The Kinetics of the Rapid Interaction of Some Cobalt(II) Chelates with Oxygen

Frances Miller, Jon Simplicio, and Ralph G. Wilkins

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. Received October 11, 1968

Abstract: The thermodynamics and kinetics of reversible uptake of O_2 in aqueous solution by certain cobalt(II) chelates have been examined. These include diethylenetriamine (dien), histamine (hist), ethylenediamine (en), and 2-aminomethylpyridine (amp) complexes. Kinetic data support the mechanism $CoL_2^{2+} + O_2 \rightleftarrows CoL_2O_2^{2+}$ (k_1, k_{-1}); $CoL_2^{2+} + CoL_2O_2^{2+} \rightleftarrows Co_2L_4O_2^{4+}$ (k_2, k_{-2}) for L = dien or histamine (any coordinated water omitted). Values for k_1, k_{-2} (from EDTA^{4-} or H$^+$ decomposition) and $k_1k_2/k_{-1}k_{-2}$ were obtained for these systems, the latter in excellent agreement with K_{O_2} obtained from oxygen-uptake experiments. In addition, values of k_1 were measured for reaction of Co(dien)(dienH)$^{3+}$, Co(hist)$_3^{2+}$, Co(amp)$_3^{2+}$, Co(amp)$_2^{2+}$, and Co(en)$_2^{2+}$ with O_2. Enthalpies and entropies of activation were obtained in all cases. The results are discussed with respect to the rate constants and the factors governing the uptake of O_2 by these species.

The ability of a variety of cobalt(II) complexes to absorb oxygen reversibly in aqueous solution has been often demonstrated.[1] An important class of such compounds is represented by the octahedral cobalt(II) ammines and polyamine chelates. Investigation of the properties of these complexes (*e.g.*, formation constants[2] and redox kinetics[3]) must therefore be made in the absence of oxygen. In the case of the cobalt(II) ammines, the oxygenation product has been well characterized as the binuclear species $(NH_3)_5CoO_2Co(NH_3)_5^{4+}$, with a peroxo grouping bridging the two cobalt atoms.[4,5] The corresponding products from the polyamine complexes are probably also peroxo-bridged dimers in solution as evidenced from stoichiometry and spectral properties, but apparently they have not been isolated and characterized as solids.[6] Fallab and Bekaroglu[7] have refocussed attention on these interesting reactions, examining the stoichiometry of the interactions, the further irreversible oxidation, and the factors governing the uptake of O_2. Apart from frequent observations that the oxygen uptake is rapid, no study of the kinetics of these interactions has been made. As part of a program of examining the mechanistic aspects of these type of oxygen carriers, we have examined the cobalt(II) chelates of the terdentate ligand, diethylenetriamine (dien), and the bidentate ligands, histamine (hist), ethylenediamine (en), and 2-aminomethylpyridine (amp). The results and behavioral patterns, including those of histidine[8] and ammonia[5] already reported, can then be assessed for this variety of complexes. As an important basis for the study, the formation constants have already been determined for all the complex ions examined here.[2]

Experimental Section

Materials. The ligands, from commercial sources, were used as the recrystallized hydrochloride salts which all had satisfactory chloride content. All chemicals used were reagent grade. Solutions of cobalt(II) nitrate were standardized by titration with EDTA using murexide indicator.

Oxygen Uptake and Rate Measurements. The ionic strength, and medium chosen, for each complex system was dictated by that used in the thermodynamic studies.[2] To a solution containing a known amount of O_2, buffer, and electrolyte, was added different amounts of cobalt(II) complex and the accompanying change of O_2 concentration was measured with a Beckman oxygen sensor. The concentration of binuclear species formed could thus be calculated. The cobalt remaining could then be partitioned between the various species in solution in amounts governed by the pH and the values of the formation constants. We used a computer to aid these calculations.[9] From these data, values for the equilibrium constants (K_{O_2}) for the oxygen uptake by the cobalt(II) complexes could be determined. The kinetics of the formation of the oxygenated species were measured in a glass Lucite stopped-flow apparatus using monitoring wavelengths of 350–420 mμ.[8] Deoxygenated solutions of the cobalt(II) complex ($\sim 10^{-4}$–10^{-2} *M*) were mixed with oxygen-containing water ($\sim 10^{-5}$–10^{-4} *M*). All formation reactions were first order and went to completion. The decomposition of the oxygenated complex ($\sim 10^{-3}$ *M*) by EDTA or buffered solution was followed by stopped-flow, Cary, or O_2-meter techniques. In all cases, dithionite gave deep red solutions rapidly and could not be used for decomposition experiments.[8] Errors in ΔH^* were ~1.0–1.5 kcal/mol.

Results and Discussion

It was clear from early formation and decomposition experiments that, unlike the histidine and ammonia work, more than one adduct species is often present in oxygenated solutions of the cobalt(II) complexes examined.

In addition, with dien and amp complexes the formation of further products, no longer capable of being decomposed to liberate oxygen, occurred within minutes of the initial oxygenation.[7] The dien and hist complexes were examined fully; for various reasons those of en and amp were less thoroughly investigated.

