

# Two dinuclear Ni<sup>II</sup>–Cd<sup>II</sup> complexes of reduced ONNO-type Schiff bases

Synthesis, crystal structures, thermal kinetic analysis and DFT studies

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Abstract Two ONNO-type Schiff bases, bis-N,N'-(salicylidene)-1,3-diaminopropane and bis-N,N'-(2-hydroxyacetophenylidene)-1,3-propanediamine, were reduced using NaBH<sub>4</sub> and converted to two phenol-amine-type tetradentate ligands, bis-N, N'-(2-hydroxybenzyl)-1,3-diaminopropane (L<sup>H</sup>H<sub>2</sub>) bis-N,N'-[1(2-hydroxyphenyl)ethyl]-1,3-diaminoand propane (LAC<sup>H</sup>H<sub>2</sub>). These ligands were used to prepare two Ni<sup>II</sup>-Cd<sup>II</sup> heterodinuclear complexes, namely [DMF NiL<sup>H-</sup> CdI<sub>2</sub>·DMF] and [DMF·NiLAC<sup>H</sup>·CdBr<sub>2</sub>·DMF] in DMF medium. The molecular structure and unit cells of these complexes have been elucidated by the use of X-ray diffraction data. The thermogravimetric analysis of the compounds revealed that as the temperature is increased, the first coordinative DMF molecule was removed from the structure followed by a second coordinative DMF molecule with the complete decomposition of the complex. The activation energies and Arrhenius pre-exponential factor of these thermal reactions were determined by the use of isothermal Coats-Redfern, nonisothermal Ozawa-Flynn-Wall and Kissinger-Akahira-Sunose methods. The results obtained for the first thermal reaction were similar since the structure of both complexes remained intact during this process. Also, the theoretical calculations of the bond lengths, bond angles and natural bond orbital analysis of

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both complexes were carried out using the algorithms embedded in Gaussian 09 software.

Keywords Heteronuclear complexes  $\cdot$  Crystal structure  $\cdot$  Thermal kinetic analysis  $\cdot$  DFT

## Introduction

Bis-N,N'-(salicylidene)-1,3-diaminopropane (LH<sub>2</sub>) is an ONNO-type Schiff base which includes two azomethine groups in its structure first used by P. Pfeifer in coordination chemistry about 90 years ago [1, 2]. It is a very popular ligand in coordination chemistry literature due to its tendency to give polynuclear complexes. It was observed to give dinuclear complexes in 1976 and trinuclear complexes in 1990 [3, 4]. From that date on, there have been vast number of studies reported related to polynuclear complexes prepared with this ligands in the literature. There are dinuclear [5-13] and trinuclear [14-20] complexes prepared by the use of LH<sub>2</sub> or its derivatives reported in the recent literature. Azomethine groups are easily reduced with NaBH<sub>4</sub> in amphyprotic solvents by the conversion of the imine bond to secondary amine [21, 22]. In this study, LH<sub>2</sub> was synthesized with 2-hydroxybenzaldehyde and 1,3propanediamine; LACH2 was synthesized with 2-hydroxvacetophenone and 1,3-diaminopropane. These Schiff bases were the reduced to amine compounds in MeOH with  $NaBH_4$  (Fig. 1).

The phenol–amine-type ligands obtained by the reduction in ONNO-type Schiff bases form very interesting coordination compounds. These ligands have a strong tendency to give polynuclear complexes [6, 22]. This study is related to the characterization of two heterodinuclear Ni<sup>II</sup>–Cd<sup>II</sup> complexes synthesized by the use of these ligands

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Fig. 1 The formula of the Schiff bases and reduced Schiff bases



Fig. 2 The structures of the complexes prepared

(Fig. 2). The ligands were characterized by element analysis, FTIR, MS and <sup>1</sup>H-NMR-<sup>13</sup>C-NMR methods. The structure of the complexes was identified by X-ray diffraction. The thermogravimetric analysis revealed that the complexes follow different decomposition patterns. Isothermal and nonisothermal–isoconversional thermokinetic analyses were used in order to bring cogent explanation to these differences.

Also theoretical calculations were carried out by using Gaussian 09W (revision D.01) software [32]. The calculations were performed by DFT/B3LYP/LanL2DZ method in a gas phase. The outer shell d electron densities and relative energy levels of Ni(II) and Cd(II) ions of the coordination compound were determined by the use of natural bond orbital (NBO) method installed in Gaussian 09. The difference between these coordination compounds was evaluated by the use of these values and the data reported in the literature.

# Experimental

#### Materials and apparatus

All the chemicals used in the experimental procedure were purchased from Merck Company, and they were used without further purification. The IR spectra were taken by the Shimadzu Infinity FTIR Spectrometer equipped with three reflectional ATR units used for with 4 cm<sup>-1</sup> accuracy. The C, H and N analyses were performed on Eurovector 3018 C, H, N, S analyzer. Metal analyses were recorded 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%):H<sub>2</sub>O<sub>2</sub>(%30) (v/v, 50-50%) with heating, diluted to 100 mL and fed to nebulizer of atomic absorption spectroscopy for metal analysis. Halogen analyses were carried out gravimetrically using AgNO<sub>3</sub> in aqueous media. Approximately 100-150 mg complex was dissolved in 5 mL HNO<sub>3</sub> (63%) by heating and diluted to 100 mL in a graduated flask. To this, solution was added excess of 0.1 M AgNO<sub>3</sub> solutions. The precipitated silver halide was filtered from a G3 glass crucible and dried in an oven at 80 °C and weighed for the halogen analysis. The mass spectra of the ligands were obtained by Shimadzu, 2010 plus with direct inlet (DI) unit with an electron impact ionizer. DI temperature was varied between 40 and 140 °C, and ionization was carried out with electrons with 70 eV energy. The NMR spectra of the ligands were recorded with a Varian brand Mercury model 400 MHz NMR spectrophotometer in d<sub>6</sub>-DMSO solution. The thermogravimetric analyses were performed by Shimadzu DTG 60H. The thermogravimetric analyses were performed between a temperature range of 30-600 °C at heating rates of 5, 10, 15, 20 and 25 °C min<sup>-1</sup> under  $N_2$ atmosphere in Pt pans. The instrument was calibrated with metallic In and Zn.

#### X-ray diffraction study

A single crystals of [NiL<sup>H</sup>·CdI<sub>2</sub>·(DMF)<sub>2</sub>] and [NiLAC<sup>H-</sup> CdBr<sub>2</sub>·(DMF)<sub>2</sub>] were analyzed on an Oxford Diffraction Xcalibur single-crystal X-ray diffractometer with a sapphire CCD detector using ΜοΚα radiation  $(\lambda = 0.71073 \text{ Å})$  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  $1.977^{\circ} \le \theta \le 26.37^{\circ}$  range for  $[NiL^{H} \cdot CdI_{2} \cdot (DMF)_{2}]$  and  $4.09^{\circ}-26.37^{\circ}$  for [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·(DMF)<sub>2</sub>]. The data of [NiL<sup>H</sup>·CdI<sub>2</sub>·(DMF)<sub>2</sub>] were collected at 301(2) K, and for other complex, they were collected at 293(2) K. The empirical absorption corrections were applied by the semiempirical method via the CrysAlis CCD software [33]. The model was obtained from the results of the cell refinement, and the data reductions were carried out using the solution software SHELXL97 [34]. The structure of the complex V was solved by direct methods using the SHELXS-97 software implemented in the WinGX package [35]. Supplementary material for structure has been deposited with the Cambridge Crystallographic Data Center as CCDC no: 1520351 [NiL<sup>H</sup>·CdI<sub>2</sub>·(DMF)<sub>2</sub>] and  $[NiLAC^{H} \cdot CdBr_{2} \cdot (DMF)_{2}]$ (deposit@ccdc.-606868 cam.ac.uk or http://www.ccdc.cam.ac.uk).

