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A facile single crystal to single crystal transition with significant structural contraction on desolvation

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Supporting Information

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S1: General methods

Starting materials and solvents were purchased from commercial sources and were used without further purification. X-ray diffraction investigations for network **2** were carried out on Station 11.3.1 of The Advanced Light Source (ALS), Lawrence Berkeley National Laboratory.[S1] Data for **1** and **3** were collected on an Agilent Gemini A-Ultra diffractometer[S2] at the University of Bath using Mo-Kα radiation, the crystal being cooled by an Agilent Cryojet.[S3]

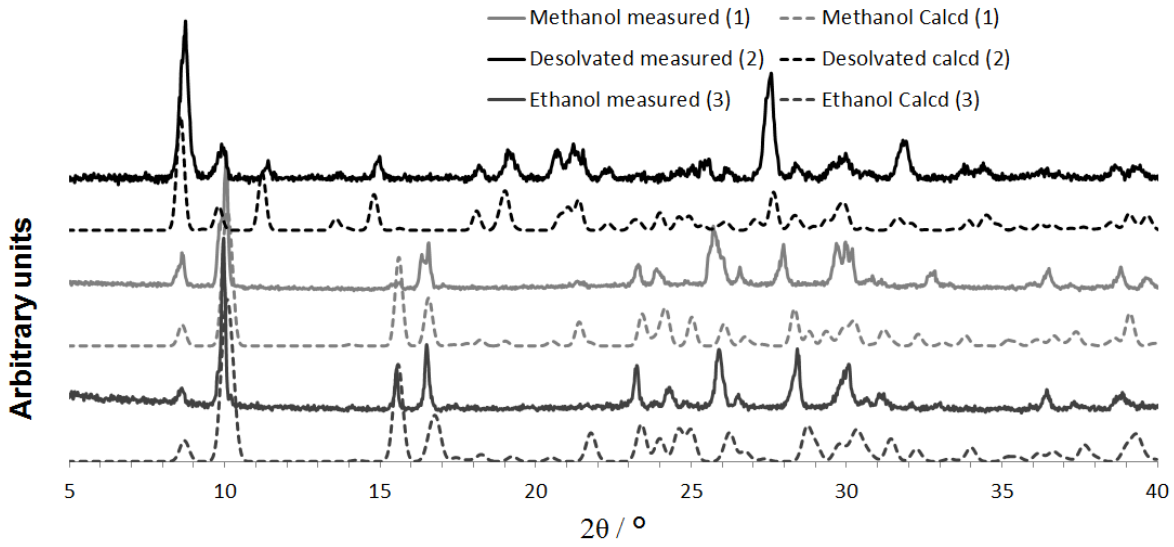
Powder X-ray diffraction patterns (PXRDs) were recorded on a Bruker AXS D8 Advance diffractometer with copper Kα radiation of wavelength 1.5406 Å at 298 K. Samples were placed on a flat plate, and measured with a 2θ range of 3-60°. The step size was 0.016° with time per step of 134.5 s. Simulated X-ray powder patterns were generated from single crystal data that were imported into PowderCell with a step size of 0.02° and time per step of 1.00 s. Characterisation of each sample was performed using 25 - 50 mg of sample. The transition from **1** to **2** was monitored by dividing a fresh 50 mg sample of **1** in half, and analysing one without air drying, followed by the second, which had been allowed to air dry for 45 minutes and had converted to **2**.

TGA experiments were carried out on a Perkin Elmer TGA 4000 Thermogravimetric Analyser. The samples were heated from 45°C to 600°C at a heating rate of 10°C/min, under a flow of nitrogen (20 mL/min).

Infrared spectra were recorded on a PerkinElmer Spectrum 100 spectrometer equipped with an ATR sampling accessory.

