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Mechanism of Formation of *trans*-Chloro-Bisdimethylglyoximato-Tertiary Phosphine Cobalt(III) Complexes and Their Isomers 1:1 Electrolytes

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The Tschugaeff reaction between cobalt chloride and dimethylglyoxime, in presence of tertiary phosphine or of nitrogen bases, in ethanol yields non charged trans-*chlorobisdimethylglyoximato-tertiary phosphine cobalt(III) complexes and / or their isomers 1:1 electrolytes, depending of the nature of axial Lewis base. The mechanism of the reaction is discussed and interpreted in term of the labilizing (kinetic) trans-effect of the Lewis base.*

Introduction

Complex of general formula *trans*-$CoCl(DH)_2L$ (L = nitrogen base, $(DH)_2$ = bisdimethylglyoximato dianion) were prepared after Tschugaeff[1] by addition of the Lewis base (1 mole) to the hot filtered reaction solution of 2.2 moles of dimethylglyoxime with 1 mole of cobalt chloride in ethanol, followed by air oxidation.

Complexes with ammonia, aliphatic or aromatic amine, pyridine and other heterocyclic nitrogen base as axial ligand L were reported.[1,2]

It was pointed out that complexes of the type $CoX(DH)_2L$ or complex cations $[Co(DH)_2L_2]^+$ ($X = Cl^-$, Br^-, I^-, NO_2^-, SCN^-) can be formed depeding on the anion in the reagent cobalt salt, the coordination properties of the ligand L, the molar ratio L/Co, the pH and reaction conditions.[2,3] On the other hand, the complex salts $[Co(DH)_2L_2]^+[CoX_2(DH)_2]^-$ ($X = Cl^-$, Br^-, I^-, NO_2^- etc.) were obtained by reaction of $[Co(DH)_2L_2]^+Cl^-$ with $K^+[CoX_2(DH)_2]^-$ ($X = CN^-$, OH^-) [4] or of $[Co(DH)_2L_2]^+CH_3COO^-$ with $H^+[CoX_2(DH)_2]^-$ [3] ($X = Cl^-$, Br^-, I^-, SCN^-).

Bis-dimethylglyoximato-triphenylphosphine- and (tri-n-butylphosphine)cobalt(III) complexes were first investigated by Schrauzer as model molecules of Vit.B_{12} group.[5]

As part of a research program devoted to the study of the coordination chemistry of a series of model molecules of Vit.B_{12} of the type CoX(chel)L (where « chel » is a planar tetradentate chelating system as bis(acetylacetone)ethylendiamine[6], bis(salicylaldehyde)-ethylendiamine,[7] bisdimethylglyoxime[5]) we reported the effect of tertiary phosphines as axial ligands on the polarographic reduction[8] of complexes $[Co(chel)H_2O\ PR_3]^+$ and $[Co(chel)(PR_3)_2]^+$ and on the solvolytic aquation of complexes $[CoCl(DH)_2PR_3]^0$.[9]

The present paper deals with the effect of the tertiary phosphine on the formation mechanism of $CoCl(DH)_2PR_3$ and/or $[Co(DH)_2(PR_3)_2]^+[CoCl_2(DH)_2]^-$ by the Tschugaeff reaction.

Tri-n-butylphosphine as axial ligand. When we attempted the preparation of $CoCl(DH)_2P(n\text{-}C_4H_9)_3$ by the Tschugaeff's procedure as reported by Schrauzer[5] red brown crystals of a product consistent with the above formula were indeed obtained but careful examination showed that it was not the above uncharged complex . From the results of the following investigations it has to be formulated as the 1:1 electrolyte $\{Co(DH)_2[P(n\text{-}C_4H_9)_3]_2\}^+\{CoCl_2(DH)_2\}^-$.

1) The electrical conductivity in nitrobenzene is higher than expected (see Table I). The product shows very low solubility in water but when dissolved in methanol it cannot be precipitated by addition of water.

2) When a methanol-water solution of the product is treated with a cation exchange resin the cation $\{Co(DH)_2[P(n\text{-}C_4H_9)_3]_2\}^+$ is adsorbed while in the eluted solution the anion $[CoCl_2(DH)_2]^-$ undergoes aquation[9] and the aquation product $CoCl(DH)_2H_2O$ is recovered (about 0.5 moles per g. atom of Co in the starting solution).

