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Synthesis, Crystal Structure, Thermal Decomposition, and XPS Studies of Homo and Heterotrinuclear Cu(II)–Cu(II)–Cu(II) and Cu(II)–Ni(II)–Cu(II) Complexes Obtained from Salpn Type Ligands[1]

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Abstract—In this study, a mononuclear CuL complex was prepared by the use of bis-*N*,*N*'-(salicylidene)-1,3-propanediamine (LH_2) and Cu^{2+} ion. $NiCl_2$ and $NiBr_2$ salt were treated with this complex in dioxane-water medium and two new complexes $[(CuL)_2NiCl_2(H_2O)_2]$ and $[(CuL)_2NiBr_2(H_2O)_2)]$ with Cu(II)–Ni(II)–Cu(II) nucleus structure were obtained. In addition to this bis-*N*,*N*'-(2-hydroxybenzyl)-1,3-diaminopropane (L^HH_2) was prepared by the reduction of LH_2 with $NaBH_4$ in MeOH medium. The treatment of this reduced complex with Cu^{2+} ion resulted a complex $[(CuL^H)_2CuCl_2]$ with a structure of Cu(II)–Cu(II)–Cu(II). The complexes prepared were characterized by the use of elemental analysis, IR spectroscopy, thermogravimetric and X-ray diffraction methods. The crystal structures of $[(CuL)_2NiBr_2(H_2O)_2]$ (CIF file CCDC 1448402) and $[(CuL^H)_2CuCl_2]$ (CIF file CCDC 1448401) complexes were elucidated. It was found that halogen ions are coordinated to terminal Cu^{2+} ions which are in a distorted square pyramid coordination sphere. It was determined that the central Cu(II), which joins terminal square pyramidal Cu(II), was coordinated only by the phenolic oxygens of the ligand while the central Ni(II) was coordinated by two phenolic oxygens of the organic ligand and two water molecules. These complexes were investigated by XPS and it was found that the terminal and central Cu^{2+} ions were different in Cu(II)–Cu(II)–Cu(II) complex. Also, the thermal degradation of the CuLH complex unit was observed to exothermic in contrast to the expectations.

Keywords: salpn type Schiff base, reduced Schiff base, heterotrinuclear complex, binding energy, XPS study

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INTRODUCTION

Bis-*N*,*N*'(salicylidene)-1,3-propanediamine (LH_2) is a ligand which has a great tendency to give polynuclear homo and heteronuclear complexes. The first dinuclear and trinuclear complexes were reported by the use of this ligand were reported in 1976 and in 1990 respectively [1, 2]. There have been so many trinuclear complexes of this tetradentate ligand prepared by the us since 1990 [3–18]. The Ni(II) and Cu(II) salts give NiL and CuL mononuclear complexes with LH_2 in weakly basic alcoholic or other organic solvents. The molecular models of these compounds have been known since 1985 [19]. It is also known that the Schiff bases could easily be converted into phenyl amines with $NaBH_4$ in alcoholic media LH_2 ligands were reduced like that and used as the reduced Shiff base ligands [20]. The reduced state of LH_2 ligand is very prone to the formation of polynuclear complexes in a similar manner [13, 21–23]. However, the nuclear structure of these trinuclear complexes is either mononuclear (Ni(II)–Ni(II)–Ni(II), Cu(II)–Cu(II)–Cu(II), Co(II)–Co(II)–Co(II), Co(III)–Co(II)–Co(III)) or dinuclear (Ni(II)–M(II)–Ni(II), M = Fe(II), Cu(II), Co(II), Mn(II), Zn(II), Cd(II), Hg(II), Pb(II)). The number of trinuclear complexes where the terminal metal ions are Cu^{2+} is highly limited. The trinuclear complex of Cu(II)–Ni(II)–Cu(II) has been reported [24, 25].

This study was related to the formation of Cu(II)–Ni(II)–Cu(II) complexes with the use of LH_2 and its reduced state bis-*N*,*N*'-(2-hydroxybenzyl)-1,3-diaminopropane (L^HH_2). In this line the original plan of this study is first the formation of mononuclear CuL and

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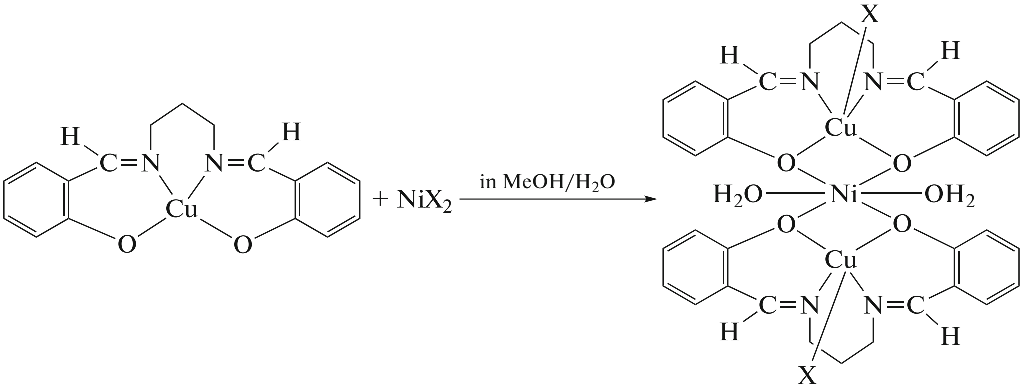
CuL^H complexes with the reaction of LH_2 or L^HH_2 using Cu(II) salts and then preparation of $[CuLNiCl_2CuL(H_2O)_2]$ (I) and $[CuLNiBr_2CuL(H_2O)_2]$ (II) complexes by the reaction of these mononuclear complexes with $NiCl_2$, $NiBr_2$, and $Ni(AcO)_2$ salts. The overall reaction is depicted in Scheme:



However, this has only worked between CuL and $NiCl_2$ and $NiBr_2$. CuL and $Ni(AcO)_2$ did not give a complex like this. When $Ni(AcO)_2$ was used, it was observed that the Cu(II) in the mononuclear CuL complex was replaced with Ni(II) resulting the formation of $[SNi(L)Cu(AcO)_2Ni(L)S]$ (S is a solvent such as dioxane or MF) type complexes given in the literature. Similarly, it was not possible to obtain the related complex with the use of the reduced ligand. However, sample with trinuclear stochimetry of $[CuL^HCuCl_2CuL^H]$ (**III**) similar to the literature with the use of reduced ligand a $CuCl_2$ [26–28].

The three complexes obtained were first characterized by the help of elemental analysis and IR spectroscopy and their thermal decomposition products were analyzed by the use of thermogravimetric (TG) methods. The complexes **II** and **III**, obtained in crystals with suitable sizes were enlightened with X-ray diffraction (XRD) method. Finally, all three-complex synthesized were subjected to XPS (X-ray photoelectron spectroscopy) study and the apparent XPS signals of Cu, O, and N atoms were investigated.

EXPERIMENTAL

Apparatus and methods. The TG-DTA studies were carried out using a Shimadzu DTG-60H apparatus. The thermogravimetric analyses were carried out in Pt pans at a rate of 10 K/min under nitrogen atmosphere. The temperature and heat calibrations of both devices were carried out using In and Pb metals. The IR spectra of the ligands and complexes were carried out by the use of Shimadzu brand Infinity model FTIR apparatus equipped with three reflection ATR unit and all IR spectra were recorded at a resolution of 4 cm^{-1}. The mass spectra were obtained by the use of a direct inlet (DI) unit of a Shimadzu 2010 Plus GCMS apparatus. C, H, and N analyses were carried out using an Eurovector 3018 CHNS analyzer while Ni and Cu analysis were completed by a GBC Avanta PM Model flame atomic absorption device. The related complex (2–3 mg) was dissolved in a mixture of HNO_3 (63%) and 1 mL H_2O_2 (30%) with heating, diluted to 100 mL, and placed into a nebulizer of the atomic absorpion device for the metal analysis. The NMR spectra of the ligands were recorded with a Varian brand Mercury model 400 MHz NMR spectrophotometer.

X-ray structure determination. A single crystal of $[CuLNiBr_2CuL(H_2O)_2]$ (**II**) and $[CuL^HCuCl_2CuL^H]$ (**III**) complexes were analyzed on an Oxford Diffraction Xcalibur Single Crystal X-ray Diffractometer with a sapphire CCD detector using MoK_α radiation (λ = 0.71073 Å) operating in $\omega/2\theta$ scan mode. The unit cell parameters were determined and refined by using the angular settings of 25 automatically centered reflections in $3.28° \le \theta \le 26.36°$ range for **III** and $2.96° \le \theta \le 26.02°$ for **II** complex. The data of **II** and **III** were collected at 293(2) and 100(2) K, respectively. The empirical absorption corrections were applied by the semi-empirical method via the Crys Alis CCD software [29]. The molecular models were obtained from the results of the cell refinement and the data reductions were carried out using the solution software SHELXL-97 [30]. The structures of complexes were solved by direct methods using the SHELXS-97 software implemented in the WinGX package [31].

Crystallographic data and structural refinements for compounds **II**, **III** are summarized in Table 1, and selected bond lengths and angles are listed in Table 2.

Supplementary material for structures **II** and **III** has been deposited with the Cambridge Crystallographic Data Centre (CCDC 1448402 (**II**), 1448401 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Synthesis of LH_2. This Schiff base was prepared via condensation reaction in EtOH under hydrothermal conditions using 2-hydroxy-benzaldehyde and 1,3-

Table 1. Crystallographic data and structure refinement of complex **II** and **III**

Parameter	Value	
	II	**III**
Formula weight	1138.41	830.22
T, K	293(2)	100(3)
Crystal size, mm	0.16 × 0.16 × 0.14	0.36 × 0.22 × 0.14
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a, Å	10.6618(4)	11.0189(7)
b, Å	15.4516(6)	15.3861(8)
c, Å	15.0511(5)	10.3441(8)
β	91.240(3)	106.959(7)
V, Å^3	2478.97(16)	1742.32(19)
Z	2	2
ρ_{calcd}, g cm^{-3}	1.616	1.583
μ, mm^{-1}	0.2902	0.2011
F(000)	1232	850
T_{max}/T_{min}	0.6868–0.6539	0.7660–0.5313
θ Range, deg	2.96–26.02	3.28–26.36
Index ranges	$-13 \le h \le 12$, $-18 \le k \le 19$, $-18 \le l \le 14$	$-13 \le h \le 13$, $-18 \le k \le 18$, $-7 \le l \le 13$
Reflections collected	4871	3489
Rreflections unique	3306	2977
R_1, wR_2 ($I > 2\sigma(I)$)	0.0494–0.1079	0.0285–0.0729
R_1, wR_2 (all)	0.0878–0.1240	0.0363–0.0755
Data/parameters	4871/310	3489/220
GOOF of F^2	1.045	1.102
Largest difference peak/hole, e Å^{-3}	0.771/–0.483	0.564/–0.311

diaminopropane. 2-Hydroxy-benzaldehyde (0.1 mol, 12.20 g) was dissolved in 120 mL of warm EtOH, then 0.05 mol (3.70 g) of 1,3-diaminopropane 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).

