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## Theoretical Study of 3d-Metal Porphyrin $\pi$ -Complexes Acetylene

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**Abstract**—The structural parameters, energies, and spectroscopic characteristics of acetylene  $\pi$ -complexes of metalloporphyrins  $M(P)(\pi-C_2H_2)$ , where M is a 3d-metal atom in different multiplicity states have been calculated by the density functional theory B3LYP method. It has been shown that the activation of the coordinated acetylene molecule is manifested in (i) a sharp weakening of its C–C bond, (ii) a 20°–40° decrease of the bond angles  $\varphi(HCC)$  and an elongation by 0.05–0.10 Å of the  $R(CC)$  bond, (iii) a long-wavelength shift of the  $\nu_{str}(CC)$  stretching mode by 300–500  $cm^{-1}$ , (iv) considerable electron density transfer from the porphyrin ring (P ring) to the  $\pi$ -ligand, and (iv) a strong displacement (0.5–0.6 Å) of the M atom from the P ring plane toward the  $\pi$ -ligand and the dome distortion of the P ring. There is a trend in the behavior of the activation effects along the 3d series and with a change in the electronic state multiplicity of the complexes.

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Metalloporphyrins have been the subject of intensive experimental and theoretical studies for several decades (see, e.g., *Porphyrin Handbook* [1] and references therein). Previously [2], we performed systematic density functional theory (DFT) calculations of molecular characteristics of five- and six-coordinate complexes of 3d metal porphyrins with  $\sigma$ -ligands like  $M(P)(\sigma-L)$  and  $M(P)(\sigma-L)_2$ , where  $P = C_{20}H_{12}N_4$ ,  $M = Ti-Ni$ , and  $\sigma-L = CO, CS, \text{ and } CN^-$ , as well as of their analogues. In [3], analogous calculations were performed for the Ti porphyrin complexes with  $\pi$ -ligands  $Ti(P)(\pi-L)$  and  $Ti(P)(\pi-L)_2$ , where  $\pi-L$  is dihapto-coordinated acetylene, ethylene, benzene, fullerene, diimine, molecular nitrogen, and related molecules. Comparison of the computation results obtained in [2] and [3] revealed several significant differences between the above  $\sigma$ - and  $\pi$ -complexes.

In accordance with the predictions of the valence state molecular model of the metalloporphyrin molecule  $M(P)$  (see [2] for details), for the Ti, Cr, Mn, and Fe carbonyl porphyrin  $\sigma$ -complexes  $M(P)(CO)_n$  ( $n = 1, 2$ ), the calculated energies of addition of the second CO group are higher than those of the first CO group, so that five-coordinate metalloporphyrins  $M(P)(CO)$  should be energetically prone to attach the second ligand and convert into the six-coordinate species  $M(P)(CO)_2$ . Conversely, five-coordinate acetylene, ethylene, diimine, and related  $\pi$ -complexes  $M(P)(\pi-L)$  are not prone to form six-coordinate  $M(P)(\pi-L)_2$  species: the M atom is strongly (by 0.5–0.6 Å) shifted

toward one  $\pi$ -ligand, while the second  $\pi$ -ligand turns out to be at a distance of 3.5–4.0 Å from the metal atom; i.e., it is weakly bound and actually displaced to the boundary of the metal coordination sphere [3].

In six-coordinate metalloporphyrins with different diamagnetic ligands  $M(P)(\sigma-L)(\sigma-L')$ , the mutual trans influence of axial  $\sigma-L$  and  $(\sigma-L')$  ligands is similar to the ligand trans influence in common octahedral transition metal complexes: a stronger bond usually becomes shorter and stronger, while a weaker bond becomes longer and weaker. In analogous  $M(P)(\pi-L)(\pi-L')$   $\pi$ -complexes, the stronger  $\pi-L$  ligand displaces the weaker  $\pi-L'$  ligand from the coordination sphere almost completely, so that the structure and properties of the remote  $M(P)(\pi-L)$  and  $\pi-L'$  moieties actually do not differ from the structures and properties of the free five-coordinate  $M(P)(\pi-L)$  complex and  $\pi-L'$  ligand.

In mixed  $\sigma\pi$ -complexes  $M(P)(\sigma-L)(\pi-L')$  in the singlet state, strong  $\pi$ -ligands like acetylene or diimine displace the carbonyl group, which, in turn, displaces weaker  $\pi$ -ligands like  $C_6H_6, C_{60}, \text{ and } N_2$ . In the triplet state, the strength of the metal– $\pi$ -ligand bond decreases much more dramatically as compared with the metal– $\sigma$  metal bond so that in the triplet state (in contrast to the singlet state) the carbonyl group displaces not only weak but also strong  $\pi$ -ligands like acetylene.

