Chapter 9

Zn(II) COMPLEXES WITH TRIDENTATE N₃S LIGAND; SYNTHESSES, SPECTROSCOPIC AND ANTIMICROBIAL PROPERTIES.

9.1 Introduction

Zinc with atomic number 30, atomic weight 65.39 and oxidation state (II) is an essential element in all living systems and plays a structural role in many proteins and enzymes. It is recognized that transcription factors regulate gene expression and the essential feature is binding to a regulatory protein in the recognition sequence of the gene. Many proteins have been found to have a zinc-containing motif that serves to bind DNA embedded in their structure. In the relevance of zinc to DM, zinc is known to be present in insulin, coordinated by three nitrogen atoms from histidines and three water molecules in an irregular octahedral environment, which is also believed to have a functional structure [1]. Surprisingly, zinc was found to have important physiological and pharmaceutical functions involving insulin-mimetic activity. In 1980, Coulston and Dandona first reported the insulin-mimetic activity of zinc ion. Although zinc(II) ion has been revealed to have an insulin-mimetic activity, zinc complexes have never been examined. Glucose normalizing effects of zinc complexes are reported [2].

Zn is regarded as one of the main healing minerals, and is found concentrated in hair, nails, nervous system, skin, liver, bones, blood and pancreas. There is an increasing amount of interest in the role of zinc in appetite control since patients with anorexia nervosa often have a low serum zinc level [3]. It is also a constituent of at least 100 enzymes in the body (25 of which specifically for food digestion) e.g. Zn forms part of the enzyme carbonic anhydrase which is required for the utilization and transport of
carbon dioxide in the body functions as an anti-oxidant, maintains normal taste and smell, essential for health of the prostate gland in males, aids wound healing and burns, boosts immunity aids, normal absorption of vitamins in the formation of insulin (component of insulin and the pancreatic enzyme), assists in the maintenance of the body's acid / alkaline balance, important for brain tissue formation, vital role in protein synthesis and promotes cell division. Deficiencies of zinc are usually the result of dietary insufficiency and deficiency causes excessive sweating, mal absorption of food, loss of taste and smell, baldness, glossitis (inflammation of tongue) stomatitis (inflammation of mouth), blepharitis (inflammation of eyelids), paronchyma (inflammation of nail/nailbed), sterility, low sperm count, dwarfism, delayed wound healing, Splenomegaly / hepatomegaly (enlarged spleen and liver) retarded growth delayed sexual maturity and white spots on nails [4]

The thiosemicarbazones of 2-acetylpyridine as well as their complexes with metals are biologically and pharmacologically active and have been the object of a considerable amount of research. There have nevertheless been relatively few studies of the coordination of thiosemicarbazones to non-transition metals, and of the biological activity of the resulting coordination compounds. The complexes of thiosemicarbazones with zinc metals constitute an especially attractive topic in view of marked differences among group 12 metals as regards both chemical behaviour and biological activity [5].

A growing number of reviews and publications have highlighted the utility of organometallic complexes in which organic chromophores are bound to metal centers for second harmonic generation. Molecular polarizabilities are frequently larger for the metallic complex than for the free chromophore because of metal-to ligand or ligand to metal charge transfer and because of the involvement of the orbitals on metals and these metal centers may act as anchors in the engineering of three-dimensional geometries giving rise to octupolar molecules. Moreover, the combination of organic and inorganic elements affords materials of relatively high mechanical and thermal stability, as is also observed for organic chromophores in inorganic host matrixes [6].
This Chapter describes the syntheses of three Zn(II) complexes with tridentate N-N-S donor thiosemicarbazone, characterization of them by various spectral techniques and their antimicrobial activities.

9.2 Experimental

9.2.1 Materials and method
The synthesis of HL4M and its characterizations are described in Chapter 2. Various Zn salts (S. D. Fine, G. R Grade) were used as received. Zinc perchlorate heptahydrate was prepared by treating Zn(II) carbonate with 1:1 perchloric acid, followed by filtration concentrating the filtrate and recrystallisation. The solvents were purified by standard procedures before use.

