CHAPTER-V

SYNTHESIS AND CHARACTERIZATION OF THE COMPLEXES OF SPIRONOLACTONE WITH Mn(II), Co(II), Ni(II) AND Cu(II)
V.1 Introduction

Spironolactone or Aldactone (7α-Acetylthio-3-oxo-17α-pregn-4-ene-21,17β-carbolactone) is a steroidal potassium-sparing diuretic and extensively used in medical practices as a multi target drug. Its backbone is steroidal nucleus with four rings. It is also included in World Health Organization’s list of essential medicines. It acts as competitive antagonist of the potent endogenous mineral-corticosteroid aldosterone i.e. it competes for the cytoplasmic aldosterone receptor. It increases the secretion of water and sodium, while decreasing the excretion of potassium, by competing for the aldosterone sensitive Na⁺/K⁺ channel in the distal tubule of the nephron.

In the present study spironolactone have been used as one of the potent bio-active ligand which has three possible coordinating sites viz. (i) carbonyl oxygen of lactone ring (ii) carbonyl oxygen of thioacetyl group (iii) carbonyl oxygen of α,β-unsaturated ring. This chapter deals with the synthesis, physico-chemical studies, magnetic studies and the spectral characterization of the complexes of spironolactone with transition metal ions Mn(II), Co(II), Ni(II) and Cu(II).
V.1.1 Medicinal Uses of Spironolactone

Widespread use of spironolactone has found it to be a safe drug to treat high blood pressure, heart failure, hypokalemia, edema, skin and hair diseases, transgender hormone therapy and various other medical conditions. It is a specific antagonist of aldosterone and is used to treat primary and secondary hyper-aldosteronism and oedematous states where secondary hyper-aldosteronism is involved (i.e. congestive heart failure, liver cirrhosis, the nephrotic syndrome and severe ascites). Spironolactone is also effective in the treatment of essential hypertension. Spironolactone in association with thiazide diuretics treats hypertension and in association with furosemide treats bronchopulmonary dyspepsia. The therapeutic mechanism of action of spironolactone involves binding to intercellular mineralocorticoids receptors (MRs) in kidney epithelial cells, thereby inhibiting the binding of aldosterone. Spironolactone has antiandrogen effects through two mechanisms: (i) it blocks the action of dihydrotestosterone on its intracellular receptor; and (ii) it interrupts ovarian steroidogenesis, lowering the levels of testosterone and other androgens. Thus, spironolactone is commonly used in the treatment of hirsutism and androgenetic alopecia in women (1-4).

Vaclavik et al. have investigated the effect of spironolactone in patient with arterial hypertension in relation to baseline blood pressure and secondary causes of hypertension and found that spironolactone treatment is effective to a similar extent both in patient with and without a secondary cause of hypertension and regardless of the baseline value of systolic blood pressure. Less effect of spironolactone have been found in patients with the highest baseline diastolic blood pressure (5).
Nakhjavani et al. have studied the short term effect of spironolactone on blood lipid profile and concluded that a daily dose of 100 mg of spironolactone may have adverse effects on the lipid profile of women with hirsutism via decreasing HDL and increasing LDL. Treatment strategies with spironolactone need to consider its metabolic consequences, particularly in subjects with baseline metabolic disorders and dyslipidaemia (6).

Pitt et al. have studied the effect of spironolactone on morbidity and mortality in patients with severe heart failure and found that treatment with spironolactone reduced the risk of death from all cardiac causes, hospitalization for cardiac causes and the combined end point of death from cardiac causes or hospitalization for cardiac causes among patients who had severe heart failure as a result of left ventricular systolic dysfunction and who were receiving standard therapy including an angiotensin-converting-enzyme (ACE) inhibitor. Spironolactone also improves the symptoms of heart failure, as measured by changes in the New York Heart Association functional class (7).

Chany et al. have conducted a retrospective study on treatment of 110 acne vulgaris women patients using spironolactone. Results of the study showed that that acne improved in the vast majority of the women and completely cleared in a large percentage during treatment with spironolactone, which further strengthens the evidence that spironolactone is an effective treatment for women with acne. Patients showed 73.1%, 75.9%, and 77.6% improvements on the face, chest, and back, respectively, which supports that spironolactone is equally effective in treating acne in multiple areas of the body. Improvements in acne regardless of the body site occurred in 85% of patients with 55% of...
patients who were completely clear and 26% of patients who were almost clear during treatment (8).

