Metal Ions Uptake Using Schiff Bases Derived from Salicylaldehyde and Appropriate Amino Compounds

Abdunnaser Etorki, Salah Ben-Saber, M. El-ajaily and Abdussalam Maihub
1. Chemistry Department, Faculty of Science, Tripoli University, Tripoli 13203, Libya
2. Pharmacy Chemistry Department, Faculty of Pharmacy, Tripoli University, Tripoli 13645, Libya
3. Chemistry Department, Faculty of Science, Benghazi University, Benghazi 1308, Libya

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Abstract: The uptake properties of the Schiff bases derived from salicylaldehyde and 4-dimethylaminobenzaldehyde, 1,8-naphthalenediamine, or 2-aminobenzoyl alcohol have been studied. These Schiff bases synthesised, characterized and subjected to complexation reactions. A series of transition and heavy metals such as Zinc (II), Cobalt (II), Lead (II), cadmium et al., formed stable complexes with the obtained Schiff bases. The Schiff bases and their complexes, for comparison, have been studied by simple conventional techniques. Various analytical parameters such as: Melting points, pH values, solubility in different solvents, infrared spectroscopy, electrical conductivity and atomic absorption spectroscopy were used. Moreover, the only Schiff base obtained from salicylaldehyde and 1,8-naphthalenediamine is considered and was subjected and evaluated for its influence on the metal ions uptake behaviour. The condition and coordination of the sites and metal ions properties agreed with the data obtained from the tools used in the analysis. With this end, a number of compounds formulated, and such Schiff base found to possess the uptake properties. The attempts have been made here to find out the best uptake properties.

Key words: Salicylaldehyde, 1,8-naphthalenediamine, 2-aminobenzoyl alcohol, Schiff bases, coordination Zinc, lead, cadmium, uptake, complexes.

1. Introduction

In the recent years, Schiff bases are widely used in the formulating of various type of application, in medical, industrial, agricultural, et al. fields. Recently, multidentate ligand introduced in different types of complexation to modern physicochemical applications such as catalytic, optical material, dyes, luminophores as well as polymer with conductance properties to biochemically relevant studies of the Schiff bases and their complexes in the points of view such as biologically active substances, antitumor, antiviral and antifungal have given a great deal of attention. Because of these applications, synthesis of new Schiff bases and their metal complexes are still the aim of many recent investigations [1-9].

Most of the preparation of Schiff bases or their complexes is strait forward and few problems might raised. One way of overcoming the problems and to improve the techniques of analysis and facilitate the application, is to introduce a new chemical agents, which are more specific in chemical activity of the target designed, special in the application carried on traces level of various ions.

Lead and cadmium are listed by the US EPA (Environmental Protection Agency) among the 129 priority pollutants [10]. Lead and cadmium are also listed among the 25 hazardous substances thought to pose the most significant potential threat to human health at priority superfund sites [11]. Lead and cadmium are listed by the EPA as class B2 and class B1...
carcinogens, respectively [12]. Most of the lead and cadmium in inner city soils and waters come from landfills and leaded paints. Landfills contain waste lead and cadmium from mining, inorganic chemicals, nonferrous metals and ammunition manufacturing, porcelain, enameling, gum and wood chemicals, paint and ink formulation and from other industrial activities such as butter production and metal smelting [13].

Humans absorb lead and cadmium in small amounts from food, water and air. Lead (II) ions inhibit a select group of enzymes, including thiol-dependent enzymes involved in heme synthesis and mitochondrial energetic [14]. Many metal ions (i.e., Zn, Pb, Cd, Hg, etc.) are extremely toxic. The toxicity depends on the chemical state of the ions. The analytical techniques with sufficient selectivity and sensitivity can be improved and introduced to determine the traces of metal ions [15]. The Schiff base from 2-aminophenol and 4-dimethylaminobenzaldehyde which considered to be bidentate as well as the complexes with Iron (III) and Cobalt (II) have been prepared and investigated [16].

The tridentate Schiff bases ligands which prepared from salicylaldehyde and 2-aminophenol, also investigated and engaged in the isolation of Mn (III) ion as a complex [17]. The bidentate Schiff base from 4-dimethylaminobenzaldehyde and 2-aminobenzoic acid found to be capable of forming complexes with different metal cations, regardless to the metal ion charge [18].

