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Design and Characterizations of Essential Metal (II)-Amino Acid: L-Arginine & L- Alanine containing Polyphosphonitrile Derivatives

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Abstract

Over the past decade, inorganic polymers, particularly polyphosphazenes, have garnered significant attention in materials science due to their unique structural versatility and tuneable properties. Polyorganophosphazenes, with the general formula [NPR_2], offer a broad range of physical and chemical characteristics, largely determined by the nature of their side groups (R), which can include Amino, Alkoxy, Aryloxy, Alkyl, or Aryl functionalities. In this study, we report the synthesis and characterization of a novel class of inorganic polymeric derivatives Metal (II)-amino acid-substituted polyphosphonitriles. These derivatives were prepared using amino acids (L-arginine and L-alanine) and side groups containing sodium, ethoxy, and phenoxy moieties. The central Metal(II) ions—Zn(II), Cu(II), Mg(II), Ca(II), and Fe(II)—are essential metals with known biological and catalytic relevance. The successful incorporation of these components was achieved through controlled polymerization and substitution reactions, resulting in structurally diverse and functionally promising materials. The synthesized polymers were characterized by their physical properties, including colour, conductivity, pH, melting point, dipole moment, and dielectric behaviour. Spectroscopic techniques such as Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD) were employed to confirm the structural features of the new materials. This study introduces a promising new class of inorganic-organic hybrid polymers with potential applications in areas such as Biomedicine, Environmental Remediation, Agricultural area and Advanced Material Engineering.

Keywords: Polyphosphonitrile, Polyorganophosphazenes, Design, Characterization, Metal-(II), Polyphosphazene, Amino acids, L- Arginine, L- Alanine

1. INTRODUCTION

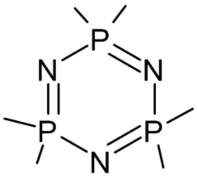
Inorganic polymers, particularly polyphosphazenes, have emerged as a versatile class of materials with wide-ranging applications due to their structural flexibility and diverse chemical functionality. Among them, polyphosphonitriles $(NPCl_2)_3$ offer a unique backbone for chemical modification, allowing the incorporation of various organic and inorganic substituents. The introduction of amino acids and essential Metal(II) ions into the polyphosphonitrile framework offers the potential to tailor physicochemical properties for specific functions, bridging the gap between biological compatibility and advanced material performance.

In recent years a growing interest has been evident in the development of polymers. Polymer comes from the Greek words ***"polus"*** which means ***"many, much"*** and ***"meros"*** which means ***"part"***. A polymer consists of a long chain of repetitive units known as monomers. Polymers are macromolecular chains composed of thousands of monomer units. Characteristics of each monomer unit contribute to the overall properties of the overall properties of the whole polymer. Polymer chemistry handles all types of reactions and chemical field's. Polymers are used in a wide range of applications. Polymers have been known to function as electrolytes since 1973, as a result of the previous decades of polymer invention **(Wright P. V., 1988)[1]**. Between 1910 and 1950, many milestones were achieved in polymer history: for example PVC, Acrylate polymers, Polyethylene and Polyamides, to name a few. This period can be truly determined as the beginning of the ***"plastic age"***. An important subgroup of polymers are polyphosphazenes, for the first time synthesized in 1897 by **H.N. Stokes (1897)[2]**. The synthesis of the phosphorus-nitrogen backbone is quite difficult and about 70 years elapsed until major advances were reported by **H. R. Allcock and R.L. Kugel (1966) [3].**

Inorganic Polymeric materials comprise a very unique area in polymer science. Presently polymers become an integral part of our day-to-day life but on the other hand possess several problems as these polymers are not biodegradable thus causing environmental pollution. As compared to organic polymers, inorganic polymers are scarcely studied whereas some of them are biodegradable and water soluble the combination of Poly Inorganic moieties and organic polymers has a high potential, high thermal stability, flame resistance and chemical resistance for future applications and has therefore attracted a lot of attention during the last decade. The inorganic polymers are classified into borates, silicones and phosphazenes. Among these phosphazenes are well known and have a significant role.

Phosphazenes:

Phosphonitrilic chloride polymers also known as Polyphosphazenes, are a class of Inorganic polymers that contain alternating phosphorus and Nitrogen atoms in the polymer backbone **(Audrieth *et al.*, 1943)[4]**.



Researchers can readily alter the bulk and surface characteristics of polyphosphazenes by varying the side groups on the phosphorous. Amino, Alkyl, Aryl, Alkoxy, Aryloxy, inorganic, or organometallic units can all be side groups. Because the connected hydrogen atoms are reactive, the Phosphonitrilic halides undergo hydrolysis and Ammonolysis processes chemically. Although these polymers have good heat resistance and do not typically depolymerize at temperatures much below 350°C, their general utility has been limited by their propensity to undergo chemical deterioration.

A comprehensive review on the inorganic polymer has been published by **H.R. Allcock, (2002)[5]** in a book (Inorganic Polymer) various aspects of Phosphonitrile derivatives viz., History, Synthetic methods, bonding structure –properties relationship, synthesis of various derivatives and their application has been discussed in great detail.

The Phosphorus Nitride compounds, which are cyclic or linear chain inorganic compounds **(Christopher W. Allen, 1994)[6]** formed by the bonding and repetition of Phosphorus and Nitrogen atoms $(P{=}N)_n$. These are one of the most interesting and attractive classes of organophosphorus compounds **(Audrieth *et al*., 1943)[4]**. The important feature of Phosphazene chemistry **(Shaw *et al*, 1962)[7]** is the method of synthesis that allows the side groups [R] to be varied over a very broad range as different side groups generate different properties. The most used phosphazene members as cyclic and linear chains are the hexacholorocyclotriphosphazene, octachlorocyclotetraphosphazene and poly (dichloro) phosphazene, respectively.

