UNIVERSITE DE NEUCHATEL
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SYNTHETIC STUDIES AND MECHANISTIC INVESTIGATIONS OF BASE – CATALYZED SUBSTITUTION ON SOME NEW COBALT (III) COMPLEXES

THESE

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Peter Comba

chimiste diplomé de l'Ecole Polytechnique Fédérale de Zurich
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Synthetic Studies and Mechanistic Investigations of Base-Catalyzed Substitution on Some New Co (III) Complexes

de Monsieur Peter Comba

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La Faculté des sciences de l'Université de Neuchâtel,
sur le rapport des membres du jury,

Messieurs W. Marty, R. Tabacchi et G. Geier
(Ecole Polytechnique Fédérale, Zurich)

autorise l'impression de la présente thèse.

Neuchâtel, le 22 juin 1981

Le doyen:

K. Bernauer

K. Bernauer

to my parents

and

to my wife Maria

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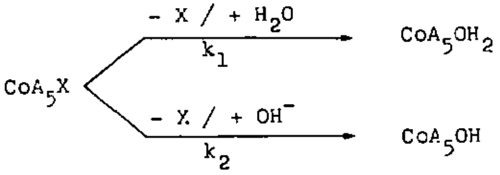
1. INTRODUCTION

The study of reaction mechanisms is pursued for different motives: by scientific curiosity which wants to look behind things, e.g. chemical transformation, or for didactic purposes, because solving mechanistic problems provides an excellent intellectual training. Moreover, the study of reaction mechanisms is from a synthetic chemist's point of view not a "l'art pour l'art" exercise since mechanistic knowledge will make it possible to select the best conditions for a desired chemical transformation rationally and with a good degree of exactitude. A few years ago, the mechanistic study of a chemical transformation still risked to be a formidable venture, a trial of patience hardly competitive with purely empirical search for "the best reaction conditions". This situation has started to change for the better: with the advent of an arsenal of highly sophisticated, accurate and rapid instrumentation for physical measurements, systematic mechanistic studies have become far more convenient to carry out.

The real benefit of systematic mechanistic study was in fact the observation that the enormous variety and complexity of chemical transformations can be reduced to a number of mechanistic prototypes. Early physical organic chemistry provides us with well known examples: e.g. the S_N1 / S_N2 classification of substitutions at tetrahedral carbon are based on observed rate laws and nucleophilicity scales have been established on the basis of rate measurements.

For inorganic reactions, mechanistic prototypes have been reckognized only much later than in carbon chemistry. The considerably greater complexity and variability of coordination centers is responsible for this lag in time.

This thesis is concerned with one of the first known mechanistic prototypes in the chemistry of octahedral coordination compounds: the base hydrolysis reaction. This reaction type has been discovered in and been widely studied with Co(III) amine complexes. In 1851, F.Claudet [1] noted the general substitutional lability of the then recently discovered Co(III) pentaammines in alkaline solution. Kinetic studies of these reactions which were typically undertaken some 80 - 100 years later have indeed shown a 10^6 - 10^{10} fold substitution rate acceleration in base, relative to neutral or acid solution [2-14,18]:



$$k_1 \ll k_2 \quad (1)$$

(charges omitted)

Analogous, though smaller accelerations are found in Cr(III), Ru(III), Os(III), Rh(III) and Ir(III) amine chemistry as well as in the chemistry of aqua complexes of many metals. In every case, the rate enhancement has been attributed to formation of a conjugate base of the complex by deprotonation of a coordinated ligand.

However, a satisfactory explanation how deprotonation of a coordinated ligand can increase the substitution lability of ligands is still lacking. This thesis is concerned with stereochemical experiments to test one of the early interpretations of this acceleration effect, viz. π- bonding between the deprotonated ligand and the metal centre in an intermediate arising after loss of the leaving group [19].

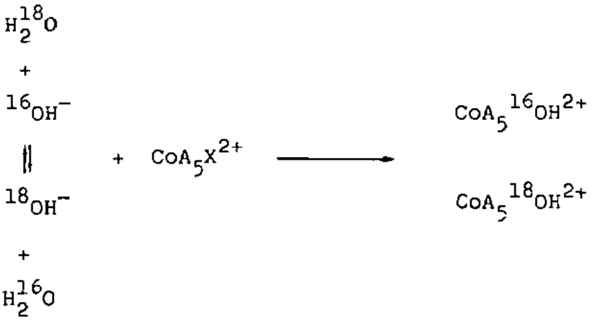
1.1. PROPOSED MECHANISMS FOR THE BASE HYDROLYSIS REACTION OF COBALT (III) PENTAAMMINE COMPLEXES

1.1.1. THE S_N2 MECHANISM

In this mechanism which was originally proposed by C.K. Ingold and coworkers [2-8] and developped further by M.L.Tobe [9] and S.C.Chan and coworkers [10], the OH^- ion displaces the leaving group in a bimolecular process (eq 2).

$$CoA_5X^{(3-n)} + OH^- \longrightarrow CoA_5OH^{3+} + X^{n-} \qquad (2)$$

S.C.Chan and coworkers [10] found that the reactivity of halogeno pentaamine Co(III) complexes with an alkaneamine ligand in base follows the same order as S_N2 substitution at saturated halogenoalkanes. Both kinetic results and comparison of activation energies, solvation energies and entropy changes were considered to support this proposal. However, the constant isotope fraction (^{18}O / ^{16}O) for base hydrolysis of Co(III) pentaamine complexes with the leaving groups Cl^-, Br^-, NO_3^- [11] (eq 3) is inconsistent with an S_N2



$$\begin{array}{c} H_2^{18}O \\ + \\ ^{16}OH^- \\ \Vert \\ ^{18}OH^- \\ + \\ H_2^{16}O \end{array} + CoA_5X^{2+} \longrightarrow \begin{array}{c} CoA_5{}^{16}OH^{2+} \\ \\ CoA_5{}^{18}OH^{2+} \end{array} \qquad (3)$$

mechanism. A constant competition ratio during base hydrolysis of Co(III) pentaamine complexes with different leaving groups but the same competition reagents such as anions X^- and H_2O (see table 2) are also inconsistent with a bimolecular S_N2 process. Measurements of activation volumes of base hydrolysis of halogeno pentaamine Co(III) complexes [13-15] give evidence for an essentially dissociative mechanism. An other important argument against an S_N2 mechanism comes from the observation that the rate of base hydrolysis increases when ammonia in halogenopentaammine Co(III) complexes is changed against more bulky monoalkylamines [16].

1.1.2. THE CONJUGATE BASE MECHANISM

A first version of these mechanisms was originally proposed by Garrick [18]: an intermediate formed by previous deprotonation of a coordinated amine function - the conjugate base - reacts with a water molecule (eq 4).

$$\begin{aligned} &\mathrm{Co(NH_3)_5X^{2+}} + \mathrm{OH^-} \overset{K}{\rightleftharpoons} \mathrm{Co(NH_3)_4NH_2X^{+}} + \mathrm{H_2O} \\ &\mathrm{Co(NH_3)_4NH_2X^{+}} + \mathrm{H_2O} \xrightarrow{k} \mathrm{Co(NH_3)_5OH^{2+}} + \mathrm{X^-} \end{aligned} \qquad (4)$$

The acceleration in base can be explained with this mechanism by the smaller charge in the conjugate base. This mechanism includes a bimolecular step, viz. the reaction of the conjugate base. This S_N2CB mechanism is inconsistent with the observed leaving group independent product distribution cited as evidence against Chan's S_N2 mechanism (cf. 1.1.1.). For associative mechanisms of any kind, the rate of product formation should be influenced by the nature and concentration of the entering nucleophile. Such influence was never observed. Basolo and Pearson [19] have further developped this model of a base hydrolysis mechanism. In their proposed mechanism the conjugate base looses the leaving group X^- in a rate determining step to form a coordinatively unsaturated intermediate state which adds a water molecule in a fast reaction (eq 5).

$$\begin{aligned} &Co(NH_3)_5X^{2+} + OH^- \overset{K_b}{\rightleftharpoons} Co(NH_3)_4NH_2X^+ + H_2O \\ &Co(NH_3)_4NH_2X^+ \xrightarrow{k} Co(NH_3)_4NH_2^{2+} \qquad (5) \\ &Co(NH_3)_4NH_2^{2+} + H_2O \xrightarrow{k'} Co(NH_3)_5OH^{2+} \end{aligned}$$

This mechanism fits the rate law (eq 6).

$$\text{rate} = \frac{k \cdot K_b\ [OH^-]}{1+K_b\,[OH^-]}\,[\text{complex}] \qquad [20] \qquad (6)$$

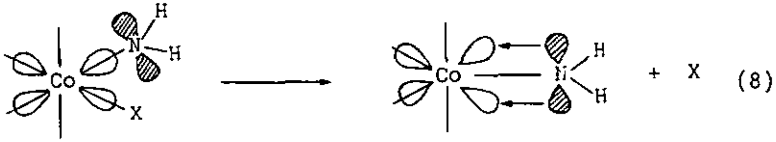
K_b for coordinated amines being smaller than 10^{-14} for most pentaamines, this reduces to the observed rate law in the usual concentration range for $[CH^-] \lesssim 1M$ (eq 7):

$$\text{rate} = k \cdot K_b\,[OH^-][\text{complex}] \qquad k \cdot K_b = k_{OH}$$

$$= k_{OH}\,[OH^-][\text{complex}] \qquad (7)$$

1.1.3. A π-STABILIZED COORDINATIVELY UNSATURATED INTERMEDIATE STATE

Basolo and Pearson [20] argue that the acceleration in alcaline aqueous solution cannot be attributed exclusively to the less positive charge of the conjugate base relative to the initial complex, in view of the results of calculations based on electrostatic theory [21] and comparisons of the rates of 2+ charged with 1+ charged complexes. An acceleration factor of less than 10^2 can be attributed to a charge effect, but the acceleration is usually greater than 10^6 [17]. There remains therefore a factor of at least 10^4. Basolo and Pearson explain this factor by $\pi\,(2p_N' \rightarrow 3d_{x^2-y^2})$ - bonding in the coordinatively unsaturated trigonal-bipyramidal intermediate (eq 8).

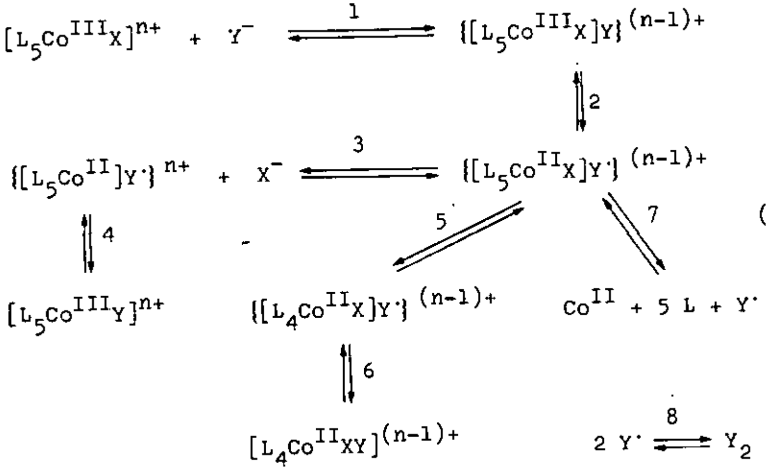


(8)

While this hypothesis is still presently widely accepted, it has never passed a more or less rigorous experimental test. We try therefore to design systems which are able to inform us whether a trigonal-bipyramidal intermediate state of chemically significant lifetime is involved in our reactions. This kind of information clearly does not prove specifically the π-bonding hypothesis since such an intermediate state could adopt a trigonal-bipyramidal configuration for other reasons. However, the observation of unambiguous stereochemical evidence for a trigonal-bipyramidal configuration of the required structure for π-bonding will satisfy a rather subtle and discriminating necessary condition for such bonding.

1.1.4. THE REDOX MECHANISM

Gillard [23] proposed another mechanism which also fits the observed rate law: $(k_1/k_{-1})k_2[OH^-][complex]$. This proposal involves an electron transfer process (eq 9):

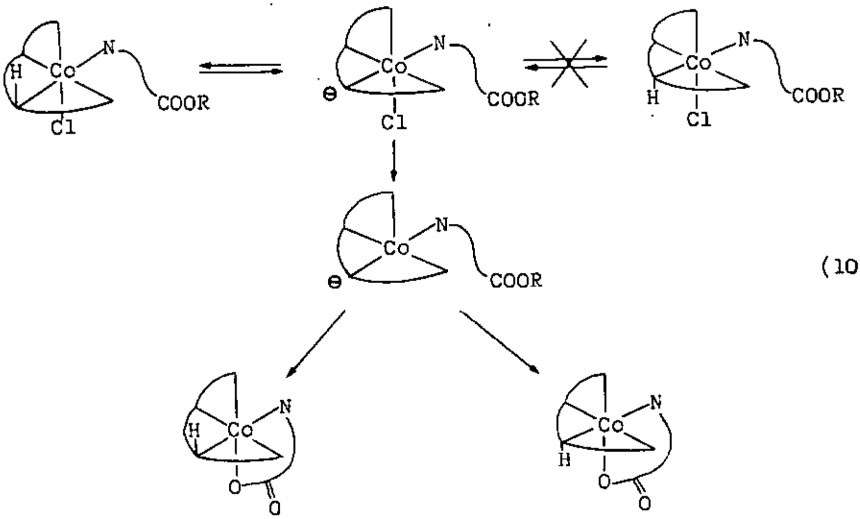


(9)

For base hydrolysis ($Y = OH^-$), the reduction of the ion pair in the preequilibrium (rate k_2) is the rate determining step. Gillard considers that the electron transfer is most likely to an excited Co(III) ion because excited states of Co(III) are better oxidising agents than the ground state [24]. Then the five coordinate Co(II) intermediate is oxidized and coordinates hydroxide in one step. Evidence for this mechanism came from comparison of redox potentials of Co(III) with other d^6 transition metals in comparison with their reactivity and from polarographic studies but a correct study of the electrochemical series shows that thermodynamically the proposed mechanism has no chance, since the free enthalpy difference $\Delta G°$ of the rate determining step is markedly positive ($E°(OH^- + e^- \rightarrow OH^-) = 1.4$ V; $E°(Co^{3+} + e^- \rightarrow Co^{2+}) = 1.8$ V (3f HNO_3); $\Delta E° = + 0.44$ V). The proposal of Gillard is also inconsistent with the observation that the rate of base hydrolysis increases with bulky amine groups which supports the idea that the loss of the leaving group must be the rate determining step [16] which is not the case in the redox mechanism. Furthermore, ^{15}N enriched ammonia should exchange rapidly with any Co(II) ammine species. $^{15}NH_3$ added to a base hydrolysis solution therefore should provide $^{15}NH_3$ - containing product which was not the case [25]. Last but not least, it would be difficult to explain full retention of configuration [26,27] in one case and full racemisation (this work) in another, similar case.

1.1.5. THE HIGH SPIN MECHANISM

Buckingham, Marty and Sargeson [28] explain the stereochemical results of the base hydrolysis of halogenopentaamine Co(III) complexes with glycine or glycine ester as a monodentate ligand by proposing a mechanism where rate determining chloride release leads to a coordinatively unsaturated intermediate state which has properties very different from ordinary Co (III) species (eq 10):



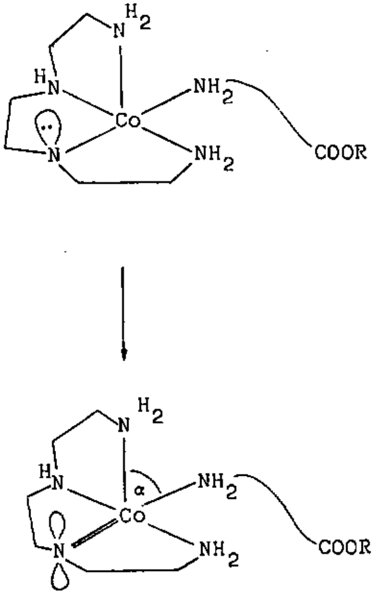
(10)

R = H, C_2H_5

tetradentate ligand = triethylenetetramine

Mutarotation at the secondary amine nitrogen centre at the junction of two coplanar five-membered chelate rings (eq 10) is observed during base hydrolysis. This mutarotation process can be excluded for the starting material and for the final products on the timescale of the experiment. It must therefore occur during the lifetime of an intermediate state arising after loss of the leaving group and which is consumed by capture of an entering ligand. Clearly nitrogen inversion can only occur if the NH proton is removed. The rates of NH deprotonation ($k_{-H} \approx 10^5 - 10^8$ $M^{-1}s^{-1}$) and reprotonation ($k_{+H} \approx 10^9 - 10^{10}$ s^{-1}) in Co(III) pentaamines and hexaamines are much faster than pyramidal inversion at coordinated amides $RR'\overset{\leftrightarrow}{N} - Co$ ($k_{inv} \approx 10^3 - 10^4$ s^{-1} in Co(III) hexaamines). From these data it was concluded that the mutarotation process had to be much faster than in hexaamines since it had to be complete within the much shorter lifetime of the coordinatively unsaturated intermediate state ($t_{1/2} \approx 10^{-8} - 10^{-10}$ s). In this case, the intermediate has to have properties different from a hexaamine such that pyramidal inversion at the nitrogen is accelerated. The authors [28] propose high-spin Co(III) or an intermediate with some transient transfer of an electron to give a $Co(II) - \dot{N}<$ radical pair.

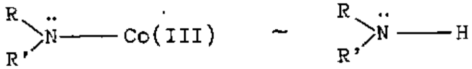
The general criterion for the rate of pyramidal inversion is the energy barrier between sp^3 and sp^2 nitrogen (if hybrid orbitals are used). Clearly, this will be lowered if there is a possibility for the $RR'N^-$ donor to participate in π-bonding of some kind and such bonding is the essential part of the Basolo and Pearson theory (cf.1.1.3.). At least some degree of π-bonding appears possible for the postulated five-coordinate intermediate state even if it is considered that the Co(trien)(glyO)Cl^{2+} system reacts with full retention at the Co(III) centre:



$120^\circ < \alpha > 90^\circ$

It is required that the limiting fully π-stabilized trigonal bipyramid is not developped since there is no rearrangement into the β_1 isomer but to any degree of distortion towards the stabilized state will correspond some degree of π-bonding. On the other hand, π-bonding is much less favorable for a high-spin Co(III) state since the accepting orbitals are partially populated and it is not clear how formation of the high-spin state could contribute to a lowering of the inversion barrier.

The proposed Co(II) - $\dot{N}RR'$ radical pair would require a high energy for its formation if we assume that a Co(III) substituent exerts a σ-bonding influence which is smaller but still comparable to that of a proton:



The formation of the radical pair would require an energy of the order of magnitude of the ionization potential of a secondary amine ($\approx$ 200 kcal/mol) which is not likely to be much compensated by stronger Co (II) - $R_2\dot{N}H$ bonding. This argument has still some merit if the analogy between Co(III) and H^+ is not good so that only 10% of the ionization energy of RR'NH would be required.

Archer [107] has invoked high-spin Co(III) intermediates in order to rationalize observed rearrangement during the lifetime of the intermediate state resulting from loss of the leaving group.

1.1.6. THE ION PAIR MECHANISM

The claimed (and later challenged [12]) observation that the relation between pseudo first order rate constants of base hydrolysis of pentaammine Co(III) complexes and the hydroxide concentration is not exactly linear when the hydroxide concentration is varied over a wide range may have suggested the ion pair mechanism (eq 11) [29].

$$\begin{array}{lcl}
[CoA_5X]^{n+} + OH^- & \underset{\text{fast}}{\overset{K_{IP}}{\rightleftharpoons}} & \{[CoA_5X]^{n+}OH^-\} \\
\{[CoA_5X]^{n+}OH^-\} & \underset{\text{r.d.s.}}{\overset{k}{\longrightarrow}} & \{[CoA_5OH]^{n+}X^-\} \qquad (11) \\
\{[CoA_5OH]^{n+}X^-\} & \underset{\text{fast}}{\rightleftharpoons} & [CoA_5OH]^{n+} + X^-
\end{array}$$

The rate law of the ion pair mechanism is not different from that of the S_N1CB mechanism. Both are given by the expression $k_{obs} = Kk[OH^-]/1 + K[OH^-]$, where in the ion pair mechanism K means the ion pairing equilibrium constant and k the rate of the ion pair rearrangement [29] and in the S_N1CB mechanism K means the conjugate base equilibrium constant and k the rate of loss of the leaving group [20]. The observed rate law is therefore not unambiguously explained by the ion pair mechanism. However, it would seem unlikely that hydroxide induces substitution so much faster than other anions - anation reactions in neutral aqueous solutions with anions such as Cl^-, N_3^-, NCS^- etc. are about 10^6 times slower [30-32]. This mechanism is also inconsistent with the effect of steric acceleration [16] since an increase in size of the substrate would decrease electrostatic anion - cation interaction. Buckingham and coworkers [33] recently obtained kinetic data for base hydrolysis of three 3+ hexaamine Co(III) complexes with tetradentate ligands 2,2',2"-triaminotriethylamine (= tren) or 2-methylamino-2',2"-diaminotriethylamine (=Metren) and NH_3. Analysis of their data enabled them to determine the degree of ion pairing and the acidity of the amine protons which lead to the conjugate base. In conclusion, they propose a combined $S_N1(IP)CB$ mechanism, in which the ion pair assists dissociation of an amine proton to give the conjugate base which rapidly looses the leaving group (eq 12).

$$\begin{tikzcd}
Co^{3+} + OH^- \arrow[r, shift left, "K_{IP}"] & Co^{3+}/OH^- \arrow[l, shift left] \arrow[r, shift left, "K_{CB}"] & Co - H^{2+} \arrow[l, shift left] \arrow[d, "k_{OH}"] \\
 & & \text{products}
\end{tikzcd} \qquad (12)$$

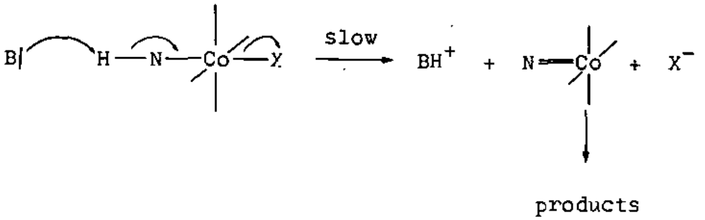
This mechanism with the two preequilibria naturally fits the same mathematical expression for the observed rate law as indicated above, where K means $K_{IP}K_{CB}$. However, the question is open, whether only the ion pair has the possibility to dissociate a proton since other kinetic and stereochemical data gave no evidence for ion pair formation ([13], this work). The best possibilities for the observation of the effects of ion-pairing are offered by highly charged complexes. Rotzinger [34] has studied the base hydrolysis of $(NH_3)_5CoNH_2Co(NH_3)_5^{5+}$ and $(\pm)$-$[en_2NH_3Co]_2NH_2^{5+}$ where the rate law (eq 13) was found:

$$\text{rate} = \frac{k\, K_B\, [\text{OH}^-][\text{complex}]}{1 + K_B[\text{OH}^-] + K_B K_B'[\text{OH}^-]^2} \qquad (13)$$

This was taken to indicate the presence of a reactive conjugate base and an unreactive ion pair with the conjugate base.

1.1.7. THE E2 - MECHANISM

Recently, R.W.Hay and P.R.Norman [35,36] proposed a concerted E2 - mechanism which is adapted from organic chemistry to explain general base catalysis [37-39]. The decrease of the second order rate constant of base hydrolysis with increasing pH may be explained with a rate determining proton transfer in the starting material. This idea is consistent with a concerted mechanism where the conjugate base is not formed in a pre-equilibrium (eq 14).



(14)

While deprotonation is certainly the rate determining step, it is not easy to decide whether release of the leaving group is concerted with it. The cited dependence of the rate on the leaving group is consistent with concertedness, but it could also be due to differences in N-H acidity caused by the different leaving groups.

1.2. EVIDENCE FOR A DISSOCIATIVE MECHANISM

One of the central problems of a mechanism of Co(III) pentaamine complexes is the question whether and to what extent the substitution process $MA_5X + Y \rightarrow MA_5Y + X$ is dissociative. In the dissociative case ([13] and references theirin) the leaving group X departs independently of the influence of Y and the five-coordinate intermediate and its second coordination sphere loose all "memory" of X before the M-Y bond begins to form. This situation will be realized in two cases:

1. when ML_5 is long lived relative to the time scale of exchange of potential ligands between the second coordination sphere and bulk solution; and
2. when X cannot be held in the second coordination sphere and passes immediately into bulk solution - as when X and ML_5 carry the same charge (e.g. $HgCl^+$ separating from $Co(NH_3)_5^{3+}$ or when X is uncharged and non polar (e.g. N_2 loss after nitrosation of $Co(NH_3)_5N_3^{2+}$).

In an interchange mechanism ([13] and references therein) exchange of X and Y occurs within a preassembled encounter complex $\{[MA_5X]Y \times H_2O\}$. M - Y bond-forming occurs before MA_5 has lost "memory" of X, that is, before the second coordination sphere has had time to relax. In particular, we have a dissociative interchange (I_D) if bond-making M - Y occurs only after the M - X bond is broken but before X is lost from the second coordination sphere.

1.2.1. ACTIVATION PARAMETERS

In the dispute over a base hydrolysis mechanism for Co(III) pentaamine complexes activation parameters are often discussed.

