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#### **CRediT** author statement

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# The effect of electronegativity upon the coordination sphere; heterodinuclear Ni(II) complexes with ONNO type Schiff bases, octahedral, square pyramidal and square planar coordination of Ni(II)

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#### Abstract

NiL.MX<sub>2</sub> heterodinuclear complexes with a nuclear structure of Ni<sup>II</sup>-M<sup>II</sup> (M = Zn, Cd, X = Cl, Br, I) were prepared in the dioxane medium by the use of an ONNO type ligand, Bis-N,N'(salicylidene)-1,3-propanediamine (LH<sub>2</sub>). The complexes prepared were characterized by the use of infrared (IR) spectroscopy, thermogravimetry (TG), semi-micro nitrogen, metal and halogen analysis. The molecular structures and unit cell properties of the compounds were elucidated by the X-ray diffraction (XRD) method. In parallel to the literature, MX<sub>2</sub> group was observed to form  $\mu$ - bridges with the phenolic oxygens of the organic ligand. The coordination sphere of NiL heterodinuclear complex in NiL group was observed to change depending upon the electronegativities of the atoms in MX<sub>2</sub> group. The electronegativities of the atoms in the MX<sub>2</sub> group affect the coordination sphere of NiL group of the heterodinuclear complex, and in parallel with the electronegativities of the atoms in MX<sub>2</sub> group, it was observed that NiL unit coordinated the solvent molecules and the coordination sphere changed. In addition to this, the coordination bonds get smaller as the number of donor atoms nearby NiL decreased. Using Gaussian 09 software, the theoretical bond lengths and bond angles were calculated and compared with the experimental data. With the Gaussian 09 software, it was determined how the occupancy levels of d orbitals of the metal atoms changed by coordination of Ni(II) ion. Also, the change of the differences between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of the complexes was monitored.

**Keywords:** Salpn type Schiff base; Heteronuclear complexes; Thermogravimetry; Theoretical calculation; DFT; NBO

# **1. Introduction**

Bis-N,N'(salicylidene)-1,3-diaminopropane (LH<sub>2</sub>) is an O<sub>2</sub>N<sub>2</sub> type tetradentate ligand known since 1946 [1]. It has a very high tendency to give polynuclear complexes. The first dinuclear complex prepared by the use of this ligand was reported in 1976 [2]. The magnetic anomaly of Ni(II) and Cu(II) complexes of this ligand was noticed in the early 1960s. However, the polynuclear complex formation of this ligand could not be verified due to the lack of X-ray methods at that time [3]. The first trinuclear Ni(II) complex of LH<sub>2</sub> ligand was reported in1990 [4]. From that time today, there have been so many dinuclear [5-7], trinuclear [4,8-13], tetranuclear [14-17] and polynuclear [18] complexes were and are still being reported in the literature. The structures of the mononuclear of Ni(II) and Cu(II) complexes of LH<sub>2</sub> has first appeared in 1985 [19]. NiL complex was found to have a square planar coordination sphere. NiL complex is dissolved in common organic solvents, attach the other coligands and solvent molecules forming square pyramidal coordination spheres [20]. In the presence of other Lewis acids result in the formation of dinuclear Ni(II) complexes with octahedral and occasionally square pyramidal coordination sphere, dinuclear [NiL.ZnBr<sub>2</sub>.x(4-picoline)] complexes have been previously reported using NiL, ZnBr<sub>2</sub> and 4-methylpyridine (4-picoline) as coligand [21]. In the reported study, depending on 4-picoline concentration, [NiL.ZnBr<sub>2</sub>.(4-picoline)<sub>2</sub>] octahedral complex or at low 4-picoline concentration [NiL.ZnBr<sub>2</sub>.(4-picoline)] square pyramidal coordination sphere was obtained. In this study, Ni-picoline nitrogen distance in square pyramidal coordination was found shorter than Ni-picoline nitrogen distance in the octahedral complex. This is probably caused by ZnBr<sub>2</sub> molecule. ZnBr<sub>2</sub> attracts the electrons of NiL unit through phenolic oxygen and attaches the coligand molecules to itself due to the decreasing electron density of Ni(II) ion. If a single coligand is attached, Ni(II) ion will attract more electrons, so the coordination bond will be shorter. If two coligands are attached, the coordination bonds will be longer. Consequently, the electronegativity of Lewis acid bound to the structure affects the coordination sphere of Ni(II) ion.

The aim of this study was to investigate the change of the coordination of Ni(II) in the NiL group, depending on the electronegativity or hardness of the Lewis acid bound to NiL group. In this study, dinuclear complexes were prepared by the use of  $ZnX_2$  (X = Br and I) and CdI<sub>2</sub> in DMF and dioxane media. In studies using ZnCl<sub>2</sub> and CdCl<sub>2</sub>, the coordination sphere has always been found to be an octahedral. It was determined by X-ray diffraction where the Ni(II) ion was in an octahedral coordination sphere by binding two DMF molecules. For this reason, iodides with lower electronegativity were used in this study. The electronegativity of Cd atom is smaller than Zn atom, similarly, the electronegativity of I atom is smaller than Br atom, in which case the coordination sphere of Ni(II) ion has been investigated. The four coordination compounds obtained were characterized by element analysis, IR spectroscopy and thermogravimetry method, then molecular models were obtained by X-ray diffraction. The basic formula of the complexes prepared are given as follows:

Ι	$[NiL \cdot ZnBr_2 \cdot (DMF)_2]$	$C_{23}H_{30}N_4O_6NiZnBr_2$
II	$[(NiL)_2 (ZnI_2)_2 \cdot (dioxane)_3]$	$C_{46}H_{56}N_4O_{10}Ni_2Zn_2I_4$
III	$[(NiL)_2 (ZnI_2)_2 \cdot (dioxane)].(dioxane)_2$	$C_{46}H_{56}N_4O_{10}Ni_2Zn_2I_4$
IV	$[(NiL \cdot CdI_2)_2]$	$C_{34}H_{32}N_4O_4Ni_2Cd_2I_2$

# 2. Experimental

The reagents supplied from Sigma-Aldrich or Merck companies used without further purification. In this study, Shimadzu IRAffinity-1 FTIR spectrometer equipped with three

reflectional ATR units was used for IR spectra with 4 cm<sup>-1</sup> accuracy. The C, H, and N analyses were performed on Eurovector 3018 CHNS analyzer. Metal analyses were carried out on GBC Avanta PM Model atomic absorption spectrometer using FAAS mode. Complex (2-3 mg) was dissolved in 1 mL HNO<sub>3</sub> (63%) with heating, diluted to 100 mL and given to nebulizer of atomic absorption spectrometer for metal analysis. Halogen analyses were performed with classical gravimetrical methods. For the halogen analyses approximately 200 mg complex was digested in a Kjeldahl flask using 6 mL HNO<sub>3</sub> (63%) and H<sub>2</sub>O<sub>2</sub> (27%) mixture (4:2, v/v) and after digestion was diluted in a 100 mL volumetric flask then was precipitated as AgX using AgNO<sub>3</sub>. The mass spectra of the ligands were obtained by a Shimadzu QP2010 Plus GCMS apparatus equipped with a direct inlet (DI) unit with an electron impact ionizer. DI temperature was varied between 40-300 °C and ionization was carried out with electrons with 70 eV energy. The NMR spectra were recorded on the Bruker Ultrashield 300 MHz NMR spectrometer using  $d_6$ -DMSO solution as the solvent. The thermogravimetric analyses were carried out by Shimadzu DTG 60H in Pt pans between a temperature range of 30-600 °C at a heating rate of 10 °C/min under N<sub>2</sub> atmosphere. The instrument was calibrated with metallic In and Zn.

