

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

5. A Introduction

Biologically non-essential but environmentally relevant, cadmium in its +II oxidation state, is capable of coordinating N, or O, or S-donor biogenic ligand. Aminoacid complexes of cadmium(II) are known and are significant in the context of physiological effects of the metal or its compound. Quite a few reviews have addressed preparation, structural and physical investigation of aminoacid complexes [1-2]. Complexes of the type $[\text{Cd}(\text{phe})_2] \cdot n\text{H}_2\text{O}$ [3], $[\text{Cd}(\text{gly})_2\text{X}_2]$ (X = Cl or Br) [4], and those that contain glycine [5-6], histidine [6], alanine [7], valine [8], proline [9], serine, asparagine, tyrosine, arginine, tryptophan, leucine [10] are documented. Solution studies included complexes of

glycine [11], aspartic acid [12], l-hydroxy proline [13], cysteine and alanine [11-14]. A number of other mixedligandhalo complexes of cadmium(II) with non-natural aminoacid as coligand have recently been documented[15]Imidazoles and its derivatives are a typical N-donor heterocyclic ligand which may mimic the histidine imidazole in coordination aspects is considered a component of biologically important molecules [15]. Due to the privileged structure [16], imidazoles including benzimidazoles have drawn immense interests owing to their potential application in the area of drugs and pharmaceuticals as antitumor [17], antiviral [18], anticancer [19], antimicrobial [20], antiprotozoal [21], and anti-inflammatory or analgesic activities [22]. Synthesis, characterization, and biological activities of mixed-halo complexes of zinc, cadmium, copper, and nickel containing meta -aminophenyl benzimidazole have been documented [23].

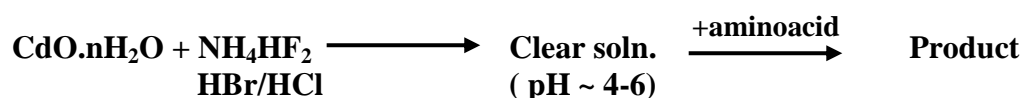
With the recognition of its valuable metallurgical properties the metal, its various compounds have found wide industrial application since 19th century. Coal and other fossil fuels also contain cadmium which is released into atmosphere on combustion. The metal is close to lead and mercury in terms of current toxicological concern. Infact, the entry of the metal in biological system induces synthesis of metallothioneins, in addition to being interfering in many other biological molecules [2].

A complex of cadmium with substituted l-methionine ligand has recently been shown to possess NLO activity [24]. A novel poly-ligand coordination polymer, $[Cd(en)(NO_3)_2(4,4'-bpy)]_n$ has been reported to possess third order NLO effect with high hyperpolarisability $|\gamma|$ value (1.7×10^{-29} esu) [25]. A dibromo bis(l-proline) cadmium(II) complex synthesised from aqueous solution reported recently has been shown to exhibit good NLO activity [26].

Despite such studies, synthesis and investigations on mixedligand complexes of cadmium remains inadequately addressed. Chemical similarity of Zn and Cd suggests that the latter may displace Zn from its biologically active site [27]. In light of this discussion, it was considered appropriate to take up work on synthesis of mixedligand cadmium(II) complex, with aminoacid-halide combination. Accordingly, an account of synthesis and characterisation of molecular complexes of the type $[\text{CdX}_2\text{L}(\text{H}_2\text{O})]$ {L= l-leucine, l-serine, l-methionine, l-cysteine, imidazole or benzimidazole; (X = F, Cl, Br or I)} , are presented in this chapter.

5.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 mixedligand complexes of cadmium(II) (**19 to 28**) are reported herein.



Protocol for synthesis of Cu (II) complexes

Synthesis of $[\text{CdF}_2(\text{Hleu})(\text{H}_2\text{O})]$ (**19**)

To a freshly prepared aqueous suspension of hydrated cadmium (II) oxide, $\text{CdO} \cdot n\text{H}_2\text{O}$, obtained from $\text{CdSO}_4 \cdot \frac{8}{3} \text{H}_2\text{O}$ (2g, 2.5m mol), solid NH_4HF_2 (0.42g, 7mol) was added just to dissolve (pH \sim 6) followed by l-leucine (0.32g, 2.5m mol) with constant stirring. The solution was concentrated on a water bath and ethanol was added when a pasty white mass was obtained (pH \sim 6) on addition of more ethanol forms white crystalline product.

It was filtered, washed with ethanol and finally by 50% ethanol then dried over fused CaCl_2 *in vacuo*. The yield was about 55%.

Synthesis of $[\text{CdF}_2(\text{Hser})(\text{H}_2\text{O})]$ (20)

To a freshly prepared aqueous suspension of hydrated cadmium (II) oxide $\text{CdO}\cdot n\text{H}_2\text{O}$ obtained from $\text{CdSO}_4\cdot \frac{8}{3}\text{H}_2\text{O}$ (2g, 2.5m mol) solid, NH_4HF_2 (0.42g, 7m mol) was added just to dissolve (pH ~ 6). Solid L-Serine (0.26g, 2.5m mol) was added with constant stirring (pH ~ 6). The solution was concentrated on a water bath to a small volume. It was cooled to room temperature and ethanol was added when a white precipitate was obtained. It was filtered, washed with ethanol and finally by 50% ethanol and dried over fused CaCl_2 *in vacuo*. The yield was about 50%.

Synthesis of $[\text{CdF}_2(\text{Hmet})(\text{H}_2\text{O})]$ (21)

To a freshly prepared aqueous suspension of hydrated cadmium (II) oxide ($\text{CdO}\cdot n\text{H}_2\text{O}$) obtained from $\text{CdSO}_4\cdot \frac{8}{3}\text{H}_2\text{O}$ (2g, 2.5m mol). Solid NH_4HF_2 (0.42g, 7m mol) was added just to dissolve (pH ~ 6) followed by L-methionine (0.73g, 2.5m mol) (pH ~ 6). The whole was concentrated on a water bath to a small volume. It was cooled to room temperature and ethanol was added when a white product was obtained. It was filtered, washed with ethanol and finally by 50% ethanol and dried over fused CaCl_2 *in vacuo*. The yield was about 60%.

Synthesis of $[\text{CdF}_2(\text{Hcys})(\text{H}_2\text{O})]$ (22)

To a freshly prepared hydrated cadmium (II) oxide, $\text{CdO}\cdot n\text{H}_2\text{O}$ obtained from $\text{CdSO}_4\cdot \frac{8}{3}\text{H}_2\text{O}$ (2g, 2.5m mol), solid NH_4HF_2 (0.42g, 7m mol) was added (pH ~ 4) followed by cysteine (0.30g, 2.5m mol). The whole was then concentrated on a water bath with occasional stirring. To this ethanol was added when a white product was obtained. It

was filtered and washed with ethanol and finally by 50% ethanol and dried over fused CaCl_2 *in vacuo*. The yield was about 55%.

Synthesis of $[\text{CdF}_2(\text{im})(\text{H}_2\text{O})](23)$

To a freshly prepared aqueous suspension of hydrated cadmium (II) oxide, $\text{CdO}\cdot n\text{H}_2\text{O}$ obtained from $\text{CdSO}_4\cdot \frac{8}{3}\text{H}_2\text{O}$ (2g, 2.5m mol) solid NH_4HF_2 (0.42g, 7m mol) was added (pH ~ 5) followed by aqueous solution of imidazole (0.17g, 2.5m mol). It was concentrated on a water bath when a white product was obtained it was cooled to room temperature and alcohol was added when a white product was obtained. It was washed with ethanol and then 50% ethanol and dried over fused CaCl_2 *in vacuo*. The yield was about 55%.

Synthesis of $[\text{CdBr}_2(\text{im})(\text{H}_2\text{O})](24)$

To a freshly prepared hydrated cadmium(II) oxide, $\text{CdO}\cdot n\text{H}_2\text{O}$ obtained from $\text{CdSO}_4\cdot \frac{8}{3}\text{H}_2\text{O}$ (2g, 2.5m mol) solid imidazol (0.17g, 2.5m mol) was added with constant stirring followed by NH_4Br (1g, 10m mol) and drops of HBr (40%, 1ml) just to dissolve (pH ~ 4). The solution was warmed on a water bath when apale brown solid was precipitated. Ethanol was added when more pale brown compound was precipitated. It was filtered and washed with ethanol and finally by 50% ethanol then dried over fused calcium chloride *in vacuo*. The yield was about 55%.

Synthesis of $[\text{CdF}_2(\text{bim})(\text{H}_2\text{O})](25)$

To a freshly prepared hydrated cadmium(II) oxide, $\text{CdO}\cdot n\text{H}_2\text{O}$ obtained from $\text{CdSO}_4\cdot \frac{8}{3}\text{H}_2\text{O}$ (2g, 2.5m mol) solid NH_4HF_2 (0.42g, 7m mol) was added (pH ~ 6) followed by benzimidazole (0.29g, 2.5m mol) in 50% ethanol. The solution was concentrated on a water bath when a white precipitated was produced. It was filtered,

washed with water and then 50% ethanol and dried over fused CaCl_2 *in vacuo*. The yield was about 65%.

Synthesis of $[\text{CdCl}_2(\text{bim})(\text{H}_2\text{O})](26)$

To a freshly prepared hydrated cadmium (II) oxide, $\text{CdO}\cdot n\text{H}_2\text{O}$ obtained from $\text{CdSO}_4\cdot \frac{8}{3}\text{H}_2\text{O}$ (2g, 2.5m mol) solid NH_4Cl (0.5g, 9m mol) was added then drop wise dil. HCl was added just to dissolved the suspension (pH ~ 4) followed by benzimidazole (0.47g, 4m mol) in 50% ethanol. The solution was concentrated on a water bath when a white precipitated was produced. It was filtered, washed with water and then 50% ethanol and dried over fused CaCl_2 *in vacuo*. The yield was about 65%.

