

Synthesis, Structure of Organophosphonyl Polyoxotungstates of Formula $[\text{C}_6\text{H}_{11}\text{P}(\text{O})]_2\text{X}^{\text{n}+}\text{W}_{11}\text{O}_{39}^{(8-\text{n})-}$ ($\text{X}^{\text{n}+}=\text{P}^{5+}, \text{Si}^{4+}, \text{B}^{3+}, \text{Ga}^{3+}$)

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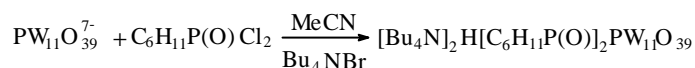
Abstract: Cyclohexanephosphonyl heteropolyundecatungstates of formula $[\text{C}_6\text{H}_{11}\text{P}(\text{O})]_2\text{X}^{\text{n}+}\text{W}_{11}\text{O}_{39}^{(8-\text{n})-}$ ($\text{X}^{\text{n}+}=\text{P}^{5+}, \text{Si}^{4+}, \text{B}^{3+}, \text{Ga}^{3+}$) have been prepared, purified and characterized by elemental analysis, IR and ^1H , ^{31}P and ^{183}W NMR.

Keywords: Polyoxometalates, organophosphorus, complex.

Derivatized polyoxometalates (POMs) have received increasing attention for the last twenty years owing to their potential in bifunctional catalysis¹. It has been recognized for a long time that the versatility of the polyoxometalates and their catalytic application can be significantly increased by grafting organic and organometallic group onto the polyoxometalate surface. Organophosphonyl derivatives of heteropolyanions have been reported previously². As the continuation, we report the synthesis and characterization of the title compounds. Sodium and potassium salt of $\text{X}^{\text{n}+}\text{W}_{11}\text{O}_{39}^{(12-\text{n})-}$ ($\text{X}=\text{P}, \text{Si}, \text{B}, \text{Ga}$) were prepared following literature³. Cyclohexanephosphonyl chloride were prepared according to published method⁴. In the presence of Bu_4NBr , to an acetonitrile solution of sodium or potassium salts of $\text{X}^{\text{n}+}\text{W}_{11}\text{O}_{39}^{(12-\text{n})-}$ ($\text{X}=\text{P}, \text{Si}, \text{B}, \text{Ga}$) was added dropwise 2 equiv of $\text{C}_6\text{H}_{11}\text{P}(\text{O})\text{Cl}_2$ in 15 ml of acetonitrile with vigorous stirring and was acidified with hydrochloric acid. The mixture was stirred about three days at room temperature.

The title compounds were obtained in 23-40% yields and all compounds have been identified by elemental analysis, IR and ^1H , ^{31}P and ^{183}W NMR.

The formulation of all tetrabutylammonium salts of $[\text{C}_6\text{H}_{11}\text{P}(\text{O})]_2\text{X}^{\text{n}+}\text{W}_{11}\text{O}_{39}^{(8-\text{n})-}$ are in agreement with elemental analysis. Their structures are proposed on the basis of NMR and IR spectroscopic data. For example, the ^{31}P NMR spectrum of the



tetrabutylammonium salt of $[\text{C}_6\text{H}_{11}\text{P}(\text{O})]_2\text{BW}_{11}\text{O}_{39}^{5-}$ in CD_3CN displays a single, sharp resonance at 35.2 ppm, in lower field by comparison with that of $\text{C}_6\text{H}_{11}\text{P}(\text{O})\text{Cl}_2$ ($\delta = 58.5$ ppm). All spectral data indicated that each $\text{C}_6\text{H}_{11}\text{PO}$ group is linked to two W atoms through two W—O—P bridges.

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