#### 2.1 X-ray crystallography

A single crystals of  $[NiL \cdot ZnBr_2 \cdot (DMF)_2]$ ,  $[(NiL)_2 \cdot (ZnBr_2)_2 \cdot (dioxane)_3]$ ,

 $[(NiL)_2 \cdot (ZnI_2)_2 \cdot (dioxane)].(dioxane)_2$  and  $[(NiL \cdot CdI_2)_2]$  were analyzed on an Oxford Diffraction Xcalibur Single Crystal X-ray Diffractometer with a sapphire CCD detector using MoKa radiation ( $\lambda = 0.71073$  A) operating in  $\omega/2\theta$  scan mode. The unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in  $2.778^{\circ} \le \theta \le 27.779^{\circ}$ range for  $[NiL \cdot ZnBr_2 \cdot (DMF)_2],$ 2.598°-27.933° for  $[(NiL)_{2} \cdot (ZnBr_{2})_{2} \cdot (dioxane)_{3}], 2.547^{\circ} - 27.789^{\circ} \text{ for } [(NiL)_{2} \cdot (ZnI_{2})_{2} \cdot (dioxane)].(dioxane)_{2} \text{ and }$ 2.608°-27.980° for [(NiL.CdI<sub>2</sub>)<sub>2</sub>]. The data for I, II and IV complexes were collected at 293(2) K and for III was collected at 200(2) K. The empirical absorption corrections were applied by the semi-empirical method via the CrysAlis CCD software [22]. The model was obtained from the results of the cell refinement and the data reductions were carried out using the solution software SHELXL97 [23]. The structure of the complexes was solved by direct methods using the SHELXS 97 software implemented in the WinGX package [24]. Supplementary material for structure has been deposited to the Cambridge Crystallographic Center CCDC no: 1949378, 1949377, 1949379. and 1949376 Data as (deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

#### 2.2 Synthesis

#### 2.2.1 Preparation of Bis-N,N'(salycilidene)-1,3-diaminopropane (LH<sub>2</sub>)

The ligand was prepared from salicylaldehyde and 1,3-propanediamine via a condensation reaction in ethanol. 0.05 mole salicylaldehyde (6.1 g) was dissolved in 50 mL EtOH under stirring and heating and was heated this solution up to the boiling point. Then 0.025 mole 1,3-propanediamine (1.85 g) was added dropwise to this solution and the final mixture was left aside for 5-6 hours and the formed yellow crystals were filtered from Buchner funnel and dried in the air.

Formula	$C_{17}H_{18}N_2O_2$
Melting Point (°C)	58
Yield (%)	90-95

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Elemental Analysis	(Expected,	%)	C: 72.32	H: 6.43	N: 9.92			
	(Found, %)	)	C: 71.95	H: 6.33	N: 10.09			
IR data (cm <sup>-1</sup> )	v <sub>О-н</sub> 2627	v <sub>C-H(Ar)</sub> 3021- 3019	v <sub>C-H(Al)</sub> 2929- 2862	v <sub>C=N</sub> 1629	$\frac{\mathcal{V}_{C=C(ring)}}{1608}$	v <sub>C-O(Ph)</sub> 1274- 1151	$\delta_{\text{C-H(Ar)}}$ 762	
$\lambda_{max}$ (243 nm)	$\varepsilon = 7045 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ in DMSO							
$\lambda_{max}$ (242 nm)	$\varepsilon = 7865 \ dz$	$m^3 mol^{-1} cm^{-1}$	in MeOH					
<sup>1</sup> HNMR ( $\delta$ , ppm) in $d_6$ -DMSO	13.51 (s) (O–H)	8.60 (s) (-CH=)	7.43 (d) (H <sub>Ar</sub> )	7.32 (t) (H <sub>Ar</sub> )	6.88 (t) (H <sub>Ar</sub> )	3.68 (t) (N–CH <sub>2</sub> )	2.01 (p) (-CH <sub>2</sub> )	
<sup>13</sup> CNMR ( $\delta$ , ppm) in $d_{\delta}$ -DMSO	166.6 161.1 132.7 132.1 119.1 118.9 116.9 58.5 (N–CH <sub>2</sub> ) 31.9 (–CH <sub>2</sub> –)							
m/z	$282 [M]^+$ 134 [HO-C $[C_6H_5]^+$	161 [HO-C <sub>6</sub> H C <sub>6</sub> H <sub>4</sub> -CH=N-C	$[I_4-CH=N-C]$ $[CH_2]^+$ 120 [	H <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> HO-C <sub>6</sub> H <sub>4</sub> -CH	] <sup>+</sup> 148 [HO-( H=N] <sup>+</sup> 107 [	C <sub>6</sub> H <sub>4</sub> -CH=N· HO-C <sub>6</sub> H <sub>4</sub> -CH	$-CH_2-CH_2]^+$ $H_2]^+$ 77	

# 2.2.2 Preparation of mononuclear NiL complex

0.01 mole LH<sub>2</sub> (2.86 g) prepared as described above was dissolved in 50 mL EtOH under heating. 10 mL of concentrated ammonia and a solution of 0.01 mole NiCl<sub>2</sub>.6H<sub>2</sub>O (2.36 g) in 50 mL hot water were respectively added to this solution under stirring. The light green bulky crystal of  $[(NiL)_2.(NH_3)_3]$  complex was precipitated in a few minutes dried at 140 °C in an oven for 4 hours. The resulting light brown material is NiL [20,21].

E	C U N O N					
Formula	$C_{17}H_{16}N_2O_2N_1$					
Melting Point (°C)	311 (decomposed over 3	860 °C, DTA	A result)			
Yield (%)	73					
Elemental Analysis	(Expected, %)	C: 60.28	H: 4.76	N: 8.27	Ni: 17.33	
	(Found, %)	C: 60.55	H: 3.17	N: 7.93	Ni: 17.19	
IR data (cm <sup>-1</sup> )	V <sub>C-H(Ar)</sub> V <sub>C-H(Al)</sub> 3061- 2922- 3030 2866	v <sub>C=N</sub> 1607	v <sub>C=C(ring)</sub> 1589- 1541	$\delta_{ ext{C-H(Al)}}$ 1475	v <sub>C-O(Ph)</sub> 1228- 1124	δ <sub>C-H(Ar)</sub> 725- 744
m/z	340 (isotope peak) 338 205 [Ni-O-C <sub>6</sub> H <sub>4</sub> -CH=N CH=NH-CH <sub>2</sub> ] <sup>+</sup> 107 [Ho	(molecular H-CH <sub>2</sub> -CH <sub>2</sub> D-C <sub>6</sub> H <sub>4</sub> -CH <sub>2</sub>	peak) 219 [] 2] <sup>+</sup> 179 [Ni 2] <sup>+</sup> 58 [Ni] <sup>+</sup>	Ni-O-C <sub>6</sub> H <sub>4</sub> -C i-O-C <sub>6</sub> H <sub>4</sub> -CH	H=NH-CH <sub>2</sub> - [=NH] <sup>+</sup> 13 <sup>4</sup>	$CH_2-CH_2]^+$ 4 $[O-C_6H_4-$

#### 2.2.3 Preparation of [NiL·ZnBr<sub>2</sub>·(DMF)<sub>2</sub>] complex (I)

0.001 mole NiL (0.339 g), prepared as described above, was dissolved in 40 mL DMF under stirring and heated up to 100-110 °C. A solution of anhydrous 0.001 mole  $\text{ZnBr}_2$  (0.226 g) in 20 mL hot MeOH was added to this solution. The mixture was rigorously stirred and left at the bench for 2-3 days and the resulting granulated crystallized green complex was filtered with a Buchner funnel and dried in air.

Formula	$C_{23}H_{30}N_4O_6NiZnBr_2$						
Yield (%)	64-70						
Elemental Analysis	(Exp, %)	C: 37.21	H: 4.07	N: 7.54	Ni: 7.90	Zn: 8.80	Br: 21.52
	(Fnd, %)	C: 36.86	H: 4.42	N: 6.99	Ni: 7.59	Zn: 8.75	Br: 20.97
IR data (cm <sup>-1</sup> )	v <sub>C-H(Ar)</sub> 3033- 3017	v <sub>C-H(Al)</sub> 2924- 2853	v <sub>C=N</sub> 1629	v <sub>C=C(ring)</sub> 1595- 1555	$\delta_{ ext{C-H(Al)}}$ 1475	v <sub>C-O(Ph)</sub> 1305- 1124	δ <sub>C-H(Ar)</sub> 753- 735

2.2.4 Preparation of  $[(NiL)_2 (ZnI_2)_2 \cdot (dioxane)_3]$  complex (II)

0.002 mole NiL (0.678 g), prepared as described above, was dissolved in 50 mL dioxane under stirring and heated up to the boiling point. A solution of 0.002 mole anhydrous ZnI<sub>2</sub> (0.638 g) in 30 mL hot MeOH was added to this solution. The resulting mixture was stirred and left at the bench for 2-3 days. The green crystals of the complex were filtered by a Buchner funnel and dried in air.