V.1.2 Side Effects of Use of Spironolactone

Even though spironolactone is a potential drug and find uses in many complex medical situations then after it has many adverse effects on human health. The most common side effect of spironolactone is urinary frequency. Other general side effects include dehydration, hyponatremia (low sodium levels), mild hypotension (low blood pressure), ataxia (muscle incoordination), drowsiness, dizziness, dry skin, and rashes. Spironolactone increases the serum levels of digoxin and interferes with digoxin assay. A number of endocrine effects have also been reported, the most common of which is gynecomastia. Because it reduces androgen levels and directly blocks androgen signaling, spironolactone can, in men, cause breast tenderness, gynecomastia (male breast development), and feminization in general, as well as testicular atrophy, reversibly reduced fertility, and loss of sexual potency. In women, spironolactone can cause menstrual irregularities, breast tenderness, amenorrhea, cloasma and breast enlargement (9-11).

The most important potential side effect of spironolactone is hyperkalemia (high potassium levels), which, in severe cases, can be life-threatening. Hyperkalemia in these people can present as a non anion-gap metabolic acidosis (12). Spironolactone may put people at a heightened risk for gastrointestinal issues like nausea, vomiting, diarrhea, cramping, agranulocytosis and gastritis. In addition, there has been some evidence suggesting an association between uses of the medication and bleeding from the stomach and duodenum, though a causal relationship between
the two has not been established. Also, spironolactone has been shown to be immunosuppressive in the treatment of sarcoidosis (13-15).

**V.1.3 Polymorphism of Spironolactone**

Spironolactone is known to crystallize from different solvents in different polymorphic forms and to undergo structural rearrangements on heating (16). Spironolactone is a steroidal diuretic having variable and incomplete oral behaviour due to its low water solubility and slow dissolution rate. Different crystalline forms of spironolactone have different solubility, dissolution rates, and as a result different bioavailability (17).

El-Dalsh et al. have reported the preparation of different solid forms of spironolactone by crystallization from acrilonitrile, absolute alcohol, chloroform and ethyl acetate. Dissolution rates of these solid forms in water-ethanol mixtures have also been found different (18).

Salole et al. have reported the preparation of three polymorphic and five solvated crystalline forms of spironolactone which were distinguishable by IR spectral, thermo-gravimetric and differential thermal analysis. These authors have also been concluded that the ability of spironolactone to recrystallize in different solid forms is due to its molecular flexibility (19).

Five solvates of spironolactone have been prepared by Beckstead and co-authors by crystallization from absolute methanol, acetonitrile, absolute ethanol, ethyl acetate and benzene. Characterization of the solvates was done using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and by FT-Raman Spectroscopy (20).
Agafonov et al. have also been obtained single crystal of two polymorphic and four solvated crystalline forms of spironolactone using different solvents and reported their crystallographic parameters, morphology and symmetry. The stability and transformation of each type of crystal have been studied by DSC, TGA and X-ray diffraction analysis (21).

V.2 Experimental

V.2.1 Materials

The synthesis of various ligands used during study has been described in chapter II. In order to synthesize complexes of spironolactone with Mn(II), Co(II), Ni(II) and Cu(II), A.R. grade MnCl$_2$.4H$_2$O, CoCl$_2$.6H$_2$O, NiCl$_2$.6H$_2$O and CuCl$_2$ were procured from Sigma-Aldrich with other solvents and used as received without further purification.

V.2.2 Synthesis of Complexes of Spironolactone with Mn(II), Co(II), Ni(II) and Cu(II).

To synthesize these complexes two types of methods i.e. conventional method and microwave irradiation method were used. A comparison between these methods is shown in Table V.3.A.

(a) Synthesis by Conventional Method

In this method hot ethanolic solution (20 ml) of spironolactone (2 mmol, 0.832 g) and saturated hot ethanolic solution of 1mmol of the respective metal chloride (0.198 g of MnCl$_2$.4H$_2$O, 0.238 g of NiCl$_2$.6H$_2$O, 0.238 g of CoCl$_2$.6H$_2$O and 0.135 g of CuCl$_2$) were mixed with constant stirring. The reaction mixture was refluxed for 8-10 hours at 80° - 90° C. The progress of reaction was monitored by Thin Layer
Chromatography. On cooling colored complexes were precipitated out. They were filtered, washed with 50% ethanol and water mixtures, dried in vacuum desiccators and recrystallized in ethanol. The Physico-chemical data of obtained solid metal complexes are shown in table V.3.A.