The capability of Schiff bases for coordination gives the advantages to form complexes, the shad of light on the natural of these ligands, the constituents of sites of coordination and the metal ion properties. The complexes of cations: such as Co (II), Ni (II) and Cu (II), Mn (II) with Schiff base derived from 2-aminophenol or 2-aminobenzoic acid with salicylaldehyde have been studied in terms of analytical chemistry from the point of gravimetry, potentiometry, molar conductance, infrared analysis and their solubility in chemical solvent. The nature of the complexes are justified to be electrolytic or non electrolytic. Most salicylaldehyde produced Schiff bases are of important significant. That can be coordinated to various metal ions whither to be bi, tri, tetra, etc. [19-22].

In this research, the authors wish to introduce and to study the Schiff base complexation in parallel with the new applications for pre concentration and metal ion uptake in ppm levels of popular transition and heavy metal ions, such as Zn, Cd and Pb in aqueous solutions, by the formation of relatively strong complexes between the ligand and the metal ions, then to be determined by AAS (atomic absorption spectrometry).

2. Experimental

2.1 Chemicals, Reagents and Apparatus

Salicylaldehyde from (Breck lan scientific supplies, UK), lead nitrate and zinc acetate from (Merck), cadmium nitrate from (Farmitalia carlo erba-Milano), 1,8-Naphthalenediamine was from (Riedle-de haen). Double distilled water. The zinc, lead and cadmium ions determination was carried out on Philips-Pu/9400x AAS (atomic absorption spectrometer).

2.2 The Preparation of the Schiff Base (L)

The Schiff base used was prepared by mixing an ethanolic solution (25 mL) of salicylaldehyde (0.05 mol = 6.106 g) with 1,8-Naphthalenediamine (0.05 mol = 7.91 g). The ethanolic solution of the aldehyde was always added slowly to the amine solution. The mixture then refluxed for 2 h. If the Schiff base did not separate, a few drops of NH₄OH or 10% NaOH solution should be added and then put in the container of the reaction containing ice. The obtained precipitate was collected by filtration through Buchner funnel, washed and recrystallized using hot ethanol and then dried at room temperature, then putted in desiccators over anhydrous CaCl₂. The dried Schiff base is ready for analysis. The yield was 65%.
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![Schiff base](image)

**Fig. 1 Schiff base 2-{[(E)-[(8-aminonaphthalen-1-yl)imino]methyl}phenol.**

2.3 The Preparation of the Complexes

The Schiff base complexes were prepared by mixing 0.005 mol (1.097, 1.54, 1.65 g) of 30 mL of saturated ethanolic solution of the metal salts (Zn(CH₃COOH)₂·2H₂O, Cd(NO₃)₂·4H₂O, Pb(NO₃)₂) respectively with the same ratio of the Schiff base (1.31 g) in the same volume of the same solvent. The mixture was refluxed for 2 h. Meanwhile, few drops of NH₄OH or 10% NaOH solution were added slowly. The complex will be separated on standing. Then the prepared solids filtrated and washed several times with hot ethanol until the filtrate becomes colorless. The complex then dried in desiccators over anhydrous CaCl₂. The dried complexes are ready for analysis. The yield was 50%. The chemical structure of the Schiff base is shown in Fig. 1.

2.4 Metal Ion Uptake Techniques

The authors have prepared a series of standard aqueous solutions of metal ions (Zn(CH₃COO)₂·2H₂O, Cd(NO₃)₂·4H₂O, Pb(NO₃)₂) in varied concentrations in ppm (20, 40, 60 ppm), then diluted and measured by the atomic absorption spectrometer. The data translated are shown in Figs. 2-4.

0.1 g of the ligand prepared from salicylaldehyde and 1,8-naphthalenediamine were treated with 20 mL of aqueous solutions of the metal ions in the previous concentrations. A few drops of dilute nitric acid were added to the mixtures. The mixtures were putted on a shaker for 45 min, after that the authors filtrated the mixtures, and the filtrate solutions were collected and metal ions determined by the AAS. The solid samples on the filter paper were dried in laboratory oven at 100 °C and kept for electrical conductivity.

2.5 Electrical Conductivity

The solid samples that were collected from the filter paper were compressed into tablets 1 mm thickness and 1.227 cm² region. The solid samples were sprightly loaded between two electrodes, DC-potential of 20 V was applied on the samples to which standard resistance was collected in series. The potential on standard resistance was measured using Metra. Hit (Germany). The temperature was stable at laboratory temperature. The obtained data are shown in the results.

