tochemistry.[13] It is likely, however, that TPE is not an extraordinary case but rather a general one. We expect that investigations similar to the present, when applied to other molecules, will lead to analogous results and complexity. Indeed, time-resolved fluorescence studies[6b,c,f] of other photochemical systems, over smaller temperature ranges without wavelength resolutions, already indicate that the fluorescence kinetics should be expected to be complex in many cases.

The question, of course, arises as to the physical significance of the different manifestations of excited-state relaxation. The following mechanisms for relaxation are proposed based on our experimental results: (1) small amplitude vibrational relaxation as indicated by picosecond hot fluorescence at low temperature; (2) conformational relaxation as indicated by viscosity controlled time-dependent bathochromic shifts in the spectrum; (3) conformational relaxation inducing electronic radiationless decay from $S_1 \rightarrow S_0$ as indicated by viscosity-dependent lifetimes; and (4) radiative decay of S_1.

We are presently examining the presence of these relaxation processes in the photochemistry of other molecules, including *cis*- and *trans*-stilbenes. It is our goal to apply the methods employed in this paper to gain a detailed understanding of the mechanism responsible for cis-trans isomerization and excited-state torsional motion in general. Potentially, these techniques could lead to a much higher level of specificity and completeness in the understanding of mechanistic photochemistry.

---

(13) Complexity of this sort, however, has been suggested on theoretical grounds, e.g., J. Michl., *J. Mol. Photochem.*, **4**, 243 (1972); H. E. Zimmerman and M. G. Steinmetz, *J. Chem. Soc., Chem. Commun.* 230 (1978).

Vibrational Studies of (Tetraphenylporphyrinato)cobalt(II) and Its Adducts with CO, NO, and O_2 in Gas Matrices

Muneteru Kozuka* and Kazuo Nakamoto

Contribution from the Todd Wehr Chemistry Building, Marquette University, Milwaukee, Wisconsin 53233. *Received July 31, 1980*

Abstract: The adducts of (tetraphenylporphyrinato)cobalt(II) (Co(TPP)) with axial ligands such as CO, ^{13}CO, NO, $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ have been studied in Ar and/or Kr matrices with the use of infrared spectroscopy. Formation of the following adducts and their axial ligand frequencies (cm^{-1}) have been confirmed: $Co(TPP)(CO)_2$, 2077 Kr, 2078 Ar; Co(TPP)(CO), 2073 Kr; $Co(TPP)(^{13}CO)_2$, 2032 Ar; Co(TPP)(NO), 1690 Kr, 1693 Ar; $Co(TPP)(^{16}O_2)$, 1278 Ar, 1272 Kr; $Co(TPP)(^{16}O^{18}O)$, 1252 and 1241 Ar; $Co(TPP)(^{18}O_2)$, 1209 Ar, 1207 Kr. The O_2 stretching frequency of $Co(TPP)(O_2)$ is the highest among those of molecular oxygen adducts of Co(II) and Fe(II) chelates known thus far. The doublet band observed for the O_2 stretching vibration of its $^{16}O^{18}O$ adduct definitely indicates the asymmetric end-on coordination of molecular oxygen. Resonance Raman spectra of Co(TPP) in matrices of respective ligands have shown the presence of the Co–ligand vibrations at 231, 237, and 345 cm^{-1} for $Co(TPP)(^{13}CO)_2$, $Co(TPP)(CO)_2$, and $Co(TPP)(O_2)$, respectively. Formation of the mixed-ligand adducts such as Co(TPP)(CO)(NO) and $Co(TPP)(CO)(O_2)$ has been confirmed, and the effect of trans-ligand interactions discussed.

Cobalt(II) chelates of porphyrins and Schiff base ligands have been the subject of extensive investigations in the past decade due to their ability to form molecular oxygen adducts. The techniques used to study these adducts include X-ray analysis, MO treatments, and electronic, ESR, and vibrational spectroscopy together with kinetic and thermodynamic measurements.[1] Very few reports are available, however, on the reactions of Co(II) chelates with other ligands such as CO and NO. As to Co(TPP) (TPP = tetraphenylporphyrinato anion), Wayland et al.[2] discussed the electronic structures and bonding of its adducts with CO, NO, O_2, $P(OCH_3)_3$ and nitrogen donors based on their ESR and electronic spectra in toluene solution. However, no detailed vibrational studies have been made on these adducts. This paper reports the infrared (IR) and resonance Raman (RR) spectra of Co(TPP) complexed with CO, ^{13}CO, NO, $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ in low-temperature gas matrices. The matrix-isolation technique is ideal for such a study since most of these adducts are stable only at very low temperatures. It should be noted that previous vibrational studies have been concentrated on molecular oxygen adducts with base ligands at the sixth coordination site. In this respect, our study is unique since $Co(TPP)O_2$ formed in inert-gas matrices can provide information about the O_2 and Co–O_2 bonds in the absence of a base ligand. Finally, matrix-isolation spectra are free from interference by solvent bands which often hinders the analysis of vibrational spectra obtained in solutions.

Experimental Section

Co(TPP) was prepared by the literature method[3] and purified by chromatography on an alumina column and recrystallization from $CHCl_3$–CH_3OH. The gases, O_2 (99.99%, Matheson), $^{18}O_2$ (92% Monsanto Research), CO (99.99%, Matheson), ^{13}CO (90.5%, Merck), NO (99.0%, Matheson), Ar (99.9995%, Matheson), and Kr (99.995%, Airco) were used without further purification. The $^{16}O^{18}O$ gas was prepared by electrical discharge of a mixture of $^{16}O_2$ and $^{18}O_2$, and its mixing ratio was determined by the relative intensities of Raman bands of each species in a mixture which was deposited on a copper cold-tip at ~15 K.[4]

Co(TPP) was vaporized from a Knudsen cell at ~430 K, and codeposited with respective gases on a CsI plate which was cooled to ~15 K by a CTI Model 21 closed-cycle helium refrigerator. A detailed design of the cell is described elsewhere.[5] IR spectra were measured on a Beckman IR-12 infrared spectrophotometer. High-resolution spectra were obtained with use of a 10-cm^{-1}/in. chart expansion, 0.8 cm^{-1}/min. chart speed, and a manual slit program. Rotation–vibration bands of standard molecules were used to calibrate the frequency reading. The miniature oven technique[4] was employed to measure the RR spectra of Co(TPP) in CO, ^{13}CO, NO, and O_2 matrices. The spectra were recorded on a Spex Model 1401 double monochromator. Detection was made with

---

* To whom correspondence should be addressed at the Chemical Research Institute of Nonaqueous Solutions, Tokoku University, Sendai 980, Japan.

(1) R. D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, **79**, 139 (1979), and references therein.

(2) B. B. Wayland, J. V. Minkiewicz, and M. E. Abd-Elmageed, *J. Am. Chem. Soc.*, **96**, 2795 (1974).

(3) P. Rothemund and A. R. Menotti, *J. Am. Chem. Soc.*, **70**, 1808 (1948).

(4) W. Scheuermann and K. Nakamoto, *Appl. Spectrosc.*, **32**, 251 and 302 (1978).

