Electronic Supplementary Information for Dalton Transactions

Supporting Information

Fluorinated Tetraolate: Prospective Ligand for the Synthesis of Polymetallic Complexes

*Haitao Zhang, Jen-Hsien Yang, and Evgeny V. Dikarev**

Department of Chemistry, University at Albany, SUNY, Albany, NY 12222

* To whom correspondence should be addressed. E-mail: dikarev@albany.edu. Phone: (518)442-4401. Fax: (518)442-3462

General Procedures. All of the manipulations were carried out in a dry, oxygen-free, dinitrogen atmosphere by employing standard Schlenk line and glove box techniques. Triphenylbismuth and hexafluoroacetylacetone (Hhfac) were purchased from Aldrich and used as received. UV-vis spectra were acquired using a Hewlett-Packard 8452A diode array spectrophotometer. The attenuated total reflection (ATR) and solution IR spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer. NMR spectra were obtained using a Bruker Avance 400 spectrometer at 400 MHz for ^{1}H and at 376.47 MHz for ^{19}F. Chemical shifts (δ) are given in ppm relative to residual solvent peak for ^{1}H and to $CFCl_3$ for ^{19}F. Elemental analysis was performed by Chemisar Laboratories Inc., Ontario, Canada. Thermogravimetric measurements were carried out under nitrogen at a heating rate of 5 °C/min using a TGA 2050 thermogravimetric analyzer, TA Instruments, Inc. The thermal decomposition/annealing of $Bi_4(hfpt)_2(hfac)_4(THF)_5$ (**4**) was studied in air at ambient pressure. The solid samples were placed into a 20 mL Coors high-alumina crucible (Aldrich) and heated at a rate of *ca.* 20 °C/min in a 120 V muffle furnace (Thermolyne). The decomposition residues were cooled by turning off the furnace power.

H_4hfpt (1):[S1] A solution of Hhfac (1.0 mL, 7mmol) in toluene (20 mL) was treated with deionized H_2O (0.51 g, 28 mmol). The reaction solution was kept at room temperature for 3 days. White crystals of H_4hfpt were collected by filtration, washed with toluene for three times, and dried under vacuum. The yield was *ca.* 90%.

$Bi_9O_7(hfac)_{13}$ (**2**):[S2] A mixture of triphenylbismuth (2.0 g, 4.5 mmol), hexafluoroacetylacetone (Hhfac) (0.74 mL, 5.3 mmol) and hexafluoropentane-2,2,4,4-tetraol (H_4hfpt) (0.47 g, 1.9 mmol) was heated at 70 °C for one hour. Anhydrous CH_2Cl_2

(20 mL) was added to the reaction mixture to yield a light-yellow powder. The solid was filtered off, washed with CH_2Cl_2 three times, and dried under vacuum. The yield was *ca.* 90%.

$Bi_4(hfpt)_2(hfac)_4(THF)_5$ (4): *Method 1*: $Bi_9O_7(hfac)_{13}$ (**2**) (0.2 g, 0.04 mmol) was dissolved in 2 mL of “wet” THF (V_{THF}:V_{H2O} = 50:1) and layered with hexanes. The resulting solution was kept at 0 °C, and the pale-yellow crystals of **4** accumulated on the walls of the tube in a course of several weeks. The yield was *ca.* 30% (based on the initial amount of bismuth).

Method 2: A mixture of $Bi_9O_7(hfac)_{13}$ (**2**) (0.2 g, 0.04 mmol) and H_4hfpt (**1**) (0.040 g, 0.16 mmol) was dissolved in 2 mL of anhydrous THF and layered with hexanes. The resulting solution was kept at 0° C, and the pale-yellow crystals of **4** accumulated on the walls of the tube in 3 days. The yield was *ca.* 90% (based on Bi). Elemental analysis (%) calcd for $C_{50}H_{48}F_{36}O_{21}Bi_4$: C 23.96, H 1.92, O 13.42, F 27.32; found: C 23.45, H 1.80, O 13.02, F 28.03; ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ = 1.84 (br, C*H*$_2$, THF), 2.43 (s, C*H*$_2$, hfpt), 3.73 (br, C*H*$_2$, THF), 6.18 (br, C*H*, hfac); ^{19}F NMR (376.47 MHz, $CDCl_3$, 22 °C): δ = -76.77 (s, C*F*$_3$, hfac), -88.15 (s, C*F*$_3$, hfpt); ATR-IR (cm^{-1}): 3135w, 2984w, 2896w, 1647s, 1597w, 1551m, 527m, 1460m, 1432w, 1370w, 1341w, 1323w, 1268m, 1254s, 1195s, 1181m, 1140s, 1111m, 1081s, 1032m, 1016m, 975m; UV/Vis (CH_2Cl_2, 22 °C): λ_{max} (ε, $M^{-1}\cdot cm^{-1}$) = 318(10977), 292(10846), 276(5230) nm.

