Reinvestigation of Na$_3$P based on single-crystal data

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Key indicators

Single-crystal X-ray study

T = 165 K

Mean σ(Na–Na) = 0.003 Å

R factor = 0.039

wR factor = 0.084

Data-to-parameter ratio = 17.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure of trisodium phosphide, Na$_3$P, known from X-ray powder diffraction data, has been refined based on single-crystal data. The compound crystallizes in the hexagonal A_3B (A = alkali metal and B = group 15 element) structure type and is isotypic with the homologous potassium phase. The framework is built of Na$^+$ and P^{3-} ions arranged in two kinds of layers perpendicular to the c axis. Two of the Na atoms and the P atom reside at positions of $\bar{6}m2$ (2b), $3m$ (4f) and $\bar{6}m2$ (2c) site symmetry, respectively.

Comment

Trisodium phosphide, Na$_3$P, has been used as a starting material for III-V semiconductor (Treece *et al.*, 1993; Khanna *et al.*, 2003), binary or multinary transition metal phosphides as a phosphorus source (Rowley & Parkin, 1993; Hector & Parkin, 1994; Xie *et al.*, 2000; Jarvis *et al.*, 2000; Yunle *et al.*, 2002; Lin *et al.*, 1992; Nuss *et al.*, 1997) and as a catalyst for olefin polymerization. In spite of those various uses, the crystal structure and lattice parameters were reported with only limited precision, relying on powder-diffraction data obtained by film methods (Brauer & Zintl, 1937). We report here the single-crystal structure of the title compound and confirm the basic structural features determined from powder diffraction; we also give more precise structural information.

The title compound, trisodium phosphide Na$_3$P, crystallizes in the hexagonal A_3B (A = alkali metals and B = group 15 elements) structure (Brauer & Zintl, 1937; Gnutzmann *et al.*, 1961), as shown in Fig. 1. The framework is built of Na$^+$ and
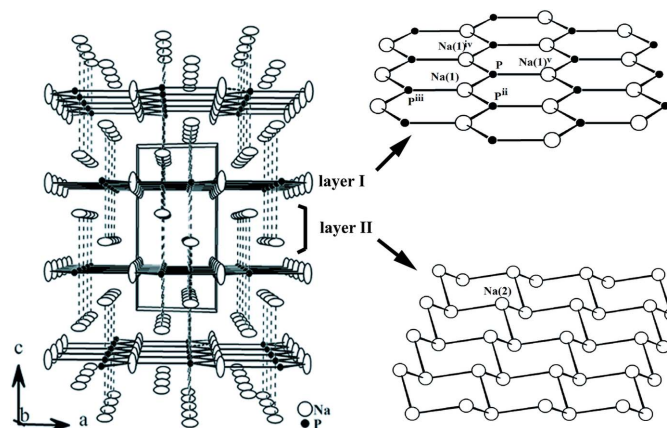

Figure 1

The structure of Na$_3$P is shown, emphasizing the layered connectivity of the Na–P network. The type I and II layers are emphasized. The stoichiometry of the type I layers is NaP and that of type II is Na$_2$. The closest Na—Na distance is between two type II layers and is highlighted by a hatched line within the unit-cell box. Displacement ellipsoids are drawn at the 60% probability level. [Symmetry codes: (ii) $x, y - 1, z$; (iii) $x - 1, y - 1, z$; (iv) $x, 1 + y, z$; (v) $1 + x, 1 + y, z$.]

P^{3-} ions arranged in two kinds of layers perpendicular to the c axis. The first layer is made up of graphite-like rings of Na1 and P atoms (layer I), and the second layer is composed of chair-form cyclohexane-like rings of Na2 atoms (layer II). P atoms are surrounded by five Na atoms in a trigonal bipyramidal arrangement. Three Na1 atoms come from layer I and two Na2 atoms come from layer II. The interatomic distances between the P and Na atoms are 2.8586 (3) Å for Na1 (solid line in Fig. 1) and 2.9053 (17) Å for Na2 (dashed line in Fig. 1). These values are in good agreement with the Na—P interatomic distances (2.875–2.987 Å) in NaP (von Schnering & Hönle, 1979). The shortest Na—Na interatomic distance is 2.977 (3) Å, between two Na2 atoms in different sheets (see Fig. 1).

Experimental

In an attempt to prepare phosphorus-containing nitrides, Na_3P was obtained by the reaction of NaN_3, TiN and P with a KI halide flux. The starting materials NaN_3 (0.0650 g, Aldrich, 99%), TiN (0.0619 g, Alfa Aesar, 99.5%), P (0.0310 g, JohnsonMatthey, 99.999%) and KI (0.3158 g) were placed into an Nb tube, which was made by welding one end of Nb tubing in an argon atmosphere, using a Centorr Associates arc furnace. After the remaining end was welded closed, the niobium tube was put into a silica tube and sealed under vacuum to protect it from oxidation during heating. The reaction tubes were heated gradually to 1073 K over 15 h and held at this temperature for 48 h. The tubes were cooled to 373 K at 3 K h^{-1}. The furnace was then turned off and the reaction tube was cooled to room temperature. After opening the Nb tube in an inert atmosphere glove-box, we observed several different crystal types, such as colorless transparent blocks, metallic shiny polyhedra and dark-red blocks. The former two crystal types were found to be KI and NbP, respectively, by means of single-crystal diffraction methods. Additionally, a powder X-ray diffraction pattern with a Scintag 2000 θ–θ diffractometer using Cu $K\alpha$ radiation showed that the dominant products are KI and unreacted TiN. A microprobe analysis of the dark-red blocks was performed with an EDAX (Thermonoran) equipped scanning electron microscope (Jeol JXA-8900R). Analysis of these crystals showed only the presence of Na and P; no other elements were detected. To prevent decomposition of the samples, the title compound was transferred from an Ar-filled glove-box to the microprobe using a specially designed portable antechamber (Ehrlich, 1995).

Crystal data

Na_3P
$M_r = 99.94$
Hexagonal, $P6_3/mmc$
$a = 4.9512 (5)$ Å
$c = 8.7874 (13)$ Å
$V = 186.56 (4)$ Å^3
$Z = 2$
$D_x = 1.779$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 196 reflections
$\theta = 3.3–40.2°$
$\mu = 0.81$ mm^{-1}
$T = 165.0 (1)$ K
Block, red
$0.10 \times 0.10 \times 0.05$ mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1999)
$T_{min} = 0.657, T_{max} = 0.960$
1495 measured reflections

155 independent reflections
115 reflections with $I > 2\sigma(I)$
$R_{int} = 0.048$
$\theta_{max} = 32.2°$
$h = -7 \rightarrow 7$
$k = -7 \rightarrow 7$
$l = -12 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.084$
$S = 1.13$
155 reflections
9 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2 + 0.2162P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}
Extinction correction: SHELXL97
Extinction coefficient: 0.16 (3)

Table 1
Selected geometric parameters (Å, °).

Na1—P	2.8586 (3)	Na2—Na2^i	2.977 (3)
Na2—P	2.9053 (17)		
P^{iii}—Na1—P	120	Na1—P—Na2	90
Na1^v—P—Na1	120	Na2^{vi}—P—Na2	180

Symmetry codes: (i) $x, y, -z + \frac{3}{2}$; (iii) $x - 1, y - 1, z$; (v) $x + 1, y + 1, z$; (vi) $x, y, -z + \frac{1}{2}$.

Data collection: SMART (Bruker, 2003); cell refinement: SAINT-Plus (Bruker, 2003); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS86 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg, 1999); software used to prepare material for publication: WinGX (Farrugia, 1999).

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