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# Synthesis, structure and spectroscopic properties of two new trinuclear nickel(II) clusters possessing solvent effect

Wen-Kui Dong<sup>a,\*</sup>, Xiao Chen<sup>a</sup>, Yin-Xia Sun<sup>a</sup>, Yu-Hua Yang<sup>a</sup>, Li Zhao<sup>a</sup>, Li Xu<sup>a</sup>, Tian-Zhi Yu<sup>b</sup>

<sup>a</sup> School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, Gansu 730070, China

<sup>b</sup> Key Laboratory of Opto-Electronic Technology and Intelligent Control (Lanzhou Jiaotong University), Ministry of Education, Lanzhou 730070, China

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# ABSTRACT

Two solvent-induced trinuclear nickel(II) clusters,  $[{NiL(CH_3OH)}_2(OAc)_2Ni] \cdot 2CH_3OH$  $(\mathbf{I})$ and  $[{NiL(C_2H_5OH)}_2(OAC)_2Ni] \cdot 2C_2H_5OH$  (II), have been synthesized by the reaction of a new Salen-type bisoxime chelating ligand of 5,5'-di(*N*,*N*'-diethylamino)-2,2'-[(1,3-propylene) dioxybis(nitrilomethylidyne)]diphenol (H2L) with nickel(II) acetate tetrahydrate in different solvents. Clusters I and II were characterized by elemental analyses, IR spectra, UV-vis absorption spectra, TG-DTA and X-ray diffraction methods. In clusters I (or II), there are two ligand moieties (which provide N<sub>2</sub>O<sub>2</sub> donors), two acetate ions, two coordinated methanol (or ethanol) molecules and two crystallizing methanol (or ethanol) molecules, which result in the formation of three slightly distorted octahedral geometries around Ni(II) ions. Interestingly, nickel(II) ions in the structures of clusters I and II are all six-coordinated geometry, but clusters I and II are grown up in different solvent. Right because of this, solvent effect cause to their different crystal structures.

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# 1. Introduction

Investigation of the structures of transition metal complexes bearing Salen-type ligand or its derivatives have been the main focus of considerable recent research interest, due to their applications in organometallic chemistry, important nonlinear optical materials [1] and interesting magnetic materials [2,3]. Some of these complexes usually possess homogeneous catalysis, which have been used as catalysts for organic reactions [4], models of reaction centers of metalloenzymes [5]. So, the study on Salentype ligands and their nickel(II) complexes are still the aim of our many current investigations [6–9]. In this paper, we report the synthesis, characterization and crystal structures of a new Salen-type bisoxime ligand, 5,5'-di(*N*,*N*'-diethylamino)-2,2'-[(1,3propylene)dioxybis(nitrilomethylidyne)]diphenol (H<sub>2</sub>L), and its corresponding trinuclear nickel clusters [{NiL(CH<sub>3</sub>OH)}<sub>2</sub>(OAc)<sub>2</sub>Ni]·  $2CH_3OH(I)$  and  $[{NiL(C_2H_5OH)}_2(OAc)_2Ni]\cdot 2C_2H_5OH(II)$  possessing solvent effect.

# 2. Experimental

# 2.1. Materials

4-(*N*,*N*'-Diethylamine)-2-hydroxybenzaldehyde was purchased from Acros Organics and recrystallized from ethanol. 1,3-Bis(aminooxy)propane was synthesized according to the method reported earlier [10]. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory.

# 2.2. Methods

Elemental analysis for Ni was detected by an IRIS ER/S-WP-1 ICP atomic emission spectrometer. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. IR spectra were recorded on a VERTEX70 FT-IR spectrophotometer, with samples prepared as KBr ( $500-4000 \text{ cm}^{-1}$ ) and CsI ( $100-500 \text{ cm}^{-1}$ ) pellets. UV-vis absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. <sup>1</sup>H NMR spectra were recorded on a Mercury-400BB spectrometer at room temperature using CDCl<sub>3</sub> as a solvent. TG–DTA analyses were carried out on a ZRY-1P thermal analyzer at a heating rate of 3 °C/min. X-ray single crystal structures were determined on a Bruker Smart APEX CCD area detector. Melting point was measured by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company, and the thermometer was uncorrected. Molar conductance value measurements were carried out on a model

<sup>\*</sup> Corresponding author. Tel.: +86 931 4938703; fax: +86 931 4956512. E-mail address: dongwk@mail.lzjtu.cn (W.-K. Dong).