#### **Thermal calculations**

Thermal dissociation activation energies ( $E_a$ ) and Arrhenius pre-exponential factors (A) of the coordination compounds were determined and compared with each other by the use of isothermal Coats-Redfern (CR) and nonisothermal Ozawa-Flayn-Wall (OFW) and Kissinger-Akahira-Sunose (KAS) methods [23–31]. The formula used in the Ozawa-Flynn-Wall (OFW) calculation was as follows [24]:

$$\ln \beta = \ln \frac{0.0048AE_a}{Rg(\alpha)} - 1.0516 \frac{E_a}{RT}$$

Kissinger–Akahira–Sunose equation stated below, which was developed approximately at same time with OFW method, has been frequently used in kinetic analysis today, [25–27].

$$ln\frac{\beta}{T^2} = \ln\frac{AE_{\rm a}}{Rg(\alpha)} - \frac{E_{\rm a}}{RT}$$

As known, the international Confederation of Thermal Analysis and Calorimetric councel (ICTAC) is recommending the use of nonisothermal studies. However, isothermal Coats–Redfern (CR) method has also been used in this study due to its similarity with the nonisothermal methods. The formula used in the CR calculations is given below [30, 31].

$$\ln \frac{g(\alpha)}{T^2} = \ln \left[ \frac{AR}{\beta E_a} \left( 1 - \frac{2RT}{E_a} \right) \right] - \frac{E_a}{RT}$$

Here the term  $\beta$  is the rate of heating in °C min<sup>-1</sup>,  $E_a$  is the activation energy in kJ mol<sup>-1</sup>, A is Arrhenius pre-exponential factor in min<sup>-1</sup>, R is gas constant in J mol<sup>-1</sup> K<sup>-1</sup> and t is a constant, T is the absolute temperature in Kelvin,  $g(\alpha)$  is the completed fraction of the reaction which is determined from h graphs, m<sub>1</sub> and m<sub>2</sub> are initial and final masses and m<sub>T</sub> is the mass remained at the temperature of the T Kelvins. The value of  $g(\alpha)$  of is simply given by  $g(\alpha) = (m_1 - m_T)/(m_1 - m_2)$ .  $E_a$  and A values were calculated from slopes and interceptions of the straight lines obtained in the plots of graphically calculated values of  $\ln\beta$ ,  $\ln(\beta/T^2)$  and  $\ln(g(\alpha)/T^2)$  against 1/T.

#### Preparation of the ligands

The first step is the synthesis of the relevant Schiff bases  $(LH_2 \text{ and } LACH_2)$  by the reaction of 1,3-propanediamine and related aldehydes. The ligands were then prepared simply by the reduction in these Schiff bases.

#### Preparation of *N*,*N*'-bis(2-hydroxyphenylidene)-1,3propanediamine (LH<sub>2</sub>)

The related Schiff base was prepared via condensation reaction in EtOH under hydrothermal conditions using 2-hydroxybenzaldehyde and 1,3-diaminepropane. 2-Hydroxybenzaldehyde (0.1 mol, 12.20 g) was dissolved in 120 mL warm EtOH; then, 0.05 mol (3.70 g) of 1, 3-diaminepropane was added to this solution and heated up to the boiling point. After cooling, yellow crystals were filtered and dried in air. Yield: 90-95%, mp: 58 °C determined by TG. Elemental Analysis, C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: 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>):  $v_{O-H}$ : 2627,  $v_{C-H(Ar)}$ : 3021–3019,  $\nu_{C-H(Aliph)}$ : 2929–2862,  $\nu_{C=N}$ : 1629,  $\nu_{C=C(ring)}$ : 1608,  $v_{C-O(Phenol)}$ : 1274–1151,  $\delta_{C-H(Ar)}$ : 762. <sup>1</sup>HNMR data in d<sub>6</sub>-DMSO (δ, ppm): 13.51 (s) (O–H), 8.60 (s) (–CH=), 7.43 (d) (HAr), 7.32(t) (HAr), 6.88 (t) (HAr), 3.68 (t) (N-CH<sub>2</sub>-), 2.01 (*p*) (-CH<sub>2</sub>-). <sup>13</sup>CNMR data in d<sub>6</sub>-DMSO ( $\delta$ , ppm): 166.6, 161.1, 132.7, 132.1, 119.1, 118.9 (CAr), 116.9 (-C=N), 58.5 (N-CH<sub>2</sub>-), 31.9 (-CH<sub>2</sub>-). MS (m/z): 282 [M]<sup>+</sup>, 161 [HO–C<sub>6</sub>H<sub>4</sub>–CH=N–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>]<sup>+</sup>, 148  $[HO-C_6H_4-CH=N-CH_2-CH_2]^+$  (base peak), 134  $[HO-C_6H_4-CH=N-CH_2-CH_2]^+$ C<sub>6</sub>H<sub>4</sub>-CH=N-CH<sub>2</sub>]<sup>+</sup>, 120 [HO-C<sub>6</sub>H<sub>4</sub>-CH=N]<sup>+</sup>, 107 [HO- $C_6H_4-CH_2$ <sup>+</sup>, 77 [ $C_6H_5$ ]<sup>+</sup>.

# Preparation of N,N-bis (2-hydroxybenzyl)-1,3-propanediamine $(L^{H}H_{2})$

3.0 g of bis-N, N'-(salicylidene)-1, 3-propanediamine (LH<sub>2</sub>) was dissolved in 70.0 mL of MeOH by rigorous stirring. The resulting solution was heated up to 50 °C adding solid NaBH<sub>4</sub> in small portions under strong mixing conditions until the solution became colorless [30, 31]. The solution was stirred for 10 min before adding 300 mL of ice water to it. The final mixture was left on the bench for 24 h. The white precipitate was filtered off and dried in air. The product was recrystallized from hot EtOH: H<sub>2</sub>O (2:1, v/v). Yield: 55-60%, mp: 107 °C. Elemental Analysis, C<sub>17</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>: Expected % C: 71.30, H: 7.74, N: 8.01; Found % C: 70.86, H: 6.69, N: 8.37. IR (cm<sup>-1</sup>):  $v_{O-H}$ : 2627,  $v_{N-H}$ : 3307,  $v_{C-H(Ar)}$ : 3055–3023,  $v_{C-H(Aliph)}$ : 2967-2823, 1606-1595,  $v_{C=C(ring)}$ :  $v_{C-O(Phenol)}$ : 1253–1099,  $\delta_{C-H(Ar)}$ : 752. <sup>1</sup>H-NMR data in d6-CH<sub>3</sub>SOCH<sub>3</sub>  $(\delta, \text{ppm})$ : 13.22 (s) (O–H), 7.12 (m) (H<sub>Ar</sub>), 6.67 (m) (H<sub>Ar</sub>), 4.73(broad) (N-H), 3.80 (m) (N-CH<sub>2</sub>-), 2.56 (m) (N-CH-), 1.15 (*m*) (-CH<sub>2</sub>-). <sup>13</sup>CNMR data in d6-DMSO (*d*, ppm): 145.41, 128.56, 127.92, 126.86, 124.85, 116.28, 65.43, 61.17, 18.62. MS (m/z): 286 (molcular peak), 179 [HO- $C_{6}H_{4}-CH_{2}-NH-CH_{2}-CH_{2}-CH_{2}-NH^{+}$ , 163 [HO-C<sub>6</sub>H<sub>4</sub>- $CH_2-NH-CH_2-CH_2-CH_2]^+$ , 150  $[HO-C_6H_4-CH_2-NH-$ CH<sub>2</sub>-CH<sub>2</sub>]<sup>+</sup>, 134 [HO-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>-NH-CH<sub>2</sub>]<sup>+</sup>, 122 [HO- $C_6H_4-CH_2-NH^+$ , 107 [HO- $C_6H_4-CH_2$ ]<sup>+</sup> (base peak), 90  $[C_6H_4-CH_2]^+$ , 77  $[C_6H_5]^+$ .

# Preparation of N,N'-bis(2hydroxyacetophenylidene)-1,3-propanediamine (LACH<sub>2</sub>)

This Schiff base was prepared via condensation reaction in EtOH under hydrothermal conditions using 2-hydroxyacetophenone and 1,3-diaminopropane. 2-Hydroxyacetophenone (0.1 mol, 13.60 g) was dissolved in 150 mL of warm EtOH; then, 0.05 mol (3.70 g) of 1,3-diaminopropane was added to it and the resulting solution was heated up to the boiling point. After cooling, yellow crystals were filtered off and dried in air. Yield: 92%, mp: 123.6 °C (determined by TG). Elemental Analysis, C<sub>19</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>: Expected % C: 73.52, H:7.14, N: 9.02; Found % C: 73.09, H: 6.35, N: 8.82 Important IR data (cm<sup>-1</sup>):  $\nu_{C-H(Ar)}$ : 3059–3017,  $\nu_{C-H(Aliph)}$ : 2944–2843,  $\nu_{C=N}$ : 1612,  $v_{C=C(ring)}$ : 1571,  $v_{C-O(Phenol)}$ : 1232–1159,  $\delta_{C-H(Ar)}$ : 754. <sup>1</sup>HNMR data in d6-DMSO ( $\delta$ , ppm): 7.06–6.97 (m) (H<sub>Ar</sub>), -6.72–6.63 (t, d) (t, d) (H<sub>Ar</sub>), 3.82 (q) (N–CH<sub>2</sub>–), 2.42–2.34 (M) (N-CH-), 1.62 (*p*) (-CH<sub>2</sub>-), 1.29-1.27 (d). <sup>13</sup>C-NMR data in d6-DMSO (δ, ppm): 157.11, 127.72, 127.52, 118.42, 115.74, 57.26, 45.01, 29.02, 22.05. MS (m/z): 310 (molcular peak), 174  $[O-C_6H_4-CCH_3=NH-CH_2-CH_2]^+$ , 162  $[HO-C_6H_4-CCH_3=NH_2-CH_2]^+$ , 148  $[HO-C_6H_4-CCH_3=NH_2-CH_2]^+$  $CCH_3 = NH_2$ <sup>+</sup> (base peak), 136 [HO-C<sub>6</sub>H<sub>4</sub>-CCH<sub>3</sub>=NH<sub>2</sub>]<sup>+</sup>, 107  $[HO-C_6H_4-CH_2]^+$ , 91  $[C_6H_4-CH_2]^+$ .

