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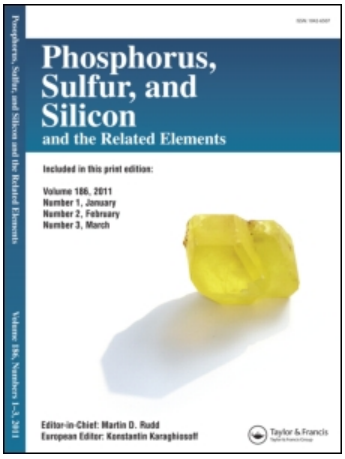

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The Study of the Mechanism of the N-Dichlorophosphoryl-P-trichloromono-phosphazene Interaction with $VOCl_3$ and Mechanism of Its Polymerization

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The Study of the Mechanism of the N-Dichlorophosphoryl-P-trichloromono-phosphazene Interaction with $VOCl_3$ and Mechanism of Its Polymerization

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The mechanism of the N-dichlorophosphoryl-P-trichloromono-phosphazene interaction with $VOCl_3$ and the mechanism of its polymerization have been studied with the RHF/3–21G method. The monomer interaction with $VOCl_3$ has been modeled, and the electron spin resonance (ESR) was measured.

Keywords N-dichlorophosphoryl-P-trichloromono-phosphazene; quantum-chemical calculation; vanadium oxotrichloride

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INTRODUCTION

N-dichlorophosphoryl-P-trichloromono-phosphazene $Cl_3PNP(O)Cl_2$ (**I**) is formed whenever PCl_5 is heated with the ammonium salt of an oxyanion, although yields vary widely according to salt chosen; ammonium sulfate gives the best yields.[1] $Cl_3PNP(O)Cl_2$ is extremely soluble in a large number of solvents, although it reacts readily with water and alcohols. The compound is soluble in benzene, carbon tetrachloride, chloroform, and other chlorinated solvents.[2] Compounds of the class X_5P_2NO are reported to be useful in the preparation of organophosphorus compounds used as insecticides, flame retardents for textiles, plasticiers, lubricating oil additives, and corrosion inhibitors. For example, the alkyl ester derivatives $(CH_3O)_5P_2NO$ and $(C_2H_5O)_5P_2NO$ are useful as insecticides.[3] The following article describes an accessible route for polydichlorophosphazene based on the polycondensation of N-dichlorophosphoryl-P-trichloromono-phosphazene (**I**).[4]

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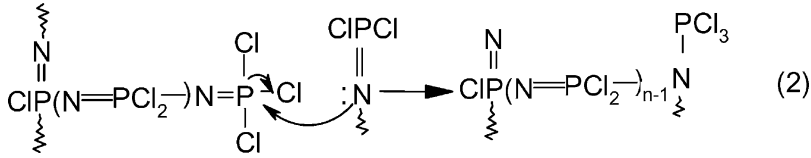
At high temperatures, **I** behaves as a difunctional compound bearing two leaving groups: $POCl_2$ and Cl^5 [Equations (1) and (2)].

$$nCl_3P{=}N{-}P(O)Cl_2 \rightarrow Cl_3P{=}N(PCl_2{=}N)_{n-1}P(O)Cl_2 + (n-1)POCl_3 \quad (1)$$



(2)

$VOCl_3$ (**2**) and VCl_4 have been used as catalysts in the Ziegler–Natta reactions for the copolymerization of ethylene and propylene.[6] Vanadium(V) forms two oxo-species, the VO^{3+} and VO_2^+ ions. The former unit is found in the oxyhalides VOX_3 (X = F, Cl, or Br) in which the VO stretching frequencies are at 1058, 1035, and 1025 cm^{-1}, respectively. In addition, however, a number of complexes of the type $VOCl_3L$ and $VOCl_32L$ have been characterized in which L can be one of a number of different oxygen or nitrogen-donor ligands. The second oxovanadium (IV) species, the VO_2^+ ion, is not well characterized.[7] Also, $VOCl_3$ can be reduced by hydrogen to the deliquescent solid $VOCl_2$. Almost all compounds containing VO^{2+} unit are blue and display two other characteristic physical properties: 1) an ESR spectrum with characteristic g values and ^{51}V hyperfine coupling (8 lines). The ESR g_{av} values for oxovanadium(IV) complexes lie in the range 1,95–2.00, i.e, close to the spin only value of 2.0023; and 2) a strong V=O stretching band in the IR in the range from 950–1000 cm^{-1}.

