SUPPLEMENTARY INFORMATION

Synthesis and characterization of new barium methylphosphonates

Klára Melánová,[a] Ludvík Beneš,[b] Jan Svoboda,[c] Vítězslav Zima,*[a] Milan Vlček,[a] Miroslava Trchová[a]

[a] *Institute of Macromolecular Chemistry of Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic. E-mail: vitezslav.zima@upce.cz*

[b] *Joint Laboratory of Solid State Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 95, 532 10 Pardubice, Czech Republic*

[c] *Institute of Organic Chemistry and Technology, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic*

Table 1: $BaCH_3PO_3 \cdot 3H_2O$

DICVOL91:

M(20) = 37.9

F(20) = 86.3(0.0037, 63)

CHEKCELL (cell refinement):

Monoclinic $P2_1/c$

a = 11.7466 (13) Å

b = 23.0236 (23) Å

c = 8.9380 (11) Å

β = 108.91 (1)°

V = 2286.74 (7) $Å^3$

$2\theta_{obs}$	d_{obs} Å	Intensity	h	k	l	$2\theta_{calc}$	d_{calc} Å	$2\theta_{obs}$-$2\theta_{calc}$
7.671	11.51630	999	0	2	0	7.674	11.51180	-0.003
8.823	10.01440	91	-1	1	0	8.829	10.00760	-0.006
11.137	7.93860	14	0	1	1	11.139	7.93700	-0.002
11.541	7.66130	10	-1	1	1	11.553	7.65340	-0.012
12.978	6.81600	42	0	2	1	12.981	6.81460	-0.003
13.335	6.63450	43	-1	2	1	13.339	6.63260	-0.004
14.015	6.31400	9	-1	3	0	14.013	6.31490	0.002
15.382	5.75600	22	0	4	0	15.382	5.75590	0.000
15.579	5.68340	16	0	3	1	15.581	5.68270	-0.002
15.934	5.55750	35	2	0	0	15.938	5.55610	-0.004
16.399	5.40120	45	-2	1	0	16.399	5.40110	0.000
17.713	5.00310	36	-2	2	0	17.711	5.00380	0.003
19.710	4.50060	22	-2	3	0	19.710	4.50050	0.000
20.877	4.25170	6	-1	5	0	20.865	4.25390	0.011
21.351	4.15830	17	0	1	2	21.351	4.15820	0.000
22.211	3.99910	47	-2	4	0	22.220	3.99750	-0.009
23.157	3.83790	54	0	6	0	23.161	3.83720	-0.004
24.011	3.70320	61	0	3	2	24.013	3.70300	-0.001
24.314	3.65780	12	-3	1	0	24.319	3.65710	-0.005
24.812	3.58550	22	1	0	2	24.822	3.58410	-0.010
25.143	3.53910	83	-2	5	1	25.127	3.54120	0.016
25.239	3.52580	164	-1	4	2	25.237	3.52600	0.002
25.479	3.49310	32	0	6	1	25.471	3.49430	0.008
25.651	3.47010	26	-1	6	1	25.660	3.46900	-0.009
26.032	3.42020	11	1	2	2	26.017	3.42210	0.015
26.320	3.38340	33	-3	0	2	26.332	3.38190	-0.012
26.608	3.34750	20	-3	1	2	26.620	3.34600	-0.012
27.458	3.24570	51	-3	2	2	27.466	3.24480	-0.008
27.643	3.22440	10	-3	4	1	27.668	3.22150	-0.026
28.243	3.15720	27	-2	6	0	28.241	3.15740	0.002

28.648	3.11360	26	0	5	2	28.642	3.11420	0.006
29.265	3.04930	10	-1	7	1	29.275	3.04820	-0.011
30.435	2.93460	21	2	0	2	30.412	2.93680	0.023
30.703	2.90970	53	-1	6	2	30.709	2.90910	-0.006
31.052	2.87770	57	0	8	0	31.050	2.87790	0.002
31.458	2.84150	15	0	6	2	31.460	2.84140	-0.002
31.594	2.82960	37	-2	7	0	31.586	2.83030	0.009
32.441	2.75760	105	-4	1	0	32.436	2.75810	0.005
34.301	2.61220	11	-4	3	0	34.301	2.61220	0.000
35.094	2.55500	28	-2	7	2	35.093	2.55500	0.000
35.334	2.53820	12	-3	6	2	35.349	2.53710	-0.015
35.959	2.49550	24	-4	4	2	35.951	2.49600	0.008
37.086	2.42220	18	1	7	2	37.068	2.42330	0.018
37.295	2.40910	16	3	1	2	37.275	2.41040	0.020
37.802	2.37790	13	-4	5	0	37.790	2.37870	0.013
38.972	2.30920	34	3	3	2	38.937	2.31120	0.034
39.091	2.30240	52	0	10	0	39.093	2.30230	-0.002
39.375	2.28650	13	-5	1	2	39.377	2.28640	-0.002
40.415	2.23000	17	-2	0	4	40.405	2.23050	0.010
40.589	2.22090	18	0	10	1	40.578	2.22150	0.012
40.959	2.20170	22	-5	3	2	40.968	2.20120	-0.009
41.181	2.19030	30	-4	7	1	41.176	2.19050	0.005
41.709	2.16380	14	-2	9	2	41.705	2.16400	0.004
42.126	2.14330	36	1	10	1	42.121	2.14360	0.005
42.565	2.12220	25	-4	7	0	42.563	2.12230	0.003
43.456	2.08080	12	-3	3	4	43.445	2.08120	0.010
44.015	2.05560	22	2	8	2	44.017	2.05550	-0.003
44.426	2.03750	14	0	3	4	44.417	2.03790	0.009
46.327	1.95830	12	-2	11	0	46.317	1.95870	0.011
46.536	1.95000	8	3	1	3	46.514	1.95090	0.023
47.412	1.91590	11	-6	2	2	47.396	1.91660	0.017
47.731	1.90390	8	-3	10	2	47.750	1.90320	-0.019
48.333	1.88160	29	-4	9	0	48.326	1.88180	0.007
49.020	1.85680	11	-4	5	4	49.028	1.85650	-0.008
49.318	1.84630	6	-6	1	0	49.324	1.84610	-0.005
50.672	1.80010	8	4	6	2	50.674	1.80000	-0.002
51.831	1.76250	20	-1	12	2	51.831	1.76250	0.001
52.354	1.74610	10	2	3	4	52.387	1.74510	-0.033
52.991	1.72660	8	-4	7	4	52.990	1.72670	0.001
53.249	1.71890	7	-6	5	0	53.269	1.71830	-0.020
54.872	1.67180	15	-4	11	0	54.876	1.67170	-0.004
56.698	1.62220	5	-6	4	4	56.692	1.62240	0.006
59.872	1.54360	8	5	7	2	59.883	1.54330	-0.011
62.084	1.49380	8	1	10	4	62.084	1.49380	0.000
64.716	1.43920	8	0	16	0	64.730	1.43900	-0.014
66.633	1.40240	8	-5	13	2	66.617	1.40270	0.016
67.377	1.38870	10	2	13	3	67.376	1.38880	0.001
67.922	1.37890	7	-8	5	3	67.908	1.37920	0.014
74.047	1.27930	8	5	5	4	74.072	1.27890	-0.025

Table 2: Anhydrous α-$BaCH_3PO_3$ prepared from $BaCH_3PO_3 \cdot 3H_2O$, dehydrated at 500°C, measured at room temperature.

