Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Synthesis, Structure and Catalytic Application of Lead(II) Complexes in Cyanosilylation Reaction

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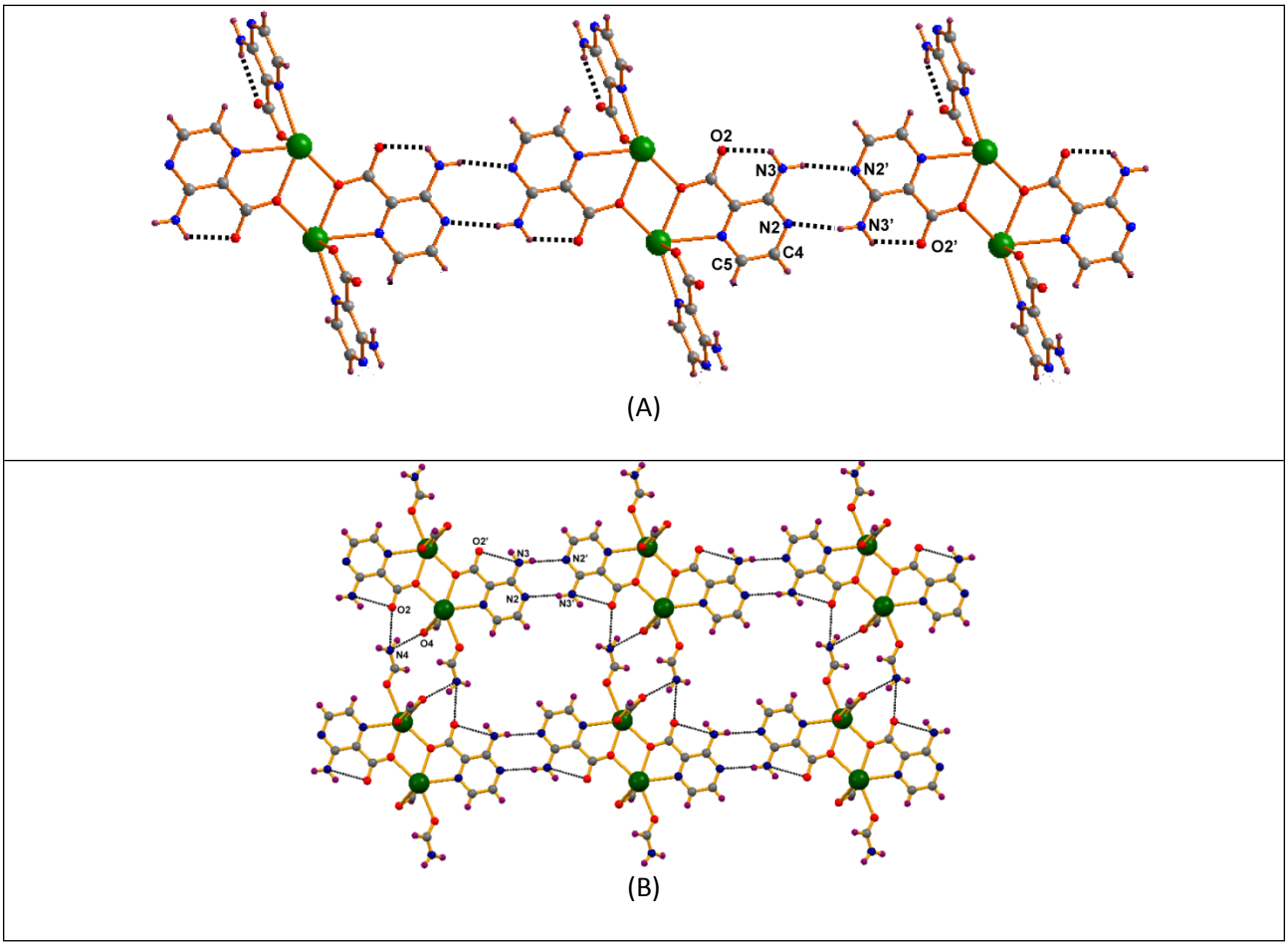
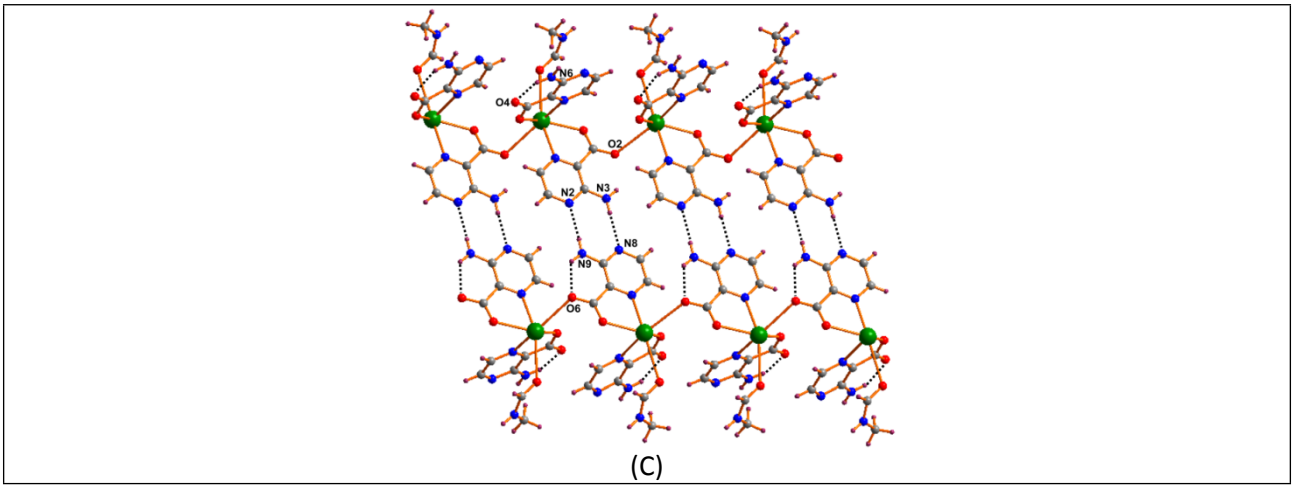


