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Base Hydrolysis and Structure of an Isomer of Chloro-4-(2-aminoethyl)-7-methyl-1,4,7,10-tetraazadecanecobalt(III) Perchlorate

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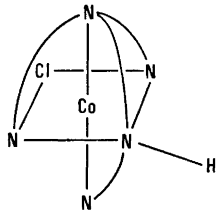
The structures and hydrolysis rate constants of isomers of the chloro-4-(2-aminoethyl)-1,4,7,10-tetraazadecanecobalt(III) ion and a 7-methyl derivative are analysed in relation to the base hydrolysis mechanism.

In a previous article [1] on the mechanism of base hydrolysis of the *sym* $[Co(trenen)Cl]^{2+}$ ion (trenen = 4-(2-aminoethyl)-1,4,7,10-tetraazadecane) it



was asserted that the reactant was that species which was deprotonated at the nitrogen *trans* to the chloride ion. This was primarily because the proton at this site exchanged faster ($\sim 10^5\times$) than any of the remaining protons in the molecule and because base hydrolysis of the chloride ion was faster than that for $[(NH_3)_5CoCl]^{2+}$ and correlated with the difference in acidity for the most acidic *trans* protons. Basolo [2] subsequently suggested that if *sym*-$[Co(trenen)Cl]^{2+}$ was *N*-methylated at the position *trans* to the chloride ion,

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the resulting complex should hydrolyse relatively slowly. Schwarzenbach and Walser [3] had prepared the appropriate ligand and a chloro-cobalt(III) ion, $[Co(Metrenen)Cl]^{2+}$, containing it. This communication presents the base hydrolysis rate constant, the proton exchange rate constant and a preliminary report of the crystal structure of this isolated complex.

The PMR spectrum, visible spectrum, and circular dichroism all indicated that the isomer of $[Co(Metrenen)Cl]^{2+}$ [3] correlated with the corresponding data obtained in the $[Co(trenen)Cl]^{2+}$ study. However, the base hydrolysis rate constant was only little less than ($\sim 1/17$) that for the latter complex (Table 1). Clearly these results appear to be in conflict with the original

Table 1. Rate constants for deuteration of $[Co(Metrenen)Cl](ClO_4)_2$, *sym*-$[Co(trenen)Cl]^{2+}$ [1] and $[Co(trenen)N_3]^{2+}$,[1] and for base hydrolysis of $[CoMetrenen)Cl](ClO_4)_2$.

Deuteration ($\mu = 2$, KCl, $T = 34°C$, [Complex] = 0.68 M, $k_{D_2O} = 3.8 \times 10^{-15}$).

pD	k, sec^{-1}	$[Co(Metrenen)Cl]^{2+}$ k_{OD^-}, $M^{-1}\,sec^{-1}$	$[Co(trenen)Cl]^{2+}$ k_{OD^-}, $M^{-1}\,sec^{-1}$	$[Co(trenen)N_3]^{2+}$ k_{OD^-}, $M^{-1}\,sec^{-1}$
			5×10^9 (1)	1.3×10^9 (1) [a]
4.50	1.0×10^{-3}	2.3×10^7 (1)	3×10^5 (1)	
4.50			1×10^5 (1)	3.4×10^6 (2)
	1.7×10^{-4}	3.6×10^9 (1)		7.6×10^6 (2) [b]
5.15	1.5×10^{-3}	7.6×10^5 (1)	$< 10^5$ (4)	7.3×10^5 (2)
5.15	1.4×10^{-4}	7.0×10^5 (3)		

Numbers in parentheses are the numbers of protons exchanged.

[a] Lowest field protons, NH.
[b] Low field protons, $-NH_2$.

Base hydrolysis of $[Co(Metrenen)Cl](ClO_4)_2$ ($\mu = 1.0$ M, $NaClO_4$, $T = 25°C$, $K_w = 13.77$, [Complex] = 10^{-3} M).

pH	k, sec^{-1}	k_{OH^-}, $M^{-1}\,sec^{-1}$	k_{OH^-}, $M^{-1}\,sec^{-1}$
8.55	1.9×10^{-5}	31	518 [a]
9.05	5.3×10^{-4}	27	
10.21	7.7×10^{-3}	28	

[a] Second order rate constant for $[Co(trenen)Cl]^{2+}$ corrected for $K_w = 13.77$ instead of $K_w = 14$.[1]

proposal [1] for the mechanism of hydrolysis of *sym*-$[Co(trenen)Cl]^{2+}$. The failure to observe a larger rate difference can be partly accounted for by the relative acidities of the *N*-protons as gauged by the proton exchange rate constants given in Table 1, in which comparisons are made with *sym*-$[Co(trenen)Cl]^{2+}$ and *sym*-$[Co(trenen)N_3]^{2+}$ ions. But the fundamental origin of these differences in proton acidity and the similarity in base hydrolysis

rate constant must be sought elsewhere. It resides in the structure of the isomer of [Co(Metrenen)Cl]$^{2+}$ upon which these measurements were made (Fig. 1). It is not that which was originally supposed, *i.e.* analogous to the line diagram.