$2\theta_{obs}$	d_{obs} Å	Intensity
9.100	9.70992	999
18.269	4.85216	4
20.969	4.23310	32
21.646	4.10228	15
21.818	4.07028	20
23.181	3.83389	20
24.691	3.60281	469
25.553	3.48321	22
26.939	3.30701	122
27.576	3.23209	142
28.495	3.12987	43
30.900	2.89150	120
31.117	2.87187	73
32.565	2.74738	33
32.768	2.73083	49
36.304	2.47258	10
37.064	2.42360	7
38.551	2.33343	34
38.981	2.30873	76
41.636	2.16739	39
42.013	2.14883	44
42.662	2.11765	19
43.371	2.08465	19
44.238	2.04576	15
46.280	1.96014	48
46.902	1.93560	50
47.091	1.92826	60

Table 3: $BaCH_3PO_3 \cdot H_2O$

DICVOL91:

M(20) = 24.8

F(20) = 44.9(0.0062, 72)

CHEKCELL:

Monoclinic $P2_1/c$, $P2_1/n$

a = 20.5115 (4) Å

b = 7.2172 (1) Å

c = 7.4920 (1) Å

β = 95.52 (1)°

V = 1103.9 (2) $Å^3$

$2\theta_{obs}$	d_{obs} Å	Intensity	h	k	l	$2\theta_{calc}$	d_{calc} Å	$2\theta_{obs}$-$2\theta_{calc}$
8.659	10.20400	999	2	0	0	8.655	10.20830	0.004
12.996	6.80690	7	-1	1	0	13.000	6.80470	-0.004
17.082	5.18660	2	0	1	1	17.083	5.18610	-0.001
17.371	5.10100	8	4	0	0	17.360	5.10410	0.011
17.896	4.95250	22	-3	1	0	17.900	4.95140	-0.004
18.656	4.75250	5	-2	1	1	18.650	4.75390	0.006
23.598	3.76710	10	-4	1	1	23.605	3.76600	-0.007
23.847	3.72840	4	0	0	2	23.846	3.72860	0.001
24.606	3.61500	3	-2	0	2	24.598	3.61620	0.008
25.038	3.55370	36	-1	2	0	25.038	3.55360	-0.001
26.179	3.40130	92	-2	2	0	26.171	3.40240	0.008
26.888	3.31320	3	0	1	2	26.892	3.31270	-0.005
27.607	3.22860	12	-1	2	1	27.602	3.22900	0.004
27.972	3.18720	26	1	2	1	27.971	3.18730	0.002
28.212	3.16060	7	-4	0	2	28.226	3.15910	-0.014
28.946	3.08210	2	-3	1	2	28.927	3.08410	0.019
30.307	2.94680	4	-4	2	0	30.309	2.94660	-0.002
30.408	2.93720	7	-6	1	1	30.414	2.93660	-0.006
30.991	2.88330	13	3	1	2	30.992	2.88310	-0.001
32.391	2.76180	7	6	1	1	32.394	2.76150	-0.003
33.104	2.70390	7	-5	2	0	33.102	2.70400	0.002
33.879	2.64380	8	-6	0	2	33.886	2.64320	-0.007
34.527	2.59570	7	-5	2	1	34.527	2.59560	-0.001
35.142	2.55160	82	1	2	2	35.148	2.55120	-0.006
36.257	2.47570	5	-6	2	0	36.256	2.47570	0.001
37.430	2.40070	2	-6	2	1	37.435	2.40040	-0.006
38.273	2.34980	5	0	1	3	38.265	2.35020	0.008
38.490	2.33700	2	-2	1	3	38.485	2.33730	0.004
39.330	2.28900	1	0	3	1	39.320	2.28960	0.011
39.706	2.26820	8	-3	3	0	39.705	2.26820	0.001

40.094	2.24720	3	2	1	3	40.113	2.24610	-0.020
40.401	2.23080	8	-9	0	1	40.399	2.23090	0.002
40.650	2.21770	10	-7	2	1	40.665	2.21690	-0.015
41.686	2.16490	1	-9	1	0	41.702	2.16410	-0.016
43.009	2.10130	2	7	1	2	43.000	2.10180	0.010
43.635	2.07260	6	-5	3	0	43.632	2.07280	0.003
43.758	2.06710	2	4	3	1	43.774	2.06640	-0.016
44.082	2.05270	2	-1	2	3	44.072	2.05310	0.009
44.347	2.04100	8	10	0	0	44.332	2.04170	0.015
44.787	2.02200	3	-1	3	2	44.785	2.02210	0.002
45.183	2.00520	4	-7	2	2	45.170	2.00570	0.013
46.139	1.96580	1	-3	3	2	46.134	1.96600	0.006
46.521	1.95060	1	-9	1	2	46.508	1.95110	0.013
46.671	1.94470	3	-10	1	1	46.672	1.94460	-0.001
47.349	1.91840	3	3	2	3	47.337	1.91880	0.013
47.897	1.89770	3	-9	2	1	47.900	1.89760	-0.003
48.071	1.89120	2	-5	2	3	48.077	1.89100	-0.005
48.801	1.86460	2	0	0	4	48.810	1.86430	-0.009
49.037	1.85620	3	-7	3	0	49.045	1.85590	-0.008
49.960	1.82410	5	9	2	1	49.952	1.82430	0.008

Table 4: anhydrous β-$BaCH_3PO_3$ prepared from $BaCH_3PO_3 \cdot H_2O$, measured at 215°C

DICVOL91:

M(20) = 29.2

F(20) = 48.5(0.0090, 46)

CHEKCELL (cell refinement):

