245. On Reactions of Oxygenated Cobalt(II) Complexes. XI. Note on the Mechanism of O_2 Uptake by Cobalt(II) Chelates with Tetra- and Pentadentate Amines

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Summary

The synthesis of two new polyamines containing 2-pyridyl and 6-methyl-(2-pyridyl) groups is described. The equilibria between H^+ and Co^{2+} and the new ligand 1,9-di(2-pyridyl)-2,5,8-triazanonane (dptn) as well as the protonation of the hydroxo complexes of 1,6-di(2-pyridyl)-2,5-diazahexane-Co(II) (Co(dpdh)) and 1-(6-methyl-2-pyridyl-6-(2-pyridyl)-2,5-diazahexane-Co(II) (Co(mdpdh)) have been studied in aqueous solution using the pH method. The coordination ability of the pyridine containing ligand dptn is compared with the chelating tendency of the analogous aliphatic amine (tetren). In spite of the lower basicity of the pyridine derivative the stability constants of its Co(II) complex is higher by a factor of thirty. The absorption spectra give evidence for a pseudooctahedral geometry of $Co(dpdh)(H_2O)_2^{2+}$ and $Co(dpdh)(H_2O)(OH)^+$. Oxygen-uptake measurements indicate the formation of binuclear peroxo species. The potentiometric equilibrium data indicate the presence of dibridged species $(dpdh)Co(O_2,OH)Co(dpdh)^{3+}$ and $(mdpdh)Co(O_2,OH)Co(mdpdh)^{3+}$. The kinetics of the rapid O_2-uptake was measured over a wide pH range on a stopped-flow apparatus. For $Co(dpdh)^{2+}$ and $Co(mdpdh)^{2+}$ we found a second order rate constant independent of pH up to pH 9, but in more alkaline solutions it increases and reaches an upper limit around pH 12.3. The data could be fitted by a rate law of the form $k_1 = (k_1'[H^+] + k_1'' K_H)([H^+] + K_H)^{-1}$. This variation with pH was explained by a rapid equilibrium $Co(dpdh)(H_2O)_2^{2+} \rightleftharpoons Co(dpdh)(H_2O)(OH)^+ + H^+(K_H)$. The enhanced rate constants of the hydroxo species must arise from a rate determining H_2O replacement by O_2, dominated by $Co–OH_2$ bond breaking and the expected ability of an OH^- group to labilize neighboring H_2O molecules. The protonation constant of the hydroxo complex obtained by equilibrium measurements ($pK_H = 11.19 \pm 0.03$) was in good agreement with that derived from kinetic data (11.12 ± 0.04). The hydrolysis of $Co(dptn)(H_2O)^{2+}$ influences the rate of O_2-incorporation in a different way. In this system retardation occurs as a result of hydrolysis ascribed to the slower leaving of OH^- compared to H_2O. This was expected if a mechanism with rate determining H_2O replacements by O_2 holds.

The addition of molecular oxygen to Co(II) complexes has recently received considerable attention [1–4]. The kinetic and mechanistic aspects of this reaction in aqueous solution have been extensively investigated [5–10]. The kinetic measurements by *Wilkins et al.* [7] were the first to support the following reaction scheme for the oxygenation of Co(II) complexes:

$$\mathrm{CoZ(H_2O)_2 + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CoZ(H_2O)O_2 + H_2O} \tag{1}$$

$$\mathrm{CoZ(H_2O)_2 + CoZ(H_2O)O_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ZCo(H_2O) \cdot O_2 \cdot (H_2O)CoZ + H_2O} \tag{2}$$

where Z represents a tetradentate ligand. The question as to which elementary step determines the rate of (1) is still unanswered. When Z is triethylenetetramine (trien), the rate constant (k_1) for the formation of the binuclear oxygenation product displays a pH dependence of the form (3)

$$k_1 = \mathrm{a[H^+] + b/[H^+] + c.} \tag{3}$$

Several mechanistic interpretations are consistent with the pH dependence of this rate constant.

1a) The loss of H_2O from the inner coordination sphere is rate determining for oxygen uptake. The increase of the oxygenation rate with increasing pH is the consequence of the hydrolysis of coordinated H_2O (4). Here the presence of a OH^- ligand would be

$$\mathrm{CoZ(H_2O)_2^{2+} \overset{K_H}{\rightleftharpoons} CoZ(H\ O)(OH)^+ + H^+} \tag{4}$$

expected to labilize the neighboring H_2O accelerating its release.

