

# Rb<sub>3</sub>P<sub>6</sub>N<sub>11</sub> and Cs<sub>3</sub>P<sub>6</sub>N<sub>11</sub>—New Highly Condensed Nitridophosphates by High-Pressure High-Temperature Synthesis

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The nitridophosphates Rb<sub>3</sub>P<sub>6</sub>N<sub>11</sub> and Cs<sub>3</sub>P<sub>6</sub>N<sub>11</sub> were synthesized by the reaction of the respective alkali azides with P<sub>3</sub>N<sub>5</sub> at 35 kbar and 1300°C using a multianvil assembly. The products were obtained as colorless crystalline powders. According to powder diffractometry it was obvious that Rb<sub>3</sub>P<sub>6</sub>N<sub>11</sub> and Cs<sub>3</sub>P<sub>6</sub>N<sub>11</sub> are isotypic to K<sub>3</sub>P<sub>6</sub>N<sub>11</sub>. The crystal structures were refined from powder diffraction data by the Rietveld method using the atomic coordinates of K<sub>3</sub>P<sub>6</sub>N<sub>11</sub> as starting values (Rb<sub>3</sub>P<sub>6</sub>N<sub>11</sub>, *P4*, *Z* = 4, *a* = 1049.74(1) pm; Cs<sub>3</sub>P<sub>6</sub>N<sub>11</sub>, *a* = 1065.15(1) pm). © 2001 Academic Press

**Key Words:** alkali metals; high-pressure chemistry; nitridophosphates; solid-state structures.

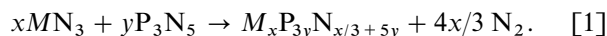
## INTRODUCTION

Ternary and multinary nitrides of the heavier alkali metals are difficult to synthesize. One of the reasons might be the fact that the binary nitrides *M*<sub>3</sub>N (*M* = Na–Cs) do not exist and thus they are not available as starting materials for synthesis.

Only a few ternary and multinary phosphorus (V) nitrides have been synthesized in the past. Furthermore, the crystal structure of P<sub>3</sub>N<sub>5</sub>, the parent compound of the nitridophosphates has been determined only recently after long-lasting efforts (1). The challenge in synthesis of phosphorus nitrides is to find appropriate crystallization conditions for these compounds. Due to the weakness of the P–N bond phosphorus nitrides easily decompose irreversibly by elimination of N<sub>2</sub> above 700°C. Moreover, phosphorus in the oxidation state +V can be easily reduced, which allows unintentional side reactions. Therefore, it is difficult to achieve a reconstructive transformation of the P–N bonds to obtain a well crystalline nitridophosphate.

Recently, we have reported on an elegant synthetic approach leading to alkali nitridophosphates using the reaction of the respective alkali azides and P<sub>3</sub>N<sub>5</sub> under

high-pressure high-temperature conditions (2). We have demonstrated that by this procedure highly condensed alkali nitridophosphates (molar ratio P:N > 1:2) are accessible that could not be synthesized by conventional methods yet. In the above-mentioned reactions the composition of the resulting products can easily be controlled by variation of the molar ratio of the starting materials MN<sub>3</sub> and P<sub>3</sub>N<sub>5</sub>. This procedure successfully has been applied to the synthesis of MP<sub>4</sub>N<sub>7</sub> (*M* = Na–Cs) yet:



Here we report on the synthesis and crystal structure determination of the hitherto unknown Rb<sub>3</sub>P<sub>6</sub>N<sub>11</sub> and Cs<sub>3</sub>P<sub>6</sub>N<sub>11</sub>, the heavier homologs of K<sub>3</sub>P<sub>6</sub>N<sub>11</sub>. The potassium nitridophosphate has been obtained by the reaction of KNH<sub>2</sub> and P<sub>3</sub>N<sub>5</sub> under ammonothermal conditions (3). The synthesis of Rb<sub>3</sub>P<sub>6</sub>N<sub>11</sub> and Cs<sub>3</sub>P<sub>6</sub>N<sub>11</sub> confirms that a broad synthetic approach to nitridophosphates can be achieved by the use of high-pressure conditions.

