Resonance Raman characterization of five-coordinate dioxygen adducts of porphyrinatocobalt(II) complexes formed in low temperature O_2 matrices†

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Resonance Raman (RR) spectra of five-coordinate dioxygen adducts of cobalt(tetramesitylporphine) and cobalt(tetramesopropylporphine) formed in low temperature O_2 matrices are reported. For the first time, all three vibrations expected for the Co—O_2 fragment, ν(O—O), ν(Co—O_2) and δ(Co—O—O), were observed for $^{16}O_2$ and $^{18}O_2$ isotopomers. These bands have been assigned based on oxygen isotope shift data as well as normal coordinate analysis of the Co—O_2 moiety. This work presents also the first observation of two distinct ν(O—O) bands due to the Co—^{16}O—^{18}O and Co—^{18}O—^{16}O isomers in 'end-on' type dioxygen adducts. The mechanism of resonance enhancement, the effect of the axial ligand on the ν(O—O) and ν(Co—O_2) frequencies and the differences in metal—O_2 bonding between cobalt and iron porphyrins are discussed.

Resonance Raman (RR) spectroscopy is a potentially effective probe for studying the structure and bonding of dioxygen adducts of heme proteins and their model compounds.[1] In favourable cases, spectral features associated with ν(O—O), ν(M—O_2) and δ(M—O—O) (M being a metal), where ν and δ are stretching and bending vibrations, respectively, can be identified in the RR spectra by using isotopically labeled compounds. Unfortunately, resonance enhancement of the ν(O—O) mode of native heme proteins and iron porphyrins has not been successful for those containing nitrogeneous axial ligands. This is probably due to the absence of the Fe—O_2 charge transfer (CT) transition in the visible range.[2] However, the ν(Fe—O_2) and δ(Fe—O—O) vibrations have been observed for a number of heme proteins.[3,4] On the other hand, the ν(O—O) and ν(Co—O_2) vibrations of dioxygen adducts of Co-substituted hemoglobin, myoglobin and their model compounds can be resonance enhanced.[5–7] However, these spectra are rather difficult to interpret because of the appearance of several oxygen isotope sensitive bands that arise from vibrational coupling between ν(O—O) and internal modes of the nitrogeneous axial ligand.[8–10]

Although a large amount of RR data is available on six-coordinate dioxygen adducts of cobalt porphyrins, only two studies have been reported, thus far, on five-coordinate Co(porphyrin)O_2 [11,12] since these compounds are extremely unstable and can be formed only in low temperature matrices. The ν(Co—O_2) stretch of Co(TPP)O_2, where TPP denotes the tetraphenylporphinato dianion, was first assigned to the band at 345 cm^{-1} in the RR spectrum of Co(TPP) cocondensed with O_2 in a low temperature O_2 matrix.[11] Recently, by using a β-pyrrole deuteriated analogue of TPP, TPP-d_8, which has no vibrations in the 350 cm^{-1} region, we[12] were able to show that the 345 cm^{-1} band is due to a TPP macrocycle mode. At that time we could not locate the ν(Co—$^{16}O_2$) vibration because it is very weak and overlapped by a strong TPP-d_8 band at 383 cm^{-1}. However, the broad shoulder at 369 cm^{-1}, observed for the $^{18}O_2$ adduct only, was assigned to the ν(Co—$^{18}O_2$) mode of Co(TPP-d_8)$^{18}O_2$.[12]

In this work we report the simultaneous observation of all three modes expected for the Co—O_2 moiety, ν(O—O), ν(Co—O_2) and δ(Co—O—O), of five-coordinate Co(TMP)O_2 and Co(MPR)O_2, where TMP and MPR denote the tetramesitylporphinato and tetramesopropylporphinato dianions, respectively. Our assignments are based on $^{16}O_2/^{18}O_2$ isotope shifts. We also performed normal coordinate analysis (NCA) based on the generalized valence force field (GVFF) model[13] and discuss the effect of the Co—O—O bond angle variation on the Co—O_2 stretching frequency. Additionally, we calculated potential energy distributions (PED) by using a standard procedure[14] to estimate the degree of vibrational mixing between ν(Co—O_2) and δ(Co—O—O).

Experimental

Compounds

H_2TMP was synthesized by the method of Hill and Williamson.[15] To remove tetramesitylchlorine contamination, H_2TMP was refluxed with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in toluene, extracted with sodium dithionite and then chromotographed over basic alumina with freshly distilled dichloromethane.[16] H_2MPR was purchased from Midcentury (Posen, IL) and used without further purification.

