Synthesis, Characterisation and Structural Derivation of Ni(II) Complexes with Diammine Derivative of 1, 2, 4-Triazole Schiff’s Base

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Abstract: Synthesis of Ni(II) Complexes with ligand 4-(2,4-diaminobenzaldimino)-3,5-dimercapto-1,2,4-triazole(L) as [NiL3], H2O, X= Pyridine, pyridine-oxide, Morpholine and picoline. Ligand [L] is synthesized by the condensation of 3,5-dimercapto-1,2,4-triazole and 2,4-diaminobenzaldehyde. The complexes are synthesized by refluxing the ligand and Ni(II) in presence of base. The complexes are characterized by the elemental analyses, magnetic moment measurement, IR, and spectral data analyses. The physical measurements and spectral data analyses and interpolation show that the ligand act as tridentate and coordinated through N and S group ligand. The ligand is a Schiff’s base derivative. The complexes of ligand and Ni(II) analyses and the structures of the complexes suggested.

Keywords: 1,2,4-triazole, 4-(2,4-diaminobenzaldimino)-3,5-dimercapto-1,2,4-triazole, Schiff’s base, IR, and Spectral data

1. Introduction

The paper is related to the study on the coordination behaviour of the Nitrogen and Sulphur bidwntate system. The ligand possess mercapti system. So a comprehensive survey of coordination behaviour of C=S, C=N and –SH is required. Nitrogen donor of many complexes studied. Thiourea and its derivatives are the simplest ligands where as many metal complexes with N and S donor system are also studied. There are numbers of works available on the coordination behaviour of Schiff’s bases of aldimes and ketamines types. The Schiff’s bases characterised by the presence of C=N double bond and are excellent chelating ligands and acyclic. The Schiff’s base metal complexes have a very special role in inorganic chemistry. They are important because they are synthesized in different fields. They are also found to have a number of pharmaceutical utility. The coordination behaviour of chelates of Schiff bases containing nitrogen, sulphur and oxygen donor atoms works already reported. Ni(II) complexes with tridented ONO donor Schiff’s base derivative derived by refluxing ethanolic solution. The low molar conductances indicate non-electrolytic nature of complexes. The µeff values of the complexes of Ni(II) indicate the octahedral around Ni(II) ions supported by electronic spectra. Metal complexes with Schiff’s base ligands derived from aromatic aldehyde with aromatic amines have been reported recently. Solution ability constants of the complexes of Schiff’s bases with various metal ions have been intensively studied. Polymetallic complexes of Fe(II), Co(II), Ni(II) and Cu(II) with ONO tridentate Schiff’s bases have been reported. Physico-Chemical studies on Cr(II), Co(II), Ni(II), and Cu(II) complexes with bidentate Schiff’s bases have been reported. The complexes have been synthesised and characterised on the basis of analytical, infrared and electronic spectral-studies-octahedral structures for Cr(III), Co(II), and Ni(II) and a square planar structure for Cu(II) complexes have been suggested. The Co(II), Ni(II) and Cu(II) complexes are non-electrolytic while Cr(III) complexes behave as electrolytic. Synthesis, spectral and magnetic studies of Ni(II) complexes of heterocyclic Schiff’s bases have been reported. The value of Racah parameter B and C were calculated by using different sitting procedures as described by Konig, to study the nephelauxetic effect which describes the fact that B values lower on complexation whereas free metal ion values are relatively higher. Jorgensen attributed the nephelauxetic effect to central field covalency and symmetry restricted covalency. The magnetic moment data coupled with electronic spectral data have suggested octahedral geometry to all the complexes. The complexes of Co(II), Ni(II) and Cu(II) with Schiff’s bases ligands prepared by condensing pyrol-2-carboxaldehyde with m-nitroaniline and p-nitroaniline complexes. The complexes derived from m-nitroaniline are ionic, paramagnetic and octahedral and the complexes of m-nitroaniline are non-ionic, paramagnetic, tetrahedral Co(II), Cu(II) and square planar Ni(II). The fungicidal activity of ligands and complexes reported against the fungicausing damage to vegetative plants at different concentrations in the form of solution or suspensions. The metal complexes reported more fungitoxic than the free ligands which is observed for four coordinated complexes of Co, Ni, and Cu with p-nitroaniline. It may be due to unsaturation of coordination number. The fungicidal activity of metal chelates were found in order of Cu, Ni, Co. The role in biological processes, of mixed ligand complexes of metal ions, Cyanopyridines with different aryl and alkyl groups found to possess various biological activities. The metal complexes of Schiff’s bases are the subject of intensive research due to their novel structural features, spectral, magnetic properties, their industrial and biological importance are much accountable. The biological activities, catalytic properties and analytical applications can be correlated to the structure of Schiff’s bases. A brief survey of work already reported as the complexes of Schiff’s bases of substituted 5-triazoles. There is great pharmacological importance of d-metal complexes of Schiff’s bases obtained from substituted 1,2,4-triazole. The Schiff’s base obtained from benzaldehyde and 4-amino-5,5-mercaptopo-5-triazole...
has been reported to form complexes with some metal ions. S.N. Dubey and Beena Kausik synthesized 4-amino-3-mercaptop-5-triazole and 5-mercaptop-3-n-propyl-5-salicylaldoxime-5-triazole and prepared complexes with Ni(II). The IR spectra of ligand and complexes have suggested the bidentate (N and S donor complexes with Ni(II). The octahedral geometry of Ni(II) complexes represented by the electronic spectral data coupled with magnetic values.

