

150. Oxygenation of Co(II) Complexes with Tripodal Ligands

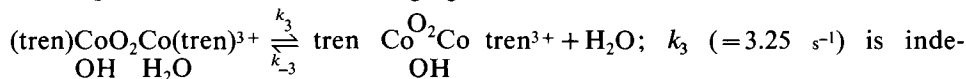
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Summary

The kinetics of O₂-uptake of five-coordinated Co²⁺/tren complexes (tren = 2,2',2''-tris(2-aminoethyl)amine) have been studied extensively. The kinetics of formation of (tren)Co(O₂,OH)Co(tren)³⁺ exhibits two steps. The rate law of O₂-addition, the first step, was of the form: rate = (k'₁[H⁺] + k''₁K_{a})/([H⁺] + K_{a}) [Co(tren)²⁺][O₂]. Second-order rate constants k'₁ = 220 ± 19 M⁻¹s⁻¹ and k''₁ = 1.8 ± .035 · 10³M⁻¹s⁻¹ agreed well from O₂-uptake and (stopped-flow) spectrophotometric measurements. The protonation constant of the hydroxo complex obtained by equilibrium measurements (spectrophotometric and by pH-titration) in anaerobic conditions (pK_a = 10.03) agreed well with that derived from kinetic data (pK_a = 9.93); k'₁ and k''₁ are about a factor 100 smaller than those for the pseudooctahedral Co(trien)(H₂O)₂²⁺. This and the fact that several other Co(II) complexes with five-coordinated geometry do not exhibit oxygen affinity led to the proposal that the oxygenation mechanism for Co²⁺/tren complexes involves fast preequilibria between Co(tren)(H₂O)₂²⁺ and Co(tren)(H₂O)₂²⁺ and only the latter is assumed to be reactive. The enhanced rate at high pH is explained by rate determining H₂O-exchange in the O₂-addition step and the ability of coordinated OH⁻ to labilize the neighbouring H₂O. This mechanism is furthermore supported by the formation of one kinetically preferred isomer of the peroxo-bridged dicobalt(III) complex (O₂ *cis* to the tertiary N-atom) and the large negative activation entropy (-30 eu). The second step is the intramolecular bridging reaction:}}



pendent of [Co(tren)²⁺] and [O₂] but exhibits a pH-dependence of the form k₃ = k'₃[H +]/(K_a + [H⁺]); k₋₃ (= 5 · 10⁻⁵ s⁻¹) was determined independently and from the two rate constants the equilibrium constant was calculated as ≈ 10⁵. The ligand combination as in Co(tren)²⁺ was shown to provide an excellent balance to form a reversible oxygen carrier; possible reasons for this are discussed.

Whereas molecular O₂ is rather unreactive towards most organic compounds it exhibits high reactivity towards most inorganic coordination compounds with multiple oxidation states. These reactions are studied for several reasons. One of them is

the interest in O₂-activation and O₂-carrier properties of metal complexes. The best characterized synthetic O₂-carriers are those of Co(II) where mononuclear superoxo-complexes and binuclear, peroxo-complexes have been isolated and characterized. Excellent recent reviews summarize the available data on this subject [1]. Despite extensive knowledge about Co-O₂-carriers there is still much activity in this field [2].

Most studies on oxygenation reactions of Co(II) species were done on octahedral complexes. The kinetics of O₂-uptake was extensively studied by *Wilkins et al.* [3]. In the case of Co(trien) (H₂O)₂²⁺ they found that the rate of O₂-incorporation increased at high pH. A possible mechanistic interpretation of the pH-dependence and the spectral change of Co(trien) (H₂O)₂²⁺ with pH was the formation of octahedral Co(trien) (H₂O)(OH)⁺ and pentacoordinate Co(trien) (OH)⁺, with the latter as the reactive species. The species Co(tren)²⁺ 1) seemed to be a promising candidate to test this interpretation. The tripodal geometry of tren (*Fig. 1a*) should favor a pentacoordinate species of the trigonal bipyramidal type [4]. Hence a thorough study of the oxygenation of Co(tren)²⁺ and of other Co(II) complexes with tripod-like ligands should bring more light into the question of the oxygenation mechanism of Co(II) complexes. Although thermodynamic and kinetic aspects of the oxygenation of Co(tren)²⁺ were studied by *Martell et al.* [5], their kinetic experiments were very incomplete. No pH-dependence was reported and, due to the lack of a concentration and wavelength dependence, the important fact that the reaction is biphasic was obviously missed. Both results are crucial to the understanding of the oxygenation mechanism of Co(tren)²⁺.

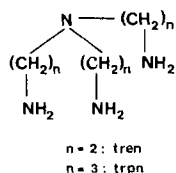


Fig. 1a. tren = 2,2',2''-tris(2-aminoethyl)amine
trpn = 3,3',3''-tris(3-aminopropyl)amine

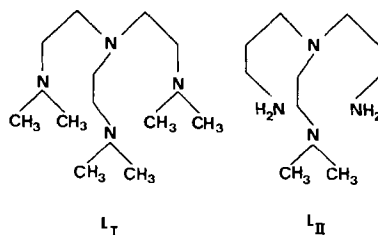


Fig. 1b. L_I = Tris(dimethylaminoethyl)amine
= Me₆tren
L_{II} = N,N-Bis(3-aminopropyl)-N',N'-dimethylethylenediamine

Additional reports on Co/tren/O₂ have appeared in the literature. *Grieb et al.* reported the syntheses and isolation of a series of binuclear peroxo-complexes with tren as the principal ligand [6]. The isolation of (tren)Co(O₂,OH)Co(tren) (C₁₀)₃ has been reported from these laboratories. The X-ray structure determination showed that the single isomer which was formed has the dioxygen *cis* to the tertiary N-atom [7].

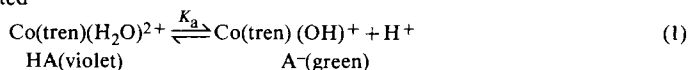
The study of Co(II) complexes with tripodal ligands as O₂-carriers appeared to be attractive from an additional point of view. The complexes with this particular

1) The notation Co(tren)²⁺ is used to denote the species formed containing these components in 1:1 ratio.

geometry, studied so far, proved to be excellent O₂-carriers in the sense that the irreversible conversion to mononuclear Co(III) complexes was almost negligible, an important property of an O₂-carrier. It seemed, therefore, desirable to extend the oxygenation studies to new Co(II) complexes with tripodal ligands. A preliminary report of part of the subject of this paper has been published earlier [8].

Experimental part. – *Materials* (see Fig. 1a–b). 2,2',2''-Tris(2-aminoethyl)amine (tren = N(CH₂CH₂NH₂)₃) [9], 3,3',3''-tris-(3-aminopropyl)amine (trpn = N(CH₂CH₂CH₂NH₂)₃) [10] and tris(2-dimethyl-aminoethyl)amine (trenMe₆, L₁) [11] were prepared by literature procedures. Tren used in some of the studies was purchased from *Strem Chem*. It was purified by fractional distillation. The amine was precipitated as trihydrochloride and three times recrystallized from ethanol/acetone. The syntheses of *N,N*-bis(3-aminopropyl)-*N,N'*-dimethylethylenediamine (L₁₁) is described elsewhere [12]²⁾.

Measurements and equipment. – Spectra: UV. and VIS. spectra were obtained on a *Cary 14* or a *Varian Techtron Spectrophotometer model 635*; both equipped with thermostated cell holders. Spectra of Co(tren)²⁺ as a function of pH and temperature were obtained using a flow-through cell which excluded O₂. At each temperature spectra were taken at 13–15 pH-values. From these spectra (Fig. 2) an acidity constant (see equ. 1) was calculated



by fitting the experimental absorbance (A_{exp}) vs. pH values at λ_{max} = 460 nm and 630 nm by equation 2:

$$K_a = \frac{(\epsilon_{\text{HA}} - \epsilon) [\text{H}^+]}{\epsilon - \epsilon_{\text{A}}} \quad (2)$$

where

$$\epsilon = \frac{A_{\text{exp}}}{[\text{Co(tren)}^{2+}]_{\text{tot}}} \quad (3)$$

From a linear ln K_a vs. 1/T plot thermodynamic quantities were calculated. K_a-values and thermodynamic quantities are listed in Table 1. The concentration of Co(tren)²⁺ in these measurements was 10⁻²M. At 25° K_a-values were also determined at 5 · 10⁻³M and 2 · 10⁻²M, as well as 2 · 10⁻⁴M by pH-titrations as described elsewhere [16].

