High blocking temperatures for DyScS endohedral fullerene single-molecule magnets

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Single molecule magnetic behavior of DyScS@C₅(6)-C₈₂ and DyScS@C₃ᵥ(8)-C₈₂ : Comparison with the Dy₂S analogues

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Abstract: Dy-based single-molecule magnets (SMMs) are of great interest due to their ability to exhibit very large thermal barriers to relaxation and therefore high blocking temperatures. One interesting line of investigation is Dy-encapsulating endohedral clusterfullerenes, in which a carbon cage protects magnetic Dy³⁺ ions against decoherence by environmental noise and allows for stabilization of bonding and magnetic interactions that would be difficult to achieve in other molecular architectures. Recent studies of such materials have focused on clusters with two Dy atoms, since ferromagnetic exchange between Dy atoms is known to reduce the rate of magnetic relaxation via quantum tunneling. Here, two new dysprosium-containing mixed-metallic sulfide clusterfullerenes, DyScS@C₅(6)-C₈₂, and DyScS@C₃ᵥ(8)-C₈₂, have been successfully synthesized, isolated, and characterized by mass spectrometry, Vis-NIR, cyclic voltammetry, single crystal X-ray diffraction, and magnetic measurements. Crystallographic analyses and redox potential values show that the deformation of the encapsulated cluster inside the fullerene cages is notably different than in the DyₓX@Cᵥ(6)-C₈₂ and DyₓX@Cᵥ(8)-C₈₂ (X = S, O). Remarkably, both isomers of DyScS@C₈₂ show open magnetic hysteresis and slow magnetic relaxation, even at zero field. Their magnetic blocking temperatures are around 7.3 K, which are among the highest values reported for clusterfullerene SMMs. The SMM properties of DyScS@C₈₂ far outperform those of the dilanthanide analogues Dy₇S@C₈₂, in contrast to the trend observed for carbide and nitride Dy clusterfullerenes.

Introduction

Given the high thermal barriers to relaxation observed in Dy-based EMFs, one may expect very high magnetic blocking temperatures and extremely long magnetic lifetimes at low temperatures. However, in most cases, the practical performance of a SMM is ultimately limited by through-barrier relaxation processes including quantum tunneling of magnetization (QTM), which compromises the magnetic relaxation lifetimes to plateau at low temperatures. Finding ways to limit QTM...
is therefore of the utmost importance in the search for
higher-performing SMMs. One promising approach is to
introduce ferromagnetic exchange between two
magnetic ions, as was demonstrated in the di-lanthanide
clusterfullerene Dy$_2$ScN@C$_{80}$. Compared to DySc$_2$N@C$_{80}$,
this compound was shown to exhibit suppressed QTM and a
higher blocking temperature $T_B = 8$ K. For this
reason, most of the recent work on EMF SMMs has been
focusing on systems with two Dy atoms, such as
Dy$_2$Sc$_3$C$_{4}(6)$-C$_{80}$, Dy$_2$Sc$_3$C$_{4}(8)$-C$_{80}$, Dy$_2$O$_2$C$_{3}(6)$-C$_{80}$,
Dy$_2$O$_2$C$_{3}(8)$-C$_{80}$, Dy$_2$O$_2$C$_{3}(9)$-C$_{80}$, Dy$_2$Sc$_3$C$_{4}(6)$-C$_{80}$,
Dy$_2$SiC$_3$O$_3$(7)-C$_{80}$ and Dy$_2$TiC$_3$O$_3$(7)-C$_{80}$. The most successful
implementation of this strategy has been in pure
dimetallofullerenes, such as Dy$_2$@C$_{60}$, which hosts strong Dy-Dy ferromagnetic exchange along a
radical Dy-Dy bond, leading to remarkable SMM
behavior with $T_B = 18$ K.$^{[13]}$

However, suppression of QTM is also possible in
single lanthanide compounds, if the magnetic ion is in a
highly symmetric environment. In fact, in non-EMF SMMs, this approach has proven to result in the highest-performing SMMs.$^{[3, 14-18]}$ A computational study focusing on hypothetical monolanthanide oxide clusterfullerenes
DyXO$_2$@C$_{60}$ ($X =$ Sc, Lu) has suggested that the Dy ligand field in these compounds, composed of oxygen and carbon from the fullerene, should provide a suitably symmetric environment to yield large thermal barriers to relaxation while simultaneously suppressing quantum tunneling.$^{[19]}$ However, while Dy$_2$O$_2$@C$_{80}$
and Dy$_2$Sc$_2$O$_2$ have been experimentally studied, their
mon-lanthanide analogues have not.

