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Some New Oxygenated Cobalt Complexes

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Cobalt(II) complexes with ornithine, 2,4-diaminobutyric acid and 2,3-diaminopropionic acid were studied as new oxygen complexes. The former complex was reversibly, while the latter two complexes were irreversibly oxygenated at room temperature. These oxygenated complexes were diamagnetic and showed electronic absorption spectra similar to that of oxygenated cobalt histidine complex, and they were assumed to be O_2-bridged binuclear complexes, $L_2Co-O_2-CoL_2$ (L: ligand). Cobalt and O_2 of the binuclear complexes existed in the state of Co(III) and O_2^{2-}, respectively. Thermodynamic measurements showed that oxygenation was an exothermal process, and deoxygenation an endothermal one. The reversibility correlated with the reduction potential of the central cobalt(III) ion and the enthalpy change of the oxygenation. Easier deoxygenation corresponded to more positive reduction potential and to smaller enthalpy change.

Since it was found that bis(salicylaldehyde)ethylenediamine cobalt (II) reversibly combined with molecular oxygen,[1] oxygen complexes of metal chelates were noted as an interesting model for the oxygen carrying compounds such as hemoglobin and hemocyanin.[2-6] Burk *et al.*[6] reported that among histidine complexes of transition metals, only the cobalt complex possessed the ability to combine reversibly with molecular oxygen. Hearon[7] explained the results as follows. Cobalt forms octahedral complexes, while the available structure of nickel and copper complexes are tetrahedral or square planar. An unpaired electron of cobalt (II) ion accounts for the stabilization of the oxygenated complex. By the combination of cobalt histidine complex with molecular oxygen, the pairing occurs between unpaired electrons from cobalt (II) ion and molecular oxygen. The binuclear structure of peroxide form was proposed from the diamagnetic nature of the oxygenated complex,[8,9] and the reactions are expected to be

$$Co^{2+} + 2HHid \rightleftharpoons Co(Hid)_2 + 2H^+ \quad (1)$$

$$2Co(Hid)_2 + O_2 \rightleftharpoons [Co(Hid)_2]_2O_2 \quad (2)$$

where HHid is histidine.

In the present research, new oxygenated cobalt complexes with 2,3-diaminopropionic acid, 2,4-diaminobutyric acid and ornithine were prepared. They were identified by elemental analyses of the isolated complex salts, the uptake oxygen gas and electronic absorption spectra of the solutions. The valency states of the central cobalt ion and coordinated molecular oxygen were estimated and thermodynamic properties were obtained. From the results, the effect of ligand-field, the redox potential of the cobalt ion and the enthalpy change on the oxygenation-deoxygenation reversibility were discussed.

Experimental

Materials. 2,3-Diaminopropionic acid and 2,4-diaminobutyric acid were obtained from Sigma Chemical Company, and histidine methyl ester and *N*-acetylhistidine were obtained from Cyclo Chemical Coorporation. The other chemicals used were of reagent grade.

Preparation of Cobalt Complex. Bis(histidinate) Cobalt(II): This chelate was synthesized according to the method of Sano and Tanabe.[10]

Found: C, 37.34; H, 4.75; N, 21.90%. Calcd for $Co(C_6H_8N_3O_2)_2 \cdot H_2O$: C, 37.41; H, 4.71; N, 21.82%.

Bis(2,3-diaminopropionate) Cobalt(II) and Bis(2,4-diaminobutyrato) Cobalt(II): These chelates were synthesized in the same way as in cobalt histidine chelate.

Found: C, 23.15; H, 5.76; N, 18.38%. Calcd for $Co(C_3H_7N_2O_2)_2 \cdot 2H_2O$: C, 23.92; H, 5.98; N, 18.60%. Pale pink powder.

Found: C, 29.46; H, 6.57; N, 16.85%. Calcd for $Co(C_4H_9N_2O_2)_2 \cdot 2H_2O$: C, 29.18; H, 6.67; N, 17.02%. Pale pink powder.

μ-Oxy-bis(Cobalt dihistidinate), $[Co(Hid)_2]_2O_2 \cdot 7H_2O$: This

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[1] P. Pfeiffer, E. Breith, E. Lubbe, and T. Tsumaki, *Ann. Chem. Liebigs*, **503**, 84 (1933).

