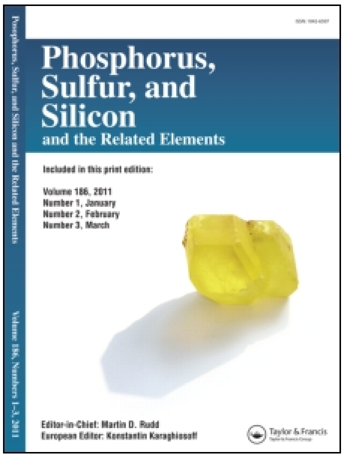

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A MODIFIED METHOD FOR PREPARATION OF A PURE OCTACHLOROCYCLOTETRAPHOSPHAZENE

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A modified method for preparing larger quantities of pure octachloro-cyclo-tetraphosphazene, in which phosphorus pentachloride reacts with ammonium chloride in 1,1,2,2-tetrachloroethane in presence of anhydrous cobalt(II) chloride and nitrogen atmosphere, has been developed. With our new method, cheaper starting materials are used, reaction time is shorter, less by-products are produced, separation of $(PNCl_2)_4$ *is easier and yielded higher than previously reported method, thus leading to a product of a good purity.*

Keywords: Cobalt (II) chloride; cyclic chlorophosphazenes; octachlorocyclotetraphosphazene; phosphorus-nitrogen compounds; phosphorus pentachloride; polyphosphazenes

INTRODUCTION

Polyphosphazenes, the largest class of inorganic macromolecules, have backbones consisting of alternating phosphorus and nitrogen atoms. The groups attached to each phosphorus atom may be organic, organometallic, or inorganic groups. Hexachlorocyclotriphosphazene and octachlorocyclotetraphosphazene, the smallest polymers of polyphosphazenes, are usually used as starting materials for preparation of higher and more complicated polyphosphazenes. Metal complexes are prepared from reactions of polyphosphazenes with certain metal compounds, and have ring nitrogen atoms coordinated to a central metal atom.[1–3] Some metallic polyphosphazene-based complexes are potential catalysts for organic transformations.[4] The literature contains many reports on properties and reactions of hexachlorocyclotriphosphazene and some reports on syntheses of the trimer, tetramer, and linear polymers.[5] In most of the hitherto reported syntheses, the tetramer produced usually needs to be extracted as a by-product from the mixture of reaction products of the trimer preparation.[6–9] Becke-Goehring[10] and Milan Kouril[11] described a direct synthesis of tetramer $(PNCl_2)_4$ using linear chlorophosphazene $(PCl_3NPCl_3)^+Cl^-$ and ammonium chloride as starting materials in an inert solvent, such as tetrachloroethane or nitrobenzene. In their method, the pure tetramer $(PNCl_2)_4$ can be directly prepared with improved yields, while the starting material, linear chlorophosphazene $(PCl_3NPCl_3)^+Cl^-$, is not easily available; the pure product can be obtained only after tedious operations (repeated solvent extractions and final heating under vacuum). Recently, we have succeeded in developing a method for direct preparation of the tetramer octachlorocyclotetraphosphazene, $(PNCl_2)_4$, in which phosphorus pentachloride reacts with ammonium chloride in 1,1,2,2–tetrachloroethane in presence of anhydrous cobalt(II) chloride in nitrogen atmosphere. The new process is characterized by shorter reaction time, simpler operation, and the formation of very little hexachlorocyclotriphosphazene and other polyphosphazene byproducts. The product is easily purified and thus of high purity. Compared with Becke-Goehring and Milan Kouril's method, the starting chemicals PCl_5 and ammonium chloride are cheap and easily available.

EXPERIMENTAL

Preparation of Octachlorocyclotetraphosphazene

1,1,2,2-tetrachloroethane and NH_4Cl were added to a four-neck flask. Before reaction, water was removed from the reaction system. Then anhydrous cobalt(II) chloride (at a ratio of $CoCl_2 : PCl_5 = 1{:}2 \sim 10$) as catalyst and PCl_5 (at a ratio of $PCl_5{:}NH_4Cl = 1{:}1 \sim 1{:}1.7$) was added, while stirring, heating, and refluxing the solution under a nitrogen atmosphere. The reaction temperature was kept between 130–140°C for 8–10 h. The gas HCl evolved was removed by water pump through a funnel inverted over the neck of the reflux condenser. The catalyst and excess ammonium chloride were removed by filtration giving a dark green solution. Solvent was removed under reduced pressure from the reaction mixture in nitrogen atmosphere and, on cooling, a viscous yellowish green solid remained. This solid was washed with absolute ethanol until colorless, and then dried to give a colorless powder (yield: 66.7%), which was recrystallized from petroleum ether (30–60°C) to give white crystals of $(PNCl_2)_4$ [yield: 25%, m.p.122.5–123.5°C] (literature: 122–124°C).

