

ELECTRONIC SUPPORTING INFORMATION

Family of Polynuclear Nickel Cage-Like Phenylsilsesquioxanes; Features of Periodic Networks and Magnetic Properties

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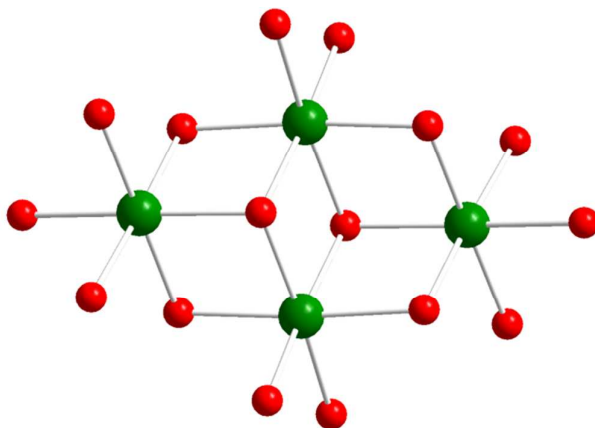


Figure S1. Fragment of crystal structure of CLMS 1 showing the organization of Ni(II) ions in the architecture. Color code: red for O, green for Ni.

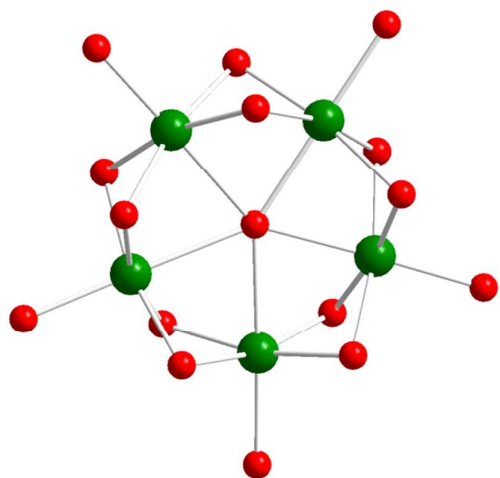


Figure S2. Fragment of crystal structure of CLMS **2** showing the organization of Ni(II) ions in the architecture. Color code: red for O, green for Ni.

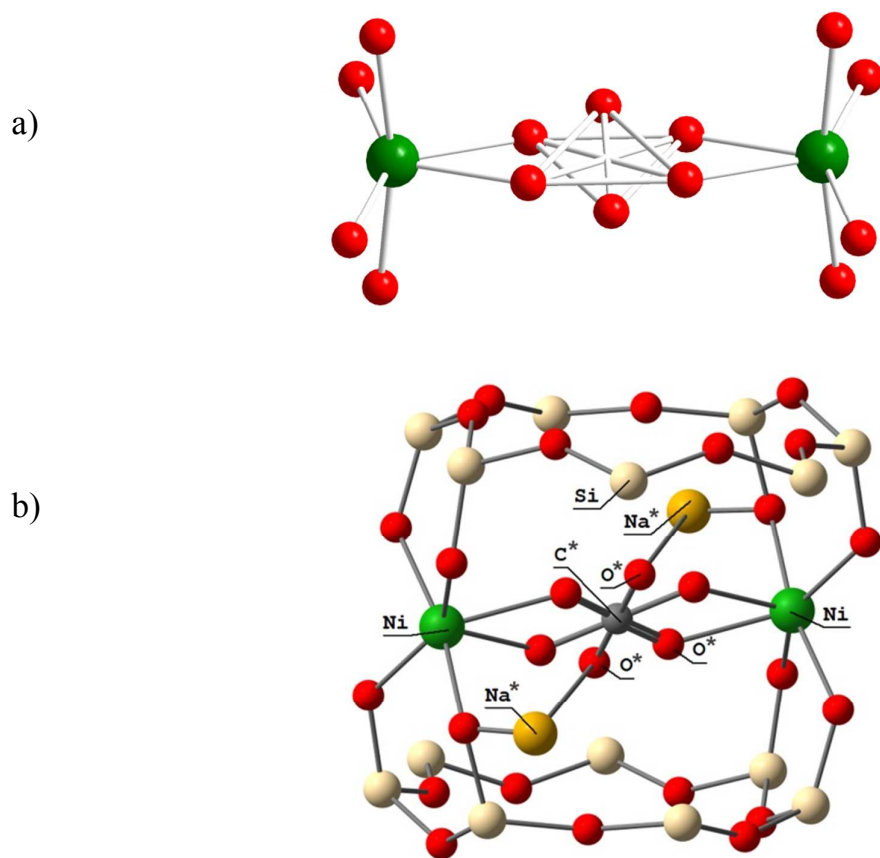


Figure S3. a) Fragment of crystal structure of CLMS **3** showing the organization of Ni(II) ions in the cage. Color code: red for O, green for Ni; b) General view of a molecular cage

fragment for CLMS **3** with encapsulated sodium bicarbonate. Color code: O – red, Si – beige, Ni – green, Na – yellow. Atoms of Na₂CO₃ moiety are marked by asterisks.