(5) D. Tevault and K. Nakamoto, *Inorg. Chem.*, **15**, 1282 (1976).

0002-7863/81/1503-2162$01.25/0

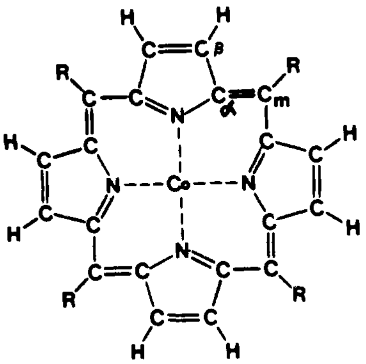


Figure 1. Structures of Co(TPP) (R = C_6H_5) and cobalt porphine (R = H).

the use of a cooled RCA C31034 photomultiplier in conjunction with a Spex digital photometer system. Excitation was provided by a Spectra-Physics Model 164 Ar ion laser. Calibration of frequency reading was made by using plasma lines from the Ar ion laser.

Results and Discussion

Co(TPP). As the first step to interpret the vibrational spectra of the Co(TPP) adducts with CO, NO, and O_2, we have studied the IR and RR spectra of Co(TPP) itself in various physical states. Figure 1 (R = C_6H_5) shows the structure of Co(TPP). For a metalloporphin (R = H) of D_{4h} symmetry, we expect $9A_{1g}$ (Raman), $8A_{2g}$ (Raman-active under resonance), $9B_{1g}$ (Raman), $9B_{2g}$ (Raman), $18E_u$ (IR), $3A_{1u}$ (inactive), $6A_{2u}$ (IR), $5B_{1u}$ (inactive), $4B_{2u}$ (inactive), and $8E_g$ (Raman) vibrations; those belonging to the former five species are in-plane whereas those belonging to the latter five species are out-of-plane modes.[6] The replacement of the hydrogen atom at the meso position by the phenyl group further increases the number of vibrations. It would be almost impossible to make completely reliable band assignments for such a large molecule even if normal coordinte analyses were carried out on Co(TPP) and its d_8 (H = D) and d_{20} (R = C_6D_5) analogues.

Previous work on the RR spectra of M(TPP) (M = Ni, Cu, and Pd),[7] Mn(TPP)X (X = Cl, Br, and I),[8] Cu(TPP),[9] and Cr(TPP)Cl,[10] does not report any band assignments. The band assignments based on TPP-d_8 and TPP-d_{20} data were first made by Burke et al.[11] on the RR spectra of $[Fe(TPP)]_2O$. Since most of the TPP vibrations are shifted only slightly by changing the central metal, we have assigned the RR spectrum of Co(TPP) on the basis of these results.

Figure 2 shows the RR spectra of Co(TPP) with the 457.9-nm excitation. Trace A is a spectrum of an Ar matrix deposited at ~15 K. Trace B was obtained by annealing the above matrix via the 15–40–15 K cycle. It is seen that three new bands appear at 518, 390, and 284 cm^{-1} while the bands at 400 and 338 cm^{-1} are weakened. These trends are more evident in the spectrum of a film (trace C) obtained by evaporating argon completely. This spectrum was exactly the same as that of Co(TPP) deposited without argon. Thus, these bands can be attributed to Co(TPP) in the condensed phase. Although the exact nature of these vibrations is not known, they serve as useful marker bands in monitoring the degree of matrix isolation.

The RR spectrum of Co(TPP) in CH_2Cl_2 solution obtained by 457.9-nm excitation was similar to those shown in Figure 2, and all the bands were found to be polarized. This is expected since the RR spectra of metalloporphyrins are dominated by the totally symmetric (A_{1g}) modes when the exciting frequency approaches that of the Soret band.[12] As expected, the vibrational frequencies of these A_{1g} modes of Co(TPP) are very similar to those of $[Fe(TPP)]_2O$.[11] Hence, we have made the following assignments based on the results obtained for $[Fe(TPP)]_2O$: 1604, Ph; 1575, $\nu(C_\beta{-}C_\beta) + \nu(C_\beta{-}H)$; 1495, $\nu(C_\beta{-}C_\beta)$; 1450, $\nu(C_\alpha{-}C_\beta) + \delta(C_\beta{-}H)$; 1376, $\nu(C_\alpha{-}N) + \delta(C_\beta{-}H)$; 1240, $\nu(C_m{-}Ph)$; 1082, $\delta(C_\beta{-}H)$; 1009, $\nu(C_\alpha{-}C_m)$; 400–390, porphin core. Here, ν and δ denote the stretching and in-plane bending modes, respectively, and all the numbers are given in cm^{-1}.

Figure 3 shows the IR spectra of Co(TPP) obtained in three physical states. Although these spectra are similar, close inspection reveals the following differences. Since the bands are sharpest in an Ar matrix, trace A shows more bands than those in other states. This is most conspicuous in the region from 760 to 700 cm^{-1}. The film spectrum (trace B) shows a band at 1100 cm^{-1} which does not appear in other states. The KBr pellet spectrum (trace C) exhibits two bands at 967 and 837 cm^{-1} which are not seen in the film spectrum.

Previously, the IR spectrum of crystalline Co(TPP) has been measured and empirical assignments proposed.[13,14] Gladkov et al.[15,16] reported complete band assignments of the IR and RR spectra of Cu^{II} porphin and its d_4, d_8, and d_{12} analogues based on normal coordinate analysis. According to their results, the IR-active normal modes which are dominated by the C_β–H bending vibrations appear at 1308 (1259), 1060–1055 (791), and 700–695 (564) cm^{-1} (the numbers in the parentheses denote the corresponding d_8 frequency). Similar bands are found at 1317 (1271), 1054 (771), and 701 (562) cm^{-1} in the IR spectrum of Co(TPP) and its d_8 analogue. In contrast to RR spectra, it was not possible to assign the phenyl group vibrations by the comparison of Co(TPP) and its d_{20} analogue since their IR spectra are too complex to interpret empirically.

Carbon Monoxide Adducts. Figure 4 shows the IR spectra of Co(TPP) codeposited with CO diluted in Ar or Kr in various ratios. The strong bands at 2149 and 2138 cm^{-1} in Ar matrices are due to CO bound to H_2O (impurity) and monomeric CO, respectively.[17] Similar bands are also seen in Kr matrices. At Ar/CO = 200 (trace A), a new band appears at 2078 cm^{-1}. This band is definitely due to CO complexed to Co(TPP) since neither CO nor Co(TPP) exhibits bands in this region. Furthermore, it is shifted to 2032 cm^{-1} when Co(TPP) is codeposited with $^{13}CO/Ar$ (trace A′). Similar experiments in Kr matrices yield two bands at 2077 and 2073 cm^{-1} (trace B). The former becomes weaker relative to the latter when the concentration of CO is decreased (trace C). Thus, it is most reasonable to assign these bands to $Co(TPP)(CO)_2$ and Co(TPP)(CO), respectively. The possibility that one of the these bands is due to Co(TPP)(CO)(H_2O) is unlikely since Co(TPP) itself did not show any indication of trace water coordination under the same experimental condition. Only the formation of the 1:1 (metal:ligand) adduct was reported previously[2]. The 1:2 adduct may be too unstable to detect by conventional techniques. Due to the reasons discussed later, it was not possible to observe such separate peaks in Ar matrices.

