

## Supporting Information

### **Direct C–N Coupling in an in Situ Ligand Transformation and the Self-Assembly of a Tetrametallic [Ni<sup>II</sup><sub>4</sub>] Staircase**

Aloke Kumar Ghosh,<sup>†</sup> Tufan Singha Mahapatra,<sup>†</sup> Rodolphe Clérac,<sup>‡,‡</sup> Corine Mathonière,<sup>§,⊗</sup>

Valerio Bertolasi,<sup>¥</sup> and Debashis Ray<sup>†,\*</sup>

<sup>†</sup> *Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India*

*Fax: (+91) 3222-82252; Tel: (+91) 3222-283324; E-mail: dray@chem.iitkgp.ernet.in*

<sup>‡</sup> *CNRS, CRPP, UPR 8641, F-33600 Pessac, France.*

<sup>‡</sup> *Univ. Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France.*

<sup>§</sup> *CNRS, ICMCB, UPR 9048, F-33600 Pessac, France.*

<sup>⊗</sup> *Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France.*

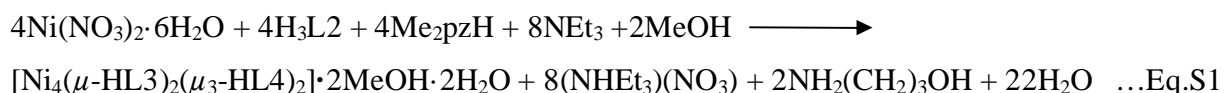
<sup>¥</sup> *Dipartimento di Scienze Chimiche e Farmaceutiche and Centro di Strutturistica Diffraattometrica, Università di Ferrara, via L. Borsari, 46, I44121 Ferrara, Italy.*

### **Experimental Section**

**Syntheses. H<sub>3</sub>L2.** To a MeOH solution (20 mL) of 2,6-diformyl-4-methylphenol (1.0 g, 6.1 mmol), 3-amino-1-propanol (0.91 g, 12.2 mmol) was added in air at room temperature (28 °C) and stirred for 2 hours and solvent was evaporated in air to get an orange colored semi-solid product after 12 hours. The obtained gummy product 2,6-bis-[(3-hydroxy-propylimino)-methyl]-4-methylphenol was washed copiously with water and hexane, and used for complex synthesis without further purification. Yield: 1.32g (78%).

**[Ni<sub>4</sub>(μ-HL3)<sub>2</sub>(μ-HL4)<sub>2</sub>]·2MeOH·2H<sub>2</sub>O (1·2MeOH·2H<sub>2</sub>O).** A MeOH solution (20 mL) of H<sub>3</sub>L2 (0.278 g, 1.00 mmol) and 3,5-dimethylpyrazole (Me<sub>2</sub>pzH) (0.96 g, 1.0 mmol) was stirred for *ca.* 40-45 minutes in air. Another MeOH solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.581 g, 2.0 mmol) was next added drop wise to previous one with stirring at room temperature. The resulting green solution

was stirred for *ca.* 10 min and a solution of NEt<sub>3</sub> (0.278 mL, 0.202 g, 2.0 mmol) was added drop wise to the reaction mixture and finally the whole mixture was stirred for another 2 hours. Finally the solvent of the reaction mixture was evaporated in air to give a green solid, which was isolated, washed with cold methanol and dried under *vacuo* over P<sub>4</sub>O<sub>10</sub>. Green crystals suitable for single crystal X-ray analysis were obtained from a saturated methanol solution after two weeks. Yield: 0.1163 g, 68%. Anal. Calcd. for C<sub>76</sub>H<sub>110</sub>Ni<sub>4</sub>N<sub>14</sub>O<sub>16</sub> (1710.62 g mol<sup>-1</sup>): C, 53.36; H, 6.48; N, 11.46. Found: C, 53.22; H, 6.32; N, 11.38. Selected FT-IR bands: (KBr, cm<sup>-1</sup>; s = strong, vs = very strong, m = medium, br = broad) 3396(br), 2921(s), 1635(s), 1559(s), 1465(vs), 1384(s), 1325(s), 1237(s), 1097(vs), 1051(s), 863(m), 816(m), 778(m), 603(m). Molar conductance,  $\Lambda_M$ : (MeOH solution) 6  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ . UV-vis spectra [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>): (MeOH solution) 665 (235), 371 (5122), 211 (17600).