Synthesis of $[\text{CdBr}_2(\text{bim})(\text{H}_2\text{O})](27)$

To a freshly prepared hydrated cadmium (II) oxide obtained from $\text{CdSO}_4\cdot \frac{8}{3}\text{H}_2\text{O}$ (2g, 2.5m mol), drop wise HBr was added (40%, 1ml) (pH ~ 4) just to dissolved the suspension, followed by benzimidazole (0.29g, 2.5m mol) in 50% alcohol. It was concentrated on a water bath and dil. NaOH solution was added when a off-white product was obtained (pH ~ 7). The compound was filtered and washed with water and finally by ethanol and dried over fused CaCl_2 *in vacuo*. The yield was about 65%.

Synthesis of $[\text{CdI}_2(\text{bim})(\text{H}_2\text{O})](28)$

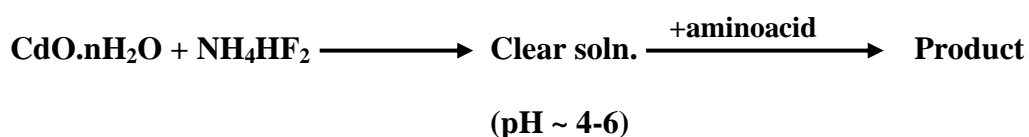
To a freshly prepared hydrated cadmium(II) oxide obtained from $\text{CdSO}_4\cdot \frac{8}{3}\text{H}_2\text{O}$ (2g, 2.5m mol), KI (2g, 12m mol) was added (pH ~ 6) followed by benzimidazole (0.29g, 2.5m mol) in 50% alcohol. It was stirred and concentrated on a water bath when a off-white product was obtained (pH ~ 6). The compound was filtered and washed with

water and finally by ethanol and dried over fused CaCl_2 *in vacuo*. The yield was about 65%.

5.C Results and Discussion

The aminoacid ligands, l-leucine, l-serine, l-methionine, l-cysteine and imidazole and benzimidazole are known to bind to cadmium(II) and examples of binary compounds abounds. The selection of l-methionine and l-cysteine were based on their propensity to bind hard cadmium(II) through sulfur donor site(s). Halides being ubiquitous in biological system are ideally suited to serve as ligands to cadmium alongside the aminoacids. Synthesis of mixedligand halo complexes shall depend on strategies that will counter formation of binary fluoro or aminoacid complexes. Our previous experience elsewhere with copper(II) in the context of preparation of mixedligand fluoro complexes suggest that a relatively higher pH value (> 6) has led to only binary fluoro complex formation [28].

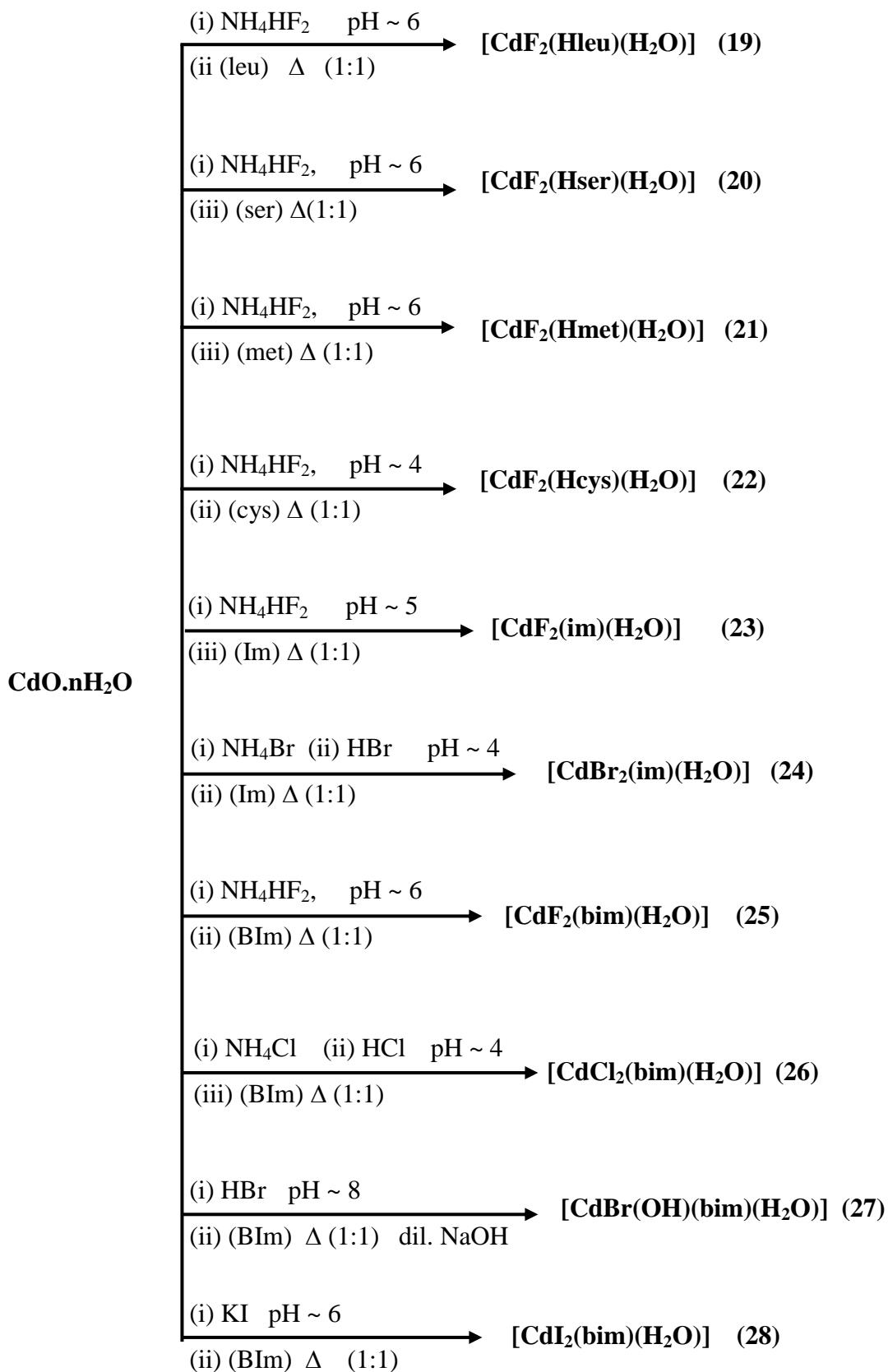
The conjecture that a pH value lower than the isoelectric point of the respective aminoacid ensure ‘zwitterionic’ form thus favouring its coordination to the metal centre has worked well on many earlier occasion [28,29]. The strategy adopted for the syntheses being described here is based on an interaction of hydrated cadmium oxide, $\text{CdO}\cdot n\text{H}_2\text{O}$ with bifluoride, HF_2^- in an acid-base type reaction followed by addition of the aminoacid coligand (Scheme 5.1).



Scheme 5.1: Formation of mixedligand fluoro cadmium(II) complexes.

The choice of NH_4HF_2 instead of HF acid not only does away with the cumbersome handling of highly corrosive and hazardous hydrofluoric acid but also offer a milder fluoridating agent at pH ~ 4 or so, a condition appropriate for coordination of aminoacids. The Cd : aminoacid: imidazole ratio has been maintained at 1 : 1 for all the synthesis in order to leave room for halide coordination. Interestingly at pH little over 6, the desired mixedligand complexes were not formed. The complexes **(19)** – **(28)** were all obtained as off-white microcrystalline water soluble compounds, stable to air and moisture (**Scheme 5.2**). The complexes **(19)** – **(24)** are soluble in water and rest are not. The complexes were molecular in nature consistent with the solution electrical conductance values (ca. 15 S). The benzimidazole complexes were all sparingly soluble in water or other common organic solvent precluding any electrical conductance measurements.

Elemental analyses (**Table 5.1**) revealed Cd : F stoichiometry 1 : 2 for all the complexes while Cd : L (L = coligand) was found to be 1 : 1. Cadmium was determined both by direct titrimetric method using EDTA as well as by Atomic Absorption Spectrophotometric (AAS) technique.



Scheme 5.2: Scheme of formation of complexes (19 – 28)

Table 5.1 : Analytical data of complexes (19-28)

Complexes	Colour	Analysis* (%)				
		Cd	^a X	C	N	H
[CdF ₂ (Hleu)(H ₂ O)] (M = 299.58)	(19) White	37.1 (37.5)	^b 11.8 (12.7)	23.4 (24.0)	4.3 (4.7)	4.4 (5.0)
[CdF ₂ (Hser)(H ₂ O)] (M = 273.4)	(20) White	41.6 (41.1)	^b 13.2 (13.9)	12.7 (13.2)	5.2 (5.1)	3.8 (3.3)
[CdF ₂ (Hmet)(H ₂ O)] (M = 317.61)	(21) White	35.9 (35.4)	^b 11.8 (12.0)	18.4 (18.9)	5.2 (4.4)	3.6 (4.1)
[CdF ₂ (Hcys)(H ₂ O)] (M = 289.47)	(22) White	40.0 (38.8)	^b 12.8 (13.1)	12.7 (12.4)	4.6 (4.8)	3.5 (3.1)
[CdF ₂ (im)(H ₂ O)] (M = 236.48)	(23) White	47.9 (47.5)	^b 15.8 (16.0)	15.7 (15.2)	11.2 (11.8)	3.1 (2.5)
[CdBr ₂ (im)(H ₂ O)] (M = 358.28)	(24) White	32.0 (31.4)	^d 44.9 (44.6)	10.1 (10.0)	7.6 (7.8)	2.0 (1.7)
[CdF ₂ (bim)(H ₂ O)] (M = 286.47)	(25) White	41.1 (39.2)	^b 13.4 (13.3)	28.5 (29.3)	9.5 (9.8)	2.8 (2.8)
[CdCl ₂ (bim)(H ₂ O)] (M = 319.47)	(26) White	35.6 (35.2)	^c 22.1 (22.2)	26.7 (26.3)	8.6 (8.8)	2.6 (2.5)
[CdBr ₂ (bim)(H ₂ O)] (M = 408.27)	(27) White	28.0 (27.5)	^d 38.8.0 (39.1)	20.4 (20.6)	6.6 (6.9)	1.8 (2.0)
[CdI ₂ (bim)(H ₂ O)] (M = 502.34)	(28) White	21.8 (22.4)	^e 49.9 (50.5)	16.1 (16.7)	4.8 (5.6)	1.9 (1.6)