Polyphosphazenes are inorganic polymers in which Nitrogen and Phosphorus atoms are alternately located and two side groups are attached to Phosphorus. Polyphosphazenes are macromolecules having inorganic elements in the backbone and organic side-groups. At least 300 different polymers of this type have been synthesized, many new types of polymers containing nitrogen and phosphorus atoms or a significant part of the polymer backbone have been synthesized, and there are many compounds of polyphosphazenes which have different properties and uses. The combination of inorganic polymers like Polyphosphazenes indicates a growing area of research and has applications in many fields[8-16] of Elastomers, Rubbers, Thermosetting, Ceramics, Coating, Adhesives, Lubricant, 3D Printing, Sensors, Ionic Conductors, Batteries, Fuel cells, Hydrogels, Fibers of Optical Materials, Stabilizers and Fire-resistant, Military-applications, Tissue-engineering, Membranes, Drug-delivery systems, Bioerodible and Bioimaging etc.

In today's reality, Bundelkhand provides one of the widest stretches of districts which are generally included one of the backward districts of India. The sufferings of the weaker section in many parts of the region appear to be increasing due partly to the deteriorating environmental conditions. The region is complex, rainfed, risky, under invested, vulnerable, ethically unique, agrarian and backward **(Mondal et al., 2016; P. Kumar et al., 2022)[17,18]**. With the collapse of monsoons and arrival of successive dry years, the inhabitants of this are now facing scarcity of water. On average the evapotranspiration rate in the region is about 1600mm, whereas the rainfall level is less than 1000mm which makes the situation worse. Additionally, the region is largely characterized by shallow red soils, undulating topography and extreme weather conditions, making the agriculture in the region more difficult leading to low crop productivity, crop intensity and higher soil loss through erosion and runoff. As a result of this nutritional problems are increasing day by day. As per the study conducted by **Mishra and Chaurasia, (2021)[19]** revealed that Utter Pradesh district of Bundelkhand region has malnutrition i.e., Underweight- 42.5 %, Stunted-39.92 %, Wasted-29.43 %. Jhansi district of Bundelkhand region is also suffering from malnutrition. Along with Jhansi six other districts are also announced as malnutrited while ***Aaganvari Centres*** and ***Mid Day Meal schemes of government*** are carried out in ***all Basic Schools of Uttar Pradesh***. The predominant crops grown in Bundelkhand region are Groundnut, Black gram, Green gram, Pigeon pea, Mustard, Chick pea, Lentil, Barley and Wheat. Low price protein rich crops like ground nut and peas assume a special significance to the farm economy as well as daily diets of local habitants of this region. Thus, in order to enhance the nutritive quality and yield of such crops by adopting the proposed technique depending upon the multi micronutrient ecofriendly biodegradable water soluble Inorganic polymer as Metal(II) amino acid Phosphonitrile derivatives which aims at minimal soil disturbance, pest and drought resistance, helps in decreasing or reverting the negative effects and ultimately increases the productivity of the crops.

My earlier published research papers **(Anupam and Chitra, 2023; 2024)**[20,21] on inorganic polymeric phosphonitrile derivatives explored their potential applications in agriculture, particularly used as fertilizers for Pea and Groundnut crops and encouraged the development of quality improvement activities such as protection of these crops, promotion of plant growth, improvement in yield, enhancement of crop quality, disease resistance and other activities.

This study focuses on the design and characterization of essential Metal(II)-amino acid; L-Arginine & L-Alanine containing polyphosphonitrile derivatives. In this L-arginine and L-alanine have used as bio-based ligands and Metal(II) ions such as Zn, Cu, Mg, Ca, and Fe have used.. By carefully controlling substitution and polymerization reactions, a new class of functional hybrid polymers has been synthesized and evaluated. These materials open new pathways for the development of next-generation inorganic polymers with potential applications in biomedical, environmental, and electronic fields.

2. MATERIALS AND METHODS:

The starting materials Phosphonitrilic Chloride Trimer: Aldrich, Amino Acids: (L-Arginine- CDH, L-Alanine- CDH) , Metals: (Zinc Powder Pure- MERCK , Iron Metal Powder- HIMEDIA, Copper Metal- RANKEM, Magnesium Metal- MERCK, Calcium Metal- HIMDIA) ,Sodium Hydroxide, Dichloromethane, Anh. Magnesium Sulphate, Ethanol, 2- Propanol, Charcoal, THF etc. all the chemicals and solvents used were of AnalaR / B. D. H. / C. D. H. / E. Merck grade.

