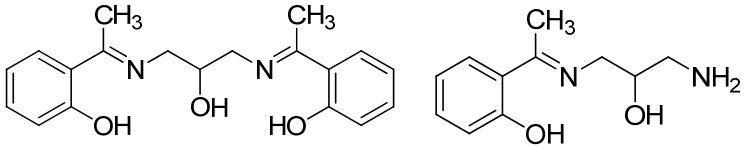
Supporting Information.

Experimental Section

Materials. The Schiff base ligand (H_3L_1) was synthesized by the reported method [a]. All other reagents and solvents used in this study are commercially available and were used without further purification. All manipulations were performed under aerobic conditions.



H_3L_1 H_2L_2

Scheme S1. The structure of H_3L_1 and H_2L_2.

Reference:

[a] S. Basak, S. Sen, G. Rosair, C. Desplanches, E. Garribba and S. Mirtra, *Aust. J. Chem.,* 2009, 62, 366.

Synthesis of Compounds.

$[Ni_4(L_1)_2(MeO)_2(MeOH)_2]$ (1) and $[Ni_6(L_1)_2(L_2)_2(OAc)_2]\cdot 2DMF$ (2)

H_3L[1](0.1903 g, 0.58 mmol) and three-ethyl amine (3 ml) were dissolved in 50ml DMF. The solution was refluxed for 30 min under stirring. Then, $Ni(OAc)_2\cdot 4H_2O$ (0.2489 g, 1 mmol) was added. This mixture was refluxed for 4 h under stirring. The green crystals of **1** were grown by slow diffusion of methanol into DMF solution. The red crystals of **2** were obtained from the DMF solution by slow evaporation at room temperature after one month. Anal. Calcd for $C_{42}H_{52}N_4Ni_4O_{10}$ (**1**): C, 49.86; H, 5.19; N, 5.69. Found: C, 50.06; H, 5.19; N, 5.56. IR (KBr pellet, cm^{-1}): 3441(s), 1601(m), 1260 (w), 1056 (m). Anal. Calcd for $C_{73}H_{93}N_{11}Ni_6O_{17}$ (**2**): C, 50.21; H, 5.28; N, 8.89. Found: C, 50.14; H, 5.36; N, 8.81. IR (KBr pellet, cm^{-1}): 3438(s), 1600(s), 1260 (w), 1048 (m).

X-ray Crystallography:

Suitable single crystals were selected for indexing and intensity data were measured on a Siemens Smart CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073Å) at 298 K. The raw data frames were intergrated into SHELX-format reflection files and corrected using SAINT program. Absorption corrections based on multiscan were obtained by the SADABS program. The

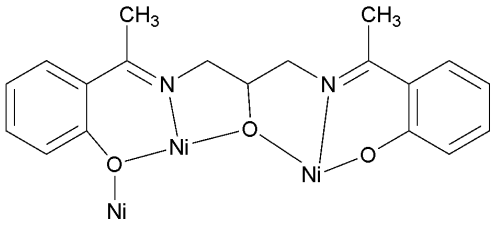
structures were solved with direct methods and refined with full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs, respectively. The coordinates of the non-hydrogen atoms were refined anisotropically, and the positions of the H-atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. Selected bond lengths and angles are listed in Table S1. CCDC 795063 (**1**) and 795064 (**2**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. In **2**, a half lattice DMF molecule is refined isotropically with a site-of-occupancy of 0.5.

Table S1. Selected Bond Lengths (Å) and Angles (deg) for **1** and **2**.

