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Supporting Information

$Pb(OF)Cu_3(SeO_3)_2(NO_3)$: A selenite fluoride nitrate with a breathing kagomé lattice

Mengsi Zhang,[a,b] Zhiying Zhao,[a] Wanwan Zhang,[a,b] Jinyang Li,[a] Xiaoying Huang,[a] and Zhangzhen He*,[a]

[a]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China

[b]University of Chinese Academy of Sciences, Beijing 100049, P. R. China

*E-mail: hcz1988@hotmail.com; hezz@fjirsm.ac.cn

Experimental details:

1. Synthesis. A mixture of 1.5 mmol CuC_2O_4 (AR, 0.2274 g), 0.5 mmol PbO (AR, 0.1116 g), 1 mmol SeO_2 (AR, 0.1110 g), 0.2 mL HNO_3, 0.1 mL HF (caution!), and 2 mL H_2O was sealed in an autoclave equipped with a 28 mL Teflon linear and heated at 230 °C for 4 days, followed by slowly cooling to room temperature for 4 days. The products of dark-brown crystals were washed with water, and then dried in air. The purity of powered samples made of crushing crystals was confirmed by powder X-ray diffraction analysis (Fig. S1). The Rietveld refinement for structural parameters was performed by GSAS-EXPGUI software.[1] The Energy dispersive X-ray spectroscopy (EDS) elemental analyses (Fig. S2) gave average molar ratios of 1.0/2.1/2.9 for Pb/Se/Cu, which is consistent with the results of single-crystal XRD structural analysis.

2. X-ray crystallographic studies. The single crystal X-ray diffraction data (XRD) for $Pb(OF)Cu_3(SeO_3)_2(NO_3)$ were collected on Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293 K. The structure was determined by direct methods and refined by full-matrix least-squares fitting on F^2 using Olex2.[2] All non-hydrogen atoms were refined with anisotropic thermal parameters. The determination program of space group was in the ShelXT program, suggesting that the space group should be either R-3m or $R3m$. The refinement in the non-centrosymmetric $R3m$ space group resulted in a much lower R_1 value, which is obviously better than the centrosymmetric handling. The structure was verified by the PLATON program,[3] and there is no missing symmetry operation. The ambiguous flack parameter (0.488) may attribute to the appearance of inversion twin, similar to the kagomé compound $Na_2Ti_3Cl_8$.[4] Pb1, Se1, Se2, and N1 atoms occupy a site of 3a symmetry position. As shown Fig. S3a, $S(1)eO_3^{2-}$ and $S(2)eO_3^{2-}$groups connected severally with O1-centered and F1-centered Cu_3 triangle in the kagomé layer, and the two kinds of Cu_3 triangles between the kagomé layer are linked by Pb^{2+} ion. Furthermore, the π-conjugated planar NO_3 triangles in the kagomé layer are aligned in a parallel fashion. This arrangements of stereoactive lone pairs of Pb^{2+} ion and SeO_3^{2-} groups as well as the π-conjugated planar NO_3 triangles may break the inversion symmetry and produce a polarization, leading to a non-centrosymmetric *R*3*m* space group. Crystallographic data and structural refinements of this compound are summarized in Table S1, and the detailed atomic positions, bond lengths and angles are listed in Tables S2-4. The results of bond valence sum (BVS) calculation of Pb1, Se1, Se2, Cu1, and N1 atoms are 2.13, 4.04, 4.16, 2.04, and 5.19, respectively, indicating that the valence states of Pb1, Se1, Se2, Cu1, and N1 atoms are +2, +4, +4, +2 and +5, respectively.

3. Magnetic Measurements. Powdered samples of $Pb(OF)Cu_3(SeO_3)_2(NO_3)$ were placed in gel capsule sample holder which were suspended in a plastic drinking straw.

measured between 2 and 300 K with various magnetic fields. Temperature dependence of magnetic susceptibility was measured at different fields using a commercial Magnetic Property Measurement System (MPMS). The isothermal magnetization was measured at different temperatures and specific heat was measured at zero field by a relaxation method using Quantum Design Physical Property Measurement System (PPMS).

4. Infrared (IR) spectra. IR spectrum analysis was performed on the Magna 750 FT-IR spectrometer with KBr pellets from 400 to 4000 cm^{-1}. The IR (Fig. S6) absorption peak at around 1375 cm^{-1} can be assigned to the characteristic peaks of NO_3^- groups,[5] and the strong absorptions at 720–420 cm^{-1} confirmed the existence of SeO_3^{2-} groups,[6] which is in agreement with the results obtained from the single crystal XRD analysis.