2. Experiment

All chemicals were used of AR grade. The compound 4-(2,4-diaminobenzaldehyde)-3,5-dimercapto-1,2,4-triazole was prepared by literature.

4-(2,4-diaminobenzaldehyde)-3,5-dimercapto-1,2,4-triazole is prepared by the condensation of thiocarbohydrazine (10.5 g, 0.1 M) and carbonsulphide (11.5 ml, 0.20 M). The mixture is taken in round bottom flask fitted with leibinger condenser containing 100 ml pyridine and refluxed on an oil bath both for one hour, from the boiling solution a precipitate is form and after cooling pale yellow prism are obtained. The pyridinium salt (4.6 gm) obtained is dissolved in hot water (20 ml) and conc. HCl (3 ml) is added. The coloured rods of free ligand separated out. The melting point of crude product is found to be 216-217 °C. The preparation of ligand is achieved by refluxing the mixture containing equimolar quantities of 4-amino-3,5-dimercapto-1,2,4-triazole and 2,4-diaminobenzaldehyde in ethanol for one hour. The volume of mixture is allowed to stand over right at room temperature. The yellow crystals are obtained. The compound is recrystallised from ethanol (C9H10N6S2).

The complexes of Ni(II) are prepared by mixing the ethanolic solution of hydrated Ni(II) separately with (0.5 ml) salt and ethanolic solution of ligand (3.6 gm, 0.5 ml). Both solution of 1:1 molar ratio is mixed together. The mixture is refluxed on water bath for 2-3 hours. On refluxion, the complexes were separated. The mixture was cooled to room temperature, filtered and washed with water and dried. The complexes and the ligand gave the satisfactory M, N and S analysis.

The alcoholic solution of 0.0051 M metal chloride and the alcoholic solution of 0.01 M ligand were mixed together with about 2 ml of appropriate base and the content were refluxed on water bath at low temperature. On cooling, the precipitate separated out. The contents on dilution with water insured the complete precipitation. The precipitate was filtered, washed with water, followed by several portion of alcoholic water and aqueous base solution. The precipitate was dried in desiccator over anhydrous CaCl2. On elemental analysis all complexes gave satisfactory of the elemental measurement. The magnetic measurement of the complexes were made on Gouy balance using appropriate calibrant. The IR recorded in KBr disc in 4000-3500 cm⁻¹. The electronic spectra of the complexes were recorded by UV-Vis-spectrophotometer.

