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Synthesis and Crystal Structure of Potassium Thorium Triphosphate, $KThP_3O_{10}$

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Potassium thorium triphosphate has been prepared by thermal synthesis at 900° C. The crystal structure has been determined from three-dimensional X-ray film data (638 independent reflexions). The crystals are monoclinic (pseudoorthorhombic) with a = 8.234(2), b = 10.187(5), c = 10.015(2) Å, β = 90°, but the structure was solved and refined in space group $P2_12_12_1$. *The positional and thermal parameters are refined by the least-squares method to R = 0.087. The thorium atom is coordinated by eight oxygen atoms, from six triphosphate chains, in the shape of a dodecahedron. Thorium–oxygen distances range from 2.37(4) Å to 2.58(4) Å. The P–O distances with terminal oxygen atoms are comparable with those in the orthophosphates. The bond lengths of phosphorus to bridging oxygen atoms are 1.65(4) Å, 1.55(3) Å, 1.58(4) Å and 1.57(5) Å.*

Introduction

A detailed investigation of phosphate compounds with the common formula $M^IM_2^{IV}(PO_4)_3$ (M^I = Li, Na, K, Rb and Cs; M^{IV} = Th, U, Zr and Hf) have been undertaken in the X-ray laboratory, Institute "Rudjer Bošković". It has included thermal syntheses[1,2] and crystal structure determinations.[3,4,5] A few compounds in this series possess ferroelectric properties.[6,7] The research in this field has been extended to polyphosphates and the main effort has been concentrated on the syntheses of thorium triphosphates and studies of their crystal structures. The geometry of the triphosphate chain and also the polymerisation of phosphates are of special interest. The only origin of information so far has been the crystal structure of $Na_5P_3O_{10}$.[8]

Experimental

Synthesis

Potassium thorium triphosphate, $KThP_3O_{10}$, was obtained by thermal synthesis from 2.2:1:0.5 molar mixture of KH_2PO_4, ThO_2 and HPO_3 (as a flux) in platinum crucible at 900° C for 24 hours. Down to 500° C the furnace was cooled slowly (50° per day) in order to obtain single crystals convenient for X-ray work. The crystals were separated from the matrix, by dissolving the soluble substances in boiling water and then washing with HNO_3 (1:1). The crystals appear in the form of thin [010] prismatic rods with dominant {101} forms. The formula was determined on the basis of the analytical data.

Anal. Calcd. for $KThP_3O_{10}$:
7.32% K, 45.32% Th, 17.40% P
Found:
7.30% K, 45.32% Th, 17.35% P

Crystallographic Data

The colourless crystals of $KThP_3O_{10}$ are of pseudoorthorhombic symmetry with a = 8.234(2), b = 10.187(5), c = 10.015(2) Å*, β = 90°, D_m = 4.175 gcm^{-3}, D_x = 4.178 gcm^{-3}, Z = 4, CuKα radiation, μ = 718.4 cm^{-1}. The crystal structure is described in space group $P2_12_12_1$.

There has been some doubt about the true symmetry of the crystals. By detailed inspection of Weissenberg photographs around [100], [010] and [001] directions, differences in intensities between some hkl and the corresponding $hk\bar{l}$ reflexions were observed. The systematic absences of the reflexions 0k0 with k = 2n + 1 were without any ambiguity. Three very weak h00 and 00l reflexions with h = 2n + 1 and l = 2n + 1 occurred (they were checked for the Renninger effect). Concerning all these facts and the solution of the Patterson synthesis the real crystal symmetry should have been monoclinic, with space group $P2_1$ and Z = 2 × 2. On the other hand no separation between the corresponding hkl and $\bar{h}kl$ reflexions at high angles was observed, indicating that the monoclinic angle β is exactly 90°. The optical properties of $KThP_3O_{10}$ were in agreement with orthorhombic symmetry. The interatomic distances calculated in the orthorhombic system were much nearer to the expected values, known from literature. For these reasons the structure description and all numerical data in the paper are based on the space group $P2_12_12_1$.

The rough estimates of unit cell dimensions were done from oscillation photographs with CuKα radiation.

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* Numbers in parentheses here and throughout this paper are the estimated standard deviations in the least significant digits.

The precise values were then deduced from zero-layer rotation patterns of single crystals taken in asymmetric (Straumanis) position and indexed by means of corresponding Weissenberg photographs, as well as from the pairs of reflexions at high angles chosen from single crystal diffraction patterns taken by a counter diffractometer.[9] The density was measured at 25° C pycnometrically with decalin as the liquid.

Equi-inclination Weissenberg photographs were taken using filtered CuKα radiation and the multiple film technique (four films). 638 independent reflexions were recorded. Out of these, 608 had observable intensities, which were measured with a microdensitometer. A crystal shaped into a sphere with radius $r = 0.0113$ cm was used to collect layer-lines h0l–h5l. The corrections for absorption (spherical crystal), Lorentz and polarization factors were made in the usual way. The factors for transforming the observed structure amplitudes on an absolute scale were found for reflexions of each layer line separately. These scale factors were improved in the course of the structure determination.