5. Thermal Analysis. Thermogravimetric analysis (TGA) was performed on the NETZSCH STA 449F3 instrument. The samples were placed in an alumina crucible, which was heated under a N_2 flow at a heating rate of 15 °C/min from room temperature to 1000 °C. The TGA curve (Fig. S7) indicates that this compound can be stable up to 400 °C. The first step starts from 400 to 465 °C, which is attributed to the release of 0.5 F_2. The observed weight loss of 2.7% is in good agreement with the theoretical value of 2.5%. Upon further heating, the second step occurs from 465 to 650 °C, corresponding to the loss of 2 SeO_2 molecules with the weight loss of 28.2%, compared to the calculated one, 29.4%. The third step in the temperature range of 650 to 840 °C, corresponds to the loss of nitrate. The observed weight loss of 6.4% is in keeping with the calculated value of 6.1%. It is noted that the final residuals of thermal analysis are not further characterized because the residuals were melted with the TGA bucket made of alumina under such high temperature.

References:

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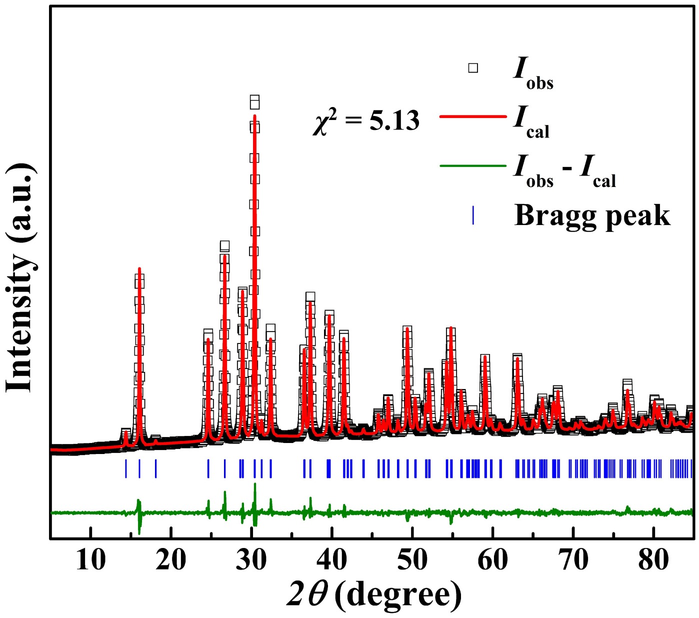

Fig. S1 Refinement of powder X-ray (Cu Kα) diffraction patterns for $Pb(OF)Cu_3(SeO_3)_2(NO_3)$.

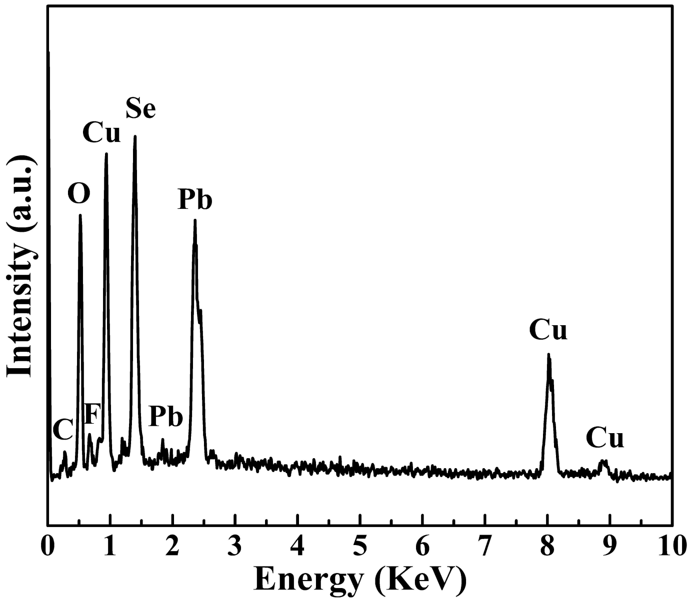

Fig. S2 The energy-dispersive spectrometry (EDS) elemental analyses of $Pb(OF)Cu_3(SeO_3)_2(NO_3)$.