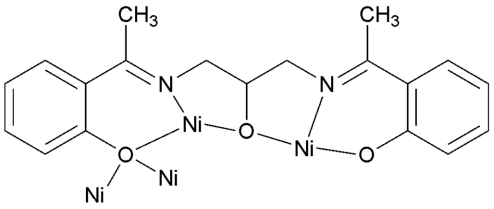
		1	
Ni(1)-O(2)	2.010(3)	Ni(1)-N(1)	2.011(4)
Ni(1)-O(1)	2.016(3)	Ni(1)-O(4)#1	2.041(3)
Ni(1)-O(4)	2.084(3)	Ni(1)-O(5)	2.145(4)
Ni(2)-O(3)	1.965(4)	Ni(2)-N(2)	1.990(5)
Ni(2)-O(4)#1	2.006(3)	Ni(2)-O(1)#1	2.010(3)
Ni(2)-O(2)	2.023(3)		
Ni(2)#1-O(1)-Ni(1)	97.05(14)	Ni(1)-O(2)-Ni(2)	96.05(14)
Ni(2)#1-O(4)-Ni(1)#1	95.64(13)	Ni(2)#1-O(4)-Ni(1)	95.00(13)
Ni(1)#1-O(4)-Ni(1)	97.46(13)		
		2	
Ni(1)-N(1)	2.028(6)	Ni(1)-O(6)	2.033(6)
Ni(1)-O(2)	2.069(5)	Ni(1)-O(4)	2.076(5)
Ni(1)-O(1)	2.079(6)	Ni(1)-O(2)#2	2.189(5)
Ni(2)-O(5)	1.970(6)	Ni(2)-N(4)	2.017(6)
Ni(2)-O(7)	2.070(6)	Ni(2)-O(4)	2.101(5)
Ni(2)-O(4)#2	2.173(6)	Ni(2)-O(2)	2.183(5)
Ni(3)-O(3)	1.822(6)	Ni(3)-N(2)	1.861(7)
Ni(3)-O(1)	1.861(6)	Ni(3)-N(3)	1.933(7)
Ni(3)-O(1)-Ni(1)	114.3(3)	Ni(1)-O(2)-Ni(2)	88.67(18)
Ni(1)-O(2)-Ni(1)#2	103.1(2)	Ni(2)-O(2)-Ni(1)#2	97.65(19)
Ni(1)-O(4)-Ni(2)	90.75(19)	Ni(1)-O(4)-Ni(2)#2	101.5(2)
Ni(2)-O(4)-Ni(2)#2	100.7(2)		

Symmetry codes: : #1, -x,-y+1,-z ; #2, -x+1,y,-z+1/2.

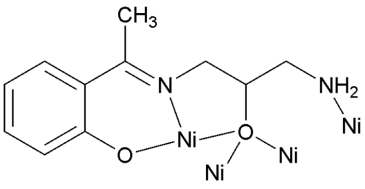
Scheme S2. Coordination modes of the ligands in the compounds.



$\eta^2:\eta^1:\eta^2:\eta^1:\eta^1:\mu_3$



$\eta^3:\eta^1:\eta^2:\eta^1:\eta^1:\mu_4$



$\eta^1:\eta^1:\eta^3:\eta^1\text{-}\mu_4$

Figure S1. The 2D supramolecular network of **1** through C-H···O interactions.

