



DEPARTAMENTO DE
QUÍMICA

UNIVERSIDAD TÉCNICA
FEDERICO SANTA MARÍA



UNIVERSIDAD TÉCNICA
FEDERICO SANTA MARÍA

How the change of the ligand from porphine, P^{2-} , to P_4 -substituted porphine, $P(P)_4^{2-}$, affects the electronic properties and the metal-ligand binding energies for the first-row transition metals: comparative study

Dr. Aleksey Kuznetsov, Assistant Professor

Department of Chemistry, Universidad Técnica Federico Santa María, Santiago, Chile

E-mail: aleksey.kuznetsov@usm.cl

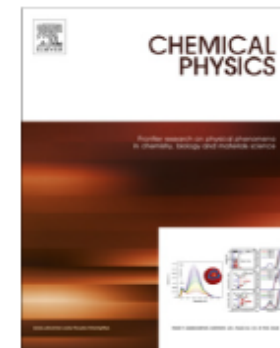


ELSEVIER

Contents lists available at [ScienceDirect](#)

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys



How the change of the ligand from L = porphine, P^{2-} , to L = P_4 -substituted porphine, $P(P)_4^{2-}$, affects the electronic properties and the M–L binding energies for the first-row transition metals M = Sc–Zn: Comparative study

Aleksey E. Kuznetsov *

Departamento de Química, Universidade Federal de São Carlos, Rodovia Washington Luiz, Km 235, Caixa Postal 676, CEP 13565-905 São Carlos, SP, Brazil

Outline

- We performed comparative DFT study, including Natural Bond Orbitals (NBO) analysis, of the binding energies between all the first-row transition metals M^{n+} ($M = \text{Sc–Zn}$) and two ligands of the similar type: porphine, P^{2-} , and its completely P-substituted counterpart, $P(P)_4^{2-}$.
- The main findings are as follows:
 - (i) complete substitution of all the pyrrole nitrogens with P-atoms does not affect the ground spin state of metalloporphyrins;
 - (ii) generally, for the $MP(P)_4$ compounds the calculated HOMO/LUMO gaps and optical gaps are smaller than for their MP counterparts;
 - (iii) the trends in the change of the binding energies between M^{n+} and $P(P)_4^{2-}/P^{2-}$ are very similar for both ligands.
- The complete substitution of the pyrrole nitrogens by the P-atoms decreases the M^{n+} -ligand binding energies; all the $MP(P)_4$ compounds studied are stable according to the calculated E_{bind} values and therefore can be potentially synthesized.

Motivation

- ❖ The structural and electronic properties along with the binding ability of porphyrins can be easily and broadly tuned by replacing one or several pyrrole nitrogens with other elements.
- ❖ The effects of the pyrrole N replacement in porphyrins with P were investigated for some porphyrins and their derivatives:
- ❖ D. Delaere, M.T. Nguyen, Chem. Phys. Lett. 376 (2003) 329.
- ❖ Y. Matano, T. Nakabuchi, H. Imahori, Pure Appl. Chem. 82 (2010) 583.
- ❖ T. Nakabuchi, Y. Matano, H. Imahori, Org. Lett. 12 (2010) 1112.
- ❖ T. Nakabuchi, M. Nakashima, S. Fujishige, H. Nakano, Y. Matano, H. Imahori, J. Org. Chem. 75 (2010) 375.
- ❖ Y. Matano, H. Imahori, Acc. Chem. Res. 42 (2009) 1193.
- ❖ Y. Matano, M. Nakashima, T. Nakabuchi, H. Imahori, S. Fujishige, H. Nakano, Org. Lett. 10 (2008) 553.
- ❖ Y. Matano, T. Nakabuchi, S. Fujishige, H. Nakano, H. Imahori, J. Am. Chem. Soc. 130 (2008) 16446.
- ❖ Y. Matano, T. Nakabuchi, T. Miyajima, H. Imahori, H. Nakano, Org. Lett. 8 (2006) 5713.
- ❖ Y. Matano, T. Miyajima, N. Ochi, T. Nakabuchi, M. Shiro, Y. Nakao, S. Sakaki, H. Imahori, J. Am. Chem. Soc. 130 (2008) 990.
- ❖ Y. Matano, T. Miyajima, T. Nakabuchi, H. Imahori, N. Ochi, S. Sakaki, J. Am. Chem. Soc. 128 (2006) 11760.
- ❖ N. Ochi, Y. Nakao, H. Sato, Y. Matano, H. Imahori, S. Sakaki, J. Am. Chem. Soc. 131 (2009) 10955.

Motivation

- ❖ It would be extremely interesting to receive answers about possible structures, properties, and reactivities of such compounds, and to figure out what differences would **complete substitution** of the pyrrole N with P cause.
- ❖ Even more significant and intriguing would be to find out:
 - what potential novel applications would these metalloporphyrins with all pyrrole nitrogens replaced with phosphorus (MP(P)_4) have?
 - Could we build catalytic systems based on them?
 - Would it be possible to use MP(P)_4 compounds as building blocks for nanotechnology?
 - What about their potential complexes with fullerenes, graphene, nanoparticles, etc.?
- ❖ The list of such questions could be growing and growing, and computational studies, of course, can be of great help here.

Motivation

- ❖ We should notice that till 2016 computational studies of metalloporphyrins with all pyrrole nitrogens replaced with P (MP(P)₄) were relatively scarce.
- ❖ They were generally represented by our previous reports on the NiP(P)₄ compound:
- ❖ J. Barbee, A.E. Kuznetsov. Revealing substituent effects on the electronic structure and planarity of Ni-porphyrins. *Comput. Theoret. Chem.* 981 (2012) 73.
- ❖ and on the series of metalloporphyrins MP(P)₄, where M = Sc, Ti, Fe, Ni, Cu, and Zn:
- ❖ A.E. Kuznetsov. Metalloporphyrins with all the pyrrole nitrogens replaced with phosphorus atoms, MP(P)₄ (M = Sc, Ti, Fe, Ni, Cu, Zn). *Chem. Phys.* 447 (2015) 36.
- ❖ **For the current research, we were motivated by the previous studies of metalloporphyrins with one and four P-atoms and by the 2013 report by Hirao and co-workers on comparative study of binding energies between several transition metals and porphine/porphine-derived ligands:**
- ❖ S. Myradalyev, T. Limpanuparb, X. Wang, H. Hirao. Comparative computational analysis of binding energies between several divalent first-row transition metals (Cr²⁺, Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, and Cu²⁺) and ligands (porphine, corrin, and TMC). *Polyhedron* 52 (2013) 96.

