COMPARATIVE STUDY BETWEEN N,N\textsuperscript{2}-BIS (ACETYLACETONE)-O-PHENYLENEDIAMINE AND (MONOACETYLACETONE)-O-PHENYLENEDIAMINE SCHIFF BASE COMPLEXES

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ABSTRACT

Co(II), Ni(II) and Cu(II) complexes formed from the Schiff base [(2Z,2Z)-4-((2-aminophenyl)imino-pent-2-en-2-ol), were prepared in situ and characterized on the basis of elemental analyses, magnetism, UV-vis., IR and ESR spectra. Thermal analyses of the complexes were studied in order to confirm the proposed structures and determine their thermal stability. Comparison between geometries, ESR and thermal studies obtained from direct condensation and in situ preparation of complexes were discussed. The in situ data show that the Schiff base form complexes with 1:1 (metal: ligand) stoichiometry with Cu(II) and Ni(II) ions compared to 2:1 (metal: ligand) formed from direct condensation between Schiff base and metal ions. However, the Co(II) in situ complex formed 1:2 (metal: ligand) stoichiometry. Square-planar geometry was suggested for the Cu(II) and Ni(II) in situ complexes, while, octahedral geometry was suggested for the Co(II) complex. The ESR spectrum of the in situ Cu(II) complex was isotropic to suggest a geometry involving grossly misaligned tetragonal axes. The thermal behavior of the complexes showed a good agreement with the formulae suggested from the analytical data. Thermal decomposition of the complexes took place in several stages. The order of stability was [Cu L(H\textsubscript{2}O)\textsubscript{3}H\textsubscript{2}O > NiL\textsubscript{2}H\textsubscript{2}O > CoL\textsubscript{2}H\textsubscript{2}O]. The thermodynamic parameters, energy of activation \(\Delta E^*\), enthalpy of activation \(\Delta H^*\), order of reaction \(n\) and entropy of activation \(\Delta S^*\) of the complexes were calculated. All the reactions were found to be first order. The high values of activation energies reveal the high stability of these complexes.

Key words: Schiff-base, IR, UV-Vis., ESR, TG, DTA.

INTRODUCTION

The chelating abilities of Schiff bases and their analytical applications have attracted remarkable attention [1-5]. O-Phenylenediamine (o-PDA) is used in the copper catalyzed synthesis of quinoxalines [6]. o-PDA is also suitable for removing elemental sulfur in mining ores, and removing aldehyde color formers in polymers. Polymeric plasticized membrane electrode based on Bis(o-phenylenediamine)-Cu(II) (Cu(II)BOPD) complex has been investigated as iodide selective electrode exhibiting anti-Hofmeister selectivity pattern [7]. Moreover, it is used as a pharmaceutical intermediate in pharmaceuticals industry [8]. Schiff bases of (o-PDA) are used in the synthesis of insecticides, dyestuff fungicides, corrosion inhibitors and pigments. A large number of Schiff bases and their complexes are of significant interest and attention are drawn to them because of their biological activity including anti-tumor, antibacterial, fungidal and anti-carcinogenic properties [1,9]. The wide range of uses of o-PDA and its Schiff bases urged us to study its Schiff base with acetyl acetone by using a different method of preparation, the in situ method, which was successfully performed by others [10], in order to throw light on the structure, mode of bonding, spectral and thermal properties of this type of compounds and to compare between this study and previous studies.

EXPERIMENTAL

All the chemicals and solvents used for the syntheses were reagent grade. All solvents were dried and purified before being used. Elemental analyses (C, H, N) were performed by the Micro analytical unit at Cairo University using HP Model MS-5988. The metal ion content was determined using atomic absorption spectrophotometer 850-Fisher Jarrell ash computer controlled. Infrared spectra were recorded on a Perkin-Elmer FT-IR type 1650 spectrophotometer in wavenumber region 4000-200 cm\(^{-1}\). The spectra were recorded as KBr pellets. The nujol muff eironic absorption spectra in the 200-1000 nm range were obtained using a Shimadzu AA-6800 spectrophotometer. The thermo-gravimetric analyses (TGA and DTA) was carried out in a dynamic nitrogen atmosphere (20 mL min\(^{-1}\)), with a heating rate of 10 °C min\(^{-1}\) using LINSELS STA PT 1000 thermal analyzer. The ESR (X-band) spectrum for the poly-crystalline sample was recorded at room temperature using a Varian E-12 spectrometer and DPPH as an external standard.

