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$Cs_4P_2Se_{10}$: A new compound discovered with the application of solid-state and high temperature NMR

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Abstract

The new compound $Cs_4P_2Se_{10}$ was serendipitously produced in high purity during a high-temperature synthesis done in a nuclear magnetic resonance (NMR) spectrometer. ^{31}P magic angle spinning (MAS) NMR of the products of the synthesis revealed that the dominant phosphorus-containing product had a chemical shift of −52.8 ppm that could not be assigned to any known compound. Deep reddish brown well-formed plate-like crystals were isolated from the NMR reaction ampoule and the structure was solved with X-ray diffraction. $Cs_4P_2Se_{10}$ has the triclinic space group P-1 with $a = 7.3587(11)$ Å, $b = 7.4546(11)$ Å, $c = 10.1420(15)$ Å, $\alpha = 85.938(2)^\circ$, $\beta = 88.055(2)^\circ$, and $\gamma = 85.609(2)^\circ$ and contains the $[P_2Se_{10}]^{4-}$ anion. To our knowledge, this is the first compound containing this anion that is composed of two tetrahedral (PSe_4) units connected by a diselenide linkage. It was also possible to form a glass by quenching the melt in ice water, and $Cs_4P_2Se_{10}$ was recovered upon annealing. The static ^{31}P NMR spectrum at 350 °C contained a single peak with a −35 ppm chemical shift and a ~7 ppm peak width. This study highlights the potential of solid-state and high-temperature NMR for aiding discovery of new compounds and for probing the species that exist at high temperature.

Keywords: NMR; Solid state; High temperature; Chalcogenides; Metal selenophosphates; Phosphorus; ^{31}P

1. Introduction

Chalcophosphates are compounds with oxidized phosphorus and at least one P–Q bond, where Q = S, Se, or Te. These compounds exhibit an impressively rich structural diversity because of the large number of stable $[P_xQ_y]^{z-}$ building blocks that can be stabilized and the variety of binding modes in which they can engage [1]. They are important in the areas of catalysis, ceramics, glasses, and molecular sieves [2–4]. Previously, solid-state nuclear magnetic resonance (NMR) has been useful in providing structural information about chalcophosphate materials [5–10]. Most notably, in selenophosphate materials there is a general correlation between the chemical shifts (CSs) of anions and the presence or absence of a P–P bond. Compounds containing a P–P bond resonate between 25 and 95 ppm whereas those that do not contain a P–P bond resonate between −115 and 5 ppm [11]. Additionally, the spectral intensity of a peak in an NMR spectrum is proportional to the number of nuclei that have the corresponding chemical environment [12]. Therefore, NMR spectroscopy is a useful tool to evaluate phase purity in cases where competing compounds have the same NMR-active nucleus.

There is little experimental data about the species that exist at high temperature although it has been proposed that different $[P_xQ_y]^{z-}$ anions exist in the melt in various equilibria [1]. Since there is ^{31}P chemical shift discrimination between P–P and non-P–P bonded selenophosphate species in room temperature solids, *in situ* ^{31}P NMR studies

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Abbreviations: CSA; Chemical shift anisotropy; MAS; Magic angle spinning

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of high-temperature syntheses can potentially provide information about the identity of ^{31}P-containing species that exist at high temperature. The known compound $Cs_4P_2Se_9$ [13] was initially chosen for a high-temperature NMR study because: (1) the synthesis temperature could be reached by our NMR probe; (2) the compound contained the interesting Se-bridged $[P_2Se_9]^{4-}$ anion; and (3) the compound melts congruently which suggests that spectra of subsequent high-temperature remelts should be similar to one another and that some correlation can be made between the remelt spectra and the spectrum of the solid compound.

In this paper, we present the new compound $Cs_4P_2Se_{10}$ which was discovered following high-temperature *in situ* NMR synthesis intended to produce $Cs_4P_2Se_9$. Room temperature solid-state ^{31}P NMR spectra of the synthetic products clearly showed that $Cs_4P_2Se_9$ was not the dominant crystalline product and the structure of $Cs_4P_2Se_{10}$ was subsequently solved with X-ray diffraction of single crystals obtained from the NMR synthesis. Synthetic conditions were varied to ascertain the important factors leading to dominant $Cs_4P_2Se_9$ or $Cs_4P_2Se_{10}$ products and high-temperature ^{31}P NMR spectra of synthetic melts were obtained and analyzed.

2. Experimental section

2.1. Sample preparation

Chemicals were used as obtained unless otherwise noted: phosphorous (MCB Reagents, Gibbstown, NJ, amorphous red), selenium shot (Tellurex Inc., Traverse City, MI, 99.999%) cesium metal, (Aldrich Chemical Co., Inc., St. Louis, MO). Phosphorous was freeze dried and Cs_2Se was prepared by a modified literature preparation [14,15]. P_2Se_5 was prepared by combining a stoichiometric amount of the elements in a pyrex ampoule, flame-sealing at a reduced pressure of ~100 mTorr, then heating to 300 °C over 6 h, holding there for 6 h, and then quenching in air. Manipulations of all starting materials were performed under a nitrogen atmosphere in a dry box (Vacuum Atmospheres Inc.).