# Preparation of bis-N,N'-[1-(2-hydroxyphenyl)ethyl]-1,3-propanediamine (LAC<sup>H</sup>H<sub>2</sub>)

3.0 g of bis-N,N'-(2-hydroxyacetophenylidene)-1,3propanediamine (LACH<sub>2</sub>) was dissolved in 100.0 mL of



Fig. 3 The pictorial illustrations of [NiL<sup>H</sup>·CdI<sub>2</sub>·(DMF)<sub>2</sub>] (a) and [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·(DMF)<sub>2</sub>] (b) complexes drawn by Pluton program

Table 1	Crystal	data	and	data	collection	values
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	$(NiL^{H} \cdot CdI_{2} \cdot (DMF)_{2})$	$(NiLAC^{H} \cdot CdBr_{2} \cdot (DMF)_{2})$
Formula weight/ g mol <sup>-1</sup>	855.45	789.52
T/K	301 (2)	293 (2)
Crystal color	Blue	Blue
Crystal system	Orthorhombic	Orthorhombic
Space group	Pbca	Pbca
a/Å	20.230 (5)	20.249 (2)
b/Å	14.607 (1)	14.881 (2)
c/Å	20.648 (4)	20.565 (1)
α	90.00	90.00
β	90.00	90.00
γ	90.00	90.00
$V/Å^3$	6101 (2)	6196.8 (11)
Ζ	8	8
Calc. density/ g cm <sup>-3</sup>	1.863	1.693
$\mu/mm^{-1}$	3.370	3.908
F (000)	3312	3152
Radiation wavelength/Å	0.71073	0.71073
$\Theta$ range/°	1.97-26.37	4.09–26.37
Index ranges	-24 < h < 24	-25 < h < 25
	-12 < k < 18	-9 < k < 18
	-25 < l < 24	-25 < l < 25
$T_{\rm max}, T_{\rm min}$	0.8284, 0.6313	0.6513, 0.2454
Reflections collected	41,369/6195	42,590/6273
Reflections unique	6195	6273
R1, wR2 (2ó)	0.0667-0.2213	0.0499-0.1391
<i>R</i> 1, w <i>R</i> 2 (all)	0.1364-0.2388	0,1105–0.1644
Data/parameters	6195/320	6273/340
GOOF of F <sup>2</sup>	0.992	1.015
Largest difference peak hole/e $Å^{-3}$	2.147, - 2.340	0.740, - 0.655
CCDC No.	1,520,351	606,868

MeOH by rigorous stirring. The resulting solution was heated up to 50 °C adding solid NaBH<sub>4</sub> in small portions under strong mixing conditions until the solution became colorless [30, 31]. The solution was stirred for 10 min before adding 500 mL of ice water to it. The final mixture was left on the bench for 24 h. The white crystals were filtered off and dried in air. The product bis-*N*,*N*-[1-(2-hydroxphenyl)ethyl]-1,3-propanediamine (LAC<sup>H</sup>H<sub>2</sub>) was recrystallized from hot EtOH. Yield: 50–55%, mp: 123–124 °C. Elemental Analysis, C<sub>19</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>: Expected % C: 72.58, H: 8.33, N: 8.90; Found % C: 72.41, H: 6.97,

N: 8.54. IR (cm<sup>-1</sup>):  $v_{O-H}$ : 2643,  $v_{N-H}$ : 3309,  $v_{C-H(Ar)}$ : 3041-3007, v<sub>C-H(Aliph)</sub>: 2968-2850, v<sub>C=C(ring)</sub>: 1608-1587,  $v_{C-O(Phenol)}$ : 1253–1109,  $\delta_{C-H(Ar)}$ : 758. <sup>1</sup>HNMR data in d6-CH<sub>3</sub>SOCH<sub>3</sub> (δ, ppm): 7.12–6.85 (*m*) (H<sub>Ar</sub>), 6.67–6.34 (t, d) (H<sub>Ar</sub>), 4, 73(broad) (N–H), 3.80 (q) (–N–CH<sub>2</sub>–), 2.56 (*m*) (N–CH–), 2.43 (*m*) (CH–CH<sub>3</sub>), 1.32 (*d*) (–CH<sub>2</sub>–). <sup>13</sup>CNMR data in d6-DMSO, ppm): 157.12, 127.90, 127.74, 127.54, 118.44, 115.77, 57.29, 57.12, 29.05, 22.07. MS (m/ z): 314 (MP), 193 [O-C<sub>6</sub>H<sub>4</sub>-CHCH<sub>3</sub>-NH-CH<sub>2</sub>-CH<sub>2</sub>- $NH^{+}$ , 164  $[O-C_{6}H_{4}-CH_{2}-NH-CH_{2}-CH_{2}-CH_{2}]^{+}$ , 150  $[O-C_6H_4-CH_2-NH-CH_2-CH_2]^+$ , 136 [HO-C6H4-CCH<sub>3</sub>=NH<sub>2</sub>]<sup>+</sup>, 121 (base peak) [HO–C6H4–CH–NH]<sup>+</sup>, 91  $[HO-C6H4-CH_2]^+$ .

#### Preparation of the complexes

The coordination compounds in this study were synthesized at a single step by the use of the template method as its analogs in the literature by the reaction of stoichiometric amount of NiCl<sub>2</sub> and CdX<sub>2</sub> (X = Br or I) salts in DMF medium.

# Preparation of [NiL<sup>H</sup>·CdI<sub>2</sub>·(DMF)<sub>2</sub>]

0.002 mol (0.565 g)of  $L^{H}H_{2}$  was dissolved in 60 mL hot DMF by constant stirring, and the solution was heated up to 100–110 °C before the addition of 0.002 mol (0.476 g) NiCl<sub>2</sub>.6H<sub>2</sub>O in 20 mL MeOH and 1.0 mL Et<sub>3</sub>N and finally 0.002 mol CdI<sub>2</sub> (0.732 g) in 20 mL hot MeOH. The final mixture was rigorously stirred and left on the bench for 5–14 days. The resulting blue crystals were filtered off, washed with MeOH and finally dried in air. Elemental Analysis, C<sub>23</sub>H<sub>34</sub>N<sub>4</sub>O<sub>4</sub>NiCdI<sub>2</sub>: Expected % C: 32.21, H: 3.99, N: 6.58, Ni: 6.84, Cd: 13.11, I: 29.85; Found % C: 31.43, H: 3.78, N: 6.38 Ni: 6.52, Cd: 12.45, I: 30.47. IR (cm<sup>-1</sup>):  $v_{N-H}$ : 3241,  $v_{C-H(Ar)}$ : 3039–3019,  $v_{C-H(Aliph)}$ : 2945–2861,  $v_{C=O(DMF)}$ : 1644,  $v_{C=C(ring)}$ : 1595–1573,  $\delta_{C-H(Aliph)}$ : 1472,  $v_{C-O(Phenol)}$ : 1308–1127,  $\delta_{C-H(Ar)}$ : 756.

# Preparation of [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·(DMF)<sub>2</sub>]

0.002 mol (0.630 g) LAC<sup>H</sup>H<sub>2</sub> was dissolved in 60 mL hot DMF under stirring and heated approximately to 100–110 °C. Then, a solution of 0.002 mol (0.476 g) NiCl<sub>2</sub>.6H<sub>2</sub>O in 20 mL MeOH and 1.0 mL Et<sub>3</sub>N and finally a solution of 0.002 mol CdBr<sub>2</sub>.4H<sub>2</sub>O (0.690 g) in 30 mL hot MeOH were added to it. The resulting brown mixture was rigorously stirred and left on the bench for 3–4 weeks. The resulting blue crystals were filtered off, washed with MeOH and finally dried in air. Elemental Analysis, C<sub>25</sub>-H<sub>34</sub>N<sub>4</sub>O<sub>4</sub>NiCdBr<sub>2</sub>: Expected % C: 38.03, H: 4.85, N: 7.09, Ni: 7.43, Cd: 14.23, Br: 20.24; Found % C: 37.29, H: 4.44,

Table 2 The selected bond lengths and angles of around coordination sphere of the complexes prepared

