Inorganica Chimica Acta, 57 (1982) 141–149

Anionopentaaminecobalt(III) Complexes with Polyamine Ligands. 18. Structure-reactivity Relationships for Epimeric Pairs of *mer*-CoCl(AA)-(2,3-tri)$^{2+}$ Complexes

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Received June 8, 1981

Two geometric isomers (red and violet), each of [CoCl(AA)(2,3-tri)]ZnCl$_4$ (AA = en, pn, tn) have been isolated from the reaction of [Co$_2$(AA)$_2$(2,3-tri)$_2$O$_2$](ClO$_4$)$_4$ with HCl. Structural assignments have been made on the basis of C-13 NMR spectra and by comparison with the related 3,3-tri complexes of known configuration. The unsymmetrical tridentate (2,3-tri) is meridionally coordinated, with the red and violet forms corresponding to the (R,S)-sec-NH proton being adjacent to, and remote from the coordinated chloro ligand, respectively. These assignments are supported by mercury(II)-assisted aquation and base hydrolysis reaction rate studies.

Introduction

As part of a continuing programme of the investigation of CoX(N$_5$)$^{n+}$ systems, we have described complexes where N$_5$ is a bidentate plus tridentate combination [1–13]. In previous work we have used the symmetrical tridentates 1,4,7-triazaheptane (diethylenetriamine = 2,2-tri) and 1,5,9-triazanonane (dipropylenetriamine = 3,3-tri). In this investigation,

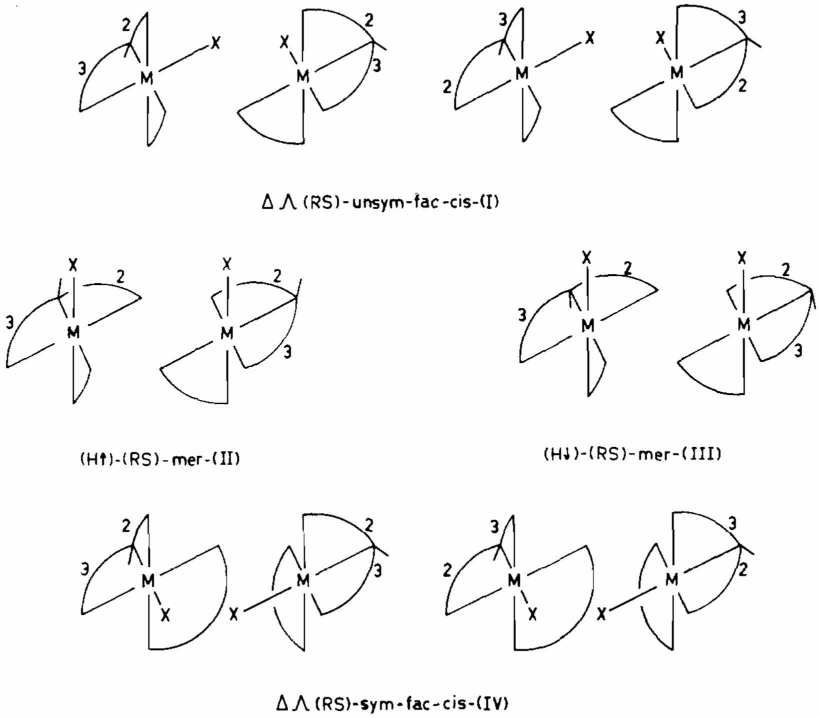

Fig. 1. The four geometric (Roman numerals) and twelve optical isomers possible for CoCl(AA)(2,3-tri)$^{2+}$.

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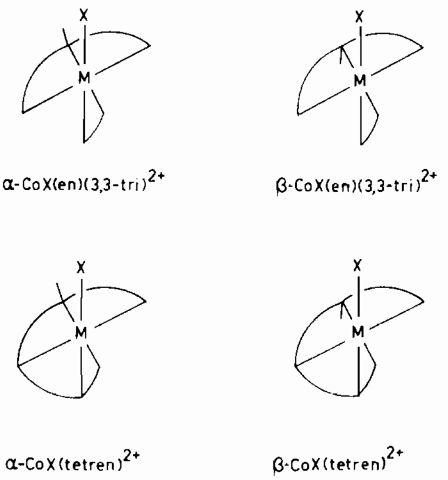
TABLE I. Analytical Data.

