CHAPTER 5

Synthesis and spectroscopic investigations of lanthanide complexes of bis-benzimidazole ligands derived from dicarboxylic acids and ortho-phenylenediamine: Luminescence, electrochemical and antimicrobial studies
INTRODUCTION

The coordination compounds derived from bio-mimic ligands have attained considerable attention by inorganic and bio-inorganic chemists. A number of such complexes have been exploited to serve as models for metallo-proteins and enzymes. Ligands having resemblance to the macro-biomolecules have been prepared and characterized in literature [1–4] by bio-coordination chemists in this regard. Imidazoles as well as benzimidazole derivatives have shown a broad biological significance [5–7] and this moiety acts as a potential coordinating/ chelating agent towards the metal ions. The coordination ability of a number of monodentate benzimidazole derivatives has been thoroughly investigated and reported [8,9]. Metal complexes of polyfunctional benzimidazole and its derivatives have attracted the attention as they are capable to generate supramolecular self-assembly via extensive hydrogen bonds [10–12]. The nature of linking group between the benzimidazole moieties in such ligands as well as that of the counter anions in the complexes probably plays important role in the formation of supramolecular architectures. The use of low-molecular weight model compounds of these biological macro-molecules has proved to be very useful and in some cases the only possible way to visualize the binding modes, structures and functions of the active sites. The presence of substituents in the tripodal moiety R₀X(CH₂BIz)ₘ₋ₙ (X = N, R = H or alkyl group, n = 0 or 1, m = 3; X = O, n = 0, m = 2 and BIz = benzimidazole), have a remarkable effect [13] on the structure and the coordinating ability of the ligand. Such tripodal ligands are especially suitable to assess the electronic and geometrical factors regulating the functions of the metallo-proteins [14,15]. The stereochemical investigations of
transition metal complexes of the tripodal ligands [1–7], bearing four potential coordinating sites have indicated a coordinatively unsaturated penta-coordinate geometry for these complexes. The formation of five coordinate square pyramidal or trigonal bipyramidal geometry strongly depends on the ligand topology, nature of the donor groups, the symmetry of the ligand and the constitution of the pendent arms or substituents. The chemistry of the analogous dipodal ligands such as HN(CH₂Imz)₂ and HN(CH₂BIm)₂ (Imz = imidazole and BIm = benzimidazole) has recently been reported [16]. These dipodal ligands, in general, result in complexes having coordinatively saturated hexa-coordinate geometry with divalent and trivalent 3d metal ions. However, to our knowledge investigations for the ligating behaviour of such dipodal ligands towards rare earth metal ions are not much reported in literature.

It is well known that rare earth metal ions are capable to expand their coordination number which can be up to eight. During the last few decades, a variety of lanthanide complexes have been shown to exhibit wide applications in medicines, radiopharmaceuticals and as MRI agents etc. [17–20]. Furthermore, several lanthanide metals complexes have received emphasis due to their potential use as luminescent materials [21] and also in the development of supramolecular photochemistry [22]. Intermolecular hydrogen bonding interactions are known to govern the formation of supramolecular structures in organic, metalloorganic as well as coordination complexes. The recent reports [23] have indicated that even protonated organic moieties can also generate three-dimensional supramolecular structures as, for example, protonated imidazole or benzimidazole etc. The protonated benzimidazole moiety contains an electron poor region associated with the imidazolium group, and a
relatively electron-rich region associated with the phenylene group. The interaction between two benzimidazolium units will be strongest when the imidazolium group of one unit lies over the phenylene moiety of the other (Scheme 1). A cation containing two protonated benzimidazoles linked by spacer such as 1,2-bis(benzimidazole-2-yl)ethane may organise itself in the solid state so that each cation overlaps favourably with other cations and this may be used to build up an excited structure.

Scheme 1. The stacking interaction. The C2 atom of the benzimidazole is indicated with an arrow.

