**Electronic Supplementary Information**

# Synthesis and structural studies of the simplest bismuth(III) oxo-salicylate complex: $[Bi_4(\mu_3\text{-}O)_2(HO\text{-}2\text{-}C_6H_4CO_2)_8]\cdot 2$ Solv (Solv = MeCN or $MeNO_2$)

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## Experimental Details

**General:** All reagents and chemicals, unless otherwise stated, were purchased from commercial sources. The acetonitrile (J. T. Baker) and nitromethane (Fisher Scientific) were used as received. NMR spectra were recorded at room temperature in $d_6$-DMSO on Bruker Avance 400 spectrometers, and the $^{1}H$ and $^{13}C$ chemical shifts were reported to tetramethylsilane (TMS). Melting points were obtained in sealed capillaries on an Electrothermal melting point instrument. Elemental analyses (C, H, N) were performed at Galbraith Laboratories.

**Synthesis:**

**Synthesis of 1·2MeCN**

$BiPh_3$ (0.11 g, 0.25 mmol) and $H_2$sal (0.10 g, 0.75 mmol) were combined and sonicated in 1.4 mL of acetonitrile at room temperature. These manipulations were done in air. The yellow solution was left for three days while crystals grew. The mother liquor was decanted and the pale orange-brown crystals were rinsed three times with 0.5 mL toluene. The crystals were then dried in *vacuo*. The crystals were identified as $[Bi_4O_2(Hsal)_8]$·2MeCN, **1**·2MeCN. Yield: 0.11 g, 86%. M.p: dec. > 300 °C. $^{1}$H-NMR (400 MHz, $d_6$-DMSO) $\delta$ (ppm) = 11.9 (s, 1H, PhO*H*), 7.65 (s, 1H, *o*-H), 7.32 (s, 1H, *p*-H), 6.80 (s, 2H, *m*-H), 2.07 (s, 1H, C$H_3$). $^{13}$C-NMR (100 MHz, $d_6$-DMSO): $\delta$ (ppm) = 173.2 (*C*=O), 159.5 (*C*-OH), 133.0 (Ar-*C*), 129.6 (Ar-*C*), 127.3 (Ar-*C*), 117.0 (Ar-*C*), 0.15 (*C*$H_3$CN). Anal. Found for **1**·2MeCN: C 35.24; H 1.83; N 1.36; Calculated (%): C 35.21; H 2.27; N 1.37.

**Synthesis of 1·2MeNO$_2$**

$BiPh_3$ (0.11 g, 0.25 mmol) and $H_2$sal (0.35 g, 2.5 mmol) were combined and sonicated in 19.0 mL of nitromethane at room temperature. All manipulations were done in air. The colorless solution was left for three days while crystals formed, then the solution was decanted. The white crystals were rinsed three times with 0.5 mL toluene before drying under vacuum. The crystals were identified as $[Bi_4O_2(Hsal)_8]$·2MeNO$_2$, **1**·2MeNO$_2$**.** Yield: 0.11 g, 83%. Melting point: decomposes > 300 °C. $^{1}$H-NMR (400 MHz, d$^6$-DMSOC): $\delta$ (ppm) = 11.9 (s, 1H, PhO*H*), 7.68 (s, 1H, *o*-H), 7.32 (s, 1H, *p*-H), 6.76 (s, 2H, *m*-H), 4.34 (s, 1H, C$H_3$). $^{13}$C-NMR (100 MHz, $d_6$-DMSO): $\delta$ (ppm) = 174.7 (*C*=O), 161.0 (*C*-OH), 134.3 (Ar-*C*), 130.5 (Ar-*C*), 118.5 (Ar-*C*),

116.8 (Ar-*C*), 63.1 (*C*$H_3NO_2$). Anal. Found for **1**·2$MeNO_2$: C 33.42; H 1.74; N 1.23; Calculated (%): C 33.38; H 2.22; N 1.34.

**Crystallographic data**

Intensities were measured on Bruker SMART 1000 diffractometer using a CCD area detector. Mo-Kα radiation ($\lambda$ = 0.71073 Å) was used in the experiments. Empirical absorption correction using the program SADABS was applied to the data ($\mu$ = 11.52 $mm^{-1}$ (**1**·2MeCN), 11.73 $mm^{-1}$ (**1**·2$MeNO_2$)). The structures were solved using direct methods and refined against $F^2$ with the SHELXTL software package.[1] All non-hydrogen atoms in the complexes were refined anisotropically. Crystallographic data collection and refinement parameters are given in **Table 1**. Figures presented in this publication were created with the programs in the Diamond (version 3.2i) software package.[2] The structures have been deposited with the Cambridge Crystallographic Database with reference numbers CCDC 979170 and 979171.

