

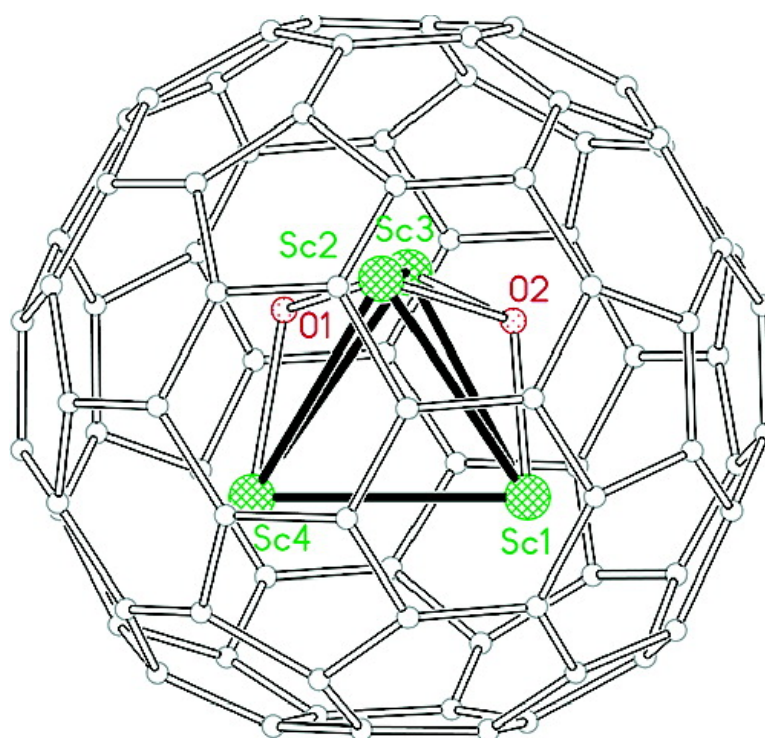
Communication

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*J. Am. Chem. Soc.*, **2008**, 130 (36), 11844-11845 • DOI: 10.1021/ja803679u • Publication Date (Web): 15 August 2008

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## A Distorted Tetrahedral Metal Oxide Cluster inside an Icosahedral Carbon Cage. Synthesis, Isolation, and Structural Characterization of $\text{Sc}_4(\mu_3\text{-O})_2@I_h\text{-C}_{80}$

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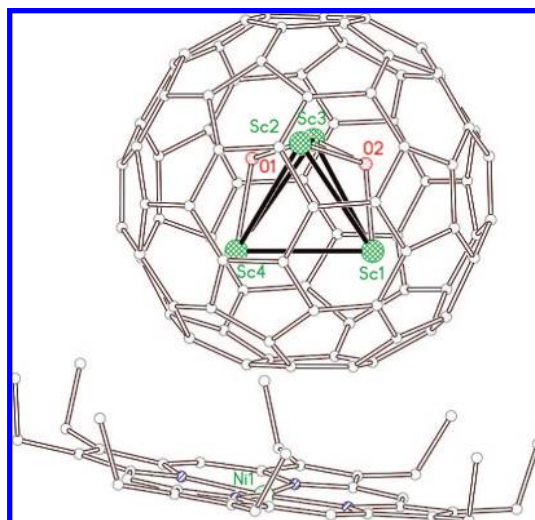
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Endohedral fullerenes involve closed carbon cages, which encapsulate an isolated atom or a group of atoms.<sup>1</sup> For example, endohedral fullerenes are known with one, two, three, or even four metal atoms trapped inside.<sup>2</sup> Additionally, there is an extensive array of endohedrals that contain metal nitride ( $\text{M}_3\text{N}$ )<sup>3</sup> or metal carbide ( $\text{M}_2\text{C}_2$ )<sup>4</sup> units on the inside. Why have no endohedrals been found with some sort of metal oxide unit on the inside? This question is particularly relevant since most endohedral metallofullerenes are prepared in an electric arc process that volatilizes graphite rods, which are doped with the appropriate metal oxide.<sup>5</sup> Here, we report the discovery of an endohedral fullerene that does encapsulate a metal oxide unit:  $\text{Sc}_4(\mu_3\text{-O})_2@I_h\text{-C}_{80}$ .

