

# Spectroscopic and Thermal Studies on Solid Complexes of 4-(2-pyridylazo)resorcinol with Some Transition Metals

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## Abstract

The preparation and characterization of  $Mn^{II}$ ,  $Fe^{II}$ ,  $Co^{II}$ ,  $Ni^{II}$ ,  $Cu^{II}$ ,  $Zn^{II}$  and  $Cd^{II}$  chelates of 4-(2-pyridylazo)resorcinol,  $H_2L$  (PAR) were reported. The solid complexes were characterized by elemental and thermal analyses, IR, molar conductance, magnetic measurements. All complexes were found to have the formulae  $[M(HL)_2]$ . The 1 : 2 (M : L) complexes showed octahedral geometry around  $M^{II}$ . The molar conductance data reveal that the chelates are non-electrolytes. IR spectra show that the ligand is coordinated to the metal ions in a terdentate manner and complexation with 4-(2-pyridylazo)resorcinol through the resorcinol OH, azo N and pyridyl N. In particular, the thermal decomposition of all the complexes of PAR is studied in nitrogen atmosphere. The final decomposition products are found to be the corresponding metal or metal oxides.

**Keywords:** Azo complexes; resorcinol; PAR; magnetic moment; thermal analysis

## 1. Introduction

Metal complexes of azo compounds containing heteroaryl ring systems find various applications. These type of molecules have several advantages, for example the azo group is photochromic, redox responsive, pH-sensitive; stabilizes low valent metal oxidation states due to the presence of a low-lying azo centred  $\pi^*$  molecular orbital, serves as a molecular switch, is used as a metal ion indicator in complexometric titration, dyes and pigments in textile industry.<sup>1–3</sup> Azo compounds are known to be involved in a number of biological reactions such as inhibition of DNA, RNA and protein synthesis, carcinogenesis and nitrogen fixation.<sup>4</sup> Furthermore, they were proved to have biological activity against bacteria and fungi. A number of papers have appeared on complexes of azo dyes, particularly on pyridylazo dyes, involving spectrophotometric<sup>5–7</sup> and chromatographic<sup>8</sup> determination and separation of higher oxidation state metal complexes.<sup>9</sup> Hetero atoms, ring size and substituents in the heterocyclic ring significantly modify the  $\pi$ -acidity of the organic ligands and affect the physical and chemical properties of the complexes. All complexation reactions of PAR with metal ions are strongly dependent on the pH of the solution because PAR is an organic ampholyte which in acidic medium can attract easily a proton to its pyridine nitrogen atom while in

basic medium its o-hydroxy group can easily dissociate (Fig. 1).

A number of simple and mixed complexes of azo compounds were synthesized and characterized.<sup>2, 3, 10–14</sup> Pandey and Narang<sup>15</sup> investigated some properties of metal complexes of monosodium 4-(2-pyridylazo)resorcinol in aqueous solution. 4-(2-pyridylazo)resorcinol (PAR) and its some complexes ( $Ni^{II}$  and  $Zn^{II}$ ) synthesized and characterized.<sup>16, 17</sup> It was concluded that PAR coordinated to the metal ions through the pyridine nitrogen and the o-hydroxyl oxygen.<sup>17–19</sup> But the thermal characterization of transition metal complexes of PAR, have not been reported earlier. The main target of the present study is to synthesize some PAR-metal chelates investigate thermal behaviour and determine the coordination capacity of this ligand, that incorporates several binding sites. The coordination behaviour of  $H_2L$  towards transition metal ions is

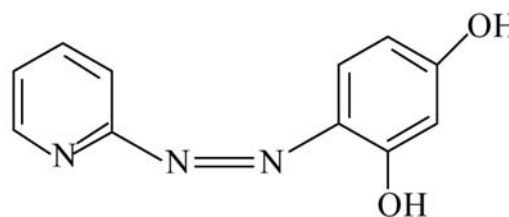


Figure 1. 4-(2-pyridylazo)resorcinol,  $H_2L$ .

investigated and the data are correlated with their molar conductance and magnetic moment measurements. The thermal decomposition of the complexes was also used to infer the structure.