* Calculated values are in parentheses. ^aX : F, Cl, Br, I; ^bF, ^cCl, ^dBr, ^eI

The complexes **(19)** – **(28)** exhibited diagnostic signatures typical of coordinated ligand. A weak band at ca. 405 cm^{-1} has been assigned to Cd – F stretch. Bands at ca. 1640 cm^{-1} and ca. 3400 cm^{-1} attributable, respectively, to ν_{HOH} (bending) and ν_{OH} (stretching) mode of water. A rather weak band observed at ca. 750 cm^{-1} has been assigned to ρ_r (H-O-H), the rocking mode of water suggesting its coordination to the metal ($\text{H}_2\text{O} \longrightarrow \text{Cd}^{2+}$). Thermal stability of these compounds beyond 200°C or so in pyrolytic experiments further augmented the coordinated nature of such water molecules.

The IR signatures (**Table 5.2**) of the different aminoacid ligands showed rather general pattern. Some common features in compounds **(19)** and **(20)** are : 1545 cm^{-1} ($\nu_{\text{as(COO)}}$), 1460 cm^{-1} ($\nu_{\text{s(COO)}}$) for the carboxylato part. We conclude that the aminoacid ligand present in zwitterionic form binds the metal through COO^- function in monodentate fashion. The shifts by $15\text{-}20\text{ cm}^{-1}$ to lower wave number in carboxylato stretching of the free ligand from those in the complexes lend credence to this conjecture.

The UV-visible spectra were recorded for some water soluble complexes (**20**, **23**, **25**). Barring a very weak absorption at around 270 nm in the UV region, there were no peaks in the visible region as would be expected of a d^{10} configuration (**Fig. 5.1**).

These complexes were screened for photoluminescence property at an excitation frequency of 270 nm and found to be strongly fluorescent showing emission maxima at ca. 365 nm for the imidazole complexes and at 395 nm for the serine complex. This luminescence behavior is believed originate from occurrence of Cd(II), a d^{10} configuration (**Fig. 5.1**).

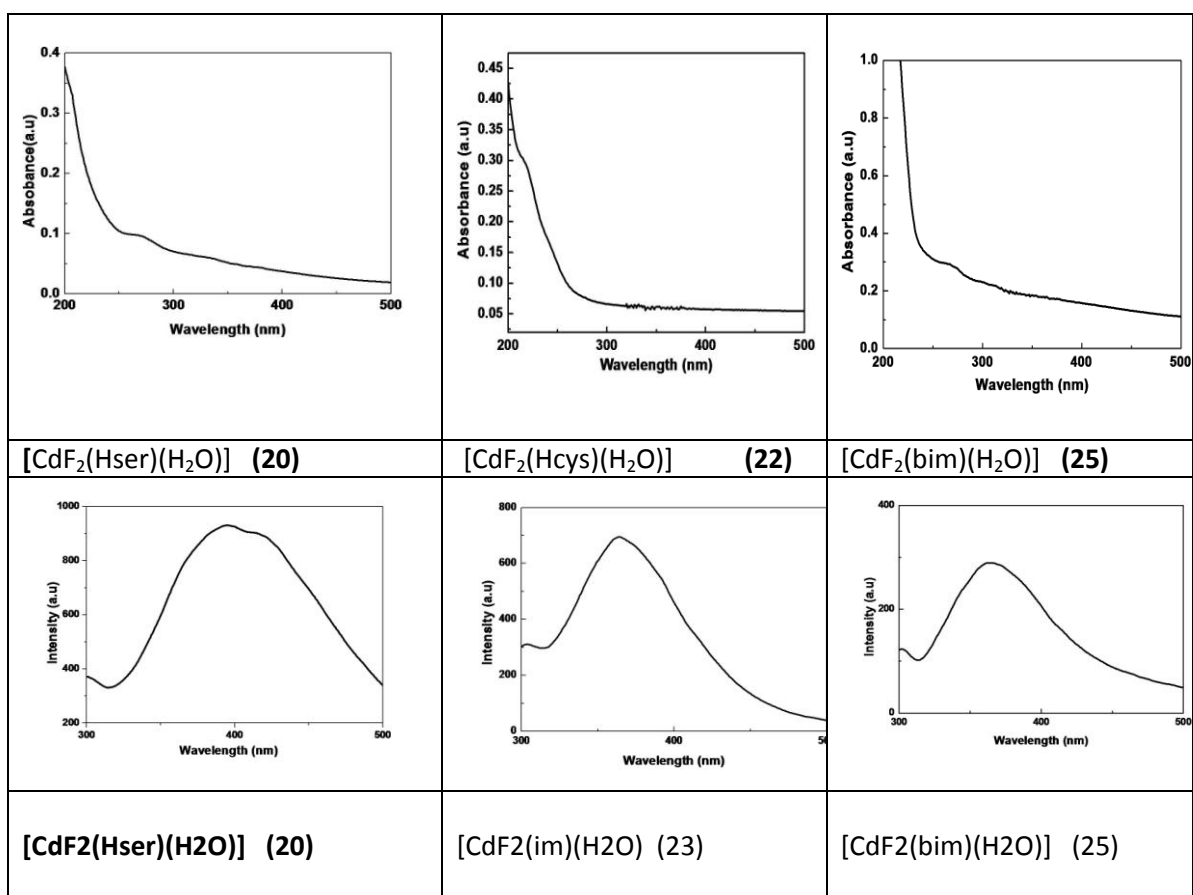


Fig.5.1 : UV-Vis. spectra of (20), (22), and (25) in $\times 10^{-3}$ aqueous solution
 Photoluminescence spectra of (20), (23) and (25)
 (PL bands at for (20) at $\lambda=395$ nm, for (23) at $\lambda=363$ nm and for (25) at $\lambda=364$ nm)

Table 5.2 : Structurally significant FT-IR data of complexes (**19** -- **28**)

Complex	IR bands (cm ⁻¹)						
	ν_{OH}	δ_{OH_2}	$\nu_{\text{COO (as)}}$	$\nu_{\text{COO (s)}}$	$\nu_{\text{(Im ring mode)}}$	$\rho_{\text{r (H}_2\text{O)}}$	
[CdF ₂ (Hleu)(H ₂ O)]	(19)	3445	1635	1545	1440	--	752
[CdF ₂ (Hser)(H ₂ O)]	(20)	3405	1640	1545	1460	--	755
[CdF ₂ (Hmet)(H ₂ O)]	(21)	3410	1620	1580	1410	--	760
[CdF ₂ (Hcys)(H ₂ O)]	(22)	3410	1620	1585	1390	--	730
[CdF ₂ (im)(H ₂ O)]	(23)	3400	1640	--	--	980	755
[CdBr ₂ (im)(H ₂ O)]	(24)	3450	1630	--	--	940	750
[CdF ₂ (bim)(H ₂ O)]	(25)	3400	1610	--	--	995	755
[CdCl ₂ (bim)(H ₂ O)]	(26)	3400	1625	--	--	980	740
[CdBr ₂ (bim)(H ₂ O)]	(27)	3450	1620	--	--	950	760
[CdI ₂ (bim)(H ₂ O)]	(28)	3410	1620	--	--	950	750

The complex **(28)** containing iodo and benzimidazole as ligands also incorporate an ‘aquo’ group as ancillary ligand. In this case, the issue of water coordination was resolved on the basis of observance of a broad and weak band 3450cm^{-1} attributable to ν_{OH} of water. Water coordination in this complex was further ascertained on the basis of a bending mode at around 760 w cm^{-1} ($\rho_{\text{H-O-H}}$) **[30]**. Simple heating experiment indicated weight loss of the compound at $\sim 200\text{ cm}^{-1}$ consistent with the loss of one water molecule. The imidazole complex $[\text{CdX}_2(\text{Im})(\text{H}_2\text{O})]$ ($\text{X}=\text{F}, \text{Br}$) revealed peaks in its FT-IR spectrum at 1545 cm^{-1} and 940 cm^{-1} corroborating its coordination to the metal centre through the sp^2 -nitrogen **[31]**. In all, a distorted tetrahedral structure appears to be most plausible for the complexes reported herein. Bands at 980 cm^{-1} and 1120 cm^{-1} observed in the complexes **24-29** are typical of benzimidazole ligand **[32]** (**Fig 5.2-5.11**).

