71. Complete Racemization in the Base Hydrolysis of Optically Active mer-{Chloro(diethylene triamine)(1,3-diaminopropan-2-ol-*N*, *N'*) cobalt(III)}tetrachlorozincate

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(7.III.80)

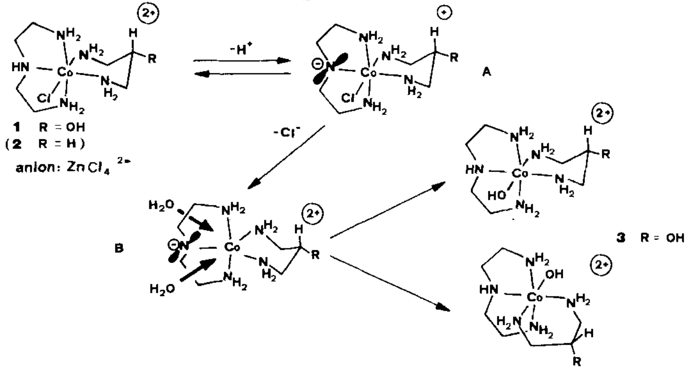
Summary

The base hydrolysis of the optically active title compound proceeds with full racemization whilst the meridional arrangement of the diethylenetriamine ligand is fully retained. The optically active hydroxo complex prepared independently with retention of configuration racemizes $\gtrsim 10^4$ times slower. This unique result is discussed in terms of the classical π-stabilization hypothesis for the base hydrolysis mechanism.

Introduction. The base hydrolysis of Co(III)-amine complexes is a prototype of an induced substitution process where deprotonation of a coordinated (amine) ligand causes some 10^5–10^8 fold acceleration [1]. It is the only reaction of Co(III)-pentaamines which may proceed with configurational rearrangement [1] [2]. However, the stereochemistry of these rearrangements is difficult to rationalize unambiguously in terms of the configuration of the supposed intermediate of reduced coordination number [3]. In this preliminary report we describe the hitherto unknown case of full racemization in the base hydrolysis of an optically active Co(III)-pentaamine complexe.

Results. Dioxygen oxidation of a stoichiometric mixture of diethylene triamine (=dien), 1,3-diaminopropan-2-ol (=dapo) and cobalt chloride hexahydrate at 0°

Scheme



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afforded a mixture of compounds from which the desired pentaamine diastereoisomer **1** *(Scheme)* was obtained by fractional crystallization. Its VIS. spectrum (λ, nm (ε, l mol^{-1} cm^{-1}): 484 (84) [max.]; 422 (32) [min.]; 372 (78) [max.]; 334 (41) [min.]) closely resembles that of **2** [4] and is distinctly different from that of diastereoisomers with facially coordinated dien or *N,O*-bonded dapo [5]. The ^{13}C-NMR. spectrum (δ, ppm: 64.10 (H–*C*–OH); 51.06, 51.00, 48.35 and 48.22 ($(H_2NCH_2CH_2)_2NH$); 43.73 and 43.42 ($H_2NCH_2CHOHCH_2NH_2$)) is consistent with meridionally coordinated dien in **1**.

The dien C-atoms in several *mer-cis* $[Co(dien)(amine)_2Cl]^{2+}$ species are pairwise isochronous (δ, ppm: 50.97–51.08, 48.00–48.20) [6] and the small splitting of the two corresponding resonances in **1** is attributed to the presence of the OH-substituent in the six-membered chelate ring which influences its conformational equilibrium position. No such splitting of the dien C-signals is expected for the *meso*-facial diastereoisomer of **1**. Finally, this assignment is supported by the successful resolution of **1** by crystallization of the arsenyl-L-tartrate salt. The optically active tetrachlorozincate salt recovered from this was characterized by its CD. spectrum *(Fig.)*.

The following reactions were carried out on **1** in water and at ambient temperature:

1) Base hydrolysis of resolved **1** *(Scheme)* was effected in a triethanolamine buffer (0.8 M, pH = 7.88). The CD. spectrum of the reaction mixture was recorded