Kinetic measurements and data analyses. – The kinetics of formation of the oxygenated species was mostly followed spectrophotometrically in a *Durrum-Gibson* stopped-flow spectrophotometer equipped with a storage oscilloscope. Solutions of Co(tren)²⁺ were prepared by mixing of Co(NO₃)₂ · 6 H₂O (*Fluka*, *p. a.*) and tren · 3 HCl under complete exclusion of O₂ in a titration vessel equipped with a combined glass electrode (UX 121, *Metrohm*). N₂ or Ar deoxygenated with V²⁺ were bubbled through all solutions for 20 min prior to raising the pH by adding small amounts of deoxygenated conc. NaOH-solution. In this way Co(tren)²⁺ was formed and the pH could be adjusted to the desired value. Airtight syringes were used to transfer the solutions to the stopped-flow drive syringes. Drive syringes and mixing chamber of the stopped-flow instrument were thermostated. Solutions of Co(tren)²⁺ thus prepared were mixed with a buffer of known O₂-concentration (2,4,6-collidine, pK_a = 7.5; borate, pK_a = 9.2) to make the pH-change negligible. At pH around the pK_a of Co(tren)(H₂O)²⁺ buffering was not necessary because the total Co(tren)²⁺-concentration was much larger than that of oxygen. These measurements revealed that the buffers had no influence on the reaction rates. All measurements were performed at constant ionic strength of 0.2 with KNO₃. Concentrations of Co(tren)²⁺ were between 2.5 · 10⁻³M – 2.5 · 10⁻²M, O₂- conc. were ranging from 6.4 · 10⁻⁵M – 2.57 · 10⁻⁴M.

Data analysis. – Earlier data were obtained by taking pictures of the oscilloscope traces. About 30 absorbance – time pairs were obtained by reading from the pictures. Most of the data were obtained in the stopped-flow apparatus of the department of *Biophysikalische Chemie des Biozentrums der Universität*

²⁾ The Author is grateful to Dr. Lotz for a gift of the ligand.

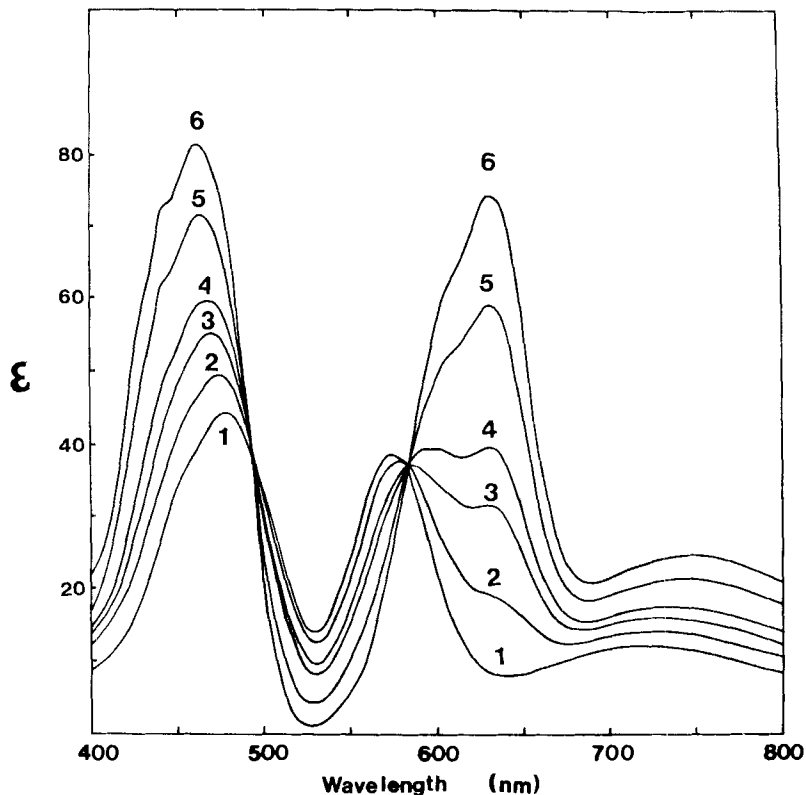


Fig. 2. Electronic absorption spectra of $\text{Co}(\text{tren})^{2+}$ at various pH: (1) 8.2, (2) 9.25, (3) 9.6, (4) 9.98, (5) 10.76, (6) 12.1

*Basel*³), modified by incorporating an optical reference system and connecting the signal and reference photomultipliers to a logarithmic amplifier, the output of this was directly proportional to the change of absorbance.

The data (1024 points) were digitized and stored with a transient recorder (type datalab DL 905) which was connected on line to a PDP 11 140 computer. Rate parameters and their standard deviations were obtained by fitting A_t vs. time curves by a nonlinear least squares method⁴). Most A_t vs. time traces could be fitted using the rate expression 4 for first-order consecutive reactions.

$$A_t - A_\infty = A_1 e^{-k_1 t} + A_2 e^{-k_2 t} \quad (4)$$

A_t and A_∞ are the absorbance of the reaction mixture at time t and infinite time. A_1 and A_2 are constants and k_1 and k_2 are rate constants. A_∞ , A_1 , A_2 , k_1 and k_2 were adjustable parameters and were optimized. For all traces the values of A_t (calc.) from equ. 4 always agreed with the observed values of A_t to a standard deviation of less than 0.5% full scale on the oscilloscope screen. Optimized values of A_0 and A_∞ agreed well with observed values. The course of the reaction was monitored at wavelengths between 345

³) The Author is grateful to Prof. C. Kirschner for the kind permission to use his stopped-flow instrument.

⁴) A program developed by Dr. C. Paul and Dr. A. Labhart was used. The use of it is gratefully acknowledged.

nm and 460 nm. Rate constants agreed well at all wavelengths. At 360–370 nm the traces could be fitted by a simple first-order rate expression

$$A_t - A_\infty = (A_0 - A_\infty) e^{-k_a t} \quad (5)$$

Most experiments were done at 420 nm. At this wavelength the absorbance difference between intermediate and product seems to be largest and an absorbance-time trace as shown in *Figure 3* is obtained. Under these conditions absorbance-time traces could be fitted with 2 exponentials even when k_1 and k_2 differed only by about 40–50%. At high pH the 2 reactions are well separated which facilitates the kinetic analysis. Some slower reactions were run with a manually driven stopped-flow mixing device as described earlier [17]. This was possible when the complex concentrations were small and the reaction slow enough ($t_{1/2} > 3$ s). In these cases no intermediate is observed and only the first reaction step can be determined. Conditions were pseudo first-order with at least a tenfold excess of O_2 over $Co(tren)^{2+}$. Absorbance vs. time traces could be fitted by the first-order rate expression 6:

$$A_\infty - A_t = A_\infty e^{-k_a^* t} \quad (6)$$

$$k_a^* = k_a [O_2]$$

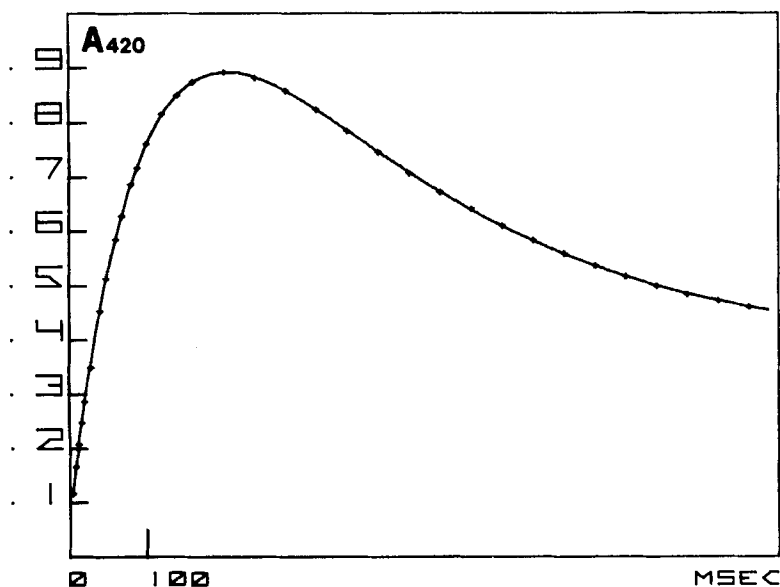


Fig. 3. Absorbance vs. time at 420 nm for the reaction of $Co(tren)^{2+}$ with O_2 at pH 9 in 0,2M borate buffer

The rate constants thus obtained agreed well with rate constants measured at high concentration when biphasic kinetics was observed. The agreement helped to confirm the accuracy of the rate constants obtained from biphasic kinetics. Some rate constants were determined by measuring the disappearance rate of oxygen using a membrane-shielded O_2 -sensor (*Clark* electrode). The electrode was inserted into a 6 ml cell, glass-jacketed to maintain constant temperature. The instrument was calibrated with air-saturated H_2O , and with deoxygenated H_2O . To ensure that the electrode response time (*ca.* 90% in 10 s) was not rate determining, $[Co(tren)^{2+}]$ had to be between $1.6 \cdot 10^{-5} M$ and $4 \cdot 10^{-5} M$ and the pH less than 8.7. First-order dependence in $Co(tren)^{2+}$ and O_2 was assumed throughout the reaction and “irreversibility” of O_2 -uptake was confirmed under the experimental conditions. This leads to the following rate law 7:

$$k \cdot t = \frac{1}{2[O_2]_0 - [Co]_0} \ln \frac{[O_2]_t [Co]_0}{[O_2]_0 [Co]_t} \quad (7)$$

$[O_2]_0$ and $[O_2]_t$ mean O_2 -concentration at time = 0 or t, resp. $[Co]_0$ and $[Co]_t$ are $Co(tren)^{2+}$ -concentrations. The perfect fit of the experimental data points of equ. 7 as shown in *Figure 4* demonstrates the validity of the assumption.

