Supplementary material

Solvent influence in the synthesis of lead(II) complexes containing benzoate derivatives.

José A. Ayllón[a*], Oriol Vallcorba[b] and Concepción Domingo.[c]

[a] *Departamento de Química, Universidad Autónoma de Barcelona, 08193-Bellaterra, Spain*

[b] *ALBA Synchrotron Light Source, 08290-Cerdanyola del Vallés, Spain*

[c] *Instituto de Ciencia de Materiales de Barcelona (CSIC), 08193 Bellaterra, Spain*.

Table S1. Crystallographic data of compound $[Pb(2MeOBz)_2(H_2O)]_n$ (**2**), measured at different temperatures.

	$[Pb(2MeOBz)_2(H_2O)]_n$ (**2**)	$[Pb(2MeOBz)_2(H_2O)]_n$ (**2**)
Empirical formula	$C_{32}H_{32}O_{14}Pb_2$	$C_{32}H_{32}O_{14}Pb_2$
Formula weigh	1054.98	1054.98
T (K)	100(2)	295(2)
Wavelength (Å)	0.72932	0.71073
System, space group	Orthorhombic, P $2_12_12_1$	Orthorhombic, P $2_12_12_1$
Unit cell dimensions		
a (Å)	7.240(4)	7.2699(4)
b (Å)	17.730(5)	17.8650(9)
g (Å)	25.480(5)	25.6381(13)
V (Å^3)	3271(2)	3329.8(3)
Z	4	4
*D*calc (g cm^3)	2.142	2.104
μ (mm^{-1})	10.970	10.168
F(000)	2000	2000
Crystal size (mm^3)	0.045 x 0.020 x 0.005	0.210 x 0.060 x 0.040
hkl ranges	-9 <= h <= 9, -23<= k <= 23 -33<= l <= 33	-7 <= h <= 9, -22<= k <= 21 -34<= l <= 33
2q range (º)	1.436 to 29.091	1.389 to 28.809
Reflections collected/ unique/[Rint]	49074/8066 [R(int) = 0.0543]	17924 / 7952 [R(int) = 0.0367]
Completeness	to θ = 25.950, 99.3%	to θ = 25.242, 99.9%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restrains/parameters	8066 / 0 / 440	7952 / 0 / 440
Goodness of fit (GOF) on F^2	1.064	1.012
Final *R* indices [$I>2\sigma(I)$]	R1 = 0.0316, wR2 = 0.0857	R1 = 0.0346, wR2 = 0.0562
R indices (all data)	R1 = 0.0321, wR2 = 0.0861	R1 = 0.0450, wR2 = 0.0593
Extinction coefficient		
Largest. Diff. peak and hole (e Å^{-3})	5.365 and -1.651	1.300 and -0.700

Table S2. Selected bond distances (Å), angles (°), and intra- and intermolecular interactions (Å) for $[Pb(2MeOBz)_2(H_2O)]_n$ (**2**) measured at 100 K.

