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Ratcheting Rotation or Speedy Spinning: EPR and Dynamics of $\text{Sc}_3\text{C}_2@C_{80}$ [†]

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Besides their technological applications, endohedral fullerenes provide ideal conditions for investigating molecular dynamics in restricted geometries. A representative of this class of systems, $\text{Sc}_3\text{C}_2@C_{80}$ displays complex intramolecular dynamics. The motion of the ^{45}Sc trimer has a remarkable effect on its electron paramagnetic resonance (EPR) spectrum, which changes from a symmetric 22-peak pattern at high temperature to a single broad lineshape at low temperature. The scandium trimer consists of two equivalent and one inequivalent metal atom, due to the carbon dimer rocking through the Sc_3 triangle. We demonstrate through first-principles molecular dynamics (MD), EPR parameter tensor averaging, and spectral modelling that, at high temperatures, three-dimensional movement of the enclosed Sc_3C_2 moiety takes place, which renders the metal centers equivalent and their magnetic parameters effectively isotropic. In contrast, at low temperatures the dynamics becomes restricted to two dimensions within the equatorial belt of the I_h symmetric C_{80} host fullerene. This restores the inequivalence of the scandium centers and causes their anisotropic hyperfine couplings to broaden the experimental spectrum.

Endohedral metallofullerenes¹ have attracted wide interest due to their properties² and applications^{3,4}, e.g., as radiotracers⁵ and contrast agents^{6,7}. Part of what makes endohedral fullerenes special is the ability of the enclosed moiety to move, e.g., rotate inside the cage^{8–10}. In paramagnetic systems, such dynamics can be studied by electron paramagnetic resonance (EPR). The first trimetallic endohedral fullerene $\text{Sc}_3\text{C}_2@C_{80}$ ^{11,12} (see xyz-file of the equilibrium structure in the ESI[†]) displays a curiously temperature-dependent EPR spectrum, a behaviour which has been attributed to the dynamics of the cage and its endohedral moiety^{13–16} using simple models assuming equivalent metal centers and either effectively isotropic or axial hyperfine tensors¹⁶. In an earlier first-principles theoretical study¹⁷ by some of the present authors, short MD simulations gave rudimentary support to the idea that the enclosed scandium trimer ratchets¹⁸ between the adjacent C_6 rings of the equatorial belt of the cage, in a 2D planar motion. The present study takes the computational investigation to an entirely different level by combining longer MD simulations and first-principles EPR calculations at both high and low temperature, providing new insight into the relationship between the temperature, dynamics, and the observed EPR spectra of the enclosed ^{45}Sc trimer. Based on the results, the validity of the previous assumptions and models of the Sc_3 dynamics can now be proven incomplete. In particular, at high temperature, the motion of the endohedral moiety becomes three-dimensional and is no longer limited to the equatorial belt of the cage. Our modelling shows that the EPR spectra of $\text{Sc}_3\text{C}_2@C_{80}$ reflect complex intramolecular dynamics which, at high temperature, effectively removes the inequivalency of the metal centers and masks the anisotropic character of the guest moiety.

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[†] Electronic Supplementary Information (ESI) available: Thorough discussion of the results, full average g - and $A(^{45}\text{Sc})$ tensors and their isotropic values at $T = 300$ K and 100 K, time variation of the isotropic EPR and chosen geometrical parameters, average hyperfine tensor orientations at 100 K, full computational details including basis sets, and the equilibrium structure of $\text{Sc}_3\text{C}_2@C_{80}$. See DOI: 10.1039/b000000x/

The EPR spectra resulting from first-principles simulations based on density functional theory (DFT) calculations at $T = 300$ K and $T = 100$ K are shown in Figure 1 (a) and (b), respectively. The best model in the high-temperature case, which reproduces the experimental observations¹⁶ quite well, is based on considering the sample movement to be in the fast-motion regime in the spectral simulation, with identical scandium atoms and isotropic EPR g - and ^{45}Sc hyperfine coupling (A) parameters. At low temperature, a solid-state spectral simulation is applied, with inequivalent scandiums, as well as anisotropic g - and $A(^{45}\text{Sc})$ tensors. The well-resolved, symmetric spectrum of 22 peaks at 300 K arises from three magnetically equivalent nuclei with spin $I = \frac{7}{2}$ and an identical, effectively isotropic hyperfine coupling constant, A_{iso} , for each. Table 1 lists the isotropic values used in the high-temperature simulation. Tables S1 and S2 in the ESI[†] list the full tensors at both temperatures. While the present modelling does not replicate the experimentally recorded spectra¹⁶ exactly, the mismatch is not significant in view of the general outcome, particularly the big qualitative difference between the high- and low-temperature behaviour.