**TABLE 1**: Selected Crystallographic Data Collection and Refinement Parameters for Compounds **1**·2 MeCN and **1**·2 $MeNO_2$.

| Compound | **1**·2MeCN | **1**·2$MeNO_2$ |
|---|---|---|
| Chemical Formula | $C_{60}H_{46}N_2O_{26}Bi_4$ | $C_{58}H_{46}N_2O_{30}Bi_4$ |
| Formula mass | 2046.91 | 2086.89 |
| Crystal System | triclinic | triclinic |
| *a*/Å | 11.041(9) | 10.948(11) |
| *b*/Å | 11.411(10) | 11.508(11) |
| *c*/Å | 14.022(12) | 13.910(14) |
| *α*/° | 69.95(1) | 68.72(1) |
| *β*/° | 68.47(1) | 68.39(1) |
| *γ*/° | 77.02(1) | 76.55(1) |
| Unit cell Volume/$Å^3$ | 1534.15(20) | 1508.5(30) |
| Temperature/*K* | 298 | 273 |
| Space Group | $P\bar{1}$ (no. 2) | $P\bar{1}$ (no. 2) |
| Number of formula units per cell/*Z* | 1 | 1 |
| Number of reflections measured | 19036 | 19447 |
| Number of independent reflections | 7278 | 7469 |
| $R_{int}$ | 0.0371 | 0.0440 |
| Final $R_1$ values ($I > 2\sigma(I)$) | 0.0256 | 0.0300 |
| Final $wR(F^2)$values (($I > 2\sigma(I)$) | 0.0541 | 0.0734 |
| Final $R_1$ values (all data) | 0.0371 | 0.0385 |
| Final $wR(F^2)$ values (all data) | 0.0574 | 0.0778 |

