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 photocromic, 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. 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. 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 and chromatographic determination and separation of higher oxidation state metal complexes. Hetero atoms, ring size and substituents in the heterocyclic ring significantly modify the $\pi$- acidity of the organic ligands and affect the phsical 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 $\text{o}$-hydroxy group can easily dissociate.

A number of simple and mixed complexes of azo compounds were synthesized and characterized. Pandey and Narang 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. It was concluded that PAR coordinated to the metal ions through the pyridine nitrogen and the $\text{o}$-hydroxyl 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.

Figure 1. 4-(2-pyridylazo)resorcinol, H$_2$L.
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), NN-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 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 λ 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 an Optic Iyvmen System conductivity meter. The thermogravimetric analysis (TG and DTG) was carried out in dynamic nitrogen atmosphere (20 mL min⁻¹) with a heating rate of 10 °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 α-Al₂O₃ 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 °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 P₂O₅. The analytical data are collected in Table 1.

3. Results and Discussion

The general reaction for the preparation of the metal complexes of H₂L is shown below:

\[ M(\text{AcO})_2 + 2\text{H}_2\text{L} \rightarrow [M(\text{HL})_2] + 2\text{AcOH} \]  (1)

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

\[ M\text{X}_2 + 2\text{H}_2\text{L} \rightarrow [M(\text{HL})_2] + 2\text{HX} \]  (2)

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

The structure formula of the ligand and their metal complexes are given in Figure 1 and 2. In all cases, 1 : 2 (M : L) solid complexes were isolated and found to have the general formula \([M(\text{HL})_2]\). 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.

IR spectra and mode of bonding: A detailed interpretation of the IR spectra of H₂L and the effect of binding with Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and Cd²⁺ ions on the vibrational frequencies of the free H₂L ligand are discussed. The IR spectra of the free ligand and its metal chelates were carried out in the 4000–400 cm⁻¹ range (Table 2). The IR spectrum of the ligand shows a broad band at 3446 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 \( \nu (\text{C–O}) \) stretching band, observed at 1187 cm⁻¹ in the free ligand, to the extent of 14–53 cm⁻¹ (1201–1240 cm⁻¹) in the complexes. However, the \( \nu (\text{N=N}) \) stretching band in the free ligand is observed at 1594 cm⁻¹. This band is shifted to lower (37–84 cm⁻¹) (1510–1557 cm⁻¹) frequency values upon complexation suggesting coordination via the azo group (M–N).¹¹, ¹⁵, ²⁰, ²¹
1631 cm$^{-1}$ due to $\nu(C=N)$ of the N3 pyridylazo nitrogen. This band is shifted to lower (25–49 cm$^{-1}$) frequencies in the complexes indicating that it has been affected upon coordination to the metal ions.\textsuperscript{11, 15} The pyridine ring vibrations at 1478 cm$^{-1}$ in H$_2$L, are observed at higher frequencies in the spectra of complexes of H$_2$L, suggesting involvement of pyridine nitrogen in bonding.\textsuperscript{15, 20} In the far-IR spectra of all complexes, the non-ligand bands observed at 418–463 and 437–517 cm$^{-1}$ region can be assigned to the $\nu$(M–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 cm$^{-1}$ as the result of $\nu$(M–O).\textsuperscript{21, 22}

Therefore, the IR spectra indicate that H$_2$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 ($\Lambda$) 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 $\pi\rightarrow\pi^*$ transition of the ligands. The band around 221 nm (in DMF) can be assigned to intra ligand of $\pi\rightarrow\pi^*$ 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.\textsuperscript{23–25}

**Solvent effect on the electronic spectra of the ligand:** The electronic absorption spectrum of the PAR was studied in various organic solvents, C$_2$H$_5$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>
<thead>
<tr>
<th>Compound</th>
<th>Color (% yield)</th>
<th>Mp, °C</th>
<th>Conductance $\Omega^{-1}$ cm$^2$ mol$^{-1}$</th>
<th>$\mu_{\text{eff}}$ (B. M.)</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Metal</th>
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<tbody>
<tr>
<td>[Mn(HL)$_2$]</td>
<td>Dark Green (96)</td>
<td>330*</td>
<td>22</td>
<td>4.88</td>
<td>54.46</td>
<td>3.28</td>
<td>17.67</td>
<td>11.21</td>
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<td>[C$_2$H$_6$N$_6$O$_4$Mn]</td>
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<td></td>
<td></td>
<td></td>
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<td>(3.34)</td>
<td>(17.39)</td>
<td>(11.37)</td>
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<td>Dark Green (98)</td>
<td>315*</td>
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<td>54.47</td>
<td>3.66</td>
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<td>(3.33)</td>
<td>(17.36)</td>
<td>(11.53)</td>
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<td>370*</td>
<td>25</td>
<td>4.81</td>
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<td>3.52</td>
<td>16.85</td>
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<td></td>
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<td></td>
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<td>(17.25)</td>
<td>(12.09)</td>
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<td>Dark Brown (43)</td>
<td>190*</td>
<td>18</td>
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<td>(53.71)</td>
<td>(3.28)</td>
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<td>337</td>
<td>12</td>
<td>Dia.</td>
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<td>3.57</td>
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<td>[Cd(HL)$_2$]</td>
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<td>17</td>
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<td>(48.86)</td>
<td>(2.98)</td>
<td>(15.54)</td>
<td>(20.79)</td>
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</table>

*Decomposition point.

