Inorganica Chimica Acta, *121* (1986) 167–174

The Synthesis and Reaction Kinetics of some Co(III) and Cr(III) Chloro Complexes of 1,4,8-Triazaoctane (2,3-tri) and the Isolation of Chiral *trans*-Dichloro[$CoCl_2(NH_3)(2,3\text{-tri})]ClO_4$

DONALD A. HOUSE

Department of Chemistry, University of Canterbury, Christchurch, New Zealand

(Received May 2, 1968)

Abstract

The reaction of 2,3-tri with $CrCl_3 \cdot 6H_2O$, dehydrated in boiling DMF, results in the formation of *mer*-$CrCl_3$(2,3-tri) and anation of hydrolysed solutions of *mer*-MCl_3(2,3-tri) (M = Co, Cr) with 6 M HCl containing $HClO_4$, forms *trans*-dichloro-*mer*-[MCl_2(2,3-tri)(OH_2)]$ClO_4 \cdot H_2O$ (M = Cr, Co; **I**, **II**). *trans*-Dinitro-*mer*-[$Co(NO_2)_2(NH_3)$(2,3-tri)]ClO_4 crystallises from the reaction between *mer*-$Co(NO_2)_3$-(2,3-tri) and aqueous 7 M ammonia, on addition of $NaClO_4 \cdot H_2O$, and *trans*-dichloro-*mer*-[$CoCl_2(NH_3)$-(2,3-tri)]ClO_4 (**III**) can be isolated by treatment of the dinitro with 12 M HCl. Reaction of *mer*-$CoCl_3$-(2,3-tri) with $C_2O_4^{2-}$, followed by addition of aqueous NH_3 and $NaClO_4 \cdot H_2O$ results in the isolation of racemic *mer*-[Co(ox)(NH_3)(2,3-tri)]$ClO_4 \cdot H_2O$. This complex was resolved into its enantiomeric forms and treatment of these with $SOCl_2$/MeOH/$HClO_4$ gave the chiral forms of *trans*-dichloro-*mer*-[$CoCl_2(NH_3)$(2,3-tri)]ClO_4 (*R* or *S* at the sec-NH center). The rates of loss of the first chloro ligand from these dichloro complexes have been measured spectrophotometrically in 0.1 M HNO_3 over a 15 K temperature range to give the following kinetic parameters; (**I**) $k_H(298) = 7.25 \times 10^{-5}$ s^{-1}, E_a = 78.5 kJ mol^{-1}, $\Delta S_{298}{}^{\#} = -69$ J K^{-1} mol^{-1}; (**II**) $k_H(298) = 4.00 \times 10^{-3}$ s^{-1}, $E_a = 89.9$, $\Delta S_{298}{}^{\#}$ = +87.5; (**III**) $k_H(298) = 3.09 \times 10^{-4}$ s^{-1}, $E_a = 103$, $\Delta S_{298}{}^{\#} = +27$. Treatment of the dichloro cations with Hg^{2+}/HNO_3 results in the generation of *mer*-M(2,3-tri)$(OH_2)_3{}^{3+}$ (M = Cr, Co; **IV**, **V**) and *trans*-diaqua-*mer*-Co(NH_3)(2,3-tri)$(OH_2)_2{}^{3+}$ (**VI**). The Co(III) cations isomerise to the *fac* configuration with (**V**) $k_{isom}(298)$ (μ = 1.0 M) = 2.97×10^{-5} s^{-1}, $E_a = 115$, $\Delta S_{298}{}^{\#} = +46$. (**VI**) $k_{isom}(298)$ (μ = 1.0 M) = 4.13×10^{-5} s^{-1}, $E_a = 113$, $\Delta S_{298}{}^{\#} = +52$.

Introduction

1,4,8-Triazaoctane (2,3-tri) is a tridentate polyamine ligand that can form a fused five and six-membered chelate ring system on coordination with a transition metal ion. Although some Co(III) complexes with this ligand have previously been reported [1–3], rather less information is known for Cr(III) [4]. One interesting feature of this ligand is that coordination of the secondary nitrogen center will generate a chiral nitrogen atom, and all 2,3-tri complexes of inert transition metal ions are potentially chiral, regardless of the coordination geometry (*mer* or *fac*). In an attempt to explore this feature and to continue our work on comparing structure–reactivity relationships of analogous Co(III) and Cr(III) polyamine complexes, we describe here the preparation of *mer*-$CrCl_3$(2,3-tri), *trans*-dinitro-*mer*-[$Co(NO_2)_2(NH_3)$(2,3-tri)]ClO_4, *mer*-[Co(ox)(NH_3)-(2,3-tri)]$ClO_4 \cdot H_2O$, racemic and chiral *trans*-dichloro-*mer*-[$CoCl_2(NH_3)$(2,3-tri)]ClO_4, and [MCl_2(2,3-tri)-(OH_2)]$ClO_4 \cdot H_2O$ (M = Co, Cr). Acid hydrolysis rates for the loss of the first chloro ligand from the dichloro complexes have been measured as well as the rates of *mer* → *fac* isomerisation of the tridentate ligand in *mer*-Co(2,3-tri)$(OH_2)_3{}^{3+}$ and *trans*-diaqua-Co(NH_3)(2,3-tri)$(OH_2)_2{}^{3+}$. Where possible, the kinetic parameters are compared with those obtained for related diethylenetriamine (2,2-tri) complexes.

