## Communications

## Iodine Supertetrahedra

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The Molecular Solid  $Sc_{24}C_{10}I_{30}$ : A Truncated, Hollow T4 Supertetrahedron of Iodine Filled with a T3 Supertetrahedron of Scandium That Encapsulates the Adamantoid Cluster  $Sc_4C_{10}^{**}$ 

Liesbet Jongen, Anja-Verena Mudring,\* and Gerd Meyer\*

Dedicated to Professor John D. Corbett on the occasion of his 80th birthday

There are two iodides of scandium (Figure 1), the rather trivial insulator  $ScI_3$  and the scandium-deficient compound  $Sc_{0.9}I_2^{[1]}$  which is metallic above and insulating below

[*] Dr. L. Jongen, Dr. AV. Mudring, Prof. Dr. G. Meyer
Institut für Anorganische Chemie
Universität zu Köln
Greinstrasse 6, 50939 Köln (Germany)
Fax: (+49) 221-470-5083
E-mail: a.mudring@uni-koeln.de
gerd.meyer@uni-koeln.de

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Figure 1. Compounds in the Sc/C/I system (binary C/I and Sc/C compounds are omitted).

approximately 100 K. At low temperatures, the excess electrons (according to  $9 \times Sc_{0.89}I_2 = (Sc^{3+})_8 \Box_1(I^-)_{18}(e^-)_6$  for a hypothetical ninefold superstructure) are localized in scandium 3d states, resulting in the presence of some divalent scandium (Sc<sup>2+</sup>), as revealed by the compound's well-resolved ESR spectrum.<sup>[2]</sup> Excess electrons may also be used for Sc–Sc bonding, as evidenced by the rather short Sc–Sc distance of 328 pm in NaSc<sub>2</sub>I<sub>6</sub><sup>[3]</sup> and supported by band-structure calculations.<sup>[2,3]</sup> The Sc–Sc bonding and Sc–I antibonding interactions must be finely tuned at the Fermi level,<sup>[2]</sup> which explains the enigmatic scandium deficiencies observed not only in Sc<sub>0.9</sub>I<sub>2</sub>, but also in CsSc<sub>0.8</sub>I<sub>3</sub>, for example.<sup>[2,4]</sup>

Excess electrons may not only be delocalized, as in metallic Sc<sub>0.9</sub>I<sub>2</sub>, or localized at the atoms (Sc<sup>2+</sup>, paramagnetic) or in bonds, but may also be used by a third partner. This is, at least in a simple (ionic) model, the case in Sc<sub>4</sub>C<sub>2</sub>I<sub>6</sub> = (Sc<sup>3+</sup>)<sub>4</sub>-(C<sub>2</sub><sup>6-</sup>)(I<sup>-</sup>)<sub>6</sub>.<sup>[5]</sup> In this compound, in addition to Coulombic Sc<sup>3+</sup>–I<sup>-</sup> interactions, there are also strong covalent Sc–C and Sc–Sc interactions, as revealed by the short Sc–Sc and Sc–C distances of 302 and 200 pm, respectively. A similar picture holds for Sc<sub>6</sub>C<sub>2</sub>I<sub>11</sub>,<sup>[5]</sup> which bears one excess electron in this model.

In an attempt to produce  $Sc_6C_2I_{11}$  in pure form for physical measurements, we have now obtained  $Sc_{2.4}CI_3$ ,<sup>[6]</sup> a slightly more scandium-rich carbide iodide than  $Sc_4C_2I_6 = Sc_2CI_3$  (Figure 1).<sup>[5]</sup> The new compound is better formulated as  $Sc_{24}C_{10}I_{30}$ , as its solid-state structure is built from molecules of this composition. The large cubic unit cell (V = 16.943(3) nm<sup>3</sup> at 293 K) contains eight crystallographically equivalent  $Sc_{24}C_{10}I_{30}$  molecules.<sup>[7]</sup> As one eighth of the unit-cell volume is 2.12 nm<sup>3</sup>, and if a space filling of 70% is assumed, each molecule has a volume of 1.48 nm<sup>3</sup> and a diameter of 1.42 nm (if it were spherical).

