The Crystal Structure of Potassium Dithorium Trisphosphate, KTh2(PO4)3*

B. Matković, B. Prodić, and M. Šljukić**

Institute Ruđer Bošković, Zagreb, Croatia, Yugoslavia
and

S. W. Peterson***

Washington State University, Pullman, Washington, U. S. A.

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The structure of $KTh_2(PO_4)_3$ has been determined from three-dimensional X-ray data. The crystals are monoclinic with a = 17.57, b = 6.863, c = 8.138 Å, $\beta = 101° 46'$, $D_x = 5.45$ g · cm^{-3}. The space group is C2/c and there are four formula units per unit cell. It follows from the interatomic distances that the compound is potassium trisphosphatodithorate defined by the formula K [Th2(PO4)3]. Nine oxygen atoms are bound to the thorium atom; their distances range from 2.26 to 2.66 Å. Eight oxygen atoms are coordinated around potassium atom; their distances range from 2.74 to 3.09 Å. The distances in the PO_4 groups do not deviate significantly from known data.

INTRODUCTION

Although there are several known structures of thorium compounds, the stereochemistry of this element is not yet well characterized. It usually involves a coordination number of eight, but other coordination numbers were also found. Up to now it has not been possible to predict from the chemical formula the coordination polyhedron or in some cases even the coordination number of the thorium atom. Only the direct experimental determination, for example, by X-ray analysis of the crystal structure, gives the answer to these questions and is therefore of considerable interest in inorganic chemistry. The crystal structure of $KTh_2(PO_4)_3$ has been studied with the purpose of determining the coordination polyhedron of oxygen atoms around the thorium atom and to establish the bond lengths between all atoms, especially Th—O. Both are of interest because the structure of this very stable compound, insoluble in all acids, was not yet known.

EXPERIMENTAL

The crystals, obtained by thermal synthesis, were colorless, transparent monoclinic prisms. Their chemical composition, determined by analysis, corresponds to

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Permanent addresses:
** Faculty of Science, the University, Sarajevo, Yugoslavia
*** Argonne National Laboratory, Argonne, Illinois, USA.

the formula $KTh_2(PO_4)_3$. The preparation of this compound was described previously[1]. It is possible to obtain single crystals in a more simple way: by heating a mixture of ThO_2, K_2HPO_4 and B_2O_3 in a platinum crucible to a temperature of 1200^0 C for 24 hours. The stoichiometric quantity of ThO_2 and an excess of K_2HPO_4 (twice the stoichiometric quantity) was used. B_2O_3 was added as a flux. Its quantity was about 6 times that of the ThO_2. The unit cell parameters were determined from oscillation and Weissenberg photographs and corrected from single crystal axial reflections (recorded by Geiger counter and calibrated with germanium). CuK α radiation was used. The obtained parameters are:

$$a = 17.57 \pm 0.014 \text{ Å}$$
$$b = 6.863 \pm 0.003$$
$$c = 8.138 \pm 0.004$$
$$\beta = 101^0\ 46' \pm 7'$$
$$Z = 4$$

The calculated density is 5.45 g. cm^{-3} and the measured density 5.44 g. cm^{-3}. The latter was determined pycnometrically using decalin as liquid. Multiple film equi-inclination Weissenberg photographs were taken around three crystallographic axes. The presence of hkl reflections only for $h + k = 2n$ and $h0l$ reflections only for $l = 2n$ indicated the space group $C2/c$ or Cc. Because the dimensions of the unit cell are very close to data obtained before for similar sodium compounds, $NaTh_2(PO_4)_3$ and $NaU_2(PO_4)_3$, which belong to the Cc group[2], at first the same space group was taken into consideration. Tests on $KTh_2(PO_4)_3$ crystals for piezoelectricity (made by the Bergman method as modified by Iitaka[3]) failed to produce a positive result. The ambiguity was resolved during the course of crystal structure determination and the $C2/c$ group was found to be correct.

The three-dimensional intensity data were recorded from crystals on multiple equi-inclination Weissenberg photographs with CuK α radiation. In order to apply absorption corrections more easily and accurately ($\mu = 1156.16$ cm.$^{-1}$) the crystals were made spherical by grinding. Such a ground specimen, mounted along the b axis (radius of sphere r = 0.083 mm, μ r = 9.6) was used for collecting $h0l$ to $h3l$ intensity data; another specimen (r = 0.067 mm, μ r = 7.7) oriented along [001] was used for collecting $hk0$ to $hk4$ reflections; $0kl$ data were collected from the specimen (r = 0.064 mm, μ = 7.4) oriented along [100]. The relative intensities were determined from the optical densities of each spot measured by means of a microdensitometer. The corrections for absorption, polarization and Lorentz-factors were made in the usual way and the structure amplitudes derived. The factors for transforming the observed structure amplitude into the absolute scale were found for reflections of each layer and with the help of these factors all structure amplitudes were scaled. These scale factors were improved in the course of structure determination.

STRUCTURE DETERMINATION

The positions of the thorium atoms were determined from Patterson projections P (u0w) and P (uv0). Their coordinates were related by the symmetry of $C2/c$ group. The signs of the structure factors calculated for these thorium positions were used with the observed structure factors to calculate the first three-dimensional Fourier synthesis from where it was possible to pick out all the atoms. These were introduced into the structure factor calculations and a second three-dimensional electron-density distribution gave very well resolved peaks for potassium and one phosphorus atom in special position on a two-fold axis and all the other atoms in general positions. The three-dimensional difference $(F_o - F_{cTh})$ Fourier synthesis confirmed the obtained positions of K, P and O atoms.

The Fourier map based on phases calculated from the thorium atoms with $C2/c$ symmetry has also $C2/c$ symmetry. However, if the Cc group is correct, we would expect the light atom peaks to be elongated, or even split. No such elongation was observed except for the peak which belongs to the potassium atom. At this point, a possible alternative of a noncentrosymmetric arrangement for potassium atoms was considered. The two most likely possibilities were: Either the space group is Cc with an approximate center of symmetry for Th, P and perhaps O atoms, or the space group is $C2/c$ and the potassium atoms are disordered, or have large

TABLE I

Fractional Coordinates for KTh₂(PO₄)₃

The thermal parameters of Th, K and P atoms are of the form $T = \exp[-(\beta_{11} h^2 + \beta_{22} k^2 + \beta_{33} l^2 + 2\beta_{12} hk + 2\beta_{13} hl + 2\beta_{23} kl)]$. Each thermal parameter is multiplied by 10^4. β_{12} and β_{23} for K (2.00) and P (4.00) are required to be zero by symmetry. Standard errors are given in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	$B(\text{Å}^2)$
Th(1.00)	0.1539 (0.0001)	0.0927 (0.0002)	0.0343 (0.0002)	6 (0.4)	14 (3)	29 (2)	1 (1)	4 (1)	−3 (2)	
K(2.00)	0.0	0.3994 (0.0034)	0.250	44 (9)	172 (48)	622 (86)	0	123 (23)	0	
P(3.00)	0.3106 (0.0006)	0.0884 (0.0014)	0.3148 (0.0013)	12 (3)	12 (16)	65 (15)	4 (6)	15 (5)	−10 (16)	
P(4.00)	0.0	−0.0986 (0.0023)	0.250	12 4	63 (28)	58 (21)		5 (8)	0	
O(5.00)	0.0686 (0.0014)	0.0256 (0.0039)	0.2423 (0.0032)							0.8 (0.4)
O(6.00)	−0.0215 (0.0018)	−0.2171 (0.0049)	0.0852 (0.0041)							1.9 (0.5)
O(7.00)	0.2263 (0.0013)	0.0459 (0.0035)	0.3354 (0.0030)							0.4 (0.4)
O(8.00)	0.3591 (0.0015)	−0.0963 (0.0041)	0.3448 (0.0033)							1.0 (0.4)
O(9.00)	0.2994 (0.0015)	0.1538 (0.0042)	0.1247 (0.0035)							1.1 (0.5)
O(10.00)	0.3463 (0.0022)	0.2690 (0.0059)	0.4144 (0.0053)							3.0 (0.7)

$R_1 = \Sigma_{hkl} ||F_o| - |F_c|| / \Sigma_{hkl} |F_o| = 0.092$ (including unobserved reflections)
$R_2 = \Sigma_{hkl} ||F_o| - |F_c|| / \Sigma_{hkl} |F_o| = 0.081$ (ommitting unobserved reflections)

