Contribution from the Laboratoire de Chimie et Biochimie Pharmacologiques et Toxicologiques,
Unité Associée au CNRS en Développement Concerté avec l'INSERM, UA 400, Université René Descartes,
45 Rue des Saints-Pères, 75270 Paris Cedex 06, France, Department of Chemistry,
Hunter College of the City University of New York, 695 Park Avenue, New York, New York 10021,
and Laboratoire de Chimie des Métaux de Transition et de Catalyse, Unité Associée au CNRS,
UA 424, Institut Le Bel, Université Louis Pasteur, 67070 Strasbourg, France

Nature of the Complexes Derived from the Reaction of 1,1-Bis(*p*-chlorophenyl)-2,2,2-trichloroethane (DDT) with Iron Porphyrins: Crystal and Molecular Structure of the Vinylidene Carbene Complex $Fe(TPP)(C{=}C(p\text{-}ClC_6H_4)_2)$

Daniel Mansuy,*[†] Jean-Paul Battioni,[†] David K. Lavallee,[‡] Jean Fischer,[§] and Raymond Weiss*[§]

Received July 30, 1987

The crystal structure of the red complex $Fe(TPP)(C{=}C(p\text{-}ClC_6H_4)_2)$ (TPP = *meso*-tetraphenylporphinato(2−)), resulting from the reduction of the insecticide DDT (1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethane) by $Fe^{II}(TPP)$ in the presence of an excess of reducing agent, has been determined by X-ray crystallography. Crystal data are as follows: triclinic, space group $P\bar{1}$, $a = 12.517$ (3) Å, $b = 18.098$ (5) Å, $c = 10.671$ (3) Å, $\alpha = 107.12$ (2)°, $\beta = 101.50$ (2)°, $\gamma = 86.93$ (2)°, $Z = 2$, $R(F) = 0.044$. The iron atom is five-coordinate and is bonded to the four pyrrole nitrogens (average Fe–N distance 1.984 Å) and to one carbon of an axial vinylidene carbene ligand (Fe–C = 1.699 Å). The complex is a highly symmetrical iron–carbene complex with no evidence of any π-interaction of the vinyl double bond with the iron. This structure is also found in solution and is clearly different from the Fe(II)-*N*-vinylporphyrin structure proposed previously by: Castro, C.; Wade, R. S. *J. Org. Chem.* **1985**, *50*, 5342.

Introduction

Organic compounds containing reactive carbon–halogen bonds such as polyhalogenomethanes, the anesthetic halothane, or benzyl halides are metabolically reduced by cytochrome P-450 with formation of stable iron–metabolite complexes.[1] From indirect evidence, it has been proposed that these complexes contain either a σ-alkyl Fe(III)–R or an Fe(II)–carbene iron–carbon bond.[1] Reduction of various polyhalogenated compounds RCX_3 by iron(II) porphyrins in the presence of a reducing agent in excess leads to the formation of many diamagnetic (porphyrin–$Fe^{II} \leftarrow CXR$) carbene complexes that have been isolated and completely characterized by many spectroscopic studies (eq 1).[2-4]

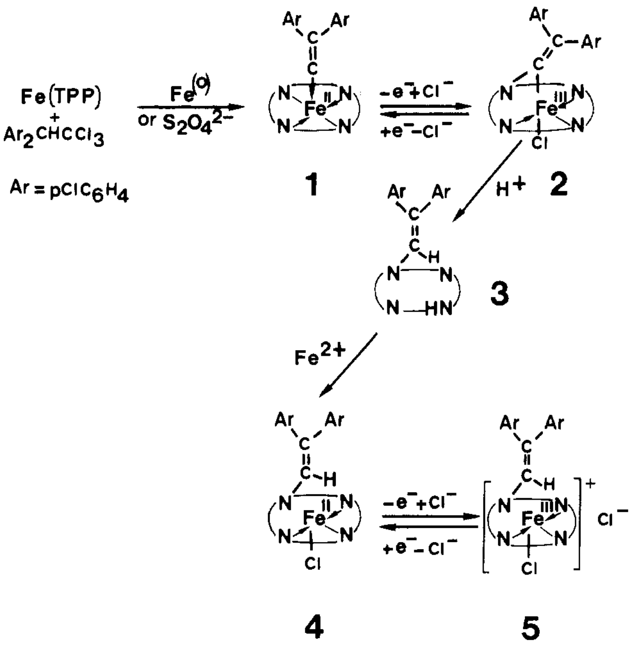
$$(P)Fe^{II} + RCX_3 \xrightarrow[-2X^-]{+2e^-} [(P)Fe^{II} \leftarrow CXR] \qquad (1)$$

In the case of the complexes derived from reduction of CCl_4, CI_4, or Cl_2CS, their respective structures $Fe \leftarrow CCl_2$, $Fe \leftarrow C \rightarrow Fe$, and $Fe \leftarrow CS$ have been established through X-ray studies.[3]

Reduction of the insecticide DDT (1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethane) by $Fe^{II}(TPP)$ (TPP = *meso*-tetraphenylporphinato(2−)) in the presence of a reducing agent in excess (iron powder or dithionite) yields a diamagnetic complex that has been assigned the vinylidene carbene structure **1** of Scheme I. This assignment has been deduced from the elemental analysis of complex **1** as well as from its UV–visible and ^1H NMR spectra, which are very similar to those of other porphyrin–Fe(II)–carbene complexes and are indicative of an axial symmetry.[2-4] A reversible one-electron oxidation of complex **1** leads to a paramagnetic ($S = {}^3/_2$) ferric complex **2** where the vinylidene ligand is inserted into an iron–nitrogen bond.[5] Its structure has been definitely established through two independent X-ray studies[5b,e] as well as by various ^1H NMR, ESR, IR, and magnetic studies.[5] Upon acidic demetalation of **2**, the *N*-vinylporphyrin **3** has been obtained.[6] Insertion of iron(II) into this *N*-vinylporphyrin gives the paramagnetic ($S = 2$) complex that has been assigned structure **4**.[7] This structure is in complete agreement with a detailed analysis of the ^1H NMR spectrum of the corresponding complex.[7b]

