

# Synthesis and Characterization of Homo and Heterobimetallic Complexes with a Dicompartamental Macrocyclic Ligand Containing Propionitrile Pendent Arms

**Golchoubian, Hamid\***<sup>+</sup>

*Department of Chemistry, University of Mazandaran, P.O. Box 47416-95447 Babol-sar, I.R. IRAN*

**Shirvan, Atie**

*Department of Chemistry, Mohammad Reza Hariri Science Foundation, Babol,  
P.O. Box 47146-38474 Babol, I.R. IRAN*

**ABSTRACT:** A binuclear macrocyclic ligand containing dissimilar  $N(\text{amine})_2O_2$  and  $N(\text{imine})_2O_2$  coordination sites sharing two phenolic oxygen atoms, was prepared by cyclic condensation of dialdehyde precursor  $L^1H_2$  with 1,3-diaminopropane. The ligand includes two propionitrile pendant arms on the amine nitrogen atoms. The homobimetallic complex  $[ZnL^2Zn(OAc)]PF_6$  was synthesized by one step procedure. Heterobimetallic complexes  $[ZnL^2M(OAc)]PF_6$  that  $M = Cu(II)$  and  $Ni(II)$ , were prepared by a trans-metallation reaction. The prepared complexes were characterized on the basis of molar conductance measurement, elemental analysis, IR, NMR and UV-Vis spectroscopy techniques. Characterization results showed that the nitrogen atoms of propionitrile pendant arms are not involved in the coordination to the metal center and also the two metal ions are bridged by two phenolic oxygen atoms and an acetate group.

**KEY WORDS:** Dicompartamental ligand, Macrocyclic, Heterobimetallic Complex, Pendent arm, Phenol based, Propionitrile arm.

## INTRODUCTION

Dinuclear ligands and their metal complexes have been attracted attention of many researchers in recent years due to their interesting catalytic properties [1], ability to stabilize unusual oxidation states [2] and importance in biomimetic studies of binuclear metalloproteins [3]. Extensive studies have been carried out on the chemistry of mono and bimetallic complexes of dicompartamental

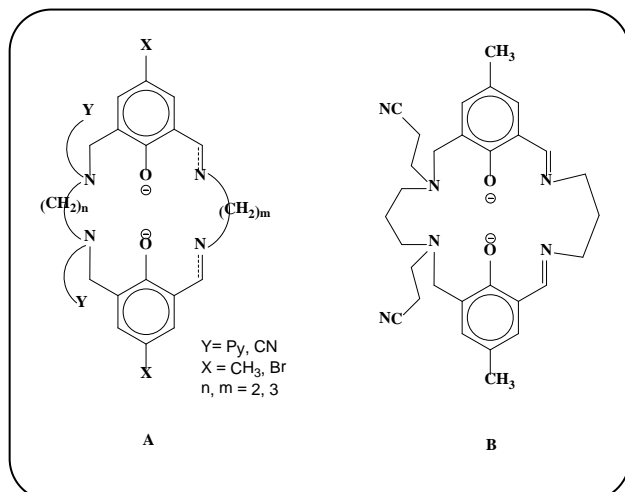
ligands. The compartmental ligands are containing two metal binding sites, that are unsymmetrical with respect to the cavity size, coordination number, geometric requirement, or the nature of the donor atoms [4,5]. Among the various types of dicompartamental ligands, special focus was on the phenol base compounds with the general structure of **A** shown in Scheme 1.

\* To whom correspondence should be addressed.

+ E-mail: h.golchoubian@umz.ac.ir

1021-9986/13/3/

7/\$/2.70



Scheme 1: Dicompartamental ligands.

Okawa and coworkers investigated the compartmental ligands with inactive pendant arms that provide two unsymmetrical tetra-coordination sites [6,7]. Researches conducted by *Bosnich* [8,9], *Busch* [10], and *Golchoubian* [11,12] shown have that by suitable design of the ligands with active pendant arms, dicompartamental ligand with hexa- and tetra coordinated sites can be achieved. These ligands potentially can provide bimetallic complexes with one coordinatively saturated and another unsaturated metal. Some types of mono and bimetallic complexes of macro-cyclic and -acyclic ligands have been prepared and their structures and reactivities were investigated in our laboratory [13-16]. In this work we prepared homo- and heterobimetallic complexes with an unsymmetrical phenol based dicompartamental ligand containing two propionitrile pendent arms as shown in type **B** in Scheme 1. This macrocyclic ligand is able to coordinate two metal ions in its different  $N(\text{amine})_2O_2$  and  $N(\text{imin})_2O_2$  compartments. Nitrile group is potentially able to coordinate to the metal ions such as  $Co(II)$ ,  $Ni(II)$ , and  $Cu(II)$  in macrocyclic complexes [17-19] and this coordination can be study by the changes of  $C\equiv N$  stretching frequency in the IR spectra [20]. The objective of this work is to investigate the influence of 1,3-diaminopropane linker ( $n = 3$  in scheme 1) on the structure of the resultant dinuclear complexes.

## EXPERIMENTAL SECTION

### Materials and measurements

All of the chemicals were of analytical grade and used without any purification. Conductance measurements

were made at  $25^\circ C$  with a Jenway 400 conductance meter on  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  samples in acetonitrile solution.  $^1H$  NMR and  $^{13}C$  NMR spectra were measured with Bruker 500 and 400 DRX Fourier Transform Spectrometers at room temperature. Infrared (IR) spectra were recorded in KBr by a single beam Bruker VECTOR22 FTIR in the range of  $400-4000 \text{ cm}^{-1}$ . Electronic spectral meagerments were carried out using UV-Vis spectrophotometer in the range of 200-800 nm. C, H, N analyses were performed on a LECO 600 CHN elemental analyzer. All samples were dried to a constant weight under high vacuum prior to analysis. The compound 2-hydroxy-3-chloromethyl-5-methylbenzaldehyde was prepared by published method [21].

### *N,N'*-bis-(2-cyanoethyl)-1,3-diaminopropane

To a methanolic solution (2mL) of 1,3-diaminopropane (20 mmol) acrylonitrile (40 mmol) was added dropwise during 40 min at room temperature. The solvent was then removed under vacuum. The desired product was obtained as a pale yellow liquid (1.74g, 97%). FT-IR ( $\nu/\text{cm}^{-1}$ ): 2246 ( $C\equiv N$  str), 3311 (b, NH str).  $^1H$  NMR (400 MHz in  $CD_3OD$ )  $\delta$  (ppm); 1.56 (br s, 2H,  $N-H$ ), 1.67 (quint, 4H,  $CH_2-CH_2-CH_2$ ), 2.52 (t, 4H,  $CH_2-CN$ ), 2.73 (t, 4H,  $CH_2-CH_2CN$ ), 2.91 (t, 4H,  $NCH_2CH_2-CH_2-N$ ).  $^{13}C$  NMR  $\delta$  (ppm); 18.7 ( $CH_2-CN$ ); 29.7 ( $CH_2-CH_2-CH_2$ ); 45.1 ( $CH_2-CH_2CN$ ); 47.8 ( $NCH_2CH_2-CH_2-N$ ), 118.8( $C\equiv N$ ).