Table 1 Calculated isotropic values of the g - and hyperfine coupling (A) tensors. Computational values from tensors averaged over 12000 snapshots in a microcanonical molecular dynamics trajectory at $T = 300$ K

T (K)	Ref.	g_{iso}	$A_{\text{iso}}^{\text{Sc1}}$	$A_{\text{iso}}^{\text{Sc2}}$	$A_{\text{iso}}^{\text{Sc3}}$	$A_{\text{iso}}^{\text{Avg.}}$
300	This work	1.9974	-16.40	-12.45	-12.88	-13.91
300 ^a	16	1.9976				17.52
Static ^b	17		-6.84	-13.92	-13.92	
Static ^c	17		-1.13	-9.28	-9.28	

^aExperimental absolute value, in the assumed $\text{Sc}_3\text{C}_2\text{@C}_{80}$ structure. Converted with $B/\text{mT} = 10^9 h\nu / (g\mu_B)/\text{MHz}$. ^bStatic first-principles calculation with the 1a isomer (with C_2 axis perpendicular to the plane of Sc_3). ^cStatic first-principles calculation with the 2a isomer (C_2 axis in the plane of Sc_3).

In the instantaneous geometries occurring in the MD simulation, the scandium trimer does not form an equilateral triangle as one of the metal atoms is not equivalent with the other two, on account of the C_2 moiety flipping through the Sc_3 plane.^{17,18} Furthermore, the EPR tensors are anisotropic. However, the dynamics of the Sc_3 moiety and the subsequent averaging cause the non-equivalence to disappear at high temperature. This is evident from Figure 2, which visualizes the scandium positions along the sampled trajectory at the two temperatures. At 300 K, the metal trimer rotates freely in three dimensions, whereas at 100 K the movement is confined to a plane that coincides with a 6-ring belt of the $I_h \text{C}_{80}$ cage. The low-temperature behaviour is commensurate with the earlier picture of the dynamics of this endohedral moiety.^{17,18} In contrast, the guest is highly dynamic at the high temperature, which is reflected in the vigorous fluctuations of the EPR parameters (see Figures S1 and S2 in the ESI[†]).

Fig. 1 Different appearance of high- and low-temperature EPR spectra of the endohedral metallofullerene $\text{Sc}_3\text{C}_2\text{@C}_{80}$. Simulated X-band (9.385 MHz) spectra at (a) 300 K (isotropic fast motion) and (b) 100 K (solid), based on the calculated, average g - and hyperfine coupling tensors from the corresponding MD simulations. Lorentzian line broadening of (a) 0.178 mT and (b) 0.6 mT has been applied, based on Ref.¹⁶.

Figure 3 illustrates why it is unjustified to consider the metal centres as equivalent. There, the EPR spectra are simulated by assuming, on the one hand, individual hyperfine tensors for all the scandium centers or, on the other hand, the same average tensor for all three. At $T = 300$ K, the equivalent model reproduces the features of the experimental spectrum, whereas the individual model produces a very different lineshape. In contrast, at $T = 100$ K, the equivalent model produces well-resolved peaks to the lineshape, whereas considering distinct scandium atoms reproduces the experimental, broad lineshape.

While the average isotropic g - and A -values determine the high-temperature spectrum, this is not the case at low temperature. Figure 4(a) compares the EPR spectral simulations using, on the one hand, full anisotropic tensors or, on the other hand, only their isotropic values. Clearly, the omission of the anisotropic parts of the tensors would result in a lineshape differing from the experimental one and, notably, the reappearance of separate peaks. At this temperature, a ratcheting jump of the ^{45}Sc trimer was observed during the sampled trajectory (see Figures S3–S5 in ESI[†]). To consider the effect that including such effects in the MD trajectory has on the spectrum, Figure 4(b) shows the EPR simulation

Fig. 2 Spatial coverage of the ^{45}Sc positions inside the C_{80} fullerene during the 300 K (left panels) and 100 K (right) simulation trajectories. The images from top to bottom depict the same data as viewed along the three different coordinate axes (x, y, and z, from top to bottom). The colors are used to distinguish between the three scandium atoms: blue and red for the equivalent Sc, and orange for the inequivalent Sc.

