

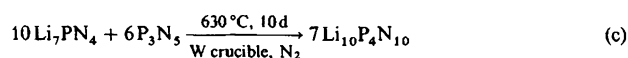
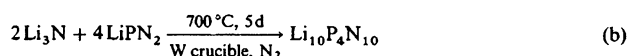
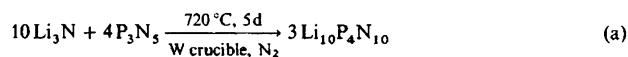
## Li<sub>10</sub>P<sub>4</sub>N<sub>10</sub>—A Lithium Phosphorus(v) Nitride Containing the New Complex Anion P<sub>4</sub>N<sub>10</sub><sup>10⊖</sup>\*\*

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Dedicated to Professor Hans Georg von Schnering on the occasion of his 60th birthday

Phosphorus(v) nitrides, like the nitrides of other light main-group elements (boron, aluminum, silicon), are potential starting compounds for the development of new ceramic materials with special properties.<sup>[1]</sup> However, a systematic entry to the class of compounds comprising binary phosphorus(v) nitrides and their ternary compounds with electropositive elements has been hindered in the past, because the methods used to prepare these compounds did not lead to defined, pure or monocrystalline products. Recently, we employed a new method to prepare defined and finely crystalline P<sub>3</sub>N<sub>5</sub>.<sup>[2]</sup> We obtained pure Li<sub>7</sub>PN<sub>4</sub>, as well as LiPN<sub>2</sub>, by reaction of the binary nitrides P<sub>3</sub>N<sub>5</sub> and Li<sub>3</sub>N. Exact structural characterization of these ternary nitrides led to the first detailed knowledge of the structure of phosphorus(v) nitrides in the solid state.<sup>[3,4]</sup> "Isolated" PN<sub>4</sub><sup>7⊖</sup> ions were found in Li<sub>7</sub>PN<sub>4</sub>, whereas, in LiPN<sub>2</sub>, which has a P–N partial structure analogous to β-cristobalite, PN<sub>4</sub> tetrahedra are vertex-linked on all sides to produce the highest conceivable degree of interconnection. Both compounds show a noticeable cation mobility in the solid state and are therefore novel lithium ion conductors.<sup>[5]</sup>

We have now discovered Li<sub>10</sub>P<sub>4</sub>N<sub>10</sub>, a new lithium phosphorus(v) nitride whose composition lies between those of Li<sub>7</sub>PN<sub>4</sub> and LiPN<sub>2</sub> and which therefore represents the first example of a phosphorus(v) nitride with an intermediate degree of condensation of PN<sub>4</sub> tetrahedra. Li<sub>10</sub>P<sub>4</sub>N<sub>10</sub> can be prepared by solid-state reaction of the binary nitrides Li<sub>3</sub>N and P<sub>3</sub>N<sub>5</sub> [Eq. (a)] as well as by reaction of LiPN<sub>2</sub> with Li<sub>3</sub>N [Eq. (b)] or of Li<sub>7</sub>PN<sub>4</sub> with P<sub>3</sub>N<sub>5</sub> [Eq. (c)]. The title compound is obtained as a colorless powder and as transparent octahedral single crystals.<sup>[6]</sup>



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Single-crystal X-ray structure analysis<sup>[7]</sup> revealed that  $\text{Li}_{10}\text{P}_4\text{N}_{10}$  has an ionic structure and contains the new complex anion  $\text{P}_4\text{N}_{10}^{10-}$ , which is isoelectronic to molecular phosphorus(v) oxide,  $\text{P}_4\text{O}_{10}$  (Fig. 1). The anion shows ideal  $T_d$  symmetry in the solid. As expected, the IR spectrum of  $\text{Li}_{10}\text{P}_4\text{N}_{10}$  displays six vibrational bands for the complex anion between  $540$  and  $1070\text{ cm}^{-1}$ .<sup>[8]</sup> The P–N bonds to the terminal nitrogen atoms of the  $\text{P}_4\text{N}_{10}^{10-}$  ion are significantly shorter than those to the bridging N atoms (P–N2  $158.1(3)$ , P–N1  $167.6(3)$  pm). This is presumably due to a greater degree of polar-bond character in the bonds between phosphorus and terminal nitrogen.

