

The Study of Magnetic Molecules Containing Cr₉ Chromium-Based Rings within Density Functional Theory

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We examine the electronic and magnetic properties of three frustrated Cr₉ molecules with a single bond defect using density functional theory method. Five non-equivalent broken-symmetry spin configurations with $S = \pm 3/2$ for Cr are considered, the corresponding differences between the total energies are calculated and the exchange interaction parameters J extracted using different scenarios. We find that the couplings for all molecules are antiferromagnetic. We also estimate the fundamental gaps and in addition, the high occupied molecular orbitals and low occupied molecular orbitals are plotted and discussed.

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1. Introduction

Molecular rings belong to a subgroup of molecular materials that are ideal for investigating electric and magnetic properties of spin coupled systems. These properties depend mostly on transitional metals embedded in the molecule. These molecules exhibit interesting physical phenomena such as magnetic memory, resonant tunneling of magnetization or hysteresis step curves of magnetization. Also these substances may find application in next generation of high density data storage devices or quantum computing.

The specific molecules, that were the object of our study, are three nanometallic chromium rings displaying the spin frustration [1, 2]. They are characterized by a antiferromagnetic exchange coupling between nearest neighboring ions. The exact chemical formulae of these rings are Cr₉F₉Cl₂(Piv)₁₇ (compound A), Cr₉F₁₁(Piv)₁₇ (compound B) and Cr₉F₁₀(Piv)₁₈ (compound C). For short we denote these molecules as Cr₉. The Piv group is pivalic acid–trimethyl acetic acid CO₂C(CH₃)₃. The original synthesized Cr₉ molecule consists of nine chromium atoms arranged in a ring. They lay almost in a single layer. Each pair of Cr atoms is connected with each other by a single fluorine bridge oriented inside a ring and two pivalic groups that span outside. Only a single pair of Cr atoms differs from this rules. Compound A (B) lacks one pivalic bridge between two Cr ions, but instead those two Cr ions are connected to Cl (F) atoms. For C one pivalic group is disconnected from one of Cr atoms and this Cr atom in turn is connected to additional F atom. Although the whole molecule consists of 292 (A and B) and 307 (C) atoms, a hydrogen saturation [3, 4] allows to reduce the number of atoms to 88 (A and B)

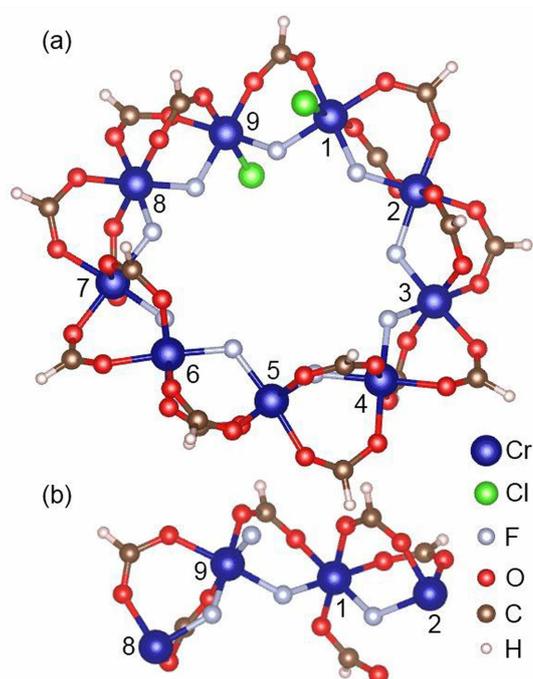


Fig. 1. The structure of the Cr₉ molecules with hydrogen atoms in place of pivalic groups. Cr 1 and Cr 9 constitute a unique pair of atoms.

and 91 (C), respectively. Simplified molecule A is presented in Fig. 1a. The molecule B is similar to A, so that the two Cl atoms are replaced by F atoms. In Fig. 1b only a fragment of molecule C with disconnected pivalic group is shown (the rest of the structure is very similar to the compound A).

In this paper we focus on obtaining and comparing magnetic properties of Cr₉ molecules, specifically the fundamental gaps and magnetic exchange parameters J , which have not been estimated before within a single framework.

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2. Computational details

The calculations are carried using density functional theory (DFT). We use SIESTA [5] computational package, which implements the pseudopotential technique. We account for the exchange and correlation effects using the Perdew–Burke–Ernzerhof (PBE) correlation functional. In our calculations we do not include spin–orbit coupling, as for the similar Cr₈ molecule it was already shown that the differences in the results are negligible [3, 6] and the single-ion anisotropy for the Cr ions is known to be very small [1–3].

