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Schiff Base Derived from p-Nitrobenzaldehyde and 1,8-Naphthalenediamine Precursor in Metal Ions Uptake

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Abstract: The characteristic coordination behavior of Schiff bases synthesized from carbonyl and primary amine compounds have been investigated and studied in different field, such as their chemistry and biological activity. Few numbers of Schiff bases were implicated in analytical aspect such as metal uptake techniques. The Schiff base and may its chelates derived from p-nitrobenzaldehyde and 1,8-naphthalenediamine were synthesized and characterized by different analytical tools. The chemical structures have been elucidated by physiochemical methods. The site of the coordination with metal ion gave this Schiff base the advantage to be used in uptake techniques, either as batch or column. The uptake studies preformed and analyzed with respect to justification of the site of coordination.

Key words: Schiff bases, chelates, physiochemical, p-nitrobenzaldehyde, 1,8-naphthalenediamine, coordination.

1. Introduction

Schiff base prepared from different aromatic ketones and aldehydes with amino compounds containing phenyl groups, spread in different directions of application. Schiff bases introduced to coordination as well to be a moiety and starting material to other chemical compounds or techniques. The simple and straightforward of synthesis gave this kind of compounds advantages of the applications. Salicylaldehyde, 2-aminobenzoic acid or 2-aminophenol as models compounds have been introduced in varieties of Schiff bases, and were studied because their activity in coordination. The azomethine group in all Schiff bases mainly dominates and influences the properties of the Schiff bases as the most sites in the Schiff base body [1].

The coordination capability of Schiff bases give them the advantages to interact with metals. In this aspect, the Schiff base considered as bidentate ligands. The characterization of the Schiff bases was facilitating by all modern tools and methods, in particular, elemental analysis, infrared and other physical methods when necessary. Heating aldehyde with primary amine in appropriate solvents, or even using microwave techniques will produce the corresponding Schiff base. The phenomena of coordination could be conjugated to the uptake techniques. Most of the transitional metal ions play a role in these reactions, because of their charge, size, electronic structure and ability to form coordinate molecules [2-4].

Schiff bases which have been synthesized, can be introduced to coordination reaction, specially, if they have either nitrogen or oxygen or sulfur atom or any unshared lone pair of electrons on atoms adjacent the

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azomethine group in order to form stable chelates with five or six membered rings. The formed chelates must gain appropriate geometry to be stable and to be handling in the chemical analysis. The electronic structures are justify the coordination numbers, as well as the geometry of coordination units [5].

The ratio of metal to ligands (M:L) in most chelates, plays a major factor and control. As long as there is limited concentration of the ligand, the chelates will be 1:1 ratio. However, increasing in ligand amount, lead to the increasing in the ratio, which produce 1:2 ratio. The increasing in the ratio controlled by the electronic structures of the metal ions and the type of the chemical geometry. Having nitro group (electron withdrawing) in para-position, and nitrogen as azomethine and as amino groups, that give the indication of the type of coordination appeared. The percentage of uptaking will be low because the influence of the nitro group, specially in para-position [6].

The chelates of $[ML(OH)_x(H_2O)_y]$ type, where M = Cd(II), Zn(II) or Pb(II), were characterized using the data from the elemental analysis, molar conductance, infrared and electronic spectra, magnetic susceptibility measurements and thermal analysis. These studies support the formation of the chelates between the metal ions and the Schiff bases. The Schiff bases derived from salicylaldehyde and 2-aminophenol or 2-aminobenzoic acid have been studied in terms of coordination chemistry using mostly the same tools as in the previous paragraph beside potentiometeric, molar conductance analysis and their solubility in different chemical solvents. The nature of the chelates can be judged to be electrolytic or non-electrolytic nature. Most nitrogen containing Schiff bases as well as salicylaldehyde containing Schiff bases produced, are of important significantance in their coordination or in their analytical and biological activity. The coordination with various metal ions whether as; bi, tri, tetra, etc. chelates can be obtained. The reactivity and the chemical structure of the Schiff bases give the shad of light on the natural of these ligands, the constituents of sites of coordination and the metal ion properties [7-10].