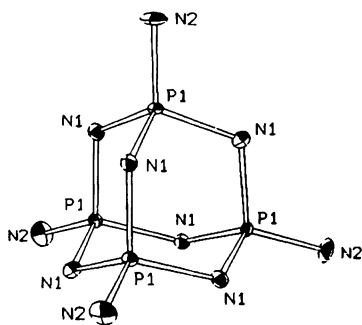


Fig. 1. Structure of the  $\text{P}_4\text{N}_{10}^{10-}$  ion in the solid state (ellipsoids drawn at 50% probability). Selected distances [pm] and angles [°] (standard deviations in parentheses): P–N2  $158.1(3)$ , P–N1  $167.6(3)$ ; N1–P–N2  $112.7(1)$ , N1–P–N1  $105.9(1)$ , P–N1–P  $116.0(2)$ .

Surprisingly, the packing of the  $\text{P}_4\text{N}_{10}^{10-}$  ions in the solid corresponds to that of molecular  $\text{As}_4\text{O}_6$  in the cubic high-temperature phase arsenolite, despite the differing compositions.<sup>[9, 10]</sup> Thus, the  $\text{P}_4\text{N}_{10}^{10-}$  ions in the solid are arranged in a zinc blende fashion, resulting in an appreciably more favorable packing of the complex anions compared with, for example, molecular phosphorus(v) oxide,  $\text{P}_4\text{O}_{10}$  (distorted body-centered arrangement).<sup>[11]</sup> It is this ionic structure formed by lithium cations and  $\text{P}_4\text{N}_{10}^{10-}$  anions which renders possible the space-saving packing, which cannot be achieved for the topologically comparable and isoelectronic, but uncharged,  $\text{P}_4\text{O}_{10}$ .

The arsenolite-like packing of the  $\text{P}_4\text{O}_{10}^{10-}$  ions in the solid forces the  $\text{Li}^{\oplus}$  ions in  $\text{Li}_{10}\text{P}_4\text{N}_{10}$  to occupy markedly different positions. In addition to trigonal-planar coordination of  $\text{Li}^{\oplus}$  ions, tetrahedral and even near-octahedral coordination by nitrogen are found. Finally, one-tenth of the  $\text{Li}^{\oplus}$  ions in  $\text{Li}_{10}\text{P}_4\text{N}_{10}$  are distributed with disorder over positions with a multiplicity higher than the actual number of atoms. The Li–N contact distances ( $193$ – $220$  pm) correspond roughly to the sum of the ionic radii<sup>[12, 13]</sup> and they increase, as expected, with the coordination number of the cations.

The close packing of the complex anions realized here is apparently caused by the tendency toward coordinative saturation of the  $\text{Li}^{\oplus}$  ions. Owing to the topology of the complex  $\text{P}_4\text{N}_{10}^{10-}$  ions, however, it is not possible to coordinate the relatively large number of  $\text{Li}^{\oplus}$  ions ( $\text{Li}^{\oplus}$ :  $\text{P}_4\text{N}_{10}^{10-} = 10:1$ ) in the same way. For this reason the  $\text{Li}^{\oplus}$  ions are distributed over positions that, from the viewpoint of crystal chemistry, are surrounded by nitrogen in an unusual number of different ways. Analogously to  $\text{Li}_7\text{PN}_4$  and  $\text{LiPN}_2$ , we expect  $\text{Li}_{10}\text{P}_4\text{N}_{10}$  to exhibit a significant lithium ion conductivity.

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$\text{Li}_3\text{N}$ , 26134-62-3;  $\text{P}_3\text{N}_5$ , 12136-91-3;  $\text{LiPN}_2$ , 60883-88-7;  $\text{Li}_7\text{PN}_4$ , 11118-04-0;  $\text{Li}_{10}\text{P}_4\text{N}_{10}$ , 133670-95-8.

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- [6] The composition of  $\text{Li}_{10}\text{P}_4\text{N}_{10}$  was determined by elemental analysis (lithium by flame photometry, phosphorus as molybdovanadatophosphate by photometry, and nitrogen as indophenol by photometry). The absence of hydrogen (N–H) was checked by IR spectroscopy.
- [7]  $\text{Li}_{10}\text{P}_4\text{N}_{10}$ :  $Fd\bar{3}m$ ,  $a = 1230.9(1)$  pm,  $Z = 8$ , Enraf-Nonius CAD4 diffractometer,  $\text{MoK}\alpha$  radiation, graphite monochromator, scan width  $2^\circ$ ,  $\omega$  scan, 958 measured reflections with  $2^\circ \leq \theta \leq 32^\circ$ , 166 symmetry-independent reflections with  $F_0 \geq 3\sigma(F_0)$ ,  $R_{\text{int}} = 0.047$ , anisotropic refinement.  $R = 0.074$ ,  $R_w = 0.042$  with  $w = 10.8/(\sigma^2(F_0))$ . Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-55175, the names of the authors, and the journal citation.
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