### Dialdehyde ligand, $L^1H_2$

2-Hydroxy-3-chloromethyl-5-methylbenzaldehyde (0.92 g, 5.0 mmol), was dissolved in 1,4-dioxane (25 mL) and anhydrous  $K_2CO_3$  (1.38 g, 2.7 mmol) was added. To the resulting mixture, *N,N'*-bis-(2-cyanoethyl)-1,3-diaminopropane (0.48 g, 2.50 mmol) was then added. The reaction mixture was stirred at reflux temperature for 6 h, and was then filtered through Celite after cooling to the room temperature. Dioxane was removed in vacuum to give a thick orange-brown oil, which was treated with an aqueous solution of HCl (15%) to reach  $pH=1$ . The yellow suspension was then extracted by  $CH_2Cl_2$  ( $3 \times 20 \text{ mL}$ ). The aqueous layer was adjusted to  $pH=7.0$  with aqueous NaOH (40%) and then to  $pH = 8.4$  by the addition of a saturated aqueous solution of  $NaHCO_3$ . The oily mixture was extracted with  $CH_2Cl_2$  ( $4 \times 20 \text{ mL}$ ) and the combined organic extracts were dried over anhydrous  $Na_2SO_4$ . Filtration and concentration under reduced

pressure gave essentially pure L<sup>1</sup>H<sub>2</sub> (0.77 g, 65%) as a pale brown oil. FT-IR (v/cm<sup>-1</sup>): 2248 (C≡N str), 1650 (C=O str), 3421 (OH str). <sup>1</sup>H NMR (400 MHz in CD<sub>3</sub>OD) δ (ppm); 1.7 (m, 2H), 2.3 (s, 6H), 2.53 (t, 4H), 2.62 (t, 4H), 2.80 (t, 4H), 3.7 (s, 4H), 7.30 (s, 2H), 7.39 (s, 2H), 9.94 (s, 2H). <sup>13</sup>C NMR δ (ppm); 16.1 (CH<sub>2</sub>CN), 20.3 (Ar-CH<sub>3</sub>), 24.8 (Ar-CH<sub>2</sub>N), 38.1 (NCH<sub>2</sub>CH<sub>2</sub>CN), 49.2 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 51.5 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 119.0 (CN), 120.7 (Ar), 125.7 (Ar), 129.0 (Ar), 131.8 (Ar), 138.3 (Ar), 157.9 (Ar), 195.5 (C=O).

### Metal complexes

#### [ZnL<sup>2</sup>Zn(μ-OAc)]PF<sub>6</sub>

To a solution of ligand L<sup>1</sup>H<sub>2</sub> (0.48 g, 1.0 mmol) in ethanol (20 mL), Et<sub>3</sub>N (3 mL, 2.0 mmol) and Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.45 g, 2.0 mmol) was added, and the reaction mixture was stirred for 3h. Then a solution of 1,3-diaminopropane (0.09 mL, 1.05 mmol) and acetic acid (0.12 mL, 2.09 mmol) in ethanol were added to the resulting solution dropwise. After stirring for one day, a saturated solution of NH<sub>4</sub>PF<sub>6</sub> in ethanol was added and the resulting yellow solid was collected and washed with ethanol (2×5 mL), ether (2×5 mL), and pentane (2×5 mL). (yield: 0.3 g, 36%). Anal. Calc. for C<sub>32</sub>H<sub>40</sub>F<sub>6</sub>N<sub>6</sub>O<sub>4</sub>PZn<sub>2</sub> (M<sub>w</sub> = 848.44 g·mol<sup>-1</sup>): C, 45.30; H, 4.75; N, 9.91%. Found: C, 45.23; H, 4.74; N, 9.50%. FT-IR (v/cm<sup>-1</sup>): 2259 (C≡N str), 1628 (C=N str), 558, 848 (PF<sub>6</sub><sup>-</sup>). <sup>1</sup>H NMR (400 MHz in DMSO) δ (ppm); 2.5 (m, 2H), 2.2 (s, 6H), 2.7 (t, 4H), 3.0 (s, 4H), 3.3 (t, 4H), 3.9 (t, 4H), 7.1 (s, 2H), 7.2 (s, 2H), 8.3 (s, 2H). <sup>13</sup>C NMR δ (ppm); 8.5, 19.9, 20.2, 23.7, 29.4, 44.8, 54.4, 57.3, 62.7, 119.2, 120.3, 124.4, 124.6, 137.3, 137.8, 164.1, 171.8, 177.3.

#### [ZnL<sup>2</sup>Cu(μ-OAc)]PF<sub>6</sub>

A solution of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (0.23 g, 1.2 mmol) in ethanol (10 mL) was added to a solution of [ZnL<sup>2</sup>Zn(OAc)]PF<sub>6</sub> (0.84 g, 1.0 mmol) in CH<sub>3</sub>CN (10 mL). The green reaction mixture was stirred for 1 h. The solution was partially concentrated at room temperature to reduce CH<sub>3</sub>CN content. Ethanol was then added in portions of (2×5 mL) and the solution was stirred overnight. The dark green solid was collected and washed with ethanol (2×5 mL), ether (2×5 mL), and pentane (2×5 mL). (0.25 g, 30%). Anal. Calc. for C<sub>32</sub>H<sub>40</sub>CuF<sub>6</sub>N<sub>6</sub>O<sub>4</sub>PZn (M<sub>w</sub> = 846.6 g / mol): C, 45.40; H, 4.76; N, 9.93%.

Found: C, 45.13; H, 4.65; N, 9.49%. FT-IR (v/cm<sup>-1</sup>): 2255 (C≡N str), 1633 (C=N str), 846, 559 (PF<sub>6</sub><sup>-</sup>).

#### [ZnL<sup>2</sup>Ni(μ-OAc)]PF<sub>6</sub>

This complex was prepared by the same method described for [ZnL<sup>2</sup>Cu(μ-OAc)]PF<sub>6</sub> except that Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O was used in place of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O. The product was obtained as a pale green solid (yield: 24%). Calc. for C<sub>32</sub>H<sub>40</sub>NiF<sub>6</sub>N<sub>6</sub>O<sub>4</sub>PZn (M<sub>w</sub> = 841.7 g·mol<sup>-1</sup>): C, 45.66; H, 4.79; N, 9.98%. Found: C, 45.93; H, 4.65; N, 10.22%. IR(v/cm<sup>-1</sup>): 2260 (C≡N str), 1631 (C=N str), 843, 559 (PF<sub>6</sub><sup>-</sup>).

