### Accepted Manuscript

Three new Salamo-type homotrinuclear nickel(II) complexes possessing solvent effects: Syntheses, structures and fluorescence properties

Lu-Mei Pu, Hai-Tao Long, Yang Zhang, Yang Bai, Wen-Kui Dong

PII: DOI: Reference:	S0277-5387(17)30155-9 http://dx.doi.org/10.1016/j.poly.2017.02.033 POLY 12500
To appear in:	Polyhedron
Received Date: Revised Date: Accepted Date:	<ul><li>22 December 2016</li><li>4 February 2017</li><li>4 February 2017</li></ul>



Please cite this article as: L-M. Pu, H-T. Long, Y. Zhang, Y. Bai, W-K. Dong, Three new Salamo-type homotrinuclear nickel(II) complexes possessing solvent effects: Syntheses, structures and fluorescence properties, *Polyhedron* (2017), doi: http://dx.doi.org/10.1016/j.poly.2017.02.033

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

# Three new Salamo-type homotrinuclear nickel(II) complexes possessing solvent effects: Syntheses, structures and fluorescence properties

### Lu-Mei Pu<sup>a,\*</sup>, Hai-Tao Long<sup>a</sup>, Yang Zhang<sup>b</sup>, Yang Bai<sup>b</sup>, Wen-Kui Dong<sup>b</sup>

<sup>a</sup> College of Science, Gansu Agricultural University, Lanzhou, Gansu, 730070, P.R.China

<sup>b</sup> School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, Gansu, 730070, P.R.China

#### Abstract

Three new solvent-induced Ni(II) complexes with the chemical formulae  $[{Ni(L)(CH_{3}OH)}_{2}(\mu - OAc)_{2}Ni]$  (1),  $[{Ni(L)(C_{3}H_{7}OH)}_{2}(\mu - OAc)_{2}Ni]$ (2) and  $[{NiL(H_2O)}_2(\mu-OAc)_2Ni]$  (3) were synthesized by the reaction of the Salamo-type ligand 4,4'-dinitro-2,2'-[1,2-ethylene-dioxybis(nitrilomethylidyne)]diphenol (H<sub>2</sub>L) with Ni(II) acetate tetrahydrate in different solvents and characterized by elemental analyses, FT-IR, UV-Vis spectra and X-ray crystallography. X-ray crystallographic analyses indicate that complexes 1, 2 and 3 have similar structures, consisting of three Ni(II) atoms, two completely deprotonated  $(L)^{2-}$  units, two  $\mu$ -acetate ions and two coordinated solvent (methanol, n-propanol and  $H_2O$ ) molecules, thereby forming slightly distorted octahedral geometries. Although the Ni(II) atoms are all hexa-coordinated in these complexes, there are obvious differences in their crystal and supramolecular structures due to solvent effects: Complex 1 forms an infinite 2D network structure, while complexes 2 and 3 form infinite 3D supramolecular structures by strong hydrogen bonding interactions.

<sup>\*</sup> Corresponding authors.

E-mail addresses: pulm@gsau.edu.cn (L.-M. Pu).

*Keywords*: Salamo-type ligand, Ni(II) complex, Crystal structure, Fluorescence property, Solvent effect

#### 1. Introduction

Schiff-base compounds constitute an important class of ligands which have been extensively investigated in coordination chemistry mainly due to their facile synthesis and easily tunable steric, electronic and catalytic properties. They are also useful in constructing supramolecular structures [1]. Nowadays Salen-type transition metal complexes have become an important research field [2]. These complexes can be used in catalysts [3,4], photonic devices [5], magnetic materials [6], models of biological [7] and electrochemical systems [8]. Furthermore, Salen-Ni(II) complexes are used extensively in the design and construction of new magnetic materials and models for the Ni(II) centers of enzymes. These complexes can be used to obtain non-linear optical materials [9], models of biological systems [10], interesting magnetic properties [11] and building blocks for cyclic supramolecular structures [12]. Thus, new materials can be produced by using these compounds, which are suitable candidates for further chemical modifications [13]. If an O-alkyl oxime moiety (-CH=N-O-(CH<sub>2</sub>)<sub>n</sub>-O-N=CH-) is used instead of a Schiff base, the larger electronegativity of the oxygen atoms is expected to affect strongly the electronic properties of the  $N_2O_2$  coordination sphere, which may lead to novel and different structures and properties of the resulting complexes [1,2]. Solvent effects can lead to better ways to control supramolecular interactions [14a]. With this in mind, we have designed synthesized Salamo-type and а ligand, 4,4'-dinitro-2,2'-[1,2-ethylene-dioxybis(nitrilomethylidyne)]diphenol (H<sub>2</sub>L), and its supramolecular trinuclear Ni(II) complexes 1, 2 and 3.

#### 2. Experimental

#### 2.1. Materials and instruments

All chemicals were of analytical reagent grade and were used without further

purification. C, H and N analyses were obtained using a GmbH VarioEL V3.00 automatic elemental analysis instrument. Elemental analyses for metals were detected with an IRIS ER/ S-WP-1 ICP atomic emission spectrometer. IR spectra were recorded on a VERTEX70 FT-IR spectrophotometer, with samples prepared as KBr (500–4000 cm<sup>-1</sup>) pellets. <sup>1</sup>H NMR spectra were determined with a German Bruker AVANCE DRX-400 spectrometer. Melting points were obtained with the use of an X4 microscopic melting point apparatus made by the Beijing Taike Instrument Limited Company and were uncorrected. Fluorescent spectra were taken on a LS-55 fluorescence photometer. X-ray single crystal structure determinations were carried out on a Bruker Smart Apex CCD diffractometer.

#### 2.2. Synthesis of the ligand $H_2L$

The main reaction steps involved in the synthesis of  $H_2L$  are given in Scheme 1.

