Supporting Information

Structure, Magnetism and Theoretical study of a Mixed-Valent Co$^{II}_3$Co$^{III}_4$ Heptanuclear Wheel: Lack of SMM Behavior despite Negative Magnetic Anisotropy

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Ab initio based methodology for the calculation of magnetic properties of polynuclear complexes

   With the spin-orbit multiplets obtained by *ab initio* calculations (CASSCF/CASPT2/RASSI-SO), the anisotropic magnetic properties for individual mononuclear fragments are calculated using the recently developed and implemented non-perturbative approach.[1] The basis of this approach is to calculate *ab initio* all angular momentum matrix elements and then all magnetic moment matrix elements on the relevant spin-orbit multiplets obtained in CASSCF/CASPT2 calculations. These matrix elements are used in a separate routine to calculate (i) magnetic properties measured directly in experiment (temperature dependent Van Vleck susceptibility tensor and powder averaged function, field dependent magnetization for different temperatures and directions and the powder magnetization) and (ii) parameters of magnetic spin Hamiltonians for different spin-orbit multiplets and groups of spin states, described by the corresponding pseudospin, (*g* tensors, zero-field splitting tensors). In calculations of magnetic properties, all spin-orbit multiplets of ligand-field type of the fragment are usually taken into account. This is important for the quantitative account of the effects of spin-orbit coupling (especially, in complexes with strong magnetic anisotropy) and of strong applied magnetic fields. Computationally, this routine (Single_Aniso) was interfaced with MOLCAS-7.0 program.[1]

For the simulation of magnetic properties of polynuclear complexes we used an approach combining the calculated magnetic properties of individual metal fragments (CASSCF/CASPT2/RASSI-SO + Single_Aniso) with the description of anisotropic exchange interaction between metal sites within the Lines model.[2] The latter begins with the isotropic exchange interactions, which would be in the absence of spin-orbit coupling on metal sites. Diagonalizing the matrix of the corresponding Heisenberg Hamiltonian, written in the basis of spin-orbit multiplets of mononuclear metal fragments, obtained from quantum chemistry calculations, gives solutions corresponding to anisotropic exchange interactions between Kramers doublets of a given metal pair. In the present case, four Kramers doublets from each cobalt(II) center have been taken into account in the exchange interaction, the Heisenberg Hamiltonian having thus the dimension of 512 x 512. The main advantage of the Lines model is that it uses one single parameter for each exchange coupled pair of metal ions, corresponding to an effective isotropic exchange interaction between them in the absence of spin-orbit coupling, to simulate the anisotropic exchange coupling. This allows avoiding of overparametrization of the simulations. For example, the Lines model was found completely adequate in the case of recently investigated Dy_3 complex[3]. These simulations are done with a specially designed routine (Poly_Aniso),[1] which was interfaced with the Single_Aniso routine treating individual metal fragments.

The described ab initio based methodology has already been successfully applied for the treatment of the effects of strong magnetic anisotropy in polynuclear transition metal complexes. Thus it allowed to explain the origin of strong anisotropy in dinuclear Co(II) complex of calyx[8]arenes[4] and to rationalize the magnetic data in Co-NC-W pairs of octacyanotungstate(V)-cobalt(II) three-dimensional networks.[5]

