Supplementary Information for :

Self-assembly and magnetic properties of a Ni(II)$_8$(μ_4-hydroxo)$_6$ Cube with μ_2-Pyrazolate as exogeneous anchillary ligand

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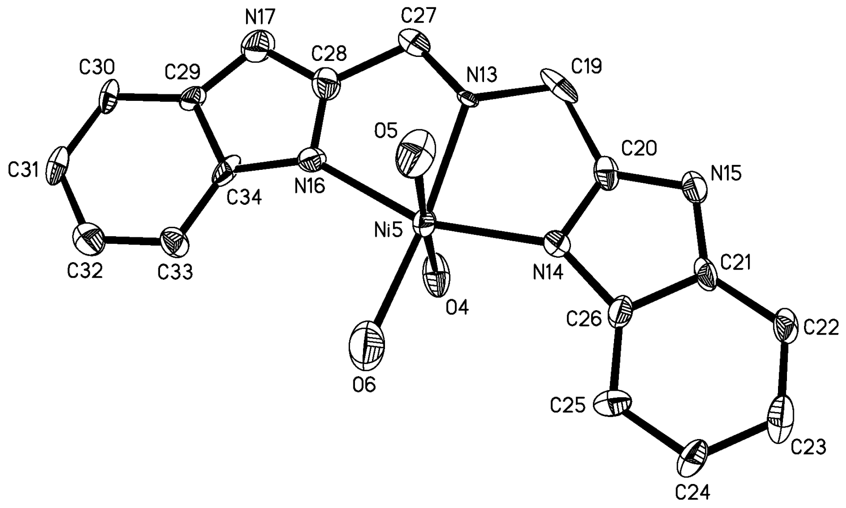


Figure S1: ORTEP diagram (30% probability thermal ellipsoids) of the $[Ni(bma)(H_2O)_3]^{2+}$ cation of **1** with the atom numbering scheme omitting hydrogen atoms for clarity.