Scheme 1. Synthetic route to the Salamo-type ligand H<sub>2</sub>L

4,4'-Dinitro-2,2'-[1,2-ethylene-dioxybis(nitrilomethylidyne)]diphenol (H<sub>2</sub>L) was prepared by a modification of the reported method [14]. An ethanol solution (10 mL) of 5-nitrosalicylicaldehyde (341.6 mg, 2.01 mmol) was added to an ethanol solution (10 mL) of 1,2-bis(aminooxy)ethane (93.4 mg, 1.00 mmol). The solution mixture was stirred at 55 °C for 5h. After cooling to room temperature, the precipitate was filtered and washed with ethanol and the ethanol/hexane (1:4). The product was dried under vacuum to give colorless microcrystals. Yield: 298.69 mg (85.14%). Mp: 202-203 °C. *Anal.* Calc. for C<sub>16</sub>H<sub>14</sub>N<sub>4</sub>O<sub>8</sub> (%): C, 49.22; H, 3.92 N, 14.33. Found: C, 49.23; H, 3.90; N, 14.36%. IR (KBr, cm<sup>-1</sup>): 3446 (w), 1629 (s), 1570 (s), 1483 (s), 1340 (s), 1272 (s), 1095 (s), 1047 (s), 1019 (s), 954 (m), 869 (s), 825 (m), 781 (s), 752 (s), 696 (m), 638 (m), 590 (s), 511 (m), 474 (m), 443 (m).

2.3. Synthesis of complexes 1, 2 and 3

The three solvent-induced Ni(II) complexes 1, 2 and 3 were obtained by the reaction of the Salamo-type ligand H<sub>2</sub>L and Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O in a 1:1 molar ratio in absolute methanol, n-propanol and H<sub>2</sub>O solvents, respectively. Single crystals of complexes 1, 2 and 3 suitable for X-ray diffraction analysis were grown using the gaseous diffusion method.

#### 2.3.1 Synthesis of complex 1

A solution of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (2.82 mg, 0.01 mmol) in methanol (3 mL) was added dropwise to a solution of H<sub>2</sub>L (3.52 mg, 0.01 mmol) in acetonitrile (3 mL) at room temperature. The color of the resulting solution turned yellow immediately, and stirring was continued for 1 h at room temperature. The solution was then filtered. After three weeks, the solvent was partially evaporated and several green prismatic single crystals suitable for X-ray crystallographic analysis were obtained. Yield: 2.50 mg (66.2%). *Anal.* Calc. for  $C_{38}H_{38}N_8Ni_3O_{22}$ ; C, 40.23; H, 3.36; N, 9.87; Ni, 15.33. Found: C, 40.21; H, 3.35; N, 9.88; Ni, 15.34%. IR (KBr, cm<sup>-1</sup>): 3447 (w), 1604 (s), 1570 (s), 1483 (s), 1311 (s), 1256 (s), 1099 (s), 688 (m), 634 (m), 557 (s), 511 (m), 476 (m), 438 (m).

#### 2.3.2 Synthesis of complex 2

A solution of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (2.82 mg, 0.01 mmol) in n-propanol (3 mL) was added dropwise to a solution of H<sub>2</sub>L (3.52 mg, 0.01 mmol) in acetonitrile (3 mL) at room temperature. The color of the resulting solution turned yellow immediately, and stirring was continued for 1 h at room temperature. The solution was then filtered and the filtrate was allowed to stand at room temperature for about three weeks. The solvent was partially evaporated and several green prismatic single crystals suitable for X-ray crystallographic analysis were obtained. Yield: 2.49 mg (62.6%). *Anal.* Calc. for C<sub>42</sub>H<sub>46</sub>N<sub>8</sub>Ni<sub>3</sub>O<sub>22</sub>: C, 42.33; H, 3.85; N, 9.41; Ni, 14.60. Found: C, 42.32; H, 3.86; N, 9.40; Ni, 14.61%. IR (KBr, cm<sup>-1</sup>): 3463 (w), 1602 (s), 1560 (s),

1479 (s), 1307 (s), 1253 (s), 1107 (s), 692 (m), 646 (m), 567 (s), 522 (m), 477 (m), 439 (m).

#### 2.3.3 Synthesis of complex 3

A solution of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (2.82 mg, 0.01 mmol) in 2-propanol (3 mL) was added dropwise to a solution of H<sub>2</sub>L (3.52 mg, 0.01 mmol) in acetonitrile (3 mL) at room temperature. The color of the resulting solution turned yellow immediately, and stirring was continued for 1 h at room temperature. The solution mixture was filtered and the filtrate was allowed to stand at room temperature for about three weeks. The solvent was partially evaporated and several green prismatic single crystals suitable for X-ray crystallographic analysis were obtained. Yield: 2.24 mg (60.7%). *Anal.* Calc. for C<sub>36</sub>H<sub>34</sub>N<sub>8</sub>Ni<sub>3</sub>O<sub>22</sub>: C, 39.07; H, 3.10; N, 10.12; Ni, 15.91. Found: C, 39.06; H, 3.07; N, 10.13; Ni, 15.73%. IR (KBr, cm<sup>-1</sup>): 3456 (w), 1635(w), 1606 (s), 1568 (s), 1483 (s), 1311 (s), 1253 (s), 1107 (s), 688 (m), 632 (m), 582 (s), 534 (m), 507 (m), 472 (m), 434 (m).

#### 2.4 X-ray crystallography of complexes 1, 2 and 3

The crystal and structure refinement data for complexes 1, 2 and 3 are given in Table 1. The single crystals of complexes 1, 2 and 3, with the approximate dimensions of  $0.23 \times 0.21 \times 0.16$ ,  $0.31 \times 0.24 \times 0.23$  and  $0.25 \times 0.23 \times 0.21$  mm, were placed on a Bruker Smart 1000 CCD area detector. The reflections were collected using graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 298(2) K. The structures were solved using the program SHELXL-97 and Fourier difference techniques, and refined by the full-matrix least-squares method on  $F^2$ . All hydrogen atoms were added in calculated positions. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were added theoretically.

Table 1 Crystal data and structure refinement for complexes 1, 2 and 3

#### 3. Results and discussion

#### 3.1. IR spectra analyses

The FT-IR spectra of H<sub>2</sub>L and its corresponding Ni(II) complexes **1**, **2** and **3** exhibit various bands in the 4000-400 cm<sup>-1</sup> region. It is obvious that the v(O–H) absorption band is near 3446 cm<sup>-1</sup> in the free ligand H<sub>2</sub>L. The free ligand H<sub>2</sub>L exhibits a characteristic C=N stretching band at 1629 cm<sup>-1</sup>, and for complexes **1**, **2** and **3** the corresponding absorption bands appear at 1604, 1602 and 1606 cm<sup>-1</sup>, indicating coordination of the Ni(II) atoms with the oxime nitrogen atoms [15c]. The C=N stretching frequencies are shifted to lower frequencies by *ca*. 23-25 cm<sup>-1</sup> upon complexation, indicating a decrease in the C=N bond order due to the coordinated bonds of the divalent metal atoms with the oxime nitrogen lone pair. The observed bands in the range 1479-1483 cm<sup>-1</sup> are attributed to the aromatic C=C skeleton vibrations [15].