## EXPERIMENTAL

### 1. Synthesis

P<sub>3</sub>N<sub>5</sub>. Phosphorus(V) nitride (P<sub>3</sub>N<sub>5</sub>) was synthesized from hexachlorocyclotriphosphazene ((PNCl<sub>2</sub>)<sub>3</sub>, p.a., Fluka) by reaction with dried gaseous ammonia (99.8%, Linde) in a quartz flow-through tube placed in a furnace (4). In the first reaction step (PNCl<sub>2</sub>)<sub>3</sub> was heated to 100°C for 10 h under flowing ammonia and then cooled down to room temperature and powdered. The procedure then was repeated at 115, 175, and 265°C, respectively. Subsequently, the crude product was heated to 600°C under evacuation (10<sup>2</sup> Pa) and finally to 950°C for 2 h under flowing ammonia.

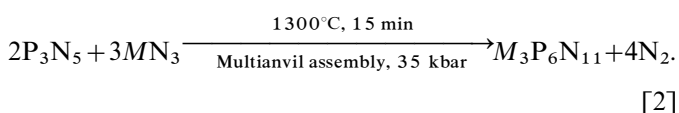
MN<sub>3</sub> (*M* = Rb, Cs). An anion exchange resin (30 g, Ionenaustauscher III(OH<sup>−</sup>), Merck) was loaded with N<sub>3</sub><sup>−</sup> ions using column technique and an 0.1 N aqueous solution of NaN<sub>3</sub> (extra pure, Merck). The respective metal chloride (2 g, p.a., Merck) was dissolved in H<sub>2</sub>O (150 ml) and the

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solution was placed onto the ion exchange resin. After the solution had passed the column, the solvent was evaporated in vacuum and single phase  $MN_3$  (checked by X-ray powder diffraction) was obtained.

$M_3P_6N_{11}$  ( $M = Rb, Cs$ ). A mixture of the respective azide  $MN_3$  and  $P_3N_5$  was mixed thoroughly in the molar ratio  $M:P = 0.5$  and charged into a hexagonal BN (hBN) capsule. The sealed capsule was subjected to the conditions of 35 kbar and 1300°C using a multianvil assembly. After maintaining the desired high-temperature and high-pressure conditions for 15 min the sample was quenched to room temperature before releasing the applied pressure. This process led to the formation of  $M_3P_6N_{11}$  as a crystalline air-stable white powder (Eq. [2]):



## 2. X-ray Diffraction Investigations

The X-ray diffraction measurements of  $Rb_3P_6N_{11}$  were carried out with a conventional transmission powder diffractometer in Debye-Scherrer geometry with  $CuK\alpha_1$  radiation. Because of the higher X-ray absorption coefficient of cesium,  $Cs_3P_6N_{11}$  was investigated with  $MoK\alpha_1$  radiation. From the diffraction patterns (Figs. 1 and 2), it was obvious that  $Rb_3P_6N_{11}$  and  $Cs_3P_6N_{11}$  are isotypic with  $K_3P_6N_{11}$  (3). The Rietveld refinement of the crystal structures was performed with the program GSAS (5) using the atomic coordinates of  $K_3P_6N_{11}$  as starting values.

Detailed crystallographic data are summarized in Table 1, the refined parameters are listed in Table 2. Table 3 gives selected interatomic distances and angles (6).

## RESULTS AND DISCUSSION

In the solid state  $Rb_3P_6N_{11}$  and  $Cs_3P_6N_{11}$  contain three-dimensional P–N network structures of corner sharing  $PN_4$  tetrahedra. Both compounds are isotypic with  $K_3P_6N_{11}$  (3). As a consequence of the molar ratio  $P:N = 6:11$  two sorts of nitrido bridges (denoted as  $N^{[2]}$  and  $N^{[3]}$ ) occur with the molar ratio 9:2. According to  ${}^3_3[(P_6^{[4]}N_9^{[2]}N_2^{[3]})^{3-}]$  these nitrogen atoms are connected to two and three neighboring phosphorus atoms, respectively. Nitrido bridges  $N^{[3]}$  have rarely been identified in phosphorus nitrides and the only representatives yet found are  $P_3N_5$  (1),  $HP_4N_7$  (7),  $P_4N_6O$  (8),  $MP_4N_7$  (2) ( $M = Na, K, Rb, Cs$ ),  $Na_3P_6N_{11}$  (9), and  $K_3P_6N_{11}$  (3). In contrast, analogous  $N^{[3]}$  connections between three Si tetrahedral centers have frequently been found in nitridosilicates and they occur exclusively in dimorphic  $Si_3N_4$  (10).