## RESULTS AND DISCUSSION

### Syntheses

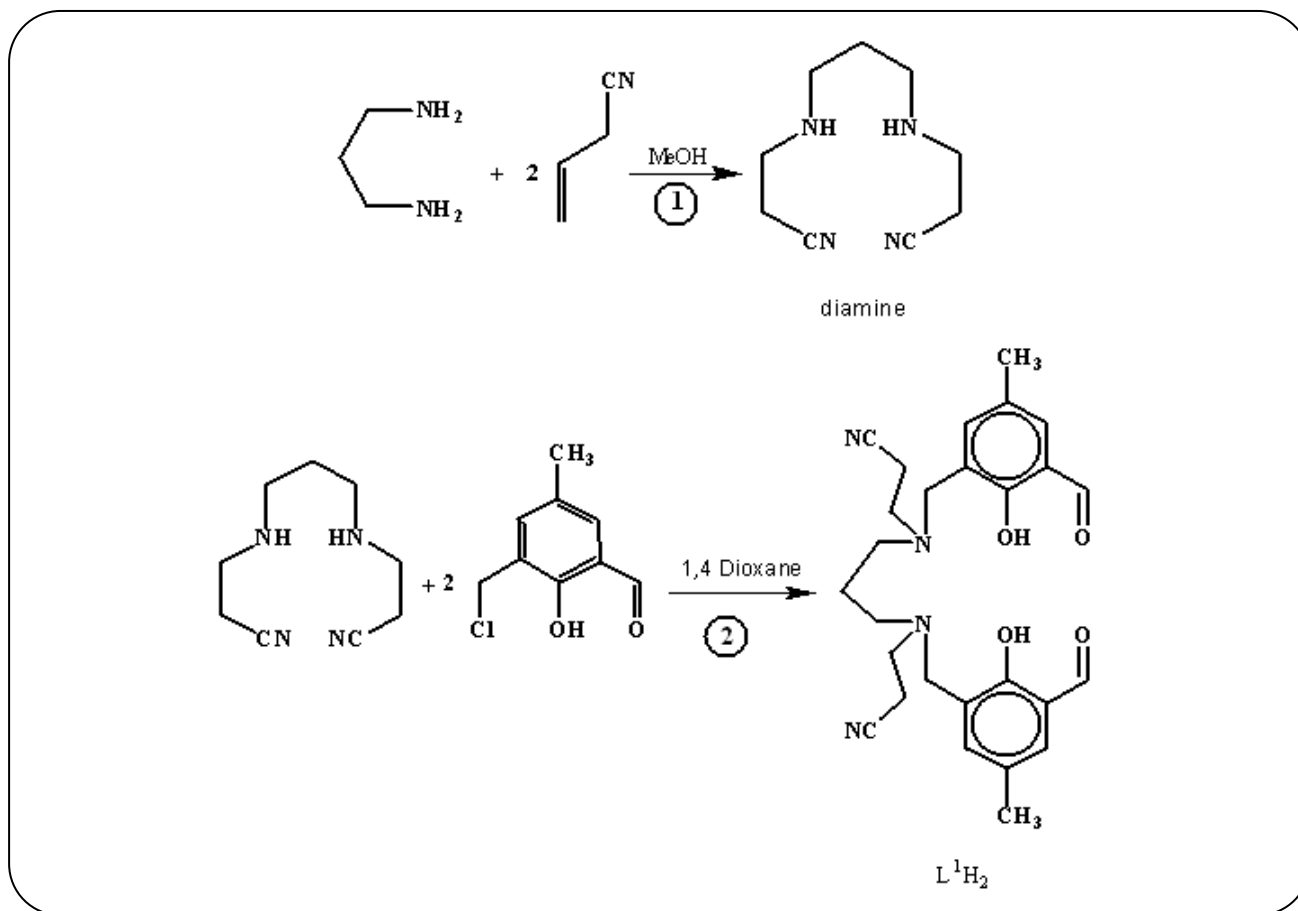
The amine moiety of the dialdehyde ligand L<sup>1</sup>H<sub>2</sub> was prepared by reaction of **1** shown in Scheme 2. This diamine compound was obtained in a high yield by condensing one part of 1,3-diaminopropane and two parts of acrylonitrile at room temperature. Reaction of one diamine molecule with two molecules of 3-chloromethyl-2-hydroxy-5-methylbenzaldehyde, in 1,4-dioxane at reflux temperature resulted in the formation of the precursor dialdehyde acyclic ligand L<sup>1</sup>H<sub>2</sub> as a viscous oil (Scheme 2, Reaction 2).

The macrocyclic homobimetallic complex [ZnL<sup>2</sup>Zn(μ-OAc)]PF<sub>6</sub> was synthesized by condensation of the dialdehyde ligand L<sup>1</sup>H<sub>2</sub> with 1,3-diaminopropane in the presence of a metal(II) ion. This complex was separated as solid from solution by the addition of saturated NH<sub>4</sub>PF<sub>6</sub>. The heterobimetallic complexes [ZnL<sup>2</sup>Cu(μ-OAc)]PF<sub>6</sub> and [ZnL<sup>2</sup>Ni(μ-OAc)]PF<sub>6</sub> were synthesized by trans-metallation reaction [7,16]. The reaction was carried out by the addition of M(OAc)<sub>2</sub>, [M= Cu(II) and Ni(II)] to the bimetallic complex [ZnL<sup>2</sup>Zn(μ-OAc)]PF<sub>6</sub> at room temperature. The synthetic route for the bimetallic complexes is shown in Scheme 3.

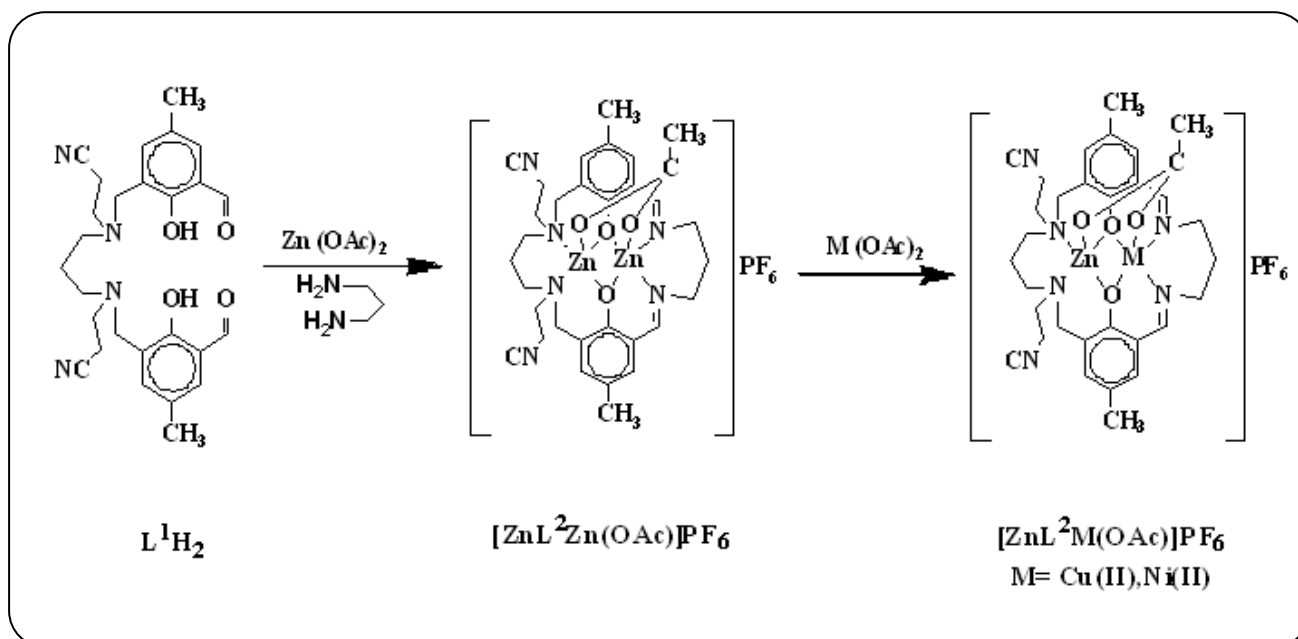
### Characterization

#### NMR spectra

The NMR spectra of the ligand shows a signal at 9.94 ppm and 195.5 ppm in <sup>1</sup>H NMR and <sup>13</sup>C NMR, respectively correspond to the aldehyde proton and aldehyde carbon. Absence of these signals and appearance of a signal at 8.3 ppm in <sup>1</sup>H NMR is associated to the iminic proton and that of 177.3 ppm



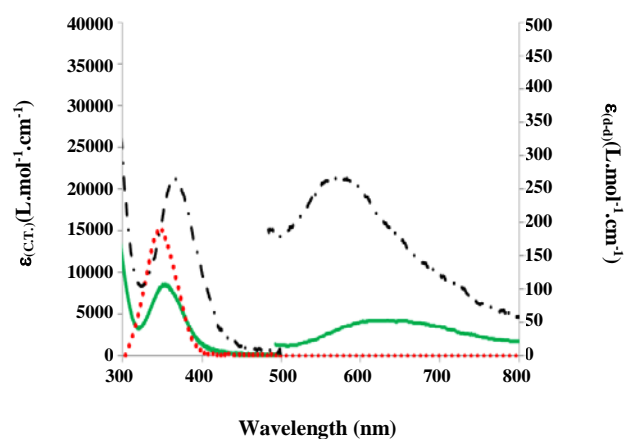
Scheme 2. Preparation of diamine (reaction 1) and dialdehyde (reaction 2) precursors.