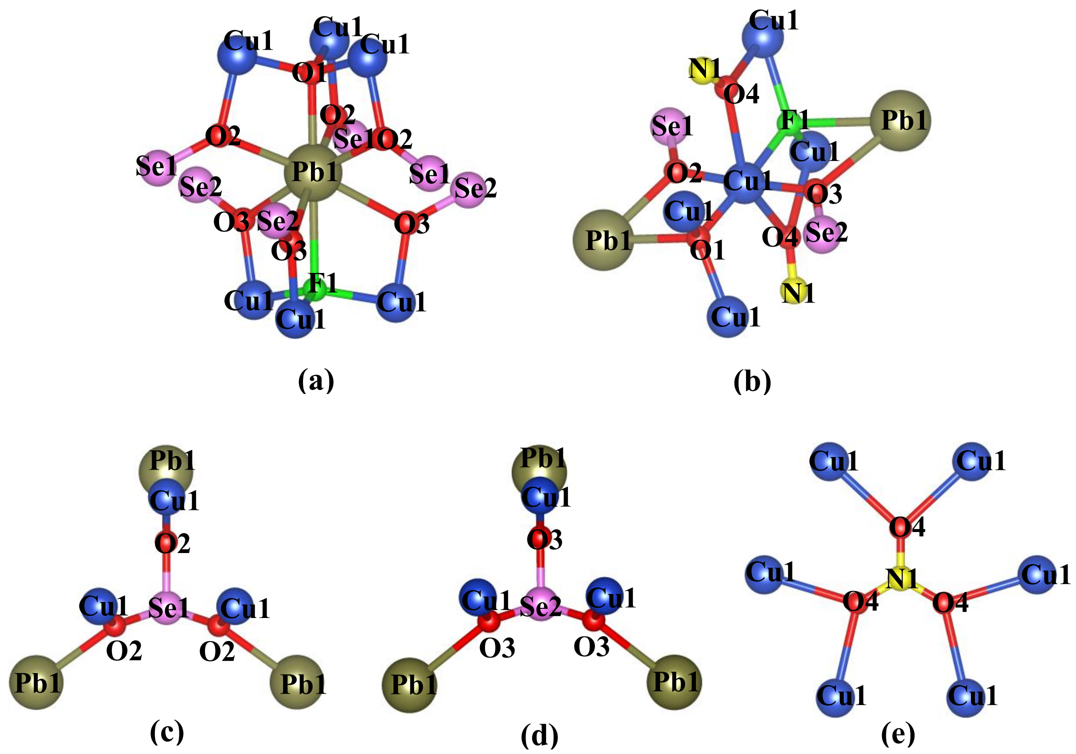

Fig. S3 Views of the coordination geometry for (a) Pb1, (b) Cu1, (c) Se1, (d) Se2, and (e) N1 atoms.

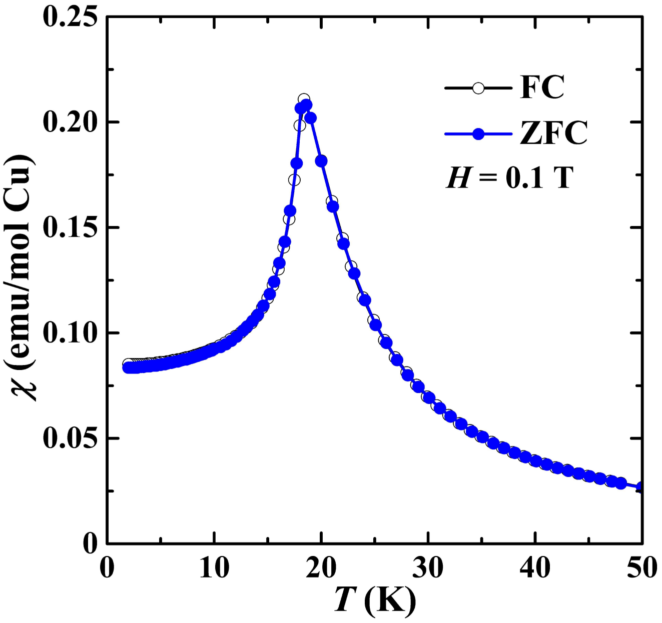

Fig. S4 ZFC and FC susceptibilities at 0.1 T.