(b) Synthesis by Microwave Method

As an alternative, a novel method of synthesis has been developed as per the principles of green chemistry, in which, either the reaction mixture was irradiated in a domestic microwave at 600 W for 2-5 minutes on alumina bed or reaction mixture in the solvent or the slurry of reaction mixture was exposed in a microwave reactor at 600 W maintaining different time intervals with respect to occasional and or definite inspection of TLC data. The mixture was cooled to room temperature and poured into ice chilled methanol and dried in vacuum over P₂O₅ (22).

The solid precipitate obtained in both the methods was separated and crystallized. Crystals were purified and recrystallized with alcohol and dried under vacuum.

V.3 Results and Discussion

V.3.1 Physical Measurements

The complexes of Spironolactone (SPL) with late 3d transition metals Mn(II), Co(II), Ni(II) and Cu(II) are coloured powdrous material and found stable at room temperatures for a long period of time. These complexes are soluble in DMSO, DMF, partially soluble in ethyl alcohol, methyl alcohol and insoluble in water and other solvents. The elemental estimations gave satisfactory results. The physical and analytical data of complexes are given in Table V.3.A.
V.3.2 IR Spectral Analysis

Characteristic infrared absorption frequencies for ligand spironolactone (SPL) and its metal complexes are reported in the Table V.3.B with their tentative assignments and the respective vibrational spectra are shown in figures V.3.B.1 to V.3.B.4. A careful study and comparison of infrared spectrum of free ligand and the metal complexes reveals that the ligand behaves as monodentate and the metal ion is coordinated through the oxygen atom of C=O group of thioacetyl group.

In case of complexes, out of three C=O stretching absorption bands, the two $\nu$(C=O)$^a$ and $\nu$(C=O)$^b$ (due to C=O stretch of lactone ring and C=O) stretch of $\alpha$, $\beta$-unsaturated ring) appear in the same frequency region (1768-1770 cm$^{-1}$) as they were in free ligand whereas the third C=O stretching absorption, $\nu$(C=O)$^c$ (due to C=O stretch of thioacetyl group) shifts to lower frequency region from 1647 to 1660 cm$^{-1}$ (23-26). This negative shifting of 33 to 46 cm$^{-1}$ in $\nu$(C=O)$^c$ clearly indicates the participation of carbonyl oxygen of thioacetyl group in metal coordination (27). This observation was further supported by positive shifting of 31-53 cm$^{-1}$ in the characteristic C-S stretching absorption, which appears at 637 cm$^{-1}$ in ligand and at 676, 668, 682 and 690 cm$^{-1}$ in case of Mn(II), Co(II), Ni(II) and Cu(II), respectively.

The IR spectra of all complexes under study showed a broad band with medium intensity in the range 3390-3500 cm$^{-1}$. These bands correspond to the O-H stretch and confirm the presence of water in the complexes. Moreover the IR spectra of complexes exhibited characteristic bands at approximately 850 cm$^{-1}$ and 550 cm$^{-1}$ assigned to rocking and wagging modes of the coordinated water molecule (28). The other characteristic peaks of the ligand viz. (C=C) stretch of $\alpha$, $\beta$-unsaturated ring, (C-O) stretch of cyclic ester group of lactone ring, (C-
H) deformation in-plane (scissoring) are found almost at the same range in all complexes which also supports the conclusions of vibrational spectral analysis.

These observations support the final structural conclusions of the complexes and the mode of bonding in them.

**V.3.3 Electronic Spectral and Magnetic Studies**

Electronic spectra of all the metal complexes of spironolactone (SPL) are recorded using MeOH, DMSO or DMF as solvent and at $10^{-3}$ to $10^{-2}$ molar concentration of samples and presented in the Figures V.3.C.1 to V.3.C.4. Characteristic absorbance bands, their tentative assignments and the results of magnetic studies are reported in Tables V.3.C. The magnetic and electronic spectral data are in relevance with proposed geometry of the complexes.