Many oxometal species have been characterized, the most stable of which are the VO^{2+} ions. The most characteristic feature of the IR spectra of oxovanadium(IV) complexes is a very strong, sharp band at 985 $\pm$ 50 cm^{-1}. This band is assigned to the V=O stretching frequency. Coordination of a ligand to the sixth octahedral position, i.e., the position trans to the V=O bond, brings about a drop of $\sim$50 cm^{-1} in the V=O stretching frequency of the parent complex.[7]

Electron paramagnetic resonance (EPR) is a very convenient tool to study the $V{=}O^{2+}$ unit (V: I = 7/2, 99.75%; S = 1/2). Hyperfine interaction with N nucleus of the N donor ligands was not observed, presumably due to the small magnitude of the hyperfine constant in EPR spectra of O and N donor ligands for $VCl_4.2L$ adducts.[8] The g values fall within a narrow range and denote the symmetry of the molecule and the nature of the orbital in which the unpaired electron is confined. On the other hand, the hyperfine interaction constants afford information of interest about the metal ligand interaction. If it is referred to the values

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of <Av>(= 1/3(A_I+2$A_\perp$), it can easily be noticed that they are significantly sensitive to 1) the nature of the donor atom, and 2) within the phosphine ligands, to the nature of the substituents on P. <Av> values are found to lie within three ranges: 91–97 G for PR_3 (R = alkyl or aryl), 100–113G for $P(OR)_3$ (R = Me, Et) or PR_2Cl, and also for O donor ligands and 100–103G for N donor ligands. Furthermore, an important observation in the case of phosphines is the existence of superhyperfine interaction with the phosphorus, which bears acceptor groups such as Cl or O. This is accompanied by an appreciable increase of <Av>. This parameter can be taken as a measure of the extent of unpaired electron delocalization on vanadium ($P \alpha 1/r^3$) so that a high value reflects a poorer transfer to the chlorine ligands, and as a consequence a lower covalency (or higher ionic character) of the V-Cl band. <Av> values that are higher than 100G are associated with phosphines having electron-withdrawing groups (Cl or OR) and also with N donor ligands (with lower nucleophilicity than that of phosphine). Higher values (about 110G) are found for compounds with O donors, where nucleophilicity is the lowest. It seems therefore that strong nucleophilies tend to delocalize unpaired electron density toward the Cl ligands, whereas weak nucleophiles leave a higher electron population on the V nucleus.[8,9]

Natural bond orbital (NBO) and topological electron density analyses have been used to investigate the electronic structure of phosphazenes [$N_3P_3R_6$] (R) H, F, Cl, Br, CH_3, CF_3, $N(C_2H_4)$; 2R) $O_2C_6H_4$), [$N_4P_4Cl_8$], and H[$NPCl_2$]4H.[10]

In this work, the mechanism of the monomer interaction with $VOCl_3$ and the mechanism of its polymerization have been studied; the model of the monomer interaction with $VOCl_3$ has been developed; and quantum chemical calculations of $VOCl_3$ interaction with $Cl_3PNP(O)Cl_2$ have been carried out.

RESULTS AND DISCUSSION

As was mentioned above, the salts of metals are capable of catalyzing the process of the "monomer" polymerization. Aiming in the study of the initial mechanism of this reaction, quantum chemical calculations of free and coordinaed to $VOCl_3$ molecules have been carried out. In Figure 1, structures of **1**+**II** **TS1**, **TS2**, **III**+**IV**, **III**+**I′**, and **IV**+**II′** are shown, and in Table I, their electron characteristics are given. The charge distribution analysis has shown that on the atom of phosphorus, a positive charge is concentrated. On the rest of the atoms, there are negative charges (Table I).