3. Results and Discussion

3.1 Physical Properties

<table>
<thead>
<tr>
<th>Schiff base</th>
<th>M. Wt.</th>
<th>C %</th>
<th>H %</th>
<th>N %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complexes</td>
<td></td>
<td>Calc</td>
<td>Found</td>
<td>Calc</td>
</tr>
<tr>
<td>LH</td>
<td>262.2</td>
<td>77.86</td>
<td>76.91</td>
<td>5.43</td>
</tr>
<tr>
<td>ZnL(OH)(H₂O)</td>
<td>361.4</td>
<td>56.45</td>
<td>55.26</td>
<td>4.43</td>
</tr>
<tr>
<td>CdL(OH)(H₂O)</td>
<td>408.4</td>
<td>49.95</td>
<td>49.85</td>
<td>3.92</td>
</tr>
<tr>
<td>PbL(OH)(H₂O)</td>
<td>503.2</td>
<td>40.54</td>
<td>40.40</td>
<td>3.18</td>
</tr>
</tbody>
</table>

The physical properties such as melting point, solubility and color are summarized in Table 1. The elemental analysis of the Schiff base and its complexes show the formation of 1:1 ratio which agreed with the theoretical values. The yields were quiet low (40%-65%). The ligands were insoluble in water and
ethanol, but soluble in THF and methanol as listed in Table 2. All the ligand and the metal complexes were stable at room temperature and non hygroscopic.

3.2 IR (Infrared Spectra)

The addition of basic solution to the mixture in order to proceed the reaction to form complexes, that confirm the deprotonation of phenolic proton, so that -O group involve in the coordination. The most probable chemical structure of the complexes, that contain ν (M-O) and ν (C=N) as sites of coordination only, and excluding ν (M-NH) from the coordination. The infrared almost in all complexes confirm such expectation [18]. The colors and spectra of the ligands show characteristic bands are summarized in Table 3.

The band at 3,300-3,500 cm⁻¹ is due to ν (N-H) and the band at 2,853-2,962 cm⁻¹ assigned to ν (C-H) [23]. A strong band in the region 1,586-1,625 cm⁻¹ in the free ligands assigned to ν (C=N) exhibits ± 5-10 cm⁻¹ shift. The spectra of the complexes indicating coordination through the azomethine nitrogen of the Schiff base and shifting of the band of ν (C=N) in the complexes as compared to the free ligand, is due to reduction of double bond character of the carbon-nitrogen bond of the azomethine group. Since ν (O-H) disappeared and the ν (M-N) and ν (M-O) bonds formed, this is further supported by the presence of bands in the region 617 cm⁻¹ [24].

The donor ability of the Schiff bases to metal ions depended on the type of the position of functional group to azomethine group. There are guidelines in the spectra of Schiff bases or in the complexes, which enable to achieve this goal. The peaks concerning (δ (OH), (δ (NH), ν (C=N), ν (M-O) and ν (M-N) indicate the differences in coordination. The remaining peaks at 3,054, 3,050 and 3,057 cm⁻¹ are consistent with the ν (NH) and confirm to be not engaged in the coordination in all complexes. No evidence of having coordination of NH₂ and C=N in the same time, if that is so, δ (OH) should be appeared. Also, no coordination of NH₂ and OH in the same time, if that is so, ν (C=N), should be without change. No bands present in the region of 420-460 cm⁻¹ which correspond to ν (M-NH) vibration.

3.3 Electrical Conductivity

The values of the electrical conductivity of the solid samples, shown in Table 4, were in the range of $2.7 \times 10^{18}-6.39 \times 10^{7}$ ohm⁻¹·cm⁻¹·mol⁻¹, confirming the non conductive nature.

<table>
<thead>
<tr>
<th>Schiff base/complexes</th>
<th>MP (°C)</th>
<th>pH</th>
<th>H₂O</th>
<th>C₂H₅OH</th>
<th>(C₂H₅)₂O</th>
<th>CHCl₃</th>
<th>THF</th>
<th>CH₃OH/Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>LH</td>
<td>216</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>ZnLXY</td>
<td>&gt; 230 d</td>
<td>&gt; 6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>CdLXY</td>
<td>&gt; 235 d</td>
<td>&gt; 6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>PbLXY</td>
<td>&gt; 233 d</td>
<td>&gt; 6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Schiff Base/complexes</th>
<th>M. Wt (g/mol)</th>
<th>IR spectra (cm⁻¹)</th>
<th>Colors</th>
</tr>
</thead>
<tbody>
<tr>
<td>LH</td>
<td>262</td>
<td>3,316,88, 1,598,33, 1,484,19, 1,416,85, 1,376,27, 1,234,44, 1,234,44, 1,165,48, 1,165,48, 1,105,57, 1,035,01, 967,99, 815,71, 752,04, 632,16.</td>
<td>Dark grey</td>
</tr>
<tr>
<td>ZnLXY</td>
<td>361.4</td>
<td>3,054,02, 1,582,79, 1,471,29, 1,400,32, 1,372,94, 1,300,84, 1,200,64, 1,041,61, 926,24, 822,37, 753,56, 671,73, 617,41</td>
<td>Black</td>
</tr>
<tr>
<td>CdLXY</td>
<td>408.4</td>
<td>3,221,84, 1,538,77, 1,455,03, 1,280,87, 1,040, 920,79, 820,67, 751,50</td>
<td>Black</td>
</tr>
<tr>
<td>PbLXY</td>
<td>503.2</td>
<td>3,057,56, 1,557,68, 1,477,25, 1,311,62, 1,243,63, 1,163,16, 1,040,79, 821,72,750,1, 688,26</td>
<td>Black</td>
</tr>
</tbody>
</table>

