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The Crystal Structure of Disodium Thorium Bisphosphate, $Na_2Th(PO_4)_2$*

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Crystals of the title compound, yielded from two preparations performed in the same way, crystallize in two different space groups, $C2/c$ and $P2_1/c$, retaining the same unit cell. Their structure has been determined by the heavy-atom method, using three sets of X-ray intensity data, the film data in $C2/c$ and the film and diffractometer data in $P2_1/c$ space groups; corresponding R values were 0.107, 0.092, and 0.044, respectively. Results obtained from these three independent determinations have shown for the most part, insignificant differences. The structure is discussed on the basis of more accurate diffractometer data.

There are eight formula units in the unit cell with dimensions (diffractometer data): $a = 0.7055(4)$, $b = 2.166(1)$, $c = 0.9095(5)$ nm, $\beta = 111.56(2)^\circ$, $V = 1.293(1)$ nm^3.

Of two crystallographically different Th atoms, one is surrounded by 10 and the other by 8 neighbouring O atoms. Their polyhedra form a weakly connected dimer sharing a common edge, defined by the two O atoms having the longest Th—O distances in the both Th polyhedra, but being nearer to one of the Th atoms.

Crystallographically different Na atoms (four in $P2_1/c$ and two in $C2/c$ space groups) are surrounded by 8 to 10 O atoms. Metal polyhedra are mutually connected by common corners, edges, and planes. Each O atom is common at least to two and at most to four metal polyhedra.

INTRODUCTION

As a continuation of our interest in alkali thorium orthophosphates which resulted in determination of the crystal structures of $KTh_2(PO_4)_3$[1] and $NaTh_2(PO_4)_3$[2] the structure of the title compound was investigated.

In a preliminary communication[3] preparation of $Na_2Th(PO_4)_2$ at 1173 K and coordination spheres of two crystallographically independent Th atoms were reported. The structure was solved on the basis of film intensity data (set I) showing the $C2/c$ crystal symmetry space group.

Another preparation, performed in the same way as the earlier one, yielded crystals with practically the same unit cell, but in the $P2_1/c$ symmetry

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* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

group. To clarify this crystal symmetry problem the structure was also solved in $P2_1/c$ group using film and diffractometer intensity data collected from crystals of the second preparation (data sets II and III, respectively). Results of these structure determinations are compared and discussed in the present paper.

EXPERIMENTAL

Crystal Data

Data set	I	II	III
a/nm	0.701	0.706	0.7055(4)
b/nm	2.15	2.17	2.166(1)
c/nm	0.912	0.915	0.9095(5)
β/°	111	112	111.56(2)
V/nm^3	1.283	1.300	1.293(1)
Z	8	8	8
Sp. g.	$C2/c$	$P2_1/c$	$P2_1/c$
M	467.958	467.958	467.958
D_m/Mg·m^{-3}	4.85	4.85	4.85
D_c/Mg·m^{-3}	4.84	4.78	4.808

Unit cell dimensions I and II were obtained from oscillation and Weissenberg photographs, and III from single crystal diffractometry after a least squares analysis of 22 reflections with 2Θ values ranging from 8° to 18°.

Crystals, ground to spheres, used for collecting intensity data sets I, II and III had radii of 0.145, 0.105 and 0.125 mm, respectively. The Weissenberg method (Cu Kα radiation, $\lambda = 154.18$ pm, $\mu = 809.44$ cm^{-1}) was used for collecting data sets I and II, while the diffractometer (Mo Kα radiation, $\lambda = 71.07$ pm, $\mu = 245.02$ cm^{-1}) gave data set III; corresponding values of μr were 11.74, 8.50 and 3.06, respectively.

Intensity Data, Structure Determinations, and Refinements

The intensity data sets I and II were collected by means of multiple equi — inclination Weissenberg photographs of the h k 0 to h k 5 levels giving 795 and 1153 independent observed reflections respectively. The intensities were measured with an optical densitometer, averaged and corrected[4] for Lorentz and polarization effects and for absorption.

The intensity data set III was collected on a Philips PW 1100 four-circle diffractometer with the $\Theta - 2\Theta$ scanning technique, a scan range of 1.20° and a scan rate of 0.04° s^{-1}. Out of 2961 reflections scanned within a quadrant ±h, k, l up to $\sin\Theta/\lambda = 0.75$, 2666 unique reflections had intensities $I > 3\sigma(I)$ and were used in the crystal-structure analysis. Three standard reflections measured every 2 hours showed small unsystematic variations with an average of 0.5(1)%. Corrections were made[5] for Lorentz and polarization effects and for absorption.

Weissenberg photographs from the crystals of the first preparation (data set I) showed reflections satisfying conditions of the $C2/c$ space group (absent reflections: h k l with $h + k \neq 2n$ and h 0 l with $l \neq 2n$). But a few very weak and diffuse spots had h k l indices with $h + k \neq 2n$ indicating thus a possibility of $P2_1/c$ space group symmetry. However, the structure was successfully solved in the $C2/c$ space group, while an attempt to solve it in the $P2_1/c$ group failed.

On the other hand, Weissenberg photographs (data set II), as well as diffractometer intensity data (data set III) from the crystals of the second preparation revealed many weak and medium but not strong h k l reflections with $h + k \neq 2n$ (about one third of the total reflections of each set) indicating distinctly the $P2_1/c$ space group. The structure was solved successfully in that space group using data set II or data set III. Excluding h k l reflections with $h + k \neq 2n$ from data sets II and III (385 and 845 reflections respectively) it was possible to »refine« the structure also in the *C*2/*c* space group.