The "nanomolecule"  $\text{Sc}_{24}\text{C}_{10}\text{I}_{30}$  has an outer envelope of 30 iodine atoms (Figure 2). A T4 supertetrahedron would consist of 35 iodine atoms (according to  $\Sigma \text{atoms} = [\frac{1}{6}(n+1)(n+2)(n+3)]$ , for a T*n* supertetrahedron, with n = 4), but as it is hollow (-1 iodine atom) and truncated at the four corners (-4 iodine atoms), there are only 30 iodine atoms in the outer shell. This truncated, hollow T4\* supertetrahedron surrounds a T3 supertetrahedron of 20 scandium atoms, which is filled



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Figure 2. Space-filling model of the  $Sc_{24}C_{10}I_{30}$  molecule. Sc blue, C black, I pink.

by a T2 supertetrahedron of 10 carbon atoms, which, in turn, is filled by a T1 tetrahedron of four scandium atoms (Figure 3). Therefore, the molecular structure of  $Sc_{24}C_{10}I_{30}$ , which can be described as  $Sc_4C_{10}Sc_{20}I_{30} = T1 + T2 + T3 + T4^*$ , is reminiscent of a Russian doll, or, in other words, the molecule has an onion-like structure.

In the  $Sc_{24}C_{10}I_{30}$  molecule, the 20 scandium atoms of the T3 supertetrahedron form 10 tetrahedra, which share common vertices and are filled with single carbon atoms. Each of the octahedral interstices of the T3 supertetrahedron





**Figure 4.** Spatial arrangement of the inner Sc<sub>4</sub> T1 tetrahedra, which are representative of the complete Sc<sub>24</sub>C<sub>10</sub>I<sub>30</sub> molecules, as viewed down the [111] direction. The similarity between the structures of Sc<sub>24</sub>C<sub>10</sub>I<sub>30</sub> and solid nitrogen is highlighted by the dashed lines, which indicate pairs of molecules, as described in the text.

interactions.

example.<sup>[11]</sup>

chalcogenide

 $Cs_8[Sn_{10}O_4S_{20}](H_2O)_{13},$ 

recently

are by no means uncommon in

although the first oxidic T5

Of course, unlike the nitrogen atoms in the  $N_2$  molecules, the  $Sc_{24}C_{10}I_{30}$  molecules are only held together by van der Waals

The  $Sc_{20}$  T3 supertetrahedron of the  $\{Sc_4C_{10}Sc_{20}\}^{30+}$  ion in its  $\{I_{30}\}^{30-}$  envelope has the same structure as the recently discovered Au<sub>20</sub> supertetrahedron.<sup>[10]</sup> A filled supertetrahedral anion was also found in

for

in

Supertetrahedra

observed

chemistry,<sup>[12]</sup>



Figure 3. Structure of the  $Sc_{24}C_{10}I_{30}$  molecule:  $Sc_4=T1$ ;  $Sc_4C_{10}=T1+T2$ ;  $Sc_4C_{10}Sc_{20}=T1+T2+T3$ ;  $Sc_4C_{10}Sc_{20}I_{30}=T1+T2+T3+T4^*$  (T4<sup>\*</sup> is the truncated, hollow T4 supertetrahedron). Sc blue, C black, I pink.

is occupied by one of the vertices of the inner Sc<sub>4</sub> T1 tetrahedron. The 10 carbon atoms have the same arrangement as the carbon atoms in adamantane (C<sub>10</sub>H<sub>16</sub>); both structures can be interpreted as fragments of the diamond lattice. They also have the same topology as the oxygen atoms in P<sub>4</sub>O<sub>10</sub>, which encapsulate a P<sub>4</sub> tetrahedron. Thus, the P<sub>4</sub>O<sub>10</sub> molecule and the Sc<sub>4</sub>C<sub>10</sub> fragment are isostructural. The shortest Sc–Sc distance in Sc<sub>24</sub>C<sub>10</sub>I<sub>30</sub> is only 276 pm, much shorter than that in Sc<sub>4</sub>C<sub>2</sub>I<sub>6</sub> (302 pm). Additionally, the Sc–C interactions of 200–210 pm in the Sc<sub>4</sub>C tetrahedra of Sc<sub>24</sub>C<sub>10</sub>I<sub>30</sub> must be regarded as strong, when compared with the Sc–C distances of approximately 230 pm observed in the Sc<sub>6</sub>C octahedra of Sc[Sc<sub>6</sub>C]I<sub>12</sub>.<sup>[8]</sup>

