# Chapter 4

**SYNTHESIS, CHARACTERIZATION AND STRUCTURAL ASSESSMENT OF NEWER MIXEDLIGAND HALO COMPLEXES OF ZINC(II) INCORPORATING BIORELEVANT COLIGANDS**

## 4.1Introduction

In recent years transition metal complexes have been used widely by many bioinorganic chemists for developing active transition metal anticancer complexes with better efficiency **[1-4]**. The presence of metal binding sites in DNA structure make different type of interactions possible such as intercalation between base pairs, minor groove binding, and major groove binding which play an important role in the efforts of the drug targeted to DNA **[5,6]**. Newer metal complexes of bioactive compounds have continuously engaged the attention of synthetic chemists. Transition

metals are particularly suitable for this purpose because they can adopt a wide variety of coordination numbers, geometries and oxidation state in comparison with carbon and other main group elements [7]. It has been observed that mixed ligand complexes behave as an efficient DNA-targeted material. The incorporation of an organic compound like α-amino acid significantly modifies the structural and biological activities of transition metal complexes [8]. The amino acids are known to coordinate with metal ion through N, O-donor ligand forming five membered chelate ring after dissociation of the acidic proton [9,10]. Zn(II) is one of the most important metal cations in biological systems as it plays an essential role in the activity of nearly 300 enzymes that catalyze approximately 50 important cellular biochemical reactions [11]. In bacteria, zinc plays a role in catalysis, protein structure and perhaps as a single molecule [12]. However, at high concentrations Zn(II) shows inhibitory action on the growth of bacterial species like*Escherichia coli*, *Streptococcus faecalis*, *Staphylococcus aureus*, *Staphylococcus epidermidis* and *Pseudomonas aeruginosa*[13]. This inhibition might be explained by the combination of Zn(II) with membrane proteins (sulfur groups) resulting in cross-linking and deactivation, which changes cell membrane permeability and disrupts transport of nutrients and wastes across the membrane [14].

The role of zinc for stabilization of protein loops in enzymes, 'zinc fingers' etc. has evoked new interest in the arena of zinc-coordination chemistry [15-17]. Discovery of 'zinc fingers' in particular has triggered intensive research on zinc-aminoacid interaction [18-20]. The zinc core in transcription factor TF III A is bound by histidine and cysteine in tetrahedral configuration.

Zinc, a redox insensitive metal [$3d^{10}$] has been known for its structural, regulatory and catalytic role in biological system second in importance only to iron. Being spectroscopically silent, developments in bio-coordination chemistry of Zn(II) has been tardy. Information on the nature of zinc-aminoacid interaction has begun to pour only recently [21,22]. So far only ten zinc-aminoacid binary compounds have been structurally characterized. ProfessorVahrenkamp's group contributed immensely to develop zinc coordination chemistry. Very recently, zinc complexes with Zn–$OH_2$ and Zn–OH motifs were synthesized and structurally characterized[23]. These complexes were implicated as suitable biomimetic systems.

In a bid to plug this lacuna and also as a part of our long-drawn program on synthesis and characterization of mixedligand halo complexes incorporating aminoacids and imidazole as coligand, we describe in this chapter preparation of some newer molecular compounds of the types [$ZnX_2L$] (X = F, L = leu, ser, phe, his,bim), [ZnBr(OH)L] (L = leu or ser), and $NH_4$[$ZnF(ser)_2(H_2O)$].$5H_2O$.The complexes with coordinated water and often coordinated hydroxide are potential candidates for 'small molecular weight' biomimetic models.

## 4.B Experimental

Reagent used, starting materials for the synthesis, the methods of chemical analysis of the complex formed and details of the instrument used for the same are as described in **Chapter 2**.The procedures for the synthesis of different mixedligandcomplexes ofzinc(II) **(11 - 19)** are described herein.

**Synthesis of  [ZnF$_2$(Hleu)(H$_2$O)].2H$_2$O      (11)**

To a freshly prepared aqueous suspension of hydrated zinc(II) oxide, ZnO.nH$_2$O, obtained from ZnSO$_4$.7H$_2$O, (2g, 6mmol), solid NH$_4$HF$_2$ (ca 0.75g, 12mmol) was added resulting a clear solution (pH ~ 6) followed by l-leucine, (0.78g, 6mmol) in hot ethanol (25%). The solution was concentrated on a water bath when a white microcrystalline product was obtained. The product was filtered, washed with water and finally by ethanol then dried over fused CaCl$_2$*in vacuuo*. The yield recorded was 55%.

**Synthesis of [ZnBr(leu)(H$_2$O)]        (12)**

To a freshly prepared aqueous suspension of hydrated zinc(II) oxide, ZnO.nH$_2$O, obtained from ZnSO$_4$.7H$_2$O (2g, 6mmol) solid NH$_4$Br (1g, 10mmol) was added. It was treated with HBr (20% in acetic acid) drop by drop with constant stirring to dissolve the suspension (pH ~ 4) followed by addition of l-luecine(0.78g, 6mmol) in hot water. The solution was concentrated in a water bath (pH ~ 3). The pH of the solution was raised to pH ~ 7-8 by adding dil. NaOH solution, whena white microcrystalline product was obtained. The product was filtered washed with water and dried over fused CaCl$_2$*in vacuuo*. The yield recorded was 65%.

**Synthesis of [ZnF$_2$(Hser)(H$_2$O)].4H$_2$O       (13)**

To a freshly prepared aqueous suspension of hydrated zinc(II) oxide, ZnO.nH$_2$O obtained from ZnSO$_4$.7H$_2$O, (2g, 6mmol), solid NH$_4$HF$_2$, (0.75g, 12mmol) was added resulting a clear solution (pH ~ 6) followed by l-serine (0.73g, 6mmol) in hot water. The solution was concentrated on a water bath, cooled to room temperature and ethanol was added when a pasty product is formed. Further addition of ethanol

yielded whitemicrocrystalline product. The product was filtered washed with ethanol and dried over fused $CaCl_2$ in*vacuuo*. The yield recorded was 50%.

**Synthesis of$NH_4[ZnF(ser)_2(H_2O)]$.$5H_2O$      (14)**

To a freshly prepared aqueous suspension of hydrated zinc(II) oxide, $ZnO.nH_2O$ obtained from $ZnSO_4.7H_2O$, (2g, 6mmol), solid $NH_4HF_2$, (1.4g, 24mmol) was added to dissolve the suspension (pH ~ 3-4), followed by l-serine (0.73g, 6mmol) in hot water. The solution was concentrated on a water bath then cooled to room temperature. Ethanol was added with constant stirring when a white micro crystalline product was obtained. It was filtered, washed with ethanol and dried over fused $CaCl_2$*in vacuuo*. The yield recorded was 30%.

**Synthesis of $[ZnBr(ser)(H_2O)]$      (15)**

To a freshly prepared aqueous suspension of hydrated zinc(II) oxide, $ZnO.nH_2O$, obtained from $ZnSO_4.7H_2O$, (2g, 6mmol), HBr (20% in acetic acid) was added drop by drop with constant stirring followed by l-serine, (0.73g, 6mmol). The solution was warmed for 15 min on a water bath, then pH of the solution was adjusted within the range of 7-8 (adding dil. NaOH solution) when a dirty white product is obtained.The product was filtered, washed with water and dried over fused $CaCl_2$*in vacuuo*. The yield recorded was 60%.

**Synthesis of $[ZnF_2(Hphe)(H_2O)]$     (16)**

To a freshly prepared aqueous suspension of hydrated zinc(II) oxide, $ZnO.nH_2O$, obtained from $ZnSO_4.7H_2O$, (2g, 6mmol), solid $NH_4HF_2$, (0.75g, 12mmol) was added resulting a clear solution (pH ~ 6) followed by phenylalanine (0.99g, 6mmol), when a

white microcrystalline product was obtained. It was filtered, washed with water and dried over fused $CaCl_2$ *in vacuuo*. The yield recorded was 55%.

**Synthesis of [ZnF$_2$(Hhis)(H$_2$O)].2H$_2$O (17)**

To a freshly prepared aqueous suspension of hydrated zinc(II) oxide $ZnO.nH_2O$ obtained from $ZnSO_4.7H_2O$ (2g,6mmol), solid$NH_4HF_2$(0.94g) was resulting a clear solution (pH~5). To it 1.08g(6mmol,)histidine was added with constant stirring. The reaction mixture was warmed on a water bath for 1 hwhen a white microcrystalline product was obtained on addition of ethanol .The compound was filtered, washed with ethanol and then dried over fused $CaCl_2$ *in vacuuo*. The yield recorded was 50%.

