The Structure of Hexasodium Bis[μ-(phosphato-*O,O'*)-pyrophosphatothorate(IV)]

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Abstract

Crystals of $Na_6[Th(PO_4)(P_2O_7)]_2$ are triclinic, space group $P\bar{1}$, with $a = 8\cdot734$ (2), $b = 8\cdot931$ (2), $c = 6\cdot468$ (1) Å, $\alpha = 93\cdot33$ (3), $\beta = 108\cdot29$ (4), $\gamma = 110\cdot10$ (4)°, $U = 442\cdot0$ Å³, $D_m = 4\cdot264$, $D_c = 4\cdot281$ Mg m^{-3}. The structure was refined to $R = 0\cdot040$ for 2475 observed reflexions $[I > 2\sigma(I)]$. A binuclear unit of Th polyhedra with a double bridge of two phosphato O atoms occurs in the structure. The Th atom exhibits ninefold coordination in the shape of a tricapped trigonal prism. Th—O distances range from 2·309 (8) to 2·785 (7) Å. The pyrophosphato group is non-linear with P—O—P 129·4 (4)°. The terminal P—O bonds range from 1·424 (7) to 1·559 (7) Å. Bridging P—O distances are 1·621 (8) and 1·630 (8) Å. The O—P—O bond angles are in the range 103·3 (4) to 117·5 (4)°. In the discrete PO_4 tetrahedron P—O bond lengths vary from 1·475 (7) to 1·577 (7) Å and O—P—O bond angles from 102·0 (4) to 116·1 (4)°. The polyhedra around Na form a three-dimensional network. The dimers of Th polyhedra fit in the holes among the Na polyhedra forming an extremely close-packed structure.

Introduction

A novel type of phosphate containing a discrete phosphato group and a pyrophosphato group was prepared by thermal synthesis. $Th(PO_3)_4$ and $NaPO_3$ in molar ratio 2:10 were heated in a platinum crucible at 1093 K for 24 h, then a 1:1 molar mixture of ThO_2 and $Na_4P_2O_7.10H_2O$ was added and heated again at 1093 K for 24 h. The furnace was slowly cooled to 773 K (50 K per day) in order to obtain single crystals suitable for X-ray work. The crystals were separated from the matrix by dissolving the soluble substances in boiling water. The chemical formula was deduced from analytical data.

Experimental

The space group was determined from Weissenberg photographs recorded with Cu $K\alpha$ radiation. The intensities were collected from a spherically shaped crystal, radius 0·047 mm, on a Philips PW 1100 computer-controlled four-circle diffractometer in the ω–2θ scan mode with graphite-monochromated Mo $K\alpha$ radiation in the range $5 < 2\theta < 64°$. 2475 observed reflexions having $I > 2\sigma(I)$ were used in the calculations. The intensities were corrected for background, Lorentz and polarization effects and for absorption $[\mu(\text{Mo } K\alpha) = 26\cdot56 \text{ mm}^{-1}]$ (Bond, 1967).

Structure determination and refinement

The Patterson map was successfully solved in $P\bar{1}$, implying a binuclear unit formed across the centre of symmetry. A Fourier synthesis based on the coordinates of the Th atom revealed the positions of three Na, three P and eleven O atoms. Refinement was by full-matrix least squares minimizing $\sum W||F_o| - |F_c||^2$. A weighting scheme of type 3 from the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) was used. $[W = W_1 . W_2$, where $W_1 = 1$ for $|F_o| \leq 30$ and $W_1 = 30/|F_o|$ for $|F_o| > 30$; $W_2 = 1$ for $\sin \theta \geq 0\cdot4$ and $W_2 = (\sin \theta)/0\cdot4$ for $\sin \theta < 0\cdot4$.]

Isotropic refinement led to $R = 0\cdot059$. In the final cycles of refinement a scale factor, the atomic coordinates and anisotropic thermal parameters (163 variables in all) were refined. Anisotropic thermal parameters are in the usual range: maximum values $U_{11} = 0\cdot037$ (3), $U_{22} = 0\cdot045$ (3) and $U_{33} = 0\cdot061$ (3) Å² for Na(3) were obtained. The final $R = 0\cdot040$ and $R_w = 0\cdot048$ for 2475 reflexions having $I > 2\sigma(I)$.

