

## Synthesis and Characterization of Organophosphazene Polyoxotungstate $[(N_3P_3)(SiW_{11}O_{39}H_2)_3]^{12-}$

Jian GONG\*, Chang Lu SHAO, Lun Yu QU

Department of Chemistry, Northeast Normal University, Changchun 130024

**Abstract:** A new organophosphazene polyoxotungstate,  $[(N_3P_3)(SiW_{11}O_{39}H_2)_3]^{12-}$ , has been prepared by reaction of hexachlorocyclotriphosphazene with undecatungstosilicate, and characterized by elemental analysis, infrared spectroscopy, and multinuclear  $^{31}P$  NMR.

**Keywords:** Polyoxotungstate, phosphazene, NMR ( $^{31}P$ ), synthesis.

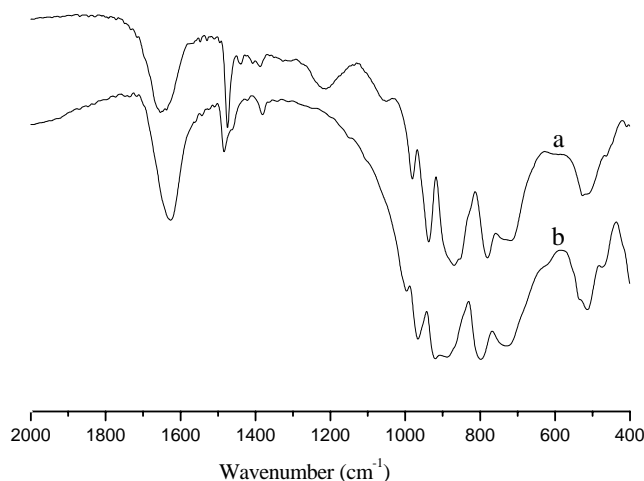
The diversity of phosphazene chemistry can be attributed to the varied reactivity of the phosphorus-halogen bond toward different nucleophiles. Of particular interest is the synthetic diversity of phosphazenes leading to a broad range of cyclophosphazenes, which exhibit a variety of different functional groups<sup>1-2</sup>. In this paper, we report the synthesis and spectroscopic characterization of the first phosphazene polyoxotungstate  $[(N_3P_3)(SiW_{11}O_{39}H_2)_3]^{12-}$ , and deduce the structure of the anion through IR and  $^{31}P$  NMR measurements.

$(Bu_4N)_6H_2[SiW_{11}O_{39}]$  was synthesized according to the published method<sup>3</sup>, and dried under vacuum for 24 h at 70 °C. To the well stirred suspension of 12 g of  $(Bu_4N)_6H_2[SiW_{11}O_{39}]$  in 100 mL of freshly distilled acetonitrile (90 °C) was added dropwise, under  $N_2$  atmosphere, 0.5 g of hexachlorocyclotriphazene in 50 mL of freshly distilled acetonitrile. The acetonitrile solution of hexachlorocyclotriphazene was added dropwise within 6 h, and the mixture was stirred at 90 °C for 140 h. The solid was separated by filtration, washed with benzene, and dried under vacuum for 24 h at 30 °C. The crude product was recrystallized from hot distilled water (2.4 g, yield 15.5%). Anal. Calcd. Si, 0.87; P, 0.96; W, 62.81; Found: Si, 0.90; P, 0.91; W, 63.11.

IR spectrum of the complex is shown in **Figure 1**. The bands at 700-1100  $cm^{-1}$  region corresponding to Keggin unit structural vibrations can be distinguished easily<sup>4</sup>, suggesting that the polyoxometallic moiety of the title complex still retains the basic framework of the Keggin structure. Compared with the IR spectrum of the  $SiW_{11}O_{39}^{8-}$ , two new peaks at 1229 and 1067  $cm^{-1}$ , appear in the IR spectrum of the title complex. The characteristic band at 1229  $cm^{-1}$  suggests existence of N=P and 1067  $cm^{-1}$  band corresponds to P-O<sup>5</sup>. It indicates that polyoxometallic anion is combined with cyclotriphazene by using P-O bond.

\* E-mail: gongj823@nenu.edu.cn

**Figure 1** IR spectra of  $[(N_3P_3)(SiW_{11}O_{39}H_2)_3]^{12-}$  (a) and  $[SiW_{11}O_{39}]^{8-}$  (b)



$^{31}P$  NMR spectrum of the title complex exhibits one line at  $-1.7$  ppm, indicating that three phosphorus atoms of the cyclotriphazene still remain the same chemical environment after the cyclotriphazene is combined with polyoxometallic anion. As we know, the  $C_s$  lacunary anion  $SiW_{11}O_{39}^{8-}$  has a hole surrounded by five oxygen atoms, one  $O_a$ , two  $O_b$  and two  $O_c$ . Obviously, two phosphoryl groups each bridges two of the five oxygen atoms that define the hole in the lacunary polyoxometallic anion. However, the results of the elemental analysis show that the rate of Si: P is 1:1, *i.e.* one cyclotriphazene molecular can be combined with three polyoxometallic anions. At the same time, one line of  $^{31}P$  NMR spectrum of the title complex indicates that one  $SiW_{11}O_{39}^{8-}$  is only combined with one phosphoryl group because of the same chemical environment of the three phosphorus atoms in the title complex. Obviously, another two edge-sharing oxygen possessed two hydrogen atoms. Why one polyoxometallic anion does not combine with two phosphoryl groups? The reason is the bigger spatial barrier.

## References

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