A recent article by Castro and Wade[8] disputed the structural assignments published previously[4,5] and shown in Scheme I. It claimed that none of the described complexes involved an iron–carbon bond. These authors proposed that the diamagnetic complex formed upon reduction of DDT by $Fe^{II}(TPP)$ (structure **1** from our assignment) is in fact an Fe(II)-*N*-vinylporphyrin complex (structure **4** of Scheme I). In order to interpret the 4-fold symmetry deduced from the ^1H NMR spectrum of this complex, they proposed strong π-bonding between iron and the *N*-vinyl

Scheme I



[†] Université René Descartes.
[‡] Hunter College.
[§] Université Louis Pasteur.

(1) (a) Wolf, C. R.; Mansuy, D.; Nastainczyk, W.; Deutschmann, G.; Ullrich, V. *Mol. Pharmacol.* **1977**, *13*, 698–705. (b) Ahr, H. J.; King, L. J.; Nastainczyk, W.; Ullrich, V. *Biochem. Pharmacol.* **1982**, *31*, 383–390. (c) Nastainczyk, W.; Ahr, H. J.; Ullrich, V. *Biochem. Pharmacol.* **1982**, *31*, 391–396. (d) Mansuy, D.; Fontecave, M. *Biochem. Pharmacol.* **1983**, *32*, 1871–1879. (e) Ruf, H. H.; Ahr, H. J.; Nastainczyk, W.; Ullrich, V.; Mansuy, D.; Battioni, J. P.; Montiel-Montoya, R.; Trautwein, A. *Biochemistry* **1984**, *23*, 5300–5306.

(2) (a) Mansuy, D. *Pure Appl. Chem.* **1980**, *52*, 681–690 and references cited therein. (b) Guérin, P.; Battioni, J. P.; Chottard, J. C.; Mansuy, D. *J. Organomet. Chem.* **1981**, *218*, 201–209. (c) Mansuy, D.; Lecomte, J. P.; Chottard, J. C.; Bartoli, J. F. *Inorg. Chem.* **1981**, *20*, 3119–3121. (d) Battioni, J. P.; Dupré, D.; Mansuy, D. *J. Organomet. Chem.* **1981**, *214*, 303–309. (e) Battioni, J. P.; Chottard, J. C.; Mansuy, D. *Inorg. Chem.* **1982**, *21*, 2056–2062. (f) Battioni, J. P.; Dupré, D.; Guérin, P.; Mansuy, D. *J. Organomet. Chem.* **1984**, *265*, 53–64.

(3) (a) Mansuy, D.; Lange, M.; Chottard, J. C.; Bartoli, J. F.; Chevrier, B.; Weiss, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 781–782. (b) Goedkin, V. L.; Deakin, M. R.; Bottomley, L. A. *J. Chem. Soc., Chem. Commun.* **1982**, 607–608. (c) Scheidt, W. R.; Geiger, D. K. *Inorg. Chem.* **1982**, *21*, 1208–1211.

(4) Mansuy, D.; Lange, M.; Chottard, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 3213–3214.

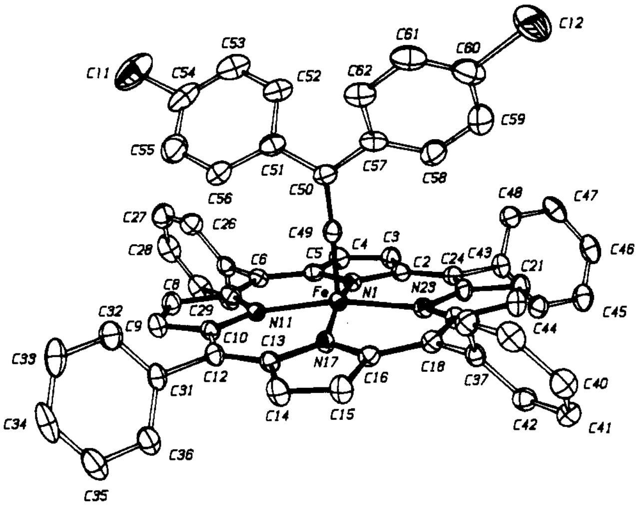


Figure 1. ORTEP plot of one molecule of complex **1**, indicating the labeling scheme used. Ellipsoids are scaled to enclose 50% of the electronic density; hydrogen atoms are omitted.

group.[8] Moreover, they proposed an Fe(III)–*N*-vinylporphyrin structure (structure **5** in Scheme I) for the complex (structure **2** from our assignment) derived from a one-electron oxidation of the diamagnetic compound **1**. Thus, they proposed structures **4** and **5** for the complexes that we have isolated and for which we have given structures **1** and **2**, respectively.

Very recently, Balch et al. have reported the X-ray crystal structure of complex **4** prepared by iron(II) insertion into the *N*-vinyl-TPPH **3**.[9] They showed clearly that this complex was distinct from the diamagnetic iron–carbene complex obtained from the reaction of Fe(TPP) with DDT in the presence of a reducing agent in excess. They also showed that there was not evidence for bonding of the iron to the vinyl group in complex **4** as suggested by Castro and Wade.[8] Their X-ray structural data are thus totally inconsistent with the structure **4** proposed by Castro and Wade for the diamagnetic complex obtained from reaction of Fe(TPP) with DDT (**1** from our assignment).