The cobalt complexes of these porphyrins were prepared by reaction of cobalt(II) chloride, $CoCl_2$, with the respective porphyrin in the presence of 2,6-dimethylpyridine in refluxing dry tetrahydrofuran, THF, under a nitrogen atmosphere. The complexes obtained were then purified by chromatography on

† *Non-SI unit employed*: 1 Torr ≈ 133 Pa.

an alumina column according to the procedure of Collman *et al.*[17]

Samples of $^{16}O_2$ (prepurified, 99.9%) and $^{18}O_2$ (97% pure) were purchased from Matheson Gas and ICON Services, respectively. 'Scrambled' dioxygen ($^{16}O_2 : {}^{16}O\,{}^{18}O : {}^{18}O_2 = 1 : 2 : 1$) was prepared *via* electrical discharge of an equimolar mixture of $^{16}O_2$ and $^{18}O_2$. Ozone formed during this process was decomposed by activated 4A molecular sieves inserted into a reaction flask. The final mixing ratio of all oxygen isotopic molecules was determined by Raman measurements of the reaction mixture.

Spectral measurements

RR spectra of five-coordinate base-free dioxygen adducts of cobalt porphyrins were obtained by using the miniature oven technique.[18] Thus, a sample of porphyrinatocobalt(II) was placed in a miniature graphite oven and heated to about 150–180 °C in a vacuum ($\approx 10^{-5}$ Torr) to remove any volatile contaminants. Then, the sample was vaporized by heating the oven to 300–350 °C and co-condensed with O_2 on a copper cold tip, which was cooled to about 25 K by a CTI Model 21 closed-cycle helium refrigerator. A back-scattering geometry was set up with a cylindrical lens to produce a line focus on the sample surface to avoid possible thermal decomposition of the samples.[19]

RR spectra were recorded on a Spex Model 1403 double monochromator fitted with a Hamamatsu R-928 photomultiplier and a Spex DM1B computer. Four scans were accumulated to obtain the RR spectra presented in this work. A Coherent Innova 100-K3 krypton ion laser was used for 406.7 nm excitation. The power at the sample was kept at *ca.* 5 mW. A spectral band pass of 4 cm^{-1} was routinely used. The accuracy of a frequency reading was ± 1 cm^{-1}.

Results and discussion

Co(TMP)O_2

The RR spectrum (406.7 nm excitation) of the $^{16}O_2$ adduct of Co(TMP) is shown in Fig. 1(A). In the high frequency region this adduct is characterized by the band at 1270 cm^{-1}, which is shifted to 1200 cm^{-1} upon $^{16}O_2/^{18}O_2$ substitution [Fig. 1(B)]. These bands are easily identified as $\nu(^{16}O—{}^{16}O)$ and $\nu(^{18}O—{}^{18}O)$, respectively, of Co(TMP)O_2. The observed isotopic shift of 70 cm^{-1} is in good agreement with the theoretically predicted value for the O—O diatomic harmonic oscillator (72 cm^{-1}). These frequencies are also in good agreement with those reported previously for Co(TPP-d_8)O_2 (RR studies[12]), Co(TPP)O_2 and Co(OEP)O_2 (IR studies[11,20]).

As was demonstrated previously,[11] the dioxygen in 'base-free' Co(TPP)O_2 takes an end-on geometry. This is based on the evidence that when a metal porphyrin reacts with $^{16}O\,{}^{18}O$ in scrambled dioxygen, the end-on adduct having non-equivalent oxygen atoms exhibits two $\nu(^{16}O—{}^{18}O)$ bands {namely ν[(metal)—^{16}O—^{18}O] and ν[(metal)—^{18}O—^{16}O]}, while the side-on adduct, having equivalent oxygen atoms, shows only one $\nu(^{16}O—{}^{18}O)$. In this study we also performed experiments with scrambled dioxygen [Fig. 1(C)]. In the high frequency region, two new bands appear in addition to those already discussed. One is clearly observed at 1241 cm^{-1}, while the second occurs at around 1230 cm^{-1} as a shoulder on the 1234 cm^{-1} porphyrin band. Thus, these bands are readily assignable to the ν[(Co)—^{16}O—^{18}O] and ν[(Co)—^{18}O—^{16}O] vibrations, respectively.[11,21] The present results clearly demonstrate that the O_2 molecule binds to Co(TMP) in the asymmetric end-on fashion. Such end-on structures are also known for six-coordinate dioxygen adducts of cobalt porhyrins,[1,8–10] cobalt-substituted heme proteins[1,5–7] and cobalt Schiff bases of the η^1 type.[22–25] However, this is the first report on the RR observation of two non-equivalent $\nu(^{16}O—{}^{18}O)$, which are characteristic of the end-on dioxygen geometry.

