CHAPTER-VII

EXPERIMENTAL

Materials and Measurements

All the reagents were of commercial grade and used as received, with the exception of Hopta and Hoptp, which were prepared according to the literature methods\textsuperscript{1,2}.

A programmable electric oven (IndFur) was used to carry out hydro(solvo)thermal reactions in which heating could be set up from room temperature to 400 °C. The FT–IR spectra were recorded on a JASCO FT-IR–410 spectrometer in the range 4000-400 cm\(^{-1}\). UV/Vis spectra were recorded on a Perkin Elmer Lambda25 UV/Vis spectrophotometer. Elemental analysis was carried out on a Perkin-Elmer 1400C analyzer. Thermogravimetric analysis was performed on a Mettler Toledo Star\textsuperscript{e} system with a heating rate of 10 °C/min under nitrogen atmosphere from room temperature to 700 °C. Magnetic susceptibility measurements were performed on a George Associate Faraday Force Magnetometer. The Non Linear Optical (NLO) experiments were performed using Nd:YAG laser beam (\(\lambda = 1064\) nm), Photo Multiplier Tube [PMT-Hammatsu Model R 2059] and a CRO [Tektranix TDS 305213]. DNA cleavage studies were performed using Biotech Submarine Gel Electrophoresis system.
7.1. Synthesis of \([\text{Ba}(\mu\text{-opta})_2(H_2O)_3]_{n^*}3nH_2O\) (1)

A mixture of 1-oxo-pyridinium-2-thioacetic acid (0.074 g, 0.40 mmol), barium hydroxide octahydrate (0.06309 g, 0.2 mmol), and ethanol (4.0 mL) was taken in a 23 mL stainless steel jacketed teflon bomb. The Teflon bomb was maintained at a temperature of 80 °C under autogenous pressure for 72 h. After cooling at a ramp of 10 °C/h to room temperature, colorless needle shaped crystals of 1 were collected by filtration, washed with diethyl ether, and then dried (0.092 g, 75% Yield). High-quality single crystals were hand picked under a microscope for X-ray investigation. Anal. Calc. for BaC_{14}H_{24}O_{12}N_{2}S_{2}: C 27.4, H 3.94, N 4.56, S 10.45 %. Found: C 27.3, H 3.89, N 4.45, S 10.39 %.

7.2. Synthesis of \([\text{Mg}(H_2O)_6]\text{(optp)}_2\) (2)

1-Oxo-pyridinium-2-thiopropionic acid (0.0498 g, 0.250 mmol), magnesium(II) acetate tetrahydrate (0.0268 g, 0.125 mmol), and water (2.5 mL) were taken in a 23 mL stainless steel jacketed teflon bomb. The Teflon bomb was maintained at a temperature of 100 °C under autogenous pressure for 72 h. After cooling at a ramp of 10 °C/h to room temperature, colorless crystals of 2 were collected by filtration, washed with diethyl ether, and then dried (0.047g, 71% Yield). Anal. Calc. for C_{16}H_{28}N_{2}O_{12}S_{2}Mg: C, 36.34; H, 5.34; N, 5.30; S, 12.13%. Found: C, 37.20; H, 5.20; N, 5.35; S, 12.24%.

7.3. Synthesis of \([\text{Co}(H_2O)_6]\text{(optp)}_2\) (3)

A mixture of 1-oxo-pyridinium-2-thiopropionic acid (0.0498 g, 0.250 mmol), cobalt(II) chloride hexahydrate (0.0297 g, 0.125 mmol), sodium hydroxide (0.010 g, 0.250 mmol) and methanol (10.0 mL) was mechanically stirred for an hour. The reaction mixture was then concentrated and transferred into a 23 mL stainless steel jacketed teflon bomb. The Teflon bomb was maintained at a temperature of 80 °C under autogenous pressure for 72 h. After cooling at a ramp of 10 °C/h to room temperature, pink colored crystals of 3 were collected by filtration, washed with deionized water followed by diethyl ether, and then dried (0.0551 g, 78% yield). Anal. Calc. for C_{16}H_{28}N_{2}O_{12}S_{2}Co: C, 34.11; H, 5.01; N, 4.97; S, 11.38%. Found: C, 35.2; H, 4.90; N, 5.14; S, 11.47%.
7.4. Synthesis of $[\text{Ni(H}_2\text{O)}_6](\text{optp})_2$ (4)

