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Electronic Supplementary Information

Renaissance of the coordination chemistry of 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (TPymT). Part II: New insights into the reaction of TPymT with $Pb(NO_3)_2$

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Physical measurements. Infrared spectra were recorded with a Varian 640 FTIR spectrometer equipped with an ATR in the 500–4000 cm^{-1} range. Raman spectra in the solid state were obtained with a FTIR Nicolet Magna 860 with Raman unit and $Nd:YVO_4$ (λ = 1064 nm) laser. Diffuse reflectance spectra were obtained with a Varian Cary 100 spectrometer using polytetrafluoroethylene (PTFE) as a reference. Simultaneous thermogravimetric (TG) and differential thermal (DTA) analyses were performed by a SDT 2960 Simultaneous DTA-TGA instrument in a dynamic air atmosphere (100 $mL\cdot min^{-1}$) from laboratory temperature to 900 °C with a 10 °C min^{-1} heating rate. Elemental analyses were performed on a Perkin Elmer 2400 CHN analyzer. Solid-state NMR experiments were performed at ambient temperature on all lead samples at B_0 = 4.7 T (Bruker AVANCE II, $\nu_L(^1H)$ = 200.13 MHz, $\nu_L(^{207}Pb)$ = 41.86 MHz). All ^{207}Pb NMR experiments were performed with a Bruker 7 mm MAS triple-resonance probe (D/H/X) using a single pulse MAS experiment at a spinning frequency of 4 kHz. The 90° pulse was 4 μs and the recycle delay was 5 s. The transmitter was stepped to high and low frequency to ensure all spinning sidebands were found. In order to identify the isotropic chemical shifts, additional experiments (not shown) were performed at a spinning frequency of 5 kHz. The reported chemical shifts are referenced to the scaled absolute frequency of tetramethylsilane (TMS) scaled by the frequency ratio, Ξ, of 20.920599% at 0.0 ppm. The chemical shifts can also be referenced to a stationary sample of $Pb(NO_3)_2$. At 295 K, its isotropic chemical shift, δ_{iso}, is –3490 ppm.[1] Chemical shifts using this method are within 2 ppm of those obtained using the absolute frequency approach. The lead-207 chemical shift tensor parameters (isotropic chemical shift, span, and skew) are reported in Table S1, and were obtained using an analysis of the spinning sideband intensities. A 1:1 intensity ratio was used for the two sites in compound **1**.

Syntheses of 1 and 2. A hot aqueous (10 mL) solution of $Pb(NO_3)_2$ (0.45 mmol, 0.149 g) was added to a suspension of **TPymT** (0.15 mmol, 0.047 g) in the same solvent (10 mL). The mixture was refluxed until all of the reactants dissolved. The resulting pale yellow solution was cooled with fast (~6 days) or slow (~4 weeks) evaporation of the solvent yielding orange large needle-like or colorless plate-like crystals of **1** and **2**, respectively.

1. Yield: 0.147 g (96.4%). *Anal.* Calc. for $C_{15}H_{13}N_{13}O_{14}Pb_2$ (1013.75): C 17.77, H 1.29, N 17.96. Found: C 17.64, H 1.35, N 18.04%.

2. Yield: 0.134 g (91.7%). *Anal.* Calc. for $C_{15}H_9N_{13}O_{12}Pb_2$ (977.72): C 18.43, H 0.93, N 18.62. Found: C 18.59, H 1.04, N 18.76%.

X-ray powder diffraction. X-ray powder diffraction for the bulk samples of **1** and **2** was carried out using a Rigaku Ultima IV X-ray powder diffractometer. The Parallel Beam mode was used to collect the data (λ = 1.541836 Å).