In [3], our attention was focused on a series of Ti porphyrin  $\pi$ -complexes in which the  $\pi$ -ligand was  $C_2H_2, C_2H_4, HCN, C_6H_6, C_{60}, N_2H_2, \text{ or } N_2$ . The present work deals with analogous B3LYP calculations

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**Table 1.** Calculated characteristics of metalloporphyrin complexes with acetylene  $M(P)(\pi-C_2H_2)$  and their anions\*

Complex	$M$	$R(MC)$	$R(CC)$	$h(M/4N)$	$\varphi(HCC)$	$\rho(M)$	$Z(C_2H_2)$	$\nu(M-C_2H_2)$	$\nu(CC)$	$E_{rel}$	$D$
$C_2H_2$	1		1.211		180.0				2071		
Sc(P)( $\pi-C_2H_2$ )	2	2.346	1.272	0.68	149.4	0.31	-0.22	407	1759	0	30
Sc(P)( $\pi-C_2H_2$ ) <sup>-</sup>	1	2.367	1.264	0.54	152.3		-0.23	247	1769	1.6	
	3	2.358	1.275	0.65	147.8	0.26	-0.30	370	1759	0	28
Ti(P)( $\pi-C_2H_2$ )	1	2.017	1.319	0.59	139.5		-0.29	597	1581	0	62
	3	2.257	1.261	0.59	155.8	1.45	-0.02	443	1793	16.8	28
Ti(P)( $\pi-C_2H_2$ ) <sup>-</sup>	2	2.025	1.318	0.57	139.4	~0	-0.35	582	1588	0	52
	4	2.256	1.265	0.55	154.8	1.41	-0.20	411	1786	23.1	
V(P)( $\pi-C_2H_2$ )	2	1.983	1.305	0.55	144.5	1.18	-0.20	590	1643	0	54
	4	2.401	1.226	0.28	172.3	2.63	0.10	216	1966	11.5	29
V(P)( $\pi-C_2H_2$ ) <sup>-</sup>	1	2.058	1.276	0.32	151.3		-0.12	484	1746	28	
	3	1.987	1.305	0.53	144.3	1.19	-0.27	572	1645	0	36
Cr(P)( $\pi-C_2H_2$ )	1	1.911	1.303	0.51	147.9		-0.12	599	1642	17.5	16
	3	2.042	1.270	0.37	152.7	2.31	-0.08	471	1763	0	22
Mn(P)( $\pi-C_2H_2$ )	2	1.994	1.266	0.36	155.1	1.14	-0.08	485	1786		26
Fe(P)( $\pi-C_2H_2$ )	1	2.101	1.239	0.24	164.4		0.04	341	1905	15.5	4
	3	3.032	1.213	0.04	179.7	2.28	0.01	64	2060	1.2	3
	5	2.221	1.234	0.43	167.6	3.87	-0.01	185	1928	0	11
Co(P)( $\pi-C_2H_2$ )	4	2.396	1.220	0.34	175.5	2.80	0.11	129	2010		10
Ni(P)( $\pi-C_2H_2$ )	3	2.595	1.215	0.20	179.0	1.78	0.11	129	2045		13.4

\* Bond lengths and bond angle are in angstroms and degrees, respectively; vibrational frequencies are in  $cm^{-1}$ ; relative multiplet energies ( $E_{rel}$ ) and decomposition energies of the complexes with retention of the multiplicity ( $D$ ) are in kcal/mol;  $M$  is the multiplicity ( $M = 2S + 1$ );  $\rho(M)$  is the spin density at the metal atom;  $Z(C_2H_2)$  is the overall effective charge at the coordinated acetylene molecule.

of the equilibrium geometry, normal mode frequencies, electron and spin density distributions, relative energies of multiplets, and other molecular characteristics for acetylene complexes of metalloporphyrins  $M(P)(\pi-C_2H_2)$  and their negative ions  $M(P)(\pi-C_2H_2)^-$  ( $P = C_{20}H_{12}N_4$ ) containing other 3d-metal atoms in different multiplicity states, as well as for their protonated forms  $M(P)(\sigma-C_2H_3)^+$  in the high-spin state. In addition, we calculated complexes of the  $Ti(P)(\pi-C_2H_2)$  type with different substituents in the P ring, as well as the tetraphenylporphyrin and phthalocyanine complexes,  $Ti(TPP)(\pi-C_2H_2)$  and  $Ti(Pc)(\pi-C_2H_2)$ , respectively. Among the experimentally studied compounds of this type, noteworthy are the  $Ti(P)(\pi-C_2H_2)$  and  $Ti(TPP)(\pi-C_2H_2)$  complexes where OEP and TPP are octaethyl- and tetraphenylporphyrins, respectively [4].

#### COMPUTATIONAL DETAILS

As previously [2, 3], all DFT calculations were performed in the B3LYP approximation [5, 6]. Geometry

optimization and normal mode frequency calculations were performed with the GAUSSIAN 03 program package [7] using the 6-31G and 6-31G\* basis sets. The energy characteristics were refined using the more extended basis set  $Gen = 6-311+G^*(M) + 6-31G^*(C, N, H, O)$ . The magnetic shielding constants  $\sigma$  of the atoms in diamagnetic complexes were calculated by the GIAO method [8, 9]. Table 1 summarizes the calculated geometries and energies of the  $M(P)(\pi-C_2H_2)$  complexes, and Table 2 presents analogous properties of Ti-acetylene  $\pi$ -complexes with different substituents in the P ring, and Table 3 lists the properties of the protonated  $M(P)(\sigma-C_2H_3^+)$  species.

