> | 1.79 | 80.1 ± 2.0 | -56 ± 4 | k |

^a ZnCl_4^{2-} salts except where noted. ^b Cl^- salt. ^cThis value is incorrectly cited in Table III, ref. 3. ^dRef. 42. ^eRef. 3. ^fIn this complex, the $\text{CH}_3\text{NH}-$ nitrogen is *trans* to the *sec*-NH group of the facially coordinated dien. ^gRef. 4. ^hThis work. ⁱ $\mu = 1.0 \text{ M}$, HNO_3 . ^jValue in parenthesis is the rate constant divided by 1.3 to convert $\mu = 1.0 \text{ M}$ HNO_3 to $\mu = 1.0 \text{ M}$ HClO_4 . ^kRef. 43. ^lNormalized from $\mu = 2.0 \text{ M}$ to $\mu = 1.0 \text{ M}$ (see ref. 30).

for these two complexes. Repetitive scan techniques established the following isosbestic points: en: 367, 429, 507; pn: 359, 430, 509; A-chxn: 361, 434, 505; B-chxn: 364, 433, 509; tn: 375, 424, 505; Me₂tn: 375, 424, 507, and the extent of reaction *versus* time was monitored from the decrease in absorbance at 380 nm. Reactions were followed for at least 6 half-lives and pseudo-first-order rate constants (k_{obs}) were calculated using 8–12 data points using previously described expressions [16]. Reproducibility was of the order of 3%. Second-order rate constants (k_{Hg}) were calculated from the expression $k_{\text{Hg}} = k_{\text{obs}} \cdot [\text{Hg}^{2+}]_i^{-1}$ and variation of $[\text{Hg}^{2+}]_i$ gave satisfactory reproducibility for k_{Hg} (Table IV). Activation parameters were computer calculated from the variation of k_{Hg} with temperature over $\sim 15 \text{ K}$ ranges (Table V) [16].

The rates of chloride release from *mer*- $\text{CrCl}(\text{AA})-(3,3\text{-tri})^{3+}$ complexes in 0.1 M HClO_4 were measured titrimetrically over 15 K temperature ranges. The starting complexes were $\text{ClO}_4^- \cdot \text{NO}_3^-$ salts, obtained by metathesis from the ZnCl_4^{2-} analogues. Weighed amounts (*ca.* 0.14 g) of these salts were dissolved in 0.1 M HClO_4 (50 ml) to give initially chloride free solutions. The well stoppered flask was placed in a temperature controlled ($\pm 0.05 \text{ K}$) water bath and after 5–7 min (to reach thermal equilibrium) an electronic timer was started. Samples (5 ml) were taken at intervals and, after quenching in ice, were analysed for released chloride by titration with standardized Hg^{2+} solution (4.88 mM) using diphenylcarbazole indicator [16]. Satisfactory end-points were obtained without prior separation of the ionic chloride. End points were not satisfactory using 1.0 M HClO_4 as the reaction medium. Infinity

volumes (V_∞) were of the order of 3 ml and corresponded to the complete release of one chloride ion per mole.

Pseudo-first-order rate constants (k_{H}) at any particular temperature were calculated from the extent of reaction (V_t) *versus* time (t) data (8–9 points) using the expression

$$t k_{\text{H}} = \ln \{ V_\infty (V_\infty - V_t)^{-1} \}$$

and V_t data were measured over at least three half-lives. Values of mean $k_{\text{H}} \pm$ standard deviation are presented in Tables VI and VII. Reproducibility was of the order of 5%.

TABLE VI. Titrimetrically Determined Pseudo-first-order Rate Constants for the Thermal Aquation of *mer*- $\text{CrCl}(\text{diamine})(\text{triamine})^{2+}$ Complexes in 0.1 M HClO_4

| Diamine | Triamine | T ($^\circ\text{C}$) | $10^5 k_{\text{obs}}$ (s^{-1}) | $10^5 k_{\text{calc}}^a$ (s^{-1}) |
|---------|----------|-----------------------------|--|---|
| en | 3,3-tri | 77.4(1) ^b | 20.1 ± 1.2 | 21.2 |
| | | 71.4(6) | 11.8 ± 1.4 | 11.7 |
| | | 70.8(6) | 11.2 ± 0.9 | 11.0 |
| | | 62.5(6) | 4.65 ± 0.2 | 4.68 |
| tn | 3,3-tri | 70.8(2) | 4.23 ± 0.2 | 4.30 |
| | | 62.5(4) | 2.19 ± 0.3 | 2.10 |
| | | 51.0(7) | 0.734 ± 0.01 | 0.734 |
| en | 2,3-tri | 70.8(4) | 3.66 ± 0.4 | 3.79 |
| | | 70.6(5) | 3.77 ± 0.3 | 3.72 |
| | | 62.5(4) | 1.83 ± 0.2 | 1.73 |
| | | 53.2(4) | 0.672 ± 0.09 | 0.683 |

^aCalculated from the activation parameters cited in Table VII. ^bNumber in parenthesis is the number of data points used in the calculation of the activation parameters.

