Supplementary Material (ESI) for Dalton Transactions

Synthesis of Bismuth and Antimony Complexes of the "Larger" Calix[n]arenes (n = 6-8); From Mononuclear to Tetranuclear Complexes.

Daniel Mendoza-Espinosa,[a] Arnold L. Rheingold,[b] Tracy A. Hanna [a]*

a. Department of Chemistry, Texas Christian University, P.O. Box 298860, Fort Worth, Texas 76129, Tel: 817-257-6197, Fax: 817-257-5851.
b. Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, m/c 0358, La Jolla, California 92093-0358
E-mail: t.hanna@tcu.edu

Electronic Supplementary Information

Crystal structure description for complex **7**.

The crystal structure of complex $[Bi_4O_2\{\mathbf{HC8}\}]_2$ **7** is illustrated in Figures S1-S3. Complex **7** displays a dimeric unit with each calixarene ligand being tetrametallated and containing five fused $Bi_2(\mu\text{-}O)_2$ four-membered rings in an overall $Bi_4O_2(OAr)_8$ core system similar to those observed in other calixarene complexes prepared in our lab (see Figure S1).[1,2] The five fused four-membered rings feature individual planarity, but they are not coplanar with each other. The calixarene ligands are in a pinched cone conformation with a C_{2v} symmetry consistent with the NMR patterns. The monomeric representation of complex **7** (Figure S1) resembles the structure of the complex ion $[(Bi(\mu_3\text{-}Cl)Cl)_4(\mu\text{-}Cl)_2\{4Li{\cdot}^{t}\mathbf{BuC8}\}(3THF)(DME)]^{2-}$ synthesized in our lab with the aid of calixanion precursors,[3] and is very similar to complex **8**.

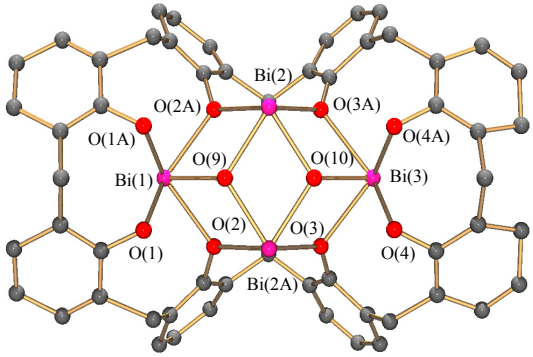

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Figure S1. Monomeric representation of complex **7** displaying the $Bi_4O_2(OAr)_8$ motif.

The overall structure of complex **7** (Figure S2) has S_4 symmetry and consists of two **HC8** units linked by a Bi_8O_4 core similar to the one found in the complex $[Bi_8O_4\{^{t}\mathbf{BuC8}\}_2]$ reported by our group.[2]

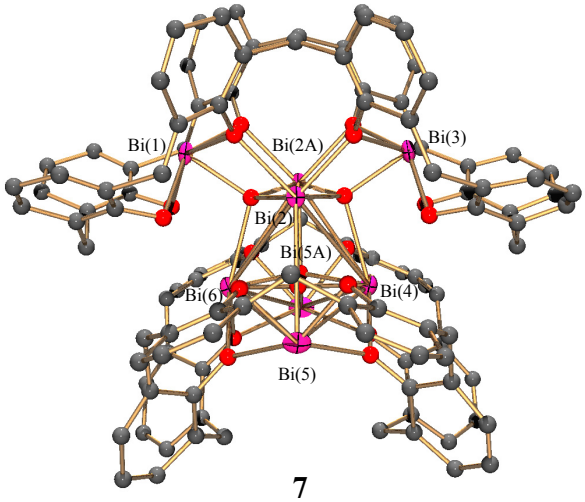

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Figure S2. Crystal structure of the dimeric $[Bi_4O_2\{\mathbf{HC8}\}]_2$ **7** complex. Hydrogen atoms and uncoordinated solvent molecules are omitted for clarity.

If the oxygen atoms of the calixarene are considered, complex **7** contains a robust Bi_8O_{20} oxo cluster (Figure S3) that contains two different types of bismuth atoms. The first type includes the bismuth atoms Bi(1), Bi(3), Bi(5) and Bi(5A), that are coordinated to four calixarene oxygens and to one bridging oxygen in a distorted square-based pyramidal geometry. The basal plane is formed by four calixarene oxygens and the apical position is occupied by the bridging oxygen.

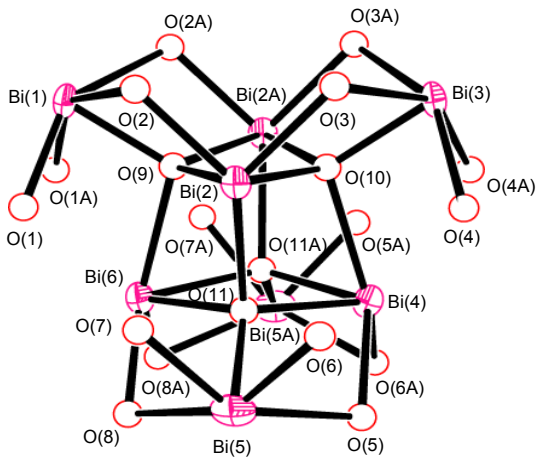

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Figure S3. Core structure of complex **7**.

The second type of bismuth atom includes Bi(2), Bi(2A), Bi(4) and Bi(6), with coordination to two oxygens from the calixarene ligand and to three bridging oxygens. The Bi_8O_{20} cluster in **7** can be more easily viewed as two Bi_4O_{10} cores that are linked by the interaction between Bi(2)-O(11), Bi(2A)-O(11A), Bi(4)-O(10) and Bi(6)-O(9) (see Figure S3). It can be noticed that a cubane-like cage is formed in the middle of the cluster by the interactions between the Bi(2), Bi(2A), Bi(4), and Bi(6) atoms and the μ_4-oxygens O(9), O(10), O(11), and O(11A). The Bi-O-Bi and O-Bi-O angles in the cubane range from 67.29° to 112.24°, far from

the ideal 90°, indicating high distortion in the cage. The robust structure of complex **7** causes relatively good air and moisture stability; no decomposition was observed after exposure to air for a period of 3 days.

General X-ray structure information. The crystallographic data and some details of the data collection and refinement of complex **7** are given in Table S1. Absorption corrections were applied by SADABS.[4] The X-ray structure of **7** was solved by direct methods and subsequent difference Fourier syntheses and refined by full matrix least-squares methods against F^2 (SHELX 97).[5] The programs ORTEP32[6] and POVRay[7] were used to generate the X-ray structural diagrams.

Table S1. Crystallographic Data and Summary of Data Collection and Structure Refinement

Crystallographic data for complex [**7**]$_2$

	[**7**]$_2$
Formula	$C_{112}H_{80}Bi_8O_{20}$
Fw	3417.60
cryst syst	Orthorhombic
space group	*P*nma
T, K	213(2)
a, Å	30.287(6)
b, Å	21.769(4)
c, Å	22.432(4)
α, deg	90
β, deg	90
γ, deg	90
V, A^3	14790(5)
Z	4
d_{calcd} g·cm^{-3}	1.535
μ, mm^{-1}	9.531
Refl collected	97048
T_{min}/ T_{max}	0.691
N_{measd}	10925
[R_{int}]	[0.1938]
R [I>2sigma(I)]	0.1159
R_w [I>2sigma(I)]	0.2590
GOF	1.038

References

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