Anionopentaaminecobalt(III) Complexes with Polyamine Ligands.

21. The Kinetics of Aquation of *unsym-fac-cis*-CoCl(dien)(bn)$^{2+}$ – A Complex Containing a Seven-membered Chelate Ring

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Received January 27, 1984

The synthesis of *unsym-fac-cis*-[CoCl(dien)(bn)]ZnCl$_4$ is described and the isomeric configuration is assigned by C-13 NMR spectroscopy. The thermal aquation rate (0.1 M HNO$_3$) was measured spectrophotometrically at 318–327 K. Calculated kinetic parameters are k_{298} = 6.37 × 10^{-5} sec^{-1} log PZ = 12.443, E_a = 95 ± 6 kJ mol^{-1}, $\Delta S_{298}^{\#}$ = –15 ± 12 J K^{-1} mol^{-1}. Corresponding kinetic parameters for the Hg^{2+}-assisted aquation rate (μ = 1.0 M) are 10^3 k_{298} = 2170 M^{-1} s^{-1}, log PZ = 11.857 E_a = 66 ± 10 and $\Delta S_{298}^{\#}$ = –26 ± 20. The order of reactivity for *unsym-fac-cis*-CoCl(dien)(AA)$^{2+}$ (AA = diamine) systems is en < (NH$_3$)$_2$ < tn < bn.

Introduction

Inert transition metal complexes of 1,4-diaminobutane (bn)[†] are not common [1]. While Co(bn)$_3^{3+}$ and the series Co(en)$_x$(tn)$_y$(bn)$_z^{3+}$ (x + y + z = 3) have been prepared [2, 3], little is known about the influence of the seven-membered ring on the lability of an associated aniono ligand.

For Co(III) complexes, a change in ring size from five to six (en to tn) results in a marked kinetic labilization. For example, in acidic solution at 25 °C, the half-lives for the loss of the first chloro ligand from *trans*-CoCl$_2$(AA)$_2^+$ are AA = en[4] :6.0 hr and AA = tn[5] :13s. Unfortunately, the AA = bn analogue has not yet been prepared, and if the labilising trend continues, this situation is unlikely to change unless a very insoluble salt can be found.

For some years, we have been working with complexes of the CoCl(dien)(AA)$^{2+}$ type and for the *unsym-fac-cis* isomers, the AA = tn [6] complex reacts 16 times faster than the AA = en [7] analog. In this letter, we describe the synthesis, characterisation, thermal aquation and Hg^{2+}-assisted aquation of the *unsym-fac-cis*-AA = bn analog of CoCl(dien)(AA)$^{2+}$.

Experimental

mer-Co(dien)Cl$_3$ was prepared as described previously [8].

unsym-fac-cis-*Chloro(diethylenetriamine)(1,4-diaminobutane)cobalt(III)tetrachlorozincate(II), [CoCl(dien)(bn)]ZnCl$_4$*

mer-CoCl$_3$(dien) (7 g) was suspended in 1:1 methanol/water (100 ml) and 1,4-butanediamine (3 ml) was added. The mixture was heated under reflux for 1 hr, during which time the brown solid dissolved to give a dark red solution. Concentrated HCl (20 ml, 12 M) containing ZnCl$_2$ (10 g) was added to the still warm solution and a small quantity (1 g) of purple-red crystals deposited, on leaving the solution at room temperature for 48 hrs. A further crop (1 g) of the crude product was obtained on evaporation of the mother liquor to half volume. Both fractions had identical i.r. spectra and were combined for recrystallisation from 50 °C 0.1 M HCl (40 ml) by addition of HCl (20 ml, 12 M) and ZnCl$_2$ (5 g).

Anal. Calcd. for CoC$_8$H$_{25}$N$_5$ZnCl$_5$: C, 19.49; H, 5.11; Co, 11.96; Cl, 35.96%. Found C, 19.23, H, 5.09; Co, 11.92; Cl, 35.72%. Visible absorption spectrum (0.1 M HCl) (λ, nm; ϵ, M^{-1} cm^{-1}): 523 max (72.4), 481 sh (58.4), 426 min (17.6), 371 max (85.3), 334 min (38.0). Final visible absorption spectrum after thermal or Hg^{2+}-assisted aquation, *unsym-fac-cis*-Co(dien)(bn)(OH$_2$)$^{3+}$: 494 max, 419 min, 360 max, 325 min.

Kinetics

The thermal aquation and Hg^{2+}-assisted aquation rates, 0.1 M HNO$_3$ (μ = 0.1 M) and HClO$_4$/Hg(NO$_3$)$_2$ (μ = 1.0 M) respectively, were measured spectrophotometrically at 500 nm using previously described techniques [9, 10]. In both cases, repeat scans (700–300 nm) showed that excellent isosbestic points were maintained during the course of the reaction, at 524, 417, 365 and 327 nm and the final absorption spectra were identical within experimental error. Activation parameters for the reactions were computer calculated from the variation of k with temperature.