From the solution treated with anion-exchange resin the cation is recovered as $\{Co(DH)_2[P(n\text{-}C_4H_9)_3]_2\}^+OH^-$ or $Co(DH)(D)[P(n\text{-}C_4H_9)_3]_2 . H_2O$ (see later) (where DH and D are dimethylglyoximato mono- and di-anion, respectively).

3) The rate of displacement of Cl^- from the anion $[CoCl_2(DH)_2]^-$ of the 1:1 electrolyte was followed by

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(1) L. Tschugaeff, *Chem. Ber.* 39, 2692 (1906); *40* 3498 (1907).

(2) Cs. Várhelyi and S. Kövendi, *J. für prakt. Chem.* *34*, 209 (1966), and literature quoted therein.

(3) R. Ripan, Cs. Várhelyi and J. Ürmösi, *Zeitsch. für anorg. und allg. Chem.* 332, 95 (1964).

(4) A. V. Ablov and G. P. Syrstova, *Russ. J. Inorg. Chem. 10*, 1079 (1965).

(5) G. N. Schrauzer and J. Kohnle, *Chem. Ber.* *97*, 3056 (1964).

(6) G. Costa, G. Mestroni, G. Tauzher, and L. Stefani, *J. Organomet. Chem.* 6, 181 (1966); G. Costa and G. Mestroni, *ibidem*, *11*, 325 (1968).

(7) G. Costa, G. Mestroni and L. Stefani, *J. Organomet. Chem. 7*, 493 (1967); G. Costa, G. Mestroni and G. Pellizer, *ibidem*, *11*, 333 (1968).

(8) G. Costa, A. Puxeddu and G. Tauzher, *Inorg. Nucl. Chem. Letters*, *4*, 319 (1968).

(9) Preceding paper.

Table I.

	Molar conductance $\Lambda_{(10^{-3}M)}$ = Ohm^{-1} cm^2 (in nitrobenzene)	$(k_{aq})_1$ x$10^6$$sec^{-1}$ (HNO$_3$ 0.01 N)	$(k_{aq})_2$ x$10^6$$sec^{-1}$
$\{Co(DH)_2[P(n\text{-}C_4H_9)_3]_2\}^+\{CoCl_2(DH)_2\}^-$	16.9	111.8	17
$CoCl(DH)_2\ P(n\text{-}C_4H_9)_3$	0	479	—

potentiometric determination of Cl^-. The plot of Cl^- concentration against time was identical to that of a solution of $H^+[CoCl_2(DH)_2]^-$ at the same molar concentration as that of the complex salt solution (Figure 1).

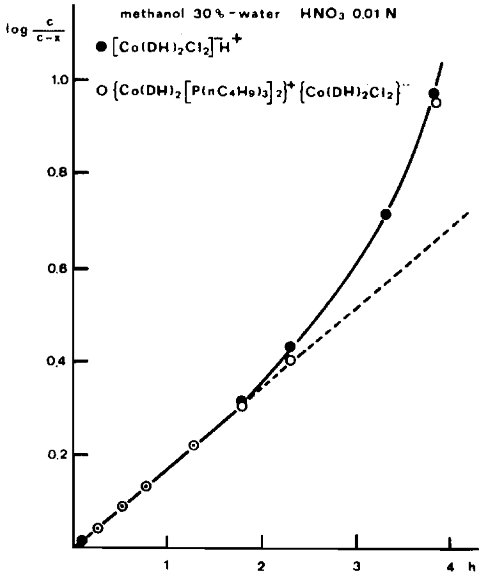


Figure 1

The pseudo-first order rate constant (methanol (30%) water; 0.01 N HNO_3, 25°C) for the reaction 1)

$$[CoCl_2(DH)_2]^- + H_2O \rightarrow CoCl(DH)_2H_2O + Cl^- \quad (1)$$

$$CoCl(DH)_2H_2O + H_2O \rightarrow [Co(DH)_2(H_2O)_2]^+ + Cl^- \quad (2)$$

were found to be identical, both from experiments with the 1:1 electrolyte $\{Co(DH)_2[P(n\text{-}C_4H_9)_3]_2\}^+\{CoCl_2(DH)_2\}^-$ and with $H^+[CoCl_2(DH)_2]^-$.

