

RefinementRefinement on F^2

$$R[F^2 > 2\sigma(F^2)] = 0.019$$

$$wR(F^2) = 0.044$$

$$S = 1.290$$

609 reflections

39 parameters

H atom refined isotropically

$$w = 1/[\sigma^2(F_o^2) + (0.0168P)^2 + 0.5112P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = -0.001$$

$$\Delta\rho_{\max} = 1.150 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.821 \text{ e } \text{Å}^{-3}$$

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

$$0.0390 (14)$$

Scattering factors from

International Tables for Crystallography (Vol. C)**Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)**

$$U_{\text{iso}} \text{ for H, } U_{\text{eq}} = (1/3)\sum_i U_{ij}U_{ii}^2 a_i^2 a_j^2 \text{ for all others.}$$

	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$
Cd	0.27185 (2)	1/4	0.40234 (5)	0.01666 (12)
Se	0.40643 (3)	3/4	0.48839 (7)	0.01405 (13)
O1	0.1357 (3)	1/4	0.6813 (6)	0.0290 (7)
O2	0.3410 (2)	0.5330 (3)	0.6386 (3)	0.0196 (4)
O3	0.3980 (3)	1/4	0.0846 (6)	0.0233 (6)
H	0.389 (4)	0.137 (8)	-0.037 (8)	0.034 (11)

Table 2. Selected geometric parameters (Å , $^\circ$)

Cd—O1	2.283 (3)	Se—O1 ⁱⁱⁱ	1.649 (3)
Cd—O2	2.245 (2)	Se—O2	1.719 (2)
Cd—O2 ⁱ	2.245 (2)	Se—O2 ^{iv}	1.719 (2)
Cd—O2 ⁱⁱ	2.372 (2)	O3—H	0.91 (4)
Cd—O2 ⁱⁱⁱ	2.372 (2)	H—O2 ^v	2.02 (4)
Cd—O3	2.312 (3)	O3—O2 ^v	2.903 (3)
O1 ⁱⁱⁱ —Se—O2	104.32 (10)	H—O—H ⁱ	93 (5)
O1 ⁱⁱⁱ —Se—O2 ^{iv}	104.32 (10)	O3—H—O2 ^v	161 (4)
O2 ^{iv} —Se—O2	96.09 (13)	O2 ^v —O3—O2 ^{vii}	70.10 (10)
Cd—O2—Cd ^{vi}	116.41 (9)		

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

Lattice parameters were determined from X-ray Guinier powder photographs (Cr $K\alpha_1$ radiation, α -quartz as internal standard) using a Huber–Guinier system 600 and the refinement program *LSUCR* (Evans *et al.*, 1963). The atomic positions were obtained from a Patterson map (Cd, Se) and successive least-squares refinements and ΔF syntheses (O, H).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Data reduction: *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1971), *ATOMS* (Dowty, 1995). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1149). Services for accessing these data are described at the back of the journal.

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Tetraammonium Tetrametaphosphate Tetrahydrate

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Abstract

The tetrametaphosphate ring in the title compound [tetraammonium *cyclo*-tetra- μ -imido-tetraphosphate tetrahydrate, $(\text{NH}_4)_4(\text{PO}_2\text{NH})_4 \cdot 4\text{H}_2\text{O}$] exhibits a chair conformation. The tetrametaphosphate rings are linked by N—H \cdots O bonds forming columns along [100]. These columns are interconnected by O—H \cdots O and N—H \cdots O hydrogen bonds through water molecules and ammonium ions. All H atoms are involved in hydrogen bonding.

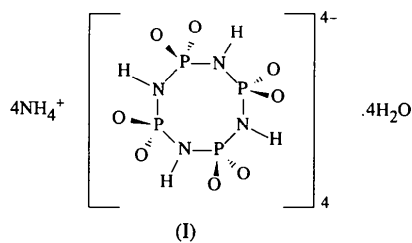
Comment

The synthesis of salts of the tetrametaphosphinic acid $\text{H}_4(\text{PO}_2\text{NH})_4 \cdot 2\text{H}_2\text{O}$ has been well investigated (Stokes, 1896; Lunkwitz & Steger, 1968; Herzog & Nielsen, 1958) but the compounds have been mainly characterized by IR spectroscopy (Corbridge & Lowe, 1954; Lunkwitz & Steger, 1968; Pustinger *et al.*, 1959; Sukova

et al., 1979) and X-ray powder diffraction (Herzog & Nielsen, 1958).

