Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary material

Screening for high-spin metal organic frameworks (MOFs): Density functional theory study on DUT-8(M_1,M_2) (with M_i = V,...,Cu)

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A1 Structural information

Table A1: Atomic positions of M1-[Ni,Ni] in Å.

Ni	4.690	4.625	6.802
Ni	4.715	4.603	3.997
N	4.721	4.654	8.914
N	4.743	4.636	1.887
O	6.292	3.302	4.323
O	3.103	3.317	6.497
O	3.094	5.879	4.258
O	6.257	5.959	6.532
O	6.003	6.199	4.293
O	5.996	3.023	6.549
O	3.417	3.005	4.278
O	3.369	6.193	6.482
C	6.533	6.499	5.411
C	6.545	2.740	5.435
C	2.843	2.755	5.384
C	2.815	6.444	5.364
H	7.290	7.284	5.411
H	7.297	1.950	5.436
H	2.061	1.996	5.384
H	2.041	7.211	5.358
H	4.412	5.546	9.273
H	5.655	4.481	9.257
H	4.109	3.932	9.267
H	4.537	5.563	1.543
H	5.645	4.360	1.527
H	4.044	3.998	1.536

A2 Magnetism in Sc and Ti systems

Table A2.1: Resulting coupling constant J [cm^{-1}] for the implementation of the range of 3d metals into the M1 model system as obtained with NRLMOL, FPLO and QE. The resulting high-spin solutions are marked red. The value of the coupling constant is only given when the following conditions is satisfy $[E_{\mathrm{LS}}, E_{\mathrm{HS}}] < E_{\mathrm{NM}}$, where E_{NM} is the energy of the non-magnetic ground state. For any other cases the tag **n.m.** is given.

NRLMOL

M1/M2	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Sc/B	**n.m.**	+117.6	+1112.6	-605.2	-796.3	**n.m.**	**n.m.**	**n.m.**	**n.m.**
A/Sc	**n.m.**	+117.6	+1113.6	-635.2	-785.1	**n.m.**	**n.m.**	**n.m.**	**n.m.**
Ti/B	+276.0	+547.1	-221.4	-270.8	-355.5	-892.1	**n.m.**	**n.m.**	**n.m.**
A/Ti	+276.0	+547.1	-233.5	-246.5	-246.5	-863.5	**n.m.**	**n.m.**	**n.m.**

FPLO

M1/M2	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Sc/B	**n.m.**	+149.9	+1139.2	-631.3	-801.0	**n.m.**	**n.m.**	**n.m.**	**n.m.**
A/Sc	**n.m.**	+149.9	+1077.1	-661.2	-869.6	**n.m.**	**n.m.**	**n.m.**	**n.m.**
Ti/B	+278.1	+544.3	-216.8	-269.9	-343.3	-877.0	**n.m.**	**n.m.**	**n.m.**
A/Ti	+278.1	+544.3	-228.4	-321.8	-367.2	-869.6	**n.m.**	**n.m.**	**n.m.**

QE

M1/M2	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Sc/B	**n.m.**	..	+1039.5	-644.6	-789.9	**n.m.**	**n.m.**	**n.m.**	**n.m.**
A/Sc	**n.m.**	..	+1039.9	-644.6	-778.3	**n.m.**	**n.m.**	**n.m.**	**n.m.**
Ti/B	+739.4	+467.5	-254.9	-278.3	-339.6	-854.5	**n.m.**	**n.m.**	**n.m.**
A/Ti	+739.4	+467.5	-266.9	-285.3	-337.1	-851.9	**n.m.**	**n.m.**	**n.m.**

Table A2.2: Magnetizations per atom in Sc and Ti based M1 model systems for the LS coupling case. For each mixed dimer, the average of both systems is taken. Calculation performed with FPLO and QE.

A	B	FPLO		QE	
		M_{A} [μ_{B}]	M_{B} [μ_{B}]	M_{A} [μ_{B}]	M_{B} [μ_{B}]
Sc	Sc	0.00	0.00	0.18	0.18
Sc	Ti	0.27	0.93	0.05	0.48
Sc	V	0.30	2.13	0.09	1.94
Sc	Cr	0.01	3.51	0.04	2.60
Sc	Mn	0.15	4.48	0.10	3.65
Sc	Fe	0.31	3.38	0.12	2.96
Sc	Co	0.08	2.08	0.04	1.84
Sc	Ni	0.12	1.00	0.05	0.98
Sc	Cu	0.00	0.00	0.00	0.00
Ti	Ti	0.11	0.11	0.15	0.15
Ti	V	0.32	2.90	0.67	1.61
Ti	Cr	1.31	3.63	0.86	2.69
Ti	Mn	1.41	4.48	0.87	3.67
Ti	Fe	1.53	3.49	0.89	3.10
Ti	Ni	1.27	1.14	0.79	1.10
Ti	Cu	1.16	0.10	0.74	0.09

