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DFT Calculations on the Interaction of Phosphazenes with Transition Metals

A thesis presented in partial fulfillment of the requirements for the degree
of Master of Science in Chemistry at Massey University, Palmerston North

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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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Chapter 1 – Introduction

1.1 The Phosphazene

The name phosphazene refers to a large class of inorganic molecules that have an unsaturated phosphorus-nitrogen back-bone¹, as shown in Figure 1.1.1.

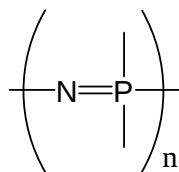


Figure 1.1.1 The PN backbone of a phosphazene.

Phosphazenes are readily functionalized by nucleophilic attack. By removing a proton from an alcohol or amine, it becomes a relatively simple process to attach different substituents to this back-bone² (see Figure 1.1.2 for an example³).

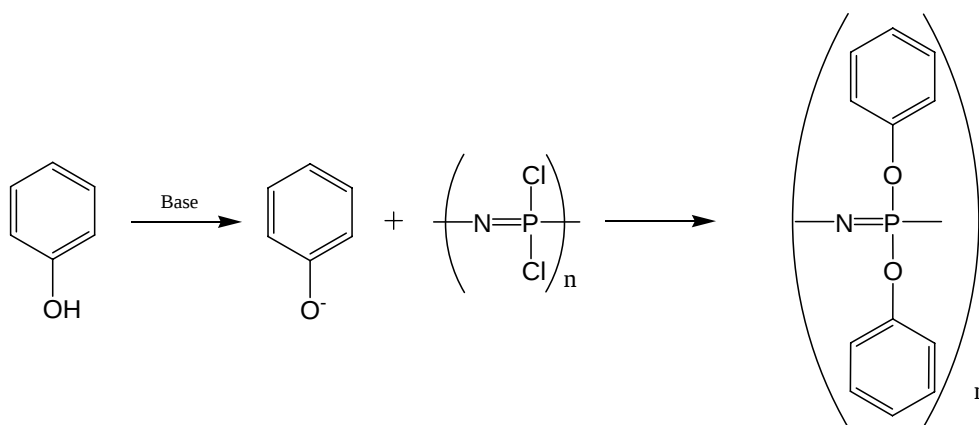


Figure 1.1.2 Example of a phosphazene substitution reaction with phenol.

Because of the greater ease of substitution of phosphazenes compared to polymers with carbon back-bones, they have been used for a variety of applications including: flame retardant materials⁴, drug delivery systems⁵, elastomers⁶, protective coatings⁷, semiconductors⁸, magnetic recording media⁹, adhesives¹⁰ and even lubricants¹¹. These are only a few of the current examples but show how important this system is.

As well as the polymer chains, phosphazenes also form cyclic molecules with varied ring sizes^{12, 13, 14}. Other heteroatoms maybe included in the ring^{15, 16, 17} (see Figure 1.1.3).

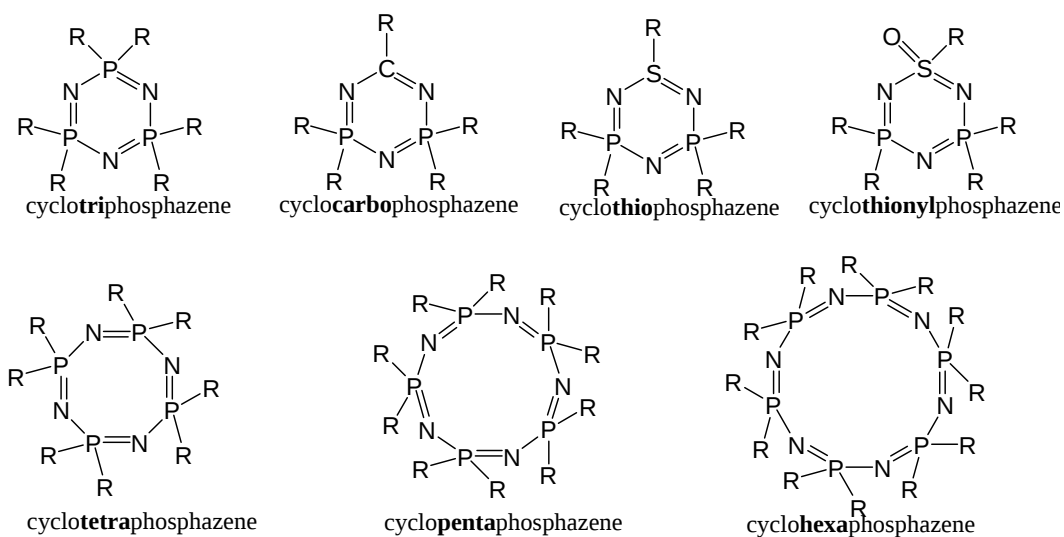


Figure 1.1.3 Examples of cyclic phosphazenes.

Cyclotriphosphazene (trimer) and cyclotetraphosphazene (tetramer) are the most studied of the cyclic phosphazenes¹⁸ as they are much more easily and cheaply synthesized¹⁹ than the other cyclic molecules and as a result provide model molecules for the polymer systems. Unlike the polymer, it is possible to get well-resolved X-ray structures of the trimer^{20, 21, 22} and tetramer^{23, 24, 25} and they can be modeled within a reasonable amount of time, which allows their behavior to be studied more thoroughly.

1.2 Phosphazene Bonding Models

Ever since the synthesis of phosphazenes, there has been much debate over the nature of the PN bonds. Many different factors need to be explained¹⁸:

- i. X-ray structures show that the PN bonds are much shorter than would be expected for a single PN bond.
- ii. Unless different substituents are attached, the PN bond remains approximately the same length no matter the size of the ring or if it is involved in a polymer.
- iii. Six membered rings have the same stabilities as eight and higher member rings despite the fact that some are planar and others are puckered.
- iv. No electronic spectral absorptions are observed in the visible or ultraviolet region above 220nm and the spectra are independent of ring size or polymer length.
- v. If electron-donating substituents are attached to the phosphorus atoms, the nitrogen atoms become electronegative enough to act as a base and accept protons or bind transition metals²⁶.
- vi. X-ray photoelectron spectroscopy shows that the core binding energies are relatively insensitive to the substituents or the ring size²⁷.
- vii. Polarographic reduction and electron spin resonance results show no evidence that the ring can be reduced to radical anions²⁸⁻³⁰.
- viii. In the linear phosphazenes there is only a very low barrier that exists to torsion of the PN bond. However, it is noted that for the polymers there is a small alternation observed for bond lengths.

The cyclotriphosphazene can be compared to the most commonly known six-membered cyclomer with multi-bonds, Benzene. Benzene consists of a hexagonal shape made up of σ bonds and out-of-plane 2p orbitals forming π bonds³¹.

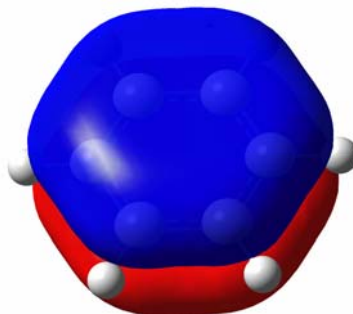


Figure 1.2.1 A benzene π orbital.

In the phosphazene, 3p orbitals on the phosphorus atoms are used for σ bond formation (bonds to the two nitrogen atoms and the two substituents). Only the 3d orbitals are left

for the formation of π bonds. Hence the first model developed by Craig and Paddock³²⁻³⁴ used a N(2p)-P(3d) overlap for π bond formation. This was developed further by Craig and Paddock³²⁻³⁴ in which the phosphorus d orbitals and the nitrogen p orbitals are able to overlap in-plane forming a π bond.

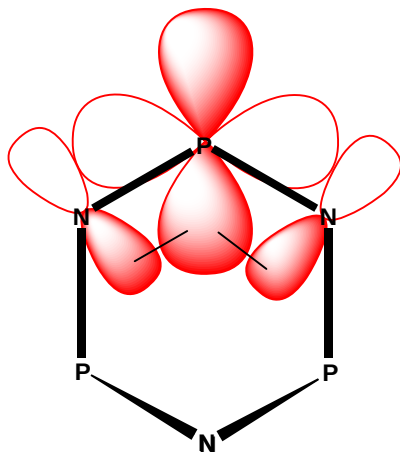


Figure 1.2.2 Craig and Paddock model of the phosphazene bonding.

Dewar³⁵ pointed out that this model did not account for the lack of UV absorbance and the independence of stability from ring planarity or size. Therefore, Dewar developed the island model in which the orbitals out-of-plane resulting in islands of electron density on the nitrogens.

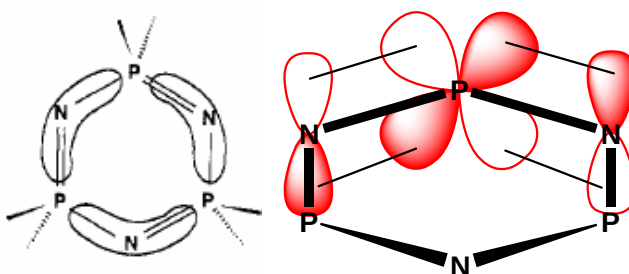


Figure 1.2.3 Dewar's island model of phosphazene bonding.

There is, however, orbital mismatch (Figure 1.2.4) that occurs making the stabilization low, which was thought to account for the lack of difference between the ring sizes and the polymers. Also the ease of changing the d orbitals, could have accounted for the low torsional activation energy for the polymers.

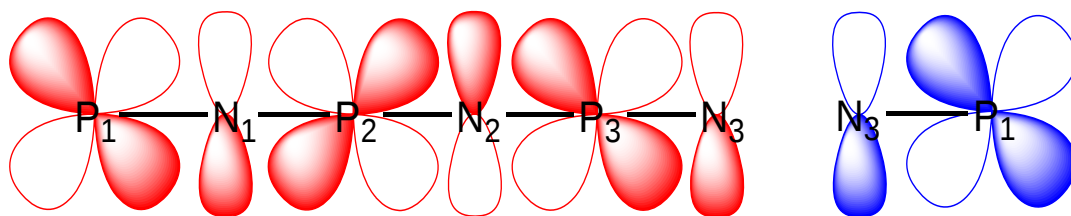


Figure 1.2.4 The Dewar island model symmetry problem.

It was not until Ferris³⁶ performed *ab initio* calculations on the phosphazene rings that it was found that the electron density was far more localized on the nitrogen than first thought. With this information, another model was developed in which there was a large zwitterionic component with the nitrogens being negatively charged and the phosphorus positively charged.

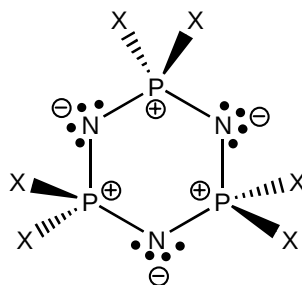


Figure 1.2.5 The Ferris zwitterionic model.

This was an improvement on the island model³⁵ in that it helped to explain the reactivity and structure of the molecule. However, it did not account for the flanking PN bond lengthening (see Section 1.4). It was not until computational chemistry advanced that it was possible to show that the bonding was not fully accounted for by the zwitterionic model but in fact had significant contributions from negative hyper-conjugation, as in CF_4 ³⁷. The combination of the zwitterionic form and negative hyper-conjugation is henceforth called the Chaplin model³⁸ (see Figure 1.2.6).

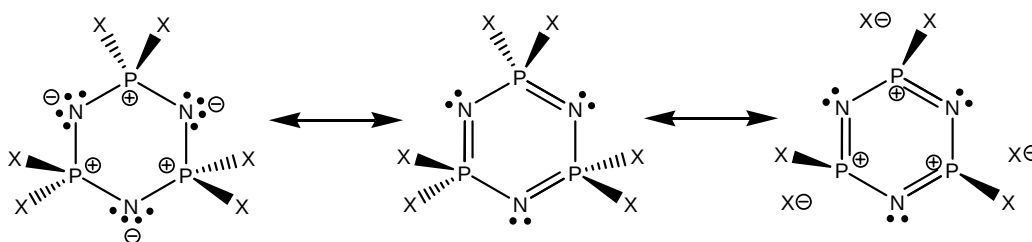


Figure 1.2.6 The Chaplin negative hyper-conjugation model.

In this model, negative hyper-conjugation accounts for around 15% of the total bonding (the exact amount depends on the substituent) with ionic bonding accounting for the rest.

The Chaplin model is currently the favoured one for phosphazenes as it accounts for all of the properties that were previously explained by the other models.

1.3 Natural Bond Orbital Analysis

Natural Bond Orbital (NBO) analysis was originally developed as a way of quantifying resonance structure contributions to molecules. NBOs are an orthonormal set of localized ‘maximum occupancy’ orbitals whose leading N/2 members give the most accurate Lewis description of the total electron density³⁹. More simply they are orbitals localized on typically one or two centres (occasionally more) that are used to describe the Lewis-like molecular bonding pattern of electrons.

The NBOs are made up of a combination of Natural Hybrid Orbitals (NHOs)⁴⁰ (h_A) which are each made up of an optimized linear combination of Natural Atomic Orbitals (NAOs)⁴¹.

$$h_A = \sum_k a_k \Theta_k^{(A)} \quad \text{Equation 1.3.1}$$

a_k = wave function coefficient, and $\Theta_k^{(A)}$ = the NAO wave function

A simplistic example is shown below:

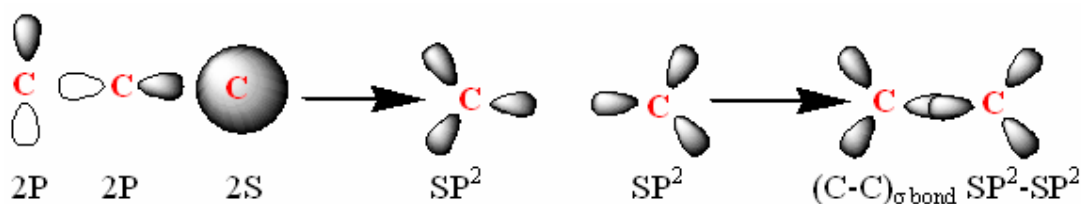


Figure 1.3.1 A schematic explanation of an NBO.

There are three classes of Lewis-like orbitals: i) core orbitals that are a pure NAO (labeled as CR in out puts); ii) lone pairs with one NHO(n_A) on the one centre (labeled as LP in out puts);

$$n_A = h_A \quad \text{Equation 1.3.2}$$

iii) the natural bond orbitals (NBO)s Ω_{AB} (labeled as BD in out puts), which consist of normalized combinations of two or more bonding NHOs on two or more centres, as in the intuitive model of chemical bonding.

$$\Omega_{AB} = a_A h_A + a_B h_B \quad \text{Equation 1.3.3}$$

a_A and a_B are polarized coefficients that must satisfy the condition $a_A^2 + a_B^2 = 1$

The difference between these coefficients provides information about the type of bond, i.e. for a covalent bond $a_A = a_B$ and for an ionic bond $a_A \gg a_B$. When $a_A \geq 0.95$ the orbitals are considered to be lone pair types.

The non-Lewis orbitals consist of two types - the antibond NBO Ω_{AB}^* and the Rydberg-type. The antibond is the orthonormal complement to the NBO or the out of phase version of the NBO (labeled as BD* in out puts).

$$\Omega_{AB}^* = a_B h_A - a_A h_B \quad \text{Equation 1.3.4}$$

While these are not intuitively considered in the Lewis model, they are very important in chemistry as they are ‘acceptor’ orbitals, and contribute to resonance and any other donor-acceptor interactions.

The Rydberg-type orbitals are one-centre NBOs that are essentially extra-valence NAOs that have little occupancy and can be ‘chemically ignored’, but are necessary for a complete quantum mechanical description of the molecule (labeled as RY in out puts).

All of these orbitals are made up of combinations of NHOs that are themselves comprised of NAOs. The NBO program is able to show all of the NAOs that contribute to the NBOs, lone pair orbitals, etc, including their occupancy and energies. Not only is the analysis able to describe the atomic components of bonding, it is also possible using second order perturbation theory (E_2) to calculate the strength of interactions such hydrogen-bonds and metal-ligand bonds.

The E_2 values provide the strength of the donor-acceptor interaction based on all of the intuitive means for describing the interaction, such as orbital occupancy, overlap and energy difference. Therefore, the E_2 values can be considered a good representation of the bond strength. The off diagonal Fock-matrix elements, $F(i,j)$, are used, $\epsilon_i - \epsilon_j$ is the difference in orbital energies and q_i is the occupancy used to weight the orbital (shown in Equation 1.3.5).

$$E_2 = \frac{q_i [F(i,j)]^2}{\epsilon_i - \epsilon_j} \quad \text{Equation 1.3.5}$$

The E_2 values provide information about the strength of the bonding and the orbitals involved in this interaction. By combining all of this information, a picture of how the metal ion interacts with the phosphazene ring can be built up.

1.4 Nucleus Independent Chemical Shift

Hückel originally developed the approximations for defining aromatic systems⁴², namely:

- i) the systems must be cyclic and planar;
- ii) there must be $(4n + 2) \pi$ electrons involved in bonding.

Hückel theory, one of the earliest forms of ‘quantum chemistry’, was able to explain the planarity and stabilisation energy of benzene. However, using this theory both borazine and phosphazene are defined as aromatic, but the theory provides no information about how aromatic these systems are. Aromaticity is a difficult property to define, but a good description uses the delocalization of electron density around a cyclic system.

One of the many methods for determining the electron delocalization of a ring is called the Nucleus Independent Chemical Shift (NICS)⁴³. It is defined as the negative of the absolute value of magnetic shielding computed at the geometrical centre of the ring. This means that the magnetic shielding in the direct centre of the ring is measured. The shielding occurs because of the electron density flowing around the ring, and is the reason that protons resonances of benzene are shifted up field in NMR measurements. However, in benzene the protons, on the outside of the ring, 2-4 Å away from the central electron density, only shift to around 7.3 ppm. By contrast, the inner protons for [18]-annulene have a shift -3.0 ppm compared to 9.8 ppm for the outer protons⁴⁴. Using this theory ³He atoms⁴⁵ or lithium(I) ions⁴⁶ have been placed in the central cavities to measure the shift. This method is however limited to those cyclic systems that can fit such ‘probes’.

Computational chemistry has been able to overcome this problem using ghost atoms (Bq). The NICS is measured by placing a ghost atom at the centre of the ring (see Figure 1.4.1). The ghost atom is a ‘probe’ as it is an atom with no basis functions and is subject to local effects without influencing the rest of the molecule. The more negative the isotropic shift becomes, the more aromatic the measured molecule is.

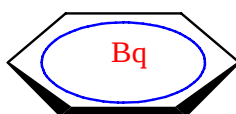


Figure 1.4.1 The ghost atom (Bq) in the centre of the benzene.

The previous method for quantifying aromaticity, i.e. aromatic stabilisation energy (ASE), agrees with the NICS method (see Figure 1.4.2), but the NICS is much simpler.

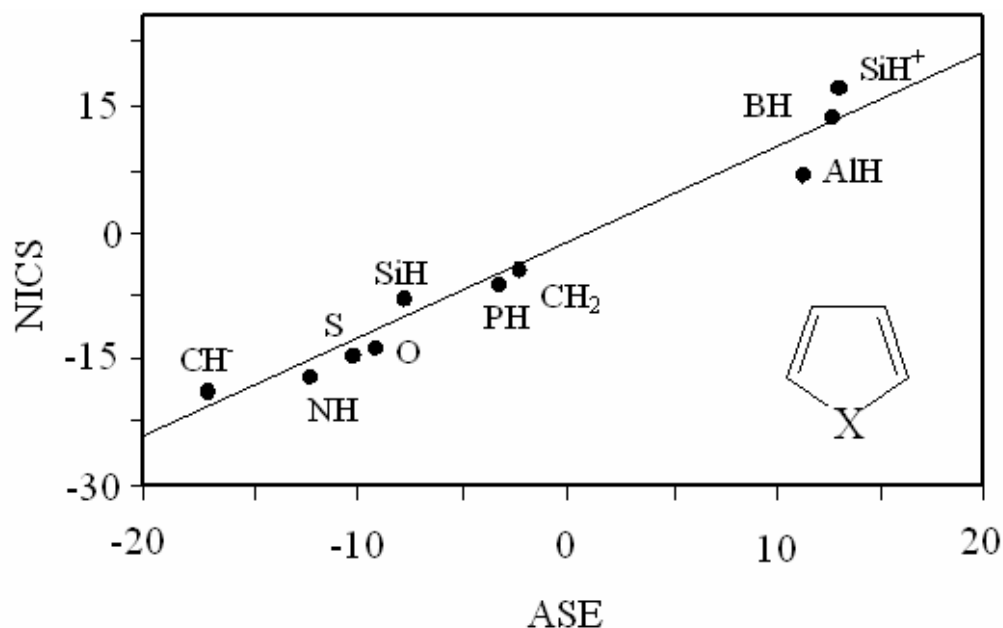


Figure 1.4.2 NICS(0) vs. ASE⁴³.

There has been some debate about the best height to place the ghost atom. The original method – NICS(0)-developed placed the ghost atom in-plane with the ring. However, there was some debate as to whether the σ bonds affected the results. To overcome this, the NICS(1)⁴⁷ approach was used where the ghost atom is held 1Å out of plane. Using this method, the effects of the σ bonds become negligible and as a result, this has become the most widely used method for determining the NICS. The NICS(1) method is perfect for planar molecules with no other groups over or near the ring but once such groups are present they can affect the ghost atom independently. In such cases, the NICS(0) method can be used. Therefore, while NICS(1) is preferred in some cases NICS(0) is still used.

1.5 Current Study

In this research project, the aim was to determine how the phosphazene interacts with transition metals, and as a result provide information about the nature of the PN bond. To the best of our knowledge, no one has used *ab initio* methods to investigate how phosphazene binds to metals despite the fact that there have been many of these complexes synthesized and structurally characterized^{48, 49, 50} (see Figure 1.5.1).

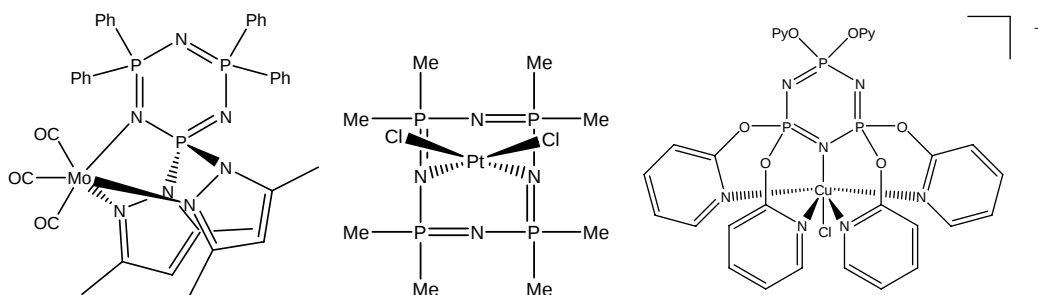


Figure 1.5.1 Examples of phosphazenes binding to transition metals.

One of the key observations when a metal binds to a phosphazene, is that the PN bonds flanking the metal lengthen by 0.01-0.04Å no matter what substituents are attached to the phosphorus⁵¹⁻⁵⁶. This behaviour shows that the purely ionic model cannot fully describe the bonding (e.g. to explain the bond lengthening). Previously, the Dewar model was used because the theory suggested that when the nitrogen lone pair bonds to the metal ion, it is no longer available for π bonding in the phosphazene therefore weaken and lengthen the flanking PN bond³²⁻³⁴. Since the Dewar model is now out-dated, it was hoped that it would be possible to explain the bond lengthening using the Chaplin model.

To test this hypothesis, a series of phosphazene complexes was modeled using the ligands shown in Figure 1.5.2.

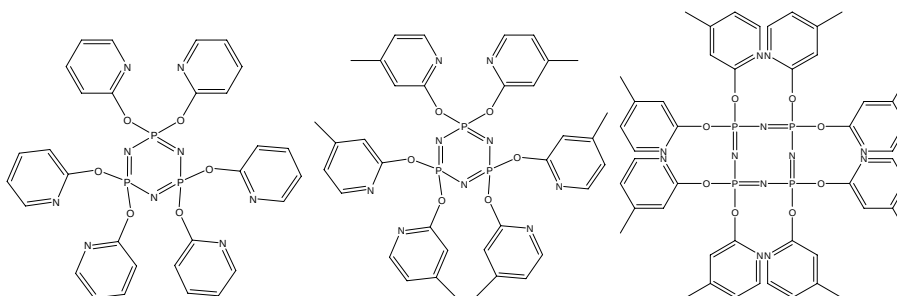


Figure 1.5.2 From left: hexakis(2-pyridyloxy)cyclotriphosphazene (L), hexakis(4-methyl-2-pyridyloxy)cyclotriphosphazene (LMe), octakis(4-methyl-2-pyridyloxy)cyclotetraphosphazene (Ltetr).

These ligands were chosen as they are able to bind a variety of different metals in an assortment of different modes, some even binding multiple metals^{57, 58} (see Figure 1.5.3). They all also display the same behaviour in which the flanking PN bonds lengthen and the dimetal species potentially show some weak communication between the metal centres⁵⁹.

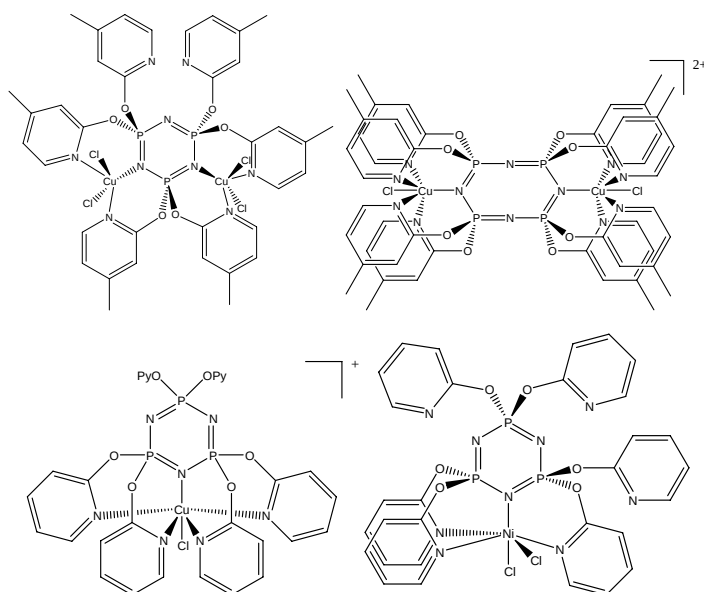


Figure 1.5.3 Examples of the Phosphazene complexes.

Chapter 3

The first part of this investigation was to determine what class of donor the phosphazene ring is. If it is a π donor or acceptor then this favours the Dewar model³⁵, but if it were a simple σ donor then this would be more consistent with the ionic or Chaplin model³⁸. Hence, this chapter provides insight to the bonding nature of the phosphazene. As the ligand is a complex molecule, the best approach to determine the donor class is to see how phosphazene binding affects the properties of the d orbitals on the transition metal ion. Their behaviour has been determined for different complexes (simplified examples for octahedral complexes are shown below in Figure 1.5.4⁶⁰).

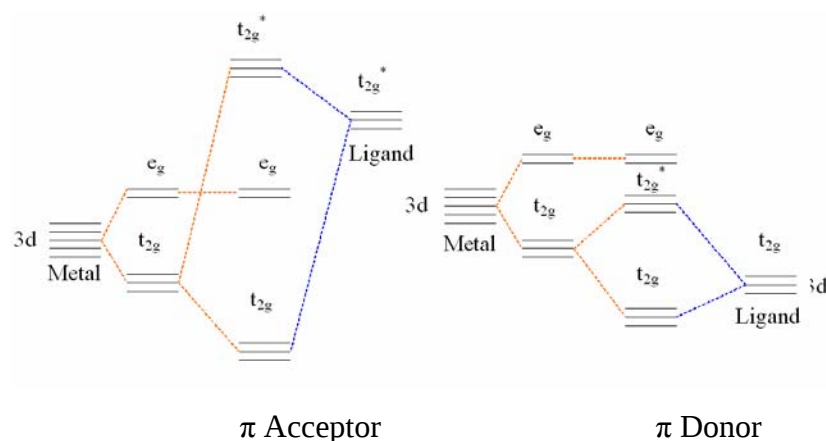


Figure 1.5.4 Examples of Donor class behaviour for an octahedral complex.

By comparing, the behaviour of the d orbitals when the metal is bound to the phosphazene to when it is not, calculations should allow the bonding type of the phosphazene to be determined.