Bond distances (Å)			
Pb(1)-O(2)	2.479(6)	Pb(1)-O(5)	2.451(5)
Pb(1)-O(6)	2.521(5)	Pb(1)-O(7)	2.714(7)
Pb(1)-O(8)	2.484(6)	Pb(1)-O(13)	2.614(5)
Pb(1)-O(1)#1	2.804(6)		
Pb(2)-O(1)	2.421(5)	Pb(2)-O(2)	2.545(6)
Pb(2)-O(3)	2.499(6)	Pb(2)-O(4)	2.543(7)
Pb(2)-O(5)	2.645(5)	Pb(2)-O(6)#2	2.593(6)
Pb(2)-O(14)	2.691(5)		
Bond angles (°)			
O(6)-Pb(1)-O(7)	79.7(2)	O(6)-Pb(1)-O(5)	52.0(2)
O(6)-Pb(1)-O(8)	94.9(2)	O(6)-Pb(1)-O(2)	121.1(2)
O(6)-Pb(1)-O(13)	81.3(2)	O(6)-Pb(1)-O(1)#1	66.5(2)
O(7)-Pb(1)-O(5)	106.2(2)	O(7)-Pb(1)-O(8)	50.1(2)
O(7)-Pb(1)-O(2)	127.9(2)	O(7)-Pb(1)-O(13)	156.0(2)
O(7)-Pb(1)-O(1)#1	83.2(2)	O(5)-Pb(1)-O(8)	79.2(2)
O(5)-Pb(1)-O(2)	69.5(2)	O(5)-Pb(1)-O(13)	72.6(2)
O(5)-Pb(1)-O(1)#1	113.5(2)	O(8)-Pb(1)-O(2)	79.2(2)
O(8)-Pb(1)-O(13)	146.9(2)	O(8)-Pb(1)-O(1)#1	132.9(2)
O(2)-Pb(1)-O(13)	75.0(2)	O(2)-Pb(1)-O(1)#1	147.9(2)
O(13)-Pb(1)-O(1)#1	75.8(2)		
O(3)-Pb(2)-O(1)	80.3(2)	O(3)-Pb(2)-O(5)	83.5(2)
O(3)-Pb(2)-O(2)	70.8(2)	O(3)-Pb(2)-O(4)	51.8(2)
O(3)-Pb(2)-O(14)	146.6(2)	O(3)-Pb(2)-O(6)#2	124.4(2)
O(1)-Pb(2)-O(5)	117.5(2)	O(1)-Pb(2)-O(2)	52.0(2)
O(1)-Pb(2)-O(4)	73.9(2)	O(1)-Pb(2)-O(14)	79.7(2)
O(1)-Pb(2)-O(6)#2	71.4(2)	O(5)-Pb(2)-O(2)	65.5(2)
O(5)-Pb(2)-O(4)	132.8(2)	O(5)-Pb(2)-O(14)	82.3(2)
O(5)-Pb(2)-O(6)#2	152.0(2)	O(2)-Pb(2)-O(4)	105.9(2)
O(2)-Pb(2)-O(14)	75.7(2)	O(2)-Pb(2)-O(6)#2	118.9(2)
O(4)-Pb(2)-O(14)	143.1(2)	O(4)-Pb(2)-O(6)#2	74.4(2)
O(14)-Pb(2)-O(6)#2	73.1(2)		

#1: -1+x,y,z #2: 1+x,y,z

Table S3. Selected bond distances (Å), angles (°), intra- and intermolecular interactions (Å) for $[Pb(2MeOBz)_2(H_2O)]_n$ (**2**), measured at 295 K.

Bond distances (Å)			
Pb(1)-O(2)	2.501(6)	Pb(1)-O(5)	2.455(6)
Pb(1)-O(6)	2.545(6)	Pb(1)-O(7)	2.711(8)
Pb(1)-O(8)	2.482(8)	Pb(1)-O(13)	2.636(5)
Pb(1)-O(1)#2	2.819(6)		
Pb(2)-O(1)	2.434(7)	Pb(2)-O(2)	2.535(7
Pb(2)-O(3)	2.522(8)	Pb(2)-O(4)	2.513(8)
Pb(2)-O(5)	2.665(6)	Pb(2)-O(6)#1	2.611(6)
Pb(2)-O(14)	2.733(5)		
Bond angles (°)			
O(6)-Pb(1)-O(7)	81.1(2)	O(6)-Pb(1)-O(5)	51.7(2)
O(6)-Pb(1)-O(8)	96.7(2)	O(6)-Pb(1)-O(2)	121.2(2)
O(6)-Pb(1)-O(13)	81.0(2)	O(6)-Pb(1)-O(1)#2	67.1(2)
O(7)-Pb(1)-O(5)	106.1(2)	O(7)-Pb(1)-O(8)	49.8(2)
O(7)-Pb(1)-O(2)	127.6(2)	O(7)-Pb(1)-O(13)	156.8(2)
O(7)-Pb(1)-O(1) #2	82.6(2)	O(5)-Pb(1)-O(8)	79.7(2)
O(5)-Pb(1)-O(2)	70.2(2)	O(5)-Pb(1)-O(13)	73.7(2)
O(5)-Pb(1)-O(1)#2	114.7(2)	O(8)-Pb(1)-O(2)	79.2(2)
O(8)-Pb(1)-O(13)	147.7(2)	O(8)-Pb(1)-O(1)#2	132.1(2)
O(2)-Pb(1)-O(13)	74.8(2)	O(2)-Pb(1)-O(1)#2	148.3(2)
O(13)-Pb(1)-O(1)#2	76.8(2)		
O(3)-Pb(2)-O(1)	83.2(2)	O(3)-Pb(2)-O(5)	84.5(2)
O(3)-Pb(2)-O(2)	71.9(2)	O(3)-Pb(2)-O(4)	50.9(2)
O(3)-Pb(2)-O(14)	148.7(2)	O(3)-Pb(2)-O(6)#1	124.6(2)
O(1)-Pb(2)-O(5)	117.4(2)	O(1)-Pb(2)-O(2)	51.5(2)
O(1)-Pb(2)-O(4)	74.4(2)	O(1)-Pb(2)-O(14)	78.6(2)
O(1)-Pb(2)-O(6)#1	72.1(2)	O(5)-Pb(2)-O(2)	66.4(2)
O(5)-Pb(2)-O(4)	133.6(2)	O(5) -Pb(2)-O(14)	81.6(2)
O(5)-Pb(2)-O(6)#1	150.8(2)	O(2) -Pb(2)-O(4)	104.4(2)
O(2)-Pb(2)-O(14)	76.8(2)	O(2) -Pb(2)-O(6)#1	120.0(2)
O(4)-Pb(2)-O(14)	143.0(2	O(4) -Pb(2)-O(6)#1	74.6(2)
O(14)-Pb(2)-O(6)#1	73.2(2)		

