Supporting Information

Syntheses and Characterization of Non-molecular Phenyl- and Methyl-Phosphonates and Ethylenediphosphonates of Thorium and Cerium.

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Table S1. Literature on tetravalent metal organophosphonate structurally characterized by powder X-ray diffraction

S.No.	Compound	Dimensionality (D)	Space group	Unit cell parameters				Reference
				a **(Å)**	***b*** **(Å)**	***c*** **(Å)**	**Non-orthogonal α/β/γ (°)**	
1)	$Zr(O_3PC_6H_5)_2$	2D	*C2/c*	9.0985(5)	5.4154(3)	30.235(2)	101.33	3
2)	$Zr(O_3PCH_2PO_3)$	3D	$P2_1$	7.589(1)	8.110(1)	5.056(1)	103.934(1)	6
3)	$Zr(HO_3PCH_2)_2NC_4H_8N(CH_2PO_3H)_2{\cdot}4H_2O$	2D	$P2_1$/c	10.7337(3)	12.8604(3)	7.8919(2)	104.91(2)	7
4)	$Zr(HO_3PCH_2)_2NC_6H_{10}N(CH_2PO_3H)_2{\cdot}5H_2O$	3D	*C2/c*	18.923(1)	16.5046(7)	7.8437(3)	91.868(3)	
5)	$Ti(O_3(CH_2)_2PO_3)$	3D	$P\bar{1}$	5.033(1)	5.092(1)	6.859(1)	95.860(1) 99.994(1) 118.217(1)	8
6)	$Ti(O_3(CH_2)_3PO_3)$	3D	*Cm2m*	5.230(1)	8.451(1)	17.400(2)		
7)	$Sn(O_3PCH_3)_2$	2D	$P2_1/c$	10.1207(10)	4.9865(4)	8.6365(7)	106.79(1)	9
8)	$Ce(O_3PC_6H_5)_2$	2D	*C2*	9.4040(3)	5.6454(2)	14.9146(5)	83.352(4)	10
9)	$Ce(O_3PCH_2COOH)_2\ H_2O$	2D	$P2_1$/a	21.3543(5)	9.8053(3)	5.1358(2)	90.731(3)	
10)	$U(O_3PC_6H_5)_2$	2D	*C2/m*	9.4559(7)	5.6769(5)A	14.9687(12)	96.539(5)	11

Table S2. Literature on tetravalent metal organophosphonates, structurally characterized by single crystal X-ray diffraction

S.No.	Compound	Dimensionality (D)	Space group	Unit cell parameters				Reference
				***a* (Å)**	***b* (Å)**	***c* (Å)**	**Non-orthogonal α/β/γ (°)**	
1)	$Zr(O_3PCH_2CH_2NC_5H_5)F_3$	2D	$P2_1/c$	12.3634(12)	9.3090(17)	9.8077(13)	112.819(8)	12
2)	$[(CH_3)_2NH_2]_2[Zr(O_3PCH_2PO_3H)_2]$	1D	$P\bar{1}$	5.4161(5)	8.4820(9)	10.2407(10)	98.482(5) 91.994(5) 102.790(5)	13
3)	$Ce[CH_2(PO_3)_2]$	3D	$P2_1/c$	7.4760(7)	8.5256(8)	9.3727(8)	101.429(1)	14
4)	α–$Ce[CH_2(PO_3)_2](H2O)$	3D	$P\bar{1}$	8.698(1)	8.730(1)	9.545(1)	71.359(1) 72.227(1) 82.787(1)	
5)	β–$Ce^{IV}[CH_2(PO_3)_2](H_2O)$	3D	$Pbca$	8.6082(4)	11.3256(5)	13.8384(6)		
6)	$Ce[CH_2(PO_3)_2](H_2O)_2$	3D	$Pna2_1$	8.840(2)	9.687(2)	8.680(2)		
7)	$Ce[C_6H_4(PO_3H)(PO_3H_2)][C_6H_4(PO_3H)(PO_3)]\cdot 2H_2O$	1D	$P\bar{1}$	9.467(1)	10.044(1)	12.671(2)	74.042(2) 78.299(2) 65.809(1)	15
8)	$Np[C_6H_4(PO_3H)_2]_2\cdot 2H_2O$	1D	$P\bar{1}$	7.886(1)	9.863(1)	12.810(2)	100.644(2) 95.617(2) 102.669(1)	
9)	$Pu[C_6H_4(PO_3H)\ (PO_3H_2)][C_6H_4(PO_3H)(PO_3)]\cdot 2H_2O$	1D	$P\bar{1}$	9.444(3)	10.021(3)	12.670(3)	74.024(2) 78.452(2) 66.042(2)	
10)	$Pu(CH_3PO_3)_2$	2D	$P2_1/c$	8.0895(12)	10.7001(10)	9.4541(14)	92.331(3)	16
11)	$Pu[CH_2(PO_3)_2](H_2O)$	3D	$P2_1/m$	6.513(3)	5.753(2)	9.023(4)	106.344(7)	
12)	$Th(O_3PCH_2PO_3)(H_2O)_2$	3D	$Pna2_1$	8.9658(4)	9.7748(5)	8.8042(4)		

13)	$(H_3O)[Th_2(O_3PC_6H_4PO_3)_2F]$	3D	$P2_1/c$	10.1611(7)	20.5782(13)	10.2490(7)	95.869(1)	
14)	$Th_2[(O_3PC_6H_4PO_3H)_2(HO_3PC_6H_4PO_3H)]$	3D	$P\bar{1}$	5.2623(4)	11.4968(8)	12.4799(9)	64.803(1) 84.129(1) 81.595(1)	17
15)	$U_2[(O_3PC_6H_4PO_3H)_2(HO_3PC_6H_4PO_3H)]$	3D	$P\bar{1}$	5.2055(10)	11.404(2)	12.408(2)	64.812(2) 84.183(2) 81.821(2)	
16)	$U(HO_3PC_6H_4PO_3H)_2 \cdot 1.5H_2O$	3D	$P\bar{1}$	7.931(3)	9.961(3)	12.952(4)	99.711(4) 95.693(4) 102.967(3)	18
17)	β–$Pu[CH_2(PO_3)_2](H_2O)$	3D	$P\bar{1}$	8.6692(5)	8.7012(5)	9.5318(6)	71.403(4) 72.248(3) 82.859(4)	19
18)	γ–$Pu[CH_2(PO_3)_2](H_2O)$		$Pbca$	8.5990(11)	11.2761(15)	13.7865(18)		
19)	$Pu[CH_2(PO_3)_2](H_2O)_3(H_2O)$		$P2_1/n$	5.2504(2)	8.2896(3)	16.4629(7)	93.912(1)	
20)	$U[CH_2\ (PO_3)_2](H_2O)$		$Pbca$	8.6227(6)	11.3457(7)	13.8635(9)		20
21)	$Np[CH_2(PO_3)_2](H_2O)_2$		$Pna2_1$	8.8418(15)	9.6381(16)	8.6627(15)		

Table S3. Pertinent details of hydrothermal synthetic reactions for homogeneous samples of compounds **1-5**

Reactants (g, mmol)		Temperature/duration	Solid product		
			Compound	Nature of sample	Yield (g, %)
$Th(OH)_4$ (0.275, 0.916)	$C_6H_5PO_3H_2$ (0.290, 1.834)	200 ˚C/4 days	$Th(O_3PC_6H_5)_2 \cdot H_2O$(**1**)	Polycrystalline	(0.350, 68)
$Th(OH)_4$ (0.357, 1.189)	$CH_3PO_3H_2$ (0.228, 2.374)	200 ˚C/4 days	$Th(O_3PCH_3)_2 \cdot H_2O$(**2**)	Polycrystalline	(0.381, 73)
$Th(OH)_4$ (0.359, 1.196)	$H_2O_3P(CH_2)_2PO_3H_2$ (0.228, 1.199)	200 ˚C/4 days	$Th(O_3P(CH_2)_2PO_3) \cdot H_2O$(**3)**	Polycrystalline	(0.359, 69)
CeO_2 (0.190, 1.103)	$CH_3PO_3H_2$ (0.345, 3.592)	200 ˚C/4 days	$Ce(O_3PCH_3)(HO_3PCH_3)$(**4**)	Single crystals	(0.150, 41)
CeO_2 (0.264, 1.533)	$H_2O_3P(CH_2)_2PO_3H_2$ (0.500, 2.630)	225 ˚C/4 days	$Ce(O_3P(CH_2)_2PO_3H)$(**5**)	Polycrystalline	(0.150, 30)

Table S4. Pertinent details of hydrothermal reactions yielding single crystals of compounds **1-3** and **5-8**

Reactants (g, mmol)			Temperature/duration	Solid product and yield
ThO_2 (0.275, 0.916)	$C_6H_5PO_3H_2$ (0.290, 1.834)	NH_4HF_2 (0.052, 0.916)	200 ˚C/15 days	$Th(O_3PC_6H_5)_2{\cdot}H_2O$(**1**) (0.310 g, 60%)
$Th(OH)_4$ (0.357, 1.189)	$CH_3PO_3H_2$ (0.400, 3.640)	NH_4HF_2 (0.034, 0.595)	200 ˚C/4 days	$Th(O_3PCH_3)_2{\cdot}H_2O$(**2**) + $Th(O_3PCH_3)F_2$(**6**) - biphasic mixture (0.311 g)
$Th(OH)_4$ (0.357, 1.189)	$CH_3PO_3H_2$ (0.228, 2.374)	NH_4HF_2 (0.067, 1.190)	200 ˚C/4 days	$Th(O_3PCH_3)_2{\cdot}H_2O$(**2**) + $Th(O_3PCH_3)F_2$(**6**) - biphasic mixture (0.331 g)
$Th(OH)_4$ (0.171, 0.571)	$CH_3PO_3H_2$ (0.056, 0.569)	NH_4HF_2 (0.032, 0.569)	200 ˚C/15 days	$Th(O_3PCH_3)F_2$(**6**) (0.1412 g, 68%)
$Th(OH)_4$ (0.359, 1.196)	$H_2O_3P(CH_2)_2PO_3H_2$ (0.228, 1.199)	NH_4HF_2 (0.0683, 1.196)	200 ˚C/4 days	$Th(O_3P(CH_2)_2PO_3){\cdot}H_2O$(**3**) + $Th(HO_3P(CH_2)_2PO_3)F{\cdot}H_2O$(**7**) - biphasic mixture (0.205 g)
CeO_2 (0.190, 1.103)	$CH_3PO_3H_2$ (0.345, 3.592)	NH_4HF_2 (0.063, 1.104)	200 ˚C/4 days	$Ce(HO_3PCH_3)_2F_2$(**8**) (0.222 g, 55%)
CeO_2 (0.264, 1.533)	$H_2O_3P(CH_2)_2PO_3H_2$ (0.500, 2.630)	NH_4HF_2 (0.087, 1.525)	225 ˚C/4 days	$Ce(O_3P(CH_2)_2PO_3H)$(**5**) (0.149 g, 30%)