Structure Determination and Refinement

The crystal structure of $KThP_3O_{10}$ was solved in the monoclinic $P2_1$ symmetry (including hkl and hkl reflexions) and also in the orthorhombic $P2_12_12_1$ symmetry. In both symmetries all atoms are in general positions (30 atoms being symmetrically independent in the monoclinic and 15 atoms in the pseudoorthorhombic case). The coordinates of the thorium atom were deduced from a three-dimensional Patterson synthesis. The potassium and phosphorus atoms were located from electron density maps based on the thorium atom. The difference Fourier technique (F_o–$F_{c_{Th}}$) was used to determine the positions of all oxygen atoms.

The structure was refined by minimizing the function $\Sigma W(|F_o|-|F_c|)^2$ using full matrix least-squares programs. All observations were given unit weights. The refinement was based on 608 observed reflexions. The atomic scattering factors for Th, K, P and O were those calculated by Hanson, Herman, Lea and Skillman.[10] The scattering factors of Th and K were corrected for anomalous dispersion according to Cromer.[11] An isotropic refinement was carried out in both symmetries without any significant differences in R values. An attempt to introduce anisotropic thermal parameters for all atoms except the oxygens was not successful, when the structure was described in terms of $P2_1$ (the potassium and the two phosphorus atoms got negative values of the β_{22} parameters). At this point the agreement factor R was 0.076. The refinement in the orthorhombic $P2_12_12_1$ symmetry with 45 positional parameters, 13 isotropic temperature factors and 12 anisotropic thermal parameters for thorium and potassium resulted in a

TABLE I. Final coordinates ($\times 10^4$) and temperature factors.

	x	y	z	B(Å^2)
Th	1381(2)	–1517(3)	2467(2)	
K	4056(12)	1831(21)	2682(16)	
P(1)	0496(16)	1233(27)	0192(12)	0.6(2)
P(2)	7738(15)	0106(24)	1282(13)	0.6(2)
P(3)	0204(18)	1149(28)	5009(14)	1.1(3)
O(1)	1530(58)	0565(74)	1190(44)	2.4(9)
O(2)	0097(40)	2569(58)	0656(33)	0.5(6)
O(3)	6206(49)	3729(71)	1199(37)	1.3(8)
O(4)	3772(40)	4579(61)	–0027(32)	0.7(6)
O(5)	1607(45)	3939(60)	3162(36)	1.3(8)
O(6)	7601(49)	1294(65)	2145(38)	2.0(9)
O(7)	4022(47)	4853(65)	4299(39)	1.5(8)
O(8)	6235(50)	3528(75)	3859(36)	1.4(8)
O(9)	1043(50)	0385(68)	3940(39)	1.7(8)
O(10)	4296(48)	2734(62)	5511(37)	1.2(8)

The anisotropic thermal parameters ($\times 10^4$) refer to the expression:

$$\exp -(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\,\beta_{12}hk+2\,\beta_{13}hl+2\,\beta_{23}kl)$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Th	0025(2)	0017(5)	0014(1)	0000(2)	0001(2)	–0000(3)
K	0096(19)	0013(39)	0083(16)	–0019(19)	–0007(16)	–0020(20)

$$R_1 = \sum_{hkl}||F_o|-|F_c||/\sum_{hkl}|F_o| = 0.087 \text{ (omitting unobserved refl.)}$$

$$R_2 = \sum_{hkl}||F_o|-|F_c||/\sum_{hkl}|F_o| = 0.088 \text{ (including unobserved refl.)}$$

final R value of 0.087 (omitting unobserved reflexions). The inter-layer scale factors were fixed at the values obtained in the isotropic refinement.

The atomic positional and thermal parameters obtained from the final refinement in $P2_12_12_1$ are listed in Table I, and observed and calculated structure factors in Table II.

TABLE II. Observed, $|F_o|$, and calculated, F_c, structure factors.