From the Cl^- concentration at the equilibrium the overall equilibrium constant $K_{aq} = 60.7 \times 10^{-8}$ was obtained. Starting from $CoCl(DH)_2H_2O$ in methanol (30%)-water solution 0.01 N HNO_3, 25°C) the rate constant for reaction 2) and the equilibrium constant $K_2 = 5.5 \times 10^{-4}$ was determined.

4) Potentiometric titration of a methanol (70%)-water solution of the complex salt with 0.1 N NaOH clearly shows two inflexion points. Each equivalence point exactly corresponds to 0.5 equivalents of NaOH per g. atom of cobalt. The titration curve (Figure 2) is superimposable to that of $H^+[CoCl_2(DH)_2]^-$ for the part subsequent to the neutralization of the strong acid, at the same molar concentration as that of the 1:1 electrolyte complex salt. It was ascertained that $\{Co(DH)_2[P(n\text{-}C_4H_9)_3]_2\}^+ClO_4^-$ is not deprotonated until pH 11.

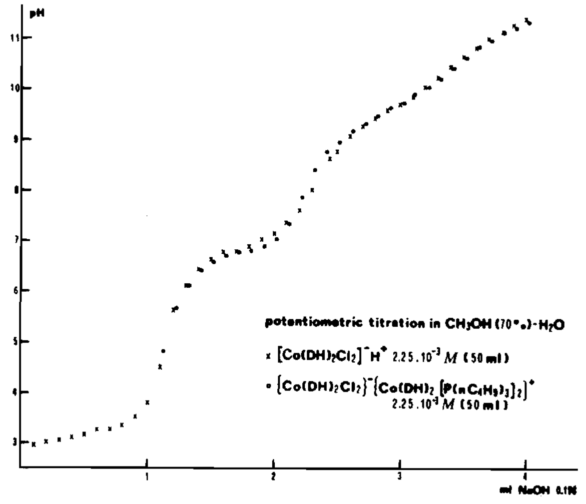


Figure 2

5) From methanol (30%)-water solution of the 1:1 electrolyte the cation can be isolated by precipitation with NaOH as the sparingly soluble $Co(DH)(D)[P(n\text{-}C_4H_9)_3]_2 . H_2O$.

By precipitation with $NaClO_4$ the perchlorate $\{Co(DH)_2[P(n\text{-}C_4H_9)_3]_2\}^+ClO_4$ is recovered in almost quantitative yield, *i.e.* 0.5 mole per g. atom of cobalt in the solution of the complex salt.

6) The 1:1 electrolyte was prepared by reaction of $\{Co(DH)_2[P(n\text{-}C_4H_9)_3]_2\}^+ClO_4^-$ or $Co(DH)(D)[P(n\text{-}C_4H_9)_3]_2 . H_2O$ in alcohol with a suspension of $H^+[CoCl_2(DH)_2]^-$. The product is obtained in almost quantitative yield. The properties of the product are identical to those of the product obtained by Tschugaeff's reaction as described above, including the I.R. spectra in the solid state.

Triphenylphosphine as axial ligand. The attempted preparation of $CoCl(DH)_2P(C_6H_5)_3$ by Tschugaeff's reaction yields about 80% of the non electrolyte complex and 20% of $\{Co(DH)_2[P(C_6H_5)_3]_2\}^+\ \{CoCl_2(DH)_2\}^-$ as can be determined by recovering the cation as perchlorate.

Non electrolyte complexes with PR_3. The uncharged complexes $CoCl(DH)_2PR_3$ can be easily obtained as pure products by reaction of less than stoichiometric amount of the tertiary phosphine with $CoCl(DH)_2H_2O$ in ethanol.

The above formulation and the distinction from the isomers 1:1 electrolyte complexes are supported by the following evidence:

1) The initial electrical conductivity of the solution in nitrobenzene is very low. It increases in water-methanol with first order rate as expected from the solvolytic aquation[9]

$$CoCl(DH)_2PR_3 + H_2O \rightarrow [Co(DH)_2H_2OPR_3]^+ + Cl^-$$

2) The chloro- and aquocomplexes are quantitatively recovered after treatment with anion exchange resin.

