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Substitution Reactions of Methylbis(dimethylglyoximato)rhodium(III) as a Function of pH

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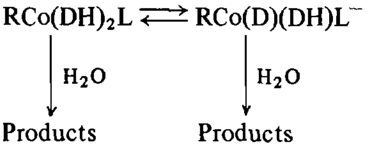
Abstract

The kinetics of axial ligation by pyridine of $CH_3Rh(DH)_2H_2O$ and the reverse hydrolysis reactions were studied in aqueous solution as a function of pH. The kinetic data indicate that the lability of this complex is strongly influenced by the extent of protonation of the equatorial chelating ring, both the doubly protonated $CH_3Rh(DH_2)(DH)L^+$ and the deprotonated $CH_3Rh(D)(DH)L^-$ species being more reactive than the species $CH_3Rh(DH)_2L$, containing intact intramolecular hydrogen bonds. A comparison is made with the behavior of the analogous Co(III) complexes.

Introduction

In our previous work [1] we reported the kinetics of the water substitution reactions of $CH_3Rh(DH)_2H_2O$ with various incoming ligands. The influence of pH on the reaction rate has not been considered, although it has been proved that the reactivity of the corresponding Co(III) complexes is strongly affected by the hydroxide ion concentration.

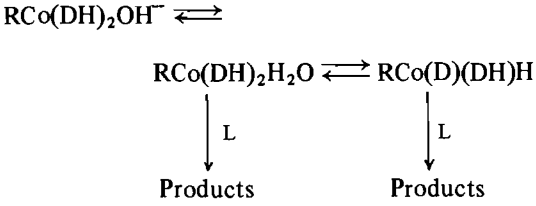
In fact, it is well established that the base hydrolysis reactions of the organocobaloximes occur via a S_NCB mechanism, involving deprotonation of the equatorial system [2, 3].



$$\begin{tikzcd} RCo(DH)_2L \arrow[r, shift left] \arrow[d, "H_2O"] & RCo(D)(DH)L^- \arrow[l, shift left] \arrow[d, "H_2O"] \\ \text{Products} & \text{Products} \end{tikzcd} \qquad (1)$$

When the leaving ligand is a substituted pyridine, the rate constant for the aquation of the conjugate base is three- to six times greater than that of the parent compound [2].

A conjugate base mechanism satisfactorily accounts also for the $[OH^-]$ dependence of axial water substitution reactions of the organoaquocobaloximes [4]. For these reactions the reactivity in alkaline medium is the result of two counteracting effects, a decrease in reactivity due to the formation of the hydroxocomplex and an increase in reactivity due to the formation of the conjugate base:



$$\begin{tikzcd} RCo(DH)_2OH^- \arrow[r, shift left] & RCo(DH)_2H_2O \arrow[l, shift left] \arrow[r, shift left] \arrow[d, "L"] & RCo(D)(DH)H_2O^- \arrow[l, shift left] \arrow[d, "L"] \\ & \text{Products} & \text{Products} \end{tikzcd} \qquad (2)$$

For the organocobaloximes examined the first effect is prevailing and a diminution of reactivity is observed in alkaline medium [4].

It appears that in any case the deprotonation of the equatorial chelating ring is associated with an increase of lability, which is attributed to the greater electron density on the cobalt atom in the anionic complex [2].

In this work we examine the pH dependence of the substitution rate for $CH_3Rh(DH)_2L$, in order to ascertain the effect of a change of the size of the metal atom. This study has been extended at low pH values with the purpose of verifying the influence on the reactivity of the formation of the cationic species $CH_3Rh(DH_2)(DH)L^+$, which are known to exist in very acidic medium [5].

Experimental

Materials

$CH_3Rh(DH)_2H_2O$ and $CH_3Rh(DH)_2Py$ were prepared as previously reported [6]. All other chemicals were analytical grade and were used without further purification. Pyridine solutions were standardized by potentiometric titration against HCl.

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General Experimental Conditions

Both the equilibrium and the kinetic measurements were carried out at 20 ± 0.1 °C. The ionic strength was maintained with $NaNO_3$ or $NaClO_4$ (when the spectrophotometric measurements were performed in the UV region).

