Preparation and Spectroscopic Studies of Cadmium(II), Zinc(II), Mercury(II) and Vanadium(IV) Chelates Azo Ligand Derived from 4-Methyl-7-hydroxycoumarin

Bayader Fathil Abass, Taghreed Mohy Al-Deen Musa, and Mahmoud Najim Abid Al-Jibouri

Department of Chemistry, College of Science, Mustansiriyah University, Baghdad, Iraq

Abstract: The present paper demonstrates the synthesis and characterization of some transition elements complexes derived from (E)-7-hydroxy-6-((4-methoxyphenyl)diazenyl)-4-methyl-2H-chromen-2-one. The ligand was prepared in the general route of azo dyes by coupling the diazonium salt of 4-methoxyaniline with 4-methyl-7-hydroxycoumarin in sodium hydroxide 10% (w/v) solution. The azo ligand was identified on the basis of elemental analyses, MS, H-NMR and FT-IR spectra. The products of complexes with the new azo dye were isolated by the direct reactions of the metal chlorides of cadmium(II), zinc(II), vanadium(IV) and mercury(II) ions with the alkaline solution of free ligand to afford the colored in the following formulas, complexes $[ML_2]_2H_2O$ formula, $M=Cd(II)$ and $Zn(II)$. However the vanadium(IV) complex was square pyramid in $[VOL_2]SO_42H_2O$ chemical formula. As well as the tetrahedral environment was suggested for mercury(II) complex in formula $[HgL_2]$. The time and mole ratio factors were studied to obtain the optimized conditions of metal complexes formations and the observed data investigated the deprotonation of the azo-dye at pH to range (7–7.5) with 30 min as time of reaction to get pure metal chelates. The TG-DSC study confirmed the thermal stability of complexes at a wide range of average heating in inert gas of analysis and the results observed from loss weight percent investigated the proposed structures of the prepared metal complexes.

Keywords: azo ligands; metal complexes of coumarin; spectroscopic studies

INTRODUCTION

The major branch of coordination chemistry has been partially allocated with the azo dyes of 4-hydroxycoumarine and their derivatives [1-2]. The inorganic complexes of chromen-2-one rings mainly could possess applications in catalysis, manufacturing of dyes and pharmaceutical drugs [3-5]. The pentagonal and hexagonal coordination complexes of dyes involving immine and hydroxyl groups have shown a wide range of applications in the diodes and solar cells fields [6-7]. The common coordination compounds derived from azo dyes of chromen-2-one have interested in wide spectrum of applications in the emission studies like fluorescence and phosphorescence [8-10].

Recently the researchers have encouraged enhancing the electronic and geometrical features of complexes of azo dyes that they would have exhibited nonlinear optical elements and printing systems [11-14]. All the above mentioned about the development of coumarin azo dyes with their chelation ability afford us to prepare and characterize new azo dye complexes of Zn(II), Cd(II), V(IV) and Hg(II) derived from (E)-7-hydroxy-6-((4-methoxyphenyl)diazenyl)-4-methyl-2H-chromen-2-one.

EXPERIMENTAL SECTION

Materials

The starting 4-methoxyaniline and 4-methyl-7-hydroxycoumarin and 4-methoxyaniline were supplied...
via Merck Company and the metal salts of VOSO$_4$·5H$_2$O, CdCl$_2$·2H$_2$O, ZnCl$_2$, CdCl$_2$ and HgCl$_2$ were supplied from Quaternary Group Merck Chemicals Companies and used as supplied without purification.

**Instrumentation**

The melting points temperature of the coumarin derivatives and metal complexes were determined on the Stuart melting point apparatus. The molecular weights of the ligand and some selected metal complexes were measured their mass spectra on a Shimadzu model GC MS QP 1000EX at college of science, Mustansiriyah University. The electronic spectra of ligand and its complexes in ethanol and DMSO solvents was determined with UV-1800 Shimadzu spectrometer apparatus. The nuclear magnetic resonance spectroscopy was carried out in $d_6$-DMSO solvent on Bruker-500 MHz NMR spectrometer. The main features of vibration frequencies of azo dye ligand and its metal complexes were scanned on Shimadzu FT-IR spectroscopy in the range (4000–200) cm$^{-1}$. The pH of the solutions was checked using a Jenway 3020 pH meter. Furthermore, the percentages of metal ions were determined with GBC 933 model FAAS at Ministry of Industry, Ibn-Cina company, Baghdad, Iraq.