[2] T. Tsumaki, This Bulletin, **13**, 252 (1938).

[3] M. Calvin and C. H. Barkelew, *J. Amer. Chem. Soc.*, **68**, 2267 (1946).

[4] R. E. Stewart, P. A. Estep, and J. J. S. Sebarstian, U. S. Bur. Mines Inform. Circ., No. 7906 (1959).

[5] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J. (1952), pp. 336—357.

[6] D. Burk, J. Z. Hearon, L. Caroline, and A. L. Schade, *J. Biol. Chem.*, **165**, 723 (1946).

[7] J. Z. Hearon, *J. Natl. Cancer Inst.*, **9**, 1 (1948).

[8] J. Z. Hearon and D, Burk, *ibid.*, **9**, 337 (1949).

[9] J. Z. Hearon, *Federation Proceedings*, **6**, 259 (1947).

[10] Y. Sano and H. Tanabe, *J. Inorg. Nucl. Chem.*, **25**, 11 (1963)

chelate was synthesized according to the above method.[10]

Found: C, 31.96; H, 5.16; N, 18.51%. Calcd for $[Co(C_6H_8N_3O_2)_2]_2O_2 \cdot 7H_2O$: C, 31.65; H, 5.27; N, 18.46%. Brown powder.

μ-Oxy-bis[Cobalt di(2,3-diaminopropionate)], $[Co(DAP)_2]_2O_2 \cdot 5H_2O$: A solution containing 2,3-diaminopropionic acid monohydrochloride (10 mmol) and cobalt(II) chloride 6-hydrate (5 mmol) in 10 m*l* of water was adjusted to pH 8.5 with a 1 N sodium hydroxide. After oxygen gas was passed for about 10 min at 10°C and 40 m*l* of acetone added, the solution was cooled. The resulting brown precipitate was collected on a funnel, washed successively with 60 per cent acetone, acetone and ether, and dried over calcium chloride under reduced pressure to give brown powder.

Found: C, 21.96; H, 5.71; N, 16.95%. Calcd for $[Co(C_3H_7N_2O_2)_2]_2O_2 \cdot 5H_2O$: C, 22.09; H, 5.83; N, 17.18%.

μ-Oxy-bis[Cobalt di(2,4-diaminobutyrate)], $[Co(DAB)_2]_2O_2 \cdot 6H_2O$: The same procedure as in the synthesis of $[Co(DAB)_2]_2O_2 \cdot 5H_2O$ was employed, using cobalt(II) chloride 6-hydrate and 2,4-diaminobutyric acid 2-hydrochloride. Brown powder.

Found: C, 26.54; H, 6.52; N, 15.40%. Calcd for $[Co(C_4H_9N_2O_2)_2]_2O_2 \cdot 5H_2O$: C, 26.45; H, 6.61; N, 15.43%.

The numbers of water were confirmed also by the weight loss at 40° and 100°C from the thermogravimetric curves of the complexes.

Apparatus and Procedures. Polarograms were obtained with a Yanagimoto recording polarograph, P. B.-104. Sample solutions contained 10^{-3} M cobalt(II) ion, 2×10^{-3} M chelating agent, 0.1 M potassium chloride, 0.05% gelatin, and 10^{-2} M potassium dihydrogen phosphate-disodium hydrogen phosphate buffer or 10^{-2} M ammonium chloride-ammonia buffer.

The stability constant of oxygenated complexes was determined with a Warburg manometer.[8] A solution of chelating ligand and a buffer solution were pipetted into the main room of reaction vessel and cobalt(II) chloride solution, into the sub-chamber of the vessel. The reaction volume was 2.00 m*l*, the final concentration of cobalt(II) ion was 10^{-2} M and the amount of chelating ligand was so arranged that the cobalt ion was completely converted to the chelate when two solutions were mixed. After the solutions were kept at the desired temperature (5—70°C) for a few minute in a water bath, cobalt solution was transferred into the main room and the mixture was shaken until equilibrium was attained. Oxygen consumption was then measured with a manometer, and the stability constant was calculated by the equation

$$K = \frac{[(CoL_2)_2O_2]}{[CoL_2]^2[O_2]}$$

where $[CoL_2]$ is the conentration of cobalt(II) chelate and $[O_2]$ is the solubility of oxygen gas under the conditions applied.