Possible errors of B3LYP calculations were exemplified by calculation of the Ti porphyrin  $\pi$ -complexes in [3]. It is worth noting once more that calculations of multiplets can be of approximate character (especially for closely spaced multiplets on the energy scale) because of the drawbacks of the single-reference approximation underlying known DFT variants. Such situations are frequently encountered in calculations

**Table 2.** Calculated geometric and spectroscopic characteristics of acetylene  $\pi$ -complexes with different rings\*

Complex	$R$ (MC)	$R$ (CC)	$h(M/4N)$	$\varphi(\text{HCC})$	$\rho(M)$	$Z$ ( $\text{C}_2\text{H}_2$ )	$\nu(M-\text{C}_2\text{H}_2)$	$\nu(\text{C}-\text{C})$	$\sigma(\text{C})$	$\sigma(\text{H})$	$E_{\text{rel}}$	$D$
Singlet state ( $C_{\text{meso}}-C_{\text{meso}}$ orientation)												
$\text{C}_2\text{H}_2$		1.211		180.0				2071	128.8	31.0	0	
Ti(P)( $\pi\text{-C}_2\text{H}_2$ )	2.017	1.319	0.59	139.5		-0.29	597	1581	-16.0	27.7	0	61.8
Ti[P(F <sub>4</sub> )]( $\pi\text{-C}_2\text{H}_2$ )	2.008	1.320	0.59	139.3		-0.24	601	1576	-20.3	27.4	0	72.1
Ti[P(Li <sub>4</sub> )]( $\pi\text{-C}_2\text{H}_2$ )	2.019	1.322	0.59	138.7		-0.34	603	1574	-9.3	28.2	0	66.3
Ti(TPP)( $\pi\text{-C}_2\text{H}_2$ )	2.015	1.320	0.59	139.2		-0.28	593	1580	-15.0	27.5	0	60.8
Ti(Pc)( $\pi\text{-C}_2\text{H}_2$ )	2.017	1.321	0.62	138.8		-0.25	585	1571	-17.0	26.5	0	65.6
Triplet state (N-N orientation)												
Ti(P)( $\pi\text{-C}_2\text{H}_2$ )	2.257	1.261	0.59	155.8	1.45	-0.02	443	1793			16.8	29.0
Ti[P(F <sub>4</sub> )]( $\pi\text{-C}_2\text{H}_2$ )	2.379	1.233	0.35	167.4	1.20	0.10	237	1921			25.2	25.5
Ti[P(Li <sub>4</sub> )]( $\pi\text{-C}_2\text{H}_2$ )	2.335	1.241	0.37	162.8	1.10	-0.02	273	1878			31.9	23.7
Ti(TPP)( $\pi\text{-C}_2\text{H}_2$ )	2.341	1.234	0.32	166.2	1.16	0.10	239	1915			27.1	24.1
Ti(Pc)( $\pi\text{-C}_2\text{H}_2$ )	2.335	1.237	0.40	165.8	0.98	0.10	277	1899			22.8	27.7

\* See notes to Table 1. TPP is tetraphenylporphyrin; Pc is phthalocyanine; Ti[P(F<sub>4</sub>)]( $\pi\text{-C}_2\text{H}_2$ ) and Ti[P(Li<sub>4</sub>)]( $\pi\text{-C}_2\text{H}_2$ ) are porphyrins in which four *meso* hydrogen atoms of the P ring are substituted by F and Li atoms, respectively (structures **2a** and **2b** in Fig. 1, see text for details);  $\sigma(\text{C})$  and  $\sigma(\text{H})$  are the magnetic shielding constants for the acetylene C and H atoms. The assignment of the  $\nu(\text{M}-\text{C}_2\text{H}_2)$  frequency of approximate, since the  $\text{M}-\text{C}_2\text{H}_2$  stretching vibration is strongly coupled to the ring vibrations.

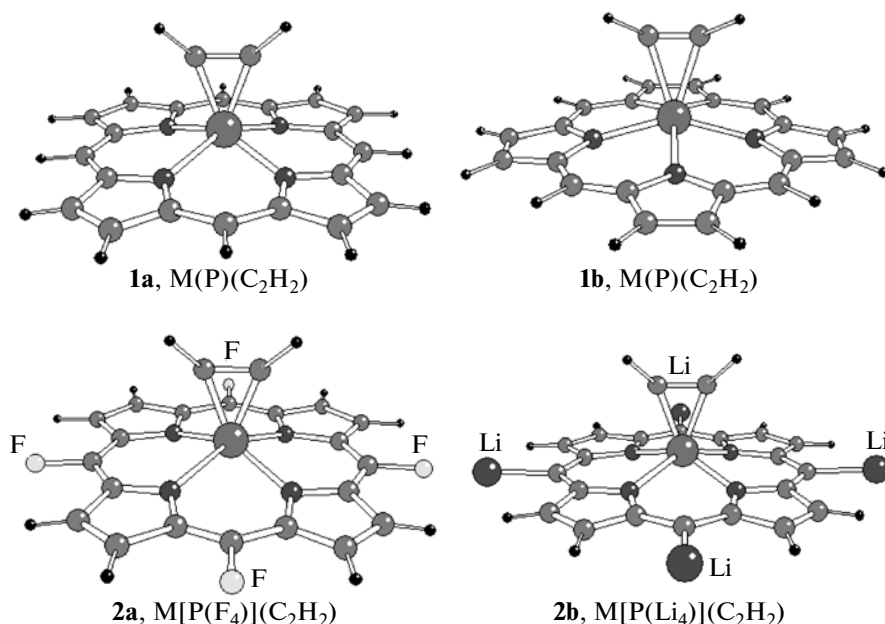
of  $\pi$ -complexes of late 3d metals (Mn(III), Co(II), etc.), where there are difficulties with the convergence of both the SCF procedure and optimization procedure. In addition, since each multiplicity value can correspond to a set of closely spaced electronic states with different electron and spin density distributions (and, hence, with different structural and spectroscopic characteristics), the choice of the lowest-lying state from this set presents a serious problem. As noted in [3], the errors of DFT calculations of relative energies of multiplets can be as large as several tenths of an electron volt, and reliable determination of the relative position of electronic states on the energy scale requires the use of multireference methods. The present work mainly deals with  $\pi$ -complexes of early 3d metals where the above difficulties are less significant, whereas for heavier 3d metals, we restricted our-