Table S5. Types of twinning, twin laws, rotation axes for generation of twinned lattices and BASF values for crystals of compounds **1** and **3-6**

Compound	**Twinning**	**Twin law**	**180° rotation axis for generation of twinned lattices**	**BASF value**
$Th(O_3PC_6H_5)_2 \cdot H_2O$(**1**)	non–merohedral	[1 0 0], [0 –1 0], [–0.540 0 –1]	[1 0 0]	0.16428
$Th(O_3P(CH_2)_2PO_3) \cdot H_2O$(**3**)	non–merohedral	[1 0 0], [0 –1 0], [–0.967 0 –1]	[1 0 0]	0.17801
$Ce(O_3PCH_3)(HO_3PCH_3)$(**4**)	non–merohedral	[–1 0 0], [0 –1 0], [–0.118 –0.674 1]	[0 0 1]	0.21176
$Ce(O_3P(CH_2)_2PO_3H)$(**5**)	non–merohedral	[-1 0 0], [0.022 1 -0.585], [0 0 –1]	[0 1 0]	0.08599
$Th(O_3PCH_3)F_2$(**6**)	merohedral	[1 0 0], [0 –1 0], [0 0 –1]	[1 0 0]	0.49118

Table S6. Wyckoff sites, atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for non–hydrogen atoms of $Th(O_3PC_6H_5)_2 \cdot H_2O$(**1**)

Atom	**Wyckoff site**	***x***	***y***	***z***	***U_{eq}**
Th(1)	2*i*	7090(1)	10813(1)	4822(1)	7(1)
Th(2)	2*i*	7814(1)	5813(1)	4827(1)	7(1)
P(1)	2*i*	4993(5)	3442(4)	3771(3)	8(1)
P(2)	2*i*	9340(5)	8447(4)	3775(3)	7(1)
P(3)	2*i*	4888(5)	8023(4)	3782(3)	9(1)
P(4)	2*i*	9446(5)	13010(4)	3778(3)	8(1)
O(1)	2*i*	6285(14)	4274(12)	4102(10)	16(3)
O(2)	2*i*	5318(13)	2038(12)	3929(9)	11(3)
O(3)	2*i*	3776(13)	3866(12)	4218(9)	11(3)
O(4)	2*i*	8206(13)	9267(12)	4078(9)	12(3)
O(5)	2*i*	9108(13)	7056(12)	3942(9)	14(3)
O(6)	2*i*	10791(14)	8876(12)	4234(9)	16(3)
O(7)	2*i*	6060(13)	7041(12)	3961(9)	11(3)
O(8)	2*i*	3525(14)	7580(12)	4090(9)	14(3)
O(9)	2*i*	5271(13)	9298(12)	4292(10)	14(3)
O(10)	2*i*	8362(13)	12039(12)	3948(9)	13(3)
O(11)	2*i*	10970(13)	12590(12)	4088(9)	12(3)
O(12)	2*i*	9342(13)	14282(11)	4277(10)	13(3)
O(1W)	2*i*	7250(14)	9239(12)	6050(9)	16(3)
O(2W)	2*i*	8324(14)	4225(12)	6059(10)	16(3)
C(1)	2*i*	4489(15)	3626(13)	2569(7)	14(4)
C(2)	2*i*	4169(17)	2568(10)	1999(10)	31(5)
C(3)	2*i*	3810(20)	2720(14)	1070(9)	46(7)
C(4)	2*i*	3780(20)	3930(17)	711(7)	46(7)
C(5)	2*i*	4100(20)	4987(13)	1281(11)	51(8)
C(6)	2*i*	4452(18)	4835(11)	2210(10)	37(6)
C(7)	2*i*	9230(15)	8597(12)	2573(7)	14(4)
C(8)	2*i*	9220(17)	7527(10)	2012(10)	31(5)
C(9)	2*i*	9130(20)	7662(14)	1085(9)	47(7)
C(10)	2*i*	9051(19)	8868(17)	718(7)	43(7)
C(11)	2*i*	9061(19)	9939(13)	1279(10)	44(7)
C(12)	2*i*	9151(18)	9803(10)	2206(10)	33(6)
C(13)	2*i*	4518(14)	8310(16)	2592(8)	14(4)
C(14)	2*i*	5616(12)	8310(20)	2102(11)	63(11)
C(15)	2*i*	5356(18)	8590(20)	1189(11)	70(10)
C(16)	2*i*	4000(20)	8880(20)	764(8)	47(8)
C(17)	2*i*	2901(15)	8880(20)	1254(11)	72(11)
C(18)	2*i*	3161(13)	8600(20)	2167(11)	54(9)
C(19)	2*i*	9218(15)	13280(16)	2582(8)	18(4)
C(20)	2*i*	7894(13)	13144(18)	2050(10)	43(7)
C(21)	2*i*	7708(15)	13380(20)	1130(10)	60(9)
C(22)	2*i*	8850(20)	13760(20)	742(8)	49(8)
C(23)	2*i*	10169(16)	13900(20)	1274(11)	62(10)
C(24)	2*i*	10356(12)	13656(18)	2194(10)	44(7)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S7. Wyckoff sites, atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for non–hydrogen atoms of $Th(O_3PCH_3)_2 \cdot H_2O$(**2**)

Atom	**Wyckoff site**	***x***	***y***	***z***	U_{eq}
Th(1)	2*i*	5212(1)	2933(1)	828(1)	20(1)
Th(2)	2*i*	4710(1)	7816(1)	4164(1)	20(1)
P(1)	2*i*	6987(1)	5122(1)	3546(1)	20(1)
P(2)	2*i*	2985(1)	9141(1)	1442(1)	19(1)
P(3)	2*i*	2967(1)	4765(1)	1897(1)	20(1)
P(4)	2*i*	6988(1)	697(1)	3074(1)	20(1)
O(1)	2*i*	6169(4)	6247(3)	3902(3)	33(1)
O(2)	2*i*	6813(4)	4806(3)	2104(3)	26(1)
O(3)	2*i*	6497(4)	3757(3)	4305(3)	32(1)
O(4)	2*i*	3197(3)	8984(3)	2888(3)	25(1)
O(5)	2*i*	3645(4)	8098(3)	707(3)	32(1)
O(6)	2*i*	3630(4)	10696(3)	1060(3)	33(1)
O(7)	2*i*	3178(4)	5933(3)	2894(3)	26(1)
O(8)	2*i*	3407(4)	3394(3)	2337(3)	27(1)
O(9)	2*i*	3908(3)	5202(3)	711(3)	25(1)
O(10)	2*i*	6683(4)	1725(3)	2079(3)	28(1)
O(11)	2*i*	6546(3)	–895(3)	2660(3)	25(1)
O(12)	2*i*	6118(4)	707(3)	4300(3)	27(1)
O(1W)	2*i*	3128(4)	2645(3)	–802(3)	27(1)
O(2W)	2*i*	6824(4)	8480(3)	5790(3)	29(1)
C(1)	2*i*	8928(6)	5923(7)	3925(6)	54(2)
C(2)	2*i*	1019(6)	8711(7)	1065(6)	51(1)
C(3)	2*i*	1063(6)	4292(6)	1359(6)	49(1)
C(4)	2*i*	8924(6)	1183(6)	3503(6)	50(1)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S8. Wyckoff sites, atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for non–hydrogen atoms of $Th(O_3P(CH_2)_2PO_3)\cdot H_2O$(**3**)

Atom	**Wyckoff site**	***x***	***y***	***z***	****U$_{eq}$***
Th(1)	4*e*	–997(1)	2136(1)	4274(1)	8(1)
P(1)	4*e*	95(4)	5362(3)	2730(3)	8(1)
P(2)	4*e*	5314(4)	4733(3)	2688(3)	8(1)
O(1)	4*e*	3(12)	3971(8)	3395(9)	16(2)
O(2)	4*e*	482(12)	6554(9)	3756(9)	18(2)
O(3)	4*e*	–1570(11)	5614(9)	1460(8)	12(2)
O(4)	4*e*	6635(12)	3663(9)	3535(9)	15(2)
O(5)	4*e*	6012(12)	6237(8)	2904(9)	15(2)
O(6)	4*e*	4720(12)	4526(8)	1122(8)	13(2)
O(1W)	4*e*	2218(12)	1956(8)	5220(9)	16(2)
C(1)	4*e*	1819(17)	5237(14)	2102(14)	17(3)
C(2)	4*e*	3478(17)	4629(14)	3179(13)	17(3)

*U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table S9. Wyckoff sites, atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for non–hydrogen atoms of $Ce(O_3PCH_3)(HO_3PCH_3)$(**4**)

Atom	**Wyckoff site**	***x***	***y***	***z***	****U$_{eq}$***
Ce(1)	2*i*	–2479(3)	7626(2)	4624(1)	13(1)
P(1)	2*i*	–1352(11)	9265(7)	7008(6)	12(1)
P(2)	2*i*	3892(11)	5608(7)	2984(6)	12(1)
O(1)	2*i*	50(30)	7408(18)	6720(15)	16(4)
O(2)	2*i*	–3320(30)	10078(19)	5871(15)	18(3)
O(3)	2*i*	510(30)	10344(18)	7004(14)	12(3)
O(4)	2*i*	1780(30)	5673(19)	4108(15)	21(3)
O(5)	2*i*	5270(30)	3560(19)	3271(14)	16(3)
O(6)	2*i*	5770(30)	6689(19)	2986(14)	15(3)
C(1)	2*i*	–3030(50)	8830(30)	8670(20)	26(5)
C(2)	2*i*	2410(50)	6310(30)	1320(20)	27(6)

*U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table S10. Wyckoff sites, atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for non–hydrogen atoms of $Ce(O_3P(CH_2)_2PO_3H)$(**5**)

Atom	Wyckoff site	*x*	*y*	*z*	*U_{eq}
Ce(1)	2*i*	7531(1)	9412(1)	–2373(1)	8(1)
Ce(2)	2*i*	2518(1)	172(1)	7410(1)	8(1)
P(1)	2*i*	4936(5)	7752(5)	1379(5)	9(1)
P(2)	2*i*	4952(5)	2454(5)	3777(5)	9(1)
P(3)	2*i*	14(5)	2516(5)	9815(5)	9(1)
P(4)	2*i*	10023(5)	7606(5)	–5062(5)	8(1)
O(1)	2*i*	5992(14)	7644(12)	–55(12)	11(2)
O(2)	2*i*	5388(14)	9177(11)	1726(12)	10(2)
O(3)	2*i*	3015(14)	8051(12)	1514(13)	12(3)
O(4)	2*i*	3933(14)	2359(12)	5265(13)	13(2)
O(5)	2*i*	4530(14)	1090(12)	3334(13)	13(3)
O(6)	2*i*	6898(14)	2234(12)	3554(13)	13(3)
O(7)	2*i*	1004(14)	2066(13)	8535(13)	13(3)
O(8)	2*i*	345(14)	1451(12)	11190(12)	12(2)
O(9)	2*i*	–1946(13)	2273(12)	10210(13)	12(3)
O(10)	2*i*	8969(13)	7462(12)	–3544(13)	12(3)
O(11)	2*i*	9594(14)	9118(12)	–6184(12)	11(2)
O(12)	2*i*	11960(14)	7857(12)	–5369(13)	13(3)
C(1)	2*i*	5070(20)	5878(17)	2744(18)	11(3)
C(2)	2*i*	4670(20)	4376(17)	2503(19)	12(4)
C(3)	2*i*	450(20)	4643(18)	9402(18)	14(3)
C(4)	2*i*	9780(20)	5836(16)	–5492(18)	11(3)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S11. Wyckoff sites, atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for non–hydrogen atoms of $Th(O_3PCH_3)\cdot F_2$(**6**)