Monoclinic $P2_1/c$

a = 8.4443 (30) Å

b = 7.2504 (27) Å

c = 7.4561 (28) Å

β = 99.80 (1)°

V = 449.83 (5) $Å^3$

$2\theta_{obs}$	d_{obs} Å	Intensity	h	k	l	$2\theta_{calc}$	d_{calc} Å	$2\theta_{obs}$-$2\theta_{calc}$
10.633	8.31310	999	1	0	0	10.623	8.32100	0.010
16.210	5.46360	51	-1	1	0	16.202	5.46640	0.008
19.115	4.63930	14	-1	1	1	19.107	4.64130	0.009
21.348	4.15870	99	2	0	0	21.339	4.16050	0.009
24.222	3.67150	27	0	0	2	24.208	3.67360	0.014
24.657	3.60770	134	-2	1	0	24.651	3.60860	0.006
25.832	3.44610	38	-2	1	1	25.829	3.44660	0.004
27.419	3.25020	81	0	2	1	27.412	3.25100	0.007
27.675	3.22070	16	-1	1	2	27.678	3.22040	-0.003
28.139	3.16860	28	1	0	2	28.151	3.16730	-0.012
29.164	3.05960	15	2	1	1	29.113	3.06490	0.051
29.544	3.02110	21	-2	0	2	29.548	3.02070	-0.004
30.250	2.95220	37	1	2	1	30.235	2.95360	0.015
32.248	2.77370	167	3	0	0	32.248	2.77370	-0.001
33.665	2.66010	20	-2	2	1	33.656	2.66080	0.009
34.606	2.58990	13	-3	1	0	34.597	2.59060	0.009
35.213	2.54660	13	2	0	2	35.208	2.54700	0.006
37.096	2.42160	17	-3	0	2	37.111	2.42060	-0.015
37.370	2.40440	12	2	1	2	37.393	2.40300	-0.023
38.583	2.33160	27	3	1	1	38.615	2.32970	-0.032
38.723	2.32350	32	0	1	3	38.778	2.32030	-0.055
40.128	2.24530	13	-1	3	1	40.154	2.24390	-0.027
41.118	2.19350	30	-3	2	1	41.124	2.19320	-0.006
43.208*	2.09210	34						
43.464	2.08040	35	4	0	0	43.467	2.08020	-0.004
44.451	2.03650	19	3	2	1	44.469	2.03570	-0.018
45.021	2.01200	10	-3	2	2	44.995	2.01310	0.026
46.087	1.96790	14	2	3	1	46.127	1.96630	-0.039
46.737	1.94200	10	-3	1	3	46.780	1.94040	-0.043

46.926	1.93470	19	-2	2	3	46.926	1.93470	0.000
47.583	1.90950	11	1	2	3	47.555	1.91050	0.028
48.083	1.89080	9	-4	1	2	48.077	1.89100	0.006
48.928	1.86010	14	-1	0	4	48.886	1.86160	0.042
50.057	1.82070	10	-3	3	0	50.016	1.82210	0.041
50.249*	1.81420	9						
52.972	1.72720	14	-1	3	3	53.011	1.72600	-0.039
53.178	1.72100	9	0	3	3	53.203	1.72020	-0.026
54.045	1.69540	14	4	2	1	54.052	1.69520	-0.007
54.243	1.68970	9	-4	1	3	54.222	1.69030	0.021
54.401	1.68520	9	1	1	4	54.401	1.68520	0.000
55.897	1.64360	14	-5	1	1	55.944	1.64230	-0.048
56.682	1.62270	15	-5	1	0	56.706	1.62200	-0.024
58.205	1.58380	12	-4	3	1	58.194	1.58400	0.012
58.567	1.57480	10	-4	3	0	58.494	1.57660	0.073
59.075	1.56250	8	1	2	4	59.044	1.56330	0.032
59.438	1.55380	8	-2	4	2	59.419	1.55430	0.018

* These diffraction lines can be caused by the reflections of copper originated from the sample holder

Table 5: $Ba(CH_3PO_3H)_2 \cdot H_2O$

Idexed by ITO12 using first 40 lines
M(20) = 90.6

TRICLINIC
a = 7.3283 Å
b = 9.3571 Å
c = 7.2909 Å
α = 94.352°
β = 110.859°
γ = 88.070°
V = 465.82 Å^3

Experimental:				Calculated:				
c.	2*theta	d [Å]	int.	h	k	l	2*theta	d [Å]
1	9.472	9.34010	100	0	1	0	9.472	9.32983
2	12.915	6.85488	18	1	0	0	12.918	6.84783
3	14.736	6.01095	30	-1	0	1	14.739	6.00547
				1	0	-1	14.739	6.00547
4	15.578	5.68768	4	0	-1	1	15.583	5.68189
5	16.093	5.50690	2	-1	1	0	16.097	5.50172
6	16.637	5.32795	1	0	1	1	16.641	5.32318
7	17.002	5.21417	9	1	1	-1	17.003	5.21045
8	18.084	4.90450	1	-1	1	1	18.078	4.90309
9	19.002	4.66928	9	0	2	0	19.009	4.66491
10	21.417	4.14769	4	1	0	1	21.422	4.14469
11	22.341	3.97809	29	0	-2	1	22.346	3.97520
12	22.975	3.86970	1	1	2	0	22.973	3.86823
13	23.124	3.84512	2	-1	2	0	23.128	3.84259
				1	-1	1	23.135	3.84142
14	23.821	3.73411	27	1	1	1	23.796	3.73627
15	24.593	3.61856	3	-2	0	1	24.596	3.61645
				2	0	-1	24.596	3.61645
16	24.740	3.59738	6	-1	0	2	24.752	3.59400
				1	0	-2	24.752	3.59400
17	24.914	3.57267	8	-1	2	1	24.918	3.57045
18	26.003	3.42533	17	2	0	0	26.003	3.42391
				2	1	-1	26.010	3.42306
19	26.199	3.40019	22	0	0	2	26.200	3.39856
20	26.799	3.32532	5	-2	1	1	26.806	3.32313
21	27.278	3.26805	4	-1	1	2	27.239	3.27130
				0	-1	2	27.284	3.26596
22	27.662	3.22352	14	2	1	0	27.666	3.22175
23	27.798	3.20806	11	-2	1	0	27.797	3.20690
24	28.240	3.15878	6	1	-2	1	28.240	3.15758
25	28.534	3.12689	7	0	1	2	28.538	3.12528
26	28.681	3.11119	6	0	3	0	28.682	3.10994
27	29.720	3.00467	13	-2	0	2	29.729	3.00273