Our assignments for the structure of complexes of Scheme I have been completely confirmed so far for complexes **2**[5b,e] and **4**[9] by X-ray structural data. In order to definitively establish the structures of Scheme I that we proposed previously, we have undertaken an X-ray study of the diamagnetic complex formed by reduction of DDT by $\mathrm{Fe^{II}}$(TPP) (**1** from our assignment). This paper reports the results of this X-ray study and shows that this complex is a pentacoordinate highly symmetrical iron–carbene complex with no evidence of any π-interaction of the vinyl double bond with the iron. All the spectroscopic results obtained for this complex are typical of porphyrin–iron(II)–carbene complexes and show that the iron–carbene structure is also present in solution.

Results and Discussion

Crystal and Molecular Structure of Complex 1. Complex **1** was prepared as described previously[4] upon reaction of Fe(TPP)Cl with DDT in the presence of iron powder in excess. It exhibited an electronic spectrum identical with that previously reported.[4,9]

Table I. Crystal Structure of Complex **1**: Positional Parameters and Their Estimated Standard Deviations[a,b]

atom	*x*	*y*	*z*	*B*, Å^2
Fe	0.01325 (3)	0.31507 (2)	0.28968 (4)	1.418 (8)
N1	−0.0551 (2)	0.2829 (1)	0.0965 (2)	1.56 (5)
C2	−0.1633 (2)	0.2850 (2)	0.0383 (3)	1.65 (6)
C3	−0.1793 (3)	0.2518 (2)	−0.1035 (3)	2.09 (7)
C4	−0.0811 (3)	0.2283 (2)	−0.1329 (3)	1.98 (7)
C5	−0.0039 (3)	0.2472 (2)	−0.0102 (3)	1.65 (6)
C6	0.1069 (2)	0.2331 (2)	−0.0016 (3)	1.71 (6)
C7	0.1825 (3)	0.2541 (2)	0.1186 (3)	1.82 (6)
C8	0.2982 (3)	0.2426 (2)	0.1281 (3)	2.09 (7)
C9	0.3452 (3)	0.2749 (2)	0.2569 (3)	2.12 (7)
C10	0.2603 (2)	0.3057 (2)	0.3279 (3)	1.63 (6)
N11	0.1593 (2)	0.2942 (1)	0.2424 (2)	1.47 (5)
C12	0.2777 (2)	0.3455 (2)	0.4637 (3)	1.72 (6)
C13	0.1945 (2)	0.3773 (2)	0.5300 (3)	1.64 (6)
C14	0.2110 (3)	0.4215 (2)	0.6686 (3)	2.26 (7)
C15	0.1120 (3)	0.4415 (2)	0.6986 (3)	2.17 (7)
C16	0.0329 (2)	0.4082 (2)	0.5795 (3)	1.66 (6)
N17	0.0839 (2)	0.3708 (1)	0.4749 (3)	1.60 (5)
C18	−0.0789 (2)	0.4133 (2)	0.5752 (3)	1.67 (6)
C19	−0.1545 (2)	0.3883 (2)	0.4564 (3)	1.62 (6)
C20	−0.2692 (3)	0.3921 (2)	0.4490 (3)	2.17 (7)
C21	−0.3162 (3)	0.3671 (2)	0.3186 (3)	2.02 (7)
C22	−0.2293 (2)	0.3462 (2)	0.2452 (3)	1.73 (6)
N23	−0.1293 (2)	0.3581 (1)	0.3307 (2)	1.59 (5)
C24	−0.2469 (3)	0.3155 (2)	0.1066 (3)	1.72 (6)
C25	0.1488 (3)	0.1940 (2)	−0.1265 (3)	1.94 (7)
C26	0.1933 (3)	0.1204 (2)	−0.1467 (3)	2.50 (8)
C27	0.2337 (3)	0.0849 (2)	−0.2618 (4)	3.18 (9)
C28	0.2300 (3)	0.1233 (2)	−0.3583 (4)	3.25 (9)
C29	0.1883 (3)	0.1957 (2)	−0.3391 (4)	3.08 (9)
C30	0.1471 (3)	0.2323 (2)	−0.2227 (3)	2.35 (7)
C31	0.3919 (2)	0.3560 (2)	0.5421 (3)	1.88 (7)
C32	0.4519 (3)	0.2940 (2)	0.5708 (3)	2.41 (7)
C33	0.5545 (3)	0.3063 (2)	0.6503 (4)	3.05 (8)
C34	0.5982 (3)	0.3797 (3)	0.7041 (4)	3.13 (9)
C35	0.5403 (3)	0.4412 (2)	0.6761 (4)	3.05 (9)
C36	0.4375 (3)	0.4303 (2)	0.5945 (3)	2.46 (8)
C37	−0.1184 (2)	0.4487 (2)	0.7028 (3)	1.61 (6)
C38	−0.0926 (3)	0.4140 (2)	0.8065 (3)	1.96 (7)
C39	−0.1276 (3)	0.4482 (2)	0.9260 (3)	2.25 (7)
C40	−0.1878 (3)	0.5155 (2)	0.9436 (3)	2.30 (7)
C41	−0.2133 (3)	0.5496 (2)	0.8415 (3)	2.08 (7)
C42	−0.1783 (3)	0.5165 (2)	0.7223 (3)	1.95 (7)
C43	−0.3616 (2)	0.3171 (2)	0.0326 (3)	1.87 (7)
C44	−0.4141 (3)	0.3876 (2)	0.0424 (3)	2.25 (7)
C45	−0.5227 (3)	0.3914 (2)	−0.0177 (4)	2.70 (8)
C46	−0.5794 (3)	0.3238 (2)	−0.0903 (4)	2.87 (8)
C47	−0.5283 (3)	0.2534 (2)	−0.1036 (4)	2.80 (8)
C48	−0.4199 (3)	0.2500 (2)	−0.0418 (3)	2.22 (7)
C49	−0.0014 (2)	0.2293 (2)	0.3175 (3)	1.73 (6)
C50	−0.0106 (3)	0.1596 (2)	0.333 (3)	2.01 (7)
C51	0.0588 (3)	0.0969 (2)	0.2679 (3)	2.38 (7)
C52	0.0139 (3)	0.0237 (2)	0.1989 (4)	2.73 (8)
C53	0.0721 (4)	−0.0322 (2)	0.1214 (4)	3.7 (1)
C54	0.1745 (4)	−0.0154 (2)	0.1113 (4)	3.72 (9)
C55	0.2244 (3)	0.0549 (2)	0.1831 (4)	3.75 (9)
C56	0.1657 (3)	0.1113 (2)	0.2625 (4)	2.90 (8)
Cl1	0.2429 (1)	−0.08266 (7)	0.0014 (1)	6.07 (3)
C57	−0.0956 (3)	0.1444 (2)	0.4027 (3)	2.27 (7)
C58	−0.1985 (3)	0.1775 (2)	0.3852 (4)	3.13 (8)
C59	−0.2781 (3)	0.1619 (2)	0.4474 (4)	3.9 (1)
C60	−0.2549 (3)	0.1131 (2)	0.5271 (4)	3.34 (9)
C61	−0.1554 (3)	0.0802 (2)	0.5466 (4)	3.07 (8)
C62	−0.0744 (3)	0.0964 (2)	0.4855 (3)	2.68 (8)
Cl2	−0.3565 (1)	0.09114 (7)	0.6016 (1)	5.58 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)$. [b] Numbering as in Figure 1.