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DDS-11D type conductivity bridge using  $1.0\times10^{-3}$  mol dm  $^{-3}$  solution in chloroform at 25  $^\circ\text{C}.$ 

# 2.3. Synthesis of the ligand $H_2L$

# 5,5'-Di(*N*,*N*'-diethylamino)-2,2'-[(1,3-

propylene)dioxybis(nitrilomethylidyne)]diphenol  $(H_{2}L)$ was prepared by the modification of the reported method [11,12]. To an ethanol solution of 4-(*N*,*N*'-diethylamine)-2hydroxybenzaldehyde (388.4 mg and 2.01 mmol) was added an ethanol solution of 1,3-bis(aminooxy)propane (106.1 mg and 1.00 mmol). The mixture solution was stirred at 55 °C for 3 h. After cooling to room temperature, the precipitate was filtered, and washed successively with ethanol and ethanol/hexane (1:4), respectively. The product was dried under vacuum, and obtained 268.47 mg of colorless microcrystal. Yield 58.8%. m.p. 85-86 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 1.17 (t, *J*=7.2 Hz, 12H), 2.10 (t, *J*=6.4 Hz, 2H), 3.36 (dd, J=7.2Hz, 8H), 4.23 (t, J=6.4Hz, 4H), 6.22 (dd, J=2.4 Hz, 4H), 6.94 (t, J=4.6 Hz, 2H), 8.06 (s, 2H), 9.89 (s, 2H). Anal. calcd. for  $C_{25}H_{36}N_4O_4$  (%): C, 65.76; H, 7.95; N, 12.27. Found: C, 65.63; H, 7.99; N, 12.21.

Colorless needle-shaped crystals of  $H_2L$  suitable for X-ray crystal analysis were grown up from the ethanol solution by slow evaporation of the solvent at room temperature.

# 2.4. Synthesis of cluster I

A solution of nickel(II) acetate tetrahydrate (24.9 mg and 0.10 mmol) in methanol (10 ml) was added dropwise to a solution of  $H_2L$  (45.7 mg and 0.10 mmol) in acetonitrile (10 ml) at room temperature. The color of the mixing solution turned to green immediately, and then continuing stirs for 4 h at room temperature. The mixture solution was filtered and the filtrate was allowed to stand at room temperature for about one week, the solvent was partially evaporated and obtained several green prismatic single crystals suitable for X-ray crystallographic analysis. Yield 23.5 mg,

#### Table 1

Crystal data and structure refinement for  $H_2L$ , clusters  $\boldsymbol{I}$  and  $\boldsymbol{II}.$ 

52.9%. Anal. calcd for  $C_{58}H_{90}N_8Ni_3O_{16}$  (%): C, 52.32; H, 6.81; N, 8.42; Ni, 13.22. Found: C, 52.21; H, 6.86; N, 8.49; Ni, 13.17.

# 2.5. Synthesis of cluster II

Cluster **II** was prepared by the same method as that of cluster **I** except changing from methanol to ethanol. Dark-green rhombohedral crystals were isolated after two weeks following the solvent was partially evaporated. Yield 21.7 mg, 46.9%. Anal. calcd for  $C_{62}H_{98}N_8Ni_3O_{16}$  (%): C, 53.67; H, 7.12; N, 8.08; Ni, 12.69. Found: C, 53.74; H, 7.19; N, 7.99; Ni, 12.61.

# 2.6. X-ray crystallography

The single crystals of H<sub>2</sub>L, clusters **I** and **II** with approximate dimensions of  $0.50 \times 0.21 \times 0.10$ ,  $0.49 \times 0.40 \times 0.37$  and  $0.31 \times 0.30 \times 0.28$  mm were placed on a Bruker Smart diffractometer equipped with Apex CCD area detector. The diffraction was collected using a graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293(2), 298(2), 298(2) K, respectively. The structures were solved by using the program SHELXS-97 [13] and Fourier difference techniques, and refined by full-matrix least-squares method on  $F^2$  using SHELXL-97 [14]. Details of the data collection and refinements are given in Table 1. All hydrogen atoms were added theoretically.