Complex	Bond lengths/Å		Bond angles/°	
$(NiL^{H} \cdot CdI_2 \cdot (DMF)_2)$	N(1)–Ni(1)	2.101 (6)	O(2)-Ni(1)-O(1)	83.10 (16)
	N(1)-H(1A)	0.85 (7)	O(2)–Ni(1)–N(2)	90.97 (18)
	N(2)–Ni(1)	2.084 (5)	O(1)–Ni(1)–N(2)	172.68 (18)
	N(2)–H(2A)	0.83 (7)	O(2)–Ni(1)–O(4)	91.95 (16)
	O(1)–Ni(1)	2.070 (4)	O(1)–Ni(1)–O(4)	94.14 (16)
	O(1)–Cd(1)	2.215 (4)	N(2)-Ni(1)-O(4)	90.33 (18)
	O(2)–Ni(1)	2.067 (4)	O(2)–Ni(1)–N(1)	172.5 (2)
	O(2)–Cd(1)	2.227 (4)	O(1)–Ni(1)–N(1)	89.5 (2)
	O(3)–Ni(1)	2.119 (4)	N(2)–Ni(1)–N(1)	96.4 (2)
	O(4)–Ni(1)	2.087 (4)	O(4)–Ni(1)–N(1)	89.71 (17)
	Br(1)–Cd(1)	2.5257 (10)	O(2)–Ni(1)–O(3)	93.45 (16)
	Br(2)–Cd(1)	2.5409 (10)	O(1)–Ni(1)–O(3)	87.19 (16)
			N(2)-Ni(1)-O(3)	88.90 (18)
			O(4)–Ni(1)–O(3)	174.56 (17)
			N(1)–Ni(1)–O(3)	85.02 (18)
			O(1)–Cd(1)–O(2)	76.30 (14)
			O(1)–Cd(1)–Br(1)	121.16 (10)
			O(2)–Cd(1)–Br(1)	120.02 (11)
			O(1)–Cd(1)–Br(2)	109.21 (10)
			O(2)–Cd(1)–Br(2)	108.55 (10)
			Br(1)–Cd(1)–Br(2)	115.36 (4)
$(NiLAC^{H} \cdot CdBr_{2} \cdot (DMF)_{2})$	N(1)–Ni(1)	2.092 (9)	N(2)-Ni(1)-O(4)	90.3 (3)
	N(1)-H(1A)	0.9100	N(2)–Ni(1)–N(1)	96.4 (3)
	N(2)–Ni(1)	2.078 (8)	O(4)–Ni(1)–N(1)	85.4 (3)
	N(2)-H(2A)	0.9100	N(2)–Ni(1)–O(1)	172.3 (3)
	O(1)–Ni(1)	2.093 (6)	O(4)–Ni(1)–O(1)	87.3 (3)
	O(1)–Cd(1)	2.238 (7)	N(1)–Ni(1)–O(1)	90.7 (3)
	O(2)–Ni(1)	2.112 (7)	N(2)–Ni(1)–O(3)	89.8 (3)
	O(2)–Cd(1)	2.239 (7)	O(4)–Ni(1)–O(3)	174.0 (3)
	O(3)–Ni(1)	2.100 (7)	N(1)–Ni(1)–O(3)	88.6 (3)
	O(4)–Ni(1)	2.087 (7)	O(1)–Ni(1)–O(3)	93.3 (3)
	I(1)–Cd(1)	2.7527 (14)	N(2)–Ni(1)–O(2)	91.0 (3)
	I(2)–Cd(1)	2.7447 (15)	O(4)–Ni(1)–O(2)	93.6 (3)
			N(1)–Ni(1)–O(2)	172.6 (3)
			O(1)–Ni(1)–O(2)	81.9 (3)
			O(3)–Ni(1)–O(2)	92.4 (3)
			O(1)-Cd(1)-O(2)	76.0 (2)
			O(1)-Cd(1)-I(2)	121.72 (17)
			O(2)-Cd(1)-I(2)	122.04 (19)
			O(1)-Cd(1)-I(1)	105.19 (17)
			O(2)–Cd(1)–I(1)	109.47 (18)
			I(2)-Cd(1)-I(1)	115.64 (4)



Fig. 4 a TG b DTA curves of the complexes. Black: [NiL<sup>H</sup>·CdI<sub>2</sub>·(DMF)<sub>2</sub>], red: [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·(DMF)<sub>2</sub>]



N:6.89, Ni: 7.36, Cd: 14.07, I: 21.46. IR (cm<sup>-1</sup>):  $v_{N-H}$ : 3246,  $v_{C-H(Ar)}$ :3061–3008,  $v_{C-H(Aliph)}$ : 2980–2862,  $v_{C=O(DMF)}$ : 1647,  $v_{C=C(ring)}$ : 1593–1568,  $\delta_{C-H(Aliph)}$ : 1481,  $v_{C-O(Phenol)}$ : 1263–1113,  $\delta_{C-H(Ar)}$ : 759–740.

#### **Results and discussion**

The pictorial representation drawn with the Pluton software of the complexes,  $[NiL^{H}\cdot CdI_2\cdot (DMF)_2]$  and  $[NiLAC^{H}-CdBr_2\cdot (DMF)_2]$ , is illustrated in Fig. 3a and b, the data collection methods and the intrinsic features of the crystals are listed in Table 1, and the related bond lengths and angles calculated from the coordination spheres are tabulated in Table 2.

As in the similar complexes reported in the literature, Ni(II) ions in both complexes were placed in an octahedral coordination sphere. On the other hand, Cd(II) ions are located in a distorted tetrahedral coordination sphere [5–7, 10]. It is high probable that the plane formed by O1N1N2O2 donor atoms in both complexes is the equatorial plane of the octahedron because coordination bond between the Ni(II) and DMF oxygens is longer than the one formed between Ni(II) and phenolic oxygens. The

calculations made with Parts program reveal the fact that the distance between Ni(II) ions and the approximate plane formed by O1N1N2O2 atoms is 0.0197 (4) Å in [NiL<sup>H-</sup> CdI<sub>2</sub>·(DMF)<sub>2</sub>] complex and 0.0346(13) Å in [NiLAC<sup>H-</sup>  $CdBr_2 \cdot (DMF)_2$ ], [36, 37]. The chelate ring formed by NiN1C8C9C10N2 atoms is in chair conformation in both complexes. Parst calculation revealed that the angle between N1C8C10N2 plane and C8C9C10 in the chelate ring is 62.22 (0.24)° in [NiL<sup>H</sup>·CdI<sub>2</sub>·(DMF)<sub>2</sub>] complex and 61.57  $(0.96)^{\circ}$  in [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·(DMF)<sub>2</sub>] complex. The angles between N1NiN2 and N1C8C10N2 planes in the chelate ring were found to be 29.49 (0.08)° in [NiL<sup>H-</sup>  $CdI_2 \cdot (DMF)_2$  and 28.16  $(0.04)^\circ$  in [NiLAC<sup>H</sup>·CdBr<sub>2</sub>-(DMF)<sub>2</sub>] complex. Both complex structures are very similar to each other. Cd(II) ion is in a distorted tetrahedral sphere. As shown in Table 2, the angles of Br1CdBr2 and I1CdI2 are approximately 115° and the angle of O1CdO2 in both complexes is around 76°. This value is very far away from the angle of tetrahedron. The TG and DTA curves of the compound are given in Fig. 4a, b.

Although these two complexes have similar structures, their TG curves are significantly different. For TG curves of these complexes, the first expectation and observations are separation of the coordinative DMF molecules from the

 Table 3 The thermoanalytical data of the complexes

Complex	1 Thermal reaction 1 mol DMF removal		2 Thermal reaction second DMF removal and decomposition		
	Temperature range/°C	Expected/found mass loss/%	Temperature range/°C	Expected mass loss (for the second mass loss of DMF molecule)/found mass loss/ % (for second mass loss of DMF molecule)– decomposition mass loss	
$(NiLAC^{H} \cdot CdBr_{2} \cdot (DMF)_{2})$ $Mw = 853.33$	1—Heating rate: 5° C min <sup>-1</sup> , 190–236/DTA peak: 226	8.55/7.76	1—Heating rate: 5° C min <sup>-1</sup> , 236–284/DTA peak: 244	—/20.738	
	2—Heating rate: 10° C min <sup>-1</sup> , 193–244/DTA peak: 233	7.85	2—Heating rate: 10° C min <sup>-1</sup> , 244–301/DTA peak: 249	21.15	
	3—Heating rate: 15° C min <sup>-1</sup> , 203–246/DTA peak: not det.	6.82	3—Heating rate: 15° C min <sup>-1</sup> , 246–313/DTA peak: 254	20.59	
	<ul> <li>4—Heating rate:</li> <li>20° C min<sup>-1</sup>, 208–252/DTA peak: not det.</li> </ul>	6.99	4—Heating rate: 20° C min <sup>-1</sup> , 252–318/DTA peak: 259	20.54	
	5—Heating rate:	7.30	5—Heating rate:	20.96	
	25° C min <sup>-1</sup> , 209–257/DTA peak: 252	Average: 7.35 ± 0.46	25° C min <sup>-1</sup> , 252–322/DTA peak: 265	Average: $20.79 \pm 0.26$	
$(NiLAC^{H} \cdot CdBr_2 \cdot (DMF)_2)$ Mw = 791.15	1—Heating rate: 5° C min <sup>-1</sup> , 149–201/DTA peak: 175	9.22/8.69	1—Heating rate: 5° C min <sup>-1</sup> , 254–316/DTA peak: 274 and 280	9.22/8.98-14.64	
	2—Heating rate: 10° C min <sup>-1</sup> , 155–220/DTA 3-peak: 179	8.85	2—Heating rate: 10° C min <sup>-1</sup> , 254–328/DTA peak: 276 and 298	8.97–17.28	
	<ul> <li>3—Heating rate:</li> <li>15° C min<sup>-1</sup>, 158–228/DTA peak: 183</li> </ul>	8.90	3—Heating rate: 15° C min <sup>-1</sup> , 251–334/DTA peak: 283 and 304	8.92–16.91	
	4—Heating rate: 15° C min <sup>-1</sup> , 160–233/DTA peak: 189	9.53	4—Heating rate: 20° C min <sup>-1</sup> , 272–360/DTA peak: 297 and 315	8.98–18.97	
	5—Heating rate:	9.12	5-Heating rate:	9.23-19.07	
	15° C min <sup>-1</sup> , 162–239/DTA peak: 191	Average: 9.02 ± 0.32	20° C min <sup>-1</sup> , 263–361/DTA peak: 299 and 316	Average: $9.02 \pm 0.12 - 17.37 \pm 1.81$	