(A)

(B)



(C)

Fig. S1 Intra- and intermolecular H-bond interactions leading to infinite 1D chains in **1** (A), and 2D sheets in **2** (B) and **3** (C)

Thermogravimetric analyses

Thermogravimetric analyses were carried out under dinitrogen in the range from room temperature to *ca.* 700 ˚C at a heating rate of 10 ˚C min^{-1}. Features of the thermal stability of complexes **1**-**6** are illustrated in Fig. S2.

Complexes **1** and **3** show a single step decomposition, the former with a weight loss of 28.4% within 291-402˚C, most likely due to loss of two ligand molecules (calcd: 28.5%), whereas the latter shows a decrease of 23.2% of its weight within 286-381˚C due to the loss of two N-methylformamides and a L1 ligand (calcd: 23.6%).

Complex **2** shows two step decompositions and loses 5.5% of its weight within 112-156˚C, most likely due to loss of one formamide molecule (calcd: 5.1%). The residue remains stable up to about 190 ˚C and then starts to release another formamide molecule and two formate anions until 330 ˚C, which corresponds to a weight loss of 15.9 % (calcd. weight loss 16.3 %) and then gradually decomposes until 396˚C.

Complex **4** exhibits a weight loss of 16.8 % in the 122-301˚C temperature range, which accounts for the total removal of 2.5 molecules of dimethylformamide and a water molecule from the lattice (calcd: 17.1%). The remaining material then starts to decompose from 302˚C until 430˚C with loss of one ligand molecule which corresponds to a weight loss of 13.8% (calcd: 14.2%).

Complex **5** exhibits a weight loss of 7.3 % in the 212-281˚C temperature range, which accounts for the total removal of two dimethylformamide and a methanol molecules from the lattice (calcd: 7.6%). The remaining material then starts to decompose from 302˚C until 377˚C with loss of three ligand molecules, two formate and a nitrate molecule which corresponds to a weight loss of 25.8% (calcd: 26.2%).

Complex **6** shows a weight loss of 13.8% between 117 and 276˚C, corresponding to the loss of two dimethylformamide molecules and a water molecule (calcd: 14.2%). Upon further heating, the complex is started to decompose from 277˚C and gradually decomposes until 700˚C.