9.2.2 Measurements
Details of various physical measurements and characterization techniques are given in Chapter 2. Details of antibacterial studies are reported in Chapter 3. The complexes were analyzed for their metal content by EDTA titration after decomposition with a mixture of perchloric acid and hydrochloric acid followed by Conc. hydrochloric acid alone.

9.2.3 Syntheses of complexes
The general method of syntheses of the Zn(II) complexes is as described below.

To a hot solution of (25 mL) of HL4M (0.05 mmol) in hot methanol was added an equimolar amount of the appropriate metal salt dissolved or suspended in methanol. The mixture was stirred for about 1 week. The yellow coloured solid so formed was filtered out, washed with methanol, ether and vacuum dried and kept over P₄O₁₀.

The complexes that we synthesized are [Zn(L4M)Cl], 43; [Zn(L4M)OAc].H₂O,44 and [Zn(L4M)ClO₄],45.
9.3 Results and discussion

The colours yields, partial elemental analyses, stoichiometries of complexes are presented in Table 9.1.

The complexes are diamagnetic and yellow in colour, insoluble in most of polar solvents but soluble in organic solvents such as dimethylformamide, dimethyl sulphoxide. The complexes are mono ligated with a 1:1:1 ratio of metal ion, ligand and gegenions. The colour of complexes indicates that the thiosemicarbazones functional group determines the colour of the solid. The analytical data indicates that the complexes present one monoanionic tridentate ligand per metal ion and fourth coordination position is occupied by mono or polyatomic anion. The molar conductivities in dimethylformamide, suggest that the complexes are non-electrolytes.

9.3.1 IR spectral investigation

Table 9.2 lists the main IR bands of HL4M and their complexes in the 4000-200 cm\(^{-1}\) region.

The spectra of the ligand shows a band of maximum intensity at 3280 cm\(^{-1}\) which is assigned to v(N-H). Absence of any broad band around 2400-2600 cm\(^{-1}\) confirms that the ligand exists in thioketo form. The \(^1\)H NMR further confirms this, which shows no signal for the S-H group. The sharp band at 1627 cm\(^{-1}\) which was assigned to v(C=N) in the ligand has shifted to lower energy and v(N-N) to higher energy in complexes suggesting coordination of azomethine nitrogen to Zn.

In the complexes v(N-H) band disappears and there appears a weak band at 674 cm\(^{-1}\) assigned to v(C-S) stretching. Vibrational coupling among thioamide groups are distributed at ca 1535, 1422, 1371 and 892 cm\(^{-1}\) identified as thioamide bands I,II, III and IV. Bands at 1371 and 892 cm\(^{-1}\) which have major contribution from v(C=S) are shifted to lower energies with reduced intensity suggesting coordination of thiolate sulphur. In the complexes coordination via the pyridine nitrogen is indicated by the shifts to higher frequencies of v(CN) + v(CC) and of the
Table 9.1
Analytical data, conductivity, magnetic moments, colours and yields of complexes of Zn(II) with HL4M

<table>
<thead>
<tr>
<th>Compound</th>
<th>Emp.formula</th>
<th>Yield (%)</th>
<th>Colour</th>
<th>µ(^d)(BM)</th>
<th>AM (^a)</th>
<th>Analytical data Found, (Calculated), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnL4MCl, 43</td>
<td>C(_3)H(_8)Cl(_4)OSZn</td>
<td>69</td>
<td>Yellow</td>
<td>Dia</td>
<td>12</td>
<td>C 40.37 (40.58) H 4.20 (4.15) N 15.29 (15.38) Zn 18.01 (17.96)</td>
</tr>
<tr>
<td>ZnL4MOAc.H(_2)O, 44</td>
<td>C(_3)H(_8)N(_4)O(_4)SZn</td>
<td>71</td>
<td>Yellow</td>
<td>Dia</td>
<td>10</td>
<td>C 41.34 (41.44) H 4.72 (4.97) N 13.69 (13.81) Zn 16.20 (16.11)</td>
</tr>
<tr>
<td>ZnL4MClO(_4), 45</td>
<td>C(_3)H(_8)Cl(_4)O(_4)SZn</td>
<td>64</td>
<td>Yellow</td>
<td>Dia</td>
<td>10</td>
<td>C 33.45 (33.66) H 3.61 (3.53) N 13.13 (13.08) Zn 15.31 (15.27)</td>
</tr>
</tbody>
</table>

