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ScY@C_{3v}(8)-C_{82}: Metal-Metal σ^2 Bond in Mixed Rare-Earth Di-metallofullerenes

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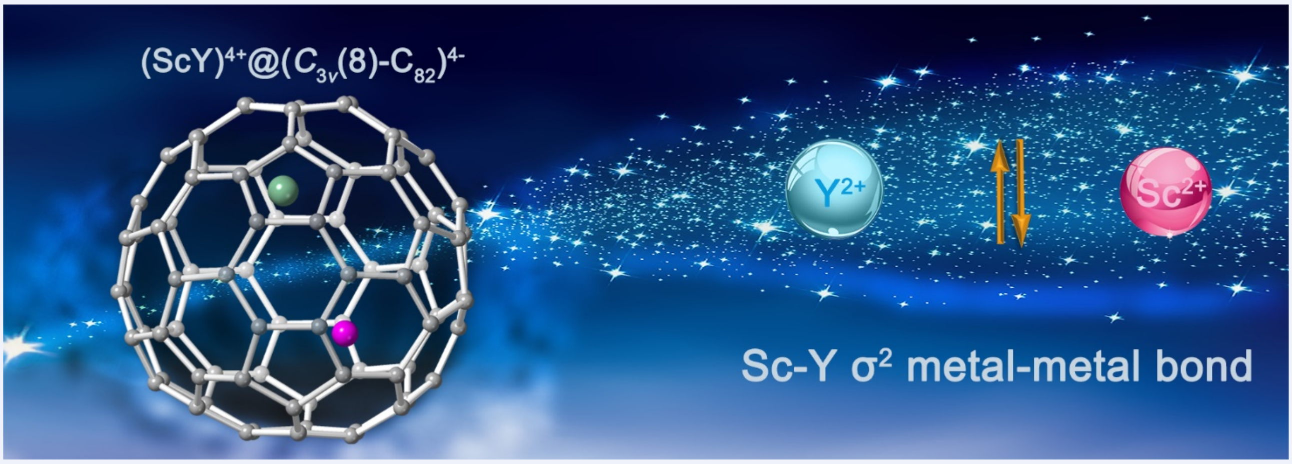
Comprehensive Summary

The experimental investigation of rare-earth metal-metal bonds remains a challenge in the study of chemical bonds. Herein, we report the synthesis and characterization of a novel heteronuclear di-metallofullerene, ScY@C_{3v}(8)-C_{82}, which contains a mixed rare-earth metal-metal bond. ScY@C_{3v}(8)-C_{82} was successfully synthesized by arc-discharging method and characterized by mass spectrometry, UV-vis-NIR spectroscopy and single-crystal X-ray diffraction crystallography, which unambiguously determined its molecular structure. Theoretical calculations were also performed to study the most likely positions of Sc-Y metallic dimer and the electronic configuration. The combined experimental and theoretical results confirmed that both Sc and Y atoms transfer two electrons to the C_{3v}(8)-C_{82} cage, i.e. $(ScY)^{4+}$@(C_{3v}(8)-$C_{82})^{4-}$. In particular a covalent Sc-Y σ^2 bond, which has never been reported before, is proven to be formed inside C_{3v}(8)-C_{82} fullerene cage. This work presents a novel di-metallofullerene containing mixed rare-earth metal-metal bond and expands the understanding of metal-metal bonding of rare earth elements.



Keywords

Fullerenes | Endohedral fullerenes | Rare earths | Chemical bond | Metal-metal bond

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Background and Originality Content

The study of metal-metal bonds has always been a focus point in the efforts of exploring chemical bonding.[1-4] The elements which can form metal-metal bond varies from the main group[5-6] to transition[7-8] and lanthanide[9-11], recently it extends to actinide[12-14] as well. To date, the majority of metal-metal bonding researches focus on the main group and transition elements.[15-17] In contrast, bonding motif investigations are relatively rare for the f-block elements as well as rare-earth metals including scandium and yttrium, as the synthesis of these metal-metal bonds remains a challenge in the traditional organometallic chemistry.[18]