In this chapter the synthesis and spectral characterization of a few lanthanide (La$^{3+}$, Pr$^{3+}$, Nd$^{3+}$, Gd$^{3+}$) complexes of the dipodal 1,2-bis(benzimidazole-2-yl)ethane dihydrochloride, L$^1$·2HCl and 1,4-bis(benzimidazole-2-onium)butane dihydrochloride, L$^2$·2HCl ligands have been given. The fluorescence and antimicrobial studies have also been performed to exploit their possible uses.
EXPERIMENTAL

Materials

All the reagents used were of analytical grade. o-phenylenediamine (E. Merck), Adipic acid (E. Merck) and Succinic acid (E. Merck) were used as received while metal salts were recrystallized and solvents were purified by standard procedures before use [24]. The salts LnCl$_3$·6H$_2$O were prepared according to the standard methods.

Instrumentation

IR spectra were recorded on a Perkin-Elmer spectrum GX automatic recording spectrophotometer as KBr disc. $^1$H and $^{13}$C NMR spectra of compounds dissolved in DMSO$_d_6$ were recorded on a Brucker AVANCE II 400 NMR spectrometer using SiMe$_4$ (TMS) as internal standard. Electronic spectra and conductivities of an aqueous solution of the complexes were recorded on a Cintra-5GBS UV-Visible spectrophotometer and Systronics-308 digital conductivity bridge, respectively, at room temperature. Fluorescence excitation and emission spectra were measured on a RF-5301PC fluorescence spectrophotometer with a 450 W xenon lamp as excitation source. The Electrospray Ionization (ESI) mass spectra were recorded on a MICROMASS QUATTRO II triple quadrupole mass spectrometer. The samples (Dissolved in methanol) were introduced into the ESI source through a syringe pump at the rate of 5mL/min. The ESI capillary was set at 3.5 kV and the cone voltage was 40 V. Microanalysis for C, H and N were obtained from Microanalytical Laboratories, CDRI, Lucknow. Thermal gravimetric analysis (TGA) data was measured from room
temperature up to 500 °C at a heating rate of 20 °C/min. The data were obtained using a Shimadzu TGA-50H instrument. Cyclic voltammograms were recorded on a CH-Instrument Electro-Chemical Analyzer using tetrabutylammonium perchlorate as a supporting electrolyte at room temperature. A three cell electrode was used containing a Pt micro cylinder working electrode, Pt wire as auxiliary electrode and Ag/AgCl as the reference electrode. The voltammograms were generated through computer stimulation giving the magnitudes of reduction, oxidation and half-wave potentials of the redox processes. Melting points reported in this work were not corrected.

**Preparation of the ligands (L\(^1\)·2HCl) and (L\(^2\)·2HCl)**

*Preparation of Ligand, [1,2-bis(benzimidazole-2-yl)ethane dihydrochloride], L\(^1\)·2HCl*

To the well grinded mixture of o-phenylenediamine (10.81 g, 100 mmol) and succinic acid (5.90 g, 50 mmol) was added 4 M hydrochloric acid (120 cm\(^3\)). The mixture was refluxed for 17 h at 120 °C and gradually cooled to room temperature and the hydrochloride of ligand L\(^1\) is separated as crystalline solid. The solid was filtered, washed with acetone and dried under vacuum at 60°C.

[Yield 69%]. Anal. Cal. (%) for C\(_{16}\)H\(_{14}\)N\(_4\)·2HCl: C, 57.3; H, 4.8; N, 16.7. Found (%): C, 57.2; H, 4.8; N, 16.5. IR (KBr): 3426m (br), 3019-2612s (br), 1623s, 1573s, 1511s, 1481w, 1461s, 1435m, 1380s, 1299m, 1264m, 1229s, 1184w, 1107w, 1020w, 924m, 898m, 817s, 763w, 732s, 620s, 510m, 433m cm\(^{-1}\). \(^1\)H NMR (300 MHz, DMSO-d\(_6\)) δ: 7.68 (m, 4 H), 7.53 (m, 4 H) aromatic protons and 3.80 (s, 4 H) aliphatic
protons; $^{13}$C NMR (75 MHz, DMSO-d$_6$) δ ppm: 113.8, 126.5, 130.6 & 149.8 (benzimidazole carbons); 24.0 (aliphatic carbon).