References


1. G. M. Sheldrick, SADABS 5.1*, Göttingen,* 1997.
2. K. Brandenburg, Diamond 3.2i*, Germany,* 1997-2012.

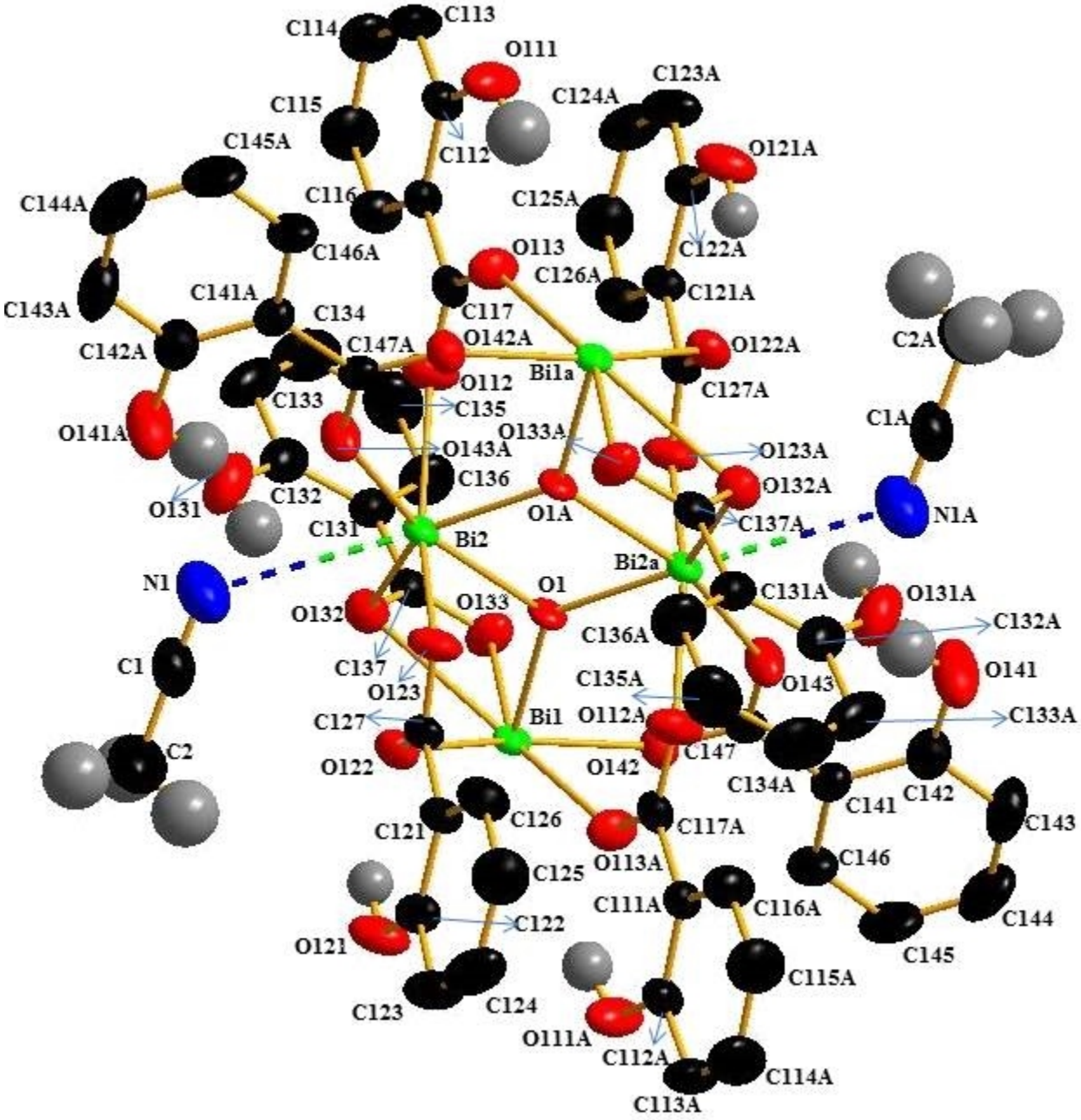


**Figure 1:** Molecular structure of **1**·2 MeCN. Anisotropic displacement parameters are shown at the 30% level. Hydrogen atoms on the salicylate ligands have been omitted for clarity.

**Table 1**: Selected Bond Distances and Angles for **1.**2MeCN*

Distances ( Å):

| | | | |
|---|---|---|---|
| Bi(1)-O(142) | 2.216(6) | Bi(2)-O(123) | 2.290(6) |
| Bi(1)-O(133) | 2.306(5) | Bi(2)-O(143)#1 | 2.368(7) |
| Bi(1)-O(113)#1 | 2.422(6) | Bi(2)-O(112) | 2.424(6) |
| Bi(1)-O(132) | 2.641(7) | O(1)-Bi(2)#1 | 2.133(5) |
| Bi(1)-O(122) | 2.689(6) | O(113)-Bi(1)#1 | 2.422(6) |
| Bi(2)-O(1)#1 | 2.133(5) | Bi(2)-N(1) | 3.063(10) |
| Bi(2)-O(1) | 2.284(6) | | |

Angles (°):

| | | | |
|---|---|---|---|
| O(1)-Bi(1)-O(142) | 94.0(2) | O(142)-Bi(1)-O(132) | 127.9(2) |
| O(1)-Bi(1)-O(133) | 87.4(2) | O(133)-Bi(1)-O(132) | 51.8(2) |
| O(132)-Bi(1)-O(122) | 74.4(2) | O(113)#1-Bi(1)-O(132) | 147.3(2) |
| O(142)-Bi(1)-O(133) | 77.9(2) | O(1)-Bi(1)-O(122) | 74.3(2) |
| Bi(1)-O(1)-Bi(2)#1 | 131.0(3) | O(1)-Bi(2)-O(123) | 86.4(2) |
| Bi(1)-O(1)-Bi(2) | 118.2(2) | O(142)-Bi(1)-O(122) | 151.4(2) |
| Bi(2)#1-O(1)-Bi(2) | 108.4(2) | O(1)#1-Bi(2)-O(1) | 71.6(2) |
| O(113)#1-Bi(1)-O(122) | 75.8(2) | O(1)#1-Bi(2)-O(123) | 79.7(2) |
| O(133)-Bi(1)-O(122) | 126.2(2) | O(1)#1-Bi(2)-O(143)#1 | 87.0(2) |
| O(1)-Bi(1)-O(113)#1 | 85.7(2) | O(1)#1-Bi(2)-O(112) | 82.9(2) |
| O(142)-Bi(1)-O(113)#1 | 77.4(2) | O(1)-Bi(2)-O(112) | 100.3(2) |
| O(133)-Bi(1)-O(113)#1 | 153.8(2) | O(123)-Bi(2)-O(112) | 158.3(2) |
| O(1)-Bi(1)-O(132) | 73.4(2) | O(143)#1-Bi(2)-O(112) | 83.4(2) |

*Symmetry transformations used to generate equivalent atoms = -x+1, -y+2, -z.

