A seven atom cluster in a carbon cage, the crystallographically determined structure of $Sc_4(\mu_3\text{-}O)_3@I_h\text{-}C_{80}$†

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The tetrahedral array of four scandium atoms with oxygen atoms capping three of the four faces found in $Sc_4(\mu_3\text{-}O)_3@I_h\text{-}C_{80}$ is the largest cluster isolated to date inside a fullerene cage.

The closed carbon cages of fullerenes can encapsulate other atoms or molecules to form endohedral fullerenes. Thus, shortly after their initial detection of C_{60}, Smalley, Kroto, Curl and co-workers reported the observation of LaC_{60} and suggested that it consisted of a lanthanum atom inside a shell of carbon atoms.[1] Subsequently, numerous endohedral fullerenes containing rare gas atoms, nitrogen atoms, or one, two, or even three electropositive metal atoms have been detected and in some cases isolated.[2] Endohedral fullerenes containing one or two diatomic molecules (*e.g.* $H_2@C_{60}$,[3] $N_2@C_{60}$,[4] $(H_2)_2@C_{70}$[5]) have also been prepared and isolated. Additionally, extensive arrays of endohedrals that contain metal carbide (M_2C_2 or M_3C_2)[6,7] or metal nitride (M_3N)[8,9] units have become available.

Recently, we reported the isolation and crystallographic characterization of $Sc_4(\mu_3\text{-}O)_2@I_h\text{-}C_{80}$ in which a metal oxide unit was encapsulated in a C_{80} cage with icosahedral symmetry.[10] In that work we also noted the presence of a related species, $Sc_4O_3C_{80}$, for which two structures were suggested: $Sc_4O_3@I_h\text{-}C_{80}$, with the additional oxygen atom as part of the internal cluster or $Sc_4(\mu_3\text{-}O)_2@I_h\text{-}C_{80}O$ with an epoxide unit on the fullerene exterior. Subsequent computational studies by Poblet and co-workers indicated that the $Sc_4O_3@I_h\text{-}C_{80}$ formulation was the more likely structure and that this would have an electronic distribution $(Sc^{3+})_4(O^{2-})_3@(I_h\text{-}C_{80}{}^{6-})$.[11] A second set of computations for $Sc_4(\mu_3\text{-}O)_3@I_h\text{-}C_{80}$ and $Sc_4(\mu_3\text{-}O)_2@I_h\text{-}C_{80}$ have produced similar results.[12] Here, we report definitive experimental data that identify $Sc_4O_3C_{80}$ as $Sc_4(\mu_3\text{-}O)_3@I_h\text{-}C_{80}$.

In order to obtain a sufficient quantity of $Sc_4O_3C_{80}$ for crystallization, a new method of sample purification was developed. As before, raw soot was obtained from the electric arc vaporization of graphite rods that were packed with 80% $Cu(NO_3)_2$ and 20% Sc_2O_3 under an air flow of 0.2 Torr min^{-1}.[10] The resulting carbon soot was collected and extracted with carbon disulfide to produce a solution that contained primarily (>95%) empty-cage fullerenes. Fig. 1 shows the chromatogram of the initial extract. The low abundance of $Sc_4O_3C_{80}$ (<0.3%) in the extract suggested that it would be impractical to initiate HPLC fraction collection at this stage. Hence, a procedure was developed to remove the bulk of the empty-cage fullerenes. Specifically, 1.5 g of fullerene extract were dissolved in 500 mL of carbon disulfide. A 4.0 g portion of solid aluminium(III) chloride was added to the stirred solution. During the 5 minutes of reaction time, the endohedral metallofullerenes were preferentially removed from solution. The mixture was filtered. The filter cake was treated with an ice–water mixture and transferred to a separatory funnel containing a saturated sodium bicarbonate solution and carbon disulfide. The endohedral fullerenes were released from the aluminium(III) chloride through the treatment with water and dissolved in the carbon disulfide layer. After several washes with deionized water, the carbon disulfide layer was filtered through a PTFE membrane. Subsequent removal of solvent *via* rotary evaporation and washing of the fullerene powder with diethyl ether resulted in an enriched endohedral sample, which contained the desired $Sc_4O_3C_{80}$. The HPLC trace for the recovered metallofullerenes is shown in Fig. 1b, which demonstrates significant removal of C_{60} and C_{70} contaminants to less than 20% and enrichment of $Sc_4O_3C_{80}$. Subsequent preparatory HPLC separation (step 2) resulted in a purified sample of $Sc_4O_3C_{80}$ as shown in Fig. 1c. Fig. 2 shows the mass spectrum of the purified sample. As seen in the inset of Fig. 2, high-resolution mass spectral analysis of the isotope peaks indicates a molecular formula of $Sc_4O_3C_{80}$.

