A Computational Study on π and σ Modes of Metal Ion Binding to Heteroaromatics $(CH)_{5-m}X_m$ and $(CH)_{6-m}X_m$ ($X = N$ and P): Contrasting Preferences Between Nitrogen- and Phosphorous-Substituted Rings[†]

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The π and σ complexation energy of various heteroaromatic systems which include mono-, di-, and trisubstituted azoles, phospholes, azines and phosphinines with various metal ions, viz. Li^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}, was calculated at the post Hartree−Fock MP2 level, MP2(FULL)/6-311+G(2d,2p)//MP2/6-31G*. The azoles and azines were found to form stronger σ complexes than the corresponding π complexes, whereas the phospholes and phosphinines had higher π complexation energy with Li^+, Mg^{2+}, and Ca^{2+} while their π and σ complexation energies were very comparable with Na^+ and K^+. The strongest π complex among the five-membered heteroaromatic system was that of pyrrole with all the metals except with Mg^{2+}, while benzene formed the strongest π complex among the six-membered heterocyclic systems. The nitrogen heterocyclic system 4H-[1,2,4] triazole and pyridazine formed the strongest σ complex among the five- and six-membered heteroaromatic systems considered. The complexation energy of the π and σ complexes of the azoles and azines was found to decrease with the increase in the heteroatom substitution in the ring, while that of phospholes and phosphinines did not vary significantly. The azoles and azines preferred to form σ complexes wherein the metal had bidentate linkage, while the phospholes and phosphinines did not show binding mode preference. In the σ complexes of both azoles and phospholes, the metal binds away form the electron-deficient nitrogen or phosphorus center.

1. Introduction

The role of metal ions has been clearly recognized and established in the regulation of enzymatic activity, function, folding, and stability of biological systems.[1−4] Following the pioneering work of Dougherty and co-workers,[5−6] the importance of cation-π interaction in biological systems was clearly established. In addition to their role in sculpting the 3-dimensional structure of biological macromolecules and their function, the significance of cation-π interactions was also recognized in the design of organic nanotubes, biological receptor models, and ionophores.[7−8] Recently, a number of experimental and theoretical studies have appeared which were aimed at understanding the cation-π interactions. These studies have revealed that cation-π interactions are arguably the strongest noncovalent interactions with high complexation energies.[9] Many of these studies were carried out on aromatic systems such as benzene and aromatic amino acid residues such as tryptophan, phenylalanine, tyrosine, histidine, etc.[10−13] Zhu et al. have employed the density functional theory to evaluate the various cation-π and cation−heteroatom complexes of nucleobases with alkali and alkaline earth metals.[14] Rodgers et al have employed the threshold collision-induced dissociation of metal complexes with xenon by guided ion beam mass spectrometry to probe the cation-π interactions.[15−19] Their study took into consideration small five- and six-membered nitrogen ring compounds with alkali metal ions, viz. Li^+, Na^+, and K^+. Earlier reports on nitrogen containing heterorings indicated that the metal ion seem to prefer bidentate binding compared to monodentate wherever possible.[20] The cation-π unit also appears to enhance the nonbonded binding strength with the adjacent arene moieties, facilitating concerted action of noncovalent interactions.[21] It has also been shown that extended π systems enhance the strength of metal ion complexation. [22−23]

Theory experiment interplay appears to be indispensable in understanding the structure, bonding, and function of metal ions. First, it is important to understand the structural preferences for the metal ion binding and also to quantify the strength of the interaction of metal ions with the aromatic systems. Our recent report on the metal ion interactions with the aromatic side chain motifs of the amino acid residues was aimed to address the same.[8] These side chain moieties are not complete representative of the various heteroaromatics present in chemical and biological systems. Thus, we realized that it is important to systematically study the metal ion interactions with the various nitrogen and phosphorus containing molecules because of their widespread occurrence.

In the present study we have employed quantum mechanical calculations to gauge the π and σ binding strengths of cations such as Li^+, Na^+, K^+, Mg^{2+}, and Ca^{2+} to a number of five- and six-membered heterocyclic ring systems, given in Chart 1.

Our objective in this study was to explore the metal ion binding to the heteroaromatics and address the following issues: (a) the relative strength of σ and π binding modes, (b) the regioselectivity of metal ion binding, and (c) all possible minima of metal ion and ring complexes. We have not come across any computational study on the metal ion binding to phosphorus containing ring systems. While metal ion binding to phospholes and phosphinines has not been widely studied, our search in the Cambridge Structural Database (CSD, CSD V5.26)[24] revealed that there are about a dozen crystal structures which have Li^+ and Na^+ bound to phosphorus systems.[25] Thus,

