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2D ^{31}P solid state NMR spectroscopy, electronic structure and thermochemistry of PbP_7

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ABSTRACT

Phase pure polycrystalline PbP_7 was prepared from the elements via a lead flux. Crystalline pieces with edge-lengths up to 1 mm were obtained. The assignment of the previously published ^{31}P solid state NMR spectrum to the seven distinct crystallographic sites was accomplished by radio-frequency driven dipolar recoupling (RFDR) experiments. As commonly found in other solid polyphosphides there is no obvious correlation between the ^{31}P chemical shift and structural parameters. PbP_7 decomposes incongruently under release of phosphorus forming liquid lead as remainder. The thermal decomposition starts at $T > 550$ K with a vapor pressure almost similar to that of red phosphorus. Electronic structure calculations reveal PbP_7 as a semiconductor according to the Zintl description and clearly shows the stereoactive Pb-6s^2 lone pairs in the electron localization function ELF.

1. Introduction

Polyphosphides are a unique class of inorganic materials with peculiar crystal chemistry, featuring a manifold of cage-, tube-, layer-like and three-dimensional phosphorus substructures [1,2], often deriving from the elements modifications. The high vapor pressure of phosphorus and the polyphosphide decomposition already at comparatively low temperatures are a severe hindrance for synthesis. Thick-walled silica tubes, high-pressure synthesis [3,4], isopiestic methods [5], salt or metal fluxes [6,7], and mineralizer techniques [8] have been used to overcome the synthetic problems and get access to the polyphosphides. Formation of fibrous materials is a further obstacle for single crystal structure determination.

The synthetic complications are a large challenge for the preparative chemist and this might explain why polyphosphide work still is a vivid field in solid state chemistry. Most recent examples are the first lead polyphosphide PbP_7 [7], the structure of BaP_3 [9], the mineralizer-assisted synthesis of deep-red transparent crystals of NaP_7 [10], the crystal growth and vibrational analyses of LiP_{15} [11], or the clathrate phase $SrNi_2P_4$ [12].

Our recent lead-flux assisted growth of PbP_7 crystals [7] under moderate high-temperature conditions led to larger quantities of the new polyphosphide. Herein we report on thermochemical data and electronic structure calculations with respect to the lead lone-pair activity and a detailed ^{31}P solid state NMR spectroscopic characterization.

2. Experimental

2.1. Synthesis and sample characterization

Crystalline samples of PbP_7 were synthesized from pieces of red phosphorus and lead granules (both abcr) with purities better than 99.9% by using the flux method. First, the phosphorus was ground to a fine powder under cyclohexane and the lead granules were washed with concentrated hydrochloric acid (VWR, 37%) and five times with boiling demineralized water to remove oxidic layers from the metallic surface. Then the elements were mixed in

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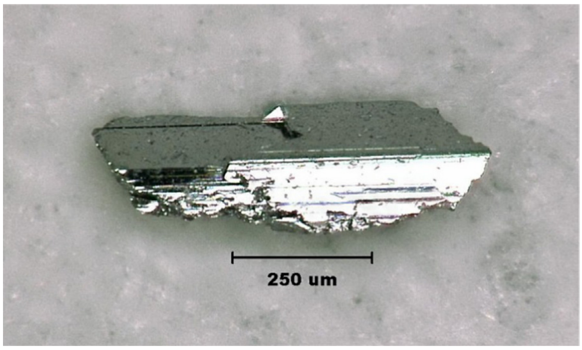

Fig. 1. Selected agglomerated crystals of PbP_7. The edge lengths of the fragment is ca. 0.5 mm.

an atomic ratio of 1:1 under cyclohexane without rubbing the mixture in order to prevent any mass loss. The dried mixtures were then cold-pressed into pellets of 6 mm diameter with a mass of about 0.5 g and sealed in evacuated quartz ampoules. The samples were heated in a muffle furnace up to 673 K within 2 d. After 6 d at that temperature, the samples were cooled to room temperature with a cooling rate of 3 K h^{-1}. The pellets were added to a 1:1 mixture of acetic acid (VWR International, 96%) and H_2O_2 (Sigma Aldrich, 35%) and placed in an ultrasonic cleaning system for 15 min to dissolve the remaining lead flux. After the pellets were decomposed, the solution was removed and the obtained crystals were stirred three times in boiling concentrated hydrochloric acid (VWR, 37%) to remove residual lead and lead chloride. Finally the product was washed three times with boiling demineralized water and acetone. The highly crystalline polyphosphide forms black crystals with edge lengths up to 1 mm (Fig. 1) and a luster reminding to crystalline black phosphorus. The mass yield of the various samples varied between 90% and 95% based on the initial amount of phosphorus. The purity of each sample was checked through a Guinier powder pattern.