	Calculated				Found			
	C%	H%	Co%	Cl%	C%	H%	Co%	Cl%
$[Co_2(en)_2(2,3\text{-tri})_2O_2](ClO_4)_4 \cdot 2H_2O$	17.92	5.37	12.56		18.06	5.11	12.67	
$[Co_2(pn)_2(2,3\text{-tri})_2O_2](ClO_4)_4$	20.65	5.42			20.40	5.38		
$[Co_2(tn)_2(2,3\text{-tri})_2O_2](ClO_4)_4$	20.65	5.42			20.89	5.43		
$[CoCl(en)(2,3\text{-tri})]ZnCl_4$-red	17.56	4.84	12.31	37.02	17.84	4.81	12.21	36.89
$[CoCl(en)(2,3\text{-tri})]ZnCl_4$-violet					17.90	4.81	12.25	36.92
$[CoCl(pn)(2,3\text{-tri})]ZnCl_4$-red	19.49	5.11			19.47	5.20		
$[CoCl(pn)(2,3\text{-tri})]ZnCl_4$-violet					19.55	5.18		
$[CoCl(tn)(2,3\text{-tri})]ZnCl_4$-red	19.49	5.11			19.61	5.13		
$[CoCl(tn)(2,3\text{-tri})]ZnCl_4 \cdot H_2O$-violet	18.80	5.33			18.86	5.23		

we describe analogous complexes using the unsymmetrical tridentate 1,4,8-triazaoctane (2,3-tri). The use of an unsymmetrical triamine could impose considerable isomeric complexity in a $CoX(AA)(ABC)^{2+}$ system as the coordinated secondary nitrogen is now asymmetric, and four geometric and twelve optical isomers can be expected (Fig. 1). However, only two isomers (red and violet) for each of the bidentate ligands en, pn and tn have been isolated and these correspond to epimerically related configurations of the sec-NH proton of the meridionally coordinated tridentate, (H↑)-R,S and (H↓)-R,S, respectively, in Fig. 1.

Thus, these isomers provide a series of epimeric pairs and structure-reactivity patterns within this series can be compared with those of similarly related isomers of $CoCl(en)(3,3\text{-tri})^{2+}$ [1, 3, 4] and $CoCl(tetren)^{2+}$ [14–18] of known configuration.



α-$CoX(en)(3,3\text{-tri})^{2+}$ β-$CoX(en)(3,3\text{-tri})^{2+}$

α-$CoX(tetren)^{2+}$ β-$CoX(tetren)^{2+}$

Fig. 2. Configurations of α- and β-$CoCl(en)(3,3\text{-tri})^{2+}$ [3, 4] and α- and β-$CoCl(tetren)^{2+}$ [14].

Experimental

N-(2-Aminoethyl)-1,3-propanediamine(1,4,8-triazaoctane = 2,3-tri) was purchased from Ames Laboratories Ltd and used as supplied. All other chemicals were the best reagent grade available. Analytical data are listed in Table I.

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 with care.

μ-Peroxobis(diamine)bis(1,4,8-triazaoctane)dicobalt(III) perchlorate

An aqueous solution (150 ml) of 2,3-tri (8 g) and the diamine (5 g pn, tn; 4 g en) was added to a stirred solution of $Co(NO_3)_2 \cdot 6H_2O$ (20 g) and $NaClO_4 \cdot H_2O$ (25 g). A rapid stream of O_2 gas was passed through the stirred, room temperature solution, and after 30 min a further 25 g of $NaClO_4 \cdot H_2O$ was added. After a further 2 hrs, the brown solid material that had deposited was collected by filtration, washed with 2-propanol and then ether and air dried. Yields were: en, 28 g, 87%; pn 70–80%; tn 28.4 g, 85%. In the case of pn, a brown oil was first formed. This was removed by decantation and reacted directly with $HCl/ZnCl_2$ (see later). The mother liquor deposited small amounts of brown crystals on standing at room temperature. Samples for analysis were recrystallised by dissolving 0.5 g of the brown solids in 60 ml 0.1 *M* $HClO_4$ at 40 °C and then adding $NaClO_4 \cdot H_2O$ (5 g). The brown solids that deposited on cooling were collected and washed as above. Greater than 90% recovery was obtained.

TABLE II. Absorption Spectral Parameters for Some *mer*-CoCl(AA)(2,3-tri)$^{2+}$ Complexes.

AA	λ_{max}	λ_{max}	λ_{min}	λ_{max}	λ_{min}
(H↑)en	532	465sh	418	363	331
red	(65.0)	(40.9)	(16.1)	(73.9)	(37.0)
(H↓)en	540	465sh	422	367	329
violet	(72.5)	(42.1)	(16.7)	(80.7)	(28.7)
(H↑)tn	523	487sh	424	370	336
red	(51.3)	(48.1)	(15.8)	(62.1)	(33.1)
(H↓)tn	536	488sh	427	374	337
violet	(51.7)	(47.0)	(15.4)	(63.0)	(25.6)
(H↑)pn	532	470sh	418	365	332
red-(A + B)[a]	(69.5)	(48.0)	(20.0)	(79.8)	(38.2)
(H↓(pn	541	470sh	422	368	330
violet-(C)[a]	(69.9)	(41.5)	(16.8)	(77.6)	(29.0)
(H↓)pn	543	470sh	422	368	330
violet-(D)[a]	(72.5)	(43.5)	(18.6)	(80.9)	(28.6)
(H↑)α-(en)	542	517sh	431	374	337
(3,3-tri) red	(75.1)	(60.1)	(13.0)	(90.1)	(30.8)
(H↓)β-(en)	542	520sh	432	375	335
(3,3-tri) violet	(70.1)	(62.0)	(13.8)	(83.0)	(31.5)

[a] Orientation of the pn ligand is not established, see Fig. 3 and text.