Computational Details

- The study performed using the Gaussian09 package.
- MP(P)_4 species first optimized within the C_2 symmetry constraints, and the resulting structures assessed using vibrational frequency analysis to probe whether or not they represent true minimum-energy geometries.
- For all the species, we considered low spin, intermediate spin, and high spin states.
- Calculations done using the split-valence 6-31G* basis set and the five functionals:
 - three hybrid, B3LYP, PBE1PBE, and B3PW91,
 - and two generalized gradient approximation (GGA), PW91 and PBE.
- The B3LYP method with the 6-31G* basis set proved to give geometries in good agreement with experiments and shown to produce the ordering of spin states of metalloporphyrin complexes reasonably well.
- The approaches used subsequently referred to as:
 - B3LYP/6-31G*, PBE1PBE/6-31G*, B3PW91/6-31G*, PW91PW91/6-31G*, and PBE1PBE/6-31G*.
- The same approaches applied to the tetrapyrrole MP species, geometry optimization within the D_{4h} constraints.
- The geometries of the ligands, P^{2-} and P(P)_4^{2-} , optimized using the same five functionals and the 6-31G* basis set.
- These approaches further employed to calculate the energies of the M^{2+} and Sc^{3+} , Mn^{4+} , Ni^{3+} ions as well.

Computational Details

- Using the B3LYP/6-31G* approach we studied the MP(P)_4 and MP (and the N_4^{2-} and P(P)_4^{2-} ligands) both in the gas phase and with implicit solvent effects from water and benzene, taken as characteristic representatives of polar and non-polar solvents ($\epsilon = 78.3553$ and 2.2706 , respectively).
- With implicit solvent effects the geometries and vibrational frequencies for the global-minimum structures for all of the MP(P)_4 and MP were calculated at the B3LYP/6-31G* level of theory using the self-consistent reaction field IEF-PCM method (UFF default model used in Gaussian09, with the electrostatic scaling factor $\alpha = 1.0$).
- The binding energies (E_{bind}) of the M–L compounds ($\text{L} = \text{P}^{2-}$ or P(P)_4^{2-}) computed using the following formula:

$$E_{\text{bind}} = E(\text{M}^{n+}) + E(\text{L}) - E(\text{M-L})$$

- where $E(\text{M-L})$ is the energy of the MP(P)_4 or MP species and $E(\text{M})$ and $E(\text{L})$ are the energies of its metal ion (M^{n+}) and ligand (L) components, respectively. For $E(\text{M}^{n+})$, we always used the ground state energy of the free metal ion regardless of the ground spin state of the M–L species.
- The full Natural Bond Orbital (NBO) analysis, using NBO version 3, was performed using the ‘pop=nbo’ command as implemented in the Gaussian09 package.

Structures and Energetics

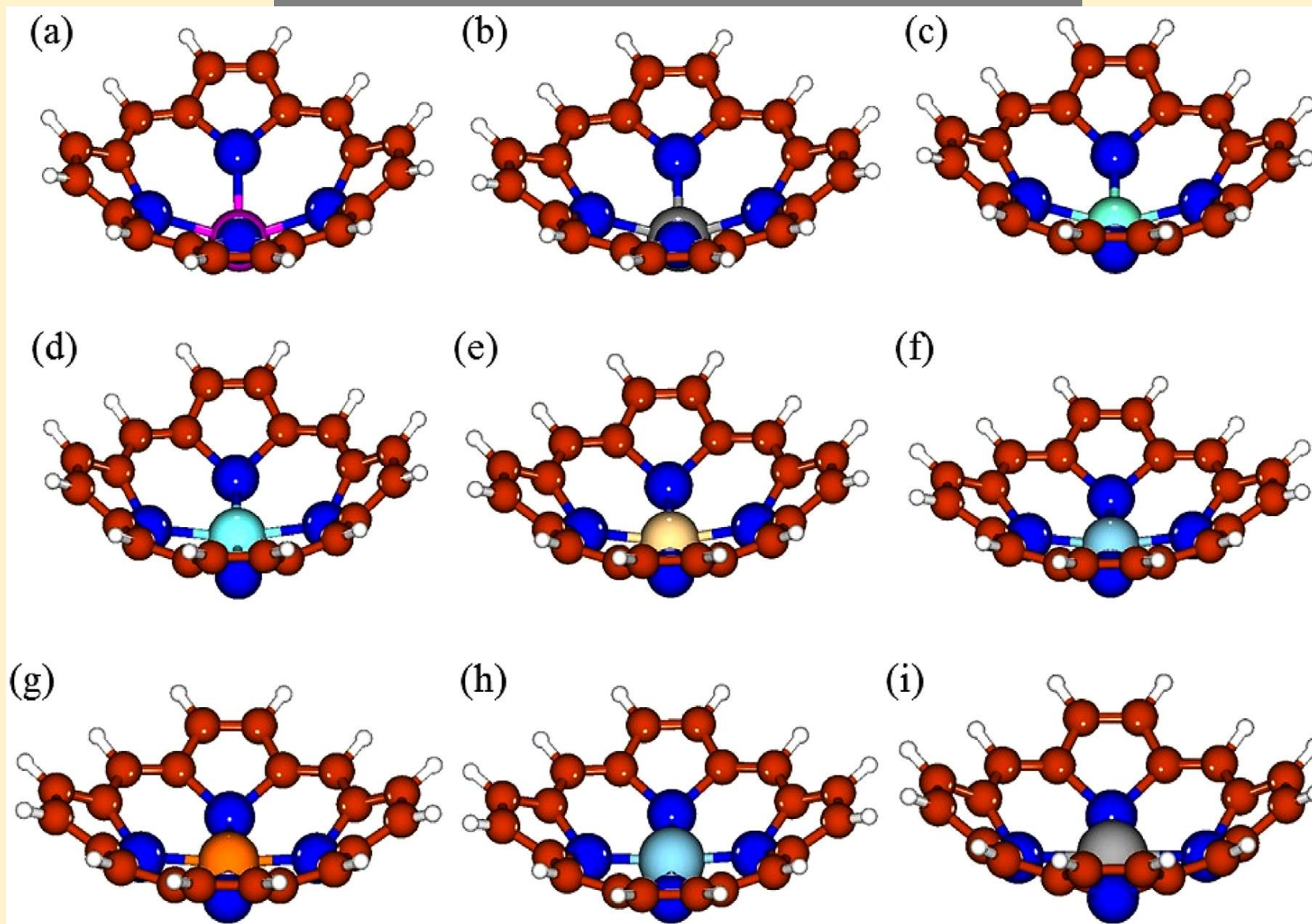


Fig. 1. Structures of the $MP(P)_4$ calculated at the B3LYP/6-31G* level: neutrals, $Sc^{II}P(P)_4$ (a), $Ti^{II}P(P)_4$ (b), $V^{II}P(P)_4$ (c), $Cr^{II}P(P)_4$ (d), $Mn^{II}P(P)_4$ (e), $Fe^{II}P(P)_4$ (f), $Co^{II}P(P)_4$ (g), $Ni^{II}P(P)_4$ (h), $Cu^{II}P(P)_4$ (i), and $Zn^{II}P(P)_4$ (j), and cations, $Sc^{III}P(P)_4$ (a'), $Mn^{IV}P(P)_4$ (e'), and $Ni^{III}P(P)_4$ (h').

