

## ELECTRONIC SUPPORTING INFORMATION

### **Structural aesthetics in molecular nanoscience: A unique Ni<sub>26</sub> cluster with a ‘rabbit-face’ topology and a discrete Ni<sub>18</sub> ‘molecular chain’**

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## Experimental Section

**Synthesis of Schiff-base ligand.** The organic ligand sacbH<sub>2</sub> was prepared in quantitative yields (~95-97%) by the condensation reaction of 2-amino-5-chlorobenzoic acid with salicylaldehyde in a molar ratio of 1:1 in refluxing MeOH. The resulting yellow microcrystalline solid was dried under vacuum and analyzed as solvent-free. Elemental analysis (%) calcd for sacbH<sub>2</sub>: C 60.99, H 3.66, N 5.08; found: C 61.06, H 3.78, N 5.04.

### Synthesis of reported compounds

**Safety note:** Perchlorate salts are potentially explosive; such compounds should be synthesized and used in small quantities, and treated with utmost care at all times.

**(NH<sub>4</sub>Et<sub>3</sub>)[Ni<sub>26</sub>(OH)<sub>4</sub>(O<sub>2</sub>CMe)<sub>19</sub>(sald)<sub>2</sub>(sacb)<sub>14</sub>(MeOH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>] (1):** To a stirred, yellow solution of sacbH<sub>2</sub> (0.06 g, 0.2 mmol) and NEt<sub>3</sub> (0.17 mL, 1.2 mmol) in MeCN/MeOH (20 mL, 5:1 v/v) was added solid Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.15 g, 0.4 mmol) followed by glacial MeCO<sub>2</sub>H (23  $\mu$ L, 0.4 mmol). The resulting green solution was stirred for 20 min, during which time all the solids dissolved and the color of the solution changed to olive-green. The solution was filtered, and the filtrate was left to evaporate slowly at room temperature. After 30 days, X-ray quality yellow-green plate-like crystals of 1·9MeCN·xMeOH·yH<sub>2</sub>O had appeared and were collected by filtration, washed with cold MeCN (2 x 2 mL) and dried under vacuum. The yield was 20 %. Elemental analysis (%) calcd for 1·10H<sub>2</sub>O: C 42.45, H 3.33, N 2.90; found: C 42.59, H 3.46, N 2.62. Selected IR data (ATR):  $\nu$  = 2926 (w), 1586 (s), 1536 (vs), 1460 (m), 1439 (s), 1404 (vs), 1349 (m), 1178 (m), 1149 (m), 1115 (m), 1034 (m), 896 (m), 848 (m), 819 (m), 791 (s), 739 (m), 674 (m), 618 (mb), 430 (m).

**(H<sub>3</sub>O)[Ni<sub>18</sub>(OH)<sub>7</sub>(O<sub>2</sub>CBu<sup>t</sup>)<sub>8</sub>(sacb)<sub>10</sub>(MeCN)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (2):** This complex was prepared in the same manner as complex 1 but using melted Bu<sup>t</sup>CO<sub>2</sub>H (46  $\mu$ L, 0.4 mmol) in place of glacial MeCO<sub>2</sub>H. After 24 days, X-ray quality green plate-like crystals of 2·11MeCN were collected by filtration, washed with cold MeCN (2 x 2 mL) and dried under vacuum. The yield was 28 %. Elemental analysis (%) calcd for 2·2MeCN: C 44.32, H 3.53, N 4.31; found: C 44.45, H 3.66, N 4.18. Selected IR data (ATR):  $\nu$  = 2957 (m), 2946 (mb), 1630 (s), 1596 (vs), 1479 (m), 1459 (m), 1440 (s), 1410 (vs), 1359 (s), 1223 (m), 1176 (m), 1150 (m), 1118 (m), 976 (m), 924 (m), 850 (m), 819 (m), 785 (s), 611 (mb), 530 (m), 459 (m).