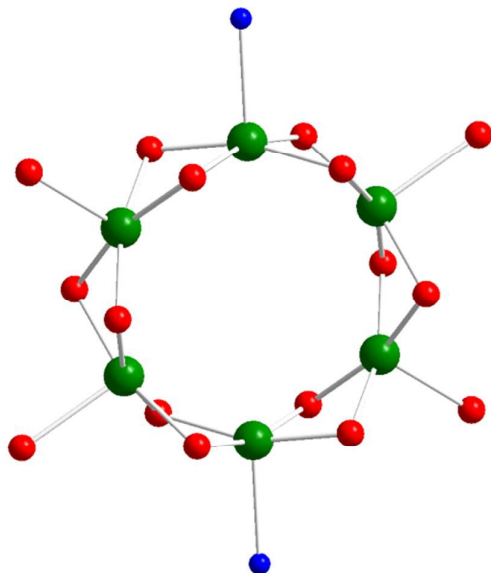


Figure S4. Fragment of crystal structure of CLMS **4** showing the organization of Ni(II) ions in the architecture. Color code: red for O, green for Ni.

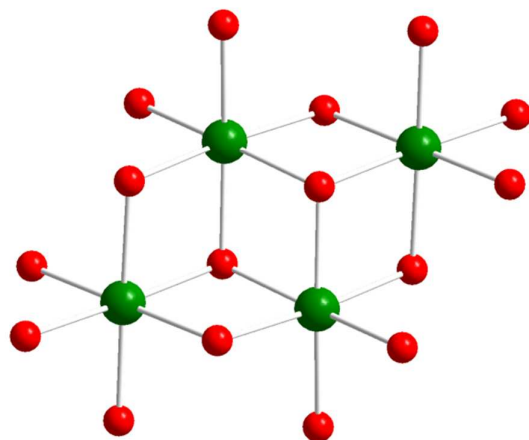


Figure S5. Fragment of crystal structure of CLMS **5** showing the organization of Ni(II) ions in the architecture. Color code: red for O, green for Ni.

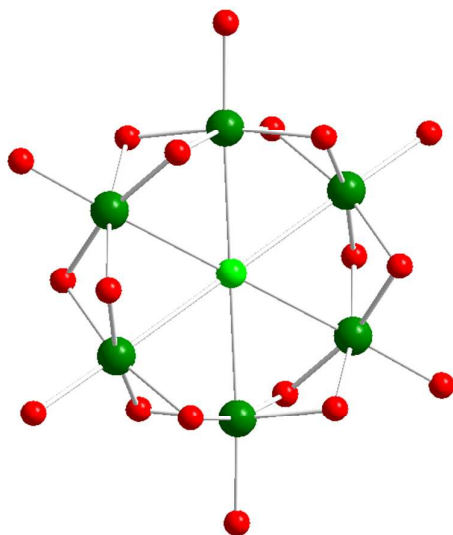


Figure S6. Fragment of crystal structure of CLMS **6** showing the organization of Ni(II) ions in the architecture. Color code: red for O, green for Ni, light green for Cl.

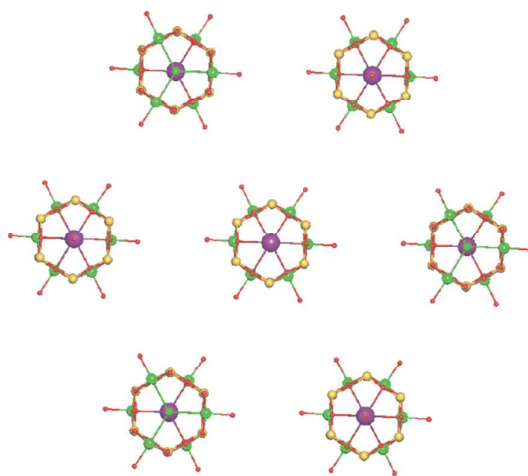


Figure S7. Fragment of the crystal packing of **6** (view along crystallographic axes *c*). Color code: O – red, Si – beige, Ni – green, Cl – light green, K – purple, Cs - violet. Carbon and hydrogen atoms are omitted.

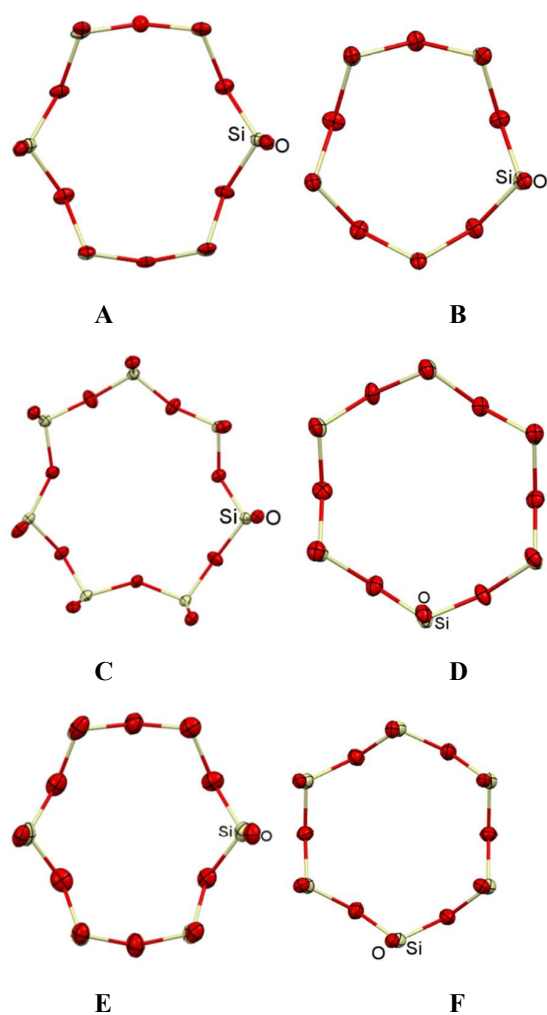


Figure S8. Top view of siloxanolate ligands in **1** (A), **2** (B), **3** (C), **4** (D), **5** (E), **6** (F). Color code: o – red, Si – beige.