Equilibrium Measurements

The proton dissociation constant of $CH_3Rh(DH)_2Py$, K_5, (Scheme 1) was determined by spectrophotometric titration of the complex in presence of a sufficiently high excess of pyridine (>0.1 M) that the ligand dissociation was also negligible in strong alkali. Concentrated solution of NaOH was added to the complex solution (2×10^{-4} M) with a microsyringe, so that the volume of the solution was increased by no more than 1%. Good isosbestic points were observed in the spectral range 360–300 nm. The pKa for the ionization process was calculated by the relation:

$$\log(A_o - A)/(A - A_\infty) = \mathrm{pH} - \mathrm{p}K_a$$

where A is the measured absorbance, A_o is the absorbance of $CH_3Rh(DH)_2Py$, and A_∞ is the absorbance of $CH_3Rh(D)(DH)Py^-$.

Kinetic Measurements

Water substitution reactions were carried out under pseudo first order conditions, with pyridine concentrations in at least tenfold excess over the complex. Generally $2-4 \times 10^{-4}$ M solutions of complex were used. The pH was maintained with borate buffers in the range 7.9–10.4 and with phosphate buffers at higher values. In the hydrolysis reactions the initial complex concentration was about 1×10^{-3} M. The pH was maintained with HNO_3 1 N below pH 2 and with phthalate buffers above this value. All reactions were followed at 430–440 nm.

Instruments

For pH measurements a pH-meter Radiometer pH M4 was used. The equilibrium studies were carried out with a Perkin-Elmer 356 double beam-double wavelength spectrophotometer. The faster reactions were followed with use of a Hi-Tech SF3 series stopped flow apparatus.

Data Analysis

The computer program used for the non-linear least squares analysis was Statistical Package for Social Sciences, version 9 (Vogelback Computing Center, Northwestern University, U.S.A.).

Results

The reaction:

$$CH_3Rh(DH)_2H_2O + Py \rightleftharpoons CH_3Rh(DH)_2Py + H_2O \tag{3}$$

was studied at $I = 1$ M ($NaNO_3$), $T = 20 \pm 0.1$ °C, and at various pH.

Scheme 1 is the minimum one consistent with both equilibrium and kinetic data.

Water Substitution Reactions

The acid dissociation constant K_1 (0.18 ± 0.08 M) was previously obtained [5].

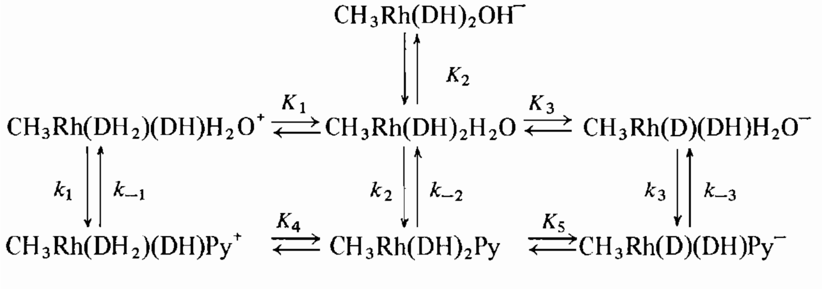
The deprotonation constant of the axial water of $CH_3Rh(DH)_2H_2O$ ($\mathrm{p}K_2 = 9.78 \pm 0.04$) has been reported in our previous work [1].

The water substitution reactions were studied at pH > 8. At this pH value only the neutral and the anionic forms of the aquocomplex and the hydroxocomplex exist in solution. The kinetic runs were performed under pseudo first order conditions, and the k_{obs} values were obtained from the linear plots of $\log(A_t - A_\infty)$ *vs.* time. Owing to the high equilibrium constant for the reaction (3) no intercept was found in the linear plots of k_{obs} *vs.* [Py], so that the k_{on} value may be calculated from the relation $k_{on} = k_{obs}/[Py]$.

The dependence of k_{on} on pH is shown in Fig. 1.

Kinetic analysis of the portion of Scheme 1 concerning water substitution leads to the relation:

$$k_{on} = \frac{k_1[H^+]/K_1 + k_2 + k_3K_3/[H^+]}{[H^+]/K_1 + 1 + (K_2 + K_3)/[H^+]} \tag{4}$$



Scheme 1.