Structural information from single-crystal X-ray investigations are only available for $\text{H}_4(\text{PO}_2\text{NH})_4 \cdot 2\text{H}_2\text{O}$ (Migchelsen *et al.*, 1965; Attig & Mootz, 1977), $\text{K}_4(\text{PO}_2\text{NH})_4 \cdot 4\text{H}_2\text{O}$, $\text{Cs}_4(\text{PO}_2\text{NH})_4 \cdot 6\text{H}_2\text{O}$ (Berking & Mootz, 1971) and $\text{K}_4(\text{H}_3\text{O})\text{Tm}[(\text{PO}_2\text{NH})_4]_2 \cdot 6\text{H}_2\text{O}$ (Sokol *et al.*, 1982). This poor level of information about tetrametaphosphimates contrasts with the well investigated structural chemistry of tetrametaphosphates (Durif, 1995) and the recently characterized crystal structures of some trimetaphosphimates (Stock & Schnick, 1996, 1997*a,b*) which are useful starting materials in the synthesis of transition metal complexes (Sokol *et al.*, 1982) and oxo-nitrido phosphates (Feldman, 1983). For the tetrametaphosphimates, only their properties as fertilizers and flame retardants have been investigated. Nothing is known about their use in synthesizing oxo-nitrido phosphates. We therefore initiated a systematic investigation using tetrametaphosphimates as precursors for the synthesis of oxo-nitrido phosphates.

The structure of the title compound, (I), is shown in Fig. 1. As in $\text{K}_4(\text{PO}_2\text{NH})_4 \cdot 4\text{H}_2\text{O}$, the P_4N_4 ring exhibits a chair conformation having the symmetry $\bar{1}$. The approximate symmetry $2/m$ with a pseudo twofold axis through P1 and P1ⁱ and a pseudo mirror plane through P2 and P2ⁱ is not attained. This lower symmetry can best be seen by comparing the torsion angles of the P—N bonds of -80.44 , 113.97 , -70.78 and -23.41° in P1—N2—P2—N1—P1ⁱ. The symmetry $2/m$ would lead to two pairs of angles having opposite signs but the same value, which obviously does not hold for compound (I). In contrast to these findings, the anion in $\text{H}_4(\text{PO}_2\text{NH})_4 \cdot 2\text{H}_2\text{O}$ exhibits a distorted boat conformation (ideal symmetry $\bar{4}$) and the P_4N_4 ring in $\text{Cs}_4(\text{PO}_2\text{NH})_4 \cdot 6\text{H}_2\text{O}$ shows the exact symmetry $\bar{4}2m$ of the saddle conformation.



Compared to the other tetrametaphosphimates, the corresponding P—N and P—O bond distances and the angles in (I) differ little. An exception is the O—P—N angles, which range from $104.77(6)$ to $111.87(6)^\circ$ (Table 1). The average values of the bond lengths and angles of all structurally investigated tetrametaphosphimates are very similar.

As found in other tetrametaphosphimates, the P_4N_4 rings are connected to form a three-dimensional network by N—H \cdots O [$\text{N}\cdots\text{O}$ $2.766(2)$ – $3.073(2)$ Å], O—

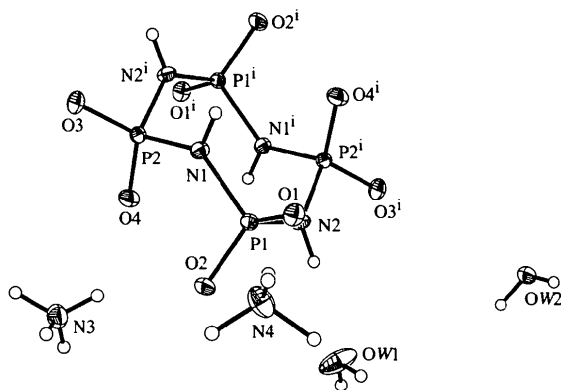


Fig. 1. Structure of compound (I) showing 50% probability displacement ellipsoids. H atoms are drawn as small circles of arbitrary radii.