Formula	$\overline{C_{46}H_{56}N_4O_{10}Ni_2Zn_2I_4}$							
Yield (%)	42							
Elemental Analysis	(Exp, %)	C: 34.94	H: 3.57	N: 3.54	Ni: 7.42	Zn: 8.27	I: 32.11	
	(Fnd, %)	C: 34.35	H: 3.41	N: 3.63	Ni: 7.25	Zn: 8.81	I: 33.36	
IR data (cm <sup>-1</sup> )	v <sub>C-H(Ar)</sub> 3021- 3008	v <sub>C-H(Al)</sub> 2924- 2850	v <sub>C=N</sub> 1618	v <sub>C=C(ring)</sub> 1595- 1558	$\delta_{\text{C-H(Al)}}$ 1473	v <sub>C-O(Ph)</sub> 1301- 1195	δ <sub>C-H(Ar)</sub> 752- 734	

2.2.5 Preparation of  $[(NiL)_2 \cdot (ZnI_2)_2 (dioxane)] \cdot (dioxane)_2 complex (III)$ 

This complex was synthesized using 0.002 mole NiL (0.678 g) and 0.002 mole anhydrous  $ZnI_2$  (0.452 g) in 50 mL dioxane-MeOH mixture (1:1, v/v) as described above for complex II.

Formula	$C_{46}H_{56}N_4O_{10}Ni_2Zn_2I_4$						
Yield (%)	26						
Elemental Analysis	(Exp, %)	C: 34.92	H: 3.57	N: 3.54	Ni: 7.42	Zn: 8.27	I: 32.13
	(Fnd, %)	C: 35.86	H: 3.81	N: 3.40	Ni: 7.31	Zn: 8.55	I: 33.57
IR data (cm <sup>-1</sup> )	v <sub>C-H(Ar)</sub> 3027- 3011	v <sub>C-H(Al)</sub> 2924- 2853	v <sub>C=N</sub> 1625	v <sub>C=C(ring)</sub> 1593- 1552	$\delta_{ ext{C-H(Al)}}$ 1475	v <sub>C-O(Ph)</sub> 1300- 1107	δ <sub>C-H(Ar)</sub> 756- 734

*Note:* In the preparation of complex II and III, a mixture of both complexes are obtained. If the solvent mixture contained a higher amount of MeOH, complex III dominates the total complex formation. However, if dioxane is predominant in the solvent mixture then complex II was formed in much higher quantities.

# 2.2.6 Preparation of $[(NiL \cdot CdI_2)_2]$ complex (IV)

This complex was synthesized using 0.002 mole NiL (0.678 g) and 0.002 mole anhydrous  $CdI_2$  (0.736 g) in dioxane as described above for complex II.

$C_{34}H_{36}N_4O_4Ni_2Cd_2I_4$						
32						
(Exp, %)	C: 28.91	H: 2.28	N: 3.96	Ni: 8.31	Cd: 15.91	I: 35.94
(Fnd, %)	C: 28.04	H: 3.11	N: 3.79	Ni: 7.94	Cd: 15.55	I: 37.87
v <sub>C-H(Ar)</sub> 3038- 3019	v <sub>C-H(Al)</sub> 2937- 2872	v <sub>C=N</sub> 1622	v <sub>C=C(ring)</sub> 1597- 1552	$\delta_{ ext{C-H(Al)}}$ 1473	v <sub>C-O(Ph)</sub> 1303- 1126	δ <sub>C-H(Ar)</sub> 752- 734
_	C <sub>34</sub> H <sub>36</sub> N <sub>4</sub> O <sub>4</sub> N 32 (Exp, %) (Fnd, %) <sup>V</sup> C-H(Ar) 3038- 3019	C <sub>34</sub> H <sub>36</sub> N <sub>4</sub> O <sub>4</sub> Ni <sub>2</sub> Cd <sub>2</sub> I <sub>4</sub> 32         (Exp, %)       C: 28.91         (Fnd, %)       C: 28.04 $\nu_{\text{C-H(Ar)}}$ $\nu_{\text{C-H(Al)}}$ 3038-       2937-         3019       2872	$\begin{array}{ccc} C_{34}H_{36}N_4O_4Ni_2Cd_2I_4\\ 32\\ (Exp, \%) & C:\ 28.91 & H:\ 2.28\\ (Fnd, \%) & C:\ 28.04 & H:\ 3.11\\ \hline \\ \nu_{C-H(Ar)} & \nu_{C-H(Al)} & \nu_{C=N}\\ 3038- & 2937- & 1622\\ 3019 & 2872 \end{array}$	$\begin{array}{cccc} C_{34}H_{36}N_4O_4Ni_2Cd_2I_4\\ 32\\ (Exp,\%) & C:28.91 & H:2.28 & N:3.96\\ (Fnd,\%) & C:28.04 & H:3.11 & N:3.79\\ \hline $v_{C-H(Ar)}$ & $v_{C-H(Al)}$ & $v_{C=N}$ & $v_{C=C(ring)}$\\ 3038- & 2937- & 1622 & 1597-\\ 3019 & 2872 & 1552 \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

#### 3. Results and Discussion

#### 3.1 X-ray diffraction

The Ortep drawings of the prepared complexes obtained from the X-ray diffraction studies are given in Fig. 1. Data collection condition and crystal properties are listed in Table 1 and bond lengths and bond angles in complex coordination spheres are shown in Table 2. Table 2 also contains the bond lengths and angles determined by the use of Gaussian 09 software for comparison purposes. There is almost no difference between the experimental results and the corresponding values obtained from the theoretical results from the theoretical programs by the use of X-ray data.

Fig. 1.

Table 1

#### Table 2

As seen from Fig. 1 Ni(II) ion has an octahedral coordination in complex I and II, a square pyramidal structure in complex III and a square planar structure in complex IV. In complex I, Ni(II) ion slightly deformed octahedral coordination sphere surrounded by two phenolic oxygens and two iminic nitrogen donors of  $L^{2-}$  and axially oriented two DMF oxygens. The two phenolic oxygens also form a  $\mu$ - bridge with Zn(II) ion of ZnBr<sub>2</sub> molecule resulting in a heterodinuclear complex. Zn(II) ion is in a distorted tetrahedral O<sub>2</sub>Br<sub>2</sub> coordination sphere. There are so many examples of this structure in the literature. Many mononuclear complexes prepared with LH<sub>2</sub> ligand can coordinate Lewis acid via phenolic oxygens resulting in dinuclear structures [5,6,25-27].

In complex II, a dioxane molecule stands between two NiL.ZnI<sub>2</sub> units and the two oxygen of this dioxane molecule coordinate the Ni(II) ion in separately NiL.ZnI<sub>2</sub> units. In addition to this case, each Ni(II) ion is coordinated one dioxane molecule from another side, consequently is occurred each establishing an  $O_4N_2$  octahedral coordination sphere around Ni(II) ion. Additionally, the phenolic oxygens of Schiff base form  $\mu$ - bridges with Zn(II) ions of ZnI<sub>2</sub> molecule constituting a distorted tetrahedral  $O_2I_2$  coordination sphere. The situation for complex III is different. Although it is formed by the same structural units (NiL, ZnI<sub>2</sub>, and dioxane) the coordination is different. Complex II and III occur at the same medium as stated in the experimental part.

Using equal amounts of NiL and  $ZnI_2$  in dioxane/MeOH mixture (50:50, v/v), a mixture of complex II and complex III is formed. Since complex II has a blue and complex III has a green color they can be mechanically separated. In complex III, one dioxane molecule coordinated two Ni(II) ions with its two oxygens connecting to NiL units. However, in our study NiL units are not coordinated with other dioxane molecules. Under these conditions, Ni(II) ions in NiL units are located in an  $O_3N_2$  square pyramidal coordination sphere. Square pyramidal coordination is not a common coordination sphere for Ni(II) ions. There are some examples of mononuclear and dinuclear complexes reported in the literature [20,21]. Again Zn(II) ions in complex III are located in the distorted tetrahedral  $O_2I_2$  coordination sphere.

Complex IV is entirely different since there are no solvent molecules coordinating NiL units and Ni(II) ion is in a square planar coordination sphere. NiL units are coordinated Cd(II) ion in CdI<sub>2</sub> by  $\mu$ - bridge through phenolic oxygens. Iodine atoms are coordinated to neighboring Cd(II) by a different  $\mu$ - bridge. Under these conditions, two [NiL·CdI<sub>2</sub>] are connected forming a heterotetranuclear complex. Here Ni(II) ions of NiL units have

approximately square planar coordination sphere and Cd(II) ions are in the  $O_2I_3$  distorted square pyramidal coordination sphere. This shows the fact that the bond angles and bond lengths displayed in Table 2, there is a very slight distortion in these parameters. On the other hand, the tetrahedral coordination sphere of Zn(II) ions in complex I, II and III are highly distorted. This fact is highly apparent from the decrease of halogen-zinc-halogen angles down to 70°.