**Synthesis of [ZnF$_2$(bim)(H$_2$O)]       (18)**

To a freshly prepared aqueous suspension of hydrated zinc(II) oxide $ZnO.nH_2O$ obtained from $ZnSO_4.7H_2O$ (2g,6mmol) solid $NH_4HF_2$(0.91g) was added resulting a clear solution (pH~5). To it 0.76g (6 mmol), benzimidazole in 50% ethanol was added with constant stirring. The mixture was heated on a water bath for 10 min when a white microcrystalline product was formed. The ppt was filtered, washed with water and finally by ethanol then dried over fused $CaCl_2$ *in vacuuo*. The yield recorded was 60%.

## 4. C  Results and Discussion

Devising strategies for simultaneous coordination of halide ligand and the coligand to zinc(II) center has been the basic objective of the work presented in this chapter. The coligands selected were l-leucine, l-serine, l-phenyl-alanine, histidineand benzimidazole.

The successful synthesis of desired mixedligandzinc(II) complexes were based on interaction of ZnO.nH$_2$O with the haloacid followed by the coligand addition(**Scheme 4.1**).

$$ZnO.nH_2O \ + \ NH_4HF_2/NH_4X \ / \ HX \quad \xrightarrow[\text{pH}\sim\text{3-7}]{\text{aminoacid}} \quad [ZnX_2(L)].nH_2O$$
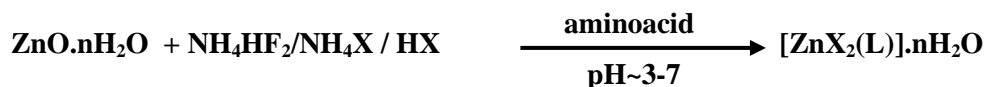
X = F or Br.
L =Hleu, Hser, Hphe,Hhis or Bim

**Scheme 4.1:** Generalized reaction strategy for the synthesis of zinc complexes.

The order of addition of reagents (i.e. halide and aminoacids etc.) was very crucial and a different sequence of adding ligand often led to binary or mixed product giving inconsistent analysis. The optimum pH condition spontaneously maintained for the different syntheses varied and was found to lie in the range 3-6 for bromo compound pH is higher and ~7-8). Use of lower amount of stoichiometric reagents and pH lower than those worked out did not favor the formation of mixedligand complexes. Again higher stoichiometric ratio of Zn : F = 1 : 8 (say) associated with drastic change in pH actually yielded quite different compounds(**Scheme 4.2**).
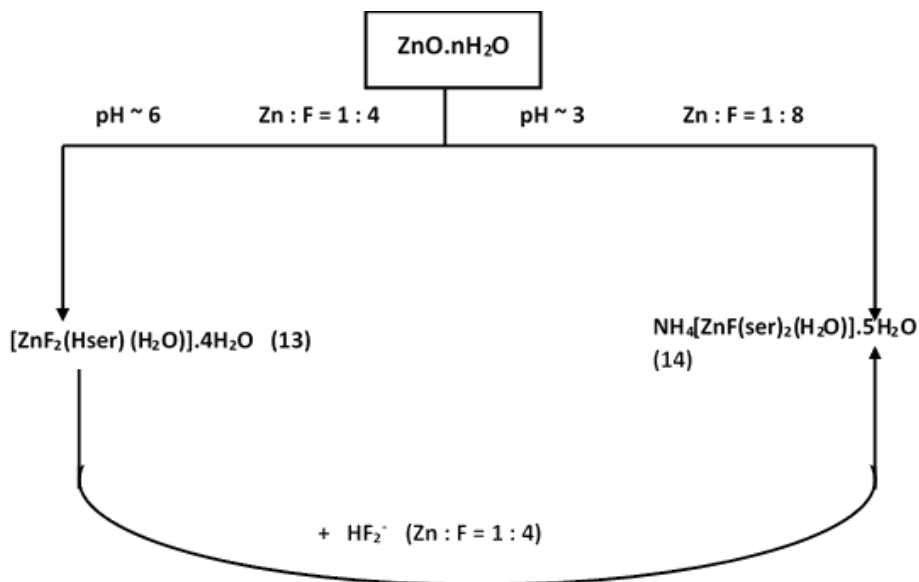


**Scheme4.2**: Formation of two different serine complexes, **(13)** and **(14)**.

Quite interestingly, the complex (**14**) can also be accessed from the complex (**13**) by addition of further amount of bifluoride ($HF_2^-$). Despite the use of higher amount of $F^-$ the number of $F^-$ coordinated per metal was one. An acidic pH (3) is believed to have caused this. This observation also validates the proposed formulations as well as the synthetic routes.

Elemental analyses (**Table 4.1**) are concordant with the formulation proposed for complexes (**11**) – (**18**).The newly synthesized Zn – complexes viz.(**13**), (**14**) and (**17**)are soluble in water and permitted conductivity measurements.The solution electrical conductance measurements ($\Lambda_M$ ) for complex (**13**), (**14**) and (**17**)revealed the values to be $< 10$ S cm$^2$ mol$^{-1}$ suggesting their nonionic character.

**Table 4.1:**  Analytical data of complexes **(11-18)**.

| Complexes | Colour | Analysis* (%) | | | | |
|---|---|---|---|---|---|---|
| | | **Zn** | **ªX** | **C** | **N** | **H** |
| [ZnF$_2$(Hleu)(H$_2$O)].2H$_2$O **(11)** (M = 288.58) | White | 22.0 (22.6) | ᵇ 13.0 (13.2) | 25.0 (25.0) | 4.6 (4.8) | 6.3 (6.6) |
| [ZnBr(leu)(H$_2$O)] **(12)** (M = 294.48) | white | 21.4 (22.2) | ᵈ 27.6 (27.1) | 24.8 (24.4) | 4.6 (4.7) | 5.1 (5.0) |
| [ZnF$_2$(Hser)( H$_2$O)].4H$_2$O **(13)** (M = 298.4) | White | 22.2 (21.8) | ᵇ 12.4 (12.7) | 12.1 (12.0) | 4.7 (4.7) | 5.9 (5.4) |
| NH$_4$[ZnF(ser)$_2$(H$_2$O)].5H$_2$O **(14)** (M = 420.3) | White | 15.6 (15.6) | ᵇ 4.6 (4.5) | 17.2 (17.1) | 9.7 (10.0) | 8.8 (9.0) |
| [ZnBr(ser)(H$_2$O)] **(15)** (M =268.3) | White | 24.4 (24.4) | ᵈ 29.5 (29.8) | 13.6 (13.4) | 5.7 (5.2) | 2.9 (3.3) |
| [ZnF$_2$(Hphe)(H$_2$O)] **(16)** (M = 286.59) | White | 22.7 (22.8) | ᵇ 14.2 (13.3) | 37.9 (37.7) | 5.3 (4.9) | 4.8 (4.5) |
| [ZnF$_2$(Hhis)(H$_2$O)].2H$_2$O **(17)** (M = 312.46) | White | 21.1 (20.9) | ᵇ12.5 (12.2) | 23.4 (23.0) | 13.4 (13.4) | 4.7 (4.8) |
| [ZnF$_2$(bim)(H$_2$O)] **(18)** (M = 239.47) | White | 27.0 (27.3) | ᵇ 15.6 (15.9) | 35.2 (35.0) | 11.5 (11.7) | 3.1 (3.3) |

