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Unsymmetrical Schiff bases functionalize as bibasic tetradentate (ONNO) and monobasic tridentate (NNO) ligands on complexation with some transition metal ions

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Abstract

Three dissymmetrical Schiff bases have been prepared by the condensation of 2-hydroxyacetophenone, ethylenediamine and several aldehydes. The electronic transitions within these Schiff bases molecules and the effect of solvents of different polarities on these transitions have been investigated by UV/vis spectroscopy. Schiff bases complexes, binary 1:1 (metal:ligand) and ternary 1:1:1 (metal:ligand): d:Lewis base, where Lewis base = imidazole or pyridine), with transition metals, Co(II), Ni(II), Cu(II), and Zn(II) have been synthesized and characterized by elemental analysis, molar conductivity and electronic absorption and IR spectra. Further, the stoichiometric ratios of the complexes in solutions and the formation constants of the interaction of Schiff base ligands with metal ions have been determined.

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Keywords: Schiff bases; Binary and ternary complexes; Metal complexes; Spectral studies; Stoichiometric determination; Formation constants

1. Introduction

Schiff bases complexes have remained an important and popular area of research due to their simple synthesis, versatility, and diverse range of applications [1,2]. Thus, Schiff bases have played a marvelous role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals [1], which has sustained their wide-spread interest over the past 150 years [2]. In the area of bioinorganic chemistry interest in Schiff bases complexes with transition and inner-transition metals has centered on the role of such complexes in providing synthetic interesting models for the metal-containing sites in metallo-proteins and -enzymes [3–11], whereas, unsymmetrical Schiff bases ligands have clearly offered many advantages over their symmetrical counterparts in the elucidation of the composition and geometry of the metal ion

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binding sites in the metallo-proteins and -enzymes, and selectivity of natural systems with synthetic materials [12,13]. Further, recent years have witnessed a great deal of interest in the synthesis and characterization of transition metals complexes containing Schiff bases as ligands due to their applications as catalysts for many reactions [14–17] and relation to synthetic and natural oxygen carriers [18].

In view of these finding and in continuation to our previous work on the Schiff bases [19–22], this piece of work has devoted with the aim to synthesize some transition metals complexes with unsymmetrical Schiff bases ligands, (R-benzaldehyde)(2-hydroxyacetophenone)ethylenediamine, and to examine their physical properties involving spectral behaviors, the inter- or intra-molecular charge transfer, the electrical conductance values and to trace complexes formation in solutions and to determine the stoichiometric ratios of the formed complexes either spectrophotometrically or by conductometric titration.

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2. Experimental

2.1. Materials and solutions

All chemicals used, ethylenediamine, 2-hydroxyacetophenone, aromatic aldehydes (*o*-hydroxybenzaldehyde, benzaldehyde, and *p*-hydroxybenzaldehyde), spectral grade organic solvents (ethanol, methanol, dimethylformamide (DMF), acetone, acetonitril, chloroform, carbontetrachloride, dichloromethane and petroleum ether), metal salts (CoCl₂·6H₂O, Ni(CH₃COO)₂·4H₂O, Cu(CH₃COO)₂·2H₂O and Zn(CH₃COO)₂·2H₂O) and Lewis bases (Imidazole and pyridine) were of extra pure products (Merck, Aldrich, Sigma or B.D.H) and have been used without further purification.

2.2. Ligand solutions

Stock solutions of the ligands $L^{1}-L^{3}$ $(1 \times 10^{-2} \text{ mol dm}^{-3})$ have been prepared by dissolving the accurate weight of each ligand in the appropriate volume of the solvent. Solutions of the required concentrations have been prepared by accurate dilution.

2.3. Metal salt solutions

Solutions $(1 \times 10^{-2} \text{ mol dm}^{-3})$ of each of the metal salts investigated have been obtained by dissolving the accurate weight of each in the appropriate volume of the solvent. The metal content of the solutions has been determined by the recommended methods of analysis [23] and the solutions of the required concentrations have been prepared by accurate dilution.

2.4. Physical measurements

The electronic absorption spectra have been recorded on a Perkin-Elmer Lambda 40 spectrophotometer equipped with a Julabo FP 40 thermostat (± 0.1 °C) using 1.0 cm matched quartz cells. IR spectra of the solid compounds have been recorded on a Shimadzu IR-408 spectrophotometer. Conductance measurements have been carried out in DMF at room temperature using Jenway 4320 conductivity meter. ¹H NMR measurements have been carried out in the microanalytical laboratory, Cairo University. HPLC measurements have been preformed at Qena Central laboratory, South Valley University. Elemental analyses for C, H, N and Cl of the ligands and solid complexes have been carried out in the microanalytical laboratories at Cairo and Assiut Universities.

2.5. Continuous variation and molar ratio methods

For purpose of continuous variation method [24], a series of solutions has been prepared by mixing ligand and metal ion solutions in varying proportions while keeping the total molar concentration of the mixed solutions constant. On the other hand, for purpose of the molar ratio method [25], a series of solutions has been prepared in which ligand concentration has kept constant, while that of metal ion has been varied for covering the molar ratios [M(II)]/[ligand] = 3.00-0.2. The spectra of all solutions prepared have been recorded within the wavelength range 300-600 nm, where a solution containing the same concentration of the ligand as that of the measured solution has been used in the reference cell to eliminate any absorption of this ligand with the absorption of the corresponding complex.

2.6. Conductance measurements

For this purpose, the relationship between the specific conductance (k) and the molar ratio [L]/[M(II)] for the different complexes formed in solution is plotted, whereas, when the concentration of the solution is $C \pmod{4m^{-3}}$, the specific conductance (k) is clearly due to $C \pmod{4m^{-3}}$, the molar conductivity (Λ) will be: $\Lambda = k/C \pmod{4m^{-1} \text{ cm}^2 \text{ mol}^{-1}}$, the conductivity per mole of electrolyte. However, correction for the dilution effect is made by multiplying the values of specific conductance by the factor (V1 + V2)/V1, in which V1 is the original volume of the metal ion solution and V2 is that of the ligand solution added. The graphs obtained have showed distinct breaks, whereas, the locations of which have given an information about the presence and stoichiometry of the different complexes liable to exist in solutions.

In the present study, the conductometric titration has been performed by titrating 25 mL of 1×10^{-3} mol dm⁻³ of the metal ion solution with 5×10^{-3} mol dm⁻³ ligand solution. The solvent used was DMF. The conductance has been measured after stirring the solution for about 2 min.

