JOURNAL OF SOLID STATE CHEMISTRY 112, 96–99 (1994)

Synthesis and Crystal Structure of the Octahedral–Tetrahedral Framework Indium Phosphate $Cs[In_2(PO_4)(HPO_4)_2(H_2O)_2]$

Sandeep S. Dhingra and Robert C. Haushalter[1]

NEC Research Institute, 4 Independence Way, Princeton, New Jersey 08540

Received July 9, 1993; accepted November 11, 1993

The reaction of $InCl_3$, H_3PO_4, $CsVO_3$, TMAOH (tetramethyl ammonium hydroxide), and H_2O in the molar ratios 2 : 6 : 1 : 1 : 125 under hydrothermal conditions at 200°C for 2 days yielded pale yellow crystals of $Cs[In_2(PO_4)(HPO_4)_2(H_2O)_2]$ (1). Phosphate (1) crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with a = 6.580(2) Å, b = 18.092(1) Å, c = 10.180(1) Å, β = 97.92(2)°, V = 1200.2(4) Å^3, Z = 4, and D_{cal} = 3.76 g cm^{-3}; R/R_w = 0.036/0.044 for 2855 reflections with $2\theta < 60.1°$ and $I \geq 3\sigma(I)$. The framework consists of corner-sharing indium octahedra and phosphate tetrahedra that form one-dimensional ribbons extending down the c axis, parallel to the crystallographic (100) plane, which interconnect to form the three-dimensional structure. The framework has large cavities in which the Cs^+ cations reside. © 1994 Academic Press, Inc.

INTRODUCTION

The increasing interest in the synthesis and structural characterization of novel metal phosphates is due largely to the diversity of structure types and abundance of metal phosphate framework compounds as well as to their potential as absorbents and as supports for catalytically active metals (1). Many inorganic phosphates with intriguing structures have been synthesized, and some possess notable ion exchange or interlayer ionic mobility (2). The largest class of phosphate open framework materials is the tetrahedral aluminophosphates (3). In the past decade a large number of aluminophosphates (3) and gallophosphates (4) have been synthesized and structurally characterized but there is very scant information on indium phosphates in the literature. The desire to incorporate sites more reactive than the main group metal cations has led to a variety of phosphate structural types containing mixed octahedral–tetrahedral frameworks (5). The heavier main group phosphates are rare and prior to our work there was only one structurally characterized indium phosphate, $Li_3[In_2(PO_4)_3]$ (6, 7). We recently reported the synthesis and novel structure of $H_3NCH_2CH_2NH_3[In_2(HPO_4)_4]$ (8), the first organically templated indium phosphate. We report here the synthesis and X-ray crystal structure of the octahedral–tetrahedral framework of an aquo-coordinated cesium indium phosphate, $Cs[In_2(PO_4)(HPO_4)_2(H_2O)_2]$ (1).

[1] To whom correspondence should be addressed.

EXPERIMENTAL

Compound 1 was synthesized by the hydrothermal method in an aqueous mixture of 2.0 $InCl_3$ (0.2 g) : 6 H_3PO_4 : 1 $CsVO_3$: 1 TMAOH : 125 H_2O and was heated at 200°C for 2 days in a 23-ml polytetrafluroethylene-coated acid digestion bomb (yield 50%). Large transparent pale yellow crystals were filtered off, washed thoroughly with water, and dried at room temperature. The product is not single phase but has 15% by weight of pale blue impurities of a vanadium phosphate. The presence of Cs, In, and P was determined by energy-dispersive X-ray analysis. Subsequent reactions with CsCl, CsOH, and Cs_2CO_3 instead of $CsVO_3$ did not yield the desired product. The