Single crystal X-ray diffraction. The X-ray data for **2** were collected at 200(2) K on a Bruker AXS SMART single crystal diffractometer with a sealed Mo tube APEX II CCD detector. The Mo radiation wavelength, 0.71073 Å, was used. Data collection and processing were performed with APEX software from Bruker AXS.[2] The crystal structures were solved by direct methods and refined using the SHELX program.[3] All non-hydrogen atoms were refined anisotropically and the positions of all hydrogen atoms were obtained from the Fourier map analysis. Figures were generated using the Mercury program.[4] $C_{15}H_9N_{13}O_{12}Pb_2$, M_r = 977.73 g mol^{-1}, orthorhombic, space group *Pccn*, a = 9.4199(3), b = 12.6344(4), c = 20.5258(5) Å, V = 2442.87(12) Å^3, Z = 4, ρ = 2.658 g cm^{-3}, μ(Mo-Kα) = 13.856 mm^{-1}, reflections: 33703 collected, 3694 unique, R_{int} = 0.0464, R_1(all) = 0.0326, wR_2(all) = 0.0698. CCDC 966468 (**2**) contains the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

1 P. A. Beckmann and C. Dybowski, *J. Magn. Reson.*, 2000, **146**, 379.

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3 G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.

4 I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. McCabe, J. Pearson and R. Taylor, *Acta Crystallogr.*, 2002, **B58**, 389.

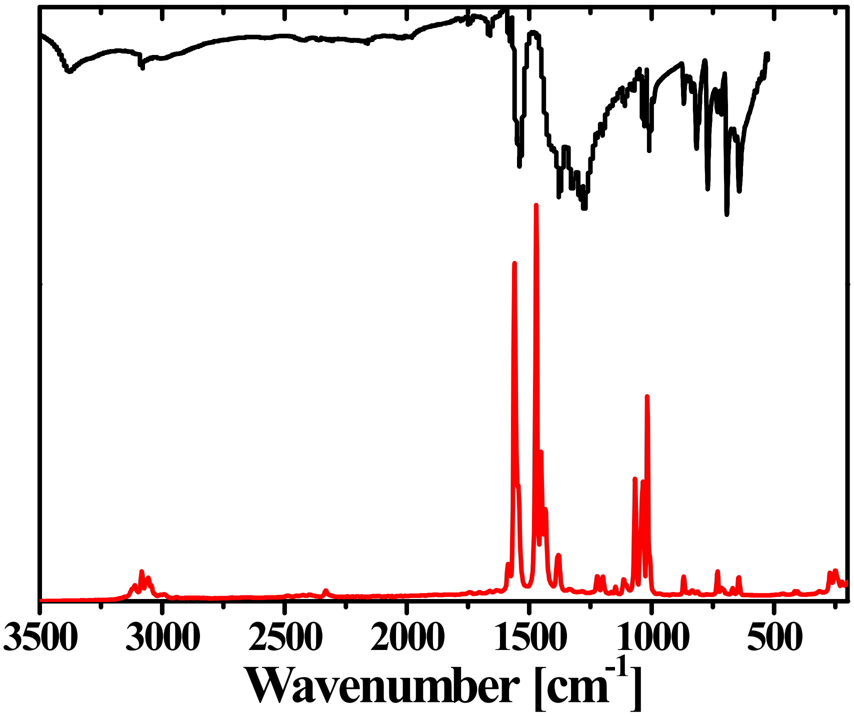

Fig. S1 The FTIR (black) and Raman (red) spectra of **1** at 298 K.