Recent studies show that fullerene cage can function as a unique system to study the rare-earth metal-metal bonding motif due to its unique coordinating environment, in which the endohedral metal units co-exist with the carbon cage by proper interactions with each other. A series of di-metallofullerene derivatives and azafullerenes have been reported, including $(M_2)^{5+}@[I_h(7)\text{-}C_{80}\text{-}R]^{5-}$ (R = CH_3 or CH_2Ph, M = Sc, Y, Gd, Tb, Dy, Ho and Er)[19-23] and $(M_2)^{5+}@(C_{79}N)^{5-}$(M = Y, La, Gd, Tb and Dy).[24-26] The combined experimental and theoretical studies revealed that these di-metallofullerenes contain rare single-electron metal-metal bond between f-block elements. On the other hand, homonuclear di-metallofullerenes such as $M_2@C_{3v}(8)\text{-}C_{82}$ (M = Sc, Y, Er and Lu)[27-30] appeared to form direct covalent σ^2 metal-metal bonds, resulting in four-electron charge transfer from the metallic dimer to the fullerene cage.

To date, the existing researches mainly concentrate on the homonuclear rare-earth di-metallofullerenes and most of the metallic dimer features single-electron bonding. However, in the aspect of heteronuclear di-metallofullerenes, the bonding motif between different rare-earth metals remains largely unknown. Early studies such as $M_1M_2@C_{80}$ (M_1M_2 = LaCe, LaPr, PrSc)[31-33] just reported ^{13}C NMR analysis and no molecular structures were provided. Other studies, such as $HoM@C_{82}$(M = Tm, Ca),[34-35] $M_2@I_h(7)\text{-}C_{80}\text{-}CH_2Ph$ (M_2 = TbGd and TbY),[22] $ErSc@C_{3v}(8)\text{-}C_{82}$ and $YLu@C_{3v}(8)\text{-}C_{82}$,[36] were all lack of crystallographic analysis to explore the metal-metal bonding inside. The only heteronuclear di-metallofullerene with crystallographic analysis, i.e. $DyEr@C_{3v}(8)\text{-}C_{82}$ was reported by Wang *et al* in 2019.[37] A two-center one-electron (2c-1e) Dy-Er single bond was found in this structure.

Herein, we report that a mixed rare-earth covalent σ^2 bond was found in a heteronuclear di-metallofullerene, namely $ScY@C_{3v}(8)\text{-}C_{82}$. It was characterized by mass spectrometry, ultraviolet-visible-near-infrared (UV-vis-NIR) absorption spectroscopy and single-crystal X-ray diffraction crystallography. Theoretical calculations also analyzed the different positions of the Sc-Y dimer in the fullerene cage as well as its electronic structure and the Sc-Y bond.

Results and Discussion

Synthesis, isolation and characterization of $ScY@C_{3v}(8)\text{-}C_{82}$

Carbon soot containing $ScY@C_{82}$ was synthesized by a modified Krätschmer-Huffman DC arc-discharge method. Hollow graphite rods filled with Sc_2O_3, Y_2O_3 and graphite powder (molar ratio of Sc : Y : C = 1 : 5 : 24) were vaporized in the arcing chamber under the atmosphere of 200 Torr Helium gas. The produced carbon soot was then collected and extracted by CS_2 for 12 h at room temperature. Then, the solution containing fullerenes was analyzed by multistage high-performance liquid chromatography (HPLC) procedures combined with matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF-MS) to confirm the isolation of $ScY@C_{82}$ (see Figure S1). The purity of the isolated compound was detected by observation of single peak by HPLC and positive-ion mode of MALDI-TOF-MS, as shown in Figure 1. The mass spectrum of $ScY@C_{82}$ shows a peak at m/z = 1117.973. In addition, the experimental and theoretical isotopic distributions match well with each other.