#1: -1+x,y,z #2: 1+x,y,z

Table S4. Crystallographic data of compound $[Pb(1,4Bzdiox)_2(H_2O)]_n$ (**4)**

Empirical formula	$C_{18}H_{16}O_9Pb$
Formula weigh	583.51
T (K)	298(2)
Wavelength (Å)	0.49603
System, space group	Orthorhombic, I *b a* 2
Unit cell dimensions	
a (Å)	28.2828(7)
b (Å)	15.4922(4)
c (Å)	8.1896(2)
V (Å^3)	3588.4(1)
Z	8
*D*calc (g cm^3)	2.160
Measured 2θ range (º), stepsize (º)	1.026 to 45.246, 0.006
Rietveld refinement details:	
Profile function	Pseudo-Voigt
2ϑ range used	1.106 to 33.000
Num. of reflections	1527
Data points	5316
Parameters	93
Restraints	91
R_{wp}	0.145
$\chi_{Rietveld}/\chi_{Pattern\text{-}Matching}$	1.147

Table S5. Crystallographic data of compound $[Pb(Ac)(Pip)_2(MeOH)]_n$ (**6**)

Empirical formula	$C_{11}H_{12}O_7Pb$
Formula weigh	463.41
T (K)	100(2)
Wavelength (Å)	0.72932
System, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	
a (Å)	7.590(7)
b (Å)	26.140(6)
c (Å)	7.250(3)
α (º)	90
β (º)	116.250(16)
γ (º)	90
V (Å^3)	1290.1(13)
Z	4
*D*calc (g cm^3)	2.386
μ (mm^{-1})	13.887
F(000)	864
Crystal size (mm^3)	0.090 x 0.070 x 0.010
hkl ranges	-10 <= h <= 10, -34<= k <= 34 -9<= l <= 9
2ϑ range (º)	3.071 to 29.088
Reflections collected/ unique/[Rint]	19645 / 3045 [R(int) = 0.0374]
Completeness	to θ = 25.950, 96.1%
Refinement method	Full-matrix least-squares on F^2
Data/restrains/parameters	3045 / 3 / 177
Goodness of fit (GOF) on F^2	1.145
Final *R* indices [$I>2\sigma(I)$]	R1 = 0.0656, wR2 = 0.1846
R indices (all data)	R1 = 0.0695, wR2 = 0.1885
Largest. Diff. peak and hole (e Å^{-3})	5.110 and -1.804

Table S6. Selected bond distances (Å), angles (°), intra- and intermolecular interactions (Å) for $[Pb(Ac)(Pip)_2(MeOH)]_n$ (**6**).

