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A Single-Crystal ESR Study on Radicals Derived from rac- and meso-1,2-Dimethyl-1,2-diphenyldiphosthine 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-diphenyldiphosthine disulfide (MePhP(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 configuration 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 (R,R and (S,S)-MePhP(S)P(S)MePh) in 1988 American Chemical Society

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S,S) and meso (R,S) 1,2-dimethyl-1,2-diphenylphosphine di-sulfide.

The molecular conformation of diphosphine disulfides in the solid state is characterized by a trans orientation of the two sulfur nuclei:

\[
\text{RS} \quad \text{PP} \quad \text{SR}
\]

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.\(^2\) 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:

\[
\text{R} \quad \text{P} \quad \text{S} \quad \text{R}
\]

Depending on the nature of the substituents several other primary and secondary radical configurations were also identified. We will now show that the two diastereoisomers 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-diphenylphosphine disulfide was synthesized from dichlorophenylphosphine sulfide and methyl magnesium iodide following a procedure analogous to the one described by Maier.\(^3\)

The two diastereoisomers 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 form was recrystallized several times from ethanol. Slow evaporation of an ethanolic solution of the racemate afforded needle-shaped crystals. Larger plate-shaped single crystals, more suitable for ESR experiments, were obtained from a slow evaporation of a pentane solution. Meso: \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.97 (m, 3, CH\(_3\)), 7.58 (m, 3, PhH), 8.13 (m, 2, PhH); \(^31\)P NMR (CDCl\(_3\)) \(\delta\) 36.5; MS, \(m/e\) (rel. intensity) 311 (100), 279 (6), 157 (100), 125 (48); mp 202 °C. Racemate: \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 2.46 (m, 3, CH\(_3\)), 7.18-7.63 (m, 5, PhH); \(^31\)P NMR (CDCl\(_3\)) \(\delta\) 37.62; MS, \(m/e\) (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-diphenylphosphine 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-diphenylphosphine Disulfide (1). Although there is no conclusive description of the crystal structure of rac-1,2-dimethyl-1,2-diphenylphosphine 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.\(^4\) 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).\(^5\) The outermost features can be assigned to the \(m_1 = 1\) and \(m_1 = -1\) 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 \(m_1 = 0\) lines, due to the non-degeneracy of the \(J = 1\), \(m_1 = 0\) and \(J = 0\), \(m_1 = 0\) energy levels (second-order splitting).\(^6\) The second radical product (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.

Figure 3. Structure of radicals 1a and 1b.

Table I. Hyperfine Tensors of Radicals 1a and 1b in rac-1,2-Dimethyl-1,2-diphenyldiphosphine Disulfide

<table>
<thead>
<tr>
<th>I</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>x</td>
</tr>
<tr>
<td></td>
<td>1143</td>
<td>1211</td>
<td>70</td>
<td>y</td>
</tr>
<tr>
<td></td>
<td>1374</td>
<td>161</td>
<td>0.137</td>
<td>z</td>
</tr>
<tr>
<td>1b</td>
<td>803</td>
<td>1042</td>
<td>-239</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>867</td>
<td>-175</td>
<td>0.950</td>
<td>y</td>
</tr>
<tr>
<td></td>
<td>1456</td>
<td>414</td>
<td>-0.043</td>
<td>z</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>I</th>
<th>g Tensor</th>
<th>Direction Cosines</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>1.994</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>2.007</td>
<td>0.139</td>
</tr>
<tr>
<td></td>
<td>2.012</td>
<td>0.018</td>
</tr>
<tr>
<td>1b</td>
<td>1.996</td>
<td>-0.085</td>
</tr>
<tr>
<td></td>
<td>2.012</td>
<td>-0.236</td>
</tr>
<tr>
<td></td>
<td>2.013</td>
<td>0.718</td>
</tr>
</tbody>
</table>

Radical 1b, exhibiting hyperfine coupling to one phosphorus nucleus, is assigned to a dissociation product resulting from a rupture of the P-P linkage (Figure 3). The estimated spin densities \( \rho_3 = 7.8\% \) and \( \rho_p = 56.3\% \) and the resulting p/s ratio of 7.2 indicate a large contribution of the phosphorus 3p orbital and a considerable flattening of the original tetrahedral geometry. The experimental hyperfine couplings of 1b are in close agreement with those observed for Ph_2PS formed in diphenylphosphine sulfide and with the values of Et_2PS in X-irradiated tetraethylphosphine disulfide. The spectrum of radical 1a is irreversibly lost upon annealing above 135 K. Further warming results in the loss of 1b at approximately 170 K.