**Procedure**

**Synthesis of azo ligand**

The azo dye was synthesized according to the modified classical procedure established in literature, by dissolving (1.83 g, 0.01 mmol) from 4-methoxyaniline in hot distilled water (10 mL) then followed by an addition of 36% (v/v) HCl (5 mL). To this solution, a cooled aqueous solution of sodium nitrite (0.45 g, 5 mmol) was added by maintaining the temperature of the reaction at 0 °C. The formed diazonium salt was gradually added to an alkaline solution of 4-methyl-7-hydroxycoumarin (0.02 mol, 3.90 g) with stirring for 30 min, after that the resulting solution was neutralized to pH of about 6.5 by addition drops of 10% NaOH. The dark orange crude was then filtered, washed several times with water and ethanol, then dried. The re-crystallization from hot ethanol afforded dark orange crystals of azo dye ligand, L, Scheme (1).

![Scheme 1. Synthesis of azo dye, HL](image)

**Synthesis of metal complexes**

The metal complexes were prepared by dissolving ZnCl$_2$ (10 mmol, 1.45 g) or CdCl$_2$.2H$_2$O (1 mmol, 1.118 g) in (15 mL) hot water and ethanolic solution of (20 mmol, 1.44 g) of azo dye, L. The mixture was stirred on water bath for 1 h then red precipitates of ZnL and CdL complexes were separated and filtered off. The Hg(II) complex was prepared by mixing (10 mmol, 1.45 g) of azo dye in (15 mL) hot ethanol with (10 mmol, 0.272 g) in (10 mL) hot water with stirring on a water bath for 2 h, the white off separated precipitate was filtered of and dried in oven at 90 °C. However, the vanadium(IV) complex was isolated in its solid state from oxovanadium sulfate penta hydrate after adjusting the mole ratios 1:2 of (M:L) with respect to dissolving VOSO$_4$·5H$_2$O in (15 mL) hot water with (20 mmol, 1.45 g) of azo dye then refluxed the mixture for 2 h. The brown precipitate was filtered, dried in air then washed several times with hot ethanol and diethyl ether, Table 1.

**RESULTS AND DISCUSSION**

**Physical Properties and Elemental Analyses**

Table 1 list the main physical properties of ligand and its complexes and show the thermal stability of almost complexes through the elevated their decomposition points. All the complexes are colored and sparingly soluble in most organic solvents except DMSO and DMF. The micro-analyses (C.H.N.) confirm the suggested chemical formula for all complexes beside the structure of azo dye. The calculation of mole ratios was in good agreement of their formation procedure and
Table 1. Some physical properties and elemental analyses of Azo dye and its complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Weight (g/mol)</th>
<th>Color</th>
<th>M.P. (°C)</th>
<th>%C Found (Calc.)</th>
<th>%H Found (Calc.)</th>
<th>%N Found (Calc.)</th>
<th>%M Found (Calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL</td>
<td>C₁₇H₁₄N₂O₄</td>
<td>Dark brown</td>
<td>178–180</td>
<td>65.00</td>
<td>4.22</td>
<td>8.88</td>
<td>--</td>
</tr>
<tr>
<td>ZnL</td>
<td>C₃₄H₂₆ZnN₄O₈</td>
<td>Red</td>
<td>&gt; 288</td>
<td>(58.232)</td>
<td>(3.89)</td>
<td>(9.36)</td>
<td>(9.22)</td>
</tr>
<tr>
<td>CdL</td>
<td>C₃₄H₂₆CdN₄O₈</td>
<td>Orange</td>
<td>&gt; 300</td>
<td>(53.33)</td>
<td>(3.90)</td>
<td>(10.01)</td>
<td>(16.22)</td>
</tr>
<tr>
<td>HgL</td>
<td>C₃₄H₂₆HgN₄O₈</td>
<td>Brown</td>
<td>277–279</td>
<td>(56.11)</td>
<td>(3.99)</td>
<td>(9.82)</td>
<td>--</td>
</tr>
<tr>
<td>VOL</td>
<td>C₃₄H₃₀N₄SO₁₄V</td>
<td>Dark brown</td>
<td>&gt; 295</td>
<td>(56.73)</td>
<td>(5.90)</td>
<td>(11.99)</td>
<td>(16.30)</td>
</tr>
</tbody>
</table>

