

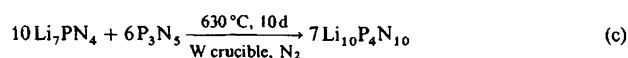
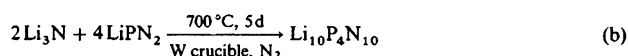
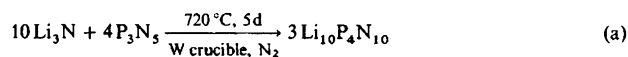
Li₁₀P₄N₁₀—A Lithium Phosphorus(v) Nitride Containing the New Complex Anion P₄N₁₀^{10⊖}**

By Wolfgang Schnick* and Ute Berger

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.^[1] 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 P₃N₅.^[2] We obtained pure Li₇PN₄, as well as LiPN₂, by reaction of the binary nitrides P₃N₅ and Li₃N. Exact structural characterization of these ternary nitrides led to the first detailed knowledge of the structure of phosphorus(v) nitrides in the solid state.^[3,4] "Isolated" PN₄^{7⊖} ions were found in Li₇PN₄, whereas, in LiPN₂, which has a P–N partial structure analogous to β-cristobalite, PN₄ 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.^[5]

We have now discovered Li₁₀P₄N₁₀, a new lithium phosphorus(v) nitride whose composition lies between those of Li₇PN₄ and LiPN₂ and which therefore represents the first example of a phosphorus(v) nitride with an intermediate degree of condensation of PN₄ tetrahedra. Li₁₀P₄N₁₀ can be prepared by solid-state reaction of the binary nitrides Li₃N and P₃N₅ [Eq. (a)] as well as by reaction of LiPN₂ with Li₃N [Eq. (b)] or of Li₇PN₄ with P₃N₅ [Eq. (c)]. The title compound is obtained as a colorless powder and as transparent octahedral single crystals.^[6]



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Single-crystal X-ray structure analysis^[7] 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, P_4O_{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 cm^{-1} .^[8] 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.

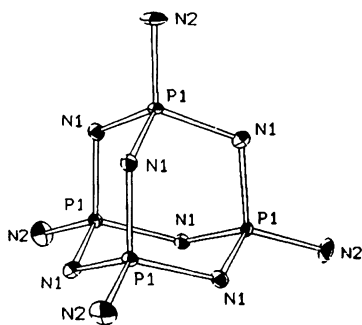


Fig. 1. Structure of the $\text{P}_4\text{N}_{10}^{10-}$ ion in the solid state (ellipsoids drawn at 50% probability). Selected distances [pm] and angles [°] (standard deviations in parentheses): P–N2 $158.1(3)$, P–N1 $167.6(3)$; N1–P–N2 $112.7(1)$, N1–P–N1 $105.9(1)$, P–N1–P $116.0(2)$.

Surprisingly, the packing of the $\text{P}_4\text{N}_{10}^{10-}$ ions in the solid corresponds to that of molecular As_4O_6 in the cubic high-temperature phase arsenolite, despite the differing compositions.^[9, 10] 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, P_4O_{10} (distorted body-centered arrangement).^[11] 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, P_4O_{10} .

The arsenolite-like packing of the $\text{P}_4\text{O}_{10}^{10-}$ ions in the solid forces the 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 Li^{\oplus} ions, tetrahedral and even near-octahedral coordination by nitrogen are found. Finally, one-tenth of the 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^[12, 13] 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 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 Li^{\oplus} ions (Li^{\oplus} : $\text{P}_4\text{N}_{10}^{10-} = 10:1$) in the same way. For this reason the 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 Li_7PN_4 and LiPN_2 , we expect $\text{Li}_{10}\text{P}_4\text{N}_{10}$ to exhibit a significant lithium ion conductivity.

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Li_3N , 26134-62-3; P_3N_5 , 12136-91-3; LiPN_2 , 60883-88-7; Li_7PN_4 , 11118-04-0; $\text{Li}_{10}\text{P}_4\text{N}_{10}$, 133670-95-8.

- [1] E. V. Borisov, E. E. Nifant'ev, *Russ. Chem. Rev.* 46 (1977) 842.
- [2] W. Schnick, J. Lücke, unpublished.
- [3] W. Schnick, J. Lücke, *J. Solid State Chem.* 87 (1990) 101.
- [4] W. Schnick, J. Lücke, *Z. Anorg. Allg. Chem.* 588 (1990) 19.
- [5] W. Schnick, J. Lücke, *Solid State Ionics* 38 (1990) 271.
- [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° , ω 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.
- [8] In the IR spectrum (KBr and PE discs, range 4000 to 150 cm^{-1}) the only vibrational bands observed were those expected on the basis of the site symmetry (T_d) of the complex $\text{P}_4\text{N}_{10}^{10-}$ anion in the solid state: $\nu_{\text{as}}(\text{P}=\text{N}_{\text{ext}})$, 1067 cm^{-1} ; $\delta(\text{P}=\text{N}_{\text{ext}})$, 541 cm^{-1} ; cage vibrations, 1000 , 839 , 778 , and 660 cm^{-1} .
- [9] K. E. Almin, A. Westgren, *Ark. Kemi B* 15 (1942) 1.
- [10] Temperature-dependent Guinier photographs revealed no phase transitions between -100 and $+120^\circ\text{C}$ for $\text{Li}_{10}\text{P}_4\text{N}_{10}$.
- [11] M. Jansen, M. Möbs, *Z. Kristallogr.* 159 (1982) 283.
- [12] A. Rabenau, *Solid State Ionics* 6 (1982) 277.
- [13] W. H. Baur, *Crystallogr. Rev.* 1 (1987) 59.