Black crystals of $Sc_4(\mu_3\text{-}O)_3@I_h\text{-}C_{80}\cdot Ni(OEP)\cdot 2C_6H_6$‡ were obtained by the slow diffusion of a saturated solution of $Sc_4O_3C_{80}$ in benzene over a benzene solution of $Ni^{II}(OEP)$ in a 7 mm od diameter tube. Fig. 3 shows a drawing of the endohedral fullerene and the adjacent porphyrin. Although the structure suffers from disorder, that disorder has been modelled and the geometry of the $Sc_4(\mu_3\text{-}O)_3$ cluster has been elucidated. Given the high symmetry of the $I_h\text{-}C_{80}$ cage and the near C_{3v} symmetry of the cluster, it is remarkable that the crystal had sufficient order to allow us to obtain structural information. There is no electron density on the outside of the carbon cage, and hence no evidence to support the formation

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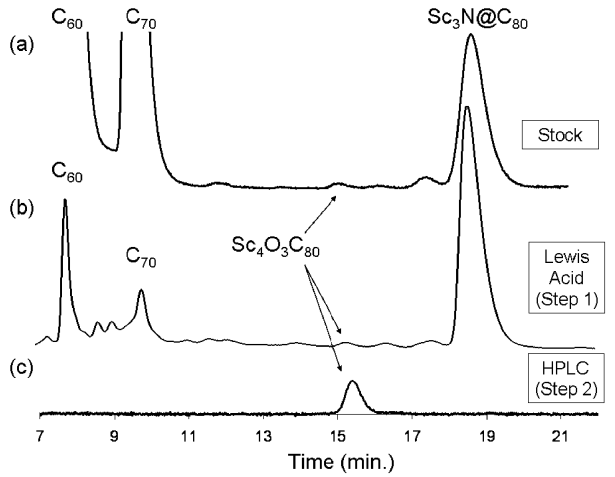

Fig. 1 Chromatograms of: (a) fullerene stock containing $Sc_4O_3C_{80}$, (b) enriched metallofullerene sample obtained after Lewis acid complexation–decomplexation step, and (c) purified $Sc_4O_3@I_h$-C_{80} after HPLC step. HPLC conditions: 0.5 mL min^{-1} xylenes, 10 × 250 mm PYE column, 360 nm UV detection, and 50 μL injections.

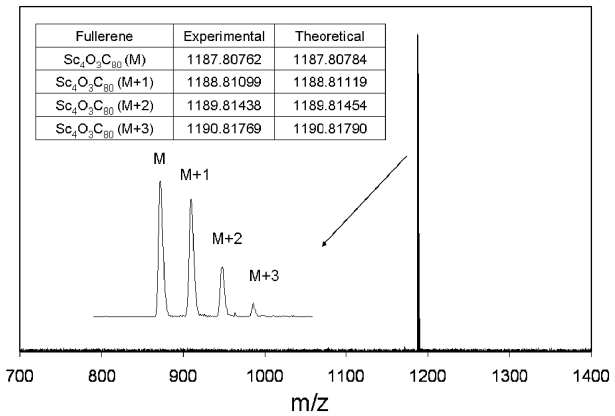

Fig. 2 MALDI mass spectral data showing the purity of the $Sc_4O_3C_{80}$ sample and the isotope analysis obtained under high resolution (inset).

