Supporting information

Triple-bridged ferromagnetic nickel(II) complexes: A combined experimental and theoretical DFT study on stabilization and magnetic coupling

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The structure of the complex **2** is shown in Figure S1 together with the atomic numbering scheme. Selected bond lengths and angles are summarized in Table S1. The dinuclear unit is formed by two independent nickel atoms, labeled Ni(1) and Ni(2), bridged by one water molecule O(3) and two μ_2-phenoxido oxygen atoms O(1) and O(2). Each of the two metal centers, Ni(1) and Ni(2) present distorted octahedral environment, being coordinated to the deprotonated chelating Schiff base ligand through the secondary amine nitrogen atoms N(1), N(3), the imine nitrogen atoms N(2), N(4) and the phenoxido oxygen atoms O(1) and O(2) respectively in facial configuration with usual bond distances (Table S1). The carboxylate oxygen atoms O(4) and O(6) of the terminally coordinated monodentate carboxylate ions, the oxygen atom O(3) of the water molecule and the bridging phenoxido atoms O(2) and O(1) complete the hexacoordination of Ni(1) and Ni(2) respectively. Thus two nickel atoms are linked through a triple oxygen bridge to form a face shared bi-octahedron, leading to a Ni-Ni distance of 2.851(1). The two phenoxido bridging angles, Ni(1)–O(1)–Ni(2) and Ni(1)–O(2)–Ni(2) are 86.3(2)°, 86.9(2)° respectively, and the water bridge angle, Ni(1)–O(3)–Ni(2) is of 85.5(2)° for complex **2**. Each bridging phenoxido oxygen atom is asymmetrically bound, with one Ni-O bond slightly longer [Ni(1)-O(2) 2.151(6)Å; Ni(2)-O(1) 2.160(6)Å] than the other [Ni(1)-O(1) 2.005(6)Å; Ni(2)-O(2) 1.991(6)Å] respectively. The Ni-O(water) bonds are identical within the experimental error [Ni(1)-O(3) 2.081(6)Å; Ni(2)-O(3) 2.099(5)Å] and these distances are comparable to those found in other reported aqua-bridged dinuclear Ni(II) complexes, which are in the range 2.09–2.25Å. The sets of four donor atoms O(1), N(2), O(4), O(3) describe the basal plane of Ni(1). The basal bond lengths around the Ni(1) atom are in the range of 1.970(7)-2.081(6)Å. The apical bond lengths are Ni(1)–O(2) 2.151(6) Å and Ni(1)–N(1) 2.146(7) Å, the

bond angle O(2)–Ni(1)–N(1) being 174.0(3) for complex **2**. Similarly in the coordination sphere of Ni(2) the basal plane consists of O(2), N(4), O(6) and O(3) with the bond lengths in the range of 1.983(7)- 2.099(5)Å. The apical bond lengths are Ni(2)-O(1) 2.160(6)Å and Ni(2)–N(3) 2.135(8)Å, the bond angle O(1)-Ni(2)-N(3) being 173.6(3)°. The two hydrogen atoms H(3A) and H(3B) of the bridging water molecule participate in strong intramolecular hydrogen bonding to the oxygen atoms O(7) and O(5) respectively of the terminally coordinated *p*-nitrobenzoate anions with D···A distances of 2.57(4) Å and 2.53(1) Å (Table S2).

