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A Single-Crystal ESR Study on Radicals Derived from rac- and meso-1,2-Dimethyl-1,2-diphenylphosphine Disulfide: Stereochemical Selection in Radical Formation

René A. J. Janssen,* Mark J. van der Woerd, Olav M. Aagaard, and Henk M. Buck

Contribution from the Department of Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands. Received November 23, 1987

Abstract: An ESR study on electron-capture phosphorus centered radicals trapped in single crystals of rac- and meso-1,2-dimethyl-1,2-diphenylphosphine disulfide (MePhP(S)(S)P(S)MePh) is reported. The principal values and axes of the g and hyperfine coupling tensors of the radical anions are determined. It is shown that X irradiation of the two diastereoisomeric compounds results in completely different radical products. The racemate yields a radical product in which the extra electron is symmetrically distributed over the two phosphorus nuclei, whereas for the meso form exclusively asymmetric electronic configurations are detected.

For many years the formation and structure of free radicals, produced by ionizing radiation, has received much attention. Numerous ESR experiments have been performed to elucidate the principles that determine the electronic structure and molecular geometry of the formed doublet species. This has resulted in a detailed understanding of the role of the nucleus at the radical center and of the influence of the surrounding ligands. Stereochemical aspects, however, are not generally included in these analyses. In the present study we report the formation of phosphorus-centered radicals in single crystals of racemic (RR and
S.S) and meso (R,S) 1,2-dimethyl-1,2-diphenyldiphosphine disulfide.

The molecular conformation of diphosphine disulfides in the solid state is characterized by a trans orientation of the two sulfur disulfides in a recent study on X-irradiated tetrasubstituted diphosphine disulfides (R,P(S)P(S)R), also possessing a trans orientation, we showed that the radiation process invariably results in the formation of an electron-capture radical product in which the unpaired electron occupies an antibonding orbital between the two phosphorus nuclei, resulting in a three-electron bond. This structure, which has been established by both single-crystal ESR and ab initio quantum chemical methods, possesses a symmetrical distribution of the unpaired electron:

Depending on the nature of the substituents several other primary and secondary radical configurations were also identified. We will now show that the two diastereoisomeric forms of the title compound give rise to completely different radical products upon X irradiation. The radiation process of the racemate involves the formation of a symmetric species with a three-electron P-P bond as described above. The meso form, on the other hand, yields exclusively asymmetric radical configurations in which the unpaired electron is mainly localized on one of the two phosphorus nuclei. The electronic structure of these radicals as determined by an interpretation of the experimental single-crystal ESR results is presented and compared with theoretical calculations.

Experimental Section

Synthesis. 1,2-Dimethyl-1,2-diphenyldiphosphine disulfide was synthesized from dichlorophenylmercury sulfide and methylmagnesium iodide following a procedure analogous to the one described by Maier. The two diastereoisomeric forms were easily separated by extraction of the crude reaction product with ethanol. The meso form, unsoluble in ethanol, was collected by filtration and recrystallized twice from chloroform. Single crystals of the meso form were prepared by slow evaporation of a chloroform solution in a stream of dry nitrogen. The racemic mixture was purified by preparative chromatography on silica gel. Racemate: 'H NMR (CDCl3) δ 7.58 (m, 3 PhH), 5.13 (m, 2 PhH); 31P NMR (CDCl3) δ 36.55; MS, m/z (rel intensity) 311 (93), 279 (6), 157 (100), 125 (48); mp 202 °C. Racemate: 'H NMR (CDCl3) δ 7.18-7.63 (m, 7 PhH), 3.16 (t, 2 PhH); 31P NMR (CDCl3) δ 37.62; MS, m/z (rel intensity) 311 (11), 279 (11), 157 (100), 125 (42); mp 144 °C.

Irradiation and ESR. Single crystals of rac- and meso-1,2-dimethyl-1,2-diphenyldiphosphine disulfide were mounted on a quartz rod and subsequently sealed in a quartz tube. The crystals were X-irradiated in a glass Dewar vessel containing liquid nitrogen (77 K) with unfiltered radiation from a Cu source operating at 40 kV and 20 mA for 6 h. ESR experiments were performed with a Bruker ER200D spectrometer interfaced with a Bruker Aspect 3000 computer and operating with a X-band standard cavity. Microwave power was set as low as possible, being 2 mW in most experiments. The crystals were rotated perpendicular to the magnetic field with a single-axis goniometer in 10° steps.