The metal ion uptake studies were done by both batch and column techniques. In the batch technique, a suspension of the resin on the metal solution of known volume and concentration was agitated for a definite period over hot plate/magnetic stirrer. The pH of the solution was adjusted using suitable buffer. The resin was filtered off, and thoroughly washed with deionized water. The metal ion concentrations in the filtrate and the washing were collected and then estimated following the proper method for the ions concerning. Dimethylglyoxime method can be used for Ni(II) and you can use Philips-Pu/9400x Atomic Absorption Spectrometer [11].

Our aims in this study to prepare a Schiff base derived from p-nitrobenzaldehyde and 1,8-naphthalenediamine which justified by its chelation with Zn(II), Cd(II) and Pb(II) ions to elucidate the capability of such Schiff base to have characteristic properties of metal uptake. However to calibrate percentage of up taking capability which were low because the influence of the nitro group [12].

2. Experiments

2.1 Chemicals, Reagents and Apparatus

All chemicals used were reagent grade. P-nitrobenzaldehyde and 1,8-naphthalenediamine from Riedle-dehaën. $Zn(CH_3CO_2)_2{\cdot}2H_2O$ and $Pb(NO_3)_2$ from E. Merck, $Cd(NO_3)_2{\cdot}4H_2O$ from Farmi Talia carlo Erba, Milano. Double distilled water was used. The elemental analysis, and Infrared spectra were carried out at South Valley University laboratories. The zinc, lead and cadmium ions determination was carried out on Philips-Pu/9400x Atomic Absorption Spectrometer. The conductivity carried out by using Metra. Hit-Germany and found to zero.

2.2 Preparation of Schiff Base

The Schiff base was prepared by mixing 60 mL hot ethanolic solution of p-nitrobenzaldehyde (1.51 g; 0.01 mol) with the same amount of hot ethanolic solution of 1,8-naphthalenediamine (1.58 g; 0.01 mol), stepwise. Few drops of dilute HCl were added to adjust the pH ≈ 4 and the obtained mixture then refluxed with stirring for 2 h. The obtained precipitate collected by filtration through Buchnner funnel, recrystallized from ethanol, and dried at room temperature in desiccators over anhydrous $CaCl_2$. The obtained yield was 65%. The product of the reaction in a ratio 1:1 gave a Schiff base with chemical structure in Fig. 1.

2.3 Metal Ion Uptake Techniques

Series of standard aqueous solutions of metal ions of Zn(II), Cd(II) and Pb(II) in their salts have been prepared in varied concentrations (20, 40 and 60 ppm), then diluted and measured by the atomic absorption spectrometer. The data translated into figures shown in Figs. 2-10. 0.10 g of the ligand (p-nitrobenzaldehyde and 1,8-naphthalenediamine) treated with 20 mL of aqueous solutions of previous concentrations. Few drops of dilute nitric acid added to the mixtures. The obtained mixtures were engaged on a shaker for 1 h and then filtrate the mixtures. The filtrate solutions were collected. The metal ions subjected for determination by the AAS (atomic absorption spectrometry). The solid samples on the filter paper were dried at 100 °C in the oven and kept for other analyses.

3. Results and Discussion

3.1 Physical Properties of the Schiff Base

The physical properties such as melting point is about 212 °C. The solubility has been preformed in different solvents and found to be soluble in hot ethanol and hot methanol and also soluble in THF (Tetrahydrofuran). However, it is not soluble in water and chloroform. The color was dark brown. The elemental analysis data of the Schiff base with molecular weight 291.3; were C; 70.20 (found = 70.50); *H* = 4.74 (found = 4.66) and *N* = 14.43 (found = 14.8) which confirm the 1:1 ratio [aldehyde:diamine]. The ligand was stable at room temperature and non-hygroscopic.

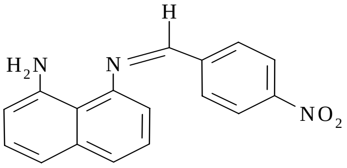


Fig. 1 The Schiff base structure.

3.2 Infrared Spectrum of the Schiff Base

The most proper chemical structure of the Schiff base, that contains ν (NH_2) and ν (C=N) groups as sites of coordination which have characteristic bands which can be summarized. The band at 3,364 cm^{-1} supports the existence of the mentioned amino group. A strong band assigned to ν (C=N) is confirmed by spectrum of the free ligand at 1,598.88 cm^{-1} [13, 14]. The existence the groups (NH_2 and C=N) in the Schiff base, is the most important side, which it count for the metal ions uptake Fig. 11.