## 2. Experimental

**Materials and methods:** All chemicals used were of the analytical reagent grade. They include 4-(2-pyridylazo)resorcinol (Fluka), ammonia solution (Riedel-de Haen), ethyl alcohol (J.J. Baker), methanol (Sigma), N,N-dimethylformamide (DMF) (Riedel-de Haen). Manganese(II), cobalt(II) and nickel(II) acetate tetrahydrate (Acros), iron(II) chloride tetrahydrate (Merck), copper(II) acetate monohydrate (Merck), zinc(II) acetate dihydrate (Merck) and cadmium(II) nitrate tetrahydrate (Merck) were used as received.

Elemental analyses and metal contents of the ligands and their complexes were measured on a LECO 932 CHNS analyser and a Perkin Elmer 800 AA Spectrometer, respectively. IR spectra between 400–4000  $\text{cm}^{-1}$  were recorded on a Jasco FT/IR-5300 spectrophotometer as KBr discs. The electronic spectra of the ligand and complexes were recorded on a Perkin Elmer  $\lambda$  20 UV/Vis. Spectrometer in various solvents. The magnetic susceptibilities were measured on powdered samples using a Sherwood Scientific MX1 Model Gouy Magnetic Susceptibility Balance. The conductance measurements were carried out using a Optic Ivymen System conductivity meter. The thermogravimetric analysis (TG and DTG) was carried out in dynamic nitrogen atmosphere (20  $\text{mL min}^{-1}$ ) with a heating rate of 10  $^{\circ}\text{C min}^{-1}$  using a Perkin Elmer Pyris 1 TGA thermal analyzer in the Central Laboratory at METU. The sample sizes ranged in mass from 3.2 to 12.2 mg. Highly sintered  $\alpha\text{-Al}_2\text{O}_3$  was used as a reference.

**Synthesis of metal complexes:** The metal complexes were prepared by the same general method. A solution of the appropriate metal chloride, nitrate or acetate (0.5 mmol) in water (15 mL) was added to the hot solution (60  $^{\circ}\text{C}$ ) of the azo compound (0.2174 g, 1 mmol) in methanol (20 mL). The pH of the mixture was raised to 7 by the addition of 10% alcoholic ammonia solution. The resulting mixture was stirred under reflux for 1 h. The resultant volume was reduced to one third by slow evaporation. The solutions were cooled and the crystals formed. The products were separated by filtration, washed with a 1 : 1 methanol-water mixture and diethyl ether, and then dried over  $\text{P}_2\text{O}_5$ . The analytical data are collected in Table 1.

## 3. Results and Discussion

The general reaction for the preparation of the metal complexes of  $\text{H}_2\text{L}$  is shown below:



where  $\text{M} = \text{Mn}^{\text{II}}, \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}$  and  $\text{Zn}^{\text{II}}$ .



where  $\text{M} = \text{Fe}^{\text{II}}$  ( $\text{X} = \text{Cl}$ ) and  $\text{M} = \text{Cd}^{\text{II}}$  ( $\text{X} = \text{NO}_3$ )

The structure formula of the ligand and their metal complexes are given in Figure 1 and 2. In all cases, 1 : 2 ( $\text{M} : \text{L}$ ) solid complexes were isolated and found to have the general formula  $[\text{M}(\text{HL})_2]$ . The results of the elemental analyses of the metal chelates of PAR, which are presented in Table 1, are in good agreement with those required by the proposed formulae.

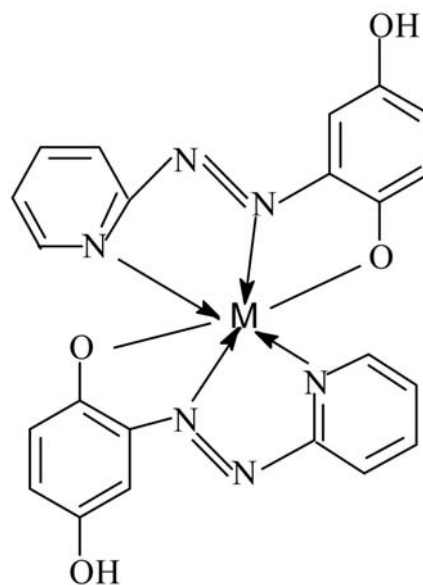


Figure 2. Suggested structural formulae of metal complexes.