Results and Discussion

New Oxygenated Cobalt Complexes. The reaction

TABLE 1. REACTION BEHAVIORS OF COBALT(II) CHELATES WITH OXYGEN GAS

Ligand	pH	Visible spectrum[a)] in the presence of O_2	Reaction with O_2	O_2-Uptake[b)] (μ*l*)	O_2 Released[b)c)] (%)	
Histidine	7.5	A	oxygenation	107	100	after 1 hr
Histidine	8.5	A	oxygenation	123	100	1 hr
Histidine	10.0	A	oxygenation	154	92	20 min
Histidine methyl ester	8.0	A	oxygenation	102	100	30 min
Histamine	9.0	C′	oxidation			
1-Methylhistidine	9.0	B	no-reaction			
N-Acetylhistidine	9.0	B	no-reaction			
Acetylacetone	9.0	B	no-reaction			
Glycine	9.0	B	no-reaction			
Alanine	9.0	B	no-reaction			
Proline	9.0	B	no-reaction			
Glutamic acid	9.0	B	no-reaction			
o-Phenanthroline	8.0	C	oxidation			
Ethylenediamine	8.0	C	oxidation			
Diethylenetriamine	8.0	C	oxidation			
Diaminopropionic acid	7.5	A	oxygenation	201	96	20 min
Diaminopropionic acid	8.5	A	oxygenation	212	85	20 min
Diaminobutyric acid	7.5	A	oxygenation	140	100	20 min
Diaminobutyric acid	8.5	A	oxygenation	182	91	20 min
Ornithine	9.0	A	oxygenation	34	100	20 min
Ornithine	10.0	A	oxygenation	93	95	20 min
Ornithine	10.0	C′				
Histidine	9.0	C′	oxidation after standing for one night at 60°C			
Diaminopropionic acid	9.0	C′				
Diaminopropionic acid	9.0	C′				

a) A: Spectra of these cobalt complexes are the same as that of oxygenated cobalt histidine complex reported by Hearon.[7]

B: Same as cobalt(II) chelate

C: Same as cobalt(III) chelate

C′: Same as cobalt(III) complex named as irreversible complex by Hearon[7]

b) Conditions of oxygen-uptake measurements;

Concentration of cobalt chelate: 10^{-2} M

Volume of the solution : 2.0 m*l*

Temperature : 30°C

c) Recovery of oxygen gas was attained by acidifying the solution after standing for the assigned time.

behaviors of various cobalt(II) chelates with oxygen gas are summarized in Table 1, which includes the three new oxygenated complexes found. Oxygen release was made by acidifying the solution, which had been contacted with air or oxygen gas for an appropriate time. As the contact time was prolonged, oxygen recovery became lower, accompanying color change. This phenomenon indicates that the oxygenated complexes are slowly oxidized to the cobalt(III) chelate. It can be deduced that if a reasonable amount of oxygen is released by acidification, the main reaction of cobalt(II) chelate by contact with oxygen gas is oxygenation, but not oxidation. Table 1 is classified according to this concept. Oxygenation, oxidation, and no-reaction could be also spectrophotometrically distinguished, because the absorption spectra of cobalt(II) chelates, cobalt(III) chelates and the oxygenated complexes differ from each other.

Cobalt(II) chelates with 2,3-diaminopropionic acid (HDAP), $\mathrm{NH_2{\cdot}CH_2{\cdot}CH}{<}\begin{smallmatrix}\mathrm{COOH}\\ \mathrm{NH_2}\end{smallmatrix}$, 2,4-diaminobutyric acid (HDAB), $\mathrm{NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH}{<}\begin{smallmatrix}\mathrm{COOH}\\ \mathrm{NH_2}\end{smallmatrix}$, and ornithine (HOrn), $\mathrm{NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH}{<}\begin{smallmatrix}\mathrm{COOH}\\ \mathrm{NH_2}\end{smallmatrix}$, are readily oxygenated. The oxygen uptake behaviors are shown in Fig. 1.