2.7. Synthesis of the (*R*-benzaldehyde)(2-hydroxyacetophenone)ethylenediamine compounds (L^1-L^3)

The compounds under investigation are: (*o*-hydroxybenzaldehyde)(2-hydroxyacetophenone)ethylenediamine (L¹), (benzaldehyde)(2-hydroxyacetophenone)ethylenediamine (L²), and (*p*-hydroxybenzaldehyde)(2-hydroxyacetophenone)ethylenediamine (L³). These Schiff bases have been prepared according to the following procedure:

0.61 g (0.01 mol) of ethylenediamine in a few amount of hot ethanol has been added dropwisely with continuous stirring to a hot ethanolic solution of 1.36 g (0.01 mol) of 2-hydroxyacetophenone followed by 1.22 g (0.01 mol) of *o*-hydroxybenzaldehyde in case of (L^1), 1.06 g (0.01 mol) of benzaldehyde in case of (L^2) and 1.22 g (0.01 mol) of *p*-hydroxybenzaldehyde in case of (L^3). The mixtures have been refluxed on water bath for about 1 h with constant stirring and then allowed to cool at room temperature. The separated solid products have been filtered off and twice crystallized from ethanol; (L^1) 1.86 g, yield 66%; (L^2) 0.77 g, yield 73%; (L^3) 1.64 g, yield 58%. The purity of the prepared compounds (L^1-L^3) has been checked using HPLC measurements. Moreover, and for the comparison purpose, the well known symmetrical compounds bis(salicylaldehyde)ethylenediamine and bis(2-hydroxyacetophenone)ethylenediamine have been prepared too and their HPLC measurements have been compared with that of (*o*-hydroxybenzaldehyde)(2-hydroxyacetophenone)ethylenediamine (L¹).

The prepared compounds (L^1-L^3) have been analyzed for their C, H and N contents, and the results obtained are in accordance with the structure postulated of each of these compounds.

The structure of these compounds can be represented schematically as follow:



where

R = o-OH; (o-hydroxybenzaldehyde)(2-hydroxyace-tophenone)ethylenediamine (L^1)

= H; (benzaldehyde)(2-hydroxyacetophenone)ethylenediamine (L^2)

= p-OH; (p-hydroxybenzaldehyde)(2-hydroxyacetophenone)ethylenediamine (L^3)

It is worthy to mention that, the asymmetric structures of the prepared $L^{1}-L^{3}$ ligands have been confirmed by the H¹ NMR spectra measurements. Thus, H¹ NMR spectra of $L^{1}(o-OH)$, as a representative ligand, in CDCl₃ has performed a singlet at σ 2.61 (3H, CH₃); two triplets at δ 2.87 and 3.95 ppm (4H, 2CH₂); a multiplet at σ 6.75– 7.29 (10H, 8H–AR–H and 2OH) and a singlets at σ 8.33 (1H, CH). The signals of the OH protons of the ligand L¹ do not appear at the normal positions around 13 ppm (in $CDCl_3$), but the spectra have showed the signals of the OH protons at lower δ value in the form of multiplets at δ (6.75–7.29) for the 10H (8H of Ar–H and 2H of 2OH). Appearance of the OH protons at lower δ value is perhaps due to the shielding of these protons through six-membered ring hydrogen bonds. It is well known [26-28] that the hydrogen bonding causes shift to a lower field. In addition, the protons of the methylene bridge do interact and have showed two triplets at δ 2.87 and 3.95 ppm. Thus, protons of a methylene bridge would show a singlets if the bridge represents an axis of symmetry which this is not representing our case. The asymmetric structure of the ligand has been confirmed as shown before. In addition, appearance of a singlet at δ 2.33 ppm for the CH₃ group of $-C(CH_3)=N-$ and, at the same time, appearance of a singlet at δ 8.33 ppm for the CH of the group -CH=N- indicate the unsymmetrical structure of the compound (L¹).

2.8. Synthesis of the binary and ternary solid complexes

The binary solid complexes have been synthesized by mixing a hot methanolic solution of each of the ligands L^1-L^3 (0.01 mol) with the appropriate amount of each metal salt (0.01 mol) of CoCl₂·6H₂O, Ni(CH₃COO)₂·4H₂O, Cu(CH₃COO)₂·2H₂O and Zn(CH₃COO)₂·2H₂O, and has dissolved in \approx 30 ml methanol. The mixtures have been refluxed on a water bath for about 3 h and then evaporated to small volumes and left overnight at room temperature. The solid complexes have been filtered off on a water pump and washed several times with cold methanol and kept in desiccator over silica gel. The yields of these synthesized binary complexes were in the range 32–48%.

On the other hand, the ternary solid complexes have been synthesized by both direct and indirect methods. For the direct method; 0.01 mol of the previously prepared binary complex in 50 ml hot methanol has been added to an equimolar amount (0.01 mol) of Lewis base imidazole or pyridine. But, in the indirect method; 0.01 mol of any ligand (L^1-L^3) has been added to 0.01 mol of metal salt solution followed by 0.01 mol of Lewis base. In each case, the mixture has been refluxed for 3–4 h, left to cool at room temperature, and the resulting precipitate has been filtered off and washed several times with cold methanol, dried and kept in desiccator over silica gel. The yields of these synthesized ternary complexes were in the range 25–33%.

The binary and ternary solid complexes have been analyzed for their carbon, hydrogen and nitrogen contents and the found elemental analyses were in satisfactory agreement with the calculated values.

(L¹; o-OH) – Found: C, 72.12; H, 6.07; N, 9.84%. Calcd for C₁₇H₁₈N₂O₂: C, 72.32; H, 6.43; N, 9.92% $(L^2; R = H)$ – Found: C, 76.58; H, 6.79; N, 10.26%. Calcd for C₁₇H₁₈N₂O: C, 76.66; H, 6.81; N, 10.52% (L¹; *p*-OH) – Found: C, 72.55; H, 6.79; N, 9.20%. Calcd for C₁₇H₁₈N₂O₂: C, 72.32; H, 6.43; N, 9.92% $[Co(L^{1}-2H)(H_{2}O)_{2}]$ – Found: C, 53.96; H, 5.60; N, 7.25%. Calcd for $C_{17}H_{20}N_{2}O_{4}Co$: C, 54.41; H, 5.37; N, 7.46%; molar conductance, 39.29 $ohm^{-1} mol^{-1} cm^2$ $[Ni(L^{1}-2H)(H_{2}O)_{2}]$ – Found: C, 54.68; H, 5.34; N, 7.67%. Calcd for C₁₇H₂₀N₂O₄Ni: C, 54.44; H, 5.37; N, 7.47%; molar conductance, 8.14 $ohm^{-1} mol^{-1} cm^2$ $[Cu(L^{1}-2H)(H_{2}O)_{2}]$ – Found: C, 53.97; H, 5.16; N, 7.48%. Calcd for C₁₇H₂₀N₂O₄Cu: C, 53.75; H, 5.31; N, 7.37%; molar conductance, 7.51 $ohm^{-1} mol^{-1} cm^2$ $[Zn(L^{1}-2H)(H_{2}O)_{2}]$ – Found: C, 53.93; H, 4.92; N, 7.98%. Calcd for C₁₇H₂₀N₂O₄Zn: C, 53.49; H, 5.28; N, 7.34%; molar conductance, 4.98 ohm⁻¹ mol⁻¹ cm² $[Co(L^1-2H)Im(H_2O)] - Found: C, 56.39; H, 5.70; N,$ 13.73%. Calcd for C₂₀H₂₂N₄O₃Co: C, 56.48; H, 5.21; N, 13.17%; molar conductance, 42.62 $ohm^{-1} mol^{-1} cm^2$