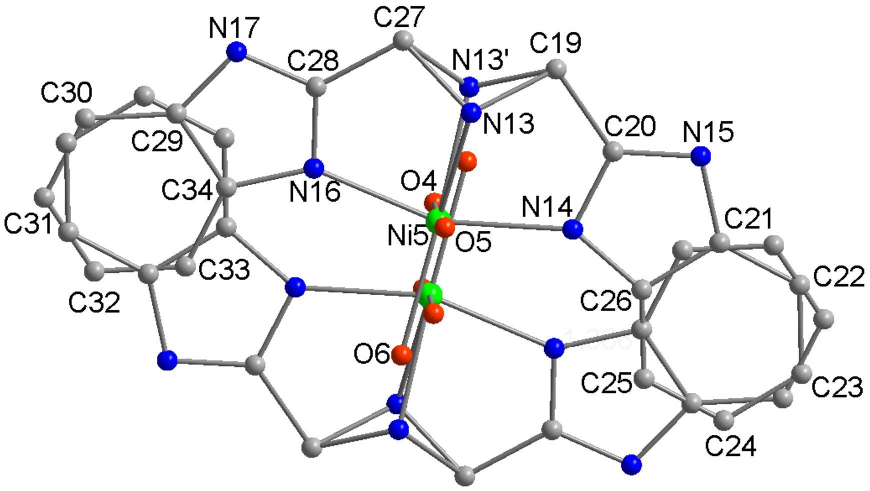
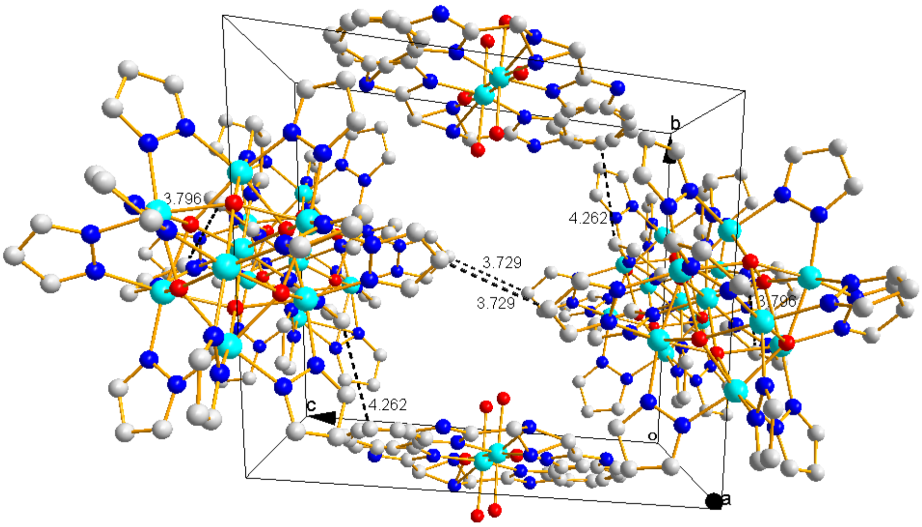
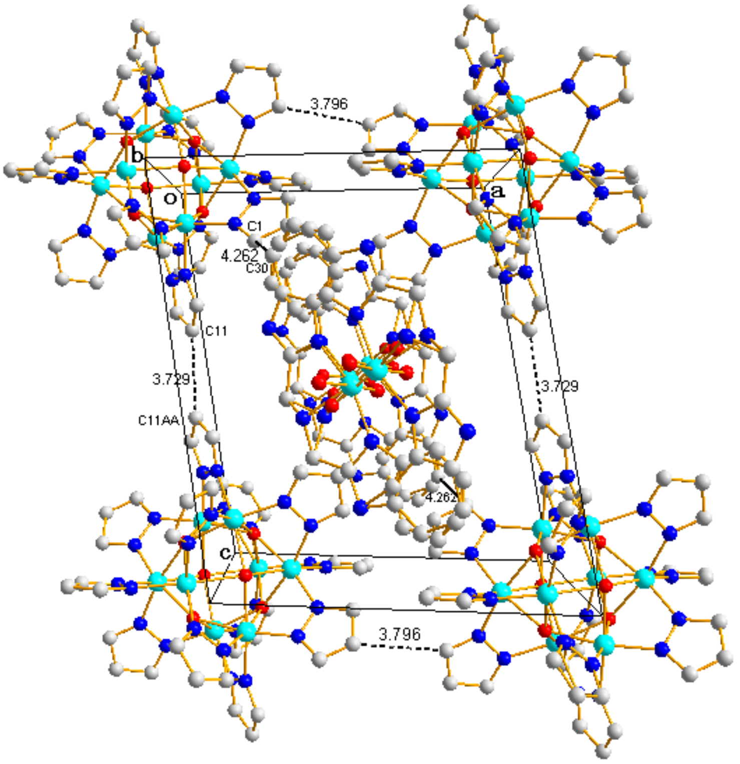


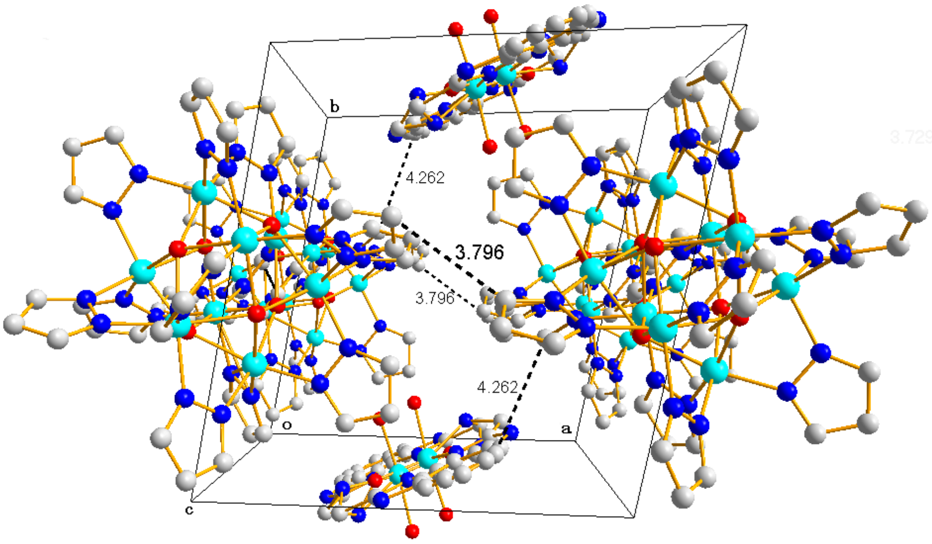
Figure S2: View of each $[Ni(bma)(H_2O)_3]^{2+}$ cation disordered over two position (hydrogen atoms are omitted for clarity)