\(^b\) Empirical formula. \(^d\) Magnetic moment \(^d\) Molar conductivity, 10\(^-3\) M solution (DMF) at 298 K.

Table 9.2
IR spectral assignments (cm\(^-1\)) of Zn(II) complexes with HL4M

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu(C=N)+)</th>
<th>(\nu(N-N))</th>
<th>(\nu(C-S))</th>
<th>(\delta(C-S))</th>
<th>(\delta_{CP})</th>
<th>(\nu(Zn_{N_{x2}}))</th>
<th>(\nu(Zn_{N_{Py}}))</th>
<th>(\nu(ZnS))</th>
<th>(\nu(ZnX))</th>
<th>(\nu(N-C))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL4M</td>
<td>1627 s</td>
<td>1010 m</td>
<td>1371 m</td>
<td>892 m</td>
<td>649 m</td>
<td>408 m</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>ZnL4MCl</td>
<td>1615 s</td>
<td>1024 m</td>
<td>1303 m</td>
<td>840 m</td>
<td>654 m</td>
<td>430 m</td>
<td>387 w</td>
<td>344 s</td>
<td>278 m</td>
<td>317 m</td>
</tr>
<tr>
<td>ZnL4MOAc.H(_2)O</td>
<td>1602 s</td>
<td>1030 m</td>
<td>1315 m</td>
<td>838 m</td>
<td>661 m</td>
<td>434 m</td>
<td>391 sh</td>
<td>347 s</td>
<td>269 m</td>
<td>298 sh</td>
</tr>
<tr>
<td>ZnL4MClO(_4)</td>
<td>1611 s</td>
<td>1028 m</td>
<td>1310 m</td>
<td>844 m</td>
<td>657 m</td>
<td>432 m</td>
<td>391 sh</td>
<td>341 s</td>
<td>279 m</td>
<td>308 m</td>
</tr>
</tbody>
</table>

\(s =\)strong; \(m =\) medium; \(w =\) weak; \(sh =\) shoulder.

Table 9.3
Electronic spectral assignments(nm) and antimicrobial activities of Zn(II) complexes with HL4M

<table>
<thead>
<tr>
<th>Compound</th>
<th>CT</th>
<th>(\pi-\pi^*)</th>
<th>(n-\pi^*)</th>
<th>Con/disc</th>
<th>1(^*)</th>
<th>2(^*)</th>
<th>3(^*)</th>
<th>4(^*)</th>
<th>5(^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL4M</td>
<td>----</td>
<td>292</td>
<td>301, 331, 390</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnL4MCl</td>
<td>386, 415</td>
<td>291</td>
<td>302, 334, 398</td>
<td>50 µg</td>
<td>+10</td>
<td>+11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnL4MOAc.H(_2)O</td>
<td>398, 425</td>
<td>288</td>
<td>302, 334, 396</td>
<td>50 µg</td>
<td>+12</td>
<td>+16</td>
<td>+10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnL4MClO(_4)</td>
<td>350, 417</td>
<td>290</td>
<td>302, 332, 392</td>
<td>50 µg</td>
<td>+9</td>
<td>+10</td>
<td></td>
<td></td>
<td>+11</td>
</tr>
</tbody>
</table>

1\(^*\)-Staphylococcus aureus; 2\(^*\)-Salmonella typhi; 3\(^*\)-Shigella sp; 4\(^*\)-Bacillus sp; 5\(^*\)-Vibrio cholera.
increase in shift of pyridine ring, out-of-plane and in-plane bending vibrations at 649 and 408 cm\(^{-1}\) assigned for HL4M by 12 to 25 cm\(^{-1}\) on complexation.

