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The Electronic Configuration and Ligand Nature of Five Coordinate Iron Porphyrin Carbene Complexes: An Experimental Study

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Supporting Information Placeholder

ABSTRACT: The five coordinate iron porphyrin carbene com-(TPP plexes [Fe(TPP)(CCl₂)] = tetraphenylporphyrin), $[Fe(TTP)(CCl_2)]$ (TTP = tetratolylporphyrin) and $[Fe(TFPP)(CPh_2)]$ (TFPP = tetra(pentafluorophenyl)porphyrin), utilizing two types of carbene ligands (CCl₂ and CPh₂), have been investigated by single crystal X-ray, XANES (X-ray Absorption Near Edge Spectroscopy), Mössbauer, NMR and UV-vis spectroscopies. The XANES unambiguously suggested the iron(II) oxidation state of the complexes. The multi-temperature and high magnetic field Mössbauer experiments, which show very large quadrupole splittings (QS, $\Delta E_{\rm Q}$), determined the S = 0 electronic configuration. More importantly, the combined structural and Mössbauer studies, especially the comparison with the low spin iron(II) porphyrin complexes with strong diatomic ligands (CS, CO and CN) revealed the covalent bond nature of the carbene ligands. A correlation between the iron isomer shifts (IS, δ) and the axial bond distances is established for the first time for these donor carbon ligands (:C-R).

The strong interest in the nature of iron porphyrin carbene complexes is directly related to the excellent catalytic performance of cytochrome P450 enzymes for numerous biochemical reactions.¹ Formation of carbene complexes of cytochrome P450 has been suggested in the reductive metabolism of polyhalogenated compounds,² oxidative metabolism of benzodioxole derivatives³ and in propylene epoxidation.⁴ The first iron (porphyrin) carbene complex [Fe(TPP)(CCl₂)] was reported in 1977.⁵ Now, iron porphyrin carbenes have been identified as versatile catalysts in various chemical reactions (e.g. cyclopropanation⁶ and N–H insertion⁷).⁸

Although of the significance, the electronic structures of iron porphyrin carbenes, as either reaction intermediates⁹ or isolated products,¹⁰ remain elusive. Theoretical calculations have been applied to this area. Zhang and coworkers claimed the predominant resonance structure of singlet $Fe^{II} \leftarrow \{:C(X)Y\}^{0,11}$ which is contrasted to the more generally accepted $Fe^{IV} = \{C(X)Y\}^{2^{-}.6b,12}$ The same group subsequently extended their results that all of the transition states and the resulting complexes have closed-shell singlet ground states.¹³ Recently, Shaik and coworkers reported the electronic structure of $[Fe(Porph)(SCH_3)(CHCO_2Et)]^{-}$ (Porph =

porphyrin).¹⁴ However, a ground state of an open-shell singlet with two antiferromagnetically coupled electrons residing on the iron(III) and carbene (-1) ligand was proposed. The authors emphasized that the bonding properties are remarkably analogous to those of the ferric heme superoxide complexes originating from Fe(II) and O_2 .¹⁵ The latter has been an intriguing problem for many years that has attracted the attentions of many groups (including ours¹⁶).¹⁷

The experimental investigations on the electronic structures of iron porphyrin carbenes also appear controversial. The oxidation state of the iron has not been definitely determined. Carbenes have been considered as carbon analogs of the porphyrin-ironoxo species ([(Porph)(Fe^V)=O]) on the basis of similarity in the electronic spectra.¹⁸ The vibrational spectral study had assigned [Fe(TPP)(CCl₂)] as a low spin iron(II) species;¹⁹ while iron(IV) was then suggested for the same complex because of the oxidationstate sensitive band at 1370 cm^{-1} .²⁰ The first Mössbauer study on the iron porphyrin carbene was reported in 1983.¹² An Fe(IV) was indicated for [Fe(TPP)(CCl₂)] based on the rather small isomer shift (δ = 0.10 mm/s) at 131 K. Recently, for the same reason Fe(IV) was suggested for [Fe(TFPP)(CPh₂)].^{6b} Again, a measurement at only one temperature was done (288 K, δ = 0.03 mm/s). Although IS is a good indicator of the oxidation state,²¹ exceptions have been found for species with strong ligand interactions.²² Hence, experimental investigations with confidence in the assignment of the iron oxidation and spin state appear highly desired.