The degree of distortion of the coordination sphere can be estimated from bond lengths and angles around the metal ion. The bond angles and the length of the complexes are given in Table 2. There are two possibilities for the formation of pentadentate coordination in complexes, namely square pyramidal and trigonal bipyramidal structures. The best method for the determination of the coordination sphere is the determination of  $\tau$  variable used since 1984 [28]. The parameter is calculated as  $\tau = (\alpha - \beta)/60$ . Here  $\alpha$  and  $\beta$  are the largest angles in the coordination sphere. If  $\tau = 1$  the structure of the coordination sphere is trigonal bipyramidal and if  $\tau = 0$  the structure of the coordination sphere is square pyramidal. The deviation from these values causes an increase in the distortion of the coordination sphere.  $\tau$ values for the coordination spheres of Ni(II) in complex III and Cd(II)in complex IV are calculated taking the angles given in Table 2, it comes out to be 0.00167 for complex III and 0.45466 for complex IV. This shows the fact that the Ni(II) in complex III is located in a slightly distorted square pyramidal and while Cd(II)ion in complex IV is in a highly deformed square pyramidal coordination sphere.

The structure of NiL compound was explained in 1985. According to it, Ni(II) ions in NiL mononuclear complex have a square planar coordination sphere [19]. However, the most striking case in this study is when a Lewis acid such as  $MX_2$  (M = Zn(II) or Cd(II), X = Cl<sup>-</sup>, Br or  $\Gamma$ ) is coordinated to NiL complex via phenolic oxygens, the electronegativity of the metal ion and halogen of Lewis acid effect the coordination around Ni(II) ion. In other words, the coordination sphere and the bond lengths of the complexes apart are affected by the electronegativity of the metal present in the complex. It also affects the magnetic susceptibility. NiL is a diamagnetic complex but acts as paramagnetic if the coordination is a square pyramidal or octahedral. This event, seen in complexes of ONNO type ligands and occurring over oxygen bridges, is known as a super magnetic exchange [29]. As in complex I, if the metal ion is in the case of halogen Cl or Br, this Lewis acid attracts some of the electrons of phenolic oxygen, so phenolic oxygen cannot deliver electrons to Ni(II) ion as in NiL mononuclear complex. In other words, the amount of electrons they offer to Ni(II) decreases. Under these situations, Ni(II) ion coordinates the solvent around itself changing the coordination sphere. If Ni(II) ion cannot find the electron donors to regain the decreasing electron density, the dinuclear complex cannot occur [30]. Since ZnBr<sub>2</sub> molecule attracts some of the electrons of the phenolic oxygen in complex I, the amount of electrons that the phenolic oxygen transfers to Ni(II) ion decrease in NiL unit. In this case, Ni(II) ion coordinates the oxygen of two solvent molecules to itself to gain electron density. If the Lewis acid used was ZnCl<sub>2</sub>, the result would be expected to be octahedral since Cl atom is more electronegative than Br atom, indeed this complex has been reported in the literature and the coordination of Ni(II) is octahedral. The difference in complex II and III is that instead of Br atoms in Lewis acid, there are I atoms. The electronegativity of I is smaller, and therefore ZnI2 unit attracts less electrons of phenolic oxygen and less electron is attracted from the dioxane molecules bound to Ni(II) ion.

As seen from Table 2 the lengths of Ni(II)–N and Ni–O in NiL unit ranged as 2.013-2.026 Å, the length of Ni(II)–O(DMF) changes between 2.134 and 2.135 Å in complex I. On the other hand, while Ni(II)–N and Ni(II)–O bond lengths in NiL unit of complex II change between 2.002 and 2.030 Å, Ni(II)–O(dioxane) distance is increased to 2.196 and 2.164 Å. It is obvious that the lengths of NiL unit do not show a significant change but the distance

between the solvent molecules is increased because Ni(II) is less affected. In complex III, Ni(II)-O and Ni(II)-N distances in NiL unit vary between 1.955 and 1.978 Å and Ni(II)-O(dioxane) distance is increased to 2.371 Å. Coordinative dioxane is shared by two NiL in this complex. That is why the increase in this distance is not surprising because the distances in NiL unit are shortened. In complex IV, there is no solvent molecule participated in the coordination, NiL unit seems to remain in mononuclear form. The Ni(II)-O and Ni(II)-N distances in this complex ranged between 1.849 and 1.875 Å. These values were reported as 1.845 and 1.901 Å for NiL mononuclear complex in the literature. Bond lengths in NiL unit relative to the mononuclear state were not affected by dinuclear complex formation. Because the electronegativities of Cd(II) ion and I atoms are not high enough. The electrons they attract from phenolic oxygens do not affect the coordination of NiL. For this reason, the coordination of Ni(II) ion in NiL unit has not changed. There was no change in NiL unit, but  $CdI_2$  unit of the complex formed the  $\mu$ - bridge over I atoms and a tetranuclear complex was formed. One I atom of each Cd(II) ion formed the  $\mu$ - bridge with the other Cd(II) ion. In this case, each Cd(II) ion had a 5-member coordination sphere and an over-deformed square pyramidal coordination sphere was formed. It is possible to say that because the  $\mu$ - bridge of I atoms gives electrons to Cd(II) ion, Cd(II) ion does not receive too many electrons from phenolic oxygen and does not affect NiL unit.

#### 3.2 Thermal analysis

TG-DTA plots of the complexes for their thermal characterization are illustrated in Fig. 2a-d and the resulting mass losses are listed in Table 3. DTA curves of four complexes are given in Fig. 3 for comparison purposes.

Fig. 2.

Fig. 3.

# Table 3

As seen in Fig. 2a and Table 3, complex I begins to decompose at 148 °C and a mass loss of 21% is observed with an endothermic reaction. This mass loss corresponds to the mass of DMF molecules coordinated. At 148 °C, DMF molecules are separated from the structure and the complex is degraded. By separating DMF molecules, NiL and ZnBr<sub>2</sub> remain in the medium and the mixture endothermic decomposes at 400 °C. This degradation is the disintegration of NiL unit. It has been previously reported that NiL molecule is broken down by an endothermic reaction at 380-400 °C. Fig. 2b shows the degradation of complex II. Complex II contains three molecules of dioxane and these dioxanes are coordinated according to X-ray diffraction data. Two dioxane molecules coordinate two NiL units through one oxygen and the other dioxane through two oxygen. An endothermic mass loss of 12.65% is observed at 97 °C followed by a loss of endothermic mass of 6.32% at 126 °C. If calculated, the first mass loss corresponds to about two dioxane molecules, the second mass loss corresponds to a single dioxane molecule, the total mass loss at 97-126 °C corresponds to three dioxane molecules. Possibly, single coordinated dioxane leaves the structure at 97 °C, and the two coordinated dioxanes begin to separate at 126 °C. Fig. 2c shows the TG-DTA curves of the complex III. X-ray results show that a dioxane molecule present in this molecule as a solvate. This solvate molecule begins to detach from the structure at 92 °C and the initial mass loss belongs to this solvate molecule and this is understood from the endothermic signal at 92 °C. The fact that the separation temperature of the dioxane molecule is lower than that

of complex II indicates that the separated molecule is solvate. The second mass loss is again endothermic and at a higher temperature, this mass loss again corresponds to a dioxane molecule and is possibly the removal of coordinated dioxane. In Fig. 2d, TG-DTA curve of complex IV is given. As it is seen, there is no mass loss up to 400 °C and the mass loss that starts at this temperature belongs to the disintegration of NiL unit as in other complexes.

Thermal analysis contributed to the characterization of complexes in this study and coordinative and solvate states of solvent molecules in complexes were determined by thermogravimetry. Thermal analysis is particularly effective in determining complex stoichiometry, especially in complexes containing solvate and coordinated solvent molecules [31]. It is possible to determine the coordinated groups clearly from TG curves. In addition, it is evident from TG curves whether the coordinated molecules are solvate or coordinative. The fact that DTA curves are also endothermic is an expected condition for these decomposition reactions. All complexes are degraded by an endothermic reaction with a curve of the same form around 400 °C, and the form of this curve is almost the same as that of the single NiL complex.

#### 3.3 Computational calculations

The occupancy levels of d orbitals of metals were determined by the use of NBO (natural bond orbital) algorithm embedded in Gaussian 09 software are listed in Table 4. ESP (electrostatic potential) diagrams showing the electron density of the complexes and the images of the HOMO and LUMO are illustrated in Fig. 4 and the energy difference between these two orbitals and the dipole moments determined from ESP diagrams are tabulated in Table 5.

#### **Fig. 4.**

#### 3.3.1 NBO analysis

Table 4 lists the electron occupancy levels and relative energy levels of d orbitals of Ni(II) and Zn(II) ion in complexes calculated by the use of NBO program, the electron density values Ni(II) ion of octahedral complex I and complex II is as expected from the classical field splitting theory [32]. The highest energy orbitals in both complexes are  $d_{yz}$  and  $d_{zx}$  orbitals which are not totally occupied. On the other hand,  $d_{x2-y2}$ ,  $d_{xy}$  and  $d_{z2}$  orbitals are much more stable and almost totally occupied this situation is in good accordance with crystal field theory for octahedral complexes. The d orbitals are split into three low and two high energy orbitals.