based on the trajectory with only the part before the ratcheting event retained. Excluding the small differences that partially result from the less complete sampling as compared to Figure 4(a), the result remains essentially the same: the anisotropic hyperfine tensors are crucial in reproducing the experimental appearance of the spectrum. The ratcheting motion brings the Sc_3C_2 moiety to a position that is equivalent to the initial position, due to the symmetry of the cage. Thus, the conclusion is that the infrequent reorientation of the Sc_3 unit along the 6-ring belt of the cage does not notably modify the measured spectrum, and can be considered merely a brief disturbance, at low temperature. At 300 K, the Sc_3 moiety is in 3D motion, visits different orientations along each of the three 6-ring belts of the cage, and undergoes much more frequent jumps that cause motional narrowing to the well-resolved 22-line spectrum.

The shapes and orientations of the anisotropic ^{45}Sc hyperfine tensors were averaged over the simulation snapshots at $T = 100$ K.

Fig. 3 Simulated X-band (9.385 MHz) EPR spectra at (a) 300 K and (b) 100 K, based on the calculated average g - and hyperfine coupling (A) tensors from the corresponding MD simulations. The individual A tensors are either considered individual or equivalent, in which case the mean tensor for all ^{45}Sc atoms is used. Lorentzian line broadening of (a) 0.178 mT and (b) 0.6 mT has been applied, based on Ref. ¹⁶.

The results (Figures S6 and S7 in the SI) partially support the earlier model¹⁶ of an axially symmetric hyperfine tensor with $A_{\perp} = 0$ and $A_{\parallel} = 3A_{\text{iso}}$. In contrast to what was assumed in Ref. ¹⁶, one of the scandiums is notably inequivalent with the other two, however. In a similar vein, our simulations showed that the tensors are not completely axial, and the orientation of their largest principal component is not perpendicular to the plane of the Sc_3 moiety, but tilted at an angle of roughly 45 degrees away from the normal of the Sc_3 plane. These facts likely contribute to the mismatch between the results of the simple model and experiment, and show how the geometrically rather small inequivalence of one of the scandium atoms can lead to large deviations in the magnetic properties.

Summarising, the dynamics of the endohedral moiety and its effect on the EPR g and ^{45}Sc hyperfine coupling tensors in $\text{Sc}_3\text{C}_2@C_{80}$ were studied using DFT, combining first-principles molecular dynamics and quantum-chemical EPR modelling. Static calculations¹⁷ and dynamical modelling over a short trajectory were not able to reproduce the features of the experimental EPR spectra. Here, more comprehensive first-principles modelling suggests that the enclosed cluster exhibits peculiar dynamics, which explains the connection of cluster dynamics with

Fig. 4 Simulated X-band (9.385 MHz) EPR spectra at 100 K, including data from either (a) all 9000 calculated snapshots or (b) only the first 5000 snapshots, before the Sc_3 moiety had jumped into a new position. Simulation based on the calculated average g and A tensors from the corresponding MD simulations, with either full tensors (Anisotropic) or only the isotropic g and A values (Isotropic). Lorentzian line broadening of 0.6 mT has been applied, based on Ref. ¹⁶.

its EPR spectra. While at low temperature the endohedral moiety undergoes ratcheting 2D motion along the equatorial belt of the C_{80} cage, at high temperature the motion is no longer restricted to one plane. To test earlier assumptions, models featuring different equivalence of the three ^{45}Sc nuclei and either effectively isotropic or anisotropic parameter tensors, were considered. The main experimental EPR observations were reproduced by the present simulations: a well-resolved 22-line spectrum arises from isotropic and equivalent, rotationally averaged ^{45}Sc atoms at high temperature (300 K). In contrast, a broad line-shape results from inequivalent metal centers with anisotropic hyperfine tensors at low temperature (100 K).

The results obtained in this work clearly show that first-principles simulations of the EPR parameters may be used to study the intricate dynamics of guest moieties in endohedral metallofullerenes, as well as the anisotropic character of their EPR parameters. This non-invasive means of spying on the caged species may benefit their potential applications as molecular sensors.