**Materials and Physical Methods.** The chemicals used were obtained from the following sources: nickel nitrate hexahydrate from S.D. Fine Chem (India); 3-amino-1-propanol from Aldrich Chemical Co. Inc. 3,5-dimethylpyrazole and 2,6-diformyl-4-methylphenol (2-hydroxy-5-methyl-benzene-1,3-dicarbaldehyde) was prepared following a literature procedure.<sup>S1</sup> All other chemicals and solvents were reagent grade materials and were used as received without further purification. The elemental analyses (C, H, N) were performed with a Perkin-Elmer model 240 C elemental analyzer. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer RX1 spectrometer. Solution electrical conductivity measurements and electronic spectra were carried out using a Unitech type U131C digital conductivity meter with a solute concentration of about 10<sup>-3</sup> M and a Shimadzu UV 3100 UV-vis-NIR spectrophotometer, respectively. The magnetic susceptibility measurements were obtained with the use of a Quantum Design MPMS-XL magnetometer. This magnetometer works between 1.8 and 350 K for dc applied field of 1000 Oe. Measurements were performed on a 16.63 mg polycrystalline sample of **1** placed in small polyethylene bags (3 × 0.5 × 0.02 cm). Experimental data were corrected for sample holder and diamagnetic contributions of the samples using experimentally determined values.

**Crystal Data Collection and Refinement for 1·2MeOH·2H<sub>2</sub>O.** The single crystal diffraction data of the complex 1·2MeOH·2H<sub>2</sub>O were collected on a Bruker APEX-II CCD X-ray diffractometer using a graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and  $\omega$ -scan method at 293 K. Information concerning X-ray data collection and structure refinement of the compound are summarized in **Table S1**. For complex 1·2MeOH·2H<sub>2</sub>O, a total of 7029 reflections were recorded with Miller indices  $h_{\min} = -14$ ,  $h_{\max} = 14$ ;  $k_{\min} = -16$ ,  $k_{\max} = 16$ ; and  $l_{\min} = -29$ ,  $l_{\max} = 29$ . In the final cycles of full-matrix least squares on  $F^2$ , all non-hydrogen atoms were assigned anisotropically except some C and O atoms, belonging to alcohol arms and CH<sub>3</sub>OH solvent molecules, which were found disordered and refined isotropically over two positions. The structure was solved using the SIR97<sup>S2</sup> program system and refined using SHELX-97 program<sup>S3</sup>. CCDC 869971 contain the supplementary crystallographic data for 1·2MeOH·2H<sub>2</sub>O. These data can be obtained free of charge [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax, +44-1223/336-033; e-mail, [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

**Table S1.** Crystallographic data for **1·2MeOH·2H<sub>2</sub>O**

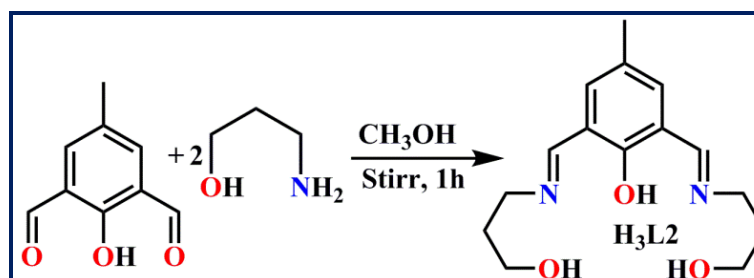
compound	<b>1·2MeOH·2H<sub>2</sub>O</b>
formula	<b>C<sub>74</sub>H<sub>98</sub>Ni<sub>4</sub>N<sub>14</sub>O<sub>12</sub>·2(CH<sub>4</sub>O)·2(H<sub>2</sub>O)</b>
FW (g.mol <sup>-1</sup> )	1710.62
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
crystal system	Monoclinic
<i>a</i> /Å	12.342(3)
<i>b</i> /Å	13.667(3)
<i>c</i> /Å	24.784(5)
$\alpha$ /°	90.0
$\beta$ /°	90.776(6)
$\gamma$ /°	90.0
<i>V</i> /Å <sup>3</sup>	4180.1(15)
<i>T</i> /K	293
<i>Z</i>	2
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.359
<i>F</i> (000)	1808
crystal size/mm	0.27 x 0.22x 0.19
$\mu$ (Mo-K $\alpha$ )/cm <sup>-1</sup>	9.58
measured Refl.ns	33554
unique ref.ns	7029
<i>R</i> <sub>int</sub>	0.2014
obs. Reflns.[ <i>I</i> ≥ 2σ( <i>I</i> )]	3686
$\theta_{\min}$ - $\theta_{\max}$ /°	1.70 -25.00
<i>hkl</i> ranges	-14, 14;-16, 16; -29,29
<i>R</i> ( <i>F</i> <sup>2</sup> ) (Obs.Reflns.)	0.0870
<i>wR</i> ( <i>F</i> <sup>2</sup> ) (All Reflns.)	0.2929
no. variables	500
goodness of fit	0.985
$\Delta\rho_{\max}$ ; $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.816; -0.677

