Magnetic anisotropy of endohedral lanthanide ions: paramagnetic NMR study of MSc2N@C80-Ih with M running through the whole 4f row†

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Paramagnetic and variable temperature 13C and 45Sc nuclear magnetic resonance studies are performed for nitride clusterfullerenes MSc2N@C80 with icosahedral Ih(7) carbon cage, where M runs through all lanthanides forming nitride clusters. The influence of the endohedral lanthanide ions on the NMR spectral pattern is carefully followed, and dramatic differences are found in peak positions and line widths. Thus, 13C lines broaden from 0.01–0.02 ppm in diamagnetic MSc2N@C80 molecules (M = La, Y, Lu) to several ppm in TbSc2N@C80 and DySc2N@C80. Direction of the paramagnetic shift depends on the shape of the 4f electron density in corresponding lanthanide ions. In TbSc2N@C80 and ErSc2N@C80 with prolate 4f-density of lanthanide ions, 13C signals are shifted down-field, whereas 45Sc peaks are shifted up-field versus diamagnetic values. In all other MSc2N@C80 molecules lanthanide ions have oblate-shaped 4f electron density, and the lanthanide-induced shift is negative for 13C and positive for 45Sc peaks. Analysis of the pseudocontact and contact contributions to chemical shifts revealed that the pseudocontact term dominates both in 13C and 45Sc NMR spectra, although contact shifts for 13C signals are also considerable. Point charge computations of the ligand field splitting are performed to explain experimental results, and showed reasonable agreement with experimental pseudocontact shifts. Nitrogen atom bearing large negative charge and located close to the lanthanide ion results in large magnetic anisotropy of lanthanide ions in nitride clusterfullerenes with quasi-uniaxial ligand field.

Importantly, both DySc2N@C80 and Dy2ScN@C80 exhibit unusually long attempt times, which are orders of magnitude longer than in other lanthanide-based SMMs.

One of the most important factors determining the SMM behaviour of lanthanide molecular magnets is the single ion magnetic anisotropy. Reliable elucidation of the ligand-field (LF) splitting of the 4f total momentum states is crucial (although not sufficient) for the correct description of magnetic properties of lanthanide SMMs. Despite the understanding that the magnetic anisotropy is an important factor determining magnetic properties of EMF, a consistent description of the LF effects in EMF has not been provided yet. The first dedicated studies of the LF in nitride clusterfullerenes have been published only recently and were motivated by the discovery of SMM behaviour in DySc2N@C80 and Dy2ScN@C80. According to the ab initio computations at the CASSCF level, the LF splitting in DySc2N@C80 is so large that its magnetization behavior at low temperature is determined solely by the ground state of the 6H15/2 manifold. Namely, the gap between the ground (mJ = ±15/2) and the first excited (mJ = ±13/2) magnetic states was predicted to be 373–415 cm−1 (ref. 7a) or 485 cm−1 (ref. 7b). Likewise, magnetization curves of DySc2N@C80 and HoSc2N@C80 measured by SQUID below 10 K are also described by only one state with mJ = ±15/2 (Dy) or mJ = ±8 (Ho). The information about excited magnetic states might be revealed...
from magnetizations studies at higher temperatures (e.g., the population of the \( m_I = \pm 13/2 \) state in DySc\(_2\)N@C\(_{80}\) near room temperature is expected to be ca. 10\%). However, with the increase of the temperature the total magnetization of the sample is decreasing dramatically and can hardly be measured reliably when only limited amount of sample is available (as it is often the case with EMF SMMs). An alternative might be the use of spectroscopic techniques, such as analysis of the fine structure in the lanthanide-based luminescence spectrum. Unfortunately, the fullerene cages of EMFs absorb light in the visible range and hence block the possibility to observe the lanthanide-based luminescence for a majority of 4f elements. So far, metal-based luminescence in EMFs could be detected only for endohedral Er\(^{3+}\) ions emitting in the near-IR range.

Solution nuclear magnetic resonance (NMR) studies can provide complimentary information on the magnetic anisotropy of lanthanide ions for the temperatures not well accessible by direct magnetization measurements. The chemical shift of a nuclei in a paramagnetic compound can be described as a sum of diamagnetic and paramagnetic terms, \( \delta^{\text{exp}} = \delta^{\text{dia}} + \delta^{\text{para}} \). In due turn, the paramagnetic shift has two major contributions, contact \( \delta^{\text{con}} \) and pseudocontact \( \delta^{\text{pc}} \). The contact (Fermi) shift results from the interaction between the nuclear spin (of \(^{13}\)C or \(^{45}\)Sc atoms in this work) and the spin-polarized electron density of the molecule (in particular in the region close to the nuclei of interest). As such, the contact shift is proportional to the hyperfine coupling constant weighed with the expectation value of the spin operator \( S_z \) of the lanthanide. The pseudocontact shift is caused by dipolar through-space interactions of the nuclear and electronic magnetic dipoles. For an \( i \)-th atom in a lanthanide-containing molecule the pseudocontact shift can be computed as:

\[
\delta^{\text{pc}} = \frac{1}{12\pi R_i^3} \left( 3 \cos^2 \theta_i - 1 \right) \left( \chi_{zz}^{Ln} - \frac{\chi_{xx}^{Ln} + \chi_{yy}^{Ln}}{2} \right) + \frac{3}{2} \left( \chi_{xx}^{Ln} - \chi_{yy}^{Ln} \right) \sin^2 \theta_i \cos 2\phi_i
\]

(1a)

where \( \chi_{\alpha\beta}^{Ln} \) are components of the magnetic susceptibility tensor of the lanthanide, whereas \( R_i \), \( \theta_i \) and \( \phi_i \) are polar coordinates of the \( i \)-th atom in the coordinate system centred on the lanthanide ion. In particular, \( R_i \) is a distance between the atom of interest and lanthanide ion, and \( \theta_i \) is an angle between quantization axis \( z \) and the vector connecting the lanthanide ion and the \( i \)-th atom. If \( \chi_{xx}^{Ln} = \chi_{yy}^{Ln} \) (i.e. the ligand field is uniaxial), eqn (1a) is simplified to:

\[
\delta^{\text{pc}} = \frac{3 \cos^2 \theta_i - 1}{12\pi R_i^3} \left( \chi_{zz}^{Ln} - \frac{\chi_{xx}^{Ln} + \chi_{yy}^{Ln}}{2} \right)
\]

(1b)

As can be seen in eqn (1), the pseudocontact shift contains information on the molecular structure and on the magnetic properties of the paramagnetic center. Paramagnetic NMR is therefore a popular structure elucidation tool for metal complexes, polymers or biomolecules. At the same time, it can be also used to determine or verify LF parameters in lanthanide complexes. The prerequisite for both types of application of NMR spectroscopy in the studies of paramagnetic molecules is the possibility to separate contact and pseudocontact contributions, since only the latter brings necessary information about molecular structure and magnetic anisotropy.

