Donor Acceptor Bond in $[\text{N}(\text{PCl}_2)_3-\text{MCl}_3$ Adducts, a DFT Study and Comparison of Results with Experimental X-Ray Data

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Received 7 July 2011; Accepted 20 September 2011

Abstract: Molecular structures of $[\text{PCl}_2\text{N}]_3\text{-MCl}_3$ adducts, $\text{M}=\text{B}, \text{Al}, \text{Ga}, \text{In}, \text{Ti}$, have been studied employing HF, B3LYP*, B3LYP, PW91, BLYP, OLYP, BP and LDA methods using DZP basis set (as defined in Amsterdam Density Functional, ADF, package). Some aspects of adduct formation like considering the difference between Front and Back dihedral angles and also ring puckering showed that the $[\text{PCl}_2\text{N}]_3\text{-AlCl}_3$ is the most stable adduct comparing the others. Based on the comparison between the X-ray and theoretical geometrical parameters of $[\text{N}(\text{PCl}_2)_3(\text{AlCl}_3)]$ and $[\text{N}(\text{PCl}_2)_3(\text{GaCl}_3)]$, the LDA method and BP, PW91 and OLYP functionals combined with DZP basis set were found to yield the most satisfactory agreement. Results showed that with surprise, the LDA(DZP) method has the maximum matching with experimental data, comparing the others.

Keywords: Donor Acceptor Bond, ADF, DFT Calculation, Adduct.

Introduction

The concept of Lewis acids and bases is commonly discussed in some inorganic chemistry text books¹. The basic concepts used to understand the origin of the chemical properties were based on the ligand field theory (LFT)². Maybe one of the first reported literatures about computation was the application of LFT to compute the electronic structure of the complexes of symmetry lower than cubic, namely five coordinated C_{3v} complexes, which only the valence metal (nd) electrons are correlated on it³. Some considerations on the proper use of computational tools in transition metal chemistry are reviewed by A. Bencini⁴. There are many reported experimental and theoretical studies about cyclophosphazenes and particularly about the cyclic chlorinated trimer which is the main argument in this article⁵⁻¹².

The tautomerism observed between cyclo- $\text{N}_3\text{P}_3\text{Cl}_4(\text{OH})_2$ and cyclo- $\text{N}_3\text{P}_3(\text{OH})_6$ with cyclo- $\text{H}_3\text{N}_3\text{P}_3(\text{OH})_3$ ^{13,14} also document the Lewis basicity of the ring nitrogen atoms. It is also known that the basicity of $\text{N}_3\text{P}_3\text{Cl}_6$ is greater than higher-member rings of cyclophosphazene. This has been proven in the separation of trimer species from other cyclic products in the presence of *conc.* H_2SO_4 which causes the formation of $[\text{N}_3\text{P}_3\text{Cl}_6\text{H}]^+$ cation¹⁵. Here are the results of studies performed about the adducts formed between cyclotriphosphazene ring, $[\text{PCl}_2\text{N}]_3$ and Lewis acids of group 13.

The Amsterdam Density Functional (ADF) package that we use its 2009.01 version is a software for first-principles electronic structure calculations and can be use by academic and industrial researchers¹⁶. It is particularly popular in the research areas of homogeneous and heterogeneous catalysis, inorganic chemistry, heavy element chemistry, various types of spectroscopy, and biochemistry. Theoretical and technical foundations of the ADF program with a survey of the characteristics of the code (numerical integration, density fitting for the Coulomb potential, and STO basis functions) are reported¹⁷.

Experimental

All the calculations have been done using the ADF 2009 program¹⁶. The local density approximation (LDA)¹⁸ has been used as the simplest level of calculation for geometry optimizations at first. To evaluate the effect of different density functional on the geometry, the geometry optimization calculations employed a variety of exchange and correlation functional containing the B3LYP, B3LYP*, BLYP, PW91, OLYP and BP¹⁹⁻²³. The HF method has also been used for comparison. The STO valence basis sets used for all cases have been double-zeta plus 3d-type polarization function (DZP).