In the title compounds  $M_3P_6N_{11}$  ( $M = Rb, Cs$ ) the  $PN_4$  tetrahedra are linked exclusively through common vertices. Within the group of highly condensed nitridophosphates (molar ratio  $P:N > 1:2$ ) this situation has only been found in the compounds  $M_3P_6N_{11}$  ( $M = Na, K$ ) and  $MP_4N_7$  ( $M = Na, K, Rb, Cs$ ). In contrast, in  $HP_4N_7$  (7), which formally represents the corresponding acid to the salts  $MP_4N_7$  and in formally isosteric  $P_4N_6O$  (8) as well as in  $P_3N_5$  (1) the  $PN_4$  tetrahedra are connected by both corners and edges.

The P–N network structure of  $Rb_3P_6N_{11}$  and  $Cs_3P_6N_{11}$  may be separated in symmetrically equivalent chains of

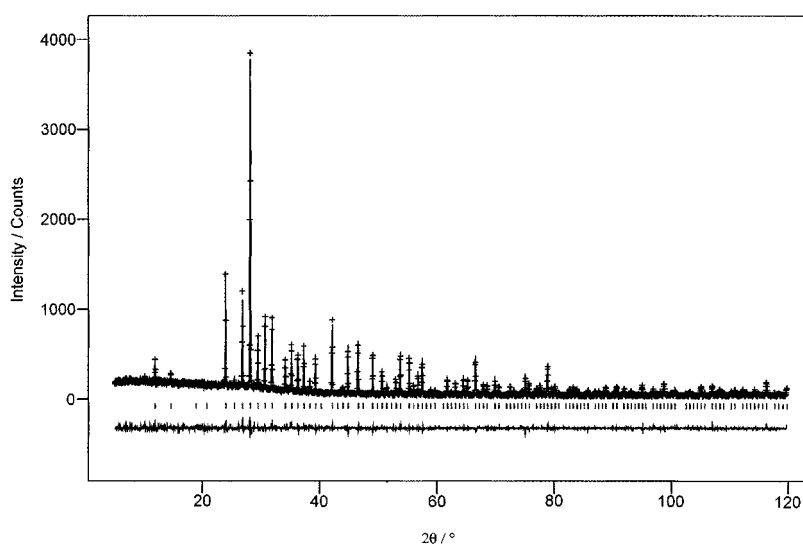


FIG. 1. Observed (crosses) and calculated (line) X-ray powder diffraction patterns as well as a difference profile of the Rietveld refinement of  $Rb_3P_6N_{11}$ . The powder pattern was obtained with a STOE Stadi P powder diffractometer ( $CuK\alpha_1$ ,  $\lambda = 154.05$  pm).

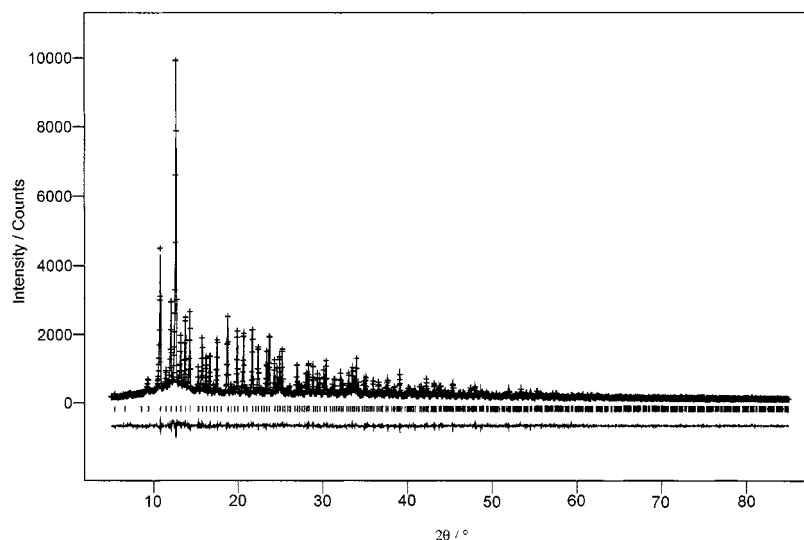


FIG. 2. Observed (crosses) and calculated (line) X-ray powder diffraction patterns as well as a difference profile of the Rietveld refinement of  $\text{Cs}_3\text{P}_6\text{N}_{11}$ . The powder pattern was obtained with a STOE Stadi P powder diffractometer ( $\text{MoK}\alpha_1$ ,  $\lambda = 70.926$  pm).

