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### **ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)**

to

# Investigating the isolation and interconversion of two diastereoisomers in an octahedral $Ni^{II}A_2(\widehat{BC})_2$ system<sup>+</sup>

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# SYNTHETIC AND CHARACTERIZATION (EXPERIMENTAL AND THEORETICAL) DETAILS

#### Materials, physical and spectroscopic measurements

All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received. Elemental analyses (C, H, N) were performed by the University of Patras microanalytical service. FT-IR spectra (4000-400 cm<sup>-1</sup>) were recorded using a Perkin Elmer 16PC spectrometer with samples prepared as KBr pellets. Solid state (diffuse reflectance) electronic spectra (1100-250 nm) were recorded on a Perkin-Elmer 330 spectrometer using spectroscopic grade MgO as reference. Magnetic susceptibilities were measured at room temperature using the Faraday method and employing a Cahn-Ventron RM-2 balance standardized with {[HgCo(NCS)<sub>4</sub>]<sub>n</sub>; diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants. Conductivity measurements were carried out at 25 °C with a Metrohm-Herisau E-527 bridge and a cell of standard design.

#### **Computational details**

All calculations were performed using the Gaussian program suite.<sup>1</sup> The geometries of all stationary points were fully optimized, without symmetry constraints, employing the 1999 hybrid functional of Perdew, Burke and Ernzerhof<sup>2-8</sup> (denoted as PBE0) as implemented in the Gaussian09 program suite. For Ni, the relativistic effective core potentials (RECP) developed by the Stuttgart group (SDD basis set) were used in conjunction with the basis set to describe the metal valence electrons, and two sets of *f* polarization functions were added,<sup>9</sup> and the 6-31G(d,p) basis set for all other main group elements, E. Hereafter, the method used in DFT calculations is abbreviated as PBE0/SDD(Ni)U6-31G(d,p)(E). All stationary points have been identified as minima. Solvent effects were accounted for by means of the Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM), this being the default self-consistent reaction field (SCRF) method.<sup>10</sup>

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B.

Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian* 09, Revision B.01, 2010.

- 2 J.P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
- 3 M. Ernzerhof and G.E. Scuseria, J. Chem. Phys., 1999, **110**, 5029-5036.
- 4 C. Adamo and V. Barone, *Chem. Phys. Lett.*, 1997, **274**, 242-250.
- 5 C. Adamo and V. Barone, J. Chem. Phys., 1999, **110**, 6158-6170.
- 6 C. Adamo, G.E. Scuseria and V. Barone, J. Chem. Phys., 1999, **111**, 2889-2899.
- 7 C. Adamo and V. Barone, *Theor. Chem. Acc.*, 2000, **105**, 169-172.
- 8 V. Vetere, C. Adamo and P. Maldivi, *Chem. Phys. Lett.*, 2000, **325**, 99-105.
- 9 A. Bergner, M. Dolg, W. Kuechle, H. Stroll and H. Preuss, *Mol. Phys.*, 1993, **80**, 1431-1441.
- 10 J. Tomasi, B. Mennucci and R. Cammi, Chem. Rev., 2005, 105, 2999-3094.

#### Preparation of trans, trans, trans-[NiCl<sub>2</sub>{(py)(ph)CO}<sub>2</sub>]·0.4H<sub>2</sub>O·0.6EtOH (1·0.4H<sub>2</sub>O·0.6EtOH)