Results and Assignment

rac-1,2-Dimethyl-1,2-diphenyldiphosphine Disulfide (1). Although there is no conclusive description of the crystal structure of rac-1,2-dimethyl-1,2-diphenyldiphosphine disulfide (1) it is known that the racemate crystallizes in the triclinic space group P1 with two molecules (R,R and S,S) in the unit cell, centrosymmetrically related to each other. After X irradiation of a single crystal of the racemate at 77 K the ESR spectrum recorded at 105 K shows the weak transitions of at least two different radical species (Figure 1). The outermost features can be assigned to the m1 = 1 and m2 = -1 absorptions of a radical with a hyperfine coupling to two indetical phosphorus nuclei (radical 1a). The large phosphorus hyperfine interaction results in a pronounced splitting between the two central m1 = 0 lines, due to the non-degeneracy of the J = 1, m2 = 0 lines (second-order splitting). The second radical product (1b) was observed at 105 K showing the features of radicals 1a and 1b.

Temperature was controlled with the aid of a variable-temperature unit operating between 90 K and room temperature. ESR parameters were obtained from a second-order analysis of the spectra.

Figure 1. Single-crystal ESR spectrum of X-irradiated rac-1,2-dimethyl-1,2-diphenyldiphosphine disulfide at 105 K showing the features of radicals 1a and 1b.

Figure 2. Angular dependence of the ESR signals due to radicals 1a and 1b.

(5) The ESR spectra of Figures 1 and 4 were obtained from randomly oriented single crystals that were transferred after the X irradiation at 77 K to an unirradiated sample tube in order to remove the overlapping central absorptions due to the irradiated quartz.
Table I. Hyperfine Tensors of Radicals 1a and 1b in rac-1,2-Dimethyl-1,2-diphenyldiphosphine Disulfide

<table>
<thead>
<tr>
<th>Radical</th>
<th>Total Tensor (MHz)</th>
<th>Isotropic (MHz)</th>
<th>Dipolar (MHz)</th>
<th>Direction Cosines</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>1122</td>
<td>1213</td>
<td>-91</td>
<td>-0.013 0.078 0.997</td>
</tr>
<tr>
<td></td>
<td>1143</td>
<td>-70</td>
<td>0.990</td>
<td>-0.136 0.024 0.988</td>
</tr>
<tr>
<td>1b</td>
<td>1374</td>
<td>161</td>
<td>0.137</td>
<td>0.988 0.075 0.998</td>
</tr>
<tr>
<td></td>
<td>803</td>
<td>-239</td>
<td>-0.311</td>
<td>0.668 -0.676 0.002</td>
</tr>
<tr>
<td></td>
<td>867</td>
<td>-175</td>
<td>0.950</td>
<td>0.250 -0.189 0.812</td>
</tr>
<tr>
<td></td>
<td>1456</td>
<td>414</td>
<td>-0.043</td>
<td>0.701 0.712 0.004</td>
</tr>
</tbody>
</table>

Table II. g Tensors of Radicals 1a and 1b

<table>
<thead>
<tr>
<th>Radical</th>
<th>g Principal Values</th>
<th>Direction Cosines</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>1.994</td>
<td>0.005 0.990 -0.140</td>
</tr>
<tr>
<td>1b</td>
<td>2.007</td>
<td>0.087 0.139 0.986</td>
</tr>
<tr>
<td></td>
<td>2.012</td>
<td>0.996 -0.018 -0.086</td>
</tr>
<tr>
<td></td>
<td>2.012</td>
<td>-0.085 0.655 0.751</td>
</tr>
<tr>
<td></td>
<td>2.012</td>
<td>0.921 -0.236 0.310</td>
</tr>
<tr>
<td></td>
<td>2.013</td>
<td>0.380 0.718 0.583</td>
</tr>
</tbody>
</table>

Table III. g Tensors of Radicals 1a and 1b

<table>
<thead>
<tr>
<th>Radical</th>
<th>g Principal Values</th>
<th>Direction Cosines</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>1.994</td>
<td>0.005 0.990 -0.140</td>
</tr>
<tr>
<td>1b</td>
<td>2.007</td>
<td>0.087 0.139 0.986</td>
</tr>
<tr>
<td></td>
<td>2.012</td>
<td>0.996 -0.018 -0.086</td>
</tr>
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</tr>
<tr>
<td></td>
<td>2.012</td>
<td>0.921 -0.236 0.310</td>
</tr>
<tr>
<td></td>
<td>2.013</td>
<td>0.380 0.718 0.583</td>
</tr>
</tbody>
</table>

Figure 3. Structure of radicals 1a and 1b. Table I. Hyperfine Tensors of Radicals 1a and 1b

Radical 1a, exhibiting hyperfine interaction of the unpaired electron with a single phosphorus nucleus.

