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Electronic Supporting Information

An Experimental and Theoretical Magneto-Structural Study of Polynuclear Ni^{II} Complexes Assembled from a Versatile bis(salicylaldehyde)diamine Polytopic Ligand.

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

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Formula	$C_{20}H_{26}N_4O_{12}Br_2Ni$	$C_{32}H_{39}N_3O_9Br_2Ni_2$	$C_{23}H_{23}N_3O_6SBr_2Ni_2$	$C_{50}H_{61}N_{11}O_{17}Br_2Ni_3$	$C_{48}H_{72}N_4O_{22}Br_4Ni_4$	$C_{45}H_{54}N_{10}O_{15}Br_4Ni_4$
M_r	732.98	886.90	746.74	1583.87	1611.58	1529.46
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group (no.)	*P21/c* (14)	*C2/c* (15)	*I2/a* (15)	*P21/c* (14)	*P-1* (2)	*P-1* (2)
a (Å)	12.3321(6)	20.9791(14)	21.9768(3)	21.6387(9)	11.7285(10)	13.3880(4)
b (Å)	9.5827(4)	14.469(2)	9.7423(10)	10.6943(12)	12.3966(13)	14.4846(5)
c (Å)	21.5074(9)	26.9753(19)	24.826(4)	27.2254(7)	12.6195(15)	14.9568(5)
α (°)	90.00	90.00	90.00	90.00	89.018(9)	106.726(3)
β (°)	94.157(4)	118.361(9)	95.237(2)	111.474(2)	70.217(9)	95.185(3)
γ (°)	90.00	90.00	90.00	90.00	64.859(9)	93.111(3)
V (Å^3)	2534.95(19)	7205.3(13)	5293.2(10)	5862.9(7)	1545.6(3)	2756.53(16)
Z	4	8	8	4	1	2
D_c (g cm^{-3})	1.921	1.635	1.874	1.794	1.731	1.843
μ(MoKα) (mm^{-1}) [a]	3.990	3.318	6.426	3.759	5.046	4.318
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Observed reflections	5889 (4775)	6345 (5721)	5329 (4677)	10308 (7841)	6058 (4762)	9673 (7112)
R_{int}	0.0438	0.0247	0.0357	0.0414	0.0267	0.0323
Parameters	378	466	337	748	329	694
GOF	1.109	1.107	1.031	1.038	1.094	1.058
R_1[b,c]	0.0560 (0.0400)	0.0349 (0.0299)	0.0538 (0.0467)	0.0608 (0.0399)	0.0556 (0.0447)	0.0744 (0.0496)
wR_2[c,d]	0.0909 (0.0843)	0.0687 (0.0666)	0.1071 (0.1030)	0.0934 (0.0862)	0.1298 (0.1239)	0.1302 (0.1192)
Largest difference in peak and hole (e Å^{-3})	1.220 and -0.638	0.920 and -0.544	2.544 and -1.891	1.175 and -0.760	1.744 and -1.010	1.037 and -0.894

[a] μ (CuKα) (mm^{-1}) in **3** and **5**.