To a pale green solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (*trans*-[NiCl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]·2H<sub>2</sub>O) (0.059 g, 0.25 mmol) in EtOH (6 mL) was added solid (py)(ph)CO (0.092 g, 0.50 mmol). The solid was immediately dissolved and the colour of the solution turned to olive green. The reaction solution was stirred for a further 15 min and filtered. Vapour diffusion of Et<sub>2</sub>O into the reaction solution gave X-ray quality, dark orange-red crystals of the product after 21 d. The crystals were collected by filtration, washed with ice-cold EtOH (2x0.5 mL) and Et<sub>2</sub>O (3x2 mL), and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub> overnight. Typical yields were in the range 50-55%. The product was analyzed satisfactorily as lattice solvent-free, *i.e.* **1**. Analytical data, calcd. for C<sub>24</sub>H<sub>18</sub>NiN<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub> (found values are in parentheses): C 58.11 (57.92), H 3.67 (3.73), N 5.65 (5.33)%. IR bands (KBr, cm<sup>-1</sup>): 3080w, 2995w, 1624s, 1583sh, 1576m, 1564s, 1522w, 1422m, 1328s, 1260mb, 1140mb, 1090w, 1062w, 1040w, 1008w, 956m, 810m, 767w, 756m, 745sh, 700m, 647w, 638sh, 540w, 512w, 460w, 427w. Solid-state (diffuse reflectance) electronic spectral data (nm): 405, 696, 810sh, 1080. Effective magnetic moment ( $\mu_{eff}$ ) at 25 °C: 3.19 BM. Molar conductivity value,  $\Lambda_M$  (MeOH, 25 °C, 10<sup>-3</sup> M): 6 S cm<sup>2</sup> mol<sup>-1</sup>. The crystalline product can be isolated (albeit in a rather poor crystal quality and a lower yield of ~30%) upon slow solvent evaporation of the reaction solution at room temperature after 2 d.

#### Preparation of cis, cis, trans-[NiCl<sub>2</sub>{(py)(ph)CO}<sub>2</sub>] (2)

To a pale green solution of NiCl<sub>2</sub>·GH<sub>2</sub>O (*trans*-[NiCl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]·2H<sub>2</sub>O) (0.059 g, 0.25 mmol) in MeCN (15 mL) was added solid (py)(ph)CO (0.092 g, 0.50 mmol). The solid was soon dissolved, and the resultant green solution was stirred for a further 15 min. The reaction solution was layered with Et<sub>2</sub>O (20 mL). Slow mixing gave X-ray quality, green crystals of the product over a period of 10 d. The crystals were collected by filtration, washed with Et<sub>2</sub>O (4x2 mL), and dried in the normal laboratory atmosphere. Typical yields were in the range 65-70%. Analytical data, calcd. for C<sub>24</sub>H<sub>18</sub>NiN<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub> (found values are in parentheses): C 58.11 (58.27), H 3.67 (3.80), N 5.65 (5.47)%. IR bands (KBr, cm<sup>-1</sup>): 3085w, 3000w, 1622s, 1588sh, 1554sh, 1523w, 1508w, 1491w, 1470w, 1455w, 1442m, 1330s, 1258m, 1155w, 1142sh, 1092w, 1067w, 1036w, 1020m, 972w, 963sh, 956m, 940w, 815w, 767w, 756m, 723w, 696m, 656w, 647sh, 550w, 510w, 455w, 445w, 420w. Solid-state (diffuse reflectance) electronic spectral data (nm): 397, 425sh, 710, 1010. Effective magnetic moment ( $\mu_{eff}$ ) at 25 °C: 3.30 BM. Molar conductivity values,  $\Lambda_{M}$  (MeOH, 25 °C, 10<sup>-3</sup> M): 70 S cm<sup>2</sup> mol<sup>-1</sup> and  $\Lambda_{M}$  (MeCN, 25 °C, 10<sup>-3</sup> M): 4 S cm<sup>2</sup> mol<sup>-1</sup>. The crystalline product can be

isolated (albeit in a rather poor crystal quality and a lower yield of  $\sim$ 25%) upon slow solvent evaporation of the reaction solution at room temperature after 5 d.