The Ar-O stretching frequency of H<sub>2</sub>L appears as a strong band at 1272 cm<sup>-1</sup>, as reported for similar Salen-type ligands [1,2,14], while Ar-O stretching frequencies of complexes **1**, **2** and **3** were observed at 1256, 1253 and 1267 cm<sup>-1</sup>, respectively. The Ar-O stretching frequencies are shifted, indicating that Ni-O bonds are formed between the Ni(II) atoms and the oxygen atoms of the phenolic groups. In addition, O-H stretching bands can be found at 3447, 3463 and 3456 cm<sup>-1</sup> in complexes **1**, **2** and **3**, respectively, which indicates the presence of methanol, n-propanol and H<sub>2</sub>O molecules, and the expected absorptions in complex **3** were observed at 1635 and *ca*. 534 cm<sup>-1</sup>, respectively. The two bands should be assigned to the bending and wagging modes of water molecules, providing evidence for the existence of coordinated water molecules [14e,14f,15c-15f].

The far-infrared spectra of complexes **1**, **2** and **3** were also obtained in the region 500-100 cm<sup>-1</sup> in order to identify frequencies due to the Ni-O and Ni-N bonds. The v(Ni-O) and v(Ni-N) vibration absorption bands are observed at 476 and 438 cm<sup>-1</sup> for complex **1**, 477 and 439 cm<sup>-1</sup> for complex **2** and at 472 and 434 cm<sup>-1</sup> for complex **3**, respectively. These assignments are consistent with the literature frequency values

[15b-15g] and similar bands are not present in the spectrum of the free ligand.

#### 3.2. UV-vis absorption spectral analyses

The UV-vis absorption spectra of the free ligand H<sub>2</sub>L and its corresponding trinuclear Ni(II) complexes **1**, **2** and **3** in the DMF solutions  $(5.0 \times 10^{-5} \text{ mol/L})$  at 298 K are shown in Fig. 1. The UV–Vis spectrum of the free ligand H<sub>2</sub>L exhibits two absorption peaks at *ca*. 375 and 448 nm, respectively. The former absorption peak at 375 nm can be assigned to the intra-ligand  $\pi$ - $\pi^*$  transition of the C=N bonds [16] and the latter one around 448 nm can be ascribed to the quinoid form of Salen-type compounds, which is sometimes absent in the corresponding Salen-type analogues [8a]. Compared with the free ligand H<sub>2</sub>L, the weak absorption band at 375 nm disappears from the UV–Vis spectra of complexes **1**, **2** and **3**, which indicates that the oxime nitrogen atoms are involved in coordination to the Ni(II) atoms [16]. Moreover, new and strong absorption bands are observed at 400, 356 and 356 nm for complexes **1**, **2** and **3**, respectively, which are assigned to L→M charge-transfer (LMCT) transitions, characteristic of transition metal complexes with an N<sub>2</sub>O<sub>2</sub> coordination sphere [17]. The differences observed in the charge-transfer (LMCT) transition peaks of complexes **1**, **2** and **3** may be caused by displacement of the coordinated solvent.

Fig 1 UV-vis absorption spectra of the ligand  $H_2L$  and its complexes 1, 2 and 3

#### 3.3 Fluorescence properties analyses

The fluorescent properties of  $H_2L$  and its corresponding complexes 1, 2 and 3 were investigated in dilute DMF solutions ( $5.0 \times 10^{-5}$  mol/L) at room temperature. The ligand  $H_2L$  does not exhibit an emission peak upon excitation at 375 nm, while complexes 1, 2 and 3 show intense photoluminescence with maximum emissions at *ca*. 319, 282 and 318 nm upon excitation at 375 nm, respectively (Fig. 2). Compared with the ligand  $H_2L$ , strong fluorescence intensities of complexes 1, 2 and 3 are observed, indicating that the fluorescence characteristic has been influenced by the introduction

of the Ni(II) atoms. Fluorescence enhancement via complexation is of high interest as its application is widely used in photochemical processes. The quench in fluorescence of the free ligand  $H_2L$  could be the result of the occurrence of a photoinduced electron transfer process owing to the presence of a lone pair of electrons on the nitrogen atoms. The process is prevented by the complexation of the free ligand  $H_2L$  with the Ni(II) atoms. Therefore, the intensities in the fluorescence can be greatly enhanced through the coordination of Ni(II) atoms. Moreover, the chelation of the ligand  $H_2L$ with the Ni(II) atoms increases the rigidity of the ligand  $H_2L$  and thus minimizes energy loss through vibrational motions, which may increase the efficiency of the emission.

#### Fig 2 Emission spectra of the ligand $H_2L$ and its complexes 1, 2 and 3

#### 3.4. Description of the crystal structures

Selected bond lengths and bond angles for complexes 1, 2 and 3 are presented in Tables 2, 3 and 4, respectively. A list of hydrogen bonding interactions in complexes 1, 2 and 3 are given in Table 5.

#### 3.4.1. Structure of complex 1

The X-ray crystal structure analysis shows that complex **1** consists of three Ni(II) atoms, two completely deprotonated  $(L)^{2-}$  units, two  $\mu$ -acetate ions and two coordinated methanol molecules (Fig. 3). The terminal Ni(II) atom (Ni2 or Ni2<sup>#1</sup>) is hexa-coordinated by two oxime nitrogen (N2 and N3) and two phenolic oxygen (O1 and O8) atoms of the deprotonated Salamo-type  $(L)^{2-}$  unit, one oxygen atom (O10) from the coordinated  $\mu$ -acetate ion and one oxygen atom (O9) from the coordinated methanol molecule. The coordination geometry around the terminal Ni(II) atom is found to be a slightly distorted octahedron. The two phenolic oxygen atoms (O1 and O8) and two oxime nitrogen atoms (N2 and N3) are in mutually *cis*-positions. The primary Ni-N and Ni-O distances are in the normal ranges (Ni2-N2 = 2.078(2), Ni2-N3 = 2.031(2), Ni2-O1 = 2.073(2), Ni2-O8 = 2.027(2), Ni2-O9 = 2.140(2) and

Ni2-O10 = 2.071(2) Å) (Table 2). The bond length between the Ni(II) atom and the apical oxygen atom (O9) is 2.140(2) Å, which is obviously longer than the distances between the Ni(II) atom and the basal oxygen and nitrogen atoms. This significant elongation has been observed previously in Ni(II) complexes with Salamo-type ligands [14f,15c].