Chapter 4

The aim of this chapter is to explain why the flanking bond lengthening (see Figure 1.5.6) occurs by identifying if there were any interactions that occur between the metal centre and the PN bonds. This included determining the strength of the interaction and the flow of electrons (i.e. to or from the PN bond). The PN bond occupancy was determined as well as the strength of the bond.

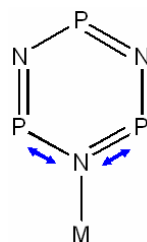


Figure 1.5.6 Flanking PN bond lengthening.

Chapter 5

The effect of the substituents on the phosphazene ring was initially investigated by determining if there is any interaction between the substituent (in this case uncoordinated pyridine) and the phosphazene ring. If any interactions are present, the effects on the ring will be examined. It has been suggested that there is an interaction between some substituents and the phosphazene ring that results in the capping substituent being held in place (see Figure 1.5.7) rather than this simply being the result of intermolecular interactions⁶¹. As the pyridine substituent contains a donor atom close

to the phosphazene ring this will provide a contrast to the acceptor nature of the metal ion thereby completing the study of how the phosphazene interacts with other systems.

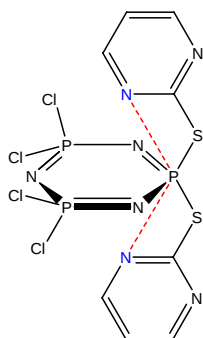


Figure 1.5.7 Example of substituent interaction with the phosphazene.

Chapter 6

The final part of this investigation will be to determine if any communication between metal centres occurs. For some of the phosphazene systems it is possible to attach multiple metal centres to the same phosphazene ring (see Figure 1.5.8). If the phosphazene system was truly aromatic, communication between metal centres should be possible. From Electron Spin Resonance (ESR) measurements small copper hyperfine coupling constants have been obtained on the $g = 2$ signal, along with a weak $g = 4$ signal via the weak coupling of the unpaired electron on each copper. The electron-electron interaction may occur via the phosphazene PN bonds or through space.

To answer this question, it will be necessary to find if there are any direct interactions between the metal centres, i.e. orbitals linking both metal centres via interactions around the ring.

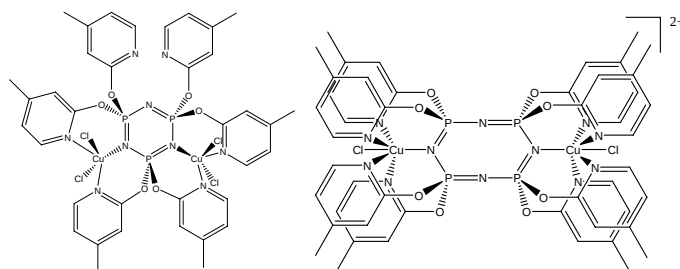


Figure 1.5.8 Phosphazenes potentially capable of metal communication.

Chapter 2 – Method

2.1 Introduction

The method was broken down into a series of stages. The first was to optimize the structure by building the molecule in GaussView⁶² based on available X-ray data⁵⁷⁻⁵⁹. The structures were then optimized to the global minima (see Figure 2.1.1), using Density Functional Theory (DFT) at the B3LYP level with a 6-31G(d) basis set and unrestricted spin (using the Gaussian03 package⁶³). The models were tested for accuracy by synthesizing the complexes according to literature methods⁵⁷⁻⁵⁹, then comparing their X-ray structures, infrared (IR) spectra and magnetic measurements with the DFT calculations.

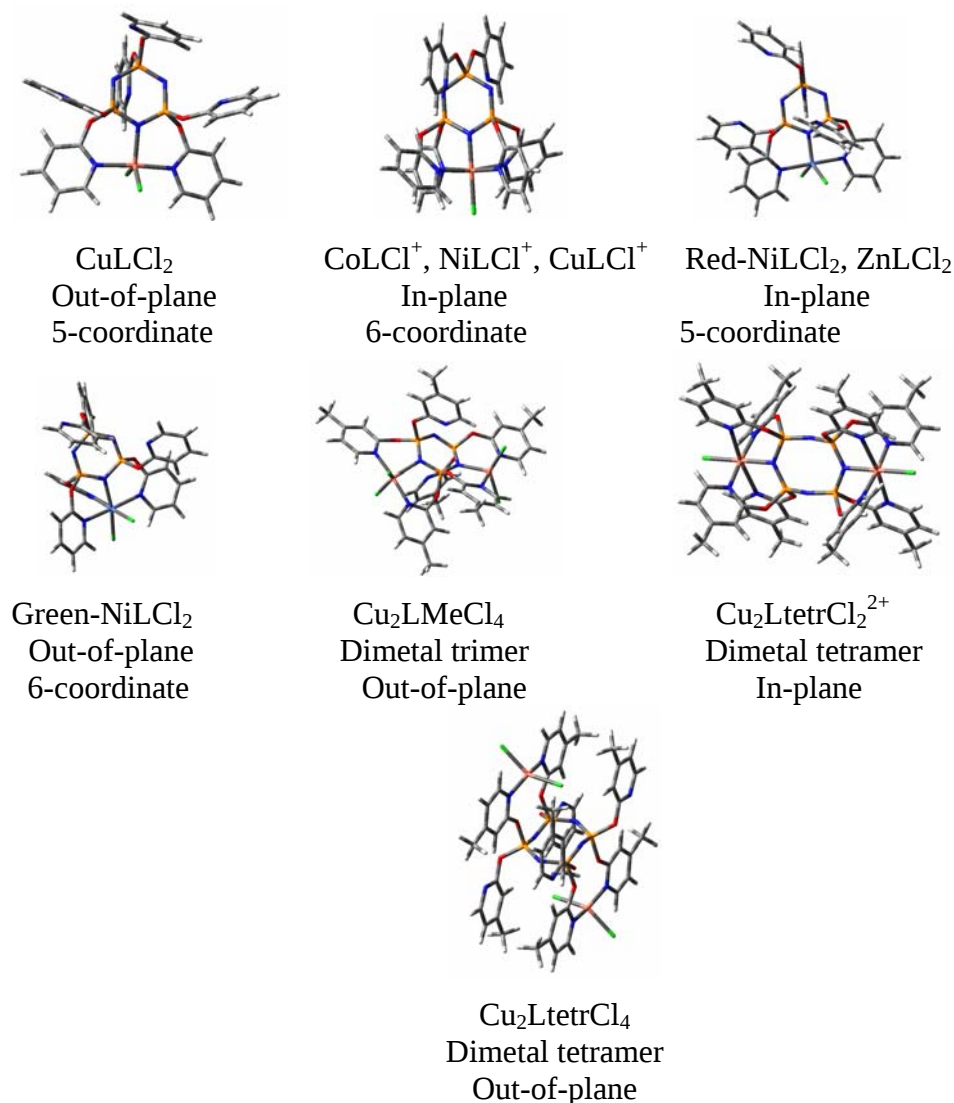


Figure 2.1.1 Examples of optimized structures (see Figure 1.5.2 for ligands).

2.2 Structural Accuracy

As a significant part of this research was to determine why the flanking PN bonds lengthened, it was necessary to determine if there was good agreement between the calculated bond parameters and those determined from X-ray analysis. This was examined by comparing the bond lengths measured in X-ray structures⁵⁷⁻⁵⁹ to the calculated values.

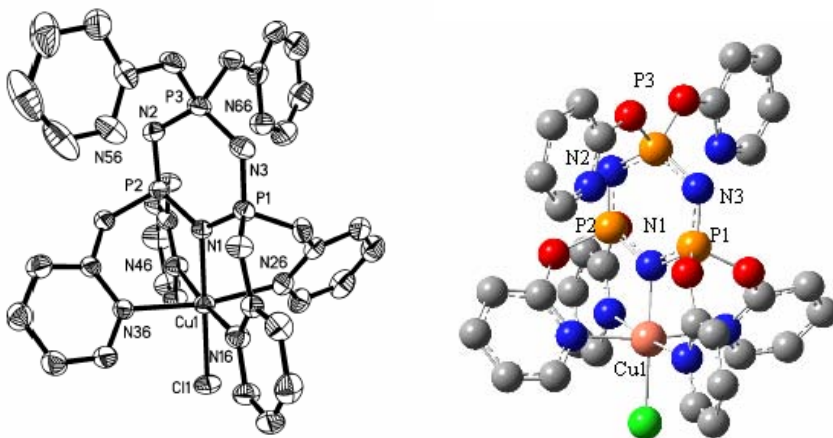


Figure 2.2.1 Comparison between an X-ray and DFT optimized structure.

The PN and N-M²⁺ bonds were examined as they are the bonds of interest in this project and relative to the phosphazene the pyridine groups were the most difficult to optimize, therefore, they will give the best indication of the model's accuracy. The accuracy was calculated as a percentage error as shown in Formula 2.2.1. The errors in bonding are displayed in Tables 2.2.1-2.2.4.

$$\text{Error}(\%) = \frac{|\text{Calculate value} - \text{X-ray value}|}{\text{X-ray value}} \times 100\% \quad \text{Formula 2.2.1}$$

The crystal structures for CoLCl₂ and CoLCl⁺ were unavailable so the DFT optimized structures were compared to similar structures to determine the orientation of the metal ions and pyridine arms, e.g. CoLMeBr₂ was used as a model for the CoLCl₂ structure and [CoLCl]CoLCl₃ as a model for CoLCl⁺. An X-ray structure of LMe is not available therefore, the bond lengthening for Cu₂LMeCl₄ will not be determined.

Single Metal Trimer Complexes

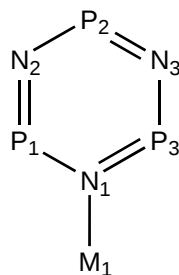


Figure 2.2.2 Atom labels for complexes in Table 2.2.1.

Table 2.2.1 Calculated bond distance errors for selected phosphazenes.

Complex	Bond Length Error (%)							Average Error (%)
	M ₁ -N ₁	N ₁ -P ₃	P ₃ -N ₃	N ₃ -P ₂	P ₂ -N ₂	N ₂ -P ₁	P ₁ -N ₁	
CuLCl ₂	3.53	1.23	0.41	1.58	1.54	0.37	0.89	1.36
CuLCl ⁺	0.49	1.61	1.34	1.02	1.52	0.29	1.34	1.09
Red-NiLCl ₂	0.00064	0.012	2.07	1.27	1.27	2.07	0.012	0.95
Green-NiLCl ₂	1.01	0.28	0.69	0.94	0.93	0.78	0.72	0.77
NiLCl ⁺	4.00	1.28	0.60	0.86	1.07	0.73	1.35	1.41
L		0.89	1.49	1.03	1.47	0.99	1.82	1.28

Cu₂LMeCl₄

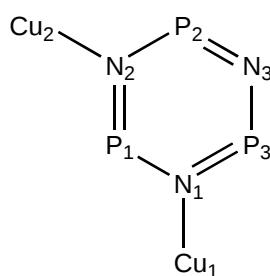


Figure 2.2.3 Cu₂LMeCl₄ atom labels.

Table 2.2.2 Calculated bond distance errors for Cu₂LMeCl₄.

Bond Length Error (%)								Average Error (%)
N ₁ -P ₁	P ₁ -N ₂	N ₂ -P ₂	P ₂ -N ₃	N ₃ -P ₃	P ₃ -N ₁	N ₁ -M ₁	N ₂ -M ₂	
0.017	0.019	0.0062	0.012	0.014	0.0062	0.0058	0.0090	0.011

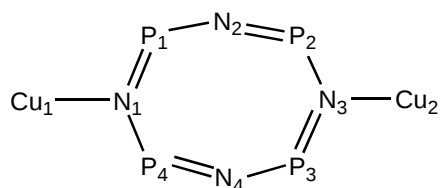


Figure 2.2.4 Cu₂LtetrCl₂²⁺ atom labels.

Table 2.2.3 Calculated bond distance errors for Cu₂LtetrCl₂²⁺.

Bond Length Errors (%)										Average Error (%)
N(1)- P(1)	P(1)- N(2)	N(2)- P(2)	P(2)- N(3)	N(3)- P(3)	P(3)- N(4)	N(4)- P(4)	P(4)- N(1)	Cu(1)- N(1)	Cu(2)- N(3)	
1.25	1.10	1.23	1.51	1.25	1.10	1.23	1.51	0.34	0.34	1.09

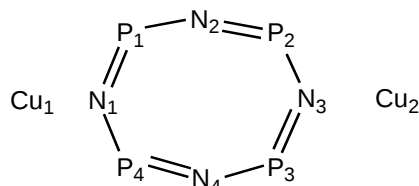


Figure 2.2.5 Cu₂LtetrCl₄ atom labels.

Table 2.2.4 Calculated bond distance errors for Cu₂LtetrCl₄.

Bond Length Errors (%)										Average Error (%)
N(1)- P(1)	P(1)- N(2)	N(2)- P(2)	P(2)- N(3)	N(3)- P(3)	P(3)- N(4)	N(4)- P(4)	P(4)- N(1)	Cu(1)- N(1)	Cu(2)- N(3)	
0.71	1.50	1.45	0.66	0.87	1.50	1.45	0.66	3.23	3.23	1.52

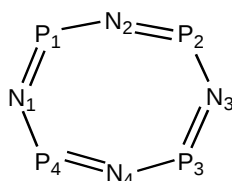


Figure 2.2.6 Ltetr atom labels

Table 2.2.5 Calculated bond length distances for Ltetr

Bond Length Errors (%)									Average Error (%)
N(1)- P(1)	P(1)- N(2)	N(2)- P(2)	P(2)- N(3)	N(3)- P(3)	P(3)- N(4)	N(4)- P(4)	P(4)- N(1)	N(1)- P(1)	
1.84	2.13	1.20	0.10	1.84	2.13	0.62	1.18	1.84	1.38

Table 2.2.6 Comparison between the calculated and observed X-ray values for the flanking PN bond lengthening

Complex	X-ray (Å)		Calculated (Å)	
	$\Delta(\text{P}_1\text{-N}_1)$	$\Delta(\text{P}_3\text{-N}_1)$	$\Delta(\text{P}_1\text{-N}_1)$	$\Delta(\text{P}_3\text{-N}_1)$
CuLCl ₂	0.019	0.017	0.013	0.010
CuLCl ⁺	0.023	0.027	0.026	0.026
Red-NiLCl ₂	0.034	0.034	0.020	0.020
Green-NiLCl ₂	0.032	0.021	0.015	0.009
NiLCl ⁺	0.016	0.016	0.014	0.014
	$\Delta(\text{P}_1\text{-N}_1)$	$\Delta(\text{P}_4\text{-N}_1)$	$\Delta(\text{P}_1\text{-N}_1)$	$\Delta(\text{P}_4\text{-N}_1)$
Cu ₂ LtetrCl ₄ (Cu 1)	0.002	0.002	0.005	0.005
	$\Delta(\text{P}_2\text{-N}_3)$	$\Delta(\text{P}_3\text{-N}_3)$	$\Delta(\text{P}_2\text{-N}_3)$	$\Delta(\text{P}_3\text{-N}_3)$
Cu ₂ LtetrCl ₄ (Cu 2)	0.002	0.002	0.005	0.005
	$\Delta(\text{P}_1\text{-N}_1)$	$\Delta(\text{P}_4\text{-N}_1)$	$\Delta(\text{P}_1\text{-N}_1)$	$\Delta(\text{P}_4\text{-N}_1)$
Cu ₂ LtetrCl ₂ ²⁺ (Cu 1)	0.037	0.034	0.044	0.044
	$\Delta(\text{P}_2\text{-N}_3)$	$\Delta(\text{P}_3\text{-N}_3)$	$\Delta(\text{P}_2\text{-N}_3)$	$\Delta(\text{P}_3\text{-N}_3)$
Cu ₂ LtetrCl ₂ ²⁺ (Cu 2)	0.037	0.034	0.053	0.044

These models all show behaviour typical of DFT calculations, i.e. the bond lengths are overestimated. However, the average error for all of the complexes was under 2% and the magnitude of the observed bond lengthening (see Table 2.2.6) was approximately, as that calculated, which indicates that a similar bond lengthening process was occurring in all the complexes. Due to the high accuracies of these calculations, it would be a reasonable assumption that the CoLCl⁺ and CoLCl₂ complexes and the bond lengthening of Cu₂LMeCl₄ were also modeled accurately.

2.3 Vibrational Accuracy

As a method for testing the accuracy of the electronic environment of the DFT model complexes, the DFT predicted IR spectra were compared to the measured spectra. The IR spectra were obtained by making the complexes according to literature methods⁵⁷⁻⁵⁹ then measuring the spectra on a Nicolet 5700 FT-IR spectrometer using KBr disks.

IR provides an effective way of measuring how well the compound has been modeled because the strengths of the bonds are dependent on the electronic environment.

The complexes being modeled in this study had complicated IR spectra. Therefore, it was necessary to select peaks in the spectra that were easily identified. The symmetric and asymmetric stretching modes of the phosphazene ring were used (see Figure 2.3.1).

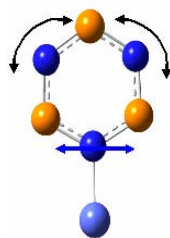
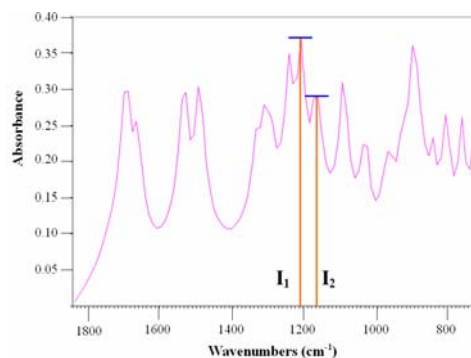


Figure 2.3.1 Phosphazene ring vibrational modes: Black is symmetric, Blue is asymmetric.

These two vibrational modes were chosen as they are very intense and sharp for all of the complexes and are specific to the ring and the metal. The comparison of the spectra was made by measuring the frequencies and the ratio of the peaks of the intensities $\{(I_1/I_2)_{\text{DFT}} \text{ to } (I_1/I_2)_{\text{measured}}\}$, where the intensity values are found using the absorbance of each peaks as shown in Figure 2.3.2. Comparisons of the vibrational data of the complexes are shown in Table 2.3.1.

CuLCl⁺ DFT Calculated Vibrational Spectrum



[CuLCl]PF₆ Measured Vibrational Spectrum

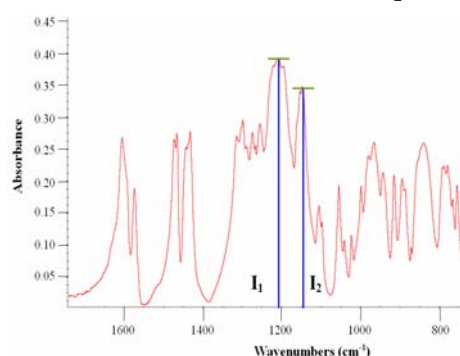


Figure 2.3.2 A comparison of DFT calculated and measured IR spectra (1800-800cm⁻¹).

Table 2.3.1 Comparisons between calculated and measured vibrational data.

Complex	Phosphazene asymmetric and symmetric ring stretching DFT (cm ⁻¹)	Phosphazene asymmetric and symmetric ring stretching Measured (cm ⁻¹)	Difference in stretching frequencies (cm ⁻¹)	Intensity Ratio DFT	Intensity Ratio Measured
CuLCl ₂	1209,1152	1227,1147	18, 5	6.7	1.2
CuLCl ⁺	1197, 1130	1209, 1147	12, 17	1.4	1.3
Green-NiLCl ₂	1190, 1157	1213, 1159	23, 2	3.5	1.2
NiLCl ⁺	1233, 1163	1218, 1161	15, 2	3.8	1.9
CoLCl ⁺	1234, 1150	1214, 1147	20, 3	3.7	1.3
CoLCl ₂	1210, 1155	1227, 1146	27, 9	7.5	1.7

The frequencies for the vibrations were accurately calculated (Table 2.3.1), differing only by 2-30cm⁻¹, but the calculated intensities were at least twice the magnitude of the measured values. This suggests that, while the electronic environment is almost correct, it is not totally accurate. The inaccuracy could be the result of basis set limitations. The

use of a higher basis set may reduce the error, but there will always be some error in such a calculation because of the DFT approximations no matter what basis set is used. Also a higher basis set would be far more expensive computationally. However, the inaccuracies that occur will only negligibly affect the electronic properties important for a qualitative bond description. Therefore, we will be able to show that the large interactions (such as the PN bond lengthening) will be accurately described. Due to computer memory constraints, the vibrational data for the dimetal complexes were not feasible in a reasonable length of time, but as the other vibrational data was accurately calculated it would be reasonable to assume that the electronic environment for these has been determined as accurately as for the mono-metal complexes.

2.4 Electronic Accuracy

In dealing with transition metals, the spin multiplicity becomes an important factor for bonding. The spin multiplicity is a property that is used to describe the number of unpaired electrons that a molecule has. For first row transition metals, the 3d orbitals are the valence orbitals. The d orbitals in most transition metal ions are not fully occupied and in first row transition metals the electrons can be arranged between the e_g and t_{2g} orbitals in a variety of different combinations (see Figure 2.4.1) resulting in different spin multiplicities. By changing the spin multiplicity, the occupancy of orbitals will be altered thereby affecting the bonding. It was therefore crucial to make sure that the complexes were modeled with the correct spin multiplicity.

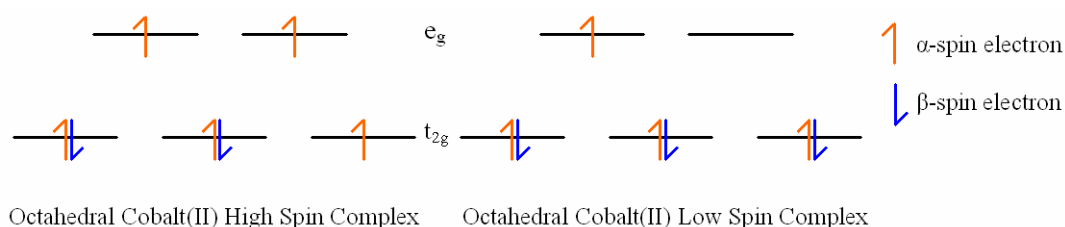


Figure 2.4.1 Example of octahedral cobalt(II) complex spin states.

To make sure that the spin multiplicity was correctly taken into account, the magnetic moments of the complexes were measured. Each electron has a magnetic moment, but when they pair, the net magnetic moment is zero. Hence, an unpaired electron makes the complex paramagnetic and therefore the magnetic moment μ_s is non-zero. By measuring the magnetic moment, it is possible to find the number of unpaired electrons¹ (see Table 2.4.1). This is done by obtaining the effective magnetic moment (μ_{eff}) using a Faraday balance (see Figure 2.4.2) to measure the magnetic susceptibility.

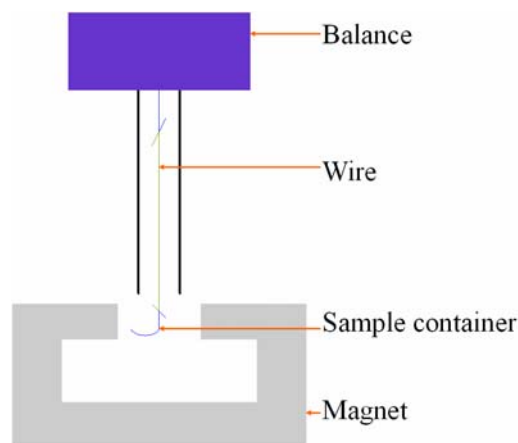


Figure 2.4.2 Schematic view of the Faraday balance.

The magnetic susceptibility was measured on the Faraday balance by first using a standard with a known magnetic moment - in this case $\text{Hg}[\text{Co}(\text{SCN})_4]$. The basis of the Faraday balance method is to measure how the weight of a sample changes when a magnetic field is applied. Using Formula 2.4.1, the magnetic susceptibility per gram (χ) can be determined.

$$\chi = \frac{\Delta W_{\text{Sample}}}{\Delta W_{\text{Standard}}} \times \frac{W_{\text{Standard}}}{W_{\text{Sample}}} \quad \text{Formula 2.4.1}$$

The molar susceptibility (χ_m) is found by multiplying the susceptibility per gram by the molar mass (M_w) (in kilograms) of the sample (see Formula 2.4.2).

$$\chi_M = \chi \times M_w \quad \text{Formula 2.4.2}$$

As the complex contained diamagnetic elements, it is therefore necessary to correct for their diamagnetism (χ_L) (see Formula 2.4.3).

$$\chi_M^{\text{cor}} = \chi_M - \chi_L \quad \text{Formula 2.4.3}$$

This corrected molar magnetic susceptibility can then be related to the effective magnetic moment by Formula 2.4.4.

$$\mu_{\text{eff}} = 797.7 (\chi_M^{\text{cor}} T)^{1/2} \quad \text{Formula 2.4.4}$$

Where T is the absolute temperature and χ_M^{cor} is the corrected molar susceptibility.

From the effective magnetic moment the spin moment and therefore the number of unpaired electrons can be approximately calculated via Formula 2.4.5. For first row transition elements $\mu_{eff} \approx \mu_s$.

$$\mu_{eff} = [s(s + 1)]^{1/2} \quad \text{Formula 2.4.5}$$

Table 2.4.1 Magnetic moments used to find multiplicity of complexes.

Complex	μ_{eff} (per metal ion)	Number of unpaired electrons
CuLCl ₂	1.76	1
CuLCl ⁺	1.81	1
Green-NiLCl ₂	2.86	2
NiLCl ⁺	3.16	2
CoLCl ⁺	4.61	3
CoLCl ₂	4.18	3
ZnLCl ₂	Diamagnetic	0
Cu ₂ LMeCl ₄	1.74	1
Cu ₂ LtetrCl ₂ ²⁺	2.03	1
Cu ₂ LtetrCl ₄	1.83	1

As ZnLCl⁺ was only a theoretical model used as a comparison, it was not possible to obtain any magnetic data. However as zinc(II) is always diamagnetic (as zinc has a filled 3d shell) the complex could be modeled as a singlet. A problem arose for the Red-NiLCl₂. The Red-NiLCl₂ complex could not be synthesized in large enough quantities for the magnetic measurements. To overcome this, both the singlet and triplet states were optimized and the lowest energy multiplicity was used. This was then reaffirmed by comparing the accuracy of the optimized structure to the X-ray structure and the colour of the complex was related back to similar nickel complexes with known spin multiplicity (see Figure 2.4.2)⁶⁴. Red five coordinate nickel species have singlet ground states, so modeling Red-NiLCl₂ as a singlet is reasonable.

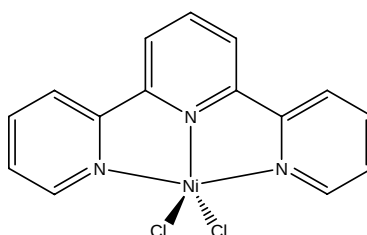


Figure 2.4.2 Five coordinate nickel analogue.

2.5 Molecular Orbital Diagram Construction

Molecular Orbital (MO) diagrams are particularly useful for analyzing multi-atom systems. This is because it is possible to pick out a specific set of orbitals for a molecule and see how they change when another part of the molecule is added or removed.

Hence, an MO analysis is ideal for the phosphazene system, but as mentioned in Section 1.4, the behaviour of d orbitals with different ligand classes is well known. Therefore, it will be possible to determine the bonding nature of the phosphazene by comparing the d orbitals when they are bound to the phosphazene and when they are not.

To achieve this, the d orbitals of the optimized structure were analysed using NBO analysis. For the unbound metal an idealized complex was created by removing all of the ligand except for the pyridine ligands around the metal ion from the optimized structure (see Figure 2.5.1). The idealized complexes were used as the uncoordinated results for metal ion, the theory being that any changes in the metal centre will be the result of coordination to the phosphazene.

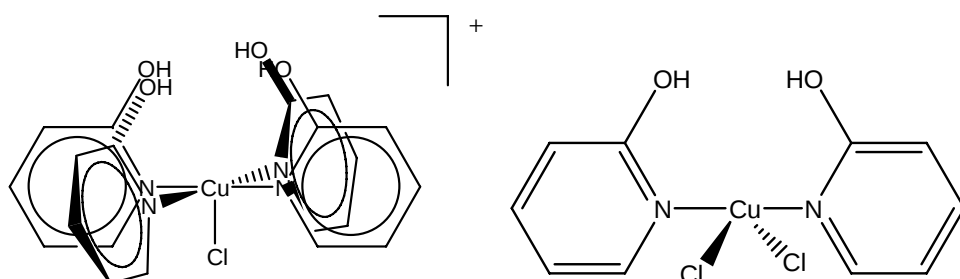


Figure 2.5.1 $\text{Cu}(\text{HOPy})_4\text{Cl}^+$ and $\text{Cu}(\text{HOPy})_2\text{Cl}_2$ the unbound phosphazene metal complex models of CuLCl^+ and CuLCl_2 respectively.