3.3 Metal Ion Uptake Techniques of the Schiff Base

The relative position of the coordinating site in the Schiff base ease 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 [11]. The presence of nitro group reduces the chelation factor as deactivating group on the aromatic ring. The concentration of the metal ions in the aqueous solutions (the filtrate) 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:

$$\text{Removal } \% = \frac{C_o - C_f}{C_o} \times 100 \qquad (1)$$

$$Q_{eqb} = \frac{(C_o - C_{eqb}) \times 20}{0.1 \times 1000} \qquad (2)$$

where, C_o = metal ion conc. in the initial solution in ppm; C_{eqb} = metal ion conc. at equilibrium; C_f = metal ion conc. in the filtrate in ppm; Q_{eqb} = adsorption capacity (mg/g).

The standard solutions of the ions used and their absorbance are shown in Figs. 2-4. The ligand shows decreasing of removal percentage when the Zn(II) ion increased up shown in the Figs. 5 and 6. It was observed also, 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. The removal percentages shown in the Figs. 7 and 8. When the concentration of Pb(II) ion increases, the removal percentage decreases, which shown in the Figs. 9 and 10. As well, the comparison can be observed from the different figures concerning the uptake behavior of the three ions used.

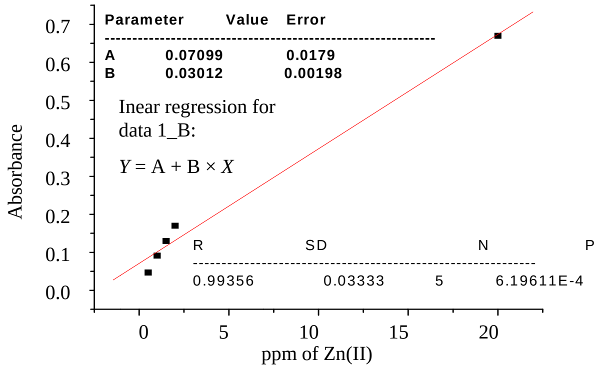


Fig. 2 **The standard solutions of Zn(II) and their absorbance values.**

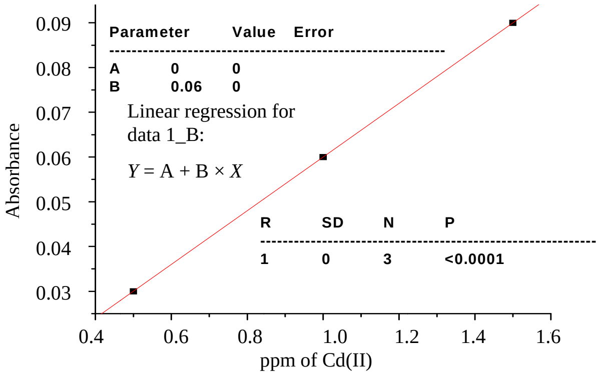


Fig. 3 **The standard solutions of Cd(II) and their absorbance values.**

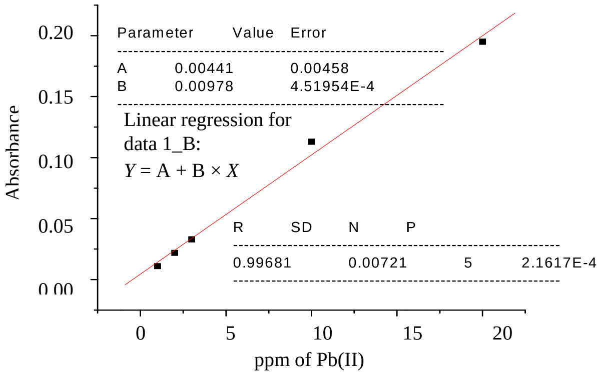


Fig. 4 **The standard solutions of Pb(II) and their absorbance values.**

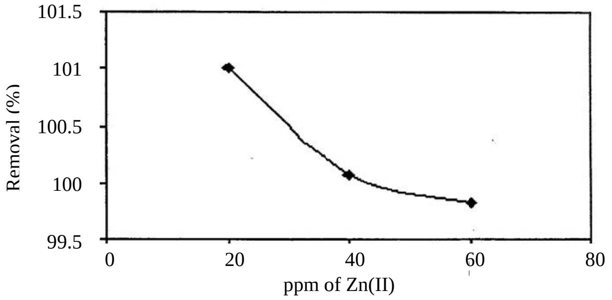


Fig. 5 **The relation between concentration of Zn(II) and the ligand removal (%).**