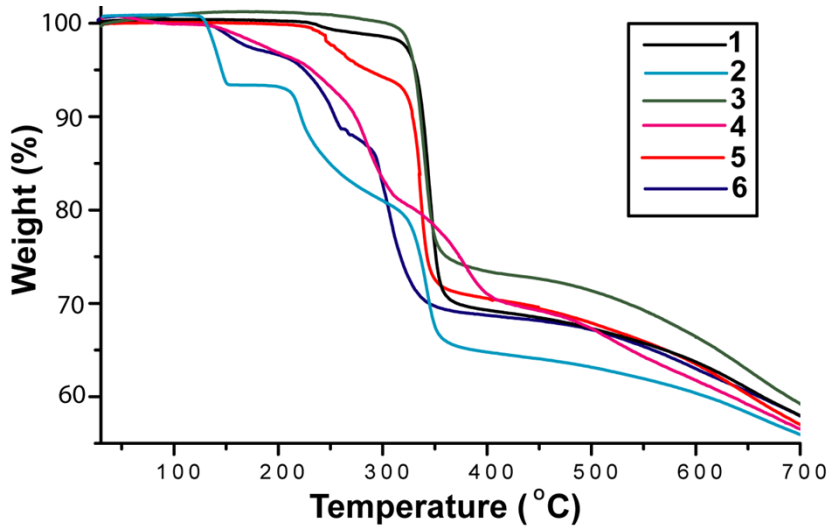


Fig. S2 Thermogravimetric curves for **1**-**6**.

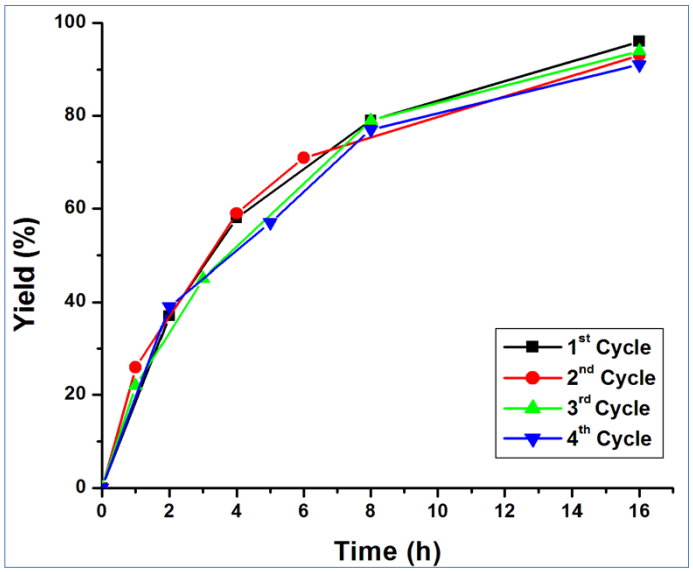
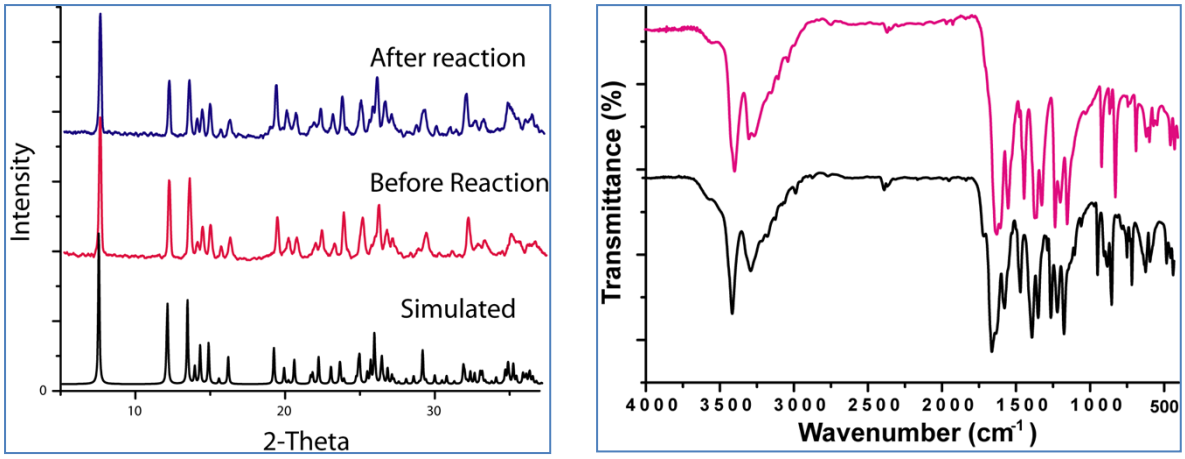


Fig. S3 Kinetic profiles in four consecutive reaction cycles employing complex **1** as catalyst in cyanosilylation reaction.