1b) At high pH a different reactive species could be present. The occurrence of both octahedral and pentacoordinate complexes in solution of $\mathrm{Co(trien)(H_2O)(OH)^+}$, as evidenced by the unusual molar absorptivity, led *Wilkins et al.* [7] to posit a trigonal bipyramidal $\mathrm{Co(trien)(OH)^+}$ complex as the reactive species in the oxygenation reaction.

2) The oxygenation process is governed by the electron-transfer. As the initial step of oxygenation an antiferromagnetic coupling of spins without *e*-transfer may occur [11] followed by a charge transfer process. This intramolecular redox process is approximated by the reaction (5) and may be facilitated by hydroxide ion. This step is complicated by the difference in the

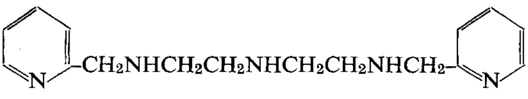
$$\begin{array}{ccc} \mathrm{Co(II)(O_2)} & \rightarrow & \mathrm{Co(III)(O_2^-)} \\ (\mathrm{t_{2g}})^5(e_\mathrm{g})^2 & & (\mathrm{t_{2g}})^6 \end{array} \tag{5}$$

electronic configuration of the two oxidation states. The energy of activation depends therefore to a great extent on the reorganization energy of the reacting species. The accepted model for the activation process in this kind of electron-transfer – suggested by *Orgel* [12] – is that electronic states in the activated complex are matched by changing bond distances and therefore the ligand field of the reactant species. The bonds must be shortened for the reductant and lengthened for the oxidant in forming the activated complex. With a stronger field less shortening for the reductant is required [13]. In spite of the puzzling arrangement of OH^- below H_2O in the spectrochemical series [14], replacement of H_2O by OH^- should provide a shorter bond in the initial complex and make it more similar to the activated complex.

Kinetic and equilibrium studies of the oxygenation of Co(II) complexes containing tetra- and pentadentate polyamines were undertaken to distinguish among these mechanistic possibilities. First we examined the kinetics of oxygen uptake in additional octahedral Co(II) chelates to test the validity of the scheme suggested by *Wilkins et al.* Subsequently we considered Co(II) chelates of the form $CoN_5(H_2O)^{2+}$. Here the pentadentate polyamine permits only a single, free coordination position for H_2O, OH^- or O_2. If the loss of H_2O is rate determining for oxygenation, then a term which decreases with increasing pH should appear in the case of $CoN_5(H_2O)$. This is ascribable to the slower exchange of OH^- as compared to H_2O.

Ligands, whose Co(II) chelates undergo reversible oxygenation were synthesized (*Schemes 1a and 1b*). Donor groups with pyridine nitrogen atoms appeared especially suitable.

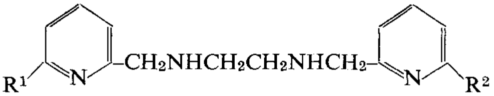
Scheme 1



dptn = 1,9-di(2-pyridyl)-2,5,8-triazanonane

As tetradentate ligands, we synthesized 1,6-di(2-pyridyl)-2,5-diazahexane (=dpdh) as well as the same ligand methylated at C(6) of one of the two pyridine rings (*Scheme 1b*).

Scheme 1b



$R^1 = R^2 = H$: dpdh = 1,6-di(2-pyridyl)-2,5-diazahexane
$R^1 = CH_3$, $R^2 = H$: mdpdh = (1-(6-methyl-2-pyridyl)-6-(2-pyridyl)-2,5-diazahexane

Experimental Part. - 1,9-Di(2-pyridyl)-2,5,8-triazanonane (dptn) was prepared by slow dropwise addition of 0.2 mol-equiv. of pyridine-2-aldehyde (*Fluka*, purum) to 0.1 mol-equiv. of diethylenetriamine (*Fluka*, puriss.) in ethanol. The *Schiff's* base was not isolated but was catalytically hydrogenated (10% Pt/C, C_2H_5OH, 1 atm H_2, RT.). The polyamine, obtained as the trihydronitrate, was recrystallized from ethanol, m.p. 185-186°.