Atom	Wyckoff site	*x*	*y*	*z*	*U_{eq}
Th(1)	4*i*	5654(1)	10000	7457(5)	8(1)
P(1)	4*i*	6355(2)	5000	2510(50)	22(2)
O(1)	4*i*	5974(9)	5000	400(50)	23(5)
O(2)	8*j*	6301(5)	8000(40)	4770(30)	19(3)
C(1)	4*i*	6983(14)	5000	1450(80)	31(9)
F(1)	4*i*	4731(5)	10000	7320(70)	10(3)
F(2)	4*i*	5326(7)	5000	8680(40)	13(4)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S12. Wyckoff sites, atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for non–hydrogen atoms of $Th(O_3P(CH_2)_2PO_3H)F{\cdot}H_2O$(**7**)

Atom	**Wyckoff site**	***x***	***y***	***z***	****U**$_{eq}$***
Th(1)	4*e*	4700(1)	10776(1)	1652(1)	7(1)
P(1)	4*e*	8134(1)	9270(1)	1981(1)	10(1)
P(2)	4*e*	3171(1)	7223(1)	2252(1)	11(1)
O(1)	4*e*	6958(3)	9583(3)	2479(3)	13(1)
O(2)	4*e*	9173(3)	8047(3)	2851(3)	15(1)
O(3)	4*e*	7488(3)	8868(3)	418(3)	15(1)
O(4)	4*e*	3816(3)	8761(3)	2466(3)	16(1)
O(5)	4*e*	1934(3)	7069(3)	2662(4)	18(1)
O(6)	4*e*	2555(4)	6809(4)	640(4)	23(1)
O(1W)	4*e*	5947(4)	10983(4)	4347(4)	26(1)
F(1)	4*e*	4425(3)	8712(3)	85(3)	14(1)
C(1)	4*e*	9204(5)	10939(5)	2323(5)	16(1)
C(2)	4*e*	4549(5)	5878(5)	3138(5)	17(1)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S13. Wyckoff sites, atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for non–hydrogen atoms of $Ce(HO_3PCH_3)_2F_2$(**8**)

Atom	**Wyckoff site**	***x***	***y***	***z***	****U**$_{eq}$***
Ce(1)	4*a*	5000	5000	7500	9(1)
P(1)	8*j*	7026(2)	6776(2)	10000	19(1)
O(1)	8*j*	6927(6)	8129(5)	10000	26(1)
O(2)	16*k*	6394(4)	6335(3)	8373(4)	24(1)
F(1)	8*j*	4105(4)	4248(3)	5000	18(1)
C(1)	8*j*	8638(10)	6391(9)	10000	34(2)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S14. Selected bond lengths (Å) for thorium compounds **1-3**

$Th(O_3PC_6H_5)_2 \cdot H_2O$**(1)**		$Th(O_3PCH_3)_2 \cdot H_2O$**(2)**		$Th(O_3P(CH_2)_2PO_3) \cdot H_2O$**(3)**	
Bond	**Bond Length**	**Bond**	**Bond Length**	**Bond**	**Bond Length**
Th(1)–O(6)#1	2.297(13)	Th(1)–O(6)#1	2.286(3)	Th(1)–O(1)	2.290(8)
Th(1)–O(4)	2.322(12)	Th(1)–O(5)#2	2.303(3)	Th(1)–O(2)#1	2.318(8)
Th(1)–O(10)	2.350(13)	Th(1)–O(10)	2.362(3)	Th(1)–O(4)#2	2.344(9)
Th(1)–O(2)#2	2.379(12)	Th(1)–O(2)	2.391(3)	Th(1)–O(3)#3	2.380(8)
Th(1)–O(9)	2.390(13)	Th(1)–O(9)#2	2.410(3)	Th(1)–O(6)#4	2.405(8)
Th(1)–O(8)#3	2.469(13)	Th(1)–O(8)	2.456(3)	Th(1)–O(5)#5	2.444(8)
Th(1)–O(1W)	2.488(13)	Th(1)–O(1W)	2.496(3)	Th(1)–O(1W)	2.491(9)
BVS	3.944	BVS	3.941	BVS	3.979
Th(2)–O(3)#4	2.296(13)	Th(2)–O(1)	2.276(3)	P(1)–O(2)	1.519(9)
Th(2)–O(1)	2.312(13)	Th(2)–O(3)#3	2.317(3)	P(1)–O(1)	1.521(8)
Th(2)–O(7)	2.351(12)	Th(2)–O(7)	2.367(3)	P(1)–O(3)	1.535(9)
Th(2)–O(5)	2.384(13)	Th(2)–O(4)	2.379(3)	P(1)–C(1)	1.809(13)
Th(2)–O(12)#5	2.410(13)	Th(2)–O(12)#3	2.403(3)	P(2)–O(4)	1.520(9)
Th(2)–O(11)#1	2.464(13)	Th(2)–O(11)#4	2.456(3)	P(2)–O(5)	1.538(9)
Th(2)–O(2W)	2.502(13)	Th(2)–O(2W)	2.508(3)	P(2)–O(6)	1.540(8)
BVS	3.916	BVS	3.942	P(2)–C(2)	1.805(13)
P(1)–O(3)	1.513(13)	P(1)–O(3)	1.506(3)	C(1)–C(2)	1.530(18)
P(1)–O(2)	1.524(13)	P(1)–O(1)	1.513(3)		
P(1)–O(1)	1.528(14)	P(1)–O(2)	1.536(3)		
P(1)–C(1)	1.801(12)	P(1)–C(1)	1.799(6)		
P(2)–O(5)	1.512(13)	P(2)–O(5)	1.513(3)		
P(2)–O(6)	1.514(14)	P(2)–O(6)	1.515(3)		
P(2)–O(4)	1.518(13)	P(2)–O(4)	1.535(3)		
P(2)–C(7)	1.800(11)	P(2)–C(2)	1.794(5)		
P(3)–O(7)	1.524(13)	P(3)–O(7)	1.499(3)		
P(3)–O(9)	1.543(14)	P(3)–O(8)	1.533(3)		
P(3)–O(8)	1.543(14)	P(3)–O(9)	1.540(3)		
P(3)–C(13)	1.793(12)	P(3)–C(3)	1.780(5)		
P(4)–O(10)	1.519(13)	P(4)–O(10)	1.501(3)		
P(4)–O(12)	1.531(13)	P(4)–O(11)	1.530(3)		
P(4)–O(11)	1.532(13)	P(4)–O(12)	1.541(3)		
P(4)–C(19)	1.798(12)	P(4)–C(4)	1.779(6)		

Symmetry transformations used to generate equivalent atoms:

$Th(O_3PC_6H_5)_2 \cdot H_2O$**(1)**: #1 –x+2,–y+2,–z+1 #2 x,y+1,z #3 –x+1,–y+2,–z+1 #4 –x+1,–y+1,–z+1 #5 x,y–1,z,

$Th(O_3PCH_3)_2.H_2O$(**2**): #1 –x+1,–y+1,–z+1 #2 x,y+1,z #3 x,y–1,z #4 –x+1,–y+1,–z,

$Th(O_3P(CH_2)_2PO_3) \cdot H_2O$(**3**): #1 –x,–y+1,–z+1 #2 x–1,y,z #3 –x–1/2,y–1/2,–z+1/2 #4 x–1/2,–y+1/2,z+1/2 #5 –x+1/2,y–1/2,–z+1/2 #6 –x+1/2,y+1/2,–z+1/2 #7 x+1,y,z #8 x+1/2,–y+1/2,z–1/2 #9 –x–1/2,y+1/2,–z+1/2

Table S15. Selected bond lengths (Å) for cerium(III) compounds **4** and **5**

$Ce(O_3PCH_3)(HO_3PCH_3)$(**4**)		$Ce(O_3P(CH_2)_2PO_3H)$**(5)**			
Bond	**Bond Length**	**Bond**	**Bond Length**	**Bond**	**Bond Length**
Ce(1)–O(3)#1	2.378(12)	Ce(1)–O(1)	2.382(11)	P(1)–O(1)	1.508(12)
Ce(1)–O(6)#2	2.382(14)	Ce(1)–O(10)	2.424(11)	P(1)–O(2)	1.534(10)
Ce(1)–O(4)	2.485(15)	Ce(1)–O(8)#1	2.439(11)	P(1)–O(3)	1.569(11)
Ce(1)–O(2)#3	2.487(16)	Ce(1)–O(5)#2	2.447(11)	P(1)–C(1)	1.784(16)
Ce(1)–O(2)	2.558(14)	Ce(1)–O(11)#3	2.558(11)	P(2)–O(4)	1.495(12)
Ce(1)–O(4)#4	2.566(14)	Ce(1)–O(2)#4	2.591(11)	P(2)–O(5)	1.540(10)
Ce(1)–O(1)	2.584(15)	Ce(1)–O(3)#4	2.615(10)	P(2)–O(6)	1.566(11)
Ce(1)–O(5)#4	2.593(13)	Ce(1)–O(12)#3	2.662(12)	P(2)–C(2)	1.796(16)
BVS	2.911	BVS	2.855	P(3)–O(7)	1.491(12)
P(1)–O(3)	1.503(13)	Ce(2)–O(7)	2.373(10)	P(3)–O(8)	1.534(12)
P(1)–O(2)	1.524(16)	Ce(2)–O(4)	2.407(11)	P(3)–O(9)	1.569(11)
P(1)–O(1)	1.576(15)	Ce(2)–O(2)#1	2.451(10)	P(3)–C(3)	1.794(15)
P(1)–C(1)	1.82(2)	Ce(2)–O(11)#2	2.459(11)	P(4)–O(10)	1.518(12)
P(2)–O(6)	1.512(13)	Ce(2)–O(5)#5	2.568(11)	P(4)–O(11)	1.539(11)
P(2)–O(4)	1.523(15)	Ce(2)–O(6)#5	2.575(10)	P(4)–O(12)	1.568(11)
P(2)–O(5)	1.575(16)	Ce(2)–O(9)#6	2.599(12)	P(4)–C(4)	1.807(14)
P(2)–C(2)	1.81(2)	Ce(2)–O(8)#6	2.602(10)	C(1)–C(2)	1.515(18)
		BVS	2.917	C(3)–C(3)#7	1.54(3)
				C(4)–C(4)#8	1.55(3)