Preparation of the Schiff base ligand:

(monoacetylacetone-o-phenylenediamine Schiff base)

The ligand (C\(_3\)H\(_7\)N\(_2\)O\(_3\)) was prepared by condensation of 0.108 g (1.00 mmol) o-phenylenediamine dissolved in EtOH to 0.100 g (1.00 mmol) of acetyl acetone dissolved in EtOH solvent and the reaction mixture stirred for 3h at 60°C. A brown precipitate was separated, filtered, washed several times with ethanol and dried in vacuum (m.p. 150°C).

Preparation of the metal complexes

All the complexes were prepared in situ using the following method. To a 0.108 g (1.00 mmol) of the o-phenylenediamine dissolved in 30 mL of EtOH was added a solution of 0.100 g (1.00 mmol) of acetylacetone dissolved in 30 mL EtOH and the reaction mixture was refluxed for 1hour. A (1.00 mmol) of the metal salts Cu(AcO)\(_2\).H\(_2\)O, 0.20 g, CoCl\(_2\).6H\(_2\)O 0.24 g and Ni(OAc)\(_2\).4H\(_2\)O , 0.25g in 15 ml ethanol was added drop wise with continuous stirring. The mixtures were then filtered, washed with cold ethanol, followed by diethyl ether and dried in vacuum desiccators.

The colors and elemental analyses of all the compounds are presented in Table 1.

RESULTS AND DISCUSSION

Infrared spectra

In order to clarify the mode of bonding and the metal ion effect on ligand, the IR spectra of the free ligand and its metal chelates were studied, Figure 1, Table 2. FT-IR spectrum of the ligand revealed absorption bands in the region of stretching vibrations of O-H and N-H bonds. Thus, the absorption band at 3449 cm\(^{-1}\) was assigned to a free NH group, which depicts the condensation of one acetyl acetone molecule (and not two molecules) to phenylene-diamine, thus forming monoacetylacetone-o-phenylenediamine Schiff base (I). The Schiff base ligand is characterized by strong bands at 1634 and 1298 cm\(^{-1}\), which are ascribed to the stretching vibrations of C=N (imine) and C-O groups, respectively [12,13].

### Table 1

<table>
<thead>
<tr>
<th>Complex</th>
<th>Preparation Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I)</td>
<td>Schiff-base</td>
</tr>
</tbody>
</table>

### Key points

- The ligand (C\(_3\)H\(_7\)N\(_2\)O\(_3\)) was prepared by condensation.
- Infrared spectra were recorded to study the bonding mode.
- Elemental analyses were carried out using HP Model MS-5988.
- The complexes were characterized using UV-vis., IR and ESR spectra.
- Thermal analyses were conducted to determine the thermal stability.

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to –OH bending [12,14]. The out-of-plane C-H deformation of the phenyl ring was observed at 756 cm⁻¹ [14]. Comparing the IR spectrum of Schiff base ligand prepared by that prepared by Sadek et.al [9] and Ismail et.al [15] where there was a lack of NH₂ band and thus attributed to the formation of \(N,N'-\)bis (acylcetone)-o-phenylenediamine and behaving as a dianionic tetradentate ligand [15].

**Table 1.** Elemental analyses of the metal complexes.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Elemental Analyses Calculated (%)</th>
<th>% M</th>
</tr>
</thead>
<tbody>
<tr>
<td>([CuL(H₂O)]\cdot3H₂O)</td>
<td>C_{11}H_{24}N_{10}Cu (Brown)</td>
<td>40.798 (41.022) 6.182 (5.901) 8.654 (8.907) 19.638 (20.026)</td>
</tr>
<tr>
<td>([CoL₂H₂O]\cdot2H₂O)</td>
<td>C_{15}H_{22}N_{10}Co (violet)</td>
<td>58.287 (58.472) 5.740 (6.117) 12.364 (12.292) 13.010 (13.428)</td>
</tr>
<tr>
<td>([NiL₂H₂O]\cdot2H₂O)</td>
<td>C_{17}H_{26}N_{10}Ni (green)</td>
<td>49.865 (50.210) 5.288 (5.382) 10.577 (10.214) 22.179 (21.680)</td>
</tr>
</tbody>
</table>