Structures and Energetics

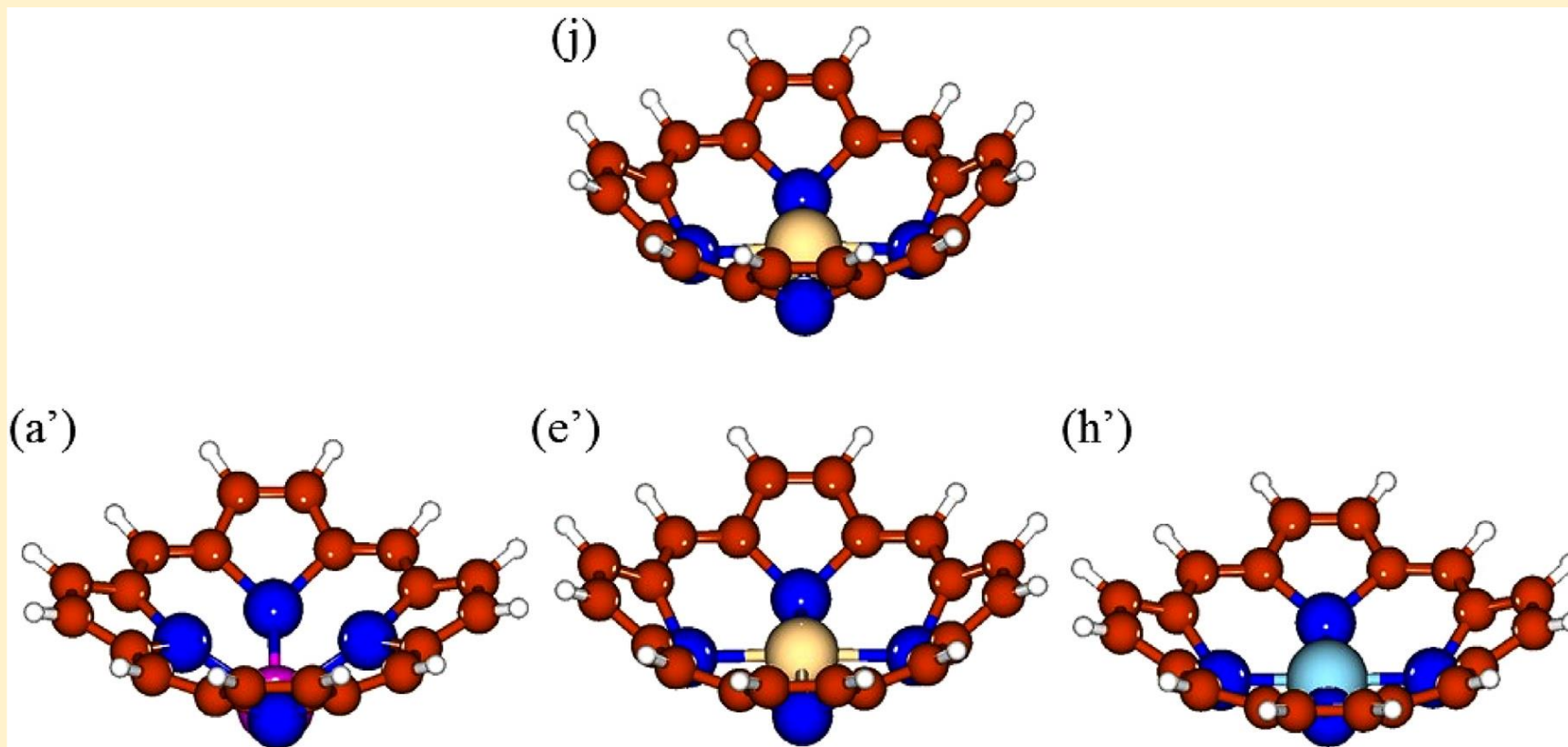


Fig. 1. Structures of the $MP(P)_4$ calculated at the B3LYP/6-31G* level: neutrals, $Sc^{II}P(P)_4$ (a), $Ti^{II}P(P)_4$ (b), $V^{II}P(P)_4$ (c), $Cr^{II}P(P)_4$ (d), $Mn^{II}P(P)_4$ (e), $Fe^{II}P(P)_4$ (f), $Co^{II}P(P)_4$ (g), $Ni^{II}P(P)_4$ (h), $Cu^{II}P(P)_4$ (i), and $Zn^{II}P(P)_4$ (j), and cations, $Sc^{III}P(P)_4$ (a'), $Mn^{IV}P(P)_4$ (e'), and $Ni^{III}P(P)_4$ (h').

Structures and Energetics

- ❖ All the $\text{MP}(\text{P})_4$ species in general accept the strongly distorted bowl-like shape.
- ❖ The distortion generally decreases along the Sc–Zn row.
- ❖ There are some structural differences between the neutral $\text{MP}(\text{P})_4$ species and their cationic counterparts:
- ❖ the $\text{Sc}^{\text{III}}\text{P}(\text{P})_4$ species possesses more pronounced bowl-like shape whereas the $\text{Mn}^{\text{IV}}\text{P}(\text{P})_4$ and $\text{Ni}^{\text{III}}\text{P}(\text{P})_4$ have less pronounced bowl-like distortions compared to their neutral counterparts.

Structures and Energetics

Table 1. Calculated properties of MP(P)₄ and MP species, B3LYP/6-31G* level of theory (gas phase).

Property		M ^c												
		Sc ^{II}	Sc ^{III}	Ti ^{II}	V ^{II}	Cr ^{II}	Mn ^{II}	Mn ^{IV}	Fe ^{II}	Co ^{II}	Ni ^{II}	Ni ^{III}	Cu ^{II}	Zn ^{II}
Ground spin state	MP(P) ₄	² A	¹ A	³ B	⁴ A	⁵ A	⁴ A	⁶ A	³ A	² A	¹ A	² B	² A	¹ A
	MP	² B	¹ A	³ B _{2g}	⁴ A	⁵ B _{2g}	⁴ B _{1g}	⁶ A	³ A	² B _{2g}	¹ A ₁	² A	² B _{1g}	¹ A _{1g}
R(M–X), Å, X = N/P	MP(P) ₄	2.43, 2.53	2.43, 2.55, 2.56	2.32	2.35	2.34	2.22	2.34	2.15, 2.20	2.16	2.12	2.17, 2.09	2.24	2.37
	MP	2.10, 2.11	2.11	2.05, 2.07	2.05	2.04	1.99, 2.02	1.99	1.99	1.97, 1.99	1.94	1.93	2.01	2.04
Angle(X ₅ –X ₄ –X ₃ –M), °, X = N/P	MP(P) ₄	27.07	47.69	32.97	24.38	11.3	12.59	–2.06	9.74	4.89	4.15	1.09	–1.29	–4.36
	MP	10.31	18.19	0.0	0.0	–0.03	0.0	0.0	0.0	0.0	0.0	–0.34	0.0	0.0
E _{bind} (M)	MP(P) ₄	24.36	44.94	25.67	26.51	27.75	26.41	97.26	28.46	29.83	31.6	61.97	31.54	29.35
	MP	29.3	50.28	30.13	31.24	32.53	30.38	101.76	32.21	33.33	34.81	65.04	35.31	33.73
Δ(HOMO/LUMO), eV ^{a, b}	MP(P) ₄	1.45/1.97	2.09	1.35/1.95	2.27/2.37	2.47/2.57	2.63/2.12	2.52/1.29	2.59/1.74	2.64/2.53	2.57	2.57/1.58	1.38/2.67	1.97
	MP	1.30/2.66	2.85	1.32/2.74	1.87/2.87	3.14/2.92	3.05/1.44	2.48/1.26	3.12/2.37	3.13/3.15	3.13	3.14/1.29	3.08/3.11	3.07
Optical gap, eV	MP(P) ₄	1.72	1.93	1.65	1.89	2.74	1.74	2.48	2.59	2.21	2.19	2.36	2.44	2.91
	MP	2.02	2.78	2.54	3.37	3.44	1.93	2.19	3.16	2.49	3.52	2.78	3.52	3.55
<S ² >	MP(P) ₄	0.76	0	2.04	3.86	6.07	3.88	8.95	2.13	0.78	0	0.77	0.76	0
	MP	0.75	0	2.01	3.77	6.02	4.15	8.84	2.03	0.81	0.0	0.78	0.75	0