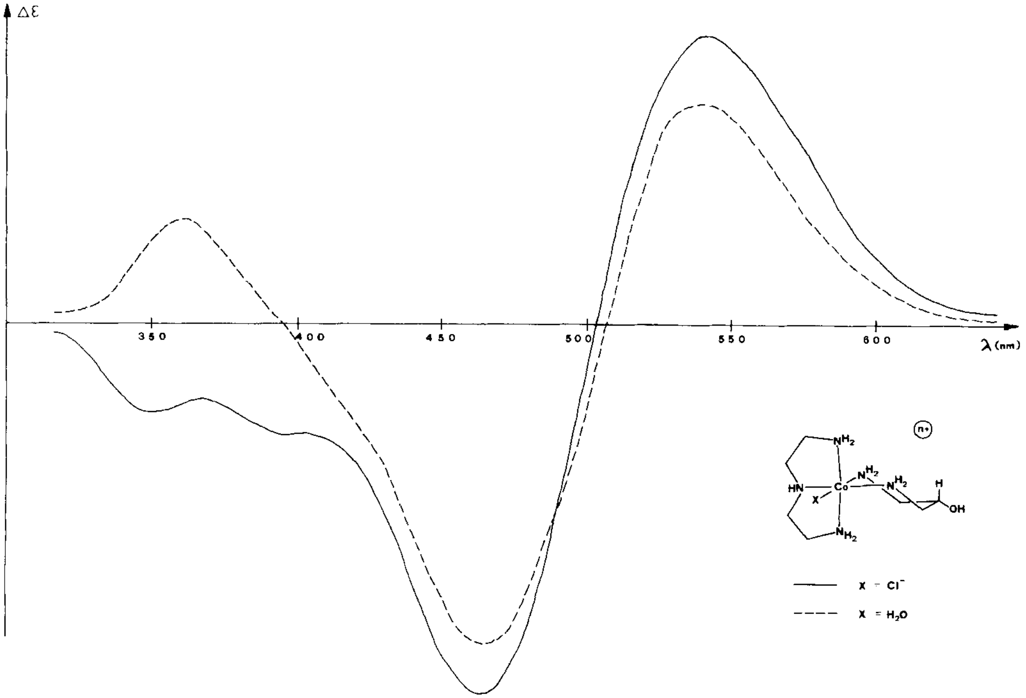

Figure. *CD. spectra of* **1** *and its corresponding aqua complex.* The scale of $\Delta\varepsilon$ (l · mol^{-1} · cm^{-1}) is arbitrary since the optical purity of the compounds is not known.

after *ca.* 60 s and corresponded to the base-line within the error, indicating complete racemization of the reaction mixture *(Fig.)*;

2) A solution of resolved **1** was treated for several days with a small excess of $AgClO_4$-solution to remove all chloride, including that coordinated to cobalt. After removing the precipitate of AgCl, the resulting aqua-ion was converted to the hydroxo complex **3** by adding the same buffer as used in the first experiment. The CD. spectrum of this mixture showed the presence of optically active hydroxo complex of the same absolute configuration as **1**. The spectrum remained unchanged for at least 3 h, ruling out racemization of **3** on the time scale of the base hydrolysis reaction;

3) The base hydrolysis reaction was carried out on racemic **1** in D_2O using a $D_2PO_4^-/DPO_4^{2-}$ buffer at pD=7.5. The ^{13}C-NMR. spectrum showed the exclusive presence of **3** (δ, ppm: 64.38 (H$-C-$OH); 49.61 (accidental isochrony of two lines) 48.13 and 48.04 [$(H_2NCH_2CH_2)_2NH$]; 44.13 and 43.36 [$H_2NCH_2CH(OH)CH_2NH_2$]).

Discussion. The spectroscopic similarities between **1** and **2** (which are the base of our structural assignment) extend to their reactivity in alcaline solution. Compounds **2** and **1** are the most reactive species in both sets of diastereoisomers. The calculated half-life of **2** is *ca.* 2.5 s at pH 7.91, 25° and μ=0.1 [4]; the diastereoisomers of **2** with facially coordinated dien react at least 3600×slower [4]. The influence of the dapo OH group on the rate may be estimated at a factor of 2–3 [7]. Optically active **3** has a racemization half-life of $>3\times10^4$ s. The observed racemization process cannot therefore be subsequent to formation of the hydroxo complex. A more involved mechanistic possibility, viz. fast preferential formation of an optically active facial hydroxo complex with subsequent rearrangement to (±)-**3** is ruled out by the observation that this facial isomer does not appreciably rearrange under the conditions of our experiments [5]. Since the (±)- and *meso*-facial isomers of **2** are quite similar in reactivity [4] we anticipate that the racemic meridional complex **3** does not arise from rearrangement of the *meso*-facial isomer.