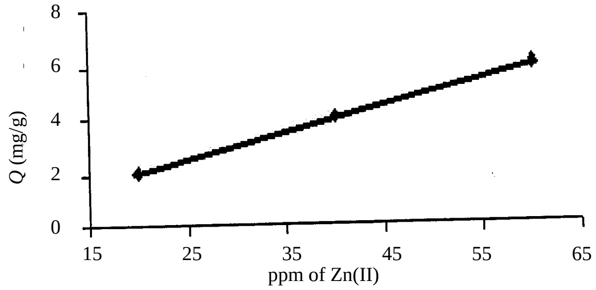


Fig. 6 **The relation between adsorption capacity and the concentration.**

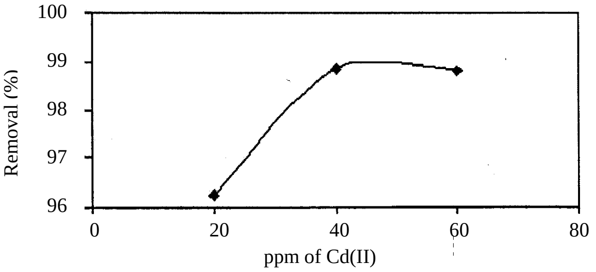


Fig. 7 **The relation between concentration of Cd(II) and the ligand removal (%).**

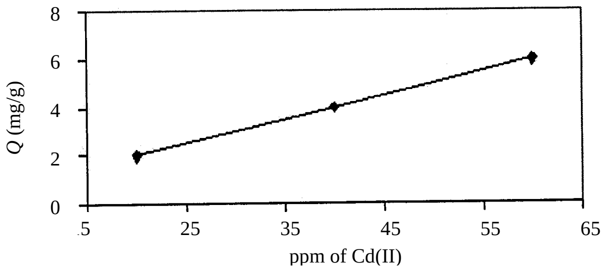


Fig. 8 **The relation between adsorption capacity and the concentration.**

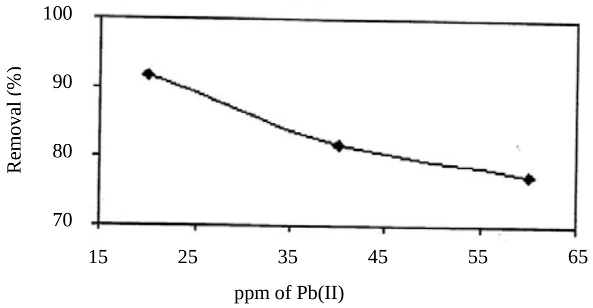


Fig. 9 The relation between concentration of Pb(II) and the ligand removal (%).