Ni(II) ion is in a square pyramidal coordination sphere in complex III and a square planar coordination sphere in complex IV. It is highly difficult to explain the crystal field splitting of these complexes by the use of the data listed in Table 4. Table 4 also includes the data calculated for NiL mononuclear complex. The occupancy values of d orbitals in the mononuclear NiL complex is highly identically calculated. The highest energy orbital  $d_{xy}$  is practically empty and other orbitals carry two electrons. Under these conditions, NiL complex expected to be diamagnetic. In fact, square planar Ni(II) complexes are diamagnetic [33].

According to the NBO data, d orbitals with at least one electron space in Ni(II) ion are seen in complex I, II and III. In addition, NBO was theoretically calculated for NiL and four orbitals were found to be full and one orbital was empty. In this case, complex I, II and III are expected to be paramagnetic and NiL to be diamagnetic, and the coordination found proves this. Only NBO results of complex IV are not fully explained. It is seen that almost two orbitals contain two electrons, but the occupancy values of the other d orbitals are 1.41, 1.66 and 1.68 electrons. If Ni(II) ion was in the square planar coordination sphere, it would be

expected that four orbitals were filled and one orbital was empty. As a result, it can be said for complex IV that the addition of  $CdI_2$  to the square planar NiL complex affects the electron order of Ni(II) ion. The electronegativities of Cd and I atoms are relatively low, it does not affect the coordination sphere of NiL complex, but it affects the electron distribution of Ni(II) ion. It is probable that the electron order on phenolic  $\mu$ - bridges is shared between Ni (II) and Cd (II) ions.

#### Table 4

#### 3.3.2 HOMO-LUMO analysis

Table 5 lists the calculated energies of HOMO and LUMO orbitals. The formation of the dinuclear complex increases the stability of HOMO and LUMO energy levels. The difference between HOMO and LUMO energies of the complex II and III are found to be lower than expected.

value in NiL complex was found as -4.949 eV. For all other  $\Delta E_{HOMO-LUMO}$ heteronuclear complexes, this value is less than -5.000. It was found that HOMO orbitals are more stable in the formation of a heteronuclear complex. A similar situation was observed in the energy levels of LUMO orbitals. LUMO orbitals of the heteronuclear complexes have shifted to more negative values. But  $\Delta E_{HOMO-LUMO}$  value is different. This difference increased in complex I, decreased in complex II and III, and did not change in complex IV. In complex I, Lewis acid ZnBr<sub>2</sub> is coordinated DMF solvent molecules. Due to its high electronegativity, ZnBr<sub>2</sub> withdraws more electrons from NiL unit. As a result, Ni(II) ion attracts more electrons from DMF molecules and the overlaps between the orbitals are strengthened, in this case the stability of HOMO orbitals increases. However, in complex II and III, ZnI<sub>2</sub> is used as Lewis acid and the coordinated solvent molecules are dioxane. Dioxane is a weaker ligand than DMF. As a result, the energy of HOMO orbitals does not decrease too much and the energy of LUMO orbitals does not increase and  $\Delta E_{HOMO-LUMO}$  value is low. In complex IV, Lewis acid used is CdI<sub>2</sub> and the solvent molecule is not coordinated because CdI<sub>2</sub> has not drawn more electrons from NiL units. The value of  $\Delta E_{HOMO-LUMO}$  remained approximately the same due to the small impact of Ni(II).

#### Table 5

#### 3.3.3 Theoretical structural analysis

Another parameter calculated from the theoretical programs is dipole moments of the complexes. The dipole moments given in Table 5 were observed to change with the electronegativity of the metal ion and geometry of the complexes. Fig. 4 shows the ESP maps of the complexes. The red regions correspond to the electron-rich and blue regions correspond to the electron-poor areas. It appears that the increase in the asymmetry of the molecules and the electronegativities of the metal ions increases the dipole moment of the complexes. Complex I is the most asymmetric complex among the complexes prepared in this study due to the presence of Zn(II) and Br<sup>-</sup> ions having the largest dipole moment value. Complex IV containing Cd(II) and  $\Gamma$  has almost a symmetrical structure and the lowest dipole moment value.

However, the theoretical dipole moment values given in Table 5 are quite identical. A dipole moment parallel to the electronegativity of the atoms in Lewis acid was calculated. While the dipole moment in the mononuclear NiL molecule was 5.618 Debye, it increased parallel to the electronegativity of Lewis acid in complex I, II and III. In the mononuclear NiL complex, it is expected to have a dipole moment due to two O and two N atoms in the cis position. Because O atoms have higher electronegativity value than N atoms. As can be seen

in complex I, II and III, when a Lewis acid is bounded to the O atoms, the dipole moment changes according to the electronegativity of the group that is bounded and this change can be calculated theoretically. However, in complex IV, the molecule has become tetranuclear and symmetrical due to the  $\mu$ - bridges made by I atoms in CdI<sub>2</sub> unit. In this case, as can be seen in Fig. 4, the center of gravity of the positive and negative charges coincide, and therefore the dipole moment is calculated low.

# 4. Conclusions

There were three different heteronuclear Ni(II) complexes with different coordination spheres prepared by the attachment of mononuclear square planar NiL complex to different Lewis acids in DMF, MeOH and dioxane mixtures. These prepared complexes were formed by adding a Lewis acid and solvent molecules to the square planar NiL complex, and the coordination of the solvent molecules affects the coordination sphere of Ni(II) ion. Thermal analysis was very helpful in determining coordinated and solvated solvent molecules. The structures of the complexes were enlightened by the X-ray diffraction method. Also, their coordination sphere evaluated by the use of the algorithms embedded in Gaussian 09. If the electronegativity of the atoms in Lewis acid increases, the square planar NiL unit turns the coordination sphere into square pyramidal and octahedral by attracting electrons from the solvent molecules. It was concluded that the electronegativity of Lewis acid used affects the coordination sphere.

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# **CRediT** author contribution statement

Yaprak Gürsoy Tuncer: Investigation. Kübra Gürpınar: Investigation. Nurcan Acar: Visualization, Data curation. Hasan Nazır: Formal analysis, Software, Validation. Ingrid Svoboda: Formal analysis, Resources. Orhan Atakol: Methodology, Supervision. Emine Kübra İnal: Conceptualization, Writing - Review & Editing.

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#### References

1. A. Martell, M. Calvin, Die Chemie Der Metallchelat-Verbindungen, Verlag Chemie, Weinheim, 1958.

2. R.J. Butcher, E. Sinn, Relation between magnetic, spectroscopic, and structural properties of bis [chloro (N-isopropyl-2-hydroxybenzylidene) aminato-. mu.-O-copper (II)] and bis (N-isopropyl-2-hydroxybenzylideneaminato) copper (II), Inorg. Chem. 15 (1976) 1604-1608.

3. M. Kato, Y. Muto, Factors affecting the magnetic properties of dimeric copper (II) complexes, Coordin. Chem. Rev. 92 (1988) 45-83.

4. C. Fukuhara, K. Tsuneyoshi, N. Matsumoto, S. Kida, M. Mikuriya, M. Mori, Synthesis and characterization of trinuclear Schiff-base complexes containing sulphur dioxide or hydrogensulphite ions as bridging groups. Crystal structure of [Zn {( $\mu$ -CH 3 CO 2)(salpd- $\mu$ -O, O') Cu} 2][salpd= propane-1, 3-diylbis (salicylideneiminate)], Dalton T. 11 (1990) 3473-3479.

5. M. Aksu, S. Durmuş, M. Sari, K. Emregül, I. Svoboda, H. Fuess, O. Atakol, Investigation on the thermal decomposition some heterodinuclear NiII-MII complexes prepared from ONNO type reduced Schiff base compounds (M II= ZnII, CdII), J. Therm. Anal. Calorim. 90 (2007) 541-547.

6. Y.N. Chen, Y.Y. Ge, W. Zhou, L.F. Ye, Z.G. Gu, G.Z. Ma, W.S. Li, H. Li, Y.P. Cai, The first Mn–Zn heterometallic dinuclear compound based on Schiff base ligand N, N'-bis (salicylidene)-1, 3-diaminopropane, Inorg. Chem. Commun. 14 (2011) 1228-1232.

7. P. Chakraborty, S. Mohanta, Mononuclear and heterometallic dinuclear, trinuclear and dimer-of-dinuclear complexes derived from single-and double-compartment Schiff base ligands having a less utilized diamine, Polyhedron 87 (2015) 98-108.