A similar method was used to determine whether alkanes bound more favourably ‘end on’ or ‘side on’ to transition metals⁶⁵. In that case, a $\text{Cr}(\text{CO})_5$ metal complex was the idealized complex used to rationalize which C-H orientation would be favourable, and the bonding mode with the lowest energy was chosen as the most favourable.

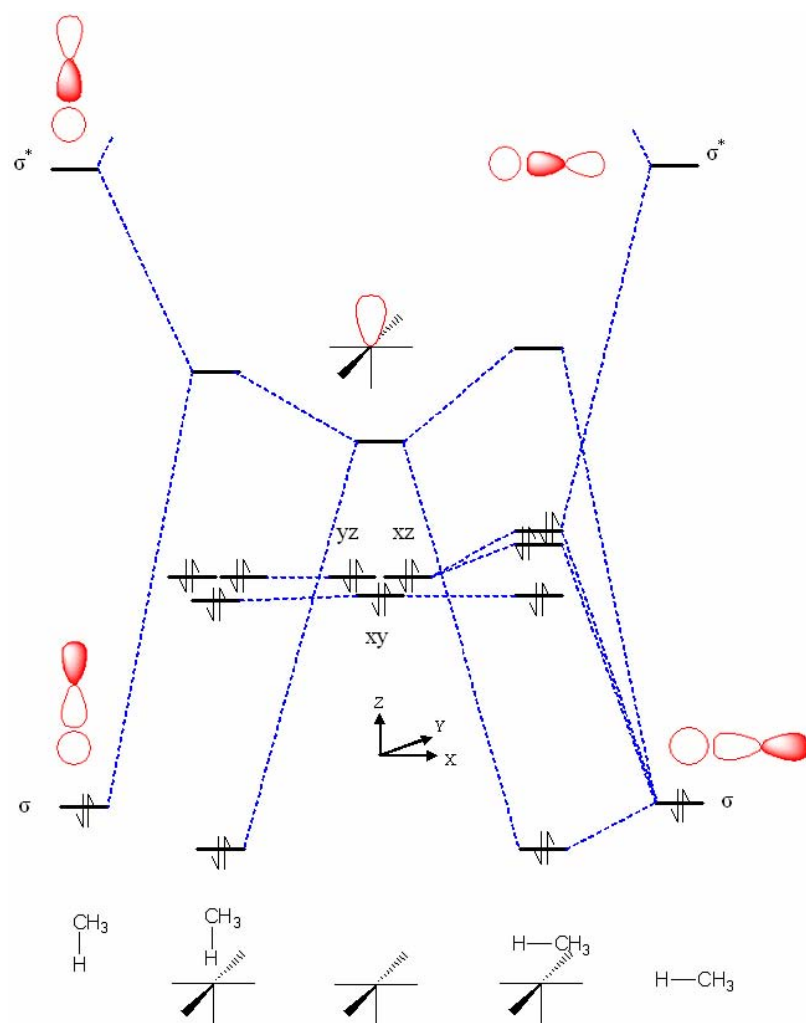


Figure 2.5.1 An example of a MO diagram being used to determine which way an alkane bonds to a transition metal.

As many of the complexes modeled in this project have doublet or triplet multiplicity, the β d orbitals will be of more interest than the α orbitals. This is because the α orbitals typically have higher occupancy than the β orbitals as a result of being the first filled by the parent atom (in this case the transition metal ion). The β orbitals, typically being less occupied by electrons from the parent atom, receive electron density from the donor (in this case the phosphazene). This results in a greater shift of energies for the β orbitals and as a result provides more information about the donor's affect on the parent atom than the α orbitals.

Chapter 3 – The Phosphazene-Metal Bond

3.1 Introduction

In this chapter, the bonding of the phosphazene to a number transition metals are investigated. Understanding the bonding nature of the phosphazene is important for the future design of ligand systems as it allows for more effective fine-tuning of the system. A key example of this is understanding why the phosphazene does not π bond to metals like benzene⁶⁶ or borazine⁶⁷ (see Figure 3.1.1).

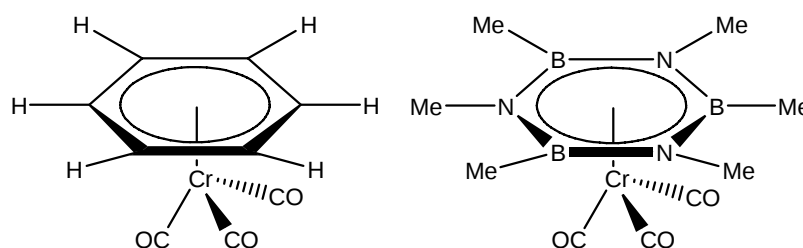


Figure 3.1.1 Examples of π complexes.

The closest example to π complexes for phosphazene is the tetramer platinum⁵¹ complex shown in Figure 3.1.2, however this is not a π type complex, since the platinum forms bonds with the ring nitrogens rather than the centre of the ring as is the case for benzene and borazine.

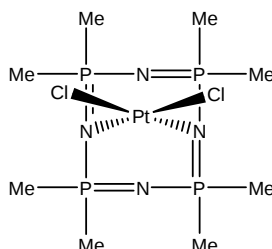


Figure 3.1.2 The tetramer platinum complex.

In all examples of phosphazenes binding to metals (excluding via ionic bonds), the metal binds to the phosphazene ring nitrogens rather than the phosphorus atoms, no matter how electron donating the substituents attached are, which suggests that the electron density is localized on the ring nitrogens. However, this is explained by all of the phosphazene bonding models (except Paddocks³²⁻³⁴) and therefore provides no distinction between them. For each of the models, the coordination of the metal to the phosphazene will result in different types of d orbital interactions with the metal. The difference in the orbital energies comes from two factors⁶⁰: i) the symmetry of the

orbitals determines which orbitals will be altered in energy (dependent on the ligand class) and ii) the electronic properties of the ligand then determine the magnitude of the change. Therefore, by classifying the bonding class of the phosphazene, the bonding nature of the PN bond will be determined.

The purpose of this chapter is to determine which donor class the phosphazene belongs to, i.e. simple σ donor, π donor or π acceptor, by observing the behaviour of the transition metal d orbitals (see Figure 1.5.4).

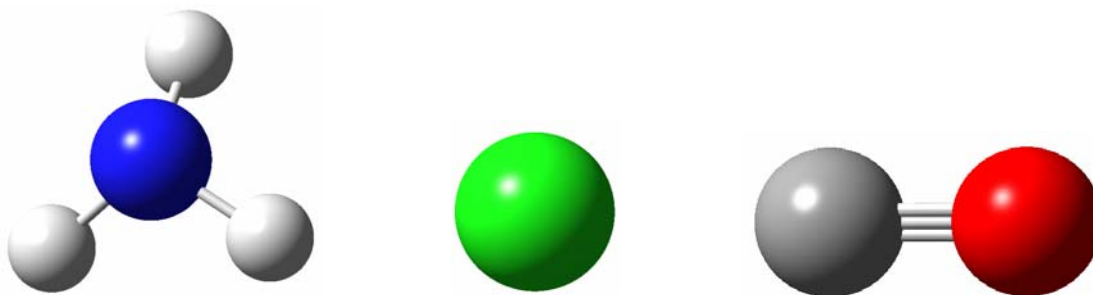


Figure 3.1.3 Examples of the donor classes. From left: ammonia (simple σ donor), chloride ion (π donor) and carbon monoxide (π acceptor).

In order to determine how the d orbitals of a metal behave when they are bound to the phosphazene a comparison must be made with the d orbitals when the metal is unbound. A MO diagram is the best way to achieve this. As well as how the d orbital occupancy changes, the wave function of the bonding orbitals has been investigated to find the atomic orbitals contributing to the bond. The investigation will be broken down into sections according to the metal geometry (six-coordinate in-plane, five-coordinate in-plane, out-of-plane, dimetal trimer and dimetal tetramer) since the similar geometries should result in similar bonding schemes. Finally, the collective behaviour for all of the complexes will be examined.

3.2 In-plane Six-coordinate Species

For all of the in-plane six-coordinate species, the local symmetry around the metal ion is C_{4v} , it being co-planar with the phosphazene ring when it forms a bond with the ring nitrogen (see Figure 3.2.1).

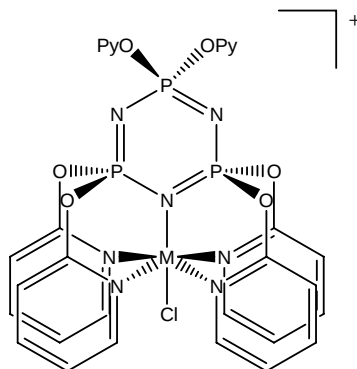


Figure 3.2.1 The structure of the in-plane six coordinate species.

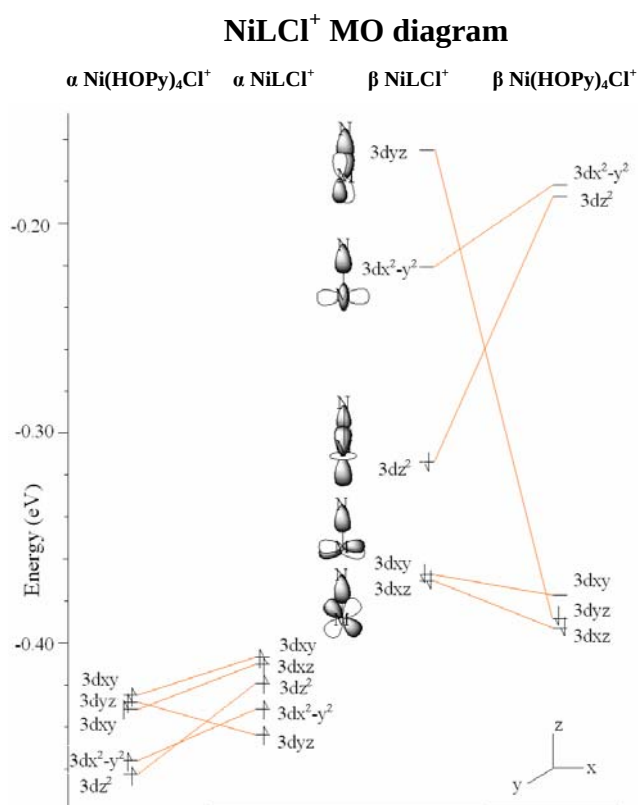
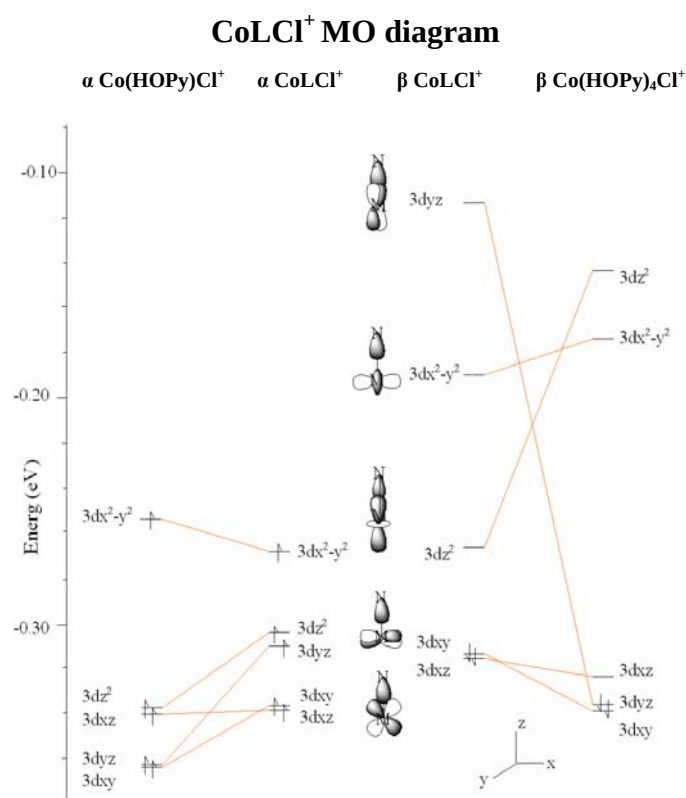


Figure 3.2.2 CoLCl⁺ and NiLCl⁺ MO diagrams comparing the metal orbitals with and without the phosphazene bound.

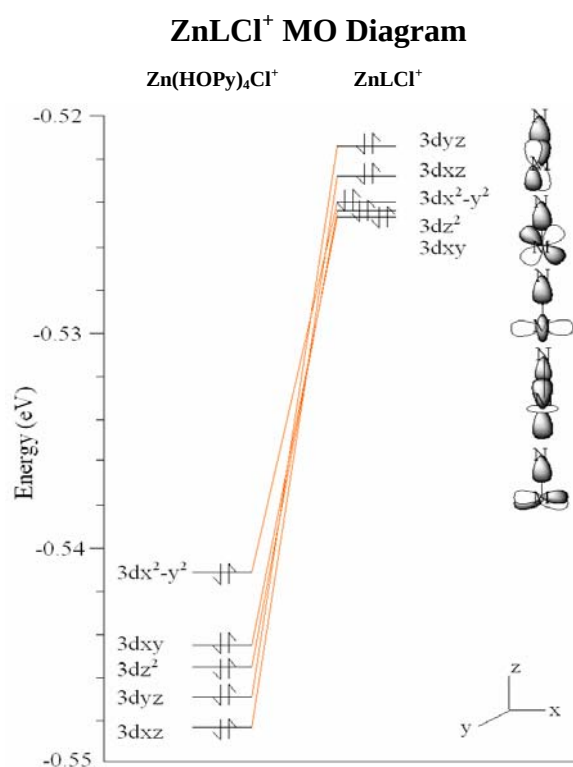
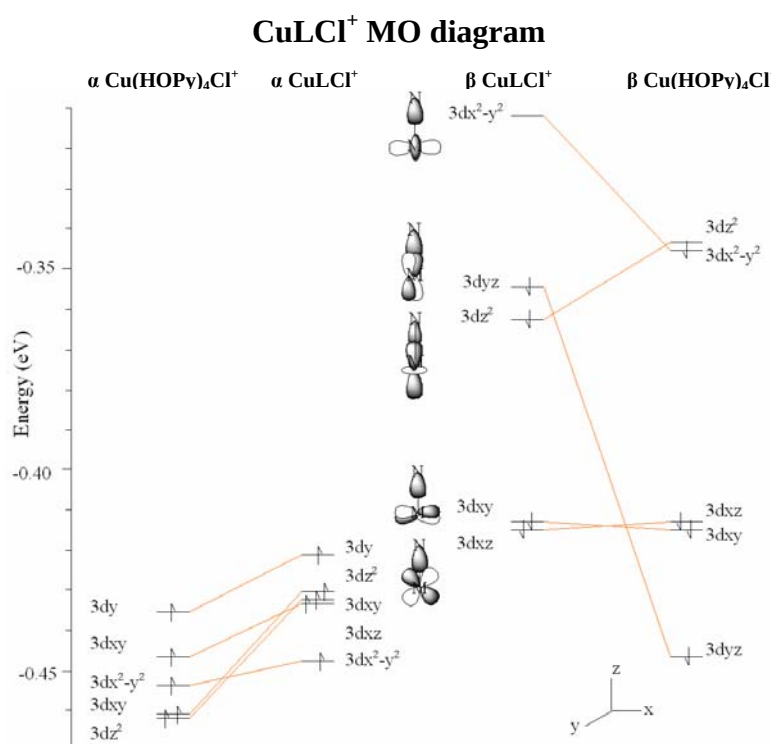


Figure 3.2.3 CuLCl⁺ and ZnLCl⁺ MO diagrams comparing the metal orbitals with and without the phosphazene bound.

From these MO diagrams (Figures 3.2.2 and 3.2.3) it can be seen that the βd_z^2 orbital is drastically lowered in energy, compared to its unbound state for the copper, cobalt and nickel complexes. The nickel and cobalt complexes have more vacancies in the d orbitals; therefore, they are able to accommodate bonding from the $\beta 3d_{x^2-y^2}$ orbital. As

expected, the zinc has a fully occupied 3d orbital set and all the orbitals increase in energy as electron density cannot flow from the ligand to the metal ion. However, it can still be observed that the $\beta 3d_z^2$ orbital increases in energy (with the exception of the $\beta 3d_{xy}$ orbital) less than the other orbitals. The occupancy of the $\beta 3d_z^2$ orbitals confirms that it is involved in the bonding (as shown in Table 3.2.1). It should be noted that the metal ions that have less occupancy in the d orbitals, have larger changes in the d_z^2 orbital occupancy as d_z^2 can accommodate more electron density.

Table 3.2.1 The occupancy change of $\beta 3d_z^2$ without and with the phosphazene attached.

Complex	Without phosphazene	With phosphazene	Difference
ZnLCl ⁺	1.98	1.99	0.01
CuLCl ⁺	0.71	0.82	0.11
NiLCl ⁺	0.11	0.74	0.63
CoLCl ⁺	0.11	0.76	0.65

Table 3.2.1 shows that there is an increase in the orbital occupancy once the metal binds to the phosphazene and this is proportional to the vacancies in the d orbitals. Cobalt is able to accommodate additional electron density, compared to copper or zinc, explaining the large difference in occupancy. The orbital responsible for this bonding, which is shown in Figure 3.2.4, would be classed as σ bonding. The σ bond is found for the cobalt, nickel, and copper complexes. Zinc forms a σ bond but as its d orbitals are fully occupied the resulting orbital is different from the other metals and this is reflected in the AO coefficients (see Table 3.2.2).

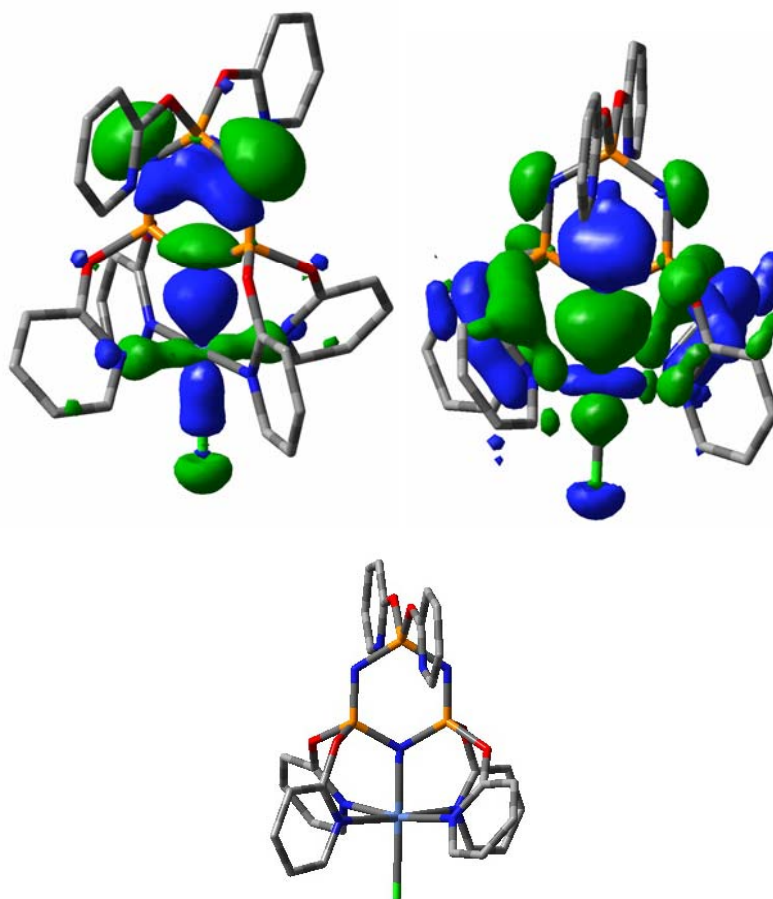


Figure 3.2.4 Left: the metal bonding orbital for CoLCl^+ , NiLCl^+ , and CuLCl^+ . Right: the metal bonding orbital for ZnLCl^+ .

Table 3.2.2 Molecular orbital coefficients for the M-N bond.

Contributing orbitals	Atomic orbital coefficients			
	CoLCl^+	NiLCl^+	CuLCl^+	ZnLCl^+
N($2p_z$)	0.2882	0.2663	0.2594	-0.2291
N(3S)	0.0031	0.0016	-0.0181	0.1097
N($3p_z$)	0.2273	0.2214	0.2254	-0.2028
M($3d_{z^2}$)	-0.1477	-0.1279	-0.2226	0.3740
M($3d_{y^2}$)	0.0533	-0.0188	0.0658	-0.1199
M($3d_{x^2}$)	0.0923	0.1464	0.1561	-0.2534
M($4d_{z^2}$)	-0.1050	-0.0893	-0.1500	0.2226
M($4d_{x^2}$)	0.0382	-0.0046	0.0449	-0.0625
M($4d_{y^2}$)	0.0643	0.0986	0.1018	-0.1411

Comparing the orbital coefficients (Table 3.2.2) shows there is always a significant contribution from the d_{z^2} orbitals but there are also contributions from d_{x^2} but little from

the d_y^2 , thus resulting in the distortion of a pure d_z^2 orbital. This occurs, because while the d_z^2 orbital is shifted down in energy, the energy difference between the d_z^2 and $d_{x^2-y^2}$ is small, resulting in a mixing of the orbitals. The key point is that it is the e_g orbitals rather than the t_{2g} orbitals involved in the bonding.

Zinc does not fit the behaviour of the other metals. The $ZnLCl^+$ complex was purely a theoretical one used for comparison. Because of its 3d orbitals being fully occupied it has significant contributions from all of the e_g orbitals.

It should also be noted that it is predominantly the p_z orbital from the phosphazene ring nitrogen contributing to the bonding orbitals with small contributions from the p_x and 3s orbitals.

3.3 In-plane Five-coordinate Species

For all of the in-plane five-coordinate species the metal is in a local C_{2v} geometry with the metal centre bound to the ring nitrogen, coplanar with the phosphazene ring (see Figure 3.3.1).

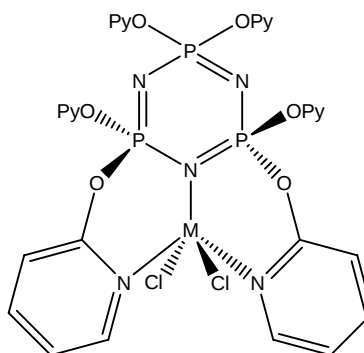


Figure 3.3.1 Example of in-plane five-coordinate species geometry.

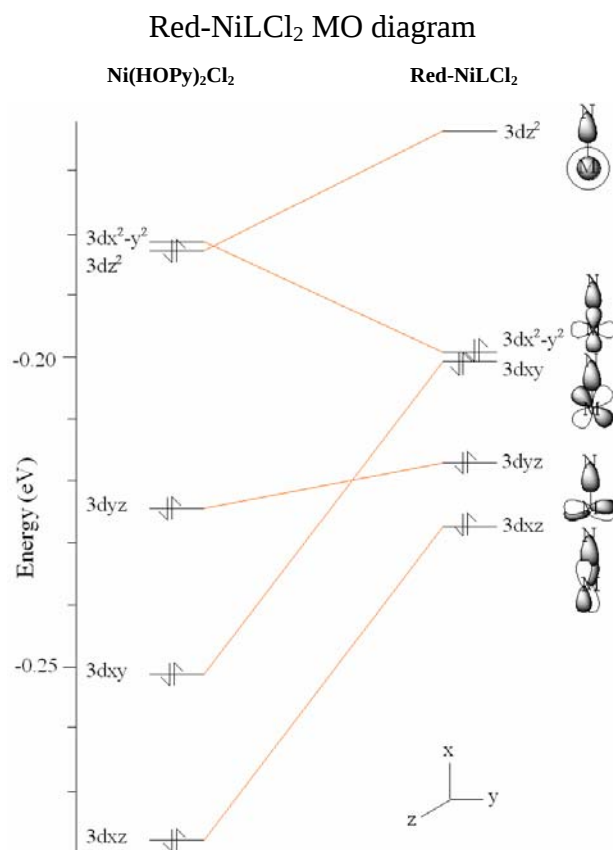
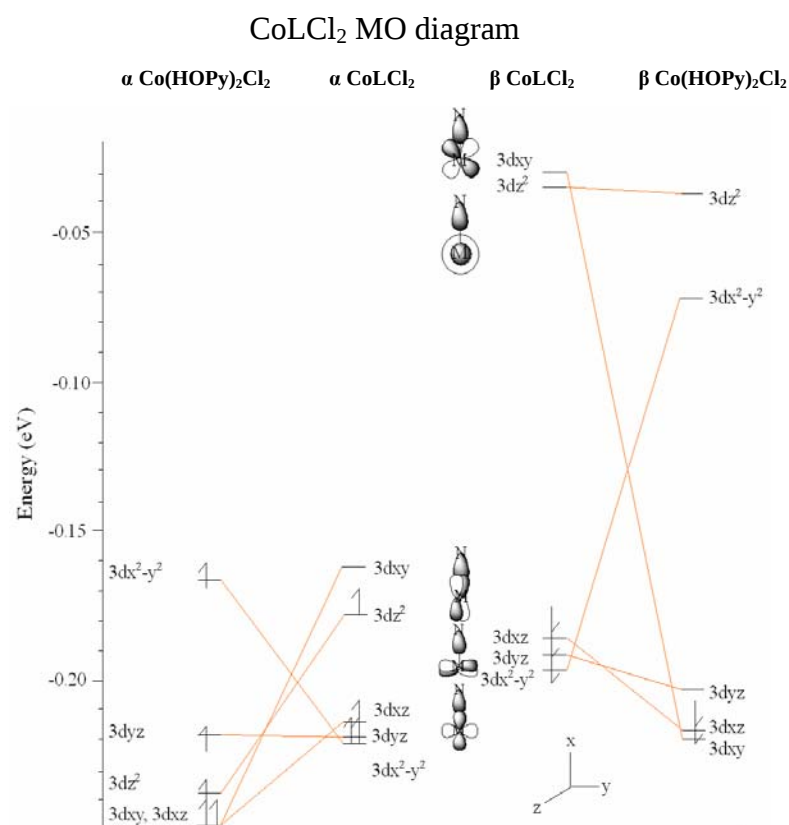


Figure 3.3.2 CoLCl₂ and Red-NiLCl₂ MO diagrams comparing the metal orbitals with and without the phosphazene bound.

ZnLCl₂ MO diagram

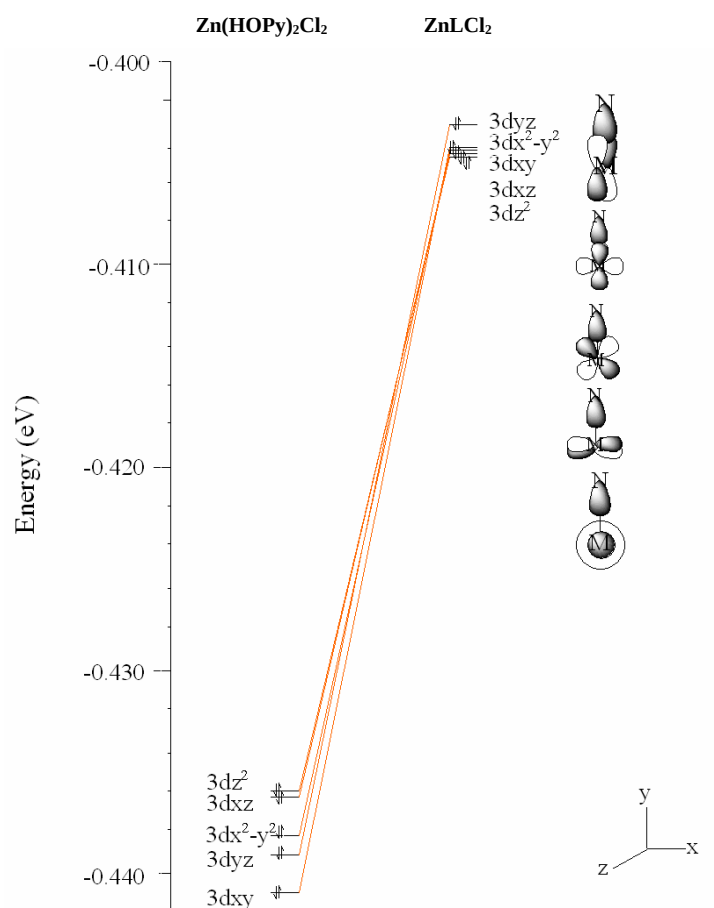


Figure 3.3.3 ZnLCl_2 MO diagrams comparing the metal orbitals with and without the phosphazene bound.