$$R_1 = \Sigma (|F_o| - |F_c|) / \Sigma |F_o|; wR_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w(F_o)^2]^{1/2}; w = 0.75/(\sigma^2(F_o) + 0.0010F_o^2)$$

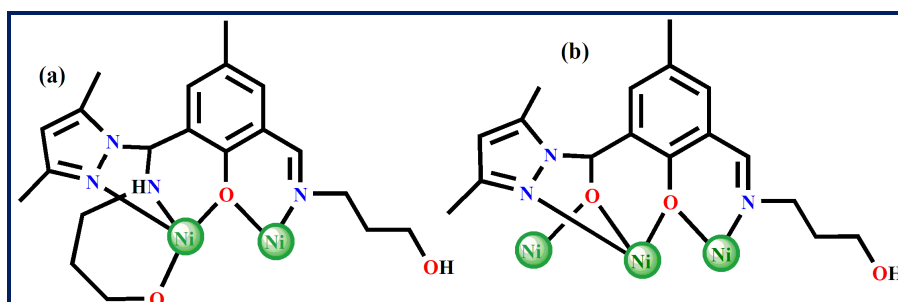
**Table S2.** Selected inter-atomic distances (Å) and angles (°) for **1**·2MeOH·2H<sub>2</sub>O

Distances			
Ni(1)-O(1)	2.040(5)	Ni(2)-N(3)	2.042(7)
Ni(1)-N(5)	2.054(7)	Ni(2)-O(4)	2.047(5)
Ni(1)-N(1)	2.068(7)	Ni(2)-N(4)	2.048(6)
Ni(1)-O(6)	2.075(6)	Ni(2)-O(3)	2.076(5)
Ni(1)-O(4)	2.094(5)	Ni(2)-O(1)	2.117(5)
Ni(1)-N(7)	2.136(6)	Ni(2)-O(3)*	2.153(5)
Angles			
O(1)-Ni(1)-N(5)	105.8(2)	N(3)-Ni(2)-O(4)	102.7(2)
O(1)-Ni(1)-N(1)	89.9(2)	N(3)-Ni(2)-N(4)	91.1(3)
N(5)-Ni(1)-N(1)	96.8(3)	O(4)-Ni(2)-N(4)	91.7(2)
O(1)-Ni(1)-O(6)	83.6(2)	N(3)-Ni(2)-O(3)	80.2(2)
N(5)-Ni(1)-O(6)	167.4(2)	O(4)-Ni(2)-O(3)	164.2(2)
N(1)-Ni(1)-O(6)	91.5(3)	N(4)-Ni(2)-O(3)	103.8(2)
O(1)-Ni(1)-O(4)	77.4(2)	N(3)-Ni(2)-O(1)	84.8(2)
N(5)-Ni(1)-O(4)	86.1(2)	O(4)-Ni(2)-O(1)	76.7(2)
N(1)-Ni(1)-O(4)	167.3(2)	N(4)-Ni(2)-O(1)	166.6(2)
O(6)-Ni(1)-O(4)	87.9(2)	O(3)-Ni(2)-O(1)	88.2(2)
O(1)-Ni(1)-N(7)	168.4(2)	N(3)-Ni(2)-O(3)*	159.3(2)
N(5)-Ni(1)-N(7)	77.4(3)	O(4)-Ni(2)-O(3)*	94.2(2)
N(1)-Ni(1)-N(7)	100.9(3)	N(4)-Ni(2)-O(3)*	100.3(2)
O(6)-Ni(1)-N(7)	91.8(2)	O(3)-Ni(2)-O(3)*	80.3(2)
O(4)-Ni(1)-N(7)	91.8(2)	O(1)-Ni(2)-O(3)*	87.6(2)
*:-x, -y, -z;			