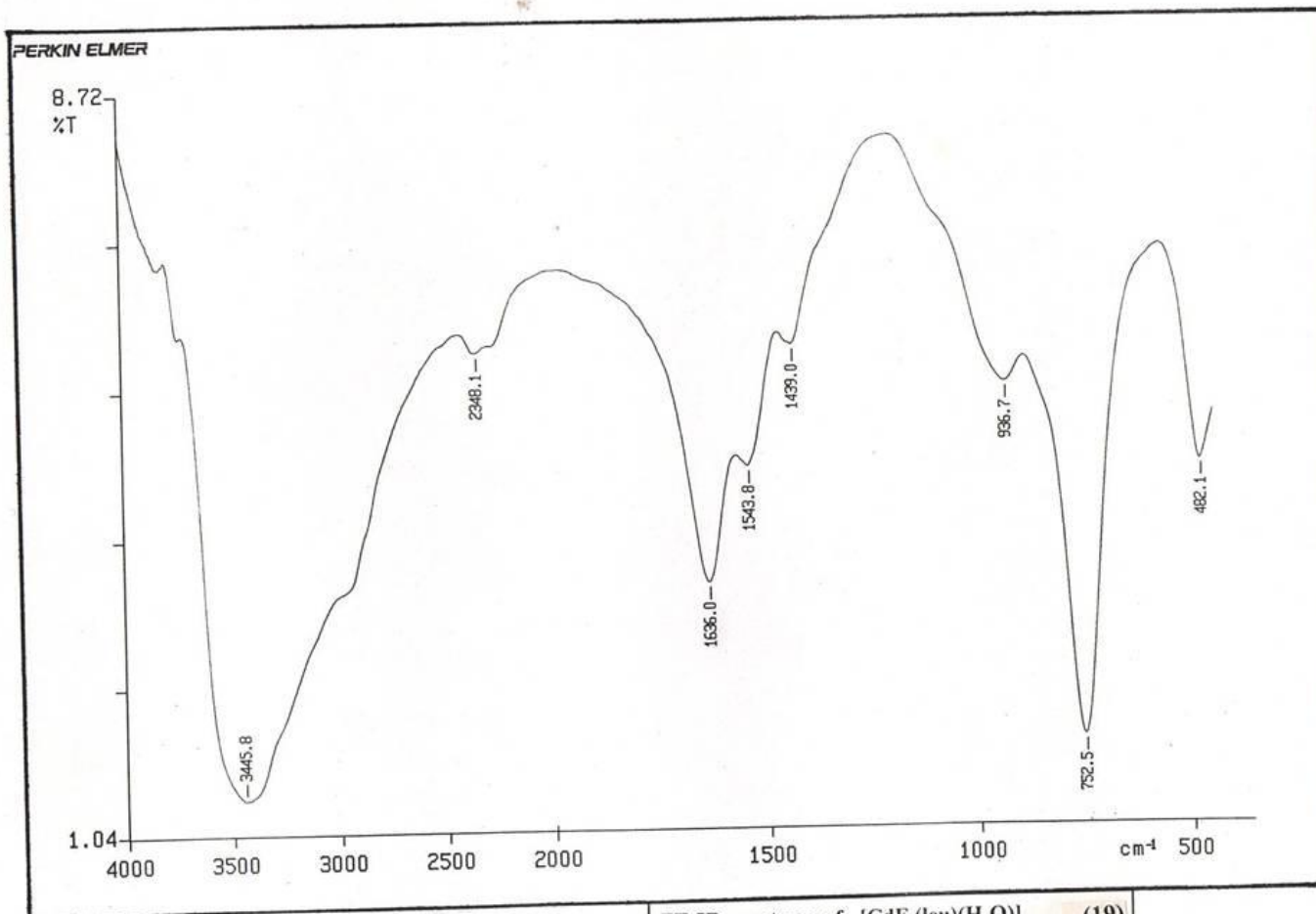


Fig. 5.2 FT-IR spectrum of $[CdF_2(leu)(H_2O)]$ (19)

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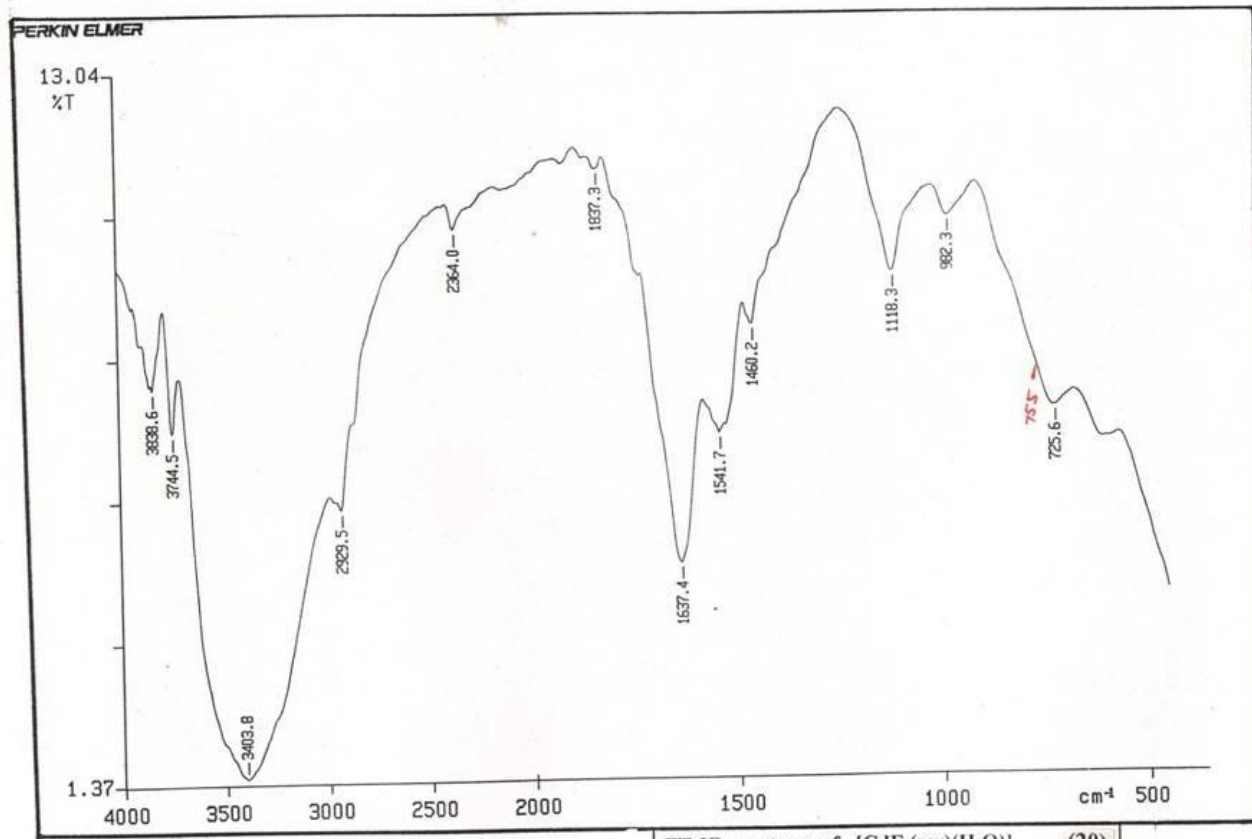
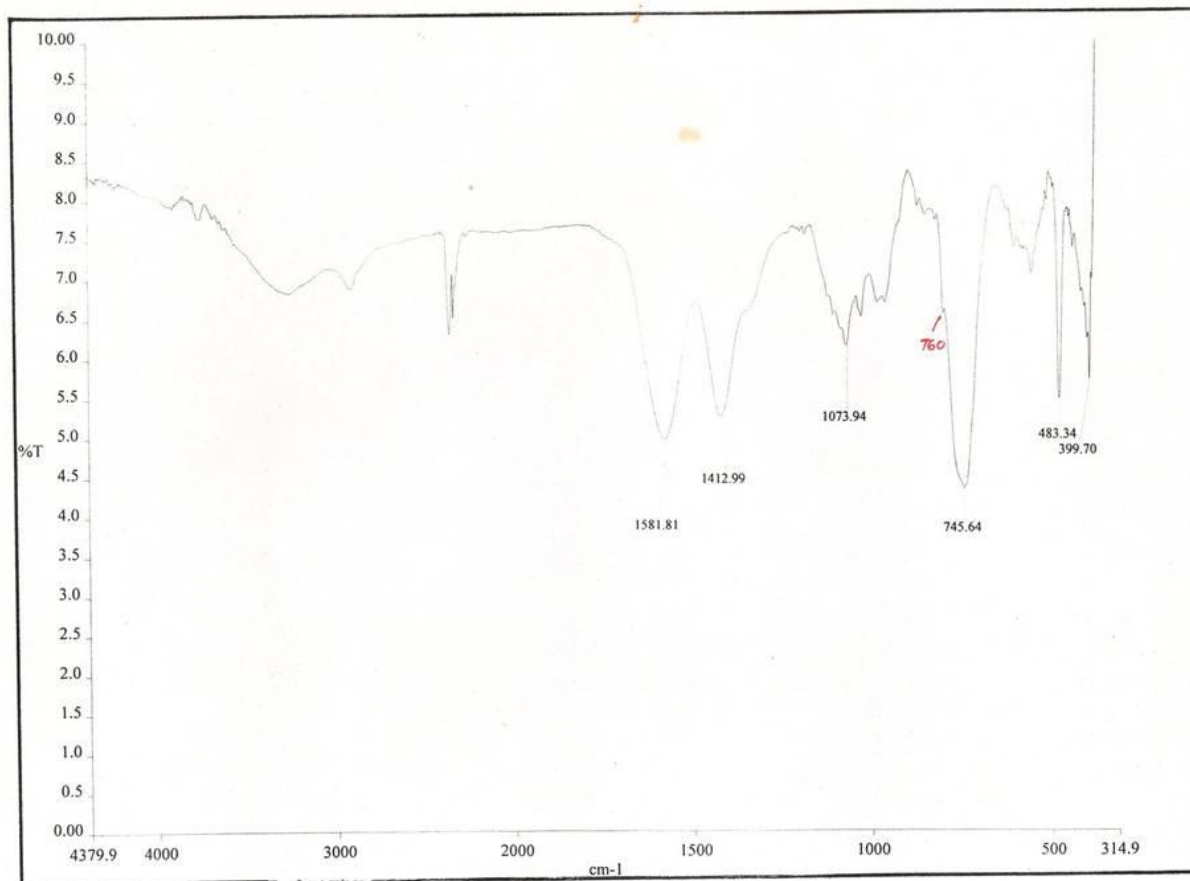