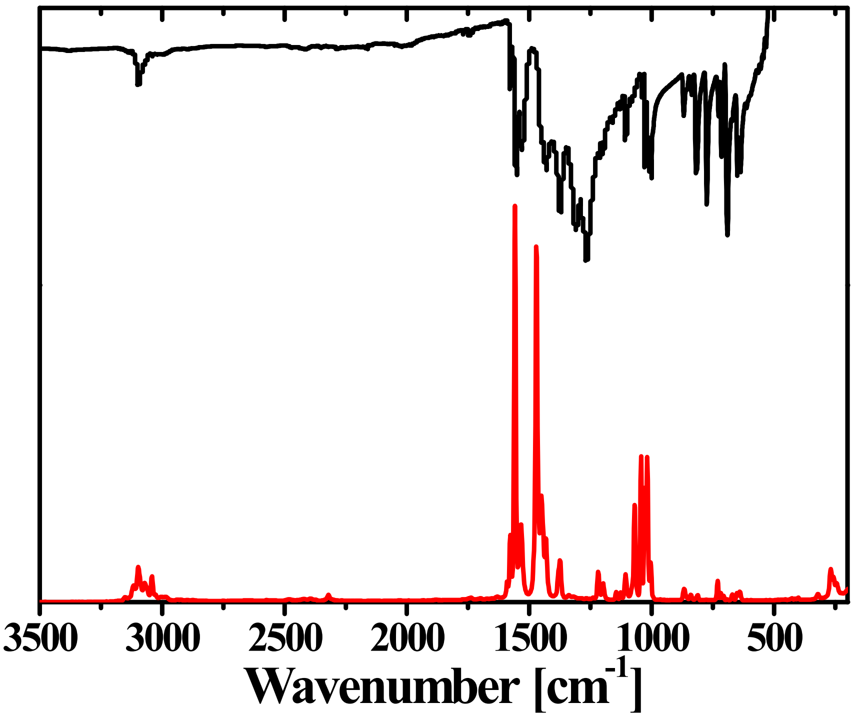

Fig. S2 The FTIR (black) and Raman (red) spectra of **2** at 298 K.

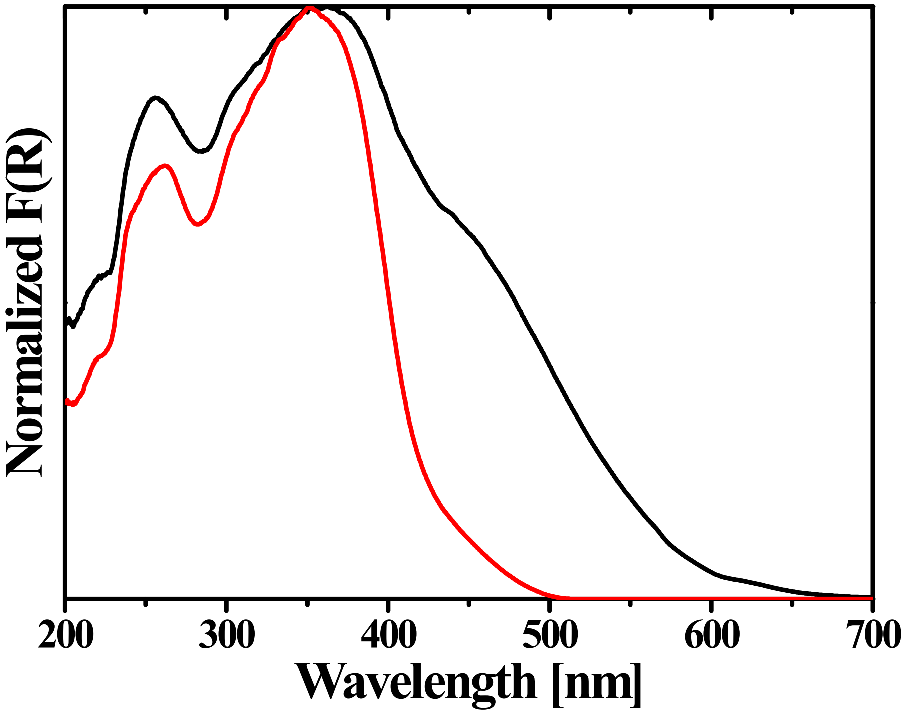

Fig. S3 The normalized Kubelka-Munk spectra of **1** (black) and **2** (red) at 298 K.