Figure 1 shows a drawing of the structure of  $\text{Sc}_4(\mu_3\text{-O})_2@I_h\text{-C}_{80}$  as obtained from X-ray crystallographic data on  $\text{Sc}_4(\mu_3\text{-O})_2@I_h\text{-C}_{80}\cdot\text{Ni}^{\text{II}}(\text{OEP})\cdot 2\text{C}_6\text{H}_6$ . However, before commenting further on the structure, we need to learn how it was prepared. Graphite rods packed with  $\text{Sc}_2\text{O}_3$  were vaporized under a flow of 300–400 Torr of helium with 6 Torr/min of air added. Although air is known to adversely affect the formation of fullerenes,<sup>6</sup> it is absolutely essential here. The raw soot was extracted with *o*-xylene, and the extract was stirred with diaminosilica gel,<sup>7</sup> which binds and removes the more reactive fullerenes. Figure 2 shows a high-pressure liquid chromatogram (HPLC) of the treated extract. In addition to the peaks due to  $\text{C}_{60}$  and  $\text{C}_{70}$  and the known endohedrals  $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ ,  $\text{Sc}_3\text{N}@D_{3h}(5)\text{-C}_{78}$ , and  $\text{Sc}_3\text{N}@D_5(6140)\text{-C}_{68}$ , two small peaks are detected at 19.3 and 20.1 min. Further chromatographic purification yields pure samples of the two compounds. The HPLC traces for the purified samples are shown in Figure 2b and c.

The compositions of the two compounds were determined to be  $\text{C}_{80}\text{O}_2\text{Sc}_4$  and  $\text{C}_{80}\text{O}_3\text{Sc}_4$  by mass spectrometry. For the former, an experimentally determined mass of 1171.812 96 amu was obtained by high resolution mass spectroscopy on samples containing  $\text{C}_{60}$ ,  $\text{C}_{70}$ , and  $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$  as internal standards and provided differentiation between the alternative formulations:  $\text{C}_{80}\text{O}_2\text{Sc}_4$  (Calcd 1171.812 92 amu),  $\text{C}_{64}\text{N}_8\text{O}_7\text{Sc}_4$  (Calcd 1171.812 09 amu), and  $\text{C}_{78}\text{N}_4\text{Sc}_4$  (Calcd 1171.835 388 amu). For the other compound,  $\text{C}_{80}\text{O}_3\text{Sc}_4$ , the experimental (1187.807 62 amu) and calculated (1187.807 84 amu) masses show similar agreement.

Studies were conducted to optimize the yield of  $\text{Sc}_4(\mu_3\text{-O})_2@I_h\text{-C}_{80}$ . When the arc process was conducted with graphite rods packed with  $\text{Sc}_2\text{O}_3$  under a flow of 300–400 Torr of helium with 6 Torr/min of dinitrogen, no  $\text{Sc}_4(\mu_3\text{-O})_2@I_h\text{-C}_{80}$  was detected in the soot. Addition of metallic copper to the graphite rods has been found to improve the yields of endohedral fullerenes, but we found no



**Figure 1.** A view of the structure of  $\text{Sc}_4(\mu_3\text{-O})_2@I_h\text{-C}_{80}\cdot\text{Ni}^{\text{II}}(\text{OEP})\cdot 2\text{C}_6\text{H}_6$ . The major sites for the  $\text{Sc}_4(\mu\text{-O})_2$  group and the  $\text{C}_{80}$  cage are shown. For clarity, the solvate molecules of benzene have been omitted.