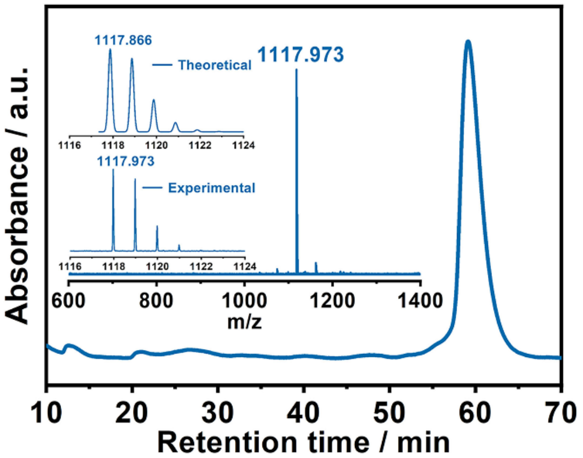

Figure 1 HPLC chromatogram of purified $ScY@C_{82}$ on the Buckyprep column with toluene as the eluent (HPLC conditions: λ = 310 nm and flow rate is 4 mL min^{-1}). The insets show the positive-ion mode MALDI-TOF mass spectrum and zoom of the experimental and theoretical isotopic distribution of $ScY@C_{82}$.

The structure of $ScY@C_{82}$ was further characterized by UV-vis-NIR absorption spectroscopy (Figure 2). UV-vis-NIR absorption is a facile method to determine the electronic structures of EMFs. The adsorption spectrum shows broad peaks at 646 and 892 nm, which are almost identical to those of $M_2@C_{3v}(8)\text{-}C_{82}$ (M = Sc, Y, Er, Lu).[27-30] This indicates that $ScY@C_{82}$ and those previously reported $C_{3v}(8)\text{-}C_{82}$ based di-EMFs have same cage isomer and electronic configuration. The encapsulated Sc and Y in $ScY@C_{3v}(8)\text{-}C_{82}$ may transfer four electrons to the $C_{3v}(8)\text{-}C_{82}$ cage and adapt low oxidation sates of Sc^{2+} and Y^{2+}.

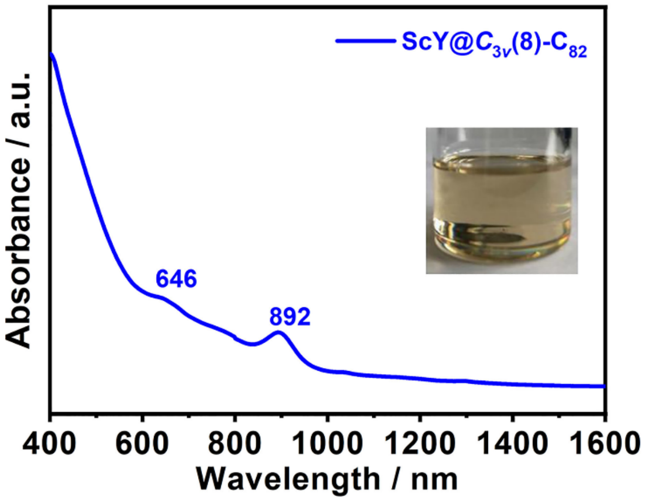

Figure 2 UV–vis–NIR adsorption spectrum of $ScY@C_{3v}(8)\text{-}C_{82}$. Inset: Photograph of the purified $ScY@C_{3v}(8)\text{-}C_{82}$ dissolved in CS_2.

Molecular and electronic structure of $ScY@C_{3v}(8)\text{-}C_{82}\cdot[Ni^{II}OEP]$

The co-crystal of $ScY@C_{82}\cdot[Ni^{II}OEP]$ was obtained by slow diffusion of benzene solution mixed with $Ni^{II}(OEP)$ (OEP = 2, 3, 7, 8, 12, 13, 17, 18-octaethylporphin dianion) into the CS_2 solution of the purified compound. The molecular structure of $ScY@C_{82}$ was unambiguously determined by single-crystal X-ray diffraction analysis and refined as $ScY@C_{3v}(8)\text{-}C_{82}\cdot[Ni^{II}(OEP)]\cdot C_6H_6$ in the monoclinic

C2/m (No. 12) space group (see details in Table S2). Figure 3 (a) shows the relationship between ScY@C_{3v}(8)-C_{82} and the co-crystallized Ni^{II}(OEP) molecule. The shortest Ni-cage distance was measured as 2.863 Å, suggesting a strong π-π interaction among them.