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

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

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

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

Compound	1	2	3	4	5	6
Ni(1)-O(1A)	2.039(2)					
Ni(1)-O(2A)	1.965(2)	2.125(2)	2.018(3)	2.059(3)	2.066(3)	2.040(4)
Ni(1)-O(3A)	1.981(2)	2.060(2)	1.982(3)	2.020(3)	2.109(3)	2.112(4)
Ni(1)-O(4A)	2.041(2)					
Ni(1)-O(1C)	2.123(2)					
Ni(1)-O(1W)	2.074(3)					
Ni(1)-O(1B)		2.040(2)	1.943(3)		2.065(3)	2.057(4)
Ni(1)-O(2B)		2.011(3)				
Ni(1)-O(1P)				2.137(3)		
Ni(1)-O(1M)					2.058(3)	
Ni(1)-N(1A)		2.130(2)	2.047(4)	2.066(3)	2.114(3)	2.098(5)
Ni(1)-N(2A)		2.135(2)	2.066(3)	2.096(3)	2.126(3)	2.104(5)
Ni(1)-N(1P)				2.077(4)		
Ni(1)-N(1C)						2.113(5)
Ni(2)-O(1A)		2.058(3)	2.041(3)	2.007(3)	2.065(3)	2.047(4)
Ni(2)-O(2A)		2.032(2)	2.019(3)	1.983(3)	2.021(3)	2.017(4)
Ni(2)-O(3A)		2.058(2)	2.014(3)			
Ni(2)-O(3A)*					2.094(3)	2 075(4)
Ni(2)-O(4A)			2.052(3)			
Ni(2)-O(1B)				2.008(3)		
Ni(2)-O(2B)			2.079(3)	1.985(3)	2.043(3)	2.008(4)
Ni(2)-O(1C)		1.980(2)				
Ni(2)-O(2C)		2.016(2)				
Ni(2)-O(1W)		2.091(2)				
Ni(2)-O(1M)					2.065(3)	
Ni(2)-O(1M)*					2.024(3)	
Ni(2)-O(1P)				2.119(3)		
Ni(2)-O(2P)				2.129(3)		
Ni(2)-N(1C)			2.015(4)			2.129(4)
Ni(2)-N(1C)*						2.081(4)
Ni(3)-O(2B)				2.071(3)		
Ni(3)-O(3B)				2.034(3)		
Ni(3)-O(2D)						2.065(4)
Ni(3)-O(3D)						2.133(4)
Ni(3)-O(1E)						2.063(4)
Ni(3)-O(2P)				2.127(3)		
Ni(3)-O(1W)				2.113(3)		
Ni(3)-N(1B)				2.065(3)		
Ni(3)-N(2B)				2.107(3)		
Ni(3)-N(1D)						2.103(5)
Ni(3)-N(2D)						2.115(5)
Ni(3)-N(1F)						2.111(5)
Ni(4)-O(1D)						2.044(4)
Ni(4)-O(2D)						2.016(4)
Ni(4)-O(3D)*						2.072(4)
Ni(4)-O(2E)						1.995(4)
Ni(4)-N(1F)						2.156(5)
Ni(4)-N(1F)*						2.082(5)

Ni(1)···Ni(2)	3.203(1)	2.954(1)	3.118(1)	3.009(1)	3.026(1)
Ni(1)···Ni(2)*				3.212(1)	3.273(1)
Ni(1)···Ni(1)*				5.417(1)	5.456(1)
Ni(2)···Ni(2)*				3.067(1)	3.159(1)
Ni(2)···Ni(3)			3.136(1)		
Ni(3)···Ni(4)					3.030(1)
Ni(3)···Ni(4)*					3.266(1)
Ni(3)···Ni(3)*					5.435(1)
Ni(4)···Ni(4)*					3.186(1)
Ni(1)-O(2A)-Ni(2)	100.79(7)	94.1(1)	101.0(1)	94.8(1)	96.5(2)
Ni(1)-O(3A)-Ni(2)	102.16(8)	95.4(1)			
Ni(1)-O(3A)-Ni(2)*				99.7(1)	102.9(2)
Ni(1)-O(1P)-Ni(2)			94.2(1)		
Ni(2)-O(2B)-Ni(3)			101.3(1)		
Ni(2)-O(2P)-Ni(3)			95.0(1)		
Ni(1)-O(1M)-Ni(2)				93.8(1)	
Ni(1)-O(1M)-Ni(2)*				103.8(1)	
Ni(2)-O(1M)-Ni(2)*				97.2(1)	
Ni(1)-N(1C)-Ni(2)					91.1(2)
Ni(1)-N(1C)-Ni(2)*					102.7(2)
Ni(2)-N(1C)-Ni(2)*					97.3(2)
Ni(3)-O(2D)-Ni(4)					95.9(2)
Ni(3)-O(3D)-Ni(4)					101.9(2)
Ni(3)-N(1F)-Ni(4)					90.4(2)
Ni(3)-N(1F)-Ni(4)*					102.3(2)
Ni(4)-N(1F)-Ni(4)*					97.5(2)