Previously, Wayland et al.[18] observed the ν(CO) of $Fe(TPP)(CO)_2$ and Fe(TPP)(CO) at 2042 and 1973 cm^{-1}, respectively, in the solid state. Similar results are reported by Eaton et al.[19]

---

(6) H. Ogoshi, Y. Saito, and K. Nakamoto, *J. Chem. Phys.*, **57**, 4194 (1972).

(7) R. Mendelsohn, S. Sunder, and H. J. Bernstein, *J. Raman Spectrosc.*, 3, 303 (1975).

(8) R. R. Gaughan, D. F. Shriver, and L. J. Boucher, *Proc. Natl. Acad. Sci., U.S.A.*, **72**, 433 (1975).

(9) J. A. Shelnutt and D. C. O'Shea, *J. Chem. Phys.*, **69**, 5361 (1978).

(10) J. A. Shelnutt, L. D. Cheung, R. C. C. Chang, Nai-Teng Yu, and R. H. Felton, *J. Chem. Phys.*, **66**, 3387 (1977).

(11) J. M. Burke, J. R. Kincaid, and T. G. Spiro, *J. Am. Chem. Soc.*, **100**, 6077 (1978).

(12) R. H. Felton and Nai-Teng Yu, *Porphyrins*, 3, 377 (1978).

(13) D. W. Thomas and A. E. Martell, *J. Am. Chem. Soc.*, **81**, 5111 (1959).

(14) J. R. Kincaid and K. Nakamoto, *J. Inorg. Nucl. Chem.*, **37**, 85 (1975).

(15) L. L. Gladkov, A. T. Gradyushko, A. M. Shulga, K. N. Solovyov, and A. S. Starukhin, *J. Mol. Struct.*, **47**, 463 (1978).

(16) K. N. Solovyov, L. L. Gladkov, A. T. Gradyushko, N. M. Ksenofontova, A. M. Shulga, and A. S. Starukhin, *J. Mol. Struct.*, **45**, 267 (1978).

(17) H. Dubost and A. Abouaf-Marguin, *Chem. Phys. Lett.*, **17**, 269 (1972).

(18) B. B. Wayland, L. F. Mehne, and J. Swartz, *J. Am. Chem. Soc.*, **100**, 2379 (1978).

(19) G. Eaton and S. Eaton, *J. Am. Chem. Soc.*, **97**, 235 (1975); J. J. Bonnet, S. S. Eaton, G. R. Eaton, R. H. Holm, and J. A. Ibers, *ibid.*, **95**, 2141 (1973).

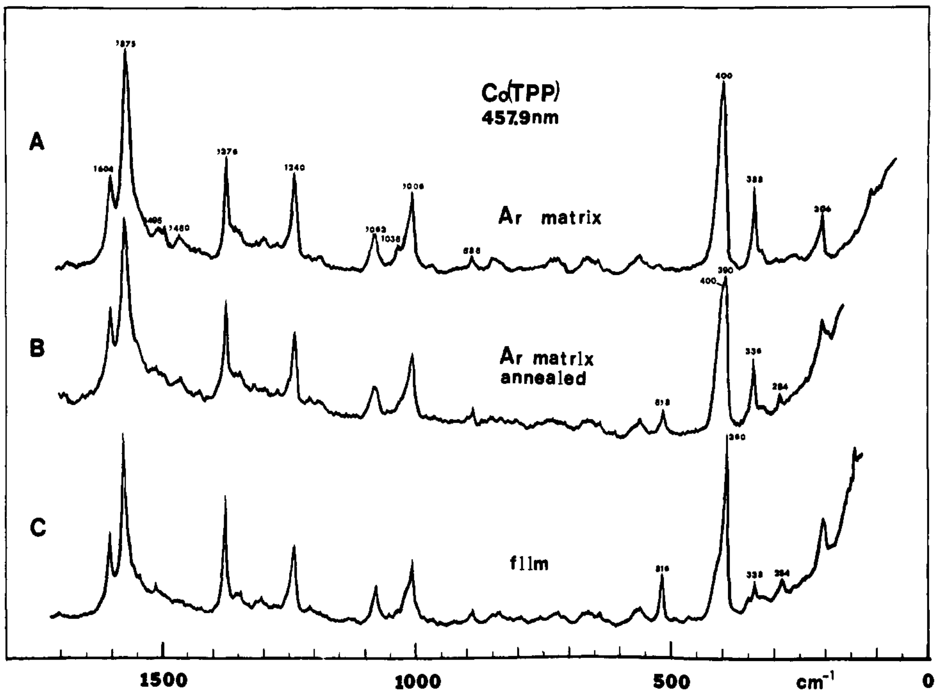


Figure 2. RR spectra of Co(TPP) in various physical states (457.9-nm excitation); A, Ar matrix; B, Ar matrix annealed (warmed to 40 K and then cooled to 15 K); C, film (warmed to 100 K and then cooled to 15 K). In B and C, frequencies are are the only for those referred to in the text. The frequencies of the remaining bands are the same as those shown in A.