Reaction with Diethylenetriamine Complexes. The

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[1] For recent accounts see L. H. Vogt, Jr., H. M. Faigenbaum, and S. E. Wiberley, *Chem. Rev.*, **63**, 269 (1963); J. A. Connor and E. A. V. Ebsworth, *Advan. Inorg. Chem. Radiochem.*, **6**, 279 (1964); S. Fallab, *Angew. Chem. Int. Ed. Engl.*, **6**, 496 (1967).

[2] L. G. Sillen and A. E. Martell, Ed., "Stability Constants of Metal–Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

[3] Traces of oxygen markedly catalyze the Co(en)$_3^{2+}$–Co(en)$_3^{3+}$ electron transfer: W. B. Lewis, C. D. Coryell, and J. W. Irvine, Jr., *J. Chem. Soc.*, S386 (1949).

[4] W. P. Schaefer, *Inorg. Chem.*, **7**, 725 (1968), and references therein.

[5] J. Simplicio and R. G. Wilkins, submitted for publication.

[6] F. P. Emmenegger, Ph.D. Thesis, Juris-Verlag, Zurich, 1963, has prepared and characterized the dark green solid, [(penten)CoO$_2$ Co(penten)](ClO$_4$)$_4$·4H$_2$O, penten = $(NH_2CH_2CH_2)_2NCH_2CH_2N(CH_2CH_2NH_2)_2$.

[7] O. Bekaroglu and S. Fallab, *Helv. Chim. Acta*, **46**, 2120 (1963); S. Fallab, *Chimia*, **21**, 538 (1967).

[8] J. Simplicio and R. G. Wilkins, *J. Amer. Chem. Soc.*, **89**, 6092 (1967).

[9] We are grateful to P. Chamberlain and G. Templeman for devising the programs used.

kinetics of uptake of O_2 by the bis(diethylenetriamine)cobalt(II) ion could be interpreted in terms of a scheme similar to that with bis(L-histidine)cobaltate(II)[8]

$$\mathrm{Co(dien)_2^{2+} + O_2 \underset{k_1,\,k_{-1}}{\rightleftarrows} Co(dien)_2O_2^{2+}} \qquad (1)$$

$$\mathrm{Co(dien)_2O_2^{2+} + Co(dien)_2^{2+} \underset{k_2,\,k_{-2}}{\rightleftarrows} (dien)_2CoO_2Co(dien)_2^{4+}} \qquad (2)$$

in which in the mono- and binuclear adduct, one of each of the two coordinated diens has a $-CH_2CH_2NH_2$ arm loosened to allow formation of the CoO_2Co unit. The values of the pseudo-first-order formation rate constants k_{obsd} with different concentrations of $Co(dien)_2{}^{2+}$ are shown in Table II. The plot of $[Co(dien)_2{}^{2+}][k_{obsd}]^{-1}$ *vs.* $[Co(dien)_2{}^{2+}]^{-1}$ is shown in Figure 1 for temperatures of 5 and 25°. The linearity required for this mechanism[8] is reasonable. The intercepts give values for $1/k_1$ and the slopes are k_{-1}/k_1k_2. The values at 25° are given in Table I. The rapid formation reactions accompanied by large optical density increases at 360–420 mμ are followed by slower reactions involving a decrease in absorbance. These are due, at least in part, to the formation of an irreversibly oxidized cobalt(III) complex which does not decompose to molecular oxygen. They may also involve the loss of dien in the formation of dibridged species of the type $(dien)_3Co_2O_2{}^{4+}$ invoked by Fallab.[7] We obviously disagree with the finding[7] that $Co(dien)_2{}^{2+}$ cannot react with oxygen to form an adduct. The decomposition of $(dien)_2CoO_2Co(dien)_2{}^{4+}$ could be effected by adding to excess EDTA at pH 10 or to buffered solutions (pH 4–5). The independence of the first-order rate constant on the concentration or nature of the decomposing agents strongly suggests that we are measuring k_{-2} in this fashion.[8] In addition, decomposition of O_2-free solutions of $Co(dien)_2{}^{2+}$ by buffer was immeasurably rapid. There were no signs from the decomposition kinetics of more than one adduct in solution, although the amount of this adduct decreased quickly on standing in solution, so that fresh solutions were always used (within 1 min of oxygenation). By combining the rate constants from the formation and decomposition studies at 25°, we can obtain an over-all formation constant ($k_1k_2/k_{-1}k_{-2} = K_{O_2}$) which is in good agreement with that obtained from equilibrated solutions (Table I). This latter value was determined in oxygenated solutions, by measuring $[O_2]$ concentrations at the point when reversible formation is complete and before any subsequent changes occur. This is easily estimated from the kinetics data and is also indicated by a dramatic slowdown in O_2 uptake.