Characterization of the Polyphosphazene Metal (II) derivatives:

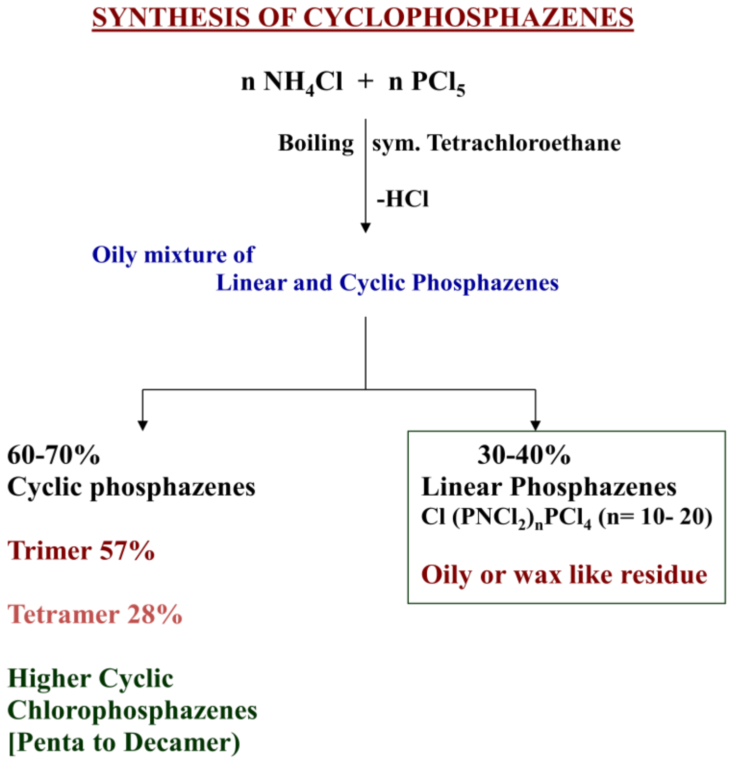
These have used without further purification and Conductivity of Water. The Melting point has determined by open capillary tube (Thiele apparatus) method. A Systronics pH meter of 0.01 readability has used for the measurement of pH. Conductance was measured with Systronics conductivity meter. 0.01M KCl solution have used as the standard reference solution.The Fourier Transform Infra-Red Spectrophotometer (FTIR) have determined by using Potassium Bromide Press Pellet Technique dispersion media through some derivatives of PerkinElmer Spectrum, Version 10.03.06 Spectrophotometer at **Indian Institute of Technology Kanpur(U.P.)**. Some derivatives of FTIR have recorded from the BRUKER Spectrometer at **Department of Chemistry, Dr. H. S. Gour (A Central) University, Sagar (M.P.) 247002**. X-rays Powder Diffraction (XRD) patterns measurements have been performed by using analytical Netherlands Model:X’Pert PRO microprobe using a monochromatic Al Kα source (1486.6eV) at **Central Research Facility,Indian Institute of Technology (IIT) Delhi.**

3. SYNTHESIS OF POLYMERS

The general procedure for the synthesis of Polyphosphazene derivatives have the common sequential steps which are given below:

1. Preparation of Phosponitrilic Chloride:

The reaction between Phosphorus Penta Chloride and Ammonia was described by **Rose in 1834**[22]



Scheme 1: The Target Polyphosphazene Derivatives were Synthesized as Outlined in scheme 1.

In recent method **(China Method)**, Phosphonitrilic compound trimer and tetramer are formed in the following two steps-

Step 1. The reaction of Sulfamic Acid is written **(Ken Toyokura *et al.*, 1979)**[23] as eq.

$$NH_2CONH_2 + SO_3 + H_2SO_4 \rightarrow 2NH_2SO_3H + CO_2$$

(Urea) (fum. Sulphuric acid) (sulphamic acid)

Urea dissolved in 100% Sulfuric Acid and 30% fuming Sulfuric acid were dropped (25 ml each).

Step 2. $PCl_5 + NH_4Cl \xrightarrow{sulphamic\ acid}$ phosphonitrilic compound

(linear or cyclic)

2. Preparation of Polyphosphazene:

(i) $(NPCl_2)_3$ and $(NPCl_2)_4$ can be prepared by Ammonolysis of PCl_5.

$$3PCl_5 + 3NH_3 \longrightarrow (NPCl_2)_3 + 9HCl$$

$$4PCl_5 + 4NH_3 \longrightarrow (NPCl_2)_4 + 12HCl$$

(ii) These compounds can be prepared by the reaction between PCl_5 and NH_4Cl in presence of $C_2H_4Cl_2$ or C_6H_5Cl or by heating PCl_5 with solid NH_4Cl at 145-160°C.

$$nPCl_5 + nNH_4Cl \xrightarrow[or\ C6H5Cl]{} (PNCl_2)_n + 4nHCl$$

$$nPCl_5 + nNH_4Cl \xrightarrow{145-160°C} (PNCl_2)_n + 4nHCl$$

Both the above reactions produce a mixture of various phosphonitrilic chlorides, but under controlled condition, high yields of $(NPCl_2)_3$ and $(NPCl_2)_4$ can be obtained. These two compounds can be separated from each other by using the fact that $(NPCl_2)_3$ sublimes in vacuum at 50°C as a white crystalline solid whereas $(NPCl_2)_4$ does not do so under these condition.