Table 2 Selected bond distances (Å) and angles (°) for complex 1.

Fig. 3 (a) Molecule structure and atom numbering scheme of complex 1 (hydrogen atoms are omitted for clarity). (b) Coordination polyhedra for the Ni(II) atoms of

complex 1

The coordination geometry of the central Ni(II) atom (Ni1) deviates slightly from ideal octahedral. The central Ni1 atom (Ni1) has an  $O_2O_2$  donor set from four  $\mu$ -phenolic oxygen atoms (O1, O8, O1<sup>#1</sup> and O8<sup>#1</sup>) of two completely deprotonated (L)<sup>2-</sup> units and each of the  $\mu$ -acetate ions bridge the central Ni1 and terminal Ni2 (or Ni2<sup>#1</sup>) atoms in the syn-syn bridging mode; as a result the central Ni1 atom finally has an  $O_2O_2O_2$  coordination environment. The primary Ni-O distances are in the normal ranges (Ni1-O1 = 2.073(2), Ni1-O1<sup>#1</sup> = 2.073(2), Ni1-O8 = 2.099(2), Ni1-O8<sup>#1</sup> = 2.099(2), Ni1-O11 = 2.018(2) and Ni1-O11<sup>#1</sup> = 2.018(2) Å) (Table 2).

In the crystal structure of complex 1, the structure is connected by four pairs of intramolecular C-H···O hydrogen bonding interactions (Table 5 and Fig. 4), which play a vital role in constructing and stabilizing the complex 1 molecules. As shown in the Fig. 5, the neighboring complex molecules are further linked into an infinite two-dimensional supramolecular network by three pairs of intermolecular hydrogen bonds (O9–H9C···O3, C5–H5···O7 and C7–H7···O7) [18].

Fig. 4 Intramolecular hydrogen bonding interactions of complex 1

Fig. 5 Part of the infinite 2D supramolecular network of complex 1

3.4.2. Structures of complexes 2 and 3

The X-ray crystal structure analyses of complexes **2** and **3** reveal that they have the same individual trinuclear neutral molecular unit  $[{(Ni(L))_2(solvent)_2}Ni]$  (the solvents are n-propanol and H<sub>2</sub>O in complexes **2** and **3**, respectively), as shown in Figs. 6 and 9, respectively, while the different solvents observed lead to the formation of the typical solvent-induced Ni(II) complexes [19].

Fig. 6 Molecule structure and atom numbering scheme of complex 2 (hydrogen atoms are omitted for clarity). (b) Coordination polyhedra for the Ni(II) atoms of complex 2

Table 3 Selected bond distances (Å) and angles (°) for complex 2.

Complex 2 consists of a linear array of three Ni(II) atoms coupled by both double  $\mu$ -phenoxo of (L)<sup>2-</sup> units and  $\mu$ -acateate anions in the syn-syn bridging mode. The terminal Ni(II) atom (Ni1 or Ni1<sup>#1</sup>) lies in a hexa-coordinated environment and adopts a distorted octahedral geometry, where the inner  $N_2O_2$  coordinated environment of the completely pentadentate (L)<sup>2-</sup> units comprise the basal plane and one oxygen atom (O10) from the  $\mu$ -acetate ion and one oxygen atom (O12) from the coordinated solvent molecule occupy the apical positions. The Ni-N and Ni-O primary distances are in the normal ranges (Ni1-N2 = 2.085(4), Ni1-N3 = 2.084(4), Ni1-O1 = 2.037(3), Ni1-O6 = 2.035(3), Ni1-O10 = 2.032(3) and Ni1-O12 = 2.116(3) Å) (Table 3). The bond length between the Ni(II) atom and the apical oxygen atom (O12) is 2.116(3) Å, which is obviously longer than the distances between the Ni(II) atom and the basal oxygen and nitrogen atoms. In addition, the central Ni2 atom is located in a hexa-coordinated environment and adopts an ideal octahedral geometry. The Ni-O primary distances are in the normal ranges (Ni2-O1 = 2.073(3), Ni1-O1<sup>#1</sup> = 2.073(3), Ni2-O6 = 2.080(3), Ni2-O6<sup>#1</sup> = 2.080(3), Ni2-O9 = 2.071(3) and Ni1-O9<sup>#1</sup> = 2.071(3)Å). The crystal structure of complex 3 is very similar to that of complex 2.

#### Fig.7 Intramolecular hydrogen bonding interactions of complex 2

Fig. 8 Part of the infinite 3D supramolecular structure showing the hydrogen bonding interactions of complex **2** 

Table 4 Selected bond distances (Å) and angles (°) for complex 3.

Fig. 9 Molecule structure and atom numbering scheme of complex **3** (hydrogen atoms are omitted for clarity). (b) Coordination polyhedra for the Ni(II) atoms of complex **3** 

The intramolecular and intermolecular hydrogen bonding interactions of complex **2** are given in Figs. 7 and 8, and those of complex **3** are given in Figs. 10 and 11, respectively. The monomeric octahedral unit and the polymeric representation of the structure are presented in Figs. 8 and 11, respectively. It is noteworthy that the coordinated solvent molecules (n-propanol or  $H_2O$ ) of complexes **2** and **3** are different from complex **1**, such solvent effects can lead to different supramolecular interactions. In complexes **2** and **3**, the neighboring complex molecules are linked into infinite three-dimensional supramolecular structures by intermolecular hydrogen bonding interactions (In complex **2**: O12–H12B…O7, C20–H20B…O3 and C3–H3…O8; in complex **3**: C9–H9A…O8 and C10–H10A…O7) (Tables 4 and 5) [20].

Table 5 Hydrogen bonding interactions [Å, °] for complexes 1, 2 and 3.

Fig.10 Intramolecular hydrogen bonding interactions of complex 3.

Fig. 11 Part of the infinite 3D supramolecular structure showing the hydrogen bonding interactions of complex **3**.