To get a full understanding of the influence of changing the metal centers A/B on the electronic and magnetic properties of the model system M1 we included Sc and Ti in the screening (see Tab. (A2.1)). Some of the results of this extended screening confirm previous assumptions, that Si and Ti tend to non-magnetic ground states. In addition some combinations of Sc and Ti with other 3d metals delivered magnetic ground states. For a more detailed insight we analyzed the magnetic moment per atom (see Tab. (A2.2)). In those calculations the initial magnetizations are 1 for Sc and 2 for Ti. It is evident that the magnetizations become very small for Sc and Ti in the LS state and with that they cannot be evaluated to calculate J, because the magnetization is only located on one atom.

A3 Spin contamination and definitions of J

A3.1 Theoretical background

In each of our calculations performed with NRLMOL, FPLO and QUANTUM ESPRESSO we calculated the ferromagnetic solution separate from the anti-ferromagnetic solution. For all calculations of the anti-ferromagnetic solution always broken symmetry is used. For unrestricted Hartree - Fock (UHF) or unrestricted Kohn - Sham (UKS) calculations, spin contamination plays an important role.
However, this scheme was only used for the ORCA calculations. For all other codes (NRLMOL, FPLO and QE) we used a restricted open-shell Kohn-Sham (ROKS) formalism, where spin contamination is not explicitly calculated.
There are many definitions for the exchange-coupling based on the broken symmetry approach

$$J_1 = -(E_{\mathrm{HS}} - E_{\mathrm{BS}})/(S^2_{\mathrm{max}}) \tag{1}$$

$$J_2 = -(E_{\mathrm{HS}} - E_{\mathrm{BS}})/(S_{\mathrm{max}} \cdot (S_{\mathrm{max}} + 1)) \tag{2}$$

$$J_3 = -(E_{\mathrm{HS}} - E_{\mathrm{BS}})/(\langle S^2 \rangle_{\mathrm{HS}} - \langle S^2 \rangle_{\mathrm{BS}}) \tag{3}$$

$$J_{\mathrm{authors}} = -(E_{\mathrm{HS}} - E_{\mathrm{BS}})/(\langle S^2 \rangle_{\mathrm{HS,ideal}} - \langle S^2 \rangle_{\mathrm{LS,ideal}}). \tag{4}$$

For the previously mentioned reason we used the definition of J_3 by evaluation of the ideal $\langle S^2 \rangle_{\mathrm{HS}}$ and $\langle S^2 \rangle_{\mathrm{LS}}$, which are based on the magnetization and with that the number of unpaired electrons (see J_{authors}).

A3.2 UKS ORCA screening

We performed the screening again with the ORCA code (Program Version 3.0.3) using the PBE functional and a triple ζ basis set with polarization function (def2-TZVP) within in the UKS scheme. The previously determined magnetizations and number of unpaired electrons (N_{A},N_{B}) as well as the multiplicity M for the high-spin state for the BSA-ORCA calculations are listed in Tab.(1). All definitions of J give the same qualitative result, so that our main result, the ferromagnetic HS-Fe family, remains fully correct (see Tab.(2,3,4)). Additionally the results from using our definition J_{authors} using ORCA are in good agreement with all our previous calculations (see Tab.(5) and paper section Results). Not converged calculations are marked with the label "n.c.". The determined trends do not depend on the definition of J or on the used calculation scheme (ROKS or UKS). Comparing the results from all the different definitions of J and the results from different numerical codes we are clearly demonstrating that our identified ferromagnetic building blocks are not an artefact of the way the calculation has been carried out.

Table 1: Number of unpaired electrons (N_A,N_B) and multiplicity M for the high-spin state for the BSA-ORCA calculations.

N_A, N_B, M	V	Cr	Mn	Fe	Co	Ni	Cu
V	3,3,7	3,4,8	3,5,9	3,4,8	3,3,7	3,2,6	3,1,5
Cr	4,3,8	4,4,9	4,5,0	4,4,9	4,3,8	4,2,7	4,1,6
Mn	5,3,9	5,4,10	5,5,11	5,4,10	5,3,9	5,2,8	5,1,7
Fe	4,3,8	4,4,9	4,5,10	4,4,9	4,3,8	4,2,7	4,1,6
Co	3,3,7	3,4,8	3,5,9	3,4,8	3,3,7	3,2,6	3,1,5
Ni	2,3,6	2,4,7	2,5,8	2,4,7	2,3,6	2,2,5	2,1,4
Cu	1,3,5	1,4,6	1,5,7	1,4,6	1,3,5	1,2,4	1,1,3

Table 2: BSA ORCA calculations evaluated with J_1. Values in cm^{-1}.