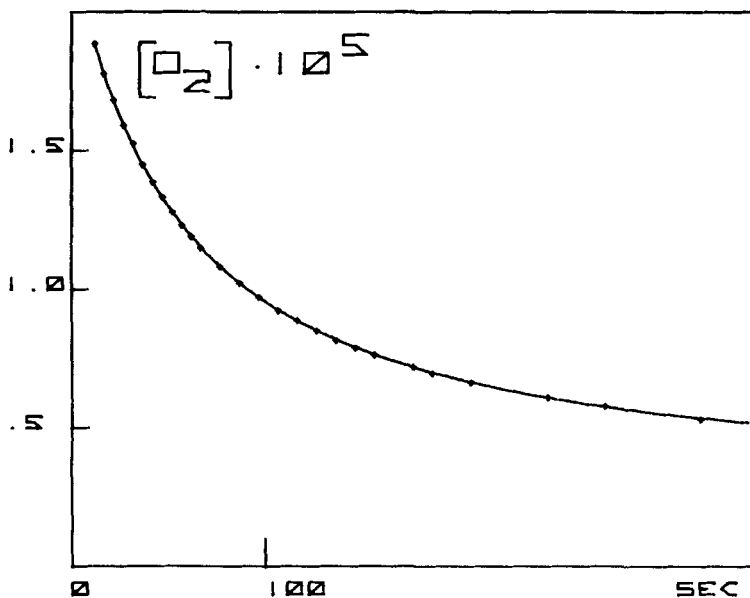


Fig. 4. Rate of O_2 -uptake (Clark electrode) of $Co(tren)^{2+}$ at pH 8.7. $[O_2]_0 = 2.03 \cdot 10^{-5} M$, $[Co(tren)^{2+}]_0 = 2.6 \cdot 10^{-5} M$. The indicated curve is the best fit of 27 data points to equation 7.

Kinetics of intramolecular redox decomposition of $(tren)Co(O_2,OH)Co(tren)^{3+}$ into Co^{2+} and O_2 . – Rate constants for this process were essentially measured as described earlier [17], but the pH-region was extended to higher pH-values. First-order rate constants were obtained from spectrophotometric and O_2 -measurements. Spectrophotometric data were obtained at 345 nm and 275 nm. Rate constants agreed well at both wavelengths. Rate constants from O_2 -measurements were obtained with the equipment described above. Preformed $(tren)Co(O_2,OH)Co(tren)^{3+}$ (pH: 8–9, 0.2M KCl) was injected into a deoxygenated buffer. Concentrations of $(tren)Co(O_2,OH)Co(tren)^{3+}$ were ranging from $4 \cdot 10^{-5} M$ – $1.2 \cdot 10^{-4} M$. At pH > 4 care has to be taken to assure that the dissociation reaction is complete so that simple first-order irreversible kinetics can be applied. This could be accomplished by using low concentrations of $(tren)Co(O_2,OH)Co(tren)^{3+}$ and addition of small amounts of EDTA. Buffers were used when necessary (HCl: pH < 2, *m*-phenylenediamine: $2.7 < pH < 4.5$, pyridine: $4 < pH < 5.5$).

Irreversible decay to mononuclear Co^{III} -complexes. – The rate of formation of irreversibly formed $Co(III)$ complexes in alkaline solution was mainly followed by monitoring the disappearance of the charge-transfer band at 345 nm or by measuring the remaining O_2 -content as a function of time.

Results. – *Co(tren)²⁺ in anaerobic conditions.* Mixing of a Co^{2+} -salt with tren under strictly anaerobic conditions affords a violet complex, an unusual colour for an octahedral Co^{2+} -complex. On addition of NaOH the colour changes to a grass green. The spectral changes as a function of pH are displayed in Figure 2. The electronic spectrum of the violet complex has been reported earlier [4]. It also has been shown that the complex has a high spin configuration and a magnetic moment of 4.67 B.M. From the striking similarity of the spectra of $Co(tren)(H_2O)_2^{2+}$ and $Co(Me_6tren)Br^+$, which is known to be trigonal bipyramidal [18], the same structure has also been proposed for the former. This assignment has been corroborated by thermochemical measurements, which revealed a higher entropy of formation for $Co(tren)^{2+}$ than for octahedral $Co(II)$ complexes [4]. Our data confirm the earlier

assignments. Five spin allowed transitions are expected in a high spin trigonal bipyramidal Co(II) complex, three of them in the visible region. The broad band centered at about 725 nm (Fig. 2) was assigned as transition to ${}^4E'$, the two other bands are assigned as transitions from the ground state ${}^4A'_2(F)$ to ${}^4A'_2(P)$ and ${}^4E''(P)$. The ${}^4A'_2(F) \rightarrow {}^4A'_2(P)$ transition has been shown to change little with change of ligand field [19] but was found to show a drastic dependence on the $N(3^\circ)\text{-Co-N}(1^\circ)$ angle [20]. With H_2O as axial ligand in $Co(tren)(H_2O)^{2+}$ this band is very symmetrical, as anticipated earlier [19], but shifts very strongly on deprotonation of the coordinated H_2O and a splitting of the band can be observed. The red shift of the ${}^4A'_2(P)$ band in the hydroxo complex could be explained by the weaker ligand field of OH^- but may be better explained by a tetrahedral distortion and a decreasing $N(3^\circ)\text{-Co-N}(1^\circ)$ angle in the $Co(tren)(OH)^+$ chromophore. The increasing intensity of all bands upon deprotonation would also fit this explanation. There was no change in shape and location of maxima between 10° and 60° . The small changes in ϵ are almost within experimental error, but show a slight increase with increasing temperature. Some of the data are shown in Table 2. The temperature dependence was intended to give some information about the occurrence of different configurations. This idea was put forward by Ciampolini *et al.* [11] on grounds of the relatively small molar extinction coefficient of $Co(tren)(H_2O)^{2+}$ compared with $Co(Me_6tren)Br^+$. The slight increase in ϵ with increasing temperature could only be explained by a small amount of weakly absorbing octahedral species in equilibrium with the pentacoordinated complex. From the temperature dependence we obtained thermodynamic quantities for K_a (equ. 1) which are shown in Table 1 together with data from other Co(II) complexes. There is a striking difference between the data in this work and in [13]. The last results were obtained from pH-titrations and at a much higher ionic strength. It may well be that this difference is due to the experimental differences. High ionic strength may afford formation of an ion pair, stabilizing the acid form (which explains the higher pK_a in [13]) and lead to a composite ΔH° (ion pair formation constant + deprotonation constant). The K_a -values are independent of the $Co(tren)^{2+}$ -concentration which shows that the spectral change with pH can be explained by the simple acid-base equilibrium 1. This explanation is strongly supported by pH-titrations in the presence and absence of O_2 (Fig. 5). If equ. 1 describes

 Table 1. Deprotonation constants (at 25°) and thermodynamic quantities for some Co(II) complexes

Complexes		K_{CoLOH}^{CoL}	(pK)	ΔH° (kcal/mol)	ΔS° (eu)	Ref.
$Co(tren)^{2+}$	a)	$9.1 \pm 0.2 \cdot 10^{-11}$	(10.03)	8.2 ± 0.5	18.7 ± 2.2	This work
$Co(tren)^{2+}$	b)	$9.4 \pm 0.3 \cdot 10^{-11}$	(10.02)			This work
$Co(tren)^{2+}$	c)	$\approx 10^{-10}$	(≈ 10.0)			This work
$Co(tren)^{2+}$	d)	$6.03 \cdot 10^{-11}$	(10.22)	0.22 ± 0.65	46 ± 2	[13]
$Co(Me_6tren)^{2+}$		$1.58 \cdot 10^{-9}$	(8.8)	8.1 ± 0.5	13 ± 1.5	[13]
$Co(TMC)^{2+}$	e)	$3.6 \cdot 10^{-9}$	(8.44)	8.1 ± 0.4	11.2	[14]
$Co(H_2O)_6^{2+}$		$1.4 \cdot 10^{-10}$	(9.85)	8.1	17.8	[15]

a) 0.2 M KNO_3 , $c_{tot} = 10^{-2}M$. b) 0.2 M KNO_3 , $c_{tot} = 2 \cdot 10^{-2}M$. c) 0.2 M KNO_3 , $c_{tot} = 2 \cdot 10^{-4}M$, pH-titration. d) 1 M $NaClO_4$. e) 0.5 M KNO_3 , TMC = 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane (see Fig. 1c).