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Methods. Microcanonical (NVE) MD simulations at 300 K (length 100 ps) and 100 K (340 ps), and the EPR parameters of extracted simulation snapshots were calculated from first principles using DFT in the CP2K¹⁹ (BLYP functional^{20,21}) and Orca^{22–24} (PBE²⁵) programmes, respectively, for the $\text{Sc}_3\text{C}_2@C_{80}$ system with zero charge and spin multiplicity of 2 (one unpaired electron). At $T = 300$ K (100 K), a total of 12000 (9000) property snapshots at 8 fs (32 fs) intervals from the end of the trajectory were calculated. EPR spectra were simulated with the EasySpin toolbox²⁶ on MATLAB²⁷, using anisotropic EPR parameter tensors averaged over the snapshots in the Eckart frame²⁸ of the Sc_3 moiety, with line broadening parameters adopted from Ref. ¹⁶. At $T = 100$ K, another set of average tensors was based on the first 5000 snapshots, to exclude the single ratcheting jump of the metal trimer observed at the end of the trajectory. See SI for more details.

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First principles modelling graphically explains how changes in the Sc-trimer motion cause the curious temperature dependence of Sc₃C₂@C₈₀ EPR spectra.

Supporting information for
Ratcheting rotation or speedy spinning:
EPR and dynamics of Sc₃C₂@C₈₀

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Contents

1	Results	S3
2	Computational details	S12
2.1	Completeness-optimised basis set for Sc	S15
2.2	Eckart frame of Sc ₃	S15
2.3	Movement of C ₂	S16

List of Tables

S1	Average g and $\mathbf{A}^{\text{Sc}}$ tensors at 300 K and 100 K	S5
S2	Average g and $\mathbf{A}^{\text{Sc}}$ tensors at 100 K before Sc ₃ reorientation	S6
S3	Average isotropic g - and A^{Sc} -values at 300 K and 100 K	S6
S4	Gaussian exponents of the scandium 21s12p10d2f basis set	S15

List of Figures

S1	The deviation Δg of the isotropic g -factor from the free-electron g -value at $T = 300$ K and 100 K	S7
S2	The isotropic A^{Sc} -values at $T = 300$ and 100 K	S8
S3	Relative tilt and rotation angles of the Sc ₃ moiety at $T = 300$ K and 100 K	S9
S4	Distances between the scandium atoms and the reference carbons of the cage at $T = 100$ K	S10
S5	Reference carbon atoms used to calculate Sc ₃ tilt and rotation angles	S11
S6	Shape and orientation of the average $\mathbf{A}^{\text{Sc}}$ tensors at 100 K	S12
S7	Shape and orientation of the average $\mathbf{A}^{\text{Sc}}$ tensors at 100 K before Sc ₃ reorientation	S12
S8	Temperature during the <i>NVE</i> simulation at 300 K	S13
S9	Temperature during the <i>NVE</i> simulation at 100 K	S14

1 Results

The full average g and $\mathbf{A}^{\text{Sc}}$ tensors are listed in Table S1. Figures S1 and S2 show the variation of the isotropic values, deviation Δg from the free-electron g -value and the hyperfine $A(^{45}\text{Sc})$ values, respectively, along the trajectories at 300 K and 100 K. At the higher temperature, the rotation of the metal trimer is quite free, as shown in the top panels of Figure S3. In the course of the low-temperature trajectory, the metal trimer made one jump to a new position with respect to the cage (see lower panels in Figure S3, as well as Figures S4 and S5 below). In order to see the effect of the jump on the tensors, they were averaged, besides over the entire thermalised trajectory, also over only the first 5000 snapshot calculations (see Table S2), where the trimer remains roughly locked into its initial position.

To indirectly consider the effect of the isotropic model of the EPR parameters, also isotropic g - and A -values were calculated from the average tensors at both temperatures. The g - and A -values are listed in Table S3. The time variation of Δg and A^{Sc} , plotted in Figures S1 and S2, shows that, while the values of the individual scandium atoms oscillate rapidly at the high temperature, the average isotropic hyperfine constant over all the three scandiums oscillates much less, which likely explains the difference between the results of the models of equivalent and inequivalent scandium atoms discussed in the article. Compared to the high-temperature trajectory, there are, at 100 K, comparatively long time ranges with well-defined, distinctly different values instead of the persistent oscillation characteristic of the 300 K simulation. The hyperfine values in Figure S2 show that one of the scandiums (*e.g.*, the inequivalent scandium at the beginning of the trajectory) clearly differs from the other two, unlike the situation at the higher temperature, which explains why the equivalent-scandium EPR spectrum differs from that appropriate to the inequivalent one.