TABLE 1
Summary of Crystallographic Data for $Cs[In_2(PO_4)(HPO_4)_2(H_2O)_2]$

Compound	$Cs[In_2(PO_4)(HPO_4)_2(H_2O)_2]$
Formula	$CsIn_2P_3O_{14}H_4$
FW	685.51
Crystal color, habit	Pale yellow, prism
a (Å)	6.580(2)
b (Å)	18.092(1)
c (Å)	10.180(1)
β (°)	97.92(2)
V (Å^3)	1200.2(4)
Z	4
Space group	$P2_1/c$ (No. 14)
D_{cal} (g cm^{-3})	3.76
μ (cm^{-1})	73.03 (Mo$K\alpha$)
Crystal size (mm)	0.20 × 0.20 × 0.20
$2\theta_{max}$ (°)	60.1
No. of data collected	3943
Data $I \geq 3\sigma(I)$	2855
No. of variables	181
Final R/R_w (%)	3.6/4.4

0022-4596/94 $6.00
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TABLE 2
Fractional Atomic Coordinates and B_{eq} Values for $Cs[In_2(PO_4)(HPO_4)_2(H_2O)_2]$ with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}
Cs(1)	0.79928(8)	0.19859(3)	0.52948(6)	1.97(2)
In(1)	1.28878(7)	0.14093(3)	0.82299(5)	0.69(2)
In(2)	0.23292(7)	0.04655(3)	0.31482(5)	0.73(2)
P(1)	0.8023(3)	0.1079(1)	0.8724(2)	0.73(6)
P(2)	0.2527(3)	−0.0133(1)	0.6287(2)	0.62(6)
P(3)	0.3281(3)	0.3018(1)	0.6397(2)	0.63(6)
O(1)	0.9764(8)	0.1541(3)	0.8342(6)	1.3(2)
O(2)	0.8001(8)	0.1175(3)	1.0285(5)	1.4(2)
O(3)	0.6006(7)	0.1381(3)	0.8034(5)	1.2(2)
O(4)	0.8328(8)	0.0256(3)	0.8492(5)	1.2(2)
O(5)	0.2683(8)	−0.0236(3)	0.4795(5)	1.0(2)
O(6)	0.2188(8)	0.0697(3)	0.6563(5)	1.0(2)
O(7)	0.4520(7)	−0.0412(3)	0.7152(5)	1.0(2)
O(8)	0.0805(7)	−0.0613(3)	0.6695(5)	1.2(2)
O(9)	0.5495(7)	0.3138(3)	0.7179(5)	1.2(2)
O(10)	0.1962(7)	0.3696(3)	0.6596(5)	0.9(2)
O(11)	0.3468(8)	0.2899(3)	0.4929(5)	1.0(2)
O(12)	0.2438(8)	0.2322(3)	0.6936(5)	1.2(2)
O(13)	1.3259(8)	0.0414(3)	0.9426(5)	1.4(2)
O(14)	0.312(1)	0.1402(3)	0.4509(5)	1.7(2)

experimental single-crystal X-ray data are summarized in Table 1 and the fractional atomic coordinates, along with the isotropic thermal parameters, of all the atoms are given in Table 2. Selected bond distances and angles are compiled in Tables 3 and 4.

RESULTS AND DISCUSSION

Single-crystal X-ray diffraction revealed the complicated octahedral–tetrahedral framework of **1**, which is built up from a relatively simple structural motif. The asymmetric unit is shown in Fig. 1 and consists of two crystallographically unique indium atoms in a slightly distorted (InO_6) octahedral geometry with the In–O bond lengths falling in the range 2.088 to 2.205 Å. Of the six oxo ligands on each In, five contact PO_4 tetrahedra, with the remaining vertex coming from the aquo ligand O(13) and O(14) (coordinated to In(1) and In(2), respectively). Two of the three unique phosphorus sites (P(1) and P(3)) are present as $(HPO_4)^{2-}$ units, sharing three oxygen atoms with each of the three adjacent indium atoms. The long P–O bond and the lack of coordination to In clearly distinguish the protonated oxygen site on the two $(HPO_4)^{2-}$ units (see Table 3). The third phosphorus center (P(2)) is present as $(PO_4)^{3-}$ with oxygens bridging to each of the four adjacent indium sites.