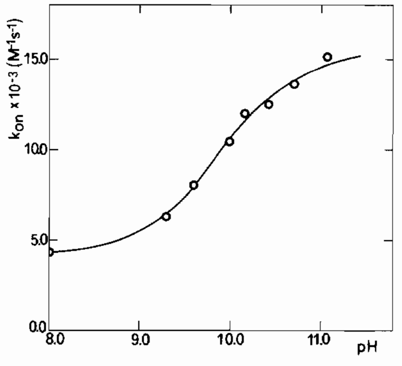


Fig. 1. Dependence of k_{on} upon pH at I = 1 M ($NaNO_3$) and T = 20 °C; the solid line is calculated from eqn. (5) and parameters contained in Table I.

At pH > 8 (4) can be simplified to:

$$k_{on} = \frac{k_2[H^+] + k_3K_3}{[H^+] + (K_2 + K_3)} \qquad (5)$$

The k_2 value ((4.23 ± 0.06) × 10^3 M^{-1} s^{-1}) has been previously measured [1] by performing the reaction in buffer solutions in the pH range 7.0–8.0, where the reaction rate is independent on $[H^+]$. The plot of $1/(k_{on} - k_2)$ *vs.* $[H^+]$ is linear in the $[H^+]$ range examined (5×10^{-10} – 8.3×10^{-12} M) and allows calculation of k_3K_3 and $K_2 + K_3$. These values were used as initial estimates in the calculation of k_3K_3 and $K_2 + K_3$ performed by a non-linear least-squares analysis (Table I).

It appears from the comparison of the $K_2 + K_3$ value with the K_2 value obtained from spectrophotometric measurements [1] that they are nearly equal, within limits of experimental error. This precludes the possibility to obtain the value of K_3 (and consequently of k_3). It should be noted that the determination of the equilibrium constants by kinetic methods has an inherently low accuracy, which may be considerably worse than suggested by the standard error, owing to systematic errors. In the present case the calculation of $[H^+]$ from the measured pH of a series of buffer solutions varying in a rather restricted pH range may constitute a considerable source of systematic errors. Consequently any estimate of the K_3 value may be hazardous and the only reliable statement is that it should not exceed the K_2 value.

The K_1 value cannot be experimentally determined, owing to the protonation of pyridine (pK_a = 5.45 at 25 °C, KNO_3 0.5 M [7]) at the pH values where the cationic complex $CH_3Rh(DH_2)(DH)H_2O^+$ is present in solution; however it is possible to calculate this value from the relation:

$$k_1 = k_{-1}k_2K_1/k_{-2}K_4 \qquad (6)$$

based on the cyclic nature of the equilibria of Scheme 1, being k_{-1}, k_{-2}, and K_4 known from the hydrolysis reactions (see below). It should be noted that this result is approximate, as k_{-1}, k_2, k_{-2}, and K_4 were measured at 20 °C, whereas K_1 was measured at 25 °C.

Kinetic and equilibrium data referring to the water substitution reactions are collected in Table I.

Hydrolysis Reactions

The hydrolysis reactions of $CH_3Rh(DH)_2Py$ were investigated in the pH range 0.3–5.9. In this pH range protonation of free pyridine shifts the equilibrium towards the formation of the aquocomplex. The reaction conforms to the first order law $-d[\text{complex}]/dt = k_{obs}[\text{complex}]$, with $k_{obs} = k_{off}$.

The dependence of k_{off} on pH is shown in Fig. 2.

From the consideration of the portion of Scheme 1 which leads to the dissociation of $CH_3Rh(DH)_2Py$ we obtain for k_{off}:

TABLE I. Summary of Kinetics and Equilibrium Data for the Water Substitution Reactions of $CH_3Rh(DH)_2H_2O$ and $CH_3Co(DH)_2H_2O$.[a]

	Rh(III)	Co(III)
k_1 (M^{-1} s^{-1})	5.5×10^4 [b]	2.25×10^3 [b]
k_2 (M^{-1} s^{-1})	$(4.23 \pm 0.06) \times 10^3$ [c]	$(1.16 \pm 0.03) \times 10^2$ [d]
k_3K_3 (M^{-2} s^{-1})	$(2.0 \pm 0.2) \times 10^{-6}$ [b]	$(8.4 \pm 0.9) \times 10^{-12}$ [e]
K_1 (M)	0.18 ± 0.08[f]	0.56[g]; 0.31 ± 0.06[h]
$K_2 + K_3$ (M)	$(1.3 \pm 0.1) \times 10^{-10}$ [b]	$(3.5 \pm 0.3) \times 10^{-13}$ [i]
K_2 (M)	$(1.7 \pm 0.2) \times 10^{-10}$ [c]	$(2.1 \pm 0.1) \times 10^{-13}$ [d]
pK_2	9.78 ± 0.04[c]	12.68 ± 0.02[d]
Q	3.64[b]	0.20[l]