Two crystallographically different Th atoms were determined by the heavy atom method in *C*2/*c* and *P*2$_1$/*c* symmetry space groups depending on the data set used. All other atoms were located from subsequent Fourier and difference maps.

Full-matrix refinements gave R values of 0.107 and 0.092 with data sets I and II respectively. The refinements were performed using anisotropic thermal parameters for non-O atoms obtained by both sets, and for four O atoms obtained by set I. The remaining O atoms (set I) and all O atoms (set II) were refined isotropically.

An anisotropic block-diagonal refinement with data set III gave the final R and R_W of 0.044 and 0.057 respectively. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with the weighting scheme $w = 1/\sigma^2(F_o)$.

Refinements in the *C*2/*c* space group with reduced (without hkl reflections with $h + k \neq 2n$) data sets II and III were performed in the same manner as the analogous refinements in the *P*2$_1$/*c* space group. An R of 0.089 was obtained for data set II, while R and R_w of 0.041 and 0.055 respectively were obtained for data set III.

Mean parameter shifts in the final cycles of the all mentioned refinements were within 0.1σ.

The final atomic coordinates obtained with refinements based on data sets I and III, showing *C*2/*c and P*2$_1$/*c* space group symmetry, respectively, are listed in Table I. Analogous atoms in both space groups are denoted by the same atomic number, but those atoms symmetrically equivalent in the *C*2/*c* group while different in the *P*2$_1$/*c* group are labelled in the latter with capital letters A and B.

Final atomic coordinates obtained by film data in the *P*2$_1$/*c* space group (set II), as well as those obtained by reduced data sets II and III, and all lists of structure factors, are available from the first author on request.

The scattering factors of Cromer and Mann were used[6] and the anomalous dispersion corrections were applied according to Cromer and Liberman.[7]

Calculations were performed mainly with the XRAY76 system[8] on a Univac 1110 computer, at the University Computing Centre of Zagreb.

Differential thermal analysis was performed on a Gebrüder Netzsch Apparatus (BRD) and powder diffraction patterns on a Philips counter diffractometer using graphite monochromated CuKα radiation.

DISCUSSION

Maximal differences of the bond lengths involving analogous atoms located by data sets II and III are 3.5σ, those by the data sets I and III 4.5σ, and those by data set I and by reduced data sets II and III are 4.3σ, where σ's are e. s. d.'s of the values obtained by film data. Corresponding mean differences, however, are in the limits of 1σ. Because of these small differences the structure has been described on the basis of the more accurate diffractometer data set III in the space group *P*2$_1$/*c*, but a few differences, which might be significant, are pointed out.

Environments of the two crystallographically different Th and four Na atoms are shown in Figures 1. and 2. A geometrical analysis of their polyhedrons according to a paper of Lippard and Russ,[9] considering criteria for a choice between dodecahedron and antiprism as the most probable polyhedra for eightfold coordination, is given in Table III. Symbols, as well as data for the perfect antiprism and dodecahedron are taken from Table I of their work.

The Th(1) atom is surrounded by eight O atoms in a distance range from 233(1) to 255(1) pm giving a mean of 246 pm, close to the sum of Th^{4+} (102 pm) and O^{2-} (140 pm) ionic radii.[10] For an eight-coordinated Th atom in $KThP_3O_{10}$,[11] Th—O distances range from 237(4) to 258(4) pm; for nine-coordinated Th atoms in $KTh_2(PO_4)_3$,[1] $NaTh_2(PO_4)_3$,[2] and $Na_6[Th(PO_4)(P_2O_7)]_2$[12] the corresponding ranges of Th—O distances are 226(4)—266(3), 227(1)—258(2), and 230.9(8)—278.5(7) pm, respectively. The Th(1) environment could be described as a distorted dodeca-

TABLE I

Fractional Positional Parameters of Atoms Based on Film Data (set I, C2/c sp. g.; × 10^3; × 10^4 for Th) and Diffractometer Data (set III, $P2_1/c$ sp. g.; × 10^4; × 10^5 for Th), Isotropic Temperature Factors (× 10^{-2} in pm², Denoted by Asterisks), or Equivalent Isotropic Temperature Factors (× 10^{-2} in pm²) Computed by the Expression $U_{eq} = {}^1/_3 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$

