

Metalloporphyrins with all the Pyrrole Nitrogens Replaced with Phosphorus Atoms, $MP(P)_4$ ($M = Sc, Ti, Fe, Ni, Cu, Zn$)

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The size, shape, and binding ability of porphyrin macrocycles can be broadly tuned by replacing one or more pyrrole nitrogens with other elements [1]. This is a highly promising approach for tuning the optical, electrochemical, and coordinating properties as well as reactivity of porphyrin species. To date, numerous efforts have been devoted to the chemical modification of the porphyrin core with C, Si, or chalcogen atoms [1]. Effects of 1 or 2 pyrrole nitrogen(s) replacement by P were studied for both bare and metallated porphyrins and their derivatives [2]. So far, no studies of free porphyrins or their metal complexes with all pyrrole nitrogens replaced with phosphorus atoms ($P(P)_4$) have been reported. Using the B3LYP/6-31G* approach, we performed the systematic investigation of transition metal-substituted $P(P)_4$ species with increasing number of d-electrons, following the sequence of electronic configurations: $3d^1 4s^2$ (Sc) \rightarrow $3d^2 4s^2$ (Ti) \rightarrow $3d^6 4s^2$ (Fe) \rightarrow $3d^8 4s^2$ (Ni) \rightarrow $3d^{10} 4s^1$ (Cu) \rightarrow $3d^{10} 4s^2$ (Zn) [3,4]. Both the neutral species, $Sc^{II}P(P)_4$, $Ti^{II}P(P)_4$, $Fe^{II}P(P)_4$, $Cu^{II}P(P)_4$, $Zn^{II}P(P)_4$, and cations, $Sc^{III}P(P)_4^+$, $Ti^{IV}P(P)_4^{2+}$, $Fe^{III}P(P)_4^+$, were studied. The Natural Bond Orbital charges on the metal centers were calculated to change from the high positive value in $Sc^{II}P(P)_4$, +0.79e, to the significant negative value, -0.19e, for $Ni^{II}P(P)_4$, and then to rise again up to significant positive value in $Zn^{II}P(P)_4$, +0.61e. All the neutral and cationic $MP(P)_4$ species studied possess one general prominent structural feature: strong deformation of the whole $MP(P)_4$ molecule which adopts pronounced bowl-like shape, compared to generally planar or slightly distorted from planar shapes of ‘parent’ metalloporphyrins (see the Figure below). Effects of solvents, both polar and non-polar, and counterions (in the case of cationic species) were investigated as well.

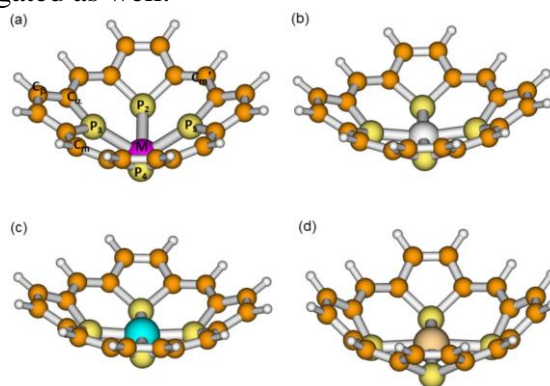


Figure 1: Calculated gas-phase structures (B3LYP/6-31G* level of theory) of the neutral $Sc^{II}P(P)_4$ (C_{1v} , 2A) (a), $Fe^{II}P(P)_4$ (C_{1v} , 3A) (b), $Ni^{II}P(P)_4$ (C_{2v} , 1A) (c), and $Zn^{II}P(P)_4$ (C_{2v} , 1A) (d) compounds.

References

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