H	K	L	10FO	10FC
4	0	0	2777	-2879
6	0	0	703	632
8	0	0	1695	1748
10	0	0	1009	-1041
1	0	1	2161	-1955
3	0	1	2594	2594
4	0	1	644	563
5	0	1	302	206
6	0	1	52	64
7	0	1	1838	-1888
8	0	1	224	-132
9	0	1	0	-34
10	0	1	421	-353
0	0	2	2405	-2332
1	0	2	870	722
2	0	2	1911	1755
3	0	2	436	-315
4	0	2	2791	2825
5	0	2	360	231
6	0	2	823	-738
7	0	2	423	-407
8	0	2	1370	-1405
9	0	2	176	-109
10	0	2	995	905
1	0	3	1318	1161
2	0	3	52	60
3	0	3	2635	-2548
4	0	3	0	-19
5	0	3	983	-876
6	0	3	495	-538
7	0	3	2023	2153
8	0	3	335	226
9	0	3	0	14
10	0	3	158	136
0	0	4	3066	3178
1	0	4	528	-329
2	0	4	784	630
3	0	4	52	-44
4	0	4	2074	-1991
5	0	4	393	-417
6	0	4	1076	973
7	0	4	226	-198
8	0	4	1121	1125
9	0	4	42	56
1	0	5	1853	-1775
2	0	5	220	-236
3	0	5	1728	1591
4	0	5	211	164
5	0	5	830	683
6	0	5	52	56
7	0	5	1741	-1892
8	0	5	297	-241
9	0	5	194	-179
0	0	6	2391	-2374
1	0	6	302	-280
2	0	6	747	532
3	0	6	52	-88
4	0	6	2482	2401
5	0	6	408	-284
6	0	6	658	-567
7	0	6	52	-52
8	0	6	1112	-1271
9	0	6	137	-229
1	0	7	1061	941
2	0	7	626	686
3	0	7	1935	-1890
4	0	7	52	-38
5	0	7	494	-424
6	0	7	145	-188
7	0	7	1394	1556
8	0	7	73	88
0	0	8	2758	2910
1	0	8	52	61
2	0	8	310	-299
3	0	8	310	-229
4	0	8	1657	-1671
5	0	8	538	-571
6	0	8	679	638
7	0	8	0	-50
8	0	8	1172	1258
1	0	9	1349	-1327
2	0	9	248	-270
3	0	9	1472	1490
4	0	9	103	117
5	0	9	485	487
6	0	9	309	380
7	0	9	1146	-1105
0	0	10	1389	-1440
1	0	10	103	-103
2	0	10	540	430
3	0	10	475	-488
4	0	10	1384	1506
5	0	10	304	363
6	0	10	500	-518
1	0	11	781	863
2	0	11	508	617
3	0	11	1119	-1268
4	0	11	165	-117
5	0	11	528	-486
0	0	12	1203	1388
1	0	12	117	160
2	1	0	2394	2387
3	1	0	2109	-1997
4	1	0	711	-602
5	1	0	1358	1308
6	1	0	1742	-1771
7	1	0	212	161
8	1	0	427	393
9	1	0	962	-1014
10	1	0	624	568
1	1	1	1896	-1935
2	1	1	1585	-1458
3	1	1	927	-1001
4	1	1	413	416
5	1	1	1739	1798
6	1	1	1299	1224
7	1	1	509	-358
8	1	1	898	-840
9	1	1	1263	-1451
10	1	1	479	-473
0	1	2	1129	-1021
1	1	2	1419	1268
2	1	2	2746	-3082
3	1	2	1275	-1039
4	1	2	264	372
5	1	2	1693	-1689
6	1	2	1347	1284
7	1	2	773	-686
8	1	2	972	-928
9	1	2	623	655
10	1	2	921	-957
0	1	3	396	-310
1	1	3	1520	1506
2	1	3	1189	1183
3	1	3	617	644
4	1	3	995	-904
5	1	3	1592	-1776
6	1	3	984	-941
7	1	3	137	-163
8	1	3	647	512
9	1	3	1225	1356
10	1	3	711	701
0	1	4	97	77
1	1	4	1223	-1263
2	1	4	2641	2838
3	1	4	636	-545
4	1	4	779	-711
5	1	4	653	376
6	1	4	1908	-1977
7	1	4	387	-252
8	1	4	549	499
9	1	4	820	-916
0	1	5	441	449
1	1	5	1609	1470
2	1	5	1607	-1663
3	1	5	851	-814
4	1	5	612	478
5	1	5	1808	-1634
6	1	5	978	749
7	1	5	307	232
8	1	5	506	-594
9	1	5	1210	-1216
0	1	6	97	-138
1	1	6	1408	1222
2	1	6	2204	-2141
3	1	6	888	-667
4	1	6	552	311
5	1	6	1490	-1449
6	1	6	1125	1126
7	1	6	608	550
8	1	6	764	-859
9	1	6	720	695
0	1	7	332	-378
1	1	7	1460	1470
2	1	7	1246	1161
3	1	7	961	770
4	1	7	824	-844
5	1	7	1404	-1467
6	1	7	1090	-1166
7	1	7	368	-435
8	1	7	580	561
0	1	8	97	76
1	1	8	1068	-954
2	1	8	1516	1557
3	1	8	1251	-1182
4	1	8	762	-692
5	1	8	1035	970
6	1	8	1233	-1302
7	1	8	177	-118
8	1	8	558	563
0	1	9	353	396
1	1	9	1213	-1151
2	1	9	1078	-1084
3	1	9	728	-808
4	1	9	275	279
5	1	9	1324	1382
6	1	9	756	710
0	1	10	490	-501
1	1	10	792	657
2	1	10	1526	-1632
3	1	10	474	-429
4	1	10	248	388
5	1	10	870	-938
6	1	10	948	884
0	1	11	223	-286
1	1	11	961	948