The unprecedented result of complete racemization during base hydrolysis, along with the absence of rearrangement of the meridional configuration may be interpreted in terms of the classical π-stabilization hypothesis [8]: The reactant will, after deprotonation of a coordinated amine function (probably the secondary amine proton in **1**) (A, *Fig.*) undergo accelerated loss of the leaving group because of the possibility of an intermediate of reduced coordination number of trigonal-bipyramidal configuration which has the proper symmetry for $\pi\,[2p(R_2N^-)\rightarrow 3\,d_{x^2-y^2}(Co)]$ overlap. The particular structure of an intermediate in which this is possible is characterized by a symmetry plane coinciding with the nodal plane of the stabilizing nitrogen orbital. Attack of incoming nucleophiles on this symmetric intermediate will lead to complete racemization. (B, *Fig.*). So far, this experimental outcome has not to our knowledge been observed. Attempts made with different pentaamine systems at trapping the postulated intermediate of reduced coordination number recently gave evidence for some leaving group dependence in the scavenging of competing nucleophiles [9] which is inconsistent with an intermediate of any chemically significant lifetime and stability. Furthermore, an attempt at observing racemization at a coordinated secondary nitrogen centre which is deprotonated in base hydrolysis was negative [10]. In order to explain why among the known optically active Co(III) pentaamines only **1** racemizes completely, we point out that a relationship has been found between the rate of base hydrolysis in Co(III)-pentaamines and all structural features in a complex which facilitate the formation of a π-stabilized, five-coordinate intermediate [11].

Since **2** has the highest base hydrolysis rate constant known to date for a Co(III)-pentaamine, it is evident that suitable stereochemical tagging as in **1** would provide (for the time being) the best candidate for observing this particular result.

This work has been supported by the *Swiss National Science Foundation* (Project 2.817.-0.77). We are grateful to Professor *R. Tabacchi* and Mr. *S. Claude* for the ^{13}C-NMR. spectra.

Experimental Part

Physical measurements. VIS. spectra were recorded on a *Unicam* SP 1800 instrument at 25±0.2°. ^{13}C-NMR. spectra were measured on a *Bruker* WP-200 instrument in the FT-mode in D_2O with internal dioxane standard (=67.45 ppm) at 25°. A *JASCO* J-500 instrument served to measure the CD. spectra at 25°.

Materials. Purissimum or reagent grade commercial chemicals were used except for the organic ligands which were of purum grade. Sodium arsenyl L-tartrate was prepared from arsenic(III) oxide, sodium hydroxide and L-tartaric acid in water at 90°.

Chloro(diethylenetriamine)(1,3-diaminopropan-2-ol) cobalt(III)tetrachlorozincate. Cobalt chloride hexahydrate (24.3 g, 0.102 mol) in water (50 ml) was mixed with diethylenetriamine (10.5 g, 0.102 mol) and 1,3-diaminopropan-2-ol (9.2 g, 0.102 mol) in water (40 ml). Dioxygen was passed through the mixture for 1 h at 0°. Hydrochloric acid (10M, 90 ml) and zinc chloride (20 g) were then added. The mixture was allowed to stand overnight at 20°. After removal of a green crystalline species (2.6 g, presumably a μ-superoxo decaamine dicobalt complex), the solution deposited red pentaamine complexes within 24 h (5.5 g) which were recrystallized from water (100 ml, pH=3)/hydrochloric acid (10M, 30 ml)/zinc chloride (10 g) to give pure **2** (3.44 g, 9.95 mmol, 6.8%) which was filtered off, washed with ethanol and ether and dried (12 h, 10^{-3} Torr). From the mother liquors, further pentaamine species can be isolated [5].

$C_7H_{23}Cl_5CoN_5OZn$	Calc.	C 16.99	H 4.68	Cl 35.82	N 14.15%
(494.86)	Found	„ 17.54	„ 4.60	„ 36.00	„ 14.02%

Resolution of **1**. The racemic complex **1** (4.5 g, 9.2 mmol) was dissolved in a mixture of water (220 ml) and ethanol (550 ml) at 0°. Lithium chloride (27.5 g) and hydrochloric acid were then added, followed by sodium arsenyl L-tartrate (2.39 g, 0.49 mmol) in ethanol (15 ml). The solution was then left at −15° for *ca.* 12 h. The less soluble diastereoisomeric salt (1.6 g) was filtered off, suspended in ethanol (20 ml), dissolved in hydrochloric acid (0.2M, 100 ml) and precipiated as the tetrachlorozincate with hydrochloric acid (10M, 25 ml) and zinc chloride (12 g) with stirring (30 min, 0°). The crystallization was complete after 48 h at −15°. Yield: 0.91 g (1.8 mmol, 19.9%). Its VIS. spectrum was identical with that of the racemate.

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