

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

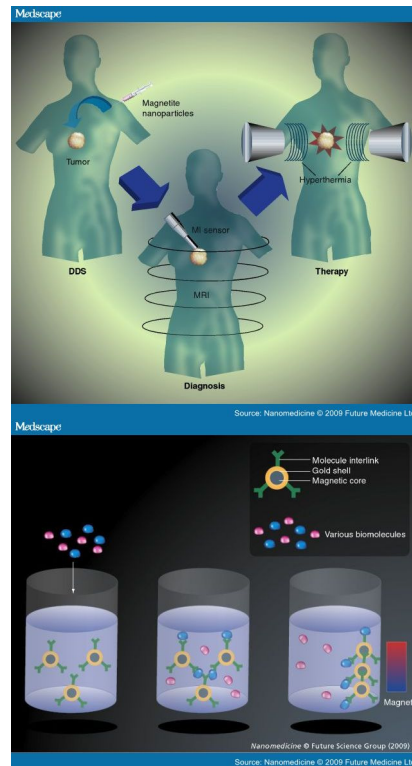
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Magneto-thermal cancer therapy, rules for magnetic particles



$\text{Gd}@\text{C}_{82}(\text{OH})_{22}$
golden mean of nanotechnology?



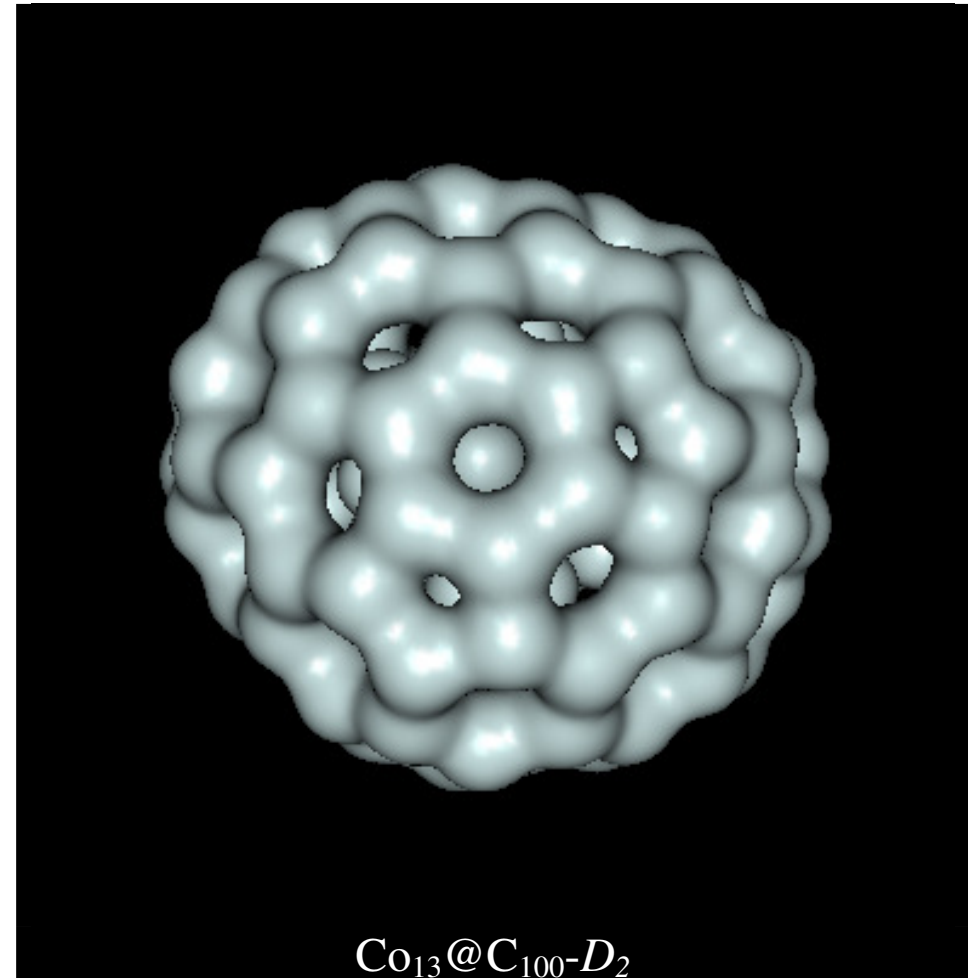
Ab initio approach

Method: DFT - density functional theory

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

Calculation: the total spin magnetic moment,
 μ_B

Software: OpenMX v.3.5 [Ozaki, 2003]



