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Coordination of Diatomic Ligands to Heme: Simply CO

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The synthesis and molecular structures of three iron(II) porphyrinates with only CO as the axial ligand(s) are reported. Two five-coordinate [Fe(OEP)(CO)] derivatives have Fe–C = 1.7077(13) and 1.7140(10) Å, much shorter than those of six-coordinate [Fe(OEP)(Im)(CO)], although ν_{C-O} is 1944–1948 cm^{-1}. The six-coordinate species [Fe(OEP)$(CO)_2$] has also been studied. The competition for π-back-bonding of two CO ligands leads to Fe–C distance of 1.8558(10) Å and ν_{C-O} being increased to 2021 cm^{-1}. The Mössbauer spectrum has a quadrupole splitting constant of 0 mm/s at 4.2 K, indicating high electronic symmetry.

Many heme-based sensing proteins that use/detect the diatomic ligands O_2, CO, or NO are known.[1−4] These sensing proteins rely on variations in the coordination number and the character of their axial ligands to induce conformational changes leading to protein activation.[1] Effects involving the trans ligand (or lack thereof) on binding diatomic molecules are important in elucidating the mechanism of small-molecule sensing proteins. To achieve a better understanding of the heme interactions involved with diatomic ligand sensing as well as broadly extending our understanding of their electronic and molecular structure, we have been investigating heme/diatomic ligand interactions.

We report for the first time the solid-state syntheses and structural characterization of unambiguously five- and six-coordinate heme CO complexes: [Fe(OEP)(CO)], [Fe(OEP)(CO)]·C_6H_6, and [Fe(OEP)$(CO)_2$].[5,6] Although these species have been previously reported in solution and the CO binding constants determined for three different porphyrins,[7] we now demonstrate the structural effects of changing the coordination environments. We compare the five-coordinate structures with those of several other diatomic ligand heme complexes, examine the effects of the addition of a sixth ligand, and note structural differences.

These adducts may elucidate important coordination chemistry features involving ligand loss, ligand switching, and ligand photolability. CO photolysis of six-coordinate heme carbonyl derivatives has been a mainstay in biophysical investigations[8] and is very efficient, with quantum yields nearing unity. The suggestion that five-coordinate heme carbonyls are less photolabile than their six-coordinate counterparts[9] generates important questions about structural differences.

We first consider the vibrational properties of five-coordinate [Fe(OEP)(CO)]. ν_{C-O} in unperturbed imidazole-ligated hemes is typically near 1970 cm^{-1}, but solid-state environmental factors can lead to variation in ν_{C-O} in the range of 1926−2000 cm^{-1}.[10,11] Thus, it is perhaps surprising to find that ν_{C-O} in [Fe(OEP)(CO)] and [Fe(OEP)(CO)]·C_6H_6 is well within this range at 1944 and 1948 cm^{-1}, respectively (Nujol mull). These values might suggest that the Fe center is involved in a significant intermolecular interaction to form a pseudo-six-coordinate complex, but this is not correct (vide infra).

The molecular structures of the two crystalline [Fe(OEP)(CO)] complexes are illustrated in Figure 1 (and Figure S1 in the Supporting Information). There are strong similarities as well as differences in their structures: the Fe out-of-plane displacements are similar at 0.20 or 0.22 Å, the off-axis tilt of the Fe−C vector is 3.8° or 2.4°, and the Fe−C−O bond angle is 177.20(8)° in both. Both forms show some ring−

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(5) The following abbreviations are used in this paper: Por, generalized porphyrin dianion; OEP, dianion of octaethylporphyrin; Deut, dianion of deuteroporphyrin; TPP, dianion of tetraphenylporphyrin.

