Designer Magnetic Superatoms

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Materials and Methods

Theoretical Method

First-principles electronic structure investigations were carried out using a molecular orbital approach within a gradient corrected density functional framework. The molecular orbitals are expressed as linear combinations of atomic orbitals formed via a combination of Gaussian functions centered at the atomic sites. The exchange correlation contributions are included within a gradient corrected (GGA) density functional as proposed by Perdew, Burke and Enzerhof (1). The actual calculations were carried out using the deMon2k software (2). For Na, Cl, V and I we employed the density functional theory (DFT) optimized DZVP basis set (3). For Mn, S and H we employed the DZVP basis set (4). The Cs atom was described using the 9 electron quasi scalar relativistic effective core potential proposed by Lenninger et al. (5) in combination with the corresponding basis set. The Au atom was described using a 19 electron relativistic effective core potential proposed by Schwerdtfeger et al. (6), in combination with the corresponding basis set.

For H, Na, S, Cl, V, Mn, and I the GEN-A2 auxiliary function set was used, and for Cs and Au the GEN-A2* auxiliary function set was used. The exchange-correlation energy was calculated from

the orbital density except for the $MnAu_{25}(SH)_{18}$ cluster. The molecular geometries and orbitals were plotted using the Schakal (7), Molekel (8) software, respectively.

To eliminate any uncertainity due to the choice of the basis set and the numerical procedure two additional complimentary schemes were used. In one scheme, all electron calculations were carried out, using the Naval Research Laboratory Molecular Orbital Library (NRLMOL) developed by Pederson and co-workers (9-11). Here the Hamiltonian matrix elements are evaluated by numerical integration over a mesh of points. The basis sets, built from a variable number of primitive Gaussians, are based on a total-energy minimization for free atoms and are optimized for all-electron density functional calculations (11). The basis sets were supplemented with a diffuse d-Gaussian to allow further variational freedom. For details of the codes and the basis sets, the reader is referred to earlier papers (9-11). The second scheme uses plane-wave basis sets within a supercell approach as implemented in the VASP code (12-14). Here, an energy cutoff of 500 eV is used, and the cluster is placed in a large cubic box of sides 20 Å in order to reduce its interaction with its images. The potential between the ion cores and the valence electrons are expressed in terms of projector augmented waves (PAW). The exchange-correlation effects are treated with the PW91 GGA functional (15). Brillouin zone integrations were carried out using only the Γ-point. Structures were relaxed using the conjugate gradient (CG) method for different fixed spin multiplicities, and without any symmetry constraints.

In general we found a very good agreement between the deMon2k, NRLMOL and VASP calculations. The results presented in the paper are based on the deMon2k calculations, with the exception of the $(Cs_8V)_2$ dimer and $(Cs_8V)_3$ trimer, for which ferromagnetic and antiferromagnetic states were calculated with the NRLMOL code.

Table S1. Electronic properties of the A_nV clusters (A = Na, and Cs; n = 1 to 12). Magnetic moments (μ), gain in energy due to alkali addition (ΔE_A), and HOMO-LUMO gaps (Gap). Magnetic moment in the immediate higher spin isomer, and the energy difference with respect to the ground state ΔE.