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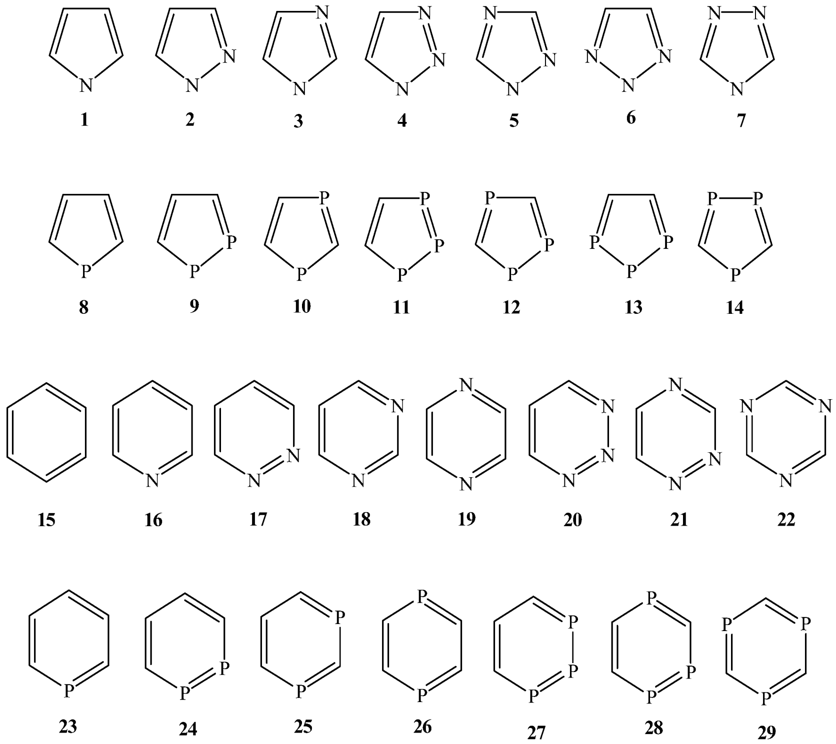
CHART 1: Various Mono-, Di-, and Trisubstituted Aromatic Compounds Considered in the Study



our present study provides the first theoretical insight on the cation-π complexation of phosphorus containing heteroaromatics, and importantly, the study also highlights the contrasts in the structural and binding affinities between the nitrogen and phosphorus containing heterocyclic systems.

2. Computational Details

All the structures considered in the study were fully optimized using the default gradient techniques as employed in the Gaussian 03 suite of program.[26] The heteroaromatic systems and their complexes with various metal ions were initially optimized at the density functional level of theory using the Becke's three parameter hybrid method with the Lee−Yang−Parr correlation functional (B3LYP) in conjugation with the 6-31G* basis set. These geometries were taken as the starting point for further optimizations at the post Hartree−Fock MP2 level with the 6-31G* basis set. Frequency calculations were then carried out to ascertain the nature of the resultant stationary point obtained and to also obtain the zero-point vibrational energy corrections. Most structures were thus characterized as minima with real frequencies. For the structures characterized as transition states, the normal mode of vibration was followed using the MOPLOT program package[27] to locate the minima connecting them. Unscaled thermochemical data obtained at the MP2/6-31G* level was used in the study. This was followed by single-point calculations at the MP2(FULL)/6-311+G(2d,2p) level on MP2/6-31G* optimized geometry. The 6-311+G(2d,2p) basis set is a split valence triple-ζ basis set which is augmented with two sets of d type polarization functions on heavy atoms and two sets of p type polarization functions on hydrogens and a set of diffuse functions each on heavy atom. For the metal−heteroaromatic complexes considered, the complexation energy (ΔE_{ele}) was calculated as the difference of the total energy of the complex and sum of the energies of the aromatic system and the metal under consideration:

$$\Delta E_{\mathrm{ele}} = E_{\mathrm{complex}} - (E_{\mathrm{hetero-aromatic}} + E_{\mathrm{M}^+})$$

The complexation energy so obtained was then corrected for the basis set superposition error (BSSE) by using the Boys−Bernardi counterpoise correction[28] scheme and also for the zero-point vibrational energy correction.

The final complexation energy, which has been reported, is defined as

$$\text{complexation energy } (\mathrm{CE}_{298}) = \Delta E_{\mathrm{ele}} + \Delta \mathrm{ZPE} + \mathrm{BSSE}$$

The complexation energy obtained at MP2(FULL)/6-311+G-(2d,2p) level was corrected for ZPE by using the values obtained at MP2/6-31G* level. The BSSE corrected complexation energy obtained at the B3LYP/6-31G* and MP2/6-31G* levels has been given in the Supporting Information. Unless otherwise specified, the complexation energies of the various metal complexes at the MP2(FULL)/6-311+G(2d,2p) level on MP2/6-31G* optimized geometries has been taken for the discussion in the paper.

3. Results and Discussion

A total of 29 aromatic compounds, which include 14 five-membered ring systems and 15 six-membered ring systems, have been considered in the study. The computational strategy involved the identification of all the possible π and σ complexes of the metal ions with the heteroaromatic systems. The results of the present work have been organized in the following way. We start our discussion with the π complexes of five-membered and six-membered rings. Next we present the σ complexes of five-membered and six-membered rings.

