

Electronic supplementary information

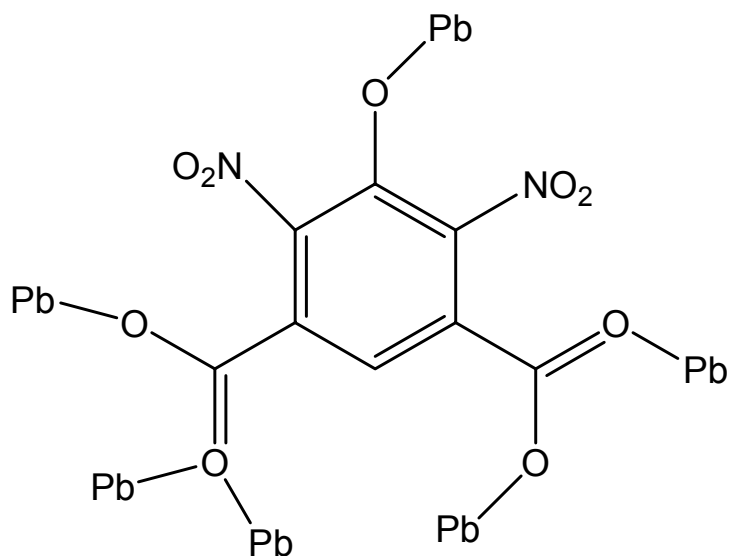


Fig. S1 Coordination mode of L_a in **1**.

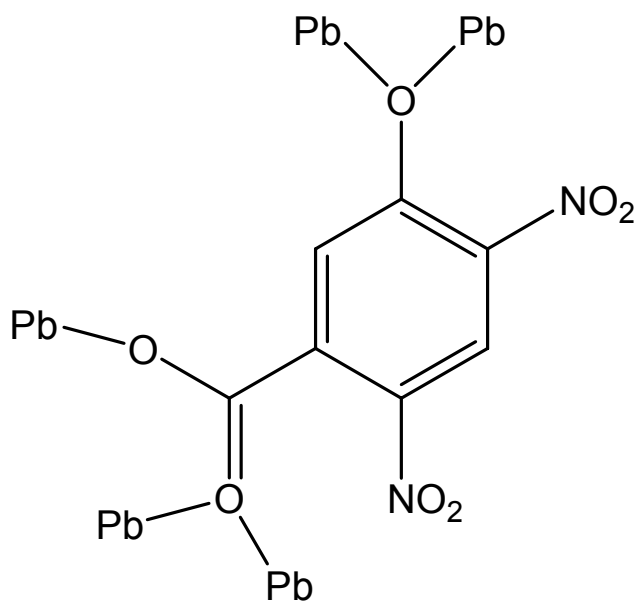


Fig. S2 Coordination mode of L_b in **2**.

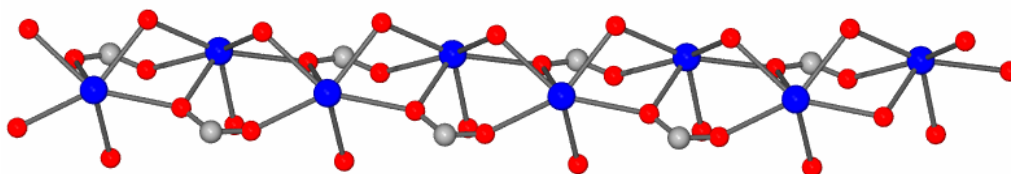


Fig. S3 View of the one-dimensional lead-oxide chain.