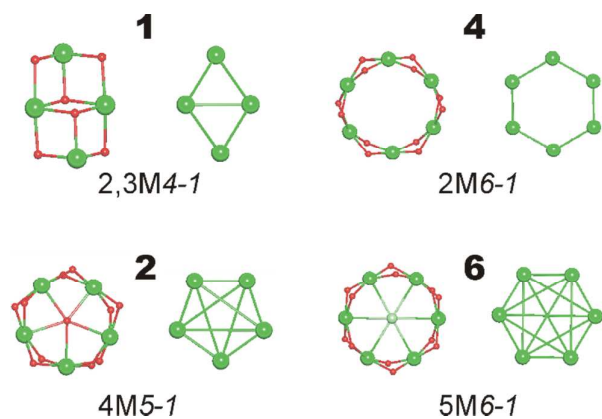


Figure 9. The Ni-containing polynuclear clusters connected by the bridged atoms (left) and the graphs for the corresponding polynuclear complexes' connectivity (right) in **1**, **2**, **4** and **6**. Color code: O - red, Ni - green, Cl - light green.

Note: Taking into account that such anions are also able to transfer spin density between d-metal ions, chemical connectivity of nickel atoms within metal-containing cluster was of interest. It was determined following the procedure described in ref. S2 to obtain the graph of Ni-containing skeleton keeping the cluster connectivity as implemented into the topospro package.^{S3} We obtained that nickel atoms in the cages of **1** - **6** form discrete clusters which belong to, respectively, 2,3M4-1, 4M5-1, 1M2-1, 2M6-1, 2,3M4-1 and 5M6-1 clusters (Figure 9) In terms of the ND*k*-*m* notation. within this notation N is equal to coordination number of topologically non-equivalent nodes, M denotes a discrete cluster (in contrast with 1-, 2- and 3-periodic architectures), *k* is the number of metal atoms in the cluster, and *m* - a classification number to distinguish topologically distinct clusters with equal ND*k* parameters. In accord with a database of topological representations of polynuclear nickel compounds,^{S4} 8 % of nickel clusters (26 of 318 discussed in ref. 15b) belong to 2M6-1 clusters. At the same time, the database contains only 4 and 3 representatives of 5M6-1 and 4M5-1 clusters. Recently, we also expanded the number of such compounds with [(PhSiO_{1.5})₁₀(NiO)₅(DMF)₇],^{15b} [(PhSiO_{1.5})₁₂(NiO)₆(H₂O)(DMSO)₉]^{15b} and [(PhSiO_{1.5})₁₂(NiO)₆(NaCl)(C₄H₈O₂)₁₃(PhCN)₂(H₂O)₂]²³ complexes. To our knowledge, **1** and **5** are the first representatives of the 2,3M4-1 clusters for nickel-containing compounds.

We would like to emphasize that two earlier publications¹⁸ reported on the distorted prismatic Ni₄-CLMSs. Note, though that compounds **1** and **5** differ from Ni₄Na₆ from ref.18 by composition (Ni₄Na₈ for **1**, Ni₄Na₄K₂ for **5**). The same should be said for the comparison of early reported Ni₆-CLMSs (isolated as alcohol complexes)^{S5} and hexanuclear complexes **4** and **6**. The more detailed discussion of structural differences could not be given here due to an absence of structural information (cif files) in CCDC for compounds from refs.18a and S5a.

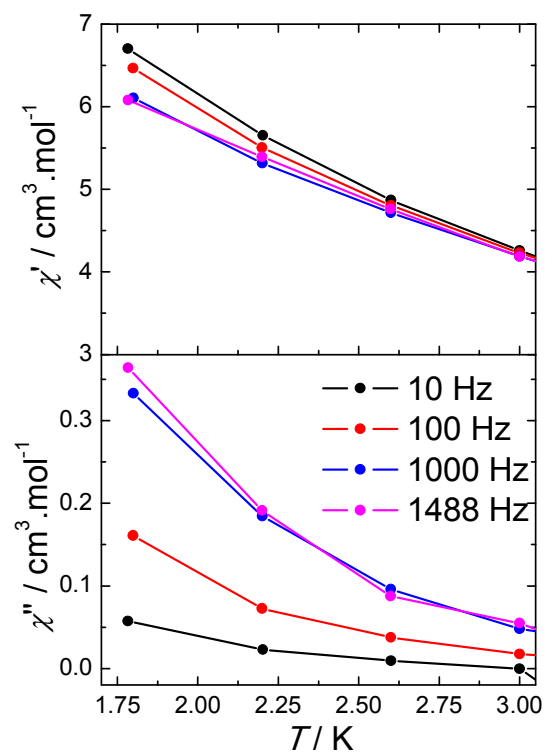


Figure S10. Temperature dependence of the in-phase (χ') and out-of-phase (χ'') susceptibilities under a zero DC-field for **1**.