For all orientations of the single crystal with respect to the magnetic field direction only a single spectrum of the two radicals 1a and 1b is observed. This absence of site splitting is in accordance with the presence of a center of symmetry in the unit cell which results in a coalignment of the S-P-P-S linkages of the magnetic field direction only a single spectrum of the two radicals was obtained by rotating the crystal in three mutual orthogonal planes (Figure 2). For that purpose one of the ESR reference axes was chosen perpendicular to the plate face, the remaining two (y, z) were directed parallel to the extinction directions in the plate face with use of a polarization microscope. A central absorption due to the irradiated quartz tube prevented the observation of the two m values for all orientations of the single crystal. For this reason the hyperfine coupling and g factor of radical 1a were evaluated from the m_x = ± 1 lines, and when possible checked with the m_y = 0 position (s). The principal values and direction cosines of the A and g tensors of radicals 1a and 1b are compiled in Tables I and II. It appears that for both species the direction of the maximum A value (A_x) is close to that of the minimum g value. This is expected because it is the direction of the phosphorus 3p orbital contributing to the singly occupied molecular orbital (SOMO).

Radical 1a is attributed to a three-electron-bond radical (Figure 3), based on the hyperfine coupling to two identical phosphorus nuclei and the values of A = 1213 MHz (A = 1/3(A_x + A_y + A_z)) and B = 161 MHz (B = A_y - A_z), which are close to the corresponding values of three-electron-bond radicals in X-irradiated tetramethyl-, tetraethyl-, and tetraphenyldiphosphine disulfides (1224 < A < 1395 MHz, 155 < B < 173 MHz)^2. The values of the isotropic (A) and dipolar (B) hydrogen couplings are commonly interpreted in terms of atomic valence and p orbital contributions to the SOMO by comparing the experimental couplings to a set of calculated values for the free atom. This analysis, using the atomic parameters compiled by Morton and Preston, results in p = 9.1% and p = 21.9% (p/s = 2.4) for each phosphorus nucleus of 1a.


Figure 5. Angular dependence of the ESR signals due to radicals 2a, 2b, and 2c.

Table III. Hyperfine Tensors of Radicals 2a, 2b, and 2c in meso-1,2-Dimethyl-1,2-diphenyldiphosphine Disulfide

<table>
<thead>
<tr>
<th>Radical</th>
<th>Total Tensor (MHz)</th>
<th>Isotropic Dipolar (MHz)</th>
<th>Direction Cosines</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>1201</td>
<td>1379</td>
<td>x: 0.978 y: 0.384 z: 0.328</td>
</tr>
<tr>
<td></td>
<td>-178</td>
<td>-105</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>1826</td>
<td>1934</td>
<td>x: 0.978 y: 0.384 z: 0.328</td>
</tr>
<tr>
<td></td>
<td>-108</td>
<td>-309</td>
<td></td>
</tr>
<tr>
<td>2c</td>
<td>2103</td>
<td>2316</td>
<td>x: 0.978 y: 0.384 z: 0.328</td>
</tr>
<tr>
<td></td>
<td>-213</td>
<td>-311</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1024</td>
<td>1231</td>
<td>x: 0.978 y: 0.384 z: 0.328</td>
</tr>
<tr>
<td></td>
<td>-108</td>
<td>-309</td>
<td></td>
</tr>
</tbody>
</table>

The ESR spectra of the X-irradiated meso form and the angular variation can be interpreted by assuming the presence of at least four different phosphorus-centered radicals. For three species a clear angular variation is observed; a fourth was undoubtedly present but could not be analyzed. A remarkable aspect of all radical species encountered in the meso compound is the fact that all hyperfine lines show an additional doublet splitting of 1.8 to 3.0 mT, probably due to proton splitting. The hyperfine coupling tensors of the three species labeled 2a, 2b, and 2c are collected in Tables III and IV. The direction cosines in these tables are listed for only one of the four possible sites. The remaining three orientations are symmetry related to (x, y, z) via (x, -y, -z), (-x, y, -z), and (-x, -y, z).