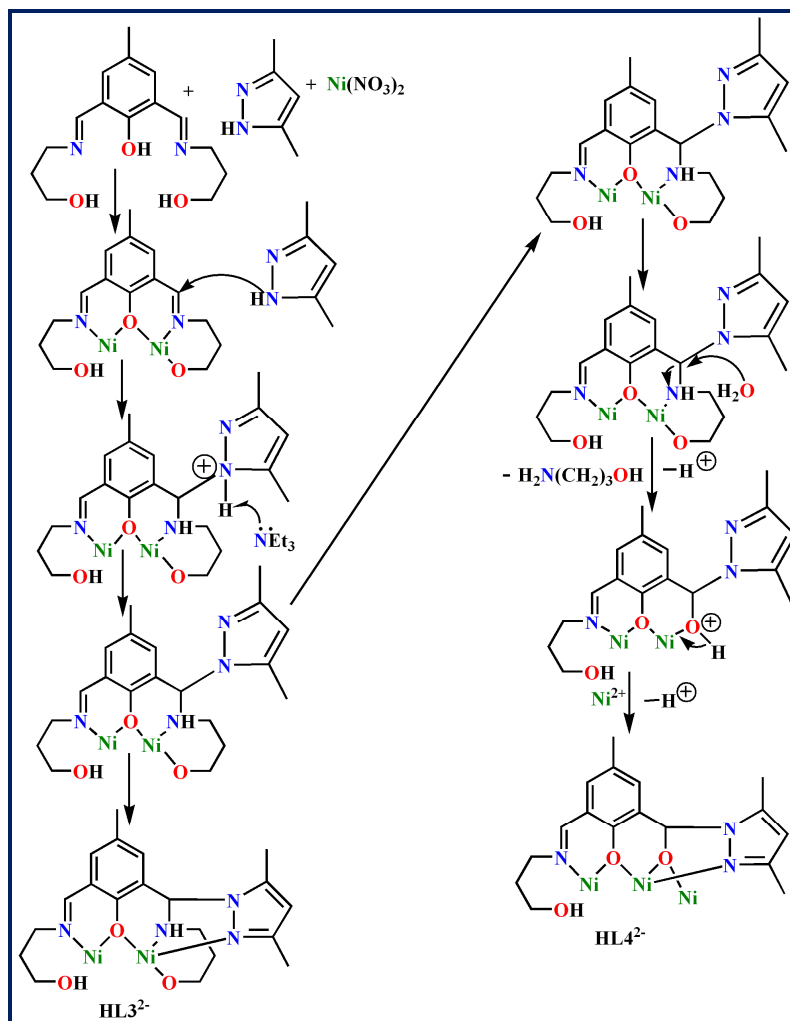
**Scheme S1.** Synthesis of H<sub>3</sub>L2



**Scheme S2.** In situ Generated Ligands HL3<sup>2-</sup> (a) and HL4<sup>2-</sup> (b) and their Coordination Modes.

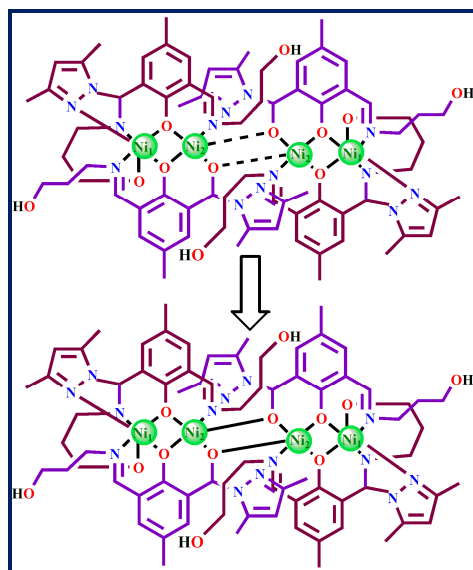


**Scheme S3.** Rationalization of the formation of nickel(II) bound ligand anions HL3<sup>2-</sup> and HL4<sup>2-</sup> through C–N coupling in complex **1**

