# STRUCTURAL AND THERMAL STUDIES OF SOME AROYLHYDRAZONE SCHIFF'S BASES–TRANSITION METAL COMPLEXES

*H. A. El-Boraey*[*]

Department of Chemistry, Faculty of Science, Menoufia University, Shebin El-Kom, Egypt

Cobalt(II), nickel(II) and copper(II) complexes of some aroylhydrazone Schiff's bases derived from isoniazide (hydrazide of isonicotinic acid) with *p*-hydroxybenzaldehyde; 2,4-dihydroxybenzaldehyde or 2-hydroxy-1-naphthaldehyde are prepared and characterized. The study reveals that the ligands coordinate in the keto form. That transformed to the enol through the loss of HCl upon heating the solid complexes. The copper(II) complexes are thermochromic in the solid-state while the cobalt(II) complex, **3** of 2,4-dihydroxybenzaldehyde moiety is solvatochromic in hot DMF. The chromisms obtained were discussed in terms of change in the ligand field strength and/or coordination geometry.

*Keywords: aroylhydrazones, electronic spectral data, IR spectral data, metal complexes, Schiff's bases, thermal studies*

## Introduction

Schiff's base metal complexes have been widely studied because of their industrial and biological applications. Studies of a new kind of (chemotherapeutic) Schiff bases are attracting the attention of biochemists [1]. Hydrazone derivatives and their metal complexes are very important due to their biological activity, particularly in the chemotherapy of cancer [2]. The tuberculostatic activity of isonicotinic hydrazide and its aroylhydrazones containing azomethine nitrogen is attributed to their ability to form stable complexes with *d*- and *f*-block metal ions [3–6]. However, through the literature survey no intensive work on their thermal properties were reported. Nowadays, the thermal analysis techniques (DTA, TG, DSC, etc.) play an important role in studying the structure of metal complexes [7–12]. Recently, the highly insulating dimeric and polymeric metal complexes of Schiff's base derived from isoniazide and salicylaldehyde were reported [13], where the study revealed that the complexes are characterized by a higher thermal stability. The ligand coordinates in the keto form to give monomeric and polymeric complexes. The keto form of the ligand in the complexes changes into enol one through the loss of HCl or HNO₃ upon heating on the solid-state. The monomeric complexes are thermochromic in both solid-state and DMF solution. The present study extends for preparation and investigation of different aroylhydrazone metal complexes, and according to our programme, the thermal behaviour and some solid-state reactions (keto-enol transformation, polymerization, etc.) of complexes will be studied.

## Experimental

All reagents were of pure analytical grade and were used as supplied from Aldrich.

### Preparation of ligands (Schiff's bases)

The Schiff's bases were prepared by condensation of isoniazide and *p*-hydroxybenzaldehyde (**L¹**), 2,4-dihydroxybenzaldehyde (**HL^II**) or 2-hydroxy-1-naphthaldehyde (**HL^III**) in (1:1) mole ratio in EtOH. The mixture was stirred with slow evaporation for 3 h. The precipitates obtained were collected, washed with EtOH several times and dried. The spectral and analytical data confirm the formation of Schiff's bases.
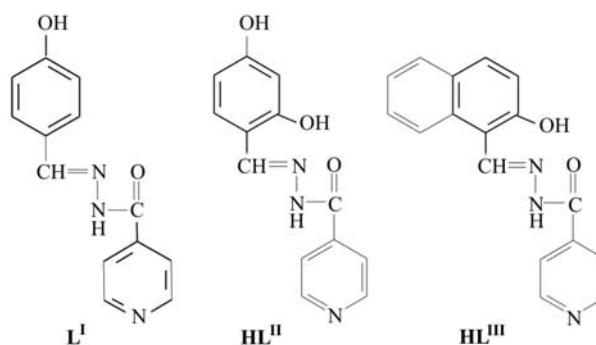


### Preparation of the complexes

Complexes **1**–**8** were prepared by template synthesis, by addition of stoichiometric amount of ethanolic solution of metal chloride to a hot ethanolic solution of iso-

