

Synthesis, Characterization and Aquation Kinetics of a New *trans* Diastereoisomer of Dichloro(*meso*-5,12-Dimethyl-1,4,8,11-tetraazacyclotetradecane)cobalt(III) Perchlorate†

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A new *trans* diastereoisomer of dichloro(*meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane)-cobalt(III) perchlorate has been prepared, and the electronic absorption and infrared spectral data studied. The assignments of the structure of the isomer have been accomplished by thorough stereochemical analysis combined with ^1H and ^{13}C NMR spectral data. Aquation kinetics have been studied at various temperatures and activation parameters determined. The results indicate a dissociative activation with retention of configuration and a distorted-square pyramidal activated complex.

The very high thermodynamic stability and extreme kinetic inertness of transition-metal complexes of tetraamine macrocyclic ligands are significant in inorganic stereochemistry, since they greatly enhance the number of potentially isolable diastereoisomers of these compounds.¹⁻⁵ Previously, Hay *et al.*⁶ described the preparation, characterization and aquation kinetics of a *cis*- and two *trans*-dichloro complexes of cobalt(III) with *meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane. Here we report the preparation, characterization and aquation kinetics of a new *trans* diastereoisomer of this complex, γ -*trans*-dichloro(*meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane)cobalt(III) perchlorate.

Experimental

Preparations.—*meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane (L). The compound L was prepared by the method of Hay and Piplani;⁷ 5 g (21.9 mmol) of it were dissolved in methanol (50 cm³) and excess of 12 mol dm⁻³ hydrochloric acid (5 cm³) added very slowly with magnetic stirring. The white precipitate of L·4HCl was collected, washed several times with diethyl ether, and dried *in vacuo*.

Sodium tris(carbonato)cobaltate(III).⁸ Cobalt(II) nitrate hexahydrate (14.6 g, 50.2 mmol) and 30% hydrogen peroxide (5 cm³) were dissolved in water (50 cm³). The solution was added dropwise with stirring to a cold slurry of sodium bicarbonate (21.0 g, 250 mmol) in water (50 cm³). The mixture was allowed to stand at 0 °C for 1 h with continuous stirring. The deep green product was filtered off, washed with cold water, then thoroughly washed with absolute ethanol and diethyl ether, and dried *in vacuo*.

trans-Dichloro(*meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane)cobalt(III) perchlorate isomers. The two diastereoisomeric α - and β -*trans*-[CoCl₂L]ClO₄ (L = *meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane) were prepared by the methods reported by Hay *et al.*⁶ γ -*trans*-Dichloro(*meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane)cobalt(III) perchlorate was prepared as follows. Freshly prepared sodium tris(carbonato)cobaltate(III) (1.0 g, 2.76 mmol) and L·4HCl (0.99 g, 2.65 mmol) were suspended in methanol-water (1 : 1,

v/v) (50 cm³). The mixture was heated on a steam bath until it turned violet. An aliquot of aqueous 12 mol dm⁻³ hydrochloric acid (10 cm³) was added dropwise to the violet filtrate. The slowness of addition of hydrochloric acid (over a period of 20 min) is crucial to the success of the synthesis of this diastereoisomer. The solution was heated further for 20 min, sodium perchlorate (2.0 g, 14.2 mmol) added, and the solution then cooled. Deep green crystals of γ -*trans*-dichloro(*meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane)cobalt(III) perchlorate obtained on cooling were filtered off, washed with ethanol, diethyl ether and dried (Found: C, 31.40; H, 6.15; N, 12.25. Calc. for C₁₂H₂₈Cl₃CoN₄O₄: C, 31.50; H, 6.20; N, 12.20%).

Instrumentation.—Electronic absorption spectra were measured on a Hitachi U-3410 spectrophotometer and the temperature of solutions controlled within ± 0.1 °C by circulating water from a constant-temperature bath. Proton and ^{13}C NMR spectra were recorded on a Bruker AM-400 NMR spectrometer, with shifts calibrated from internal tetramethylsilane. Infrared spectra were determined from Nujol mulls sandwiched between KRS-5 plates and from KBr pellets using a JASCO FT/IR-300E spectrophotometer. Kinetic measurements of the aquation reactions of γ -*trans*-[CoCl₂L]⁺ were carried out using 0.10 mol dm⁻³ HNO₃ as solvent. The reactions were monitored at 317 nm, and excellent first-order plots were obtained in all cases.