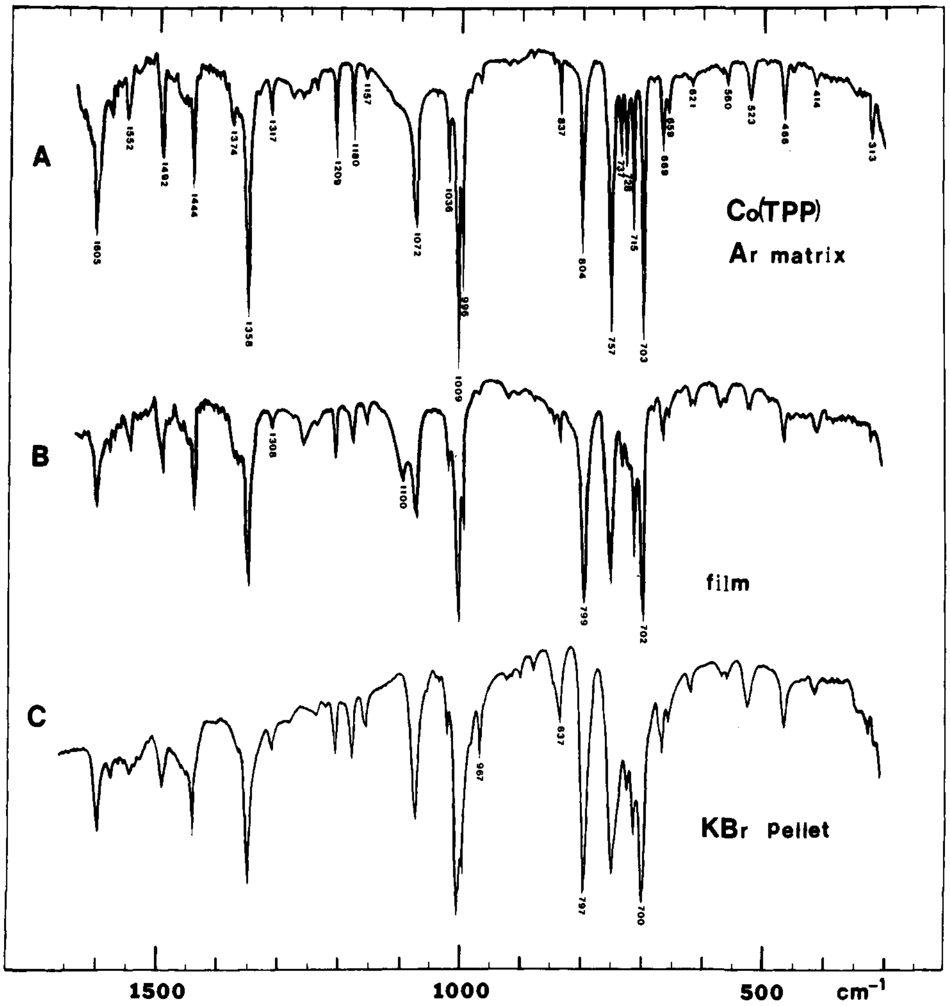


Figure 3. IR spectra of Co(TPP) in various physical states: A, Ar matrix (15 K); B, film (15 K); C, KBr pellet (300 K). In B and C, frequencies are shown only for those referred to in the text.

for Ru(TPP)(CO)$_2$ (2005 cm^{-1}) and Ru(TPP)(CO) (1945 cm^{-1}). Then, the order of ν(CO) (cm^{-1}) for the 1:1 adducts is Co(TPP)(CO) (2073) ≫ Fe(TPP)(CO) (1973) > Ru(TPP)(CO) (1945). A similar order is obtained for the 1:2 adducts: Co(TPP)(CO)$_2$

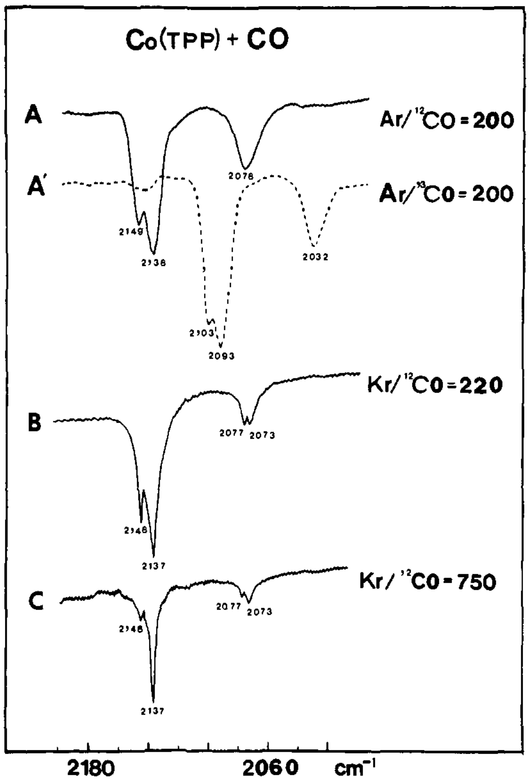


Figure 4. IR spectra of cocondensation products of Co(TPP) with CO in Ar or Kr matrices at 15 K.

(2077) > Fe(TPP)(CO)$_2$ (2042) > Ru(TPP)(CO)$_2$ (2005). In general, the ν(CO) is governed by two factors: (1) σ donation from CO to the metal which tends to increase ν(CO) and is maximized at the M–C–O angle of 120°, and (2) π back-donation from the metal to CO which tends to decrease ν(CO) and is maximized at the M–C–O angle of 180°. The above frequency order seems to indicate that the degree of π back-bonding increases in the order Co(II) < Fe(II) < Ru(II). According to MO calculations,[20] π back-bonding is stronger in Fe(TPP) than in Co(TPP) since the d-level manifold is raised in going from Co(TPP) to Fe(TPP). Additional support comes from the fact that the Fe–C–O bond in Fe(TPP)(CO)(py) is linear[21] while the Co–C–O bond in Co(TPP)(CO) could be bent.[2]

In the M(TPP)(CO)$_{1,2}$ series discussed above, the ν(CO) of the 1:2 adduct is always higher than that of the 1:1 adduct. This is understandable since the second CO group decreases the degree of π back-bonding due to competition between two trans CO groups. Due to the reason discussed above, this trans π effect is much smaller for Co(TPP)(CO)$_2$ than for Fe(TPP)(CO)$_2$. The small difference in ν(CO) between Co(TPP)(CO)$_2$ and Co(TPP)(CO) may be accounted for on this basis.

In general, the CO complexes exhibit relatively sharp IR-active ν(CO) (half-bandwidth ~5 cm^{-1}) in inert-gas matrices.[22] In fact, the half-bandwidth of the ν(CO) of Co(TPP)(CO)$_n$ (n = 1, 2) in Kr matrices (traces B and C) are on the order of 5–6 cm^{-1}. However, Ar matrices give only a single broad band (half-bandwidth ~16 cm^{-1}), indicating that the ν(CO) of the 1:1 and 1:2 adducts are probably overlapped. Another factor contributing to its broadness is the decreasing rigidity of the matrix in going from Kr to Ar.[22]

A further confirmation of the adduct formation has been made by observing low-frequency vibrations. Since these vibrations are very weak, extremely thick deposits are necessary to observe them in matrix-isolation IR spectra. In contrast, RR spectroscopy normally requires only dilute samples since metalloporphyrin vibrations are strongly resonance enhanced. Several metal-ligand vibrations have already been observed by RR spectroscopy.[11,23-25] We have, therefore, attempted to observe them in inert-gas matrices by RR spectroscopy. However, new bands due to adduct formation were not discernible in the low-frequency region. When Co(TPP) was deposited in pure ^{12}CO matrices, two new bands were observed at 248 and 237 cm^{-1} which were shifted to 244 and 231 cm^{-1}, respectively, by the ^{12}CO–^{13}CO substitution (Figure 5). Other bands were insensitive to the isotope substitution and found to be attributable to Co(TPP) itself (see Figure 2). Previously, Huber et al.[26] assigned the M–C stretching frequencies of Cu(CO)$_n$, Ag(CO)$_n$, and Au(CO)$_m$ (n = 1–3, m = 1, 2) at 375–325, ~250, and <200 cm^{-1}, respectively. Thus, the bands observed near 240 cm^{-1} may be assigned to the Co–C stretching modes of the Co(TPP)(CO)$_n$ adducts although they conceivably contain slight Co–C–O bending character.[27] The bands at 248 and 237 cm^{-1} have been assigned to Co(TPP)(CO) and Co(TPP)(CO)$_2$, respectively, due to the following reasons. (1) In general, the higher the ν(CO), the lower the ν(Co–C). Since the ν(CO) of the 1:2 adduct is higher than that of the 1:1 adduct (vide supra), the ν(Co–C) of the former should be lower than that of the latter. (2) The relative intensities of these two peaks are consistent with the expectation that the 1:2 adduct should be dominant in pure CO matrices.