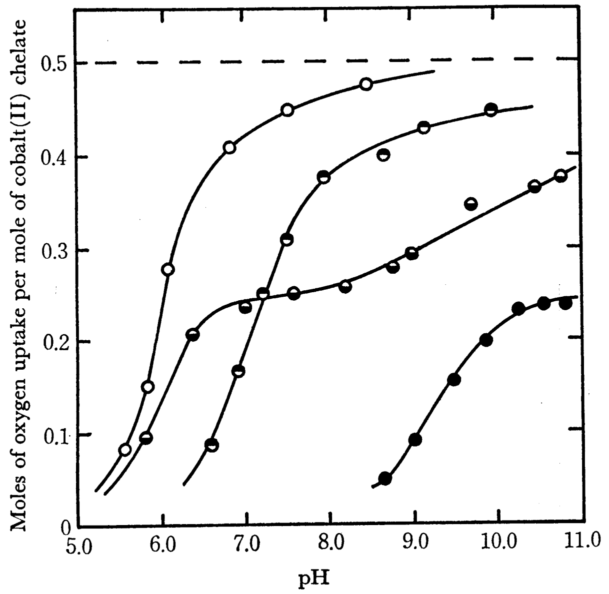

Fig. 1. Oxygen uptake of Cobalt(II) chelates.
○: Co(DAP)$_2$; ◒: Co(Hid)$_2$; ◓: Co(DAB)$_2$;
●: Co(Orn)$_2$
concentration of the chelates: 10^{-2}M
volume: 2 m*l*
temperature: 30°C

The reversibility of oxygenation-deoxygenation was studied by measuring the color change of solution, which occurred by aeration and thereafter by bubbling nitrogen gas. The anaerobic solutions are slightly pink, but they become deep amber in the oxygenation process. The oxygenated ornithine complex can be easily deoxygenated, but the DAP and the DAB complexes are hardly deoxygenated at room temperature. The reversibility increases in the order

$$\begin{array}{l}[\mathrm{Co(DAP)_2}]_2\mathrm{O_2} < [\mathrm{Co(DAB)_2}]_2\mathrm{O_2} \\ \quad\text{(partially deoxygenated)} \\ \qquad\qquad \ll [\mathrm{Co(Orn)_2}]_2\mathrm{O_2} < [\mathrm{Co(Hid)_2}]_2\mathrm{O_2} \\ \qquad\qquad\qquad \text{(reversibly deoxygenated)}\end{array}$$

It has been considered that the imidazole ring is essential for the specific oxygenation of cobalt histidine chelate. Any oxygenated cobalt(II) chelates with amino acids, which did not have imidazole ring, were not found up to date, and further more the chelate with 1-methylhistidine, imidazole of which is blocked, is not oxygenated. However, the chelate with *N*-acetylhistidine, the amino group of which is blocked but not imidazole, does not absorb oxygen gas, and this shows that amino group is also dispensable. On the other hand, the new oxygenated complexes indicate that the imidazole ring is not always necessary. But it can be stated that the ligands having two nitrogen doners and a carboxyl or a carbonyl group are suitable. Carboxyl or carbonyl group seems to play an important role in the oxygenation reversibility, because the histidine chelate and the histidine methyl ester chelate are reversibly oxygenated, but not the histamine chelate.

Magnetic Properties and Electronic Absorption Spectra. Magnetic moments of the oxygenated cobalt complexes were obtained at 25°C with the Gouy balance. Oxygenated complexes of Co(DAP)$_2$, Co(DAB)$_2$, and Co(Orn)$_2$ showed 0.17, 0.14, and 0.15 Bohr magnetons, respectively. As reported on diamagnetic [Co(Hid)$_2$]$_2$O$_2$,[8] such small moments can be attributed to cobalt(II) chelate impurity resulting from incomplete oxygenation, and the new oxygenated complexes should be diamagnetic. Figure 2 show the electronic absorption spectra of the new oxygenated cobalt complexes. The shape