3.1. π Complexes. *Five-Membered Heterocyclic Systems*. Out of the 14 π complexes considered in this category, only 9 could be located and were characterized as minima on the potential energy surface. All our attempts to obtain the π complex (with any metal) of imidazole **3** and triazoles **4**, **5**, and **7** were futile. Sustained efforts on the putative structures for the π complexes yielded σ complexes, viz. **3**(σ^3), **4**(σ^8), **5**(σ^{10}), and **7**(σ^{14}), upon geometry optimization. In case of pyrazole **2**, a stable π complex

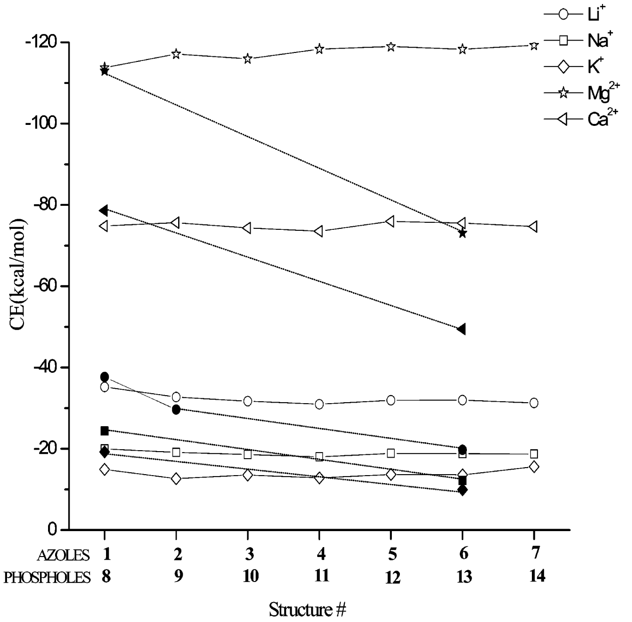


Figure 1. The variation in the π complexation energy (CE) in kcal/mol of the five-membered ring system at the MP2(FULL)6-311+G-(2d,2p)//MP2/6-31G* level. The phospholes are represented by hollow symbols, while the azoles are represented by solid symbols.

with Li^+ alone could be located while it converged to a more stable σ complex (**2**(σ^2)) with the rest of the metals. Figure 1 presents the π complexation energy of the five-membered heterocyclic systems with the various metal ions.

A steep decrease in the π complexation energy of the azoles was observed with the increase in the nitrogen atom substitution in the ring. In case of Li^+ complex of azoles, the complexation energy was found to decrease by about 8 kcal/mol from pyrrole **1** to pyrazole **2** (diazole) and by about 10 kcal/mol from **2** to **6** (triazole). In contrast, for phospholes the increase in the heteroatom substitution in the ring led to a slight increase in the complexation energy. Here, the maximum increase in the complexation energy was observed for the Mg^{2+} phosphole complexes, which was about 2−3 kcal/mol from mono- to disubstitution and about 2 kcal/mol from di- to trisubstituted phospholes. Pyrrole formed the strongest π complex among the five-membered heterocyclic systems with all the metals except Mg^{2+}. With Mg^{2+}, 1H-[1,3,4] triphosphole **14** formed the strongest π complex. All the Mg^{2+} phosphole complexes were found to be more stable than pyrrole Mg^{2+} complex.

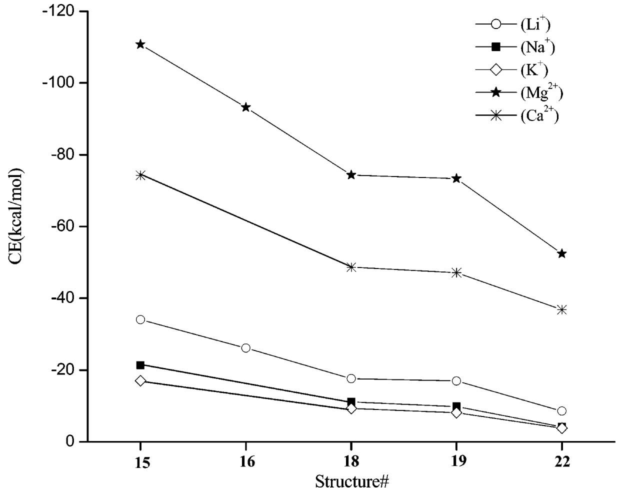


Figure 2. The π complexation energy (CE) in kcal/mol of benzene and the mono-, di-, and trisubstituted azines at the MP2(FULL)6-311+G(2d,2p)//MP2/6-31G* level.

