Fluorescence, Biological Activity and Spectroscopic Studies of Azo-linked Schiff Base Ligand Type (ONO) and Its Complexes with Cr\textsuperscript{III}, Co\textsuperscript{II} Ni\textsuperscript{II} and Cd\textsuperscript{II} Ions

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Abstract

The precursor [W] \((2-(2-(naphthalen-5-yl) diazenyl)-4-amino-3-hydroxynaphthalene-1-sulfonic acid)\) was synthesized from reaction of diazonium salt with 1-amino-2-naphtol-4-sulfonic acid. Then the tridentate Schiff base ligand type ONO was synthesized from the reaction of the precursor with salicyaldehyde in 1:1 mole ratio to produce the ligand \(H_2L\) \((2-(2-(naphthalen-5-yl) diazenyl)-4-(2-hydroxynaphthalen-3-yl)methyleneamino)-3-hydroxy salicyalene-1-sulfonic acid)\), the reaction achieved in methanol as a solvent under reflux. Spectroscopic methods IR, U.V, \(^1H, ^13C\)-NMR was used to characterize the ligand. Complexes of \([Cr^{III}, Co^{II}, Ni^{II}\) and \(Cd^{II}\) \) ions were also prepared through reaction of ligand with metal salts in 2:1 mole ratio at reflux, using KOH as a base, ethanol as a solvent. Chloride content, molar conductivity and melting point measurements along with I.R and U.V-Vis, atomic absorption (A.A) spectroscopy were used to characterize the complexes. \(^1H\)-NMR spectroscopy was used to characterize Cd complex. Thermal analysis was used to insure the presence of crystallized \(H_2O\) molecule in the complexes structure. The following formula was proposed for Cr complex: \(K[Cr(L)_2].H_2O\), while \(Co^{II}, Ni^{II}\) and \(Cd^{II}\) complexes have the \(K_2[M(L)_2].H_2O\) formula. The biological activity of the prepared compounds was studied. Fluorescence properties of the prepared compounds were studied (at room temperature) which indicate that the ligand may behave as strong fluorescent emitter. The complexes also showed fluorescence characteristic with the ligand. The ligand revealed high relative intensity and its fluorescence peak were also shifted to the lower or higher wavelength when compared with the complexes.

Keywords: Azo linked Schiff base, metal complexes, fluorescence properties, biological activity.
Introduction

Due to the important and interesting properties of Schiff bases and their transition metal complexes such as ability to bind heavy metal atoms, undergo tautomerism, exhibit catalytic reduction, many of them have been synthesized [1]. Azo Schiff base compounds contain both azo and azomethine groups, are commonly synthesized by coupling a diazonium reagent with an aromatic aldehyde to form an azo aldehyde [2]. Many azo compounds have been used in industry due to their versatile applications in various fields, including liquid crystalline, dyes for different materials, and lasers [3]. Sulfonated azo dyes are the most numerous of the manufactured synthetic dyes [4]. Moreover, complexes with conjugated π systems containing aromatic rings favour the development of fluorescent materials. [5, 6] In this work we reported the synthesis and characterization of new azo linked Schiff base and its some metal complexes; the biological activity and fluorescence properties of the prepared compounds were studied.

Experimental

Melting point of the synthesized compounds was measured using an electrothermal apparatus stuart. FT–IR Testscan Shimadzu (FT-IR)- 8300 series spectrophotometer in the range (4000– 400 cm⁻¹) was used to obtain the Infrared spectra using potassium bromide discs, at College of Education for pure science Ibn- Al- Haitham/ Baghdad University. U.V–Vis spectrophotometer SP-3000 plus type Optima, in the range (200– 1100 nm) was used to obtain the electronic spectra of the compounds, with concentration (10⁻³) mole L⁻¹ of samples in DMSO at 25°C using quartz cell of (1.0) cm length. Eutech 150 conductivity meter was used to obtain the molar conductivity of the complexes at (25 °C) for (10⁻³) M solutions of the samples in DMSO. Elemental microanalysis was performed on a (C.H.N) analyser, Eurovector EA 3000 A at Al–al Bayt University, Jordan. "H-NMR Spectra for the ligand and Cd complex were recorded in DMSO-d₆ using Brucker, model: ultra-shield 300 MHz apparatuses, origin: Switzerland and are reported in ppm (s), at Al –al Bayt University, Jordan. PerkinElmer instruments by SII, Diamond TG/DTA, Thermogravimetric/ Differential thermal analyser was used to study the thermal properties of the compounds. The fluorometric analysis was carried out using Perkin ElmerLS-55 spectrofluorometric at room temperature (298 K), the last two measurements were achieved at College of Education for pure science Ibn- Al- Haitham/ Baghdad University.