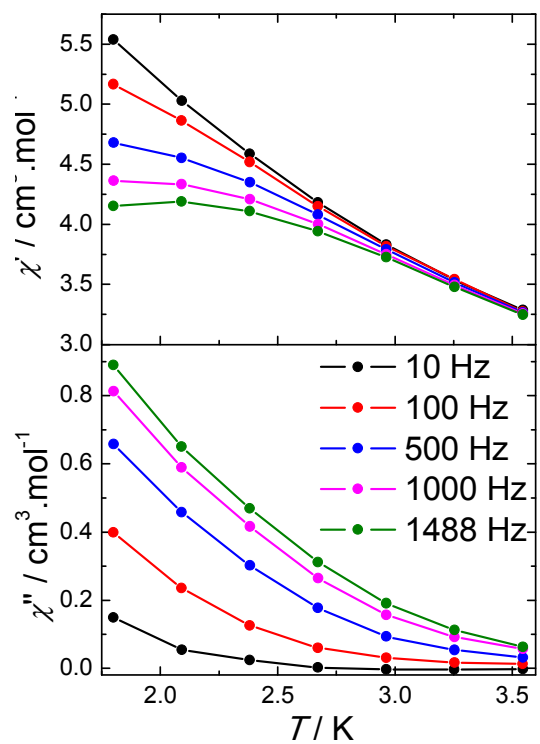


Figure S11. Temperature dependence of the in-phase (χ') and out-of-phase (χ'') susceptibilities under a 900 Oe DC-field for **1**.

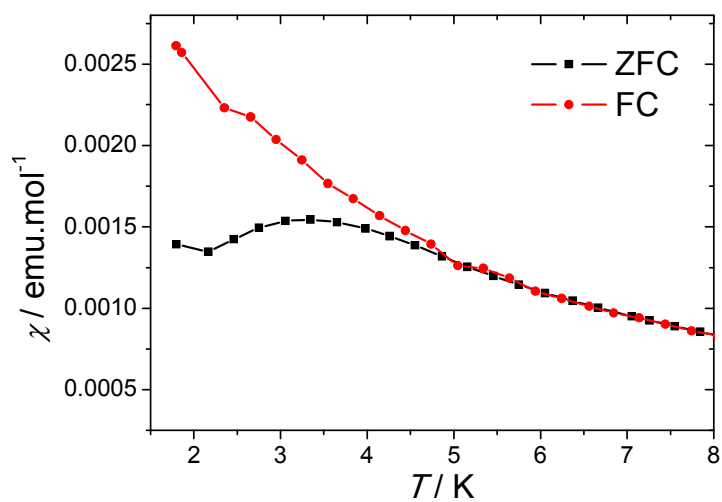


Figure S12. ZFC/FC curves measured under a 100 Oe field for **2**.

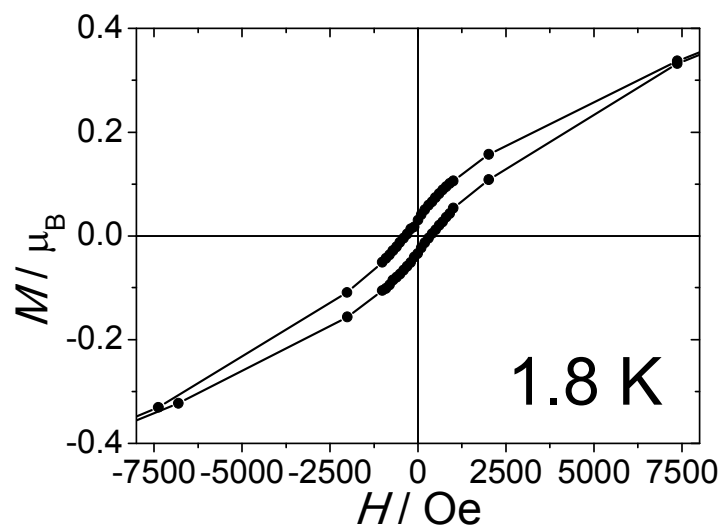


Figure S13. Hysteresis loop for **2** at 1.8 K.

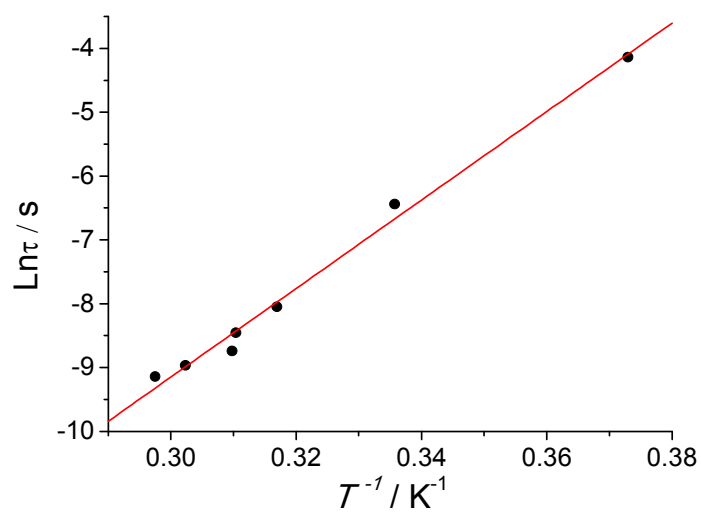


Figure S14. Temperature dependence of the relaxation time for **2**. The red solid line corresponds to the best Arrhenius fit.