The compound 43 shows a medium intensity band at 289 cm\(^{-1}\) indicating terminal rather than bridging chlorine. Asymmetric and symmetric stretching vibrations of the acetate grouping in 44 appear at 1585 and 1441 cm\(^{-1}\) respectively. The difference between \(\nu_{\text{asym}}(\text{COO})\) and \(\nu_{\text{sym}}(\text{COO})\) is 142 cm\(^{-1}\), which reflects the unidentate coordination mode of acetate group [7]. A medium intensity band at 3325 cm\(^{-1}\) indicates presence of non-coordinated water. The compound 45 shows broad bands at 1150, 1028 and 920 cm\(^{-1}\), suggesting mono coordinated [8] perchlorate group.

9.3.2. Electronic spectra
The electronic spectral data of complexes are listed in Table 9.3.

The principal ligand HL4M has a band at 292 nm due to \(\pi \rightarrow \pi^*\) transition. This band is almost unchanged in the spectra of complexes. The ligands also shows broad bands at 301 nm and a shoulder at lower energy (331 nm) due to \(n \rightarrow \pi^*\) transitions associated with the azomethine linkage. This band in the complex has shown a bathochromic shift due to the donation of a lone pair of electrons to metal and hence the coordination of azomethine. The broad shoulder centered at 390 nm in the ligand was assigned to \(\pi \rightarrow \pi^*\) of the thioamide chromophore which suffers a blue shift in the complex due to thio enolisation. The moderately intense band for the complexes in the region 350-425 nm is assigned to S\(\rightarrow\)Zn(II) LMCT. The LMCT maxima of the complexes show line broadening with a tale running in to the visible part of the spectra. Except this the complexes show no appreciable absorption in the region above 450 nm in dimethylformamide solution and also in polycrystalline state. The results are in consistent with the d\(^{10}\) electronic configuration of Zn(II) ion [9].

9.3.3 \(^1\)H NMR spectra
The \(^1\)H NMR signals of the ligand and complexes are listed in Table 9.4.

The ligand HL4M has a signal at \(\delta\) 8.77 ppm due to N-H proton, which disappears on D\(_2\)O exchange. Protons of C-CH\(_3\) are observed at \(\delta\) 3.35 ppm. A multiplet around \(\delta\) 3.81 ppm is due to protons of morpholine ring. Protons of
aromatic ring are found between $\delta$ 7.46 to 8.25 ppm. In complexes signals due to N-H is absent, supporting thio enolisation. Deprotonation of $^3$NH in complexes is reflected by the lack of $N^3$H signal (singlet) that appears at $\delta$ 8.77 ppm in the spectrum of HL4M. The coordination via pyridine nitrogen causes their pyridine protons signals to shift much more with respect to their positions in the free ligand spectrum. The signals due to protons of pyridine ring show splitting. This may be due to the dissymmetry caused by the non planarity of the ligand on complexation [10]. The down field shift in 44 of the acetate resonance ($\delta$, 1.99) compared with that of the ionic acetate suggests interaction of the acetate with the metal centers in solution [11].

9.3.4 $^{13}$C NMR spectra
Coordination of the ligand via the azomethine nitrogen is indicated in the spectra of all the complexes by the down field shift of the methyl carbon signal. Coordination via the sulphur atom is indicated by the up field shift of the $^{8}$C signals. Among the pyridine carbon signals, by far the most affected by complexation is that of $^3$C, which shifts up field in all those spectra in complexes, this may be attributed to coordination via the pyridine nitrogen. The methyl and morpholine ring carbon signals lie at practically the same position as in free ligands.