 $[Co(L^{1}-2H)Py(H_{2}O)] - Found: C, 60.76; H, 5.82; N,$ 9.29%. Calcd for C₂₂H₂₃N₃O₃Co: C, 60.55; H, 5.31; N. 9.63%: molar conductance. 41.61 $ohm^{-1} mol^{-1} cm^2$ $[Ni(L^{1}-2H)Im(H_{2}O)] - Found: C, 65.00; H, 5.13; N,$ 13.19%. Calcd for C₂₀H₂₂N₄O₃Ni: C, 56.51; H, 5.22; N, 13.18%; molar conductance, 8.44 $ohm^{-1} mol^{-1} cm^2$ $[Ni(L^1-2H)Py(H_2O)] -$ Found: C, 60.41; H, 5.67; N, 9.93%. Calcd for C₂₂H₂₃N₃O₃Ni: C, 60.59; H, 5.32; N, 9.64%; molar conductance, 5.53 $ohm^{-1} mol^{-1} cm^2$ $[Cu(L^{1}-2H)Im(H_{2}O)] -$ Found: C, 56.13; H, 5.21; N, 12.92%. Calcd for C₂₀H₂₂N₄O₃Cu: C, 55.87; H, 5.16; N, 13.03%; molar conductance, 7.11 $ohm^{-1} mol^{-1} cm^2$ $[Cu(L^{1}-2H)Py(H_{2}O)] - Found: C, 59.37; H, 5.21; N,$ 9.90%. Calcd for C₂₂H₂₃N₃O₃Cu: C, 59.92; H, 5.26; N, 9.53%; molar conductance, 7.82 ohm⁻¹ mol⁻¹ cm² $[Zn(L^1-2H)Im(H_2O)] -$ Found: C, 55.84; H, 5.41; N, 12.24%. Calcd for C₂₀H₂₂N₄O₃Zn: C, 55.63; H, 5.14; N, 12.98%; molar conductance, 13.49 $ohm^{-1} mol^{-1} cm^2$ $[Zn(L^{1}-2H)Py(H_{2}O)] - Found: C, 59.37; H, 4.94; N,$ 9.28%. Calcd for C₂₂H₂₃N₃O₃Zn: C, 59.67; H, 5.25; N, 9.59%; molar conductance, 8.49 $ohm^{-1} mol^{-1} cm^2$ $[Co(L^2-H)Cl(H_2O)_2]$ – Found: C, 52.30; H, 5.33; Cl,

[Co(L -11)Cl(11₂O)₂] – Found. C, 52.50, 11, 5.55, Cl, 8.66; N, 7.09%. Calcd for $C_{17}H_{21}ClN_2O_3Co: C, 51.73;$ H, 5.11; Cl, 8.96; N, 7.10%; molar conductance, 47.67 ohm⁻¹ mol⁻¹ cm²

 $[\text{Ni}(\text{L}^2-\text{H})\text{Ac}(\text{H}_2\text{O})_2] - \text{Found: C, 54.89; H, 5.63; N, } \\ 7.06\%. \text{ Calcd for } C_{19}\text{H}_{24}\text{N}_2\text{O}_5\text{Ni: C, 54.58; H, 5.54; N, } \\ 6.70\%; \text{ molar conductance, 5.48 ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$

 $\begin{array}{l} [Cu(L^2-H)Ac(H_2O)_2] - Found: \ C, \ 53.34; \ H, \ 5.68; \ N, \\ 6.63\%. \ Calcd \ for \ C_{19}H_{24}N_2O_5Cu: \ C, \ 53.96; \ H, \ 5.48; \\ N, \ 6.62\%; \ molar \ conductance, \ 9.37 \ ohm^{-1} \ mol^{-1} \ cm^2 \\ [Zn(L^2-H)Ac(H_2O)_2] - Found: \ C, \ 54.01; \ H, \ 5.82; \ N, \\ 6.13\%. \ Calcd \ for \ C_{19}H_{24}N_2O_5Zn: \ C, \ 53.72; \ H, \ 5.46; \ N, \\ 6.60\%; \ molar \ conductance, \ 4.93 \ ohm^{-1} \ mol^{-1} \ cm^2 \end{array}$

 $\label{eq:cond} \begin{array}{l} [Co(L^2-H)Cl\cdot Py(H_2O)] - Found: C, 58.50; H, 4.19; Cl, \\ 7.89; N, 9.45\%. Calcd for C_{22}H_{24}ClN_3O_2Co: C, 57.97; \\ H, 5.08; Cl, 7.76; N, 9.22\%; molar conductance, \\ 47.23 \ ohm^{-1} \ mol^{-1} \ cm^2 \end{array}$

 $[Ni(L^2-H)Ac \cdot Im(H_2O)] - Found: C, 56.50; H, 5.00; N, 11.55\%. Calcd for C_{22}H_{26}N_4O_4Ni: C, 56.44; H, 5.38; N, 11.97\%; molar conductance, 5.36 ohm⁻¹ mol⁻¹ cm²$

 $[\text{Ni}(\text{L}^2-\text{H})\text{Ac·Py}(\text{H}_2\text{O})] - \text{Found: C, 60.31; H, 5.02; N, } \\ 8.47\%. \text{ Calcd for } C_{24}\text{H}_{27}\text{N}_3\text{O}_4\text{Ni: C, 60.16; H, 5.47; N, } \\ 8.77\%; \text{ molar conductance, 5.05 ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$

$$\label{eq:cull_harmonic} \begin{split} & [Cu(L^2-H)Ac\cdot Im(H_2O)] - \text{Found: C, 56.40; H, 4.96; N,} \\ & 12.17\%. \ Calcd \ for \ C_{22}H_{26}N_4O_4Cu: \ C, \ 55.91; \ H, \ 5.13; \\ & \text{N, 11.96\%; molar conductance, 11.80 } ohm^{-1} \ mol^{-1} \ cm^2 \\ & [Cu(L^2-H)Ac\cdot Py(H_2O)] - \text{Found: C, 58.89; H, 5.26; N,} \\ & 8.84\%. \ Calcd \ for \ C_{24}H_{27}N_3O_4Cu: \ C, \ 59.56; \ H, \ 5.41; \\ & \text{N, $ 8.68\%; molar conductance, $ 11.79 } ohm^{-1} \ mol^{-1} \ cm^2 \end{split}$$

 $[Co(L^3-H)Cl(H_2O)_2]$ – Found: C, 49.78; H, 4.88; Cl, 8.52; N, 6.55%. Calcd for $C_{17}H_{21}ClN_2O_4Co$: C, 49.59;

H, 5.14; Cl, 8.61; N, 6.80%; molar conductance, 37.17 ohm $^{-1}$ mol $^{-1}$ cm 2

 $[Ni(L^{3}-H)Ac(H_{2}O)_{2}] - Found: C, 52.52; H, 5.41; N, 6.68\%. Calcd for C_{19}H_{24}N_{2}O_{6}Ni: C, 52.45; H, 5.56; N, 6.44\%; molar conductance, 6.02 ohm⁻¹ mol⁻¹ cm²$

 $[Cu(L^3-H)Ac(H_2O)_2] - Found: C, 52.39; H, 5.84; N, 6.38\%$. Calcd for $C_{19}H_{24}N_2O_6Cu: C, 51.87; H, 5.50; N, 6.37\%$; molar conductance, 3.24 ohm⁻¹ mol⁻¹ cm²