**Single-crystal X-ray diffraction studies.** Crystals of complexes 1 and 2 were selected and mounted onto a cryoloop using inert oil.<sup>[S1]</sup> Diffraction data were collected at 150.0(2) K on a Bruker X8 Kappa APEX II Charge-Coupled Device (CCD) area-detector diffractometer controlled by the APEX2 software package<sup>[S2]</sup> (Mo K $\alpha$  graphite-monochromated radiation,  $\lambda$  = 0.71073 Å), and equipped with an Oxford Cryosystems Series 700 cryostream monitored remotely with the software interface Cryopad.<sup>[S3]</sup> Images were processed with the software SAINT,<sup>[S4]</sup> and absorption effects corrected with the multi-scan method implemented in SADABS.<sup>[S5]</sup> The structures have been solved by direct methods employed in SHELXS-97,<sup>[S6,S7]</sup> allowing the immediate location of the metals. The other non-Hydrogen atoms of the complexes were located from difference Fourier maps calculated by successive full-matrix least-squares refinement cycles on  $F^2$  using SHELXL-2013,<sup>[S7,S8]</sup> and effectively refined with anisotropic displacement parameters. For both complexes 1 and 2, the lattice groups were disordered and could not be modeled properly; thus the program SQUEEZE,<sup>[S9]</sup> a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. Information concerning crystallographic data collection and structure refinement details is summarized in Table S1. Crystallographic data (excluding structure factors) for the structures of complexes 1 and 2 have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication numbers: CCDC-1023378 (1), -1023379 (2). Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 2EZ, UK; FAX: (+44) 1223 336033, or online via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk).

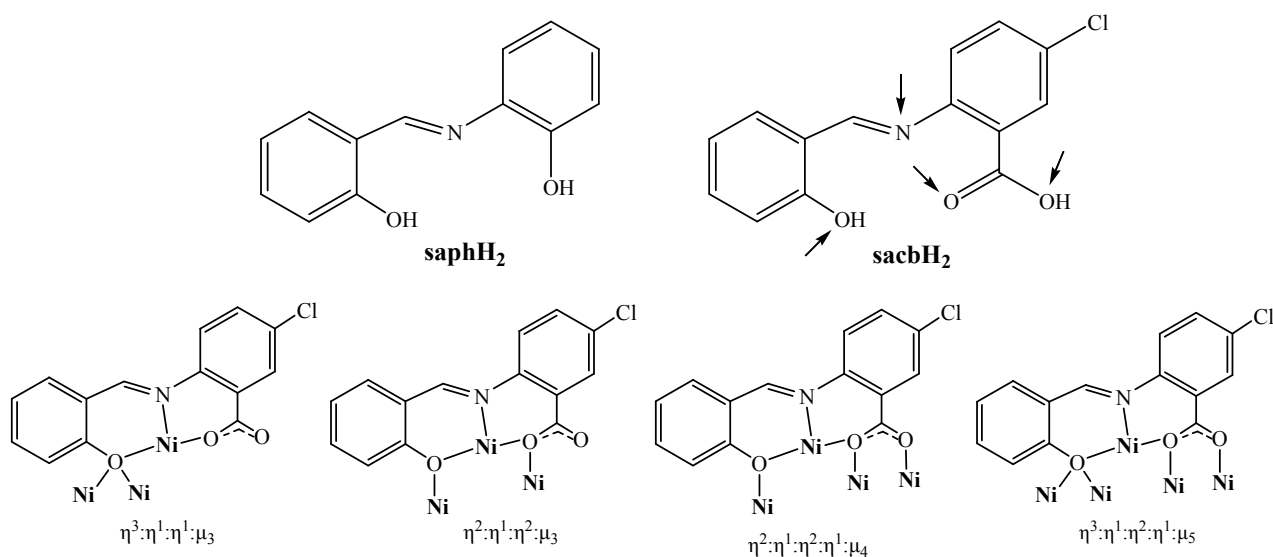
**Table S1. Crystallographic Data for Complexes 1·9MeCN·xMeOH·yH<sub>2</sub>O and 2·11MeCN**

Parameter	1·9MeCN·xMeOH·yH <sub>2</sub> O	2·11MeCN
Formula	C <sub>275</sub> H <sub>232</sub> N <sub>24</sub> Ni <sub>26</sub> O <sub>123</sub> Cl <sub>14</sub>	C <sub>210</sub> H <sub>211</sub> N <sub>25</sub> Ni <sub>18</sub> O <sub>64</sub> Cl <sub>12</sub>
Formula weight / g mol <sup>-1</sup>	7374.48	5591.22
Crystal type	Yellow-green plates	Green plates
Crystal size / mm <sup>3</sup>	0.21 × 0.21 × 0.09	0.28 × 0.08 × 0.05
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
$a$ / Å	25.959(1)	22.442(2)
$b$ / Å	45.854(2)	21.074(2)