*   helboraey@yahoo.com

niazide and the appropriate aldehyde in (1:1:1) mole ratio. A precipitate was formed after stirring in air for 1 h. Petroleum-ether (60–80) was added to assist a good precipitation. The precipitate obtained was filtered off, washed subsequently by EtOH several times and dried over $CaCl_2/P_4O_{10}$. Elemental analyses (C, H and N) were carried out at the microanalytical centre, Cairo University, Egypt. Metal(II) contents were determined by standard complexometric titration. KBr-IR spectra were recorded using a Perkin-Elmer 1430 spectrophotometer. Electronic spectra were measured in Nujol mulls using a Perkin-Elmer Lambda-4B spectrophotometer. Magnetic susceptibility measurements were carried out at room temperature on a modified Gouy-type magnetic balance, Herts SG8 5HJ England. Diamagnetic corrections were calculated from the values given by Selwood and Pascall's constants [14]. The molar conductivity measurements were done in DMF ($10^{-3}$ M) using a Tacussel conducometer type CD6N. The thermal analyses (TG and DTA) were carried out using a Shimadzu DTA/TG-50 with a heating rate of $10°C$ $min^{-1}$, in presence of nitrogen atmosphere. The flowing rate of $N_2$ was 30 $cm^3$ $min^{-1}$.

## Results and discussion

The prepared complexes are stable in air at room temperature. Generally, they are sparingly soluble in most organic solvents. Complexes **1**–**3** and **5** have an appreciable solubility in hot DMF. The molar conductance value of these complexes are considerably lower than those of univalent electrolytes in that solvent, indicating coordination of the chloride ions [15]. Complexes **4**, **6**–**8** are sparingly soluble or insoluble in hot DMF. This behaviour may be attributed to their dimeric nature in the solid-state.

### IR spectra

IR spectral data of the free Schiff's bases and their metal complexes are given in Table 2. The spectra of ligands **HL$^{II}$** and **HL$^{III}$** display a splitted band in the range 3230–2600 $cm^{-1}$ that is assigned to $\nu$(OH---N) or $\nu$(NH---O) [16], which confirms the tautomerism in these ligands. Ligand **L$^{I}$** displays a medium band at ca. 3230 $cm^{-1}$ is assigned to $\nu$NH of secondary amide. The spectra of all ligands display also bands in the regions 1680–1650, 1630–1620, 1610–1580 and 1560–1550 $cm^{-1}$ due to amide I, $\nu$(C=N) (azomethine of aromatic Schiff's bases), $\nu$(C=C) of pyridine/phenyl or naphthyl rings and amide II, respectively [17]. The bands at 1330–1290, 1170–1130 and 700–650 $cm^{-1}$ are assigned to $\delta$(C–OH) of phenol or naphthol moiety, $\nu$(C–O) of phenol/naphthol moiety and $\gamma$C–OH of phe-

nol/naphthol moiety, respectively [17]. The careful investigation of the spectra of the complexes and their corresponding ligands indicated that:

- The bands of $\nu$NH and amide II appear in the spectra of both ligands and complexes at the same position, confirming that NH moiety does not participate in the coordination. The observed minor shift to lower frequency of $\delta$NH (amide II) for some complexes may be due to its presence in chelate system rather than the open system of the ligands.

- The bands of amide I, and $\nu$C=N (sometimes screened by the strong band of pyridine/phenyl or naphthyl rings at 1600 $cm^{-1}$ are shifted to lower frequency on complexation, due to their participation in the mode of coordination. Cu(II) complex **2** is characterized by the appearance of an additional strong band at 1725 $cm^{-1}$ due to $\nu$(C=O) of ketoenamine tautomer of phenolic ring of the tautomerism of the Schiff's base, the data suggest the presence of such complex in a mixture of two tautomeric forms [18].

    For **HL$^{III}$**, the $\delta$(C–OH) of naphtholic skelton at 1330 $cm^{-1}$ and C–OH deformation of naphtholic skelton at 690 $cm^{-1}$ disappeared on complexation, confirming the deprotonation of naphtholic (OH) through the coordination with metal ions. This was also confirmed by the observed shift of $\nu$(C–O) of naphtholic skelton from 1160 $cm^{-1}$ (in the ligand) to 1140 $cm^{-1}$ (in the complexes). This behaviour was not observed in the spectra of complexes of *p*-hydroxybenzaldehyde moiety (**L$^{I}$**), instead, the above three bands appear in their normal positions. This indicates that **HL$^{III}$** behaves as monobasic tridentate ligand whereas **L$^{I}$** behaves as a neutral bidentate ligand.

