$S(1^{i})\cdots S(3^{v})$	4,157 (5)	Ge—S(3)	2,184 (4)
$S(2^{iv})\cdots S(5^{iii})$	4,353 (5)	Ge—S(2)	2,203 (4)
$S(2^{iv})\cdots S(3^{v})$	3,675 (5)	$Ge—S(6^{x})$	2,205 (4)
$S(3^{v})\cdots S(5^{iii})$	3,914 (5)	$S(3)\cdots S(4^{ix})$	3,709 (5)
Cd(3)—$S(1^{i})$	2,540 (4)	$S(3)\cdots S(6^{x})$	3,584 (5)
$Cd(3)—S(6^{iii})$	2,545 (4)	$S(2)\cdots S(4^{ix})$	3,573 (5)
$Cd(3)—S(5^{vi})$	2,546 (4)	$S(2)\cdots S(6^{x})$	3,510 (5)
$Cd(3)—S(4^{vii})$	2,566 (4)	$S(4^{ix})\cdots S(6^{x})$	3,595 (5)
$S(1^{i})\cdots S(6^{iii})$	4,302 (5)	$S(2)\cdots S(3)$	3,468 (4)
$S(1^{i})—Cd(1)—S(5^{ii})$	123,7 (2)	$S(5^{vi})—Cd(3)—S(6^{iii})$	111,6 (2)
$S(1^{i})—Cd(1)—S(3)$	113,5 (2)	$S(4^{vii})—Cd(3)—S(5^{vi})$	110,6 (2)
$S(1^{i})—Cd(1)—S(6)$	111,5 (2)	$S(4^{vii})—Cd(3)—S(6^{iii})$	94,5 (2)
$S(3)—Cd(1)—S(5^{ii})$	112,7 (2)	$S(1^{i})—Cd(4)—S(5^{i})$	116,8 (2)
$S(3)—Cd(1)—S(6)$	84,9 (2)	$S(1^{i})—Cd(4)—S(2^{viii})$	124,2 (2)
$S(5^{ii})—Cd(1)—S(6)$	102,9 (2)	$S(1^{i})—Cd(4)—S(4^{iv})$	98,9 (2)
$S(1^{i})—Cd(2)—S(5^{iii})$	122,1 (2)	$S(2^{viii})—Cd(4)—S(4^{iv})$	85,7 (2)
$S(1^{i})—Cd(2)—S(2^{iv})$	111,4 (2)	$S(2^{viii})—Cd(4)—S(5^{i})$	116,5 (2)
$S(1^{i})—Cd(2)—S(3^{v})$	108,2 (2)	$S(4^{iv})—Cd(4)—S(5^{i})$	101,6 (2)
$S(2^{iv})—Cd(2)—S(5^{iii})$	118,1 (2)	$S(4^{ix})—Ge—S(3)$	116,7 (2)
$S(2^{iv})—Cd(2)—S(3^{v})$	90,8 (2)	$S(4^{ix})—Ge—S(2)$	109,5 (2)
$S(3^{v})—Cd(2)—S(5^{iii})$	99,4 (2)	$S(4^{ix})—Ge—S(6^{x})$	110,4 (2)
$S(1^{i})—Cd(3)—S(6^{iii})$	115,5 (2)	S(2)—Ge—S(3)	104,5 (2)
$S(1^{i})—Cd(3)—S(5^{vi})$	112,1 (2)	$S(2)—Ge—S(6^{x})$	105,5 (2)
$S(1^{i})—Cd(3)—S(4^{vii})$	111,3 (2)	$S(3)—Ge—S(6^{x})$	109,5 (2)

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

Les corrections d'absorption ont été réalisées à l'aide du programme de J. A. Ibers d'après la méthode analytique décrite par de Meulenaer & Tompa (1965).

Résolution de la structure: *MULTAN*80 (Main et *al.*, 1980). Affinement de la structure: *ORXFLS* (Busing, 1971) modifié par P. Laruelle. Tracé des figures: *MOLVIEW* (Cense, 1990). Calcul des distances et des angles interatomiques: *ORFFE* (Busing, Martin & Levy, 1964).

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Les listes des facteurs de structure et des facteurs d'agitation thermique anisotrope ont été déposées au dépôt d'archives de l'UICr (Référence: DU1119). On peut en obtenir des copies en s'adressant à: The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

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$Ba[H_3IO_6]$

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Abstract

Barium orthoperiodate was synthesized and its structure determined by single-crystal X-ray diffraction. The structure consists of Ba^{2+} and $(H_3IO_6)^{2-}$ ions alternately located on the trigonal axis (*c* axis). The IO_6 polyhedron has D_3 symmetry, but is greatly distorted from a regular octahedron. A three-dimensional network of IO_6 octahedra is formed through short O—H···O hydrogen bonds. The H atom is positionally disordered.

Comment

As some periodates show non-water-soluble characteristics, the title compound was synthesized in order to investigate its solubility in water.