9.3.5 Two-dimensional NMR techniques
Two dimensional correlation spectroscopy assist in determining the connectivity of a molecule showing proton-proton (COSY) as well as carbon-proton coupling (HMQC). Chemists can now readily glean information about spin-spin coupling and the exact connectivity of atoms in molecules through techniques called multidimensional NMR spectroscopy. The most common multidimensional techniques utilize two-dimensional NMR (2D NMR) and go by acronyms such as COSY, HETCOR, and a variety of others. The two-dimensional sense of 2D NMR spectra does not refer to the way they appear on paper but instead reflects the fact that the data are accumulated using two radio frequency pulses with a varying time delay between them. The result is an NMR spectrum with the usual one-dimensional spectrum along the horizontal
and vertical axes, and a set of correlation peaks that appear in the x-y field of the graph.

When 2D NMR is applied to $^1$H NMR it is called $^1$H-$^1$H correlation spectroscopy (COSY). COSY spectra are exceptionally useful for deducing proton-proton coupling relationships. 2D NMR spectra indicate coupling between hydrogens and the carbons to which they are attached. In this case, it is called heteronuclear correlation spectroscopy (HETCOR, or C-H HETCOR). When ambiguities are present in the one-dimensional $^1$H and $^{13}$C NMR spectra, a HETCOR spectrum can be very useful for assigning precisely which hydrogens and carbons are producing their respective peaks.

In a COSY spectrum, the ordinary one-dimensional $^1$H spectrum is shown along both the horizontal and the vertical axes. Meanwhile, the x-y field of a COSY spectrum is similar to a topographic map and can be thought of as looking down on the contour lines of a map of a mountain range. Along the diagonal of the COSY spectrum is a view that corresponds to looking down on the ordinary one-dimensional spectrum of compound though each peak were a mountain. The one-dimensional counterpart of a given peak on the diagonal lies directly below that peak on each axis. The peaks on the diagonal provide no new information relative to that obtained from the one-dimensional spectrum along each axis. The important and new information from the COSY spectrum, however, comes from the correlation peaks ("mountains") that appear off the diagonal (called "cross peaks"). If one starts at a given cross peak and imagines two perpendicular lines (i.e., parallel to each spectrum axis) leading back to the diagonal, the peaks intersected on the diagonal by these lines are coupled to each other. Hence, the peaks on the one-dimensional spectrum directly below the coupled diagonal peaks are coupled to each other. The cross peaks above the diagonal are mirror reflections of those below the diagonal; thus the information is redundant and only cross peaks on one side of the diagonal need be interpreted. The x-y field cross-peak correlations are the result of instrumental parameters used to obtain the COSY spectrum. First, one chooses a starting point in the COSY spectrum [Fig.9.1] from which to begin tracing the coupling relationships [12]. A peak whose
Table 9.4

$^1$H NMR assignments of N-N-S donor and its zinc(II) complexes. (All absorptions are in (δ) ppm)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^2$NH</th>
<th>$^1$CH</th>
<th>$^2$CH</th>
<th>$^3$CH</th>
<th>$^4$CH</th>
<th>$^5$CH</th>
<th>$^6$CH</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL4M</td>
<td>8.77</td>
<td>7.89</td>
<td>7.27</td>
<td>7.34</td>
<td>7.34</td>
<td>2.62</td>
<td>3.72-3.84</td>
</tr>
<tr>
<td>ZnL4MCl</td>
<td>---</td>
<td>7.81</td>
<td>7.25</td>
<td>7.10</td>
<td>7.23</td>
<td>2.61</td>
<td>3.72-3.82</td>
</tr>
<tr>
<td>ZnL4MOAc.H$_2$O</td>
<td>---</td>
<td>7.80</td>
<td>7.24</td>
<td>7.00</td>
<td>7.21</td>
<td>2.59</td>
<td>3.72-3.86</td>
</tr>
<tr>
<td>ZnL4MClO$_4$</td>
<td>---</td>
<td>7.81</td>
<td>7.26</td>
<td>7.12</td>
<td>7.20</td>
<td>2.61</td>
<td>3.72-3.82</td>
</tr>
</tbody>
</table>

