First-principles study and design of cobalt carbides and metallofullerenes for magneto-thermal cancer therapy

Andrew Kuznetsov

ATG:Biosynthetics, Merzhausen, Germany
Magneto-thermal cancer therapy, rules for magnetic particles

Gd@C$_{82}$(OH)$_{22}$
golden mean of nanotechnology?
**Ab initio** approach

**Method:** DFT - density functional theory

GGA-PBE - generalized gradient approximation [Perdew, Burke, Ernzerhof, 1996]

**Calculation:** the total spin magnetic moment, $\mu_B$

**Software:** OpenMX v.3.5 [Ozaki, 2003]
**d-Electrons and their spins in transition metals**

The diagram shows the periodic table of the elements, highlighting transition metals. The table lists elements from groups I to VIII, with a focus on d-block elements. The periodic table is colored to distinguish between s, p, and d elements, with d-block elements highlighted in red. The table includes information on atomic numbers, symbols, and electron configurations for selected elements.
Scheme of experiments

Co$_5$, Co$_{13}$

- carbides
  - “saturation”, “asymmetry”

- fullerenes
  - “screen effect”, “orientation effect”

optimal carrier
Co<sub>5</sub> and Co<sub>13</sub> clusters

Co<sub>5</sub>-<i>D</i><sub>3h</sub>  
Co<sub>13</sub>-<i>I</i><sub>h</sub>

bottom-up

to an observer

<table>
<thead>
<tr>
<th></th>
<th>Co&lt;sub&gt;5&lt;/sub&gt;-&lt;i&gt;D&lt;/i&gt;&lt;sub&gt;3h&lt;/sub&gt;</th>
<th>Co&lt;sub&gt;13&lt;/sub&gt;-&lt;i&gt;I&lt;/i&gt;&lt;sub&gt;h&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>total magnetic moment</td>
<td>13.00 µ&lt;sub&gt;B&lt;/sub&gt;</td>
<td>31.00 µ&lt;sub&gt;B&lt;/sub&gt;</td>
</tr>
<tr>
<td>magnetic moment per Co-atom</td>
<td>2.60 µ&lt;sub&gt;B&lt;/sub&gt;</td>
<td>2.39 µ&lt;sub&gt;B&lt;/sub&gt;</td>
</tr>
</tbody>
</table>
Magnetic activity of carbides $\text{Co}_5\text{C}_n$ (a) and $\text{Co}_{13}\text{C}_n$ (b) depending on the number of carbon atoms.
Isomers of Co$_5$C$_5$ and Co$_{13}$C$_{6,12}$ complexes

Co$_5$C$_5$

Co$_{13}$C$_6$

Co$_{13}$C$_{12}$

symmetric

asymmetric (cap)

chain
Magnetism of isomers of Co$_5$C$_5$ (a) and Co$_{13}$C$_{6,12}$ (b) complexes
Endohedral metallofullerenes and their characteristics

<table>
<thead>
<tr>
<th></th>
<th>Co₅@C₆₀-I₇</th>
<th>Co₅@C₈₀-I₇</th>
<th>Co₁₃@C₈₀-I₇</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>total magnetic moment</strong></td>
<td>10.47 µ_B &lt;</td>
<td>11.78 µ_B &lt;</td>
<td>27.00 µ_B</td>
</tr>
<tr>
<td><strong>magnetism per Co-atom</strong></td>
<td>2.16 µ_B &lt;</td>
<td>2.39 µ_B &gt;</td>
<td>2.08 µ_B</td>
</tr>
<tr>
<td><strong>related to pure Co cluster</strong></td>
<td>80.5 % &lt;</td>
<td>90.6 % &gt;</td>
<td>87.1 %</td>
</tr>
<tr>
<td><strong>length of Co–C bond</strong></td>
<td>2.18 Å &lt;</td>
<td>2.33 Å &gt;</td>
<td>2.09 Å</td>
</tr>
<tr>
<td><strong>number of Co–C bonds</strong></td>
<td>5 &gt;</td>
<td>2 &lt;</td>
<td>12</td>
</tr>
</tbody>
</table>

\[ M \sim \langle L \rangle / N, \]

where \( M \) is the magnetic moment per Me-atom of given complex (µ_B), \( \langle L \rangle \) is the average Me–C bond length in Å, and \( N \) is the total number of Me–C bonds in the complex.
The size of fullerene cage depending on the metal cluster insertion
Along and across oriented Co$_5$ cluster in the C$_{70}$-$D_{5h}$ fullerene

along orientation

![Chemical structure]

2.19 $\mu_B$/Co-atom

> 

across orientation

![Chemical structure]

1.80 $\mu_B$/Co-atom
Conclusion

- Magnetic moment (MM) is strongly correlated to the effective hybridisation between $d$-electrons of core cobalt cluster and $p$- or $\pi$-electrons of carbon shell, which is closely related to the average bond length and the number of bonds

1a. MM of the $\text{Co}_m\text{C}_n$ complexes is decreased monotonically with the growing number of C-atoms

1b. MM of the $\text{Co}_m\text{C}_n$ isomers is increased steadily with the decreasing number of Co–C bonds

1c. MM of the Co carbide isomers is improved with the loss of symmetry

2a. MM of the Co clusters embedded into fullerenes is dropped down with the decreasing size of carbon cage

2b. MM of the confined Co cluster is depended on its position in the carbon cage

- Complex $\text{Co}_5@\text{C}_{80}$ is a good candidate for a cancer treatment
Publications

Kuznetsov A. From carbides to Co\textsubscript{5} and Co\textsubscript{13} metallofullerenes: first-principles study and design // Am. J. Biomed. Eng. (in prep. 2011).

Kuznetsov A. Magnetic properties of endohedral complexes Co\textsubscript{5}@C\textsubscript{n} depending upon the size and symmetry of fullerenes as well as orientation of cobalt cluster // Comp. Mater. Sci. (in press 2011).

Kuznetsov A. Magnetic moments of carbides Co\textsubscript{13}C\textsubscript{1-12}: a density functional investigation // Actual Problems of Applied Physics 2011, Sevastopol, Ukraine, 18-21 October (2011).

Tereshchuk P., Kuznetsov A. Magnetism of Co\textsubscript{13} cluster embedded into fullerenes of different size and form // 219th ECS Meeting, The Electrochemical Society, Montreal, Canada, 1-6 May 2011.

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