				2	0	-2	29.729	3.00273
28	30.181	2.95987	1	1	2	-2	30.190	2.95794
29	30.601	2.92011	7	2	2	-1	30.581	2.92099
30	30.765	2.90491	6	0	-3	1	30.762	2.90416
31	31.475	2.84101	19	0	-2	2	31.464	2.84095
				1	3	-1	31.474	2.84007
				1	3	0	31.484	2.83926
32	31.652	2.82549	3	-1	3	0	31.658	2.82402
33	31.936	2.80098	2	-2	2	1	31.946	2.79921
34	32.299	2.77033	6	2	2	0	32.296	2.76968
35	32.443	2.75840	11	0	3	1	32.442	2.75752
36	32.521	2.75192	8	-2	2	0	32.523	2.75086
37	33.187	2.69818	1	2	0	1	33.185	2.69748
38	33.294	2.68975	3	-1	3	1	33.289	2.68933
				1	0	2	33.304	2.68812
39	33.641	2.66282	4	0	2	2	33.646	2.66159
40	34.208	2.61994	1	1	-1	2	34.209	2.61904
41	34.782	2.57797	1	2	1	1	34.790	2.57659
42	36.622	2.45256	1	-2	2	2	36.626	2.45155
43	36.738	2.44505	3	1	3	-2	36.718	2.44561
				1	3	1	36.742	2.44406
44	37.085	2.42294	2	-1	0	3	37.081	2.42252
				1	0	-3	37.081	2.42252
45	37.277	2.41093	5	2	3	-1	37.266	2.41094
46	37.619	2.38975	2	1	1	-3	37.618	2.38916
47	37.747	2.38199	3	1	-2	2	37.726	2.38258
				3	1	-1	37.764	2.38025
48	38.390	2.34354	3	-3	1	1	38.388	2.34300
49	38.915	2.31310	6	-3	0	2	38.920	2.31218
				2	2	1	38.893	2.31370
				3	0	-2	38.920	2.31218
50	39.085	2.30340	4	-2	0	3	39.093	2.30237
				-1	1	3	39.086	2.30276
				2	0	-3	39.093	2.30237
51	39.605	2.27434	4	2	1	-3	39.583	2.27499
				3	1	-2	39.618	2.27301
52	39.972	2.25431	3	0	-4	1	39.966	2.25403
53	40.602	2.22079	2	0	3	2	40.607	2.21993
				1	2	-3	40.611	2.21971
				3	1	0	40.589	2.22088
54	40.764	2.21231	1	-3	1	0	40.729	2.21357
				1	4	0	40.745	2.21273
55	40.936	2.20341	4	-1	4	0	40.931	2.20309
56	41.760	2.16179	3	0	4	1	41.760	2.16125
57	42.310	2.13496	2	-3	2	1	42.305	2.13466
58	42.443	2.12859	4	2	2	-3	42.437	2.12834
59	43.152	2.09522	2	0	-2	3	43.143	2.09515
60	43.338	2.08667	4	-1	2	3	43.335	2.08630
				1	-3	2	43.311	2.08738
61	43.639	2.07294	3	2	0	2	43.642	2.07234
62	43.922	2.06024	3	2	-3	1	43.921	2.05980

63	44.018	2.05596	1	3	2	0	44.004	2.05612
64	44.381	2.03999	3	2	-1	2	44.387	2.03924
65	44.651	2.02829	2	-3	2	2	44.630	2.02870
				1	4	-2	44.640	2.02829
66	44.924	2.01658	3	2	3	1	44.918	2.01638
67	45.156	2.00678	2	-2	2	3	45.157	2.00627
				2	1	2	45.134	2.00721
68	45.294	2.00098	4	-3	0	3	45.263	2.00182
				1	4	1	45.283	2.00096
				2	4	-1	45.292	2.00059
				3	0	-3	45.263	2.00182
69	45.676	1.98513	3	0	2	3	45.659	1.98536
				1	3	-3	45.659	1.98535
				1	3	2	45.693	1.98396
				3	1	-3	45.677	1.98462
70	47.021	1.93140	1	-3	1	3	47.020	1.93103
71	47.140	1.92680	1	3	-1	1	47.124	1.92699
72	47.285	1.92123	4	-2	4	0	47.272	1.92129
				-2	4	1	47.253	1.92204
				2	-2	2	47.288	1.92071
73	48.062	1.89196	2	-1	4	2	48.053	1.89190
				1	1	3	48.072	1.89120
74	48.777	1.86588	1	0	5	0	48.764	1.86597
75	49.746	1.83176	1	0	-5	1	49.738	1.83167
76	50.182	1.81687	1	1	5	-1	50.179	1.81660
77	50.431	1.80848	1	-4	0	2	50.428	1.80822
				1	-4	2	50.427	1.80824
				4	0	-2	50.428	1.80822
78	50.773	1.79710	3	-3	2	3	50.775	1.79667
				-2	0	4	50.765	1.79700
				-1	5	0	50.763	1.79707
				2	0	-4	50.765	1.79700
79	51.455	1.77485	1	0	3	3	51.459	1.77439
80	52.377	1.74577	3	2	4	1	52.363	1.74585
81	53.522	1.71108	1	4	0	0	53.481	1.71196
				4	2	-2	53.496	1.71153
				4	2	-1	53.525	1.71065
82	53.918	1.69943	1	0	0	4	53.912	1.69928
				1	-3	3	53.928	1.69882
83	54.488	1.68301	1	-4	0	3	54.481	1.68289
				0	-4	3	54.450	1.68378
				4	0	-3	54.481	1.68289
84	54.840	1.67301	2	3	1	-4	54.849	1.67245
				4	1	-3	54.824	1.67315
85	55.244	1.66175	1	-4	2	2	55.239	1.66156
86	56.241	1.63462	2	-3	3	3	56.239	1.63436
				2	5	-2	56.234	1.63452
87	57.035	1.61373	1	1	3	3	57.023	1.61375
				4	2	-3	57.049	1.61309
88	57.446	1.60316	1	-4	2	0	57.423	1.60345
				2	1	3	57.433	1.60319

Table 6: $Ba(CH_3PO_3H)_2$

TREOR90:

M(20) = 14

F(20) = 17.0(0.013828, 86)

CHEKCELL (cell refinement):

Monoclinic $P2_1/m$

a = 11.5798 (28) Å

b = 15.5863 (54) Å

c = 4.8983 (21) Å

β = 98.58 (1)°

V = 874.19 (8) $Å^3$

$2\theta_{obs}$	d_{obs} Å	Intensity	h	k	l	$2\theta_{calc}$	d_{calc} Å	$2\theta_{obs}$-$2\theta_{calc}$
7.731	11.43520	999	1	0	0	7.721	11.44980	0.010
13.760	6.43550	29	-1	2	0	13.746	6.44240	0.015
15.488	5.72150	29	2	0	0	15.478	5.72500	0.010
20.959	4.23860	40	1	0	1	20.954	4.23960	0.005
22.211	4.00240	9	-2	0	1	22.203	4.00380	0.008
22.898	3.88380	50	-2	1	1	22.934	3.87790	-0.035
23.310	3.81610	46	3	0	0	23.307	3.81660	0.003
24.121	3.68960	12	-1	4	0	24.127	3.68870	-0.006
25.019	3.55920	69	-2	2	1	25.004	3.56130	0.015
25.807	3.45230	76	2	0	1	25.806	3.45240	0.001
26.035	3.42260	18	-3	2	0	25.996	3.42760	0.039
27.512	3.24210	30	-3	0	1	27.512	3.24200	0.000
29.867	2.99160	45	-3	2	1	29.849	2.99330	0.018
31.242	2.86300	33	4	0	0	31.248	2.86250	-0.006
31.937	2.80220	38	3	0	1	31.946	2.80150	-0.009
33.287	2.69160	44	-4	2	0	33.347	2.68700	-0.060
33.912	2.64340	32	-4	0	1	33.918	2.64300	-0.006
36.016	2.49370	6	-3	4	1	36.039	2.49220	-0.023
36.759	2.44500	10	-1	0	2	36.771	2.44420	-0.012
38.114	2.36120	6	-2	0	2	38.129	2.36030	-0.015
38.853	2.31790	20	4	0	1	38.860	2.31750	-0.007
39.333	2.29070	66	5	0	0	39.346	2.29000	-0.013
41.015	2.20060	36	-5	0	1	41.007	2.20100	0.008
41.282	2.18700	11	-4	4	1	41.276	2.18730	0.007
44.801	2.02300	7	0	7	1	44.801	2.02300	0.000
46.292	1.96130	3	5	0	1	46.315	1.96030	-0.023
47.384	1.91860	6	3	0	2	47.363	1.91940	0.021
47.626	1.90940	12	6	0	0	47.655	1.90830	-0.029
47.855	1.90080	5	5	2	1	47.847	1.90110	0.008
48.093	1.89190	4	-6	1	0	48.033	1.89420	0.060