- For **HL$^{II}$**, the spectra display two bands at 1330 and 1300 $cm^{-1}$ due to $\delta$(C–OH of the phenolic skelton), two bands at 700 and 650 $cm^{-1}$ ($\gamma$C–OH) and two bands at 1170 and 1130 $cm^{-1}$ ($\nu$C–O). This doublet nature of the peaks for each type is due to the presence of two phenolic (–OH) substituents on the phenyl ring [19]. On complexation, the two bands at 1300 and 650 $cm^{-1}$ of $\delta$(C–OH) and ($\gamma$C–OH) disappeared, whereas the bands at 1330 and 700 $cm^{-1}$ still present. This indicates that one phenolic –OH is deprotonated (*o*-substituent) whereas the other one does not (*p*-substituent). On the other hand, one of the two $\nu$C–O of phenol (1170 $cm^{-1}$) appears nearly in its position as for the ligand, whereas the other shifts to lower frequency, (from 1130 for ligand to 1090 $cm^{-1}$ for complexes). This behaviour indicates that **HL$^{II}$** behaves as monobasic tridentate ligand and has free *p*-OH group. Furthermore, the bands at 570–470, 460–420 and 340–305 $cm^{-1}$ which are not present in the spectra of the free hydrazones are assigned to $\nu$(M–O), $\nu$(M–N) and terminal $\nu$(M–Cl), respectively [20]. The dimeric nature of the complexes was

also supported by the appearance of a new band within the range 740–720 cm$^{-1}$, of di-μ oxo bridged ring vibration [21].

## Electronic spectra and room temperature magnetic moments (μ_eff)

### Co(II) complexes

The spectrum of cobalt(II) complex, **1** shows a multiple strong band in the range 710–600 nm, and its magnetic moment value (4.56 BM) typified tetrahedral geometry [22]. The spectra of cobalt(II) complexes, **3** and **6** exhibit two absorption bands in the range 700–680 and at 530 nm, indicating an octahedral geometry around cobalt(II) ion [22]. The room temperature magnetic moment values (Table 1) are lower than those corresponding to the high-spin value for monomeric complexes, due to the spin coupling via phenolic or naphtholic oxygen bridges [23] (vide IR spectra).

### Ni(II) complexes

The spectra of nickel(II) complexes, **4** and **7** show bands in the range 710 and 500 nm, due to high spin five coordinate geometry [24]. The lower magnetic moment values for nickel(II) complexes are attributed to the spin coupling via phenolic or naphtholic oxygen bridges [23], (vide IR spectra).

### Cu(II) complexes

The observed broad absorption band in the spectra of copper(II) complexes near 560–550 nm suggests a square planar environment around copper(II) ion [24]. The magnetic moment values of copper(II) complexes, **2** and **5** (Table 1) are within the normal range of monomeric copper(II) complexes. For copper(II) complex, **8** the value of magnetic moment is lower than that of the monomeric one suggesting copper–copper interaction through naphtholic oxygen bridges [23]. On the basis of the above discussion, together with elemental analysis data, molar conductance and thermogravimetric analysis (Tables 1–3) the Formula 1 can be suggested.

## Thermal studies

DTA and TG data of the investigated complexes are given in Fig. 1, Table 3. The curves are characterized by endothermic peaks in the temperature range 25–327°C, assigned to loss of solvents of crystallization (except for complexes **3** and **5**), as indicated from TG mass losses in that temperature range. The appearance of more than one endothermic DTA peak confirms that the solvents are not isoenergetically bound and thus their elimination takes place via different steps. For cobalt(II) complex **3** and copper(II) complex **5** of ligand (**L^{II}**), the TG curves show no mass loss in the indicated temperature range. Indicat-

