Electronic Supporting Information

The Important Role of the Anion Coligands in Promoting Structural and Magnetic Diversity in Polynuclear Ni(II) Complexes with a versatile bis(2-methoxyphenol)diaminehexadentate Mannich Base ligand. An Experimental and Theoretical Magneto-Structural Study

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Refine special details: In general, the quality of the crystals was quite poor. Several crystals of compounds were measured and the structures were solved from the best data we were able to collect. Anisotropic temperature factors were assigned to all atoms except for hydrogen atoms and the following atoms: C3M, O3M and O3W (for **1**), N1X and O1X (for **2**), O1M (for **4**) and all carbon, nitrogen and oxygen atoms (for **5**). For compound **2**, disordered azide and methanol molecules were considered at the Na coordination site. The occupancies of both ligands were fixed at 0.5. Attempts to identify the methanol solvent molecules failed in compound **2**. Instead, a new set of F^2 (hkl) values with the contribution from solvent molecules withdrawn was obtained by the SQUEEZE procedure implemented in PLATON-94 (A.L. Spek, *PLATON-94,A Multipurpose Crystallographic Tool*, University of Utrecht, TheNetherlands, 1994). Refinement reduced R_1 to 0.0415 for **2**. Attempts to solve disorder problems with crystallization methanol molecules failed in compound **3** and **4**. Instead, a new set of F^2 (hkl) values with the contribution from solvent molecules withdrawn was obtained by the SQUEEZE procedure. The compound **5** was poorly diffracting and there was almost no significant diffraction at angles above 22.5 deg., therefore no reflections were measured above this value. The structure was found to be highly disordered, every atom, except Ni(1), being disordered over two positions with occupancy factors of 0.6 and 0.4. Hydrogen atoms are riding their parent atoms with an

isotropic temperature factor arbitrarily chosen as 1.2 times that of the respective parent except for hydrogen atoms pertaining to solvent molecules that were not located.

Table S1.- Crystallographic data for complexes **1**-**6**

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Formula	$C_{46}H_{74}N_{10}O_{12}Ni_2$	$C_{93}H_{142}N_{20}O_{21}Na_2Ni_4$	$C_{48}H_{76}N_{16}O_{12}Ni_4$	$C_{54}H_{90}N_{16}O_{18}Ni_4Na_2$	$C_{44}H_{60}N_4O_8Cl_4Ni_4$	$C_{54}H_{78}N_4O_{14}Ni_3$
M_r	1076.57	2157.08	1304.09	1532.24	1149.60	1183.33
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group (no.)	*P21/n*	*C2/c*	*P-1*	*P-1*	*P21/n*	*C2/c*
a (Å)	13.3901(3)	39.938(7)	11.0288(14)	11.4753(7)	10.6316(13)	25.3316(14)
b (Å)	20.2174(4)	19.592(3)	11.4646(15)	11.5055(9)	20.125(3)	13.2982(7)
c (Å)	18.9053(5)	13.763(2)	13.467(3)	14.3852(15)	12.1235(15)	20.1791(11)
α (°)	90.00	90.00	112.640(2)	72.546(8)	90.00	90.00
β (°)	92.532(2)	109.256(2)	108.893(2)	86.577(7)	113.762(9)	122.9930(10)
γ (°)	90.00	90.00	97.485(2)	80.135(6)	90.00	90.00
V (Å^3)	5112.9(2)	10167(3)	1422.1(4)	1785.0(3)	2374.1(5)	5701.4(5)
Z	4	4	1	1	2	4
D_c (g cm^{-1})	1.399	1.409	1.523	1.425	1.608	1.379
μ(MoK_a) (mm^{-1})	0.806	0.816	1.377	1.125	1.843	1.046
T (K)	100	100	100	100	100	100
Observed reflections	11679 (7243)	11835 (9692)	6390 (3895)	6292 (5077)	3098 (1176)	5006 (3684)
R_{int}	0.0450	0.0380	0.0673	0.0295	0.1295	0.0426
Parameters	656	627	350	404	209	347
GOF	0.908	1.070	0.943	1.066	0.850	1.007
R_1[a, b]	0.0763(0.0436)	0.0509 (0.0415)	0.0962 (0.0566)	0.0825 (0.0701)	0.1716 (0.0638)	0.0663 (0.0446)
wR_2[c]	0.1001 (0.0954)	0.1147 (0.1095)	0.1346 (0.1208)	0.2115 (0.1995)	0.1123 (0.0901)	0.1093 (0.0965)
Largest difference in peak and hole (e Å^{-3})	1.064 and -0.517	0.941 and -0.344	0.718 and -0.424	1.848 and -1.248	0.519 and -0.418	0.468 and -0.256

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] Values in parentheses for reflections with $I > 2\sigma(I)$.