In Ref. 1, a frozen-solution EPR spectra of the system was modeled by assuming an axially symmetric hyperfine tensor for each Sc, with the principal components $A_{\perp} = 0$ and $A_{\parallel} = 3A_{\text{iso}}$. In the study, two orientations of the hyperfine tensors were tested, either perpendicular to the Sc_3 plane, or parallel to it, with the former found to better, albeit not perfectly, match the experimentally measured spectrum. Because the tensor orientations are readily available from first-principles calculations, the validity of the assumption is easily tested. Figures S6 and S7 show a visual representation of the rough shape and orientation of the hyperfine tensors of each scandium, calculated from the tensors averaged both over all snapshots and only the first 5000 snapshots, respectively (in the latter again to exclude jump-like ratcheting motion of the the metal trimer).

While the jump-like motion of the Sc_3 moiety is seen to slightly affect the tensor shapes, the overall result is that, during the sampled trajectory, all the ^{45}Sc hyperfine tensors are almost axially symmetric, with one of the principal components clearly larger than the two others. The orientation

of the distinct principal axis is neither exactly parallel nor perpendicular to the Sc_3 plane. This, however, may also be affected by the limited trajectory length where the metal trimer does not thoroughly sample all of the available phase space. In any case, contrary to the assumption made in Ref. 1, the scandium centers are not equivalent, and especially the relative size of the principal components of the distinct scandium is smaller than that of the other two Sc centers.

Table S1: Total g and $\mathbf{A}$ tensors (in MHz) of the three ^{45}Sc atoms, averaged over 12000 (at 300 K) and 9000 (100 K) evenly spaced (in 8 fs and 32 fs intervals, respectively) snapshots from microcanonical molecular dynamics trajectories, after transformation of the instantaneous tensors into the Eckart frame of the Sc_3 subsystem. The standard error of mean $s = \sigma/\sqrt{N}$ is used to estimate the error limits, where σ is the standard deviation and N is the number of snapshots.

T (K)	Tensor		x	y	z
300	$\mathbf{g}$	x	1.99684 ± 0.00002	0.00005 ± 0.00001	-0.00006 ± 0.00001
		y	-0.00001 ± 0.00001	1.99769 ± 0.00001	0.00020 ± 0.00001
		z	-0.00003 ± 0.00001	0.00021 ± 0.00001	1.99775 ± 0.00001
	$\mathbf{A}^{\text{Sc1}}$	x	-22.88 ± 0.13	0.05 ± 0.08	0.15 ± 0.13
		y	0.05 ± 0.08	-16.90 ± 0.09	6.21 ± 0.08
		z	0.15 ± 0.13	6.21 ± 0.08	-9.42 ± 0.16
	$\mathbf{A}^{\text{Sc2}}$	x	-20.65 ± 0.11	0.53 ± 0.06	-0.95 ± 0.09
		y	0.53 ± 0.06	-12.95 ± 0.10	-5.68 ± 0.07
		z	-0.95 ± 0.09	-5.68 ± 0.07	-3.76 ± 0.16
	$\mathbf{A}^{\text{Sc3}}$	x	-19.88 ± 0.11	0.82 ± 0.12	-0.27 ± 0.03
		y	0.82 ± 0.12	-2.88 ± 0.19	1.02 ± 0.05
		z	-0.27 ± 0.03	1.02 ± 0.05	-15.89 ± 0.09
	$\mathbf{A}^{\text{avg}}$	x	-21.14 ± 0.09	0.47 ± 0.05	-0.36 ± 0.06
		y	0.47 ± 0.05	-10.91 ± 0.10	0.52 ± 0.03
		z	-0.36 ± 0.06	0.52 ± 0.03	-9.69 ± 0.11
100	$\mathbf{g}$	x	1.99765 ± 0.00002	0.00025 ± 0.00001	-0.00015 ± 0.00001
		y	0.00022 ± 0.00001	1.99735 ± 0.00001	-0.00022 ± 0.00001
		z	0.00012 ± 0.00001	-0.00016 ± 0.00001	1.99868 ± 0.00001
	$\mathbf{A}^{\text{Sc1}}$	x	-21.77 ± 0.12	7.40 ± 0.11	8.42 ± 0.11
		y	7.40 ± 0.11	-22.99 ± 0.08	3.11 ± 0.07
		z	8.42 ± 0.11	3.11 ± 0.07	-16.31 ± 0.15
	$\mathbf{A}^{\text{Sc2}}$	x	-20.43 ± 0.14	-7.52 ± 0.10	9.31 ± 0.13
		y	-7.52 ± 0.10	-25.40 ± 0.05	-1.68 ± 0.08
		z	9.31 ± 0.13	-1.68 ± 0.08	-19.12 ± 0.17
	$\mathbf{A}^{\text{Sc3}}$	x	-17.14 ± 0.08	-0.81 ± 0.08	-0.07 ± 0.04
		y	-0.81 ± 0.08	-3.86 ± 0.21	-0.23 ± 0.04
		z	-0.07 ± 0.04	-0.23 ± 0.04	-14.66 ± 0.07
	$\mathbf{A}^{\text{avg}}$	x	-19.78 ± 0.10	-0.31 ± 0.04	5.88 ± 0.07
		y	-0.31 ± 0.04	-17.42 ± 0.07	0.40 ± 0.02
		z	5.88 ± 0.07	0.40 ± 0.02	-16.70 ± 0.10