Experimental

The polyamine ligand, *N*-(2-aminoethyl)-1,3-propanediamine(1,4,8-triazaoctane, 2,3-tri) was obtained from Aldrich Chemical Co. and used as supplied. This material had the expected ^{13}C NMR spectrum (53.71, 48.23, 42.48, 39.66, 34.71 ppm) and this technique showed that no other carbon containing species were present. All other chemicals were the best reagent grade available. ^{13}C NMR spectra were recorded in DMF using a Varian CFT 20 with dioxane (67.39 ppm) as an internal reference. A Varian DMS 100 recording spectrophotometer was used for all visible absorption spectral measurements. $Co(NO_2)_3$(2,3-tri) and $CoCl_3$(2,3-tri) were prepared as previously described [1]. In all prepara-

0020-1693/86/$3.50a

tions, the salts were removed from solution by filtration through sintered glass funnels. The products were washed with 2-propanol and then ether and air dried. In all cases except the oxalato, the perchlorate salts described here are readily soluble in DMF.

CAUTION. Although we have experienced no difficulties with the perchlorate salts of the complexes mentioned herein, these complexes should be treated as potentially explosive and handled accordingly.

trans-Dinitro-mer-dinitro(ammine)(1,4,8-triazaoctane)cobalt(III)perchlorate, $[Co(NO_2)_2(NH_3)(2,3\text{-tri})]ClO_4$

Trinitro(2,3-tri)cobalt(III) (10 g) was heated in 100 ml of aqueous 7 M NH_3 solution (50 ml H_2O, 50 ml conc. NH_3). The non-electrolyte slowly dissolved to give an orange solution (30 min, 80 °C). $NaClO_4 \cdot H_2O$ (20 g) was added and yellow crystals of the perchlorate deposited. Heating was continued for a further 30 min and the product (13 g) filtered from the hot solution. A sample for analysis (2 g) was recrystallised from hot water (50 ml, 80 °C) by addition of $NaClO_4 \cdot H_2O$ (5 g) and ice cooling. *Anal.* Calc. for $[Co(NO_2)_2(NH_3)(C_5H_{15}N_3)]ClO_4$: C, 15.61; H, 4.72; N, 21.85. Found: C, 15.43; H, 4.99; N, 21.93%. ^{13}C NMR spectrum: 54.62, 49.86, 42.76, 39.65, 27.16 ppm. Visible absorption spectrum (H_2O): 446 max. (222), 407 min. (140).

trans-Dichloro-mer-dichloro(ammine)(1,4,8-triazaoctane)cobalt(III)perchlorate, $[CoCl_2(NH_3)(2,3\text{-tri})]ClO_4$

The *trans*-dinitro (1.25 g) was suspended in 12 M HCl (10 ml) and warmed to about 80 °C. Effervescence occurred and the solution colour changed from yellow to red to lime green (*ca.* 20 min). $HClO_4$ (2 ml, 70%) was then added and grass-green crystals deposited from the warm solution. After ice cooling, the product was collected by filtration in an almost quantitative yield. The product was recrystallised from 0.1 M HCl by addition of HCl (12 M) and $HClO_4$. *Anal.* Calc. for $[CoCl_2(NH_3)(C_5H_{15}N_3)]ClO_4$: C, 16.52; H, 4.99; N, 15.41. Found: C, 16.33; H, 5.04; N, 15.24%. ^{13}C NMR spectrum: 56.02, 49.12, 43.21, 39.21, 28.04 ppm. Visible absorption spectrum: (3 M HCl: 631 max. (35.9), 554 min. (14.3), 463 max. (44.3), 443 min. (42.7). (DMF): 629 max. (39.4), 554 min. (16.6), 469 max. (45.7), 453 min. (44.5).

trans-Diaqua-*mer*-$Co(NH_3)(2,3\text{-tri})(OH_2)_2^{3+}$ was generated in solution by dissolving the dichloro in 0.82 M HNO_3 containing 5.74×10^{-2} M $Hg(NO_3)_2$. Visible absorption spectrum: 485 max. (61.0), 422 min. (28.4). After 24 h at room temperature the visible absorption spectrum of *fac*-$Co(NH_3)(2,3\text{-tri})(OH_2)_2^{3+}$ was recorded: 496 max. (65.0), 424 min. (21.5).

trans-Dichloro-mer-dichloro(aqua)(1,4,8-triazaoctane)cobalt(III)perchlorate Monohydrate, $[CoCl_2(2,3\text{-tri})(OH_2)]ClO_4 \cdot H_2O$

Trichloro(1,4,8-triazaoctane)cobalt(III) (2 g) was heated in 0.1 M $HClO_4$ (70 ml) until all the non-electrolyte had dissolved (by hydrolysis) (*ca.* 10 min). An equal volume of 12 M HCl and 10 ml of 70% $HClO_4$ were then added and the solution allowed to cool spontaneously to room temperature. Green needles deposited in an almost quantitative yield during the cooling period. *Anal.* Calc. for $[CoCl_2(C_5H_{15}N_3)(OH_2)]ClO_4 \cdot H_2O$: C, 15.70; H, 5.00; N, 10.98. Found: C, 15.52, H, 5.41 N, 11.13%. ^{13}C NMR spectrum: 57.29, 49.28, 42.48, 39.66, 28.02 ppm. Visible absorption spectrum: this complex hydrolyses with a half-life of 5 min at room temperature in 0.1 M HNO_3 and even in 3 M HCl we were unable to measure reproducible data. The first band maxima is at approximately 630 nm [2].

mer-Oxalato(ammine)(1,4,8-triazaoctane)cobalt(III)perchlorate Monohydrate, $[Co(ox)(NH_3)(2,3\text{-tri})]ClO_4 \cdot H_2O$