References:

S1) a) E. Bouwman, J. C. Huffman, E. B. Lobkovsky, G. Christou *Inorg. Chem.*, 1992, **31**, 4436; b) E. Bouwman, K. G. Caulton, G. Christou, K. Folting, C. Gasser, D. N.

Hendrickson, J. C. Huffman, E. B. Lobkovsky, J. D. Martin, P. Michel, H. L. Tsai, Z. Xue *Inorg. Chem.*, 1993, **32**, 3463.

S2) E. V. Dikarev, H. Zhang, B. Li *Angew. Chem. Int. Ed.*, 2006, **45**, 5448.

Thermogravimetric Data

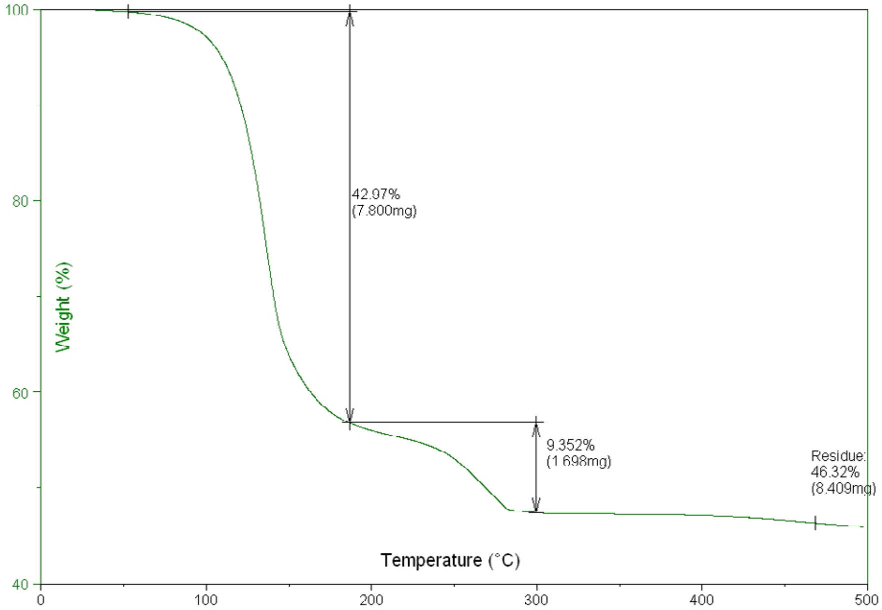

Figure S1. TGA diagram of $Bi_4(hfpt)_2(hfac)_4(THF)_5$ (**4**) recorded under nitrogen.