Table S2: Total g and $\mathbf{A}$ tensors (in MHz) of the three ^{45}Sc atoms at 100 K, averaged over the first 5000 evenly spaced (32 fs) snapshots from microcanonical molecular dynamics trajectories, after transformation of the instantaneous tensors into the Eckart frame of the Sc_3 subsystem. The standard error of mean $s = \sigma/\sqrt{N}$ is used to estimate the error limits, where σ is the standard deviation and N is the number of snapshots.

T (K)	Tensor	x	y	z
100	$\mathbf{g}$	x	1.997649 ± 0.000014	0.000250 ± 0.000005
		y	0.000221 ± 0.000005	1.997353 ± 0.000007
		z	0.000120 ± 0.000012	-0.000162 ± 0.000009
	$\mathbf{A}^{\text{Sc1}}$	x	-27.14 ± 0.14	14.89 ± 0.04
		y	14.89 ± 0.04	-25.72 ± 0.03
		z	15.51 ± 0.05	5.06 ± 0.08
	$\mathbf{A}^{\text{Sc2}}$	x	-25.33 ± 0.16	-14.09 ± 0.03
		y	-14.09 ± 0.03	-25.12 ± 0.04
		z	15.83 ± 0.05	-4.49 ± 0.07
	$\mathbf{A}^{\text{Sc3}}$	x	-19.82 ± 0.05	0.21 ± 0.02
		y	0.21 ± 0.02	7.51 ± 0.10
		z	-1.81 ± 0.02	0.39 ± 0.05
	$\mathbf{A}^{\text{avg}}$	x	-24.10 ± 0.10	0.34 ± 0.02
		y	0.34 ± 0.02	-14.45 ± 0.05
		z	9.85 ± 0.03	0.32 ± 0.02

Table S3: Isotropic g - and A -values of the corresponding tensors of the three ^{45}Sc atoms, averaged over 12000 (at 300 K) and 9000 (100 K) evenly spaced snapshots from microcanonical molecular dynamics trajectories. The standard error of mean $s = \sigma/\sqrt{N}$ is used to estimate the error limits, where σ is the standard deviation and N is the number of snapshots.

T (K)	Ref.	g_{iso}	$A_{\text{iso}}^{\text{Sc1}}$ (MHz)	$A_{\text{iso}}^{\text{Sc2}}$ (MHz)	$A_{\text{iso}}^{\text{Sc3}}$ (MHz)	A_{iso}^a (MHz)
300	This work	1.99743 ± 0.00001	-16.40 ± 0.06	-12.45 ± 0.08	-12.88 ± 0.08	-13.91 ± 0.08
100	This work	1.99790 ± 0.00001	-20.36 ± 0.06	-21.65 ± 0.03	-11.89 ± 0.08	-17.96 ± 0.08
100 ^b	This work	1.99766 ± 0.00001	-23.04 ± 0.03	-20.96 ± 0.03	-7.87 ± 0.06	-17.29 ± 0.06
300 ^c	1	1.9976				17.52
Static ^d	2		-6.84	-13.92	-13.92	
Static ^e	2		-1.13	-9.28	-9.28	

^aAverage over the three Sc atoms

^bFirst 5000 snapshots

^cExperimental, in the assumed $\text{Sc}_3@\text{C}_{82}$. Converted with $B/\text{mT} = 10^9 h\nu/(g\mu_B)/\text{MHz}$.

^dFirst-principles, static calculation with the 1a isomer.

^eFirst-principles, static calculation with the 2a isomer.

Figure S1: The deviation of the isotropic g -factor from the free-electron g -value $g_e = 2.0023193$, $\Delta g = g_{\text{iso}} - g_e$, during the simulation at $T = 300$ K (top) and 100 K (bottom).

Figure S2: Isotropic hyperfine coupling constants of the three ^{45}Sc nuclei (blue, red and green lines), and their mean value (black line), during the simulations at $T = 300$ K (left panel) and 100 K (right).