Results and Discussion

There are potentially four geometric isomers that can be formed from the reaction between *mer*-CoCl$_3$-

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[†] Abbreviations used: en = NH$_2$(CH$_2$)$_2$NH$_2$ tn = NH$_2$(CH$_2$)$_3$NH$_2$, bn = NH$_2$(CH$_2$)$_4$NH$_2$, dien = NH$_2$(CH$_2$)NH(CH$_2$)$_2$NH$_2$.

0020-1693/84/$3.00

TABLE I. C-13 NMR Spectra [12].

	dien	bn
unsym-fac-cis- $CoCl(dien)(bn)^{2+\,a}$	55.78, 54.69, 45.49[b], 44.79[b]	44.98[b], 44.35[b] 28.82, 28.18
unsym-fac-cis- $CoCl(dien)(NH_3)_2{}^{2+}$	55.60, 54.64, 45.00, 44.55	
sym-fac-cis- $CoCl(dien)(NH_3)_2{}^{2+}$	55.45, 44.2	
mer-cis- $CoCl(dien)(NH_3)_2{}^{2+}$	50.92, 48.24	

[a] In 0.1 *M* HCl, relative to dioxane at 67.39 ppm. [b] There is some uncertainty as to the assignment of these C-resonances, but there is no doubt as to the dien configuration.

(dien) and a diamine, *viz.*, *sym-fac-cis*, *unsym-fac-cis* and two *mer-cis* forms [11].

The reaction between *mer*-$CoCl_3$(dien) and 1,4-diaminobutone gives a low yield of one isomeric form as all crops of [CoCl(dien)(bn)]$ZnCl_4$ from fractional crystallisation had identical i.r. spectra. This form is assigned to the *unsym-fac-cis*-configuration on the basis of the C-13 NMR spectrum for the dien-C atoms (Table I), where the resonance positions are sensitive to the dien configuration [12]. The visible absorption and i.r. spectrum also support this assignment as they are similar to the related *unsym-fac-cis*-[CoCl(dien)(AA)]$ZnCl_4$ (AA = en, tn) analogs. Kinetic parameters for the aquation of *unsym-fac-cis*-[CoCl(dien)(bn)]$ZnCl_4$ are given in Tables II and III.

The rate of loss of the chloro ligand in aqueous acidic solution is about 15X that of the analogous six-membered ring and about 250X that of the analogous five-membered ring isomer. Indeed, *unsym-fac-cis*-CoCl(dien)(bn)$^{2+}$ is one of the most labile Co(III) chloropentaamine complexes so far investigated [10, 11]. The increase in lability of *unsym-fac-cis*-CoCl(dien)(AA)$^{2+}$ in the order en < $(NH_3)_2$ < tn < bn does not appear to be related to any pattern in the activation parameters (Table III).

TABLE II. Rate Constants for the Thermal and Hg^{2+}-Assisted Aquation of *unsym-fac-cis*-[CoCl(dien)(bn)] $ZnCl_4$.[a]

Thermal Aquation (0.1 *M* HNO_3)

T °C [K]	10^4 k_{obs} (s^{-1})	10^4 k_{calc}[b] (s^{-1})
45.2 [318.4]	7.04 ± 0.11(1)[c]	7.25
47.7 [320.9]	10.1 ± 0.2(1)	9.59
51.5 [324.7]	14.0 ± 0.14(1)	14.5
54.2 [327.4]	19.6 ± 0.4(1)	19.4

Hg^{2+}-Assisted Aquation (μ = 1.0 *M*; $HClO_4$, $Hg(NO_3)_2$)

T °C [K]	[$HClO_4$] (*M*)	$[Hg^{2+}]_i$ (m*M*)	10^3 k_{obs} (s^{-1})	10^3 k_{Hg} (M^{-1} s^{-1})	10^3 $k_{Hg\,calc}$[b] (M^{-1} s^{-1})
10.5 [283.7]	0.94	20.9	11.7 ± 0.14(7)[c]	560 ± 7	558
6.4 [279.6]	0.94	20.9	7.76 ± 0.25(4)	371 ± 12	371

unsym-fac-cis-[CoCl(dien)(tn)]$ZnCl_4$ [6]
Hg^{2+}-assisted aquation[d] (μ = 1.0 *M*; $HClO_4$, $Hg(NO_3)_2$)

T °C [K]	[$HClO_4$] (*M*)	$[Hg^{2+}]_i$ (m*M*)	10^3 k_{obs} (s^{-1})	10^3 k_{Hg} (M^{-1} s^{-1})	10^3 $k_{Hg\,calc}$[b] (M^{-1} s^{-1})
25.3 [298.5]	0.94	20.9	3.01 ± 0.24(4)[c]	144 ± 12	129
22.9 [296.1]	0.88	44.7	4.51 ± 0.36(4)	101 ± 8	105
20.0 [293.2]	0.94	20.9	1.49 ± 0.08(4)	71.5 ± 4	81.0
	0.88	44.7	3.46± 0.17(4)	77.6± 4	
15.1 [288.3]	0.82	64.5	3.69± 0.19(4)	57.2 ± 3	51.8
10.6 [283.8]	0.82	64.4	2.19± 0.12(4)	33.9 ± 2	33.9

[a] All rate constants were determined spectrophotometrically by monitoring the change in absorbance at 500 nm, with time. [Co(III)] ~ 1 X 10^{-3} *M*. [b] Calculated from the activation parameters cited in Table III. [c] Numbers in parenthesis are the number of individual kinetic determinations used to calculate the mean ± standard deviation, and used for the calculation of the activation parameters. Where only a single kinetic run was performed, the standard deviation was estimated from the mean of 8–10 point-by-point calculations over >3 half-lives. [d] Isosbestic points at 516, 421, 358 and 323 nm.