In this study, we report the synthesis, isolation, structural characterization and SMM properties of new
mixed metallic dysprosium-based sulfide clusterfullerenes, DySc$_2$S@C$_{80}$ and DySc$_2$S@C$_{82}$. Both crystallographic analyses and electronic studies show that the replacement of one Dy by Sc exerts a noticeable influence on the conformation of the encapsulated cluster inside the fullerene cages. Remarkably, both isomers show open magnetic hysteresis loops at temperatures below 7 K, indicating SMM behavior. The magnetic blocking temperatures for both isomers are around $T_B = 7.3$ K, much lower than for sulfur-ligated SMMs.$^{[20, 22]}$ and among the highest temperatures reported for a
pristine EMF. Of particular note, this $T_B$ far exceeds that of Dy$_2$S@C$_{82}$ ($T_B = 2$ K) to our knowledge. Analysis of magnetic relaxation times at zero-field and under a moderate
magnetic field suggests the presence of some degree of
QTM at zero-field; nonetheless, the lifetimes are found to
be much longer than those of Dy$_2$S@C$_{82}$, even at zero field. This result points to the promise of mono-
dysprosium clusterfullerenes to achieve excellent SMM behavior.

### Results and Discussion

#### Preparation, purification and spectroscopic characterizations of DySc$_2$S@C$_{82}$

Generally, the dimetallic sulfide clusterfullerenes
were prepared via two synthetic methods. Dunsch et al.
introduced the sulfur source using solid guanidinium thiocyanate (CH$_3$N$_2$HSCN), in addition to graphite powder.$^{[23]}$ Using this method, only one isomer of Sc$_2$S@C$_{82}$ was obtained as a minor product along
with major products of Sc$_2$N@C$_{82}$ and Sc$_2$N@C$_{78}$. Our
group introduced SO$_2$ as the sulfur source to produce
SCFs as major products with a few minor products, such as oxide cluster metallofullerenes (OCFs).$^{[24-26]}$ In order to produce mixed-metallic sulfide clusterfullerenes, soots containing DySc$_2$S@C$_{80}$ were produced by a modified direct current and discharge method.$^{[27]}$ As source material, Dy$_2$O$_2$, Sc$_2$O$_3$ and graphite powder were mixed in a weight ratio of 2:1:3, and packed in graphite rods. The arc synthesis was carried out under
210 torr He and 20 torr SO$_2$ as the source of sulfur. The soot was then Soxhlet extracted with CS$_2$ for 12 hours.
As shown in Figure 1, DySc$_2$S@C$_{82}$ and DySc$_2$S@C$_{84}$ were obtained along with a family of Sc$_2$S@C$_n$ (2n = 82-90). The experience of Sc$_2$S@C$_{80}$ is attributed to the presence of a small lead compound. Similar to the previously reported results with NH$_3$, the formation of empty
fullerenes was largely suppressed and a relatively high selectivity in the production of sulfide clusterfullerenes was observed with SO$_2$. Multistage HPLC separation procedures were employed to isolate and purify them (see Figures S1-S3, Supporting Information). The purity of the isolated DySc$_2$S@C$_{82}$ (I, II) were established by HPLC and MALDI-TOF mass spectrometry (Figure 1B, Supporting Information). Both compounds are reasonably pure although slight impurities of Sc$_2$S@C$_{82}$ are still observed due to their very similar retention times.

![Figure 1. MALDI-TOF spectra of the extract showing the existence of DySc$_2$S@C$_n$ (2n = 82, 84) and a family of Sc$_2$S@C$_n$ (2n = 82-90).](image-url)
The distribution of the metal-sulfide bond lengths in the DyScS cluster due to the possible different electron densities at those positions are highlighted in orange. The second major orientation, which is shown in blue, is modeled with Sc2/Dy2A (with fractional occupancy of 0.24), Dy3/Sc3A (with fractional occupancy of 0.38) and S2S (with fractional occupancy of 0.31) (Figure 3a). Note that both orientations of the DyScS cluster in DyScS@C6 are analogous to that of the C8@C6 @ fullerene.

For DyScS@C8, there are fourteen sites for the Dy20 atom (including the metal positions generated by the crystallographic mirror plane). Two sites are found for the sulfide atom, and both of them reside on the crystallographic mirror plane. The multiple positions for Dy/Sc atoms indicate that the DyScS cluster tends to move more freely in the C8@C6 cage compared to the motion in the C6@C6 cage, because the cage carbon signals are averaged to give an apparent C8 symmetry to the fullerene. Similar internal dynamic behavior for Sc2 and M2@C8 analogous to that of the Sc2 and M2@C6 cage previously.