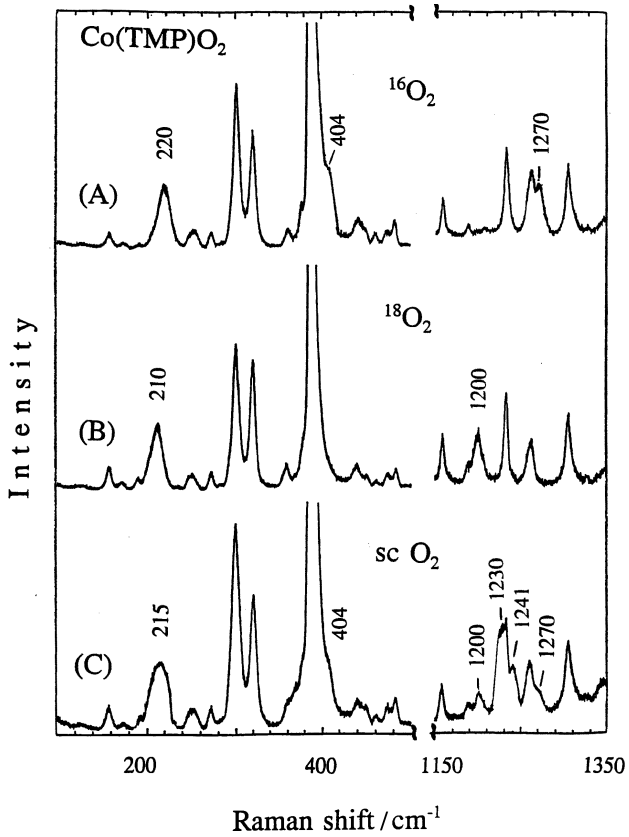

Fig. 1 Resonance Raman spectra of Co(TMP) co-condensed with dioxygen at 25 K (406.7 nm excitation). (A) $^{16}O_2$; (B) $^{18}O_2$; (C) scrambled O_2.

In the low frequency region the RR spectrum of the $^{16}O_2$ adduct of Co(TMP) exhibits two oxygen isotope sensitive bands at 404 (as a shoulder on a very strong porphyrin band at around 390 cm^{-1}) and 220 cm^{-1} [Fig. 1(A)]. Upon $^{16}O_2/^{18}O_2$ substitution these bands are downshifted; the 404 cm^{-1} band disappears since it is apparently shifted under the strong 390 cm^{-1} macrocycle band, while the 220 cm^{-1} band is shifted to 210 cm^{-1}. Based on our previous work[12] and also on NCA calculations (*vide infra*), we assign the 404 and 220 cm^{-1} bands to the $\nu(Co—{}^{16}O_2)$ and $\delta(Co—{}^{16}O—{}^{16}O)$ modes, respectively. We also tried to determine the $\nu(Co—{}^{18}O_2)$ frequency from the difference spectrum (A) − (B) and by using a fitting procedure. However, due to inadequate experimental conditions we were not able to get a clear-cut result.

When scrambled oxygen is used [Fig. 1(C)] the band at 404 cm^{-1} practically disappears since its intensity is 1/4 of that presented in Fig. 1(A). Obviously, the expected $\nu(Co—{}^{16}O{}^{18}O)$ and $\nu(Co—{}^{18}O{}^{16}O)$ bands are hidden under the porphyrin band. Thus, the only oxygen isotope sensitive band seen is at 215 cm^{-1}. Although four Co—O—O bending vibrations are expected when scrambled dioxygen is reacted with the cobalt(II) porphyrin, we observe only a broad and symmetric band at 215 cm^{-1} since their frequencies are expected to be close (within 10 cm^{-1}).