Cluster	Ground State			Next isomer	
	μ (μ_B)	ΔE_A (eV)	Gap (eV)	μ (μ_B)	ΔE (eV)
NaV	4			2	0.67
Na_2V	5	0.71	0.44	3	0.13
Na_3V	4	0.78	0.53	6	0.00
Na_4V	5	0.97	0.37	3	0.09
Na_5V	4	1.18	0.57	6	0.17
Na_6V	5	1.11	0.57	3	0.28
Na_7V	4	1.09	0.43	6	0.14
Na_8V	5	1.34	0.69	3	0.51
Na_9V	6	0.97	0.30	4	0.09
$Na_{10}V$	5	0.86	0.29	3	0.05
$Na_{11}V$	4	0.84	0.31	2	0.11
$Na_{12}V$	1	1.00	0.18	3	0.05
CsV	4			2	0.57
Cs_2V	5	0.45	0.15	3	0.06
Cs_3V	4	0.52	0.38	6	0.06
Cs_4V	5	0.52	0.35	3	0.14
Cs_5V	6	0.61	0.29	4	0.08
Cs_6V	5	0.64	0.28	3	0.08
Cs_7V	4	0.70	0.29	6	0.00
Cs_8V	5	0.84	0.22	7	0.14
Cs_9V	6	0.62	0.31	4	0.04
$Cs_{10}V$	5	0.51	0.35	3	0.17
$Cs_{11}V$	4	0.67	0.24	6	0.02
$Cs_{12}V$	5	0.42	0.25	3	0.02
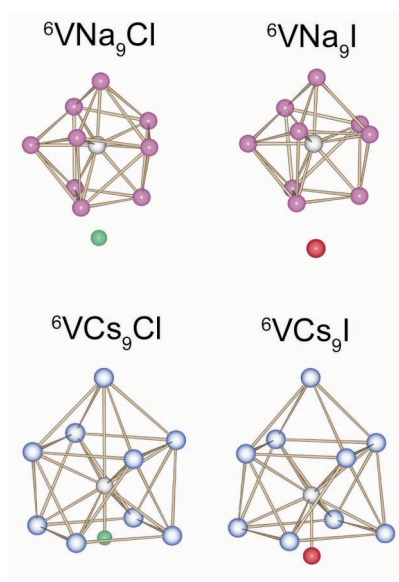
Figure S1. The ground state structure of VNa$_9$Cl, VNa$_9$I, VCs$_9$Cl and VCs$_9$I clusters. The green and the red circles correspond to Cl and I atoms respectively
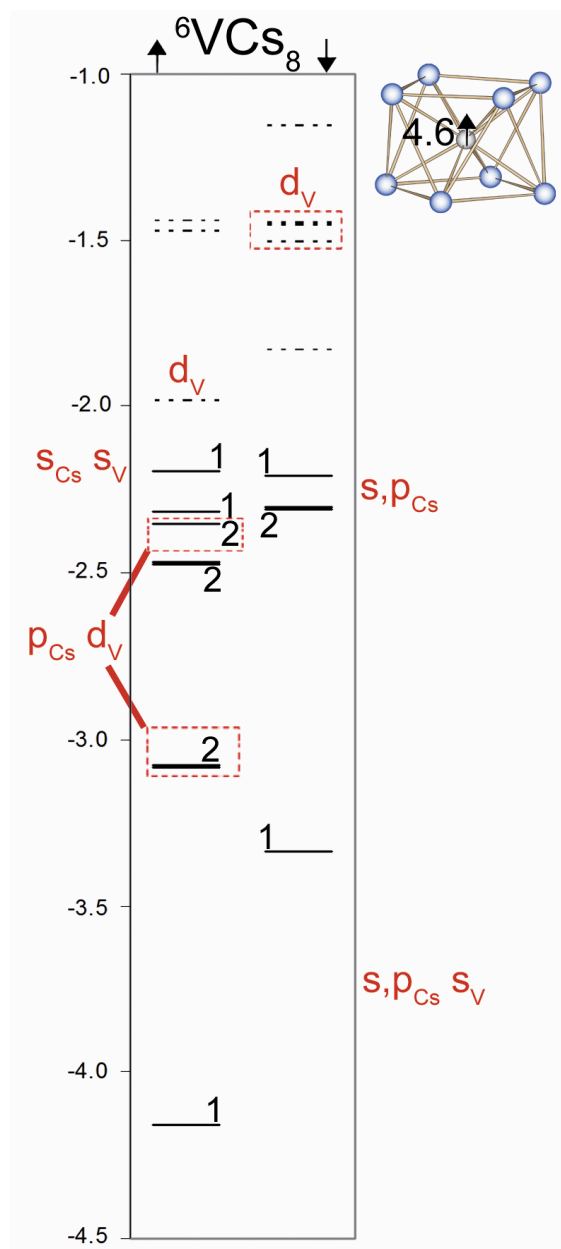
Figure S2. One electron energy levels in VCs_8. The majority and minority levels are shown.

Continuous lines correspond to the filled levels while the dotted lines correspond to the unfilled

states. For each level, the degeneracy and atomic composition has been marked. The optimized

geometry of VCs_8 and the atomic spin moment at the V sites are also given.

$^6(VCs_8)_3$

$5\mu_B$
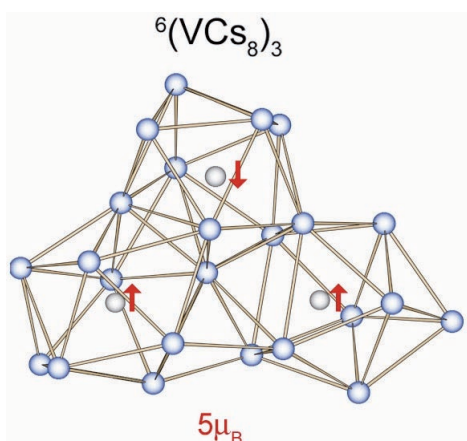
Figure S3. The lowest energy structure of a $(VCs_8)_3$ trimer. The arrows indicate the direction of V local spin moments. V atoms with `up' spins form the longer side of the triangle. The superscripts indicate spin multiplicity.

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