

Crystal Structures and Optical Properties of Two Layered Lead Halide Phosphites $\text{Pb}_3(\text{HPO}_3)\text{Cl}_4 \cdot \text{H}_2\text{O}$ and $\text{Pb}_3(\text{HPO}_3)_2\text{Cl}_2 \cdot \text{H}_2\text{O}$

Zong-Jie Zhao,^{a,c} Yu-Zheng Yan,^b Jia-Jian Fu,^a Hong-Yan Wu,^a Jian-Han Zhang^{*a,c}

a. School of Resources & Chemical Engineering, Sanming University, Sanming, 365004, PR China

b. Straits Institute of Technology, Sanming University, Sanming, 365004, PR China

c. College of Chemical Engineering, Fuzhou University, Fuzhou, 350000, PR China

Table S1. Selected Bond lengths for $\text{Pb}_3(\text{HPO}_3)\text{Cl}_4 \cdot \text{H}_2\text{O}$ and $\text{Pb}_3(\text{HPO}_3)_2\text{Cl}_2 \cdot \text{H}_2\text{O}$.

Compound	Atom-Atom	Length(Å)	Atom-Atom	Length(Å)	
$\text{Pb}_3(\text{HPO}_3)\text{Cl}_4 \cdot \text{H}_2\text{O}$	P1-O2	1.547(7)	Pb3-Cl2f	3.081(3)	
	P1-O3	1.529(7)	Pb3-Cl3g	3.127(2)	
	P1-O1	1.525(6)	Pb3-Cl3f	3.441(2)	
	P2-O5	1.546(7)	Pb4-O4	2.519(7)	
	P2-O6	1.522(7)	Pb4-O5	2.885(7)	
	P2-O4	1.515(6)	Pb4-Cl6	2.930(3)	
	Pb1-O1	2.575(6)	Pb4-Cl4	2.966(2)	
	Pb1-O2	2.911(6)	Pb4-Cl5	2.980(2)	
	Pb1-Cl1	2.952(2)	Pb4-Cl8h	3.078(3)	
	Pb1-Cl7a	2.978(2)	Pb4-Cl1i	3.114(3)	
	Pb1-Cl2	2.980(3)	Pb4-Cl5d	3.159(2)	
	Pb1-Cl2b	3.014(3)	Pb5-O4	2.400(6)	
	Pb1-Cl3	3.022(2)	Pb5-O6h	2.553(6)	
	Pb1-Cl8a	3.070(3)	Pb5-O5h	2.560(7)	
	Pb2-O1	2.380(6)	Pb5-O8	2.862(8)	
	Pb2-O3c	2.509(6)	Pb5-O7	2.951(7)	
	Pb2-O2c	2.671(7)	Pb5-Cl7	2.922(2)	
	Pb2-O7	2.771(7)	Pb5-Cl5	3.104(2)	
	Pb2-O8	2.877(7)	Pb5-Cl1b	3.181(2)	
	Pb2-Cl3	2.972(3)	Pb5-Cl3	3.372(3)	
	Pb2-Cl4d	2.995(2)	Pb6-O6	2.499(7)	
	Pb2-Cl5	3.347(2)	Pb6-O5h	2.710(7)	
	Pb2-Cl8e	3.246(2)	Pb6-Cl8	2.965(3)	
	Pb3-O3	2.434(6)	Pb6-Cl4h	3.004(2)	
	Pb3-O2c	2.520(7)	Pb6-Cl7	3.030(3)	
	Pb3-Cl4d	2.994(3)	Pb6-Cl5j	3.061(2)	
	Pb3-Cl1c	3.029(3)	Pb6-Cl6h	3.123(3)	
	Pb3-Cl7f	3.034(2)	Pb6-Cl6k	3.173(2)	
	a: $1-x, 1-y, 1-z$; b: $1-x, -y, 1-z$; c: $1/2-x, 1/2+y, 1/2-z$; d: $-x, 1-y, 1-z$; e: $-1/2+x, 3/2-y, -1/2+z$; f: $-1/2+x, 1/2-y, -1/2+z$; g: $1/2-x, -1/2+y, 1/2-z$; h: $1/2-x, -1/2+y, 3/2-z$; i: $-1/2+x, 1/2-y, 1/2+z$; j: $1/2-x, 1/2+y, 3/2-z$; k: $1/2+x, 3/2-y, 1/2+z$.				
	Compound	Atom-Atom	Length(Å)	Atom-Atom	Length(Å)
	$\text{Pb}_3(\text{HPO}_3)_2\text{Cl}_2 \cdot \text{H}_2\text{O}$	P1-O1	1.500(9)	Pb2-O2	2.450(6)
		P1-O2	1.531(6)	Pb2-O2b	2.451(6)
P1-O2a		1.531(6)	Pb2-Cl2f	3.129(2)	
P2-O3		1.499(9)	Pb2-Cl2g	3.129(2)	