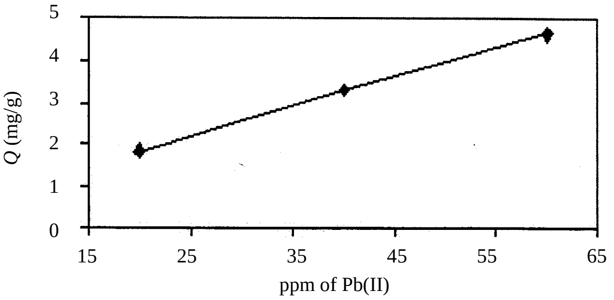
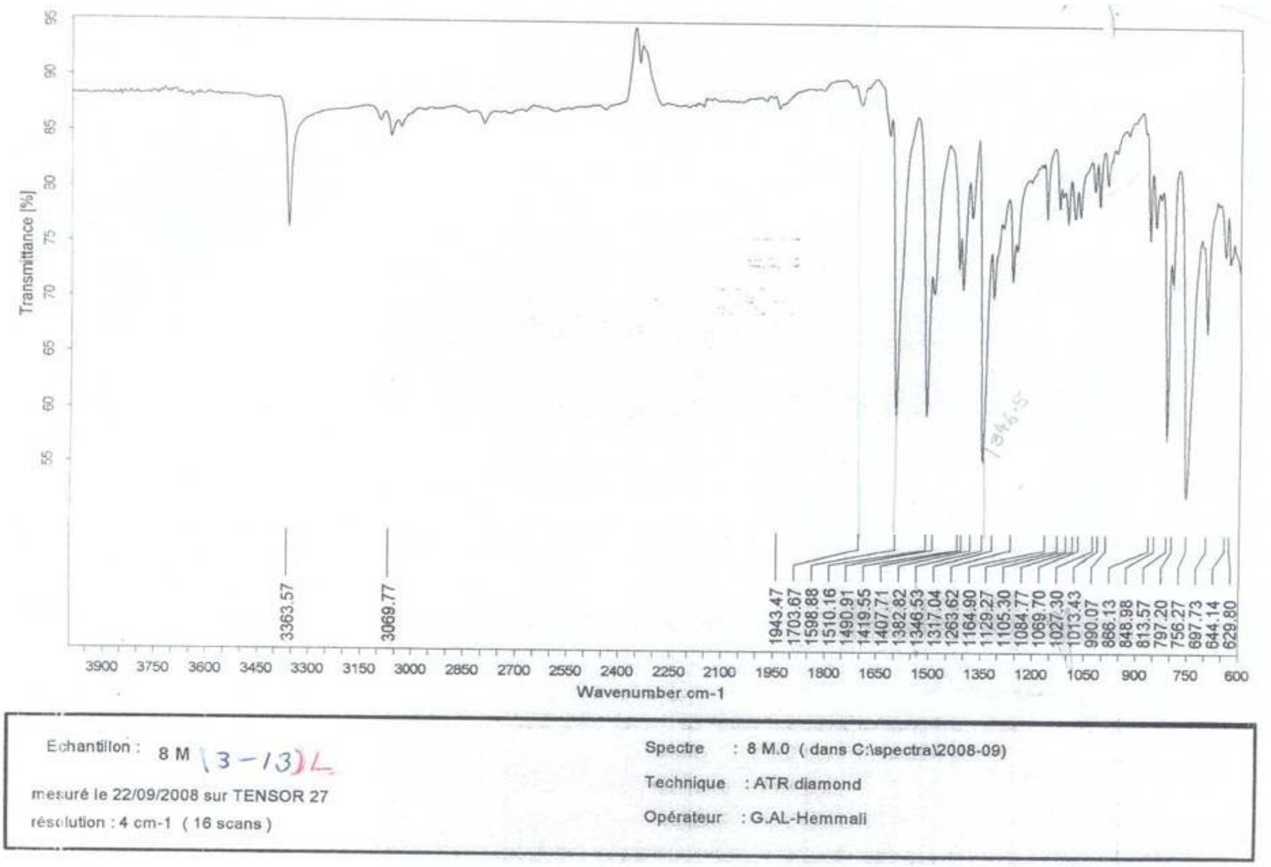


Fig. 10 The relation between adsorption capacity and the concentration.



Echantillon : 8 M (3 – 13)L
mesuré le 22/09/2008 sur TENSOR 27
résolution : 4 cm-1 (16 scans)

Spectre : 8 M.0 (dans C:\spectra\2008-09)
Technique : ATR diamond
Opérateur : G.AL-Hemmali

Fig. 11 The infrared spectrum of the Schiff base.

4. Conclusions

The strait forward methods of synthesis of Schiff base and the great deal of the Schiff bases characters introduced in complexation of divalent metal ions with the Schiff base containing electron withdrawing group substituent in para-position to evaluated the site of coordination as shown in the structure of the Schiff base. The uptake behavior of the Schiff base was measured and estimated. It was observed that the ligand shows clear decreasing of removal percentage when the Zn(II) ion increased up. Also 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. When the concentration of Pb(II) ion increases the removal percentage decreases. In general the factors in the uptake of the Schiff base can be referred to the site of coordination (there is only a nitrogen atom involves in the coordination), as well the presence of nitro group (deactivating group) reduces the electron availability in the trapping action.

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