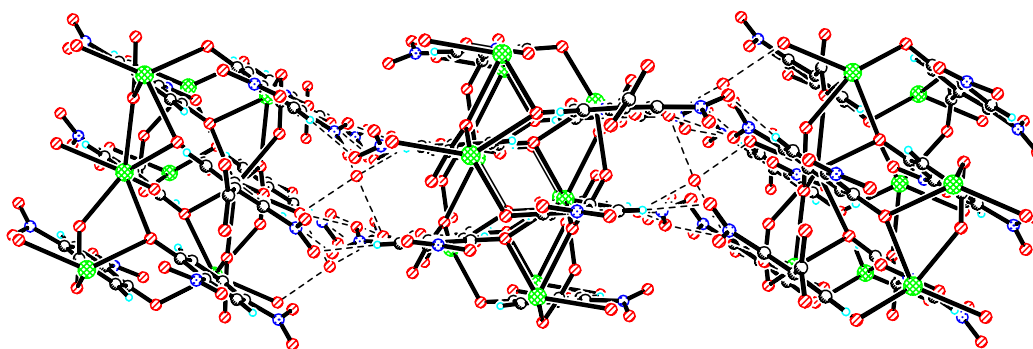


Fig. S4 View of the three-dimensional supramolecular architecture of **2** along *a* axis.

Synthesis and Structure description of $\{[\text{Pb}_{1.5}(\text{L})] \cdot (\text{H}_2\text{O})_{1.5}\}_n$ (**3**):

Using $\text{Pb}(\text{NO}_3)_2$ instead of the mixture of $\text{Pb}(\text{NO}_3)_2$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ under the same conditions, **3**‡§ was generated. X-ray crystallographic study shows that the organic ligand in **3**, different from those observed in **1** and **2**, is not dinitrified owing to the absence of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, but entirely deprotonated (L). There exist two unique Pb^{II} atoms in the asymmetry unit (Fig. S5), the Pb1 is coordinated by four oxygen atoms from two deprotonated hydroxyl groups and two carboxylate groups of different L ligands, in a pseudo trigonal bipyramidal geometry with O4A and O4B axial ($\angle\text{O4A-Pb-O4B} = 142.2(8)^\circ$), O1 and O1A equatorial ($\angle\text{O1-Pb-O1A} = 96.2(8)^\circ$),¹ the average Pb1–O bond distance is 2.45 Å. Whereas the Pb2 center is in a highly distorted pyramidal geometry, three oxygen atoms from one deprotonated hydroxyl group and two carboxylate groups of different L ligands comprise the basal plane, the Pb2 center derivates from the basal plane by 0.5617 Å. In contrast to the high coordination numbers of the large radius Pb^{II} atom, only a few examples containing low three-coordinated Pb^{II} atoms were obtained.² Two Pb2 and one Pb1 atoms share two hydroxyl oxygen atoms and two carboxylate oxygen atoms to generate a trinuclear unit (Fig. S6), in which the neighboring Pb...Pb distance is 4.099 Å, slightly longer than that in **2**. The no dinitrified L ligand acts as a μ_5 -bridge and extends the trinuclear units into a three-dimensional framework with large channels containing free water molecules as spacer fillers (Fig. S7, S8). The intramolecular hydrogen bonds between water molecules and carboxylate groups as well as between water molecules and water molecules further stabilize the framework.

References

‡ Synthesis of **3**: The procedure was similar to the synthesis of **1** and **2** except for using $\text{Pb}(\text{NO}_3)_2$ (0.50 mmol, 165.6 mg) instead of the mixture of $\text{Pb}(\text{NO}_3)_2$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Yellow block crystals of **3** were obtained (yield: 81.0 mg, 47% based on Pb). Elemental analysis (%): calcd. for $\text{C}_8\text{H}_6\text{Pb}_{1.5}\text{O}_{6.5}$ (516.93): C 18.59, H 1.17; found: C 18.57, H 1.21. IR (KBr, cm^{-1}): 3503 (bs), 1565 (s), 1504 (m), 1435 (m), 1383

(m), 1337 (s), 1263 (m), 1140 (w), 815 (m), 715 (s), 565 (s)

§ Crystal data for **3**: $M_r = 516.93$, Monoclinic, Space group $C2/c$, $a = 10.000(9)$ Å, $b = 13.05(1)$ Å, $c = 15.55(1)$ Å, $\beta = 99.85(1)^\circ$, $V = 2000(3)$ Å³, $Z = 8$, $T = 173(2)$ K, $\rho_{\text{calcd}} = 3.433$ g cm⁻³, A total of 5887 reflections were collected, of which 1758 were unique reflections, $R(\text{int}) = 0.0815$, $\mu(\text{MoK}\alpha) = 25.260$ mm⁻¹, parameters = 154, $GOF = 1.048$, $R_I = 0.0481$, $wR_2 = 0.1230$ ($I \geq 2\sigma(I)$) and $R_I = 0.0695$, $wR_2 = 0.2083$ for all data. CCDC: 288166 for **3**.

