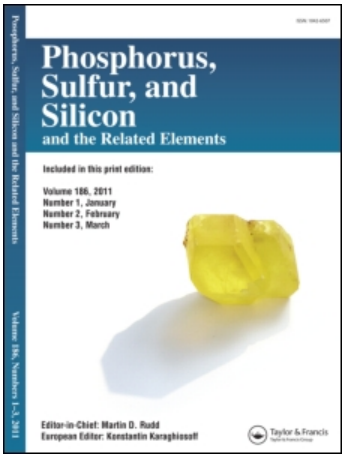

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Synthesis and Theoretical Study of Vanadium Oxotrichloride Complex of Hexachlorotriphosphazene and *Ab Initio* Investigations of Some Simple Cyclic Triphosphazenes

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SYNTHESIS AND THEORETICAL STUDY OF VANADIUM OXOTRICHLORIDE COMPLEX OF HEXACHLOROTRIPHOSPHAZENE AND *AB INITIO* INVESTIGATIONS OF SOME SIMPLE CYCLIC TRIPHOSPHAZENES

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$N_3P_3Cl_6 \cdot VOCl_3$ results from the reaction between vanadium oxotrichloride and hexachlorotriphosphazene in dichloroethane. Vanadium oxotrichloride coordination with nitrogen atom in the phosphonitrile ring was detected from the IR spectrum of the product. Quantum-chemistry calculations for $(NPX_2)_3$ ($X = H$, F, Cl, NH_2) were carried out as well. A comparative study of some basic characteristics of the simple cyclotriphosphazenes' electronic structures was carried out. Quantum-chemistry calculations also were done for the complex of hexachlorophosphazene with vanadium oxotrichloride. It is shown that the nitrogen atom in phosphazenes plays an essential role for donor-acceptor interactions and is the most preferable atom for binding with a vanadium atom.

Keywords: Quantum-chemical calculation; triphosphazenes; vanadium oxotrichloride

Phosphazenes, inorganic hetero-ring and chain compounds containing alternate phosphorus and nitrogen atoms in their skeletons, are unique carriers for transition metals, owing to their ability to serve as versatile multifunctional ligands.[1,2]

So far many products have been reported from the interactions of cyclophosphazenes with metal halides. In most cases, the structures of the adducts are not known, but at least two different classes appear to exist. In the first group, a complex is formed by ionization of a halide ion from phosphorus and complexation of it to a metal halide.[3–12] The second group of metal halide phosphazene complexes includes those

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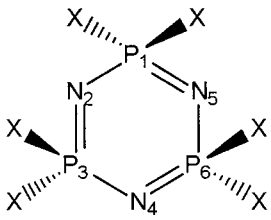
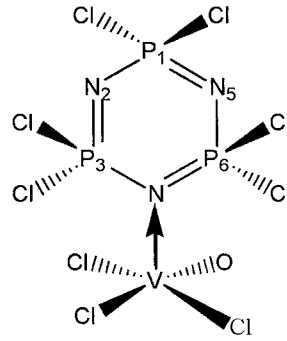


X=H(1), F(2), Cl(3), NH_2(4)



[$VOCl_3$ (5)] (6)

FIGURE 1 Structures of the studied compounds (**1–6**).

compounds that are formed by coordination of the metal to the skeletal nitrogen atom.[13–18]

The reaction of trichlorooxovanadium (V) with a number of monodentate oxygen and nitrogen donor ligands (L) and bidentate ligands (B) results in the formation of $VOCl_3$2L and $VOCl_3$B respectively.[19–22]

By using standard ab initio methods, the electronic structures, vibrational spectra and optimal geometries of cyclo-$(NPX_2)_3$ with X = H, F, Cl were investigated.[23–32]

In this article we carried out both theoretical and experimental studies. Electronic structures of the cyclic triphosphazenes shown in Figure 1, are calculated by using two ab initio methods: Hartree-Fock (HF) and Density Functional Theory (DFT). Quantum-chemistry modeling of the $VOCl_3$ interaction with $N_3P_3Cl_6$ (see system 6 in Figure 1) is also carried out. The total electronic energy variations dependence on the V–N_4 distances changes is discussed.