3) From the titration curve only one equivalence point can be clearly seen (1 equivalent of NaOH per mole of $CoCl(DH)_2PR_3$) corresponding to the titration of the aquocomplex. The pK_a's of several aquocomplexes $CoCl(DH)_2PR_3$ are reported in the preceeding paper.

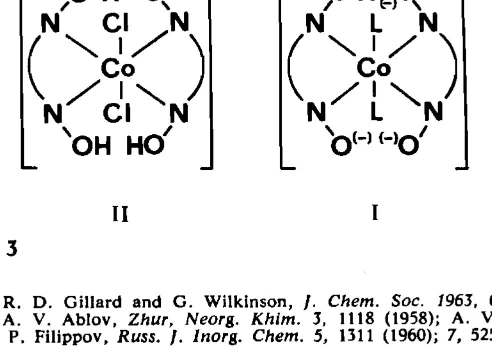
No evidence for the equilibrium between 1:1 electrolyte and uncharged complex was observed.

Discussion

From the above evidence there can be little doubt that in aqueous or alcohol-water solution the product of Tschugaeff's reaction using $P(n\text{-}C_4H_9)_3$ as Lewis base consists of $\{Co(DH)_2[P(n\text{-}C_4H_9)_3]_2\}^+$ and of the aquation products of the initially present $[CoCl_2(DH)_2]^-$, *i.e.* $CoCl(DH)_2H_2O$ and $[Co(DH)_2(H_2O)_2]^+$. The aquocomplexes behave as mono and diacid respectively. The structure of the product in the solid state is less certain, while it is identical to that of the solid product of the reaction of $H^+[CoCl_2(DH)_2]^-$ with $\{Co(DH)_2[P(n\text{-}C_4H_9)_3]_2\}^+$ as appears from I.R. spectra. The low solubility in water may suggest that in the solid state uncharged species should exist. This is not inconsistent with the 1:1 electrolyte properties in solution if one considers that the acid $H^+[CoCl_2(DH)_2]^-$ was formulated by Gillard and Wilkinson[10] as the uncharged species $[CoCl_2(DH)(DH)_2)]^0$ (I) (where DH_2 is dimethylglyoxime) while by splitting off a proton even the cation could be formulated as the uncharged species $\{Co(DH)(D)[P(n\text{-}C_4H_9)_3]_2\}^0$ (II). This formulation was previously proposed by Ablov for the anhydro-bases as $[Co(DH)(D)(Py)_2]^0$.[11]

It can be seen that the uncharged complexes I and II differ from the anionic and cationic species respectively only by the shift of the proton (Figure 3).

As far as the mechanism of formation of the 1:1 electrolytes is concerned the following interpretation can be proposed.



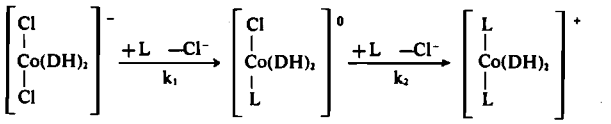
II I

Figure 3

By the reaction of $CoCl_2 \cdot 6\,H_2O$ with dimethylglyoxime in alcohol the dichloroanion $[CoCl_2(DH)_2]^-$ is first formed; by addition of the Lewis base L in the stoichiometric ratio L/Co = 1:1, ligand substitution of Cl^- by L takes place and $CoCl(DH)_2L$ is formed. When the axial ligand L exerts a strong *trans*-effect further displacement of Cl^- ligand can occur before the complete consumption of $[CoCl_2(DH)_2]^-$.

As a limiting case the ligand $L = P(n\text{-}C_4H_9)_3$ is entirely used to form $[Co(DH)_2L_2]^+$ and the 1:1 electrolyte is obtained as the sole product.

