



# SYNTHESIS AND SPECTROSCOPIC STUDY OF DIVALENT METAL COMPLEXES WITH 4-HYDROXY-6-METHYL-3-((Z)-4-METHYLPHENYL-AZO)-2H-PYRAN-2-ONE LIGAND

Mahmoud Najim Al-Jibouri,<sup>[a]</sup> Taghreed M. Musa<sup>[a]</sup> and Al-Ameen Bariz Omar Ali<sup>[a]</sup>

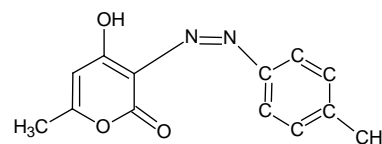
**Keywords:** azo dye, metal complexes, 4-hydroxy-6-methyl-3-((Z)-4-methylphenylazo)-2H-pyran-2-one ligand

Six chelate complexes of 4-hydroxy-6-methyl-3-((Z)-4-methylphenylazo)-2H-pyran-2-one (HL) ligand with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were synthesized and characterized by elemental analysis, magnetic susceptibility measurements, electronic, <sup>1</sup>H, <sup>13</sup>C NMR and IR spectral studies. The ligand is coordinated to the metals through its deprotonated pyrane-oxygen and the azo-group. Mn(II), Co(II), Cu(II) and Ni(II) complexes have octahedral geometry around the central atoms. The molar conductance measurements on chloride-ion containing Zn(II) and Cd(II) complexes confirmed that chloride ions are bound in the coordination sphere, and the most probable geometry around the central atoms is likely to be tetrahedral.

\* Corresponding Authors

E-Mail: mahmoudnajim71@yahoo.com

[a] Chemistry Department, College of Science, Al-Mustansiriya University, Baghdad, Iraq



**Figure 1.** Structure of the 4-hydroxy-6-methyl-3-((Z)-4-methylphenylazo)-2H-pyran-2-one ligand

## Introduction

Azo compounds, characterized by the presence of one or more azo ( $-N=N-$ ) groups in the molecule, are widely used as dyes and form complexes with various metals.<sup>1-11</sup> The azo compounds are usually prepared by the reaction of diazo species obtained in the diazotisation of aromatic primary amines and a coupling agent.<sup>2</sup> The versatile ligating behaviour of azo compounds had evoked considerable interest because its metal complexes have shown better usability in dye industry than the parent azo dyes.<sup>3-11</sup> Furthermore, the toxicity of azo dyes used as parent or complexed materials in dye industry is generally lower than the toxicity of the starting compounds, e.g. the azo-compounds formed from diazotized benzidines with maleic ester cannot be converted back to benzidine in human body which suggests that these dyes are not mutagenic as the parent amines.<sup>8</sup>

Since the metal-azo dyes complexes are more specific and selective than the pure azo dyes due to their better fiber affinity and improved light fastness, therefore the structure and properties of various pyrazolone-like derivatives have been studied.<sup>4-8</sup> For example, complexes of Ni(II), Co(II), Mn(II), Cu(II), La(III), Ce(III), Th(IV) or VO<sub>2</sub>(V) cations with 4-*p*-methoxyphenylazopyrazolone, Cu(II) and Co(II) complexes of 1-isonicotinoyl-3-methyl-4-phenylazopyrazolones,<sup>4,5</sup> or the synthesis and characterization of macrocyclic ligands prepared by the condensation of dehydroacetic acid with 1,2-phenylenediamine and 1,3-propylenediamine were reported.<sup>7</sup>

*p*-Tolylazo-4-hydroxy-6-methylpyran-2-one and its complexes with Mn(II), Co(II), Ni(II), Cu(II), Cd(II) and Zn(II) have not been characterized so far.

## Experimental

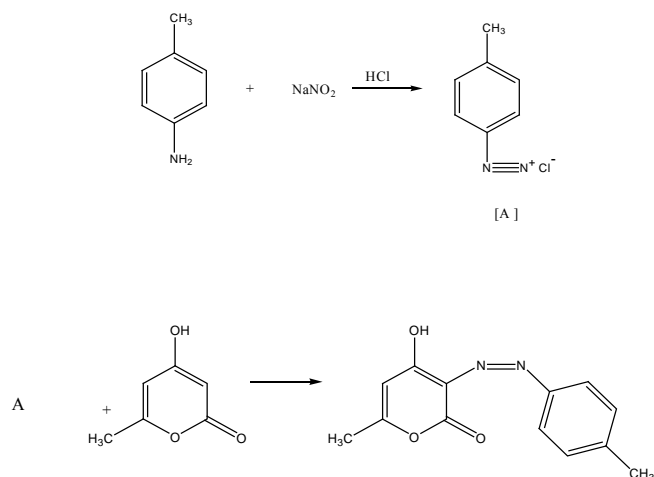
### Materials and methods

All the chemicals used for synthetic purposes were of Analar grade. Solvents like methanol, nitric acid, chloroform, *N,N*-dimethylformamide and ethanol were Sigma Aldrich products and used as received. Commercial methanol was purified by distillation.