TABLE III. Kinetic Parameters for the Thermal and Hg^{2+}-Assisted Aquation of some *unsym-fac-cis*-$CoCl(dien)(AA)^{2+}$ systems at 298.2 K.

AA	10^7 k_H (s^{-1})	E_a (kJ mol^{-1})	$\Delta S_{298}^{\#}$ (J K^{-1} mol^{-1})	Ref.
en	2.56	110	−8	[7]
$(NH_3)_2$	19.2	95	−44	[14]
tn	43.0	73	−111	[6]
bn	637	95 ± 6	−15 ± 12	a
AA	10^3 k_{Hg} (M^{-1} s^{-1})	E_a (kJ mol^{-1})	$\Delta S_{298}^{\#}$ (J K^{-1} mol^{-1})	
en	14.9	58	−93	[7]
$(NH_3)_2$	77.6	65.3	−55	[14]
tn	~100			[14]
	126	64 ± 3	−56 ± 6	a
bn	2170	66 ± 10	−26 ± 20	a

[a] This work.

We have argued previously [13], on the basis of molecular mechanics calculations, that the driving force for these thermal aquation ractions is the ease in which the five coordinate intermediate (generated by a dissociative mechanism) can distort to a trigonal bipyramid. In the *unsym-fac-cis*-$CoCl(dien)(AA)^{2+}$ series, such a distortion is facilitated by increasing flexibility of the bidentate ligand. Flexibility, while qualitatively easy to visualise, is difficult to quantitatively define. However, one parameter which seems to reflect the steric constraints of the (AA) group is the N–N distance along the octahedral edge – the so called 'bite distance'. Published crystal structures allow us to calculate this distance as en (2.68 Å), $(NH_3)_2$ (2.78 Å), tn (2.83 Å) and bn (2.82 Å).

It would not be expected that this 'bite distance' will increase monotonically with increasing ring size. Indeed, with large rings, involving considerable twisting, the N–N edge distance will decrease as the N atoms are no longer forced to adopt a distance constrained by the ring. The maximum distance may have been reached with tn or bn.

Extending this argument to the effects of distortion on the aquation rate, we would expect that for *unsym-fac-cis*-$CoCl(dien)(AA)^{2+}$ systems with a very large AA ring, a rate decrease relative to the tn or bn analogs may be observed, as the ends of the diamine will have an influence rather like two independent monoamines where $k_H(max) \sim 20 \times 10^{-7}$ s^{-1} at 25 °C. This estimate is calculated from the relationship [10] $\log k_{Hg} = 0.96 \log k_H + 4.36$ with $k_{Hg}(max) \sim 50 \times 10^3$ M^{-1} s^{-1} (25 °C) for *unsym-fac-cis*-$CoCl(dien)(monoamine)_2{}^{2+}$ [14].

Kinetic data for the Hg^{2+}-assisted aquation of *unsym-fac-cis*-$CoCl(dien)(AA)^{2+}$ (AA = tn, bn) are reported in Tables II and III. Low temperatures were required for the latter to give measurable half-lives under the pseudo-first-order conditions used. Nevertheless, reasonable activation parameters were obtained (Table III) from the two temperatures used, and 10^3 k_{Mg} extrapolated to 25 °C (2170 M^{-1} s^{-1}) is in satisfactory agreement with the value (2140 M^{-1} s^{-1}) calculated from the previously cited relationship [10] between k_H and k_{Hg} using 10^7 k_H = 637 s^{-1} at 25 °C.

Like the thermal aquation, the order of chloro lability for the Hg^{2+}-assisted aquation of *unsym-fac-cis*-$CoCl(dien)(AA)^{2+}$ is en < $(NH_3)_2$ < tn < bn. Indeed, there is a linear relationship between log k_{Hg} and log k_H as already suggested [10]. The second order rate constant for the Hg^{2+}-assisted aquation of *unsym-fac-cis*-$CoCl(dien)(bn)^{2+}$ at 25 °C is one of the largest recorded for a Co(III) chloropentaamine and is comparable with those reported for *cis*-$CoCl(tn)_2(monoamine)^{2+}$ with two independent six-membered rings [10, 15].

Acknowledgements

We thank the New Zealand Universities Grants Committee for providing funds to purchase instruments used in this research and the University of Canterbury for research grant 591695.

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