	P2-O4	1.534(7)	Pb2-Cl1f	3.380(4)
	P2-O4b	1.534(7)	Pb3-O4	2.474(6)
	Pb1-O1c	2.395(9)	Pb3-O4h	2.474(6)
	Pb1-O2b	2.622(6)	Pb3-O5	2.763(2)
	Pb1-O2	2.622(6)	Pb3-Cl2	2.891(4)
	Pb1-O4d	2.700(6)	Pb3-Cl1	3.031(2)
	Pb1-O4e	2.700(6)	Pb3-Cl1i	3.031(2)
	Pb2-O3	2.327(9)	Pb3-Cl1j	3.077(4)

a: $x, 1/2-y, z$; **b:** $x, 3/2-y, z$; **c:** $2-x, 1/2+y, 1-z$; **d:** $1-x, -1/2+y, 1-z$; **e:** $1-x, 2-y, 1-z$; **f:** $1+x, y, z$; **g:** $1+x, -1+y, z$; **h:** $x, 5/2-y, z$; **i:** $x, 1+y, z$; **j:** $-x, 1/2+y, 2-z$.

Table S2. Selected bond angles for $\text{Pb}_3(\text{HPO}_3)\text{Cl}_4 \cdot \text{H}_2\text{O}$ and $\text{Pb}_3(\text{HPO}_3)_2\text{Cl}_2 \cdot \text{H}_2\text{O}$.

Compound	Atom-Atom-Atom	Angle(°)	Atom-Atom-Atom	Angle(°)
$\text{Pb}_3(\text{HPO}_3)\text{Cl}_4 \cdot \text{H}_2\text{O}$	O3-P1-O2	108.2(4)	O6-P2-O5	107.5(4)
	O1-P1-O2	109.4(4)	O4-P2-O5	109.7(4)
	O1-P1-O3	112.8(4)	O4-P2-O6	113.3(4)

a: $1/2-x, -1/2+y, 1/2-z$; **b:** $1/2-x, 1/2+y, 3/2-z$.

Compound	Atom-Atom-Atom	Angle(°)	Atom-Atom-Atom	Angle(°)
$\text{Pb}_3(\text{HPO}_3)_2\text{Cl}_2 \cdot \text{H}_2\text{O}$	O2a-P1-O2	111.8(5)	O4b-P2-O4	111.9(5)
	O1-P1-O2	111.6(3)	O3-P2-O4	109.9(3)
	O1-P1-O2a	111.6(3)	O3-P2-O4b	109.9(3)

a: $x, 1/2-y, +z$; **b:** $x, 3/2-y, +z$.