In the field of endohedral metallofullerenes, paramagnetic NMR was mainly used for the structural studies. Several Ce-EMFs, anion of Pr@C\(_{82}\), three isomers of Tm@C\(_{82}\), Sm@C\(_{80}\) and Sm@C\(_{82}\) (ref. 18) were characterized by \(^{13}\)C NMR. The variable-temperature \(^{45}\)Sc NMR study was also reported for CeSc\(_2\)N@C\(_{80}\). The dominant contribution of the pseudocontact shift in Ce-EMFs was postulated based on the analysis of the temperature dependence in the framework of Bleaney’s theory. The size of the contact term contribution in the paramagnetic NMR spectra of EMFs remains unclear. Our group recently reported paramagnetic NMR study of HoM\(_2\)N@C\(_{80}\) and Ho\(_2\)MN@C\(_{80}\) (M = Sc, Y, Lu). \(^{13}\)C and \(^{45}\)Sc signals of these molecules could be identified in spite of the severe broadening induced by Ho\(^{3+}\) ions. This study showed that paramagnetic NMR spectroscopy when combined with the analysis of the ligand field splitting, can provide information on the magnetic state of lanthanide ions in EMFs.

In this work we report on a systematic paramagnetic NMR study of MSc\(_2\)N@C\(_{80}\) compounds with all lanthanides forming nitride clusterfullerenes (M = La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm) and concomitant calculations of the ligand field splitting in these molecules. The main goal is to provide a consistent and uniform description of the magnetic states of lanthanide ions in these molecules based on the ligand field computations verified by experimental NMR data. The manuscript is organized in several parts. First, we describe the results of experimental NMR measurements, including the temperature dependence and relaxation times. Then, we perform a thorough analysis of the NMR data to separate contact and pseudocontact contributions to paramagnetic shifts. This section is followed by the brief analysis of the molecular structures. Then point-charge calculations of the ligand field splitting are described, which give the desired description of the single ion magnetic anisotropy in the series of MSc\(_2\)N@C\(_{80}\) molecules across the whole 4f row. Reliability of the computed LF patterns is then verified by comparison of the computed and experimental pseudocontact shifts.

**Experimental and computational details**

In this work we will consider exclusively MSc\(_2\)N@C\(_{80}\) compounds with the \( \text{I}_6(7) \) carbon cage (Fig. 1). Hereafter the compounds will be abbreviated as 1M, where M denotes the corresponding lanthanide (e.g., LaSc\(_2\)N@C\(_{80}\) is denoted hereafter as 1La). All studied compounds were synthesized using the arc-discharge method in the presence of nitrogen source such as NH\(_3\) (ref. 21) or guanidine thiocyanate, and then separated using chromatography as described in the ESI Fig. S1–S5. The synthesis of 1Ce, 1Nd, 1Pr, 1Dy, 1Ho, and 1Lu in our group was described earlier. 1La, 1Pr, 1Tb, 1Er and 1Tm were...
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Fig. 1 DFT-optimized molecular structure of representative 

MSc₃N@C₈₀ (1P). Praseodymium ion (shown green) is at the
distance of 2.225 Å from the central nitrogen atom (blue), whereas two
Sc–N distances are 1.939 and 1.936 Å. Carbon atoms are shown in grey
(pentagon–hexagon–hexagon junctions, PHJJs) and orange (triple
hexagon junctions, THJJs). In (b), the plane of the cluster is normal to
the paper. Thin cyan lines denote shortest Pr–C distances: 2.508 Å
(C1), 2.553 Å (C2), 2.591 Å (C3), and 2.658 Å (C4).

synthesized for this work using guanidine thiocyanate as a
nitrogen source, whereas 1Tb and 1Y were synthesized using
NH₃ as a reactive gas. Note that the synthesis and characterization
of 1Y,²⁵ 1La,²⁶ 1Ce,²³ 1Tb,²⁷ and 1Er²⁸ was also reported by other groups using somewhat different conditions. Gd also
forms mixed-metal nitride clustertogether with Sc²⁹ but
neither 13C nor 45Sc NMR signals could be detected for 1Gd, so
this molecule will not be discussed hereafter.

The 125 MHz 13C NMR and 121.5 MHz 45Sc NMR measure-
ments were performed on a Bruker Avance 500 spectrometer
equipped with a multiprobe head 1H/13C. The measurements
were performed for compounds dissolved in CS₂ with d₅-
aacetone placed in a coaxial tube as a lock; in special cases d₅-
acetic acid was also used as a solvent. Typically the
spectra were measured at each 10 K in the temperature rage
form 268 to 308 K.

Longitudinal relaxation rates (R₁) were measured using
inversion recovery pulse sequence with different delays between
π and π/2 pulses. The values were determined from the slope of
the linear fit of ln(1/ln(1)) versus τ (delay). Transversal relaxation
rates (R₂) were measured using Carr–Purcell–Meiboom–Gill
(CPMG) pulse sequence.²⁸ The values were determined from
slopes of linear fit of –ln(1) versus τ (delay). In case of broad line
width, R₂ cannot be determined by CPMG-pulse sequence because
the relaxation is too fast. Conservative estimation of R₂ values
in such cases can be done by measuring the line width at
half peak maximum. However, R₂ is estimated by this procedure
includes the line broadening and inhomogeneity of the magnetic
field (R₂ = y2B²/2 + R₂) and therefore the T₂ time determined
from the line width is shorter than the real one.

DFT optimization of molecular coordinates was performed
at the B3LYP level using the Firefly code. The basis sets were def2-
SVP [5,1,1/3,1/1] for carbon atoms,³¹ def2-TZVP [6,2,1,1/4,1,1/1,1/1]
for nitrogen,³² and Stuttgart–Cologne effective core potentials for
Sc (ECP10MDF)³³ and lanthanides (4f-in-core ECP-MWB-II)³⁴ with
{3,1,1,1,1,1/2,1,1/4,1/1,1/1,1/1} and {3,1,1,1,1,1,1,1,1,1/2,1,1/1,1/1,1/1,1/1,1/1,1/1,1/1,1/1,1/1,1/1} valence parts, respectively. Spin density and hyperfine
coupling constants in GdSc₂N@C₈₀ were computed at the PBE
level using the specially tailored SARC basis set of TZVP quality³⁵
combined with either DKH or ZORA scalar relativistic corrections
implemented in the ORCA package.³⁶ To compute the Bader
(QTAI) charges, full electron calculations were performed at
the PBE/SARC-TZVP level with DKH scalar relativistic corrections
using ORCA. To avoid poor reliability of the full electron DFT treatment
of the 4f elements, Y was used to model the charges of the
lanthanides from Tb to Tm, whereas La was used to model Ce, Pr,
and Nd. QTAI computations of the atomic charges were then
performed with the AIMP³⁷ code. Point charge calculations of the
ligand field splitting, magnetic susceptibility tensors, and 4f electron
densities were performed using so1ion (Cfield) routine in
McPhase code.³⁸ Molecular structures and isosurfaces were visualized
with the help of VMD.³⁹

Results and discussion

NMR spectroscopy

13C and 45Sc NMR spectra at 288 K. Fig. 2 and 3 show 13C and
45Sc NMR spectra of 1M compounds measured at 288 K (the
temperature is chosen as the center of the temperature interval
used in the variable temperature NMR studies, see below).