Scattering factors given by Cromer & Mann (1968) were used. Anomalous-dispersion corrections were included for Na, P and Th (Cromer & Liberman,

Table 1. *Final atomic coordinates* ($\times 10^4$, *for* Th $\times 10^5$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^2$)

U_{eq} is derived from the anisotropic thermal parameters by

$$U_{eq} = \tfrac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	U_{eq}
Th	33402 (2)	29080 (2)	7553 (3)	0·64 (1)
Na(1)	−125 (5)	1311 (5)	3616 (7)	2·60 (13)
Na(2)	1781 (6)	5632 (5)	3998 (7)	2·45 (13)
Na(3)	5847 (7)	10346 (7)	2930 (11)	4·80 (20)
P(1)	8631 (2)	1274 (2)	−1448 (3)	0·96 (6)
P(2)	7737 (2)	3582 (2)	896 (3)	1·05 (6)
P(3)	3781 (3)	2970 (2)	5926 (3)	0·97 (6)
O(1)	7249 (8)	−51 (7)	−797 (11)	1·38 (18)
O(2)	10349 (8)	1625 (7)	98 (11)	1·50 (18)
O(3)	8571 (10)	1018 (10)	−3750 (11)	2·37 (24)
O(4)	8182 (7)	2870 (7)	−1124 (10)	1·22 (17)
O(5)	8927 (9)	3518 (8)	2947 (10)	1·86 (20)
O(6)	7948 (8)	5282 (8)	450 (13)	2·03 (20)
O(7)	5902 (8)	2501 (7)	732 (11)	1·65 (18)
O(8)	2570 (8)	3341 (8)	4056 (10)	1·51 (19)
O(9)	4984 (9)	2470 (9)	4924 (11)	2·07 (21)
O(10)	4667 (8)	4449 (7)	7714 (10)	1·11 (18)
O(11)	2762 (8)	1670 (7)	7068 (10)	1·37 (18)

Fig. 1. Projection of the structure along z, showing the co-ordination of the Th dimer.

1970). The calculations were carried out on the Univac 1100 computer at the University Computing Centre in Zagreb with the XRAY system (Stewart *et al.*, 1976). The atomic coordinates are listed in Table 1.*