Expansion of the asymmetric unit along the crystallographic c axis in the bc plane yields a one-dimensional ribbon as shown in Fig. 2. The aquo ligands on the InO_6 octahedra lie in the plane of the ribbons and the tetrahedral $(HPO_4)^{2-}$ unit, P(3), shares its three oxygens only with

TABLE 3
Selected Bond Distances (Å) in $Cs[In_2(PO_4)(HPO_4)_2(H_2O)_2]$ with Their Standard Deviations in Parentheses

Cs(1)–O(1)	3.612(6)	In(2)–O(4)	2.117(5)
Cs(1)–O(1)	3.261(6)	In(2)–O(5)	2.090(5)
Cs(1)–O(2)	3.328(6)	In(2)–O(7)	2.139(5)
Cs(1)–O(3)	3.419(5)	In(2)–O(8)	2.107(5)
Cs(1)–O(5)	3.196(5)	In(2)–O(10)	2.180(5)
Cs(1)–O(8)	3.367(6)	In(2)–O(14)	2.205(6)
Cs(1)–O(9)	3.405(5)	P(1)–O(1)	1.511(5)
Cs(1)–O(9)	3.373(5)	P(1)–O(2)	1.601(6)
Cs(1)–O(11)	3.380(5)	P(1)–O(3)	1.515(5)
Cs(1)–O(12)	3.220(5)	P(1)–O(4)	1.524(6)
Cs(1)–O(14)	3.364(6)	P(2)–O(5)	1.548(5)
In(1)–O(1)	2.088(5)	P(2)–O(6)	1.550(5)
In(1)–O(3)	2.089(5)	P(2)–O(7)	1.559(5)
In(1)–O(6)	2.130(5)	P(2)–O(8)	1.530(5)
In(1)–O(11)	2.126(5)	P(3)–O(9)	1.577(5)
In(1)–O(12)	2.108(5)	P(3)–O(10)	1.531(5)
In(1)–O(13)	2.168(5)	P(3)–O(11)	1.532(5)
		P(3)–O(12)	1.509(5)

TABLE 4
Selected Bond Angles (°) in $Cs[In_2(PO_4)(HPO_4)_2(H_2O)_2]$ with Their Standard Deviations in Parentheses

O(1)–In(1)–O(3)	174.4(2)	O(4)–In(2)–O(5)	104.2(2)
O(1)–In(1)–O(6)	90.4(2)	O(4)–In(2)–O(7)	87.5(2)
O(1)–In(1)–O(11)	87.5(2)	O(4)–In(2)–O(8)	92.4(2)
O(1)–In(1)–O(12)	83.7(2)	O(4)–In(2)–O(10)	82.4(2)
O(1)–In(1)–O(13)	95.7(2)	O(4)–In(2)–O(14)	167.0(2)
O(3)–In(1)–O(11)	91.4(2)	O(5)–In(2)–O(7)	94.8(2)
O(3)–In(1)–O(12)	90.9(2)	O(5)–In(2)–O(8)	91.0(2)
O(3)–In(1)–O(13)	89.8(2)	O(5)–In(2)–O(10)	173.3(2)
O(3)–In(1)–O(6)	90.9(2)	O(5)–In(2)–O(14)	88.4(2)
O(6)–In(1)–O(11)	177.4(2)	O(7)–In(2)–O(8)	174.0(2)
O(6)–In(1)–O(12)	88.9(2)	O(7)–In(2)–O(10)	86.6(2)
O(6)–In(1)–O(13)	86.6(2)	O(7)–In(2)–O(14)	88.5(2)
O(11)–In(1)–O(12)	92.4(2)	O(8)–In(2)–O(10)	87.4(2)
O(11)–In(1)–O(13)	92.2(2)	O(8)–In(2)–O(14)	90.2(2)
O(12)–In(1)–O(13)	175.4(2)	O(10)–In(2)–O(14)	85.1(2)
O(1)–P(1)–O(2)	107.8(3)	O(5)–P(2)–O(6)	109.0(3)
O(1)–P(1)–O(3)	109.2(3)	O(5)–P(2)–O(7)	110.5(3)
O(1)–P(1)–O(4)	112.3(3)	O(5)–P(2)–O(8)	110.5(3)
O(2)–P(1)–O(3)	107.1(3)	O(6)–P(2)–O(7)	110.0(3)
O(2)–P(1)–O(4)	106.2(3)	O(6)–P(2)–O(8)	111.7(3)
O(3)–P(1)–O(4)	113.9(3)	O(7)–P(2)–O(8)	105.1(3)
O(9)–P(3)–O(10)	108.9(3)		
O(9)–P(3)–O(11)	108.6(3)		
O(9)–P(3)–O(12)	106.9(3)		
O(10)–P(3)–O(11)	111.4(3)		
O(10)–P(3)–O(12)	112.1(3)		
O(11)–P(3)–O(12)	108.7(3)		
In(1)–O(1)–P(1)	137.5(3)	In(2)–O(4)–P(1)	135.0(3)
In(1)–O(3)–P(1)	140.7(3)	In(2)–O(5)–P(2)	134.3(3)
In(1)–O(6)–P(2)	135.3(3)	In(2)–O(7)–P(2)	133.7(3)
In(1)–O(11)–P(3)	132.9(3)	In(2)–O(8)–P(2)	135.9(3)
In(1)–O(12)–P(3)	148.7(3)	In(2)–O(10)–P(3)	130.2(3)