[c] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{½}$

Table S2.Selected bond lengths (Å) and angles (degrees) for complexes 1-6.

Compound	1	2	3	4	5	6
Ni1-O1A	2.024(2)	2.031(1)	1.987(3)	2.068(3)	2.049(12)	2.110(2)
Ni1-O3A	2.138(2)	2.121(1)	2.002(3)	2.084(3)	2.041(12)	2.015(2)
Ni1-N1A	2.091(3)	2.087(2)	2.110(4)	2.142(5)	2.134(16)	2.118(3)
Ni1-N2A	2.088(3)	2.094(2)	2.121(3)	2.136(5)	2.109(12)	2.150(3)
Ni1-N1N	2.118(3)	2.088(2)	2.220(4)	2.133(5)		
Ni1-N4N			2.194(4)			
Ni1-O1B	2.063(2)			2.098(5)		2.047(2)
Ni1-O2B						2.052(2)
Ni1-O1A’		2.092(1)				
Ni1-Cl1					2.482(5)	
Ni1-Cl1’					2.501(4)	
Ni2-O1A	2.077(2)		1.954(4)		1.984(12)	2.062(2)
Ni2-O2A			2.194(3)		2.347(10)	2.090(2)
Ni2-O3A				2.022(4)	2.002(11)	
Ni2-O4A				2.215(3)	2.165(17)	
Ni2-O1B	2.017(2)	2.034(1)				
Ni2-O2B				2.027(5)		
Ni2-O3B	2.118(3)	2.028(1)				
Ni2-N1B	2.099(3)	2.162(2)				
Ni2-N2B	2.077(3)	2.147(2)				
Ni2-N1N	2.105(3)		2.048(4)	2.077(4)		
Ni2-N4N		2.190(2)	2.102(4)	2.070(5)		
Ni2-N4N’		2.206(2)	2.162(3)	2.075(5)		
Ni2-Cl1					2.463(7)	
Ni2-Cl2					2.278(7)	
Ni2-O1M			2.042(3)			
Ni2-O1W						2.018(2)
Ni1-Ni2	2.8129(6)		3.2025(8)	3.0407(9)	3.372(4)	3.5946(6)
Ni1-Ni2’			3.321(1)	5.891(1)	3.350(3)	
Ni1-Ni1’		2.8085(6)	5.7451)	8.814(1)	3.531(3)	6.7782(8)
Ni2-Ni2’		3.4003(6)	3.092(1)	3.1978(8)	5.721(4)	
Ni1-O1A-Ni2	86.58(9)		108.7(2)		113.4(5)	118.99(10)
Ni1-O1B-Ni2	87.17(10)					
Ni1-N1N-Ni2	83.54(11)		102.1(2)	92.5(2)		
Ni1-N1N-Ni1’		84.53(8)				
Ni1-O1A-Ni1’		85.86(5)				
Ni2-N4N-Ni2’		101.36(7)	93.0(1)	101.0(2)		
Ni1-N4N-Ni2			102.1(2)			
Ni1-N4N-Ni2’			94.6(1)			
Ni1-O3A-Ni2				95.5(1)	111.9(7)	
Ni1-Cl1-Ni2					86.0(12)	
Ni1-Cl1’-Ni2					84.9(2)	
Ni1-Cl1-Ni1’					90.2(2)	

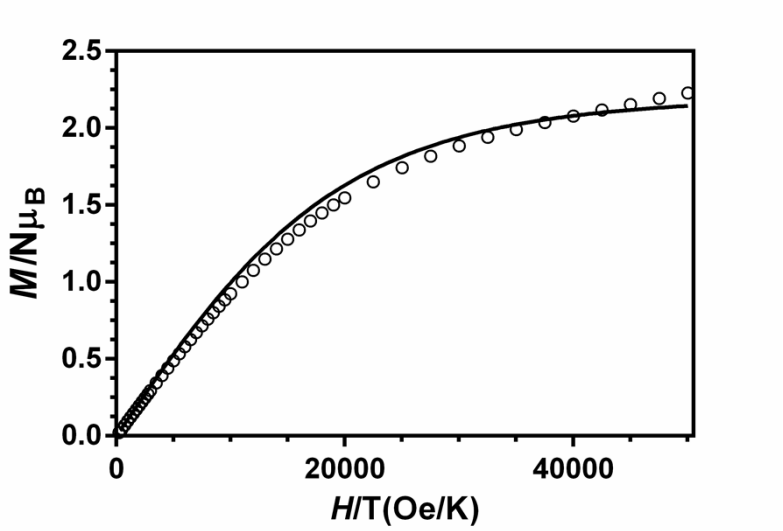

Figure S1.- Field dependence of the magnetization for 6. The solid black line corresponds to the Brllouin function for $S = 1$ with g = 2.2.