d-Electrons and their spins in transition metals

ПЕРИОДИЧЕСКАЯ СИСТЕМА ХИМИЧЕСКИХ ЭЛЕМЕНТОВ Д.И.МЕНДЕЛЕЕВА																	
Периоды	Ряды	Г Р У П П Ы Э Л Е М Е Н Т О В															
		I		II		III		IV		V		VI		VII		VIII	
		а	б	а	б	а	б	а	б	а	б	а	б	а	б	б	
1	1	Н водород 1,008															Не гелий 4,003
2	2	Li литий 6,941	Be бериллий 9,0122	B бор 10,811	C углерод 12,011	N азот 14,007	O кислород 15,999	F фтор 18,998									Ne неон 20,179
3	3	Na натрий 22,99	Mg магний 24,312	Al алюминий 26,982	Si кремний 28,086	P фосфор 30,974	S сера 32,064	Cl хлор 35,453									Ar аргон 39,948
4	4	K калий 39,102	Ca кальций 40,08	Sc скандий 44,956	Ti титан 47,956	V ванадий 50,941	Cr хром 51,996	Mn марганец 54,938	Fe железо 55,845	Co кобальт 58,933	Ni никель 58,7						Kr криптон 83,8
5	5	Cu медь 63,546	Zn цинк 65,37	Ga галлий 69,72	Ge германий 72,59	As мышьяк 74,922	Se селен 78,96	Br бром 79,904									Xe ксенон 131,3
6	6	Rb рубидий 85,468	Sr стронций 87,62	Y иттрий 88,906	Zr цирконий 91,22	Nb ниобий 92,906	Mo молибден 95,94	Tc технеций (99)	Ru рутений 101,07	Rh родий 102,906	Pd палладий 106,4						
7	7	Ag серебро 107,868	Cd кадмий 112,41	In индий 114,82	Sn олово 118,69	Sb сурьма 121,75	Te теллур 127,6	I йод 126,905									
8	8	Cs цезий 132,905	Ba барий 137,34	Лантаноиды		Hf гафний 178,49	Ta тантал 180,948	W вольфрам 183,85	Re рений 186,207	Os осмий 190,2	Ir иридий 192,22	Pt платина 195,09					
9	9	Au золото 196,967	Hg ртуть 200,59	Tl таллий 204,37	Pb свинец 207,19	Bi висмут 208,98	Po полоний [210]	At астат [210]									
10	10	Fr франций [223]	Ra радий [226]	Актинοиды		Rf резерфордий [261]	Db дубний [262]	Sg сигборгий [263]	Bh борий [264]	Hn ханний [265]	Mt мейтнерий [266]						
Высшие оксиды		R ₂ O	RO	R ₂ O ₃	RO ₂	R ₂ O ₅	RO ₃	R ₂ O ₇	RO ₄								
Летучие водородные соединения					RH ₄	RH ₃	H ₂ R	HR									
Л А Н Т А Н О И Д Ы																	
57	La	58	Ce	59	Pr	60	Nd	61	Pm	62	Sm	63	Eu	64	Gd	65	Tb
66	Dy	67	Ho	68	Er	69	Tm	70	Yb	71	Lu						
72	Hf	73	Ta	74	W	75	Re	76	Os	77	Ir	78	Pt	79	Au	80	Hg
81	Tl	82	Pb	83	Bi	84	Po	85	At	86	Rn						
87	Fr	88	Ra	89	Ac	90	Th	91	Pa	92	U	93	Np	94	Pu	95	Am
96	Cm	97	Bk	98	Cf	99	Es	100	Fm	101	Md	102	No	103	Lr		
104	Rf	105	Db	106	Sg	107	Bh	108	Hn	109	Mt	110		111		112	