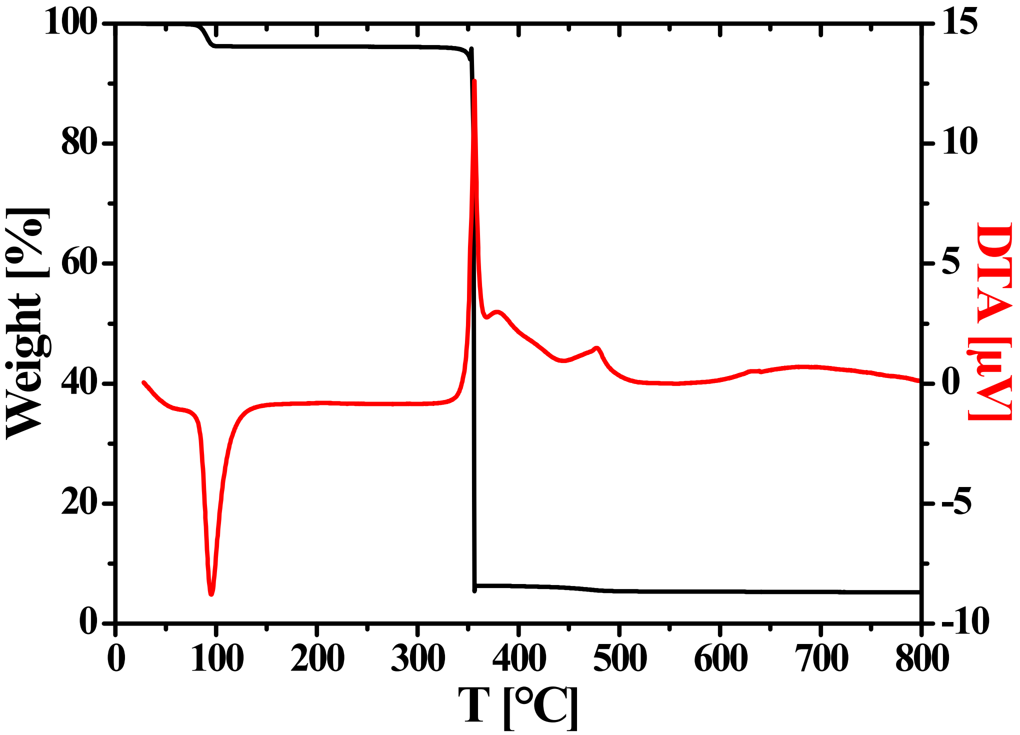

Fig. S4 Simultaneous TG/DTA analyses of **1** performed in a dynamic air atmosphere.

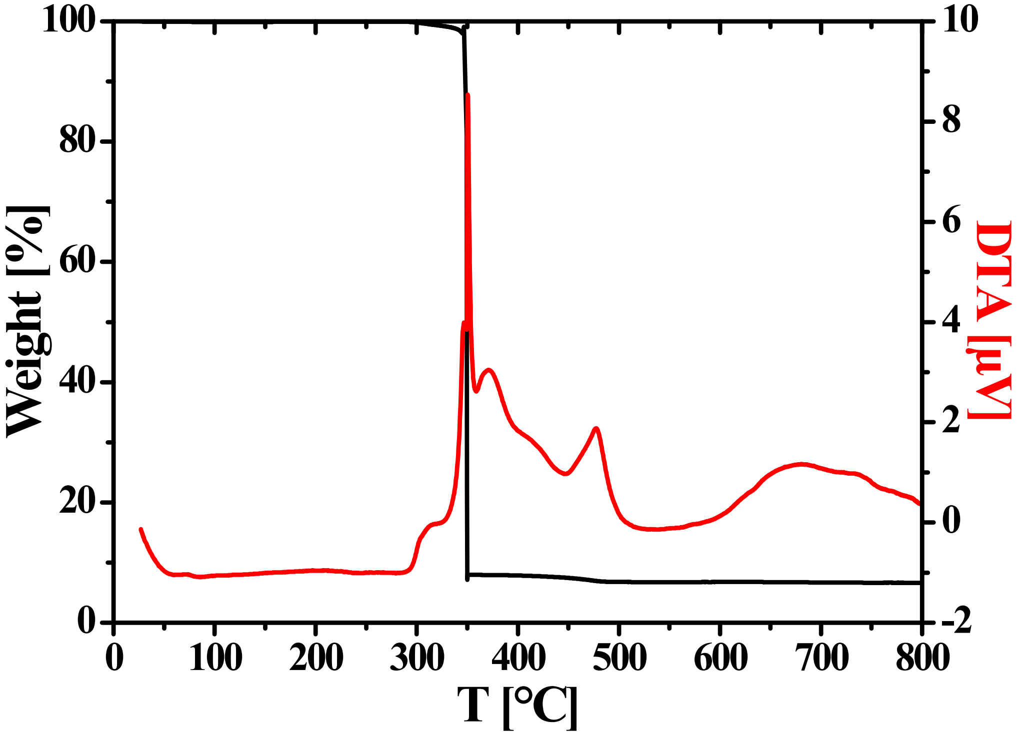

Fig. S5 Simultaneous TG/DTA analyses of **2** performed in a dynamic air atmosphere.