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TABLE I Bond Lengths and Mulliken Charges Calculated with RHF/3–21G for 1+II TS1, TS2, III+IV, III+I', IV+II'

Atoms	1+II	TS1	III+IV	Atoms	III+I′	TS2	IV+II′
	Bond Lengths (Å)						
P6-N5	1.614	1.762	4.283	V14-N5	1.731	2.155	5.372
N5-P1	1.614	1.736	1.562	N5-P1	1.580	1.658	1.534
P6-O7	1.530	1.660	1.539	V14-O13	1.522	1.514	1.510
P6-Cl8	2.196	2.147	2.148	V14-Cl12	2.208	2.215	2.155
P6-Cl9	2.196	2.216	2.165	V14-Cl10	2.245	2.309	2.161
V14-N5	5.651	1.925	1.731	N16-P15	1.532	1.548	1.534
V14-O13	1.511	1.512	1.520	N16-P17	1.603	1.624	1.599
V14-Cl10	2.152	2.208	2.230	P15-N5	5.168	1.720	1.606
V14-Cl11	2.161	2.859	5.299	P15-Cl21	2.161	3.519	5.328
V14-Cl12	2.161	2.188	2.214	P15-Cl23	2.175	2.169	2.191
P6-Cl11	5.375	2.383	2.155	V11-Cl21	1.713	2.281	2.160
	Mulliken Charges (ē)						
P1	1.246	1.223	1.138	N5	−1.045	−1.255	−1.291
Cl2	−0.117	−0.107	−0.096	V14	1.571	1.410	1.424
Cl3	−0.122	−0.221	−0.154	P1	1.178	1.032	1.242
Cl4	−0.122	−0.096	−0.082	O7	−0.359	−0.291	−0.284
N5	−1.298	−1.290	−1.069	Cl12	−0.476	−0.340	−0.372
P6	1.605	1.266	1.161	Cl10	−0.562	−0.473	−0.386
O7	−0.653	−0.844	−0.683	N16	−1.303	−1.319	−1.344
Cl8	−0.268	−0.084	−0.139	P15	1.255	1.556	1.741
Cl9	−0.268	0.089	−0.161	P17	1.658	1.574	1.626
Cl10	−0.365	−0.386	−0.480	Cl21	−0/092	−0.450	−0.384
Cl11	−0.384	−0.293	−0.144	Cl23	−0.359	−0.119	−0.205
Cl12	−0.384	−0.372	−0.473			–	
O13	−0.295	−0.260	−0.368				
V14	1.427	1.553	1.550				

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The modeling of the N-dichlorophosphoryl-P-trichloromonophosphazene interaction with $VOCl_3$ has been carried out to investigate the state of the free molecules relative to their charge and orbitals. The orbitals of N5 that enter in the HOMO are the most active ones and participate in the donor–acceptor interaction.

LUMO of $VOCl_3$ formed by the AO of vanadium plays the role of the acceptor orbital. Thus, the most probable points of attack are these two atoms (V and N5), and the orbitals' interaction proceeds between them.

The analysis of the bond length changes has shown that the bond V-N5 strengthening causes the bonds P1-N5 and P6-N5 weakening. Simultaneously, the bond between V and Cl atoms increase (Table I).