Fast rotation of the MSc₃N cluster inside the highly
symmetric C₈₀–I₃ carbon cage results in the averaging of the
carbon signals, leaving only two 13C NMR peaks with a 3 : 1
intensity ratio. The higher intensity peaks corresponds to the 60
carbon atoms at the pentagon–hexagon–hexagon junctions
(PHHJ), whereas the lower intensity peak is due to the 20 atoms
at the triple hexagon junctions (THJ, see Fig. 1). The chemical
shift of the PHHJ carbons in diamagnetic 1M compounds is
bracketed by the 1La and 1Lu values, 144.76 and 143.99 ppm,
respectively. Likewise, the THJ signal varies from 138.08 ppm in
1La to 136.90 ppm in 1Lu. Chemical shifts of the THJ and PHHJ

Fig. 2 13C NMR spectra of 1M compounds measured in CS₂ at 288 K.
Note the different scale in the left and right panels; for a better
comparison, the spectrum of 1Y is shown in both panels.
carbon atoms in 1Y are intermediate between those of 1La and 1Lu (see Table 1). Thus, depending on the size of the endohe
dral cluster, the diamagnetic 13C values are subject to change
within the range of ca. 1 ppm (see also ref. 40) which should be
taken into account in the analysis of the paramagnetic shi
ds of Table 1 and used to compute paramagnetic shifts were obtained by approxi-
mating the 13C chemical shifts by a quadratic function of the
Shannon radii of metal ions (see ESI Fig. S6†).

The measurement of the 13C NMR spectra of paramagnetic
EMFs is complicated by the considerable line broadening.
However, thanks to the simple two-line spectrum of the C80
molecule, the signals are detectable even when they are
severely broadened as in 1Tb or 1Dy. In 1Ce, 1Pr, 1Nd, 1Tb, 1Dy,
and 1Ho the 13C signals are shifted up-field with respect to the
diamagnetic values. The magnitude of the paramagnetic shift
varies from few ppm in 1Ce, 1Pr, and 1Nd to tens of ppm in 1Tb,
1Dy, and 1Ho (Fig. 2 and Table 1). On average, lanthanide-
duced shifts of the THJ carbons are more pronounced than
those of the PHHJ carbons.

In 1Er and 1Tm the lanthanide-induce shi
d (down-field). The PHHJ and THJ 13C signals of 1Er are coin-
ciding near the room temperature and appear at 153.2 ppm, but
can be resolved at higher or lower temperatures as discussed
below. In 1Tm, the stronger lanthanide-induced shift of the THJ
signal pushes it to a lower field than that of the PHHJ (in all
other 1M compounds the PHHJ signal appears at lower field
than that of the THJ carbons). Direction of the lanthanide-
duced paramagnetic shift is determined by a magnetic
anisotropy of the lanthanide ion (see ref. 41 for recent exam-
pies), and hence experimental NMR data gives information at
least on the sign of the anisotropy. This question will be dis-
cussed in more details below.

In 45Sc NMR spectra, all 1M compounds exhibit one relat-
ively broad peak (Fig. 3). The 45Sc chemical shifts of the
diamagnetic 1La and 1Lu are 198 and 200 ppm, respectively,
whereas in paramagnetic 1M molecules the 45Sc signal position
ranges from −233 ppm in 1Er to 1892 ppm in 1Dy. The
peak width varies from 30–40 ppm for the diamagnetic 1Lu
and 1La and paramagnetic 1Ce, 1Pr, 1Nd and 1Er, to ca. 70–80 ppm
for the 1Tb, 1Dy, 1Ho, and 1Tm.

Variable temperature NMR studies. Temperature depend-
en of paramagnetic NMR shifts can be used as an additional
parameter to distinguish the contact and pseudocontact
contributions as well as to clarify the extent of the magnetic
anisotropy. Fig. 4 and 5 show variations of 13C and 45Sc NMR
spectra in the temperature range 268–308 K. To quantify the
temperature variation, we will use the Δ268(δ) parameter, which
is the difference of the chemical shifts measured at 308 and
268 K.

Temperature variation of the peak positions is in line with
the single-temperature δpara values. Namely, the compounds
with strong paramagnetic shifts exhibit enhanced variation of
the peak position with the temperature and vice versa. Likewise,
the sign of the Δ268(δ) values is opposite to the sign of the δpara
shifts. The only exclusion is the PHHJ signal of 1Tm, for which
both δpara and Δ268(δ) parameters are positive. Since this signal

Table 1 Shannon ionic radii of lanthanides and chemical shifts of 1M molecules measured at 288 K

<table>
<thead>
<tr>
<th>1M</th>
<th>R(M3+)</th>
<th>δ</th>
<th>Δν1/2</th>
<th>δ∥</th>
<th>δ⊥</th>
<th>Δ308</th>
<th>δ∥</th>
<th>Δ308</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>0.900</td>
<td>144.11</td>
<td>1.5</td>
<td>144.11</td>
<td>—</td>
<td>—</td>
<td>137.11</td>
<td>—</td>
</tr>
<tr>
<td>La</td>
<td>1.032</td>
<td>144.76</td>
<td>2.0</td>
<td>144.76</td>
<td>—</td>
<td>—</td>
<td>138.08</td>
<td>138.08</td>
</tr>
<tr>
<td>Ce</td>
<td>1.010</td>
<td>142.69</td>
<td>15.1</td>
<td>144.63</td>
<td>—1.94</td>
<td>0.73</td>
<td>135.73</td>
<td>137.89</td>
</tr>
<tr>
<td>Pr</td>
<td>0.990</td>
<td>142.55</td>
<td>41.8</td>
<td>144.51</td>
<td>—1.96</td>
<td>0.72</td>
<td>131.59</td>
<td>137.73</td>
</tr>
<tr>
<td>Nd</td>
<td>0.983</td>
<td>142.69</td>
<td>50.5</td>
<td>144.47</td>
<td>—1.78</td>
<td>0.25</td>
<td>129.91</td>
<td>137.67</td>
</tr>
<tr>
<td>Tb</td>
<td>0.923</td>
<td>105.6</td>
<td>579</td>
<td>144.20</td>
<td>—38.6</td>
<td>8.6</td>
<td>98.0</td>
<td>137.25</td>
</tr>
<tr>
<td>Dy</td>
<td>0.912</td>
<td>97.5</td>
<td>905</td>
<td>144.15</td>
<td>—46.7</td>
<td>10.2</td>
<td>61.6</td>
<td>137.18</td>
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<tr>
<td>Ho</td>
<td>0.901</td>
<td>119.1</td>
<td>284</td>
<td>144.11</td>
<td>—25.0</td>
<td>—</td>
<td>74.2</td>
<td>137.12</td>
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<tr>
<td>Er</td>
<td>0.890</td>
<td>153.23</td>
<td>45</td>
<td>144.08</td>
<td>9.15</td>
<td>2.12</td>
<td>153.23</td>
<td>137.05</td>
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<tr>
<td>Tm</td>
<td>0.880</td>
<td>144.83</td>
<td>17.2</td>
<td>144.04</td>
<td>0.79</td>
<td>0.34</td>
<td>151.97</td>
<td>137.00</td>
</tr>
<tr>
<td>Lu</td>
<td>0.861</td>
<td>143.99</td>
<td>1.2</td>
<td>143.99</td>
<td>—</td>
<td>—</td>
<td>136.90</td>
<td>136.90</td>
</tr>
</tbody>
</table>

* Ionic radii are in Å, chemical shifts are in ppm, line width Δν1/2 in Hz. 13C chemical shifts are determined with precision to the second decimal except for 1Tb, 1Dy, and 1Ho, which are determined to the first decimal. The diamagnetic shifts were estimated from the polynomial fit of the δ(1M)-versus-R(M3+) data for 1Y, 1La, and 1Lu. The values are obtained by subtracting the 45Sc chemical shift of 1La (1Ce, 1Pr, 1Nd) or 1Lu (other compounds).
has the smallest $\delta_{\text{para}}$ value (0.79 ppm), we cannot exclude that uncertainties in the estimation of the $\delta_{\text{para}}$ value may play a role here. More likely, however, is that the pseudocontact and contact contributions have opposite signs and compensate each other in this molecule.