8. S. Öz, Ü. Ergun, M. Yakut, I. Svoboda, A. Atakol, E.K. İnal, N. Yılmaz, O. Atakol, Synthesis, crystal structure, chromatographic seperation, and thermogravimetric investigation of a ONNO type asymmetric Schiff base and its trinuclear complexes, Russ. J. Coord. Chem. 40 (2014) 571-582.

9. A. Hazari, A. Das, P. Mahapatra, A. Ghosh, Mixed valence trinuclear cobalt (II/III) complexes: Synthesis, structural characterization and phenoxazinone synthase activity, Polyhedron 134 (2017) 99-106.

10. A. Hazari, C.J. Gómez-García, M.G. Drew, A. Ghosh, Rare examples of diphenoxidobridged trinuclear NiII2FeIII complexes with a reduced salen type Schiff base ligand: Structures and magnetic properties, Polyhedron 138 (2017) 145-153.

11. S. Ghosh, A. Ghosh, Coordination of metalloligand [NiL](H2L= salen type N2O2 Schiff base ligand) to the f-block elements: Structural elucidation and spectrophotometric investigation, Inorg. Chim. Acta. 442 (2016) 64-69.

12. P. Seth, A. Figuerola, J. Jover, E. Ruiz, A. Ghosh, Antiferro-to ferromagnetic crossover in diphenoxido bridged NiII2MnII complexes derived from N2O2 donor Schiff base ligands, Polyhedron 117 (2016) 57-63.

13. A. Hazari, S. Giri, C. Diaz, A. Ghosh, Unusual site selection of NCS– in trinuclear complexes of Cu (II) and Ni (II) with a reduced N2O2 donor Schiff base: Structural, theoretical and magnetic studies, Polyhedron 118 (2016) 70-80.

14. M. Mikuriya, S. Ikenoue, R. Nukada, J.W. Lim, Synthesis and structural characterization of tetranuclear zinc (II) complexes with a linear array, B. Chem. Soc. Jpn. 74 (2001) 101-102.

15. R. Kurtaran, L.T. Yıldırım, A.D. Azaz, H. Namli, O. Atakol, Synthesis, characterization, crystal structure and biological activity of a novel heterotetranuclear complex:[NiLPb (SCN) 2 (DMF)(H2O)] 2, bis-{[μ-N, N'-bis (salicylidene)-1, 3-propanediaminato-aqua-nickel (II)](thiocyanato)(μ-thiocyanato)(μ-N, N'-dimethylformamide) lead (II)}, J. Inorg. Biochem. 99 (2005) 1937-1944.

16. A.D. Khalaji, H. Hadadzadeh, K. Fejfarova, M. Dusek, Metal-dependent assembly of a tetranuclear copper (II) complex versus a 1D chain coordination polymer of cobalt (III) complex with N2O2-chelating Schiff-base ligand: Synthesis, characterization and crystal structures, Polyhedron 29 (2010) 807-812.

17. D. Bandyopadhyay, D. Karmakar, G. Pilet, M. Fleck, Synthesis and crystal structure of two new heteropolynuclear [NiIICdIICdIINiII] and [NiIICdIINiII] Schiff base complexes involving bridging chlorine and oxygen functions, Polyhedron 30 (2011) 2678-2683.

18. M. Mikuriya, N. Tsuru, S. Ikemi, S. Ikenoue, High nuclearity in a zinc (II) complex with 1, 3-bis (salicylamino)-2-propanol, Chem. Lett. 27 (1998) 879-880.

19. M.G. Drew, R.N. Prasad, R. Sharma, Structures of (N,N'-trimethylenedisalicylidene aminato) nickel (II)(1) and (N, N'-trimethylenedisalicylideneaminato) copper (II)(2), Acta Crystallogr. C. 41 (1985) 1755-1758.

20. Y. Elerman, M. Kabak, O. Atakol, An N, N'-bis (salicylidene)-1, 3-propanediaminenickel complex, Acta Crystallogr. C. 49 (1993) 1905-1906.

21. O. Atakol, H. Nazir, C. Arici, S. Durmus, I. Svoboda, H. Fuess, Some new Ni–Zn heterodinuclear complexes: square-pyramidal nickel (II) coordination, Inorg. Chim. Acta. 342 (2003) 295-300.

22. CrysAlis C. CrysAlis RED, version 1.171. Oxford Diffraction Ltd., Abdingdon, UK, 2002.

23. G.M. Sheldrick, SHELXS 97 and SHELXL 97, Program for Crystal Structure Solution and Refinement, University of Göttingen, Germany, 1997.

24. L.J. Farrugia, WinGX suite for small-molecule single-crystal crystallography, J. Appl. Crystallogr. 32 (1999) 837-838.

25. M.L. Colon, S.Y. Qian, D. Vanderveer, X.R. Bu, Chiral bimetallic complexes from chiral salen metal complexes and mercury (II) halides and acetates: the anionic groups interact with Cu (II) in apical position, Inorg. Chim. Acta. 357 (2004) 83-88.

26. L.K. Das, C.J. Gómez-García, M.G. Drew, A. Ghosh, Playing with different metalloligands [NiL] and Hg to [NiL] ratios to tune the nuclearity of Ni (II)–Hg (II) complexes: Formation of Di-, Tri-, Hexa-and nona-nuclear Ni–Hg clusters, Polyhedron 87 (2015) 311-320.

27. L. Tatar, O. Atakol, D. Ülkü, M. Aksu, {[μ-Bis (salicylidene)-1, 3-propanediaminato]copper (II)} dichlorozinc (II), Acta Crystallogr. C. 55 (1999) 923-925.

28. A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, Synthesis, structure, and spectroscopic properties of copper (II) compounds containing nitrogen–sulphur donor ligands; the crystal and molecular structure of aqua [1, 7-bis (N-methylbenzimidazol-2'-yl)-2, 6-dithiaheptane] copper (II) perchlorate, Dalton T. 7 (1984) 1349-1356.

29. C. Zeyrek, A. Elmali, Y. Elerman, Super-exchange interaction in a chair-piperazine bridged dicopper (II/II) complex: synthesis, crystal structure, magnetic properties and molecular orbital calculations, Z. Naturforsch. B. 61 (2006) 237-242.

30. A. Atakol, H. Nazir, I. Svoboda, M.L. Aksu, O. Atakol, Synthesis, crystal structure, theoretical calculations and thermal characterization of two heterodinuclear Ni II–Zn II complexes prepared from ONNO-type symmetrical Schiff base and its reduced derivative, J. Therm. Anal. Calorim. 139 (2020) 1863-1882.

31. S. Durmuş, Ü. Ergun, J.C. Jaud, K.C. Emregül, H. Fuess, O. Atakol, Thermal decomposition of some linear trinuclear schiff base complexes with acetate bridges, J. Therm. Anal. Calorim. 86 (2006) 337-346.

32. J.R. Gispert, Coordination Chemistry, Wiley-VCH, Weinheim, 2008.

33. N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, second ed., Elsevier, Oxford, 2012.

# The List of Figures

**Fig. 1.** The Ortep drawings of the complexes prepared, a.  $[NiL \cdot ZnBr_2 \cdot (DMF)_2]$  (I), b.  $[(NiL)_2 \cdot (ZnI_2)_2 \cdot (dioxane)_3]$  (II), c.  $[(NiL)_2 \cdot (ZnI_2)_2 \cdot (dioxane)_2]$  (III), d.  $[(NiL \cdot CdI_2)_2]$  (IV).

**Fig. 2.** TG-DTA curves a.  $[NiL \cdot ZnBr_2 \cdot (DMF)_2]$  (**I**), b.  $[(NiL)_2 \cdot (ZnI_2)_2 \cdot (dioxane)_3]$  (**II**), c.  $[(NiL)_2 \cdot (ZnI_2)_2 \cdot (dioxane)].(dioxane)_2$  (**III**), d.  $[(NiL \cdot CdI_2)_2]$  (**IV**), black: TG; red, blue, green, pink: DTA curve.

**Fig. 3.** DTA curves of the complexes prepared in this study, red: complex **I**, blue: complex **II**, green: complex **III**, purple: complex **IV**.