Oxalic acid dihydrate (4.5 g, 1.2 mole equivalent) was added to a suspension of *mer*-$CoCl_3(2,3\text{-tri})$ (8.5 g) in water (80 ml) and the mixture was heated at 80 °C for about 15 min to give a clear blue solution. $NaClO_4 \cdot H_2O$ (20 g) was added and, after ice cooling, 30 ml of concentrated aqueous NH_3 solution. Any precipitated $Na_2C_2O_4$ was removed by filtration and the now purple coloured solution was heated at 80 °C. The colour changed to pink and red crystals of the product (9 g) deposited from the hot solution after about 15 min. These were collected by filtration from the ice cooled solution. A small quantity (1 g) was recrystallised for analysis from 30 ml of 80 °C 0.2 M NH_3 solution by addition of $NaClO_4 \cdot H_2O$ (5 g) and ice cooling. *Anal.* Calc. for $[Co(C_7H_{18}N_4O_4)]ClO_4 \cdot H_2O$: C, 21.10; H, 5.10; N, 14.10. Found: C, 21.25; H, 5.17; N, 14.31%. Visible absorption spectrum (0.1 M HNO_3): 503 max. (103), 421 min. (12.0), 355 max. (155), 331 min. (97.5). ^{13}C NMR spectrum (0.1 M NH_3): 56.57, 49.51, 42.75, 38.42, 27.58.

Resolution of Racemic mer-$[Co(ox)(NH_3)(2,3\text{-tri})]ClO_4 \cdot H_2O$

The method of resolution followed the procedures described previously [5, 6] using 2 g of the racemic perchlorate in 100 ml of buffer and 2 g of dibenzyol-(+)-tartaric acid in 60 ml, both at 80 °C. On spontaneous cooling, a pink crystalline mass of the less soluble diastereoisomeride (associated with the (+) cation) deposited, and this (2 g) was collected by filtration after 20 min at room temperature. The perchlorate salt of the (−)-cation (0.7 g, 70% optically pure) was obtained from the mother liquor after 24 h, by addition of $NaClO_4 \cdot H_2O$ (10 g). *Anal.*

Calc. for $[Co(C_7H_{18}N_4O_4)][C_{18}H_{13}O_8]\cdot 2H_2O$: C, 46.73; H, 5.49; N, 8.72. Found: C, 46.10; H, 4.95; N, 7.86%. CD spectrum (DMF:3 M HCl, 50:50) (λ, nm; $\Delta\epsilon$, M^{-1} cm^{-1}): 545, +0.717; 513, 0; 485, −0.600; 410, −0.017; 368, −0.076; 352, 0; 335, +0.092; 312, 0. ORD spectrum for the (+)-cation (0.1 M HNO_3) (λ, nm; [M], $°M^{-1}$ m^{-1}: 589, +695; 558, 0; 520, −2630; 476, 0; 455, +490; 408, 0; 325, −129; 368, 0; 355, +206; 345, 0.

$(+)_{450}$-trans-Dichloro-mer-dichloro(ammine)(1,4,8-triazaoctane)cobalt(III)perchlorate, $(+)_{450}$ trans-$[CoCl_2(NH_3)(2,3\text{-tri})]ClO_4$

The less soluble diastereoisomeride (+)-$[Co(ox)(NH_3)(2,3\text{-tri})][C_{18}H_{13}O_8]\cdot 2H_2O$ (1.5 g) was suspended in thionyl chloride (10 ml) and methanol (15–20 ml) was added cautiously and dropwise (use gloves and an efficient fume hood) until the vigorous effervescence that initially occurred, had virtually ceased. During this process the solid dissolved and HCl fumes were evolved. The bright pink solution was gently warmed at about 30–40 °C and the colour changed through purple to green (10 min). Addition of 60% $HClO_4$ (5 ml) resulted in the precipitation of grass green crystals which were collected from the ice cooled solution by filtration. These were recrystallised from 0.5 M HCl (25 ml) by addition of an equal volume of 12 M HCl and 60% $HClO_4$ (10 ml) to give 0.3 g of $(+)_{450}$-$[CoCl_2(NH_3)(2,3\text{-tri})]ClO_4$. CD spectrum (0.1 M HNO_3): 620, −0.223; 535, −0.043; 480, −0.098; 422, 0; 405, +0.014; 390, 0. ORD spectrum (0.1 M HNO_3): 670, −348, 600, 0; 580, +43.5; 555, 0; 530, −43.5; 518, 0; 450, +333; 330, 0.

(−)-*trans*-Diaqua-*mer*-$Co(NH_3)(2,3\text{-tri})(OH_2)_2{}^{3+}$ was generated in solution by dissolving $(+)_{450}$-*trans*-$[CoCl_2(NH_3)(2,3\text{-tri})]ClO_4$ in 0.82 M HNO_3 containing 5.74×10^{-2} M $Hg(NO_3)_2$. CD spectrum; 565, +0.384; 535, 0; 474, −1.02; 408, 0; 365, +0.167. ORD spectrum: 630, +230; 605, 0; 589, −270; 530, −2460; 486, 0; 450, +2120; 358, 0. This slowly isomerised to the (−)-*fac* isomer over 24 h at room temperature. CD spectrum: 560, +0.641; 535, 0; 471, −1.18; 406, 0; 340, +0.218.