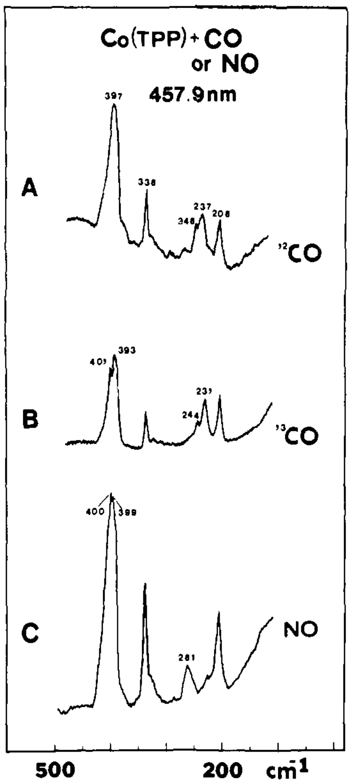


Figure 5. RR spectra (457.9-nm excitation) of Co(TPP) deposited in pure ^{12}CO (A), ^{13}CO (B), and NO (C) matrices at 15 K.

Nitric Oxide Adducts. Trace A of Figure 6 shows the IR spectrum of NO in an Ar matrix. According to Fateley et al.,[28] the bands at 1875, 1866, and 1778 cm^{-1} are due to the NO monomer, the symmetric and antisymmetric stretching vibrations of the cis dimer, respectively. The shoulder band at 1766 cm^{-1}

---

(20) A. Dedieu, M. M. Rohmer, and A. Veillard in "Metal-Ligand Interactions in Organic Chemistry and Biochemistry", B. Pullman and N. Goldblum, Eds., Part 2, Reidel, Dordrecht, Holland, 1977, p 101.

(21) S. M. Peng and J. A. Ibers, *J. Am. Chem. Soc.*, **98**, 8032 (1976).

(22) M. Moskovits and G. A. Ozin, "Cryochemistry", Wiley, New York, 1976.

(23) N. Ohta, W. Scheuermann, K. Nakamoto, Y. Matsuda, S. Yamada, and Y. Murakami, *Inorg. Chem.*, **18**, 457 (1979).

(24) J. M. Burke, J. R. Kincaid, S. Peters, R. R. Gagne, J. P. Collman, and T. G. Spiro, *J. Am. Chem. Soc.*, **100**, 6083 (1978).

(25) J. Kincaid and K. Nakamoto, *Spectrosc. Lett.*, **9**, 19 (1976).

(26) H. Huber, E. P. Kündig, M. Moskovits, and G. A. Ozin, *J. Am. Chem. Soc.*, **97**, 2097 (1975).

(27) For example, see L. H. Jones, R. S. McDowell, and M. Goldblatt, *J. Chem. Phys.* **48**, 2663 (1968).

(28) W. Fateley, H. Bent, and B. Crawford, Jr., *J. Chem. Phys.*, **31**, 204 (1959).

Table I. Structures and Vibrational Frequencies (cm^{-1}) of 1:1 Complexes

compd	type	$\nu(^{16}O_2)$	$\nu(^{16}O^{18}O)$	$\nu(^{18}O_2)$	$\Delta\nu^a$	$\nu(^{16}O_2)/\nu(^{18}O_2)$	ref
$Co(TPP)(O_2)^b$	asym	1278	1252, 1241	1209	68	1.05	*c*
$Co(HDTT)(py)(O_2)^d$	asym	1137		1078	59	1.05	36
$Co(TPP)(1\text{-}MeIm)(O_2)$	asym	1142		1071	71	1.07	37
hemoglobin(O_2)	asym	1132^e		1065	67	1.06	39, 38, 32
$Li(O_2)^b$	sym	1097	1067	1035	61	1.06	40
$Pd(O_2)^b$	sym	1024	996	967	57	1.06	41
$Ni(O_2)^b$	sym	966	940	914	52	1.06	41
$Fe(O_2)^b$	sym	946	931	911	35	1.04	42
$Ti(OEP)(O_2)$	sym	898					43
$Mn(TPP)(O_2)$	sym	$(844)^f$		803			37

[a] $\nu(^{16}O_2) - \nu(^{18}O_2)$. [b] Inert-gas matrices. [c] Present work. [d] Co(HDTT):(7,8,15,16,17,18-Hexahydro-3,12-dinitrobenzo[*e,m*][1,4,8,11]-tetraazacyclotetradecinato)cobalt(II). [e] Average frequency of two bands at 1156 and 1107 cm^{-1} which are split by Fermi resonance (ref 39). [f] Hidden by the solvent band at 844 cm^{-1} (ref 37).

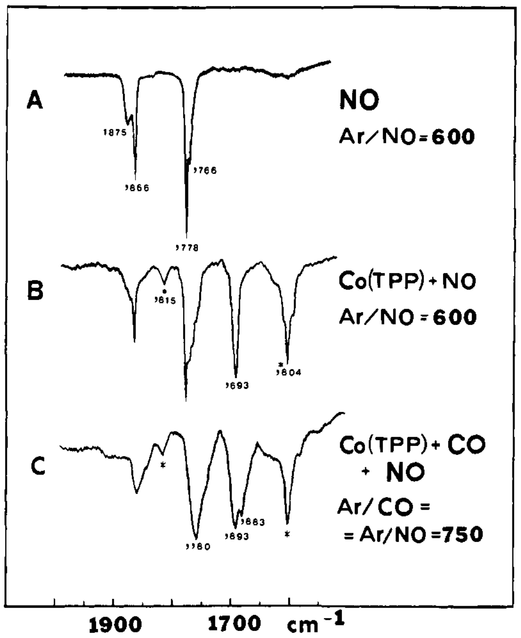


Figure 6. IR spectra of NO (A), Co(TPP) + NO (B), and Co(TPP) + CO + NO (C) in Ar matrices at 15 K. The asterisks indicate the Co(TPP) bands.

may correspond to the antisymmetric vibration of the trans dimer.[29] Trace B is the spectrum of Co(TPP) codeposited with NO diluted in Ar. Two bands at 1815 and 1604 cm^{-1} are due to Co(TPP). A new band appears strongly at 1693 cm^{-1} while the NO monomer band at 1875 cm^{-1} is weakened. The former band is always sharp and its frequency remains unaffected by the change in the Ar/NO ratio from 30 to 2500. We have, therefore, assigned this band to the 1:1 adduct, Co(TPP)(NO). Previously, the ν(NO) of nitrosylporphyrins have been observed for the following compounds: Co(TPP)(NO), ~1700 cm^{-1};[2] Fe(TPP)(NO), 1700 cm^{-1};[30] $Fe(TPP)(NO)_2$, 1870 and 1690 cm^{-1};[30] Mn(TPP)(NO), 1760 cm^{-1};[31] Cr(TPP)(NO), 1700 cm^{-1};[31] hemoglobin-NO, 1615 cm^{-1}.[32] In the present work, we could not obtain any definitive evidence for the formation of $Co(TPP)(NO)_2$ even when relatively high concentrations of NO were used.