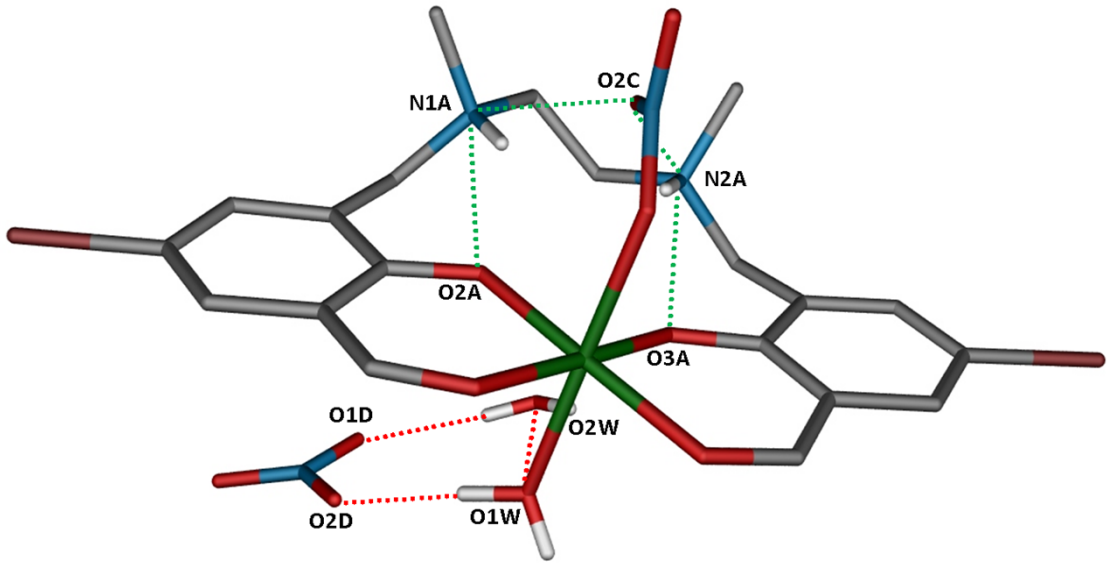

Figure S1. A perspective view of the structure of **1** together with intramolecular (green dotted lines) and intermolecular (red dotted lines) hydrogen bonds.

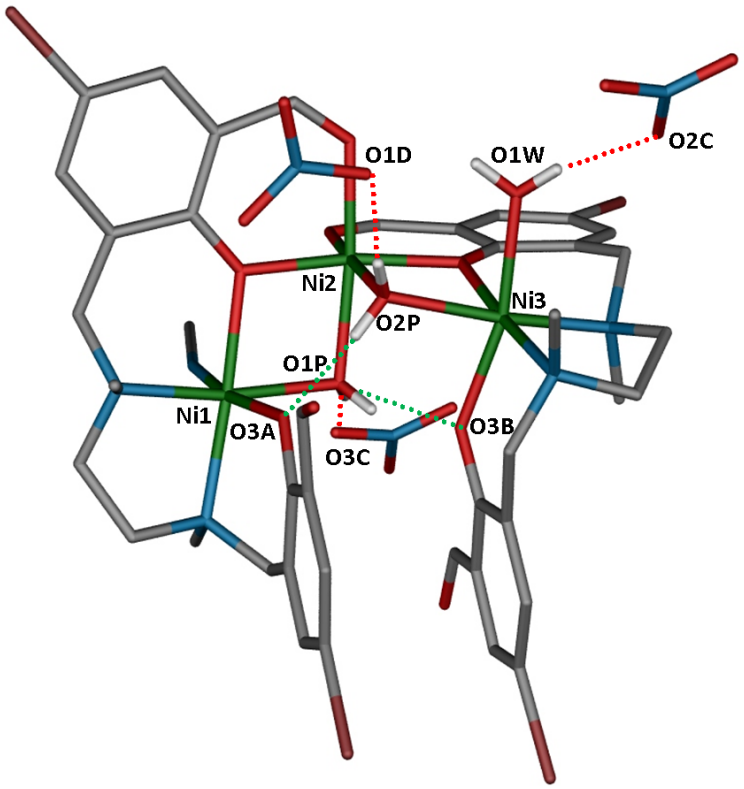

Figure S2. A perspective view of the structure of **4** together with intramolecular (green dotted lines) and intermolecular (red dotted lines) hydrogen bonds.