Scheme 3. Synthesis scheme for preparation of dinuclear complexes.

**Table 1: Molar conductivity values of the complexes in acetonitrile solution.**

Compound	$\Lambda_m$ of the complexes, ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ , at 25°C)
$[\text{ZnL}^2\text{Zn}(\mu\text{-OAc})]\text{PF}_6$	136
$[\text{ZnL}^2\text{Cu}(\mu\text{-OAc})]\text{PF}_6$	127
$[\text{ZnL}^2\text{Ni}(\mu\text{-OAc})]\text{PF}_6$	134
1:1 electrolytes	120–160
1:2 electrolyses	220–300

**Fig. 1: The electronic absorption spectra of the heterodinuclear complex.**

in  $^{13}\text{CNMR}$  belongs to the iminic carbon of  $[\text{ZnL}^2\text{Zn}(\mu\text{-OAc})]\text{PF}_6$ . These results indicate complete closure of the ligand.  $^1\text{HNMR}$  and  $^{13}\text{CNMR}$  of this complex show the signals corresponding to half of the molecule that is indicative of a symmetrical structure.

### Conductometric data

Conductometric data of the synthesized bimetallic complexes in acetonitrile at 25°C are presented in Table 1. The molar conductance,  $\Lambda_m$  of all these complexes are in agreement with expected range of the value for two-ion electrolytes. The results are consistent with their formulas [22] and confirm the present of one acetate ion in the inner coordination sphere and one  $\text{PF}_6^-$  ion in the secondary coordination sphere of the complexes. This characterization in agreement with our pervious results with ethylenediamine link in place of 1,3-diaminopropan [16].

### Infrared spectra

The IR spectra of acyclic ligand  $\text{L}^1\text{H}_2$  show the  $\text{C}=\text{O}$  and  $\text{C}\equiv\text{N}$  stretching bands at  $1650\text{ cm}^{-1}$  and  $2248\text{ cm}^{-1}$ , respectively. The vibration at  $1650\text{ cm}^{-1}$  shifts to  $1630\text{ cm}^{-1}$  due to transformation of  $\text{C}=\text{O}$  aldehyde band to  $\text{C}=\text{N}$  imin band in the cyclic complexes [23,24]. The IR spectra of the complexes are nearly identical. Two sharp bands at  $550$  and  $840\text{ cm}^{-1}$  in these complexes, attributed to the anti- symmetric stretching and anti-symmetric bending vibration of  $\text{PF}_6^-$ , respectively [25,26]. The  $\text{C}\equiv\text{N}$  stretching band in the complexes appears approximately in the same position as the free ligand indicating that the nitrogen atoms of the propionitrile pendant arms are not involved in coordination to metal center. In the dinuclear complexes anti-symmetric and symmetric vibration of the acetate group appears at  $1580$  and  $1440\text{ cm}^{-1}$ , respectively. The small separation between the two vibration modes (less than  $150\text{ cm}^{-1}$ ) indicates bridging acetate in the complex [16, 27].

### Electronic absorption spectra

The Electronic absorption spectra of the synthetic complexes were recorded in acetonitrile solutions over the range of 200-800 nm (Fig. 1). This region includes d-d transitions and some metal-ligand charge transfers. The visible spectrum of the complex  $[\text{ZnL}^2\text{Cu}(\mu\text{-OAc})]\text{PF}_6$  shows a band at about 600 nm assigned to the d-d transition of the copper center. The d-d transition of nickel(II) in  $[\text{ZnL}^2\text{Ni}(\mu\text{-OAc})]\text{PF}_6$  complex causes a broad peak in this region. The observed bands at 270 nm and round 350-370 nm in the binuclear complexes are attributed to the azomethine linkage [28,29] and intraligand  $\pi\text{-}\pi^*$  transition, respectively [29].

### CONCLUSIONS

The dicompartmental macrocyclic ligand containing  $\text{N}(\text{amine})_2\text{O}_2$  and  $\text{N}(\text{imine})_2\text{O}_2$  coordination sites with two propionitrile pendant arms were synthesized by a stepwise method and the homo and heterobimetallic complexes were prepared. Characterization results show that the  $-\text{CN}$  moieties of the pendant arms are not participate in binding to the metal ions. All attempts to obtain single crystals of the desired quality for X-ray crystallography to determine their structure have been failed. However, the comparison of the characterization results with those analogous complexes that their

structures were established by x-ray crystallography confirms the structure shown in Scheme 3 (see supplementary materials Figs. S1-S8).

#### Acknowledgement

We are grateful for the financial support of Mazandaran University of the Islamic Republic of Iran.

Received : Feb. 8, 2014 ; Accepted : Jun. 9, 2014

#### REFERENCES

- [1] Golchoubian H., Nemati Kharat Ghaziani A., Hydrogen Peroxide Oxidation of Mono-and Disubstituted Alkylarenes Catalyzed by Dinuclear Co(III)-Cu(II) Macrocyclic Complex, *Polish J. Chem.*, **79**, p. 825-830 (2005).
- [2] Rezvani A., Hadadzadeh H., Synthesis, Electrochemical Properties and Spectroscopic Studies of Mono and Dinuclear Zn (II) Polypyridyl Complexes with Phenylcyanamide Ligands, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **28**, p. 63-70 (2009).
- [3] Babcock G.T., Vickery L.E., Palmer G., The Electronic State of Heme in Cytochrome Oxidase II. Oxidation-Reduction Potential Interactions and Heme Iron Spin State Behavior Observed in Reductive Titrations, *J. Bio. Chem.*, **253**, p. 2400-2411 (1978).
- [4] Sreedaran S., Bharathi K.S., Rahiman A.K., Jagadish L., Kaviyarasan V., Narayanan V., Novel Unsymmetrical Macrocyclic Dicompartamental Binuclear Copper (II) Complexes Bearing 4-and 6-Coordination Sites: Electrochemical, Magnetic, Catalytic and Antimicrobial Studies, *Polyhedron*, **27**, p. 2931-2938 (2008).
- [5] Yonemura M., Nakamura Y., Usuki N., Okawa H., Macrocyclic Effects Upon Isomeric Cu<sup>II</sup>M<sup>II</sup> and M<sup>II</sup>Cu<sup>II</sup> Cores. Formation with Unsymmetric Phenol-Based Macrocyclic Ligands, *J. Chem. Sci.*, **112**, p. 291-310 (2000).
- [6] Yonemura M., Matsumura Y., Furutachi H., Ohba M., Okawa H., Fenton D.E., Migratory Transmetalation in Diphenoxo-Bridged Cu(II)M(II) Complexes of a Dinucleating Macrocyclic Ligand with N (amine)<sub>2</sub>O<sub>2</sub> and N(imine)<sub>2</sub>O<sub>2</sub> Metal-Binding Sites, *Inorg. Chem.*, **36**, p. 2711-2717 (1997).
- [7] Yonemura M., Ohba M., Takahashi K., Okawa H., Fenton D.E., Dinuclear Cu<sup>II</sup>M<sup>II</sup> Complexes of a Phenol-Based Macrocyclic Ligand with N(amine)<sub>2</sub>O<sub>2</sub> and N(imine)<sub>2</sub>O<sub>2</sub> Metal-Binding Sites: the Effect of Chloride Ligation Upon the Site Selectivity of Metal Ions, *Inorg. Chim. Acta*, **283**, p. 72-79 (1998).
- [8] Fraser C., Johnston L., Rheingold A.L., Haggerty B.S., Williams G. K., Whelan J., Bosnich B., Bimetallic Reactivity, Synthesis, Structure and Reactivity of Homo-and Heterobimetallic Complexes of a Binucleating Macrocyclic Ligand Containing 6-and 4-Coordination Sites, *Inorg. Chem.*, **31**, p. 1835-1845(1992).
- [9] McCollum D.G., Hall L., White C., Ostrander R., Rheingold A.L., Whelan J., Bosnich B., Bimetallic Reactivity. Preparation and Characterization of Symmetrical Bimetallic Complexes of a Binucleating Macrocyclic Ligand, Cytim, Containing 6-and 4-Coordinate Sites, *Inorg. Chem.*, **33**, p. 924-933(1994).
- [10] Rybak-Akimova E.V., Alcock N.W., Busch D.H., Dicompartamental Ligands with Hexa-and Tetradentate Coordination Sites: One-Step Synthesis of Ligands and Metal Complexes and Their X-Ray Structure Analysis, *Inorg. Chem.*, **37**, p. 1563-1574 (1998).
- [11] Golchoubian H., Baktash E., Welter R., Preparation and Characterization of Mono-and Hetero-Dinuclear Complexes with a Dicompartamental Macrocyclic Ligand Containing Hexa-and Penta-Coordination Sites, *Inorg. Chem. Commun.*, **10**, p. 1035-1039 (2007).
- [12] Golchoubian H., Mardani H.R., Bruno G., Amiri Rudbari H., Synthesis of Mono-and Heterodinuclear Complexes with Unsymmetrical Phenol-Based Dicompartamental Ligand Containing Hexa-and Tetradentate Coordination Sites: An Unusual Methyl Elimination in Coordination Chemistry, *Inorg. Chim. Acta*, **383**, p. 250-256 (2012).
- [13] Niazi Rahnema A., Golchoubian H., Pritchard R., Preparation of Monometallic Complexes of Non-Macrocyclic Ligands, *Bull. Chem. Soc. Jpn*, **78**: 1047-1053 (2005).
- [14] Golchoubian H., Baktash E., Welter R., Synthesis and Characterization of Mono-and Heterodinuclear Complexes with Dicompartamental Macrocyclic Ligand Containing Hexa-and Pentadentate Coordination Sites, *Inorg. Chem. Commun.*, **10**: 120-(2007).