**Table 1** Elemental analysis, magnetic and electronic spectral data for the complexes

| No. | Compound | Colour | Calc. (found)% | | | | μ_eff BM | Λ_m/ cm$^2$ Ω$^{-1}$ mol$^{-1}$ in DMF | Electronic spectra/ nm |
|-----|----------|--------|------|------|------|------|------|------|------|
| | | | C | H | N | M | | | |
| | ligand **L^I** | buff | – | – | – | – | – | – | – |
| 1 | [CoL$^I$Cl$_2$]·(2H$_2$O+1.5EtOH) | green | 40.3 (39.9) | 5.0 (5.1) | 8.8 (8.5) | 12.3 (12.0) | 4.65 | 21.9 | 710–600 s/br |
| 2 | [CuL$^I$Cl$_2$]·5H$_2$O | greenish-brown | 33.5 (33.2) | 4.5 (4.2) | 9.9 (9.3) | 13.6 (13.1) | 1.97 | 28.6 | 500 br |
| | ligand **HL^{II}** | pale-orange | – | – | – | – | – | – | – |
| 3 | [CoL$^{II}$(H$_2$O)Cl]$_2$·0.5EtOH | brown | 42.6 (42.0) | 3.5 (3.6) | 11.0 (9.5) | 15.5 (15.0) | 3.2 | 21.9 | 700–600s/ br |
| 4 | [NiL$^{II}$Cl]$_2$·4EtOH | yellow-orange | 46.1 (46.0) | 4.9 (5.0) | 9.5 (10.5) | 13.2 (12.6) | 2.08 | a | 710 w, 590 s |
| 5 | [CuL$^{II}$Cl]·2H$_2$O+0.25EtOH | orange-red | 40.2 (40.3) | 3.9 (3.8) | 10.4 (10.0) | 15.7 (15.7) | 1.84 | 61.3 | 550 br |
| | ligand **HL^{III}** | yellow | – | – | – | – | – | – | – |
| 6 | [CoL$^{III}$(H$_2$O)Cl]$_2$·(2H$_2$O+2EtOH) | red | 48.8 (48.4) | 4.7 (4.6) | 9.0 (8.2) | 12.6 (12.6) | 3.0 | b | 680 br, 530 br |
| 7 | [NiL$^{III}$Cl]$_2$·10H$_2$O | red | 43.0 (43.0) | 4.6 (4.7) | 8.9 (8.4) | 13.3 (13.0) | 2.12 | b | 585 s/br, 500 s |
| 8 | [CuL$^{III}$]$_2$Cl$_2$·(2H$_2$O+2EtOH) | red | 50.3 (49.7) | 4.4 (4.4) | 9.3 (9.7) | 14.0 (13.9) | 1.26 | a | 560 br |

a – partially soluble, b – insoluble

ing that the corresponding endothermic DTA peak is assigned to lattice or chemical rearrangement of the compounds. From the DTA curves, the desolvation process was followed by another asymmetric endothermic peak (sometimes splitted). This peak is assigned to completion of the desolvation process together with the loss of HCl molecules as indicated from TG mass loss, to give the dimeric or polymeric complexes with the enol form of the ligands. Complex **8** completes its desolvation during the decomposition of the enolic form.

### Co(II) complexes

DTA and TG curves (Fig. 1) pointed that the formed enolic intermediates of cobalt(II) complexes **1**, **3** and **6** are generally unstable and spontaneously decomposed. The exothermic DTA peaks in the temperature range 346–604°C are assigned to the decomposition of di-μ-chloro bridge (for **1**) or di-μ-oxo four-membered ring [25] (for **3** and **6**). The compounds complete their decomposition through exothermic processes to give a mixture of CoO and carbon as a final product [12] for



**Formula 1**

complexes **3** and **6**, respectively, (vide TG data, Table 2). Cobalt(II) complex **3**, is solvatochromic in DMF where its brown colour changes into green in hot DMF and is attributed to geometry change, as indicated from the electronic spectra. The observed shift of (*d–d*) transition band of the brown form from 700–680 to 720–580 nm (multiple strong band) for the green form indicates change in coordination geometry from octahedral to terahedral, respectively [22]. The observed solvatochromic behaviour can also be explained on the basis of dehydrating action of DMF along with its basic character. The two factors enhance the removal of water as well as HCl. The removal process is followed by conformational changes of the four-membered di-μ-oxo-bridge to give the distorted enolic tetrahedral configuration. This change can be represented as follows:



**Fig. 1** DTA and TG curves of complexes **1–8**

$[CoL^{II}(H_2O)Cl]_2 \cdot 0.5EtOH$

Complex **3**, keto (brown)

$$\xrightarrow{\text{DMF, } -(2H_2O+2HCl+0.5EtOH)} [CoL^{II}]_2$$

enol (green)
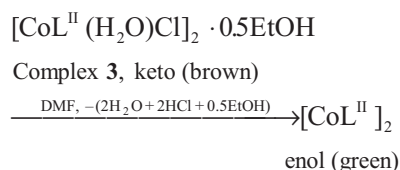
*Ni(II) complexes*

The thermal investigation indicated that the enolic forms obtained during the heating of nickel(II) complexes **4** and **7** are thermally stable up to 320 and 365°C, respectively. The structure of the enolic forms were confirmed from electronic spectra, magnetic susceptibility measurements and IR spectra. Electronic spectra of the solid complexes and their heated forms up to 270°C (for **4**) and 350°C (for **7**) are significantly different. The observed (*d–d*) bands in the range 710–500 nm deformed and shifted to become a single broad band centered at 500 nm, indicating a change in coordination geometry towards the planar configuration. This change was also confirmed by magnetic susceptibility measurements which give diamagnetic properties for the heated forms. On the other hand, IR spectra of the heated forms show no characteristic peaks for ν(NH), amide I and amide II.