48.582	1.87410	4	-6	0	1	48.602	1.87330	-0.020
49.121	1.85470	3	-6	2	0	49.154	1.85360	-0.033
52.091	1.75580	4	-5	2	2	52.047	1.75720	0.044
55.450	1.65710	8	-2	9	0	55.432	1.65760	0.018
55.644	1.65180	4	6	2	1	55.599	1.65300	0.045
56.242	1.63560	2	7	0	0	56.239	1.63570	0.003
56.645	1.62500	2	-7	0	1	56.646	1.62490	-0.001
57.993	1.59040	5	-7	2	1	57.978	1.59070	0.015
64.995	1.43490	4	2	8	2	65.020	1.43440	-0.025
65.137	1.43210	7	-8	0	1	65.152	1.43180	-0.015

Table 7: $Ba_2(CH_3PO_3H)_2(CH_3PO_3)\cdot 4H_2O$

Idexed by ITO12 using first 40 lines
M(20) = 16.9

TRICLINIC
a = 9.7728 Å
b = 11.7776 Å
c = 8.7245 Å
α = 103.489°
β = 117.642°
γ = 73.861°
V = 848.08 Å^3

	Experimental:						Calculate:	
No	2θ	d [Å]	int.	h	k	l	2θ	d [Å]
1	7.885	11.20286	100	0	1	0	7.868	11.22815
2	10.424	8.47948	2	1	0	0	10.414	8.48762
3	11.790	7.50018	2	-1	0	1	11.782	7.50545
				1	1	0	11.757	7.52118
4	14.289	6.19345	3	-1	1	0	14.256	6.20786
5	14.758	5.99778	2	0	1	1	14.752	6.00033
6	15.799	5.60472	2	0	2	0	15.773	5.61407
7	19.975	4.44154	1	1	1	1	19.966	4.44352
8	20.625	4.30288	2	-1	2	0	20.600	4.30809
9	20.924	4.24222	4	-1	0	2	20.933	4.24035
				2	0	0	20.916	4.24381
10	23.768	3.74065	2	0	3	0	23.754	3.74272
11	24.076	3.69343	5	-1	1	2	24.087	3.69168
				1	2	1	24.050	3.69730
12	24.351	3.65236	2	2	2	-2	24.325	3.65613
13	26.488	3.36233	4	0	-2	2	26.469	3.36471
14	27.875	3.19813	5	-1	3	0	27.861	3.19968
15	28.290	3.15214	3	2	3	-2	28.270	3.15431
16	28.401	3.14008	3	2	1	1	28.381	3.14223
17	29.198	3.05612	2	-1	2	2	29.188	3.05710
18	29.801	2.99565	1	1	3	1	29.813	2.99444
19	30.524	2.92629	2	1	4	-1	30.519	2.92681
20	30.646	2.91495	2	1	1	2	30.635	2.91597
21	30.891	2.89238	2	2	2	1	30.906	2.89095
22	31.275	2.85768	2	0	-3	2	31.255	2.85952
23	31.512	2.83680	2	1	4	0	31.510	2.83693
24	31.870	2.80571	14	0	4	0	31.855	2.80704
25	32.088	2.78712	2	2	4	-1	32.086	2.78733
26	32.364	2.76397	2	-2	2	2	32.335	2.76646
27	33.786	2.65089	2	2	4	-2	33.757	2.65310
28	33.908	2.64156	2	1	4	-2	33.897	2.64243
29	35.337	2.53800	1	0	4	1	35.342	2.53760

30	35.471	2.52871	1	-1	3	2	35.483	2.52790
				0	3	2	35.478	2.52819
31	35.588	2.52067	3	-1	4	0	35.582	2.52108
32	37.299	2.40888	1	-1	4	1	37.328	2.40708
				0	-4	2	37.276	2.41031
				4	2	-2	37.299	2.40884
33	37.606	2.38987	1	4	1	-1	37.612	2.38952
34	37.725	2.38266	1	1	-4	1	37.716	2.38316
				2	0	2	37.710	2.38356
35	38.282	2.34923	2	1	5	-1	38.276	2.34957
				2	1	2	38.301	2.34812
				3	0	1	38.294	2.34853
36	38.608	2.33016	1	-2	3	2	38.620	2.32945
				1	3	2	38.608	2.33014
37	40.123	2.24559	7	0	5	0	40.122	2.24563
38	40.811	2.20932	2	1	5	-2	40.801	2.20983
39	40.937	2.20279	1	1	0	3	40.951	2.20205
40	41.926	2.15310	2	-2	4	0	41.906	2.15405
41	42.102	2.14448	1	-4	0	3	42.114	2.14393
				-2	4	1	42.123	2.14348
				0	4	2	42.125	2.14340
42	42.758	2.11312	1	3	3	1	42.764	2.11283
43	42.832	2.10961	2	3	5	-1	42.821	2.11012
44	43.288	2.08846	2	0	5	1	43.313	2.08729
				1	-2	3	43.276	2.08902
45	47.177	1.92496	2	2	5	1	47.184	1.92468
				3	4	1	47.187	1.92459
46	48.305	1.88259	1	1	6	-2	48.310	1.88244
				5	1	-3	48.276	1.88368
47	49.090	1.85433	1	1	3	3	49.090	1.85432
48	49.484	1.84048	2	-2	5	0	49.481	1.84059

Table 8: $Ba_2(CH_3PO_3H)_2(CH_3PO_3)$

Idexed by ITO12 using first 40 lines
M(20) = 26.3

TRICLINIC
a = 9.2837 Å
b = 12.0084 Å
c = 7.4711 Å
α = 95.661°
β = 91.916°
γ = 81.388°
V = 819.34 Å^3