In the crystal of ScY@C_{3v}(8)-C_{82}, the whole molecule, including the fullerene cage and the encapsulated metallic dimer, shows two equivalent orientations with the same occupancy of 0.5. The two equivalent orientations are mirror-related due to the crystallographic mirror plane of the *C2/m* space group, as is shown in Figure S2. Inside the C_{3v}(8)-C_{82} cage, Sc ion is ordered and only two sites (Sc1 and Sc2) are observed, showing the occupancy of 0.388(3) and 0.112(3), respectively. Y ion, on the other hand, shows slight degree of disorder with four metal sites, i.e., Y1, Y2, Y3 and Y4. The total occupancy for Y1 to Y4 is 0.5. Y1 is assigned as the major Y site as it possesses a much higher occupancy of 0.261(2), compared to those of the other three sites (0.067(2), 0.086(2) and 0.086(2) for Y2-Y4, respectively). Moreover, corresponding metal sites ($Sc1_m$, $Sc2_m$, $Y1_m$, $Y2_m$, $Y3_m$ and $Y4_m$) with the same occupancy are generated via the mirror-related counterparts ascribed to the same crystallographic mirror plane (see Figure S2). Considering the previous crystallographic studies of Sc_2@C_{3v}(8)-C_{82} and Y_2@C_{3v}(8)-C_{82},[29-30] we select the major Sc and Y sites in ScY@C_{3v}(8)-C_{82} for further analysis (see Figure 3). Computational results about the metal positions inside the fullerene are commented in the following sections.

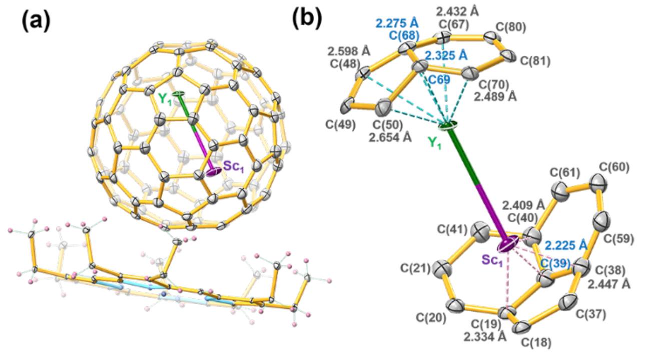

Figure 3 (a) ORTEP drawing of ScY@C_{3v}(8)-C_{82}·[Ni^{II}OEP] with 10% thermal ellipsoids. Only one cage orientation and the major Sc (Sc1 with 0.388 occupancy) and Y (Y1 with 0.261 occupancy) sites are shown. For clarity, the solvent molecules and minor metal sites are omitted. (b) Detailed structure of the encapsulated Sc1 and Y1 (major sites) interacting with the closest aromatic fragments of the C_{3v}(8)-C_{82} cage.

According to crystallographic analysis, the distance between Sc and Y (major sites) is determined to be 3.674(7) Å. This Sc-Y distance is slightly larger than the Y-Y distance (3.596 Å) and the Sc-Sc distance (3.36 Å) in M_2@C_{3v}(8)-C_{82} (M = Sc and Y). The details of metal-cage distances and metal sites in C_{3v}(8)-C_{82} cage are illustrated in Figure 4. For ScY@C_{3v}(8)-C_{82}, the Sc1 site is located near [5, 6, 6] carbon junction (at the vertex of two hexagons and one pentagon) with the shortest Sc-C distances ranging from 2.225 to 2.447 Å. The Y1 site resides close to a [5, 6] carbon bond (between a pair of adjacent pentagon and hexagon rings), with the shortest Y-C distance of 2.275 to 2.325 Å (see Figure3 (b) and Figure 4).

Figure 4 presents the molecular structures of Y_2@C_{3v}(8)-C_{82}, ScY@C_{3v}(8)-C_{82} and Sc_2@C_{3v}(8)-C_{82}, which show that the replacement of Y by Sc has a notable impact on the position of metal ion inside the same cage. It can be clearly seen that after one of the Y ions in Y_2@C_{3v}(8)-C_{82}[30] is substituted by Sc, the Sc ion in ScY@C_{3v}(8)-C_{82} prefers to locate near [5, 6, 6] carbon junction rather than the pentagon ring for Y ions in Y_2@C_{3v}(8)-C_{82}. The remaining Y site still resides close to the [5, 6] carbon bond, and the shortest Y-C distances do not change drastically (within 0.1 Å). Therefore, for Y1 sites, the metal-cage interaction appears to be identical in Y_2@C_{3v}(8)-C_{82} and ScY@C_{3v}(8)-C_{82}. Overall, the position of Sc-Y dimer inside C_{3v}(8)-C_{82} is in fact comparable to the Y-Y dimer in C_{3v}(8)-C_{82} cage, which indicates that the metal-metal interaction between Sc-Y is likely similar to that of the Y-Y, that is, it seems to be a σ^2 bond.

