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Kinetics of Aquation of *trans*-Chloro-Tertiary Phosphine-Co^{III}-Bisdimethylglyoximato Complexes

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The kinetics of the aquation reaction of trans-*chloro-tertiary phosphine-Co^{III}-bisdimethylglyoximato complexes and pKa of the corresponding aquo-complexes have been examined in order to determine the* trans-*effect of the tertiary phosphine on the chloro and aquo axial ligand respectively. The aquation rates, the pKa of the aquo-complexes, and half-wave potentials of reduction of the aquo-complexes at d.m.e. correlated with the pKa of the phosphine. The results are discussed in term of σ-donor character of the phosphine and trasmission of electronic effect through the cobalt atom. The effect of the planar chelating system on the kinetic properties in model molecules of vitamin B_{12} is discussed.*

Introduction

The nature of the effects of one ligand and their transmission to another ligand through the central metal ion constitutes one of the main problems in coördination chemistry. These interactions (*cis* and *trans* effects) can be observed in the ground state as well as in the thermodynamic and kinetic aspects of chemical reactivity. Coordination chemistry of Co^{III} complexes of vitamin B_{12} group,[1] porphirins[2] and phtalocyanines,[3] are examples where these studies could be particularly useful.

The opportunity for studying these effects and for comparing the behaviour of complexes of biological interest with that of other Co^{III} complexes was further improved since several series of co^{III} chelates containing an approximately planar chelating system and a variety of axial ligands, including a σ-bonded carbon ligand, were proposed as model molecules.[4-6] Trans-effects were mostly studied in square-planar Pt^{II} complexes with emphasis in the kinetic aspects[7] while the kinetic data for the biologically important Co^{III} complexes are more sparse,[2,8,9,1b]

Among the model molecules the axial ligand substitution and aquation were investigated in Co^{III} dimethylglyoximates.[10] The problem of the transmission of electronic effects of the ligands (cis and *trans* effects) was recently tackled by N.M.R. technique in Co^{III} dimethylglyoximates,[11a] bis(acetylacetone)ethylendiamine and bis(salicylaldehyde)ethylendiamine complexes.[11b]

The well known stabilizing effect exhibited by phosphine ligands on the low oxidation states, hydrido and organometallic derivatives of transition metals was considered in the chemical investigations of Co^{III} dimethylglyoximates.[12]

We recently reported the marked influence of some tertiary phosphines on the polarographic half-wave potentials ($E_{1/2}$) for the formal $Co^{III} \rightarrow Co^{II}$ reduction of model molecules of Vit. B_{12}.[13]

As another consequence of trans-effect we cxplain the nature of the complexes obtained by the Tschugaeff's reaction from $CoCl_2$, dimethylglyoxime and Lewis bases as depending on the σ-donor properties[14] of the ligand.

The above observations prompted us to choose a suitable series of co^{III} dimethylglyoximates of the type $ClCo(DH)_2PR_3$ (DH = dimethylglyoximato monoanion) to evaluate the kinetic effect of tertiary phosphines as axial ligands using the aquation reaction as a test.

Trans-effect. The trans-effect has been observed for numerous reactions of Pt^{II} but it is not nearly as well defined for the reaction rates in the octahedral complexes.

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Table I.

PR_3	pK_a (PR_3) *a*	pK_a (PR_3) *b*	pK_a $[H_2OCo(DH)_2PR_3]^+$	k_{aq} $[ClCo(DH)_2PR_3]^\circ$ $\times 10^6 sec^{-1}$	$E_{1/2}$ $[H_2OCo(DH)_2PR_3]^+ClO_4^-$ (V. *vs.* S.C.E.)
$P(C_6H_5)_3$	2.73	3.05	7.10	111.6	–0.150
$P(C_6H_5)_2(C_2H_5)$	—	4.92	7.80	135.0	–0.320
$P(C_2H_5)_3$	8.69	8.65	8.10	890.5	–0.485
$P(n\text{-}C_4H_9)_3$	8.43	8.89	8.10	958	–0.525
$P(cyclo\text{-}C_6H_{11})_3$	9.70	9.05	8.20	very fast	–0.270

[a] Values extrapolated to 100% water from potentiometric titration in nitromethane - water - mixed solvents - C. A. Streuli, Anal. Chem. 32, 985 (1960) - relative value accurate to ±0.02 pK. [b] Calculated from the equation $pK_a = 7.85 – 2.67\Sigma\sigma^*$ (cfr. 15).