2	1	11	807	893
3	1	11	682	674
4	1	11	538	-596
5	1	11	867	-1002
0	1	12	97	101
2	1	12	1219	1209
3	1	12	321	235
2	2	0	799	-690
3	2	0	2446	-2580
4	2	0	803	736
5	2	0	1113	-969
6	2	0	572	-411
7	2	0	1654	1703
8	2	0	362	-305
9	2	0	0	42
10	2	0	348	266
1	2	1	476	279
2	2	1	726	-659
3	2	1	459	-432
4	2	1	2421	-2513
5	2	1	287	-213
6	2	1	1480	1299
7	2	1	880	784
8	2	1	1321	1393
9	2	1	278	227
10	2	1	1012	-1081
0	2	2	1606	1510
1	2	2	2983	3373
2	2	2	412	-261
3	2	2	1946	1939
4	2	2	1370	-1245
5	2	2	1113	1045
6	2	2	163	119
7	2	2	1708	-1834
8	2	2	626	519
9	2	2	0	24
10	2	2	330	-236
0	2	3	2175	-2332
1	2	3	198	-265
2	2	3	612	370
3	2	3	1208	1122
4	2	3	2050	1929
5	2	3	465	-254
6	2	3	1324	-1096
7	2	3	709	-586
8	2	3	1062	-1176
9	2	3	196	89
10	2	3	966	1103
0	2	4	1640	-1662
1	2	4	1612	1595
2	2	4	577	466
3	2	4	2753	-2748
4	2	4	877	639
5	2	4	1487	-1272
6	2	4	137	153
7	2	4	1649	1641
8	2	4	503	-466
9	2	4	289	-298
0	2	5	1756	1789
1	2	5	1028	899
2	2	5	814	-709
3	2	5	821	-710
4	2	5	1866	-1831
5	2	5	193	-224
6	2	5	1130	1131
7	2	5	582	-482
8	2	5	1167	1219
9	2	5	371	358
0	2	6	1208	1159
1	2	6	2012	-2046
2	2	6	148	-88
3	2	6	1365	1456
4	2	6	723	-774
5	2	6	821	-562
6	2	6	416	425
7	2	6	1426	-1446
8	2	6	498	473
0	2	7	2050	-2150
1	2	7	345	-467
2	2	7	300	186
3	2	7	806	-495
4	2	7	1710	1730
5	2	7	222	195
6	2	7	837	-748
7	2	7	657	-663
8	2	7	1147	-971
0	2	8	372	-269
1	2	8	800	743
2	2	8	346	318
3	2	8	1690	-1608
4	2	8	946	815
5	2	8	858	-761
6	2	8	299	-321
7	2	8	1015	1168
0	2	9	1457	1463
1	2	9	470	573
2	2	9	896	-538
3	2	9	580	478
4	2	9	1473	-1520
5	2	9	365	-312
6	2	9	691	725
7	2	9	628	562
0	2	10	882	802
1	2	10	1459	-1394
2	2	10	185	-133
3	2	10	1163	1098
4	2	10	662	-745
5	2	10	440	509
6	2	10	385	404
0	2	11	1465	-1655
1	2	11	576	-596
2	2	11	209	258
3	2	11	479	504
4	2	11	1156	1113
0	2	12	680	-565
1	2	12	875	757
2	2	12	450	536
2	3	0	248	-284
3	3	0	1970	2126
4	3	0	763	-671
5	3	0	1664	-1675
6	3	0	771	-636
7	3	0	665	-598
8	3	0	102	94
9	3	0	1398	1578
10	3	0	272	278
1	3	1	641	-688
2	3	1	1804	1709
3	3	1	190	-290
4	3	1	1248	-1260
5	3	1	640	667
6	3	1	1359	-1525
7	3	1	349	333
8	3	1	1146	1027
9	3	1	590	454
0	3	2	473	376
1	3	2	1756	-1945
2	3	2	1053	-833
3	3	2	1482	-1382
4	3	2	430	-369
5	3	2	2121	2181
6	3	2	401	122
7	3	2	803	713
8	3	2	558	-470
9	3	2	1050	-1152
0	3	3	0	-75
1	3	3	920	930
2	3	3	2496	-2621
3	3	3	720	-665
4	3	3	1074	742
5	3	3	549	-527
6	3	3	2022	1979
7	3	3	497	418
8	3	3	1142	-1240
9	3	3	395	360
0	3	4	345	-242
1	3	4	1772	1760
2	3	4	1010	830
3	3	4	2078	2056
4	3	4	703	-590
5	3	4	1899	-1799
6	3	4	1100	-1005
7	3	4	271	-78
8	3	4	167	251
9	3	4	1362	1424
0	3	5	0	13
1	3	5	590	-580
2	3	5	2021	2075
3	3	5	531	359
4	3	5	817	-733
5	3	5	683	688
6	3	5	1603	-1762
7	3	5	220	235
8	3	5	1131	1255
0	3	6	606	493
1	3	6	1718	-1734
2	3	6	1019	-666
3	3	6	1232	-1176
4	3	6	284	-207
5	3	6	1845	1960
6	3	6	144	100
7	3	6	666	625
8	3	6	518	-538
0	3	7	327	-200
1	3	7	837	842
2	3	7	1622	-1630
3	3	7	691	-642
4	3	7	1122	903
5	3	7	375	-332
6	3	7	1234	1247
7	3	7	183	139
8	3	7	864	-774
0	3	8	191	-159
1	3	8	1901	1886
2	3	8	631	409
3	3	8	1144	944
4	3	8	500	-404
5	3	8	1226	-1228
6	3	8	554	-528
0	3	9	102	53
1	3	9	571	-484
2	3	9	1722	1759
3	3	9	259	270
4	3	9	594	-565
5	3	9	650	685
6	3	9	880	-1008
0	3	10	208	212