Table S3. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Pb}_3(\text{HPO}_3)\text{Cl}_4 \cdot \text{H}_2\text{O}$ and $\text{Pb}_3(\text{HPO}_3)_2\text{Cl}_2 \cdot \text{H}_2\text{O}$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Compound	Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})$
$\text{Pb}_3(\text{HPO}_3)\text{Cl}_4 \cdot \text{H}_2\text{O}$	Pb2	2190.3(2)	3423.7(5)	3826.2(2)	13.40(13)
	Pb5	2884.0(2)	4086.1(5)	6225.5(2)	13.23(13)
	Pb3	692.5(3)	1387.3(4)	1485.4(3)	14.79(12)
	Pb1	4536.9(3)	1136.2(5)	3644.3(3)	16.62(13)
	Pb4	568.3(3)	6363.8(5)	6348.2(3)	18.72(13)
	Pb6	4397.4(3)	6255.4(4)	8558.5(3)	16.71(13)
	P2	2468.4(16)	7986(3)	7056.0(16)	10.8(6)
	Cl4	-675.1(16)	8769(3)	6701.3(16)	14.4(6)
	Cl7	4400.0(16)	6144(3)	6719.5(16)	15.1(6)
	Cl3	4032.3(17)	3692(3)	4736.4(16)	16.1(6)
	P1	2573.7(15)	-400(3)	2940.3(16)	10.1(5)
	Cl1	5715.5(17)	-1341(3)	3265.8(17)	17.0(6)
	Cl5	972.3(16)	3806(3)	5240.9(16)	15.0(6)
	Cl2	5972.1(17)	1201(3)	5161.8(17)	18.0(6)
	Cl6	937.8(17)	8720(3)	5163.8(17)	18.9(6)
	Cl8	5624.6(18)	8728(3)	8247.4(17)	19.6(6)
	O2	3377(4)	-1351(7)	2823(4)	16.3(17)
	O7	2469(4)	1281(7)	5136(5)	22(2)
	O5	1656(4)	8888(7)	7186(4)	16.3(17)
	O8	2513(4)	6230(7)	4844(5)	25(2)
	O6	3098(4)	7865(8)	7899(4)	19.4(17)
	O3	1954(4)	-224(8)	2090(4)	16.1(16)
	O1	2866(4)	1192(7)	3347(4)	16.7(17)
	O4	2203(4)	6385(7)	6661(4)	17.4(17)
Compound	Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})$
$\text{Pb}_3(\text{HPO}_3)_2\text{Cl}_2 \cdot \text{H}_2\text{O}$	Pb3	999.6(7)	12500	8723.5(4)	15.57(19)
	Pb1	6432.6(7)	7500	3898.7(4)	17.26(19)
	Pb2	8111.3(7)	7500	6766.3(4)	16.27(19)
	P1	8338(5)	2500	5295(2)	9.1(7)
	Cl2	-2747(5)	12500	7713(2)	20.4(8)
	P2	3510(5)	7500	7570(2)	13.5(8)
	Cl1	-591(7)	7500	9125(3)	37.2(11)
	O2	7166(9)	4814(11)	5422(4)	15.0(15)
	O4	2285(9)	9821(12)	7520(4)	22.1(17)
	O3	4807(13)	7500	6780(6)	17(2)
	O1	10152(13)	2500	5934(7)	21(2)
O5	4730(20)	12500	9514(9)	55(4)	

Table S4. Mulliken charges for Pb, Cl, and P atoms in $\text{Pb}_3(\text{HPO}_3)\text{Cl}_4 \cdot \text{H}_2\text{O}$ and $\text{Pb}_3(\text{HPO}_3)_2\text{Cl}_2 \cdot \text{H}_2\text{O}$.

Compound	Atoms	Mulliken Charge (e)	
$\text{Pb}_3(\text{HPO}_3)\text{Cl}_4 \cdot \text{H}_2\text{O}$	Pb1	1.139	
	Pb2	1.309	
	Pb3	1.14	
	Pb4	1.074	
	Pb5	1.283	
	Pb6	1.17	
	Cl1	-0.532	
	Cl2	-0.561	
	Cl3	-0.548	
	Cl4	-0.518	
	Cl5	-0.541	
	Cl6	-0.569	
	Cl7	-0.521	
	Cl8	-0.546	
	P1	2.000	
	P2	2.012	
	$\text{Pb}_3(\text{HPO}_3)_2\text{Cl}_2 \cdot \text{H}_2\text{O}$	Pb1	1.455
		Pb2	1.311
Pb3		1.225	
Cl1		-0.571	
Cl2		-0.543	
P1		2.021	
P2		1.999	