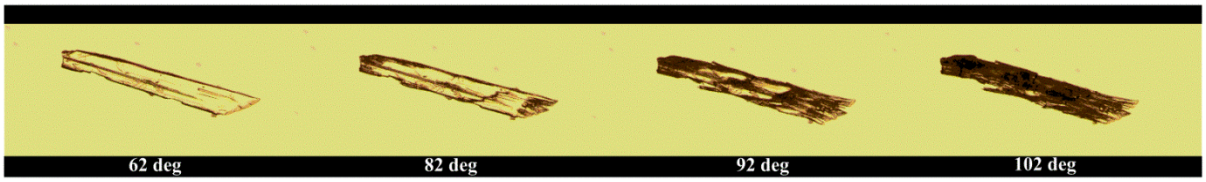
Hot stage microscopy analysis was conducted on complex **1** using a Mettler Toledo FP82 hot stage equipped with a Leica DM1000 microscope. A single crystal of the complex was placed on a glass slide in oil, and heated from 30 °C to a final temperature of 200 °C at a rate of 10 °C per minute.

S2: PXRD data for 1 – 3.



Note: Intermittent variation in peak intensity and location has be attributed to labile interactions between the CP and solvent molecules resulting in localised changes to electron density.

S3: Rapid heating of crystalline 1.



Rapid heating of a single crystal sample of **1** yielded microcrystalline particles. Rate of heating: 10 °C per minute. PXRD analysis of the degraded crystal was found to match the simulated pattern of crystalline **2**.

S4: Crystallographic data for 1 – 3.

Single crystal X-ray data was collected on an Agilent Gemini A-Ultra diffractometer equipped with a Cryojet crystal cooling apparatus. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. Details of treatment of disorder *etc* are included in the cif files.

Table 1. Crystallographic Data for **1** and **2**.

	1	**2**	**3**
formula	$C_{22}H_{18}O_{11}Pb_2$	$C_{20}H_8O_8Pb_2$	$C_{44}H_{30}O_{19}Pb_4$
formula weight	872.74	790.64	1691.44
crystal system	monoclinic	triclinic	monoclinic
space group	*I*2/*a*	$P\bar{1}$	*I*2
a, Å	10.037(2)	9.3790(4)	9.988(2)
b, Å	17.698(4)	10.0130(3)	17.698(4)
c, Å	12.687(3)	10.3180(4)	12.489(3)
α, °	90	100.148(3)	90
β, °	96.75(3)	91.407(3)	95.59(3)
γ, °	90	107.941(3)	90
V, Å	2238.1(8)	904.22(6)	2197.1(8)
Z	4	2	2
ρ_{calc}, g/cm^3	2.590	2.904	2.557
reflns measured	6767	13225	24817
unique reflections	2606	5621	5531
no. obsd (I > 2σ(I))	2043	3486	4802
R_1	0.0406	0.0505	0.0479
wR_2	0.0875	0.1064	0.0846
GOF	1.008	1.016	1.031
temp, K	100(2)	100(2)	149.9(2)

S5: Selected bond lengths and angles 1 – 3.

*Bond lengths and angles for **1**.*

Bond lengths (Å)			
Pb(1)-O(1)	2.416(6)	Pb(1)-O(5)	2.647(8)
Pb(1)-O(3)#1	2.439(5)	O(4)-Pb(1)#3	2.520(6)
Pb(1)-O(4)#2	2.520(6)	O(3)-Pb(1)#1	2.439(5)
Pb(1)-O(2)	2.529(6)		
Bond angles (°)			
O(1)-Pb(1)-O(3)#1	82.98(19)	O(4)#2-Pb(1)-O(2)	126.31(18)
O(1)-Pb(1)-O(4)#2	74.4(2)	O(1)-Pb(1)-O(5)	132.3(2)
O(3)#1-Pb(1)-O(4)#2	85.30(18)	O(3)#1-Pb(1)-O(5)	83.0(2)

O(1)-Pb(1)-O(2)	52.67(18)	O(4)#2-Pb(1)-O(5)	148.6(2)
O(3)#1-Pb(1)-O(2)	80.40(19)	O(2)-Pb(1)-O(5)	80.1(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y,-z+1 #2 x+1,y,z #3 x-1,y,z