There exists a linear free energy relationship (LFER) for the free energy of activation $\Delta G^{\neq}$:

$$\Delta G^{\neq} = \alpha \Delta G^{\circ} + \text{constant} \qquad (15)$$

where the Brønsted slope is

$$\alpha = (\partial G^{\neq} / \partial G^{\circ})_{p,T} \qquad (16)$$

It can be shown that the slope α is 1.0 for dissociative mechanisms whereas it is 0.5 for associative mechanisms [13 and references therein]. For the base hydrolysis of halogeno pentaammine Co(III), a LFER of $\alpha = 1.0$ was found [40].

It is clear that a LFER of unit slope exists for the enthalpy of activation $\Delta H^{\neq}$ if it exists for $\Delta G^{\neq}$. Powell's enthalpy of the transition state ΔH_T [41] which is nothing else than $\Delta H^{\neq} - \Delta H^{\circ}$ reflects this situation and it is really constant for base hydrolysis of $Co(NH_3)_5X^{2+}$ - complexes where $X^- = Cl^-, Br^-, I^-, NO_3^-$ (ΔH_T = 163.3 kJ mol^{-1} ± 4 [42]).

The activation entropies $\Delta S^{\neq}$ for an S_N1CB - mechanism are expected to be in the order of 40 cal mol^{-1} deg^{-1} [43] since the first step of the reaction - the formation of the conjugate base - can easily be compared with a deprotonation of an aqua complex, where activation parameters are available. To the second step - abstraction of the leaving group - an activation entropy of about 0 may be attributed from comparison with the well known values of aquation reactions. The measured values -

some are listed in table 1 (see too references [43] and [44]) - are in good agreement with these estimates but

complex	$\Delta S^{\neq}$ (cal $deg^{-1}mol^{-1}$)	ref.
$Co(NH_3)_5F^{2+}$	+ 16.6	45.10
$Co(NH_3)_5Cl^{2+}$	+ 32.4	45,10
$Co(NH_3)_5Br^{2+}$	+ 35.4	45,10
$Co(NH_3)_5I^{2+}$	+ 46.4	46,10
$Co(NH_3)_5NCS^{2+}$	+ 42.0	47
$Co(NH_3)_5NO_2^{2+}$	+ 44.0	48
$Co(NH_3)_5NO_3^{2+}$	+ 43.1	40
$Co(NH_3)_5N_3^{2+}$	+ 30.3	49
$Co(NH_3)_5SO_4^{+}$	+ 24.6	50,51

table 1 : selected activation entropies for base hydrolysis of some Co(III) pentaammines

they are not with an S_N2 mechanism.

In an interpretation of these activation parameters it should be pointed out that (1) the average values for a D or an I_D mechanism might be about the same, (2) the interpretation of a mechanism consisting of two or more steps is very difficult, (3) all estimates have been made with very simple models and (4) activation parameters are quasithermodynamic quantities and therefore very difficult to interpret exactly. Nevertheless, the observed activation parameters are not inconsistent with an S_N1CB mechanism.

The measurement of the volume of activation $\Delta V^{\neq}$ by high presure kinetics ($\delta \ln k / \delta p)_T = -\Delta V^{\neq} / RT$ becomes increasingly important. Data for one-step mechanisms are relatively easily interpreted in terms of atomic motion only [13]. But one intriguing problem remains: in base hydrolysis an overall reaction is measured and the results are interpreted by a stepwise mechanism. Direct comparison therefore becomes very difficult. However, first results are available [14,15] and they are in full agreement with a dissociative mechanism. Kitamura [14] found an activation volume for the base hydrolysis of the chloro pentaammine Co(III) complex of + 33.4 ml mol^{-1} which he interprets in terms of a S_N1CB mechanism and Balt [15] found good agreement of this value with his calculated one.

1.2.2. COMPETITION EXPERIMENTS

The competition of the possible intermediate states for other nucleophiles (Y) than water or hydroxide added during base hydrolysis of Co(III) pentaamine complexes allows to distinguish a dissociative process - where a common, leaving group - independent five - coordinate intermediate with a chemically significant lifetime is built up from other mechanistic possibilities (eq 17).

$$\left.\begin{array}{l} CoA_5 - H \\ CoA_5 \end{array}\right\} \begin{array}{l} \xrightarrow{H_2O \text{ or } OH^-} CoA_5OH \\ \xrightarrow{Y \text{ or } Y\,/\,H^+} CoA_5Y \end{array}$$

$$\left.\begin{array}{l} CoA_5X - H \\ CoA_5X \end{array}\right\} \begin{array}{l} \xrightarrow{H_2O \text{ or } OH^-} CoA_5OH + X \\ \xrightarrow{Y \text{ or } Y\,/\,H^+} CoA_5Y + X \end{array} \qquad (17)$$

When a common intermediate is produced in a dissociative mechanism, the competition ratio CoA_5OH / CoA_5Y should be independent of the leaving group X and only vary with the nucleophile added, whereas for any concerted bimolecular mechanism it will be dependent on the nature of both X and Y. Numerous competition experiments have been done in the last 15 years and some of them are listed in table 2.

complex a)	Y	[Y],M	% CoA_5Y	ref.
$Co(NH_3)_5Cl^{2+}$	N_3^-	0.5	4.9	12
$Co(NH_3)_5Cl^{2+}$	N_3^-	1.0	8.5	12
$Co(NH_3)_5Cl^{2+}$	NCS^-	"	5.5	12
$Co(NH_3)_5Br^{2+}$	N_3^-	"	8.7	12
$Co(NH_3)_5I^{2+}$	"	"	10.0	12
$Co(NH_3)_5NO_3^{2+}$	"	"	10.4	12
$Co(NH_3)_5DMSO^{3+}$	"	"	12.3	52
$Co(NH_3)_5OP(OMe)_3^{3+}$	"	"	12.5	52
$Co(NH_3)_5OC(NH_2)_2^{3+}$	"	"	12.0	52
cis-$CoNH_3en_2Cl^{2+}$	"	"	24	53
trans-$CoNH_3en_2Cl^{2+}$	"	"	24	53
$Co(NH_2CH_3)_5Cl^{2+}$	"	0.5	35.9	16
$CobampdapoCl^{2+}$	"		6.5	27
$CobampdapoBr^{2+}$	"	"	6.0	27
$CobamptmdCl^{2+}$	"	"	8	26
$CobamptmdBr^{2+}$	"	"	9	26
$CobampenCl^{2+}$	"	"	9	26
α-$CodiendapoCl^{2+}$	"	"	63.6	this work
α-$CodiendapoCl^{2+}$	"	0.5	47.1	" "
α-$CodiendapoCl^{2+}$	"	0.25	28.3	" "
α-$CodiendapoBr^{2+}$	"	1.0	61.7	" "
α-$CodiendapoBr^{2+}$	"	0.5	48.3	" "
α-$CodiendapoBr^{2+}$	"	0.25	30.4	" "

a) for abbreviations see 2.1.

table 2 : selected competition values

In competition experiments with $Co(NH_3)_5X^{n+}$ - complexes, Reynolds [58] found a competition ratio which was about 10% higher for 3+ complexes than for 2+ complexes. He interprets these results by an I_D mechanism. However, it seems obvious that a change in charge could increase the concentration of competing nucleophiles in the solvent sheath surrounding the initial species (cf.3.1.). Of course, an increase in charge could also favour the ion pairing (increase of K_{IP} in eq 18). However, no kinetic evidence for ion pairing with added nucleophiles was found [13,59]. Measurements of the rate of Co - X rupture in base showed no significant difference in cases with or without added nucleophile.

1.2.3. STERIC ACCELERATION

One of the most important results of the last years supporting a dissociative mechanism is the increase of the base hydrolysis rate on going from pentaammine Co(III) complexes to more and more sterically hindered pentakis(alkylamine) Co(III) complexes. Sargeson and coworkers [16] have found that base hydrolysis of pentakis(alkylamine) Co(III) complexes show an acceleration of a factor of more than 10^5 when the amines vary from NH_3 to CH_3NH_2, $n\text{-}C_3H_7NH_2$ and $i\text{-}C_4H_9NH_2$ (table 3). It could be shown that this marked acceleration can be attributed to steric effects for the following reasons:

CoA_5Cl^{2+} A	k_{OH} $M^{-1}s^{-1}$	k_{aq} 10^8 s^{-1}	k_{ex} a) 10^{-4}	k_{ex} b) 10^{-6}	ref.
NH_3	0.25	1.7	5	3	16,54,55
cis NH_3 tr CH_3NH_2	0.64	-	-	-	16
CH_3NH_2	3800	37	30	30	56,57
$n\text{-}C_3H_7NH_2$	11000	-	-	-	16
$i\text{-}C_4H_9NH_2$	150000	180	-	-	16

a) cis amine protons

b) trans amine protons

table 3 : steric acceleration

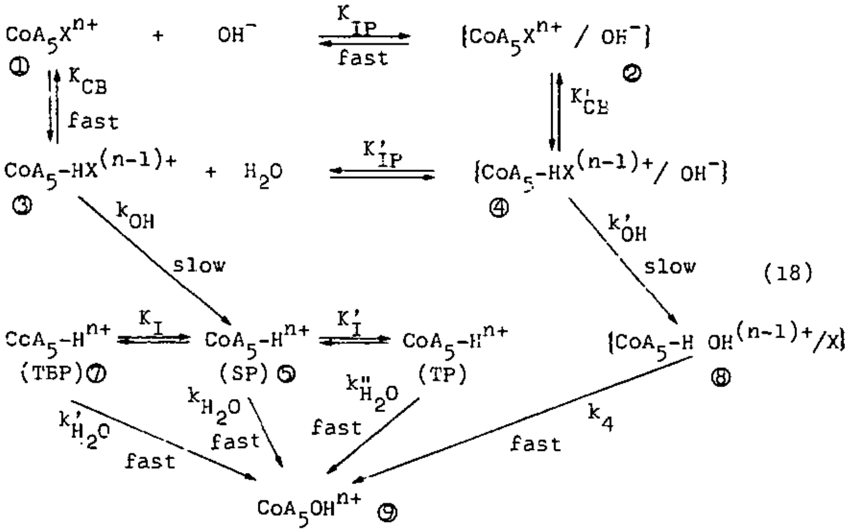
There exists a linear free energy relationship (LFER) between the logarithm of the proton exchange rate of the coordinated amines and the pK_a-value [16,60]. Because there is no possibility to directly measure the pK_a of coordinated amines ($pK_a > 14$), this direct proportionality must be accepted as the only measure of the acidity of the coordinated amines. Comparison of the proton exchange rates of the complexes with deuterated ammonia and methylamine as amine ligands show that the proton exchange for cis or trans amine protons differ by less than a factor of about 5 (table 3). The difference in base hydrolysis rate of about 10^4 cannot therefore be attributed to the basicity differences of the conjugate base. Competition experiments which were made on the same systems are also in agreement with a dissociative mechanism. The increase of the competition ratio from about 4% to 36% (cf. table 2) is consistent with a more stabilized coordinatively unsaturated intermediate state due to steric strain in starting materials and products.

1.2.4. STEREOCHEMICAL CHANGE

If base hydrolysis of Co(III) pentaamine complexes really follows an S_N1CB mechanism - and much evidence for this exists now as was shown in the preceding sections - the configurations of the final products should only reflect the geometry of the intermediate state of reduced coordination number and therefore be independent of the leaving group. Products from competition with other nucleophiles than water therefore should also have the same configuration. Most published results show this feature. However, base hydrolysis of N-methyl-2,2',2"-triaminotriethylamine ammine Co(III) complexes with different leaving groups such as Cl^-, Br^- and NH_3 show a marked difference from this behaviour [61]. Buckingham and coworkers interpret this by either a purely dissociative process in which the solvent sheath of the coordinatively unsaturated intermediate state has had no time to rearrange and therefore still reflects the environment of the initial species or by an I_D process where the loss of the leaving group is accompanied by some small degree of bond making with the nucleopile. Both interpretations are consistent with the observation that the stereochemistry seems to be influenced by the charge of the initial species.

1.3. CONCLUSION

Concluding the discussion of all proposed mechanisms, we see that there exists considerable evidence for the formation of leaving-group independent coordinatively unsaturated intermediate states in base hydrolysis of Co(III) pentaamine complexes. These intermediate states may arise from the well established S_N1CB - mechanism. If reactive ion pairs with OH^- (S_N1IP) are included, the pattern presented in eq 18 is obtained.



(18)

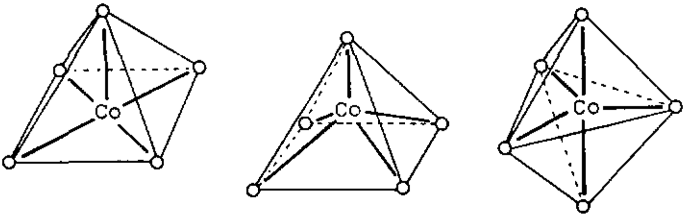
- The conjugate base ③ may be produced by dissociation of an amine proton in the starting material ① or in the ion pair ②, produced by starting material ① and a hydroxide anion. The fraction of both pathways depends on the values of the equilibrium constants K_{CB}, K_{IP} and K'_{CB}. Subsequent loss of the leaving group leads to the coordinatively unsaturated intermediate state ⑤. This reaction is normally rate determining, but there exist cases where the deprotonation of the coordinated amine function is slower than loss of the leaving group. In these cases each act of deprotonation leads to reaction of the conjugate base (cf.1.1.7.).

- The coordinatively unsaturated intermediate state ⑤ which results from loss of the leaving group from the conjugate base ③ has first square pyramidal configuration ⑤. Relaxation to a trigonal bipyramidal ⑦ or a tetragonal pyramidal configuration ⑥ should have rates which are faster than reprotonation or bond formation to the entering nucleophile ($k_{relax} \cong 10^{12}$-10^{14} s^{-1} [61]). If base hydrolysis follows the route via the coordinatively unsaturated intermediate ③, the stereochemistry in the products will be predicted from the values of the constants K_I and K'_I which reflect the stabilities of the three possible configurations. In the case of a π-stabilized intermediate state (this work) $K_I \gg 1 > K'_I$ (if the rearrangement of the square pyramidal configuration is faster than reprotonation or bond formation to the entering nucleophile). In the case of $N_{py} \rightarrow Co(III)$ - backbonding [26,27] K_I, $K'_I < 1$ or bond formation to the entering nucleophile is faster than rearrangement of the initial square pyramidal species. Henderson and Tobe have recently demonstrated [62] that the geometry of the ligand sphere has a big influence on K_I.

- The route via intermediate ④ symbolizes a possible I_D mechanism without a coordinatively unsaturated intermediate. This route possibly explains unusual stereochemical results [61] . It is obvious that this behaviour becomes important with increasing charge of starting materials.
- Unusual stereochemical results [61] and changes in competition ratios using differently charged leaving groups [61,52,58] show the need for having additional information on the rearrangement lability of the first coordination sphere on the time scale of the life-time of the coordinatively unsaturated intermediate state. It is evident that the structure of this environment is reflected in both product distribution and product configuration.

1.4. THE CONFIGURATION OF THE COORDINATIVELY UNSATURATED INTERMEDIATE STATE

There exist in principle three possible configurations for five coordinate intermediate states, two may be termed as pentahedra, one is a hexahedron [63] (fig.1).



square
pyramid
(pentahedron)

tetragonal
pyramid
(pentahedron)

trigonal
bipyramid
(hexahedron)

figure 1 : possible configurations for the coordinatively unsaturated intermediate states

The square pyramid arises from an octahedral complex by loss of a ligand without subsequent rearrangement. The four small triangular faces are essentially blocked against attack of incoming nucleophiles. Attack at the square bottom face will lead to retention of configuration. The two other polyhedra are the result of some rearrangement subsequent to loss of a ligand. The faces are now all open to attack by nucleophiles and this allows for configurational rearrangement.

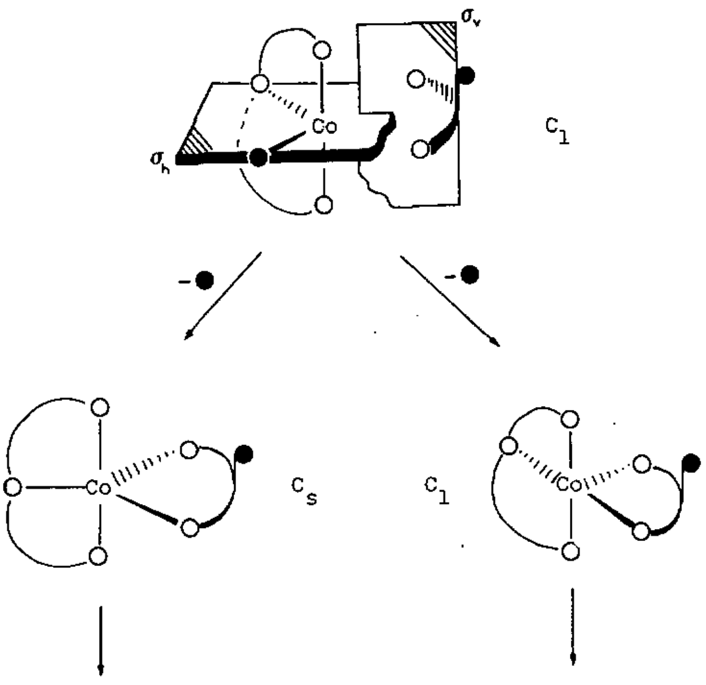
1.4.1. THE STEREOCHEMICAL CONCEPT

The stereochemistry of starting materials and products is normally easy to detect whereas the configuration of the intermediates is not, especially when the intermediates are short-lived as it is the case in base hydrolysis where their lifetime is at the diffusion controlled limit [64]. In these cases a *stereochemical relationship* between the configuration of starting materials and products is very useful. The following conditions must be fulfilled [26]:

- The intermediate is short lived enough that attack of incoming nucleophiles is faster than multiple rearrangements.
- In a first state immediately following metal-leaving-group rupture, the intermediate state has square pyramidal configuration.
- In subsequent rearrangement the ligand motion should be as small as possible.
- The attack of an incoming nucleophile is in principle the reverse of the first step, viz. attack of the nucleophile at a square bottom face of a square pyramid.

Stereochemical changes are essentially easy to detect when the starting material is optically active. In these cases we observe retention or inversion of the configuration - a chiral intermediate is the consequence - or racemisation - an achiral intermediate is the consequence - or a mixture of all.

Our work aims at designing and testing a suitable ligand system which should enable us to distinguish whether the intermediate has pentahedral or hexahedral configuration (fig.2).



racemisation

retention

figure 2 : a possible system to detect the configuration of the intermediate state

It is evident that full racemisation in such a system would be consistent with the only achiral intermediate state which is a trigonal bipyramid and would have the possibility to be stabilized by π-bonding.

2. RESULTS

2.1. ABBREVIATIONS

A	amine ligand
bach	1,3-bis-(aminomethyl)-isochinolin
bamp	2,6-bis-(aminomethyl)-pyridine
dapo	1,3-diaminopropane-2-ol
dien	2,2'-diaminodiethylamine
dimen	1,2-dimethylethylenediamine
dmso	dimethylsulfoxide
dpt	3,3'-diaminodipropylamine
en	ethylenediamine
ept	2,3-diaminoethylpropylamine
H_2dipic	pyridine-2,6-dicarboxylic acid
tmd	1,3-diaminopropane
χ	mer-syn-N [a,b]
χ'	mer-anti-N [a,b]
π	(±)fac-exo-O [a,c]
π'	(±)fac-endo-O [a,c]
ω	meso-fac-exo-O [a]
ω'	meso-fac-endo-O [a]
π NNO	(±)fac-tridentate dapo [a]
ω NNO	meso-fac-tridentate dapo [a]

a) This nomenclature refers to the coordination of an aliphatical triamine ligand, dapo and a monodentate ligand to a Co(III) center (cf. fig.8).

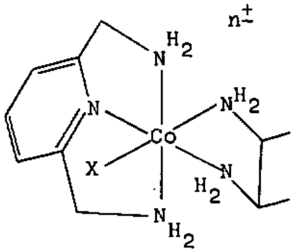
b) The orientation of the secondary amine proton is assigned from the base hydrolysis rate and structure comparisons with related compounds [65,66].

c) The orientation of the hydroxo group is assigned by the stereochemical course and the relative rates of the coordination of the dangling OH-group (cf.2.6.2.).

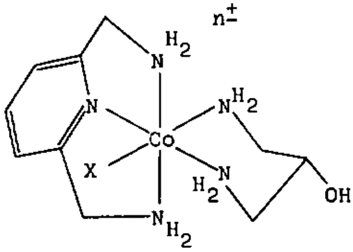
2.2. TYPE OF COMPOUNDS

Our stereochemical concept for the bonding characteristics in the coordinatively unsaturated intermediate state (cf. 1.4.1.) required us to develop mixed ligand Co(III) complexes of the general formula [Co(meridionally coordinated tridentate ligand)(bidentate ligand)(leaving group)]$^{\pm n}$, where either the tridentate or the bidentate ligand are prochiral. This, together with the prochiral unit constituted by the other chelate ligand coordinated at the Co(III) center plus the leaving group creates a chiral complex (fig.2). The possibility of a π bond between the π system of a pyridine donor and the $d_{x^2-y^2}$ orbital of Co(III) in the coordinatively unsaturated intermediate state and the influence of this bond on the configuration of this intermediate have been examined previously in pentaamines [26,27]. The change of the coordination sphere from CoA_5X to CoA_3O_2X allows to analyse electronic effects in base hydrolysis and on the properties of the coordinatively unsaturated intermediate state involved. Recently, Henderson and Tobe [62] proposed a correlation between the ring size and arrangement of chelate ligands and the base hydrolysis rate. They found that all structural features favouring the formation of a π-stabilized trigonal-bipyramidal intermediate give rise to an increase in the base hydrolysis rate constant.

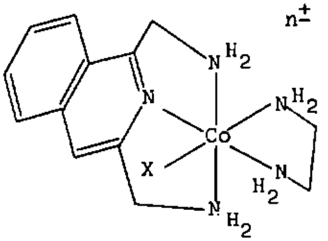
In this work, a stereochemical test of this structure-reactivity correlation has been carried out. This test makes use of the clearly defined stereochemical consequences of this π bonding effect.



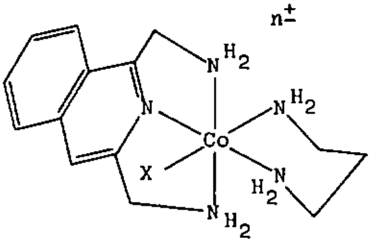
①
Co bamp dimen $X^{n\pm}$



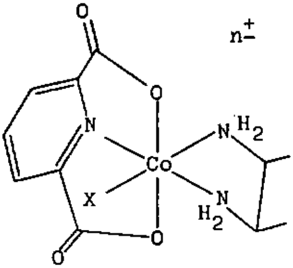
②
Co bamp dapo $X^{n\pm}$



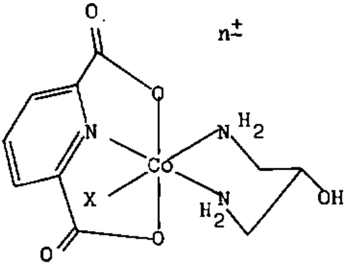
③
Co bach en $X^{n\pm}$



④
Co bach tmd $X^{n\pm}$

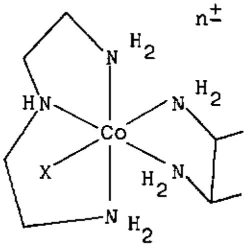


⑤
Co dipic dimen $X^{n\pm}$



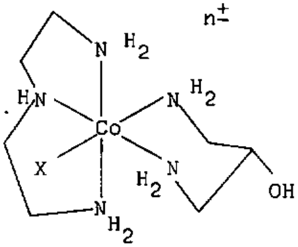
⑥
Co dipic dapo $X^{n\pm}$

figure 3



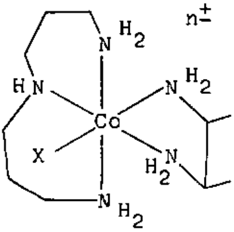
⑦

x-Co dien dimen $X^{n\pm}$



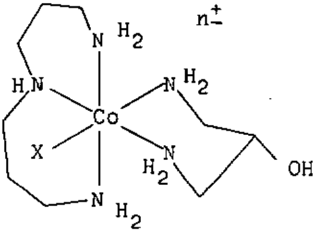
⑧

x-Co dien dapo $X^{n\pm}$



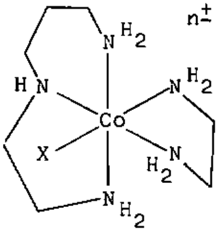
⑨

x-Co dpt dimen $X^{n\pm}$



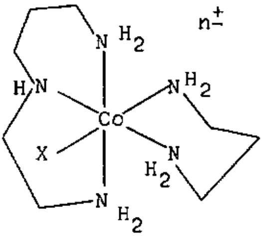
⑩

x-Co dpt dapo $X^{n\pm}$



⑪

x-Co ept en $X^{n\pm}$



⑫

x-Co ept tmd $X^{n\pm}$

figure 3 (cont.)

figure 3 : examples for chiral mixed ligand Co(III) complexes of the general formula [Co(meridionally coordinated tridentate ligand)(bidentate ligand)(monodentate ligand)]$^{\pm n}$

② : ref. [26,27]

⑥ : this work, ref. [67]

⑧ : this work, ref. [68]

⑩ : this work

2.3. REACTIONS

Comparison of base hydrolysis rates with the rates of spontaneous aquation allows to estimate the reactivity of the conjugate base. In previous work [21,43,44,17] acceleration factors of about $10^5 - 10^{10}$ have been found. Competition experiments allow to examine the characteristics of the substitution reaction (associative or dissociative, stepwise or synchronous) and to estimate the lifetime of the intermediate state relative to other starting materials. Adequate description of the base hydrolysis reactivity requires the knowledge of the rates of many individual reaction steps: The rate of deuterium exchange gives a relative measure of the acidity of the NH protons and thus of the relative ease by which different possible conjugate bases are formed. The rate of base hydrolysis is usually a composite quantity (cf. 1.1.2.) reflecting the deprotonation step as well as the rate determining loss of the leaving group. The immediate hydrolysis product, arising from scavenging of solvent by the coordinatively unsaturated intermediate state may undergo various subsequent reactions: isomerization may be accompanied by spectral change in the UV/VIS region; change in optical activity may occur at the same or a different rate and needs to be specified separately. In the presence of coordinating anions, the primary hydroxo or aqua complex may undergo anation (substitution of OH^-/ OH_2 by anions) concurrently. Another possibility of forming aniono complexes is by way of scavenging anions concurrently with solvent scavenging. Subsequent hydrolysis of this anion competition product may also be observed. These possibilities, all of which have been observed in this work are summarized in fig. 4.