www.calc.ru



Д.И. Менделеев
1834-1907

СИМВОЛ ЭЛЕМЕНТА

ПОРЯДКОВЫЙ НОМЕР

Rb 37
РУБИДИЙ

НАЗВАНИЕ ЭЛЕМЕНТА

ОТНОСИТЕЛЬНАЯ АТОМНАЯ МАССА

РАСПРЕДЕЛЕНИЕ ЭЛЕКТРОНОВ ПО СЛОЯМ

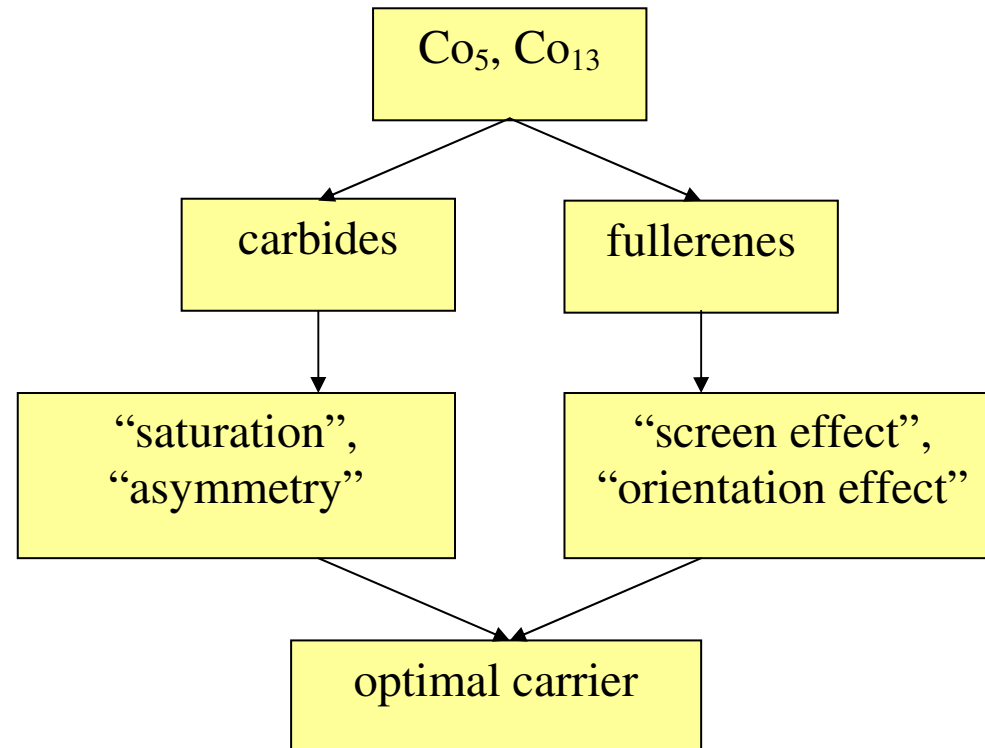
- s-элементы
- p-элементы
- d-элементы
- f-элементы

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
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4s² 3d¹ 3d² 3d³ 3d⁴ 3d⁵ 3d⁶ 3d⁷ 3d⁸ 3d¹⁰

Sc	Ti	V	Cr	Mn	Fe
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Scheme of experiments

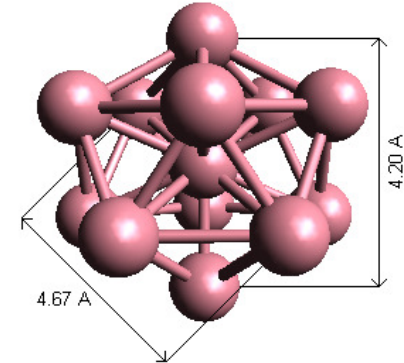
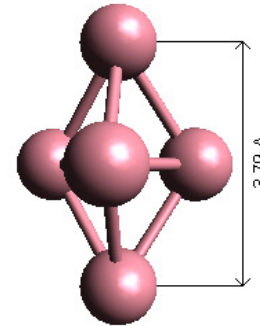