Five different spin configurations with $s = \pm 3/2$ for Cr ions were calculated for three Cr₉ molecules. The considered spin configurations were as follows: (i) all spin up (with total spin of molecule $S = 27/2$), (ii) spin down on Cr 1 ($S = 21/2$), (iii) spin down on Cr 1 and 9 ($S = 15/2$), (iv) spin down on Cr 4, 6, and 8 ($S = 9/2$), (v) spin down on Cr 2, 4, 6, and 8 ($S = 3/2$). The Cr sites are numbered in Fig. 1.

3. Results and discussion

The ground state found for the Cr₉ molecules corresponds to the total spin $S = 3/2$ and is denoted as AF. The ferromagnetic (FM) configuration corresponds to the highest total energy. In fact, it turned out that for all Cr₉ molecules the energies of the (i)–(v) configurations are arranged from highest to lowest. Magnetic moments (MM) obtained for specific Cr ions for both AF (with total MM $m = 3 \mu_B$) and FM ($m = 27 \mu_B$) state are in Table I. The values of magnetic moments for the remaining atoms are close to 0. The magnetic moments are strongly localized on Cr ions.

By performing two calculations [7, 8] of the Kohn–Sham high occupied molecular orbital (HOMO) energy, one for the N particle system and another for the $N + 1$ particle system with 1 extra electron one can obtain estimates of the fundamental gap as

$$E_g = E_H^{N+1} - E_H^N, \quad (1)$$

where E_H^{N+1} (E_H^N) stands for HOMO energy of the $N + 1$ (N) particle system. The high occupied–low occupied molecular orbital (HOMO–LUMO) gap for N -particle system and the HOMO energies for $N + 1$ (E_H^{N+1}) and N (E_H^N) particle systems, as well as fundamental gap determined according to Eq. (1) for Cr₉ molecules in the AF and FM states are listed in Table II.

Additionally we present in Fig. 2 the plots of HOMO and LUMO levels in energy range [HOMO–0.15 eV:HOMO] and [LUMO:LUMO+0.15 eV] for the Cr₉ molecules in ground AF state.

For A and B molecules the plots suggest that LUMO states are spread over Cr ions located opposite the unique Cr pair. The HOMO levels in A compound are located mainly on one of unique Cr ion and connected Cl atom and partially on second unique Cr ion, but not on second Cl atom. In contrast, for B molecule HOMO levels are spread over the pair of unique Cr ions and additional

TABLE I

Magnetic moments in units of μ_B found using Mulliken analysis for Cr ions.

	Cr1	Cr2	Cr3	Cr4	Cr5	Cr6	Cr7	Cr8	Cr9
A AF	2.93	-2.89	2.90	-2.89	2.90	-2.92	2.91	-2.91	2.91
A FM	2.95	2.93	2.94	2.93	2.94	2.96	2.95	2.94	2.92
B AF	2.85	-2.90	2.88	-2.93	2.93	-2.89	2.89	-2.90	2.89
B FM	2.87	2.95	2.91	2.97	2.97	2.93	2.93	2.94	2.91
C AF	2.96	-2.92	2.92	-2.91	2.88	-2.89	2.89	-2.87	2.87
C FM	2.97	2.96	2.96	2.96	2.92	2.94	2.94	2.90	2.89

TABLE II

Fundamental gaps and HOMO energies for N and $N + 1$ particle system for Cr₉ molecules in the AF and FM states. All values in eV.

	A		B		C	
	AF	FM	AF	FM	AF	FM
$E_L^N - E_H^N$	1.08	0.88	0.64	0.35	0.68	0.48
E_H^{N+1}	-3.99	-2.47	-2.17	-2.43	-3.49	-2.38
E_H^N	-4.58	-4.55	-4.26	-4.16	-4.14	-4.13
$E_H^{N+1} - E_H^N$	0.59	2.08	2.09	1.73	0.65	1.75

two F atoms. Interesting behavior is observed for the third molecule C where HOMO levels are located on disconnected pivalic group, while LUMO levels are mainly delocalized over a large portion of the ring. These results are similar to the ones obtained for heteronuclear octametallc Cr₇Cd and Cr₇Ni rings in [8]. In the heterometallic rings the HOMO levels were strongly localized on a substituting ions Cd and Ni which can be considered analogous to the unique Cr pair in Cr₉ rings. Similarly the LUMO states were delocalized over Cr ions opposite to the substituting ions. The main difference is that the HOMO and LUMO orbitals for Cr₉ are not as symmetrical as the ones for Cr₇Cd and Cr₇Ni. This can be easily attributed to the fact that the Cr₉ rings are strongly distorted and lack proper symmetry, whereas the Cr₇Cd and Cr₇Ni are highly regular.