Red and violet isomers of chloro(diamine) (1,4,8-triazaoctane)cobalt(III) tetrachlorozincate(II) [CoCl(AA)(2,3-tri)]ZnCl$_4$

The crude μ-peroxo complexes, prepared above, (20 g) were stirred into 4 *M* HCl (120 ml) containing ZnCl$_2$ (30 g). The solutions were heated on a steam bath (*ca.* 80 °C) until effervescence ceased (*ca.* 1 hr) during which time the red isomers crystallised. These were filtered from the hot solutions and washed with 2-propanol, then ether and air dried. The more soluble violet isomers were obtained from the mother liquor after standing overnight at room temperature. Total yields of ZnCl$_4^{2-}$ salts were: en 92%; pn 62%; tn 56%. The crude products were recrystallised from HCl by the addition of ZnCl$_2$ until constant IR and C-13 NMR spectra were obtained.

In the case of AA = pn, there was evidence for two violet isomers in later crystal crops and it is evident from the C-13 NMR spectrum that the 'red isomer' is also an isomeric mixture. These presumably arise from the two possible modes of coordination of the pn ligand [19, 20].

Chemical Analysis

Co was determined by decomposing the complexes with ammonium peroxodisulphate and estimating the Co(II) spectrophotometrically at 620 nm as the thiocyanate complex in aqueous acetone [21]. Non-perchlorate halogen was determined by potentiometric titration with standard AgNO$_3$ using a Radiometer pH-meter. The complexes were decomposed with sodium hydroxide and acidified with HNO$_3$ prior to titration. C and H analyses were performed by Prof. A. D. Campbell of the University of Otago, New Zealand.

Spectral Measurements

The visible absorption spectra were obtained using a Varian Superscan recording spectrophotometer. The same instrument was used for all Hg^{2+}-assisted aquation rate data. Data for the extinction coefficients were obtained in 0.1 *M* HClO$_4$ at 20–25 °C using matched 1.00 cm quartz cells with 0.1 *M* HClO$_4$ in the reference beam. A mean of three determinations was used to obtain the data cited in Table II. Infrared spectra were determined in KBr discs using a Shimadzu IR-27G infrared spectrophotometer. C-13 NMR spectra (Table III) were run in

TABLE III. C-13 NMR Data.[a]

	2,3-tri					en		
(en)(2,3-tri)red	56.94,	50.50,	43.08,	39.12,	27.26	45.83,	45.17	
violet	55.34,	49.69,	43.31,	39.36,	27.69	46.01,	44.85	
(tn)(2,3-tri)red	56.01,	49.67,	42.48,	39.40,	27.20	39.40,	39.27,	25.83
violet	55.42,	49.89,	43.17,	39.41,	27.64	39.41,[b]		25.56
						pn		
(pn)(2,3-tri)violet-(C)[c]	55.19,	49.79,	43.44,	39.28,	27.89	17.77,	51.07,	53.77
			43.29		27.55	17.93		53.67
violet-(D)[c]	55.52,	49.85,	43.50,	39.40,	27.81	17.15,	50.39,	55.39
			43.29	39.29	27.53	17.24		55.22
red(A + B)[c]	57.25,	50.31,	43.77,	39.11,	27.40	17.93,	51.01,	55.18
	57.10	50.05	42.93	39.03		17.78	50.39	54.46
	56.35			38.92		17.30		53.53

[a] 150–200 mg of the ZnCl$_4^{2-}$ salts in 0.1 *M* HCl with dioxane as an internal standard. [b] This resonance is twice the intensity of the other six. [c] Orientation of the pn ligand is not established, see Fig. 3 and text.

TABLE IV. Observed and Calculated Rate Constants for the Hg^{2+}-assisted Aquation of Some *mer*-$CoCl(AA)(ABA)^{2+}$ Complexes (μ = 1.0 *M*, $HClO_4$).[a]