The chloride salts of Mn(II), Ni(II), Cu(II), Cd(II) and Zn(II) were used for the synthesis of the complexes.

### Synthesis of 3-(4-methylphenyl)azotriacetic lactone, HL

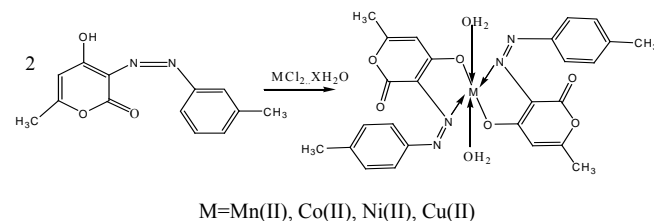
4-Methylaniline (0.01 mol, 1.08 g) was first diazotised with NaNO<sub>2</sub> and HCl, and the resulting solution was slowly added dropwise to a well cooled alkaline solution of 4-hydroxy-6-methyl-2-pyranone (0.02 mol, 1.266 g). The mixture was allowed to stand for 2 h. The product, 6-methyl-3-((Z)-(4-methylphenyl)azo)-4-hydroxypyran, HL, was filtered, washed successively with 0.001 M HCl then with distilled water (Scheme 1). The product was recrystallized from methanol and stored over anhydrous calcium chloride in a desiccator. The molecular formula is C<sub>12</sub>H<sub>13</sub>N<sub>2</sub>O<sub>3</sub>, Elem. Anal.: Found (calcd.): %C=62.33 (63.93), %N=10.66 (11.47), %H=4.22(4.95).



Scheme 1. Synthesis of HL azo ligand

### Synthesis of metal complexes

Methanolic solutions of metal salts were added dropwise to the solution of HL ligand in the same solvent under stirring. The mixture was refluxed on a steam bath for about 2-3 hours. The metal salt to ligand ratio was kept at 1:2. The precipitated complexes were filtered, washed with water, methanol and dried. These were recrystallized from  $\text{CH}_3\text{Cl}-\text{CH}_3\text{OH}$  mixture and stored over anhydrous  $\text{MgSO}_4$  in a desiccators (Scheme 2).



Scheme 2. Synthesis of M(II) (M=Cu, Ni, Mn, Co) complexes with HL azo ligand.

### Physical measurements

The elemental analyses (CHN) of the free ligand were carried out using Carlo Erba CHN analyzer. The metal content analyses were conducted using FAAS on Shimadzu 670AA flame atomic spectrometer with standard addition method.<sup>12</sup> The UV-visible spectra were recorded using 0.001 M solutions of ligand and complexes in methanol and DMF, respectively. The IR spectra of the compounds were recorded in KBr discs. The NMR spectra were obtained using  $\text{DMSO}-d_6$  as solvent and TMS as internal standard on a Bruker 300MHz NMR spectrometer. The magnetic susceptibility was determined at room temperature on Sherwood magnetic susceptibility instrument which was calibrated  $\text{Hg}[\text{Co}(\text{NCS})_4]$ . The chloride-ion content of the zinc(II) and Cd(II) chelates were determined by conductometric titration after dissolving the complexes in least volume of  $\text{HNO}_3$  and dilution with 10 % ethanol.

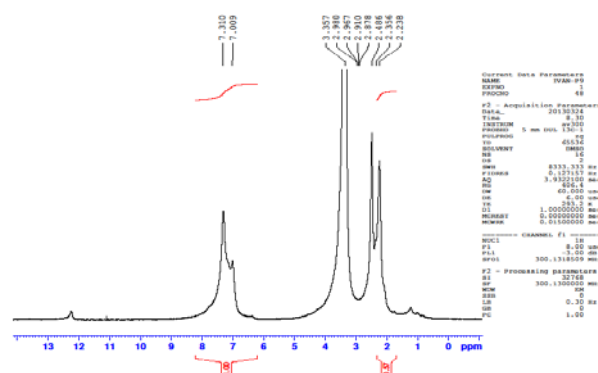
## Results and discussion

The synthesis route for the metal complexes can be seen in Scheme 3. The complexes are stable solids in air, with varying shades of brown coloration and their structures were established from their elemental analyses, infrared, electronic, or NMR spectra and magnetic moment measurements. The results obtained from CHN and metal content analysis (Table 1 and Figure 2) are in good agreement with the data calculated for 1:2 metal-ligand ratio for Mn, Co, Ni or Cu and and 1:1 ratio for Zn or Cd complexes.<sup>12</sup> The complexes are completely soluble in DMF and DMSO, partially soluble in other polar solvents such as acetonitrile and methanol but are completely insoluble in non-polar organic solvents. The low molar conductance values obtained ( $10-33 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ) for the complexes in DMF indicates their non-electrolyte nature.<sup>13</sup> The decomposition points of complexes are high enough thus the loss of water is probably proceeded even before melting/observable decomposition.