**IR spectra and mode of bonding:** A detailed interpretation of the IR spectra of  $\text{H}_2\text{L}$  and the effect of binding with  $\text{Mn}^{\text{II}}, \text{Fe}^{\text{II}}, \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Zn}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$  ions on the vibrational frequencies of the free  $\text{H}_2\text{L}$  ligand are discussed. The IR spectra of the free ligand and its metal chelates were carried out in the 4000–400  $\text{cm}^{-1}$  range (Table 2). The IR spectrum of the ligand shows a broad band at 3446  $\text{cm}^{-1}$ , which can be attributed to the phenolic OH group. This band is still broad in all complexes, which renders it difficult to attribute to the involvement of phenolic OH group in coordination. The involvement of the deprotonated phenolic OH group in chelation is confirmed by the blue-shift of the  $\nu(\text{C}-\text{O})$  stretching band, observed at 1187  $\text{cm}^{-1}$  in the free ligand, to the extent of 14–53  $\text{cm}^{-1}$  (1201–1240  $\text{cm}^{-1}$ ) in the complexes. However, the  $\nu(\text{N}=\text{N})$  stretching band in the free ligand is observed at 1594  $\text{cm}^{-1}$ . This band is shifted to lower (37–84  $\text{cm}^{-1}$ ) (1510–1557  $\text{cm}^{-1}$ ) frequency values upon complexation suggesting coordination via the azo group (M–N).<sup>11, 15, 20, 21</sup> The IR spectrum of the ligand revealed a sharp band at

**Table 1:** Analytical and Physical Data of Metal Complexes of 4-(2-Pyridylazo)resorcinol

Compound	Color (% yield)	Mp, °C	Conductance $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	$\mu_{\text{eff}}$ (B. M.)	Conctects (found/calcd.) %			
					C	H	N	Metal
[Mn(HL) <sub>2</sub> ] [C <sub>22</sub> H <sub>16</sub> N <sub>6</sub> O <sub>4</sub> Mn]	Dark Green (96)	330*	22	4.88	54.46 (54.67)	3.28 (3.34)	17.67 (17.39)	11.21 (11.37)
[Fe(HL) <sub>2</sub> ] [C <sub>22</sub> H <sub>16</sub> N <sub>6</sub> O <sub>4</sub> Fe]	Dark Green (98)	315*	26	4.94	54.47 (54.57)	3.66 (3.33)	17.29 (17.36)	11.18 (11.53)
[Co(HL) <sub>2</sub> ] [C <sub>22</sub> H <sub>16</sub> N <sub>6</sub> O <sub>4</sub> Co]	Black (98)	370*	25	4.81	53.93 (54.22)	3.52 (3.31)	16.85 (17.25)	11.65 (12.09)
[Ni(HL) <sub>2</sub> ] [C <sub>22</sub> H <sub>16</sub> N <sub>6</sub> O <sub>4</sub> Ni]	Dark Green (59)	370*	10	2.88	54.11 (54.25)	3.40 (3.31)	16.91 (17.25)	11.78 (12.05)
[Cu(HL) <sub>2</sub> ] [C <sub>22</sub> H <sub>16</sub> N <sub>6</sub> O <sub>4</sub> Cu]	Dark Brown (43)	190*	18	1.05	53.20 (53.71)	3.37 (3.28)	16.64 (17.08)	12.72 (12.92)
[Zn(HL) <sub>2</sub> ] [C <sub>22</sub> H <sub>16</sub> N <sub>6</sub> O <sub>4</sub> Zn]	Brown (96)	337	12	Dia.	53.23 (53.51)	3.57 (3.26)	16.71 (17.02)	13.33 (13.24)
[Cd(HL) <sub>2</sub> ] [C <sub>22</sub> H <sub>16</sub> N <sub>6</sub> O <sub>4</sub> Cd]	Green (98)	315*	17	Dia.	48.24 (48.86)	2.94 (2.98)	15.24 (15.54)	21.19 (20.79)

\*Decomposition point.