$(-)_{450}$-*trans*-$[CoCl_2(NH_3)(2,3\text{-tri})]ClO_4$ can be similarly isolated starting with (−)-$[Co(ox)(NH_3)(2,3\text{-tri})]ClO_4$.

mer-Trichloro(1,4,8-triazaoctane)chromium(III), $CrCl_3(2,3\text{-tri})$

$CrCl_3\cdot 6H_2O$ (10 g) was boiled in DMF (40 ml) until the solution was a deep violet colour and the volume reduced by about 10 ml. This solution was cooled to 120 °C and 2,3-tri (4.5 ml) slowly added with good magnetic stirring. The temperature rose to almost boiling and a microcrystalline grey–brown powder (9.5 g, 92%) deposited. The product was filtered from the cooled solution. An attempt to recrystallise this non-electrolyte from 0.1 M $HClO_4$/6 M HCl gave *trans*-dichloro-*mer*-$[CrCl_2(2,3\text{-tri})(OH_2)]ClO_4\cdot H_2O$. *Anal.* Calc. for $CrCl_3(C_5H_{15}N_3)$: C, 21.79; H, 5.49; N, 15.25. Found: C, 21.68; H, 5.66; N, 15.19%.

trans-Dichloro-mer-Dichloro(aqua)(1,4,8-triazaoctane)chromium(III)perchlorate Monohydrate, $[CrCl_2(2,3\text{-tri})(OH_2)]ClO_4\cdot H_2O$

This complex (red–brown needles) was prepared from *mer*-$CrCl_3(2,3\text{-tri})$ as for the Co(III) analog. *Anal.* Calc. for $[CrCl_2(OH_2)(C_5H_{15}N_3)]ClO_4\cdot H_2O$: C, 15.99; H, 5.10; N, 11.18. Found: C, 15.76; H, 5.43; N, 11.13%. Visible absorption spectrum (3 M HCl): 583 max. (22.3), 563 min. (20.6), 498 max. (38.2), 459 min. (30.1), 419 max. (38.1).

mer-$Cr(2,3\text{-tri})(OH_2)_3{}^{3+}$ was generated in solution by dissolving the above complex in 0.82 M HNO_3 containing 5.74×10^{-2} M $Hg(NO_3)_2$. Visible absorption spectral parameters were recorded after 24 h at room temperature: 481 max. (46.7), 425 min. (21.0), 376 max. (37.6).

Kinetics

The rates of loss of the first chloro ligand from the dichloro complexes were measured spectrophotometrically in 0.1 M HNO_3, and the rates of *mer* → *fac* isomerisation for $Co(2,3\text{-tri})(OH_2)_3{}^{3+}$ and $Co(NH_3)(2,3\text{-tri})(OH_2)_2{}^{3+}$ were similarly measured in Hg^{2+}/HNO_3 solutions [7]. Table I lists the spectrophotometric data used in the kinetic analysis, with first order rate constants (Tables II and III) being calculated from absorbance *vs.* time data at fixed wavelengths (Table I). Activation parameters (Tables IV and V) were calculated from the variation of k_{obs} with temperature [8] over a 15 K temperature range.

Results and Discusion

Synthesis and Structural Assignments

Four new Co(III) and two Cr(III) complexes of 1,4,8-triazaoctane have been isolated as crystalline solids, *viz.* $[Co(NO_2)_2(NH_3)(2,3\text{-tri})]ClO_4$, (±)–, (+)– and (−)– $[CoCl_2(NH_3)(2,3\text{-tri})]ClO_4$, $[CoCl_2(2,3\text{-tri})(OH_2)]ClO_4\cdot H_2O$, $[Co(ox)(NH_3)(2,3\text{-tri})]ClO_4\cdot H_2O$, $[CrCl_3(2,3\text{-tri})]$ and $[CrCl_2(2,3\text{-tri})(OH_2)]ClO_4\cdot H_2O$, although the Co(III) dichloroaqua had previously been characterised in solution [2]. The two Cr(III) complexes are isomorphous with their Co(III) analogs and hence have analogous structures. The tridentate ligand has previously [1] been assigned to a *mer* configuration in $Co(NO_2)_3(2,3\text{-tri})$ and $CoCl_3(2,3\text{-tri})$ and a consistent pattern of C atom resonances in the ^{13}C NMR spectra of the Co(III) complexes, together with the above isomorphism, suggests that this configuration is retained in all the

TABLE I. Spectrophotometric Data for the Kinetic Studies

Reaction	Medium	Observed isosbestic points (nm) (final spectrum (nm))	Monitoring wavelength (nm)
$CrCl_2(2,3\text{-tri})(OH_2)^+ \rightarrow$ $CrCl(2,3\text{-tri})(OH_2)_2^{2+} + Cl^-$	0.1 M HNO_3	422, 454, 569 (492 max., 442 min., 392 max.)	380
$CoCl_2(2,3\text{-tri})(OH_2)^+ \rightarrow$ $CoCl(2,3\text{-tri})(OH_2)_2^{2+} + Cl^-$	0.1 M HNO_3	411, 456, 600 (535)[a] (597 max., 499 max., 383 max.) (600 max., 505 max., 390 max.)[b]	380
$CoCl_2(NH_3)(2,3\text{-tri})^+ \rightarrow$ $CoCl(NH_3)(2,3\text{-tri})(OH_2)^{2+} + Cl^-$	0.1 M HNO_3	406, 475, 599 (490sh, 490 max, 440 min.)	430
mer-$Co(2,3\text{-tri})(OH_2)_3^{3+} \rightarrow$ fac-	2.00×10^{-2} M Hg^{2+} 0.95 M HNO_3	489, 498 (514 max., 431 min., 361 max., 345 min.) (412 max., 433 min., 370 max., 350 min.)[b]	530
mer-$Co(NH_3)(2,3\text{-tri})(OH_2)_2^+ \rightarrow$ *fac*-	5.74×10^{-2} M Hg^{2+} 0.82 M HNO_3	471, 570 (496 max., 424 min.)	520

[a] Region of close contact. [b] Ref. 2.