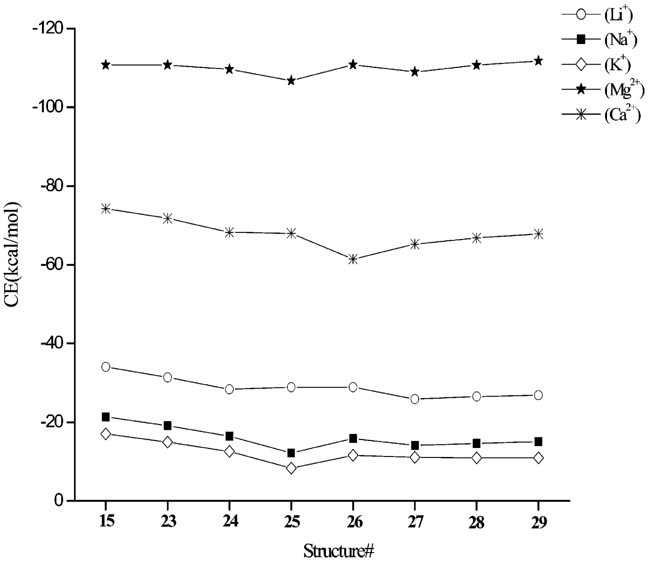
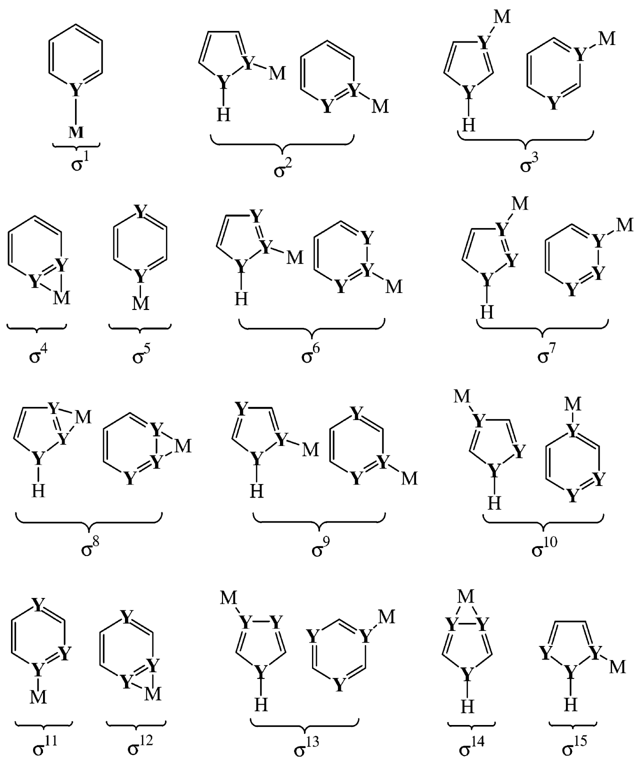


Figure 3. The π complexation energy (CE) in kcal/mol of the mono-, di-, and tri substituted phosphinines at the MP2(FULL)6-311+G(2d,-2p)//MP2/6-31G* level.

Six-Membered Heterocyclic Systems. Out of the 15 π complexes, our geometry optimization efforts yielded only 12 stationary points on the potential energy surface, with all efforts to locate the π complexes for **17**, **20**, and **21** turning out to be futile. The putative starting geometry to locate the π complex for **17**, **20**, and **21** invariably ended up collapsing to σ complexes of the types **17**(σ^4), **20**(σ^6), and **21**(σ^{12}), respectively. However, a stable π complex of pyridine **16** could be obtained with Li^+ and Mg^{2+}, while it collapsed to **16**(σ^1) with Na^+, K^+, and Ca^{2+}. The Na^+, K^+, and Ca^{2+} π-complexes of pyrimidine **18** and K^+ complex of pyrazine **19** were characterized as transition state, while the K^+ complex of 1,3,5-triazine **22** was characterized as a second-order saddle point. The remaining stationary points were all characterized as minima. In the cases where the π complex was not characterized as minima, geometry optimization following the normal mode of vibration resulted in the σ complex. The π complexation energy of the azines and the phosphinines with the various metals is given in Figure 2 and Figure 3, respectively. The strongest π complex among the six-membered ring systems was formed by Benzene (**15**), while triazine **22** formed the weakest π complex. In general, the substitution of carbon ring with either nitrogen or phosphorus led to a decrease in the complexation energy. A small deviation to this generalization was observed for the Mg^{2+} phosphinine complexes. It was observed that with Mg^{2+}, phosphinines form π complexes with almost the same complexation energy as Mg^{2+} benzene complexes. In case of Li^+ complexes of azines, the complexation energy decreased by about 10 kcal/mol from mono- to disubstitution and by about 16 kcal/mol from mono- to trisubstitution. This decrease in complexation energy was about 20 and 40 kcal/mol from mono- to di- and mono- to trisubstituted azines, respectively, if the Mg^{2+} complexes were considered. Such a marked decrease in the complexation energy with the increase in the heteroatom substitution was not observed in the phosphinines. For the phosphinines, the decrease in the complexation energy as one move from mono- to di- and from di- to trisubstitution was only about 2−3 kcal/mol. As seen with the phospholes, Mg^{2+} shows a preference to bind to the phosphinine analogues.

Previous studies indicated that sequential replacement of carbon or methine units in benzene skeleton does not lead to

CHART 2: Various σ Complexes Considered in the Study



loss of aromaticity.[29] Neither the partial charges nor the nuclear independent chemical shift values (NICS) which are popular aromaticity index to gauge aromaticity show any linear correlation with the complexation energy.

