

Published in final edited form as:

Inorg Chem. 2006 September 4; 45(18): 7050–7052.

Coordination of Diatomic Ligands to Heme: Simply CO

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Abstract

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 $\nu_{\text{C-O}}$ 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 distances of 1.8558 (10) Å and $\nu_{\text{C-O}}$ is 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 O₂, CO, or NO are known.^{1–4} These sensing proteins rely on variations in 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. In order 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-coordinate and six-coordinate heme CO complexes: [Fe(OEP)(CO)], [Fe(OEP)(CO)].C₆H₆, and [Fe(OEP)(CO)₂].^{5,6} Although these species have been previously reported in solution and CO binding constants determined for three different porphyrins,⁷ we now demonstrate the structural effects of changing coordination environments. We compare the five-coordinate structures with those of several other diatomic ligand heme complexes, examine 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 counterparts⁹ generates important questions about structural differences.

We first consider the vibrational properties of five-coordinate [Fe(OEP)(CO)]. $\nu_{\text{C-O}}$ in unperturbed imidazole-ligated hemes is typically near 1970 cm^{-1} , but solid-state environmental factors can lead to variation in $\nu_{\text{C-O}}$ in the range of 1926 to 2000 cm^{-1} .^{10,11} Thus, it is perhaps surprising to find that $\nu_{\text{C-O}}$ in [Fe(OEP)(CO)] and [Fe(OEP)(CO)].C₆H₆ is

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well within this range at 1944 cm^{-1} and 1948 cm^{-1} , respectively (Nujol mull). These values might suggest that the iron 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 $[\text{Fe}(\text{OEP})(\text{CO})]$ complexes are illustrated in Figure 1 (and Fig. S1). There are strong similarities as well as differences in their structures: the iron out-of-plane displacements are similar at 0.20 \AA or 0.22 \AA , the off-axis tilt of the Fe–C vector is 3.8° or 2.4° , and the Fe–C–O bond angle is $177.20(8)^\circ$ in both. Both forms show some ring–ring interactions although these lead to some strong differences as well. Figure 2a shows the pairwise interactions in $[\text{Fe}(\text{OEP})(\text{CO})]$, 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 $[\text{Fe}(\text{OEP})(\text{CO})]$ (Figure 2a) is similar to that of both crystalline forms of $[\text{Fe}(\text{OEP})(\text{NO})]$ for which little por-phyrin overlap is observed.¹² The closest intermolecular contact to the iron in $[\text{Fe}(\text{OEP})(\text{CO})]$ is 3.12 \AA whereas in $[\text{Fe}(\text{OEP})(\text{CO})]\cdot\text{C}_6\text{H}_6$ the closest contact to iron is 3.58 \AA . In the two $[\text{Fe}(\text{OEP})(\text{NO})]^+$ 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 $[\text{Fe}(\text{OEP})(\text{CO})]\cdot\text{C}_6\text{H}_6$ (Figure 2b) are comparable although slightly larger than in the isoelectronic $[\text{Fe}(\text{OEP})(\text{NO})]^+$ complexes. The porphyrin core conformation in $[\text{Fe}(\text{OEP})(\text{CO})]$ is nearly planar whereas that in $[\text{Fe}(\text{OEP})(\text{CO})]\cdot\text{C}_6\text{H}_6$ displays modest core ruffling. The average equatorial Fe–N_p distances are $1.988(2)\text{ \AA}$ and $1.984(3)\text{ \AA}$ for the unsolvated and solvated forms. The very short Fe–N_p bond distances reflect the strong bonding interaction and low-spin state of iron. Significantly, the axial ligand-induced equatorial (Fe–N_p) bond distance differences observed in five-coordinate $[\text{Fe}(\text{por})(\text{NO})]$ derivatives¹² are not observed; individual Fe–N_p distances are tightly clustered.