The Cu(II), Co(II) and Ni(II) complexes gave broad bands at 3460, 3444 and 3448 cm⁻¹ respectively, assigned either to coordinated water [16,17], or to –OH group, whereas, the band at 3396 cm⁻¹ disappeared, together with the shifting of ν N-H bending band from 1504 cm⁻¹ in the ligand to 1518 cm⁻¹ upon complexation indicating the contribution of the NH₂ group in complex formation. Two ν C=N bands were observed in the Co(II) complex, one of them is at about the same position as that in the ligand, whereas the second band is blue shifted indicating the coordination of one of the two C=N groups of the two ligands to the metal ion. ν C=N band is red shifted in the Ni(II) complex, also indicating its coordination to the metal ion. The ν C-O band at 1298 cm⁻¹ is shifted to lower frequency by ~ (20-42 cm⁻¹), thus it is suggested that the –OH group is deprotonated and oxygen atom of this (C-O) group is bonded to the metal ions. New bands in the ranges 356–420 cm⁻¹ for the Cu, Co and Ni complexes, due to ν M-N and ν M-O [18] were detected. The IR suggests that ( mono acetylacetone-o-phenylenediamine ) coordinates to the metal ions in a tridentate fashion through NNO; whereas N,N'-bis (acylcetone)-o-phenylenediamine coordinated through NNOO tetradeutate mode [15]. Ismail et.al have shown that metal ions have coordinated to water, enolic –OH and C=N (imino N atoms).

**Table 2.** Characteristic IR and electronic absorption spectral data of the ligand and its metal complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν O-H cm⁻¹</th>
<th>ν NH₂ cm⁻¹</th>
<th>ν C=N cm⁻¹</th>
<th>ν C-O cm⁻¹</th>
<th>ν N-H bending cm⁻¹</th>
<th>ν M-O or M-N</th>
<th>(\lambda_{max}) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>3449</td>
<td>3396(b)</td>
<td>1634</td>
<td>1298</td>
<td>1504</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>([CuL(H₂O)]\cdot3H₂O)</td>
<td>3460(b)</td>
<td>-</td>
<td>1630</td>
<td>1322</td>
<td>1518</td>
<td>364, 393</td>
<td>525</td>
</tr>
<tr>
<td>([CoL₁₂H₂O]\cdot2H₂O)</td>
<td>3444</td>
<td>-</td>
<td>1637</td>
<td>1278</td>
<td>1519</td>
<td>356, 394</td>
<td>513,635, 677</td>
</tr>
<tr>
<td>([NiL₂H₂O]\cdot2H₂O)</td>
<td>3448</td>
<td>-</td>
<td>1654</td>
<td>1256</td>
<td>1518</td>
<td>364, 393</td>
<td>430, 590</td>
</tr>
</tbody>
</table>

**Electronic Absorption Spectra**

The UV-visible absorption spectrum of the \([CuL(H₂O)]\cdot3H₂O\) prepared in situ, showed a band at 525 nm which may be assigned to \(\lambda_{a} \rightarrow \lambda_{b} \) and is consistent with a square planar[19,20] or a distorted tetragonal [21] geometry for this complex. The NiL₂H₂O showed two bands at 430 and 590 nm assigned as \(\lambda_{a} \rightarrow \lambda_{b} \) and \(\lambda_{a} \rightarrow \lambda_{c} \) attributed to the presence of this complex in the square-planar structure [12,12,20,22]. As for the cobalt complex CoL₂H₂O, three bands were observed at 513, 635 and 677 nm respectively assignable to the \(\lambda_{a} \rightarrow \lambda_{b} \) transitions in an octahedral structure. The Ni(II) complex reported in this work, is diamagnetic confirming consequently, four coordinate, square planar geometry [24,25] ruling out the presence of paramagnetic, tetrahedral form. The room temperature magnetic moments of the copper(II) complexes are expected to be higher than the spin-only value of 1.73 B.M. as a result of an orbital contribution and spin-orbit coupling, which mixes in the higher terms into the ground term. As a result, 1.90-2.20 B.M. magnetic values are usually observed for mononuclear copper(II) complexes, regardless of stereo-chemistry [26]. A magnetic moment was found to be 1.884 B.M which lies within the expected value for one electron. The Co(II) complex has a magnetic moment of 5.12 B.M. corresponding to an octahedral geometry.