Bond distances (Å)			
Pb(1)-O(6)	2.536(7)	Pb(1)-O(3)	2.796(9)
Pb(1)-O(7)	2.66(1)	Pb(1)-O(4)	2.475(8)
Pb(1)-O(5)	2.63(1)	Pb(1)-O(6)#3	2.54(1)
Pb(1)-O(3)#1	2.84(1)	Pb(1)-O(5)#2	2.70(1)
Bond angles (°)			
O(6)-Pb(1)-O(3)	120.8(3)	O(6)-Pb(1)-O(7)	75.4(3)
O(6)-Pb(1)-O(4)	74.1(3)	O(6)-Pb(1)-O(5)	50.3(3)
O(6)-Pb(1)-O(6)#3	66.5(3)	O(6)-Pb(1)-O(3)#1	151.5(3)
O(6)-Pb(1)-O(5)#2	108.5(3)	O(3)-Pb(1)-O(7)	163.5(3
O(3)-Pb(1)-O(4)	48.8(3)	O(3)-Pb(1)-O(5)	96.8(3)
O(3)-Pb(1)-O(6)	107.4(3	O(3)-Pb(1)-O(3)#1	73.8(3)
O(5)#2-Pb(1)-O(3)	92.7(3)	O(7)-Pb(1)-O(4)	144.7(3)
O(7)-Pb(1)-O(5)	96.5(3)	O(7)-Pb(1)-O(6)#3	75.1(3)
O(7)-Pb(1)-O(3)#1	90.3(3)	O(7)-Pb(1)-O(5)#2	83.9(3)
O(4)-Pb(1)-O(5)	77.1(3)	O(4)-Pb(1)-O(6)#3	76.8(3)
O(4)-Pb(1)-O(3)#1	108.7(3)	O(4)-Pb(1)-O(5)#2	122.5(3)
O(5)-Pb(1)-O(6)#3	115.9(3)	O(5)-Pb(1)-O(3)#1	157.9(3)
O(5)-Pb(1)-O(5)#2	66.0(3)	O(6)#3-Pb(1)-O(3)#1	86.2(3)
O(6)#3-Pb(1)-O(5)#2	159.0(3)	O(3)#1-Pb(1)-O(5)#2	94.0(3)

#1: -x,1-y,1-z #2: 1-x,1-y,1-z #3: 1-x,1-y,2-z

Supplementary Figures

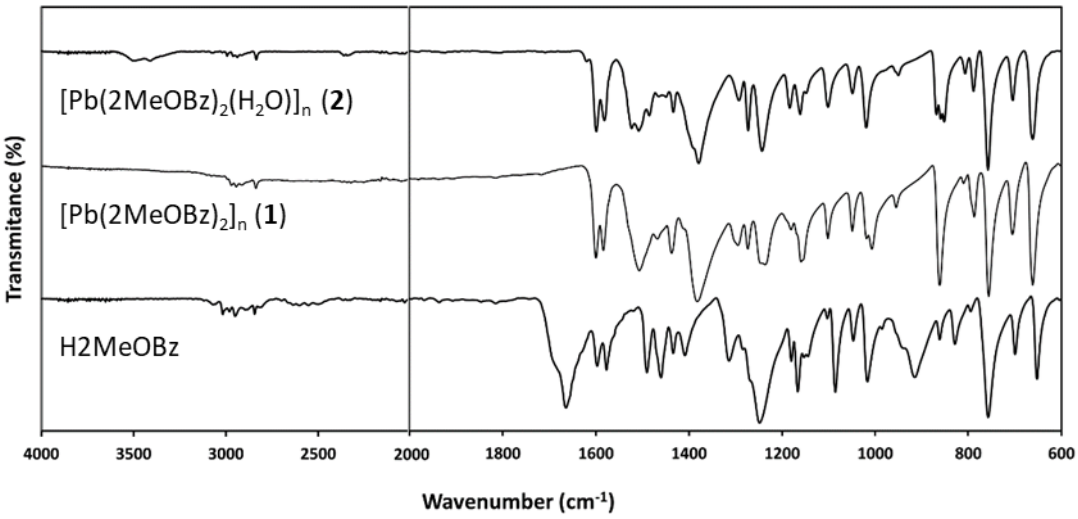

Figure S1. ATR-FTIR spectra of 2-methoxybenzoic acid (*bottom*) and of compounds $[Pb(2MeOBz)_2]_n$ (**1**) (*middle*) and $[Pb(2MeOBz)_2(H_2O)]_n$ (**2**) (*up*).