* Calculated values are in parentheses.
ªX : F, Cl, Br;   ᵇF , ᶜCl , ᵈBr,  M = mol. wt.
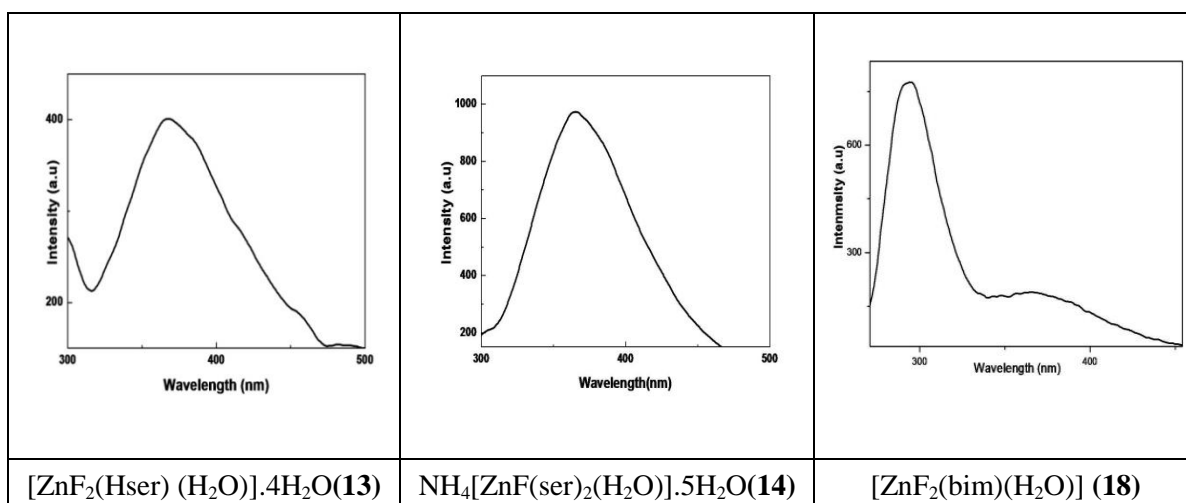
The UV-visible spectra of representative water soluble compounds, **13,14,17 and 18**were rather straightforward showing no absorption in the visible range in keeping with the occurrence of $d^{10}$ configuration of zinc(II) **(Fig. 4.1)**. A band at ca.265nm routinely observed in these complexes are ligand based transition.

The photoluminescence spectra of representative complexes of **(13)** and **(14)**in aqueous solution at ambient temperature,revealed the compounds to be fluorescent showing emission peaks at 370nm at an excitation of 260nm and that of **(18)** at 300nm at an excitation of 245nm **(Fig. 4.2)**.
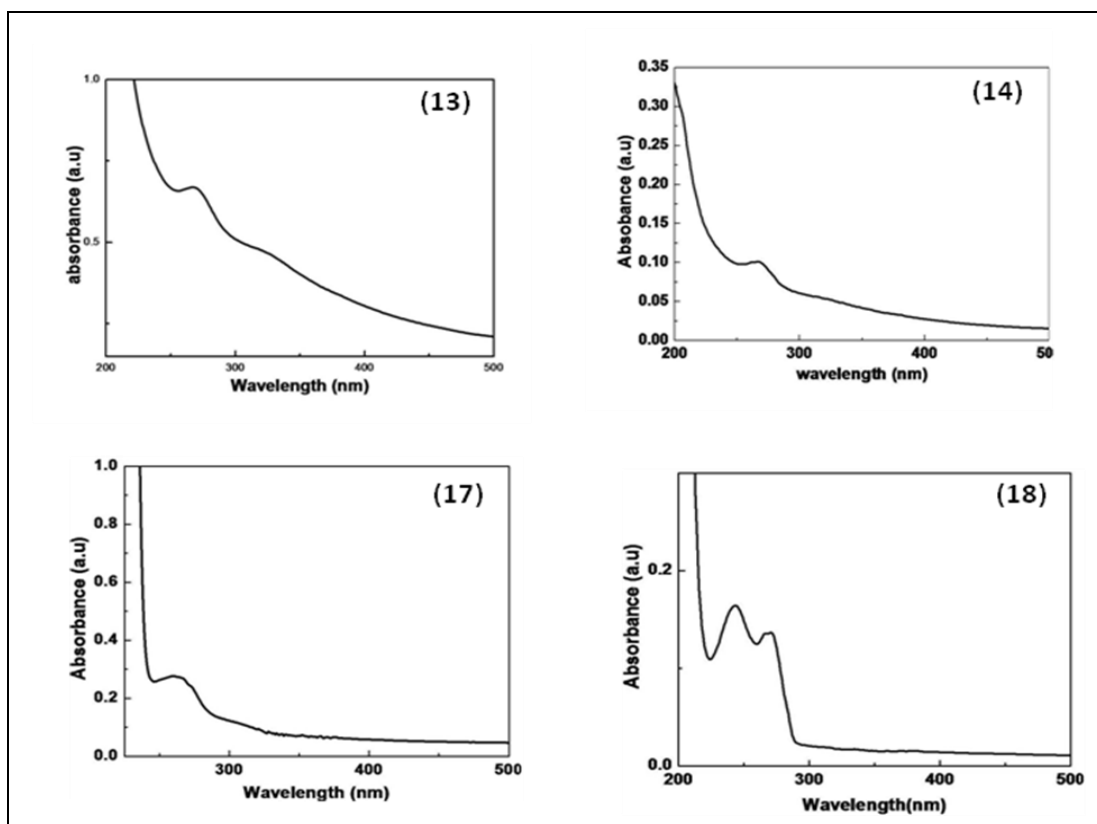


**Fig. 4.1:** UV-Vis spectra of zinc(II) compounds **(13), (14), (17)** and **(18)**

(For **(13)**,at $\lambda$= 270nm, for**(14)**,at $\lambda$= 273nm,for**(17)** at $\lambda$= 260nm and for (18) at $\lambda$=245nm, 271nm)

| [ZnF₂(Hser) (H₂O)].4H₂O(13) | NH₄[ZnF(ser)₂(H₂O)].5H₂O(14) | [ZnF₂(bim)(H₂O)] (18) |

**Fig. 4.2:** Photoluminescence spectra of zinc(II) compounds **(13)**, **(14)** and **(18)**

(Transitionsfor **(13)** at λ= 369nm, for **(14)** at λ=365nm and for **(18)** at λ= 293nm)

The vibrational spectroscopy has been very useful for elucidating structures of the complexes **(Table 4.2)**. The complexes **(11)**,**(13)**, **(14)**, **(17) and (18)** presumably incorporates coordinated water molecules as is evident from the occurrence of bands at ~ 3445 cm$^{-1}$ ($\nu_{OH}$), 1640 cm$^{-1}$ ($\delta_{H2O}$) and 835 cm$^{-1}$ ($\rho_{rH2O}$)**(Fig. 4.3–4.8)**. Thermal stability of complex **(11)** when heated in a closed silica vessel till about $300^\circ$C further augmented this inference. The coligand amino acids in the complexes **(11), (13), (16)** and **(17)** are believed to occur in zwitterionic dipolar charged forms presumably binding the metal ion via its carboxylato-oxygen in monodentate fashion**[24]**. For complexes **(11)** - **(18)**, bands at 3435 (br) cm$^{-1}$ assignable to $\nu_{OH}$ coupled with weak absorption near 825 cm$^{-1}$ confirms water coordination. For the anionic complexes **(14)**, the amino acid, serine is believed to be present in its ionic form (c.f. [ZnBr(H₂O)ser], **(15)** where serine ligand is also conjectured to be ionic). Bands at 1585 cm$^{-1}$ {$\nu_a$ (COO)}, ~ 1435cm$^{-1}$ {$\nu_s$ (COO)}, and 1025 cm$^{-1}$ {$\rho_r$ (CH₃)} amongst others, were very characteristic. A 1385 s cm$^{-1}$ ($\delta$ NH₂ of NH₄$^+$) and 3150 cm$^{-1}$ ($\nu_{N-H}$

stretching) band and a positive chemical test confirmed the presence of $NH_4^+$ ion in the complex (**14**). Thus one terminal halide, one aquo, and two chelated N,O-ligated amino acidatogroup complete the six coordination around zinc(II) in the complex (**14**) (**Fig.4.12**). For the complex (**12**) and (**15**)also, a chelated N,O-bonded amino acidatogroup plus a halo and an aquo group make up the four coordination around the metal center (**Fig.4.12**).The symmetric and asymmetric FT-IR features associated with the carboxylato group of the amino acid coligand were invariant in all the complexes irrespective of the composition. This we believe is due to carboxylato (-COO) coordination utilizing one oxygen end in all the cases.