TABLE II
Observed and Calculated Structure Factors for KTh₂(PO₄)₃

H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
0	2	0	327.1	314.8	18	4	0		—11.4	9	1	—1	222.2	—221.4	1	5	2	158.0	—144.8
0	4	0	369.5	—404.4	19	1	0	271.3	246.2	9	3	1	244.4	—239.8	1	5	—2	367.3	—321.7
0	6	0	461.5	—476.5	19	3	0	54.7	—52.0	9	3	—1	367.7	—372.3	1	7	2	120.7	—94.0
0	8	0		—22.7	20	0	0	266.8	268.6	9	5	1	68.0	—74.2	1	7	—2	166.1	—156.7
1	1	0	318.6	304.2	20	2	0	87.8	87.5	9	5	—1	68.4	77.2	2	0	2	488.7	—545.0
1	3	0		—22.6	21	1	0		—11.0	9	7	1	141.5	139.0	2	0	—2	119.3	84.2
1	5	0	194.6	—175.0	22	0	0	115.8	—166.8	9	7	—1	223.6	—224.6	2	2	2	216.6	—193.5
1	7	0	149.4	—121.9	0	2	1	132.5	—117.0	10	2	1	194.0	178.8	2	2	—2		—0.1
2	0	0	259.8	—237.5	0	4	1	118.2	—118.6	10	2	—1	47.8	49.7	2	4	2	274.6	260.5
2	2	0	163.7	—107.5	0	6	1		—7.2	10	4	1	168.5	160.1	2	4	—2		—15.3
2	4	0	142.4	134.9	0	8	1	45.3	40.2	10	4	—1	32.5	—38.9	2	6	2	343.3	303.7
2	6	0	163.9	137.8	1	1	1	280.3	—270.7	10	6	1	70.9	—56.2	2	6	—2	100.7	—83.9
2	8	0		29.4	1	1	—1	256.4	—267.0	11	1	1	252.3	246.9	3	1	2	485.4	—558.9
3	1	0	363.3	—382.1	1	3	1	530.4	—532.3	11	1	—1	133.0	123.2	3	1	—2	423.7	—418.9
3	3	0		41.0	1	3	—1	342.7	—322.6	11	3	1	500.7	511.7	3	3	2		42.8
3	5	0	361.7	354.1	1	5	1	66.8	—56.7	11	3	—1	282.5	305.2	3	3	—2	122.0	120.2
3	7	0	195.5	174.9	1	5	—1		17.7	11	5	1	102.7	107.4	3	5	2	464.8	458.4
4	0	0	341.2	—342.8	1	7	1	253.9	234.1	11	5	—1	58.4	—45.5	3	7	2	260.5	240.6
4	2	0	149.2	—137.0	1	7	—1	224.5	—217.5	11	7	1	230.1	—262.9	3	7	—2	181.1	165.6
4	4	0	208.0	214.6	2	2	1	266.2	—245.0	11	7	—1	183.5	186.4	4	0	2	255.7	—248.9
4	6	0	265.5	257.0	2	2	—1	657.0	—696.8	12	2	1	279.2	264.6	4	0	—2	727.9	—728.1
4	8	0		7.2	2	4	1	255.6	—246.3	12	2	—1	268.5	261.5	4	2	2	139.7	—122.3
5	1	0		—21.4	2	4	—1	436.4	430.0	12	4	1	181.7	173.3	4	2	—2	209.9	—228.9
5	3	0		9.7	2	6	1	114.0	94.0	12	4	—1	210.0	—216.6	4	4	2	158.6	150.5
5	5	0		—4.6	2	6	—1	176.1	—158.2	12	6	1	103.1	—98.1	4	4	—2	369.5	352.8
5	7	0		—22.5	2	8	1	218.9	227.3	12	6	—1	100.8	98.2	4	6	2	122.5	108.5
6	0	0	677.1	704.4	2	8	—1	361.8	—372.2	13	1	1	92.7	—79.3	4	6	—2	465.8	442.5
6	2	0	151.4	131.3	3	1	1	73.3	—66.2	13	1	—1	105.6	87.6	5	1	2	255.8	263.7
6	4	0	360.4	—365.6	3	1	—1	139.3	—110.6	13	3	1	127.9	—116.9	5	1	—2	69.2	—65.7
6	6	0	394.5	—399.7	3	3	1	103.3	—74.4	13	3	—1	180.8	178.5	5	3	2	34.9	—39.9
6	8	0		—6.6	3	3	—1	213.0	—222.7	13	5	1	40.5	—47.6	5	3	—2		16.1
7	1	0	334.0	348.9	3	5	1		—27.8	13	5	—1	35.9	—34.3	5	5	2	195.8	—170.2
7	3	0	153.8	—153.5	3	5	—1	105.5	73.2	13	7	1	52.7	50.4	5	5	—2	83.6	59.4
7	5	0	342.1	—360.3	3	7	1		23.2	14	2	1	253.5	—259.6	5	7	2	131.0	—121.4
7	7	0	195.5	—194.5	3	7	—1	122.0	—113.1	14	2	—1	319.4	—305.0	5	7	—2	64.7	51.3
8	0	0	85.4	61.9	4	2	1	410.8	410.5	14	4	1	169.2	—171.0	6	0	2	479.6	582.7
8	2	0		—3.2	4	2	—1	211.7	197.4	14	4	—1	194.2	177.1	6	0	—2	212.8	187.1
8	4	0	52.9	—42.0	4	4	1	313.4	310.7	14	6	1	61.8	63.5	6	2	2	169.6	147.9
8	6	0	68.8	—52.2	4	4	—1	224.5	—200.8	14	6	—1	121.5	—117.7	6	2	—2	131.6	135.0
8	8	0		5.0	4	6	1	142.3	—142.7	15	1	1	163.9	—157.4	6	4	2	216.8	—203.5
9	1	0	298.3	—292.3	4	6	—1	85.0	57.3	15	1	—1	239.8	—232.6	6	4	—2	121.1	—105.4
9	3	0	100.0	66.4	4	8	1	278.8	—289.9	15	3	1	264.6	—259.3	6	6	2	286.5	—267.6
9	5	0	251.4	251.8	4	8	—1	138.9	147.7	15	3	—1	377.7	—388.3	6	6	—2	197.4	—178.6
9	7	0	128.1	116.4	5	1	1	325.1	334.9	15	5	1	67.4	—57.9	7	1	2	283.5	296.0
10	0	0	402.1	—386.5	5	1	—1	200.5	187.8	15	5	—1	74.0	70.5	7	1	—2	469.0	492.4
10	2	0	154.5	—151.2	5	3	1	539.5	577.1	16	2	1		—7.9	7	3	2	35.0	—26.5
10	4	0	191.8	192.4	5	3	—1	489.3	510.1	16	2	—1	147.5	—126.2	7	3	—2	73.6	—56.4
10	6	0	263.4	277.2	5	5	1	98.4	87.5	16	4	1		—16.1	7	5	2	216.6	—212.3
11	1	0	187.8	—183.1	5	5	—1	99.0	—82.1	16	4	—1	117.1	105.4	7	5	—2	111.1	—332.5
11	3	0		14.4	5	7	1	283.4	—289.7	17	1	1	140.5	131.1	7	7	2	146.8	—130.6
11	5	0	152.4	135.7	5	7	—1	252.6	239.0	17	1	—1	106.6	84.5	7	7	—2	176.1	—159.8
11	7	0	90.0	85.8	6	2	1	194.7	175.1	17	3	1	290.3	273.8	8	0	2	220.7	—194.8
12	0	0	301.8	276.9	6	2	—1	233.9	222.5	17	3	—1	165.6	153.2	8	0	—2	331.8	348.5
12	2	0	129.0	103.8	6	4	1	134.6	104.2	17	5	1	38.3	39.6	8	2	2	78.1	—57.1
12	4	0	156.3	—150.9	6	4	—1	175.4	—172.7	17	5	—1	32.4	—31.3	8	2	—2	156.7	134.4
12	6	0	184.4	—189.7	6	6	1		—21.9	18	2	1	272.7	274.7	8	4	2	144.3	122.0
13	1	0	440.0	433.3	6	6	—1	115.6	96.5	18	2	—1	234.2	234.1	8	4	—2	138.5	—121.1
13	3	0	73.8	—61.6	6	8	1	51.6	—39.6	18	4	1	177.0	203.2	8	6	2	117.2	103.3
13	5	0	331.3	—354.9	6	8	—1	152.6	166.7	19	1	1	42.2	41.7	8	6	—2	176.1	—175.7
13	7	0	178.7	—190.8	7	1	1	221.7	—208.9	19	1	—1	128.6	111.9	9	1	2	378.7	—368.2
14	0	0	300.1	295.0	7	1	—1	95.3	—76.6	19	3	1	67.8	76.9	9	1	—2	201.2	—179.9
14	2	0	132.3	113.9	7	3	1	300.3	—311.4	19	3	—1	195.6	198.5	9	3	2	69.8	60.6
14	4	0	151.2	—136.9	7	3	—1	67.8	—60.6	20	2	1	127.5	—137.8	9	3	—2	120.5	72.2
14	6	0	150.3	—156.8	7	5	1	44.7	—13.5	20	2	—1	90.2	—85.9	9	5	2	377.6	391.2
15	1	0	156.8	—144.0	7	5	—1	78.7	52.1	21	1	1	105.1	—129.4	9	5	—2	147.1	147.3
15	3	0	44.6	48.9	7	7	1	184.4	182.8	21	1	—1	169.7	—160.3	9	7	2	198.8	204.6
15	5	0	109.9	127.6	7	7	—1		—25.1	21	3	—1	203.7	—280.9	9	7	—2	81.6	64.7
16	0	0	312.6	—285.2	8	2	1	320.0	—307.2	0	0	2	354.8	347.8	10	0	2	318.8	—338.9
16	2	0	94.6	—89.1	8	2	—1	574.4	—618.0	0	2	2	55.6	48.6	10	0	—2	613.3	—643.1
16	4	0	155.8	161.6	8	4	1	217.7	—228.9	0	4	2	222.2	—228.6	10	2	2	165.3	—130.4
16	6	0	178.4	212.8	8	4	—1	370.9	367.4	0	6	2	272.2	—274.6	10	2	—2	221.3	—198.3
17	1	0	211.0	—175.3	8	6	1	96.5	88.0	0	8	2		—11.6	10	4	2	232.9	250.4
17	3	0	44.2	43.8	8	6	—1	149.9	—137.6	1	1	2	181.0	164.4	10	4	—2	315.2	316.4
17	5	0	149.6	189.4	8	8	1	205.8	226.5	1	1	—2	299.2	331.5	10	6	2	262.9	261.3
18	0	0		20.8	8	8	—1	313.8	—320.4	1	3	2		—16.7	10	6	—2	399.2	392.1
18	2	0		25.0	9	1	1	162.9	—145.9	1	3	—2	161.6	—174.8					