**Line width and relaxation times.** Variation of the line width, which is especially well pronounced in the $^{13}$C NMR spectra, points to the substantial change of relaxation times across the lanthanide row. A transverse relaxation time $T_2$ can be estimated using the relation $T_2 = (\pi \Delta r_{1/2})^{-1}$, where $\Delta r_{1/2}$ is the peak width at its half maximum. The $\Delta r_{1/2}$ values determined for PHHJ signals at 288 K are listed in Table 1. For $^{1}Tm$ we have also measured $T_2$ and $T_1$ times directly using Carr–Purcell–Meiboom–Gill pulse sequence and inversion recovery method, which gave 50 ms and 66 ms at 288 K, respectively (see ESI Fig. S7 and S8† for other temperatures). As might be anticipated, $T_1$ is longer than $T_2$, and the $T_2^*$ value of 19 ms determined by the line width method underestimates the real $T_2$ time but gives correct order of the value. Direct measurements of shorter relaxation times is beyond the possibilities of our spectrometer. In diamagnetic $^{1}M$ compounds, the nuclei spin relaxation times are much longer.44 For instance, $T_2$ and $T_1$ times of the PHHJ carbons in $^{1}Y$ are 17 and 23 s, respectively. Note that $T_2$ determined from the CPMG pulse sequence for diamagnetic $^{1}Y$ is significantly longer than might be estimated from the line width ($T_2^* = 0.2$ s), which shows that the line width for such narrow signals is limited by the instrument.

Comparison of the $\Delta r_{1/2}$ values for $^{13}$C peaks in $^{1}M$ series (Fig. 1 and Table 1) reveals dramatic influence of the lanthanide on the nuclei spin relaxation. For instance, $^{13}$C nuclei spins in $^{1}Dy$ ($T_2 \approx 0.3$ ms) relax ca. $5 \times 10^4$ times faster than in diamagnetic $^{1}Y$ ($T_2 = 17$ s). The plot of $\Delta r_{1/2}$ versus $\delta_{\text{para}}$ for the PHHJ carbons along the $^{1}M$ series can be well fit by a parabola (see ESI Fig. S9†). This fact points to the prevailing contribution of the pseudocontact shift in the total paramagnetic shift since the relaxation rate in paramagnetic molecules has $R^4$ dependence on the distance between the nuclei and paramagnetic center, whereas the pseudocontact shift scales as $R^{-3}$ (eqn (1)).

The broadening of $^{45}$Sc signals along the $^{1}M$ series is not so pronounced as for carbon signals because the $^{45}$Sc quadrupole moment broadens the peaks even in diamagnetic molecules. The $^{45}$Sc signals in $^{1}Dy$, $^{1}Tb$, $^{1}Ho$, and $^{1}Tm$ are roughly two times broader than in the $^{1}Y$ (Fig. 3), which can be ascribed to a paramagnetic effect. At the same time, in $^{1}Ce$, $^{1}Pr$, $^{1}Nd$, and $^{1}Er$ the line width is comparable to that of diamagnetic $^{1}Y$, which means that the spin relaxation rate in these molecules is still determined by a quadrupole effect.

The line width exhibits substantial decrease at lower temperatures (Fig. 4 and 5). For instance, $^{45}$Sc signals measured at 268 K are roughly twice broader than at 308 K (Fig. 5). In some previous works, temperature dependence of the $^{45}$Sc line width was used to estimate rotation barrier of the endohedral clusters.19,41 If the line width is directly proportional to the rotational correlation time, the plot $\ln(\Delta r_{1/2})$ versus $T^{-1}$ gives a straight line with the slope proportional to the activation energy. In this work, none of the $^{1}M$ molecules gave straight line in the $\ln(\Delta r_{1/2})$ versus $T^{-1}$ coordinates, preventing thus further analysis of the data. The broadening at low temperature should result from the interplay of the slowing of the cluster dynamics and the electron spin contribution, which can hardly be separated at this moment.

**Separation of contact and pseudocontact shifts**
The localized “buried” nature of the 4f electrons in lanthanides implies that the contact contribution to the paramagnetic shift should be rather small. Typically, the values become negligible when the nucleus of interest is separated by more than four
magnetic NMR, and several schemes were proposed to solve it. Unfortunately, all methods allowing analytical deviation of linearizable equations are based on Bleaney’s assumption that LF splitting is less than the thermal energy and hence expansion of the magnetic susceptibility in reciprocal temperature series is limited to $T^{-2}$. This assumption is definitely not fulfilled for 1M molecules, and hence the results of these calculations may give only qualitative estimation at best (see also ref. 41a for a detailed discussion of the limitations of Bleaney’s theory). Another assumption usually applied is that the system is either purely axially (LF operator described in phenomenological $B_0^2$ parameters is limited to the $B_0^2$ term), or its rhombic anisotropy can be described solely by a $B_2^2$ parameter. The sum of contact and pseudocontact shifts can be then described as:

$$\delta_0^{\text{para}} = F_i (S_j \parallel_i) + C_i (B_0^2 G_i + 6B_2^2 H_i)$$

The first term is the contact shift, where $F_i$ is proportional to a Fermi coupling constant, and $(S_j \parallel_i)$ is the expectation value of the spin projection operator $S_i$ for a given lanthanide. The second term is the pseudocontact shift, $C_i$ is a numerical factor specific for each lanthanide and tabulated by Bleaney et al., whereas $G_i$ and $H_i$ are structural factors (compare to eqn (1a)). If rhombic anisotropy is negligible, the second term reduces to $\delta_0^{\text{para}} = C_i B_0^2 G_i$ (compare to eqn (1b)).

Reilley’s method. Following the method proposed by Reilley et al., eqn (2) can be written in the form:

$$\frac{\delta_0^{\text{para}}}{(S_j \parallel_i)} = F_i + C_i \left( B_0^2 G_i + \sqrt{6}B_2^2 H_i \right)$$

The plot $\delta_0^{\text{para}}/(S_j \parallel_i)$ versus $C_i/(S_j \parallel_i)$ along the lanthanide series is expected to give a straight line, if all molecules are isostructural, and the $F_i$ value and LF parameters are not changing along the series. Contact and pseudocontact shifts can be then computed from the intercept and the slope.

Fig. 6 shows $\delta_0^{\text{para}}/(S_j \parallel_i)$ versus $C_i/(S_j \parallel_i)$ plots for two NMR signals measured for 1M molecules. $^{13}\text{C}$ PPHJ and $^{45}\text{Sc}$ shifts can be roughly linearized if 1Tm values are excluded from the set; the $\delta_0^{\text{con}}$ and $\delta_0^{\text{pc}}$ shifts computed from the linear fits are listed in Tables 2 and 3. The $^{13}\text{C}$ THJ shifts cannot be fitted by a straight line in these coordinates (see ESI Fig. S10f).