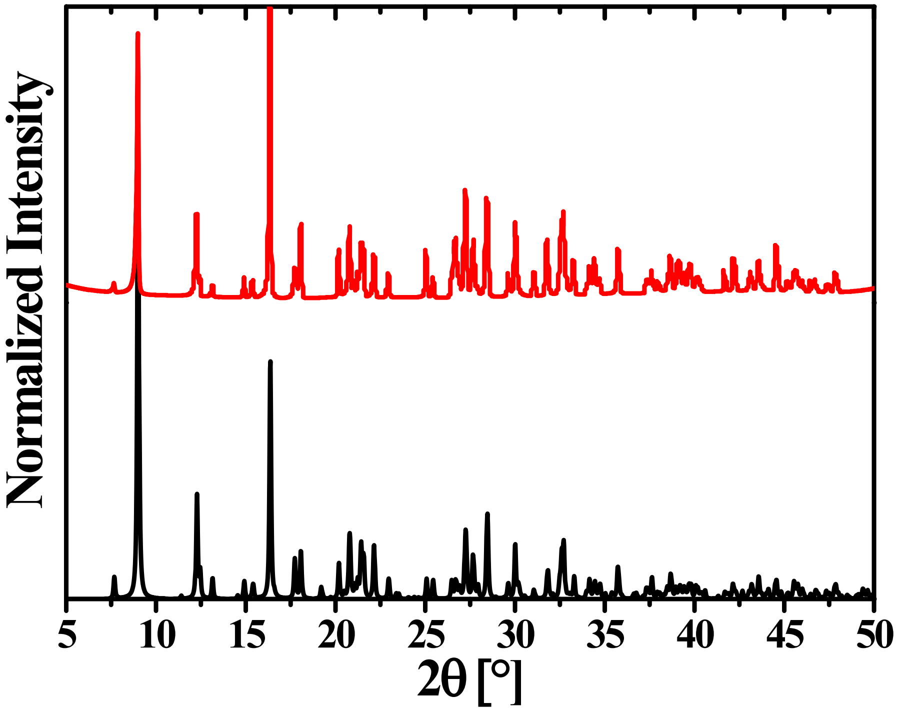

Fig. S6 Calculated (black) and experimental (red) X-ray powder diffraction patterns of **1**.

