J Therm Anal Calorim (2009) 98:377–385
DOI 10.1007/s10973-009-0302-2

The effect of ligand basicity on the thermal stability of heterodinuclear Ni^{II}–Zn^{II} complexes

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Received: 10 November 2008 / Accepted: 16 January 2009 / Published online: 6 August 2009

Abstract Four complexes of the nuclear structure Ni^{II}–Zn^{II} were prepared with bis-*N*,*N*′-(salicylidene)-1,3-propanediamine (LH_2), bis-*N*,*N*′-(salicylidene)-2,2′-dimethyl-1,3-propanediamine ($LDMH_2$) and the reduced derivatives of these Schiff bases, bis-*N*,*N*′-(2-hydroxybenzyl)-1,3-propanediamine (L^HH_2), bis-*N*,*N*′-(2-hydroxybenzyl)-2,2′-dimethyl-1,3-propanediamine (LDM^HH_2). The complexes were characterized using IR spectroscopy, elemental analysis and thermogravimetric methods. The stoichiometry of the complex molecules were found to be $NiL{\cdot}ZnCl_2{\cdot}(DMF)_2$, $NiLDM{\cdot}ZnCl_2{\cdot}(DMF)_2$, $NiL^H{\cdot}ZnCl_2{\cdot}(DMF)_2$ and $NiLDM^H{\cdot}ZnCl_2{\cdot}(DMF)_2$. The molecular models of the complexes prepared with the reduced Schiff bases were determined according to the X-ray diffraction method. It is seen that in these complexes Ni(II) is in octahedral and Zn(II) is in tetrahedral coordination sphere. Ni(II) ion is coordinated between two nitrogen and two oxygen donors of the ligand and oxygen donors of the two DMF molecules. Zn(II) ion on the other hand is coordinated between two oxygen of the organic ligand forming two μ bonds. It also coordinates two Cl ions. The thermogravimetric analysis showed that the complex $NiLDM^H{\cdot}ZnCl_2{\cdot}(DMF)_2$ containing methyl groups is more stable than the other complex $NiL^H{\cdot}ZnCl_2{\cdot}(DMF)_2$ containing reduced Schiff base. The coordinative DMF molecules in $NiLDM^H{\cdot}ZnCl_2{\cdot}(DMF)_2$ were thermally cleaved. However, the cleavage of DMF molecules $NiL^H{\cdot}ZnCl_2{\cdot}(DMF)_2$ resulted in the thermal degradation of the complex. In order to explain the TG data of the ligands were titrated in non-aqueous medium and their basicity strengths were determined. It was found that the basicity of the ligands containing two methyl groups were stronger. It is understood that the two methyl groups increase the negative charge density on nitrogen causing an increase in complex stability.

Keywords Thermal decomposition · Dinuclear complexes · Basicity order · Potentiometric titration · Thermal stability

Introduction

Bis-*N*,*N*′-(salicylidene)-1,3-propanediamine (LH_2) is a ligand which is highly prone to forming multi nuclear complexes [1–4]. Ni(II) and Cu(II) complexes of this ligand have square planar coordination sphere and the molecular structures of these complexes determined using X-ray diffraction method are given in literature [5]. In the presence of a Lewis acid, these square planar complexes coordinate to the Lewis acid from their phenolic oxygens and form binuclear complexes [6–11]. Ni(II) and Cu(II) ions in these binuclear complexes can also be coordinated with a nitrogen containing ligand such as Py or a solvent such as DMF [12–14]. Bis-*N*,*N*′-(salicylidene)-1,3-propanediamine (LH_2) is easily reduced with $NaBH_4$ in amphiprotic medium and turn into an ONNO type phenol–amine ligand [15]. In this study, bis-*N*,*N*′-(salicylidene)-1,3-propanediamine (LH_2) and bis-*N*,*N*′-(salicylidene)-2,2′-dimethyl-1,3-propanediamine

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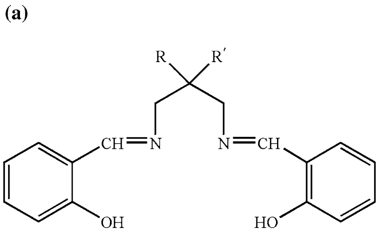
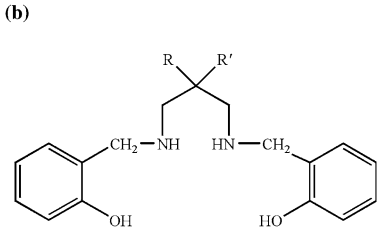