T °C [K]	$[H^+]$ *M*	10^2 $[Hg^{2+}]^b$ *M*	10^3 $k_{obs}{}^c$ s^{-1}	10^3 $k_{Hg}{}^d$ M^{-1} s^{-1}	10^3 k_{Hg} calc^e M^{-1} s^{-1}
violet-(H↓)-$CoCl(tn)(2,3\text{-}tri)^{2+}$					
7.2[280.4]	0.76	9.34	1.76 ± 0.07	18.8 ± 0.7	18.9
10.7[283.9]	0.82	6.45	1.82 ± 0.04	28.2 ± 0.6	28.5
			1.94 ± 0.04	30.1 ± 0.6	
			1.77 ± 0.08	27.5 ± 1.3	
13.1[286.3]	0.82	6.45	2.42 ± 0.12	37.5 ± 1.8	37.6
			2.42 ± 0.04	37.5 ± 0.9	
15.8[289.0]	0.82	6.45	3.32 ± 0.04	51.5 ± 0.6	51.1
			3.25 ± 0.06	50.4 ± 0.9	
			3.31 ± 0.04	51.4 ± 0.6	
18.7[291.9]	0.82	6.45	4.69 ± 0.07	72.7 ± 1.1	70.6
			4.43 ± 0.05	68.7 ± 0.7	
red-(H↑)-$CoCl(tn)(2,3\text{-}tri)^{2+}$					
10.7[283.9]	0.76	9.34	1.07 ± 0.02	11.4 ± 0.2	11.7
13.1[286.3]	0.76	9.34	1.50 ± 0.08	16.0 ± 0.9	15.0
15.8[289.0]	0.76	9.34	1.82 ± 0.03	19.5 ± 0.3	19.8
18.4[291.6]	0.82	6.45	1.68 ± 0.06	26.0 ± 0.9	25.7
18.7[291.9]	0.76	9.34	2.57 ± 0.02	27.5 ± 0.2	26.5
	0.82	6.45	1.57 ± 0.07	24.3 ± 1.1	
22.6[295.8]	0.82	6.45	2.56 ± 0.09	39.7 ± 1.4	38.9
	0.88	4.47	1.73 ± 0.07	38.7 ± 1.6	
25.0[298.2]	0.88	4.47	2.22 ± 0.04	49.7 ± 0.9	49.1
violet-(H↓)-$CoCl(en)(2,3\text{-}tri)^{2+}$					
25.0[298.2]	0.76	9.34	0.546 ± 0.005	5.84 ± 0.05	5.83
31.1[304.3]	0.76	9.34	1.13 ± 0.02	12.1 ± 0.2	11.9
45.1[318.3]	0.88	4.47	2.28 ± 0.04	51.0 ± 0.9	54.6
52.5[325.7]	0.94	2.09	2.46 ± 0.07	118 ± 3.4	113
red-(H↑)-$CoCl(en)(2,3\text{-}tri)^{2+}$					
25.0[298.2]	0.76	9.34	0.418 ± 0.005	4.47 ± 0.05	4.42
31.1[304.3]	0.76	9.34	0.698 ± 0.01	7.47 ± 0.1	7.94
45.1[318.3]	0.82	6.45	1.88 ± 0.05	29.1 ± 0.8	28.0
	0.94	2.09	0.631 ± 0.007	30.2 ± 0.3	
56.0[329.2]	0.88	4.47	2.98 ± 0.1	66.6 ± 2.2	69.3
	0.94	2.09	1.49 ± 0.06	71.3 ± 2.9	
			1.42 ± 0.02	67.9 ± 0.9	
			1.41 ± 0.02	66.9 ± 1.0	
violet-(H↓)-$CoCl(pn)(2,3\text{-}tri)^{2+}$					
37.2[310.4]	0.76	9.34	3.38 ± 0.08	36.3 ± 0.9	37.3
45.1[318.3]	0.82	6.45	5.46 ± 0.07	84.6 ± 1.1	82.4
	0.94	2.09	1.78 ± 0.07	85.1 ± 3.3	
52.5[325.7]	0.94	2.09	3.38 ± 0.06	162 ± 3	167
red-(H↑)-$CoCl(pn)(2,3\text{-}tri)^{2+}$					
37.2[310.4]	0.76	9.34	1.26 ± 0.02	13.5 ± 0.2	14.0
45.1[318.3]	0.82	6.45	1.95 ± 0.05	30.2 ± 0.8	28.4

(continued on facing page)

TABLE IV. *(continued)*

T °C [K]	$[H^+]$ *M*	10^2 $[Hg^{2+}]^b$ *M*	10^3 k_{obs}^{c} s^{-1}	10^3 k_{Hg}^{d} M^{-1} s^{-1}	10^3 k_{Hg} calc^e M^{-1} s^{-1}
56.0[329.2]	0.88	4.47	3.00 ± 0.014	67.1 ± 3.1	71.3
	0.94	2.09	1.54 ± 0.03	73.7 ± 1.4	
β-violet-(H↓)-CoCl(en)(3,3-tri)$^{2+}$					
7.2[280.4]	0.94	2.09	2.39 ± 0.25	114 ± 12	
10.7[283.9]	0.94	2.09	3.74 ± 0.3	179 ± 14	
α-red(H↑)-CoCl(en)(3,3-tri)$^{2+}$					
18.45[291.6]	0.76	9.34	1.98 ± 0.04	21.2 ± 0.4	21.4
	0.82	6.45	1.60 ± 0.06	24.9 ± 0.9	
	0.88	4.47	0.821 ± 0.016	18.4 ± 0.4	
	0.94	2.09	0.447 ± 0.007	21.4 ± 0.3	
22.6[295.8]	0.88	4.47	1.47 ± 0.03	32.9 ± 0.7	32.5
25.0[298.2]	0.88	4.47	1.87 ± 0.06	41.8 ± 1.3	41.2
31.1[304.3]	0.94	2.09	1.53 ± 0.05	73.2 ± 2.4	74.0