Co₅ and Co₁₃ clusters

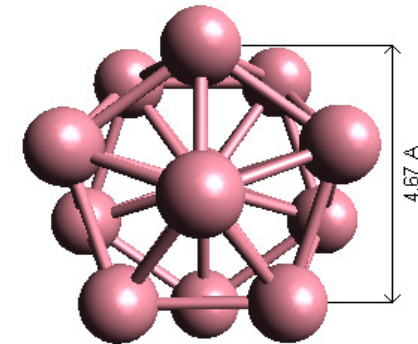
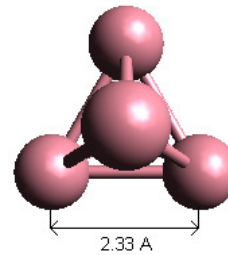
Co₅-D_{3h}

Co₁₃-I_h

bottom-up



to an observer



total magnetic moment
magnetic moment per Co-atom

13.00 μ_B

2.60 μ_B

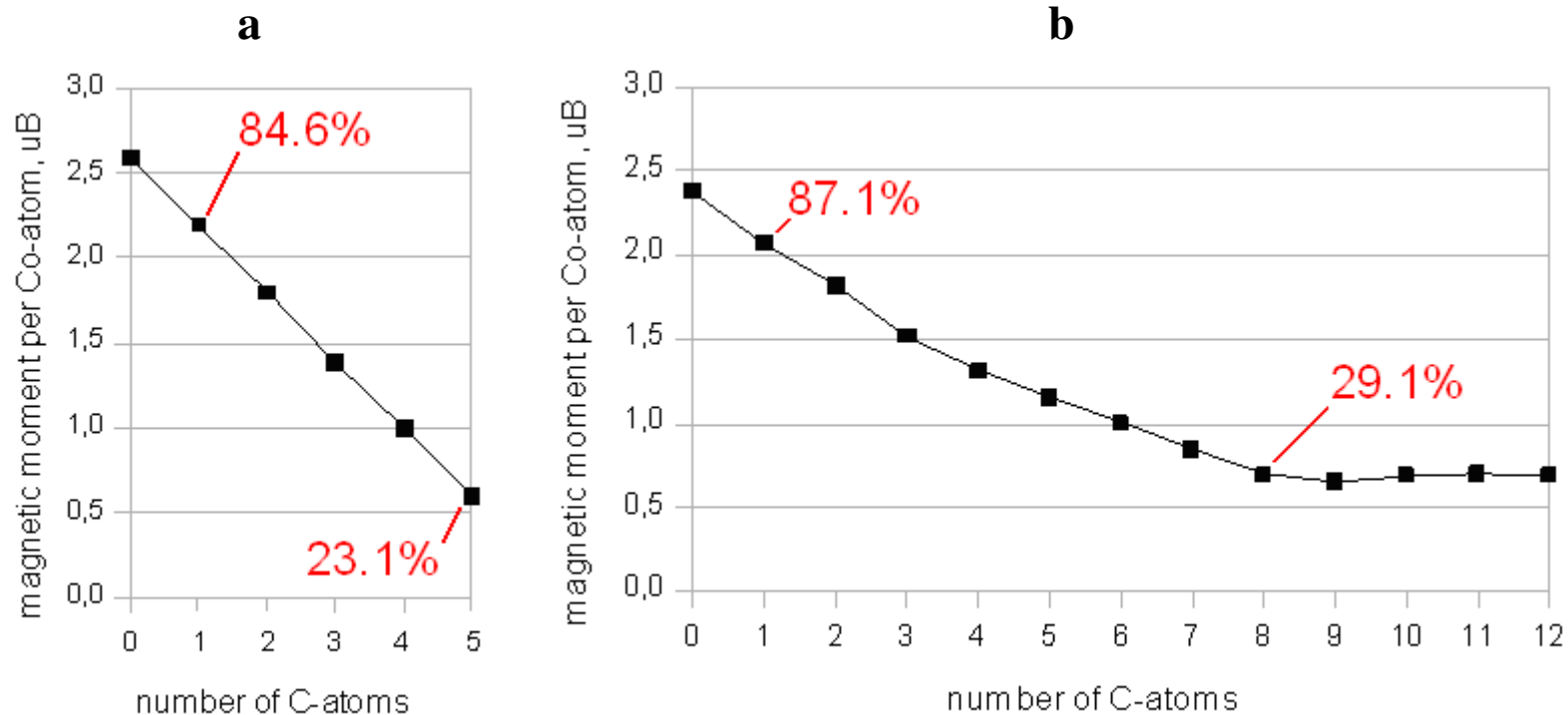
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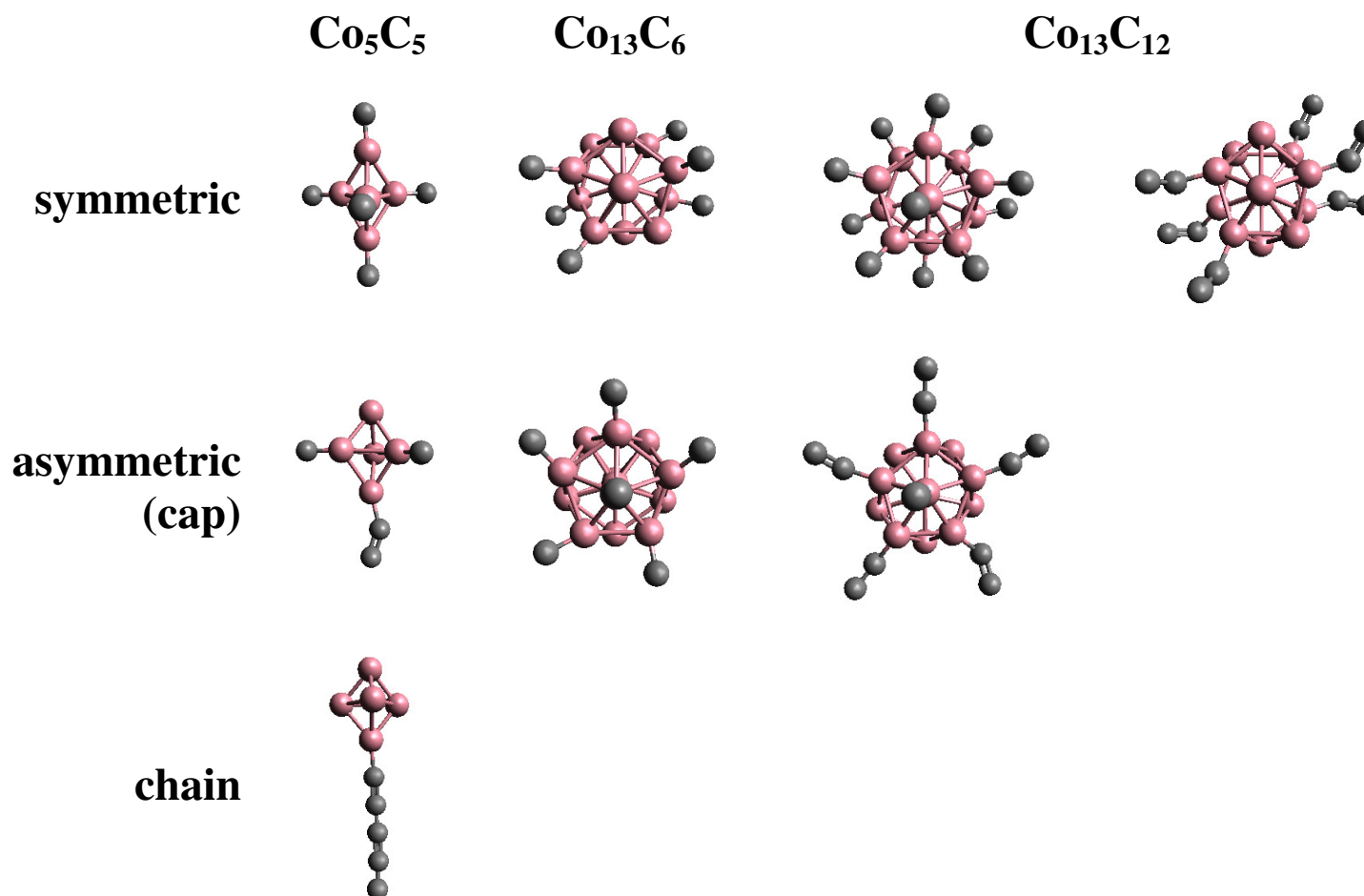
31.00 μ_B