The absolute values of $\delta_0^{\text{con}}$ shifts for the PPHJ carbons are 2–4 times smaller than those of $\delta_0^{\text{para}}$. Furthermore, the $\delta_0^{\text{con}}$ and $\delta_0^{\text{pc}}$ shifts of $^{1}\text{Ce}$, $^{1}\text{Pr}$, $^{1}\text{Nd}$, $^{1}\text{Er}$, and $^{1}\text{Tm}$, have opposite signs. For $^{1}\text{Nd}$ this analysis predicts mutual compensation of $\delta_0^{\text{con}}$ and $\delta_0^{\text{pc}}$, but uncertainties of 1–2 ppm make the analysis of the small values rather ambiguous.

The ratio between $\delta_0^{\text{con}}$ and $\delta_0^{\text{pc}}$ for the $^{45}\text{Sc}$ chemical shifts is smaller than for the $^{13}\text{C}$ counterparts, and the contact term contribution drops to less than 10% for the majority of lanthanides; the largest relative $\delta_0^{\text{con}}$ values of ca. 20% are found in $^{1}\text{Nd}$ and $^{1}\text{Ho}$. Thus, although uncertainty of the fit is rather high, the dominance of the pseudocontact term is beyond any doubt.

Deviations from the straight line in eqn (3) are usually considered to be an indication of the loss of the isostructurality along the series. This can hardly be the case for the 1M series since molecular structures determined by single-crystal X-ray diffraction for some of them are very similar (subject to vary with lanthanide contraction, see below). More likely, other assumptions used in the model are not valid. In particular, Reilley’s approach implies that the LF parameters are not changing along the lanthanide row, which is most probably not correct for the 1M molecules.

Parameter-free models. The requirement of the constant LF parameters is one of the obvious weak points of Reilley’s approach, which can be circumvented by combining the data on two or more nuclei and excluding $B_0^2$ and $B_2^2$ terms in eqn (3). For an uniaxial system ($B_2^2 = 0$), the 2-nuclei parameter-free model is obtained by plotting $\delta_0^{\text{para}}/(S_j \parallel_i)$ versus $\delta_0^{\text{para}}/(S_j \parallel_i)$, which should give a straight line for the isostructural series (ref. 46):

$$\delta_0^{\text{para}}/(S_j \parallel_i) = \left( F_i - F_j + \frac{G_j}{G_i} \right) + \frac{G_j}{G_i} \frac{\delta_0^{\text{para}}}{(S_j \parallel_i)}$$

The slope of the line is a ratio of the structural factors $G_j/G_i$, and the intercept is a difference of $F_i$ and $F_jG_i/G_j$. For the molecules with a rhombic anisotropy ($B_2^2 \neq 0$), the parameter-free model can be obtained in a similar fashion by simultaneous analysis of chemical shifts of three different nuclei. In the latter case linearization gives the equation of a plane (ref. 47):

$$\frac{\delta_0^{\text{para}}}{(S_j \parallel_i)} = (F_i - F_k D_{ik} + F_k E_{ik}) + D_{ik} \frac{\delta_0^{\text{para}}}{(S_j \parallel_i)} + E_{ik} \frac{\delta_0^{\text{para}}}{(S_j \parallel_i)}$$

where coefficients $D_{ik}$ and $E_{ik}$ are functions of the structural parameters $G_i$ and $H_i$ from eqn (3), see ref. 47a for full details.

Fig. 7 visualizes analysis of all chemical shifts for 1M molecules within parameter free models. The 3D plot corresponds to the 3-nuclei method, whereas projections on the coordinate planes allow evaluation of the 2-nuclei method for three different combination of nuclei. In the 3-nuclei model, all data...
Table 2 Contact and pseudocontact $^{13}$C chemical shifts in 1M molecules

<table>
<thead>
<tr>
<th>1M</th>
<th>$\langle S_z \rangle^a$</th>
<th>$C_j^a$</th>
<th>PHJJ $\delta^{con}$</th>
<th>PHJJ $\delta^{pc}$</th>
<th>DFT $\delta^{con}$</th>
<th>DFT $\delta^{pc}$</th>
<th>PCM $\delta^{con}$</th>
<th>PCM $\delta^{pc}$</th>
<th>$\Delta_t^{106ke}$ 268</th>
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<tr>
<td>Ce</td>
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<td>0.3</td>
<td>0.4</td>
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<td>Pr</td>
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<td>-4.0</td>
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<td>-7.7</td>
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<td>1.4</td>
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<td>1.1</td>
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<td>Tb</td>
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<td>Ho</td>
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<td>Tm</td>
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$^a$ $\langle S_z \rangle$ and $C_j$ values are adopted from ref. 44a. $^b$ PBE/SARC-TZVP calculations. $^c$ The values are obtained as $\delta^{pc} = \delta^{para}(exp) - \delta^{con}(DFT)$. $^d$ "PCM" stands for point charge model. $^e$ $\Delta_t^{106ke}$ values are computed using PCM approach and include only $\delta^{pc}$ contribution.

Table 3 Contact and pseudocontact $^{45}$Sc chemical shifts in 1M molecules

<table>
<thead>
<tr>
<th>1M</th>
<th>Reilley 2-nuc $e$</th>
<th>Reilley 2-nuc $b$</th>
<th>PCM $\delta^{con}$</th>
<th>PCM $\Delta_t^{106ke}$ 268</th>
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<tr>
<td>Ce</td>
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<td>17</td>
<td>-2</td>
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<tr>
<td>Tb</td>
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</tr>
<tr>
<td>Dy</td>
<td>-110</td>
<td>13</td>
<td>1472</td>
<td>1679</td>
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<td>Ho</td>
<td>-87</td>
<td>10</td>
<td>578</td>
<td>862</td>
</tr>
<tr>
<td>Er</td>
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<tr>
<td>Tm</td>
<td>-32</td>
<td>4</td>
<td>-773</td>
<td>-213</td>
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</table>

$^e$ Obtained using the fit of eqn (4a) together with $^{13}$C-PHJJ shifts, and then subtracting $\delta^{con}(^{13}$C) values estimated by Reilley’s approach. $^b$ The value was not included in the fit; inclusion of 1Pr shift worsened the fit from $R^2 = 0.96$ to $R^2 = 0.87$, but gave the values closer to those obtained by Reilley’s approach. $^c$ The values are obtained as $\delta^{pc} = \delta^{para}(exp) - \delta^{con}(2-nuc)$. $^d$ "PCM" stands for point charge model. $^e$ $\Delta_t^{106ke}$ values are computed using PCM approach and include only $\delta^{pc}$ contribution.

DFT calculations of contact shifts. Independent computations of contact shifts are possible using quantum chemical approaches. DFT computations of lanthanide-containing molecules for systems other than 4f$^7$ cannot be reliable (unless 4f-in-core effective core potentials are used, but this approach cannot be used if spin properties related to the 4f electrons are of interest). However, the $F_i$ value usually remains the same for the whole lanthanide row, and hence computations can be performed for Gd analogues. Recently, such calculations provided accurate estimation of the contact shifts in a series of Tb complexes.$^{19}$

Fig. 7 Three-nuclei 3D plot in $\delta^{para}/\langle S_z \rangle$ coordinates for $^{45}$Sc, $^{13}$C-PHJJ and $^{13}$C-PHJJ chemical shifts in 1M series ($T = 288$ K). Red spheres are 3D data; blue, green, and black circles are projections on coordinate planes. Red grid shows a fitted plane (1Pr was not included in the fit).
atoms further away from the Gd ion is the same as for the Gd itself.