[Zn(L³–H)Ac(H₂O)₂] – Found: C, 51.92; H, 5.47; N, 6.86%. Calcd for $C_{19}H_{24}N_2O_6Zn$: C, 51.66; H, 5.48; N, 6.34%; molar conductance, 4.06 ohm⁻¹ mol⁻¹ cm²

 $\begin{array}{l} [Co(L^3-H)Cl \cdot Im(H_2O)] - \mbox{Found: C, 51.90; H, 5.16; Cl,} \\ 7.56; N, 12.97\%. Calcd for C_{20}H_{23}ClN_4O_3Co: C, \\ 52.00; H, 5.02; Cl, 7.68; N, 12.13\%; molar conductance, \\ 46.16 \ ohm^{-1} \ mol^{-1} \ cm^2 \end{array}$

 $[Co(L^{3}-H)Cl \cdot Py(H_{2}O)] - Found: C, 56.21; H, 5.38; Cl, 7.67; N, 8.64\%. Calcd for C_{22}H_{24}ClN_{3}O_{3}Co: C, 55.88; H, 5.12; Cl, 7.50; N, 8.89\%; molar conductance, 49.89 ohm⁻¹ mol⁻¹ cm²$

[Ni(L³–H)Ac·Im(H₂O)] – Found: C, 54.64; H, 5.43; N, 11.61%. Calcd for $C_{22}H_{26}N_4O_5Ni$: C, 54.46; H, 4.50; N, 11.55%; molar conductance, 7.51 ohm⁻¹ mol⁻¹ cm² [Ni(L³–H)Ac·Py(H₂O)] – Found: C, 58.29; H, 5.18; N, 8.57%. Calcd for $C_{24}H_{27}N_3O_5Ni$: C, 58.10; H, 5.48; N, 8.47%; molar conductance, 6.27 ohm⁻¹ mol⁻¹ cm² [Cu(L³–H)Ac·Im(H₂O)] – Found: C, 53.22; H, 4.98; N, 10.99%. Calcd for $C_{22}H_{26}N_4O_5Cu$: C, 53.93; H, 5.35; N, 11.43%; molar conductance, 2.39 ohm⁻¹ mol⁻¹ cm²

 $[Cu(L^3-H)Ac\cdotPy(H_2O)] -$ Found: C, 57.64; H, 5.06; N, 8.31%. Calcd for $C_{24}H_{27}N_3O_5Cu$: C, 57.54; H, 5.43; N, 8.39%; molar conductance, 3.43 ohm⁻¹ mol⁻¹ cm²

3. Results and discussion

3.1. Electronic absorption spectra of $L^1 - L^3$ solutions in organic solvents of different polarities

With the aim to attain information about the types of the electronic transitions and interaction liable to exist in solutions, the electronic spectra have been measured of the subject compounds (L^1-L^3) in several organic solvents of different polarities, ethanol, methanol, chloroform, carbon tetrachloride, dichloromethane, acetonitril and dimethylformamide (DMF). Generally, the recorded spectra of L^1-L^3 in different organic solvents have displayed three main absorption bands (cf Table 1). The UV band appeared in the range 280–291 nm is assignable to the localized electronic transition of the benzenoid system of the compounds. Such an assignment is achieved from its higher energy, lower wavelength, and higher molar absorptivity.

The second band has been observed in the range 315– 330 nm as a broad and/or a shoulder band. This band can be ascribed to the π - π^* transitions of the benzenoid system of the compounds strongly overlapped with n- π^* electronic transition that involves the nonbonding electrons

Table I			
Electronic absorption spectral bands of th	e Schiff bases $L^1 - L^3$ solutions.	1×10^{-3} mol dm ⁻³ , in pure	organic solvents at 25 °C

Solvents	$L^1(\mathbf{R} = o \cdot \mathbf{OH})$		$L^2(R = H)$		$L^{3}(\mathbf{R}=p-\mathbf{O}$	H)	Assignment	
	λ_{\max}	\$emax	\$emax	λ_{\max}	λ_{\max}	$\epsilon_{ m max}$		
Ethanol	281	1.15	_	_	_	_	$\pi - \pi^*$, within aromatic system	
	320 b	2.53	323	5.40	323	6.79	π - π^* , within C=N gps	
	_	_	379 sh	2.30	379 sh	2.30	Intramolecular CT transition	
	394 b	0.52	390	2.39	390 b	2.40	Intramolecular CT transition	
Methanol	285 sh	2.04	_	_	_	_	$\pi - \pi^*$, within aromatic system	
	317 b	7.86	320 b	6.00	321 b	6.20	π - π^* , within C=N gps	
	380 sh	2.07	384 b	1.33	376 b	3.02	Intramolecular CT transition	
	395	2.26	-	_	403 b	2.97	Intramolecular CT transition	
CHCl ₃	_	_	_	_	_	_	$\pi - \pi^*$, within aromatic system	
	321 b	5.88	_	_	330 b	2.47	$\pi - \pi^*$, within C=N gps	
	_	_	_	_	_	_	Intramolecular CT transition	
	399 b	0.28	390 sh	0.98	394 b	1.25	Intramolecular CT transition	
CCl	_	_	_	_	_	_	$\pi - \pi^*$, within aromatic system	
	321 b	5.88	326 b	10.57	323 b	11.30	$\pi - \pi^*$, within C=N gps	
	_	_	_	_	_	_	Intramolecular CT transition	
	399 b	0.28	409 sh	0.33	_	_	Intramolecular CT transition	
CH ₂ Cl ²	_	_	_	_	_	_	$\pi - \pi^*$, within aromatic system	
2	319	10.70	319 b	9.04	320 b	10.05	$\pi - \pi^*$, within C=N gps	
	_	_	_	_	_	_	Intramolecular CT transition	
	399 b	0.35	399 sh	0.73	394 b	0.83	Intramolecular CT transition	
CH ₃ CN	_	_	_	_	_	_	$\pi - \pi^*$, within aromatic system	
-	317	10.05	319 b	7.12	316 b	6.64	$\pi - \pi^*$, within C=N gps	
	_	_	388 sh	1.03	_	_	Intramolecular CT transition	
	391 b	0.50	_	_	394 b	1.07	Intramolecular CT transition	
DMF	291 sh	8.70	_	_	_	_	$\pi - \pi^*$, within aromatic system	
	317 b	6.79	317 b	8.53	315 b	7.73	$\pi - \pi^*$, within C=N gps	
	_	_	_	_	_	_	Intramolecular CT transition	
	403 sh	0.40	390 sh	0.93	394 sh	0.83	Intramolecular CT transition	

 $\lambda = \text{nm}; \epsilon = 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}; \text{ sh, shoulder; b, broad.}$

of the azomethine nitrogen atom. A similar assignment was described by Jaffe et al. [29]. This assignment is substantiated by the fact that the position of this band suffers small solvent shifts where changing the polarity of the medium (cf Table 1).

Table 1 also indicates that the λ_{max} of $L^1(R = o$ -OH) observed at 320 nm has the lower molar absorptivity value relative to that of the other compounds in ethanol. This comes in confirmation with $n-\pi^*$ nature where the *n*-electrons of the two *o*-OH groups (L¹) are blocked by the strong H-bonding established between the azomethine nitrogen and the *o*-OH groups as represented schematically below.