H \cdots O [$\text{O}\cdots\text{O}$ $2.666(2)$ – $2.732(2)$ Å] and O—H \cdots N hydrogen bonds [$\text{O}\cdots\text{N}$ $3.224(2)$ Å]. In compound (I), all H atoms are involved in hydrogen bonding. H1 forms N1—H1 \cdots O1 [$\text{N}\cdots\text{O}$ $2.933(2)$ Å] hydrogen bonds resulting in columns of tetrametaphosphimate rings along [100]. These columns are further stabilized by N1 \cdots H12—OW1—H11 \cdots O1 connections [$\text{N}\cdots\text{OW}\cdots\text{O}$ $3.224(2)$, $2.711(2)$ Å] (Fig. 2). The H atoms of OW2 are solely involved in the interconnection of the columns [$\text{O3}\cdots\text{H21}$ —OW2—H22 \cdots O2; $\text{O}\cdots\text{OW}\cdots\text{O}$ $2.732(2)$, $2.666(2)$ Å]. The

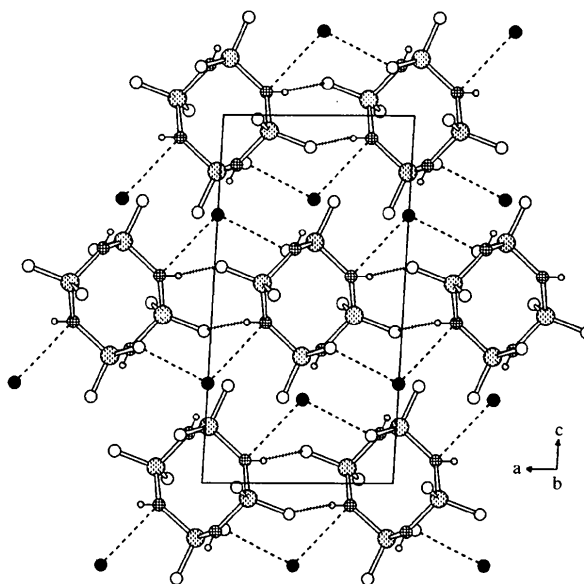


Fig. 2. View of the crystal packing of the tetrametaphosphimate rings along [010] showing the connectivity of the P_4N_4 rings by hydrogen bonding between the rings (crosses) and through OW1 (dashes) forming columns along [100]. The ammonium ions, OW2 and the H atoms bound to the water molecules are omitted for clarity. (P = large hatched, N = medium hatched, H = small open, O = medium open, OW1 = medium black circles.)

ammonium ions take part in the extended hydrogen bonding by bridging *via* the lone pairs of OW2, N4—H42...OW2...H31—N3 (N...O...N 2.801, 2.858 Å). They interconnect the columns and the P₄N₄ rings in the columns [N3—H32...O3, N3—H33...O2, N3—H34...O1, N4—H41...O1, N4—H43...O2, N4—H44...O3; N...O 2.821 (2), 2.887 (2), 2.810 (2), 2.766 (2), 2.908 (2) and 3.030 (2) Å, respectively].

Analogous to (NH₄)₂(PO₂NH)₃.CH₃OH and (NH₄)₃-(PO₂NH)₃.H₂O, the ammonium ions are distorted from ideal tetrahedral geometry.