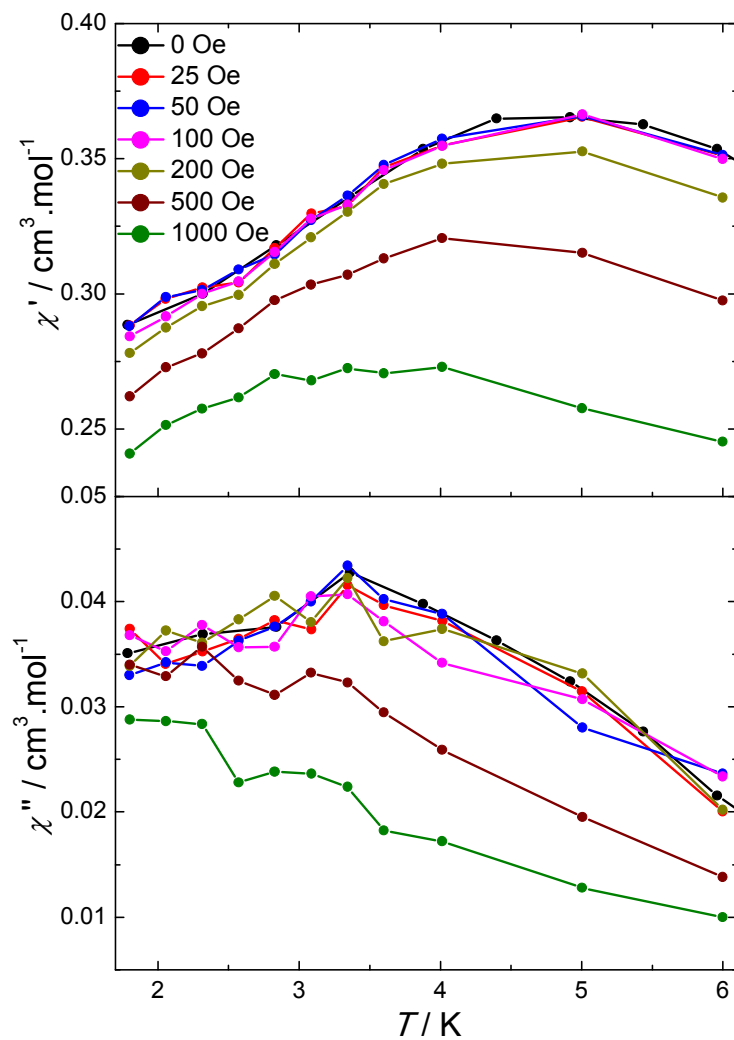


Figure S15: Temperature dependence of the ac susceptibilities (500 Hz) for various DC fields for **2**.

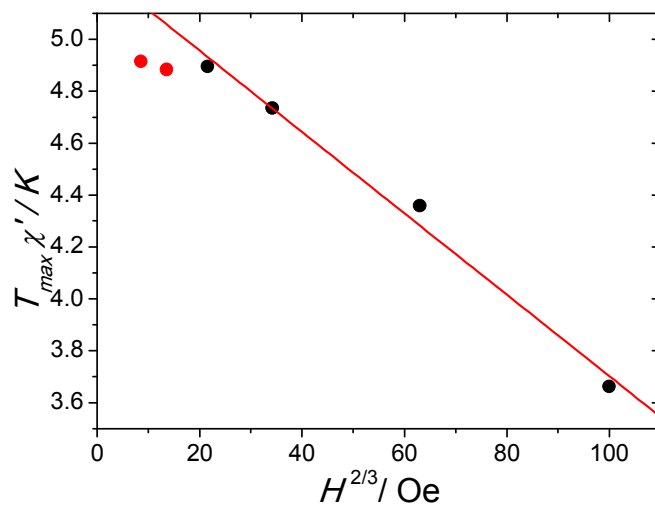


Figure S16 : Almeida-Thouless line for **2**.

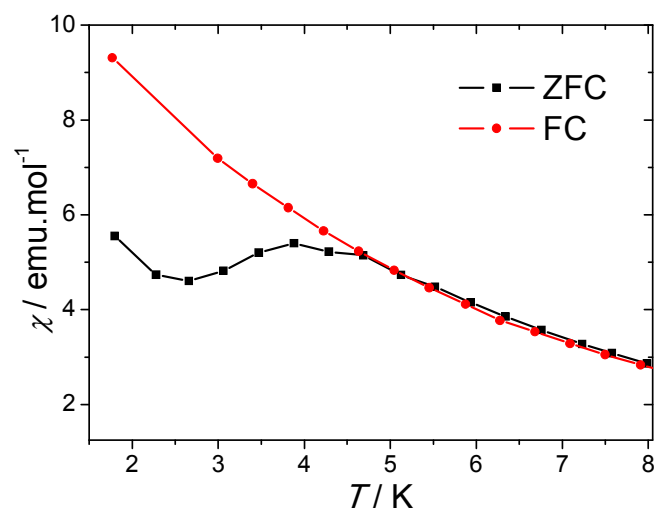


Figure 17. ZFC/FC curves for **4** measured under a 100 Oe field.