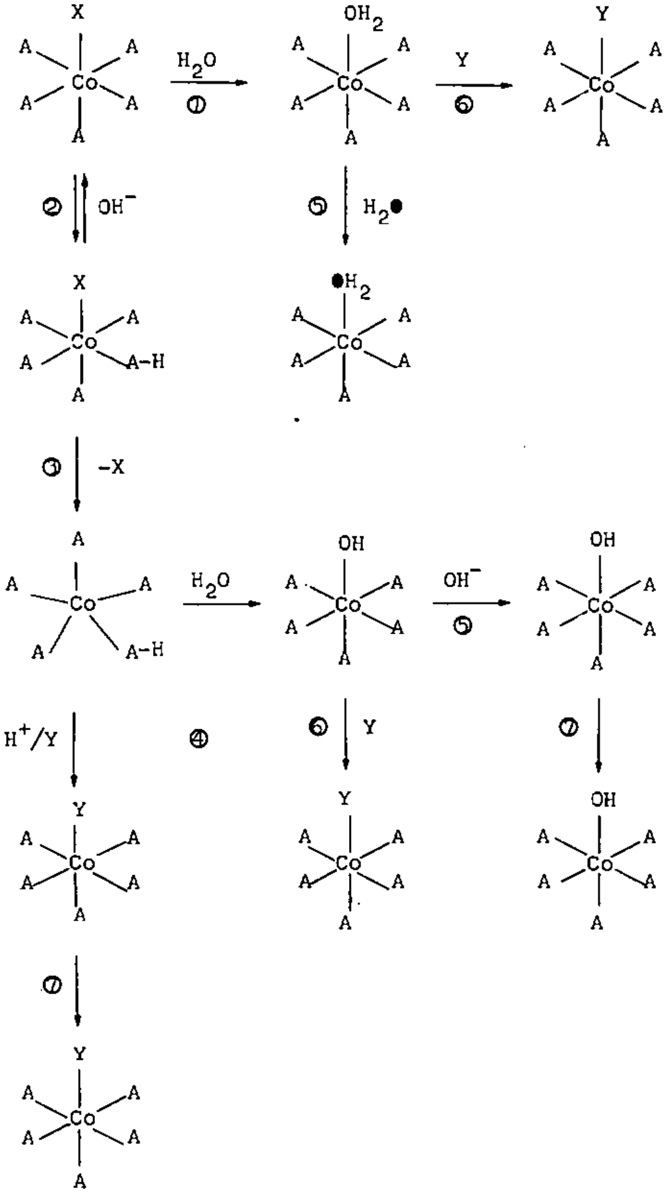


figure 4

figure 4 : reactions studied in our systems:

① spontaneous hydrolysis	$(k_{H_2O}\ [s^{-1}])$
② proton exchange	$(k_{OD}\ [M^{-1}s^{-1}])$
③ base hydrolysis	$(k_{OH}\ [M^{-1}s^{-1}])$
④ competition	(% CoA_5Y)
⑤ racemisation	$(k_{OH}\ [M^{-1}s^{-1}])$
⑥ anation	$(k_{an};\ k'_{an}\ [s^{-1}])$
⑦ isomerisation	$(k_{is}\ [s^{-1}])$

2.4. METHODS OF SYNTHESIS AND RESOLUTION OF CHIRAL COMPOUNDS

2.4.1. SYNTHESIS OF Co dipic A A $X^{\pm n}$ - COMPLEXES

Complexes with meridionally coordinated $dipic^{2-}$, two amine ligands and a monodentate ligand contain the chromophore CoA_3O_2X where the two oxygen donors occupy trans positions. Our work in this area aimed at developing good synthetic routes and methods to assign their structures. A general route to the synthesis of mixed ligand Co(III) systems with amine ligands is the oxidation of the corresponding labile Co(II) complexes. Fallab and coworkers [70,71] have shown that dioxygen oxidation of species with at least three nitrogen donors generally gives binuclear μ-peroxo species which normally undergo redox decomposition to lead to mixed ligand Co(III) compounds. However, dioxygen oxidation of an equimolar mixture of sodium pyridine-2,6-dicarboxylate, ethylenediamine and Co(II) nitrate hexahydrate in water at 0 °C gave dark brown reaction mixtures from which pyridine-2,6-dicarboxylic acid and $Coen_2OH_2X^{n+}$ were isolated after acidification (eq 19). Only a small amount (<1%) of Co dipic en OH_2^+ was detected by ^{1}H-NMR and IR spectroscopy in a solid fraction obtained by adding acetic acid to the reaction mixture. We interpret this result by disproportionation of the binuclear Co(II) precursor complex (eq 19).

$$\begin{tikzcd}
Co^{2+} + dipic^{2-} + en \arrow[r, rightleftharpoons] & Co^{II}dipic\ en\ OH_2 \arrow[dl, "O_2"'] \arrow[d, "O_2"] \\
{[Co^{III}dipic\ en\ OH_2]^+} & {[Co\ (en)_2\ (OH_2)_2]^{3+} + [Co\ dipic_2]^-}
\end{tikzcd} \qquad (19)$$

This hypothesis is supported by the observation that dioxygen oxydation of the same reaction mixture in presence of an excess of sodium nitrite did not yield the desired Co dipic en NO_2 - complex but a compound which was found by chromatographic analysis and individual characterization of the components to be a mixture of cis-[Co en_2 $(NO_2)_2]_2$ [Co dipic $(NO_2)_3$] and trans-[Co en_2 $(NO_2)_2]_2$ [Co dipic $(NO_2)_3$] ($\approx$ 1 : 0.7; ^{1}H-NMR).

We therefore have chosen an alternative approach, starting from Co(III) complexes with substitutionally labile ligands. This method has prcedent in recent work [72-74] . One possible starting material is the $Co(CO_3)_2AA^-$ - ion (eq 20).

$$C(NH_2)_3\ [Co\ en\ (CO_3)_2]\ +\ H_2dipic\ +\ H_2O\ \longrightarrow$$

$$[Co\ dipic\ en\ OH]\ +\ CO_2\ +\ C(NH_2)_3HCO_3 \qquad (20)$$

$$[Co\ dipic\ en\ OH]\ +\ HX\ \longrightarrow\ [Co\ dipic\ en\ OH_2]X$$

The pure hydroxo complex was only isolated in very small amounts, but treatment of the crude material, probably a mixture of hydroxo and carbonato complexes, with acids afforded salts of the aqua complexes in very high yields. Solutions of the hydroxo complex were prepared by deprotonation of the aqua ion which is a weak acid with $pK_a = 7.48 \pm 0.05$ (determined by potentiometric titration at 25.0 ± 0.1 °C, $\mu = 1.0$ ($NaClO_4$)). Deprotonation is accompanied by a spectral change of the lower energy spectral band to lower frequencies (fig. 5).

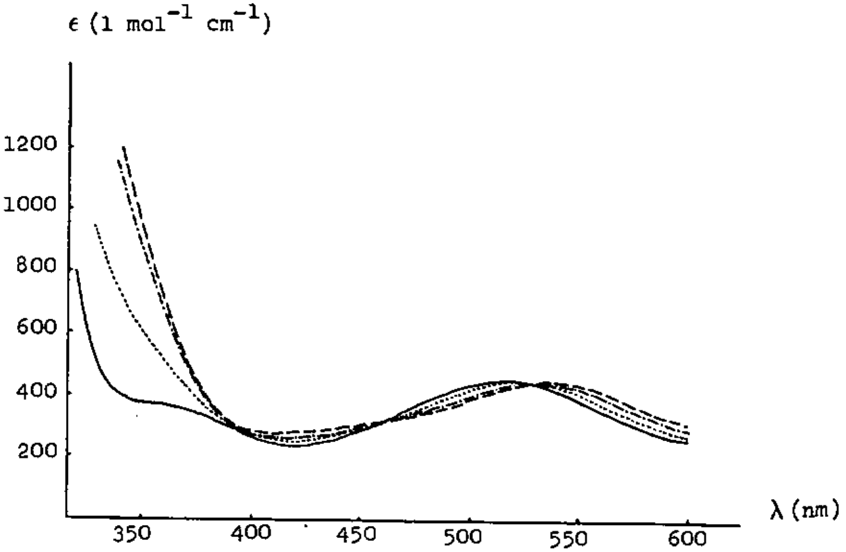


figure 5 : spectral change during deprotonation of Co dipic en OH_2^+ at $\mu = 1.0$ and 25.0 ± 0.1 °C

—— pH = 6.50
········ pH = 7.33
—·—·· pH = 8.02
---- pH = 9.30

Another suitable starting material are Erdmann's salt type Co A A $(NO_2)_4$ - species. They react with H_2dipic in water to give the corresponding nitro complexes (eq 21).

$$\begin{tikzcd} \mathrm{Co\ A\ A\ (NO_2)_4^-} + \mathrm{H_2dipic} \arrow[rr, "1\ \mathrm{h}\ 80\ ^\circ\mathrm{C}"] & & \mathrm{Co\ dipic\ A\ A\ NO_2} \arrow[d] \arrow[dl] \\ & \mathrm{Co\ dipic\ A\ A\ ONO} & \mathrm{Co\ dipic\ A\ A\ OH_2^+} \end{tikzcd} \qquad (21)$$

In the diammine series, three different species could be isolated to all of which we attribute a structure where the ammine ligands are trans to each other (cf. 2.5.1.). First a yellow brown compound precipitated which is sparingly soluble in either water or dimethyl sulfoxide. It is not retained on both cation or anion exchange resins (Dowex 50W X8, 50-100 mesh; Dowex 1 X8, 100-200 mesh respectively). This fact together with its VIS-spectrum which is typical of a chromophore with N-bound nitrite is compatible with a trans-Co dipic A_2 NO_2 - complex. As a second product a purple water-insoluble species, presumably trans-Codipic A_2 ONO could be isolated. After some days, crystals of the presumably aquated complex were filtered off. This violet water-soluble trans-Co dipic A_2 OH_2^+ - ion shows retention on a Dowex 50W X8, 50-100 mesh column. The same synthetic route applied to Co dapo $(NO_2)_4^-$ led directly to a violet sparingly water soluble compound, probably the Co dipic dapo ONO - complex which has no retention on a Dowex 50W X8, 50-100 mesh column.

Uncharged aniono complexes were prepared by two principal different routes. The sparingly water soluble azido, nitro an thiocyanato complexes in the ethylenediamine series were obtained by anation of the corresponding aqua complex in neutral aqueous solutions containing the anion at 1M concentration at 25 °C (eq 22).

$$\text{Co dipic en } OH_2^{+} + X^{-} \longrightarrow \text{Co dipic en X} + H_2O \quad (22)$$

The formation of the azido complex was followed kinetically (cf. 2.6.7.). In other experiments we tried to thermally dehydrate the different solid salts of the aqua complex. Heating X-ray powder photographs were taken of samples at heating rates of 1 or 6 °C/min. (fig. 6). In most cases ($X = NO_3^-$, Br^-, CH_3COO^-, $(SO_4^{2-})_{\frac{1}{2}}$) redox decomposition of the samples occurred at temperatures lower than or close to the temperature of dehydration. On the other hand, for $X = Cl^-$ and $C_2O_4H^-$, the set of powder lines of the starting materials disappeared and a new set arose (fig. 6). Thermal analysis with on-line mass spectral monitoring of gaseous reaction products established that the process was strictly stoichiometric (fig. 7). There was no evolution of CO_2 (g).

These two thermal reactions could be carried out on a preparative scale (eq 23 and 24) and the reaction products gave satisfactory analyses.

$$\text{Co dipic en } OH_2\ Cl\ (s) \xrightarrow{\sim 200\ ^\circ C} \text{Co dipic en Cl (s)} + H_2O\ (g) \quad (23)$$

$$\text{Co dipic en } OH_2\ C_2O_4H\ (s) \xrightarrow{\sim 100\ ^\circ C} \text{Co dipic en } O_4C_2H\ (s) + H_2O\ (g) \quad (24)$$

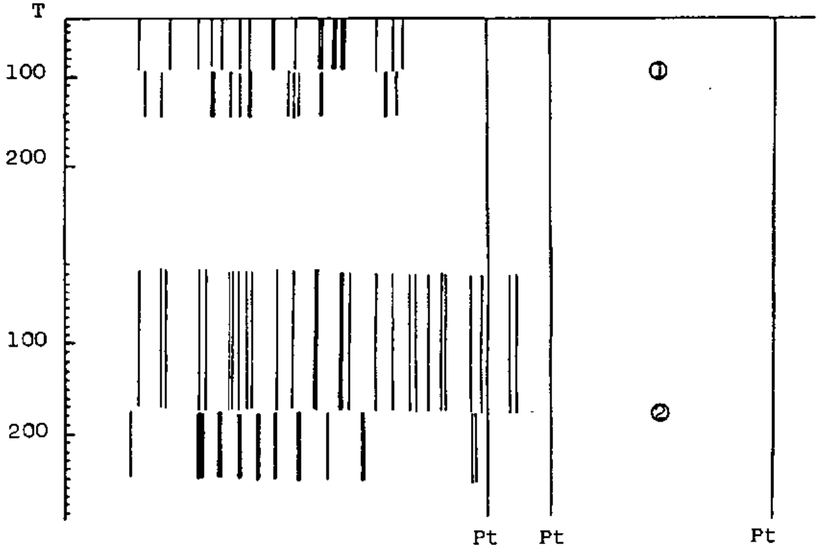


figure 6 : heating X-ray powder photographs of [Co dipic en OH_2]C_2O_4H (s) (①) and [Co dipic en OH_2]Cl (s) (②). Fe K_α - irradiation; heating rate = 1 °C/min

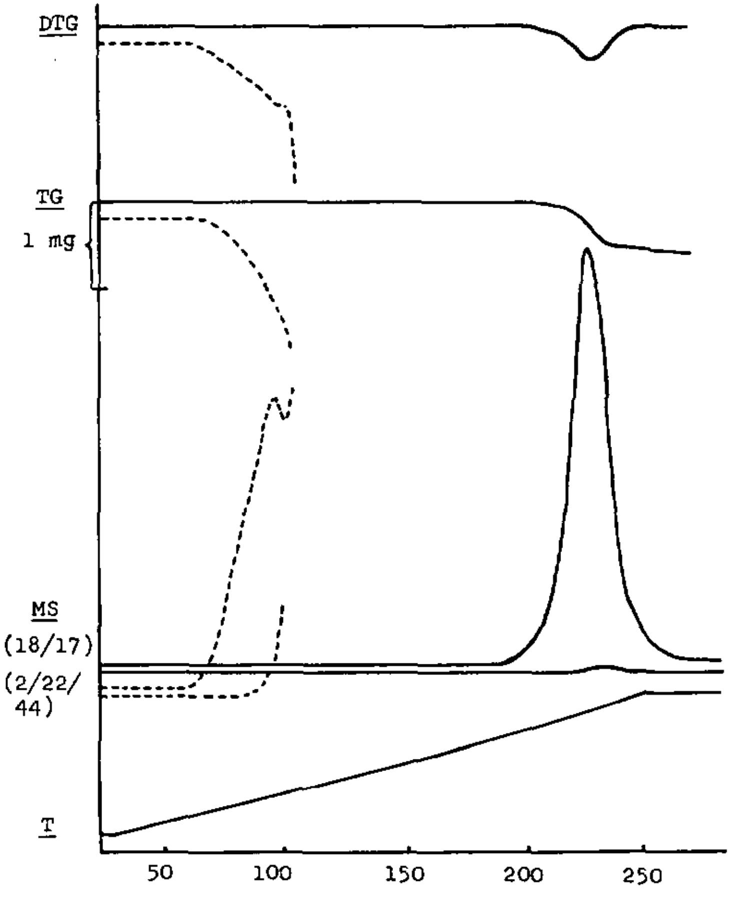


figure 7 : DTG, TG and MS spectrum of the complexes [Co dipic en OH_2]Cl (s) (———) and [Co dipic en OH_2]C_2O_4H (s) (.........) heating rate: 6 °C/min; 10 mg (chloride), 25 mg (oxalate)

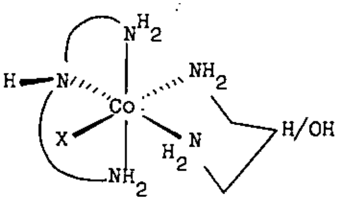
The chloro complex proved insoluble in water but was soluble in dmso. A solution of the chloro complex in dmso treated with Hg^{2+} or Ag^{+} (eq 25) led to the dmso - complex which was precipitated as the nitrate or perchlorate salts.

$$\text{Co dipic en Cl} + AgNO_3 \xrightarrow{\text{dmso}} [\text{Co dipic en dmso}]NO_3 + AgCl\ (s) \qquad (25)$$

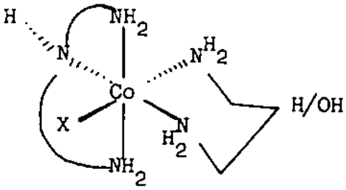
Its VIS - spectra is very similar to that of the corresponding aqua ion (cf. table 4). A cursory investigation of its aquation was therefore made by ^{1}H-NMR in D_2O , making use of the significant difference of chemical shifts of free and coordinated dmso (cf. 2.6.7.).

2.4.2. SYNTHESIS OF Co dien dapo X $^{\pm n}$ and Co dpt dapo X $^{\pm n}$ COMPLEXES

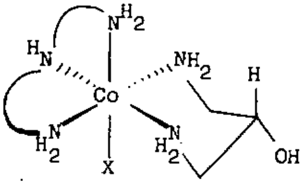
Dioxygen oxidation of aqueous solutions of Co(III) chloride hexahydrate, dien or dpt and dapo in stoichiometric ratios at 0 °C afforded a dark-brown solution, presumably containing the binuclear μ-peroxo complex with the desired mixed ligand sphere [71,72,75]. The crude solution was treated with hydrochloric acid and zinc chloride at 0 °C. The colour changed to dark green. After one night at room temperature, a green cristalline substance, most likely a binuclear μ-superoxo complex, was filtered off from the solution which had turned dark red. The desired mononuclear chloro complexes precipitated during the next few days as tetrachlorozincate salts and were recristallized from water at 0 °C and precipitated by addition of hydrochloric acid and zinc chloride. There exist six geometric isomers of the type [Co dien dapo X]$^{n+}$ and two with dapo as a tridentate ligand [Co dien dapo]$^{3+}$ (fig. 8). The $\varkappa$ and $\varkappa'$ isomers have meridionally coordinated dien. They differ only in the orientation of the secondary amine proton. No such isomerism is possible for the other isomers. Both mer-structures are chiral. Dissymmetry may be considered to arise from the OH-group remote from the donor atom by two atoms. The π and π' isomers differ from each other by the orientation of the OH-group in the dapo ligand. While the π'-isomer has the possibility to coordinate the OH-group which gives the πNNO-isomer there exists no such possibility for the π-isomer without previous rearrangement of the ligand sphere. Both isomers are chiral. An analogous difference exists for the two



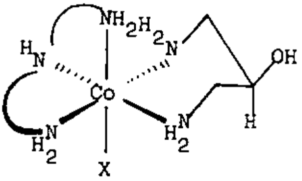
(χ')



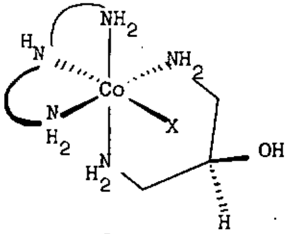
(χ)



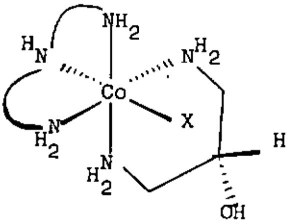
(π')



(π)



(ω')



(ω)

figure 8

πNNO ωNNO

figure 8 (cont.) : the geometrical isomers of $[\text{Co AAA dapo X}]^{n+}$ and $[\text{Co AAA dapo}]^{3+}$ (AAA = dien or dpt)

meso-fac structures ω and ω'. There exist therefore two geometrical isomers for complexes with tridentate coordinated dapo, the chiral πNNO - isomer and the meso ωNNO - isomer.

In the dien series, five different isomers were isolated and characterised (χ, χ', π, π', πNNO) by their CD-, VIS-, IR-, ^{1}H-NMR- and ^{13}C-NMR-spectra (cf. 2.5.2.) and by their base hydrolysis kinetics (cf. 2.6.). The yield of the different mononuclear chloro complexes is strongly dependent of the reaction temperature and the time between the end of the preparation and the precipitation of the product. It was shown by ion exchange chromatography (Dowex 50W X2; 100-200 mesh) that a fresh reaction mixture of the mononuclear pentaamine Co(III) - complexes contained no πNNO - isomer. The κ- aqua compound isomerizes in acid solution to afford a π- type isomer. Dioxygen oxidation of the labile Co(II) precursor complex gave the π' - isomer in very small isolated yield only and the κ'-isomer was never found. The last was prepared from the κ'-azido complex by addition of hydrochloric acid and precipitated as the tetrachlorozincate salt.

The bromo complexes were prepared either by reacting the corresponding hydroxo complexes prepared by silver (I) or mercury (II) assisted hydrolysis of the chloro compounds with hydrobromic acid and zinc bromide or by reacting the corresponding azido complexes with hydrobromic acid.

The azido complexes were either obtained from neutral aqueous solutions of the corresponding chloro or aqua complexes with an excess of sodium azide or by hydrolysis of the corresponding chloro complexes in alcaline solutions in presence of an excess of sodium azide. The azido compounds were crystallized as tetrachlorozincate salts by addition of zinc chloride and lithium chloride. Base hydrolysis of the κ- chloro complex in sodium azide containing solution afforded a mixture of the κ- and κ'-isomers in a ratio of about 1 : 1.5 (^{1}H-NMR). These mixtures were precipitated fractionally from aqueous solutions by addition of sodium antimonyl - L - tartrate.

In the dpt - series only one isomer was isolated which was characterised by its CD-, VIS- and ^{13}C-NMR-spectra as the κ- isomer (cf. ref. [75-78]).

2.4.3. RESOLUTION OF ENANTIOMERS

All complexes resolved in this work are cations. They were resolved by precipitation of the less soluble diastereomeric salt with an optically active anion, such as sodium arsenyl - L - tartrate or sodium antimonyl - L - tartrate. To aqueous solutions - the presence of lithium chloride increased in some cases the optical yield - of the complexes was added half an equivalent of the optically active anion. The precipitate was recristallized from aqueous solutions containing the resolving reagent. This procedure was repeated until constant ellipticity was reached.

2.5. SPECTROSCOPY AND STRUCTURAL ASSIGNMENTS

2.5.1. Co dipic A A X $^{\pm n}$ - COMPLEXES

The tridentate ligand dipic^{2-} is coordinated meridionally as in all known complexes of this ligand for which X-ray structure determinations exist [79-81].