stoichiometric and it is based on flame atomic absorption data. The flame atomic absorption spectroscopy for metal contents (M%) in the solid complexes are experimentally
determined through standard addition method and the observed analyses are in good agreement with
the calculated data confirming the structures of all the prepared complexes. However the molar conductivity
measurements reveals that all complexes do not show
electrolytic nature [15], except vanadium(IV) complex
solution in DMF that exhibits conductivity motion due
to the presence of sulfate counter ion in the structure.

Mass Spectra

The mass spectrum of azo-dye ligand showed peak
at molecular ion m/e = 310 which indicates the unstable
molecular weight of the expected C₁₇H₁₄N₂O₄ formula due
to losing methoxy and methyl groups in the gas-phase of
GC conditions for the MS spectra then confirms
formation of the azo dye [13]. The peaks observed at
around m/e = 116 and 89 would be resulted from cleavage
of chromen ring and points of −CH₃ and −OH respectively
[12]. As well as the mass spectrum of vanadium (II)
complex shows weak intensity peak at 747 that is allocated
to the molecular ion of complex in the gas phase [14,17].

NMR Spectra

The H and ¹³C-NMR were displayed only for the azo
dye with chemical shifts in (ppm) units and are relative to
residual proton solvent signals. The spectrum of the
ligand is in a good agreement with the number of protons
and their assignments of nuclear spins of Ar-H and
methyl protons. The ¹H-NMR spectrum of the ligand, Fig. 1 shows a singlet signal at δ (7.9–8.99) ppm
corresponding to the −C=C−H of chromen ring. The
peak showed at around δ (14.50) ppm was also recorded
in the ligand spectrum, due to the −OH proton that is
directly attached to C7 of chromen ring. The doublet of
doublet peaks at around δ (12.45) ppm reflects mainly
the spin coupling of aromatic protons adjacent to each
other in aromatic substituted [12-13]. Furthermore, the
aliphatic protons of −CH₃ groups attached at C-4 were
resonated at around 4.43.

The ¹³C-NMR spectrum of azo ligand showed multiple peaks at 75 ppm related to −CH3 aliphatic
carbon atom and 96 ppm related to −C=OH moiety [12-
13]. The peaks at 125–135 ppm may be related to
resonance of aromatic carbon atoms while the
deshielded −C=N−N− and −C=C− of coumarin may be
assigned to effect of withdrawing groups and showed at
145–165 ppm, respectively. As well as the H-NMR
spectrum of CdL complex displayed remarkable changes
in some resonated aromatic protons and disappearance
of −OH moiety. These data of NMR confirmed the
coordination of Cd(II) ion with the HL azo dye through
−C=N− and OH with deprotonation in the chelation
reaction. As well as the deshielded protons of −HC=CH−
of chromene ring and hydrated water molecules was
download shifted due to the electron donation of the
active site toward the empty orbitals of Cd(II) ion [16-17].
**Fig 1.** H NMR of azo ligand in DMSO-$d_6$ solvent