**Mn(II) Complex**

The electronic transition from the ground state term $^6A_1$ of high spin tetrahedral Mn(II) to higher energy terms are spin forbidden as the higher energy terms are of different (quartet) multiplicity. The observed spectra of the manganese (II) complex with the ligand exhibit bands at 18083, 21276, 25641 and 27027 cm$^{-1}$ assigned tentatively to the transitions: $^6A_1 \rightarrow ^4T_1$ (G), $^6A_1 \rightarrow ^4T_2$ (G), $^6A_1 \rightarrow ^4A_1, ^4E$ (G) and $^6A_1 \rightarrow ^4T_2$ (D) respectively. These electronic spectral transitions of manganese complex with the ligands are typical of tetrahedral environment around the manganese (29-31).

The absorption bands at 25641, and 27027 cm$^{-1}$ are almost merged into each other which clearly reveals that the excited energy terms $^4T_2$ (D) and $^4A_1, ^4E$ (G) lies very closely. The highest energy transition $^6A_1 \rightarrow ^4T_2$ (D) is generally merge with ligand transitions. No
distinction could be made between internal absorption of ligand, charge transfer and d-d bands above wavenumber 30000 cm\(^{-1}\) (32-33).

Complex of bivalent manganese are known in both high spin (S=5/2) and low spin (S = 1/2) states. Because of the additional stability of the half filled d-orbitals manganese (II) generally forms high spin complex which has an orbitally degenerate \(^6\)S ground state term and the spin only magnetic moment of 5.9 ± 0.1 BM is expected which will be independent of the temperature and of stereochemistry (34).

The magnetic susceptibility measurements have been carried out in the polycrystalline state at room temperature and the results are given in Table V.3.C. The manganese (II) complex with SPL has magnetic moment value 5.94 BM indicating the presence of five unpaired electrons and hence it is high spin complex with tetrahedrally coordinated manganese (35).

**Co(II) Complex**

In an octahedral field of Co (II), \(d^7\)-system, three spin allowed transitions are anticipated because of splitting of the free ion, ground \(^4\)F and the accompanying \(^4\)P term. The ground state term, for high spin octahedral Co(II) (\(d^7\)), is \(^4\)T\(_{1g}\). However in the high spin octahedral systems the \(^4\)A\(_{2g}\) (F) level is usually close to the \(^4\)T\(_{1g}\) (P) level and transition to these levels are close together. All transitions in Co(II) complexes are spin allowed transitions unlike Mn(II) complex (36).

Co(II) complex of SPL exhibit absorption bands at 10621, 18099 and 19417 cm\(^{-1}\) which are attributed to the transitions \(^4\)T\(_{1g}\)(F) \(\rightarrow\) \(^4\)T\(_{2g}\)(F) (\(v_1\)), \(^4\)T\(_{1g}\)(F) \(\rightarrow\) \(^4\)A\(_{2g}\)(F) (\(v_2\)) and \(^4\)T\(_{1g}\)(F) \(\rightarrow\) \(^4\)T\(_{1g}\)(P) (\(v_3\)) respectively, indicative of octahedral geometries for the Co(II) complex. The highest energy transition \(^4\)T\(_{1g}\)(F) \(\rightarrow\) \(^4\)T\(_{1g}\)(P) (\(v_3\)) is generally merge with ligand
internal transitions. Since $^4A_{2g}$ state is derived from a $t_{2g}^3 \ e_g^4$ electronic configuration and the $^4T_{1g}(F)$ ground state is derived from $t_{2g}^5 \ e_g^2$ configuration, the $^4T_{1g}(F) \rightarrow ^4A_{2g}(F) (\nu_2)$ transition is essentially a two electron process, it is therefore weaker by about a factor of $10^{-2}$ than the other transitions and often appears as a shoulder. One characteristic transition for octahedral environment around Co(II) ion is $^4T_{1g}(F) \rightarrow ^4T_{2g}(F) (\nu_1)$which generally occurs in the near IR region. (37-39).

The magnetic susceptibility measurements have been carried out in the polycrystalline state at room temperature and the results are presented in Table V.3.C. The observed magnetic moment of the complex lie in the range 4.70-5.81 BM, which correspond to three unpaired electrons. This indicates a quartet ground state term $^4F$ ($S = 3/2$) which is the case of Co (II) ($d^7$) and it may be obtained weak field i.e. high spin octahedral configuration (40-41).