	Data set I					Data set III			
Atom	x	y	z	U_{eq}/U	Atom	x	y	z	U_{eq}
Th(1)	0	726(1)	2500	2(1)	Th(1)	25515(7)	17740(2)	24422(5)	0.92(1)
Th(2)	0	2968(1)	2500	2(1)	Th(2)	24342(7)	—4685(2)	24780(6)	1.12(1)
P(1)	—323(2)	189(1)	152(3)	4(1)	P(1A)	—723(5)	630(2)	1470(4)	1.1(1)
					P(1B)	5704(5)	596(2)	3488(4)	1.1(1)
P(2)	—187(2)	—65(1)	378(3)	3(1)	P(2A)	716(5)	3165(2)	3697(4)	1.1(1)
					P(2B)	4436(5)	3153(2)	1182(4)	1.2(1)
Na(1)	378(4)	62(1)	10(4)	5(2)	Na(1A)	—3656(10)	1871(4)	67(10)	3.1(3)
					Na(1B)	—1249(11)	1869(4)	4776(10)	3.6(3)
Na(2)	—105(4)	—190(1)	60(6)	10(2)	Na(2A)	1457(11)	4376(4)	442(9)	2.9(3)
					Na(2B)	3582(12)	4394(4)	4531(9)	3.0(3)
O(11)	—518(7)	191(3)	1(7)	4(1)*	O(11A)	—2761(16)	630(5)	57(11)	1.6(3)
					O(11B)	7686(17)	591(6)	4912(11)	2.1(4)
O(12)	—132(6)	197(2)	108(6)	4(1)*	O(12A)	1011(19)	570(6)	813(14)	2.5(4)
					O(12B)	3860(18)	552(6)	4055(15)	2.6(4)
O(13)	—293(8)	128(2)	247(9)	10(4)	O(13A)	—426(15)	1214(5)	2429(12)	1.7(3)
					O(13B)	5461(15)	1176(5)	2503(12)	1.6(3)
O(14)	—301(6)	248(2)	257(7)	5(3)	O(14A)	—516(14)	53(5)	2516(11)	1.5(3)
					O(14B)	5501(15)	14(5)	2476(12)	1.6(3)
O(21)	31(7)	—80(2)	479(10)	5(3)	O(21A)	2879(15)	3312(6)	4775(11)	1.8(3)
					O(21B)	2227(15)	3300(6)	107(11)	1.7(3)
O(22)	—289(6)	—54(2)	500(6)	3(1)*	O(22A)	—398(15)	3030(5)	4834(12)	1.7(3)
					O(22B)	5498(15)	3017(6)	22(12)	1.9(3)
O(23)	—290(7)	—121(2)	296(6)	4(2)	O(23A)	—144(17)	3740(6)	2662(13)	2.2(3)
					O(23B)	5348(16)	3712(5)	2230(12)	1.8(3)
O(24)	—205(8)	—10(2)	269(8)	5(1)*	O(24A)	561(17)	2617(5)	2621(12)	1.9(4)
					O(24B)	4588(18)	2591(5)	2247(13)	1.9(4)

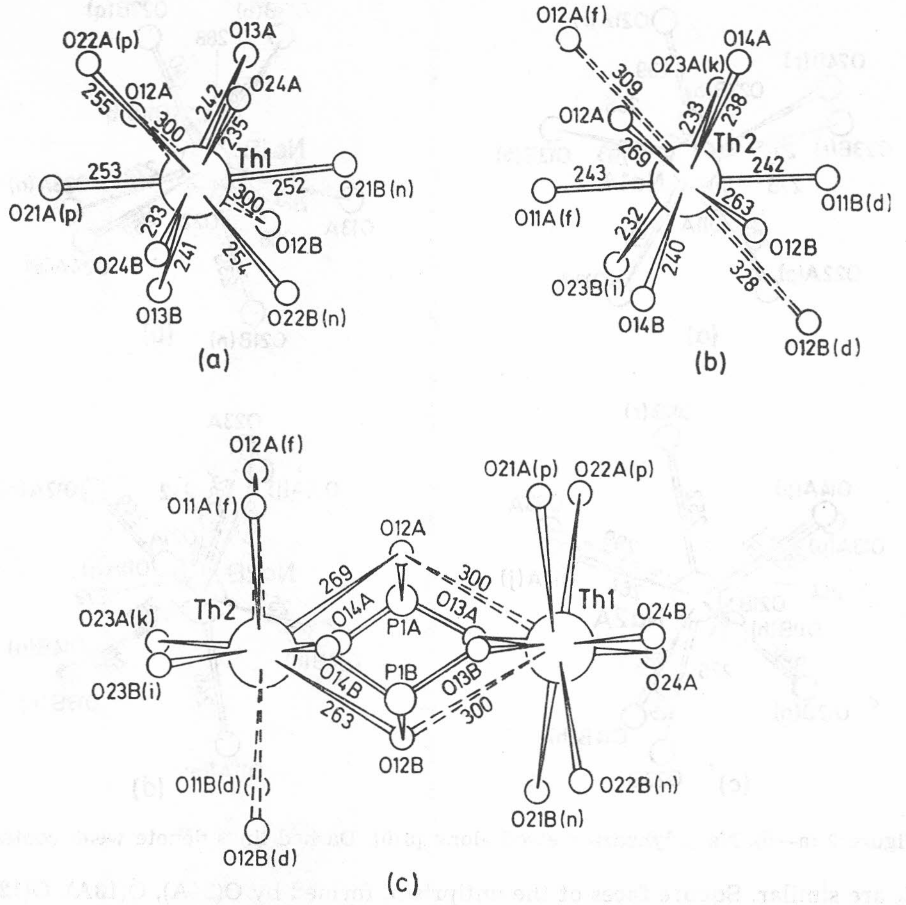

Figure 1 (a, b). Th polyhedra viewed along [010]. (c) Mutual positions of Th (1) and Th (2) polyhedra viewed along [100]. Dashed lines denote weak contacts.

hedron (Table III) with an angle A_T of 89.9(3)° between the mean planes through atoms of two intersecting trapezoids. This angle is practically equal to that for the ideal dodecahedron, but there is a large mean displacement d_T of 31 pm of the atoms from the mean plane through one of the trapezoids, equal to that for the ideal antiprism. Further, the closest O atoms in the Th(1) neighbourhood are O(12A) and O(12B), both of them at a distance of 300(1) pm from Th(1). These two atoms can be included in the Th coordination sphere if the following considerations are accepted. The thorium covalent radius (165 pm)[10] might be taken as approximately equal to its van der Waals radius for a high coordination number. As the van der Waals radius of the O atom[13] is 140 pm, a Th—O distance of 305 pm would be obtained as the sum of van der Waals radii and consequently as a limit for an O atom to belong to the Th coordination sphere. In that case the Th polyhedron is a distorted antiprism with centered square faces. That is because the angle A_T of 65.1(2)° is nearer to that of the ideal antiprism than to that of the ideal dodecahedron, while the displacements d_T and