Similar to phospholes, the complexation energy of the di- and trisubstituted isomers of phosphinines was also found to be highly competitive. The phospholes and phosphinines form stronger π complexes compared to their nitrogen counterparts. Owing to the diagonal relationship between carbon and phosphorus, there seem to be higher propensity for π delocalization between carbon and phosphorus. This preference to have a higher π complexation for phosphorus over the nitrogen compounds may be understood due to the higher compatibility of the carbon and phosphorous orbitals for delocalization.

3.2. σ Complexes. The 28 heterocyclic systems considered in the study provide a possibility to realize large number of σ complexes with the metal ions. The di- and trisubstituted analogues display multiple ways in which a metal ion can bind with the σ lone pair of the heteroatom. Chart 2 presents the various σ binding modes that have been considered. The σ complexes of azoles and azines with Li^+, Na^+, and K^+ have been studied experimentally by Rodgers et al. by the threshold collision-induced dissociation method. In Figure 4, a correlation of the experimentally and theoretically obtained complexation energy at MP2(FULL)/6-311+G(2d,2p) level has been plotted. Clearly, the complexation energies computed are in excellent agreement with the experimental results, which firmly establish that the level of theory employed is adequate enough to give quantitative results. The order of the binding energies of a given hetero aromatic system with various metals considered is as follows: $Mg^{2+} > Ca^{2+} > Li^+ > Na^+ > K^+$.

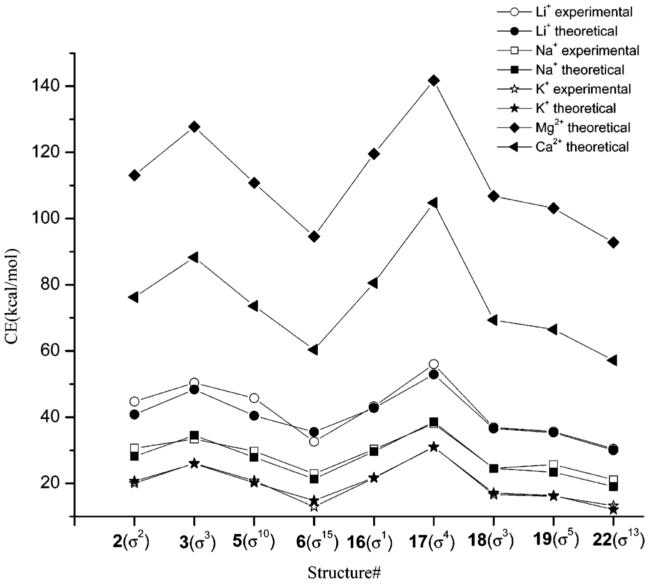


Figure 4. The variation of the σ complexation energy (CE) in kcal/mol of the various nitrogen heterocyclic systems and the experimental values are included for comparison where available.

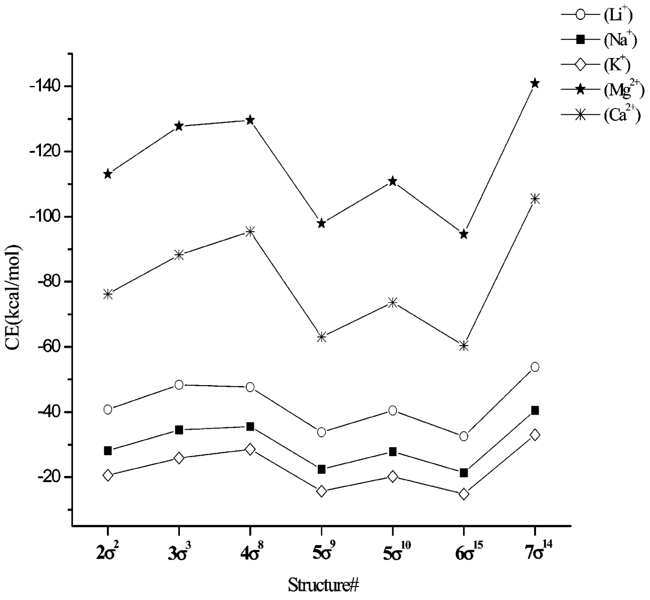


Figure 5. The σ complexation energy (CE) in kcal/mol of the di- and trisubstituted azoles at the MP2(FULL)6-311+G(2d,2p)//MP2/6-31G* level.