Co(MPR)O_2

Next we measured the RR spectra of Co(MPR)O_2 to observe the $\nu(Co—{}^{16}O_2)$ and $\nu(Co—{}^{18}O_2)$ vibrations, which are expected to have less interference from the porphyrin core deformation mode near 390 cm^{-1}.[1,26] Fig. 2(A) shows the RR spectrum (406.7 nm excitation) of the $^{16}O_2$ adduct of Co(MPR). It exhibits three bands at 1262, 402 (shoulder) and

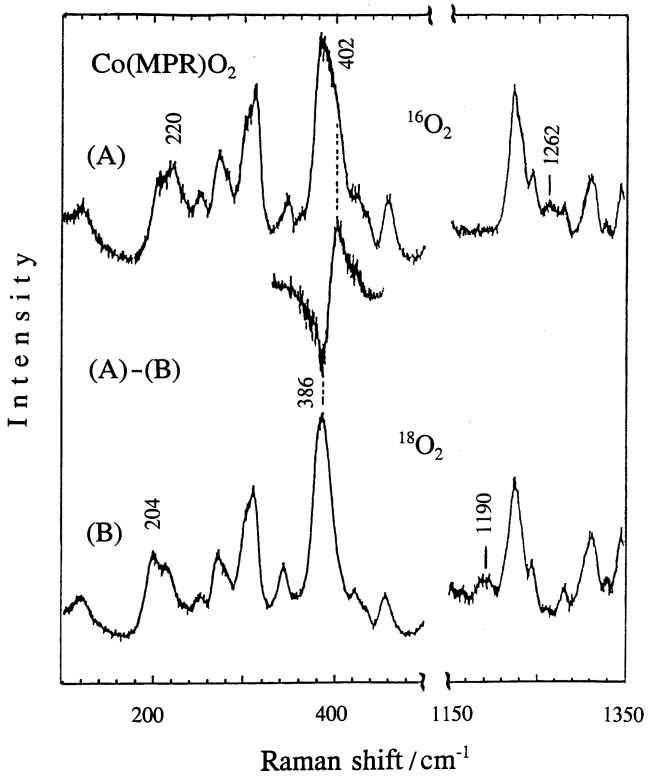

Fig. 2 Resonance Raman spectra of Co(MPR) co-condensed with dioxygen at 25 K (406.7 nm excitation). (A) $^{16}O_2$; (B) $^{18}O_2$. (A) – (B) is the difference spctrum.

220 cm^{-1}. These bands are identified as the $\nu(^{16}O—^{16}O)$, $\nu(Co—^{16}O_2)$ and $\delta(Co—^{16}O—^{16}O)$ modes, respectively, confirming our previous assignments.[12] Upon $^{16}O_2/^{18}O_2$ substitution these bands are shifted to 1190, 386 and 204 cm^{-1}, respectively [Fig. 2(B)]. As can be seen in the middle trace, the difference spectrum (A) – (B) clearly shows the presence of two bands at 402 and 386 cm^{-1}.

Mechanism of RR enhancement

Fig. 1 and 2 show that only weak RR enhancement can be achieved for all three modes expected for the Co—O_2 moiety of Co(TMP)O_2 and Co(MPR)O_2 by using 406.7 nm excitation. No marked differences were noted for RR enhancements by excitation at 413.1 and 415.4 nm.

Thus far, at least three mechanisms have been proposed to account for resonance enhancement of axial vibrations such as $\nu(Co—O_2)$ in metalloporphyrin complexes, namely one direct and two indirect mechanisms. The direct mechanism assumes the presence of a metal—O_2 charge transfer (CT) transition. In cobalt porphyrins, the axial ligand (L) → Co CT transition may occur from filled σ or π ligand orbitals to vacant metal d orbitals, whereas Co → L CT transition may occur from the partially filled d orbitals to vacant π ligand orbitals.[1] Since such CT transitions are localized in the Co—L linkage, the Co—L distance is expected to change appreciably when the laser wavelength is chosen in the Co → L CT region.[27] Although we have not been able to measure the electronic spectrum of Co(porphyrin)O_2 in low temperature O_2 matrices, we anticipate the presence of a strong Soret band at around 410 nm for arylporphyrins and around 390 nm for alkylporphyrins.[28] The fact that the $\nu(Co—O_2)$ and $\nu(O—O)$ vibrations are only weakly enhanced by violet lines from a krypton ion laser does not necessarily exclude the direct mechanism of RR enhancement of these modes. However, a very weak enhancement of these vibrations in Co(MPR)O_2 by violet lines (practically *no enhancement* by using argon ion blue and green lines) and the observation of $\nu(O—O)$ upon yellow excitation (*vide infra*) seem to suggest that the direct mechanism is not responsible for the observed phenomenon. It is interesting to note that the $\nu(Co—O_2)$ and $\nu(O—O)$ stretches of (six-coordinate) oxycobaltmyoglobin, $CoMbO_2$, and oxycobalthemoglobin, $CoHbO_2$, are enhanced through the L → Co CT transition $[\pi^*(\pi_g^*O_2/d_{xz}) \rightarrow \sigma^*(d_{z^2}Co/\pi_g^*)]$ underlying the Soret band.[5] These observations seem to suggest that the nature of the Co—O_2 CT transition is affected strongly upon coordination of a base ligand in the position *trans* to the bound dioxygen.