Figure 1 displays a perspective view of the structure of complex **1** used for all atoms. Figure 2 shows a formal diagram of the porphinato core displaying the perpendicular displacements in units of 0.01 Å of each atom of the core from the mean plane of the

---

(5) (a) Mansuy, D.; Lange, M.; Chottard, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6437–6439. (b) Chevrier, B.; Weiss, R.; Lange, M.; Chottard, J. C.; Mansuy, D. *J. Am. Chem. Soc.* **1981**, *103*, 2899–2901. (c) Mansuy, D.; Morgenstern-Badarau, I.; Lange, M.; Gans, P. *Inorg. Chem.* **1982**, *21*, 1427–1430. (d) Latos-Grazynski, L.; Cheng, R. J.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1981**, *103*, 4270–4272. (e) Olmstead, M. M.; Cheng, R. J.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 4143–4148. (f) Balch, A. L.; Cheng, R. J.; La Mar, G. N.; Latos-Grazynski, L. *Inorg. Chem.* **1985**, *24*, 2651–2656. (g) Battioni, J. P.; Lexa, D.; Mansuy, D.; Savéant, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 207–215.

(6) Lange, M.; Mansuy, D. *Tetrahedron Lett.* **1981**, 2561–2564.

(7) (a) Mansuy, D.; Battioni, J. P.; Dupré, D.; Sartori, E.; Chottard, G. *J. Am. Chem. Soc.* **1982**, *104*, 6159–6161. (b) Balch, A. L.; Chan, Y. W.; La Mar, G. N.; Latos-Grazynski, L.; Renner, M. K. *Inorg. Chem.* **1985**, *24*, 1437–1443.

(8) Castro, C. R.; Wade, R. S. *J. Org. Chem.* **1985**, *50*, 5342–5351.

(9) Balch, A. L.; Chan, Y. W.; Olmstead, M. M.; Renner, M. W. *J. Org. Chem.* **1986**, *51*, 4651–4656.

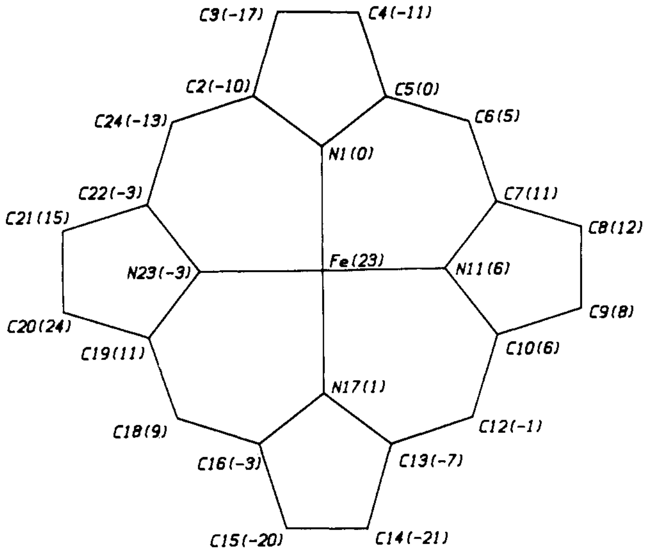


Figure 2. Stick-bond model of the 24-atom core of the porphyrin macrocycle of complex **1**, giving in 0.01 Å units the displacement of each atom with respect to the 24-atom core mean plane.

Table II. Selected Bond Lengths (Å) and Angles (deg) of Complex **1**^{a,b}

Fe–N1	1.991 (2)	N1–Fe–C49	96.6 (1)
Fe–N11	1.980 (2)	N11–Fe–C49	96.3 (1)
Fe–N17	1.982 (2), 1.984 (1)	N17–Fe–C49	96.6 (1)
Fe–N23	1.985 (2)	N23–Fe–C49	96.1 (1)
Fe–C49	1.689 (3)		
Pyrroles			
N–C_α	1.364 (1)	C_α–N–C_α	104.4 (1)
C_α–C_β	1.432 (1)	N–C_α–C_β	110.6 (1)
C_β–C_β	1.347 (2)	C_α–C_β–C_α	107.1 (1)
C_α–C_m	1.391 (1)	N–C_α–C_m	125.6 (1)
		C_α–C_m–C_α	122.8 (1)
		C_α–C_m–C_{phe}	118.5 (1)
Phenyl Rings			
C_m–C_{phe}	1.495 (2)	C–C–C	120.00 (6)
C_{phe}–C_{phe}	1.386 (1)		
Ligand			
C49–C50	1.336 (4)	Fe–C49–C50	176.7 (3)
C50–C51	1.482 (4), 1.48 (3)	C49–C50–C51	117.5 (3)
C50–C57	1.490 (4)	C49–C50–C57	120.4 (3)
C54–C11	1.743 (4), 1.745 (2)	C–C–C	120.0 (1)
C60–C12	1.746 (4)		
C–C	1.385 (1)		

[a] Estimated standard deviations in parentheses. [b] Numbering as in Figure 1; C_α, C_β, C_m, and C_{phe} are respectively the α- and β-carbons of the pyrrole rings, the meso carbons, and the quaternary carbons of the phenyl groups.