The VIS-spectral data of most of the new compounds are listed in table 4. Since the chromophores have low symmetry, the position of the maxima is influenced by the relative intensity of overlapping components of the spectral bands. For example, the long wave length maximum of Co dipic$_2^-$ occurs at slightly higher frequencies than that of Co dipic dien$^+$, contrary to a simple prediction based on donor atom positions in the spectrochemical series. This is mainly due to the distorted coordination geometry caused by the dipic^{2-}- ligand. The band positions have therefore limited value in determining the set of donor atoms. However, structural assignment of the three trans-[Co dipic $(NH_3)_2$ X]$^{n+}$ complexes may be supported by the VIS-spectral properties. The yellow-brown species, a non-electrolyte, has the low energy transition (derived from octahedral $^1A_{1g} \rightarrow {}^1T_{1g}$) at 465 nm and the second transition (derived from octahedral $^1A_{1g} \rightarrow {}^1T_{2g}$) is not observed because of overlap with a strong charge transfer transition. Both are characteristic for N-bound Co(III) - nitro complexes (cf. table 4). On the other hand the two other isomers have VIS-spectral properties which are characteristic for Co dipic A A X $^{\pm n}$- species with a ligand X with an oxygen donor.

substance	λ nm / ε l mol^{-1} cm^{-1} (min, max, sh)
[Co dien dipic] Cl	518/209.1(max);461/121.8(min);434/138.8(max);393/90.5(min)
NH_4[Co $dipic_2$]	512/656(max);428/69(min);383(sh)
[Co en_2 $(NO_2)_2]_2$	514/307(max);488/289(min)
[Co dipic $(NO_2)_3$]	
cis-[Co en_2 $(NO_2)_2]^+$ a)	437/177.8(max)
trans-[Co en_2 $(NO_2)_2]^+$ a)	430/199.5(max)
Na_2[Co dipic $(NO_2)_3$]	520/319(max);484/264(min)
[Co dipic $(NH_3)_3$] NO_3	537/227(max);410/42(min);436(sh);340(sh)
trans-[Co dipic $(NH_3)_2$ NO_2]	465/121.4(max);414/58(min)
trans-[Co dipic $(NH_3)_2$ ONO] b)	524(max);438(min);360(max)
trans-[Co dipic $(NH_3)_2$ OH_2] NO_2	520(max);425(min);350(sh)
Co dipic en OH	507/242.2(max);410/46.4(min);340(sh)
[Co dipic en OH_2] X	
X = NO_3^-, Cl^-, Br^-, $\frac{1}{2}SO_4^{2-}$, CH_3COO^-, $C_2O_4H^-$	518/243.3(max);418/43.5(min);358/165(max);348/162.1(min)
Co dipic en Cl c)	520/255.1(max);437/67.7(min);375(sh)
Co dipic en N_3 c)	510/301(max);445/169(min)

table 4

Co dipic en SCN c)	520/345(max);440/257(min)
[Co dipic en dmso]NO_3	512(max);430(min);370(sh)
[Co dipic dapo ONO]	532/228(max);460/87(min)

table 4 (cont.) : VIS-spectral parameter of Co dipic A A $X^{\pm n}$ - complexes and related compounds in distilled water at 25.0 ± 0.1 °C

a) ref.[82]

b) reflection spectrum

c) solvent: dmso

Infrared spectroscopy of the complexes containing dipic^{2-}, two ammonia or a diamine and a monodentate ligand served as a useful characteristic of the species. Although the spectra were not fully analysed, the comparison with reference spectra and literature values [83-87] allowed to determine some bands of diagnostic value. Coordinated dipic^{2-} has the following characteristic bands: 1080 - 1090 cm^{-1} (intense, sharp), 910 - 920 cm^{-1}, 680 - 695 cm^{-1}. The carbonyl band for coordinated dipic^{2-} (1670 - 1630 cm^{-1}) lies between the lines for free H_2dipic (1700 cm^{-1}) and free dipic^{2-} (1600 cm^{-1}). The C≡N - stretching frequencies occurs at 2100 cm^{-1} for the N-bounded thiocyanato complex [83] and the azide ion absorbs at 2040 cm^{-1} and 1335 cm^{-1} in the azido complex [84]. For the presumed O- and N-bonded nitro complexes, none of the characteristic frequences of the nitrite ion have been observed [85] in the spectra of the dipic complexes and we cannot presently identify the NO_2 bonding mode with certainty. Linkage isomerism is also possible for dmso [86] and this ligand has been considered to be oxygen-bonded in $[Co\,(NH_3)_5\,dmso]^{3+}$ [87] on the base of a low energy shift of the ν_{SO} streching frequency to about 930 - 950 cm^{-1}. In [Co dipic en dmso]NO_3, a strong broad band at 930 cm^{-1} with shoulders at 940 cm^{-1} and 960 cm^{-1} is assigned to this vibration. This band does not appear in [Co dipic en OH_2]NO_3 and we infer bonding through oxygen in this dmso complex.

The ^{1}H-NMR spectra typically show a relatively complex seven- to thirteen-line pattern for the three aromatic protons of coordinated dipic^{2-} (fig. 9). In contrast, a two line pattern with a coupling constant of less than

1 Hz is found for H_2dipic (8.38 ppm) and Na_2dipic (8,01 ppm) in D_2O and this feature has been used to test for free dipic^{2-} in reaction mixtures. In the Co dipic en X $^{n+}$ series, the ethylenediamine methylene protons generally appear as two quintet patterns (intensity ratio about 1 : 4 : 6 : 4 : 1) owing to very similar coupling to vicinal CH and NH protons (fig. 9). In alcaline solutions containing the hydroxo complex (X = OH), the amine functions are deuterated and the resulting methylene proton pattern may be described phenomenologically as two sets of doublets with some mutual effect on the line intensities (fig. 9).

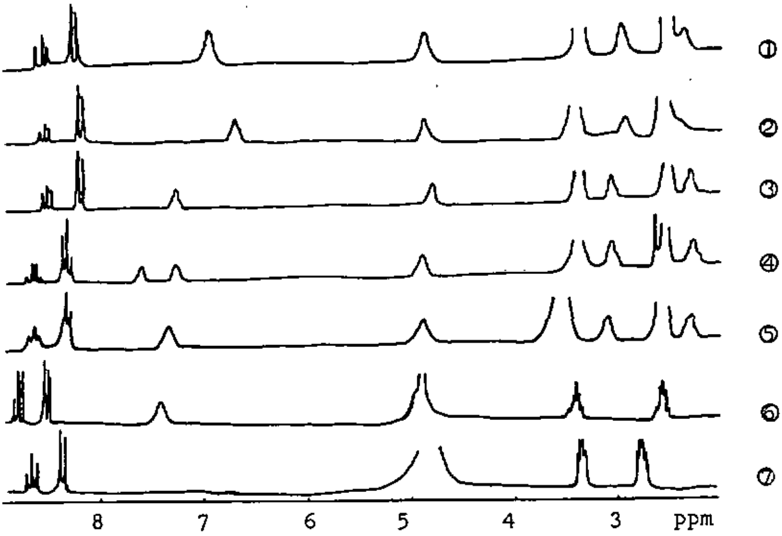


figure 9 : 200 MHz ^{1}H-NMR spectra of [Co dipic en X]$^{n+}$ complexes in DMSO-d_6 (① - ⑤) or D_2O (⑥ , ⑦) relative to internal TSP.
① : X = N_3^-; ② : X = NO_2^-; ③ : X = Cl^-;
④ : X = dmso; ⑤ : X = OH_2; ⑥ : X = OH_2;
⑦ : X = OH^-

On the whole, these patterns are sharp and simple owing to the large inequivalence of the methylene groups adjacent to the cis and trans amine functions relative to the unidentate ligands.

The amine protons are observed in acid D_2O / D_2SO_4 solutions (pD ≈ 3). They exchange slowly in this medium. The two NH_2 - groups are strongly nonequivalent in Co dipic en $X^{\pm n}$ species, one occuring at about 7.3 ppm and the other near 4.8 ppm (fig. 9), thus overlapping with the HOD - signal. The last is observed in DMSO-d_6 - solutions. In Co dipic en dmso$^+$ dissolved in DMSO-d_6 the NH_2 protons at low field give rise to two separate resonances. In Co dipic dapo OH_2^+ the same inequivalence is observed for both NH_2 - functions, but no such splitting is observed in Co dipic en Cl. Inequivalence as observed in the first two cases is attributed to solvation effects and has been observed previously [88,89]. Since this inequivalence of the amine protons in the ethylenediamine series is influenced by the leaving group, we may assign them to the amine function cis to the leaving group. An irradiation experiment on Co dipic en OH_2^+ ion showed that the ethylenediamine methylene protons at low field couple to the amine group at low field, cis to the leaving group (fig. 10).

Yoneda and coworkers [90] have found for Co A_5 Cl^{2+} complexes that trans NH_2 - protons appear at higher field. The observed positions for the amine protons in $[Co\ dipic\ (NH_3)_3]^+$ in D_2O (5.2 ppm (3 H) and 3.7 ppm (6 H)) can serve as a guide in the structural assignment in $[Co\ dipic\ (NH_3)_2\ X]^{n+}$ complexes. For the three different unidentate ligands X = H_2O (D_2O), NO_2 (DMSO-d_6) and ONO

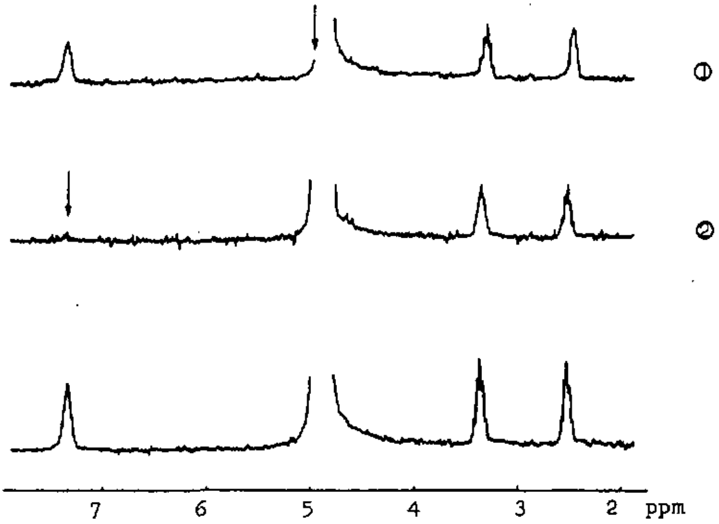


figure 10 : 200 MHz ^{1}H-NMR spectra of [Co dipic en OH_2]$^+$
in D_2O / D_2SO_4 relative to internal TSP
①: irradiated at 4.93 ppm
②: irradiated at 7.34 ppm

(DMSO-d_6), amine proton signals are found at 4.1, 4.4 and 3.6 ppm, respectively. This is consistent with the position of ligand X trans to the pyridine nitrogen donor and therefore a trans arrangement of the two ammine ligands.

2.5.2. Co AAA dapo X $^{n+}$ - COMPLEXES

The VIS - spectral parameters of these complexes are listed in table 5. The differences between complexes with meridionally and facially coordinated dien are qualitatively the same as for Co dien tmd X $^{n+}$ - complexes [75]. In the region of the transitions at lower energy (components of the parent octahedral $^1A_{1g} \rightarrow {}^1T_{1g}$ transition) the absorption band is split for the Co AAA dapo X $^{n+}$ isomers. The change of intensities of the two bands in this region (460 - 495 nm, 530 - 545 nm for AAA = dien; ~560 nm for AAA = dpt) owing to different distortions of the octahedral symmetry is a good means for assigning facial or meridional coordination of the tridentate ligand (fig. 11).

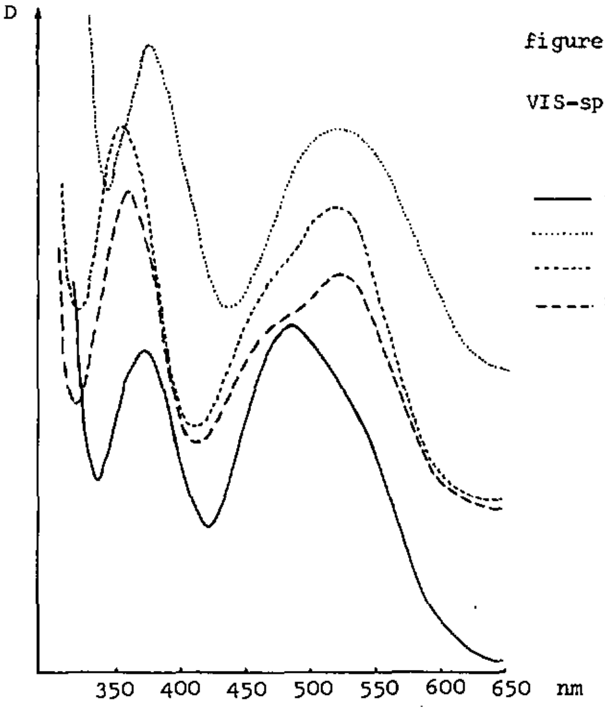


figure 11 :

VIS-spectra of

substance	λnm / ε l mol^{-1} cm^{-1} (min, max, sh)
x- $[Co\ dien\ dapo\ Cl]^{2+}$	530(sh);484/79(max);422/29.4(min);372/73.4(max);334/39.1(min)
π- $[Co\ dien\ dapo\ Cl]^{2+}$	535/73.7(max);495(sh);422/21.8(min);370/100(max);328/35(min)
π'- $[Co\ dien\ dapo\ Cl]^{2+}$	532/71.8(max);490(sh);420/20(min);368/90(max);322/45(min)
πNNO- $[Co\ dien\ dapo]^{3+}$	474/58(max);402/13.9(min);344/84.8(max);305/22.9(min)
πNNO- $[Co\ dien\ dapo]^{2+}$ (deprot.)	484/61(max);429/27(min);380/111.4(max);354(sh);320/61(min)
x- $[Co\ dien\ dapo\ N_3]^{2+}$	510/262(max);435/64(min)
x- $[Co\ dien\ dapo\ Br]^{2+}$	540(sh);482/87(max);428/51(min)
x- $[Co\ dien\ dapo\ OH_2]^{3+}$	474/94.3(max);410/30(min);342/59(max);330/34.6(min)
π- $[Co\ dien\ dapo\ N_3]^{2+}$ a)	516/345.5(max);440/72.1(min)
π- $[Co\ dien\ dapo\ Br]^{2+}$ a)	532/71(max);490(sh);422/21(min);370/96(max);330/33(min)
π- $[Co\ dien\ dapo\ OH_2]^{3+}$	484/83(max);408/21(min);346/80(max);321/21(min)
π'- $[Co\ dien\ dapo\ OH_2]^{3+}$	480/81(max);408/20(min);340/78(max);322/34(min)
x'- $[Co\ dpt\ dapo\ Cl]^{2+}$	520/67.3(max);434/22(min);376/87(max);342/51(min)

table 5 : VIS-spectral parameter of Co AAA dapo $X^{\pm n}$ - complexes
in distilled water of pH ≅ 3 ($HClO_4$) at 25.0 ± 0.1 °C
a) ref. [91]

In all known cases, one of the two low-energy absorption bands has a higher extinction coefficient for facial and a smaller extinction coefficient for meridional coordination. The high energy band of the πNNO - isomer is very sensitive to deprotonation of the coordinated OH - group and the pK_a - value ($pK_a = 2.74 \pm 0.05$; determined by potentiometric titration at 25.0 ± 0.1 °C; $\mu = 1.0$ ($NaClO_4$)) was thus also measured spectrophotometrically (fig. 12) to give agreement with the first result ($pK_a = 2.72$; $T = 25.0 \pm 0.1$ °C; $\mu = 1.0$ ($NaClO_4$)).

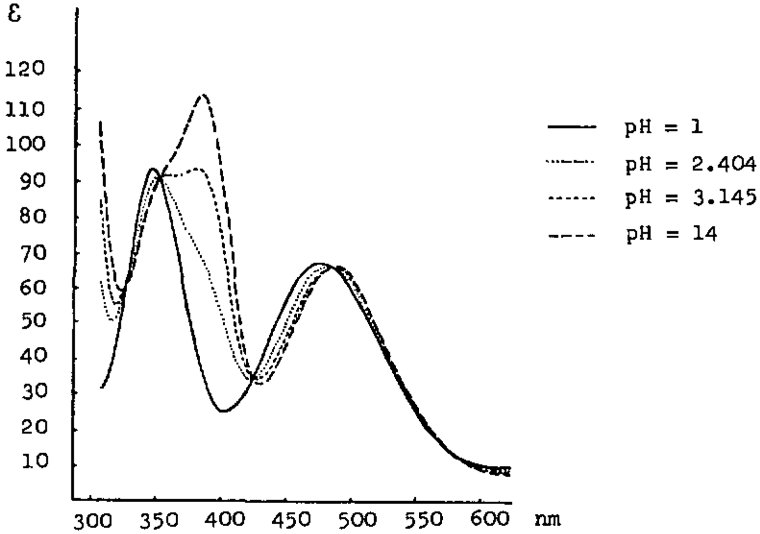


figure 12 : VIS-spectra of πNNO-[Co dien dapo]$^{3+}$ in various buffers [69]

All compounds show the usual two CD-absorption bands in the region of the low energy transition (derived from octahedral $^1A_{1g} \rightarrow {}^1T_{1g}$) with opposite sign. The CD spectra in the region of the second transition (derived from octahedral $^1A_{1g} \rightarrow {}^1T_{2g}$) are very sensitive to the leaving group. The isomers with meridionally coordinated dien or dpt have phenomenologically nearly the same CD-spectra as [Co bamp dapo Cl]$^{2+}$ [26,27] which also has a meridionally coordinated tridentate amine ligand (fig. 13).This similarity is attributed to the same source, viz. the OH - group of dapo as the only disturber of symmetry of all three chromophores in question. It destroys the time-average mirror plane present in the analogous tmd complex.

Optically active facial isomers are easily distinguished from meridional ones by their intensities of the transitions. The optical activity of the x- isomers may be attributed to a conformational effect induced by the OH substituent of dapo [26,92]. The resulting disturbance of symmetry is remote from the chromophore and causes a small CD - effect. On the other hand, the optical activity of the π- type isomers arises from a configurational effect, a dissymetric position of the ligand atoms. Their CD - intensities are therefore ~5 - 6 times higher.

The ^{1}H-NMR spectra of Co dien dapo X $^{\pm n}$ - complexes were compared with the dien- and dapo-complexes in the dipic series (fig. 14). The signal of the secondary dien amine proton has the highest chemical shift. Its exchange rate in complexes with meridionally coordinated dien is higher than that of all other cis amine protons (cf. 2.6.3.).

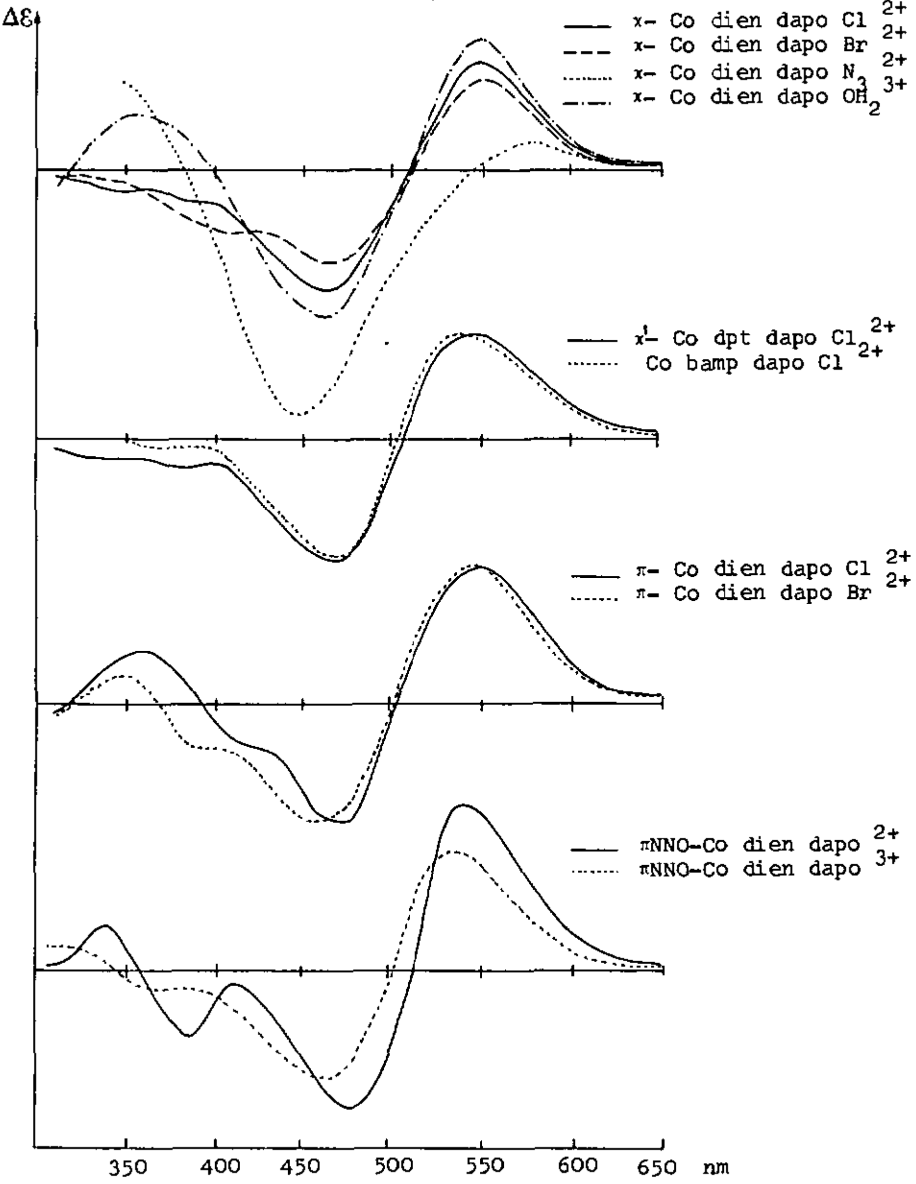


figure 13 : CD - spectra of optically active Co(III) complexes with dapo and either dien, dpt or bamp (arbitrary ordinate scale).

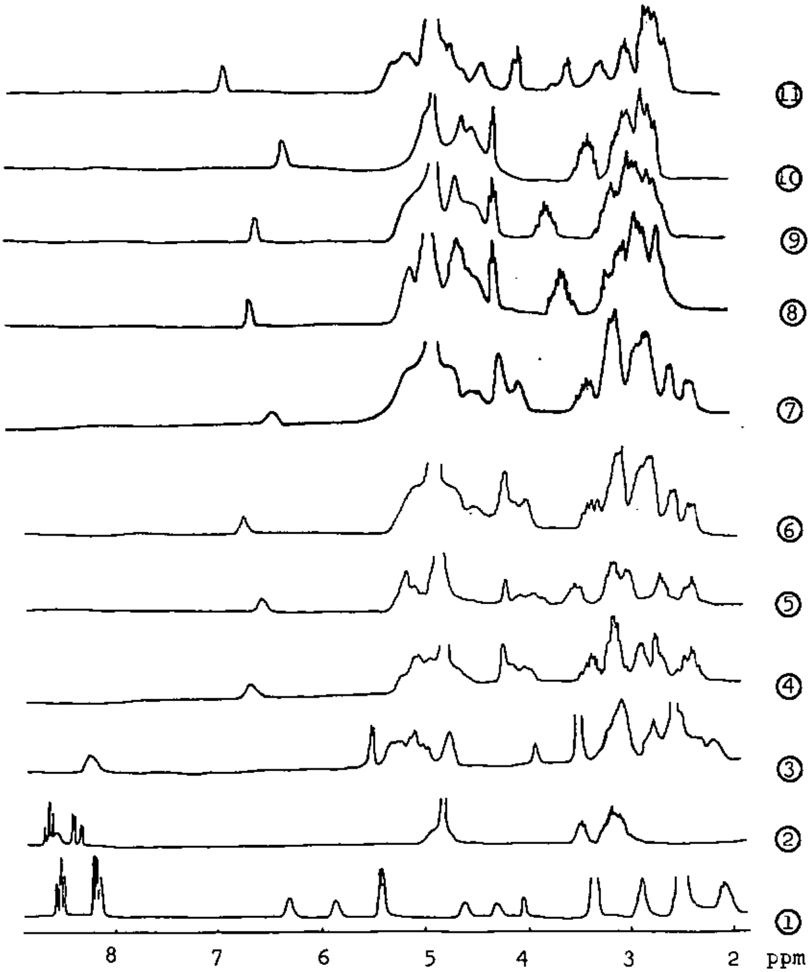


figure 14 : 200 MHz ^{1}H-NMR spectra in DMSO-d_6 (① - ③) or D_2O/D_2SO_4 (④ - ⑪) relative to TSP :

① Co dipic dapo ONO

② Co dipic dien $^+$

③ κ- Co dien dapo Cl^{2+}
④ κ- Co dien dapo Cl^{2+}
⑤ κ- Co dien dapo Br^{2+}
⑥ κ- Co dien dapo N_3^{2+}
⑦ κ'- Co dien dapo N_3^{2+}
⑧ π- Co dien dapo Cl^{2+}
⑨ π- Co dien dapo Br^{2+}
⑩ π- Co dien dapo N_3^{2+}
⑪ π'- Co dien dapo Cl^{2+}

In the same complexes, the trans amine protons have the lowest chemical shifts and the highest exchange rates (cf. 2.6.3.). They normally appear at higher field than the cis amine protons [90,93], and it is well known that their exchange is slower in CoA_5Cl^{2+} complexes than in cis amine protons [94]. The cis amine protons of dapo and dien are partly buried under the HOD signal. They all can be observed when spectra are carried out in DMSO-d_6 - solutions. The main difference in ^{1}H-NMR spectroscopy between the κ and κ' isomers of the azido complex lies in the different chemical shift of the secondary amine protons (fig. 14).

^{13}C-NMR spectroscopy is perhaps the simplest method to distinguish and to structurally characterize the different isomers of Co dien AA X^{n+}- and Co dpt AA X^{n+}- complexes. Owing to the differences in symmetry between κ-, π- and ω-type isomers (cf. fig. 8), the number of ^{13}C-NMR signals are different. Since there are symmetry equivalent carbon nuclei, the number of lines is reduced in κ and ω isomers.

This is strictly true only for species with no other than methylene carbons. For x dapo complexes, the two pairs of dien carbons are only nearly equivalent (see below). Furthermore, their chemical shifts show nearly no influence of the leaving group X (fig. 15). The attribution of the different signals to specific carbon atoms is possible by comparison of the spectra of the different isomers with each other and with other complexes containing coordinated dien, dpt or dapo (fig. 15, table 6).