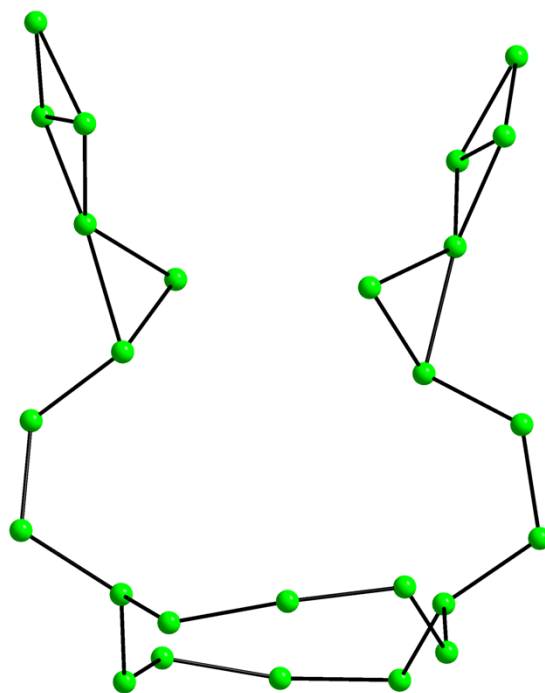
$c / \text{\AA}$	32.608(2)	52.993(5)
$\beta / ^\circ$	94.904(3)	90.197(4)
Volume / $\text{\AA}^3$	38671(3)	25063(4)
$Z$	4	4
$D_c / \text{g cm}^{-3}$	1.267	1.482
$\mu / \text{mm}^{-1}$	1.398	1.524
$\theta$ range	2.42 - 26.37	1.76 - 25.00
Index ranges	$-30 \leq h \leq 30$ $-54 \leq k \leq 54$ $-38 \leq l \leq 38$	$-26 \leq h \leq 26$ $-24 \leq k \leq 25$ $-62 \leq l \leq 62$
Reflections collected	371801	179512
Independent reflections	68057 ( $R_{\text{int}} = 0.0923$ )	21874 ( $R_{\text{int}} = 0.0832$ )
Final $R$ indices [ $I > 2\sigma(I)$ ] <sup>a,b</sup>	$R1 = 0.0838$ $wR2 = 0.1875$	$R1 = 0.0917$ $wR2 = 0.2066$
Final $R$ indices (all data)	$R1 = 0.1328$ $wR2 = 0.2176$	$R1 = 0.1230$ $wR2 = 0.2201$
$(\Delta\rho)_{\text{max,min}} / \text{e \AA}^{-3}$	2.564 and -1.994	1.143 and -0.925

<sup>a</sup>  $R1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$ .

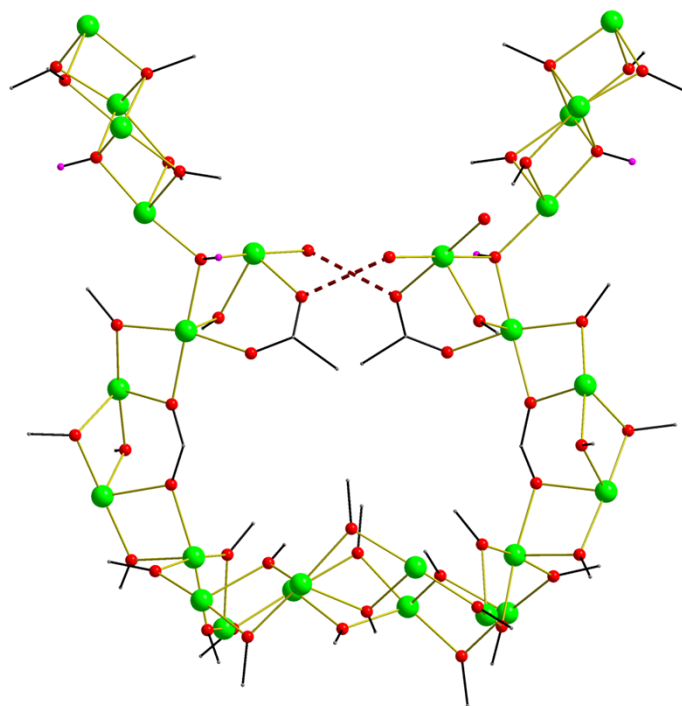
<sup>b</sup>  $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$ ,  $w = 1/[\sigma^2(F_o^2) + [(ap)^2 + bp]]$ , where  $p = [\max(F_o^2, 0) + 2F_c^2]/3$ .