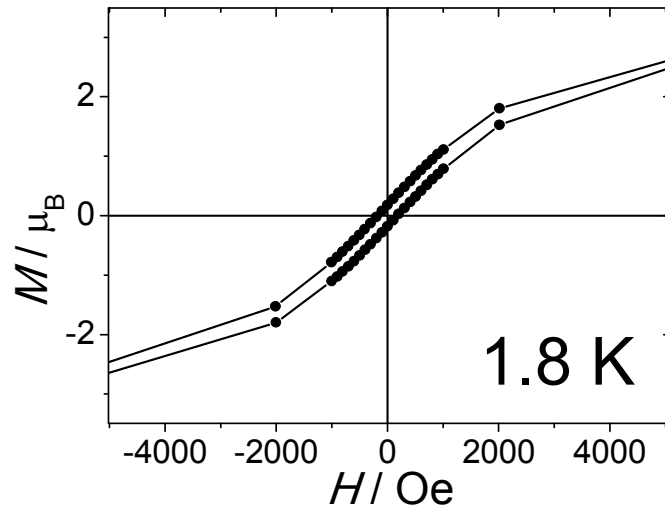


Figure S18. Hysteresis loop for **4** at 1.8 K.

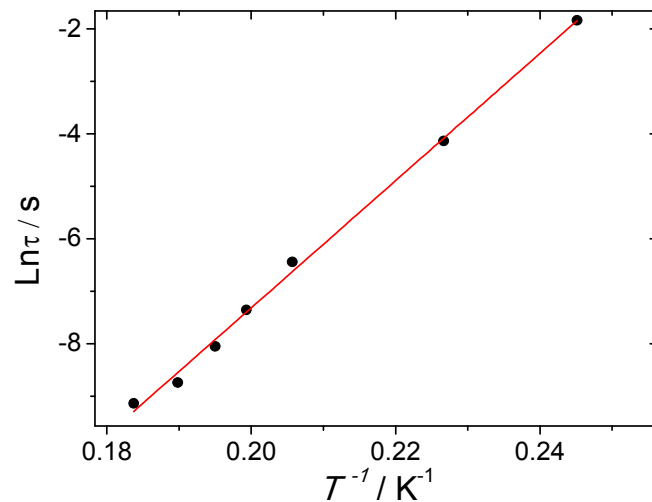


Figure S19. Temperature dependence of the relaxation time for **4**. The red solid line corresponds to the best Arrhenius fit.

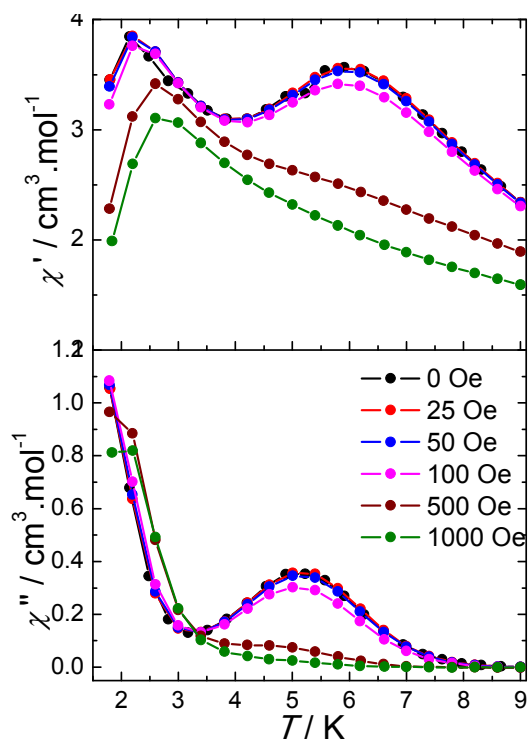


Figure S20. Temperature dependence of the ac susceptibilities (500 Hz) for various DC fields for **4**.

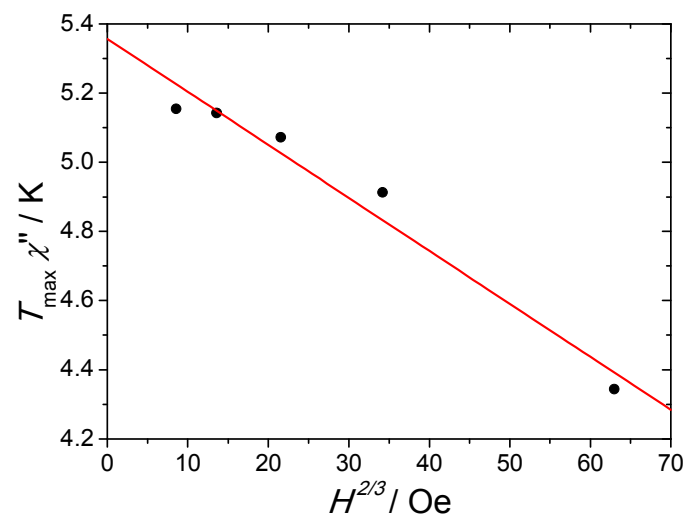


Figure S21. Almeida-Touless (AT) model line for 4.

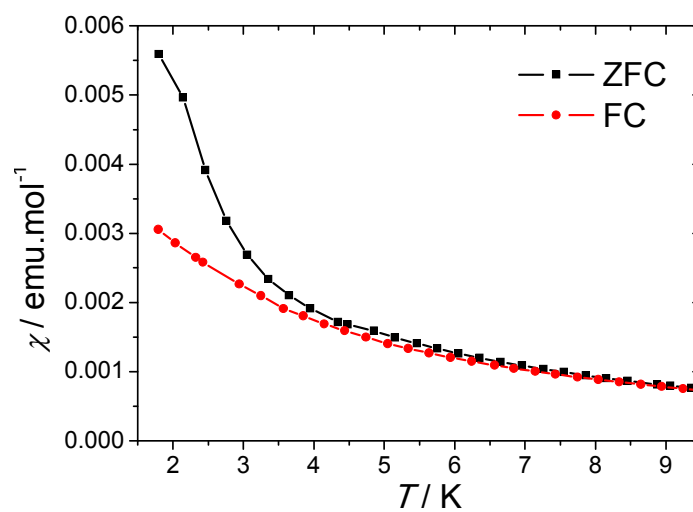


Figure S22. ZFC/FC curves measured under a 100 Oe DC field for 5.