TABLE II. Observed and Calculated Pseudo-first-order Rate Constants for the Loss of the First Chloro Ligand from some *trans*-dichloro-2,3-tri Complexes of Cr(III) and Co(III) in 0.1 M HNO_3

Complex[a]	*T* (°C) [K]	$10^4 k_{obs}$ [b] (s^{-1})	$10^4 k_{calc}$ [c] (s^{-1})
$CrCl_2(2,3\text{-tri})(OH_2)^+$	60.1 [333.3]	20.5 ± 0.41	20.3
	54.6 [327.8]	12.5 ± 0.16	12.6
	49.5 [322.7]	8.10 ± 0.12	8.02
	39.9 [313.1]	3.27 ± 0.04	3.27
	25.0 [298.2]		0.725
$CoCl_2(2,3\text{-tri})(OH_2)^+$	25.0 [298.2]		40.0
	22.8 [296.0]	29.9 ± 1.0	30.6
	19.4 [292.6]	20.2 ± 0.4	20.0
	14.3 [287.5]	10.3 ± 0.2	10.4
$CoCl_2(NH_3)(2,3\text{-tri})^+$	42.1 [315.3]	30.7 ± 0.7	29.8
	38.8 [312.0]	18.9 ± 0.5	19.6
	33.7 [306.9]	9.73 ± 0.2	10.1
	29.4 [302.6]	5.92 ± 0.1	5.67
	25.0 [298.2]		3.09
	21.2 [294.4]	1.80 ± 0.1	1.80

[a] Perchlorate salts. [b] Mean ± the standard deviation of at least two determinations at each temperature. [c] Calculated from the activation parameters cited in Tables IV and V.

perchlorate salts described here, as well as for $CrCl_3$-(2,3-tri). *trans*-Dichloro-*mer*-[$CrCl_2(2,3\text{-tri})(OH_2)$]-$ClO_4 \cdot H_2O$ was fortuitously isolated in an attempt to re-anate a hydrolysed solution of *mer*-$CrCl_3(2,3\text{-tri})$ in HCl containing $HClO_4$. *mer*-$CoCl_3(2,3\text{-tri})$ behaves similarly, but the corresponding dien complex could not be isolated from hydrolysed solutions of *mer*-$CoCl_3$(dien), and only the starting material was recovered.

The *trans*-dichloro configuration is assigned mainly on the basis of the visible absorption spectra, with band maxima at about 600 mn. We are less certain about the *trans* configuration for the dinitro, although the sequence of colour changes in 12 M HCl, orange to red and then more slowly to green, is characteristic of this configuration [9].

Kinetics

Kinetic parameters associated with the rate of loss of the first chloro ligand from *trans*-dichloro-*mer*-$MCl_2(2,3\text{-tri})(OH_2)^+$ (M = Co, Cr) are listed in Table 5.

It has been observed previously that the replacement of a five-membered en ring by a six-membered tn ring causes considerable labilisation of the first chloro ligand in *trans*-dichloro-bis(diamine)cobalt(III) complexes, whereas this effect is not observed for the

TABLE III. Observed and Calculated Pseudo-first-order Rate Constants for the *mer* → *fac* Isomerisation of Some Co(III) 2,3-tri Complexes μ= 1.0 M)

Complex	T (°C) [K]	$10^4\ k_{obs}$ [a] (s^{-1})	$10^4\ k_{calc}$ [b] (s^{-1})
$Co(2,3\text{-tri})(OH_2)_3^{3+}$ [c]	54.6 [327.8]	19.8 ± 0.4	19.7
	49.6 [322.8]	10.2 ± 0.2	10.3
	44.2 [317.4]	4.99 ± 0.04	4.95
	40.3 [313.5]	2.86 ± 0.03	2.87
	25.0 [298.2]		0.297
$Co(NH_3)(2,3\text{-tri})OH_2)_2^{3+}$[d]	53.4 [326.6]	23.7 ± 1.0	24.2
	48.8 [322.0]	13.5 ± 0.5[c]	13.1
		13.7 ± 0.2	
	45.0 [318.2]	7.58 ± 0.2	7.83
	40.5 [313.7]	4.20 ± 0.2	4.17
	25.0 [298.2]		0.413

[a] Mean ± standard deviation of at least two determinations at each temperature. [b] Calculated from the activation parameters cited in Table V. [c] In 2.0×10^{-2} M $Hg(NO_3)_2$, 0.95 M HNO_3 (μ = 1.0 M). [d] In 5.74×10^{-2} M $Hg(NO_3)_2$, 0.82 M HNO_3 (μ = 1.0 M).

TABLE IV. Kinetic Parameters for the First Step in the Acid Hydrolysis of comparable *trans*-Dichloro Co(III) and Cr(III) Complexes at 298.2 K

Ligand	Co(III)			Cr(III)			References Co(III); Cr(III)
	k_H (s^{-1})	E_a (kJ mol^{-1})	$\Delta S_{298}^{\#}$ ($JK^{-1}\ mol^{-1}$)	k_H (s^{-1})	E_a (kJ mol^{-1})	$\Delta S_{298}^{\#}$ ($JK^{-1}\ mol^{-1}$)	
$(NH_3)_4$	1.8×10^{-3}	99	+36 (44)[a]	4.5×10^{-5}	91	−25	b; c
$(en)_2$	3.5×10^{-5}	110	+59 (36)	2.2×10^{-5}	97	−17	d; e
$(tn)_2$	5.33×10^{-2}	89	+29 (18)	2.08×10^{-5}	102	+1	f; g
$(Me_2tn)_2$	5.57×10^{-3}	97	+28 (14)	2.25×10^{-5}	104	+5	h; h
(en)(tn)	3.96×10^{-4}	101	+21 (34)	1.93×10^{-5}	98	−5	i; i
(*R*,*S*)-(2,3,2-tet)	1.5×10^{-5}	102	+4 (19)	3.23×10^{-6}	107	0	j, k; l
(*RR*,*SS*)-(3,2,3-tet)	5.4×10^{-5}	103	+17 (69)	1.06×10^{-6}	95	−50	k; m
(*RSSR*)-cyclam	1.1×10^{-6}	103	−13 (27)	2×10^{-8}	116	−8	n; o
(*RSSR*)-teta	9.3×10^{-4}	107	+54 (56)	1.26×10^{-5}	93	−37	p, q; r
$(2,3\text{-tri})(OH_2)$	4.00×10^{-3}	89.9 ± 2.9	+87.5 ± 5 (88)	7.25×10^{-5}	78.5 ± 0.6	−69 ± 1.2	s; s