[a]As $ZnCl_4^{2-}$ salts, *ca.* 1 mg/ml. [b]Initial $[Hg^{2+}]$. [c]Observed pseudo-first-order rate constant. [d]$k_{Hg} = k_{obs}$ $[Hg^{2+}]^{-1}$. [e]Calculated from the activation parameters cited in Table VI.

TABLE V. Observed and Calculated Rate Constants for the Base Hydrolysis of Some *mer*-CoCl(AA)(ABA)$^{2+}$ Complexes (μ = 0.1 *M*, NaCl).[a]

T °C [K]	pH $[10^8$ $[OH^-], M]^b$	10^4 k_{obs}^{c} (s^{-1})	10^3 k_{OH}^{d} $(M^{-1}$ $s^{-1})$	10^3 k_{OH} calc^e $(M^{-1}$ $s^{-1})$
red-(H↑)-CoCl(tn)(2,3-tri)$^{2+}$				
15.5 [288.7]	6.7 [2.92]	4.86	16.6	16.8
20.4 [293.6]	6.5 [2.78]	9.24	33.2	32.5
25.0 [273.2]	6.2 [2.35]	13.1	55.7	59.2
	6.1 [1.64]	10.2	62.2	
violet-(H↓)-CoCl(tn)(2,3-tri)$^{2+}$				
20.4 [293.6]	7.5[27.8]	13.6	4.89	4.55
25.0 [298.2]	7.0[13.1]	12.5	9.54	9.38
30.75[303.9]	6.4 [4.87]	11.0	22.6	22.3
35.5 [308.7]	6.2 [4.33]	19.3	44.6	45.2
red-(H↑)-CoCl(en)(2,3-tri)$^{2+}$				
20.4 [293.6]	7.1 [11.1]	6.40	5.76	5.70
25.0 [298.2]	6.85[9.25]	10.2	11.0	11.2
30.75[303.9]	6.4 [4.87]	12.2	25.0	25.0
35.5 [308.7]	6.2 [4.33]	21.0	48.5	48.2
violet-(H↓)-CoCl(en)(2,3-tri)$^{2+}$				
25.0 [298.2]	7.6 [52.0]	6.50	1.25	1.24
30.75[303.9]	7.2 [30.8]	7.57	2.46	2.49
35.5 [308.7]	7.0 [27.4]	12.2	4.45	4.41

(continued overleaf)

TABLE V. *(continued)*

T °C [K]	pH [10^8 [OH^-], *M*]^b	10^4 k_{obs}^{c} (s^{-1})	10^3 k_{OH}^{d} (M^{-1} s^{-1})	10^3 k_{OH} calc^e (M^{-1} s^{-1})
red-(H↑)-CoCl(pn)(2,3-tri)$^{2+}$				
20.4 [293.6]	7.3 [17.5]	8.40	4.80	4.62
25.0 [298.2]	6.8 [8.24]	6.33	7.68	7.98
30.75 [303.9]	6.5 [6.14]	9.06	14.8	15.4
35.5 [308.7]	6.3 [5.46]	14.9	27.3	26.2
violet-(H↑)-CoCl(pn)(2,3-tri)$^{2+}$				
20.4 [293.6]	8.1 [110]	11.2	1.02	1.01
26.5 [299.7]	7.4 [32.8]	7.12	2.17	2.20
34.7 [307.9]	6.9 [21.7]	13.1	6.04	6.00

[a] As $ZnCl_4^{2-}$ salts. Zn^{2+} does not interfere below pH = 8. [b] $-\log[OH^-] = pK_{wc} + 0.105 - pH$. [c] Observed pseudo-first-order rate constant ± 5%. [d] $k_{OH} = k_{obs}[OH^-]^{-1}$. [e] Calculated from the activation parameters cited in Table VII.

0.1 *M* HCl using previously described techniques [22, 23].

Kinetic Data

Rates of Hg^{2+}-assisted aquation were determined in $Hg^{2+}/HClO_4$ solution (μ = 1.0 *M*), prepared by dissolving $Hg(NO_3)_2 \cdot H_2O$ in $HClO_4$ and standardising with chloride solution [24]. Small amounts of the $ZnCl_4^{2-}$ salts (*ca.* 1 mg/ml) were dissolved in the solvent at the appropriate temperature in a 1.00 cm spectrophotometer cell. After establishing that satisfactory isosbestic points could be obtained by repeated spectral scans, absorbance *vs.* time data were measured at 550 nm using the fixed wavelength mode and a scale expansion of 0.1 absorbance. These low Co(III) concentrations, and consequent high instrument sensitivity were required to provide a suitable Hg^{2+}: complex ratio for pseudo-first-order kinetics [25].