H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
11	1	2	58.0	48.2	2	4	3	233.3	-200.9	13	1	-3	114.6	97.8	6	0	-4	88.2	61.8
11	1	-2	251.6	-243.8	2	4	-3	282.4	245.6	13	3	3	235.3	-223.2	6	2	4	161.4	149.7
11	3	2		11.2	2	6	3	132.0	104.9	13	3	-3	209.6	194.1	6	2	-4	85.3	80.3
11	3	-2	54.1	44.4	2	6	-3	109.7	-88.8	13	5	3		-14.5	6	4	4	276.2	-278.7
11	5	2	26.9	-27.1	2	8	3	155.9	173.4	13	5	-3		-36.9	6	4	-4	155.7	-103.8
11	5	-2	239.0	231.7	2	8	-3	217.2	-229.7	14	2	3	356.9	-346.4	6	6	4	314.7	-323.5
11	7	2	49.7	-47.8	3	1	3	134.4	128.3	14	2	-3	95.8	-95.7	6	6	-4	78.2	-64.6
11	7	-2	142.4	146.0	3	1	-3	208.1	-210.1	14	4	3	253.7	-258.2	7	1	4	75.7	58.6
12	0	2	346.8	318.6	3	3	3	257.1	253.2	14	4	-3	124.0	108.2	7	1	-4	416.0	391.9
12	0	-2		18.1	3	3	-3	324.2	-339.3	14	6	-3		-1.1	7	3	4		-9.9
12	2	2	79.5	65.6	3	5	3	110.0	90.5	15	1	3	107.9	-87.0	7	3	-4	88.5	-73.6
12	2	-2	73.8	62.1	3	5	-3	37.2	52.6	15	1	-3	175.7	-171.2	7	5	4	80.6	-75.8
12	4	2	180.8	-181.3	3	7	3	115.5	-106.1	15	3	3	155.1	-139.2	7	5	-4	429.6	-428.6
12	4	-2		-36.8	3	7	-3	211.4	-207.3	15	3	-3	267.2	-299.9	7	7	4	40.6	-36.5
12	6	2	211.8	-213.6	4	2	3	377.9	375.1	15	5	3	33.8	-37.3	7	7	-4	193.1	-207.1
12	6	-2	73.3	-61.3	4	2	-3	107.7	102.3	15	5	-3	59.9	57.3	8	0	4	267.4	-245.9
13	1	2	230.9	224.5	4	4	3	251.6	241.0	16	2	3	105.3	90.8	8	0	-4	439.3	390.8
13	1	-2	269.8	265.3	4	4	-3		-25.5	16	2	-3	249.5	-230.9	8	2	4	114.6	-106.7
13	3	2	75.0	-83.8	4	6	3	104.7	-87.6	16	4	3	96.2	98.2	8	2	-4	139.9	117.7
13	3	-2	74.2	-61.3	4	6	-3		27.8	16	4	-3	182.5	174.6	8	4	4	150.5	125.1
13	5	2	229.3	-236.6	4	8	3	210.8	-228.4	17	1	3	123.3	127.7	8	4	-4	280.4	-282.1
13	5	-2	296.5	-292.7	4	8	-3		-7.9	17	1	-3		31.7	8	6	4	195.5	181.8
13	7	-2	135.0	-134.9	5	1	3	205.0	208.4	17	3	3	223.2	244.0	8	6	-4	291.6	-284.6
14	0	2	77.6	53.3	5	1	-3	202.7	202.6	17	3	-3		-2.0	9	1	4	297.2	-308.7
14	0	-2	262.1	248.3	5	3	3	250.3	244.1	18	2	3	157.0	167.2	9	1	-4	48.5	-51.7
14	2	2	43.4	26.9	5	3	-3	409.8	431.8	18	2	-3	327.5	318.8	9	3	4	42.1	25.0
14	2	-2	78.3	69.5	5	5	3		33.8	18	4	-3	32.4	-211.9	9	3	-4		-13.1
14	4	2	55.2	-35.0	5	5	-3	116.6	-87.3	19	1	3	35.6	-33.4	9	5	4	247.7	266.3
14	4	-2	189.4	-196.3	5	7	3	186.0	-175.6	19	1	-3	162.5	142.5	9	5	-4		14.0
14	6	2	64.9	-73.8	5	7	-3	257.2	258.5	19	3	-3	241.9	248.5	9	7	-4	43.5	20.3
14	6	-2	202.9	-204.9	6	2	3	91.4	-65.9	20	2	-3	64.5	55.1	10	0	4	209.5	-176.7
15	1	2	252.2	-213.0	6	2	-3	521.2	499.4	21	1	-3	87.7	-83.7	10	0	-4	322.7	-290.1
15	1	-2	44.1	33.2	6	4	3		37.4	21	3	-3	121.1	-157.1	10	2	4	119.6	-95.9
15	3	2	44.7	41.2	6	4	-3	395.6	-371.7	0	0	4	303.5	300.3	10	2	-4	78.9	-72.0
15	3	-2		-13.5	6	6	3		14.2	0	2	4	178.2	180.9	10	4	4	127.4	99.4
15	5	2	200.7	201.0	6	6	-3	172.9	148.8	0	4	4	207.3	-195.3	10	4	-4	184.6	173.2
15	5	-2	71.1	-60.5	6	8	3	303.1	307.4	0	6	4	232.5	-222.4	10	6	4	103.1	100.9
16	0	2	408.8	-389.3	6	8	-3	238.1	-233.6	0	8	4		6.4	10	6	-4	128.7	186.7
16	0	-2	382.0	-363.9	7	1	3	454.0	-459.5	1	1	4	146.7	-143.7	11	1	4	170.5	149.7