selves to the brief discussion of the most general qualitative trends.

## RESULTS AND DISCUSSION

### *Neutral M(P)( $\pi\text{-C}_2\text{H}_2$ ) Complexes and M(P)( $\pi\text{-C}_2\text{H}_2$ )<sup>-</sup> Anions*

According to the calculations, the  $\pi$ -complexes of early 3d metals in the ground state correspond to low- and medium-spin doublet (M = Sc), singlet (Ti), doublet (V), and triplet (Cr) states with structures of symmetry close to  $C_{2v}$  (Fig. 1) in which the porphyrin ring P has a dome conformation and the active  $\text{M}-\text{C}_2$  fragment has a shape of an isosceles triangle with the acetylene C-C bond oriented parallel to the line either between the opposite *meso* carbon atoms (structure **1a** for M = Sc and Ti) or between the nitrogen atoms of



**Fig. 1.** Structures of acetylene  $\pi$ -complexes of metalloporphyrins. In structures **1a** and **1b**, the  $C_2H_2$  molecule is parallel to the  $C_{meso}-C_{meso}$  and N-N lines, respectively. In structure **2a** and **2b**, all *meso* H atoms are substituted by F and Li atoms, respectively.

the P ring (structure **1b** for  $M = V$  and Cr). Different mutual orientations of  $C_2H_2$  and the P ring have almost no effect on the geometry of the  $M-C_2$  moiety, and the barrier to rotation of acetylene about the molecular axis does not exceed a few kcal/mol and slowly decreases in going from Sc to Cr. The  $C_2H_2$  molecule in the complexes has a negative charge, which monotonically decreases from  $-0.2e$  for  $M = Sc$  to  $-0.1e$  for  $M = Cr$ . The molecule acts as an electron density acceptor and the P ring, as an electron density donor. The shift of the metal  $h(M/4N)$  normally to the P ring plane toward  $C_2H_2$  is significant in all complexes and monotonically decreases from 0.7 (Sc) to 0.5 Å (Cr). An analogous monotonic shortening is typical of the  $R(MC_2)$  distance between the metal atom and the acetylene molecule (from 2.35 (Sc) to 1.98 Å (V) with a small elongation for Cr, 2.04 Å). The  $\nu(M-C_2H_2)$  stretching vibration frequency changes oppositely to the  $R(M-C_2H_2)$  distance: it increases from 410  $cm^{-1}$  for Sc to 590–600  $cm^{-1}$  for Ti and V and decreases to 470  $cm^{-1}$  for Cr. The bond energies  $D(M-C_2H_2)$  (hereinafter, the decomposition energies for  $M(P)(C_2H_2) \rightarrow M(P) + C_2H_2$  with retention of the spin are given) increase from  $\sim 30$  (Sc) to 54–62 kcal/mol (Ti, V) and then decreases again to  $\sim 22$  kcal/mol (Cr). The effect of activation of the acetylene molecule in the metal coordination sphere are most pronounced for the singlet  $Ti(P)(C_2H_2)$  complex, where the bond energy  $D(Ti-C_2H_2)$  is maximal: the deviation of the  $\varphi(HCC)$  angle from the straight one is as large as  $40^\circ$ , the  $R(CC)$  distance becomes 0.11 Å longer and closer to the common length of the C–C double bond, the

$\nu_{str}(CC)$  frequency is shifted toward lower wavelengths by almost 500  $cm^{-1}$  as compared with the corresponding characteristics of the isolated  $C_2H_2$  molecule (see [3] for details). The weakest activation effect are observed for the triplet  $Cr(P)(C_2H_2)$  complex, which has the lowest bond energy  $D(Cr-C_2H_2)$ : here, the  $\varphi(HCC)$  angle decreases by  $28^\circ$ , the  $R(CC)$  distance becomes 0.06 Å longer, and the  $\nu_{str}(CC)$  frequency decreases by  $\sim 300$   $cm^{-1}$ . The Sc and V complexes have an intermediate position:  $Sc(P)(C_2H_2)$  is closer to  $Cr(P)(C_2H_2)$  while  $V(P)(C_2H_2)$  is closer to  $Ti(P)(C_2H_2)$ ; however, in all cases, the changes in geometric and spectroscopic characteristics of the coordinated acetylene molecule remain considerable and can be easily monitored by IR and NMR spectroscopy.