Five-Membered Heterocyclic Systems. The σ complexation energy of the azoles with various mono- and dications is presented in Figure 5. All the complexes were characterized as minima on the potential energy surface. Among the disubstituted azoles, imidazole **3**(σ^3) had higher complexation than pyrazole **2**(σ^2). The complexation energy of **2**(σ^2) was lower by over 5 kcal/mol with monocations and over 10 kcal/mol with dications compared to **3**(σ^3). In case of traizoles, the metal always preferred to bind in a bidentate fashion. For triazole **4** and **7**, stable σ complexes **4**(σ^8) and **7**(σ^{14}) could be located wherein the metal had a bidentate linkage. All attempts to locate a stationary point for the complexes of the type **4**(σ^6)**,** **4**(σ^7), or **7**(σ^{13}), where the metal has monodentate linkage converged to the stable complex **4**(σ^8) and **7**(σ^{14}). In the case of 1H-[1,2,4] triazole **5**, where the metal (in monodentate linkage) can bind at two electron-rich nitrogen sites (**5**(σ^9) and **5**(σ^{10})), the metal always preferred to bind away from the electron-deficient nitrogen center. The **5**(σ^{10}) isomer was preferred over **5**(σ^9) isomer by about 5 kcal/mol with monocations and by about 10 kcal/mol with dications. Among the various azole isomers, **2**, **3**, **4, 5**, **6**, and **7** the stability of the σ complex decreased in the following order: **7**(σ^{14}) > **4**(σ^8) > **3**(σ^3) > **2**(σ^2) > **5**(σ^{10})

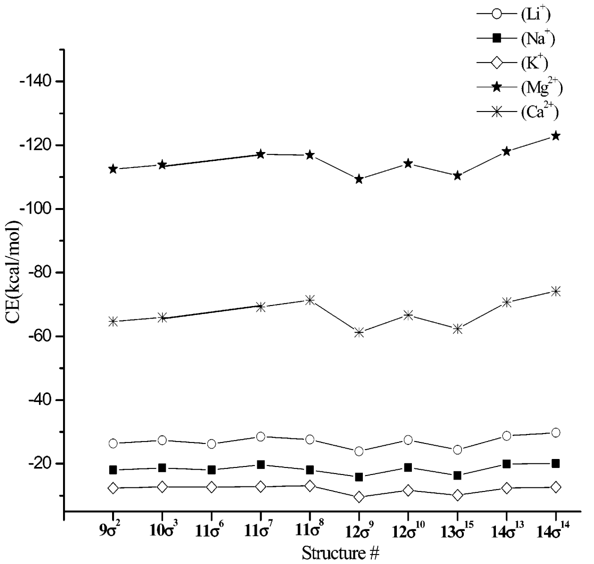


Figure 6. The σ complexation energy (CE) in kcal/mol of the di- and trisubstituted phospholes at the MP2(FULL)6-311+G(2d,2p)//MP2/6-31G* level.

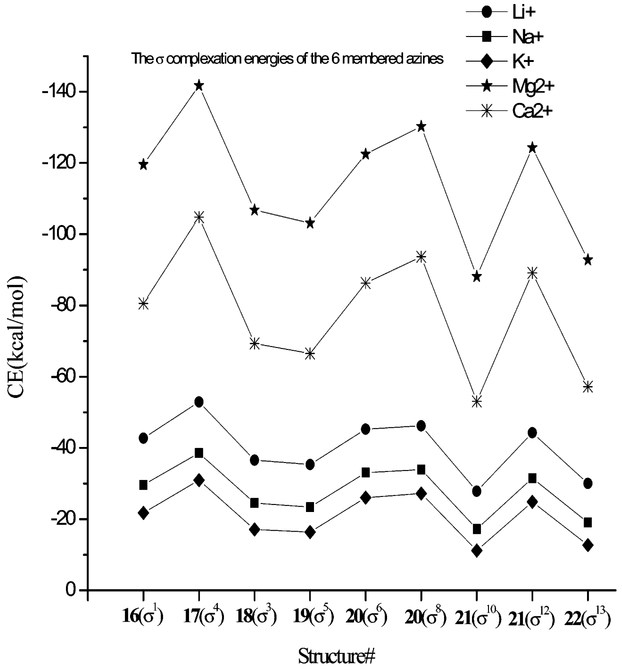


Figure 7. The σ complexation energy (CE) in kcal/mol of the mono-, di-, and trisubstituted azines at the MP2(FULL)6-311+G(2d,2p)//MP2/6-31G* level.

> **5**(σ^9) > **6**(σ^{15}). The following points emerged after analyzing the stability of the σ-complexes: (a) the metal preferentially binds in a bidentate fashion whereever possible; (b) the complexes with metal in bidentate linkage always had higher complexation energy than those with metal in monodentate linkage; (c) for complexes with monodentate linkage with the metal, the complexation energy was greater when the metal-binding center was away from the electron-deficient nitrogen center; (d) The complexation energy for the disubstituted azoles was found to be higher than that for the trisubstituted azoles.