[a] Data referring to Rh(III) reactions are collected at 20 °C, except for K_1, which was measured at 25 °C; data referring to Co(III) reactions are collected at 25 °C. [b] This work. [c] From ref. 1. [d] From ref. 2. [e] Calculated from data of ref. 2 as $k'_{on}K'_{c2} = k'_{off}K_fK'_{cL}$ (symbols of ref. 2). [f] From ref. 5. [g] From ref. 15. [h] From ref. 11. [i] From ref. 4. [l] Calculated from data of refs. 2 and 4, as explained in the Discussion.

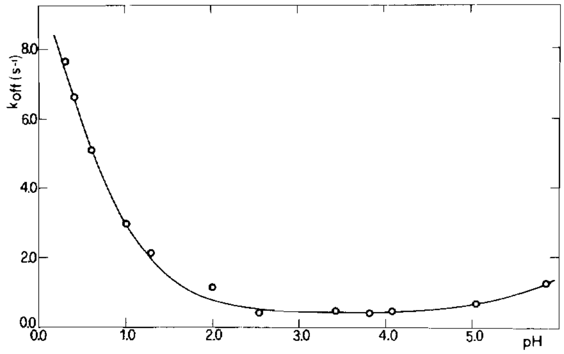


Fig. 2. Dependence of k_{off} upon pH at I = 1 M ($NaNO_3$) and T = 20 °C; the solid line is calculated from eqn. (7) and parameters contained in Table II.

TABLE II. Summary of Kinetic and Equilibrium Data for the Hydrolysis Reactions of $CH_3Rh(DH)_2Py$ and $CH_3Co(DH)_2Py$^{a}.

	Rh(III)	Co(III)
k_{-1} (s^{-1})	12.9 ± 0.09^b	2.9 ± 0.3^b
k_{-2} (s^{-1})	$(4.6 \pm 0.5) \times 10^{-1\ b}$	$(5.52 \pm 0.15) \times 10^{-2\ c}$
k_{-3} (s^{-1})	0.97 ± 0.15^b	$(1.63 \pm 0.1) \times 10^{-1\ c}$
K_4 (M)	0.39 ± 0.05^b	0.84 ± 0.15^b
K_5 (M)	$(2.2 \pm 0.1) \times 10^{-10\ b}$	$(2.4 \pm 0.6) \times 10^{-14\ c}$
pK_5	9.65 ± 0.02^b	13.61 ± 0.09^c

[a] Data referring to Rh(III) reactions are collected at 20 °C; data referring to Co(III) reactions are collected at 25 °C. [b] This work. [c] From ref. 2.

$$k_{off} = \frac{k_{-1}[H^+]/K_4 + k_{-2} + k_{-3}K_5/[H^+]}{[H^+]/K_4 + 1 + K_5/[H^+]} \qquad (7)$$

At sufficiently high $[H^+]$, the terms containing $[H^+]$ in the denominator may be neglected, so that:

$$k_{off} = \frac{k_{-1}[H^+] + k_{-2}K_4}{K_4 + [H^+]} \qquad (8)$$

The k_{-2} value (Table II) has been determined by carrying out the reaction in the pH range 3.0–4.5, where the reaction rate is independent on $[H^+]$. The plot of $1/(k_{off} - k_{-2})$ *versus* $1/[H^+]$ is linear and allows a preliminary calculation of k_{-1} and K_4. The values reported in Table II have been calculated by a non-linear least-squares analysis on the basis of these preliminar estimates.*

At pH > 6.0 the absorbance variation becomes too small, so that k_{-3} and K_5 cannot be determined by kinetic methods. The K_5 value has been obtained by spectrophotometric titration with NaOH of $CH_3Rh(DH)_2Py$, in the presence of a sufficient excess of pyridine to prevent ligand dissociation. Consequently, the k_{-3} value can be calculated on the basis of the relation:

$$k_{-3} = k_{-2}k_3K_3/k_2K_5 \qquad (9)$$

Discussion

It appears from the data of Table I that the deprotonation constant of the axial water (pK_2) is strongly influenced by the nature of the central atom.

