The Preparation and Characterization of Divalent Copper, Nickel, Cobalt and Manganese Complexes of Some Schiff Base Ligands

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ABSTRACT. Co(II), Mn(II), and Cu(II) Complexes of Schiff bases which are derived from the condensation of 3-amino-1,2,4-triazole and salicylaldehyde (L1), p-hydroxy benzaldehyde (L2) and vaniline (L3), have been prepared and investigated by spectrophotometric, conductometric and analytical measurements. L1 is coordinated through the iminic nitrogen and phenolic oxygen atoms. L2 and L3 are bonded through the imino nitrogen and one ring nitrogen atoms as bidentate ligands. Most of these complexes behave as a non-electrolyte while some as a 1:1 electrolyte. The structural configurations have been proposed by the corresponding electronic transition.

Introduction

Schiff bases are important ligands in chemistry, because of their biological aspects and their application in the field of colour photography[1-3]. It was therefore of interest to try to study the complexing properties of the Schiff bases derived from 3-amino-1,2,4-triazole and salicylaldehyde (L1); p-hydroxybenzaldehyde (L2); and vaniline (L3) with Co(II), Mn(II), Ni(II) and Cu(II). In the present paper we report on the preparation and characterization of these complexes. The composition and stability constants of chelates formed in solution as well as the proposed structures are elucidated from the spectral behaviour of the chelates.
Experimental

I. Materials and Solutions

All the chemicals used were of analytical grade reagents. Schiff bases were prepared by condensation of equimolar quantities of the amine and the aldehydes in dry ethanol[4]. The solid ligands obtained were recrystallized from ethanol. The elemental analysis confirmed the suggested structure of these compounds. The ligands prepared have the formula:

\[
\begin{align*}
N & \quad N=CH \\
N & \quad N \\
H & \qquad X
\end{align*}
\]

\(x = \text{o - OH (L)}, \ p\text{-OH (L), } \text{p-OH, m - OCH}_3 (L_3)\).

Stock solutions (1 × 10^{-2} mol. dm^{-3}) of the ligands and the metal salts CoCl_2.6H_2O, MnCl_2.4H_2O, NiCl_2.6H_2O and Cu(NO_3)_2.6H_2O were prepared by dissolving accurately weighed amount of each in ethanol. The metal solutions are standardized by recommended methods of analysis[5]. Solutions for absorbance and conductance measurements of the desired concentration were obtained by accurate dilution of the stock solutions with ethanol.

II. Synthesis of Solid Complexes

The solid complexes were prepared by mixing ethanolic solutions of calculated amounts of the ligand and metal salt. The resulting solution was refluxed for \(\approx 1\) hr. The solid complexes which precipitated were filtered off, washed with ethanol, recrystallized from ethanol and dried. Microanalysis of C, H and N was undertaken by the microanalytical unit, Cairo University (see Table 1).

The conductance values were measured at 25 ± 0.1°C with a WPA CM 25 conductivity meter. The electronic spectra in the UV and visible regions were recorded on a Shimadzu 240 spectrophotometer using 1 cm matched silica cells. The infrared spectra were recorded (4000-200 cm^{-1}) on a Perkin-Elmer 599 B spectrophotometer as KBr disks.

Results and Discussion

The formation of the complexes in ethanolic solution is established on the bases of the shifts in the absorption maxima of the ligands[6].

The band of the free ligands at \(\lambda_{\text{max}}\) 335 (L), 330 (L) or 325 (L_3) nm is red shifted to 405-415 nm (L), 348-435 nm (L) and 365-375 nm (L_3) on complexation to the metals (Fig. 1). Due to the electron withdrawing character of 1,2,4-triazole ring[7], it is suggested that, the free ligand is assigned to excitation of \(\pi\)-electrons of exocyclic and cyclic C = N[3] influenced by the intramolecular charge transfer (CT) originating
from the aryl moiety to the nitrogen hetero ring. Hence, the observed red shift which confirms the complex formation can be attributed to the expected easier (CT) in the complexed ligand as a result of the high positive charge of the coordinated metal ion which facilitates this transition.