The variation in the complexation energy of phosphole with various metal ions is depicted in Figure 6. It was interesting to note that a cursory look at Figure 6, especially comparisons with Figure 5, revealed that the extent of variation in the complexation energies of phosphole was much smaller either from one system to the other, whether the complex was of mono- or bidentate type. In sharp contrast to the complexation energy difference of about 5−15 kcal/mol between the two regio isomers of disubstituted azoles, the corresponding difference for the disubstituted phospholes, **9**(σ^2) and **10**(σ^3), was approximately about 1/10 of that of azoles! Thus, the regioselectivity of the disubstituted phospholes was virtually insignificant compared to the azoles. 1H-[1,2,3] triphosphole **11** formed three types of σ complexes; **11**(σ^6), **11**(σ^7), and **11**(σ^8), where the metal binds to the phosphorus center in monodentate fashion in the first two and bidentate fashion in the third. Similarly, the trisubstituted phosphole **14** also formed two different σ complexes depending on whether the metal had monodentate linkage **14**(σ^{13}) or bidentate linkage **14**(σ^{14}). The remaining triphosphole isomers **12** and **13** had metal in the monodentate linkage. The complexation energy of these σ complexes were quite competitive, irrespective of the metal ion. It was interesting to note that in the case of phospholes, both the mono- and bidentate complexes were found to be minima on the potential energy surface. This was in contrast to the situation with azoles, where most monodentate complexes were not even stationary points, when an alternative possibility existed for the bidentate complexation. However, the energy difference between the mono- and bidentate complexes of phospholes was marginal, albeit bidentate was preferred in most cases. All attempts to locate a complex of the type σ^6 for **11** with dications converged to the more stable σ^8 type complex where the metal has bidentate linkage. 1H-[1,2,4] triphosphole **12** formed stable complex of the types σ^9 and σ^{10} and like the nitrogen analogue **5**, the metal preferred to bind away from the electron-deficient phosphorus atom. The complex **12**(σ^{10}) was about 3−4 kcal/mol (with monocations) and about 5 kcal/mol (with dications) more stable than **12**(σ^9).

Six-Membered Heterocyclic Systems. The variation in the complexation energy of various mono-, di-, and trisubstituted azines is presented in Figure 7. The σ complexation energy of azines was found to be higher than the corresponding σ complex energy of phosphinines with any of the metals considered. All the azines σ complexes considered were characterized as minima on the potential energy surface, with the exception of **20**(σ^6). Like the azoles, the azines also preferred to form a σ complex where the metal has bidentate linkage. In the case of pyridazine **17**, though there exists the possibility to form two σ complexes of the types **17**(σ^2) and **17**(σ^4), the more stable **17**(σ^4) (metal has a bidentate linkage) alone could be located. Similarly for 1,2,3-triazine **20,** the complex of the type σ^7 could not be located on the potential energy surface. Although a complex of the type σ^6 could be located where the metal had monodentate linkage, it was characterized as a transition state and, following the normal mode of vibration, led to the more stable complex (σ^8) where the metal had bidentate linkage. The same was observed for [1,2,4] triazine **21**. This aromatic system could form four σ complexes of the type **21**(σ^9), **21**(σ^{10}), **21**(σ^{11}), and **21**(σ^{12}), wherein the first three complexes had monodentate metal linkage while **21**(σ^{12}) had bidentate linkage. Out of the four, **21**(σ^9) and **21**(σ^{11}) collapsed to **21**(σ^{12}). Between **21**(σ^{10}) and **21**(σ^{12}), the latter was more stable by over 15 kcal/mol with monocations and by over 30 kcal/mol with dications compared to **21**(σ^{10}). Among the azines, the complexation energy seemed to gradually decrease with the increase in the heteratom substitution in the ring system. Like the azoles, the bidendate complexes of azines had higher complexation energy, well over 15 and 30 kcal/mol for the mono- and dications, respectively, when compared to corresponding σ complexes, which had metals with monodentate linkage.

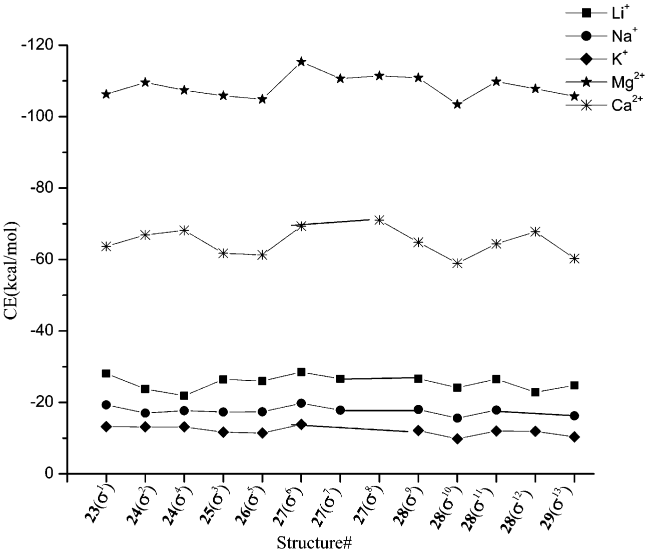


Figure 8. The σ complexation energy (CE) in kcal/mol of the mono-, di-, and trisubstituted phosphinines at the MP2(FULL)6-311+G(2d,-2p)//MP2/6-31G* level.