Symmetry transformations used to generate equivalent atoms for $Ce(O_3PCH_3)(HO_3PCH_3)$(**4**): #1 –x,–y+2,–z+1 #2 x–1,y,z #3 –x–1,–y+2,–z+1 #4 –x,–y+1,–z+1 #5 x+1,y,z

$Ce(O_3P(CH_2)_2PO_3H)$(**5**): #1 –x+1,–y+1,–z+1 #2 –x+1,–y+1,–z #3 –x+2,–y+2,–z–1 #4 –x+1,–y+2,–z #5 –x+1,–y,–z+1 #6 –x,–y,–z+2 #7 –x+2,–y+1,–z–1 #8 –x,–y+1,–z+2

Table S16. Selected bond lengths (Å) for thorium and cerium(IV) compounds **6**–**8**

$Th(O_3PCH_3)F_2$(**6**)		$Th(HO_3P(CH_2)_2PO_3)F{\cdot}H_2O$(**7**)		$Ce(HO_3PCH_3)_2F_2$(**8**)	
Bond	**Bond Length**	**Bond**	**Bond Length**	**Bond**	**Bond Length**
Th(1)–O(2)	2.285(15)	Th(1)–O(2)#1	2.290(3)	Ce(1)–O(2)	2.246(4)
Th(1)–O(2)#1	2.285(15)	Th(1)–O(1)	2.336(3)	Ce(1)–O(2)#1	2.246(4)
Th(1)–F(2)#2	2.339(8)	Th(1)–O(4)	2.346(3)	Ce(1)–O(2)#2	2.246(4)
Th(1)–F(2)	2.339(8)	Th(1)–O(3)#2	2.376(3)	Ce(1)–O(2)#3	2.246(4)
Th(1)–F(1)#3	2.43(3)	Th(1)–O(5)#3	2.381(3)	Ce(1)–F(1)#3	2.331(2)
Th(1)–F(1)	2.469(12)	Th(1)–F(1)#2	2.401(2)	Ce(1)–F(1)#4	2.331(2)
Th(1)–F(1)#4	2.61(3)	Th(1)–F(1)	2.423(2)	Ce(1)–F(1)#5	2.331(2)
Th(1)–O(1)#5	2.636(14)	Th(1)–O(1W)	2.577(4)	Ce(1)–F(1)	2.331(2)
Th(1)–O(1)#6	2.636(14)	BVS	4.220	BVS	3.832
BVS	3.934	P(1)–O(1)	1.524(3)	P(1)–O(2)#7	1.519(4)
P(1)–O(1)	1.41(3)	P(1)–O(2)	1.529(3)	P(1)–O(2)	1.519(4)
P(1)–O(2)#8	1.64(2)	P(1)–O(3)	1.534(3)	P(1)–O(1)	1.569(6)
P(1)–O(2)	1.64(2)	P(1)–C(1)	1.798(4)	P(1)–C(1)	1.771(10)
P(1)–C(1)	1.75(4)	P(2)–O(5)	1.500(3)		
		P(2)–O(4)	1.507(3)		
		P(2)–O(6)	1.586(4)		
		P(2)–C(2)	1.782(5)		
		C(1)–C(2)#1	1.541(6)		

Symmetry transformations used to generate equivalent atoms for:

$Th(O_3PCH_3).F_2$(**6**): #1 x,–y+2,z #2 x,y+1,z #3 –x+1,–y+2,–z+1 #4 –x+1,–y+2,–z+2 #5 x,y+1,z+1 #6 x,y,z+1 #7 x,y–1,z #8 x,–y+1,z #9 x,y–1,z–1 #10 x,y,z–1

$Th(HO_3P(CH_2)_2PO_3H){\cdot}F{\cdot}H_2O$(**7**) : #1 –x+3/2,y+1/2,–z+1/2 #2 –x+1,–y+2,–z #3 –x+1/2,y+1/2,–z+1/2 #4 –x+3/2,y–1/2,–z+1/2 #5 –x+1/2,y–1/2,–z+1/2

$Ce(HO_3PCH_3)_2.F_2$(**8**): #1 –x+1,–y+1,z #2 x+0,–y+1,–z+3/2 #3 –x+1,y+0,–z+3/2 #4 x,–y+1,z+1/2 #5 –x+1,–y+1,–z+1 #6 –x+1,–y+1,–z+2 #7 x,y,–z+2

Table S17. Nonbonding O(W)···O distances (Å), indicative of hydrogen bonding, in thorium compounds **1–3** and **7**

$Th(O_3PC_6H_5)_2 \cdot H_2O$(**1**)		$Th(O_3PCH_3)_2 \cdot H_2O$(**2**)		$Th(O_3P(CH_2)_2PO_3) \cdot H_2O$(**3**)		$Th(HO_3P(CH_2)_2PO_3)F \cdot H_2O$(**7**)	
Nonbonding O(W)···O	**Distance (Å)**	**Nonbonding O(W)···O**	**Distance (Å)**	**Nonbonding O(W)···O**	**Distance (Å)**	**Nonbonding O(W)···O**	**Distance (Å)**
O(1W)···O(3)	2.838(18) Å	O(1W)···O(6)	2.806(4) Å	O(1W)···O(6)	2.878(10) Å	O(1W)···O(1)	2.876(5) Å
O(1W)···O(8)	2.584(18) Å	O(1W)···O(9)	2.831(4) Å	O(1W)···O(1)	2.849(10) Å	O(1W)···O(2)	2.934(5) Å
O(1W)···O(5)	2.820(18) Å	O(1W)···O(2)	2.781(4) Å	O(1W)···O(5)	2.615(10) Å	O(1W)···O(3)	2.999(4) Å
O(1W)···O(12)	2.867(19) Å	O(1W)···O(11)	2.636(4) Å	O(1W)···O(3)	2.788(11) Å	O(1W)···O(4)	2.989(4) Å
O(2W)···O(11)	2.607(18) Å	O(2W)···O(12)	2.833(4) Å			O(1W)···O(5)	2.947(4) Å
O(2W)···O(2)	2.824(18) Å	O(2W)···O(1)	2.842(4) Å			O(1W)···O(6)	2.988(4) Å
O(2W)···O(9)	2.854(18) Å	O(2W)···O(8)	2.636(4) Å				
O(2W)···O(6)	2.828(18) Å	O(2W)···O(4)	2.790(4) Å				

Table S18. Observed and calculated thermal % weight losses for the formation thermal decomposition ThP_2O_7/CeP_2O_7 residue for compounds **1**-**6** and **8**.

Compound	**Observed % weight loss**	**Calculated % weight loss for ThP_2O_7/CeP_2O_7**
$Th(O_3PC_6H_5)_2 \cdot H_2O$(**1**)	17	27.78
$Th(O_3PCH_3)_2 \cdot H_2O$(**2**)	7.55	7.32
$Th(O_3P(CH_2)_2PO_3) \cdot H_2O$(**3**)	7.38	6.89
$Ce(O_3PCH_3)(HO_3PCH_3)$(**4**)	3.06	4.58
$Ce(O_3P(CH_2)_2PO_3H)$(**5**)	2.30	3.99
$Th(O_3PCH_3)F_2$(**6**)	12.15	−11.52
$Ce(HO_3PCH_3)_2F_2$(**8**)	16.77	14.69

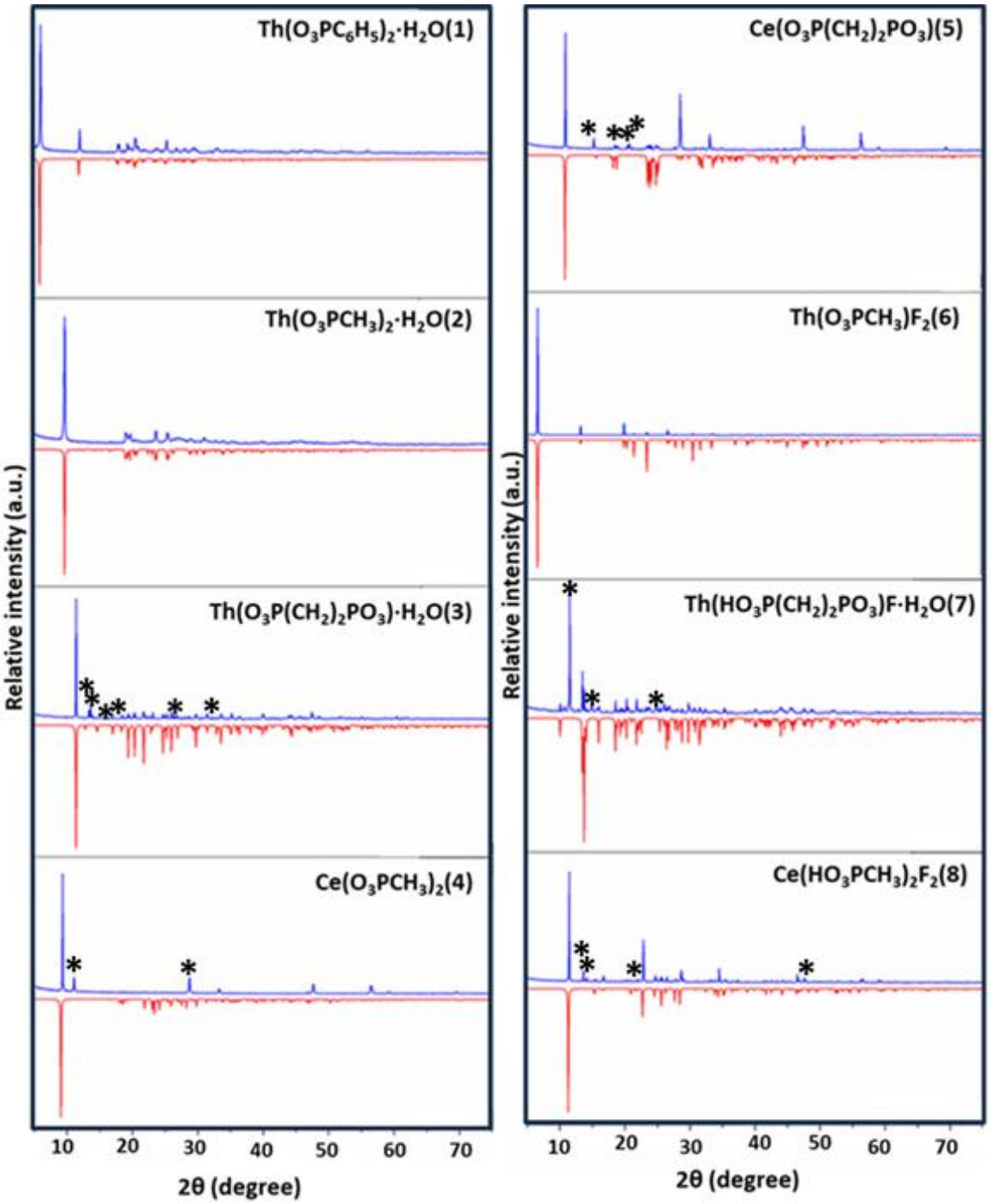

Figure S1. Simulated (red) and observed (blue) powder XRD patterns of compounds **1-8** (* represents unidentified reflections in the case of compounds **3**, **4**, **5**, **7** and **8**).