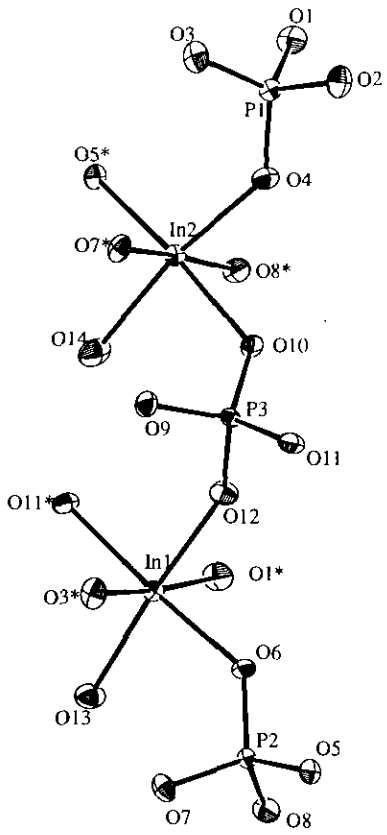

FIG. 1. ORTEP representation of the asymmetric unit of the anionic framework in $Cs[In_2(PO_4)(HPO_4)_2(H_2O)_2]$.

the indium octahedra of the ribbons. The other $(HPO_4)^{2-}$ unit, P(1), shares only one oxygen with an InO_6 octahedron with the remaining two O atoms shared with the ribbons above and below. Similarly, the phosphorus center (P(2)) present as the $(PO_4)^{3-}$ unit shares two of its oxygen atoms within the ribbons and the other two with the ribbons above and below. Thus the three-dimensional structure can be envisioned as the interconnection of these ribbons, propagating down the *c* axis, with four other ribbons which are generated by a *c* glide. This mode of connectivity is illustrated in Fig. 3, which is a view perpendicular to the crystallographic (001) plane.

The framework has large voids in which the Cs^+ ions are trapped as charge-compensating countercations. There are 10 short ionic contacts between the Cs^+ and the oxygen sites of the anionic framework, in the range 3.196 to 3.419 Å (see Table 3 for details), and 1 long contact of 3.612 Å, contributing 5% to the total valence sum of 1.03 for the cesium ion. The environment around the cesium cation is shown in Fig. 4.

The title compound was found to be isostructural to a cesium vanadium(III) phosphate recently synthesized (9). The necessity of $CsVO_3$ in the synthesis could perhaps be rationalized by the aforementioned vanadium phosphate providing the nucleation sites for the crystallization of the cesium indium phosphate. While there were no large amounts of V present in (**1**), trace amounts of vanadium in (**1**) cannot be completely ruled out because the peaks for Cs and V overlap in the EDX analysis.