**Fig. 4.** The theoretically calculated ESP maps of the complexes prepared and their HOMO and LUMO images.

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Donomotono	Complexes						
Parameters	Ι	II	III	IV			
Molar mass/ g mol <sup>-1</sup>	710.41	1580.70	1404.88	1410.45			
T/ K	293(2)	293(2)	200(2)	293(2)			
Crystal color	blue	blue	green	red			
Crystal system	monoclinic	monoclinic	monoclinic	triclinic			
Space group	Cc	$P2_1/n$	$P2_1/n$	P-1			
a /Å	10.5384(7)	10.6740(10)	10.6009(6)	9.4637(10)			
b /Å	15.1458(8)	16.7230(2)	12.4509(7)	9.5815(6)			
c /Å	17.5110(10)	15.310(2)	20.8520(10)	12.498(10)			
Alpha /°	90.00	90.00	90.00	94.171(8)			
Beta /°	98.763(8)	91.689(9)	100.204(6)	109.820(10)			
Gamma /°	90.00	90.00	90.00	112.316(9)			
$V/Å^3$	2762.3(3)	2731.7(5)	2708.7(3)	959.50(169			
Ζ	4	2	2	1			
Calc. density/ g cm <sup>-3</sup>	1.708	1.922	1.938	2.441			
$\mu / \text{mm}^{-1}$	4.478	3.862	3.895	5.319			
F (000)	1424	1536	1536	660			
Radiation	0.71073	0.71073	0.71073	0.71073			
wavelength /Å							
$\theta$ range /°	2.778 - 27.779	2.598 - 27.933	2.547 - 27.789	2.608 - 27.980			
Index ranges	$-13 \le h \le 11$ ,	$-13 \le h \le 13$ ,	$-13 \le h \le 7$ ,	$-12 \le h \le 12$ ,			
-	$-17 \le k \le 18$ ,	$-20 \le k \le 21$ ,	$-16 \le k \le 11$ ,	$-12 \le k \le 12$			
	$-21 \le 1 \le 21$	$-19 \le 1 \le 19$	$-24 \le l \le 26$	$-14 \le l \le 16$			
Reflections collected	4730	5883	5763	4127			
<b>Reflections unique</b>	4122	3026	3275	3464			
R1, wR2 (2ó)	0.0474 - 0.1308	0.02045-0.2224	0.065 - 0.1101	0.0434 - 0.0548			
<i>R</i> 1, w <i>R</i> 2 (all)	0.0443 - 0.1257	0.0984 - 0.2870	0.1360 - 0.1385	0.1253 - 0.1338			
Data / Parameters	4730/316	5883/307	5763/307	4127/226			
GOOF of $F^2$	1.117	1.053	1.094	1.088			
Largest difference peak hole /e Å <sup>-3</sup>	0.708 - (-1.193)	1.377 – (-1.231)	1.085 - (-1.021)	1.142 - (-2.230)			
CCDC No	1949378	1949377	1949379	1949376			
Crystal Dimensions	0.48×0.40×0.32	0.26×0.10×0.08	0.36×0.04×0.02	0.24×0.22×0.12			

# Table 1

Data collection conditions and crystal data of the complexes.

# Table 2

The selected bond lengths and angles of the around coordination spheres of the complexes and theoretical bond lengths and angles for comparison.

	Experimentally	Theoretically	Experimentally	Theoretically
Complex	measured	calculated	measured	calculated
1	bond lengths	bond lengths	bond angles	bond angles
Ι	Br1 Zn1 2.330(15)	Br1 Zn1 2.330	Zn1 O2 Ni1 100.1(12)	Zn1 O2 Ni1 100.1
	Br2 Zn1 2.312(16)	Br2 Zn1 2.312	N1 Ni1 O1 90.3(13)	N1 Ni1 O1 90.6
	Zn1 O1 1.984(6)	Zn1 O1 1.984	N1 Ni1 O2 169.1(13)	N1 Ni1 O2 169.7
	Zn1 O2 2.013(5)	Zn1 O2 2.013	O1 Ni1 O2 78.8(11)	O1 Ni1 O2 79.1
	Ni1 N1 2.017(7)	Ni1 N1 2.018	N1 Ni1 N2 99.9(15)	N1 Ni1 N2 100.1
	Ni1 O1 2.018(5)	Ni1 O1 2.018	O1 Ni1 N2 169.6(14)	O1 Ni1 N2 169.0
	Ni1 O2 2.026(6)	Ni1 O2 2.026	O2 Ni1 N2 91.0(13)	O2 Ni1 N2 91.2
	Ni1 N2 2.034(7)	Ni1 N2 2.035	N1 Ni1 O3 88.6(13)	N1 Ni1 O3 88.3
	Ni1 O5 2.134(5)	Ni1 O5 2.134	O1 Ni1 O3 91.8(12)	O1 Ni1 O3 91.8
	Ni1 O4 2.135(6)	Ni1 O4 2.135	O2 Ni1 O3 92.3(12)	O2 Ni1 O3 92.5
			N2 Ni1 O3 86.6(14)	N2 Ni1 O3 86.2
			N1 Ni1 O4 90.3(13)	N1 Ni1 O4 90.1
			O1 Ni1 O4 90.6(11)	O1 Ni1 O4 90.9
			O2 Ni1 O4 89.1(12)	O2 Ni1 O4 89.4
			N2 Ni1 O4 91.2(13)	N2 Ni1 O4 91.2
			O3 Ni1 O4 177.4(13)	O3 Ni1 O4 177.6
			O1 Zn1 O2 80.0(11)	O1 Zn1 O2 80.2
			O1 Zn1 Br2 112.2(10)	O1 Zn1 Br2 112.8
			O2 Zn1 Br2 116.5(9)	O2 Zn1 Br2 116.3
			O1 Zn1 Br1 111.6(9)	O1 Zn1 Br1 111.4
			O2 Zn1 Br1 111.7(9)	O2 Zn1 Br1 111.8
			Cl2 Zn1 Br1 118.6(6)	Cl2 Zn1 Br1 118.3
Π	N1 Ni1 2.030(11)	N1 Ni1 2.030	Ni1 O1 Zn1 100.5(4)	Ni1 O1 Zn1 100.5
	N2 Ni1 2.012(14)	N2 Ni1 2.012	Nil O2 Znl 100.2(4)	Nil O2 Znl 100.2
	O5 N11 2.196(8)	05 Nil 2.196	OI N11 O2 79.7(4)	OI N11 O2 79.7
	O6 N11 2.164(9)	06 Nil 2.164	OI N11 N2 169.9(5)	OI N11 N2 169.9
	OI N11 $2.002(9)$	OI N11 2.002	O2 N11 N2 90.5(5)	O2 N11 N2 90.4
	O1 Zn1 2.006(8)	OI ZnI 2.006	OI NII NI 90.4(4)	OI NII NI 90.5
	O2  N11  2.005(9) O2  7a1  2.012(10)	$O_2 N_{11} 2.006$ $O_2 T_{\pi} 1.2.012$	O2 N11 N1 169.5(4)	02 N11 N1 169.5
	$O_2 Zn_1 2.012(10)$ $Z_{n1} I_2 2.510(2)$	02 Zn1 2.015 Zn1 12 2 510	$N_2 N11 N1 99.3(0)$	NZ NII NI 99.0
	$Z_{n1} I_{12} Z_{n1} I_{12} Z_{n2} I_{12} $	$Z_{n1} I_{12} Z_{.519}$	O1 N11 O4 91.2(4) O2 Ni1 O4 01 $2(4)$	O1 N11 O4 91.2 O2 N51 O4 01 2
	$\Sigma 111 11 2.320(2)$	ZIII II 2.320	$N_2 N_{11} O_4 91.3(4)$	N2 Ni1 04 91.5
			N1 N11 O4 00.5(5)	N1 N11 O4 92 5
			O1 Ni1 O3 91 8(3)	01  Nil 03 91 8
			O2 Ni1 O3 87 1(3)	O2 Ni1 O3 87 1
			N2 Ni1 O3 90 2(4)	N2 Ni1 O3 90 2
			N1 Ni1 O3 89 6(4)	N2 Ni1 O3 89 6
			$O_{26}^{-1}$ Ni1 O3 176 3(3)	026 Ni1 03 176 3
			O1 Zn1 O2 79 5(4)	O1 Zn1 O2 79 5
			O1 Zn1 $I_2$ 116 5(3)	O1 $Zn1$ 12 116 5
			O2 Zn1 I2 113.7(2)	O2 Zn1 I2 113.7
			O1 Zn1 I1 112 $1(3)$	O1 Zn1 I1 112.1
			O2 Zn1 I1 114.8(3)	O2 Zn1 I1 114.8
			I2 Zn1 I1 115.4(8)	I2 Zn1 I1 115.4
III	N1 Ni1 1.972(7)	N1 Ni1 1.972	O1 Ni1 O2 77.9(2)	O1 Ni1 O2 77.9
	N2 Ni1 1.978(6)	N2 Ni1 1.978	O1 Ni1 N1 91.7(3)	O1 Ni1 N1 91.6
	O1 Ni1 1.955(5)	O1 Ni1 1.955	O2 Ni1 N1 169.2(2)	O2 Ni1 N1 169.2