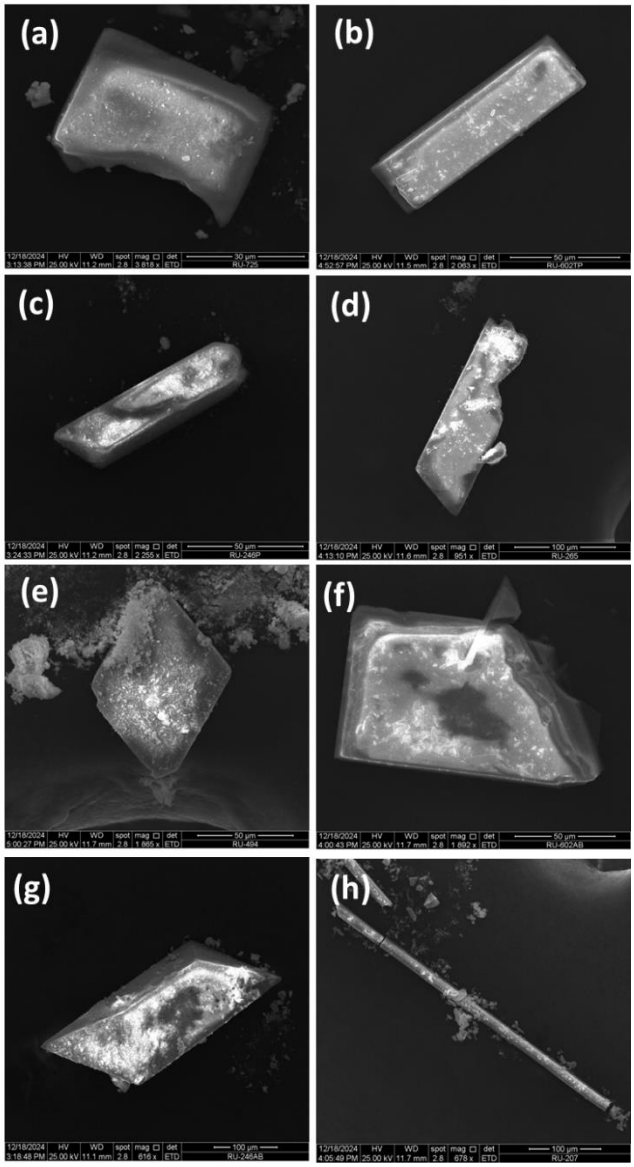

Figure S2. Scanning electron microscopy (SEM) images of crystallites of (a) $Th(O_3PC_6H_5)_2 \cdot H_2O$(**1**), (b) $(Th(O_3PCH_3)_2 \cdot H_2O$(**2**), (c) $Th(O_3P(CH_2)_2PO_3) \cdot H_2O$(**3**), (d) $Ce(O_3PCH_3)(HO_3PCH_3)$(**4**), (e) $Ce(O_3P(CH_2)_2PO_3H)$(**5**), (f) $Th(O_3PCH_3)F_2$(**6**), (g) $Th(O_3P(CH_2)_2PO_3H)F_2 \cdot H_2O$(**7**) and (h) $Ce(HO_3P(CH_3)_2F_2$(**8**).

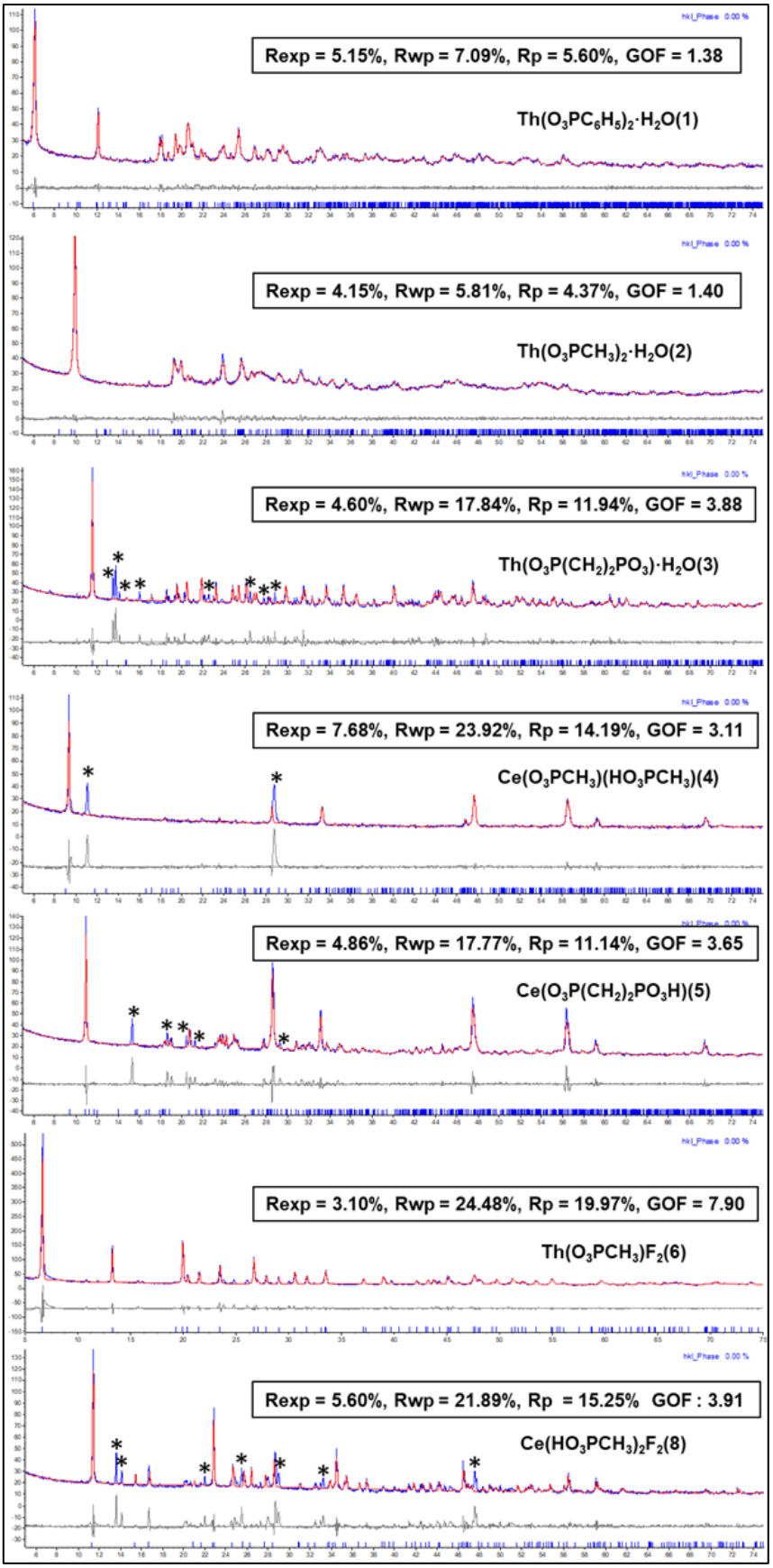

Figure S3. Final Labile fit XRD data plots of compounds **1**-**6** and **8**. Measured (blue) and calculated (red) intensities and difference curve (grey) are shown. Vertical bars

(blue) at the bottom indicate the positions of the Bragg reflections. The values of agreement factors and goodness of fit are presented. (* represents unidentified reflections in the case of compounds **3**, **4**, **5**, and **8**).

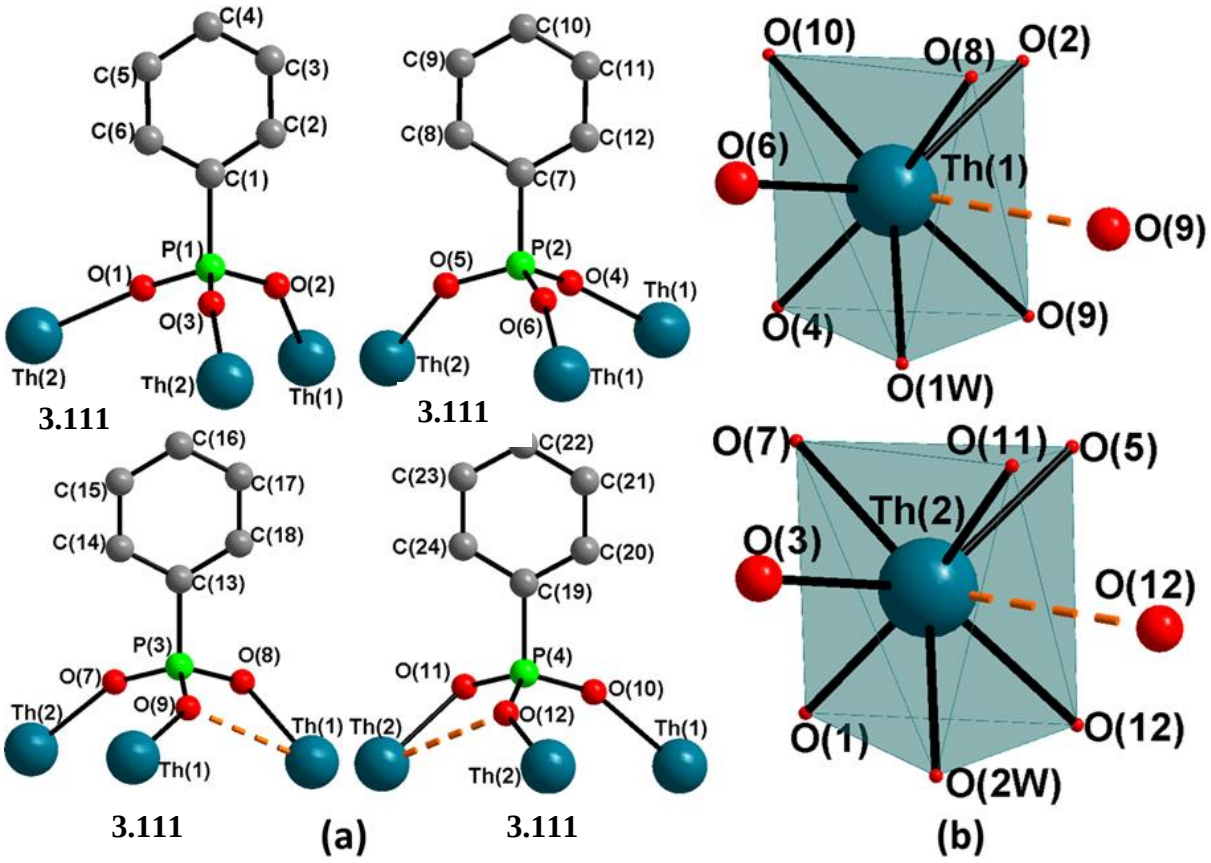

Figure S4. (a) Coordination mode of phenylphosphonate moieties to Th^{4+} cations along with Harris notation and (b) mono-capped trigonal prismatic ThO_7 polyhedra in $Th(O_3PC_6H_5)_2 \cdot H_2O$(**1**).