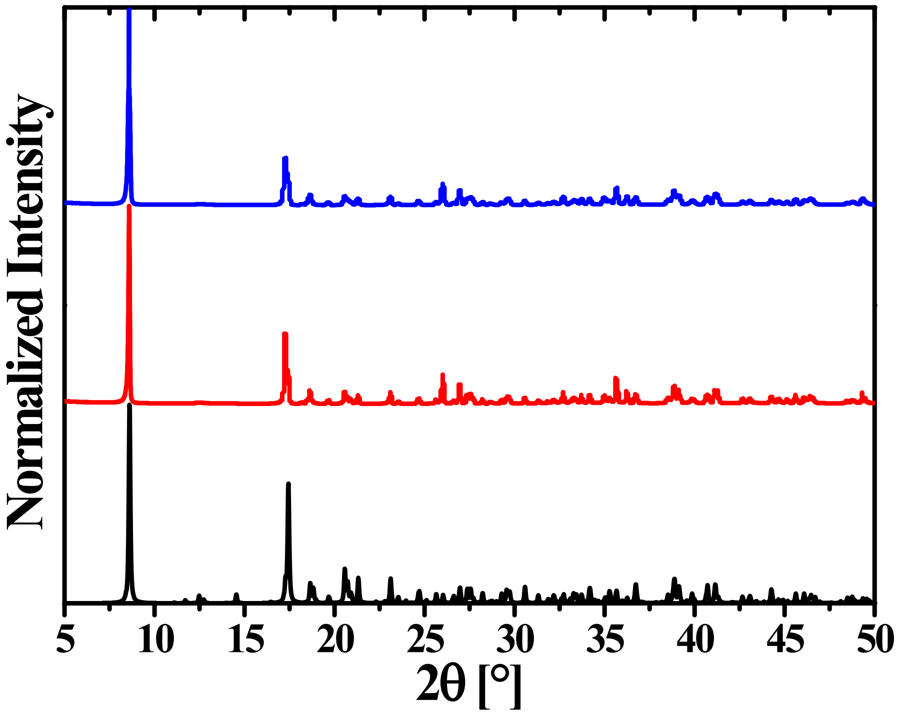

Fig. S7 Calculated (black) and experimental (red) X-ray powder diffraction patterns of **2**, and the powder pattern of the sample (blue) obtained after annealing of the raw material of **1** at 200 °C for 10 min.

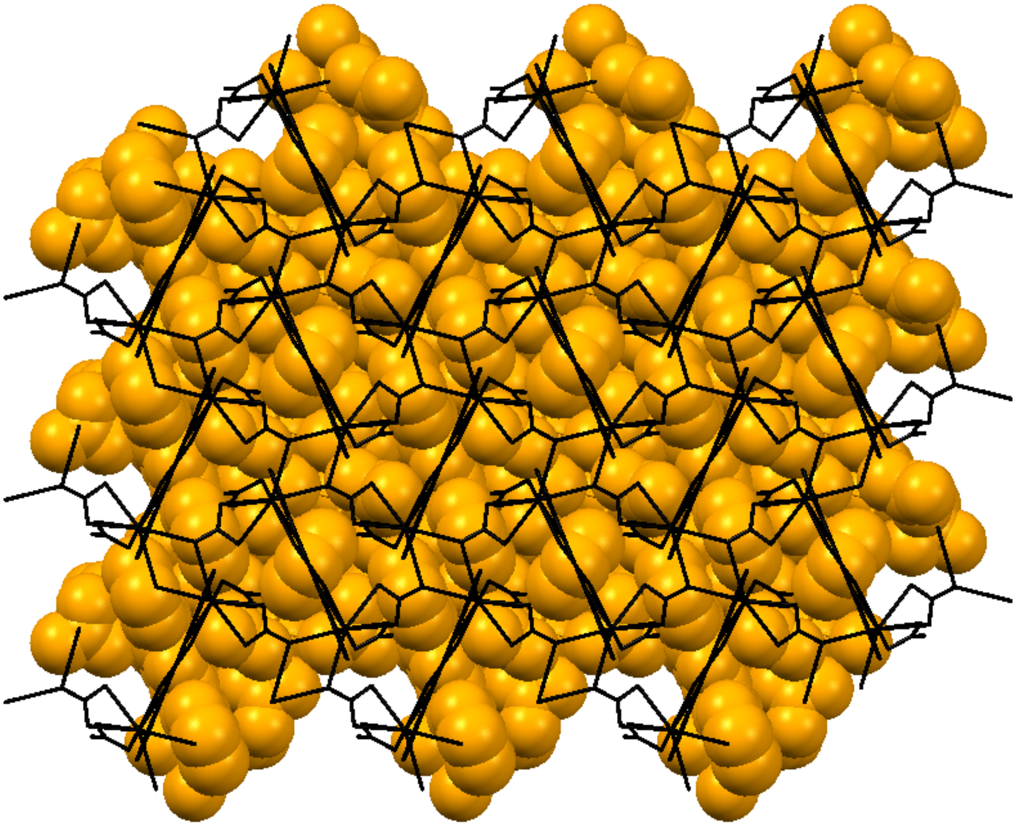

Fig. S8 Crystal packing of 2D sheets of **2**.