#### 4. Conclusion

In complexes 1, 2 and 3, the ligand  $H_2L$  is completely deprotonated as a tetradentate  $(L)^{2-}$  dianion and there are two solvent molecules coordinating to the two terminal Ni(II) atoms. These complexes have elongated octahedral coordination environments with an unusually long bond from the hexa-coordinated Ni(II) centers to the oxygen atoms of the apical coordinated solvent molecules for the terminal Ni(II) atoms, and distorted octahedral geometries for the central Ni(II) atom. These complexes exhibit abundant hydrogen bonding interactions in the solid state. UV-vis spectra clearly indicate the structures of the three complexes are different from the

ligand (H<sub>2</sub>L). X-ray crystal structures reveal that the structures of complexes 1, 2 and 3 are very similar except for the difference of the coordinated solvent molecules. Interestingly, the existence of solvent effects leads to slight differences in the crystal and supramolecular structures of complexes 1, 2 and 3.

#### Supplementary data

CCDC 1522520-1522522 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

#### Acknowledgements

This work was supported by the National Natural Science Foundation of China (21361015), which is gratefully acknowledged.

#### References

- [1] (a) P.G. Cozzi, Chem. Soc. Rev. 33 (2004) 410;
  - (b) S. Akine, T. Taniguchi, T. Nabeshima, Inorg. Chem. 43 (2004) 6142;
  - (c) S. Akine, W.K. Dong, T. Nabeshima, Inorg. Chem. 45 (2006) 4677;
  - (d) S. Akine, A. Akimoto, T. Shiga, H. Oshio, T. Nabeshima, Inorg. Chem. 47 (2008) 875;
  - (e) T. Nabeshima, M. Yamamura, Pure Appl. Chem. 85 (2013) 763.
- [2] (a) D. Braga, L. Maini, M. Polito, E. Tagliavini, F. Grepioni, Coord. Chem. Rev. 246 (2003) 53;
  - (b) L. Xu, L.C. Zhu, J.C. Ma, Y. Zhang, J. Zhang, W.K. Dong, Z. Anorg. Allg. Chem. 14 (2015) 2520;
  - (c) S. Akine, T. Nabeshima, Dalton Trans. (2009) 10395;
  - (d) S. Akine, F. Utsuno, T. Taniguchi, T. Nabeshima, Eur. J. Inorg. Chem. 49 (2010) 3143;
  - (e) J.C. Ma, X.Y. Dong, W.K. Dong, Y. Zhang, L.C. Zhu, J.T. Zhang, J. Coord. Chem. 69 (2016) 149;
  - (f) W.K. Dong, Y.X. Sun, C.Y. Zhao, X.Y. Dong, L. Xu, Polyhedron 29 (2010) 2087;(g) P.A. Vigato, S. Tamburini, Coord. Chem. Rev. 252 (2008) 1871.
- [3] S.M. Aylor, R.M. Supkowski, R.L. La Duca, Inorg. Chim. Acta 361 (2008) 317.
- [4] (a) S.S. Sun, C.L. Stern, S.T. Nguyen, J.T. Hupp, J. Am. Chem. Soc. 126 (2004) 6314;
  (b) T. Katsuki, Coord. Chem. Rev. 140 (1995) 189.
- [5] (a) H. Miyasaka, N. Matsumoto, H. Okawa, N. Re, E. Gallo, C. Floriani, J. Am. Chem. Soc. 118 (1996) 981;
  - (b) E. Bayol, T. Gurten, A.A. Gurtena, M. Erbil, Mater. Chem. Phys. 112 (2008) 624;
  - (c) T. Gao, P.F. Yan, G.M. Li, G.F. Hou, J.S. Gao, Inorg. Chim. Acta 361 (2008) 2051;
  - (d) X.Q. Song, P.P. Liu, Z.R. Xiao, X. Li, Y.A. Liu, Inorg. Chim. Acta 438 (2015) 232;
  - (e) P.P. Liu, L. Sheng, X.Q. Song, W.Y. Xu, Y.A. Liu, Inorg. Chim. Acta 434 (2015) 252;
  - (f) X.Q. Song, Y.J. Peng, G.Q. Chen, X.R. Wang, P.P. Liu, W.Y. Xu, Inorg. Chim. Acta 427 (2015) 13.
- [6] (a) T.K. Ronson, H. Adams, M.D. Ward, Inorg. Chim. Acta 358 (2005) 1943;
  - (b) Y.H. Feng, C. Wang, J.X. Xu, L. Xu, D.Z. Liao, S.P. Yan, Z.H. Jiang, Inorg. Chem. Commun. 11 (2008) 549;
  - (c) X.Q. Song, P.P. Liu, Y.A. Liu, J.J. Zhou, X.L. Wang, Dalton Trans. 45 (2016) 8154;
  - (d) W.K. Dong, J.C. Ma, L.C. Zhu, Y.X. Sun, S.F. Akogun, Y. Zhang, Cryst. Growth. Des. 16 (2016) 6903;
  - (e) W.K. Dong, J.C. Ma, L.C. Zhu, Y.X. Sun, S.F. Akogun, Y. Zhang, New J. Chem. 40 (2016) 6998.
- [7]. (a) H.L. Wu, Y.C. Bai, Y.H. Zhang, Z. Li, M.C. Wu, C.Y. Chen, J.W. Zhang, J. Coord. Chem. 67 (2014) 3054;

(b) H.L. Wu, G.L. Pan, Y.C. Bai, H. Wang, J. Kong, F.R. Shi, Y.H. Zhang, X.L. Wang, Res.
Chem. Intermed. 41 (2015) 3375;
(c) H.L. Wu, C.P. Wang, F. Wang, H.P. Peng, H. Zhang, Y.C. Bai, J. Chin. Chem. Soc.
(2015) 1028;
(d) C.Y. Chen, J.W. Zhang, Y.H. Zhang, Z.H. Yang, H.L. Wu, G.L. Pan, Y.C. Bai, J. Coord.
Chem. 68 (2015) 1054;
(e) H.L. Wu, Y.C. Bai, Y.H. Zhang, G.L. Pan, J. Kong, F.R. Shi, X.L. Wang, Z. Anorg. Allg.
Chem. 640 (2014) 2062;

(f) H.L. Wu, G.L. Pan, Y.C. Bai, Y.H. Zhang, H. Wang, F.R. Shi, X.L. Wang, J. Kong, J. Photochem. Photobio. B 135 (2014) 33;

(g) H.L. Wu, G.L. Pan, Y.C. Bai, H. Wang, J. Kong, F.R. Shi, Y.H. Zhang, X.L. Wang, J. Chem. Res. 38 (2014) 211.