**Table 2** IR spectral data for the complexes

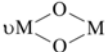| No. | Compound | IR/cm$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|---|
| | | νNH | ν(OH–N) (NH–O) | amide I | νC=N azometh. | νC=C arom. | amide II |
| **L$^I$** | | 3230(m) | – | 1660(s) | 1620(s) | 1600(s) | 1560(s) |
| **1** | $[CoL^ICl_2]\cdot(2H_2O+1.5EtOH)$ | 3230(m) | – | 1640(s) | 1610(s) | 1590(s) | 1559(m) |
| **2** | $[CuL^ICl_2]\cdot5H_2O$ | 3230(m) | – | 1725(s) 1645(s) | 1610(m/s) | 1590(m) 1585(m) | 1555(m) |
| **HL$^{II}$** | | – | 3230–2600(m/s) | 1650(sh) | 1630(s) | 1610(m) 1585(s) | 1550(s) |
| **3** | $[CoL^{II}(H_2O)Cl]_2\cdot0.5EtOH$ | 3230(m) | – | 1630(m) | 1610(s/br) | 1610(br) | 1550(m) |
| **4** | $[NiL^{II}Cl]_2\cdot4EtOH$ | 3230(m) | – | 1630(m) | 1610(s/br) | 1580(m) | 1550(m) |
| **5** | $[CuL^{II}Cl]\cdot2H_2O+0.25EtOH$ | 3230(m) | – | 1640(s) | 1610(s) | 1585(m) | 1550(s) |
| **HL$^{III}$** | | – | 3220–2720(m/s) | 1680(s) | 1630(s) | 1600(m) 1580(m) | 1550(s) |
| **6** | $[CoL^{III}(H_2O)Cl]_2\cdot(2H_2O+2EtOH)$ | 3200(m) | – | 1635(m) | 1615(s) | 1600(m) 1585(m) | 1535(s) |
| **7** | $[NiL^{III}Cl]_2\cdot10H_2O$ | 3220(m) | – | 1640(sh) | 1612(sh) | 1600(s) 1590(s) | 1555(m) |
| **8** | $[CuL^{III}]_2Cl_2\cdot(2H_2O+2EtOH)$ | 3220(m) | – | 1630(s) | 1615(s) | 1595(s) 1585(s) | 1555(s) |

| No. | Compound | δC–OH | νC–O | υM⟨O⟩M | νM–O | νM–N | νM–Cl |
|---|---|---|---|---|---|---|---|
| **L$^I$** | | 1290(s) | 1170(s) | – | – | – | – |
| **1** | $[CoL^ICl_2]\cdot(2H_2O+1.5EtOH)$ | 1290(s) | 1170(s) | – | 470(m) | 420(m) | 310(s) |
| **2** | $[CuL^ICl_2]\cdot5H_2O$ | 1290(s) | 1170(s) | – | 520(m) | 450(m) | 320(m) |
| **HL$^{II}$** | | 1330(s) 1300(s) | 1170(s) 1130(s) | – | – | – | – |
| **3** | $[CoL^{II}(H_2O)Cl]_2\cdot0.5EtOH$ | 1330(s) | 1170(s) 1090(m) | 740(m) | 525(m) | 460(m) | 330(m) |
| **4** | $[NiL^{II}Cl]_2\cdot4EtOH$ | 1330(s) | 1170(s) 1090(s) | 720(m) | 540(m) | 460(m) | 305(m) |
| **5** | $[CuL^{II}Cl]\cdot2H_2O+0.25EtOH$ | 1330(s) | 1170(s) 1090(s) | – | 530(s) | 460(s) | 305(s) |
| **HL$^{III}$** | | 1330(s) | 1160(s) | – | – | – | – |
| **6** | $[CoL^{III}(H_2O)Cl]_2\cdot(2H_2O+2EtOH)$ | – | 1140(s) | 745(s) | 530(m) | 445(m) | 330(m) |
| **7** | $[NiL^{III}Cl]_2\cdot10H_2O$ | – | 1140(m) | 746(m) | 500(m) | 420(m) | 340(m) |
| **8** | $[CuL^{III}]_2Cl_2\cdot(2H_2O+2EtOH)$ | – | 1140(s) | 715 | 520(m) | 450(m) | 320(m) |

s – strong, m – medium, sh – shoulder, br – broad

This behaviour confirms the structural changes due to the coordination of the ligands in their enol form through the loss of HCl molecule. These solid-state reactions can be represented as follows:

$$[NiL^{II}Cl]_2 \cdot 4EtOH \xrightarrow{270°C, -4(EtOH+2HCl)} [NiL^{II}]_2$$

Complex **4**  ⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀ enol - form

keto - form  ⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀ (square planar)

$$[NiL^{III}Cl]_2 \cdot 10H_2O \xrightarrow{350°C, -(10H_2O+2HCl)} [NiL^{III}]_2$$