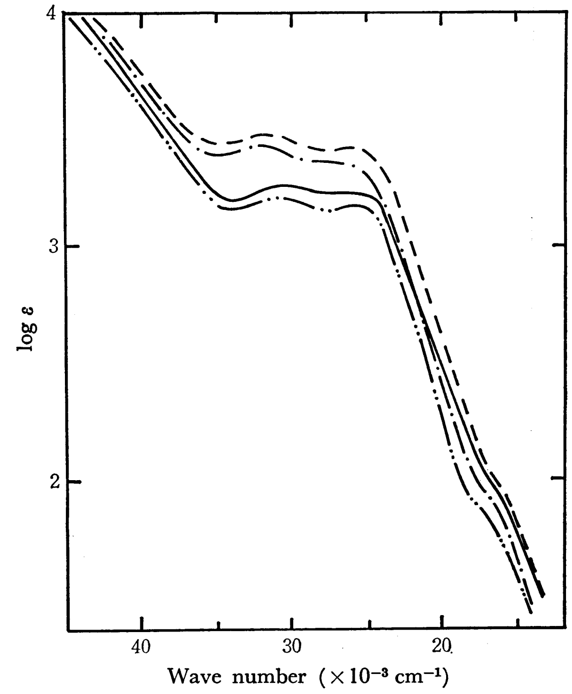

Fig. 2. Electronic absorption spectra of oxygenated cobalt complexes.
——: [Co(Hid)$_2$]$_2$O$_2$ ------: [Co(DAP)$_2$]$_2$O$_2$
- · -: [Co(DAB)$_2$]$_2$O$_2$ -··-: [Co(Orn)$_2$]$_2$O$_2$
pH: 9.00 (except for pH 10.00 in [Co(Orn)$_2$]$_2$O$_2$)

of the spectra resembles that of the oxygenated histidine complex, but are quite different from those of the cobalt(II) chelates (Fig. 3) and the cobalt(III) chelates[11] (Fig. 4). From these results, the new oxygenated complexes may be regarded as diamagnetic O_2-bridged binuclear cobalt complexes like the histidine complex, in which one unpaired electron from each of the cobalt(II) ions is paired with each of two unpaired electrons from molecular oxygen.

Valency States of Cobalt and Coordinated Molecular Oxygen in Oxygenated Cobalt Complexes. Figure 5 shows the polarograms obtained with cobalt(II) DAP chelate ($Co(DAP)_2$), the oxygenated complex ($[Co(DAP)_2]_2O_2$), and the cobalt(III) chelate ($[Co(DAP)_2]^+$).[12] The oxygenated complex, $[Co(DAP)_2]_2O_2$, show three waves. The first wave (a) must be the reduction wave of cobalt(III) to cobalt(II), since an identical wave is observed with the cobalt(III) chelate,

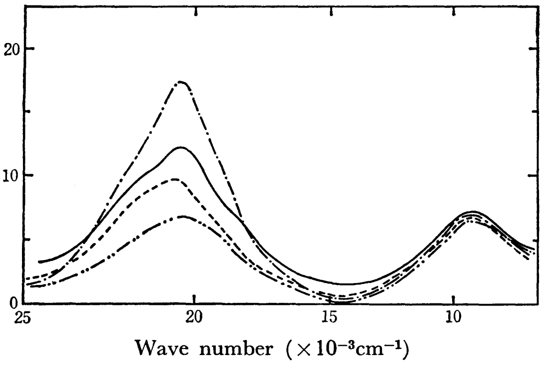

Fig. 3. Electronic absorption spectra of cobaltous chelates.
——: $Co(Hid)_2$ ------: $Co(DAP)_2$
- · -: $Co(DAB)_2$ -··-: $Co(Orn)_2$ pH: 9.00

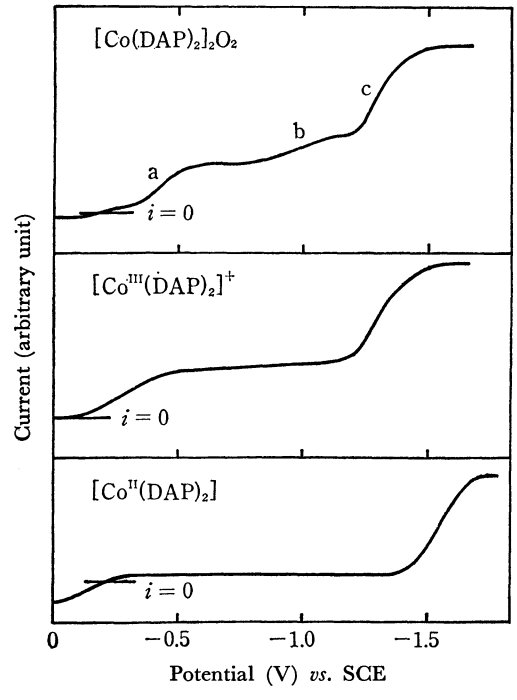

Fig. 5. Polarograms of cobalt(II) chelate, cobalt(III) chelate and the oxygenated complex with diaminopropionic acid. pH: 8.70