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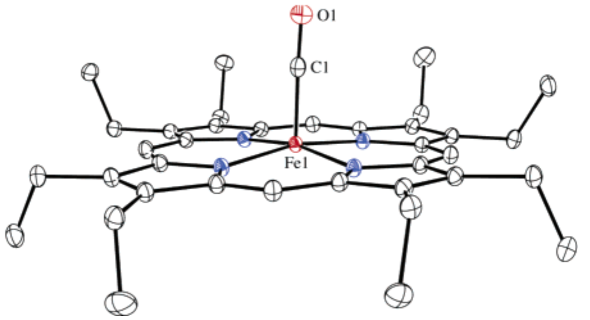

Figure 1. Thermal ellipsoid plot of [Fe(OEP)(CO)] (50% probability ellipsoids). H atoms are omitted for clarity.

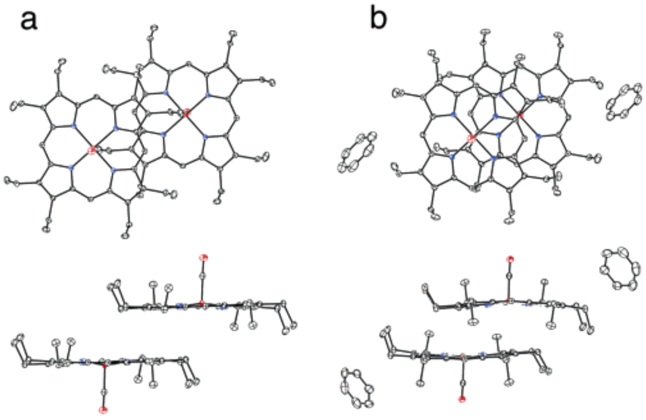

Figure 2. ORTEP plots (50% probability ellipsoids) of [Fe(OEP)(CO)] (a) and [Fe(OEP)(CO)]·C_6H_6 (b) displaying the pairwise interactions. In part a, the 24-atom mean-plane separation is 3.42 Å and the lateral shift of the two ring centers is 6.76 Å. The Fe···Fe distance is 7.58 Å. The corresponding distances in part b are 3.46, 3.88, and 5.20 Å, respectively.

ring interactions, although these lead to some strong differences as well. Figure 2a shows the pairwise interactions in [Fe(OEP)(CO)], while the equivalent packing in the benzene solvate is shown in Figure 2b. In both cases, there is inversion symmetry; metrical information is given in the figure caption. The inter-ring packing pattern in the unsolvated form of [Fe(OEP)(CO)] (Figure 2a) is similar to that of both crystalline forms of [Fe(OEP)(NO)], for which little porphyrin overlap is observed.[12] The closest intermolecular contact to the Fe in [Fe(OEP)(CO)] is 3.12 Å, whereas in [Fe(OEP)(CO)]·C_6H_6, the closest contact to Fe is 3.58 Å. In the two [Fe(OEP)(NO)]$^+$ structures (isoelectronic to the CO's), however, there is a large porphyrin ring overlap with the π system of an adjacent molecule acting as a pseudo sixth ligand.[13] The tighter interactions in [Fe(OEP)(CO)]·C_6H_6 (Figure 2b) are comparable to, although slightly larger than, those in the isoelectronic [Fe(OEP)(NO)]$^+$ complexes. The porphyrin core conformation in [Fe(OEP)(CO)] is nearly planar, whereas that in [Fe(OEP)(CO)]·C_6H_6 displays modest core ruffling. The average equatorial Fe−N_p distances are 1.988 (2) and 1.984(3) Å for the unsolvated and solvated forms, respectively. The very short Fe−N_p bond distances reflect the strong bonding interaction and low-spin state of Fe. Significantly, the axial-ligand-induced equatorial (Fe−N_p) bond distance differences observed in five-coordinate [Fe(por)(NO)] derivatives[12] are not observed; individual Fe−Np distances are tightly clustered.