2.2. *Solid state NMR spectroscopy*

Solid state NMR spectra were obtained at 202.404 MHz, using 90° pulses of 6.3 μs length, a relaxation delay of 6000 s and a spinning frequency of 10 kHz using a Bruker DSX 500 spectrometer. Radiofrequency driven dipolar recoupling (RFDR) experiments were undertaken at 121.440 MHz, using a spinning speed of 25.0 kHz, and two dipolar mixing times of 1.6 and 0.32 ms, respectively. The 2D data matrix contained 26 t_1 values, which were incremented at 40 μs.

2.3. *Thermogravimetry/high temperature gas balance*

The thermal decomposition behavior of PbP_7 under its own equilibrium vapor pressure has been analyzed using an advanced high-temperature gas balance [13]. In contrast to standard TG measurements, the experimental setup of the HTGB allows the determination of mass changes under equilibrium conditions. Thereby, the vapor phase is enclosed in a silica ampoule and thus realizes an equilibrium in permanent contact with the solid state. The application of the HTGB allows the analysis of solid–gas equilibria in the working range from 0.01 till 15 bar at temperatures up to 1373 K. The current measurements were carried out with an overall weight of 139 mg of starting material PbP_7 in an evacuated silica ampoule ($V = 16$ cm^3), applying a heating rate of 10 K h^{-1} while heating up to 973 K and a cooling rate of 10 K h^{-1} down to ambient temperature. The maximum temperature has been chosen after mass constancy was reached at $T > 733$ K.

2.4. *Computational details*

Self-consistent ab initio band structure calculations were performed with the LMTO method in its scalar relativistic version (program LMTO-ASA 47) [14]. A detailed description may be found elsewhere [15]. Three-dimensional grids of the electron localization function (ELF) [16,17] were calculated. By definition the values for ELF are confined to the range 0–1. Regions in space for which the Pauli principle does not increase the kinetic energy of the electrons can be identified as areas in which pairing of electrons with opposite spins play an important role. Thus, high values of ELF can be treated as equivalent to covalent bonds or lone pairs. The Crystal Orbital Hamiltonian population (COHP) method was used for the bond analysis [18]. COHP gives the energy contributions of all electronic states for a selected bond. The values are negative for bonding and positive for antibonding states. With respect to the well-known COOP diagrams, we plot – COHP(E) to obtain positive values for bonding states.

3. Results and discussion

3.1. *Synthesis, crystal chemical description and lone-pair formation*

Liquid lead was repeatedly used as flux medium for the growth of phosphide, arsenide, or silicide phases in single crystalline form [19–23]. It is remarkable, that crystals of Hittorf phosphorus can be crystallized from melts of white phosphorus in excess lead [23]. The polyphosphide PbP_7, however, was not observed during these studies.

Before discussing the electronic structure and detailed ^{31}P solid state NMR spectroscopic data we briefly redraw to the crystal chemical description of the PbP_7 structure ($P2_1/c$, $a = 970.70(11)$, $b = 673.34(10)$, $c = 1243.89(18)$ pm, $\beta = 122.55(1)°$ [7]; relevant interatomic distances are listed in Table 1). A view of the PbP_7 unit cell along the *a* axis is shown in Fig. 2. The phosphorus atoms built up a complex three-dimensional polyphosphide network in which the lead cations fill cages. The phosphorus substructure of PbP_7 derives from the structures of black phosphorus and α-arsenic. The monomeric structural motifs are P_6 hexagons that are trans-edge-shared, forming strands that extend in *a* direction (emphasized by the blue ellipsoids in Fig. 1). The P–P bond lengths range from 219 to 225 pm, close to the P–P single bond length of 223 pm, suggesting single bond character (two-electron-two-center bonds). From a geometrical point of view, the ellipsoids are arranged in a strongly distorted hexagonal rod packing. Neighboring strands are condensed via the P1 atoms. At the right-hand part of Fig. 2 we present a cutout of the structure of black phosphorus [24]. The P–P distances within the hexagons of 223 and 225 pm

Table 1
Interatomic distances (units of pm) in the structure of PbP_7. The two- (2b) and three-bonded (3b) P atoms are indicated.

Pb	1	P1	283.2	P4(3b)	1	P6	218.8
	1	P6	292.6		1	P3	221.4
	1	P6	297.2		1	P2	225.0
	1	P4	317.5	P5(3b)	1	P5	220.7
	1	P2	321.8		1	P6	220.8
	1	P1	332.9		1	P7	220.9
P1(2b)	1	P7	220.5	P6(2b)	1	P4	218.8
	1	P3	222.2		1	P5	220.8
P2(3b)	1	P7	222.2	P7(3b)	1	P1	220.5
	1	P3	223.0		1	P5	220.9
	1	P4	225.0		1	P2	222.2
P3(3b)	1	P4	221.4				
	1	P1	222.2				
	1	P2	223.0				