In metal(porphyrin)L_2 (D_{4h} symmetry) or metal(porphyrin)L (C_{4v} symmetry) complexes, the out-of-plane vibration (A_{1g} and A_1, respectively) can couple with in-plane porphyrin core vibrations of the same symmetry and borrow intensity from the latter.[29] Spiro[30] suggests, however, that such vibrational coupling would be rather weak since the internal coordinates are orthogonal. He prefers direct coupling of the axial ligand vibration to the in-plane electronic transition. Thus, in Co(porphyrin)O_2, the $\nu(Co—O_2)$ mode of A_1 symmetry may be enhanced by the $\pi \rightarrow \pi^*$ transition of the porphyrin core since it alters the Co—O and O—O bond lengths. If so, their excitation profiles should follow that of the electronic absorption spectrum. Then the observed enhancement should be the strongest in the Soret region and become much weaker in the α and β regions.[1,29] Even in the Soret region, however, excitation of the $\nu(Co—O_2)$ and $\nu(O—O)$ modes is expected to be rather weak since the $\pi \rightarrow \pi^*$ transitions are highly localized in the porphyrin core. Thus, the Co—O and O—O bond distances may not change appreciably[27] and the RR enhancement of the $\nu(Co—O_2)$ and $\nu(O—O)$ modes may be weak. In fact, we observed only a very weak $\nu(^{18}O—^{18}O)$ band at 1200 cm^{-1} for Co(TMP)$^{18}O_2$ with excitation at 568.2 nm from a krypton ion laser. This band disappears upon $^{18}O_2/^{16}O_2$ isotopic substitution. Obviously, the $\nu(^{16}O—^{16}O)$ band is too weak to be observed, since it is hidden under a medium to strong porphyrin band (probably B_{2g} mode, which corresponds to ν_{27} of the TPP macrocycle).[31] Thus, we conclude that the $\nu(Co—O_2)$ and $\nu(O—O)$ modes of five-coordinate dioxygen adducts of Co(porphyrins) are probably resonance enhanced through the indirect mechanism proposed by Spiro.[30]

Influence of ligand basicity on the *ν*(O—O) frequency

When the O_2 molecule binds to Co(II) (d^7), the Co—O_2 bond is formed mainly by σ donation from d_{z^2} (Co) to the antibonding $\pi_g^*(O_2)$ orbital, which is only slightly counteracted by π donation in the oposite direction. There is abundant evidence to indicate that nearly one electron is transferred to the dioxygen *via* σ-bonding.[22,23] Thus, the canonical form of the dioxygen adduct can be expressed as Co(III)—O_2^-. In general, the $\nu(O—O)$ frequency decreases as the negative charge on the $2p\pi^*$ orbital of dioxygen increases *via* electron donation from the porphyrin core through the Co atom. Thus, the more acidic the porphyrinato ligand, the less electron density on the metal ion and less σ donation to the dioxygen, resulting in a weaker Co—O_2 bond and a stronger O—O bond. Accordingly, the observed order of the $\nu(O—O)$ frequencies: Co(TPP-d_8)O_2 (1281 cm^{-1}) > Co(OEP)O_2 (1275 cm^{-1}) > Co(TMP)O_2 (1270 cm^{-1}) > Co(MPR)O_2 (1262 cm^{-1}) reflects the order of ligand basicity of these porphyrins. Although the opposite trend is expected for $\nu(Co—O_2)$,[32] it was not possible to confirm it for five-coordinate Co(por)O_2 since their frequencies were too close (404 ± 2–3 cm^{-1}) (Table 1).