- [15] Golchoubian H., Rostami L., Kariuki B., Preparation of Heterodinuclear Complexes with Phenol-Based Compartmental Ligands Containing Hexa-and Tetradentate Coordination Sites, *Polyhedron*, **29**, p. 1525-1533 (2010).
- [16] Golchoubian H., Fateh D.S., Bruno G., Rudbari H.A., Homo and Heterodinuclear Complexes Derived From Unsymmetrical Macrocyclic Ligands with Two Coordination Sites: Removal of a Pendant Arm and Migration of Copper Ion Upon Cyclization, *J. Coord. Chem.*, **65**, p. 1970-1991 (2012).
- [17] Yonemura M., Arimura K., Inoue K., Usuki N., Ohba M., Okawa H., Coordination-Position Isomeric  $M^{II}Cu^{II}$  and  $Cu_{III}M^{II}$  ( $M = Co, Ni, Zn$ ) Complexes Derived from Macrocyclic Compartmental Ligands, *Inorg. Chem.*, **41**, p. 582-589 (2002).
- [18] Furutachi H., Fujinami S., Suzuki M., Ōkawa H., Dinuclear  $Co^{II}M^{II}$  ( $M = Pb$  or  $Co$ ) Complexes Having a "Co (salen)" Entity in a Macrocyclic Framework: Ligand Modulation Effect and Neighboring Metal (II) Effect Upon Oxygenation at the "Co (Salen)" Center, *J. Chem. Soc. Dalton Trans.*, 2761-2769 (2000).
- [19] Inoue K.J., Ohba M., Okawa H., Heterodinuclear  $M^{II}Ni^{II}$  ( $M = Co, Ni, Cu, Zn$ ) Complexes of a Macrocyclic Compartmental Ligand. Anomalous EPR of  $Cu^{II}Ni^{II}$  Complex by Coordination of 1-Methylimidazole, *Bull. Chem. Soc. Jpn.*, **75**, p. 99-107 (2002).
- [20] Farona M.F., Bremer N.J., Sussinonitrile Derivatives of Halogenopentacarbonyl manganese(I), *J. Am. Chem. Soc.*, **88**, p. 3735-3740 (1966).
- [21] Sun G.C., He Z.H., Li Z.J., Yuan X.D., Yang Z.J., Wang G.X., Liu C.R., Facile Synthesis of 1, 6-Bis (2-furyl)-2, 5-bis (2-hydroxy-3-formyl-5-methylbenzyl)-2, 5-diazahexane: a New Dinucleating Ligand, *Molecules*, **6**, p. 1001-1005 (2001).
- [22] Geary W.J., The Use of Conductivity Measurements in Organic Solvents for the Characterisation of Coordination Compounds, *Coord. Chem. Rev.*, **7**, p. 81-122 (1971).
- [23] Robinson J.W., "Practical Handbook of Spectral Data", Wiley-Interscience: New York (1997).
- [24] Silverstein R.M., Bassler G.C., "Spectrometric Identification of Organic Compound", Wiley & Sons: New York (1988).
- [25] Dolphin D.A. Wick, "Tabulation of Infrared Spectral Data", Wiley-Interscience: New York (1977).
- [26] Nakamuta K., "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 4th Ed., Section II.8. Wiley-Interscience: New York (1988).
- [27] Deacon G.B., Phillips R.J., Relationships Between the Carbon-Oxygen Stretching Frequencies of Carboxylate Complexes and the Type of Carboxylate Coordination, *Coord. Chem. Rev.*, **33**: 227-250 (1980).
- [28] Furutachi H., Ishida A., Miyasaka H., Fukita N., Ohba M., Ōkawa H., Koikawa M.,  $Fe^{II}Pb^{II}$  and  $Fe^{III}$  Complexes of Macrocyclic Compartmental Ligands: Different Cyclization in Stepwise Template Synthesis Using  $Fe^{II}/Pb^{II}$  or  $Fe^{III}/Pb^{II}$  pairs, *J. Chem. Soc., Dalton Trans.*, 367-263 (1999).
- [29] Shi Q., Cao R., Li X., Luo J., Hong M., Chen Z., Syntheses, Structures, Electrochemistry and Magnetic Properties of Chain-Like Dicyanamide Manganese (III) and Iron (III) Complexes with Salen Ligand, *New J. Chem.*, **26**, p. 1397-1401 (2002).

## Supplementary materials

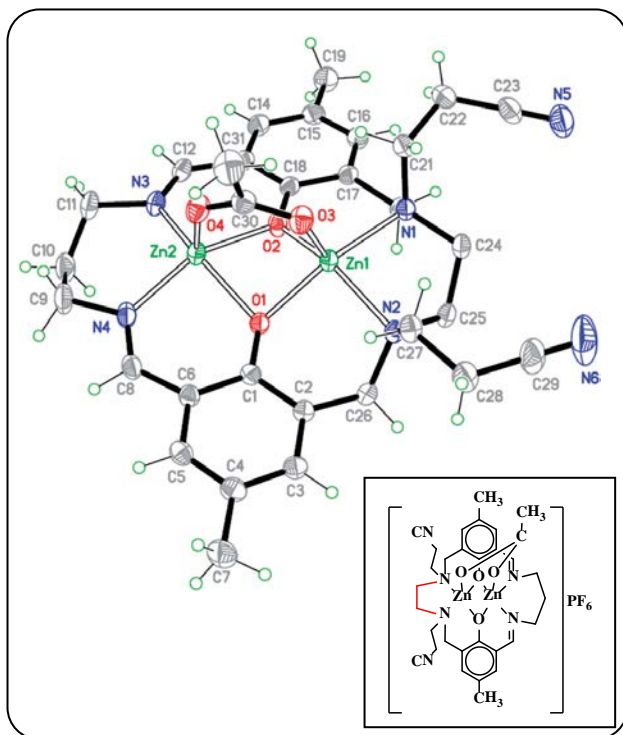


Fig. S1: The structure of similar complex to  $[ZnL^2Zn(\mu-OAc)]PF_6$  that was published before Golchoubian, H.; Sadeghi Fateh, D.; Bruno, G.; Amiri Rudbari, H. J. *Coord. Chem.* 2012, 65, 1970.

