DFT Calculations on the Interaction of Phosphazenes with Transition Metals

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Abstract

The electronic structure of substituted cyclic phosphazenes has been investigated using Density Functional Theory (DFT) and Natural Bond Order (NBO) analysis. NBO analysis shows covalent, ionic and negative hyper-conjugation interactions all contribute to the electronic structure of cyclic phosphazenes.

The geometric and electronic structural changes that occur when transition metals are coordinated to the nitrogen atom of the phosphazene ring have been analyzed using the NBO model. The bonding of transition metal ions with the ring nitrogen on the phosphazene was investigated by modeling hexakis(2-pyridyloxy)cyclotriphosphazene, hexakis(4-methyl-2-pyridyloxy)cyclotriphosphazene and octakis(2-pyridyloxy)cyclotetraphosphazene with different metal ions (Co(II), Ni(II), Cu(II), Zn(II)) in their assorted configurations with DFT as implemented in the Gaussian03 package.

First-row transition metals bind to the phosphazene ring with simple σ donor behaviour via the ring nitrogen. The lengthening of the PN bonds adjacent to the coordinated metal centre is a result of electron density being removed from the PN bonding orbitals and going into the 4s orbital of the metal ion.

Investigating the pyridine substituents on the phosphazene ring showed that these can affect the PN bonds in a similar fashion, although weaker, to the transition metals. This effect is the result of the pyridine nitrogen lone pair affecting the negative hyper-conjugation component of the PN bond.

Coupling between two metal atoms coordinated to the phosphazene ring was investigated by DFT calculations, which showed molecular orbitals in both the tricyclic and tetracyclic phosphazene capable of providing an ‘electron density bridge’ between the metal centres. These results are in accord with ESR and magnetic susceptibility results, which can be explained in terms of weak antiferromagnetic coupling between metal ions.

The cyclic phosphazenes are model compounds for polyphosphazenes and the results obtained from this work will provide insight into the electronic properties of this important class of inorganic polymers.

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