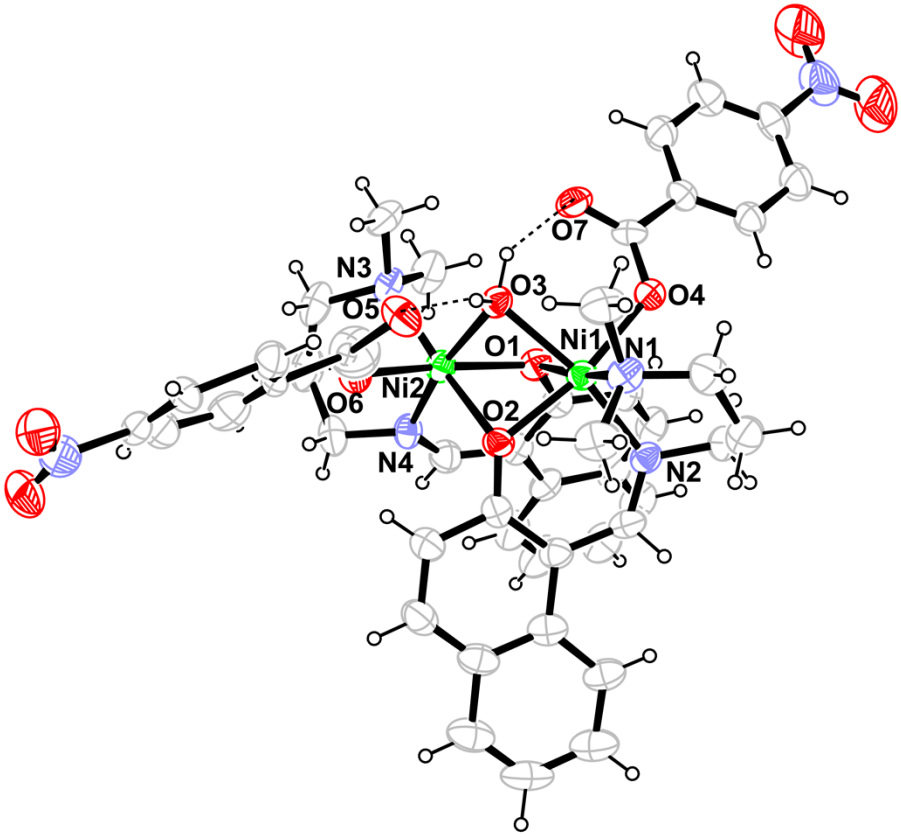

Figure S1. ORTEP view of the asymmetric unit of **2** with ellipsoids at the 30% probability level.

Table S1. Bond distances (Å) and angles (º) in the metal coordination spheres of complex **2**

Ni(1) – O(1)	2.005(6)	Ni(2) – O(1)	2.160(6)
Ni(1) – O(2)	2.151(6)	Ni(2) – O(2)	1.991(6)
Ni(1) – O(3)	2.081(6)	Ni(2) – O(3)	2.099 (5)
Ni(1) – O(4)	2.036(7)	Ni(2) – O(6)	2.046(6)
Ni(1) – N(1)	2.146(7)	Ni(2) – N(3)	2.135(8)
Ni(1) – N(2)	1.970(7)	Ni(2) – N(4)	1.983(7)
O(1)-Ni(1)-O(2)	79.2(2)	O(1)-Ni(2)-O(6)	86.7(3)
O(1)-Ni(1)- O(3)	80.2(2)	O(1)-Ni(2)-N(3)	173.6(3)
O(1) -Ni(1) - O(4)	166.4 (3)	O(1)-Ni(2)-N(4)	98.6(3)
O(1) -Ni(1) - N(1)	100.9(3)	O(2)-Ni(2)-O(3)	79.1(2)
O(1) -Ni(1) - N(2)	89.6(3)	O(2)-Ni(2)-O(6)	164.5(3)
O(2) -Ni(1) - O(3)	76.0(2)	O(2)-Ni(2)-N(3)	102.0(3)
O(2) -Ni(1) - O(4)	88.9(2)	O(2)-Ni(2)-N(4)	89.6(2)
O(2) -Ni(1) - N(1)	174.1(3)	O(3)-Ni(2)-O(6)	91.4(2)
O(2) -Ni(1) - N(2)	98.2(3)	O(3)-Ni(2)-N(3)	97.7(3)
Ni(1) -O(3)- Ni(2)	85.5(2)	O(3)-Ni(2)-N(4)	168.3(2)
O(3)- Ni(1) - O(4)	90.7(2)	O(6)-Ni(2)-N(3)	91.3(3)
O(4) -Ni(1) - N(1)	90.4(3)	O(6)-Ni(2)-N(4)	99.0(3)
O(4) -Ni(1) - N(2)	98.6(3)	N(1)-Ni(1)-N(2)	87.8(3)
Ni(1)- O(1)- Ni(2)	86.3(2)	O(1)-Ni(2)-O(2)	79.3(2)
Ni(1)- O(2)- Ni(2)	86.9(2)	O(1)-Ni(2)-O(3)	76.3(2)

Table S2. Hydrogen bonding distances (Å) and angles (º) for the complex **2**

Compound	D−H···A	D—H	D··· A	A···H	∠D—H···A
2	O(3)–H(3A)···O(7)	0.97	2.57(4)	1.73	143
	O(3) –H(3B)···O(5)	0.97	2.53(1)	1.69	142
	O(1S)–H(1S)···O(7)	0.82	2.81(4)	2.21	130