**Fig 2.** H-NMR of CdL complex in DMSO-$d_6$ solvent

**IR Spectra of the Ligand and Complexes**

The IR spectra of the synthesized complexes in CsI were compared with that of the azo dye. The spectra of the complexes showed the absorption bands characteristic of the ligand with some differences ascribed to the formation of respective ion associated, which showed the more characteristic infrared spectral bands of the free ligand and its complexes. The broad absorption at 3500 cm$^{-1}$ is assigned to $-OH$ of coumarin azo ligand. The strong band at 1651 is associated to $-C=O$ of chromene ring while the strong band at 1623 cm$^{-1}$ is associated with $-CH=CH-$ of aromatic and - rings respectively [12,15] as given in Fig. 3. The appearance of new band at 1477 cm$^{-1}$ confirms the formation of azo $-N=N-$ moiety. The remarkable changes
Fig 3. FT-IR spectrum of azo dye, HL in KBr disc

on –N=N– to lower frequencies at 1450–1433 cm⁻¹ confirm the coordination of ligand via nitrogen atom with M–N formation beside the –C=O shift and supports the bidentate neutral ligand behavior as shown in Fig. 3. The vanadyl complex in Fig. 4 exhibits new band at 950.633 and 590 cm⁻¹ confirming V=O and V–N bands [14-17].

Electronic Spectra and Magnetic Susceptibility

The azo ligand showed one strong absorption around 379 nm which was assigned to intra-ligand charge transfer of –N=N– moiety, then confirms the formation of azo dye due to the high intensity band located near the visible region. On comparison the UV-Visible spectra of all complexes with the spectrum of the free ligand in DMSO solvent, it is noted that the new weak bands observed at around (490–380) nm are consistent with the chelation of empty orbitals of Hg(II), Zn(II), Cd(II) and V(IV) ions [18-19] with the lone pairs of the donating atoms in the active sites of azo dye. The intra-ligand charge transfer of –N=N– moiety was shifted to longer or shorter wavelengths due to the linkage of lone

Fig 4. FT-IR spectrum of VOL complex in CsI disc
pair to the empty orbitals of metal ions in the region (380–500) nm, Table 2. The diamagnetic properties of zinc (II), cadmium (II) and mercury(II) complexes with the association of elemental analyses confirm the tetrahedral environment. The red solution of vanadium (IV) complex displayed two spin-allowed peaks at 650 and 490 nm that are attributed to $^2A_g \rightarrow ^2B_{1g}$ and $^2A_g \rightarrow ^2B_{2g}$ transitions respectively [20]. The value of magnetic moment of solid complex of vanadium(II) at 27 °C to 1.80 BM revealed the presence of unpaired electron in its outer level 3d$^1$ and make it forms the possibility of five-coordinate complex with a bi dentate azo-dye ligand through two active site –N=N and –OH groups [18-19].

**Thermal Analysis of C1 and C2 Complexes**

The thermal stability of zinc(II) and cadmium(II) complexes was screened with TG-DTA analyses in the nitrogen atmosphere and presented in Table 3. The losing of weak points like M–Cl and methyl groups were shown in the first stages of analyses at range (190–270) °C temperature while the final stage of analysis for C1 complex was accomplished at (300–450) °C to give the stable phase of zinc(II) oxide [20]. As well as the hydrated cadmium(II) complex showed three stages of thermal analysis with losing of crystalline water at around (160–280) °C. The data observed from weight loss (%w) would be in agreement with the theoretical data.