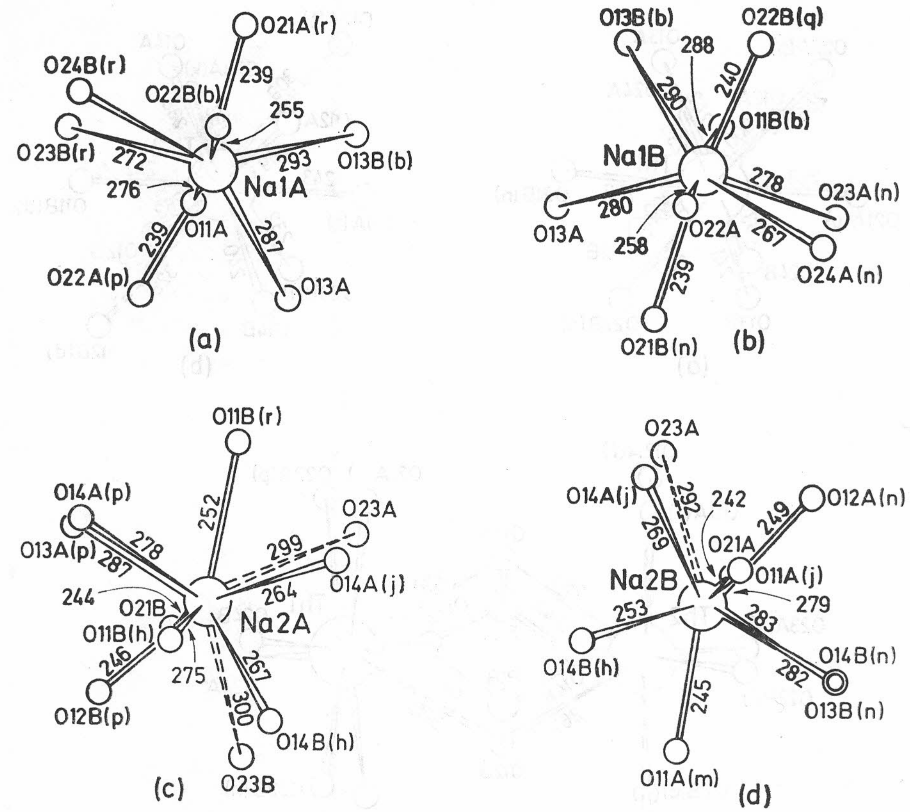

Figure 2 (a—d). Na polyhedra viewed along [010]. Dashed lines denote weak contacts.

d_S are similar. Square faces of the antiprism, formed by O(24A), O(13A), O(12B), O(22Bn) and O(22Ap), O(12A), O(13B), O(24B), are centred with the O(21Bn) and O(21Ap) atoms, respectively, and therefore a tenfold coordination is accomplished.

The Th(2) atom is surrounded by eight O atoms. Six shorter Th(2)—O distances range from 232(1) to 243(1), while two longer ones of 269(1) and 263(1) pm involve the O(12A) and O(12B) O atoms. The mean value of these Th(2)—O distances of 245 pm is close to that of Th(1). The Th(2) polyhedron satisfies conditions for an antiprism better than for a dodecahedron. The antiprism square faces formed by O(14A), O(23Ak), O(11Af), O(12A) and O(14B), O(23Bi), O(11Bd), O(12B) atoms are centered with O(12Af) and O(12Bd) atoms, respectively. But the two latter O atoms, having Th(2)—O distances of 309(1) and 328(1) pm, most probably do not participate in the Th(2) coordination sphere.

The Na(1A) and Na(1B) atoms are eight-coordinated. Their polyhedra are intermediates between the ideal dodecahedron and antiprism. The corresponding A_T values are nearly midway between those for the ideal polyhedra, but the displacements d_T and d_S indicate that distorted dodecahedra are more acceptable. The Na(1A)—O distances range from 239(1) to 293(1) pm and the

TABLE II

Relevant Interatomic Distances (pm) and Angles (°). The Me - - O Lines Denote the Distances Involving Distant O Atoms Having Diminished or Slight Probabilities of Belonging to the Metal Polyhedra

Th polyhedra

Th(1) -– O(12A)	300(1)	Th(2) — O(11Af)	243(1)
Th(1) -– O(12B)	300(1)	Th(2) — O(11Bd)	242(1)
Th(1) — O(13A)	242(1)	Th(2) — O(12A)	269(1)
Th(1) — O(13B)	241(1)	Th(2) — O(12B)	263(1)
Th(1) — O(21Ap)	253(1)	Th(2) - - O(12Af)	309(1)
Th(1) — O(21Bn)	252(1)	Th(2) - - O(12Bd)	328(1)
Th(1) — O(22Ap)	255(1)	Th(2) — O(14A)	238(1)
Th(1) — O(22Bn)	254(1)	Th(2) — O(14B)	240(1)
Th(1) — O(24A)	235(1)	Th(2) — O(23Ak)	233(1)
Th(1) — O(24B)	233(1)	Th(2) — O(23Bi)	232(1)