2.39 μ_B

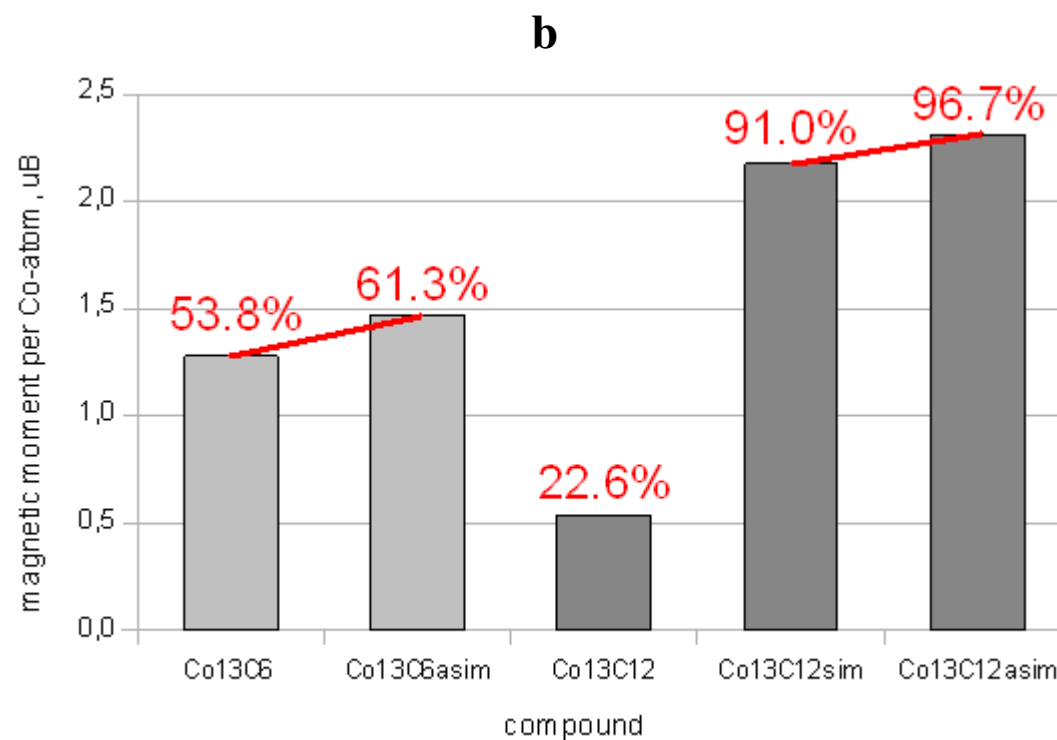
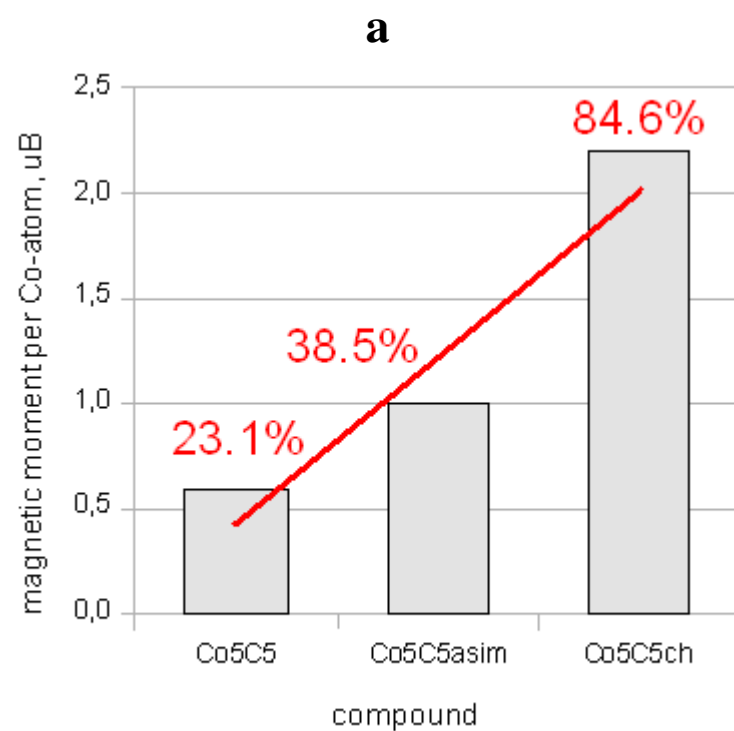
Magnetic activity of carbides Co_5C_n (a) and Co_{13}C_n (b) depending on the number of carbon atoms