**Table 4.2:**　Structurally significant FT-IR data of complexes **(11 – 18)**.

| Complex | | IR bands ($cm^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | $\nu_{COO\ (as)}$ | $\nu_{COO\ (s)}$ | $\nu_{OH}$ | $\delta(H_2O)$ | $\delta_{NH_2}\ NH_4^+$ | $\nu_{O\text{-}O}$ | $\rho_r\ (H_2O)$ |
| [ZnF$_2$(Hleu)(H$_2$O)].2H$_2$O | **(11)** | 1585 | 1450 | 3440 | 1620 | 1405 | – | 830 |
| [ZnBr(leu)(H$_2$O)] | **(12)** | 1590 | 1450 | 3435 | 1660 | 1410 | – | 835 |
| [ZnF$_2$(Hser)(H$_2$O)].4H$_2$O | **(13)** | 1590 | 1440 | 3555 | – | 1385 | – | 906 |
| NH$_4$[ZnF(ser)$_2$(H$_2$O)].5H$_2$O | **(14)** | 1590 | 1430 | 3520 | 1635 | 1415 | – | 850 |
| [ZnBr(ser)(H$_2$O)] | **(15)** | 1588 | 1385 | 3420 | 1630 | – | – | 832 |
| [ZnF$_2$(Hphe)(H$_2$O)] | **(16)** | 1590 | 1410 | 3540 | 1625 | – | – | 835 |