- 1 P. Klüfers and J. Schuhmacher, *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 1863.
- 2 (a) D. J. Teff, J. C. Huffman and K. G. Caulton, *Inorg. Chem.*, 1995, **34**, 2491; (b) D. J. Teff, J. C. Huffman and K. G. Caulton, *Inorg. Chem.*, 1996, **35**, 2981; (c) K. W. Terry, K. Su, T. D. Tilley and A. L. Rheingold, *Polyhedron*, 1998, **17**, 891.

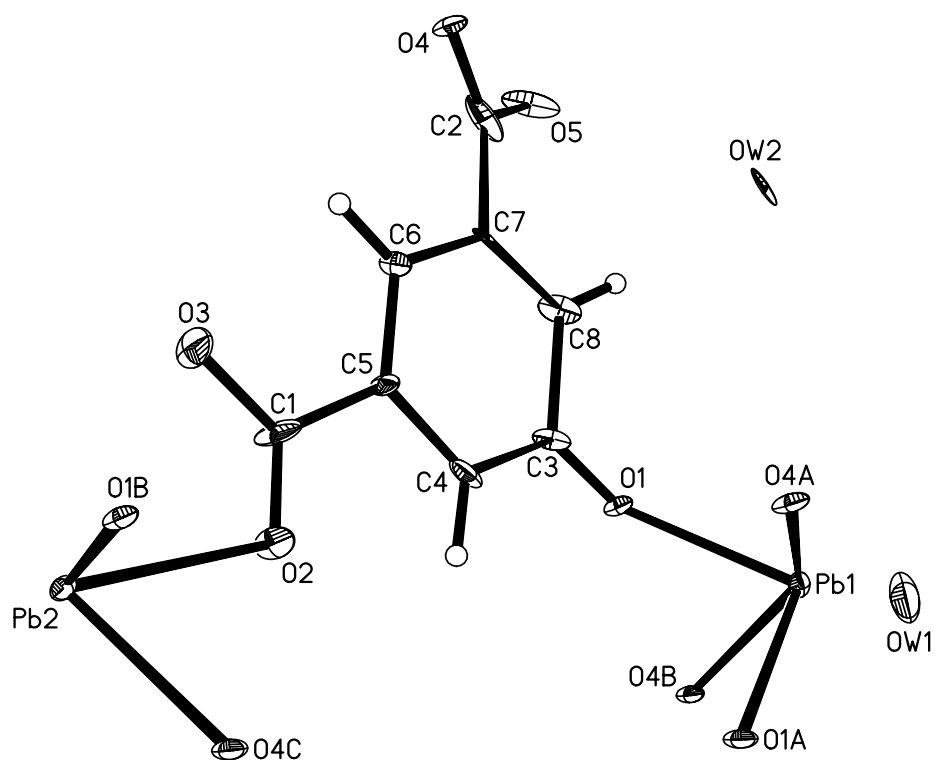


Fig. S5 Perspective view of the coordination geometries of two unique Pb^{II} centers and the entirely deprotonated organic ligand (L) with 30% probability ellipsoids.

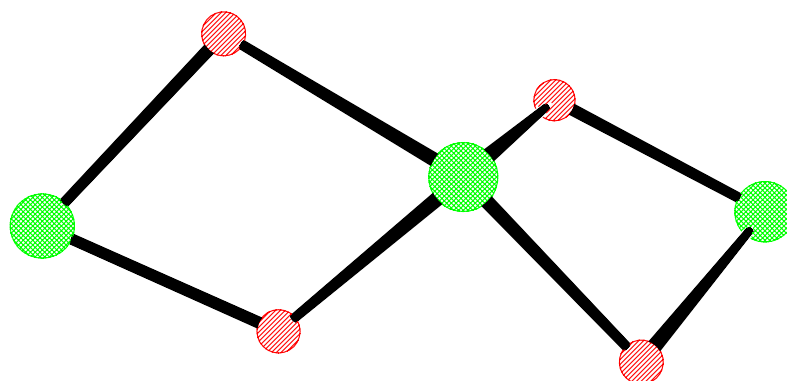


Fig. S6 View of the trinuclear unit.