Radical 2a is assigned to a three-electron-bond P-S radical (Figure 6). The estimated atomic orbital spin densities of the central phosphorus atom $\rho_0 = 10.3\%$ and $\rho_p = 44.4\%$ are relatively close to the values found in recent studies on similar radicals generated in tetrasubstituted diphenphane disulfides and trialkylyphosphine sulfides and selendimes. The isotropic hyperfine coupling (3 orbital contribution) of 2a (1379 MHz) is somewhat smaller than that for these related species (1619-1776 MHz), whereas the dipolar interaction (3p orbital contribution) is larger (326 MHz vs 245-315 MHz). This results in an increased p/s ratio of 4.3 for 2a, which is probably due to a small widening of the tetrahedral angle between the P-S bond and the bonds with the remaining three substituents.

Radical 2b is characterized by a high isotropic phosphorus hyperfine coupling (4164 MHz, $\rho_p = 14.4\%$) and a relatively small dipolar interaction ($\beta_p = 164 MHz, \rho_p = 25.3\%$) resulting in a p/s ratio of 1.8. Similar species have not been encountered so far in X-irradiated diphenphane disulfides. This complicates the identification of a radical structure for 2b. The relatively low p/s ratio points to a trigonal-bipyramidal (TBP) radical structure, either with an equatorial (TBP-e) or an apical (TBP-a) location of the unpaired electron. TBP-e structures, identified in tetramethyl- and tetraethyldiphosphine disulfides, exhibit hyperfine coupling to two phosphorus nuclei and their magnitudes are clearly different from those of 2b. We therefore propose a TBP-a like species with the SOMO pointing away from the substituents (Figure 6).

The third species, radical 2c, exhibits hyperfine coupling to two distinct $I = 1/2$ nuclei. The central phosphorus nucleus apparently bears a large amount of spin density since both the isotropic and anisotropic hyperfine couplings are very large, viz., $A_{iso} = 2316 MHz$ and $A_{iso} = 373 MHz$. In fact these values are approximately two times the values of the symmetrical three-electron-bond radical and of the racemate (vide supra). Nevertheless, the possibility that the large coupling is the result of the splitting of one $m_j = 1$ and $m_j = -1$ lines of a phosphorus triplet can be ruled out since the expected $m_j = 0$ transitions are absent. The weak absorptions in the $g = 2$ region of the ESR spectra of the meso form (Figure 4) are not related to the strong lateral absorptions because they are found to be much more persistent upon annealing the single crystal. A second possibility, that the large splitting is the result of a radical pair, one of whose components is a phosphonyl type radical, seems unlikely because no transitions were observed in the half-field region between 70 and 260 mT. This leads to the conclusion that radical 2c is a phosphorus centered radical, exhibiting a large hyperfine coupling to one $^{31}P$ nucleus and a small one to a second. The value of $A_{iso}$ for the central phosphorus atom is appreciably larger than that for the other radicals encountered in X-irradiated disulfide disulfides. We tentatively assign 2c to a radical with an asymmetric three-electron-P-S bond in which the unpaired electron is mainly localized on one of the two phosphorus nuclei (Figure 6). The spin density distribution, estimated from the hyperfine coupling parameters, amounts to

---

Table V. Calculated Isotropic and Anisotropic Hyperfine Coupling Constants for R,R- and meso- Phosphoryl Radicals

<table>
<thead>
<tr>
<th>Radical</th>
<th>Nucleus</th>
<th>(A^\text{iso} )</th>
<th>(B )</th>
<th>Direction cosines</th>
</tr>
</thead>
<tbody>
<tr>
<td>R,R</td>
<td>P, P</td>
<td>0.602 1089</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S, S</td>
<td>0.011</td>
<td></td>
<td></td>
</tr>
<tr>
<td>meso</td>
<td>P, P</td>
<td>0.602 1091</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S, S</td>
<td>0.011</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Relative to the axis system in Figure 7.

\( \rho_m = 17.3\% \) and \( \rho_p = 50.8\% \) for the central atom, and \( \rho_m = 1.0\% \) and \( \rho_p = 11.3\% \) for the adjacent phosphorus nucleus. The directions of the dipolar hyperfine couplings of the two nuclei are inclined by an angle of 13° and therefore almost parallel, supporting the three-electron-bond assignment. Quantum chemical calculations have shown that the magnitudes of \( A^\text{iso} \) in a three-electron-bound phosphoranyl radical can vary strongly with the substituents, possibly accounting for the large angle between the three-electron bond and the remaining three substituents, possibly accounting for the large angle between the three-electron bond and the remaining three substituents.