The carbon atoms in the dien and dpt ligands in several mer-cis-[Co dien A_2 X$]^{n+}$ - species are pairwise nearly or perfectly isochronous [95,96]. The small splitting of the two or three corresponding resonances is attributed to the presence of the OH - group in the six membered chelate ring which influences its conformational equilibrium position. This small, distant effect is transduced to the carbon atoms of the tridentate ligands.

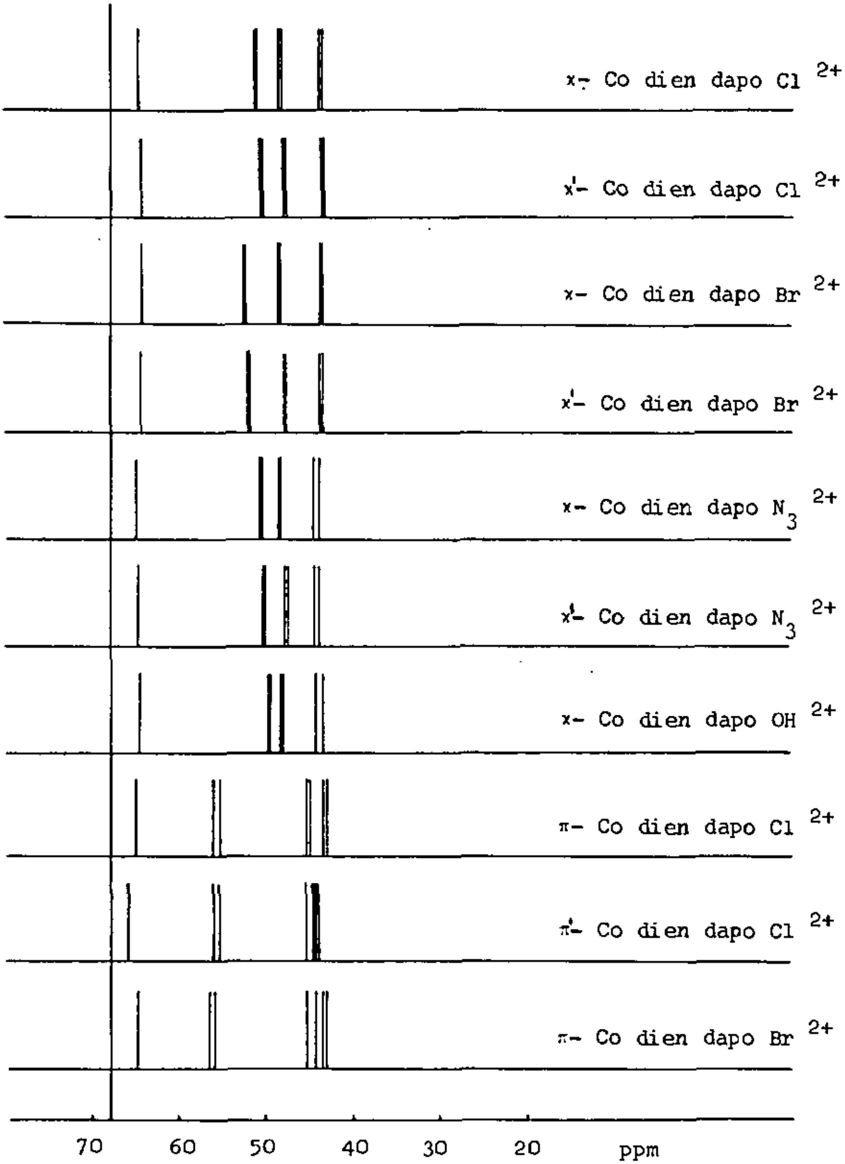


figure 15: 50.32 MHz ^{13}C NMR-spectra in D_2O/D_2SO_4 relative to internal Dioxan (67.4 ppm)

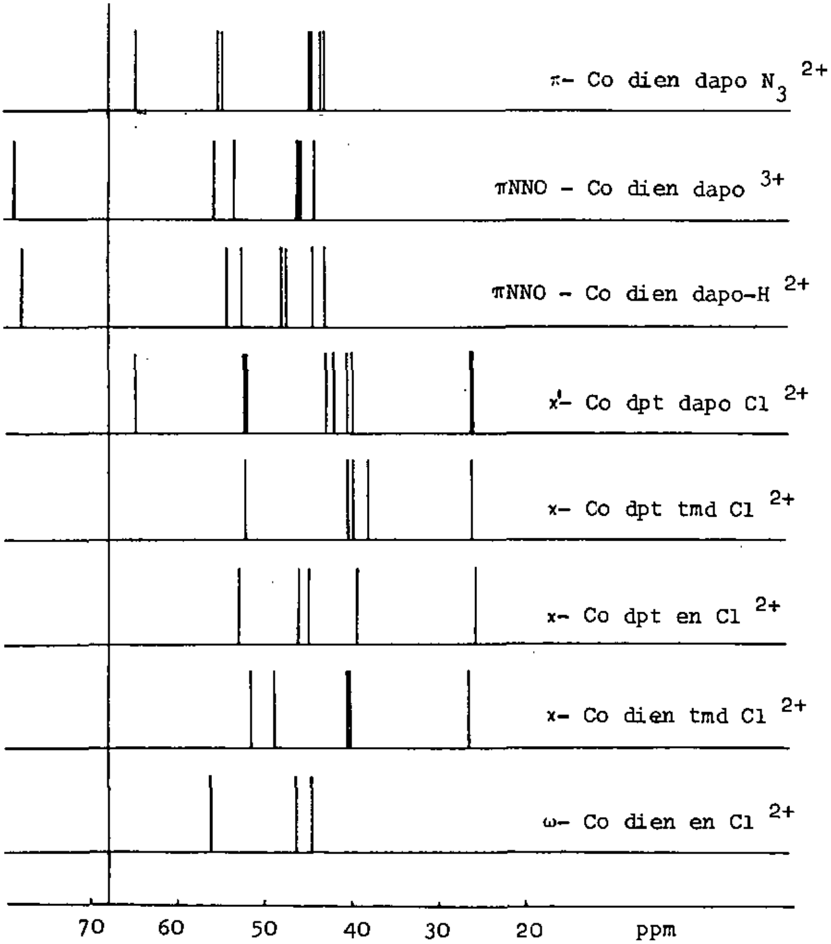


figure 15 (cont.)

substance	a)	b)	c)
κ-CodiendapoCl^{2+}	64.1	51.0;51.0;48.3;48.2	43.6;43.4
κ'-CodiendapoCl^{2+}	64.0	50.3;50.1;47.8;47.4	43.4;43.2
κ-CodiendapoBr^{2+}	63.8	52.1;52.0;48.2;48.1	43.5;43.2
κ'-CodiendapoBr^{2+}	63.2	51.3;51.1;47.2;47.1	43.1;43.0
κ-CodiendapoN_3^{2+}	64.5	50.3;50.1;48.2;48.1	44.2;43.6
κ'-CodiendapoN_3^{2+}	64.3	49.9;49.8;47.4;47.1	44.0;43.5
κ-CodiendapoOH^{2+}	64.4	49.6;49.6;48.1;48.0	44.1;43.4
π-CodiendapoCl^{2+}	64.6	55.7;55.0;45.0;44.7	43.0;42.7
π'-CodiendapoCl^{2+}	65.3	55.8;53.9;45.043.9	44.1;43.6
π-CodiendapoBr^{2+}	64.5	56.2;55.7;45.2;44.1	43.4;42.9
π-CodiendapoN_3^{2+}	64.4	54.8;54.3;44.4;44.2	43.2;42.8
πNNO-Codiendapo^{3+}	78.2	55.2;52.9;45.5;43.8	45.5;45.5
πNNO-Codiendapo^{2+}	77.4	54.0;52.4;44.4;43.0	47.9;47.4
κ'-CodptdapoCl^{2+}	64.4	51.9;51.6;40.2;39.5;25.8;25.7	42.5;41.6
κ-CodpttmdCl^{2+}	25.6	51.6;39.9;25.4	39.3;37.7
κ-CodptenCl^{2+}		52.4;38.9;25.2	45.7;44.5
κ-CodientmdCl^{2+}	25.9	50.8;48.2	39.8;39.5
ω-CodienenCl^{2+}		55.6;45.8	44.0

table 6 : 50.32 MHz ^{13}C-NMR chemical shifts of aqueous solutions relative to internal dioxan (67.4 ppm) in ppm

a) tertiary carbon of dapo

b) methylene carbons of dien or dpt

c) methylene carbons of dapo

2.6. REACTIVITY AND STEREOCHEMISTRY IN BASE CATALYZED SUBSTITUTION PROCESSES

Base hydrolysis of all complexes in aqueous buffer solutions ($\mu = 1.0$ M, $NaClO_4$ or NaN_3; 25.0 ± 0.1 °C) was followed spectrophotometrically (VIS), by stopped flow methods (SF) or with CD-spectroscopy (CD). When pseudo first order kinetics were observed, plots of $\log (D - D_\infty)$ against time were linear for at least three half-lives. The observed rate law for base hydrolysis is consistent with that usually found for base hydrolysis of Co(III) pentaamine complexes: $k_{obs} = k_{OH}[OH^-]$ (cf. 1.1.2.). The products of each reaction were analysed by their ^{13}C-NMR-, VIS- and CD-spectra for optically active materials.

In this chapter, the data tables list the values of k_{OH} (base hydrolysis) or of k_{OD} (proton exchange). The corresponding values of k_{obs} are calculated by multiplying k_{OH} or k_{OD} by the pertinent OH^- or OD^- concentration from the given pH or pD values. pK_w values are indicated in each table.

2.6.1. BASE HYDROLYSIS RATES OF Co(III) COMPLEXES WITH MERIDIONALLY COORDINATED dien, dapo AND A MONODENTATE LEAVING GROUP

The base hydrolysis rate of x-[Co dien dapo Cl]$^{2+}$ is within the error the same as that of x-[Co dien tmd Cl]$^{2+}$ [65]. The influence of the dapo hydroxy group is therefore even less important than that observed for the Co bamp AA X - systems where AA = tmd or dapo [26]. The x-isomers of Co dien dapo X - complexes with X = Cl^-, Br^- and N_3^- respectively have the highest base hydrolysis rates measured so far in Co(III) pentaamine chemistry. This feature is discussed in terms of the π-bonding model (cf. 3.). Data are presented in tables 7-9. The initial product of base hydrolysis is shown by their ^{13}C-NMR spectra to be $\geq$95% x-[Co dien dapo OH]$^{2+}$ ion. This isomerizes slowly to π-[Co dien dapo OH]$^{2+}$. The observed rate constant for this reaction was measured at 25 °C or 45 °C in the same reaction medium as base hydrolysis. It is independent of the OH^- concentration at pH $\gtrsim$ 6.6. This subsequent isomerisation of the x-[Co dien dapo OH]$^{2+}$ is therefore at least 50 times slower than the measured base hydrolysis rates. Data are presented in table 10.

Buffer	pH a)	$k_{OH}[M^{-1}s^{-1}]$	Method
Pyridine	5.821	$1.19\ 10^5$	CD b)
Pyridine	5.821	$1.09\ 10^5$	VIS c)
Pyridine d)	6.104	$1.43\ 10^5$	CD e)
Triethanolamine	8.246	$1.11\ 10^5$	SF f)
Tris	8.255	$1.22\ 10^5$	SF f)
Diethanolamine	9.239	$1.06\ 10^5$	SF f)
Ethanolamine	9.792	$9.83\ 10^4$	SF f)
Methylamine	10.988	$1.24\ 10^5$	SF f)

$k_{OH} = (1.13 \pm 0.093)\ 10^5\ M^{-1}s^{-1}$

table 7 : base hydrolysis rates of x-$[\text{Co dien dapo Cl}]^{2+}$
T = 25.0 ± 0.1 °C; $\mu = 1.0$ ($NaClO_4$); buffer concentration: 0.1 M; $[Co]_{tot} \cong 2 \cdot 10^{-3}$ M

a) $pK_w = 13.77$

b) $\lambda = 460$ nm

c) $\lambda = 305$ nm

d) measured in 1M NaN_3

e) $\lambda = 491$ nm

f) $\lambda = 300$ nm

base hydrolysis rate of x-$[\text{Co dien tmd Cl}]^{2+}$ in the same conditions: $k_{OH} = 1.14\ 10^5\ M^{-1}s^{-1}$

Buffer	pH [a]	$k_{OH}[M^{-1}s^{-1}]$
Triethanolamine	8.239	$1.34\ 10^6$
Tris	8.253	$1.49\ 10^6$
Tris	8.274	$1.49\ 10^6$
Diethanolamine	9.219	$1.37\ 10^6$
Diethanolamine	9.238	$1.36\ 10^6$
Ethanolamine	9.705	$1.35\ 10^6$

$k_{OH} = (1.40 \pm 0.072)\ 10^6\ M^{-1}s^{-1}$

table 8 : base hydrolysis rates of $\varkappa$-$[\text{Co dien dapo Br}]^{2+}$
$T = 25.0 \pm 0.1$ °C; $\mu = 1.0$ $(NaClO_4)$; buffer
concentration: 0.1 M; $[Co]_{tot} \cong 2 \cdot 10^{-3}$ M;
SF; $\lambda = 342$ nm
a) $pK_w = 13.77$

Buffer	pH [a]	$k_{OH}[M^{-1}s^{-1}]$	Method
Tris	8.274	$1.67\ 10^2$	CD [b]
Diethanolamine	9.219	$1.22\ 10^2$	CD [b]
Diethanolamine	9.219	$1.30\ 10^2$	VIS [c]
Diethanolamine	9.238	$1.45\ 10^2$	VIS [c]
Ethanolamine	9.745	$1.14\ 10^2$	VIS [c]
Ethanolamine	9.818	$1.12\ 10^2$	VIS [c]

$k_{OH} = (1.32 \pm 0.21)\ 10^2\ M^{-1}s^{-1}$

table 9 : base hydrolysis rates of $\varkappa$-$[\text{Co dien dapo } N_3]^{2+}$
$T = 25.0 \pm 0.1$ °C; $\mu = 1.0$ $(NaClO_4)$; buffer
concentration: 0.1 M; $[Co]_{tot} \cong 2 \cdot 10^{-3}$ M
a) $pK_w = 13.77$
b) $\lambda = 490$ nm
c) $\lambda = 390$ nm

Buffer	T [°C]	pH [a]	k_{obs} $[s^{-1}]$
$HClO_4$ 1M	45.0	0	1.97 10^{-5}
Pyridine	45.0	6.200	26.7
N-ethyl-morpholine	45.0	8.070	55.6
Tris	45.0	8.450	55.7
Tris	25.0	8.500	4.8 10^{-5}
Diethanolamine	25.0	9.450	6.29 10^{-5}
Ethanolamine	25.0	9.472	5.65 10^{-5}
Methylamine	25.0	10.0	5.33 10^{-5}

$k_{obs} = (5.52 \pm 0.62)\ 10^{-5}\ s^{-1}$ $(T = 25.0\ °C;\ pH \gtrsim 6.6)$

table 10 : isomerisation rate of the base hydrolysis product of x-[Co dien dapo X]$^{2+}$
$\mu = 1.0$ ($NaClO_4$); buffer concentration: 0.1 M
$[Co]_{tot} \cong 2\ 10^{-3}$ M; VIS; $\lambda = 485$ nm
a) $pK_w = 13.77$

2.6.2. BASE HYDROLYSIS RATES OF Co(III) COMPLEXES WITH FACIALLY COORDINATED dien, dapo AND A MONODENTATE LIGAND

In this chapter we report preliminary kinetic studies of the isomers with facially coordinated dien to support by kinetic data structure and base hydrolysis mechanism of the isomers with meridionally coordinated dien. ^{13}C-NMR-, VIS- and CD- spectral analysis of the final products of the complexes reacted in alcaline aqueous solutions show that both π and π' isomers lead to the πNNO-[Co dien dapo]$^{3+}$ ion in two reation phases. As expected [65], this rate is much smaller than the base hydrolysis rate of π -[Co dien dapo Cl]$^{2+}$. It is accelerated by a factor of 24 in the π' isomer and this rate effect warrants further study. It appears consistent with the possibility of participation of the dapo hydroxy group in the transition state (fig. 16).

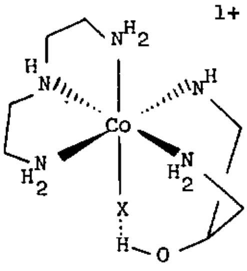


figure 16 : hypothetical transition state of base hydrolysis of π'-[Co dien dapo Cl]$^{2+}$

This would therefore support the structural assignment 𝕋' = (±)fac-endo-OH.

Both 𝕋 and 𝕋' isomers lead to cyclized product at the end of the second, slower reaction phase. The second phase is 10^4 × faster in the 𝕋' isomer relative to the 𝕋 isomer and this impressive rate difference clearly supports the hypothesis that the 𝕋' isomer is the one that cyclizes without the necessity of rearrangement at Co, i.e. (±)fac-endo-OH.

An independent argument in favor of this assignment comes from the observation that the 𝕋-isomer cyclizes with inversion of configuration (fig. 17). This is consistent with the need for rearrangement at Co in the (±)fac-exo-OH hydroxo complex. The stereochemical course is probably partial racemization with some net inversion from the qualitative observations made so far.

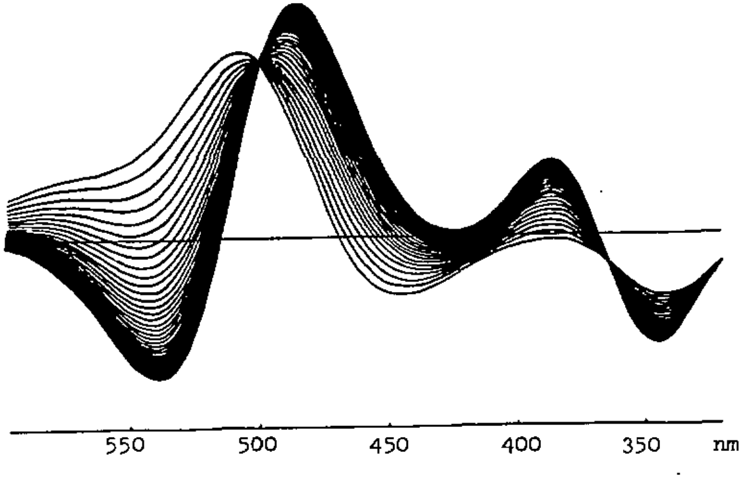


figure 17 : stereochemical change during base hydrolysis of 𝕋 - $[\text{Co dien dapo Cl}]^{2+}$ (pH = 11.11; μ = 1.0 T = 25.0 ± 0.1 °C; t = 30 min.;[97])

Buffer/ Base	pH [a]	$k_{OH}[M^{-1}s^{-1}]$	Method
NaOH	12.665	26.41	SF [b]
NaOH	12.506	21.44	SF [b]
Methylamine	10.910	23.90	CD [c]
Ethanolamine	9.750	23.09	CD [c]
Ethanolamine	9.750	29.68	VIS [b]
Diethanolamine	9.200	24.55	CD [c]
Diethanolamine	9.200	29.40	VIS [b]

$k_{OH} = 25.50 \pm 3.14 \ M^{-1}s^{-1}$

table 11 : base hydrolysis rates of $\mathbf{T}$-[Co dien dapo Cl]$^{2+}$
$T = 25.0 \pm 0.1$ °C; $\mu = 1.0$ ($NaClO_4$); buffer-concentration: 0.1 M; $[Co]_{tot} \cong 2 \cdot 10^{-3}$M; [93]
a) $pK_w = 13.77$
b) $\lambda = 305$ nm
c) $\lambda = 502$ nm

base hydrolysis rate of $\mathbf{T}'$-[Co dien dapo Cl]$^{2+}$:

$k_{OH} = 1.32 \ 10^2 \ M^{-1}s^{-1}$

($T = 25.0 \pm 0.1$ °C; $\mu = 1.0$ ($NaClO_4$); pH = 8.483 (Triethanolamine, 0.1 M); $[Co]_{tot} \cong 2 \cdot 10^{-3}$ M; VIS, $\lambda = 310$ nm)

Buffer	pH $^{a)}$	$k_{OH}[M^{-1}s^{-1}]$	Method
Methylamine	12.978	159.1	SF
Methylamine	13.040	184.2	SF
Methylamine	13.083	184.8	SF
Tris	8.253	180.9	VIS

$k_{OH} = 177.2 \pm 12.2 \ M^{-1}s^{-1}$

table 12 : base hydrolysis rates of π-$[\text{Co dien dapo Br}]^{2+}$
T = 25.0 ± 0.1 °C; $\mu = 1.0$ ($NaClO_4$); buffer-concentration: 0.1 M; $[\text{Co}]_{tot} \cong 2 \cdot 10^{-3}$ M; [91];
$\lambda = 334$ nm
a) $pK_w = 13.77$

Buffer / Base	pH $^{a)}$	$k_{OH}[M^{-1}s^{-1}]$
Methylamine	10.970	$6.997 \ 10^{-2}$
NaOH	12.875	$4.871 \ 10^{-2}$
NaOH	12.699	$4.436 \ 10^{-2}$

$k_{OH} = (5.435 \pm 1.370) \ 10^{-2} \ M^{-1}s^{-1}$

table 13 : base hydrolysis rates of π-$[\text{Co dien dapo } N_3]^{2+}$
T = 25.0 ± 0.1 °C; $\mu = 1.0$ ($NaClO_4$); buffer-concentration: 0.1 M; $[\text{Co}]_{tot} \cong 2 \ 10^{-3}$M;
$\lambda = 370$ nm; VIS; [98]
a) $pK_w = 13.77$

2.6.3. PROTONEXCHANGE RATES OF Co(III) COMPLEXES WITH MERIDIONALLY COORDINATED dien, dapo AND A MONODENTATE LIGAND

The proton exchange rates were measured for x-[Co dien dapo Cl]$^{2+}$, x-[Co dien dapo Br]$^{2+}$, x-[Co dien dapo N$_3$]$^{2+}$, x-[Co dien dapo N$_3$]$^{2+}$ and x-[Co dien tmd Cl]$^{2+}$, whose ^{1}H-NMR spectra are shown in fig. 14. The measurements were performed in 1 M acetate or 1 M formiate buffer solutions or in diluted D_2SO_4 solutions at 20 ± 2 °C and 25 ± 2 °C at different ionic strengths. Plots of log (peak surface) vs. time were constant for at least three half lives. The data fit the usually observed rate law $k_{obs} = k_{D_2O} + k_{OD}[OD^-]$ [94], but was measured only in the alcaline region. The rate constants of the primary and secondary amines are directly comparable as shown in eq 28. Proton exchange at the primary amine functions is best described as a consecutive reaction system:

$$\mathrm{NH_2} \xrightarrow[k_1]{OD^-} \mathrm{NHD} + \mathrm{OH^-}$$

$$\mathrm{NHD} \xrightarrow[k_2]{OD^-} \mathrm{ND_2} + \mathrm{OH^-} \qquad (26)$$

and the following expression for peak surface = f(t) holds as in biphasic kinetics:

$$S_t = s_{ND_2}[NH_2]_o + (s_{NH_2} - s_{ND_2})[NH_2]_o\, e^{-k_1 t} + (s_{NHD} - s_{ND_2})\,[k_1[NH_2]_o / (k_2 - k_1)]\,\left\{e^{-k_1 t} - e^{-k_2 t}\right\} \qquad (27)$$

Considering that the specific peak surfaces of NH_2 and NHD give a 2 : 1 ratio and that for reasons of mass conservation $k_1 = 2\ k_2$, this reduces to

$$S_t = s_{NH_2}[NH_2]_o\ e^{-k_1 t} - s_{NH_2}[NH_2]_o\ (e^{-k_1 t} - e^{-k_2 t})$$

where the observed rate constant is that of the second reaction, $NHD \longrightarrow ND_2$.

$$S_t = s_{NH_2}[NH_2]_o\ e^{-k_2 t} \qquad (28)$$

Data are presented in tables 14 - 17.

The protons trans to the acido group always exchange faster than the sec. amine proton with the exception of the tmd complex. The consequence of this result together with the stereochemical observations for the site of deprotonation and formation of the reactive conjugate base are discussed in chapter 3.3..