coordination sphere and mass loss due to DMF removal reaction, respectively. Therefore, the first mass loss is attributed to this process. However, in  $[NiLAC^{H} \cdot CdBr_{2-}(DMF)_{2}]$  complex the DMF molecules are removed from the structure in a two-step procedure. Both of these thermal reactions are endothermic. On the other hand, the removal of DMF seems to take place by a single-step process in  $[NiL^{H} \cdot CdI_{2} \cdot (DMF)_{2}]$ . However if we look more carefully at the curves, we can see that removal of DMF molecules is in fact a two-step process in  $[NiL^{H} \cdot CdI_{2} \cdot (DMF)_{2}]$  complex.

The detailed curves in Fig. 5 which depict only the region where the mass loss takes place clearly illustrate the fact that the [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·(DMF)<sub>2</sub>] complex also gives a two-step DMF removal reaction. However, the other complex [NiL<sup>H</sup>·CdI<sub>2</sub>·(DMF)<sub>2</sub>] gives a shoulder around 280 °C in TG and two endothermic signal around 280 and 305 °C in DTA plots. These two endothermic reactions are not clearly visible since they occur very close to each other. The thermos analytical data obtained from the TG curves are listed in Table 3.





**Fig. 6 a** The linear lines obtained by OFW methods for [NiL<sup>H</sup>·CdI<sub>2</sub>. (DMF)<sub>2</sub>]. **b** The KAS results of [NiL<sup>H</sup>·CdI<sub>2</sub>·(DMF)<sub>2</sub>] complex: black:  $g(\alpha) = 0.2$ , red:  $g(\alpha) = 0.3$ , green:  $g(\alpha) = 0.4$ , blue:  $g(\alpha) = 0.5$ , brown:  $g(\alpha) = 0.6$ , orange:  $g(\alpha) = 0.7$ , dark green:  $g(\alpha) = 0.8$ . **c** The CR results of [NiL<sup>H</sup>·CdI<sub>2</sub>·(DMF)<sub>2</sub>] complex: black: 5 °C min<sup>-1</sup>, red: 10 °C min<sup>-1</sup>, green: 15 °C min<sup>-1</sup>, blue: 20 °C min<sup>-1</sup>, brown: 25 °C min<sup>-1</sup>. **d** The lines obtained for [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·(DMF)<sub>2</sub>] complex by the OFW method: black:  $g(\alpha) = 0.2$ , red:  $g(\alpha) = 0.3$ , green:

 $g(\alpha) = 0.4$ , blue:  $g(\alpha) = 0.5$ , brown:  $g(\alpha) = 0.6$ , orange:  $g(\alpha) = 0.7$ , dark green:  $g(\alpha) = 0.8$ . **e** The KAS results of [NiLAC<sup>H</sup>·CdBr<sub>2</sub>. (DMF)<sub>2</sub>] complex: black:  $g(\alpha) = 0.2$ , red:  $g(\alpha) = 0.3$ , green:  $g(\alpha) = 0.4$ , blue:  $g(\alpha) = 0.5$ , brown:  $g(\alpha) = 0.6$ , orange:  $g(\alpha) = 0.7$ , dark green:  $g(\alpha) = 0.8$ . **f** The CR results of [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·(DMF)<sub>2</sub>] complex: black: 5 °C min<sup>-1</sup>, red: 10 °C min<sup>-1</sup>, green: 15 °C min<sup>-1</sup>, blue: 20 °C min<sup>-1</sup>, brown: 25 °C min<sup>-1</sup>

Table 4 The thermokinetic analysis results of the complexes prepared

Complex	Method					
	OFW		KAS		CR	
	$E_{\rm a}$ /kJ mol <sup>-1</sup>	$A/\min^{-1}$	$E_{\rm a}/{\rm kJ}~{\rm mol}^{-1}$	$A/\min^{-1}$	$E_{\rm a}/{\rm kJ}~{ m mol}^{-1}$	$A/\min^{-1}$
$(NiL^{H}.Cdl_{2}.(DMF)_{2})$	$g(\alpha) = 0.2; 148.17 \pm 2.63$	$(9.82 \pm 0.35) \times 10^{14}$	$g(\alpha) = 0.2; 169.18 \pm 2.77$	$(4.21 \pm 0.14) \times 10^9$	$\beta = 5; 98.71 \pm 0.80$	$(2.77 \pm 0.09) \times 10^9$
	$g(\alpha) = 0.3; 155.61 \pm 3.00$	$(7.60 \pm 0.29) \times 10^{15}$	$g(\alpha) = 0.3; 205.96 \pm 3.48$	$(2.90 \pm 0.09) \times 10^{12}$	$\beta = 10; 93.06 \pm 0.33$	$(1.23 \pm 0.08) \times 10^9$
	$g(\alpha) = 0.4; 126.36 \pm 2.15$	$(5.38 \pm 0.19) \times 10^{12}$	$g(\alpha) = 0.4; 160.52 \pm 1.86$	$(6.04 \pm 0.14) \times 10^9$	$\beta = 15; 102.51 \pm 0.54$	$(1.52 \pm 0.02) \times 10^{10}$
	$g(\alpha) = 0.5; 131.22 \pm 1.77$	$(1.71 \pm 0.05) \times 10^{13}$	$g(\alpha) = 0.5; 181.16 \pm 1.99$	$(6.79 \pm 0.15) \times 10^9$	$\beta = 20; 103.64 \pm 0.60$	$(2.12 \pm 0.02) \times 10^{10}$
	$g(\alpha) = 0.6; 124.90 \pm 3.45$	$(3.44 \pm 0.18) \times 10^{12}$	$g(\alpha) = 0.6; 167.73 \pm 1.52$	$(2.59 \pm 0.05) \times 10^9$	$\beta = 25; 90.34 \pm 0.77$	$(8.00 \pm 0.13) \times 10^8$
	$g(\alpha) = 0.7; 124.81 \pm 3.66$	$(3.32 \pm 0.19) \times 10^{12}$	$g(\alpha) = 0.7; 178.48 \pm 4.21$	$(2.94 \pm 0.13) \times 10^9$		
	$g(\alpha) = 0.8; 120.12 \pm 3.28$	$(1.04 \pm 0.06) \times 10^{12}$	$g(\alpha) = 0.8; 164.29 \pm 1.58$	$(1.01 \pm 0.02) \times 10^9$		
	Average = $133.03 \pm 3.14$		Average = $175.33 \pm 2.87$		Average = $97.59 \pm 0.71$	
$(NiLAC^{H} \cdot CdBr_{2} \cdot (DMF)_{2})$	$g(\alpha) = 0.2; 311.60 \pm 13.39$	$(1.47 \pm 0.39) \times 10^{39}$	$g(\alpha) = 0.2; 320.09 \pm 13.85$	$(4.48 \pm 0.43) \times 10^{27}$	$\beta = 5; 280.94 \pm 21.87$	$(1.49 \pm 0.11) \times 10^{32}$
	$g(\alpha) = 0.3; 281.68 \pm 5.63$	$(3.33 \pm 0.15) \times 10^{32}$	$g(\alpha) = 0.3; 288.78 \pm 5.77$	$(1.05 \pm 0.14) \times 10^{24}$	$\beta = 10; 203.86 \pm 4.89$	$(1.36 \pm 0.03) \times 10^{23}$
	$g(\alpha) = 0.4; 261.47 \pm 11.37$	$(1.25 \pm 0.12) \times 10^{30}$	$g(\alpha) = 0.4; 268.29 \pm 12.01$	$(4.88 \pm 0.48) \times 10^{21}$	$\beta = 15; 189.43 \pm 7.76$	$(3.03 \pm 0.12) \times 10^{21}$
	$g(\alpha) = 0.5; 218.02 \pm 2.09$	$(7.17 \pm 0.15) \times 10^{24}$	$g(\alpha) = 0.5; 221.74 \pm 2.31$	$(2.23 \pm 0.05) \times 10^{16}$	$\beta = 20; 89.89 \pm 1.92$	$(4.30 \pm 0.20) \times 10^9$
	$g(\alpha) = 0.6; 223.97 \pm 4.88$	$(2.61 \pm 0.12) \times 10^{25}$	$g(\alpha) = 0.6; 227.90 \pm 4.78$	$(8.00 \pm 0.38) \times 10^{16}$	$\beta = 25; 86.73 \pm 2.25$	$(2.04 \pm 0.11) \times 10^9$
	$g(\alpha) = 0.7; 170.59 \pm 9.33$	$(1.13 \pm 0.14) \times 10^{18}$	$g(\alpha) = 0.7$ ; 166.19 $\pm$ 8.77	$(8.41 \pm 0.93) \times 10^9$		
	$g(\alpha) = 0.8; 152.59 \pm 4.13$	$(7.93 \pm 0.46) \times 10^{16}$	$g(\alpha) = 0.8; 155.97 \pm 3.89$	$(5.04 \pm 0.77) \times 10^9$		
	Average = $231.42 \pm 8.87$		Average = $255.56 \pm 9.03$		Average = $170.17 \pm 11.94$	