Here we report three iron porphyrin carbene complexes [Fe(TPP)(CCl₂)], [Fe(TTP)(CCl₂)] and [Fe(TFPP)(CPh₂)], which were characterized by various spectroscopies. The ORTEP diagrams of the three structures are given in Figure 1 and S1. The 24-atom mean planes and the orientations of the axial ligands are available in Figure S2. As can be seen, the [Fe(TFPP)(CPh₂)]^{6b} and the new [Fe(TFPP)(CPh₂)]·1.5C₆H₆, both arylcarbene structures show ruffled conformation, which is contrasted to the saddled confordichlorocarbene mation of the [Fe(TPP)(CCl₂)] and [Fe(TTP)(CCl₂)]. The difference between the two types of carbene can also be seen from the key structural parameters, which are given in Table 1. The CPh₂ is more sterically bulky than CCl₂. To avoid the steric interactions with the peripheral phenyl groups, CPh₂ tends to align itself along the Fe–N_P vectors which results in a small dihedral angle to the closest N_P–Fe–C_{carbene} plane (φ =

Table 1. Selected Structural Parameters of Iron Porphyrin Carbene Complexes and Related Species

complex	$\Delta_{24}^{a,b}$	$\Delta_4^{a,b}$	Fe–C ^a	(Fe–N _p) _{av} ^{a,c}	Fe-L ^a	Fe-C-X ^d	$\pmb{\varphi}^{d,e}$	τ ^{d,f}	ref ^g
				Carbene Comp	exes				
[Fe(TPP)(CCl ₂)]	0.17	0.20	1.726(3)	1.972(6)		124.68(17), 124.69(17)	40.81	1.6	tw
[Fe(TTP)(CCl ₂)]	0.19	0.20	1.7295(15)	1.980(9)		124.34(9), 125.23(9)	40.30	0.0	tw
[Fe(TFPP)(CPh ₂)]·1.5C ₆ H ₆	0.30	0.23	1.789(2)	1.9847(9)		122.11(15), 124.27(16)	17.14	2.3	tw
[Fe(TFPP)(CPh ₂)]	0.29	0.24	1.767(3)	1.966(3)		122.3(2), 126.1(3)	13.88	2.7	6b
$[Fe(TPP)(C=C(p-C C_6H_4)_2)]$	0.23	0.22	1.689(3)	1.984(1)		176.7(3)		NA ^h	27
[Fe(TPP)(CCl ₂)(H ₂ O)]			1.83(3)	1.984(4)	2.13(3)	NA ^h		NA ^h	28
[Fe(TFPP)(CPh ₂)(1-MeIm)]	0.12	0.10	1.827(5)	1.973(4)	2.168(4)	124.2(4), 124.8(4)	19.36	0.0	6b
				Related Compl	exes				
[Fe(OEP)(CO)]	0.20	0.20	1.7140(11)	1.988(2)		177.20(8)		3.8	23
[Fe(OEP)(CO)]·C ₆ H ₆	0.22	0.20	1.7077(13)	1.984(3)		177.20(11)		2.4	23
[Fe(OEP)(CS)]	0.23	0.22	1.662(3)	1.982(5)		176.3(2)		~4	29
[K(222)][Fe(TPP)(CN)](100K)	0.23	0.17	1.8783(10)	1.986(7)		177.19(10)		6.3	25

^{*a*}Values in angstroms. ^{*b*}Displacement of iron atom from the 24-atom (Δ_{24}) or the four pyrrole nitrogen atoms (Δ_4) mean plane. The positive numbers indicate a displacement towards the C_{ligand}. ^{*c*}Average distance between the iron and porphyrin nitrogen atoms. ^{*d*}Angle values in degrees. ^{*e*}Dihedral angle between the carbene ligand plane (which is denoted by the C_{carbene} atom and the two bonded atoms) and the plane of the closest N_p–Fe–C_{carbene}. ^{*f*}The tilt of the Fe–C vector off the normal to the 24-atom mean plane. ^{*a*}NA = not available.



Figure 1. Side-on ORTEP diagrams of (a) [Fe(TPP)(CCl₂)], (b) [Fe(TTP)(CCl₂)] and (c) [Fe(TFPP)(CPh₂)]. Thermal ellipsoids of all atoms are contoured at the 50% probability level. Hydrogen atoms and solvent molecules are not shown for clarity.

13~17°). This is compared to the large φ angle (~40°) of the CCl₂ ligands which nearly bisect the N_P–Fe–N_P angles. The relatively large iron out of plane displacements (Δ_{24} and Δ_4) and the longer

Fe–C_{carbene} distances of the two [Fe(TFPP)(CPh₂)] structures are also consistent with the steric effect of CPh₂. The key structural parameters of the well-studied, low spin [Fe(II)(Porph)(XY)] (XY=CO,²³ CS²⁴ and CN⁻²⁵) are also given in Table 1. It is seen the Δ_{24} (and Δ_4), and the (Fe–N_p)_{av} distances of the carbene complexes are in the range of 0.17~0.30 and 1.96~1.99 Å. Both parameters, which are sensitive to the electronic configuration of the central metal,²⁶ are similar to those of the [Fe(Porph)(XY)] analogues. Except [Fe(TPP)(C=C(*p*-CIC₆H₄)₂)], all the carbene complexes show Fe–C–X angles ~120°, which is consistent to the sp² hybridized carbon atoms and in contrast with the XY ligands which bond to heme in a linear fashion (~177°).