1631  $\text{cm}^{-1}$  due to  $\nu(\text{C}=\text{N})$  of the N3 pyridylazo nitrogen. This band is shifted to lower (25–49  $\text{cm}^{-1}$ ) frequencies in the complexes indicating that it has been affected upon coordination to the metal ions.<sup>11, 15</sup> The pyridine ring vibrations at 1478  $\text{cm}^{-1}$  in H<sub>2</sub>L, are observed at higher frequencies in the spectra of complexes of H<sub>2</sub>L, suggesting involvement of pyridine nitrogen in bonding.<sup>15, 20</sup> In the far-IR spectra of all complexes, the non-ligand bands observed at 418–463 and 437–517  $\text{cm}^{-1}$  region can be assigned to the  $\nu(\text{M}-\text{N})$  stretching vibrations of the azo and N3 pyridylazo nitrogen, respectively. Conclusive evidence regarding the bonding of oxygen to the metal ions is provided by the occurrence of bands at 517–533  $\text{cm}^{-1}$  as the result of  $\nu(\text{M}-\text{O})$ .<sup>21, 22</sup>

Therefore, the IR spectra indicate that H<sub>2</sub>L behaves as monobasic acid and the coordination sites being ArOH, N=N and the N3 atom of the pyridylazo moiety.

**Molar conductance data:** The solubility of the complexes in DMF permitted determination of the molar conductivity ( $\Lambda\text{m}$ ) of  $10^{-3}$  M solutions at 25 °C and, by comparison, the electrolytic nature for each complex. The

low values of the molar conductance data listed in Table 1 indicate that the complexes are nonelectrolytes.

**Magnetic susceptibility and electronic spectra measurements:** The electronic spectra for PAR and its complexes recorded in various solvent such as EtOH and DMF are given in Table 3. The effect of pH change for absorption spectra was also performed by adding 0.1 M HCl and KOH. The electronic spectral data of the ligand exhibit 3 bands in the UV region. The band appearing in the range of 241–393 nm is attributed to  $\pi-\pi^*$  transition of the ligands. The band around 221 nm (in DMF) can be assigned to intra ligand of  $\pi-\pi^*$  transition. The other two bands observed in the region of 382–393 and 395 nm (a shoulder in EtOH) are attributed to  $n-\pi^*$  electronic transitions.<sup>23–25</sup>

**Solvent effect on the electronic spectra of the ligand:** The electronic absorption spectrum of the PAR was studied in various organic solvents, C<sub>2</sub>H<sub>5</sub>OH and DMF. The  $\lambda_{\text{max}}$  of the ligand shows slightly red shift in DMF compared to EtOH solution (Fig. 3). Moreover, in the electronic absorption spectra of PAR, a shoulder around 395

**Table 2:** Selected IR Data (4000–400  $\text{cm}^{-1}$ ) of 4-(2-Pyridylazo)resorcinol and Its Complexes

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{N}=\text{N})$	Pyridine ring	$\nu(\text{C}-\text{O})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{N})$ (azo)
Ligand(H <sub>2</sub> L)	1631 s	1594 m	1478 s	1187 s	–	–	–
[Mn(HL) <sub>2</sub> ]	1582 s	1557 m	1499 w	1240 s	517 w	454 w	431 w
[Fe(HL) <sub>2</sub> ]	1606 m	1547 m	1478 m	1207 s	533 w	452 w	418 w
[Co(HL) <sub>2</sub> ]	1591 s	1510 s	1469 m	1201 s	517 w	498 w	463 w
[Ni(HL) <sub>2</sub> ]	1596 m	1545 m	1509 w	1211 s	531 w	517 w	428 w
[Cu(HL) <sub>2</sub> ]	1594 s	1548 m	1476 w	1212 s	516 w	450 w	424 w
[Zn(HL) <sub>2</sub> ]	1606 m	1545 m	1514 m	1207 s	531 w	437 w	420 w
[Cd(HL) <sub>2</sub> ]	1596 m	1543 m	1505 w	1202 s	532 w	476 w	422 w

s: sharp, m: medium, w: weak

nm which cannot be seen clearly in DMF solution of the ligand becomes more clear in the ethanol solution. And the band appearing in 221 nm in DMF attributed to  $n-\pi^*$  electronic transition cannot be seen in EtOH solution of the ligand.