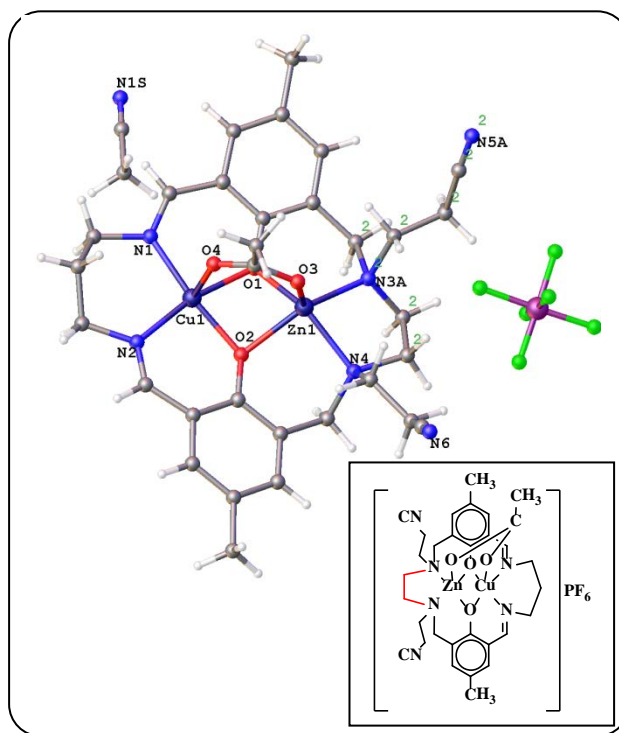


Fig. S2: The structure of similar complex to  $[ZnL^2Cu(\mu-OAc)]PF_6$  that was published before Golchoubian, H.; Sadeghi Fateh, D.; Bruno, G.; Amiri Rudbari, H. J. *Coord. Chem.* 2012, 65, 1970.

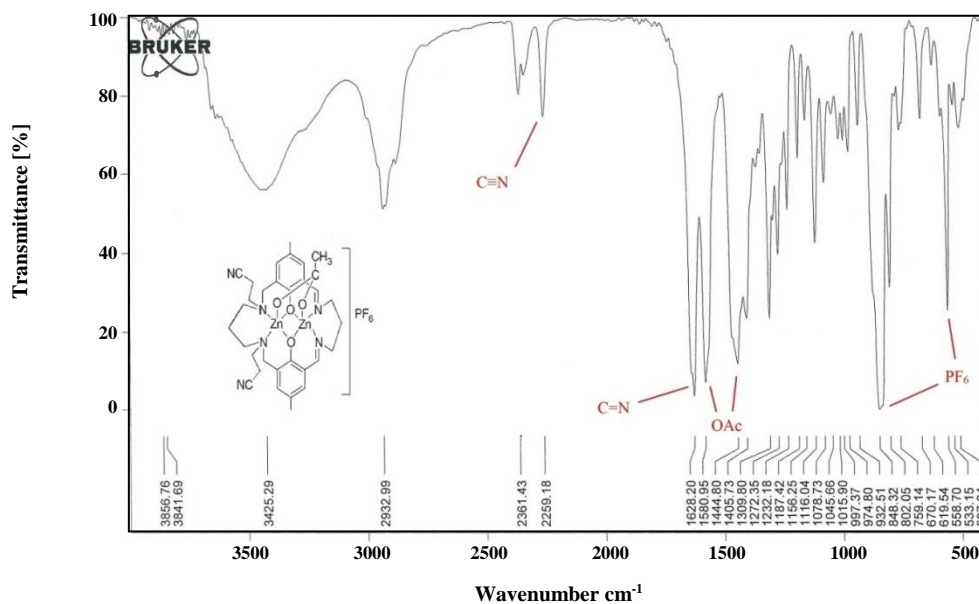


Fig. S3: IR spectrum of  $[ZnL^2Zn(\mu-OAc)]PF_6$ .



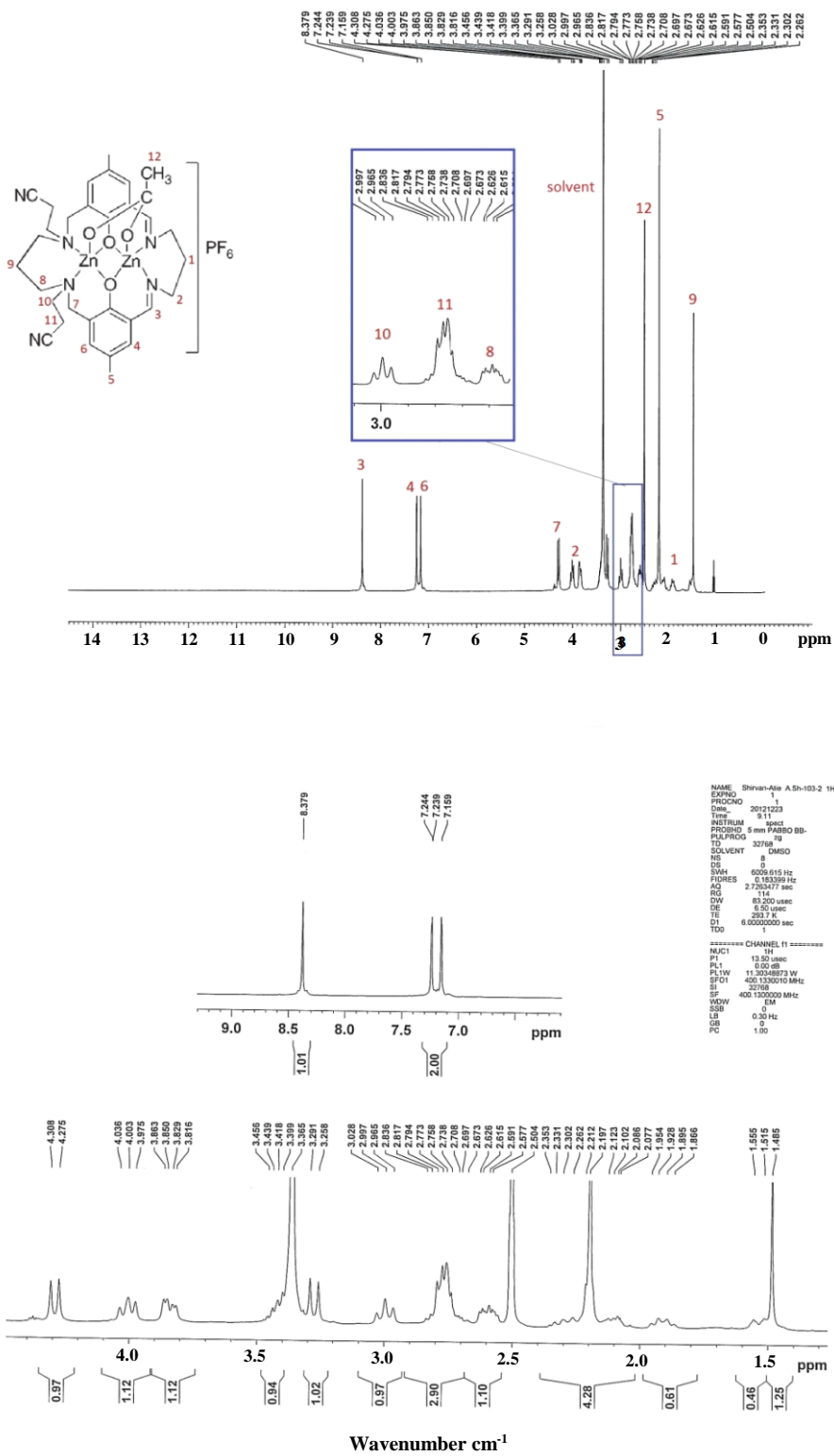


Fig. S4:  $^1\text{H}$  NMR spectrum of  $[\text{ZnL}^2\text{Zn}(\mu\text{-OAc})]\text{PF}_6$ .