[a] Calculated from the expression $\Delta S_{298}^{\#}Co(III) + \Delta S_{298}^{\#}Cr(III) = 19$ assuming the values for Cr(III), (see discussion). [b] Ref. 28. [c] Ref. 29. [d] Ref. 30. [e] Ref. 31. [f] Ref. 32. [g] Refs. 10, 33. [h] Ref. 34. [i] Ref. 35. [j] Ref. 15. [k] Ref. 36. [l] Ref. 37. [m] Ref. 12. [n] Ref. 38. [o] Ref. 39. [p] Ref. 40. [q] Ref. 41. [r] Ref. 42. [s] This research.

TABLE V. Kinetic Parameters for the Acid Hydrolysis and *mer* → *fac*-Isomerisation of some Co(III) Triamine Complexes at 298 2 K

Complex	Acid hydrolysis[a]			References
	$10^5\ k$ (s^{-1})	E_a (kJ mol^{-1})	$\Delta S_{298}^{\#}$ ($JK^{-1}\ mol^{-1}$)	
trans-dichloro-*mer*-$CoCl_2(NH_3)(dien)^+$	39.8[b]	106	+36	c
trans-dichloro-*mer*-$CoCl_2(NH_3)(2,3\text{-tri})$	30.9[b]	103 ± 2	+27 ± 4	d
	Isomerisation[e]			
mer-$Co(dien)(OH_2)_3^{3+}$	24.7	109	+42	f
mer-$Co(2,3\text{-tri})(OH_2)_3^{3+}$	2.97	115 ± 1	+46 ± 2	d
trans-diaqua-*mer*-$Co(NH_3)(dien)(OH_2)_2^{3+}$	162	100	+29	f
trans-diaqua-*mer*-$Co(2,3\text{-tri})(NH_3)(OH_2)_2^{3+}$ [g]	4.13	113 ± 3	+52 ± 6	d

[a] Rate of loss of first chloro ligand (0.1–0.3 M HNO_3). [b] Spectrophotometrically determined rate constants. [c] Ref. 11. [d] This research. [e] In 0.02 M $Hg(NO_3)_2$, 0.95 M HNO_3 (μ = 1.0 M). [f] Ref. 7. [g] In 0.0574 M $Hg(NO_3)_2$, 0.82 M HNO_3 (μ = 1.0 M).

Cr(III) analogs [10]. However, this labilising effect in Co(III) complexes is decreased as the six-membered ring is incorporated into linear of macrocylic tetraamine ligands (Table IV). This decreases in the six-membered ring labilising effect is now reflected in the present linear triamine system as the rate of loss of the first chloro ligand from *trans*-$CoCl_2(NH_3)$-(2,3-tri)$^+$ approximately equals that observed for *trans*-$CoCl_2(NH_3)$(dien)$^+$ [11].

The six-membered ring labilising effect (tn *vs.* en) has been attributed to the larger ring allowing a more ready distortion to a five-coordinate intermediate [12] and this is supported by recent molecular mechanics calculations [13]. However, in fused ring systems, the ready distortion of the six-membered ring may be restricted by the positions of secondary NH protons. Thus, systems with a readily available fold axis e.g., *RRRR,SSSS-trans*-$CoCl_2$(cyclam)$^+$ [14] or *RR,SS-trans*-$CoCl_2$(2,3,2-tet)$^+$ [15] aquate very much faster than isomeric analogs where this fold axis is absent. In the present system, as for the dien analog, the two chloro ligands are not equivalent and only loss of the chloro ligand remote from the sec-NH proton will allow the ready generation of a five-coordinate intermediate. Consequently, if the chloro adjacent to the sec-NH proton is the more labile [3, 11] the rate of reaction will not be markedly influenced by ring size effects.

Although the kinetic parameters for *trans-mer*-$CoCl_2$(2,3-tri)$(OH_2)^+$ are reported in Table IV, there are virtually no directly comparable Co(III) analogs. Certainly, the replacement of NH_3 by OH_2 causes a moderate increase (X13) in chloro lability, but the opposite effect has been observed for the *mer* → *fac* isomerisation of Co(dien)$(OH_2)_3^{3+}$ relative to Co-(NH_3)(2,3-tri)$(OH_2)_2^{3+}$ where replacement of NH_3 by H_2O causes a X7 decrease in rate [7]. For the present 2,3-tri system the replacement of NH_3 by H_2O results in a X2 decrease for the *mer* → *fac* isomerisation. It should be noted that these k_{obs} comparisons are well within the range where reversals of order may be expected if a temperature other than 25 °C was considered, as the values for the energy and entropy of activation are by no means comparable.