16	2	2	168.9	-165.5	7	1	-3		-0.1	1	1	-4	511.2	576.6	11	1	-4	336.3	-305.6
16	2	-2	127.9	-102.6	7	3	3	65.0	74.4	1	3	4		30.7	11	3	4	37.3	-38.5
16	4	2	208.0	212.0	7	3	-3	101.0	-75.9	1	3	-4	68.8	-62.8	11	3	-4	101.2	84.4
16	4	-2	210.5	206.9	7	5	3		4.3	1	5	4	149.2	122.4	11	5	4	135.8	-124.8
16	6	-2	224.3	219.5	7	5	-3	236.5	242.2	1	5	-4	478.8	-448.0	11	5	-4	287.1	293.6
17	1	2	127.9	-112.8	7	7	3		-12.4	1	7	4	100.6	97.1	11	7	-4	140.0	154.4
17	1	-2	335.1	-309.0	7	7	-3	377.5	-374.9	1	7	-4	230.8	-225.8	12	0	4	391.0	447.0
17	3	2		6.7	8	2	3	230.8	-250.8	2	0	4	325.0	-307.2	12	0	-4	118.7	-106.3
17	3	-2	76.3	58.2	8	2	-3	298.2	-290.7	2	0	-4	303.6	323.2	12	2	4	164.3	152.4
17	5	-2	263.4	286.8	8	4	3	183.4	150.5	2	2	4	104.8	-91.2	12	2	-4		-26.0
18	0	2	167.2	145.1	8	4	-3	127.0	118.4	2	2	-4	117.2	109.1	12	4	4	221.4	-231.3
18	0	-2	129.0	-113.4	8	6	3	112.9	-95.1	2	4	4	211.0	195.6	12	4	-4		25.1
18	2	2	61.2	50.5	8	6	-3		-7.6	2	4	-4	162.9	-128.1	12	6	-4	99.3	105.2
18	2	-2		-32.2	9	1	3	223.9	-229.1	2	6	4	277.6	265.8	13	1	4	229.3	195.3
18	4	2	76.4	-82.0	9	1	-3		10.9	2	6	-4	166.4	-140.5	13	1	-4	240.7	208.8
19	1	2	186.5	203.4	9	3	3	390.7	-361.2	3	1	4	270.7	-282.9	13	3	4	28.7	-30.6
19	1	-2	168.2	146.0	9	3	-3		-0.7	3	1	-4	245.3	-253.2	13	3	-4		-25.8
19	3	2	27.7	-36.6	9	5	3	35.4	43.2	3	3	4	108.1	106.2	13	5	4	154.4	-177.6
19	3	-2	24.0	-20.5	9	5	-3		-15.3	3	3	-4	68.9	59.4	13	5	-4	202.9	-222.9
20	0	2	154.9	172.0	9	7	3	209.9	-206.3	3	5	4	302.9	286.0	14	0	4	135.2	-104.1
20	0	-2	257.4	241.0	9	7	-3	214.7	195.3	3	5	-4	215.5	181.4	14	0	-4	511.0	475.5
20	2	2	70.8	73.3	10	2	3	164.4	-153.5	3	7	4	135.5	126.5	14	2	4	61.4	-41.4
20	2	-2	105.9	104.3	10	2	-3	171.5	155.6	3	7	-4	113.6	95.6	14	2	-4	218.5	204.8
21	1	-2	178.2	168.1	10	4	3	146.7	157.7	4	0	4		18.1	14	4	4	74.3	62.8
21	3	-2	11.3	-15.3	10	4	-3	88.8	-81.3	4	0	-4	445.8	-437.2	14	4	-4	250.3	-256.9
22	0	-2	103.4	-119.5	10	6	3		-19.9	4	2	4		-19.3	14	6	-4	259.8	-314.3
0	2	3	316.3	-313.2	11	1	3	187.2	184.7	4	2	-4	148.3	-138.5	15	1	4	188.5	-176.8
0	4	3	210.6	-207.9	11	3	3	306.0	294.0	4	4	4		14.5	15	1	-4	181.4	169.2
0	6	3	139.6	122.4	11	3	-3	196.4	190.9	4	4	-4	203.6	184.0	15	3	4	36.7	34.5
0	8	3	178.4	176.2	11	5	3	26.4	45.1	4	6	4		2.7	15	3	-4		-12.7
1	1	3	234.6	-248.8	11	5	-3	31.9	-23.9	4	6	-4	264.3	249.0	15	5	4	120.5	-111.9
1	1	-3	163.0	-170.5	12	1	3	121.9	132.3	5	1	4	335.6	339.9	16	0	4	179.8	-165.6
1	3	3	569.0	-576.9	12	2	3	166.8	140.7	5	1	-4	265.4	-319.9	16	0	-4	154.0	-135.8
1	3	-3	199.3	-163.1	12	2	-3	457.3	486.8	5	3	4	121.1	-117.4	16	2	4	82.6	-63.8
1	5	3	148.6	-122.2	12	4	3	121.4	108.0	5	3	-4	53.8	40.2	16	2	-4	52.9	-50.4
1	5	-3	129.3	96.8	12	4	-3	366.9	-367.4	5	5	4	357.0	-329.4	16	4	-4	103.2	97.0
1	7	3	310.2	305.3	12	6	3		-13.9	5	5	-4	283.5	248.2	17	1	4		-4.2
1	7	-3	87.9	-76.1	12	6	-3	136.4	127.8	5	7	4	155.4	-157.3	17	1	-4	284.0	-259.8
2	2	3	286.8	-295.3	13	1	3	150.6	-135.3	5	7	-4	169.4	156.4	17	3	4		11.0
2	2	-3	398.0	-437.3						6	0	4	406.7	427.8	17	3	-4	62.6	58.0