According to X-ray analysis, the metal-N-O angles in Co(TPP)(NO).[33] and Fe(TPP)(NO)[34] are 135 and 149°, respectively. These compounds exhibit ν(NO) near 1700 cm^{-1}. Thus, relatively

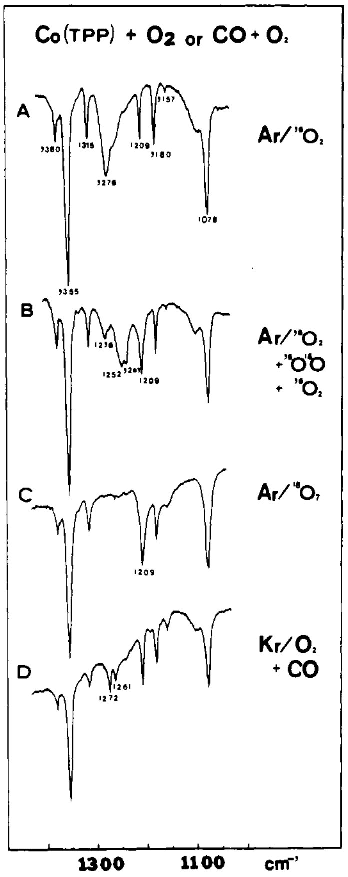


Figure 7. IR spectra of cocondensation products of Co(TPP) with O_2 (15 K). In all cases, the dilution ratio (matrix gas/total ligand gas) was 750. In B, the $^{16}O_2/^{16}O^{18}O/^{18}O_2$ ratio was 3/5/2. In D, the $^{16}O_2$/CO ratio was 1.

low ν(NO) are indicative of bent metal-N-O bonds. In accordance with these observations, Wayland and Olson[30] assigned the 1870- and 1690-cm^{-1} bands of $Fe(TPP)(NO)_2$ to a linear Fe^{II}-NO^+ and a bent Fe^{II}-NO^- groups, respectively.

The RR spectrum of Co(TPP) deposited in a pure NO matrix is shown in trace C of Figure 5. The bands at 400, 398, 338, and 206 cm^{-1} are due to Co(TPP) itself (Figure 2). A broad band at 261 cm^{-1} may be an overlap of the NNO bending vibration of the NO dimer[35] and the Co-NO stretching mixed with the Co-N-O bending vibration.

Molecular Oxygen Adducts. Trace A of Figure 7 shows the IR spectrum of Co(TPP) codeposited with $^{16}O_2$ diluted in Ar ($Ar/^{16}O_2$ = 750) at ~15 K. The band at 1278 cm^{-1} has been

---

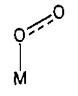
(29) W. A. Guillory and C. E. Hunter, *J. Chem. Phys.*, **50**, 3516 (1969).
(30) B. B. Wayland and L. W. Olson, *J. Am. Chem. Soc.*, **96**, 6037 (1974).
(31) B. B. Wayland, L. W. Olson, and Z. U. Siddiqui, *J. Am. Chem. Soc.*, **98**, 94 (1976).
(32) C. H. Barlow, J. C. Maxwell, W. J. Wallace, and W. S. Caughey, *Biochem. Biophys. Res. Commun.*, **55**, 91 (1973).
(33) W. R. Scheidt and J. L. Hoard, *J. Am. Chem. Soc.*, **95**, 8281 (1973).
(34) W. R. Scheidt and M. E. Frisse, *J. Am. Chem. Soc.*, **97**, 17 (1975).
(35) J. R. Durig and M. G. Griffin, *J. Raman Spectrosc.*, **5**, 273 (1976).
(36) T. Szymanski, T. W. Cape, R. P. Van Duyne, and F. Basolo, *J. Chem. Soc., Chem. Commun.*, 5 (1979).

assigned to the $\nu(O_2)$ of the 1:1 adduct, $Co(TPP)(O_2)$, due to the following reasons. (1) All other bands were observed for Co(TPP) itself. (2) When the matrix was warmed to 40 K, only this band disappeared. (3) The shape and frequency of this band did not change when the Ar/O_2 ratio was changed from 2500 to 30. (4) When Co(TPP) was codeposited with $^{18}O_2$ diluted in Ar, the 1278-cm^{-1} band disappeared and the band at 1209 cm^{-1} became stronger than the ligand band at 1180 cm^{-1} (trace C). This result clearly indicates that the 1278-cm^{-1} band was shifted to 1209 cm^{-1} by the $^{16}O_2$–$^{18}O_2$ substitution.

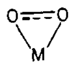
Table I lists the vibrational frequencies and structures of typical 1:1 ($metal/O_2$) complexes. In general, 1:1 molecular oxygen adducts are classified into two types; the superoxo type which exhibits $\nu(O_2)$ in the 1200–1130-cm^{-1} region and the peroxo type which exhibits $\nu(O_2)$ in the 935–800-cm^{-1} region.[1] As is shown in Table I, however, the cocondensation products of metal atoms such as Li,[40] Au,[44] Pd,[41] Ni,[41] Pt,[41] and Fe[42] with O_2 in inert-gas matrices exhibit their $\nu(O_2)$ between these two regions. The $\nu(O_2)$ of $Co(TPP)(O_2)$ observed in this work is clearly outside of the superoxo range and is higher than that of $Co(TPP)(1\text{-MeIm})O_2$ by 136 cm^{-1}.[37] We attribute this large shift to the effect of the axial ligand in the latter since such a base increases the negative charge on the O_2 via the σ or π donation (for the MO discussion, see next section).

Recently, we have found a similar trend for $[Co(salen)]_2O_2$[45] and its pyridine adduct $[Co(salen)py]_2O_2$;[46] the former exhibits $\nu(O_2)$ at 1011 cm^{-1} ($\nu(^{18}O_2)$ at 943 cm^{-1}) whereas the latter shows $\nu(O_2)$ at 888 cm^{-1} ($\nu(^{18}O_2)$ at 833 cm^{-1}). Thus, coordination of pyridine at the axial position lowered $\nu(O_2)$ by 123 cm^{-1} in this case. It was not possible, previously, to make such comparisons since no data were available on $\nu(O_2)$ of molecular oxygen adducts without base ligands. Apparently, the effect of a base ligand on $\nu(O_2)$ is substantial, and this should be reflected on all other properties of molecular oxygen adducts. These examples demonstrate that the $\nu(O_2)$ can be varied in a wide range depending upon the nature of the metal which is governed by its surrounding groups.