In the cubic unit cell ( $Pa\bar{3}$ ), the Sc<sub>24</sub>C<sub>10</sub>I<sub>30</sub> molecules are arranged in the same way as the nitrogen atoms in solid

supertetrahedron was  $Na_{26}Mn_{39}O_{55}$ .<sup>[13]</sup>

In Sc<sub>24</sub>C<sub>10</sub>I<sub>30</sub> (with C<sup>4-</sup> and I<sup>1-</sup>), scandium has an oxidation state of slightly less than +3 (+2.92), if a purely ionic model is considered. Hence, there are two excess electrons per molecule, according to  $(Sc^{3+})_{24}(C^{4-})_{10}(I^-)_{30}(e^-)_2$ . These electrons can be expected to reside in the empty Sc<sub>4</sub> tetrahedron, in analogy to the 20 electrons that occupy 10 bonding orbitals (four-center, two-electron (4c–2e) bonds) in the naked Au<sub>20</sub> cluster.<sup>[10]</sup> Indeed, extended Hückel molecular orbital (EHMO) calculations for  $\{Sc_4\}^{10+}$ , as well as for  $\{Sc_4C_{10}Sc_{20}\}^{30+}$  reveal similar bonding pictures.<sup>[14]</sup> In both cases, the HOMO is a 4c–2e orbital (Figure 5). Of course, the empty Sc<sub>4</sub> tetrahedron could also be filled with two hydrogen atoms, which would consume the two electrons. Although the

only

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**Figure 5.** The HOMOs for the {Sc<sub>4</sub>}<sup>10+</sup> tetrahedron (left) and the {Sc<sub>4</sub>C<sub>10</sub>Sc<sub>20</sub>}<sup>30+</sup> cluster (right), as well as the molecular orbital diagram for {Sc<sub>4</sub>C<sub>10</sub>Sc<sub>20</sub>}<sup>30+</sup>, obtained from EHMO calculations.

hydrogen atoms in related compounds usually occupy octahedral sites, which are displaced away from the center towards a triangular face of the octahedron, the possibility that hydrogen atoms occupy the  $Sc_4$  tetrahedron cannot be completely ruled out. However, the yield was not enhanced when hydrogen was deliberately added to the reaction, either as  $ScH_2$  or as hydrogen gas, which diffuses through the tantalum container at the chosen reaction temperature.

In the Sc/C/I system (Figure 1),  $Sc_7CI_{12} = (Sc^{3+})\{(Sc^{3+})_6 (C^{4-})(e^{-})_{5}$  (I<sup>-</sup>)<sub>12</sub>, in which single carbon atoms occupy the centers of scandium octahedra, is certainly the most stable compound.<sup>[8]</sup> In Sc<sub>6</sub>C<sub>2</sub>I<sub>11</sub> and Sc<sub>4</sub>C<sub>2</sub>I<sub>6</sub>, C<sub>2</sub> (ethanide) units occupy the scandium octahedra.<sup>[5]</sup> In  $Sc_4C_2I_6$ , the octahedra share trans edges to form chains. Every second octahedron is distorted in such a way that it can also be described as two tetrahedra sharing a common edge. As mentioned above,  $Sc_{24}C_{10}I_{30}$  is only slightly more reduced than  $Sc_4C_2I_6 =$  $Sc_{20}C_{10}I_{30}$ . Thus, it can be argued that the incorporation of an empty  $Sc_4$  tetrahedron stabilizes the  $Sc_{24}C_{10}I_{30}$  oligomer. Oligomers are rather uncommon in the chemistry of interstitially stabilized rare-earth-metal halide clusters. With scandium, the bromides  $Sc_{19}Z_4Br_{28}$  (Z = Mn, Fe, Ru, Os) are known.<sup>[15]</sup> These compounds contain the  $R_{16}Z_4X_{20}$  oligomer (R = rare-earth metal, X = halogen) first observed for  $Y_4RuI_5$ .<sup>[16]</sup> The component  $R_{16}Z_4$  cluster consists of four edge-sharing R<sub>6</sub>Z octahedra. Carbon atoms in tetrahedral interstices are known from RbPr<sub>5</sub>C<sub>2</sub>Cl<sub>10</sub>.<sup>[17]</sup> In this compound, two Pr<sub>4</sub>C tetrahedra share a common face to form a Pr<sub>5</sub> trigonal bipyramid, which encapsulates a C<sub>2</sub> unit.

The crystal structure of  $Sc_{24}C_{10}I_{30}$  consists of molecules of the same composition, which are packed in the same way as the nitrogen atoms in solid nitrogen. The molecules have an onion- or Russian-doll-like structure,  $(e^{-})_2Sc_4C_{10}Sc_{20}I_{30}$ , and contain two excess electrons, which reside in the inner  $Sc_4$  tetrahedron and occupy a 4c–2e orbital.