$C_{16}H_{26}N_8O_9$ (474.43) Calc. C 40.5 H 5.5 N 23.6% Found C 40.2 H 5.5 N 23.3%

1,6-Di(2-pyridyl)-2,5-diazahexane (dpdh) was similarly prepared by a modification of the previously described method [15] and obtained as the tetrahydronitrate, m.p. 171-172°.

$C_{14}H_{22}N_8O_{12}$ (494.37) Calc. C 34.01 H 4.49 N 22.67% Found C 34.11 H 4.61 N 22.04%

Mdpdh was analogously synthesized by addition of 6-methylpyridine-2-aldehyde to 5-(2-pyridyl)-1,4-diazapentane [16] followed by catalytic hydrogenation (10% Pd/C, C_2H_5OH, 1 atm H_2, RT.). This ligand was likewise isolated as the tetrahydronitrate, m.p. 173-174°.

$C_{15}H_{24}N_8O_{12}$ (508.42) Calc. C 35.4 H 4.76 N 22.04% Found C 35.42 H 4.72 N 21.83%

The protonation constants of the ligands as well as the stability constants of the Co(II) complexes and protonation constants of the hydroxo-complexes were determined by pH titrations of 10^{-2}M solutions of dptn · HNO_3 with O_2- and CO_2-free 0.2 N NaOH. In all titrations as well as in all kinetic measurements, the ionic strength was 0.2 (KNO_3, *Merck p.a.*). The temperature was 25 ± 0.1°. A compensator E 388 with Dosimat and combined glass electrode (UX 121, *Metrohm*) was used in pH measurements.

Solutions of $Co(dptn)^{2+}$ and $Co(dpdh)^{2+}$ used in the titrimetric determinations were kept completely oxygen free by purging with V^{2+}-deoxygenated nitrogen or argon for 15 min before analysis. Deoxygenated nitrogen was blown across the surface of the solution during the titration. $CoSO_4 \cdot 7\,H_2O$ was present substoichiometrically (90%) with respect to the ligand. The computer program 'VARIAT' developed by *Kaden & Zuberbühler* [17] was employed for the evaluation of the data. Ultraviolet and visible spectra of the oxygen complexes were obtained on a *Cary* 14 Spectrometer. The spectra of $Co(dpdh)^{2+}$ and $Co(mdpdh)^{2+}$ were measured with a *Varian* Techtron Spectrophotometer Model 635 using a quartz flow-through cell which excluded oxygen during filling the cell and during the measurement. The cell compartment was purged with nitrogen. A *Fieldlab* Oxygen Analyser with a *Clark* electrode was used to measure O_2 uptake. The kinetics of formation of the oxygenated species was followed in a *Durrum-Gibson* stopped-flow apparatus. Solutions of Co(II) complexes prepared under complete exclusion of oxygen were mixed with basic buffer solutions of known oxygen concentration. Buffer solutions used were: collidine ($pK=7.5$), borate ($pK=9.2$) and 2-*t*-butylaminoethanol ($pK=11.3$). The concentrations of buffers were 0.2. The absorbance changes were monitored at absorbance maxima as well as other wavelengths with identical results.

The kinetic curves were evaluated on the basis of the previously cited model, eq. (1) and (2). Application of the steady-state approximation to the formation of the mononuclear O_2-complex (1) and under the condition that the binuclear, singly bridged product (2) is formed irreversibly we get the following expression (6):

$$\frac{d[\text{peroxy species}]}{dt} = k_{\text{exp}}[O_2] = \frac{k_1 k_2 [\text{CoZ}]^2 [O_2]}{k_{-1} + k_2[\text{CoZ}]} \tag{6}$$

which simplifies to $k_{\text{exp}} = k_1[\text{CoZ}]$ at high [CoZ]. This approximation is valid at concentrations greater than 10^{-4} M for $Co(dptn)^{2+}$ and $4 \cdot 10^{-3}$ M for $Co(dpdh)^{2+}$ and $Co(mdpdh)^{2+}$. Experimental conditions in all three systems were selected such that $[CoZ^{2+}]$ exceeded $[O_2]$ by at least a factor 10–15. Thus the experimental rates were pseudo first order. Some kinetic curves for the reaction of $Co(dptn)^{2+}$ with O_2 were evaluated by the method of initial velocities. Kinetic parameters were calculated by least squares fitting on a *Hewlett Packard* 9830.