- [8] (a) S. Akine, T. Taniguchi, T. Nabeshima, Chem. Lett. 30 (2001) 682;
  - (b) W.K. Dong, J.C. Ma, L.C. Zhu, Y. Zhang, X.L. Inorg. Chim. Acta 445 (2016) 140.
- [9] (a) H. Miyasaka, N. Matsumoto, H. Okawa, N. Re, E. Gallo, C. Floriani. J. Am. Chem. Soc. 118 (1996) 981;
  - (b) E. Bayol, T. Gurten, A.A. Gurtena, M. Erbil. Mater. Chem. Phys. 112 (2008) 624;
  - (c) X.Q. Song, P.P. Liu, Y.A. Liu, J.J. Zhou, X.L. Wang, Dalton Trans. 45 (2016) 8154.
- [10] (a) P.G. Lacroix, Eur. J. Inorg. Chem. 2 (2001) 339;
  - (b) H.L. Wu, G.L. Pan, Y.C. Bai, H. Wang, J. Kong, F.R. Shi, Y.H. Zhang, X.L. Wang, J. Coord. Chem. 66 (2013) 2634.
- [11] (a)T.K. Ronson, H. Adams, M.D. Ward, Inorg. Chim. Acta 358 (2005) 1943.
  - (b) Y.H. Feng, C. Wang, J.X. Xu, L. Xu, D.Z. Liao, S.P. Yan, Z.H. Jiang, Inorg. Chem. Commun. 11 (2008) 549.
  - (c) Y.H. Feng, C. Wang, G.F. Xu, Y. Ouyang, D.Z. Liao, S.P. Yan, Inorg. Chem. Commun. 11 (2008) 341.
- [12] A.K. Sharma, F. Lloret, R. Mukherjee, Inorg. Chem. 46 (2007) 5128.
- [13] C. Policar, F. Lambert, M. Cesario, Eur. J. Inorg. Chem. 12 (1999) 2201.
- [14] (a) W.K. Dong, X.N. He, H.B. Yan, Z.W. Lv, X. Chen, C.Y. Zhao, X.L. Tang, Polyhedron 28 (2009) 1419;
  - (b) W.K. Dong, J. Zhang, Y. Zhang, N. Li, Inorg. Chim. Acta 444 (2016) 95;
  - (c) S. Akine, T. Taniguchi, W.K. Dong, T. Nabeshima, J. Org. Chem. 70 (2005) 1704;
  - (d) W.K. Dong, X.L. Li, L. Wang, Y. Zhang, Y.J. Ding, Sens. Actuators B 229 (2016) 370;
  - (e) W.K. Dong, F. Zhang, N. Li, L. Xu, Y. Zhang, J. Zhang, L.C. Zhu, Z. Anorg, Allg. Chem. 642 (2016) 532;

<sup>(</sup>f) W.K. Dong, J.G. Duan, Y.H. Guan, J.Y. Shi, C.Y. Zhao, Inorg. Chem. Acta 362 (2009) 1129.

[15] (a) H.F. Xu, S.H. Zhang, Y.M. Jiang, X.X. Zhong, F. Gao, Chinese J. Struct. Chem. 23 (2004) 808;

(b) A. Majumder, G.M. Rosair, A. Mallick, N. Chattopadhyay, S. Mitra, Polyhedron 25 (2006) 1753;

(c) W.K. Dong, Y.X. Sun, Y.P. Zhang, L. Li, X.N. He, X.L. Tang, Inorg. Chim. Acta 362 (2009) 117;

(d) W.K. Dong, S.F. Akogun, Y. Zhang, Y.X. Sun, X.Y. Dong, Sens. Actuators B 238 (2017) 723;

(e) L.Q. Chai, J. J. Huang, H. S. Zhang, Y. L. Zhang, J. Y. Zhang, Y. X. Li, Spectrochim. Acta, Part A 131 (2014) 526;

(f) L.Q. Chai, G. Liu, J.Y. Zhang, J.J. Huang, J.F. Tong, J. Coord. Chem. 66 (2013) 3926;

(g) L.Q. Chai, H.S. Zhang, J.J. Huang, Y.L. Zhang, Spectrochim. Acta, Part A 137 (2015) 661.

[16] (a) L. Wang, J.C. Ma, W.K. Dong, L.C. Zhu, Y. Zhang, Z. Anorg, Allg. Chem. 642 (2016) 834;

(b) L.Q. Chai, G. Wang, Y.X. Sun, W.K. Dong, L. Zhao, X.H. Gao, J. Coord. Chem. 65 (2012) 1621.

(c) P. Wang, L. Zhao, Synth. React. Inorg. Met. Org. Nano Met. Chem. 46 (2016) 1095.

(d) Y.X. Sun, L. Wang, X.Y. Dong, Z.L. Ren, W.S. Meng, Synth. React. Inorg. Met. Org. Nano Met. Chem. 43 (2013) 599;

(e) Y.X. Sun, W.K. Dong, L. Wang, L. Zhao, Y.H. Yang, Chinese J. Inorg. Chem. 25 (2009) 1478;

(f) X.Y. Dong, Y.X. Sun, L. Wang, L. Li, J. Chem. Res. 36 (2012) 387;

(g) L. Zhao, L. Wang, Y.X. Sun, W.K. Dong, X.L. Tang, X.H. Gao, Synth. React. Inorg. Met. Org. Nano Met. Chem. 42 (2012) 1303;

(h) L. Zhao, X.T. Dang, Q. Chen, J.X. Zhao, L. Wang, Synth. React. Inorg. Met. Org. Nano Met. Chem. 43 (2013) 1241;

(i) P. Wang, L. Zhao, Spectrochim. Acta, Part A 135 (2015) 342.

[17] L. Gomes, E. Pereira, B. Castro de, J. Chem. Soc., Dalton Trans. (2000) 1373.