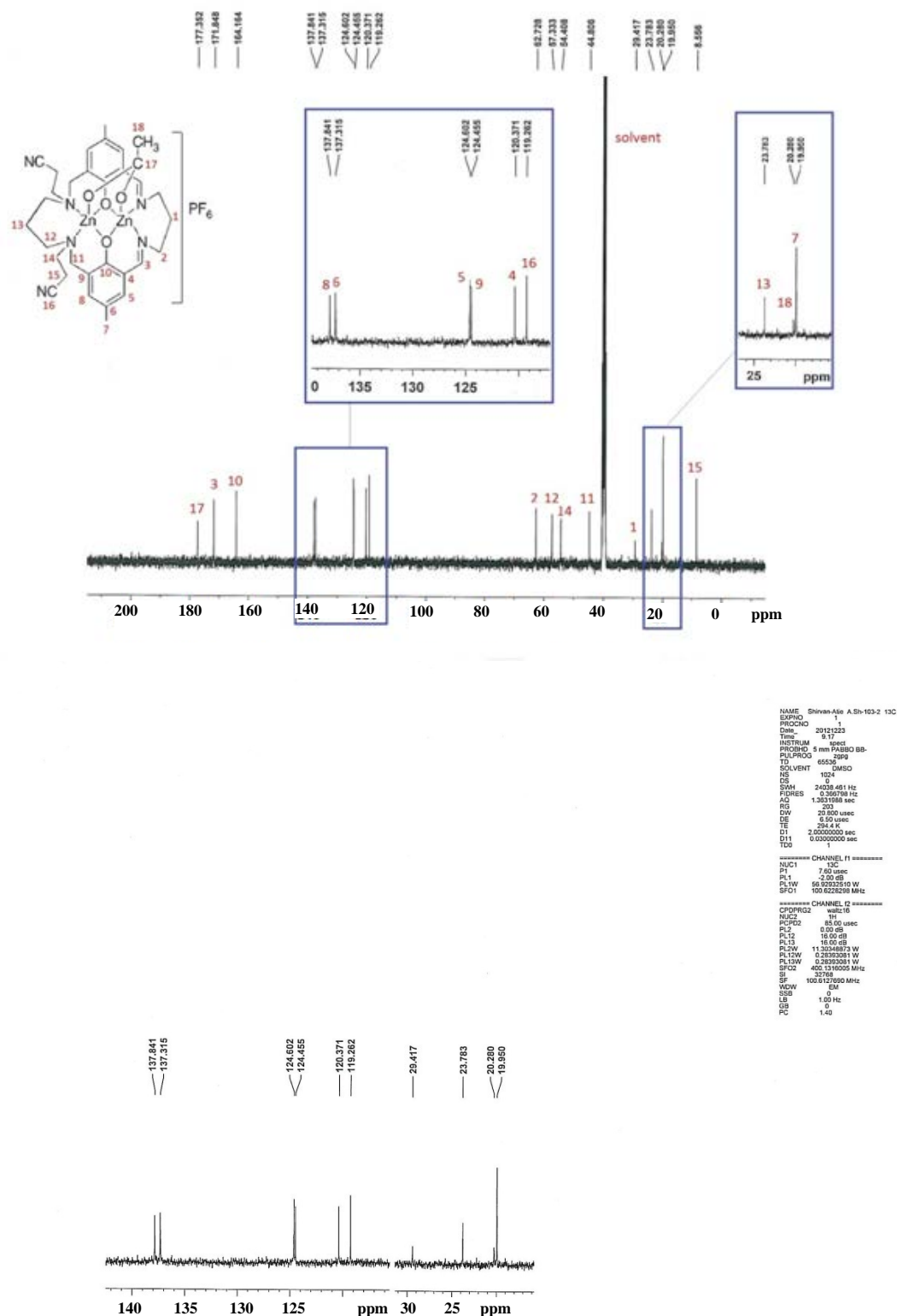


Fig. S5: <sup>13</sup>C NMR spectrum of  $[ZnL^2Zn(\mu-OAc)]PF_6$ .

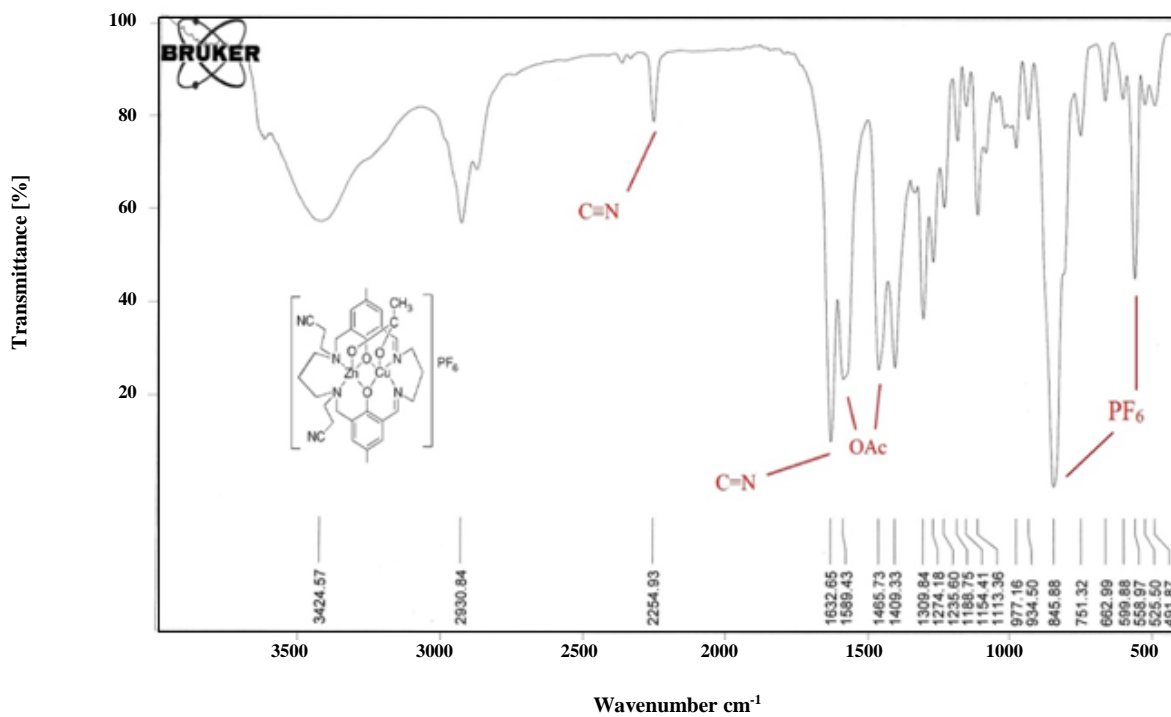


Fig. S6: IR spectrum of  $[\text{ZnL}^2\text{Cu}(\mu\text{-OAc})]\text{PF}_6$ .