| [ZnF$_2$(Hhis)(H$_2$O)].2H$_2$O | **(17)** | – | – | 3421 | 1627 | – | – | 834 |
| [ZnF$_2$(bim)(H$_2$O)] | **(18)** | – | – | 3500 | 1630 | – | – | 831 |
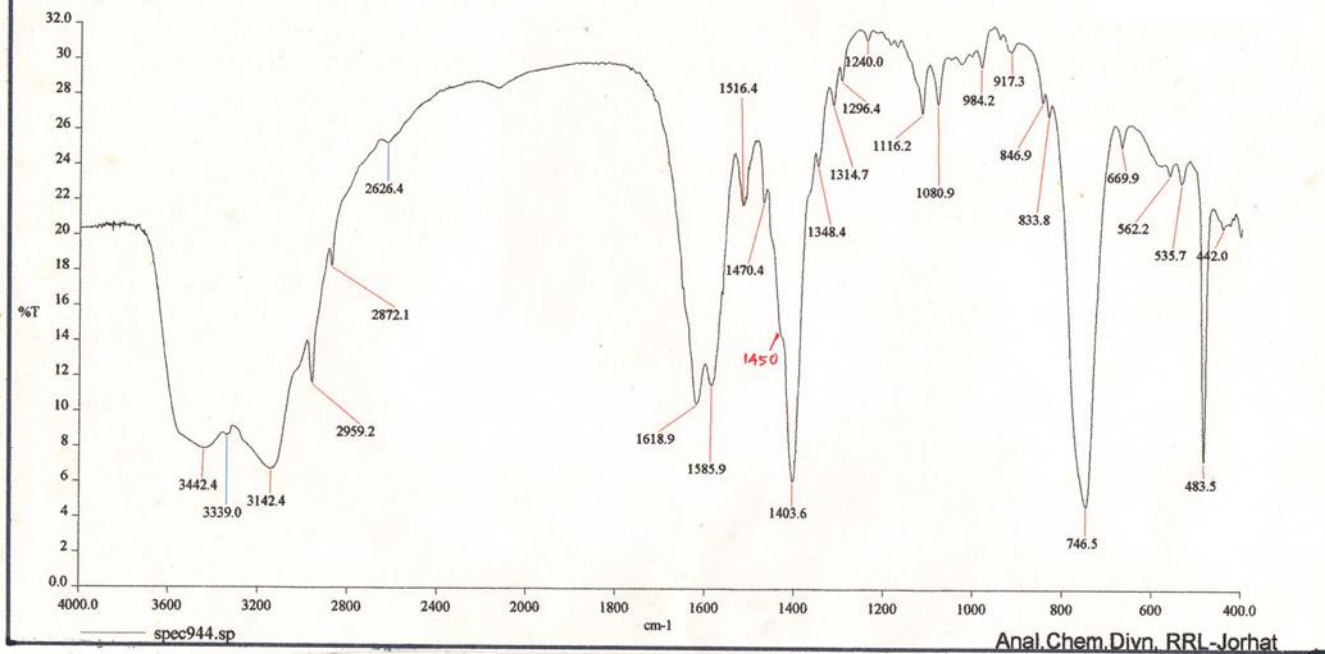
**Fig. 4.3:** FT-IR spectrum of $[ZnF_2(Hleu)(H_2O)].2H_2O$ **(11)**
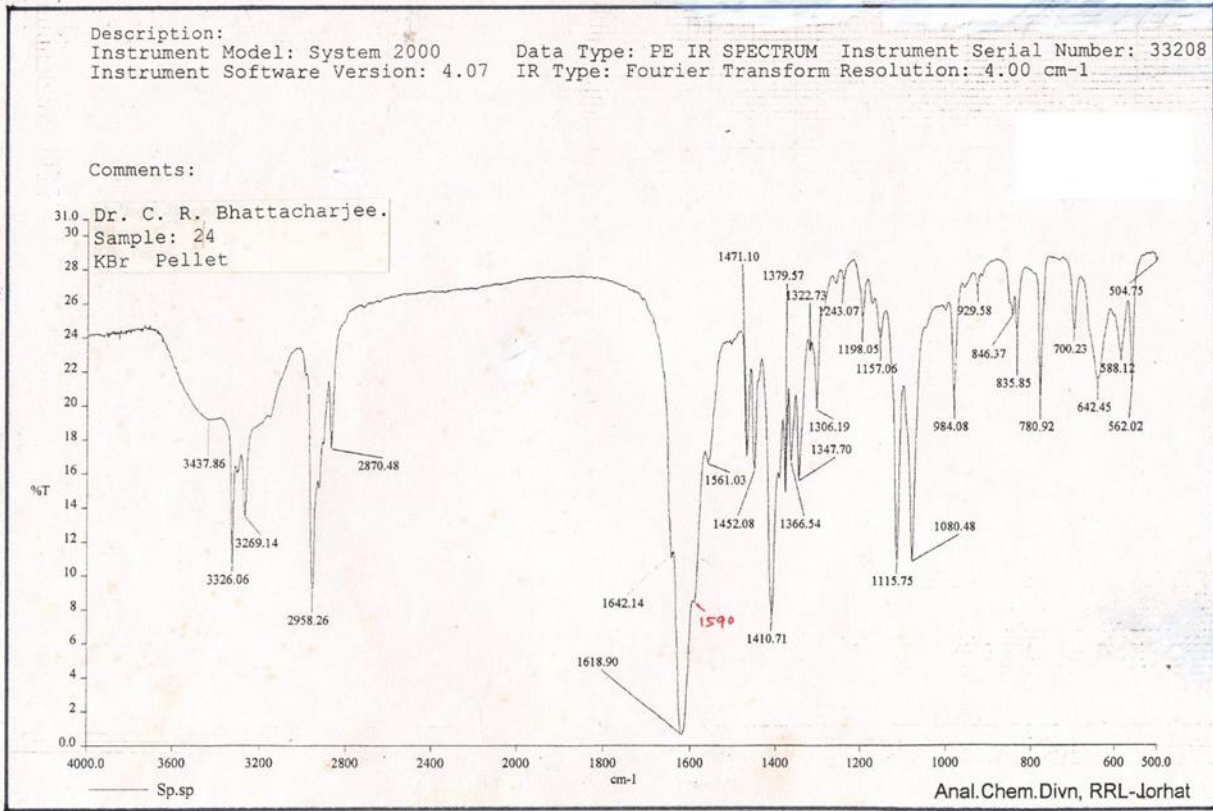
**Fig. 4.4:** FT-IR spectrum of [ZnBr(leu)(H$_2$O)] **(12)**
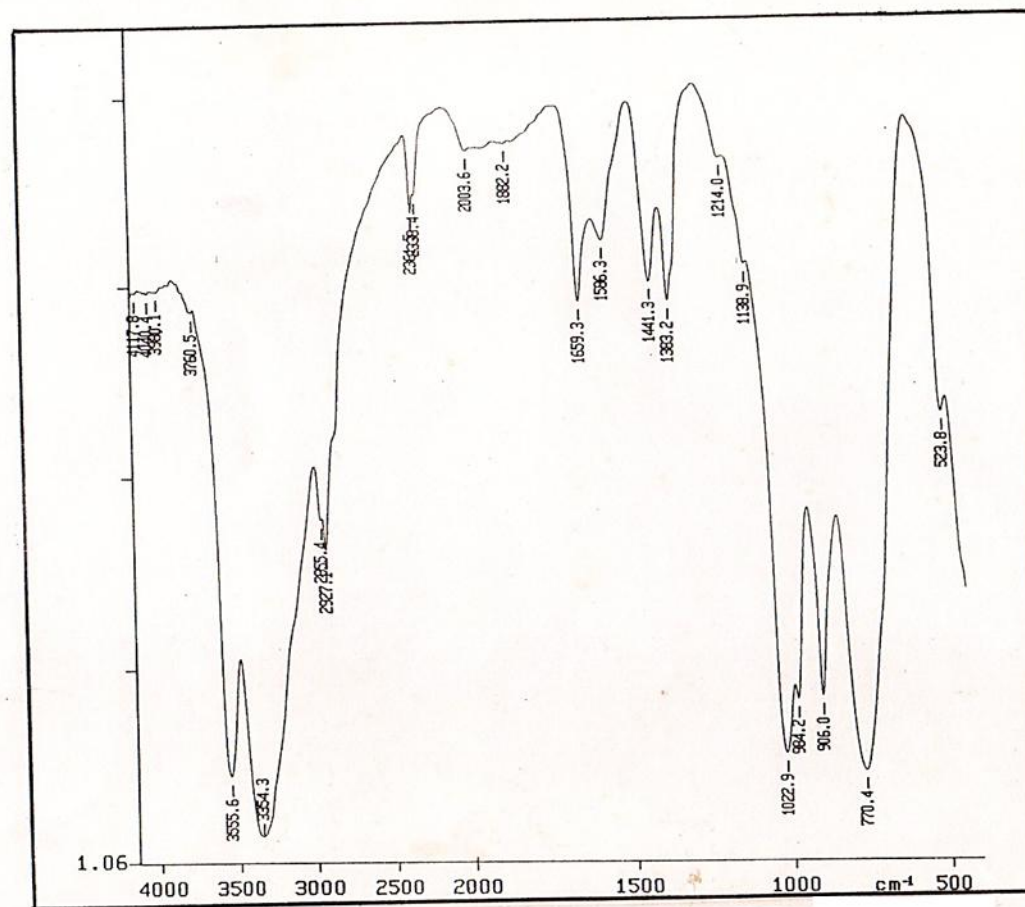
**Fig. 4.5:** FT-IR spectrum of $[ZnF_2(Hser)(H_2O)].4H_2O$ **(13)**
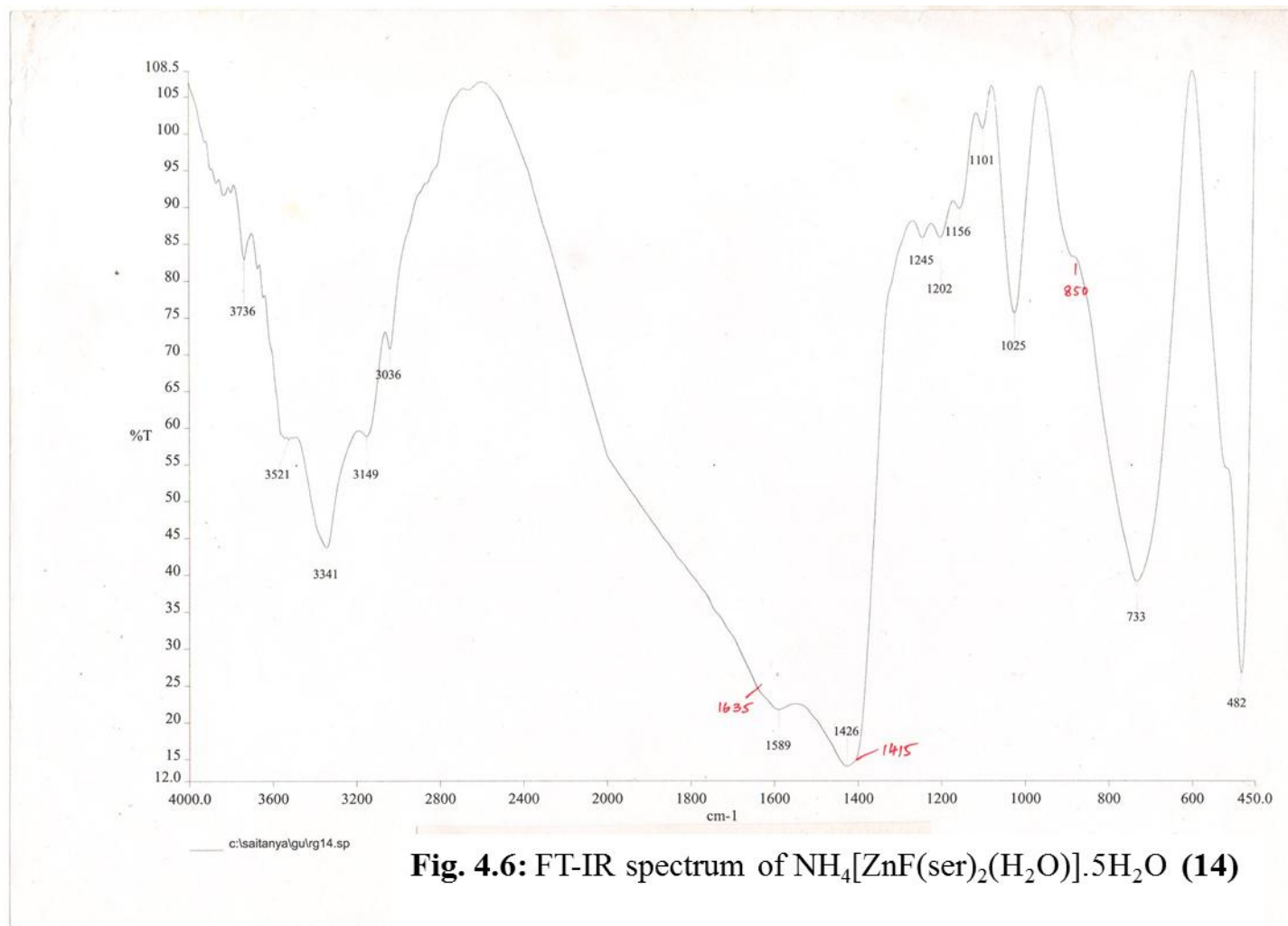
**Fig. 4.6:** FT-IR spectrum of NH$_4$[ZnF(ser)$_2$(H$_2$O)].5H$_2$O **(14)**
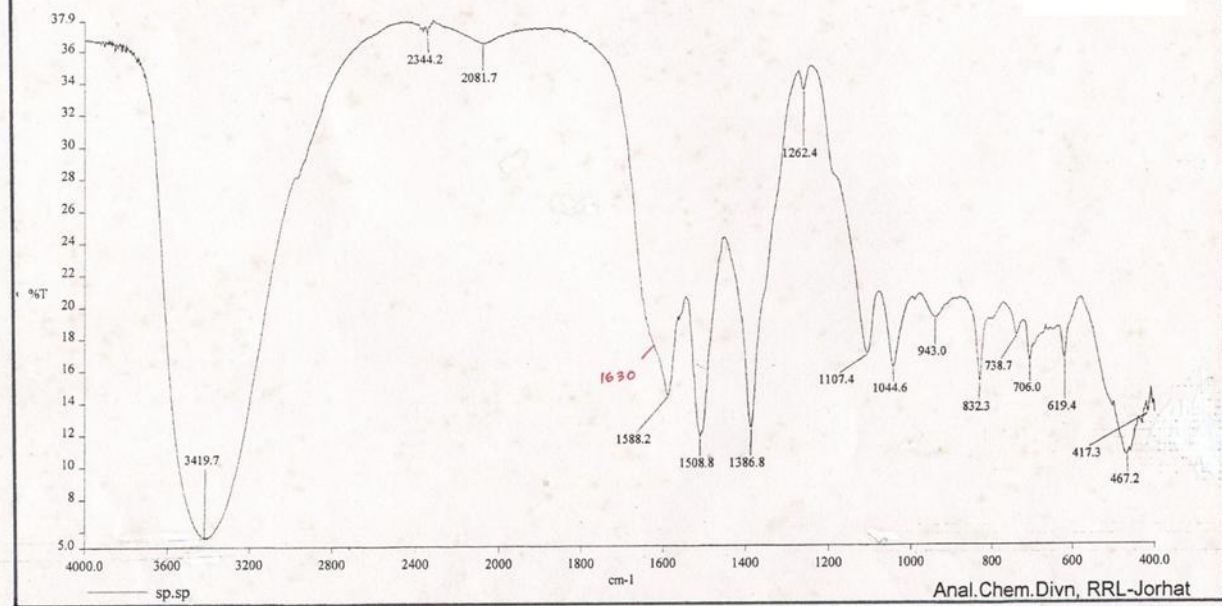
**Fig. 4.7:** FT-IR spectrum of $[ZnBr(ser)(H_2O)]$ **(15)**
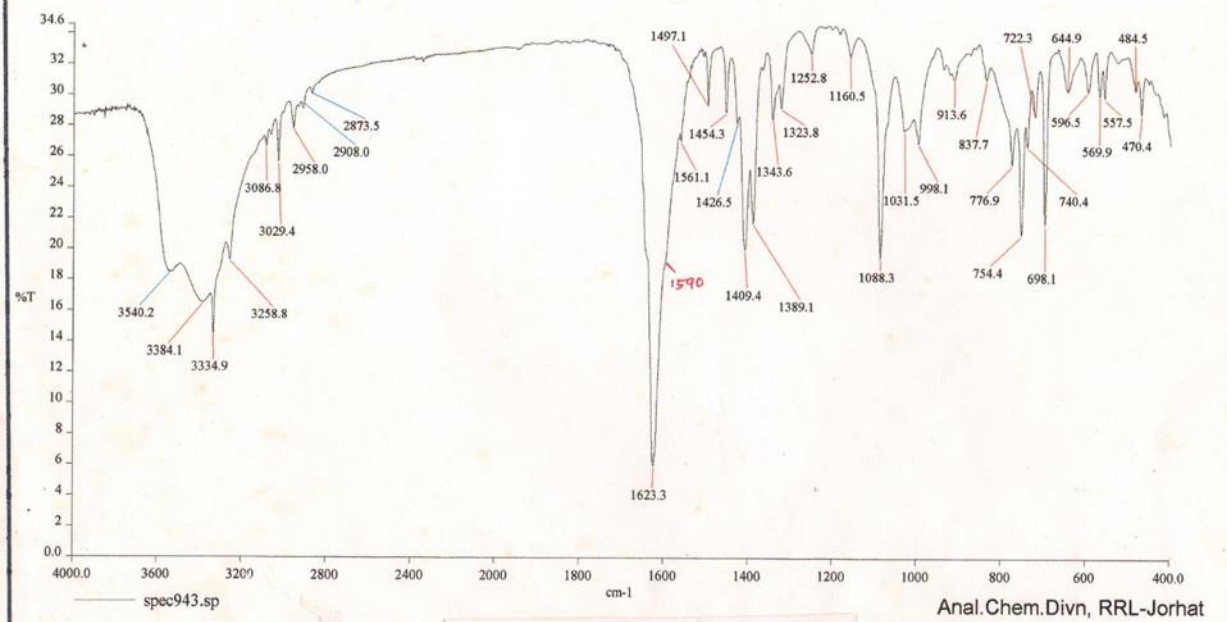
**Fig. 4.8:** FT-IR spectrum of $[ZnF_2(Hphe)(H_2O)]$  **(16)**