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	O1 Zn1 1.990(6)	O1 Zn1 1.990	O1 Ni1 N2 169.1(3)	O1 Ni1 N2 169.1			
	O2 Ni1 1.965(6)	O2 Ni1 1.965	O2 Ni1 N2 91.6(3)	O2 Ni1 N2 91.6			
	O2 Zn1 2.009(5)	O2 Zn1 2.009	N1 Ni1 N2 98.7(3)	N1 Ni1 N2 98.7			
	O3 Ni1 2.372(5)	O3 Ni1 2.372	O1 Ni1 O3 91.7(2)	O1 Ni1 O3 91.6			
	Zn1 I2 2.540(12)	Zn1 I2 2.540	O2 Ni1 O3 92.4(2)	O2 Ni1 O3 92.4			
	Zn1 I1 2.555(12)	Zn1 I1 2.555	N1 Ni1 O3 90.6(2)	N1 Ni1 O3 90.6			
			N2 Ni1 O3 91.8(2)	N2 Ni1 O3 91.6			
			O1 Zn1 O2 76.0(2)	O1 Zn1 O2 76.1			
			O1 Zn1 I2 113.3(17)	O1 Zn1 I2 113.3			
			O2 Zn1 I2 115.6(16)	O2 Zn1 I2 115.6			
			O1 Zn1 I1 115.0(17)	O1 Zn1 I1 115.0			
			O2 Zn1 I1 113.5(17)	O2 Zn1 I1 113.5			
			I2 Zn1 I1 116.9(4)	I2 Zn1 I1 116.9			
IV	N1 Ni1 1.857(6)	N1 Ni1 1.857	Ni1 O1 Cd1 100.7(2)	Ni1 O1 Cd1 100.7			
	N2 Ni1 1.875(6)	N2 Ni1 1.865	Ni1 O2 Cd1 107.3(2)	Ni1 O2 Cd1 107.3			
	O1 Ni1 1.849(5)	O1 Ni1 1.850	O1 Ni1 N1 95.1(2)	O1 Ni1 N1 95.1			
	O1 Cd1 2.425(5)	O1 Cd1 2.424	O1 Ni1 O2 83.6(2)	O1 Ni1 O2 83.6			
	O2 Ni1 1.865(5)	O2 Ni1 1.865	N1 Ni1 O2 170.6(2)	N1 Ni1 O2 170.6			
	O2 Cd1 2.238(5)	O2 Cd1 2.238	O1 Ni1 N2 168.1(2)	O1 Ni1 N2 168.0			
	Cd1 I1 2.697(8)	Cd1 I1 2.697	N1 Ni1 N2 92.6(3)	N1 Ni1 N2 92.6			
	Cd1 I2 2.754(9)	Cd1 I2 2.754	O2 Ni1 N2 90.3(2)	O2 Ni1 N2 90.3			
	Cd1 I2 3.065(10)	Cd1 I2 3.065	O2 Cd1 O1 63.9(17)	O2 Cd1 O1 63.9			
			O2 Cd1 I1 117.3(14)	O2 Cd1 I1 117.3			
			O1 Cd1 I1 99.6(12)	O1 Cd1 I1 99.6			
			O2 Cd1 I2 110.4(14)	O2 Cd1 I2 110.4			
			O1 Cd1 I2 91.8(12)	O1 Cd1 I2 91.9			
			I1 Cd1 I2 131.2(3)	I1 Cd1 I2 131.2			
			O2 Cd1 I2 96.2(13)	O2 Cd1 I2 96.2			
			O1 Cd1 I2 158.5(11)	O1 Cd1 I2 158.5			
			I1 Cd1 I2 97.0(3)	I1 Cd1 I2 97.0			
			I2 Cd1 I2 87.3(2)	I2 Cd1 I2 87.3			
			Cd1 I2 Cd1 92.7(2)	Cd1 I2 Cd1 92.7			

# **Table 3**The thermoanalytical data of the complexes prepared.

2nd Thermal Reaction 1st Thermal Reaction Coordinative or solvated DMF or dioxane loss Thermal decomposition of NiL Complex Mass loss reaction Found Observed temperature Expected Observed temperature Found range/ °C range/ DTA peak/ °C mass loss/ % mass loss/ % mass loss/ % Ι Coordinative DMF loss 148.93 - 235.6220.56  $21.22 \pm 0.15$ 401.95 - 438.20  $13.92\pm0.31$ / 200.33 / 421.14 Π Coordinative first 97.41 - 126.09 6.32  $6.37 \pm 0.03$ 402.37 - 431.67  $13.54\pm0.27$ dioxane loss / 116.69 / 419.80 Coordinative dioxane 126.09 - 150.5912.65  $12.22 \pm 0.14$ / 140.82 loss III Solvate dioxane loss 11.79 92.90 - 135.80  $10.23 \pm 0.17$ 402.27 - 440.49 $18.05 \pm 1.96$ / 113.69 / 423.46 Coordinative dioxane  $6.21\pm0.12$ 178.98 - 229.755.88 / 211.89 loss IV 400.5 - 446.88 $24.35 \pm 1.42$ / 419.47 This decomposition is the first thermal reaction.

Table 4	
Occupancy and relative energy levels of d orbitals of the metal ions in complexes.	

		Central Atoms					
Complex	Orbital		Ni Zn				
		Charge/ e	Relative energy/ eV	Charge/ e	Relative energy/ eV		
Ι	d <sub>xy</sub>	1.97070	-0.28716	1.99635	-0.60960		
	d <sub>zx</sub>	1.70502	-0.26950	1.99772	-0.61408		
	$d_{yz}$	1.07966	-0.23170	1.99655	-0.60844		
	d <sub>z2</sub>	1.93698	-0.31654	1.99624	-0.60957		
	d <sub>x2-y2</sub>	1.95718	-0.28425	1.99575	-0.60905		
II	d <sub>xy</sub>	1.94755	-0.28936	1.99712	-0.61176		
	d <sub>zx</sub>	1.69126	-0.27678	1.99795	-0.61253		
	$d_{yz}$	1.1653	-0.24590	1.99673	-0.61128		
	d <sub>z2</sub>	1.94958	-0.31721	1.99723	-0.61212		
	d <sub>x2-y2</sub>	1.90231	-0.28222	1.99656	-0.61190		
III	$d_{xy}$	1.65517	-0.27116	1.99722	-0.61270		
	d <sub>zx</sub>	1.65102	-0.28325	1.99734	-0.61243		
	$d_{yz}$	1.96345	-0.32043	1.99670	-0.61277		
	d <sub>z2</sub>	1.90422	-0.27145	1.99721	-0.61244		
	d <sub>x2-y2</sub>	1.48519	-0.30237	1.99734	-0.61302		
IV	$d_{xy}$	1.93473	-0.31131	1.99846	-0.62634		
	d <sub>zx</sub>	1.66494	-0.25805	1.99935	-0.62708		
	$d_{yz}$	1.98474	-0.32134	1.99872	-0.62843		
	d <sub>z2</sub>	1.41303	-0.27529	1.99888	-0.62807		
	d <sub>x2-y2</sub>	1.68788	-0.25432	1.99903	-0.62649		
NiL	$d_{xy}$	0.3286	-0.14287				
	d <sub>zx</sub>	1.86985	-0.22360				
	$d_{yz}$	1.90097	-0.22521				
	d <sub>z2</sub>	1.86360	-0.20962				
	d <sub>x2-y2</sub>	1.96873	-0.27000				

# Table 5

Theoretically calculated HOMO and LUMO energy values and dipole moments of the complexes.

Complex	E <sub>HOMO</sub> / eV	$E_{LUMO} / eV$	$\Delta E / eV$	μ / D
Ι	-6.099	-2.476	3.623	9.177
II	-5.755	-2.809	2.946	8.081
III	-5.805	-3.071	2.734	8.299
IV	-5.862	-2.326	3.536	1.495
NiL	-4.949	-1.421	3.528	5.618

<u>3.5</u>















# Highlights

- Ni(II) complex of ONNO type LH<sub>2</sub> ligand has a square planar coordination sphere. •
- Zn(II) and Cd(II) halides are coordinated to NiL by  $\mu$ -bridge over phenolic oxygen. •
- The electronegativity of atom in the halide affects the coordination sphere of NiL. •
- If ZnCl<sub>2</sub> or ZnBr<sub>2</sub> is attached, the coordination sphere is inevitable octahedral.
- If CdI<sub>2</sub> is attached, the coordination sphere remains as a square pyramidal. •

#### **Declaration of interests**

 $\boxtimes$  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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