H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
17	5	—4	170.3	231.5	1	1	6	241.3	—247.7	1	3	7	214.3	—209.1	7	1	8	142.8	—139.9
18	0	4	327.1	250.8	1	1	—6	228.7	237.4	1	3	—7	190.2	161.7	7	1	—8	112.3	89.2
18	0	—4	208.9	—191.7	1	3	6		24.6	2	2	7	148.5	122.6	7	3	8	20.9	9.1
18	2	4	31.0	74.0	1	3	—6		—35.0	2	2	—7	122.1	—111.1	7	3	—8	48.0	—41.5
18	2	—4	88.1	—77.4	2	0	6	457.3	—530.7	3	1	7	165.4	169.1	8	0	8	226.0	—265.5
19	1	—4	45.3	37.6	2	0	—6	254.8	251.1	3	1	—7	168.0	—179.3	8	0	—8	384.3	376.7
19	3	—4	21.1	—12.7	2	2	6	191.9	—198.1	3	3	7	262.8	265.1	8	2	8	88.8	—103.7
20	0	—4	341.5	320.5	2	2	—6	102.8	93.0	3	3	—7	313.8	—304.9	8	2	—8	154.9	151.5
20	2	—4	120.1	124.2	3	1	6	181.9	—176.7	4	2	7	188.8	185.0	9	1	8	117.7	—115.5
21	1	—4	167.4	172.7	3	1	—6		27.9	4	2	—7	235.2	—221.4	9	1	—8	218.0	188.7
0	2	5	288.9	—294.6	3	3	6	51.1	37.3	5	1	7		3.5	9	3	—8	68.8	—44.8
0	4	5	252.8	—236.8	3	3	—6		—8.9	5	1	—7	102.5	79.9	10	0	8	93.5	93.9
0	6	5	108.3	96.2	4	0	6	199.8	178.5	5	3	—7		—1.2	10	0	—8		—24.2
1	1	5	156.5	—166.8	4	0	—6	413.2	—429.5	5	3	—7	76.0	57.2	10	2	—8	73.3	—40.6
1	1	—5		30.5	4	2	6	78.0	73.3	6	2	7	261.1	—261.7	11	1	—8	186.6	—175.7
1	3	5	274.3	—295.9	4	2	—6	154.5	—128.2	6	2	—7	370.6	365.3	11	3	—8	46.4	42.9
1	3	—5	121.2	105.8	5	1	6	266.5	276.6	7	1	7	197.9	—181.4	12	0	—8	260.7	—233.5
2	2	5	111.5	—93.5	5	1	—6	211.3	—328.8	7	1	—7	205.1	189.9	12	2	—8	95.1	—86.7
2	2	—5	316.9	—346.2	5	3	6	40.8	—35.5	7	3	7	302.3	—297.2	13	1	—8	44.1	34.1
3	1	5	148.1	174.2	5	3	—6	104.7	94.4	7	3	—7	334.1	301.6	13	3	—8		—3.5
3	1	—5	270.0	—286.4	6	0	6	211.6	187.3	8	2	7	39.7	—50.5	14	0	—8	259.5	252.3
3	3	5	290.5	274.1	6	0	—6		—43.9	8	2	—7		11.9	14	2	—8	93.0	85.9
3	3	—5	421.6	—452.4	6	2	6	127.3	110.8	9	1	7	100.9	100.0	15	1	—8	253.2	251.7
4	2	5	447.5	481.3	6	2	—6		6.0	9	1	—7	133.7	—121.8	15	3	—8	33.6	—32.6
4	2	—5	129.4	—156.9	7	1	6	66.6	—55.2	9	3	7	157.2	149.9	16	0	—8	121.7	129.0
5	1	5	120.8	103.4	7	1	—6	208.7	185.5	9	3	—7	328.0	—219.5	16	2	—8	34.4	46.7
5	1	—5	193.8	181.8	7	3	6		16.3	10	2	7	202.0	217.5	17	1	—8	85.7	—100.6
5	3	5	128.6	111.1	7	3	—6		—16.4	10	2	—7	248.1	—243.0	0	2	9	197.5	—209.7
5	3	—5	220.7	215.2	8	0	6	330.0	—314.3	11	1	7	83.1	70.1	0	4	9	126.4	—136.6
6	2	5	211.7	—198.3	8	0	—6	370.9	328.5	11	1	—7	85.2	—65.8	1	1	9	77.0	—59.3
6	2	—5	336.5	309.9	8	2	6	121.3	—108.4	11	3	7	101.8	105.6	1	1	—9	136.9	127.7
7	1	5	137.9	—135.6	8	2	—6	165.5	157.2	11	3	—7	166.3	—148.9	1	3	9	67.5	—72.7
7	1	—5	144.6	124.3	9	1	6	258.4	—233.7	12	2	7	118.3	—130.7	1	3	—9	196.2	194.0
7	3	5	307.3	—289.1	9	1	—6	232.9	215.2	12	2	—7	229.9	217.9	2	2	9	149.5	161.6
7	3	—5	240.4	229.7	9	3	6	88.7	83.7	13	1	7	110.6	—137.6	2	2	—9		4.2
8	2	5	202.2	—182.6	9	3	—6		—21.5	13	1	—7	241.1	223.3	3	1	9	173.9	171.7
8	2	—5	151.6	—134.7	10	0	6		5.9	13	3	—7	347.2	350.0	3	1	—9	159.6	—139.8
9	1	5	67.2	59.8	10	0	—6	246.6	—221.5	14	2	—7	136.3	125.7	3	3	9	288.0	—297.9
9	1	—5	288.9	—269.8	10	2	6		4.9	15	1	—7	94.0	—71.3	3	3	—9	241.4	—244.0
9	3	5	133.6	115.0	10	2	—6		—87.3	15	3	—7	121.8	—124.5	4	2	9	85.5	100.3
9	3	—5	453.9	—462.8	11	1	6	188.9	182.3	16	2	—7	188.7	—203.0	4	2	—9	257.8	—268.3
10	2	5	375.3	377.4	11	1	—6	404.1	—382.5	17	1	—7	128.5	—125.6	5	1	9	73.8	—72.8
10	2	—5	349.9	—314.2	11	3	6	61.0	—52.0	17	3	—7	189.3	—208.8	5	1	—9	46.7	—41.2
11	1	5	185.5	158.5	11	3	—6	75.6	62.2	18	2	—7	49.8	60.5	5	3	9	92.1	—77.7
11	1	—5	146.4	111.3	12	0	6	197.8	208.0	19	1	—7	157.5	168.3	6	2	9	82.7	—181.2
11	3	5	237.9	215.6	12	0	—6	295.6	—250.3	0	0	8	95.5	—52.7	6	2	—9	165.8	159.8
11	3	—5	115.3	97.4	12	2	6	88.5	87.4	0	2	8	41.2	—21.8	7	1	—9	156.2	152.3
12	2	5	77.0	—51.2	12	2	—6	118.8	—106.4	0	4	8	42.4	26.5	7	3	—9	207.0	225.9
12	2	—5	259.8	239.5	13	1	6	75.0	67.9	1	1	8	186.0	—178.2	9	1	—9	96.8	—73.9
13	1	5	117.4	—107.4	13	1	—6	119.8	92.5	1	1	—8	229.6	201.5	9	3	—9	114.8	—119.9
13	1	—5	175.6	161.6	13	3	6	41.4	—26.1	1	3	8	71.7	62.9	10	2	—9	252.6	—296.1
13	3	5	217.0	—206.7	13	3	—6		—1.2	1	3	—8	38.0	—41.1	11	1	—9	120.4	—114.0
13	3	—5	313.8	268.3	14	0	6	151.6	—161.5	2	0	8	214.5	—233.6	11	3	—9	176.5	—177.2
14	2	5	187.8	—194.6	14	2	6	287.1	245.9	2	0	—8	376.4	377.4	12	2	—9	75.2	80.0
14	2	—5	80.3	66.7	14	2	—6	59.2	—70.4	2	2	8	88.5	—71.7	13	1	—9	117.5	126.6
15	1	5	43.8	—29.4	15	1	6	104.8	101.0	2	2	—8	178.2	167.4	0	0	10	131.4	—154.9
15	1	—5	167.0	—147.6	15	1	—6	255.8	—255.1	3	1	8		—24.5	1	1	10	254.2	—253.3
15	3	5	41.0	—45.8	15	3	6	213.4	192.2	3	1	—8	128.5	110.9	1	1	—10	84.1	92.8
15	3	—5	274.9	—265.4	15	3	—6	66.3	—60.3	3	3	8		—0.7	2	0	—10	177.5	211.5
16	2	5	169.1	175.8	16	0	—6		—7.1	3	3	—8		—16.9	2	2	10	57.8	87.1
16	2	—5	350.1	—343.8	16	2	—6	46.3	—27.6	4	0	8	230.1	239.5	2	2	—10	127.8	139.4
17	1	5	105.9	149.7	17	1	—6	242.4	—232.4	4	0	—8	180.4	—165.2	4	0	—10		—6.5
17	1	—5		—23.3	17	3	—6	56.6	51.3	4	2	8	94.3	98.4	4	2	—10		—14.6
17	3	—5	90.3	—81.5	18	0	—6	321.5	—301.4	4	2	—8	120.3	—81.4	5	1	—10	201.2	—213.3
18	2	—5	124.7	128.0	18	2	—6	106.9	—112.5	5	1	8	262.5	252.8	6	0	—10	210.7	—223.3
19	1	—5	162.1	151.9	19	1	—6		—10.6	5	1	—8	259.9	—253.9	6	2	10	66.3	—84.8
19	3	—5	213.3	240.7	19	3	—6		—5.6	5	3	8	42.1	—33.3	7	1	—10		14.7
20	2	—5	111.3	136.1	20	0	—6	134.0	154.2	5	3	—8	38.6	34.1	8	0	—10	149.0	164.4
21	1	—5	49.8	—52.8	0	2	7	380.8	—370.7	6	0	8	76.7	93.1	9	1	—10	39.7	52.9
0	0	6	129.3	107.3	0	4	7	291.5	—274.5	6	0	—8	257.1	—225.7	9	3	—10	139.3	177.0
0	2	6	108.4	84.6	0	6	7	85.2	94.5	6	2	8	50.9	47.1	10	0	—10	95.2	119.4
0	4	6	131.4	—104.9	1	1	7	175.8	—166.5	6	2	—8	114.7	—110.4					
0	6	6	105.7	—100.6	1	1	—7	112.5	97.8										