The short axial Fe–C distance of $1.7140(11)\text{ \AA}$ in $[\text{Fe}(\text{OEP})(\text{CO})]$ is shorter than those of the six-coordinate imidazole adducts by $\sim 0.03\text{--}0.06\text{ \AA}$.^{10,14} This might suggest stronger Fe→C π -back-donation, but the relatively normal $\nu_{\text{C-O}}$ 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 $[\text{Fe}(\text{OEP})(\text{CO})]\cdot\text{C}_6\text{H}_6$ is $1.7077(13)\text{ \AA}$; the possibly slightly shorter Fe–C distance is not consistent with the 4 cm^{-1} increase in $\nu_{\text{C-O}}$, 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 $\nu_{\text{C-O}}$. As we have noted for a different series of six-coordinate carbonyl derivatives,¹⁰ there is a strong correlation between $\nu_{\text{C-O}}$ and the Fe–C/C–O bond lengths, this question is being examined in more detail for OEP derivatives.

The structures of other $[\text{Fe}(\text{OEP})(\text{XY})]^+ \cdot 0$ adducts (XY = NO or CS) are available for comparison. Structural parameters for five- and six-coordinate species are listed in Table 1. The iron out-of-plane displacement of $[\text{Fe}(\text{OEP})(\text{CO})]$ is seen to be at the low end of the range. In all cases, the addition of a sixth ligand leads to a decreased iron 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 COs are the system that experiences the largest increase in Fe–C bond distance (from $1.7140(11)\text{ \AA}$ to $1.7733(12)\text{ \AA}$ in $[\text{Fe}(\text{OEP})(\text{CO})(1\text{-MeIm})]$).¹⁴ Interestingly, the Fe–C bond would appear to have changed minimally when the trans ligand is the weakly coordinating tetrahydrofuran ligand in $[\text{Fe}(\text{Deut})(\text{CO})(\text{THF})]$. 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 SI) at low temperature reproducibly afford crystals of $[\text{Fe}(\text{OEP})(\text{CO})_2]$. Analysis of crystals of $[\text{Fe}(\text{OEP})(\text{CO})_2]$ gave the structure displayed in Figure

3; the complex has a required inversion center. As might be expected, the competition from two COs for π -backbonding from the central iron 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 iron(II).¹⁵ The porphyrin core is planar; core diagrams for all three complexes are given in Figure S2.

Mössbauer spectra for [Fe(OEP)(CO)] are consistent with an isolated five-coordinate iron 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 isomer shift of 0.31 mm/s, this increases to a QS of 0.176 mm/s and an isomer shift of 0.18 mm/s at 298 K. Spectra in applied magnetic field for this complex confirmed that it is a diamagnetic species. Complete data are in Table S1.

Five-coordinate coordinate carbonyl hemes have been structurally characterized and compared with related five- and six-coordinated 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.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

We thank the NIH for support (GM-38401, W.R.S.) and the NSF for X-ray instrumentation (CHE-0443233). We thank Prof. Timothy Sage for useful discussions.

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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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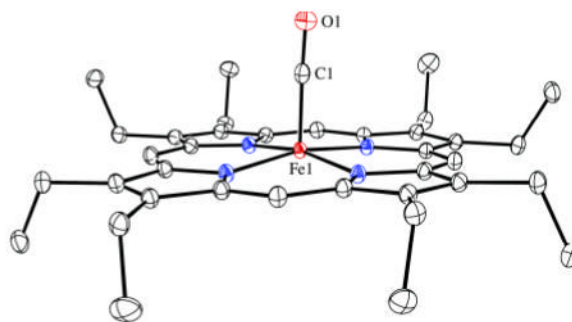


Figure 1. Thermal ellipsoid plot of [Fe(OEP)(CO)] (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

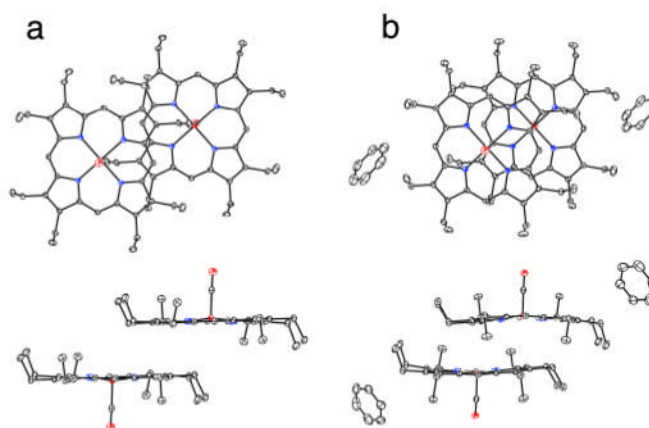


Figure 2. ORTEP plots (50% probability ellipsoids) of [Fe(OEP)(CO)] (a) and [Fe(OEP)(CO)].C₆H₆ (b) displaying the pairwise interactions. In (a) the 24-atom mean plane separation is 3.42 Å and the lateral shift of the two ring centers is 6.76 Å. The Fe···Fe distance is 7.58 Å. The corresponding distances in (b) are 3.46, 3.88, and 5.20 Å, respectively.