	Experimental:						Calculate:	
No	2θ	d [Å]	int.	h	k	l	2θ	d [Å]
1	7.444	11.86593	100	0	1	0	7.473	11.81958
2	13.038	6.78504	2	-1	1	0	13.045	6.78126
3	13.402	6.60117	3	0	-1	1	13.446	6.57963
4	14.628	6.05071	2	0	1	1	14.655	6.03976
5	14.941	5.92472	5	0	2	0	14.979	5.90979
6	16.539	5.35564	1	1	2	0	16.589	5.33946
7	19.658	4.51242	2	2	1	0	19.680	4.50740
8	21.772	4.07875	5	-2	1	0	21.767	4.07976
				1	-2	1	21.802	4.07315
9	22.527	3.94370	4	0	3	0	22.550	3.93986
				2	1	-1	22.483	3.95132
10	22.667	3.91963	14	2	2	0	22.698	3.91435
11	23.892	3.72145	5	0	0	2	23.923	3.71666
12	24.385	3.64725	2	0	-1	2	24.396	3.64574
13	24.501	3.63024	2	0	-3	1	24.529	3.62620
14	24.690	3.60292	6	2	-1	1	24.706	3.60063
15	24.806	3.58632	3	2	2	-1	24.836	3.58202
16	25.014	3.55702	10	-2	1	1	25.044	3.55283
				1	3	-1	25.044	3.55285
17	25.636	3.47209	5	-1	0	2	25.668	3.46785
				1	1	-2	25.688	3.46516
18	25.971	3.42802	3	1	0	2	26.015	3.42237
19	26.219	3.39614	3	-2	2	0	26.263	3.39063
20	26.540	3.35580	4	0	3	1	26.570	3.35216
				2	2	1	26.539	3.35598
21	27.320	3.26181	8	1	1	2	27.341	3.25930
22	27.519	3.23860	10	2	3	0	27.561	3.23380
23	27.643	3.22435	6	1	-3	1	27.707	3.21706
24	27.816	3.20473	4	-1	1	2	27.812	3.20519
25	28.425	3.13739	4	2	-2	1	28.466	3.13296
26	29.337	3.04194	6	-2	2	1	29.367	3.03891
27	30.559	2.92305	3	1	2	2	30.582	2.92093

28	31.417	2.84513	4	-3	0	1	31.384	2.84800
				0	-3	2	31.461	2.84126
				3	0	-1	31.384	2.84800
29	31.756	2.81551	4	-1	2	2	31.717	2.81893
30	31.972	2.79701	4	3	1	1	31.968	2.79733
31	33.474	2.67484	5	3	-1	1	33.474	2.67481
32	33.609	2.66442	4	-3	1	1	33.595	2.66551
				2	-3	1	33.619	2.66365
33	34.340	2.60936	3	3	3	0	34.337	2.60957
34	34.491	2.59828	2	2	2	2	34.537	2.59491
35	34.890	2.56947	3	-2	3	1	34.913	2.56781
36	34.992	2.56218	2	2	3	-2	35.054	2.55779
37	36.211	2.47867	1	0	0	3	36.225	2.47778
38	36.867	2.43610	2	-1	3	2	36.885	2.43495
39	37.350	2.40571	2	-3	2	1	37.320	2.40756
				-1	0	3	37.383	2.40362
				3	3	1	37.383	2.40365
40	37.983	2.36705	4	0	-2	3	37.993	2.36642
				0	5	0	38.035	2.36392
41	38.516	2.33548	3	1	2	-3	38.518	2.33540
				2	3	2	38.500	2.33644
42	38.769	2.32081	4	3	1	2	38.797	2.31923
43	39.145	2.29942	2	-1	1	3	39.177	2.29759
				3	4	0	39.110	2.30139
44	39.513	2.27886	2	2	4	-2	39.582	2.27499
45	40.278	2.23728	2	4	1	-1	40.300	2.23616
46	41.106	2.19411	3	0	5	1	41.118	2.19352
47	41.171	2.19081	3	4	1	1	41.212	2.18872
				4	2	-1	41.181	2.19032
48	41.495	2.17447	3	-2	3	2	41.476	2.17538
49	42.339	2.13304	2	2	-1	3	42.343	2.13284
50	43.252	2.09008	2	2	5	1	43.290	2.08837
51	43.539	2.07698	1	2	4	2	43.575	2.07535
52	43.852	2.06288	1	3	3	2	43.904	2.06057
53	44.318	2.04227	2	2	-2	3	44.367	2.04013
54	45.260	2.00193	1	4	1	-2	45.296	2.00041
55	45.537	1.99038	2	1	3	3	45.508	1.99159
56	45.611	1.98732	2	1	6	0	45.618	1.98703
57	45.947	1.97359	2	3	1	-3	45.998	1.97151
58	46.039	1.96984	2	0	6	0	46.037	1.96993
59	46.705	1.94331	2	-3	0	3	46.699	1.94354
60	47.360	1.91795	1	1	5	2	47.404	1.91627
61	47.603	1.90872	3	3	0	3	47.627	1.90781
62	48.224	1.88559	2	-2	5	1	48.233	1.88524
				2	3	3	48.224	1.88559
63	48.407	1.87889	2	3	-1	3	48.435	1.87786
64	48.675	1.86915	1	-3	1	3	48.701	1.86823
				-1	6	0	48.641	1.87038
65	48.858	1.86260	2	0	-1	4	48.845	1.86307
66	49.090	1.85432	1	5	1	0	49.053	1.85564
67	49.449	1.84169	1	1	1	-4	49.468	1.84104