1	3	10	1253	-1336
2	3	10	583	-637
3	3	10	700	-711
4	3	10	282	-353
5	3	10	1424	1271
0	3	11	224	-177
1	3	11	495	485
2	3	11	1216	-1383
3	3	11	377	-432
4	3	11	686	548
0	3	12	147	-107
2	3	12	565	435
1	4	0	1541	-1943
2	4	0	93	-115
3	4	0	1484	1578
4	4	0	1751	1760
5	4	0	898	810
6	4	0	1048	-1031
7	4	0	1120	-1074
8	4	0	985	-925
9	4	0	296	-281
0	4	1	1234	-1465
1	4	1	1004	1172
2	4	1	533	504
3	4	1	1685	-1660
4	4	1	1285	1233
5	4	1	747	594
6	4	1	869	-835
7	4	1	1554	1485
8	4	1	941	-849
9	4	1	219	189
0	4	2	1919	2220
1	4	2	1146	1319
2	4	2	1017	-864
3	4	2	1363	-1372
4	4	2	2104	-2060
5	4	2	907	734
6	4	2	583	566
7	4	2	1021	837
8	4	2	1167	1112
9	4	2	92	79
0	4	3	913	886
1	4	3	1559	1660
2	4	3	371	-305
3	4	3	1840	1921
4	4	3	1136	-1043
5	4	3	596	-440
6	4	3	762	747
7	4	3	1467	-1398
8	4	3	760	647
9	4	3	334	345
0	4	4	2566	-2768
1	4	4	1364	-1294
2	4	4	310	288
3	4	4	1282	1209
4	4	4	1029	841
5	4	4	793	723
6	4	4	674	-604
7	4	4	1084	-1084
8	4	4	880	-903
9	4	4	179	-118
0	4	5	1005	-956
1	4	5	1333	1312
2	4	5	396	370
3	4	5	1711	-1657
4	4	5	1156	967
5	4	5	588	-610
6	4	5	854	-788
7	4	5	1069	1092
8	4	5	657	-763
9	4	5	204	185
0	4	6	1229	1112
1	4	6	1199	-936
2	4	6	1001	-837
3	4	6	1392	1193
4	4	6	1752	-1700
5	4	6	679	-662
6	4	6	483	477
7	4	6	802	957
8	4	6	1014	944
0	4	7	1453	1414
1	4	7	860	723
2	4	7	416	-395
3	4	7	1227	1191
4	4	7	1232	-1111
5	4	7	546	519
6	4	7	650	596
7	4	7	1180	-1272
8	4	7	752	818
0	4	8	1797	-1803
1	4	8	1172	-1013
2	4	8	633	-562
3	4	8	1133	1082
4	4	8	1314	1232
5	4	8	633	674
6	4	8	699	-701
0	4	9	1140	-1129
1	4	9	1041	1021
2	4	9	572	566
3	4	9	891	-896
4	4	9	893	895
5	4	9	492	506
6	4	9	606	-501
0	4	10	906	850
1	4	10	686	797
2	4	10	498	-397
3	4	10	845	-857
4	4	10	1182	-1307
0	4	11	694	755
1	4	11	626	-663
2	4	11	326	-341
3	4	11	1322	1267
4	4	11	721	-773
1	4	12	684	-652
2	5	0	2074	-2192
3	5	0	0	-84
4	5	0	1050	983
5	5	0	876	660
6	5	0	1909	1836
7	5	0	304	266
8	5	0	868	-878
9	5	0	199	-196
1	5	1	1800	2117
3	5	1	1240	1219
4	5	1	831	236
5	5	1	2213	-2057
6	5	1	389	432
7	5	1	816	396
8	5	1	576	-452
9	5	1	1689	1674
0	5	2	0	60
1	5	2	725	726
2	5	2	2750	2964
3	5	2	811	784
4	5	2	404	-263
5	5	2	463	-376
6	5	2	1622	-1615
7	5	2	283	-225
8	5	2	934	1021
9	5	2	326	-184
0	5	3	332	262
1	5	3	1671	-1638
2	5	3	164	-169
3	5	3	823	-708
4	5	3	408	-364
5	5	3	1688	1636
6	5	3	413	329
7	5	3	481	582
8	5	3	242	277
9	5	3	1470	-1392
0	5	4	245	-184
1	5	4	570	557
2	5	4	2102	-2224
3	5	4	806	-356
4	5	4	1087	840
5	5	4	348	-229
6	5	4	1781	1719
7	5	4	609	495
8	5	4	673	-620
0	5	5	384	-270
1	5	5	1581	1663
2	5	5	310	225
3	5	5	721	766
4	5	5	650	623
5	5	5	1763	-1774
6	5	5	143	-88
7	5	5	582	373
8	5	5	245	206
0	5	6	780	714
1	5	6	336	247
2	5	6	2113	2330
3	5	6	439	319
4	5	6	466	-522
5	5	6	332	229
6	5	6	1373	-1286
7	5	6	373	-429
8	5	6	1022	935
0	5	7	189	177
1	5	7	1767	-1634
2	5	7	266	164
3	5	7	1347	-1233
4	5	7	412	252
5	5	7	1898	1708
6	5	7	152	-133
7	5	7	348	269
0	5	8	0	-23
1	5	8	392	270
2	5	8	1761	-1725
3	5	8	316	-211
4	5	8	672	580
5	5	8	397	292
6	5	8	1272	1388
7	5	8	345	221
0	5	9	833	-505
1	5	9	1228	1293
2	5	9	270	223
3	5	9	779	770
4	5	9	387	427
5	5	9	1730	-1528
6	5	9	329	245
0	5	10	0	28
1	5	10	185	115
2	5	10	1522	1521
3	5	10	406	447
0	5	11	207	317
1	5	11	1254	-1036
2	5	11	186	168