[18] (a) L. Xu, Y.P. Zhang, J.Y. Shi, W.K. Dong, Chin. J. Inorg. Chem. 23 (2007) 1999;

(b) L. Xu, Y.P. Zhang, L. Wang, J.Y. Shi, W.K. Dong, Chin. J. Struct. Chem. 27 (2008) 183;(c) Y.X. Sun, S.T. Zhang, Z.L. Ren, X.Y. Dong, L. Wang, Synth. React. Inorg. Met. Org. Nano Met. Chem. 43 (2013) 995;

(d) Y.X. Sun, X.H. Gao, Synth. React. Inorg. Met. Org. Nano Met. Chem. 41 (2011) 973;

(e) Y.X. Sun, L. Xu, T.H. Zhao, S.H. Liu, G.H. Liu, X.T. Dong, Synth. React. Inorg. Met. Org. Nano Met. Chem. 43 (2013) 509;

(f) W.K. Dong, J.H. Feng, X.Q. Yang, Synth. React. Inorg. Metal Org. Nano Met. Chem. 37 (2007) 189;

(g) W.K. Dong, C.E. Zhu, H.L. Wu, T.Z. Yu, Y.J. Ding, Synth. React. Inorg. Met. Org. Nano Met. Chem. 37 (2007) 61.

- [19] W.Y. Bi, X.Q. Lv, W.L. Chai, W.J. Jin, J.R. Song, W.K. Wong, Inorg. Chem. Commun. 11 (2008) 1316.
- [20] (a) W.K. Dong, S.J. Xing, Y.X. Sun, L. Zhao, L.Q. Chai, X.H. Gao, J. Coord. Chem. 65 (2012) 1212;

(b) W.K. Dong, G. Li, Z.K. Wang, X.Y. Dong, Spectrochim. Acta, Part A 133 (2014) 340;

(c) W.K. Dong, C.Y. Zhao, Y.X. Sun, X.L. Tang, X.N. He, Inorg. Chem. Commun. 12 (2009) 234;

(d) W.K. Dong, X. Li, C.J. Yang, M.M. Zhao, G. Li, X.Y. Dong, Chin. J. Inorg. Chem. 30 (2014) 1911;

(e) W.K. Dong, J.C. Ma, Y.J. Dong, L.C. Zhu, Y. Zhang, Polyhedron 115 (2016) 228;

(f) W.K. Dong, L.C. Zhu, Y.J. Dong, J.C. Ma, Y. Zhang, Polyhedron 117 (2016) 148;

(g) Y.J. Dong, X.Y. Dong, W.K. Dong, Y. Zhang, L.S. Zhang, Polyhedron 123 (2017) 305.

#### Table 1 Crystal data and structure refinement for complexes 1, 2 and 3

bond	Dis. (Å)	bond	Dis. (Å)	bond	Dis. (Å)
Ni1-O1	2.073(2)	Ni1-011	2.018(2)	Ni2-09	2.140(2)
Ni1-O1 <sup>#1</sup>	2.073(2)	Ni1-O11 <sup>#1</sup>	2.018(2)	Ni2-O10	2.031(2)
Ni1-O8	2.099(2)	Ni2-O1	2.034(2)	Ni2-N2	2.078(2)
Ni1-O8 <sup>#1</sup>	2.099(2)	Ni2-08	2.027(2)	Ni2-N3	2.085(3)
bond	angles (°)	bond	angles (°)	bond	angles (°)
01-Ni1-O8	78.09(7)	01-Ni1-011	87.95(8)	O1-Ni1-O1 <sup>#1</sup>	180
O1-Ni1-O8 <sup>#1</sup>	101.91(7)	O1-Ni1-O11 <sup>#1</sup>	92.05(8)	O8-Ni1-O11	90.06(8)
O8-Ni1-O1 <sup>#1</sup>	101.91(7)	O8-Ni1-O8 <sup>#1</sup>	180	O8-Ni1-O11 <sup>#1</sup>	89.94(8)
O11-Ni1-O1 <sup>#1</sup>	92.05(8)	O11-Ni1-O8 <sup>#1</sup>	89.94(8)	O11-Ni1-O11 <sup>#1</sup>	180
O1 <sup>#1</sup> -Ni1-O8 <sup>#1</sup>	78.09(7)	O1 <sup>#1</sup> -Ni1-O11 <sup>#1</sup>	87.95(8)	O8 <sup>#1</sup> -Ni1-O11 <sup>#1</sup>	90.06(8)
01-Ni2-O8	80.66(8)	01-Ni2-O9	89.17(8)	O1-Ni2-O10	94.83(9)
O1-Ni2-N2	86.05(1)	O1-Ni2-N3	166.75(9)	08-Ni2-O9	91.21(8)
O8-Ni2-O10	90.03(9)	08-Ni2-N2	166.69(1)	O8-Ni2-N3	88.00(9)
O9-Ni2-O10	175.96(9)	O9-Ni2-N2	88.01(1)	09-Ni2-N3	84.21(1)
O10-Ni2-N2	91.66(1)	O10-Ni2-N3	91.99(1)	N2-Ni2-N3	105.12(1)
Ni1-O1-Ni2	97.37(8)	Ni1-O1-C1	133.09(2)	Ni2-O1-C1	125.09(2)
Ni1-O8-C12	132.72(2)	N3-O5-C9	112.9(3)	Ni1-O8-Ni2	96.75(8)
Ni2-O10-C18	125.5(2)	Ni2-08-C12	128.64(2)	Ni2-09-C17	125.7(2)
Ni2-N2-C7	123.5(2)	Ni1-O11-C18	131.5(2)	O2-N1-O3	122.4(3)
Ni2-N3-C10	123.6(2)	Ni2-N3-O5	128.7(2)	Ni2-N2-O4	127.2(2)

Table 2 Selected bond distances (Å) and angles (°) for complex 1.

Symmetry transformations used to generate equivalent atoms: <sup>#1</sup> 1-x, -y, 1-z.