Table 9.5

$^{13}$C NMR spectral assignments of HL4M and its zinc(II) complexes (All absorptions are in ppm)

<table>
<thead>
<tr>
<th>Compound</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>C6</th>
<th>C7</th>
<th>C8</th>
<th>C9</th>
<th>C10</th>
<th>C11</th>
<th>C12</th>
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</thead>
<tbody>
<tr>
<td>HL4M</td>
<td>137.82</td>
<td>120.78</td>
<td>124.51</td>
<td>119.80</td>
<td>148.77</td>
<td>185.51</td>
<td>13.86</td>
<td>150.24</td>
<td>52.25</td>
<td>52.25</td>
<td>66.66</td>
<td>66.66</td>
</tr>
<tr>
<td>ZnL4MCl</td>
<td>131.58</td>
<td>129.05</td>
<td>149.01</td>
<td>122.56</td>
<td>138.07</td>
<td>156.22</td>
<td>17.66</td>
<td>168.27</td>
<td>48.99</td>
<td>48.98</td>
<td>65.28</td>
<td>65.28</td>
</tr>
<tr>
<td>ZnL4MOAc.H$_2$O</td>
<td>135.84</td>
<td>129.17</td>
<td>150.35</td>
<td>122.69</td>
<td>142.33</td>
<td>172.62</td>
<td>17.05</td>
<td>159.89</td>
<td>48.99</td>
<td>48.99</td>
<td>65.28</td>
<td>65.28</td>
</tr>
<tr>
<td>ZnL4MClO$_4$</td>
<td>136.93</td>
<td>131.28</td>
<td>149.40</td>
<td>124.79</td>
<td>143.42</td>
<td>176.48</td>
<td>17.61</td>
<td>166.87</td>
<td>48.99</td>
<td>48.99</td>
<td>65.28</td>
<td>65.28</td>
</tr>
</tbody>
</table>
assignment is relatively apparent in the one-dimensional spectrum is a good point of reference. For the compound, 45 the singlet from the alpha hydrogen at 7.99 ppm is quite obvious and readily assigned. If we find the peak on the diagonal that corresponds to this, an imaginary line can be drawn parallel to the vertical axis that intersects a correlation peak in the x-y field off the diagonal. From here a perpendicular imaginary line can be drawn back to its intersection with the diagonal peaks. At its intersection we see that this diagonal peak is directly above the one-dimensional spectrum peak at δ 7.2 ppm. Thus, the alpha hydrogen is coupled to the hydrogen whose signal appears at δ 7.2 ppm. It is now clear that the peak at δ 7.2 ppm is due to the hydrogen on the 3C of pyridine ring. Moving back up to the diagonal from each of these cross peaks indicates that the hydrogen whose signal appears at δ 7.8 ppm is coupled to the hydrogens whose signals appear at δ7.2 ppm. The hydrogen at δ 7.4 ppm is coupled with hydrogen at δ 7.2 ppm.

The hydrogens at δ 3.8 ppm and δ 3.6 ppm are therefore the two hydrogens on the carbon of morpholine moiety. Thus, from the COSY spectrum we can quickly see which hydrogens are coupled to each other. Furthermore, from the reference starting point, we can "walk around" a molecule, tracing the neighbouring coupling relationships along the molecule's carbon skeleton as we go through the COSY spectrum [13].

COSY spectrum of the compound 45 is consistent to an AMX spin system. Aromatic protons of the pyridine ring appear at δ 7.4 (d, J=7.5 Hz; 7.22(t, J= 7.2 Hz) 7.28(dd,J=7.4 &2.4 Hz) and 7.3(d , J= 8.1 Hz) respectively. Aliphatic protons of the 3C were observed as singlet and protons of morpholino moiety are observed as multiplet.