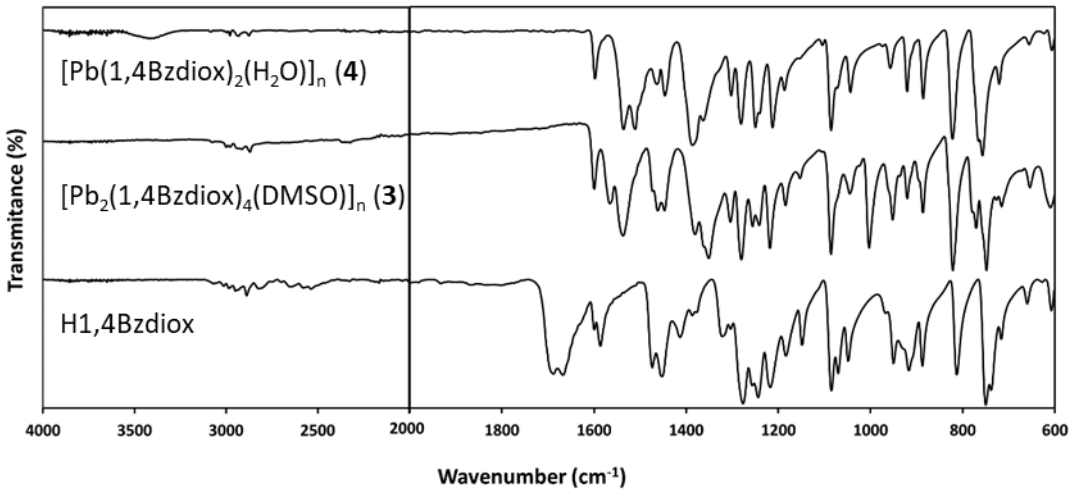

Figure S2. ATR-FTIR spectra of 1,4-benzodioxan-5-carboxylic acid (*bottom*) and of compounds $[Pb_2(1,4Bzdiox)_4(DMSO)]_n$ (**3**) (*middle*) and $[Pb(1,4Bzdiox)_2(H_2O)]_n$ (**4**) (*up*).

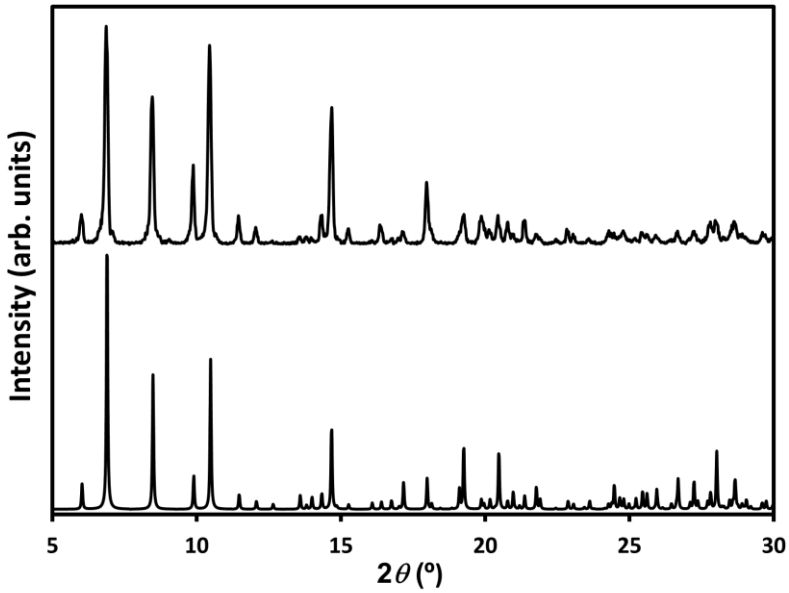

Figure S3. Comparison of powder XRD patterns collected at room temperature *(up)* for $[Pb(2MeOBz)_2(H_2O)]_n$ (**2**) with the one calculated from single-crystal structural data at 295 K *(down)*.