The longer wavelength band(s) in the recorded spectra of the compounds L^1-L^3 observed in the range 380–410 nm can be ascribed to the transition within the whole

molecule essentially as intramolecular charge transfer (CT) interaction. The CT seems to originate from the aryl moiety, whereas, the positive charge azomethine carbon atom is the acceptor center. Table 1 reveals that, the position of the CT band is quite sensitive to the nature of the constituent, R, attached to the aldehyde moiety. Generally, for compounds L^1-L^3 , the excitation energy of this band decreases as the electron donor power of the constituent, R, is increased according to the following sequence:

$L^{1}(R = o-OH) > L^{3}(R = p-OH) \approx L^{2}(R = H)$

From the previous order, it could be emphasized that the λ_{max} of CT band of the L¹ (R = *o*-OH) compound is longer than that of other compounds (L² and L³) due to the established H-bonding between the *o*-OH groups and the azomethine nitrogen which, in turn, results in high electron density on the oxygen atom of the *o*-OH groups. This will, of course, leads to a higher contribution of electrons on the azomethine double bond, i.e. the π -electron cloud is more delocalized and consequently is easier to be excited. This behavior substantiates the CT character of this band.

In DMF as a solvent, the spectra of L^1-L^3 have displayed a broad or a shoulder band ranged between 390 and 410 nm. This band can be attributed to an intermolec-

ular CT transition [30] taking place thorough the interaction between the solute and solvent molecules via H-bonding [31].

Further, data given in Table 1 indicate the absence of any band in the range 320–330 nm in the spectra of $L^2(R = H)$ in CHCl₃, (in contrast to the spectra of the other compounds, L^1 and L^3 , in CHCl₃). Instead, a shoulder band has been observed around 390 nm. This may be due to the overlapping of these bands with other intramolecular CT band supposed to appear \approx 390 nm.

On the other hand, the data in Table 1 reveal the absence of any absorption band due to intramolecular CT interaction in case of the recorded spectra of the compounds $L^{1}(R = o$ -OH) and $L^{3}(R = p$ -OH) in CCl₄ as demonstrated. This can be interpreted on the principle of the difficult CT interaction in the solute molecules of these compounds in CCl₄ as a solvent.

3.2. Electronic absorption spectra and stoichiometry of the complexes formed in solution

Electronic absorption spectra of the free methanolic L^{1} – L^{3} solutions and the spectra of the complexes solutions resulting from adding the metals salts solutions to each ligand solution have been measured. Generally, it is evident that addition of metal ion to the ligand solution causes distinguishable changes in the visible absorption spectra of the ligand. This behavior suggests an instantaneous complex formation in solution from the reaction of each of the ligands under investigation with each of the metal ions used.

The longer wavelength band(s) of each free ligand $(L^{1}-L^{3})$ at 317–403 nm has acquired a red shift on complex formation with the metal ion. A new shoulder has been observed at a longer wavelength (in range of 390–435 nm) in case of the complex solution of L^{1} with Co(II), Ni(II) and Cu(II), L^{2} and L^{3} with Co(II) and Cu(II). This behavior can be explained as follows.

The longer wavelength band observed in the spectrum of the free ligands $L^{1}-L^{3}$ can be assigned to an intramolecular CT transition liable to take place within the solute molecule. Thus the red shift observed in the λ_{max} of this band on complex formation with the divalent transition metal ions Co(II), Ni(II), and Cu(II) can be interpreted on the principle of an expected easier CT transition within the complexed Schiff bases ($L^{1}-L^{3}$) rather than within the free ones. This is due to the positive charge of the coordinating metal ions. On the other hand, the observed new shoulder around 440 nm in the spectra of the complexes solutions can be likely ascribed to an intermolecular transition from the ligands molecules to the vacant orbitals localized on the coordinated metal ions, i.e. $L \rightarrow MCT$.

Aiming to determine the stoichiometry of the different complexes liable to form in solution from the interaction of Co(II), Ni(II), Cu(II) and Zn(II) ions with the compounds under investigation, L^1-L^3 , two different spectrophotometric methods, continuous variation (CV) [24] and

molar ratio (MR) of Yoe and Jones [25] methods, and conductometric titration method have been applied. Thus, the curves plotted for CV method are characterized either by one clear maximum located at ligand mole fraction equals to ≈ 0.50 and/or ≈ 0.70 , for most cases, or by a shoulder accompanied by a maximum located also at the same ligand mole fraction values; i.e. ≈ 0.50 and/or 0.70. This behavior clearly indicates that the stoichiometry of the different complexes formed in solution from the reaction of the ligands (L¹–L³) with the metal ions Co(II), Ni(II), Cu(II) and Zn(II) is 1:1 and/or 1:2 (M:L).

It is to be noted that for the complexes of Ni(II) with $L^{1}(R = o$ -OH), Cu(II) and Ni(II) with $L^{2}(R = H)$ the CV plots have possessed a well-defined shoulder at a mole fraction of the ligand near 0.55 and a well characterized peak at ≈ 0.70 . This behavior can be explained on the basis that 1:1 complexes species are formed in solution but, they disproportionate to form 1:2 (metal to ligand) complexes species where the latter are more stable. Such a disproportionate reaction can be represented by the following equation:

$2ML(solution) \rightleftharpoons ML^2(solution) + M(solution)$

In addition, results of the MR method have supported the results of the CV method. It is evident that, the relationships obtained for the MR method are characterized by one or two breaks located at molar ratios [M(II)]/[L]equals to 1.0 and/or 2.0. This indicates that the stoichiometric ratio of the complexes, which are liable to form in solution from the reaction of each of the ligands L^1 (R = o-OH) with Co(II), Ni(II), Cu(II) and Zn(II), and $L^{2}(R = H)$ with Co(II), Cu(II), Zn(II) and $L^{3}(R = p-OH)$ with Co(II) is 1:1 (M:L), while the stoichiometry of reacting L², L³ with Ni(II) is 1:1 and 1:2 (M:L) depending on the nature of both the metal ion and the ligand. Thus, the plots of absorbance vs [M]/[L] molar ratio for Ni(II)- L^2 , and Ni(II)- L^3 , indicate the formation of 1:1 complex species. After complete formation of 1:1 complexes, new complex species are being formed, but these are unstable. Therefore, the absorbance decreases again beyond a ratio of [M]/[L] equals to 1.6 which reveals a decomposition of the complexes formed in solution with higher ratio of metal to ligand.

Further evidence has been given by the conductometric titration method. Thus, on plotting the specific conductance values, as a function of [L]/[M(II)] molar ratio, it is evident that, the titration curves obtained are straight lines for the majority of the points recorded, and these lines are accompanied with breaks corresponding to the stoichiometric ratios of the complexes formed in solutions. Moreover, it is apparent that, the breaks take place at the molar ratios 1:1 and/or 1:2 metal to ligand, which are in a good agreement with those determined spectro-phometrically.