In summary, the structure of the three-dimensional

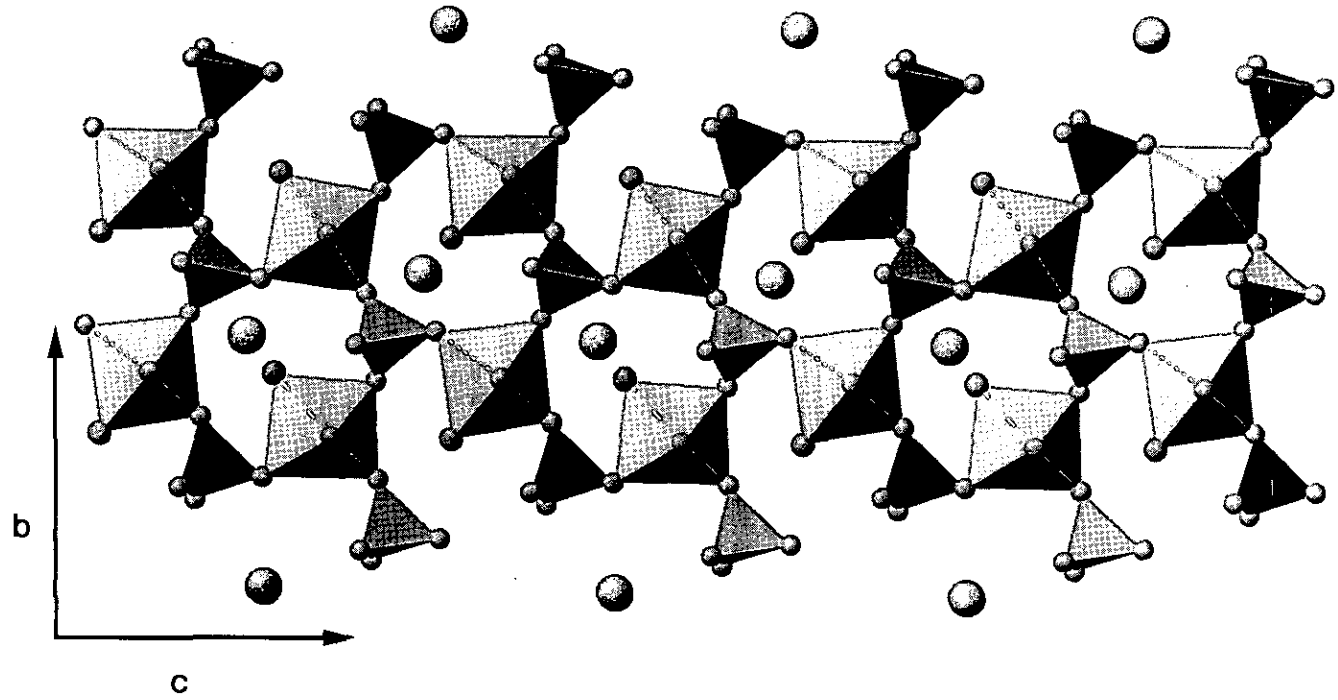

FIG. 2. Polyhedral drawing of the one-dimensional ribbon showing the connectivity of the indium octahedra and the phosphorus tetrahedra. The view is perpendicular to the (100) plane.