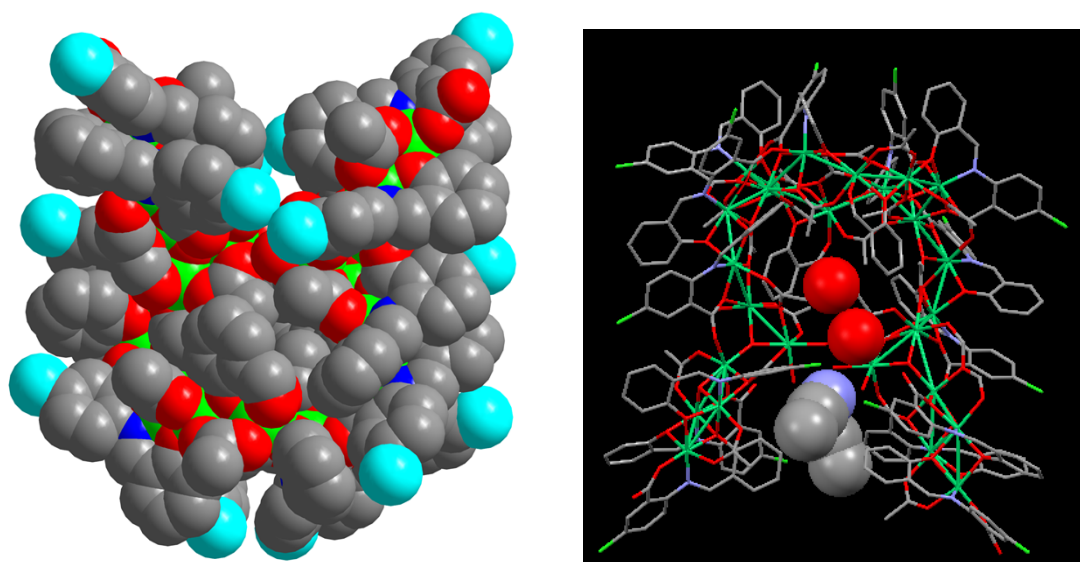
**Scheme S1.** (top) Structural formulas and abbreviations of the ligands discussed in the text; (bottom) their crystallographically established coordination modes in complexes **1** and **2**.



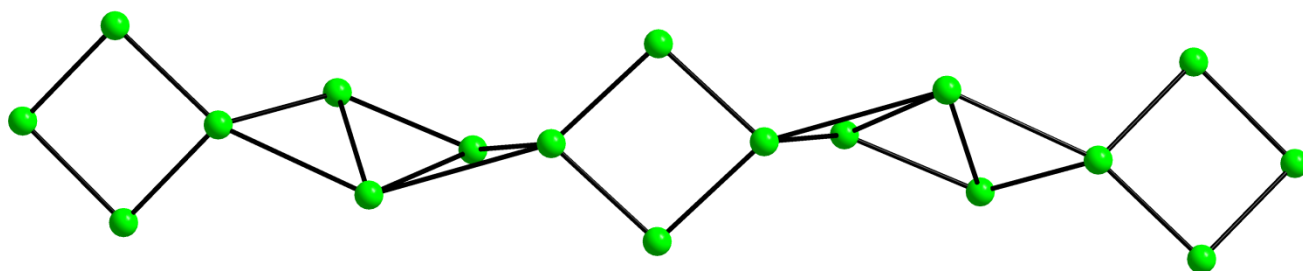
**Fig. S1.** The  $\text{Ni}_{26}$  ‘bunny-rabbit’-face topology with the black lines indicating the  $\text{Ni}^{2+}\dots\text{Ni}^{2+}$  vectors.