Results and Discussion

γ -*trans*-[CoCl₂L]ClO₄ is green and has an electronic spectrum typical of a *trans*-CoCl₂N₄⁺ chromophore,⁹ which is significantly different from those of the α - and β -*trans* isomers (Table 1). As shown in Fig. 1, the IR spectrum of γ -*trans*-[CoCl₂L]ClO₄ is significantly different from those of the α - and β -*trans* isomers reported by Hay *et al.*,⁶ the γ -*trans* isomer having a $\nu(\text{NH})$ band at 3222 cm⁻¹, which is shifted to higher frequency relative to those of the other two isomers (Table 2). The ^1H NMR spectra of the α - and β -*trans*-[CoCl₂L]ClO₄ were reported by Hay *et al.*,⁶ the ^1H and ^{13}C NMR spectra and the distortionless enhancement by polarization transfer (DEPT) spectra of α - and γ -*trans*-[CoCl₂L]ClO₄ obtained in this work are deposited as supplementary material (SUP 57032). Note that the proton NMR spectrum of α -*trans*-[CoCl₂L]ClO₄ obtained in this work is slightly different from that reported previously (Table 3). The data for γ -*trans*-[CoCl₂L]ClO₄ given

† Supplementary data available (No. SUP 57032, 7 pp.): Proton, ^{13}C and DEPT NMR spectra of α - and γ -*trans*-[CoCl₂L]ClO₄. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Electronic absorption spectral data for the isomers of *trans*-[CoCl₂L]ClO₄ in acetonitrile solution

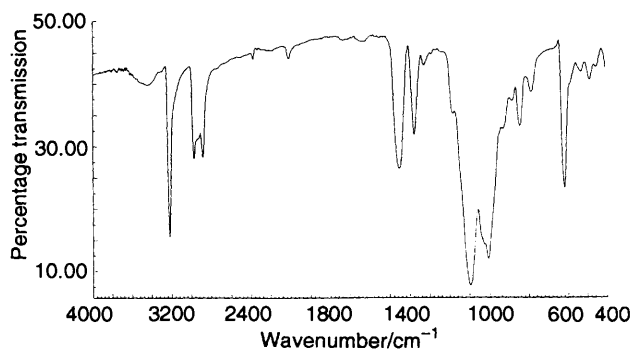
Isomer	$\lambda_{\max}^a/\text{nm}$	$\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$
γ - <i>trans</i> -[CoCl ₂ L]ClO ₄	629	46
	446 (sh)	38
	376 (sh)	81
	310	1964
α - <i>trans</i> -[CoCl ₂ L]ClO ₄ ^b	625	34
	455 (sh)	45
	390 (sh)	181
β - <i>trans</i> -[CoCl ₂ L]ClO ₄ ^b	318	1975
	625	28
	460 (sh)	29
	390	61
	317	1100

^a sh = shoulder. ^b Data from ref. 6.**Table 2** Infrared spectral data for the *trans*-[CoCl₂L]ClO₄ isomers

Isomer	$\tilde{\nu}(\text{NH})/\text{cm}^{-1}$
γ - <i>trans</i> -[CoCl ₂ L]ClO ₄	3222
α - <i>trans</i> -[CoCl ₂ L]ClO ₄ ^a	3195
β - <i>trans</i> -[CoCl ₂ L]ClO ₄ ^a	3190