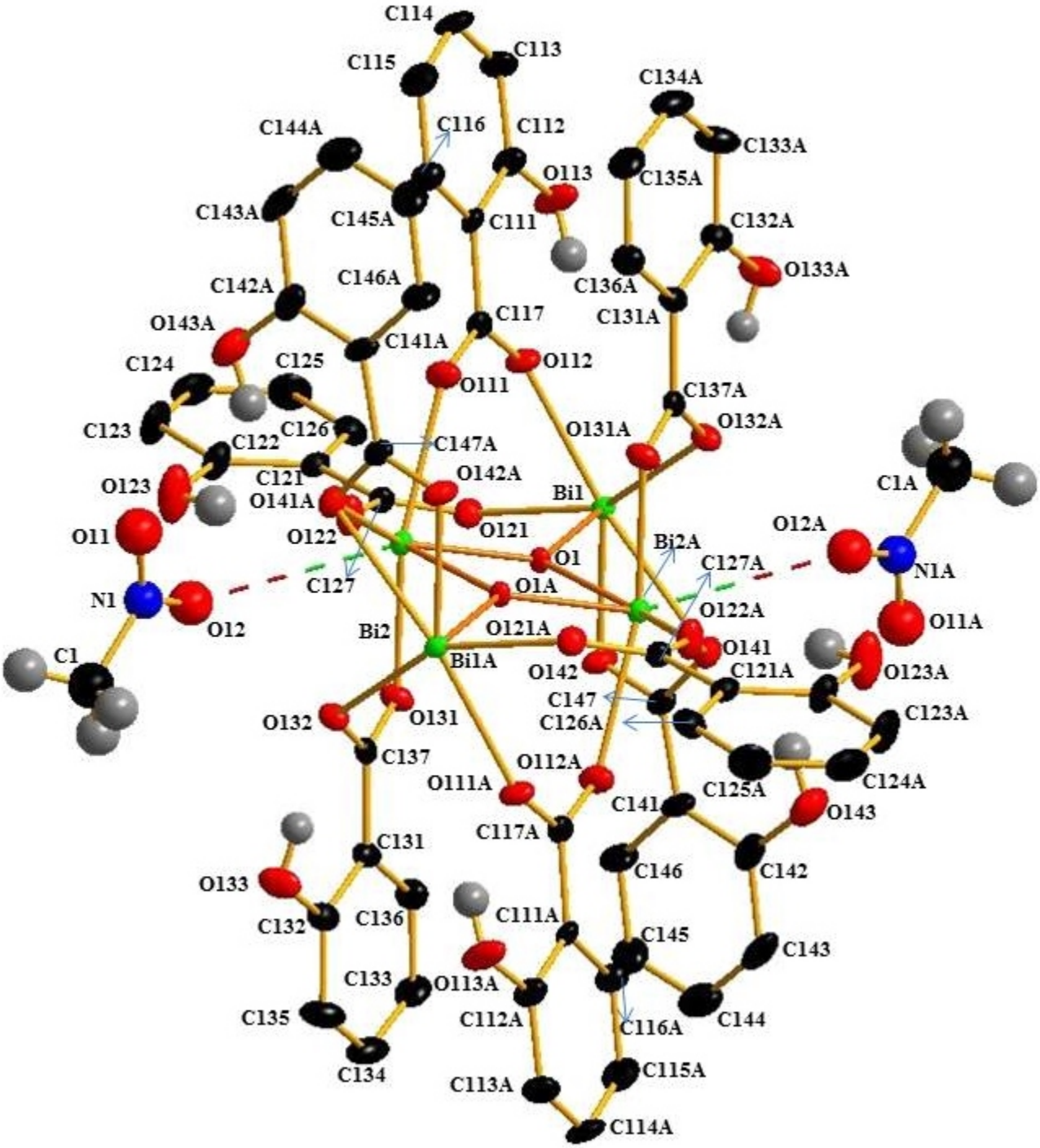


**Figure 2**: Molecular Structure of **1**·2 $MeNO_2$. Anisotropic displacement parameters are shown at the 30% level. Hydrogen atoms on the salicylate ligands have been omitted for clarity.