**Preparation of ligand, [1,4-bis(benzimidazole-2-onium)butane dihydrochloride], $L^2$·2HCl**

o-phenylenediamine (10.81 g, 100 m mol) and adipic acid (7.3 g, 50 mmol) were dissolved in 120 mL 6 M hydrochloric acid. The colourless solution, after being heated to reflux for 17 h, turned blue. On cooling, green crystals of the dihydrochloride salt were obtained. The crystals were filtered, washed with diethylether, and dried under vacuum. The crystals were treated in ethanol with activated carbon under refluxed for 2 h. After filtration, colourless crystals were obtained upon cooling to room temperature. A hot solution of the product (2g) in ethanol (45 mL) and water (15 mL) was prepared. Slow cooling of this solution lead to the formation of colourless crystalline product.

[Yield 70%]. Anal.Cal. (%) for C$_{18}$H$_{20}$N$_4$·2HCl: C, 59.17; H, 6.02; N, 15.34; Found (%): C, 58.96; H, 6.03; N, 15.24; IR (cm$^{-1}$): $\nu_{\text{max}}$ 2670-2510 (brs), 1950 (w), 1672(m), 1619(s), 1568(s), 1513(m), 1485(m), 1456(s), 1391(m), 1377(m), 1312(m), 1291(m), 1216(s), 1195(s), 1145(w), 1032(m), 976(m), 868(s), 737 (s), 653(s), 616(s), 437(s), 384(m). $^1$H NMR (300 MHz, solvent DMSO-d$_6$, 298 K, δ ppm): 7.77 (m, 4H), 7.52 (m, 4H) aromatic protons, 3.24 (m, 4H) and 2.00 (m, 4H) aliphatic protons. $^{13}$C NMR (75 MHz, DMSO-d$_6$) δ ppm: 115.8, 127, 131.5 & 152 (benzimidazole carbons); 26.0 (aliphatic carbon).
General procedure for the synthesis of the complexes (1–4), \([\text{Ln}(\mathcal{L}^1)\text{Cl}_3\text{H}_2\text{O}] \) (Ln = La, Pr, Nd and Gd)

An ethanolic solution (10 mL) of \(\text{LnCl}_3\cdot6\text{H}_2\text{O}\) was dropped to a magnetically stirred hot solution of the ligand \((\mathcal{L}^1\cdot2\text{HCl})\) (0.674 g, 2 mmol) taken in 20 mL ethanol. The stirring was continued for 1 h at room temperature giving precipitates in the solution. The precipitates of (1-4) were filtered off, washed with ethanol and dried under vacuum. Attempts for the recrystallization of the complexes in different solvents could not provide single crystals suitable for X-ray crystallographic studies.

General procedure for the synthesis of the complexes (5–8), \([\text{Ln}({\mathcal{L}}^2)\text{Cl}_3\text{H}_2\text{O}]\cdot2\text{H}_2\text{O} \) (Ln = La, Pr, Nd and Gd)

An ethanolic solution (10 mL) of the rare earth metal chloride \((\text{LnCl}_3\cdot6\text{H}_2\text{O})\) was dropped to a magnetically stirred hot solution of the ligand \((\mathcal{L}^2\cdot2\text{HCl})\) (0.798 g, 2 mmol) taken in 25 mL ethanol. After 1h stirring, precipitation in the solution occurs. The precipitates of (5-8) were filtered off, washed with ethanol and dried under vacuum. However, attempts for the recrystallization of the complexes in different solvents could not provide single crystals suitable for X-ray crystallographic studies.

\([\text{La}({\mathcal{L}}^1)\text{Cl}_3\text{H}_2\text{O}] \) (1)