References

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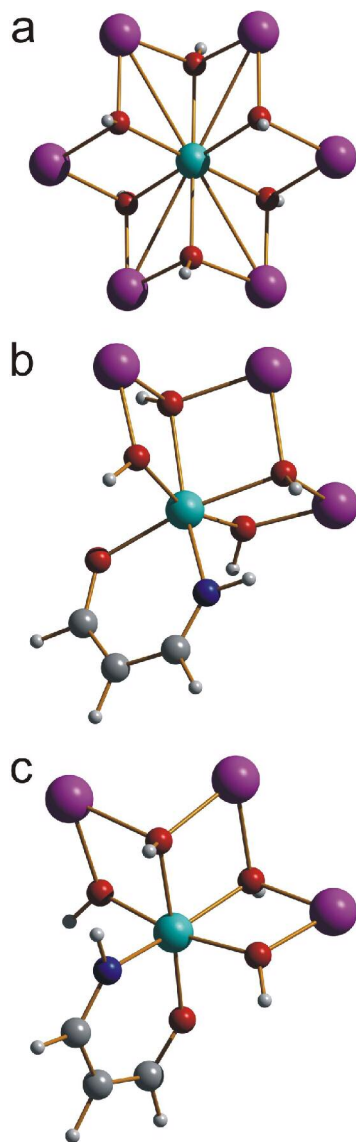
Figure 1S. Structural model A used in ab initio calculations of the mononuclear fragments, for the central Co(II) site (a), for the marginal Co(II) site (b), and for the Co(III) site (c). Color scheme: turquoise Co, red O, green F, blue N, pink Li$^+$, grey C, white H.
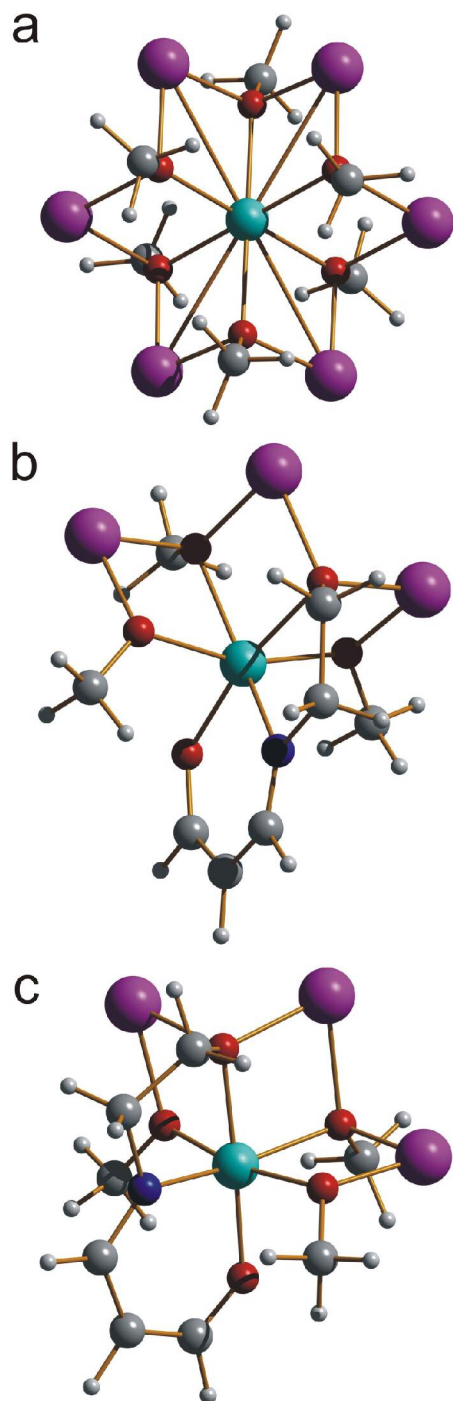
Figure 2S. Structural model B used in ab initio calculations of the mononuclear fragments, for the central Co(II) site (a), for the marginal Co(II) site (b), and for the Co(III) site (c). Color scheme: turquoise Co, red O, green F, blue N, pink Li$^+$, grey C, white H.

Table S1. Spin-orbit energies of low-lying states for the Co(III) fragments (cm^{-1})