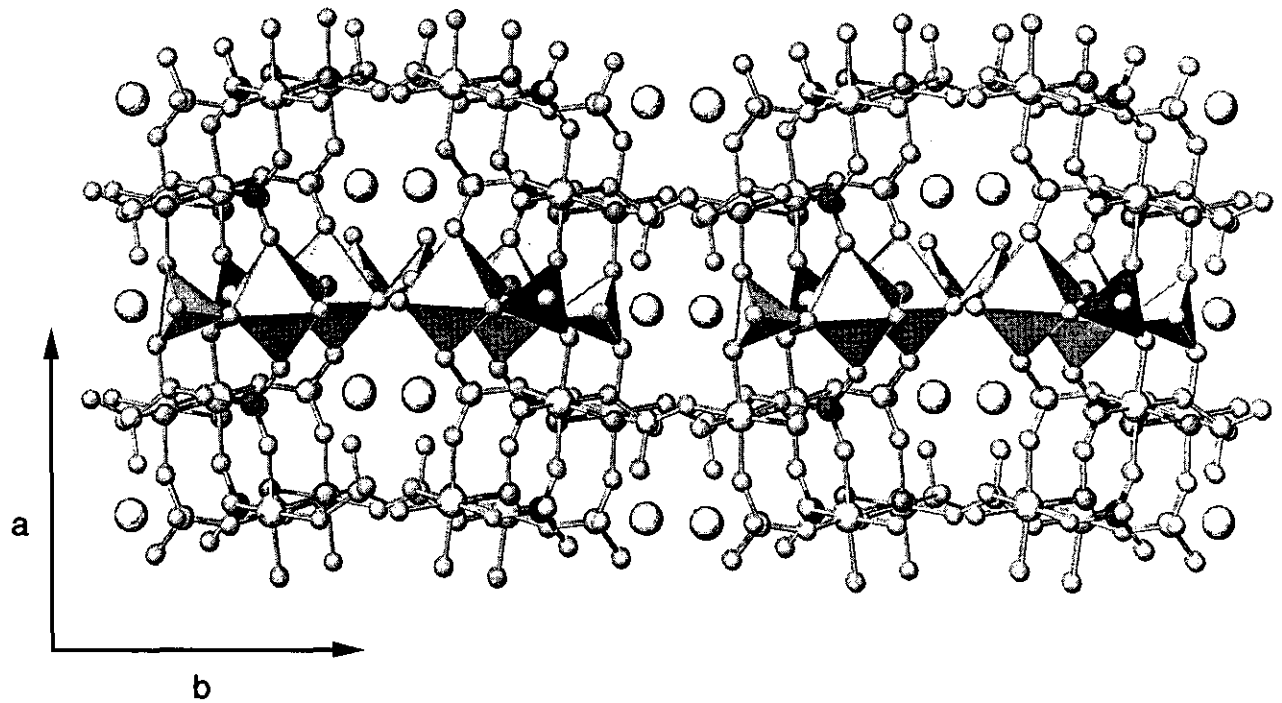

FIG. 3. View of the framework depicting the interconnection of the ribbons, shown in Fig. 2, that run parallel to [001] to form the three-dimensional solid. The view is perpendicular to the (001) plane.

framework cesium indium phosphate $Cs[In_2(PO_4)(HPO_4)_2(H_2O)_2]$ shows that complicated structures can be synthesized by simple octahedral–tetrahedral structural motifs. The aquo ligand coordinated to the metal center is in fact very rare and further investigation of the indium phosphate system appears likely to exhibit new structure types and coordination environments around the metal.

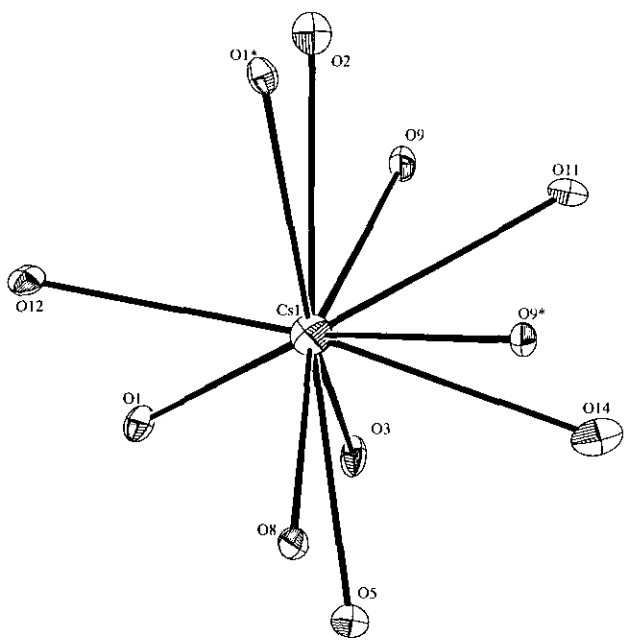

FIG. 4. ORTEP representation of the coordination environment around the Cs^+ cation.

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