The above discussion pertains to low- and medium-spin state in which the vacant AOs of the M atom favor the formation of rather strong  $M-C_2H_2$  bonds. In the excited high-spin states, these bonds become longer (by 0.24 and 0.42 Å for  $M = Ti$  and V, respectively) and weaker with the simultaneous sharp decrease in the activation effects for the acetylene molecule. However, calculations show that the triplet state for  $Ti(P)(C_2H_2)$  and the quartet state for  $V(P)(C_2H_2)$  retain some “residual” stability to decomposition with removal of  $C_2H_2$  and, presumably, can exist in the free state.

According to calculations (Table 1), the extra electron in the  $M(P)(C_2H_2)^-$  anions is accepted into the antibonding  $\pi$ -MO of the porphyrin ring P, so that the  $M(P^-)(C_2H_2)$  structure corresponds best of all to these anions. In this structure, the electron and spin density

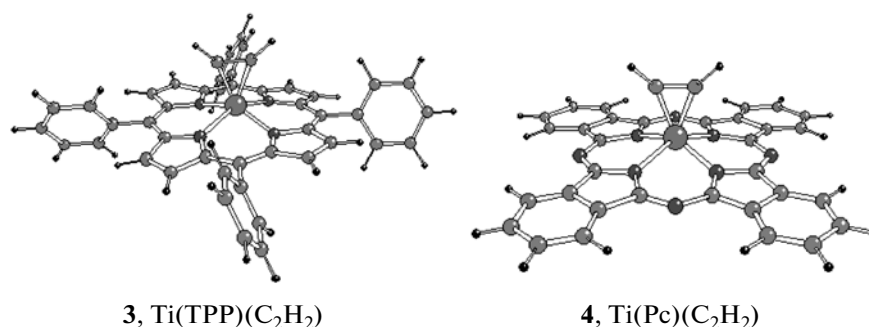


Fig. 2. Structures of acetylene  $\pi$ -complexes of titanium tetraphenylporphyrin (**3**) and phthalocyanine (**4**).

distributions in the  $M-C_2H_2$  moieties is slightly disturbed and little differs from those in the initial neutral  $M(P)(C_2H_2)$  molecules with the same  $M$  atom and the multiplicity lower by unity. Indeed, Table 1 demonstrates that the structural and spectroscopic characteristics of the  $M-C_2H_2$  moiety in the anions are almost quantitatively consistent with the characteristics of the corresponding (“preceding”) neutral systems, for example, in the pairs  $Ti(P)(C_2H_2)^-$  (doublet)– $Ti(P)(C_2H_2)$  (singlet),  $V(P)(C_2H_2)^-$  (triplet)– $V(P)(C_2H_2)$  (doublet), etc. The adiabatic electron affinity (the difference between total energies of the optimized  $M(P)(C_2H_2)^-$  and  $M(P)(C_2H_2)$  structures) is about 25 kcal/mol for the Sc, Ti, and V complexes and increases to 40 kcal/mol for the triplet  $Cr(P)(C_2H_2)$ . The energy of  $C_2H_2$  elimination with retention of the spin for the anions is always lower than for the neutral precursors with a minimal difference of 4 kcal/mol for  $M = Sc$  and a more significant difference of 10–15 kcal/mol for  $M = Ti, V,$  and  $Cr$ .

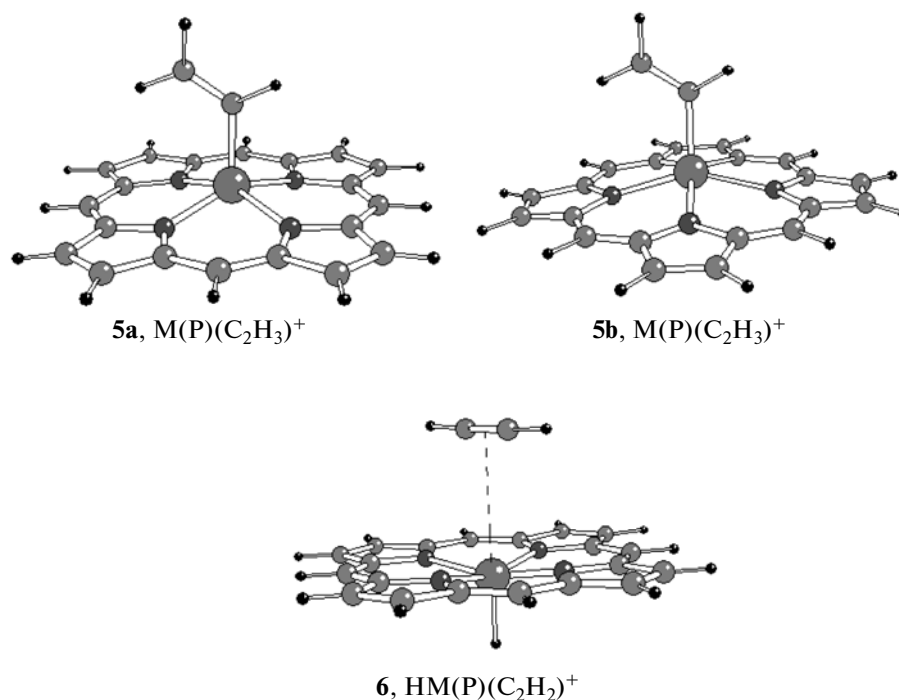
#### Complexes with More Complicated Rings of TPP, Pc, and Others