R = R′= H, bis-*N*,*N*′-(salicylidene)-
1,3-propanediamine (LH_2)
R = R′= CH_3, bis-*N*,*N*′-(salicylidene)-
2,2 -dimethyl-1,3-propanediamine ($LDMH_2$)



R = R′ = H, bis-*N*,*N*′-(2-hydroxybenzyl)-
1,3-propanediamine (L^HH_2)
R = R′ = CH_3, bis-*N*,*N*′-(2-hydroxybenzyl)-
2,2 -dimethyl-1,3-propanediamine (LDM^HH_2)

Fig. 1 The formulas of ligands **a** LH_2, $LDMH_2$, **b** L^HH_2 and LDM^HH_2

($LDMH_2$) are reduced to obtain bis-*N*,*N*′-(2-hydroxybenzyl)-1,3-propanediamine (L^HH_2), bis-*N*,*N*′-(2-hydroxybenzyl)-2,2′-dimethyl-1,3-propanediamine (LDM^HH_2). Heterodinuclear complexes are obtained from both the Schiff bases (LH_2 and $LDMH_2$) and the reduced Schiff bases (L^HH_2 and LDM^HH_2) in the presence of $ZnCl_2$ in DMF medium. The formulas of the ligands LH_2, $LDMH_2$, L^HH_2 and LDM^HH_2 are given in Fig. 1a and b.

The molecular models of the complexes similar to **I** ($NiL{\cdot}ZnCl_2{\cdot}(DMF)_2$) and **II** ($NiLDM{\cdot}ZnCl_2{\cdot}(DMF)_2$) are reported in literature [16, 17]. The X-ray diffraction studies of the complexes **III** ($NiL^H{\cdot}ZnCl_2{\cdot}(DMF)_2$) and **IV** ($NiLDM^H{\cdot}ZnCl_2{\cdot}(DMF)_2$) which gave suitable crystals were carried out and the complexes **I–IV** were thermogravimetrically analyzed. The four complexes prepared were characterized with IR and elemental analyses. They were later studied thermogravimetrically. The two Schiff base ligands; bis-*N*,*N*′-(salicylidene)-1,3-propanediamine, bis-*N*,*N*′-(salicylidene)-2,2′-dimethyl-1,3-propanediamine and the two reduced Schiff bases; bis-*N*,*N*′-(2-hydroxybenzyl)-1,3-propanediamine,bis-*N*,*N*′-(2-hydroxybenzyl)-2,2′-dimethyl-1, 3-propanediamine were titrated with $HClO_4$ in acetonitrile solvent to determine their relative basicity strengths in order to explain the TG data.

Experimental

Chemicals

1,3-diaminopropane (Merck), 2,2′-dimethyl-1,3-propanediamine (Merck), salisylaldehyde (Fluka), ethanol (Riedel-deHaën), methanol (Riedel-deHaën), nickel(II) chloride hexahydrate (Aldrich), zinc(II) chloride (Merck), sodium boronhydride (Fluka), acetonitrile (Riedel-deHaën), perchloric acid (Merck) were used without further purification.

Preparation of the ligands

Schiff bases LH_2 and $LDMH_2$ were prepared by the condensation reaction of 1,3-diaminopropane, 2,2′-dimethyl-1,3-propanediamine and salicylaldehyde in ethanol. They were recrystallised in 1:1 $EtOH{:}H_2O$ mixture. LH_2; melting point 58–59 °C, reaction yield >90%, color yellow; $LDMH_2$; melting point 97–98 °C, reaction yield >95%, color yellow.

Approximately 3.0 g of these Schiff bases were dissolved in 50 mL MeOH by mixing and $NaBH_4$ was added to this solution in drop wise manner until a colorless solution was obtained. The resulting solution was poured into approximately 250 mL icy water and kept on the bench for 24 h. The white colored organic precipitate formed at the end of this period is the reduced Schiff base. It was recrystallised from 70% EtOH. L^HH_2; melting point 106–108 °C, reaction yield >75%, color white; LDM^HH_2; melting point 95–96 °C, reaction yield >90%, color white.

Preparation of the complexes

Four complexes were prepared using the same method. 0.001 mol ligand (LH_2, $LDMH_2$, L^HH_2, LDM^HH_2) was solved in 40 mL hot DMF. Solution of 0.2 mL Et_3N and 0.001 mol (0.238 g) $NiCl_2{\cdot}6H_2O$ in 0.20 mL hot MeOH was added to this solution. Afterwards solution of 0.001 mol (0.136 g) $ZnCl_2$ in 10 mL hot MeOH was added and the mixture thus prepared was kept on the bench for 2–3 days. The crystals which precipitated at the end of this period were filtered and dried in air.