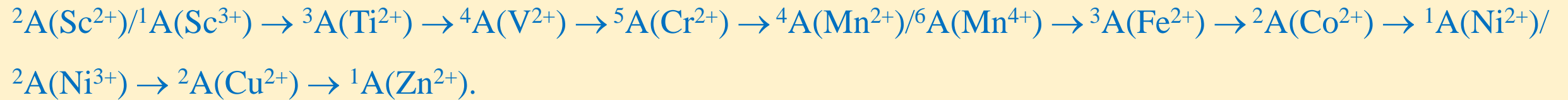
^a α/β values.

^b Gaps, eV, given as HOMO–LUMO energy differences.

^c For Sc, Mn, and Ni both neutral and cationic ground-state structures are given.

Structures and Energetics

I. In general, with all five density functionals employed, both the MP(P)_4 and their MP counterparts have the same calculated ground spin states which change along the transition metal row as follows:



Exceptions:

- (i) $\text{Ti}^{\text{II}}\text{P(P)}_4$, at the PBE1PBE/6-31G* and B3PW91/6-31G* levels the singlet C_1 is lower in energy than the triplet C_2 by 3.8 and 4.6 kcal/mol, respectively;
- (ii) $\text{Mn}^{\text{IV}}\text{P(P)}_4$, four hybrid functionals employed produced the ${}^6\text{A}$ as the ground state whereas both PW91PW91/6-31G* and PBE1PBE/6-31G* gave the ${}^2\text{A}$ as the ground state.

Thus, complete substitution of all the pyrrole nitrogens with P-atoms does not generally affect the ground spin state of metalloporphyrins.

Structures and Energetics

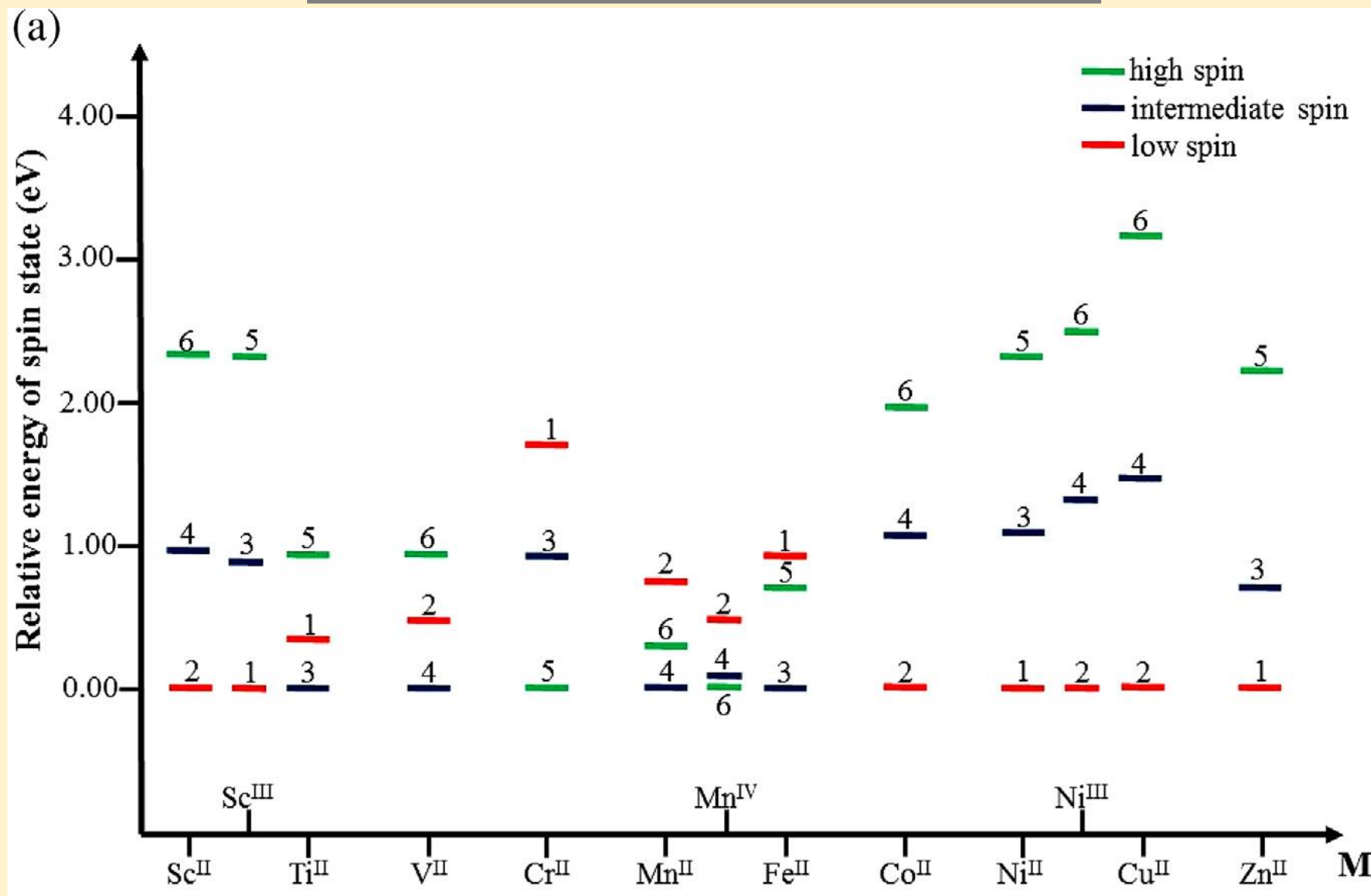


Fig. 3. Relative stabilities of spin states of the $\text{MP}(\text{P})_4$ (a) and MP (b) species (in eV), calculated at the B3LYP/6-31G* level. The ground state is set to 0 eV. Spin multiplicity $2S+1$ is indicated in the chart.