IR Spectra

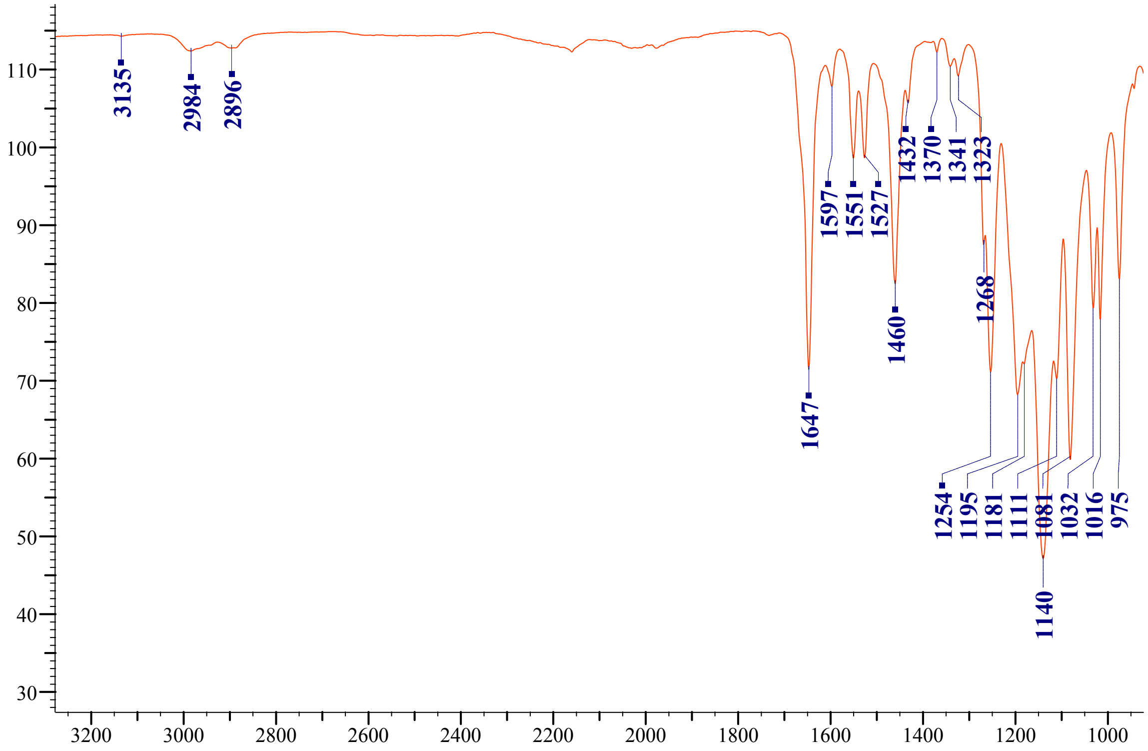

Figure S2. The attenuated total reflection (ATR) spectrum of $Bi_4(hfpt)_2(hfac)_4(THF)_5$ (**4**).

NMR Spectra

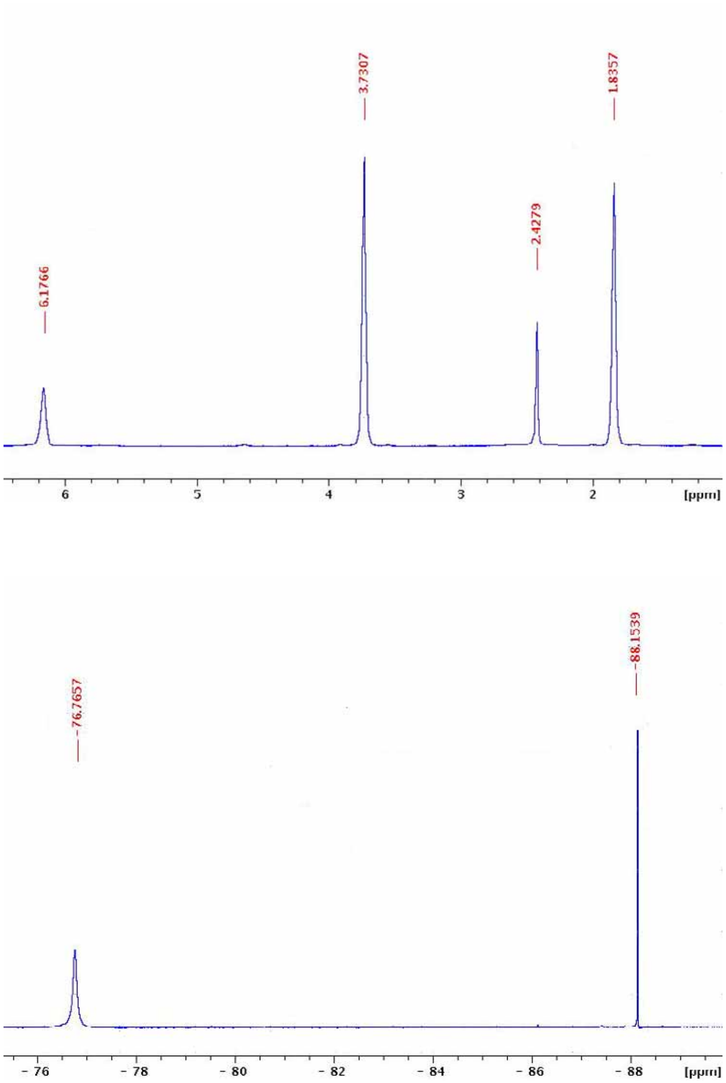

Figure S3. ^{1}H (top) and ^{19}F (bottom) NMR spectra of $Bi_4(hfpt)_2(hfac)_4(THF)_5$ (**4**) at 22 °C in $CDCl_3$.