[White, m.p. >300°C, yield 45%]. Anal. Cal. (%) for \(\text{C}_{32}\text{H}_{30}\text{N}_8\text{O}\text{LaCl}_3\): C, 48.78; H, 3.84; N, 14.22. Found (%): C, 48.75; H, 3.80; N, 14.19. Molar conductance, \(\Lambda_m\) (in \(10^{-3}\) M CH$_3$OH): 29.4 ohm$^{-1}$cm$^2$mol$^{-1}$. ESI-Mass: \(m/z = 789\) (18%),
[La(L\(^1\))\(_2\)Cl\(_3\)H\(_2\)O+2H\(^+\)]; \textit{m/z} = 788 (15%), [La(L\(^1\))\(_2\)Cl\(_3\)H\(_2\)O+H\(^+\)]; \textit{m/z} = 787 (20%), [La(L\(^1\))\(_2\)Cl\(_3\)H\(_2\)O\(^+\)]; \textit{m/z} = 769 (48%), [La(L\(^1\))\(_2\)Cl\(_3\)]; \textit{m/z} = 733 (31%), [La(L\(^1\))\(_2\)Cl\(_2\)]; \textit{m/z} = 699 (29%), [La(L\(^1\))\(_2\)Cl+H\(^+\)]; \textit{m/z} = 664 (32%) [La(L\(^1\))\(_2\)2H\(^+\)], \textit{m/z} = 401 (19%), [La(L\(^1\))]+H\(^+\)]; \textit{m/z} = 271(22%), [La(L\(^1\)/2)+2H\(^+\)]. \(^1\)H NMR (DMSO-d\(_6\), ppm) \(\delta\): 7.68 (m, 8H, ring proton), 7.53 (m, 8H, ring protons), 3.98 (s, 8H, CH\(_2\)), 2.3 (s, O-H of water).

**[Pr (L\(^1\))\(_2\)Cl\(_3\)H\(_2\)O] (2)**

[White, m.p. >300 °C, Yield 52%]. Anal. Cal. (%) for C\(_{32}\)H\(_{39}\)N\(_8\)OPrCl\(_3\): C, 48.66; H, 3.83; N, 14.19. Found (%): C, 48.60; H, 3.83; N, 14.10. Molar conductance, \(\Lambda_m\) (in 10\(^{-4}\) M CH\(_3\)OH): 27.5 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\). ESI-Mass: \textit{m/z} = 790 (24%), [Pr(L\(^1\))\(_2\)Cl\(_3\)H\(_2\)O]\(^+\); \textit{m/z} = 788 (10%), [Pr(L\(^1\))\(_2\)Cl\(_3\)H\(_2\)O-H]\(^+\); \textit{m/z} = 787 (17%), [Pr(L\(^1\))\(_2\)Cl\(_3\)H\(_2\)O-2H]\(^+\); \textit{m/z} = 771 (22%), [Pr(L\(^1\))\(_2\)Cl\(_3\)]\(^+\); \textit{m/z} = 736 (32%), [Pr(L\(^1\))\(_2\)Cl\(_2\)+H]\(^+\); \textit{m/z} = 701 (28%), [Pr(L\(^1\))\(_2\)Cl+2H]\(^+\); \textit{m/z} = 664 (30%) [Pr(L\(^1\))\(_2\)+H]\(^+\), \textit{m/z} = 403 (21%), [Pr(L\(^1\))+2H]\(^+\); \textit{m/z} = 270 (19%), [Pr(L\(^1\)/2)]\(^+\). \(^1\)H NMR (DMSO-d\(_6\), ppm) \(\delta\): 7.97(m, 8H, ring proton), 7.54 (m, 8H, ring protons), 3.97 (s, 8H, CH\(_2\)), 2.2 (s, O-H of water).

**[Nd(L\(^1\))\(_2\)Cl\(_3\)H\(_2\)O] (3)**

[White, m.p. >300 °C, Yield 53%]. Anal. Cal. (%) for C\(_{32}\)H\(_{30}\)N\(_8\)ONdCl\(_3\): C, 48.45; H, 3.81; N, 14.13. Found (%): C, 48.41; H, 3.10; N, 14.11. Molar conductance, \(\Lambda_m\) (in 10\(^{-3}\) M CH\(_3\)OH): 25 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\). ESI-Mass: \textit{m/z} = 792 (24%), [Nd(L\(^1\))\(_2\)Cl\(_3\)H\(_2\)O]\(^+\); \textit{m/z} = 791 (14%), [Nd(L\(^1\))\(_2\)Cl\(_3\)H\(_2\)O-H]\(^+\); \textit{m/z} = 790 (22%), [Nd(L\(^1\))\(_2\)Cl\(_3\)H\(_2\)O-2H]\(^+\); \textit{m/z} = 789 (11%), [Nd(L\(^1\))\(_2\)Cl\(_3\)H\(_2\)O-3H]\(^+\); \textit{m/z} = 774 (19%), [Nd(L\(^1\))\(_2\)Cl\(_3\)]\(^+\); \textit{m/z} = 738 (31%), [Nd(L\(^1\))\(_2\)Cl\(_2\)]\(^+\), \textit{m/z} = 703 (26%), [Nd(L\(^1\))\(_2\)Cl+H]\(^+\);
\[ m/z = 666 \text{ (28\%)}; \text{[Nd(L\textsuperscript{1})\textsubscript{2}]}^+; m/z = 405 \text{ (22\%)}; \text{[Nd(L\textsuperscript{1})+H]}^+; m/z = 273 \text{ (20\%)}, \text{[Nd(L\textsuperscript{1}/2)]}^+. \] 