There are not many cases where it is possible to compare Rh(III) systems with analogous Co(III) systems, but the available data suggest a considerable similarity between the pK_a of the coordinated water. For $Rh(NH_3)_5H_2O^{3+}$ and $Co(NH_3)_5H_2O^{3+}$, in the same experimental conditions, pK_a are 5.9 and 5.7, respectively [7]. For *trans*-$Rh(en)_2(H_2O)_2^{3+}$, at 26.4 °C and I = 1 M ($NaClO_4$), the pK_{a1} and pK_{a2} values (relative to the deprotonation of the first and second water molecule) are 4.4 and 7.6 [8]. For *trans*-$Co(en)_2(H_2O)_2^{3+}$ at 25 °C and I = 1 M ($NaNO_3$) these values are 4.45 and 7.94 [8]. For $Rh(TPPS)(H_2O)_2^{3-}$ (TPPS = *meso*-tetrakis(p-sulphonatophenyl)porphinato) pK_{a1} = 7.0 pK_{a2} = 9.8, at 25 °C and 1 M $NaClO_4$ [9]; for $Co(TPPS)(H_2O)_2^{3-}$ pK_{a1} = 7.02 and pK_{a2} = 9.76, in the same experimental conditions [10]. Consequently, the diminution of 3–4 units in the pK_2 value is somewhat surprising and could suggest a weaker *trans* influence of the methyl group in the rhodium derivative.

The effect of the change of the metal atom on the acidity of the equatorial protons cannot be discussed, because of the lack of comparison data. We can only attempt a comparison with the effect of the variation of the R group for a series of organocobaloximes [3]. For these compounds the increase of the acidity constants of the equatorial proton of the pyridine derivative, with decreasing electron donor power of R, generally parallels the increase of the deprotonation constants of the axial water of the aquo derivative. On this basis an increase of acidity of the equatorial proton of $CH_3Rh(DH)_2Py$, concomitant with the lowering of pK_2, is to be expected and could be ascribed to a diminution of the *cis* influence of the CH_3 group in the rhodium complexes.

Moreover, the independence of K_1 and K_4 on the metal atom is in accord with the independence of the equatorial deprotonation constants of $RCo(DH_2)(DH)H_2O^+$ on the nature of the R group [11].

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*Kinetic data for the acid hydrolysis of $CH_3Co(DH)_2Py$ are not available. As their knowledge should be interesting in view of a comparison, this reaction has been examined in the proton concentration range 0.05–0.5 M HNO_3, at 25 °C and 1 M $NaNO_3$. Also for this complex the dependence of k_{off} on $[H^+]$ is described by eqn. (7), revealing the formation of the species $CH_3Co(DH_2)(DH)Py^+$. Kinetic and equilibrium data for the hydrolysis of $CH_3Co(DH)_2Py$ are listed in Table II.

It should be noted that the equatorial proton of $CH_3Rh(DH)_2Py$ is slightly more acidic than the axial proton of $CH_3Rh(DH)_2H_2O$ ($pK_5 < pK_2$), whereas for the analogous cobalt complexes the pK_a of the equatorial proton is at least one unit higher than the pK_a of the axial proton [2, 3]. This result suggests a further weakening of the hydrogen bond in the rhodium complex, as a result of the larger Rh ion in the constrained geometry of the tetradentate ligand. Indeed ^1H NMR spectra of $M(DH)_2PyCl$ show the equatorial proton resonance at $\delta = 12.05$ ppm for M = Rh and $\delta = 18.01$ ppm for M = Co [12], and structural data relative to $M[(DO)(DOH)pn]Cl_2$ complexes* indicate the lengthening of the O····O distance of the intramolecular hydrogen bond for the Rh(III) complex (O····O distance = 2.448(5) Å for Co and 2.626(4) Å for Rh) [13].

The reactivity of the methylbis(dimethylglyoximato)rhodium(III) complex is strongly affected by the degree of protonation of the equatorial chelating system. In fact, both the doubly protonated $CH_3Rh(DH_2)(DH)L^+$ and the deprotonated $CH_3Rh(D)(DH)L^-$ species are more labile than are the hydrogen bonded $CH_3Rh(DH)_2L$ species.