Crystallographic Section

X-ray powder diffraction data were collected on a Bruker D8 Advance diffractometer (Cu K_α radiation, focusing Göbel Mirror, LynxEye one-dimensional detector, step of 0.02^o 2θ, 20 ^oC). The crystalline samples under investigation were grounded and placed in the dome-like airtight zero-background holders inside a glove box.

Selected single crystal of **4** suitable for X-ray crystallographic analysis was used for structural determination. The X-ray intensity data were measured at 173(2) K (Bruker KRYOFLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (λ = 0.71073 Å) operated at 1800 W power. The crystal was mounted on a goniometer head with silicone grease. The detector was placed at a distance of 6.140 cm from the crystal. A total of 1850 frames were collected with a scan width of 0.3° in ω and an exposure time of 20 s/frame. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm to a maximum 2θ angle of 56.54° (0.75 Å resolution). The final cell constants are based upon the refinement of the *XYZ*-centroids of several thousand reflections above 20 $\sigma(I)$. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the empirical method (SADABS).

The structure was solved and refined by full-matrix least squares procedures on F^2 using the Bruker SHELXTL (version 6.12) software package. The coordinates of bismuth atoms were found in direct method *E* maps. The remaining atoms were located after an alternative series of least-squares cycles and difference Fourier maps. The hydrogen atoms were included in idealized positions for structure factor calculations. One hexafluoroacetylacetonate ligand was found to exhibit a two-fold disorder. The fluorine atoms of some CF_3 groups and the carbon atoms of THF molecules appeared to be disordered. This disorder was modeled in each individual case. Anisotropic displacement parameters were assigned to all non-hydrogen atoms, except the disordered fluorine, carbon and oxygen atoms.

Powder X-Ray Diffraction Study of Decomposition of $Bi_4(hfpt)_2(hfac)_4(THF)_5$.

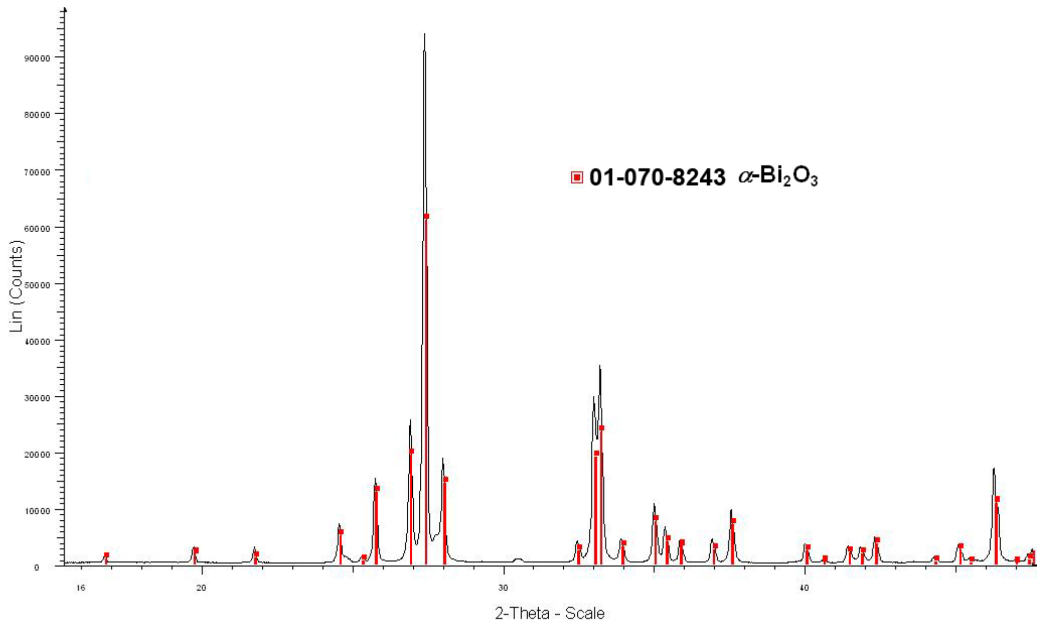

Figure S4. Powder X-ray diffraction pattern of decomposition residues of $Bi_4(hfpt)_2(hfac)_4(THF)_5$ (**4**) annealed at 600 °C for 72 hours.