In these species, the $\beta 3d_{x^2-y^2}$ orbital is the primary bonding orbital, as shown by its decrease in energy (Figures 3.3.2 and 3.3.3). This is because the $\beta 3d_z$ orbital interacts in an axial fashion with the two pyridine groups, thus causing the $\beta 3d_{x^2-y^2}$ to be favoured for bonding to the phosphazene nitrogen. Once again, this is reflected in the occupancy increase of the $\beta 3d_{x^2-y^2}$ orbital (Table 3.3.1).

Table 3.3.1 Occupancy of the $\beta 3d_{x^2-y^2}$ orbital for in-plane 5-coordinate species

Complex	Without phosphazene	With phosphazene	Difference
CoLCl_2	0.22	0.95	0.72
Red-NiLCl_2	0.65	0.98	0.32
ZnLCl_2	0.99	0.99	0.00

The effects of the vacant orbitals are much more apparent for cobalt since it is able to accommodate more electron density in the $\beta 3d_{x^2-y^2}$ orbital than nickel or zinc. However,

it is reassuring that the $\beta 3d_{x^2-y^2}$ orbital is participating to the greatest extent forming a σ bond with the ring nitrogen as shown in Figure 3.3.4.

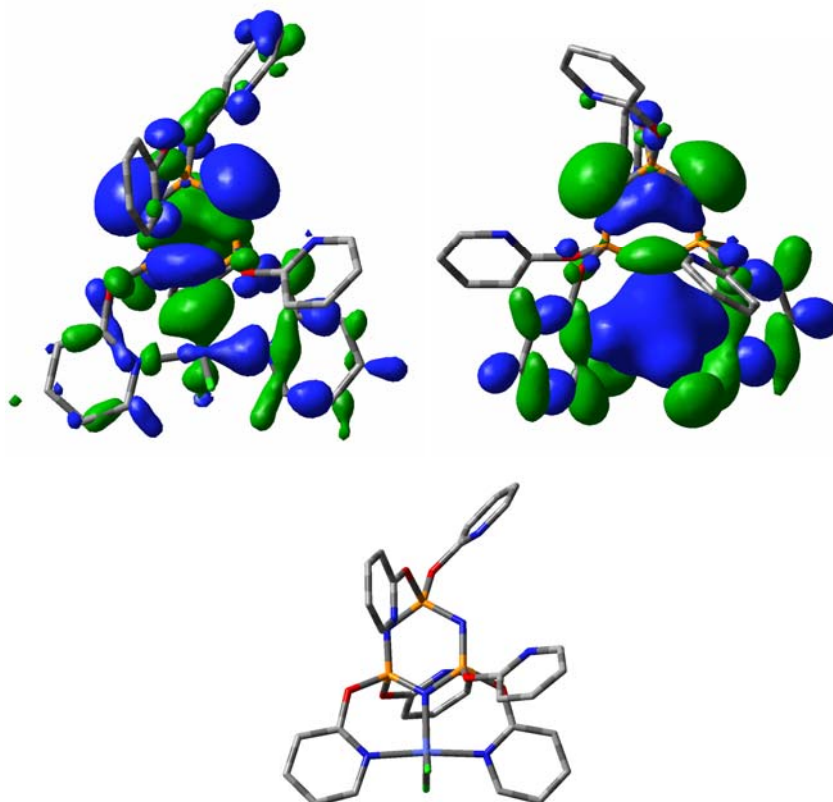


Figure 3.3.4 Left: CoLCl_2 and Red-NiLCl_2 metal bonding orbital. Right: ZnLCl_2 metal bonding orbital.

Table 3.3.2 Molecular orbital coefficients

Atomic Orbitals	Complexes MO coefficients		
	CoLCl_2	Red-NiLCl_2	ZnLCl_2
$\text{N}(1)(2p_x)$	0.2742	0.2457	-0.1534
$\text{N}(1)(2p_z)$	-0.0583	-0.1196	-0.0264
$\text{N}(1)(3p_x)$	0.2177	0.2106	-0.1130
$\text{M}(3s)$	0.0352	0.0372	-0.1111
$\text{M}(4s)$	-0.0571	-0.0554	0.2239
$\text{M}(3d_{z^2})$	0.0814	0.1401	-0.0100
$\text{M}(3d_{y^2})$	0.0496	-0.0451	0.0037
$\text{M}(3d_{x^2})$	-0.1290	-0.0940	0.0020
$\text{M}(4d_{z^2})$	0.0600	0.0917	-0.0159
$\text{M}(4d_{y^2})$	0.0345	-0.0251	-0.0091
$\text{M}(4d_{x^2})$	-0.0852	-0.0568	-0.0100

The atomic orbitals for the σ bond contain predominately $\beta 3d_{x^2-y^2}$ character (see Table 3.3.2) although the coefficients are much smaller than for the six-coordinate in-plane species. There are several of these weakly σ bonding orbitals that make up for the low coefficients. There is still a small contribution from the d_{z^2} orbital because of the orbitals remaining close in energy.

3.4 Out-of-plane Trimer Species

The out-of-plane trimer species do not fit any specific structure-the only common feature is that the metal ion is out-of-plane with the phosphazene ring. The CuLCl_2 complex has the copper ion held in five-coordinate geometry with the copper held 25° out of plane but still forms a bond to the ring nitrogen. The Green- NiLCl_2 complex has the nickel ion held in an octahedral geometry coordinating to only three of the pyridine groups, which results in it being bound to the ring nitrogen 12° out of plane (see Figure 3.4.1).

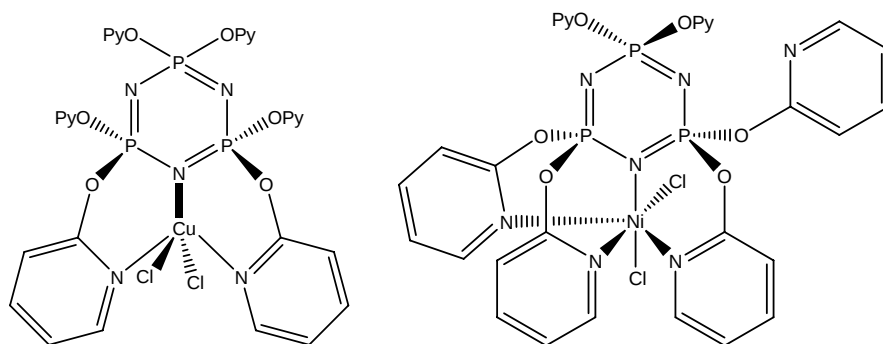


Figure 3.4.1 Structures of the out-of-plane complexes. Left: CuLCl_2 Right: Green- NiLCl_2

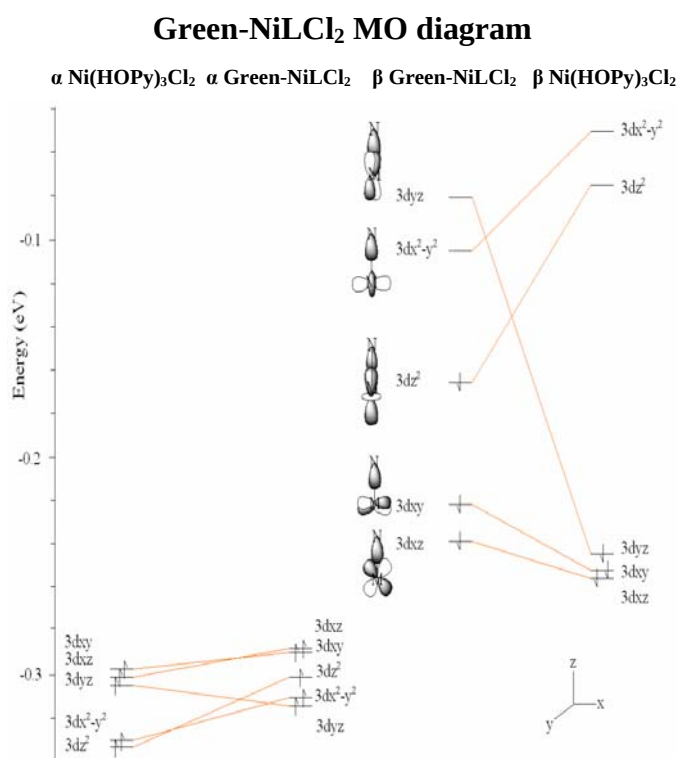
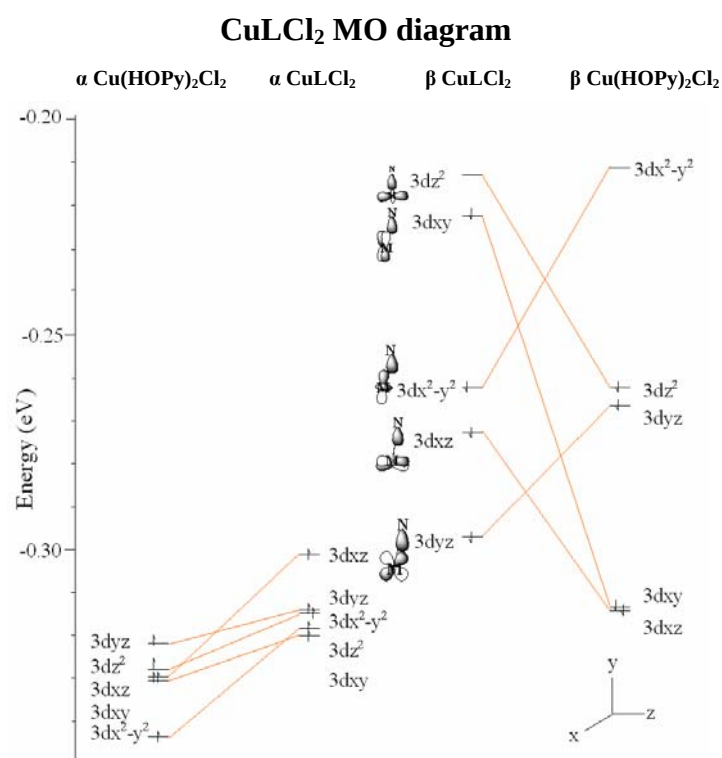


Figure 3.4.2 CuLCl₂ and Green-NiLCl₂ MO diagrams.

Hence, for Green-NiLCl₂ (Figure 3.4.2), the result is that the bonding is a combination of that observed for the in-plane five-coordinate and in-plane six-coordinate species. This means that the $\beta 3d_{z^2}$ and $\beta 3d_{x^2-y^2}$ orbitals are strongly involved in bonding. Because of the metal just being shifted enough to reduce the out-of-phase interactions, the $\beta 3d_{x^2-y^2}$ orbital is able to contribute to the bonding without greatly affecting the

direct overlap of the $\beta 3d_z^2$ orbital thus maintaining the σ bond. For the CuLCl_2 complex (Figure 3.4.2) the metal ion is 25° out-of-plane so, while it forms a σ bond with the $\beta 3d_z^2$ orbital, it is strained so the bond also contains $\beta 3d_{x^2-y^2}$ character (Figure 3.4.3) as a result of this distortion. CuLCl_2 also has another weak bonding mode - a π like bond using the $\beta 3d_{yz}$ orbital (Figure 3.4.3). However, in both cases it is the nitrogen lone pair providing a large amount of the bonding character.

Table 3.4.1 Comparison of 3d orbital occupancy with and without the phosphazene attached for CuLCl_2 .

$\beta 3d_{x^2-y^2}$		$\beta 3d_z^2$		$\beta 3d_{yz}$	
Without phosphazene	With phosphazene	Without phosphazene	With phosphazene	Without phosphazene	With phosphazene
0.58	0.86	0.82	0.69	0.86	0.98

The orbital occupancies (Table 3.4.1) confirm what the MO diagram shows, i.e. the $\beta 3d_{x^2-y^2}$ and $\beta 3d_{yz}$ orbitals (Figure 3.4.3) both become far more populated when bound to the phosphazene, but the $\beta 3d_z^2$ orbital still has a reasonable occupancy and therefore can still be involved in bonding which is reflected by its relatively large coefficient in Table 3.4.2.

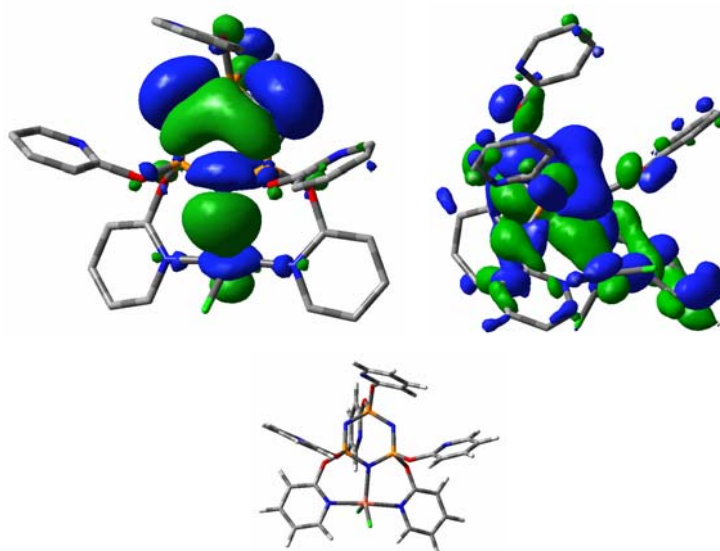


Figure 3.4.3 CuLCl_2 metal bonding orbitals Left: $\beta 182$, Right $\beta 180$.

Table 3.4.2 Atomic orbital coefficients for CuLCl₂.

Atomic orbital	Molecular Orbital Coefficients	
	β_{182}	β_{180}
N(2P _x)	-0.1993	0.1500
N(2P _y)	0.1028	-0.0742
N(2P _z)	0.1641	0.1233
N(3P _x)	-0.1911	0.1256
N(3P _z)	0.1257	0.0816
Cu(3d _{x²})	-0.1873	0.1148
Cu(3d _{y²})	0.0371	-0.0713
Cu(3d _{z²})	0.1490	-0.0429
Cu(3d _{xy})	0.1841	-0.0784
Cu(3d _{xz})	0.0879	-0.0803
Cu(3d _{yz})	-0.0319	0.1393
Cu(4d _{x²})	-0.1161	0.0697
Cu(4d _{y²})	0.0210	-0.0448
Cu(4d _{z²})	0.0882	-0.0251
Cu(4d _{xy})	0.1124	-0.0491
Cu(4d _{xz})	0.0528	-0.0496

The energy difference for the metal orbitals is much larger for Green-NiLCl₂ than for CuLCl₂ and as a result the nickel forms two bonding orbitals, one with more pure d_{z²} character and the other with more pure d_{x²-y²} character with negligible contributions from the t_{2g} orbitals. The occupancy (Table 3.4.3) shows a large increase for both e_g orbitals which fits the large change in energy.

Table 3.4.3 Comparison of d orbital occupancy with and without the phosphazene attached for Green-NiLCl₂.

$\beta 3d_{x^2-y^2}$		$\beta 3d_{z^2}$	
Without phosphazene	With phosphazene	Without phosphazene	With phosphazene
0.1472	0.4014	0.1754	0.6540

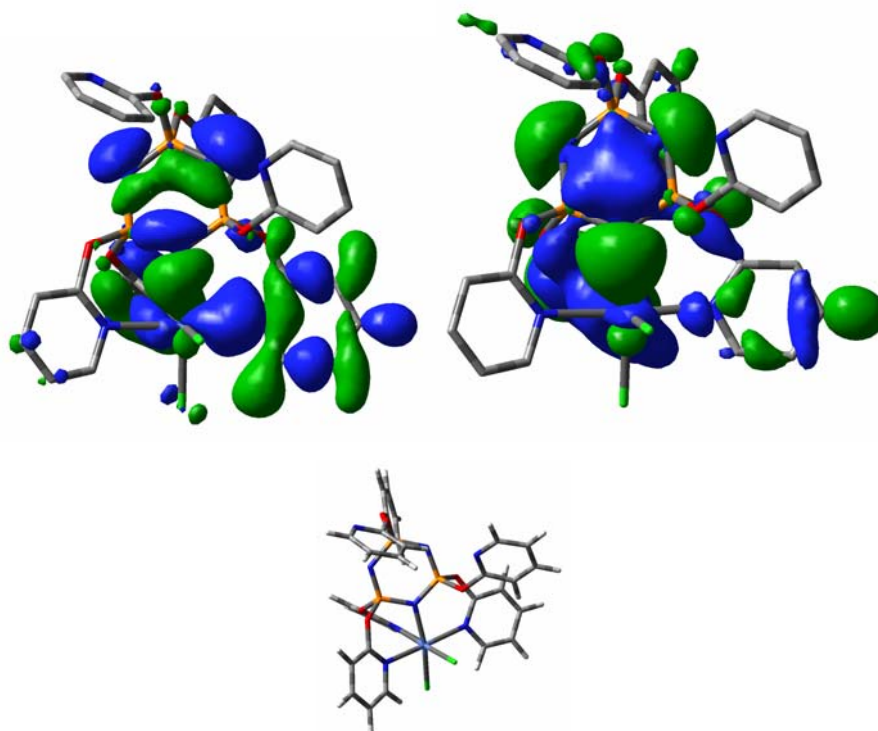


Figure 3.4.4 Green-NiLCl₂ bonding orbitals Left: 183β, Right:155α.

Table 3.4.3 Molecular Orbital coefficients for the Green-NiLCl₂ bonding orbitals.

Atomic Orbitals	Atomic orbital coefficients	
	155 α	183 β
N(2P _z)	0.1652	0.2092
N(2P _y)	-0.1095	-0.0604
N(3s)	0.2155	0.0768
N(3P _z)	0.1254	0.1818
Ni(3d _{z²})	0.1513	0.0645
Ni(3d _{y²})	-0.0803	0.0318
Ni(3d _{x²})	-0.0712	-0.0970
Ni(4d _{z²})	0.0916	0.0473
Ni(4d _{y²})	-0.0459	0.0192
Ni(4d _{x²})	-0.0405	-0.0664

In the orbital plots and the atomic coefficients (Table 3.4.3), it can be seen that the d_{x²-y²} contributions are much smaller than the d_{z²} orbitals for either of the orbitals. This is consistent with the MO diagram and orbital occupancies, the β 3d_{z²} being lower in energy and higher in occupancy than the β 3d_{x²-y²} orbitals.

3.5 Dimetal Trimer Species

The dimetal trimer species refers to a complex where two metal ions coordinate to the phosphazene ring (see Figure 3.5.1). In this example, the copper ions are coordinated with identical symmetry in a trigonal bipyramidal geometry with the metal centres held 28° out of plane with the phosphazene ring.

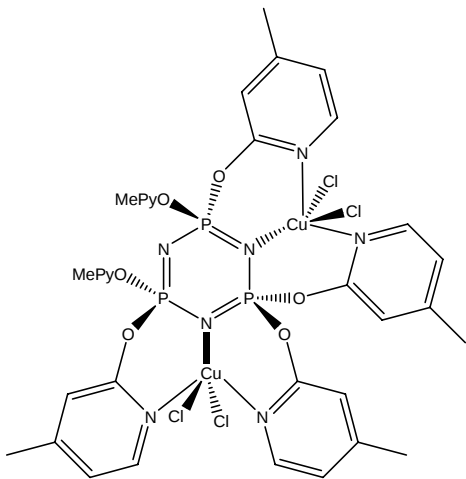


Figure 3.5.1 $\text{Cu}_2\text{LMeCl}_4$ geometry.

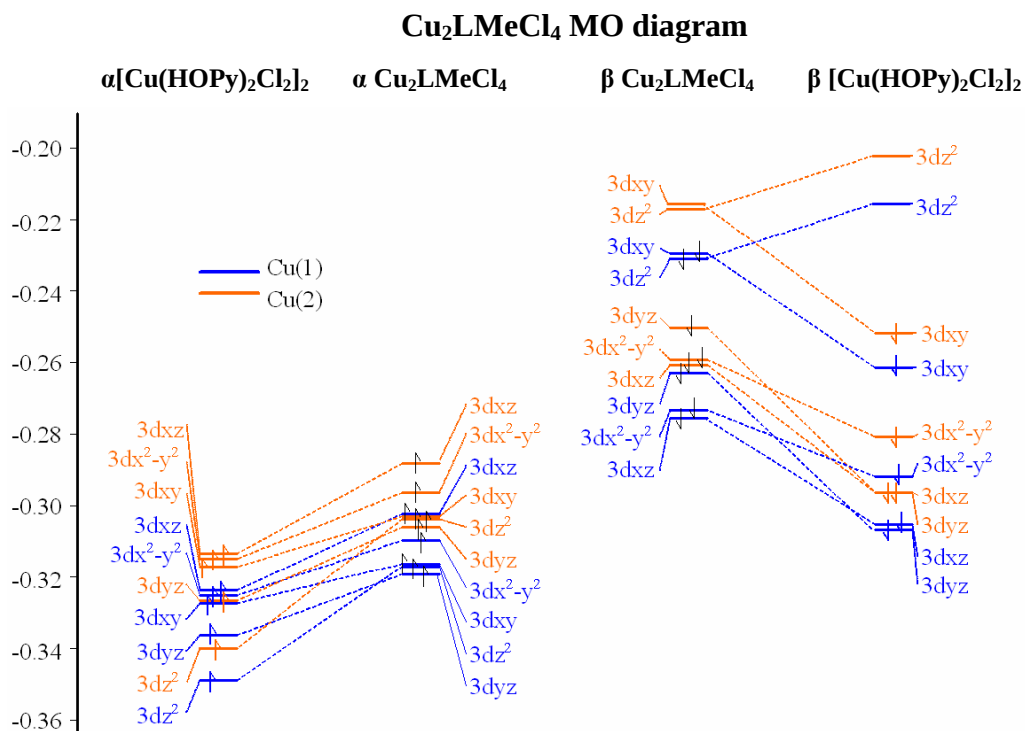


Figure 3.5.2 $\text{Cu}_2\text{LMeCl}_4$ MO diagram.

One of the copper orbitals has been shifted in energy relative to the other copper orbital, however, the shifting between orbitals remains the same. The $\beta 3d_z^2$ orbital has been shifted down (typical behaviour of a simple σ donor), however, as the $\beta 3d_z^2$ orbital was

only slightly shifted the $\beta 3d_{x^2-y^2}$ still has enough occupancy to contribute to the bonding. The occupancy of the orbitals also reflects the shifted $\beta 3d_{x^2-y^2}$ orbital, by the decrease in occupancy and the slight increase in $\beta 3d_z^2$ occupancy (Table 3.5.1). It should be noted that these changes are very small and both orbitals still have enough occupancy to contribute significantly to the bonding.

Table 3.5.1 Occupancy changes for the $\beta 3d_{x^2-y^2}$ and $\beta 3d_z^2$ orbitals.

Copper	$\beta 3d_{x^2-y^2}$			$\beta 3d_z^2$		
	Without Phosphazene	With Phosphazene	Difference	Without Phosphazene	With Phosphazene	Difference
1	0.93	0.92	-0.01	0.57	0.74	0.16
2	0.93	0.91	-0.01	0.56	0.73	0.17

The σ bonding orbital found for $\text{Cu}_2\text{LMeCl}_4$ (Figure 3.5.3) is similar to the CuLCl_2 bonding orbital. While it appears to be $d_{x^2-y^2}$ in character, it is mostly d_z^2 with contributions from d_{xy} and d_{xz} . As in CuLCl_2 , the metal centres are far enough out of ring-plane so that the t_{2g} orbitals are able to contribute to the bonding.

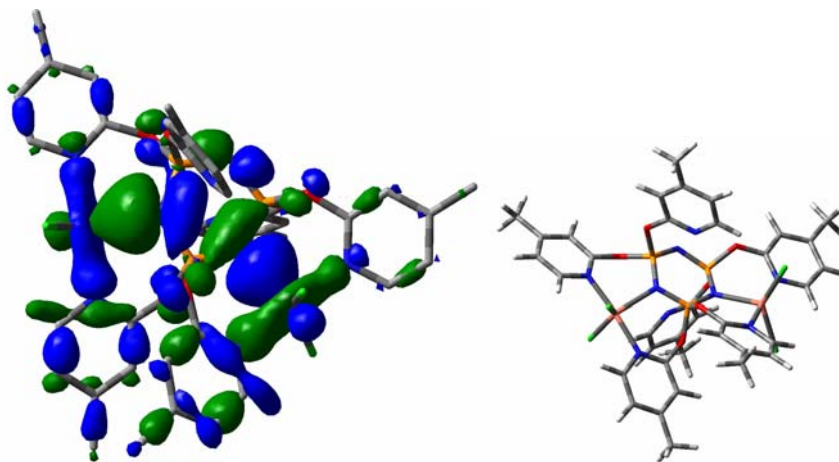


Figure 3.5.3 Metal bonding orbital of $\text{Cu}_2\text{LMeCl}_4$.

Table 3.5.2 Atomic orbital coefficients contributing to the bonding orbitals

Atomic Coefficients	Bonding orbital
Cu(1)(3d _{x²})	0.0305
Cu(1)(3d _{y²})	-0.1018
Cu(1)(3d _{xy})	0.1282
Cu(1)(3d _{xz})	0.0547
Cu(1)(4d _{xy})	0.0753
N(1)(2P _x)	-0.0745
N(1)(3s)	0.1182
N(1)(3P _x)	-0.0550
Cu(2)(3d _{x²})	0.0306
Cu(2)(3d _{y²})	-0.1022
Cu(2)(3d _{xy})	-0.1283
Cu(2)(3d _{xz})	0.0560
Cu(2)(4d _{xy})	-0.0632
N(2)(2P _x)	0.0746
N(2)(3s)	0.1181
N(2)(3P _x)	0.0550

As before, it should be noted that the nitrogen part of the orbital still consists of some form of sp² hybrid. Table 3.5.2 showed that the 4d_{xy} coefficient sign of each of the copper ions were different, which is reflected by the alternating colours (representing the different phases) of the molecular orbital plot (see Figure 3.5.3). This suggests that the metal ions are influencing each other – to be discussed in Chapter 6.

3.6 Dimetal Tetramer Species

The tetramer species are better models for the phosphazene polymer⁶⁸, therefore two examples of the tetramer (Figure 3.6.1) were investigated, both with two metals coordinated. $\text{Cu}_2\text{LtetrCl}_2^{2+}$ has the copper ions bound co-planar with the phosphazene ring in identical C_{4v} environments with a bond to the phosphazene ring nitrogen. $\text{Cu}_2\text{LtetrCl}_4$ is used as a comparison since the copper ions are held in a strained square planar geometry with the metal centres held at 81° to the ring plane, but there are no signs of coordination of the metal to the phosphazene ring.

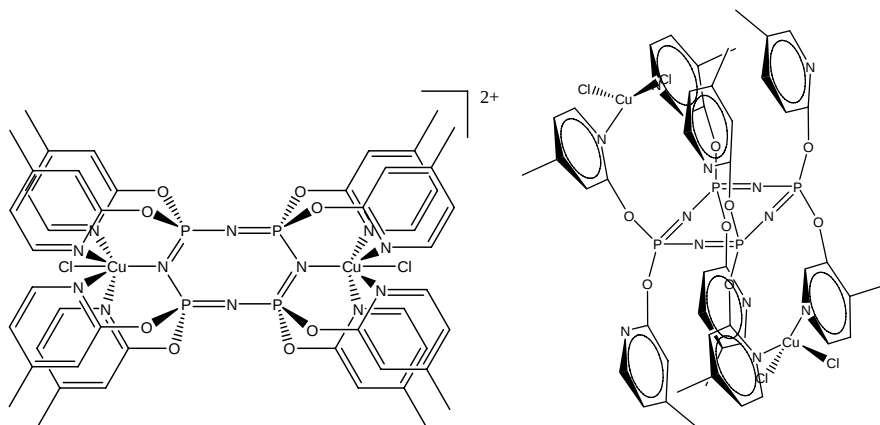


Figure 3.6.1 Dimetal Tetramer species Left: $\text{Cu}_2\text{LtetrCl}_2^{2+}$ Right: $\text{Cu}_2\text{LtetrCl}_4$ ⁵⁹.