24-atom core. Positional parameters are indicated in Table I, and selected interatomic distances and angles are presented in Table II.

The iron atom is five-coordinate. It is bonded to the four porphinato nitrogens (N_p) and to one carbon atom of the vinylidene carbene moiety. The average Fe–N_p distance is 1.984 (1) Å. This distance is clearly consistent with the presence of a five-coordinate, low-spin iron(II) center: (i) it is not significantly different from the average Fe–N_p distance found in the five-coordinate low-spin iron(II)-thiocarbonyl complex Fe(OEP)(CS) (1.982 (5) Å),[3c] and (ii) it is only slightly shorter than the average distance of 1.998 (11) Å found for six-coordinate low-spin iron(II) porphyrin complexes. Accordingly, it is known that a change in the coordination number from 6 to 5 causes a modest radial contraction of the porphinato core.[10]

The iron–vinylidene carbene carbon bond distance of 1.699 (3) Å is similar to that of 1.675 Å present in the μ-carbido bis(tetraphenylporphyrin) derivative[3b] in which a single carbon atom is bridging two iron porphyrins in a linear Fe–C–Fe bonding unit. It is also only slightly longer than the Fe–C bond of a porphyrin Fe–CS complex.[3c] The Fe—C49═C50 moiety is nearly linear (Figure 1), the corresponding angle being 176.7 (3)°. Moreover, the Fe–C bond is tipped only by 0.2°; thus, it lies almost normal to the mean plane of the ring. The C49–C50 bond distance of 1.336 (4) Å corresponds to a normal double bond. The displacement of the metal from the four N_p nitrogen mean plane is 0.23 Å from the 24-atom-core mean plane. The perpendicular displacement of the core atoms from their mean plane (Figure 2) indicates only a slight ruffling of the core. The vinylidene moiety of the ligand is nearly planar. Its mean plane lies almost perpendicular to the mean plane of the porphyrin ring. The dihedral angle between the mean plane of the vinylidene group and the mean plane of the porphyrin ring is 86.6°.

The structural data of complexes **1** and **4**[9] show clearly that they are not iron *N*-vinylporphyrins in which the *N*-vinyl group would be π-bonded to iron. Accordingly, in complex **1**, the two distances between iron and the vinylic carbons of the axial ligand are very different (1.689 (3) and 3.024 (3) Å), contrary to what was observed in Mo(TPP)(PhC≡CPh), in which an acetylene ligand is π-bonded to the metal.[11]

It is noteworthy that, as discussed previously,[9] the X-ray structural data published on complex **2**[5b,e] derived from a one-electron oxidation of **1** are in complete agreement with the bridged structure **2** involving a σ Fe–C bond (Scheme I) and are inconsistent with an iron(III)–*N*-vinylporphyrin structure (**5** in Scheme I), which would involve a π-bond between the iron and the vinyl group, as proposed by Castro and Wade.[8]

Structure of Complex 1 in Solution. The UV–visible spectra of C_6H_6 solutions prepared from crystals of the same sample of complex **1** as the one used for this structural study are identical with those previously published[4] for complexes obtained upon reaction of DDT with Fe(TPP) in the presence of iron powder. Moreover, these spectra of C_6H_6 solutions of **1** are very similar to that obtained for crystals of **1** crushed between two glass plates, except for a broadening and slight red-shift (about 10 nm for the Soret band and 4 nm for the 520-nm band) of the peaks, as is typically found when UV–visible spectra of complexes in solution are compared with those of the same complexes in the solid state.[5c,12] This is good evidence for a symmetrical carbene structure of complex **1** both in the crystalline state and in solution. Accordingly, the UV–visible spectrum of complex **1** is very similar to those of the previously described Fe^{II}(TPP)(carbene) pentacoordinated complexes, which all exhibit a Soret peak around 415 nm and a band around 520 nm with a shoulder at 550 nm.[2] Moreover, the ^{1}H NMR spectrum of complex **1**[4] is typical of diamagnetic iron(II)–TPP complexes with full 4-fold symmetry. This type of spectrum has been previously found for all reported Fe(TPP)(carbene) complexes and corresponds well to the structure of Figure 1. The UV–visible and ^{1}H NMR spectra of complex **1** are clearly different from those of the iron(II)–*N*-vinylporphyrin and –*N*-alkylporphyrin complexes.[7,9,13] Compared data on complex **1** (this work) and **4**[9] show that the complex obtained by reaction of DDT with Fe(TPP)[4] is an iron(II)–vinylidene carbene complex (structure **1**) and not an iron(II)–*N*-vinylporphyrin complex as speculated by Castro and Wade.[8] A significant factor in the arguments of these authors was their report that treatment of **1** or **2** by CF_3COOD resulted in the nondeuteriated *N*-vinylporphyrin *N*-(CAr_2═CH)TPPH instead of *N*-(CAr_2═CD)TPPH. However, Balch and co-workers found that reaction of **2** with

---

(10) Scheidt, W. R.; Reed, C. A. *Chem. Rev.* **1981**, *81*, 543–555.