improvement in the formation of  $\text{Sc}_4(\mu_3\text{-O})_2@I_h\text{-C}_{80}$  when copper was added to the  $\text{Sc}_2\text{O}_3$ -packed graphite rods.<sup>8</sup> However, we have found that increasing the air flow does improve the production of  $\text{Sc}_4(\mu_3\text{-O})_2@I_h\text{-C}_{80}$  and that a flow of 12 Torr/min is optimal. Packing graphite rods with copper nitrate along with scandium oxide has been shown to suppress empty cage fullerene formation and facilitate the production of  $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ .<sup>9</sup> The copper nitrate decomposes in the arc and serves as a source of  $\text{NO}_x$ . To determine the effect of copper nitrate on the formation of  $\text{Sc}_4(\mu_3\text{-O})_2@I_h\text{-C}_{80}$ , we prepared a series of rods packed with various amounts of copper nitrate. The results indicate that increasing content of copper nitrate dramatically improves the yield of  $\text{Sc}_4(\mu_3\text{-O})_2@I_h\text{-C}_{80}$ . Optimal conditions for formation of  $\text{Sc}_4(\mu_3\text{-O})_2@I_h\text{-C}_{80}$  were an air flow of 0.2 Torr/min with graphite rods packed with 80%  $\text{Cu}(\text{NO}_3)_2$  and 20%  $\text{Sc}_2\text{O}_3$ , which leads to a 12% yield from the soluble extract. The low  $\text{Sc}_2\text{O}_3$  content minimizes its use, and recycling waste soot is advised.<sup>10</sup> At this point, we can rank the source of oxygen and its inclusion in  $\text{Sc}_4(\mu_3\text{-O})_2@I_h\text{-C}_{80}$  as follows:  $\text{NO}_x$  from copper nitrate >  $\text{O}_2$  from air  $\gg$  O from  $\text{Sc}_2\text{O}_3$ .

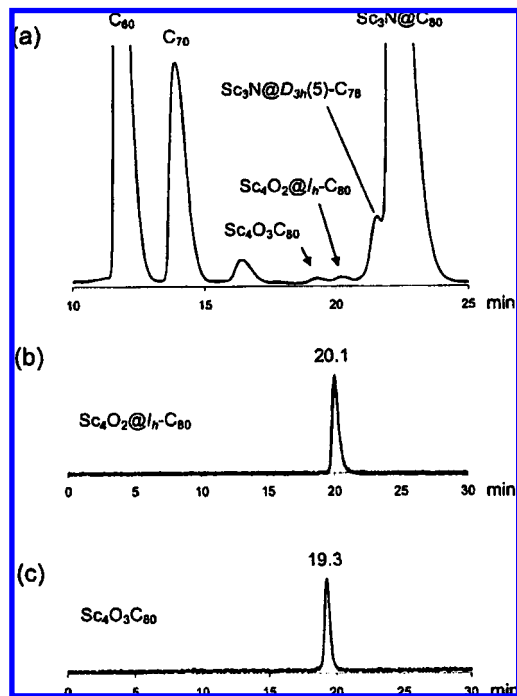
Black blocks of  $\text{Sc}_4(\mu_3\text{-O})_2@I_h\text{-C}_{80}\cdot\text{Ni}^{\text{II}}(\text{OEP})\cdot 2\text{C}_6\text{H}_6$  were obtained by diffusion of a benzene solution of the endohedral fullerene into a benzene solution of  $\text{Ni}^{\text{II}}(\text{OEP})$  and utilized in the crystal structure determination.<sup>11</sup>

Figure 1 shows a drawing of  $\text{Sc}_4(\mu_3\text{-O})_2@I_h\text{-C}_{80}$  and the adjacent  $\text{Ni}^{\text{II}}(\text{OEP})$  molecule, which as usual cradles the endohedral within

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**Figure 2.** HPLC chromatograms of (a) the xylene extract after 2 h of SAFA prepurification and (b and c) the final isolated samples of  $\text{Sc}_4(\mu_3\text{-O})_2@I_h\text{-C}_{80}$  and  $\text{C}_{80}\text{O}_3\text{Sc}_4$ , respectively.

the eight ethyl groups. The structure shows the presence of the  $I_h\text{-C}_{80}$  cage that is common to many endohedrals containing the  $\text{M}_3\text{N}$  unit. Two orientations of this cage are present in the crystal. The  $I_h\text{-C}_{80}$  cage encapsulates a distorted tetrahedral set of scandium atoms with bridging oxygen atoms asymmetrically positioned on two of the triangular faces of the  $\text{Sc}_4$  tetrahedron. This unit is disordered over three orientations with occupancies of 0.50, 0.30, and 0.20. For the major site, the Sc–O distances (Å) are as follows: Sc1–O2, 1.964(14); Sc2–O2, 2.005(14); Sc2–O1, 2.11(2); Sc3–O1, 1.83(4); Sc3–O2, 2.056(13); Sc4–O1, 2.090(14). These distances are within the range of Sc–O bond lengths (1.87–2.29 Å) observed for other scandium complexes containing a bridging oxide group.<sup>12,13</sup> The Sc2–Sc3 distance (2.946(7) Å) is short while the other Sc–Sc distances show considerable variation: Sc1–Sc2, 3.066(8); Sc1–Sc3, 3.379(6); Sc1–Sc4, 3.120(5); Sc2–Sc4, 3.329(5); Sc3–Sc4, 3.214(5).