The formation of $(NPCl_2)_n$ takes place through the following steps[24,25]:

$PCl_5 + NH_4Cl \rightarrow NH_4PCl_6$ (Ammonium hexachloro phosphate-unstable product)

$$NH_4PCl_6 \xrightarrow{Decomposition} NH.PCl_3 + 3HCl$$

$$NH.PCl_3 \xrightarrow{Condensation} (NPCl_2)_n + nHCl$$

3. Preparation[26-31] and Separation of Metal(II) amino acids (L-Arginine and L-Alanine) Phosphonitrile Derivatives:

3.1. Synthesis of Polymer Metal (II) Arginine Sodium Phosphonitrilic Derivative (Compound A-1)

This polymer was synthesized by mixing hexachlorocyclotriphosphazene (HCCP, $N_3P_3Cl_6$) (1g, 2.87mmol) with 1N-NaOH (10%) in a three-necked, round bottom flask equipped with a water condenser, magnetic stirrer bar and a pressure equalizing addition funnel and stirring the mixture for 30 min. Then we gradually added 2.5 g (14.35mmol) of Arginine and treated it for 45 min at 30°C, then Metals such as Zn, Cu, Mg, Ca and Fe (in calculated amounts) were added to the reaction mixture and stirred at room temperature. The reaction mixture was then heated at 65°C in reflux for 4 days. The mixture was then cooled to 25°C and 2-propanol (10 ml) was added, followed by removal of all the solvent. The precipitate was dissolved in CH_2Cl_2 solution and extraction was completed against deionized water. The dichloromethane layer was dried over anh. $MgSO_4$, filtered and then dried under vacuum for 96 hours. The yield of inorganic polymer based on Metal (II) Arginine Sodium Phosphonitrilic derivative was found to be 83%.

3.2. Synthesis of Polymer Metal (II) Alanine Sodium Phosphonitrilic Derivative

(Compound A-2)

Initial, the polymer was synthesized in a dry three-necked round bottom flask equipped with a water condenser, magnetic stirrer bar, thermometer and pressure equalizing addition funnel, in which a mixture of Hexachlorocyclotriphosphazene (HCCP, $N_3P_3Cl_6$, 1g, 2.87mmol) and 1N-NaOH, (10%) was stirred in a reflux condenser for 30 minutes. Next we slowly added 2.5 g (28.06mmol) of Alanine and treated it for 45 minutes at 30°C. Then Metals such as Zn, Cu, Mg, Ca and Fe (in calculated amounts) were added to the reaction mixture and it was stirred at room temperature. The reaction mixture was then heated at 65°C under reflux for 4 days. The mixture was then cooled to 25°C and 2-propanol (10 ml) was added, after which all the solvent was removed. The precipitate was dissolved in CH_2Cl_2 solution and extraction was completed against deionized water. The dichloromethane layer was dried over anh. $MgSO_4$, filtered and then dried under vacuum for 96 hours. The yield of polymeric Metal (II) Alanine based on Sodium Phosphonitrilic Derivative was 86%.

3.3. Synthesis of Polymer Metal (II) Arginine Ethoxy Phosphonitrilic Derivative

(Compound A-3)

The polymer was synthesized according to the following protocol. Hexachlorocyclotri Phosphazene (HCCP, $Cl_6N_3P_6$) (1g, 2.87mmol) was mixed with 86.8g of C_2H_5ONa in 100 ml distilled water and allowed to heat at 37°C for 1 h. 2.5g (14.35mmol) of Arginine was added and then the reaction mixture was refluxed at 55°C for 32 h. Now Zinc powder (15.32mmol), Copper powder (15.74mmol), Magnesium powder (41.67mmol), Calcium powder (25mmol) and Iron powder (17.63mmol) were added to this solution. The reaction mixture was then stirred for 96 h and the temperature was allowed to rise to 73°C. The mixture was then cooled to 25°C and 2-propanol (10 ml) was added, after which all the solvent was removed and dried thoroughly and again washed with 25 ml ice cold water. Now 2 g de-colorizing charcoal was added and digested for 15min. The precipitate was dissolved in THF solution, again deionized water extraction was completed. The sample was dried over anh. $CaCl_2/MgSO_4$ and then kept in vacuum for four days. The yield of polymer based on Metal(II) Arginine Ethoxy Phosphonitrilic derivative was found to be 72%.

3.4. Synthesis of Polymer Metal (II) Alanine Ethoxy Phosphonitrilic Derivative

(Compound A-4)

Initially, hexachlorocyclotriphosphazene (HCCP, $N_3P_3Cl_6$) (1g, 2.87mmol) was mixed with 86.8 g C_2H_5ONa in 100 ml distilled water and allowed to heat at 25°C for 1 h. Alanine (2.5 g, 28.06mmol) solution was added and then the reaction mixture was refluxed at 55°C for 32 h. Now Zinc powder (15.32mmol), Copper powder (15.74mmol), Magnesium powder (41.67mmol), Calcium powder (25mmol) and Iron powder (17.63 mmol) were added to this solution. Then the reaction mixture was stirred for 96 h and the temperature was allowed to rise to 73°C. The mixture was then cooled to 25°C and 2-propanol (10 ml) was added, after which all the solvent was removed and dried thoroughly and again washed with 25 ml ice cold water. Now 2 g de-colorizing charcoal was added and digested for 15 minutes. The precipitate was dissolved in THF solution and again the extraction was completed with deionized water. The sample was dried over anh. $CaCl_2/MgSO_4$ and then kept in vacuum for four days. The yield of polymeric Metal (II) Alanine based Ethoxy Phosphonitrilic derivative was found to be 77%.

3.5. Synthesis of Polymer Metal (II) Arginine Phenoxy Phosphonitrilic Derivative (Compound A-5)

First, a phenolate solution was prepared by stirring phenol and alkali Metal hydroxide in a dispersing agent. Then hexachlorocyclotriphosphazene (HCCP, $N_3P_3Cl_6$) (1g, 2.87mmol) and Arginine were added to the phenolate solution and the reaction was stirred at 42°C for 18 hours. Now Zinc powder (15.32 mmol), Copper powder (15.74 mmol), Magnesium powder (41.67 mmol), Calcium powder (25 mmol) and Iron powder (17.63 mmol) were added to this solution. The reaction mixture was then stirred for about 48 hours and the temperature was allowed to rise to 94°C. The dispersing agent was then removed by distillation, and the unreacted raw material was removed by washing and filtration, then the crude product was obtained and the polymer Metal (II) Arginine Phenoxy Phosphonitrilic Derivative was obtained by washing and drying the crude product. The yield of the product was found to be 72%.