$(NiLAC^{H} \cdot CdBr_2 \cdot (DMF)_2)$	Experimental bond lengths/Å	Theoretical bond lengths/Å	$(NiL^{H} \cdot CdI_{2} \cdot (DMF)_{2})$	Experimental bond lengths/Å	Theoretical bond lengths/Å
N1-Ni1	2.101 (6)	1.99672	N1 Ni1	2.092 (9)	1.98579
N2-Ni1	2.084 (5)	1.99227	N2 Ni1	2.078 (8)	1.97975
O1-Ni1	2.070 (4)	1.91395	O1 Ni1	2.093 (6)	1.93202
O1-Cd1	2.215 (4)	2.27546	O1 Cd1	2.238 (7)	2.26261
O2-Ni1	2.067 (4)	1.91531	O2 Ni1	2.112 (7)	1.92934
O2-Cd1	2.227 (4)	2.27531	O2 Cd1	2.239 (7)	2.26981
O3dmf-Ni1	2.119 (4)	3.09201	O3dmf Ni1	2.100 (7)	3.09347
O4dmf-Ni1	2.087 (4)	4.06586	O4dmf Ni1	2.087 (7)	3.29466
Br1-Cd1	2.5257 (10)	2.63299	I1 Cd1	2.7527 (14)	2.82023
Br2-Cd1	2.5409 (10)	2.64888	I2 Cd1	2.7447 (15)	2.84309
Ni1-Cd1	3.2854 (9)	3.23914	Ni1-Cd1	3.3438 (17)	3.33114
Ni1 O1 Cd1	100.05 (17)	100.92683	Ni1 O1 Cd1	101.0 (3)	104.875
Ni1 O2 Cd1	99.79 (17)	100.890	Ni1 O2 Cd1	100.4 (3)	104.697
O2 Ni1 O1	83.10 (16)	82.513	N2 Ni1 N1	96.4 (3)	97.662
O2 Ni1 N2	90.97 (18)	92.075	N2 Ni1 O1	172.3 (3)	170.805
O1 Ni1 N2	172.68 (18)	172.673	N1 Ni1 O1	90.7 (3)	89.888
O2 Ni1 N1	172.5 (2)	172.949	N2 Ni1 O2	91.0 (3)	90.620
O1 Ni1 N1	89.5 (2)	92.261	N1 Ni1 O2	172.6 (3)	171.471
N2 Ni1 N1	96.4 (2)	92.704	O1 Ni1 O2	81.9 (3)	115.652
O1 Cd1 O2	76.30 (14)	67.405	O1 Cd1 O2	76.0 (2)	67.715
O1 Cd1 Br1	121.16 (10)	114.295	O1 Cd1 I2	121.72 (17)	112.023
O2 Cd1 Br1	120.02 (11)	114.848	O2 Cd1 I2	122.04 (19)	113.002
O1 Cd1 Br2	109.21 (10)	107.228	O1 Cd1 I1	105.19 (17)	111.606
O2 Cd1 Br2	108.55 (10)	106.862	O2 Cd1 I1	109.47 (18)	110.133
Br1 Cd1 Br2	115.36 (4)	129.381	I2 Cd1 I1	115.64 (4)	127.142

Table 5 The comparison of the theoretical and experimental bond lengths and angles

The presence of the first step was attributed to the formation of square pyramidal Ni(II) complex as intermediate.  $\begin{bmatrix} NiLAC^{H} \cdot CdBr_{2} \cdot (DMF)_{2} \end{bmatrix} \rightarrow \begin{bmatrix} NiLAC^{H} \cdot CdBr_{2} \cdot DMF \end{bmatrix} \\ + DMF_{(gas)} \begin{bmatrix} NiL^{H} \cdot Cdl_{2} \cdot (DMF)_{2} \end{bmatrix} \rightarrow \begin{bmatrix} NiL^{H} \cdot Cdl_{2} \cdot DMF \end{bmatrix} \\ + DMF_{(gas)}$ 

There are similar Schiff base complexes of Ni(II)–Zn(II) prepared in the literature, and it was reported that there were square pyramidal and octahedral complexes formed depending upon the ligand concentration [5]. It was not possible to obtain a mononuclear NiL<sup>H</sup>-type complex with  $L^{H}H_{2}$  ligand. Although a CuL<sup>H</sup> complex has been reported to be synthesized and isolated recently [38], there was no report about the NiL<sup>H</sup> complex in the literature. On the other hand, the TG curves show clearly that the intermediate product [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·DMF] formed during the reaction is much more stabile because of this intermediate remained stable between 210 and 250 °C and the second DMF molecule immediately removed in [NiL<sup>H</sup>·CdI<sub>2</sub>. (DMF)] and the decomposition of the complex has began

because of NiL<sup>H</sup> complex cannot isolated at room temperature, and in this case NiL<sup>H</sup> complex cannot be stable at 250 °C. For this reason, decomposition of NiL complex begins with the removal of the second DMF molecule from [NiL<sup>H</sup>·CdI<sub>2</sub>·(DMF)2] complex. As a result, the first and second DMF losses cannot be distinguished from each other at the DTA curves. The removal of the first DMF molecule is much more apparent in [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·DMF] complex. In addition, the first and second DMF losses can be seen in the DTA curve of the [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·DMF] complex. This situation indicates that the NiLAC<sup>H</sup> mononuclear complex is more stable than the mononuclear NiL<sup>H</sup> complex. Therefore, the difference between these two thermal reactions was investigated by the use of thermal kinetic methods such as nonisothermal-isoconversional Ozawa-Flynn-Wall (OFW) and Kissinger-Akahira-Sunose (KAS) and isothermal Coats-Redfern (CR) methods. The activation energy and the Arrhenius pre-exponential of the first thermal reaction were determined [25-31]. OFW and KAS calculations were carried out at heating rates of 5, 10, 15, 20 and 25 °C min<sup>-1</sup> determining

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the T values corresponding to the points at  $g(\alpha)$  0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8, and 1/T values were plotted against  $\ln\beta$  for OFW and against  $\ln(\beta/T^2)$  for KAS method. For CR, the  $g(\alpha)$  values for each heating rate were calculated against different temperatures. So, five lines were obtained for the five different heating rates and temperatures. All these lines are depicted in Fig. 6a–f, and the  $E_a$  and A values determined from Fig. 6a–f are listed in Table 4.

Mononuclear complexes prepared by the use of reduced ONNO-type Schiff bases are very scarce, and Ni(II) complex prepared from reduced ONNO-type Schiff bases has not been reported yet. Recently, preparation, isolation and characterization of a CuL<sup>H</sup> complex have been reported [38]. However, some of the reduced ONNO-type Schiff bases give abundant amount di-, tri- and polynuclear complexes. The polynuclear complexes of these ligands are highly stable. The kinetic analysis results reported in Table 4 belong to the reaction of the removal of the first DMF group from the structure. DTA curves clearly show the formation of [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·DMF] complex after the removal of the first DMF molecule from the structure of [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·(DMF)<sub>2</sub>] complex, and then, second DMF molecule removes from the structure. This case is different for the  $[NiL^{H} \cdot CdBr_{2} \cdot DMF]$  complex. The final temperature of the second DMF molecule removal reaction is not clear. Thermokinetic analysis results makes it apparent that  $[NiLAC^{H} \cdot CdI_{2} \cdot (DMF)_{2}]$  complex is more stable than [NiL<sup>H</sup>·CdI<sub>2</sub>·(DMF)<sub>2</sub>]. The thermokinetic results for the reactions of two complexes involving the cleavage of a DMF molecule are given in Table 4. The  $E_a$  value for the reaction of [NiLAC<sup>H</sup>·CdI<sub>2</sub>·(DMF)<sub>2</sub>] is significantly higher than the one for the reaction of  $[NiL^{H} \cdot CdI_{2} \cdot (DMF)_{2}]$ . This case clearly indicates that the thermal stability of  $[NiLAC^{H} \cdot CdI_{2} \cdot (DMF)_{2}]$  is higher. The magnitude of the activation energy is the indication of the stability of the compound. The greater activation energy corresponds to higher thermal stability of the compound. The results reported in Table 4 are different from each other. Especially, the data found by the isothermal CR method are highly different than the data obtained by these of non isothermal methods. Although the Ea values obtained from by the use of OFW and KAS methods were found to be comparable, the values of the pre-exponential constants were erratic and were not comparable. The reason for this discrepancy was most probably the immediate removal of the second DMF molecules just after the removal of the first molecule leaving a highly unstable mononuclear complex behind, which immediately decomposes with the removal of the second DMF group. The [NiLAC<sup>H</sup>·CdBr<sub>2-</sub> DMF] complex formed after the removal of DMF molecule from the structure of [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·(DMF)<sub>2</sub>] is much more stabile that the corresponding complex of 
 Table 6
 The electron density and relative energy levels of the central atoms around coordination spheres