Description and discussion of the structure

Coordination around the thorium atom

Polyhedra around two Th atoms related by the centre of symmetry form a dimer sharing O(10)^{ii} and O(10)^{v} with a Th$\cdots$Th^{iv} distance of 4·2520 (4) Å (Fig. 1). The Th atom is coordinated by nine O atoms from four pyrophosphato groups [O(1)^{iii}; O(2)^{i}; O(6)^{iv}; O(7)] and three phosphato tetrahedra [O(8), O(9); O(10)^{ii}, O(11)^{ii}; O(10)^{v}] (Figs. 1 and 2). Two pyrophosphato groups related by the centre of symmetry act as bidentate bridging ligands to Th and Th^{iv}, coordinating O(6) and O(7) to each Th atom (Fig. 1). Isolated P(3) tetrahedra repeated by the centre of symmetry form two bridges with O(10)^{ii} and O(10)^{v} between Th and Th^{iv}. However the P(3) tetrahedron also acts as a bidentate cyclic ligand coordinating O(8), O(9) and O(10)^{ii}, O(11)^{ii} to the same Th atom. Thus O(10)^{ii} and O(10)^{v} are shared by both polyhedra (Figs. 1 and 2). The coordination polyhedron around Th can be described as either a tricapped trigonal prism (Fig. 1) with O(2)^{i}, O(9) and O(10)^{ii} centring rec-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36275 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
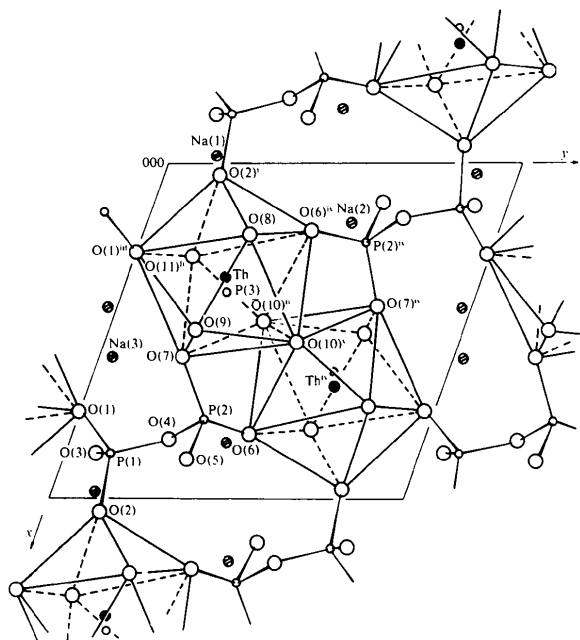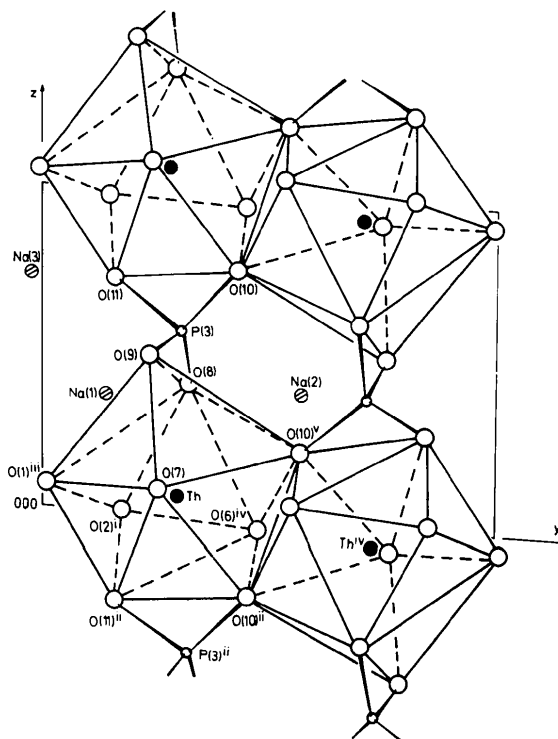

Fig. 2. Projection of the structure along x. The role of the P(3) tetrahedra: bidentate cyclic [O(8),O(9); O(10)^{ii},O(11)^{ii}], bridging [O(10)^{ii},O(10)^{v}]. Dimers of Th polyhedra are connected by P(3) tetrahedra along z.

Table 2. *Interatomic distances* (Å) *and angles* (°)

Within the Th polyhedron

Th—O(1)ⁱⁱⁱ	2·427 (6)	O(2)ⁱ···O(8)	2·656 (7)
Th—O(2)ⁱ	2·347 (6)	O(2)ⁱ···O(11)ⁱⁱ	3·290 (11)
Th—O(6)ⁱᵛ	2·309 (8)	O(6)ⁱᵛ···O(8)	3·191 (10)
Th—O(7)	2·391 (8)	O(6)ⁱᵛ···O(10)ⁱⁱ	2·664 (8)
Th—O(8)	2·479 (7)	O(6)ⁱᵛ···O(10)ᵛ	2·955 (12)
Th—O(9)	2·750 (7)	O(6)ⁱᵛ···O(11)ⁱⁱ	3·413 (11)
Th—O(10)ᵛ	2·325 (5)	O(7)···O(9)	3·058 (11)
Th—O(10)ⁱⁱ	2·785 (5)	O(7)···O(10)ᵛ	3·099 (10)
Th—O(11)ⁱⁱ	2·392 (6)	O(7)···O(10)ⁱⁱ	2·892 (10)
O(1)ⁱⁱⁱ···O(2)ⁱ	2·844 (11)	O(7)···O(11)ⁱⁱ	2·829 (8)
O(1)ⁱⁱⁱ···O(7)	2·882 (9)	O(8)···O(9)	2·408 (11)
O(1)ⁱⁱⁱ···O(8)	3·594 (10)	O(8)···O(10)ᵛ	3·122 (9)
O(1)ⁱⁱⁱ···O(9)	2·961 (8)	O(9)···O(10)ᵛ	3·297 (10)
O(1)ⁱⁱⁱ···O(11)ⁱⁱ	2·884 (9)	O(10)ⁱⁱ···O(10)ᵛ	2·871 (9)
O(2)ⁱ···O(6)ⁱᵛ	2·755 (9)	O(10)ⁱⁱ···O(11)ⁱⁱ	2·389 (8)