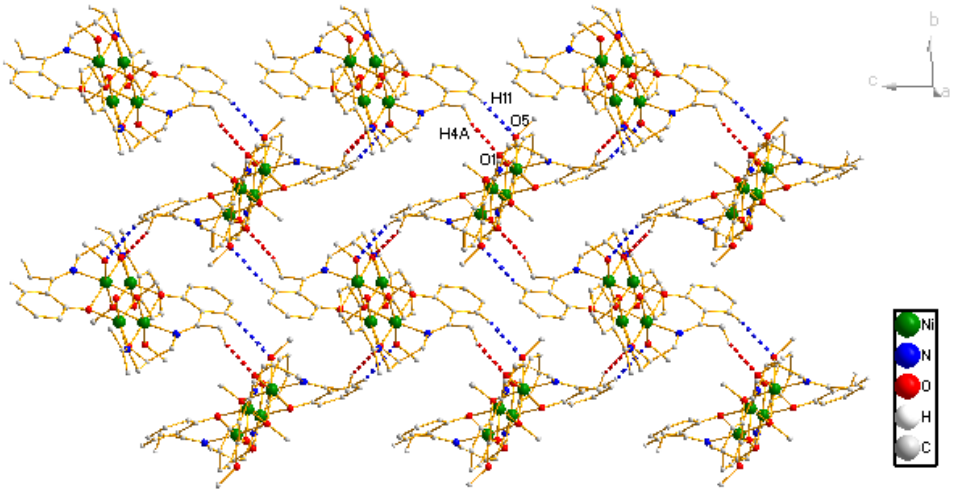
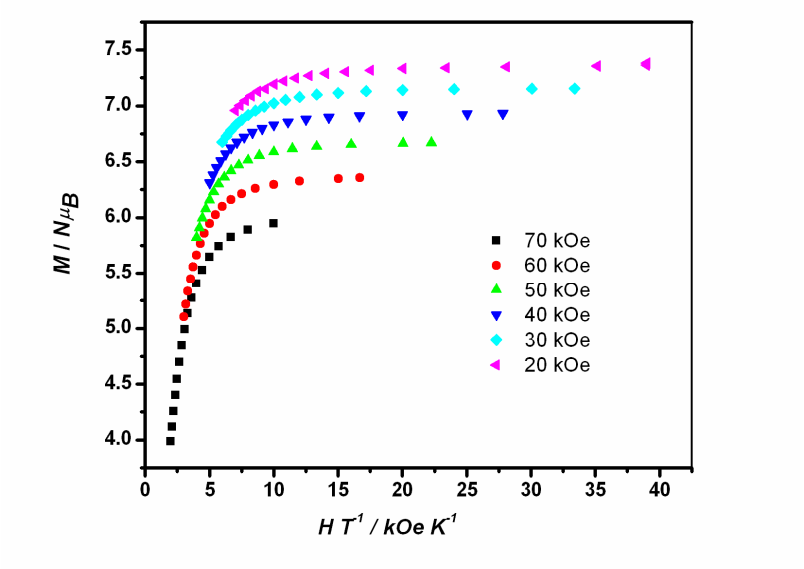
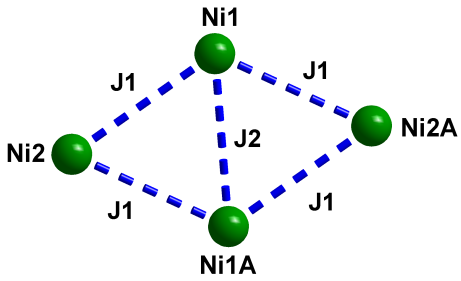


Figure S2. Plot of the reduced magnetization ($M/N\mu_B$) vs H/T of **1** at the indicated applied fields.



Fitting of the magnetic properties of 1.



$$\chi_{\mathrm{M}}=\frac{Ng^2\beta^2}{3kT}\times\frac{\begin{array}{c}(6e^{-17x}+24e^{-8x}+54e^{7x}+96e^{28x})+84e^{8b}+30e^{14b}+6e^{18b}+168e^{4a+4b}+60e^{4a+10b}+12e^{4a+14b}\\+60e^{6a+8b}+30e^{8a+6b}+6e^{8a+10b}+12e^{10a+8b}\end{array}}{\begin{array}{c}(e^{-20x}+2e^{-17x}+2e^{-8x}+2e^{7x}+2e^{28x})+7e^{8b}+5e^{14b}+3e^{18b}+e^{20b}+14e^{4a+4b}+10e^{4a+10b}+6e^{4a+14b}\\+10e^{6a+8b}+5e^{8a+6b}+3e^{8a+10b}+e^{8a+12b}+6e^{10a+8b}+e^{12a+8b}\end{array}}$$

where $a=-J_1/kT$, $b=-J_2/kT$ and $x=D/3kT$

Reference: A. Escuer, M. Font-Bardía, S. B. Kumar, X. Solans. R. Vicente, Polyhedron 1999, 18, 909.