1-Oxo-pyridinium-2-thiopropionic acid (0.498 g, 0.250 mmol), nickel(II) acetate tetrahydrate (0.031 g, 0.125 mmol), and water (2.5 mL) were taken in a 23 mL stainless steel jacketed teflon bomb. The Teflon bomb was maintained at a temperature of 130 °C under autogenous pressure for 96 h. After cooling at a ramp of 10 °C/h to room temperature, green colored crystals of 4 were collected by filtration, washed with diethyl ether, and then dried (0.053 g, 75% yield). Anal. Calc. for $\text{C}_{16}\text{H}_{28}\text{N}_2\text{O}_{12}\text{S}_2\text{Ni}$: C, 33.12; H, 5.01; N, 4.97; S, 11.38% : Analytical results Found: C, 35.23; H, 4.90; N, 5.23; S, 11.47%.

7.5. Synthesis of $[\text{Zn(H}_2\text{O)}_6](\text{optp})_2$ (5)

A mixture of 1-oxo-pyridinium-2-thiopropionic acid (0.0498 g, 0.250 mmol), zinc(II) acetate dihydrate (0.0274 g, 0.125 mmol), and water (2.5 mL) was taken in a 23 mL stainless steel jacketed teflon bomb. The Teflon bomb was maintained at a temperature of 150 °C under autogenous pressure for 120 h. After cooling at a ramp of 10 °C/h to room temperature, colorless crystals of 5 were collected by filtration, washed with diethyl ether, and then dried (0.0554g, 78% yield). Anal. Calc. for $\text{C}_{16}\text{H}_{28}\text{N}_2\text{O}_{12}\text{S}_2\text{Zn}$: C, 33.72; H, 4.95; N, 4.92; S, 11.25%. Found: C, 34.75; H, 4.75; N, 5.25; S, 11.37%.

7.6. Synthesis of $[\text{Cu(optp})(\mu-\text{optp})(\text{H}_2\text{O})]_n\cdot2\text{nH}_2\text{O}$ (6)

A mixture of 1-oxo-pyridinium-2-thiopropionic acid (0.0498g, 0.250 mmol), copper(II) sulphate pentahydrate (0.0312g, 0.125 mmol), sodium hydroxide (0.020 g, 0.250 mmol) and ethanol (10.0 mL) was mechanically stirred for an hour. The reaction mixture was then concentrated and transferred into a 23 mL stainless steel jacketed teflon bomb. The Teflon bomb was maintained at a temperature of 85 °C under autogenous pressure for 72 h. After cooling at a ramp of 10 °C/h to room temperature, peacock blue colored crystals of 6 were collected by filtration, washed with deionized water followed by diethyl ether, and then dried (0.045 g, 70% yield). Anal. Calc. for $\text{C}_{16}\text{H}_{32}\text{N}_2\text{O}_{25}\text{S}_2\text{Cu}$: C, 37.39; H, 4.31; N, 5.45; S, 12.47%. Found: C, 38.40; H, 4.12; N, 5.60; S, 12.58%.
7.7. Synthesis of 

$[\text{Co(tmb)}_2(4,4^\prime\text{-bpy})_2(\text{H}_2\text{O})_2](\text{Htmb})_2$ (7)

Cobalt acetate tetrahydrate (0.0311 g, 0.125 mmol), 2,4,6-trimethylbenzoic acid (0.041 g, 0.250 mmol), 4,4$^\prime$-bpy (0.039 g, 0.250 mmol) and water (2.5 mL) were stirred together for 30 minutes, sealed in a 23 mL Teflon-lined stainless steel bomb, and kept at 100 °C under autogenous pressure for 72 h. After cooling at a ramp of 10 °C/h to room temperature, pink colored crystals of 7 were collected by filtration, washed with deionized water followed by diethyl ether, and then dried (0.0858 g, 65% yield). Anal. Calc. for $\text{C}_{60}\text{H}_{66}\text{N}_4\text{O}_{10}\text{Co}$: C, 67.85; H, 6.26; N, 5.28%. Found: C, 68.25; H, 6.02; N, 5.60%.