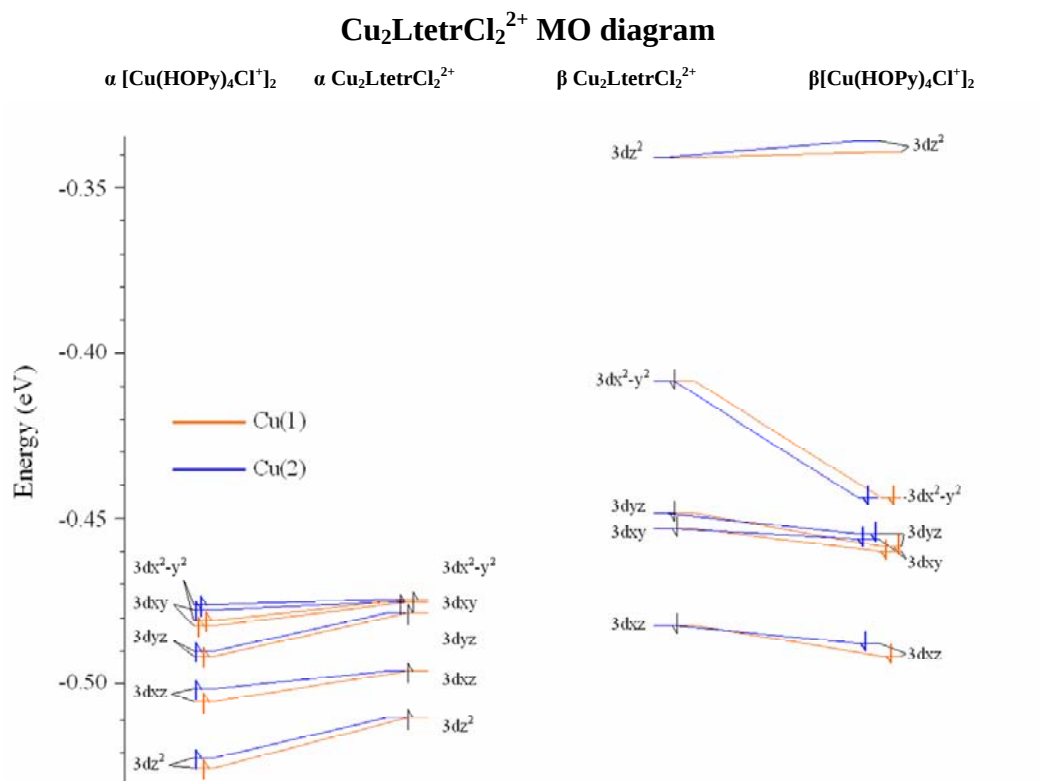


Figure 3.6.2 MO diagrams of $\text{Cu}_2\text{LtetrCl}_2^{2+}$.

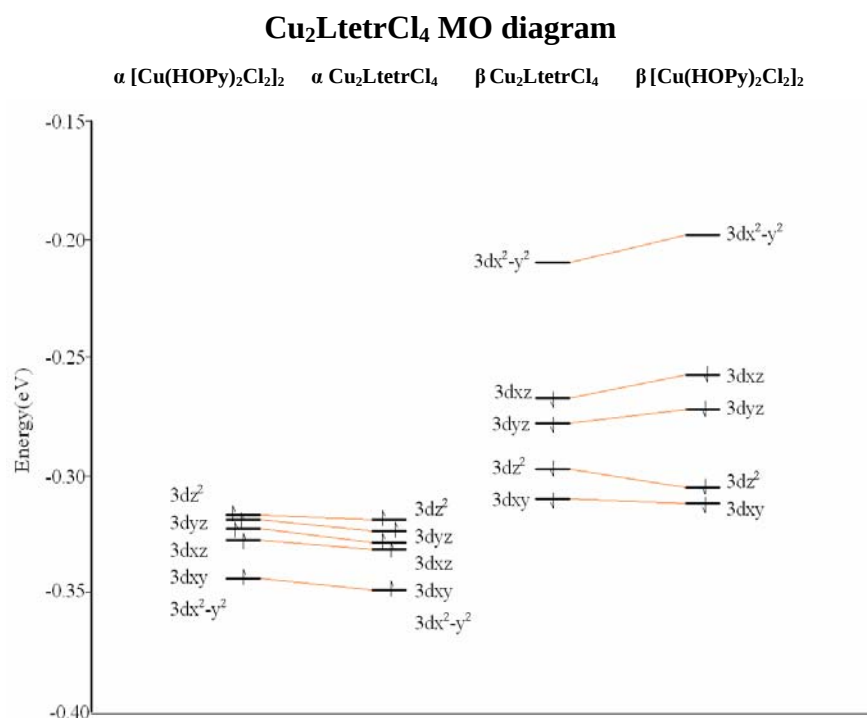


Figure 3.6.3 MO diagrams of Cu₂LtetrCl₄.

The Cu₂LtetrCl₂²⁺ MO diagram shows that there is only a slight decrease in the $\beta 3d_z^2$ orbital suggesting simple σ donor behaviour. The $\beta 3d_{x^2-y^2}$ orbital is still the lowest e_g orbital and therefore has a large occupancy (see Table 3.6.1) and significant contribution to the bonding (see Table 3.6.2). The Cu₂LtetrCl₄ MO diagram showed that despite the fact that there was no apparent bonding to the phosphazene, there was some small interaction resulting in the shifting of the d orbitals. This is reflected with the almost negligible change in the orbital occupancy (see Table 3.6.1)

Table 3.6.1 Occupancies of the $\beta 3d_{x^2-y^2}$ and $\beta 3d_z^2$

Complex	$\beta 3d_{x^2-y^2}$ orbital occupancy			$\beta 3d_z^2$ orbital occupancy		
	Without Phosphazene	With Phosphazene	Difference	Without Phosphazene	With Phosphazene	Difference
Cu ₂ LtetrCl ₂ ²⁺ (Cu 1)	0.9396	0.8137	-0.1259	0.3720	0.4613	0.0893
Cu ₂ LtetrCl ₂ ²⁺ (Cu 2)	0.9500	0.8156	-0.1374	0.3648	0.4600	0.0952
Cu ₂ LtetrCl ₄ (Cu 1)	0.5348	0.5548	0.0200	0.8967	0.9867	0.0890
Cu ₂ LtetrCl ₄ (Cu 2)	0.5348	0.5548	0.0200	0.8967	0.9867	0.0890

The bonding orbital for $\text{Cu}_2\text{LtetrCl}_2^{2+}$ shows both metals are in identical environments with the nitrogen orbitals consisting of mainly p_x character, possibly because of the square geometry of the tetramer as opposed to the hexagonal geometry of the trimer. The contributing metal orbital is the $\beta 3d_{x^2-y^2}$ as shown in Table 3.6.2. The lone-pair orbital of $\text{Cu}_2\text{LtetrCl}_4$ shows the nitrogen orbitals that are typically associated with metal bonding having no overlap with the copper ion orbitals. As expected from the negligible change in metal ion behaviour it would be reasonable to assume that the copper is not directly bonding to the phosphazene ring nitrogen at all.

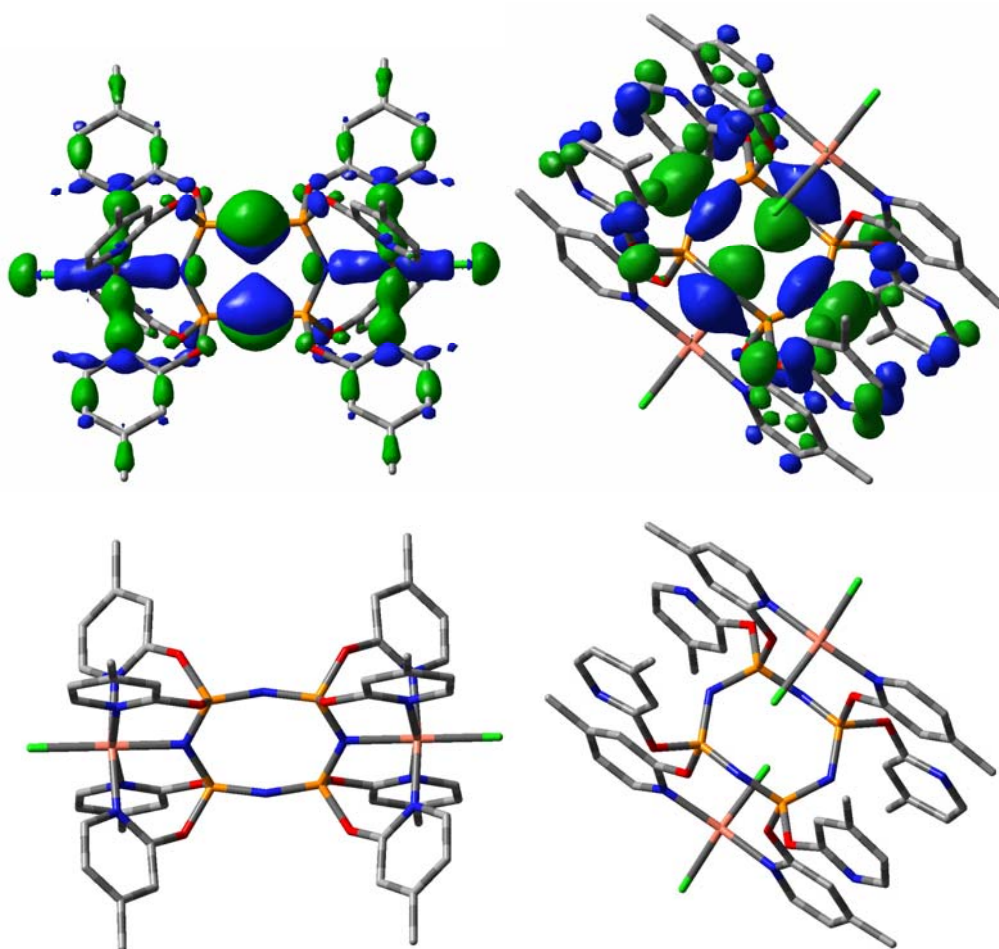


Figure 3.6.4 Orbital picture Right: $\text{Cu}_2\text{LtetrCl}_2^{2+}$ metal bonding orbital. Left: $\text{Cu}_2\text{LtetrCl}_4$ lone pair orbital.

Table 3.6.2 Molecular orbital coefficients

Atomic orbital	Atomic orbital Coefficients	
	$\text{Cu}_2\text{LtetrCl}_2^{2+}$	$\text{Cu}_2\text{LtetrCl}_4$
N(1)(3P _x)	0.103	0.0417
N(3)(3P _x)	-0.103	-0.0417
Cu(1)(4s)	0.101	0
Cu(1)(3d _{x²})	-0.212	0
Cu(1)(3d _{y²})	0.239	0
Cu(1)(4d _{x²})	-0.138	0
Cu(1)(4d _{y²})	0.141	0
Cu(2)(4s)	0.103	0
Cu(2)(3d _{x²})	-0.217	0
Cu(2)(3d _{y²})	0.245	0
Cu(2)(4d _{x²})	-0.141	0
Cu(2)(4d _{y²})	0.144	0

3.7 Collective Properties

The previous sections describe the effects on the metal d orbitals as the result of metal-coordination to the phosphazene. The behaviour found is typical of a simple σ donor and so with this information, it was possible to extend this study. By using the E_2 values, it is possible to estimate the strength of the M-N bonds (see Chapter 1) as shown in Figure 3.7.1.

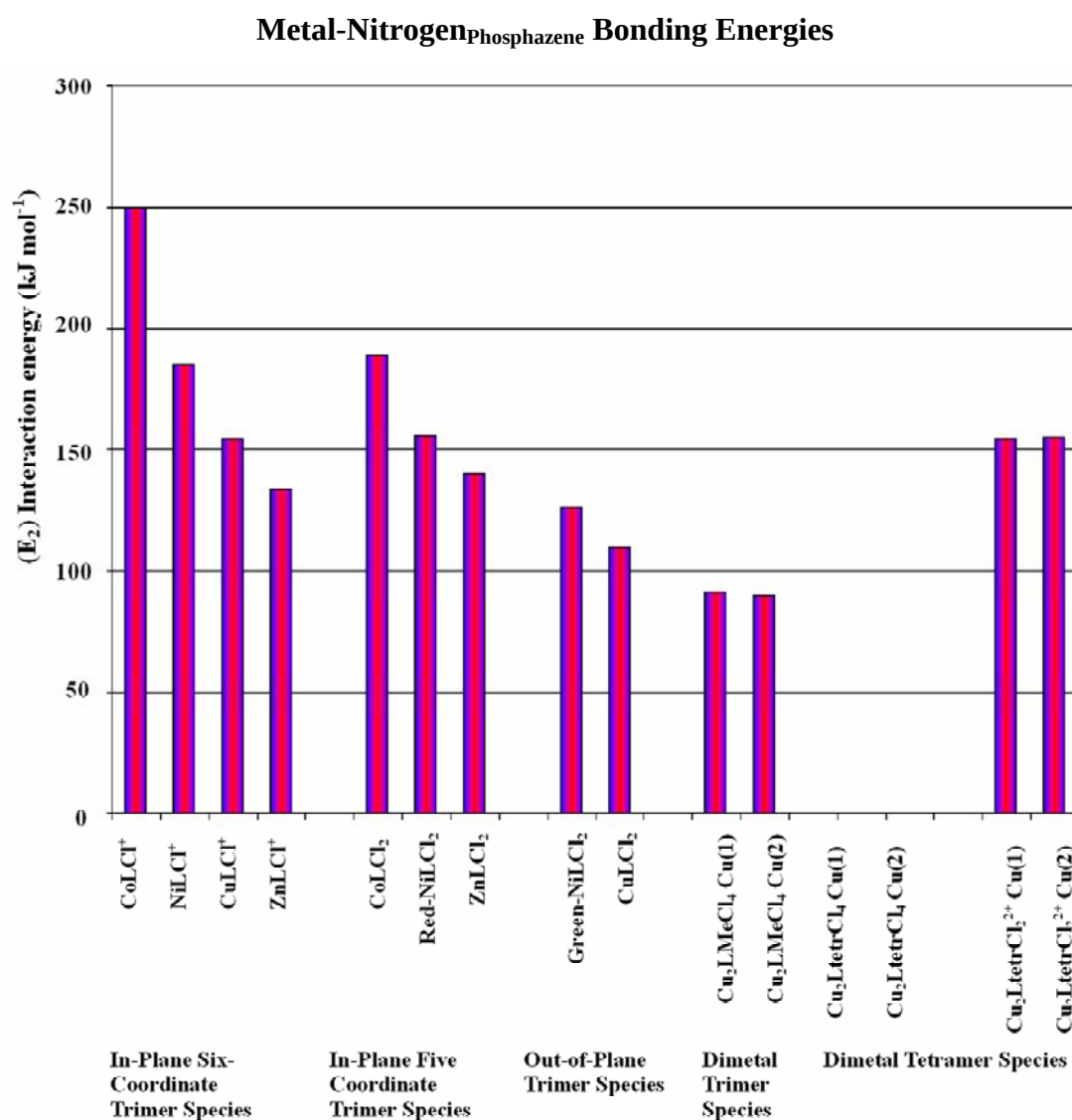


Figure 3.7.1 Metal-Nitrogen_{phosphazene} bonding energies

Figure 3.7.1 shows the metal in the six-coordinate complexes is bound much more strongly than in the five-coordinate species, and in the out-of-plane species the binding is weaker still. The Cu₂LMeCl₄ complex shows much weaker bonding than its single metal ion analogue (CuLCl₂) which is most likely due to the reduction of electron density in the phosphazene ring as a result of two metal ions binding. Cu₂LtetrCl₂²⁺

shows the same trend, with weaker bonds than its single copper analogue (CuLCl^+). $\text{Cu}_2\text{LtetrCl}_4$ shows no bonding to the phosphazene ring at all as expected from the previous results. The NBO E_2 interactions show which phosphazene orbitals donate to the metal ions. The electron donor orbital from the phosphazene can be regarded as a lone pair from the ring nitrogen, consisting of 33% s and 66% p character for the trimer and 23% s and 77% p character for the tetramer. Using Pauling's valence bond theory terminology, these could crudely be called sp^2 orbitals (see Figure 3.7.2). The tetramer orbital is not perfectly sp^2 as the result of a more linear geometry to the PN bond. When the metal bonds to the tetramer it takes on a more rectangular shape with the PNP angle of 128° as opposed to the trimer with an angle of 120° .

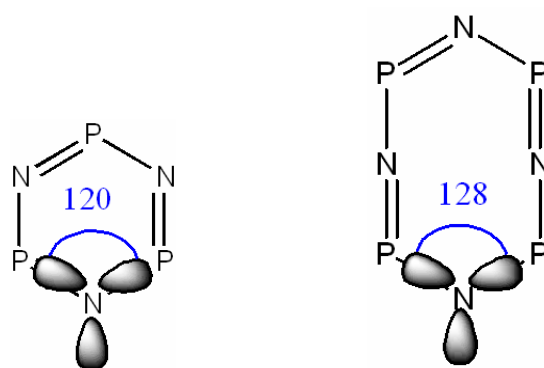


Figure 3.7.2 A schematic view of the phosphazene bonding orbital.

3.8 Conclusion

In this chapter we showed that the phosphazene is a simple σ donor ligand acting via the nitrogen's lone pair of electrons. Since the same result is found for the trimer and the tetramer, it is a reasonable assumption that the polymer also acts as a σ donor. The six-coordinate in-plane species have stronger bonding energies than the five-coordinate in-plane species, which are stronger than the out-of-plane species. When two metals bind to the same phosphazene ring the electron density is shared between the two metal centres resulting in the bonds being weaker than for the single metal analogues. The simple σ donor behaviour of phosphazene is consistent with the Chaplin³⁸ or ionic³⁶ bonding model, but provides no explanation why the flanking PN bonds lengthen - this will be discussed in Chapter 4.

Chapter 4 - Bond Lengthening of Flanking PN bonds

4.1 Introduction

A common feature observed when a metal coordinates to a phosphazene ring nitrogen is that the flanking PN bonds lengthen by 0.01-0.04 Å (see Figure 4.1.1).

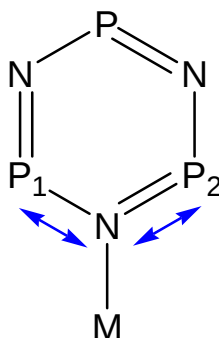


Figure 4.1.1 Schematic view of the bond lengthening.

This feature occurs in many different phosphazenes regardless of whether or not the phosphazene pendant substituents coordinate to the metal ion⁵¹⁻⁵⁶. It is therefore not a substituent effect but a feature of the phosphazene coordination.

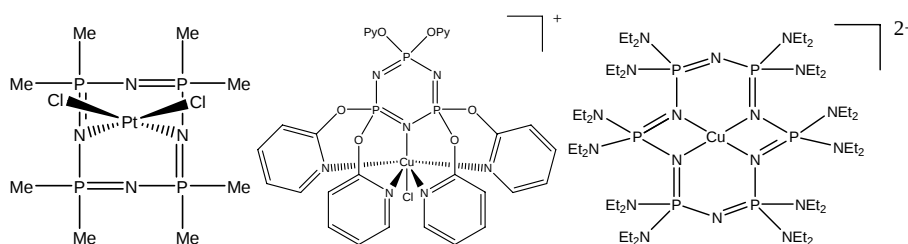


Figure 4.1.2 Examples of phosphazenes with known bond lengthening.

Paddock theorized that this was a result of electron density being removed from the PN bond via the 2p orbital on the ring nitrogen as it coordinates to the metal ion, resulting in the bond being weaker and therefore lengthening³²⁻³⁴. A similar principle was applied for the Dewar model³⁵ (see Figure 4.1.2).

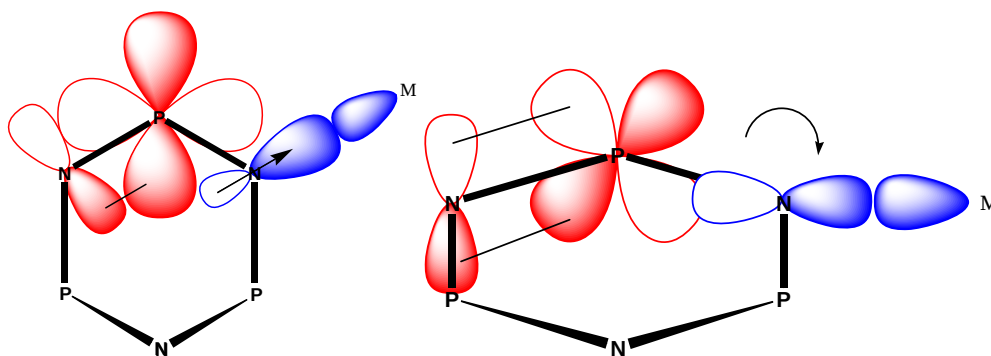


Figure 4.1.3 Right: The Paddock theory for bond lengthening. Left: Dewar theory for bond lengthening.

Both the Paddock³²⁻³⁴ and Dewar³⁵ models have since been disproven (as described in Chapter 1). The ionic model provided a different theory, the metal ion binding resulted in electron density being removed from the nitrogen making it less negatively charged therefore reducing the ionic bonding component in the ring hence resulting in weaker bonds. This theory remains valid as part of the Chaplin³⁸ model but metal binding could also effect the negative hyper-conjugation - this will be investigated in this chapter.

From the previous chapter, it was determined that the phosphazene is a simple σ donor, which is not consistent with either the Paddock or the Dewar model but can be explained in terms of the ionic or Chaplin model. In order to determine the reason for the bond lengthening, the flow of electron density to, or from, the PN bond must be determined. There are only two reasons that a bond will weaken and therefore lengthen, i) electron density is removed from the bonding orbitals or ii) electron density is being added to anti-bonding orbitals. NBO E_2 values determine if the PN bond acts as a donor or acceptor of electron density towards the metal ion. Once the direction of the electron flow is determined, the effect on the negative hyper-conjugation can be analysed. As the negative hyper-conjugation is responsible for the aromatic behaviour, changes in the aromaticity of the phosphazene will be a result of effects on the negative hyper-conjugation.

4.2 Interactions

In order to gauge which way the electron density is flowing, the E_2 values were examined to see if the PN bonds are acting as donors or acceptors and hence, whether the electron density is going to or coming from the flanking PN bonds.

The NBO E_2 values show there is an interaction of approximately 5-20 kJ mol⁻¹ resulting from the flanking PN bond donating electron density to the metal ion's 4s orbital for all of the complexes (see Figure 4.2.1). There is no significant electron donation from the metal ions to the PN bond. Therefore, the bond lengthening is a result of electron density being removed from the PN bonding orbital.

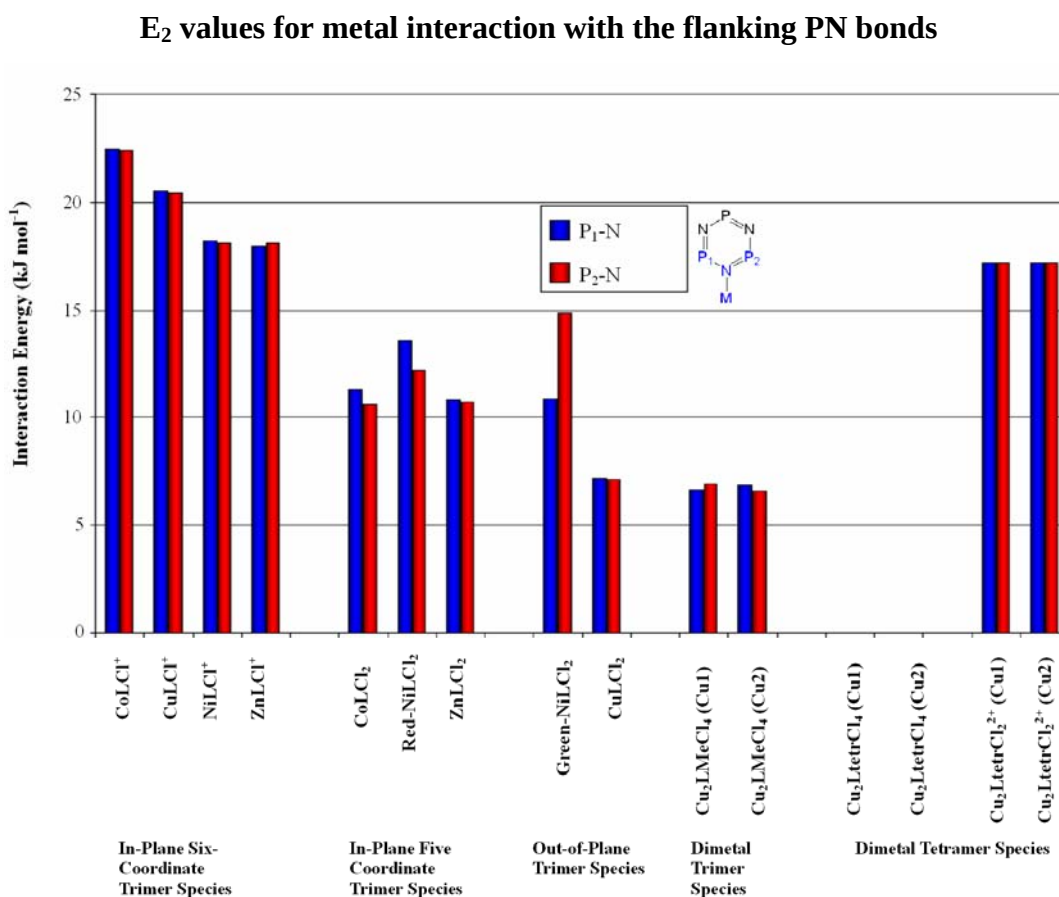


Figure 4.2.1 Comparison of the flanking PN bond interaction with the metal ion.

The interaction strength is much greater in the six-coordinate in-plane species than the five-coordinate in-plane species because of the metal ions being held closer to the flanking PN bonds. When the metal ion is moved away from the bonds, the interaction strength decreases proportionally for both a six-coordinate and five-coordinate species. For the dimetal species, the interaction strength is approximately the same as for their

single metal analogues, showing that the effect is dependent on the metal's ability to accommodate electron density and the distance of the metal ion from the flanking bonds. The distance dependence is displayed in Figures 4.2.2 and 4.2.3.

CuLCl_2

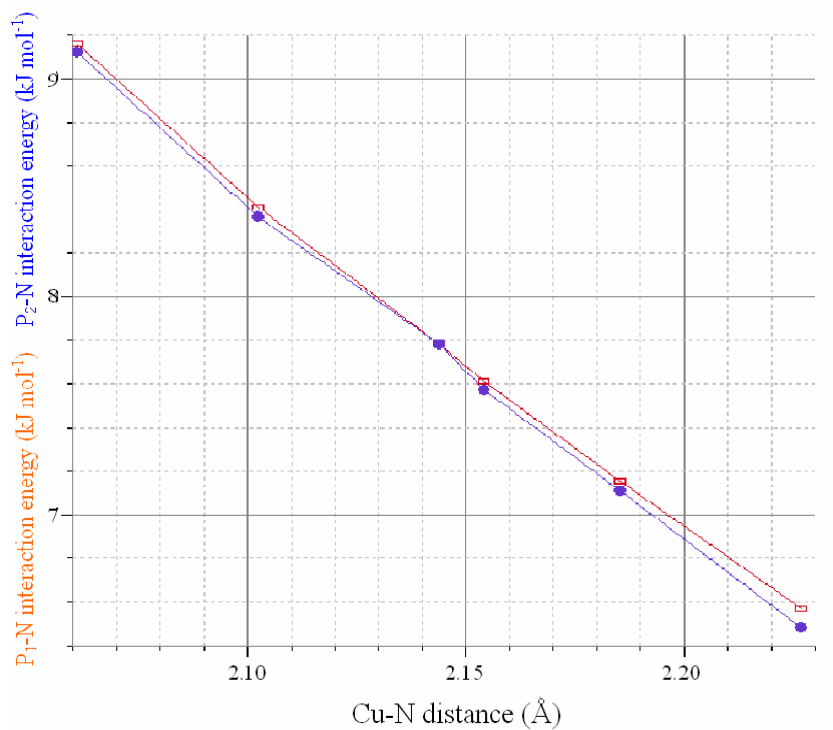


Figure 4.2.2 A comparison of metal nitrogen distance to interaction strength for CuLCl_2 .