Results and Discussion

One of the best optimized structures for $[\text{NPCl}_2]_3\text{AlCl}_3$ which has shown very good agreements to its X-ray crystallographic data, including the X-ray structure, is presented in Figure 1.

Figure 1. X-ray molecular structure $[\text{NPCl}_2]_3\text{AlCl}_3$ and its PW91/DZ optimized geometry. Some nomenclatures in optimized geometry have been omitted for clarity.

The bond lengths of the $[\text{NPCl}_2]_3\text{AlCl}_3$ adduct which derived from its crystallographic data at various calculations and calculated related errors are given in Table 1. Meanwhile, the ADF software has restriction so that we could not define exact nomenclature as there was in Crystallographic results. Figure 2 shows the comparison of the results:

Figure 2. Comparison of calculated Al-N Bond lengths with exp. Al-N bond of $[\text{NPCl}_2]_3\text{AlCl}_3$ adduct.

As one can see from this figure, although all the methods have shown acceptable results, with less than 6.6% error, the LDA (DZP) method has shown the least error (0.7%) from the x-ray crystallographic data. Considering the average errors of various calculations, mentioned in the last row of Table 1, one can find the next trend for overall bond of $[\text{NPCl}_2]_3\text{AlCl}_3$ adduct (for adoption to experimental Data).

Adoption: LDA > BP > BLYP > HF > PW91 > B3LYP* > B3LYP > OLYP

Related errors: $0.7 < 2.2 < 2.9 < 4.5 < 5.3 < 6.0 < 6.1 < 6.6$

This trend confirms the LDA method as the best one between selected methods and levels of calculation for bond distances of $[\text{NPCl}_2]_3\text{AlCl}_3$ adduct. There are two crystallographic data, one for aluminum adduct and the other for gallium adduct^{24,25,26}. The curves of all donor-acceptor bond lengths for five mentioned adducts have been shown in Figure 3.

Figure 3. Comparison of donor-acceptor bond lengths for all adducts (and experimental for Al and Ga).

There is not actual bond between two cores if the calculated bond length is too much. Figure 3 indicates that except for Al, the OLYP is not a good level of calculation, because the calculated bond lengths are more than 3.5 angstrom.

Comparing the actual bond length of gallium adduct ($2.048 \text{ \AA}$) with calculated one ($2.3 - 2.8 \text{ \AA}$) confirms this deduction. The non regular curve of boron adduct in Figure 3 suggests that there is a difference between this adduct and the others. The experimental attempt for synthesis of $[\text{PCl}_2]_3\text{-BCl}_3$ adduct has been done in 2008 but the colorless crystals obtained

from the procedure were characterized to be the starting material, $[\text{PCl}_2\text{N}]_3$, not any adduct. At the same time, the adducts of $[\text{PCl}_2\text{N}]_3\text{-AlCl}_3$ and $[\text{PCl}_2\text{N}]_3\text{-GaCl}_3$ have been synthesized successfully.

Figure 3 shows that the calculated bond lengths for $[\text{PCl}_2\text{N}]_3\text{-AlCl}_3$ and $[\text{PCl}_2\text{N}]_3\text{-GaCl}_3$ adducts are a little more than experimental in all cases. If we can accept this advantage for the other adducts which have no X-ray data, then the LDA method would be the best method comparing the others. The calculated bond length for B-N, around $3.4 \text{ \AA}$, suggests that there is no actual donor-acceptor bond between boron and nitrogen and maybe this is the reason of non successful efforts for its synthesis. Furthermore, the most successful polymerizations of $(\text{PNCI}_2)_3$ involved using the catalyst BCl_3 ²⁶. This means that we can expect the BCl_3 constitute a weaker adduct with the cyclic trimer and recognizing this firmly, will help us finding the reason for the experimental evidence.