Fig. 5.3

FT-IR spectrum of [CdF₂(ser)(H₂O)] (20)

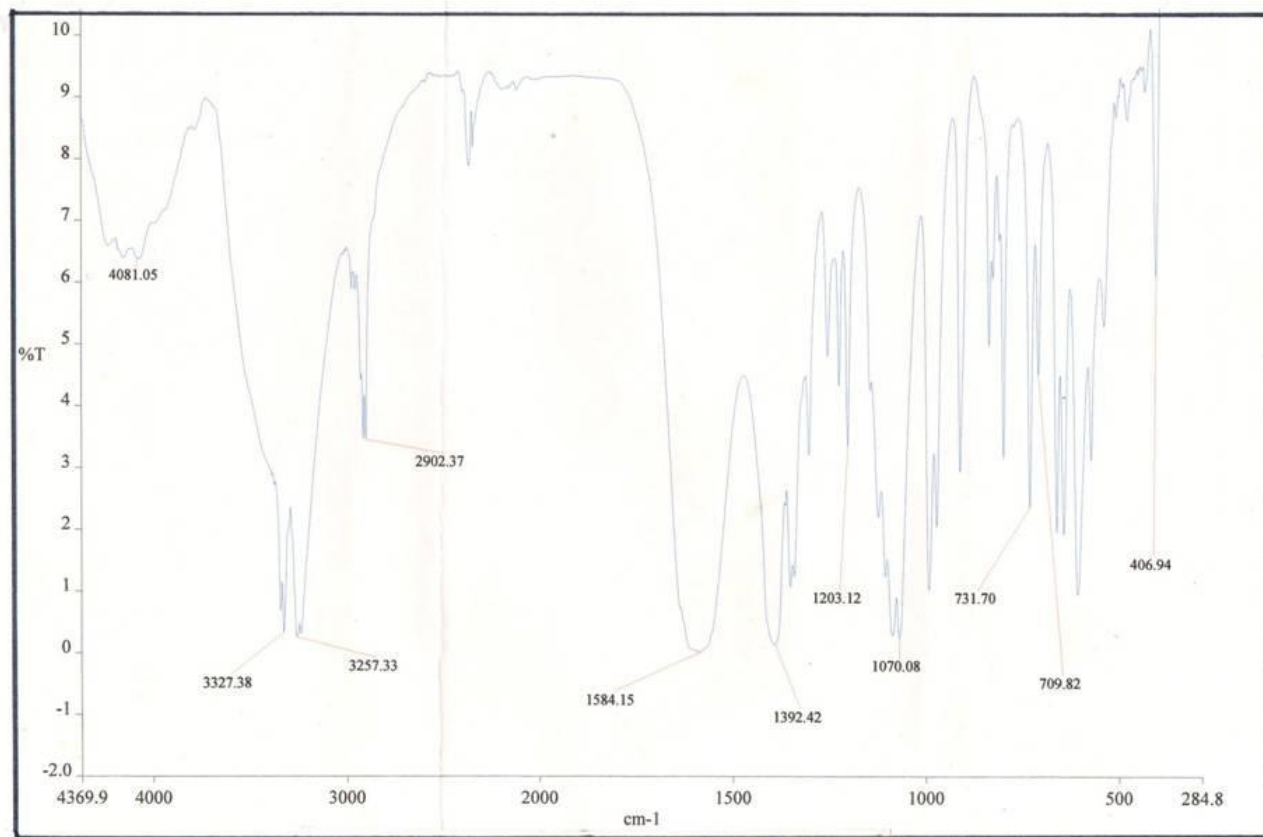
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X: 1 scan, 4.0cm⁻¹, smooth



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Fig. 5.4

FT-IR spectrum of [CdF₂(met)(H₂O)] (21)



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Fig. 5.5 FT-IR spectrum of [CdF₂(cys)(H₂O)] (22)

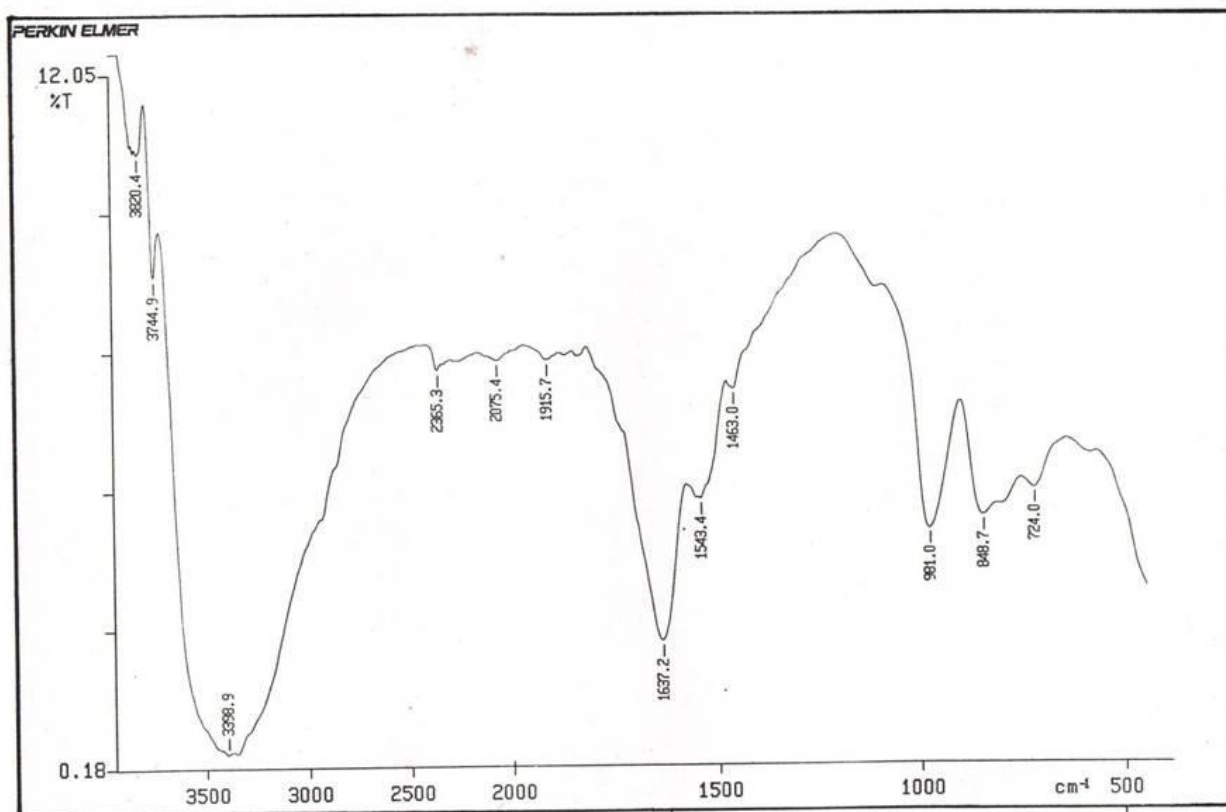
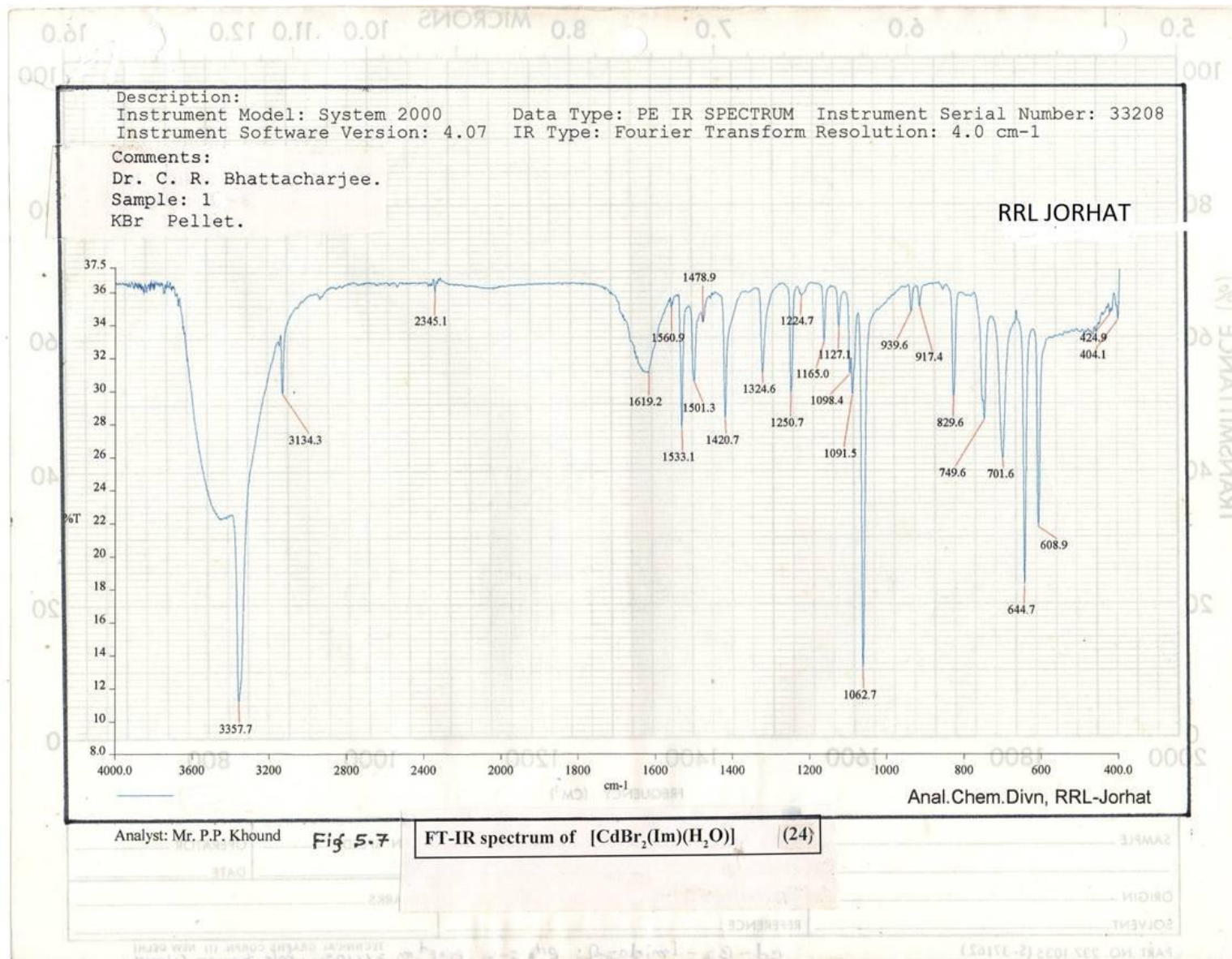
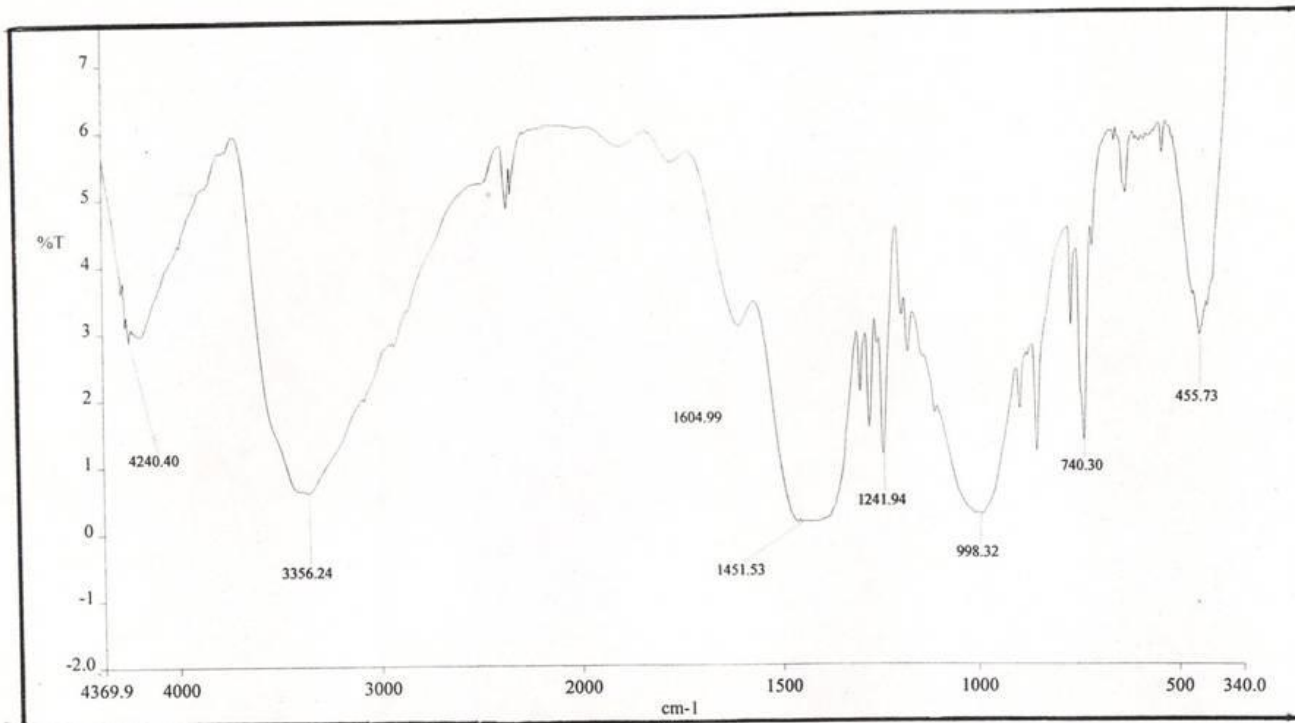