The synthesis that produced $Cs_4P_2Se_{10}$ as the dominant P-containing product was performed by combining Cs_2Se (0.186 g, 0.53 mmol), P_2Se_5 (0.124 g, 0.27 mmol), and Se (0.192 g, 2.4 mmol) which were subsequently ground together in an agate mortar and pestle to increase homogeneity. This resulted in a reaction stoichiometry with the nominal composition "$Cs_4P_2Se_{16}$" or an excess of six equivalents of Se relative to the $Cs_4P_2Se_{10}$ stoichiometry. The extra Se in the reaction stoichiometry was added to favor the production of $Cs_4P_2Se_{10}$ rather than $Cs_4P_2Se_9$ [13]. Approximately 75 mg of this mixture was loaded into a fused silica ampoule, sealed at ~100 mTorr, and placed in the high-temperature NMR probe. The sample was then heated at a rate of 10 °C/min, with pauses in the temperature ramp to collect isothermal NMR spectra. After reaching the maximum temperature of 600 °C and collecting an NMR spectrum, the sample was cooled back to room temperature at a rate of 10 °C/min, again pausing for spectral collection. The total time spent above room temperature was ~6 h. A room temperature ^{31}P NMR spectrum following the *in situ* synthesis contained a dominant isotropic peak at −52.8 ppm and integration of all the spectral peaks indicated that $Cs_4P_2Se_{10}$ was >99% of the total P-containing compounds (Fig. 1A). Powder X-ray diffraction indicated that elemental Se also remained in the final products. It was also possible to prepare $Cs_4P_2Se_{10}$ with a conventional high-temperature furnace using the same stoichiometry and a heating/cooling profile of a similar length. Crystals of $Cs_4P_2Se_{10}$ were air and moisture stable over a period of at least several hours.

$Cs_4P_2Se_9$ was produced in high purity by combining Cs_2Se (0.281 g, 0.82 mmol), P_2Se_5 (0.186 g, 0.41 mmol), and Se (0.032 g, 0.41 mmol) in a fused silica ampoule. This resulted in a "$Cs_4P_2Se_8$" reaction stoichiometry and under these Se starved conditions, $Cs_4P_2Se_9$ is favored. The ampoule was subsequently sealed under a reduced pressure of ~100 mTorr and allowed to react in a furnace. The sample was heated to 700 °C over 12 h, held at 700 °C for 12 h, and then cooled to room temperature over 12 h. The room temperature ^{31}P NMR spectrum had a dominant isotropic peak at −39.9 ppm and integration of all the spectral peaks indicated that $Cs_4P_2Se_9$ was >90% of the

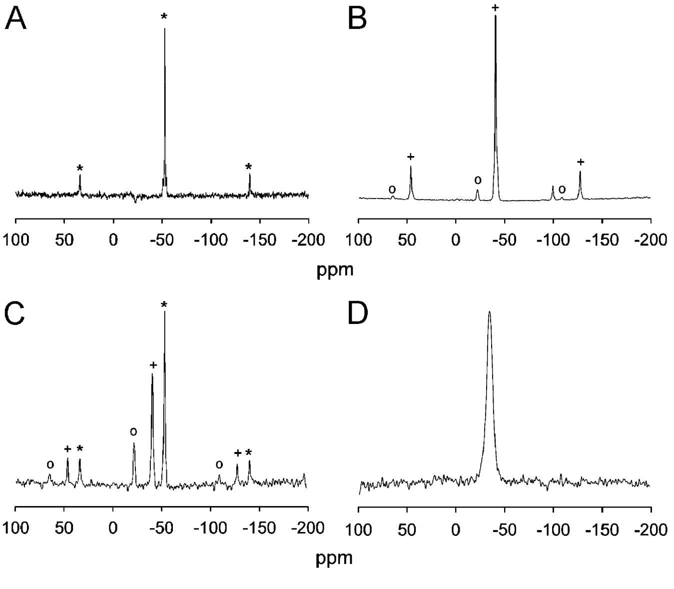

Fig. 1. Ambient temperature ^{31}P MAS NMR spectra of the final products of: (A) a "$Cs_4P_2Se_{16}$" reaction stoichiometry indicating $Cs_4P_2Se_{10}$ as the dominant ^{31}P-containing species at −52.8 ppm; (B) a "$Cs_4P_2Se_8$" reaction stoichiometry indicating $Cs_4P_2Se_9$ as the dominant ^{31}P-containing species at −39.9 ppm; and (C) a "$Cs_4P_2Se_{12}$" reaction stoichiometry that produced $Cs_4P_2Se_9$ and $Cs_4P_2Se_{10}$ in a ~3:5 ratio. Panel D displays the static ^{31}P NMR spectrum of a 350 °C melt of the products in C. The peak with a chemical shift of −22.0 ppm in panels B and C was not assigned and the peak at −99.8 ppm in panel B was not assigned. For spectra A–C, the spinning frequency was 14 kHz and spinning sidebands are grouped with the corresponding isotropic peak using like symbols with *≡$Cs_4P_2Se_{10}$, +≡$Cs_4P_2Se_9$, and o≡unassigned peak with −22.0 ppm isotropic shift.