\(^1\text{H NMR (DMSO-d\textsubscript{6}, ppm)}\ \delta: \text{7.68 (m, 8H, ring proton), 7.52 (m, 8H, ring protons), 4.78 (s, 8H, CH\textsubscript{2}), 2.1 (s, O-H of water).} \]

\textbf{[Gd(L\textsuperscript{1})\textsubscript{2}Cl\textsubscript{3}H\textsubscript{2}O]} (4)

[White, m.p. >300 °C, Yield 60\%]. Anal. Cal. (%) for C\textsubscript{32}H\textsubscript{30}N\textsubscript{8}OGdCl\textsubscript{3}: C, 47.67; H, 3.75; N, 13.90. Found (%): C, 47.62; H, 3.82; N, 13.90. Molar conductance, \(\Lambda_m\) (in 10\textsuperscript{-3} M CH\textsubscript{3}OH): 38.7 ohm\textsuperscript{-1}cm\textsuperscript{2}mol\textsuperscript{-1}. ESI-Mass: \(m/z = 806 \text{ (22\%)}, \text{[Gd(L\textsuperscript{1})\textsubscript{2}Cl\textsubscript{3}H\textsubscript{2}O]}^+; m/z = 788 \text{ (20\%)}, \text{[Gd(L\textsuperscript{1})\textsubscript{2}Cl\textsubscript{3}]}^+; m/z = 753 \text{ (30\%)}, \text{[Gd(L\textsuperscript{1})\textsubscript{2}Cl+H]}^+; m/z = 716 \text{ (24\%)}, \text{[Gd(L\textsuperscript{1})\textsubscript{2}Cl]}^+; m/z = 682 \text{ (26\%)}, \text{[Gd(L\textsuperscript{1})\textsubscript{2}+2H]}^+; m/z = 680 \text{ (21\%)}, \text{[Gd(L\textsuperscript{1})\textsubscript{2}]}^+; m/z = 548 \text{ (18\%)}, \text{[Gd(L\textsuperscript{1}/2)-H]}^+. \(^1\text{H NMR (DMSO-d\textsubscript{6}, ppm)}\ \delta: \text{7.54 (m, 8H, ring proton), 7.88 (m, 8H, ring protons), 4.06 (s, 8H, CH\textsubscript{2}), 2.2 (s, O-H of water).} \]

\textbf{[La(L\textsuperscript{2})\textsubscript{2}Cl\textsubscript{3}H\textsubscript{2}O\textsubscript{-}2H\textsubscript{2}O]} (5)

[White, m.p. >300 °C, Yield 66\%]. Anal. Cal. (%) for C\textsubscript{36}H\textsubscript{42}N\textsubscript{8}O\textsubscript{3}LaCl\textsubscript{3}: C, 49.13; H, 4.81; N, 12.73. Found (%): C, 49.10; H, 4.79; N, 12.69. Molar conductance, \(\Lambda_m\) (in 10\textsuperscript{-3} M CH\textsubscript{3}OH): 24.5 ohm\textsuperscript{-1}cm\textsuperscript{2}mol\textsuperscript{-1}. ESI-Mass: \(m/z = 849 \text{ (22\%)}, \text{[La(L\textsuperscript{2})\textsubscript{2}Cl\textsubscript{3}H\textsubscript{2}O+2H]}^+; m/z = 830 \text{ (15\%)}, \text{[La(L\textsuperscript{2})\textsubscript{2}Cl\textsubscript{3}+H]}^+; m/z = 793 \text{ (26\%)}, \text{[La(L\textsuperscript{2})\textsubscript{2}Cl\textsubscript{2}]}^+; m/z = 758 \text{ (32\%)}, \text{[La(L\textsuperscript{2})\textsubscript{2}Cl+H]}^+; m/z = 721 \text{ (35\%)}, \text{[La(L\textsuperscript{2})\textsubscript{2}]}^+; m/z = 430 \text{ (21\%)}, \text{[La(L\textsuperscript{2})\textsubscript{2}+H]}^+; m/z = 283 \text{ (25\%)}, \text{[La(L\textsuperscript{2}/2)]}^+. \(^1\text{H NMR (DMSO-d\textsubscript{6}, ppm)}\ \delta: \text{7.78 (m, 8H, ring proton), 7.52 (m, 8H, ring protons), 3.34 (s, 8H, CH\textsubscript{2}), 2.54(s, 8H, CH\textsubscript{2}), 2.1 (s, O-H of water).} \]
[Pr(L²)₂Cl₃H₂O]·2H₂O (6)