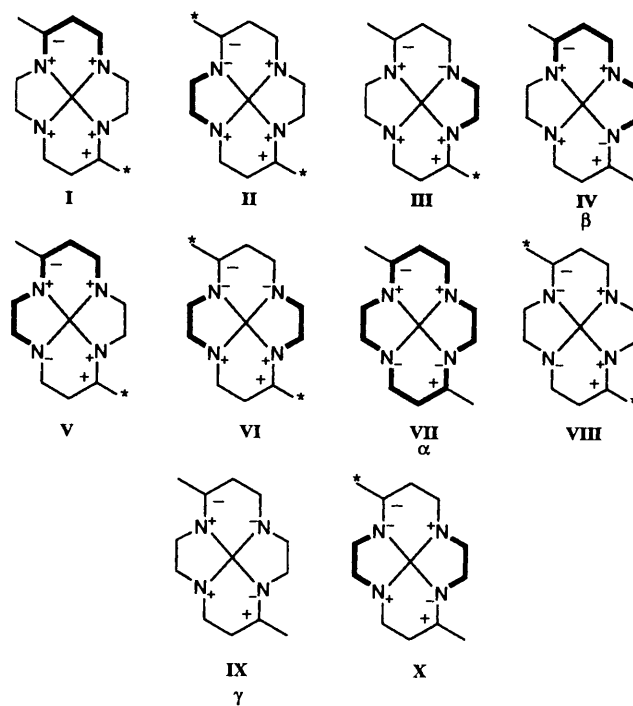
^a Data from ref. 6.**Table 3** Proton and ¹³C NMR spectral data (δ , J in Hz) of the α -, β - and γ -*trans*-[CoCl₂L]ClO₄ isomers in (CD₃)₂SO solution

Isomer	¹ H		¹³ C
	CH ₃	NH	
γ - <i>trans</i> -[CoCl ₂ L]ClO ₄ ^a	1.31 (d, $J = 6.3$)	6.36, 5.77	18.1, 32.3, 44.9, 49.2, 50.4, 52.0
α - <i>trans</i> -[CoCl ₂ L]ClO ₄ ^a	1.33 (d, $J = 6.2$)	6.63, 5.53	18.2, 35.9, 48.7, 50.2, 52.7, 53.9
α - <i>trans</i> -[CoCl ₂ L]ClO ₄ ^b	1.41 (d, $J = 7.3$)	6.62, 5.52	
β - <i>trans</i> -[CoCl ₂ L]ClO ₄ ^b	1.40 (d, $J = 7.3$)	6.63, 5.52	

^a This work. ^b Data from ref. 6.**Fig. 1** The IR spectrum of γ -*trans*-[CoCl₂L]ClO₄ (KBr disc)

in Table 3 indicate that this isomer has two equatorial methyl groups and an inversion centre.

There are four asymmetric nitrogens in [CoCl₂L]ClO₄. The presence of these asymmetric centres affords the possibility of ten diastereoisomers, I–X in Fig. 2. Four of the isomers (VI–IX) are centrosymmetric and only two of these (VII and IX) have two equatorial methyl groups. Isomer VII is the structure assigned to the α -*trans*-[CoCl₂L]⁺ by Hay *et al.*,⁶ therefore, the only possible structure for the γ -*trans*-[CoCl₂L]⁺ isomer, which is centrosymmetric and has two equatorial methyl

**Fig. 2** Configurations of the *trans*-[CoCl₂L]⁺ isomers. A plus sign at an asymmetric centre indicates that the hydrogen atom is above the plane of the macrocycle, and a minus sign that it is below the plane. *gauche* Conformations of the five-membered chelate rings and chair conformations of the six-membered chelate rings are indicated by thicker lines. The axial methyl groups are indicated with asterisks**Table 4** Configurations of the stereoisomers of *trans*-[CoCl₂L]⁺

Isomer	Configurations of the six asymmetric centres					
	N ¹	N ⁴	C ⁵	N ⁸	N ¹¹	C ¹²
γ - <i>trans</i> -[CoCl ₂ L] ⁺	IX	<i>RS</i>	<i>RS</i>	<i>SR</i>	<i>SR</i>	<i>SR</i>
α - <i>trans</i> -[CoCl ₂ L] ⁺	VII	<i>SR</i>	<i>RS</i>	<i>SR</i>	<i>RS</i>	<i>SR</i>
β - <i>trans</i> -[CoCl ₂ L] ⁺	IV	<i>RS</i>	<i>RS</i>	<i>SR</i>	<i>RS</i>	<i>SR</i>

Table 5 Rate constants at various temperatures (± 0.1 °C) and activation parameters for the aquation of γ -*trans*-[CoCl₂L]ClO₄ in 0.10 mol dm⁻³ HNO₃

$T/^\circ\text{C}$	$10^4 k_{\text{aq}}/\text{s}^{-1}$
15.0	1.61
20.0	3.37
25.0	5.72
30.0	9.44
35.0	15.2
40.0	24.6
45.0	38.4
50.0	55.5
$\Delta H^\ddagger = 74.7 \pm 1.8 \text{ kJ mol}^{-1}$	
$\Delta S^\ddagger_{298} = -57.3 \pm 5.9 \text{ J K}^{-1} \text{ mol}^{-1}$	