All the XCl_3 ($\text{X} = \text{B}, \text{Al}, \text{Ga}, \text{In}, \text{Tl}$) has triangular planar geometry, but they find somehow a little distortion after producing an adduct. The magnitude of this distortion can be considered as the stability of adducts. Wherever there is more distortion, there is more stability and of course, the less bond length of the adduct.

Figure 5 shows the calculated Cl-X-N angles in various Methods and levels (all using DZP basis set) in which $\text{X} = \text{B}, \text{Al}, \text{Ga}, \text{In}, \text{Tl}$. Except for the boron case as an abnormal adduct, the other adducts, specially the aluminum and gallium cases, show interesting results. In fact, there is no significant difference between BP, BLYP, LDA and PW91 levels for Cl-X-N angle, but the OLYP level gave the least value for this angle, so it would be the worst case.

Figure 4. Calculated X-N bond length, PW91(DZP).

The Cl-Al-N and Cl-Ga-N angles are less than related experimental angles in all calculations, so maybe one can say that the more calculated value for this angle, the more adaption to x-ray results. As one can see, the investigated N-X-Cl angle is becoming less as we come down from Al to Tl in group 13 of periodic table. It means that the XCl_3 moiety of adduct is becoming more planar from Al to Tl. The trend of N-X-Cl angle, calculated in LDA method, would be as following:

$$\text{Tl} - \text{N} - \text{Cl} < \text{In} - \text{N} - \text{Cl} < \text{Ga} - \text{N} - \text{Cl} < \text{Al} - \text{N} - \text{Cl}$$

We choose the $[\text{PCl}_2\text{N}]_3\text{-AlCl}_3$ adduct as the best one hereafter. All calculated bond lengths and bond angles with related errors are collected in Table 1 and Table 2. Although we found the best results in LDA(DZP) method, we consider the PW91(DZP) as a good level of GGA method (and close to LDA in results) henceforward according to the simplicity of LDA method in the calculation.

Table 1. Bond lengths of [NPCl₂]₃AlCl adduct and related errors, calculated in various methods and levels.

Empirical Bond length(A)			Calculated Bond length(A)									
			Methods / Error									
Crystallographic nomenclature	Bond length(A)	Equivalent Cal. nomenclature	LDA (%Error)	B3LYP* (%Error)	B3LYP (%Error)	PW91 (%Error)	OLYP (%Error)	BLYP (%Error)	BP (%Error)	HF (%Error)		
1 Al-N	1.982	Al-N	2.036 (2.7)	2.196 (10.8)	2.199 (10.9)	2.131 (7.5)	2.179 (9.9)	2.174 (9.7)	2.117 (6.8)	2.153 (8.6)		
2 P2-N2	1.561	P2-N3	1.571 (0.6)	1.609 (3.1)	1.608 (3.0)	1.607 (2.9)	1.802 (15.4)	1.595 (2.2)	1.588 (1.7)	1.580 (1.2)		
3 P2-N1	1.6521	P2-N6	1.647 (-0.3)	1.670 (1.1)	1.671 (1.1)	1.664 (0.7)	1.660 (0.5)	1.680 (1.7)	1.669 (1.0)	1.645 (-0.4)		
4 P1-N2	1.572	P1-N3	1.582 (0.6)	1.800 (14.5)	1.800 (14.5)	1.800 (14.5)	1.800 (14.5)	1.603 (2.0)	1.598 (1.6)	1.800 (14.5)		
5 P2(A)-N1	1.652	P5-N6	1.647 (-0.3)	1.670 (1.0)	1.671 (1.2)	1.665 (0.8)	1.660 (0.5)	1.679 (1.6)	1.669 (1.0)	1.645 (-0.4)		
6 P1-N(2A)	1.572	P1-N4	1.582 (0.6)	1.800 (14.5)	1.800 (14.5)	1.800 (14.5)	1.800 (14.5)	1.604 (2.0)	1.588 (1.0)	1.800 (14.5)		
7 P2(A)-N(2A)	---	P5-N4	1.572	1.607	1.608	1.607	1.660	1.595	1.598	1.580		
8 ¹ Al-Cl	2.109	¹ Al-Cl	2.108 (0.0)	2.155 (2.2)	2.161 (2.5)	2.130 (1.0)	2.130 (1.0)	2.144 (1.7)	2.132 (1.1)	2.111 (0.1)		
9 ¹ P2-Cl	1.969	¹ P2-Cl	1.986 (0.9)	2.038 (3.5)	2.038 (3.5)	2.020 (2.6)	2.010 (2.1)	2.041 (3.7)	2.014 (2.3)	1.980 (0.6)		
10 ¹ P1-Cl	1.975	¹ P1-Cl	1.999 (1.2)	2.090 (5.8)	2.090 (5.8)	2.090 (5.8)	2.090 (5.8)	2.053 (3.9)	2.029 (2.7)	2.090 (5.8)		
11 ¹ P2(A)-Cl	1.969	¹ P5-Cl	1.987 (0.9)	2.038 (3.5)	2.040 (3.6)	2.019 (2.5)	2.010 (2.1)	2.041 (3.7)	2.014 (2.3)	1.979 (0.5)		
Average Error for each level			0.7	6.0	6.1	5.3	6.6	2.9	2.2	4.5		