EXPERIMENTAL SECTION

$VOCl_3$ and $N_3P_3Cl_6 \cdot VOCl_3$ are very sensitive to air and/or moisture. All manipulations on them were carried out in a pure nitrogen or argon atmosphere. For the reason, Glove box techniques were used. Solvents were distilled and dried by appropriate agents before using. Vanadium oxotrichloride and hexachlorocyclotriphosphazene were purchased from Fluka. Infrared spectra were measured as KBr pellets on Bio-Rad FT-IR Spectrometer. Elemental analyses were carried out on 175C Fotometer Merck SQ 118, Simaa 6000 Model.

Reaction of $VOCl_3$ with Hexachlorocyclotriphosphazene

1,2 Dichloroethane (10 ml) was added to a 100 ml flask containing 0.5965 gram ($3.448 * 10^{-3}$ mmol) of $VOCl_3$.

$$(PNCl_2)_3 + VOCl_3 \rightarrow (PNCl_2)_3 \cdot VOCl_3 \quad (1)$$

The solution was cooled in N_2/acetone slush bath. Then newly sublimed hexachlorocyclotriphosphazene dissolved in 10 ml 1,2 dichloroethane was added slowly. At room temperature, the colour of solution changed (from red to dark red). Solution was refluxed 1 h; it was left for 1 week at room temperature for precipitating. Residue was obtained from the mixture by using a centrifuge. The solid was washed with 1,2 dichloroethane three times. After drying, the elemental analyses, Electron Spin Resonance (ESR), and infrared (IR) spectroscopy of the solid were carried out.

To regenerate hexachlorocyclotriphosphazene, $N_3P_3Cl_6 \cdot VOCl_3$ was hydrolysed by cold water. The atomic absorption analysis (Perkın-Elmer-SIMAA 6000) was carried out for the vanadium determination in the hydrolyzed solution (found for $N_3P_3Cl_6 \cdot VOCl_3$: V, 9.94%; calculated: V, 9.77%). Spectrophotometric analysis for Cl determination was done on UV visible spektrophotometre (Shimadzu, 2101 PC) (found: Cl, 20.35%; calculated: Cl, 20.42%). Nitrogen analysis of solid part was carried out on Carlo-Erba 1106 Elemental Analyser (found N, 8.01%, calculated N, 8.00%).

The same reaction was done by using different ratios of hexachlorocyclotriphosphazene/$VOCl_3$, but the same results were obtained. In ESR, there was no peak about vanadium. It tells in favor of the V(5+) oxidation state as to $VOCl_3 \cdot N_3P_3Cl_6$. Also, the peak absence tells us that the molecule $[VOCL_4]^- \cdot [N_3P_3Cl_5]^+$ is not being formed.

IR values of $N_3P_3Cl_6$ (cm^{-1}): 520, 600, 874, 1252, 1315. IR values of the complex (cm^{-1}): 417, 533, 805, 984, 1096, 1220, 1320.

METHOD OF AB INITIO CALCULATIONS

Ab initio calculations for four different cyclotriphosphazene systems $(NPX_2)_3$ (X = H, F, Cl, NH_2) and the complex $[N_3P_3Cl_6 \cdot VOCl_3]$ were done, aiming to study the dependence between electronic structure of phosphazene ring and the nature of atom or atomic group attached to the phosphorus atom. The systems' electronic structures were calculated by means of HF and DFT methods. The Becke's three-parameter hybrid functional[33] combined with the Lee, Yang, and Parr (LYP) correlation functional[34] and denoted as B3LYP[35] was employed in the DFT calculations. Ab initio molecular orbital calculations were performed

by using the standard GAUSSIAN 98W program package[36] for the STO-3G[37,38] and 6-31G(d,p)[39] basis sets. There are many experimental x-ray structure data for some high-symmetric derivatives[40–48] with small deviations from symmetric planar phosphazene rings, which are ascribed to solid-state effects. Geometries of the structures have been taken from the x-ray data. For quantum-chemistry calculations, the ring of $(NPX_2)_3$ is taken as regular and planar ring (D_{3h} symmetry). Experimental data indicates that the P—N bond length is not a simple function of substituents electro-negativity. To study the mechanism of $VOCl_3$ interaction with $N_3P_3Cl_6$, the electronic structure of a free molecule $VOCl_3$ was calculated in addition.

