The Ligation of Phosphine Derivatives and the Oxygen-binding Properties of the Cobalt Mesoporphyrin IX Dimethyl Ester in Toluene

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The coordination of phosphine derivatives and some other bases to the cobalt mesoporphyrin IX dimethyl ester in toluene has been spectrophotometrically investigated. The coordination equilibrium constants were determined for each base, and found to be of this sequence (25 °C) : $P(C_4H_9)_3 \gg P(OCH_3)_3 > P(C_6H_5)_3 > S(CH_3)_2 > As(C_6H_5)_3$. The reversible oxygenation of the penta-coordinate complexes formed as above was investigated at lower temperatures (−20—−80 °C): the corresponding equilibrium constants were found to be in the following sequence (−80 °C): $P(C_4H_9)_3 > P(OCH_3)_3 > S(CH_3)_2 > P(C_6H_5)_3 > As(C_6H_5)_3$. These relations were discussed in terms of the σ-donating ability of a ligand coordinated *trans* to oxygen.

The reversible oxygenation of cobalt porphyrin has been the subject of considerable interest in recent years. EPR spectral evidence for the reversible oxygen uptake by the penta-coordinate cobalt porphyrins in a frozen organic solution at the temperature of liquid nitrogen has already been presented.[1,2] The success in the replacement of iron by cobalt in hemoglobin and myoglobin[3] particularly stimulated investigations of the amine-ligation and oxygen-binding properties of cobalt porphyrins.[4–6]

In the present work we investigated the effects of such axial ligand as $P(C_6H_5)_3$, $P(C_4H_9)_3$, $P(OCH_3)_3$, $As(C_6H_5)_3$, and $S(CH_3)_2$ on the reversible oxygenation of cobalt porphyrins. Among these bases, phosphine, phosphite, and arsine derivatives are usually considered to have not only σ-donor but also π-acceptor properties. Particularly, triphenylphosphine, a good π-acceptor, is very frequently used in the field of organometallic chemistry to stabilize the low-valent state of metal complexes. It would be interesting, therefore, to compare the effects of the ligation of phosphine derivatives on the oxygenation of cobalt porphyrins with those of the amine ligation.

In this report, we will present thermodynamic data on the ligation and oxygenation of the cobalt mesoporphyrin IX dimethyl ester in toluene solutions. The bonding properties of phosphine derivatives as well as the effect of the bases coordinated *trans* to oxygen on the oxygen-binding ability will be discussed in comparison with those of unsaturated amines.

During the course of the present work, Wayland *et al.*[7–9] reported EPR studies of tetraphenylporphyrin-cobalt(II) coordinated with PR_3 or $(POR)_3$, and their dioxygen complexes. The results of the EPR measurements of our cobalt porphyrin system completely agreed with those reported by these authors. Therefore, the results of our EPR measurements will be omitted.

Experimental

Materials. The mesoporphyrin IX dimethyl ester (Sigma Chemical Co.) was used without further purification. The Co(II) mesoporphyrin IX dimethyl ester (CoP) was prepared according to the established method.[10] Reagent-grade toluene was purified by the usual method and used as the solvent. The trimethylphosphite and dimethylsulfide were also distilled *in vacuo* prior to use. All the other chemicals were of a reagent grade and were used without special pretreatment.

Measurements. The coordination equilibria of CoP were measured by means of a spectrophotometric titration procedure (Hitachi spectrophotometer EPS-3T). Aliquots of a ligand solution (1—10^{-3} M in toluene) were added to 3.6 ml of a toluene solution of CoP (*ca.* 5×10^{-6} M) from a calibrated micro syringe (Terumo MS 10). The absorption spectra in the range from 350 to 400 nm were recorded after each addition of the ligand solution. The equilibrium constants of coordination (K) were derived from the changes in the absorbance at 394 nm. The constants were found to be independent of the wavelengths. Dilution corrections were kept small, and good isosbestic points were obtained. The cell temperature was controlled to ±0.2 °C in the 10—30 °C range by the use of Haake's thermostat, type "F." The temperature was measured by means of an inserted copper-constantan thermocouple.

The oxygenations were carried out in an optical cell mounted in a Pyrex Dewar. For a typical measurement, a 4-ml portion of a toluene solution containing CoP (10^{-5}—10^{-6} M) and a ligand (10^{-1}—10^{-4} M) was placed in the cell and nitrogen gas was bubbled in from a cylinder. The oxygenation temperature (−20—−80 °C) was controlled by introducing cold nitrogen gas purged from the liquid-nitrogen container into the Pyrex Dewar mounted in the sample compartment of the spectrophotometer; it was kept constant within ±0.5 °C. The temperature was measured by the thermocouple attached to the outside of the sample cell.