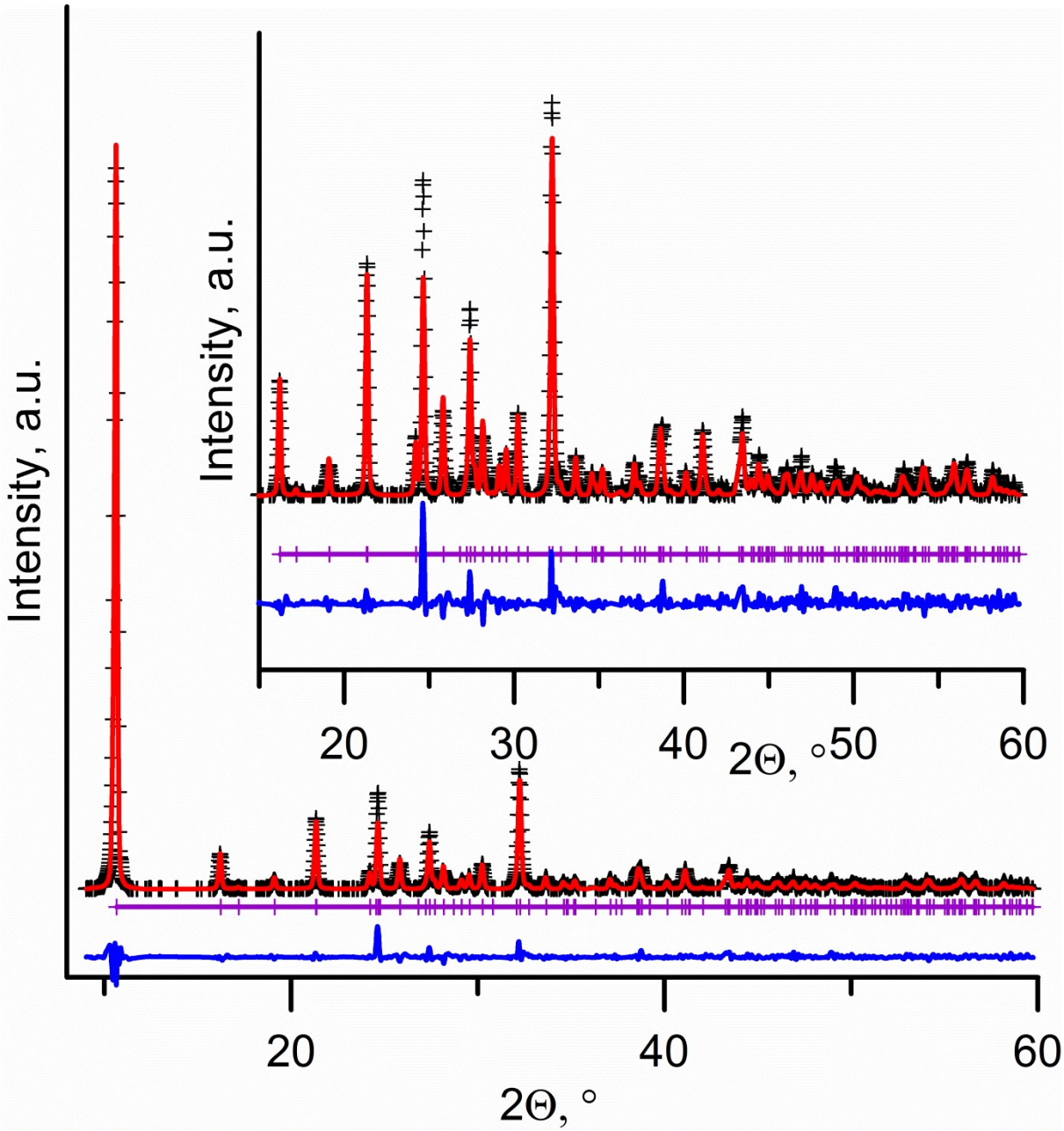

Figure S1. X-Ray powder pattern of β-$BaCH_3PO_3$ with final Rietveld and difference plots.

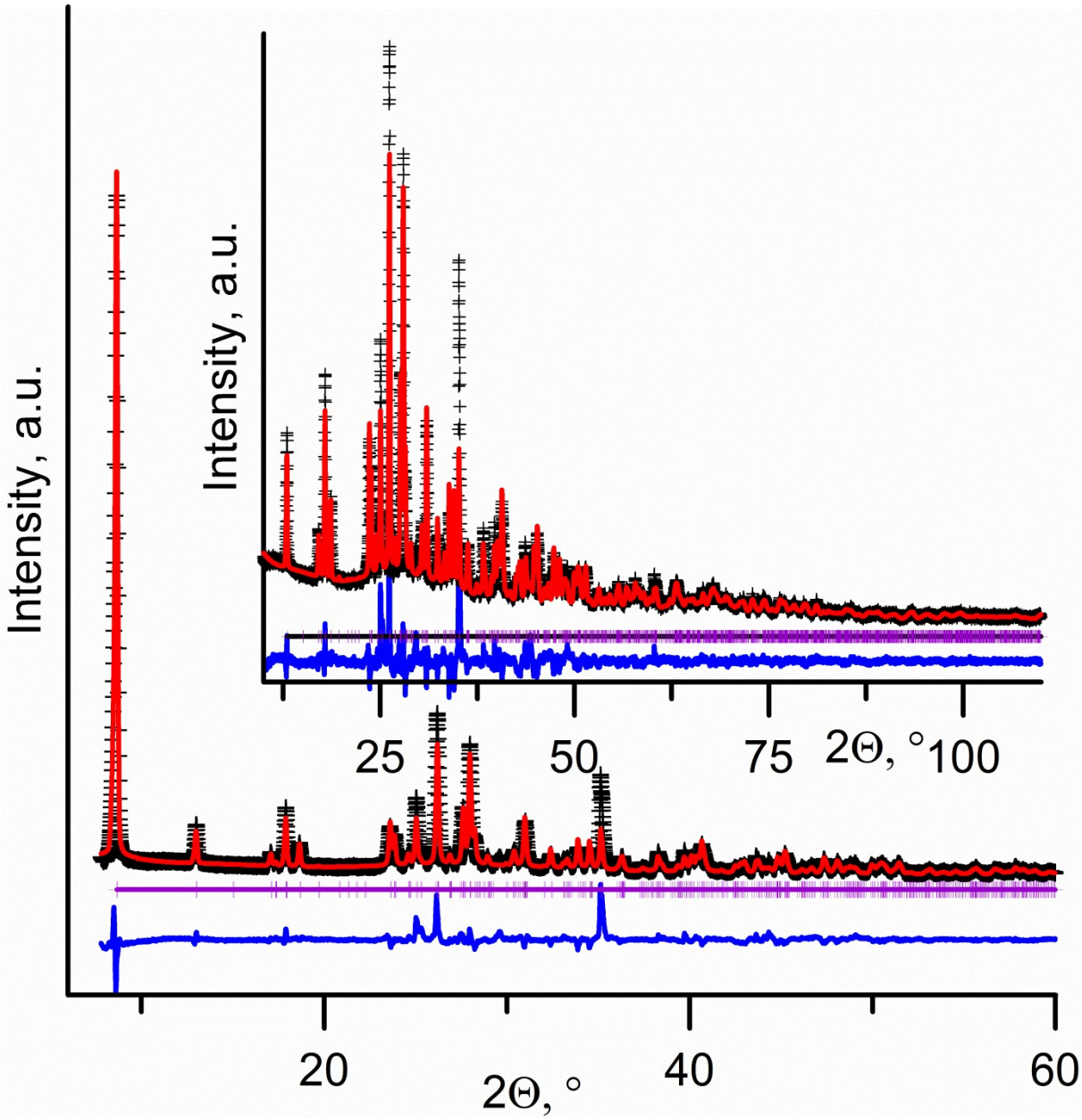

Figure S2. X-Ray powder pattern of $BaCH_3PO_3 \cdot H_2O$ with final Rietveld and difference plots.