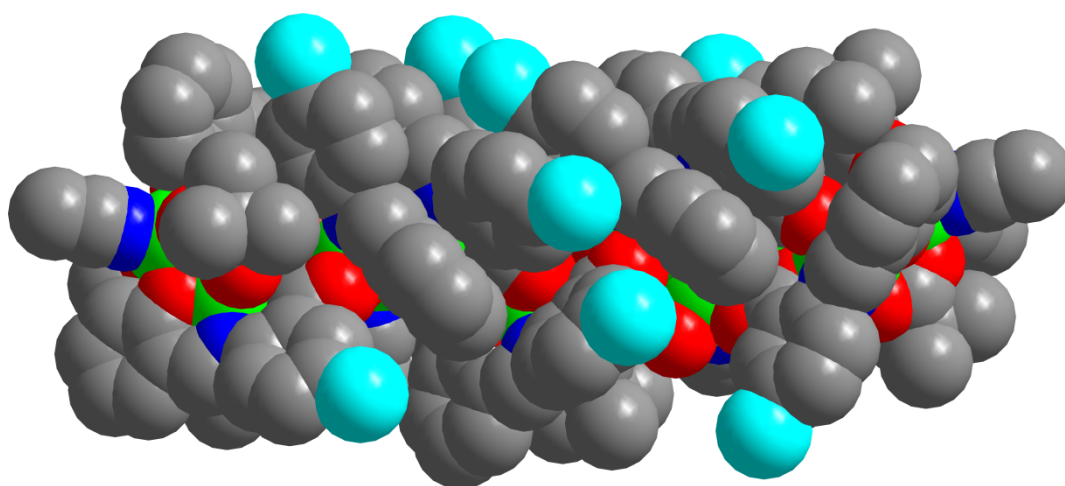
**Fig. S2.** The  $\text{Ni}_{26}$  core emphasizing at the two strong intramolecular H-bonding interactions (brown dashed lines), which serve to “close out” the  $\text{Ni}_{18}$  “head”.