Rates of base hydrolysis were determined in 0.1 *M* NaCl using the previously described pH-stat technique [26, 27].

Calculations

Second order rate constants k_{Hg} for the Hg^{2+}-assisted aquation reaction were calculated from the spectrophotometrically determined pseudo-first-order rate data as described previously [28] and the values are cited in Table IV.

Second order rate constants, k_{OH} (Table V) for the base hydrolysis reactions were calculated from the pseudo-first-order trace of OH^- uptake *vs.* time [27]. The set pH values were converted to [OH^-] using the expression

$$-\log[OH^-] = pK_{wc} + \log \gamma_{\pm} - pH$$

where $\log \gamma_{\pm} = 0.105$ for μ = 0.1 *M*, and pK_{wc} = 14.129, 13.951, 13.779, 13.607 and 13.458 at 15, 20, 25, 30 and 35 °C [29]. The pH meter was calibrated with 0.01 *M* borax, pH = 9.276, 9.225, 9.180, 9.139 and 9.102 at T = 15, 20, 25, 30 and 35 °C [30]. All activation parameters (Tables VI and VII) were computer calculated from the variation of rate constant with temperature using standard equations [27].

Results

Structural Assignments

The HCl decomposition of the μ-peroxo pentaamines, $Co_2(AA)_2(2,3\text{-tri})_2O_2^{4+}$, results in the isolation of two (violet and red) CoCl(AA) (2,3-tri)$^{2+}$ isomers (AA = en, tn). This reaction is now a standard route to the formation of $CoCl(N_5)^{2+}$ systems with polyamine ligands [31]. These violet and red isomers are assigned to structures II and III respectively (Fig. 1) on the following basis.

(a) Increasing the size of the chelate rings in an m,n-tri polyamine results in the increased stabilisation of the meridional configuration [32, 33]. Thus, no facial Co(III) complexes with 3,3-tri are known, and the rate of *mer* → *fac* isomerisation of Co(m,n-tri)$(OH_2)_3^{3+}$ is 2,2-tri greater than 2,3-tri, with 3,3-tri and 3,4-tri decomposing to Co(II) [32–34]. Consequently a meridional configuration is expected for the 2,3-tri ligand.

(b) While all 5 carbon atoms of the 2,3-tri ligand are expected to be C-13 distinguishable regardless of geometric configuration, the close similarity of the C-13 spectra of the red and violet forms (Table III) suggests either a III/II or I/IV relationship (Fig.

TABLE VI. Kinetic Parameters for the Hg^{2+}-assisted Aquation of Some *mer*-CoCl(AA)(ABA)$^{2+}$ Complexes at 298.2 K and μ = 1.0 *M*, $HClO_4$.

Complex		10^3 k_{Hg} (M^{-1} s^{-1})	Ea (kJ mol^{-1})	log PZ	$\Delta S^{\#}_{298.2}$ (JK^{-1} mol^{-1})	Ref.
(H↓)-CoCl(tn)(2,3-tri)$^{2+}$	(violet)	139	78.1 ± 1.6	12.833	−7.5 ± 3	a
(H↑)-CoCl(tn)(2,3-tri)$^{2+}$	(red)	49.1	70.7 ± 2.4	11.073	−41 ± 5	a
(H↓)-CoCl(en)(2,3-tri)$^{2+}$	(violet)	5.82	87.7 ± 2.2	13.147	−1.5 ± 5	a
(H↑)-CoCl(en)(2,3-tri)$^{2+}$	(red)	4.42	72.4 ± 1.2	10.331	−55.5 ± 3	a
(H↓)-CoCl(pn)(2,3-tri)$^{2+}$	(violet)	10.1	82.3 ± 3.2	12.43	−15 ± 7	a,b
(H↑)-CoCl(pn)(2,3-tri)$^{2+}$	(red)	4.35	73.6 ± 3.8	10.53	−51 ± 8	a,b
(H↓)-CoCl(en)(3,3-tri)$^{2+}$	(violet)	1000	85	14.9	+33	a,c,d
(H↑)-CoCl(en)(3,3-tri)$^{2+}$	(red)	41.2	72.3 ± 6	11.29	−37 ± 12	a,c
(H↓)-CoCl(en)(2,2-tri)$^{2+}$		5.21	81.5 ± 1.2	11.98	−23 ± 4.5	e
(H↓)-CoCl(NH_3)$_2$(2,2-tri)$^{2+}$		21.4				f,g
(H↓)-CoCl($EtNH_2$)(2,2-tri)$^{2+}$		169				f,g
(H↓)-CoCl(tn)(2,2-tri)$^{2+}$		250				h,i

[a]This research. [b]The orientation of the unsymmetric pn ligand within the complex is not known. [c]Refs. 1, 3, 4. [d]Only two temperatures used to determine the activation parameters. [e]Ref. 8. [f]Sec-NH proton orientation not established with confidence. [g]Ref. 28. [h]D. A. House, unpublished research. [i]Ref. 9.