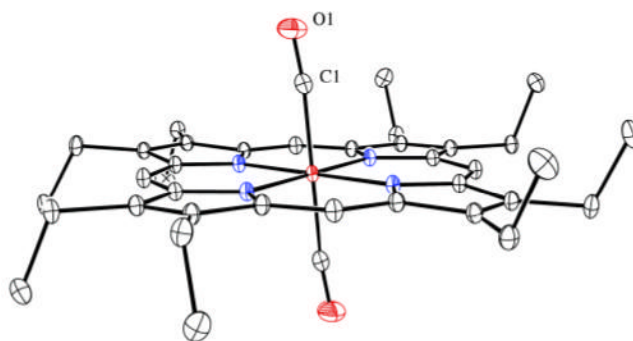


Figure 3. Thermal ellipsoid plot of $[\text{Fe}(\text{OEP})(\text{CO})_2]$. The Fe–C vector is tilted from the heme normal by 5.9° ; the C and O atoms are shifted laterally by 0.14 and 0.56 Å, respectively.

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non-hydrogen atoms were refined anisotropically. Hydrogen atoms were
idealized with the standard SHELXL-97 idealization methods. Hydrogen atoms
were placed at calculated geometries and allowed to ride on the position of
the parent atom. Hydrogen thermal parameters were set to 1.2\times the

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The structure is a iron octaethylporphyrin bound axially carbon monoxide.
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C(B4) C 0.11003(11) 0.60644(10) 0.28702(8) 0.0138(2) Uani 1 1 d . . .
C(B5) C 0.23544(11) 0.61527(10) 0.60354(8) 0.0141(2) Uani 1 1 d . . .
C(B6) C 0.32926(11) 0.55353(10) 0.66172(8) 0.0139(2) Uani 1 1 d . . .
C(B7) C 0.63515(11) 0.18589(10) 0.67284(8) 0.0141(2) Uani 1 1 d . . .
C(B8) C 0.66104(11) 0.10607(10) 0.61890(8) 0.0135(2) Uani 1 1 d . . .
C11 C 0.64141(11) -0.00261(11) 0.28789(9) 0.0163(2) Uani 1 1 d . . .
H11A H 0.6147 -0.0329 0.2364 0.020 Uiso 1 1 calc R . .
H11B H 0.6373 -0.0630 0.3454 0.020 Uiso 1 1 calc R . .
C12 C 0.77913(13) 0.01917(12) 0.26990(11) 0.0258(3) Uani 1 1 d . . .
H12A H 0.8336 -0.0521 0.2599 0.039 Uiso 1 1 calc R . .
H12B H 0.8091 0.0419 0.3234 0.039 Uiso 1 1 calc R . .
H12C H 0.7831 0.0818 0.2148 0.039 Uiso 1 1 calc R . .
C21 C 0.46465(13) 0.17777(11) 0.13144(8) 0.0188(2) Uani 1 1 d . . .
H21A H 0.3735 0.1876 0.1159 0.023 Uiso 1 1 calc R . .