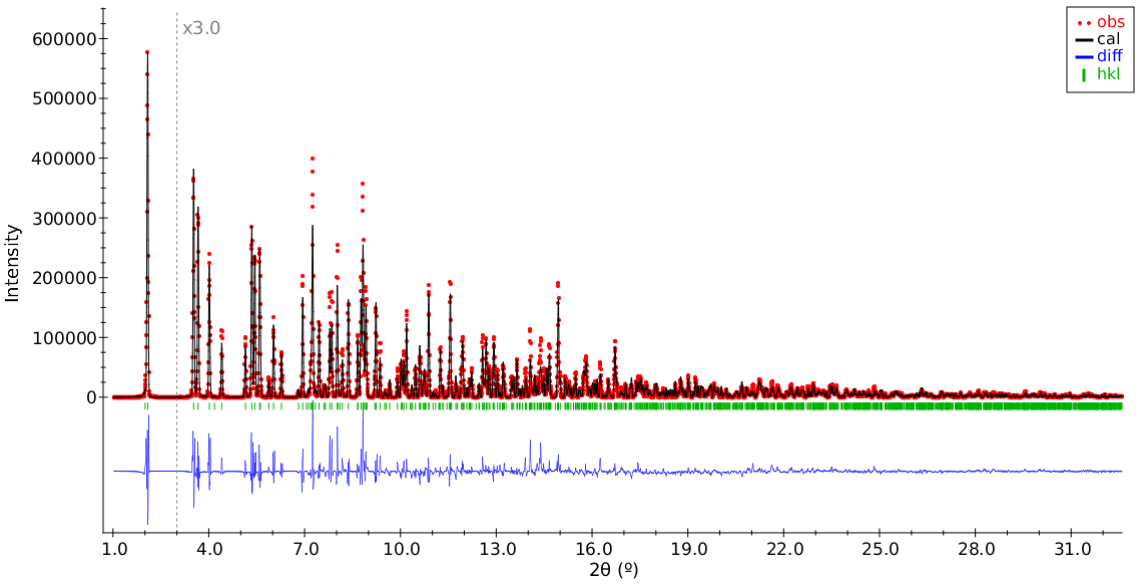

Figure S4. Rietveld fit of $[Pb(14Bzdiox)_2(H_2O)]_n$ (**4)** to SR-XRPD data, showing calculated (**black**), observed (**red**), and difference (**blue**) intensities.