O(12A) . . . O(12B)	290(2)	O(11Af) . . . O(12A)	310(2)
O(12A) . . . O(13A)	250(2)	O(11Af) . . . O(12Af)	250(2)
O(12A) . . . O(13B)	323(2)	O(11Af) . . . O(14B)	278(1)
O(12A) . . . O(21Ap)	307(2)	O(11Af) . . . O(23Ak)	360(2)
O(12A) . . . O(22Ap)	321(2)	O(11Af) . . . O(23Bi)	281(1)
O(12B) . . . O(13A)	318(2)	O(11Bd) . . . O(12B)	299(2)
O(12B) . . . O(13B)	250(2)	O(11Bd) . . . O(12Bd)	252(2)
O(12B) . . . O(21Bn)	304(2)	O(11Bd) . . . O(14A)	282(1)
O(12B) . . . O(22Bn)	331(2)	O(11Bd) . . . O(23Ak)	281(1)
O(13A) . . . O(21Bn)	268(1)	O(11Bd) . . . O(23Bi)	346(2)
O(13A) . . . O(22Ap)	288(2)	O(12A) . . . O(12Af)	296(2)
O(13A) . . . O(24A)	311(2)	O(12A) . . . O(12B)	290(2)
O(13B) . . . O(21Ap)	272(1)	O(12A) . . . O(14A)	246(2)
O(13B) . . . O(22Bn)	287(2)	O(12A) . . . O(14B)	320(2)
O(13B) . . . O(24B)	312(2)	O(12Af) . . . O(14A)	321(2)
O(22Ap) . . . O(21Ap)	241(2)	O(12Af) . . . O(23Ak)	307(2)
O(22Ap) . . . O(24A)	275(2)	O(12Bd) . . . O(12B)	304(2)
O(22Ap) . . . O(24B)	361(1)	O(12Bd) . . . O(14B)	326(2)
O(22Bn) . . . O(21Bn)	242(2)	O(12Bd) . . . O(23Bi)	312(2)
O(22Bn) . . . O(24A)	359(1)	O(12B) . . . O(14A)	308(2)
O(22Bn) . . . O(24B)	271(2)	O(12B) . . . O(14B)	245(2)
O(24A) . . . O(21Bn)	291(1)	O(14A) . . . O(23Ak)	290(2)
O(24A) . . . O(24B)	298(2)	O(14B) . . . O(23Bi)	292(2)
O(24B) . . . O(21Ap)	289(1)	O(23Ak) . . . O(23Bi)	306(2)

O(12A) - - Th(1) - - O(12B)	57.7(3)	O(11Af) — Th(2) — O(11Bd)	165.0(4)
O(12A) - - Th(1) - - O(13A)	53.6(4)	O(11Af) — Th(2) — O(12A)	74.5(4)
O(12A) - - Th(1) — O(13B)	72.2(3)	O(11Af) — Th(2) — O(12B)	119.3(4)
O(12A) - - Th(1) — O(21Ap)	66.8(4)	O(11Af) — Th(2) -– O(12Af)	52.1(4)
O(12A) - - Th(1) — O(21Bn)	106.0(4)	O(11Af) — Th(2) -– O(12Bd)	125.8(4)
O(12A) - - Th(1) — O(22Ap)	70.2(3)	O(11Af) — Th(2) — O(14A)	118.1(3)
O(12A) - - Th(1) — O(22Bn)	129.5(3)	O(11Af) — Th(2) — O(14B)	70.3(4)
O(12A) - - Th(1) — O(24A)	126.4(4)	O(11Af) — Th(2) — O(23Ak)	98.5(4)
O(12A) - - Th(1) — O(24B)	138.2(4)	O(11Af) — Th(2) — O(23Bi)	72.7(4)
O(12B) - - Th(1) — O(13A)	70.8(3)	O(11Bd) — Th(2) — O(12A)	120.2(4)
O(12B) - - Th(1) — O(13B)	53.7(4)	O(11Bd) — Th(2) — O(12B)	72.6(4)
O(12B) - - Th(1) — O(21Ap)	106.5(4)	O(11Bd) — Th(2) - - O(12Af)	130.0(4)
O(12B) - - Th(1) — O(21Bn)	66.1(4)	O(11Bd) — Th(2) - - O(12Bd)	49.7(4)
O(12B) - - Th(1) — O(22Ap)	126.9(3)	O(11Bd) — Th(2) — O(14A)	72.0(4)
O(12B) - - Th(1) — O(22Bn)	72.8(3)	O(11Bd) — Th(2) — O(14B)	113.8(4)
O(12B) - - Th(1) — O(24A)	137.5(4)	O(11Bd) — Th(2) — O(23Ak)	72.5(4)
O(12B) - - Th(1) — O(24B)	128.3(4)	O(11Bd) — Th(2) — O(23Bi)	94.0(4)
O(13A) — Th(1) — O(13B)	117.4(4)	O(12A) — Th(2) — O(12B)	66.0(4)
O(13A) — Th(1) — O(21Ap)	110.1(3)	O(12A) — Th(2) - - O(12Af)	61.1(3)
O(13A) — Th(1) — O(21Bn)	65.7(3)	O(12A) — Th(2) - - O(12Bd)	126.0(3)