# 3. Results and discussion

#### 3.1. Molar conductances

Clusters I and II are soluble in chloroform, DMF, DMSO, but not soluble in acetone, ethanol, methanol, ethyl acetate and hexane. Molar conductance values of clusters I and II at  $25 \,^{\circ}$ C of  $10^{-3} \,\text{mol}\,\text{dm}^{-3}$  chloroform solutions are 0.4 and  $0.5 \,\Omega^{-1} \,\text{cm}^2 \,\text{mol}^{-1}$ , respectively, indicating that clusters I and II are non-electrolyte [15]. These imply that all the acetate groups in clus-

	H <sub>2</sub> L	I	II
Empirical formula	$C_{25}H_{36}N_4O_4$	$C_{58}H_{90}Ni_8N_3O_{16}$	C <sub>62</sub> H <sub>98</sub> N <sub>8</sub> Ni <sub>3</sub> O <sub>16</sub>
Formula weight	456.58	1331.51	1387.61
Temperature (K)	293(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Monoclinic, C2/c	Triclinic, P-1	Triclinic, P-1
Unit cell dimensions (Å, °)			
а	29.922(3)	12.6579(15)	12.5101(10)
b	4.9686(5)	13.4477(16)	12.6121(14)
С	16.8353(17)	21.541(2)	13.2552(16)
β	99.345(2)	88.648(3)	67.4280(10)
Volume (Å <sup>3</sup> )	2469.7(4)	3256.0(6))	1742.5(3)
Z, Calculated density (Mg/m <sup>3</sup> )	4, 1.228	2, 1.358	1, 1.322
Absorption coefficient (mm <sup>-1</sup> )	0.084	0.928	0.870
F(000)	984	1412	738
Crystal size (mm)	$0.50 \times 0.21 \times 0.10$	$0.49 \times 0.40 \times 0.37$	$0.31 \times 0.30 \times 0.28$
heta range for data collection (°)	1.38-25.01	1.80-25.01	1.67-25.00
Limiting indices	$-35 \le h \le 31, -5 \le k \le 5, -11 \le l \le 20$	$14 \le h \le 15, -15 \le k \le 15, -19 \le l \le 25$	$-14 \le h \le 14, -12 \le k \le 14, -15 \le l \le 14$
Reflections collected/unique	5817/2164	17,051/11,292	9117/6056
	$[R_{\rm int} = 0.0668]$	$[R_{\rm int} = 0.0312]$	$[R_{int} = 0.0304]$
Completeness to $\theta$	$100\% (\theta = 25.01^{\circ})$	98.5% (θ=25.01°)	98.7% (θ=25.01°)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9917 and 0.9592	0.7252 and 0.6591	0.7927 and 0.7742
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	2164/0/152	11292/0/773	6056/0/422
Goodness-of-fit on F <sup>2</sup>	1.002	1.013	1.011
Final R indices [I > 2sigma(I)]	$R_1 = 0.0555, wR_2 = 0.1297$	$R_1 = 0.0736$ , $wR_2 = 0.1820$	$R_1 = 0.0668, wR_2 = 0.1581$
R indices (all data)	$R_1 = 0.1648, wR_2 = 0.1836$	$R_1 = 0.1392, wR_2 = 0.2388$	$R_1 = 0.1152, wR_2 = 0.1968$
Largest diff. peak and hole (e Å <sup>-3</sup> )	0.186 and -0.146	0.931 and -0.950	0.664 and -0.810



Fig. 1. Infrared absorption spectra of H<sub>2</sub>L, clusters I and II.

ters I and II are always held in the coordination sphere in solution or solid state.

# 3.2. IR spectra

IR spectra of H<sub>2</sub>L and its clusters I and II are given in Fig. 1. IR spectra indicate that clusters I and II have similar structures. The free ligand H<sub>2</sub>L exhibits Ar–O and C=N stretching bands at 1298 and 1599 cm<sup>-1</sup>, respectively, which are shifted to lower frequencies by *ca*. 54 and 16 cm<sup>-1</sup> upon complexation. This lowering of energy results from the M–O and M–N interaction upon complexation and is similar to that reported for nickel(II) clusters [16]. In addition, O–H stretching bands can be found at 3431 (or 3427) cm<sup>-1</sup> in cluster I (or II), providing the evidence for existence of crystallizing methanol (or ethanol) molecules.