7.8. Synthesis of 

{$\{[\text{Ni(tmb)}_2(\mu-4,4^\prime\text{-bpy})(\text{H}_2\text{O})_2](4,4^\prime\text{-bpy})\}_n$ (8)

A mixture of nickel acetate tetrahydrate (0.0311 g, 0.125 mmol), 2,4,6-trimethyl benzoic acid (0.041 g, 0.250 mmol), 4,4$^\prime$-bipyridyl (0.039 g, 0.250 mmol) and water (2.5 mL) was stirred for 30 minutes, sealed in a 23 mL Teflon-lined stainless steel bomb, and kept at 75 °C under autogenous pressure for 72 h. After cooling at a ramp of 10 °C per hour to room temperature, green colored crystals of {$\{[\text{Ni(tmb)}_2(\mu-4,4^\prime\text{-bpy})(\text{H}_2\text{O})_2](4,4^\prime\text{-bpy})\}_n$ (8) were collected by filtration, washed with deionized water followed by diethyl ether, and then dried (0.0641 g, 70%). Anal. Calc. for $\text{C}_{40}\text{H}_{42}\text{N}_4\text{O}_{6}\text{Ni}$: C, 65.50; H, 5.77; N, 7.64%. Found: C, 66.23; H, 5.49; N, 7.51%

7.9. Synthesis of $[\text{Cu(tmb)}(2,2^\prime\text{-dpa})(\text{Cl})].\text{CH}_3\text{OH}$ (9)

A mixture of copper chloride dihydrate (0.0213 g, 0.125 mmol), 2,4,6-trimethylbenzoic acid (0.041 g, 0.250 mmol), 2,2$^\prime$-dipyridylamine (0.0426 g, 0.250 mmol) and methanol (3 mL) was stirred for 30 minutes, sealed in a 23 mL Teflon-lined stainless steel bomb, and kept at 80 °C under autogenous pressure for 72 h. After cooling at a ramp of 10 °C/h to room temperature, bluish green colored crystals of 9 were collected by filtration, washed with deionized water followed by diethyl ether, and then dried (0.0351 g, 65% Yield). Anal. Calc. for $\text{C}_{20}\text{H}_{20}\text{N}_3\text{O}_2\text{ClCu}$: C, 55.43; H, 4.65; N, 9.7%. Found: C, 55.35; H, 4.52; N, 9.60 %.
7.10. Synthesis of [Cu(2,2'-bpy)₂(Cl)]NO₃·3H₂O (10)

A mixture of copper chloride dihydrate (0.0213 g, 0.125 mmol), 2,4,6-trimethylbenzoic acid (0.041 g, 0.250 mmol), 2,2'-bipyridyl (0.039 g, 0.250 mmol) and 1N nitric acid (3 mL) was taken in a 23 mL Teflon-lined stainless steel bomb, sealed and kept at 80 °C under autogenous pressure for 72 h. After cooling at a ramp of 10 °C/h to room temperature, blue colored crystals of 10 were collected by filtration, washed with deionized water followed by diethyl ether, and then dried (0.0461 g, 70% yield). Anal. Calc. for C₂₀H₂₂N₅O₆ClCu: C, 45.55; H, 4.20; N, 13.28%. Found: C, 45.12; H, 4.04; N, 12.95%.

7.11. Synthesis of [Co(tmb)₂(imi)₂] (11)

A mixture of cobalt acetate tetrahydrate (0.0311 g, 0.125 mmol), 2,4,6-trimethylbenzoic acid (0.041 g, 0.250 mmol), imidazole (0.017 g, 0.250 mmol), and water (2.5 mL) was homogenized for 30 minutes. It was then sealed in a 23 mL Teflon-lined stainless steel bomb, and kept at 150 °C under autogenous pressure for 72 h. After cooling at a ramp of 10 °C per hour to room temperature, magenta colored crystals of [Co(C₁₀H₁₁O₂)₂(C₃H₄N₂)₂] were collected by filtration, washed with de-ionized water followed by diethyl ether, and then dried (0.0442 g, 68 %). Anal. Calc. for C₂₆H₃₀N₄O₄Co: C, 59.88; H, 5.80; N, 10.74% : Found: C, 60.40; H, 5.45; N, 10.93%.