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H21B H 0.5068 0.1010 0.1210 0.023 Uiso 1 1 calc R . .
 C22 C 0.52649(16) 0.27340(13) 0.06697(10) 0.0282(3) Uani 1 1 d . . .
 H22A H 0.5139 0.2713 0.0025 0.042 Uiso 1 1 calc R . .
 H22B H 0.6182 0.2607 0.0788 0.042 Uiso 1 1 calc R . .
 H22C H 0.4870 0.3495 0.0783 0.042 Uiso 1 1 calc R . .
 C31 C 0.11401(12) 0.55857(12) 0.12695(8) 0.0192(2) Uani 1 1 d . . .
 H31A H 0.0250 0.6003 0.1211 0.023 Uiso 1 1 calc R . .
 H31B H 0.1158 0.4820 0.1112 0.023 Uiso 1 1 calc R . .
 C32 C 0.19947(16) 0.62794(16) 0.05853(10) 0.0334(3) Uani 1 1 d . . .
 H32A H 0.1693 0.6378 -0.0044 0.050 Uiso 1 1 calc R . .
 H32B H 0.2875 0.5862 0.0630 0.050 Uiso 1 1 calc R . .
 H32C H 0.1967 0.7046 0.0729 0.050 Uiso 1 1 calc R . .
 C41 C 0.00477(11) 0.70902(10) 0.27463(8) 0.0155(2) Uani 1 1 d . . .
 H41A H 0.0067 0.7540 0.2099 0.019 Uiso 1 1 calc R . .
 H41B H 0.0185 0.7605 0.3158 0.019 Uiso 1 1 calc R . .
 C42 C -0.12585(12) 0.67093(11) 0.29681(9) 0.0200(2) Uani 1 1 d . . .
 H42A H -0.1925 0.7399 0.2893 0.030 Uiso 1 1 calc R . .
 H42B H -0.1279 0.6262 0.3608 0.030 Uiso 1 1 calc R . .
 H42C H -0.1409 0.6223 0.2546 0.030 Uiso 1 1 calc R . .
 C51 C 0.13683(12) 0.71548(10) 0.61793(9) 0.0170(2) Uani 1 1 d . . .
 H51A H 0.1143 0.7680 0.5573 0.020 Uiso 1 1 calc R . .
 H51B H 0.1726 0.7602 0.6561 0.020 Uiso 1 1 calc R . .
 C52 C 0.01644(13) 0.67419(12) 0.66574(10) 0.0249(3) Uani 1 1 d . . .
 H52A H -0.0465 0.7418 0.6736 0.037 Uiso 1 1 calc R . .
 H52B H 0.0381 0.6239 0.7265 0.037 Uiso 1 1 calc R . .
 H52C H -0.0196 0.6304 0.6278 0.037 Uiso 1 1 calc R . .
 C61 C 0.36280(12) 0.57186(11) 0.75340(8) 0.0173(2) Uani 1 1 d . . .
 H61A H 0.3334 0.6544 0.7558 0.021 Uiso 1 1 calc R . .
 H61B H 0.4569 0.5564 0.7587 0.021 Uiso 1 1 calc R . .
 C62 C 0.30452(14) 0.49457(13) 0.83620(9) 0.0241(3) Uani 1 1 d . . .
 H62A H 0.3333 0.5085 0.8937 0.036 Uiso 1 1 calc R . .
 H62B H 0.3318 0.4126 0.8339 0.036 Uiso 1 1 calc R . .
 H62C H 0.2111 0.5131 0.8340 0.036 Uiso 1 1 calc R . .
 C71 C 0.68766(12) 0.18096(11) 0.76535(8) 0.0170(2) Uani 1 1 d . . .
 H71A H 0.7045 0.2593 0.7677 0.020 Uiso 1 1 calc R . .
 H71B H 0.7702 0.1272 0.7727 0.020 Uiso 1 1 calc R . .
 C72 C 0.59808(14) 0.14053(14) 0.84566(9) 0.0256(3) Uani 1 1 d . . .
 H72A H 0.6355 0.1423 0.9040 0.038 Uiso 1 1 calc R . .
 H72B H 0.5856 0.0609 0.8463 0.038 Uiso 1 1 calc R . .
 H72C H 0.5155 0.1924 0.8382 0.038 Uiso 1 1 calc R . .
 C81 C 0.75305(11) -0.00600(10) 0.63676(8) 0.0155(2) Uani 1 1 d . . .
 H81A H 0.7189 -0.0642 0.6111 0.019 Uiso 1 1 calc R . .
 H81B H 0.7611 -0.0360 0.7044 0.019 Uiso 1 1 calc R . .
 C82 C 0.88487(13) 0.00863(12) 0.59375(11) 0.0262(3) Uani 1 1 d . . .
 H82A H 0.9429 -0.0657 0.6094 0.039 Uiso 1 1 calc R . .
 H82B H 0.9181 0.0676 0.6178 0.039 Uiso 1 1 calc R . .
 H82C H 0.8783 0.0334 0.5263 0.039 Uiso 1 1 calc R . .
 C1 C 0.26187(12) 0.26712(11) 0.49735(8) 0.0159(2) Uani 1 1 d . . .
 O1 O 0.18732(9) 0.20987(9) 0.52230(7) 0.02251(19) Uani 1 1 d . . .
 C90 C 0.84363(16) 0.73398(16) 0.98868(12) 0.0359(4) Uani 1 1 d . . .
 H90A H 0.8286 0.6557 1.0061 0.043 Uiso 1 1 calc R . .
 C91 C 0.90715(16) 0.77079(18) 0.90674(13) 0.0399(4) Uani 1 1 d . . .
 H91A H 0.9363 0.7182 0.8676 0.048 Uiso 1 1 calc R . .
 C92 C 0.92837(18) 0.88518(19) 0.88154(14) 0.0469(5) Uani 1 1 d . . .
 H92A H 0.9719 0.9113 0.8249 0.056 Uiso 1 1 calc R . .
 C93 C 0.8863(2) 0.96126(19) 0.93885(16) 0.0560(6) Uani 1 1 d . . .
 H93A H 0.9013 1.0395 0.9220 0.067 Uiso 1 1 calc R . .
 C94 C 0.8223(2) 0.9229(2) 1.02077(15) 0.0569(6) Uani 1 1 d . . .
 H94A H 0.7924 0.9749 1.0602 0.068 Uiso 1 1 calc R . .
 C95 C 0.80212(19) 0.80932(18) 1.04512(12) 0.0437(4) Uani 1 1 d . . .
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 N2 0.0124(4) 0.0119(4) 0.0127(4) -0.0028(3) 0.0006(3) -0.0013(3)
 N3 0.0129(4) 0.0123(4) 0.0124(4) -0.0032(3) 0.0005(3) -0.0014(3)
 N4 0.0122(4) 0.0137(4) 0.0127(4) -0.0045(3) 0.0004(3) -0.0010(3)
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 C(M2) 0.0138(5) 0.0116(5) 0.0159(5) -0.0025(4) 0.0019(4) -0.0014(4)
 C(M3) 0.0144(5) 0.0153(5) 0.0139(5) -0.0046(4) 0.0004(4) -0.0035(4)
 C(M4) 0.0132(5) 0.0113(5) 0.0154(5) -0.0029(4) 0.0008(4) -0.0006(4)
 C(A1) 0.0119(5) 0.0124(5) 0.0137(5) -0.0039(4) 0.0012(4) -0.0020(4)
 C(A2) 0.0120(5) 0.0141(5) 0.0131(5) -0.0041(4) 0.0007(4) -0.0032(4)