$\text{PN}_4$  tetrahedra which run along [100], [010], and [001] (Fig. 3). Linkage of these chains is achieved by  $\text{N}^{[2]}$  as well as  $\text{N}^{[3]}$  atoms. Channels of  $\text{P}_8\text{N}_8$  rings run along [100], [010], and [001] in which alkali ions are situated. The distances M–N to the alkali cations (Rb–N, 287–341 pm; Cs–N, 301–349 pm) correspond with the sum of the respective ionic radii (11).

The P–N bond length in  $M_3\text{P}_6\text{N}_{11}$  ( $M = \text{Rb}, \text{Cs}$ ) are in the typical range (P– $\text{N}^{[2]}$ , 159–162 pm; P– $\text{N}^{[3]}$ , 170–171 pm)

(1). As expected the average values for P– $\text{N}^{[2]}$  are significantly smaller than those for P– $\text{N}^{[3]}$ . The bond angles N–P–N vary between 102 and 120°. The bond angles P– $\text{N}^{[2]}$ –P range from 119° to 131° in  $M_3\text{P}_6\text{N}_{11}$ , being typical for phosphorus(V) nitrides (1). The sum of angles at the  $\text{N}^{[3]}$  bridges amounts to nearly 360° for both  $\text{Rb}_3\text{P}_6\text{N}_{11}$  and  $\text{Cs}_3\text{P}_6\text{N}_{11}$ , therefore these N atoms may be considered as  $\text{sp}^2$  hybridized. Both bond lengths and angles are in good accordance with those found in  $\text{K}_3\text{P}_6\text{N}_{11}$ .

There are two different atomic sites  $M1$  and  $M2$  for the alkali ions in  $M_3\text{P}_6\text{N}_{11}$  ( $M = \text{Rb}, \text{Cs}$ ).  $M1$  is coordinated by

TABLE 1  
Crystallographic Data for  $M_3\text{P}_6\text{N}_{11}$  ( $M = \text{Rb}, \text{Cs}$ )

Formula	$\text{Rb}_3\text{P}_6\text{N}_{11}$	$\text{Cs}_3\text{P}_6\text{N}_{11}$
$M_r$ (g/mol)	596.20	738.52
Crystal system	Cubic	Cubic
Space group	$P4_132$ (No. 213)	$P4_132$ (No. 213)
Lattice constants (pm)	$a = 1049.74(1)$	$a = 1065.15(1)$
Cell volume ( $10^6$ pm <sup>3</sup> )	1156.76(2)	1208.47(2)
Z	4	4
Diffractometer	Stoe STADI P	Stoe STADI P
$\lambda$ (pm)	154.050	70.926
T (°C)	25(2)	25(2)
Profile range	$5^\circ \leq 2\theta \leq 120^\circ$	$5^\circ \leq 2\theta \leq 85^\circ$
Data points	11480	8000
Observed reflections	208	926
Positional param.	9	9
Profile param.	7	7
Background param.	3	3
$R_p$	0.0979	0.0487
$wR_p$	0.1077	0.0618
$R_F$	0.0612	0.0812
$\chi^2$	0.5998	0.812

TABLE 2  
Atom Coordinates and Isotropic Displacement Factors  
(pm<sup>2</sup>) of  $M_3\text{P}_6\text{N}_{11}$  ( $M = \text{Rb}, \text{Cs}$ )