The intensity of the ESR spectra of 2a, 2b, and 2c decreases slowly upon annealing and the signals are irreversibly lost above 240 K.

Quantum Chemical Calculations

In this section we present a quantum chemical description of symmetrical three-electron-bound radicals in racemic and meso diphosphine disulfide radical anions. Since a full calculation on the two diastereoisomeric forms of the title compound would be very time consuming the calculations were restricted to (R,R)- and meso-1,2-dimethylphosphine disulfide, thereby replacing the phenyl groups by hydrogen atoms. Unrestricted Hartree–Fock (UHF) calculations were performed in order to obtain a theoretical geometry at which the hyperfine coupling parameters could be evaluated. Throughout the calculations a split valence 4-31G basis set\(^{15,16}\) implemented with a single set of six second-order Gaussians was constrained to the point symmetry of the precursor molecules: \( C_2 \) for R,R and \( C_3 \) for meso. Except for the CH bond lengths and the HCP bond angles which were simultaneously evaluated by using two variables, all molecular parameters were fully optimized in an analytical gradient procedure. This resulted in true energy minima for both the R,R and meso forms (Figure 7). Their structures are characterized by a relatively long P–P bond of 2.748 Å and a SPP bond angle of 142.2°. This elongation of the SPP bond is the result of the antibonding nature of the SOMO of these radicals. The isotropic and anisotropic (dipolar) hyperfine couplings were evaluated from the wave function by computing the expectation values of the corresponding operators:

\[
A^\text{iso} = (8\pi/3)g\beta g_N S_3 \left\langle \Psi_0 | \sum_{i<j} r_{ij} \hat{S}_i \hat{S}_j | \Psi_0 \right\rangle
\]

\[
B_{ij} = -3g\beta g_N S_3 \left\langle \Psi_0 | \left( \sum_{i<j} \frac{r_{ij}^2 \hat{S}_i \hat{S}_j}{r^5} \right) | \Psi_0 \right\rangle
\]

After diagonalization of the \( B_{ij} \) matrix the three principal values are obtained, together with their directions relative to the molecular framework. The results of these calculations for the R,R and meso radical anions are compiled in Table V.

The hyperfine properties of the R,R and meso-1,2-dimethylphosphine disulfide radical anion are in quantitative agreement with experiment. The two phosphorus nuclei hold most of the unpaired electron density. The value for \( A^\text{iso} \) is approximately 10% too small compared with radical 1a, whereas the dipolar couplings deviate approximately 17% from experiment. The direction of the largest principal value of the dipolar hyperfine coupling, corresponding to the direction of the phosphorus 3p orbital contributing to the SOMO, makes an angle of 29.1° with the P–P bond. From the direction cosines in Table V it appears that the dipolar couplings of the two phosphorus nuclei are inclined by a small angle of 5.6°. This is a consequence of the \( C_3 \) symmetry of the R,R radical and indicates that the two phosphorus nuclei are not strictly magnetically equivalent for all orientations of a magnetic field.

Although the experiments do not reveal a symmetric three-electron-bond structure for the meso form, the calculations predict a stable geometry for the meso-1,2-dimethylphosphine disulfide radical anion. The hyperfine properties of this radical are very similar to the R,R couplings. However, by symmetry constraint (\( C_3 \)) the principal directions of the dipolar couplings are now completely aligned and hence the phosphorus nuclei are magnetically equivalent.

Discussion

The present study reveals that there are major differences between the radicals generated in rac- and meso-1,2-dimethyl-1,2-diphenyldisulfide disulfide. It is noteworthy that, besides a difference in the nature of the radical configurations, stronger ESR absorptions are found for the meso form than for the racemate, indicating a more efficient electron-capture process. There is no doubt that some variations in the radical configurations between racemate and meso could be expected in advance, because in principle the two diastereoisomers are different compounds. However, their difference is small since it concerns merely the stereochemistry around the phosphorus nuclei. The formation of a specific radical product is usually explained by taking into account the different properties of the substituents such as electronegativity. These arguments cannot be used to account for...
the present observations. The fact that no symmetrical three-electron-bond species are detected for the meso form can also not
be explained by a possible wrong symmetry of the expected SOMO
with respect to geometry of the parent molecule. In fact the CI
point symmetry fits excellently to a hypothetical symmetric ant-
tibonding orbital. This is confirmed by the quantum chemical
calculations that predict stable geometries for both the racemic
and meso form.