For $C_{17}H_{18}N_2O_2$
anal. calcd., %: C, 72.32; H, 6.43; N, 9.92.
Found, %: C, 71.95; H, 6.33; N, 10.09.

IR data (ν, cm^{-1}): 2627 ν(O–H), 3021–3019 ν(C–H$_{Ar}$), 2929–2862 ν(C–H$_{Aliph}$), 1629 ν(C=N), 1608 ν(C=C$_{ring}$), 1274–1151 ν(C–O$_{Phenol}$), 762 δ(C–H$_{Ar}$). λ_{max}, nm (ε, L mol^{-1} cm^{-1}): 243 (7045) in DMSO; 242 (7865) in MeOH. ^{1}H NMR data: (CH_3COCH_3-d_6; δ, ppm): 13.51 (s. O–H), 8.60 (s. –CH=), 7.43 (d. H$_{Ar}$), 7.32 (t. H$_{Ar}$), 6.88 (t. H$_{Ar}$), 3.68 (t. N–CH$_2$–), 2.01 (p. –CH$_2$–). ^{13}C NMR (CH_3COCH_3-d_6; δ, ppm): 166.6, 161.1, 132.7, 132.1, 119.1, 118.9 (C$_{Ar}$), 116.9 (–C=N), 58.5 (N–CH$_2$–), 31.9 (–CH$_2$–). MS (*m/z*): 282 [M]$^+$, 161 [HO–C_6H_4–CH=N–CH$_2$–CH$_2$–CH$_2$]$^+$, 148 [HO–C_6H_4–CH=N–CH$_2$–CH$_2$]$^+$ (BP = base peak), 134 [HO–C_6H_4–CH=N–CH$_2$]$^+$, 120 [HO–C_6H_4–CH=N]$^+$, 107 [HO–C_6H_4–CH$_2$]$^+$, 77 [C_6H_5]$^+$.

Synthesis of L^HH_2. 3.0 g of LH_2 was dissolved in 70.0 mL of MeOH by stirring and heating. This solution was heated up to 50°C and to this solution solid $NaBH_4$ in small portions was added until colorless under strong mixing [32–35]. After 10 min of stirring, 300 mL of ice water was added to it. The final mixture was left to stand for 24 h. After filtration, the white precipitate was air-dried. The product L^HH_2 was

Table 2. Selected bond distances (Å) and angles (deg) for **II** and **III**

Bond	*d*, Å	Bond	*d*, Å
	II		
N(1)–Cu(1)	1.972(4)	O(3)–H(3*A*)	0.86(2)
N(2)–Cu(1)	1.978(4)	O(3)–H(3*B*)	0.81(2)
O(1)–Cu(1)	1.968(3)	Ni(1)–O(3)	2.025(3)
O(1)–Ni(1)	2.087(3)	Ni(1)–O(2)	2.080(3)
O(2)–Cu(1)	1.967(3)	Ni(1)–O(1)	2.087(3)
O(2)–Ni(1)	2.080(3)	Cu(1)–Br(1)	2.8242(8)
O(3)–Ni(1)	2.025(3)		
	III		
N(1)–Cu(1)	1.994(2)	O(2)–Cu(2)	1.9108(16)
N(1)–H(1*A*)	0.82(3)	O(2)–Cu(1)	1.9632(16)
N(2)–Cu(1)	1.995(2)	Cu(1)–Cl(1)	2.5091(7)
N(2)–H(2*A*)	0.86(3)	Cu(1)–Cu(2)	2.9138(3)
O(1)–Cu(2)	1.919(15)		
O(1)–Cu(1)	1.9823(16)		
Angle	ω, deg	Angle	ω, deg
	II		
O(3)Ni(1)O(3)	180.0(3)	O(2)Cu(1)N(2)	91.57(15)
O(3)Ni(1)O(2)	89.65(13)	O(1)Cu(1)N(2)	165.35(16)
O(2)Ni(1)O(2)	180.0(2)	N(1)Cu(1)N(2)	94.11(18)
O(3)Ni(1)O(1)	91.19(13)	O(2)Cu(1)Br(1)	100.95(9)
O(2)Ni(1)O(1)	105.21(11)	O(1)Cu(1)Br(1)	102.14(9)
O(1)Ni(1)O(1)	180.0(16)	N(1)Cu(1)Br(1)	91.40(13)
O(2)Cu(1)O(1)	80.04(12)	N(2)Cu(1)Br(1)	91.18(12)
O(2)Cu(1)N(1)	166.30(15)		
O(1)Cu(1)N(1)	91.66(15)		
	III		
O(2)Cu(1)O(1)	78.09(7)	N(1)Cu(1)Cl(1)	103.10(6)
O(2)Cu(1)N(1)	164.01(8)	N(2)Cu(1)Cl(1)	99.08(6)
O(1)Cu(1)N(1)	92.91(7)	O(2)Cu(1)Cu(2)	40.55(5)
O(2)Cu(1)N(2)	93.17(7)	O(1)Cu(1)Cu(2)	40.86(4)
O(1)Cu(1)N(2)	168.75(8)	N(1)Cu(1)Cu(2)	133.48(6)
N(1)Cu(1)N(2)	93.88(8)	N(2)Cu(1)Cu(2)	132.53(6)
O(2)Cu(1)Cl(1)	89.93(5)	Cl(1)Cu(1)Cu(2)	76.179(16)
O(1)Cu(1)Cl(1)	88.09(5)	O(2)Cu(2)O(2)	180.0(10)