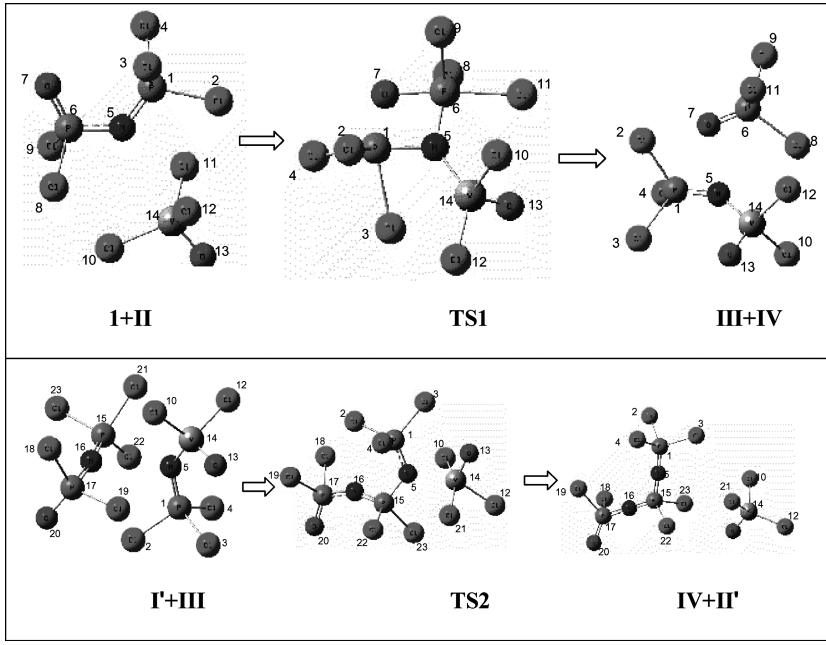

FIGURE 1 Structures of **1**+**II TS1, TS2, III**+**IV, III**+**I, IV**+**II** calculated with RHF/3–21G.

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In this way, the atom N5 attachment to V makes it possible for the bond P1-N5 to break up and one atom of Cl dissociate from V with its forthgoing attachment to the radical PCl_2O. As a result of this, the molecule $POCl_3$ is extracted, and a new radical particle is formed.

It is capable of interacting with the new "monomer" according to Figure 1. From this a dimer is formed, and the $VOCl_3$ molecule is freed, which plays the role of catalyst in the reaction given.

At the next step of the chain's growth, one more $VOCl_3$ is attached to the atom of nitrogen connected to the group $POCl_2$. The mechanism is repeated with the trimer formation, etc.

The ESR measurements were performed by the Bruker EMX spectrometer. The spectra of three samples (**1**, **2**, **3**) were recorded at the frequency $\nu = 9.45$ GHz, modulating field amplitude M = 1G, and power level P = 2 mW.

The recorded ESR spectra have absorption lines in the magnetic field range 3000–4000 G (see Figure 2). The most simple spectrum of (**1**) unambiguously points out that the observed spectrum (Figure 2) is the hyperfine structure pattern of V ions with nuclear spin I = 7/2.

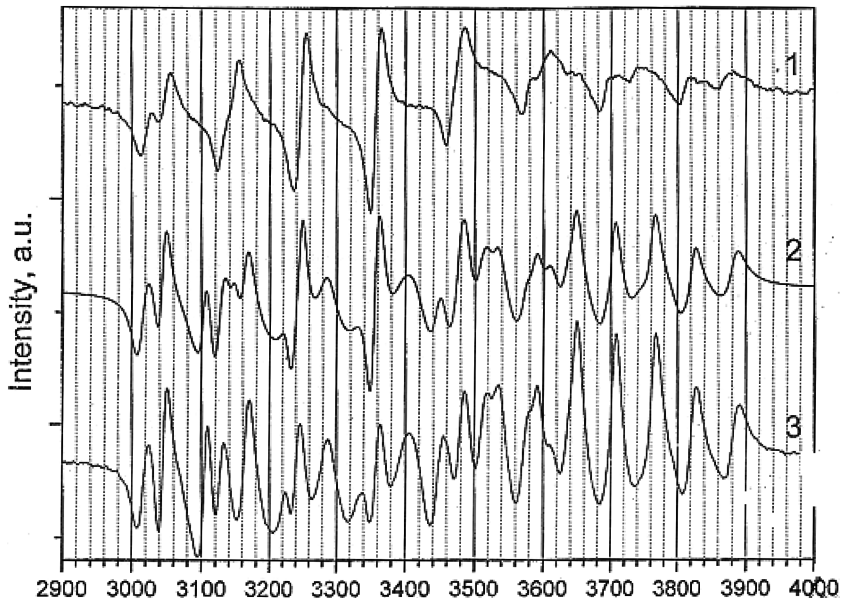

FIGURE 2 Observed ESR spectrum.