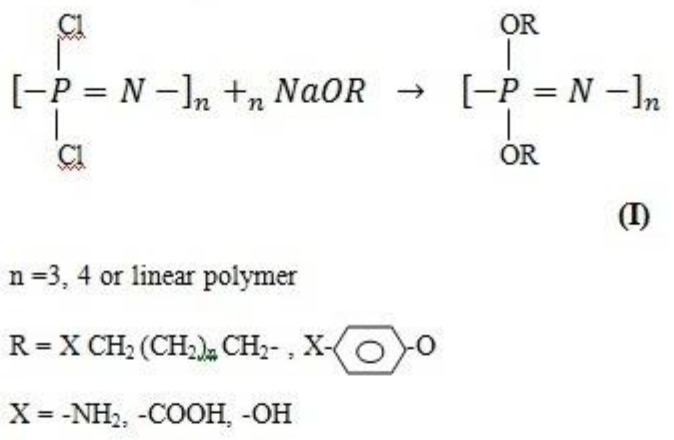
3.6. Synthesis of Polymer Metal (II) Alanine Phenoxy Phosphonitrilic Derivative (Compound A-6)

First, phenol and alkali metal hydroxide were added to a dispersing agent and stirred to prepare a phenolate solution. Then hexachlorocyclotriphosphazene (HCCP, $N_3P_3Cl_6$) (1g, 2.87 mmol) and Alanine were added to the phenolate solution, stirred and reacted for 18 hours at 42°C. Now Zinc powder (15.32 mmol), Copper powder (15.74 mmol), Magnesium powder (41.67mol), Calcium powder (25 mmol) and Iron powder (17.63 mmol) were added to this solution. Then the reaction mixture was stirred for 48 hours and the temperature was allowed to rise to 94°C. The dispersing agent was removed by distillation, and the unreacted raw material was removed by washing, filtering, then the crude product was obtained and after washing and drying the crude product, polymer Metal (II) Alanine Phenoxy Phosphonitrilic derivative was obtained. The yield of the product was found to be 69%.

A summary of the reactions involved in the synthesis of the above six derivatives is as follows-

Scheme I. Preparation[27,32] of Alkoxy and Phenoxy Phosphonitrile Derivatives

We have now synthesized polymers whose derivatives contain organic groups covalently bonded to the terminal phosphorus atom on the chain. Where in the organic compound will first react with chloride ions that are attached to one or both of the terminal phosphorus atoms on the chain, after the reaction, two organic groups are substituted on the terminal phosphorus atoms and the organic compound terminal phosphorus atoms, and the terminal organic groups are phenoxy and alkoxy group substituents, respectively. By treating phosphonitrile polymers with sodium salts of suitable Alkoxy or Phenoxy derivatives [=P-OR] the final product is formed a stable compound alkoxy or phenoxy sodium phosphonitrile polymer derivative. This stability is only a direct result of the organic substitution at the terminal phosphorus atoms of the chain. This invention relates to the synthesis of linear phosphonitrile chloride polymers. We have also found that if substitution occurs at the phosphorus atoms in the internal $PNCl_2$- units, an immediate decrease in thermal stability is observed.



$$[-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{P}}=N-]_n +_n NaOR \rightarrow [-\overset{\overset{OR}{|}}{\underset{\underset{OR}{|}}{P}}=N-]_n$$

(I)

n =3, 4 or linear polymer

R = X $CH_2(CH_2)_nCH_2$- , X-C_6H_4-O

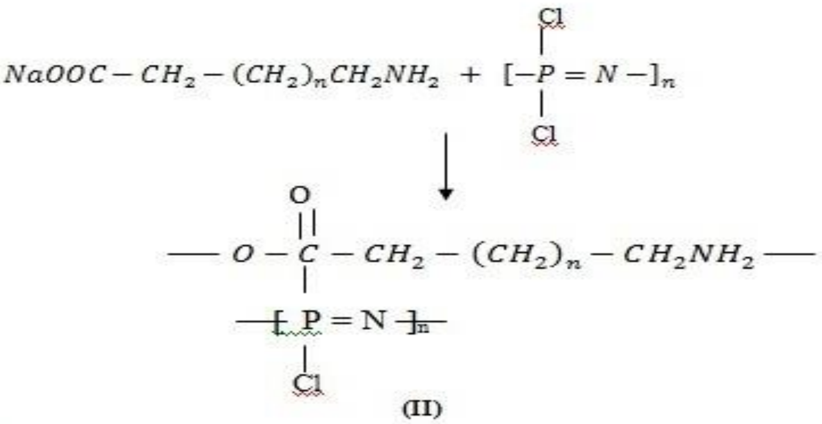
X = $-NH_2$, -COOH, -OH

Scheme-II. Insertion of Amino Acid (L-Arginine or L-Alanine)

We choose L-Arginine and L-Alanine amino acids for this research. As we know, L-Arginine (Arg) is an essential amino acid involved in various human metabolic processes including ammonia detoxification, protein accretion, hormone secretion, immune modulation and other biosynthetic pathways**(G. Wu et al., 2021)[33], (M. C. Pedrazini et al., 2024)[34]**. L-arginine leads to the production of nitric oxide **(G. Wu et al., 2021)[33], (M. C. Pedrazini et al., 2024)[34]**, which relaxes blood vessels, as well as increases blood flow and regulates blood pressure. Reduces cholesterol which helps maintain heart health **(Bode-Böger et al., 1998)[35]**. L-Arginine helps in hormone production in the body, maintaining normal glucose levels while producing insulin in diabetics **(Kazakov et al., 2024)[36]**. L-arginine(Arg) improves blood flow; including strengthening the immune system or accelerating the wound healing process after injury, as well as helping prevent infections and diseases **(J. Jang, et al., 2024)[37]**.