In all the complexes one of the azo nitrogens and the oxygen of deprotonated enolic hydroxyl group take part in the coordination with the central metal ions (Figure 1). The Zn(II) and Cd complexes were diamagnetic and all others showed expected magnetic moment values.

### NMR spectra

Both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the ligand confirmed the proposed structure and all the peaks could be assigned.<sup>12</sup> The Figure 2 shows the  $^1\text{H}$  NMR spectrum of Cd(II) complex that records clear shift in signals of  $-\text{OH}$ ,  $-\text{CH}=\text{C}-\text{O}-$  and less shift in absorptions of Ar-H resonances in the regions 6.4-7.8 ppm and 12.33 ppm, respectively. Furthermore, the shielded resonances of  $-\text{CH}_3$  groups were recorded at 2.3-3.3 ppm. The distinct changes in the absorptions of  $^1\text{H}$  NMR for the ligand support the coordination nitrogen  $-\text{N}=\text{N}-$  in  $\beta$ -position and  $-\text{OH}$  of 2-pyranone moiety upon deprotonation.<sup>13</sup>

Figure 2.  $^1\text{H}$  NMR spectrum of Cd(II) complex in  $\text{DMSO}-d_6$  solution

### FTIR spectra

The important IR spectral bands and their assignment are shown in Table 2. The free ligand in KBr shows a broad band at  $3500 \text{cm}^{-1}$  which belongs to an intra hydrogen-bound OH-group, thus it confirms the existence of the enol tautomeric form of the free azo ligand.

**Table 1.** Physical properties and elemental analysis of the prepared ligand HL and its metal complexes.

Compound	Molecular weight, g mol <sup>-1</sup>	Color	M.P., °C	Λ, S mol <sup>-1</sup> cm <sup>2</sup>	M-content, % Calcd. (found)	Cl-content, % Calcd. (found)
HL	244.3	Dark yellow	122-124	8		—
[MnL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	577.5	Dark brown	244-246	12	9.51(9.01)	
[CoL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	581.5	Red	266 <sup>d</sup>	20	10.13(9.22)	
[NiL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	581.3	Dark yellow	288 <sup>d</sup>	33	10.10(9.55)	
[CuL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	586.2	Red	320 <sup>d</sup>	17	10.84(10.44)	
[ZnLCl(H <sub>2</sub> O)]	362.1	Orange	317 <sup>d</sup>	19	18.06(16.11)	9.79(9.09)
[CdLCl(H <sub>2</sub> O)]	409.2	Brown	279 <sup>d</sup>	30	27.46(26.55)	8.66(8.36)

d=decomposition

**Table 2.** Selected infrared vibrations of HL ligand and its metal complexes (cm<sup>-1</sup>).

Compound	νC=O, ν-OH	νC=CH, νN=N-	νM-N, νM-O	νAr-C-H, νC-O (pyranone)
HL	1690-1678(s), 3500(br)	1630, 1520-1480		3010(w), 2966(m), 1215
[MnL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	1680-1658(s), 3520	1620, 1500-1420	550(m), 470(w)	3060(w), 2982(m), 1216
[CoL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	1670-1640(s), 3612	1590, 1480-1470	488, 422	3066, 2952, 1206
[NiL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	1675-1662(s), 3522	1591, 1501-1469	476, 410	3100, 2872, 1222
[CuL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	1653-1639(s), 3444(br)	1588, 1511-1433	560(w), 455(m)	3050, 2950, 1189
[ZnLCl(H <sub>2</sub> O)]	1675-1645(s), 3550	1604, 1544-1501	477-455, 422(m)	3108(w), 1198(s)
[CdLCl(H <sub>2</sub> O)]	1680-1641(s), 3255(m)	1533, 1450-1433	489(m), 400(w)	3022(w), 1118(m)

s=strong, m=medium, br=broad, w=weak

The strong absorptions at 1520-1480 cm<sup>-1</sup> and 1690-1678 cm<sup>-1</sup> regions are typical for the an -N=N- and C=O pyranone moieties, respectively.<sup>16</sup> The strong absorptions in the region 1215 cm<sup>-1</sup> may be attributed to C-O-C stretching corresponded to triacetic lactone structure.<sup>17</sup>