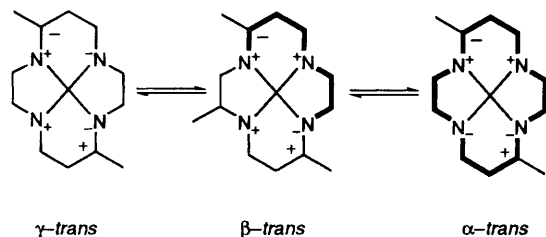
groups, is structure IX. The configurations of the chiral centres of these stereoisomers are given in Table 4.

It is interesting that the three isomers with two equatorial methyl groups, IV, VII and IX, are the structures assigned to the *trans*- β -, α - and γ -diastereoisomers, respectively.⁶ A scheme for the isomerization reactions of these three diastereoisomers is shown in Fig. 3. All the other diastereoisomers of *trans*-[CoCl₂L]⁺ containing one or two axial methyl groups are relatively unstable.

The structure of γ -*trans*-[CoCl₂L]⁺ IX indicates that the two co-ordinated chlorides in this complex are kinetically

Table 6 Rate constants and activation parameters for the aquation of the isomers of $\text{trans}[\text{CoCl}_2\text{L}]^+$ at $25.0 \pm 0.1^\circ\text{C}$ and $I = 0.10 \text{ mol dm}^{-3}$

Isomer	$k_{\text{aq}}/\text{s}^{-1}$	Relative rate	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{JK}^{-1} \text{mol}^{-1}$
$\gamma\text{-trans}[\text{CoCl}_2\text{L}]^+$	5.72×10^{-4}	10.4	74.7 ± 1.8	-57.3 ± 5.9
$\alpha\text{-trans}[\text{CoCl}_2\text{L}]^+{}^a$	2.4×10^{-4}	4.4	69 ± 4	-84 ± 12
$\beta\text{-trans}[\text{CoCl}_2\text{L}]^+{}^a$	0.55×10^{-4}	1.0	76 ± 4	-72 ± 13

^a Data from ref. 6.**Fig. 3** Reaction scheme for the configurational isomerizations of the $\text{trans}[\text{CoCl}_2\text{L}]^+$ isomers; key as in Fig. 2

equivalent. The rate constants and activation parameters for the aquation of this complex ion are given in Table 5. The entropy of activation is $-57.3 \pm 5.9 \text{ J K}^{-1} \text{ mol}^{-1}$, the negative value indicating dissociative activation with retention of configuration.^{6,10} At 25.0°C this isomer is two times more reactive than the $\alpha\text{-trans}$ isomer and *ca.* eleven times more reactive than the $\beta\text{-trans}$ isomer (Table 6). The relatively high reactivity of the $\gamma\text{-trans}$ isomer is mainly due to the entropy factor; as shown in Table 6, the ΔS^\ddagger_{298} values for the aquation reactions of $\alpha\text{-}$ and $\beta\text{-trans}[\text{CoCl}_2\text{L}]^+$ reported by Hay *et al.*⁶ are substantially more negative than that of $\gamma\text{-trans}[\text{CoCl}_2\text{L}]^+$.

It is interesting that $\beta\text{-trans}[\text{CoCl}_2\text{L}]^+$ has a fold line and can readily form a folded *cis* complex. However, at 25.0°C $\beta\text{-trans}[\text{CoCl}_2\text{L}]^+$ is four and *ca.* eleven times less reactive to aquation than the $\alpha\text{-trans}$ and $\gamma\text{-trans}$ isomers, respectively, which cannot fold. If the structure of the activated complex for the aquation reaction were a trigonal bipyramid, a large degree of folding of the macrocycle would be required to reach the transition state, and the rates for the reactions for the $\alpha\text{-}$ and $\gamma\text{-}$

trans complexes, which cannot fold, would be much slower than that of the $\beta\text{-trans}$ isomer. Therefore, the activated complex is probably not a folded trigonal bipyramid, but a distorted square pyramid.¹¹⁻¹³

Acknowledgements

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