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C(A3 0.0115(5) 0.0143(5) 0.0137(5) -0.0024(4) -0.0001(4) -0.0025(4)
C(A4 0.0116(5) 0.0108(5) 0.0148(5) -0.0013(4) 0.0006(4) -0.0019(4)
C(A5 0.0146(5) 0.0104(5) 0.0146(5) -0.0029(4) 0.0022(4) -0.0028(4)
C(A6 0.0144(5) 0.0132(5) 0.0135(5) -0.0044(4) 0.0020(4) -0.0040(4)
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C(A8 0.0111(5) 0.0135(5) 0.0139(5) -0.0021(4) 0.0010(4) -0.0018(4)
C(B1 0.0129(5) 0.0131(5) 0.0161(5) -0.0059(4) 0.0009(4) -0.0025(4)
C(B2 0.0142(5) 0.0143(5) 0.0145(5) -0.0056(4) 0.0004(4) -0.0034(4)
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C(B7 0.0122(5) 0.0166(5) 0.0133(5) -0.0025(4) -0.0008(4) -0.0022(4)
C(B8 0.0115(5) 0.0143(5) 0.0138(5) -0.0013(4) -0.0002(4) -0.0019(4)
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C12 0.0174(6) 0.0204(6) 0.0406(8) -0.0120(6) 0.0046(5) -0.0002(5)
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C31 0.0199(6) 0.0209(6) 0.0154(5) -0.0032(4) -0.0040(4) 0.0009(5)
C32 0.0356(8) 0.0452(9) 0.0164(6) 0.0006(6) 0.0019(6) -0.0087(7)
C41 0.0150(5) 0.0122(5) 0.0177(5) -0.0010(4) -0.0019(4) -0.0007(4)
C42 0.0156(5) 0.0179(6) 0.0261(6) -0.0054(5) 0.0013(5) -0.0017(4)
C51 0.0206(6) 0.0115(5) 0.0190(6) -0.0051(4) 0.0031(4) -0.0016(4)
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C61 0.0217(6) 0.0167(6) 0.0162(5) -0.0070(4) 0.0017(4) -0.0064(4)
C62 0.0305(7) 0.0288(7) 0.0157(6) -0.0060(5) 0.0016(5) -0.0113(6)
C71 0.0163(5) 0.0188(6) 0.0161(5) -0.0034(4) -0.0028(4) -0.0028(4)
C72 0.0287(7) 0.0339(8) 0.0156(6) -0.0043(5) 0.0004(5) -0.0103(6)
C81 0.0147(5) 0.0144(5) 0.0159(5) -0.0008(4) -0.0011(4) -0.0009(4)
C82 0.0159(6) 0.0178(6) 0.0399(8) 0.0000(5) 0.0051(5) 0.0014(5)
C1 0.0174(5) 0.0157(5) 0.0141(5) -0.0045(4) -0.0011(4) 0.0007(4)
O1 0.0230(5) 0.0236(5) 0.0222(5) -0.0052(4) 0.0018(4) -0.0079(4)
C90 0.0318(8) 0.0388(9) 0.0344(8) 0.0032(7) -0.0126(7) -0.0086(7)
C91 0.0283(8) 0.0496(11) 0.0401(9) -0.0057(8) -0.0053(7) -0.0052(7)
C92 0.0316(9) 0.0629(13) 0.0403(10) 0.0121(9) -0.0116(7) -0.0185(9)
C93 0.0691(14) 0.0386(11) 0.0576(13) 0.0107(9) -0.0372(11) -0.0175(10)
C94 0.0782(16) 0.0481(12) 0.0430(11) -0.0123(9) -0.0265(11) 0.0053(11)
C95 0.0459(10) 0.0529(11) 0.0276(8) 0.0006(7) -0.0127(7) -0.0034(9)