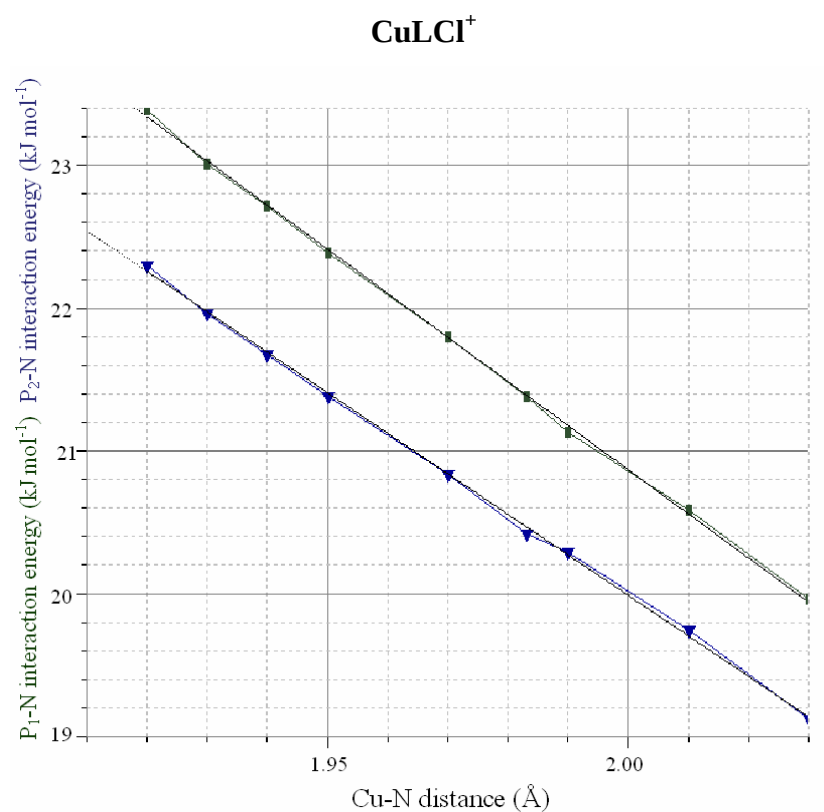


Figure 4.2.3 A comparison of metal nitrogen distance to interaction strength for CuLCl⁺.

Figures 4.2.2 and 4.2.3 show a linear relationship between the acceptor-donor interaction energy and the metal-ring nitrogen distance, confirming that the distance between the metal ion and the bonds has a large affect on the interaction, which would be the expected behavior for the 4s orbital over a short distance. The comparison between the six-coordinate in-plane and five-coordinate out-of-plane also shows that this behaviour is independent of the metal's geometry.

To provide evidence that this interaction is affecting the bonding of the phosphazene, a comparison of bond occupancy versus the interaction energy was made (see Figure 4.2.4).

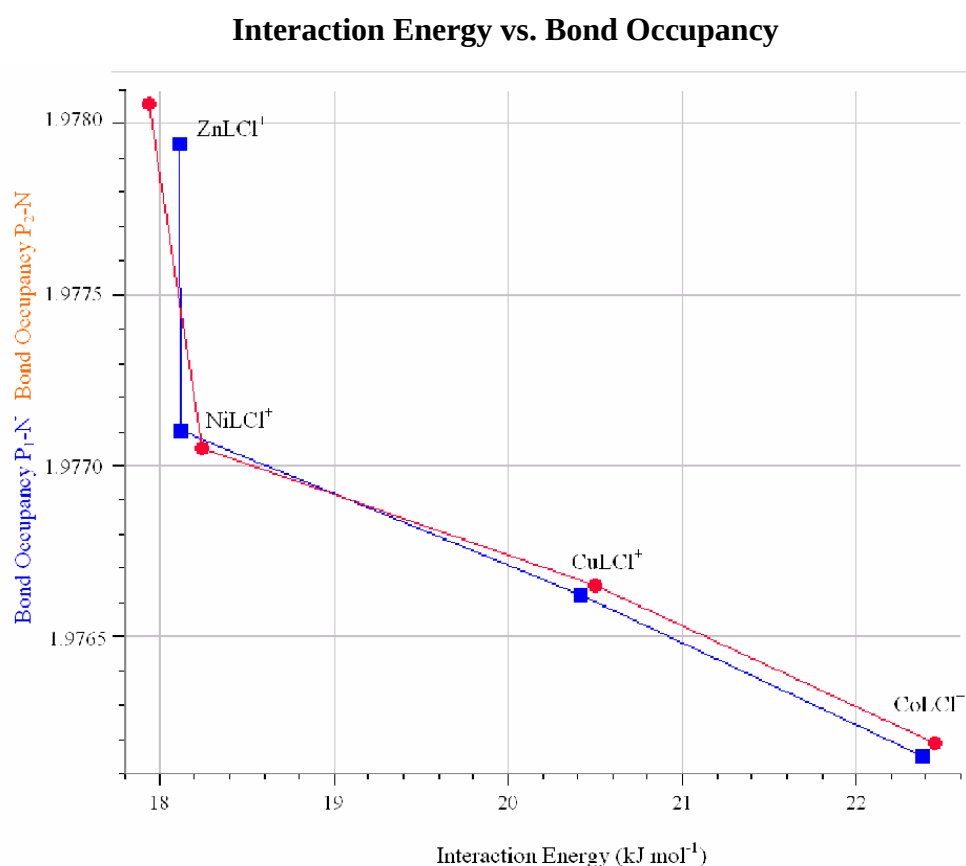


Figure 4.2.4 Interaction Energy vs. bond occupancy.

A linear relationship for nickel, copper and cobalt is clearly observed (see Figure 4.2.4) showing that for these complexes the bond occupancy is directly proportional to the interaction energy. Zinc is an outlier for this, which is most likely due to its filled 3d shell. Having a full 3d shell means that there will be higher occupancy in the 4s orbital which leaves less room for the PN bond electrons to go into. A direct relationship between the bond lengthening and the interaction was not found possibly due to substituent effects (to be discussed in Chapter 5). While the NBO E_2 values have shown the direction of electron flow, they are unable to determine whether the electron density is being removed from the ionic, σ or negative hyper-conjugation components of the PN bond.

4.3 Aromaticity Calculations

While the previous sections in this chapter have focused on the bond lengthening from the metal's point of view, this section approaches it from the phosphazene side. Despite the fact that the interaction responsible for bond lengthening has been identified it did not explain specifically which part of the bond was donating electron density to the 4s orbital of the metal. The electron density could be coming from the ionic part, negative hyper-conjugation part, or both. While the phosphazene bonding remains very complicated, it is still possible to get information about the bonding by measuring a collective property, in this case the aromaticity of the phosphazene ring. As the negative hyper-conjugation is responsible for all of the aromatic behaviour of the phosphazene, any changes in aromaticity are the result of changes to the negative hyper-conjugation.

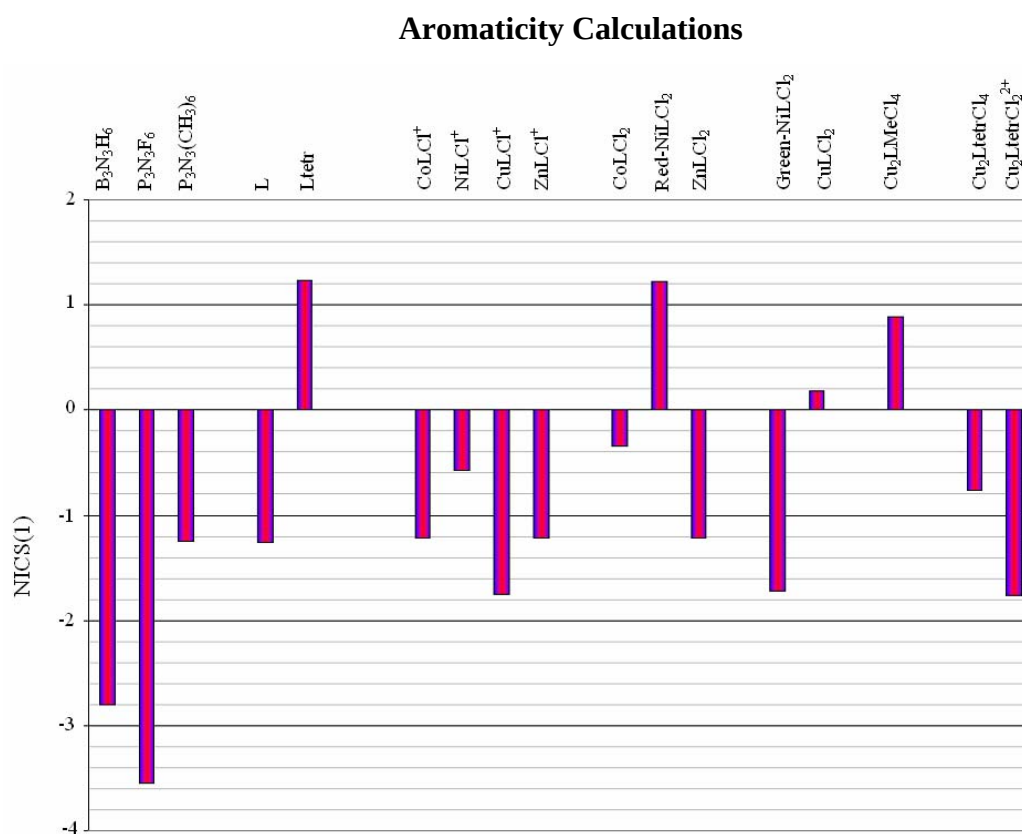


Figure 4.3.1 NICS(1) values for the complexes, free ligands and reference molecules.

As a method of confirming results, reference molecules were measured. The NICS(1) values were consistent with Chaplin's model i.e. strong electron-withdrawing groups increase the aromatic character of the phosphazene e.g. compare the NICS(1) P₃N₃F₆ (-3.5) to P₃N₃(CH₃)₆ (-1.23). This method has severe limitations in the presence of transition metals, as shifting of the ghost atom can occur directly because of the

magnetism of the metal. While these values may be affected by the transition metals, the free ligand results are not. The tetramer is far less aromatic (+1.2) than the trimer (-1.3) possibly a result of only having two pyridines interacting with a larger ring compared to the trimer (see Chapter 5).

To see if there was any relationship between the bonding of the metal to the phosphazene, a comparison was made between the aromaticity and the interaction between the PN bond and the 4s orbital of the metal ion.

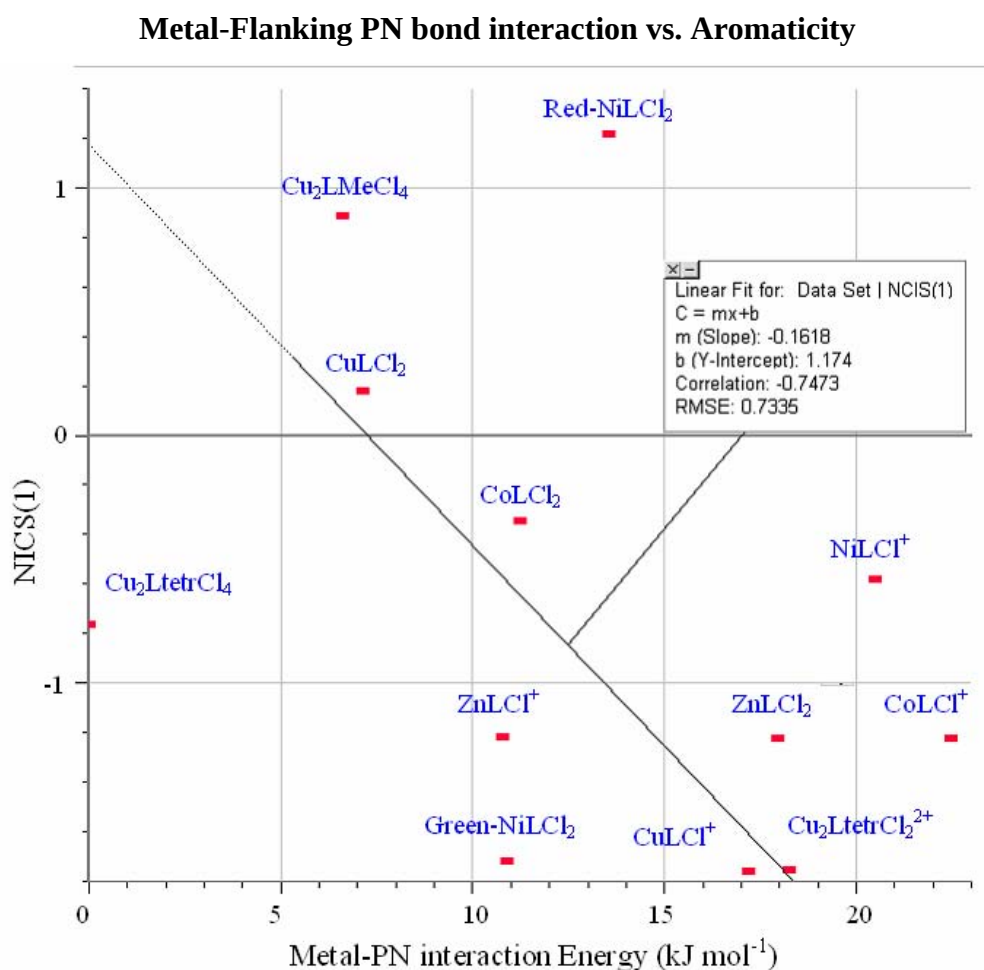


Figure 4.3.2 Comparison between NICS(1) and metal-flanking PN bond interaction.

Despite how scattered the results are, there is an ill-defined trend between the Metal-PN interaction and the NICS(1) values. As the interaction strength increases the aromaticity increases, suggesting that the negative hyper-conjugation contribution to the bonding has increased. This is possibly the result of the ionic part of the bonding being reduced by the metal taking electron density from the nitrogen shifting the ratio of negative hyper-conjugation and ionic bonding.

4.4 Conclusion

The bond lengthening that is observed in all phosphazene when a transition metal is coordinated is the result of electron density being removed from PN bonding orbitals going into the 4s orbitals of the metal (see Figure 4.4.1). Because the interaction occurring via the metal 4s orbital is independent of the geometry for the same metal, only the distance between the metal ion and the flanking PN will affect the bond lengthening. The metal dependence relates to the ability to accommodate electron density. This means that a metal with fewer 3d electrons can accommodate more electron density from the flanking PN bonds which results in greater lengthening. While this phenomena has only been studied for the first row transition metals it is plausible that the same mechanism occurs with heavier metals, but using their 5s or 6s orbitals instead.

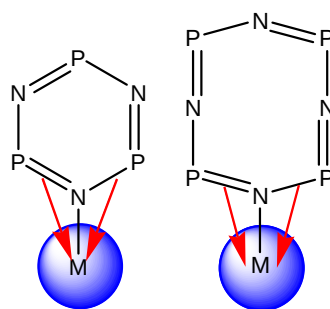


Figure 4.4.1 Schematic view of the metal 4s interaction with the flanking PN bonds.

The aromaticity calculations suggest, although not convincingly, that the electron density is being removed from the ionic part of the bonding. It would be necessary to separate the effect of shifting of the metals on the ghost atom from that of the aromatic shifting to confirm this, but it stands to reason, the ionic nature of the bond will be reduced by a positively charged centre bonded to the negatively charged nitrogen (see Figure 4.4.2).

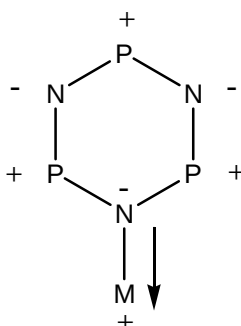


Figure 4.4.2 Schematic view of the metal ions affect on the ionic bonding of the phosphazene.

However, it is unlikely that only one part of the bonding being is affected by the metal bonding. Having a positively charged centre bonding to the nitrogen would also reduce the nitrogen's ability to be involved in negative hyper-conjugation thereby weakening PN bond. It is clear that electron density is being removed from the PN bonds resulting in bond lengthening, and this fits the simple σ donor class of the phosphazene as no back bonding to the phosphazene ring is occurring.

Chapter 5 – The Substituent - Phosphazene Interaction

5.1 – Introduction

Many studies have been performed on the phosphazene by varying the substituents attached to the phosphorus to see how electron withdrawing or donating groups affect the PN bond. The most common examples are the use of different halogens^{69, 70} (as shown in Figure 5.1.1).

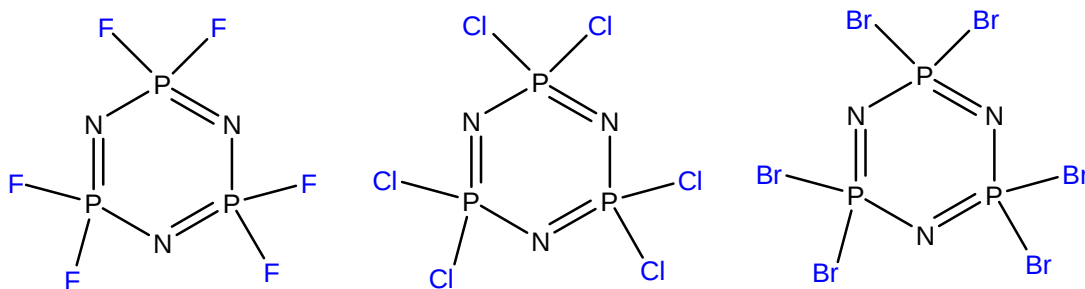


Figure 5.1.1 Examples of common substituents attached to the phosphazene ring for computational analysis.

While such comparisons are crucial for the understanding of the PN bond in phosphazenes, they neglect to explain what happens when larger groups with different functionalities that are able to directly interact with the ring are attached (e.g. see Figure 5.1.2). It is also important to know why these groups pack in the solid-state, and explain why some pyridine polymer systems are unstable⁷¹.

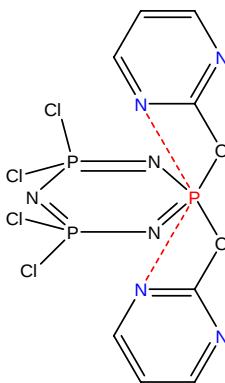


Figure 5.1.2 Example of donor acceptor interactions between pyrimidine and ring phosphorus.

In this chapter, the interaction of a pyridine substituent with the phosphazene system will be analysed. In systems with pyridines attached, the pyridine ring nitrogen is always seen weakly interacting with the ring phosphorus. According to the ionic

bonding model of the phosphazene, the phosphorus is positively charged and this attracts the lone pair on the pyridine nitrogen resulting in a donor-acceptor interaction⁵⁵. The only other possibility is that it is the result of crystal packing, weak intermolecular interactions causing the molecule to pack in a particular way in solid state. Neither of these theories explain why the substituent always sits over the centre of the ring.

In this section, the trimer (L) and tetramer (Ltetr) (see Figure 5.1.3) will be investigated to determine if there is any electron donation from the pyridine nitrogen to the phosphazene ring and, if so, which atoms are accepting electron density. In addition, it will examine how this interaction affects that bonding nature of the phosphazene ring, the bond occupancy and aromaticity of the phosphazene ring.

Both of the trimer and tetramer have the same groups attached, however, the tetramer has the capping pyridine nitrogen held closer the phosphorus (2.76 Å) than the trimer's capping pyridine nitrogen (2.88 Å) - both of which are much less than the sum of the van der Waals radii of P and N (3.35 Å)²⁴. This large difference suggests that the interaction is stronger in the tetramer than the trimer. Another interaction present in the trimer is the flanking pyridine interacting with the phosphorus atom. The pyridine nitrogen is held only 3.00 Å away from the phosphorus, suggesting some form of interaction. However, in the tetramer the phosphorus pyridine nitrogen distance is 3.48 Å, which is greater than the sum of van der Waals radii (3.35 Å)²⁴ and therefore is not likely to be a significant interaction.

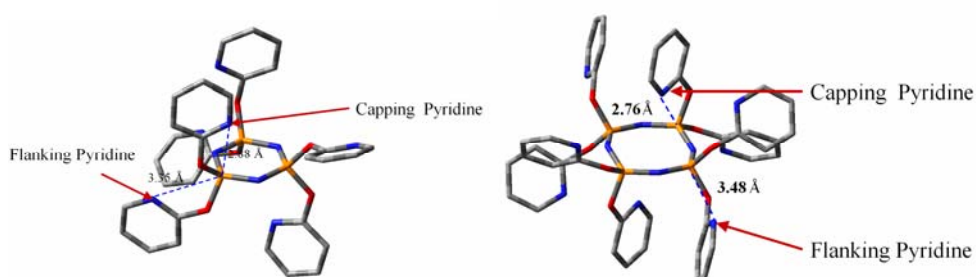


Figure 5.1.3 Phosphazene groups investigated for pyridine interaction. Left: Trimer:
Right Tetramer

5.2 The interactions of the capping pyridine ring with the phosphazene ring

In this section, the NBO E_2 values were used to see if the lone pair on the pyridine nitrogen is donating any electron density to any part of the phosphazene ring, or if instead, the pyridine itself is accepting electron density from the phosphazene ring.

Trimer capping pyridine interactions

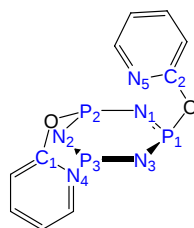


Figure 5.2.1 Labels for the capping pyridines and phosphazene.

Table 5.2.1 Interactions between the capping pyridine and trimer phosphazene ring.

Donor	Acceptor	Energy (kJ mol ⁻¹)
BD C(1)–N(4)	LP P(2)	6.15
LP N(4)	LP P(2)	18.49
LP N(4)	LP P(3)	6.15
LP N(4)	BD* P(2)-N(1)	1.42
LP N(4)	BD* P(2)-N(2)	1.42
LP N(4)	BD* P(3)-N(3)	0.59
BD C(2)–N(5)	LP P(1)	7.23
LP N(5)	LP P(1)	18.66
LP N(5)	LP P(2)	3.39
LP N(5)	LP P(3)	3.68
LP N(5)	BD* P(1)-N(1)	1.42
LP N(5)	BD* P(1)-N(3)	1.51
LP N(5)	BD* P(2)-N(1)	0.54
LP N(5)	BD* P(3)-N(3)	0.59

The E_2 values show that there is a donor-acceptor interaction between the pyridine lone-pair and the phosphorus that attached to it (18.49 kJ mol⁻¹ for P(2) and 18.66 kJ mol⁻¹ for P(1)). There are other similar but weaker interactions with the other phosphorus atoms in the ring (e.g. 3.39 kJ mol⁻¹ between N(5) and P(2)). There are also interactions

with the anti-bonding orbitals of the PN bonds (e.g. 1.42 kJ mol^{-1} between N(5) and P(1)-N(1)). Thus, while the donor-acceptor interaction suggested in the literature⁶¹ exists, there are other interactions that result in the pyridine being held directly over the phosphazene ring, a feature that appears to be common for all cyclophosphazenes as proved by seeing the same behaviour in the tetramer analogue.

Tetramer capping pyridine interactions

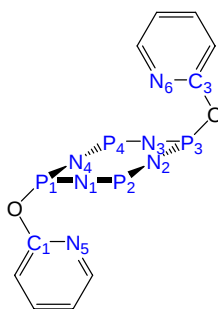


Figure 5.2.2 Capping pyridines and phosphazene labels.

Table 5.2.2 Capping pyridine interactions with the tetramer phosphazene ring.

Donor	Acceptor	Energy (kJ mol ⁻¹)
BD N(5)-C(1)	LP P(1)	6.02
BD N(5)-C(1)	LP P(2)	1.46
LP N(5)	LP P(1)	21.42
LP N(5)	LP P(2)	6.39
LP N(5)	LP P(3)	1.55
LP N(5)	LP P(4)	3.64
LP N(5)	BD* P(1)-N(1)	1.84
LP N(5)	BD* P(1)-N(4)	1.75
LP N(5)	BD* N(1)-P(2)	0.92
LP N(5)	BD* P(4)-N(4)	0.59
BD N(6)-C(3)	LP P(3)	6.02
BD N(6)-C(3)	LP P(4)	1.46
LP N(6)	LP P(1)	0.79
LP N(6)	LP P(2)	3.63
LP N(6)	LP P(3)	21.42
LP N(6)	LP P(4)	5.65
LP N(6)	BD* P(2)- N(2)	0.59
LP N(6)	BD* N(2)- P(3)	1.75
LP N(6)	BD* P(3)-N(3)	1.84
LP N(6)	BD* N(3)-P(4)	0.92
LP N(6)	BD* P(4)-N(4)	0.38

The tetramer exhibits the same behaviour as the trimer with the interaction between the pyridine nitrogen and the phosphorus it is attached to (e.g. $21.42 \text{ kJ mol}^{-1}$ between N(5) and P(1)). Weaker interactions with the other phosphorus atoms (e.g. 6.39 kJ mol^{-1} between N(5) and P(2)), and the PN anti-bonding orbitals (e.g. 1.84 kJ mol^{-1} between N(5) and the P(1)-N(1) bond) are also observed. However, the interaction strength is almost double that of the trimer species, possibly as a result of the phosphazene being able to flex, thus, allowing a stronger interaction.

To see how the lone-pair interaction with the bonds affects this interaction, the pyridine nitrogen to phosphazene ring distance was varied. The distance was varied by constraining the P-O-C angle as shown in Figure 5.2.3, then relaxing the rest of the molecule.

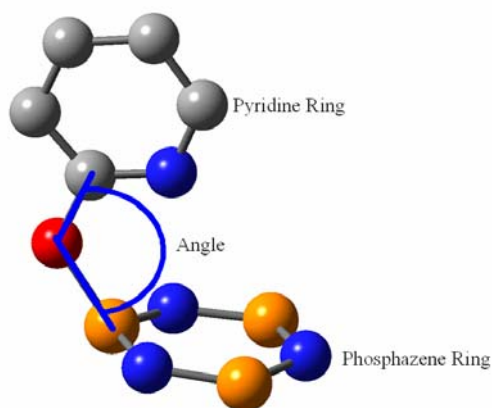


Figure 5.2.3 Angle adjusted.

As changes in the phosphazene bond lengths were very small, the bond occupancy was used to determine the affect on the bonds. The bond occupancy is far more sensitive to the electron density of the bonds and will therefore show greater changes.

Capping Pyridine

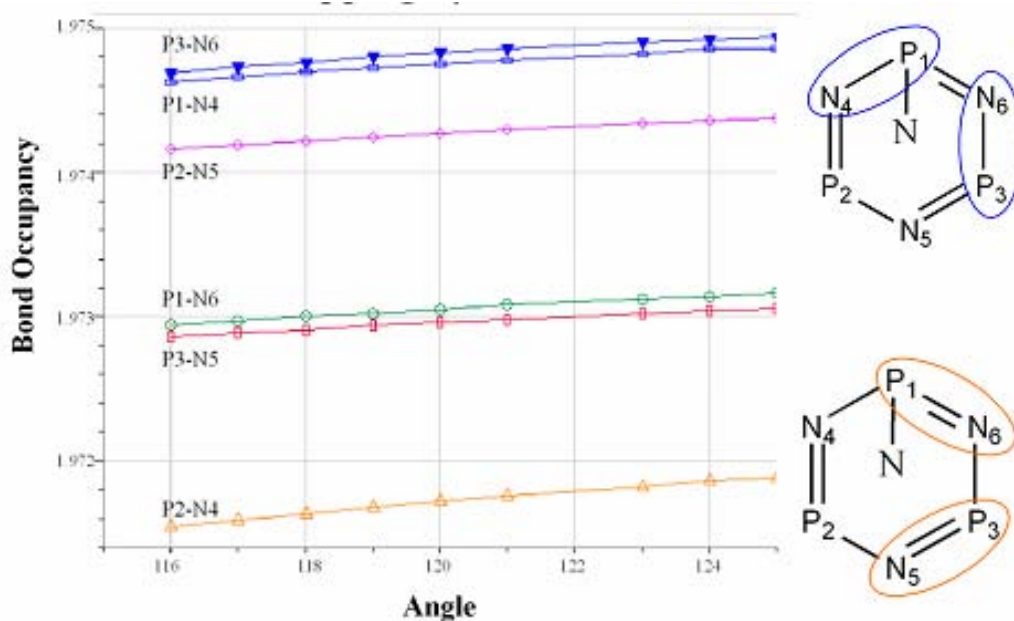


Figure 5.2.4 Bond occupancy versus P-O-C angle.

While there appears to be an almost linear relationship between the bond occupancy and the angle of the P-O-C bond, the change is very small and would be unlikely to be the cause of the bond lengthening that has been observed. In spite of this, it does show that the pyridine is having an almost equal affect on all of the bonds. This interaction with all of the bonds is explained by viewing Figure 5.2.5.

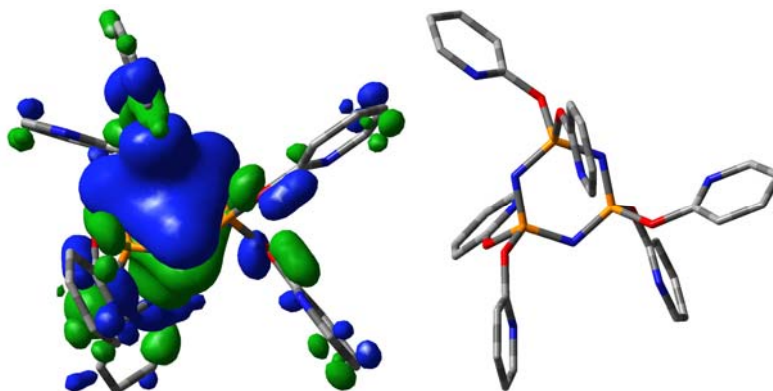


Figure 5.2.5 MO responsible for interactions observed in Table 5.2.1.