Isomers of Co_5C_5 and $\text{Co}_{13}\text{C}_{6,12}$ complexes

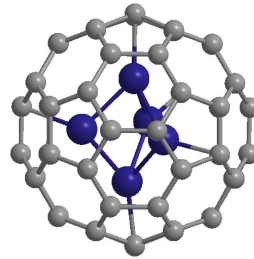


Magnetism of isomers of Co_5C_5 (a) and $\text{Co}_{13}\text{C}_{6,12}$ (b) complexes

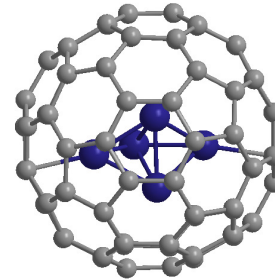


Endohedral metallofullerenes and their characteristics

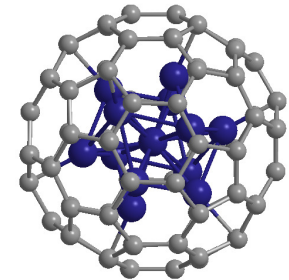
$\text{Co}_5@C_{60}-I_h$



$\text{Co}_5@C_{80}-I_h$



$\text{Co}_{13}@C_{80}-I_h$

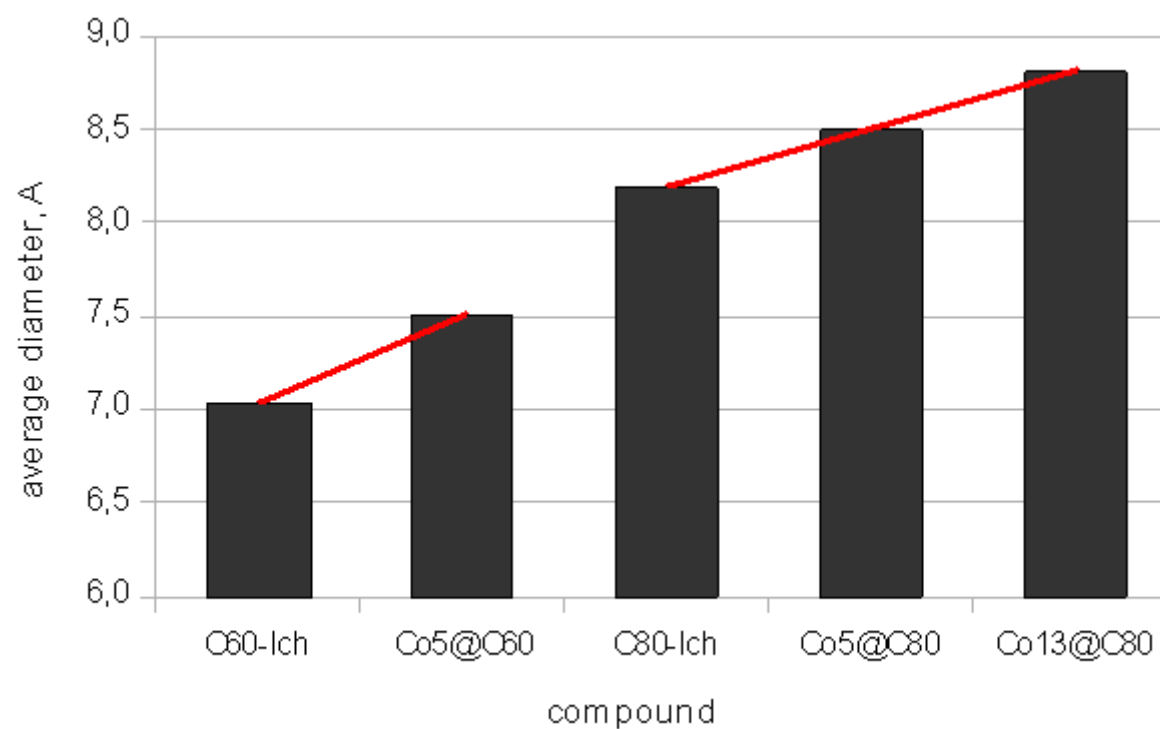


total magnetic moment	10.47 μ_B	<	11.78 μ_B	<	27.00 μ_B
magnetism per Co-atom	2.16 μ_B	<	2.39 μ_B	>	2.08 μ_B
related to pure Co cluster	80.5 %	<	90.6 %	>	87.1 %
length of Co–C bond	2.18 Å	<	2.33 Å	>	2.09 Å
number of Co–C bonds	5	>	2	<	12

$$M \sim \langle L \rangle / N,$$

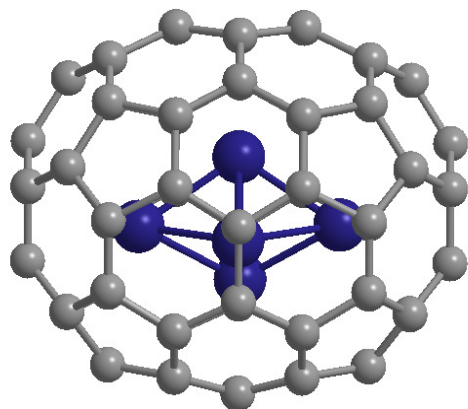
where M is the magnetic moment per Me-atom of given complex (μ_B), $\langle L \rangle$ is the average Me–C bond length in Å, and N is the total number of Me–C bonds in the complex

The size of fullerene cage depending on the metal cluster insertion



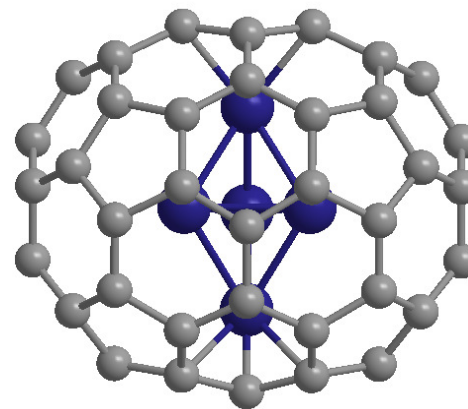
Along and across oriented Co₅ cluster in the C₇₀-D_{5h} fullerene

along orientation



2.19 μ_B /Co-atom

across orientation



1.80 μ_B /Co-atom

>

Conclusion

- Magnetic moment (MM) is strongly correlated to the effective hybridisation between *d*-electrons of core cobalt cluster and *p*- or π -electrons of carbon shell, which is closely related to the average bond length and the number of bonds
 - 1a.* MM of the Co_mC_n complexes is decreased monotonically with the growing number of C-atoms
 - 1b.* MM of the Co_mC_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_5 and Co_{13} metallofullerenes: first-principles study and design // Am. J. Biomed. Eng. (in prep. 2011).

Kuznetsov A. Magnetic properties of endohedral complexes $\text{Co}_5@C_n$ 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 $\text{Co}_{13}\text{C}_{1-12}$: a density functional investigation // Actual Problems of Applied Physics 2011, Sevastopol, Ukraine, 18-21 October (2011).

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

Kuznetsov A., Korvink J. From DNA-structures to a NanoSwarm // DECOI 2006: Design of Collective Intelligence, International Summer School on Collective Intelligence and Evolution, Amsterdam, Holland, 7-11 August (2006).

Acknowledgements

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