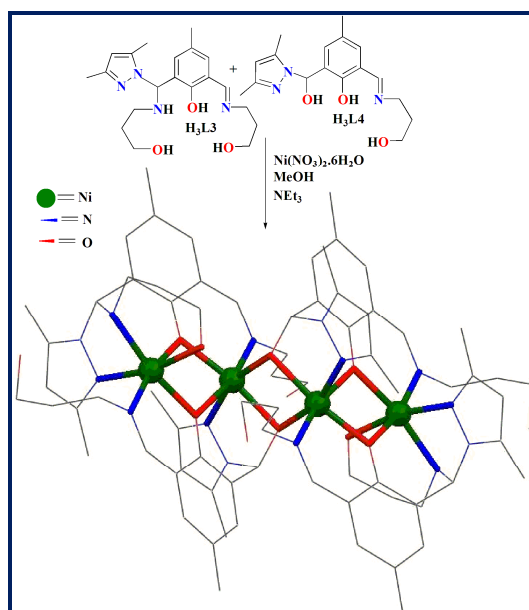


In methanolic  $NEt_3$  medium the nickel(II) bound pro-ligand  $HL2^{2-}$  initiates a nucleophilic attack of 3,5-dimethylpyrazolate anion on one imine carbon of one ligand arm to generate an intermediate for  $HL3^{2-}$  and  $HL4^{2-}$ . This results in formation of a new  $C_{imine}-N_{pz}$  bond between imine C of ligand and imidazolate N favoring new coordination of second pyrazole N to  $Ni(II)$  in  $HL3^{2-}$ . In the second step, the  $Ni^{II}$  bound  $H_2L3^{2-}$  species with loosely bound propanolate arm undergoes hydrolysis in dilute  $NEt_3$  medium leading to the transformation of  $Ni^{II}$  bound  $H_2L3^{2-}$  fragment to  $Ni^{II}$  bound  $H_2L4^{2-}$  species.

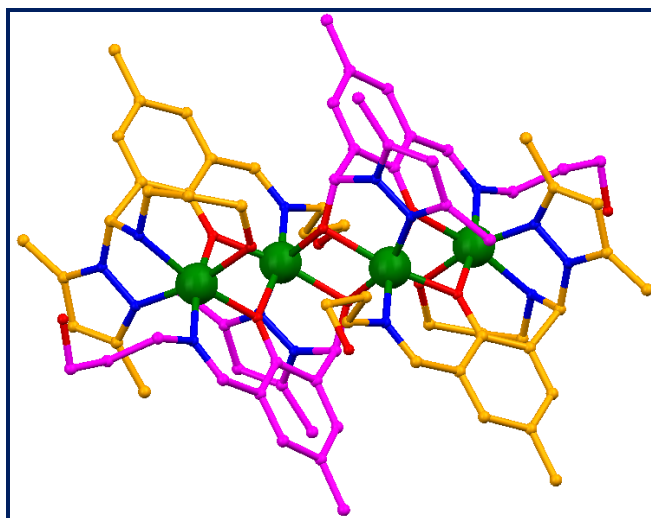
**Scheme S4.** Self-aggregation of dimetallic precursors *via* ligand modification



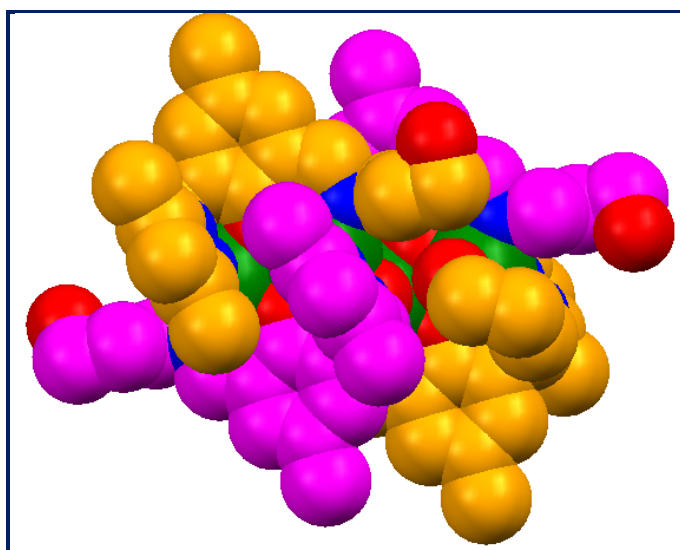
**Scheme S5.** Hitherto unknown in Situ generated ligands for the  $\{\text{Ni}_4\}$  assembly