K-edge XANES have been done to determine the iron oxidation states of the carbene complexes. $[Fe(TPP)(CS)]^{24}$ and [Fe(TPP)CI] were also prepared and tested as references. The normalized (top) and the first derivative (bottom panel) of the XANES spectra are given in Figure 2. It is seen both the pre-edge features A' and the first absorption edge (7112.9 eV) of $[Fe(TPP)(CCl_2)]$ and $[Fe(TFPP)(CPh_2)]$ are identical to those of the ferrous [Fe(TPP)(CS)], suggesting the same oxidation states. This position is consistent with calculations on the Fe(II) complexes with square-pyramidal geometry.³⁰ In contrast, the peaks of [Fe(TPP)CI] which shift towards higher energy due to the higher valence state of iron(III) appeared at 7113.9 eV.³¹ Hence, the finger print analysis determined the iron(II) oxidation state of $[Fe(TPP)(CCl_2)]$ and $[Fe(TFPP)(CPh_2)]$.

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Figure 3. 4.2 K Mössbauer spectra of $[Fe(TPP)(CCl_2)]$ (top) and $[Fe(TFPP)(CPh_2)]$ (bottom) recorded under 9T applied magnetic field.

Two types of carbene complexes were further studied by Mössbauer spectroscopy on the solid state to determine the electron configurations. In Table 2, the isomer shifts and quadrupole splittings of the known porphyrin carbene complexes are given. Also given are the Mössbauer parameters of the [Fe(Porph)(XY)] (XY=CO, CS, CN⁻) analogues. As it is seen, although the isomer shifts of the current samples show apparent temperature dependence (~50% change) with smaller isomer shifts at higher temperatures due to the second order Doppler shift,³² all the values (0.02~0.19) are between those of the ferrous [Fe(Porph)(XY)] (-0.03~0.37 mm/s). The current samples show unusually large magnitude of the quadrupole splitting ($|\Delta E_0|$ = 2.2~2.5 mm/s), which are larger than all the known low spin iron(II) heme complexes. The large $|\Delta E_0|$, however, are comparable to those of the five- $(2.24(1))^{33}$ and six-coordinate (-2.15~-2.31 mm/s) oxyheme complexes.³⁴ It is interesting to note that both dioxygen and carbene show bent ligand geometry (Fe-O-O=122~132°).¹⁶

The two samples were further studied under strong magnetic fields (3, 6 and 9 T) which gives more insight into the ligand nature. An illustration of the fits to spectra is given in Figure 3; information on all fits are found in the Table S2. The high field results definitely assigned the low spin S = 0 states as determined by high-quality fits to applied-field experiments. The fits suggest high rhombicity in the electric field gradient (EFG) with n being 0.90 (CCl₂) and 0.60 (CPh₂). Both values are fairly large for a low spin species, and compared to ~0.2 and 0.5 for oxyheme³⁵ and cytochrome c respectively.^{34b} Interestinly, [Fe(TFPP)(CPh₂)] shows negative QS which is consistent to the DFT prediction,¹ but opposite to that of [Fe(TPP)(CCl₂)].³⁶ The principal component of the EFG, V_{zz} is approximately given by the Equation 1, where k is the scaling factor and the n_i values are the effective populations of the appropriate 3d orbitals.³⁷ As d_{xy} is a nonbonding orbital, the contribution to V_{zz} comes from the imbalance in electron densities in the other d orbitals. A smaller

Table 2. Selected Mössbauer Parameters for Iron Porphyrin Carbene Complexes and Related Species

 $n_{x^2-y^2}$ which would contribute to the negative QS is presumed because of the electron deficient nature of the TFPP macrocycle that induced less density of the $d_{x^2-y^2}$ orbital.

$$V_{zz} = k \Big[n_{x^2 - y^2} - n_{z^2} + n_{xy} - \frac{1}{2} \big(n_{xz} + n_{yz} \big) \Big]$$
(1)