The effect of pH on the rate constant for oxygen uptake by the bis species is interesting (Table II). By using a [ligand]/[cobalt] ratio of 75, it was possible to examine the bis species (present in ≥98%) even at a pH value as low as 7.5. The second-order formation rate constant (k_1, obtained as $k_{obsd}/[Co(dien)_2{}^{2+}]$ at high cobalt concentration) is independent of $[H^+]$ at pH 9.5–10.5, but increases at lower pH until at pH 7.5 it is some 15 times higher in value. Changing the [ligand]/[cobalt] ratio from 3 to 75 had only a 15% increase in the rate constant at pH 10. These results can be explained in terms of a reactive protonated form of $Co(dien)_2{}^{2+}$.

$$\begin{array}{ccc} \mathrm{Co(dien)_2^{2+} + H^+} & \overset{K}{\rightleftarrows} & \mathrm{Co(dien)_2H^{3+}} \\ k_1\downarrow O_2 & & k_1{}^{H}\downarrow O_2 \\ \text{adduct} & & \text{adduct} \end{array}$$

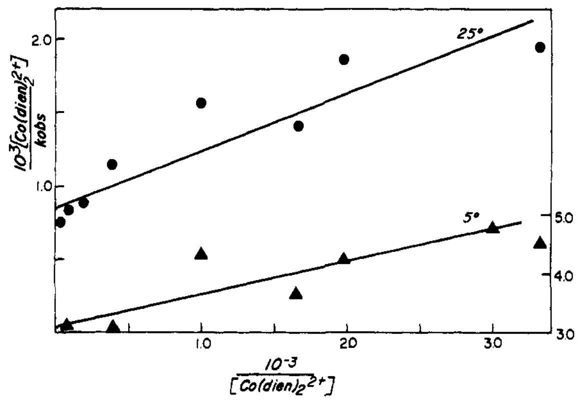

Figure 1. Plots of $10^3[Co(dien)_2{}^{2+}]/k_{obsd}$ *vs.* $10^{-3}/[Co(dien)_2{}^{2+}]$; $I = 0.20\ M$; pH 10; [dien]/[Co] = 3 or 10. The left ordinate refers to 25°, the right ordinate to 5°.

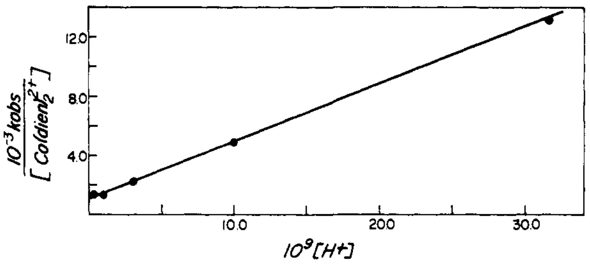

Figure 2. Plot of $10^{-3}k_{obsd}/[Co(dien)_2{}^{2+}]$ *vs.* $10^9[H^+]$; $I = 0.35\ M$ except pH 7.5, $I = 1.0\ M$.

For such a mechanism, relation 3 can be deduced. If $K[H^+] \ll 1$, then approximation 4 follows and this is shown to hold in our case by the linear plot of k_{obsd} against $[H^+]$, Figure 2. We can thus obtain a value for k_1, but for only the product $k_1{}^{H}K$. These are 1.0×10^3 M^{-1} sec^{-1} and 3.9×10^{11} M^{-2} sec^{-1} at 25°.

$$k_{obsd} = (k_1 + k_1{}^{H}K[H^+])(1 + K[H^+])^{-1} \qquad (3)$$

$$k_{obsd} = k_1 + k_1{}^{H}K[H^+] \qquad (4)$$

We can make a reasonable estimate of $k_1{}^{H}$ if we consider the structure of the protonated form to contain *one* of the two diens only coordinated through two nitrogens and having a free $-NH_3{}^+$ group. Such a species would be expected (from the discussion below) to react more rapidly than the fully nitrogen coordinated system, designated $CoN_6{}^{2+}$, and would be approximately simulated by $Co(tetraen)(H_2O)^{2+}$ which has a k_1 value 10^5 M^{-1} sec^{-1} at 25°.[10] We can use this as a reasonable estimate of $k_1{}^{H}$. The value then for K is 4×10^6 M^{-1} which is satisfyingly close to that of $Co(pentenH)^{3+}$ for which the corresponding protonation constant is 8×10^6 M^{-1}. In the latter complex also a coordinated $-NH_2$ group in a CoN_6 system is detached and protonated.[11] The protonated ion $Co(dien)(dienH)^{3+}$ will be in very small concentration in the high pH range where the bis is dominant and also in the low pH range where only the *mono* will be important,

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(10) J. Simplicio and R. G. Wilkins, unpublished; tetraen = $NH_2CH_2CH_2(NH\ CH_2CH_2)_3NH_2$. This complex has a marked affinity for O_2 with $K_{O_2} > 10^{10}$ for the 2:1 Co:O_2 compound. We are grateful to R. Yelin for a sample of the purified ligand.

(11) G. Schwarzenbach and P. Moser, *Helv. Chim. Acta*, **36**, 581 (1953).