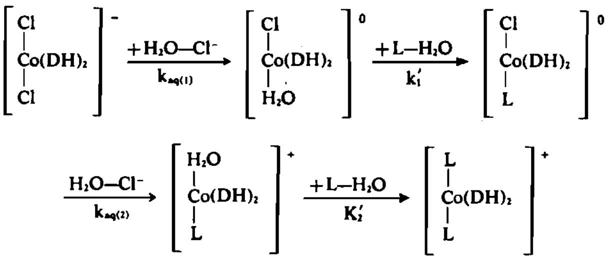
In the alternative case $[CoCl_2(DH)_2]^-$ is completely consumed with formation of $CoCl(DH)_2L$



$$\begin{bmatrix} Cl \\ | \\ Co(DH)_2 \\ | \\ Cl \end{bmatrix}^- \xrightarrow[k_1]{+L\ -Cl^-} \begin{bmatrix} Cl \\ | \\ Co(DH)_2 \\ | \\ L \end{bmatrix}^0 \xrightarrow[k_2]{+L\ -Cl^-} \begin{bmatrix} L \\ | \\ Co(DH)_2 \\ | \\ L \end{bmatrix}^+$$

The extent of formation of the 1:1 electrolyte depends thus on the labilizing (kinetic) *trans*-effect of the ligand L.

This conclusion is still valid when the intermediate aquation of the chlorocomplexes can occur:



$$\begin{bmatrix} Cl \\ | \\ Co(DH)_2 \\ | \\ Cl \end{bmatrix}^- \xrightarrow[k_{aq(1)}]{+H_2O-Cl^-} \begin{bmatrix} Cl \\ | \\ Co(DH)_2 \\ | \\ H_2O \end{bmatrix}^0 \xrightarrow[k_1']{+L-H_2O} \begin{bmatrix} Cl \\ | \\ Co(DH)_2 \\ | \\ L \end{bmatrix}^0$$

$$\xrightarrow[k_{aq(2)}]{H_2O-Cl^-} \begin{bmatrix} H_2O \\ | \\ Co(DH)_2 \\ | \\ L \end{bmatrix}^+ \xrightarrow[K_2']{+L-H_2O} \begin{bmatrix} L \\ | \\ Co(DH)_2 \\ | \\ L \end{bmatrix}^+$$

Moreover, if the anation reactions are rapid as compared with aquation the extent of the 1:1 electrolyte formed would depend on the ratio of the reaction rates $k_{aq(1)}$ and $k_{aq(2)}$.

The kinetic condition for the almost complete formation of the complex salt when $L = P(n\text{-}C_4H_9)_3$ is verified if one assumes as an indication of the kinetic *trans*-effect of L the relative values of the aquation rate constants in methanol (30%)-water 0.01 N HNO_3, *i.e.* $k_{aq(2)} = 479 \times 10^{-6} sec^{-1}$ and $k_{aq(1)} = 111.8 \times 10^{-6} sec^{-1}$ while k_{aq} for $CoCl(DH)_2H_2O$ is $17 \times 10^{-6} sec^{-1}$.

On the other hand $P(C_6H_5)_3$ represents an intermediate case since in this case both isomers are formed (20% of the 1:1 electrolyte).

The *trans*-effect of aromatic and heterocyclic nitrogen bases which yield mainly the non electrolytes $CoX(DH)_2L$ by Tschugaeff's reaction[2,11-13] appears thus to be comparatively lower than that of $P(n\text{-}C_4H_9)_3$.

Experimental Section

$\{Co(DH)_2[P(n\text{-}C_4H_9)_3]_2\}^+\{CoCl_2(DH)_2\}^-$. a) *Tschugaeff's reaction.* $CoCl_2 \cdot 6\,H_2O$ (5 g.; 21 mmoles) were reacted with dimethylglyoxime (5.5 g.; 47

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(10) R. D. Gillard and G. Wilkinson, *J. Chem. Soc. 1963*, 6041.

(11) A. V. Ablov, *Zhur, Neorg. Khim. 3*, 1118 (1958); A. V. Ablov and M. P. Filippov, *Russ. J. Inorg. Chem. 5*, 1311 (1960); *7*, 525 (1962).

(12) A. V. Ablov and G. P. Syrstova, *Zhur. Obsh. Khim. 25*, 1304 (1955); *Zhur. Neorg. Khim. 1*, 687 (1956).