#### Conversion of 2 into 1

Solid **2** (0.099 g, 0.20 mmol) was dissolved in EtOH (15 mL) under moderate heating (40 °C). The resultant olive green solution was stirred for 2 h at this temperature (no reflux is needed) and filtered. Vapour diffusion of Et<sub>2</sub>O into this solution resulted in X-ray quality, dark orange-red crystals within a period of 2 weeks; the unit cell of a crystal was almost identical with that of the authentic complex  $1\cdot0.4H_2O\cdot0.6EtOH$  prepared by the direct 1:2 reaction between NiCl<sub>2</sub>·6H<sub>2</sub>O and (py)(ph)CO in EtOH (*vide supra*). The crystals were collected by filtration, washed with Et<sub>2</sub>O (2x2 mL) and dried *in vacuo* over anhydrous CaCl<sub>2</sub> for 2 d. The yield of the conversion was 42%. The orange-red product analyzed satisfactorily as lattice solvent-free, *i.e.* **1**. Analytical data, calcd. for C<sub>24</sub>H<sub>18</sub>NiN<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub> (found values are in parentheses): C 58.11 (58.73), H 3.67 (3.61), 5.65 (5.58)%. The IR and diffuse reflectance spectra of this sample are superimposable with the corresponding spectra of the authentic complex  $1\cdot0.4H_2O\cdot0.6EtOH$ . Effective magnetic moment ( $\mu_{eff}$ ) at 25 °C: 3.14 BM. The complex can be isolated (albeit in a rather poor crystal quality and a lower yield of ~30%) upon slow solvent evaporation of the green solution at room temperature over a period of 4 d.



Fig.S1 Solid-state (diffuse reflectance) electronic spectrum of the diastereoisomer 1.



Fig. S2 Solid-state (diffuse reflectance) electronic spectrum of the diastereoisomer 2.

Equilibrium geometries and stability of the *cis*- and *trans*-  $[NiCl_2(H_2O)_4]$  species in solution Taking into account that NiCl\_2·6H\_2O could exist as octahedral *cis*- $[NiCl_2(H_2O)_4]$  and *trans*- $[NiCl_2(H_2O)_4]$  species in MeCN and EtOH solutions, we calculated the geometries and stability of the two diastereoisomers (geometrical isomers) employing the PBE0/SDD(Ni)U6-31G(d,p)(E) computational protocol (Fig.S3).



**Fig. S3** Equilibrium geometries of the *cis*- and *trans*-[NiCl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] diastereoisomers in MeCN, (**a**), and EtOH, (**b**), solutions calculated at the PBE0/SDD(Ni)U6-31G(d,p)(E) level of theory.

Inspection of Fig.S3 reveals that the solvent has practically no effect on the structures of the *cis*and *trans*-[NiCl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] isomers. Waizumi et al.<sup>11</sup> reported the Ni-Cl and Ni-O bond lengths of *cis*-[NiCl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] complex to be in the ranges 2.374(1)-2.397(1) Å and 2.058(3)-2.080(3) Å, respectively, using single-crystal X-ray crystallography. Employing single-crystal X-ray data, assisted by neutron data, Ptasiewicz-Bak and co-workers<sup>12</sup> reported Ni-Cl bond lengths of 2.371(1) Å and 2.395(1) Å, and Ni-O bond distances in the range 2.053(1)-2.081(1) Å at 295 K for this stereoisomer. For *trans*-[NiCl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>], which has higher energy than the *cis* isomer, singlecrystal X-ray data at room temperature for NiCl<sub>2</sub>·6H<sub>2</sub>O (which contains the *trans* isomer) have revealed<sup>13</sup> Ni-Cl and Ni-O bond lengths of 2.38 Å and 2.10 Å, respectively. The corresponding data at room temperature, obtained from single-crystal neutron-diffraction data,<sup>14</sup> have been reported to be 2.359(7) Å (Ni-Cl) and 2.05(1) Å (Ni-O). It is worth noting that the Ni-Cl and Ni-O bond lengths of the *cis* and *trans* isomers, calculated at the PBE0/SDD(Ni)U6-31G(d,p)(E) level of theory, are in excellent agreement with the experimental data.