Table I. Kinetic Data for Cobalt(II) Complex–O_2 Interaction at 25°

Reactant	k_1, M^{-1} sec^{-1}	ΔH_1*, kcal/mol	ΔS_1,* eu	k_{-2}, sec^{-1}	K_{kin},[a] M^{-2}	K_{thermo},[b] M^{-2}
CoN_6						
$Co(dien)_2^{2+}$	1.2×10^3	10	−12	1.6×10^{-2}	1.6×10^8	3.0×10^8
$Co(hist)_3^{2+}$	6.8×10^4	8	−8	...	...	...
$Co(amp)_3^{2+}$	47	~17	~+5	...	...	...
$Co(en)_3^{2+}$	$\leq 10^4$					
$Co(NH_3)_6^{2+}$[c]	$\leq 10^3$					
CoN_5O						
$Co(NH_3)_5(H_2O)^{2+}$[c]	2.5×10^4	4	−25	56		$\sim 6 \times 10^6$
$Co(tetraen)(H_2O)^{2+}$	$\sim 10^5$			(ΔH_{-2}* = 18 ΔS_{-2}* = +9)		
CoN_4O_2						
$Co(hist)_2(H_2O)_2^{2+}$	1.8×10^4	5	−23	1.4×10^{-2} (ΔH_{-2}* = 13 ΔS_{-2}* = 37)	2.9×10^8	2.5×10^8
Co(L-histidine)$_2$[d]	3.5×10^3	5	−25	0.47	5.5×10^8[e]	3.0×10^8[e] 7.2×10^6
$Co(en)_2(H_2O)_2^{2+}$	4.7×10^5	15	+19	1.5×10^{-3}	...	...
$Co(amp)_2(H_2O)_2^{2+}$	7.2×10^2	6	−25	...	...	...

[a] Value of $k_1k_2/k_{-1}k_{-2}$. [b] From O_2 uptake measurements. [c] Reference 5. [d] Reference 8. [e] At 4°.

Table II. Kinetic Data for Formation of Oxygen Adducts

I = 0.20 M, pH 10.0			Temp = 25.0°, $[Co(dien)_2^{2+}] = 5.0 \times 10^{-3}$ M		
Temp, °C	$[Co(dien)_2^{2+}]$,[a] mM	k_{obsd}, sec^{-1}	pH	I, M	k_{obsd}, sec^{-1}
25.0	20.0[b]	26	10.5	0.35	4.7
25.0	12.6	17	10.0	0.36[c]	5.4
25.0	10.0	12	10.0	0.35	4.7
25.0	8.0	9.9	10.0	0.24	5.7
25.0	5.0	5.7	9.5	0.35	4.9
25.0	2.5	2.2	9.5	0.24	5.7
25.0	1.0	0.64	9.0	0.35	6.6
25.0	0.60	0.43	9.0	0.24	7.2
25.0	0.51	0.27	8.5	0.35	11
25.0	0.30	0.15	8.5	0.24	11
15.0	20.0[b]	14	8.0	0.35	24
15.0	12.6	9.0	7.5	1.0[c]	67
5.0	20.0[b]	7.0	8.0	0.24[d]	3.7
5.0	12.6	4.1	7.0	0.24[e]	2.8
5.0	2.5	0.83			
5.0	1.0	0.23			
5.0	0.60	0.16			
5.0	0.51	0.12			
5.0	0.30	0.066			

Temp, °C	pH	$[Co(hist)_2(H_2O)_2^{2+}]$, mM	[hist], mM	k_{obsd}, sec^{-1}	$10^{-4}k_{obsd}$/[bis], M^{-1} sec^{-1}
25.0	8.2	1.6	0.10	28	1.7
25.0	9.1	0.50	0.28	11	2.1
25.0	7.9	1.3	0.29	35	2.6
25.0	10.0	0.60	1.1	19	3.2
25.0	9.0	2.3	1.3	66	2.9
25.0	10.0	0.81	1.5	23	2.9
25.0	9.5	2.4	2.1	81	3.4
25.0	10.0	1.9	4.6	115	5.4
25.0	10.0	0.55	8.8	53	9.6
15.0	8.8	1.4	0.18	15	1.1
15.0	8.8	1.6	0.45	27	1.6
15.0	10.0	0.83	0.93	15	1.7
15.0	9.7	2.5	1.1	53	2.2
15.0	9.4	0.80	1.4	15	1.9
15.0	10.0	0.36	2.8	8.7	2.4
15.0	10.0	0.57	5.5	26	4.5
15.0	10.3	0.26	6.6	12	4.4
5.0	8.2	1.9	0.03	20	1.0
5.0	9.1	0.84[f]	0.51	11	1.3
5.0	10.0	0.84[f]	0.51	10	1.2
5.0	10.0	1.9	1.2	27	1.6
5.0	9.7	2.0	2.2	46	2.3
5.0	10.0	3.3	2.3	58	2.1
5.0	9.4	1.9	2.6	50	2.6
5.0	10.0	4.6	3.6	100	2.7
5.0	10.3	0.08	58	19	24[g]