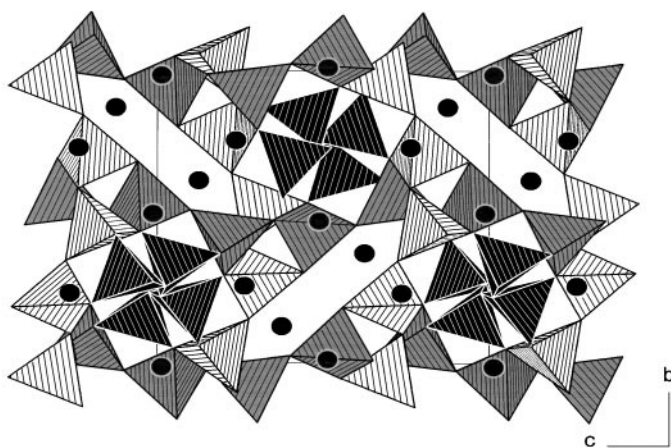
Atom	Wyckoff position	x	y	z	$U_{\text{iso}}^a$
$M1$	$4a$	$\frac{3}{8}$	—	—	305(6)
		$\frac{3}{8}$	—	—	289(5)
$M2$	$8c$	0.76289(7)	—	—	164(4)
		0.77134(4)	—	—	188(3)
P	$24e$	0.06985(16)	0.21067(20)	0.29797(20)	63(5)
		0.06753(16)	0.20064(19)	0.29230(21)	98(5)
$\text{N}1$	$24e$	0.0102(5)	0.3497(6)	0.2761(5)	56(13)
		0.0067(6)	0.3390(6)	0.2757(5)	125(17)
$\text{N}2$	$12d$	$\frac{1}{8}$	0.1905(4)	0.4405(4)	56(13)
		$\frac{1}{8}$	0.1810(4)	0.4310(4)	115(22)
$\text{N}3$	$8c$	0.1997(4)	—	—	56(13)
		0.1938(4)	—	—	96(29)

<sup>a</sup>  $U_{\text{iso}}$  is defined as  $\exp(-8\pi^2 U_{\text{iso}} \sin^2 \theta / \lambda)$ . The displacement factors of  $\text{Rb}_3\text{P}_6\text{N}_{11}$  were constrained to be equal.

**TABLE 3**  
Interatomic Distances (pm) and Angles ( $^{\circ}$ ) in  $M_3P_6N_{11}$   
( $M = Rb, Cs$ )

Compound	$Rb_3P_6N_{11}$	$Cs_3P_6N_{11}$
$M1-N2^{[2]}$	333.3(2) $6 \times$	342.3(2)
$-N3^{[3]}$	318.6(7) $2 \times$	334.4(8)
$M2-N1^{[2]}$	287.4(6) $3 \times$	301.4(5)
$-N1^{[2]}$	310.4(5) $3 \times$	318.7(6)
$-N2^{[2]}$	341.4(5) $3 \times$	349.3(6)
$P-N1^{[2]}$	159.0(5)	159.5(5)
$-N1^{[2]}$	160.5(7)	162.0(6)
$-N2^{[2]}$	161.8(4) $2 \times$	161.3(4)
$-N3^{[3]}$	171.3(2) $3 \times$	170.7(2)
$N1^{[2]}-P-N1^{[2]}$	112.5(3)	113.8(3)
$N1^{[2]}-P-N2^{[2]}$	113.0(2)	111.7(3)
$N1^{[2]}-P-N3^{[3]}$	106.6(2)	106.7(2)
$N1^{[2]}-P-N2^{[2]}$	111.2(3)	110.9(3)
$N1^{[2]}-P-N3^{[3]}$	107.8(4)	108.2(4)
$N2^{[2]}-P-N3^{[3]}$	105.2(3)	105.0(3)
$P-N1^{[2]}-P$	131.3(4)	130.7(4)
$P-N2^{[2]}-P$	111.7(4)	112.4(4)
$P-N3^{[3]}-P$	119.5(7)	119.4(1)

8 N atoms while  $M2$  is coordinated by 9 N atoms. According to MAPLE calculations (12–14) only  $N^{[2]}$  atoms contribute to the coordination of  $M2$  while a small coor-



**FIG. 3.** Crystal structure of  $Rb_3P_6N_{11}$  and  $Cs_3P_6N_{11}$ . View along  $[100]$ . The structure can be described from symmetrically equivalent chains of  $PN_4$  tetrahedra along  $[100]$ ,  $[010]$ , and  $[001]$  (black, white, and gray, respectively). The alkali metal atoms are drawn as black circles.

dinative contribution of  $N^{[3]}$  atoms has to be included in the coordination sphere of  $M1$  (Table 3).

The synthesis of  $Rb_3P_6N_{11}$  and  $Cs_3P_6N_{11}$  shows that a broad and elegant synthetic approach to nitridophosphates is possible by use of high-pressure reaction conditions. This approach may be also applied to other nonmetal-nitrides like nitridosilicates or nitridoborates. The use of the metal azides is specifically useful in those cases when the respective nitrides are not available.

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