The far-infrared spectra of clusters **I** and **II** are 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 IR spectrum of cluster **I** (or **II**) shows vibrational absorption frequencies at 496 (or 496) and 422 (or 426) cm<sup>-1</sup>, which are assigned to  $\nu$ (Ni–N) and  $\nu$ (Ni–O), respectively. These assignments are consistent with the literature frequency values [17–19].

#### 3.3. UV-vis absorption spectra

UV-vis absorption spectra of the ligand (H<sub>2</sub>L) and its corresponding trinuclear nickel(II) clusters I and II in the dilute chloroform solutions at 298 K are shown in Fig. 2. The spectral shapes of clusters I and II are similar to each other, and different from the shape of the ligand  $(H_2L)$ . The absorption spectrum of the free ligand (H<sub>2</sub>L) shows absorption peaks at 337 nm. This is the characteristic peak for any Salen-type ligands due to  $\pi - \pi^*$  transitions [20,21]. Noteworthy is that there is a broad absorption around 373 nm, which is seen in the corresponding Salen analogues. The absorption is ascribed to the keto-NH form of Salen-type compounds [12,22]. Compared with the absorption peak of ligand, the corresponding absorption peak of clusters I and II is observed at 345 and 346 nm, respectively, which is bathochromically shifted by ca. 8 and 9 nm, indicating that the coordination of Ni(II) ions with L<sup>2–</sup> units. Noteworthy is that the same of UV-vis absorption spectra of clusters I and II can clearly indicate the similar structure of the clusters.



Fig. 2. UV-vis absorption spectra of H<sub>2</sub>L, clusters I and II.

# 3.4. Thermal properties

Thermal decomposition process of cluster I can be divided into four stages. The first stage is at 40–55 °C. The TG curve shows that the weight loss corresponding to this temperature range is 5.1% that roughly coincides with the value of 4.8%, calculated for the loss of two crystallizing methanol molecules from the outer of cluster I. The second stage starts from 86 to 94 °C with the weight loss of 5.0%, which corresponds to the loss of two methanol molecules which takes part in coordination to the nickel atoms. The third stage degradation temperature is in the range of 202-248 °C with the mass loss of 9.3%, in which two coordinated acetate ions are removed with theoretical loss of 8.9%. The solid remains stable up to 329 °C and the fourth weight loss starts at around 335-347 °C with decomposition of the compound. The TG curve shows around 81.9% weight loss at 365 °C indicating the complete removal of organic part of the compound. The main product was NiO with a residual value of 18.1% (theoretical residual value was 16.8%).

Thermal decomposition of cluster **II** also occurs in four stages. The initial weight loss occurs in the range 46–68 °C. The TG curve shows that weight loss corresponding to this temperature range is 7.2% consistent with 6.6%, calculated for loss of two crystallizing ethanol molecules. The second stage is 88–97 °C with weight loss of 7.0%, which corresponds to the loss of two ethanol molecules coordinated to Ni. The third stage degradation temperature is in the range 230–256 °C with mass loss of 9.1%, in which two coordinated acetate ions decompose with theoretical loss of 8.5%. The solid remains stable up to 340 °C and the fourth weight loss starts at around 346–357 °C with further decomposition of the compound. The TG trace of cluster **II** shows 82.2% weight loss at 377 °C indicating complete removal of organic fragments and NiO with a residual value of 17.8% (theoretical residual value was 16.1%).

#### 3.5. Crystal structures and solvent effect

#### 3.5.1. Ligand H<sub>2</sub>L

The crystal structure of  $H_2L$  was determined by X-ray crystallography. The  $H_2L$  is sufficiently stable to resist scrambling of the C=N bonds, which may be ascribed to lower reactivity of the oxime C=N bonds toward nucleophiles. The molecule adopts a V-shaped conformation, the dihedral angle between the two halves of the molecule being  $89.77(4)^\circ$ . There is one half-molecule in the asymmetric unit, with a crystallographic twofold rotation axis passing through the central C atom (Figs. 3 and 4). The oxime groups and phenolic alcohols have trans-conformation, and there is a strong intramolecular hydrogen bond,  $O2-H2\cdots N1$ 



Fig. 3. The molecule structure of H<sub>2</sub>L with the atom numbering. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level.