Rather high σ values of the coordinates and interatomic distances (Tables I and III) and some large ΔF values (Table II) might be explained by the pseudosymmetry.

TABLE III. Interatomic distances and angles in $KThP_3O_{10}$.

A	B	C	Distances (Å) A–B	Distances (Å) A–C	Angles (degrees) A–B–C
			Within dodecahedron		
O(1)	Th	O(3)	2.48(6)	3.72(7)	99(2)°
O(2)	Th	O(3)	2.43(4)	3.46(5)	91(1)
O(3)	Th	O(6)	2.41(4)	2.89(8)	74(2)
O(5)	Th	O(6)	2.58(4)	4.38(7)	123(2)
O(6)	Th	O(8)	2.41(6)	3.06(8)	70(2)
O(8)	Th	O(1)	2.37(4)	2.77(9)	70(2)
O(9)	Th	O(1)	2.45(6)	2.79(5)	67(1)
O(10)	Th	O(1)	2.38(4)	3.49(9)	92(2)
O(1)	Th	O(5)		3.14(7)	77(2)
O(2)	Th	O(5)		3.13(6)	77(1)
O(2)	Th	O(6)		2.85(6)	72(1)
O(2)	Th	O(9)		3.05(8)	77(2)
O(3)	Th	O(8)		2.67(4)	68(1)
O(3)	Th	O(9)		2.83(7)	71(2)
O(5)	Th	O(9)		3.37(6)	84(1)
O(5)	Th	O(10)		2.88(6)	71(1)
O(6)	Th	O(10)		2.91(6)	75(2)
O(8)	Th	O(10)		2.90(6)	75(1)
			Within the triphosphate chain		
O(1)	P(1)	O(2)	1.48(5)	2.42(8)	110(3)
O(2)	P(1)	O(3)	1.48(5)	2.46(6)	111(3)
O(3)	P(1)	O(4)	1.51(4)	2.50(6)	105(2)
O(4)	P(1)	O(1)	1.65(4)	2.56(5)	109(3)
O(1)	P(1)	O(3)		2.51(5)	114(3)
O(2)	P(1)	O(4)		2.52(7)	107(2)
O(4)	P(2)	O(5)	1.55(3)	2.38(6)	106(2)
O(5)	P(2)	O(6)	1.42(5)	2.51(9)	119(2)
O(6)	P(2)	O(7)	1.49(6)	2.46(7)	106(3)
O(7)	P(2)	O(5)	1.58(4)	2.47(6)	111(3)
O(4)	P(2)	O(6)		2.49(5)	110(3)
O(4)	P(2)	O(7)		2.46(5)	104(2)
O(7)	P(3)	O(8)	1.57(5)	2.31(7)	100(3)
O(8)	P(3)		1.45(4)	2.47(7)	114(2)
O(9)	P(3)		1.49(5)	2.46(8)	113(3)
O(10)	P(3)		1.46(6)	2.49(8)	110(2)
O(7)	P(3)			2.44(5)	105(3)
O(8)	P(3)			2.44(6)	114(4)
P(1)	O(4)	P(2)			120(2)
O(4)	P(2)	O(7)			103(2)
P(2)	O(7)	P(3)			146(3)
			Potassium-oxygen distances ≤ 3.24 Å		
O(1)	K		2.87(5)		
O(3)	K		3.01(6)		
O(5)	K		2.98(5)		
O(6)	K		3.02(4)		
O(7)	K		3.24(5)		
O(8)	K		2.76(6)		
O(9)	K		3.15(5)		
O(10)	K		2.98(4)		

Unfortunately the number of the corresponding hkl and $\bar{h}kl$ reflexions with differences in intensities recorded by the film method has been too small to determine the symmetry uniquely.