The TGA analysis of representative compounds, **13,14,16** and **17** were recorded (**Fig.4.9 and Table 4.3**) and the patterns obtained were found to be rather similar. The weight loss processes were not very clear cut, though the initial step near $> 200^{\circ}C$ in all of these seems to be the loss of water molecules and (or) fluoride. The weight loss in the higher temperature range could not be assigned to any specific moieties.



| TGA traces of [ZnF$_2$(Hser)(H$_2$O].4H$_2$O **(13)** | TGA traces of NH$_4$[ZnF(ser)$_2$(H$_2$O)].5H$_2$O **(14)** |
| TGA traces of [ZnF$_2$(Hphe)(H$_2$O)] **(16)** | TGA traces of [ZnF$_2$(Hhis)(H$_2$O)].2H$_2$O **(17)** |
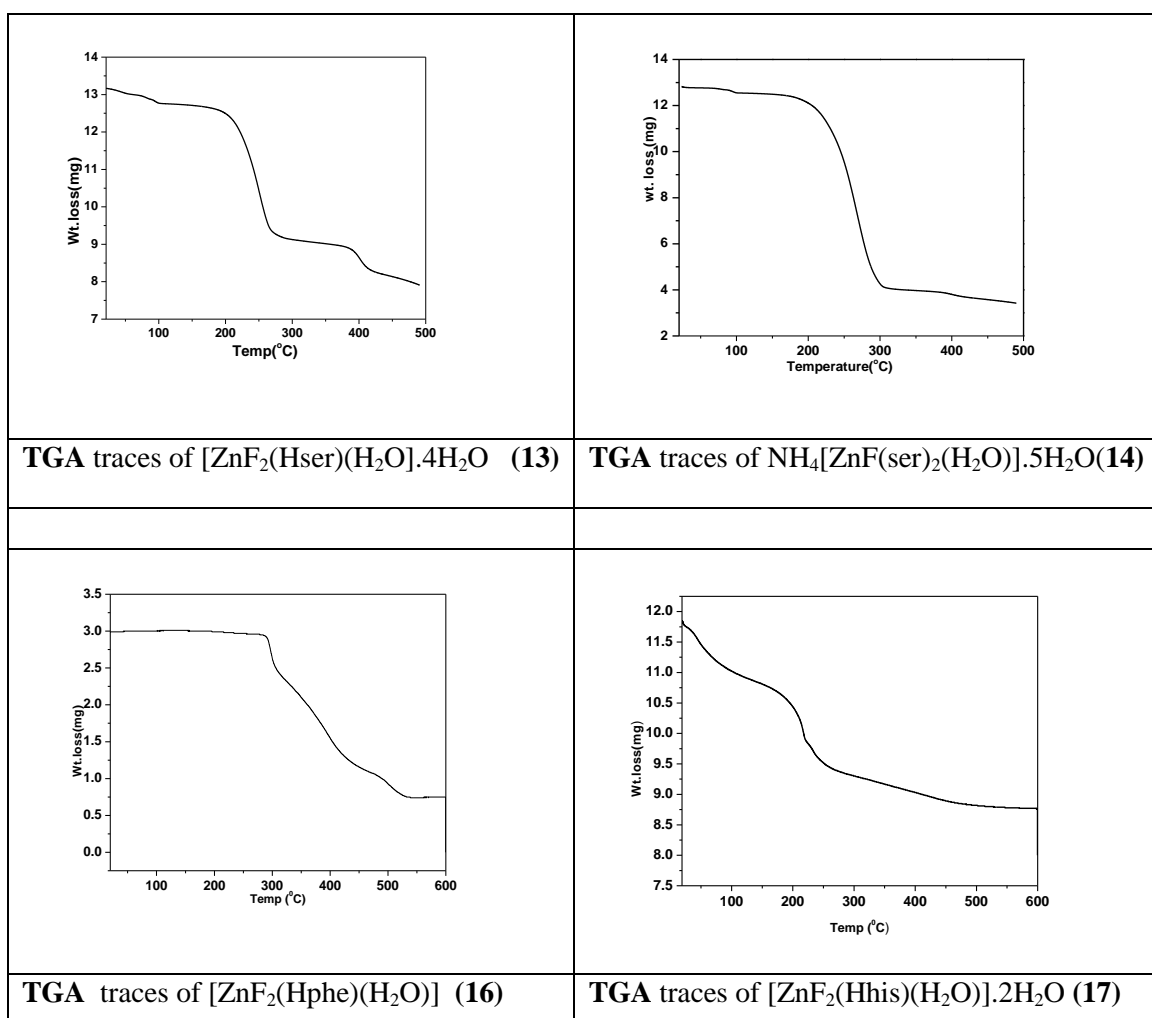
**Fig. 4.9:** TGA spectra of zinc (II) compounds **(13), (14), (16)** and **(17)**

**Table. 4.3:** TGA data of selected Zn complex **(13)**, **(14)**, **(16)** and**(17)**

| Compound | TGA plateau ($^0$C) | % of mass loss | | Process |
|---|---|---|---|---|
| | | observed | calculated | |
| [ZnF$_2$(Hser)(H$_2$O].4H$_2$O **(13)** (M = 298.3) | 22 -- 275<br>280 -- 488 | 29.8<br>10.1 | 30.1<br>12.7 | Loss of water molecules<br>Loss of two F atoms |
| NH$_4$[ZnF(ser)$_2$(H$_2$O)].5H$_2$O **(14)** M = 420.3 | 25 -- 425 | 73.4 | 75.5 | Loss of six water molecules and two F atoms |
| [ZnF$_2$(Hphe)(H$_2$O)] **(16)** M= 286.58 | 285 -- 300<br>300 -- 503 | 12.88<br>56.2 | 13.26<br>57.6 | Loss of two F atoms<br>Loss of the organic ligand (Hphe) |
| [ZnF$_2$(Hhis)(H$_2$O)].2H$_2$O **(17)** M= 294.46 | 21 -- 163<br>165 -- 347 | 11.4<br>17.8 | 11.5<br>17.9 | Loss of two water molecules<br>Loss of two F atoms and one water molecule |

The coordination geometry around zinc(II) in these complexes **(13)** and **(14)** comprises of one/two terminal fluoride, one/two bidentate [N,O] serine completing five coordination. Binding of one aquo group to zinc(II) may possibly lead to a six– coordinate distorted octahedral structure. Attempts to resolve this by X-ray crystallography proved futile as good quality single crystals capable of giving good reflection could not be obtained. X-ray quality crystals could not be grown. Needle shaped crystals of NH$_4$[ZnF$_2$(ser)].4H$_2$O, however, could be obtained from aqueous solution as well as a mixture of aqueous–ethanol solution. Poor reflectance did not permit any X-ray analysis probably due to lack of any well-defined single crystals. In the absence of any such concrete evidence, the formula of complexes **(13)** and **(14)** were shown without any coordinated water molecule, though, its occurrence within the coordination sphere may not be ruled out. Efforts to obtain iodo complexes using KI / HI did not work under several experimental condition tried in the laboratory probably owing to lesser propensity for coordination of larger I⁻ towards Zn(II).