Measurement techniques

C, H, N element analysis of the complexes were made on Leco 932 CHNS analyser. Ni and Zn analysis were made on GBC Avanta PM AAS equipment. Chlorine analysis was made gravimetrically with the help of $AgNO_3$. IR spectra were obtained on a Perkin Elmer Spectrum 100 FTIR spectrometer using the ATR attachment.

Thermogravimetric analyses were carried out on Shimadzu DTG-60 H equipment in Pt pans under N_2 atmosphere. Heating rate was 10 °C/min. Curves were recorded between 30 and 750 °C. The pans were cleaned with O_2 at 750 °C.

All potentiometric measurements were carried out in an 80-mL jacketed titration cell thermostated at 25.0 ± 0.1 °C and under nitrogen atmosphere. An Orion 960 automatic titrator, equipped with a combined pH electrode (Ingold) containing a filling solution of 0.1 M NaCl was used for measuring the cell emf values. Titration of the ligands was carried out in MeCN and 0.034 M $HClO_4$ was used as titrant.

The intensity data were collected at room temperature using an Enraf-Nonius CAD 4 diffractometer [18] with MoKα radiation with $\omega/2\theta$ scan mode. The cell parameters were determined from a least-squares refinement of 25 centered reflections in the range of $2.46 \leq \theta \leq 23.41°$ in **III**, $2.12 \leq \theta \leq 26.29°$ in **IV**. Three standard reflections that were periodically measured for every 120 min during data collection showed no significant intensity variations. The ranges of h, k, l are $0 \leq h \leq 15$, $0 \leq k \leq 21$, $0 \leq l \leq 23$ in **III**, $0 \leq h \leq 11$, $-12 \leq k \leq 12$, $-22 \leq l \leq 21$ in **IV**, respectively. There were 4,422 reflections were collected for complex **III** 3572 of were utilized, the number of reflections collected for complex **IV** were 4,081 of which 2,898 were utilized for structural determinations and refinement according to $I \geq 2\sigma(I)$. Cell refinement and data reduction were carried out using CAD4 Express [18]. The structures were solved by direct method using the program SHELXS97 and refined using SHELXL97 [19] in the WinGX package [20]. All non-hydrogen atoms were refined isotropically and then anisotropically by full matrix least squares method. All the hydrogen atoms were placed geometrically and refined as riding with $U_{eq}(H) = 1.2U_{iso}(C)$.

Results and discussion

Important IR data and elemental analysis results of the ligands and complexes are given in Table 1. The data in Table 1 are in agreement with the formulas given in Fig. 1a and b. The band seen at 1,652 cm^{-1} in the IR spectra is the stretching vibration of the carbonyl group in DMF. $\nu_{C=N}$ stretching vibrations of complexes **I** and **II** are seen at 1,620 cm^{-1}. In Schiff bases which contain an aliphatic carbon attached to the iminic nitrogen $\nu_{C=N}$ vibration band is observed at wave numbers bigger than 1,630 cm^{-1}. However, it is a known fact that these vibration bands shift 10–25 cm^{-1} towards lower energy. These vibrations for ligands (LH_2 and $LDMH_2$) are observed at 1,642; 1,644 cm^{-1} have moved to lower

Table 1 Elemental analysis results and important IR data of the complexes and ligands (L^HH_2 and LDM^HH_2)

Complex	Elemental analysis								IR data/cm^{-1}								
	Expected/%				Found/%				ν_{O-H}	ν_{N-H}	ν_{C-H} (Ar)	ν_{C-H} Aliph	$\nu_{C=N}$	$\nu_{C=C}$(Ar)	δ_{CH2}	ν_{C-O}	δ_{C-H} (Ar)
	C	N	Ni	Zn	C	N	Ni	Zn	–	–	3048–3014	2964–2921	1649	1627	1594	1477	758
I NiL·$ZnCl_2$·$(DMF)_2$	44.46	9.01	9.44	10.52	44.53	8.76	9.38	10.65	–	–	3052–3012	2973–2917	1651	1628	1596	1472	755
II NiLDM·$ZnCl_2$·$(DMF)_2$	46.24	8.62	9.04	10.07	45.84	8.43	8.86	9.58	–	3252–3218	3054–3021	2963–2928	1657	–	1602	1487	759
III NiL^H·$ZnCl_2$·$(DMF)_2$	44.17	8.96	9.38	10.45	43.79	8.47	9.07	10.26	–	3283–3254	3055–3018	2970–2918	1654	–	1598	1489	759
IV NiLDM^H·$ZnCl_2$·$(DMF)_2$	45.95	8.57	8.98	10.01	45.52	8.41	9.11	9.48	–	–	–	–	–	–	–	–	–
L^HH_2	71.30	9.78	–	–	71.56	9.11	–	–	2710–2628	–	755	–	–	–	–	–	–
LDM^HH_2	72.57	8.90	–	–	73.02	8.47	–	–	2715–2624	–	759	–	–	–	–	–	–