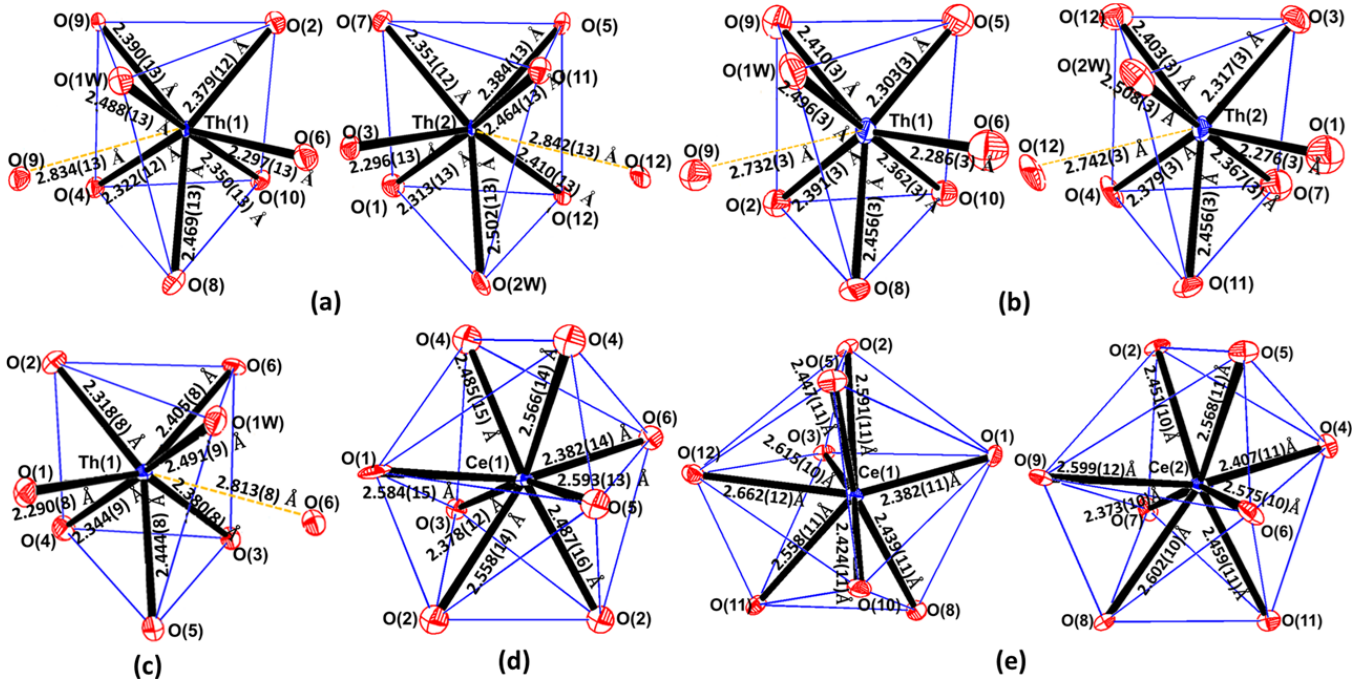

Figure S5. ORTEP representations of coordination spheres of Th^{4+} and Ce^{3+} ions of (a) $Th(O_3PC_6H_5)_2 \cdot H_2O$(**1**), (b) $Th(O_3PCH_3)_2 \cdot H_2O$(**2**), (c) $Th(O_3P(CH_2)_2PO_3) \cdot H_2O$(**3**), (d) $Ce(O_3PCH_3)(HO_3PCH_3)$(**4**) and (e) $Ce(O_3P(CH_2)_2PO_3H)$(**5**).

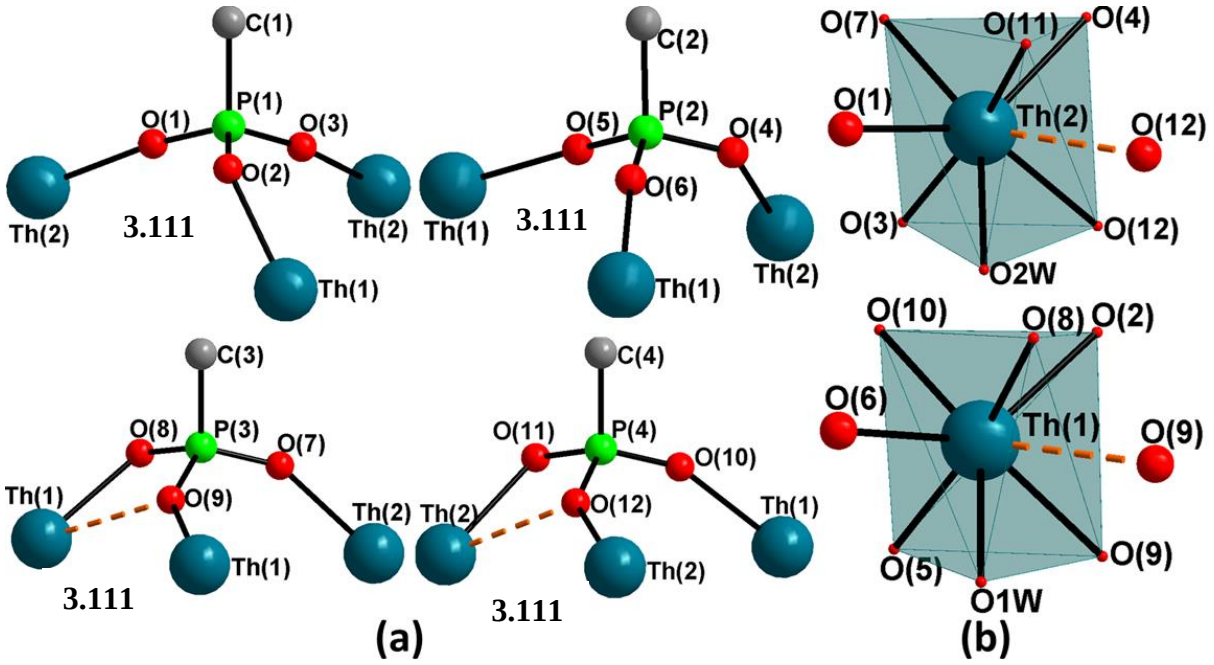

Figure S6. (a) Coordination mode of methylphosphonate moieties to Th^{4+} cations along with Harris notation and (b) mono-capped trigonal prismatic ThO_7 polyhedra in $Th(O_3PCH_3)_2 \cdot H_2O$(**2**).

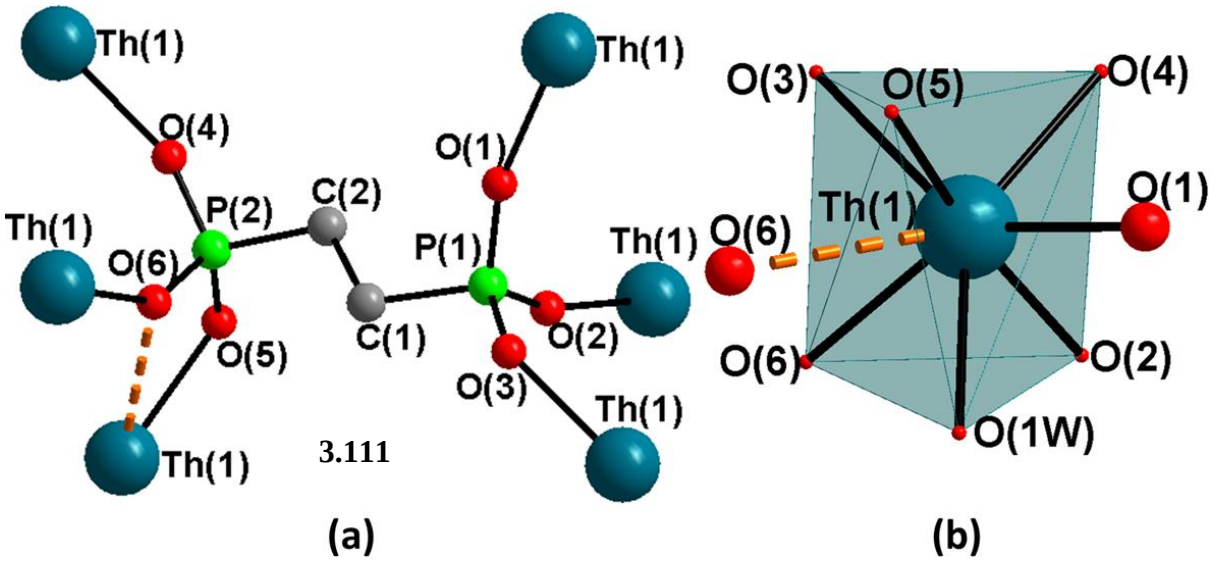

Figure S7. (a) Coordination mode of 1, 2-ethylenediphosphonate moiety to Th^{4+} cations along with Harris notation and (b) Mono-capped trigonal prismatic polyhedra in $Th(O_3P(CH_2)_2PO_3) \cdot H_2O$(**3**).