Complex **7**  ⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀ enol - form

keto - form  ⠀⠀⠀⠀⠀⠀⠀⠀⠀⠀ (square planar)

DTA and TG data (Table 3) indicated that the complexes start their decomposition at 320 and 365°C to give NiO and a mixture of NiO and carbon as a final product [12] (vide TG data) for complexes **4** and **7**, respectively.

## Cu(II) complexes

DTA curve (Fig. 1) of the greenish brown monomeric copper(II) complex **2** display a splitted strong DTA peak in the temperature range 156–223°C. From TG data (Table 3), this peak represents a loss of three molecules of water of crystallization together with one HCl molecule giving a polymeric dark green form at 223°C (in which the ligand coordinates in its enol form as monobasic bidentate ligand). Therefore, the complex **2** is characterized by thermochromic properties. As indicated from magnetic moment and spectroscopic measurements, the observed thermochromism is attributed to geometry and structural changes. The electronic absorption spectra indicated that the complex displays a geometry changes in both DMF and in the solid-state upon heating. The observed broad band in the 780–700 nm range (in Nujol mull) of the spectrum of the dark green form is indicative of five coordinate copper(II) [26]. This geometry change was also confirmed by IR spectra. Where the dark green form

**Table 3** Thermal data for the complexes

| No. | Temperature/°C | | Mass loss/% | Reaction | Leaving species |
|---|---|---|---|---|---|
| | DTA | TG | calc. (found) | | |
| **1** | 25–125 | 25–125 | 3.8 (3.8) | a | $-H_2O$ |
| | 135–327 | 135–327 | 8.6 (8.7) | a+d | $-(H_2O+0.5EtOH)$ |
| | 327–364 | 327–364 | 17.2 (17.5) | d | $-(HCl+EtOH)$ |
| | 364–604* | – | – (–) | b (decomposition of di-μ-chloro-bridge) | |
| **2** | 25–156 | 25–156 | 7.7 (7.6) | a | $-2H_2O$ |
| | 156–223 | 156–223 | 19.4 (19.4) | a | $-3(H_2O+HCl)$ |
| | 238–600* | | | b | |
| **3** | 40–100 | 40–100 | – | – | lattice or chemical rearrangement |
| | 150–384 | 150–384 | 17.3 (17.4) | a+b+formation of enolic form | $-(2H_2O+2HCl+0.5EtOH)$ |
| | 425–481* | | | b (decomposition of di-μ-oxo bridge) | |
| | | at 536 | 24.4 (24.6)● | remain | $\equiv 2CoO+3C$ |
| **4** | 25–170 | 25–170 | 15.6 (15.6) | d | $-3EtOH$ |
| | 170–270 | 170–270 | 13.4 (13.1) | d+formation of enolic form | $-(2HCl+EtOH)$ |
| | 320–600* | 270–410 | (54.8) | b | – |
| | – | at 410 | 16.8 (16.5)● | remain | $\equiv 2NiO$ |
| **5** | 25–100 | 25–100 | – | – | lattice or chemical rearrangement |
| | 150–290 | 150–265 | 20.8 (20.2) | a+b+formation of enolic form | $-(2H_2O+HCl+0.25EtOH)$ |
| | 327–600* | 265–540 | (62.5) | b | |
| | – | at 540 | 17.3 (17.3)● | remain | $\equiv Cu_2O$ |
| **6** | 25–100 | 25–100 | 3.8 (3.9) | a | $-2H_2O$ |
| | 100–350 | 100–350 | 21.5 (21.4) | a+b+formaiton of enolic form | $-(2H_2O+2EtOH+2HCl)$ |
| | 350–600* | 350–558 | (54.7) | b (decomposition of di-μ-oxo-bridge) | |
| | | at 558 | 19.9 (20.0)● | remain | $\equiv 2CoO+3C$ |
| **7** | 25–100 | 25–100 | 5.6 (5.5) | a | $-3H_2O$ |
| | 100–210 | 110–210 | 11.3 (11.4) | a | $-6H_2O$ |
| | 210–350* | 210–350 | 9.5 (10.0) | a+formation of enolic form | $-(H_2O+2HCl)$ |
| | 365–600* | 350–500 | (54.0) | b | |
| | | at 500 | 19.5 (19.3)● | remain | $\equiv 2NiO+3C$ |
| **8** | 25–125 | 25–125 | 3.9 (3.7) | a | $-2H_2O$ |
| | 125–265 | 125–248 | 8.1 (8.1) | formation of enolic form | $-2HCl$ |
| | 285–600* | 248–450 | (66.5) | b | |
| | | at 45°C | 21.5 (21.7)● | remain | $\equiv 2CuO+3C$ |