In MeCN and EtOH solutions of NiCl<sub>2</sub>·6H<sub>2</sub>O, the [NiCl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] species can be either the trans- or the cis-isomer, where cis- $[NiCl_2(H_2O)_4]$  is slightly more stable than the trans- $[NiCl_2(H_2O)_4]$  isomer by only 0.2 and 1.7 Kcal/mol at the PBE0/SDD(Ni)U6-31G(d,p)(E) and BP86/SDD(Ni)U6-31G(d,p)(E) levels of theory, respectively. Therefore, the cis- and trans- $[NiCl_2(H_2O)_4]$  isomers coexist in equilibrium in the MeCN and EtOH solutions, and the nucleophilic substitution reactions of the coordinated  $H_2O$  molecules by the (py)(ph)CO nucleophiles (that proceeds through the  $S_N^1$  mechanism) could afford both the various *cis*- and *trans*-[NiCl<sub>2</sub>{(py)(ph)CO}<sub>2</sub>] isomers (Scheme 1 of the main body of the Communication). It is evident that the cis/trans selectivity in the  $[NiCl_2(H_2O)_4]$  entity is not a thermodynamically driven process. Probably the effect of H bonds and kinetics induced by the solvent might be responsible for the observed diastereoisomeric selectivity in  $[NiCl_2((py)(ph)CO)_2]$  in MeCN and EtOH solutions. It should be noticed that solvation and H bond formation are in favour of the trans- $[NiCl_2(H_2O)_4]$  isomer in EtOH solution, thus accounting well for the isolation of *trans, trans, trans*- $[NiCl_2((py)(ph)CO]_2]$  (1) from the EtOH solution. In MeCN solutions, H bonds are missing and therefore the formation of one of the *cis* (considering the chlorido ligands) diastereoisomers is favoured with respect to one of the trans (again considering the chlorido ligands) diastereoisomers, in excellent agreement with the experiment which revealed the isolation of *cis, cis, trans*- $[NiCl_2((py)(ph)CO]_2]$  (2) from this solvent.

- 11 K. Waizumi, H Masuda and H. Ohtaki, Inorg. Chim. Acta, 1992, 192, 173-181.
- 12 H. Ptasiewicz-Bak, I. Olovsson and G.J. McIntyre, *Acta Crystallogr., Sect. B*, 1999, **55**, 830-840.
- 13 J. Mizuno, J. Phys. Soc. Jpn., 1961, 16, 1574-1580.
- 14 R. Kleinberg, J. Chem. Phys., 1969, 50, 4690-4696.

## **STRUCTURAL INFORMATION**

#### Experimental for single-crystal X-ray crystallography

Dark orange-red crystals of 1.0.4H<sub>2</sub>O.0.6EtOH (0.09x0.20x0.20 mm) and green crystals of 2 (0.04x0.24x0.26 mm), respectively, were taken from the mother liquor and immediately cooled to -93 °C (1.0.4H<sub>2</sub>O.0.6EtOH) and -103 °C (2). X-ray diffraction data were collected on a Rigaku R-AXIS SPIDER Image Plate diffractometer using graphite-monochromated Mo K $\alpha$  radiation. Data collection ( $\omega$ -scans) and processing (cell refinement, data reduction and empirical absorption correction) were performed using the CrystalClear program package.<sup>1</sup> The structures were solved by direct methods using SHELXS-97<sup>2</sup> and refined by full-matrix least-squares techniques on  $F^2$  with SHELXL, ver. 2014/6<sup>3</sup>. The H atoms were located by difference maps and refined isotropically, except those of the partially occupied EtOH and H<sub>2</sub>O lattice solvent molecules in  $1.0.4H_2O.0.6EtOH$  which were introduced at calculated positions as riding on bonded atoms. Further crystallographic details for  $1.0.4H_2O.0.6EtOH$ :  $2\vartheta_{max}=54^\circ$ ,  $(\Delta/\sigma)_{max}=0.001$ , F(000)=1094, cell parameters from 15663 reflections,  $R_1$  (all data)=0.0635,  $wR_2(I>2\sigma(I))=0.1258$ . The highest peak in the difference Fourier map for this structure is 1.22 e at 1.25 Å from H25A. Further crystallographic details for **2**:  $2\vartheta_{max}=54^\circ$ ,  $(\Delta/\sigma)_{max}=0.001$ , F(000)=1016, cell parameters from 13728 reflections,  $R_1$  (all data)=0.0434,  $wR_2(I>2\sigma(I))=0.0730$ . The highest peak in the difference Fourier map for this structure is 0.33 e at 0.89 Å from NI'. Most structural plots were drawn using the Diamond 3 program package.<sup>4</sup> Important crystallographic data are listed in Table S1, while selected interatomic distances and angles are listed in Tables S2 and S3. Full details can be found in the CIF files.