(11) De Cian, A.; Colin, J.; Schappacher, M.; Ricard, L.; Weiss, R. *J. Am. Chem. Soc.* **1981**, *103*, 1850–1851.

(12) Mahy, J. P.; Battioni, P.; Mansuy, D.; Fischer, J.; Weiss, R.; Mispelter, J.; Morgenstern-Badarau, I.; Gans, P. *J. Am. Chem. Soc.* **1984**, *109*, 1699–1706.

(13) (a) Lavallée, D. K. *Bioinorg. Chem.* **1975**, *6*, 219–227. (b) Anderson, O. P.; Kopelove, A. B.; Lavallée, D. K. *Inorg. Chem.* **1980**, *19*, 2101–2107. (c) Lançon, D.; Cocolios, D.; Guilard, R.; Kadish, K. M. *J. Am. Chem. Soc.* **1984**, *106*, 4472–4478.

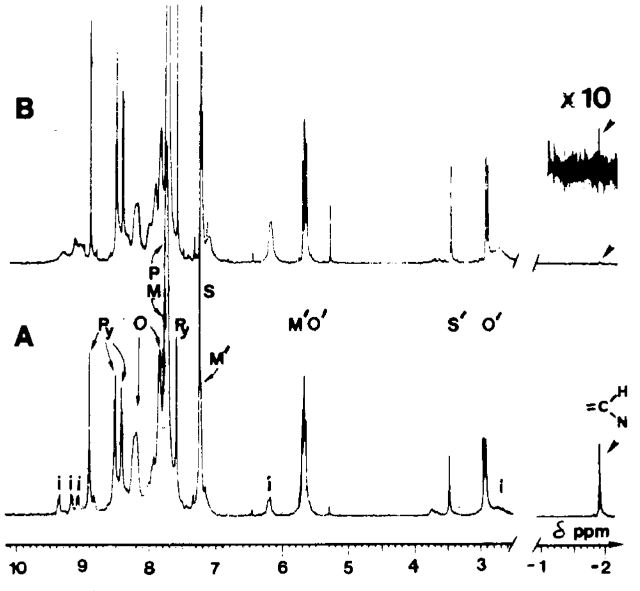


Figure 3. ^{1}H NMR spectra of the crude product obtained by treatment of complex **1** with (A) CF_3COOH or (B) CF_3COOD: Py = pyrrole; O, M, and P = ortho, meta, and para protons of the *meso*-phenyl groups; O′ and M′ = ortho and meta protons of the phenyl groups of the vinyl moiety; S = $CHCl_3$; S′ = CH_3OH; i = signals corresponding to a secondary product, the *N*,*N*′-vinyl-bridged TPP.[6,20] In the case of spectrum B the region between −1 and −2 ppm is also given after a 10-fold increase of the amplitude.

CF_3COOD led to the *N*-vinylporphyrin **3** with 95% deuteriation of the vinylic proton.[7b,9] We reproduced this reaction and obtained almost identical results. Moreover, we reinvestigated the reaction of complex **1** with CF_3COOD described by Castro and Wade.[8] Upon reaction of pure complex **1** in CH_2Cl_2 with an excess of aerated CF_3COOH, the solution turned green within 1 min. After washing of this solution with water and aqueous ammonia, *N*-(CAr_2=CH)TPPH (**3**) was obtained with a very high yield (~ 90%). Its ^{1}H NMR spectrum (Figure 3) shows clearly the presence of the vinylic proton at −1.9 ppm. When the same reaction was performed with CF_3COOD, a similar yield of *N*-(CAr_2=CD)TPPH was obtained. Its ^{1}H NMR spectrum (Figure 3) shows that it contains less than 2% *N*-(CAr_2=CH)TPPH.

We verified that treatment of *N*-(CAr_2=CH)TPPH by CF_3COOD under identical conditions did not lead to any H/D exchange. Thus, whatever the mechanism of the reaction between **1** and CF_3COOH may be, our results are consistent with structure **1** but not with structure **4** for the complex derived from Fe(TPP) and DDT. These results are different from those reported by Castro and Wade indicating that treatment of **1** by CF_3COOD led to nondeuteriated **3**. In that regard, it is noteworthy that when the reaction between **1** and CF_3COOD was performed under strictly anaerobic conditions, it was slower and led to mixtures of *N*-(CAr_2=CD)TPPH and *N*-(CAr_2=CH)TPPH (ratio between 90:10 and 80:20) with lower yields (around 70%). Moreover, we noticed that the yields were considerably lower when the reactions were performed on crude complex **1** derived from reaction of Fe(TPP) with DTT and iron powder.

All the presently available data on complexes **1** and **2** formed upon reaction of Fe(TPP) with DDT and iron powder, including (i) the X-ray structures of complexes **1** (this work), **2**,[5b,e] and **4**,[9] (ii) the UV–visible and ^{1}H NMR spectra of these complexes, and (iii) the results of their acidic demetalation, are in complete agreement with the structures of Scheme I. In particular, they clearly establish the existence of iron–carbene and σ iron–carbon bonds in complexes **1** and **2**, respectively.

Experimental Section

Physical Measurements. UV–visible spectra were obtained by using an Aminco DW2 spectrophotometer. ^{1}H NMR spectra were run at 20 °C on a Bruker MW 250 spectrometer operating at 250 MHz.

Preparation of Compounds. Samples of compounds **1**,[4] **2**,[5] and **3**[6] were prepared as described previously.

Structure Determination of Complex 1. Suitable dark blue single crystals of **1** were obtained by slow evaporation of CH_2Cl_2/MeOH solutions at room temperature.

