

Supporting Information

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SI 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 et al. (1). The actual calculations were carried out using the deMon2k software (2). For all the atoms we employed the gradient corrected optimized double zeta valence polarized basis set (3) and the GEN-A2 auxiliary function set. The exchange-correlation potential was calculated via a numerical integration on an adaptive grid from the orbital density (4). To determine the geometry and spin multiplicity of the ground state, the configuration space was sampled by starting from several initial configurations and spin multiplicities and optimizing the geometry employing the quasi-Newton Levenberg-Marquardt method (5). All structures were fully optimized in delocalized redundant coordinates without imposing any symmetry constraints, to allow for full variational freedom. The molecular

geometries and orbitals were plotted using the Molekel software (6). To eliminate any uncertainty due to the choice of the basis set and the numerical procedure one additional complimentary scheme was used. All electron calculations were carried out, using the Naval Research Laboratory Molecular Orbital Library (NRLMOL) developed by Pederson and coworkers (7–9). 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 (9). 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 (7–9). In general we found a very good agreement between the deMon2k and NRLMOL calculations. The results presented in the paper are based on the deMon2k calculations, with the exception of the $(\text{FeMg}_8)_2$ dimer for which the ferromagnetic and antiferromagnetic states were calculated with the NRLMOL code.

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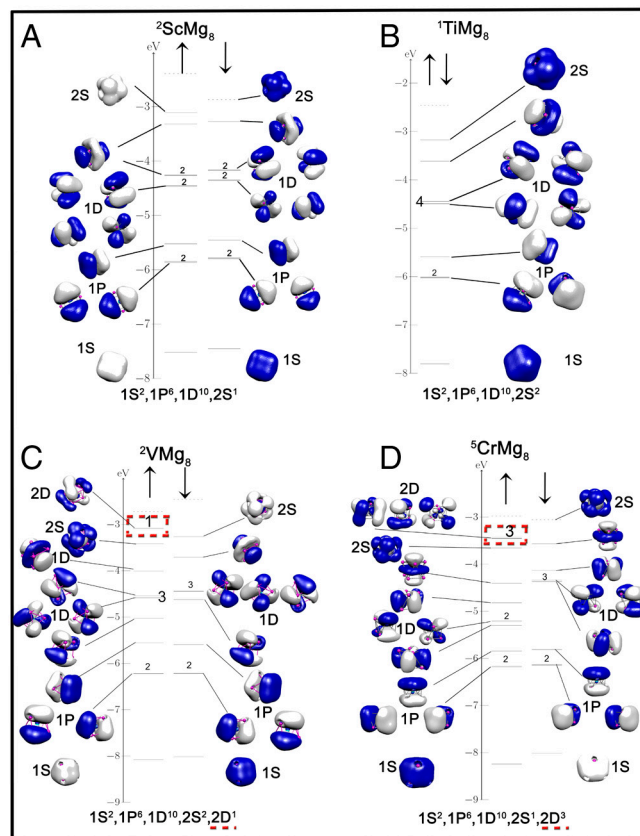


Fig. S1. The one electron energy levels and orbital wavefunction isosurfaces (isoval = 0.01 a.u.) in the TMMg₈ clusters. (A) TM = Sc, (B) TM = Ti, (C) TM = V, and (D) TM = Cr. The majority and minority levels are shown. Continuous lines correspond to the filled levels, whereas the dotted lines correspond to the unfilled states. For each level, the angular momentum and their occupancy has been marked. The 2D occupied energy levels are highlighted in a dotted red box.

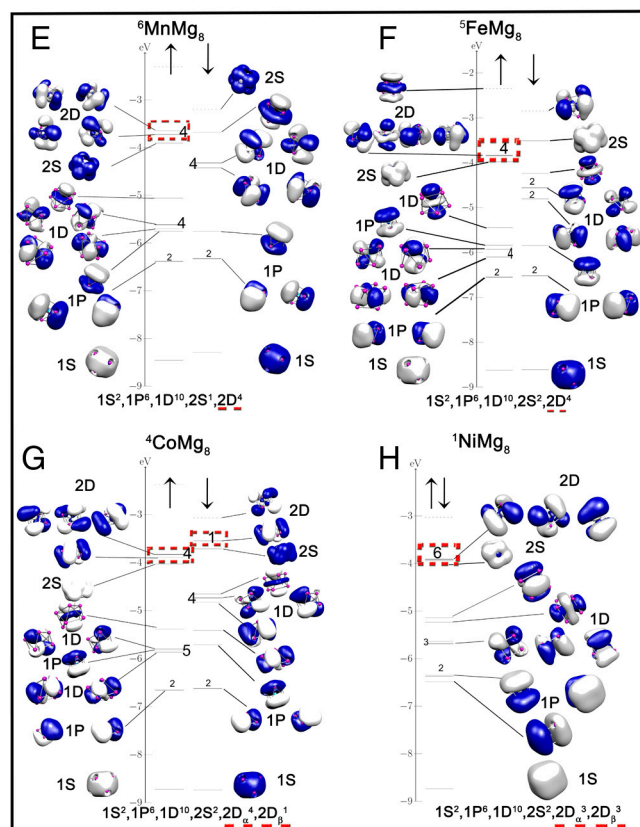


Fig. S2. The one electron energy levels and orbital charge wavefunction isosurfaces (isoval = 0.01 a.u.) in the TMMg_8 clusters. (E) TM = Mn, (F) TM = Fe, (G) TM = Co, and (H) TM = Ni. See caption of Fig. S1.

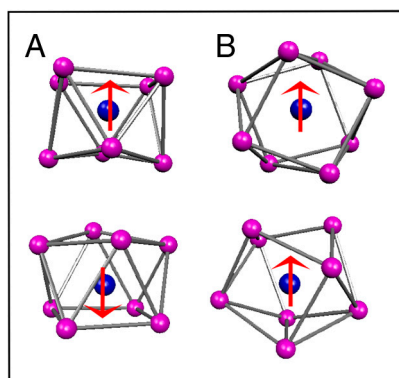


Fig. S3. The lowest energy structure and next spin isomer of the $(\text{FeMg}_8)_2$ dimer. (A) The antiferromagnetic ($0 \mu_B$) and (B) the ferromagnetic state ($4 \mu_B$) state. Arrows indicate the direction of Fe local spin moments.