TABLE VII. Kinetic Parameters for the Base Hydrolysis of Some *mer*-CoCl(AA)(ABA)$^{2+}$ Complexes at 298.2 K and μ = 0.1 *M*, NaCl.

Complex		10^{-3} k_{OH} (M^{-1} s^{-1})	Ea (kJ mol^{-1})	log PZ	$\Delta S^{\#}_{298.2}$ (JK^{-1} mol^{-1})	Ref.
(H↓)-CoCl(tn)(2,3-tri)$^{2+}$	(violet)	9.38	114 ± 2	24.045	207 ± 4	a
(H↑)-CoCl(tn)(2,3-tri)$^{2+}$	(red)	59.2	95.0 ± 2	21.4	156 ± 10	a
(H↓)-CoCl(en)(2,3-tri)$^{2+}$	(violet)	1.24	92.4 ± 2	19.284	116 ± 4	a
(H↑)-CoCl(en)(2,3-tri)$^{2+}$	(red)	11.2	107 ± 1	22.718	182 ± 2	a
(H↓)-CoCl(pn)(2,3-tri)$^{2+}$	(violet)	1.83	93.6 ± 1.5	19.653	123 ± 3	a
(H↑)-Co(pn)(2,3-tri) $^{2+}$	(red)	7.98	86.7 ± 4	19.09	112 ± 8	a
(H↓)-CoCl(en)(3,3-tri)$^{2+}$	(violet)	2.2				b
(H↑)-CoCl(en)(3,3-tri)$^{2+}$	(red)	2.8				b
(H↓)-CoCl(tetren)$^{2+}$		1.7 × 10^3	(343.2 K)			c
(H↑)-CoCl(tetren)$^{2+}$		3.5 × 10^3	(343.2 K)			c
		35	100		171	c
		84	133	28.18	286	d
(H↓)-CoCl(en)(2,2-tri)$^{2+}$		30				b
(H↓)-CoCl(tn)(2,2-tri)$^{2+}$		502	83.3 ± 2	20.29	135 ± 4	e,f
(H↑)-CoCl(tn)(3,3-tri)$^{2+}$		27.5	102 ± 3	22.39	175 ± 6	e

[a]This research. [b]R. W. Hay and K. B. Nolan, *J. Inorg. Nucl. Chem., 38,* 2118 (1976); R. W. Hay, personal communication. [c]Ref. 17, k_{OH} values at 343.2 K. [d]Ref. 18. [e]Ref. 9. [f]P. Comba and W. Marty, personal communication.

1). (c) The α(red)- and β-(violet)-CoCl(en)(3,3-tri)$^{2+}$ isomers [1] are known [3, 4] to be epimerically related as in structures III and II (Fig. 1) respectively. The solid state colour and visible absorption spectral parameters (Table II) for the red and violet CoCl(AA)(2,3-tri)$^{2+}$ isomers are similar to those of the α- and β-CoCl(en)(3,3-tri)$^{2+}$ forms, supporting the structural assignment. (d) Chemical interconversions of the red and violet CoCl(en)(3,3-tri)$^{2+}$ isomers [1] are paralleled in the related isomers of

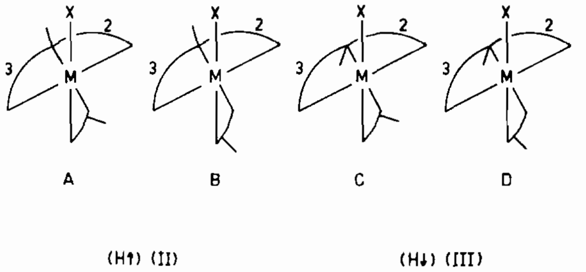


Fig. 3. Potential geometric isomers for *mer*-CoCl(pn)(2,3-tri)$^{2+}$. Each of these isomers contains two chiral centers, RS(*N*) and RS(*C*).

CoCl(en)(2,3-tri)$^{2+}$ [19]. (e) In terms of current structure-reactivity theory [9, 10, 13, 35–37] isomers of structure II (violet) are expected to react more rapidly in aquation or Hg^{2+}-assisted aquation, than those of structure III (red). For a dissociative mechanism, isomers of structure II can more easily distort towards a trigonal bipyramid transition state than those of structure III, because of the favourable orientation of the sec-NH proton. This prediction is in agreement with the observation [8] that β-(violet)-CoCl(en)(3,3-tri)$^{2+}$ has an aquation rate of 10 times, and an Hg^{2+}-assisted aquation rate of *ca.* 24 times that of the α(red)-isomer (Table VI). The violet/red isomeric pairs of CoCl(AA)(2,3-tri)$^{2+}$ all show a similar Hg^{2+}-assisted aquation rate relationship (Table VI).