On the other hand, it has been found that the conductance has changed from (7.9–39.6), (6.1–15.9), (39.5–59.1) and $(1.0-8.8) \times 10^{-6}$ ohm⁻¹ cm² mol⁻¹ during the titration of each Co(II), Ni(II), Cu(II) and Zn(II) metal ion solutions, respectively, with all the ligands (L^1-L^3) used. With respect to the same ligand, the specific conductance value generally runs according to the following sequence:

This is in agreement with the general order of stability of the complexes of these metal ions which has been established before by Grinberg and Yatsimirsk [32] and by Irving and Williams [33]. This behavior clearly indicates that the anions of the ligands $L^{1}-L^{3}$ are coordinated to the metal ions Co(II), Ni(II), Cu(II) and Zn(II). This fact is in accordance with the results of the elemental analyses of the synthesized solid complexes. Thus, the chemical reactions liable to take place in solution between the metal ions Co(II), Ni(II), Cu(II) and Zn(II) and the ligands $L^{1}-L^{3}$ to form 1:1 and/or 1:2 (M:L) complexes can be represented by the following chemical equations:

$$\begin{split} H_{2}L + M(II) &\rightleftharpoons LM(II) + 2H^{+} \ (1:1 \ complex) \\ 2H_{2}L + M(II) &\rightleftharpoons (L)^{2}M(II) + 4H^{+} \ (1:2 \ complex) \\ where \ H_{2}L &= (o \text{-OH}) \ compound \ (L^{1}) \\ HL + M(II) &\rightleftharpoons LM(II) + H^{+} \ (1:1 \ complex) \\ 2HL + M(II) &\rightleftharpoons L^{2}M(II) + 2H^{+} \ (1:2 \ complex) \\ where \ HL &= L^{2} \ and \ L^{3}. \end{split}$$

3.3. Evaluation of the apparent formation constants of the different metal chelates formed

The data obtained from the two spectrophotometric methods, CV and MR, which were used in this work to establish the stoichiometry of the metal complexes, were also utilized for the determination of the formation constants ($K_{\rm f}$) of such complexes making use the following equations [34]:

$$K_{\rm f} = \frac{A/A_{\rm m}}{\left(1 - A/A_{\rm m}\right)^2 C} \quad \text{for (1:1 L:M) complexes}$$
$$K_{\rm f} = \frac{A/A_{\rm m}}{4C^2 \left(1 - A/A_{\rm m}\right)^3} \quad \text{for (2:1 L:M) complexes}$$

where $A_{\rm m}$ is the limiting absorbance value corresponding to the maximum formation of the complex and A is the absorbance at a given metal ion concentration C.

The mean $K_{\rm f}$ values obtained for the metal complexes under investigation are given in Table 2.

Examination of the results shown in this Table 2 reveals that the order of stability of the 1:1 or 1:2 complexes of a given ligand runs according to the following sequence:

This is in agreement with the general order of the stability of the complexes of these metal ions which is established before [29]. Meanwhile, the stability of each metal complexed with the different ligands used decreases according to the sequence:

$$L^{3}(R = p-OH) > L^{1}(R = o-OH) > L^{2}(R = H)$$

This is in somewhat in agreement with decreasing electron releasing character of the substituents in the same direction which results in a decrease in the basicity of the azomethine nitrogen of the ligand and, consequently, the tendency toward complex formation is expected to decrease. For example the ligand $L^3(R = p$ -OH) has a tendency to act as a good σ -donor owing to the expected high basicity of the two bonding sites (the two azomethine nitrogen atoms) of L^3 as the result of the high electron releasing power of the OH group in the *para* position in $L^3(p$ -OH) relative to that of the nonsubstituted L^2 (R = H) or even of the OH hydroxyl in the *ortho* position in $L^1(o$ -OH).

3.4. Characterization of the solid complexes isolated in presence and absence of imidazole or pyridine as a Lewis base

The results of the chemical analyses of the different synthesized solid products of the reaction of each of the ligands L^1-L^3 with the metal ions Co(II), Ni(II), Cu(II) and Zn(II) have suggested the formation of the 1:1 (ligand:metal) and 1:1:1 (ligand:metal:Lewis base) chelates. The suggested general formulae of the obtained chelates are $[M(L^1-2H)(Lewis)(H_2O)],$ $[M(L^{1}-2H)(H_{2}O)_{2}],$ [M(L- $[M(L-H)(Lewis)X(H_2O)]$ $H X (H_2 O)_2$ and where $L^{1}(R = o-OH), L (L^{2}(R = H) \text{ or } L^{3}(R = p-OH)), X = Cl^{-1}$ or CH_3COO^- and Lewis base = imidazole (Im) or pyridine (Py). This indicates that the deprotonated ligands $L^{1}-L^{3}$ have coordinated to the metal ion.

The molar conductance values of the DMF solutions $(1 \times 10^{-3} \text{ mol dm}^{-3})$ of the different synthesized metal complexes have been determined and have been shown in the experimental part following the elemental analysis data for each synthesized complex. It is evident that the molar conductance values for all the synthesized complexes of the ligands $L^{1}-L^{3}$ with Co(II) in absence and/ or presence of Lewis base are in the rang 37– 50 ohm⁻¹ mol⁻¹ cm², while with the other metals (Ni(II), Cu(II) and Zn(II)) the values are in the range 2–14 ohm⁻¹ mol⁻¹ cm². This suggests the nonelectrolyte nat-

Table 2

Apparent formation constant values (K_f) of the L^1-L^3 complexes with different transition metals

Ligand	Co(II) complex		Ni(II) complex		Cu(II) complex		Zn(II) complex	
	1:1	1:2	1:1	1:2	1:1	1:2	1:1	1:2
$L^1(R = o - OH)$	1.98×10^{5}	_	_	18.10×10^{8}	2.50×10^{5}	_	_	5.48×10^{8}
$L^2(R = H)$	_	3.24×10^{8}	_	4.31×10^{8}	_	4.36×10^{8}	_	2.25×10^{8}
$L^{3}(R = p - OH)$	_	32.90×10^{8}	3.30×10^{5}	_	_	37.50×10^{8}	_	22.06×10^{8}

ure of these complexes as reported [35]. Accordingly, one can deduce that in the different metal complexes under investigation, the anions Cl^- or CH_3COO^- are coordinated to the metal ion as displayed in the molecular formulae of these complexes, shown hereafter. However, this conclusion is reasonable since in 1:1 or 1:1:1 complexes each of the metal ions studied is still having unoccupied coordination sites. This is based on the expected tendency of the studied metal ions to form complexes with high coordination number, six, for Co(II), Ni(II), Cu(II) and Zn(II).

On the other hand, the electronic absorption spectra of the methanolic solutions of the different synthesized, binary and, ternary complexes have been recorded in the wavelength range 250–750 nm.

The electronic absorption spectra of Co(II)–(L¹–L³) complexes are characterized by a weak crystal field broad band or a shoulder (552–597 nm) ($\varepsilon_{max} = 13-183 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) followed by a long tail into the low energy region. This behavior suggests an octahedral structure for these complexes, [36] and is assigned to $4T_{1g}(F) \rightarrow 4T_{1g}(P)$ transitions [37]. The observed visible band in the recorded spectra of Co(II)–(L¹–L³) complexes in the range 368–382 nm ($\varepsilon_{max} = 2660-3490 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) can be ascribed to an intramolecular CT transition within the complexed Schiff bases molecules.