A B

Fig. S4 A) Powder XRD curves of **1** (the red and blue curves refer to before and after the catalysis reaction and the black curve is the theoretical one). B) FT-IR spectra of **1** (the black and pink curves were obtained before and after the cyanosilylation reaction, respectively).

Calculation of the yield in the Cyanosilylation reaction

The -CH peak of benzaldehyde (reactant) appears as 10.048 ppm and the 2-phenyl-2-((trimethylsilyl)oxy)acetonitrile (product) appears at 5.531 ppm.

Total amount of complex: unreacted benzaldehyde + 2-phenyl-2-((trimethylsilyl)oxy)acetonitrile = 1+ 27.6 = 28.6

Percentage of the unreacted benzaldehyde: 100/28.6 = 3.5%

Conversion of benzaldehyde = yield of 2-phenyl-2-((trimethylsilyl)oxy)acetonitrile = 100-3.5 = 96.5%

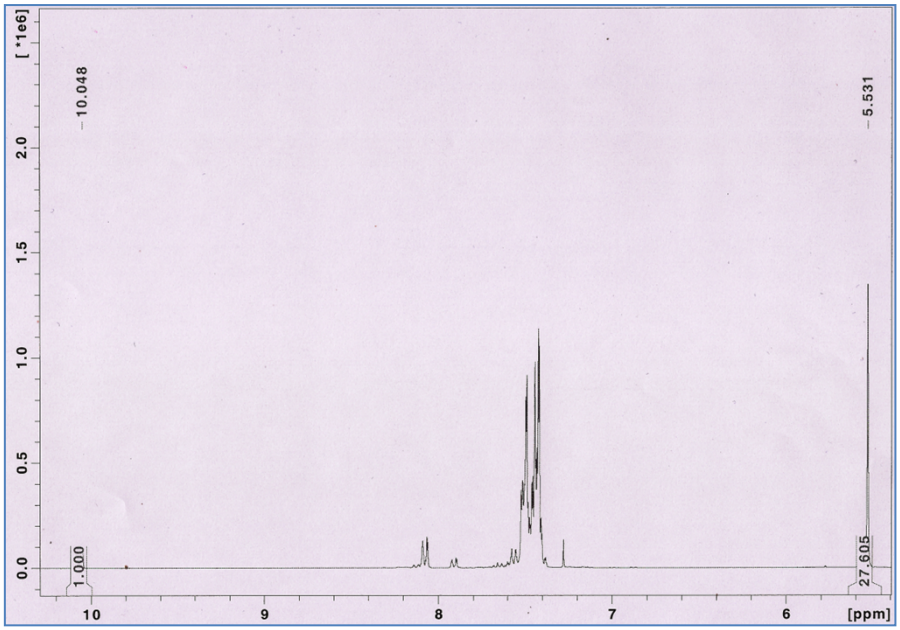


Fig. S5 Example of integration in the ^{1}H-NMR spectrum for the determination of cyanosilylation reaction products (Table 1, Entry 4).

Table S1: Crystal data and structure refinement details for Complexes 1-3			
Identification name	**1**	**2**	**3**
Formulae	$C_{20}H_{16}N_{12}O_8Pb_2$	$C_{14}H_{16}N_8O_{10}Pb_2$	$C_{24}H_{26}N_{14}O_{10}Pb_2$
Mol. wt.	966.83	870.73	1084.97
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
Temperature /K	296	296	296
Wavelength /Å	0.71073	0.71073	0.71073
a /Å	7.7520(3)	7.6846(4)	7.6487(5)
b /Å	7.8081(3)	8.0250(4)	12.2700(7)
c /Å	11.2756(5)	10.1201(5)	18.3447(12)
α/°	85.184(2)	102.495(2)	81.365(2)
β/°	86.853(2)	99.181(2)	87.259(2)
γ/°	67.1140(10)	112.272(2)	73.959(2)
V/ Å^3	626.36(4)	543.33(5)	1635.82(18)
Z	1	1	2
Density/Mgm^{-3}	2.563	2.661	2.203
Abs. Coeff. /mm^{-1}	13.496	15.544	10.355
F(000)	448	400	1024
Refl. collected	7136	10973	18025
Refl. unique	2550	2225	5514
Max. 2θ/°	26.37	26.41	24.70
Ranges (h, k, l)	-9 <= h <= 9 -9 <= k <= 9	-9 <= h <= 9 -10 <= k <= 10	-8<= h <=8 -13<= k <=14