A systematic search in reciprocal space using a Philips PW1100/16 automatic diffractometer showed that crystals of **1** belong to the triclinic system. The unit-cell dimensions and their standard deviations were obtained and refined at −100 °C with Mo Kα radiation ($\lambda = 0.70926$ Å) by using 25 carefully selected reflections and the standard Philips software. Final results: $C_{56}H_{36}N_4Cl_2Fe$, mol wt 915.71, $a = 12.517$ (3) Å, $b = 18.098$ (5) Å, $c = 10.671$ (3) Å, $\alpha = 107.12$ (2)°, $\beta = 101.50$ (2)°, $\gamma = 86.93$ (2)°, $V = 2264$ Å^3, $Z = 2$, $d_{calcd} = 1.343$ g·cm^{-3}, $\mu = 4.935$ cm^{-1}, $F_{000} = 944$, space group $P\bar{1}$.

A nearly parallelepipedic crystal of 0.20 × 0.30 × 0.30 mm dimensions was cut out from a cluster of crystals, glued at the end of a copper wire, and mounted on a rotation-free goniometer head. All quantitative data were obtained from a Philips PW1100/16 four-circle automatic diffractometer, controlled by a P852 computer, using graphite-monochromated radiation and standard software at −100 °C (achieved by a locally built low-temperature device). The vertical and horizontal apertures in front of the scintillation counter were adjusted to minimize the background counts without loss of net peak intensity at the 2σ level. The full scan width used for the $\theta/2\theta$ flying step scan was $\Delta\theta = (0.9 + 0.143 \tan\theta)°$ with a step width of 0.05° and a scan speed of 0.024° s^{-1}. A total of 10962 +h,k,l and −h,k,l reflections were recorded ($4° < \theta < 57°$). The resulting data set was transferred to a PDP11/60 computer, and for all subsequent computations, with the exception of a local data-reduction program, the Enraf-Nonius SPD/PDP package was used.[14] The standard reflections measured every hour during the entire data-collection period showed no significant trend. The raw step-scan data were converted to intensities by using the Lehmann–Larsen method[15] and then corrected for Lorentz, polarization, and absorption factors, the latter computed by the empirical method of Walker and Stuart[16] since face indexation was not possible (absorption factors were between 0.82 and 1.11). A unique data set of 5903 reflections having $I < 3\sigma(I)$ was used for determining and refining the structure.

The structure was solved by direct methods MULTAN[17] in space group $P\bar{1}$, assumed on the basis of E_{hkl} statistics. After refinement of the heavy atoms, a difference Fourier map revealed maxima of residual electronic density close to the positions expected for the hydrogen atoms: they were introduced into structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors such as $B(H) = 1 + B_{eqv}(C)$ Å^2, but not refined. Full least-squares refinement minimizing $\sum w(F_o - F_c)^2$ converged to $R(F) = 0.044$ and $R_w(F) = 0.064$, with $w(F^2) = (\sigma\text{counts}^2 + (pI)^2)^{-1}$. The unit weight observation was 1.19 for $p = 0.08$. A final difference map revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients come respectively from ref 18 and 19.

Acidic Demetalation of Complex 1. A 200-mg sample of complex **1**, which was obtained after purification by recrystallization from CH_2Cl_2–pentane, was dissolved in 100 mL of CH_2Cl_2 and added into 2 mL of CF_3COOH (or CF_3COOD). The originally red-brown solution turned green within 1 min. After it had been stirred 15 min, the solution was washed with aqueous ammonia (2 M). After evaporation of the solvent, the ^{1}H NMR and UV–visible spectra of the crude product were recorded. They were in complete agreement with the data previously published for compound **3**.[6] Purification was achieved by crystallization of **3** from CH_2Cl_2 and pentane (170 mg, yield 90%). When the reaction was performed under these conditions with CF_3COOD instead of CF_3COOH, very similar yields of *N*-(CAr_2=CD)TPPH were obtained.

When the reaction was performed under anaerobic conditions with CF_3COOD, the characteristic green color appeared more slowly (within about 5 min), and the ^{1}H NMR spectrum of the crude product was indicative of a mixture of *N*-(CAr_2=CH)TPPH and *N*-(CAr_2=CD)T-

---

(14) Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., Van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.

(15) Lehmann, M. S.; Larsen, F. *Acta Crytallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1974**, *A30*, 580–584.

(16) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 159.

(17) (a) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1970**, *B26*, 274–295. (b) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1971**, *A27*, 368–376.

(18) Cromer D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2b.

(19) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(20) Wisnieff, T. J.; Gold, A.; Evans, S. A. *J. Am. Chem. Soc.* **1981**, *103*, 5616–5618.

PPH (15:85). The yields were lower (about 70%).

Acknowledgment. D.K.L. is grateful for a Fullbright Research Scholar award and the generous support of the National Cancer Institute of the NIH (Grant CA 25427).

Registry No. **1**, 72042-21-8; DDT, 50-29-3; Fe(TPP), 16591-56-3.

Supplementary Material Available: Table III, listing U_{ij} for all nonhydrogen atoms, Table IV, listing hydrogen atom parameters, Table V, listing the full set of bond distances, and Table VI, listing the full set of bond angles (15 pages); Table VII, listing observed and calculated structure factor amplitudes (×10) for all observed reflections (25 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of California, Berkeley, California 94720