	V	Cr	Mn	Fe	Co	Ni	Cu
V	209.35	-99.43	-110.83	-477.77	-489.95	-887.39	-1217.62
Cr	-102.49	-366.91	-217.38	-275.69	-409.70	-712.20	**n.c**
Mn	-109.18	-216.36	-127.46	-132.19	-167.19	-260.62	-358.98
Fe	-476.30	-272.66	-134.62	160.69	83.22	163.8	149.61
Co	-481.87	-420.37	-177.68	18.27	**n.c.**	-117.80	-210.01
Ni	-884.28	-708.02	-258.62	166.59	-145.38	-396.20	-331.41
Cu	-995.84	-276.19	-354.13	100.50	-217.14	-325.32	-1053.68

Table 3: BSA ORCA calculations evaluated with J_2. Values in cm^{-1}.

	V	Cr	Mn	Fe	Co	Ni	Cu
V	157.02	-77.33	-88.66	-371.60	-367.46	-633.85	-811.75
Cr	-79.72	-293.53	-177.86	-220.55	-318.66	-534.15	**n.c**
Mn	-87.34	-177.02	-106.21	-108.15	-133.75	-202.71	-269.24
Fe	-370.46	-218.13	-110.15	128.55	64.72	122.76	106.86
Co	-361.40	-326.95	-142.14	14.21	**n.c.**	-84.14	-140.01
Ni	-631.63	-531.02	-201.15	124.94	-103.841	-264.14	-198.85
Cu	-663.89	-197.28	-265.60	71.79	-144.76	-195.19	-526.84

Table 4: BSA ORCA calculations evaluated with J_3. Values in cm^{-1}.

	V	Cr	Mn	Fe	Co	Ni	Cu
V	202.61	-99.43	-116.49	-472.94	-464.09	-827.63	-1347.60
Cr	-102.50	-356.08	-216.07	-269.34	-403.93	-752.25	**n.c.**
Mn	-114.78	-215.07	-126.20	-132.33	-175.30	-309.73	-600.86
Fe	-471.34	-266.42	-134.75	158.34	83.60	178.51	219.62
Co	-456.70	-414.52	-186.31	18.34	**n.c.**	-119.69	-263.50
Ni	-824.71	-747.96	-307.44	181.69	-146.95	-378.16	-340.63
Cu	-1130.18	-377.13	-592.26	147.40	-272.49	-334.84	-854.42

Table 5: BSA ORCA calculations evaluated with J_{authors}. Values in cm^{-1}.

	V	Cr	Mn	Fe	Co	Ni	Cu
V	157.01	-81.19	-98.52	-390.16	-367.46	-693.23	-1217.59
Cr	-83.71	-293.52	-183.41	-220.53	-334.57	-640.96	**n.c.**
Mn	-97.01	-182.54	-106.21	-111.52	-178.32	-266.02	-538.45
Fe	-388.96	-218.12	-113.58	128.55	67.96	147.29	187.01
Co	-361.39	-343.29	-157.94	14.92	**n.c.**	-92.03	-210.01
Ni	-690.82	-637.21	-263.99	149.93	-113.56	-264.14	-248.56
Cu	-995.79	-345.23	-531.17	125.61	-217.14	-243.95	-526.89

A4 All-electron and PAW DOS

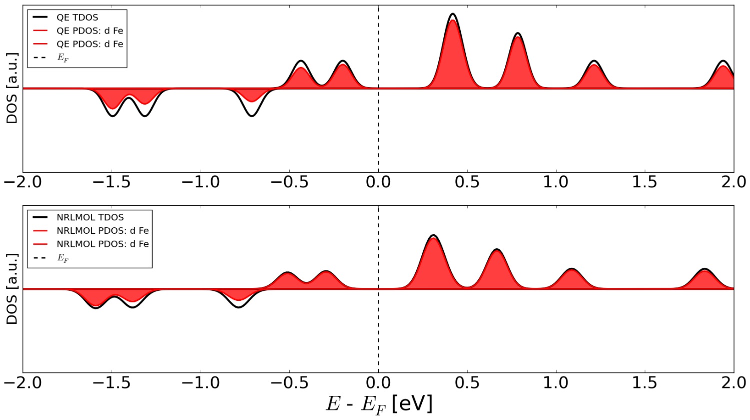

Figure A4: Comparison between the density of states for M1-[Fe,Fe] calculated with NRLMOL and QE. There is qualitative as well as quantitative agreement between PAW and all-electron DOS.