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;
All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
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N2 C(A4 1.3794(14) . ?
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C(A1 C(B1 1.4472(16) . ?

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C(A6) C(B6) 1.4451(16) . ?
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C(A8) C(B8) 1.4452(16) . ?
C(B1) C(B2) 1.3627(16) . ?
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C(B3) C(B4) 1.3593(17) . ?
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C(B7) C(B8) 1.3597(16) . ?
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C11 C12 1.5268(18) . ?
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C21 C22 1.5304(19) . ?
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C22 H22C 0.9800 . ?
C31 C32 1.520(2) . ?
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C1 O1 1.1259(16) . ?
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C(A3) C(M1) H(MA) 117.3 . . ?
C(A5) C(M2) C(A4) 124.70(11) . . ?
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C(A4) C(M2) H(MB) 117.7 . . ?
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C(A7) C(M3) H(MC) 117.5 . . ?
C(A6) C(M3) H(MC) 117.5 . . ?
C(A1) C(M4) C(A8) 124.69(11) . . ?
C(A1) C(M4) H(MD) 117.7 . . ?
C(A8) C(M4) H(MD) 117.7 . . ?
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N1 c(A1) c(B1) 111.01(10) . . ?
C(M4) c(A1) c(B1) 124.15(11) . . ?
N1 c(A2) c(M1) 124.67(10) . . ?
N1 c(A2) c(B2) 111.08(10) . . ?
C(M1) c(A2) c(B2) 124.24(11) . . ?
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N2 c(A3) c(B3) 110.98(10) . . ?
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N2 c(A4) c(M2) 124.76(11) . . ?
N2 c(A4) c(B4) 111.11(10) . . ?
C(M2) c(A4) c(B4) 124.08(11) . . ?
C(M2) c(A5) N3 124.61(10) . . ?
C(M2) c(A5) c(B5) 124.21(11) . . ?
N3 c(A5) c(B5) 111.14(10) . . ?
N3 c(A6) c(M3) 124.66(11) . . ?
N3 c(A6) c(B6) 111.48(10) . . ?
C(M3) c(A6) c(B6) 123.79(11) . . ?
N4 c(A7) c(M3) 125.08(11) . . ?
N4 c(A7) c(B7) 111.14(10) . . ?
C(M3) c(A7) c(B7) 123.77(11) . . ?
C(M4) c(A8) N4 124.42(11) . . ?
C(M4) c(A8) c(B8) 124.24(11) . . ?
N4 c(A8) c(B8) 111.25(10) . . ?
C(B2) C(B1) C(A1) 106.38(10) . . ?
C(B2) C(B1) C11 128.40(11) . . ?
C(A1) C(B1) C11 125.16(11) . . ?
C(B1) C(B2) C(A2) 106.56(10) . . ?
C(B1) C(B2) C21 128.88(11) . . ?
C(A2) C(B2) C21 124.46(11) . . ?
C(B4) C(B3) C(A3) 106.76(10) . . ?
C(B4) C(B3) C31 127.33(11) . . ?
C(A3) C(B3) C31 125.88(11) . . ?
C(B3) C(B4) C(A4) 106.42(10) . . ?
C(B3) C(B4) C41 127.59(11) . . ?
C(A4) C(B4) C41 125.94(11) . . ?
C(B6) C(B5) C(A5) 106.53(10) . . ?
C(B6) C(B5) C51 128.04(11) . . ?
C(A5) C(B5) C51 125.34(11) . . ?