- 1 CrystalClear, Rigaku/MSC Inc., The Woodlands, TX, USA, 2005.
- 2 G. M. Sheldrick, Acta Crystallogr., Sect. A, 2008, 64, 112–122.
- 3 G. M. Sheldrick, Acta Crystallogr., Sect. C, 2015, 71, 3–8.
- 4 *DIAMOND: Crystal and Molecular Structure Visualization*, Ver. 3.1, Crystal Impact GbR, Bonn, Germany, 2011.

Parameter	<b>1</b> •0.4H₂O·0.6EtOH	2
Formula	C <sub>25.2</sub> H <sub>22.4</sub> N <sub>2</sub> NiO <sub>3</sub> Cl <sub>2</sub>	$C_{24}H_{18}N_2NiO_2Cl_2$
F <sub>w</sub>	530.86	496.01
Crystal system	Monoclinic	Orthorhombic
Space group	P2 <sub>1</sub> /n	Pcan
a/Å	10.5379(2)	7.9540(1)
b/Å	9.1919(2)	13.9375(3)
c/Å	25.3211(5)	19.6479(4)
α/°	90.0	90.0
β/°	95.362(1)	90.0
γ/°	90.0	90.0
V/Å <sup>3</sup>	2441.95(9)	2178.14(7)
Z	4	4
$\rho_{\text{calcd}}/\text{g cm}^{-3}$	1.444	1.513
T/K	180	170
Radiation/µ (mm <sup>-1</sup> )	Μο Κα (1.043)	Μο Κα (1.160)
RefIns collected /unique (R <sub>int</sub> )	21709/5319 (0.049)	19717/2366 (0.049)
Reflns with I>2 $\sigma$ (I)	4036	1816
No. of parameters	393	177
$R_1[I>2\sigma(I)], wR_2$ (all data)	0.0449, 0.1441	0.0306, 0.0819
$GOF(F^2)$	1.09	1.13
$\Delta \rho_{\rm max} / \Delta \rho_{\rm min}$ (e Å <sup>-3</sup> )	1.22/-0.50	0.33/-0.40
CCDC number	1949392	1949393

**Table S1** Crystal data and structure refinement for compounds *trans, trans, trans*. [NiCl<sub>2</sub>{(py)(ph)CO}<sub>2</sub>] $\cdot 0.4H_2O \cdot 0.6EtOH$  (1 $\cdot 0.4H_2O \cdot 0.6EtOH$ ) and *cis, cis, trans*-[NiCl<sub>2</sub>{(py)(ph)CO}<sub>2</sub>] (**2**)

		Distances	
Ni-Cl1	2.417(1)	Ni1-N1	2.046(2)
Ni1-Cl2	2.397(1)	Ni1-N2	2.049(3)
Ni1-01	2.095(2)	C6-O1	1.239(4)
Ni1-02	2.088(2)	C18-O2	1.236(4)
		Angles	
Cl1-Ni1-Cl2	178.0(1)	01-Ni1-N2	103.1(1)
Cl1-Ni1-O1	90.1(1)	O2-Ni1-N1	99.1(1)
Cl1-Ni1-O2	90.0(1)	O2-Ni1-N2	78.9(1)
Cl1-Ni1-N1	91.3(1)	N1-Ni1-N2	177.3(1)
Cl1-Ni1-N2	86.9(1)	C5-C6-O1	118.7(3)
Cl2-Ni1-O1	88.3(1)	C7-C6-O1	119.7(3)
Cl2-Ni1-O2	91.6(1)	C5-C6-C7	121.6(3)
Cl2-Ni1-N1	89.7(1)	C17-C18-O2	118.3(3)
Cl2-Ni1-N2	92.3(1)	C19-C18-O2	119.6(3)
01-Ni1-O2	178.0(1)	C17-C18-C19	122.0(3)
O1-Ni1-N1	78.9(1)		