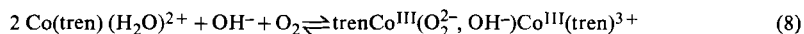
Table 2. *Electronic spectra of pentacoordinated Co(II) complexes at 20°*

Complexes	$\lambda_{\max}(\text{nm})$	ϵ_{molar}	Assignment	Ref.
Co(tren)(H ₂ O) ²⁺	724	12.2(12.4) ^{a)}	$^4A_2' \rightarrow ^4E'(F)$	This work
	573	40(42) ^{a)}	$^4A_2' \rightarrow ^4A_2'(P)$	This work
	479	47(50) ^{a)}	$^4A_2' \rightarrow ^4E''(P)$	This work
	≈ 455	≈ 38(sh)	b)	
Co(tren)(OH) ⁺	747	25	$^4A_2' \rightarrow ^4E'(F)$	This work
	632	73	$^4A_2' \rightarrow ^4A_2'(P)$	
	≈ 606	≈ 60(sh)		
	464	83	$^4A_2' \rightarrow ^4E''(P)$	
	≈ 445	≈ 75(sh)		
Co(Me ₆ tren)Br ⁺	813 ^{c)}	29		[11]
	620–640 ^{c)}	128		
	502–505 ^{c)}	112		

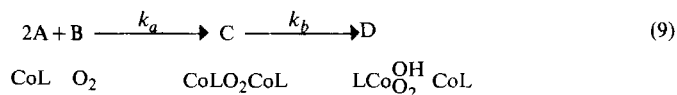
a) 50°. b) The $^4E''(P)$ -band is expected to split when the symmetry of the molecule is lower than D_{3h} [19]. c) In CHCl₃.

the spectral changes as a function of OH⁻ and knowing that the Co:O₂:OH stoichiometry is as shown in equ. 8 the two titration curves should intersect at pH = pK_a as is observed (Fig. 5). The pH-titration demonstrates that the green complex in solution is a mononuclear complex rather than a binuclear μ -hydroxo-complex as was proposed earlier [21]. However, from more concentrated solutions of Co(tren)²⁺ a solid dinuclear complex, (tren)Co(OH)Co(tren) (ClO₄)₃ can be isolated which shows an OH⁻ stretch vibration typical for μ -hydroxo-bridges [22].

Kinetics of formation. – The green and violet form of Co(tren)²⁺ react readily with molecular oxygen to form a kinetically and thermodynamically stable μ -peroxo, μ -hydroxo complex (see equ. 8).



The OH-bridge in solution can be inferred from pH-titrations (Fig. 5) and the final product of oxygenation can be isolated and its X-ray structure has been determined [7]. The electronic spectrum is constant over the pH-range 12 > pH > 4 and the temperature range studied and shows small deviations below 300 nm at pH > 12. It is characterized by a broad high intensity band at about 345 nm ($\epsilon = 7250$) and a shoulder at 275 nm ($\epsilon = 6720$). The first ligand field band appears as a very ill defined shoulder at about 480 nm ($\epsilon = 460$). The second ligand field band is obscured. The two intense bands which are exhibited by all μ -peroxo-, μ -hydroxo-dico-balt(III) complexes have been assigned as charge transfer transitions from O₂²⁻ (π^*) to Co(III) d σ^* orbitals [23]. The occurrence of the high intensity absorption bands render electronic absorption spectroscopy a convenient method for following the rate of formation of the oxygenated species. The reaction of Co(tren)²⁺ with O₂ exhibits biphasic kinetics at 420 nm of the form



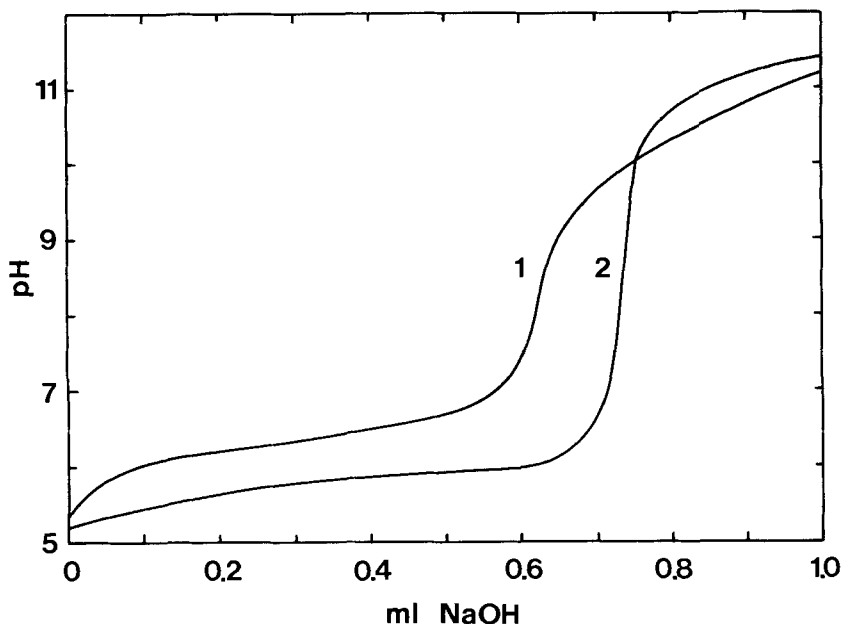


Fig. 5. Potentiometric titration of $\text{tren} \cdot 3 \text{HCl}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1,05:1 ratio) under N_2 (1) and under O_2 (2)

At $[\text{Co}(\text{tren})^{2+}] \gg [\text{O}_2]$ the absorbance vs. time traces were successfully treated in terms of two consecutive first order reactions consistent with accumulation and decay of an intermediate as displayed in *Figure 3*. Stopped-flow traces could be fitted perfectly using a function of the form (equ. 4)⁵⁾. The reaction became monophasic at 360–370 nm and $\text{pH} < 10$. This can only be due to the fact that $\epsilon_C = \epsilon_D$. Under these conditions only k_a is measured which helps to assign k_a to the faster and k_b to the slower reaction phase. The problem of separating the two reactions could be circumvented in two ways: 1) A wavelength was chosen at which A_1 and A_2 have opposite sign. This allowed to discern small differences in rate constants; 2) The first step (k_a) proved to be pseudo first-order and could be speeded up by increasing the $\text{Co}(\text{tren})^{2+}$ -concentration.

The concentration dependence showed that the rate of O_2 -disappearance and formation of the intermediate was first-order in $[\text{Co}(\text{tren})^{2+}]$ and $[\text{O}_2]$ (10).

$$-\frac{d[\text{O}_2]}{dt} = \frac{d[\text{intermediate}]}{dt} = k_a [\text{Co}(\text{tren})^{2+}] [\text{O}_2] \quad (10)$$

5) The evaluation of concentrations A, B, C and D and the optical density changes as a function of time is straightforward and can be found in [24]. In this special case

$$A_1 = \frac{\epsilon_C [\text{O}_2]_0 \cdot k_1 [\text{Co}]_0}{k_3 - k_1 [\text{Co}]_0} + \frac{\epsilon_D \cdot [\text{O}_2]_0 k_3}{k_1 [\text{Co}]_0 - k_3} \quad A_2 = \frac{(\epsilon_C - \epsilon_D) \cdot k_1 [\text{Co}]_0 [\text{O}_2]_0}{k_1 [\text{Co}]_0 - k_3}$$

This rate law holds over the concentration range studied ($1.5 \cdot 10^{-5} \text{M} - 2.5 \cdot 10^{-2} \text{M}$). No second-order term in $[\text{Co}(\text{tren})^{2+}]$ could be found; k_a values were the same for the green and the violet form of $\text{Co}(\text{tren})^{2+}$ if both forms were mixed with an air-saturated buffer of the same pH. This result shows that the two forms equilibrate rapidly compared to the rate of O_2 -uptake; k_a was essentially pH-independent between pH 8–9, and increased with pH levelling off at $\text{pH} > 11$. This kind of pH-profile (Fig. 6), which clearly resembles the profile of an acid-base titration curve, has been found for several $\text{Co}(\text{II})$ -complexes with open chain tetradentate ligands and octahedral complex geometry. The curve indicated represents a least-squares best fit to a single pK_a value using an equation of the form 11.

$$k_a = \frac{k'_a[\text{H}^+] + k''_a K_a}{[\text{H}^+] + K_a} \quad (11)$$

The pH-independent second-order rate constants were found to $k'_a = 219 \pm 20 \text{M}^{-1} \text{s}^{-1}$ and $k''_a = 1820 \pm 35 \text{M}^{-1} \text{s}^{-1}$ and $K_a = 1.18 \pm 0.2 \cdot 10^{-10} \text{M}$. Activation parameters were obtained at pH 8.3 from an *Arrhenius* plot at 4 different temperatures between 16° and 36° using the relationship $\Delta E^\ddagger = \Delta H^\ddagger + RT$. Second-order rate constants as well as activation parameters are summarized in Table 3 along with those of $\text{Co}(\text{trien})^{2+}$.