**Ni(II) Complex**

Ni(II) is the only common $d^8$ ion and its spectroscopic and magnetic properties have accordingly been extensive studied. In a cubic field three spin allowed transitions are expected because of splitting of free ion, ground $^3F$ term and the presence of the $^3P$ term. Ni(II) is a $d^8$ system where $^3A_{2g}(F)$ is the ground state. The excited states with same multiplicity are $^3T_{2g}(F)$, $^3T_{1g}$ (F) and $^3T_{1g}$ (P) (42). The electronic absorption spectra of the Ni (II) complexes were recorded at room temperature using DMSO as solvent.

The electronic spectrum of the present Ni(II) complex of spironolactone as ligand showed three spin allowed bands at 12853 ($\nu_1$), 16542 ($\nu_2$) and 26109 cm$^{-1}$ ($\nu_3$) which are assignable to tentative assignments viz. $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow$
$^3T_{1g}$ (P). These transitions suggests the octahedral geometry of the Ni(II) complex. The lowest energy transition ($\nu_1$) occurs almost in the near IR region. (43-45).

The magnetic susceptibility measurements have been carried out in the polycrystalline state at room temperature and the results are presented in Table V.3.C. The magnetic behaviour of bivalent nickel complexes depends upon the nature of the ligand and geometry of the complexes. Ni(II) complex show the magnetic moment value in the range of 3.08-3.3 BM which is correspond to two unpaired electrons and consistency with octahedral environment around Ni(II). The present Ni(II) complex exhibit paramagnetic behaviour due to the presence of two unpaired electrons (46-47).

**Cu(II) Complex**

Cu (II) gives rise to only one free ion ground term $^2D$, which is twofold spin and orbitally degenerate. $^2D$ free ion term is split into ground state $^2E_g$ and excited state $^2T_{2g}$ terms. In a perfect octahedral $d^9$ complex, a single absorption band with good intensity corresponding to the spin allowed transition $^2E_g \rightarrow ^2T_{2g}$ is expected in the region 11000-16000 cm$^{-1}$. On distortion to $D_{4h}$ symmetry, these terms further splits into $^2B_{1g}$, $^2A_{1g}$, $^2E_g$ and $^2B_{2g}$ levels. Excitation can now occur from the ground state $^2B_{1g}$ to the $^2A_{1g}$, $^2E_g$ and $^2B_{2g}$. In case of extreme distortion leading to the square planar geometry a multiple band with three components corresponding to the three transitions is observed (48-49).

In the present case of Cu(II) complex with spironolactone a single asymmetric broad band, in the region 9891-14285 cm$^{-1}$, is observed. The broadness of the band confirms the splitting of octahedral free ion terms ($^2E_g$ and $^2T_{2g}$) into new terms $^2B_{1g}$, $^2A_{1g}$, $^2E_g$ and $^2B_{2g}$ on distortion to $D_{4h}$.
symmetry and the expected three transitions \( ^2B_{1g} \rightarrow ^2A_{1g} \), \( ^2B_{1g} \rightarrow ^2E_g \) and \( ^2B_{1g} \rightarrow ^2B_{2g} \). The broadness of the band may be because these transitions are similar in energy thus giving rise to only one broad band. These data suggest John-Teller distortion i.e. a tetragonally distorted octahedral geometry around Cu(II) ion (50-51).

A high intense peak in the range 25773-26109 cm\(^{-1}\) present in electronic spectra of both the Cu (II) complexes which is assigned for Cl→ Cu(II) charge transfer band (LMCT) (52-53).