Synthesis of the precursor 2-(2-(naphthalen-5-yl)diazenyl)-4-amino-3-hydroxynaphthalene-1-sulfonic acid

He compound was synthesized as described in literature [7, 8].1-naphthyl amine (1.43g, 10.00 mmol), in water (10 ml) and concentrated hydrochloric acid (2.62 ml, 30.00 mmol) was mixed and stirred until a clear solution was obtained. The mixture cooled to 0– 5°C and sodium nitrite solution (0.76g, 10.00 mmol) in water (5 ml) were then added dropwise, keeping the temperature below 5°C. For an additional 1h (in an ice bath) the resulting mixture was stirred. After that a little urea was added and was buffered using solid sodium acetate (solution 1). (2.4g, 10.00 mmol) of (1-Amino-2-naphtol-4-sulfonic acid) was dissolved in 10 ml aqueous NaOH (10 mmol) solution, then cooled to 0-5°C using ice bath (solution 2). This solution was then gradually added as portions to cooled solution 1, the mixture resulted was continually stirred for 2 hrs. at 0-5°C,., the crude precipitate was filtered by acidification and washed by cold water several times. Yield 71%, m.p (292 °C dec.).
Synthesis of the ligand [H$_2$L]

To (3.00 g, 7.63 mmol) of the precursor (W) dissolved in 25 ml of methanol, it was added (0.93 g, 7.63 mmol) of salicyldehyde in 10 ml of methanol with 3-4 drops of glacial acetic acid, refluxed for 2 hrs., cooled at room temperature for 15 minutes, filtered off, the precipitate was collected with 10ml of cold dry methanol. Yield 57%, m.p (250°C).

Synthesis of the complex K[Cr(L)$_2$].H$_2$O

The complex was prepared by adding (0.14 g, 2.41 mmol) of potassium hydroxide dissolved in 10 ml ethanol with stirring and heating to a solution of (0.60 g, 1.21 mmol) of chromium (III) chloride hexahydrate dissolved in 10 ml ethanol was added to ligand solution. The resulting mixture was refluxed for 2 hrs. Washed with ethanol and recrystallized. Yield 54%, Dec. (over 320 °C).

Synthesized of K$_2$[Co(L)$_2$]H$_2$O, K$_2$[Ni(L)$_2$]H$_2$O and K$_2$[Cd(L)$_2$]H$_2$O

A similar method to that mentioned in preparation of Cr$^{III}$ complex was used to prepare the complexes of H$_2$L with Co$^{II}$, Ni$^{II}$, and Cd$^{II}$ ions; Table (1) shows the reactant quantity of the complexes and their physical properties.

Biological activity

It was studied the antibacterial activity of the prepared ligand [H$_2$L] and its complexes using the agar diffusion technique. Staphylococcus aureus, Escherichia coli, Psedomonas aeruginosa, Bacillus subtilis and Candida albicans were the organism tested in this study. The agar media were inoculated with test organisms and a solution of the tested compound (100 µg/ml) was placed separately in (6 mm diameter)cups in the agar medium. The inhibition zones were measured after 24 hours’ incubation, alone solution of DMSO studied and showed no activity against organisms.

Results and discussion

New acyclic tridentate ligand type ONO donor atoms have been synthesized. The ligand H$_2$L was synthesized by the condensation reaction of precursor [w] with salycaldihyde in 1:1 molar ratio using methanol as a solvent according to the general route shown in Scheme (1). The ligand contains two labile protons H$_2$L, by removing these protons an anionic (-2) tridentate system is formed.