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- [6] Synthesis:  $Sc_{2.4}CI_3 = Sc_{24}C_{10}I_{30}$  was obtained as a by-product in an attempt to synthesize Sc<sub>6</sub>C<sub>2</sub>I<sub>11</sub>, starting from ScI<sub>3</sub>, scandium, and graphite (molar ratio 1:1:1). ScI<sub>3</sub> was synthesized from the elements and sublimed under high vacuum at 1193 K. Scandiummetal pieces and graphite were used as purchased. All starting materials and products were stored and manipulated in an argon-filled glove box (MBraun, Garching). The reaction was carried out in a sealed tantalum container, jacketed with a fusedsilica tube, at a temperature of 1123 K. After two weeks, the reaction mixture was cooled by turning off the power to the furnace. Good quality blue-black single crystals of Sc<sub>24</sub>C<sub>10</sub>I<sub>30</sub> were obtained, along with a black powder and single crystals of Sc<sub>6</sub>C<sub>2</sub>I<sub>11</sub>. X-ray powder diffraction at room temperature (transmission mode, Imaging Plate Guinier Camera G670 (Huber, Rimsting)), monochromatic  $Mo_{K\alpha}$  radiation) revealed that the product mainly consists of two phases, Sc<sub>6</sub>C<sub>2</sub>I<sub>11</sub> and  $Sc_4C_2I_6$ .  $Sc_{24}C_{10}I_{30}$  could not be detected by X-ray powder diffraction at room temperature.
- [7] Crystal data and structure refinement: A suitable single crystal  $(0.3 \times 0.2 \times 0.2 \text{ mm})$  was sealed in a glass capillary in an argonfilled glove box. Intensity data were collected at room temperature on an IPDS I diffractometer, and at 130 K on an IPDS II diffractometer (both Stoe, Darmstadt). 130(2) K: cubic, Pa3 (No. 205); a = 2551.82(5) pm, V = 16.6169(6) nm<sup>3</sup>; Z = 8,  $\rho_{calcd} =$ 4.002 g cm<sup>-3</sup>; 1.38 <  $\theta$ /° < 24.99; Mo<sub>Ka</sub> radiation ( $\lambda$  = 71.073 pm);  $F(000) = 17232; \mu = 12.973 \text{ mm}^{-1}; 139853 \text{ reflections measured},$ 4879 unique, 3997 observed; R1 = 0.0281, wR2 = 0.0654 (for  $I_0 >$  $2\sigma(I_0)$ ). 293 K: cubic,  $Pa\bar{3}$  (No. 205); a=2568.4(3) pm, V= 16.943(3) nm<sup>3</sup>; Z=8,  $\rho_{calcd}=3.925 \text{ g cm}^{-3}$ ;  $2.24 < \theta/^{\circ} < 23.85$ ; Mo<sub>Ka</sub> radiation ( $\lambda = 71.073 \text{ pm}$ ); F(000) = 17232;  $\mu =$ 12.723 mm<sup>-1</sup>; 51375 reflections measured, 4346 unique, 2331 observed; R1 = 0.0668, wR2 = 0.1378 (for  $I_0 > 2\sigma(I_0)$ ). The data were processed with the program SHELX-97 [G. M. Sheldrick, SHELX-97, Universität Göttingen, 1997]. Scattering factors were taken from: A. J. C. Wilson, International Tables for Crystallography, Vol. C, Mathematical, Physical and Chemical Tables, Kluwer, Dordrecht, The Netherlands, 1995. Numerical absorption corrections were performed after crystal-shape optimization using the programs XRED and XSHAPE [Stoe, XRED 1.01 and XSHAPE 1.01, Darmstadt, 1996]. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fizkarlsruhe.de), on quoting the depository numbers CSD-414259 (130 K) and CSD-414260 (293 K).
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Raleigh, NC, USA, **1998**.] with the following parameters (double-zeta functions):  $H_{ij}$  [eV],  $\zeta_1$ , coefficient 1,  $\zeta_2$ , coefficient 2: Sc: 4s -7.05, 1.5, 0.5172, 0.9, 0.587; 4p -3.98, 1.14, 1.0, 0.0, 0.0; 3d -8.35, 4.4, 0.359, 2.0, 0.766; C: 2s -19.66, 1.98, 0.7931, 1.24, 0.2739; 2p -10.86, 2.2, 0.2595, 0.96, 0.8026.

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