The short axial Fe−C distance of 1.7140(11) Å in [Fe(OEP)(CO)] is shorter than those of the six-coordinate imidazole adducts by ∼0.03−0.06 Å.[10,14] This might suggest stronger Fe → C π back-donation, but the relatively normal ν_{C-O} value suggests that the Fe π donation into the CO π^* orbitals is similar to that of the six-coordinate species. This would then suggest that it is the σ-bonding component that leads to the shorter Fe−C bond distance. The distance in [Fe(OEP)(CO)]·C_6H_6 is 1.7077(13) Å; the possibly slightly shorter Fe−C distance is not consistent with the 4-cm^{-1} increase in ν_{C-O}, again suggesting the importance of σ bonding. We thus conclude that differences in the σ-bonding component of Fe−C have no or modest effects on ν_{C-O}. As we have noted for a different series of six-coordinate carbonyl derivatives,[10] there is a strong correlation between ν_{C-O} and the Fe−C/C−O bond lengths; this question is being examined in more detail for OEP derivatives.

The structures of other [Fe(OEP)(XY)]$^{+,0}$ adducts (XY = NO or CS) are available for comparison. Structural parameters for five- and six-coordinate species are listed in Table 1. The Fe out-of-plane displacement of [Fe(OEP)(CO)] is seen to be at the low end of the range. In all cases, the addition of a sixth ligand leads to a decreased Fe atom displacement and in most cases to an increase in the length of the Fe−X(XY) bond. Although this increase is never large, the CO's are the system that experiences the largest increase in the Fe−C bond distance {from 1.7140(11) to 1.7733(12) Å in [Fe(OEP)(CO)(1-MeIm)]}.[14] Interestingly, the Fe−C bond would appear to have changed minimally when the trans ligand is the weakly coordinating tetrahydrofuran (THF) ligand in [Fe(Deut)(CO)(THF)]. Unfortunately, the relatively low precision of this structure (from ∼25 years ago) is not adequate to comment on further but clearly merits further attention.

Although solutions of Fe(OEP) and CO will always be mixtures of mono- and bis-CO species, crystallization experiments (see the Supporting Information) at low temperature reproducibly afford crystals of [Fe(OEP)$(CO)_2$]. Analysis of crystals of [Fe(OEP)$(CO)_2$] gave the structure displayed in Figure 3; the complex has a required inversion center. As might be expected, the competition from two CO's for π back-bonding from the central Fe leads to increased Fe−C bond distances of 1.8558 (10) Å, which is also consistent with the observed asymmetric stretch of 2021 cm^{-1}. The CO ligands are tilted off-axis as shown with other metrical information given in Figure 3. Perhaps as a consequence of the competition for bonding with two CO ligands, the equatorial Fe−N_p bonds are at the very long end of values expected for low-spin Fe^{II}.[15] The porphyrin

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Table 1. Notable Bonding Parameters for [Fe(OEP)(CO)] and Related Compounds

complex	Fe−XY[a]	X−Y[a]	Fe−X−Y[b]	Fe−Np[a]	Fe−L_{ax} [a]	ΔFe[c]	ν_{X-Y}[d]	ref
[Fe(OEP)(CO)]	1.7140(11)	1.1463(12)	177.20(8)	1.988(2)		0.20	1944[e]	tw
[Fe(OEP)(CO)]·C_6H_6	1.7077(13)	1.1259(16)	177.20(11)	1.984(3)		0.22	1948[e]	tw
[Fe(OEP)(NO)]	1.722(2)	1.167(3)	144.4(2)	2.004(15)		0.29	1666[e]	12
[Fe(OEP)(NO)]	1.7307(7)	1.1677(11)	142.74(8)	2.010(13)		0.27	1673[e]	12
$[Fe(OEP)(NO)]^+$	1.6528(13)	1.140(2)	173.19(13)	1.994(5)		0.32	1838[e]	13
$[Fe(OEP)(NO)]^+$	1.644(3)	1.112(4)	176.9(3)	1.994(1)		0.29	1868[e]	16
[Fe(OEP)(CS)]	1.662(3)	1.559(3)	176.3(2)	1.982(5)		0.23	1292[e]	17
[Fe(Deut)(CO)(THF)]	1.706(5)	1.144(5)	178.3(14)	1.98(3)	2.127(4)	0.10	1955[f]	18
[Fe(OEP)(CO)(1-MeIm)]	1.744(5)	1.158(5)	175.1(4)	2.000(3)	2.077(3)	0.00	1965[g]	19
[Fe(OEP)(CO)(1-MeIm)]	1.7733(12)	1.1413(15)	175.67(11)	2.010(4)	2.0544(9)	0.02	1980[e]	20
$[Fe(OEP)(NO)(1\text{-}MeIm)]^+$	1.6465(17)	1.135(2)	177.28(17)	2.003(5)	1.9889(16)	0.02	1921[e]	21
[Fe(TPP)(NO)(1-MeIm)]	1.750(2)	1.182(3)	137.7(2)	2.008(13)	2.173(2)	0.04	1628[e]	22
[Fe(OEP)(CS)(1-MeIm)]	1.703(4)	1.563(4)	172.2(2)	2.001(4)	2.112(3)	0.10	1272[e]	23
$[Fe(OEP)(CO)_2]$	1.8558(10)	1.1216(13)	173.95(9)	2.0133(7)	1.8558(10)	0.00	2021[e]	tw