The observed pseudo-first order rate constant k_{aq} for the reaction

$$ClCo(DH)_2L + H_2O \rightarrow [H_2OCo(DH)_2L]^+ + Cl^-$$

seems suitable for assessing the relative activating influence of substituents in a series of analogous compounds undergoing the same reaction.

The compounds chosen for this investigation represent a suitable series of analogous complexes to allow an evaluation of the importance of inductive effects on these rate of reaction.

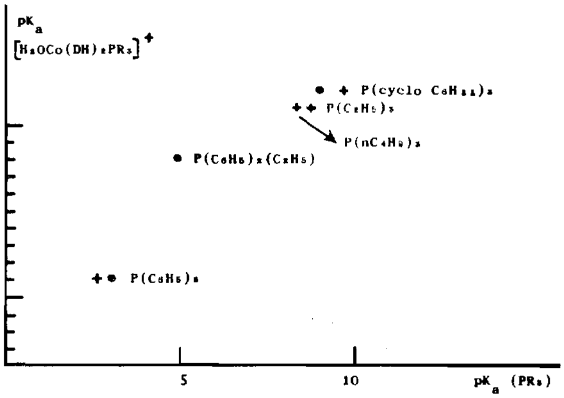

Figure 1.
+ $pK_a(PR_3)$: experimental values by potentiometric titration in nitromethane-water extrapolated to 100% H_2O
○ $pK_a(PR_3)$: calculated from eq. $pK_a = 7.85 – 2.67\Sigma\sigma^*$ (15)

Results and discussion

The trans-structure of the bisdimethylglyoximatocobalt(III) complexes of the type $ClCo(DH)_2PR_3$ investigated in the present paper and the maintenance of the trans-stereochemistry in the axial ligand substitution reaction is assumed.[10]

The solvolytic aquation in methanol (30%)-water

$$ClCo(DH)_2PR_3 + H_2O \rightarrow [H_2OCo(DH)_2PR_3]^+ + Cl^-$$

obeys first order kinetics and goes to completion.

The rate constants k_{aq} are reported in Table I together with the pK_a of the tertiary phosphine ligand, the pK_a of the corresponding aquocomplex cation $[H_2OCo(DH)_2PR_3]^+$ and the half wave potential ($E_{1/2}$) of the irreversible monoelectronic reduction at the dropping mercury electrode (vs. satured calomel electrode).

It can be seen from the above data that:

a) The pK_a of the aquocomplex cation increases as the basicity of the tertiary phosphine ligand increases, the plot of the pK_a (aquocomplex) against pK_a (phosphine) yields a straight line, (Figure 1). Only the pK_a of $[H_2OCo(DH)_2P(C_6H_5)_3]^+$ is lower than expected from the pK_a of $P(C_6H_5)_3$.

b) The rate constant for the aquation reaction increases as the pK_a of the aquocomplex increases.

c) The $E_{1/2}$ values shift to more negative potentials as the pK_a of the complex increases (with exception of $P(cycloC_6H_{11})_3$).

The first correlation reflects a thermodynamic *trans-effect*. The order of decreasing acidity of the aquocomplexes $P(C_6H_5)_3 < P(C_6H_5)_2(C_2H_5) < P(n\text{-}C_4H_9)_3 < P(cyclo\text{-}C_6H_{11})_3$ is the same as that of increasing σ-donor character of the tertiary phosphine.[15] The decreasing acidity of the aquocomplex can be attributed to the relative increase of the effective charge on the metal atom (weakening the metal-oxygen bond) as was proposed for the $[H_2OPtA_2L]^{n+}$ complexes.[16]

The correlation b) between rates of aquation and pK_a of the aquocomplex reflects the connection between the thermodynamic and the kinetic *trans*-effect. A similar correlation was found for the acidity of *trans*-$[H_2OCo(en)_2L]^{2+}$ decreasing in the order L = = NCS^-, NO_2^-, Cl^-, OH^- which is the same, with the exception of NO_2^-, as the order of increasing effect of L on the rate of hydrolysis of *trans*-$[ClCo(en)_2L]^+$.[17]

The increase of the rate of acid hydrolysis of $[ClCo(en)_2(X\text{-}py)]^{2+}$ with the base strength of substituted pyridine ligand X-Py (pyridine, β-picoline, α-picoline, γ-methoxypyridine) was also attributed to changes in the inductive effect of X–Py.[18]

Although the steric condition (and π-bonding contribution) are not the same for all the tertiary phosphines examined, it can be suggested that the change in reaction rates must be attributed mainly to changes in the inductive effect of the inert ligand as reflected by the pK_a of the phosphine.[15]

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(15) Wm. A. Henderson and C. A. Streuli, *J. Am. Chem. Soc. 82*, 5791 (1960).
(16) Ref. 7) p. 367.
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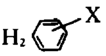
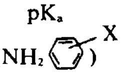
Table II.