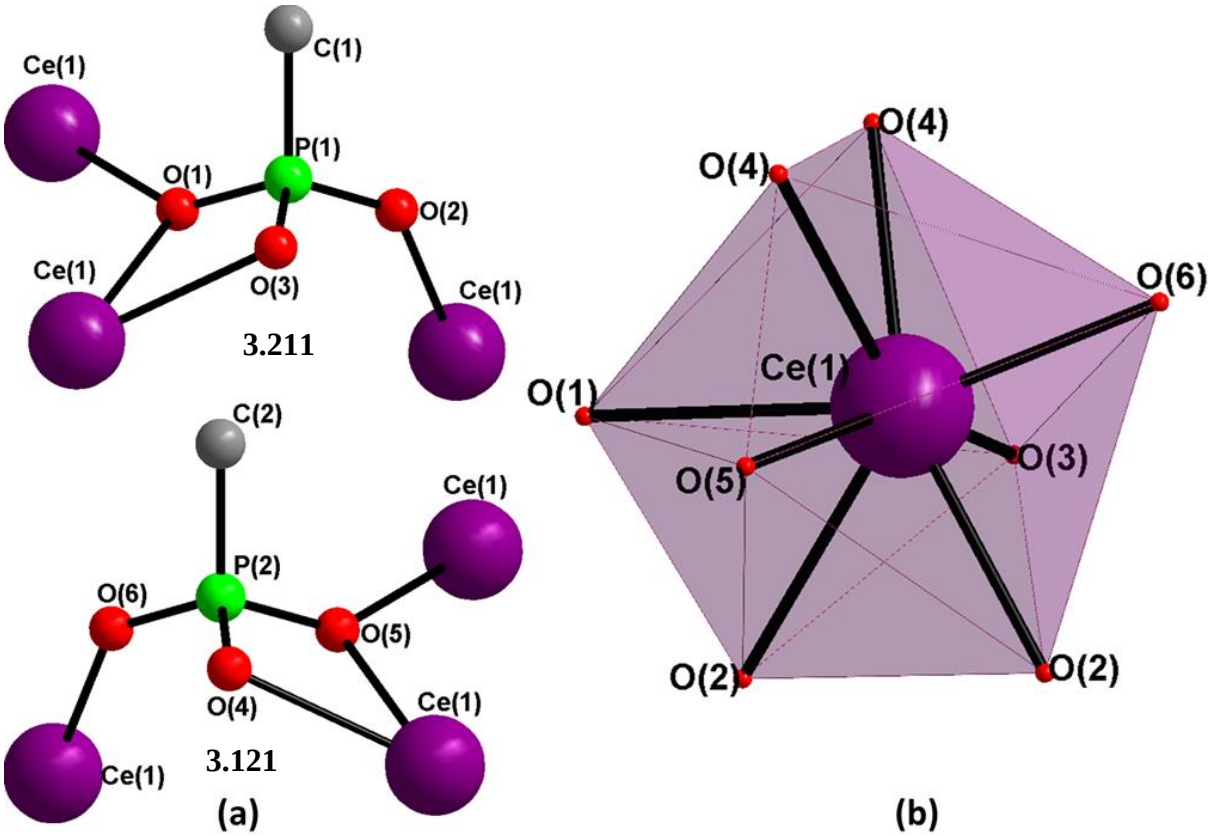

Figure S8. (a) Coordination mode of methylenephosphonate moieties to Ce^{3+} cations along with Harris notation and (b) CeO_8 dodecahedron in $Ce(O_3PCH_3)(HO_3PCH_3)$(**4**).

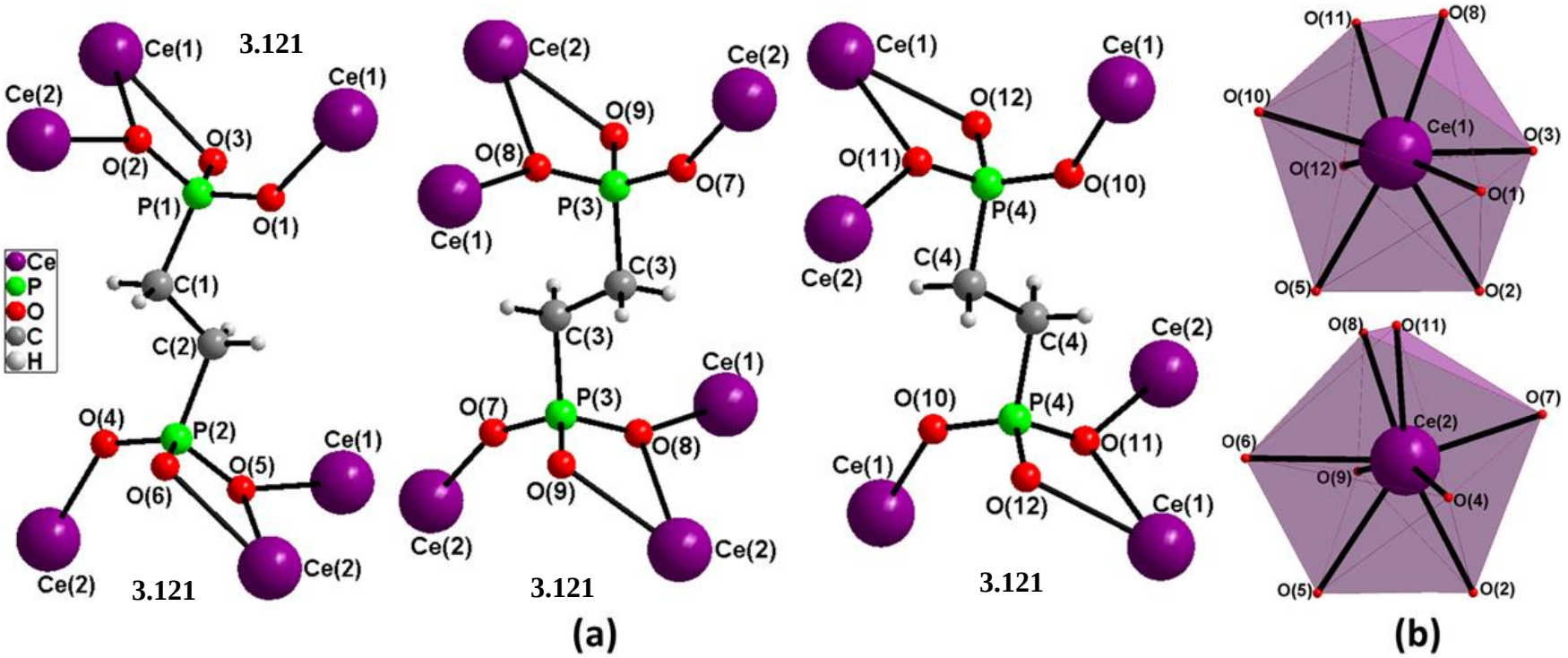

Figure S9. (a) Coordination mode of 1, 2-ethylenediphosphonate moieties to Ce^{3+} cations along with Harris notation and (b) dodecahedron polyhedral in $Ce(O_3P(CH_2)_2PO_3H)$(**5**).

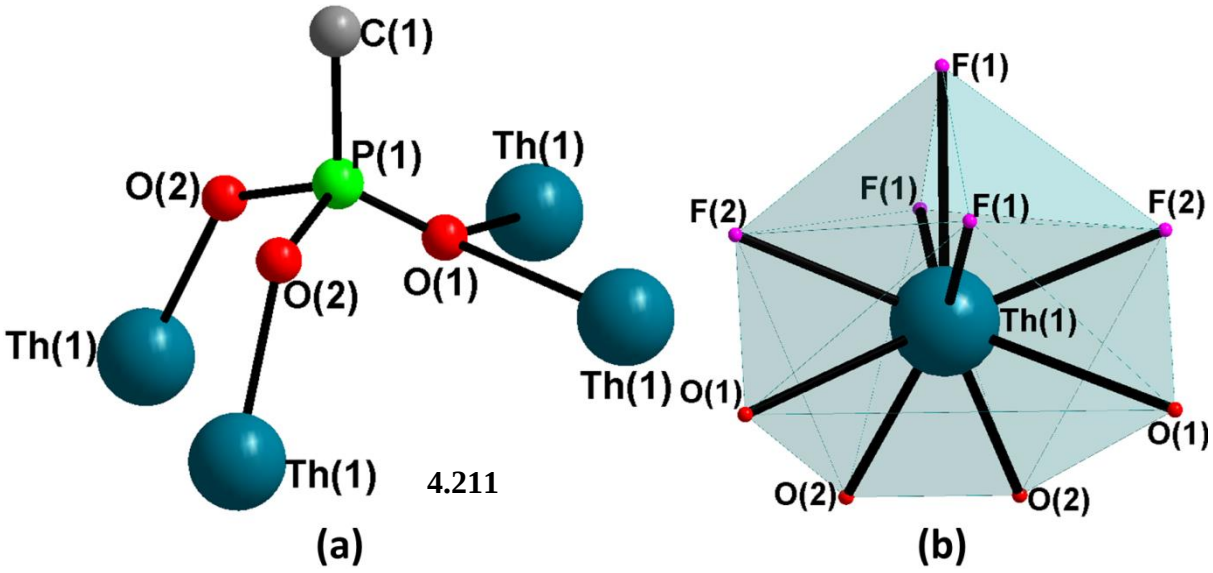

Figure S10. (a) Coordination mode of methylphosphonate moiety to Th^{4+} cations along with Harris notation and (b) ThO_4F_5 coordination polyhedron in $Th(O_3PCH_3)F_2$(**6**).

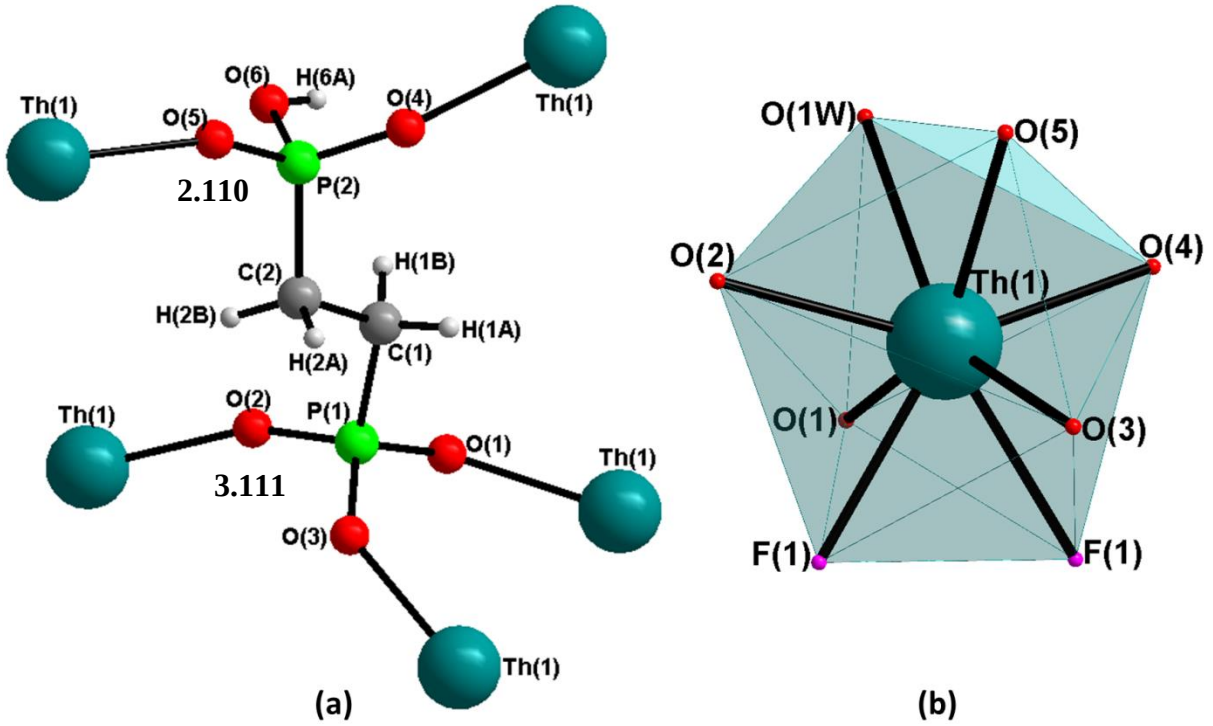

Figure S11. (a) Coordination mode of 1, 2-ethylenediphosphonate moiety to Th^{4+} cations along with Harris notation and (b) dodecahedron polyhedra in $Th(O_3P(CH_2)_2PO_3H)F{\cdot}H_2O$(**7**).