Until now, we considered complexes with the “bare” porphyrin ring  $P = C_{20}H_{12}N_4$ . As is known, such complexes are unstable to association and have been little studied, so that their calculations are often of model and predictive character. The question arises of how much these results can be useful in going to “actually existing” protected metal tetraphenylporphyrins  $M(TPP)$  or when the phthalocyanine (Pc) ring stands in place of the porphyrin ring  $P$ . We considered this question using analogous B3LYP calculations of a series of titanium  $\pi$ -complexes  $Ti(TPP)(C_2H_2)$ ,  $Ti(Pc)(C_2H_2)$  (structures **3** and **4**, Fig. 2), and substituted derivatives  $Ti[P(F_4)](C_2H_2)$  and  $Ti[P(Li_4)](C_2H_2)$  (structures **2a** and **2b**, respectively, Fig. 1) in their singlet and triplet states (in the latter two complexes, all four H atoms at the *meso* carbon atoms are substituted by fluorine and lithium atoms, respectively). The computation results are summarized in Table 2. As is seen, in the singlet state, the structural and vibrational characteristics of the  $Ti-C_2H_2$  moiety change only

slightly both on going from the bare  $P = C_{20}H_{12}N_4$  ring to the substituted TPP or phthalocyanine Pc and upon the substitution of F and Li atoms for the  $H_{meso}$  atoms. Extrapolation allows us to assume that the structural and vibrational characteristics of  $M-C_2H_2$  moieties and the trends in their behavior found by means of calculations of model metalloporphyrins  $M(P)$  will be satisfactorily (at least, at the semiquantitative level) transferred to their more complicated protected and *meso*-substituted analogues, as well as to phthalocyanines. We also believe that the same conclusion is valid for  $M-C_2H_4$ ,  $M-N_2H_2$ , and other moieties, i.e., with ethylene, diimine, and other  $\pi$ -ligands in the states where the antibonding  $\pi$ -MO remains vacant.

The most perceptible differences are those for the magnetic shielding constants (we here discuss relative changes in  $\sigma(C)$ ) at the acetylene C atoms and for the bond energies  $D(Ti-C_2H_2)$ . The differences are maximal for *meso*-substituted metalloporphyrins: for the F-substituted complex  $M[P(F_4)](C_2H_2)$ , the bond energy increases by  $\sim 11$  kcal/mol, while  $\sigma(C)$  decreases by  $\sim 4$  ppm; for the Li-substituted analogue  $M[P(Li_4)](C_2H_2)$ , both  $D(Ti-C_2H_2)$  and  $\sigma(C)$  increase by  $\sim 4.5$  kcal/mol and  $\sim 7$  ppm, respectively, as compared with the characteristics of the initial  $M(P)(C_2H_2)$  complex. Inasmuch as the F and Li atoms occupy the outermost positions on the electronegativity scale, we can assume that, in the case of other *meso* substituents with intermediate electronegativities, the changes will fall within these ranges. Going from the bare  $P$  ring to substituted TPP has almost no effect (within the calculation error) on  $D(Ti-C_2H_2)$  and  $\sigma(C)$ , and for phthalocyanine, a perceptible change (in increase by 4 kcal/mol) is observed only for the  $D(Ti-C_2H_2)$  energy.

The above discussion pertains to the singlet state. In the triplet state where one electron is excited into the antibonding  $\pi$ -MO of the ring and the  $Ti-C_2H_2$  interaction and acetylene polarization become sharply weaker, the effect of the  $P$ -ring substituents is more clearly pronounced. As compared with the singlet, the  $D(Ti-C_2H_2)$  energy in the triplet decreases severalfold, the  $R(M-C_2H_2)$  distance becomes 0.06–0.08 Å longer, and the  $\nu_{str}(M-C_2H_2)$  frequency decreases by 70–200



**Fig. 3.** Structures of protonated acetylene complexes. In structures **5a** or **5b**, the vinyl  $C_2H_3$  groups are coplanar with the planes containing the M atom and the  $C_{meso}-C_{meso}$  or N–N lines, respectively. In structure **6**, the M atom is protonated, and the acetylene molecule is displaced from the metal coordination sphere.

$cm^{-1}$ . Correspondingly, the  $\phi(HCC)$  angle in the acetylene molecule increases by  $15^\circ-20^\circ$ ,  $R(CC)$  becomes  $0.03 \text{ \AA}$  shorter, and  $\nu_{str}(CC)$  increases by  $70-200 \text{ cm}^{-1}$ . This is accompanied by a change of the mutual orientation of  $C_2H_2$  and  $Ti(P)$ : in the singlet, the C–C is coplanar with the plane containing the M atom and the opposite  $C_{meso}$  atoms, and in the triplet, this bond is coplanar with the plane containing the M atom and the opposite nitrogen atoms of the P ring.