Table II *(Continued)*

Temp, °C	pH	$[Co]_{total}$, m*M*	$[hist]_{total}$, m*M*	$[Co(hist)_2H_2O_2^{2+}]$, m*M*	[hist], m*M*	k_{obsd}, sec^{-1}
25.0[h]	8.2	2.0	6.0	0.54	0.012	1.2
25.0	8.2	2.0	6.0	0.54	0.012	1.0
25.0	9.1	1.0	2.0	0.34	0.019	0.37
25.0	8.8	2.0	2.0	0.15	0.015	0.10
5.0	7.9	5.0	50.0	3.1	0.069	39
5.0	8.2	5.0	15.0	1.9	0.027	20
5.0	8.2	2.0	8.0	0.58	0.018	1.7
5.0	7.9	1.3	13.0	0.39	0.019	0.53
5.0	8.5	1.0	4.0	0.29	0.018	0.43
5.0	7.9	1.0	10.0	0.24	0.015	0.30
5.0	7.9	1.0	6.0	0.14	0.010	0.12
5.0	7.9	1.0	4.0	0.086	0.0053	0.046

		$I = 1.0\ M$ KCl, Borate Buffer			
Temp, °C	pH	$[Co(en)_2(H_2O)_2^{2+}]$, m*M*	$[Co(en)_3^{2+}]$, m*M*	k_{obsd}, sec^{-1}	$10^{-5}k_{obsd}/[bis]$, $M^{-1}\ sec^{-1}$
25.0	9.4	0.13	10.0	58	4.5
25.0	9.6	0.077	20.0	38	5.0
25.0	10.0	0.046	10.0	17	3.7
25.0	10.6	0.025	9.7	11.5	4.6
25.0	10.8	0.011	6.0	5.1	4.8
25.0	10.9	0.022	11.0	11.5	5.2
15.0	10.0	0.068	9.0	12.6	1.85
5.0	10.3	0.051	5.0	3.3	0.65

Temp, °C	pH	$[Co(amp)_2(H_2O)_2^{2+}]$, m*M*	[amp], m*M*	k_{obsd}, sec^{-1}	$10^{-3}k_{obsd}/[bis]$, $M^{-1}\ sec^{-1}$
25.0	7.0	3.4	0.30	2.5	0.70
25.0	7.3	3.4	2.3	3.7	1.1
25.0	7.6	3.7	4.1	5.0	1.3
15.0	7.0	3.7	0.14	1.9	0.50
15.0	7.6	4.2	1.2	2.6	0.61
15.0	7.3	4.8	2.1	3.3	0.69
5.0	7.0	3.8	0.10	1.2	0.32
5.0	7.6	4.5	0.74	1.3	0.29
5.0	7.3	5.3	1.3	1.7	0.32

[a] $[dien]_{total} = 3[Co]_{total}$. Calculations indicated that this species represented 97–99% of the total cobalt. We assumed 100%. Similar results were obtained when a tenfold excess of dien was used. [b] Ionic strength = 0.27 *M*. [c] $[dien]_{total}/[Co]_{total} = 75$; in others ratio = 10 ($I = 0.35\ M$) or 3 ($I = 0.24\ M$). [d] Contains $8.9 \times 10^{-3}\ M$ $Co(dien)(H_2O)_3^{2+}$ and $0.4 \times 10^{-3}\ M$ $Co(dien)_2^{2+}$. [e] Contains $8.3 \times 10^{-3}\ M$ $Co(dien)(H_2O)_3^{2+}$ and $0.2 \times 10^{-3}\ M$ $Co(dien)_2^{2+}$. [f] These runs show independence of pH *per se*. [g] Point A in Figure 3. This run also gives k_{tris} directly as $k_{obsd}/[tris] = 2.0 \times 10^4\ M^{-1}\ sec^{-1}$. [h] Negligible amounts of tris present in this set of runs.

unless extremely large amounts of ligand are present. This would account for it not being detected in potentiometric measurements.[2] It is observed here only because of its enhanced kinetic reactivity toward O_2, compared with the nonprotonated form. The rate constant for the $Co(histidine)_2$–O_2 reaction is independent of pH from 8 to 11,[8] and this reflects the weak basicity of the carboxylate group which is believed detached in forming the binuclear complex. In two experiments, $Co(dien)(H_2O)_3^{2+}$ was the predominant species (Table II). The uptake of O_2 was decidedly slower and the rate could in large part be accounted for by the small amount of bis present. The rate constant for oxygenation of the *mono* is at least ten times smaller than that for the bis species.

Reaction with Histamine Complexes. A simple experiment showed that hydroxo species are not important in the formation kinetics, unlike that observed with the cobalt(II)-diglycine–O_2 system.[12] Two solutions identical in all respects except for having different total ligand concentrations and different pH values (9 and 10) had the same reaction half-lives (Table II). The rates of formation of the oxygen adduct were studied over a wide range of [histamine]/[cobalt] ratio and pH (Table II). At sufficiently high cobalt concentrations the reaction was second order and with a contribution from the bis and tris complexes, $Co(hist)_2(H_2O)_2^{2+}$ and $Co(hist)_3^{2+}$ of k_{bis} and k_{tris} to the rate of oxygen uptake, (5) and (6) hold

$$k_{obsd} = k_{bis}[bis] + k_{tris}[tris] \tag{5}$$

$$k_{obsd}/[bis] = k_{bis} + k_{tris}K_3[hist] \tag{6}$$

where K_3 is the formation constant of the tris species and [hist] is the free unprotonated ligand concentration. The appropriate linear plots are shown in Figure 3 with the intercepts of value k_{bis} and the slopes $k_{tris}K_3$. The value of k_{tris} at 5° was also determined directly by measuring k_{obsd} at very high [hist] when only the tris contributes (Table II). In addition, the value of k_{bis} was obtained from measurements on solutions in which the tris species was missing. The [mono] present was shown not to contribute to the rate. It was in such solutions that the effect of the concentration of $[Co(hist)_2(H_2O)_2^{2+}]$ on the