Fig. 5.6 FT-IR spectrum of $[CdF_2(lm)(H_2O)]$ (23)

02/06/14 12:47 DR.P.K.BORUAH G.U.
X: 1 scan, 4.0cm⁻¹, flat, smooth





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Fig. 5.8

FT-IR spectrum of [CdF₂(BIm)(H₂O)] (25)

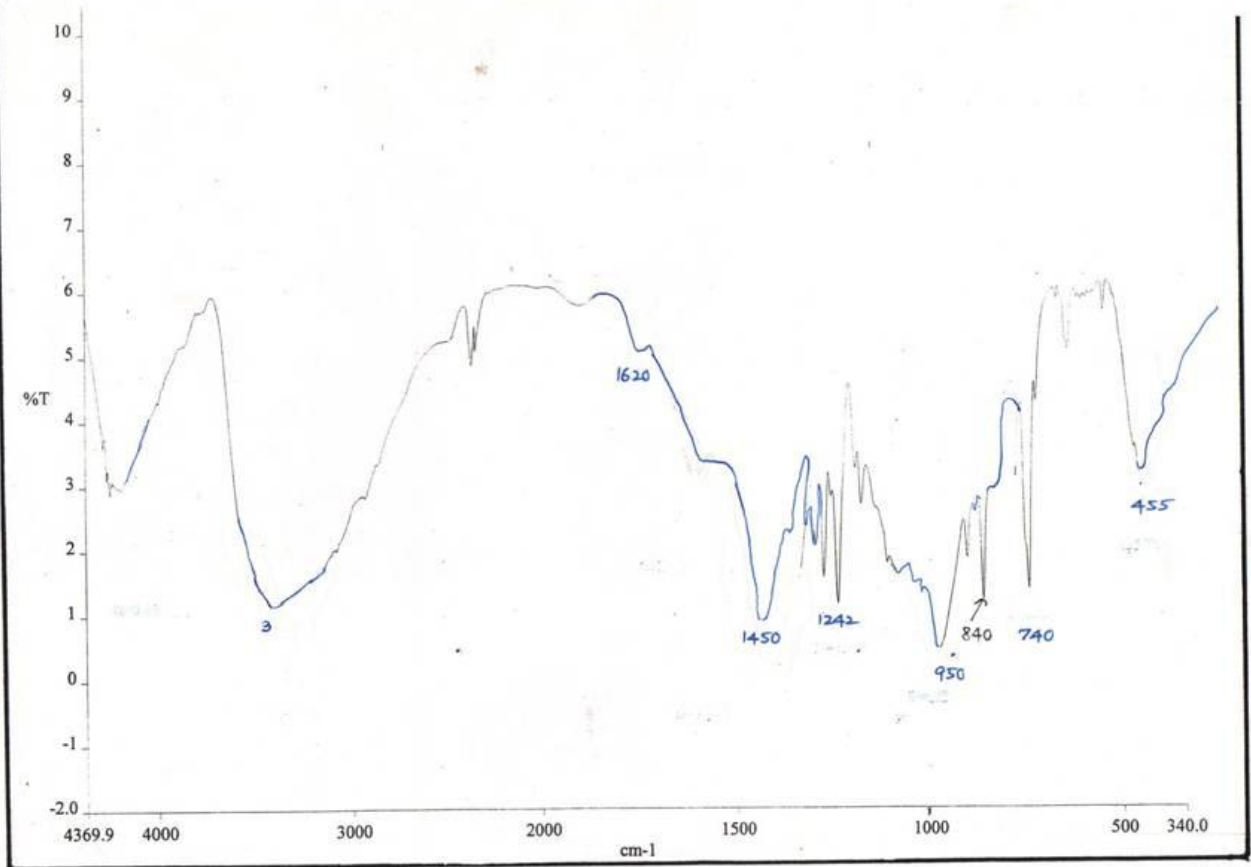
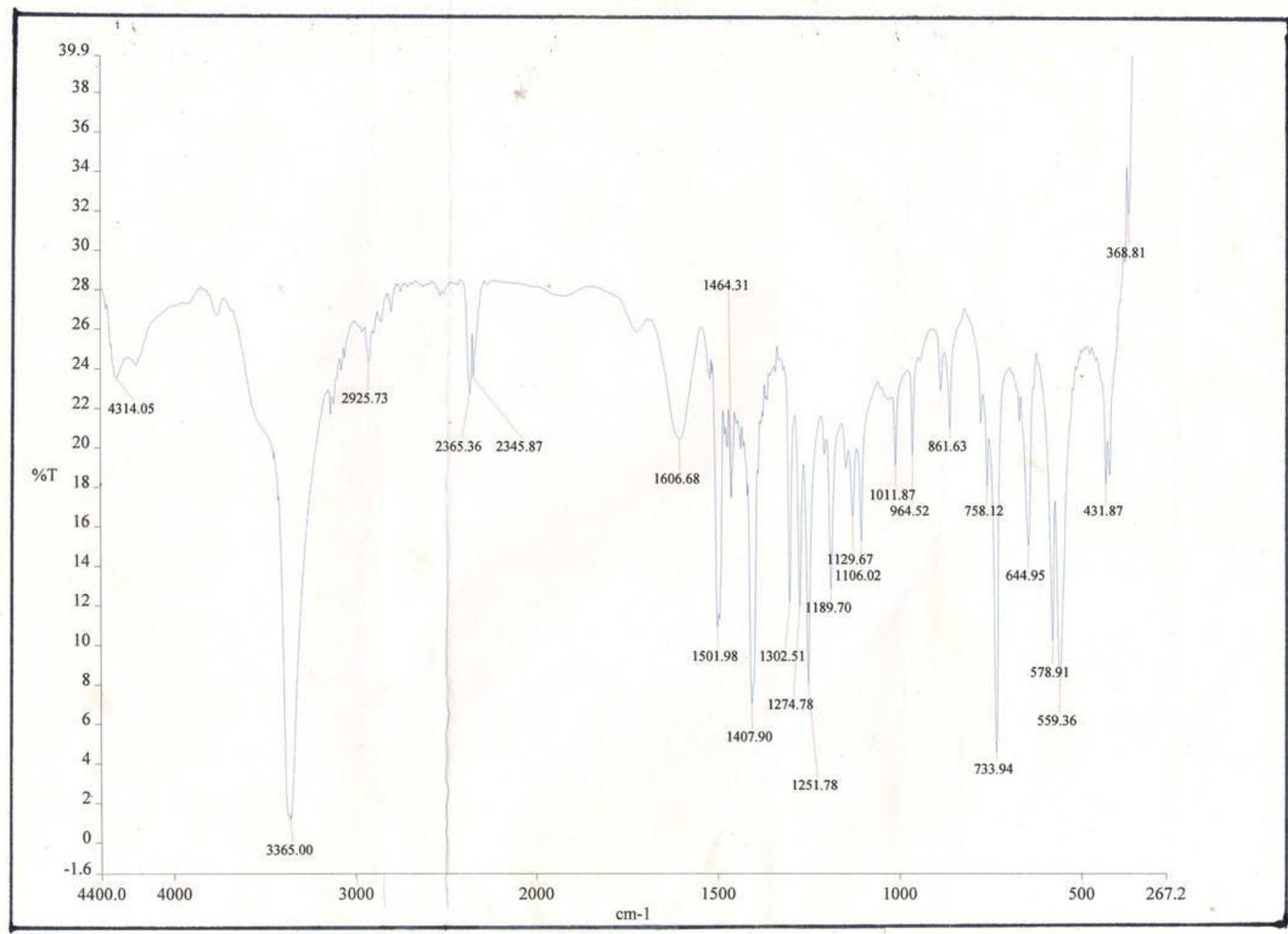