On the other hand, L-Alanine is a non-essential amino acid, as the human body can make it from other amino acids. Provides energy to the body during fasting, thereby increasing physical performance and endurance. Improves muscle growth and repair L-Alanine also improves neurotransmitter regulation, including supporting prostate health. Although we don't need to eat certain foods to get the required amount, consuming higher amounts of L-Alanine can be beneficial for several reasons **(P. Mantuano et al., 2020)[38]; (V. Rovelli et al., 2022)[39]**.

Similarly Sodium salt of Amino acids was reacted with Chlorophosphonitrile to prepare aminoacid phosphonitrile derivatives.

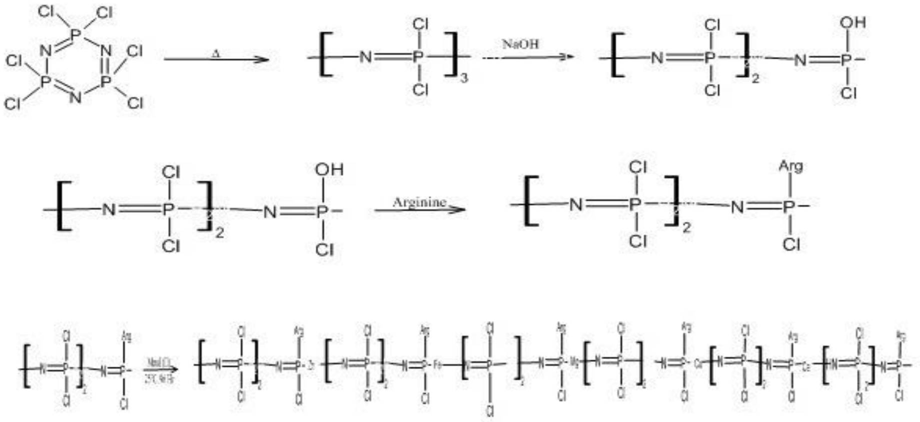


(II)

eg-

Step 3. Preparation[27,30,31,40,41] of Polymer Metal (II) Phosphonitrilic derivatives

We have prepared polymeric Metal(II) phosphonitrile derivatives by reacting phosphonitrile and amino acids with metal salts such as Zn, Cu, Mg, Ca, Fe etc. forming water soluble compounds and have overcome the micronutrient deficiencies caused by spraying of these compounds on Agricultural crops.



4. RESULT AND DISCUSSION

The Polymer Metal (II) Aminoacid: L-Arginine and L- Alanine Phosphonitrilic Derivatives have been synthesized by using nucleophilic substitution reaction. The synthesized polymer have been confirmed and identified by Physical Parameters like Colour, M.P., Yield, Dipole moment[42], pH[43-44], Conductance[42,46] and Dielectric properties[47,48] etc. and Spectral Analysis[49-55] FTIR, X-Ray Differecation study and EDX Spectrum.

Analytical Data:

4.1. COMPOUND A-1. Polymer Metal (II) Arginine Sodium Phosphonitrilic Derivative

Yield: 83%, Colour: Concrete Grey, Melting Point: 172-176ºC, Dipole moment (40ºC in Benzene): 0.97±0.1D, P^H: 6.5, Conductance: 1.6, Dielectric Constant: 2.73±0.04.

Infrared Bands in KBr (cm^{-1}) :1349.50 cm^{-1} (–P=N Stretching -Phosphazene ring), 1205.72cm^{-1} (P–N=P ring), 601.70 cm^{-1} (P-N ring stretching), 525.54 cm^{-1} (N-P-Cl Bending),1002.00 cm^{-1} (O-P ring), 3486.15 cm^{-1} (–NH$_2$(NH$_4^+$) Stretching(strong Absorption), 1246.41 cm^{-1} (C–N Bending and Stretching),1554.20 cm^{-1} and 1402.33 cm^{-1} (Carboxyl(COO$^-$) Bending Assymetric), 927.50cm^{-1} (Zn-P), 624.13 cm^{-1} (Cu-P), 795.12 cm^{-1} (Mg-P), 802.11 cm^{-1} and 1141.91 cm^{-1} (Ca-P), 640.91 cm^{-1} (Fe-P). XRD: Crystalline Solid polymer.

4.2. COMPOUND A-2. Polymer Metal (II) Alanine Sodium Phosphonitrilic Derivative

Yield: 86%, Colour: Grey Purple, Melting Point: 163-165ºC, Dipole moment (40ºC in Benzene): 0.92±0.1D, P^H: 7.1, Conductance: 1.8, Dielectric Constant: 2.76±0.02.