Oxygen and nitrogen from cylinders were mixed by means of a mixing apparatus equipped with two calibrated flowmeters, and a mixture of a given composition was introduced into the solution of penta-coordinate CoP complexes. Complete spectra from 340 to 500 nm were recorded after each equilibration.

Determination of the Equilibrium Constant. The equilibrium constant, K, of the ligation of CoP, as expressed by:

$$\mathrm{CoP} + \mathrm{L} \overset{K}{\rightleftharpoons} \mathrm{CoPL} \tag{1}$$

was determined graphically by spectrophotometric titration without direct measurements of the extinction coefficients of the complexes, using the Ketelaar method,[11] as is shown below:

$$\frac{1}{A_0 - A} = \frac{1}{K(\varepsilon_{\mathrm{CoP}} - \varepsilon_{\mathrm{CoPL}})[\mathrm{CoP}]_t[\mathrm{L}]_t} + \frac{1}{(\varepsilon_{\mathrm{CoP}} - \varepsilon_{\mathrm{CoPL}})[\mathrm{CoP}]_t} \tag{2}$$

where

A_0: absorbance of the starting solution ([L]=0)

A: absorbance of the solution containing ligand ($[L]_t$)

ε_{CoP}, ε_{CoPL}: molar extinction coefficients of CoP, CoPL

$[CoP]_t$: molar concentration of the total CoP($[CoP]_t=[CoP]+[CoPL]$)

$[L]_t$: molar concentration of the total ligand ($[L]_t=[L]+[CoPL]$)

By plotting $1/(A_0-A)$ against $1/[L]_t$, a straight line should be obtained. From the intercept and the slope of the straight line, K can be derived. In the concentration range of the ligand studied, hexa-coordinate complexes, $CoPL_2$, were not formed, which is in accordance with the results of EPR studies.[7]

The equilibrium constant, K_{O_2}, of the reversible oxygenation of the penta-coordinate CoP expressed by:

$$\mathrm{CoPL} + \mathrm{O_2} \overset{K_{O_2}}{\rightleftharpoons} \mathrm{CoPL\cdot O_2} \qquad (3)$$

can be derived similarly to K from the plot of $1/(A_0—A)$ against $1/P_{O_2}$:

$$\frac{1}{A_0-A}=\frac{1}{K_{O_2}(\varepsilon_{CoPL}-\varepsilon_{CoPL\cdot O_2})[CoPL]_t}\frac{1}{P_{O_2}}+\frac{1}{(\varepsilon_{CoPL}-\varepsilon_{CoPL\cdot O_2})[CoPL]_t} \qquad (4)$$

The oxygenation equilibria were measured at appropriate intervals between −25 and −80 °C. When K_{O_2} was small ($L=P(C_6H_5)_3$ and $As(C_6H_5)_3$), oxygenation was investigated only near −80 °C.

Results

Ligand Binding. Figure 1 shows typical ligand-titration spectra obtained when $P(C_4H_9)_3$ was added, step by step, to a CoP solution at 11.8 °C. It is apparent from the figure that the absorbance in the Soret region (~397 nm) gradually decreases with the increase in the concentration of $P(C_4H_9)_3$ and that the spectral change is well characterized by isosbestic points. The addition of the other ligands to the CoP solution was found to cause similar changes in the Soret region. No appreciable shift was observed in the Soret band, however.