L NH_2 	pK_a (NH_2 )	pK_a $[H_2OCo(DH)_2L]^+$	k_{aq} [e] $\times 10^6 sec^{-1}$
p-OCH_3	5.29 [a]	6.69 [c]	53.9
m-CH_3	4.73 [b]	6.87 [c]	62.5
p-CH_3	5.08 [b]	6.88 [c]	69.3
o-CH_3	4.42 [b]	7.09 [c]	118.6
2,4,6$(CH_3)_3$	4.38 [b]	8.25 [d]	228.1

[a] N. F. Hall and M. R. Sprinkle, *J. Am. Chem. Soc.*, *54*, 3469 (1932). [b] R. N. Beale, *J. Chem. Soc.*, 4494 (1954). [c] A. V. Ablov, B. A. Bovykin, and N. M. Samus, *Zh. Neorg. Khim.*, *11*, (8), 1832 (1966), Chem. Abstr., *65*, 17777e (1966); values in 0.1 *M* $NaClO_4$ at 25°. [d] Value obtained in the same conditions as *c*. [e] Values at 35° in methanol (30%)-water.

Steric factors are probably responsible of the high ratio of aquation of $ClCo(DH)_2P(C_6H_5)_3$ and of $ClCo(DH)_2P(cyclo\text{-}C_6H_{11})_3$ which are likely to be distorted owing to the bulkiness of the phosphine.

Though the kinetics of the aquation reaction is consistent with either S_N1 or S_N2 mechanism, the above correlation suggests a S_N1 mechanism.

Pentacoordinate structure of the type RCo(chel) (where « chel » is a tetradentate approximately planar ligand) can exist either in corrinoids [1d] and in model molecules.[1d,5,6] The dissociation mechanism was suggested also from the kinetics of ligand substitution in Co^{III}hematoporphyrin.[2]

As far as the polarographic reduction is concerned, the shift of $E_{1/2}$ of the irreversible reduction is connected with the activation energy required for the electronic rearrangement preceeding the electron-transfer at the d.m.e. as is shown by the correlation between the activation energy and excitation energy of the Co^{III}-ammonia complexes $[Co(NH_3)_5L]^{2+}$.[19]

The shift of $E_{1/2}$ can be explained if the energy difference between the first unoccupied and the last occupied orbital increases with increasing σ-donor properties of the phosphine ligand. This negative charge is distributed in the delocalized molecular orbitals of the planar conjugate chelating system including the Co atom.

Preliminary kinetic data of the aquation reaction of $ClCo(DH)_2NH_2C_6H_4X$(Table II) shows that the rate of aquation is lower than expected from the proton affinity of the amine ligand as compared with phosphine ligands. This result is to be interpreted by assuming a stronger interaction of the latter ligands with the cobalt atom through a σ bond and possibly through a contribution of a π-back donation. The *trans*-effect P>N is in agreement with the soft character of the co^{III}bisdimethylglyoximato moiety and is confirmed by the decreasing rates of hydrolysis in the series $ClCo(DH)_2H_2O$ ($k_{aq} = 4.8\times10^{-5}sec^{-1}$), $BrCo(DH)_2H_2O$ ($k_{aq} = 3.9\times10^{-5}sec^{-1}$), $ICo(DH)_2H_2O$ ($k_{aq} = 2.5\times10^{-5}sec^{-1}$, 35°C) [10b] and by the order of nucleophilicity in the anation reaction of $H_2OCo(DH)_2NO_2$ and $H_2OCo(DH)_2I$.[10g]

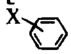
The cobaltic ion shows mild class (b) character also in the cobalamins.[1b]

From comparison of kinetic properties in corrinoids and in other naturally occurring cobaltic complexes it was pointed out [1b,9] that the equilibria for the ligand substitution reaction are in most cases very rapidly established while these reactions are in general slow among the pentammine, pentacyano and bis-dimethylglyoximato-Co^{III} complexes.

Even the Co^{III}-hematoporphirins were recently shown to be kinetically labile toward substitution reaction of axial ligands.[2]

It can be now pointed out that when trans-dichloro complexes containing NH_3, en, and $(DH)_2$ as ligands in the equatorial plane, are compared (Table III), the bisdimethylglyoximato complexes show a relatively higher rate of aquation.