## DFT study

The structure of the Zn(II) complex [ZnF$_2$(Hleu)(H$_2$O)] **(11)** was fully optimized using BLYP functional and DNP basis sets as implemented in the DMol3 program **[25,26]**. In order to confirm the stability of the complexes we performed vibrational frequencies calculations at the optimized structure with the same level of theory.

The DFT optimized geometries of zinc complex [ZnF$_2$(Hleu)(H$_2$O)] **(11)**is shown in **Fig.4.10**. In the vibrational frequency calculations, no imaginary frequency is observed for the compound which suggests that the optimized compound signifies stable structure i.e., shows local minima in the potential energy surfaces. Structural parameters are given in **Table 4.4**.

**Table 4.4:** DFT Bond lengths (Å) and bond angles (°) of [ZnF$_2$(Hleu)(H$_2$O)]**(11)**

| Structural parameters | Complex |
|:---:|:---:|
| Zn—F1 | 1.974 |
| Zn —F2 | 1.824 |
| Zn —O1 | 2.180 |
| Zn — O2 | 2.095 |
| F1— Zn —F2 | 130.80 |
| F1— Zn —O1 | 106.11 |
| O1— Zn —O2 | 90.92 |
| O2— Zn —F1 | 88.89 |

**Table 4.5:** DFT computed energy value and dipole moment data of **(11)**

| Compound | DFT computed energy values | | | | |
|---|---|---|---|---|---|
| | LUMO (eV) | HOMO (eV) | $\Delta E_{(E_{LUMO}-E_{HOMO})}$ | Hardness(eV) $\eta = \dfrac{E_{LUMO} - E_{HOMO}}{2}$ | Dipole moment (D) |
| [ZnF$_2$(Hleu)(H$_2$O)] **(11)** | -1.3284 | -6.27712 | 4.94872 | 2.47436 | 9.2825 |
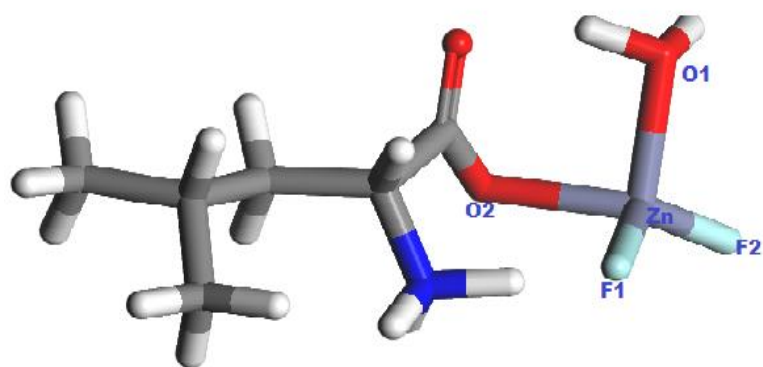
**Fig.4.10:**Optimized structure of [ZnF$_2$(Hleu)(H$_2$O)] **(11)**
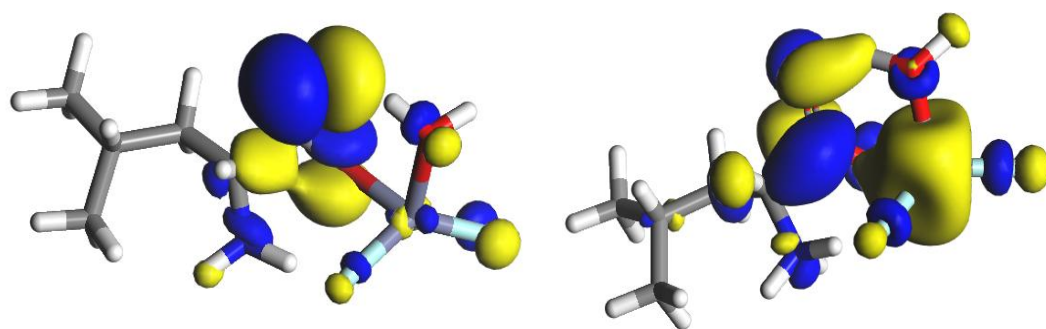


**Fig. 4.11:**HOMO, LUMO energy diagram of [ZnF$_2$(Hleu)(H$_2$O)] **(11)**

Based on analytical and spectroscopic evidences, the complexes leaving aside complex **(14)** were all conjectured to be four coordinate with a distorted tetrahedral geometry **(Fig. 4.12)**.Proposed structure of the zinc complexes are given below:
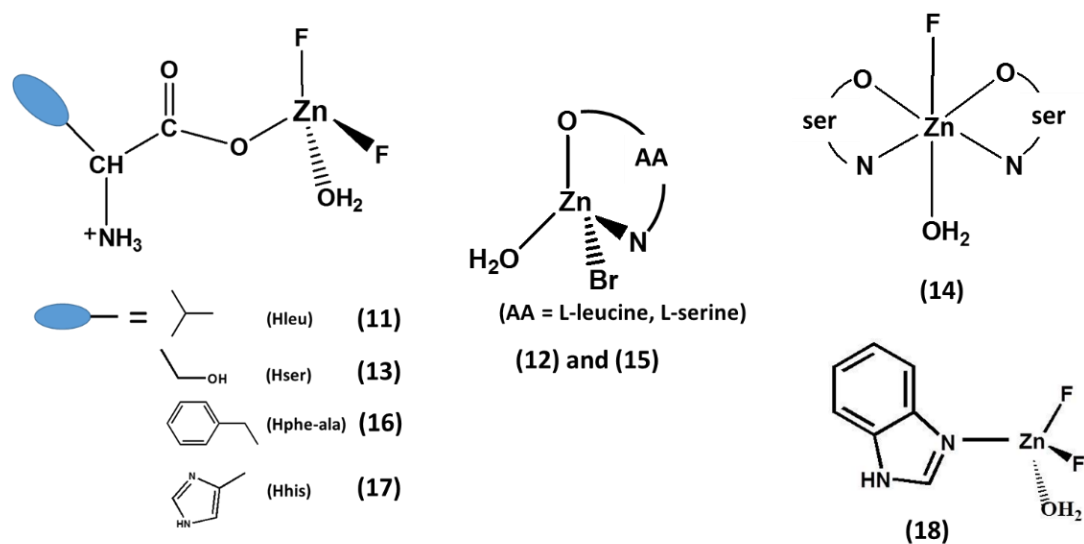


**Fig. 4.12:** Tentative structure of complexes (**11**) – (**18**).

Aqueous medium, simpler reaction strategy are the redeeming feature of the work described in this chapter.

$$\text{ZnO.nH}_2\text{O}$$

(i) NH$_4$HF$_2$, pH ~ 6
(ii) (leu) Δ (1:1) → **[ZnF$_2$(Hleu)(H$_2$O)]. 2H$_2$O (11)**

(i) NH$_4$Br, (ii) HBr pH ~ 8
(iii) (leu) Δ (1:1) → **[ZnBr(leu)(H$_2$O)] (12)**

(i) NH$_4$HF$_2$, pH ~ 6
(iii) (ser) Δ (1:1) → **[ZnF$_2$(Hser)(H$_2$O)].4H$_2$O (13)**