Fig. 4. Electronic absorption spectra of cobaltic chelates.
——: $[Co(Hid)_2]^+$ ------: $[Co(DAP)_2]^+$
- · -: $[Co(DAB)_2]^+$ -··-: $[Co(Orn)_2]^+$
pH: 9.00

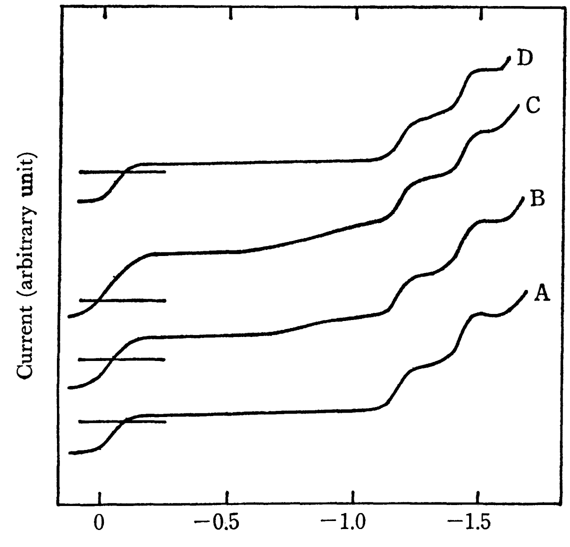

Fig. 6. Polarograms of cobalt histidine chelates.
A: solution of $Co^{II}(Hid)_2$ in the absence of air
B: after passing O_2 for 30 sec in solution A
C: after passing O_2 for 30 sec in solution B
D: after passing N_2 for 30 min in solution C
pH: 8.70

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11) Cobalt(III) chelate solutions were prepared by blowing oxygen gas into the cobalt(II) chelate solutions for one day at 60°C, and valency state of the cobalt (III) was confirmed by the polarograms (Ref. 12).

12) B. Jaselskins, *J. Amer. Chem. Soc.*, **80**, 1283 (1958)

TABLE 2. REDOX POTENTIAL OF Co(III)/Co(II) AND $H_2O_2/2H_2O$, STABILITY CONSTANTS OF OXYGENATED COBALT COMPLEXES ($[CoL_2]_2O_2$), AND ENTHALPY CHANGES OF OXYGENATION

$[CoL_2]_2O_2$	L=Hid	L=Orn	L=DAB	L=DAP
Co(III)/Co(II) (V)	−0.03	−0.15	−0.27	−0.41
$H_2O_2/2H_2O$ (V)	−0.97	−0.97	−0.97	−0.96
Stability, K[a)]	6.6×10^5	2.7×10^5	7.2×10^6	9.1×10^7
$\Delta H_{30°C}$ (kcal/mol)	−25.5	−19.6	−26.7	−29.3

pH: 8.70 (pH: 10 for Orn)
Temperature: 30°C
a) $K = \dfrac{[(CoL_2)_2O_2]}{[CoL_2]^2\,[O_2]}$

but not with the cobalt(II) chelate. The second wave (b) is observed only with oxygenated complexs. Although the exact value can not be measured, because of little overlap with wave (c), the half-wave potential (−0.96 V *vs.* SCE) is nearly equal to the reduction potential of hydrogen peroxide (−0.95 V). The potential is independent of the kind of oxygenated complexes, and wave (b) might result from hydrogen peroxide produced in the reduction process of cobalt(III) to cobalt(II):

$$[L_2Co^{III}\text{-}O_2^{2-}\text{-}Co^{III}L_2] \xrightarrow[2H^+]{2e^-} 2Co^{II}L_2 + H_2O_2$$

The last wave (c) is attributed to the reduction of cobalt(II) to metallic cobalt.