Table S1 Lead-207 chemical shift tensor parameters for **1** and **2**

Compound	δ_{iso}/ppm	Ω/ppm	κ
1 (needles), site 1	–3005(2)	370(20)	–0.65(0.1)
1 (needles), site 2	–2920(1)	550(20)	–0.50(0.2)
2 (plates)	–2973(2)	570(20)	–0.10(0.1)

Table S2 Selected bond lengths (Å) and bond angles (°) for **2**

Bond lengths					
Pb(1)–N(1)	2.674(3)	N(2)–C(1)	1.333(4)	O(3)–N(6)	1.244(4)
Pb(1)–N(3)	2.701(3)	N(3)–C(2)	1.332(5)	O(4)–N(7)	1.245(5)
Pb(1)–N(5)	2.679(3)	N(3)–C(5)	1.326(5)	O(5)–N(7)	1.256(5)
Pb(1)–O(1)	2.690(3)	N(4)–C(2)	1.319(5)	O(6)–N(7)	1.227(5)
Pb(1)–O(3)#1	2.744(3)	N(4)–C(3)	1.335(6)	C(1)–C(2)	1.494(5)
Pb(1)–O(4)	2.642(3)	N(5)–C(7)	1.334(3)	C(3)–C(4)	1.376(7)
Pb(1)–O(5)	2.740(4)	N(5)–C(8)	1.337(4)	C(4)–C(5)	1.372(7)
N(1)–C(1)	1.329(4)	O(1)–N(6)	1.263(5)	C(6)–C(7)	1.486(6)
N(1)–C(6)	1.337(3)	O(2)–N(6)	1.225(4)	C(8)–C(9)	1.378(5)
Bond angles					
N(1)–Pb(1)–N(3)	59.93(9)	O(4)–Pb(1)–O(5)	46.96(11)	N(3)–C(2)–C(1)	116.1(3)
N(1)–Pb(1)–N(5)	61.58(8)	O(5)–Pb(1)–O(3)#1	91.47(12)	N(3)–C(5)–C(4)	121.6(5)
N(5)–Pb(1)–N(3)	121.27(9)	N(6)–O(1)–Pb(1)	97.8(2)	N(4)–C(2)–C(1)	117.8(3)
N(1)–Pb(1)–O(1)	66.44(9)	N(6)–O(3)–Pb(1)#2	137.3(3)	N(4)–C(3)–C(4)	123.3(5)
N(1)–Pb(1)–O(5)	142.66(12)	N(7)–O(4)–Pb(1)	99.9(2)	N(5)–C(7)–C(6)	117.1(2)
N(1)–Pb(1)–O(3)#1	75.41(9)	N(7)–O(5)–Pb(1)	94.8(2)	N(5)–C(8)–C(9)	122.2(4)
N(3)–Pb(1)–O(3)#1	84.40(12)	C(1)–N(1)–Pb(1)	122.7(2)	C(1)–N(1)–C(6)	115.9(3)
N(3)–Pb(1)–O(5)	154.77(12)	C(2)–N(3)–Pb(1)	122.0(2)	C(1)#3–N(2)–C(1)	114.9(4)
N(5)–Pb(1)–O(1)	76.95(9)	C(5)–N(3)–Pb(1)	119.3(3)	C(2)–N(4)–C(3)	115.3(4)
N(5)–Pb(1)–O(3)#1	76.68(10)	C(6)–N(1)–Pb(1)	120.7(2)	C(5)–N(3)–C(2)	117.3(4)
N(5)–Pb(1)–O(5)	81.53(12)	C(7)–N(5)–Pb(1)	121.2(2)	C(7)–N(5)–C(8)	116.5(3)
O(1)–Pb(1)–N(3)	84.87(11)	C(8)–N(5)–Pb(1)	121.5(2)	O(2)–N(6)–O(1)	120.1(4)
O(4)–Pb(1)–N(1)	127.57(10)	N(1)#3–C(6)–N(1)	123.5(4)	O(2)–N(6)–O(3)	121.8(4)
O(4)–Pb(1)–N(3)	138.00(12)	N(2)–C(1)–N(1)	124.9(3)	O(3)–N(6)–O(1)	118.1(3)
O(4)–Pb(1)–N(5)	84.21(11)	N(4)–C(2)–N(3)	126.2(3)	O(4)–N(7)–O(5)	118.1(4)
O(1)–Pb(1)–O(3)#1	140.62(9)	N(5)–C(7)–N(5)#3	125.8(4)	O(6)–N(7)–O(4)	119.8(4)
O(1)–Pb(1)–O(5)	112.86(11)	N(1)–C(1)–C(2)	117.1(3)	O(6)–N(7)–O(5)	122.0(4)
O(4)–Pb(1)–O(1)	67.96(10)	N(1)–C(6)–C(7)	118.3(2)	C(3)–C(4)–C(5)	116.3(4)
O(4)–Pb(1)–O(3)#1	136.66(12)	N(2)–C(1)–C(2)	118.0(3)	C(8)–C(9)–C(8)#3	116.8(5)