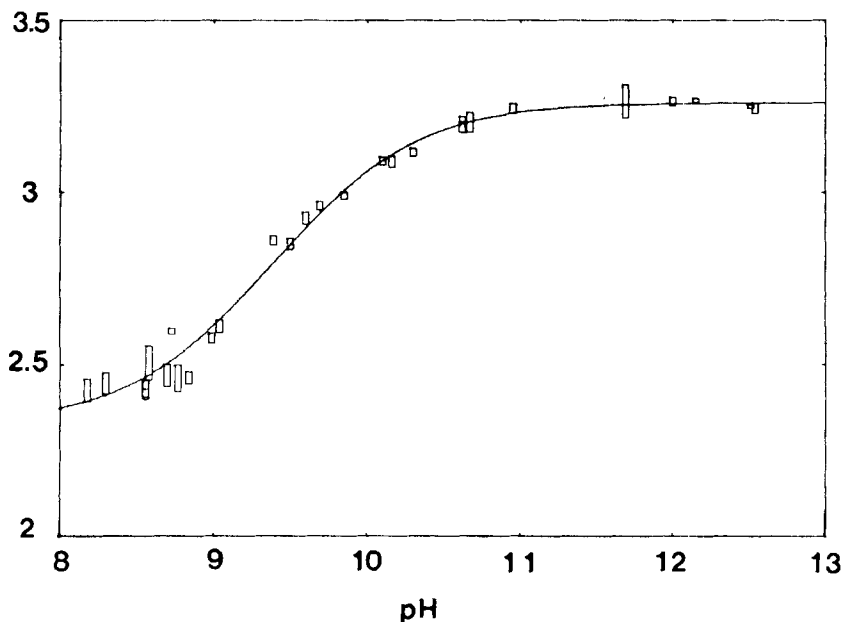


Fig. 6. Influence of pH on the rate of O_2 -addition to $\text{Co}(\text{tren})^{2+}$ in aqueous solution containing several buffers (25°). The parameters are $k'_1 = 220 \pm 19 \text{M}^{-1} \text{s}^{-1}$, $k''_1 = 1820 \pm 35 \text{M}^{-1} \text{s}^{-1}$, $K_a = 1.18 \pm 0.2 \cdot 10^{-10} \text{M}$.

The second (intramolecular) step was strictly first-order and the rate constant independent of the concentration of cobalt and oxygen. The experimental results are compatible with the following rate law.

$$-\frac{d[\text{intermediate}]}{dt} = k_b[\text{intermediate}] \quad (12)$$

Table 3. Kinetic data for the reaction of Co(II) complexes with O₂ in water at 25°

Complexes	$k_1(\text{M}^{-1}\text{s}^{-1})$	$\text{p}K_a^{\text{a}}$ ($\text{p}K_a^{\text{b}}$)	$\Delta H^\ddagger(\text{kcal/mol})$	$\Delta S^\ddagger(\text{eu})$	Ref.
Co(tren)(H ₂ O) ²⁺	219 ± 20	9.93 ± 0.07 (10.03)	5.1 ± 0.5	-29.6 ± 3.5	This work
Co(tren)(OH) ⁺	1820 ± 35				This work
Co(trien)(H ₂ O) ₂ ²⁺	2.5 · 10 ⁴	11.2 ± 0.1	7.1	-15	[3]
Co(trien)(H ₂ O)(OH) ⁺	2.8 · 10 ⁵				[3]

^a) $\text{p}K_a$ from kinetic measurements. ^b) $\text{p}K_a$ from spectrophotometric titration under O₂ exclusion (see Fig. 2).

k_b was independent of pH up to about pH 10 and decreased with increasing pH. At pH > 12 the log k_{obs} vs. pH plot has the slope -1. Figure 7 shows the best fit to the experimental data using an equation of the form 13.

$$k_b = \frac{k_b'[\text{H}^+]}{[\text{H}^+] + K_b} \quad (13)$$

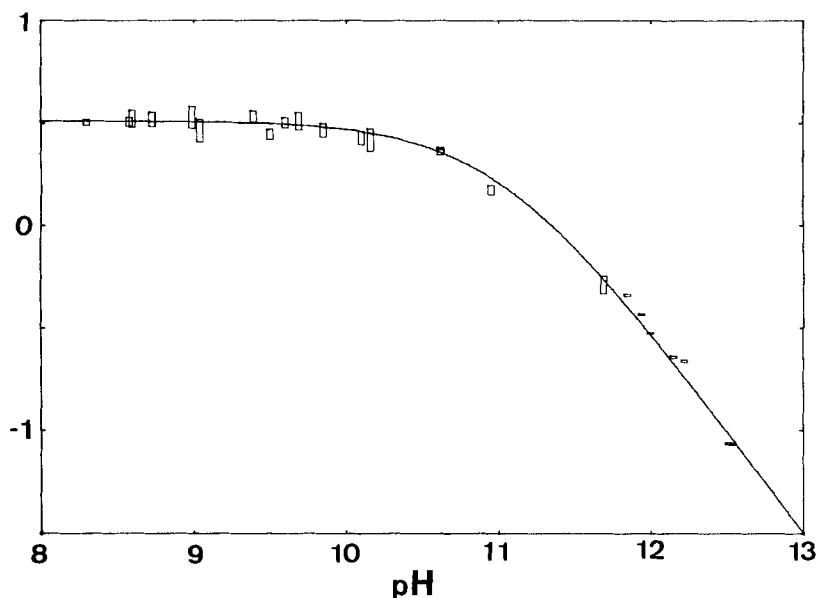


Fig. 7. Influence of pH on the rate of intramolecular bridging reaction of Co/tren/O₂. The parameters are $k_3 = 3.25 \pm 0.15 \text{ s}^{-1}$, $K_a = 9.76 \pm 0.45 \cdot 10^{-12} \text{ M}$.

Activation parameters were obtained at pH 9 and calculated from an Arrhenius plot (see Table 4). At pH 12.2 k_b decreased slightly with increasing temperature; $\Delta H_{\text{obs}}^\ddagger \approx -2 \text{ kcal/mol}$. This step leads undoubtedly to the doubly-bridged (tren)Co^{III}(O₂²⁻, OH-)Co^{III}(tren)³⁺. Its spectrum did not change for weeks and no irreversible conversion to mononuclear Co^{III} complexes could be observed at pH 8–10. This

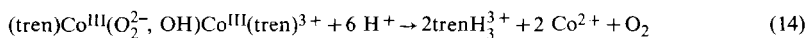
result is in qualitative agreement with the one found by *Martell et al.* who reported some conversion to mononuclear complexes after 3 months [5]. On the contrary, $(\text{trpn})\text{Co}(\text{O}_2, \text{OH})\text{Co}(\text{trpn})^{3+}$ decayed very fast to a species which did not liberate molecular O_2 upon acidification. The half live of the oxygenated species at pH 9 and 25° is 20 min as compared to several months for $\text{tren}/\text{Co}/\text{O}_2$.

Table 4. Kinetic data for the intramolecular bridging reaction in binuclear μ -peroxo-dicobalt(III) complexes and H_2O -exchange rates in mononuclear Co(III) complexes

Complexes	$k_3(\text{s}^{-1})$	$K_3(\text{M})^{\text{a}}$	$\Delta H^\ddagger(\text{kcal/mol})$	$\Delta S^\ddagger(\text{eu})$	Ref.
$\text{trenCo}^{\text{III}}\text{O}_2^2-\text{Co}^{\text{III}}\text{tren}$ H ₂ O OH	3.25 ± 0.15		11.5 ± 1.5	-17.5 ± 2.5	This work
$\text{trenCo}^{\text{III}}\text{O}_2^2-\text{Co}^{\text{III}}\text{tren}$ OH OH	$< 10^{-2}$	$9.8 \pm 0.5 \cdot 10^{-12}$			This work
$\text{trienCo}^{\text{III}}\text{O}_2^2-\text{Co}^{\text{III}}\text{trien}$ H ₂ O OH	2.0		11,0	-21	[3]
$\text{trienCo}^{\text{III}}\text{O}_2^2-\text{Co}^{\text{III}}\text{trien}$ OH OH	$\approx 1.2 \cdot 10^{-2}$	$1.2 \cdot 10^{-11}$			[3]
$\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$	$5.8 \cdot 10^{-6}$ b)		26.6 ± 0.3	6.7 ± 1	[32]

^a) From kinetic measurements. ^b) H_2O -exchange rate.