Structures and Energetics

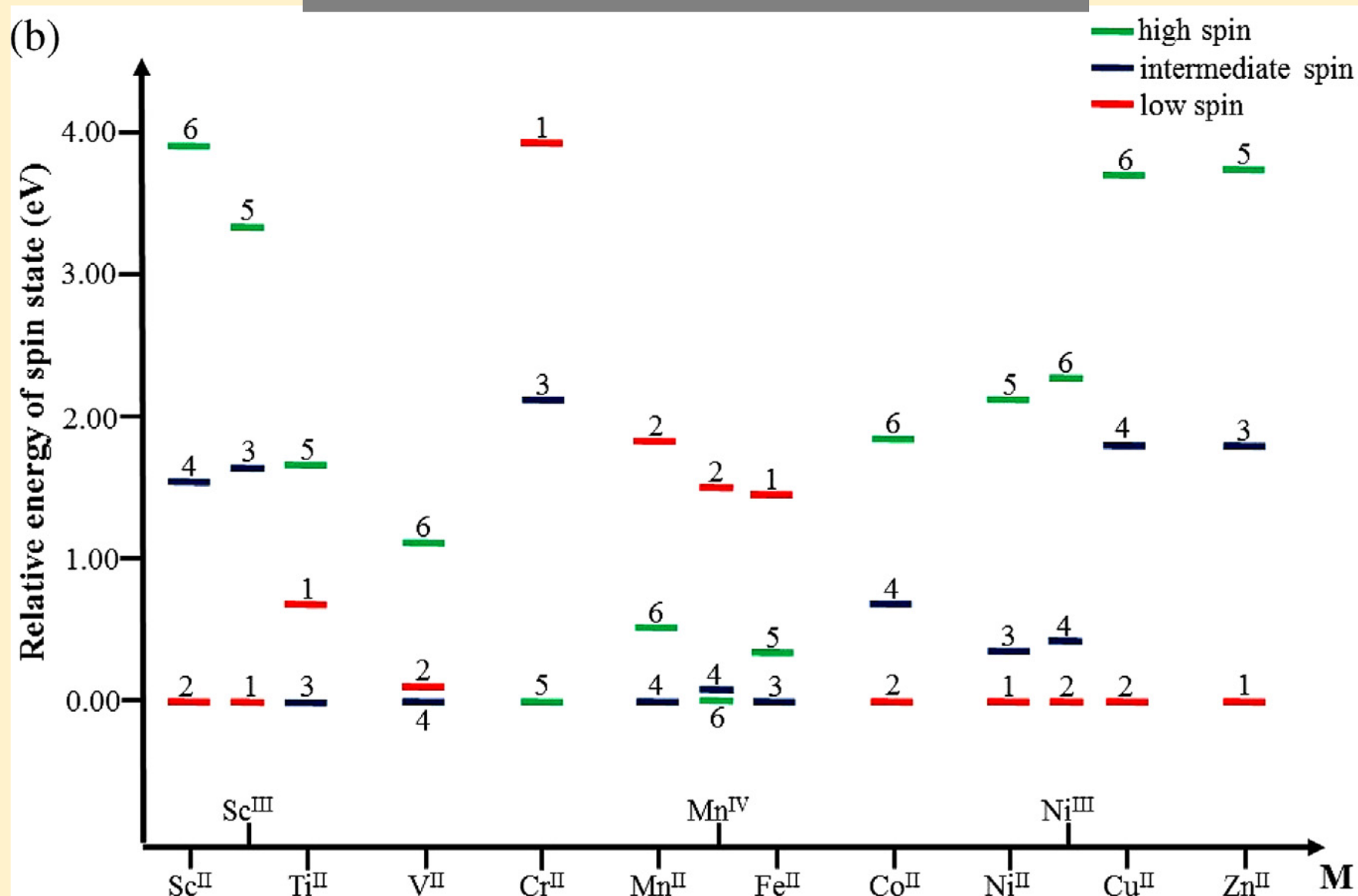


Fig. 3. Relative stabilities of spin states of the $\text{MP}(\text{P})_4$ (a) and MP (b) species (in eV), calculated at the B3LYP/6-31G* level. The ground state is set to 0 eV. Spin multiplicity $2S+1$ is indicated in the chart.

Structures and Energetics

II. All the $\text{MP(P)}_4/\text{MP}$ couples have the same ordering of spin states at all the levels of theory used.

The differences observed:

(i) $\text{Ti}^{\text{II}}\text{P(P)}_4/\text{Ti}^{\text{II}}\text{P}$, for $\text{Ti}^{\text{II}}\text{P}$ the ^3A is the ground state with all the functionals employed,

whereas for $\text{Ti}^{\text{II}}\text{P(P)}_4$ PBE1PBE and B3PW91 gave the ^1A as the ground state.

(ii) $\text{Mn}^{\text{IV}}\text{P(P)}_4/\text{Mn}^{\text{IV}}\text{P}$, $\text{Mn}^{\text{IV}}\text{P(P)}_4$ has the ^2A the ground state at the PW91PW91/6-31G* and PBEPBE/6-31G* levels,

whereas the $\text{M}^{\text{IV}}\text{P}$ calculated to have the ^6A as the ground state with all the functionals employed.

(iii) $\text{Mn}^{\text{II}}\text{P(P)}_4/\text{Mn}^{\text{II}}\text{P}$, $\text{Mn}^{\text{II}}\text{P(P)}_4$ has the $^4\text{A} \rightarrow ^2\text{A} \rightarrow ^6\text{A}$ sequence with the PW91PW91 and PBEPBE functionals,

whereas the $\text{Mn}^{\text{II}}\text{P}$ has the $^4\text{A} \rightarrow ^6\text{A} \rightarrow ^2\text{A}$ sequence with all the functionals employed.

(iv) $\text{Fe}^{\text{II}}\text{P(P)}_4/\text{Fe}^{\text{II}}\text{P}$, $\text{Fe}^{\text{II}}\text{P(P)}_4$ has the $^3\text{A} \rightarrow ^1\text{A} \rightarrow ^5\text{A}$ sequence with the PW91PW91 and PBEPBE functionals,

whereas the $\text{Fe}^{\text{II}}\text{P}$ counterpart has the $^3\text{A} \rightarrow ^1\text{A} \rightarrow ^5\text{A}$ sequence with all the functionals employed.

Structures and Energetics

III. For the energy differences (spacings, or splittings) between the ground state and the closest low-lying spin states the following trends observed:

- (i) From Sc through Mn, the spacing range for MP(P)_4 is smaller or essentially equal to the spacing range for MP.
- (ii) From Mn^{2+} through Ni^{2+} the situation becomes opposite.
- (iii) Finally, for Cu and Zn the situation with the spacings restores.