Infrared Bands in KBr (cm^{-1}) :1350.63 cm^{-1} (–P=N Stretching -Phosphazene ring) , 1183.33cm^{-1} (P–N=P ring), 787.66 cm^{-1} (P-N ring stretching), 525.54 cm^{-1} (N-P-Cl Bending),1068.92 cm^{-1} (O-P ring), 3453.19 cm^{-1} (–NH$_2$(NH$_4^+$) Stretching(strong Absorption), 1142.52 cm^{-1} (C–N Bending and Stretching),3029.13cm^{-1} and 2103.01 cm^{-1} (C–H Stretching and Bending), 601.11 cm^{-}1 (C=O), 1576.28 cm^{-1} and 1411.00 cm^{-1} (Carboxyl(COO$^-$) Bending Assymetric), 928.92cm^{-1} (Zn-P), 601.11 cm^{-1} (Cu-P), 878.94 cm^{-1} (Mg-P), 824.94 cm^{-1} (Ca-P), 624.50 cm^{-1} (Fe-P). XRD: Crystalline Solid polymer.

4.3. COMPOUND A-3. Polymer Metal (II) Arginine Ethoxy Phosphonitrilic Derivative.

Yield: 72%, Colour: Neon Blue, Melting Point: 189-192ºC, Dipole moment (40ºC in Benzene): 0.94±0.1D, P^H: 7.4, Conductance: 2.9, Dielectric Constant: 2.68±0.02.

Infrared Bands in KBr (cm^{-1}) :1142.52 cm^{-1} (–P=N Stretching -Phosphazene ring), 1183.33cm^{-1} (P–N=P ring), 602.46 cm^{-1} (P-N ring stretching), 525.54 cm^{-1} (N-P-Cl Bending), 1068.92 cm^{-1} (O-P ring), 3421.02 cm^{-1} (–NH$_2$(NH$_4^+$) Stretching(strong Absorption), 1243.71 cm^{-1} (C–N Bending and Stretching),2953.90cm^{-1}, 2186.61cm^{-1}and 1131.05 cm^{-1} (C–H Stretching and Bending),1470.47cm^{-1} (Carboxyl(COO$^-$) Bending Assymetric), 928.92cm^{-1} (Zn-P), 624.50 cm^{-1} (Cu-P), 878.94 cm^{-1} (Mg-P), 824.99 cm^{-1} (Ca-P), 646.28 cm^{-1} (Fe-P). XRD: Crystalline Solid polymer.

4.4. COMPOUND A-4. Polymer Metal (II) Alanine Ethoxy Phosphonitrilic Derivative

Yield: 77%, Colour: Ultramarine Blue, Melting Point: 203.5ºC, Dipole moment (40ºC in Benzene): 0.89±0.3D, P^H: 6.7, Conductance: 3.2, Dielectric Constant: 2.70±0.04.

Infrared Bands in KBr (cm^{-1}) :1356.19 cm^{-1} (–P=N Stretching -Phosphazene ring) , 1192.23cm^{-1} (P–N=P ring), 1005.14 cm^{-1} (P-N ring stretching), 525.21cm^{-1} (N-P-Cl Bending), 1086.06 cm^{-1} (O-P ring), 3520.57 cm^{-1} (–NH$_2$(NH$_4^+$) Stretching(strong Absorption),1102.23 cm^{-1} (C–N Bending and Stretching),3005.94cm^{-1}, 2943.78cm^{-1}, 2650.19cm^{-1}and 1474.23 cm^{-1} (C–H Stretching and Bending), 1710.92cm^{-1}(>C=O Stretching), 580.02cm^{-1} (C=O), 1577.11cm^{-1} and 1413.73cm^{-1} (Carboxyl(COO^-) Bending Assymetric), 936.52cm^{-1} (Zn-P), 626.87 cm^{-1} (Cu-P), 878.32 cm^{-1} (Mg-P), 840.53 cm^{-1} (Ca-P), 648.94 cm^{-1} (Fe-P). XRD: Crystalline Solid polymer.

4.5. COMPOUND A-5. Polymer Metal (II) Arginine Phenoxy Phosphonitrilic Derivative.

Yield: 72%, Colour: Dark Pastel Shade of Red, Melting Point: 142ºC, Dipole moment (40ºC in Benzene): 0.98±0.1D, P^H: 6.9, Conductance: 2.4, Dielectric Constant: 2.57±0.02.

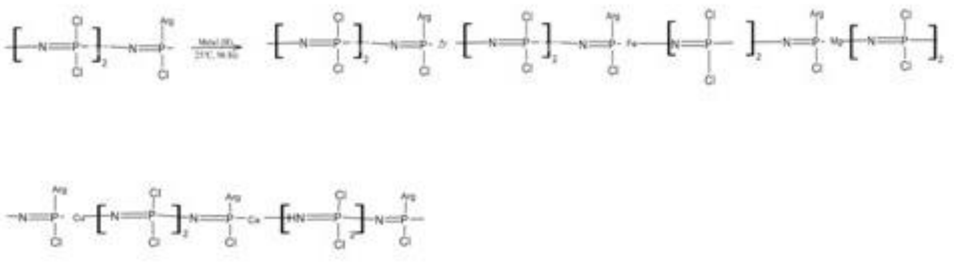
Infrared Bands in KBr (cm^{-1}) :1392.55 cm^{-1} (–P=N Stretching -Phosphazene ring) , 1161.22cm^{-1} (P–N=P ring), 602.71 cm^{-1} (P-N ring stretching), 521.24cm^{-1} (N-P-Cl Bending), 1058.46 cm^{-1} (O-P ring), 3496.21 cm^{-1} ($-NH_2(NH_4^+)$ Stretching(strong Absorption),1243.93 cm^{-1} (C–N Bending and Stretching),3001.01cm^{-1}, 2950.19cm^{-1}, 2876.15cm^{-1}and 1454.43 cm^{-1} (C–H Stretching and Bending), 1710.54cm^{-1}(>C=O Stretching), 571.24cm^{-1} (C=O), 1583.52cm^{-1} 1539.09 cm^{-1} and 1402.20cm^{-1} (Carboxyl(COO^-) Bending Assymetric), 1602.62 cm^{-1}(C-O Phenolic), 920.77cm^{-1} (Zn-P), 602.71 cm^{-1} (Cu-P), 880.38 cm^{-1} (Mg-P), 805.79 cm^{-1} (Ca-P), 640.01 cm^{-1} (Fe-P). XRD: Crystalline Solid polymer.