[White, m.p. > 300 °C, Yield 56%]. Anal. Cal. (%) for C₃₆H₄₂N₈O₃PrCl₃: C, 49.02; H, 4.80; N, 12.70. Found (%): C, 49.00; H, 4.81; N, 12.70. Molar conductance, λₐ (in 10⁻³ M CH₃OH): 21 ohm⁻¹cm²mol⁻¹. ESI-Mass: m/z = 850 (21%), [Pr(L²)₂Cl₃H₂O+H]⁺; m/z = 831 (18%), [Pr(L²)₂Cl₃]⁺; m/z = 797 (24%), [Pr(L²)₂Cl₂+2H]⁺; m/z = 759 (29%), [Pr(L²)₂Cl-H]⁺; m/z = 725 (31%), [Pr(L²)₂+H]⁺, m/z = 432 (26%), [Pr(L²)]⁺, m/z = 287 (24%), [Pr(L²/2)+H]⁺. ¹H NMR (DMSO-d₆, ppm) δ: 7.54 (m, 8H, ring proton), 7.35 (m, 8H, ring protons), 3.42 (s, 8H, CH₂), 2.84 (s, 8H, CH₂), 2.2 (s, O-H of water).

[Nd(L²)₂Cl₃H₂O]·2H₂O (7)

[White, m.p. >300 °C, Yield 54%]. Anal. Cal. (%) for C₃₆H₄₂N₈O₃NdCl₃ : C, 48.84; H, 4.78; N, 12.66. Found (%): C, 48.81; H, 4.71; N, 12.64%. Molar conductance, λₐ (in 10⁻³ M CH₃OH): 33.5 ohm⁻¹cm²mol⁻¹. ESI-Mass: m/z = 854 (19%), [Nd(L²)₂Cl₃H₂O+H]⁺; m/z = 834 (21%), [Nd(L²)₂Cl₃-H]⁺; m/z = 800 (23%), [Nd(L²)₂Cl₂+H]⁺; m/z = 763 (27%), [Nd(L²)₂Cl]⁺; m/z = 727 (31%), [Nd(L²)₂]⁺, m/z = 581 (26%), [Nd(L²/2)]⁺. ¹H NMR (DMSO-d₆, ppm) δ: 7.33 (m, 8H, ring proton), 7.14 (m, 8H, ring protons), 3.76 (s, 8H, CH₂), 2.21 (s, 8H, CH₂), 2.3 (s, O-H of water).

[Gd(L²)₂Cl₃H₂O]·2H₂O (8)

[White, m.p. >300 °C, Yield 56%]. Anal. Cal. (%) for C₃₆H₄₂N₈O₃GdCl₃: C, 48.13; H, 4.71; N, 12.47. Found (%): C, 48.11; H, 4.70; N, 12.42. Molar conductance, λₐ (in 10⁻³ M CH₃OH): 24 ohm⁻¹ cm²mol⁻¹. ESI-Mass: m/z = 868 (21%), [Gd(L²)₂Cl₃H₂O+2H]⁺; m/z = 848 (15%), [Gd(L²)₂Cl₃]⁺; m/z = 813 (24%),
[Gd(L₂Cl₂+H)]⁺; m/z = 776 (31%), [Gd(L₂Cl)]⁺, m/z = 742 (32%), [Gd(L₂)₂+H]⁺, m/z = 741 (30%), [Gd(L₂)₂]⁺, m/z = 595 (28%), [Gd(L²/2)]⁺. ¹H NMR (DMSO-d₆, ppm) δ: 7.6 (m, 8H, ring proton), 7.45 (m, 8H, ring protons), 3.47 (s, 8H, CH₂), 2.42 (s, 8H, CH₂), 2.2 (s, O-H of water).