The variation in the complexation energy of the various mono-, di-, and trisubstituted phosphinines with various metal ions is presented in Figure 8. Though most of the phosphinine σ complexes were characterized as minima, a few exceptions did exist. The σ complexes **23**(σ^1) with Mg^{2+}, **24**(σ^4) with all the metals except K^+, **28**(σ^{10}) with Mg^{2+}, and **28**(σ^{12}) with Li^+, Mg^{2+}, and Ca^{2+} were characterized as transition states. Following the normal mode of vibration resulted in complexes wherein the metal was displaced from the plane of the ring. The **27**(σ^7) collapsed to **27**(σ^6) and **27**(σ^8) with K^+ and Ca^{2+}, respectively. **27**(σ^8) with all monocations collapsed to a complex that has monodentate linkage, while **28**(σ^{12}) with Na^+ collapsed to **28**(σ^9), a structure with monodentate linkage. The σ complexation energies of phosphinine were found to be lower than their azines counterparts. Unlike the azines, phosphinine didnot show high binding mode preference. Such complexes where the metal had bidentate linkage such as **24**(σ^4), **27**(σ^8), and **28**(σ^{12}) all had complexation energies comparable to the complexes that had monodentate linkage. Also, in such complexes the metal was slightly displaced from the plane of the ring. All the bidentate complexes where the metal lies in the plane of the ring, with the exception of **23**(σ^4) of K^+, were characterized as a transition state, and the minimum was one wherein the metal was displaced from the plane of the ring.

3.3. Comparison of the π and σ Complexes. *Five-Membered Heterocyclic Systems.* The σ complexation energy of the azoles was found to be much higher than the π complexation energy. The Li^+ σ complex of pyrazole **2** had a complexation energy 10 kcal/mol greater than that of the π-complex. Similarly, the σ complexation energy of trisubstituted azole **6** is about 5−10 kcal/mol (with monocations) and about 14−20 kcal/mol (with dications) greater than the π complexation energy. The disubstituted phospholes **9** and **10** preferred to form stronger π complexes with Li^+, Mg^{2+}, and Ca^{2+}, while for Na^+ and K^+, π and σ had comparable energies. If the trisubstituted phospholes were to be considered then in general, the π complexes were either more stable or had comparable π and σ complexation energies.

Six-Membered Heterocyclic Systems. The σ complex of azines were found to be almost 2 times more stable than the π complex with most of the metal ions. For the azines, increase in the heteroatom substitution in the ring led to a decrease in both the σ and π complexation energy. The π complexation energy of monosubstituted phosphinine **23** was higher than the σ complex for Li^+, Mg^{2+}, and Ca^{2+}, while for Na^+ and K^+, both the complexation energies are almost identical. For **24**, **25**, and **26,** the disubstituted phosphinines, the π complexes were either more stable or had comparable complexation energies with the σ complex. The trisubstituted phosphinine **27** formed more stable σ complex with most of the metal ions, while for the other two isomers **28** and **29**, the π and σ complexes had comparable complexation energy.

The current study revealed that metal ion-binding strength of both π and σ complexes are similar between the five- and six-membered ring systems. However, there is strong contrast between the nitrogen- and phosphorus-susbtsituted systems. The π complexation of phosphorus-containing ring systems are much stronger than that of nitrogen-containing ring systems. Perhaps this is due to higher compatibility of carbon and nitrogen π orbitals owing to the diagonal relationship.

Conclusions

The paper presents the σ and π complexation energies of heterocyclic ring systems such as azoles, phospholes, azines, and phosphinines with cations such as Li^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}. The theoretical study reveal that azoles and azines form stronger σ complexes, which is in agreement with earlier experimental and computational studies. In sharp contrast, the phospholes and phosphinines form stronger π complexes with the metal ions Li^+, Mg^{2+}, and Ca^{2+}. With Na^+ and K^+ there is little difference between the π and σ complexation energies for phosphorus heteroaromatics. The π and σ complexation energy of azoles and azines is found to decrease as the heteroatom substitution increases in the ring. In contrast, the complexation energies of both phosphole and phosphinines show little dependence on the number of phosphorus atoms in the ring. The complexation energy of a given heteroaromatic system with various metals followed the order $Mg^{2+} > Ca^{2+} > Li^+ > Na^+ > K^+$. Among the chosen metals, Mg^{2+} show a higher propensity to bind to the phosphorus systems while forming a π complex. The phosphinine Mg^{2+} complexes were found to have comparable complexation energy to benzene Mg^{2+} complex. The metal preferred to bind in the bidentate fashion to azoles and azines, whereas for the phospholes and phosphinines, no such binding preference was observed. For both azoles and phospholes, the metal binds away from the electron-deficient heteroatom. Thus, the present computational study revealed a very important contrast between nitrogen- and phosphorus-containing heteroaromatics. The strong π bonding ability of the phospholes and phosphinines is worthwhile for experimental verification.

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Supporting Information Available: The BSSE corrected complexation energies of the σ and $\pi-$ complexes at the MP2-(FULL)/6-311+G(2d,2p)//MP2/6-31G*, B3LYP/6-31G* and MP2/6-31G* level and the principal geometric parameters of the complexes at the MP2/6-31G*. This material is available free of charge via the Internet at http://pubs.acs.org.

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