The polarograms of cobalt histidine complexes are shown in Fig. 6. The *i-E* curve is deformed by passing air or oxygen gas through the solution, but it slowly returns to the original shape by bubbling nitrogen gas. The first wave of polarograms obtained with the anaerobic solution is the oxidation wave, which might be attributed to the oxidation of cobalt(II) to cobalt(III) (A and D in Fig. 6). As oxygenation proceeds by aeration, the negative current decreases and simultaneously positive current increases (B and C in Fig. 6), but the half-wave potential remains almost constant (−0.03 V). These solutions give the second wave at the same potential (−0.97 V) as that of $[Co(DAP)_2]_2O_2$, *i.e.* the reduction potential of hydrogen peroxide. The current increases with the increase in positive current of the first wave, but the ratio of the former current to the latter is somewhat smaller than unity. This may be caused by the difference in both diffusion currents. Caglioti *et al.*[13)] also reported that the polarograms of $[Co(Hid)_2]_2O_2$ showed the redox wave of cobalt(III)/cobalt(II) and the reduction wave of hydrogen peroxide. The third and fourth waves may be due to the reduction of cobalt(II) to cobalt(I) and cobalt(I) to cobalt(0), respectively. The other oxygenated complexes, $[Co(DAB)_2]_2O_2$ and $[Co(Orn)_2]_2O_2$ show a similar polarographic behavior. The reduction potentials of the central cobalt(III) ions and O_2-type oxygen are given in Table 2.

These results lead to the conclusion that the coordinated molecular oxygen accepts two electrons from two cobalt(II) ions to attain the state of O_2^{2-}, and at the same time, two cobalt(II) ions are oxidized to cobalt(III) ions.

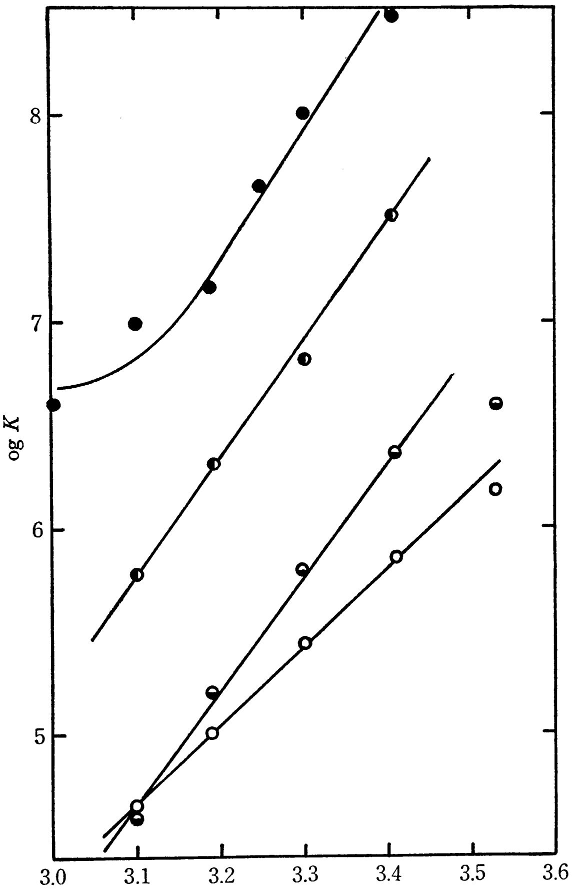

Fig. 7. Stabilities of oxygenated cobalt complexes.
○: $[Co(Orn)_2]_2O_2$; ◓: $[Co(Hid)_2]_2O_2$;
◐: $[Co(DAB)_2]_2O_2$; ●: $[Co(DAP)_2]_2O_2$;
pH=8.70 (pH=10.0 for $[Co(Orn)_2]_2O_2$)
$K=[(CoL_2)_2O_2]/[CoL_2]^2\cdot[O_2]$

Accordingly, two electrons of O_2^{2-} must be returned to the cobalt(III) ions by deoxygenations. This is confirmed by the fact that the oxygenated complexes, of which the central cobalt(III) ion gives more positive reduction potential, can be more easily deoxygenated.

Thermodynamics of Oxygenation of Cobalt Chelates. In Table 2, are presented the stability constants of the oxygenated complexes and the enthalpy changes of the oxygenation calculated from Fig. 7. Oxygenation is an exothermal process and the enthalpy change is larger in irreversible oxygenation than in the reversible one. In other words, deoxygenation, an endothermal pro-

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[13)] V. Caglioti, P. Silvestroni, and C. Futlani, *J. Inorg. Nucl. Chem.*, **13**, 90 (1960) cess, occurs when the enthalpy change of the oxygenation is small. The histidine complex is unique, because $[Co(Hid)_2]_2O_2$ is more easily deoxygenated than $[Co(Orn)_2]_2O_2$ in spite of the higher enthalpy change. This may be due to the presence of the imidazole ring, although no definite explanation can be given.