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One can see the additional splitting of components towards the edges of spectra on both left- and right-hand side, which can be assigned to the existence of two types of V complexes in the sample. Besides, the spectra recorded arise from solutions. So, the observed increase of component line width apart from the center of the spectra (Figure 2) must be associated with molecular tumbling effects (in liquid solvents).

The well known line with the approximation of each hyperfine line in the case of tumbling effects is as follows:

$$dH = \alpha + \beta M_1 + jM_{II}^2,$$

where M_I is quantum number of nüclear magnetic moment, and β, j are parameters that depend on the tumbling rate.

The computer modeling of spectrum 1 with using the Bruker <win EPR> Simfonia program succeded (Figure 2) at following values of fitted parameters.

For the first type of V complexes, $A_1 = 109G$, $g_1 = 1{,}966$, $\alpha_1 = 14G$, $\beta = -2G$, $\gamma = 1G$.

It must be noted that values of the hyperfine interaction constant A and g factors for both types of V centers are typical for vanadium complexes.

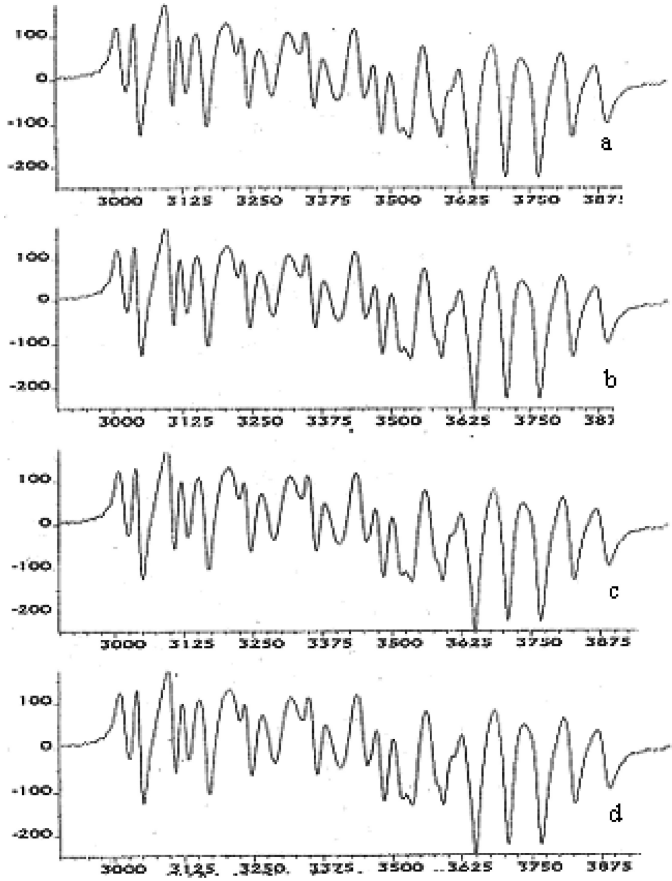

FIGURE 3 Simulation ESR spectrum.

In contrast to spectrum **1**, which is rather simple, spectra **2** and **3** are much more complicated. However, from Figure 2 one can note that some lines in spectra **2** and **3** have the same resonance fields as in spectrum **1**. The intensity of these lines decreases towards spectrum **3**. This means that the spectra **2** and **3** contain a contribution from essentially the same V-complexes as in spectrum **1**.

Spectrum **3** is obtained when we can substract from spectrum **1** with the appropriate scale factor spectrum **2**. Figure 3 shows the result of spectrum **3**.

