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Preliminary Communication

Preparation and Structure of Disodium Thorium Bisphosphate, $Na_2Th(PO_4)_2$

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$Na_2Th(PO_4)_2$ was investigated as a part of our study in the structure chemistry of alkali thorium and zirconium orthophosphates[1–3].

SYNTHESIS

The preparation of $Na_2Th(PO_4)_2$, as described in literature,[4] could not be reproduced successfuly. The crystals used in this investigation were obtained by heating 1.3 : 1.0 : 3.0 molar mixture of $Na_4P_2O_7 \cdot 10H_2O$, ThO_2 and $NaPO_3$ (as flux) in a platinum crucible at 900 °C for six hours. In order to obtain larger single crystals, convenient for crystal studies, the furnace was kept for 72 hours at 900 °C and then cooled slowly (90 K per day) to 500 °C. The crystals were separated from the matrix by dissolving the solubles in boiling water. The formula of the compound was proved from analytical data:

$Na_2Th(PO_4)_2$ calc'd: 9.83% Na; 49.58% Th; 13.24% P
found: 9.80% Na; 49.40% Th; 12.96% P.

Disodium thorium bisphosphate is insoluble in water, but soluble in inorganic acids. If the heating temperature during the synthesis is higher the more stable compound[3] $NaTh_2(PO_4)_3$, will be obtained, even at the same molar ratio of starting materials.

CRYSTAL DATA AND STRUCTURE

The crystals of disodium thorium bisphosphate are monoclinic, with $a = 7.01\ (1)$, $b = 21.50\ (3)$, $c = 9.12\ (1)$ Å, $\beta = 111.0^0\ (0.3)$; $d_c = 4.84$ and $d_m = 4.85$ g/cm^3. The piezo-electric effect was not detected. The space group is C2/c with $Z = 8$. The crystal data were obtained from oscillation and Weissenberg photographs.

The structure has been determined using 795 independent non-zero hk0—hk5 reflections recorded on multiple film Weissenberg photographs and solved by Patterson and three-dimensional electron density synthesis followed by least squares refinement. The structure of $Na_2Th(PO_4)_2$ is composed of discrete PO_4 groups with oxygen atoms attached also to thorium and sodium atoms in the shape of very distorted polyhedra. There are two thorium atoms which occupy special positions (4e) on the two-fold axes in the space group C2/c; two sodium, two phosphorus and eight oxygen atoms are in general positions (8f). Th (1) atom is surrounded by ten oxygen atoms and Th (2) atom is eight coordinated (Fig. 1 and Table I).

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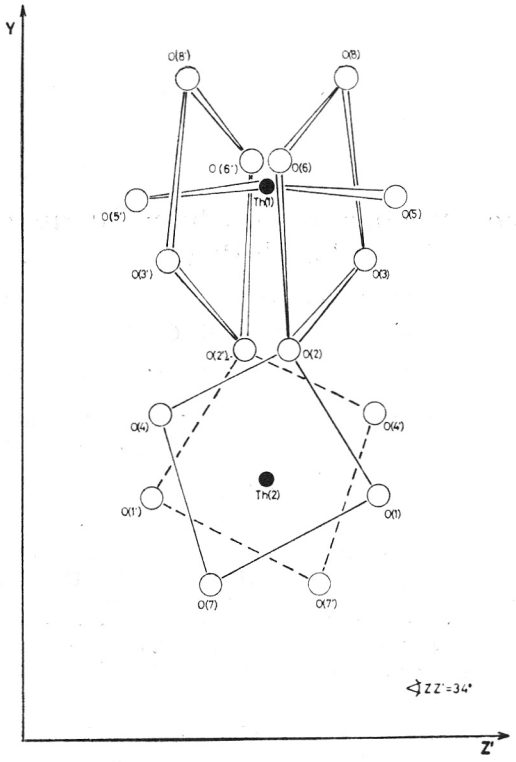

Fig. 1. The projection of thorium polyhedra onto the YZ' plane.

TABLE I.

Interatomic distances/Å and angles within thorium polyhedra. Primed number denotes the atom related by symmetry operation of twofold axis

A	B	C	A—B	B—C	A—B—C
O(2)	Th(1)	O(8)	3.00(4)	2.34(6)	139(2)°
O(3)	Th(1)	O(6)	2.38(5)	2.48(4)	122(2)°
O(5)	Th(1)	O(5′)	2.47(7)	2.47(7)	171(1)°
O(1)	Th(2)	O(4)	2.29(7)	2.40(5)	115(2)°
O(2)	Th(2)	O(7)	2.54(4)	2.28(4)	117(1)°

The oxygen atoms from two symmetrically independent phosphate tetrahedra coordinate thorium atoms in the following way: the P (1) tetrahedron acts as bidendate ligand both to Th (1) and Th (2) atoms and as a monodentate ligand to symmetrically related Th (2) atom. The P (2) tetrahedron is bidendate ligand to Th (1) and monodendate to Th (2) and to symmetrically related Th (1) atom. The bond lengths and angles in PO_4 groups do not deviate significantly from the results obtained earlier. Both sodium atoms are surrounded by nine oxygen atoms in the range from 2.39 to 3.09 Å. The present

R value determined on the basis of isotropic temperature factors is 12.4%. Further refinement of the structure is in course.

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SAŽETAK

Preparacija i struktura dinatrij—torij—bisfosfata, $Na_2Th(PO_4)_2$

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Opisana je preparacija dinatrij—torij—bisfosfata. Kristali toga spoja monoklinski su s $a = 7.01(1)$, $b = 21.50(3)$, $c = 9.12(1)$, Å, $\beta = 111.0(0.3)^0$; $d_c = 4.84$, a $d_m = 4.85$ g/cm^3. Prostorna grupa je C2/c sa $Z = 8$. Struktura je rješavana iz trodimenzionalnih rendgenskih podataka. Udaljenosti torij—kisik variraju od 2.29 do 2.54 (3.00) Å, a natrij—kisik od 2.39 do 3.09 Å. Udaljenosti u PO_4-skupinama ne razlikuju se bitno od poznatih podataka. Utočnjavanje strukture je u toku.

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