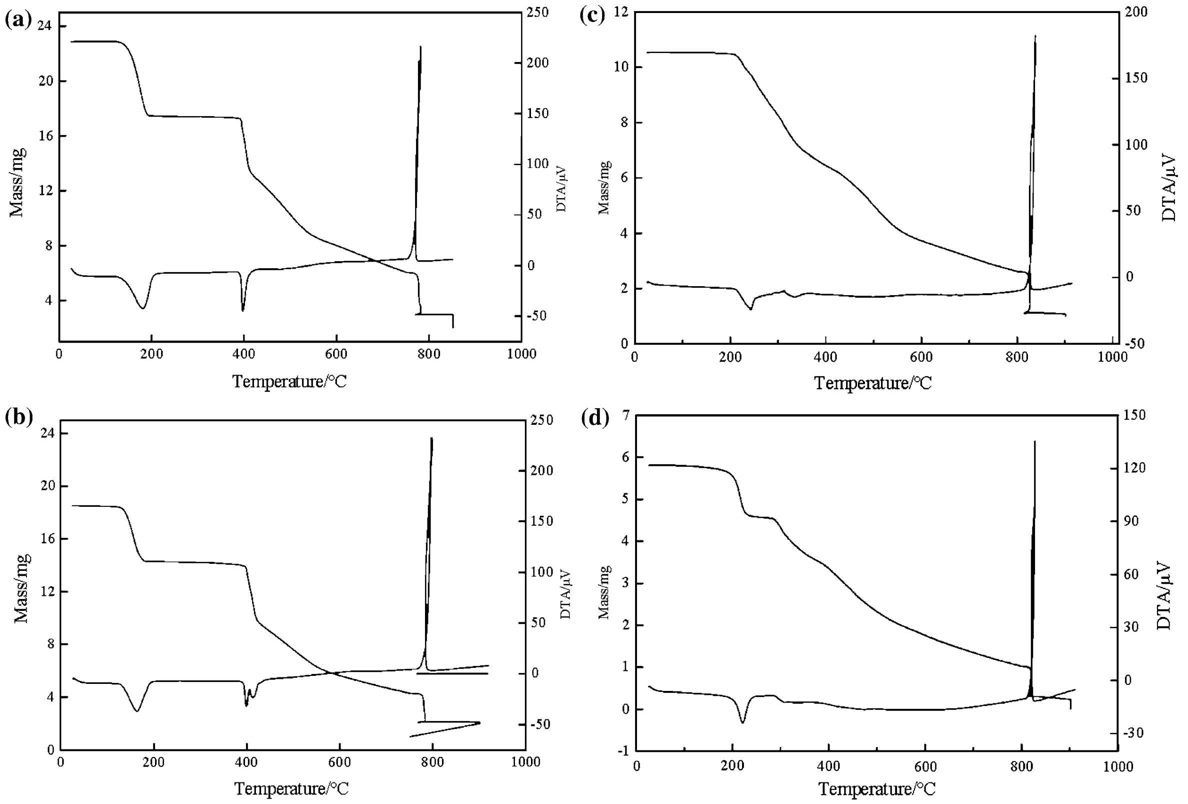


Fig. 2 The curves of complexes **a I**, **b II**, **c III**, and **d IV**

energy by 20 cm^{-1}. This shows that iminic nitrogens participate in coordination [21].

In complexes **III** and **IV** stretching bands are observed at $\nu_{N\text{–}H}$ 3,283–3,218 cm^{-1}. These $\nu_{N\text{–}H}$ bands in ligands are observed at 3,326–3,268 cm^{-1}. Since LH_2 and $LDMH_2$ complexes do not carry N–H bonds these bands are not observed in complexes **I** and **II**. However, when the ligand is reduced C=N group is convert to C–NH. In this case $\nu_{N\text{–}H}$ band becomes clearly visible and $\nu_{C=N}$ band disappears for complexes **III** and **IV**.