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(12) C. Tanford, D. C. Kirk, Jr., and M. K. Chantooni, Jr., *J. Amer. Chem. Soc.*, **76**, 5325 (1954).

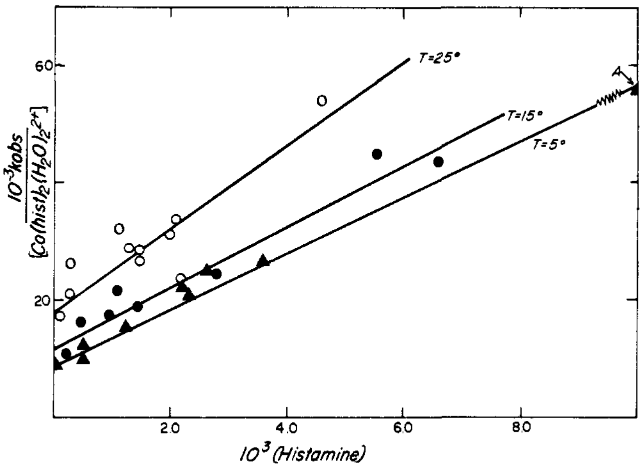


Figure 3. Plots of $10^{-3}k_{\text{obsd}}/[\text{Co(hist)}_2(\text{H}_2\text{O})_2{}^{2+}]$ *vs.* 10^3[hist]; $I = 1.0\ M$; point A represents 240 (*y*) *vs.* 58 (*x*).

rate was examined (Table II) so as to give values for reaction of this species of k_1 and the composite rate constants k_{-1}/k_1k_2 (see reaction schemes 7 and 8), analogous to the dien case (Figure 4). The value of k_{-2} was determined from acid decomposition experiments (rate constant independent of pH 3.6–4.7) with freshly oxygenated solutions originally containing little tris

$$\text{Co(hist)}_2(\text{H}_2\text{O})_2{}^{2+} + \text{O}_2 \underset{k_1,\,k_{-1}}{\rightleftarrows} \text{Co(hist)}_2(\text{H}_2\text{O})\text{O}_2{}^{2+} + \text{H}_2\text{O} \qquad (7)$$

$$\text{Co(hist)}_2(\text{H}_2\text{O})\text{O}_2{}^{2+} + {}'\text{Co(hist)}_2(\text{H}_2\text{O})_2{}^{2+} \underset{k_2,\,k_{-2}}{\rightleftarrows} (\text{hist})_2(\text{H}_2\text{O})\text{CoO}_2\text{Co(hist)}_2(\text{H}_2\text{O})^{4+} \qquad (8)$$

species. The rates of spectral change and (complete) oxygen release at pH 4 were similar. The values for K_{O_2} obtained from kinetic and O_2 measurements are in good agreement and close to that of Hearon, *et al.*[13] (Table I). With solutions in which tris and bis species were in comparable concentrations, the fast oxygenation was followed by slower changes. Decomposition of the oxygen adducts generated from such solutions showed two rates, from spectral and oxygen measurements. The faster was identical with that of the k_{-2} process of (8). The slower had a first-order rate constant = 8.9×10^{-4} sec^{-1} at 25°, $I = 1.0\ M$ KNO_3. These observations will be commented on below.

Reaction with Other Complexes. The uptake of O_2 by some other complexes was also studied (Table II). The Co(II)–en system showed such a marked affinity for oxygen that $5 \times 10^{-4}\ M$ $[\text{Co(en)}_3{}^{2+}]$ reduced a $2 \times 10^{-4}\ M$ oxygen solution to less than $10^{-5}\ M$, so that accurate oxygen-uptake constants would be difficult to measure. All the oxygen was recoverable, on acidification, even 30 min after oxygenation. The rate of oxygen uptake by the Co(II)–en system could be explained solely in terms of $[\text{Co(en)}_2(\text{H}_2\text{O})_2{}^{2+}]$ even although the concentration of the tris species far exceeded that of the bis (Table II). The rates were too rapid to measure if the concentration of bis was increased, by lowering the $[\text{en}]_\text{T}/[\text{Co}]_\text{T}$ ratio. As with the histamine system, the formation process was followed by slower changes and adjustment of the