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C(B5 C(B6 C(A6 106.34(10) . . . ?
 C(B5 C(B6 C61 128.82(11) . . . ?
 C(A6 C(B6 C61 124.81(11) . . . ?
 C(B8 C(B7 C(A7 106.78(10) . . . ?
 C(B8 C(B7 C71 128.51(11) . . . ?
 C(A7 C(B7 C71 124.68(11) . . . ?
 C(B7 C(B8 C(A8 106.19(10) . . . ?
 C(B7 C(B8 C81 127.93(11) . . . ?
 C(A8 C(B8 C81 125.82(11) . . . ?
 C(B1 C11 C12 112.86(10) . . . ?
 C(B1 C11 H11A 109.0 . . . ?
 C12 C11 H11A 109.0 . . . ?
 C(B1 C11 H11B 109.0 . . . ?
 C12 C11 H11B 109.0 . . . ?
 H11A C11 H11B 107.8 . . . ?
 C11 C12 H12A 109.5 . . . ?
 C11 C12 H12B 109.5 . . . ?
 H12A C12 H12B 109.5 . . . ?
 C11 C12 H12C 109.5 . . . ?
 H12A C12 H12C 109.5 . . . ?
 H12B C12 H12C 109.5 . . . ?
 C(B2 C21 C22 112.60(11) . . . ?
 C(B2 C21 H21A 109.1 . . . ?
 C22 C21 H21A 109.1 . . . ?
 C(B2 C21 H21B 109.1 . . . ?
 C22 C21 H21B 109.1 . . . ?
 H21A C21 H21B 107.8 . . . ?
 C21 C22 H22A 109.5 . . . ?
 C21 C22 H22B 109.5 . . . ?
 H22A C22 H22B 109.5 . . . ?
 C21 C22 H22C 109.5 . . . ?
 H22A C22 H22C 109.5 . . . ?
 H22B C22 H22C 109.5 . . . ?
 C(B3 C31 C32 112.65(11) . . . ?
 C(B3 C31 H31A 109.1 . . . ?
 C32 C31 H31A 109.1 . . . ?
 C(B3 C31 H31B 109.1 . . . ?
 C32 C31 H31B 109.1 . . . ?
 H31A C31 H31B 107.8 . . . ?
 C31 C32 H32A 109.5 . . . ?
 C31 C32 H32B 109.5 . . . ?
 H32A C32 H32B 109.5 . . . ?
 C31 C32 H32C 109.5 . . . ?
 H32A C32 H32C 109.5 . . . ?
 H32B C32 H32C 109.5 . . . ?
 C(B4 C41 C42 111.37(10) . . . ?
 C(B4 C41 H41A 109.4 . . . ?
 C42 C41 H41A 109.4 . . . ?
 C(B4 C41 H41B 109.4 . . . ?
 C42 C41 H41B 109.4 . . . ?
 H41A C41 H41B 108.0 . . . ?
 C41 C42 H42A 109.5 . . . ?
 C41 C42 H42B 109.5 . . . ?
 H42A C42 H42B 109.5 . . . ?
 C41 C42 H42C 109.5 . . . ?
 H42A C42 H42C 109.5 . . . ?
 H42B C42 H42C 109.5 . . . ?
 C(B5 C51 C52 111.45(10) . . . ?
 C(B5 C51 H51A 109.3 . . . ?
 C52 C51 H51A 109.3 . . . ?
 C(B5 C51 H51B 109.3 . . . ?
 C52 C51 H51B 109.3 . . . ?
 H51A C51 H51B 108.0 . . . ?
 C51 C52 H52A 109.5 . . . ?
 C51 C52 H52B 109.5 . . . ?
 H52A C52 H52B 109.5 . . . ?
 C51 C52 H52C 109.5 . . . ?
 H52A C52 H52C 109.5 . . . ?
 H52B C52 H52C 109.5 . . . ?
 C(B6 C61 C62 113.80(10) . . . ?
 C(B6 C61 H61A 108.8 . . . ?
 C62 C61 H61A 108.8 . . . ?
 C(B6 C61 H61B 108.8 . . . ?
 C62 C61 H61B 108.8 . . . ?
 H61A C61 H61B 107.7 . . . ?
 C61 C62 H62A 109.5 . . . ?
 C61 C62 H62B 109.5 . . . ?
 H62A C62 H62B 109.5 . . . ?
 C61 C62 H62C 109.5 . . . ?
 H62A C62 H62C 109.5 . . . ?
 H62B C62 H62C 109.5 . . . ?

