

Preparation and Crystallographic Characterization of the Polyphosphate TIPO₃

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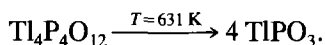
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Chemical preparation and crystallographic data are specified for thallium polyphosphate. TIPO₃ crystallizes in the monoclinic system, space group $P2_1/n$, with the following unit-cell parameters: $a = 12.270(7)$ Å; $b = 4.263(2)$ Å; $c = 6.328(4)$ Å; $\beta = 96^\circ.72(3)$; $Z = 4$. This compound is isotypic with two previously described polyphosphates, namely RbPO₃ and CsPO₃. © 1991 Academic Press, Inc.

Introduction

Crystallographic studies have been carried out for two thallium condensed phosphates: the cyclotetraphosphate Tl₄P₄O₁₂ (1) and the cyclotriphosphate Tl₃P₃O₉ (2). These two compounds are transformed, by heating, to a long-chain polyphosphate, TIPO₃ (3). The transformations are not reversible and proceed according to the process:



TIPO₃ has not been studied up to now.

Chemical Preparation

During experiments made to prepare a thallium–lithium phosphate, TIPO₃ single crystals were obtained accidentally in a flux containing 0.546 g of Li₂CO₃, 14 g of Tl₂CO₃, and 4.5 cm³ of H₃PO₄ heated at 473 K for 3 days. Crystals of TIPO₃ grow as needles.

Powder samples were prepared from a stoichiometric mixture of Tl₂CO₃ and

(NH₄)₂HPO₄. The initial heating temperature was 523 K and produced an amorphous material which crystallized after calcination at 573 K for 4 days.

Crystallographic Study

Single crystal study by the Weissenberg technique shows this compound to be isotypic with the two polyphosphates CsPO₃ (4) and RbPO₃ (5).

The powdered sample was studied by X-ray diffraction. Data were recorded with a Philips Norelco diffractometer using copper $K\alpha_{1,2}$ radiation and operating at a low scan speed [$1/8^\circ(\theta) \text{ min}^{-1}$]. An indexed powder diagram is provided in Table I. Intensities reported in this table are peak heights above the background. Unit-cell dimensions refinement was obtained from a least squares refinement using the angular data of the powder diffractogram. Table II compares the crystallographic constants of TIPO₃ with those of CsPO₃ and RbPO₃. It reveals that these three condensed phosphates are isotypic.

TABLE I
INDEXED POWDER DIAGRAM FOR TIPO₃

<i>hkl</i>	<i>d</i> _{cal.}	<i>d</i> _{obs.}	<i>I</i> _{obs.}	<i>hkl</i>	<i>d</i> _{cal.}	<i>d</i> _{obs.}	<i>I</i> _{obs.}
200	6.09	6.09	14	311	2.581	2.580	4
101	5.87	5.88	12	112	2.524	2.524	9
101	5.34	5.33	26	410	2.479	2.480	23
110	4.02	4.02	15	212	2.418	2.417	21
301	3.609	3.610	57	411	2.385	2.385	6
210	3.493	3.494	37	501	2.368	2.370	7
111	3.450	3.450	38	402	2.328	2.327	6
111	3.331	3.330	18	212	2.262	2.262	15
301	3.243	3.244	13	510	2.116	2.116	10
211	3.144	3.143	100	120	2.100	2.098	6
400	3.046	3.045	24	511	2.070	2.072	16
211	2.970	2.969	20	600	2.031	2.030	19
202	2.936	2.936	25				

TABLE II
MAIN CRYSTALLOGRAPHIC FEATURES FOR TIPO₃, CsPO₃, AND RbPO₃

Polyphosphate	Space group	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	<i>Z</i>	Ref.
TIPO ₃	<i>P</i> 2 ₁ / <i>n</i>	12.270(7)	4.263(2)	6.328(4)	96.72(3)	4	This study
CsPO ₃	<i>P</i> 2 ₁ / <i>n</i>	12.71	4.32	6.83	97	4	(4)
RbPO ₃	<i>P</i> 2 ₁ / <i>n</i>	12.123(2)	4.228(2)	6.479(2)	96.3(3)	4	(5)

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