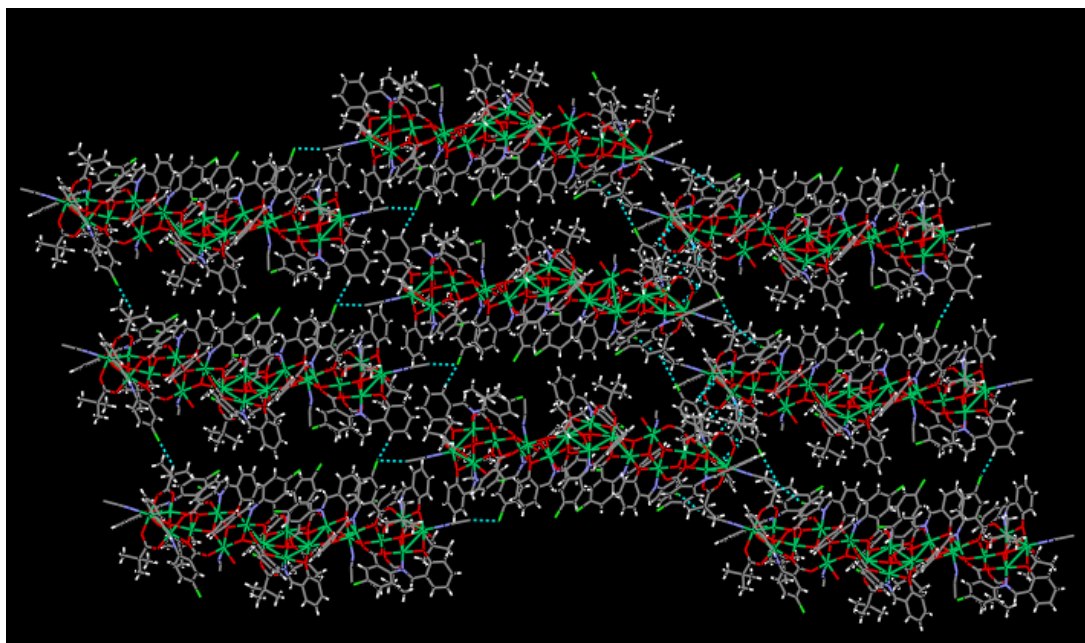


**Fig. S3.** (left) Space-filling representation of the  $\text{Ni}_{26}$  cluster anion. (right) The solvent-accessible area within the voids of  $\text{Ni}_{26}$ . A close examination of the crystal packing of **1** reveals that there are no significant intermolecular interactions between neighboring  $\text{Ni}_{26}$  anions; the shortest  $\text{Ni}\cdots\text{Ni}$  distance between neighboring units is  $\sim 7.23$  Å, with nearest neighbours oriented perpendicular to one another. Color scheme:  $\text{Ni}^{\text{II}}$  green, O red, N blue, C dark gray, Cl cyan.

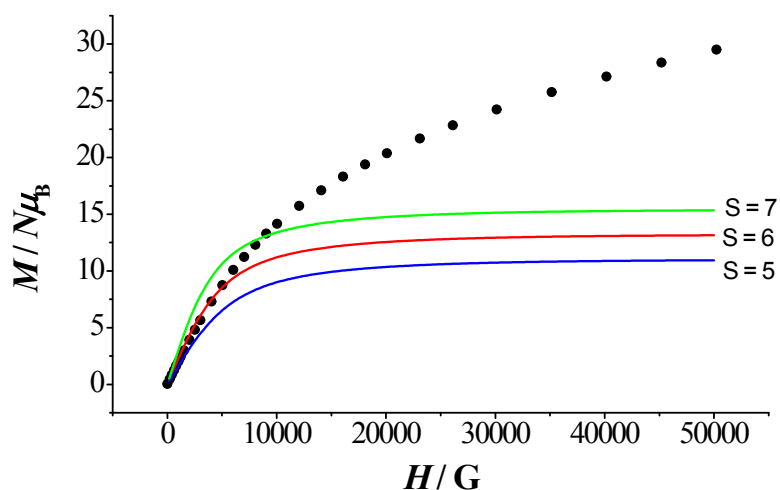


**Fig. S4.** The  $\text{Ni}_{18}$  'molecular-chain'-like topology comprising adjacent  $\text{Ni}_4$  squares and  $\text{Ni}_3$  triangles; the black lines indicate the  $\text{Ni}^{2+}\cdots\text{Ni}^{2+}$  vectors.

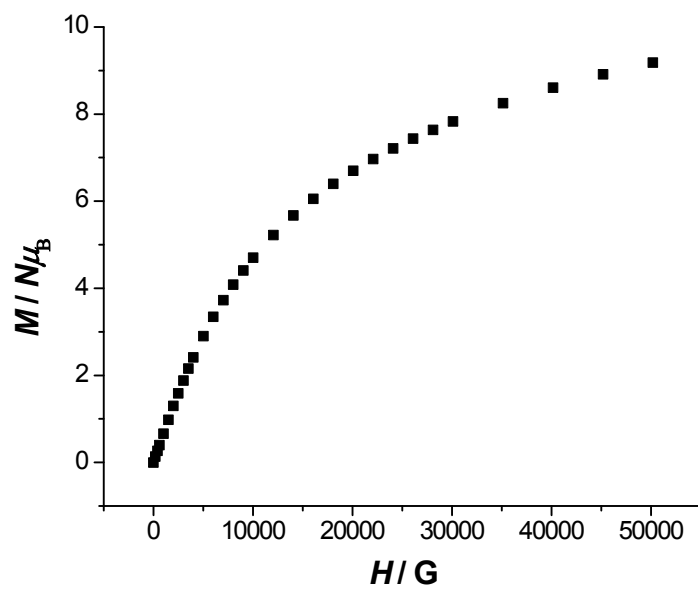




**Fig. S5.** (top) Space-filling representation of the nanotubular  $\text{Ni}_{18}$  cluster cation. Color scheme:  $\text{Ni}^{\text{II}}$  green, O red, N blue, C dark gray, Cl cyan. (bottom) The puckering of the  $\text{Ni}_{18}$  clusters in the crystal resulted from the presence of weak intermolecular C-H...Cl contacts.