(1) *a*-axis



(2) *b*-axis



(3) *c*-axis

Figure S3: Packing plot of **1** viewed along *a*-axis (1), *b*-axis (2), *c*-axis (3), respectively. H atoms and DMSO solvent molecules were omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for complex **1**.

Ni(1)-N(1)	2.009(5)	Ni(3)-O(3)	2.194(4)
Ni(1)-N(9)	2.027(5)	Ni(3)-Ni(1)#1	2.9868(10)
Ni(1)-N(8)	2.040(6)	Ni(4)-N(6)	2.030(5)
Ni(1)-O(3)#1	2.148(4)	Ni(4)-N(7)	2.030(5)
Ni(1)-O(1)	2.179(4)	Ni(4)-N(12)	2.031(5)
Ni(1)-O(2)#1	2.183(4)	Ni(4)-O(3)	2.158(4)
Ni(1)-Ni(2)	2.9575(11)	Ni(4)-O(1)	2.168(4)
Ni(1)-Ni(3)#1	2.9867(10)	Ni(4)-O(2)#1	2.169(4)
Ni(1)-Ni(4)	2.9973(10)	Ni(4)-Ni(2)#1	2.9967(10)
Ni(2)-N(2)	2.019(5)	O(2)-Ni(4)#1	2.169(4)
Ni(2)-N(3)	2.023(4)	O(2)-Ni(1)#1	2.183(4)
Ni(2)-N(11)	2.033(5)	O(2)-H(2A)	0.820(10)
Ni(2)-O(1)	2.150(4)	O(3)-Ni(1)#1	2.148(4)
Ni(2)-O(2)	2.180(4)	O(3)-Ni(2)#1	2.183(4)
Ni(2)-O(3)#1	2.183(4)	N(10)-Ni(3)#1	2.018(5)
Ni(2)-Ni(3)	2.9748(10)	Ni(5)-N(13)	2.006(15)
Ni(2)-Ni(4)#1	2.9968(10)	Ni(5)-O(5)	2.042(11)
Ni(3)-N(4)	2.015(5)	Ni(5)-N(14)	2.051(10)
Ni(3)-N(5)	2.015(5)	Ni(5)-N(16)	2.078(10)
Ni(3)-N(10)#1	2.018(5)	Ni(5)-O(4)	2.094(10)
Ni(3)-O(2)	2.169(4)	Ni(5)-N(13')	2.100(14)
Ni(3)-O(1)	2.180(4)	Ni(5)-O(6)	2.138(18)
N(1)-Ni(1)-N(9)	93.8(2)	Ni(1)-Ni(2)-Ni(4)#1	89.42(3)
N(1)-Ni(1)-N(8)	95.3(2)	Ni(3)-Ni(2)-Ni(4)#1	89.91(3)
N(9)-Ni(1)-N(8)	96.3(2)	Ni(2)-Ni(3)-Ni(1)#1	90.52(3)
N(1)-Ni(1)-O(3)#1	90.3(2)	N(13)-Ni(5)-O(5)	61.4(6)
N(9)-Ni(1)-O(3)#1	92.55(18)	N(13)-Ni(5)-N(14)	79.4(4)
N(8)-Ni(1)-O(3)#1	169.22(18)	O(5)-Ni(5)-N(14)	88.8(4)
N(1)-Ni(1)-O(1)	93.87(19)	N(13)-Ni(5)-N(16)	81.0(4)
N(9)-Ni(1)-O(1)	170.51(17)	O(5)-Ni(5)-N(16)	86.5(4)
N(8)-Ni(1)-O(1)	88.61(18)	N(14)-Ni(5)-N(16)	159.7(4)
O(3)#1-Ni(1)-O(1)	81.79(14)	N(13)-Ni(5)-O(4)	113.6(6)
N(1)-Ni(1)-O(2)#1	171.0(2)	O(5)-Ni(5)-O(4)	174.9(5)
N(9)-Ni(1)-O(2)#1	90.35(17)	N(14)-Ni(5)-O(4)	90.4(4)
N(8)-Ni(1)-O(2)#1	92.18(18)	N(16)-Ni(5)-O(4)	92.6(4)
O(3)#1-Ni(1)-O(2)#1	81.56(14)	N(13)-Ni(5)-O(6)	157.8(6)
O(1)-Ni(1)-O(2)#1	81.32(14)	O(5)-Ni(5)-O(6)	96.5(6)
Ni(2)-Ni(1)-Ni(4)	89.68(3)	N(14)-Ni(5)-O(6)	101.6(4)
Ni(3)#1-Ni(1)-Ni(4)	89.67(3)	N(16)-Ni(5)-O(6)	98.5(5)
Ni(1)-Ni(2)-Ni(3)	91.17(3)	O(4)-Ni(5)-O(6)	88.6(6)