Redox decomposition of $(\text{tren})\text{Co}(\text{O}_2, \text{OH})\text{Co}(\text{tren})^{3+}$ in acid solution. – As has been shown before [15] the final product of oxygenation of $\text{Co}(\text{tren})^{2+}$ decays in acid solution according to equ. 14.



This reaction can be viewed as an intramolecular electron transfer and goes to completion at all pH-values studied ($0 < \text{pH} < 5.5$). The rate was found to be pH-dependent. In this study the pH-range was extended to values > 3 which resulted in the finding of a pH-independent region. The experimental data (*Fig. 8*) could be fitted to the following rate law.

$$-\frac{d[\text{Co}(\text{O}_2, \text{OH})\text{Co}^{3+}]}{dt} = \frac{d[\text{O}_2]}{dt} = (1.6 \pm 0.08 \cdot [\text{H}^+] + 5.25 \pm 0.6 \cdot 10^{-5}) [\text{Co}(\text{O}_2, \text{OH})\text{Co}^{3+}] \quad (15)$$

This rate law holds between pH 1 and 5.5. In this pH-region the formation of O_2 and disappearance of $(\text{tren})\text{Co}(\text{O}_2, \text{OH})\text{Co}(\text{tren})^{3+}$ follows first-order kinetics. Below pH 1 the decay traces had to be fitted by 2 consecutive first-order processes. This complicated reaction is not discussed in this paper.

Discussion. – The rate of oxidative addition of molecular O_2 to octahedral Co(II) complexes has been explained by assuming that ligand exchange is rate-determining [3][16]. Several questions concerning reactive species remained open. In the case

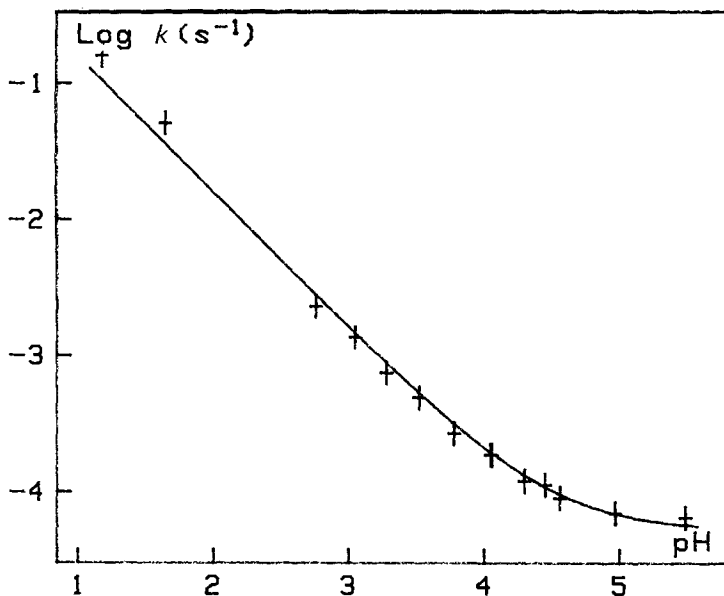
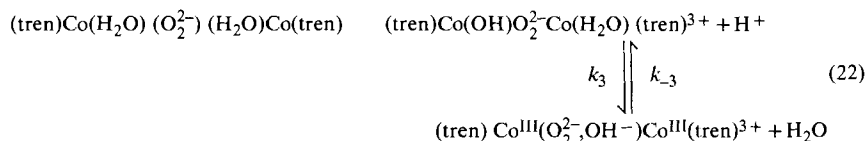
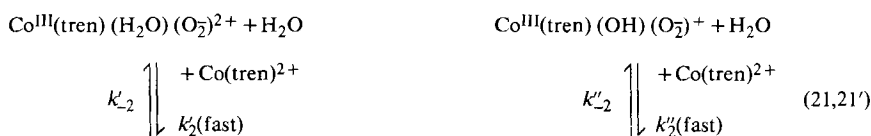
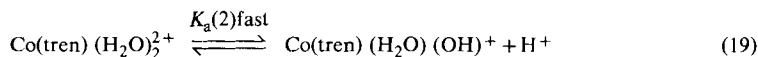
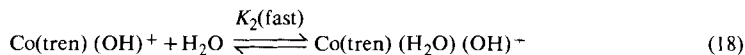
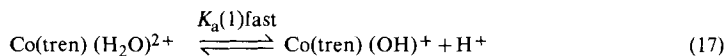
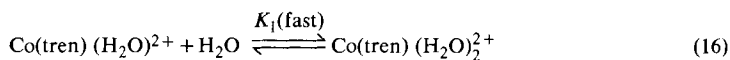


Fig. 8. Influence of pH on the rate of internal redox decay of $(tren)Co(O_2,OH)Co(tren)^{3+}$. Parameters are $k_H = 1.6 \pm 0.12 M^{-1} s^{-1}$, $k_{-3} = 5.2 \pm 0.6 \cdot 10^{-5} s^{-1}$.

of $Co(trien)^{2+}$ a pentacoordinate trigonal bipyramidal complex was proposed to be a possible reactive species [3]. Hence, complexes with tripod ligands appeared likely to give further information about the mechanism of oxygenation of $Co(II)$ complexes as these ligands show a strong propensity to form trigonal bipyramidal complexes.

$Co(tren)^{2+}$ exists in a violet and green form depending on pH. Temperature and pH-dependence of the electronic spectrum corroborated the assignment of a pentacoordinate trigonal bipyramidal geometry. Both forms react readily with molecular O_2 . The striking difference between the two tetradentate systems $Co(trien)^{2+}$ and $Co(tren)^{2+}$ (the two ligands have about the same donor strength) is the much slower rate of O_2 -addition to the latter. This result is rather surprising. Indeed we expected a much faster rate of oxygenation of $Co(tren)^{2+}$ considering its geometry. *Wilkins* considered a pentacoordinated $Co(trien)(OH)^+$ as a minor component in alkaline solutions of $Co(trien)^{2+}$, but as the possible reactive species towards O_2 . A mechanistic scheme that is compatible with the presented experimental data and accounts for the small rate is depicted by the following equations.

Scheme 1



This scheme is consistent with the assumption of irreversible consecutive first-order reactions with second-order rate constants k'_1 and k'_1 and a first-order rate constant k_3 . This can be easily understood from the experimental conditions $[\text{Co}(\text{tren})^{2+}] \gg [\text{O}_2]$ (hence k'_1 and k'_1 are pseudo first-order rate constants) and the fact that the intermediates $(\text{tren})\text{Co}(\text{H}_2\text{O}) (\text{O}_2)\text{Co}(\text{OH}) (\text{tren})^{3+}$ and $(\text{tren})\text{Co}(\text{OH}) (\text{O}_2) (\text{OH})\text{Co}(\text{tren})^{2+}$ are formed quantitatively as well as the product $(\text{tren})\text{Co}(\text{O}_2, \text{OH})\text{Co}(\text{tren})^{3+}$ ⁶⁾. Reactions 16–19 are considered to be fast, 16 and 18 being rapid preequilibria between 5- and 6-coordinate species and only the latter are assumed to be reactive toward O_2 . The $[\text{Co}(\text{tren})^{2+}]$ -dependence (equ. 10) requires that only one Co(II) species is involved in the rate-controlling step. The pH-dependence for the first reaction is explained by rapid acid base equilibria and rate-determining H_2O -exchange in the O_2 addition step. The following rate law can be derived and is in agreement with the functional form of equ. 11.

$$k = \frac{k_1[\text{H}^+] + k'_1 \cdot K_a(2)}{[\text{H}^+] (1 + 1/K_1) + K_a(2) (1 + 1/K_2)} \quad (23)$$

The pH-independent rate constants are given by equ. 24 and 25.

$$k_a = \frac{k_1 K_1}{1 + K_1} \quad (24) \quad k'_a = \frac{k'_1 K_2}{1 + K_2} \quad (25)$$

The rate at the inflection point is given by equ. 26.

$$k_{\text{obs}} = \frac{1 + 1/K_2}{1 + 1/K_1} K_a(2) \quad (26)$$

6) This has been verified by the finding that the two reaction amplitudes are independent of $[\text{Co}(\text{tren})^{2+}]$ at constant $[\text{O}_2]$ under the experimental conditions ($[\text{Co}(\text{tren})^{2+}] \gg [\text{O}_2]$) and the potentiometric titration under O_2 and N_2 (see Fig. 5) which ascertained a stoichiometry given in equ. 9 with the equilibrium on the side of the product.