| A		B		C		Octahedral parent term
Co2	Co3	Co2	Co3	Co2	Co3	
0.0	0.0	0.0	0.0	0.0	0.0	$^1A_{1g}$
893.4	2080.5	1645.6	2737.9	1763.8	2865.8	$^1T_{1g}$
953.2	2148.1	1712.6	2783.2	1815.9	2884.1	
976.5	2178.5	1772.5	2862.5	1862.2	2959.2	
1076.5	2413.7	2000.9	3199.6	2761.4	4545.6	$^5T_{2g}$ + $^3T_{1g}$
1080.6	2417.7	2018.1	3214.2	2897.2	4630.6	
2148.4	2943.3	2711.0	3715.8	3057.0	4707.7	
2184.5	3009.7	2772.4	3721.6	4390.4	5741.2	
2228.3	3016.3	2793.9	3788.5	4392.2	5742.7	
2960.5	4328.3	3766.3	4702.8	4459.9	5794.7	
3062.7	4354.8	3904.5	4809.5	4467.8	5823.8	
3133.1	4380.0	4085.1	4877.1	4488.0	5835.1	
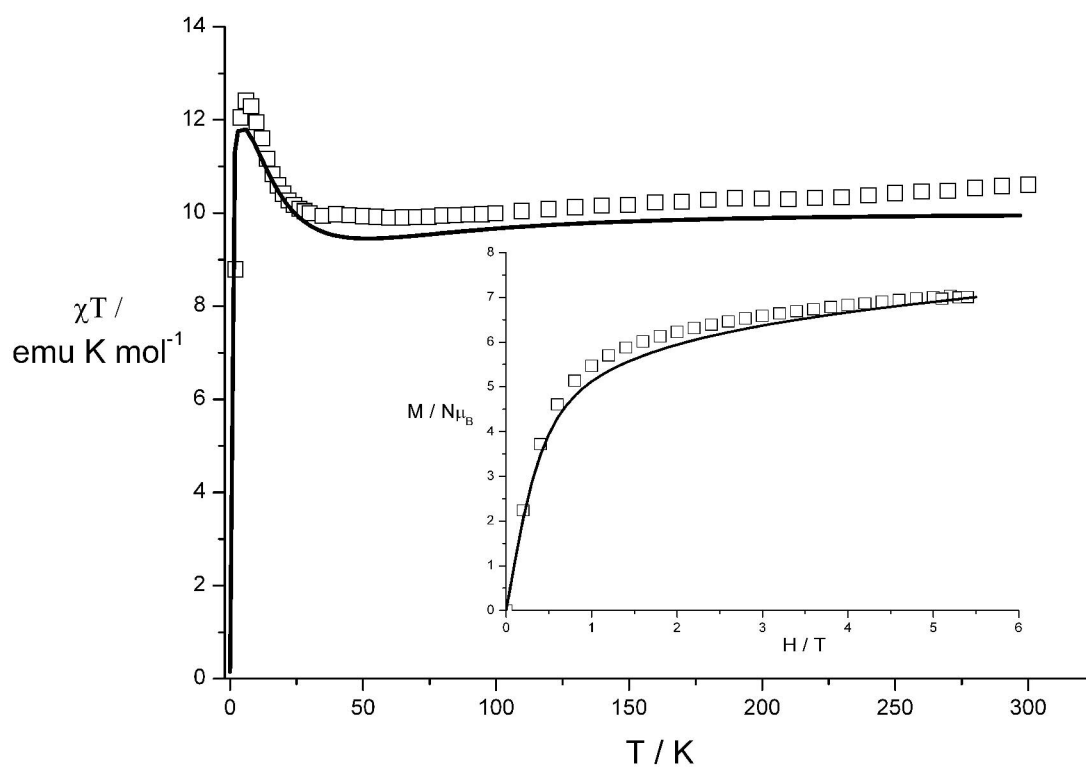
Figure 3S. Experimental temperature dependence of the product of molar magnetic susceptibility with temperature χT (squares) measured on powders compared with the ab initio calculated magnetic susceptibility ($J_1=2.0$ cm^{-1}, $J_2=5.6$ cm^{-1}, $zJ'=-0.005$ cm^{-1}) within the structural model B for the cobalt sites (line). Inset: the measured molar magnetization at 2K (squares) compared with the ab initio calculated for the structural model A and the same exchange parameters (line).

Table S2. Exchange spectrum (cm^{-1}) of low-lying Kramers doublets of the [Co$^{II}_3$Co$^{III}_4$(L)$_6$(MeO)$_6$] complex calculated in three structural approximations.

A	B	C
J_1=1.4 cm^{-1}, J_2=5.6 cm^{-1}, zJ'=-0.01 cm^{-1}	J_1=2.0 cm^{-1}, J_2=5.6 cm^{-1}, zJ'=-0.005 cm^{-1}	J_1=1.5 cm^{-1}, J_2=5.5 cm^{-1}, zJ'=-0.03 cm^{-1}
0.00	0.00	0.00
4.90	5.69	5.22
23.29	23.06	22.81
26.18	26.14	25.51
200.49	176.44	233.24
205.35	185.99	241.42