recrystallized from hot EtOH–H_2O (2 : 1, v/v). Yield, 55–60%, mp = 107°C.

For $C_{17}H_{22}N_2O_2$

anal. calcd., %:	C, 71.30;	H, 7.74;	N, 8.01.
Found, %:	C, 70.86;	H, 6.69;	N, 8.37.

IR data (ν, cm^{-1}): 3307 ν(N–H), 3055–3023 ν(C–H_{Ar}), 2967–2823 ν(C–H_{Aliph}), 1606–595 ν(C=C_{ring}), 1253–1099 ν(C–O_{Phenol}), 752 δ(C–H_{Ar}). ^1H NMR data (CH_3COCH_3-d_6; δ, ppm): 13.22 s., 7.12 m., 6.67 m., 4.73 br., 3.80 m., 2.56 m., 1.15 m. ^{13}C NMR (CH_3COCH_3-d_6; δ, ppm): 155.41, 151.23, 143.27, 126.92, 128.56, 124.85, 65.43, 61.17, 18.62. MS (*m/z*): 286 (molecular peak), 179 $[HO–C_6H_4–CH_2–NH–CH_2–CH_2–CH_2–NH]^+$, 163 $[HO–C_6H_4–CH_2–NH–CH_2–CH_2–CH_2]^+$, 150 $[HO–C_6H_4–CH_2–NH–CH_2–CH_2]^+$, 134 $[HO–C_6H_4–CH_2–N–CH_2]^+$, 122 $[HO–C_6H_4–CH_2–NH]^+$, 107 $[H–C_6H_4–CH_2]^+$ (base peak), 90 $[C_6H_4–CH_2]^+$, 77 $[C_6H_5]^+$.

Synthesis of I. *First stage preparation of CuL.* 1.410 g (0.005 mol) LH_2 was dissolved in 50 mL EtOH; 1.0 mL Et_3N and 0.850 g $CuCl_2 \cdot 2H_2O$ solution in 20 mL hot water were added to it. The resulting mixture was kept on the bench for 5–6 h and the dark green crystals were filtered off. It has no definite melting point and decomposes above 260°C. Yield, 60–80%.

For $C_{17}H_{16}N_2O_2Cu$

anal. calcd., %:	C, 59.38;	H, 4.68;	N, 8.14;	Cu, 18.48.
Found, %:	C, 58.82;	H, 4.37;	N, 7.92;	Cu, 17.56.

IR data (ν, cm^{-1}): 3048–3018 ν(C–H_{Ar}), 2954–2869 ν(C–H_{Aliph}), 1618 ν(C=N), 1599 ν(C=C_{ring}), 1317–1149 ν(C–O_{Phenol}), 756 δ(C–H_{Ar}).

Second stage preparation of trinuclear complex. 0.687 g (0.002 mol) CuL 60 mL was dissolved in hot dioxane heated at its boiling point. A solution of 0.238 g (0.001 mol) $NiCl_2 \cdot 6H_2O$ in 40 mL of MeOH–H_2O (1 : 1, v/v) was added to it. The solution was kept at the bench for 2–3 days and precipitated crystals were filtered off and dried in air. Yield, 27%.

For $C_{42}H_{52}N_4O_{10}Cl_2Cu_2Ni$ (**I**)

anal.	C,	H,	N,	Cl,	Cu,	Ni,
calcd., %:	49.03;	5.09;	5.63;	6.89;	12.35;	5.70.
Found, %:	C,	H,	N,	Cl,	Cu,	Ni,
	48.81;	4.49;	5.63;	7.12;	12.30;	5.88.

IR data (ν, cm^{-1}): 2627 ν(O–H), 3021–3019 ν(C–H_{Ar}), 2929–2862 ν(C–H_{Aliph}), 1629 ν(C=N), 1608 ν(C=C_{ring}), 1274–1151 ν(C–O_{Phenol}), 762 δ(C–H_{Ar}).

Synthesis of II was carried out in two stages as mentioned above and the second stage was the synthesis of complex **II** by using CuL (0.687 g) and NiBr2 (0.219 g, 0.001 mol).

For $C_{42}H_{52}N_4O_{10}Br_2Cu_2Ni$

anal. calcd., %:	C, 45.14;	H, 4.68;	N, 5.01;	Br, 14.30;	Cu, 11.32;	Ni, 5.25.
Found, %:	C, 44.67;	H, 5.43;	N, 4.91;	Br, 14.94;	Cu, 11.32;	Ni, 4.96.

IR data (ν, cm^{-1}): 3023–3010 ν(C–H_{Ar}), 2941–2854 ν(C–H_{Aliph}), 1631–1624 ν(C=N), 1610 ν(C=C_{ring}), 1278–1159 ν(C–O_{Phenol}), 752 δ(C–H_{Ar}).