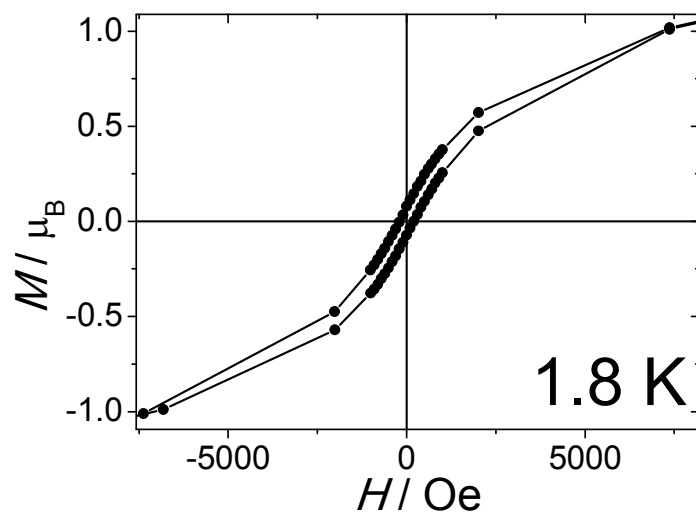


Figure S23. Hysteresis loop for **5** at 1.8 K.

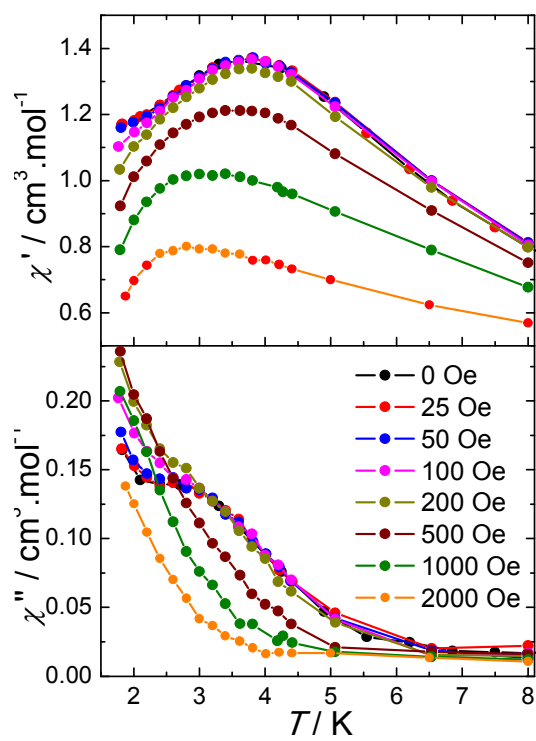


Figure S24. Temperature dependence of the ac susceptibilities for various DC fields for **5**.

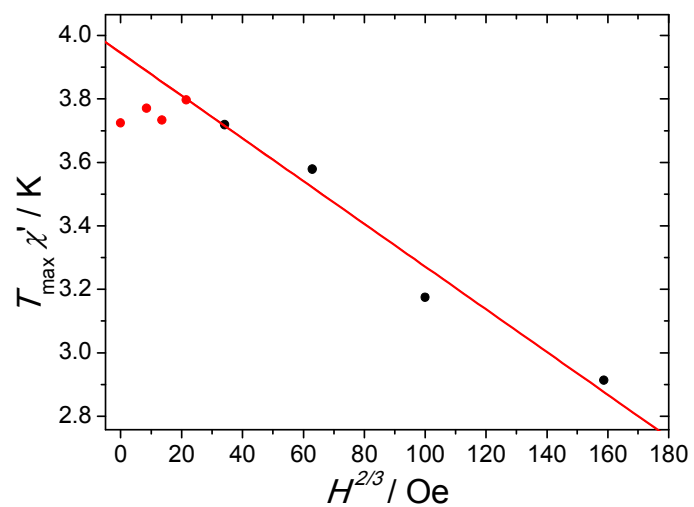


Figure S25. AT line for 5.

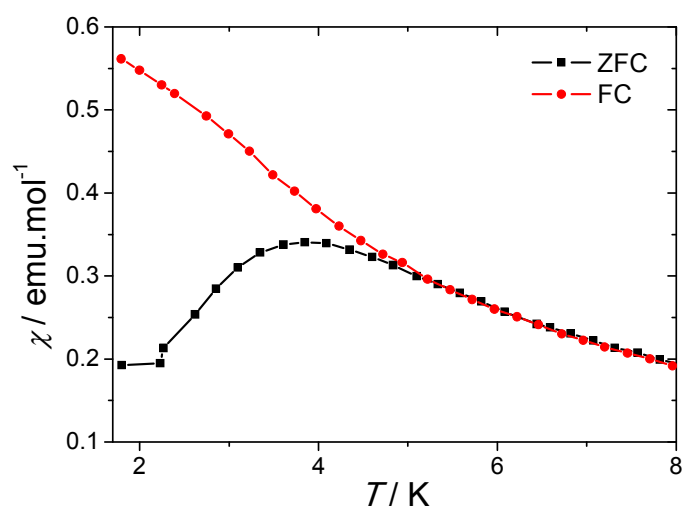


Figure S26. ZFC/FC curves measured under a 50 Oe DC field for 6.