Torsion angles					
Pb(1)–N(1)–C(1)–N(2)	169.08(19)	Pb(1)–O(5)–N(7)–O(6)	–171.6(4)	C(3)–N(4)–C(2)–N(3)	0.6(8)
Pb(1)–N(1)–C(6)–N(1)#3	–170.1(2)	Pb(1)#2–O(3)–N(6)–O(1)	–147.1(3)	C(3)–C(4)–C(5)–N(3)	–1.4(9)
Pb(1)–N(3)–C(2)–N(4)	–166.5(4)	Pb(1)#2–O(3)–N(6)–O(2)	31.5(7)	C(5)–N(3)–C(2)–N(4)	–0.4(7)
Pb(1)–N(5)–C(7)–N(5)#3	–170.4(2)	N(1)–C(1)–C(2)–N(3)	–2.4(5)	C(6)–N(1)–C(1)–N(2)	–1.5(4)
Pb(1)–N(1)–C(1)–C(2)	–10.2(4)	N(1)–C(1)–C(2)–N(4)	177.8(4)	C(8)–N(5)–C(7)–N(5)#3	–0.2(2)
Pb(1)–N(1)–C(6)–C(7)	9.9(2)	N(1)–C(6)–C(7)–N(5)	–12.84(19)	C(1)–N(1)–C(6)–C(7)	–179.3(2)
Pb(1)–N(3)–C(2)–C(1)	13.7(5)	N(1)–C(6)–C(7)–N(5)#3	167.16(19)	C(1)#3–N(2)–C(1)–C(2)	–179.9(3)
Pb(1)–N(3)–C(5)–C(4)	167.3(5)	N(1)#3–C(6)–C(7)–N(5)#3	–12.84(19)	C(2)–N(4)–C(3)–C(4)	–1.1(9)
Pb(1)–N(5)–C(7)–C(6)	9.6(2)	N(2)–C(1)–C(2)–N(3)	178.3(3)	C(2)–N(3)–C(5)–C(4)	0.9(8)
Pb(1)–N(5)–C(8)–C(9)	170.6(2)	N(2)–C(1)–C(2)–N(4)	–1.5(5)	C(3)–N(4)–C(2)–C(1)	–179.6(5)
Pb(1)–O(1)–N(6)–O(2)	–15.1(4)	N(4)–C(3)–C(4)–C(5)	1.6(10)	C(5)–N(3)–C(2)–C(1)	179.8(4)
Pb(1)–O(1)–N(6)–O(3)	163.5(3)	N(5)–C(8)–C(9)–C(8)#3	–0.2(3)	C(6)–N(1)–C(1)–C(2)	179.2(3)
Pb(1)–O(4)–N(7)–O(5)	–5.1(5)	C(1)–N(1)–C(6)–N(1)#3	0.7(2)	C(7)–N(5)–C(8)–C(9)	0.4(5)
Pb(1)–O(4)–N(7)–O(6)	171.4(4)	C(1)#3–N(2)–C(1)–N(1)	0.8(2)	C(8)–N(5)–C(7)–C(6)	179.8(2)
Pb(1)–O(5)–N(7)–O(4)	4.8(5)				