Synthesis of III. Reduced Schiff base L^HH_2 (0.572 g, 0.002 mol) was dissolved in 40 mL of dioxane by heating up to 70°C. Et_3N (0.5 mL) and a solution of $CuCl_2 \cdot 2H_2O$ (0.510 g, 20 mL) in hot MeOH–H_2O (1 : 1, v/v) were added to this mixture. The resulting mixture was kept on the bench for 48 h; the crystalized green complex was filtered off and dried in air.

For $C_{34}H_{40}N_4O_4Cl_2Cu_3$

anal. calcd., %:	C, 49.19;	H, 4.85;	N, 6.75;	Cl, 8.54;	Cu, 22.96.
Found, %:	C, 49.03;	H, 4.71;	N, 7.16;	Cl, 8.40;	Cu, 22.14.

IR data (ν, cm^{-1}): 3170 ν(N–H), 3033–3012 ν(C–H_{Ar}), 2947–2872 ν(C–H_{Aliph}), 1595 ν(C=C_{ring}), 1275–1076 ν(C–O_{Phenol}), 748 δ(C–H_{Ar}).

RESULTS AND DISCUSSION

The X-ray diffraction images of $[CuLNiBr_2CuL(H_2O)_2]$ (**II**) and $[CuL^HCuCl_2CuL^H]$ (**III**)

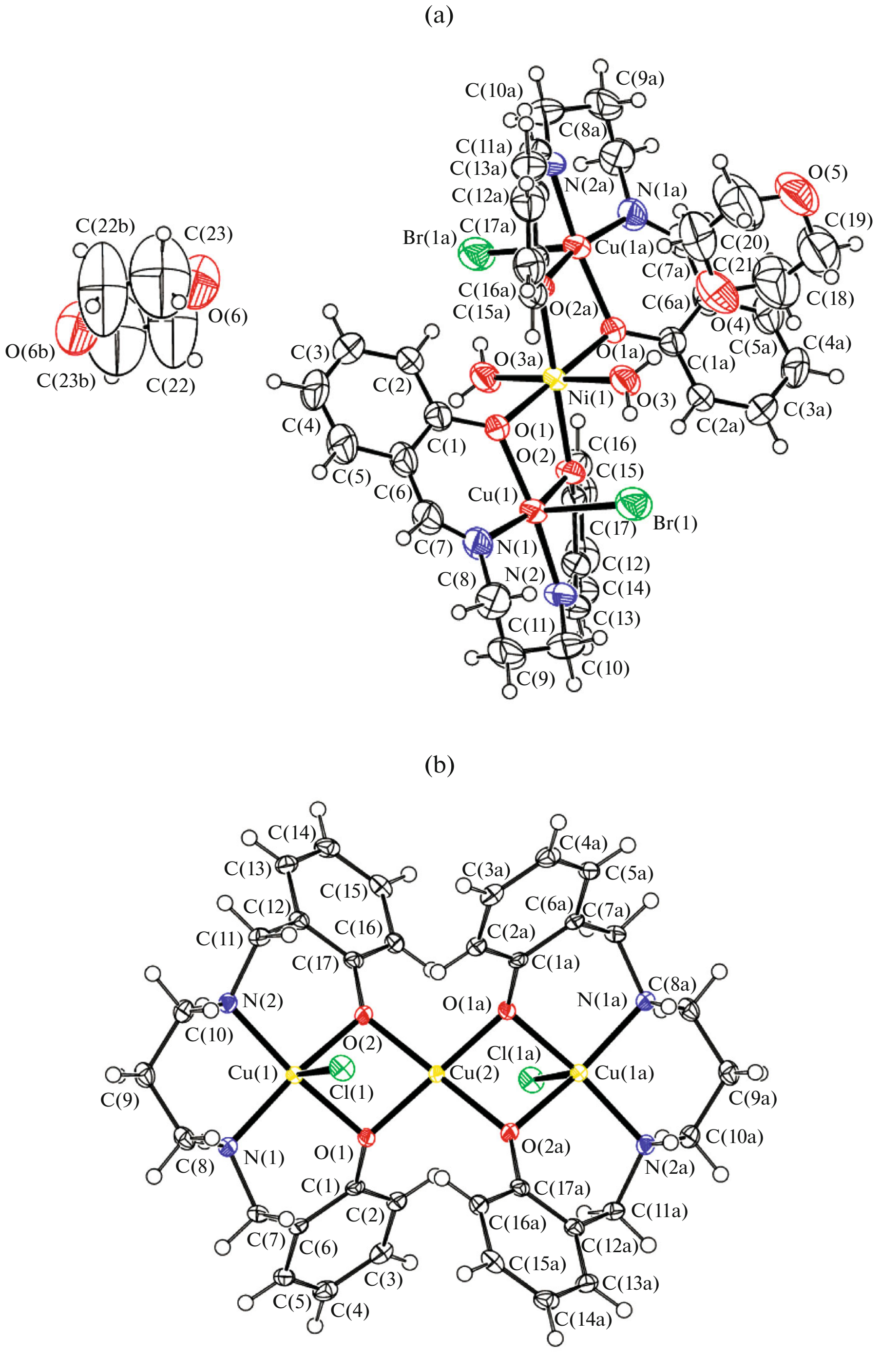


Fig. 1. Ortep picture of complexes **II** (a) and **III** (b).

complexes drawn with Ortep program are given in Fig. 1 [31].