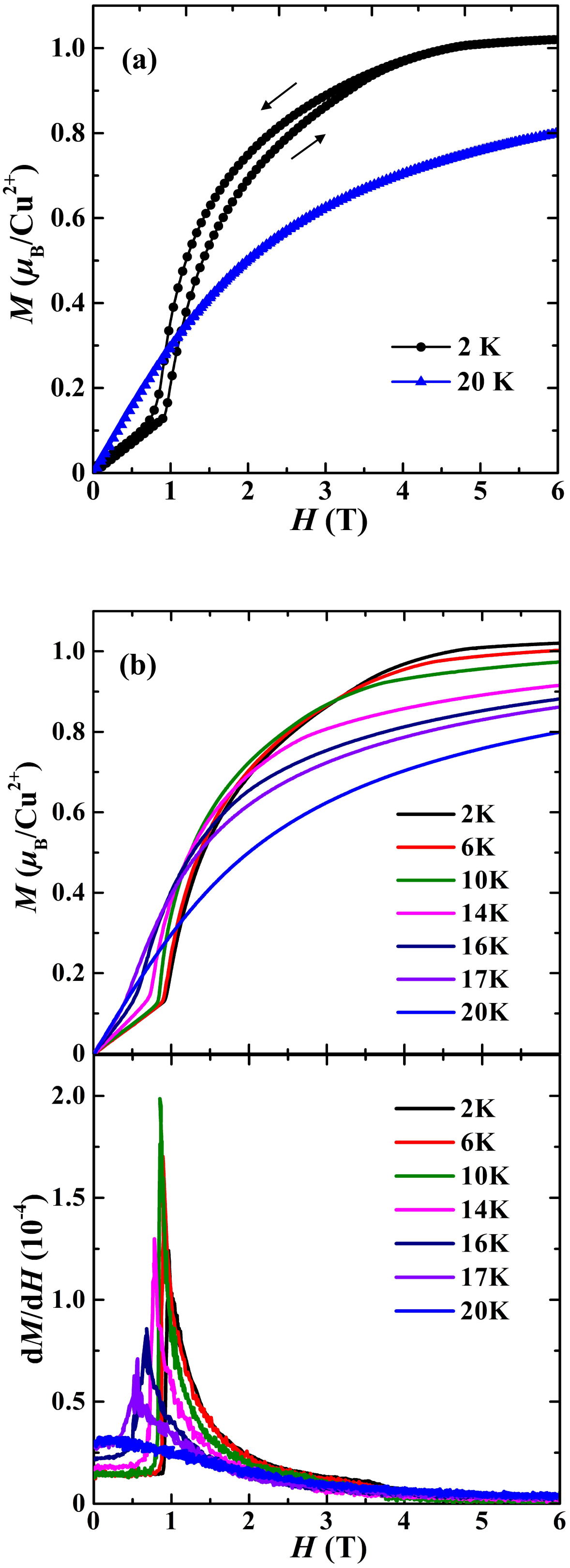

Fig. S5 (a) The hysteresis of $Pb(OF)Cu_3(SeO_3)_2(NO_3)$ at 2 and 20 K. (b) The magnetization curves (0–6 T) measured from 2 to 20 K.

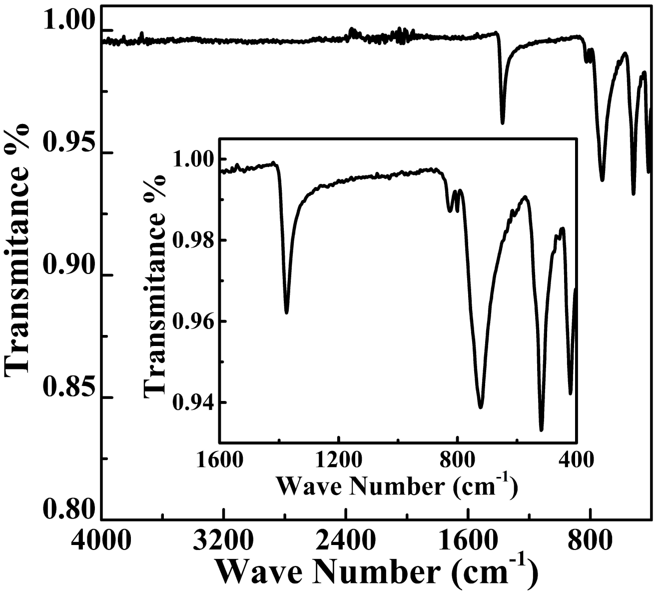

Fig. S6 IR spectra of Pb(OF)$Cu_3(SeO_3)_2(NO_3)$.