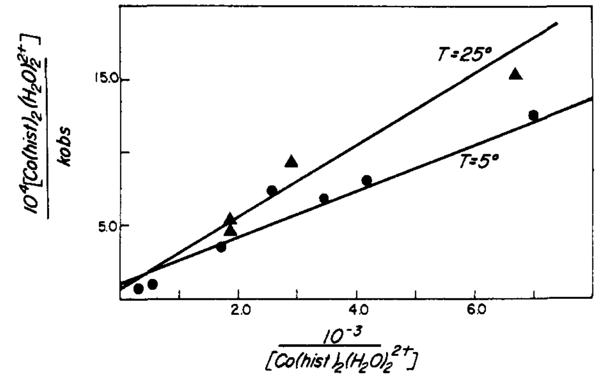
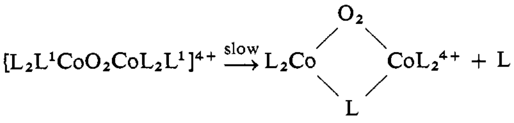


Figure 4. Plots of $10^4[\text{Co(hist)}_2(\text{H}_2\text{O})_2]/k_{\text{obsd}}$ *vs.* $10^{-3}[\text{Co(hist)}_2(\text{H}_2\text{O})_2]$; $I = 1.0\ M$.

oxygenated solution from pH ~8 to pH ~4.0–4.7 revealed two independently decomposing species $k_{\text{obsd}} = 1.5 \times 10^{-3}$ sec^{-1} and 0.3×10^{-3} sec^{-1} at 25°. The study of the formation of the cobalt(II)–2-aminomethylpyridine–O_2 adduct (Table II) showed that the bis and tris species both contribute to the rate. From plots of the form of (5) and (6), the values shown in Table I are obtained. Equilibria and decomposition measurements would have been difficult, however, in view of the rapid formation of another species from the initially formed reversible oxygen adduct.

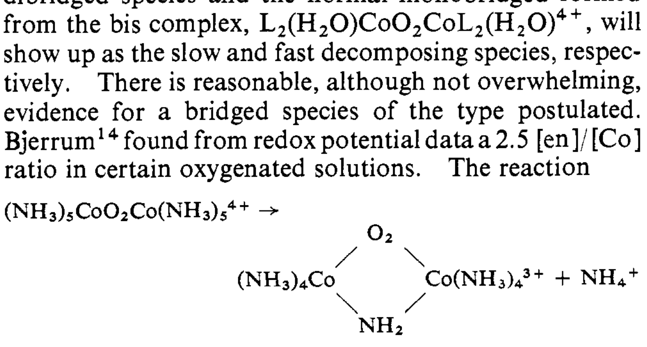
Processes Subsequent to Oxygenation. The slow changes which followed the rapid oxygenation process with the complexes of the bidentate ligands probably did not involve the breakdown of the peroxo bridge since the oxygen was completely recoverable even at the end of this slow step. The slow rate appeared qualitatively to be insensitive to metal, ligand, and hydroxide concentrations although no accurate studies were made. The slow step was observed only when the tris species was present in the original solutions and the magnitude of the slow change paralleled its amount. The slow change could be associated with the formation of a dibridged species, *e.g.*

$$2\text{CoL}_3{}^{2+} + \text{O}_2 \overset{\text{rapid}}{\rightleftarrows} [\text{L}_2\text{L}^1\text{CoO}_2\text{CoL}_2\text{L}^1]^{4+}$$



$$[\text{L}_2\text{L}^1\text{CoO}_2\text{CoL}_2\text{L}^1]^{4+} \xrightarrow{\text{slow}} \text{L}_2\text{Co}\underset{\text{L}}{\overset{\text{O}_2}{\diamond}}\text{CoL}_2{}^{4+} + \text{L}$$

in which L^1 represents one ended association of L. This dibridged species and the normal monobridged formed from the bis complex, $\text{L}_2(\text{H}_2\text{O})\text{CoO}_2\text{CoL}_2(\text{H}_2\text{O})^{4+}$, will show up as the slow and fast decomposing species, respectively. There is reasonable, although not overwhelming, evidence for a bridged species of the type postulated. Bjerrum[14] found from redox potential data a 2.5 [en]/[Co] ratio in certain oxygenated solutions. The reaction



$$(\text{NH}_3)_5\text{CoO}_2\text{Co(NH}_3)_5{}^{4+} \rightarrow (\text{NH}_3)_4\text{Co}\underset{\text{NH}_2}{\overset{\text{O}_2}{\diamond}}\text{Co(NH}_3)_4{}^{3+} + \text{NH}_4{}^+$$

with some analogy to ours is known to occur in aqueous

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[13] J. Z. Hearon, D. Burk, and A. L. Schade, *J. Natl. Cancer Inst.*, **9**, 337 (1949), report a value of 4.7×10^7 at 23°.

[14] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, p 215.

ammonia, although very slowly at 35°. Finally, these slow changes and the production of more than one oxygenated species do not occur with Co(tetraen)$(H_2O)^{2+}$ or Co(histidine)$_2$, where ligand bridging cannot be conceived.