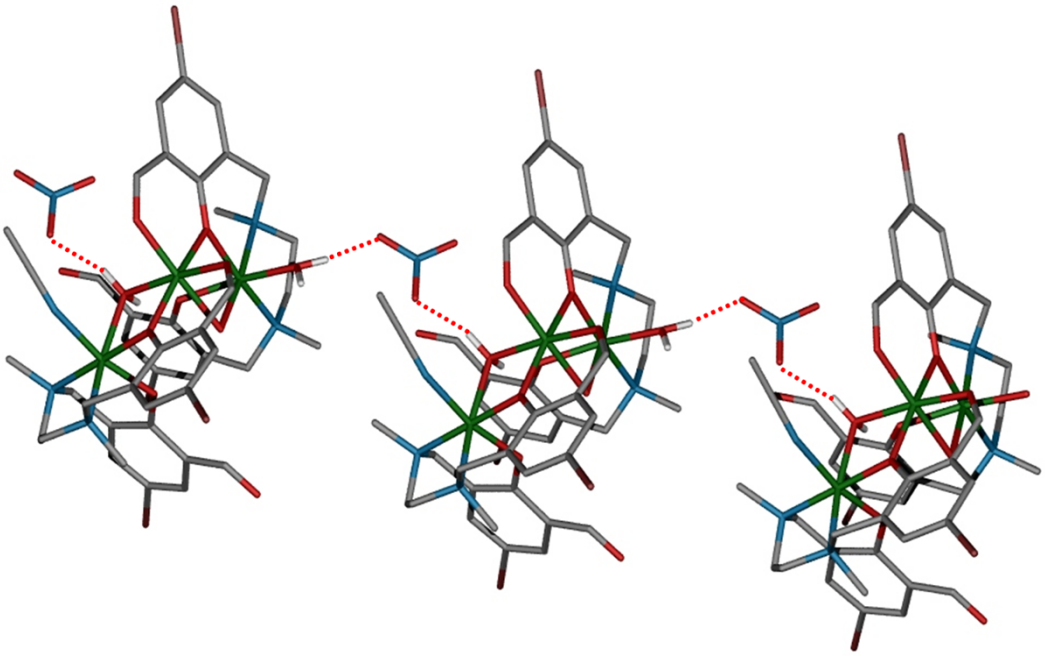

Figure S3. A perspective view of the structure of **4** together with intermolecular (red dotted lines) hydrogen bonds forming a chain running along the *b* axis.

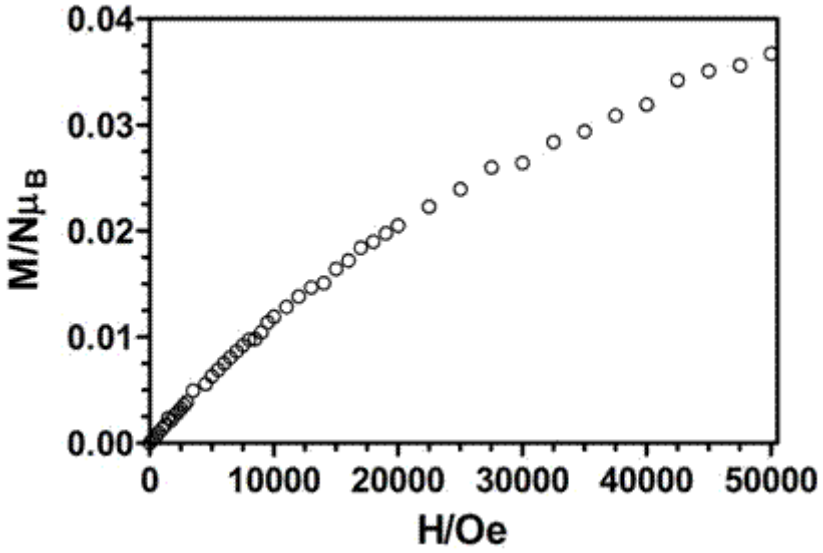

Figure S4. Field dependence of the magnetization for **2**.

Table S3. Spin densities of compound **2-6**.

Atoms	2	3	4	5	6A	6B
Ni1	+1.6907	+1.6554	+1.6610	−1.6873	+1.6683	+1.6711
Ni2	−1.7206	+1.7375	−1.7230	−1.7203	+1.6797	+1.6804
Ni3	–	–	+1.6718	+1.6872	+1.6683	+1.6711
Ni4	–	–	–	+1.7203	+1.6797	+1.6804
$O_{phenoxo}$	+0.0083 −0.0059	+0.0900[a]	+0.0624[a] −0.0166[a]	−0.0000[a,d] +0.0001[a,d]	+0.0758[a]	+0.0722[a]
$O_{aldehyde}$	−0.0380	+0.0455[a]	−0.0598	−0.0344 +0.0344	+0.0414[a]	+0.0449[a]
$O_{acetate}$	–	+0.0595[a]	–	−0.0410[a] +0.0410[a]	+0.0474[a]	+0.0472[a]
O_{acac}	+0.0476[a] −0.0592[a]	–	–	–	–	–
$O_{methoxide}$	–	–	–	−0.0554 +0.0554	–	–
O_{water}	−0.0292	–	−0.0592[a,c] +0.0161	–	–	–
N_{en}[b]	+0.0640[a]	+0.0677[a]	+0.0916[a]	−0.0625[a] +0.0626[a]	+0.0703[a]	+0.0707[a]
N_{SCN}	–	+0.0690	–	–	–	–
$N_{acetonitrile}$	–	–	+0.0454	–	–	–
N_{azide}					+0.1944[e]	+0.1889[e]

[a] Mean values.[b] From the ethylenediamine moiety of the ligand. [c] Bridged molecules. [d] Due to the symmetry of the system. [e] Sum of the three *N* atoms of the azide ligand.