FT-IR spectra

I.R. spectrum for ligand H$_2$L. Figure (1) displayed a broad band at (3365.8) cm$^{-1}$ may due to interference of the phenolic and sulphonic OH groups [9,10,11]. On the other hand, the spectrum displayed band of weak intensity at (2972.3) cm$^{-1}$, this band may due to intramolecular hydrogen bonding (OH…N) group [12]. The bands at 1624, (1155.3– 1124.5) cm$^{-1}$ can be attributed to stretching of (C=N) imine and (C–N) groups respectively. The disappearance of amine (NH$_2$) band in the spectrum, and appearance of imine (C=N) band, which reveals the formation of Schiff base ligand [13,14,15]. In the spectra of the complexes the imine (C=N) band shifted to lower frequency and appeared at (1616.2-1585.4) cm$^{-1}$ for complexes of Cr$^{III}$, Co$^{II}$, Ni$^{II}$ and Cd$^{II}$ ions respectively. The shift to lower frequency can be attributed to the participation of the iminic nitrogen atom in the coordination to the metal [16,17,18]. This can be explained by the movement of electrons from the iminic nitrogen to

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the metal ion (delocalisation of metal electron density into the ligand π-system) [19,20] as a result of coordination process. The ligand spectrum reveals a band at (1489.1) cm⁻¹ may refer to (N=N) azo group [21], this band, in the infrared spectra of the complexes, did not show any wave number shift and appeared at (1489.1-1485.2) cm⁻¹ for complexes of CrIII, CoII, NiII and CdII ions respectively, which may be explained by non-participation of azo nitrogen atoms in complex formation [22]. The orientation of azomethine and azo groups on azo Schiff base ligands are in such a way that coordination of the two groups to the metal ion is not possible, thus, the azo group is left free and uncoordinated while the azomethine group preferentially coordinated to the metal ion [16, 23, 24,25]. On the other hand the two bands at (1384.9 and 1340.0) cm⁻¹ referred to υ(C–O) of salycaldehyde and 1-amino-2-naphtol-4-sulfonic acid in the free ligand have been shifted to lower frequency and appeared at (1327.0-1386.8) cm⁻¹ for complexes CrIII, CoII, NiII and CdII ions respectively. This shift confirming the coordination of oxygen atoms of the two phenolic groups to the metal [26,27]. The presence of adsorbed water molecules in the complexes structure can be revealed by a broad band at (3421.7-3452.6) cm⁻¹ which indicates OH group of water molecules [2]. Finally, the spectra showed new bands at (518.7-567.2), (466.8-534.9) and (424.5-486.6) cm⁻¹ can be referred to υ(M–N), υ(M–O)car. and υ(M–O) naphth for complexes CrIII, CoII, NiII and CdII ions respectively. These new bands confirmed the coordination of the ligand to the metal ion through imin nitrogen and phenolic oxygen atoms. These results are supported by several reports [28, 29]. Finally, the spectrum of the ligand showed bands at (1278.8) cm⁻¹ can be attributed to the υasyn(SO3–H) and υsym(SO3–H) [30]. The characteristic bands are shown in Table (2).

U.V-Vis spectra

The (U.V-Vis) spectrum for H₂L, Figure (2), Shows bands of shortest wave length presenting at (245,260) nm may assigned to π–π* transition of the aromatic rings of azo-linked Schiff base ligand [2]. The band at 300 nm may refer to the imine n–π* transition and this absorption may belong to the keto amine quinoid tautom form of the ligand [31,32]. Finally the band at 420nm in the ligand spectrum may be attributed to the azo group (N=N)[11]. In each case the spectrum showed intense peaks in the (U.V) region at (245-290 nm) for CrIII, CoII, NiII and CdII complexes can be assigned to π–π* transition of the aromatic rings [2]. While the band at (305nm) in the free ligand shifted to longer wave lengths in the complexes and appeared at (315-360 nm) for complexes [CrIII, CoII, NiII and CdII] the shift may be resulted from the coordination process, confirming the imine nitrogen participation in coordination to the metal atom [33]. The N=N band of the free ligand at 420 did not shift in the corresponding metal complexes which reveals that the diazo group didn’t participate in complex formation, therefore it was concluded from the electronic spectra that the azo-linked Schiff base ligand coordinated to the metal atom through the carbaldehyic and naphtholic oxygen beside the imine nitrogen [2].

Finally, the bands in the visible region can be related with d-d transitions. The CrIII complex shows a band at 626nm assignable to 4A₂g→4T₁g(p) suggesting distorted octahedral geometry around CrIII ion [34,35,36]. The CoII complex shows a band at 650 nm and 710nm assignable to 4T₁g→4T₁g(p) and 4T₁g→4A₂g(F) suggesting distorted octahedral geometry around CoII ion [34,35,36,37]. The NiII complex shows a band at 510nmassignable to 3A₂g→ 3T₁g suggesting distorted octahedral geometry around NiII ion. The Cd (II) metal ion of this complex belongs to d⁴⁰ system and these metals do not have (d–d) transition. The octahedral geometry was proposed around Cd(II) ion. The characteristic peaks are summarized of the ligands and complexes in Table (3). The molar conductance of the complexes in (DMSO) is summarized in Table (3). From the above data, the following formula was proposed for Cr complex: K[M(L)₂]. H₂O, while Co, Ni and Cd complexes have the K₂[M(L)₂].H₂O formula.

