

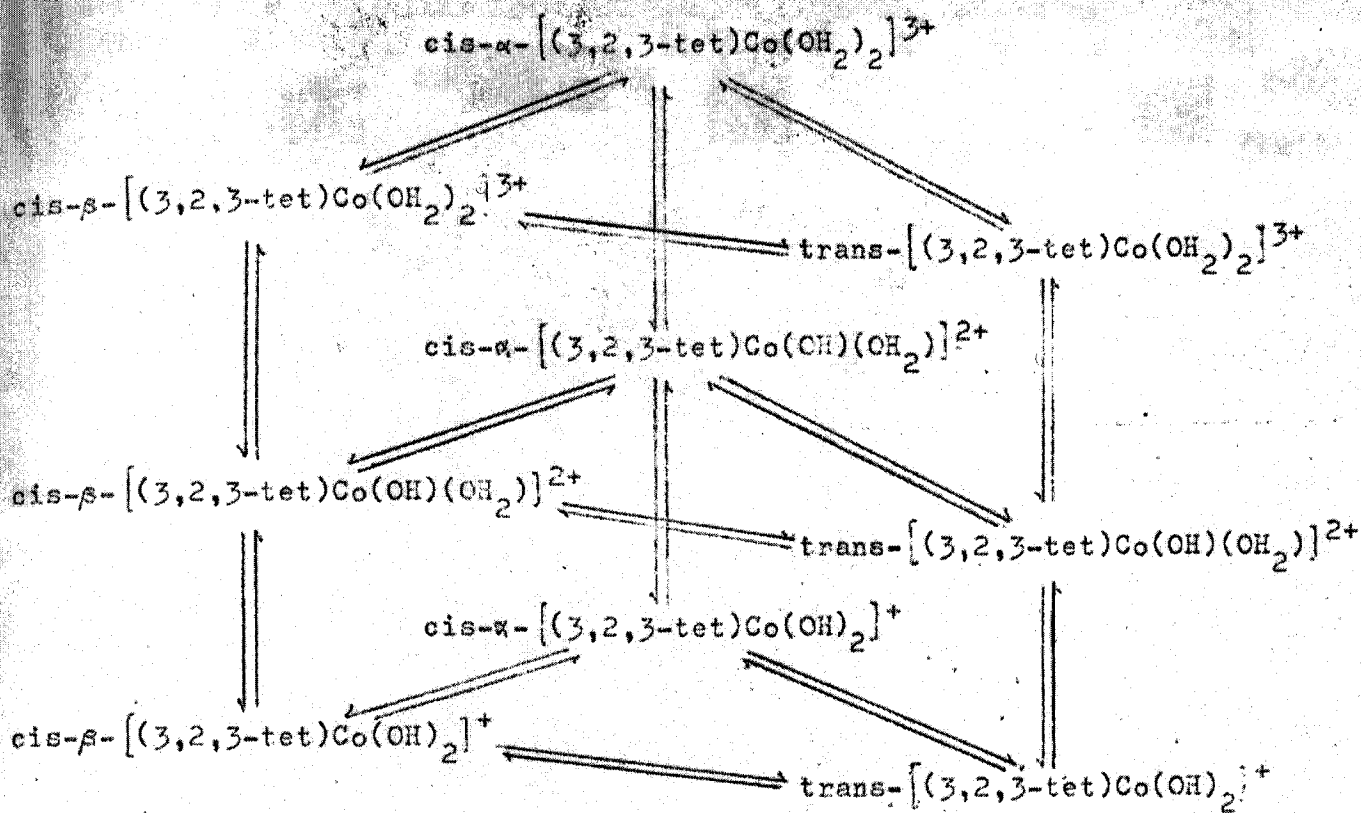


where $\text{N}_4 = 2,3,2\text{-tet}$ or $3,2,3\text{-tet}$. The rate constants at 25.15°C and the corresponding Eyring-Polanyi activation parameters are:

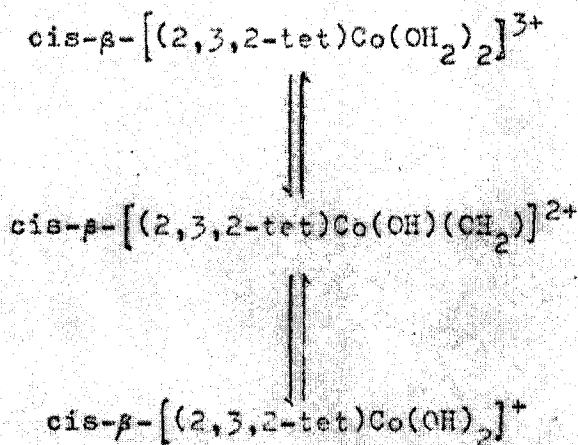
$\text{cis-}\beta\text{-}[(2,3,2\text{-tet})\text{CoCO}_3]^+$	
Water - catalysed Pathway	Hydronium-ion-catalysed Pathway
k at $25.15^\circ\text{C} = 1.03 \times 10^{-4} \text{s}^{-1}$	k at $25.15^\circ\text{C} = 1.66 \times 10^{-1} \text{M}^{-1} \text{s}^{-1}$
$\Delta H^\ddagger = 94.62 \pm 2.23 \text{kJmol}^{-1}$	$\Delta H^\ddagger = 36.59 \pm 0.02 \text{kJmol}^{-1}$
$\Delta S^\ddagger = -3.94 \pm 1.50 \text{JK}^{-1} \text{mol}^{-1}$	$\Delta S^\ddagger = -137.10 \pm 1.48 \text{JK}^{-1} \text{mol}^{-1}$

$\text{cis-}\beta\text{-}[(3,2,3\text{-tet})\text{CoCO}_3]^+$	
Water - catalysed Pathway	Hydronium-ion-catalysed Pathway
k at $25.15^\circ\text{C} = 3.87 \times 10^{-5} \text{s}^{-1}$	k at $25.15^\circ\text{C} = 2.67 \times 10^{-2} \text{M}^{-1} \text{s}^{-1}$
$\Delta H^\ddagger = 72.17 \pm 0.14 \text{kJmol}^{-1}$	$\Delta H^\ddagger = 71.97 \pm 0.19 \text{kJmol}^{-1}$
$\Delta S^\ddagger = -87.31 \pm 3.52 \text{JK}^{-1} \text{mol}^{-1}$	$\Delta S^\ddagger = -33.65 \pm 1.26 \text{JK}^{-1} \text{mol}^{-1}$

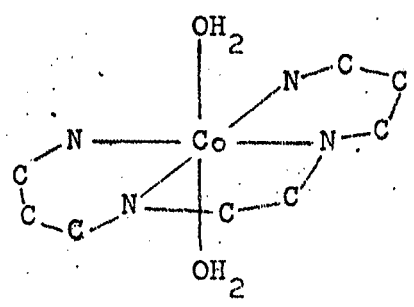
The $\text{cis-}\beta\text{-}[(3,2,3\text{-tet})\text{Co}(\text{OH}_2)_2]^{3+}$ product of hydrolysis further undergoes isomerisation to the $\text{trans-}[(3,2,3\text{-tet})\text{Co}(\text{OH}_2)_2]^{3+}$ form and, quite possibly, $\text{cis-}\alpha\text{-}[(3,2,3\text{-tet})\text{Co}(\text{OH}_2)_2]^{3+}$, and exists in dynamic equilibrium with these latter. The isomerisations are accompanied by various proton transfer equilibria involving diaqua, hydroxo aqua and dihydroxo species giving an overall complex equilibrium system:



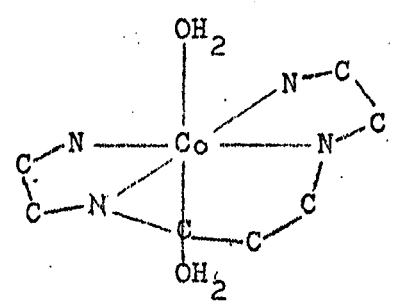
The $\text{cis-}\beta\text{-}[(2,3,2\text{-tet})\text{Co}(\text{OH}_2)_2]^{3+}$ product of hydrolysis does not isomerise but undergoes acid dissociation of the type:



This difference is explained in terms of the greater thermodynamic stability, arising from steric factors, of the trans-[(3,2,3-tet)Co(OH₂)₂]³⁺ ion compared with the trans-[(2,3,2-tet)Co(OH₂)₂]³⁺ ion (or of that of the cis-β-[(2,3,2-tet)Co(OH₂)₂]³⁺ ion compared with the cis-β-[(3,2,3-tet)Co(OH₂)₂]³⁺ ion); i.e. the cationic cis-β-[(3,2,3-tet)Co(OH₂)₂]³⁺ species undergoes further isomerisation to trans-[(3,2,3-tet)Co(OH₂)₂]³⁺ because



is
a
stabler
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This has been rationalised in terms of the greater length and flexibility of the 3,2,3-tet ligand as compared with the 2,3,2-tet ligand. The greater length and flexibility of the former ligand has also been used to account for the thermodynamic stability and formation during isomerisation of some amount of cis-α-[(3,2,3-tet)Co(OH₂)₂]³⁺, cis-α-[(3,2,3-tet)Co(OH)(OH₂)]²⁺ and cis-α-[(3,2,3-tet)Co(OH)₂]⁺ species.