Decreasing wavenumber values belong to the -C=O and -N=N- groups in the IR spectra of the complexes clearly indicates a bidentate monobasic coordination of the HL ligand through oxygen of the deprotonated -OH group and the β-N-atom of the -N=N-group, respectively. The strong absorptions in the range of 1544-1420 cm<sup>-1</sup> entirely reveals the shifting of electron pair of -N=N- group toward metal ions. All the metal(II) complexes showed a broad absorptions in the region 3220-3612 cm<sup>-1</sup> which entirely belong to the coordinated water molecules.<sup>16</sup>

The far-infrared spectra of metal complexes in CsI discs showed weak absorptions in the regions 412-560 and 400-470 cm<sup>-1</sup> confirming the presence M-N and M-O bonds, and the spectra of Zn and Cd-complexes contains the vibrations belongs to M-Cl, M-N and M-O bonds as well.

#### Electronic spectral data and magnetic moments

The electronic absorption bands of complexes are very similar to the bands of the ligand. This showed that no structural changes occurred on complexation, however, a slight shift in the absorption maxima of >C=O and -N=N bands may have occurred as the consequence of their participation in the coordination. The dark yellow solution of HL in methanol displays two high intensity peaks at 233 and 410 nm. These bands belong to the chromophores -N=N- group and substituted benzenoid ring.<sup>15,19</sup>

The cobalt complex was brown in color with a red tinge. This is typical for the octahedral geometry around cobalt(II).<sup>19,20</sup> The appearance of the band at 572 may be

due to <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>A<sub>2g</sub> transition in an octahedral environment, although the magnetic moment value (3.82 B.M) was found to be too low for an octahedral geometry.<sup>19,20</sup>

The Mn(II) complex showed spectral bands which were overlapped with CT bands. The band observed at 540 nm could very well be due to <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>T<sub>1g</sub> transition. The magnetic moment value of 5.54 B.M. indicated octahedral geometry.<sup>18</sup>

**Table 3.** Electronic spectra, molar conductance and magnetic moments of the prepared metal complexes

Compound	λ <sub>max</sub> nm	ν, cm <sup>-1</sup>	Λ, S cm <sup>2</sup> mol <sup>-1</sup>	μ, B.M.
HL	333 410	30030 24390	-	-
[MnL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	299 540	33448 18518	25	5.54
[CoL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	315 572	31746 17482	14	3.82
[NiL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	396 656	25252 15243	19	2.65
[CuL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	267 388	37253 25773	33	1.70
[ZnLCl(H <sub>2</sub> O)]	280 355	35714 28169	10	0
[CdLCl(H <sub>2</sub> O)]	300 440	33333 25000	18	0

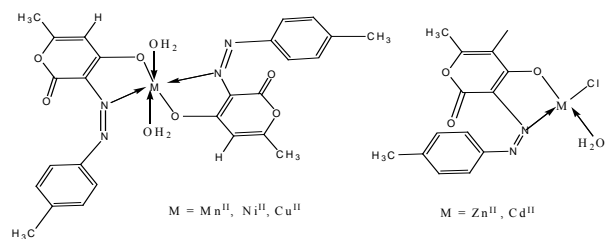
λ=molar conductance in DMF solutions at 0.001 M concentration.

The spectrum of Ni(II) complex was very conspicuous with bands at 396 nm and 656 nm belonging to the  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$  and the  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$  transitions respectively.<sup>21</sup> These bands are characteristic for octahedral geometry around nickel. The magnetic moment value of 2.65 B.M also pointed out the octahedral geometry for Ni(II) complexes. The brown colored copper complex showed bands at the lower end of the visible region. This complex has a magnetic moment of 1.70 BM.

The solutions of zinc(II) and cadmium (II) complexes in DMF showed high intensity peaks in the regions 280-300 and 355-400 nm that may be ascribed to intra-ligand charge transfer INCT and LMCT transitions respectively.<sup>23,24</sup>

## Conclusion

The octahedral geometry for Cu(II), Ni(II), Co(II) or Mn(II) complexes and tetrahedral geometry for Zn(II) or Cd(II)-complexes was proposed on the basis of elemental analyses, molar conductivity measurements, magnetic measurements and NMR or FTIR spectra. The infrared spectral studies revealed that the  $\beta$ -nitrogen of N=N group and the enolized oxygen atom of pyranone ring participate in bonding with the metal ions forming a five-membered ring chelates.



**Scheme 3.** Structures of M(II) complexes with 4-hydroxy-6-methyl-3-[(Z)-(4-methylphenyl)azo]-2H-pyran-2-one.

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