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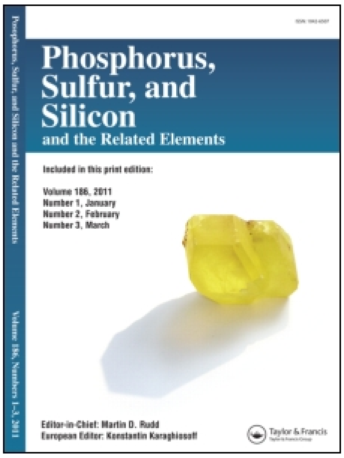

Phosphorus, Sulfur, and Silicon and the Related Elements

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Synthesis and Characterization of the Novel Tetraphosphorus Trisulfide Boron Triiodide $(P_4S_3).(BI_3)$ Adduct: X-Ray Powder Diffraction, ^{31}P Mas NMR, IR and Raman Spectroscopy

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Synthesis and Characterization of the Novel Tetraphosphorus Trisulfide Boron Triiodide $(P_4S_3)\cdot(BI_3)$ Adduct: X-Ray Powder Diffraction, ^{31}P Mas NMR, IR and Raman Spectroscopy

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$(P_4S_3)\cdot(BI_3)$ was prepared and characterized by X-ray Powder Diffraction, ^{31}P MAS NMR, IR and Raman Spectroscopy. Density functional calculations (B3LYP) were carried out.

Keywords: Tetraphosphorus trisulfide boron triiodide adduct; density functional theory; ^{31}P MAS NMR spectroscopy; X-ray powder diffraction; Raman spectroscopy

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INTRODUCTION

Several investigations were published concerning the vibrational frequencies of α-P_4Se_3 , β-P_4Se_3 and the related cage-like molecules P_4S_3, As_4S_3 and As_4Se_3 [1]. Recently, Blachnik et al. published the Lewis acid-bases adduct from the reaction of P_4Se_3 with $NbCl_5$. The crystal structure of $(P_4Se_3)\cdot(NbCl_5)$ showed that the Nb-P bonding is formed with an basal phosphorus atom. In contrast to this species the structure of β-$(P_4S_4)\cdot(NbCl_5)$, formed from P_4S_3 and $NbCl_5$, two $NbCl_5$ units are coordinated on the basal phosphorus atoms [2].

Pure yellow tetraphosphorus trisulfide boron triiodide $(P_4S_3)\cdot(BI_3)$ was prepared by reaction of stoichiometric amounts of P_4S_3 and BI_3 in CS_2.

COMPUTATIONAL RESULTS

Density functional calculations were carried out for both the apical and the basal Lewis acid-base adducts. A 6-31G(d) basis-set was utilized for the phosphorus, sulfur and boron atoms and a DZP basis-set for iodine. Moreover, a quasi-relativistic pseudopotential was used for iodine.

At the considered level of theory (B3LYP) this adduct formation represents an endothermic reaction in the gas phase. In solid state, the lattice energy plays an important role to stabilize this adduct and therefore needs to be considered. For chemically similar compounds the lattice energy lies in the range of 25±5 kcal mol^{-1} which explains the stability of the formed adducts in the solid state. In addition, the reaction entropy has a large influence on the reaction. At B3LYP level the apical and the basal isomers are separate by only 1.71 kcal mol^{-1} in favor at the basal complex. The adduct formation of $(P_4S_3)\cdot(BI_3)(s)$ is assumed to be a slightly exothermic reaction although these adducts are not stable in the gas phase. Both the electronic situation and the thermodynamics should slightly favor the formation of the basal P-B adduct.

EXPERIMENTAL RESULTS

The product formed has been characterized by Raman and IR spectroscopy, solid-state ^{31}P MAS NMR and X-ray powder diffraction.

Vibrational assignments for the normal modes of both possible Lewis acid-base adducts have been made on the basis of comparison between theoretically obtained and experimentally observed Raman and IR data. The experimental vibrational data show the best agreement for the apical adduct.

Additionally, solid-state ^{31}P MAS NMR spectra were recorded of $(P_4S_3)\cdot(BI_3)$ and P_4S_3 for reference using a single pulse aquisition and spinning speeds up to 30 kHz. The spectrum of $(P_4S_3)\cdot(BI_3)$ shows one isotropic shift for the apical and two isotropic shifts (intensity 2 : 1) for the basal phosphorus atoms. The strong high frequency ^{31}P shift of roughly $\delta = +51$ ppm for the resonance of the apical phosphorus atom of $(P_4S_3)\cdot(BI_3)$ compared with those of P_4S_3 indicates the formation of an apical adduct.

Based on these data it was possible to solve the structure by means of a X-ray powder diffraction experiment. The Rietveld structure refinement clearly shows that P_4S_3 forms an apical BI_3 adduct with a fairly long P-B distance of 2.42 Å. The phosphorus-boron bond length is larger than the sum of the covalent radii of 1.88 Å but significantly shorter than the sum of the van der Waals radii.

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