Experimental

The starting material H₄(PO₂NH)₄.2H₂O was obtained according to the literature (Steger & Lunkwitz, 1961) by hydrolysis (333 K, 48 h) of (PNCl₂)₄ in dioxane. (NH₄)₄(PO₂NH)₄.4H₂O was prepared by the reaction of an aqueous solution of ammonia (10%) with a stoichiometric amount of the acid followed by precipitation with acetone. Large single crystals of up to 3 mm edge length were grown by diffusion-controlled addition of acetone to a 1 × 10⁻² M aqueous solution of (I). Suitable crystals can also be grown by recrystallization from a hot saturated aqueous solution at 277 K.

Crystal data

(NH₄)₄(PO₂NH)₄.4H₂O

M_r = 456.18

Monoclinic

*P*2₁/*n*

a = 6.5295 (8) Å

b = 11.0584 (7) Å

c = 12.2954 (7) Å

β = 92.920 (6)°

V = 886.65 (13) Å³

Z = 2

D_x = 1.709 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 44 reflections

θ = 6.53–15.14°

μ = 0.497 mm⁻¹

T = 173 (2) K

Platelet

1.19 × 0.34 × 0.18 mm

Colourless

Data collection

Siemens *P4* diffractometer

ω scans

Absorption correction:

numerical, *HABI-*

TUS (Herrendorf &

Baernighausen, 1993)

T_{min} = 0.832, *T_{max}* = 0.923

4404 measured reflections

2042 independent reflections

1916 reflections with

I > 2σ(*I*)

R_{int} = 0.010

θ_{max} = 27.49°

h = -9 → 8

k = -14 → 14

l = -15 → 15

3 standard reflections

every 97 reflections

intensity decay: 2.07%

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.026

wR(*F*²) = 0.078

S = 1.124

2042 reflections

124 parameters

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.478 e Å⁻³

Δρ_{min} = -0.348 e Å⁻³

Extinction correction:

SHELXL93 (Sheldrick, 1993)

H atoms were refined using a riding model, starting from Fourier coordinates *w* = 1/[σ²(*F_o*²) + (0.0407*P*)² + 0.6573*P*] where *P* = (*F_o*² + 2*F_c*²)/3

Extinction coefficient:

0.0059 (16)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

P1—O2	1.5006 (11)	P2—O4	1.4920 (11)
P1—O1	1.5105 (11)	P2—O3	1.5121 (11)
P1—N1	1.6588 (13)	P2—N2'	1.6689 (13)
P1—N2	1.6729 (13)	P2—N1	1.6818 (13)
O2—P1—O1	115.41 (6)	O4—P2—N2'	111.87 (6)
O2—P1—N1	110.56 (6)	O3—P2—N2'	104.77 (6)
O1—P1—N1	106.48 (6)	O4—P2—N1	107.28 (6)
O2—P1—N2	107.29 (7)	O3—P2—N1	106.98 (6)
O1—P1—N2	109.90 (6)	N2'—P2—N1	106.79 (6)
N1—P1—N2	106.91 (6)	P1—N1—P2	128.61 (8)
O4—P2—O3	118.52 (7)	P2'—N2—P1	130.10 (8)

Symmetry code: (i) 1 - *x*, -*y*, 1 - *z*.

Table 2. Hydrogen-bonding geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O1 ⁱ	0.899	2.042	2.933 (2)	170.90
N2—H2...OW1 ⁱⁱ	0.860	2.075	2.927 (2)	170.86
N3—H31...OW2 ⁱⁱⁱ	0.848	2.021	2.858 (2)	169.27
N3—H32...O3 ⁱ	0.880	1.945	2.821 (2)	172.78
N3—H33...O2	0.864	2.073	2.887 (2)	156.92
N3—H34...O1 ^{iv}	0.932	1.892	2.810 (2)	168.20
N4—H41...O1	0.997	1.788	2.766 (2)	166.25
N4—H42...OW2 ^v	0.997	1.824	2.801 (2)	166.02
N4—H43...O2 ^{vi}	0.983	1.933	2.908 (2)	171.08
N4—H44...O3 ^{vii}	1.099	2.149	3.030 (2)	135.29
N4—H44...OW1 ^{viii}	1.099	2.224	3.073 (2)	132.38
OW1—H11...O4 ^{viii}	0.860	1.852	2.711 (2)	176.65
OW1—H12...N1 ^{viii}	0.783	2.475	3.224 (2)	160.55
OW2—H21...O3 ^{ix}	0.774	1.976	2.732 (2)	165.31
OW2—H22...O2 ^{viii}	0.868	1.803	2.666 (2)	171.98