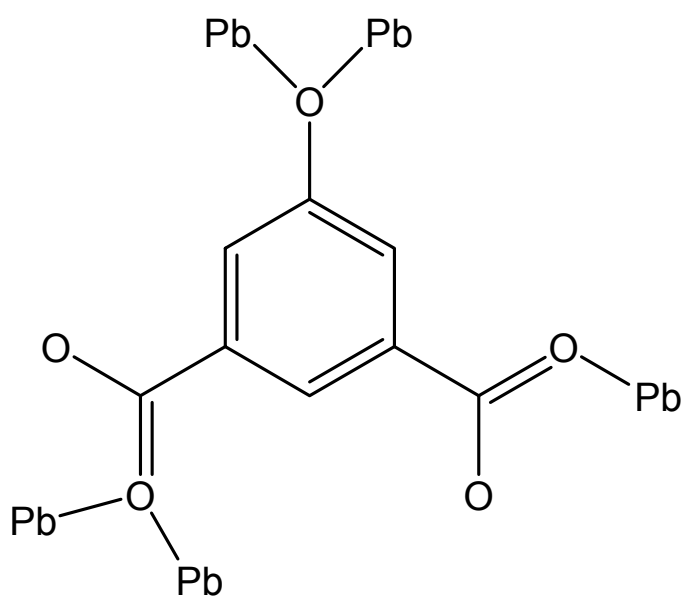


Fig. S7 Coordination mode of L in 3.