The calculations were done on a CAE 90–40[12] computer in Zagreb and an IBM 370/155[13] computer in Uppsala.

Description and Discussion of the Structure

The thorium atom is coordinated by eight oxygen atoms from six chains; O(1) and O(5) from one chain, O(2) and O(6) from an other one, and the remaining four oxygen atoms O(3), O(8), O(9) and O(10) from four different chains (Figure 1). The coordination polyhedron around thorium is a dodecahedron. The crystal structure consists of thorium polyhedra connected by triphosphate chains. The structure is very close-packed. The only existing cavities are occupied by potassium atoms.

Coordination around Thorium

The thorium–oxygen distances in the dodecahedron range from 2.37(4) Å to 2.58(4) Å (Table III and Figure 2). Their mean value of 2.44 Å is near to the sum of the ionic radii (2.42 Å). The Th–O distances in this structure are in agreement with those in literature: e.g. for compounds with coordination number eight these values range from 2.40 Å to 2.68 Å as in $Th(OH)_2CrO_4$,[14] $Th(OH)_2SO_4$[15] and $Th(C_5H_7O_2)_4$.[16] In $KTh_2(PO_4)_3$[3] with coordination number nine the Th–O distances of 2.26 Å to 2.66 Å could also be compared with those in $KThP_3O_{10}$ (with exception of one very short distance of 2.26 Å).

The oxygen–oxygen distances, the edges of dodecahedron, vary over a wide range from 2.67(4) to 4.38(7) Å. Considering the influence of the ligand geometry on the regularity of the coordination polyhedron this structure could be compared with chelate complexes.[17]

Triphosphate Chain

The triphosphate chain is composed of three PO_4 tetrahedra with common corners (Figure 3). Bridging oxygen atoms O(4) and O(7) form longer P–O bonds than the others; their values are 1.65 Å, 1.55 Å, 1.58 Å and 1.57 Å (Table III). The remaining P–O bond lengths in the triphosphate chain do not deviate significantly from the values in orthophosphates. They range from 1.42(5) Å to 1.51(4) Å. The only known triphosphate structure of $Na_5P_3O_{10}$[8] is rather different in its nature from the $KThP_3O_{10}$ structure; the triphosphate chain is not coordinated to any metal atom and besides it is traversed by a two-fold axis. Thus the regularity of the triphosphate chain is quite preserved. In the $KThP_3O_{10}$ structure all oxygen atoms in the chain (except the two bridging) are coordinated to thorium atoms