Apparently, the addition process of an extra electron to the
diphosphine disulfides is able to discriminate between the several
possible radical configurations in a highly selective way. It is
conceivable that the difference in the formation of the various
and geometric radical configurations is a consequence of the
kinetics of the electron-capture process, rather than the result
of (small) differences in total energy between the final radical
products. In general electron-capture will lead to detectable
electron-gain centers provided there is a relatively fast relaxation
of the electron acceptor.~ The relaxation may take the form of
bond stretching or bending, or bond breaking, and it should lead
to sufficiently deep traps to give detectable radical species. A
possible explanation for the formation of a symmctric species in
the racemate and asymmetric structures in the meso form can
be obtained by assuming that the extra electron reacts with the
tiny-bonding orbital. This is confirmed by the quantum chemical
point symmetry fits excellently to a hypothetical symmetric an-
tibonding orbital. The oxygen transport proteins, hemoglobin (Hb)
and myoglobin (Mb), have been carefully studied in the oxygen-oxygen stretching region. Included in the study are the cobalt analogues of myoglobin (MbCo), hemoglobin
(HbCo), and its isolated subunits (acap and βcap) as well as the iron/cobalt mixed hemoglobin hybrids, (αacapβcap)2 and (αacapβcap)3.

The spectra of the O2(O2) adducts have been measured in both normal
H2O and deuterated (D2O) buffers for each of the proteins. Strong bands located at ~1135, ~1096, and ~1065 cm−1
in H2O solution are identified with v(3O=O), v(2O=O), and v(1O=O), respectively. Shifts of these bands in D2O solution
and the selective appearance of weaker features in the spectra of particular isotopic oxygen adducts are interpreted as the
consequence of vibrational coupling of v(O=O) with internal modes of the proximal and/or the distal histidylimidazole. The
plausibility of this interpretation is supported by the observation of similar behavior in model compound systems which is
documented here and in earlier studies. All of the major and minor features observed in the spectra of the proteins can be
explained without requiring the existence of two liganded (O2) conformers, in contrast to earlier interpretations. In addition,
based on the results of model compound studies, the frequency observed for v(O=O) indicates that the bound dioxygen is hydrogen
bonded to the distal histidylimidazole in these protein systems. However, the present interpretation argues that the frequency
shifts of v(3O=O) observed upon replacement of H2O by D2O cannot be taken as evidence for this distal side hydrogen bonding.
Finally, it is suggested that the spectroscopic consequences of such coupling not only complicate the interpretation of oxygen
adduct spectra but also (in a positive light) may provide a powerful spectroscopic probe of subtle structural perturbations once
they are more fully understood and properly calibrated.

Abstract: The resonance Raman (RR) spectra of the oxygen adducts of cobalt-substituted heme proteins have been carefully
studied in the oxygen–oxygen stretching region. Included in the study are the cobalt analogues of myoglobin (MbCo), hemoglobin
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documented here and in earlier studies. All of the major and minor features observed in the spectra of the proteins can be
explained without requiring the existence of two liganded (O2) conformers, in contrast to earlier interpretations. In addition,
based on the results of model compound studies, the frequency observed for v(O=O) indicates that the bound dioxygen is hydrogen
bonded to the distal histidylimidazole in these protein systems. However, the present interpretation argues that the frequency
shifts of v(3O=O) observed upon replacement of H2O by D2O cannot be taken as evidence for this distal side hydrogen bonding.
Finally, it is suggested that the spectroscopic consequences of such coupling not only complicate the interpretation of oxygen
adduct spectra but also (in a positive light) may provide a powerful spectroscopic probe of subtle structural perturbations once
they are more fully understood and properly calibrated.

Resonance Raman Studies of Dioxygen Adducts of
Cobalt-Substituted Heme Proteins and Model Compounds.
Vibrationally Coupled Dioxygen and the Issues of Multiple
Structures and Distal Side Hydrogen Bonding

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The oxygen transport proteins, hemoglobin (Hb) and myoglobin
(Mb), are perhaps the most thoroughly studied of all biomolecules.1 Despite intensive effort by many research groups and an
extensive body of accumulated knowledge, questions remain un-
answered, even at a rather fundamental level. In fact, knowledge of
the details of O2 structure and bonding at the heme site remains
incomplete. Thus, issues such as the importance of distal side
hydrogen bonding between the bound O2 and the heme pocket
distal histidine2–7 and even the number of stable structures7–9 remain controversial.

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