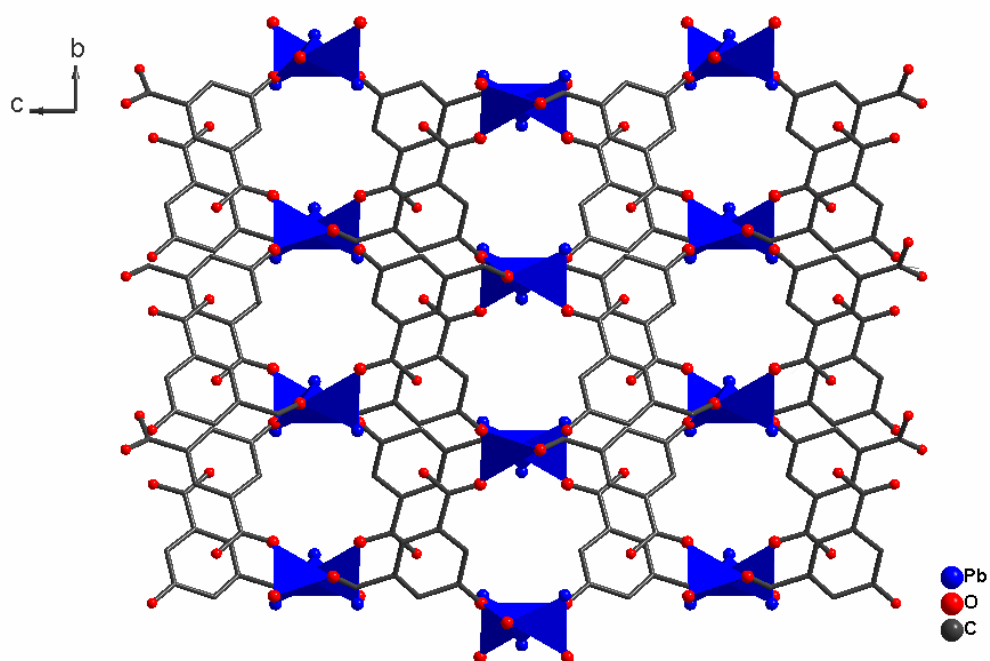
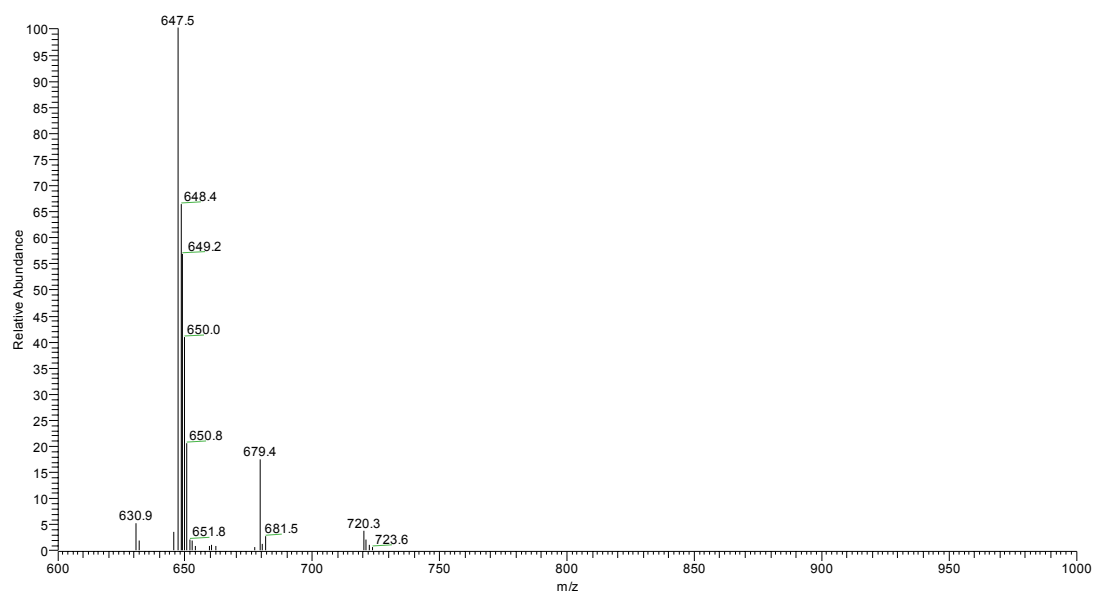
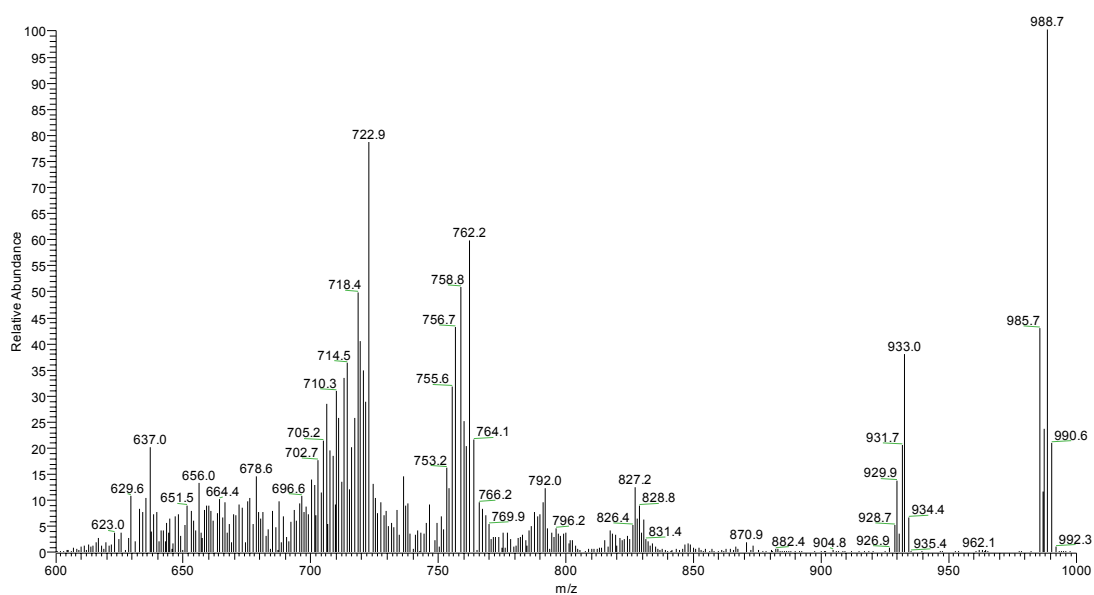


Fig. S8 View of the three-dimensional framework of **3** along *a* axis, the free water molecules were omitted for clarify.



(a)



(b)

Fig. S9 Mass spectrogram of the solution (a) and the cluster structure of **1** (b).