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Supporting Information

A Novel Ni_4 Complex Exhibiting Microsecond Quantum Tunneling of the Magnetization

Guillem Aromí,[a,*] Elisabeth Bouwman,[b] Enrique Burzurí,[c] Chiara Carbonera,[c] J. Krzystek,[d] Fernando Luis,[c] Christoph Schlegel,[e] Joris van Slageren,[e,f,*] Stefania Tanase,[b] Simon J. Teat,[g,h]

[a] *Departament de Química Inorgànica, Facultat de Química, Universitat de Barcelona, Diagonal 647, E-08028 Barcelona, Spain. Tel: +34 934039760, Fax: +34 934907725.*

[b] *Co-ordination and Bio-Inorganic Chemistry, Leiden Institute of Chemistry, Gorlaeus Laboratories, P.O.Box 9502, 2300 RA Leiden, The Netherlands.*

[c] *Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, y Departamento de Física de la Materia Condensada, C/ Pedro Cerbuna 12, 50009-Zaragoza, Spain.*

[d] *National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310 USA.*

[e] *1. Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, D-70550 Stuttgart, Germany.*

[f] *School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK. Tel: +44 1159513523, Fax: +44 1159513563.*

[g] *Daresbury Laboratory, Daresbury, Warrington, Cheshire, WA4 4AD, UK.*

[h] *Light Source, Lawrence Berkeley Lab, 1 Cyclotron Rd, MS2-400, Berkeley, CA 94720.*

Supplementary Material

Table S1. Selected interatomic distances (Å) and angles (deg.) for complex **1**.

Ni1–O1	2.052(2)	O2–Ni2–O21	155.39(9)
Ni1–O2	2.073(2)	O2–Ni2–N21	98.78(10)
Ni1–O4	2.075(2)	O3–Ni2–O21	118.26(9)
Ni1–O5	2.146(3)	O3–Ni2–N21	101.26(9)
Ni1–O11	1.985(3)	O21–Ni2–N21	88.91(10)
Ni1–N11	2.023(3)	O1–Ni3–O3	81.57(8)
Ni2–O1	2.033(2)	O1–Ni3–O4	81.03(8)
Ni2–O2	2.032(2)	O1–Ni3–O6	88.79(9)
Ni2–O3	2.009(2)	O1–Ni3–O31	173.34(9)
Ni2–O21	2.004(2)	O1–Ni3–N31	98.76(9)
Ni2–N21	1.986(2)	O3–Ni3–O4	82.23(8)
Ni3–O1	2.042(2)	O3–Ni3–O6	169.29(9)
Ni3–O3	2.082(2)	O3–Ni3–O31	99.81(8)
Ni3–O4	2.045(2)	O3–Ni3–N31	95.67(9)
Ni3–O6	2.259(2)	O4–Ni3–O6	91.70(9)
Ni3–O31	1.976(2)	O4–Ni3–O31	92.67(8)
Ni3–N31	2.018(3)	O4–Ni3–N31	177.90(9)
Ni4–O2	2.084(2)	O6–Ni3–O31	89.24(9)
Ni4–O3	2.096(2)	O6–Ni3–N31	90.38(10)
Ni4–O4	2.082(2)	O31–Ni3–N31	87.61(9)
Ni4–O7	2.120(2)	O2–Ni4–O3	79.94(8)
Ni4–O41	2.010(2)	O2–Ni4–O4	81.74(8)
Ni4–N41	2.039(2)	O2–Ni4–O7	90.63(8)
Ni1···Ni2	3.1061(6)	O2–Ni4–O41	90.00(8)
Ni1···Ni3	3.1211(6)	O2–Ni4–N41	171.89(9)
Ni1···Ni4	3.1149(6)	O3–Ni4–O4	81.01(8)
Ni2···Ni3	3.0508(6)	O3–Ni4–O7	162.92(8)
Ni2···Ni4	3.1020(6)	O3–Ni4–O41	98.35(8)
Ni3···Ni4	3.1295(6)	O3–Ni4–N41	93.86(9)
N42–H···O31	2.662(3)	O4–Ni4–O7	83.57(8)
N32–H···O21	2.889(3)	O4–Ni4–O41	171.70(8)
N22–H···O41	2.625(3)	O4–Ni4–N41	102.60(8)

O1–H···O1S	2.734(4)	O1–Ni2–O21	88.81(9)
O7–H···O11	2.644(3)	O1–Ni2–N21	175.15(9)
O1–Ni1–O2	80.18(8)	O2–Ni2–O3	83.30(8)
O1–Ni1–O4	80.07(8)	O7–Ni4–O41	95.85(9)
O1–Ni1–O5	90.93(11)	O7–Ni4–N41	96.64(9)
O1–Ni1–O11	171.58(9)	O41–Ni4–N41	85.70(9)
O1–Ni1–N11	98.18(11)	Ni1–O1–Ni2	98.97(10)
O2–Ni1–O4	82.17(8)	Ni1–O1–Ni3	99.34(9)
O2–Ni1–O5	168.30(10)	Ni2–O1–Ni3	96.94(9)
O2–Ni1–O11	93.91(9)	Ni1–O2–Ni2	98.34(9)
O2–Ni1–N11	98.02(10)	Ni1–O2–Ni4	97.05(8)
O4–Ni1–O5	88.85(9)	Ni2–O2–Ni4	97.82(9)
O4–Ni1–O11	93.25(9)	Ni2–O3–Ni3	96.45(8)
O4–Ni1–N11	178.19(11)	Ni2–O3–Ni4	98.17(9)
O5–Ni1–O11	94.08(11)	Ni3–O3–Ni4	97.03(8)
O5–Ni1–N11	90.72(11)	Ni1–O4–Ni3	98.50(8)
O11–Ni1–N11	88.53(12)	Ni1–O4–Ni4	97.05(8)
O1–Ni2–O2	81.63(9)	Ni3–O4–Ni4	98.61(8)
O1–Ni2–O3	83.59(8)		