The disordered positions of the DyScS cluster in DyScS@C8 are shown in Figure S7 (Supporting Information). The major orientation of the DyScS cluster, which is modeled with Sc2/Dy2A (with fractional occupancy of 0.18), Dy1/Sc1A (with fractional occupancy of 0.28) and S1S (with fractional occupancy of 0.34), is highlighted in orange, as shown in Figure 3b. This configuration is analogous to the major site of the Sc8 cluster in Sc8@C6, as well as the major site of the Dy8 cluster in Dy8@C6. It’s worth noting that the Sc1i/1A1i site (with fractional occupancy of 0.14) shows almost identical occupancies with respect to Sc2/Dy2A (with fractional occupancy of 0.18). Thus, it’s reasonable to assign the DyScS cluster involving Sc1/Dy1A (with fractional occupancy of 0.14), Dy2/Sc2A (with fractional occupancy of 0.14) and S1S (with fractional occupancy of 0.34) to the second major orientation considering their occupancies and the bonding distances (Figure 3b). Both orientations share a common sulfide. This result is in agreement with the previous study that showed that two major crystallographic Dy@X sites exist for Dy2@C8 (X = S, O),[9,10] DFT calculations for Dy2@C8 also confirmed that the two most stable conformers are almost isoenergetic within 0.2 kJ mol−1.[9]
ligand field. Of particular interest of are the short metal-sulfur bond lengths of 2.15 Å to 2.50 Å, which is expected to result in a strong axial field and therefore large single-ion anisotropy. As has been seen in other Dy-based EMFs. For comparison, we searched the Cambridge Structural Database (CSD) for any molecules reporting Dy-S bonds (57 structures with 194 Dy-S bonds) and plotted the bond distances as a histogram (Figure 4). The median bond length is found to be 2.82 Å, and nearly all lengths are greater than 2.60 Å, significantly larger than Dy-S bonds in DyScS@C62. The only exceptions are Dy-S bonds with Dy-S lengths between 2.4 Å and 2.5 Å, and a coordination polymer with a Dy-S length of 2.98 Å. From this analysis, it is evident that the fullerene cage in DyScS@C62 stabilizes Dy-S bonds that are far shorter than typical. A similar analysis was recently performed for Dy-O@C62, where short Dy-O bond lengths stabilized by the fullerene cage were found to result in a very large anisotropy barrier (predicted to be on the order of 1400 cm–1) and good SMM performance.

Furthermore, a computational study of the hypothetical EMFs DyScO@C82, which are oxide analogues of the presently studied EMFs, concluded that the predicted local environments of Dy coordinated by oxygen and carbon, which are similar to the local environments we observe in DyScS@C62, are of sufficiently high symmetry to quench QTM up to the third excited states. Therefore, both isomers of DyScS@C62 appear to possess structures well-suited for establishing large thermal barriers to relaxation while also suppressing QTM.

**Figure 3.** Perspective drawings show (a) the predominant sites of the DyScS cluster in DyScS@C3(6)-C62 and DyScS@C3(8)-C62, respectively. Interestingly, the Dy-S-Sc angle varies from 105.5°/107.8° in DyScS@C3(6)-C62 to 84.1°/85.7° in DyScS@C3(8)-C62. In other words, the DyScS cluster is much less compressed in DyScS@C3(6)-C62 than in DyScS@C3(8)-C62. Different cluster shapes within isomeric cages were also reported for other Sc-based cluster fullerenes. For example, the Sc-S-Sc angle for ScS@C3(6)-C62 (156.6°) is also larger than that reported for ScS@O@C3(8)-C62 (131°) (see Table S1, Supporting Information). Undoubtedly, the cage structure plays an important role on the endohedral cluster shape. However, if a cluster contains more metal ions, the dimetallic cluster shape in different isomers is much less flexible. For example, the DyScS cluster exhibits almost identical Dy-S bond lengths and cluster geometry in DyS@C3(6)-C62 and in DyS@C3(8)-C62 (94.4°). Similarly, the Dy-O angle of the major cluster in DyO@C3(6)-C62 (138.8°) is comparable to that in DyO@C3(8)-C62 (139°) (see Table S1, Supporting Information). Thus, cage structures and metal ion sizes exert critical effects on the conformations of the clusters. Moreover, the electrochemical results also confirmed that the substitution of the metal in the metal cluster exerts a noticeable influence on their electrochemical behavior (Figure S8 and Table S2, Supporting Information).