3. Result and Discussion

The formation of complexes represented by the physical measurements as magnetic moment measurements values, electronic spectra and IR values, change from free state of metal ions ligand. The magnetic moment values are tabulated as;

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Complexes</th>
<th>( \mu (BM) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[NiL3H3O]</td>
<td>2.85</td>
</tr>
<tr>
<td>2</td>
<td>[NiL3Py]</td>
<td>2.79</td>
</tr>
<tr>
<td>3</td>
<td>[NiL(Mor)]</td>
<td>2.84</td>
</tr>
<tr>
<td>4</td>
<td>[NiL(α-Pic)]</td>
<td>2.85</td>
</tr>
<tr>
<td>5</td>
<td>[NiL(α-Pic-O)]</td>
<td>2.78</td>
</tr>
</tbody>
</table>

Ni(II) complexes generally forms four coordinated tetrahedral or planar and six coordinated octahedral complexes depending upon the electronegativity and geometry of the ligand. If the complex is diamagnetic, it can have either square planar or trigonal bipyramidal configuration. If the complex is paramagnetic, then the configuration is octahedral geometry. In an octahedral field the triplet \( T_2^g \) lies lower in energy than the doublet \( E_g \). The electronic configuration in ground state is \( (t_2g)^2(E_g)^{2n} \) in which only one arrangement of the electrons and therefore non-degenerate and not liable to Jahn-Teller distortion. The six ligands are identical one may expect the complexes to be quite regular. The two \( e_g \) electrons are spin parallel and since there is no resultant orbital angular momentum once the degeneracy of the d-orbitals is lifted, magnetic moment should be close to the spin only value of 2.8 BM. The first excited triplet level \( (T_2^g) \) has essentially
of mixed ligand complexes are lower than high spin Octahedral Ni(II) complexes. The magnetic moment values are straightforward and are in the range expected for studies on the spectral behaviour of complexes with D₄h symmetry. The expected range of second and third ligand field strength and expected to fall in the range of absorption bands are:

The complexe compounds of divalent Ni(II) have been obtained in different stereochemistry but the complexes with coordination number four and six are most common. The Ni(II) ion has ⁵⁻ ground state and the next higher state having the same multiplicity is ⁶⁻. The transition in octahedral geometry in weak field are as: ²A₂g(F)→5T₂g(F), 3υ₁→(i)

²A₂g(F)→3T₁g(F), 3υ₂→(ii)

²A₂g(F)→3T₁g(P), 3υ₃→(iii)

The value of ²A₂g(F) → ³T₂g(F) is directly taken to be ligand field strength and expected to fall in the range of 8000-11,500 cm⁻¹. 

3. Electronic Spectra of Complexes

The electronic spectra of Ni(II) complexes under investigation have been studied, the bands are obvious in the region 200-450 nm, however, the bands are absent in the region beyond 450 or 470 nm, clearly show the absence of tetrahedral geometry of complexes. Had, the complexes possess tetrahedral geometry, they would have exhibited the strong absorption band in the region 650-800 nm. Hence, octahedral geometry for the complexes is predicted. The band positions are not clearly observed due to obscuring by ligand absorption and charge transfer bands. The band in the region 220-260 nm are assigned to ³υ₁→ ³π* whereas the bands in the region 320-480 nm are assigned to combination of ³υ₁→ ³π* and ¹A₂g(F)→ ³T₂g(P). The bands ~ 460 nm are assigned as combination of bands of charge transfer and ¹A₂g(F)→ ³T₂g(P).