The introduction of the unsymmetric (RS)-1,2-diaminopropane ligand will allow two forms each of structures (II) and (III), depending on the mode of coordination of the diamine (Fig. 3). The A(II)/C(III) and B(II)/D(III) pairs should be related by chemical interconversion, but the A(II)/D(III) *etc.* pairs will not be interconvertable. While we have been able to separate two violet isomers (Table III) by fractional crystallisation, the red isomer appears (C-13 NMR) to be a mixture of the A and B forms.

This red isomeric mixture has been used for reaction rate studies with no evidence for kinetically distinguishable forms, implying that the A and B isomers in the mixture react at the same rate within a factor of 2.

Kinetic Data

Epimerically related pairs of isomers of Co(III) polyamine complexes have previously been isolated for CoCl(AA)(3,3-tri)$^{2+}$ (AA = en [3, 4], tn [7]) and CoCl(tetren)$^{2+}$ [14–16] (Fig. 2), and some *trans*-$CoCl_2(N_4)^+$ systems, *e.g.* (RR, SS)-/(RS)-*trans*-$CoCl_2$(2,3,2-tet)$^{2+}$ [38–40] may also be considered as proton-inversion related forms.

One isomer is usually thermodynamically more stable than the other, and for the pentaamines, base hydrolysis of the violet forms followed by anation with HCl, results in more or less conversion to the red isomer.

There are, however, a number of systems where only one isomeric form is known, especially with 2,2-tri, *e.g.* (H↓)-*mer*-CoCl(en)(2,2-tri)$^{2+}$ (structure II) [2, 5, 6] and the assignment of the orientation [28] of the sec-NH proton in such cases is difficult in the absence of an X-ray crystal structure.

The kinetic parameters for the rate of Hg^{2+}-assisted aquation and base hydrolysis of 4 epimerically related isomeric *mer*-CoCl(AA)(m,n-tri)$^{2+}$ pairs are presented in Tables VI and VII.

In every case, the Hg^{2+} assisted aquation rate for the violet-(H↓)-isomer (III in Fig. 1) is greater than the corresponding red-(H↑)-form (II in Fig. 1) with rate ratios varying from 24 for m = n = 3, AA = en to 1.3 for m = 2, n = 3, AA = en. In each case, the violet-(H↓)-form has a more positive activation energy and entropy.

Although Hg^{2+}-assisted aquation rates have not been measured for the epimerically related CoCl(tetren)$^{2+}$ isomeric pair, the rates of aquation (which normally parallel those of Hg^{2+}-assisted aquation [25]) are in the order β(H↓) > α(H↑) [14, 41] with a β/α rate ratio of 2.7.

For base hydrolysis (Table VII), the pattern of reactivity is reversed, and the red-(H↑)-isomers are the more labile, with rate ratios varying from 9.0 for n = 2, n = 3, AA = en to 1.3 for m = n = 3, AA = en. Here, however, no clear pattern of activation energy or entropy is apparent, but the lability order is preserved for the related CoCl(tetren)$^{2+}$ systems [17].

In these *mer*-CoCl(AA)(m,n-tri)$^{2+}$ systems, base hydrolysis is believed [20] to occur via deprotonation of the sec-NH proton in the planar Co-($-N(CH_2)_mNH(CH_2)_nN-$) component of the polyamine ligand and in certain $CoCl_2(N_4)^+$ complexes this deprotonation can be rate determining [42].

Such systems are characterised by general base catalysis, and more negative activation energies and entropies ($E_a \sim 50$ kJ mol^{-1}, $\Delta S_{298} \sim 70$ J K^{-1} mol^{-1}) [42, 43] than those observed here, and have so far been restricted to $CoCl_2(N_4)^+$ complexes. The observation that there is a leaving group effect, $k_{Br}/k_{Cl} \sim 8$, in systems where deprotonation is rate-determining has lead to the proposal for a concerted E2 mechanism for the base hydrolysis reaction [42]. Such a sophistication may not be necessary as the 'leaving group effect' may be explained by differing electronic effects of Cl and Br on the acidity of the sec-NH proton. Proton exchange rates for similar complexes with different leaving groups would go some way to solving this problem.

Despite these difficulties, the epimeric system described here, may provide some information as to the direction of attack of the approaching OH$^-$ nucleophile towards the labile proton. Although it is tempting to suggest that a *cis* attack relative to the leaving group is more favourable than a possible *trans* attack, as it is complexes which contain the labile proton oriented in this direction (structure III, Fig. 1) that are more reactive, this may be too great an extrapolation.

Certainly, it appears that the sec-NH-proton oriented towards the leaving group is slightly more acidic than that in the alternative configuration.

Acknowledgements

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

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