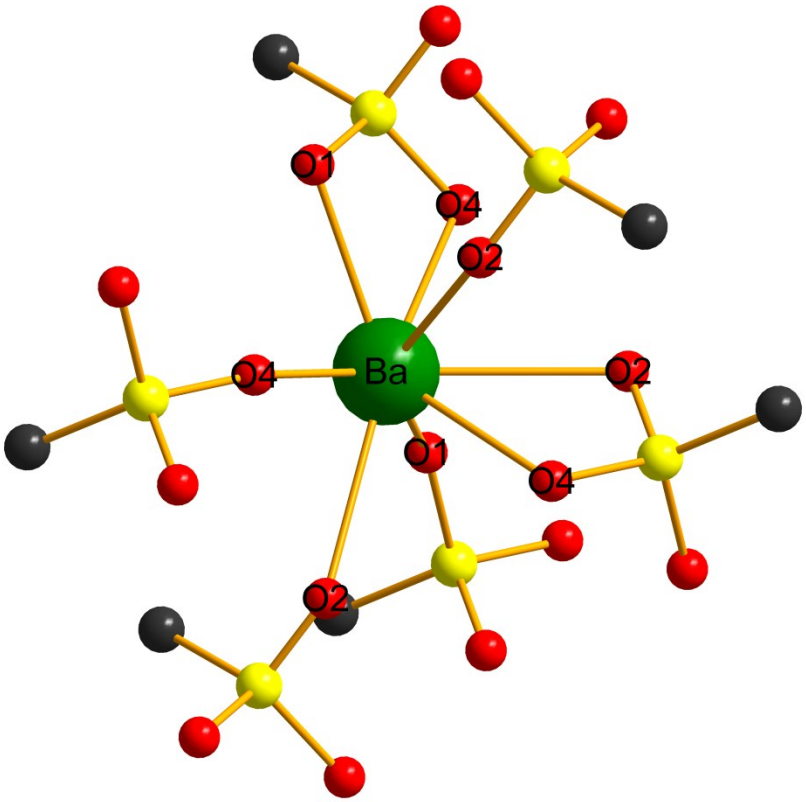

Figure S3. Bonding of the methylphosphonate ligands to the Ba atom in β-$BaCH_3PO_3$.

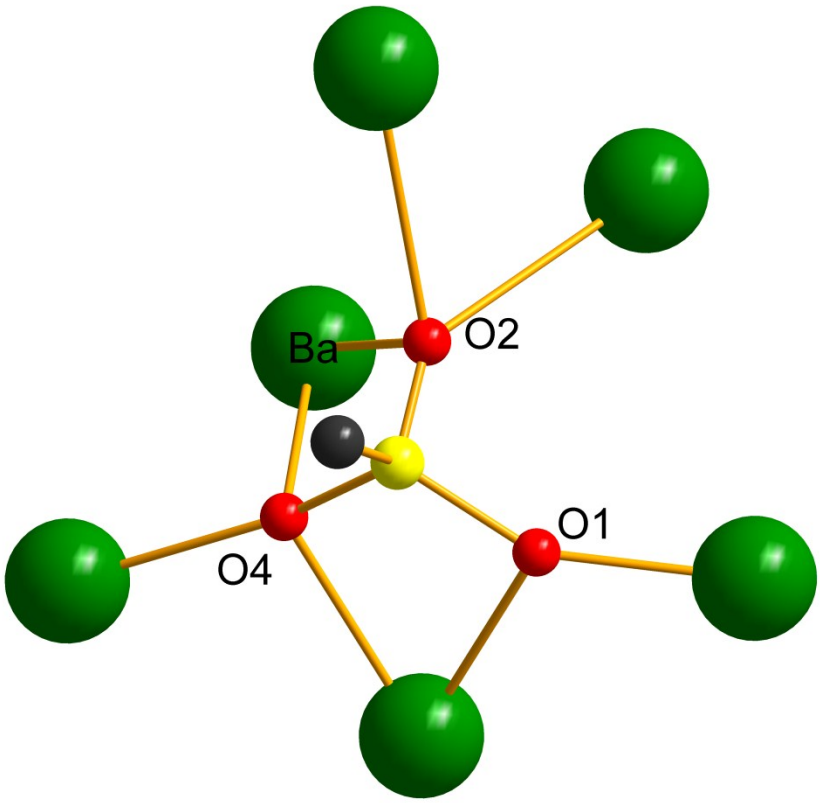

Figure S4. Coordination environment of the methylphosphonate ligand in β-$BaCH_3PO_3$.

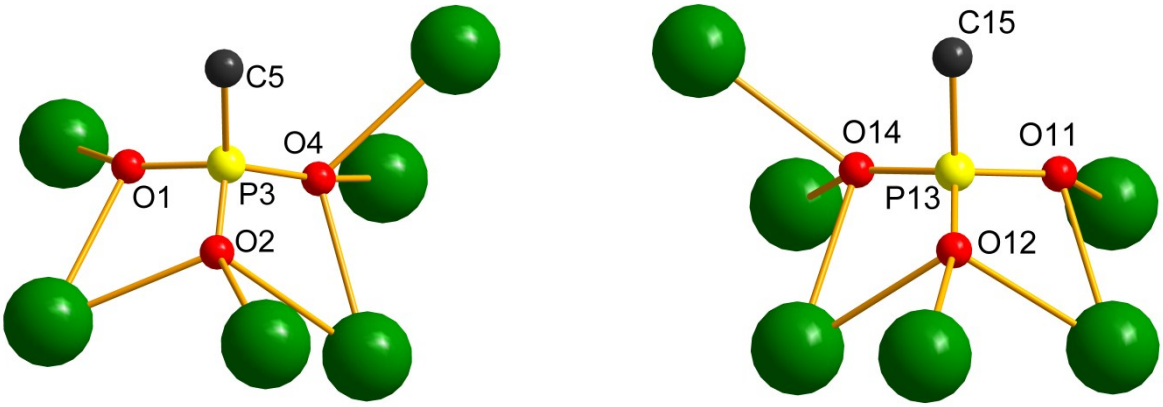

Figure S5. Coordination environment of the methylphosphonate ligands in $BaCH_3PO_3 \cdot H_2O$.

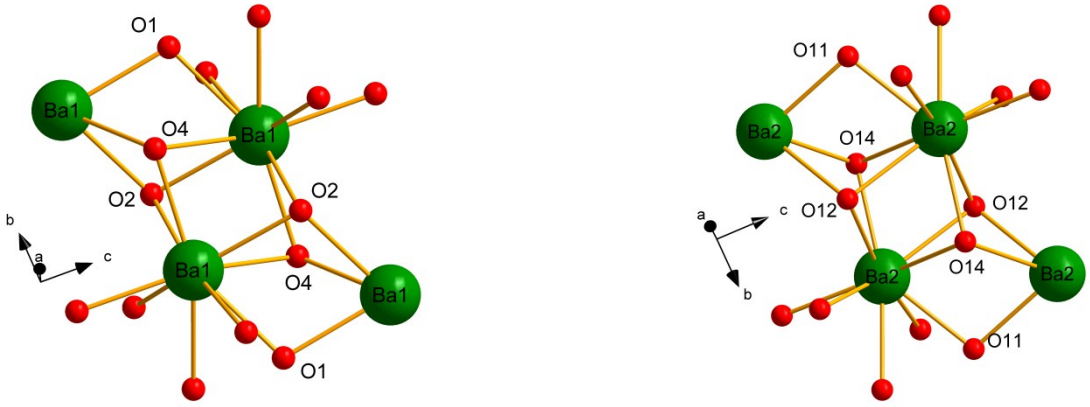

Figure S6. Fragment showing a connection between the Ba atoms in $BaCH_3PO_3 \cdot H_2O$.