Fig. 4. Packing diagram of H<sub>2</sub>L along *b*-axis. H atoms are omitted for clarity.



Fig. 5. The molecule structure of cluster I with the atom numbering. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. Each of the nickel atoms sit in an octahedral geometry.



Fig. 6. Packing diagram of cluster I along a-axis. H atoms are omitted for clarity.

(d(O2-H2) = 0.820 Å, d(H2...N1) = 1.918 Å, d(O2...N1) = 2.640(2) Å, O2-H2...N1 = 146.35°) involving the hydroxy group and adjacent oxime N atoms [9].

#### 3.5.2. Clusters I and II

Two new clusters **I** and **II**, possessing coordinated methanol and ethanol molecules, respectively, have been synthesized successfully through changing of solvent, which can help to study the influence of solvent effect in the formation and structure of the clusters.

X-ray crystallographic analysis of cluster I reveals a symmetric trinuclear structure. It crystallizes in the monoclinic system, space group C2/c, and the unit cell contains two crystallographically independent but chemical identical trinuclear clusters, molecules A and B (Fig. 5). Both molecules A and B consist of three nickel(II) ions, two L<sup>2–</sup> units, two acetate ions, two coordinated methanol molecules and two crystallizing methanol molecules. In molecule A, the terminal nickel atom (Ni2) is six-coordinated by two nitrogen atoms (N1 and N2) and two oxygen atoms (O3 and O4) in the N<sub>2</sub>O<sub>2</sub> moieties of the ligand, one oxygen atom (O6) from the bridging acetate anion and one oxygen atom (O7) from the coordinated ethanol molecule. Consequently, around Ni2 atom is a slightly distorted octahedral geometry. In addition, the central nickel (Ni1)



Fig. 7. The molecule structure of cluster II with the atom numbering. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. Each of the nickel atoms sit in an octahedral geometry.

Intermolecule H-bond (Å, °) details for clusters I and II.								

D−H···A	d(D–H)	$d(H \cdot \cdot \cdot A)$	∠DHA	$d(D \cdots A)$
Cluster I				
07-H7···016 <sup>i</sup>	0.820	1.802	175.04	2.620
014-H14015	0.820	1.792	176.72	2.611
015-H15…012 <sup>ii</sup>	0.820	1.892	169.15	2.702
016-H16…05 <sup>iii</sup>	0.820	1.911	170.71	2.724
Cluster II				
07–H7···08 <sup>iv</sup>	0.820	1.832	171.85	2.646
08–H8···05 <sup>v</sup>	0.821	1.969	169.18	2.779

Symmetry codes: (i) x, y, z - 1; (ii) -x + 1, -y, -z + 1; (iii) -x + 2, -y, -z + 1; (iv) -x + 1, -y + 1, -z + 2; (v) x, y, z - 1.

coordination sphere is completed by four  $\mu$ -phenoxo oxygen atoms (O3, O4, O3# and O4#) from two [NiL] chelates, and both of oxygen atoms (O5 and O5#) from two acetate anions which adopts a familiar  $\mu$ O-C-O fashion [9,23,24], and also constitute octahedral geometry. Compared with molecule A, molecule B is similar in the structural features but distinct in some bond distances and angles. Furthermore, the trinuclear structure is stabilized by two  $\mu$ -acetato ligands, which neutralize the whole charge of cluster I (Fig. 6).

The single crystal structures of clusters I and II are isomorphous and isostructural, so the structural features of cluster II are very similar to those of cluster I except the difference of coordinated solvent molecules (Fig. 7). Noticeably is that the structure of cluster II only contains a trinuclear cluster.

Intermolecular hydrogen bonds are existed and given in Table 2. In cluster **I**, there are four strong hydrogen bonds (include molecules A and B), 07–H7…16, 014–H14…015, 015–H15…012 and 016–H16…05, but only two hydrogen bonds exist in cluster **II**, 07–H7…08 and 08–H8…05. Every O atom from crystallizing methanol or ethanol molecules exhibits obviously strong intermolecular interactions with two nearest O atoms, one from acetate anion and one from coordinated methanol or ethanol molecule at same time.