	-14 <= l <= 14	-12 <= l <= 12	-21<= l <= 21
Complete to 2θ (%)	99.5	99.9	99.2
Refl. with I > 2σ(I)	2475	2167	4373
Data/ Restraints/Parameters	2550/ 0/ 190	2225 / 0/ 154	5514 / 0 / 453
Goof (F^2)	1.166	1.190	1.141
R1 [I > 2s(I)]	0.0214	0.0187	0.0384
wR2 [I > 2s(I)]	0.0540	0.0458	0.1015
R1 [all data]	0.0220	0.0192	0.0504
wR2 [all data]	0.0544	0.0462	0.1102

Table S1: Crystal data and structure refinement details for Complexes 4-6

Identification name	**4**	**5**	**6**
Formulae	$C_{27.5}H_{35.5}N_{14.5}O_{11.5}Pb_2$	$C_{44}H_{48}N_{24}O_{24}Pb_5$	$C_{28}H_{32}N_{14}O_{11}Pb_2$
Mol. wt.	1167.58	2333.01	1155.05
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	C2/m	$P2_1/c$
Temperature /K	296	296	296
Wavelength /Å	0.71073	0.71073	0.71073
a /Å	14.468(3)	28.1919(17)	7.8443(4)
b /Å	13.261(2)	19.7200(10)	22.1845(13)
c /Å	19.861(4)	11.8904(8)	21.7657(13)
α/°	90.00	90.00	90.00
β/°	90.964(7)	111.140(2)	90.842(2)
γ/°	90.00	90.00	90.00
V/ $Å^3$	3809.9(12)	6165.5(6)	3787.3(4)
Z	4	4	4
Density/Mgm^{-3}	2.036	2.513	2.026
Abs. Coeff. /mm^{-1}	8.903	13.708	8.953
F(000)	2232	4328	2200
Refl. collected	66637	46755	43363
Refl. unique	7794	5832	6930
Max. 2θ/°	26.37	25.41	25.36
Ranges (h, k, l)	-18 <= h <=18 -16 <= k <=16 -24 <= l <= 24	-33 <= h <=33 -23 <= k <=23 -14 <= l <= 14	-9<= h <=9 -26<= k <=26 -26 <= l <= 26
Complete to 2θ (%)	99.9	99.4	99.6
Refl. with I > 2σ(I)	6291	4847	4943
Data/ Restraints/Parameters	7794 / 1 / 388	5832 / 24 / 412	6930 / 0 / 397
Goof (F^2)	1.058	1.060	1.047
R1 [I > 2s(I)]	0.0429	0.0626	0.0526
wR2 [I > 2s(I)]	0.1037	0.1732	0.1172
R1 [all data]	0.0573	0.0728	0.0862
wR2 [all data]	0.1095	0.1793	0.1269