O(13A) — Th(1) — O(22Ap)	70.7(3)	O(12A) — Th(2) — O(14A)	57.6(4)
O(13A) — Th(1) — O(22Bn)	120.5(4)	O(12A) — Th(2) — O(14B)	77.6(4)
O(13A) — Th(1) — O(24A)	81.4(4)	O(12A) — Th(2) — O(23Ak)	118.5(4)
O(13A) — Th(1) — O(24B)	159.9((4)	O(12A) — Th(2) — O(23Bi)	143.3(4)
O(13B) — Th(1) — O(21Ap)	66.7(3)	O(12B) — Th(2) - - O(12Af)	126.5(3)
O(13B) — Th(1) — O(21Bn)	108.7(3)	O(12B) — Th(2) - - O(12Bd)	60.7(3)
O(13B) — Th(1) — O(22Ap)	120.5(4)	O(12B) — Th(2) — O(14A)	75.7(4)
O(13B) — Th(1) — O(22Bn)	70.9(4)	O(12B) — Th(2) — O(14B)	58.0(4)
O(13B) — Th(1) — O(24A)	160.6(4)	O(12B) — Th(2) — O(23Ak)	140.3(5)
O(13B) — Th(1) — O(24B)	82.3(4)	O(12B) — Th(2) — O(23Bi)	118.4(4)
O(21Ap) — Th(1) — O(21Bn)	125.0(4)	O(12Af) - - Th(2) - - O(12Bd)	172.7(3)
O(21Ap) — Th(1) — O(22Ap)	56.7(4)	O(12Af) - - Th(2) — O(14A)	70.6(3)
O(21Ap) — Th(1) — O(22Bn)	124.6(4)	O(12Af) - - Th(2) — O(14B)	114.7(4)
O(21Ap) — Th(1) — O(24A)	113.1(4)	O(12Af) - - Th(2) — O(23Ak)	67.2(4)
O(21Ap) — Th(1) — O(24B)	72.9(4)	O(12Af) - - Th(2) — O(23Bi)	108.3(3)
O(21Bn) — Th(1) — O(22Ap)	125.0(4)	O(12Bd) - - Th(2) — O(14A)	113.9(3)
O(21Bn) — Th(1) — O(22Bn)	57.0(4)	O(12Bd) - - Th(2) — O(14B)	68.0(3)
O(21Bn) — Th(1) — O(24A)	73.4(4)	O(12Bd) - - Th(2) — O(23Ak)	107.7(4)
O(21Bn) — Th(1) — O(24B)	113.4(4)	O(12Bd) - - Th(2) — O(23Bi)	65.2(3)
O(22Ap) — Th(1) — O(22Bn)	160.2(4)	O(14A) — Th(2) — O(14B)	125.9(4)
O(22Ap) — Th(1) — O(24A)	68.3(3)	O(14A) — Th(2) — O(23Ak)	76.0(4)
O(22Ap) — Th(1) — O(24B)	96.8(4)	O(14A) — Th(2) — O(23Bi)	156.9(4)
O(22Bn) — Th(1) — O(24A)	96.0(4)	O(14B) — Th(2) — O(23Ak)	158.0(4)
O(22Bn) — Th(1) — O(24B)	67.4(4)	O(14B) — Th(2) — O(23Bi)	76.3(4)
O(24A) — Th(1) — O(24B)	79.3(4)	O(23Ak) — Th(2) — O(23Bi)	82.4(4)

Na polyhedra

Na(1A) — O(11A)	276(1)	Na(1B) — O(11Bb)	288(2)
Na(1A) — O(13A)	287(1)	Na(1B) — O(13Bb)	290(1)
Na(1A) — O(13Bb)	293(1)	Na(1B) — O(13A)	280(2)
Na(1A) — O(21Ar)	239(1)	Na(1B) — O(21Bn)	239(1)
Na(1A) — O(22Bb)	255(1)	Na(1B) — O(22A)	258(1)
Na(1A) — O(22Ap)	239(1)	Na(1B) — O(22Bq)	240(1)
Na(1A) — O(23Br)	272(1)	Na(1B) — O(23An)	278(1)
Na(1A) — O(24Br)	267(1)	Na(1B) — O(24An)	267(1)
Na(2A) — O11Bh)	275(1)	Na(2B) — O(11Aj)	279(1)
Na(2A) — O(11Br)	252(1)	Na(2B) — O(11Am)	245(1)
Na(2A) — O(12Bp)	246(2)	Na(2B) — O(12An)	249(2)
Na(2A) — O(13Ap)	287(1)	Na(2B) — O(13Bn)	282(1)
Na(2A) — O(14Bh)	267(1)	Na(2B) - - O(23A)	292(1)
Na(2A) — O(14Aj)	264(1)	Na(2B) — O(14Bh)	253(2)
Na(2A) — O(14Ap)	280(1)	Na(2B) — O(14Bn)	283(1)
Na(2A) — O(21B)	244(1)	Na(2B) — O(21A)	242(1)
Na(2A) - - O(23A)	299(2)	Na(2B) — O(14Aj)	269(1)
Na(2A) - - O(23B)	300(1)		

Phosphate groups

P(1A) — O(11A)	154(1)	P(1B) — O(11B)	152(1)
P(1A) — O(12A)	155(2)	P(1B) — O(12B)	157(2)
P(1A) — O(13A)	151(1)	P(1B) — O(13(B)	152(1)
P(1A) — O(14A)	154(1)	P(1B) — O(14B)	154(1)
P(2A) — O(21A)	151(1)	P(2B) — O(21B)	154(1)
P(2A) — O(22A)	154(1)	P(2B) — O(22B)	153(1)
P(2A) — O(23A)	154(1)	P(2B) — O(23B)	153(1)
P(2A) — O(24A)	152(1)	P(2B) — O(24B)	153(1)

O(11A) — P(1A) — O(12A)	107.8(6)	O(11B) — P(1B) — O(12B)	109.5(7)
O(11A) — P(1A) — O(13A)	111.9(6)	O(11B) — P(1B) — O(13B)	112.3(6)
O(11A) — P(1A) — O(14A)	111.3(6)	O(11B) — P(1B) — O(14B)	111.0(6)
O(12A) — P(1A) — O(13A)	109.4(7)	O(12B) — P(1B) — O(13B)	108.5(7)
O(12A) — P(1A) — O(14A)	105.0(7)	O(12B) — P(1B) — O(14B)	103.9(7)
O(13A) — P(1A) — O(14A)	111.2(6)	O(13B) — P(1B) — O(14B)	111.2(6)