The O_2 molecule may bind to the metal either in the asymmetric end-on (**1**) or symmetric side-on fashion (**2**). Distinction of these



1



2

two geometries can be made by using the isotope scrambling technique.[40,41] For **1**, a four-peak spectrum is expected since the $\nu(O_2)$ of the M–$^{16}O^{16}O$, M–$^{16}O^{18}O$, M–$^{18}O^{16}O$, and M–$^{18}O^{18}O$ species are different. However, the latter should give a three-peak spectrum since only one adduct is formed with $^{16}O^{18}O$. Trace B of Figure 7 shows the IR spectrum of Co(TPP) cocondensed with a mixture of these isotopic oxygens diluted in Ar. In addition to the bands at 1278 ($^{16}O_2$ adduct) and 1209 cm^{-1} (an overlap of the $\nu(^{18}O_2)$ with a ligand band), two bands are observed at 1252 and 1241 cm^{-1} which can be assigned to the Co–$^{16}O^{18}O$ and Co–$^{18}O^{16}O$ species, respectively. These assignments are based on the previous work on oxyhemerythrin by Kurtz et al.,[47] who attributed the bands at 845, 825, 818, and 797 cm^{-1} to the Fe–$^{16}O^{16}O$, Fe$^{16}O^{18}O$, Fe–$^{18}O^{16}O$, and Fe–$^{18}O^{18}O$, respectively. The separation of the two central peaks is 11 cm^{-1} for $Co(TPP)O_2$ and 7 cm^{-1} for oxyhemerythrin. The ratio of these two values (1.57) is close to that of the $\nu(O_2)$ of these two compounds ((1252–1241)/(825–818) = 1.52). In contrast to $Co(TPP)O_2$, all the $M(O_2)_n$ (n = 1, 2) type adducts in inert-gas matrices take the symmetric side-on structure (**2**) as evidenced by the isotope scrambling technique.[41,44]

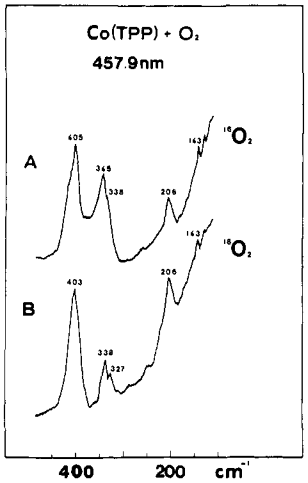


Figure 8. RR spectra (457.9-nm excitation) of Co(TPP) deposited in pure $^{16}O_2$ (A) and $^{18}O_2$ (B) matrices at 15 K.

Table II. Effect of Coordination on Vibrational Frequencies (cm^{-1})

L	$\nu(L)^a$	$\nu(HbL)^b$	$\Delta\nu/\nu(L)$	$\nu(Co(TPP)L)$	$\Delta\nu/\nu(L)$	$\nu(CoL)$
CO	2144^c	1951^c	0.09	2073^d	0.03	248^d
NO	1875^d	1615^e	0.14	1693^d	0.10	$(261)^{d,f}$
O_2	1580^g	1132^h	0.28	1278^d	0.19	345^d

[a] Free state. [b] Hemoglobin(Hb)–L adduct. [c] Reference 50. [d] Present work. [e] Reference 32. [f] Uncertain (see text). [g] Reference 51. [h] Reference 39.

Figure 8 shows the RR spectra of Co(TPP) deposited in pure $^{16}O_2$ and $^{18}O_2$ matrices at ~15 K. The band at 345 cm^{-1} in a $^{16}O_2$ matrix shifted to 327 cm^{-1} when $^{18}O_2$ was used as the matrix gas. Thus, these bands have been assigned to the Co–O_2 stretch. The band at 338 cm^{-1} is due to Co(TPP) (see Figure 2). Thus far, $\nu(Co–O_2)$ are known for 2:1 adducts such as $[Co(salen)B]_2O_2$ (542 cm^{-1} for B = py and 535 cm^{-1} for B = pyO)[46] and $[Co(salen)]_2O_2$ (533 and ~380 cm^{-1}).[45] No information was available on $\nu(Co–O_2)$ of 1:1 adducts such as $Co(TPP)O_2$. On the other hand, $\nu(Fe–O_2)$ of 1:1 adducts are known for oxyhemoglobin (567 cm^{-1})[48] and $Fe(T_{piv}PP)(1\text{-MeIm})O_2$ (568 cm^{-1}).[24] The relatively low $\nu(Co–O_2)$ value of $Co(TPP)O_2$ indicates that the Co–O_2 bond of this adduct is much weaker than those of the other adducts mentioned above.

Trends in Vibrational Frequencies. Table II compares the vibrational frequencies of the three ligands (L) in the free state with those of the adducts with hemoglobin (Hb) and Co(TPP). The relative shifts, $\Delta\nu/\nu(L)$ of these ligand vibrations follow the order O_2 > NO > CO, in both cases, and are slightly larger for the hemoglobin than for the Co(TPP) series. According to current MO theories[2,49] the π^* orbital of the X≡Y ligand splits into two levels (π^*_a and π^*_b) due to the bending of the M—X≡Y bond, and the main interaction (σ type) occurs between the metal d_{z^2} and the ligand π^*_a orbitals as shown in Figure 9. It is known

---

[37] R. D. Jones, J. R. Budge, P. E. Ellis, Jr., J. E. Linard, D. A. Summerville, and F. Basolo, *J. Organomet. Chem.*, **181**, 151 (1979).

[38] J. C. Maxwell, J. A. Volpe, C. H. Barlow, and W. S. Caughey, *Biochem. Biophys. Res. Commun.*, **58**, 166 (1974).

[39] J. O. Alben, *Porphyrins*, **3**, 334 (1978).

[40] L. Andrews, *J. Chem. Phys.*, **50**, 4288 (1969).

[41] H. Huber, W. Klotzbücher, G. A. Ozin, and A. Vander Voet, *Can. J. Chem.*, **51**, 2722 (1973).

[42] S. Abramowitz, N. Acquista, and I. W. Levin, *Chem. Phys. Lett.*, **50**, 423 (1977).

[43] R. Guilard, M. Fontesse, P. Fournari, C. Lecomte, and J. Protas, *J. Chem. Soc., Chem. Commun.*, 161 (1976).

[44] D. McIntosh and G. A. Ozin, *Inorg. Chem.*, **15**, 2869 (1976).

[45] M. Suzuki, T. Ishiguro, M. Kozuka, and K. Nakamoto, to be submitted for publication.

[46] K. Nakamoto, M. Suzuki, T. Ishiguro, M. Kozuka, Y. Nishida and S. Kida, *Inorg. Chem.*, **19**, 2822 (1980).

[47] D. M. Kurtz, Jr., D. F. Shriver, and I. M. Klotz, *J. Am. Chem. Soc.*, **98**, 5033 (1976).

[48] H. Brunner, *Naturwissenschaften*, **61**, 129 (1974).

[49] For example, see A. Dedieu, M. M. Rohmer, and A. Veillard, *J. Am. Chem. Soc.*, **98**, 5789 (1976).

[50] J. O. Alben and W. S. Caughey, *Biochemistry*, **7**, 175 (1968).

[51] G. Herzberg, "Spectra of Diatomic Molecules", Van Nostrand, New York, 1950.