TABLE VII. Activation Parameters for the Aquation of some $\text{MCl}(\text{N}_5)^{2+}$ Complexes at 298.2 K^a

| M | (N ₅) | 10 ⁷ k _H (s ⁻¹) | E _a (kJ mol ⁻¹) | ΔS [#] (J K ⁻¹ mol ⁻¹) |
|-----------------|--|--|---|---|
| Cr | (NH ₃) ₅ | 95 | 89.3 | -50 |
| Co | (NH ₃) ₅ | 17.6 | 96.7 | -39 |
| Cr | (MeNH ₂) ₅ | 2.48 | 113 | -2 |
| Co | (MeNH ₂) ₅ | 367 | 91.8 | -30 |
| Cr ^b | <i>sfac</i> -(en)(dien) | 224 | 89.2 | -43 |
| Co | <i>sfac</i> -(en)(dien) | 0.94 | 113 | -7 |
| Cr | <i>sfac</i> -(tn)(dien) | 218 | 91.0 | -37 |
| Co | <i>sfac</i> -(tn)(dien) | 2.16 | 110 | -10 |
| Cr ^c | <i>ufac</i> -(Metn)(dien) | 37 | 93 | -45 |
| Co | <i>ufac</i> -(Metn)(dien) | 30.7 | 107 | +3 |
| Cr ^d | <i>mer</i> -(en)(3,3-tri) ^e | 5.34 | 99.2 ± 4 | -40 ± 8 |
| Co | <i>mer</i> -(en)(3,3-tri) ^e | 213 | 95 | -25 |
| Cr ^d | <i>mer</i> -(tn)(3,3-tri) ^e | 5.04 | 82.8 ± 3 | -96 ± 6 |
| Co | <i>mer</i> -(tn)(3,3-tri) ^e | 870(calc) ^f | | |
| Cr ^d | <i>mer</i> -(en)(2,3-tri) ^e | 2.87 | 90.9 ± 3.4 | -73 ± 7 |
| Co ^g | <i>mer</i> -(en)(2,3-tri) ^e | 37(calc) ^h | | |

^aData from refs. cited in ref. 1 unless otherwise stated. ^bRef. 3. ^cRef. 4. ^dThis research. ^eIn this complex the *sec*-NH proton is remote from the coordinated chloro ligand (Fig. 1). ^fCalculated by multiplying the value for the (H⁺) isomer (ref. 1) by 5. ^gRef. 44. ^hCalculated from the k_{Hg} data [44] using eqn. (1).

Results and Discussion

The reaction of 1,5,9-triazanone (3,3-tri) with $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ dehydrated at 190 °C in DMSO results in a satisfactory yield (~60%) of olive green $\text{CrCl}_3(3,3\text{-tri})$. This non-electrolyte is isomorphous with the analogous *mer*- $\text{CoCl}_3(3,3\text{-tri})$ [17–19], and can thus be assigned to the meridional configuration. Such an assignment is entirely consistent with the observation that *mer*- $\text{Cr}(3,3\text{-tri})_2^{3+}$ is the only isomer so far isolated when two moles of 3,3-tri are coordinated to Cr(III) [20] and also with the general observation that complexes with 3,3-tri in the facial configuration are rather uncommon [21].

$\text{CrCl}_3(3,3\text{-tri})$ dissolves in dilute HClO_4 with hydrolysis and on anation with HCl, in the presence of HClO_4 , dark green *trans*-dichloro- $[\text{CrCl}_2(3,3\text{-tri})(\text{OH}_2)]\text{ClO}_4$ is obtained (Table II). The preparation of $\text{CrCl}_3(3,3\text{-tri})$ and $[\text{CrCl}_2(3,3\text{-tri})(\text{OH}_2)]\text{ClO}_4$ parallel the recently described isolation of $\text{CrCl}_3(2,3\text{-tri})$ and *trans*-dichloro- $[\text{CrCl}_2(2,3\text{-tri})(\text{OH}_2)]\text{ClO}_4$ [22]. In both cases the *mer* configuration of the triamine is retained during the hydrolysis/anation reactions.