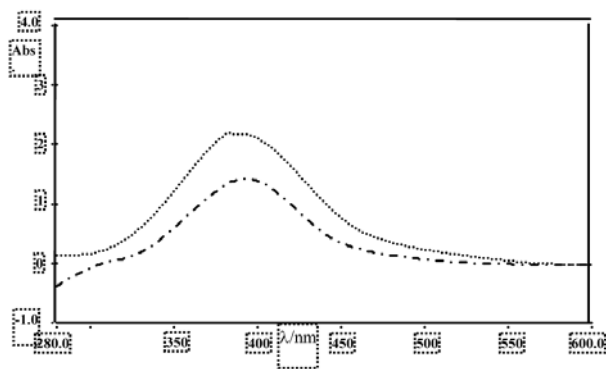


Figure 3. Electronic absorption spectra of PAR in EtOH (.....) and DMF (- · - · - ·)

**pH effect on the electronic absorption:** The effect of pH change on the electronic absorption spectra of the ligand was studied in EtOH solution by adding a small amount of 0.1M HCl and KOH. The  $\lambda_{\max}$  of the ligand (382 nm) in ethanolic solution is not effected by adding a small amount of 0.1M HCl. However, the electronic absorption spectra of this compound change considerably when adding a small amount of 0.1M KOH in ethanolic solution. After adding two drops of 0.1M KOH to ethanolic solution of the ligand, the  $\lambda_{\max}$  appearing around 382 nm in the spectra of the neutral ethanolic solutions of the ligand shift to 404 nm and the intensity of this band slightly increases. Furthermore, a new band appears around 303 nm indicating the ligand exist in the anionic form in basic solutions probably due to phenolic group (Fig.4, Table 3).

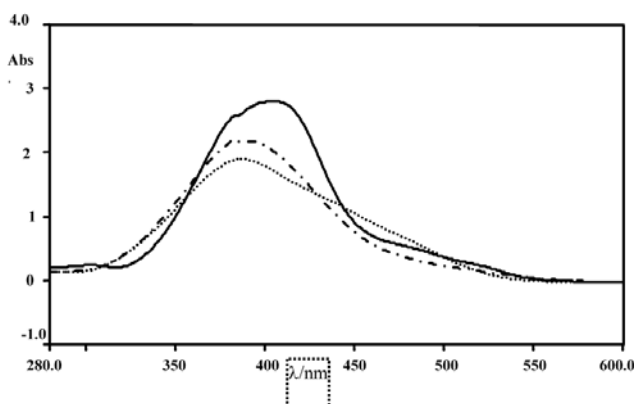


Figure 4. Electronic absorption spectra of PAR in EtOH (- · - · - ·); EtOH+HCl (.....) and EtOH + KOH (—)