Buffer	pD [a)]	k_{OD}(secA)	k_{OD}(trans)	k_{OD}(cis)
Acetate	4.539	$5.78\ 10^6$	$2.04\ 10^7$	-
Formiate	4.641	$5.71\ 10^6$	$1.84\ 10^7$	-
Acetate	4.645	$6.83\ 10^6$	$2.64\ 10^7$	-
Formiate	4.878	$5.70\ 10^6$	$2.00\ 10^7$	-
Acetate	5.045	$6.80\ 10^6$	$2.06\ 10^7$	-
Formiate	5.091	$5.33\ 10^6$	$2.18\ 10^7$	-
Acetate	5.237	$5.94\ 10^6$	$1.65\ 10^7$	$\leq 10^5$

k_{OD} (sec-A) = $(5.97 \pm 0.56)\ 10^6 \cdot M^{-1}s^{-1}$
k_{OD} (trans) = $(2.06 \pm 0.28)\ 10^7\ \ M^{-1}s^{-1}$
k_{OD} (cis) $\leq 10^5\ \ M^{-1}s^{-1}$

Acetate [b)]	5.045	$3.30 \cdot 10^6$	$1.10\ 10^7$	-
Acetate [c)]	5.045	$7.97\ 10^6$	$1.92\ 10^7$	-

table 14 : exchange rates of the amine protons of x-[Co dien dapo Cl]$^{2+}$ in $M^{-1}s^{-1}$
T = 20 ± 2 °C; $\mu = 1.0$; buffer concentration: 1.0 M; $[Co]_{tot}$ = 0.1 M; [99]

a) $pK_{D_2O} = 14.869$; pD = pH + 0.4
b) $\mu = 0.5$
c) T = 25 °C

Buffer	pD a)	k_{OD}(secA)	k_{OD}(trans)	k_{OD}(cis)
Formiate	4.878	1.01 10^7	3.76 10^7	-
Acetate	5.237	1.17 10^7	4.50 10^7	$\leq 10^5$

table 15 : exchange rates of the amine protons of x-[Co dien dapo Br]$^{2+}$ in $M^{-1}s^{-1}$
T = 20 ± 2 °C; $\mu = 1.0$; buffer concentration: 1.0 M; $[Co]_{tot}$ = 0.1 M; [99]
a) $pK_{D_2O} = 14.869$; pD = pH + 0.4

table 16 : Preliminary experiments show that the exchange rates of the secondary amine protons of x- Co dien dapo N_3^{2+} and x'- Co dien dapo N_3^{2+} differ by a factor of about 3.

Buffer	pD a)	k_{OD}(secA)	k_{OD}(trans)	k_{OD}(cis)
Acetate	5.563	2.69 10^6	2.44 10^6	-
Acetate	5.899	2.62 10^6	2.32 10^6	$\leq 10^5$

table 17 : exchange rates of the amine protons of x-[Co dien tmd Cl]$^{2+}$ in $M^{-1}s^{-1}$
T = 20 ± 2 °C; $\mu = 1.0$; buffer concentration: 1.0 M; $[Co]_{tot}$ = 0.1 M; [99]
a) $pK_{D_2O} = 14.869$; pD = pH + 0.4

2.6.4. THE ANATION RATE OF THE κ-[Co dien dapo OH]$^{2+}$ AND κ-[Co dien dapo OH$_2$]$^{3+}$ IONS AND THE DETERMINATION OF THE pK$_a$ - VALUE OF THE AQUA COMPLEX

The anation rate was measured in aqueous buffer solutions containing sodium azide. The measurements were performed spectrophotometrically using base hydrolysed solutions of the chloro complex. Under pseudo-first order conditions, the rate is independent of the azide concentration in the range of $0.05 < [N_3^-] < 1$ M (table 18). Anation is discribed by the following reaction system:

$$\begin{array}{l} CoOH_2^{3+} \overset{K_a}{\rightleftharpoons} CoOH^{2+} + H^+ \\ CoOH^{2+} + N_3^- \xrightarrow{k^{OH}} CoN_3^{2+} + OH^- \\ CoOH_2^{3+} + N_3^- \xrightarrow{k^{OH_2}} CoN_3^{2+} + H_2O \end{array} \qquad (29)$$

The corresponding rate law is well known:

$$\text{rate} = -\frac{d[Co]}{dt}\text{tot} = k[Co]_{tot}[N_3^-] \qquad (30)$$

and under pseudo first order conditions:

$$\text{rate} = k[Co]_{tot} = (k^{OH}[CoOH^{2+}] + k^{OH_2}[CoOH_2^{3+}])[N_3^-]$$

$$k = (k^{OH}\underbrace{\frac{[CoOH^{2+}]}{[Co]_{tot}}}_{r} + k^{OH_2}\underbrace{\frac{[CoOH_2^{3+}]}{[Co]_{tot}}}_{1-r})[N_3^-] \qquad (31)$$

With the acidity constant of the aqua ion

$$K_a = \frac{[H^+]\,[CoOH^{2+}]}{[CoOH_2{}^{3+}]} \qquad (32)$$

the fraction of hydroxo complex r becomes

$$r = \frac{K_a}{K_a + [H^+]}$$

and the rate constant k can be shown to be a linear function of r (eq 33) with the intercept k^{OH_2} and the slope $k^{OH} - k^{OH_2}$

$$k = r\,(k^{OH} - k^{OH_2}) + k^{OH_2} \qquad (33)$$

Linearisation of the plot k_{obs} vs. pH therefore assists in determining the pK_a value of x–[Co dien dapo OH_2]$^{3+}$ as well as in determining the observed rate constants for the hydroxo and the aqua ion (cf. table 18, fig. 18):

$pK_s = 5.92 \pm 0.2$
$k^{OH} = 2.10\ 10^{-2}\ s^{-1}$
$k^{OH_2} = 1.0\ 10^{-3}\ s^{-1}$

The products of the reaction were analysed by ^{13}C-NMR spectroscopy and found to be the equilibrium mixture of x– and x'–[Co dien dapo N_3]$^{2+}$ (ratio ~ 6 : 4).

Buffer	pH $^{a)}$	$[N_3]_{tot}$	k_{obs} s^{-1}
Diethanolamine	9.65	1.0	$2.17 \cdot 10^{-2}$
Diethanolamine	9.52	1.0	$2.10 \cdot 10^{-2}$
N-ethylmorpholine	8.43	1.0	$2.14 \cdot 10^{-2}$
Triethanolamine	7.65	1.0	$1.98 \cdot 10^{-2}$
Pyridine	6.41	1.0	$1.29 \cdot 10^{-2}$
Pyridine	6.27	1.0	$1.34 \cdot 10^{-2}$
Pyridine	5.95	1.0	$1.12 \cdot 10^{-2}$
Azide	5.72	1.0	$8.78 \cdot 10^{-3}$
Azide	5.60	1.0	$6.60 \cdot 10^{-3}$
Azide	4.92	1.0	$2.94 \cdot 10^{-3}$
Azide	4.56	1.0	$1.09 \cdot 10^{-3}$
N-ethylmorpholine	8.43	0.85	$2.04 \cdot 10^{-2}$
N-ethylmorpholine	8.43	0.77	$2.17 \cdot 10^{-2}$
N-ethylmorpholine	8.43	0.70	$2.07 \cdot 10^{-2}$
N-ethylmorpholine	8.43	0.50	$2.13 \cdot 10^{-2}$
N-ethylmorpholine	8.43	0.25	$2.04 \cdot 10^{-2}$
N-ethylmorpholine	8.43	0.10	$2.24 \cdot 10^{-2}$
N-ethylmorpholine	8.43	0.05	$1.93 \cdot 10^{-2}$

table 18 : anation rates of x-$[Co\ dien\ dapo\ OH]^{2+}$ and x-$[Co\ dien\ dapo\ OH_2]^{3+}$ with N_3^-
$T = 25.0 \pm 0.1$ °C; $\mu = 1.0$ M; buffer concentration: ≥ 0.1 M; $[Co]_{tot} \cong 1 \cdot 10^{-3}$ M; [99]
a) $pK_w = 13.77$

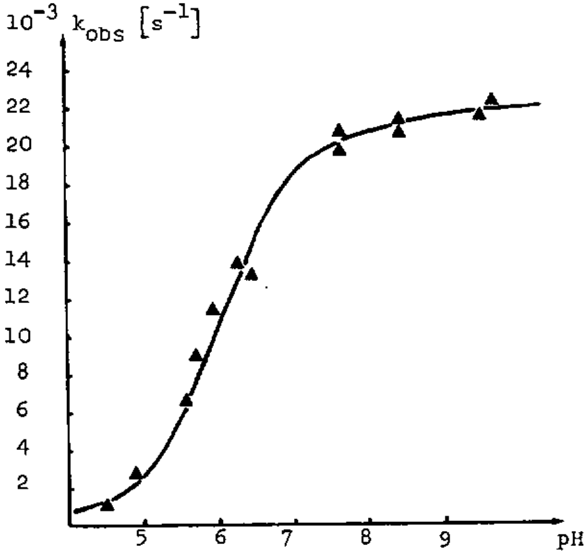


figure 18 : anation rates of ϰ-[Co dien dapo OH]$^{2+}$ and ϰ-[Co dien dapo OH$_2$]$^{3+}$ with N_3^-
$[N_3^-] = 1$ M; $\mu = 1.0$; T = 25.0 ± 0.1 °C

2.6.5. THE STEREOCHEMISTRY OF BASE HYDROLYSIS OF COMPLEXES WITH MERIDIONALLY COORDINATED dien, dapo AND A MONODENTATE LIGAND

The optically active χ-$[\mathrm{Co\ dien\ dapo\ Cl}]^{2+}$ and χ-$[\mathrm{Co\ dien\ dapo\ Br}]^{2+}$ complexes racemize to (100 ± 2) % during base hydrolysis. On the timescale of these experiments, the meridional arrangement of dien is preserved to ≥ 95 %. However, the mer-hydroxo complex racemizes faster than base hydrolysis of the chloro and bromo species in the pH range accessible for CD kinetics using conventional mixing techniques [99]. The stereochemistry of these substitutions remains therefore undetermined by these experiments. Earlier experiments first suggested some retention of configuration on a much longer timescale for the hydroxo ion but this could subsequently be attributed to some rearrangement of the aqua ion in acidic solution (cf. 2.6.1.). This rearrangement process in acidic solution interferes with attempted preparations of χ-Co dien dapo X^{2+} species where X is a very good leaving group such as NO_3^-, $CH_3SO_3^-$ or others. It is expected that base hydrolysis in these cases is much faster than racemization of the χ- hydroxo complex and if complete racemization were observed on the timescale of the complex with X, the stereochemistry of the substitution could be deduced directly. However, this method would be sensitive to the presence of small amounts of rearranged or ring-cosed products.

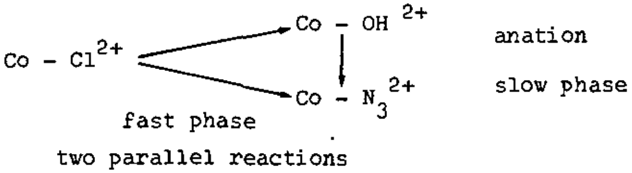
Another method consists in examining the stereochemistry of anion competition products in the base hydrolysis of χ-$[\mathrm{Co\ dien\ dapo\ X}]^{2+}$ species (X=Cl,Br). These reactions may be carried out e.g. in 1 M N_3^- and the azido complex resulting both from competition as well as from anation must be racemic if a symmetrical, trigonal-bipyramidal intermediate state of reduced coordination number is involved. In the possible case where only partial racemisation of the immediate products occurred, this would be detected by some retention (or possibly inversion) of optical activity in the azide competition product provided this does not racemize on the timescale of the experiments. On the other hand, the hydroxo ion will racemize faster than base hydrolysis of the two starting materials and the hydroxo complex from this source will give racemic azido complex by anation in the achiral medium used. The utility of this method will depend on the amount of competition which has been shown to be very high (cf. 2.6.6.). The base hydrolysis kinetics of χ-[Co dien dapo X]$^{2+}$ (X = Cl^-,Br^-) were followed in different buffered azide media ([pyridine] = 0.1 M; pH = 5.95 - 6.10; $[N_3^-]$ = 0.5 - 2 M; μ = 1.0 or 2.05). The change in CD intensity was followed at 491 nm at a sensitivity of 0.2 m°/cm. Pseudo first-order, uniphasic kinetics were observed (cf.table 7) and in all runs, Θ_∞ coincided with the base line run with the buffer solution alone. These measurements were done at the maximum value of Θ on the most sensitiv scale and, given the high competition values, an accuracy of at least ± 2% is assigned. The result is therefore (100 ± 2) % racemisation.

In a blank experiment, the CD intensity of optically active χ-azido complex was monitored at 491 nm in one of the previously used pyridine buffers (pH = 5.85). No decrease in CD intensity was found for at least 30 min. and therefore, in the above experiments, the presence of racemic azido complex is not due to racemization after its formation.

2.6.6. KINETICALLY MEASURED COMPETITION RATIOS OF Co(III) COMPLEXES WITH MERIDIONALLY COORDINATED dien, dapo AND A MONODENTATE LIGAND

The base hydrolysis reaction kinetics of χ-[Co dien dapo X]$^{2+}$ (X = Cl^-, Br^-) in the presence of N_3^- (0.25 - 1 M) and buffer (pyridine / $HClO_4$; pH = 7.96 - 8.04; $\mu = 1.0$) at 25 °C are biphasic. Both phases are accompanied by an increase in optical density at 514 nm (X = Cl^-) or 530 nm (X = Br^-), consistent with formation of the χ-azido complex. The formation of this compound has been verified by ^{13}C NMR (cf. 2.6.4.) and is essentially quantitative at the end of the reaction sequence. The pseudo-first order rate constants of these two reaction phases were determined by nonlinear regression using a computer programme [34,101]. The rate constants are relatively close to each other under the conditions of the experiment and the analysis is therefore subject to a larger error (± 21%) than usually found for uniphasic kinetics. Nevertheless, the rapid reaction phase has a rate constant ($k_{obs} = 0.146\ s^{-1}$; pH = 8.04 for X = Cl^- and $k_{obs} = 2.86\ s^{-1}$; pH = 8.04 for X = Br^-) close to that of base hydrolysis of the halogeno complexes ($k_{obs} = 0.208\ s^{-1}$ for X = Cl^- and $k_{obs} = 2.58\ s^{-1}$ for X = Br^-; values calculated from k_{OH} for pH = 8.04, cf. table 7,8) under these conditions. The slow phase has a rate constant ($k_{obs} = 2.25\ 10^{-2}\ s^{-1}$) close to that for anation of the hydroxo product ($k_{obs} = 2.10\ 10^{-2}\ s^{-1}$) and it is independent of the leaving group. Under these conditions, base hydrolysis of the azido complex will make but a negligible contribution ($k_{obs} = 2.44\ 10^{-4}\ s^{-1}$, calculated from k_{OH} for pH = 8.04, cf. table 9).

We interpret these observations by the following sequence of transformations (chelate ligands dien and dapo are omitted):



(34)

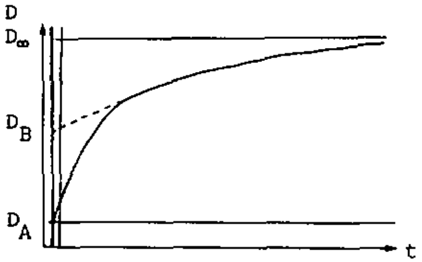
The azido complex therefore arises both from competition (fast phase) and from subsequent anation of the hydroxo complex (slow phase).

In order to determine the amount of competition, the initial concentration of the azido complex (ε_{514} = 256 M^{-1} cm^{-1}; ε_{530} = 231 M^{-1} cm^{-1}) has to be determined at the beginning of the slow phase by extrapolation to t = 0. The stopped-flow kinetics have been monitored at 514 nm and at 530 nm, the isosbestic points of Co - Cl $^{2+}$ and Co - OH $^{2+}$ and Co - Br $^{2+}$ and Co - OH $^{2+}$, respectively, where ε= 72 $M^{-1}cm^{-1}$ (X = Cl^-) and ε= 65 $M^{-1}cm^{-1}$ (X = Br^-).

In stopped-flow kinetics, care has to be taken in defining the zero-point of the time axis. This was found to be variable and the following procedure was used: The value of the optical density of the solution of starting material (without base) was recorded as a horizontal trace on the oscilloscope. To this was superimposed a kinetic trace of the biphasic reaction sequence in alcaline azide solution, maintaining the oscilloscope settings. With the aid of the computer programme, the best parameters of the following sum of exponentials:

$$Y = A\ e^{-k_1 t} + B\ e^{-k_2 t} + C$$

was fitted to the curve. The function thereby obtained was then used to find the value of Y(t=0). In an iterative procedure, arbitrary values of t = 0 and t = -1 sec were used to calculate the coordinates of the crossing point with the horizontal trace of the starting material. This intersection point was then used along with a second, arbitrary point to calculate a new intersection point. This procedure was continued until the intersection point remained invariant. For the corresponding value was calculated the extrapolated value of y for the second exponential alone (eq 35).



(35)

The following relations hold:

$$D_A = \varepsilon_{CoCl}\,[CoCl^{2+}] \qquad (36)$$

$$D_B = \varepsilon_{CoOH}\,[CoOH^{2+}] + \varepsilon_{CoN_3}\,[CoN_3^{2+}]_{comp} \qquad (37)$$

At the isosbestic point between $CoCl^{2+}$ amd $CoOH^{2+}$, $\varepsilon_{CoOH} = \varepsilon_{CoCl}$ At the end of the fast phase, the reaction mixture contains but $CoOH^{2+}$ and $CoN_3{}^{2+}$:

$$[CoOH^{2+}] = [Co]_{tot} - [CoN_3{}^{2+}]_{comp} \qquad (38)$$

Thus,

$$D_B = [Co]_{tot}\,\varepsilon_{CoCl} + [CoN_3{}^{2+}]_{comp.}\,(\varepsilon_{CoN_3} - \varepsilon_{CoCl}) \qquad (39)$$

and

$$[CoN_3{}^{2+}]_{comp} = \frac{D_B - [Co]_{tot}\,\varepsilon_{CoCl}}{\varepsilon_{CoN_3} - \varepsilon_{CoCl}} \qquad (40)$$

The competition values were calculated from this formula and are presented in table 19 and figure 19. A formula of the same type is also easily derived from

$$D = \varepsilon_C [A]_o + (\varepsilon_A - \varepsilon_C)[A]_o\, e^{-k_1 t} + (\varepsilon_B - \varepsilon_C)\, \frac{k_1 [A]_o}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t}\right) \qquad [100]$$

the general expression for any system exhibiting biphasic kinetics (A,B,C: starting material, intermediate (s), product(s)).

X	$[N_3^-]$	number of runs	$\% \ CoN_3^{2+}$
Cl^-	1.0	6	63.6 ± 5.74
Cl^-	0.5	2	47.1 ± 2.78
Cl^-	0.25	1	28.3
Br^-	1.0	1	61.7
Br^-	0.5	1	48.3
Br^-	0.25	1	30.4

table 19 : competition ratios of x-$[Co\ dien\ dapo\ X]^{2+}$

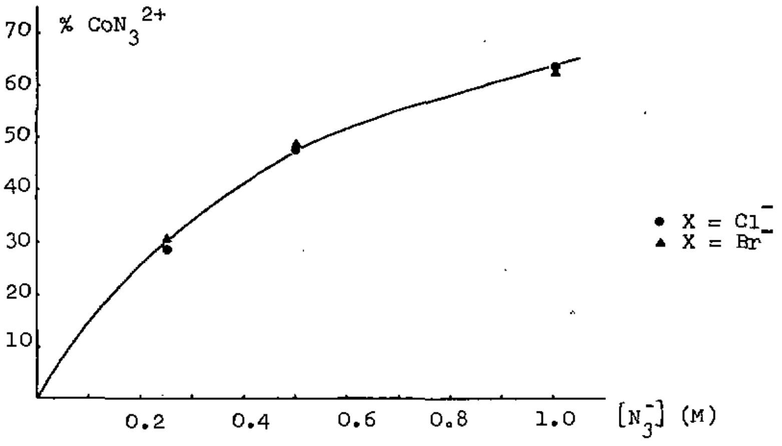


figure 19 : competition ratios of x-$[Co\ dien\ dapo\ X]^{2+}$

2.6.7. THE REACTIVITY OF Co(III) COMPLEXES WITH dipic^{2-}, TWO AMINE LIGANDS AND A MONODENTATE LIGAND

Preliminary studies of the reactivity of these complexes show that the change of charge and / or the change of the electronic structure about the Co(III) - ion lead to a marked but not very high difference in substitution ractivity. The most important change can be observed in the deprotonation equilibrium of the aqua complex. The pK_a value of $[Co\ dipic\ en\ OH_2]^+$ is 7.48 ± 0.013, i.e. about half an order of magnitude higher than for Co(III) pentaamine complexes. This is presumably due to the lower charge. On the other hand the spontaneous aquation rate of $[Co\ dipic\ en\ dmso]^+$ in neutral water at $T \cong 25$ °C and $\mu = 2 \cdot 10^{-2}$ with $k_{aq} = 9.88\ 10^{-5}\ s^{-1}$ lies in the same order of magnitude expected for Co(III) pentaamine complexes ($[Co\ (NH_3)_5\ dmso]^{3+}$; T = 25 °C; $\mu = 0.1$; $k_{aq} = 2 \cdot 10^{-5}\ s^{-1}$ [102]). The anation rate of $[Co\ dipic\ en\ OH_2]^+$ is also comparable with observed values for Co(III) pentaamine complexes [43] which are normally in a range of about $10^{-6}\ s^{-1}$ for solutions containing 1 M N_3^- ($k_{an} = 1.1\ 10^{-6}\ s^{-1}$; 1 M N_3^-; T = 25 °C).

3. DISCUSSION

3.1. AZIDE COMPETITION

When Co(III) pentaamine complexes are base hydrolysed in presence of competing nucleophiles Y such as azide, thiocyanate, nitrite, sulfate, methanol or others, a procuct mixture of CoA_5OH^{n+} and CoA_5Y^{m+} results (cf. 1.2.2.), where the amount of CoA_5Y^{m+} generally is rather small (about 10-30% for solutions of 1 M Y; tables 2 and 20). The product ratios CoA_5OH^{n+} / CoA_5Y^{m+} show but a very small dependence of the leaving group [52,58,102]. These results are usually taken to indicate a common intermediate of reduced coordination number [12] and the competition ratios are taken to be a relative measure of the lifetime of this inermediate state [64]. The competition of x-[Co dien dapo X]$^{2+}$ (X= Cl$^-$, Br$^-$) for azide of 63 % suggests that this system has the most stable intermediate state of reduced coordination number observed so far. This remarkable stabilisation is also reflected in the highest base hydrolysis rate of a chloro Co(III) aliphatic pentaamine complex ever measured so far. For a completely unselective intermediate state formed in 1 M N_3^- / 55.6 M H_2O, a product mixture containing only 1.8% azido complex is predicted. So far, all competition experiments have given higher amounts of azido complex and this can be interpreted in terms of selectivity of an intermediate [20].

Some anomalies in ion competition such as a small leaving group dependence and nonlinear plots of the ratio CoA_5Y^{m+} /

CoA_5OH^{n+} vs. concentration of the competing ion are discussed in more recent papers in terms of a dissociative interchange mechanism with ion pairing in the intermediate state [58,102]. We note that plots of competition ratio vs. concentration of the competing ion are generally nonlinear and are only approximatively linear for low competition ratios and in a limited concentration range. Our results (cf. 2.6.6.) fit the function $F(Y) = [Y] / (1-R_m^{-1})$ $(R_m = k_Y / k_{H_2O})$, which is the general expression for competition in the absence of ion pairing [34]. Independently, the fact that the azido complex resulting from base hydrolysed optically active chloro complex in azide containing solutions is completely racemic can only be interpreted with an achiral intermediate state, which would not be the case for any interchange mechanism. This result is certain to a high degree of accuracy of the measurements owing to the high competition ratio. Sargeson and coworkers [52] observed that the competition ratios in Co(III) pentaamine complexes differ only by a factor of about 5 in changing the competing nucleophiles over a wide range. They argue that the rate controlling step is the abstraction of the nucleophile from the solvent sheath surrounding the reactant. Ion pairing concerted with the rate determining step should afford a much greater difference in competition ratios. In the limiting dissociative mechanism, the observation that the competition ratios are slightly dependent on the charge of the leaving group is explained by differences in the relative rates of anion capture and rearrangement of the solvent sheath. The leaving group dependence implies that the solvent sheath remains the same as in the starting complex or is at least still influenced by the starting material. Anion capture is therefore faster or comparable in rate with rearrangement of the solvent sheath.

The observation of a leaving group dependence for substrates of different charge is, however, not necessarily consistent with a concerted substitution process with dissociative activation (I_D). It can be seen as a consequence of extremely short lifetimes in a stepwise substitution. The observed absence of anion-dependent terms in the rate law for substitution for a variety of substrates and entering nucleophiles is inconsistent with concerted substitution and so is the general lack of correlation between competition ratios and the expected stability of ion aggregates with the reactants.

3.2. IMPLICATIONS OF RACEMISATION DURING BASE HYDROLYSIS

The high stabilisation of the intermediate state has the stereochemical consequence of full racemisation during base hydrolysis. In this sense the intermediate has effectively lost all memory of the optically active starting compound and it is therefore evident that the leaving group is completely abstracted from the first coordination sphere before entering of the new ligand. It is furthermore evident that attack of H_2O which affords a racemic product with the same configuration as the starting material from an optically active complex must be an attack at a fully achiral trigonal bipyramidal state.

If we exclude deprotonation at a primary amine cis to the leaving group (cf. 2.6.3., 3.3.), there exist two possible trigonal bipyramidal intermediate states with meridional configuration of dien (fig. 20).

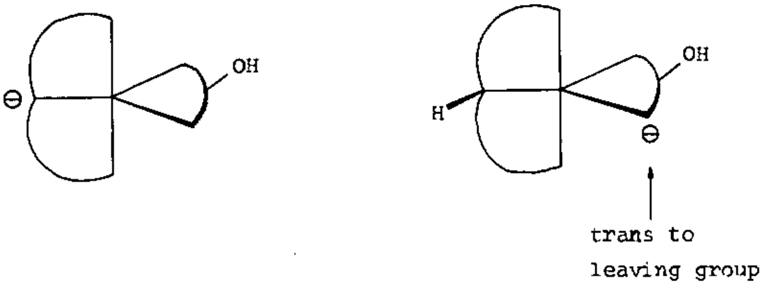


figure 20 : a chiral and an achiral trigonal bipyramidal intermediate state

Only the conjugate base deprotonated at the secondary amine affords an achiral intermediate state with the possibility of π-bonding. It has been argued that deprotonation induces dissymmetry in the intermediate which affects the product stereochemistry [104]. Therefore, complete racemization is not expected to be consistent with deprotonation trans to the leaving group.