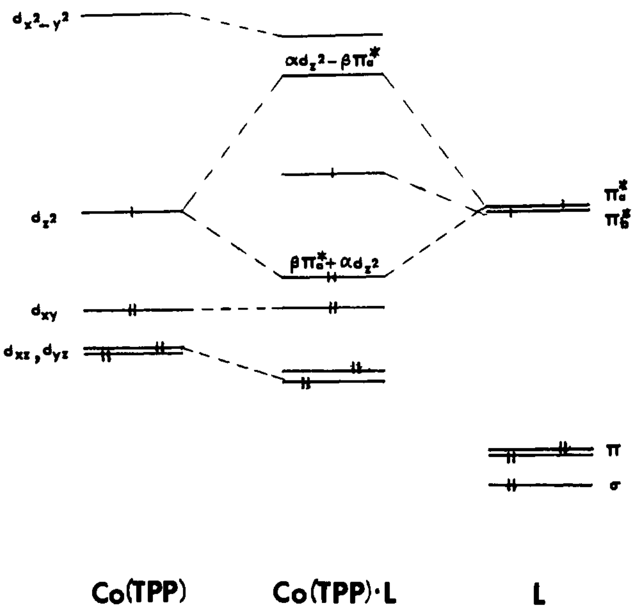


Figure 9. Schematic MO diagram for the bent Co(TPP)L adduct.

that the π^* level is raised monotonically in going from O_2 to NO to CO.[2] Suppose that the π^* level is much lower, slightly lower, and higher for O_2, NO, and CO, respectively, relative to the d_{z^2} level. Then, the net electron drift from the metal to the antibonding π^* orbital would increase in the order CO < NO < O_2, and this could account for the observed trend in the $\Delta\nu/\nu(L)$ values. The effect of the base ligand on $\nu(O_2)$ discussed in the preceding section can also be understood in terms of the same MO scheme since electron donors such as 1-MeIm and py raise the d_{z^2} orbital, thus shifting more electrons to the O_2.[49]

It should be noted that the order of $\Delta\nu(\nu(L)$ for the HbL series has no direct relationship with the thermodynamic stability order of these adducts: NO ≫ CO > O_2.[52] This is understandable since the latter is a function of ΔG (=G(HbL) − G(Hb) − G(L)) while the former depends only upon the change in the L bond order due to complexation. Thus, it includes no ΔS or ΔH effect of structural changes in Hb upon adduct formation. Although the stability constants are not available for the Co(TPP)L series, the fact that Co(TPP)NO can be isolated as crystals whereas Co(TPP)O_2 exists only in solution[2] or in inert-gas matrices at low temperatures seems to suggest the similar stability order.

Mixed-Ligand Adducts. Previously, Wayland et al.[2] detected the formation of Co(TPP)(CO)(O_2) by ESR spectroscopy. We have, therefore, carried out cocondensation reactions of Co(TPP) with CO + O_2 and CO + NO diluted in Ar or Kr. It was not possible to study the NO + O_2 system since O_2 immediately oxidizes NO. Trace D of Figure 7 shows the IR spectrum of Co(TPP) codeposited with a mixed gas, CO + O_2, diluted in Kr (Kr/O_2 = Kr/CO = 750). All the bands except those at 1272 and 1261 cm^{-1} can be identified as the Co(TPP) bands. Co(TPP)O_2 exhibits $\nu(O_2)$ at 1272 cm^{-1} in Kr matrices. Thus, the 1261-cm^{-1} band has been assigned to the $\nu(O_2)$ of Co(TPP)(CO)(O_2). Trace C of Figure 6 shows the IR spectrum of Co(TPP) codeposited with a mixed gas, CO + NO, diluted in Ar (Ar/CO = Ar/NO = 750). As discussed in the preceding section, the band at 1693 cm^{-1} is due to the ν(NO) of Co(TPP)(NO). We have, therefore, assigned the band at 1683 cm^{-1} to Co(TPP)(CO)(NO). The low-frequency shift of $\nu(O_2)$ or ν(NO) caused by the CO coordination at the trans position can be understood in terms of its donor ability which makes the O_2 or NO more electronegative.[49]

Table III. Vibrational Frequencies (cm^{-1}) of Co(TPP) Adducts in Ar and Kr Matrices

	IR[a]	RR[a]
adduct	ν(CO), ν(NO), $\nu(O_2)$	ν(Co–L)
Co(TPP)$(CO)_2$	2078 [Ar], 2077 [Kr]	237 [CO]
Co(TPP)(CO)	2073 [Kr]	248 [CO]
Co(TPP)$(^{13}CO)_2$	2032 [Ar]	231 [^{13}CO]
Co(TPP)(^{13}CO)		244 [^{13}CO]
Co(TPP)(NO)	1693 [Ar], 1690 [Kr]	261 [NO][c]
Co(TPP)($^{16}O_2$)	1278 [Ar], 1272 [Kr]	345 [$^{16}O_2$]
Co(TPP)($^{16}O^{18}O$)	1252 [Ar] 1241 [Ar]	
Co(TPP)($^{18}O_2$)	1209 [Ar], 1207 [Kr]	
Co(TPP)(CO)(O_2)	2089 [Ar] 2089 [Kr] 1261 [Ar] 1261 [Kr]	
Co(TPP)(CO)(NO)	~2078 [Ar][c] ~2077 [Kr][b] 1683 [Ar] 1685 [Kr]	

[a] The matrix gas used is shown in the brackets. [b] Overlap with Co(TPP)$(CO)_n$ bands. [c] Uncertain.

In the high-frequency region, a new ν(CO) appeared at 2089 cm^{-1} when Co(TPP) was codeposited with CO + O_2 diluted in Ar. This frequency is higher than ν(CO) of Co(TPP)(CO) (2073 cm^{-1}), indicating that the CO of the latter complex acted as a σ donor. In the case of CO + NO, no such new ν(CO) was observed probably because the difference in electronic properties between CO and NO is too small to warrant a separate peak due to Co(TPP)(CO)(NO).

Table III summarizes the frequencies of the L and Co–L vibrations of the Co(TPP)L and Co(TPP)LL′ series obtained in this work. The vibrational frequencies of the Co(TPP) core of these adducts were almost identical with those of Co(TPP) itself. Previously, Woodruff et al.[53] measured the RR spectra of oxy- and deoxycobalt(II) myoglobins containing several Co^{II} porphyrins and concluded that neither environmental nor specific axial ligand electronic effects cause any appreciable distortion of the Co–porphyrin core since their vibrational frequencies change very little by these effects. Apparently, a similar conclusion is applicable to the present study.

Acknowledgment. This work was supported by a grant from National Science Foundation (CHE-7915169). The authors acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support and are grateful to Professor James Kincaid of the University of Kentucky for his generous gifts of Co(TPP) and its deuterio derivatives and to Professor Masatatsu Suzuki of Kyushu University for his helpful discussions.

---

(52) E. Antonini and M. Brunori, *Front. Biol.*, **21**, 276 (1971).

(53) W. H. Woodruff, D. H. Adams, T. G. Spiro, and T. Yonetani, *J. Am. Chem. Soc.*, **97**, 1695 (1975).