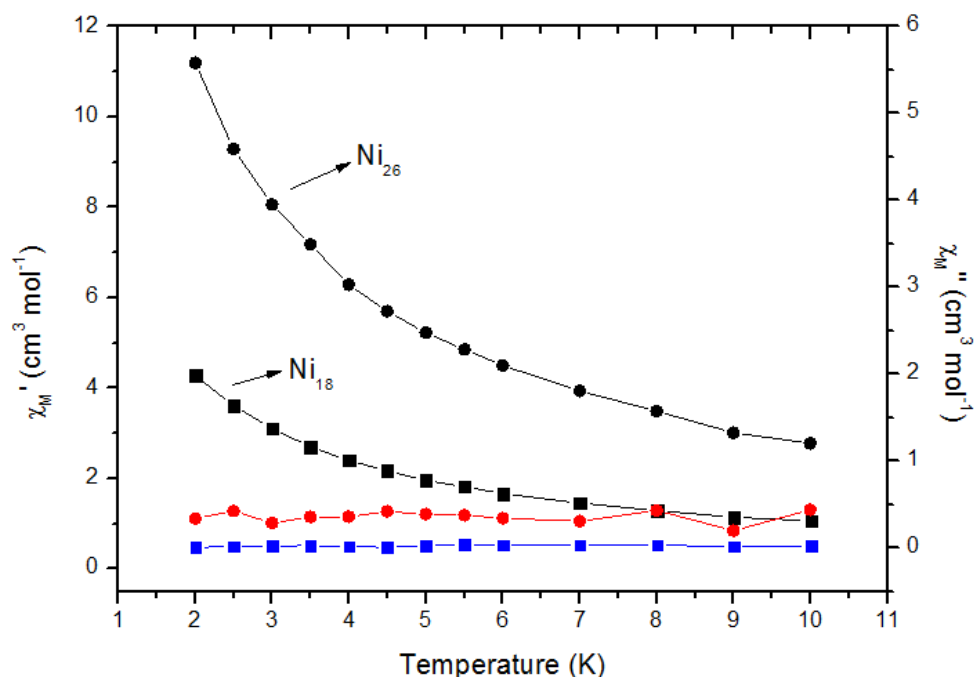


**Fig. S6.** Plot of magnetization ( $M$ ) versus field ( $H$ ) for complex  $1 \cdot 10\text{H}_2\text{O}$  at 2 K. The solid, colored lines are the different fits of the data to the corresponding Brillouin functions for  $S = 5, 6$  and  $7$  with  $g = 2.2$ .



**Fig. S7.** Plot of magnetization ( $M$ ) versus field ( $H$ ) for complex  $2 \cdot 2\text{MeCN}$  at 2 K.

**Fig. S8.** The in-phase (as  $\chi_M' T$ ) vs  $T$  ac susceptibility signals for  $1 \cdot 10\text{H}_2\text{O}$  (●) and  $2 \cdot 2\text{MeCN}$  (■), under a 4 G oscillating field operating at a frequency of 1000 Hz.



**Fig. S9.** The in-phase ( $\chi_M'$ , top) and out-of-phase ( $\chi_M''$ , bottom) vs  $T$  ac susceptibility signals for **1**·10H<sub>2</sub>O (●) and **2**·2MeCN (■), under a 4 G oscillating field operating at a frequency of 1000 Hz.

### Additional magnetic discussion:

In cases such as **1** and **2**, as well as for the majority of polynuclear 3d-metal clusters with a non-zero ground state, the resultant molecular  $S$  value is a consequence of the many competing (predominantly) antiferromagnetic interactions that prevent (frustrate) perfectly antiparallel spin alignments. This is particularly true when triangular subunits are present, since an antiferromagnetically-coupled triangle cannot contain spins that are all aligned antiparallel with both neighbours. The ground state then becomes extremely difficult to predict from a structural examination and simple spin-up/spin-down considerations. In fact, the net molecular  $S$  is dependent on the precise topology of the  $M_x$  ( $M$  = metal) framework and very sensitive to the relative strengths of the competing interactions. Crucial to the latter in Ni<sup>II</sup> chemistry is the fact that Ni-OR-Ni interactions within triangular units are often of similar magnitude, either weakly antiferromagnetic or, occasionally, weakly ferromagnetic.<sup>[S10]</sup>

### References:

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