RESULTS AND DISCUSSION

As seen from the IR spectrum data, the phosphazene trimer has a symmetric structure, but in the complex this symmetric structure is broken. For this reason, strong stretching P—N (1252 cm^{-1}) peak in the trimer decreases to 1096–1220 cm^{-1} and splits into two peaks. This means that nitrogen atom of trimer is coordinated with vanadium. When the complex is being formed, electron density on the $P—N_4$ bond decreases. The decrease is supposed to be attributed to the decrease in the π-electron interaction on the skeletal bonds. The coordination can be explained by the lone pair of electrons participation in an sp^2-orbital of the cyclophosphazene formation. The pair of electrons does not any longer participate in the π-system of the ring.

For the compound obtained from reaction of the phosphazene monomer and $VOCl_3$, the peak at 994 cm^{-1} represents V=O band, and peaks at 1215 ve 1322 cm^{-1} represent P—N and P=N stretching frequency. The ESR measurements on solid $N_3P_3Cl_6 \cdot VOCl_3$ indicated no signal, and this is compatible with the oxidation state for vanadium V^{5+} where the electron confiquration is formally d^0.

Geometrical and Electronic Structure of Cyclo-$(NPX_2)_3$

To explore the coordination capabilities of various phosphazenes to $VOCl_3$, their electronic structure was studied. Calculated geometries and some experimental data of the cyclo-$(NPX_2)_3$ with X=H, F, Cl and NH_2 are compared in Table I. As the table shows, the best results that agree with the experimental data for all X are calculated by HF method with the basis set 6-31G(d). Some basic characteristics of the electronic structure calculated for all compounds under study show the symmetric charge distribution on atoms (see Table II).

TABLE I Structural Parameters of $(NPX_2)_3$ as Determined by Ab Initio Geometry Optimizations in Various Basis Sets

X	Basis set	Method	R_{N-P}	R_{P-X}	P–N–P	N–P–N
Cl	STO-3G	HF	1.72	2.10		
		DFT	1.74	2.16	110.02	129.93
	6-31G(d)	HF	1.57	1.99	123.76	116.24
			(1.581)[a]	(1.993)	(121.4)	(118.4)
		DFT	1.60	2.03		
	DZP	HONDO	1.58	1.99	123.90	116.10
F	STO-3G	HF	1.71	1.61	111.86	128.44
		DFT	1.75	1.66	108.97	131.05
	6-31G(d)	HF	1.56	1.53	123.42	116.56
			(1.570)	(1.529)	(120.4)	(119.6)
		DFT	1.59	1.56		
	DZP	HONDO	1.59	1.54	123.50	116.50
H	STO-3G	HF	1.77	1.38	108.95	131.04
		DFT	1.78	1.42	107.37	132.62
	6-31G(d)	HF	1.59	1.39	123.41	116.59
		DFT	1.61	1.41	118.70	
	DZP	HONDO	1.61	1.40	123.70	116.60
NH_2	STO-3G	HF	1.73	1.73	107.95	122.91
		DFT	1.75	1.82	106.86	125.23
	6-31G(d)	HF	1.59	1.67	124.07	114.18
		DFT	1.75	1.80	106.87	125.23

[a]Values in parentheses represent the mean values as determined from the crystal structure.[40,44]

Ab initio calculations of cyclo-$(NPX_2)_3$ molecules (X=H, F, Cl, NH_2) were carried out by using basis sets that differ in the number of polarization functions on the P, Cl and N atoms. In Figure 2 the charge changes for the N, P atoms and X substituent are given for different

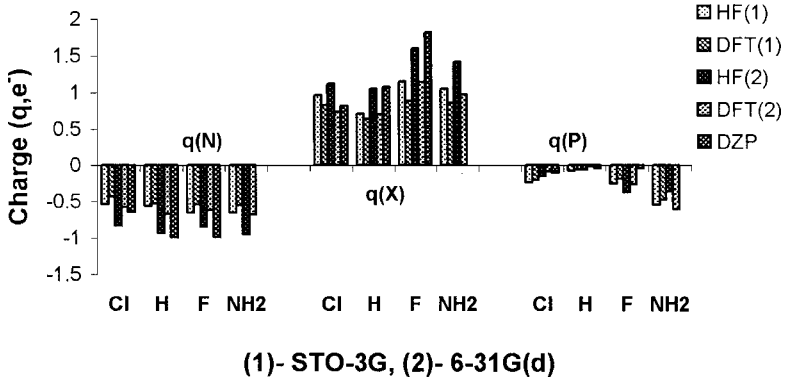


FIGURE 2 The charges on the N, X, and P atoms dependency on the method and basis set chosen.