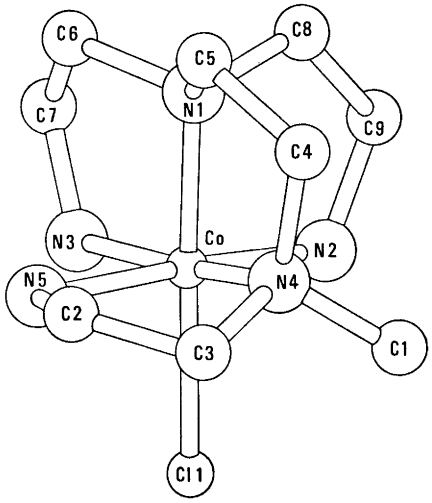

Fig. 1.

The structure was determined in a single crystal X-ray diffraction analysis of the salt $(+)_{440}$[Co(Metrenen)Cl](ClO$_4$)$_2$. The crystals are orthorhombic, space group $P2_12_12_1$, with unit cell dimensions $a = 13.330(11)$ Å, $b = 15.371(17)$ Å, $c = 9.237(8)$ Å. $D_m = 1.77 \pm 0.03$ g cm^{-3} and, with $Z = 4$, $D_c = 1.742 \pm 0.008$ g cm^{-3}. All independent intensities with sin θ/λ less than 0.704 were measured using a Picker FACS-1 single crystal diffractometer operating in its 2θ-scan mode, each scan being over 1.9 degrees at a rate of 1 degree per min. Background counts were made for 20 sec at each end of the scan range. The incident radiation was graphite-monochromated Mo$K\alpha$. 1303 of the measured reflections had net intensities (peak minus time-corrected background counts) greater than or equal to three times their corresponding estimated standard deviations (calculated from counting statistics only), and these were used to solve and refine the crystal structure by Patterson, heavy-atom Fourier and full-matrix least squares methods. The R factor is at present 0.069 and refinement is continuing.[4]

The apparent anomaly which existed between the base hydrolysis rate constants for the *sym*-[Co(trenen)Cl]$^{2+}$ ion and this [Co(Metrenen)Cl]$^{2+}$ ion has vanished with the disclosure of the basic structural difference between these complexes. However, it is still rather surprising that one N-proton is so acidic and that the base hydrolysis rate constant is so high for the [Co(Metrenen)Cl]$^{2+}$ ion relative to the corresponding constants for the [Co(NH$_3$)$_5$Cl]$^{2+}$ ion. The origin of both these effects may lie in the considerable

distortion from regular octahedral symmetry of the $[Co(Metrenen)Cl]^{2+}$ ion revealed by the crystal structure analysis (Table 2) and predicted from a strain energy minimization study.[5] Recently large steric acceleration effects

Table 2. Current values of the bond lengths (in Ångström) and bond angles (in degrees) in the direct environment of the Co(III) ion. The estimated standard deviations (distances $\times 10^3$, angles $\times 10$) are given in parentheses.

Bond lengths			
Co – Cl1	2.248(5)	Co – N3	1.945(16)
Co – N1	1.923(11)	Co – N4	1.989(16)
Co – N2	1.958(16)	Co – N5	2.027(16)
Bond angles			
Cl1 – Co – N2	88.2(6)	N1 – Co – N4	87.4(6)
Cl1 – Co – N3	91.5(5)	N1 – Co – N5	97.2(6)
Cl1 – Co – N4	94.5(5)	N2 – Co – N3	90.8(7)
Cl1 – Co – N5	87.8(5)	N2 – Co – N4	96.5(7)
N1 – Co – N2	86.6(7)	N3 – Co – N5	86.8(6)
N1 – Co – N3	87.2(6)	N4 – Co – N5	86.4(6)

were observed for base hydrolysis of chloropentakis(alkylamine)cobalt(III) ions of the form $[CoA_5Cl]^{2+}$ ($A = CH_3NH_2$, n-$C_3H_7NH_2$, i-$C_4H_9NH_2$) [6] and it was asserted that non-bonded interactions strained the molecule in the ground state. Angular deformations arising from strain of this kind in the $[Co(CH_3NH_2)_2Cl]^{2+}$ ion have since been observed in crystals.[7]

One other $[Co(Metrenen)Cl]^{2+}$ isomer has recently been isolated and evidence for the existence of another has also been obtained. The results of a complete study of all these isomers will be presented later.

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