Symmetry transformations used to generate equivalent atoms: #1(A) -x,-y+1,-z #2 -x+1,-y+2,-z+1

Synthesis of the complex

A solution of $Ni(OAc)_2\cdot 2H_2O$ (224.0 mg, 0.9 mmol) in MeOH (10 mL) was mixed with a solution of pyrazolate (82.5 mg, 1.2 mmol) in MeOH (10 mL). After 10 min of stirring, to the resulting green solution bis(2-benzimidazolylmethyl)amine (bma) solid (55.4 mg, 0.2 mmol) was added, immediately leading to an azury solution. The mixture was stirred overnight and most of the solvent (ca. 80%) was removed under reduced pressure. The light blue precipitate formed was filtered off, washed with small amount of methanol and diethyl ether, and dried under vacuum. Blue cubelike crystals were obtained by recrystalization in DMSO in one week, which are air stable and suitable for X-ray diffraction analysis. Yield: ca. 50%. Further reactivity studies have shown that pyrazolate and BMA ligands are amount chemically changeable. For example, the reaction ratio of $Ni(OAc)_2\cdot 2H_2O$, pyrazolate and bma in 1:1:1 also presents the same product, however the complex only crystallized from DMSO solution.

Computational Details

In our calculations, we employed the experimental structures that take into account small variations in the geometry induced by intermolecular interactions that may result in large changes in the calculated exchange coupling constants due to the strong dependence of the magnetic properties with structural parameters. Calculations with the B3LYP functional[1] were performed with NWChem code[2,3] using the quadratic convergence approach and a guess function generated with the Jaguar 6.5 code.[4] The triple-ζ all electron Gaussian basis set proposed by Schaefer *et al.* was employed.[5]