A drawing of the structure is shown in Fig. 1. The structure comprises Ba^{2+} and $(H_3IO_6)^{2-}$ ions, with the Ba^{2+} ion at the origin and the I atom at $0,0,\frac{1}{2}$. Six O atoms coordinate to an I atom with I—O bond lengths of 1.879 (2) Å. The IO_6 coordination octahedron has D_3 symmetry: one threefold axis of rotation and three twofold rotation axes perpendicular to the former through the central I atom. Therefore, the octahedron is highly symmetric but distorted from a regular octahedron. The distortion is characterized by (*a*) the angle between the I—O bond and the trigonal axis being 53.5 (1)°, smaller than that of 54.8° for a regular octahedron, (*b*) by an elongation of the octahedron along the trigonal axis, and (*c*) by the fact that the two faces perpendicular to the trigonal axis are rotated with respect to each other by an angle of 17.7 (2)°, which shows that the octahedron is twisted around the trigonal axis. Thus, the distortion is fairly large in contrast to the distortions observed in related compounds, *e.g.* $Cd[H_3IO_6].3H_2O$ (Braibanti, Tiripicchio, Bigoli & Pellinghelli, 1970) and $Mg[H_3IO_6].3H_2O$ (Bigoli, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1970).

The H atom is positionally disordered at two equivalent sites [0.8 (2) Å apart] so that a half H atom is attached to each O atom. The IO_6 octahedra are linked through hydrogen bonds to form an infinite

three-dimensional network in the crystal, as shown in Fig. 2. Such a hydrogen bond is also reported for $(NH_4)_2[H_3IO_6]$ (Helmholtz, 1937) and resembles those of KDP-type crystals in the paraelectric phase (KDP is KH_2PO_4) (West, 1930; Nelmes, 1987). The O—H bond has a distance of 0.90 (10) Å and the O···O distance is short at 2.517 (4) Å. The title compound presumably undergoes a transition at some lower temperature into a phase with ordered H atoms, as in KDP (Nelmes, 1987). The shortest Ba···O contact is 2.916 (2) Å.

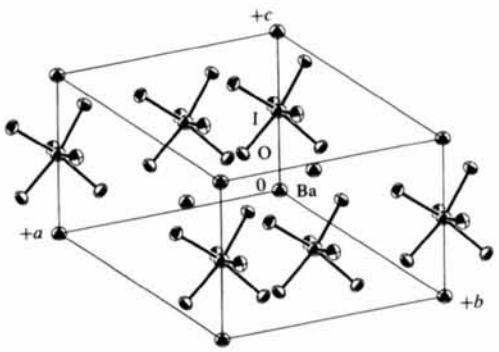

Fig. 1. An *ORTEP*II (Johnson, 1976) view of the title structure. The H atoms have been omitted. Displacement ellipsoids are drawn at the 80% probability level.

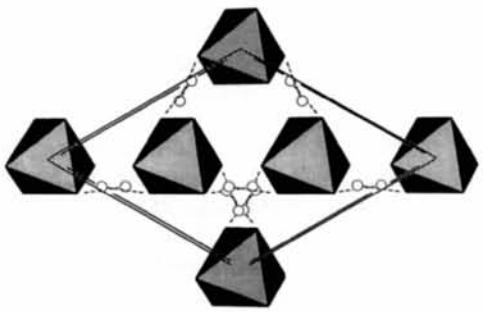

Fig. 2. A projection of the structure along **c**, showing the hydrogen-bond formation and the disordered H atoms (circles). Polyhedra represent the IO_6 groups; dashed lines represent the hydrogen bonds. The Ba atoms are not shown.

Experimental

Very small colourless and pseudo-hexagonal prismatic crystals of $Ba[H_3IO_6]$ were isolated by sedimentation from an aqueous solution of $BaCO_3$ and H_5IO_6. The crystals obtained were barely soluble in water.

Crystal data

$Ba[H_3IO_6]$
M_r = 363.3
Trigonal
$R32$
a = 7.6178 (9) Å
c = 7.2537 (7) Å
V = 364.54 (4) Å^3
Z = 3
D_x = 4.96 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 11–12.5°
μ = 14.5 mm^{-1}
T = 297 K
Prism
0.16 × 0.06 × 0.06 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
T_{min} = 0.36, T_{max} = 0.42
1131 measured reflections
491 independent reflections
685 observed reflections [$I > 3\sigma(I)$]
R_{int} = 0.020
θ_{max} = 25°
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 13$
$l = -2 \rightarrow 14$
4 standard reflections monitored every 150 reflections
intensity decay: 0.6%

Refinement

Refinement on F
R = 0.011
wR = 0.014
S = 1.29
251 reflections
15 parameters
All H-atom parameters refined
$w = 4F/[\sigma^2(F) + (0.007F)^2]$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: *TEXSAN* (Molecular Structure Corporation, 1992)
Extinction coefficient: secondary, 0.199 (6) × 10^{-5}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

B_{iso} for H; $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for Ba, I and O.

	x	y	z	B_{eq}/B_{iso}
Ba	0	0	0	0.964 (5)
I	0	0	1/2	0.981 (5)
O	0.2262 (4)	0.0831 (3)	0.3457 (3)	0.94 (3)
H†	0.26 (1)	−0.01 (1)	0.33 (2)	2.7 (5)

† Occupancy = 0.5.