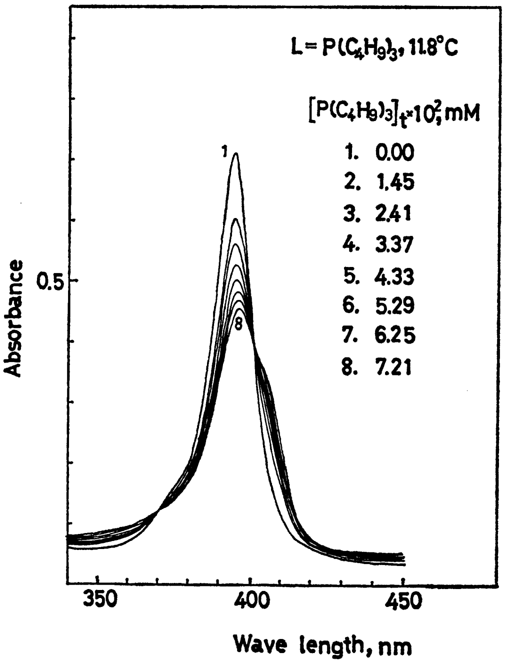

Fig. 1. The spectrophotometric titration spectrum for the determination of K at 11.8 °C for $L=P(C_4H_9)_3$. Spectrum 1 is that of 5.5×10^{-6} M Co mesoporphyrin IX dimethyl ester and 2−8 are at concentration of tri-*n*-butylphosphine added: 1.45, 2.41, 3.37, 4.33, 5.29, 6.25 and 7.21×10^{-5} M, respectively.

Figure 2 shows the plots of $1/(A_0—A)$ (394 nm) against $1/[L]_t$ at 11.8, 15.3, and 20.5 °C respectively. Straight lines were obtained in the plots, indicating that Eq. (2) is valid. Ligand titrations were further performed with $P(OCH_3)_3$, $P(C_6H_5)_3$, $S(CH_3)_2$, and $As(C_6H_5)_3$; all were found to give rise to a similar relation. The equilibrium constant, K, of the reaction (1) was then calculated for each ligand at various temperatures. The results are summarized in Fig. 3 as well as in the third column of Table 1, where the

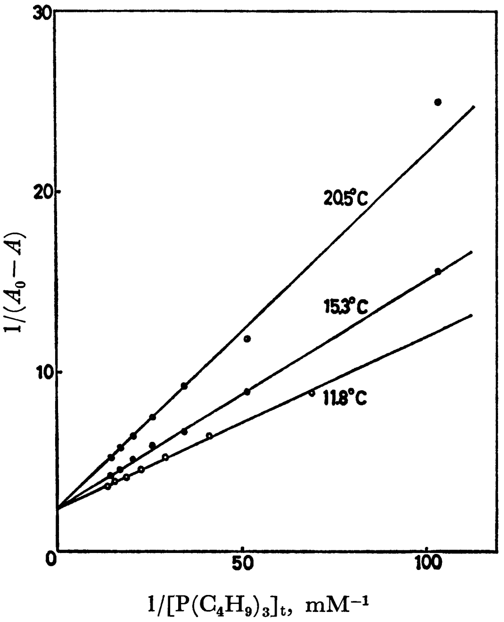

Fig. 2. $1/(A_0-A)$ as a function of the reciprocal tri-*n*-butylphosphine molar concentration added, $1/[P(C_4H_9)_3]_t$ for three temperatures.
○ 11.8 °C, ● 15.3 °C, ◑ 20.5 °C

Table 1. Thermodynamic data for equilibrium, $\mathrm{CoP+L} \overset{K}{\rightleftharpoons} \mathrm{CoP\cdot L}$

L	Temp., °C	K, M^{-1}	ΔG, kcal/mol	ΔH, kcal/mol	ΔS, e.u.
$P(C_6H_5)_3$	9.3	62.3	−2.3	−7.0	−17
	16.0	41.8	−2.1		
	26.0	30.4	−2.0		
$P(C_4H_9)_3$	11.8	24.2×10^3	−5.7	−13.3	−27
	15.3	18.6×10^3	−5.6		
	20.5	12.1×10^3	−5.5		
$P(OCH_3)_3$	16.9	63.1	−2.4	−6.9	−15
	19.6	58.9	−2.4		
	25.4	45.1	−2.3		
$S(CH_2)_2$	11.0	33.8	−2.0	−4.5	− 9
	21.5	24.9	−1.9		
	26.0	22.5	−1.9		
$As(C_6H_5)_3$	15.3	4.7	−0.9	−5.2	−15
	20.6	4.6	−0.9		
	24.9	3.5	−0.7		