3.3. PROTON EXCHANGE RATES AND THE SITE OF DEPROTONATION

The site of deprotonation in the conjugate base is dicussed controversially in the literature. Coordinated aliphatic amines normally have pK_a - values greater than 14 and thus are not measurable in aqueous solutions. Consequently, they cannot be determined separately from the usual rate law of base hydrolysis. Measurements of the exchange rates of the amine protons with the deuterated solvent by ^1H-NMR - techniques establish the N-H acidities on a relative scale [33]. Our measurements show once more that isolated exchange rates have no necessary implication on the base hydrolysis mechanism, because it is not necessary that the most acidic amines afford the most reactive conjugate base, provided the exchange rate is faster than base hydrolysis. An increase in acidity by a factor of about 4 in the case of the amine protons trans to the leaving group relative to the secondary amine which presumably affords the most reactive conjugate base does not necessarily provide an argument against our hypothesis of deprotonation of the secondary amine function in the reactive conjugate base. In any alkaline solution there will be comparable concentrations of the two conjugate bases arising from trans and secondary amine deprotonation. Secondary amine deprotonation is still about 10 times faster than base hydrolysis of coordinated chloride. Protons at amines trans to the leaving group normally exchange faster than the ones cis to the leaving group [94,105]. Nordmeyer [106] postulates that usually the amines cis to the leaving group are deprotonated. This affords the unique possibility for π-stabilisation of the five-coordinate intermediate state even in early stages of base hydrolysis. Independently of the arguments mentioned above, a system comparable to ours with a tertiary amine function in the place of the secondary amine presumably deprotonated in the conjugate base (x-$[\text{Co Medien dapo X}]^{2+}$) could be used to test our assertion. This complex would be expected to change its reactivity totally (competition ratio, stereochemistry, base hydrolysis rate).

If the conjugate base is deprotonated at the secondary amine function, the rate of the exo-NH and endo-NH species (x and x') should differ by the deprotonation rate difference of the two amine functions (cf. eq 7), since the reprotonation rates can be expected to be diffusion controlled. In the case of the azido complexes the deprotonation rate difference has been shown to be about 3 (cf. 2.6.3.). In the case of the proposed S_N1CB mechanism with deprotonation at the secondary amine function, the pure Co - X abstraction rates could be detected. For all other mechanisms, the rate differences of the x and x' isomers will be unequal to the proton exchange differences.

3.4. THE REACTIVITY OF THE BASE HYDROLYSIS PRODUCTS

In addition to the high competition ratio and the complete racemisation observed in the products of base hydrolysis the high stabilisation of the coordinatively unsaturated intermediate state has a third unique effect. The anation rate of the hydroxo product is unusually high (cf. ref. [43]). Optically active x-$[\mathrm{Co\ dien\ dapo\ OH}]^{2+}$ has a very high racemisation rate (cf. 2.6.5.) which is indicative of a rather high lability of the coordinated hydroxy group. The observation that the hydroxo complex racemizes faster than the chloro and bromo species is unusual since normally OH^- is a much poorer leaving group than Cl^- or Br^- ($t_{\frac{1}{2}}$ for solvent exchange of trans $[\mathrm{Co\ en_2\ NH_3\ OH}]^{2+}$: 200 h) [121,122]. A high anation rate could therefore be expected because anation of the hydroxo complex with azide means nothing else but competition with azide during water exchange in the hydroxo complex when we presume the same substitution mechanism, viz. S_N1CB with deprotonation at the secondary amine. High lability of coordinated hydroxide could also be observed in π- and π'- isomers, where the relatively fast ring closure with the dapo hydroxy group is taken to express a competition situation between H_2O and diamine-bound dangling hydroxide at the stage of the coordinatively unsaturated intermediate state. The ring-closure rate along with a presumably small selectivity of the intermediate state implies a high lability of the hydroxy group.

The high racemisation rate of optically active hydroxo species was an intriguing factor in the stereochemical analysis of the base hydrolysis. However it is now clear that racemisation is due to the achiral stabilized coordinatively unsaturated intermediate state subsequent to loss of the leaving group. From the competition experiments, the hydroxo complex formed during base hydrolysis of optically active t-[Co dien dapo X]$^{n+}$ is inferred to be racemic and racemisation is therefore not due to any reaction of the hydroxo complex. Attack of the two competing nucleophiles water and azide takes place at the same intermediate state and the azido product which is completely stable in the medium of our experiments is shown to be 100 ± 2 % racemic (cf. 2.6.5.).

3.5. THE UNIQUENESS OF THE OBSERVED RESULTS

Most Co(III) pentaamine complexes react with partial retention of configuration [107] and competition ratios (tables 2 and 20) as well as the ratio of base hydrolysis to aquation rates (acceleration factors, cf. table 20) and anation rates (cf. ref. [43]) normally indicate a lesser stabilisation of the intermediate as observed in this work. Why this unique result? Tobe and Henderson [62] recently noted that the base hydrolysis rate increases with all structural features of the complex that facilitate the formation of a trigonal bipyramidal intermediate of the type shown in fig. 21.

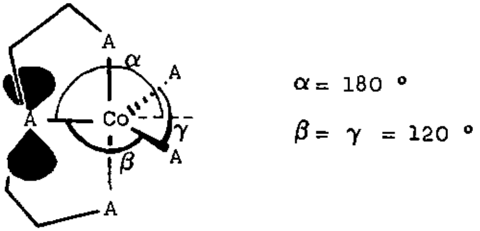


figure 21 : best geometry for π-stabilisation in the intermediate of reduced coordination number

Such a relationship is possible since factors which stabilize the coordinatively unsaturated intermediate state will also exert their influence on the preceding transition state and therefore on the rate of leaving group release. As mentioned above, deprotonation at a cis amine provides the best stabilisation. Furthermore, Henderson and Tobe point out that the species has the best chance to be stabilized by π-bonding if two 5-membered chelate rings fix the amide function in the plane of the Co(III)-$d_{x^2-y^2}$ orbital because this arrangement is the most favorable for the required planarization of the secondary amine function. Furthermore, the remaining equatorial positions are best occupied by two monodentate amines or a six membered chelate to accommodate the ideal 120 ° angle in the trigonal bipyramidal intermediate. Our chloropentaamine complex fulfills all these conditions and has indeed the highest base hydrolyses rate observed so far for a chloropentaamine complex with saturated amine ligands. A test for the importance of the factors mentioned above could be made on similar systems with different combinations of six- and five - membered chelates such as x-[Co dpt dapo X]$^{n+}$, x-[Co dien dimen X]$^{n+}$, x-[Co dpt dimen X]$^{n+}$, x-[Co ept AA X]$^{n+}$ etc. (cf. fig. 3).

3.6. THE REACTIVITY OF THE CONJUGATE BASE

The stabilisation of the conjugate base is in fact better reflected by the acceleration ratio k_{OH} / k_{aq} of base hydrolysis against spontaneous aquation (table 20) than by base hydrolysis rates alone. In this analysis, differences in the N-H acidities should be taken into account. From proton exchange data, they are known to vary $\leq 10^2$ fold for related substances which is much smaller than the observed differences in k_{OH}. The acceleration factors compared with competition ratios and stereochemical changes during base hydrolysis give the best appraisal of the degree of stabilisation of the corresponding intermediates.
We therefore propose the following interpretation:

1. The stabilisation of the pentakisalkylamine complexes arises at least partly from steric strain i.e. the transition states producing and consuming the intermediate are destabilized.
2. The unique result of full retention in the case of Co bamp dapo X $^{n+}$ complexes [26,27] cannot exclusively be due to the impossibility of π-stabilisation but the square pyramidal intermediate is likely to be stabilized by π-backbonding (see below).
3. x-[Co dien dapo Cl]$^{2+}$ and x-[Co dien en Cl]$^{2+}$ have very similar acceleration factors and this is consistent with similar stabilization of the intermediates and argues against strong steric acceleration in the dapo complex.

Most important for the reactivity of the conjugate base are all structural conditions which fix the amide-π-orbital in the plane of the Co(III) $d_{x^2-y^2}$ - orbital plane. However, comparison of the isolated acceleration factors is likely to be misleading and it appears necessary to wait for complementation of the results presented in table 20)

substance	$k_{aq}[s^{-1}]$	$k_{OH}[M^{-1}s^{-1}]$	k_{OH}/k_{aq}	$\%CoN_3^{2+}(1M\ N_3^-)$	ref.
$Co(NH_3)_5Cl^{2+}$	$1.8\cdot10^{-6}$	0.26	$1.44\cdot10^5$	8.5	12,43.54,109
$Co(NH_3)_5Br^{2+}$	$6.5\cdot10^{-6}$	1.4	$2.15\cdot10^5$	8.7	12,43,109
$Co(NH_3)_5CH_3SO_3^{2+}$	$2.0\cdot10^{-4}$	55	$2.75\cdot10^5$	10.1	94,110
$Co(NH_3)_5SO_4^+$	$8.9\cdot10^{-7}$	$4.9\cdot10^{-2}$	$5.51\cdot10^5$	5.8	43,44
$Co(NH_3)_5dmso^{3+}$	$2\cdot10^{-5}$	5.4	$2.7\cdot10^5$	12.8	58,102
cis-$Coen_2NH_3Cl^{2+}$	$4.2\cdot10^{-7}$	2.7 a)	$6.43\cdot10^6$	24	43,44,53
cis-$Coen_2NH_3Br^{2+}$	$1.6\cdot10^{-6}$	22 a)	$1.38\cdot10^7$	24	44,53
sym-$CotrenenCH_3SO_3^{2+}$	$2.6\cdot10^{-5}$	$7.6\cdot10^4$	$2.92\cdot10^9$	47.7	94,110
$Co(CH_3NH_2)_5Cl^{2+}$	$3.7\cdot10^{-5}$	$3.4\cdot10^2$	$9.19\cdot10^6$	48.6	16
$CobampdapoCl^{2+}$	$1\cdot10^{-5}$	$3\cdot10^3$	$3\cdot10^8$	6.5	26,27
$CobampdapoBr^{2+}$	$4.1\cdot10^{-5}$	$1.5\cdot10^4$	$3.66\cdot10^8$	6	26,27
$CobampenCl^{2+}$	$1.6\cdot10^{-6}$	480	$3\cdot10^8$	9	26,27,88
κ-$CodienenCl^{2+}$	$1.78\cdot10^{-7}$	$1\cdot10^4$ a)	$5.6\cdot10^{10}$	-	108
κ-$CodiendapoCl^{2+}$	$5.65\cdot10^{-6}$ b)	$1.13\cdot10^5$	$2\cdot10^{10}$	63.6	this work
π-$CodientmdCl^{2+}$	$4.3\cdot10^{-6}$	46 a)	$1.07\cdot10^7$	-	65
ω-$CodientmdCl^{2+}$	$2.16\cdot10^{-7}$	3.5 a)	$1.62\cdot10^7$	-	65
κ-$CodpttmdCl^{2+}$	$1.74\cdot10^{-5}$	$9.17\cdot10^3$ a)	$5.27\cdot10^8$	-	65
κ-$CodptenCl^{2+}$	$2.13\cdot10^{-5}$	$2.9\cdot10^3$ a)	$1.35\cdot10^8$	-	65
κ-CodptenCl	$1.16\cdot10^{-5}$	$7.3\cdot10^2$ a)	$6.3\cdot10^7$	-	65

table 20

table 20 : acceleration factors and competition ratios of base hydrolysis reactions of some selected pentaamine Co(III) complexes at T = 25 °C and $\mu = 1.0$

a) estimated from other ionic strength

b) estimated from analogous tmd complex

by the missing competition and stereochemical data. We point out that it is indeed the lifetime at the coordinatively unsaturated intermediate state, reflected by competition ratios, which answers the question concerning the stability of the intermediate state, which indeed is dependent on the activation barrier leading to the products. All rate or acceleration values are dependent on the activation barrier leading to the intermediate state and therefore give no direct information about the relative stability of the intermediate state. However it is clear from the Hammond postulate that an increase in the stability of the intermediate will decrease the activation energy of the leaving group release step in some way, but there is no evidence for a direct relationship as we can see from table 20. We argue that one of the most important factors for π-stabilisation is the positioning of the amide orbital in the plane of the Co(III) $d_{x^2-y^2}$ orbital. Some stereochemical results on Co tren, Co Metren and Co trenen complexes [33,61,94,105,110] support this hypothesis. A clear answer could arise from investigating $[\text{Co ept AA X}]^{\pm n}$ complexes.

The role of the π-stabilizing nitrogen p orbital is clarified by a series of experiments with [Co bamp dapo X]$^{2+}$ complexes (fig. 22)[26,27].

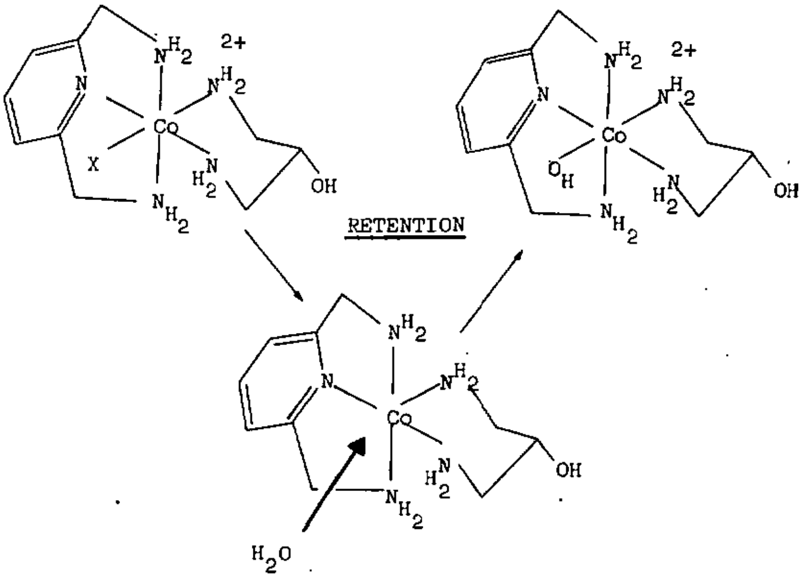


figure 22 : full retention in base hydrolysis of [Co bamp dapo X]$^{n+}$

There is a pyridine nitrogen as a potential donor of a π-stabilizing orbital. Although the system is structurally very similar to ours, full retention of configuration is observed. This retention is proved not to be due to a concerted attack of H_2O at a trigonal bipyramidal intermediate state deprotonated only at the amine trans to the leaving group because full retention is observed also in the azide competition product performed in solutions where the presence of HN_3 can be excluded. The pyridine nucleus has accessible π^* orbitals and a square pyramidal intermediate state can be stabilized by Co(III) to pyridine backbonding. This backbonding contribution may in fact be strong enough to exclude rearrangement to a trigonal bipyramid before attack of the entering nucleophile and thus be responsible for the observed retention of configuration. There is a ligand field spectral evidence for such $\pi \rightarrow \pi^*$ backbonding in $Co(bipy)_3^{3+}$ [112], $Co(phen)_3^{3+}$ [112] and $Copy_4X_2^+$ [113]. An open question is whether the pyridine nitrogen orbitals would fulfill the necessary conditions for π-bonding. An answer to these questions could come from a similar series of experiments with dipic complexes where Co(III) to pyridine backbonding should in fact be much smaller due to the electrophilic carboxylato groups. However, the experiments with the bamp complexes (full retention) and with the dien complexes (full racemisation) provide us with good evidence for the reality of π-stabilisation. This is because we can exclude a stabilisation by release of steric strain effects in the case of Co bamp complexes as we find for the pentakisalkylamine series. The comparable Co dien complexes are much more stabilized than both types of complexes mentioned above and stabilisation by steric strain release effects may therefore be excluded in this case too. The competition results in the Co dien and Co bamp species are strikingly different (64% vs. 8% in 1 M N_3^-) and this difference is hard to accommodate by differences in outer-sphere aggregate stabilities since the two classes of complexes are structurally very similar. This provides an argument against a concerted mechanism of base hydrolysis in these cases.

One question remains. The configuration and lifetime of the coordinatively unsaturated intermediate state in the case of the pentakisalkylamine Co(III) complexes may be interpreted with the steric strain in the hexacoordinated species, with Co (III) to pyridine backbonding in the case of CobampAAX^{n+} complexes and with amide to Co(III) π-bonding in the case of CodienAAX^{n+} complexes. Where does the stabilisation in all other cases come from? It is very important to point out that the stabilisation in each case cannot be explained by only one effect. Steric strain may be more or less important in each case and π-stabilisation can only be excluded in the CobampAAX^{n+} complexes where full retention is observed. In each case it is very important to see that questions regarding the possibility of π-bonding can only be answered clearly in a very limited number of cases. One important fact needs to be reemphasized: Trigonal bipyramidal geometry is required only for maximum stabilization by π-bonding.

3.7. CONSEQUENCES FOR THE π - STABILISATION HYPOTHESIS

Returning to the isolated case of base hydrolysis of x-[Co dien dapo X]$^{2+}$ we repeat that all experiments are clearly in good agreement with a limiting S_N1CB mechanism which consists of the sequence: a fast deprotonation equilibrium forming a very reactive conjugate base by deprotonation at the secondary amine function of dien. This species looses the leaving group in the rate determining step, which is fast relative to other pentaamines. The resulting coordinatively unsaturated intermediate state is strongly stabilized relative to other systems. It shows no evidence for ion pairing and is completely achiral. In a following fast reaction it captures nucleophiles present in the solvent sheath surrounding it. By its stabilization, it shows high selectivity for azide. Thus all necessary structural conditions for π-stabilization are fulfilled in this reaction. This is more than could ever be proven for comparable systems but no further conclusions are possible. We are not presently able to imagine any laboratory experiment to really prove the existence of the inferred π-bonding. Orbital energy calculations could lead further.

4. EXPERIMENTAL PART

4.1. PHYSICAL MEASUREMENTS

IR spectra were recorded either on a Perkin Elmer 521 or a Beckman IR 4250 instrument in the region of 4000 - 200 cm^{-1} by means of KBr or CsBr pellets. VIS spectra were measured on Cary 14, Unicam SP 1800 or Uvikon 810 instruments at 25.0 ± 0.1 °C unless stated otherwise. A Jasco J - 500 instrument served to measure the CD spectra at 25.0 ± 0.1 °C. ^1H- and ^{13}C-NMR spectra were recorded on Bruker WP 200, Bruker HX 90 or Bruker HX 90E instruments, all in the FT mode at 25 °C or on a Perkin Elmer R 12B 60 MHz NMR instrument. pH measurements were performed with a Metrohm E 388 compensator or with a Metrohm 605 pH-meter. The Phillips C 11 electrode (1 M $NaClO_4$) was calibrated by titration of a standard Titrisol HCl solution (Merck) with a standard Titrisol NaOH solution (Merck) at constant ionic strength (1.0 M; $NaClO_4$). The kinetics were all measured under pseudo first order conditions in complex. They were performed on a Jasco J - 500 instrument (CD), on a Unicam SP 1800 or a Uvikon 810 instrument (VIS), on a Dionex (Durrum) D - 110 instrument (stopped flow), on a Bruker WP 200 instrument (H-exchange) or on a Perkin Elmer R 12B 60 MHz NMR instrument (^1H-NMR). Thermoanalyses were performed on a Mettler TM1 thermobalance coupled to a Balzers Quadrupole QMG 101 mass spectrograph system via steel capillary. Heating X-ray powder photographs were taken on a Nonius Lenné camera using Fe K_α irradiation. The heating rate was 1 °C / min.. C,H,N,Cl, Br, and S were analysed by the Mikrolabor at the ETH Zurich.

4.2. MATERIALS

Purissimum or reagent grade commercial chemicals were used except for the organic ligands which were of purum grade. Sodium arsenyl tartrate was prepared from arsenic(III) oxide, sodium hydroxide and tartaric acid in water at 90 °C [114].

4.3. SYNTHESIS OF COMPLEXES

Upon recovery, all compounds were washed with acetone or ethanol and ether and dried in vacuo (12 - 24 h; $1\text{-}10\cdot10^{-3}$ torr, 20 °C) before characterisation.

4.3.1. Co(III) COMPLEXES WITH MERIDIONALLY COORDINATED TRIDENTATE pyridine - 2,6 - dicarboxylate, TWO AMINES AND A MONODENTATE LIGAND, INCLUDING STARTING MATERIALS AND REFERENCE SUBSTANCES

[(Diethylenetriamine)(pyridine-2,6-dicarboxylato)cobalt(III)] chloride [111]

Trichloro diethylenetriamine cobalt(III) [115,116] (3 g; 0.01 mol) and pyridine-2,6-dicarboxylic acid (1.86 g; 0.01 mol) were dissolved together in the minimum amount of water. After three days purple red crystals deposited from the solution on adding lithium chloride. They were recrystallized twice from hot water at pH = 9 (ammonia). Yield: 2.8 g (0.077 mol; 77.2 %).

$C_{11}H_{16}N_4O_4ClCo$	Calc.	C 36.43	H 4.45	N 15.65	%
(362.66)	Found	" 36.28	" 4.61	" 15.71	%

Ammonium[bis(pyridine-2,6-dicarboxylato)cobaltate(III)]

Cobalt(II) nitrate hexahydrate (15 g; 0.05 mol) and pyridine-2,6-dicarboxylic acid (16.7 g; 0.1 mol) were suspended in water (100 ml) together with charcoal. Dioxygen was passed through the mixture for 1 h at 80 °C. The complex was precipitated from the violet solution by adding ammonium chloride. The violet crystals were recristallized twice from hot water. Yield: 6.04 g (0.025 mol; 49.9 %).

$C_{14}H_{10}N_3O_8Co$	Calc.	C 41.29	H 2.48	N 10.32	%
(407.14)	Found	" 41.24	" 2.57	" 10.28	%

Bis[dinitro bis(ethylenediamine)cobalt(III)][trinitro(pyridine-2,6-dicarboxylato)cobaltate(III)]

A stream of dioxygen was passed through an aqueous solution (90 ml) of cobalt(II) chloride hexahydrate (20 g; 0.084 mol), pyridine-2,6-dicarboxylic acid (15,7 g; 0.093 mol), sodium nitrite (20,3 g; 0.29 mol) and ethylenediamine (5.5 g; 0.092 mol) during 16 hours. At the end of the reaction, an orange brown precipitate was filtered off. It was recrystallized twice from hot water. Yield: 12.4 g (0.038 mol; 44.7 %).

$C_{15}H_{35}N_{16}O_{18}Co_3$	Calc.	C 19.92	H 3.90	N 24.78	Co 19.55	%
(904.341)	Found	" 19.87	" 3.86	" 23.83	" 19.3	%

Sodium [trinitro (pyridine-2,6-dicarboxylato)cobaltate(III)]

a. Bis[dinitro(bis ethylenediamine)cobaltate(III)]trinitro (pyridine-2,6-dicarboxylato)cobalt(III) (5 g; 0.0055 mol) was passed through a cation exchange resin (Dowex 50W X2; H^+- form). The eluate was precipitated by adding sodium perchlorate. Yield: 1.67 g (0.0038 mol; 68.4 %).

b. The dinitro bis(ethylenediamine)cobaltate(III) - cation from the bis[dinitro bis(ethylenediamine)cobaltate(III)][trinitro(pyridine-2,6-dicarboxylato)cobalt(III)] (5 g; 0.0055 mol) was precipitated as the perchlorate salt by adding sodium perchlorate (3.09 g; 0.022 mol). The sodium salt of the anionic component deposited from the filtrate and was recristallized once from water. Yield: 0.92 g (0.0021 mol; 37.8 %)

$C_7H_7N_4O_{12}CoNa_2$	Calc.	C 18.93	H 1.59	N 12.62	%
(444.066)	Found	" 19.09	" 1.25	" 12.34	%

[(Pyridine-2,6-dicarboxylato)triammine cobalt(III)] nitrate

Carbonato tetraammine cobalt(III) nitrate (9.96 g; 0.04 mol)[117] and pyridine-2,6-dicarboxylic acid (6.68 g; 0.04 mol) were stirred together in water (200 ml). When the effervescence of carbon dioxide ceased, ammonia was added. After a few days, dark violet crystals were collected from the violet solution. They were recrystallized twice from hot aqueous ammonia (pH ~ 10. Yield: 3.0 g (0.011 mol; 27.3 %).

$C_7H_{12}N_4O_8Co$	Calc.	C 24.94	H 3.59	N 20.77	%
(337.139)	Found	" 24.91	" 3.59	" 20.62	%

(Pyridine-2,6-dicarboxylato)nitro diammine cobalt(III)

Potassium tetranitro bis ammine cobalt(III) [118] (5.2 g; 0.016 mol) and pyridine-2,6-dicarboxylic acid (2.75 g; 0.016 mol) were dissolved in the minimum amount of water. When the effervescence of nitrous gases ceased, the solution had a yellow-brown colour. The solution was kept in the dark at ambient temperature for a week. Then the red brown crystals were filtered off and recrystallized from hot water. Yield: 3.8 g (0.012 mol; 78.1 %).