TableS2Selectedbondlengths(Å)andangles(°)forcomplextrans,tran

Distances							
Ni1-Cl1	2.376(1)	Ni1-N1	2.054(2)				
Ni1-01	2.160(1)	C6-O1	1.242(2)				
Angles							
Cl1-Ni1-Cl1'	104.7(1)	01-Ni1-N1	77.2(1)				
Cl1-Ni1-O1	166.6(1)	01-Ni1-N1'	95.4(1)				
Cl1-Ni1-O1'	85.6(1)	N1-Ni1-N1'	169.9(1)				
Cl1-Ni1-N1	93.5(1)	C5-C6-O1	117.6(2)				
Cl1-Ni1-N1'	92.7(1)	C7-C6-O1	119.8(2)				
01-Ni1-01'	85.7(1)	C5-C6-C7	122.7(2)				

**Table S3** Selected bond lengths (Å) and angles (°) for complex *cis, cis, trans*-[NiCl<sub>2</sub>{(py)(ph)CO}<sub>2</sub>] (2)<sup>*a*</sup>

<sup>a</sup> Symmetry code to generate equivalent atoms: (') x, -y+1, -z+3/2.

#### Short description of the supramolecular features of complexes 1.0.4H<sub>2</sub>O.0.6EtOH and 2

Table S4 summarizes the H-bonding interactions in the structure of  $1.0.4H_2O.0.6EtOH$ . Chains of *trans, trans, trans*-[NiCl<sub>2</sub>{(py)(ph)CO}<sub>2</sub>] molecules parallel to the *b* axis are formed through C3-H(C3)…Cl1 (*x*, 1+*y*, *z*) and C15-H(C15)…Cl2 (*x*, -1+*y*, *z*) H bonds; the chains are linked in pairs through C2-H(C2)…Cl1 (3/2-*x*, 1/2+*y*, 1/2-*z*) H bonds, Fig.S5. Interactions of the pairs of chains through C10-H(C10)…Cl2 (-1+*x*, *y*, *z*) H bonds results in the formation of layers parallel to the (001) plane, Fig.S6. The layers are stacked parallel to the *c* axis interacting through C14-H(C14)…Cl2 (1-*x*, -*y*, -*z*) H bonds generating the 3D architecture of the structure, Fig.S7. The positions of the lattice H<sub>2</sub>O and EtOH molecules are also indicated in Fig.S7 with bold violet lines. The O atoms of H<sub>2</sub>O and EtOH are at distances 3.20(1) and 3.876(6) Å from the Cl2 ligands, respectively, indicating the possible existence of intermolecular H bonds.

The *cis, cis, trans*-[NiCl<sub>2</sub>{(py)(ph)CO}<sub>2</sub>] molecules in the crystal structure of **2** interact through C3-H(C3)…Cl1' (1/2+*x*, 1/2+*y*, 3/2-*z*) H bonds (Table S5, Fig.S8,b) and through  $\pi$ - $\pi$  stacking interactions involving the centrosymmetrically-related C7/C8/C9/C10/C11/C12 and C7''/C8''/C9''/C10''/C11''/C12'' phenyl rings at a distance of 3.46 Å [symmetry code: ('') 1-*x*, 1-*y*, 2-*z*]. Layers parallel to the (001) plane are formed through the above mentioned H bonds (Fig.S9, left); the layers are further stacked along the *c* axis thus forming the 3D architecture of the structure (Fig.S9, right).



**Fig.S4** Fully labelled structure of the molecule *trans, trans, trans*- $[NiCl_2{(py)(ph)CO}_2]$  that is present in the crystal of  $1.0.4H_2O.0.6EtOH$ . The thermal ellipsoids are at the 50% probability level.



**Fig.S5** Pairs of chains of *trans, trans, trans*-[NiCl<sub>2</sub>{(py)(ph)CO}<sub>2</sub>] molecules parallel to *b* axis in the crystal structure of  $1.0.4H_2O.0.6EtOH$ . The dashed cyan lines represent the C3-H(C3)…Cl1 (*x*, 1+*y*, *z*) and C15-H(C15)-Cl2 (*x*, -1+*y*, *z*) H bonds, and the orange ones represents the C2-H(C2)…Cl1 (3/2-*x*, 1/2+*y*, 1/2-*z*) H bonds. Metric parameters are listed in Table S4.