It has been suggested that the isomer shifts of the iron will decrease both with an increase in ligand σ donation and iron π -back donation to the ligand.³⁸ At the entire temperature range the IS [Fe(TPP)(CCl₂)] are approximately half those of of [Fe(TFPP)(CPh₂)], which suggests the CCl₂ bonds more strongly to iron than does the CPh₂. This is in agreement with the relatively shorter axial bond distance of [Fe(TPP)(CCl₂)] as well as the larger η value of 0.90. This is also in accordance with the experimental difficulty in isolating a CPh₂ derivative with a simple porphyrin such as TPP.^{6b} Interestingly, a similar pattern is seen in the [Fe(Porph)(XY)] complexes. The CS has been considered as a better σ -donor and π -acceptor than CO;²⁴ and both are stronger than the cyanide which is a typical σ donor. This sequence is well consistent with the axial distance and IS, that the stronger bonding corresponds to shorter bond distances and smaller IS. In figure 4, the relationship between the axial Fe-C distances and the isomer shifts is plotted. All the five ligands have lone pair of electrons on the donor carbon atoms (:C-R). The correlations between the two parameters for the diatomic ligands and/or carbene ligands are clearly evident. We note this is the first time that such experimental data have been marshalled for a possible correlation. The axial distances of the two carbene complexes are between 1.73~1.79 Å, closer to those of the carbonyl (1.7140(11)) and thiocarbonyl (1.662(3)), but shorter than that of the cyano analogue (1.8783(10) Å). [Fe(TPP)(CS)] and [Fe(TPP)(CCl₂)] showed similarly significant Raman bands (1368 and 1369 cm⁻¹) suggesting their similarly strong π -acceptor ligands.¹⁹ This is consistent with the similar IS and QS values of the two complexes (Table 2).





Figure 2. Comparison of the Fe *K*-edge XANES (top) and its first derivative (bottom) of the carbene and reference complexes.

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In summary, we have characterized two types of five coordinate iron porphyrin carbene complexes. The solid state XANES and Mössbauer studies unambiguously determined the iron(II) S = 0 states of the products. A combined investigation of the crystal structural data and the Mössbauer parameters, including the comparison with the diatomic ligands (CS, CO and CN⁻), present a clear picture of the covalent bond nature of the carbene ligands. In particular, a correlation has been established for the first time between the iron isomer shifts and the axial distances of the :C–R ligated porphyrin complexes. The work shall push forward the understanding on the nature of the carbene ligands.

ASSOCIATED CONTENT

Supporting Information

Materials and methods, complete structural details for three complexes, thermal ellipsoid diagrams and mean plane diagrams of the three structures, multi-temperature and high magnetic field Mössbauer spectra and tables of [Fe(TPP)(CCl₂)] and [Fe(TFPP)(CPh₂)], details of XANES, UV-vis spectra, ¹H NMR and ¹³C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interests.

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Figure 4. The relationship between the axial Fe–C distance and the isomer shift. The two parameters are based on the measurements at the same or the closest available temperatures. The blue line is fitted for CS CO and CN^- and the red line for all the five ligands.

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Complex	τV		s ^a	rof
Complex	1, К	ΔEQ	0	ref
Ca	arbene con	nplexes		
[Fe(TPP)(CCl ₂)]	295	2.23	0.02	tw
	275	2.26	0.04	tw
	225	2.26	0.06	tw
	175	2.27	0.08	tw
	125	2.28	0.09	tw
	75	2.29	0.10	tw
	25	2.29	0.10	tw
[Fe(TPP)(CCl ₂)] _{HMF} ^b	4.2	+2.30	0.10	tw
		η = 0.90		tw
[Fe(TPP)(CCl ₂)]	131	2.28	0.10	12
[Fe(TFPP)(CPh ₂)]	300	2.41	0.09	tw
	250	2.44	0.15	tw
	200	2.45	0.16	tw
	150	2.46	0.18	tw
	100	2.47	0.18	tw
	50	2.48	0.19	tw
	35	2.48	0.19	tw
[Fe(TFPP)(CPh ₂)] _{HMF} ^b	4.2	-2.48	0.18	tw
		$\eta = 0.60$		tw
[Fe(TFPP)(CPh ₂)]	288	2.34	0.03	6b
		-2.37(<i>S</i> = 0)	0.10	11
[Fe(II)(Porp	h)(XY)]		
[Fe(OEP)(CS)]	293	1.95	-0.03	24
	4.2	1.93	0.08	24
[Fe(OEP)(CO)]	298	1.81	0.14	23
	4.2	1.84	0.27	23
[K(222)][Fe(TPP)(CN)]	25	1.83	0.37	25
Oxyiro	n porphyrii	n complexes		
PCN-224FeO ₂	100	2.24	0.38	33
[Fe(TpivPP)(1-MeIm)(O ₂)]	4.2	2.10	0.29	39

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1 70

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Fe-C distance (Å)

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*CPh

§ (mm/s)

CPh.

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