DISCUSSION

The product $(PNCl_2)_4$ was characterized by XRD (D/Max–IIIB) and IR(KBr pellets) performed on a Alpha Centaur IR–10300E spectrometer (Mattson Instruments Ltd).

In XRD patterns, the main peaks were respectively d = 3.84 (220), d = 3.43 (310), d = 7.68 (110), d = 5.24 (101), and d = 2.98 (002); (in Figure 1).

In IR 1287 cm^{-1} (N = P), 896 cm^{-1} (N-P), 795 cm^{-1} (N-P), 576 cm^{-1} (P-Cl), 521 cm^{-1} (P-Cl); the same as in literature. Yield of $N_4P_4Cl_8$ was influenced by the NH_4Cl : PCl_5 (mol) ratio. When the NH_4Cl/PCl_5 (mol) ratio was varied between 1 and 1.8 (Figure 2), highest yield of $N_4P_4Cl_8$ was obtained at the ratio 1:1.5.

Effect of the $CoCl_2$: PCl_5 ratio on yield of $N_4P_4Cl_8$ is shown in Table I. When $CoCl_2$: PCl_5 ratio was 1:2 ~ 2.5, the product obtained was mainly $N_4P_4Cl_8$. Largest yield of $N_4P_4Cl_8$ was obtained at the ratio 1:2.5. At ratio 1:3 ~10, most of the crude product was hexachlorocyclotriphosphazene $N_3P_3Cl_3$(m.p 114°C).

RESULTS

Experimental studies showed that to obtain a satisfactory yield of the pure tetramer the following combination of conditions proved to be

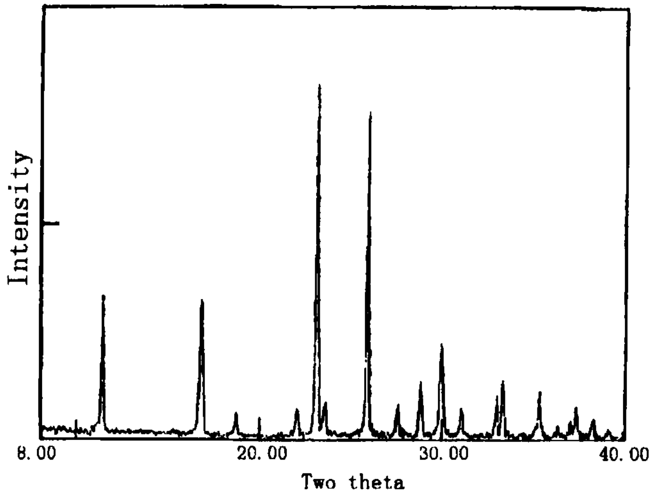

FIGURE 1 The XRD spectrum of $N_4P_4Cl_8$.

TABLE I Effect of $CoCl_2$:PCl_5 Ratio on Yield of Crude Product

$CoCl_2$: PCl_5 ratio	1 : 3 ~ 10	1 : 2.5	1:2
Main product	$N_3P_3Cl_6$	$N_4P_4Cl_8$	$N_4P_4Cl_8$
mp (°C)	105 ~ 110	123.5 ~ 124	123.5 ~ 124
Yield, crude product (%)		66.7	54.3

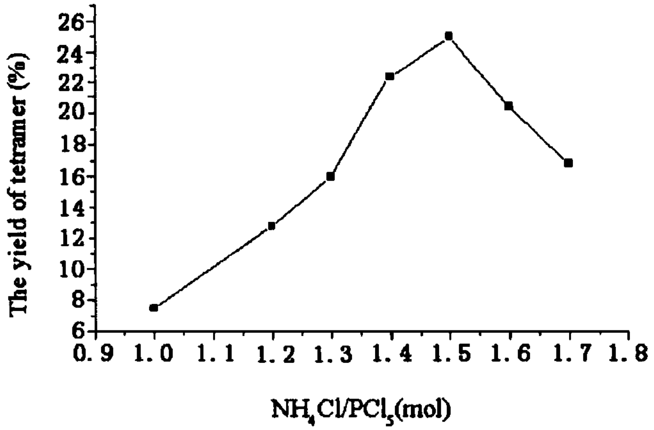

FIGURE 2 Yield of the tetramer vs NH_4Cl/PCl_5 ratio. 1. Reaction temperature at 130–140°C; 2. $CoCl_2$: PCl_5 (molar ratio) = 1 : 2.5.

optimum: (1) appropriately large quantities of cobaltous chloride; (2) suitable reaction temperature range (e.g., 130–140°C); (3) NH_4Cl/PCl_5(mol) = 1.5:1 (Figure 1), the reaction temperature was at 130–140°C and the catalyst quantity was the same as in Figure 1.

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