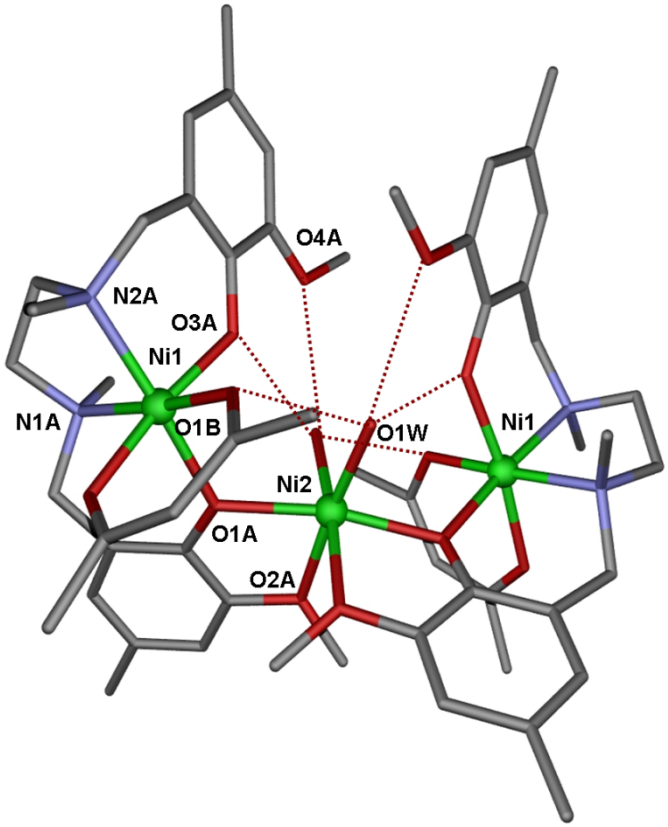

Figure S2.- A perspective view of the structure of **6** together with the intramolecular hydorgen bonds (dotted lines).

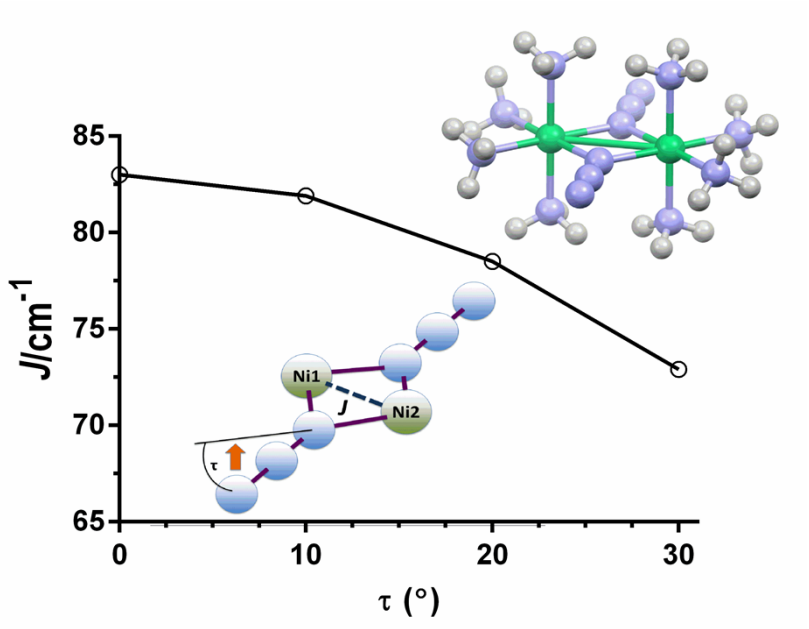

Figure 3.- Dependence of *J* with the τ angle (inset bottom) for the double EO-azide bridged dinuclear Ni^{II} planar model $[Ni_2(\mu\text{-}EO)_2(NH_3)_8]^{2+}$(inset top).