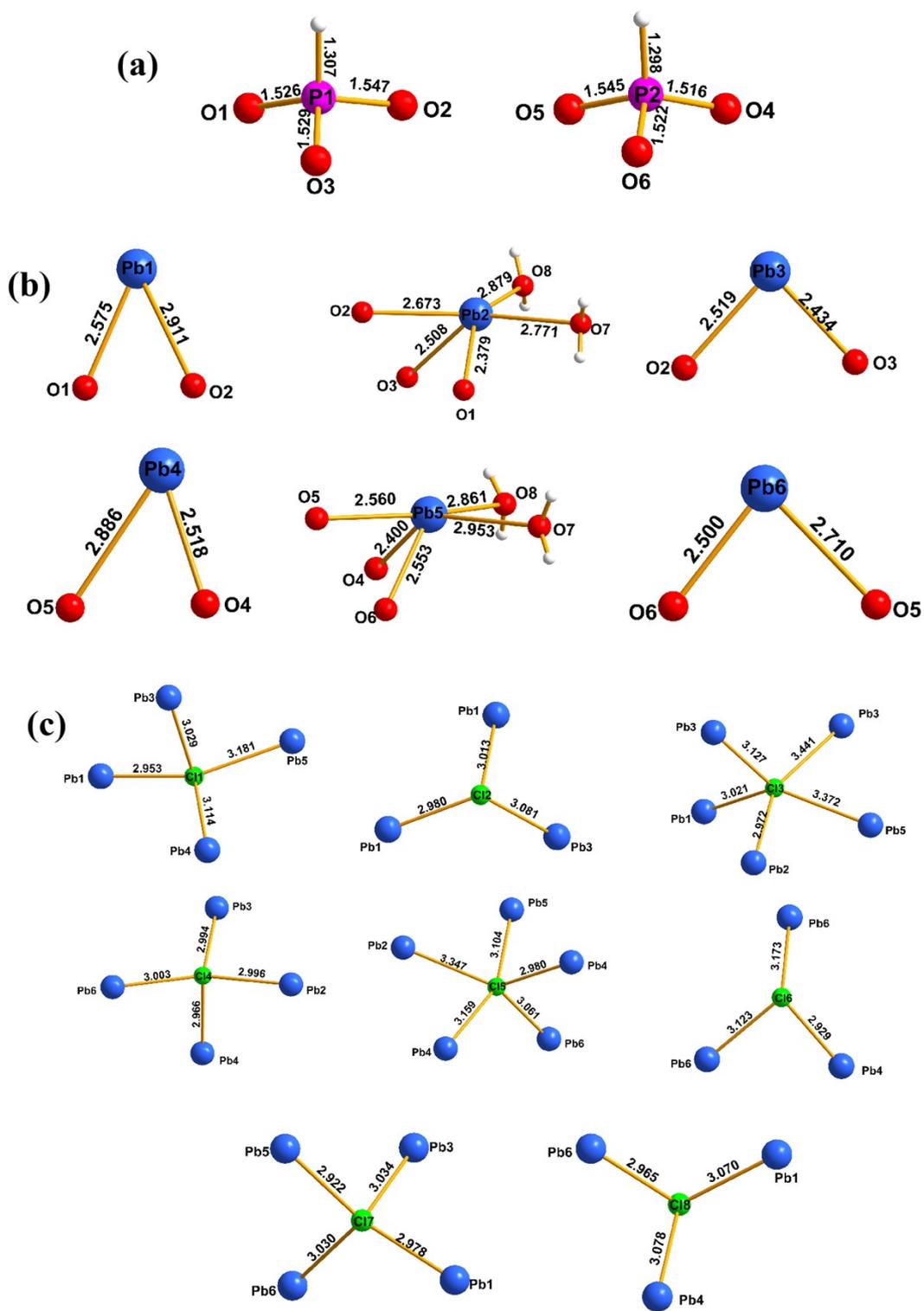


Figure S1. The coordinated environments of Pb (a), P (b) and Cl (c) atoms in $\text{Pb}_3(\text{HPO}_3)\text{Cl}_4 \cdot \text{H}_2\text{O}$.