[a] In angstroms. [b] In degrees. [c] Displacement from the 24-atom mean plane. [d] In reciprocal centimeters. [e] Nujol mull. [f] THF. [g] CD_2Cl_2 solution.

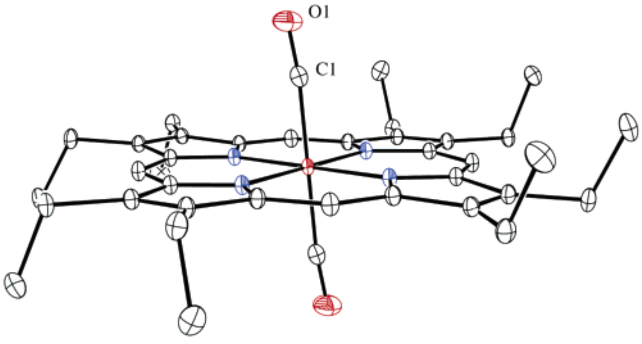

Figure 3. Thermal ellipsoid plot of $[Fe(OEP)(CO)_2]$. The Fe−C vector is tilted from the heme normal by 5.9°; the C and O atoms are shifted laterally by 0.14 and 0.56 Å, respectively.

core is planar; core diagrams for all three complexes are given in Figure S2 in the Supporting Information.

Mössbauer spectra for [Fe(OEP)(CO)] are consistent with an isolated five-coordinate Fe center. The quadrupole splitting is much larger (1.84 mm/s, 4.2 K) than that observed for six-coordinate carbonyls (typically less than 0.7 mm/s), strongly indicative of a d-orbital asymmetry consistent with five-coordination. The isomer shift value of 0.27 mm/s is similar to that of the six-coordinate derivatives; the relatively low value is consistent with strong and effectively equivalent covalency among the occupied Fe 3d orbitals in all derivatives. The six-coordinate derivative is much more symmetric, with a quadrupole splitting of 0 or near 0 at 4.2 K and an isomer shift of 0.31 mm/s; this increases to a quadrupole splitting of 0.176 mm/s and an isomer shift of 0.18 mm/s at 298 K. Spectra in the applied magnetic field for this complex confirmed that it is a diamagnetic species. Complete data are given in Table S1 in the Supporting Information.

Five-coordinate coordinate carbonyl hemes have been structurally characterized and compared with related five- and six-coordinate diatomic complexes. Although the biological importance of five-coordinate carbonyl hemes is not known, proteins have been described that have spectroscopic properties that may be associated with this adduct.[9,24]Additional spectroscopic and photophysical studies on these carbonyl complexes are in prospect.

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Supporting Information Available: Syntheses, figures, and crystallographic data are available (including CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.

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