**Thermogravimetric (TGA) and differential thermal analysis (DTA):**

Thermogravimetric (TG) and differential thermal analyses (DTA) for the metal complexes were carried out within the temperature range from 25-1000 °C at a heating rate of 10 °C/min in N₂ atmosphere. It was noted that the thermal behaviour of Co(II), Ni(II) and Cu(II) complexes depends on the nature of the metal ion, Figure 2., Table 3. The thermal behavior of the complexes showed good agreement with the formulae suggested from the analytical data, Table 3, Figure 2. The thermal decomposition of the complexes took place in several stages. The TG curve of \([CuL(H₂O)]\cdot3H₂O\) complex showed a mass loss of 16.300 % (calc. 16.690 %) between 55-240 °C due to the loss of three water.
molecules in the first stage. Between the temperature 240-350 °C, a percentage loss of 45.551 was observed (calculated 45.743 %) due to the loss of C$_8$H$_6$N$_2$ + the coordinated water molecule and the corresponding activation energy amounted to 103.925 KJ/mol and finally a percentage loss of 32.770 (calculated 33.00 %) due to the decomposition of the complex to CuO + 2C in the temperature range 350-480 °C, with corresponding activation energy amounting to 189.143 KJ/mol. A remaining of 5.380 % is attributed to the evolution of a CH$_4$ molecule (4.95%) during the process of decomposition.

Table (3): TGA of the studied complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>T / °C</th>
<th>% mass loss Found (calc.)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CuL.(H$_2$O)] 3H$_2$O</td>
<td>55-240</td>
<td>16.300 (16.690)</td>
<td>3 H$_2$O</td>
</tr>
<tr>
<td></td>
<td>240-350</td>
<td>45.551 (45.743)</td>
<td>C$_8$H$_6$N$_2$ + H$_2$O</td>
</tr>
<tr>
<td></td>
<td>350-480</td>
<td>32.770 (33.00)</td>
<td>CuO + 2C</td>
</tr>
<tr>
<td>[CoL$_2$.H$_2$O]</td>
<td>68-269</td>
<td>28.030 (27.150)</td>
<td>C$_6$H$_5$N$_2$ + H$_2$O</td>
</tr>
<tr>
<td></td>
<td>269-450</td>
<td>24.913 (25.607)</td>
<td>C$_6$H$_4$N$_2$ + C</td>
</tr>
<tr>
<td></td>
<td>450-617</td>
<td>46.720 (47.365)</td>
<td>Co + C$_8$H$_16$ + CO$_2$</td>
</tr>
<tr>
<td>[NiL.H$_2$O]</td>
<td>204-289</td>
<td>45.332 (46.055)</td>
<td>C$_6$H$_4$N$_2$ + H$_2$O</td>
</tr>
<tr>
<td></td>
<td>289-434</td>
<td>38.380 (38.840)</td>
<td>NiO + C$_3$H$_6$</td>
</tr>
</tbody>
</table>

On the other hand, The TGA of Cu(II) complex [Cu$_2$(L)(H$_2$O)$_6$](SO$_4$)$_2$·2H$_2$O (2) prepared by Ismail et.al [15] shows loss in weight within the temperature range 50–180 °C, due to removal of the lattice and coordinated water molecules. The dehydrated complex is thermally stable up to 360 °C, after which SO$_4^{2−}$ ions were removed. Finally the complex undergoes decomposition of the organic ligand at 800 °C, whereupon the final product [Cu$_2$(O)$_2$(CO)$_2$] is formed.

Comparing the decomposition pattern of the two different copper complexes, it seems that the latter complex is decomposed at a higher temperature due to its presence as a dimer.

The DTA of [CuL(H$_2$O)].3H$_2$O showed one broad splitted endothermic peak centered at 90 and 150 °C, together with two small exothermic peaks at 170 and 200 °C which is in accord with the dehydration of outer and decomposition of the coordinated water molecules. Two other strong exothermic peaks were observed at 325°C and 420 °C due to the decomposition of the rest of the complex.

The TG of [NiL.H$_2$O] showed the mass loss in two steps only. The first step 204-289 °C owing to the loss of C$_6$H$_4$N$_2$ + coordinated H$_2$O (found: 45.288 %, calculated: 46.055 %). The second step between the temperature range 289-434 °C attributed to the loss of NiO + C$_2$H$_4$ molecule (found: 38.380 %, calculated 38.840 %). A (16.338%) which is remaining is attributed to the evolution of C$_3$H$_6$ molecule (15.850%).

The DTA curve exhibits two exothermic peaks. The first is at 117 °C is due to the loss of the coordinated water molecule to the Ni(II) ion [27,28].
together with the loss of part of the organic ligand. The second peak which is a split peak centered at 210, 240°C is due to the decomposition of the rest of the complex.