- **Complete substitution of all pyrrole N's with P-atoms 'closes' the spacings between the ground spin state and the closest spin state for $\text{M}^{2+/3+}$ with the number of (unpaired) d-electrons increasing from 0 to 4 ($\text{M}^{n+} = \text{Sc}^{2+/3+}$, Ti^{2+} , V^{2+} , and Cr^{2+}) and for M^{2+} with completely filled d-shell ($\text{M}^{2+} = \text{Cu}^{2+}$ and Zn^{2+}).**
- **Complete substitution of all pyrrole N's with P-atoms 'opens' the spacings between the ground spin state and the closest spin state for M^{n+} with half- and more than half-filled d-shell and decreasing number of unpaired d-electrons ($\text{M}^{n+} = \text{Mn}^{2+/4+}$, Fe^{2+} , Co^{2+} , and Ni^{2+}).**

Electronic Properties

Table 2. Gas-phase optical gaps (eV) for the $M^{n+}P(P)_4$ and $M^{n+}P$ species calculated at the TD-B3LYP/6-31G*//TD-PBE1PBE/6-31G*//TD-B3PW91/6-31G*//TD-PW91PW91/6-31G*//TDPBEPBE/6-31G* levels.

M Gap, eV	Sc ²⁺ (Sc ³⁺)	Ti ²⁺	V ²⁺	Cr ²⁺	Mn ²⁺ (Mn ⁴⁺)	Fe ²⁺	Co ²⁺	Ni ²⁺ (Ni ³⁺)	Cu ²⁺	Zn ²⁺
MP(P) ₄	1.72(1.93)//	1.65//	1.89//	2.74//	1.74(2.48)//	2.59//	2.21//	2.19(2.36)//	2.44//	2.91//
	1.80(2.03)//	1.85//	1.96//	2.49//	1.79(2.61)//	2.31//	2.35//	2.34(1.11,2.59)//	2.56//	2.96//
	1.78(1.99)//	1.78//	1.93//	2.39//	1.75(2.27)//	2.34//	2.24//	2.23(2.41)//	2.45//	2.73//
	1.66(1.86)//	1.61//	1.83//	1.65//	1.57(1.60)//	0.99//	0.93//	2.71(2.19)//	2.32//	2.29//
	1.66(1.86)	1.61	1.84	1.65	1.57(1.60)	0.97	0.93	2.71(2.19)	2.32	2.29
MP	2.02(2.78)//	2.54//	3.37//	3.44//	1.93(2.19)//	3.16//	2.49//	3.52(2.78)//	3.52//	3.55//
	1.59(2.96)//	2.06//	3.50//	3.55//	1.90(2.33)//	3.26//	2.55//	3.61(2.95)//	3.62//	3.64//
	2.04(2.87)//	2.57//	2.11//	3.47//	1.91(2.25)//	3.43//	2.52//	3.53(2.80)//	3.55//	3.58//
	1.80(2.54)//	2.31//	2.12//	3.13//	2.42(1.31)//	2.73//	1.43//	2.99(2.34)//	2.36//	2.32//
	1.80(2.54)	2.26	2.13	3.13	2.43(1.29)	2.73	1.43	2.97(2.34)	2.36	2.31

Electronic Properties

- ❖ For MP(P)_4 the HOMO/LUMO gaps and optical (TDDFT) gaps are noticeably smaller than for MP counterparts, both in the gas phase and in implicit solvents, with some exclusions (Sc-, Ti-, V-, and Mn-compounds).
- ❖ **Complete substitution of all the pyrrole nitrogens with P-atoms in the porphyrin core generally ‘closes’ the calculated HOMO/LUMO gap, which can be explained by stabilization of the MP(P)_4 LUMOs.**
- ❖ The $\text{M}^{2+}\text{P(P)}_4$ HOMO/LUMO gaps are generally not significantly affected by the effects of implicit solvents.
- ❖ The MP(P)_4 TDDFT gaps are generally noticeably smaller than the MP TDDFT gaps.
- ❖ This trend is kept for both neutral and cationic species with the exception of $\text{Mn}^{4+}\text{P(P)}_4$.
- ❖ The optical gaps for the all three cationic MP(P)_4 studied are larger than the optical gaps for their neutral MP(P)_4 counterparts (the only exclusion being $\text{Ni}^{3+}\text{P(P)}_4$).
- ❖ As expected, the GGA functionals give significantly lower values of both the HOMO/LUMO and optical gaps than the three hybrid functionals employed, with several exclusions: V^{2+}P and Mn^{2+}P .

Binding Properties

Table 3. Gas-phase binding energies, E_{bind} (eV), for $M^{n+}P(P)_4$ and $M^{n+}P$ in the ground states, B3LYP/6-31G*//PBE|PBE/6-31G*//B3PW91/6-31G*//PW91PW91/6-31G*//PBEPBE/6-31G* levels, without ZPE.

Positive values mean bound species.

M	Sc ²⁺ (Sc ³⁺)	Ti ²⁺	V ²⁺	Cr ²⁺	Mn ²⁺ (Mn ⁴⁺)	Fe ²⁺	Co ²⁺	Ni ²⁺ (Ni ³⁺)	Cu ²⁺	Zn ²⁺
E_{bind} , eV										
MP(P) ₄	24.36(44.94)//	25.67//	26.51//	27.75//	26.41(97.26)//	28.46//	29.83//	31.60(61.97)//	31.54//	29.35//
	24.11(44.43)//	26.49//	26.17//	27.32//	25.75(96.42)//	27.84//	29.21//	30.49(60.90)//	30.79//	28.65//
	24.05(44.49)//	26.45//	26.27//	27.39//	25.95(96.98)//	28.10//	29.35//	30.77(61.43)//	30.93//	28.61//
	24.85(45.48)//	26.72//	27.75//	28.71//	27.84(99.19)//	30.20//	31.72//	32.95(62.26)//	32.48//	29.41//
	24.78(45.34)	26.66	27.68	28.60	27.69(98.95)	30.06	31.58	32.80(62.04)	32.32	29.25
MP	29.30(50.28)//	30.13//	31.24//	32.53//	30.38(101.76)//	32.21//	33.33//	34.81(65.04)//	35.31//	33.73//
	29.35(50.09)//	30.11//	30.76//	32.54//	30.09(101.43)//	31.91//	32.98//	34.02(64.36)//	35.07//	33.52//
	29.19(50.04)//	30.02//	30.70//	32.45//	30.12(101.55)//	32.25//	33.02//	34.10(64.63)//	35.00//	33.35//
	13.11(34.14)//	14.29//	15.44//	16.73//	14.86(86.34)//	16.93//	17.97//	19.20(48.29)//	19.49//	17.36//
	−6.27(14.67)	−5.12	−3.97	−2.71	−4.60(66.81)	−2.55	−1.50	−0.27(28.74)	0.02	−2.11

Binding Properties

- ❖ E_{bind} calculated for the $M^{n+}P$ compounds using the three hybrid functionals are significantly higher than those calculated for their $M^{n+}P(P)_4$ counterparts, the difference being several eV.
- ❖ E_{bind} calculated for Sc^{3+} and Ni^{3+} are almost twice larger than for Sc^{2+} and Ni^{2+} , and E_{bind} calculated for Mn^{4+} are almost three times (for MnP) or almost four times (for $MnP(P)_4$) as large as E_{bind} for Mn^{2+} .
- ❖ For MP, the PW91 functional gives much lower E_{bind} , and the PBE functional gives essentially no chemical bonding between M^{2+} and P^{2-} .
- ❖ For $MP(P)_4$ the GGA calculated $M^{n+}-P(P)_4^{2-}$ binding is comparable or even a little stronger than calculated with the three hybrid functionals.
- ❖ Thus, the hybrid functionals including fraction of the Hartree–Fock exchange should be considered as the most suitable candidates for describing the chemical bonding in the metalloporphyrins and their derivatives, including tetraphosphoroporphyrins, and GGA functionals should be used with high caution for this purpose, if used at all.