In the IR spectrum of the ligands only the phenolic stretching bands $\nu_{O\text{–}H}$ are observed at energies lower than expected. The reason for this is the strong hydrogen bond between the phenolic O–H and iminic and aminic nitrogen atoms. This hydrogen bond may cause the proton of the base to be transferred onto nitrogen atom and move the $\nu_{O\text{–}H}$ vibration to lower energy by 700–1,000 cm^{-1} [22]. In this study $\nu_{O\text{–}H}$ vibrations of the ligands are observed at 2,715–2,625 cm^{-1}.

TG is one of the most efficient methods in determination of complex stoichiometries [23]. The TG curves of the complexes are given in Fig. 2a–d. Full thermoanalytical data of the complexes are given in Table 2.

Mass loss in the first thermal reactions of complexes **I**, **II** and **IV** is observed at temperatures between 135 and 240 °C. This mass loss corresponds to the two DMF molecules in the expected complex stoichiometry. In contrast, in complex **III**, termination of the first thermal reaction is observed clearly after decomposition is initiated at 203 °C. In complexes **I** and **II** ligands are Schiff bases whereas in complexes **III** and **IV** ligands are reduced Schiff bases. If the ligand is a Schiff base, DMF molecules start to break off at around 135 °C and the reaction is completed about at 200 °C. DTA peaks are observed around 161–177 °C. This is close to the results cited in literature [23]. If the ligand is reduced Schiff base (phenol amine) DMF break off takes place at higher temperatures. In complex **IV**, thermal reaction which starts at around 160 °C is completed at around 240 °C. In complexes **I** and **II** second thermal reaction starts around 380 °C and continues up to 650 °C. In complex **IV** the complex is stabile for by 35 °C after the completion of the DMF removal reaction at 230 °C. Second thermal reaction starts at around 270 °C and continues up to 700 °C. This second decomposition reaction of the complexes **I**, **II** and **IV** are similar, but their initiation temperatures are different. It is considered that in these reactions organic ligand start to decompose first and in parallel to the organic ligand's decomposition $ZnCl_2$ leaves the structure. O_2 was added to the medium at around 750 °C and a strong exothermic peak appeared in all four curves. This exothermic peak is the result of the combustion of the carbon particles formed

Table 2 Thermoanalytical data of the complexes

Complex	1. Thermal reaction Decomposition of DMF molecules			2. Thermal reaction Decomposition of the complex		Remnant metal oxide (NiO)	
	Temperature range/°C	Mass loss expected/%	Mass loss observed/%	Temperature range/°C	Mass loss observed/%	Mass loss expected/ %	Mass loss observed/%
I NiL·$ZnCl_2$·$(DMF)_2$	135–202 DTA peak 177	23.50	23.56 ± 0.14	380–700	43.40 ± 1.26	12.02	12.18 ± 0.46
II NiLDM·$ZnCl_2$·$(DMF)_2$	128–185 DTA peak 161	22.48	22.67 ± 0.37	380–685	49.72 ± 2.15	11.50	11.70 ± 0.15
III NiL^H·$ZnCl_2$·$(DMF)_2$	203- DTA peak 238	23.35	No measurement	Indefinite initiation and termination temperatures	–	11.94	10.78 ± 0.45
IV $NiLDM^H$·$ZnCl_2$·$(DMF)_2$	162–230 DTA peak 219	22.34	21.39 ± 0.64	270–718	56.07 ± 3.10	11.43	10.58 ± 0.22

during decomposition of the ligand. The mass remaining after the formation of this peak corresponds to NiO as shown in Table 2. Curve of complex **III** is different from the other three curves. This complex remains unchanged up to 203 °C but starting from this temperature onward it undergoes a constant decomposition up to 700 °C. In this complex the upper limit where the DMF molecules leave the structure is unknown. From the curves in Fig. 2a–d we can suggest that complex **III** is formed with the DMF molecules alone. DMF molecules make coordination in other complexes as well but these complexes remain stable with Ni–Ligand–$ZnCl_2$ nucleus after the DMF molecules are thermally separated. It is considered that in complex **III** Ni–ligand–$ZnCl_2$ units also start to decompose with the separation of DMF. However, in complexes **I**, **II** and **IV** the complex remaining after the separation of the DMF molecules maintains its stability.

$$\mathrm{Ni[ligand]\cdot ZnCl_2\cdot (DMF)_2} \xrightarrow[-2\mathrm{DMF}]{\Delta} \mathrm{Ni[ligand]\cdot}$$

$$\mathrm{ZnCl_2} \xrightarrow{-\mathrm{ZnCl_2}} \mathrm{Ni[ligand]} \rightarrow \text{decomposition}$$