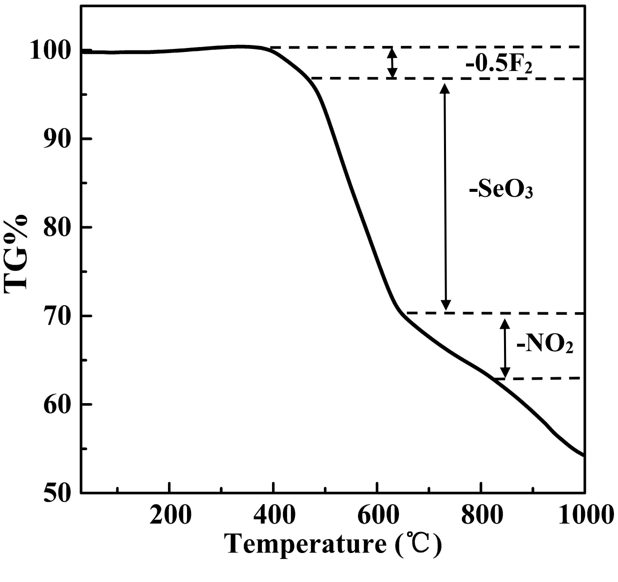

Fig. S7 The TGA curve for Pb(OF)$Cu_3(SeO_3)_2(NO_3)$.

Table S1 Crystal data and structure refinements for $Pb(OF)Cu_3(SeO_3)_2(NO_3)$.

Compound	$Pb(OF)Cu_3(SeO_3)_2(NO_3)$
formula weight	748.74
T, K	room temperature
λ, Å	0.71073
space group	$R3m$
a, Å	6.6973(1)
c, Å	18.5548(3)
V, Å^3	720.75(2)
Z	3
D_{calcd}, g cm^{-3}	5.175
μ, mm^{-1}	31.657
GOF on F^2	1.103
Flack factor	0.488(9)
R_1, wR_2 $[I > 2\sigma(I)]$[a]	0.0146, 0.0355
R_1, wR_2 (all data)	0.0146, 0.0355

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, and $wR_2 = \{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$.

Table S2 Atomic coordinates ($\times10^4$) and equivalent isotropic displacement parameters (Å$^2\times10^3$) for $Pb(OF)Cu_3(SeO_3)_2(NO_3)$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Pb(1)	6667	3333	3501(1)	12(1)
Se(1)	3333	6667	3669(1)	11(1)
Se(2)	6667	3333	6497(1)	11(1)
Cu(1)	5071(1)	4929(1)	5082(1)	12(1)
F(1)	3333	6667	5313(5)	13(1)
O(1)	6667	3333	4800(5)	9(2)
O(2)	4665(5)	5335(5)	4052(3)	18(1)
O(3)	5348(5)	4652(5)	6112(3)	22(1)
O(4)	1059(5)	2118(11)	5130(4)	37(2)
N(1)	0	0	5120(8)	14(2)

Table S3 Anisotropic displacement parameters (Å^2×10^3) for $Pb(OF)Cu_3(SeO_3)_2(NO_3)$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb(1)	12(1)	12(1)	11(1)	0	0	6(1)
Se(1)	12(1)	12(1)	8(1)	0	0	6(1)
Se(2)	13(1)	13(1)	8(1)	0	0	6(1)
Cu(1)	15(1)	15(1)	11(1)	-1(1)	1(1)	11(1)
F(1)	12(2)	12(2)	16(4)	0	0	6(1)
O(1)	8(2)	8(2)	12(4)	0	0	4(1)
O(2)	28(2)	28(2)	9(2)	0(1)	0(1)	22(3)
O(3)	37(3)	37(3)	12(2)	-1(1)	1(1)	33(3)
O(4)	17(2)	8(2)	83(5)	3(3)	2(1)	4(1)
N(1)	12(2)	12(2)	16(5)	0	0	6(1)

Table S4 Bond lengths [Å] and angles [deg] for $Pb(OF)Cu_3(SeO_3)_2(NO_3)$.