Hyperfine coupling constants for carbon atoms in GdSc2N@C80 span the range from −0.041 MHz to 0.096 MHz, and the averaging over the whole carbon cage yields the values of 0.015 and 0.010 MHz for the PHHJ and THJ carbons, respectively. The pseudocontact shifts computed for 13C atoms using these constants are listed in Table 2. Remarkably, the DFT-computed values for the PHHJ carbons are quite close to those obtained by Reilley’s method. If we tentatively suggest that the agreement between the theory and experiment is equally well for the THJ carbons, their contact shifts should be 35% smaller than those of PHHJs. Furthermore, relative contributions of the contact term in total paramagnetic shifts of the THJ carbons are much smaller than for the PHHJ carbons.

For the 45Sc hyperfine coupling constant, the PBE-DKH approximation with tailored SARC-TZVP basis set gives the average value of −0.27 MHz. An increasing the basis set to def2-TZVP or inclusion of the spin–orbit coupling corrections give the values of −0.26 MHz and −0.28 MHz, respectively, whereas switching to ZORA scalar relativistic method reduces the 45Sc hyperfine coupling constant to −0.21 MHz. If hybrid PBE0 functional is used instead of PBE with SARC-TZVP basis, predicted DKH and ZORA values are −0.35 and −0.49 MHz, respectively. The use of PBE-DKH/TZVP constants for estimation of the 45Sc contact shifts in 1M molecules yields unrealistically high values (625 ppm for 1Tb, 560 ppm for 1Dy, etc.). It should be noted that computation of the 45Sc hyperfine coupling constants is less straightforward than for 13C nuclei because of the subtle balance between the valence- and core–shell spin polarizations, which often have opposite signs in transition metals.49 Due to this reason, prediction of the 45Sc hyperfine coupling constant meets serious difficulties even for the Sc-based EMFs radicals such as Sc2N@C80 (ref. 50), where coupling constants are large and dominated by SOMO contribution. Reliable prediction of the core–shell spin polarization becomes even more problematic for paramagnetic molecules, in which the spin density on the Sc atoms is largely induced by spin polarization (such as in 1M). We have to admit that DFT prediction of small 45Sc coupling constants in 1M can hardly be reliable at this moment and refrain from further discussion of DFT-computed $\sigma_{\text{con}}(45\text{Sc})$ values.

Temperature dependence of chemical shifts. If Bleaney’s conditions are satisfied, the temperature dependence of chemical shifts can be also used to distinguish contact and pseudocontact terms: whereas the contact term scales as $T^{-1}$, the pseudocontact term has $T^{-2}$ dependence. If one of the terms dominates, plot $\delta_{\text{para}}$ versus $T^{-1}$ or $T^{-2}$ should give a straight line, whose intercept is close to $\delta_{\text{dia}}$. In due turn, a large deviation of the intercept from the reference $\delta_{\text{dia}}$ value signals that the corresponding contribution is small. This simple yet efficient approach was employed before to prove the dominance of pseudocontact shift in Ce-based EMFs. However, this approach can give reliable results only if the pseudocontact term has real $T^{-2}$ dependence, and if one the terms dominates. If LF splitting is larger than the thermal energy, contribution of $T^{-3}$ and higher terms cannot be ignored,51 and results of the linear fitting become inconclusive. In the 1M series, only for 1Ce is the intercept of the $\delta_{\text{para}}(T^{-2})$ plot close to $\delta_{\text{dia}}$ for all three nuclei (see ESI Table S1†). For all other lanthanides, the intercepts of $\delta_{\text{para}}(T^{-1})$ and $\delta_{\text{para}}(T^{-2})$ linear fits give rather irregular set of data, sometimes with large deviations from $\delta_{\text{dia}}$ for both $T^{-1}$ and $T^{-2}$ plots (ESI Table S1†). Thus, large magnetic anisotropy of lanthanide ions in 1M molecules prevents the use of temperature dependence for distinguishing contact and pseudocontact contributions to paramagnetic chemical shifts. Good results obtained for the 1Ce in $\delta_{\text{para}}(T^{-2})$ fits are in part due to the small $(S_e)_{1\text{Ce}}$ value (Table 2), which makes the contact term negligible.

Geometry parameters of 1M molecules

For the further analysis of the magnetic state and the LF splitting of lanthanide ions in the 1M compounds it is necessary to take into account a variation of the molecular geometry parameters along the series. Namely, a significant decrease of the ionic radii of lanthanides from La to Lu cannot be ignored, especially when magnetic anisotropy is large. Therefore, to obtain a consistent set of the molecular geometry parameters along the whole 4f row for the subsequent LF calculations (see next section), we performed DFT optimization of all structures using the B3LYP functional and 4f-in-core basis set for lanthanides. The M–N and averaged Sc–N bond lengths are listed in ESI Table S2† and are plotted versus Shannon ionic radii of M$^{3+}$ ions in Fig. 9. As expected, the decrease of the ionic radii from La to Lu results in the gradual decrease of the M–N distance (from 2.241 Å in 1La to 2.133 Å in 1Lu). At the same time, since the carbon cage remains the same, the increase of the lanthanide size also leads to the simultaneous decrease of the Sc–N bond lengths (compare 1.929 Å in 1La to 1.979 Å in 1Lu) so that the cluster size remains more or less the same along the whole series. Single-crystal X-ray structures were reported earlier for 1La,16 1Ce,19 1Gd,17 1Tb,17 and 1Er,20 and experimental bond length values also confirm this trend. Namely, in the 1La–1Ce–1Gd–1Tb–1Er the lanthanide–nitrogen bond is decreasing as 2.196(4)–2.184(2)–2.149(10)–2.126(11)–2.089(9) Å. The averaged Sc–N distance is varying as 1.932(7)–1.938(2)–1.918(9)–1.949(8)–1.968(6) Å, respectively, i.e. there is a gradual decrease from 1La/1Ce to 1Tb to 1Er (note
that 1Gd deviates from the trend). A comparison to the computed data shows that DFT overestimates the M–N distances by ca. 0.04–0.06 Å, whereas the error for the Sc–N distances is smaller than 0.01 Å. Overall, DFT-optimized bond lengths give reasonable estimation of the experimental values.

Significant variation of the bond lengths in nitride clusters can be also inferred from the analysis of the FTIR absorption spectra. In the frequency range of 500–800 cm⁻¹, all nitride clusterfullerenes have a characteristic antisymmetric metal–nitrogen stretching vibration with medium to strong absorption intensity, whose frequency correlates with the metal–nitrogen bond length and therefore can be used for the analysis of the LF in nitride clusterfullerenes. Recently we showed that the point charge model employing scaled Bader charges can reasonably reproduce the ab initio (CASSCF) computed ligand field splitting in DySc₂N@C₈₀, which enables the use of this simple approach for other 1M compounds. To calculate the LF splitting in this work we used B3LYP-optimized coordinates discussed above and Bader charges for nitrogen, scandium, and four closest carbon atoms (denoted C1–C4 in Fig. 1; since the cage carbon atoms have very small contribution to the LF, it is sufficient to consider only few nearest atoms, their QTAIM charges are listed in the ESI Table S2†).