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

The structure was determined using the reflections *hkl*, *hk̄l*, *h̄kl* and *h̄k̄l*. All H atoms could be unambiguously located after the anisotropic refinement of all non-H atoms. The ω-scan width was 1.2° with an ω-scan rate of 2.5° min⁻¹. The background-to-signal ratio was 0.5.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Sheldrick, 1994). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL*, *KPLOT* (Hundt, 1979). Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1143). Services for accessing these data are described at the back of the journal.

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$\text{Na}_{13}\text{K}_4\text{Ga}_{47.45}$: a New Sodium Potassium Gallide Phase Containing Trimeric Icosahedral Gallium Clusters

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Abstract

$\text{Na}_{13}\text{K}_4\text{Ga}_{47.45}$ was isolated from a melt prepared from the elements taken in the atomic proportion 3:1:12. It crystallizes in the trigonal $R\bar{3}m$ space group [$a =$

16.325 (3), $c = 35.135$ (5) Å]. The structure results from the packing of icosahedral Ga_{12} units and trimeric Ga_{28} units. The latter are formed by the condensation of three Ga_{12} units by triangular-face sharing. The interpolyhedral space is filled with K^+ and Na^+ cations.

Comment

The structure of $\text{Na}_{13}\text{K}_4\text{Ga}_{47.45}$ contains three different clusters: icosahedron *A* with $\bar{3}m$ symmetry located at the $3a$ special position (0,0,0), icosahedron *B* centered around the $9d$ position (1/2,0,1/2) with $2/m$ symmetry and icosahedral trimer *C* centered around the $6c$ position

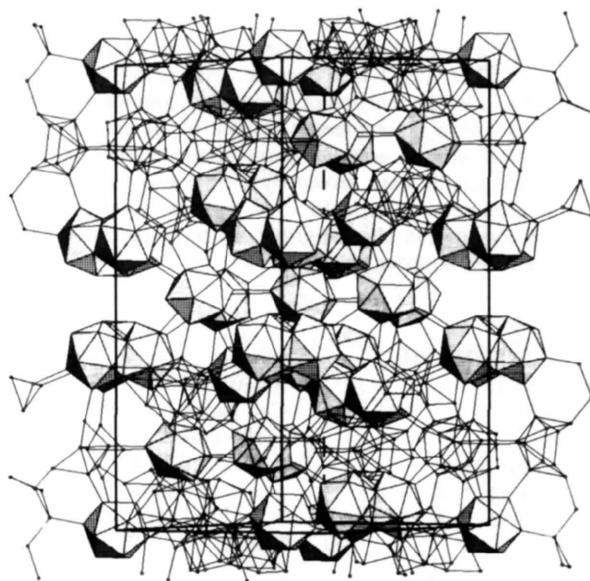


Fig. 1. Representation of the structural packing in $\text{Na}_{13}\text{K}_4\text{Ga}_{47.45}$. The unit cell contains 12 monomeric and 3 trimeric icosahedral gallium units.

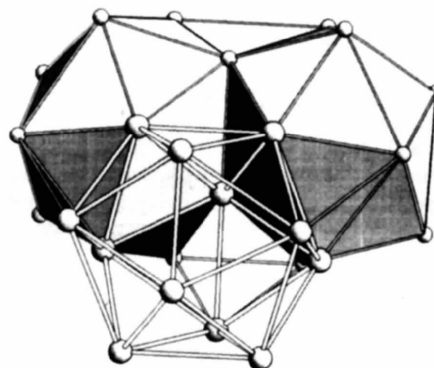


Fig. 2. The trimeric icosahedral unit resulting from the condensation of three icosahedra by face sharing. Each icosahedron shares two faces (five vertices) with its neighbours.