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Radical 1a, attributed to a three-electron-bond radical (Figure 3), based on the hyperfine coupling to two identical phosphorus nuclei and the values of \( A_{iso} = 1213 \text{ MHz} \) (\( A_{iso} = \frac{1}{2} (A_{xx} + A_{yy} + A_{zz}) \) and \( B_{iso} = 161 \text{ MHz} \) (\( B_{iso} = A_{xx} - A_{zz} \)), which are close to the corresponding values of three-electron-bond radicals in X-irradiated tetramethyl-, tetraethyl-, and tetraphenyldiphosphinesulphides (1224 < \( A_{iso} < 1395 \text{ MHz} \), 155 < \( B_{iso} < 173 \text{ MHz} \)). The values of the isotropic \( A_{iso} \) and dipolar \( B_{iso} \) hyperfine couplings are commonly interpreted in terms of atomic valence s 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 \( \rho_3 = 9.1\% \) and \( \rho_p = 21.9\% \) (p/s = 2.4) for each phosphorus nucleus of 1a.

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>-178</td>
<td>-1.050 0.775 0.624</td>
</tr>
<tr>
<td>2b</td>
<td>1826</td>
<td>-108</td>
<td>0.978 -0.203 0.057</td>
</tr>
<tr>
<td>2c</td>
<td>2103</td>
<td>-213</td>
<td>0.371 -0.357 0.857</td>
</tr>
<tr>
<td></td>
<td>2156</td>
<td>-78</td>
<td>0.099 0.683 0.723</td>
</tr>
<tr>
<td></td>
<td>2120</td>
<td>186</td>
<td>0.186 0.701 -0.688</td>
</tr>
<tr>
<td></td>
<td>2689</td>
<td>373</td>
<td>0.387 0.780 -0.492</td>
</tr>
<tr>
<td></td>
<td>81</td>
<td>139</td>
<td>0.167 0.278 0.946</td>
</tr>
<tr>
<td></td>
<td>114</td>
<td>-25</td>
<td>0.829 -0.559 0.018</td>
</tr>
<tr>
<td></td>
<td>222</td>
<td>83</td>
<td>0.533 0.781 -0.324</td>
</tr>
</tbody>
</table>

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

Figure 6. Structure of radicals 2a, 2b, and 2c.

Table IV. g Tensors of Radicals 2a, 2b, and 2c

<table>
<thead>
<tr>
<th>Radical</th>
<th>g x</th>
<th>g y</th>
<th>g z</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>1.997</td>
<td>0.784</td>
<td>0.460</td>
</tr>
<tr>
<td></td>
<td>-0.417</td>
<td>0.879</td>
<td>0.088</td>
</tr>
<tr>
<td>2b</td>
<td>0.000</td>
<td>0.174</td>
<td>0.770</td>
</tr>
<tr>
<td></td>
<td>-0.614</td>
<td>0.126</td>
<td>0.905</td>
</tr>
<tr>
<td>2c</td>
<td>0.016</td>
<td>-0.428</td>
<td>0.621</td>
</tr>
<tr>
<td></td>
<td>0.657</td>
<td>0.887</td>
<td>0.438</td>
</tr>
<tr>
<td></td>
<td>0.188</td>
<td>0.148</td>
<td>0.787</td>
</tr>
<tr>
<td></td>
<td>-0.486</td>
<td>0.781</td>
<td>0.287</td>
</tr>
</tbody>
</table>

Figure 6. Structure of radicals 2a, 2b, and 2c.

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 undoubtly present but could not be analyzed in detail. 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 $\rho_p = 0.103$ and $\rho_p = 0.444$ are relatively close to the values found in recent studies on similar radicals generated in tetrasubstituted diphosphine disulfides and trialkylphosphine sulfides and selendines. The isotropic hyperfine coupling (3s orbital contribution) of 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 ($A^{iso} = 1934$ MHz, $\rho_p = 14.4\%$) and a relatively small dipolar interaction ($B_{ps} = 186$ 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 diphosphine 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 tetraethylphosphine 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 $B_{ps} = 373$ MHz. In fact these values are approximately two times the values of the symmetrical three-electron-bond radical 1a (the racemate (vii supra). Nevertheless, the possibility that the large coupling is the result of the splitting of $m_1$ = 1 and $m_2$ = -1 lines of a phosphorus triplet can be ruled out since the expected $m_1 = 0$ 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 phosphoryl 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 31P 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 diphosphine disulfides. We tentatively assign 2c to a radical with an asymmetric three-electron-P-P 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 14.4\% and 44.4\%.