The lone pair from the pyridine ring is able to provide sufficient electron density to the phosphazene ring resulting in a ‘spreading’ of the orbitals forming the π -like bond, allowing the pyridine to donate electron density to all of the phosphorus atoms and PN bonds.

5.3 The interaction of the flanking pyridine with the trimer phosphazene ring

Another interaction that is present in the trimer, but not always found in the tetramer and other species, is the flanking pyridine donor-acceptor interaction with the phosphorus attached to it, without it being held directly over the phosphazene ring.

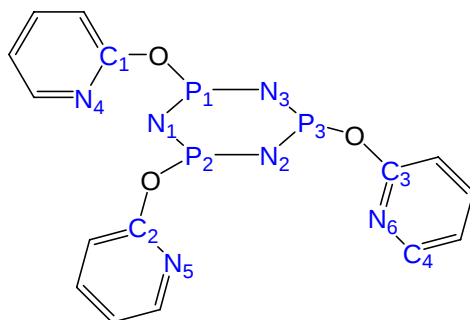


Figure 5.3.1 Labels for flanking pyridines and phosphazene.

Table 5.3.1 Flanking pyridine interactions with phosphazene.

Donor	Acceptor	Energy (kJ mol ⁻¹)
BD C(1)-N(4)	LP P(1)	5.56
LP N(4)	LP P(1)	13.14
LP N(4)	BD* P(1)-N(3)	5.06
LP N(4)	BD* P(1)-N(1)	5.06
BD C(2)-N(5)	LP P(2)	5.48
LP N(5)	LP P(2)	6.56
LP N(5)	BD* P(2)-N(1)	1.63
LP N(5)	BD* P(2)-N(2)	3.77
BD N(6)- C(3)	LP P(3)	1.00
BD N(6)- C(4)	LP P(3)	4.69
LP N(6)	LP P(3)	8.54
LP N(6)	BD* P(3)-N(3)	1.21
LP N(6)	BD* P(3)-N(2)	3.39

The flanking pyridine has interactions that are far more specific. It is only interacting with the phosphorus attached to it and its flanking bonds. These interactions are slightly weaker than the capping pyridine's interaction (e.g. 35.00 kJ mol⁻¹ between N(4) and P(1)). As they are specific to the flanking PN bonds they could provide an explanation for the variance observed in the lengthening (described in Chapter 4). Some interactions

between the pyridine and the PN bonds (e.g. 5.06 kJ mol⁻¹ between N(4) and the P(1)-N(1) bond) are of the order of the metal-PN interactions (e.g. 7.15 kJ mol⁻¹ for CuLCl₂). The bond occupancy was compared to the P-O-C angle (Figure 5.2.7) to determine how strongly these interactions affect the bonding around the phosphazene.

Flanking Pyridine

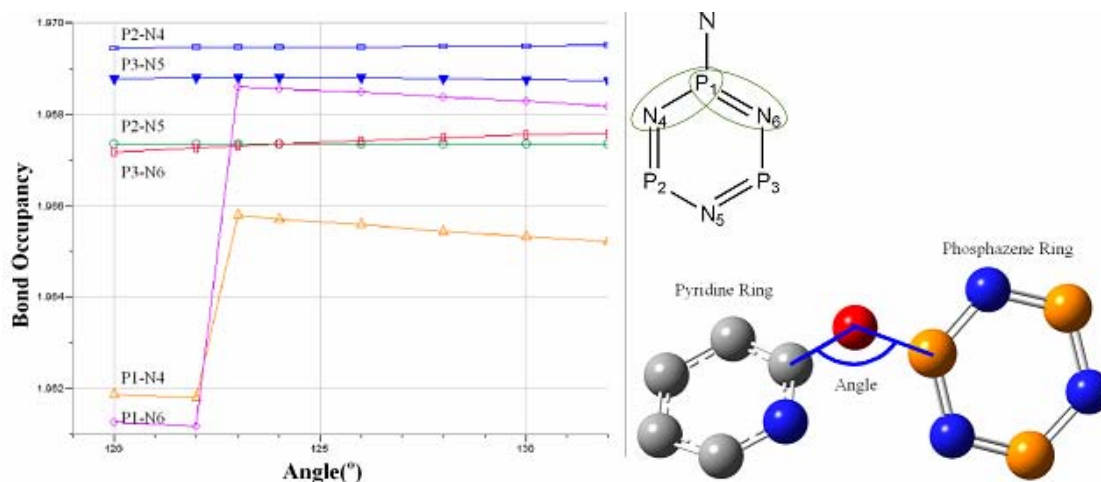


Figure 5.2.7 Flanking pyridine P-O-C angle versus bond occupancy.

Figure 5.2.7 shows only the flanking PN bonds drastically change as the pyridine is moved. As the lone pair of the pyridine nitrogen is moved away, the bond occupancy increases, possibly because of the negative hyper-conjugation part of the bonding increasing its contribution.

5.4 Aromaticity Calculations

In order to understand what part of the PN bonding is affected by the pyridine, the aromaticity of the phosphazene was calculated as the pyridines were moved away from the ring. The reason behind this is that the negative hyper-conjugation is responsible for the ring current in the phosphazene and therefore the aromaticity. If the aromatic behaviour is changed then it is reasonable to assume that the negative hyper-conjugation is changed.

The capping pyridine angle was adjusted gradually changing the distance between the phosphazene ring and the pyridine (see Figure 5.4.1). The NICS(0) value was measured in the ring plane to limit the effects of the pyridine directly interacting with the ghost atom.

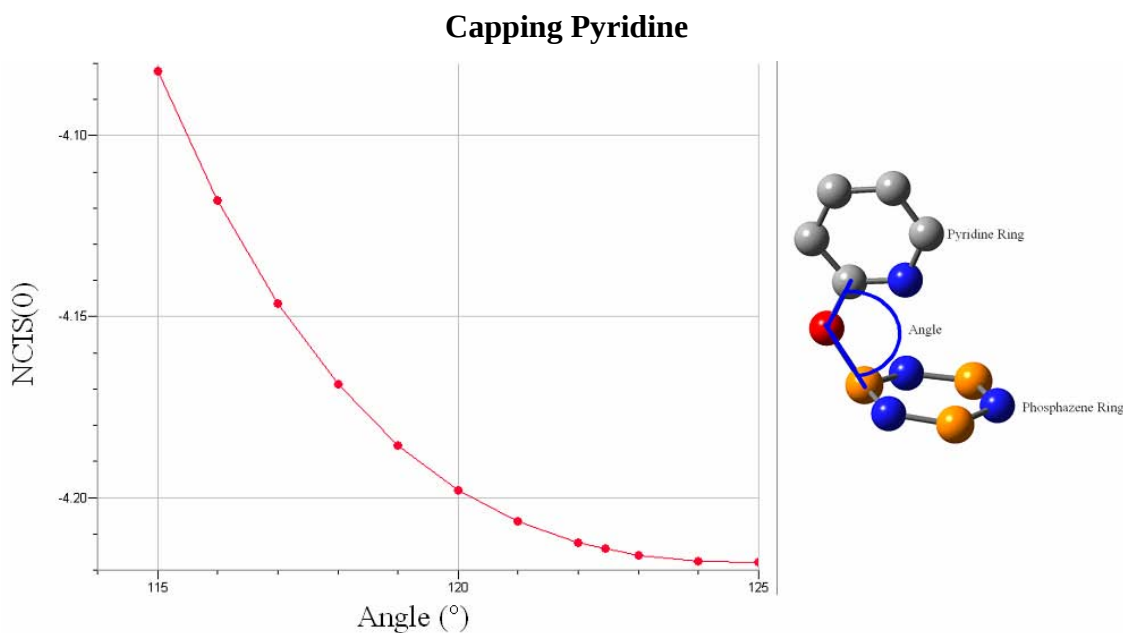


Figure 5.4.1 NICS(0) vs. bond angle for trimer capping pyridine.

Figure 5.3.1 shows an exponential increase in aromaticity as the pyridine is moved away from the phosphazene ring. This can be explained by referring back to the interactions in Section 5.2. There is a significant donation of electron density from the pyridine lone-pair to the phosphorus atoms. Because of increased electron density being supplied to the phosphorus atoms they are less able to accommodate, or requires less, electron density from the negative hyper-conjugation. Therefore, as the pyridine is moved away less electron density is available for the phosphorus atom causing increased contributions from the negative hyper-conjugation (see Figure 5.4.2).

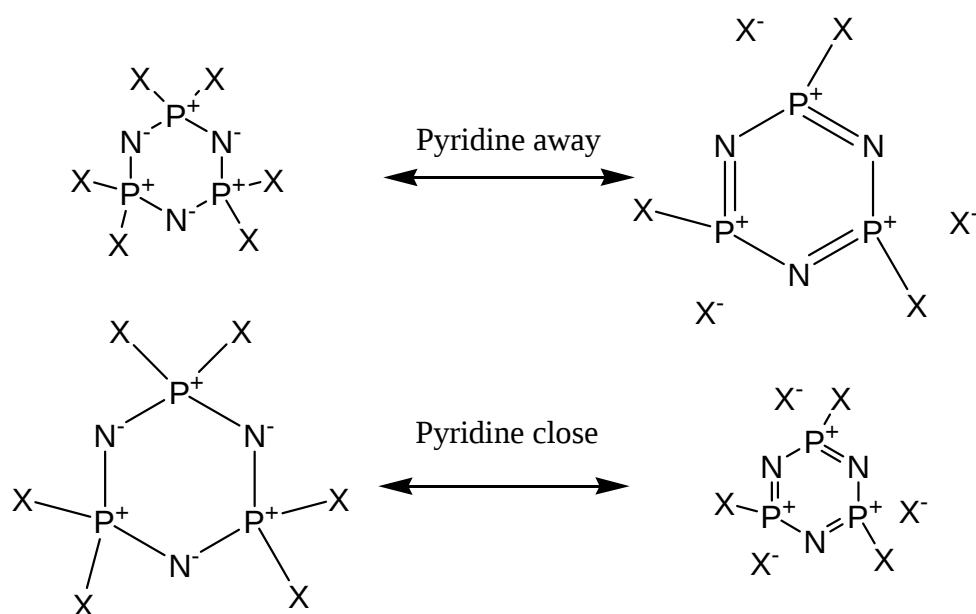


Figure 5.4.2 The effect of the pyridine distance on the bonding nature of the phosphazene.

The same approach for the flanking pyridine was used to see how localized the effect of the pyridine donor acceptor interactions with the phosphorus atom is. The P-O-C angle was varied and the NICS(0) was measured (see Figure 5.4.3), based on the theory that if the effect is localized then it will only have a small effect on the aromaticity of the entire system.

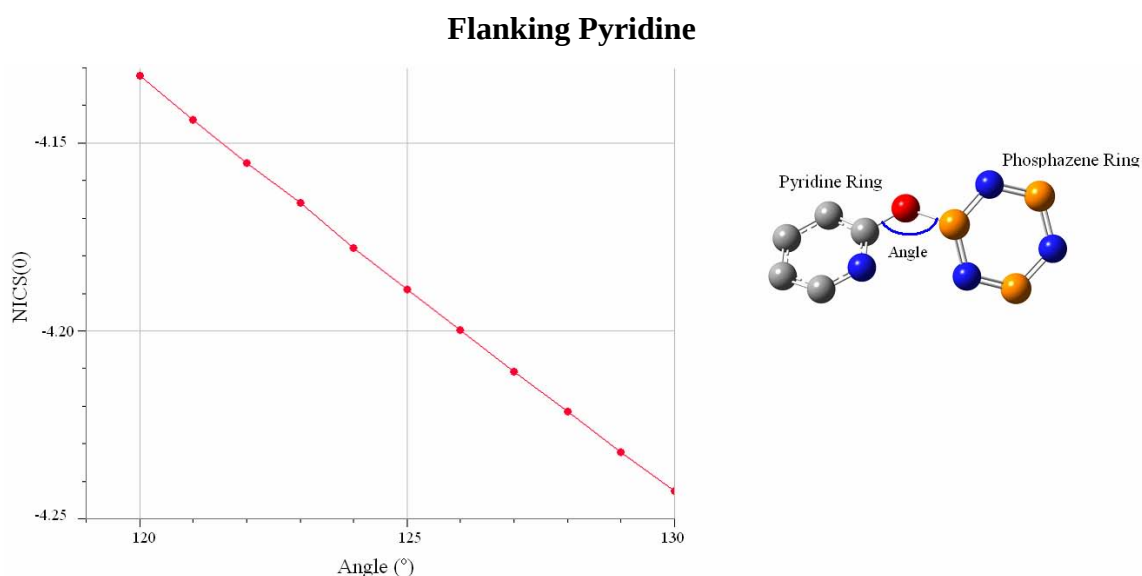


Figure 5.3.3 NICS(0) versus trimer flanking pyridine angle.

While the phosphazene showed an increase in aromaticity as the pyridine was moved away, the effect was linear and was less than that observed for the capping pyridines. From

this result, it can be said that the effect of the flanking pyridine interaction does affect the electron delocalization of the phosphazene ring, but not to the same extent as the capping pyridine.

5.5 Conclusion

It can be concluded that the pyridine lying directly over the phosphazene ring (capping pyridine) is a result of interactions between the nitrogen in the pyridine and phosphorus atoms and the PN bonds, rather than a feature of packing in the crystal lattice. Because of the electron density being provided by the pyridine nitrogen, the negative hyperconjugation becomes less necessary for the phosphorus atoms to obtain electron density. This interaction is stronger for the tetramer, which is reflected by the shorter $P_{\text{Phosphazene}}-N_{\text{Pyridine}}$ distance and is possibly due to greater flexibility of the tetramer phosphazene ring. It would be a reasonable assumption that this behaviour would occur for all of the cyclic analogues of the phosphazene, but would be unlikely to occur for the polymer.

The flanking pyridine interaction is of a reasonable strength, comparable to the metal-PN interaction (refer to Chapter 4). It is the presence of this interaction that could explain why a direct relationship between the metal-PN interaction and the bond lengthening could not be found. This interaction appears as if it should be far more common than the capping pyridine one. It would seem that for the flanking pyridine other interactions could take precedence (e.g. intermolecular interactions) such as in the case of the tetramer. As the tetramer is typically hailed as a better model for the polymer than the trimer⁶⁸, it would be difficult to say if such interactions occur in the polymer, but they could be the reason for the cleaving of the polymer in the presence of pyridine pendant groups.

Chapter 6 – Metal-Metal Communication

6.1 Introduction

Previous bonding models of phosphazenes such as Paddock's³²⁻³⁴ suggest that if two metal ions were attached to a cyclic phosphazene, communication between the two metal centers could occur. To the best of our knowledge only two phosphazene complexes have been developed that have two metal ions attached to the phosphazene via the ring nitrogens^{57, 59} where magnetic and Electron Spin Resonance (ESR) data are available; these complexes will be referred to as $\text{Cu}_2\text{LtetrCl}_2^{2+}$ and $\text{Cu}_2\text{LMeCl}_4$ (see Figure 6.1.1).

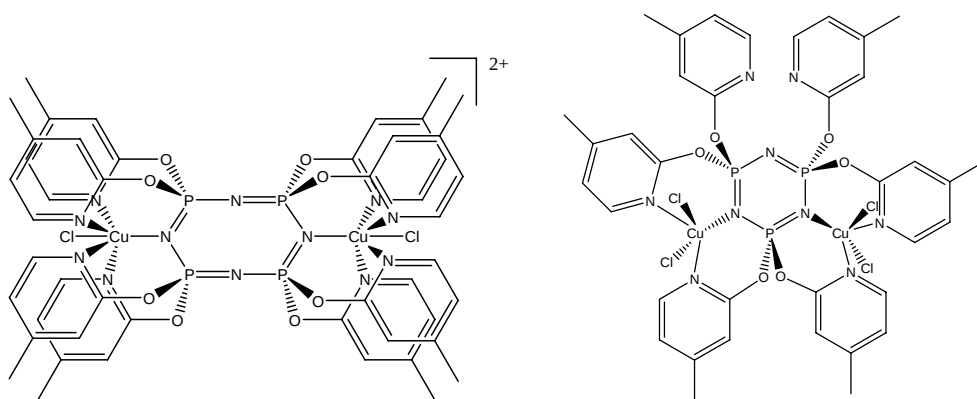


Figure 6.1.1 Dimetal phosphazene systems investigated Left: $\text{Cu}_2\text{LtetrCl}_2^{2+}$ Right: $\text{Cu}_2\text{LMeCl}_4$.

Metal-metal communication can occur as a result of coupling between magnetic spin systems. The coupling can occur in two ways: ferromagnetically and antiferromagnetically. Ferromagnetically means that all of the particles (metal ions in these examples) have the spin orientated in the same direction (see Figure 6.1.2), resulting in an increase of the magnetic susceptibility. However, in antiferromagnetism the spins of the particles alternate (see Figure 6.1.2), reducing the magnetic susceptibility.

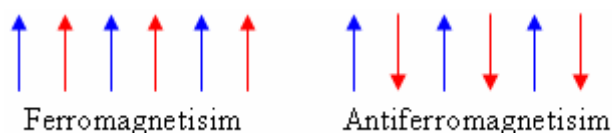


Figure 6.1.2 Difference between Antiferromagnetic and Ferromagnetic spin orientations.

Antiferromagnetism is a common form of metal-metal communication which occurs as a result of metal ions getting sufficiently close to each other allowing the metals to magnetically interact, or it can occur through a bridge⁷². The bridge typically associated with antiferromagnetic coupling is one with π bonding, such as an aromatic system (Figure 6.1.3).

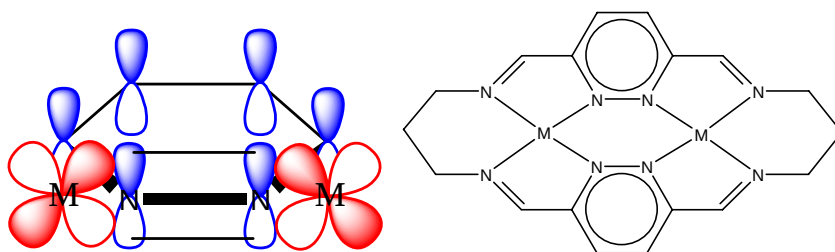


Figure 6.1.3 A schematic view of metal communication using pyridazine⁷².

The π bonding allows electron density to pass from one metal centre to the other, providing a means of coupling (see Figure 6.1.4), which is known as Superexchange⁷³.

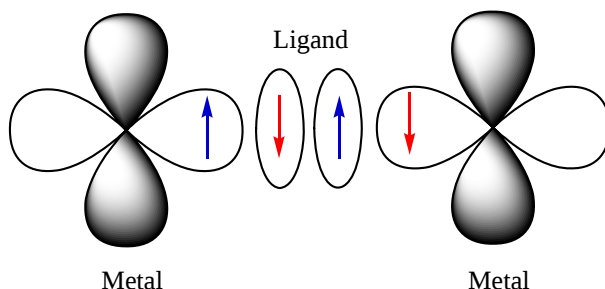


Figure 6.1.4 A schematic diagram of Superexchange via a ligand causing antiferromagnetic coupling.

To determine if a complex is ferromagnetic or antiferromagnetic the magnetic susceptibility (χ) is measured as a function of temperature⁷⁴ (see Figure 6.1.5). The magnetic moment (μ_{eff}) can then be calculated.

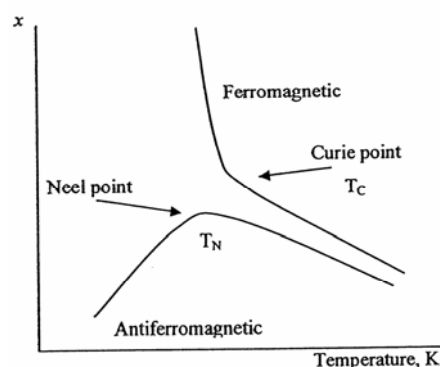


Figure 6.1.5 The different behaviour of antiferromagnetic and ferromagnetic systems as the temperature changes (χ = magnetic susceptibility).

In the case of a ferromagnetic system, the magnetic susceptibility will increase as the temperature decreases. In contrast, for an antiferromagnetic system the magnetic susceptibility will increase as the temperature decreases until the Neel point, once past this point the magnetic susceptibility decreases drastically.

For the complex, $\text{Cu}_2\text{LMeCl}_4$, the calculated curves of χ and μ_{eff} versus temperature can be fitted to the observed values assuming a spin coupled system with a best fit parameter of $2J = -1 \text{ cm}^{-1}$ which suggests a weak interaction⁵⁷ (see Figure 6.1.6). Preliminary results⁵⁹ suggest $\text{Cu}_2\text{LtetrCl}_2^{2+}$ exhibits a similar behaviour and will also have a low $2J$ value (see Figure 6.1.6).

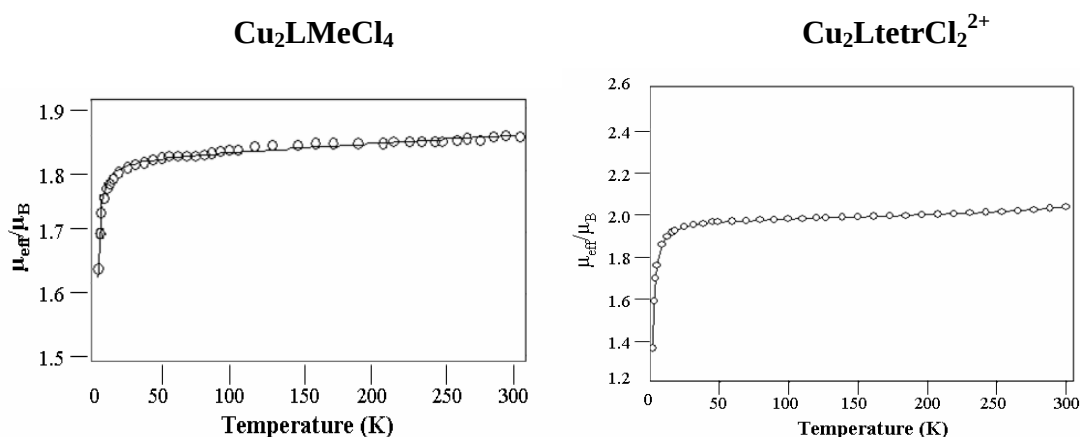


Figure 6.1.6 The magnetic moments (μ_{eff}) measured at different temperatures. Left $\text{Cu}_2\text{LMeCl}_4$, Right: $\text{Cu}_2\text{LtetrCl}_2^{2+}$.

Another way of detecting metal-metal interactions is ESR spectroscopy. An ESR spectrum for a single copper(II) ion should show four hyperfine coupling bands. This

can be explained by considering the energy levels of the unpaired electron (see Figure 6.1.7).

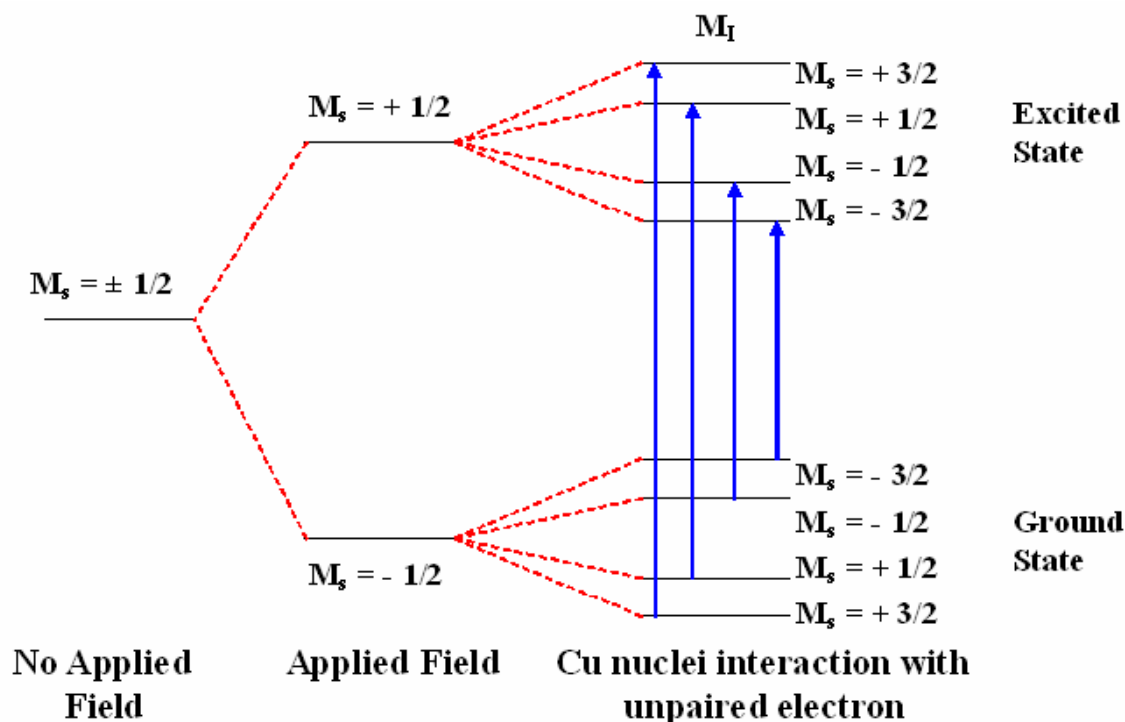


Figure 6.1.7 Energy level diagram for an unpaired electron on an uncoupled copper (II) ion in a magnetic field.

The transition rules $\Delta M_s = \pm 1$ and $\Delta M_I = 0$, predict four allowed transitions.

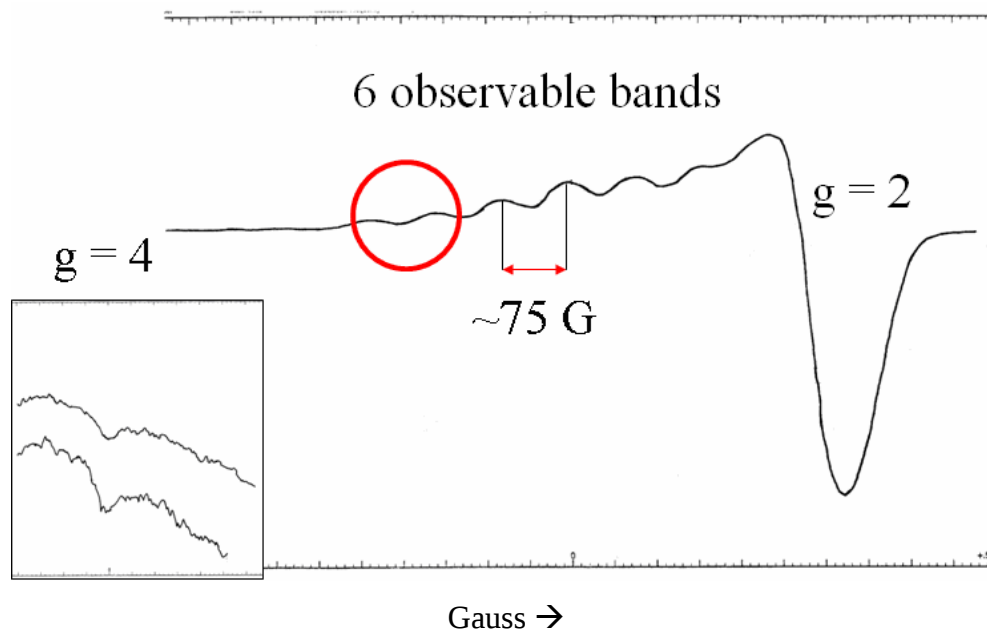
The general equation is:

$$2nI + 1 = \text{number of bands} \quad \textbf{Formula 6.1.1}$$

where n is the number of nuclei and I is the nuclear spin ($I = 3/2$ for Copper).

If the two copper(II) ions are acting completely independently of each other when bound to the phosphazenes only four bands should be observed. However, in the measured ESR of $\text{Cu}_2\text{LtetrCl}_2^{2+}$ (see Figure 6.1.8), six hyperfine bands are observed with a possible seventh present. $\text{Cu}_2\text{LMeCl}_4$ (see Figure 6.1.8) has four bands with others possibly present (five-coordinate copper makes hyperfine bands difficult to observe).