**Figure 4.** Histogram of Dy-S bond lengths reported in the Cambridge Structural Database (CSD). The orange rectangle shows the range of Dy-S bond lengths observed in the two isomers of DyScS@C62.

**SMM Properties for DyScS@C3(6)-C62 and DyScS@C3(8)-C62**

Both isomers of DyScS@C62 show slow magnetic behavior at low temperature. Figure 5 shows the magnetic hysteresis loops taken while slowly ramping the field (2.5 mT sec–1) at 2 K. Both compounds show broad, open loops with a typical “waist-restricted” shape that is characteristic of many SMMs. In these compounds, the widest hysteresis is seen at moderate magnetic fields, where quantum tunneling relaxation is suppressed and magnetic relaxation is at its slowest.
blocking temperatures reported for lanthanide-nonmetal DyScS@C, virtually identical for the two isomers (7.33 K), as shown in Figure 5, inset. The magnetic blocking temperature at a temperature sweep rate of 5 K under zero-field-cooled (ZFC) and field-cooled (FC) conditions, in each case taken upon warming at a rate of 5 K min⁻¹ under an applied field of 0.3 T. Both isomers also show irreversibility in magnetization, both isomers also show irreversibility in magnetization. The main panel shows magnetic hysteresis loops taken at 2 K with a slow field sweep rate of 2.5 mT sec⁻¹. The transition behavior of the two isomers shows very similar hysteretic behavior, subtle differences may be seen. In particular, the hysteresis loop of DyScS@C(8)-C₃ shows slightly more waist-restriction near zero field. As with all SMMs, the magnetic lifetime than DyScS@C(6)-C₃, this suggests that, under a magnetic field, the waist restriction is considerably reduced or even eliminated. Near H = 7 T, the loops narrow considerably as quantum tunneling becomes active and increases the rate of magnetic relaxation in these compounds. In particular, dysprosium nitride clusters, where isotopes of dysprosium sit in the two extremes, with a moderate degree of ferromagnetic exchange suppressed quantum tunneling. Most notably, DyScS@C(6)-C₃ outperforms the monolanthane analogues DyN@C₆ while that DyScS@C(8)-C₃ shows slightly broader hysteresis behavior. However, theblocking temperature reported for lanthanide-nonmetal, with the field is swept at a rate of 10 mT sec⁻¹. The coercive field (Hₑ) for each isomer is plotted at 5 K vs. temperature (Figure 6a and 6b). At the field-sweep rate used for this experiment (10 mT sec⁻¹), the coercive field for DyScS@C(6)-C₃ and T = 7 K, we then turn to measurements of the magnetic relaxation dynamics. Characteristic magnetic relaxation times as a function of temperature are typically collected using DC saturation-relaxation experiments, as shown in Figure 7. In these experiments, a field of 5 T is applied to the sample at a fixed temperature, and then rapidly ramped down to either 0 T or 0.3 T. Once the target field is hit, the DC magnetization is monitored as a function of time. The resulting decay in magnetization is fit to a model to extract a magnetic lifetime for the given temperature and magnetic field. The decay curves were also fit to a single-exponential function to extract a magnetic lifetime for the given temperature and magnetic field. The decay curves were also fit to a single-exponential function to extract a magnetic lifetime for the given temperature and magnetic field. The decay curves were also fit to a single-exponential function to extract a magnetic lifetime for the given temperature and magnetic field.
Based on the waist-restricted shapes of the magnetic hysteresis loops, the application of a moderate magnetic field is expected to suppress quantum tunneling relaxation and therefore limit in longer magnetic lifetimes. Indeed, this behavior is observed for both isomers of DyScS@C₆, with longer magnetic relaxation times on the order of minutes for the zero-field data, and hours for the 0.3 T data. Interestingly, this effect is more pronounced for DyScS@C₆(6)-C₆ than for DyScS@C₆(8)-C₆, as predicted by the former’s greater degree of waist-restriction seen in the hysteresis loops. At zero field, DyScS@C₆(8)-C₆ shows faster relaxation than DyScS@C₆(6)-C₆ by about an order of magnitude; under a 0.3 T field, the trend is reversed.