Assuming that only the pentacoordinate species is present in detectable concentrations, equ. 26 simplifies to $k_{\text{obs}} = (K_1/K_2) K_a(2) = K_a(1)$. The agreement between the deprotonation constant determined independently with the one found from the pH-dependence of the rate constant corroborates what was said above. In the following some evidence is given in support of the proposed equilibria 16 and 18 and the assumption of the reactive hexacoordinate complexes.

a) The much larger rate of oxygenation of $\text{Co}(\text{trien})^{2+}$, compared to $\text{Co}(\text{tren})^{2+}$, can readily be explained by assuming that only a small amount of reactive species $\text{Co}(\text{tren})(\text{H}_2\text{O})_2^{2+}$ is in equilibrium with $\text{Co}(\text{tren})(\text{H}_2\text{O})^{2+}$ (ca. 1% would be necessary). In fact, assuming a dissociative mechanism, as proposed by *Wilkins* for the oxygenation of octahedral $\text{Co}(\text{II})$ complexes, the pentacoordinated $\text{Co}(\text{tren})(\text{H}_2\text{O})^{2+}$ would be expected to react with O_2 near the diffusion controlled limit;

b) A close look at the activation parameters of the two systems shows that the reaction of $\text{Co}(\text{tren})^{2+}$ with molecular O_2 is characterized by a larger negative entropy term somewhat counterbalanced by a smaller ΔH^* . The strongly negative ΔS^* may reflect an activated complex which is composed of a higher number of molecules. This is consistent with the participation of an additional H_2O molecule besides O_2 or a pre-equilibrium 16. The smaller ΔH^* in $\text{Co}(\text{tren})^{2+}$ again may be explained by a pre-equilibrium and/or a weaker $\text{Co}-\text{OH}_2$ bond in $\text{Co}(\text{tren})(\text{H}_2\text{O})_2^{2+}$. It is agreed that it is certainly always difficult to make a very strong statement about activation parameters;

c) The propensity of tripod ligands with amine-donor atoms to form pentacoordinate complexes is due to steric factors. If the assumption of an equilibrium 16 is correct the introduction of additional steric hindrance should even further slow down the reaction. The $\text{Co}(\text{II})$ complex with hexamethylated tren, L_I proved to be unreactive towards O_2 and $\text{Co}(L_{II})$ absorbs O_2 very slowly, and no peroxo-complex can be obtained in aqueous solution. It is of interest to note that two pentacoordinate $\text{Co}(\text{II})$ complexes have been reported to be unreactive towards O_2 . $\text{Co}L_{III}$ (for L_{III} see *Fig. 1c*) is pentacoordinate, most likely square pyramidal and does not exhibit any oxygen affinity at all [14] whereas the octahedral $\text{Co}(\text{cyclam})(\text{H}_2\text{O})_2^{2+}$ forms stable peroxo-compounds [25]. $\text{Co}L_{IV}$ (for L_{IV} see *Fig. 1c*) was reported to be very stable to oxidation and does not react with O_2 [26]. Again the related ligand L'_{IV} forms an octahedral $\text{Co}(\text{II})$ complex which reacts with O_2 [27].

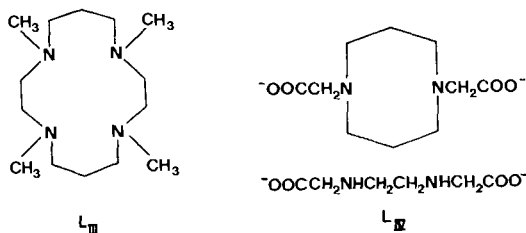


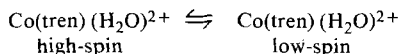
Fig. 1c. L_{III} = 1,5,8,12-Tetramethyl-1,5,8,12-tetraazacyclotetradecane

d) Synthetic work and a kinetic study showed that only one of 3 possible isomers is formed upon oxygenation of $\text{Co}(\text{tren})^{2+}$ [17]. An X-ray structure revealed the

stereospecifically preferred isomer is the one with the tertiary amino groups *cis* to the peroxo bridge [7]. If the replacement of H_2O in $\text{Co}(\text{tren})(\text{H}_2\text{O})_2^{2+}$ is rate-limiting in the oxygenation reaction, the substitution must occur in the most labile position which must be *cis* to the tertiary amino group. This labilisation is suggested by looking at models and certainly by the known tendency of *tren* to form a trigonal bipyramidal geometry. *Madan et al.* noted an anomalously fast aquation rate for $\text{Co}^{\text{III}}(\text{tren})\text{Cl}_2^+$ where the labile Cl^- is the one *cis* to the tertiary N-atom [28]. In the course of ^{17}O -line broadening studies *Hunt et al.* [29] also noted two rate constants for the pseudooctahedral $\text{Ni}(\text{tren})(\text{H}_2\text{O})_2^{2+}$ and a ratio of water exchange rates at 25° of *ca.* 10–20. In this experiment the site of the faster exchanging H_2O molecule could not be identified but again is suggested to be *cis* to the tertiary N-atom. The structure of the deprotonated complex in equ. 19 is determined by the more acidic H_2O *trans* to the tertiary N-atom. The acidity of coordinated H_2O is mainly determined by the charge on the metal and the metal-oxygen bond length. The bond length must be longer in the more labile position. This position now is additionally labilised by the OH^- *trans* to the tertiary N-atom. Hydrolysis of coordinated H_2O is known to labilize neighboring H_2O -molecules [3]. The preferred formation of the isolated isomer throughout the pH region of study is therefore consistent with the proposed mechanism;

e) A mechanism in which the is rate-limiting exchange of the apical H_2O in the five-coordinate complex followed by rearrangement can be excluded. This conclusion is based on previous results where we showed [16] that in complexes like $\text{CoL}(\text{H}_2\text{O})_2^{2+}$ – as opposed to $\text{CoL}(\text{H}_2\text{O})_2^{2+}$ – the incorporation of O_2 is retarded at higher pH due to the formation of $\text{CoL}(\text{OH})^+$ and the slower exchange of OH^- compared to H_2O . Hence, for $\text{Co}(\text{tren})(\text{H}_2\text{O})_2^{2+}$ the rate of O_2 -uptake inverse to OH^- would be expected whereas for $\text{Co}(\text{tren})(\text{H}_2\text{O})_2^{2+}$ a pH-dependence as shown in *Figure 6* should result.

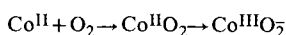
Most of above observations can also be understood in terms of an associative mechanism, *i. e.* the addition of O_2 to the five-coordinate $\text{Co}(\text{tren})(\text{H}_2\text{O})_2^{2+}$ 7). Two reasons are especially decisive to discount an associative mechanism: The pH-profile and more importantly the small rate constant compared with $\text{Co}(\text{trien})(\text{H}_2\text{O})_2^{2+}$. In an associative mechanism the rate is expected to approach the diffusion-controlled limit if high-spin five-coordinate $\text{Co}(\text{tren})(\text{H}_2\text{O})_2^{2+}$ is assumed to be reactive. However, there is an alternative explanation: It is not unlikely that the high-spin complexes are not reactive and small amounts of low-spin $\text{Co}(\text{tren})(\text{H}_2\text{O})_2^{2+}$ is the reactive species:



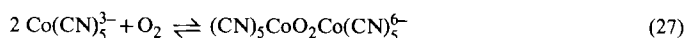
This would explain the small rate constant. The pH-dependence had to be explained by a shift of the above equilibrium to the right if H_2O is replaced by OH^- .

7) The referees of this article prefer this interpretation. From their point of view the experimental data are best explained by a simple addition of O_2 to the penta-coordinate $\text{Co}(\text{II})$ complexes. The higher reactivity of $\text{Co}(\text{tren})(\text{OH})^+$ is accounted for by assuming a smaller reorganizational energy for the hydroxo-complex compared with the aquo-complex. The lack of reactivity of the $\text{Co}(\text{II})$ complexes with ligands depicted in *Figures 1b* and *1c* is explained by the high stability of these complexes and/or steric hindrance in the attack of O_2 .

Certainly these mechanisms and the one depicted above (and preferred) are kinetically indistinguishable. It is hoped that new, specially designed ligands help to distinguish between the mechanisms. Independent of this unresolved question the tentative conclusion is that high spin five-coordinated Co(II) complexes do not react with O₂. We can only speculate about the reason for the observed lack of O₂-affinity: the process of oxygenation is one of intramolecular electron transfer with the addition of O₂ to Co(II) (in most cases determined by ligand exchange and rate-limiting) followed by electron transfer.

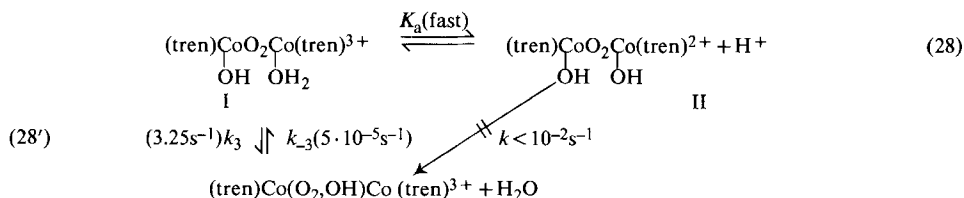


During the activation process some reorganization has to occur to bring the geometry close to Co(III). This may afford a very high activation energy, especially in the case of high-spin five-coordinate complexes because of the well known instability of five-coordinate Co(III) amine complexes. On the other hand it has been known for a long time that the five-coordinated low-spin Co(CN)₅³⁻ reacts readily with O₂ according to equ. 27 [30].