**Electronic absorption spectra of the complexes:** Electronic absorption spectra of the complexes were recorded in DMF and EtOH solutions (Table 3).  $Mn^{II}$ ,  $Fe^{II}$ ,  $Co^{II}$ ,  $Ni^{II}$ ,  $Cu^{II}$ ,  $Zn^{II}$  and  $Cd^{II}$  chelates show four bands at 209–239, 220–267, 257–292 and 366–409 nm which are attributed to the  $\pi-\pi^*$  and  $n-\pi^*$  transitions, respectively, within the  $H_2L$  ligand. In the electronic spectra of some complexes, there is a band around 304–326 nm. This band is assigned as a CT transition.<sup>24, 25</sup> Although the position of CT band of all complexes do not regular variation in DMF and EtOH solvents, it may be concluded from Table 3 that the CT transition bands in DMF solution usually show a little more red shift than those of in EtOH solutions. The UV spectrum of  $Mn^{II}$  complex show three bands at 488–491, 529–527 and 711–721 nm (Table 4) assignable to  ${}^4T_{1g} \rightarrow {}^6A_{1g}$ ,  ${}^4T_{2g}(G) \rightarrow {}^6A_{1g}$  and  ${}^4T_{1g}(D) \rightarrow {}^6A_{1g}$  transitions,<sup>11</sup> respectively, which lie in the same range as reported for octahedrally coordinated  $Mn^{II}$  ion. The magnetic moment (4.88 B.M.) is an additional evidence for an octahedral structure. The magnetic moment of the iron(II) complex has been found to be 4.94 B.M., which is within the range of values corresponding to high-spin octahedral complexes of iron(II) ions. From the electronic spectra, it is observed that, the  $Fe^{II}$  chelate exhibits a band at 514–544 nm, which may be assigned to the  ${}^5T_{2g} \rightarrow {}^5E_g$  transition in octahedral geometry of the complex.<sup>15</sup> The band observed at 316 nm which is not observe in DMF can be attributed to ligand-to-metal charge transfer band. For the cobalt complex, the magnetic moment (4.81 B. M.) is within the range of octahedral cobalt(II) complexes. The UV spectrum shows a band of medium intensity at 531–514 nm which is assigned to the transition  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P) (v_3)$ , but the transition  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F) (v_2)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F) (v_1)$  of an octahedral cobalt(II) complex cannot be observe. The band at 319–326 nm refers to the charge transfer transition (L–MCT). The magnetic moment of the  $Ni^{II}$  complexes has been found to be 2.88 B. M., which is within the range of values corresponding to octahedral geometry. The UV spectra of  $Ni^{II}$  complex is consistent with the formation of an octahedral geometry with the appearance of two bands at:  $v_1 = (535-523 \text{ nm}): {}^3A_{2g} \rightarrow {}^3T_{2g}$  and  $v_2: (575-552 \text{ nm}): {}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ . But  $v_3: {}^3A_{2g} \rightarrow {}^3T_{1g}(P)$  can not be observe. The band at 318–323 nm refers to the charge transfer band (L–MCT). The UV spectra of  $Cu^{II}$  complex gives the band centered at 845 nm (in DMF), which may be assigned to  ${}^2E_g \rightarrow {}^2T_{2g}$  transition in an approximately octahedral environment ( $\mu_{\text{eff}} = 1.05 \text{ B.M.}$ ). The zinc and cadmium complexes are diamagnetic and are likely to octahedral.<sup>11, 15, 21</sup> Unfortunately, the some expected weak d–d transition in the visible region for some complexes cannot be detected even with concentrated solution. It may be lost in the low energy tail of the charge transfer transition.<sup>24, 25</sup>

**Thermogravimetric (TG) analysis:** The TG for the metal complexes was carried out within the temperature range from room temperature up to 1000 °C. Thermal

**Table 3:** Electronic bands and d–d transitions of PAR and its metal complexes

Compound	EtOH	DMF
Ligand (H <sub>2</sub> L)	241, 382, 395s	221, 259, 393
H <sub>2</sub> L (EtOH + HCl)	242, 389, 437	
H <sub>2</sub> L (EtOH + KOH)	244, 303, 384s, 404, 490s	
[Mn(HL) <sub>2</sub> ]	217, 235, 262, 304, 398, 488, 529, 711	236, 261, 268, 304, 401, 491, 527s, 721
[Fe(HL) <sub>2</sub> ]	217, 239, 261, 316, 404, 514	287, 407, 510, 544s
[Co(HL) <sub>2</sub> ]	217, 246, 319, 452, 514	224, 238, 292, 326, 366, 467s, 531,
[Ni(HL) <sub>2</sub> ]	217, 239, 269, 318, 409, 523, 552s	211, 231, 263, 323, 407, 535, 575
[Cu(HL) <sub>2</sub> ]	212, 220, 257, 384, 530	239, 267, 280, 408, 525, 845
[Zn(HL) <sub>2</sub> ]	219, 238, 265, 317, 500	228, 268, 321, 410, 538
[Cd(HL) <sub>2</sub> ]	209, 220, 262, 317, 384, 404, 514	228, 242, 266, 284, 400, 514

s: shoulder

data of the complexes are given in Table 4. The correlations between the different decomposition steps of the complexes with the corresponding weight losses are discussed in terms of the proposed formulae of the complexes.