#### Protonated $M(P)(C_2H_3)^+$ Forms

In [3], we showed for titanium compounds that the protonation of the  $M(P)(C_2H_2)$   $\pi$ -complex can occur at two sites: the proton can be attached to the acetylene molecule to form the vinyl complex  $M(P)(C_2H_3)^+$  and to the metal atom to form the opposite axial  $\sigma$ -bond M–H. Both structures correspond to local minima of the potential energy surface; however, in the second structure of  $Ti(P)(C_2H_3)^+$ , which is considerably less favorable than the first structure, the trans influence of the Ti–H bond is so strong that the  $C_2H_2$  molecule is actually displaced from the metal coordination sphere, being at a distance of  $3.0 \text{ \AA}$  from the metal, and turns out to be weakly, if at all, bound to the  $Ti(P)H^+$  residue. Since acetylene is a “strong”  $\pi$ -ligand, an analogous pattern is expected for related complexes with ethylene, benzene, and other weaker  $\pi$ -ligands: in all cases, protonation at the metal atom

should be accompanied by decomposition of the complex with displacement of the  $\pi$ -ligand.

Protonation of the coordinated acetylene molecule can occur without a barrier and is accompanied by considerable electron density rearrangement in the  $M-C_2H_2$  moiety: one  $\pi$ -bond in acetylene is broken, the C–H bond forms, the  $\pi-C_2H_2$  complex converts into the high-spin vinyl  $\sigma$  form with structure **5a** or **5b** (Fig. 3). The positive charge initially localized at the proton is transferred to the  $M(P)$  porphyrin and is mainly distributed over the P ring. The oxidative number of the metal atom increases by unity, although its effective charge (according to Mulliken) changes only by tenths of an electron charge. In the complexes with early 3d metals, the vinyl group is a weak electron acceptor and has a small negative charge, which decreases in magnitude along the 3d series and, beginning with  $M = Cr$ , changes sign to positive, so that in the complexes of late 3d metals, the vinyl group acts as a weak donor.

According to our calculations, in structure **5a** of  $M(P)(\sigma-C_2H_3)^+$  ions, the vinyl C–C bond is coplanar with the plane containing the M atom and the opposite  $C_{meso}$  atoms of the P ring. The geometric and spectroscopic parameters of the  $M-(\sigma-C_2H_3)^+$  moiety depend rather weakly on the nature of M atom (Table 3). In the lowest-lying high-spin states, on going from Ti to Mn, the  $R(CC)$  and  $R(CH)$  bond lengths and  $\phi(HCC)$  angles of the vinyl group vary within narrow limits of  $0.04$  and  $0.01 \text{ \AA}$  and a few degrees, respec-

**Table 3.** Calculated energetic characteristics of protonated acetylene complexes  $M(P)(\sigma-C_2H_3)^{+*}$ 

Complex	$M$	$R$ ( $MC_M$ )	$R$ (CC)	$R$ ( $C_MH$ )	$h(M/4N)$	$\Phi$ ( $MC_M C$ )	$\rho(M)$	$Z$ ( $C_2H_3$ )	$\nu(M-C_2H_3)$	$\nu(CC)$	$E_{rel}$	$D$
$C_2H_3$	2		1.310	1.083						1678		
Ti(P)( $\sigma-C_2H_3$ ) <sup>+</sup>	1	2.021	1.349	1.094	0.45	123.6		-0.08	557	1618		48
V(P)( $\sigma-C_2H_3$ ) <sup>+</sup>	2	1.974	1.342	1.092	0.43	122.8	1.20	-0.03	559	1615		43
Cr(P)( $\sigma-C_2H_3$ ) <sup>+</sup>	1	1.938	1.340	1.091	0.38	122.5		0.03	565	1611	25.9	
	3	1.950	1.348	1.090	0.30	125.6	2.38	0.06	553	1595	0	
Mn(P)( $\sigma-C_2H_3$ ) <sup>+</sup>	2	1.991	1.326	1.088	0.22	124.2	3.37	0.00	466	1651		
Fe(P)( $\sigma-C_2H_3$ ) <sup>+</sup>	1	1.871	1.344	1.088	0.26	124.7		-0.06	583	1580	27.1	
	3	1.966	1.328	1.086	0.20	124.2	2.22	0.09	447	1630	0	39
	5	1.975	1.333	1.093	0.36	124.2	2.91	-0.16	479	1635	13.8	
Co(P)( $\sigma-C_2H_3$ ) <sup>+</sup>	2	1.883	1.328	1.090	0.15	127.5		-0.05	548	1668	0	
	4	1.983	1.327	1.087	0.28	119.2	2.47	0.09	407	1631	22.4	
	6	2.070	1.334	1.092	0.46	124.6	3.11	-0.05	369	1625	30.4	
Ni(P)( $\sigma-C_2H_3$ ) <sup>+</sup>	1	1.953	1.313	1.085	0.15	124.5		0.16	486	1681	0	
	3	1.903	1.324	1.086	0.15	125.6	1.18	0.08	481	1684	7.8	

\* See notes to Table 1.  $C_M$  is the acetylene carbon atom bound to the metal atom.