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-bond 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-dimethylidiphosphine 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 on phosphorus and sulfur was used (radial exponents 0.55, S 0.65).\(^{17}\) The UHF procedure was followed by removal of the last spin contaminant with use of the annihilation operator.\(^{18}\)

The molecular geometry of the two diastereoismeric radical anions was constrained to the point symmetry of the precursor molecules: \(C_2\) for \(R,R\) and \(C_1\) 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°.\(^{12}\) This elongation of the SPP bond is the direct 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.

The present study reveals that there are major differences between the radicals generated in rac- and meso-1,2-dimethylidiphosphine 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 C\textsubscript{1} point symmetry fits excellently to a hypothetical symmetric antibonding 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 differentiation in the formation of the various electronic 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.\textsuperscript{19} 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 symmetric species in the racemate and asymmetric structures in the meso form can be obtained by assuming that the extra electron reacts with the parent molecules from a direction perpendicular to the plane of the phosphorus and sulfur nuclei. The electron will then first encounter one methyl and one phenyl group for the meso molecules and two methyl or two phenyl groups for the enantiomers \(R,R\) and \(S,S\). Discrimination between a symmetric and an asymmetric radical product can then be rationalized by a difference in the rate of molecular relaxation (e.g., bond bending) in the solid state between the small methyl group and the large phenyl substituent. For the meso form the electron adds preferentially to the side of the methyl group rather than to the side with the phenyl substituent, resulting in an asymmetric radical configuration. For the molecules of the racemate \((R,R\) and \(S,S)\) there is no difference between the relaxation rate of the two sides of the molecule and hence a symmetric electron-capture product is formed. In the light of the present results further experimental and theoretical study on stereochemical selection in radical formation will be necessary.

Acknowledgment. This investigation has been supported by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO). We thank G. C. Groenenboom for assistance in the quantum chemical calculations.

Registry No. 1, 13639-75-3; 1a, 115181-91-4; 1b, 115093-24-8; 2, 13639-76-4; 2a, 115181-92-5.

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

Alan Bruha and James R. Kincaid*

Contribution from the Chemistry Department, Marquette University, Milwaukee, Wisconsin 53233. Received September 23, 1987

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 (Mb\textsubscript{Co}), hemoglobin (Hb\textsubscript{Co}), and its isolated subunits (\(\alpha\text{Co}\) and \(\beta\text{Co}\)) as well as the iron/cobalt mixed heme hybrids, (\(\alpha\text{Co}\beta\text{Fe}\))\textsubscript{2} and (\(\alpha\text{Fe}\beta\text{Co}\)). The spectra of the \(\text{O}_2\), \(\text{O}_2\text{(H}_2\text{O)}\), and scrambled oxygen (\(\text{O}_2\text{H}_2\text{O}\), \(\text{O}_2\text{H}_2\text{O}\)\textsubscript{2}, 1:2:1) adducts have been measured in both normal (\(\text{H}_2\text{O}\)) and deuteriated (\(\text{D}_2\text{O}\)) buffers for each of the proteins. Strong bands located at \(\sim 1135\), \(\sim 1096\), and \(\sim 1065 \text{ cm}^{-1}\) in \(\text{H}_2\text{O}\) solution are identified with \(\nu(\text{O}_2\text{H})\), \(\nu(\text{O}_2\text{D})\), and \(\nu(\text{O}_2\text{D})\), respectively. Shifts of these bands in \(\text{D}_2\text{O}\) 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 \(\nu(\text{O}_2\text{H})\) 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 (\(\text{O}_2\)) conformers, in contrast to earlier interpretations. In addition, based on the results of model compound studies, the frequency observed for \(\nu(\text{O}_2\text{H})\) 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 \(\nu(\text{O}_2\text{D})\) observed upon replacement of \(\text{H}_2\text{O}\) by \(\text{D}_2\text{O}\) 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.

The oxygen transport proteins, hemoglobin (Hb) and myoglobin (Mb), are perhaps the most thoroughly studied of all biomolecules.\textsuperscript{1} Despite intensive effort by many research groups and an extensive body of accumulated knowledge, questions remain unanswered, even at a rather fundamental level. In fact, knowledge of the details of \(O_2\) structure and bonding at the heme site remains incomplete. Thus, issues such as the importance of distal side hydrogen bonding between the bound \(O_2\) and the heme pocket distal histidine\textsuperscript{2-7} and even the number of stable structures\textsuperscript{8-9} remain controversial.