Table III.

	k_{aq} sec^{-1}
$[NH_3{-}Co(NH_3)_4{-}Cl]^{2+}$	0.6×10^{-6} [a]
trans$[Cl{-}Co(NH_3)_4{-}Cl]^+$	1.8×10^{-5} [b]
» $[NH_3Co(en)_2{-}Cl]^{2+}$	3.3×10^{-7} [c]
» $[Cl{-}Co(en)_2{-}Cl]^+$	3.2×10^{-5} [b]
» $[Cl{-}Co(DH)_2{-}Cl]^-$	2.7×10^{-4} [d]
»  $NH_2{-}Co(DH)_2{-}Cl$	0.5×10^{-4} to 2.3×10^{-4}
» $PR_3{-}Co(DH)_2{-}Cl$	1.1×10^{-4} to $1.\times10^{-3}$
» $PPh_3Co(BAE){-}Br$	very fast
» $PPh_3Co(salen){-}Br$	very fast

[a] See ref. 20. [b] R. G. Pearson and F. Basolo, *J. Phys. Chem.*, *59*, 304 (1955). [c] F. Basolo and R. G. Pearson, *Adv, Inorg. Chem. and Radiochem.*, 3, 5 (1961). [d] See ref. 10d.

Moreover the present results show that trans labilizing ligands such as $P(n\text{-}But)_3$ or $P(cyclo\text{-}C_6H_{11})_3$ increase the rate of aquation of chloro-Co^{III}bisdimethylglyoximato complexes by an order of magnitude or more.

It can be concluded that as in the ground state and thermodynamic effects even the kinetic *trans*-effects are mainly due to the charge donation to the cobalt-atom via the σ-bond.

It was suggested [2] that when Co^{III} ion is chelated in a macrocycle having delocalized electronic structure, the complex loses its transition metal character and might be kinetically labile. The extent to which this happens is likely to be strongly dependent on the structure of the planar chelating system acting as acceptor of the donated charge.

Thus the halogeno Co^{III}-bis(acetylacetone)ethylendiiminato and Co^{III}-bis(salicylaldehyde)ethylendiimina-

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(20) J. Lewis and R. G. Wilkins, «Modern Coordination Chemistry», 1960, Interscience Publ., p. 129.

to complcx are aquated much faster than the Co-bisdimethylglyoximato (unpublished results).

In addition to the extended analogies with the chemical behaviour of Vit.B_{12} group complexes, which can be observed with several conjugate chelating systems as ligands in the equatorial plane it can be concluded that even as far as the kinetic properties are concerned, the behaviour of Co chelates as model molecules could be determined by a suitable choice of the chelating macrocycle.

The study of different complexes of the type XCo-(chel)Y could be thus an useful approach to the understanding of the relationships between steric and electronic structure and model properties.

Experimental Section

Materials. The preparation of the complexes is reported and discussed in a separate paper[14] concerning the formation reaction mechanisms.

All other chemicals were reagent grade.

Kinetic studies. The chloro-complexes were dissolved in methanol.

The calculated volume of stock-solutions of chloro-complexes in methanol were pipetted into volumetric flasks and made up to volume with water, to obtain the desired concentration of the complexes in mixed solvent methanol (30%)-water (70%) in volume. The solutions were rapidly transferred to a water-jacketed conductivity cell (25°C ± 0.05°C). Molar concentrations from 2 to 4×10^{-4} were adopted.

The aquation reaction was followed by measuring the conductivity with a S.I.S. « Halosis » bridge, « magic eye » type.

The rate constants were determined from the equation $\ln \Delta C = -kt + \text{const.}$, where C is the conductivity and $\Delta C = C_{t+\Delta t} - C_t$.

It was ascertained that the aquation reaction goes to completion by comparing the limiting value of the molar conductivity of the solution with the calculated value for a solution of $[H_2OCo(DH)_2L]^+Cl^-$. The latter figure was calculated from the independently determined molar conductivity of the $[H_2OCo(DH)_2L]^+ClO_4^-$ and of KCl in the same solvent and concentration.

Potentiometric titrations. 50 ml of 2×10^{-3} *M* solutions of $[H_2OCo(DH)_2L]^+ClO_4^-$ complexes in methanol(30%)-water were titrated at 25 °C with 0.1 *N* NaOH using a Beckman Model G pH-meter.

The pK_a values calculated from the usual plots of pH against log b/(a–b) at the point where (a–b) = b (b = conc. added base; b = initial conc. of aquo-complex).

For the $[H_2OCo(DH)_2P(cyclo\text{–}C_6H_{11})_3]^+ClO_4^-$ complex, which easily loses the phosphine in basic solution, the pK_a was calculated from the first points of the titration curve (in the acid range) using the equation $pK_a = pH + \log \dfrac{a-b}{b}$.

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