*exo, a – dehydration, b – decomposition, d – desolvation, ● – final product percent

shows no characteristic peaks for amide I ($\nu$CO), but shows peaks for $\nu$NH, $\nu$(CO) of free ketonenamine, and amide II ($\delta$NH), i.e., the heated complex exists in two tautomeric forms. The reduced magnetic moment value (1.36 BM) of the dark-green form is an evidence for polymerization through di-chloro-oxo-bridge [23]. So, the discussed scope is given in the following:

$$[CuL^1Cl_2] \cdot 5H_2O \xrightarrow{223°C, \ -(5H_2O + HCl)} [CuL^1Cl]_n$$

Complex **2**,                     polymeric green form

keto greenish - brown          (five coordinate)

square planar
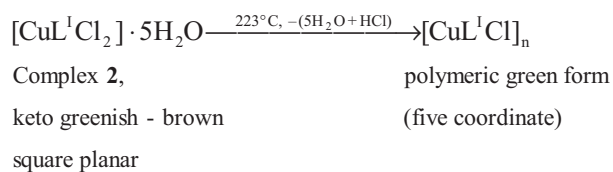
However, the DTA and TG curves (Fig. 1) illustrated that the polymeric dark green form starts its decomposition at 238°C. The observed exothermic DTA peak with a maximum at 272°C is assigned to the decomposition of four-membered ring [25]. The thermal investigation of copper(II) complexes (the orange-red **5** and red **8**) show that, their colour continuously changed to brownish-yellow and brown upon being heated in the solid-state up to 265 and 248°C, respectively. The electronic spectra in Nujol mulls of the solid complexes are similar to those of the heated forms. The square planar keto complexes were only deformed in the enol form during heating course. The reduced magnetic moment values (1.02 and 1.16 BM) for the enolic forms of **5** and **8**, respectively, indicating the presence of copper–copper interaction through di-$\mu$-oxo bridge [23]. The IR spectra of the heated forms show no characteristic peaks for $\nu$NH, amide I and amide II, confirming the structural change due to coordination of the ligand in its enol form through the loss of HCl molecules. In addition, IR spectrum of the heated form of complex, **5** displays a new band at 725 cm$^{-1}$, characteristic of di-$\mu$-oxo-bridge. This band is still present in the spectrum of the heated form of complex **8**. The change in colour may be attributed to change in the strength and symmetry of the ligand field. Probably caused by the increased molecular vibration and conformational changes of the di-$\mu$-oxo bridge upon heating [15]. The observed changes can be represented as follows:

$$[CuL^{II}Cl] \cdot (2H_2O + 0.25EtOH)$$

Complex **5**, keto - form, orange - red

$$\xrightarrow{265°C, \ -(2H_2O + HCl + 0.25EtOH)} [CuL^{II}]_2$$

enol - form, brownish - yellow

$$[CuL^{III}]_2Cl_2 \cdot (2H_2O + 2EtOH)$$

Complex **8**, keto - form, red

$$\xrightarrow{248°C, \ -(2H_2O + 2HCl)} [CuL^{III}]_2$$

enol - form, brown
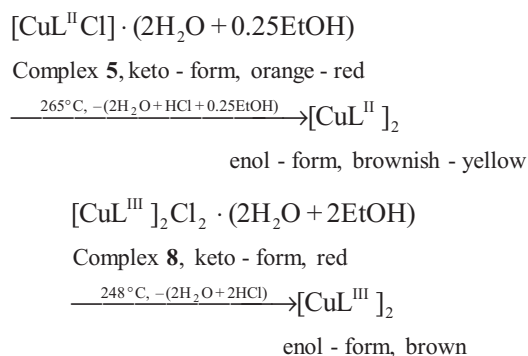
DTA and TG data (Table 3) indicated that the enolic forms are thermally stable over the temperature range 248–327°C. The complexes **5** and **8** start their decomposition at 327 and 285°C, respectively. The final product is Cu$_2$O and a mixture of CuO+carbon for complexes **5** and **8**, respectively [12]. For all investigated complexes the final products for decomposition reactions were established by means of TG/DTA and IR.