When the second Y ion in Y_2@C_{3v}(8)-C_{82} is replaced by Sc, i.e. in Sc_2@C_{3v}(8)-C_{82},[29] the Sc ion (Sc2 site) locates near to a [5, 6] carbon bond, which is adjacent to the [5, 6] bond the original Y ion (Y1 site) is close to (see Figure 4). Though the other Sc ion (Sc1 site) still locates near the original [5, 6, 6] carbon junction, it is slightly shifted to the adjacent [5, 6, 6] carbon junction. In general, the arrangements of metal ion positions in Y_2@C_{3v}(8)-C_{82}, ScY@C_{3v}(8)-C_{82} and Sc_2@C_{3v}(8)-C_{82} suggest that, for these di-metallofullerenes with σ^2 bonding interaction, the preferred positions of metal ions intend to facilitate both metal-metal interactions and metal-cage interactions.

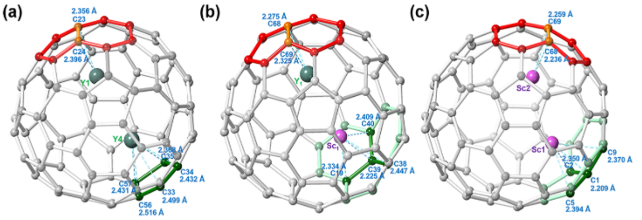

Figure 4 Molecular structures of (a) Y_2@C_{3v}(8)-C_{82}[30] (b) ScY@C_{3v}(8)-C_{82} (c) Sc_2@C_{3v}(8)-C_{82}[29]. The drawing shows the metal-cage relationships in the same perspective view. The closest metal-cage distances are labelled in blue. (Above: [5, 6] carbon bond is marked in orange and the aromatic sections around are in red. Below: [5, 6, 6] carbon junction, pentagon ring and the surrounding aromatic fragments are highlighted in green.)

Computational Analysis of ScY@C_{3v}(8)-C_{82}

To study the position and describe the Sc-Y bond inside C_{3v}(8)-C_{82} cage, DFT studies were performed (see Computational details). Several positions of the dimer inside the cage were analyzed based on the different occupations of the Sc and Y atoms in the crystal structure (Figure S5). Interestingly, all the initial positions considered led to two final positions that are degenerate within the error of the methodology (see Table 1 and a and b in Figure 5). Furthermore, when we exchange the positions of Sc and Y (a *vs* a' or b *vs* b', Figure 5) no significant changes in their energies are observed. All of these positions define an equatorial region on the C_{3v}(8)-C_{82} cage where the dimer can be located, as shown in Figure 5b, in good agreement with the disorder found for the metal positions in the X-ray structure (Figure S2). Similar results were obtained by Popov and co-workers when they simulated Y_2@C_{3v}(8)-C_{82}.[38] The degeneracy of all these positions, alongside with the C_{3v} symmetry of the cage, suggest that the Sc-Y dimer ~~has a high degree of freedom~~ can rotate inside the fullerene along this equatorial belt. The ~~rotation of the~~ Sc-Y dimer does not significantly alter the distance, ranging between 3.49 Å and 3.55 Å, when changing the position in this belt. When the dimer is aligned alongside the C_3 axis of the cage, Sc-Y distance is enlarged leading to a far less stable structure (see Table 1). This is probably due to a larger space in the cage along this axis, thus the stronger metal-cage interaction does not allow for a full metal-metal interaction. It is remarkable that the Sc-Y initial distances of around 3.2 Å are always enlarged by around 0.3 Å during the geometry optimization process.