*Bond lengths and angles for **2**.*

Bond lengths (Å)			
Pb(1)-O(7)	2.414(8)	Pb(2)-O(5)	2.330(8)
Pb(1)-O(1)	2.448(7)	Pb(2)-O(3)	2.407(8)
Pb(1)-O(4)#1	2.461(7)	Pb(2)-O(6)	2.639(8)
Pb(1)-O(2)	2.506(7)	O(4)-Pb(1)#3	2.461(7)
Pb(1)-O(1)#2	2.719(8)	O(8)-Pb(2)#1	2.410(7)
Bond angles (°)			
O(7)-Pb(1)-O(1)	86.9(3)	O(2)-Pb(1)-O(1)#2	101.2(2)
O(7)-Pb(1)-O(4)#1	80.5(3)	Pb(1)-O(1)-Pb(1)#2	110.5(3)
O(1)-Pb(1)-O(4)#1	73.8(2)	O(5)-Pb(2)-O(3)	80.5(3)
O(7)-Pb(1)-O(2)	80.6(3)	O(5)-Pb(2)-O(8)#3	76.1(2)
O(1)-Pb(1)-O(2)	53.3(2)	O(3)-Pb(2)-O(8)#3	88.8(3)
O(4)#1-Pb(1)-O(2)	124.4(2)	O(5)-Pb(2)-O(6)	52.0(2)
O(7)-Pb(1)-O(1)#2	147.3(2)	O(3)-Pb(2)-O(6)	78.5(3)
O(1)-Pb(1)-O(1)#2	69.5(3)	O(8)#3-Pb(2)-O(6)	127.8(3)
O(4)#1-Pb(1)-O(1)#2	71.5(3)		

Symmetry transformations used to generate equivalent atoms:
#1 x,y-1,z #2 -x+2,-y+1,-z #3 x,y+1,z