Complex **II** contains two additional dioxane molecules. The coordination of the both complexes are similar in both CuL and CuL^H units of terminal Cu complexes. Both have distorted square pyramidal structure. The terminal Cu^{2+} ions are coordinated by two phenolic oxygens of two iminic and one chloride ion. Central Ni^{2+} ion is coordinated by four phenolic oxygens and two water molecules in an octahedral coordination sphere O(6).

In the complex **III** which contains reduced ligands, the terminal Cu^{2+} ion is in a similar coordination sphere but coordinated only four phenolic oxygens. A five-member square pyramidal coordination is very common for Cu(II) complexes [26–28]. Similarly, a four-member coordination is also very common for Cu(II) complexes, but Cu^{2+} ions make sometime a distorted square-planar coordination [26, 27]. In our study, Cu(II) seems to be in a square planar coordination since programs solve the molecules on symmetry basis. The octahedral coordination is an expected situation for central Ni^{2+} ion. The central Ni(II) in these type trinuclear complexes was always found to be in octahedral coordination in the literature [2, 13, 14, 16, 17]. There is some difference in chelate rings formed in the complex. Looking at the data listed in Table 2 the chelate rings formed by the terminal Cu(II) are different. The six membered Cu–N(1)–C(8)–C(9)–C(10)–N(2) chelate is in chair conformation for both compounds. However, the chair confirmation formed by the reduced ligand is more ideal. The angles between these chelate planes can easily be determined by the use of the Parst program [36]. In complex **III**, the angle between the C(8)–C(9)–C(10) and N(1)–C(8)–C(10)–N(2) planes was 56.63(0.22)° and the angle between the N(1)–C(8)–C(10)–N(2) and N(1)–Cu–N(2) planes was determined to be 47.00(0.09)°. Two angles are very close to each other. However, the ligand in complex **II** is a Schiff base and the same angles in complex **II** were 59.74(0.07)° and 28.14(0.01)°, respectively. The chelate ring in complex **III** is in a much-stressed form. This is obviously due to the imine bonds in Schiff base. The imine bond is a double bond between C and N and this makes the torsion angles of C(8)C(9)N(1)Cu and C(9)C(10)N(2)Cu smaller. These torsion angles were 61.9(2)° and –60.7(2)° in reduced ligand or complex **III** while it reduces to 52.0(6)° and –52.4(6)° in complex **II**.

There is a different situation when the square pyramidal structures of terminal Cu^{2+} ions are compared. The following equation, which shows that the five-membered coordination are in square pyramid or trigonal pyramid structures undifferently how distorted they are, is frequently used [37].

$$T = (\alpha - \beta)/60.$$

Here, α and β are two largest angles around Cu^{2+} ion. As τ value approaches to zero the coordination sphere is closer to the square pyramidal structure. Similarly, if this value goes to unity then the coordination is most likely to be trigonal bipyramid. Figure 1 clearly reveals that the coordination spheres obtained in this study were square pyramid. The τ value for complex **III** and **II** are observed to be 0.0158 and 0.079, respectively (Table 2). In summary, the coordination of the complexes obtained by the use of Schiff base is much closer to the ideal structure. On the other hand, the chelate rings are much more distorted from the ideal structure. In these types of complexes, it is highly difficult to determine the coordinated H_2O molecules since elemental analysis do not give definite information about it.

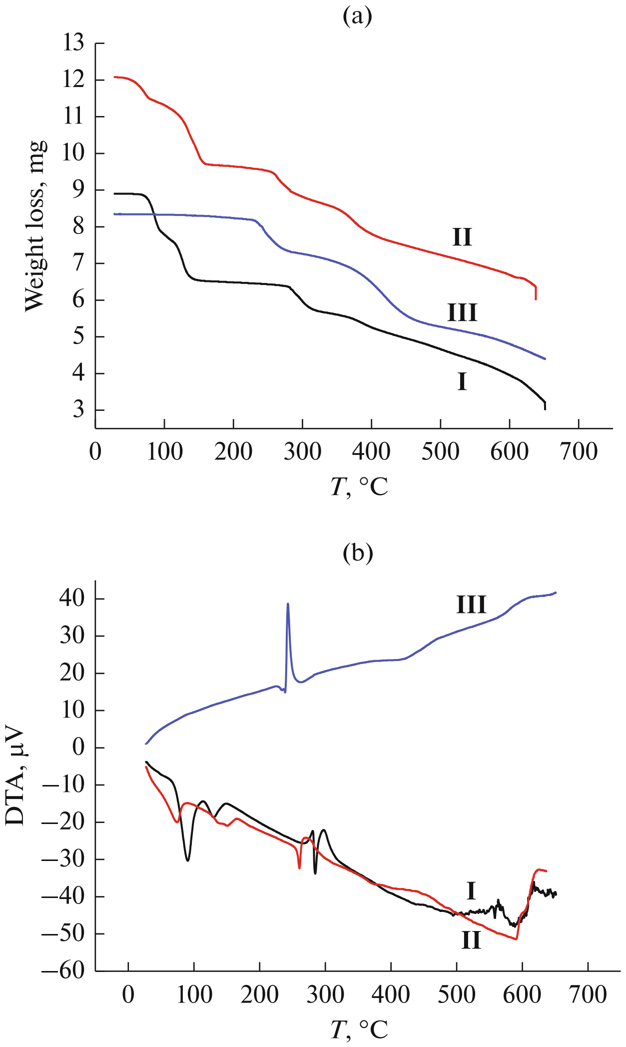


Fig. 2. The comparative TG (a) and DTA (b) curves of complexes **I**–**III**.