Binding Properties

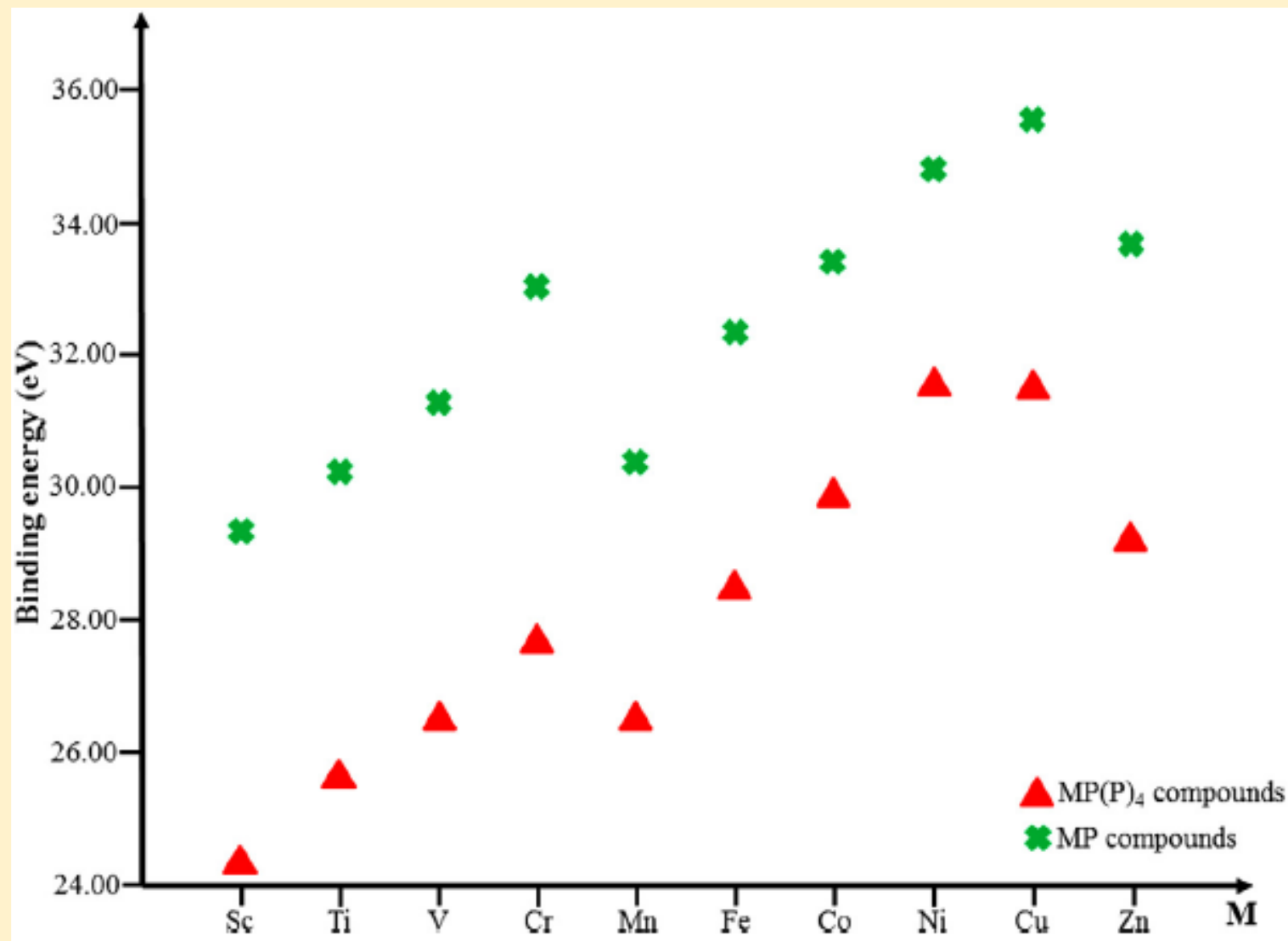


Fig. 4. Gas-phase binding energies, E_{bind} (eV), for the $\text{M}^{2+}\text{P(P)}_4$ (red signs) and M^{2+}P (green signs) compounds in their ground states as exemplified by calculations at the B3LYP/6-31G* level. ZPE energies not included.

Binding Properties

Table 4. Gas-phase NBO charges, e, at the M and P/N centers in the $M^{n+}P(P)_4$ and $M^{n+}P$ species in their ground states calculated at the B3LYP/6-31G* level.

Property		M												
		Sc ^{II}	Sc ^{III}	Ti ^{II}	V ^{II}	Cr ^{II}	Mn ^{II}	Mn ^{IV}	Fe ^{II}	Co ^{II}	Ni ^{II}	Ni ^{III}	Cu ^{II}	Zn ^{II}
Q _M	MP(P) ₄	0.79	0.92	0.36	0.47	0.38	0.30	0.67	0.20	−0.05	−0.19	−0.09	0.24	0.61
	MP	1.81	1.95	1.48	1.29	1.20	1.40	1.61	1.18	1.02	0.93	0.94	1.11	1.28
Q _{P/N}	MP(P) ₄	0.42, 0.50	0.46, 0.51	0.54	0.53	0.51	0.54	0.51	0.55, 0.62	0.64	0.68	0.71, 0.69	0.54	0.45
	MP	−0.71, −0.73	−0.65	−0.68	−0.64	−0.62	−0.64	−0.66	−0.60, −0.62	−0.60	−0.56	−0.57	−0.61	−0.65

Binding Properties

Table 5. The stabilization energies E(2), kcal/mol, from the second order perturbation theory analysis of Fock matrix in NBO basis for the MP(P)₄ species, M = Sc–Zn, at the B3LYP/6-31G* level of theory.