Results and Discussion. – The measured acidity constants of the new ligand dptn are compared with analogous values of tetren and dien (*Table 1*). As tetren, dptn forms a triply protonated species in moderately acid solutions: $dptnH_3^{3+}$. However,

Table 1. *Equilibrium constants for the combinations of various ligands with* H^+ $pK^{H_nL}_{H_{(n+1)}L}$ *and* Co^{2+} (*log* $K^{CoL}_{Co,L}$) *at 25°*

Ligand	$pK^{H_3L}_{H_4L}$	$pK^{H_2L}_{H_3L}$	$pK^{HL}_{H_2L}$	pK^{L}_{HL}	$\log K^{CoL}_{Co,L}$	$pK^{CoLOH}_{Co,L}$	Ref.
dptn		4.02	7.17	8.97	14.84	11.51	this work
tetren[a])		8.08	9.1	9.68	13.3		[18]
dien[b])		4.34	9.13	9.94	8.1		[19]
dpdh	[c])	1.6 ± 0.02	5.52 ± 0.01	8.35 ± 0.01	12.24 ± 0.07	11.2 ± 0.03	
dpdh	1.62	1.81	5.45	8.23	12.8		[15][d])
dpdh	1.8	2.0	5.47	8.23	12.0		[20][e])

[a]) Tetraethylenepentamine.
[b]) Diethylenetriamine.
[c]) Strong acid.
[d]) I = 0.1 (KNO_3).
[e]) I = 0.1 (KCl).

the stepwise deprotonation (pK_1, pK_2, pK_3) corresponds closely to that of dienH_3^{3+}. As a consequence of the reduced basicity of the two terminal nitrogen atoms the three protons must reside on the three neighboring amino nitrogen atoms. In the case of tetrenH_3^{3+} the two terminal, primary nitrogens and the innermost, secondary amine must undoubtedly be protonated to achieve the greatest possible separation of the positive charges. Thus a meaningful comparison can only be made between dptnH_3^{3+} and dienH_3^{3+}. There is a striking difference in the pK values representing the dissociation of the second and third proton (pK_2, pK_3). The basicity of the adjacent secondary amines is reduced in dptn because of the inductive effect of the aromatic rings. For dienH_2^{2+} and tetrenH_2^{2+} the K_2/K_3 ratio is only slightly greater than the statistical factor.

The stabilities of the Co(dptn)$^{2+}$ and Co(tetren)$^{2+}$ complexes differ clearly. The higher stability of Co(dptn)$^{2+}$ is not surprising, although ordinarily there exists a parallel between metal binding and proton affinity [21]. However, as was shown by *Anderegg* [22], this correlation has to be modified for ligands which for instance, contain a pyridine ring. Protonated complexes such as Co(dptn)H^{3+} or Co(dptn)H_2^{4+} do not appear under the experimental conditions employed here.

Further we repeated *Martells* [15] and *Grünwedels* [20] measurements of the acid dissociation constants of dpdh and the stability constants of Co(dpdh)$^{2+}$ and determined the protonation constants of the hydroxocomplexes of the two tetradentate ligands. All results are summarized in *Table 1*. Some of the results are used in the interpretation of the kinetic data.

The formation of binuclear complexes can be unambiguously inferred from the quantitative determination of the oxygen incorporation. In a typical determination 1.7 mmol of the Co(II) complex, mixed with an air-saturated buffer solution of an appropriate pH, consumes 0.85 ± 0.02 mmol oxygen. The pH titration of Co(dpdh)$^{2+}$ in the presence of oxygen demonstrates the consumption of an additional half proton per complex ion. This indicates the formation of a single hydroxo bridge (7), *cf. Fig. 2*. With Co(dptn)$^{2+}$

$$\underset{P_1}{(Z)\,(H_2O)CoO_2Co(H_2O)\,(Z)^{4+}} \rightleftharpoons \underset{P_2}{ZCo^{O_2}_{OH}CoZ^{3+}} + H_3O^+ \qquad (7)$$

there was no indication of such additional bridging, as is found in all peroxo complexes of type P_1. In an earlier communication *Fallab et al.* described the oxygenation of diethylenetriamine-1,7-diacetatocobalt(II) [23]. Here a more stable, doubly bridged complex is formed upon release of an acetato ligand above pH 8 (8). This possibility was examined for (dptn)CoO_2Co(dptn)$^{4+}$.