Ligand field in 1M molecules

Reliable determination and verification of the cluster bond lengths discussed in the previous section is crucial for the analysis of the LF in nitride clusterfullerenes. Recently we showed that the point charge model employing scaled Bader charges can reasonably reproduce the ab initio (CASSCF) computed ligand field splitting in DySc₂N@C₈₀, which enables the use of this simple approach for other 1M compounds. To calculate the LF splitting in this work we used B3LYP-optimized coordinates discussed above and Bader charges for nitrogen, scandium, and four closest carbon atoms (denoted C1–C4 in Fig. 1; since the cage carbon atoms have very small contribution to the LF, it is sufficient to consider only few nearest atoms, their QTAIM charges are listed in the ESI Table S2†).

The central nitrogen atom gives the main contribution to the LF in nitride clusterfullerenes because of its large negative charge (Bader charge −1.7) and close distance to the lanthanide...
ca. by ions, degeneracy of the ions is well seen for non-Kramers ions (Pr, Tb, Ho). For these deviation from the uniaxial symmetry induced by the two Sc densities in exhibits only small variation with temperature. For instance, properties. A sar are results, 4f densities such predicted to have predominant contribution to the magnetic account, an approximate degeneracy of the ion. When the contribution of the Sc ions is also taken into overall LF splitting, 571 cm\(^{-1}\). The two-fold degenerate ground state with the large Lanthanide ions with oblate 4f-density. The ground magnetic state of the ions with oblate shape of the 4f electron density (Ce, Pr, Nd, Tb, Dy, Ho; see ref. 54 and Fig. 11a for 4f density in 1Dy) has the largest \(J_z\) value (5/2 in 1Ce, 4 in 1Pr, 9/2 in 1Nd, 6 in 1Tb, 15/2 in 1Dy, and 8 in 1Ho), and the energy of the other \(m_j\) states is gradually increasing with the decrease of the \(|m_j|\) values. The gaps between the neighboring \(m_j\) states are also getting smaller with the decrease of the \(|m_j|\) value. The deviation from the uniaxial symmetry induced by the two Sc ions is well seen for non-Kramers ions (Pr, Tb, Ho). For these ions, degeneracy of the \(\pm m_j\) states is not enforced, but remains rigorous in the uniaxial ligand field produced by a single nitride ion. When the contribution of the Sc ions is also taken into account, an approximate degeneracy of the \(\pm m_j\) states holds only for large projections of the total momentum, whereas for the levels with \(|m_j| = 1\) the splitting becomes significant. A mixing of the \(m_j\) states is also substantial for small \(|m_j|\) values showing that the \(m_j\) is not a “good” quantum number anymore.

The practical importance of the states with small \(|m_j|\) values in ions with oblate 4f density is rather limited because the LF splitting in 1M is very large (Fig. 10). The smallest overall LF splitting, 571 cm\(^{-1}\), is found in 1Ho, whereas the largest LF splitting is reaching 1915 cm\(^{-1}\) in 1Ce. The gap between the ground state and the first excited state in 1Ce (1075 cm\(^{-1}\)), 1Pr (849 cm\(^{-1}\)), 1Nd (364 cm\(^{-1}\)), 1Tb (384 cm\(^{-1}\)), and 1Dy (382 cm\(^{-1}\)) is so large that even at room temperature the ground magnetic state with the largest \(J_z\) projection is predicted to have predominant contribution to the magnetic properties. As a result, 4f density in such 1M molecules exhibits only small variation with temperature. For instance, 4f densities in 1Dy calculated at 2 K and 288 K can hardly be distinguished by eye (Fig. 11a).

The two-fold degenerate ground state with the large \(J_z\) projection and a significant gap to the first excited state are prerequisites for the SMM behaviour,\(^{54}\) and hence the data in Fig. 10 show that slow magnetization reversal can be expected for all 1M compounds (except for the 1Gd, 1Er and 1Tm). The SMM behaviour with exceptionally long attempt time is already discovered for 1Dy.\(^{3,4}\) Field-induced SMM behaviour is also found in non-Kramers 1Ho,\(^{5}\) albeit on a much shorter timescale than in 1Dy. The rigorous protection of the two-fold degeneracy of the ground magnetic state in Kramers ions makes them more attractive for single ion magnetism, and we expect 1Ce and 1Nd to be the next candidates for the SMM behaviour in nitride clustercfeculene as already detected in some organometallic complexes of Ce\(^{55}\) and Nd.\(^{56}\) It should be however noted that the magnetization reversal barrier in 1Dy is smaller than expected from its LF splitting,\(^{4}\) which indicates that the mechanism for the magnetization reversal in 1M compounds is more complex and may include, for instance, Raman-like process.\(^{5}\)

**Lanthanide ions with prolate 4f-density.** The LF splitting pattern in 1Er and 1Tm is completely different because of the prolate shape of the 4f electron density of these lanthanides (Fig. 11b). The ground state for these lanthanides has the lowest \(J_z\) projection (\(m_j = \pm 1/2\) in 1Er and \(m_j = 0\) in 1Tm). The energy is increasing with the increase of the \(|m_j|\) values, and the density of states is higher in the low energy part of the spectrum, whereas at higher energies the energy levels are distributed sparser. As a result of such level distribution, variation of the temperature has profound effect on the magnetic anisotropy of 1Tm and 1Er. As can be seen in Fig. 11b, an increase of the temperature dramatically changes 4f electron density distribution in 1Er and makes it almost isotropic. Thus, the room-temperature magnetic properties of 1Er and 1Tm result from the contribution of several \(m_j\) states.
1Er is the only compound in the whole 1M series for which spectroscopic data on the lanthanide-based luminescence are available. At helium temperatures the luminescence spectra of 1Er exhibit the fine structure due to the Er-based transitions in the $^4I_{13/2} \rightarrow ^4I_{11/2}$ manifold. Unfortunately, emission from several molecular/cluster sites complicates the fine structure and makes assignment less straightforward. The energy gap between the two lowest energy LF states determined in ref. 57, 28/37 cm$^{-1}$, compares reasonably to the 37 cm$^{-1}$ gap between the $m_I = \pm 1/2$ and $m_I = \pm 3/2$ states in our calculations, however the overall splitting determined in the optical measurements, 330 cm$^{-1}$, is considerably smaller than the value of 554 cm$^{-1}$ predicted by the point-charge model.

### Computed versus experimental pseudocontact chemical shifts

LF calculations allow direct estimation of the magnetic susceptibility tensor at different temperatures using Van Vleck formulae, and therefore enable computations of the pseudocontact chemical shifts using eqn (1a) or (1b) given the atomic coordinates are known (e.g. from DFT calculations) and they are not changing with temperature. Comparison between experimental and computed chemical shifts can be used then to evaluate reliability of the computed ligand field splitting levels. Rotation of the nitride cluster inside the carbon cage means that the values computed for individual carbon atoms should be averaged. Recently we found that the static model (simple averaging of the values) and the averaging of the values computed over molecular dynamics trajectory give comparable results for 1Ho,57 and therefore only static model is applied in this work.

In the 1M molecules with oblate 4f-density eqn (1a) and (1b) give identical values of the pseudocontact shift because $\chi_{xx}$ and $\chi_{yy}$ components of the magnetic susceptibility tensor are virtually equal. In the 1Er and 1Tm molecules, the difference between $\chi_{xx}$ and $\chi_{yy}$ values is rather large, and hence eqn (1a) is to be used. The pseudocontact shifts computed for the THJ and PHHJ carbons as well as for the Sc atoms at $T = 288$ K are listed in Table 2 and 3 along with the computed $\Delta_{\text{obs}}$ values. Fig. 11 plots pseudocontact shift isosurfaces in 1Dy and 1Er as examples of lanthanides with oblate and prolate 4f density shapes, respectively.

