

Abstract

Macrocycles have been a central subject in both synthetic and material chemistry utilizing their potential not only in host-guest chemistry but also as gas storage and modelling of biological systems. Families of organic macrocycles has far reaching impact on an extremely large area of molecular and supramolecular chemistry, spanning the fields of coordination and material chemistry. In contrast, inorganic macrocycles are far less investigated due to various factors affecting their synthesis, reactivity and purification. In spite of these challenges, it has been possible to assemble inorganic macrocycles. The high bond energy of P-N bond with relatively lower polarity, leads to the development of a new class of macromolecular chemistry. Phosph(III)azane dimers of the type $[\text{CIP}(\mu\text{-NR})_2]$ are excellent building blocks for the formation of a range of inorganic macrocycles. The present work deals with the syntheses of inorganic-organic hybrid macrocycles using cyclodiphosph(III)azane $[\text{CIP}(\mu\text{-N}^t\text{Bu})_2]$ as a inorganic building block. Some new examples of inorganic-organic hybrid macrocycles: $[\{(\text{O}=\text{P}(\mu\text{-N}^t\text{Bu}))_2\}\{\text{O}(\text{CH}_2)_2\text{N}(\text{Me})(\text{CH}_2)_2\text{O}\}]_2$ (**2**) $[(\text{HOCH}_2)(\text{Me})\text{C}(\text{CH}_2\text{O})_2(\mu\text{-}\{\text{P}_2(\mu\text{-N}^t\text{Bu})_2\})_2(-\text{OCH}_2)_2\text{C}(\text{Me})(\text{CH}_2\text{OH})]$ (**3**) and $[(\text{HOCH}_2)(\text{Me})\text{C}(\text{CH}_2\text{O})_2(\mu\text{-}\{(\text{O}=\text{P})_2(\mu\text{-N}^t\text{Bu})_2\})_2(-\text{OCH}_2)_2\text{C}(\text{Me})(\text{CH}_2\text{OH})]$ (**4**) were synthesized by using different organic linkers and characterized by using SCXRD, HRMS and heteronuclear NMR spectroscopy. The macrocycles containing P^{III} units were air and moisture sensitive and by oxidizing the phosphorus from +3 to +5 state, these macrocycles became air stable.