Figure S3: Relative tilt (angle between plane normals) and rotation in degrees between the plane formed by Sc_3 and the plane formed by the reference carbons of the cage (see Figure S5), at $T = 300$ K (top) and 100 K (bottom).

Figure S4: Distances between the scandium atoms and the reference carbons (see Figure S5) of the cage, at $T = 100$ K.

Figure S5: Reference carbon atoms used in the distance and angle plots. C17, C40 and C53 form a plane roughly along one 6-ring belt of the cage, while C31 is at the “top” of the cage relative to that plane. The tilt of the Sc_3 plane relative to the C17–C40–C53 plane is defined as the angle between the normal vectors of the two planes. The relative rotation of the planes is defined as the angle between two vectors, one of which is on the C17–C40–C53 plane (*e.g.*, a vector from one atom to the midpoint between the two other atoms) and the other is a projection to that plane of a vector lying on the Sc_3 plane.

Figure S6: Graphical representation of the shape and orientation of the $\mathbf{A}$ tensors of each scandium, as viewed from the front of the Sc_3 moiety (left picture) or top (right), averaged over the full trajectory at $T = 100$ K. The ellipsoids are drawn with each axis corresponding to one principal value of the corresponding tensor. The scaling is the same for all nuclei, but chosen for visual purposes only.

Figure S7: Graphical representation of the shape and orientation of the $\mathbf{A}$ tensors of each scandium, as viewed from the front of the Sc_3 moiety (left picture) or top (right), averaged over the first 5000 calculations (the part of trajectory before Sc_3 “jumps”) at $T = 100$ K. The ellipsoids are drawn with each axis corresponding to one principal value of the corresponding tensor. The scaling is the same for all nuclei, but chosen for visual purposes only.

2 Computational details

The studied system consists of a C_{80} carbon cage enclosing three scandium metal atoms and a carbon dimer, denoted $\text{Sc}_3\text{C}_2@\text{C}_{80}$, with zero charge and

doublet electronic state (*i.e.*, spin multiplicity $2S + 1 = 2$, $S = 1/2$). The scandium trimer forms a not-quite-equilateral triangle, where two scandiums remain practically identical during the simulations, whereas the third one is inequivalent to them, due to the orientation of the carbide C_2 unit that librates towards the non-identical scandium.

Molecular dynamics trajectories were calculated with density functional theory (DFT), using the BLYP functional [3, 4] as implemented in the CP2K [5] software package version 2.4 (at 300 K) and 2.5 (100 K). A cubic simulation cell with 12 Å long edges and a timestep of 2 fs was used in the simulations, along with a cutoff energy of 600 Ry and self-consistent field (SCF) convergence threshold of 10^{-6} . The ^{45}Sc (^{12}C) core electrons were described using the norm-conserving GTH-BLYP-q11 (GTH-BLYP-q4) pseudopotential [6–8], and valence electrons with Gaussian DZV-GTH-PADE [9] (DZVP-GTH-BLYP [10]) basis sets optimised for the GTH pseudopotentials.

The 300 K trajectory was started from a geometry-optimised structure of the neutral isomer 2a reported by Taubert *et al.* [2]. The full trajectory consists of three parts: an initial microcanonical NVE simulation (duration 87.4 ps), an equilibrating, canonical NVT simulation (172.6 ps) with a canonical sampling/velocity rescaling (CSV) [11] thermostat enabled, and a final microcanonical NVE simulation (100.0 ps) from which the property calculation snapshots were extracted. In the NVT simulation, the time constants of 100 fs (most of the region) and 1 fs were used for the thermostat, with little difference in the results. Figure S8 shows the temperature during the production NVE part of the 300 K simulation.

Figure S8: Temperature of the production NVE part of the 300 K MD simulation.

The 100 K trajectory was started from the same equilibrium geometry as the high-temperature trajectory, and consists of two parts: an initial canonical NVT trajectory (20 ps) with the CSV thermostat enabled, and using 1 fs and 100 fs time constant regions, followed by a microcanonical NVE simulation (340 ps), from which the property calculation snapshots were ex-

tracted. Figure S9 shows the temperature during the production *NVE* part of the 100 K simulation.

Figure S9: Temperature of the production *NVE* part of the 100 K MD simulation.