The Sc-Y metallic unit presents 6 valence electrons, of which 4 are transferred to the C_{3v}(8)-C_{82} cage. This leaves 2 electrons that occupy a metal-metal σ orbital (see Figure 6 and Figure S6), which allows to describe the bond in the Sc–Y heterodimer in a very similar way as Sc–Sc and Y–Y homodimers inside the same C_{3v}(8)-C_{82} cage (see Figure S7). The system shows a spin singlet ground state, leaving the triplet state 14.1 kcal/mol above it, in the best case scenario, which corresponds to the Sc-Y dimer aligned with the C_3 axis.

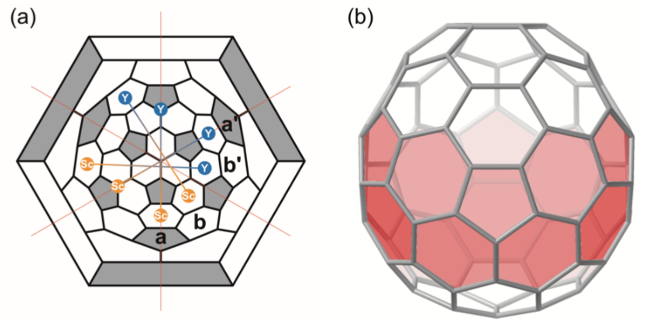

Figure 5 (a) Schlegel diagram with computed positions for the inner dimer of ScY@C_{3v}(8)-C_{82}. Positions a/b and a'/b' are equivalent but the positions of Sc and Y are exchanged. (b) Highlighted equatorial region of C_{3v}(8)-C_{82} ~~for the stabilization of~~ that corresponds to the lowest-energy positions of the Sc-Y dimer inside the cage.

Table 1 Relative energies, most representative distances and bond parameters for different positions of Sc-Y dimer in ScY@C_{3v}(8)-C_{82}.[a]

Position	Spin state	ΔE	Sc-Y	Sc-C[b]	Y-C[b]	ρ_{bcp}[c]	∇^2_{bcp}[d]
a	Singlet	0.5	3.548	2.31	2.49	0.18	-0.24
a'	Singlet	0.0	3.550	2.30	2.50	0.18	-0.29
b	Singlet	0.7	3.510	2.31	2.52	0.19	-0.31
b'	Singlet	0.7	3.487	2.29	2.54	0.19	-0.23
C_3	Triplet	14.7	4.308	2.27	2.46	0.08	-0.15

[a] Energies in kcal·mol^{-1} and distances in Å. [b] Average distances. [c] Electronic density in e·Å^{-3}. [d] Laplacian of the density in e·Å^{-5}.

In this triplet state, the Sc-Y distance is enlarged to 4.31 Å and only one electron occupies the metal-metal σ orbital (the other unpaired electron is now occupying a cage orbital). For all the different positions of the inner dimer in ScY@C_{3v}(8)-C_{82}, we have found that a bond critical point (BCP) is present in between the two metal atoms according to Quantum Theory of Atoms in Molecules (QTAIM) theory.[39] Bader postulated that the presence of a BCP between two atoms is a necessary and sufficient criterion for the atoms to be bonded. The values of the density at the BCP and its Laplacian are rather similar for the singlet states, but significantly lower for the triplet state with only one bonding electron (Table 1). Table 2 shows a comparison of Sc-Y, Sc-Sc and Y-Y computed bond parameters inside C_{3v}(8)-C_{82}. Y-C distances are somewhat larger than Sc-C ones in line with the different size of the metal ions. Consequently, the Y-Y and Y-Sc distances are slightly smaller than Sc-Sc ones. The densities at BCP are rather similar for the three systems, but the Laplacian for the heterodimer is somewhat smaller. Delocalization indices, δ(A,B), which provide a quantitative measure of the degree of electron sharing between the atoms A and B, have been proposed as a measure of bond order.[40] A value of δ(Sc,Y) = 0.610 is found for the Sc-Y heterodimer, which is very similar to those found for the Sc-Sc and Y-Y homodimers (see Table 2). The values obtained for Y_2@C_{3v}(8)-C_{82} are consistent with those previously presented in the literature using slightly different computational settings.[41]

Table 2 Comparison of representative distances and Bader bond parameters for ScY@C_{3v}(8)-C_{82}, Sc_2@C_{3v}(8)-C_{82} and Y_2@C_{3v}(8)-C_{82}.[a]