$C_7H_9N_4O_6Co$	Calc.	C 27.65	H 2.98	N 18.42	%
(304.11)	Found	" 27.34	" 3.24	" 18.47	%

[(Pyridine-2,6-dicarboxylato)diammine aqua cobalt(III)] nitrite

A concentrated solution of (pyridine-2,6-dicarboxylato) nitro diammine cobalt(III) (2 g; 0.0063 mol) in water of pH = 7 was aquated by heating the solution for about 1 h at about 80 °C. The violet crystals were filtered off. Yield: 1.36 g (0.0042 mol; 65 %).

$C_7H_{11}N_4O_7Co$	Calc.	C 26.10	H 3.44	N 17.39	%
(322.13)	Found	" 26.06	" 3.18	" 17.52	%

(Pyridine-2,6-dicarboxylato)(ethylenediamine) hydroxo cobalt(III) hemihydrate

Guanidinium bis carbonato (ethylenediamine)cobaltate(III) [119,120] (9.9 g; 0.033 mol) and pyridine-2,6-dicarboxylic acid (5.55 g; 0.033 mol) were dissolved in water with stirring (300 ml). During a strong effervescence of carbon dioxide, the solution turned violet. After about 30 h, acetone was added to precipitate a crude mauve mixture probably containing hydroxo-, aqua- and carbonato complexes. It was recrystallized twice from hot water at pH~8 (sodium hydroxide). Yield: 1.4 g (0.0045 mol; 13.7 %).

$C_9H_{13}N_3O_{5.5}Co$	Calc.	C 34.85	H 4.22	N 13.55	%
(310.15)	Found	" 34.74	" 4.36	" 13.37	%

Because of the small yield of this synthesis, solutions or this compound were normally produced by deprotonation of (pyridine-2,6-dicarboxylato)ethylenediamine aqua cobalt(III) salts ($pK_a = 7.48$).

Aniono[(pyridine-2,6-dicarboxylato)ethylenediamine aqua cobalt(III)]

The crude product of the reaction of guanidinium bis carbonato ethylenediamine cobaltate(III) with pyridine-2,6-dicarboxylic acid was used as the starting material. To a suspension of this complex mixture (3.9 g) in water were added various concentrated acids. Effervescence of carbon dioxide and colour change to red-violet could be observed. From these solutions, the corresponding salts of aqua complexes were filtered off in yields of about 60 % respective to bis carbonato ethylenediamine cobaltate(III).

perchlorate:

$C_9H_{13}N_3O_9ClCo$	Calc.	C 26.92	H 3.26	N 10.46	Cl 8.83 %
(401.604)	Found	" 26.73	" 3.26	" 10.32	" 8.69 %

nitrate:

$C_9H_{13}N_4O_8Co$	Calc.	C 26.69	H 3.60	N 15.39	%
(364.159)	Found	" 26.60	" 3.51	" 15.30	%

chloride:

$C_9H_{13}N_3O_5ClCo$	Calc.	C 32.02	H 3.88	N 12.45	Cl 10.50 %
(337.607)	Found	" 31.86	" 3.75	" 12.37	" 10.41 %

bromide:

$C_9H_{13}N_3O_8BrCo$	Calc.	C 28.29	H 3.43	N 11.00	Br 20.92 %
(382.063)	Found	" 28.36	" 3.50	" 11.06	" 19.67 %

acetate:

$C_{11}H_{16}N_3O_7Co$	Calc.	C 36.58	H 4.47	N 11.63	%
(361.199)	Found	" 36.28	" 4.33	" 11.70	%

sulfate dihydrate:

$C_{18}H_{30}N_6O_{16}Co_2S$	Calc.	C 29.36	H 4.11	N 11.41	%
(736.40)	Found	" 29.05	" 4.08	" 11.32	%

hydrooxalate:

$C_{11}H_{14}N_3O_{10}Co$	Calc.	C 32.29	H 3.94	N 10.27	%
(409.197)	Found	" 32.45	" 4.04	" 10.31	%

Chloro(pyridine-2,6-dicarboxylato)ethylenediamine cobalt(III)

Finely powdered [(pyridine-2,6-dicarboxylato)ethylenediamine aqua cobalt(III)] chloride (5g; 0.015 mol) was heated for about 3 h at 218 °C in a drying oven. Yield: 4.73 g (0.015 mol; 100%).

$C_9H_{11}N_3O_4ClCo$	Calc.	C 33.82	H 3.47	N 13.15	Cl 11.09	%
(319.592)	Found	" 33.99	" 3.50	" 13.03	" 11.03	%

Hydrogenoxalato(pyridine-2,6-dicarboxylato)ethylenediamine cobalt(III)

Finely powdered (pyridine-2,6-dicarboxylato)ethylenediamine aqua cobalt(III)hydrooxalate (3.73 mg; 9.115 10^{-6}mol) was heated for about 3 h at 114 °C in a drying oven. Yield: 3.57 mg (9.126 10^{-6}mol; 100 %).

$C_{11}H_{12}N_3O_8Co$	loss of weight	Calc.	4.40 %
(373.166)		Found	4.3 ± 0.1 %

[(Pyridine-2,6-dicarboxylato)ethylenediamine dimethylsulfoxide cobalt(III)]nitrate

Chloro(pyridine-2,6-dicarboxylato)ethyenediamine cobalt(III) (5 g; 0.16 mol) and silver nitrate (2.66 g; 0.16 mol) were stirred together in the minimum amount of dimethylsulfoxide. After removal of the silver chloride precipitate (after 1 h), the solution was allowed to stand in the refrigerator overnight. The precipitate was filtered off and recrystallized twice from dmso solutions, satturated with lithium perchlorate, which were added to a mixture of n-propanol and ether (~1 : 1). Yield: 3.28 g (0.0077 mol; 48.3 %)

$C_{11}H_{17}N_4O_8SCo$	Calc.	C 31.14	H 4.04	N 13.21	%
(424.277)	Found	" 30.31	" 4.05	" 11.76	%

Azido(pyridine-2,6-dicarboxylato)ethylenediamine cobalt(III)

(pyridine-2,6-dicarboxylato)ethylenediamine aqua cobalt(III) chloride (1.5 g; 0.0044 mol) was stirred in an aqueous solution (150 ml) containing sodium azide (20 g; 0.31 mol). The sparingly soluble violet crystalline product was filtered off after 2 weeks. The precipitate was washed with water and dried at 50 °C (72 h). Yield: 1.27 g (0.0039 mol; 88.5 %).

$C_9H_{11}N_6O_4Co$	Calc.	C 33.14	H 3.40	N 25.77	%
(326.158)	Found	" 33.17	" 3.66	" 25.55	%

Nitro(pyridine-2,6-dicarboxylato)ethylenediamine cobalt(III)

(pyridine-2,6-dicarboxylato)ethylenediamine aqua cobalt(III) chloride (1.5 g; 0.0044 mol) was stirred in an aqueous solution (150 ml) containing sodium nitrite (15 g; 0.37 mol). The dark red platelets were filtered off after one week. The sparingly soluble nitro complex was washed with water and dried at 90 °C (24 h). Yield: 1.32 g (0.004 mol; 90.9 %).

$C_9H_{11}N_4O_6Co$	Calc.	C 32.74	H 3.36	N 16.97	%
(330.144)	Found	" 32.71	" 3.43	" 16.84	%

Thiocyanato(pyridine-2,6-dicarboxylato)ethylenediamine cobalt(III)

(pyridine-2,6-dicarboxylato)ethylenediamine aqua cobalt(III) chloride (1.5 g; 0.0044 mol) and ammonium thiocyanate (20 g; 0.26 mol) were stirred together. The violet precipitate was filtered off after two weeks. The crystalline product was washed with water and dried at 90 °C. Yield: 1.36 g (0.004 mol; 90.3 %).

$C_{10}H_{11}N_4O_4SCo$	Calc.	C 35.09	H 3.24	N 16.38	%
(342.220)	Found	" 34.99	" 3.26	" 16.30	%

Nitrito(pyridine-2,6-dicarboxylato)(1,3-diaminopropane-2-ol)cobalt(III)

A stirred aqueous solution of sodium tetranitro(diaminopropane-2-ol)cobalt(III) (cf. ref.[118]) (2.5 g; 0.007 mol) and pyridine-2,6-dicarboxylic acid (1.1 g; 0.007 mol) was heated to about 80 °C during 1 h. The solution became blood-red. After one day the violet crystals were filtered off. Yield: 0.3 g (0.0008 mol; 11.33 %).

$C_{10}H_{15}N_4O_8Co$	Calc.	C 31.76	H 4.00	N 14.81	%
(378.185)	Found	" 31.66	" 4.01	" 14.36	%

4.3.2. Co(III) COMPLEXES WITH A TRIDENTATE DIALKYLTRIAMINE, 1,3 -diaminopropan - 2 - ol AND A MONODENTATE LIGAND

[Chloro(diethylenetriamine)(1,3-diaminopropane-2-ol) cobalt(III)] tetrachlorozincate

An aqueous solution (300 ml) of cobalt chloride hexahydrate (145.8 g; 0.612 mol) of 0 °C was mixed with an aqueous solution (240 ml) of diethylenetriamine (63 g; 0.612 mol) and 1,3-diaminopropane-2-ol (55.2 g; 0.612 mol) at 0 °C. During the slow addition of the ligands to the cobalt(II) solution, the temperature was kept at 0 °C. Then, O_2 was passed through the mixture for 1 h at 0 °C. A solution of zinc chloride (120 g; 0.88 mol) in hydrochloric acid (10 M; 540 ml) were added dropwise within 3 h always at 0 °C. The brown mixture was allowed to stand at ambient temperature overnight. After removal of a green crystalline species, presumably a μ-superoxo decaamine dicobalt complex (16.4 g), the solution deposited red and violet cobalt(III) pentaamine complexes within 24 to about 150 h. The different crops were recrystallized from the minimum amount of water (0 °C) by adding zinc chloride (0.67 g / g complex) and hydrochloric acid 10 M (3.35 ml / g complex). By this method, four different isomers of the chloro complex could be isolated: χ-, π-, π'- and πNNO-species (see below). Yield of all isolated complexes: 98.17 g (0.18 mol; 32.1 %).

χ-[Chloro(diethylenetriamine)(1,3-diaminopropane-2-ol) cobalt(III)]tetrachlorozincate

The first crop in the recrystallisation of the combined precipitates isolated 1 and 2 days after the above synthesis gave pure red χ- isomer. Yield: 44.0 g (0.09 mol; 14.7 %).

$C_7H_{23}N_5Cl_5CoZn$	Calc.	C 16.99	H 4.68	N 14.15	Cl 35.82 %
(494.862)	Found	" 17.54	" 4.60	" 14.02	" 36.00 %

π-[Chloro(diethylenetriamine)(1,3-diaminopropane-2-ol) cobalt(III)]tetrachlorozincate

The second precipitate of the recrystallisation for the χ isomer and the precipitates of the synthesis above after 3 and 4 days were combined in a recrystallisation to give the pure violet π- isomer. Yield: 15.48 g (0.03 mol; 5.1 %).

$C_7H_{23}N_5Cl_5OCoZn$	Calc.	C 16.99	H 4.68	N 14.15	Cl 35.82 %
(494.862)	Found	" 17.24	" 4.56	" 13.93	" 36.03 %

A better yield of this isomer is obtained when the ligands and the cobalt(II) salt are mixed at ambient temperature and the oxygenated peroxo-complex is heated for about 3/4 h to 80 °C after treatment with zinc chloride and hydrochloric acid. By this method yields of the π-isomer up to 20 % were obtained.

τ'-[Chloro(diethylenetriamine)(1,3-diaminopropane-2-ol) cobalt(III)]tetrachlorozincate

The second crop of the mother liquor of the recrystallisation for the τ - isomer (above) was recrystallized a second time to yield 0.1 g (0.2 mmol; 0.03 %) of mauve platelets of the τ'- isomer.

$C_7H_{23}N_5Cl_5OCoZn$	Calc.	C 16.99	H 4.68	N 14.15	Cl 35.82 %
(494.862)	Found	" 16.95	" 4.46	" 13.95	" 35.43 %

τNNO-[Chloro(diethylenetriamine)(1,3-diaminopropane-2-ol) cobalt(III)]tetrachlorozincate chloride

All crops which were collected from the synthesis above after more than 4 days including the third fraction of the recrystallization for the τ-isomer were combined and recrystallized to give the pure orange τNNO-isomer. Yield: 21.79 g (0.04 mol; 7.2 %).

$C_7H_{23}N_5Cl_5OCoZn$	Calc.	C 16.99	H 4.68	N 14.15	Cl 35.82 %
(494.862)	Found	" 17.09	" 4.58	" 13.97	" 35.93 %

A better yield of this isomer was realized when the cobalt(II)/ ligand mixture was not cooled and the peroxo complex treated with zinc chloride and hydrochloric acid was heated to 80 °C until the effervescence of O_2 ceased.

x-[Azido(diethylenetriamine)(1,3-diaminopropane-2-ol) cobalt(III)] tetrachlorozincate

x- chloro(diethylenetriamine)(1,3-diaminopropane-2-ol) coblt(III) tetrachlorozincate (8,5 g; 0.017 mol) was dissolved in 26 ml of a triethanolamine buffer (pH = 9.5) containing sodium azide (2 M). The colour immediately turned purple. After two minutes lithium chloride (5.8 g; 0.14 moles) and zinc chloride (7 g; 0.05 moles) were added to the cooled solution (0 °C). The dark purple precipitate was immediately filtered off. Yield: 6.6 g (0.013 mol; 77.4 %).

$C_7H_{23}N_8Cl_4OZn$	Calc.	C 16.77	H 4.62	N 22.35	Cl 28.28 %
(501.429)	Found	" 16.81	" 4.43	" 22.18	" 28.18 %

This complex was analysed by ^{13}C-NMR to be a 1 : 1 - mixture of the syn-NH and anti-NH isomers.

Recrystallization of the mixture of both isomers from concentrated aqueous solution containing sodium antimonyl tartrate (0.7 g / g complex) afforded the pure, optically active x-isomer. The antimonyl tartrate salt was dissolved in slightly acid solution (pH≅5) and precipitated by addition of lithium chloride and zinc chloride.

Treatement of the azido complex with concentrated hydrobromic or hydrochloric acid gave the pure bromo or chloro complexes respectively which are precipitated by addition of zinc bromide or zinc chloride.

ϰ-[Bromo(diethylenetriamine)(1,3-diaminopeopane-2-ol) cobalt(III)] tetrachlorozincate

ϰ- chloro(diethylenetriamine)(1,3-diaminopeopane-2-ol) cobalt(III) tetrachlorozincate (10 g; 0.02 mol) and silver nitrate (17.16 g; 0.1 mol) were dissolved in the minimum amount of water and stirred together at ambient temperature in the dark for 3 days. After removal of the silver chloride precipitate, hydrobromic acid (48%; 157 ml) and zinc bromide (30 g; 0.13 mol) were added. The solution was then evaporated in a desiccator over sulfuric acid in the refrigerator. The first three fractions (collected after 1,2,3 days) contained the pure ϰ-isomer. Yield: 5.35 g (0.007 mol; 37.3 %).

$C_7H_{23}N_5Br_5OCoZn$	Calc.	C 11.72	H 3.23	N 9.77	Br 55.71	%
(717.142)	Found	" 11.90	" 3.14	" 9.93	" 55.45	%

π-[Azido(diethylenetriamine)(1,3-diaminopropane-2-ol) cobalt(III)] tetrachlorozincate [91]

π- chloro(diethylenetriamine)(1,3-diaminopropane-2-ol) cobalt(III) tetrachlorozincate (5 g; 0.01 mol) was dissolved in the minimum amount of water containing sodium azide (1.5 g; 0.02 mol). After three weeks in the dark at ambient temperature, violet crystals were filtered off. They were recrystallized once from water by adding lithium chloride and zinc chloride. Yield: 0.43 g (8.58 mmol; 8.58 %).

$C_7H_{23}N_8Cl_4OZn$	Calc.	C 16.77	H 4.62	N 22.35	%
(501.429)	Found	" 16.44	" 4.47	" 21.86	%

π-[Bromo(diethylenetriamine)(1,3-diaminopropane-2-ol) cobalt(III)] tetrachlorozincate [91]

π-[chloro(diethylenetriamine)(1,3-diaminopropane-2-ol) cobalt(III)] tetrachlorozincate (5 g; 0.01 mol) was dissolved in the minimum amount of water. To this solution, silver nitrate (8.58 g; 0.05 mol) was added and the mixture was stirred at ambient temperature in the dark for 6 days. After removal of the silver chloride precipitate, hydrobromic acid (48 %; 100 ml) and zinc bromide (15 g; 0.07 mol) were added. Half of the solvent was evaporated at 40 °C and after one day violet crystals could be filtered off. Yield: 1.73 g (2.4 mmol; 24.12 %).

$C_7H_{23}N_5Br_5OCoZn$	Calc.	C 11.72	H 3.23	N 9.77	%
(717.142)	Found	" 11.82	" 3.20	" 9.48	%

x-[Chloro(dipropylenetriamine)(1,3-diaminopropane-2-ol) cobalt(III)] tetrachlorozincate

To an aqueous solution (50 ml) of cobalt(II) chloride hexahydrate (24.3 g; 0.102 mol) an aqueous solution of dipropylenetriamine (13.38 g; 0.012 mol) and 1,3-diaminopropane-2-ol (9.2 g; 0.102 mol) was added. Dioxygen was passed through the stirred and cooled (0 °C) solution for 1 h. Zinc chloride (50g; 0.37 mol) and hydrochloric acid (10 M; 85 ml) were added to the cooled solution. The solution was allowed to stand at ambient temperature (2 days). The mauve crystalline product was then filtered off and recrystallized once from cold water by adding zinc chloride

(2 g; 0.015 mol) and hydrochloric acid (10 M; 10.05 ml). Yield: 1.2 g (0.002 mol; 2.25 %).

$C_9H_{27}N_5Cl_5OCoZn$	Calc.	C 20.67	H 5.20	N 13.39	%
(522.916)	Found	" 20.55	" 5.13	" 13.31	%

4.4.RESOLUTION OF THE COMPLEXES

x-[Chloro(diethylenetriamine)(1,3-diaminopropane-2-ol)cobalt(III)]tetrachlorozincate

Racemic x-[chloro(diethylenetriamine)(1,2-diaminopropane-2-ol)cobalt(III)] tetrachlorozincate (13.2 g; 0.027 mol) was dissolved in an aqueous aolution of lithium chloride 0.24 M (132 ml at 0 °C. Sodium arsenyl L - tartrate (12.7 g; 0.027 mol) in water (42 ml) was then added. A precipitate forms which was filtered off immediately, washed with ethanol and ether and dried in a stream of air. Yield: 15.6 g.

The less soluble diastereoisomeric salt was recrystallized from an aqueous solution of lithium chloride 1.92 M (500 ml) at 0 °C by addition of sodium arsenyl L - tartrate (3.6 g; 0.0074 mol) in water (12 ml). The red crystals were filtered off after one night at -15 °C. The precipitate was washed with ethanol and ether and air-dried. Yield : 5.25 g.

The arsenyl L -tartrate salt was dissolved in hydrochloric acid (0.1 M; 35 ml). Hydrochloric acid (10 M; 15 ml) was added and the complex was precipitated as the tetrachlorozincate salt by adding zinc chloride (6 g; 0.044 mol). Yield: 4.05 g (0.0082 mol; 60.74 % of the less soluble antipode). Ellipticity of the product: $\Theta^{25}_{463} = -\ 705\ \mathrm{l\ M^{-1}\ m^{-1}}$.

In a second application of this procedure were obtained 2.25 g (0.0045 mol; 33.3 % based on the less soluble antipode in the starting material. Ellipticity of the product: $\Theta^{25}_{463} = -\ 862\ \mathrm{l\ M^{-1}\ m^{-1}}$.

After applying the procedure a third time, the ellipticity was constant within the error: $\Theta^{25}_{463} = -\ 858\ \mathrm{l\ M^{-1}\ m^{-1}}$.

All mother liquours were separated in two groups, one which contained more of the less soluble arsenyl L- tartrate diastereoisomer and one with the more soluble one. These two solutions were adsorbed on an ion exchange resin (Dowex 50W X2; H^+ - form) individually. Washing with water (pH =3; HCl) removed all foreign anions and the cation was eluted with HCl (5 M) to give a concentrated aqueous solution from which the tetrachlorozincates were regenerated by adding zinc chloride. Both enantiomers were prepared by these procedures, using sodium arsenyl L - or D - tartrates.

x-[Bromo(diethylenetriamine)(1,3-diaminopropane-2-ol) cobalt(III)] tetrabromozincate

Racemic x-[bromo(diethylenetriamine)(1,3-diaminopropane-2-ol)cobalt(III)] tetrabromozincate (10.0 g; 0.014 mol) was dissolved in an aqueous solution of lithium chloride 0.24 M (80 ml) at 0 °C. Sodium arsenyl L - tartrate (6.59 g; 0.014 mol) in water (22 ml) was added. The precipitate was immediately filtered off, washed with ethanol and ether and air dried. Yield: 12.3 g.

The arsenyl L- tartrate salt obtained was recrystallized from an aqueous solution of lithium chloride (1.92 M; 380 ml) at 0 °C by addition of sodium arsenyl L -tartrate (1.9 g; 0.004 mol)in water (6.3 ml). After one night at -15 °C, the precipitate was collected, washed with ethanol and ether and air dried. Yield: 4.8 g.

The arsenyl L - tartrate salt was dissolved in the minimum amount of hydrobromic acid. Hydrobromic acid (48 %; 3 ml / g complex) was added and the complex was precipitated as the tetrabromozincate salt by adding zinc bromide (6.8 g; 0.03 mol). Yield: 2.82 g (0.0039 mol; 56.2 %).

x-[Azido(diethylenetriamine)(1,3-diaminopropane-2-ol)cobalt(III)]tetrachlorozincate

Recrystallisation of a mixture of the and isomers from sodium antimonyl L - tartrate containing aqueous solutions gave the pure, optically active x-isomer (cf. p.140).

π-[Chloro(diethylenetriamine)(1,3-diaminopropane-2-ol)cobalt(III)] dichloride

Racemic π-chloro(diethylenetriamine)(1,3-diaminopropane-2-ol)cobalt(III)dichloride (17 g; 0.047 mol) was dissolved in water (20 ml; 30 °C). 15 ml of an aqueous solution of sodium arsenyl L - tartrate (11.55 g; 0.024 mol; 30 °C) were added dropwise to the first solution. The precipitate, collected after ½ h at ambient temperature, was washed with ethanol and ether and air-dried. Yield: 9.73 g (0.023 mol; 96 % based on the less soluble antipode). Ellipticity of the product: Θ^{25}_{554}= 3200 l M^{-1} m^{-1}.

π-[Bromo(diethylenetriamine)(1,3-diaminopropane-2-ol)cobalt(III)] dibromide

Racemic π-bromo(diethylenetriamine)(1.3-diaminopropane-2-ol)cobalt(III)dibromide (15.7 g; 0.032 mol) was dissolved in water (30 ml; pH = 3 ($HClO_4$)). 25 ml of an aqueous solution of sodium arsenyl L - tartrate (7.79 g; 0.016 mol) were added to the first solution. After 12 h at 0 °C, the precipitate was filtered off. Yield: 4.58 g (0.0079 mol; 49.7 % based on the less soluble antipode). Ellipticity of the procuct: Θ^{25}_{566} = 3849 l M^{-1} m^{-1}.

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6. ABSTRACT

Synthesis and structural assignements of two types of compounds are reported: Co(III) complexes with meridionally coordinated pyridine-2,6-dicarboxylate, two amines or an aliphatic diamine and a monodentate ligand, and Co(III) complexes with a meridionally or facially coordinated aliphatic triamine and di- or terdentate diaminopropane-2-ol. The reactivity of the neutral or 1+ charged triamine complexes has been investigated cursorily and appears not to be much different from the well known pentaamine complexes.

The new Co(III) pentaamine complexes gave important kinetic and stereochemical results. They are discussed in terms of the well known π- stabilisation hypthesis of Basolo and Pearson. The kinetic results are in good agreement with a limiting S_N1CB mechanism. Proton exchange measurements are discussed in terms of a deprotonation of the secondary amine function cis to the leaving group competing with deprotonation trans to the leaving group. The resulting conjugate base proved to be very reactive and loss of the leaving group affords a relatively highly stabilized achiral coordinatively unsaturated intermediate state. This species shows no evidence for ion pairing. In a fast reaction step, this attacks any nucleophile present in the solvent sheath surrounding the intermediate state.

7. CURRICULUM VITAE

I was born July 7, 1953 as a son of Ernst and Irma Comba-Preisig. After six years of primary school and three years of Junior High School in Rorschach, I entered the high school of St.Gallen in autumn 1969 where I graduated 1973 (Maturität). From 1973 to 1977 I studied Chemistry at the Swiss Federal Institute of Technology (ETH) in Zurich. In November 1977 I graduated as dipl. Chem. ETH. In December 1977 I started graduate studies in coordination chemistry at ETH Zurich with Prof. Dr. Werner Marty as the thesis supervisor. This work was continued at the University of Neuchâtel from January 1980 to May 1981. At the University of Neuchâtel I was appointed teaching assistant. In addition, during the whole studies I worked as a chemistry teacher. For the last three years I tought chemistry at the High School of Baden. In spring 1980 I married Maria Kern.

Neuchâtel, May 1981 Peter Comba