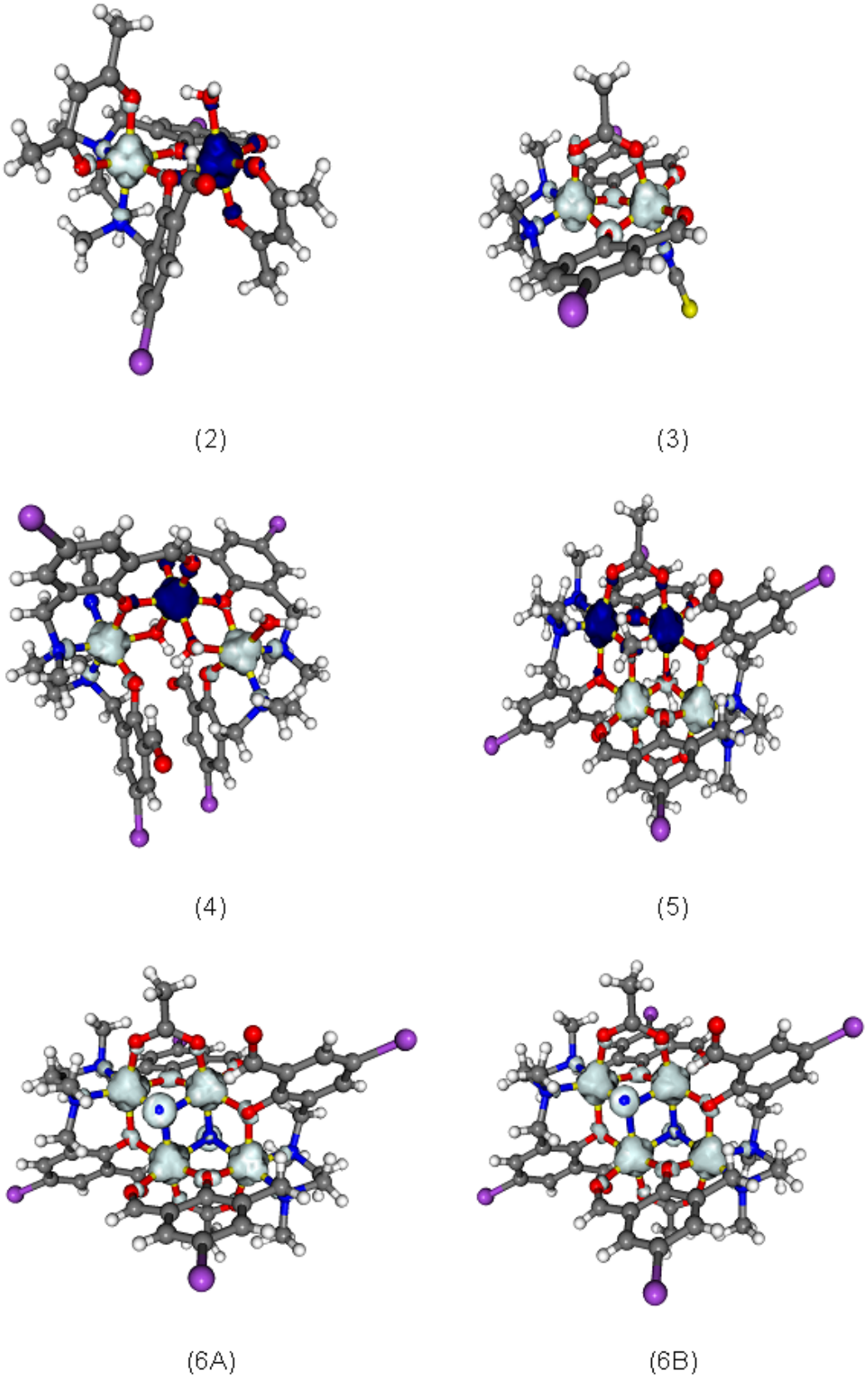

Figure S5. Calculated spin densities for structures **2-6**. The isodensity surfaces represented correspond to a cut-off value of 0.012 e bohr^{-3}. Grey and blue colors correspond to positive and negative values, respectively.