Solid-State and Solution Chemistry of Calcium *N*-(Phosphonomethyl)glycinate

Paul H. Smith and Kenneth N. Raymond*

Received August 26, 1987

The solid-state and solution chemistry of the calcium salt of *N*-(phosphonomethyl)glycine (glyphosate) has been investigated. The molecular structure of the calcium salt, $CaC_3H_6NO_5P{\cdot}2H_2O$, has been determined by single-crystal X-ray diffraction. The structure is polymeric. The calcium atom is seven-coordinate with four oxygen atoms from three different phosphonate groups, one carboxylate oxygen from yet another glyphosate, and two water oxygens. Each glyphosate is in turn bonded to four different calcium atoms through both the phosphonate and carboxylate ends. The nitrogen atom is protonated and therefore does not bind to the calcium. The compound crystallizes in space group $P\bar{1}$ with $Z = 2$ and $a = 5.4336$ (7) Å, $b = 7.9530$ (10) Å, $c = 10.3868$ (9) Å, $\alpha = 74.576$ (8)°, $\beta = 78.495$ (9)°, and $\gamma = 83.044$ (10)°. The final residuals for 159 variables refined against the 1047 data for which $F^2 > 3\sigma(F^2)$ were as follows: agreement $R = 2.09\%$ and $R_w = 3.50\%$. Calcium-selective-electrode titration data were used to determine the stability constant ($\log \beta_{ML} = 3.35$ (1)) and showed no evidence for an ML_2 complex. The solubility product (K_{sp}) and the formation constant (K_1) of calcium glyphosate (CaHL) were determined by analysis of total calcium in a series of saturated solutions of calcium glyphosate dihydrate containing increasing amounts of the dipotassium salt of glyphosate. The values of $\log K_{sp}$ and $\log K_1$ are −5.32 (2) and 2.04 (9), respectively.

Introduction

The introduction of *N*-(phosphonomethyl)glycine (glyphosate) as a commercial herbicide in the 1970s[1] has been described as a revolutionary advance in agriculture.[2] The utility of this compound is based on its unique properties: (1) It is absorbed by all green plant material, is translocated throughout the plant, and then kills the entire plant, including roots or rhizomes. (2) It inhibits a specific plant enzyme and as a result is not toxic to animals. (3) On contact with soil it is immobilized and inactivated, so that it only affects plant material it immediately contacts. (4) In the soil it is degraded within a period of days by soil organisms to CO_2, PO_4^{3-}, and NH_3.

Although complexation certainly must play a role in property 3, relatively little is known about the coordination behavior of this potentially tridentate ligand. A study by Wauchope et al.[3] first examined the acid solution equilibria of glyphosate. Subsequently, Madsen et al.[4] determined the stability constants of the divalent complexes ML^- (M = Cu, Zn, Mn, Ca, and Mg; L = glyphosate trianion) and redetermined the protonation constants. More recently, Motekaitis and Martell[5] redetermined the protonation constants of the glyphosate ligand, redetermined the stability constants for a number of the ML^- species, and examined other divalent as well as trivalent metal ion complexes.

While the structure of the zwitterionic free acid, $HO_2CCH_2NH_2^+CH_2PO_3H^-$, has been determined,[6] no structure determination of a glyphosate complex has been published. The complex calcium salt $Ca(H_2L)_2(H_3L)_2$[7] has been examined. In this salt there are neutral zwitterionic glyphosate molecules and monoanions in which the carboxylate groups are deprotonated. However, the coordination of the Ca^{2+} ions from both glyphosate species is only through phosphonate oxygens. Recently an NMR study of the platinum complexes of glyphosate[8] has presented the first information about the structure of a glyphosate metal complex involving coordination via the nitrogen.

We have prepared the sparingly soluble salt of the glyphosate dianion $CaHL{\cdot}2H_2O$ and examined its solid-state structure. We have also determined its solubility product and reinvestigated its solution equilibria (reported to involve the species CaL^-, CaHL, and CaL_2^{4-}).[5] The equilibrium constants reported by Motekaitis and Martell were determined by pH potentiometric titrations on the assumption of a homogeneous solution, and so that study assumed the absence of any solid/solution equilibrium. Furthermore, any equilibrium reaction that does not evolve or consume protons in the pH range studied is relatively insensitive to pH potentiometry. The stability constant (log *K*) reported by Motekaitis and Martell for the reaction $CaL^- + L^{3-} = CaL_2^{4-}$ is 2.62.[5] Such a low stability constant results in the putative CaL_2^{4-} species being formed only when L^{3-} is the major ligand species, i.e., above the pH of the last protonation constant, 10.142. As seen in the species distribution curve calculated by Motekaitis and Martell (Figure 6 of ref 5), the CaL_2 species becomes significant only above pH 10. Thus, the dominant reaction in the pH range where CaL_2 is reported to be formed does not evolve or consume protons. In the present study direct measurement of calcium concentration, by chemical analysis or a calcium ion selective electrode, has been used to characterize the equilibrium reactions and their thermodynamic constants. We conclude that there is no evidence for a CaL_2^{4-} species. Furthermore, even the glyphosate trianion coordinates to calcium only through the phosphonate group, with little or no involvement of the nitrogen.

Experimental Section

General Considerations. All chemicals were reagent grade. The glyphosate was obtained as the pure crystalline acid (99.9%) from Monsanto. The pH (not p[H$^+$]) was monitored by a Fisher Accumet Model 825 MP pH meter and glass pH electrode, calibrated at pH 7.00 and 10.00. Microanalytical and atomic absorption analyses were performed

---

* To whom correspondence should be addressed.

(1) Grossbard, E.; Atkinson, D. *The Herbicide Glyphosate*; Butterworths: London, 1985.

(2) Holly, K. In ref 1, pp 451–453.

(3) Wauchope, D. *J. agric. Food Chem.* **1976**, *24*, 717.

(4) Madsen, H. E. L.; Christensen, H. H.; Gottlieb-Petersen, C. *Acta Chem. Scand., Sect. A* **1978**, *A32*, 79.

(5) Motekaitis, R. J.; Martell, A. E. *J. Coord. Chem.* **1985**, *14*, 139.

(6) Knuuttila, P.; Knuuttila, H. *Acta Chem. Scand., Sect. B* **1979**, *B33*, 623.

(7) Knuuttila, P., personal communication.

(8) Appleton, T. G.; Hall, J. R.; McMahon, I. J. *Inorg. Chem.* 1986, *25*, 726.

0020-1669/88/1327-1056$01.50/0