A careful analysis of spectra permits us to find the 15 most intense lines that are equidistantly spaced in the magnetic field. Other lines apparently arise due to the fact that the substracting procedure cannot

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be done perfectly. It is highly possible, because parameters α_1,β, G, and γ are slightly different for subtracted contribution to spectra from these for same V complexes, for example, due to a little different ratio resolution.

The 15 equidistant lines in the spectrum can be found much more easily if some type of Fourier filtering is applied in order to eliminate the unnecessary lines. For example, the result for biexponential filtering is shown in Figure 3d.

The distance between lines on the spectrum in Figure 3c is approximately two lines are smaller than for spectrum in Figure3a. This means that this contribution results from vanadium complexes coupled by exchange interaction. In the case of that, exchange constant $J_{ex} >> A$. It is expected that for the hyperfine splitting with distance between lines A/2 and effective nuclear spin, $I_{cf} = 2I_v = 7$. That is what we observe in the experiment.

The ESR simulation of this contribution to spectra **2** and **3** is rather useful due to the above mentioned imperfectness of the subtraction procedure and small evolution (dependence) of the spectrum's form on the exchange parameter in the range from Jex >A to Jex >> A. But the

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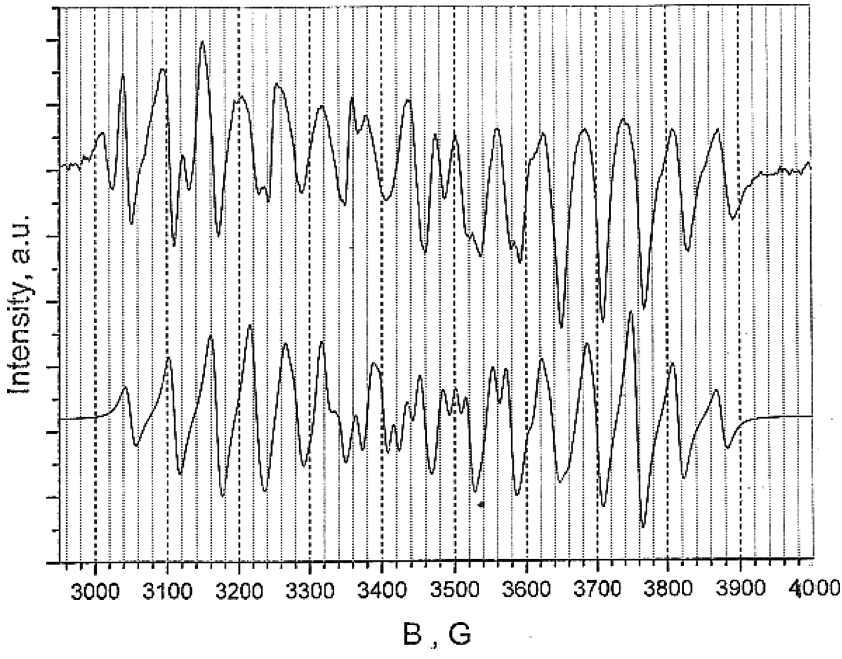

FIGURE 4 Comparison experimental and simulation peaks.

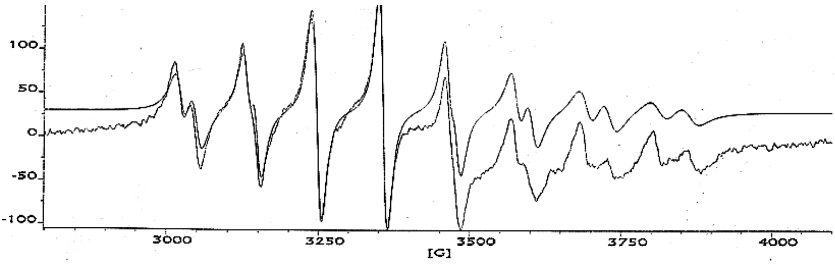

FIGURE 5 Experimental and simulated peaks.

main features of the spectra (15 lines, the decreasing of lines amplitude in the center of spectrum) are reproducible.