$\text{Cu}_2\text{LtetrCl}_2^{2+}$ ESR Spectrum



$\text{Cu}_2\text{LMeCl}_4$ ESR Spectrum

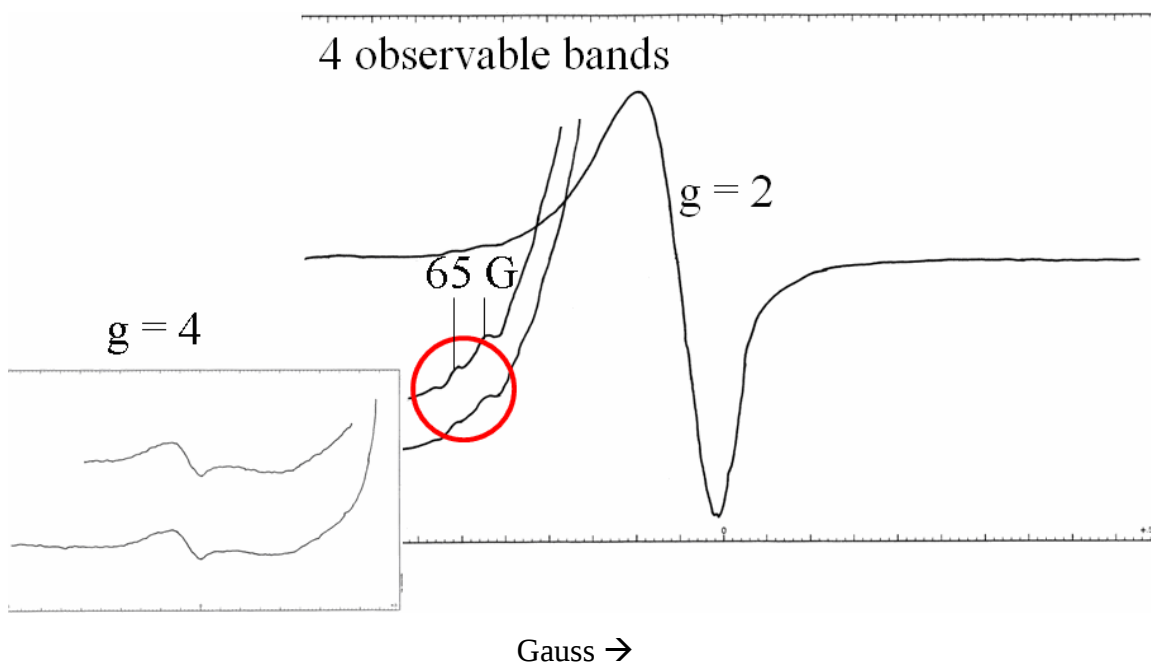


Figure 6.1.8 ESR spectra (frozen solution) of the complexes Top: $\text{Cu}_2\text{LtetrCl}_2^{2+}$
Bottom: $\text{Cu}_2\text{LMeCl}_4$.

Formula 6.1.1, predicts seven hyperfine bands in the ESR spectrum if two copper ions are interacting. The additional bands occur as a result of the unpaired electrons being able to interact, further splitting up the energy levels. Another typical feature of a single copper ESR spectrum is that the hyperfine splitting is 150-200 G. However, in $\text{Cu}_2\text{LtetrCl}_2^{2+}$, the splitting is ~75 G and 65 G for $\text{Cu}_2\text{LMeCl}_4$ (see Figure 6.1.8). Further

proof that the two copper ions are coupled with each other is that a weak band is observed in the $g = 4$ region as a result of the $\Delta M_s = \pm 2$ transition becoming allowed. This is consistent with the unpaired electron and the copper nuclei interacting with each other.

Both the magnetic susceptibility and ESR measurements suggest that the metal ions are antiferromagnetically coupled. However, these measurements provide no information as to how the coupling is occurring. There are three possible ways in which the coupling could occur: when two molecules come together to form a dimer via intermolecular bridges; when metal ions are held close enough together they can couple through space; or the phosphazene ligand could be acting as an intramolecular bridge between the metal ions, facilitating Superexchange.

The X-ray structures^{57, 59} of both $\text{Cu}_2\text{LtetrCl}_2^{2+}$ and $\text{Cu}_2\text{LMeCl}_4$ (see Figure 6.1.9) show that in the solid state there are no interactions between the copper or chloride ions that could account for the coupling. Due to the steric hindrance, resulting from the bulky ligand, it is unlikely that the ions would get close enough (intermolecularly) to allow for any interaction in frozen solution.

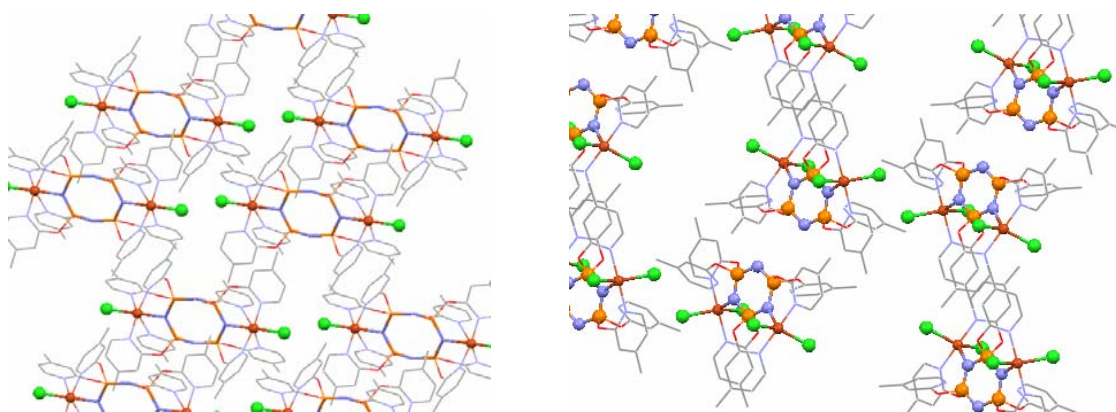


Figure 6.1.9 Packing structure of complexes, Left: $\text{Cu}_2\text{LtetrCl}_2^{2+}$, Right: $\text{Cu}_2\text{LMeCl}_4$.

Another feature that the X-ray structures^{57, 59} (see Figure 6.1.10) show is that the Cu-Cu distance for $\text{Cu}_2\text{LtetrCl}_2^{2+}$ is 8.55 Å and 6.47 Å for $\text{Cu}_2\text{LMeCl}_4$, suggesting coupling through space is unlikely.

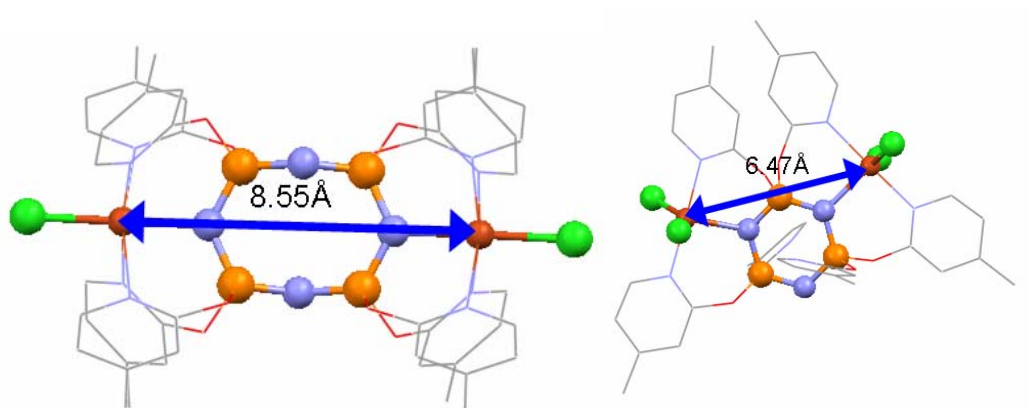


Figure 6.1.10 Cu-Cu distances, Left: $\text{Cu}_2\text{LtetrCl}_2^{2+}$, Right: $\text{Cu}_2\text{LMeCl}_4$

This leaves coupling as a result of a Superexchange mechanism occurring via the phosphazene ring. In order to explain this phenomenon the occupied orbitals containing the copper ions were examined to see if any overlap of electron density occurs between the two metal ions.

6.2 Molecular Orbitals Involved in Metal-Metal Communication.

Only one occupied orbital simultaneously involving the two metal ions in $\text{Cu}_2\text{LtetrCl}_2^{2+}$ was found which could provide a pathway for an electron-electron coupling interaction (see Figure 6.2.1). No other metal based orbitals displayed an overlap of electron density between metal orbitals.

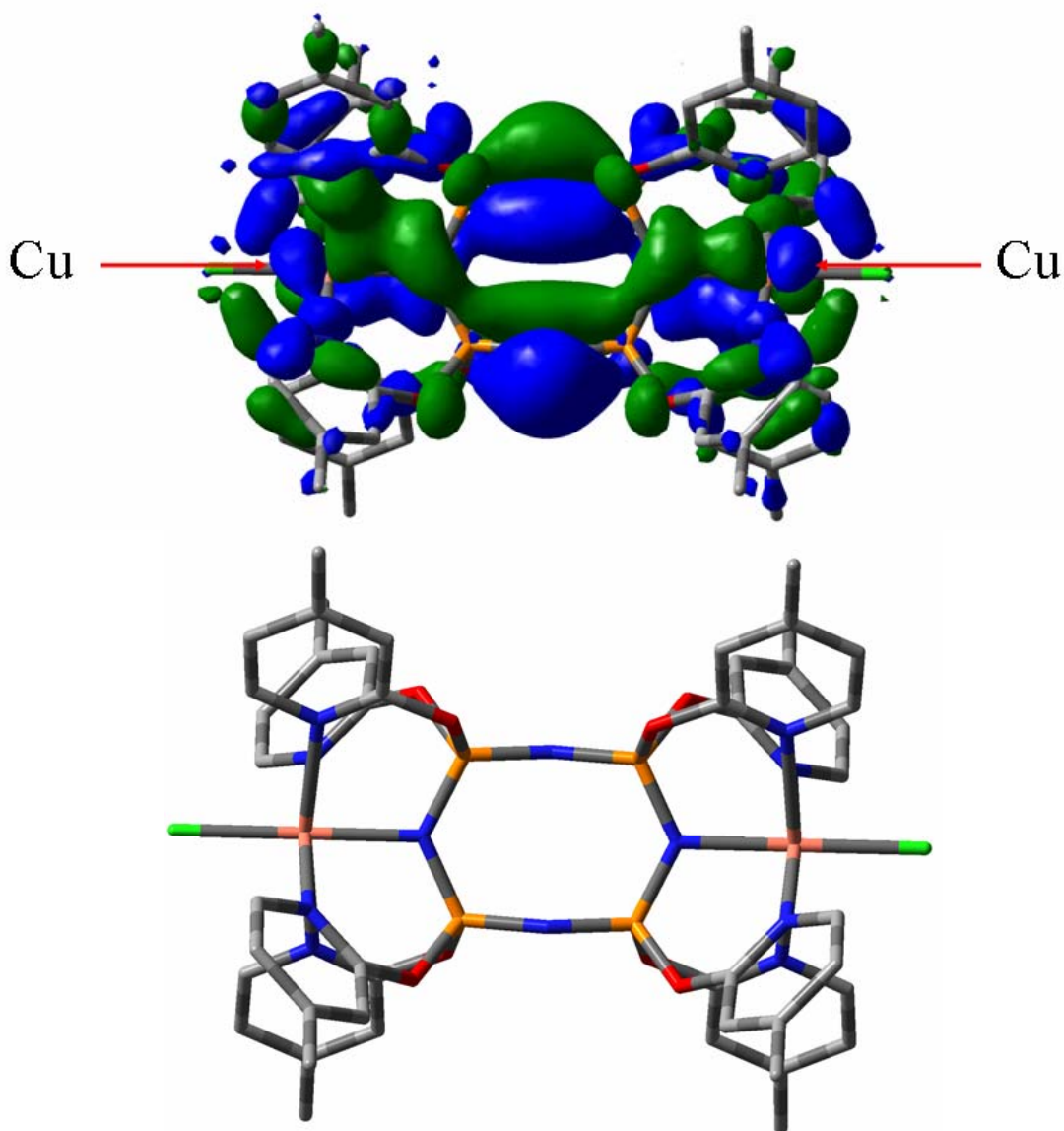


Figure 6.3.1 $\text{Cu}_2\text{LtetrCl}_2^{2+}$ 'electron density bridge' orbital.

While the orbital is initially complicated to look at, the coefficients (see Table 6.2.1) show that the molecular orbital is comprised mainly of the copper d_{xy} and the p orbitals of the phosphazene ring nitrogens with negligible contributions from the phosphorus atomic orbitals.

Table 6.2.1 Atomic orbital coefficients for the $\text{Cu}_2\text{LtetrCl}_2^{2+}$ ‘electron density bridge’.

Atomic Orbital	Coefficient
N(1)(2P _y)	-0.069
N(1)(3P _y)	– 0.090
N(2)(2P _z)	0.266
N(2)(3S)	– 0.099
N(2)(3P _z)	0.194
N(4)(2P _z)	0.284
N(4)(3S)	0.102
N(3)(2P _y)	– 0.066
N(3)(3P _y)	– 0.087
Cu(2)(3d _{xy})	0.223
Cu(2)(4d _{xy})	0.137
Cu(1)(3d _{xy})	– 0.231
Cu(1)(4d _{xy})	– 0.141

A simplified view of the ‘electron density bridge’ orbital is shown in Figure 6.3.2. Only the 2p orbitals from the phosphazene ring nitrogens are involved, there being no significant contributions from the phosphorus atoms (i.e. orbital coefficient magnitudes less than 0.009), which is behaviour that would be expected for the ionic component of the bonding, not the negative hyper-conjugation component. This is counter intuitive as negative hyper-conjugation accounts for the aromatic behaviour of the phosphazene, and aromaticity is typically associated with a ring’s ability to allow metal communication.

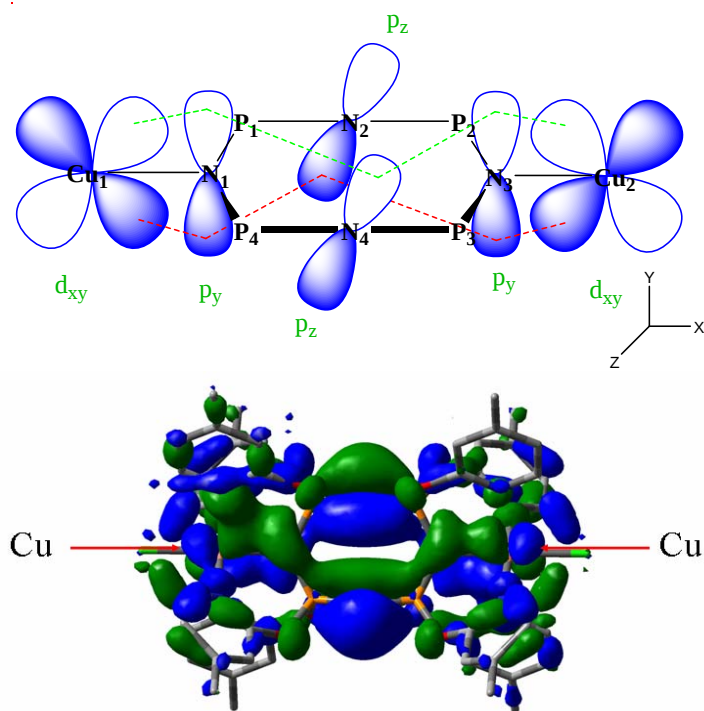


Figure 6.2.2 A schematic view of the ‘electron density bridge’ for $\text{Cu}_2\text{LtetrCl}_2^{2+}$.

The weak overlap of the orbitals probably occurs because the metal centres are directly opposite to each other in identical environments. The ‘pulling’ effect of each positive metal ion on the phosphazene causes the nitrogen lone pairs on N(2) and N(4) to ‘spread’, forming the ‘electron density bridge’ between the metal centres, hence allowing the observed coupling between the metal centres.

Although an ‘electron density bridge’ orbital was found for $\text{Cu}_2\text{LMeCl}_4$ (see Figure 6.2.3) it was different owing to the fact that the copper atoms are out-of-plane with the smaller trimer ring.

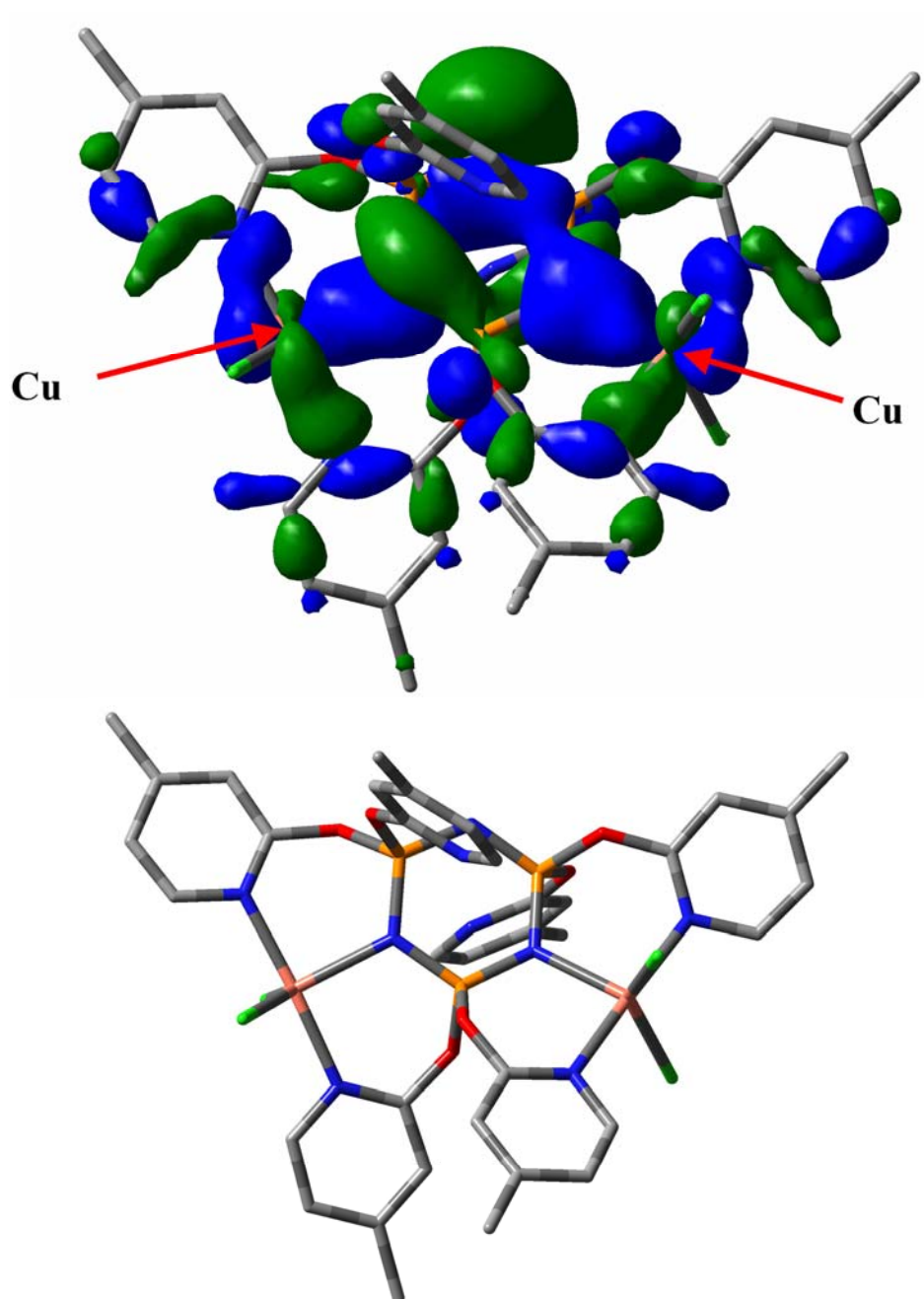


Figure 6.2.3 ‘Electron density bridge’ for $\text{Cu}_2\text{LMeCl}_4$.

As with $\text{Cu}_2\text{LtetrCl}_2^{2+}$, the orbital initially appears complex, however, the MO coefficients reveal its main components (see Table 6.2.2).

Table 6.2.2 Coefficients of the Cu₂LMeCl₄ electron density bridge.

Atomic Orbital	Coefficient
Cu(1)(3d _{x²})	-0.190
Cu(1)(3d _{y²})	0.111
Cu(1)(4d _{x²})	-0.116
N(1)(2p _z)	0.152
N(1)(3p _z)	0.135
N(3)(2s)	0.103
N(3)(2p _y)	0.324
N(3)(3s)	0.201
N(3)(2p _y)	0.214
Cu(2)(3d _{x²})	-0.186
Cu(2)(3d _{y²})	0.112
Cu(2)(4d _{x²})	-0.114
N(2)(2p _z)	-0.153
N(2)(3p _z)	-0.135

The orbital consists mainly of the nitrogen N(3) and N(4) p orbitals and the d_{x²-y²} orbitals of the copper ions. The copper ions are 28° out-of-plane with the phosphazene ring plane, which means the nitrogen atoms use the p_z orbitals to interact with the metal atomic orbitals. The ‘electron density bridge’ can then be formed via the p_y orbital on N(1) weakly overlapping with the p_z orbitals of the coordinated nitrogens. This is similar to the overlap observed for Cu₂LtetrCl₂²⁺ and could occur as the result of having two metal ions drawing electron density towards themselves changing the orbitals enough to allow them to overlap (or spread). Once again, the phosphorus atoms make a negligible contribution (i.e. orbital coefficient magnitudes less than 0.009) to the orbital as expected since the ionic part of PN bonding, with the electron density localized on the ring nitrogens, is the most significant.

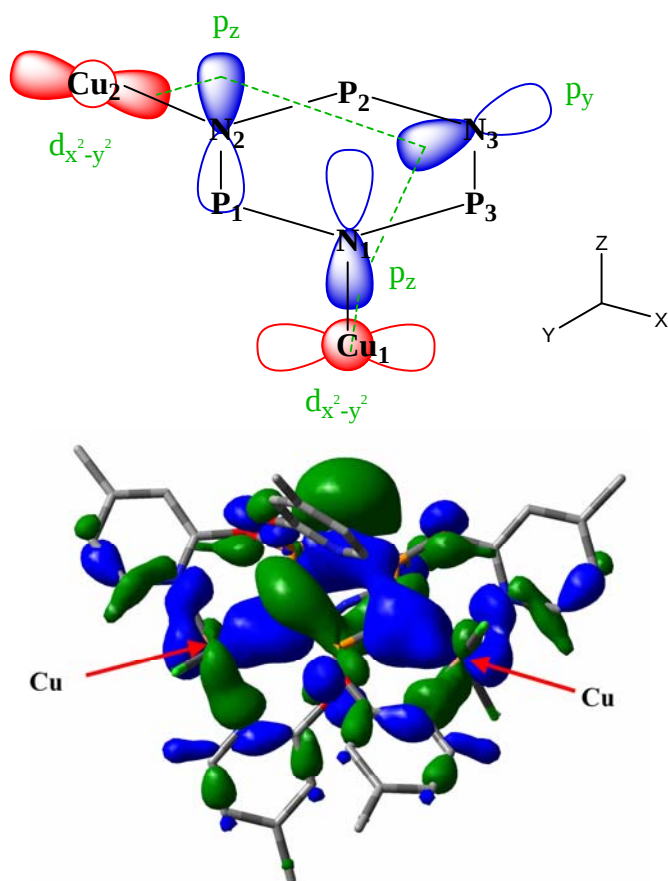


Figure 6.2.4 Schematic view of the $\text{Cu}_2\text{LMeCl}_4$ 'electron density bridge'.

6.3 Conclusion

Magnetic susceptibility and ESR measurements indicate that some form of interaction is occurring between the metal centres. By examining the occupied orbitals of $\text{Cu}_2\text{LtetrCl}_2^{2+}$ and $\text{Cu}_2\text{LMeCl}_4$, 'electron density bridges' between the metal centres are found. It is therefore plausible that communication between metal centers could occur via the 'electron density bridge' on the phosphazene ring, which would explain the metal-metal coupling observed in the ESR and magnetic susceptibility measurements. Not only is it a possibility that communication is occurring via the phosphazene, but it is in fact occurring via the ionic part of the PN bonding rather than the negative hyperconjugation component, which is typically associated with the aromatic behaviour of the phosphazene. While the aromaticity calculations (Chapter 4) were subject to severe limitations there was a large enough difference to show that $\text{Cu}_2\text{LMeCl}_4$ (0.8875) is less aromatic than $\text{Cu}_2\text{LtetrCl}_2^{2+}$ (-1.7575), which is possibly because the metal centres for $\text{Cu}_2\text{LtetrCl}_2^{2+}$ are on opposite ends of the phosphazene therefore the ring current remains evenly distributed.

The formation of the 'electron density bridge' may be the result of having two metals pulling the electron density of the uncoordinated nitrogen atoms towards them (see Figure 6.5.1), thus resulting in a 'spreading' of the p orbitals, forming the electron density bridge.

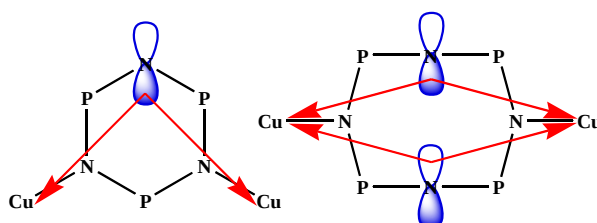


Figure 6.5.1 Pulling of the copper ions.

While no metal-metal communication on polymer or higher cyclic systems has been reported, it is plausible that weak communication could occur, provided that the metal binds directly to the nitrogen of the PN back bone and the ratio of metal atoms to PN units is sufficiently high to causing the spreading of nitrogen p orbitals without breaking the bonds.

Chapter 7 – Overall Conclusions

This study of cyclophosphazenes binding transition metals via the phosphazene ring nitrogen has revealed a great deal of information about the phosphazene itself. The investigation has shown that phosphazenes behave as simple σ donors, which is consistent with the current theory of bonding (i.e. the Chaplin model³⁸) for the phosphazene. They bond via the lone pair on the ring nitrogen, which can be regarded as being in approximately an sp^2 hybrid orbital. The metal binds with the d_z^2 or $d_{x^2-y^2}$ orbitals, which confirms the simple σ donor nature of the phosphazene, forming bonds with a calculated bond strength of the order of 150 kJ mol^{-1} . As this behaviour is observed in both the trimer and tetramer, it would be a fair assumption that the polymer will behave in the same way.

The flanking PN bond lengthening that occurs when a metal coordinates to the phosphazene has been a feature of PN bonding that was previously unexplained. Theories had been developed for this phenomenon by Paddock and Dewar that were based on previous models of the phosphazene³²⁻³⁵. Simple σ donor behaviour for phosphazenes as found in this study does not explain the bond lengthening so the system was further investigated. This revealed that there was a donation of electron density from the flanking PN bond to the 4s orbital of the metal ion. The interaction is approximately 10% of the metal-phosphazene bonding strength. This interaction was independent of the metal ion geometry being only dependent on the distance of the metal centre from the PN bonds and the metal's ability to accept electron density. The aromaticity calculations suggest that the ratio of the negative hyper-conjugation to ionic bonding components increase when the metal is coordinated, however, due to the shifting effect of the metal ion this could not be confirmed. It would be reasonable to assume that this effect would also be present in the metal-rich polymer and other higher cyclomer systems.

The pendant substituent effect provided a direct contrast to the metal ion. Rather than withdrawing electron density from the phosphazene, the lone pair of the pyridine nitrogen donates electron density to the phosphazene ring. The pendant pyridine interacts with the phosphazene in two different modes; either capping or flanking. The capping pyridine interacts with all of the phosphorus atoms in the ring and the PN

bonds. The flanking pyridine has more specific interaction between the phosphorus atom that the pyridine is attached to and the flanking PN bonds. These substituent effects are significant enough to alter the bond lengths, explaining why there is not a direct relationship between the interaction of the PN flanking bond with the 4s orbital of the metal and the bond lengthening. The aromaticity calculations show that as the pyridine – phosphazene distance increases, the phosphazene ring becomes more aromatic. This occurs because as the pyridine lone pair donates electron density to the phosphorus atoms. The phosphorus atoms therefore require less of a contribution from negative hyper-conjugation to provide the phosphorus with electron density.

Two metal ions have the potential to communicate via the phosphazenes. In contrast to aromatic π systems that commonly facilitate metal communication, the phosphazene has electron density flowing in and out-of-ring plane. An ‘electron density bridge’ links metal ions and is formed because of the metals pulling equally and oppositely resulting in the nitrogen-p orbitals of the phosphazene ring being spread. These calculations explain the weak coupling that is observed in the magnetic susceptibility and ESR measurements and could be extended to polymer and cyclic systems.

Not only has this study revealed much information about the behaviour of cyclophosphazenes, it has also provided a new approach to studying such systems. Rather than refining the calculations to provide more accurate models of the bonding their interaction with a well-known system, the transition metal, was studied.

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