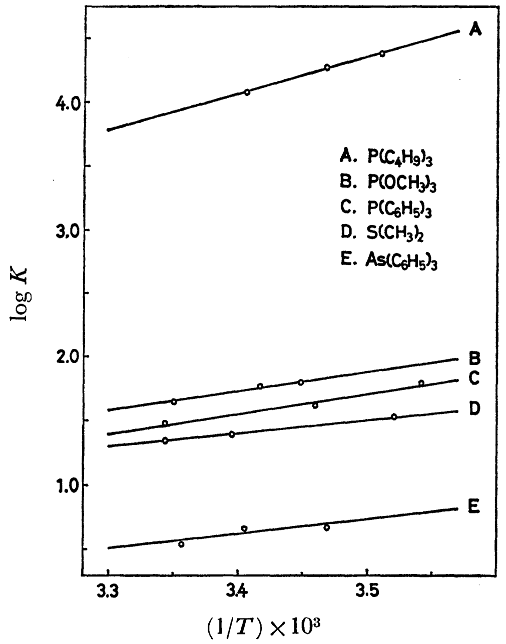

Fig. 3. The van't Hoff plots of K for L=$P(C_4H_9)_3$ (A), $P(OCH_3)_3$ (B), $P(C_6H_5)_3$ (C), $S(CH_3)_2$ (D) and $As(C_6H_5)_3$ (E).

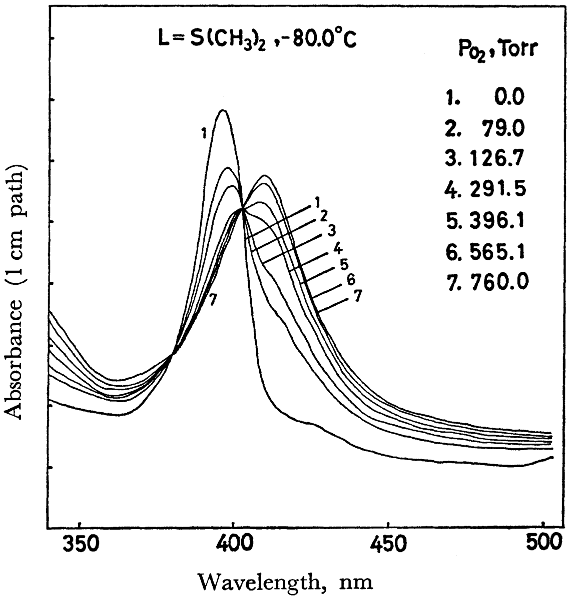

Fig. 4. The spectrophotometric titration for the determination of K_{O_2} at −80.0 °C for L=$S(CH_3)_2$. Spectrum 1 is that of 1 : 1 complex between cobalt mesoporphyron IX dimethyl ester and dimethylsulfide and 2—7 are at partial pressure of oxygen: 79.0, 126.7, 291.5, 396.1, 565.1 and 760.0 Torr, respectively.

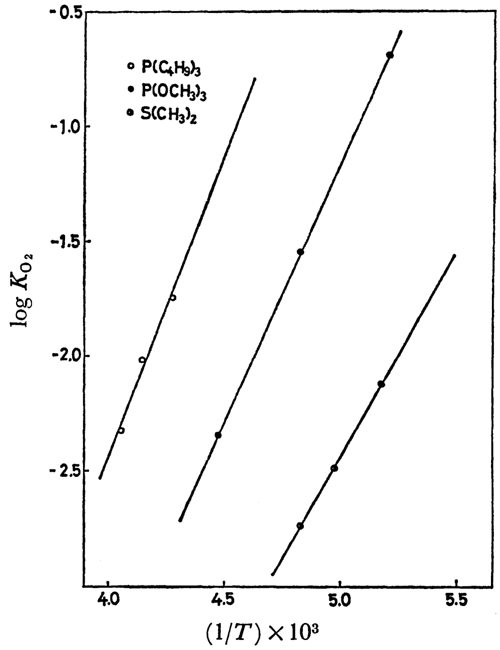

Fig. 5. The van't Hoff plots of K_{O_2} for L=$P(C_4H_9)_3$ (○), $P(OCH_3)_3$ (●) and $S(CH_3)_2$ (◑).

TABLE 2. THERMODYNAMIC DATA FOR REACTION,

$$CoP\cdot L+O_2 \overset{K_{O_2}}{\rightleftharpoons} CoP\cdot L\cdot O_2$$

L	Temp., °C	K_{O_2}, Torr^{-1}	ΔH, kcal/mol	$\Delta S^{a)}$, eu
$P(C_6H_5)_3$	−82.0	$(3.8\pm0.1)\times10^{-3}$	—	—
$P(C_4H_9)_3$	−26.5 −32.0 −39.5	$(4.7\pm0.5)\times10^{-3}$ $(9.6\pm0.6)\times10^{-3}$ $(18.0\pm2.0)\times10^{-3}$	−11.8	−59
$P(OCH_3)_3$	−49.5 −66.0 −81.0	$(4.5\pm1.1)\times10^{-3}$ $(28.4\pm1.5)\times10^{-3}$ $(203.4\pm20.0)\times10^{-3}$	−10.3	−57
$S(CH_3)_2$	−66.0 −72.0 −80.0	$(1.8\pm0.8)\times10^{-3}$ $(3.3\pm0.2)\times10^{-3}$ $(7.6\pm0.4)\times10^{-3}$	−8.1	−52
$As(C_6H_5)_3$	−79.0	$(1.5\pm0.2)\times10^{-3}$	—	—

a) Standard State of 1 Torr O_2.

corresponding thermodynamic quantities are also presented in the last three columns.