$\mathbf{I}, \mathbf{II}$ and $\mathbf{IV}$complexes

$$\mathrm{Ni[ligand]\cdot ZnCl_2\cdot (DMF)_2} \xrightarrow[-2\mathrm{DMF}]{\Delta}$$

$$\mathrm{Ni[ligand]} + \mathrm{ZnCl_2} \rightarrow \text{decomposition}\,\mathbf{III}\,\text{complex}$$

The complexes are formed by the coordination of $ZnCl_2$ from the phenolic oxygens. Since $ZnCl_2$ attracts the electrons of the phenolic oxygens, phenolic oxygens can transfer less electrons to Ni(II) and in turn Ni(II) ion coordinates DMF molecules to compensate this electron deficient. If the nitrogen atom of the organic ligand has sufficient amount of electron density, it is considered that the complex will maintain its existence even after the DMF molecules leave the structure. However, in the case of complex **III** the electron density on the aminic nitrogen atoms of the organic ligand is insufficient and the complex starts to decompose after the DMF molecules leave the complex structure. In order to understand charge density on the nitrogen atoms of L^HH_2 and LDM^HH_2 these ligands were potentiometrically titrated in MeCN. Potentiometric titration in non-aqueous solvents is one of the simplest methods that give an idea about the acidity and basicity strengths of organic acids and bases [24]. The basicity of organic matter can be determined from the half-neutralization potential on the potentiometric titration curves. Half-neutralization potentials in MeCN of the phenol amine compounds titrated in this study are given in Table 3. LDM^HH_2 has a more positive half-neutralization potential. This is in contrast to what is expected. L^HH_2 acts as a stronger base. The hydrogen bond formed between phenolic OH group and the aminic nitrogen is considered to create this effect.

Table 3 Half-neutralization potentials of ligands in MeCN

Ligands	1. half neutralization potentials/mV	2. half neutralization potentials/mV
LH_2	204.4 ± 3.5	306.7 ± 0.6
$LDMH_2$	252.0 ± 1.4	358.0 ± 1.5
L^HH_2	−60.8 ± 0.5	91.7 ± 1.9
LDM^HH_2	−38.2 ± 1.3	210.0 ± 4.5

Standard deviation for three results

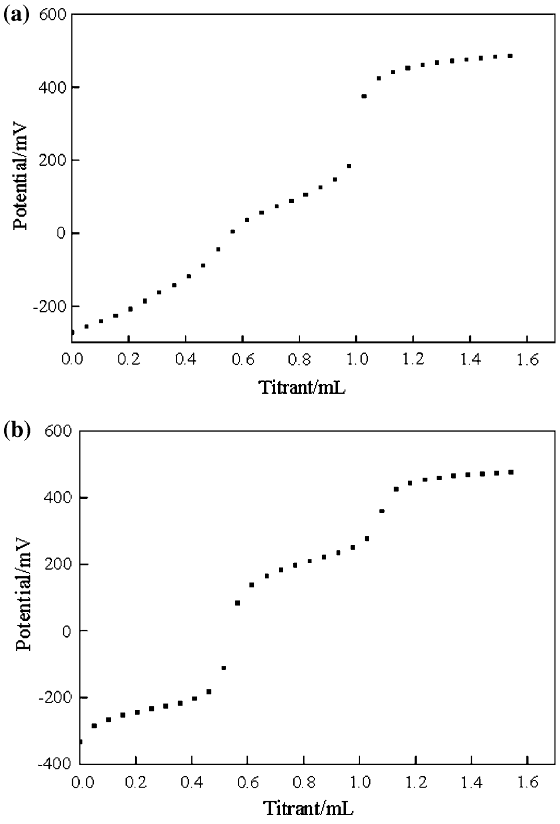


Fig. 3 Titration curves of **a** bis-*N*,*N*′-(2-methoxybenzyl)-1,3-propanediamine and **b** bis-*N*,*N*′-(2-methoxybenzyl)-2,2′-dimethyl-1,3-propanediamine

A strong hydrogen bond is known to exist between phenolic OH group and aminic and iminic nitrogen atoms. Due to this hydrogen bond hydrogen can be partially transferred to the nitrogen atom [25–27]. The higher the electron density of the aminic nitrogen atoms, the stronger the phenolic hydrogen will be bonded to this nitrogen. In this case it is not possible to determine the status of the charge density on the nitrogen atoms by potentiometric titration.

Therefore, in order to determine the electron density on the aminic nitrogen atoms, phenolic groups have been transformed into methoxide groups and titrated in MeCN.

Since no hydrogen bonds are formed with methoxy groups electron density of the nitrogen atoms can be determined more clearly.