Atom	Orbital	Occupancy	Energy
(NiLAC <sup>H</sup> ·C	$CdBr_2 \cdot (DMF)_2)$		
Ni	dxy	1.98411	- 0.27503
Ni	dxz	1.89553	-0.26860
Ni	dyz	0.87339	- 0.19839
Ni	$dx^2y^2$	1.96500	- 0.27150
Ni	$dz^2$	1.97814	- 0.30411
Cd	dxy	1.99906	- 0.60449
Cd	dxz	1.99979	- 0.60620
Cd	dyz	1.99730	- 0.60134
Cd	$dx^2y^2$	1.99788	- 0.60375
Cd	$dz^2$	1.99772	- 0.60505
$(NiL^H \cdot CdI_2)$	$(DMF)_2)$		
Ni	dxy	1.95486	- 0.27368
Ni	dxz	1.57125	- 0.24083
Ni	dyz	1.50882	-0.25378
Ni	$dx^2y^2$	1.81378	- 0.25943
Ni	$dz^2$	1.82272	- 0.28358
Cd	dxy	1.99836	- 0.60785
Cd	dxz	1.99882	- 0.60919
Cd	dyz	1.99785	- 0.60678
Cd	$dx^2y^2$	1.99885	-0.60782
Cd	$dz^2$	1.99832	- 0.60867

[NiL<sup>H</sup>·CdI<sub>2</sub>·DMF] formed with a similar manner from the [NiL<sup>H</sup>·CdI<sub>2</sub>·(DMF)<sub>2</sub>] complex. This is verified with the TG data where the boundaries of the first and second thermal DMF reaction are clearly visible in TG curves of [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·DMF] complex. We think that the differences can be been explained by the results obtained from theoretical programs. Therefore, the theoretical bond lengths, bond angles and the HOMO-LUMO diagrams were calculated by the use of DFT/B3LYP/LanL2DZ algorithm embedded in Gaussian 09 software. In addition, the occupancy level of the d orbitals of the central atoms and relative energy levels were calculated with natural bond-order (NBO) analysis by using the atomic coordinates obtained from X-ray data as input. The bond lengths, bond angles in the coordination sphere and the occupancy levels of the 3d orbitals of Ni(II) and 4d orbitals of Cd(II) are given in Tables 5 and 6, respectively. The steric conditions created by the methyl groups effect the overlapping feature of the nitrogen donor groups. Therefore, the high probability of HOMO orbitals around central Ni(II) ion of  $[NiLAC^{H} \cdot CdBr_{2} \cdot (DMF)_{2}]$  complex is shown in Fig. 7. In contrary, this probability for the other complex is weak. The calculated average energy levels of HOMO and LUMO orbitals for both complexes show that [NiLAC<sup>H-</sup> CdBr<sub>2</sub>·(DMF)<sub>2</sub>] complex is more stable. The HOMO, [NiLAC<sup>H</sup>.CdBr<sub>2</sub>.DMF]



HOMO, calculated energy level: -5.888 eV



LUMO, calculated energy level: -2.072 eV

Fig. 7 The HOMO and LUMO orbitals of the complexes prepared

LUMO energy levels and  $\Delta E$  for [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·(DMF)<sub>2</sub>] complex are -5.888, -2.072 and 3.816 eV, respectively. These values for the other complex are -5.709, -2.105 and 3.604 eV. As expected,  $\Delta E$  value of the [NiLAC<sup>H-</sup>CdBr<sub>2</sub>·(DMF)<sub>2</sub>] complex is greater than [NiL<sup>H</sup>·CdI<sub>2</sub>·(DMF)<sub>2</sub>].

The most probable explanation of this difference is the fact that after being located between Cd(II) ions extracts electrons from the oxygen atoms decrease the electron density going from these oxygen atoms to nickel ion. That is why the central Ni(II) atom binds two solvent molecules. The bond lengths indicate that they are coordinatively bounded. When we look at the bond lengths given in Table 6, it is seen that the biggest difference between the experimental and theoretically calculated values was between the oxygen atoms of the coordinated DMF groups and the central Ni(II) ion. The experimental values were determined as 2.119 and 2.087 Å come out as 4.06 and

[NiL<sup>H</sup>.CdI<sub>2</sub>.(DMF)<sub>2</sub>]



HOMO, calculated energy level: -5.709 eV



LUMO, calculated energy level: -2.105 eV

3.09 Å in theoretical calculations. The same situation exists in HOMO-LUMO diagram. Figure 7 indicates that the central Ni(II) ion of [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·(DMF)<sub>2</sub>] complex overlaps in a stronger manner. Figure 7a shows that the central ion of compound [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·(DMF)<sub>2</sub>] makes a much stronger overlapping with the HOMO orbitals. Figure 7b, on the other hand, indicates that the overlapping of the central atom of compound [NiL<sup>H</sup>·CdI<sub>2</sub>·(DMF)<sub>2</sub>] is not as strong as the corresponding ion of [NiLACH-CdBr<sub>2</sub>·(DMF)<sub>2</sub>] complex. The experimental bond lengths of N1-Ni and N2-Ni of [NiL<sup>H</sup>·CdI<sub>2</sub>·(DMF)<sub>2</sub>] complex (2.093 and 2.112 Å) are longer than the corresponding bonds in [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·(DMF)<sub>2</sub>] complex (2.070 and 2.067 Å). It is possible that the two methyl groups increase electron-donating capacities of the nitrogen donors. That is why it can be claimed that the intermediate product of [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·(DMF)<sub>2</sub>] complex is more stable than the intermediate product of [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·DMF]. The

occupancy levels of the central ions obtained by NBO analysis are listed in Table 6. It is not logical to expect any energy differences between 4d orbitals of the both coordination compound since Cd(II) ion is in d<sup>10</sup> state. In fact, since the occupancy levels of 4d orbitals of Cd(II) ion are very close to 2.00, the energy levels of 4d orbitals are not different from each other. If we think that the O<sub>2</sub>N<sub>2</sub> donors are coordinated along x and y and the oxygens of the DMF molecules z axes, it is obvious that the most effected orbitals are  $dx^2 - y^2$ ,  $dz^2$  and dxy orbitals. According to the data listed in Table 6, this seems to be the case for [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·(DMF)<sub>2</sub>] complex. However, the  $dx^2 - y^2$ orbital of [NiL<sup>H</sup>·CdI<sub>2</sub>·(DMF)<sub>2</sub>] complex does not follow this trend. This is an evidence that the locations of the nitrogen donors of the [NiL<sup>H</sup>·CdI<sub>2</sub>·(DMF)<sub>2</sub>] compound are not suitable for overlapping. That is causes the resulting intermediate of formed in the thermal analyses being higly unstable and decompose immediately. On the other hand, thermogravimetric data of the [NiLAC<sup>H</sup>·CdBr<sub>2</sub>·(DMF)<sub>2</sub>] complex do not explicitly prove that the compound NiLAC<sup>H</sup> formed after the removal of DMF groups is highly stabile. What it proves is that it is at least more stable than the corresponding NiL<sup>H</sup> of the other complex. It is a known fact that one cannot expect a complete accordance with the thermokinetic analysis if the compound gives no stable product as a result of thermal dissociation process. The thermal kinetic applications are based upon certain assumptions [24]. The validity of the Kissinger equation has been disputed in recent days [39].

## Conclusions

Two Ni<sup>II</sup>–Cd<sup>II</sup> dinuclear complexes with similar structures have been prepared. Their structures have been characterized by the X-ray diffraction methods. Thermogravimetric analysis differences between two complexes were explained by the use of thermal kinetic analysis and theoretical calculations. Two consecutive removals of DMF molecule from the complexes observed during the thermal degradation reactions. The activation energies of the first thermal removal of the DMF molecule were calculated by the use of thermal kinetic methods developed by Ozawa-Flynn-Wall, Kissinger-Akahira-Sunose and Coats-Redfern. Markedly, higher activation energy for [NiLACH-CdBr<sub>2</sub>·(DMF)2] complex was observed, and therefore, this complex and its intermediates were more thermally stable. Thermally, stability of this complex was attributed to the more suitable position of the donor nitrogens of LACHH2.