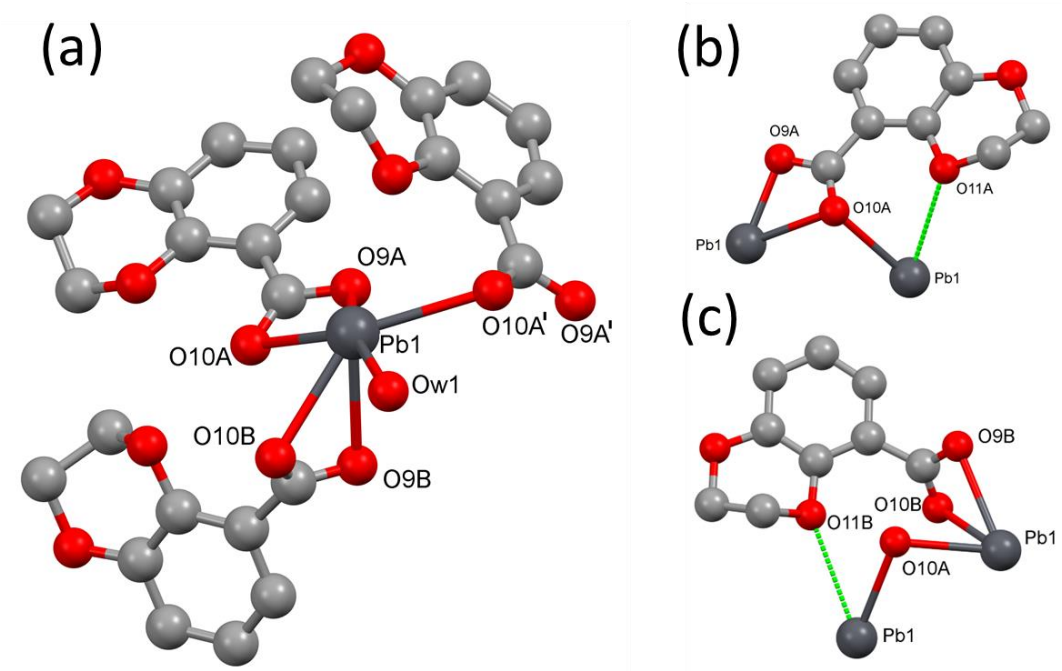

Figure S5. (a) Coordination sphere of each independent Pb(II) in 4. Hydrogen atoms are omitted for clarity. Only covalent Pb-O bonds are depicted. (b) and (c) Coordination modes of each independent 14Bzdiox ligand; distances longer than 2.74 Å are indicated with light green sticks. Color codes: dark gray (Pb), red (O), gray (C).

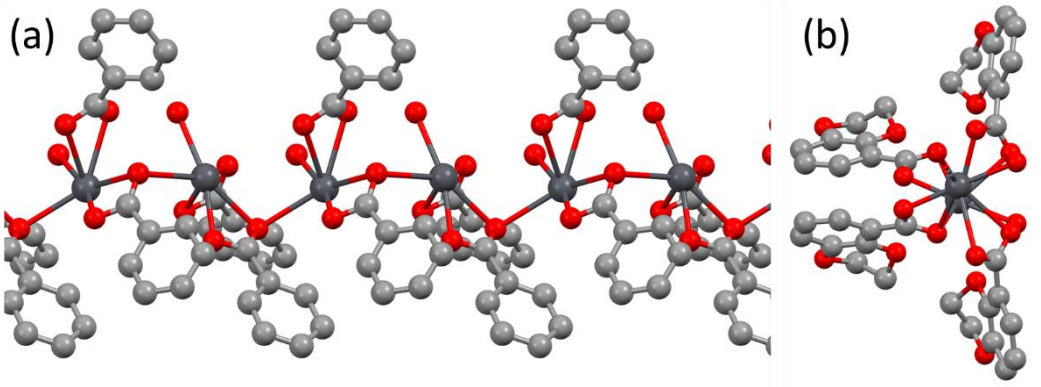

Figure S6. Crystal structure of compound **4**: (a) chain view along *c* axis, (b) chain view along *a* axis.

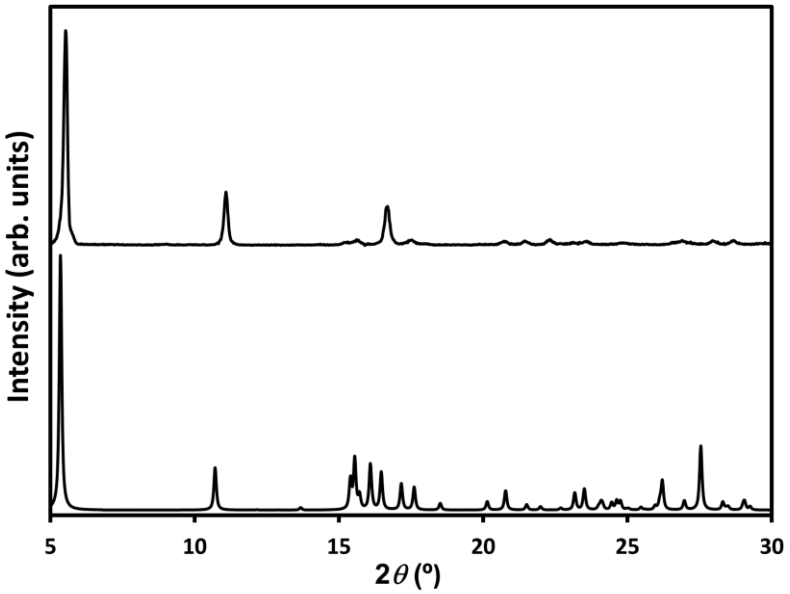

Figure S7. Comparison of powder XRD pattern collected at room temperature for $[Pb(Pip)_2(H_2O)]_n$ (**1**) *(down)* with the one calculated from single-crystal structural data at 100 K of $[Cd(Pip)_2(H_2O)]_n$ *(up)*.[1]