In the range of 9—26 °C, the coordination capability of the ligands was qualitatively given by:

$$P(C_4H_9)_3 \gg P(OCH_3)_3 > P(C_6H_5)_3 > S(CH_3)_2 > As(C_6H_5)_3$$

Oxygen Binding. Figure 4 shows the spectral changes in CoPL under various oxygen partial pressures from 0 to 760 Torr at −80 °C (L=$S(CH_3)_2$). The CoP coordinated with the other ligands gave spectral changes similar to those in the case of $S(CH_3)_2$; the absorption peak of the penta-coordinate complex (deoxy form) decreased, step by step, upon oxygenation, while another absorption peak originating from the oxygenated form appeared in the longer-wavelength region. The spectral change was reversible with respect to the ambient oxygen pressure; the original spectrum was restored when nitrogen gas was bubbled into the CoPL solution.

Among the ligands studied, the oxygenation reached a saturation under 760 Torr at −80 °C with $P(C_4H_9)_3$ or $P(OCH_3)_3$ while only a partial oxygenation was observed with $P(C_6H_5)_3$, $S(CH_3)_2$, or $As(C_6H_5)_3$, even at −80 °C. Figure 5 shows the van't Hoff plots of K_{O_2}. The K_{O_2} values as well as the related thermodynamic parameters are presented in Table 2.

In the temperature range studied (−20 °C——80 °C), the K_{O_2} values for CoPL decreased in the following order of ligands coordinated *trans* to oxygen:

$P(C_4H_9)_3 > P(OCH_3)_3 > S(CH_3)_2 > P(C_6H_5)_3 > As(C_6H_5)_3$

This order was parallel with that of the ligation capability of L except $S(CH_3)_2$ and $P(C_6H_5)_3$ were reversed. Despite the large difference in the value of K for $P(C_4H_9)_3$ ($\log K = 4.08$ at 20 °C) and $P(OCH_3)_3$ ($\log K = 1.77$ at 20 °C), the K_{O_2} values for $P(C_4H_9)_3$ ($\log K_{O_2} = -1.2$ at -50 °C) and $P(OCH_3)_3$ ($\log K_{O_2} = -2.3$ at -50 °C) were not very different from one another, suggesting that K and K_{O_2} are not determined by common factors alone.

Discussion

Ligand Binding: The importance of σ-bonding properties between ligand and metal ion has previously been recognized. Recently, it has been suggested that the π-bonding properties are also important for unsaturated amines to form a cobalt-oxygen adduct.[5,6] The importance of π-bonding properties has been well accepted for the derivatives of phosphine, leading to the stabilization of low-valent organometallic complexes.[12] Here, we shall comparatively discuss the bonding properties of unsaturated amines, phosphorous, and arsenic bases on the basis of their ligation equilibria to CoP.

We first presume that the pK_a of the conjugate acid is a measure of the σ-donor property of a base. Unfortunately, the pK_a of phosphorous and arsenic bases is little known. From the literature[13] we adopt 8.43 and 2.73 respectively as the pK_a values of $P(C_4H_9)_3$ and $P(C_6H_5)_3$. The pK_a of $P(OCH_3)_3$ was estimated to be about 3.5. The estimation was carried out on the basis of the linear relationship observed between the half-neutralization potential and pK_a for a series of tertiary phosphorous bases.[13,14] The pK_a of $As(C_6H_5)_3$ must be very low. We presumed it to be 0.0 ± 0.5 on the basis of the results of a potentiometric titration of periodic-group V_a triaryls.[15]

The log K values given in Table 1 were then plotted against the pK_a estimated as above for each base in Fig. 6a, together with the corresponding plots for unsaturated amines due to Stynes *et al.*[6] As is shown in Fig. 6a, unsaturated amines were found to stabilize their complexes more strongly than phosphorous and arsenic bases at the same pK_a, while fairly good straight lines were obtained between log K and pK_a for the two base groups. Especially, it should be noticed that the slope of the straight line ($\partial \log K / \partial \, pK_a$) was greater for the phosphorous and arsenic bases (0.4) than for the amines (0.1). The greater dependence of log K on pK_a must mean that the σ-donor properties of the ligand predominantly control the stability of the complex.