temperature motions. With both possibilities, the initial refinement proceeded normally in the C2/c space group. The least squares refinement using ORFLS program[4] was based on a unit weighing system. The coordinates and isotropic temperature factors were refined until the shifts in the atomic coordinates were less than standard deviations. In the course of this refinement the R index decreased to 10%. With anisotropic temperature factors for Th, K and P atoms the R index decreased to 9.2% (including unobserved reflections). When the calculated structure factors are based on the thorium atom only, the value for the R index is 21%. A high individual temperature factor (B = 6.8 (± 0.7) Å²) for the potassium atom was obtained during the cycles of refinement with isotropic temperature factors. When anisotropic thermal parameters were introduced, the potassium atom thermal parameters, especially β_{33}, were still high and physically quite unlikely. They indicated that further investigation is necessary for the potassium atom location. But all attempts to refine the structure in the alternative non-centric Cc group or to find the occupancy factor for the potassium atom in C2/c group led to no improvement. So we conclude that the C2/c space group is correct and that the potassium atoms have large temperature motions. It is also probable that undetected departures from crystal sphericity have caused the absorption correction to be in error (μ is large). That resulted in physically too high potassium thermal parameters.

The atomic coordinates and temperature factors are listed in Table I. The observed and calculated structure factors are listed in Table II. The atomic scattering factors used in these calculations were from International Tables for X-ray Crystallography (1962)[5]. The real, but not the imaginary part of the anomalous dispersion correction has been applied. Bond distances and angles were computed using the Busing, Martin and Levy, ORFFE, Fortran function and error program (1964)[6]. The experimental work and the determination of the thorium atom coordinates were done at Institute Ruđer Bošković. The work was continued at Washington State University, where one of the authors (B. M.) had a postdoctoral fellowship. The three-dimensional Fourier synthesis, the refinement cycles and the calculation of bond lengths and angles were carried out on the IBM 709 computer at the Washington State University Computing Center.

<div align="center">DESCRIPTION AND DISCUSSION OF THE STRUCTURE</div>

The numbering of the atoms, which is the same in all figures and tables, is explained and listed in Table III. The bond distances and angles are listed in Table IV. The projection along [010] is shown in Fig. 1.

All PO₄ tetrahedra are discrete groups, that is, no oxygen atom is common to two phosphorus atoms. Each oxygen atom, in addition to being bonded to the phosphorus atom, is also attached to the thorium atom, because the distances between the thorium atom and the nine nearest atoms range from 2.26 to 2.66 Å, as shown in Table IV and Fig. 2, where thorium-oxygen distances are represented by straight lines. The next closest oxygen atom O(10.66) is 3.77 Å from the thorium atom Th (1.00). So it is reasonable to assign thorium the coordination number nine. Such a polyhedron is shown in Fig. 3 (a) and (b). The oxygen atoms which belong to this polyhedron are connected in the picture by straight and broken lines in two different ways and indicate two possibilities of drawing the Th-polyhedron. The coordination of the thorium atom involves nine oxygen atoms from seven PO₄ groups (Fig. 2). Each Th-polyhedron shares three edges with three neighboring polyhedra because of the nine oxygen atoms surrounding the thorium atom, six belong also to the other three Th-polyhedra, e. g. in Fig. 4 the Th (1.00) polyhedron shares the edges defined by the oxygen atoms O(5.00)—O(7.00), O(5.44)—O(7.44), and O(9.00)——O(9.66) with the neighboring polyhedra which belong to the thorium atoms Th (1.04), Th (1.44) and Th (1.06). These polyhedra with sharing edges are related by symmetry operations of the c-glide plane and the centre of

TABLE III

Numbering of Atoms

Atoms are designated by a three place number which identifies the atom, the cell translation and the symmetry transformation. Only those atoms are numbered which are mentioned in the tables or figures.

The atoms	The coordinates
Th (1.10); O (6.10)	x, y + 1, z.
Th (1.01); P (3.01); O (6.01); O (7.01); O (8.01); O (9.01); O (10.01)	1/2 − x, 1/2 + y, 1/2 − z.
O (10.21)	1/2 − x, 1/2 + y − 1, 1/2 − z.
Th (1.02); P (3.02); P (4.02); O (5.02); O (6.02); O (7.02); O (9.02)	−x, −y, −z.
O (10.53)	1/2 + x − 1, 1/2 − y, 1/2 + z − 1.
O (8.73)	1/2 + x − 1, 1/2 − y − 1, 1/2 + z − 1.
Th (1.04)	x, −y, 1/2 + z.
Th (1.44); O (5.44); O (7.44)	x, −y, 1/2 + z − 1.
Th (1.05); O (5.05); O (6.05); O (7.05)	−x, y, 1/2 − z.
Th (1.06); O (9.06); O (10.06)	1/2 − x, 1/2 + y − 1, 1/2 + z − 1.
O (9.37); O (10.37)	1/2 + x − 1,

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TABLE IV

Interatomic distances and angles in $KTh_2(PO_4)_3$

Standard errors are given in parenthesis

A	B	C	Distances (Å)		Angles (degrees)
			A — B	A — C	A — B — C
Within Th-polyhedron					
O(6.02)	Th(1.00)	O(5.44)	2.48(0.03)	2.43(0.04)**	56+
O(7.00)	Th(1.00)	O(9.00)	2.54(0.02)	2.46(0.04)**	58
O(5.44)	Th(1.00)	O(7.44)	2.66(0.03)	2.72(0.03)	64
O(5.00)	Th(1.00)	O(7.00)	2.52(0.03)	2.72(0.03)	65
O(9.06)	Th(1.00)	O(9.00)	2.41(0.03)	2.72(0.06)	67
O(9.00)	Th(1.00)	O(7.44)	2.54(0.03)	2.80(0.04)	68
O(7.44)	Th(1.00)	O(9.06)	2.45(0.02)	2.76(0.04)	69
O(8.01)	Th(1.00)	O(9.06)	2.38(0.03)	2.73(0.04)	69
O(10.21)	Th(1.00)	O(5.00)	2.26(0.04)	2.78(0.05)	71
O(5.00)	Th(1.00)	O(6.02)	*	2.93(0.04)	72
O(8.01)	Th(1.00)	O(6.02)	*	2.86(0.04)	72
O(7.00)	Th(1.00)	O(10.21)	*	2.88(0.05)	74
O(10.21)	Th(1.00)	O(7.44)	*	2.91(0.05)	76
O(8.01)	Th(1.00)	O(5.00)	*	3.03(0.04)	76
O(7.00)	Th(1.00)	O(8.01)	*	3.09(0.04)	78
O(10.21)	Th(1.00)	O(5.44)	*	3.21(0.05)	81
O(8.01)	Th(1.00)	O(9.00)	*	3.32(0.04)	85
O(5.44)	Th(1.00)	O(9.06)	*	3.47(0.04)	86
O(6.02)	Th(1.00)	O(9.06)	*	3.34(0.04)	86
O(10.21)	Th(1.00)	O(9.00)	*	3.64(0.05)	99
O(5.00)	Th(1.00)	O(5.44)	*	4.09(0.01)	104
O(7.00)	Th(1.00)	O(7.44)	*	4.12(0.01)	111
O(10.21)	Th(1.00)	O(6.02)	*	3.93(0.05)	112
O(6.02)	Th(1.00)	O(7.44)	*	4.19(0.04)	117
O(7.00)	Th(1.00)	O(9.06)	*	4.22(0.04)	117
O(5.00)	Th(1.00)	O(9.00)	*	4.44(0.04)	122
O(8.01)	Th(1.00)	O(5.44)	*	4.45(0.04)	124
O(5.44)	Th(1.00)	O(9.00)	*	4.74(0.04)	131
O(7.00)	Th(1.00)	O(6.02)	*	4.58(0.04)	132
O(8.01)	Th(1.00)	O(7.44)	*	4.49(0.04)	137
O(10.21)	Th(1.00)	O(8.01)	*	4.40(0.05)	143
O(5.00)	Th(1.00)	O(9.06)	*	4.69(0.04)	144
O(10.21)	Th(1.00)	O(9.06)	*	4.46(0.05)	145
O(5.00)	Th(1.00)	O(7.44)	*	4.76(0.03)	147
O(6.02)	Th(1.00)	O(9.00)	*	4.84(0.04)	149
O(7.00)	Th(1.00)	O(5.44)	*	5.07(0.03)	154
Within the phosphate groups					
O(6.00)	P(4.00)	O(5.05)	1.55(0.03)	2.43(0.04)	106 (2)
O(6.05)	P(4.00)	O(5.00)			
O(5.00)	P(4.00)	O(6.00)	1.49(0.03)	2.47(0.04)	109 (2)
O(5.05)	P(4.00)	O(6.05)			
O(5.00)	P(4.00)	O(5.05)	*	2.44(0.05)	110 (2)
O(6.00)	P(4.00)	O(6.05)	*	2.63(0.06)	117 (3)
O(7.00)	P(3.00)	O(9.00)	1.55(0.02)	2.46(0.04)	103 (1)
O(9.00)	P(3.00)	O(10.00)	1.58(0.03)	2.46(0.05)	104 (2)
O(8.00)	P(3.00)	O(7.00)	1.52(0.03)	2.51(0.04)	110 (1)
O(8.00)	P(3.00)	O(9.00)	*	2.55(0.04)	110 (2)
O(10.00)	P(3.00)	O(7.00)	1.54(0.04)	2.58(0.04)	113 (2)
O(8.00)	P(3.00)	O(10.00)	*	2.59(0.05)	116 (2)

(+) With standard error of 1⁰; * Already mentioned; ** Also within phosphate group.