### Table 2. Electronic spectra and molar extinction coefficients for complexes

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Molar Conc.</th>
<th>nmλ</th>
<th>$\Sigma L.mol^{-1} cm^{-1}$</th>
<th>Assignment</th>
<th>$\mu$ (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOL</td>
<td>$1 \times 10^{-3}$</td>
<td>655</td>
<td>110</td>
<td>$^2A_g \rightarrow ^2B_{1g}$</td>
<td>1.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>490</td>
<td>90</td>
<td>$^2A_g \rightarrow ^2B_{2g}$</td>
<td>Dia</td>
</tr>
<tr>
<td></td>
<td></td>
<td>380</td>
<td>2900</td>
<td>LMCT</td>
<td>Dia</td>
</tr>
<tr>
<td></td>
<td></td>
<td>455</td>
<td>8000</td>
<td>MLCT</td>
<td>Dia</td>
</tr>
<tr>
<td>ZnL</td>
<td>$1 \times 10^{-4}$</td>
<td>390</td>
<td>27000</td>
<td>INCT</td>
<td>Dia</td>
</tr>
<tr>
<td></td>
<td></td>
<td>280</td>
<td>13000</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>Dia</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500</td>
<td>20000</td>
<td>INCT</td>
<td>Dia</td>
</tr>
<tr>
<td>CdL</td>
<td>$1 \times 10^{-5}$</td>
<td>470</td>
<td>12700</td>
<td>MLCT</td>
<td>Dia</td>
</tr>
<tr>
<td></td>
<td></td>
<td>250</td>
<td>30000</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>Dia</td>
</tr>
<tr>
<td></td>
<td></td>
<td>455</td>
<td>11700</td>
<td>MLCT</td>
<td>Dia</td>
</tr>
<tr>
<td>HgL</td>
<td>$1 \times 10^{-5}$</td>
<td>300</td>
<td>10000</td>
<td>INCT</td>
<td>Dia</td>
</tr>
</tbody>
</table>

Dia = Diamagnetic, LMCT and MLCT are charge transfer from ligand to metal or vice-versa, and INCT = Intra-ligand charge transfer bands

### Table 3. Thermo gravimetric analysis (TGA) of the metal complexes

<table>
<thead>
<tr>
<th>No.</th>
<th>Molecular formula</th>
<th>Temp. range (°C)</th>
<th>Mass loss%</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>[ZnL$_2$]</td>
<td>190–270</td>
<td>6.43</td>
<td>Loss of Cl and –OH, -2OCH$_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300–450</td>
<td>33.84</td>
<td>Further dissociation of the organic ligand (C$_8$H$_6$N$_2$) with formation of ZnO + Zn$_3$N$_2$ as final product</td>
</tr>
<tr>
<td></td>
<td></td>
<td>160–280</td>
<td>16.01</td>
<td>Loss of 2 hydrated H$_2$O molecules, –OCH$_3$</td>
</tr>
<tr>
<td>C2</td>
<td>[CdL$_2$]·2H$_2$O</td>
<td>290–390</td>
<td>10.06</td>
<td>Loss of 2 hydrated H$_2$O molecules, –OCH$_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400–560</td>
<td>52.13</td>
<td>Loss of phenyl, 2Cl anion and decomposition of the organic (2C$_6$H$_5$N$_2$O)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>441–541</td>
<td>15.16</td>
<td>Loss of (C$_6$H$_5$CH$_3$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>541–930</td>
<td>6.16</td>
<td>Further dissociation of the organic ligand (2C) with formation of CdO as final product</td>
</tr>
</tbody>
</table>
O O
N
CH₃

M(II)=Zn, Cd and Hg ions

Scheme 2. Structures of metal complexes

and supports their structures [21-22].

**CONCLUSION**

According to the results obtained from elemental analyses, FT-IR, NMR and EI-MS spectra and electronic spectra in ethanol and DMSO solvents, the tetrahedral geometry was identified for zinc(II), cadmium(II) and mercury(II) complexes, while the vanadium(IV) complex was square-pyramid of five coordination number via optimization the mole ratios 2:1 of ligand azo to the metal ion. The thermal analyses and molar conductivity measurements confirmed the square-pyramid around vanadium(IV) ion and tetrahedral environment around zinc(II), cadmium(II) and mercury(II) ions, Scheme 2.

**ACKNOWLEDGMENTS**

Authors are so grateful for service laboratories at Mustansiriyah University, College of Science, Department of Chemistry facilitating of FT-IR, UV-Visible spectra and magnetic moments measurements. As well as the authors appreciated the role of University of Baghdad, Ibn-Haitham Education College for pure sciences for carrying out the thermal analyses.

**REFERENCES**


[20] Esmaeilzadeh, M.A., 2019, Composite prepared from a metal-organic framework of type MIL-101(Fe) and morin-modified magnetite nanoparticles for extraction and speciation of vanadium(IV) and vanadium(V), Microchim. Acta, 186, 14.