The Mn<sup>II</sup> complex with the general formula [Mn(C<sub>22</sub>H<sub>16</sub>N<sub>6</sub>O<sub>4</sub>)] is thermally decomposed in two successive decomposition steps. These two steps occur within the temperature range 95–520 °C with an estimated mass loss 79.20% (calculated mass loss = 82.01%) are reasonably accounted for the decomposition of the ligand molecules leaving MnO<sub>2</sub> residue.

The Fe<sup>II</sup> complex, [Fe(C<sub>22</sub>H<sub>16</sub>N<sub>6</sub>O<sub>4</sub>)], is thermally decomposed in three successive decomposition steps within the temperature range 70–625 °C. These decomposition steps of estimated mass loss 84.00% which is responsibly accounted for the decomposition of the ligand molecules with a final oxide residue of FeO.

The Co<sup>II</sup> complex, with the general formula [Co(C<sub>22</sub>H<sub>16</sub>N<sub>6</sub>O<sub>4</sub>)], shows decomposition pattern of three stages. The first steps with estimated mass loss of 43.57%, found within the temperature range 350–570 °C. Corresponding to loss of one ligand molecule (calculated mass loss = 43.95%). The second steps with estimated mass loss of 21.43%, found within the temperature range 570–645 °C. Corresponding to loss of pyridylazo group; C<sub>5</sub>H<sub>4</sub>N<sub>3</sub> (calculated mass loss = 21.77%). The remaining decomposition steps with an estimated mass loss 19.30% which is due to loss of the second ligand molecule leaving CoO residue occurring within the temperature range 645–845 °C (calculated mass loss = 18.90%). The total estimated mass loss is 84.30% (total calculated mass loss = 86.62%).

The Ni<sup>II</sup> complex with the formula [Ni(C<sub>22</sub>H<sub>16</sub>N<sub>6</sub>O<sub>4</sub>)] was thermally decomposed in two successive decomposition steps. The first estimated mass loss of 40.00% (calculated mass loss = 40.48%) within the temperature range 265–500 °C can be attributed to the liberation of one ligand molecule except OH. The second step occur within the temperature range 500–700 °C with an estimated mass loss 47.90% (calculated mass loss = 47.47%), which is reasonably accounted for the loss of the other ligand molecule leaving Ni as residue with total estimated mass loss 87.90% (total calculated mass loss = 87.95%).

The Cu<sup>II</sup> complex with the general formula [Cu(C<sub>22</sub>H<sub>16</sub>N<sub>6</sub>O<sub>4</sub>)] was thermally decomposed in two successive decomposition steps. The first estimated mass loss of 20.80% within the temperature range 180–210 °C may be attributed to the liberation of pyridylazo group; C<sub>5</sub>H<sub>4</sub>N<sub>3</sub> (calculated mass loss = 21.56%). The remaining step of decompositions occur within the temperature range 210–900 °C with an estimated mass loss of 62.30% (calculated mass loss = 62.27%) which corresponds to the loss of ligand molecules leaving CuO residue with a total estimated mass loss 83.10% (total calculated mass loss = 83.83%).

The Zn<sup>II</sup> complex, with the general formula [Zn(C<sub>22</sub>H<sub>16</sub>N<sub>6</sub>O<sub>4</sub>)], shows decomposition pattern of three stages. The first step with estimated mass loss of 16.00%, found within the temperature range 40–350 °C. Corresponding to loss of pyridine group; C<sub>5</sub>H<sub>4</sub>N (calculated mass loss = 15.81%). The second and third steps with an estimated mass loss 68.30% which is due to loss of the ligand molecules leaving ZnO residue occurring within the temperature range 350–595 °C (calculated mass loss = 67.70%). The total estimated mass loss is 84.30% (total calculated mass loss = 83.52%).