The electron paramagnetic resonance (EPR) parameters, g and hyperfine ($\mathbf{A}$) tensors for each scandium were calculated using snapshot geometries extracted from the MD trajectories at constant intervals of 8 fs at 300 K (a total of 12000 snapshots), and 32 fs (a total of 9000 snapshots) at 100 K. The snapshots were selected starting from the last step of each trajectory towards the beginning, thus using the best-equilibrated part of the micro-canonical trajectory. The EPR parameters were calculated for each snapshot geometry with the Orca program system [12–14] version 3.0.3, using the resolution of the identity (RI) approximation [15] and the PBE functional [16, 17]. The grid and integration accuracy parameters were set to 7, and SCF convergence to “tight”. An uncontracted, completeness-optimised Gaussian basis set (dubbed co-r, 21s12p10d2f, *vide infra*) was used for scandium, while Def2-SVP and Def2-QZVPP [18, 19] basis sets were employed for cage and C₂ carbons, respectively.

Simulations of the EPR spectra were calculated with the EasySpin toolbox version 5.1.7 [20] on MATLAB R2015b [21]. The g and $\mathbf{A}^{\text{Sc}}$ tensors used in the simulations are listed in Tables S1 and S2. In simulations based on isotropic constants, the g - and A -values of Table S3 were used. The experiment-related simulation settings, which were not available from first-principles calculations, were gathered from Ref. 1, to produce comparable figures. The X-band microwave frequency was not specified in the reference, and hence the value 9.385 MHz from the EasySpin documentation was used. High-temperature (300 K) simulations were run with the “garlic” program of EasySpin, applying Lorentzian broadening with full width at half maximum (FWHM) of 0.178 mT. Low-temperature (100 K) simulations were run with the solid-state “pepper” program of EasySpin, with the second-order perturbation theory approximation and Lorentzian broadening with FWHM of 0.6 mT. No Gaussian broadening was applied. The direct matrix-diagonalization

method was not applicable for this system due to very high resource requirements.

2.1 Completeness-optimised basis set for Sc

The co-r basis set shown in Table S4 was optimised using Kruununhaka 2.0.1 basis set tool kit [22] by following the isotropic values of the g and $\mathbf{A}^{\text{Sc}}$ tensors, as well as the A_{33} element of the SD contribution to the $\mathbf{A}$ tensor, as calculated using Orca version 2.8 in a small ScH_2 test system with the OLYP [23] functional and the RI approximation, setting the grid and integration accuracy to 7.

Table S4: Gaussian exponents of the completeness-optimised, uncontracted 21s12p10d2f basis set for scandium.

s	p	d	f
40238445.	2880.2919	626.53701	2.7179697
15582491.	1163.3533	232.03955	0.21356169
5601176.1	435.67808	83.123739	
1790589.7	161.81055	30.375595	
672553.42	57.892302	10.687894	
233927.39	20.042841	3.6495037	
77153.397	7.7789602	1.3569478	
23754.441	2.7506261	0.48991826	
7590.6403	1.0139505	0.17798017	
2345.3225	0.35374221	0.65559727E-01	
957.09586	0.13879297		
279.65475	0.56359098E-01		
105.05810			
40.461758			
12.087544			
3.3285515			
1.3642222			
0.39733190			
0.12672184			
0.51834597E-01			
0.20287268E-01			

2.2 Eckart frame of Sc_3

For comparison and averaging anisotropic properties between differently oriented snapshots, an in-house built program was used to transform the calculated g and $\mathbf{A}^{\text{Sc}}$ tensors from the laboratory frame to the Eckart frame [24, 25] of the Sc_3 subsystem. The equilibrium geometry used in the transformation was based on the structure that the MD simulations were started

from. To ensure that it is consistent with the MD simulations, a geometry optimization was performed with CP2K using the same functional and SCF settings as in the MD simulations, which resulted in almost no changes in the geometry, with differences between the old and new Sc positions being 0.036 and 0.049 Å (larger for the inequivalent scandium). The equilibrium structure is released as a separate Supporting Information file.

2.3 Movement of C₂

The C₂ unit librates inside the Sc₃ triangle during the simulated trajectories. The movement is faster at 300 K, whereas at 100 K it is slower and, to some extent, it is possible to distinguish the two isomers 1a (C₂ perpendicular to the Sc₃ plane) and 2a (in the Sc₃ plane), found in Ref. 2. Despite the occasional perpendicular orientation, the libration mainly takes place towards one distinct scandium atom, and preserves the roles of the scandium atoms during the calculated trajectory. At 300 K, the dynamical motion of the system averages the scandium atoms effectively equivalent.

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