O(1)ⁱⁱⁱ—Th—O(11)ⁱⁱ	73·5 (2)	O(8)—Th—O(6)ⁱᵛ	83·5 (3)
O(2)ⁱ—Th—O(1)ⁱⁱⁱ	73·1 (2)	O(8)—Th—O(9)	54·5 (2)
O(2)ⁱ—Th—O(6)ⁱᵛ	72·6 (2)	O(8)—Th—O(10)ⁱⁱ	144·2 (2)
O(2)ⁱ—Th—O(8)	66·7 (2)	O(8)—Th—O(10)ᵛ	81·0 (2)
O(2)ⁱ—Th—O(9)	104·9 (2)	O(8)—Th—O(11)ⁱⁱ	154·3 (2)
O(2)ⁱ—Th—O(10)ⁱⁱ	123·8 (2)	O(9)—Th—O(1)ⁱⁱⁱ	69·4 (2)
O(2)ⁱ—Th—O(10)ᵛ	132·7 (3)	O(9)—Th—O(6)ⁱᵛ	132·2 (3)
O(2)ⁱ—Th—O(11)ⁱⁱ	88·0 (2)	O(9)—Th—O(10)ⁱⁱ	131·3 (2)
O(7)—Th—O(1)ⁱⁱⁱ	73·5 (2)	O(9)—Th—O(10)ᵛ	80·6 (2)
O(7)—Th—O(11)ⁱⁱ	72·5 (2)	O(10)ᵛ—Th—O(6)ⁱᵛ	70·2 (2)
O(7)—Th—O(8)	126·4 (2)	O(10)ⁱⁱ—Th—O(1)ⁱⁱⁱ	121·4 (2)
O(7)—Th—O(9)	72·6 (2)	O(10)ⁱⁱ—Th—O(6)ⁱᵛ	70·2 (3)
O(7)—Th—O(10)ⁱⁱ	67·4 (2)	O(10)ᵛ—Th—O(10)ⁱⁱ	67·7 (2)
O(7)—Th—O(10)ᵛ	82·2 (2)	O(10)ⁱⁱ—Th—O(11)ⁱⁱ	54·3 (2)
O(8)—Th—O(1)ⁱⁱⁱ	94·2 (2)	O(11)ⁱⁱ—Th—O(6)ⁱᵛ	93·1 (3)

Within the pyrophosphato group

P(1)—O(1)	1·559 (7)	O(1)···O(4)	2·495 (9)
P(1)—O(2)	1·432 (6)	O(2)···O(3)	2·396 (9)
P(1)—O(3)	1·475 (8)	O(2)···O(4)	2·460 (10)
P(1)—O(4)	1·621 (8)	O(3)···O(4)	2·481 (12)
P(2)—O(4)	1·630 (8)	O(4)···O(5)	2·487 (9)
P(2)—O(5)	1·424 (7)	O(4)···O(6)	2·429 (11)
P(2)—O(6)	1·521 (8)	O(4)···O(7)	2·572 (11)
P(2)—O(7)	1·527 (7)	O(5)···O(6)	2·485 (11)
O(1)···O(2)	2·457 (8)	O(5)···O(7)	2·384 (8)
O(1)···O(3)	2·595 (11)	O(6)···O(7)	2·570 (9)