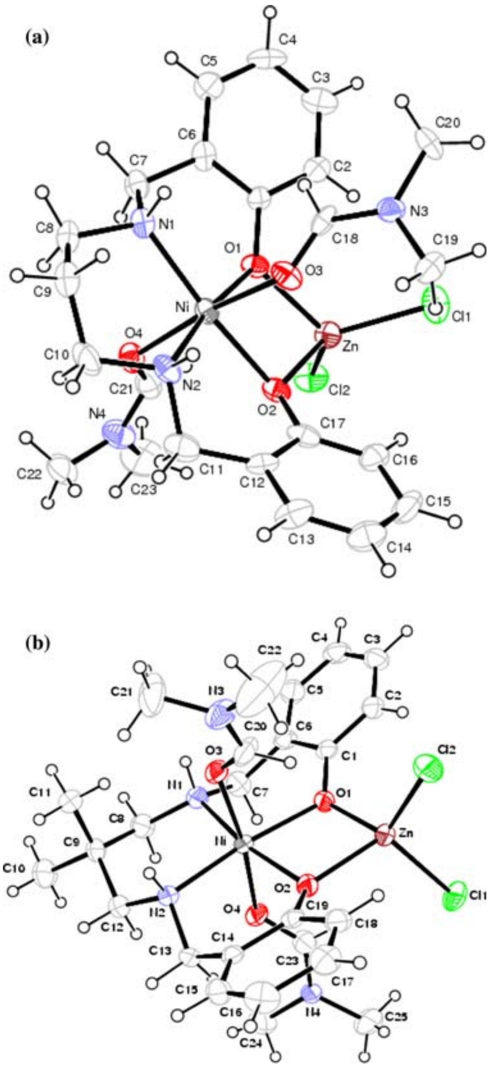


Fig. 4 The molecular structure and atomic labeling scheme of the complex **a III** and **b IV**. Displacement ellipsoids are drawn at the 30% probability level

The titration curves $LDMH_2$ and LDM^HH_2 obtained in acetonitrile medium are given in Fig. 3a, b as an example. It is seen that 1. half neutralization potentials for bis-*N*,*N*′-(2-methoxybenzyl)-1,3-propanediamine −185 mV, bis-*N*,*N*′-(2-methoxybenzyl)-2,2′-dimethyl-1,3-propanediamine −235 mV, respectively. These values show that the nitrogen atoms of bis-*N*,*N*′-(2-methoxybenzyl)-2,2′-dimethyl-1,3-propanediamine have higher electron density. Due to this higher electron density, the bi-nuclear complex remains somewhat more stable after thermal separation of the DMF molecules from this ligands complex.

This is also seen in bond lengths. Suitable crystals of complexes **III** and **IV** have been prepared and their molecular models have been obtained by X-ray diffraction method. Figure 4 shows the PLATON drawing [28] for complexes **III** (a) and **IV** (b) and their selected

Table 4 Crystallographic and experimental data for the complexes

	III	**IV**
Chemical formula	$C_{23}H_{34}Cl_2N_4NiO_4Zn$	$C_{25}H_{38}Cl_2N_4NiO_4Zn$
Formula mass	625.52	653.57
Temperature/K	293(2)	293(2)
Wavelength/Å	0.71073	0.71073
Crystal system, space group	Orthorhombic, P bca	Triclinic, P 1
Unit cell dimensions/Å, °		
a	13.5670(4)	8.8388(2)
b	19.5534(5)	10.0071(3)
c	20.8782(3)	17.8197(4)
α	–	101.120(2)
β	–	101.007(2)
γ	–	99.514(2)
Volume/Å^3	5538.6(2)	1484.32(6)
Z	8	2
Calculated density/mg m^{-3}	1.500	1.462
Absorption coefficient/mm^{-1}	1.774	1.658
F (000)	2592	680
Crystal size/mm	0.12 × 0.15 × 0.60	0.15 × 0.20 × 0.60
θ_{max}/°	23.41	26.29
Index range	$0 \le h \le 15$, $0 \le k \le 21$, $0 \le l \le 23$	$0 \le h \le 11$, $-12 \le k \le 12$, $-22 \le l \le 21$
Number of reflections used	3572	2898
Number of parameters	316	334
R_{int}	0.0487	0.0448
R	0.0595	0.589
R_w	0.1115	0.1272
Goodness of fit	0.997	1.024
$\Delta\rho_{min}$, $\Delta\rho_{max}$/e Å^{-3}	−0.678, 0.554	−0.648, 0.667

crystallographic and experimental data are given in Table 4, some of the important coordinative bond lengths and angles are tabulated in Tables 5 and 6, respectively.