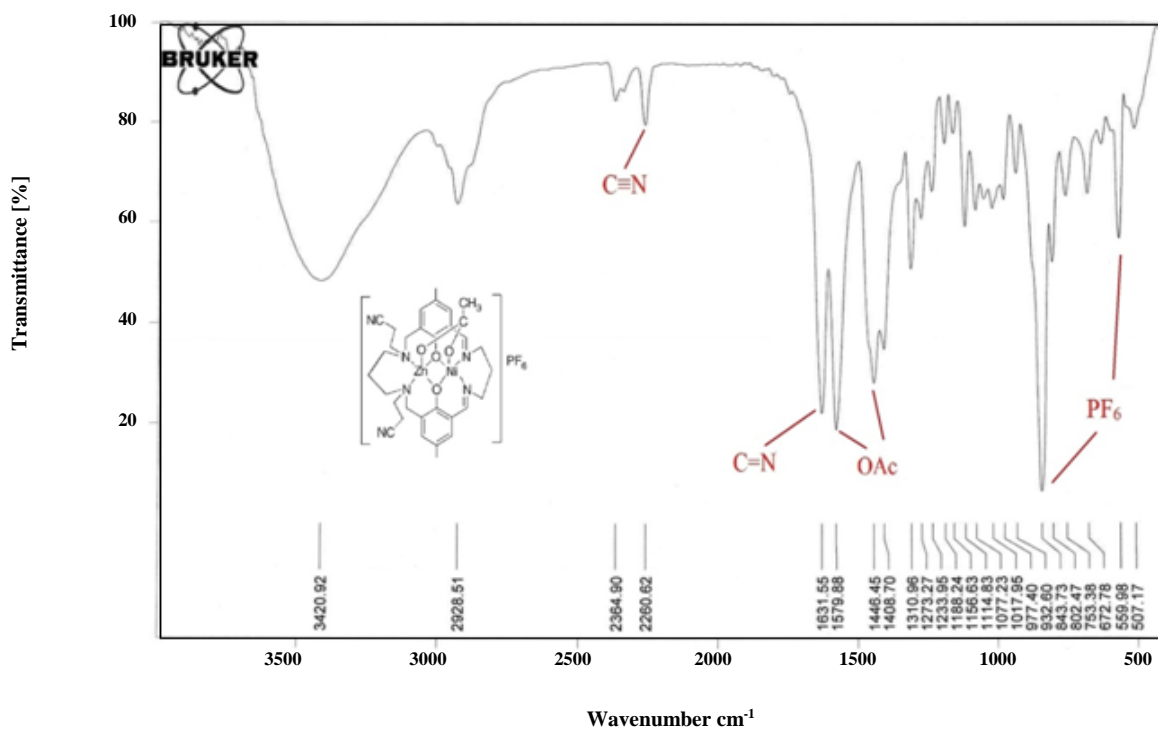


Fig. S7: spectrum of  $[\text{ZnL}^2\text{Ni}(\mu\text{-OAc})]\text{PF}_6$ .

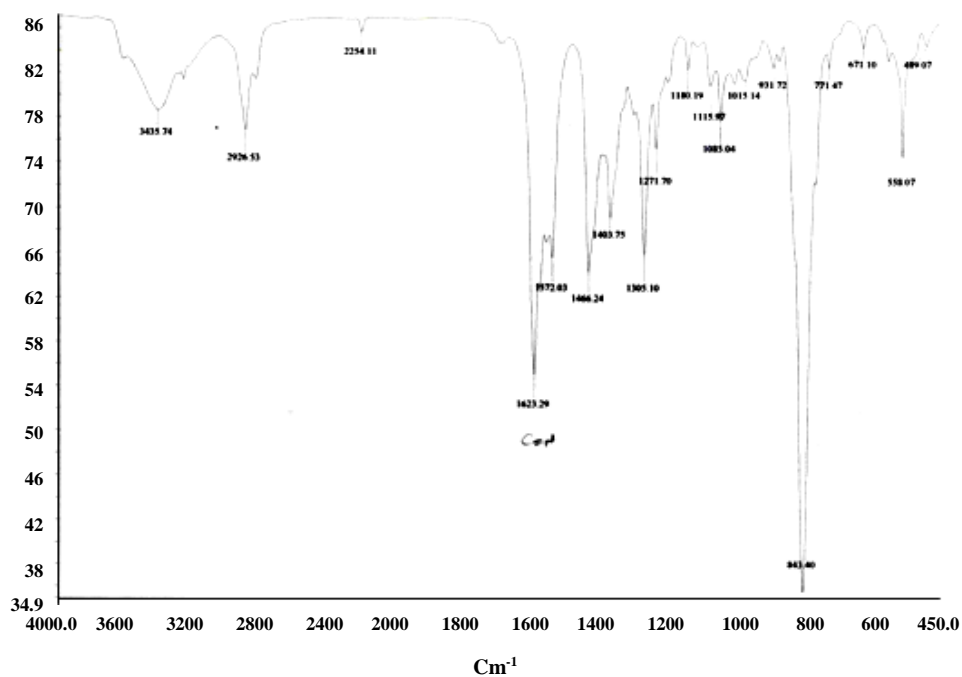


Fig. S8: The IR spectrum of similar complex to  $[ZnL^2Cu(\mu-OAc)]PF_6$  that its structure was confirmed by X-ray crystal structure and published before Golchoubian, H.; Sadeghi Fateh, D.; Bruno, G.; Amiri Rudbari, H. *J. Coord. Chem.* 2012, 65, 1970.

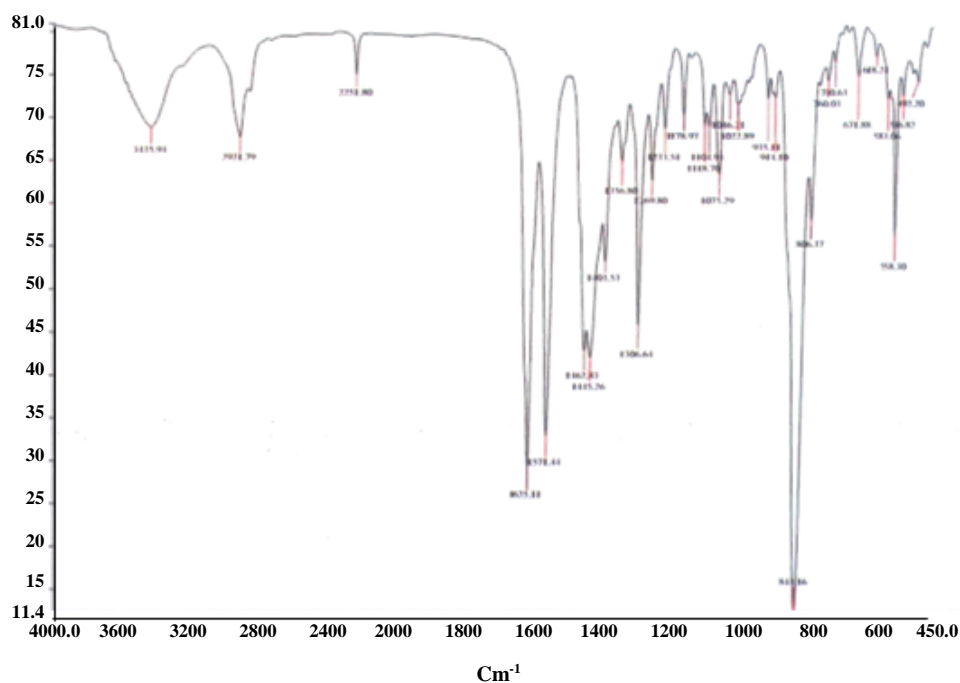


Fig. S9: The IR spectrum of similar complex,  $[ZnL^2Zn(\mu-OAc)]PF_6$  that its structure was confirmed by X-ray crystal structure and published before ; Golchoubian, H.; Sadeghi Fateh, D.; Bruno, G.; Amiri Rudbari, H. *J. Coord. Chem.* 2012, 65, 1970.