TABLE III

The exchange couplings between the Cr(III) ions following from the models $\alpha - \gamma$. All values in meV.

	Model α		Model β			Model γ			Experiment		
	J	J_{19}	J	J_{19}	J_{NN}	J	J_{19}	J_{12}	J	J_{19}	J_{12}
A	4.7	0.5	4.7	0.6	-0.3	4.8	0.7	4.3	1.4	0.7	1.4
B	5.1	2.2	5.1	2.1	0.5	4.8	1.9	6.2	1.5	0.5	1.4
C	4.7	1.3	4.7	1.5	-0.4	4.8	1.5	3.9	1.5	0.01	0.8

Following the established methodology [6, 9] and comparing combinations of DFT energy differences with those of the Ising models, we have estimated the exchange integrals J between chromium ions within the standard broken symmetry approach [9] for three different models of couplings α , β and γ . In the first model α we consider J for nearest neighbours (NN) for eight pairs of Cr ions

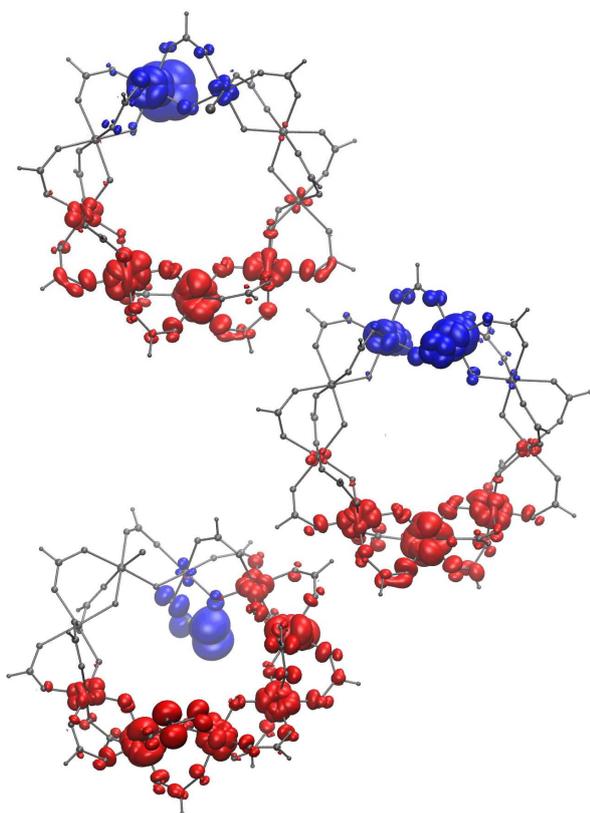


Fig. 2. Isosurface plots of the HOMO (blue) and LUMO (red) levels in the AF state for A (top), B (middle) and C (bottom) Cr_9 molecule for isovalues of ± 0.05 a.u. Orbitals with energy that fall in the [HOMO-0.15 eV:HOMO] and [LUMO:LUMO+0.15 eV] energy windows are plotted.

and J_{19} for unique pair of Cr ions. The second model β is the enrichment of the first by taking into account the next NN couplings J_{NN} . The third model γ is an extension of the first model, considering another coupling J_{12} for the chromium ion pairs (1,2) and (8,9). The exchange interaction parameters obtained for Cr_9 are presented in Table III.

The couplings J and J_{12} are close to those found within DFT for the eight-numbered molecules [4, 9] and consistent with earlier estimations for Cr_9 [10] and Cr_8Cd [11] but significantly overestimate the experimental values given in Table III [1, 2]. The couplings J_{19} found here are overestimated too, but they are much weaker than the J values found here. This finding agrees qualitatively with experiment.

From the point of view of the classification of spin frustration [1, 12, 13], the DFT predictions assign all the Cr_9 molecules to a group characterized by the second type. However, the experimental values indicate that in the variant C the third type is realized, as the ratio J_{12}/J does not exceed the corresponding critical value [2, 12, 14].

4. Conclusions

We have carried out the systematic SIESTA-based DFT calculations for the Cr_9 molecules. We have shown that exchange couplings are consistent with other DFT estimates for the Cr_9 and Cr_8 family. We have confirmed the localization of the magnetic moments on the Cr ions. We also shown that the fundamental gaps obtained from $N/N + 1$ system are greater than those gained from the Kohn–Sham HOMO and LUMO levels for N particle system. Finally it was shown that the HOMO orbitals tend to be localized in places where a bond defect has been introduced to the ring.

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