The Cd<sup>II</sup> complex with the formula [Cd(C<sub>22</sub>H<sub>16</sub>N<sub>6</sub>O<sub>4</sub>)] was thermally decomposed in three successive decomposition steps. In the first two steps, estimated mass loss of 19.90% (calculated mass loss = 19.62%) within the temperature range 270–355 °C can be attributed to the liberation of pyridylazo group (C<sub>5</sub>H<sub>4</sub>N<sub>3</sub>). The last decomposition step occur within the temperature range 355–620 °C with an estimated mass loss 57.10% (calculated mass loss = 56.64%), which is reasonably accounted for the loss of the ligand molecule leaving CdO as residue with total estimated mass loss 77.00% (total calculated mass loss = 76.26%).

## 4. Conclusions

The design and synthesis of complexes of PAR proved to be as straightforward as expected, giving high yields of the complexes in simple, one pot reactions. As anticipates, the ligand coordinates six coordinate transition metal ions to give octahedral complexes. The

**Table 4:** Thermoanalytical results (TG, DTG) of metal complexes

Complex	TG range (°C)	DTGmax (°C)	Estimated (% , calculated)		Assignment	Metallic residue
			Mass loss	Total mass loss		
[Mn(HL) <sub>2</sub> ]	95–520	330, 378	79.20 (82.01)	79.20 (82.01)	Loss of ligand molecules	MnO <sub>2</sub>
[Fe(HL) <sub>2</sub> ]	70–625	315, 375, 456	84.00 (83.95)	84.00 (83.95)	Loss of ligand molecules	FeO
[Co(HL) <sub>2</sub> ]	300–570	370	43.57 (43.95)		Loss of one ligand molecule	
	570–645	580	21.43 (21.77)		Loss of C <sub>5</sub> H <sub>4</sub> N <sub>3</sub> group	
	645–845	800	19.30 (18.90)	84.30 (84.62)	Loss of another ligand molecule	CoO
[Ni(HL) <sub>2</sub> ]	265–500	370	40.00 (40.48)		Loss of one ligand molecule except OH	
	500–700	520	47.90 (47.47)	87.90 (87.95)	Loss of another ligand molecule	Ni
[Cu(HL) <sub>2</sub> ]	180–210	190	20.80 (21.56)		Loss of C <sub>5</sub> H <sub>4</sub> N <sub>3</sub> group	
	210–685	560	62.30 (62.27)	83.10 (83.83)	Loss of ligand molecules	CuO
[Zn(HL) <sub>2</sub> ]	40–350	337	16.00 (15.81)		Loss of C <sub>5</sub> H <sub>4</sub> N group	
	350–595	480, 552	68.30 (67.70)	84.30 (83.52)	Loss of ligand molecules	ZnO
[Cd(HL) <sub>2</sub> ]	270–355	315, 335	19.90 (19.62)		Loss of C <sub>5</sub> H <sub>4</sub> N <sub>3</sub> molecule	
	355–620	510	57.10 (56.64)	77.00 (76.26)	Loss of ligand molecules	CdO

proposed general structures of the complexes are shown in Fig. 2.

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## Povzetek

V članku je opisana sinteza in karakterizacija Mn<sup>II</sup>, Fe<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup> in Cd<sup>II</sup> kelatov 4-(2-piridilazo)resorcinola, H<sub>2</sub>L (PAR). Karakterizacija kompleksov zajema elementno in termično analizo, IR spektroskopijo, molsko prevodnost in magnetne meritve. Kompleksi imajo formulo [M(HL)<sub>2</sub>] z oktaedrično koordinacijo M<sup>II</sup> in ne ionizirajo. IR spectri kažejo na štirištevno koordinacijo liganda z resorcinolno OH, azo N in piridilnim N atomom. Termični razpad kompleksov v dušiku daje ustrezne kovine ali kovinske okside.