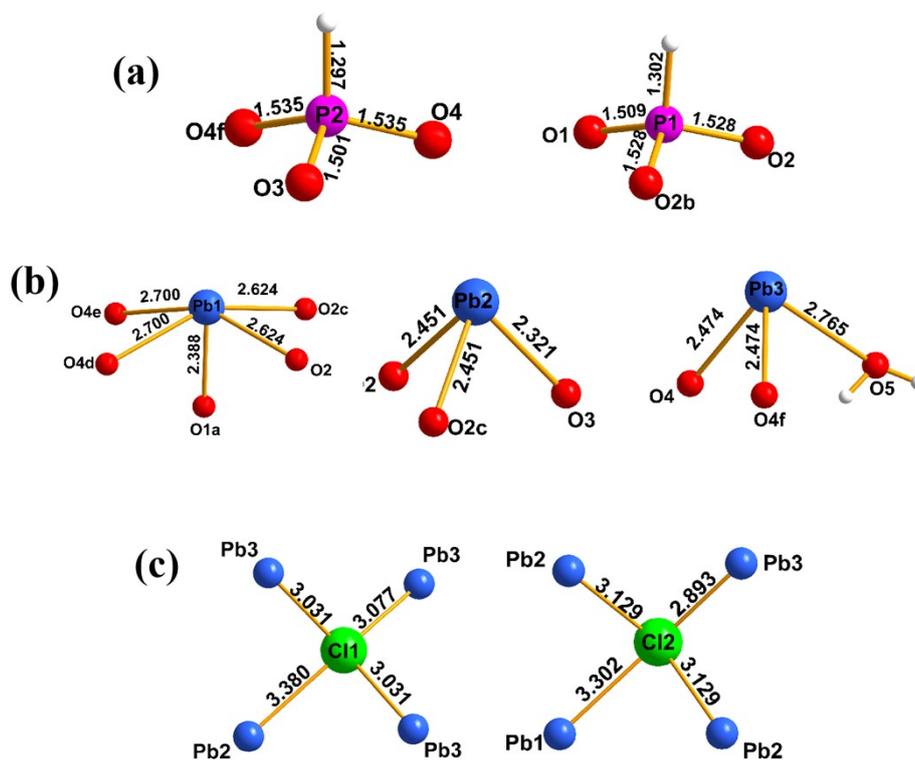


Figure S2. The coordinated environments of Pb (a), P (b) and Cl (c) atoms in $\text{Pb}_3(\text{HPO}_3)_2\text{Cl}_2 \cdot \text{H}_2\text{O}$.