The half life for the loss of the first chloro ligand from *trans*- $\text{CrCl}_2(3,3\text{-tri})(\text{OH}_2)^+$ in 0.1 M HNO_3 at 40 °C is 23.5 min which can be compared with a value of 35.3 min obtained under the same conditions for *trans*- $\text{CrCl}_2(2,3\text{-tri})(\text{OH}_2)^+$ [22].

TABLE VIII. Non-hydrogen Atom Coordinates for *mer*- $[\text{CrCl}(\text{en})(3,3\text{-tri})]\text{ZnCl}_4$

| Atom | x/a | y/b | z/c |
|-----------------|------------|------------|------------|
| Cation (Fig. 1) | | | |
| Cr | 0.94223(8) | 0.52055(5) | 0.74913(7) |
| Cl(5) | 1.0860(1) | 0.48807(9) | 0.5486(1) |
| N(1) | 0.8484(5) | 0.3870(3) | 0.7383(5) |
| C(1) | 0.7310(7) | 0.3545(3) | 0.5802(6) |
| C(2) | 0.5722(6) | 0.4144(4) | 0.5315(6) |
| C(3) | 0.6085(6) | 0.5050(4) | 0.4612(6) |
| N(4) | 0.7179(5) | 0.5696(3) | 0.5831(4) |
| C(5) | 0.7390(7) | 0.6531(3) | 0.4840(6) |
| C(6) | 0.8233(6) | 0.7328(3) | 0.5868(6) |
| C(7) | 1.0161(6) | 0.7203(3) | 0.6564(6) |
| N(2) | 1.0529(5) | 0.6500(3) | 0.7876(5) |
| N(5) | 1.1516(5) | 0.4769(3) | 0.9410(4) |
| C(8) | 1.0867(7) | 0.4572(4) | 1.0925(6) |
| C(9) | 0.9630(6) | 0.5336(4) | 1.1113(5) |
| N(6) | 0.8329(5) | 0.5443(3) | 0.9505(4) |
| Anion | | | |
| Zn | 0.49555(6) | 0.25000 | 1.00468(7) |
| Cl(1) | 0.2012(1) | 0.25128(8) | 0.8994(1) |
| Cl(2) | 0.5823(2) | 0.39554(9) | 1.0526(2) |
| Cl(3) | 0.6577(2) | 0.1803(1) | 0.8531(1) |
| Cl(4) | 0.5479(2) | 0.1691(1) | 1.2436(2) |

Diamines (en, pn, chxn, tn, Me₂tn) react with *mer*- $\text{CrCl}_3(3,3\text{-tri})$, suspended in DMF, at about 100–120 °C to give pink precipitates of (presumably) $[\text{CrCl}(\text{diamine})(3,3\text{-tri})]\text{Cl}_2$. *mer*- $\text{CrCl}_3(2,3\text{-tri})$ reacts similarly, and the properties of the $\text{CrCl}(\text{diamine})(2,3\text{-tri})^{2+}$ complexes will be described in a future publication.

The crude chloride salts of $\text{CrCl}(\text{diamine})(3,3\text{-tri})^{2+}$ were recrystallized, purified and characterized as ZnCl_4^{2-} salts (Table I). The visible absorption spectra are (Table III) entirely consistent with a $\text{CrCl}(\text{N}_5)^{2+}$ chromophore with absorption maxima at ~520 and ~380 nm, the former having a more or less pronounced shoulder at ~480 nm. On replacement of the coordinated chloro ligand by H₂O, to give $\text{Cr}(\text{diamine})(3,3\text{-tri})(\text{OH}_2)^{3+}$, the colour changes from pink to orange, and symmetrical absorption bands at ~480 and ~370 nm are observed.

There are three possible topological arrangements for a $\text{MX}(\text{bidentate})(3,3\text{-tri})^{n+}$ ligands combination, viz, *s-fac*-, *u-fac*- and *mer* [1]. Of these, only the *u-fac* is potentially chiral (assuming a symmetrical diamine), and there is an additional source of isomerism in the *mer*-configuration in that the *sec*-NH proton can be adjacent to, or remote from the

coordinated monodentate ligand. The two *mer*-[CoCl(en)(3,3-tri)]ZnCl₄ isomers previously isolated [11–13], differ only in respect of the *sec*-NH proton position. In the present series of Cr(III) complexes, the *mer*-configuration was expected to be retained, but the position of the *sec*-NH proton could not easily be assigned. The problem was compounded by the fact that the IR spectrum of [CrCl(en)(3,3-tri)]ZnCl₄ did not correspond to the IR spectrum of either of the two previously established Co(III) isomers [11] nor were any of the [MCl(en)(3,3-tri)]ZnCl₄ (M = Co, Cr) isomers isomorphous.