The ligand binding to CoP may generally be associated not only with the donation of electrons from the ligand to the cobalt atom (σ-bonding), but also with the interaction of the d-orbitals of cobalt with the π^* and/or π-orbitals of the ligand (π-bonding). Thus, it follows from Fig. 6a that unsaturated amines participate in their binding to CoP *via* the π-interacting properties more significantly than do the phosphorous and arsenic bases.

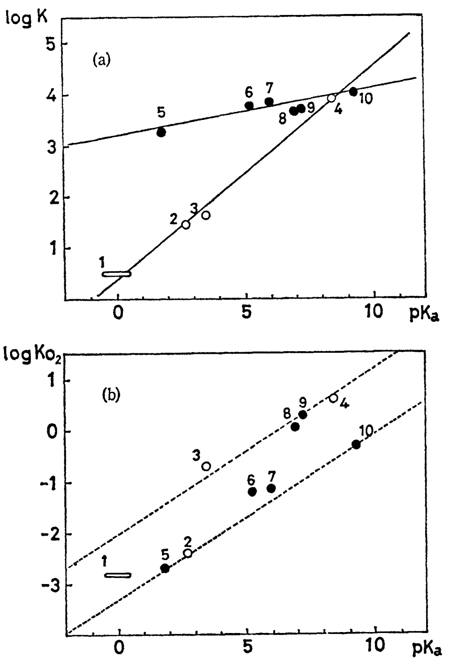

Fig. 6. The plots of pK_a of ligands against log K(a) or log K_{O_2}(b).
Open circles: $As(C_6H_5)_3$(1), $P(C_6H_5)_3$(2), $P(OCH_3)_3$ (3), $P(C_4H_9)_3$(4) Solid circles: 4-CN-pyridine(5), pyridine(6), 4-*t*-Bu-pyridine(7), imidazole(8), 1-Me-imidazole(9), 4-NH_2-pyridine(10).

Contrary to expectation, the π-bonding properties of phosphorous and arsenic bases appeared to be weaker than those of unsaturated amines. It seems that this can be explained by such factors as the contraction of the orbitals of the cobalt ion (divalent and low spin) and the expansion of the orbitals of the phosphorous atom as compared with those of the nitrogen atom. This explanation is not inconsistent with the thermodynamic observations that the binding of unsaturated amines to CoP is accompanied by larger heats and smaller entropy changes when compared with those of the phosphorous and arsenic bases.

Oxygen Binding. In the same way as in the case of ligand binding to CoP, the log K_{O_2} values were plotted against the pK_a of the ligands. The results are shown in Fig. 6b. It is apparent from Fig. 6b that the oxygen-binding properties of the complexes are promoted by larger pK_a values of the ligands, just as in the case of ligand binding, although the linear relation is only approximate. Nevertheless, it is interesting to note that the slope of the straight line for phosphorous and arsenic bases was roughly identical with that for pyridine bases, in contrast with the case for the ligand binding. In other words, the oxygen-binding properties of CoPL, in which L is the amine, seem to depend more strongly on the pK_a of L than does their ligation to CoP, suggesting that the σ-donating properties of L are important for the oxygen binding.

According to the molecular orbital model proposed by Wayland *et al.*,[8] the cobalt-oxygen binding is considered to be principally a covalent bonding of the singly occupied cobalt(II), d_{z^2}, and the signly occupied oxygen σ-orbital that results from the splitting the π^* degeneracy: also, a ligand molecule, L, elevates in proportion to the donating ability of L, the d_{z^2} cobalt and stabilizes the cobalt-oxygen bond. The low π^*-orbital energy of oxygen will tend to localize the covalent σ pair on oxygen, causing a decline in the cobalt-oxygen $d\pi$—$p\pi$ bonding. In consequence, the π-bonding properties of L are considered to contribute to only a little to the cobalt-oxygen bonding.

The poor relationship between $\log K_{O_2}$ and pK_a may indicate that the ligands coordinated *trans* to oxygen also control oxygen-binding not only by σ-donating ability but also with other factors such as π-donating ability and/or the degree of polarization induced upon oxygenation.

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