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# THORIUM ORTHOPHOSPHATES

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## Abstract

## Full Text

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## CHEMISTRY

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## THORIUM ORTHOPHOSPHATES

(Presented by Academician I. I. Chernyayev, 26 IV 1965)

Thorium with the orthophosphate ion can give several types of salts: normal thorium phosphate  $\text{Th}_3(\text{PO}_4)_4 \cdot n\text{H}_2\text{O}$  <sup>(1,3,9)</sup>, acid phosphates  $\text{Th}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ ,  $\text{Th}(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  <sup>(4,5)</sup>, and compounds of the double-salt type:  $\text{Na}_2\text{O} \cdot 4\text{ThO}_2 \cdot 3\text{P}_2\text{O}_5$ ;  $\text{Na}_2\text{O} \cdot \text{ThO}_2 \cdot \text{P}_2\text{O}_5$ ;  $5\text{Na}_2\text{O} \cdot 2\text{ThO}_2 \cdot 3\text{P}_2\text{O}_5$ ;  $\text{K}_2\text{O} \cdot 4\text{ThO}_2 \cdot 3\text{P}_2\text{O}_5$ ;  $\text{K}_2\text{O} \cdot \text{ThO}_2 \cdot \text{P}_2\text{O}_5$ ;  $6\text{K}_2\text{O} \cdot 3\text{ThO}_2 \cdot 4\text{P}_2\text{O}_5$  <sup>(6,7)</sup>. The latter, apparently, are complex compounds of the following composition:  $\text{NaTh}_2(\text{PO}_4)_3$ ;  $\text{Na}_2\text{Th}(\text{PO}_4)_2$ ;  $\text{Na}_5\text{Th}(\text{PO}_4)_3$ ;  $\text{KTh}_2(\text{PO}_4)_3$ ;  $\text{KTh}(\text{PO}_4)_2$ , and  $\text{K}_{12}\text{Th}_3(\text{PO}_4)_8$ , respectively.

Phosphates of a similar type were also obtained with alkaline-earth metals ( $\text{MeO} \cdot \text{ThO}_2 \cdot \text{P}_2\text{O}_5$ , where  $\text{Me} = \text{Ca}, \text{Sr}, \text{Ba}$ ) <sup>(8)</sup>. All compounds of alkali and alkaline-earth metals were synthesized by fusing thorium oxide or chloride with phosphates of the corresponding metals.

In the literature we found no indications of other methods for obtaining thorium phosphate complexes and, in particular, of the possibility of isolating them from aqueous solutions. In this connection, we undertook an investigation, by physicochemical analysis methods, of several aqueous systems containing thorium and phosphate ion. In addition, we attempted to synthesize certain thorium phosphate complexes from aqueous saturated solutions of alkali-metal and ammonium phosphates.

In equimolar (0.01 M) series of the systems  $\text{Th}(\text{NO}_3)_4\text{—H}_3\text{PO}_4\text{—H}_2\text{O}$ ,  $\text{Th}(\text{NO}_3)_4\text{—NaH}_2\text{PO}_4\text{—H}_2\text{O}$ , and  $\text{Th}(\text{NO}_3)_4\text{—Na}_2\text{HPO}_4\text{—H}_2\text{O}$ , the specific electrical conductivity, pH, and thorium content in the liquid phase were measured. At the extremal points the solid phase was studied.

As the results of the investigation showed, in the first two systems the conductivity and pH curves have one extremum, corresponding to the formation of the neutral thorium phosphate  $\text{Th}_3(\text{PO}_4)_4 \cdot n\text{H}_2\text{O}$ . Analysis of the isolated solid phase also corresponds to this compound (see Table 1).