¹ Average bond lengths are reported for both experimental and calculations.

The calculated FTIR spectrum of this adduct using PW91(DZP) method has been shown in Figure 5.

Some of the related frequencies with absorption Intensity more than 8, are collected in Table 3. One of the most important calculated frequencies is the simultaneous symmetric stretching of P(2)-N(3) and P(5)-N(4) bonds, which should be observed at 1041 cm^{-1} . The two near calculated frequencies at 965 and 952 are due to non-symmetric stretching of mixed P-N bonds. The vibrations of P-N bonds in similar compounds observed^{27,28} between $1245\text{--}1300\text{ cm}^{-1}$.

Figure 5. Average of Cl-X-N angle, calculated in various methods and levels.

The next frequency, 730 cm^{-1} , is due to simultaneous symmetric stretching of P(2)-N(6) and P(5)-N(6) bonds which effect on Al-N bond too. The Al-N bond compress when the two mentioned bonds pull, but the Al center is without any movement. The five later vibrations mentioned in Table 3 is related to breathing of cyclotriphosphazene ring, calculated between $497\text{--}582\text{ cm}^{-1}$. Consider the N6 atom in the center of a triangle containing Al, P2 and P5. The two frequencies, 367 and 377 cm^{-1} , is related to out of plane movement of the N6 in this triangle. The symmetric stretching of Al-N bond should be observed at 232 cm^{-1} and finally, the rocking motion of cyclotriphosphazene ring calculated at $204\text{--}209\text{ cm}^{-1}$. The cyclotri-phosphazene ring has vibrations like a cradle in these frequencies.

Table 2. Bond angels of $[\text{NPCl}_2]_3\text{AlCl}_3$ adduct and related errors, calculated in various methods and levels.