## Conclusions

In the present study, cobalt(II), nickel(II) and copper(II) complexes of some aroylhydrazone Schiff's bases derived from isoniazide with *p*-hydroxybenzaldehyde; 2,4-dihydroxybenzaldehyde or 2-hydroxy-1-naphthaldehyde are prepared and characterized, the study reveals that:

- the ligands coordinate in the keto form that transformed to the enol through loss of HCl upon heating the solid complexes, to give the dimeric or polymeric (complex **2**) complexes
- the enolic intermediates of cobalt(II) complexes, are thermally unstable whilst that of nickel(II) and copper(II) complexes, are thermally stable
- cobalt(II) complex **3** of 2,4-dihydroxybenzaldehyde moiety is solvatochromic in hot DMF
- copper(II) complex **2** presents in two tautomeric forms as a result of tautomerization of the Schiff's base
- copper(II) complexes **5** and **8** are only deformed in the enol form during heating course
- the complexes obtained are characterized by the presence of different solvents of crystallization with different nature of interaction

## References

1 A. M. Mishra, J. Indian Chem. Soc., 76 (1999) 35.

2 F. A. French and E. J. Blanz, Cancer Res., 28 (1968) 2419.

3 S. Pal, Snog. Chem., 41 (2002) 4843.

4 Z. Y. Yang, R. D. Yang, F. S. Li and K. B. Yu, Polyhedron, 19 (2000) 2599.

5 B. Singh, R. Sriuastava, K. K. Narang and V. P. Singh, Synth., React. Inorg. Met. Org. Chem., 29 (1999) 1867.

6 V. Puri and B. V. Agarwal, J. Indian Chem. Soc., 75 (1998) 27.

7 E. Szunyogová, K. Györyová, J. Kovárová and E. Juhászová, J. Therm. Anal. Cal., 71 (2003) 967.

8 A. M. Donia, H. A. El-Boraey and M. F. El-Samalehy, J. Therm. Anal. Cal., 73 (2003) 987.

9 M. Amirnasr, R. Houriet and S. Meghdadi, J. Therm. Anal. Cal., 67 (2002) 523.

10 D. Czakis-Sulikowska, A. Czylkowska and A. Malinowska, J. Therm. Anal. Cal., 65 (2001) 505.

11 M. Olczak-Kobza and M. Cichecka, J. Therm. Anal. Cal., 66 (2001) 379.

12 S. U. Din and M. Umar, J. Therm. Anal. Cal., 58 (1999) 61.

13 A. M. Donia and H. A. El-Boraey, J. Anal. Appl. Pyrolysis, 63 (2002) 69.

14 P. W. Selwood, 'Magnetochemistry' Interscience Publisher Inc., New York 1956.

15 A. M. Donia and H. A. El-Boraey, Transition Met. Chem., 18 (1993) 315.

16 A. D. Garnovskii, A. L. Nivorozhkin and V. I. Minkin, Coord. Chem. Rev., 126 (1993) 1.

17 J. B. Lambert, H. F. Shurvell, L. Verbit, R. G. Cooks and G. H. Stout, 'Organic Structural Analysis', Macmillan, New York 1976, p. 235.

18 J. Costamagna, J. Vargas, R. Latorre, A. Alvarado and G. Mena, Coord. Chem. Rev., 119 (1992) 67.

19 F. A. Aly, M. Gaber, R. M. Issa and F. A. El-Saied, Bull. Soc. Chim., 4 (1988) 661.

20 A. Z. El-Sonbati, Transition Met. Chem., 16 (1991) 45.

21 M. Mohan, A. Kumar, M. Kumar and N. K. Jha, Inorg. Chim. Acta, 136 (1987) 65.

22 D. Gajapathy, S. Govindarajan, K. C. Patil and H. Monohar, Polyhedron, 2 (1983) 865.

23 F. A. El-Saied, M. M. Aly, M. T. Abd El-Al and A. M. Anwar, Polish J. Chem., 67 (1993) 1.

24 A. B. P. Lever, 'Inorganic Electronic Spectroscopy', Elsevier, Amsterdam 1968, p. 333.

25 A. M. Donia, Thermochim. Acta, 32 (1998) 187.

26 F. Jalilehvand, Y. Ishii, M. Hidai and Y. Fukuda, J. Chem. Soc., Dalton Trans., (1996) 3251.