In other cases where the  $I_h\text{-C}_{80}$  cage is present,<sup>3a</sup> the stabilization of this particular  $\text{C}_{80}$  isomer is attributed to the presence of a  $-6$  charge ion in the cage, which gives it a closed shell. If a similar situation pertains with  $\text{Sc}_4(\mu_3\text{-O})_2@I_h\text{-C}_{80}$ , then the  $\text{Sc}_4(\mu_3\text{-O})_2$  cluster should have a  $+6$  charge, which could be achieved with the presence of a mixed valence unit,  $(\text{Sc}^{3+})_2(\text{Sc}^{2+})_2(\text{O}^{2-})_2$ . Such an electron distribution is consistent with the presence of a short Sc–Sc distance between Sc2 and Sc3 as the  $(\text{Sc}^{2+})_2$  portion. Note also that Sc1 and Sc4, which are more widely separated, are positioned immediately above the porphyrin in positions that are remarkably similar to those found for the  $\text{Sc}^{3+}$  ions in many crystals containing the  $\text{Sc}_n\text{M}_{3-n}\text{N}@I_h\text{-C}_{80}\cdot\text{Ni}^{\text{II}}(\text{OEP})$  unit.<sup>14</sup>

To our knowledge, the  $\text{Sc}_4(\mu_3\text{-O})_2$  cluster is the largest unit found in an endohedral fullerene. Despite the presence of this large cluster within the  $I_h\text{-C}_{80}$  cage, the scandium to carbon contacts are similar

to those seen in related endohedrals. In  $\text{Sc}_4(\mu_3\text{-O})_2@I_h\text{-C}_{80}$ , the two closest Sc–C distances for each scandium atom are Sc1, 2.016(4), 2.113(6); Sc2, 2.277(4), 2.348(5); Sc3, 2.210(4), 2.370(5); Sc4, 2.231(4), 2.285(4) Å. For comparison the comparable distances in  $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$  are Sc1, 2.255(4), 2.282(3); Sc2, 2.272(4), 2.272(4); Sc3, 2.243(4), 2.307(4) Å.<sup>15</sup> Likewise, there are no unusual interactions of the oxygen atoms of the cluster with the carbon cage. For the major orientation, the closest carbon to oxygen contacts are: O1 - 2.721(19); O2 - 2.562(19) Å.

The structure of  $\text{C}_{80}\text{O}_3\text{Sc}_4$  remains to be determined. Likely structures are  $\text{Sc}_4\text{O}_3@I_h\text{-C}_{80}$ , with the additional oxygen atom as part of the internal cluster or  $\text{Sc}_4(\mu_3\text{-O})_2@I_h\text{-C}_{80}\text{O}$  with an epoxide unit on the fullerene exterior.<sup>16</sup> Preliminary crystallographic data have revealed the presence of a tetrahedral-like  $\text{Sc}_4$  cluster within the fullerene cage.

**Acknowledgment.** We thank the National Science Foundation (Grants CHE-0716843 to A.L.B. and M.M.O., CHE-0547988 to S.S.), the DOE GAANN Fellowship (P200A060323 to S.S.), and the Lucas Research Foundation for financial support.

**Supporting Information Available:** Preparative and separation information for  $\text{Sc}_4(\mu_3\text{-O})_2@I_h\text{-C}_{80}$ . X-ray crystallographic data for  $\text{Sc}_4(\mu_3\text{-O})_2@I_h\text{-C}_{80}\cdot\text{Ni}^{\text{II}}(\text{OEP})\cdot 2(\text{C}_6\text{H}_6)$  in CIF format. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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JA803679U