O(1)—P(1)—O(2)	110·4 (4)	O(4)—P(2)—O(6)	100·8 (4)
O(1)—P(1)—O(3)	117·5 (4)	O(4)—P(2)—O(7)	109·1 (3)
O(1)—P(1)—O(4)	103·3 (4)	O(5)—P(2)—O(6)	115·0 (4)
O(2)—P(1)—O(3)	111·0 (5)	O(5)—P(2)—O(7)	107·7 (4)
O(2)—P(1)—O(4)	107·3 (3)	O(6)—P(2)—O(7)	115·0 (4)
O(3)—P(1)—O(4)	106·4 (5)	P(1)—O(4)—P(2)	129·4 (4)
O(4)—P(2)—O(5)	108·8 (4)		

Within the phosphato group

P(3)—O(8)	1·475 (7)	O(8)···O(10)	2·386 (7)
P(3)—O(9)	1·561 (9)	O(8)···O(11)	2·521 (10)
P(3)—O(10)	1·497 (6)	O(9)···O(10)	2·595 (11)
P(3)—O(11)	1·577 (7)	O(9)···O(11)	2·655 (11)
O(8)···O(9)	2·408 (12)	O(10)···O(11)	2·389 (8)

O(8)—P(3)—O(9)	104·9 (4)	O(9)—P(3)—O(10)	116·1 (4)
O(8)—P(3)—O(10)	106·8 (4)	O(9)—P(3)—O(11)	115·6 (4)
O(8)—P(3)—O(11)	111·3 (4)	O(10)—P(3)—O(11)	102·0 (4)

Table 2 (cont.)

Na···O distances ≤ 3·048 Å

Na(1)···O(2)ⁱ	2·452 (9)	Na(3)···O(1)ⁱˣ	2·531 (9)
Na(1)···O(3)ⁱⁱⁱ	2·840 (12)	Na(3)···O(3)ˣⁱⁱ	2·509 (9)
Na(1)···O(3)ˣ	2·310 (10)	Na(3)···O(7)ˣⁱ	2·454 (10)
Na(1)···O(5)ⁱ	2·399 (10)	Na(3)···O(7)ⁱᵛ	2·961 (8)
Na(1)···O(8)	2·344 (7)	Na(3)···O(9)ᵛⁱ	2·672 (12)
Na(1)···O(11)	2·697 (7)	Na(3)···O(9)ᵛ	2·926 (10)
Na(1)···O(11)ᵛⁱⁱ	2·757 (7)	Na(3)···O(11)ⁱˣ	2·495 (11)
Na(2)···O(4)ⁱᵛ	2·355 (8)	Na(2)···O(6)ⁱᵛ	3·048 (10)
Na(2)···O(5)ᵛ	2·403 (10)	Na(2)···O(8)	2·372 (10)
Na(2)···O(5)ⁱ	2·407 (7)	Na(2)···O(9)ᵛ	2·584 (8)

Symmetry code

(i)	x − 1,	y,	z		
(ii)	x,	y,	z − 1		
(iii)	1 − x,	−y,	−z		
(iv)	1 − x, 1 − y,	−z			
(v)	1 − x, 1 − y,	1 − z			
(vi)	x, y + 1,	z			

(vii)	−x,	−y,	1 − z
(viii)	x,	y,	z + 1
(ix)	1 − x,	−y,	1 − z
(x)	x − 1,	y,	z + 1
(xi)	−x,	1 − y,	1 − z
(xii)	x,	1 + y,	1 + z