$$(dtda)CoO_2Co(dtda) + H_2O \rightleftharpoons (dtda)Co^{O_2}_{OH}(dtda)^- + H^+ \qquad (8)$$

Models showed that coordination of all five *N*-donor groups introduced severe strain in the terminal chelate ring. The spectrum of the binuclear species exhibited a charge transfer band at 322 nm typical for a singly bridged O_2 complex ($\varepsilon = 1.2 \cdot 10^4 \text{M}^{-1}\,\text{L}\,\text{cm}^{-1}$) as well as a shoulder at 425 nm ($\varepsilon = 1.7 \cdot 10^3$). The two doubly bridged complexes have maxima at 378 nm (dpdh, $\varepsilon = 7.4 \cdot 10^3$) and 387 nm (mdpdh, $\varepsilon = 5.2 \cdot 10^3$).

Next we considered the rate of O_2 incorporation in the two Co(Z)$(H_2O)_2^{2+}$ systems. The pH dependence of k_1 for the case of Z = dpdh is given in *Figure 3*. The measured

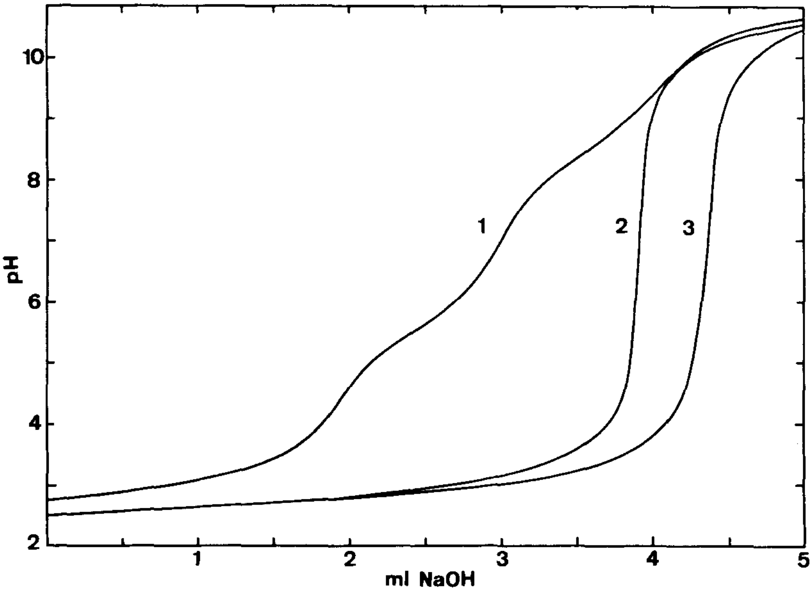


Fig. 2. *Potentiometric titrations of dpdh · $4HNO_3$* (1.1 · 10^{-3} M) (1), 1.1:1 molar ratio of dpdh to Co(II) under a nitrogen atmosphere (2), 1.1:1 molar ratio of dpdh to Co(II) under an oxygen atmosphere.

values were fitted to eq. 3. The indicated curve represents the best fit to the data. The increase of the rate with increasing pH is explicable by a hydrolytic reaction (9).

$$Co(dpdh)(H_2O)_2^{2+} \rightleftharpoons Co(dpdh)(H_2O)(OH)^+ + H^+ \qquad (9)$$

As anticipated, a OH^- ligand labilizes the neighboring H_2O ligand and accelerates its release from the coordination sphere. Spectroscopic evidence does not support the participation of detectable amounts of a pentacoordinate complex as the reactive species at high pH. The coordination geometry of the Co(II)-dpdh complex was