Table S2: Hydrogen bond geometry (Å, °) in complexes 1-6.						
Complex	D-H---A	D-H (Å)	H···A (Å)	D···A (Å)	<D−H···A(°)	Symmetry
1	N(3)–H(3A)····N(2)	0.86	2.22	3.067(5)	167	-1-x,1-y,-z
	N(3)–H(3B)····O(2)	0.86	2.10	2.731(5)	130	-
	N(6)–H(6A)····O(2)	0.86	2.22	3.078(6)	174	x,y,1+z
	N(6)–H(6B)····O(4)	0.86	2.08	2.716(6)	130	-
	C(4)–(4)····N(5)	0.93	2.61	3.236(6)	125	-x,1-y,1-z
	C(10)–(10)····O(4)	0.93	2.44	3.147(5)	132	x,1+y,z
2	N(3) –H(3A) ····N(2)	0.86	2.24	3.093(4)	173	2-x,1-y,-z
	N(3) –H(3B) ····O(2)	0.86	2.09	2.721(4)	130	-
	N(4) –H(4A)····O(3)	0.86	2.21	3.063(5)	173	-x+1, -y+1, -z+1
	N(4) –H(4B)····O(2)	0.86	2.28	2.850(5)	124	x, y+1, z+1
	N(4) –H(4B)····O(4)	0.86	2.28	3.016(6)	144	-x, -y+1, -z+1
	C(3) –H(3) ····O(5)	0.93	2.35	3.047(6)	132	-
3	N(3)–H(3A)····N(8)	0.86	2.22	3.082(9)	177	1-x,1-y,-z
	N(3)–H(3B)····O(2)	0.86	2.10	2.728(9)	129	-
	N(6) –H(6A)····N(11)	0.86	2.33	3.181(11)	170	1-x,2-y,1-z
	N(6)–H(6B)····O(4)	0.86	2.05	2.679(11)	130	-
	N(14)-H(14A)····O(4)	0.86	2.01	2.806(11)	154	x,1+y,z
	N(9)–H(9A)····N(2)	0.86	2.18	3.033(9)	175	1-x,1-y,-z
	N(9)–H(9B)····O(6)	0.86	2.11	2.727(9)	128	-
	N(9)–H(9B)····O(6)’	0.86	2.32	2.953(8)	130	2-x,1-y,-z
	N(12)--H(12A)····N(5)	0.86	2.14	2.970(11)	163	1-x,2-y,1-z
	N(12)–H(12B)····O(8)	0.86	2.03	2.673(10)	131	-
	N(12 –H(12B)····O(8)’	0.86	2.00	2.839(10)	165	1+x,y,z
	C(4)–H(4)····O(5)	0.93	2.40	3.322(8)	171	-1+x,y,z
	C(14)–H(14)····O(1)	0.93	2.46	3.374(9)	169	x,-1+y,z
4	N(3) –H(3A) ····N(11)	0.86	2.36	3.210(13)	172	1+x,y,z
	N(3) –H(3B) ····O(2)	0.86	2.11	2.731(12)	129	-
	N(6) –H(6A) ····O(6)	0.86	1.96	2.806(8)	169	x,1/2-y,1/2+z
	N(6) –H(6B) ····O(4)	0.86	2.03	2.668(8)	131	-
	N(9) –H(9A) ····O(8)	0.86	2.20	2.954(9)	147	-x,1-y,-z
	N(9) –H(9B) ····O(6)	0.86	2.06	2.689(9)	130	-
	O(9) –H(9O) ····O(2)	0.91	1.94	2.830(9)	165	1-x,1/2+y,1/2-z
	O(9)–H(10O) ····O(8)	1.10	1.78	2.822(9)	156	1+x,y,z
	O(9) –H(10O) ····N(9)	1.10	2.52	3.200(9)	119	1-x,1-y,-z
	N(12)–H(12A) ····N(2)	0.86	2.12	2.978(13)	174	-1+x,y,z
	N(12) –H(12B) ····O(8)	0.86	2.04	2.677(12)	130	-
	C(9) –H(9) ····O(1)	0.93	2.54	3.281(9)	137	x,1/2-y,1/2+z
	C(14) –H(14) ····O(2)	0.93	2.41	3.205(11)	143	x,1+y,z
5	N(3)–H(3A)····O(4)	0.86	2.49	3.33(2)	166	1/2-x,1/2-y,1-z
	N(3)–H(3B)····O(2)	0.86	2.05	2.67(2)	129	-
	N(6)–H(6A)····N(8)	0.86	2.22	3.077(16)	174	1/2+x,1/2-y,z
	N(6)–H(6B)····O(4)	0.86	2.05	2.673(16)	128	-
	N(9)–H(9A)····N(5)	0.86	2.31	3.150(15)	166	-1/2+x,1/2-y,z
	N(9)–H(9B)····O(6)	0.86	2.03	2.666(16)	130	-
	N(12)–H(12A) ····O(11)	0.86	2.52	3.37(5)	170	x,y,1+z
	N(12)–H(12A)····O(12)	0.86	2.12	2.80(4)	136	x,y,1+z
	N(12)–H(12B)····O(8)	0.86	2.03	2.63(6)	126	-
	C(9) –H(9)····O(11)	0.93	2.60	3.310(17)	133	1/2-x,1/2+y,-z