tangular faces or a monocapped square antiprism with O(9) centring a square face (Fig. 1). If the Th—O distances are compared with the sum of the ionic radii (2·42 Å) (Pauling, 1960) three categories of bond distances in the Th polyhedron are evident: (*a*) 2·309 (8)–2·392 (6) Å which are less than 2·42 Å, (*b*) 2·427 (6) and 2·479 (7) Å, and (*c*) 2·750 (7) and 2·785 (7) Å which are considerably larger than the sum of the ionic radii (Table 2). In the structure of K|Th₂(PO₄)₃|, with ninefold coordination of Th, the values of the Th—O distances range from 2·26 (4) to 2·66 (3) Å (Matković, Prodić, Šljukić & Peterson, 1968). The Th—O distances in the present structure are in the wide range 2·309 (8)–2·785 (7) Å. A larger scattering of Th—O distances can be expected for high coordination numbers. In |Th(OH)(NO₃)₃(H₂O)₃|₂, with elevenfold coordination, Th—O distances are Th—O(OH) 2·36 (3) (in bridge); Th—O(H₂O) 2·53 (3); Th—O(NO₃) 2·65 (6) Å (Johansson, 1968). A further example of eleven coordination is the structure of Th(NO₃)₄.5H₂O with Th—O(H₂O) distances in the range 2·438–2·473 (10) Å and Th—O(NO₃) distances 2·528 (10)–2·618 (10) Å (Ueki, Zalkin & Templeton, 1966). For twelve coordination, the lengthening of the Th—O distances is more pronounced. In the structure of [C(NH₂)₃]₂[Th(CH₃COO)₆], with icosahedral coordination of Th, Th—O distances of 2·5 and 2·8 Å were observed (Molodkin & Ivanova, 1966). Long Th—O distances, 2·50–2·80 (5) Å, occurred also in the structure of |Mg(H₂O)₆||Th(NO₃)₆|.2H₂O with icosahedrally coordinated Th (Šćavničar & Prodić, 1965).

In the structure of the title compound there are two very long distances: Th—O(9) 2·750 (7), and Th—O(10)ⁱⁱ 2·785 (7) Å (Table 2). If these O atoms are excluded from the Th coordination sphere a mono-

capped trigonal prism is obtained. However, preference was given to ninefold coordination since it occurs more frequently than sevenfold for Th. The Th$\cdots$Th distance of 4·2520 (4) Å appearing in the dimer is somewhat longer than the 3·988 (3) Å found in [Th(OH)(NO$_3$)$_3$(H$_2$O)$_3$]$_2$ with Th—OH—Th bridges (Johansson, 1968). The shortest Th$\cdots$Th contact outside the dimer is 5·7182 (3) Å.

Pyrophosphato and phosphato groups

Both pyrophosphato and discrete phosphato groups are involved in the coordination around Th. In the pyrophosphato group two terminal O atoms |O(3), O(5)| and a bridging atom |O(4)| are not coordinated to Th. A pyrophosphato group forms a bridge in the Th dimer [O(6),O(7)] but also connects Th dimers along x [through O(2)] and y [though O(1)] forming an infinite sheet (Fig. 1). The isolated P(3) tetrahedron acts as a bidentate cyclic ligand [O(8),O(9); O(10)^{ii},O(11)^{ii}] forming two bridges between Th and Th^{iv} by O(10)^{ii} and O(10)^{v}. It also joins Th polyhedra in the z direction (Fig. 2). The pyrophosphato group is non-linear with the P(1)—O(4)—P(2) angle 129·4 (4)°. The terminal P—O bonds in both tetrahedra range from 1·424 (7) to 1·559 (7) Å. Bridging P—O distances P(1)—O(4) and P(2)—O(4) are 1·621 (8) and 1·630 (8) Å, respectively. The O—P—O bond angles in the pyrophosphato group are in the range 103·3 (4)– 117·5 (4)°. In the P(3) tetrahedron P—O bond lengths vary from 1·475 (7) to 1·577 (7) Å and O—P—O bond angles from 102·0 (4) to 116·1 (4)°. Bond lengths and angles in the pyrophosphato and phosphato groups are in accord with literature data given for PO$_4$ tetrahedral geometry (Corbridge, 1974).

Sodium environment

The Na(1) and Na(2) polyhedra repeated by the operation of a centre of symmetry form dimers whereas the Na(3) polyhedra are joined into an infinite chain along z (Fig. 3). The coordination spheres around Na(1) and Na(3) are composed of seven O atoms in an arrangement which can be roughly described as a monocapped trigonal prism. Na(2) has a distorted octahedral environment. Two discrete PO$_4$ tetrahedra and three pyrophosphato groups are involved in the coordination of each Na.