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(C=N)</th>
<th>$\nu$(N=N)</th>
<th>Pyridine ring</th>
<th>$\nu$(C=O)</th>
<th>$\nu$(M–O)</th>
<th>$\nu$(M–N)</th>
<th>$\nu$(M–N) (azo)</th>
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<tr>
<td>Ligand(H$_2$L)</td>
<td>1631 s</td>
<td>1594 m</td>
<td>1478 s</td>
<td>1187 s</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<td>[Mn(HL)$_2$]</td>
<td>1582 s</td>
<td>1557 m</td>
<td>1499 w</td>
<td>1240 s</td>
<td>517 w</td>
<td>454 w</td>
<td>431 w</td>
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<tr>
<td>[Fe(HL)$_2$]</td>
<td>1606 m</td>
<td>1547 m</td>
<td>1478 m</td>
<td>1207 s</td>
<td>533 w</td>
<td>452 w</td>
<td>418 w</td>
</tr>
<tr>
<td>[Co(HL)$_2$]</td>
<td>1591 s</td>
<td>1510 s</td>
<td>1469 m</td>
<td>1201 s</td>
<td>517 w</td>
<td>498 w</td>
<td>463 w</td>
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<tr>
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<td>1596 m</td>
<td>1545 m</td>
<td>1509 w</td>
<td>1211 s</td>
<td>531 w</td>
<td>517 w</td>
<td>428 w</td>
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<tr>
<td>[Cu(HL)$_2$]</td>
<td>1594 s</td>
<td>1548 m</td>
<td>1476 w</td>
<td>1212 s</td>
<td>516 w</td>
<td>450 w</td>
<td>424 w</td>
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<tr>
<td>[Zn(HL)$_2$]</td>
<td>1606 m</td>
<td>1545 m</td>
<td>1514 m</td>
<td>1207 s</td>
<td>531 w</td>
<td>437 w</td>
<td>420 w</td>
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<tr>
<td>[Cd(HL)$_2$]</td>
<td>1596 m</td>
<td>1543 m</td>
<td>1505 w</td>
<td>1202 s</td>
<td>532 w</td>
<td>476 w</td>
<td>422 w</td>
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</table>

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–π* electronic transition cannot be seen in EtOH solution of the ligand.

**Electronic absorption spectra of the complexes:**

Electronic absorption spectra of the complexes were recorded in DMF and EtOH solutions (Table 3). MnII, FeII, CoII, NiII, CuII, ZnII and CdII chelates show four bands at 209–239, 220–267, 257–292 and 366–409 nm which are attributed to the π–π* and n–π* transitions, respectively, within the H₂L ligand. In the electronic spectra of some complexes, there is a band around 304–326 nm. This band is assigned as a CT transition.24, 25 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 MnII complex show three bands at 488–491, 529–527 and 711–721 nm (Table 4) assignable to 4T₁g(D) → 6A₁g transitions, 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 5T₂g → 5Eg transition in octahedral geometry of the complex.15 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 4T₁g(F) → 4T₁g(P) (ν₃), but the transition 4T₁g(F) → 4A₂g(F) (ν₂) and 4T₁g(F) → 4T₂g(F) (ν₁) 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 NiII complex has been found to be 2.88 B.M., which is within the range of values corresponding to octahedral geometry. The UV spectra of CuII complex gives the band centered at 845 nm (in DMF), which may be assigned to 2Eg → 2T₂g transition in an approximately octahedral environment (μ eff = 1.05 B.M.). The zinc and cadmium complexes are diamagnetic and are likely to octahedral.11, 15, 21 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.24, 25

**Thermogravimetric (TG) analysis:**

The TG for the metal complexes was carried out within the temperature range from room temperature up to 1000 °C. Thermal
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 MnII complex with the general formula [Mn(C_{22}H_{16}N_{6}O_{4})] 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%) which is reasonably accounted for the decomposition of the ligand molecules leaving MnO residue.

The FeIII complex, [Fe(C_{22}H_{16}N_{6}O_{4})], 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 reasonably accounted for the decomposition of the ligand molecules leaving FeO residue.

The CoII complex, with the general formula [Co(C_{22}H_{16}N_{6}O_{4})], shows decomposition pattern of three stages. The first steps with estimated mass loss of 43.57%, found within the temperature range 350–570 °C, that corresponds to the loss of one ligand molecule (calculated mass loss = 43.95%). The second steps with estimated mass loss of 40.00%, found within the temperature range 350–595 °C (calculated mass loss = 40.48%) within the temperature range 270–355 °C can be attributed to the liberation of pyridine group; C_5H_4N (calculated mass loss = 19.90%). The remaining step of decomposition steps within the temperature range 40–350 °C (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 CoO residue occurring within the temperature range 645–845 °C (calculated mass loss = 83.52%) total calculated mass loss = 86.62%.

The NiII complex with the formula [Ni(C_{22}H_{16}N_{6}O_{4})] 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 may be attributed to the liberation of pyridylazo group; C_5H_4N_3 (calculated mass loss = 21.56%). The remaining step of decompositions occur within the temperature range 210–900 °C with an estimated mass loss 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 CuII complex with the general formula [Cu(C_{22}H_{16}N_{6}O_{4})] 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_5H_4N_3 (calculated mass loss = 21.56%). The remaining step of decompositions occur within the temperature range 210–900 °C with an estimated mass loss 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 ZnII complex, with the general formula [Zn(C_{22}H_{16}N_{6}O_{4})], 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_5H_4N (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 CdII complex with the formula [Cd(C_{22}H_{16}N_{6}O_{4})] 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_5H_4N_3). The last decomposition step occurs within the temperature range 355–620 °C with an estimated mass loss 77.00% (calculated mass loss = 76.26%) which is reasonably accounted for the loss of the ligand molecule leaving CdO as residue with total estimated mass loss 84.30% (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
proposed general structures of the complexes are shown in Fig. 2.

5. Acknowledgements

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6. References


Povzetek


Karipcin and Kabalcilar: Spectroscopic and Thermal Studies on Solid Complexes ...