LH = Free Schiff base, M. Wt = molecular weight, IR = infrared, X = hydroxide group, Y = water molecule.
3.4 The Metal Ion Uptake of Chelating Ligand (L)

The relative position of the three coordinating site in the Schiff base eases the accessibility of such sites by the metal ions, and this is one of the aspects influencing the metal ion uptake behavior of the ligand. The concentration of the metal ions in the aqueous solutions (the filtrate solutions) after, they treated with the ligand and quantitative determined by the atomic absorption spectrometer can be preformed. From the data, the percentage of the metal ion uptake (removal percentage) and the adsorption capacity were calculated using the following relationships:

\[
\text{Removal \%} = \frac{C_o - C_f}{C_o} \times 100 \quad Q_{eqb} = \frac{(C_o - C_{eqb}) \times 10^{-2}}{0.1 \times 10^{3}}
\]

where:
- \(C_o\) is metal ion concentration in the initial solution in ppm;
- \(C_f\) is metal ion concentration in the filtrate in ppm;
- \(C_{eqb}\) is metal ion concentration at equilibrium.

The standard solutions of the ions used and their absorbance are shown in Figs. 2-4. It was observed that with an increase in the concentration of Cd (II) ion the extent of removal percentage increased up to certain stage, beyond which there was no further increase in the Cd (II) ion removal percentage shown in Fig. 2. The ligand shows decreasing of removal percentage when the Zn (II) ion increased up also shown in Fig. 6a. The ligand did not work with Pb (II) ion Fig. 7.

4. Conclusions

The complexation of series divalent metal ions with Schiff base containing substituents of various position of sites has been evaluated as shown in Fig. 9. Since the conformational structure of the Schiff bases is planar and completely conjugated double bonds. That agreed with the only chemical structure of the complexes obtained. The uptake behavior of the Schiff base was measured and estimated. It was observed that with an increase in the concentration of Cd (II) ion the extent of removal percentage increased up to certain stage, beyond which there was no further increase in the Cd (II) removal percentage (Figs. 5 and 6). The ligand

<table>
<thead>
<tr>
<th>Solid sample</th>
<th>Zn (II) solutions</th>
<th>Cd (II) solutions</th>
<th>Pb (II) solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L+20 ppm L+40 ppm L+60 ppm</td>
<td>L+20 ppm L+40 ppm L+60 ppm</td>
<td>L+20 ppm L+40 ppm L+60 ppm</td>
</tr>
<tr>
<td>Volt/mV</td>
<td>0.07</td>
<td>0.35</td>
<td>0.15</td>
</tr>
<tr>
<td>Conductivity</td>
<td>2.698</td>
<td>1.462</td>
<td>6.394</td>
</tr>
</tbody>
</table>

Table 4 The voltage and the calculated electrical conductivity $10^{-7}$ ohm$^{-1}$·cm$^{-1}$ of the solid samples which filtrated from the aqueous solutions.

![Linear Regression for Data1_B](image)

Fig. 2 The standard solutions of Cd (II) and their absorbance values.
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Fig. 3  The standard solutions of Zn (II) and their absorbance values.

Fig. 4  The standard solutions of Pb (II) and their absorbance values.

Fig. 5  The relation between concentration of Cd (II) and the ligand removal percentage.

Fig. 6  The relation between adsorption capacity and the concentration for Cd (II).
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Fig. 7 The relation between concentration of Zn (II) and the ligand removal percentage.

Fig. 8 The relation between adsorption capacity and the concentration for Zn (II).

Fig. 9 The expected chemical structures of the complexes and the appropriate sites of coordination X, Y = OH− and H2O molecules.

shows decreasing of removal percentage when the Zn (II) ion increased up (Figs. 7 and 8). The ligand did not work well with Pb (II) ion.

References