A kinetic study of this reaction is hampered by the occurrence of dimeric and may be even polymeric species in the reactant mixture. It is noteworthy that so far the oxygenation of only few low-spin Co(II) systems has been studied kinetically: Co-myoglobin (CoMb) and Co-hemoglobin (CoHb). Both are artificial hemoproteins, which have been prepared by an anaerobic recombination of apomyoglobin and apohemoglobin with cobaltous porphyrins. Both exhibit reversible oxygenation and CoHb even shows a high degree of cooperativity. The rate constant for the oxygenation of proto-CoMb is $3.6 \cdot 10^7 \text{ M}^{-1}\text{s}^{-1}$. ($\Delta E^\ddagger = 9.2 \text{ kcal/mol}$, $\Delta S^\ddagger = 7.6 \text{ eu}$) [31]. This is strikingly higher than found for the polyamine complexes.

The second step (C → D) is strictly first-order and is certainly the intramolecular bridging reaction (22). This explanation is in accord with the one given for Co/trien/O₂. The perfect fit of the experimental data points by one exponential is in agreement with the occurrence of only one isomer in the final product. Hence, it is safe to conclude that the intermediate exists as a single isomer as well. The pH-dependence (Fig. 7) is best understood in terms of a scheme in which 2 species are in a rapid acid base equilibrium:



The slope -1 shows that reaction from II does not occur to any significant extent in the pH-region of study. This reflects the slower exchange rate of OH⁻ as compared to H₂O. The rate of the bridging reaction ($k_3 = 3.25\text{s}^{-1}$) must be considered high for H₂O exchange on a Co(III) center⁸⁾, but is only slightly higher than k_3 found in

⁸⁾ H₂O-exchange rate must be $> 3.25\text{s}^{-1}$.

Co/tren/ O_2 (see *Table 4*). The enhancement obviously is the result of a much lower activation energy as compared to H_2O -exchange rates in $Co(NH_3)_5(H_2O)^{3+}$. This effect is somewhat counterbalanced by a less favorable ΔS^\ddagger . The low ΔH^\ddagger may reflect the problem of assigning oxidation states if there are redox-active, noninnocent, ligands. So far only few quantitative kinetic studies of substitution reactions on Co(III) peroxo-complexes have been undertaken. The few examples indicate that the peroxo-group causes a strong labilizing effect, which is not limited to the *trans* position as would be expected in view of the structural ground-state *trans*-effect exerted by O_2^{2-} [33]. The negative ΔS^\ddagger is consistent with the anticipated loss of rotational freedom in the activated complex because only a *cisoid*-configuration would lead to a μ -hydroxo-bridged complex. The slightly decreasing rate constant at $pH = 12.3$ with increasing temperature gives an unreasonable ΔH^\ddagger value for a one step reaction which is necessarily a positive quantity. But ΔH_{obs}^\ddagger can readily be understood in terms of our mechanism and analyzed as the difference of the enthalpy term for the fast acid-base preequilibrium ΔH_3^\ddagger and the activation energy for the intramolecular bridging step 29.

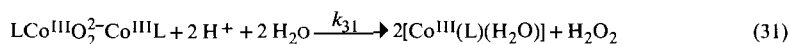
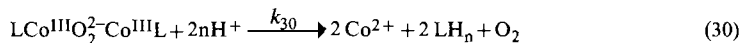
$$H_{obs}^\ddagger = \Delta H_3^\ddagger - \Delta H_3^\ddagger \quad (29)$$

The dissociation of an acid is usually an endothermic process, *i. e.* the higher temperature favors dissociation and diminishes the concentration of the reactive species (I in equ. 28). So ΔH_{obs}^\ddagger can become negative if ΔH_3^\ddagger is large enough. From $H_{obs}^\ddagger \approx -2 \text{ kcal mol}^{-1}$ and the known value for ΔH_3^\ddagger (obtained from measurements at $pH 9$) ΔH_3^\ddagger calculates to $\approx 14 \text{ kcal mol}^{-1}$. This procedure to calculate ΔH_3^\ddagger is justified because of the slope -1 .

At this stage the product spectrum does not change for weeks at $pH 8-9$ and no loss of reversibly bound O_2 has been found. The same unique kinetic stability towards irreversible decomposition has been noticed by *Martell et al.* [27] with tripod-like ligands, *e. g.* Co/uedda/ O_2 and Co/sdtma/ O_2 ⁹⁾. *Martell* tentatively explains this inhibition of "final oxidation" by the ligand structure. In an earlier report we concluded from our work that besides charge and steric hindrance the easy formation of the μ -hydroxo-bridge and along with this the position of equilibrium 28' are responsible for the rate of irreversible decomposition [34]. This proposal was tested with Co/trpn/ O_2 . Trpn is like tren a tripod-like ligand but due to the propylene, rather than ethylene-groups linking the amino N-atoms, steric crowding should aggravate the formation of the additional μ -hydroxo-bridge. The difference of the kinetic stability of the two systems is striking. The half-lives being several months for Co/tren/ O_2 and only about 20 min for Co/trpn/ O_2 . This result certainly disproves the assumption that exclusively the tripod-like ligand geometry imparts the high kinetic stability of these complexes. Unfortunately the low stability precludes a more thorough investigation of the system Co/trpn/ O_2 . From additional properties of Co/tren/ O_2 it is evident that the Co(II)-ligand combination as in $Co(tren)^{2+}$ provides an excellent balance to form reversible O_2 -carriers. This can be seen from the quantitative reversibility. Virtually 100% O_2 can be recovered upon acidification. Addition of base regenerates the O_2 -complex. As many as 20 oxygenation-deoxy-

⁹⁾ uedda = Ethylenediamine-*N,N*-diacetic acid, sdtma = *N,N*-Bis(2-aminoethyl)glycine.

generation cycles have been performed on a given sample with no significant decrease of the CT-band. This is in marked contrast to the Co/trien/O₂ system. There acidification to pH < 2 leads to a considerable irreversible side reaction (31) and titration to an alkaline pH does not regenerate 100% of the O₂-complex. The amount of side reaction depends on pH and is strongly influenced by anions [35]. The factors which determine the degree of reversibility and the mechanism leading to mononuclear Co(III) products are not well understood. The degree of reversibility in acid solution (equ. 30 and 31) is given by $k_{30}/k_{30} + k_{31}$. The rate constants k_{30} and k_{31} are defined by equ. 30 and 31.



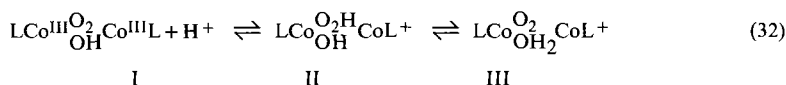
The step leading to the formation of Co²⁺ and O₂ occurs by intramolecular electron transfer. The energy barrier to electron transfer is imposed by the *Franck-Condon* restriction. Step 31 has to be considered a substitution reaction which may be accelerated by protonation of the peroxo-group. These reactions have not been studied for a wide range of complexes and structures, hence any speculation as to the reasons for the difference in these 2 systems appears to be premature.

Reaction 14 has been discussed in an earlier paper [17]. The rate of dissociation has been found to be H⁺-catalyzed between 1 < pH < 4 and levelled off at pH < 1. We explained this with the assumption of the protonation of the peroxo-complex and rate determining opening of the hydroxo-bridge¹⁰). Extension to pH > 4 (*Fig. 8*) leads again to a pH-independent rate, which was calculated to $5.25 \cdot 10^{-5} \text{ s}^{-1}$ and must be explained as the non H⁺-assisted opening of the hydroxo-bridge (k_{-3} in (28')). From k_3 ($= 3.25 \pm 0.15 \text{ s}^{-1}$) and k_{-3} an equilibrium constant K_3 can be calculated to $\approx 10^{+5}$. This figure demonstrates clearly what *Martell* calls "lock-in" of O₂ by the hydroxo bridge. It should be noted that it fits well into our explanation of the high kinetic stability of the Co/tren/O₂ carrier. Equilibrium 28' is extremely shifted to the unreactive doubly-bridged complex.

Further investigations with new tripodal ligands to corroborate the given mechanistic ideas are being pursued in this laboratory.

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¹⁰⁾ The site of protonation which causes the accelerated cleavage is most likely the hydroxo-bridge, but the more basic group is expected to be the peroxo-group. As expected, protonation of the peroxo group has been shown to slow down the rate of intramolecular electron transfer and a better explanation of the pH-dependence may be given by assuming the tautomeric equilibrium 32 and III as the reactive species.



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