The reliability of the point charge model in calculations of the magnetic susceptibility can be evaluated comparing experimental and computed $\delta^\text{pc}$ shifts (Fig. 12). As experimental values we use the results of Reilley’s approach for $^{13}$C-PHHJ signal and the values from the 2-nuclei fitting for $^{45}$Sc shifts. Details for the $^{13}$C-THJ shifts are not discussed in the text but can be found in the ESI Fig. S11†.

As can be seen in Fig. 12, reasonably good correlation exists between experimental and computed data. If 1Tm and 1Tb are not included in the set, the linear correlation with the intercept set to zero gives $R^2$ values of 0.98 and 0.99 for the PHHJ and $^{45}$Sc shifts, respectively. Note also that the $^{45}$Sc $\delta^\text{pc}$ shifts from the 2-nuclei model are very close to the total $\delta^\text{para}$ shifts. Thus, we can tentatively use $^{45}$Sc chemical shifts of paramagnetic mixed-metal nitride clusterfullerenes to evaluate the size of the magnetic anisotropy of the endohedral lanthanide ions without rather complicated and sometimes hardly possible estimation of the contact term.

It should be also noted that the slope of the linear fit in Fig. 12 is close to 0.9 for $^{45}$Sc but is near 1.4 for $^{13}$C-PHHJ. The slope for an analogous fit for the $^{13}$C-THJ signals (see ESI Fig. S11†) is close to 0.9. As follows from eqn (1) and our earlier studies of the Ho-based NCFSs,57,79 the structural factor also plays an important role in determining the $\delta^\text{pc}$ values, and dynamic nature of the $^{13}$C shifts in 1M molecules (i.e. averaging over the cluster rotation) makes calculation less straightforward than for the $^{45}$Sc shifts. For instance, in 1Ho the term $(3\cos^2 \theta - 1)/12\pi R^3$ (denoted hereafter as $G_3$) computed in this work at the B3LYP level is $-3.30 \times 10^{-3} - 1.29 \times 10^{-3}$ Å$^{-3}$ for the PHHJ/THJ carbons, respectively. At the same time, our recent PBE computations using Y as a model for Ho gave the values of $-7.37 \times 10^{-4} - 5.59 \times 10^{-4}$ Å$^{-3}$, respectively. Along the 1M series, the $G_3$ values for carbon atoms vary by 15-20%, from $-3.91 \times 10^{-4} - 1.13 \times 10^{-3}$ Å$^{-3}$ in 1Ce to $-3.16 \times 10^{-4} - 1.31 \times 10^{-3}$ Å$^{-3}$ in 1Er. Since the slope of the linear fit between experimental and calculated $\delta^\text{pc}$ values for THJ carbons is closer to 1, we propose that B3LYP level gives correct values for the THJ carbons, whereas $G_3$ factors for the PHHJs are underestimated (and therefore the slope is close to 1.4). Thus, the use of paramagnetic $^{13}$C chemical shifts for analysis of the magnetic anisotropy of the endohedral lanthanide ions meets certain difficulties caused by the uncertainties in the structural factor when endohedral cluster is rotating on the NMR time scale. On the contrary, the $G_3$ term for $^{45}$Sc is almost independent on the level of theory employed to calculate it. Moreover, its variation along the whole 1M series is below 1% because the shortening of the M-N distance in the cluster is balanced by the elongation of the Sc-N distance. Such indifference to the structural factor makes the $^{45}$Sc chemical shifts more suitable for the analysis of the magnetic anisotropy in mixed-metal nitride clusterfullerenes.

Computed $\Delta_{\text{obs}}$ values reasonably agree with experimental data for THJ carbon and Sc signals, but are rather far from the experimental values of the PHHJ carbons. The latter is likely to
be due to the larger relative contribution of the contact shift for the PHHJ carbons, which is not taken into account in PCM computations of $\Delta_{268}^{308}$. This is especially well seen for the 1Tm based on its magnetic anisotropy, negative $\Delta_{268}^{308}$ value is expected for the pseudocontact shift, but positive for the contact shift. A small positive $\Delta_{268}^{308}$ value observed experimentally for the 1Tm-PHHJ carbon is therefore due to the compensation of both terms. On the contrary, the pseudocontact contribution in the 1Tm-THJ chemical shift is much larger than the contact counterpart, and the experimental $\Delta_{268}^{308}$ value is negative in good agreement with the results of computations.

1Tm and 1Tb are important deviations from the general trend (Fig. 12). Especially noticeable is the 1Tb value for the $^{45}$Sc shift, which is predicted to be much more positive than experimentally observed (Fig. 12). In other words, whereas the point charge model predicts that the LF splitting in 1Tb and 1Dy is quite similar (Fig. 10), from the $^{45}$Sc NMR spectra it follows that the LF splitting in 1Tb should be considerably smaller. Interestingly, recent ab initio CASSCF calculations predict that the LF splitting in 1Tb is indeed smaller than in 1Dy,\(^7\) which would give better agreement with experimental NMR shifts. Similarly, correct prediction of the experimental values for 1Tm require reliable estimation of a considerable number of the LF splitting levels (Fig. 10), rather than only 1–2 excited states needed for other 1M molecules. Inability of the point charge model to correctly treat all states may be also the reason of the noticeable deviations well seen for 1Tm values in Fig. 12. Therefore, both 1Tb and 1Tm values provide convenient training set to be considered in future computational studies. At the current moment we can conclude that the point charge model gives qualitatively correct predictions of the LF splitting in lanthanide EMFs but fails to describe more subtle effects. More advanced approaches would be needed to address this problem,\(^4\) but this task goes beyond the scope of this work.

Conclusions

In this work we have performed the first systematic paramagnetic NMR study of MSc$_2$N@C$_{80}$ molecules with M running through all lanthanides capable of forming nitride fullerene clusters (M = La, Ce, Pr, Nd, Tb, Dy, Ho, Er, Tm, Lu). Analysis of the whole set of data enabled separation of the contact and pseudocontact contributions to the paramagnetic shifts. We showed that the contact shift of $^{13}$C nuclei may be rather large, although pseudocontact term is still larger. For the $^{45}$Sc shifts, the pseudocontact term dominates. Since pseudocontact term is directly dependent on the magnetic anisotropy, the $^{45}$Sc NMR spectra are found to be especially useful for the studies of magnetic properties of lanthanide ions in clusterfullerenes.

Interpretation of the paramagnetic NMR data required modelling of the ligand field splitting in MSc$_2$N@C$_{80}$ molecules, which was accomplished using the point charge model. Although quite simple, this approach provided semi-quantitative agreement with experimental data. Considerable deviations between experimental and computed chemical shifts are found only for TmSc$_2$N@C$_{80}$ and TbSc$_2$N@C$_{80}$. We showed that the main contribution to the ligand field is from the nitride ion, which results in an almost uniaxial ligand field. For the lanthanides with oblate shape of the 4f density (i.e. all lanthanides except for Er and Tm) the ground magnetic state in MSc$_2$N@C$_{80}$ has the largest $J_z$ projection with rather large gap to higher energy states (with smaller $m_y$ values). It shows that MSc$_2$N@C$_{80}$ molecules with Kramers lanthanide ions are especially promising in the field of single molecule magnetism. Yet, more refined treatment of the ligand field splitting might be needed to fully account for all experimental data.

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Notes and references