A single crystal X-ray structure analysis* of [CrCl(en)(3,3-tri)]ZnCl₄ (Fig. 1) establishes our expectation of a retained *mer*-configuration for the triamine and also shows that the *sec*-NH proton is remote from the coordinated chloro ligand, corresponding to the (H↓)-*β-mer*-[CoCl(en)(3,3-tri)]ZnCl₄ isomer [13]. The reason for the lack of isomorphism between *β-mer*-[MCl(en)(3,3-tri)]ZnCl₄ (M = Co, Cr) is apparently due to a change in conformation of a six-membered ring. In the Co(III) complex one six-membered ring is chair, while the other is twist but in the Cr(III) analog both rings are chair.

An additional source of isomerism is introduced for AA = pn as this unsymmetrical diamine has two alternate modes of coordination in a *mer*-configuration. The NH₂CH₂- end of the diamine can be *trans*

to the coordinated *sec*-NH of the triamine or *trans* to the coordinated chloro ligand [24]. The complex used in this study could have either configuration or be a mixture of both isomeric forms as unpublished work from these laboratories indicate that separation of such isomers by fractional crystallization is rather difficult [25, 26].

The use of chxn as a *cis/trans*- isomeric mixture does result in the formation of two separable *β-mer*-CrCl(chxn)(3,3-tri)²⁺ isomers (A and B). Only the isomer containing the *trans*-chxn is capable of existing in chiral forms and preliminary results indicate the B isomer can be resolved with the α -bromo- π -camphorsulfonate anion. Complexes containing *cis*-chxn have not been widely investigated as the diamine stereochemistry requires axial (presumed unfavourable) coordination [27]. However, molecular models indicate that both axial (*cis*-chxn) or equatorial (*trans*-chxn) coordination seem possible in the present system [28].

From a kinetic point of view, this present series of complexes is interesting in two respects. Firstly, the coordinated chloro ligand is particularly inert to aquation and secondly, this series provides the first instance of a 'non-replaced ligand effect' in an homologous group of closely related Cr(III) complexes.

The *mer*-CrCl(diamine)(3,3-tri)²⁺ (diamine = N–C–C–N skeleton) complexes are among the least reactive CrCl(N₅)²⁺ complexes reported for both thermal and Hg²⁺-assisted chloride release reactions [1, 29, 30]. Note, however, that CrCl(en)(2,3-tri)²⁺ is even slower (Table V).

Assuming that all the CrCl(diamine)(3,3-tri)²⁺ complexes under investigation have the same *mer*-(H↓) configuration, we can see from Table V that changing the diamine from a five-membered chelate ring (en, pn, chxn-A) to a six-membered ring (tn, Me₂tn) results in a 4–5 fold increase in rate for Hg²⁺-assisted aquation. This is the first time that such a 'ring size effect', so common in Co(III) chemistry, has been observed for Cr(III). The chelate ring size effect is best illustrated in data accumulated for the rate of loss of the first chloro ligand in acidic solution from *trans*-[MCl₂(diamine)₂]⁺ (M = Co, Cr) complexes [31][†]. For M = Co, changing the diamine from en to tn results in a 1.7 × 10³ increase in aquation rate, whereas for M = Cr, the rate of aquation is independent of the ring size. Similar effects are observed for the thermal or Hg²⁺-assisted chloride release in the *s-fac*-MCl(diamine)(dien)²⁺ (M = Co, Cr) systems [1], although here the rate increase from en to tn for M = Co is much less dramatic. Consequently it is reasonably safe to assume that in Co(III) chemistry, the replacement of en by tn in