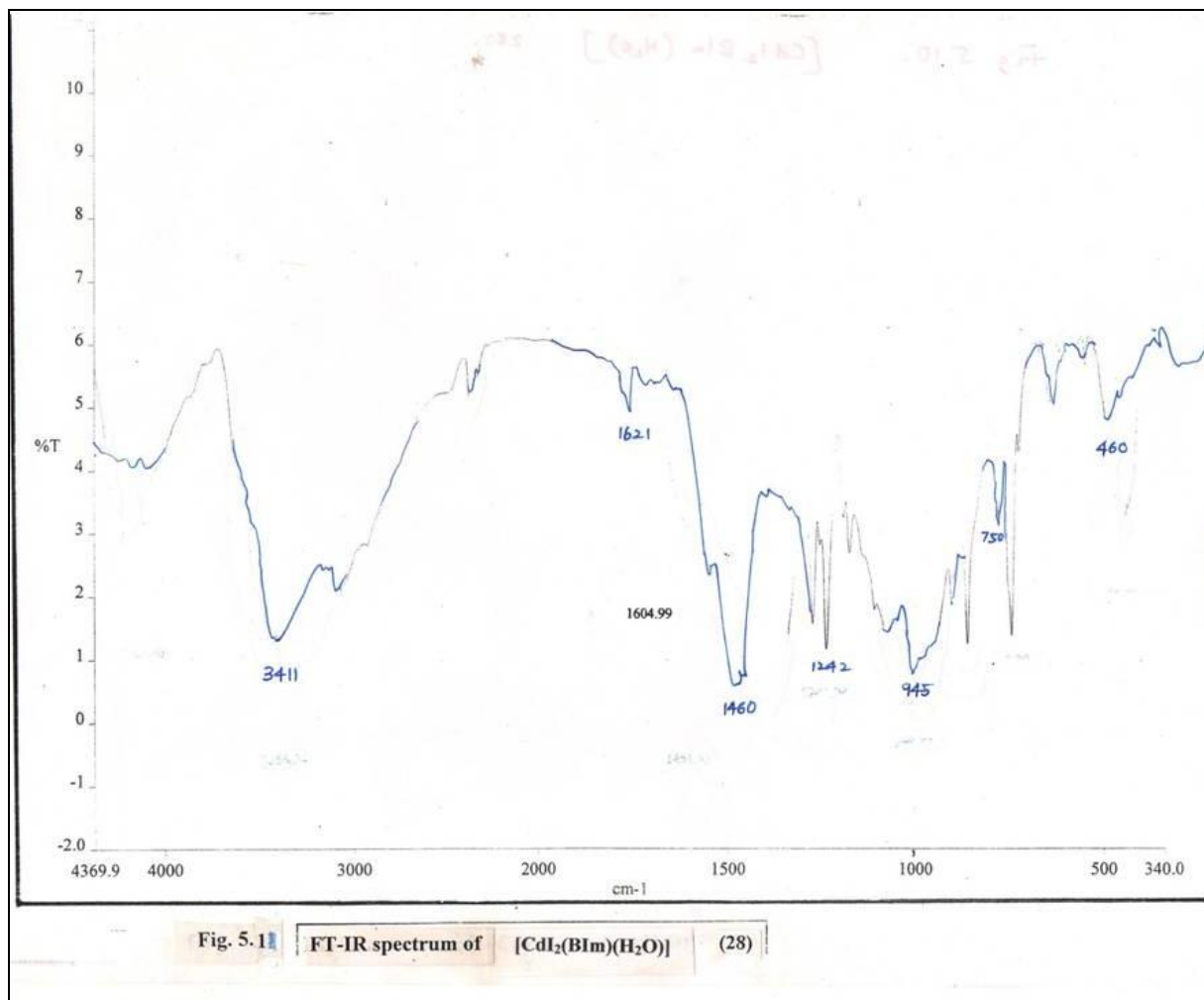
Fig. 5.9 FT-IR spectrum of [CdCl₂(BIm)(H₂O)] (26)



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Fig. 5-10

FT-IR spectrum of [CdBr(OH)(BIm)(H₂O)] (27)



In order to further validate the composition of the complexes, TGA experiments for some selected compounds, **20**, **22**, **25** were carried out. The TGA profiles are shown in **Fig. 5.3** and the data are given in **Table 5.3**. The TGA patterns are not quite similar as would be expected for similar type of composition. The first step reflected water loss from each of the complexes. Quite different behavior were, however, noted in the second thermal transition which matched with loss of the organic coligand for **22** and **25** while fluorides were lost preferentially over the coligand in compound **20**.

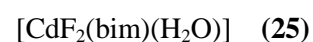
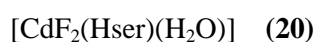
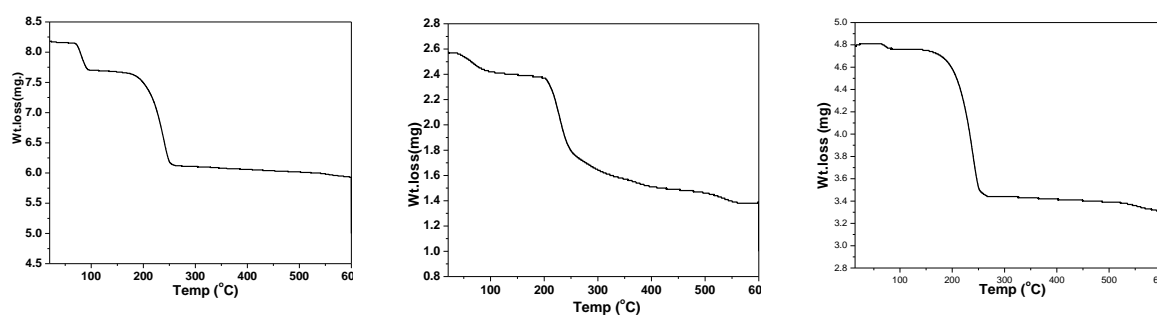


Fig.5.12: TGA spectra of cadmium complexes, (**20**), (**22**) and (**25**)

Table 5.3: TGA data of the compounds (**20**, **22**, **25**)

Compound	TGA Plateau(⁰ C)	% of weight loss		Process
		observed	calculated	
[CdF ₂ (Hser)(H ₂ O)] (20) M= 273.47	157--206	19.1	19.7	Loss of one water and two F atoms.
[CdF ₂ (Hcys)(H ₂ O)] (22) M= 289.45	40 --100	6.1	6.2	Loss of water molecule
	100--570	40.5	41.8	Loss of organic ligand (Hcys)
[CdF ₂ (bim)(H ₂ O)] (25) M= 286.52	31--123	6.25	6.28	Loss of water molecule
	144--562	40.23	41.21	Loss of organic ligand (bim)