Figures 4 and 5 are examples that show the experimental (upper) and simulated (below) spectra.

The second one was calculated for spin Hamiltonian:

$$H = g\beta B(\bar{S}_1 + \bar{S}_2) + A(\bar{S}_1\bar{I}_1 + \bar{S}_2\bar{I}_2) + J_{ex}\ \bar{S}_1\bar{S}_2$$

with the following parameters: Jex = 8000G, $A_1 = A_2 = 115$, $g_1 = g_2 =$ 1.95 and line width of each component $\Delta H = 15G$. These value of A and g are very close to values of those directly extracted from the spectrum in Figure 3. A = 120G and g = 1.958.

CONCLUSIONS

The modeling of the monomer interaction with $VOCl_3$ has been carried out, and parameters of $VOCl_3$ interaction with $Cl_3PNP(O)Cl_2$ have been calculated with RHF/6-31G(d). It is worth paying attention to the fact that both in the dimer and "monomer" have the atom of nitrogen bound with the leaving group $POCl_2$ and the atoms orbitals are represented with the maximal weight of coefficients. It must be noted that in our case, the dipole–dipole interaction is a negligible one, because otherwise the subtracted spectrum would contain not 15 but $15 \times 2 = 30$ lines (approximately of the some intensity) due to additional zero fields splitting.

EXPERIMENTAL

$VOCl_3$ and $Cl_3PNP(O)Cl_2$ are very sensitive to air and/or moisture. All manipulations on them were carried out in a pure nitrogen or argon atmosphere. For this reason, glove box techniques were used. Solvents were distilled and dried by appropriate agents before using. Vanadium oxotrichloride and hexachlorocyclotriphosphazene were

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purchased from Fluka. Elemental analyses were carried out on 175C Fotometer Merck SQ 118, Simaa 6000 Model. ESR measurements were performed on a Bruker EMX-series spectrometer.

Reaction of $VOCl_3$ with P-Trichloro N-Dichlorophosphoril Monophosphazene

1,2-Dichloroethane (10 mL) was added to a 100 mL flask containing $VOCl_3$ (0.011 mol, 1.93 g). The solution was cooled in a liquid nitrogen and acetone mixture. Then P-trichloro N-dichloro phosphoril monophosphazene dissolved in 1,2 dichloroethane (10 mL) was added slowly. When the temperature of mixture was at room temperature, it became brown. Then it was refluxed 1 h, and the solvent was distilled. A liquid-like oil was obtained. Elemental analysis and ESR analyses of this liquid were carried out. When the addition operation of P-trichloro N-dichloro phosphoril monophosphazene to $VOCl_3$ solution was carried out at room temperature, the color changed immediately to deep brown (Equation 3).

$$Cl_3PNPOCl_2 + VOCL_3 \rightarrow Cl_3PN - (PNCl_2)_n - POCl_2VOCl_2 \qquad (2)$$

The atomic absorption analysis (Perkin-Elmer SIMAA 6000) was carried out for the vanadium and phosphorus determination in the hydrolyzed solution (found for $N_3P_3Cl_6 \cdot VOCl_3$: V, 8.12%; calculated: V, 7.52%, found P, 21.71%, calculated N, 20.86%). Spectrophotometric analysis for Cl determination was performed on a UV visible spectrophotometer (Shimadzu, 2101 PC) (found: Cl, 58.24%; calculated: Cl, 60.48%).

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COMPUTATIONAL METHODS

All calculations for the N-dichlorophosphoryl-P-trichloromonophosphazene interaction with $VOCl_3$ were performed at the HF/3–21G level of theory using the Gaussian 98 package.[11] For both TS found, its reactant and product has been confirmed by intrinsic reaction coordinate (IRC) calculations. The molecular structures along the IRC were fully optimized at the same level of theory.

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