Discussion

Theoretical methods based on density functional theory have been extensively employed since some time ago to study the spin states from simple molecules[6] to polynuclear metal clusters.[7] Such methodology also allows to obtain all the exchange coupling constants that are present in polynuclear transition metal complexes.[8,9] In order to calculate the n $\boldsymbol{J_{ij}}$ exchange coupling constants of a polynuclear complex, we must at least perform $n+1$ energy calculations of different spin configurations that correspond to single-determinant Kohn-Sham solutions.[8] Such spin configurations must be selected in such way that it is possible to solve a system of n equations with n unknowns, the $\boldsymbol{J_{ij}}$ values. However, in order to minimize the effects of a low symmetry or, even, a dependence of the calculated J values on the selected set of spin configurations, we have chosen some extra confirmations. This procedure allow us to discern the presence of non-negligible interactions between the second neighbours or some dependence of the configurations on our results as well as to obtain a more accurate estimation for the mean value of the exchange coupling constants. In this way, eight calculations were performed on the Ni_8 complex in order to obtain the two exchange coupling constants by least-squares fitting for the following spin configurations: a high spin (S = 8), three S = 2 ({Ni_{1A}, Ni_{3A}}, {Ni_{1A}, Ni_{2A}} and {Ni_1, Ni_{1A}}) and four S=0 ({Ni_1, Ni_3, Ni_{1A}, Ni_{3A}}, { Ni_1, Ni_2, Ni_{1A}, Ni_{2A}}, {Ni_2, Ni_4, Ni_{1A}, Ni_{3A}}, and { Ni_3, Ni_4, Ni_{1A}, Ni_{2A}}) spin distributions, where only the spin-down centers are indicated in the notation used here.

According to the description of the structure in the manuscript, only two different exchange interactions appear in Ni_8 complex, that correspond to the edge of a cube (J_a) and to the diagonal of cube face (J_b). Whilst in the first case a pyrazole and two hydroxo (μ_4-OH) groups are involved as bridging ligands, in J_b only a μ_4-OH ligand mediates between the nickel(II) ions. Actually, more exchange couplings can be considered due to the low symmetry of the complex; however, since small changes in the geometrical parameters we have preferred to use a simple topology of the magnetic interaction with only two different exchange coupling constants. An analysis of the validity of this approach has been done in our theoretical study. In this situation, the considered spin Hamiltonian can be expressed as follows:

$$H = -J_a\left[\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_4 + \hat{S}_2\hat{S}_3 + \hat{S}_3\hat{S}_4 + \hat{S}_{1A}\hat{S}_{2A} + \hat{S}_{1A}\hat{S}_{4A} + \hat{S}_{2A}\hat{S}_{3A} + \hat{S}_{3A}\hat{S}_{4A} + \hat{S}_1\hat{S}_{3A} + \hat{S}_2\hat{S}_{4A} + \hat{S}_3\hat{S}_{1A} + \hat{S}_4\hat{S}_{2A}\right]$$
$$-J_b\left[\hat{S}_1\hat{S}_3 + \hat{S}_2\hat{S}_4 + \hat{S}_{1A}\hat{S}_{3A} + \hat{S}_{2A}\hat{S}_{4A} + \hat{S}_1\hat{S}_{4A} + \hat{S}_2\hat{S}_{3A} + \hat{S}_1\hat{S}_{2A} + \hat{S}_4\hat{S}_{3A} + \hat{S}_3\hat{S}_{2A} + \hat{S}_4\hat{S}_{1A} + \hat{S}_2\hat{S}_{1A} + \hat{S}_3\hat{S}_{4A}\right]$$

, where $\boldsymbol{S_i}$ are the local spin operators of each paramagnetic center. The results obtained for J_a and J_b using seven equations from eight different spin distributions are: –6.1 ± 2.5 and –58 ± 3 cm^{-1}. The found standard deviations are larger than those usually obtained, that can be related to the low symmetry of the Ni_8 complex.[10] In fact, to consider a new exchange coupling between the closest second neighbours (cube diagonal) don't allow us to reduce these deviations. Even more, when these extra exchange couplings are included in the fit of the experimental curves, them are cancelled out and a good fit is obtained using only two exchange couplings. Moreover, from the previous study in dinuclear complexes where only one atom make up the exchange pathway, the small or moderate variations considered for the exchange coupling constants can be reproduced by small changes in some geometrical parameters such as the NiONi angle.[8a,9a] Thus, we can conclude that the moderate standard deviations are connected to the process of the modelization by increasing of the molecular symmetry.

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