The electronic absorption spectra of Ni(II)–(L^1-L^3) are characterized by a broad band or a shoulder covering the long wavelength region 540–553 nm ($\varepsilon_{max} = 13-$ 340 dm³ mol⁻¹ cm⁻¹) where the spectra exhibit long tail into the near infrared region. This behavior can be assigned to an octahedral $3A_{2g} \rightarrow 3T_{1g}(P)$ transition [36]. Further, the absorption band observed in the recorded spectra of these complexes in the range 396–399 nm ($\varepsilon_{max} = 2230-$ 7530 dm³ mol⁻¹ cm⁻¹) can be ascribed to an intramolecular CT transition within the complexed Schiff bases molecules.

The electronic absorption spectra of Cu(II)–(L¹–L³) complexes are characterized by a broad band or a shoulder covering the region 550–574 nm ($\varepsilon_{max} = 190$ –400 dm³ mol⁻¹ cm⁻¹). In addition, such spectra exhibit a long tail into near infrared region. Since it has been described before that octahedral Cu(II) complexes give rise to one absorption band in the region ≈600 nm which often exhibit a tail into the near infrared region [36]. Therefore octahedral structure can be proposed for the studied Cu(II)–(L¹–L³) complexes.

It is worthy to note that the relatively higher molar absorption of the observed weak crystal field absorption shoulders in the spectra of the different studied Cu(II)– (L^1-L^3) complexes can be attributed to the expected centric structure of these complexes, i.e. distorted octahedral structure [38]. Again one recalls that the well-defined visible absorption band appeared in the spectra of all examined Cu(II) complexes in the range 351–357 nm ($\varepsilon_{max} = 2260-8510 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) can be assigned to an intramolecular CT transition liable to take place within the complexed Schiff bases molecules.

The electronic absorption spectra of $Zn(II)-L^3$ are characterized by a shoulder ≈ 550 nm (having very low molar absorption) with a tail into near infrared region that could be assigned as d-d band and the complex $Zn(II)-L^3$ has a d-d transition. However, it is hard to detect any d-d band in the spectra of $Zn(II)-L^1$ and (L^2) complexes. Therefore, the structures of these complexes are difficult to be assigned but for $Zn(II)-L^3$ complex, octahedral structure can be proposed. Furthermore, the well-defined visible absorption band appeared in the spectra of $Zn(II)-(L^1-L^3)$ in the range 343-351 nm $(\varepsilon_{max} = 740-10,100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$ can be assigned to intramolecular CT transitions liable to take place within the complexed Schiff base molecule.

In addition to the previous given discussion, it is necessary to refer that the bands observed in the ranges 368–382, 396–399, 351–357 and 343–351 nm in the spectra of Co(II), Ni(II), Cu(II) and Zn(II) complexes with L^1-L^3 are quite sensitive to the change of the metal ion and the molecular structure of the ligand. Comparing the position of this band on transfer from metal ion to another with the same ligand reveals that λ_{max} of this band shifts (in general) to lower energy in the following order:

 $Co(II) > Ni(II) \approx Cu(II) > Zn(II)$

This indicates that this band is corresponding to ligand to metal CT. This is in agreement with the reported trend [36] where it is concluded that λ_{max} of LMCT shifts to longer wavelengths as the metal becomes more readily reducible. Further confirmation of assigning this band as LMCT transition, is attained by comparing the λ_{max} on changing the ligand with the same given metal ion. As a general trend, λ_{max} of this band acquires a shift to longer wavelengths as the electron releasing power of the constituent (R), attached to the phenyl moiety is increased. Such a shift indicates an easier electronic transfer to the metal ion. With respect to Co(II)–(L¹–L³) complexes as an example, the order was found to be

 $L^1>L^3>L^2$

In the ultraviolet region, the bands observed in the ranges 272–282, 268–270, 274–279 and 270–276 nm in spectra of Co(II), Ni(II), Cu(II) and Zn(II)– (L^1-L^3) , respectively, can be ascribed to an intraligand electronic transition, because bands in these regions are sensitive enough to the type of metal ion used.

The electronic absorption spectra of the mixed-ligand complexes showed some minor changes in the position and intensity of the CT bands. This behavior confirms coordination of Lewis bases (Im or Py) in the mixed-ligand complexes. The substitution of H_2O by a Lewis base may result in a change of the type of orbital from which the electron is transferred to the metal ion. The d–d bands displayed by the mixed-ligand complexes are located almost at the same positions as in the spectra of the binary chelates, indicating that the geometry around the metal ions is not change [39].

On the other hand, to reach a conclusive idea about the structure of metal chelates with the subject ligands, infrared spectra of the free ligands (L^1-L^3) and their complexes were recorded. In such cases, an insight view in the type of bonds formed between the ligand and the central metal ion can be gained from a careful investigation of the spectrum of the complex essentially in comparison to that of the free ligand, and accordingly, the tentative assignment of some of the important bands has been made. With respect to the ligands L^1-L^3 , instead of an expected sharp strong band at 3500 cm^{-1} due to stretching vibration of OH groups, a broad band appeared covering the range 2500-3500 cm⁻¹. This band includes both C-H and hydrogen bonded OH stretching frequencies. This assignment is reasonable since some literature report [40-42] a frequency of hydrogen bonded OH near 2800 cm⁻¹. Similar absorption band was observed in the region $2600-2800 \text{ cm}^{-1}$ in the spectra of bis(salicylidene)diamine [42]. This band disappears in the IR spectra of the corresponding metal chelates where instead a weak band appears near 3000 cm^{-1} which is assignable to the stretching of C-H. This also indicates that the phenolic oxygen is coordinated to the metal ion. Furthermore, the phenolic C–O stretching vibrations appeared at 1280–1295 cm⁻¹ in the IR spectra of L^1-L^3 was found to have an appreciable shift to lower frequency in the IR spectra of the corresponding metal chelates confirming its coordination to the metal ion [9,43,44]. The IR spectra of all complexes show a broad band in the region $3050-3600 \text{ cm}^{-1}$. This indicates that water molecules exist in the complexes prepared.

A strong band in the region $1595-1645 \text{ cm}^{-1}$ is observed in the IR spectra of all ligands (L^1-L^3) , which may be assigned to the stretching vibration of the azomethine group [45]. Generally this band is shifted to lower frequencies on complexation. Thus, it suggests that coordination of each of the ligand under investigation with the studied metal ions takes place through the nitrogen azomethine. However, the shift of this band to lower frequencies reveals that the bond order of the -C=N- linkage is lowered upon their coordination to the metal ion.

The two bands appeared in the IR spectra of the free ligands and in the IR spectra of the corresponding metal chelates in the regions $1530-1580 \text{ cm}^{-1}$ and $1430-1455 \text{ cm}^{-1}$ are assigned to C=C stretching vibrations of the aromatic system. The observed shifts to lower or higher frequencies may be due to the involvement of C=C band in some mesomeric interactions upon the formation of chelate rings.

In addition, the IR spectra of the complexes of ligands $L^2(R = H)$ and $L^3(R = p$ -OH) have shown the Co-Cl (stretch) bands in the range of 665–820 cm⁻¹ in case of cobalt complexes and the C=O (vs or s) stretch bands, belonging to the acetate group, in the range of 1690–1720 cm⁻¹ in the Ni, Cu, and Zn complexes.