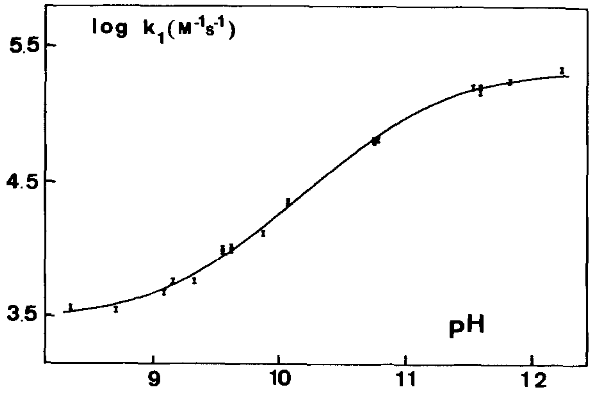


Fig. 3. *Dependence of oxygen-uptake rate of Co(II)-dpdh on pH*

inferred from the variation of the absorption spectra between pH 8 and 12.5. In the absence of oxygen Co(II) salts (10^{-3}M) are completely complexed by dpdh ($1.1 \cdot 10^{-3}$M) at pH 5.5 with the formation of a pink-colored complex. The spectrum of this complex can be interpreted as that of the pseudooctahedral $Co(dpdh)(H_2O)_2^{2+}$. For regular octahedral complexes with cubic symmetry such as $Co(H_2O)_6^{2+}$, $Co(NH_3)_6^{2+}$ and $Co(en)_3^{2+}$ theory predicts two bands in the visible region [24] originating from transitions between the ground state and two quartet excited states. The stronger band is due to the transitions between $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and appears at 450–500 nm. A band at lower energy, found at 540 nm in $Co(NH_3)_6^{2+}$ and 535 nm in $Co(en)_3^{2+}$ was identified as the transition $^4T_{1g} \rightarrow {}^4A_{2g}$ [25]. Both bands are of low intensity ($\varepsilon < 10$). Lowering the symmetry from cubic to tetragonal should cause a splitting of the $^4T_{1g}(P)$ state which is triply degenerate whereas the band $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ cannot be split by fields of lower symmetry. The $Co(dpdh)(H_2O)_2^{2+}$ spectrum is consistent with such a coordination geometry. The complex exhibits a maximum at 484 nm ($\varepsilon = 13.9$) and two ill-defined shoulders at 520 nm ($\varepsilon = 7.5$) and 465 nm ($\varepsilon = 12$). The deprotonated species $Co(dpdh)(H_2O)(OH)^+$ has two shoulders at 535 nm ($\varepsilon = 10.1$) and 500 nm ($\varepsilon = 14.4$) and a double peak at 475 nm ($\varepsilon = 17.2$) and 445 nm ($\varepsilon = 17.1$). It is possible that this splitting is due to a *trans*-configuration. From these spectroscopic and kinetic measurements we conclude that the simple reaction scheme suffices to explain the experimental data. The pH dependence (10)

$$\begin{tikzcd}
Co^{II}Z(H_2O)_2^{2+} \arrow[r, "+O_2,\ k_1'"] \arrow[d, shift right, "K_H"'] & Co^{III}Z(H_2O)(O_2^-)^{2+} + H_2O \arrow[d, shift right] \\
H^+ + Co^{II}Z(H_2O)(OH)^+ \arrow[r, "+O_2,\ k_1''"] \arrow[u, shift right] & Co^{III}Z(OH)(O^-)^+ + H_3O^+ \arrow[u, shift right]
\end{tikzcd}$$

derivable from this scheme is in agreement with the functional form of eq. (3). The rate constants (k_1', k_1'') and equilibrium constants (K_H) for several systems including

$$k_1 = k_1'[H^+] + k_1'' \cdot K_H/[H^+] + K_H \qquad (10)$$

$Co(trien)^{2+}$ are compared (*Table 2*). The rate constants vary by a factor ≈400 and we consider these to be consistent with a common mechanism for all systems. Steric