The structure of cadmium complex, [CdF₂(Hser)(H₂O)] (**20**) has been fully optimized using BLYP functional and DNP basis sets as implemented in the program DMol3 [33,34]. In order to confirm the stability of the complex vibrational frequencies calculations were performed at the optimized structure with the same level of theory. The DFT optimized geometries of cadmium complex, [CdF₂(Hser)(H₂O)] (**20**) is shown in **Fig.5.12**. In the vibrational frequency calculations, no imaginary frequency is observed for the compound signifying stable structures (shows local minima in the potential energy surfaces). Structural parameters are given in **Table 5.5**. From **Fig. 5.12**, it is observed that in complex the cadmium ion forms a four-coordinate distorted tetrahedral structure. Values of HOMO-LUMO gap are given in **Table 5.6**. It is observed from the table that ΔE and Hardness values are quite higher for the complex, which suggests the stability of the complex. Similarly, the structure of another cadmium complex, [CdF₂(bim)(H₂O)] (**25**) has also been fully optimized using BLYP functional and DNP basis sets as implemented in the program DMol3 [32]. In

order to confirm the stability of the complex we performed vibrational frequencies calculations at the optimized structure with the same level of theory. The DFT optimized geometries of cadmium- benzimidazole complex [CdF₂(bim)(H₂O)] (**25**) is shown in **Fig.5.15**. In this compound also the vibrational frequency calculations, no imaginary frequency is observed for the compound [CdF₂(bim)(H₂O)] (**25**), which suggests that the optimized compounds signify stable structures i.e., shows a local minima in the potential energy surfaces. Structural parameters for the compound [CdF₂(bim)(H₂O)] (**25**) are given in **Table 5.7**. From **Fig. 5.15**, it is observed that in the complex cadmium metal forms a four co-ordinate distorted tetrahedral structure. Values of HOMO-LUMO gap are given in **Table 5.8**. It is noted that ΔE and Hardness values are quite higher for the complex, suggesting the stability of the complex. The DFT computed bond angles and bond lengths are furnished in **Table 5.4** and the selected reactivity parameters are provided in **Table 5.5** for [CdF₂(Hser)(H₂O)] (**20**).

Table 5.4: DFT computed bond lengths(Å) and bond angles(°) for [CdF₂(Hser)(H₂O)] (**20**)

Structural parameters	Bond length (Å) and bond angle (°)
Cd—F1	2.145
Cd—F2	2.081
Cd—O1	2.533
Cd—O2	2.356
Cd—O3	
F1—Cd—F2	146.88
O1—Cd—F2	68.31
O1—Cd—O2	88.24
O2—Cd—F1	92.52
O2—Cd—O3	2.145

Table 5.5 : DFT Selected reactivity parameters for the compound **(20)**

Compound	DFT computed energy values				
	LUMO (eV)	HOMO (eV)	$\Delta E(E_{LUMO}-E_{HOMO})$ (eV)	Hardness(eV) $\eta = \frac{E_{LUMO} - E_{HOMO}}{2}$	Dipole moment (D)
[CdF ₂ (Hser)(H ₂ O)] (20)	-2.018	-6.380	4.362	2.181	9.673

The DFT computed bond angles and bond lengths are furnished in **Table 5.6** and the selected reactivity parameters are provided in **Table 5.7** for [CdF₂(bim)(H₂O)] **(25)** .

Table 5.6 : DFT bond lengths (Å) and bond angles (°) of [CdF₂(bim)(H₂O)] **(25)**

Structural parameters	Benzimidazole Complex
Cd—F1	2.108
Cd—F2	2.073
Cd—O	2.239
Cd—N	2.413
F1—Cd—O	80.13
N—Cd—F2	86.65
O—Cd—N	127.64
F2—Cd—F1	147.67

Table 5.7: Selected reactivity parameters [CdF₂(bim)(H₂O)] (**25**)

Compound	DFT energy values				
	LUMO (eV)	HOMO (eV)	$\Delta E_{(LUMO-HOMO)}$ (eV)	Hardness(eV) $\eta = \frac{E_{LUMO} - E_{HOMO}}{2}$	Dipole moment (D)
[CdF ₂ (BIm)(H ₂ O)] (25)	-6.045	-6.383	0.338	0.169	8.9804

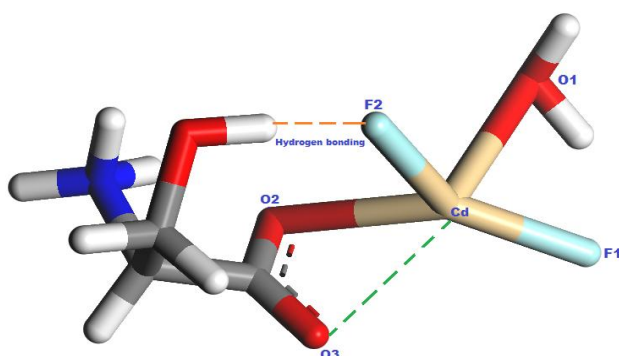


Fig. 5.13 : Optimized structure of [CdF₂(Hser)(H₂O)] (**20**)

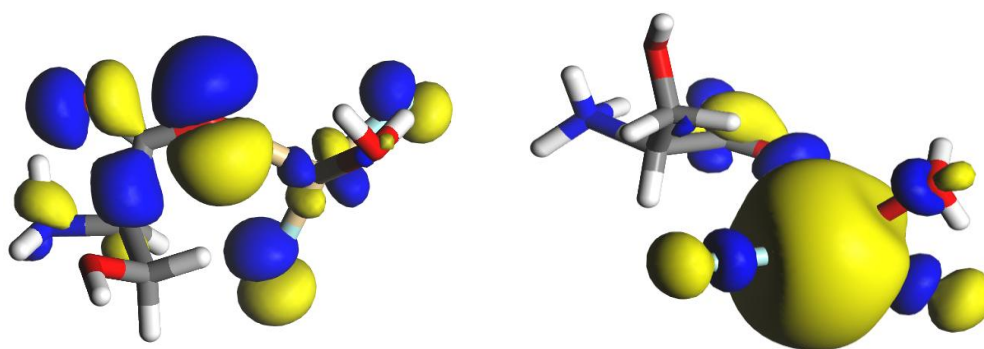


Fig. 5.14 HOMO and LUMO of [CdF₂(Hser)(H₂O)] (**20**)

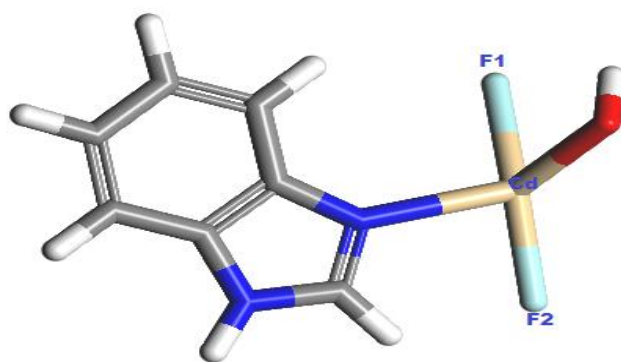


Fig. 5.15 Optimized structure $[\text{CdF}_2(\text{bim})(\text{H}_2\text{O})]$ (25)

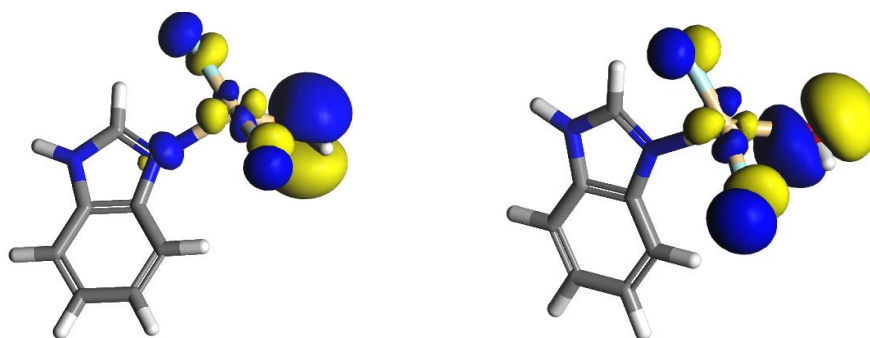
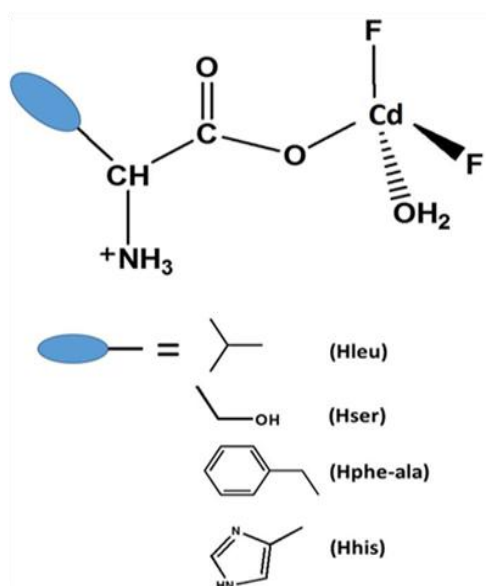
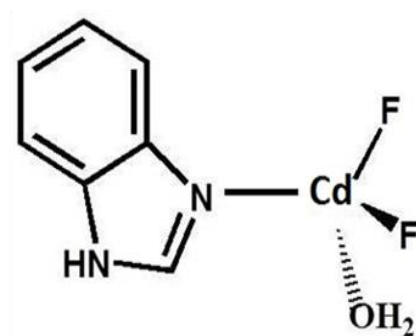


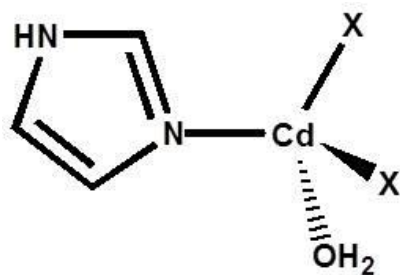
Fig. 5.16 HOMO and LUMO of $[\text{CdF}_2(\text{bim})(\text{H}_2\text{O})]$ (25)



Distorted tetrahedral
19 - 22



Distorted tetrahedral
25 - 28



Distorted tetrahedral, 23, 24 (X = F, Br)

Fig. 5.17 : Tentative molecular structure of Cd(II) complexes

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