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#### References

- Calvin M, Barkelew CH. The oxygen carrying synthetic chelate compounds. J Am Chem Soc. 1946;68:2267–73.
- Martell A, Calvin M. Die Chemie der Metallchelat Verbindungen. Verlag Chemie GMBH: übersetzt von Hermann Specker; 1958. p. 199–200.
- Butcher RJ, Sinn E. Relation between magnetic, spectroscopicand structural properties of Bis[chloro(N-isopropyl-2-hydroxybenzylidene)amine ato-µ-O-copper(II)] and Bis(N-isopropyl-2-hydroxybenzylidenamine ato)copper(II). Inorg Chem. 1976;15:1604–9.
- 4. Fukuhara C, Tsuneyoshi K, Matsumoto N, Kida S, Mikuriya M, Mori M. Synthesis and characterization of trinuclear Schiff bases base complexes containing sulphure dioxide or hydrogensulphide ions as bridging group. JCS Dalton Trans. 1990;11:3473–9.
- Atakol O, Nazir H, Arıcı C, Durmuş S, Svoboda I, Fuess H. Some New Ni-Zn heterodinuclear complexes:square-pyramidal nickel(II) coordination. Inorg Chim Acta. 2003;342:295–300.
- Aksu M, Durmuş S, Sarı M, Emregül KC, Svoboda I, Fuess H, Atakol O. Investigation of thermal decomposition some heterodinuclear Ni<sup>II</sup>-M<sup>II</sup> complexes prepared from ONNO type reduced Schiff bases base compounds. J Therm Anal Cal. 2007;90:541–7.
- Wang JH, Yan PF, Li GM, Zhang JW, Chen P, Suda M, Einaga Y. N, N'-bis(2-hydroxy-methoxybenzylidene)-1,3-diaminopropane dimeric 4f and 3d–4f heterodinuclear complexes. Inorg Chim Acta. 2010;363:3706–13.
- Feng X, Zhou LL, Shi ZQ, Shang JJ, Wu XH, Wang LY, Zhou JG. Synthesis, crystal structure, and luminescence property of a new zinc (II) complex with Schiff-base containing triazole propane ancillary ligand. Synth React Inorg Met Org Nano Metal Chem. 2013;43:1093–8.
- Chacraborty P, Mohanta S. Mononuclear and heterometallic dinuclear, trinuclear and dimer-of-dinuclear complexes derived from single- and double-compartment Schiff bases base ligands having a less utilized diamine. Polyhedron. 2015;87:98–108.
- Kanta Das L, Gomez-Garcia CJ, Drew MGB, Ghosh A. Plying with different metalloligands [NiL] and Hg to [NiL] ratios to tune the nuclearity of Ni(II)-Hg(II) complexes. Polyhedron. 2015;87:311–20.
- Yardan A, Hopa C, Yahsi Y, Karahan A, Kara H, Kurtaran R. Two new heterodinuclear Schiff bases base complexes: synthesis, crystal structure and thermal studies. Spectrochim Acta A. 2015;137:351–6.
- Daier VA, Riviere E, Mallet-Ladeira S, Moreno DM, Hureau C, Signorella SR. Synthesis, characterization and activity of imidazolate-bridged and Schiff-base dinuclear complexes as models of Cu, Zn-SOD. A comparative study J Inorg Biochem. 2016;163:162–75.
- Kopotkov VA, Korchagin DV, Talantsev AD, Morgunov RB, Yagubskii EB. Binuclear cyano-bridged complex derived from [Mn-III(salpn)] and [Fe-III(CN)(6)]: synthesis, structure and magnetic properties. Inorg Chem Comm. 2016;64:27–30.
- Uhlenbrock S, Wegner R, Krebs B. Synthesis and characterization of novel Tri- and hexanuclear zinc complexes with biomimetic chelate ligands. JCS Dalton Trans. 1996;18:3731–6.
- Ülkü D, Ercan F, Atakol O, Dinçer FN. Bis{(µ-acetato)[µbis(salicylidene)-1,3-propanediamine ato](dimethylsulphoxide) nickel(II)}nickel(II). Acta Cryst. 1997;C53:1056–7.
- Biswas S, Diaz C, Ghosh A. The first triple phenoxido-bridged triangular N<sup>II</sup>Cu<sup>II</sup><sub>2</sub> Compleses with a N<sub>2</sub>O<sub>2</sub> Donor di-Schiff bases Base and Pseudohalide (N(CN)<sup>-</sup><sub>2</sub> or NCS<sup>-</sup>) Ligands. Polyhedron. 2013;51:96–101.
- Ghosh S, Aromi G, Gamez P, Ghosh A. The impact anionmodulated structural variation on the magnetic coupling in trinuclear heterometallic Cu<sup>II</sup>-Co<sup>II</sup> complexes derived from a salen type schiff bases base ligand. Eur J Inorg Chem. 2014;21: 3341–9.

- Saha S, Sasmal A, Choudhury CR, Gomez-Garcia CJ, Garribba E, Mitra S. A new double phenoxide-bridged trinuclear Cu(II)-Schiff bases base complex. Polyhedron. 2014;69:262–9.
- Hazari A, Ghosh A. Trinuclear complexes of [CuL] (H2L = N, N'-bis(salicylidene)-1,4-butanediamine e) with HgX2 (X = N3-, NCO-). Polyhedron. 2015;87:403–10.
- Ida Y, Ghosh S, Ghosh A, Nojiri H, Ishida T. Strong ferromagnetic exchange interactions in hinge-like Dy(O2Cu)(2) complexes involving double oxygen bridges. Inorg Chem. 2015;54: 9543–55.
- Aneetha H, Pannerselvam K, Liao TF, Lu TH, Chung CS. Syntheses, structures, spectra and redox properties of alkoxo and phenoxo-bridged diiron complexes. JCS Dalton Trans. 1999;16:2689–94.
- 22. Reglinski J, Taylor M, Kennedy AR. Hydrogenated Schiff bases base ligands. Inorg Chem Comm. 2006;9:736–9.
- Vyazovkin S, Burnham AK, Criado JM, La Perez-Maqueda, Popescu C, Sbirazzuoli N. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. Thermochim Acta. 2011;520:1–19.
- 24. Koga N. Ozawa's kinetic method for analysing thermoanalytical curves. J Therm Anal Cal. 2013;113:1527–41.
- Zianna A, Vecchio S, Gdaniee M, Czapik A, Hadzidimitriou A, Lalia-Kantouri M. Synthesis, thermal analysis and spectroscopic and structural characterizations of zinc(II) complexes with salicylaldehydes. J Therm Anal Cal. 2013;112:455–64.
- Çılgı GK, Çetişli H, Donat R. Thermal kinetic analysis of uranium salts. J Therm Anal Cal. 2014;115:2007–20.
- Kullyyakool S, Danvirutai C, Siriwong K, Noisong P. Determination of kinetic triplet of the synthesized Ni<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.8H<sub>2</sub>O by non-isothermal and isothermal kinetic methods. J Therm Anal Cal. 2014;115:1497–507.

- Abdel-Kader NS, Amine RM, El-Ansary AL. Complexes of Schiff bases base of benzopyran-4-one derivative. J Therm Anal Cal. 2016;123:1695–706.
- Sarada K, Muraleedharan K. Effect of addition of silver on the thermal decomposition kinetics of copper oxalate. J Therm Anal Cal. 2016;123:643–51.
- Soliman AA, Linert W. Investigations on new transition metal chelates of the 3-methoxy-salicylidene-2-amine othiophenol Schiff bases base. Thermochim Acta. 1999;338:67–75.
- Ebrahimi HP, Hadi JS, Abdulnabi ZA, Bolandnazar Z. Spectroscopic, thermal analysis and DFT computational studies of salentype Schiff bases base complexes. Spectrochim Acta Part A. 2014;117:485–92.
- Frisch MJ, Trucks GW et al. Gaussian 09, Revision D.01. Gaussian Inc. Wallingford CT. 2009.
- Oxford Diffraction CrysAlis CCD and CrysAlis RED, Version 1.170.14, Oxfordshire (England): Oxford Diffraction, 2002.
- Sheldrick GM. SHELXS-97 and SHEXL-97, program for crystal structure solution and refinement. Göttingen: University of Göttingen; 1997.
- 35. Farrugia LJ. WinGX suite for small-molecule single-crystal crystallography. J Appl Cryst. 1999;32:837–8.
- Spek AL. Structure validation in chemical crystallography. Acta Cryst. 2009;D65:148–55.
- 37. Spek AL. J Appl Cryst. 2003;36:7-13.
- 38. Hazari A, Kanta DL, Bauza A, Frontera A, Ghosh A. Exploring the coordinative adaptation and molcular shapes of trinuclear Cu<sup>1</sup><sub>2</sub>M<sup>II</sup> (M = Zn/Cd) complexes derived from salen type Schiff bases. JCS Dalton Trans. 2016;45:5730–40.
- Svoboda R, Malek J. Is the Kissinger Equation obsolete today? J Therm Anal Cal. 2014;115:1961–7.