Table 2. *Kinetic parameters for Co(II) complex-oxygen intraction at 25°*

System	k_1 ($M^{-1}s^{-1}$)	pK_H(kin.)	pK_H(thermo)	Ref.
$Co(dpdh)(H_2O)_2^{2+}$	$3 \pm 0.2 \cdot 10^3$	11.12 ± 0.04	11.19 ± 0.03[a]	this work
$Co(dpdh)(H_2O)(OH)^+$	$2.15 \pm 0.1 \cdot 10^5$			this work
$Co(mdpdh)(H_2O)_2^{2+}$	$4.2 \pm 0.3 \cdot 10^2$	11.35 ± 0.1	11.3 ± 0.1[b]	this work
$Co(mdpdh)(H_2O)(OH)^+$	$2.9 \pm 0.2 \cdot 10^4$			this work
$Co(trien)(H_2O)_2^{2+}$	$2.5 \cdot 10^4$			[7]
$Co(trien)(H_2O)(OH)^+$	$2.8 \cdot 10^5$			[7]
$Co(dptn)(H_2O)^{2+}$[c]	$1.65 \pm 0.2 \cdot 10^5$	11.4 ± 0.1	11.5[a]	this work
$Co(dptn)(OH)^+$	$< 2 \cdot 10^3$			this work

[a] Potentiometric titration.
[b] Spectrophotometric tiration.
[c] T = 18°.

hindrance appears to retard O_2-incorporation. This trend is also verified in the case of the dimethylated ligand 1,6-bis(6-methylpyridyl(2))-2,5-diazahexane [26], for which k_1' was evaluated as $140 \pm 40 \text{M}^{-1}\text{s}^{-1}$. Such behaviour is in agreement with a mechanism in which H_2O replacement by O_2 is rate determining, dominated by Co–OH_2 bond breaking and with the supposition that the rate of H_2O exchange in complexes of similar structure¹) is faster, the greater the electron density at the metal center [29]. This is undoubtedly a function of the distance of the donor, from the metal center, which is determined, among others by steric factors. The OH^- acceleration is greater in the $Co(dpdh)^{2+}$ and $Co(mdpdh)^{2+}$ system than with $Co(trien)^{2+}$. In both systems additional, complicated reactions occur after the oxygenation step, as judged by further spectral changes, which are not discussed in the framework of the present work.

The rate constant determined for O_2 incorporation in $Co(dptn)^{2+}$ $k_1 = 1.65 \cdot 10^5 \text{M}^{-1}\text{s}^{-1}$ agrees quite well with the value reported by *Wilkins et al.* for the reaction of $Co(tetren)^{2+}$ with O_2 ($\approx 10^5 \text{M}^{-1}\text{s}^{-1}$) [7]. In the present work we have considered chiefly the influence of hydrolysis of $Co(dptn)(H_2O)^{2+}$ on the rate of oxygenation (11). As *Figure 4* shows, in contrast to the pH dependence of the oxygenation found in complexes of the type $Co(Z)(H_2O)_2^{2+}$, a retardation occurs in systems with pentadentate ligands as a result of hydrolysis. This finding confirms a mecha-

$$Co(dptn)(H_2O)^{2+} \overset{K_H(11)}{\rightleftharpoons} Co(dptn)(OH)^+ + H^+ \qquad (11)$$

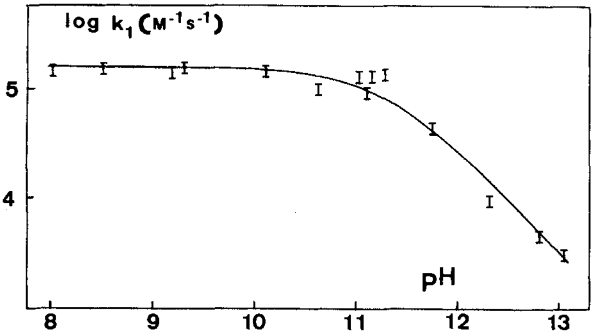


Fig. 4. *Dependence of oxygen-uptake rate of Co(II)-dptn on pH*

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¹) Similar structure means octahedral (O_h) or pseudooctahedral (*e.g.* D_{4h}, C_{4v}) geometry. Solutions of $Co(dpdh)(H_2O)_2^{2+}$ consist undoubtedly of several isomers depending on the ligand topologies. The possible modes of wrapping a linear quadridentate ligand (*e.g.* trien or dpdh) about a cobalt(II) ion give rise to the following isomers: *α-cis* (D, L), *β-cis* (D, L) and *trans*. However, in addition to the topological isomers, several isomeric possibilities arise from the manner in which the secondary *N*-atoms coordinate. Furthermore two additional isomers (β_1 and β_2) arise in the hydroxo-complex $Co(dpdh)(H_2O)(OH)^+$. For references see [27]. The isomeric structures and the ratios of the various isomers in our systems are not known with any certainty, but there is good evidence that more than one isomer exists. This can be inferred from the kinetic behaviour of the oxygenated species [28]. Consequently our k_1 values may be averages of similar values of several isomers, because it is difficult to see clearly differences in k_1 values smaller than 3.