As it can be seen in Fig. 4a and b Ni(II) ions are in an octahedral and Zn(II) ions in a tetrahedral coordination sphere.

In complex **III** distances between Ni(II) and the DMF oxygen's are found to be 2.060 and 2.096 Å. In complex **IV** these distances are found as 2.109 and 2.140 Å. Bonds in complex **IV** are clearly longer. This shows that there is less electron requirement for the Ni(II) in complex **IV**. Since the nitrogen atoms of the ligand in complex **IV** have higher electron densities the bond between Ni(II) and DMF is longer. Ni(II) ion in complex **III** needs more electrons, therefore it attracts the electrons of the DMF molecules and the respected bond length is shorter. Therefore, the temperature at which the DMFs leave the structure goes up to 200 °C.

Table 5 Selected bond lengths (Å) for complexes

III		**IV**	
Zn···Ni	3.0534(19)	Zn···Ni	3.1156(11)
Zn–O1	1.989(7)	Zn–O1	1.977(4)
Zn–O2	1.986(7)	Zn–O2	2.006(4)
Zn–Cl1	2.218(3)	Zn–Cl1	2.229(2)
Zn–Cl2	2.253(3)	Zn–Cl2	2.232(2)
Ni–O1	2.079(7)	Ni–O1	2.048(4)
Ni–O2	2.084(7)	Ni–O2	2.062(4)
Ni–O3	2.060(8)	Ni–O3	2.109(4)
Ni–O4	2.096(7)	Ni–O4	2.140(4)
Ni–N1	2.074(8)	Ni–N1	2.055(5)
Ni–N2	2.073(8)	Ni–N2	2.078(5)

As seen from Fig. 4a and b, in both complexes Ni(II) ion has O_4N_2 and Zn(II) ion has O_2Cl_2 coordination sphere. Ni(II) ion is coordinated between two phenolic oxygen and two iminic nitrogen of the organic ligand. These two phenolic oxygen and two iminic nitrogen donors form a basal plane. Ni(II) ions are located approximately at the middle of this basal plane. The oxygen atoms of two DMF molecules coordinate Ni(II) ion up and down of the basal

Table 6 Selected bond angles (°) for complexes

III		IV	
Zn–O1–Ni	97.2(3)	Zn–O1–Ni	101.43(19)
Zn–O2–Ni	97.2(3)	Zn–O2–Ni	99.96(18)
O1–Zn–O2	84.3(3)	O1–Zn–O2	80.64(17)
O1–Ni–O2	79.7(3)	O1–Ni–O2	77.66(16)
O1–Ni–O3	91.6(3)	O1–Ni–O3	92.84(18)
O1–Ni–O4	93.2(3)	O1–Ni–O4	94.13(17)
N1–Ni–O2	171.8(3)	N1–Ni–O2	170.11(19)
N2–Ni–O1	172.2(3)	N2–Ni–O1	169.96(19)
Cl1–Zn–Cl2	114.85(13)	Cl1–Zn–Cl2	113.63(8)
Ni–Zn–Cl1	123.43(11)	Ni–Zn–Cl1	121.63(6)
Ni–Zn–Cl2	121.64(10)	Ni–Zn–Cl2	124.65(6)

plane. Therefore, Ni(II) ion is in an octahedral coordination sphere. Two DMF oxygen are in apical position. As seen from Table 5 the bond lengths around the Ni(II) ion in complex **III** and **IV** vary between 2.060–2.096 and 2.048–2.140 Å. The bond lengths in the basal plane in complex **III** are 2.079, 2.084, 2.074 and 2.073 Å and they are very close to each other. The bond lengths in apical positions were found to be 2.060 and 2.096 Å in the complex **III** and they do not differ from each other very much. The bond lengths in the basal plane and apical positions of complex **IV** were found to be between 2.048–2.072 and 2.109–2.140 Å. These values are also very close to each other. However, the bonds in the basal plane of complex **IV** are shorter and the bonds at apical positions are considerable longer than those of complex **III**. This shows that the coordinative bonds in the basal plane of complex **IV** are more stabile than those in complex **III**. This may be attributed to the fact that higher electron density of the nitrogen atoms in LDM^{H2-}. Only the coordination sphere of Ni(II) in complex **III** is close to ideal. Complex **IV** has a more distorted coordination sphere. The bond angles support this fact. The coordination sphere of Zn(II) ion is a distorted tetrahedral. $ZnCl_2$ molecule forms a μ bridge with phenolic oxygens.

Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC 687246 for complex **III** and CCDC 687245 for complex **IV**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2, 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements The authors also thank the Ankara University Scientific Research Fund (Project No: 20070705118) for their support.

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