TABLE II Some Electronic Structure Data of Cyclo-$(NPX_2)_3$ in Various Basis Sets and Methods

X	Basis set	Method	$E_{(SCF)}$ (a.u.)	E_{HOMO}	E_{LUMO}	q_N	q_P	q_X	Q_{P-X}	Q_{N-P}/Q_{V-P}
Cl	STO-3G	HF	−3899.00	−0.353	0.098	−0.53	0.96	−0.23	0.15	0.22
		DFT	−3905.64	−0.228	0.086	−0.43	0.83	−0.20	0.13	0.21
	6-31G(d)	HF	−3942.55	−0.438	0.080	−0.83	1.12	−0.15	0.30	0.47
		DFT	−3949.63	−0.308	−0.095	−0.57	0.73	−0.08	0.26	0.43
	DZP[a]	Ab initio (HONDO/7)		−0.435	0.088	−0.64	0.82	−0.10		
F	STO-3G	HF	−1759.98	−0.296	0.328	−0.65	1.15	−0.25	0.16	0.22
		DFT	−1764.68	−0.141	0.090	−0.54	0.89	−0.18	0.14	0.19
	6-31G(d)	HF	−1782.43	−0.479	0.182	−0.85	1.60	−0.37	0.34	0.51
		DFT	−1787.60	−0.333	0.001	−0.62	1.14	−0.26	0.34	0.44
	DZP	Ab initio (HONDO/7)		−0.489	0.199	−0.99	1.82	−0.04		
H	STO-3G	HF	−1175.19	−0.245	0.388	−0.56	0.71	−0.07	0.31	0.20
		DFT	−1177.92	−0.084	0.160	−0.52	0.64	−0.06	0.28	0.20
	6-31G(d)	HF	−1188.98	−0.381	0.173	−0.93	1.05	−0.06	0.34	0.49
		DFT	−1191.88	−0.256	0.022	−0.67	0.70	−0.01	0.30	0.47
	DZP	Ab initio (HONDO/7)		−0.384	0.144	−0.99	1.07	−0.04		
NH_2	STO-3G	HF	−1501.21	−0.240	0.393	−0.65	1.05	−0.54	0.26	0.22
		DFT	−1505.73	−0.099	0.140	−0.55	0.86	−0.47	0.19	0.21
	6-31G(d)	HF	−1519.34	−0.356	0.206	−0.95	1.41	−0.06	0.35	0.50
		DFT	−1505.73	−0.099	0.140	−0.55	0.86	−0.48	0.21	0.21

[a]From Breza.[32]

methods and basis sets. When the 6-31G(d) basis set is taken instead of STO-3G, this causes substantial polarization of charges on the N and P atoms of the heterocycle. The negative charge increase on the N atom and positive charge increase on the P atom are observed for all X substituents under this change (see Figure 2). It happens due to the nature of bonds that are being formed as a result of different orbitals overlapping. For the compound with X=Cl, d-orbitals of chlorine are involved in the interaction with the heterocycle that causes an additional system of π-bonds formation.

As a result, new channels for the electronic density redistribution are being formed. In this case, the homogenous delocalization on the atoms takes place. The Cl atom replacement by NH_2 groups causes the increase of negative charges on the N atoms of the heterocyclic system and substituent X. At the same time, the positive charges on the atoms of phosphorus also increase. Multi-orbital interaction in the systems with Cl and N leads to the more strong bonds formation in the heterocycle of the phosphazene.