Table 2. *Selected geometric parameters* (Å, °)

I—O	1.879 (2)		
O—I—O^{i}	88.2 (1)	O—I—O^{ii}	83.1 (1)
O—I—O^{iii}	102.4 (1)	O—I—O^{iv}	166.1 (1)
Short contacts			
Ba···O	2.927 (2)	Ba···O^{v}	2.916 (2)
O···O^{vi}	2.957 (4)		
Hydrogen bonds			
O—H	0.90 (10)	O···O^{vii}	2.517 (4)
H···O^{vii}	1.68 (9)	H···H^{vii}	0.8 (2)
I—O···H	113 (7)	O—H···O^{vii}	154 (10)

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

Intensity data were corrected for Lp effects. The validity of the refined absorption correction was confirmed by a subsequent refinement including a ψ-scan absorption correction, which

produced a comparable T_{max}/T_{min} ratio. The structure was solved by Patterson methods and *DIRDIF*92 (Beurskens *et al.*, 1992). The position of the H atom was deduced from difference Fourier maps. Structure refinement was performed using *TEXSAN* (Molecular Structure Corporation, 1992). Graphics were produced using *ORTEP*II (Johnson, 1976) and *CHARON* (Lauher, 1989). All computations were performed on an IRIS INDIGO.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: OH1082). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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KYP_4O_{12}

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Abstract

Potassium yttrium cyclotetraphosphate is isostructural with $RbNdP_4O_{12}$. The structure is built up from $P_4O_{12}^{4-}$ cyclotetraphosphate anions linked by YO_8 polyhedra to form a three-dimensional framework, which delimits intersecting tunnels in which the K^+ ions are located. The P_4O_{12} ring anion is centrosymmetric.

Comment

The cyclotetraphosphates corresponding to the general formula $M^1LnP_4O_{12}$ are well known (Hong, 1975*a*,*b*; Koizumi, 1976*a*; Koizumi & Nakano, 1978; Averbuch-Pouchot & Durif, 1983; Durif, Averbuch-Pouchot & Guitel, 1983). The compounds obtained for M^1 = K and Ln = Sm, M^1 = Rb and Ln = Nd, and M^1 = NH_4 and Ln = Pr and Nd, are isostructural (Ferid, Ariguib & Trabelsi, 1987; Koizumi & Nakano, 1977; Masse, Guitel & Durif, 1977). The title compound is isostructural with the compounds of this series. In the present work we report its chemical preparation and structural investigation.

This structure contains the centrosymmetrical cyclotetraphosphate ring anion $P_4O_{12}^{4-}$. As shown in the projection onto the *ab* plane, the P_4O_{12} rings form layers perpendicular to the *c* axis at $z = 0$ and 1/2. The YO_8 polyhedra interconnect the P_4O_{12} rings to form a three-dimensional framework. This disposition creates intersecting tunnels in which the K atoms reside. All the K^+ and Y^{3+} ions are located on twofold axes in the $z = 1/4$ and $z = 3/4$ planes. The coordination around the Y atom forms a lozenge antiprism which shares its two lozenge faces with two neighbouring KO_{10} polyhedra. The YO_8 polyhedra are isolated from one another since they do not share any O atoms. This type of isolation appears responsible for the good fluorescence properties shown in lanthanide compounds, such as those of the series $M^1NdP_4O_{12}$ (M^1 = Li, Na and K) (Otsuka, Miyazawa, Yamada, Iwasaki & Nakano, 1977; Chinn & Hong, 1975; Tsujimoto, Fukuda & Fukai, 1977; Tofield, Weber, Damen & Liao, 1975). The shortest Y···Y distance [5.978 (1) Å] has a value between those of the corresponding Nd···Nd distances in $NaNdP_4O_{12}$ (5.719 Å) (Koizumi, 1976*b*) and $RbNdP_4O_{12}$ (6.129 Å). The structures of KYP_2O_7 (Hamady, Zid & Jouini, 1994) and the related compound $RbYP_2O_7$ (Akrim, Zambon, Metin & Cousseins, 1993) display shorter Y···Y distances of 5.423 and 5.30 Å, respectively. In the KO_{10} polyhedron, the K—O distances exhibit a

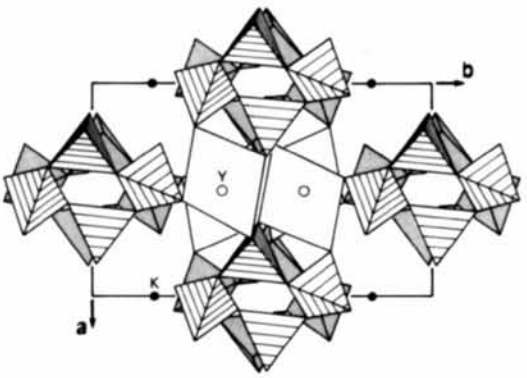

Fig. 1. The KYP_4O_{12} structure projected along the *c* axis showing the P_4O_{12} rings.

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