O(21A) — P(2A) — O(22A)	104.3(6)	O(21B) — P(1B) — O(22B)	103.9(6)
O(21A) — P(2A) — O(23A)	107.6(6)	O(21B) — P(1B) — O(23B)	109.1(6)
O(21A) — P(2A) — O(24A)	113.5(6)	O(21B) — P(1B) — O(24B)	112.6(7)
O(22A) — P(2A) — O(23A)	112.3(7)	O(22B) — P(1B) — O(23B)	112.4(7)
O(22A) — P(2A) — O(24A)	110.6(7)	O(22B) — P(1B) — O(24B)	110.2(7)
O(23A) — P(2A) — O(24A)	108.6(6)	O(23B) — P(1B) — O(24B)	108.6(6)

Symmetry code

(a) x + 1, y, z
(b) x — 1, y, z
(c) — x + 1, — y + 1, — z + 1
(d) — x + 1, — y, — z + 1
(e) — x, — y + 1, — z
(f) — x, —y, — z
(g) — x, — y, — z + 1
(h) — x + 1, y + 1/2, — z + 1/2
(i) — x + 1, y — 1/2, — z + 1/2
(j) — x, y + 1/2, — z + 1/2
(k) — x, y — 1/2, — z + 1/2
(m) x + 1, — y + 1/2, z + 1/2
(n) x, — y + 1/2, z + 1/2
(p) x, — y + 1/2, z — 1/2
(q) x — 1, — y + 1/2, z + 1/2
(r) x — 1, — y + 1/2, z — 1/2

Na(1B)—O distances from 239(1) to 290(1) pm with mean values of 266 and 268 pm, respectively. In some other structures with six- and seven-coordinated Na atoms, the Na—O distances range from 227(1) to 283(1) pm for water,[14] and from 234(1) to 293(1) for phosphate or from 231(1) — to 305(1) pm for pyrophosphate[12] O atoms. Assuming that the Na covalent radius[10] of 157 pm is nearly equal to the van der Waals radius for a Na atom with a high coordination number, 297 pm might be accepted as an approximate sum of van der Waals radii of Na and O atoms. The O atoms with the Na—O distances that are nearly in the limit of this evaluated sum might be considered to belong to the Na coordination sphere.

The Na(2A) atom is surrounded by eight O atoms with the Na—O distances ranging from 244(1) to 287(1) pm. The next two O atoms, O(23A) and O(23B), which are 299(2) and 300(2) pm from the Na(2A) atom, complete the Na(2A) coordination sphere to ten. Similarly, the Na(2B) atom is surrounded by eight O atoms with the Na—O distances ranging from 242(2) to 283(1) pm; the next O atom, O(23A), which is 292(1) pm from the Na(2B) atom, completes its coordination sphere to nine. If, for the purpose of comparing the four Na polyhedra, only the eight atoms nearer to the Na(2A), as well as to the Na(2B) atoms are considered, corresponding polyhedra could be described formally, also as intermediates between the ideal dodecahedron and antiprism (Table III).

Each metal atom is coordinated by two pairs of O atoms from two different phosphate groups acting as bidentate ligands. Other O atoms are coordinated monodentately. The shortest metal—O bonds are realized by monodentately coordinated O atoms. Each of the P(1A) and P(1B) phosphate groups acts as a bidentate ligand for one Th(2) and three Na atoms, while each of the P(2A) and P(2B) phosphate groups acts as a bidentate ligand for one Th(1) and one Na atom. Each of the O atoms belongs at least to two, but mostly to four metal polyhedrons. P—O bond lengths within P tetrahedra range from 151(1) to 157(2) pm and O—P—O bond angles from 103.9(7) to 113.5(6)° with corresponding means of 153 pm and 109.4°, respectively (Table II).

The metal polyhedra are mutually connected by common corners, edges, and planes formed by O atoms. Corresponding Th . . . Th, Th . . .Na, and Na . . . Na distance ranges, considering neighbouring metal polyhedra, are 485.9(3) — 546.3(2), 384(1) — 420(1), and 322(1) — 559(1) pm, respectively.

TABLE III

Geometry of the Metal Polyhedra. d_T *is the Average Displacement of O Atoms, Determining a Dodecahedron Trapezoid, from their Mean Plane, and* d_S *is the Average Displacement of O Atoms from the Mean Plane Through a Square Face of an Analogous Antiprism (e. s. d.'s of the Displacements are within 1 pm);* A_T *is the Angle Between Mean Planes Through two Interescting Dodecahedron Trapezoids*

Metal atoms	Atoms of intersecting dodecahedron trapesoid pairs	d_T/pm	d_S/pm	A_T/°
Th(1)*	O(13A), O(13B), O(24B), O(24A) O(22Bn), O(21Bn), O(22Ap), O(21Ap)	10 31	18,16	89.9(3)
Th(1)**	O(13B), O(24B), O(24A), O(13A) O(22Bn), O(12B), O(12A), O(22Ap)	10 16	11,11	65.1(2)
Th(2)	O(14B), O(13Bi), O(23Ak), O(14A) O(11Bd), O(12B), O(12A), O(11Af)	11 61	1,4	76.8(3)
Na(1A)	O(21Ar), O(13Bd), O(13A), O(22Ap) O(22Bb), O(24Br), O(23Br), O(11A),	9 1	51,22	84.3(3)
Na(1B)	O(21Bn), O(13A), O(13Bd), O(22Bq) O(11Bb), O(23An), O(24An), O(22A)	13 4	52,24	84.6(3)
Na(2A)	O(11Br), O(14Aj), O(14Bh), O(12Bp) O(21B), O(13Ap), O(14Ap), O(11Bh)	10 4	0,63	81.9(4)
Na(2B)	O(12An), O(14Aj), O(14Bh), O(11Am) O(11Aj), O(14Bn), O(13Bn), O(21A)	6 4	66,0	83.9(3)
	Perfect antiprism	37 37	0,0	77.4
	Perfect dodecahedron	0 0	31,31***	90.0