Normal coordinate analysis

Previously we carried out NCA on a triatomic Co—O—O moiety of Co(MPR)O_2 by using a set of four force constants.[12] In this work we performed NCA on a bent Co—O—O fragment of Co(TMP)O_2. Since no X-ray data are

Table 1 The ν(O—O), ν(M—O_2), and δ(M—O—O) frequencies (in cm^{-1}) of five-coordinate dioxygen adducts of cobalt and iron porphyrins

Compound	ν(O—O)	ν(M—O_2)	δ(M—O—O)	References
Co(TPP-d_8)O_2	1281	?	216	12
Co(OEP)O_2	1275	407	217	21, 12*b*
Co(TMP)O_2	1270	404	220	this work
Co(MPR)O_2	1262	402	220	this work
Fe(TPP-d_8)O_2	1195	508	345	19
Fe(OEP)O_2	1192	509	?	19
Fe(TMP)O_2	1188	516	343	19

available on five-coordinate Co(porphyrin)O_2 complexes, we used the molecular parameters, which were varied in the following ranges: the O—O distance (R_1) from 1.15 to 1.30 Å, the Co—O distance (R_2) from 1.90 to 2.10 Å, and the Co—O—O angle (θ) from 90° to 180°. Since we were not able to observe the ν(Co—$^{18}O_2$), these parameters were adjusted so that the calculated frequency of ν(Co—$^{18}O_2$) becomes 385 cm^{-1}, that is, almost the same frequency as that observed for Co(MPR)$^{18}O_2$. The best fit of data including both dioxygen isotopomers was obtained for: $R_1 = 1.20$ Å, $R_2 = 2.00$ Å and $\theta = 137.5°$. These values are very close to those used in the Fe(Pc)O_2 calculations,[33] where Pc is the phthalocyanato dianion. A set of six force constants obtained was: $K(R_1) = 7.43$, $K(R_2) = 1.63$, $H(\theta) = 0.26$, $K(R_1, R_2) = 0.10$, $K(R_1, \theta) = 1.8 \times 10^{-5}$, and $K(R_2, \theta) = 0.13$ mdyn $Å^{-1}$. Then we calculated frequency dependences of the ν(^{16}O—^{16}O), ν(Co—$^{16}O_2$), δ(Co—^{16}O—^{16}O) modes (and the same for the $^{18}O_2$ derivative) as a function of θ. The results shown in Fig. 3 clearly indicate that the ν(O—O) frequencies do not change much with variation of θ, whereas the ν(Co—O_2) and δ(Co—O—O) frequencies change dramatically. For example, in the range from 130° to 150°, a slight change of θ (*i.e.*, of 5°) induces a downshift of ν(Co—O_2) and an upshift of δ(Co—O—O) by as much as 10 cm^{-1}. Thus, observation of these low frequency modes is highly important in estimating the Co—O—O angle.

We also calculated the potential energy distributions (PED) for ν(^{16}O—^{16}O), ν(Co—$^{16}O_2$) and δ(Co—^{16}O—^{16}O) as a function of θ as presented in Fig. 4. These results show very small degrees of mixing among these three modes.

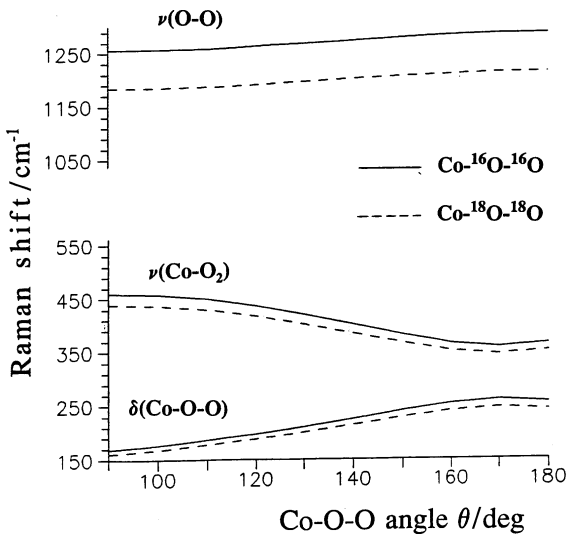

Fig. 3 Plots of theoretical ν(O—O), ν(Co—O_2) and δ(Co—O—O) as a function of the Co—O—O angle (θ). The curves are calculated by using K(O—O), K(Co—O) and H(Co—O—O) values of 7.43, 1.63, and 0.26 mdyn $Å^{-1}$, respectively (see text for details).