4.6. COMPOUND A-6. Polymer Metal (II) Alanine Phenoxy Phosphonitrilic Derivative

Yield: 69%, Colour: Reddish Grey, Melting Point:129ºC, Dipole moment (40ºC in Benzene): 0.96±0.2D, P^H: 6.1, Conductance: 2.7, Dielectric Constant: 2.62±0.03.

Infrared Bands in KBr (cm^{-1}) :1387.25 cm^{-1} (–P=N Stretching -Phosphazene ring), 12.03.86cm^{-1} (P–N=P ring), 618.90 cm^{-1} (P-N ring stretching), 521.63cm^{-1} (N-P-Cl Bending), 1070.54 cm^{-1} (O-P ring), 3393.12 cm^{-1} ($-NH_2(NH_4^+)$ Stretching(strong Absorption),1178.37 cm^{-1} (C–N Bending and Stretching),3079.16cm^{-1}, 3013.02cm^{-1}, 2941.82cm^{-1}and 1455.08 cm^{-1} (C–H Stretching and Bending), 1710.23cm^{-1}(>C=O Stretching), 579.39cm^{-1} (C=O), 1599.59cm^{-1} 1451.33 cm^{-1} , 698.03 cm^{-1} and 546.42cm^{-1} (Carboxyl(COO^-) Bending Assymetric), 1611.25 cm^{-1}(C-O Phenolic), 967.04cm^{-1} (Zn-P), 618.99 cm^{-1} (Cu-P), 876.68 cm^{-1} (Mg-P), 744.02 cm^{-1}and 1148.92 cm^{-1} (Ca-P), 698.03 cm^{-1} (Fe-P). XRD: Crystalline Solid polymer.

On the basis of all these techniques the assumed structures are :



5. CONCLUSION

These studies reveal the successful synthesis of six polyphosphazenes A-1, A-2, A-3, A-4, A-5 and A-6 (polymer metal(II) arginine sodium phosphonitrilic derivative, polymer metal(II) alanine sodium phosphonitrilic derivative, polymer metal(II) arginine ethoxy phosphonitrilic derivative, polymer metal(II) alanine ethoxy phosphonitrilic derivative, polymer metal(II) arginine phenoxy phosphonitrilic derivative and polymer metal(II) alanine phenoxy phosphonitrilic derivative) via nucleophilic substitution reaction of chlorine atoms and their further characterization. Their successful synthesis is an advantage of this synthesis system among economical methods based on both inorganic phosphorus-nitrogen chemistry and renewable amino acids and metal (II) cations X-ray diffraction (XRD) elucidates the crystalline structure and size of these phosphonitrile derivatives.

There are three main classes of micronutrients: inorganic, chelate and organic complexes. Inorganic sources such as sulfates of Cu, Mg,Ca, Fe and Zn are the most common metal salts used in the fertilizer industry because they are readily available to plants and soluble in water. Till date no compounds containing phosphonitrile have been used for supply micronutrients to plants. This work mainly focuses on the synthesis of phosphonitrile cyclic derivatives and polymers containing amino acids with metal salts because phosphonitrile itself decomposes to yield phosphate and ammonia which are environmentally friendly and are used as fertilizers for plants.

Polyphosphazenes have many attractive properties found in their elastomeric applications, ceramics, coating adhesives, lubricants, 3D printing, optical properties, sensors, proton conducting polymers, stabilizers, fire resistant military, fire retardant membranes and biological applications. Due to their special properties, polyphosphazenes find many uses in various industries. The effect of phosphonitrile derivatives prepared on agricultural crops (pea and groundnut) to overcome malnutrition has been discussed in detail in a previously published research paper **(Anupam and Chitra, 2023; 2024)** **[20,21]**. Derivatives of phosphonitrile are exploring new applications as smart fertilizers, soil conditioners and plant growth enhancers. Through their advancements, biotechnology and nanotechnology can greatly improve the efficiency of agriculture. They are bound to micronutrients. These inorganic polymers are sprayed on protein-rich crops like peas and groundnuts to increase crop quality and yield, thereby increasing the financial income of farmers.

6. RECOMMONDATION

The foliar spray of these synthesized derivatives are useful for inhancing quality and yield of Agricultural crops which all have been reported in my two earliar research papers mainly on Pea crop and Groundnut crop**(Anupam and Chitra, 2023; 2024)** **[20,21]**. Thus keeping in view of the above said reasons by implementing the suggested technique that relies on environmental friendly, water soluble compound known as phosphonitrile derivative. These derivatives has very low cost and its minute quantity is sufficient for inhancing nutritive value of the crops like Pea and Groundnut as per needed daily life. Application of these derivatives on the agricultural crops like Pea and Groundnut helps in increasing the soil fertility, drought resistance, disease resistant and ultimately improves the overall yield of the crop compare to other fertilizers.

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