For the compounds with X=H a small negative charge is observed on the H atom. In this case hydrogen and phosphorus interact with σ-bond formation. As seen from Figure 2, there is no one-valued dependency on the parameters of calculations in the charge changes for all X substituents. When the number of functions in the basis set grows, calculations show a considerable redistribution of electron density on bonds. This also concerns the N—P and P—X bonds (see Figure 3), and as a consequence of the charge redistribution, the bonds' lengths decrease (see Table I).

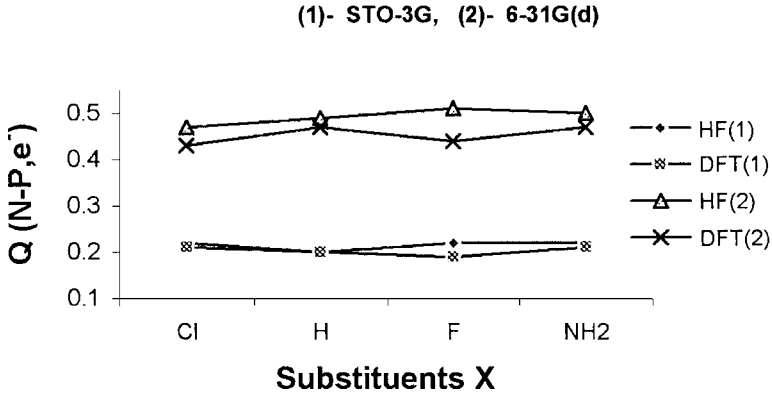


FIGURE 3 The electron density changes on the N–P bond of heterocycle and their dependence on the method and basis set chosen.

The donor-acceptor interaction between cyclo-$(NPX_2)_3$ molecules (with X=H, F, Cl, NH_2) and $VOCl_3$ was studied, based on the perturbation theory application to the data on their electronic structures. The nature of the frontier HOMO and LUMO plays an essential role in this interaction and the compounds' chemical reactivity. As the analysis of the LCAO coefficients on the HOMO and LUMO of reacting molecules shows, their maximal values belong to the N_4 atom on the HOMO and V atom on the LUMO. The pertrubation theory makes it possible to calculate the total energy change (ΔE) for the two interacting orbitals (the HOMO as donor and the LUMO as acceptor) in the case when the bond between the atom N_4 of the phosphazene and atom V of $VOCl_3$ is being formed.[49,50] The energy variations ΔE_{ij} for interacting frontier orbitals is calculated from the following equation:

$$\Delta E_{ij} = \frac{q_N q_V}{R_{V-N}\varepsilon} + 2\sum_{HOMO}\sum_{LUMO}\frac{\left(C_i^{HOMO} C_j^{LUMO}\Delta\beta_{V-N}\right)^2}{E_i^{HOMO} - E_j^{LUMO}},$$

where R_{V-N} is the distance between atoms N_4 and V; ε is the dielectric constant; C_i^{HOMO}, C_j^{LUMO} are AO coefficients on the HOMO and LUMO of atoms N_4 and V; $\Delta\beta_{V-N}$ is the resonance integral variation under the orbitals of the N_4 and V atoms interaction at the R_{V-N} distance; and, finally, E_i^{HOMO}, E_j^{LUMO} are energies of the HOMO and LUMO of isolated molecules $(NPX_2)_3$ and $VOCl_3$.

In Figure 4 the values of ΔE_{ij} are given for different X. As seen from the Figure 4, the bond V–N_4 becomes the most stable when X=Cl and X=NH_2 (their ΔE_{ij} are maximal). Inconsiderable energy changes are observed for phosphazenes with X=H and X=F. Thus, the probability of the complex (phosphazene-$VOCl_3$) formation increases in the row of H, F, Cl, NH_2. The experiments show that the reaction of

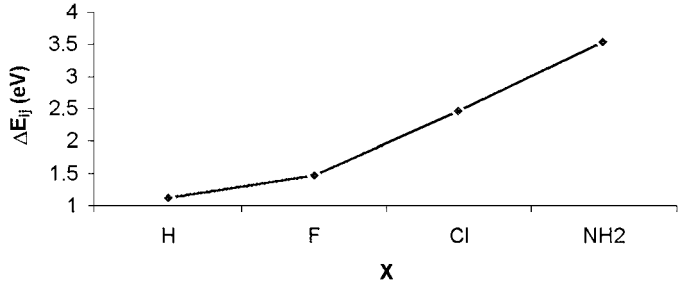


FIGURE 4 ΔE_{ij} variations (bond V–N_4) for different X.

hexachlorocyclotriphosphazene with $VOCl_3$ gives a stable compound. The same is to be said about phosphazene with X=NH_2.