#### 3.5.3. Solvent effect

Comparing clusters I and II, the ratio of ligands and the nickel(II) ions are both 2:3. Every terminal Ni atom forms two six-membered rings with two salicylaldoxime moieties and the acetates adopt familiar role to reinforce the structures by the bridging between the adjacent nickel(II) ions. Here, solvent effect on the nickel(II) clusters cause to their different crystal structures, in which methanol (or ethanol) molecules are coordinated to Ni2 and Ni4 in cluster I (or Ni2 in cluster II) [25].

It is clearly revealed the influence of solvent effect in selected bond distances (Å) and bond angles (°) for clusters I and II. In cluster I, the distance from O7 (coordinated methanol molecule) to plane of N1–N2–O3–O4 is 2.072(2) Å and O7–Ni2 is 2.138(2) Å, so we confirm that Ni2 is not coplanar with N1–N2–O3–O4 plane and slightly deviates toward O6 from the acetate anion. The dihedral angle of N1–Ni2–O3 and N2–Ni2–O4 is 6.24(3)° (molecules A), and the dihedral angle of N5–Ni4–O10 and N6–Ni4–O11 is 6.55(3)° (molecules B).

Cluster **II** shows distance from O7 (coordinated ethanol molecule) to plane of N1–N2–O3–O4 (2.068(3)Å) is shorter than O7–Ni2 (2.133(2)Å). As same as cluster **I**, Ni2 is also not coplanar with N1–N2–O3–O4 plane and slightly deviates toward O6 from the acetate anion. And the dihedral angle of N1–Ni2–O3 and N2–Ni2–O4 is  $4.92(2)^{\circ}$ .

The appearance of Ni2 deviates toward O6 in clusters I and II may be attributed to electrostatic attraction of acetate anion. Further, the dihedral angle of two planes (N1–Ni2–O3 and N2–Ni2–O4) in cluster II ( $4.92(2)^{\circ}$ ) is smaller than that in cluster I ( $6.24(3)^{\circ}$  or  $6.55(3)^{\circ}$ ), due to larger steric hindrance of coordinated ethanol



Fig. 8. Packing diagram of cluster II along *b*-axis. H atoms are omitted for clarity.

molecules than the coordinated methanol molecules. So, it is easily found solvent effect on clusters **I** and **II** cause to their differences in crystal structures (Fig. 8).

#### 4. Conclusions

Based on the data, description and discussion above, a new Salen-type bisoxime chelating ligand, 5,5'-di(N,N'-diethylamino)-2,2'-[(1,3-propylene)dioxybis(nitrilomethylidyne)]diphenol(H<sub>2</sub>L), and its two solvent-induced trinuclear nickel(II) cluster,  $[{NiL(CH_3OH)}_2(OAc)_2Ni] \cdot 2CH_3OH(I) \text{ and } [{NiL(C_2H_5OH)}_2(OAc)_2$ Ni]·2C<sub>2</sub>H<sub>5</sub>OH (II), have been synthesized and structurally characterized. Molar conductance values of clusters I and II in chloroform indicate that clusters I and II is non-electrolyte and all the acetate groups in clusters I and II are held in the coordination sphere. In IR spectra of clusters I and II, O-H stretching bands are found at 3431 and 3427 cm<sup>-1</sup>, implying existence of crystallizing and coordinated methanol and ethanol molecules, respectively. UV-vis spectra clearly indicated the structures of two clusters are similar and different from the ligand (H<sub>2</sub>L). X-ray crystal structures reveal that the structural features of clusters I and II are very similar except the difference of coordinated solvent molecules. Interestingly, the existence of solvent effect on clusters I and II cause to their slight differences in crystal structures.

#### 5. Supplementary material

Crystallographic data for the structure analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos: 684103 for H<sub>2</sub>L, 652648 for cluster I and 684102 for II. Copies of these information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mails: linstead@ccdc.cam.ac.uk; deposit@ccdc.cam.ac.uk, direct line: +44 1223 762910; tel.: +44 1223 336408; fax: +44 1223 336033).

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# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2009.08.037.

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