Of more significance in Table IV are the Co(III)/Cr(III) comparisons. It is now apparent that the most important kinetic parameter distinguishing the difference in primary aquation rates between analogous *trans*-dichloro Co(III) and Cr(III) complexes is the activation entropy. For Co(III) systems this parameter is generally positive, whereas for Cr(III) cases, a more negative value is observed [16]. Indeed, there is an approximate correlation $\Delta S_T{}^{\#}$Co(III) + $\Delta S_T{}^{\#}$Cr(III) = 19 and in Table IV the values in parenthesis under $\Delta S_{298}{}^{\#}$Co(III) are calculated from this expression.

Mechanistically, the general concensus is that the aquation of Cr(III) complexes is more associative [17] than for Co(III) systems. Assuming that solvent assisted chloride release for Cr(III) involves prior hydration of the leaving group in the transition state, the resulting loss of entropy will have a negative contribution to $\Delta S^{\#}$ as observed.

On the other hand, it has been argued that for certain Cr(III) complexes (mainly *trans*-$CrCl_2$(macrocycle)$^+$) that steric crowding would inhibit an associative process [18]. Indeed, steric efforts do seem to be important for Cr(III) as illustrated by the 1000 fold increase in aquation rate for *trans*-$CrCl_2$(tet *a*)$^+$ (tet *a* = C-meso-Me_6cyclam) when compared with *trans*-$CrCl_2$(cyclam)$^+$ (Table IV), but in both systems a negative $\Delta S^{\#}$ is observed. It is also the case, however, that Co(III) systems are even more sensitive to changes in the non-replaced ligands than are Cr(III) systems. This has been attributed [13] to the generation of a more fully developed trigonal bipyramid intermediate for Co(III) in agreement with the observation that the propensity for stereochemical change during the aquation is more pronounced for Co(III). It is difficult to predict how such a change in intermediate stereochemistry [trigonal bipyramid for Co(III) *vs.* square planar for Cr(III)] would influence $\Delta S^{\#}$, but the constant difference of ~19 J K^{-1} mol^{-1} could be attributed to more bond reorganisation occurring in the transition state during the aquation of Co(III) *trans*-dichloro systems.

Thus, our interpretation of the currently available information is that for *trans*-dichloro tetraamine complexes, both Co(III) and Cr(III) aquate via an essentially dissociative mechanism and that the difference between the two systems is the generation of a more fully developed trigonal bipyramid intermediate for Co(III).

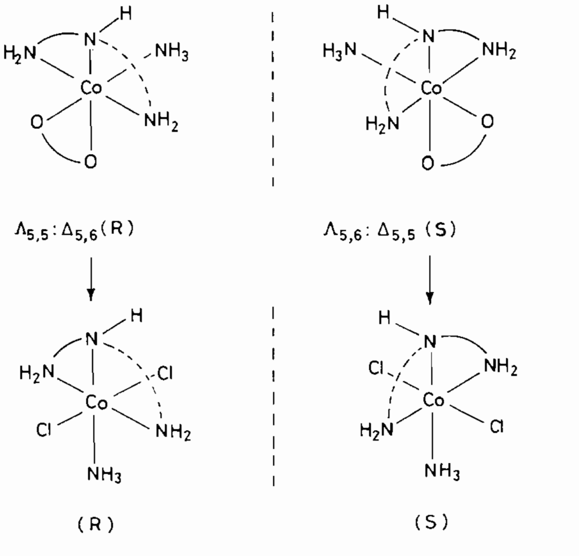
Optical Activity

As mentioned in the 'Introduction', 2,3-tri is a prochiral ligand as, on coordination, a single asymmetric nitrogen center is generated, and we have succeeded in preparing $(+)_{450}$-*trans*-$[CoCl_2(NH_3)$-(2,3-tri)$]ClO_4$.

The number of examples where the sole source of optical activity is due to a single asymmetric nitrogen atom is not large and includes $Co(NH_3)_4$-(sarcosine)$^{2+}$[19] and $Co(NH_3)_4$(N-Me-en)$^{3+}$ [30]. The present system is unique in that it is the first *trans* dichloro Co(III) complex where the chirality arises from a single sec-NH asymmetric center. All previous examples of chiral *trans* dichloro N_4 systems e.g. *trans*-$CoCl_2$N-Me-en)$_2^+$ [21] or *trans*-$CoCl_2$(linear tetraamine)$^+$ [22–24] contain two asymmetric centers.

For $(+)_{450}$-*trans*-$CoCl_2(NH_3)$(2,3-tri)$^+$, the rotational intensity is similar to that observed for analogous complexes with two assymmetric centers and about half that of analogous complexes with an asymmetric carbon atom adjacent to a coordinated nitrogen, e.g. (–)-$CoCl_2$(R-pn)$_2^+$ [25].

At this stage, we are uncertain as to the absolute configuration of the asymmetric nitrogen atom in $(+)_{450}$-*trans*-$CoCl_2(NH_3)(2,3\text{-tri})^+$, (*R* or *S*). We can, however, make a tentative assignment on the basis of the following argument. We commence by assuming that the parent oxalato has the same configuration as that established for *mer*-$[Co(ox)(NH_3)(dien)]NO_3$ [26], *i.e.* with the sec-NH proton adjacent to the NH_3 ligand. The less soluble diastereoisomeride, $(+)$-$Co(ox)(NH_3)(2,3\text{-tri})^+$ (from which the $(+)_{450}$-*trans* dichloro was derived) can be assigned to the Δ absolute configuration on the basis of its CD spectrum [5, 6], but this assignment requires further analysis as it is uncertain as to which ring pair will dominate the CD intensity. A Δ configuration with the 5,6 membered ring pair (ox, tn) dominant will give rise to the (*R*) configuration at the sec-NH, whereas a Δ configuration with the 5,5 ring pair (ox, en) dominant gives the (*S*) sec-NH configuration (Scheme 1). We have argued previously [27], that for oxalato complexes it will be the five-membered ring pairs that dominate, and on this basis the resulting $(+)_{450}$-*trans* dichloro should have the (*S*) absolute configuration.