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$^1$H-NMR

The $^1$H-NMR spectrum of $\text{H}_2\text{L}$ is shown in Figure (3), the spectrum showed a signal at ($\delta=$9.15 ppm) may be due to OH proton of sulfonic acid group [38]. The multiplet chemical shifts at ($\delta=7.04$–$8.68$ ppm) range could be due to protons of aromatic rings [2]. The sharp signal at chemical shift ($\delta=8.95$ ppm) can be attributed to the proton of the azomethine group (N=C–H) [37]. Keto hydrazone tautomer for the prepared ligand confirmed by the small chemical shifts of the NH proton of azo group which observed at the range ($\delta=3.40$–$4.45$ ppm) [22]. The broad signal at the range ($\delta=4.90$–$5.90$ ppm) may be considered to the OH proton in the salycaldehyde ring, because of intramolecular hydrogen bonding with the nitrogen atom on the naphthalene ring [2]. The naphtholic OH proton chemical shift were shown around ($\delta=10.30$ ppm) due to deprotonation by KOH before complex formation. The sharp signal at chemical shift ($\delta=9.00$ ppm) can be due to the proton of the azomethine (N=C–H) group. The $^{13}$C-NMR spectrum of $\text{H}_2\text{L}$, Figure (4) in DMSO–$d_6$ solvent shows the multiplet chemical shifts at ($\delta=118.8$–$129.7$ ppm) range could be assignable to C–C aromatic. The chemical shifts at the range ($\delta=136.6$–$145.2$ ppm) can be attributed to C–S, C–O, C–N and C–C groups. The chemical shift at the range ($\delta=158$–$167$ ppm) can be attributed to C=C of aromatic rings. The chemical shift at ($\delta=173.0$ ppm) can be attributed to the azomethine group C=N. The carbonyl group C=O resulted from the tautomerization in the azo-linked Schiff base compounds was observed around ($\delta=193$ ppm) [40].

Thermal analysis

Azo-linked Schiff base ligands and their metal complexes were tested by thermogravimetric analysis in the (50.0–500.0) °C temperature range to explain the thermal decomposition process. The adsorbed water molecule lost from all the complexes at the range (92–100) °C. The thermograph of the tested complex show in Figure (9). Comparison between the ligand and its complexes reveals that the complexes were more thermally stable [2,41].

Biological activity

The biological activity of the ligand $\text{H}_2\text{L}$ and its complexes were studied by using inhibition method [39,40,41,42] for four types of pathogenic bacteria and Candida albicans fungi. Two kinds of bacteria were gram positive staphylococcus aureu and Bacillus subtilis, the other two were gram negative escherichiacoli and psedomonas Aeruginosa. The ligand shows good inhibition diameter to escherichiacoli, while Cr complex was very active against psedomonas Aeruginosa. Mn complex shows inhibition effect against staphylococcus aureu. In general, the complexes were more active than the ligand under similar conditions due to that the polarity of the metal ion considerably reduces as a result of the chelation, because the donor groups partially sharing the positive charge of the metal. Electron delocalization over the whole chelate ring may increase the lipophilic character of the metal atom, which as a result, favours its permeation through the lipid layer of the cell membrane [43]. The compounds didn’t show any antifungal activity against candida albicans. The measured zones of inhibition against the growth of different microorganisms are listed in Table (4).

Fluorescence studies

It can be seen in Table 1 that generally; the intensities of the ligand are higher than its metal complexes. When the ligand is coordinated to metal, the fluorescence intensity decreased,

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because of quenching effect of the transition metal, when bounded to the ligand during coordination, the charge transfer transition from the ligand to metal ions occurred. In the complexes spectra, the fluorescence peak was shifted to higher wavelength in Cd complex, lower wavelength in Co complex compared to the ligand and no change observed in Cr and Ni complex. The ligand emitted at 638 nm when excited at 624, while the Cr complex fluoresced at 638 nm when excited at 577 nm, Co complex emitted at lower wavelength, 563 nm when excited at 498 nm, finally Cd complex emitted at 657 nm when excited at 630nm [5,6].