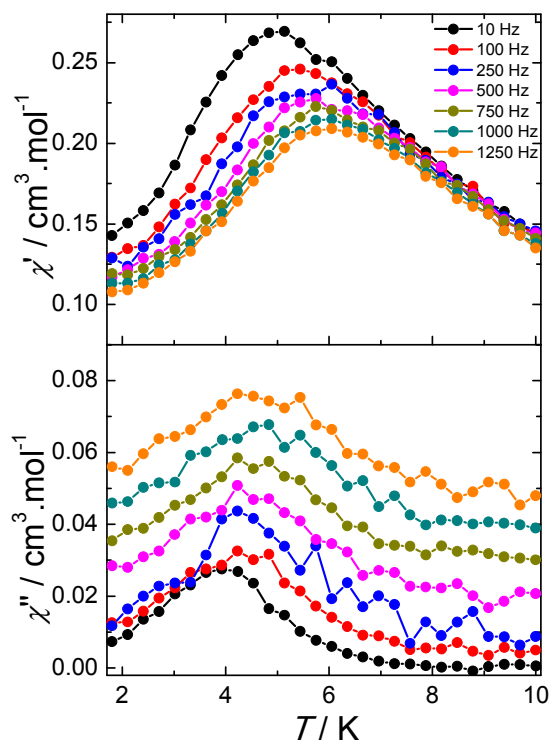


Figure S27. Temperature dependence of the in-phase (χ') and out-of-phase (χ'') susceptibilities under a zero DC-field for **6**.

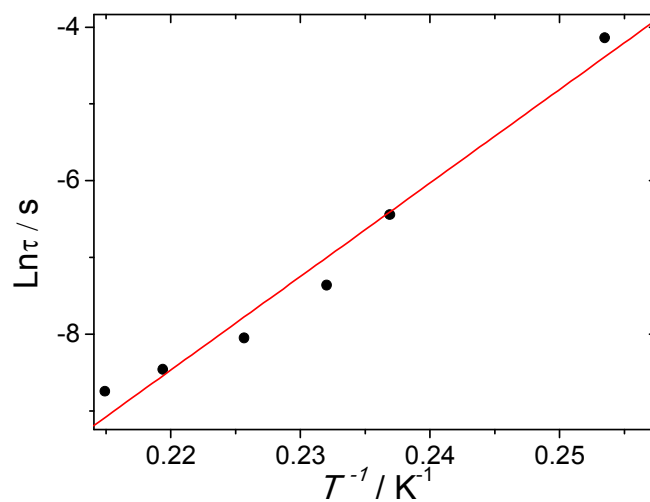


Figure S28 Temperature dependence of the relaxation time for **6**. The red solid line corresponds to the best Arrhenius fit.

References

- S1. (a) Pashchenko, V.; Brendel, B.; Wolf, B.; Lang, M.; Lyssenko, K.; Shchegolikhina, O.; Molodtsova, Y.; Zherlitsyna, L.; Auner, N.; Schütz, F.; Kollar, M.; Kopietz, P.; Harrison, N. Synthesis, Structure and Magnetic Properties of a Novel Linear CuII-Trimer Complex. *Eur. J. Inorg. Chem.* **2005**, 4617-4625. (b) Korlyukov, A. A.; Eskova, M. A.; Tkachenko, I. M.; Kononevich, Y. N.; Shchegolikhina, O. I.; Muzafarov, A. M. Heteroligand nickel siloxane with 4-vinylbenzyl substituents. *Mendeleev Comm.* **2015**, *25*, 226–228.
- S2. Kostakis, G. E.; Blatov, V. A.; Proserpio, D. M. A method for topological analysis of high nuclearity coordination clusters and its application to Mn coordination compounds. *Dalton Trans.* **2012**, *41*, 4634-4640.
- S3. Blatov, V. A.; Shevchenko, A. P.; Proserpio, D. M. Applied Topological Analysis of Crystal Structures with the Program Package ToposPro. *Cryst. Growth Des.* **2014**, *14*, 3576-3586.
- S4. Wix, P.; Kostakis, G. E.; Blatov, V. A.; Proserpio, D. M.; Perlepes, S. P.; Powell, A. K. A Database of Topological Representations of Polynuclear Nickel Compounds. *Eur. J. Inorg. Chem.* **2013**, 520-526.
- S5. (a) Shchegolikhina, O. I.; Zhdanov, A. A.; Igonin, V. A.; Ovchinnikov, Yu. E.; Shklover, V. E.; Struchkov, Yu. T. *Organomet. Chem. USSR* 1991, *4*, 39 (*Metalloorg. Khim.*, 1991, *4*, 74). (b) Cornia, A.; Fabretti, A. C.; Gatteschi, D.; Palyi, G.; Rentschler, E.; Shchegolikhina, O. I.; Zhdanov, A. A. Molecule-Based Magnets: Ferro- and Antiferromagnetic Interactions in Nickel(II) Cyclohexasiloxanolate Sandwich Complexes. *Inorg. Chem.* 1995, *34*, 5383-5387.