C(B7 C71 C72 113.07(10) . . ?
 C(B7 C71 H71A 109.0 . . ?
 C72 C71 H71A 109.0 . . ?
 C(B7 C71 H71B 109.0 . . ?
 C72 C71 H71B 109.0 . . ?
 H71A C71 H71B 107.8 . . ?
 C71 C72 H72A 109.5 . . ?
 C71 C72 H72B 109.5 . . ?
 H72A C72 H72B 109.5 . . ?
 C71 C72 H72C 109.5 . . ?
 H72A C72 H72C 109.5 . . ?
 H72B C72 H72C 109.5 . . ?
 C(B8 C81 C82 112.19(10) . . ?
 C(B8 C81 H81A 109.2 . . ?
 C82 C81 H81A 109.2 . . ?
 C(B8 C81 H81B 109.2 . . ?
 C82 C81 H81B 109.2 . . ?
 H81A C81 H81B 107.9 . . ?
 C81 C82 H82A 109.5 . . ?
 C81 C82 H82B 109.5 . . ?
 H82A C82 H82B 109.5 . . ?
 C81 C82 H82C 109.5 . . ?
 H82A C82 H82C 109.5 . . ?
 H82B C82 H82C 109.5 . . ?
 O1 C1 Fe1 177.20(11) . . ?
 C95 C90 C91 120.28(18) . . ?
 C95 C90 H90A 119.9 . . ?
 C91 C90 H90A 119.9 . . ?
 C90 C91 C92 119.60(19) . . ?
 C90 C91 H91A 120.2 . . ?
 C92 C91 H91A 120.2 . . ?
 C93 C92 C91 119.98(19) . . ?
 C93 C92 H92A 120.0 . . ?
 C91 C92 H92A 120.0 . . ?
 C94 C93 C92 119.64(19) . . ?
 C94 C93 H93A 120.2 . . ?
 C92 C93 H93A 120.2 . . ?
 C95 C94 C93 119.9(2) . . ?
 C95 C94 H94A 120.1 . . ?
 C93 C94 H94A 120.1 . . ?
 C90 C95 C94 120.63(19) . . ?
 C90 C95 H95A 119.7 . . ?
 C94 C95 H95A 119.7 . . ?

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| <u>_diffn_measured_fraction_theta_max</u> | .999 |
| <u>_diffn_reflns_theta_full</u> | 31.00 |
| <u>_diffn_measured_fraction_theta_full</u> | .999 |
| <u>_refine_diff_density_max</u> | .546 |
| <u>_refine_diff_density_min</u> | -.479 |
| <u>_refine_diff_density_rms</u> | .058 |

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 ^d | νX–Y ^c | 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 ₆ H 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-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) | 1.558 (10) | 0.00 | 2021 ^e | tw |

^a Å

^b degrees.

^c cm⁻¹

^d Displacement from 24-atom meanplane.

^e Nujol mull.

^f THF.

^g CD₂Cl₂ solution.