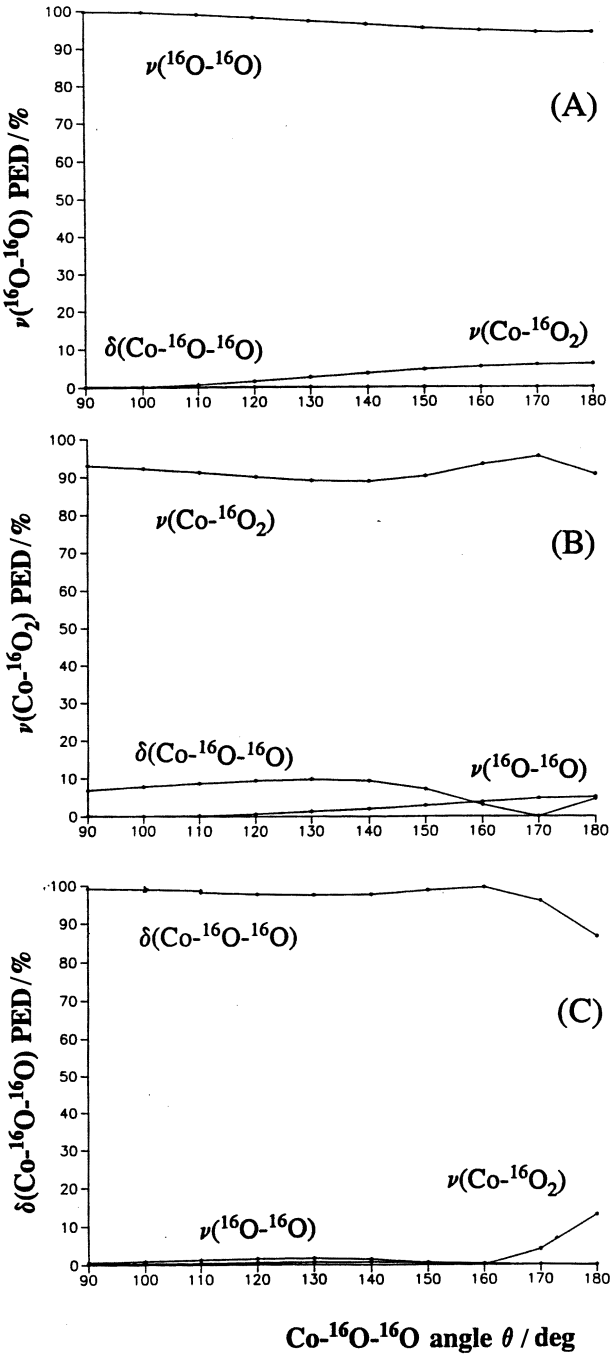

Fig. 4 Potential energy distributions (PED) for: (A) ν(^{16}O—^{16}O); (B) ν(Co—$^{16}O_2$); (C) δ(Co—^{16}O—^{16}O) as a function of the Co—^{16}O—^{16}O angle (θ).

Metal ion effect: Co(III) *versus* Fe(III) in five- and six-coordinate porphyrin dioxygen adducts as heme protein model compounds

Five-coordinate M(porphyrin)O_2 cannot be directly used as model compounds for heme proteins. However, they can serve as a potential probe for understanding the influence of the steric, electronic and other environmental factors on dioxygen binding in naturally occurring heme proteins. The main difficulty in studying these base-free compounds is that they are very unstable and can be obtained exclusively in low temperature matrices.

In contrast to Co(porphyrin), reaction of O_2 with Fe(porphyrin) in the gas phase leads to formation of two types of five-coordinate dioxygen adducts.[19,21] The major product exhibits the ν(^{16}O—^{16}O) mode in the 1188–1223 cm^{-1} range, while the minor one shows it at around 1105 cm^{-1}.[19,21] These

bands have been assigned to the end-on and the side-on isomers, respectively.[21] The latter is thermally unstable and converts reversibly to the end-on isomer upon raising the temperature. These two Fe(porphyrin)O_2 isomers are formed because there are two possible electronic ground state configurations that have been proposed for the square planar Fe(TPP): $(d_{xy})^2(d_{xz}\,d_{yz})^3(d_{z^2})^1$ [34] and $(d_{xy})^2(d_{z^2})^2(d_{xy}\,d_{yz})^2$.[35] The former tends to favour the formation of the end-on, whereas the latter tends to prefer the symmetric side-on structure. Since the energy gap between these two electronic states is small, both isomers are produced in the reaction of Fe(II)(porphyrin) with O_2. The nature of the Fe—O_2 bond in these end-on dioxygen adducts is not fully understood. However, it has been suggested[22,23] that the Fe—O_2 bond is formed by σ donation from the antibonding π_g^* of O_2 to the $3d_{z^2}$ orbital of the iron atom, which is counteracted by π donation from the iron $3d_\pi$ orbitals to the dioxygen antibonding π_g^* orbitals.