Single-Crystal X-ray Diffraction Study of $Bi_4(hfpt)_2(hfac)_4(THF)_5$.

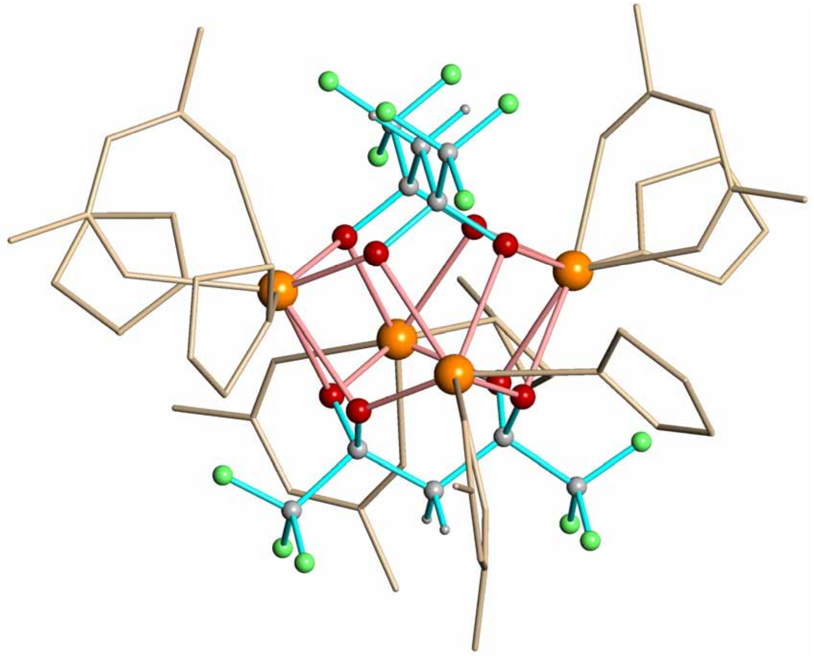

Figure S5a. Molecular structure of $Bi_4(hfpt)_2(hfac)_4(THF)_5$ (**4**). Fluorine and hydrogen atoms of THF and hexafluoroacetylacetonate ligands are omitted for clarity. The hfpt ligands and their coordination to Bi atoms are highlighted with different colors. Only one orientation of disordered groups is shown.

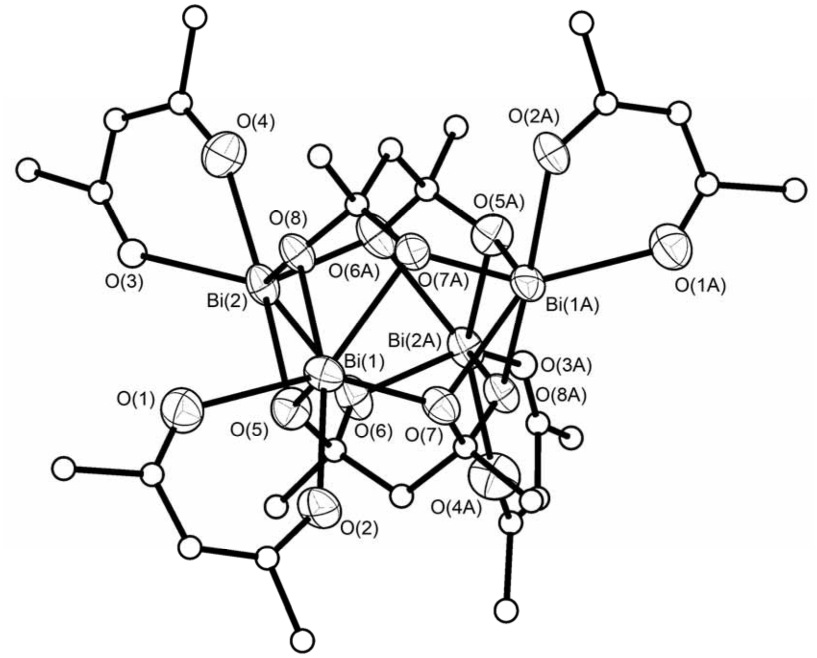

Figure S5b. Perspective drawing of $Bi_4(hfpt)_2(hfac)_4(THF)_5$ (**4**). Carbon and disordered oxygen atoms are shown as spheres of arbitrary radii. Metal and oxygen atoms are represented by thermal ellipsoids at the 40% probability level. THF molecules, fluorine and hydrogen atoms are omitted for clarity. Only metal and oxygen atoms are labeled.