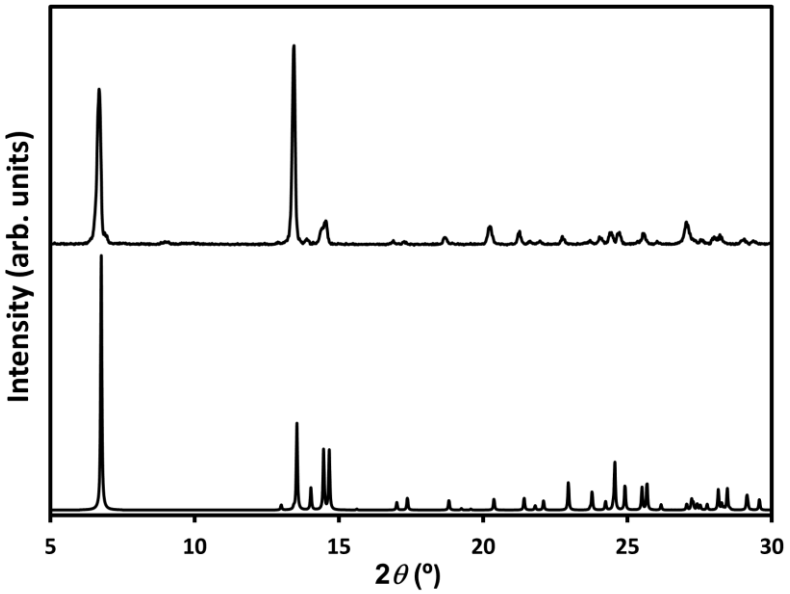

Figure S8. Comparison of powder XRD pattern collected at room temperature for $[Pb(Ac)(Pip)(MeOH)]_n$ (**5**) (*up*) with the one calculated from single-crystal structural data at 100 K (*down*).

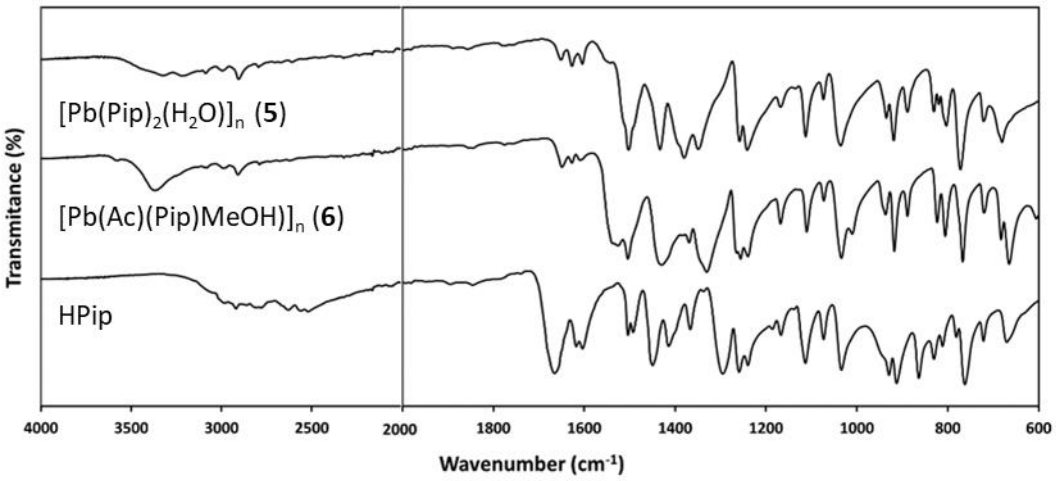

Figure S9. ATR-FTIR spectra of piperonylic acid (*bottom*) and of compounds $[Pb(Ac)(Pip)(MeOH)]_n$ (**6**) (*middle*) and $[Pb(Pip)_2(H_2O)]_n$ (**5**) (*up*).

Reference

[1] Ejarque, D.; Sánchez-Férez, F.; Ayllón, J.A.; Calvet, T.; Font-Bardia, M.; Pons, J. Diverse Structures and Dimensionalities in Zn(II), Cd(II), and Hg(II) Metal Complexes with Piperonylic Acid. *Cryst. Growth Des.* **2020**, *20*, 383–400, doi:10.1021/acs.cgd.9b01317