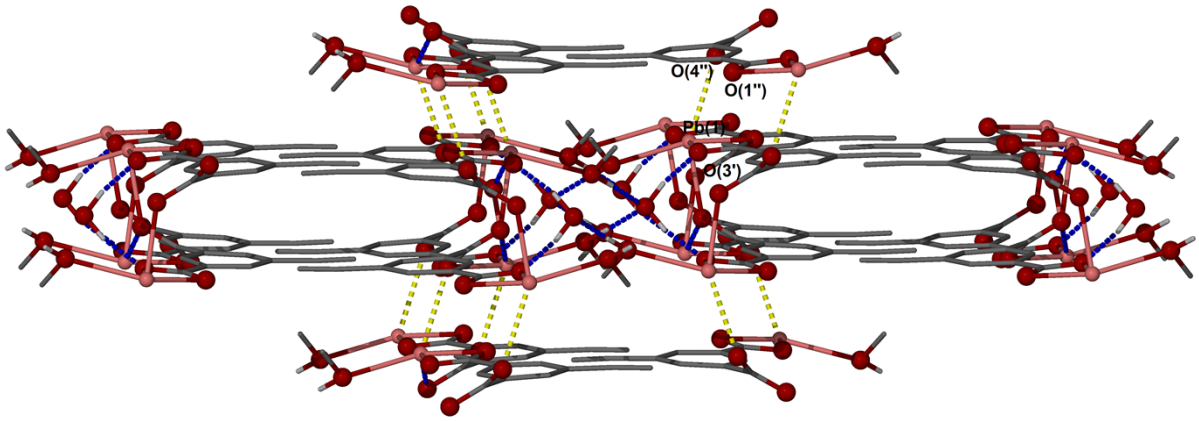
*Bond lengths and angles for **3**.*

Bond lengths (Å)			
Pb(2)-O(7)	2.321(11)	Pb(1)-O(4)#4	2.601(11)
Pb(2)-O(5)#1	2.384(10)	Pb(1)-O(9)	2.641(5)
Pb(2)-O(6)#2	2.483(7)	Pb(1)-O(5)	2.861(9)
Pb(2)-O(8)	2.565(7)	O(4)-Pb(1)#1	2.601(11)
Pb(2)-O(4)	2.623(10)	O(5)-Pb(2)#4	2.384(10)
Pb(1)-O(3)#3	2.414(7)	O(6)-Pb(2)#2	2.483(7)
Pb(1)-O(1)	2.427(10)	O(3)-Pb(1)#3	2.414(7)
Pb(1)-O(2)	2.451(8)	Pb(1)-O(4)#4	2.601(11)
Bond angles (°)			
O(7)-Pb(2)-O(5)#1	76.8(4)	O(3)#3-Pb(1)-O(4)#4	84.3(3)
O(7)-Pb(2)-O(6)#2	82.4(3)	O(1)-Pb(1)-O(4)#4	71.2(4)
O(5)#1-Pb(2)-O(6)#2	86.2(3)	O(2)-Pb(1)-O(4)#4	125.3(3)
O(7)-Pb(2)-O(8)	52.0(4)	O(3)#3-Pb(1)-O(9)	78.4(2)
O(5)#1-Pb(2)-O(8)	127.7(4)	O(1)-Pb(1)-O(9)	131.3(2)
O(6)#2-Pb(2)-O(8)	78.1(2)	O(2)-Pb(1)-O(9)	78.6(3)
O(7)-Pb(2)-O(4)	76.3(3)	O(4)#4-Pb(1)-O(9)	148.5(3)
O(5)#1-Pb(2)-O(4)	75.5(3)	O(3)#3-Pb(1)-O(5)	147.6(3)
O(6)#2-Pb(2)-O(4)	154.4(3)	O(1)-Pb(1)-O(5)	72.3(3)
O(8)-Pb(2)-O(4)	99.0(3)	O(2)-Pb(1)-O(5)	98.9(3)
O(3)#3-Pb(1)-O(1)	83.1(3)	O(4)#4-Pb(1)-O(5)	68.2(3)
O(3)#3-Pb(1)-O(2)	82.9(3)	O(9)-Pb(1)-O(5)	133.8(3)
O(1)-Pb(1)-O(2)	54.5(3)	Pb(1)#1-O(4)-Pb(2)	108.6(4)

Symmetry transformations used to generate equivalent atoms: #1 x-1,y,z
#2 -x+1,y,-z+2 #3 -x+1,y,-z+1 #4 x+1,y,z

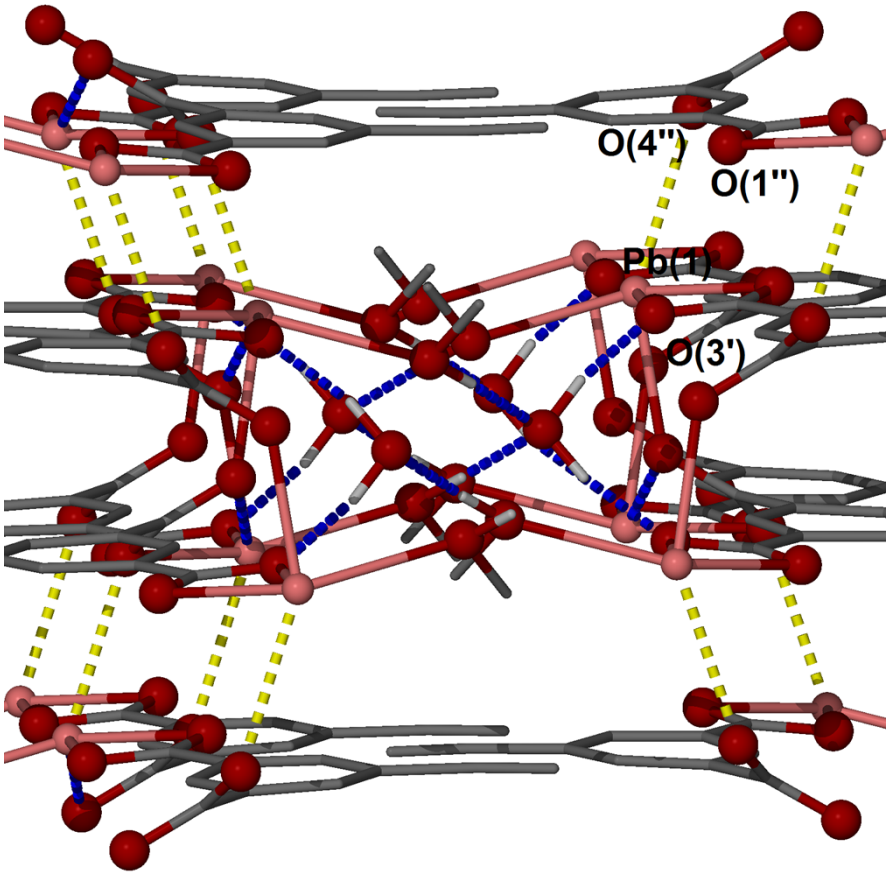
S6: Expanded Figure 4.