One of the most effective methods to determine the complex stoichiometry is thermogravimetry [15]. Figure 2a shows the thermogravimetric curves for all three complexes in a comparative manner. It is clear that the first process is the decomposition of water from complexes **I** and **II**. Figure 2b shows the DTA curves for the thermal reactions given in a comparative manner. The first thermal reaction in complex **I** and **II** is endothermic.

The central Ni^{2+} ions in complex **I** and **II** are coordinated with two H_2O molecules as well as two phenolic oxygens. The XRD data show that in complex **II** the coordination includes two oxygen molecules as well water molecules. The molecular model of complex **II** cannot be presented since it was not possible to grow its crystals to the appropriate dimensions. However, the thermo gravimetric results show that two water molecules are present in the molecule as a coordinated solvent. The first thermal reaction is most probably is

Table 3. The thermoanalytical data of complexes **I**–**III**

Complex	Thermal reaction							
	loss of H_2O or H_2O + dioxane (1)			loss of dioxane or H_2O + dioxane (2)			(3)	
	temperature range, °C	weight loss, %		temperature range, °C	weight loss, %		temperature range, °C	weight loss, % (found)
		exptd	found		exptd	found		
$(CuL)_2NiCl_2(H_2O)_2(C_4H_8O_2)_2$ (**I**)	68–102 DTA peak: 90.72 (endo)	11.55	11.77 ± 0.22	114–147 DTA peak: 130.07 (endo)	11.55	12.31 ± 0.40	266–287 DTA peak: 273	6.85
$(CuL)_2NiBr_2(H_2O)_2(C_4H_8O_2)_2$ (**II**)	67–93 DTA peak: 86.62 (endo)	3.50	3.73 ± 0.11	126–173 DTA peak: 163.04 (endo)	15.75	14.99 ± 0.30	265–289 DTA peak: 273	6.26
$(CuL^H)_2CuCl_2$ (**III**)	230–247 DTA peak: 246 (exo)	Most probably trinuclear complex decomposes	8.04 ± 0.38					

the removal of H_2O molecules from the structure. The weight loss which takes place between 68–102°C belonging to removal of two H_2O from complex **I** do not match the expected value, while the weight loss in complex **II** which takes place at 67–93°C corresponds to the removal of two H_2O molecules (found 3.73 ± 0.11%; exptd 3.50%). Table 3 lists the thermodynamic data related to these complexes. The thermal reaction (2) took place in complex **II** corresponds to the loss of two dioxane molecules. The weight loss in the thermal reaction (1) of complex **I** was found to be 11.77 ± 0.22%. This value is much higher than the value expected for the removal of two H_2O molecules. However, if one thinks that the structure contains two dioxane molecules it can be concluded that there were one H_2O and one dioxane molecule removed from the structure (exptd 11.55%; found 11.77 ± 0.22%). Again, the weight loss found in the second thermal weight loss of the complex **I** also matches the removal of one H_2O and one dioxane molecules from the structure (exptd 11.55%; found 12.31 ± 0.40%). TG and DTA curves of complex **I** and **II** are in the same form. The thermal reaction (3) observed starts at 260°C. It is probable that after the removal of the coordinated H_2O molecules the trinuclear complex completely decomposes into terminal CuL and central Ni(II) units. After this temperature, thermal decomposition of CuL complex takes place. In the literature, it was reported that the CuL and NiL complexes starts to decompose at temperature with a similar TG curve [15, 34]. The TG and DTA curves of complex **III** are entirely different. This complex was obtained by the template synthesis using the reduced ligand and $CuCl_2$. It was not possible to obtain mononuclear complexes by template synthesis. The XRD data show that the central Cu^{2+} ion is only coordinated by four phenolic oxygens. As seen from Fig. 2b, no weight loss is observed at the hydrothermal temperature range because a water or dioxane molecule was not coordinated on the complex molecule.

It is most probably due to the fact that terminal CuL^H units are not stable, and for this reason the mononuclear CuL^H unit could not be obtained in a stable form. At the template synthesis, the CuL^H units are formed and trimerised by central Cu^{2+} ion. During the thermal analysis when the temperature reaches to 240°C complex **III** decomposes into terminal CuL^H and central Cu(II). The instable CuL^H units begin to decomposition in an exothermic manner at this temperature. The exothermic peak observed in DTA curve of complex **III** in Fig. 2c corresponds to this decomposition process. At this temperature, the trinuclear complex decomposes with a small weight loss. If this is the case, then the electron densities of Cu^{2+} ions must be very different. The XPS scanning data of Cu^{2+} ions and O and N atoms are comparatively listed in Fig. 3.