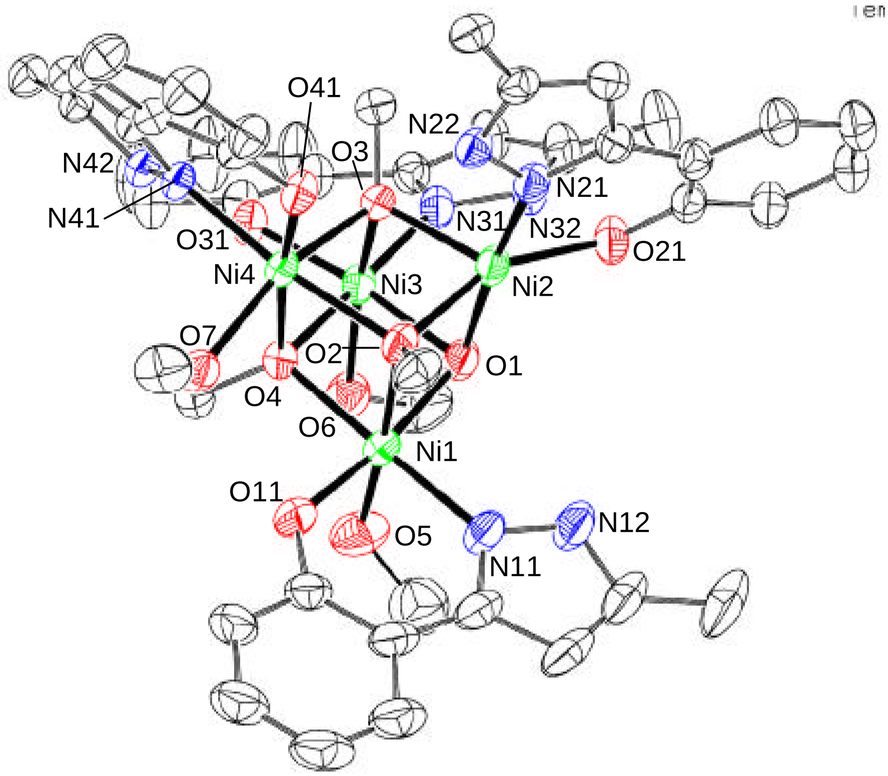

Figure S1. ORTEP representation at the 50% level of probability of complex $[Ni_4(OH)(OMe)_3(Hphpz)_4(MeOH)_3]$. Only heteroatoms are labeled and hydrogen atoms are not shown.

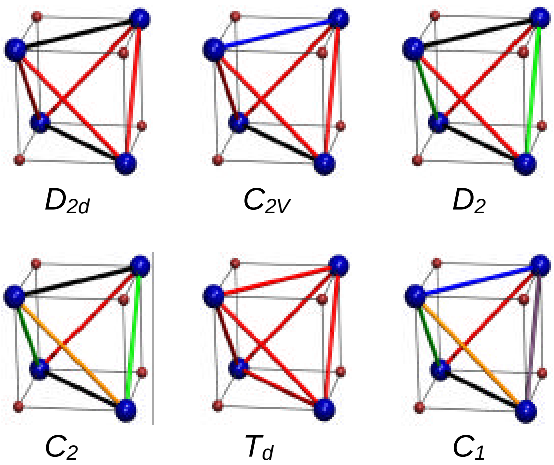

Figure S2. Idealized symmetry groups of complexes with a $[Ni_4O_4]$ core, with the distribution of intramolecular magnetic interactions. Blue and red balls are Ni and O atoms, respectively. Each type of interaction is represented by a different color of the bars connecting Ni atoms.

Among the collection of compounds in the Cambridge Structure Database, only two examples display pentacoordinated Ni^{II} centers (two of the four metals in each case).[55, 56] In D_{2d} or S_4 symmetry there are two different sets (of 2 and 4, respectively) of pairwise exchange couplings (Figure S1). Complexes with this symmetry constitute the largest group (34 examples, e.g. [8, 57]). The next largest group is that of C_2 symmetry in which there are four different sets of exchange couplings with 2, 2, 1, and 1 members, respectively (8 cases, e.g. [58, 59]). The other symmetries are less common: C_{2v} (three sets of couplings with 4, 1, and 1 members, respectively; 3 examples),[16, 60] C_1 (all couplings different, 3 examples),[39, 40] D_2 (three sets of couplings with 2, 2, and 2 members, respectively; 2 examples)[61, 62] and T_d (all coupling constants equal, 1 example).[63] This survey shows that **1** is one of the few $[Ni_4O_4]$ cubanes with no (idealized) symmetry elements at all.