The composition of the complexes formed in ethanolic solution between each of Co(II), Mn(II), Ni(II) and Cu(II) and Schiff bases L₁ - L₃, is determined by the spec-
Spectra of $1 \times 10^{-4}$ mol. dm$^{-3}$ of L$_1$ (a), $1.2 \times 10^{-3}$ mol. dm$^{-3}$ of Li with $6 \times 10^{-4}$ mol. dm$^{-3}$ Mn(II) (b), Co(II) (c), Ni(II) (d) and Cu(II) (e).

The conductometric titration results of 25 ml of $1 \times 10^{-3}$ mol. dm$^{-3}$ metal ion solution against ($1 \times 10^{-2}$ mol. dm$^{-3}$) ligand solution (Fig. 4 as a representative example) are in accordance with the results obtained from the spectroscopic measurements.
FIG. 2. Molar ratio method for M-L₃ chelates:

- a - Mn(II), λ = 370 nm, Mn(II) = 1 × 10⁻⁴ mol. dm⁻³
- b - Co(II), λ = 375 nm, Co(II) = 1 × 10⁻⁴ mol. dm⁻³
- c - Ni(II), λ = 365 nm, Ni(II) = 1 × 10⁻⁴ mol. dm⁻³
- d - Cu(II), λ = 368 nm, Cu(II) = 1 × 10⁻⁴ mol. dm⁻³

FIG. 3. Job's continuous variation method for M-L₃ chelates:

- a - Mn(II), λ = 370 nm, total concentration = 2 × 10⁻⁴ mol. dm⁻³
- b - Co(II), λ = 375 nm, total concentration = 1 × 10⁻⁴ mol. dm⁻³
- c - Ni(II), λ = 365 nm, total concentration = 1 × 10⁻⁴ mol. dm⁻³
- d - Cu(II), λ = 368 nm, total concentration = 2 × 10⁻⁴ mol. dm⁻³
The molar conductivities of the synthesized complexes in $1 \times 10^{-3}$ mol. dm$^{-3}$ DMF solution (Table 1) reveal that Cu(II)-L$_1$(1:1), Cu(II)-L$_2$(1:1, 1:2); Co(II), Ni(II)-L$_3$(1:2) and Cu(II)-L$_3$(1:1) complexes are in the range of those given for 1:1 electrolytes. The other complexes behave as a non-electrolytes$^{[10]}$.

![Graph showing specific conductance vs. ml added of ligand](image)

**FIG. 4.** Conductometric titration of 25 ml ($1 \times 10^{-3}$ mol. dm$^{-3}$) of a – Mn(II), b – Co(II), c – Ni(II) and d – Cu(II) with $1 \times 10^{-2}$ mol. dm$^{-3}$ L$_1$.

The conditional stability constants ($K_c$) of the complexes are determined spectrophotometrically$^{[11]}$. The values obtained together with the corresponding free energy of formation are given in Table (2). The results reveal that the stability of the metal chelates for the different ligands varies in the order $L_1 > L_2 > L_3$.

The high tendency of $L_1$ to form complexes relative to the other ligands can be attributed to the formation of high stable six-membered chelate ring. On the other hand, ligands can form less stable four-membered chelate ring. Moreover, the results given in Table (2), show that the stability of the metal chelates for the same ligand are in agreement with the general order of stability of these metal ion complexes$^{[12]}$. Comparison of the principal ir bands of the free ligands with their metal complexes Table (3), show the following:
The Preparation and Characterization of Divalent.