Effect of Ligand-Field on Oxygenation. Cobalt chelates with glycine, alanine, proline, and glutamic acid are neither oxygenated nor oxidized, whereas the chelates with *o*-phenanthroline (phen), ethylenediamine (en), and diethylenetriamine (dien) are oxidized immediately after oxygenation (Table 1).

From the spectrochemical series or the strength order of ligand-field,

$$\text{oxalate} < \text{glycine} < \text{en} \sim \text{dien} < \text{phen} \quad \text{(ligand)}$$

$$F^- < O < N < C \quad \text{(donor atom)},$$

it might be reasonable to consider that ligand-field of (N–O) type ligands, glycine, 1-methylhistidine, and *N*-acetylhistidine is weaker than of that (N–N) type ligands, en, dien, phen, and histamine. As observed above, ligands available to the oxygenation are (N–N) type compounds with a carboxyl or carbonyl group at the α position to an amino group. In such a situation, carboxyl or carbonyl group probably weakens the coordination power of the nitrogen atom. This anticipation is ascertained by the fact that ligand-field absorption band (20.3 kK) of cobalt(II) histidine methyl ester chelate appears at the frequency region between those of (N–N) type histamine chelate (20.5 kK) and (N–O) type glycine chelate (20.0 kK).

These results and polarographic data suggest that an important factor of oxygenation is the strength of ligand-field and at least medium strenght is favorable for reversible oxygenation.

Effect of Solvent on Deoxygenation. In aqueous solution, $[Co(DAP)_2]_2O_2$ and $[Co(DAB)_2]_2O_2$ are hardly deoxygenated, and irreversibly oxidized slowly even at room temperature and rapidly at higher temperatures (Fig. 8). However, in the solution containing more than 60 per cent ethanol, those complexes can be deoxygenated at higher temperatures. Although the experiments in other organic solvents could not be carried out, because of the low solubility of oxygenated complexes, it can be expected that oxygenated complexes are more easily deoxygenated in nonpolar solvents than in aqueous solution.

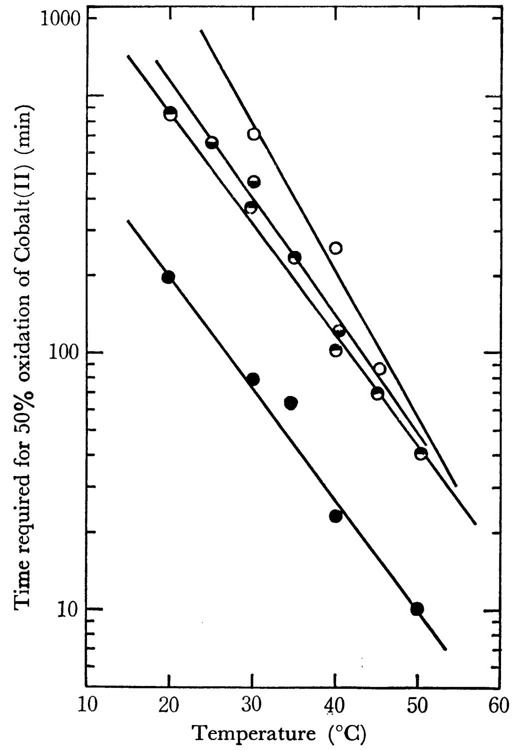

Fig. 8. Oxidation of oxygenated cobalt complexes.
○: $[Co(Hid)_2]_2O_2$ ◓: $[Co(Orn)_2]_2O_2$
◒: $[Co(DAB)_2]_2O_2$ ●: $[Co(DAP)_2]_2O_2$
pH: 8.70 (except for pH 10.00 in $[Co(Orn)_2]_2O_2$)

In this paper, discussion was made mainly from the viewpoint of the ligand-field strength of the chelating agents. Changes of entropy and enthalpy might be important, because reduction potential of the central cobalt(II) ion is related to the free energy. In order to understand more closely the reversible mechanism the entropy effect must be considered.

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