The magnetic susceptibility measurements have been carried out in the polycrystalline state at room temperature and the results are presented in Table V.3.C. The magnetic behaviour of bivalent copper complexes depends upon the nature of the ligand and geometry of the complexes. The Cu (II) complex of Spironolactone show magnetic moment in the range 1.87-1.92 BM, is slightly higher than the spin-only value 1.73 BM expected for one unpaired electron, which offers possibility of an octahedral geometry (54-55).
Table- V.3.A
Physico-chemical Data of Complexes of SPL with Mn(II), Co(II), Ni(II) and Cu(II)
(C.M. = Conventional method, M.M. = Microwave method)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Complexes</th>
<th>Color</th>
<th>M.P. (°C)</th>
<th>Reaction period</th>
<th>Yield %</th>
<th>Elemental analysis Calculated (Found) %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C.M. Hrs. M.M. min.</td>
<td>C.M. M.M. C</td>
<td>H</td>
</tr>
<tr>
<td>1</td>
<td>[Mn(H₂O)₂(SPL)₂]Cl₂</td>
<td>Brown</td>
<td>208±2</td>
<td>8.5 3.4</td>
<td>38 56</td>
<td>57.93 (57.83) 6.89 (6.81)</td>
</tr>
<tr>
<td>2</td>
<td>[Co(H₂O)₄(SPL)₂]Cl₂</td>
<td>Dark green</td>
<td>210±1</td>
<td>9.0 3.2</td>
<td>43 55</td>
<td>55.69 (55.49) 7.02 (6.89)</td>
</tr>
<tr>
<td>3</td>
<td>[Ni(H₂O)₄(SPL)₂]Cl₂</td>
<td>Dark Green</td>
<td>205±1</td>
<td>9.4 4.3</td>
<td>41 58</td>
<td>55.70 (55.63) 7.02 (6.92)</td>
</tr>
<tr>
<td>4</td>
<td>[Cu(H₂O)₄(SPL)₂]Cl₂</td>
<td>Bluish Black</td>
<td>202±2</td>
<td>10.0 4.5</td>
<td>37 59</td>
<td>55.44 (55.36) 6.98 (6.89)</td>
</tr>
</tbody>
</table>
Table- V.3.B
Vibrational Spectral Assignments (cm⁻¹) of Complexes of SPL with Mn(II), Co(II), Ni(II) and Cu(II)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Ligand/Complexes</th>
<th>Carbonyl groups</th>
<th>ν(C=O) ¹</th>
<th>ν(C=O) ²</th>
<th>ν(C=O) ³</th>
<th>ν(C=C) ⁴</th>
<th>ν(C-O) ⁵</th>
<th>ν(C-S) ⁶</th>
<th>δ(C-H)</th>
<th>ν(O-H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SPL</td>
<td></td>
<td>1769</td>
<td>1673</td>
<td>1693</td>
<td>1616</td>
<td>1240</td>
<td>637</td>
<td>1458</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>[Mn(H₂O)₂(SPL)₂]Cl₂</td>
<td>1768</td>
<td>1670</td>
<td>1660</td>
<td>1618</td>
<td>1237</td>
<td>676</td>
<td>1460</td>
<td>3419</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>[Co(H₂O)₄(SPL)₂]Cl₂</td>
<td>1769</td>
<td>1676</td>
<td>1653</td>
<td>1619</td>
<td>1227</td>
<td>668</td>
<td>1456</td>
<td>3405</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>[Ni(H₂O)₄(SPL)₂]Cl₂</td>
<td>1768</td>
<td>1671</td>
<td>1654</td>
<td>1616</td>
<td>1245</td>
<td>682</td>
<td>1456</td>
<td>3394</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>[Cu(H₂O)₄(SPL)₂]Cl₂</td>
<td>1770</td>
<td>1670</td>
<td>1647</td>
<td>1617</td>
<td>1248</td>
<td>690</td>
<td>1452</td>
<td>3445</td>
<td></td>
</tr>
</tbody>
</table>

¹ = (C=O) stretch of lactone ring, ² = (C=O) stretch of α, β-unsaturated ring, ³ = (C=O) stretch of thioacetyl group,
⁴ = (C=C) stretch of α, β-unsaturated ring, ⁵ = (C-O) stretch of cyclic ester group of lactone ring, ⁶ = (C-S) stretch of thioacetyl group, ⁷ = (C-H) deformation in-plane (scissoring).
### Table- V.3.C