Dimer	A-B	A-C[b]	B-C[b]	ρ_{bcp}[c]	∇^2_{bcp}[d]	δ(A,B)	Ref
Sc-Y	3.550	2.30	2.50	0.18	-0.29	0.610	This work
Sc-Sc	3.576	2.30	2.35	0.17	-0.40	0.684	This work
Y-Y	3.544	2.46	2.51	0.19	-0.43	0.641	This work
Y-Y	3.656			0.19	-0.32	0.629	[41]

[a] Distances in Å. [b] Average distances. [c] Electronic density in e·Å^{-3}. [d] Laplacian of the density in e·Å^{-5}.

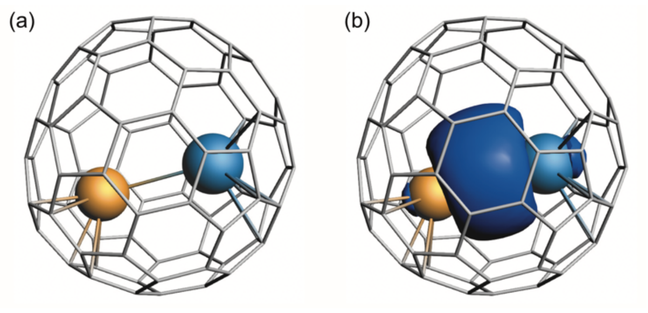

Figure 6 (a) Computed structure of ScY@C_{3v}(8)-C_{82}. (b) Metal-metal bonding orbital in ScY@C_{3v}(8)-C_{82}.

Table 3 Relative energies and representative distances for different positions of the dimer in ScY@C_{3v}(8)-C_{82} considering the nearest porphyrin ring.[a]

Position	Spin state	ΔE	Sc-Y	Sc-C[b]	Y-C[b]
a	Singlet	0.5	3.566	2.29	2.50
a'	Singlet	0.3	3.485	2.29	2.51
b	Singlet	0.0	3.530	2.30	2.53
b'	Singlet	0.0	3.489	2.30	2.54

[a] Energies in kcal·mol^{-1} and distances in Å. [b] Average distances.

Besides, the effect of the porphyrin on the position of the Sc-Y dimer was also analyzed. The porphyrin plane stablishes π-π interactions with the cage with a certain angle with its C_3 axis, near its sumanene pattern (see Figure S8). The effect of the porphyrin upon the position of the Sc-Y dimer inside the cage seems minimal (see Table 3). The previously obtained results of the Sc-Y dimer along the equatorial region of low-energy positions are maintained when considering the porphyrin.

Conclusions

In summary, a novel heteronuclear di-metallofullerene, ScY@C_{3v}(8)-C_{82} was successfully synthesized and characterized by mass spectrometry, UV-vis-NIR spectroscopy, single-crystal X-ray diffraction crystallography and theoretical calculations as well. The experimental and computational studies revealed that there is a formal transfer of four electrons from the Sc-Y dimer to the C_{3v}(8)-C_{82} cage, i.e. $(ScY)^{4+}$@$(C_{3v}(8)\text{-}C_{82})^{4-}$ and, therefore, the existence of a mixed rare-earth Sc-Y σ^2 bond inside the cage. Furthermore, the values of densities at bond critical point and the delocalization indices calculated according to QTAIM theory show very similar values in comparison with M_2@C_{3v}(8)-C_{82} (M = Y, Sc) homodimers, thus confirming an analogous σ^2 metal-metal bond. In addition, DFT calculations found that the effect of the porphyrin upon the position of the Sc-Y dimer seems minimal. This work presents, to our best knowledge, the first mixed rare-earth metal-metal σ^2 bonding motif in a molecular compound, which not only expands the family of heteronuclear di-metallofullerenes, but also, more importantly, provides new understanding for the f-block metal-metal bonds.

Experimental

Spectroscopic study

The positive-ion mode matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) (Bruker, Germany) was employed for the mass characterization. The UV-vis-NIR spectra of the purified ScY@C_{82} was measured in CS_2 solution with a Cary 5000 UV-vis-NIR spectrophotometer (Agilent, USA).