7.12. Synthesis of [Ni(tmb)₂(imi)₂] (12)

A mixture of nickel acetate tetrahydrate (0.0311 g, 0.125 mmol), 2,4,6-trimethylbenzoic acid (0.041 g, 0.250 mmol), imidazole (0.017 g, 0.250 mmol), and water (2.5 mL) was homogenized for 30 minutes. It was then sealed in a 23 mL Teflon-lined stainless steel bomb, and kept at 150 °C under autogenous pressure for 72 h. After cooling at a ramp of 10 °C per hour to room temperature, green colored crystals of [Ni(C₁₀H₁₁O₂)₂(C₃H₄N₂)₂] were collected by filtration, washed with de-ionized water followed by diethyl ether, and then dried (0.0475 g, 73 %). Anal. Calc. for C₂₆H₃₀N₄O₄Co: C, 59.91; H, 5.80; N, 10.75% : Found: C, 60.80; H, 5.77; N, 10.94%.
7.13. Synthesis of $\{[\text{Ni(tmb)}_2(\text{H}_2\text{O})_3].2\text{H}_2\text{O}\}_n$ (13)

Nickel acetate tetrahydrate (0.0311 g, 0.125 mmol), and 2,4,6-trimethylbenzoic acid (0.041 g, 0.250 mmol) were dissolved in aqueous medium (2.5 mL). The mixture was sealed in a 23 mL Teflon-lined stainless steel bomb, and held at 70 °C for 72 h. The bomb was cooled naturally to room temperature and pale green colored crystals of $\{[\text{Ni(tmb)}_2(\text{H}_2\text{O})_3].2\text{H}_2\text{O}\}_n$ were obtained. Then the crystals were collected by filtration, washed with de-ionized water followed by diethyl ether, and then dried (0.048 g, 81.2 %). Anal. Calc. for C$_{20}$H$_{32}$O$_9$Ni: C, 50.56; H, 6.79 %; Found: C, 51.61; H, 6.48 %.

7.14. Synthesis of $\{[\text{Co(tmb)}_2(\text{H}_2\text{O})_3].2\text{H}_2\text{O}\}_n$ (14)

Cobalt acetate tetrahydrate (0.0311 g, 0.125 mmol), and 2,4,6-trimethylbenzoic acid (0.041 g, 0.250 mmol) were dissolved in aqueous medium (2.5 mL). The mixture was sealed in a 23 mL Teflon-lined stainless steel bomb, and held at 70 °C for 72 h. The bomb was cooled naturally to room temperature and pink colored crystals of $\{[\text{Co(tmb)}_2(\text{H}_2\text{O})_3].2\text{H}_2\text{O}\}_n$ were obtained. Then the crystals were collected by filtration, washed with de-ionized water followed by diethyl ether, and then dried (0.046 g, 79 %). Anal. Calc. for C$_{20}$H$_{32}$O$_9$Ni: C, 50.56; H, 6.79 %; Found: C, 51.61; H, 6.48 %.

7.15. Synthesis of $[\text{Cu}_2(\mu-\text{tmb})_4(\text{CH}_3\text{OH})_2]$ (15)

For the synthesis of 15, a mixture of copper acetate monohydrate (0.0311 g, 0.125 mmol), 2,4,6-trimethylbenzoic acid (0.0205 g, 0.125 mmol), and caffeine (0.0242 g, 0.125 mmol) were mixed in methanol (2.5 mL). After stirring for half an hour, the mixture was placed in a 23 mL Teflon-lined reactor and heated at 85 °C in an oven for three days. Then the reactor was cooled slowly to room temperature; dark green colored crystals of $[\text{Cu}_2(\mu-\text{tmb})_4(\text{CH}_3\text{OH})_2]$ were collected by filtration, washed with de-ionized water followed by diethyl ether, and then dried (0.0460 g, 87.7%). In this synthesis caffeine finds its use as a mineralizer. Anal. Calc. for C$_{42}$H$_{52}$O$_{10}$Cu$_2$: C, 59.77; H, 6.21%: Found: C, 59.68; H, 6.13%.
7.16. **Synthesis of Cd(tmb)(phen)$_2$(NO$_3$)$_2$.CH$_3$OH (16)**

A mixture of cadmium nitrate tetrahydrate (0.0385 g, 0.125 mmol), 2,4,6-trimethylbenzoic acid (0.041 g, 0.250 mmol), 1,10-phen (0.0495 g, 0.250 mmol) CH$_3$OH (1.5 mL) and water (1.5 mL) was sealed in a 23 mL Teflon-lined stainless steel bomb, and kept at 85 °C under autogenous pressure for 72 h. After cooling at a ramp of 10 °C/h to room temperature, colorless crystals of 16 were collected by filtration, washed with deionized water followed by diethyl ether, and then dried (0.0592 g, 65% yield). Anal. Calc. for C$_{35}$H$_{31}$N$_5$O$_6$Cd: C, 57.58; H, 4.28; N, 9.59%. Found: C, 57.42; H, 4.01; N, 9.20%.

References