TABLE 2. The stability constants ($K_F$, L·mol$^{-1}$) and energy of formation ($-\Delta G$, Kcal·mol$^{-1}$) for Cu(II), Ni(II), Co(II) and Mn(II) - Schiff base complexes.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>M : L ratio</th>
<th>$L_1$</th>
<th>$L_2$</th>
<th>$L_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_F$</td>
<td>$\Delta G$</td>
<td>$K_F$</td>
<td>$\Delta G$</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>1:1</td>
<td>$9.92 \times 10^6$</td>
<td>9.60</td>
<td>$4.44 \times 10^6$</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>-</td>
<td>-</td>
<td>$2.65 \times 10^{11}$</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>1:1</td>
<td>$9.89 \times 10^{12}$</td>
<td>17.83</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co(II)</td>
<td>1:1</td>
<td>$5.60 \times 10^{12}$</td>
<td>17.50</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>-</td>
<td>-</td>
<td>$6.65 \times 10^3$</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>1:1</td>
<td>$2.59 \times 10^6$</td>
<td>8.80</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$L_1 (x = o-\text{OH}), L_2 (x = p-\text{OH})$ and $L_3 (x = p-\text{OH}, m-\text{OCH}_3)$

1. The free ligand $L_1$ shows a broad band at 3050 cm$^{-1}$ which is assigned to the intramolecular hydrogen bonded $\nu_o$-OH stretching. The disappearance of this band in the ir spectra of $L_1$ complexes indicates that the o-OH group is taking part in complexation. This is supported by the lowering of the phenolic $\nu_C$-O stretching of $L_1$ on complexation. The band observed at 3200 cm$^{-1}$ in the spectra of ligands $L_2$ and $L_3$ can be ascribed to the $\nu_OH$ stretching of p-OH group of the aldehydic moiety. The presence of broad band in the ir spectra of all complexes in the region 3350-3500 cm$^{-1}$, except of Mn(II) with $L_2$ & $L_3$, suggests the presence of coordinated water molecules$^{[13]}$. On the other hand, the phenolic $\nu_C$-O stretching of the ligands $L_2$ and $L_3$ does not show a marked shift on complexation, a result which excludes a coordination through the oxygen atom of the p-OH group.

2. The free ligands show two bands in the regions 1605-1615 cm$^{-1}$ and 1670-1672 cm$^{-1}$. Due to electron withdrawing character of the triazole ring$^{[7]}$, the high frequency band can be assigned to the stretching vibration of the central azomethine $\nu_C = N$ and the lower frequency is due to the stretching of the ring $\nu_C = N$. Thus, in $L_1$ complexes, the ring $\nu_C = N$ does not show a marked shift while the central azomethine $\nu_C = N$ shows a blue shift. This suggests that $L_1$ is coordinated to the metal ion through the central azomethine nitrogen atom. This leads to electronic shifts from ring nitrogen atoms towards the azomethine nitrogen atom. On the other hand, for $L_2$ and $L_3$ complexes, the frequency shift of both ring $\nu_C = N$ and central $\nu_C = N$ suggests that the neutral molecules of $L_2$ and $L_3$ are coordinated to the metal ion as bidentate ligands through one nitrogen atom of triazole ring and the azomethine nitrogen atom. This is supported by the elemental analysis of the solid complexes formed (Table 1).