As far as the substitution reactions in alkaline medium are concerned, the rhodium derivative shows an increased reactivity both in the anation and in the hydrolysis reactions. For the analogous cobalt complexes the lability towards water substitution decreases in alkaline medium [4]. This comparison may be expressed in a more quantitative way by means of the ratio $Q = k_3K_3/k_2(K_2 + K_3)$ [4]. If Q is greater than 1 an acceleration in the rate is observed in alkaline medium; if Q is equal to 1 the rate is independent on $[OH^-]$; if Q is less than 1 a rate retardation is observed in basic solution. For the reaction of the rhodium complex with pyridine $Q = 3.64$; for the analogous reaction of the cobalt complex a value of 0.20 may be calculated from the k_3K_3 value of ref. 2 and the $K_2 + K_3$ value of ref. 4. The last parameter has been found for the reaction with NH_3, but is obviously independent on the nature of the incoming ligand.

The different behaviour of the Rh and Co complexes may be caused either by a relatively higher lability of the conjugate base (*i.e.* a higher k_3/k_2 ratio) or by a relatively greater acidity of the equatorial proton (*i.e.* a higher $K_3/(K_2 + K_3)$) for the rhodium derivative. Unfortunately, we were not able to obtain separate values for k_3 and K_3, but only the product k_3K_3 so that a choice between these possibilities cannot be made.

Some useful indications may be derived from consideration of the strictly related base hydrolysis reactions. In this case the acceleration in rate due to the formation of the conjugate base is rather small ($k_{-3}/k_{-2} = 2.1$) and very similar to that observed for the cobalt derivative ($k_{-3}/k_{-2} = 2.9$) [2]. The lability ratio for the inverse water substitution reactions (k_3/k_2) would probably be almost independent of the metal atom. On the other hand, as outlined above, the comparison of the acidity of the equatorial proton of $CH_3M(DH)_2Py$ with that of the axial proton of $CH_3M(DH)_2H_2O$ indicates a higher relative acidity of the equatorial proton of the rhodium derivative ($K_5/K_2 = 1.3$ for M = Rh and 0.11 for M = Co). It is very probable that this also occurs for the equatorial proton of the aquocomplex (*i.e.* for K_3/K_2). In this hypothesis the different behavior of $CH_3Rh(DH)_2H_2O$ and $CH_3Co(DH)_2H_2O$ towards the water substitutions in alkaline medium should be mainly due to a greater extent of formation of the conjugate base (*i.e.* a greater $K_3/(K_2 + K_3)$ value) for the rhodium complex.

Whereas positive catalysis by hydroxide ions on the axial substitution reactions of octahedral complexes containing acidic protons is well known, acid catalyzed processes are rather uncommon [14]. Acid catalysis is generally noted when the leaving group is the anion of a weak acid. Incipient protonation of the leaving group in the transition state has been invoked to account for the catalytic effect [14]. As protonation of the bonded axial ligands cannot occur in the present case, the higher lability of the examined complexes in very acidic medium should be attributed to the formation of the cationic species $CH_3Rh(DH_2)(DH)L^+$, doubly protonated at the planar chelate, which have been previously reported [5]. Additional support to this comes from the consideration that the organocobaloximes, for which formation of cationic species have been demonstrated from both spectrophotometric [15] and kinetic measurements [11, 16], show quite similar behaviour in very acidic solutions, whereas $RCo[(DO)(DOH)pn]H_2O^+$ complexes, for which no evidence of protonation has been found [17], do not show any catalytic effect of H^+ [18].

The increase of lability due to the formation of the cationic complexes is about of the same order of magnitude as that due to the formation of the anionic complexes in the substitution reactions in alkaline medium (k_1/k_2 and k_{-1}/k_{-2} range from 10 to 50). For the base hydrolysis reactions of the organocobaloximes the increased lability was ascribed to the increase of the electron density on the cobalt atom due to the deprotonation of the equatorial chelate [2]. Such an explanation cannot be valid for the increased lability of the cationic complexes. As both in anionic and in cationic complexes one of the two intramolecular hydrogen bonds is disrupted, it seems

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*The ligand (DO)(DOH)pn differs from the ligand $(DH)_2$ for the replacement of one O···H···O bridge by a $-(CH_2)_3-$ group.

reasonable to suppose that the higher lability of these derivatives may be caused by a lesser rigidity of the planar chelating ring, which could for instance promote the bending of the two individually planar DH units and the lengthening of the bond *trans* to the alkyl group.

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