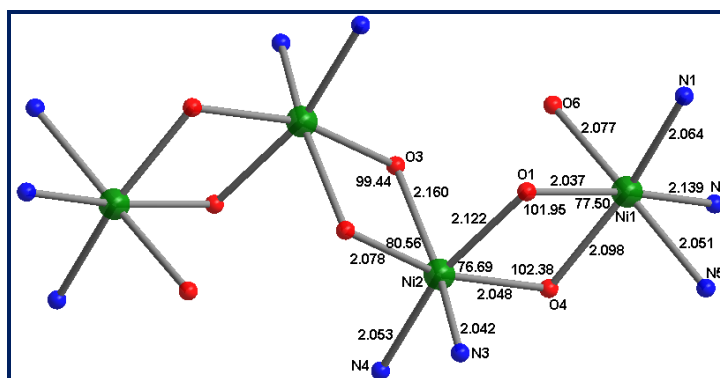




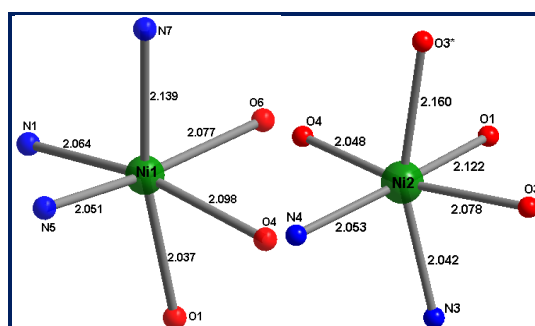
**Figure S1.** Ball-stick view along crystallographic *c* axis showing ligand skeletons in yellow and pink; red, O; blue, N; green, Ni.



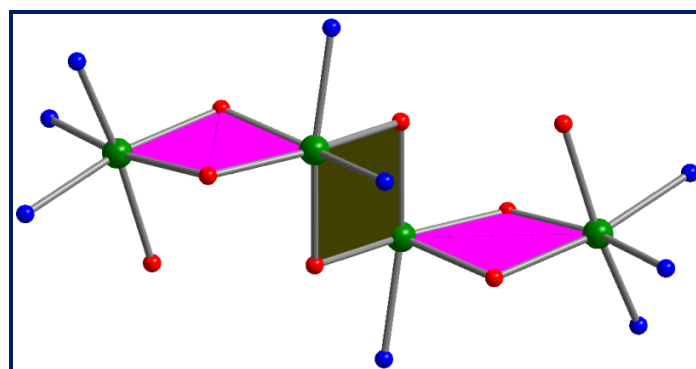
**Figure S2.** Space-fill representation along the crystallographic *c* axis. Carbon skeletons HL3<sup>2-</sup> and HL4<sup>2-</sup> are presented in yellow and pink; blue, N; red, O; green, Ni.



(a)

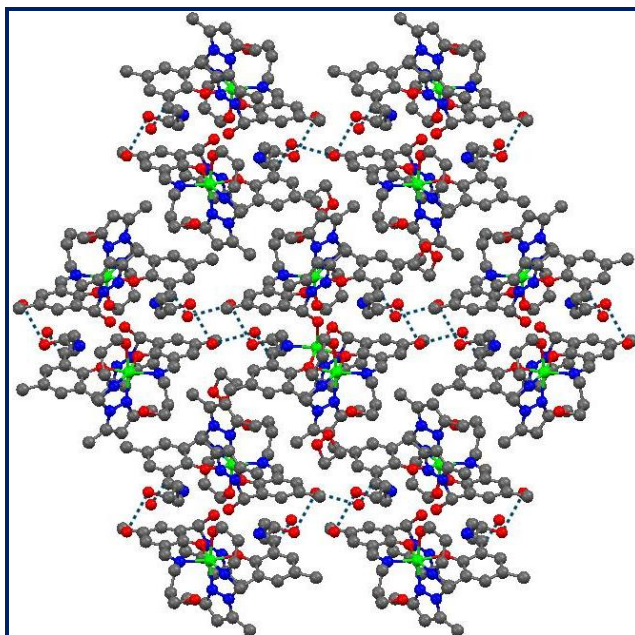


(b)