of a fullerene epoxide. The C_{80} cage has two orientations: one is a half molecule that utilizes the crystallographic mirror to generate the other half while the other is disordered with respect to the mirror plane. The occupancies of these two orientations refined to 0.452(2) and 0.548(2). The $Sc_4(\mu_3\text{-}O)_3$ cluster inside the I_h-C_{80} cage is also disordered. Two well-defined orientations of the $Sc_4(\mu_3\text{-}O)_3$ unit, which consists of a nearly tetrahedral array of four scandium atoms with oxygen atoms bridging three of the four faces of the tetrahedron, were found. The set Sc1, Sc2, Sc3, Sc4, O1, O2, and O3, which is shown in Fig. 3 and 4, has the highest occupancy and gave the clearest indication of the oxygen positions. A third orientation with low occupancy is also present and was partially modelled. The occupancies of the three orientations of the $Sc_4(\mu_3\text{-}O)_3$ clusters are 0.2291(11), 0.1535(10), and 0.1172(13), respectively. The presence of multiple orientations of the $Sc_4(\mu_3\text{-}O)_3$ unit is consistent with the computational study that indicated that there was little energetic discrimination between different locations of the cluster inside the I_h-C_{80} cage.[11]

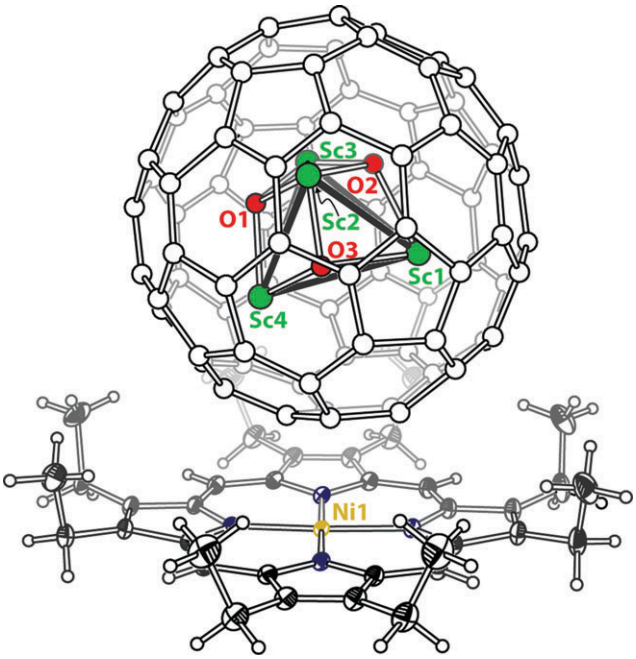

Fig. 3 A view of the structure of $Sc_4(\mu_3\text{-}O)_3@I_h$-$C_{80}$·Ni(OEP)·$2C_6H_6$ with 50% thermal contours for the porphyrin atoms and, for clarity, uniformly sized circles for the atoms of the endohedral fullerene and the hydrogen atoms. Only the major site for the $Sc_4(\mu_3\text{-}O)_3$ cluster with 0.45 fractional occupancy is shown along with one orientation of the fullerene cage.

Table 1 contains the Sc–Sc and Sc–O distances within the $Sc_4(\mu_3\text{-}O)_3$ cluster and compares these values to the corresponding values for the $Sc_4(\mu_3\text{-}O)_2$ cluster and to the recently published computational values.[10,11] In the $Sc_4(\mu_3\text{-}O)_3$ cluster, the Sc–Sc distances fall into two clear groups. The separations between Sc atoms that are bridged by two oxygen atoms (Sc1–Sc2, Sc2–Sc3, and Sc3–Sc4) are shorter than the distances between scandium atoms that are bridged by only one oxygen atom (Sc 1–Sc3, Sc1–Sc4, Sc3–Sc4). As the calculated values show, this distinction was also predicted by the computations and the agreement between the computed and experimental values is very good.[11] The experimental and computed Sc–O distances also show good agreement for O1 and O2. Refinement of O3 was difficult because of its proximity to the atoms of the other orientations of the $Sc_4(\mu_3\text{-}O)_2$ cluster and the Sc–O3 distances are affected by this problem. In general the Sc–Sc and Sc–O distances in $Sc_4(\mu_3\text{-}O)_3@I_h$-$C_{80}$ are similar to those in $Sc_4(\mu_3\text{-}O)_2@I_h$-$C_{80}$.