Magnetic Moments and Electronic Spectral Data of Complexes of SPL with Mn(II), Co(II), Ni(II) and Cu(II)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Complex</th>
<th>Rf value</th>
<th>$\mu_{\text{eff}}$ (BM)</th>
<th>Electronic Spectral Bands (cm$^{-1}$)</th>
<th>Tentative assignments</th>
<th>Expected Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Mn(H$_2$O)$_2$(SPL)$_2$]Cl$_2$</td>
<td>(0.85)$^a$</td>
<td>5.94</td>
<td>18083, 21276, 25641, 27027</td>
<td>$^6$A$_1$→$^3$T$_1$ (G), $^6$A$_1$→$^3$T$_2$ (G)</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$^6$A$_1$→$^4$A$_1$, $^4$E (G), $^6$A$_1$→$^4$T$_2$ (D)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>[Co(H$_2$O)$_4$(SPL)$_2$]Cl$_2$</td>
<td>(0.68)$^c$</td>
<td>4.91</td>
<td>10621, 16625, 19417</td>
<td>$^4$T$_1g$(F)→$^4$T$_2g$ (F),$^4$T$_1g$(F)→$^4$A$_2g$ (F)</td>
<td>Octahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$^4$T$_1g$(F)→$^4$T$_1g$ (P)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>[Ni(H$_2$O)$_4$(SPL)$_2$]Cl$_2$</td>
<td>(0.75)$^b$</td>
<td>3.18</td>
<td>12853, 16542, 26109</td>
<td>$^3$A$_{2g}$(F)→$^3$T$<em>2g$(F),$^3$A$</em>{2g}$ (F)→$^3$T$_1g$ (F)</td>
<td>Octahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$^3$A$_{2g}$ (F)→$^3$T$_1g$ (P)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>[Cu(H$_2$O)$_4$(SPL)$_2$]Cl$_2$</td>
<td>(0.70)$^e$</td>
<td>1.86</td>
<td>9891-14285 cm$^{-1}$ (Asymmetric broad band)</td>
<td>$^2$B$<em>{1g}$→$^2$A$</em>{1g}$, $^2$B$<em>{1g}$→$^2$B$</em>{2g}$, $^2$B$_{1g}$→$^2$E$_g$</td>
<td>Distorted Octahedral</td>
</tr>
</tbody>
</table>

Figure V.3.B.1 Vibrational Spectrum of $[\text{Mn(H}_2\text{O)}_2(\text{SPL})_2]\text{Cl}_2$
Figure V.3.B.2 Vibrational Spectrum of \([\text{Co(H}_2\text{O)}_4\text{(SPL)}_2]\text{Cl}_2\)
Figure V.3.B.3 Vibrational Spectrum of $[\text{Ni(H}_2\text{O)}_4\text{(SPL)}_2]\text{Cl}_2$
Figure V.3.B.4 Vibrational Spectrum of [Cu(H₂O)₄(SPL)₂]Cl₂
Figure V.3.C.1 UV-visible Spectrum of $[\text{Mn(H}_2\text{O)}_2(\text{SPL})_2]\text{Cl}_2$
Figure V.3.C.2 UV-visible Spectrum of $[\text{Co(H}_2\text{O)}_4\text{(SPL)}_2]\text{Cl}_2$
Figure V.3.C.3 UV-visible Spectrum of \([\text{Ni(H}_2\text{O)}_4\text{(SPL)}_2]\text{Cl}_2\)
Figure V.3.C.4 UV-visible Spectrum of $[\text{Cu(H}_2\text{O)}_4\text{(SPL)}_2\text{]}\text{Cl}_2$
V.4 Conclusion

IR spectral studies have shown that spironolactone behaves as monodentate ligand in complexes with Mn(II), Co(II), Ni(II) and Cu(II) where metal coordination occurs through the carbonyl oxygen atom of thioacetyl group. Vibrational spectroscopic analysis also confirms the presence of coordinated water molecules in all complexes. The electronic spectral assignments are characteristic to the geometries adopted by metal ion in ligand environments. On the basis of the tentative electronic spectral assignments it is inferred that the Mn(II) complex of spironolactone possess tetrahedral geometry, Co(II) and Ni(II) complexes adopts octahedral geometry while the Cu(II) complex found to have tetragonally distorted octahedral environment around the metal ion. These structural conclusions based on spectral studies were further supported by the observed value of magnetic moments and the physico-chemical studies.

Magnetic susceptibility measurements at room temperature exhibit paramagnetic character for all complexes. The complexes synthesized by novel green method are at par with conventional synthesis and in all cases yield was found to be better than conventional synthesis.
Figure V.4.1 Tentative Structure of Complex of SPL with Mn(II)

Figure V.4.2 Tentative Structure of Complexes of SPL where M= Co(II), Ni(II) and Cu(II)
V.5 References