Potassium—oxygen distances $\leqslant 3.61$ Å

K(200)	O(8.01)	2.74(0.03)
K(200)	O(5.00)	2.84(0.03)
K(200)	O(6.10)	2.94(0.04)
K(200)	O(6.02)	3.09(0.03)
K(200)	O(10.53)	3.61(0.04)

The shortest Th...O distance which do not belong to Th-polyhedron (in Å)

Th(1.00)	O(10.06)	3.77(0.04)

The shortest P...O distances which do not belong to the phosphate groups (in Å)

P(4.00)	O(10.37)	3.37(0.04)
P(3.00)	O(7.01)	3.38(0.03)

The shortest O...O distances which do not belong to a phosphate group or a Th-polyhedron (in Å)

O(10.00)	O(6.01)	3.08(0.05)
O(6.00)	O(10.21)	

The shortest distances between the other atoms (in Å)

Th(1.00)	P(4.02)	3.18(0.01)
K(2.00)	P(4.00)	3.42(0.03)
Th(1.00)	K(2.00)	4.09(0.01)

symmetry at ¼ or ¾ a axis and form infinite sheets parallel to the b and c axes. The sheets are not comparable with those of the silicates; here the sheet indicates the close-packed assemblage of thorium, oxygen and phosphorus atoms which are in general positions. The sheets of polyhedra are joined together by phosphate groups whose phosphorus atoms are in special position, on two-fold axes. These phosphate groups act as bridges, and form a three-dimensional network. There are two types of phosphate group coordinations: bidentate cyclic and bridging. PO_4 oxygen atoms with phosphorus on the two-fold axis belong to four Th-polyhedra, to two of them as bidentate cyclic. Those oxygens, whose phosphorus atom is in a general position, belong to five Th-polyhedra, to one of them as bidentate cyclic.

The packing of the thorium atoms and the phosphate groups is very close except along a two-fold axis where holes between PO_4 tetrahedra exist. The potassium atoms are located in these holes on two-fold axes. The nearest neighbors of the potassium atoms are oxygen atoms. Their distances range from 2.74 to 3.09 Å and are equal to or greater than the sum of the ionic radii. The resulting eightfold coordination *e. g.* around K(2.00) may be considered to arise from oxygens O(8.01), O(5.00), O(6.10), O(6.02) and their pairs
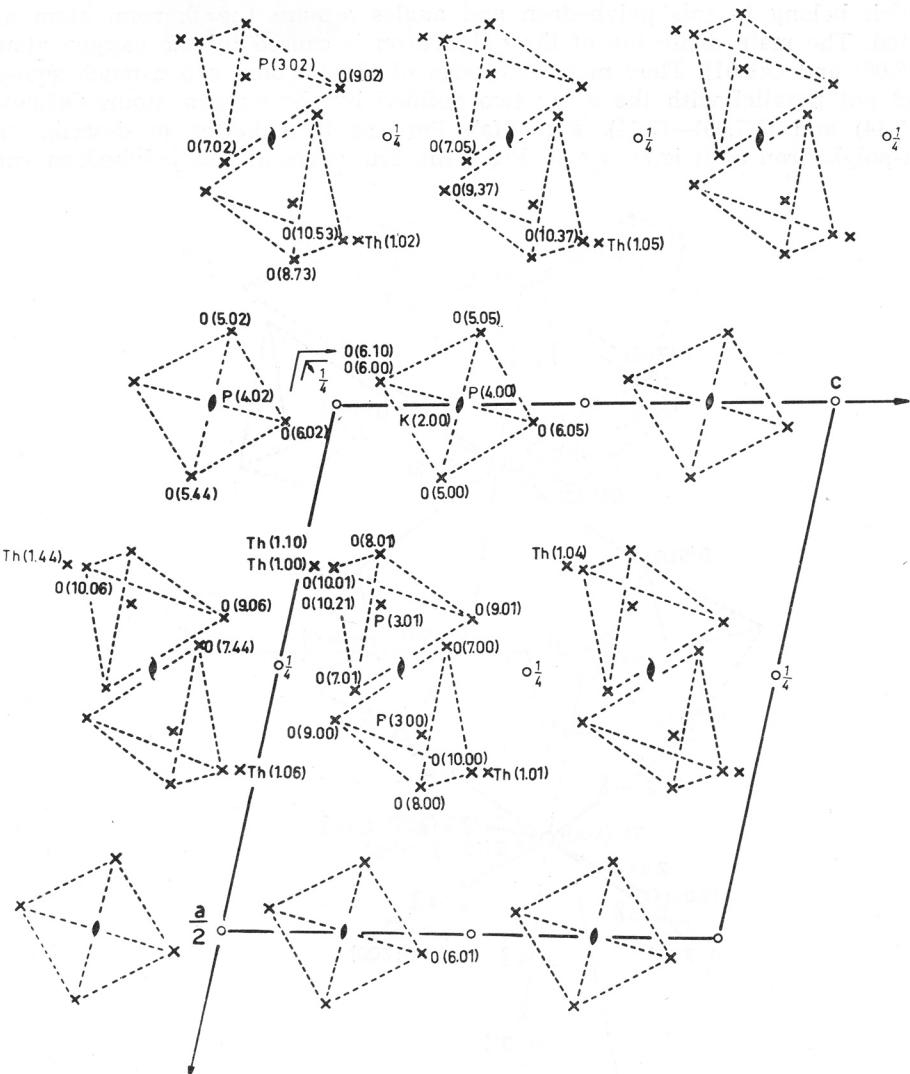
Fig. 1. Projection of the structure of $KTh_2(PO_4)_3$ on a plane normal to [010]. Oxygen atoms from the phosphate groups are connected by broken lines. Only those atoms are numbered which are mentioned in the text or tables.

related by the symmetry of the two-fold axis. On the basis of interatomic distances the compound can be described as potassium trisphosphatodithorate defined by the formula $K[Th_2(PO_4)_3]$. The close packing of all atoms with some short Th—O distances, among which is one very short, makes the $KTh_2(PO_4)_3$ compound very stable.

A trigonal prism with additional ligands outside each of the rectangular faces is the presumable polyhedron in stereochemistry for coordination nine. The Th-polyhedron in $KTh_2(PO_4)_3$ is very distorted. Its geometry can be best understood from Table IV where all distances between the oxygen atoms

which belong to this polyhedron and angles around the thorium atom are listed. The main distortion of the polyhedron is caused by the oxygen atoms O(9.06) and O(8.01). They make one edge of the trigonal prism much shorter and not parallel with the other two defined by the oxygen atoms O(5.00)—O(5.44) and O(7.00)—(7.44), Fig. 3 (a). Perhaps it is better to describe the Th-polyhedron as it is shown in Fig. 3 (b). The edges of this polyhedron vary
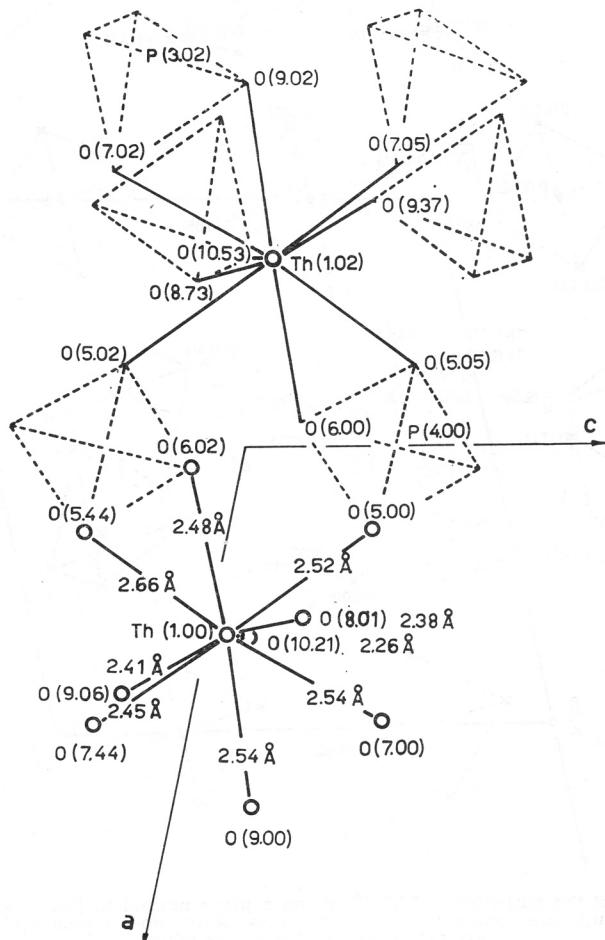
Fig. 2. A view down two KTh₂(PO₄)₃ groups related by the center of symmetry. Thorium-oxygen atoms are connected by straight lines. Projections of the seven phosphate groups whose oxygen atoms belong to the Th (1.02) polyhedron are represented by broken lines. Oxygen atoms O (10.53) and O (8.73) belong to two different phosphate groups translated by the cell along the b axis.