Na(1) and Na(1)^{vii} at a distance of 3·055 (7) Å form their dimer with the common face formed by O(3)^{iii}, O(3)^{x}, O(11) and O(11)^{vii}. Six O atoms are disposed at the apices of a distorted trigonal prism with Na$\cdots$O distances 2·310 (10)–2·840 (12) Å; a seventh neighbour, O(2)^{i}, at 2·452 (9) Å is beyond the quadrilateral face.

Na(2) and Na(2)^{xi} at a distance of 3·594 (7) Å form their dimer with common edge O(5)^{i}–O(5)^{v}. The
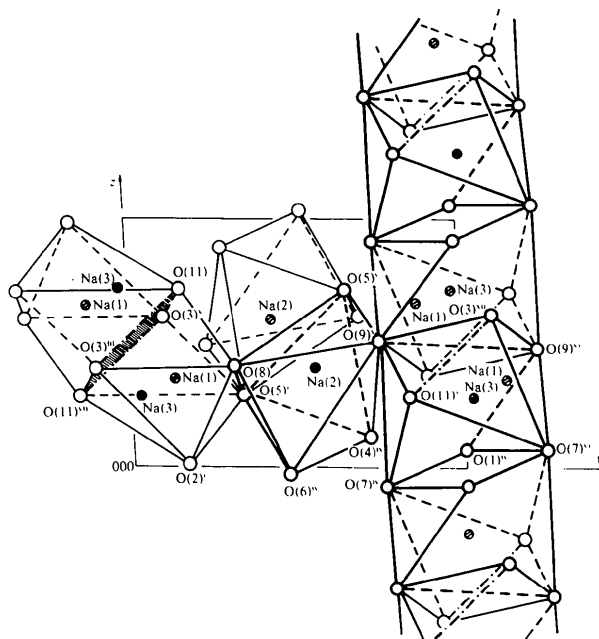

Fig. 3. Projection of the structure along x, illustrating the environments around Na(1), Na(2) and Na(3). The Na(1) and Na(1)^{vii} polyhedra form a dimer sharing the face |O(3)^{iii},O(3)^{x},O(11),O(11)^{vii}|. Na(2) and Na(2)^{xi} distorted octahedra share the edge |O(5)^{i}–O(5)^{v}|. To avoid overlapping of the Na(1) and Na(3) polyhedra, a partial illustration |for Na(1) at y = 0 and for Na(3) at y = 1| is given. The Na(3) polyhedra with common edge |O(9)^{v},O(9)^{vi}| and two common corners |O(7)^{iv},O(7)^{vi}| form an infinite chain along z. The chain of Na(3) polyhedra is linked with Na(1) dimers (connecting line indicated · — · — ·). The Na(2) dimer joins these chains along y.
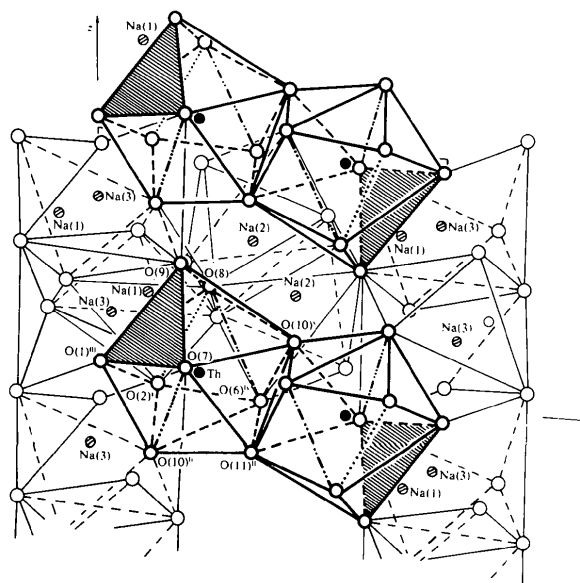

Fig. 4. Projection of the structure along x. Dimers of Th polyhedra fit in the holes appearing among the Na polyhedra. The Na and Th polyhedra share O atoms as follows: Na(1) and Th |O(2)^{i}–O(8), indicated by dotted line|; Na(2) and Th |O(6)^{ix}–O(8), indicated by · · — · · —|; Na(3) and Th |O(7),O(9),O(1)^{iii}, shaded, and also O(7)–O(11)^{ii}, indicated by · · · — · · · —|.