Scheme 1. Absolute configurations of *mer*-$[Co(ox)NH_3)(2,3\text{-tri})]^+$ and *trans*-dichloro-*mer*-$CoCl_2(NH_3)(2,3\text{-tri})^+$. Five-membered chelate rings are denoted —— and six-membered rings – – –.

Acknowledgement

We thank the New Zealand Universities Grants Committee for providing funds to purchase instruments used in this research.

References

1 A. R. Gainsford and D. A. House, *J. Inorg. Nucl. Chem., 32,* 688 (1970).
2 M. C. Couldwell and D. A. House, *J. Inorg. Nucl. Chem., 33,* 2583 (1971).
3 D. A. House, A. R. Gainsford and J. W. Blunt, *Inorg. Chim. Acta, 57,* 141 (1982).
4 C. L. Sharma and T. K. De, *J. Indian Chem. Soc., 58,* 119 (1981).
5 D. A. House, *Inorg. Chim. Acta, 60,* 145 (1982).
6 G. R. Brubaker and D. P. Schaefer, *Inorg. Chem., 10,* 968 (1971).
7 D. A. House, *Inorg. Chim. Acta, 30,* 281 (1978); Foo Chuk Ha and D. A. House, *Inorg. Chim. Acta, 38,* 167 (1980).
8 A. J. Cunningham, D. A. House and H. K. J. Powell, *J. Inorg. Nucl. Chem., 33,* 572 (1971).
9 G. G. Schlessinger, 'Inorganic Laboratory Preparations', Chem. Pub. Co., New York, 1962, p. 247.
10 M. C. Couldwell and D. A. House, *Inorg. Chem., 11,* 2024 (1972).
11 M. C. Couldwell and D. A. House, *Inorg. Chem., 13,* 2949 (1974).
12 D. Yang and D. A. House, *Inorg. Chem., 21,* 2999 (1982).
13 D. A. House and R. J. Maclagan, *Aust. J. Chem., 37,* 239 (1984).
14 C. J. Cooksey and M. L. Tobe, *Inorg. Chem., 17,* 1558 (1978).
15 R. Niththyananthan and M. L. Tobe, *Inorg. Chem., 8,* 1589 (1969).
16 D. A. House and O. Nor, *Inorg. Chim. Acta, 72,* 195 (1983).
17 T. W. Swaddle, *Coord. Chem. Rev., 14,* 217 (1974).
18 E. Bang and O. Mønsted, *Acta Chem. Scand., Ser. A, 36,* 353 (1982).
19 B. Halpern, A. M. Sargeson and K. R. Trunbull, *J. Am. Chem. Soc., 88,* 4630 (1966).
20 D. A. Buckingham, L. G. Marzilli and A. M. Sargeson, *J. Am. Chem. Soc., 89,* 825 (1967).
21 W. T. Robinson, D. A. Buckingham, G. Chandler, L. G. Marzilli and A. M. Sargeson, *J. Chem. Soc., Chem. Commun.,* 539 (1969).
22 H. G. Hamilton and M. D. Alexander, *J. Am. Chem. Soc., 89,* 5056 (1967).
23 B. Bosnich, J. MacB. Harrowfield and H. Boucher, *Inorg. Chem., 14,* 815, 828 (1975).
24 A. M. Sargeson and G. H. Searle, *Inorg. Chem., 6,* 787 (1968).
25 C. J. Hawkins, E. Larsen and I. Olsen, *Acta Chem. Scand., 19,* 1915 (1965).
26 M. C. Couldwell, D. A. House and B. R. Penfold, *Inorg. Chim. Acta, 13,* 61 (1975).
27 D. A. House and V. McKee, *Inorg. Chem., 23,* 4237 (1984).
28 R. C. Link, *Inorg. Chem., 8, 1016 (1969).*
29 D. W. Hoppenjans, J. B. Hunt and C. R. Gregoire, *Inorg. Chem., 7,* 2506 (1968).
30 S. C. Chan, *Aust. J. Chem., 20,* 595 (1967).
31 D. J. MacDonald and C. S. Garner, *J. Inorg. Nucl. Chem., 18,* 219 (1961).
32 I. R. Jonasson, R. S. Murray, D. R. Stranks and Y. K. Yandell, *Proc. Int. Conf. Coord. Chem., 12,* 32 (1969).
33 M. C. Couldwell and D. A. House, *Inorg. Nucl. Chem. Lett., 7,* 947 (1971).
34 D. A. House, *Inorg. Chem., 25,* 1671 (1986).
35 M. C. Couldwell, D. A. House and H. K. J. Powell, *Inorg. Chem., 12,* 617 (1973).
36 M. D. Alexander and H. G. Hamilton, *Inorg. Chem., 8,* 2131 (1969).

37 C. Kutal and A. W. Adamson, *Inorg. Chem.*, *12*, 1990 (1973).

38 C. K. Poon and M. L. Tobe, *J. Chem. Soc. A*, 2069 (1967).

39 E. Campi, J. Ferguson and M. L. Tobe, *Inorg. Chem.*, *9*, 1781 (1970).

40 W. K. Chan and C. K. Poon, *J. Chem. Soc. A*, 3087 (1971).

41 J. A. Kernahan and J. F. Endicott, *Inorg. Chem.*, *9*, 1504 (1970).

42 D. Yang and D. A. House, *Inorg. Chim. Acta Lett.*, *64*, 167 (1982).