(i) NH$_4$HF$_2$, pH ~ 3-4
(ii) (ser) Δ (1:1) → **NH$_4$[ZnF(ser)$_2$(H$_2$O].5H$_2$O (14)**

(i) HBr, pH ~ 8
(iii) (ser) Δ (1:1) → **[ZnBr(ser)(H$_2$O)] (15)**

(i) NH$_4$HF$_2$ , pH ~ 6
(ii) (phe.ala) Δ (1:1) → **[ZnF$_2$(Hphe)H$_2$O] (16)**

(i) pH ~ 6
(iii) Δ (1:1) → **[ZnF$_2$(Hhis)(H$_2$O)].2H$_2$O (17)**

(i) (Im) pH ~ 6
(ii) Δ (1:1) → **[ZnF$_2$(bim)(H$_2$O)] (18)**
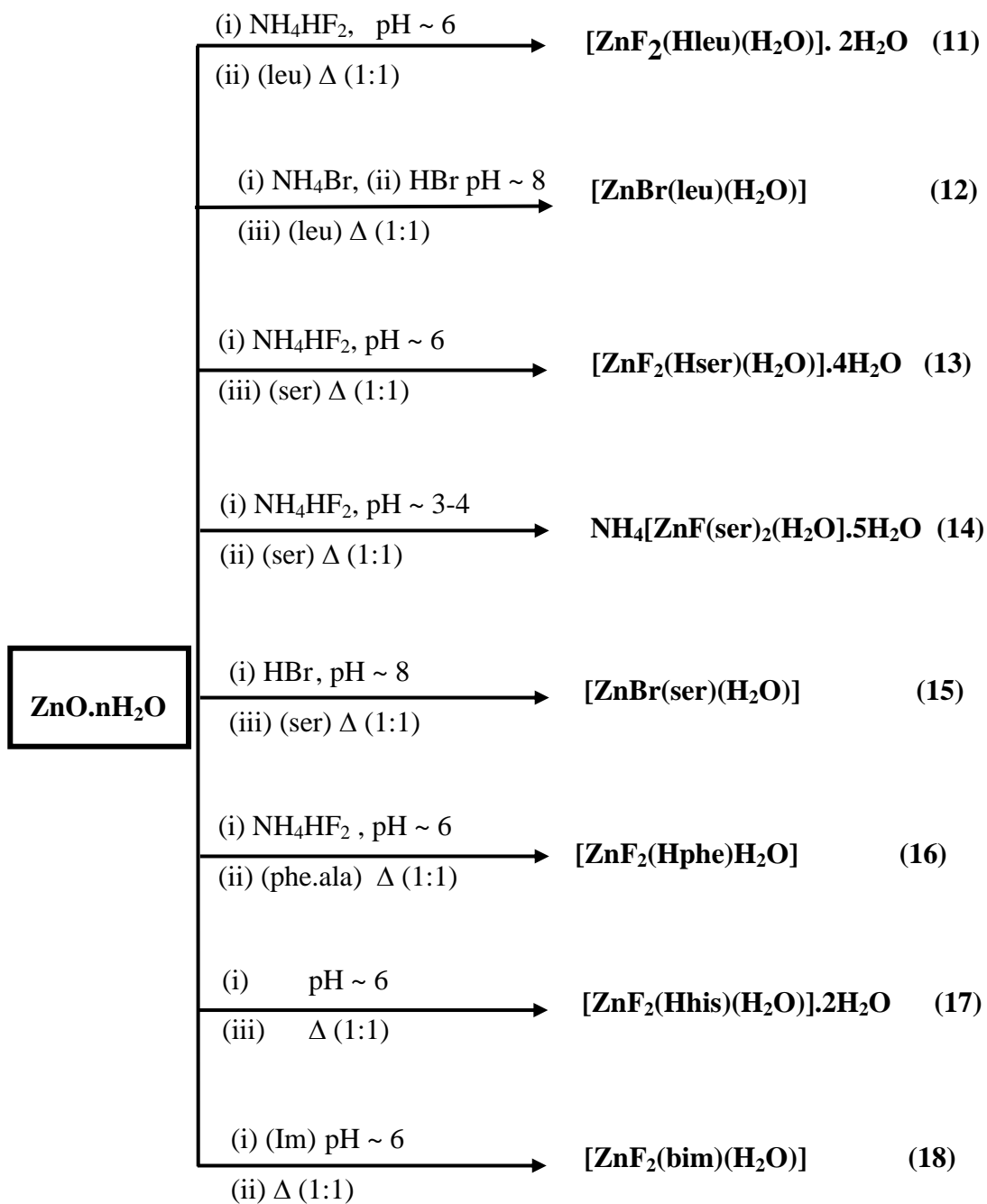
**Scheme 4.3:** Formation of complexes (**11 – 18**).

**References**

1.  H.K. Liu, P.J. Sadler, **Acc. Chem. Res.**, 2011, **44**, 349.

2.  U. Jungwirth, C.R. Kowol, B.K. Keppler, C.G. Hartinger, W. Berger, P. Heffeter,**Antioxid. Redox Signal**, 2011, **15,** 1085.

3.  S.L.H. Higgins, T.A. White, B.S.J. Winkel, K.J. Brewer, **Inorg. Chem.**, 2011, **50,**463.

4.  M. Cusumano, M.L. Di Pietro, A. Giannetto, **Inorg. Chem.**,2006, **45**, 230.

5.  C. Li, S.L. Liu, L.H. Guo, D.P. Chen, **Electrochem. Commun.**, 2005, **7**, 23.

6.  L.H. Hurley, **Nat. Rev.**, 2002, **2**, 188.

7.  J.R.J. Sorenson, **Chem. Br.**, 1984, **20**, 1110.

8.  P. Kumar, A.K. Singh, J.K. Saxena, D.S. Pandey, **J. Organomet. Chem.**, 2009, **694**, 3570.

9.  C.M. Metcalfe, S. Spey, H. Adams, J.A.J. Thomas, **Chem. Soc. Dalton Trans.**, 2002,4732.

10. A. Amboise, B.J. Maiya, **Inorg. Chem.**,2000, **39**, 4256.

11. (a) I. Bertini, F. Briganti, A. Scozzafava, Zinc proteins, in: G. Berthon (Ed.), **Handbook of Metal–Ligand Interaction in Biological Fluids: Bioinorganic Chemistry,** Marcel Dekker, New York, 1995.
    (b) A.S. Prasad, Functional roles of zinc, in: G. Berthon (Ed.), **Handbook of Metal–Ligand Interactions in Biological fluids: Bioinorganic Medicine**, Marcel Dekker, New York, 1995.

12. R.R. Chrichton, **Biological Inorganic Chemistry: An Introduction, Elsevier**, **Oxford**, 2008.

13. D.K. Blencowe, A.P. Morby, **FEMS Microbiol. Rev.**, 2003, **27**, 291.

14. J. Yao, Y. Liu, H.G. Liang, C. Zhang, J.Z. Zhu, X. Qin, M. Sun, S.S. Qu, Z.N. Yu, **J.Therm. Anal. Calorim.**, 2005, **79**, 39.

15. S. Atmaca, K. Gul, R. Cicek, Turk. **J. Med. Sci.**, 1998, **28**,595.

16. S. Ranganathan, N. Jayaraman, R. Roy, **Tetrahedron**, 1992, **48**, 92.

17. H. Boerzel, M. Koeckert, W. Bu, B. Spingler, S.J. Lippard, **Inorg. Chem.**, 2003, **42**, 1504.

18. M. Gelinsky, H. Vahrenkamp, **Eur. J. Inorg.**, 2002, 2458.

19. T. Spiro (ed.) **Zinc Enzymes**, Wiley, New York, 1983.

20. M.S. Lee, G.P. Gippert, K.V. Soman, D.A. Case, P.E. Wright, **Science**, 1989, **245**, 635.

21. R.J.P. Williams, **Polyhedron**, 1987, **6**, 61.

22. G. Perkin, **Chem. Rev.**, 2004, **104**, 699.

23. M. Rombach, M. Gelinsky, H. Vahrenkamp, **Inorg. Chim. Acta**, 2002, **334**, 25.

24. C. Djordjevic, N. Vuletic, B.A. Jacobs, E. Sinn, **Inorg. Chem.**, 1997, **36**, 1798.

25. B. Delly **J. Chem. Phys.**, 1990, **92**, 508.

26. C. Lee, W. Yang, R.G. Parr, **Phys. Rev. B**, 1988, **37**, 785.

✼ ✼ ✼ ✼ ✼