*Red crystals of [CrCl(en)(3,3-tri)]ZnCl₄(C₈H₂₅N₅Cl₅-CrZn), $M_R = 485.95$ are monoclinic, space group $P2_1$, with $a = 7.932(2)$, $b = 14.711(4)$, $c = 8.312(2)$ Å, $\beta = 104.06(2)^\circ$, $V = 940.85$ Å³, $Z = 2$, $D_{\text{calc}} = 1.71$ g cm⁻³, $D_{\text{meas}} = 1.61$ g cm⁻³, $\mu_{\text{calc}} = 13.18$ cm⁻¹. X-ray diffraction data at -130 °C were collected on a 0.14 × 0.14 × 0.06 mm crystal for 2235 independent reflections having $2\theta < 55^\circ$ and for $+h$, $+k$, $\pm l$, on a Nicolet R3m automated four-circle diffractometer using graphite-crystal monochromated Mo K α radiation, $\lambda = 0.71069$ Å and $\theta - 2\theta$ scans. The space group was determined from systematic absence ($0k0$, $k = 2n + 1$) and confirmed by the structure analysis. The non-unique data were averaged and the data corrected for Lorentz, polarization, anomalous dispersion, check reflection fluctuations and absorption effects. For the last, the max. and min. transmission factors were 0.88 and 0.74. The structure was solved by heavy atoms, Patterson and conventional difference Fourier synthesis methods (SHELXTL) [23]. The final residues for 180 variables refined against all the data were $R_F = 3.40\%$ and $R_w = 3.92\%$. In the final cycles and structure factor calculations, hydrogen atoms were included in idealized calculated positions and all non-hydrogen atoms were refined using anisotropic thermal parameters. The inverted structure gave residual values of $R_F = 5.10\%$ and $R_w = 6.18\%$. We thus concluded the chirality has been established unequivocally. Atom coordinates are listed in Table VIII and observed bond lengths (Å) are Cr–Cl = 2.287(3), Cr–N (mean) = 2.096(5) with the en ring in the δ -conformation (dihedral angle = 51.4°).

[†]See especially Table IV of this paper.

any particular complex will result in labilization of a leaving group.

Mechanistically, the general consensus is that both thermal and Hg^{2+} -assisted chloride release reactions from Co(III) proceed via a dissociative path and an intermediate of reduced coordination number. Indeed, there is a reasonable correlation between k_{Hg} and k_{H} for Co(III) systems [30] viz.

$$\log k_{\text{Hg}} = 0.96 \log k_{\text{H}} + 4.36 \quad (1)$$

We have rationalized the observed ring size effect on the dissociative chloride release reactions of Co(III) complexes in terms of the flexible six-membered ring allowing a more ready distortion to a trigonal-bipyramid five-coordinate intermediate [32].

The thermal aquation of $\text{CrCl}(\text{N}_5)^{2+}$ systems is thought to proceed via an interchange mechanism (I) [33]. The I mechanism may be further subdivided into two classes: I_d in which the leaving and entering groups are only weakly bound in the transition state; and I_a where more substantial bonding between both groups is involved. Support for the I_a mechanism in Cr(III) is found in the recent description of a seven-coordinate $\text{Cr}(\text{N}_5)(\text{OH}_2)_2^{3+}$ complex [34].

It is considerably more difficult to predict the influence of non-replaced ligands on (I) mechanisms as the site of attack of the incoming water molecule is unknown. In general terms, steric effects are expected to manifest themselves in the approach of the nucleophile, rather than in the release of the leaving group. The data in Table IX show that there is no correlation between $k_{\text{H}}[\text{Co(III)}]$ and $k_{\text{H}}[\text{Cr(III)}]$.

The question now is 'what is the mechanism of Hg^{2+} -assisted chloride release in Cr(III) systems?' A previous summary of the available data suggests an essentially dissociative mechanism [29] and it is argued that the preformed Cl-Hg^+ species in the

$(\text{N}_5)\text{Cr-Cl-Hg}(\text{aq})^{4+}$ adduct will be a better leaving group than Cl^- .

However, if the data presented in Table VIII are used to support an associative mechanism for the thermal aquation of Cr-Cl systems, then it must also be argued that Hg^{2+} -assisted aquation of analogous Cr-Cl systems is associative as well.

While there is no correlation between $k_{\text{Hg}}[\text{Co(III)}]$ and $k_{\text{Hg}}[\text{Cr(III)}]$, there does appear to be some sort of relationship between $k_{\text{H}}[\text{Cr(III)}]$ and $k_{\text{Hg}}[\text{Cr(III)}]$ in that slow k_{H} corresponds to slow k_{Hg} and vice versa. There is insufficient data to establish more than this approximate trend and there are some inconsistencies.