As for the cobalt complex CoL₃.H₂O, three steps were detected. In the first step, between 68-260°C, the loss was found to be 28.030% (calculated: 27.150%) due to the loss of C₄H₆N₂ + the coordinated H₂O molecule with activation energy 156.968 KJ/mol. Then between 269-450°C, the % loss found was to be 24.983% (calculated 25.607%) owing to the loss of the second C₄H₆N₂ + C molecule, with an activation energy of 149.984 KJ/mol. The third step between 450-617°C was attributed to the decomposition of the rest of the complex to Co + CO + C₂H₆ molecules, (found: 47.850%, calculated 47.395%) with activation energy 76.455 KJ/mol.

The DTA of Col₃.H₂O gave exothermic peaks at 80, 150, 220, 340, 425, 510 and 680°C due to the decomposition of the complex [29].

There were no data available in the literature to compare between them and the prepared Co(II) and Ni(II) complexes.

From the DTA data, the thermodynamic parameters ΔE*'(activation energy), ΔH*(enthalpy of activation), n(order of the reaction) and ΔS*(entropy) were calculated by the Horowitz-Metzger equations [30,31] and the results are shown in Table 4. The values of the collision factor, Z, were calculated based on the following relation:

$$Z = \Delta S' \exp(\Delta H' / R T_0)$$

where R= molar gas constant, T0 = the rate of heating (10 K/min), ΔS' = the entropy of activation, K and h are the Boltzman and Planck's constants, respectively. The change of the entropy ΔS' values for all complexes are of the same magnitude within the range (-0.226 - 0.243 KJ / mol K). The negative values for the entropies of activation indicate that the activated complexes have more ordered structure than the reactants and the reactions are slower than normal [32]. The negative values of ΔS' make the dissociation process non-spontaneous. All the reactions were found to be approximately first order. The high values of activation energies reveal the high stability of chelation in these complexes [33]. Comparing ΔE* of [CuL(H₂O)].3H₂O with that of [NiL.H₂O], it was found that the former possess a higher value, since as the radius of the metal ion decreases, the binding between it and the ligand increases. ΔE* of the Co(II) complex is more ordered than the reactants and/or the reactions are slower than normal [32]. The negative activation indicate that the activated complexes have more ordered structure than the reactants and/or the reactions are slow, whereupon, all the reactions are slow, whereupon, they obtained positive ΔH* values which means that the decomposition processes are endothermic.

X-band EPR:
The X-band EPR spectrum of the [CuL(H₂O)].3H₂O complex in the solid-state was measured at room temperature and gave a disymmetric isotropic broad band having no hyperfine structure, Figure 3. When there is a slow-motion regime, the rotational diffusion is slow, so that the spectrum loses its similarity to the isotropic limiting case. The lines broaden and distort [34]. Also, the broadening can be due to dipolar exchange and unresolved hyperfine interactions in the solid state [35] or due to the tumbling motion of the molecules [36]. The calculated g-value was found to be equal to 2.145. Figure (2), to suggest a geometry involving grossly misaligned tetragonal axes [37]. Aₙ = 139 x 10⁶ cm⁻¹. On the other hand, [CuL(H₂O)].3H₂O (2) [15], prepared by Ismail et. al. gave two g-values, gₓ ≈ gᵧ which indicates that the unpaired electron is predominantly in the dₓz-orybital giving 3B₁g as the ground state. The observed data show that the g-values are >2.0023 and hence the metal–ligand bonding in this complex is essentially covalent.

The proposed structures for the in situ prepared complexes are shown in Figure 4.

![Figure (3): X-band EPR spectrum of the [CuL(H₂O)].3H₂O complex in the solid-state.](image)

CONCLUSION

1. Preparation of Schiff base and its complexes derived from o-phenylenediamine and acetylacetone were performed in situ in order to compare between them and those prepared previously by normal condensation method.
2. It was found that the in situ method gives (monoacetylacetone)-o-phenylenediamine Schiff base compared to N,N'-bis (acetylacetone)-o-phenylenediamine obtained by condensation method.
3. The activation energy for decomposing the in situ (mono) copper (II) complex is lower than that of the dimeric complex prepared by condensation which was expected due to the presence of two Cu(II) ions.
The proposed structures for complexes:
(a) [CuL.H₂O].3H₂O  (b) [CoL₂.H₂O]  (c)  [NiL.H₂O]

REFERENCES