(13) Cs. Várhelyi and B. Bohm, Studia Univ. Babes-Bolyai, *Ser. Chemia 8*, 113 (1963); 9, 55 (1964); cfr. C. A. *61*, 14161b (1964); 62, 15642b (1964).

mmoles) in 200 ml of boiling ethanol. To the hot filtered solution 5 ml tri-n-butylphosphine (20 mmoles) were added dropwise. After cooling brown crystals were obtained Recrystallized from ethanol.

b) To an alcoholic solution of $\{Co(DH)_2[P(n\text{-}C_4H_9)_3]_2\}^+ClO_4^-$ or $Co(DH)(D)[P(n\text{-}C_4H_9)_3]_2 . H_2O$ a suspension of finely powdered $CoCl_2(DH)(DH_2)$ in alcohol was added by stirring. The product was filtered (~100% yield) and recrystallized from ethanol.

$\{Co(DH)_2[P(C_6H_5)_3]_2\}^+\{CoCl_2(DH)_2\}^-$. By the method b) the 1:1 electrolyte was obtained in almost quantitative yield. Recrystallized from methanol.

$CoCl(DH)_2PR_3$ (R = $P(n\text{-}C_4H_9)_3$; $P(C_2H_5)_3$; $P(cyclo\text{-}C_6H_{11})_3$). $CoCl(DH)_2H_2O$ (3.4 g.; 10 mmoles) prepared after Babko and Korotun[14] was suspended in ethanol (100 ml) and treated dropwise under stirring at room temperature with the appropriate tertiary phosphine (6-7 mmoles). $P(cyclo\text{-}C_6H_{11})_3$ was added as ethereal solution. The brown solution was concentrated by evaporation of the solvent and the precipitated product was filtered and washed with water.

The product is purified by recrystallization from ethanol or by precipitation from the ethanolic conc. solution with sat.aqueous solution of KCl.

$CoCl(DH)_2\ P(C_2H_5)(C_6H_5)_2$; $CoCl(DH)_2\ P(C_6H_5)_3$: were prepared by the same procedure as above. The $P(C_6H_5)_3$ was added as ethereal solution. The reaction was performed at 40-60°C and the product precipitated spontaneously from the reaction solution. Recrystallized from ethanol.

$[Co(DH)_2H_2OL]^+ClO_4$ (L = $P(n\text{-}C_4H_9)_3$; $P(C_2H_5)_3$; $P(C_2H_5)(C_6H_5)_2$; $P(C_6H_5)_3$; $P(cyclo\text{-}C_6H_{11})_3$. To a freshly prepared conc. ethanol solution of $[Co(DH)_2(H_2O)_2]^+ClO_4^-$ [15] (4.2 g.; 10 mmoles) the appropriate phosphine (6-7 mmoles) was added dropwise (solid phosphines were added as conc.ethereal solutions). After stirring (1 h.) at room temperature the solvent was evaporated and the product was precipitated at 0°C by addition of sat.solution of $NaClO_4$ slightly acidified as above.

The aquocomplexes were obtained also by solvolytic aquation of the corresponding $CoCl(DH)_2PR_3$ in conc. water-methanol solution in the presence of $NaClO_4 + HClO_4$.

$[Co(DH)_2L_2]^+ClO_4^-$ (L = $P(n\text{-}C_4H_9)_3$; $P(C_2H_5)(C_6H_5)_2$; $P(C_6H_5)_3$). $CoCl(DH)_2H_2O$ or $[Co(DH)_2(H_2O)_2]^+ClO_4^-$ were reacted with the appropriate phosphine in the molar ratio 1:2. The product was filtered and purified by precipitation with sat. $NaClO_4$ from ethanol solution followed by washing with water and drying.

Potentiometric titrations: were performed in methanol (70%)-water solution with 0.1 N NaOH using a Beckman Model G pH-meter.

Kinetic measurements: were performed in 0.01 N HNO_3 methanol (30%)-water solution at 25° by potentiometric determination of Cl^- released by solvolytic aquation, using the following cell:

$$Ag \mid AgCl \begin{array}{c}\text{complex}\\ \text{solution } 0.01\text{ N } HNO_3\end{array} \Bigg| \begin{array}{c}KNO_3\\ \text{agar}\end{array} \Bigg| \ KCl\ \text{sat.}Hg_2Cl_2 \mid Hg$$

The average Cl^- concentration was calculated from calibration plots obtained by replacing the complex solution in the left half-cell with solution of known NaCl concentration in the same solvent and experimental conditions as for the complexes.