3. New bands appear in the region 465-320 cm$^{-1}$ may be assigned to $\gamma M \rightarrow N^{[14,15]}$. Thus, according to the previously discussed results, the structural formula of 1:1 of M:L chelates are as follows:
TABLE 3. Infrared spectral band assignments (cm⁻¹) in the region 4000-200 cm⁻¹ of Schiff base triazoles and their complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν OH</th>
<th>ν C = N</th>
<th>ν C - O</th>
<th>ν M - N</th>
</tr>
</thead>
<tbody>
<tr>
<td>L₁ (x = o-OH)</td>
<td>3050</td>
<td>1670</td>
<td>1285</td>
<td>-</td>
</tr>
<tr>
<td>L₁ - Cu(II)</td>
<td>3300(br)</td>
<td>1660</td>
<td>1270</td>
<td>460(w)</td>
</tr>
<tr>
<td>L₁ - Ni(II)</td>
<td>3400(br)</td>
<td>1660</td>
<td>-</td>
<td>359(vs)</td>
</tr>
<tr>
<td>L₁ - Co(II)</td>
<td>3500(br)</td>
<td>1675</td>
<td>1580sh</td>
<td>-</td>
</tr>
<tr>
<td>L₁ - Mn(II)</td>
<td>3460(br)</td>
<td>1675</td>
<td>1270</td>
<td>392(m)</td>
</tr>
<tr>
<td>L₂ (x = p-OH)</td>
<td>1672</td>
<td>1260(s)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>L₂ - Cu(II)</td>
<td>3350(br)</td>
<td>1675</td>
<td>1300(w)</td>
<td>460</td>
</tr>
<tr>
<td>L₂ - Ni(II)</td>
<td>3400(br)</td>
<td>1650(br)</td>
<td>1300(m)</td>
<td>460</td>
</tr>
<tr>
<td>L₂ - Co(II)</td>
<td>3400(br)</td>
<td>1655</td>
<td>1300(m)</td>
<td>460</td>
</tr>
<tr>
<td>L₂ - Mn(II)</td>
<td>1600</td>
<td>1300</td>
<td>460(s)</td>
<td>-</td>
</tr>
<tr>
<td>L₃ (vanilin)</td>
<td>3200(br)</td>
<td>1672</td>
<td>1300</td>
<td>-</td>
</tr>
<tr>
<td>L₃ - Cu(II)</td>
<td>3400(br,s)</td>
<td>1600(s)</td>
<td>-</td>
<td>460</td>
</tr>
<tr>
<td>L₃ - Ni(II)</td>
<td>3400(br)</td>
<td>1675(br)</td>
<td>1310(s)</td>
<td>390</td>
</tr>
<tr>
<td>L₃ - Co(II)</td>
<td>3450(br)</td>
<td>1680</td>
<td>1300(m)</td>
<td>395</td>
</tr>
<tr>
<td>L₃ - Mn(II)</td>
<td>1600</td>
<td>1310(s)</td>
<td>465</td>
<td>-</td>
</tr>
</tbody>
</table>

br = broad, vs = very strong, w = weak, s = strong and m = medium.

\[ \text{I} \quad \text{M - L₁ (1:1)} \]
The electronic spectra of the synthesized complexes in DMF are consistent with tetrahedral geometry for 1:1 complexes, but spectra of the 1:2 (M:L) complexes can be interpreted in terms of an octahedral geometry. The bands centered at about 16000 cm\(^{-1}\) in the spectra of 1:1 complexes are similar to those of other tetrahedral complexes. The spectra of 1:2 complexes show a strong band at around 27000 cm\(^{-1}\) consistent with octahedral geometry. The observed strong band in the region 30000-28570 cm\(^{-1}\) in the spectra of all complexes are due to \(\pi-\pi^*\) transition within the central C = N group.

References

تحضير وتشخيص متراكبات النحاس والنيكل والكوبالت والمنجنيز الثنائية التكافؤ مع بعض قواعد شيف

فاطمة صديق حسن، عديلة السعدي محمد، عزة جبر و علي جاد.
قسم الكيمياء، كلية العلوم، جامعة الملك عبد العزيز، جدة، المملكة العربية السعودية.
و قسم الكيمياء، كلية العلوم بأسوان، جامعة أسوان، مصر.

المستخلص: تم تحضير متراكبات الكوبالت والمنجنيز والنيكل والنحاس مع قاعدة شيف المشفرة من 3- أمين - 4،0،4- نتريゾل والسلسلد (L1)، باراهيدروكسي بنزالد هيد (L2) والفانيدين (L3) وقت دراسة التماثلات باستعمال القياسات الطيفية والتشابهية والتحليلية. وقد وجد أن (L1) يرتبط بذرتي البيتروجين الأميني والأكسجين الفينيل، بينما (L2) و (L3) ترتبط بذرة البيتروجين الأميني وأحد ذرات البيتروجين الحلقي، كليجاند ثنائي المخلب.

معظم هذه المتراكبات تسلك مسلك لا إلكتروليتات، بينما البعض يسلك مسلك إلكتروليت (1: 1).

هذا ودراسة الانتقالات الإلكترونية أمكن اقترح التركيب الثنائي للمتراكبات.