HETCOR or HMQC cross-peak correlations
In a HETCOR spectrum a 13C spectrum is presented along one axis and a 1H spectrum is shown along the other. Cross peaks relating the two types of spectra to each other are found in the x-y field. Specifically, the cross peaks in a HETCOR spectrum indicates which hydrogens are attached to which carbons in a molecule, or
Fig. 9.1 $^1$H-NMR spectrum of the zinc complex 45
Fig. 9.1 COSY spectrum of the zinc complex 45
Fig. 9.2 $^{13}$C-NMR spectrum of the zinc complex 45
Fig. 9.2 HMQC spectrum of the zinc complex 45
there is no diagonal spectrum in the x-y field like that found in the COSY. If imaginary lines are drawn from a given cross peak in the x-y field to each respective axis, the cross peak indicates that the hydrogen giving rise to the 

$^1\text{H}$ NMR signal on one axis is coupled (and attached) to the carbon that gives rise to the corresponding $^{13}\text{C}$ NMR signal on the other axis. Therefore, it is readily apparent which hydrogens are attached to which carbons. Fig. 9.2 shows schematic counter plots of the HMQC spectrum of the compound. The spectrum suggests a (A-a) – (M-m) - (X-x) system [14] that A and a, M and m and C and c, respectively are directly connected. The vertical dimensions represents the $^{13}\text{C}$ chemical shift scale and horizontal that of the protons. The cross peaks indicate one bond, $^1\text{H}$-$^{13}\text{C}$ bond in they correlate protons and carbon signals of the atoms directly attached. The $^1\text{H}$ and $^{13}\text{C}$ connectivities made on the basis of HMQC spectrum is in agreement with $^1\text{H}$ and $^{13}\text{C}$ spectral assignments.

The HETCOR spectrum for 45 is shown in the Fig. 9.2. Having interpreted the COSY spectrum already, we have known precisely which hydrogens of the compound produce each signal in the IH spectrum. If an imaginary line is taken from the doublet of the proton spectrum at 7.8 ppm (vertical axis) out to the correlation peak in the x-y field and then dropped down to the $^{13}\text{C}$ spectrum axis (horizontal axis), it is apparent that the $^{13}\text{C}$ peak at 180-158 ppm is produced by the pyridynyl carbon of ligand. Having assigned the $^1\text{H}$ NMR peak at 2.6 ppm to the hydrogen on the methyl carbon of the molecule tracing out to the correlation peak and down to the $^{13}\text{C}$ spectrum indicates that the $^{13}\text{C}$ NMR signal at 13 - 20 ppm arises from the methyl carbon (carbon 2). Finally, from the $^1\text{H}$ NMR peaks at 3.4 - 3.6 for the two hydrogens on the carbon, our interpretation leads us out to the cross peak to the $^{13}\text{C}$ peak at 63 ppm. From the studies the structures assigned for the representative complexes are as follows,
9.4 Biological studies

The antibacterial activity of all the new compounds was assayed against two Gram positive and nine Gram negative clinical pathogens and the results are tabulated in Table 9.3. All the new complexes were found to be more active against the pathogens than the ligands. Compound 44 is moderately active against *Bacillus sp* and showed high activity against *Staphylococcus aureus*, *Salmonella typhi* and *Shigella sp*. Compounds 43 and 45 had relatively low activity against *Staphylococcus aureus* and *shigella sp*. Among the compounds, the acetate complex 44 is the most reactive. But its activity was found to be lower than Cu(II) complexes. The Zn(II) complexes exhibited activity comparable to that of Cu(II) complexes only at high concentrations. Perchlorate complex 45 showed very little activity against *Vibrio cholera*. The MIC values were found to be almost similar to Cu(II) complexes showing their importance in antimicrobial uses.
9.5 Concluding remarks

In this Chapter an attempt was made to elucidate the structure of three zinc complexes of a thiocarbonyl morpholino moiety which provides a backbone for the N-N-S donor ligand. The structure proposed tentatively for the complexes was tetrahedral. By synthesizing these compounds, we were heading towards the designing of synthetic models of sulphur-rich zinc complexes. Enhancement of antimicrobial behaviour upon complexation could be utilized for pharmacological applications.
References