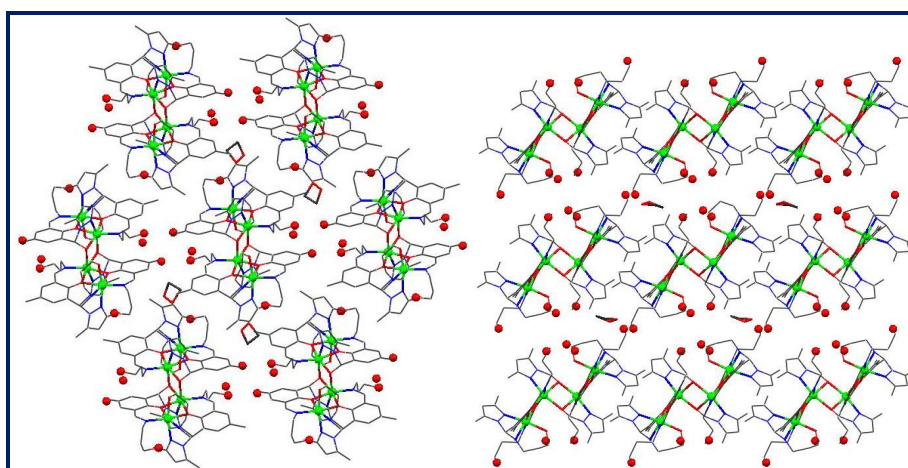


(c)

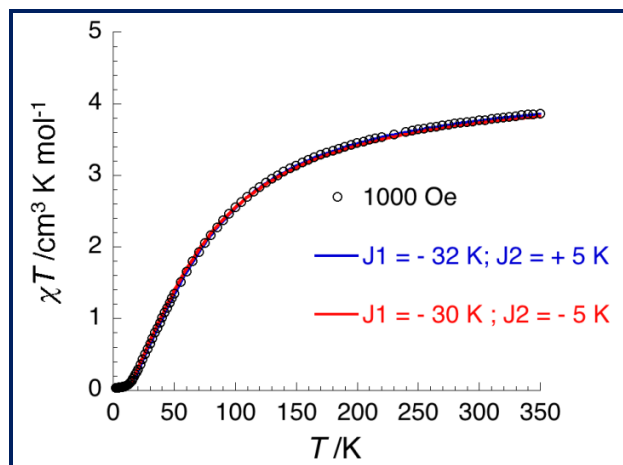
**Figure S3.** (a) Staircase like core structure of **1** with coordination sphere bond lengths and angles. (b) Different donor atoms around Ni1 and Ni2. (c) Staircase arrangements of three Ni<sub>2</sub>O<sub>2</sub> planes.



**Figure S4.** Ball-stick representations of **1** showing hydrogen-bonds (along *a* axis).



**Figure S5.** Packing along crystallographic *a* (left) and *b* (right) axes.



**Figure S6.** Thermal dependence of the  $\chi T$  product ( $\chi$  being the molar magnetic susceptibility defined by  $M/H$ ) measured at 1000 Oe for **1**. Dots: experimental points; Lines: Simulations using the MAGPACK<sup>S4</sup> program following Hamiltonian:  $\hat{H} = -2J_1(S_{\text{Ni1}} \cdot S_{\text{Ni2}} + S_{\text{Ni1}^*} \cdot S_{\text{Ni2}^*}) - 2J_2 S_{\text{Ni2}} \cdot S_{\text{Ni2}^*}$ . The  $g$  factor has been fixed as 2.09.

## References

- S1. (a) Furniss, B. S.; Hannaford, A. J.; Rogers, V.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*; 4th ed., Longman: London and New York, **1978**; Ch VI, p 881. (b) Gagne, R. R.; Spiro, C. L.; Smith, T. J.; Hamann, C. A.; Thies, W. R.; Shiemke, A. K. *J. Am. Chem. Soc.* **1981**, *103*, 4073-4081.
- S2. Altomare, A.; Burla, M.C.; Camalli, M.; Cascarano, G.L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A.G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.*, **1999**, *32*, 115-119.
- S3. Sheldrick, G. M. SHELX-97, *Program for Crystal Structure and Refinement*, University of Göttingen, Germany, **1997**.
- S4. Borrás-Almenar, J. J., Clemente-Juan J. M., Coronado, E., Tsukerblat, J. *Comput. Chem.*, **2001**, *22*, 985-991.