Typically, the only active relaxation in SMMs is fit with the Orbach equation, according to:

\[ \tau = \tau_0 \exp \left( \frac{-U_{\text{eff}}}{k_B T} \right) \]  

(1)

Where \( U_{\text{eff}} \) is the effective energy barrier to thermal relaxation, \( \tau_0^{-1} \) is the attempt frequency, and \( k_B T \) is the Boltzmann constant times the temperature. However, this linear relation, in general, only fits at high temperatures where other relaxation mechanisms are not active. Without high-temperature relaxation data from AC susceptibility measurements, it is difficult to draw definite conclusions about the mechanisms for the observed magnetic relaxations. In these compounds, the thermal Orbach barrier to relaxation based on the magnetic anisotropy would be expected to be on the order of several hundred K based on results from other Dy-based EMFs. How these barriers cannot be fit with the present data, QTM relaxation is in principle temperature-independent and therefore at 0T it would be expected to plateau as the temperature is decreased. In our 0T data, however, a definite temperature-dependence of the relaxation times is observed down to the lowest temperature measured. Given that the field-dependence of the relaxation times and the waist-restricted hysteresis loops indicate that QTM is present and active, without high-temperature relaxation data to Orbach processes yielded barriers between 3 K and 14 K and \( \tau_0 \) between 2 s and 11 s (Figure S15 and Table S8, Supporting Information).

Once again, it is of interest to compare the SMM performance of DyScS@C₆ to those of DyS@C₆, which were reported to display a non-waist-restricted hysteresis loop consistent with suppressed quantum tunneling of magnetization due to Dy-Dy ferromagnetic exchange. Interestingly, even though DyScS@C₆ does not display such a complete suppression of tunneling, its magnetic relaxation times far exceed those of DyS@C₆, even at zero field. At 1.8 K, the C₆ and C₈ isomers of DyScS@C₆ show zero-field magnetic lifetimes around 10 s and 100 s, respectively. For DyScS@C₆, these lifetimes are 1390(40) s and 150(1) s, respectively. Application of a 0.3 T magnetic field further increases these values up to 1.202(1)×10⁴ s and ∼5×10⁴ s, respectively. For the same isomers of DyS@C₆, the lifetimes are long at 1.8 K in zero field (10⁴ s to 10⁶ s), but are suppressed by the application of moderate magnetic fields.

The difference in behavior between DyScS@C₆ and DyS@C₆ may be rationalized on the basis of the Dy-Dy exchange interaction in DyS@C₆. Even though the ferromagnetic Dy-Dy interaction seems to suppress quantum tunneling, the overall observed relaxation times still plateau as temperature is decreased. This behavior can be explained by the fact that the exchange interaction is weak in di-lanthanide clusters, leading to low-lying excited exchange states. As a result, low-energy Orbach processes, with barriers 15.2 K (C₆(6)-C₆) and 6.5 K (C₆(8)-C₆), dominate the relaxation at low temperatures in DyS@C₆. DyScS@C₆ has no such ferromagnetic exchange. Therefore, QTM is not as completely suppressed, but the exchange relaxation pathway is not available. Therefore, changing from mono-lanthanide to di-lanthanide clusters represents a tradeoff. In some Dy-based EMFs, the tradeoff of exchange relaxation for QTM suppression results in better performance for the dilanthanide. In the Dy
sulfide clusters, however, the monolanthanide evidently far outperforms the dilanthanide.

Conclusion

In this work, two new dysprosium-containing mixed dimetallic sulfide clusterfullerenes, namely, DyScS@C_{62} (I, II), have been successfully synthesized and characterized by mass spectrometry, Vis-NIR, cyclic voltammetry, single crystal X-ray diffractionometry, and magnetic measurements. Crystallographic analyses revealed that DyScS@C_{62} (I, II) possess C_{6}(6)-C_{62} and C_{8}(8)-C_{62} cages, respectively. Notably, the metal ion size of the cluster exhibits a critical effect on the conformation of the cluster in the fullerene cages. Results from redox potentials also show that replacement of the metal in the metal cluster exerts a noticeable influence on their electrochemical behavior. Both isomers of DyScS@C_{62} are found to show very similar single molecule magnetic behavior with open hysteresis loops at low-temperature. The magnetic blocking temperatures and magnetic lifetimes far exceed those for the dimetallic sulfide EMF, Dy S@C_{62}. This result underlines the promise of ECFs with single Dy atoms and short metal-nonmetal contacts. Therefore, the (so far unreported) compound DyScO@C_{62} may be expected to perform very well as a SMM. Furthermore, a recent report has shown that the identity of the diamagnetic metal in a Dy cluster can have a large impact on the SMM properties, so the full series of compounds DyMX@C_{62} (M = Y, Sc, Lu; X = O, S) is a fruitful research direction.

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