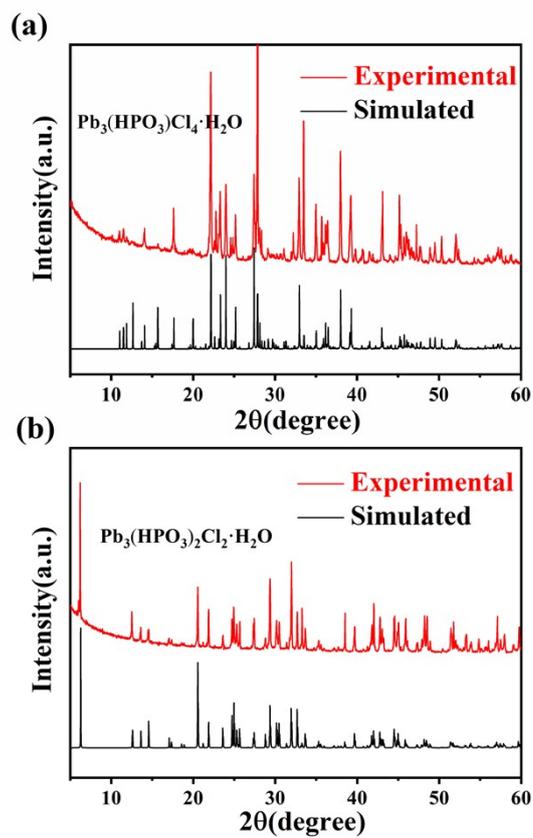


Figure S3. Simulated and experimental XRD patterns of $\text{Pb}_3(\text{HPO}_3)_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ (a) and $\text{Pb}_3(\text{HPO}_3)\text{Cl}_4 \cdot \text{H}_2\text{O}$ (b).

Figure S4. Electron microscope image and EDS mapping of $\text{Pb}_3(\text{HPO}_3)_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ (a) and $\text{Pb}_3(\text{HPO}_3)\text{Cl}_4 \cdot \text{H}_2\text{O}$ (b). The EDS quantitative analysis for $\text{Pb}_3(\text{HPO}_3)_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ (c) and $\text{Pb}_3(\text{HPO}_3)\text{Cl}_4 \cdot \text{H}_2\text{O}$ (d).

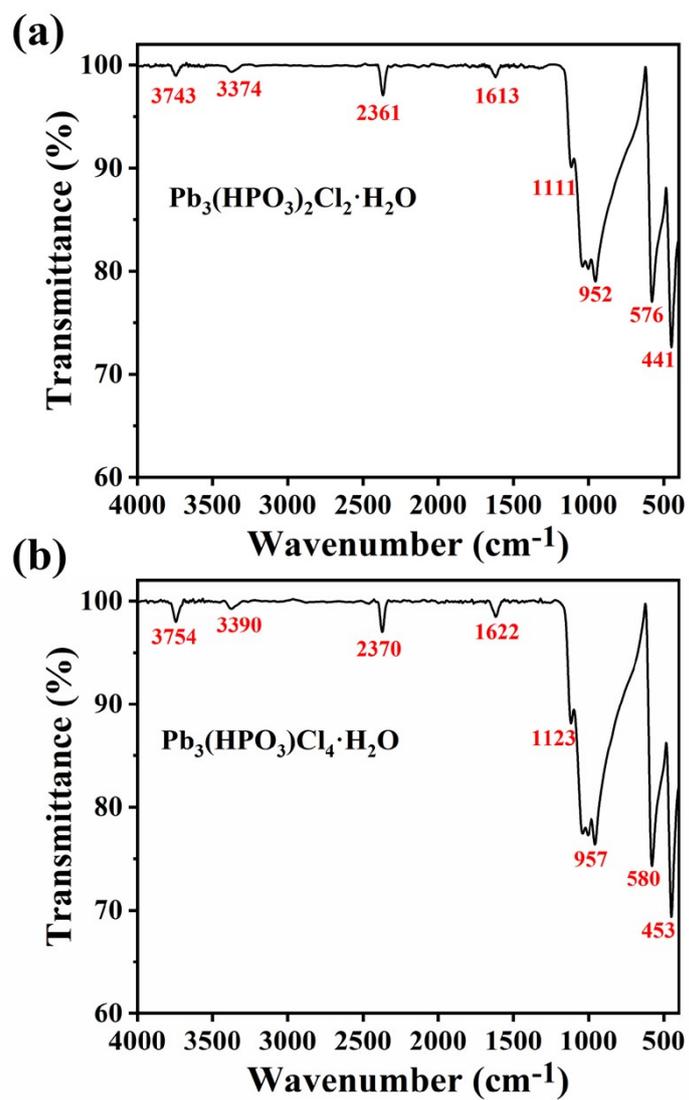


Figure S5. Infrared absorption spectra of $\text{Pb}_3(\text{HPO}_3)\text{Cl}_4 \cdot \text{H}_2\text{O}$ (a) and $\text{Pb}_3(\text{HPO}_3)_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ (b).