tively, and slightly differ from the characteristics of the isolated  $C_2H_3$  radical, and the  $R(M-C_2H_3)$  bond becomes only  $\sim 0.03$  Å shorter. The  $\nu_{str}(CC)$  and  $\nu_{str}(CH)$  frequencies are slightly shifted toward longer wavelengths, by 50–100  $cm^{-1}$ . The calculated energies of elimination of the vinyl radical with the homolytic  $M-C_2H_3$  bond cleavage in the complexes are 43–48 kcal/mol and are comparable ( $\sim 10$  kcal/mol lower) with the  $D(M-C_2H_2)$  energies in the initial neutral  $\pi$ -complex. The overall decrease in energy upon the protonation of the acetylene  $\pi$ -complexes of metalloporphyrins is estimated at  $\sim 225$ – $265$  kcal/mol, which considerably exceeds the proton affinity of the free  $C_2H_2$  molecule ( $\sim 151$  kcal/mol [10]).

As already mentioned, for the strong singlet  $\pi$ -complex  $Ti(P)C_2H_2$ , the protonation of acetylene is clearly preferred over the protonation of the metal atom (structure **6** in Fig. 3). The question arises as to how the relative energy of these two alternative protonated structures (**5a** and **6**) will change for complexes with weaker  $M$ -ligand bonds, for example, when acetylene is substituted by ethylene or other weak  $\pi$ -ligands, as well as when Ti is substituted by its heavier neighbors in the  $3d$  series. In [3], we found that, for the weak dinitrogenyl complex  $Ti(P)N_2$  where the calculated  $Ti-N_2$  bond energy is less than 10 kcal/mol, both structures are close in energy, although the protonation of the  $N_2$  molecule remains slightly more preferable. Inasmuch as  $C_2H_2$  and  $N_2$  occupy the outermost positions in the series of  $\pi$ -ligands in the strength of their bond with the metal atom, we can assume that for the  $Ti(P)L$  complexes with other  $\pi$ -ligands  $L$  characterized by intermediate metal-ligand bond energies, the protonation of the

ligand also remains energetically more favorable. As for substitution of Ti by other  $3d$  atoms, our analogous B3LYP calculations of the triplet  $Cr(P)(C_2H_3)^+$  and  $Fe(P)(C_2H_3)^+$  complexes demonstrate that, in these cases as well, protonation of acetylene to form the vinyl complex is considerably more favorable than protonation of the metal atom.

To conclude, it is pertinent to make several general remarks on the results obtained for the  $M(P)(\pi-C_2H_2)$  complexes containing late  $3d$ -metal atoms, which are computationally more complicated. Since the  $3d$  AOs of the metal atoms are filled by electron pairs or unpaired electrons and the bonding  $M-C_2H_2$  interactions become weaker, most complexes are considerably less stable to decomposition with elimination of the  $C_2H_2$  molecule as compared with the above complexes. The calculated  $D(M-C_2H_2)$  energies for these complexes rarely exceed 10 kcal/mol, even for low- and medium-spin states. Inasmuch as the B3LYP approximation tends to systematically overestimate these energies [3, 11, 12], we assume that the “actual” stability of such complexes can be even lower. For adequate analysis of trends in the behavior of properties of similar weakly bound compounds (and especially for quantitative estimates of absolute values), more accurate approximations should be used. In some cases, the spin characteristics like  $S(S+1)$  calculated by us at the B3LYP level significantly differ from standard values, which points to the multireference character of wave functions and insufficient “adequacy” of the B3LYP approximation. Therefore, only few structures with late  $3d$  atoms are presented in Table 1 for which the B3LYP computation results are believed to be most reliable. These data demonstrate that a decrease in  $D(M-$

C<sub>2</sub>H<sub>2</sub>) is accompanied by a considerable elongation of the metal–acetylene distance to 2.2–2.3 Å or more, a decrease in the  $\nu(\text{M}-\text{C}_2\text{H}_2)$  frequency to 200 cm<sup>-1</sup> or lower, and a sharp weakening of the activation effects of the weakly coordinated C<sub>2</sub>H<sub>2</sub> molecule, for which the geometric and vibrational characteristics are close to those of the free C<sub>2</sub>H<sub>2</sub> molecule. Comprehensive systematic analysis requires the use of considerably more sophisticated multireference approaches, which is still beyond the capability of our computers.

These methodical difficulties mainly refer to weakly bound  $\pi$ -complexes M(P)( $\pi$ -C<sub>2</sub>H<sub>2</sub>). For considerably stronger protonated  $\sigma$ -complexes M(P)<sup>+</sup>( $\sigma$ -C<sub>2</sub>H<sub>3</sub>), the B3LYP approximation is more adequate. The decomposition energies of these ions with elimination of the C<sub>2</sub>H<sub>3</sub> vinyl radical decrease rather slowly along the 3d series, but remain higher than 20–30 kcal/mol. According to calculations (Table 3), the medium-spin triplet state is most favorable for the Fe(P)<sup>+</sup>( $\sigma$ -C<sub>2</sub>H<sub>3</sub>) ion and the low-spin doublet and singlet states are most favorable for Co(P)<sup>+</sup>( $\sigma$ -C<sub>2</sub>H<sub>3</sub>) and Ni(P)<sup>+</sup>( $\sigma$ -C<sub>2</sub>H<sub>3</sub>), respectively.

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