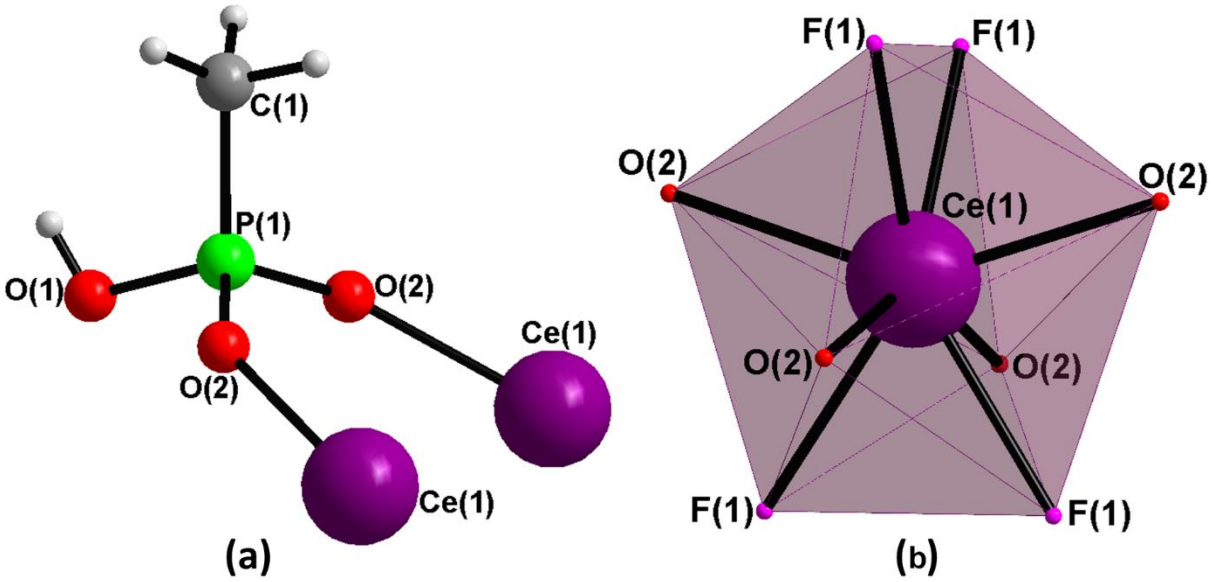

Figure S12. (a) Coordination mode of methylphosphonate moiety to Ce^{4+} cations along with Harris notation and (b) dodecahedron polyhedral in $Ce(HO_3PCH_3)_2F_2$(**8**).

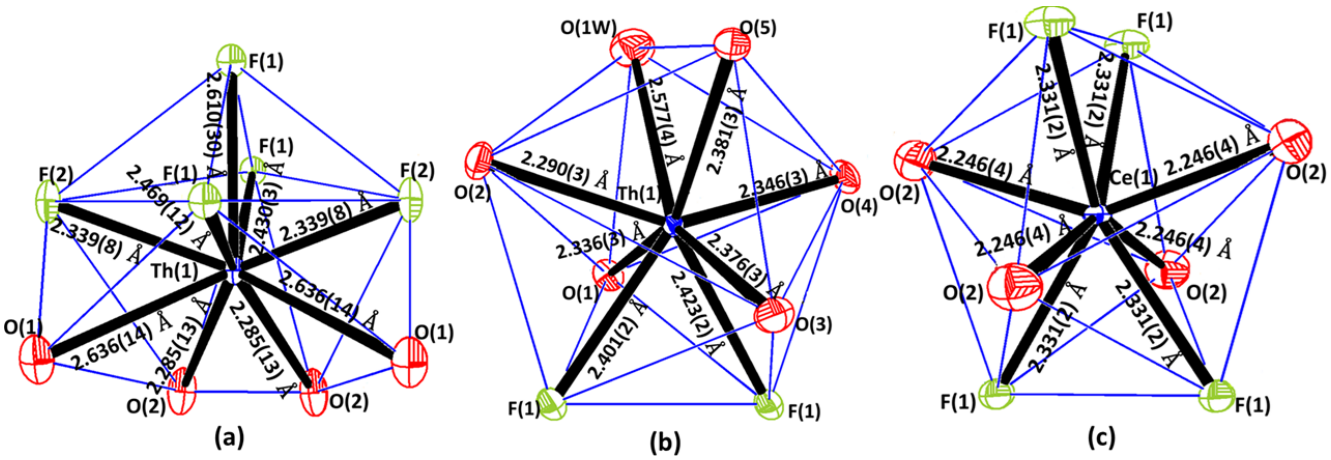

Figure S13. ORTEP representations of coordination spheres of Th, Ce ions in (a) $Th(O_3PC_6H_5)F_2$(**6**), (b) $Th(O_3P(CH_2)_2PO_3H)F{\cdot}H_2O$(**7**) and (c) $Ce(HO_3PCH_3)_2F_2$(**8**).

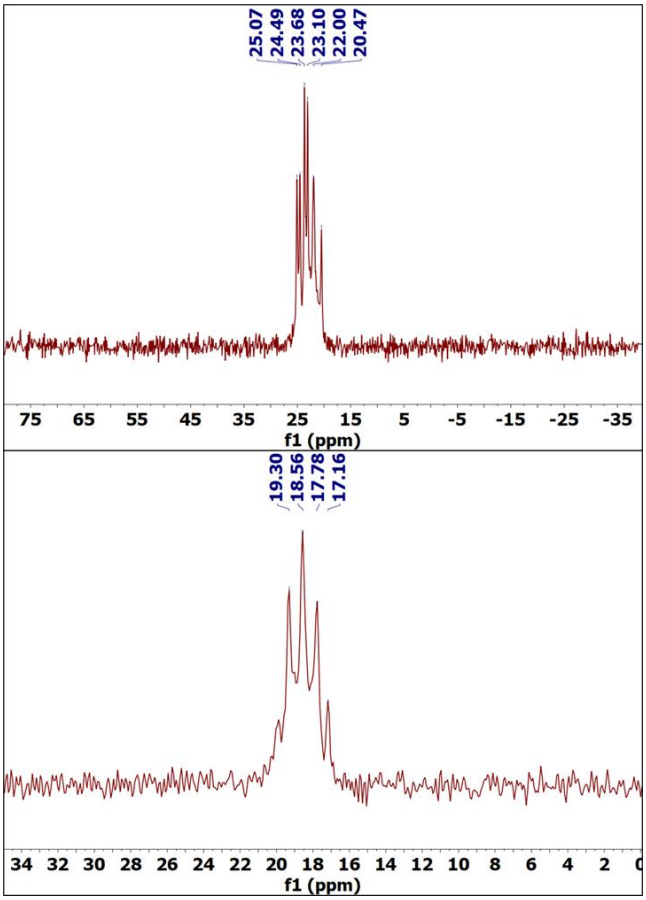

Figure S14. ^{13}C MAS NMR spectra of (top) $Th(O_3P(CH_2)_2PO_3)\cdot H_2O$(**3**). and (bottom) $H_2O_3P(CH_2)_2PO_3H_2$ acid.

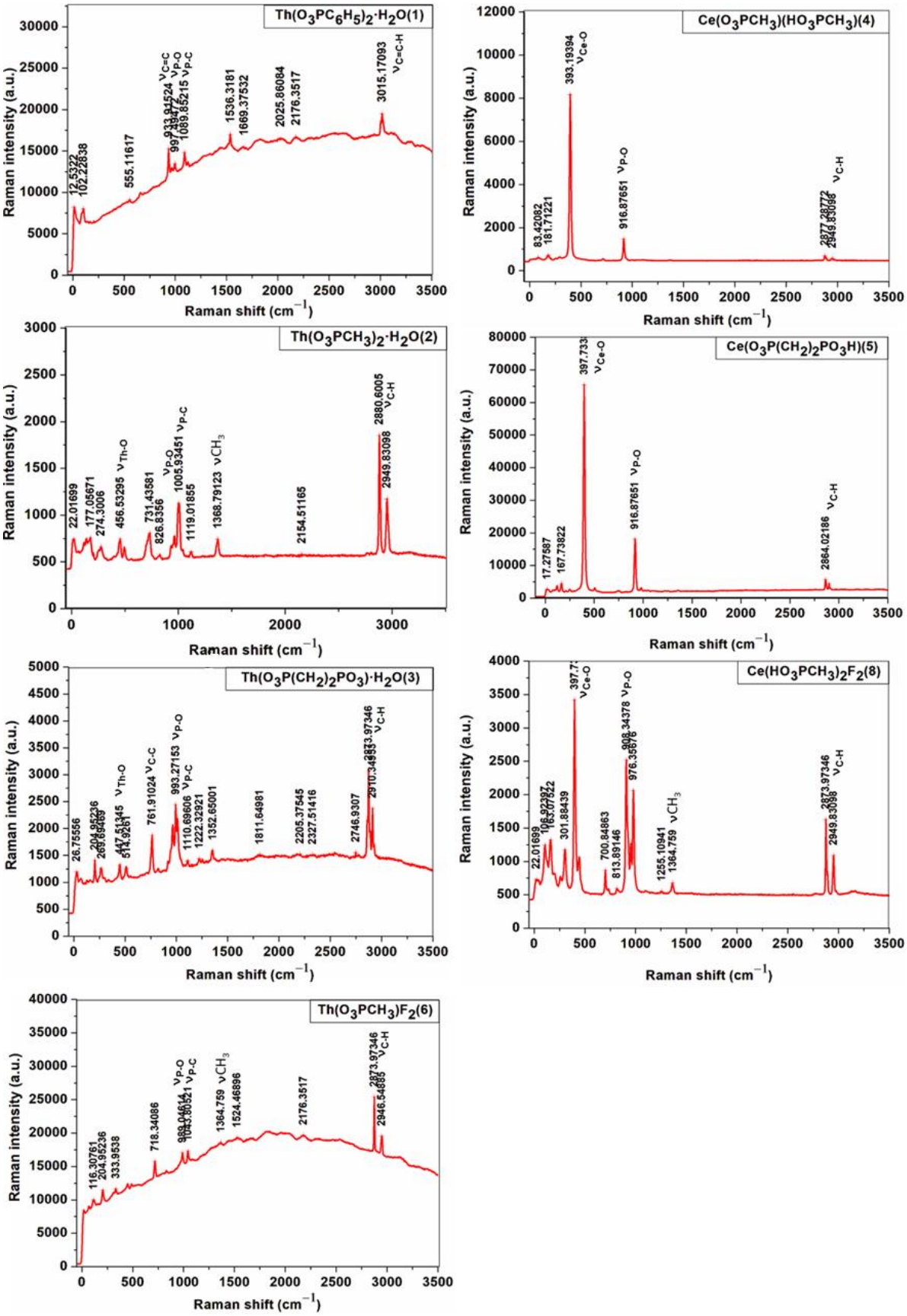

Figure S15. Solid-state Raman spectra of (left) thorium and (right) cerium compounds, **1**-**6** and **8**.