**Table 2:** Selected Bond Distances (Å) and Angles (°) for **1**.2MeNO$_2$.*

| | | | |
|---|---|---|---|
| Distances: | | | |
| Bi(1)-O(1) | 2.092(3) | Bi(2)-O(1)#1 | 2.274(3) |
| Bi(1)-O(121) | 2.233(3) | Bi(2)-O(131) | 2.285(3) |
| Bi(1)-O(142) | 2.303(3) | Bi(2)-O(122) | 2.382(3) |
| Bi(1)-O(112) | 2.418(3) | Bi(2)-O(111) | 2.434(3) |
| Bi(1)-O(141) | 2.631(3) | O(1)-Bi(2)#1 | 2.274(3) |
| Bi(1)-O(132)#1 | 2.714(3) | Bi(2)-O(12) | 3.103(4) |
| Bi(2)-O(1) | 2.117(3) | | |
| | | | |
| Angles: | | | |
| Bi(1)-O(1)-Bi(2) | 131.77(14) | O(1)-Bi(1)-O(132)#1 | 73.51(10) |
| Bi(1)-O(1)-Bi(2)#1 | 117.34(12) | O(121)-Bi(1)-O(132)#1 | 150.39(11) |
| Bi(2)-O(1)-Bi(2)#1 | 108.67(12) | O(142)-Bi(1)-O(132)#1 | 128.11(10) |
| O(1)-Bi(1)-O(121) | 93.94(11) | O(122)-Bi(2)-O(111) | 84.10(12) |
| O(1)-Bi(1)-O(142) | 87.37(11) | O(1)-Bi(2)-O(1)#1 | 71.33(12) |
| O(121)-Bi(1)-O(142) | 76.41(12) | O(1)-Bi(2)-O(131) | 78.64(11) |
| O(1)-Bi(1)-O(112) | 84.33(11) | O(1)#1-Bi(2)-O(131) | 86.63(11) |
| O(121)-Bi(1)-O(112) | 76.20(12) | O(1)-Bi(2)-O(122) | 86.76(11) |
| O(142)-Bi(1)-O(112) | 150.70(11) | O(1)#1-Bi(2)-O(122) | 156.91(11) |
| O(1)-Bi(1)-O(141) | 73.41(10) | O(131)-Bi(2)-O(122) | 81.84(12) |
| O(121)-Bi(1)-O(141) | 127.30(11) | O(1)-Bi(2)-O(111) | 83.11(11) |
| O(142)-Bi(1)-O(141) | 52.63(10) | O(1)#1-Bi(2)-O(111) | 99.94(11) |
| O(112)-Bi(1)-O(141) | 147.81(10) | O(131)-Bi(2)-O(111) | 157.49(11 |

*Symmetry transformations used to generate equivalent atoms = -x, -y+1, -z+1

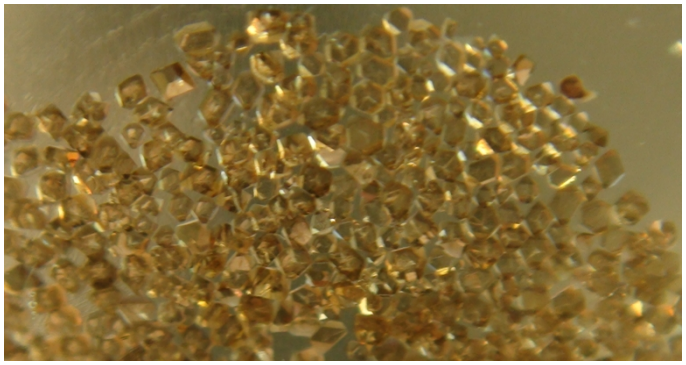

**Figure 3:** The prismatic crystals of $[Bi_{38}O_{44}(HSal)_{26}(Me_2CO)_{16}(H_2O)_2]\cdot(Me_2CO)_4$ oxo-cluster.