	C(18) –H(18)····O(10)	0.93	2.62	3.55(4)	179	-
	C(8) –H(8) ····O(1)	0.93	2.57	3.164(16)	122	-
6	N(3)-H(3N)····O(2)	0.86	1.94	2.627(16)	135	-
	N(4)-H(4N)····O(4)	0.86	2.00	2.655(16)	132	-
	N(9)-H(9N)····O(6)	0.86	2.03	2.673(12)	131	-
	N(10)-H(10N)····O(8)	0.86	2.05	2.673(11)	129	-
	C(17)-H(17A)····N(12)	0.97	2.65	3.431(13)	138	-x+1, -y+2, -z+1
	C(17)-H(17B)····N(8)	0.97	2.68	3.472(14)	139	-x+2, -y+2, -z+1
	C(20)-H(20)····O(8)	0.93	2.48	3.222(13)	136	x-1, y, z
	C(14)-H(14)····O(6)	0.93	2.55	3.286(13)	137	x+1, y, z
	C(3)-H(3)····O(2)	0.93	2.40	3.203(14)	145	x+1, y, z
	C(9)-H(9)····O(4)	0.93	2.46	3.217(14)	139	x-1, y, z

Table S3: Selected bond distances (Å) and angles (°) for complexes 1-6

	Bond distances		Bond angles		Bond angles
1					
Pb1–O3	2.271(3)	O3–Pb1–O1	84.05(11)	O3–Pb1–N1	82.31(11)
Pb1–O1	2.403(3)	O3–Pb1–O1	81.26(11)	O1–Pb1–N1	64.12(9)
Pb1–O1’	2.531(3)	O1–Pb1–O1	66.26(11)	O1–Pb1–N1	128.90(9)
Pb1–N4	2.585(3)	O3–Pb1–N4	67.29(11)	N4–Pb1–N1	78.62(11)
Pb1–N1	2.608(3)	O1–Pb1–N4	135.70(11)	Pb1–O1–Pb1	113.74(11)
		O1–Pb1–N4	135.42(11)		
2					
Pb1–O3	2.335(3)	O3–Pb1–O1	84.03(10)	O1–Pb1–N1	127.78(8)
Pb1–O1	2.415(2)	O3–Pb1–O1’	86.68(10)	O3–Pb1–O5	84.13(15)
Pb1’–O1	2.555(2)	O1–Pb1–O1’	65.25(9)	O1–Pb1–O5	138.76(11)
Pb1–N1	2.613(3)	O3–Pb1–N1	76.68(10)	O1–Pb1–O5	152.58(11)
Pb1–O5	2.686(4)	O1–Pb1–N1	64.03(9)	N1–Pb1–O5	74.82(11)
		Pb1–O1–Pb1	114.75(9)		
3					
Pb1–O1	2.454(5)	O3-Pb1-O1	130.4(2)	O7-Pb2-N10	67.1(2)
Pb1–O3	2.387(6)	O3-Pb1-N1	79.5(2)	O5-Pb2-N10	73.1(2)
Pb1–N4	2.487(6)	O1-Pb1-N1	65.72(18)	N7-Pb2-N10	92.9(2)
Pb1–N1	2.481(6)	O3-Pb1-N4	66.9(2)		
Pb2–O5	2.443(5)	O1-Pb1-N4	75.4(2)		
Pb2–O7	2.338(5)	N1-Pb1-N4	84.8(2)		
Pb2–N10	2.501(6)	O7-Pb2-O5	122.9(2)		
Pb2–N7	2.477(6)	O7-Pb2-N7	77.0(2)		
Pb1-O9	2.855(1)	O5-Pb2-N7	65.60(17)		
Pb2–O10	2.880(9)				
4					
Pb1–O1	2.444(5)	O1–Pb1–O3	90.70(16)	O5–Pb2–N10	79.2(2)
Pb1–O3	2.454(4)	O1–Pb1–N1	64.9(2)	O7–Pb2–O3	139.59(17)
Pb1–N1	2.519(7)	O3–Pb1–N1	85.24(19)	O5–Pb2–O3	62.23(15)
Pb1–O5	2.530(5)	O1–Pb1–O5	139.26(18)	N10–Pb2–O3	83.50(18)
Pb2–O7	2.469(5)	O3–Pb1–O5	65.50(16)	O7–Pb2–N4	85.16(19)
Pb2–O5	2.536(5)	N1–Pb1–O5	79.9(2)	O5–Pb2–N4	117.15(18)