**Antimicrobial assays**

The antimicrobial screening was performed by reported method [25], against the micro-organisms Pseudomonas aeruginosa, Bacillus cirroflagellosus, Aspergillus niger and Penicillium notatum, using the concentration 1 mg/mL of test solutions in DMSO. The standards used were Greseofulvin and Norfloxacin against fungi and bacteria respectively.

**Molecular model computations**

CSChem-3D-MOPAC software [26] has been used to get the minimum energy perspective plots for the geometries of the complexes. This provides the most stable (ground state) arrangement of the ligand environment around the metal ions. The structural parameters like relevant bond lengths and bond angles were also computed.

**Calculations for spectroscopic parameters (βav, b½, δ, P_exp & P_cal)**

The nephelauxetic effect is a measure of the degree of covalency (βav) of the M–ligand bond(s) in the complexes. There is a considerable reduction in the magnitude of the radial integral regarding the metal ions valence orbitals in the process of complex formation. Nephelauxetic ratio, βav [27] can be calculated from the relation
\[ \beta_{av} = \frac{1}{2} \sum_{n=1}^{n} \frac{v_{\text{comp}}}{v_{\text{aq}}} \]  

\( \beta_{av} = \frac{1}{2} \sum_{n=1}^{n} \frac{v_{\text{comp}}}{v_{\text{aq}}} \) where \( v_{\text{comp}} \) and \( v_{\text{aq}} \) are the energies (cm\(^{-1}\)) of the f–f bands observed in the complexes and their aquo counter parts, respectively. The f-orbitals when involved in covalent bond formation with the ligand, the metal ion 4f wave function \( \phi_{4f} \) is expressed [28] by the expression

\[ < \phi_{4f} | = (1 - b)^{1/2} < 4f| - b^{1/2} < \phi_{\text{ligand}} | \]  

where \( b^{1/2} \) measures the amount of 4f–ligand orbital mixing and is calculated [29] from the relation

\[ b^{1/2} = \left[ \frac{(1 - \beta_{av})}{2} \right]^{1/2} \]  

The positive and negative values of \( b^{1/2} \) for a complex correspond to covalent and ionic characters, respectively. The Sinha’s covalency parameter \( \delta \), which is a function of the nephelauxetic ratio \( \beta_{av} \), is calculated from the equation [30]

\[ \delta = \frac{(1 - \beta_{av})}{\beta_{av}} \times 100 \]  

The oscillator strength is defined as the measure of the intensity of the absorption bands arising from the f–f transition. Its magnitudes for the experimentally observed absorption bands termed as \( P_{\text{exp}} \) is calculated from the following expression [31].
where $\nu$, $\varepsilon$ and $\eta$ are the energy (cm\(^{-1}\)) of transition, molar extinction coefficient and the refractive index of the medium, respectively. The calculated oscillator strength ($P_{\text{calc}}$) is computed [32] from the relation given by eq (6), which expresses the ligand field interaction with the 4f\(^n\) radial eigen function of the central ion causing a mixing of higher configuration of opposite parity into the 4f\(^n\) configuration giving rise to induced electronic dipole transitions i.e.

$$P_{\text{calc}} = \sum_{\lambda=2,4,6} T_{\lambda} \nu(f^N \psi_j || U^\lambda || f^N \psi'_f)^2 (2J + 1)^{-1}$$

where $\nu$ is the energy of the transition, $\psi_j \leftrightarrow \psi'_f$ and $U^\lambda$ is the unit tensor operator connecting the initial and the final states via three phenomenological parameters $T_{\lambda}$ ($\lambda = 2$, $4$ and $6$). These three parameters are related to radial part of the 4f\(^n\) wave functions, the wave functions of the perturbing configurations, the refractive index of the medium and the ligand field parameters.