Quantum-Chemical Modeling of the $VOCl_3$ Interaction with $N_3P_3Cl_6$

Let us consider in more details the interaction between $VOCl_3$ and $N_3P_3Cl_6$. Some electronic characteristics of the investigated molecules are given in Table III. Below, wave functions are shown for $VOCl_3$:

$$\varphi^{\mathrm{HOMO}} \approx -0.21d_{xz}^{\mathrm{V}} - 0.58p_z^{\mathrm{O}} + 0.16p_z^{\mathrm{Cl}};$$
$$\varphi^{\mathrm{LUMO}} \approx 0.14p_z^{\mathrm{V}} + 0.46d_{z2}^{\mathrm{V}} - 0.48d_{xz}^{\mathrm{V}} + 0.59d_{x2-y2}^{\mathrm{V}}.$$

As seen, the LUMO is capable of playing an important role in the Cl interaction with other organic molecules, as it was mentioned before. Analysis of the nature of the frontier orbitals of $VOCl_3$ shows that HOMO consists of π-orbitals of metal, oxygen and chlorine. Analysis of the phosphazene structures relative to their atomic charges and properties of molecular orbitals has shown that the most probable place for the attack in the molecule of phosphazene is nitrogen in the heterocycle. This atom is represented with the highest weight in the HOMO.

Oxochlorovanadyl binds with the atom of nitrogen for the account of its free d_π-orbitals that form the LUMO (see Figure 5). The charges distribution under different X (see Table III) bears the evidence of the fact that the negative charge decrease on the atom of nitrogen is the result

TABLE III Data on the Electronic Structure of $VOCl_3$ and its Complex with $(NPCl_2)_3$, Calculated by the HF Method

Systems	$VOCl_3$		$VOCl_3 + (NPCl_2)_3$	
Parameter	STO-3G	6-31G(d)	STO-3G	6-31G(d)
E_{HOMO} (a.u.)	−0.419	−0.474	−0.336	−0.410
E_{LUMO} (a.u.)	0.084	−0.035	0.051	−0.004
q_{V} (ē)	1.17	1.11	1.08	1.09
q_{O} (ē)	−0.22	−0.34	−0.25	−0.35
q_{Cl} (ē)	−0.32	−0.26	−0.42	−0.33
q_{N4} (ē)	—	—	−0.53	−1.10
$Q_{\mathrm{V—O}}$ (ē)	0.43	0.25	0.42	0.24
$Q_{\mathrm{V—Cl}}$ (ē)	0.23	0.30	0.20	0.28
$Q_{\mathrm{V—N}}$ (ē)	—	—	0.20	0.09