Na···O distances range from 2·355 (8) to 3·048 (10) Å. A seventh neighbour, O(7)^v, at 3·345 (7) Å no longer belongs to the Na(2) environment, so that a geometrical environment analogous to Na(1) and Na(3) does not occur.

The Na(3) polyhedra related by a centre of symmetry, sharing an edge defined by O(9)^v and O(9)^{vi}, are joined to the Na(3) polyhedra translated along z through two common corners [O(7)^{iv} and O(7)^{vi}]. Thus an infinite ribbon of Na(3) polyhedra is formed (Fig. 3). Na(3) is surrounded by six O atoms located at the corners of a distorted trigonal prism with Na···O distances from 2·454 (10) to 2·961 (8) Å; a seventh oxygen, O(3)^{xii}, centring the vertical prism face is at 2·509 (9) Å.

Crystal packing

The polyhedra around Na(1) and Na(3) share the O(3)^{iii}–O(11) edge. Hence, the Na(1) dimer units are attached to an infinite chain of Na(3) polyhedra in the xz plane. The Na(1) and Na(2) polyhedra have the common edge O(5)^i–O(8). The Na(2) and Na(3) polyhedra share the corner occupied by O(9)^v. The Na(2) dimer units connect these chains along y in a three-dimensional framework of Na polyhedra (Fig. 3). The Na and Th polyhedra share elements as follows: Na(1) and Th with the common edge O(2)^i–O(8); Na(2) and Th with the common edge O(6)^{iv}–O(8); Na(3) and Th with the common face O(7), O(9), O(1)^{iii}

and also with the common edge O(7)–O(11)^{ii}. Thus the dimers of Th polyhedra fit in the holes among the Na polyhedra forming an extremely close-packed structure (Fig. 4).

References

BOND, W. L. (1967). *International Tables for X-ray Crystallography*. Vol. II, pp. 295–298. Birmingham: Kynoch Press.

CORBRIDGE, D. E. C. (1974). *The Structural Chemistry of Phosphorus*, p. 262. Amsterdam: Elsevier.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

JOHANSSON, G. (1968). *Acta Chem. Scand.* **22**, 389–398.

MATKOVIĆ, B., PRODIĆ, B., ŠLJUKIĆ, M. & PETERSON, S. W. (1968). *Croat. Chem. Acta*, **40**, 147–161.

MOLODKIN, A. K. & IVANOVA, O. M. (1966). *Zh. Neorg. Khim.* **11**, 2456–2477.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca, New York: Cornell Univ. Press.

ŠĆAVNIČAR, S. & PRODIĆ, B. (1965). *Acta Cryst.* **18**, 698–702.

STEWART, J. M., MACHIN, P. A., DICKINSON, C., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

UEKI, T., ZALKIN, A. & TEMPLETON, D. H. (1966). *Acta Cryst.* **20**, 836–841.

Untersuchungen an Polyhalogeniden.
2.* Cesiumdicyanotriiodid

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Abstract

Cs[I(ICN)$_2$], C$_2$CsI$_3$N$_2$, is orthorhombic, space group *Pmmn* (No. 59) with $a = 16·494$ (4), $b = 6·726$ (1), $c = 4·592$ (1) Å, $V = 509·4$ Å^3, $D_c = 3·688$ Mg m^{-3}, $Z = 2$. The compound may be prepared in aqueous solution by addition of two molecules of ICN to one

formula unit of CsI. The crystal structure has been solved by direct methods from diffractometer data and refined by full-matrix least squares to $R = 0·057$ for 512 reflections. The structure can be interpreted as a package of pentahalide-analogous anions [I(ICN)$_2$]$^-$ and Cs$^+$ cations in layers. The anionic groups of symmetry *mm2* are angular with φ(I–I$^-$–I) = 123·12 (5)° and d(I$^-$–I) = 3·306 (1) Å. The distance d(I–C) = 2·08 (2) Å is lengthened, the distance

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* Teil 1: Tebbe (1980).