General Conclusions

The kinetic data from this and previous work are summarized in Table I. Different ionic strengths had to be used for each study, but it was shown that this would only slightly modify the rate constants and that, therefore, a discussion of trends is quite valid. With the single exception of histamine, the fully nitrogen-coordinated CoN_6 system is less reactive than the corresponding CoN_5O or CoN_4O_2 systems and this is shown by NH_3, en, amp, and dien complexes. Indeed, if the concentration of CoN_6 relative to CoN_5O or CoN_4O_2 cannot be obtained sufficiently high, its contribution to the rate of O_2 uptake is not detectable. This occurs with en and also NH_3 and amp at lower temperatures. Apparently a coordinated H_2O group is more easily replaced than a coordinated $-NH_2$ group by O_2 in the first reaction of the two-step mechanism. The rate constants k_1 for reaction of all the lower species, except $Co(en)_2(H_2O)_2^{2+}$, are within a factor of about 20 of each other, with $\Delta H^* = 4\text{–}6$ kcal/mol and $\Delta S^* \sim 25$ eu. These similar values reflect the common process of O_2 replacement in the Co–O position.[8,15] The Co–O breakage in the peroxo species (represented by k_{-2}) also appear to be only slightly dependent on the chelating ligands coordinated to the cobalt(II).

The factors governing the ability of a cobalt(II) complex to pick up O_2 are quite complicated and apparently not attributable to any one specific feature of the complex. Complexes with a highly negative E^0 value tend not to pick up O_2, but redox potentials alone cannot be used diagnostically, since, for example, $Co(NH_3)_5(H_2O)^{2+}$ ($E^0 = -0.37$ V)[15] absorbs O_2 rapidly, whereas $Co(phen)_3^{2+}$ with virtually the same potential ($E^0 = -0.40$)[16] does not interact with O_2 over long periods. Fallab[1] has made the supportable contention that the complex must contain three donor nitrogen atoms as a *minimum* requirement for O_2 uptake. The unreactivity of $Co(NH_3)_4(H_2O)_2^{2+}$ shows that a $Co(N_4O_2)$ system will not necessarily be O_2-active, however.[5] The type of nitrogen and oxygen donor in the complex must be also considered. Qualitatively, it appears that those complexes unreactive to O_2 have ligand systems such as carboxyl and heterocyclic groupings. These can effectively withdraw electron density from the metal center thus hindering the electron transfer from the cobalt to the peroxo oxygen, which is apparently required in the formation of the binuclear species. This is also consistent with the greater tendency of nitrogen to donate electrons to cobalt(II) compared with oxygen. In addition, in certain iridium complexes it has been shown that as the electronegativity of the substituents on Ir decreases, the strength of bonding of O_2 to the iridium increases (evidenced by the degree of reversibility and O–O bond length).[17]

This preference for O_2 uptake by complexes containing nitrogen rather than oxygen donors has important implications with the peptide and amino acid amide derivatives of cobalt(II). It appears that cobalt(II) is not easily able to promote ionization of the peptide hydrogen in basic medium and in this respect differs from copper(II) and nickel(II).[18] However, since such an ionization would almost certainly result in a switch from Co-peptide O to cobalt-peptide N bonding (if it resembled Cu(II) and Ni(II) behavior), the ionized species would be expected to be more sensitive to O_2 in solution. Thus, interaction with oxygen might serve as an indicator of cobalt(II)-coordinated peptide ionization. This idea is supported by the small amount of data available. Thus, glycylglycine but not glycylproline or glycylsarcosine complexes of cobalt(II) pick up oxygen in basic medium.[19] Our observation that asparagine but not aspartate complexes pick up O_2 around a pH $\sim$12 can also only be easily explained by invoking deprotonated amide coordination in the former case. We are exploring this idea further.

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(15) The second-order rate constants for the reactions $Co(NH_3)_5H_2O^{2+} + NH_3 \rightarrow Co(NH_3)_6^{2+} + H_2O$ and $Co(en)_2(H_2O)_2^{2+} + en \rightarrow Co(en)_3^{2+} + 2H_2O$ are $\sim 10^6$ and 3×10^5 M^{-1} sec^{-1}, respectively, at 25° (H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **4**, 1061 (1965); R. G. Pearson and R. D. Lanier, *J. Amer. Chem. Soc.*, **86**, 765 (1964)). These involve substitution by neutral molecules NH_3 and en, rather than O_2.

(16) R. G. Yalman, *Inorg. Chem.*, 1, 16 (1962); E. Paglia and C. Sironi, *Gazz. Chim. Ital.*, **87**, 1125 (1957); R. Farina and R. G. Wilkins, *Inorg. Chem.*, 7, 514 (1968).

(17) J. A. McGinnety and J. A. Ibers, *Chem. Commun.*, **235** (1968).

(18) See, for example, R. B. Martin, M. Chamberlin, and J. T. Edsall, *J. Amer. Chem. Soc.*, **82**, 495 (1960).

(19) E. M. Crook and B. R. Rabin, *Biochem. J.*, **68**, 177 (1958); P. Tong and N. C. Li, *J. Amer. Chem. Soc.*, **86**, 1293 (1964).