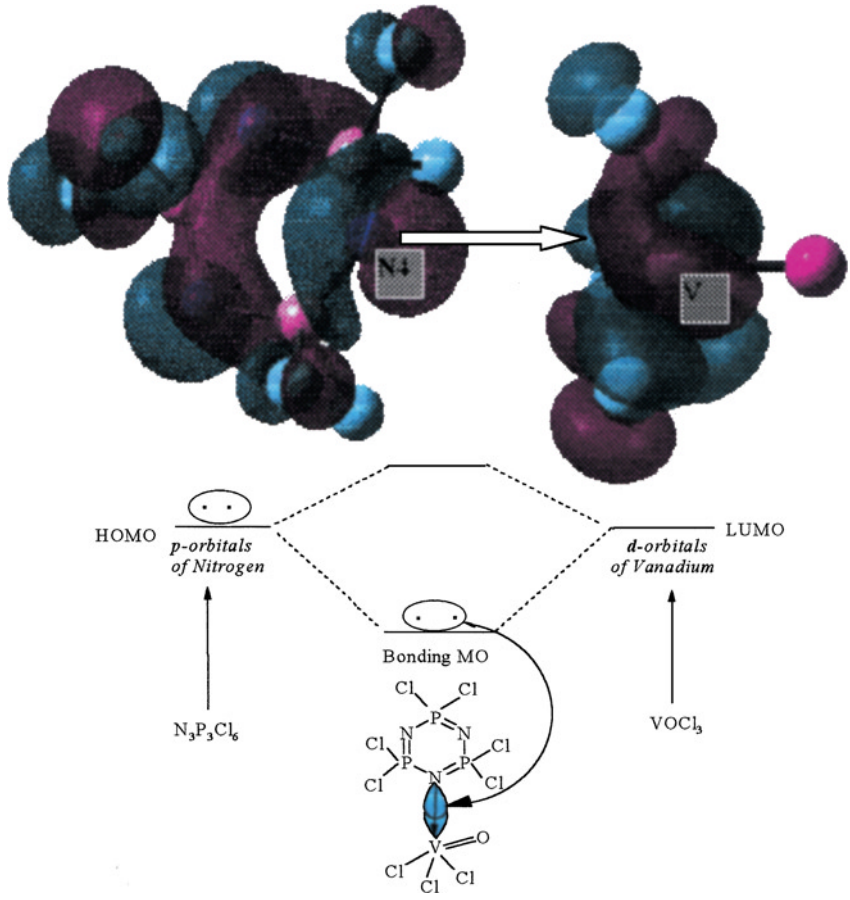


FIGURE 5 The HOMO and LUMO overlapping on the atoms of hexachlorocyclophosphazene and $VOCl_3$.

of $VOCl_3$ approaching to the atom. Simultaneously, positive charge on the atom of vanadium decreases as well. The vanadium approaching to the atom of nitrogen causes the growth of electron density on the $V{-}N_4$ bond.

At the same time, the $N_4{-}P_3$ and $N_4{-}P_6$ bonds in the heterocycle become weaker, while the $P_3{-}N_2$ and $P_6{-}N_5$ bonds become stronger. It is to be emphasized that the $V{-}N_4$ bond formation causes weakening of the bond V—Cl.

Let us analyze electronic energy changes in the system $[VOCl_3 + (NPCl_2)_3]$ as the result of varying the distance between atoms V and N_4 (see Figure 6). As seen from Figure 6, the minimum of electron energy

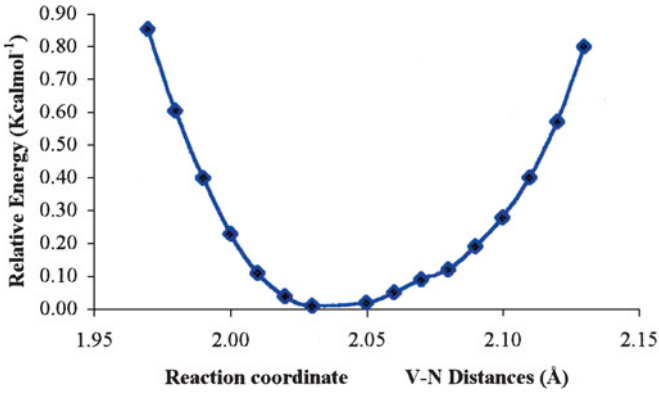


FIGURE 6 The dependence of the electronic energy in the system [$VOCl_3 + (NPCl_2)_3$] on the length of the V–N_4 bond.

in the complex is achieved under the bond V–N_4 length equal to 2.035Å. Electronic parameters of the complex are given in Table III.

CONCLUSION

Reaction of $VOCl_3$ with hexachloro-cyclotriphosphazene allowed to obtain the $VOCl_3 \cdot (NPCl_2)_3$complex. The bond in the complex is being formed for the account of interaction between the vanadium atom and the nitrogen atom of hexachlorocyclophosphazene. A few ab initio methods were used to calculate electronic stuctures of some simple cyclic triphosphazenes $(NPX_2)_3$ (X=H, F, Cl, NH_2) with the STO-3G and 6-31G(d,p) basis sets that differ in the number of polarisation functions on the P and N atoms. The results of the study show that the choice of the basis set for the electronic structure calculations is of great importance when experimental data for the complexes obtained are to be explained.

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