IR Spectral Study of Complexes

<table>
<thead>
<tr>
<th>S.N. o.</th>
<th>Complexes</th>
<th>NH (cm⁻¹)</th>
<th>OH (cm⁻¹)</th>
<th>SH (cm⁻¹)</th>
<th>M⁻N (cm⁻¹)</th>
<th>M⁻S (cm⁻¹)</th>
<th>M⁻O (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>C₆H₄N₅S₂</td>
<td>326 5</td>
<td>256 5</td>
<td>310 275</td>
<td>450</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>[NiL₃(H₂O)]</td>
<td>286 0</td>
<td>255 5</td>
<td>300 270</td>
<td>-</td>
<td>270</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>[NiL₃]</td>
<td>286 0</td>
<td>255 5</td>
<td>310 275</td>
<td>-</td>
<td>270</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>[NiL₃(Mor)]</td>
<td>255 5</td>
<td>254 5</td>
<td>315 270</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>[NiL₃(OH)]</td>
<td>254 5</td>
<td>315 270</td>
<td>-</td>
<td>270</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is somewhat different to analyse the spectra of tetrahedral complexes because of the effect of spin orbital coupling. The reliable identifying characteristic of Tf complexes have been suggested. The first criterion for distinguishing between two cases in the value of extinction coefficient of the band at maximum. Practically, all tetrahedral complexes have rather intense blue or green colour due to presence of an absorption band in the red part of the visible region.

The electronic spectra of Ni(II) complexes under investigation have been studied, the bands are obvious in the region 200-450 nm, however, the bands are absent in the region beyond 450 or 470 nm, clearly show the absence of tetrahedral geometry of complexes. Had, the complexes possess tetrahedral geometry, they would have exhibited the strong absorption band in the region 650-800 nm. Hence, octahedral geometry for the complexes is predicted. The band positions are not clearly observed due to obscuring by ligand absorption and charge transfer bands. The band in the region 220-260 nm are assigned to ³υ₁→ ³π* whereas the bands in the region 320-480 nm are assigned to combination of ³υ₁→ ³π* and ¹A₂g(F)→ ³T₂g(P). The bands ~ 460 nm are assigned as combination of bands of charge transfer and ¹A₂g(F)→ ³T₂g(P).
Important absorption bands in IR spectrum of the ligand and their assignment:

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Frequencies (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>3270</td>
<td>(N-H) stretching</td>
</tr>
<tr>
<td>2.</td>
<td>3025</td>
<td>(C-H) stretching</td>
</tr>
<tr>
<td>3.</td>
<td>2565</td>
<td>(S-H) stretching</td>
</tr>
<tr>
<td>4.</td>
<td>1525 1445</td>
<td>Skeletal vibration of benzene ring</td>
</tr>
<tr>
<td>5.</td>
<td>760</td>
<td>(C-H)</td>
</tr>
<tr>
<td>6.</td>
<td>700</td>
<td>N (~C-S)</td>
</tr>
</tbody>
</table>

IR spectra of ligand and complexes have been studied and their band positions of important active groups and those of M – N and M – S have been tabulated. The band positions have been assigned on the basis of works reported earlier$^{55-66}$. Thesharp and strong bands near 3270 cm$^{-1}$, 3025 cm$^{-1}$, 700 cm$^{-1}$ have been assigned to stretching ($\nu$(vib)) vibrations. The lower values of -NH bands are assigned due to H – bonding — intramolecular / intermolecular$^{61-66}$. In complexes, the -NH frequency is lower which may be due to the coordination of one of the three - NH$_2$ in complex formation and others remain free. The aromatic ring vibrations are observed as expected in the spectra of the complexes. The bands in the lower range near 315, 275 cm$^{-1}$ are assigned to M-N and M-S respectively.

5. Conclusion

From the elemental analyses, magnetic moment measurements, electronic and IR spectral studies, Author concluded that Ni(II) forms the octahedral complexes with the ligand 4-(2,4-diaminobenzaldehydeiminio)-3,5-dimercaptop-1,2,4-triazole(L) and in presence of suitable base. The Author on the basis of physical measurements proposed the structure of the complexes.

Acknowledgement

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References


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