Nevertheless, we do observe a small but marked ring size effect for the Hg^{2+} -assisted aquation in *mer*- $\text{CrCl}(\text{AA})(3,3\text{-tri})^{2+}$ complexes which may be indicative of some (I_d) contribution. We could have hardly used a complex with a more favourable geometry to encourage a dissociative mechanism. The ends of the meridionally coordinated triamine are nicely poised to fold towards the position vacated by the leaving group (Fig. 1) and one end of the coordinated diamine can also move in the same direction, given sufficient flexibility in the diamine chain. Consequently, the replacement of en by tn causes a five-fold rate increase.

Indeed, the Hg^{2+} -assisted chloride release reactivity order of $\text{en} < \text{Me}_2\text{tn} < \text{tn}$ for *mer*- $\text{CrCl}(\text{diamine})(3,3\text{-tri})^{2+}$ parallels that observed for the thermal aquation of the first chloro ligand in *trans*- $\text{CoCl}_2(\text{diamine})_2^+$ systems [32] where a D mechanism is firmly established.

We also note that the six-membered ring effect observed for Hg^{2+} -assisted aquation is not reflected in the thermal aquation data (Table VIII). For the thermal aquation, k_{H} (298.2) values are quite similar for *mer*- $\text{CrCl}(\text{diamine})(3,3\text{-tri})^{2+}$ (diamine = en, tn). Nevertheless, the activation parameters are sufficiently different to make simple k_{H} comparisons unreliable. Indeed, at 70.8 °C k_{H} (en) is about three

TABLE IX. k_{Hg} ($\mu = 1.0 \text{ M}$) and k_{H} Data for Comparable $\text{MCl}(\text{N}_5)^{2+}$ Systems ($\text{M} = \text{Co}, \text{Cr}$) at 298.2 K

| N_5 | Co(III) | | Cr(III) | |
|--|--|--|---|--|
| | $10^7 N k_{\text{H}}^a$ (s^{-1}) | $10^3 \times k_{\text{Hg}}$ ($\text{M}^{-1} \text{s}^{-1}$) | $10^7 \times k_{\text{H}}^a$ (s^{-1}) | $10^3 \times k_{\text{Hg}}^b$ ($\text{M}^{-1} \text{s}^{-1}$) |
| (H \downarrow)- <i>mer</i> -(tn)(3,3-tri) | ~870(calc) | ~3000(calc) ^c | 5.0 | 2.7 |
| (H \downarrow)- <i>mer</i> -(en)(3,3-tri) | 213 | 1000 ^d | 5.3 | 0.6 |
| (H \downarrow)- <i>mer</i> -(en)(2,3-tri) | ~37(calc) | 139 ^d | 2.9 | 0.18 |
| <i>ufac</i> -(N-Me-tn)(dien) | 30.7 | ~120(calc) ^c | 37 | 2.0 |
| (NH $_3$) $_5$ | 17.6 | 122 ^e | 95 | 48 |
| <i>sfac</i> -(tn)(dien) | 2.16 | 47.4 ^e | 218 | 21.6 |
| <i>sfac</i> -(en)(dien) | 0.94 | 4.9 ^e | 224 | 22.0 |

^aData from Table VII. ^bData from Table V. ^cCalculated from the k_{H} value using eqn. (1). ^dRef. 44. ^eData from ref. 1.

times greater than k_H (tn). Consequently, we have no evidence to suggest a mechanism other than the normally accepted I_a process for the thermal aquation.

One other mechanistically important feature of this present series of complexes is that (apart from $\text{CrCl}(\text{tetren})^{2+}$) they are the first Cr(III) complexes to contain a polyamine system with the sec-NH donor group in a meridional configuration [35]. This structural feature, when found in Co(III) systems, results in an increase in the rate of base hydrolysis by some three orders of magnitude when compared with isomeric analogues where this feature is absent [35].

Preliminary results indicate that for $\beta\text{-mer-CrCl}(\text{en})(3,3\text{-tri})^{2+}$, base hydrolysis is about 16 times faster than $\text{sym-fac-CrCl}(\text{en})(\text{dien})^{2+}$ [3]. This is in the expected direction but not nearly as dramatic as the Co(III) examples [$\beta\text{-mer-CoCl}(\text{en})(3,3\text{-tri})^{2+}$, $k_{\text{OH}}(298.2) = 2.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$; $\text{sym-fac-CoCl}(\text{en})(\text{dien})^{2+}$, $k_{\text{OH}}(298.2) = 4.71 \text{ M}^{-1} \text{ s}^{-1}$ [1, 36].

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