Table 1 lists the ν(O—O), ν(M—O_2) and δ(M—O—O) frequencies of the known Co and Fe(por)O_2 end-on adducts. As is clearly seen, all cobalt complexes exhibit ν(O—O) at much higher and ν(M—O_2) at much lower frequencies than the corresponding iron complexes. In general, the ν(O—O) frequency reflects the charge density on the dioxygen: the larger the negative charge on the $2p\pi_g^*$ orbital of dioxygen the lower the ν(O—O) and the higher the ν(M—O_2) frequencies. Thus, the low ν(M—O_2) and high ν(O—O) frequencies reflect weaker M—O_2 and stronger ν(O—O) bonds in the Co than in the Fe complexes. In other words, the results presented in Table 1 suggest that the net negative charge on the dioxygen is less in the five-coordinate cobalt than in the analogous iron complexes.

When a base ligand (in most cases imidazole, pyridine or their derivatives) coordinates to the axial position (*trans* to dioxygen), the ν(O—O) band shifts markedly to lower frequency while the ν(M—O_2) band shifts upward as shown in Table 2. These trends indicate clearly that the *trans* axial ligand increases electron donation to the metal d orbitals, thus enhancing the M—O_2 bond strength and consequently weakening the O—O bond by increasing the net negative charge on the antibonding π_g^* (O_2) orbitals. This effect was quantitatively demonstrated for a series of Co(TPP-d_8)(base)O_2 complexes, where the ν(O—O) frequency decreased linearly as the pK_a of the base increased.[44]

Observed changes in the ν(O—O) and ν(M—O_2) frequencies are more dramatic for cobalt than iron complexes, as expected from the differences in the nature of the Co—O_2 and Fe—O_2 bonds.[22,23] This metal ion effect must be attributed to the multiple bond character of the Fe—O_2 bond relative to the single Co—O_2 bond. In fact, the ν(Fe—O_2) mode is at around 570 cm^{-1} while the ν(Co—O_2) mode is near 520 cm^{-1} in M(por)(base)(O_2). Consequently, coordination of a base ligand causes a downshift of the ν(O—O) band by 'only' 50 cm^{-1} in iron complexes but by 100–150 cm^{-1} in six-coordinate cobalt dioxygen compounds.

Table 2 The ν(O—O) and ν(M—O_2) frequencies (in cm^{-1}) of six-coordinate dioxygen adducts of various cobalt and iron porphyrins and heme proteins

Compound	ν(O—O)	ν(M—O_2)	References
Co(OEP-d_4)(py)O_2	1145	521	36
Co(TPP)(pip)O_2	1142	519	37
Co(PF)(DMI)O_2	1151	527	36, 6
Fe(OEP)(pip)O_2	?	574	38
Fe(TPP)(pip)O_2	1157	575	37
Fe(PF)(NMI)O_2	1159	568	39, 26
$CoHbO_2$	1138	537	7, 19, 5
$CoMbO_2$	1138	539	7, 5
HbO_2	1107	567	40, 41
MbO_2	1103	572	42, 43

Abbreviations: py = pyridine; pip = piperidine; DMI = 1,2-dimethylimidazole; NMI = *N*-methylimidazole; PF = 'picket-fence' porphyrin.

The metal—O_2 stretching frequencies of six-coordinate dioxygen adducts of cobaltous and ferrous porphyrin model compounds are in fairly good agreement with those of hemoglobin (HbO_2), myoglobin (MbO_2) and their cobalt analogues (Table 2). On the other hand, previous infrared[45] and RR studies[5,7,19,46] of these compounds show several oxygen isotope sensitive bands in the ν(O—O) region that have caused controversy in their assignments. Yu and coworkers[5,6] and Potter *et al.*[45] attributed the observed multiple band pattern to two discrete conformers of the dioxygen adducts. Later, Kincaid and coworkers[8–10] have shown that the observed spectra can be interpreted in terms of a single conformer and that the appearance of the multiple oxygen isotope sensitive bands arises from 'vibrational resonance coupling' of the ν(O—O) mode with internal modes of the *trans*-axial histidylimidazole fragment. Using this approach the exact ν(O—O) frequency can be calculated from the observed RR spectra. The existence of a single dioxygen conformer has also been confirmed by Miller and Chance[47] in their recent FT-IR studies on MbO_2.

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