On transfer from the binary to the mixed-ligand complexes, it has been found that the IR spectral bands appearing in the high frequency region have slightly altered in the case of L^1-L^3 mixed-ligand complexes. This behavior indicates that coordination of the Lewis base nitrogen (Im, Py) decreases the electron demand of the positive charge localized on the metal ion.

Based on the foregoing discussion, it could be concluded that the Schiff bases ligands L^2 and L^3 act as monobasic tridentate ONN ligands in 1:1 and 1:1:1 complexes while the ligand $L^1(R = o$ -OH) acts as bibasic tetradentate ONNO ligand in 1:1 and 1:1:1 complexes where an expected fiveand six-membered chelate rings are formed. Hence, one can draw the following structures for the chelates formed.



(1) = 1:1 complexes of Schiff bases L² and L³ (II) = 1:1:1 complexes of Schiff bases L² and L³ (III) = 1:1 complexes of Schiff base L¹ (R=*o*-OH) (IV) = 1:1:1 complexes of Schiff base L¹ (R=*o*-OH) R = H (L²) and *p*-OH (L³) X = Cl² or CH₃COO⁻

Lewis base = imidazole (Im) or pyridine (Py)

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2007.02.023.

References

- [1] M.K. Taylor, J. Reglinski, D. Wallace, Polyheron 23 (2004) 3201.
- [2] S. Yamada, Coordin. Chem. Rev. 192 (1999) 537.
- [3] A.A. Khandar, S.A. Hosseini-Yazdi, S.A. Zarei, Inorg. Chim. Acta 358 (2005) 3211.
- [4] P.K. Mascharak, Coordin. Chem. Rev. 225 (2002) 201.
- [5] J.G. Muller, L.A. Kayser, S.J. Paikoff, V. Duarte, N. Tang, R.J. Perez, S.E. Rokita, C.J. Burrows, Coordin. Chem. Rev. 185–186 (1999) 761.
- [6] D.P. Kessissoglou, Coordin. Chem. Rev. 185-186 (1999) 837.
- [7] J.W. Pyrz, A.L. Roe, L.J. Stern, L. Que, J. Am. Chem. Soc. 107 (1985) 614.
- [8] V.E. Kaasjager, L. Puglisi, E. Bouwman, W.L. Driessen, J. Reedijk, Inorg. Chim. Acta 310 (2000) 183.
- [9] A.S. Al-Shihri, Spectrochim. Acta A 60 (2004) 1189.
- [10] D.S. Frausto, R.J.P. Williams, The Biological Chemistry of the Elements, Clarendon Press, Oxford, 1991.

- [11] W. Kaim, B. Schwederski, Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life, Wiley, New York, 1996.
- [12] N. Daneshvar, A.A. Entezami, A.A. Khandar, L.A. Saghatforoush, Polyheron 22 (2003) 1437.
- [13] X.R. Bu, C.R. Jackson, D.V. Derveer, X.Z. You, Q.J. Meng, R.X. Wang, Polyheron 16 (1997) 2991.
- [14] Y.P. Cai, C.Y. Su, A.W. Xu, B.S. Kang, Y.X. Tong, H.Q. Liu, S. Jie, Polyheron 20 (2001) 657.
- [15] G. Henrici-Oleivé, S. Olivé, Coordination and catalysis, Weinheim, Verlag Chemie, New York, 1977; The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide, Springer, Verlag, Berlin, New York, 1984.
- [16] P.K. Battacharya, Proc. Indian Acad. Sci. (Chem. Sci.) 102 (1990) 247
- [17] A.M. El-Hendawy, A.H. Alkubaisi, A. El-Kourashy, M.M. Shanab, Polyheron 12 (1993) 2343.
- [18] P.J. McCarthy, R.J. Hovey, K. Ueno, A.E. Martell, J. Am. Chem. Soc. 77 (1955) 5820.
- [19] M.H. Abou-El-Wafa, A.A. Mohamed, U.M. Rabie, M.R. Mahmoud, Bull. Fac. Sci. Assiut Univ. 19 (1990) 115.
- [20] M.R. Mahmoud, A.M. El-Nady, M.H. Abou-El-Wafa, U.M. Rabi, J. Chin. Chem. Soc. 37 (1990) 381.
- [21] M.H. Abou-El-Wafa, U.M. Rabie, Rev. Roum. Chim. 46 (2001) 723.
- [22] U.M. Rabie, M.H.M. Abou-El-Wafa, Rev. Roum. Chim. 49 (2004) 863.
- [23] A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, 3rd ed., Longman, London, 1961.
- [24] P. Job, Ann. Chem. Phys. 2 (1928) 113.
- [25] J.H. Yoe, A.L. Jones, Ind. Eng. Chem. Analyst Ed. 16 (1944) 111.

- [26] R.S. Drago, Physical Methods for Chemists, 2nd ed., Saunders College Publishing, Mexico, 1992.
- [27] L.W. Reeves, W.G. Schneider, Can. J. Chem. 35 (1957) 251.
- [28] W.G. Schneider, J. Phys. Chem. 66 (1962) 2653.
- [29] H.H. Jaffe, S.J. Yeh, R.W. Gardner, J. Mol. Spectrosc. 2 (1958) 120; H.H. Jaffe, M. Orehin, Theory and Application of Ultraviolet Spectroscopy, John Willey and Sons, New York, 1982.
- [30] M.A. El-Gahami, Z.A. Khfagi, S.A. Ibrahim, Can. J. Appl. Spectrosc. 36 (1991) 108.
- [31] S.A. Ibrahim, M.S.K. Youssef, Can. J. Chem. 62 (1984) 2841.
- [32] A.R. Grinberg, K.B. Yatsimirsk, Bull. Acad. Sci. USSR. Div. Chem. Sci. (1952) 239.
- [33] H. Irving, R.J.P. Williams, J. Chem. Soc. (1953) 3192.
- [34] I.M. Issa, R.M. Issa, M.S. Abd-All, Egypt. J. Chem. 14 (1971) 81.
- [35] W.J. Geary, Coordin. Chem. Rev. 7 (1971) 81.
- [36] A.B.P. Lever, Inorganic Electronic Spectroscopy, 2nd Ed., Elsevier, Amsterdam, New York, 1984.
- [37] C.K. Jorgensen, Absorption Spectra and Chemical Bonding in Complexes, Addison-Wesly, Pergamon Press, Oxford, 1962.
- [38] M.C. Day, J. Selbin, Theoretical Inorganic Chemistry, Reinhold, New York, 1969.
- [39] M.H. Abou El-Wafa, A.M. Hammam, N.M. Rageh, Synth. React. Inorg. Met. 28 (7) (1998) 1235.
- [40] A.W. Baker, A.T. Shulgin, J. Am. Chem. Soc. 81 (1959) 1523.
- [41] K. Ueno, A.E. Martell, J. Phys. Chem. 60 (1956) 1270.
- [42] H.H. Freedman, J. Am. Chem. Soc. 83 (1961) 2900.
- [43] B.S. Garg, D. Nandan Kumar, Spectrochim. Acta A 59 (2003) 229.
- [44] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1978.
- [45] J.E. Kovacic, Spectrochim. Acta A 23 (1967) 183.