	E(2), kcal/mol						
	Sc ^{II}	Sc ^{III}	Ti ^{II}	V ^{II}	Cr ^{II}	Mn ^{II}	Mn ^{IV}
'Direct' ^a	190.4/293.3	816.95	214.8/291.96	358.58/230.78	265.84/239.5	0/506.5	319.58/220
'Indirect' ^a	278.27/189.43	403.34	291.53/332.8	114.04/216.4	42.87/124.59	804.01/229.42	189.53/70
Total ^b	483.7/467.7 //	816.95/403.34 //	506.76/624.33 //	589.36/330.44 //	505.34/167.46 //	506.5/1033.43 //	539.58/259.53 //
	951.4	1220.29	1131.09	919.8	672.8	1539.93	799.11
	Fe ^{II}	Co ^{II}	Ni ^{II}	Ni ^{III}	Cu ^{II}	Zn ^{II}	
'Direct'	231.1/495.65	313.98/389.2	232.5	288.09/372.73	0/119.12	0	
'Indirect'	261.3/208.3	66.12/65.45	106.76	610.3/588.71	789.1/406.7	1610.34	
Total	726.75/469.6 //	703.18/131.57 //	232.5/106.76 //	660.82/1199.01 //	119.12/1195.8 //	0/1610.34 //1610.34	
	1196.35	834.75	339.26	1859.83	1315		

^aThe analysis is carried out by examining all possible interactions between 'filled' (donor) Lewis-type natural bonding orbitals (NBOs) and 'empty' (acceptor) non-Lewis NBOs and estimating their energetic importance by 2nd-order perturbation theory. Since these interactions lead to loss of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbitals, they are referred to as 'delocalization' corrections to the zeroth-order natural Lewis structure.

'Direct' interactions are those involving all the M–P NBOs, and 'indirect' interactions are all other possible interactions involving the NBOs on metal centers and on other atoms.

For the non-singlet structures, E(2)'s are given separately for α- and β-orbitals.

^bTotal values are as follows: sum of the 'direct' energies; sum of the 'indirect' energies; sum of both energies.

Binding Properties

- ❖ The trends in the change of the E_{bind} between M^{2+} and $P(P)_4^{2-}/P^{2-}$ ligands are very similar for both ligands, with a few exceptions.
- ❖ Similar E_{bind} trends are observed in the implicit solvents as well.
- ❖ In addition, E_{bind} 's calculated in the implicit solvents are significantly lower than those calculated in the gas phase, the drop of E_{bind} is especially large with the implicit effects of water.
- ❖ This can be explained by the significant stabilization of doubly charged M^{2+} and $P^{2-}/P(P)_4^{2-}$ ions in solvents, especially in the polar solvent as water, compared to the relatively smaller stabilization of the neutral $MP/MP(P)_4$.

Binding Properties

- ❖ The relative binding energies in the MP and MP(P)_4 complexes are determined by a balance of various factors:
 - ✓ change of the M^{n+} ground state from the free ion form to the ion bound in the complex;
 - ✓ ‘direct’ interactions involving all the M-P NBOs;
 - ✓ ‘indirect’ interactions which are all other possible interactions, i.e., the metal-to-ligand p back-donation and the ligand-to-metal charge transfer;
 - ✓ in the case of $\text{M}^{3+/4+}$ ions, we should take into account pure electrostatic interactions between the cation and the ligand overcoming all other interactions.
- ❖ The E_{bind} differences between MP and MP(P)_4 can be explained by the stronger electrostatic interactions between M^{2+} and P^{2-} : the P^{2-} ligand should possess higher charge density on the N’s compared to the more diffuse charge density on the P-atoms in the P(P)_4^{2-} ligand.
- ❖ Also, more diffuse orbitals (both occupied and empty) on the P-atoms of the P(P)_4^{2-} ligand can suit worse for the interactions with the M^{2+} d-orbitals (including donation and back-donation).

Conclusions and Perspectives

- ❖ Complete substitution of all pyrrole N's with P-atoms does not affect the ground spin state of metalloporphyrins.
- ❖ All MP(P)_4 and their MP counterparts possess the same ordering of spin states.
- ❖ Complete substitution of all pyrrole N's 'closes' the spacings between the ground spin state and the next spin state for $\text{M}^{2+/3+}$ with the number of d-electrons increasing from 0 to 4 and for M^{2+} with completely filled d-shell.
- ❖ Complete substitution of all pyrrole N's 'opens' the spacings between the ground spin state and the closest spin state for M^{n+} with half- and more than half-filled d-shell and decreasing number of unpaired d-electrons.
- ❖ For MP(P)_4 the calculated HOMO/LUMO gaps are noticeably smaller than for their MP counterparts.
- ❖ Complete substitution of all pyrrole N's in the porphyrin core generally 'closes' the calculated HOMO/LUMO gap.
- ❖ The TDDFT gaps for MP(P)_4 are noticeably smaller than the optical gaps for their MP counterparts.
- ❖ The optical gaps for the all three cationic MP(P)_4 are larger than the optical gaps for their neutral MP(P)_4 counterparts.

Conclusions and Perspectives

- ❖ Binding energies calculated for the $M^{n+}P$ compounds using the three hybrid functionals are significantly higher than those calculated for their $M^{n+}P(P)_4$ counterparts, the difference being several eV.
- ❖ Hybrid functionals including fraction of the Hartree–Fock exchange should be considered as the most suitable candidates for describing the chemical bonding in the metalloporphyrins and their derivatives, including tetraphosphoroporphyrins, and GGA functionals should be used with high caution for this purpose, if used at all.
- ❖ The trends the E_{bind} change between M^{2+} and $P(P)_4^{2-}/P^{2-}$ are very similar for both ligands, with a few exceptions.
- ❖ The relative E_{bind} in the MP and $MP(P)_4$ complexes are determined by a balance of ‘direct’ interactions involving all the M–P NBOs and ‘indirect’ interactions such as the metal-to-ligand p back-donation and the ligand-to-metal charge transfer.
- ❖ The MP/ $MP(P)_4$ E_{bind} differences can be explained by the stronger electrostatic interactions between M^{2+} and P^{2-} .
- ❖ Also, more diffuse P-atom orbitals of the $P(P)_4^{2-}$ ligand can suit worse for the interactions with the M^{2+} d-orbitals.

Conclusions and Perspectives

Based on our current findings, we raise the following questions, which are of high interest for the follow-up research:

- (i) How strong will transition metals of the second (and probably third) row interact with the P(P)_4^{2-} ligand? How stable will those compounds be compared to their tetrapyrrole counterparts?
- (ii) What structures, electronic, and optical properties will M^{n+} complexes with larger derivatives of the P(P)_4^{2-} ligands, analogous to phthalocyanine, have?
- (iii) Can MP(P)_4 compounds form complexes with fullerenes, similar to regular metalloporphyrins? If yes, what would be structures and properties of those complexes?
- (iv) What about building blocks for nanotechnology formed by the MP(P)_4 compounds, for example, stacks of these species?

Acknowledgements

- ✓ The organizing committee of the VISTA Seminars for the opportunity to participate.
- ✓ This work was supported by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) Grant “Estudo Teórico Computacional de Sistemas Nanoestruturados com Potencial Aplicação Tecnológica”, number 402313/2013-5, approved in the call N° 70/2013 Bolsa de Atração de Jovens Talentos – BJT – MEC/MCTI/CAPES/CNPq/FAPs/Linha 2 – Bolsa de Atração de Jovens Talentos – BJT.
- ✓ The computational resources of the centers Centro Nacional de Processamento de Alto Desempenho em São Paulo, Núcleo de Tecnologia da Informação, and Centro Nacional de Processamento de Alto Desempenho – UFC are highly appreciated.