in length from 2.43 to 3.93 Å including two shorter distances which are part of the phosphate groups adjoining the Th-polyhedron. The Th-polyhedron represented in this way is a pentagon with two ligands on both sides which belong to two phosphate groups. It has some similarity to a pentagonal bipyramid, the polyhedron with one ligand on both sides of a pentagon. Pentagonal bipyramidal was found to be the coordination polyhedron of

seven oxygen atoms around the zirconium atom in the structure of $Zr_4(OH)_6(CrO_4)_5(H_2O)_2$[7]. One expects only one ligand on both sides of the pentagon if the oxygen atoms are not bonded to each other. Oxygen atoms in the phosphate group are closer than is normal for atoms from separate
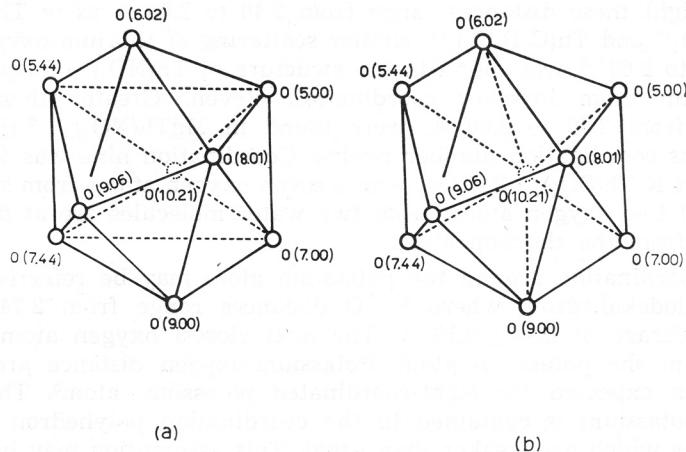
Fig. 3 The coordination polyhedron of oxygen atoms around the thorium atom. Oxygen atoms are connected by straight and broken lines in two different ways and indicate two possibilities of drawing the Th-polyhedron: (a) as a trigonal prism with additional ligands outside each of the rectangular faces and (b) as a pentagon with two ligands on both sides.
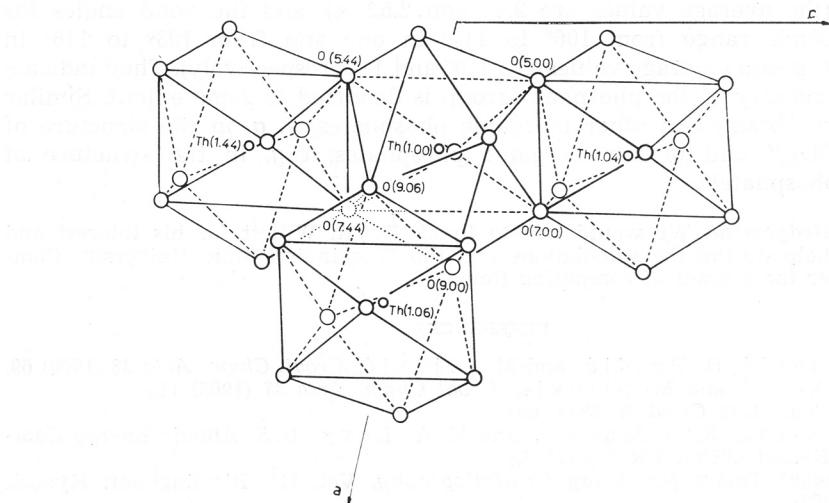
Fig. 4 A view down the Th-polyhedra with sharing edges.

molecules and thus the coordination can be nine if four atoms are from two phosphate groups. The pentagon in the Th-polyhedron is not regular, because its sides are not equal and the atoms in the corners are not coplanar.

The values of Th—O distances vary over a wide range from 2.26 to 2.66 Å. The scatter is much greater than the accuracy of the experiment (0.04 Å). It is interesting to compare these distances with those already found in other thorium compounds, e. g., thorium—oxygen distance in ThO_2 (fluorite type structure) is 2.41 Å[8]; in other compounds where the thorium atom has coordination eight these distances range from 2.40 to 2.68 Å as in $Th(OH)_2CrO_4$[9], $Th(OH)_2SO_4$[10] and $Th(C_5H_7O_2)_4$[11]; similar scattering of thorium-oxygen distance from 2.42 to 2.62 Å was found in the structure of $Th(NO_3)_4 \cdot 5H_2O$[12,13], where the thorium atom involves coordination eleven. Greater thorium-oxygen distances, from 2.50 to 2.80 Å, were found in $MgTh(NO_3)_6 \cdot 8H_2O$[14], where thorium has coordination number twelve. Coordination nine was found in the structure of $K_4Th(SO_4)_4 \cdot 2H_2O$[15], where seven oxygen atoms from six sulphato-groups and two oxygen atoms from two water molecules are at distance 2.30 to 2.58 Å from the thorium atom.

The coordination around the potassium atom may be referred to a very distorted dodekahedron, where K—O distances range from 2.74 to 3.09 Å with an average of 2.90 ± 0.19 Å. The next closest oxygen atom O(10.53) is 3.61 Å from the potassium atom. Potassium-oxygen distance are somewhat longer than expected for eight-coordinated potassium atom[5]. They indicate that the potassium is contained in the coordination polyhedron by electrostatic forces which are weaker than usual. This assumption may be confirmed by the K thermal parameters, which are the highest of the whole structure.

The distances within the phosphate groups do not deviate significantly from the results obtained before. The P—O distances range from 1.49 to 1.55 Å in one PO_4 group and from 1.52 to 1.58 Å in another (average values are 1.52 and 1.55 Å); the O—O distances range from 2.43 to 2.63 Å and from 2.46 to 2.59 Å (the average values are 2.48 and 2.52 Å), and the bond angles for O—P—O bonds range from 106° to 117° in one and from 103° to 116° in another PO_4 group (average values are 110° and 111° respectively). They indicate that the symmetry of the phosphato group is distorted to some extent. Similar results were obtained in other inorganic phosphates, e. g. in the structure of $Cu_5(PO_4)_2(OH)_4$[16] and in some organic phosphates, e. g. in the structure of triphenyl phosphate[17].

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IZVOD

Kristalna struktura kalij ditorij trisfosfata

B. Matković, B. Prodić, M. Šljukić i S. W. Peterson

Struktura KTh₂(PO₄)₃ određena je iz trodimenzionalnih podataka metodom rendgenske strukturne analize. Kristali su monoklinski sa a = 17,57, b = 6,863, c = = 8,138 Å, β = 101° 46′, prostorna grupa C2/c, Z = 4. Na temelju strukturnih podataka i međuatomskih razmaka ustanovljeno je da je spoj kalij trisfosfatoditorat, K[Th₂(PO₄)₃]. U koordinacijski poliedar torijeva atoma ulazi devet kisikovih atoma iz sedam fosfatnih grupa. Udaljenosti torij—kisik variraju od 2,26 do 2,66 Å. Koordinacioni poliedar kalijeva atoma čini osam kisikovih atoma, udaljenosti kalij—kisik variraju od 2,74 do 3.09 Å. Udaljenosti u PO₄ grupama ne razlikuju se od poznatih podataka.

INSTITUT »RUĐER BOŠKOVIĆ«
ZAGREB, JUGOSLAVIJA
     I
WASHINGTON STATE UNIVERSITY
   PULLMAN, WASH., U. S. A.