nism in which H_2O replacement by O_2 (12) is rate determining. The experimental

$$\mathrm{Co(dptn)(H_2O)^{2+} + O_2 \rightleftharpoons Co(dptn)O_2^{2+} + H_2O} \tag{12}$$

values in *Figure 4* are best fitted by a function of the form (13). The equilibrium constant $K_H = 10^{11,4 \pm 0,1}$ determined from the pH dependence of k_1 is in good agree-

$$k_1 = k_1' \cdot [H^+]/[H^+] + K_H \tag{13}$$

ment with the hydrolysis constants derived from titrimetric measurements (*cf. Table 2*). As indicated by the pH profile (*Figure 4*), the species $\mathrm{Co(dptn)(OH)^+}$ exhibits only minor activity with respect to O_2 exchange in the pH range examined *i.e.* the ligand exchange (14) of the hydroxo-complex proceeds at least a factor of

$$\mathrm{Co(dptn)(OH)^+ + O_2 \rightleftharpoons Co(dptn)O_2^{2+} + OH^-} \tag{14}$$

100 slower, indicating the slower exchange of OH^- compared to H_2O.

All our kinetic results of oxygen uptake of systems of the types $\mathrm{CoZ(H_2O)_2}$ and $\mathrm{CoZ(H_2O)}$ lend themselves to the interpretation that H_2O replacement by O_2 governs the rate of oxygenation of Co(II) complexes (1).

We think that the acceleration at higher pH values in the $\mathrm{Co(trien)^{2+}}$ system is also due to a simple acid-base equilibrium (4) and an enhanced replacement of H_2O by the labilizing OH^- ligand. Based on magnetic circular dichroic (MCD) spectra of a series of four-, five- and six-coordinate Co(II) complexes *Kaden et al.* [30] assigned a pseudooctahedral geometry to $\mathrm{Co(trien)(H_2O)_2^{2+}}$ and $\mathrm{Co(trien)(H_2O)(OH)^+}$. The visible spectra of pentacoordinate Co(II) complexes consist of three absorption regions centered around 850 nm, 670 nm and 500 nm with molar absorptivities in the range of 50 to 150. The visible spectrum of $\mathrm{Co(trien)(H_2O)(OH)^+}$ does not exhibit these three bands but has only one band at 545 nm ($\varepsilon = 30.2$) and a shoulder at 510 nm ($\varepsilon = 25$). $\mathrm{Co(trien)(H_2O)_2^{2+}}$ has one band at 484 nm ($\varepsilon = 8$) and a shoulder at 460 nm ($\varepsilon = 6.6$) with normal extinction coefficients for an octahedral Co(II) complex [7]. The relatively strong absorption of $\mathrm{Co(trien)(H_2O)(OH)^+}$ must be explained by a distorted *cis*-complex of lower symmetry (C_{4v})2). Unfortunately there are only few results on spectral changes due to hydrolysis in Co(II) complexes.

The data in *Table 2* show a decrease in the rate of oxygenation with decreasing strength of the nitrogen donor and decreasing number of coordinated nitrogen donors. Previous studies of Ni(II) and Co(II) complexes showed that the presence of coordinated nitrogen donors causes a significant increase in the rate of ligand substitution and solvent exchange [32]. Labilization of coordinated solvent by polydentate amine ligands may be understood by a model in which electron donation from the amine donor reduces the effective charge of the central metal ion thereby reducing

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2) We found a similar spectral change in the system

$$\mathrm{Co(dmtrien)(H_2O)_2^{2+} \rightleftharpoons Co(dmtrien)(H_2O)(OH)^+ + H^+}$$

(dmtrien = 4,7-dimethyl-1,4,7,10-tetraazadecane). The geometry of the two complexes would be expected to be *cis* because the methyl substituents enhance the stabilities of the 'angular' configuration at the central amine donor atoms such that *trans*-complexes with this ligand might not be obtainable [31].

the enthalpy of activation and labilizing the solvent [33]. Further detailed mechanistic studies are in progress in these laboratories.

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