Empirical Bond Angles			Calculated Bond Angles (Methods/Error)							
Crystallographic nomenclature	Bond Angle	Equivalent cal. nomenclature	LDA (%Error)	B3LYP* (%Error)	B3LYP (%Error)	PW91 (%Error)	OLYP (%Error)	BLYP (%Error)	BP (%Error)	HF (%Error)
1 N2-P2-N1	116.51	N3-P2-N6	116.6 (0.1)	121.1 (3.9)	120.9 (3.8)	121.7 (4.5)	121.6 (4.4)	117.6 (0.9)	117.5 (0.8)	120.2 (3.2)
2 N(2A)-P2(A)-N1	---	N4-P5-N6	116.5	121.1	120.9	120.8	121.6	117.7	117.5	120.2
3 N2-P1-N(2A)	115.42	N3-P1-N4	116.2 (0.7)	119.7 (3.7)	119.7 (3.7)	119.7 (3.7)	119.7 (3.7)	116.5 (0.9)	116.8 (1.2)	119.7 (3.7)
4 P1-N2-P2	125.33	P1-N3-P2	124.8 (-0.4)	116.5 (-7.0)	116.7 (-6.9)	116.2 (-7.3)	115.9 (-7.5)	124.3 (-0.8)	124.1 (-1.0)	116.1 (-7.4)
5 P1- N(2A)-P2(A)	---	P1-N4-P5	124.8	116.6	116.7	116.3	116.0	124.3	124.1	116.1
6 P2-N1- P2(A)	117.68	P2-N6-P5	119.6 (1.6)	121.5 (3.2)	121.7 (3.4)	120.8 (2.6)	120.8 (2.7)	117.4 (-0.2)	117.9 (0.2)	123.0 (4.5)
7 Cl-P1-Cl	102.84	Cl-P1-Cl	102.8 (0.0)	100.8 (-2.0)	100.8 (-2.0)	100.8 (-2.0)	100.8 (-2.0)	102.4 (-0.4)	102.5 (-0.3)	100.8 (-2.0)
8 Cl-P2-Cl	104.75	Cl-P2-Cl	105.0 (0.2)	104.3 (-0.4)	104.4 (-0.3)	104.3 (-0.4)	104.3 (-0.4)	104.3 (-0.4)	104.6 (-0.1)	105.1 (0.3)
9 Cl- P2(A)-Cl	---	Cl-P5-Cl	105.0	104.4	104.4	104.3	104.3	104.4	104.6	105.1
10 ¹ Cl-Al-Cl	112.44	¹ Cl-Al-Cl	114.7 (2.0)	114.4 (1.7)	114.4 (1.7)	114.1 (1.5)	113.5 (0.9)	113.6 (1.0)	114.43 (1.8)	113.6 (1.0)
11 ¹ N-Al-Cl	106.32	¹ N-Al-Cl	103.5 (-2.7)	103.9 (-2.3)	104.0 (-2.2)	104.3 (-1.9)	105.1 (-1.1)	103.8 (-2.4)	103.9 (-2.3)	105.0 (-1.2)
Average Error for each level			0.2	0.1	0.2	0.1	0.1	-0.2	0.0	0.3

¹Average bond angles are reported for both experimental and calculations.

Table 3. Calculated frequencies and related absorption Intensity for $[\text{PCl}_2\text{N}]_3\text{-AlCl}_3$ adduct, PW91(DZP).

Frequency, cm^{-1}	Absorption Intensity (Km/mole)	Frequency, cm^{-1}	Absorption Intensity (km/mole)
198.185360	43.230191	525.097586	28.070726
204.182931	8.203172	540.114492	66.924728
232.525013	31.176488	540.941599	47.559648
367.282559	22.792879	561.273395	61.352417
376.850398	65.222285	582.392269	471.493092
446.967871	42.363302	730.436060	56.911300
474.046453	236.787447	951.988503	42.710483
496.758103	315.745354	965.360109	661.005724
510.820699	142.114887	1041.406343	1003.231081

Another aspect of adduct formation which could be considered, will be the distortion that takes place in the ring structure and due to this, the ring takes a chair like shape that affects the bond lengths of the ring. We divided the adduct structure into two parts, namely front and back sections. This is clearly shown in Figure 8 and the results are shown in Table 4.

Figure 6. Comparison of N-X-Cl angle of adducts (calculated in LDA(DZP)).**Table 4.** Front and back angle in adduct structures, PW91(DZP).

Adduct	$[\text{NPCl}_2]_3\text{BCl}_3$	$[\text{NPCl}_2]_3\text{AlCl}_3$	$[\text{NPCl}_2]_3\text{GaCl}_3$	$[\text{NPCl}_2]_3\text{InCl}_3$	$[\text{NPCl}_2]_3\text{TlCl}_3$
Front angle	13.7	22.2	21.0	20.3	20.5
Back angle	8.6	1.3	5.8	6.0	2.9

As it can be seen from the Table 4, there is not a large difference between the front and back angles in the first adduct ($[\text{NPCl}_2]_3\text{BCl}_3$) in comparison with the others. This means that again there is no specific interaction between BCl_3 and $[\text{NPCl}_2]_3$. The more difference between these two angles means that the donor acceptor bond is stronger. Figure 7 shows the results as curves.