**Fig.S6** A layer of pairs of chains of molecules *trans, trans, trans*- $[NiCl_2\{(py)(ph)CO\}_2]$  parallel to the (001) plane in the crystal structure of  $1 \cdot 0.4H_2O \cdot 0.6EtOH$ . The dashed light green lines indicate the C10-H(C10)…Cl2 (-1+*x*, *y*, *z*) H bonds. The other color codes are the same with those used in Fig.S5. Metric parameters are listed in Table S4.



**Fig.S7** Layers of pairs of chains of molecules *trans, trans, trans*-[NiCl<sub>2</sub>{(py)(ph)CO}<sub>2</sub>] parallel to the *c* axis in the crystal structure of  $1 \cdot 0.4H_2O \cdot 0.6EtOH$ . The dashed dark green lines represent the C14-H(C14)…Cl2 (1-*x*, -*y*, -*z*) H bonds. The other color codes are the same with those used in Figs. S5 and S6. Metric parameters are listed in Table S4. The positions of the lattice H<sub>2</sub>O and EtOH molecules are indicated with bold violet lines.



**Fig.S8** a) Fully labelled structure of the molecule *cis, cis, trans*- $[NiCl_2\{(py)(ph)CO\}_2]$  that is present in the crystal of **2**. Symmetry operation: (') *x*, 1-*y*, 3/2-*z*. The thermal ellipsoids are at the 50% probability level. The dashed light green lines represent the intramolecular C1-H(C1)····Cl1 and (its symmetry equivalent) C1'-H(C1')····Cl1' H bonds. b) Intermolecular interactions between neighbouring mononuclear octahedral molecules in the crystal structure of **2**. The dashed cyan and orange lines represent H-bonding and  $\pi$ - $\pi$  stacking interactions, respectively. Metric parameters for the H bonds are listed in Table S5.



**Fig.S9** (Left) Layers of molecules *cis, cis, trans*- $[NiCl_2{(py)(ph)CO}_2]$  parallel to the (001) plane in the crystal structure of **2**. (Right) Stacking of the layers along the *c* axis in the crystal structure of **2**. The color codes are the same with those used in Fig.S8.

Table S4 Parameters (Å, °) for the H bonds in the crystal structure of complex 1.0.4H<sub>2</sub>O.0.6EtOH

D-H···A <sup>a</sup>	D-H	Н…А	D····A	D-H···A	Symmetry of A				
C3-H(C3)…Cl1	0.93(4)	2.72(4)	3.647(3)	163(3)	x, 1+y, z				
C15-H(C15)…Cl2	0.88(4)	2.93(4)	3.737(3)	152(3)	x, -1+y, z				
C2-H(C2)…Cl1	0.96(4)	2.78(3)	3.523(3)	135(2)	3/2- <i>x</i> , 1/2+y, 1/2-z				
C10-H(C10)…Cl2	0.96(4)	2.82(4)	3.616(3)	142(3)	-1+ <i>x, y, z</i>				
C14-H(C14)…Cl2	0.96(4)	2.83(4)	3.755(3)	160(3)	1-x, -y, -z				
0									

<sup>a</sup> C2, C3, C14 and C15 are aromatic 2-pyridyl carbon atoms, while C10 belongs to a phenyl ring; these atoms are not labelled in Fig.1

Table S5 Parameters (Å, °) for the crystallographically independent H bonds in the crystal structure of complex 2.

D-H····A <sup>a</sup>	D-H	Н…А	D…A	D-H···A	Symmetry of A				
Intramolecular									
C1-H1…Cl1	0.96(2)	2.59(2)	3.260(2)	128(2)					
Intermolecular									
C3-H3…Cl1'	0.94(2)	2.67(2)	3.342(2)	129(2)	1/2+x, 1/2+y, 3/2-z				
<sup>a</sup> C3 is the aromatic carbon atom of the N(1)-containing 2-pyridyl ring; this carbon atom is not labelled in Fig.2.									