Pb2–N10	2.539(6)	O7–Pb2–O5	128.80(19)	O3–Pb2–N4	60.33(16)
Pb2–O3	2.677(5)	O7–Pb2–N10	64.67(19)	Pb1–O5–Pb2	109.89(19)
Pb2–N4	2.688(6)	N10–Pb2–N4	71.2(2)	Pb1–O3–Pb2	107.77(16)
5					
Pb1–N1	2.436(12)	N1–Pb1–O1	66.2(4)	O11–Pb3–O9	76.0(5)
Pb1–O1	2.477(10)	N1–Pb1–O3	82.9(4)	O4–Pb3–O9	106.3(4)
Pb1–O3	2.481(10)	O1–Pb1–O3	131.0(3)	O4–Pb3–O9’	148.2(5)
Pb1–O5	2.584(10)	N1–Pb1–O5	78.8(4)	O9–Pb3–O9	45.0(6)
Pb1–N4	2.711(10)	O1–Pb1–O5	127.4(3)	O7–Pb2–O6	118.7(4)
Pb2–O7	2.360(18)	O3–Pb1–O5	78.0(3)	O6–Pb2–O6’	92.4(5)
Pb2–O6	2.479(11)	N1–Pb1–N4	79.5(4)	O7–Pb2–N10	67.5(8)
Pb2–N10	2.56(2)	O1–Pb1–N4	74.9(3)	O6–Pb2–N10	74.0(5)
Pb2–O5	2.750(10)	O3–Pb1–N4	62.4(3)	O7–Pb2–O5	80.5(2)
Pb1–N7	2.793(10)	O5–Pb1–N4	136.6(3)	O6–Pb2–O5	49.4(3)
Pb3–O7	2.44(2)	N1–Pb1–N7	74.8(4)	O6–Pb2–O5	140.4(3)
Pb3–O4	2.567(11)	O1–Pb1–N7	73.5(3)	N10–Pb2–O5	84.4(3)
Pb3–O11	2.58(2)	O3–Pb1–N7	135.0(3)	O7–Pb2–O5	80.5(2)
Pb3–O9	2.729(16)	O5–Pb1–N7	59.8(3)	O6–Pb2–O5	140.5(3)
Pb4–O12	2.22(2)	N4–Pb1–N7	145.2(4)	O6–Pb2–O5	49.4(3)
Pb4–O2	2.504(13)	O7–Pb3–O4	108.3(4)	O5–Pb2–O5’	160.6(4)
		O4–Pb3–O4	96.1(5)	O12–Pb4–O2	79.3(6)
		O7–Pb3–O11	160.4(6)	O2–Pb4–O2’	76.4(6)
		O4–Pb3–O11	84.3(4)	O12–Pb4–O13	83.8(7)
		O7–Pb3–O9	85.9(6)	O2–Pb4–O13	156.3(6)
		O4–Pb3–O9	148.2(5)	O2–Pb4–O13	116.5(5)
		O4–Pb3–O9	106.3(4)	Pb1–O5–Pb2	141.7(4)
		O11–Pb3–O9	76.0(5)	Pb2–O7–Pb3	112.5(9)
		O7–Pb3–O9	85.9(6)		
6					
Pb1–O7	2.456(6)	O7–Pb1–O1	132.7(2)	O5–Pb2–O3	133.4(3)
Pb1–O1	2.485(8)	O7–Pb1–O3	73.5(2)	O5–Pb2–O1	73.8(3)
Pb1–O3	2.534(7)	O1–Pb1–O3	120.6(3)	O3–Pb2–O1	120.3(3)
Pb1–N1	2.570(9)	O7–Pb1–N1	79.3(3)	O5–Pb2–N5	80.5(3)
Pb1–N11	2.634(8)	O1–Pb1–N1	64.0(3)	O3–Pb2–N5	63.2(3)
Pb2–O5	2.459(7)	O3–Pb1–N1	75.8(3)	O1–Pb2–N5	76.5(3)
Pb2–O3	2.465(7)	O7–Pb1–N11	63.7(2)	O5–Pb2–N7	63.3(2)
Pb2–O1	2.528(7)	O1–Pb1–N11	78.3(3)	O3–Pb2–N7	78.9(2)
Pb2–N5	2.595(9)	O3–Pb1–N11	131.7(2)	O1–Pb2–N7	131.2(3)
Pb2–N7	2.635(9)	N1–Pb1–N11	75.2(3)	N5–Pb2–N7	74.6(3)