Expanded 1:



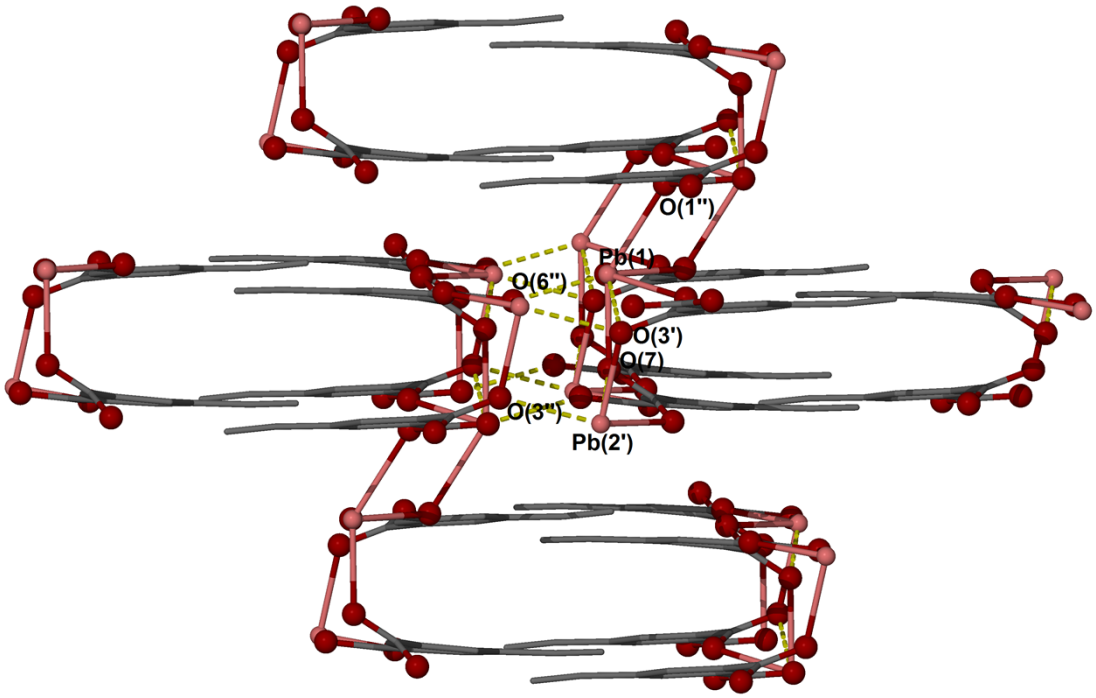
More detailed view of the interactions between chains of **1**. Initially, hydrogen bonding dominates with two secondary interactions between Pb(1)-O(3') and Pb(1)-O(4''), with O(1'') labelled to show the slip between chains when solvents are eliminated to form **2**.

Enlarged Metal Coordination Region:



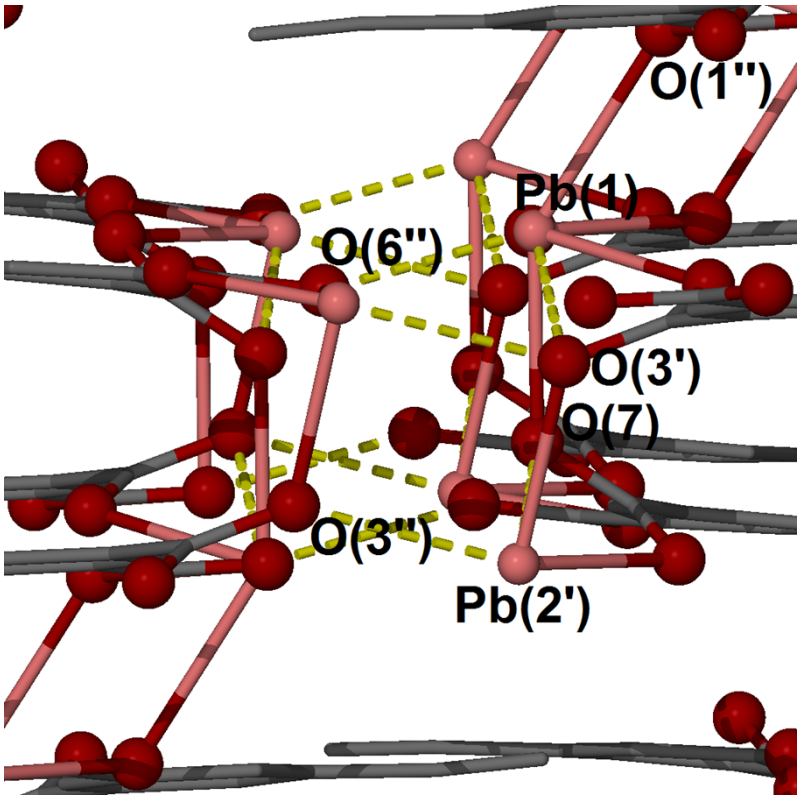
Here the coordination environment of the lead(II) in **1** is shown in greater clarity.

Expanded 2:



Conversion to **2** sees a primary Pb(1)-O(1'') bond form by slipping of the chains. Lost hydrogen bonds are replaced by secondary interactions between Pb(1) and O(6'') and Pb(2) and O(3'').

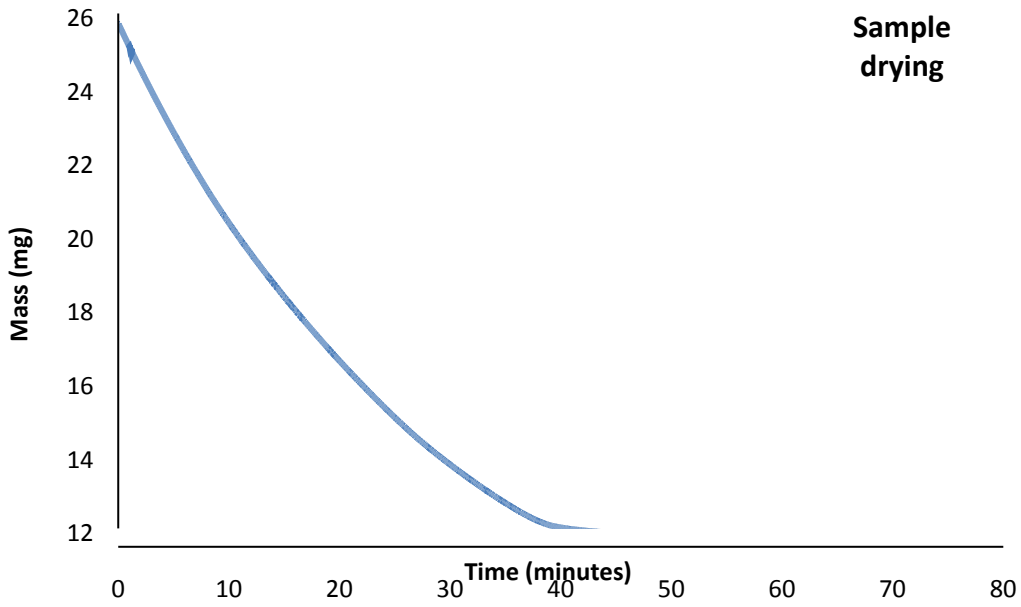
Enlarged Metal Coordination Region:



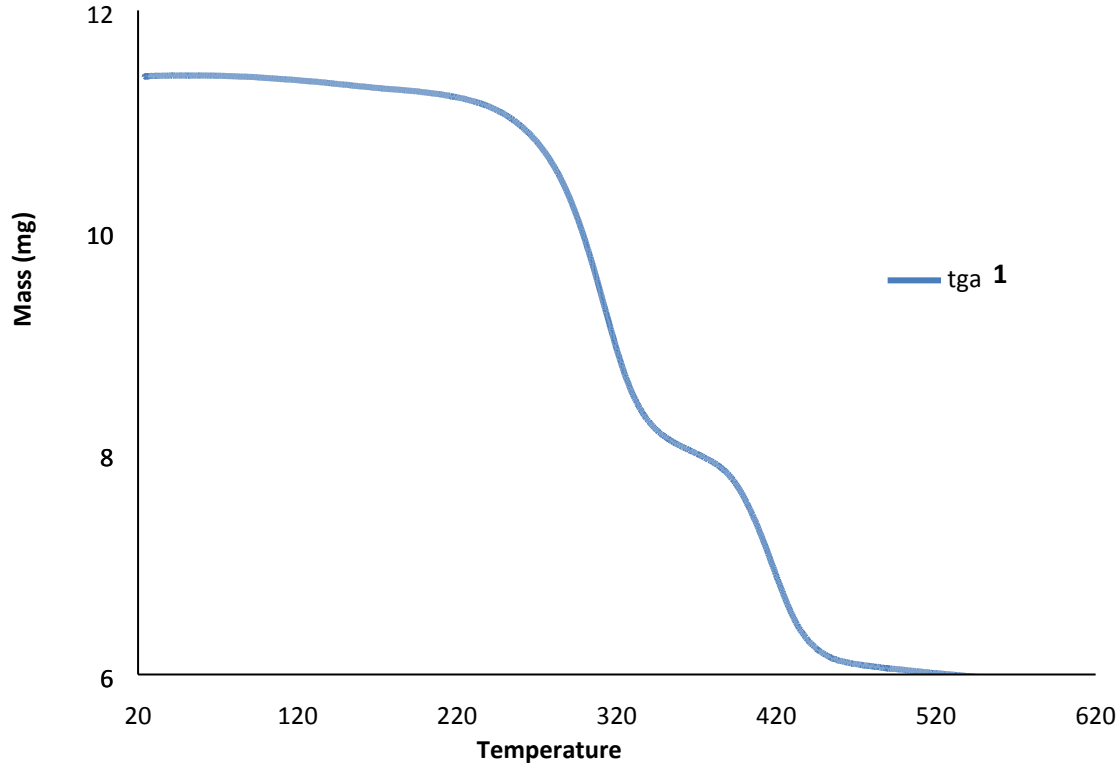
Here the coordination environment of the lead(II) centres in **2** are shown in greater clarity.

S7: TGA analysis of 1.

Thermogravimetric analysis was used to better understand the desolvation behaviour of **1**. A fresh, methanol moistened sample was placed on the balance under a constant stream of nitrogen and the loss of weight monitored. After approximately 34 minutes 90% of the solvent mass had been lost, and 99% solvent loss was observed after 48 minutes. Monitoring was continued for 14 hours to allow the sample weight to completely equilibrate. After this time the converted sample of **2** was heated to 600 °C, whereupon the sample degraded to lead(II) oxide in a two-step process beginning at 200 °C and reaching completion at 480 °C (observed mass loss: 45%, predicted mass loss: 44%).



Pre-drying of a solvated sample of **1** freshly removed from mother-liquor on the TGA balance under a stream of nitrogen at ambient temperature.



TGA analysis of **1** once a steady weight was attained post-drying

S8: References:

S1: Station13.3.1, The Advanced Light Source. www.als.lbl.gov/als/techspecs/bl11.3.1.html.
S2: Agilent Gemini A-Ultra Diffractometer http://www.chem.agilent.com/en-US/Products/Instruments/x-raycrystallography/smallmoleculesystem/geminiultra/pages/default.aspx
S3: Agilent CryojetXL http://www.chem.agilent.com/en-US/Products/Instruments/x-raycrystallography/accessories/cryojetxl/pages/default.aspx