When Fig. 3a is examined it is easily seen that complexes **I** and **II** give a signal maximum at 397 eV. This value was observed to shift 0.5 V higher potential in complex **III**. In complexes **I** and **II**, there is only one type N atom since all N atoms have the same chemical environment. That is why only a single signal was observed. However, in complex **III** the nitrogen atoms are in secondary amine form and they are supposed to be rich in electrons. Therefore, the binding energy must decrease. However, a completely reverse case is observed here. In complex **II** there needed more energy to snatch an electron from the N atom in complex **II**. In that case, the electrons on the N atoms are largely transferred to terminal Cu(II)

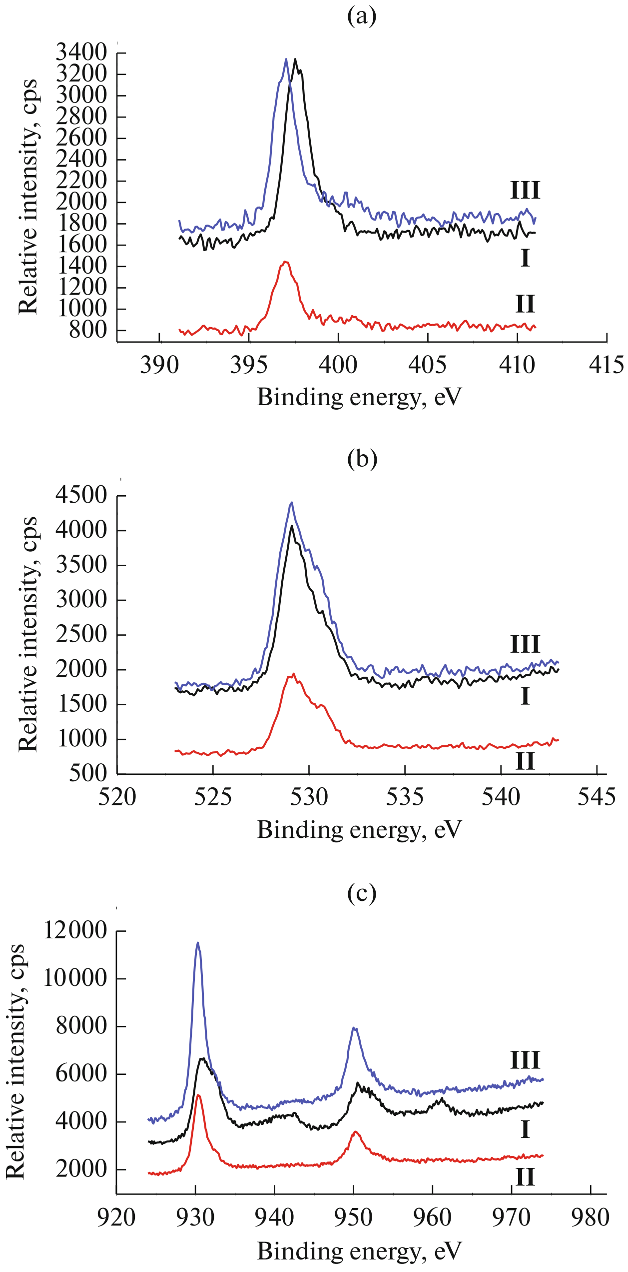


Fig. 3. XPS scanning curves of 1*s* electrons of N (a), O (b), Cu (c) atoms in the complexes **I**–**III**.

atoms. This situation is clearly apparent in IR spectra. The ν(N–H) vibrations are observed at 3307 cm^{-1} in when the reduced ligand is in its free state and shifts to 3170 cm^{-1}. There is a shift of approximately 137 cm^{-1} to lower energy. The fact that the vibrational frequency of the donor atoms shifts to the lower energy values after they make coordination bond has been known for a long time. However, the shift here is higher than the normal value. The IR data also show that there is an extensive electron transfer from N atom to the reduced ligand.

Figure 3b shows the situation of the O atoms in three complexes. There are three types of oxygen atoms, namely oxygen of water, phenolic oxygen, and oxygen of dioxane ($C_4H_8O_2$). The H_2O molecules form a coordination bond. Therefore, there must be a small difference between these three different types of oxygens. When we focus on curves of complexes **I** and **II** there is a shoulder at 531 eV in addition to the signal observed at 529 eV which is absent in the curve of complex **III**.

The most surprising result in XPS studies was observed for the 2*p* electrons of Cu atoms. As known the electrons of Cu atom which give distinctive signals are the *p* electrons and this situation is entirely specific to Cu atoms. The $2p^{1/2}$ and $2p^{3/2}$ electrons give XPS signals about 930 and 950 eV, respectively, and both these signals are observed in the presence of Cu atoms [38]. There are two signals expected from complexes **I** and **II** coming from $2p^{1/2}$ and $2p^{3/2}$ electrons since they contain only one type of Cu atom. This is the situation in Fig. 3c which contains two signals at 930 and 950 eV. However, the situation is entirely different for complex **III**. Here there are two different Cu atoms with different chemical environments. The chemical surroundings of the terminal and central Cu atoms are different. Also, the chemical environment of the terminal Cu(II) atoms in complex **III** differs from those in complexes **I** and **II**. This is also clearly apparent in Fig. 3b. The signals of complex **III** show a slight shift towards the higher energy. The central Cu(II) is different. There are two weak signals at 942 and 961 eV in Fig. 3b. This is most probably due to the central Cu(II) atom. These sorts of great differences are not very common in XPS studies. However, it is the case here. These findings show that the central Cu atoms joining to CuL^H units resulting a much stretched complex. It is most probable that the strong exothermic signals observed at 240°C are due to this highly stretched structure. However, there is not a cogent explanation of this situation.

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