The $(Sc_4(\mu_3\text{-}O)_3)^{6+}$ and $(Sc_4(\mu_3\text{-}O)_2)^{6+}$ clusters found in these endohedrals have no precedent in the known chemical

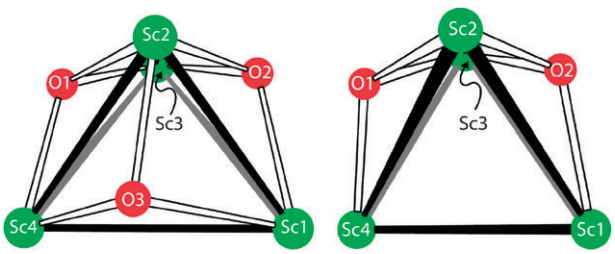

Fig. 4 Comparison of the scandium oxide clusters in $Sc_4(\mu_3\text{-}O)_3@I_h$-$C_{80}$ on the left and $Sc_4(\mu_3\text{-}O)_2@I_h$-$C_{80}$ on the right.

Table 1 Crystallographic and computed distances within the scandium oxide clusters of $Sc_4(\mu_3\text{-}O)_3@I_h\text{-}C_{80}$ and $Sc_4(\mu_3\text{-}O)_2@I_h\text{-}C_{80}$[a]

	$Sc_4(\mu_3\text{-}O)_3@I_h\text{-}C_{80}$			$Sc_4(\mu_3\text{-}O)_2@I_h\text{-}C_{80}$[b]	
	Exp.	Calc.[c]		Exp.	Calc.[c]
Sc1–Sc2	3.001(2)	2.98–2.99	Sc1–Sc2	3.066(8)	3.25–3.30
Sc1–Sc3	3.500(2)	3.42–3.45	Sc1–Sc3	3.379(6)	3.25–3.30
Sc1–Sc4	3.396(2)	3.42–3.45	Sc1–Sc4	3.120(5)	3.21–3.48
Sc2–Sc3	3.013(2)	2.98–2.99	Sc2–Sc3	2.946(7)	2.94–3.00
Sc2–Sc4	3.024(2)	2.98–2.99	Sc2–Sc4	3.392(5)	3.25–3.30
Sc3–Sc4	3.399(2)	3.42–3.45	Sc3–Sc4	3.214(5)	3.25–3.30
Sc2–O1	2.050(6)		Sc2–O1	2.11(2)	
Sc3–O1	1.939(6)		Sc3–O1	1.83(4)	
Sc4–O1	1.961(5)		Sc4–O1	2.090(14)	1.98–2.01
Sc1–O2	2.088(7)		Sc1–O2	1.964(14)	
Sc2–O2	2.003(7)	1.99	Sc2–O2	2.005(14)	
Sc3–O2	2.037(10)		Sc3–O2[c]	2.056(13)	
Sc1–O3	2.23(2)		—	—	—
Sc2–O3	1.82(2)		—	—	—
Sc4–O3	1.74(2)		—	—	—

[a] Distances in angstroms (Å). [b] Data from ref. 10. [c] Data from ref. 11.

behaviour of scandium. The stable oxide of scandium is the ionic solid Sc_2O_3, which was the starting material employed in this study. Other oxides of scandium have only been detected in the gas phase. These are Sc_2O, ScO, and ScO_2.[13,14] Thus, our studies along with those of endohedral fullerenes containing the $(M_3N)^{6+}$ unit demonstrate the ability of fullerenes to entrap chemical entities that have not been detected outside the carbon cage.

In summary, $Sc_4(\mu_3\text{-}O)_3@I_h\text{-}C_{80}$ has been isolated and examined by single crystal X-ray diffraction. Bond lengths within the $(Sc_4(\mu_3\text{-}O)_3)^{6+}$ unit agree with those previously computed.[11]

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Notes and references

‡ *Crystal data*: $Sc_4(\mu_3\text{-}O)_3@I_h\text{-}C_{80}$·Ni(OEP)·2benzene, black parallelepiped, $C_{128}H_{56}Sc_4N_4O_3Ni$, M = 1936.32, monoclinic, space group $C2/m$, a = 25.2780(6) Å, b = 15.1136(4) Å, c = 19.8016(5) Å, β = 95.1670(10)°, V = 7534.3(3) Å^3 at 100(2) K, μ(synchrotron radiation, λ = 0.77490 Å) = 0.663 mm^{-1}, Z = 4. Reflections collected, 167 616; R_{int} 0.038. Refinement of 31 951 reflections, 851 parameters, and 37 restraints yielded wR_2 = 0.304 for all data and a conventional R_1 = 0.100 based on 27 614 reflections with $I > 2\sigma(I)$.

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