Conclusions

From the above data, the following formula was proposed for Cr complex: K[Cr(L)2]. H2O, while Co, Ni and Cd complexes have the K2[M(L)2].H2O formula. Also, it was concluded that the azo-linked Schiff base ligand coordinated to the metal atom through the salicylic and naphtholic oxygen beside the imine nitrogen atoms It was revealed from the biological activity studies that the complexes are more active than the ligand under similar experimental conditions. Fluorescence studies showed that the intensity of the ligand is higher than its metal complexes, also in the complexes spectra the fluorescence peak was shifted to higher wavelength in Cd complex, lower wavelength in Co complex compared to the ligand and no change observed for Cr and Ni complexes.

References


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### Table (1): Reactant quantity of the prepared H\(_2\)L complexes and their some physical properties

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<th>Empirical formula</th>
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<th>Wt of metal salt (g)</th>
<th>Wt of product (g)</th>
<th>Yield %</th>
<th>Microanalysis found (calc) %</th>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>M%</td>
</tr>
<tr>
<td>H(_2)L</td>
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<td>250</td>
<td>-</td>
<td>-</td>
<td>57</td>
<td>65.10</td>
</tr>
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<td>65.18</td>
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<tr>
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<td>0.36</td>
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<td>0.32</td>
<td>46</td>
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<td>260 Dec.</td>
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<td>0.36</td>
<td>52</td>
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### Table (2) Infrared spectral data (wave number \(\nu\) \(\text{cm}^{-1}\)) of the ligand and complexes

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<th>(\nu(\text{OH}))</th>
<th>(\nu(\text{C=N}))</th>
<th>(\nu(\text{N=N}))</th>
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<th>(\nu(\text{M–N}))</th>
<th>(\nu(M–O)_{\text{as}})</th>
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<td>K[Cr(L)(_2)].H(_2)O</td>
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<td>1616.2</td>
<td>1489.1</td>
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https://doi.org/10.30526/30.3.1607
Table (3): Electronic spectral data of the ligands and complexes

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Table (4): Biological activity of ligand and complexes

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<th>Staphylococcus aureus (G+)</th>
<th>Escherichia coli (G-)</th>
<th>Pseudomonas aeruginosa (G-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2L$-</td>
<td>-</td>
<td>+++</td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>$K_2[Cr(L)_2]_2H_2O$</td>
<td>+</td>
<td>+</td>
<td></td>
<td>+++</td>
</tr>
<tr>
<td>$K_2[Co(L)_2]_2H_2O$</td>
<td>-</td>
<td>+++</td>
<td></td>
<td>+++</td>
</tr>
<tr>
<td>$K_2[Ni(L)_2]_2H_2O$</td>
<td>+++</td>
<td>-</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>$K_2[Cd(L)_2]_2H_2O$</td>
<td>+++</td>
<td>-</td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>

(-) = No inhibition = inactive,  (+) = (2-4) mm = active,  (++) = (5-7) mm = more active,  (+++) = (8-13) mm = highly active: 6-10, (+++): 11-15, (+++++): 16-20 mm

**Figure (1):** FT-IR spectrum of the ligand [H$_2$L]

**Figure (2):** FT-IR spectrum of K[Cr(L)$_2$].H$_2$O Complex
**Figure (3):** FT-IR spectrum of K$_2$[Cd(L)$_2$].H$_2$O Complex

**Figure (4):** Electronic spectrum of the ligand [H$_2$L]

**Figure (5):** Electronic spectrum of the K[Co(L)$_2$].H$_2$O Complex

https://doi.org/10.30526/30.3.1607
Figure (6): $^1$H-NMR spectrum of the ligand [H$_2$L]

Figure (7): $^{13}$C-NMR spectrum of the ligand [H$_2$L]

Figure (8): $^1$H-NMR spectrum of K$_2$[Cd(L)$_2$].H$_2$O Complex
Figure (9): Thermograph of $K_2[Fe(L)_2].H_2O$

Figure (10): Emission spectra of the ligand

Figure (11): Emission spectra of $K_2[Co(L)_2].H_2O$
Figure (12): Emission spectra of $\text{K}_2[\text{Cd(L)}].\text{H}_2\text{O}$

Scheme (1): Synthesize route of the ligand ($\text{H}_2\text{L}$)
Scheme (2): Synthesize route of the complexes

Where:
- M = Co, Ni and Cd : n = 2
- M = Cr : n = 2