Figure 7. The FTIR spectrum of $[\text{PCl}_2\text{N}]_3\text{-AlCl}_3$ adduct, PW91(DZP).

Some of the related frequencies with absorption Intensity more than 8, are collected in table 3. During the adduct formation, the cyclotriphosphasene ring puckers and its bonds take the different lengths. These bond lengths are compared in the form of trends in Table 5. We define the two nearest P-N bond to acid center as the front pair, so we have two P-N bonds as middle and finally, two P-N bonds as back. As it can be seen, the two by two bonds are different in all adducts.

Table 5. Comparison of three types of P-N bond lengths in $[\text{N}(\text{PCl}_2)_3]\text{MCl}_3$ adducts, PW91(DZP).

Adduct	Front P-N bonds	Middle P-N bonds	Back P-N bonds
$[\text{N}(\text{PCl}_2)_3]\text{BCl}_3$	1.598	1.615	1.800
	1.598	1.615	1.800
$[\text{N}(\text{PCl}_2)_3]\text{AlCl}_3$	1.664	1.607	1.800
	1.665	1.607	1.800
$[\text{N}(\text{PCl}_2)_3]\text{GaCl}_3$	1.634	1.610	1.801
	1.633	1.612	1.800
$[\text{N}(\text{PCl}_2)_3]\text{InCl}_3$	1.636	1.609	1.800
	1.636	1.609	1.800
$[\text{N}(\text{PCl}_2)_3]\text{TlCl}_3$	1.630	1.610	1.800
	1.631	1.610	1.800

From all data given above, it can be concluded that the aromaticity of cyclophosphazene's ring, which attached to MCl_3 , is not typical of aromatic compounds, because in traditional aromatic rings won't pucker if any substituent attached to them, while the six P-N bonds of $[\text{N}(\text{PCl}_2)_3]$ divided to 3 pairs as mentioned above²⁹.

Conclusion

Comparison of calculated Al-N Bond lengths with exp. Al-N bond of $[\text{NPCl}_2]_3\text{AlCl}_3$ adduct, found from X-Ray data, showed interesting result. Although maybe we expect somehow the high level methods such as B3LYP or B3LYP* show the nearest results to the x-ray crystallographic data for Al-N bond, but it did not occur. In fact, the trend for adoption of this bond to the experimental datum has been shown as following:

The bond length of the adducts became more as we go from up to down of group 13. It means that the strongest acid-base bond is within the $[\text{PCl}_2\text{N}]_3\text{-AlCl}_3$ adduct. On the other hands, the acid-base bond strength for the group 13 adduct of cyclotriphosphazene, $[\text{PCl}_2\text{N}]_3$, would be as the following trend:

One of the most important advantages of this research is about calculation results of BCl_3 and its related adduct. The nitrogen atoms bear the most population, 52.66%, of the HOMO in the trimer molecule, and as it is expected this electron pair is located on P_z orbital of the nitrogen. The next most populated atom in HOMO of cyclotriphosphazene ring is one of the chlorine atoms which specifies 26.27% of the HOMO to itself. This proportion is almost half of electron density that nitrogen contributes and due to this, it is concluded that the tendency interacting with an empty orbital of a Lewis acid is doubled. Kapička *et. al.* also reported that HOMO in the molecular structure of trimer species has e' symmetry and is consisted of two π -radial nonbonding MOs which is suitable for σ -interaction with an electron acceptor in the ring plane direction³⁰.

Acknowledgment

This work has been supported by the University of Payame Noor (Iran). We would like to thank the Mashhad branch of Payame Noor University, for further support of this research.

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