Table S1. Crystallographic Data and Structure Refinement Parameters for $Bi_4(hfpt)_2(hfac)_4(THF)_5$ (**4**).

formula	$Bi_4O_{21}C_{50}H_{48}F_{36}$
fw	2504.80
crystal system	monoclinic
space group	*C2/c*
a (Å)	16.824(3)
b (Å)	31.843(6)
c (Å)	16.016(3)
α (deg)	90.00
β (deg)	120.491(3)
γ (deg)	90.00
V (Å^3)	7394(2)
Z	4
ρ_{calcd} (g·cm^{-3})	2.250
μ (mm^{-1})	9.648
transm factors	0.2755–0.4167
temp (K)	173(2)
data/restr/params	8673/79/478
$R1$,[a] $wR2$[b]	
$I > 2\sigma(I)$	0.0490, 0.1163
all data	0.0691, 0.1284
quality-of-fit[c]	1.023

[a] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

[c] Quality-of-fit = $[\Sigma[w(F_o^2-F_c^2)^2]/(N_{\mathrm{obs}}-N_{\mathrm{params}})]^{1/2}$, based on all data.

Table S2. Selected Bond Distances [Å] and Angles [°] for $Bi_4(hfpt)_2(hfac)_4(THF)_5$ (**4**). Atom labeling corresponds to Figure S5b.

Distances		Angles		Angles	
Bi(1)–O(1)	2.621(7)	O(1)–Bi(1)–O(2)	71.0(2)	O(3)–Bi(2)–O(4)	65.9(4)
Bi(1)–O(2)	2.352(6)	O(1)–Bi(1)–O(5)	86.9(2)	O(3)–Bi(2)–O(5)	127.7(3)
Bi(1)–O(5)	2.158(6)	O(1)–Bi(1)–O(7)	151.3(2)	O(3)–Bi(2)–O(6)	121.1(4)
Bi(1)–O(7)	2.158(6)	O(1)–Bi(1)–O(7A)	139.8(2)	O(3)–Bi(2)–O(6A)	121.3(4)
Bi(1)–O(7A)	2.606(6)	O(1)–Bi(1)–O(8)	100.3(2)	O(3)–Bi(2)–O(8)	134.2(4)
Bi(1)–O(8)	2.535(6)	O(2)–Bi(1)–O(5)	84.7(2)	O(4)–Bi(2)–O(5)	146.6(2)
Bi(2)–O(3)	2.767(16)	O(2)–Bi(1)–O(7)	80.8(2)	O(4)–Bi(2)–O(6)	154.8(2)
Bi(2)–O(4)	2.341(7)	O(2)–Bi(1)–O(7A)	146.4(2)	O(4)–Bi(2)–O(6A)	83.4(3)
Bi(2)–O(5)	2.604(6)	O(2)–Bi(1)–O(8)	154.7(2)	O(4)–Bi(2)–O(8)	80.7(2)
Bi(2)–O(6)	2.548(7)	O(5)–Bi(1)–O(7)	85.5(2)	O(5)–Bi(2)–O(6)	51.60(19)
Bi(2)–O(6A)	2.181(6)	O(5)–Bi(1)–O(7A)	106.0(2)	O(5)–Bi(2)–O(6A)	105.7(2)
Bi(2)–O(8)	2.180(5)	O(5)–Bi(1)–O(8)	70.8(2)	O(5)–Bi(2)–O(8)	69.1(2)
Bi(1)···Bi(1A)	3.9393(10)	O(7)–Bi(1)–O(7A)	68.8(2)	O(6)–Bi(2)–O(6A)	72.4(3)
Bi(1)···Bi(2)	3.8892(8)	O(7)–Bi(1)–O(8)	103.2(2)	O(6)–Bi(2)–O(8)	102.6(2)
Bi(2)···Bi(2A)	3.8206(9)	O(7A)–Bi(1)–O(8)	52.22(16)	O(6A)–Bi(2)–O(8)	82.5(2)