X-ray Crystallographic Study

The black block crystals of ScY@C_{3v}(8)-C_{82} were obtained by slow diffusion of the CS_2 solution of the metallofullerene compound into the benzene solution of [Ni^{II}(OEP)]. Single-crystal X-ray data of ScY@C_{3v}(8)-C_{82} was collected at 120 K on a diffractometer (Bruker D8 Venture) equipped with a CCD collector. The multiscan method was used for absorption correction. The structure was solved using direct methods[42] and refined on F^2 using full-matrix least-squares using the SHELXL2015 crystallographic software packages.[43] Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters. CCDC-2238278 (ScY@C_{3v}(8)-C_{82}) contains the supplementary crystallographic data for this article. Details of crystallographic data can be found in Supplementary information (Table S2).

Computational details

DFT calculations were carried out with the ADF 2019 package[44] using PBE0 exchange-correlation functional in combination with Slater triple-ζ polarization (TZP) basis set quality.[45-47] Frozen cores were described by means of single Slater functions, consisting of shell 1s for C, and of 1s to 3p for Sc, of 1s to 4p for Y. Scalar relativistic corrections were included by means of the ZORA formalism. Dispersion corrections by Grimme were also included.[48] A data set collection of computational results is available in the ioChem-BD repository and can be accessed via https://doi.org/10.19061/iochem-bd-2-60.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2021xxxxx.

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Entry for the Table of Contents

ScY@C_{3v}(8)-C_{82}: Metal-Metal σ^2 Bond in Mixed Rare-Earth Di-metallofullerenes

Lihao Zheng,[a] Yannick Roselló,[b] Yingjing Yan,[a] Yang-Rong Yao,[a] Xiaolin Fan,[a] Josep M. Poblet,[b] Antonio Rodríguez-Fortea*,[b] and Ning Chen*,[a]

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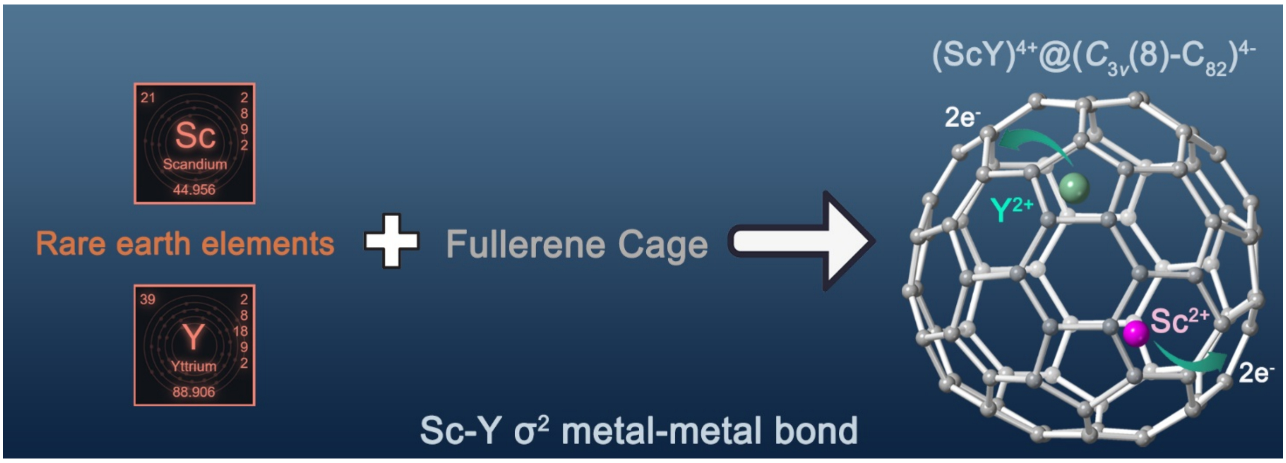

A heteronuclear di-metallofullerene, ScY@C_{3v}(8)-C_{82}, which contains a mixed rare-earth metal-metal bond, was successfully synthesized and characterized. The combined experimental and theoretical results confirm that both Sc and Y atoms transfer two electrons to the C_{3v}(8)-C_{82} cage. In particular, a covalent Sc-Y σ^2 bond, which has never been reported before, is proven to be formed inside C_{3v}(8)-C_{82} fullerene cage.