Pb(1)-F(1)#1	2.823(8)	O(2)#3-Pb(1)-O(3)#4	78.67(10)
Pb(1)-O(1)	2.409(9)	O(2)-Pb(1)-O(3)#1	173.89(17)
Pb(1)-O(2)#2	2.537(6)	O(2)#2-Pb(1)-O(3)#4	173.89(17)
Pb(1)-O(2)#3	2.537(6)	O(2)#2-Pb(1)-O(3)#5	78.67(10)
Pb(1)-O(2)	2.537(6)	O(2)#3-Pb(1)-O(3)#5	173.89(17)
Pb(1)-O(3)#4	2.694(6)	O(2)-Pb(1)-O(3)#4	78.67(10)
Pb(1)-O(3)#5	2.694(6)	O(2)-Pb(1)-O(3)#5	78.67(10)
Pb(1)-O(3)#1	2.694(6)	O(3)#1-Pb(1)-F(1)#1	60.15(11)
Se(1)-O(2)#6	1.700(6)	O(3)#5-Pb(1)-F(1)#1	60.15(11)
Se(1)-O(2)#7	1.700(6)	O(3)#4-Pb(1)-F(1)#1	60.15(11)
Se(1)-O(2)	1.700(6)	O(3)#1-Pb(1)-O(3)#4	97.37(15)
Se(2)-O(3)#2	1.689(6)	O(3)#1-Pb(1)-O(3)#5	97.37(15)
Se(2)-O(3)	1.689(6)	O(3)#4-Pb(1)-O(3)#5	97.37(15)

Se(2)-O(3)#3	1.689(6)	O(2)#7-Se(1)-O(2)	103.8(2)
Cu(1)-F(1)	2.061(2)	O(2)#6-Se(1)-O(2)#7	103.8(2)
Cu(1)-O(1)	1.924(3)	O(2)#6-Se(1)-O(2)	103.8(2)
Cu(1)-O(2)	1.970(6)	O(3)#3-Se(2)-O(3)#2	103.4(2)
Cu(1)-O(3)	1.937(5)	O(3)#3-Se(2)-O(3)	103.4(2)
Cu(1)-O(4)	2.391(4)	O(3)#2-Se(2)-O(3)	103.4(2)
Cu(1)-O(4)#6	2.391(4)	F(1)-Cu(1)-O(4)#6	72.97(12)
N(1)-O(4)	1.228(6)	F(1)-Cu(1)-O(4)	72.97(12)
N(1)-O(4)#8	1.228(6)	O(1)-Cu(1)-F(1)	176.1(3)
N(1)-O(4)#9	1.228(6)	O(1)-Cu(1)-O(2)	88.0(3)
O(1)-Pb(1)-F(1)#1	180.0	O(1)-Cu(1)-O(3)	96.3(3)
O(1)-Pb(1)-O(2)#2	66.25(12)	O(1)-Cu(1)-O(4)#6	106.89(12)
O(1)-Pb(1)-O(2)#3	66.25(12)	O(1)-Cu(1)-O(4)	106.89(12)
O(1)-Pb(1)-O(2)	66.25(12)	O(2)-Cu(1)-F(1)	88.1(3)
O(1)-Pb(1)-O(3)#5	119.85(11)	O(2)-Cu(1)-O(4)#6	88.1(2)
O(1)-Pb(1)-O(3)#1	119.85(11)	O(2)-Cu(1)-O(4)	88.1(2)
O(1)-Pb(1)-O(3)#4	119.85(11)	O(3)-Cu(1)-F(1)	87.6(3)
O(2)-Pb(1)-F(1)#1	113.75(12)	O(3)-Cu(1)-O(2)	175.7(3)
O(2)#2-Pb(1)-F(1)#1	113.75(12)	O(3)-Cu(1)-O(4)	90.7(2)
O(2)#3-Pb(1)-F(1)#1	113.75(12)	O(3)-Cu(1)-O(4)#6	90.7(2)
O(2)#3-Pb(1)-O(2)	104.88(14)	O(4)-Cu(1)-O(4)#6	145.8(2)
O(2)#2-Pb(1)-O(2)	104.88(14)	O(4)#9-N(1)-O(4)#8	119.98(5)
O(2)#2-Pb(1)-O(2)#3	104.88(14)	O(4)-N(1)-O(4)#8	119.98(5)
O(2)#3-Pb(1)-O(3)#1	78.67(10)	O(4)#9-N(1)-O(4)	119.98(5)
O(2)#2-Pb(1)-O(3)#1	78.67(10)		

Symmetry transformations used to generate equivalent atoms: #1 x+1/3,y-1/3,z-1/3; #2 -x+y+1,-x+1,z; #3 -y+1,x-y,z; #4 -x+y+1/3,-x+2/3,z-1/3; #5 -y+4/3,x-y+2/3,z-1/3; #6 -y+1,x-y+1,z; #7 -x+y,-x+1,z; #8 -x+y,-x,z; #9 -y,x-y,z.