### Table 1

### Results of the analysis of thorium phosphates

Compound	Found, % Th	Found, % P	Found, % Me*	Calculated, % Th	Calculated, % P	Calculated, % Me*
$\text{Th}_3(\text{PO}_4)_4 \cdot 15\text{H}_2\text{O}$	15.30	9.67	—	50.03	9.69	—
$\text{NaTh}_2(\text{PO}_4)_3 \cdot 4.5\text{H}_2\text{O}$	43.08	9.00	2.68	43.08	8.63	2.14
$(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot 2.85\text{H}_2\text{O}$	41.78	11.84	5.25	42.33	11.30	5.11
$\text{KTh}(\text{PO}_4)(\text{OH})_2 \cdot 3.5\text{H}_2\text{O}$	50.09	6.72	8.92	50.09	6.68	8.44
$\text{NaTh}(\text{PO}_4)(\text{OH})_2 \cdot 4.5\text{H}_2\text{O}$	49.89	6.35	4.87	49.89	6.65	4.94

\* Me = N, K, Na.

Investigation of the liquid phase showed that, as the amount of phosphate ion in the solution increases, the concentration of thorium decreases and at the extremal point (ratio  $\text{PO}_4^{3-}/\text{Th}^{4+} = 1.33$ ) is equal to zero. Further increase

an increase in the concentration of phosphate ion in the liquid phase does not affect the quantitative precipitation of thorium or the composition of the solid phase. In the system  $\text{Th}(\text{NO}_3)_4\text{--Na}_2\text{HPO}_4\text{--H}_2\text{O}$  there is a gradual change in the specific electrical conductivity and pH within the range of the ratio  $\text{PO}_4^{3-}/\text{Th}^{4+}$  from 0 to 1.3, and simultaneous formation of a solid phase is observed; moreover, quantitative precipitation of thorium occurs at the ratio of  $\text{PO}_4^{3-}$  to  $\text{Th}^{4+}$  corresponding to the formation of  $\text{Th}_3(\text{PO}_4)_4$ . Within the range of the ratio  $\text{PO}_4^{3-}/\text{Th}^{4+} = 1.33\text{--}2.5$ , a sharp decrease in electrical conductivity is noted, without a change in the concentration of thorium in the solution, which indicates further coordination of the phosphate ion by the thorium orthophosphate precipitate. This is confirmed by analysis of the solid phase, whose composition corresponds to the compound  $\text{NaTh}_2(\text{PO}_4)_3 \cdot n\text{H}_2\text{O}$  (see Table 1).

In the systems studied, we were unable to observe the formation of any other thorium phosphates, and we turned to the study of the reactions of thorium nitrate with phosphates of alkali metals in concentrated (with respect to phosphate ion) aqueous solutions.

It was established that, when an approximately 70% aqueous solution of thorium nitrate is mixed with a twentyfold excess of saturated solutions of trisubstituted ammonium and sodium phosphates and disubstituted potassium phosphate, white, readily filterable precipitates are formed. According to chemical analysis (Table 1), in the air-dry state the latter have the compositions:  $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ ,  $\text{NaTh}(\text{PO}_4)(\text{OH})_2 \cdot 4.5\text{H}_2\text{O}$ , and  $\text{KTh}(\text{PO}_4)(\text{OH})_2 \cdot 3.5\text{H}_2\text{O}$ . The individuality of the thorium phosphate complexes obtained was confirmed by repeated reproduction of the synthesis, by thermography, and by recording infrared absorption spectra.

All the synthesized phosphorus-containing thorium compounds are stable in air, practically insoluble in water and in organic solvents, and sparingly soluble in solutions of mineral acids.

In contrast to thorium orthophosphate  $\text{Th}_3(\text{PO}_4)_4 \cdot 17\text{H}_2\text{O}$ , from which removal of water is difficult and occurs over a broad temperature interval (100–800°), dehydration of  $\text{NaTh}_2(\text{PO}_4)_3 \cdot 17\text{H}_2\text{O}$ ;  $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ ;  $\text{NaThPO}_4(\text{OH})_2 \cdot 4.5\text{H}_2\text{O}$  and  $\text{KTh}(\text{PO}_4)(\text{OH})_2 \cdot 3.5\text{H}_2\text{O}$  is accomplished on heating to ~450°.

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*Note: Figure translations are in progress. See original paper for figures.*

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