* assuming that O(12A) and O(12B) are not involved in the Th(1) polyhedron

** assuming that O(12A) and O(12B) are involved in the Th(1) polyhedron

*** assuming a metal-ligand bond distance of about 260 pm

It may be assumed that the Th(1) and Th(2) polyhedra with the shortest Th . . . Th distance of 485.9(3) pm make a weakly connected dimer sharing the common edge formed by the O(12A) and O(12B) atoms, Figure 1(c). These O atoms with the longest Th(2)—O bonds and only weak contact to the Th(1) atom are among those with the longest P—O bonds. They are probably affected by a stretching effect between the two Th atoms in the process of compound formation and crystallization. Perhaps it is significant that in the few relatively higher differences in interatomic bond distances, obtained by data sets I and III, are just those involving the O(12) atom in the $C2/c$ and the corresponding O(12A) and O(12B) atoms in the $P2_1/c$ space group. The Th(2)—O(12) distance of 251(4) pm in $C2/c$ and the corresponding distances Th(2)—O(12A) of 269(1) pm and Th(2)—O(12B) of 263(1) pm in $P2_1/c$ make differences of 4.5 and 3.0 σ. It may be supposed that these O atoms and consequently, more or less, other non-Th atoms may remain after the crystallization process fixed in positions slightly displaced from those which are energetically the mostly suitable. In this case, a change in space group symmetry but essentially the same structural arrangement could be assumed, thus keeping unit cell dimensions unchanged. In accordance with these assumptions, a differential thermal analysis did not show any features indicative of a phase transformation. Neither powder diffraction patterns of samples from the two different preparations nor powder

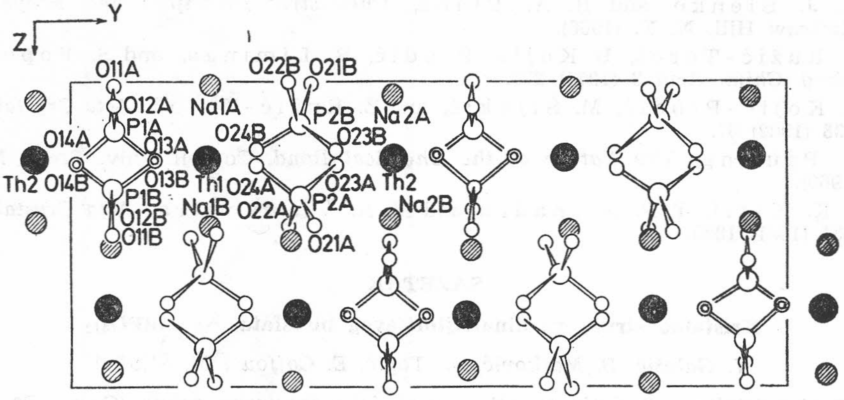

Figure 3. Projection of the structure viewed along [100] showing distribution of Th and Na atoms and phosphate groups within a unit cell.

patterns generated from analogous single crystal data showed any significant differences in intensity maxima.

It can be seen in Figure 3 that the structure has some layer like character. Layers of metal atoms are parallel with the XY plane with Th atoms at nearly 1/4 and 3/4 and with Na atoms at roughly 0 and 1/2 of *c* levels. P atoms are between the metal layers and each of the phosphate groups gives two O atoms to the Th and two others to the Na layers. In this way, a strong connection between the metal layers is achieved. The same is valid for the C2/c space group, only the Th atoms are exactly at the 1/4 and 3/4 levels along *c*.

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SAŽETAK

Kristalna struktura dinatrijtorijevog bifosfata, $Na_2Th(PO_4)_2$

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Spoj kristalizira u dvije različite simetrijske prostorne grupe ($C2/c$ i $P2_1/c$), a pritom zadržava istu jediničnu ćeliju. Strukturna određivanja vršena su na temelju filmskih i difraktometrijskih rendgenskih podataka. U grupi $C2/c$ struktura je utočnjena na temelju filmskih podataka ($R = 0,107$) a u grupi $P2_1/c$ na temelju filmskih ($R = 0,092$) i difraktometrijskih ($R = 0,044$) podataka. Razlike među tako dobivenim rezultatima, većinom su bile beznačajne.

Osam formulskih jedinica nalazi se u elementarnoj ćeliji slijedećih dimenzija (navedeni su difraktometrijski podaci kao najtočniji): $a = 0,7055(4)$ nm, $b = 2,166(1)$ nm, $c = 0,9095(5)$ nm, $\beta = 111,56(2)°$, $V = 1,293(1)$ nm^3.

Dva kristalografski različita torijeva atoma okružena su s 8 odnosno 10 bližih kisikovih atoma. Njihovi poliedri preko zajedničkog brida čine slabo povezani dimer. Kisikovi atomi iz zajedničkog brida bliži su jednom nego drugom torijevu atomu, ali u većoj udaljenosti od njih nego ostali kisikovi atomi unutar oba poliedra.

Dva kristalografski različita natrijeva atoma u grupi $C2/c$, odnosno četiri u grupi $P2_1/c$ okruženi su s 8 do 10 obližnjih kisikovih atoma. Metalni poliedri međusobno su povezani zajedničkim uglovima, bridovima i plohama, tako da je svaki kisikov atom zajednički najmanje za dva, a najviše za četiri metalna poliedra.