The concentrations of the complexes were in the range $1 - 1.8\times10^{-3}$ *M*. The kinetic data were plotted, according to the equation $k = \dfrac{2{,}303}{t} \log \dfrac{c}{c-x}$.

In the aquation kinetic of $[CoCl_2(DH)_2]^+$ the deviation from linearity was ascribed to the removal of a second chloro ion from the complex. The rate constant for this complex was obtained from the straight line portion of the graph.

Conductance measurements: were performed in nitrobenzene with a Halosis (S.I.S.) conductivity bridge and a jacketed cell thermostated at 25°C.

Exchange resin experiments: 0.5 g. (0.47 mmoles) of $Co(DH)_2[P(n\text{-}C_4H_9)_3]_2\}^+\{CoCl_2(DH)_2\}^-$ obtained by procedure a) were dissolved in 100 ml of ethanol (70%)-water solution and passed through a column filled with Dowex 1X anion-exchange resin (in the OH^- form).

From the eluted solution after evaporation of the ethanol 0.32 g. (~95% yield) of $Co(DH)(D)[P(n\text{-}C_4H_9)_3]_2 . H_2O$ were recovered and identified by analysis. By the same procedure as above, using a Dowex 50W cation-exchange resin (in the H^+ form) 0.11 g. (~10% yield) of $CoCl(DH)_2H_2O$ were recovered and identified by analysis.

Compound	Analyses % C Calcd.	C Found	H Calcd.	H Found	N Calcd.	N Found
$CoCl(DH)_2\ P(C_2H_5)_3$	38.0	37.9	6.6	6.5	12.7	12.8
$CoCl(DH)_2\ P(n\text{-}C_4H_9)_3$	45.6	45.5	7.8	7.9	10.6	10.6
$CoCl(DH)_2\ P(C_2H_5)(C_6H_5)_2$	49.0	49.0	5.4	5.5	10.4	10.4
$CoCl(DH)_2\ P(C_6H_5)_3$	53.2	53.1	5.0	4.9	9.5	9.4
$CoCl(DH)_2\ P(cyclo\text{-}C_6H_{11}) . 1/2H_2O$	50.9	50.8	7.9	8.2	9.1	9.1
$[Co(DH)_2H_2O\ P(C_2H_5)_3]^+ClO_4^- . 1/2H_2O$	31.5	31.5	6.0	6.1	10.5	10.2
$[Co(DH)_2H_2O\ P(n\text{-}C_4H_9)_3]^+ClO_4^-$	39.5	40.2	7.1	7.4	9.2	9.2
$[Co(DH)_2H_2O\ P(C_2H_5)(C_6H_5)_2]^+ClO_4^- . H_2O$	41.4	41.6	5.2	5.2	8.8	8.9
$[Co(DH)_2H_2O\ P(C_6H_5)_3]^+ClO_4^-$	46.7	46.7	4.7	4.6	8.4	8.3
$[Co(DH)_2H_2O\ P(cyclo\text{-}C_6H_{11})_3]^+ClO_4^- . H_2O$	44.3	44.3	7.3	7.3	8.0	8.0
$\{Co(DH)_2[P(n\text{-}C_4H_9)_3\}^+ClO_4^-$	48.5	48.3	8.6	8.4	7.1	7.1
$\{Co(DH)_2[P(C_2H_5)(C_6H_5)_2]_2\}^+ClO_4^- . H_2O$	51.8	52.0	5.6	5.6	6.7	6.7
$\{Co(DH)_2[P(C_6H_5)_3]_2\}^+ClO_4^-$	57.9	57.9	4.9	5.0	6.1	6.1
$Co(DH)(D)[P(n\text{-}C_4H_9)_3]_2 . H_2O$	54.1	54.2	9.8	9.7	7.9	8.2
$\{Co(DH)_2[P(n\text{-}C_4H_9)_3]_2\}^+\{CoCl_2(DH)_2\}^-$	45.6	45.4	7.8	7.6	10.6	10.6
$\{Co(DH)_2[P(C_6H_5)_3]_2\}^+\{CoCl_2(DH)_2\}^-$	53.2	53.3	5.0	5.1	9.5	9.4
	Cl				Co	
$CoCl(DH)_2H_2O$	10.4	10.2			17.2	17.4

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