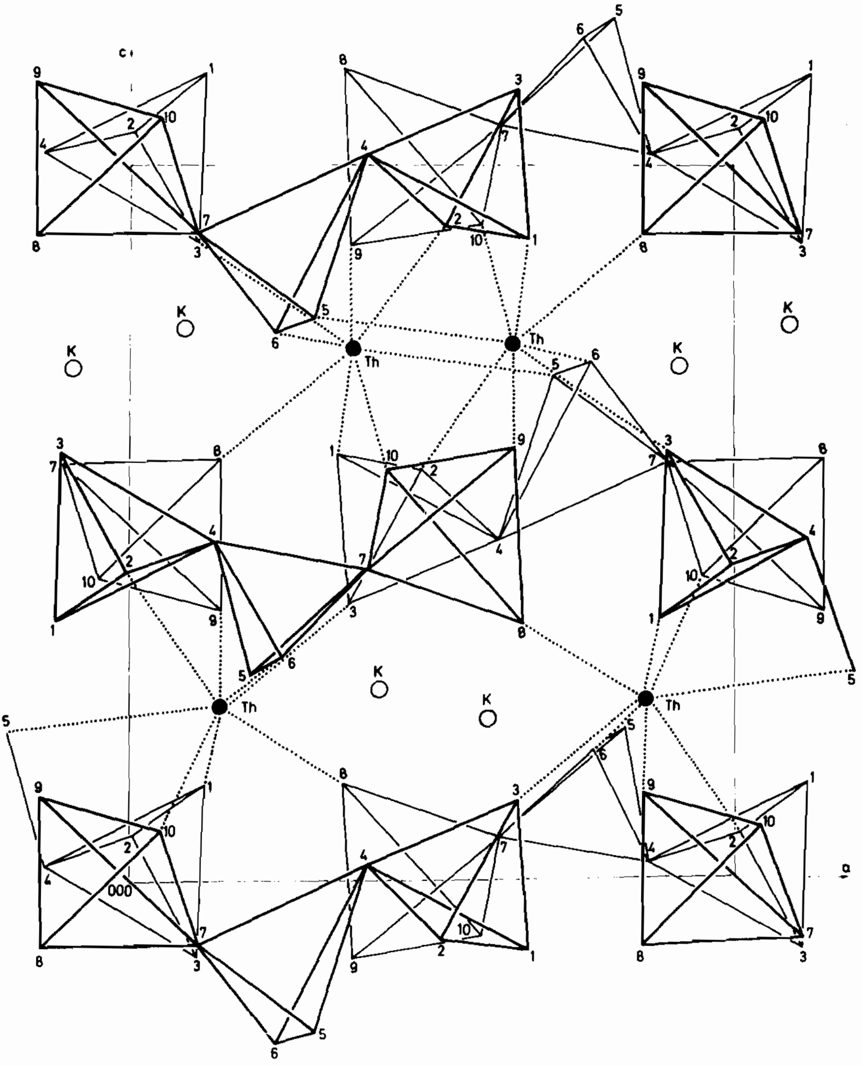

Figure 1. (010) projection of the structure $KThP_3O_{10}$.

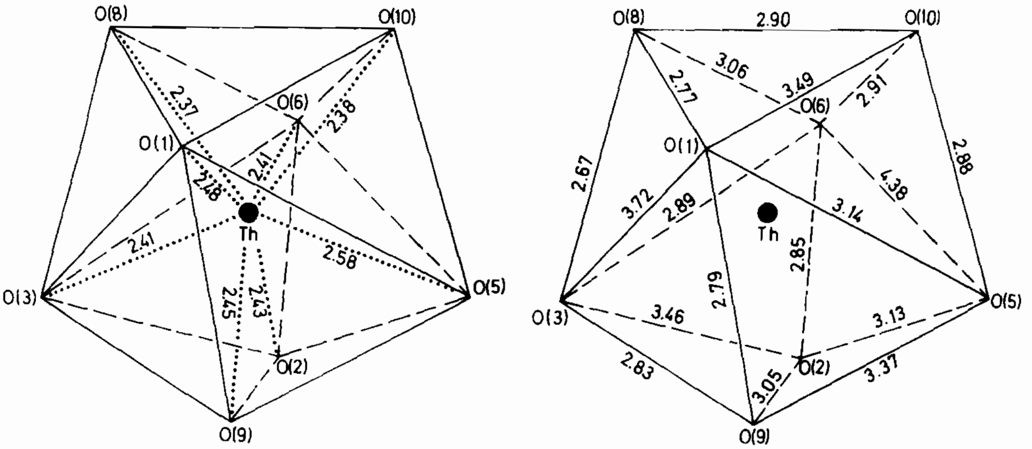

Figure 2. Th–O bond lengths and O–O distances in dodecahedron.

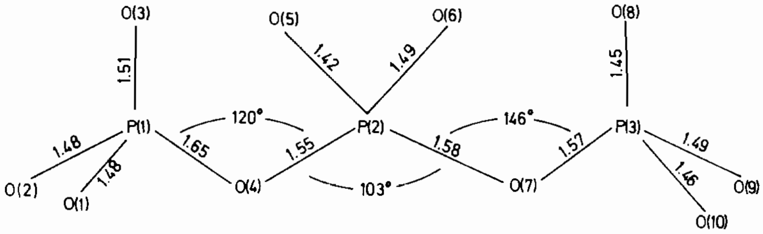

Figure 3. Triphosphate chain in $KThP_3O_{10}$.

and it is reasonable to expect some deformation of the triphosphate chain. In spite of that the obtained values of P–O bond lengths in $KThP_3O_{10}$ are in good agreement with the values of 1.65 Å for bridging oxygen atom and 1.50 Å for the others in $Na_5P_3O_{10}$[8] structure. As to the angles, the value of 120° for P(1)–O(4)–P(2) angle is nearly equal to the value (119°) in $Na_5P_3O_{10}$; on the contrary, the P(2)–O(7)–P(3) angle, 146°, is much larger. The asymmetric shape of the triphosphate chain in $KThP_3O_{10}$ is due to different contributions of the oxygen atoms in the formation of coordination polyhedra. Terminal oxygen atoms from the neighbouring P(1) and P(2) tetrahedra are engaged in pairs [O(1) and O(5); O(2) and O(6)] to two thorium polyhedra, while the remaining atom O(3) to the third (Figure 1). The oxygen atoms from P(2) and P(3) tetrahedra are coordinated to five different dodecahedra.

Potassium environment

The potassium atom is surrounded by eight oxygen atoms disposed at the corners of irregular polyhedron. Potassium–oxygen contacts with the values from 2.76 Å to 3.24 Å indicate their electrostatic character.

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