bond	Dis. (Å)	bond	Dis. (Å)	bond	Dis. (Å)
Ni1-01	2.037(3)	Ni1-N2	2.085(4)	Ni2-O6	2.080(3)
Ni1-O6	2.035(3)	Ni1-N3	2.084(4)	Ni2-O6 <sup>#2</sup>	2.080(3)
Ni1-O10	2.032(3)	Ni2-O1	2.073(3)	Ni2-O9	2.017(3)
Ni1-O12	2.116(3)	Ni2-O1 <sup>#2</sup>	2.073(3)	Ni2-O9 <sup>#2</sup>	2.017(3)
bond	angles (°)	bond	angles (°)	bond	angles (°)
01-Ni1-O12	89.78(1)	O1-Ni2-O1 <sup>#2</sup>	180.000(1)	Ni1-O1-Ni2	97.40(1)
O1-Ni1-N2	87.00(1)	O1 <sup>#2</sup> -Ni2-O6 <sup>#2</sup>	78.48(1)	C1-O1-Ni1	125.7(3)
01-Ni1-N3	167.38(1)	O1-Ni2-O6 <sup>#2</sup>	101.52(1)	C1-O1-Ni2	132.2(3)
06-Ni1-O1	80.34(1)	01-Ni2-O6	78.48(1)	Ni1-O6-Ni2	97.25(1)
O6-Ni1-O12	89.54(1)	O1 <sup>#2</sup> -Ni2-O6	101.52(1)	C16-O6-Ni1	126.5(2)
O6-Ni1-N2	166.92(1)	O6 <sup>#2</sup> -Ni2-O6	180.0	C16-O6-Ni2	132.5(3)
O6-Ni1-N3	87.41(1)	O9 <sup>#2</sup> -Ni2-O1 <sup>#2</sup>	87.90(1)	C21-O9-Ni2	132.5(3)
O10-Ni1-O1	92.96(1)	O9-Ni2-O1	87.90(1)	C21-O10-Ni1	125.2(3)
O10-Ni1-O6	91.67(1)	O9 <sup>#2</sup> -Ni2-O1	92.10(1)	Ni1-O12-H12	118.7(1)
O10-Ni1-O12	177.16(1)	O9-Ni2-O1	92.10(1)	C18-O12-Ni1	131.1(3)
O10-Ni1-N2	92.27(2)	O9-Ni2-O6 <sup>#2</sup>	90.89(1)	C18-O12-H12	110.0(1)
O10-Ni1-N3	90.41(1)	O9 <sup>#2</sup> -Ni2-O6 <sup>#2</sup>	89.11(1)	O4-N2-Ni1	127.7(3)
N2-Ni1-O12	87.11(2)	09-Ni2-O6	89.11(1)	C7-N2-Ni1	123.7(3)
N3-Ni1-O12	87.08(1)	O9 <sup>#2</sup> -Ni2-O6	90.89(1)	O5-N3-Ni1	128.1(3)
N3-Ni1-N2	105.03(1)	O9-Ni2-O9 <sup>#2</sup>	180.0	C10-N3-Ni1	123.2(3)

Table 3 Selected bond distances (Å) and angles (°) for complex 2.

Symmetry transformations used to generate equivalent atoms: <sup>#2</sup> -x, 1-y, 1-z.

	bond	Dis. (Å)	bond	Dis. (Å)	bond	Dis. (Å)	
	Ni2-O11	2.011(4)	Ni2-N3	2.088(4)	Ni1-09	2.072(4)	
	Ni2-O1	2.041(3)	Ni2-N2	2.107(4)	Ni1-O9 <sup>#3</sup>	2.072(4)	
	Ni2-O6	2.047(3)	Ni1-O6	2.065(3)	Ni1-O1	2.084(3)	
	Ni2-O10	2.079(4)	Ni1-O6 <sup>#3</sup>	2.065(3)	Ni1-O1 <sup>#3</sup>	2.084(3)	
	bond	angles (°)	bond	angles (°)	bond	angles (°)	
	O1-Ni1-O6	77.88(13)	O1-Ni1-O9	90.54(14)	01-Ni1-O1 <sup>#3</sup>	180	
	O1-Ni1 -O6 <sup>#3</sup>	102.12(13)	O1-Ni1-O9 <sup>#3</sup>	89.46(14)	O6-Ni1-O9	90.67(14)	
	O6-Ni1-O1 <sup>#3</sup>	102.12(13)	O6-Ni1-O6 <sup>#3</sup>	180	O6-Ni1-O9 <sup>#3</sup>	89.33(14)	
	O9-Ni1-O1 <sup>#3</sup>	89.46(14)	O9-Ni1-O6 <sup>#3</sup>	89.33(14)	O9-Ni1-O9 <sup>#3</sup>	180	
	O1 <sup>#3</sup> -Ni1-O6 <sup>#3</sup>	77.88(13)	O1 <sup>#3</sup> -Ni1-O9 <sup>#3</sup>	90.54(14)	O6 <sup>#3</sup> -Ni1-O9 <sup>#3</sup>	90.67(14)	
	01-Ni2 -O6	79.25(13)	O1-Ni2 -O10	88.33(15)	01-Ni2-O11	94.09(16)	
	01-Ni2 -N2	86.65(15)	O1-Ni2 -N3	165.49(16)	O6-Ni2-O10	92.62(14)	
	O6-Ni2 -O11	91.18(15)	O6-Ni2 -N2	165.76(15)	O6-Ni2-N3	87.17(15)	
	O10-Ni2-O11	175.82(14)	O10 -Ni2 -N2	88.89(17)	O10-Ni2-N3	87.22(17)	
	O11-Ni2-N2	87.85(17)	O11 -Ni2 -N3	91.23(18)	N2-Ni2-N3	107.05(17)	
	Ni1-O1-Ni2	97.49(13)	Ni1 -01-C1	134.5(3)	Ni2-O1-C1	126.5(3)	
	Ni2-N3-C10	124.6(4)	Ni2 -06-C16	128.2(3)	Ni1-O6-Ni2	97.88(13)	
	Ni1-O6-C16	132.7(3)	Ni2 -N2-O4	128.1(3)	Ni1-09-C17	130.2(4)	
	Ni2-O11-C17 <sup>#3</sup>	128.4(4)	Ni2 -N3-O5	127.5(3)	Ni2-N2-C7	124.3(4)	
Symmetry transformations used to generate equivalent atoms: <sup>#3</sup> 1-x, 1-y, 1-z.							

Table 4 Selected bond distances (Å) and angles (°) for complex 3.

Table 5 Hydrogen bonding interactions  $[\text{\AA}, ^{\circ}]$  for complexes 1, 2 and 3

























### **Graphical Abstract:**



### **Graphical Abstract:**

Three new solvent-induced Ni(II) complexes with the chemical formulae  $[{Ni(L)(solvent)}_2(\mu$ -OAc)\_2Ni] (the solvent is methanol, n-propanol and H<sub>2</sub>O in complexes **1**, **2** and **3**, respectively) were synthesized by the reaction of the Salamo-type ligand

4,4'-dinitro-2,2'-[1,2-ethylene-dioxybis(nitrilomethylidyne)]diphenol (H<sub>2</sub>L). Interestingly, the existence of a solvent effect leads to slight differences in the crystal and supramolecular structures of complexes **1**, **2** and **3**.