CHAPTER 2

EXPERIMENTAL DETAILS

2.1 General considerations:

All the reactions were carried out using water as a solvent and in air, unless specified otherwise. Metal salts, substituted benzoic acids and other reagents were used as purchased. The starting materials and reaction products are air stable and hence were routinely prepared under normal laboratory conditions without any special precautions. The pH of the solutions was determined using short-range pH paper as well as electronic pH meter (Model PHAN, Lab India). The infrared spectra of the samples were recorded on a IR Prestige-21 Fourier transform (SHIMADZU) (4000-250 cm\(^{-1}\)) infrared (IR) spectrometers and as KBr diluted pellets on a Shimadzu FTIR-8101A spectrophotometer at Department of Chemistry, Goa University. The samples for the IR were prepared as KBr diluted pellets in the solid state and the signals referenced to polystyrene bands. Electronic spectra were recorded using matched quartz cells on a Shimadzu (UV-2450) spectrophotometer at Department of Chemistry, Goa University. The metal content was analysed by EDTA / gravimetric method following standard procedures. The insoluble 4-nbAH obtained on acid treatment of the complexes was weighed as described earlier [78]. The water content of the synthesized complexes was estimated by Karl-Fischer titration. NMR spectra were recorded on a Bruker WT 300 MHz FT-NMR spectrophotometer, NIO, Donapaula, Goa. The C, H and N analyses were performed on a HEKA Tech Euro EA elemental analyzer. Thermal decomposition studies were performed in an electric furnace (Newtronic) fitted with a temperature controller in silica crucibles. TG-DTA measurements were performed simultaneously using the STA-409CD device (Netzsch). The thermal investigations were performed in Al\(_2\)O\(_3\) crucibles using a heating rate of 4 K/min and purged in an air stream of 75 ml/min. EDX analysis was performed with a Philips ESEM XL 30 scanning electron microscope equipped with an EDAX analyzer. X-ray powder patterns were recorded in transmission geometry using a STOE STADI P diffractometer (CuK\(_\alpha \) = 1.54056 Å) at Institut für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel, Germany and on X-ray diffractometer, system APD 2000, Ital Structures (Italy) at Department of
Chemistry, Goa University. STOE Image Plate Diffraction System and on an AED-II four circle diffractometer, using graphite-monochromated Mo-Kα radiation (λ=0.71069Å). Single crystal X-ray diffraction study was performed at the single crystal X-ray facility at School of Chemistry, University of Hyderabad, Institute für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel, Germany and at IIT Kanpur.

2.2. Synthesis of the bivalent metal carboxylates

2.2.1. Preparation of [Mg(H2O)6]2(4-nba)2·2H2O [75]

Method I: A mixture of magnesium carbonate (0.84 g, 10 mmol) and 4-nitrobenzoic acid (4-nbaH) (3.34 g, 20 mmol) was taken in water (50 ml) and heated on a steam bath. The insoluble starting materials slowly started dissolving accompanied with brisk effervescence. The heating of the reaction mixture was stopped when there was no more evolution of CO2. At this stage the reaction mixture was almost clear and the pH was close to neutral. The hot solution was filtered and kept for crystallization. The rectangular crystalline blocks that separated were filtered, washed thoroughly with ether and dried in vacuo. The crystals obtained in this method were suitable for X-ray structure investigations. Yield 4.5 g (90%).

Anal. Found (calcd) for C14H24MgN2O16: Mg 4.70 (4.86), 4-nbaH 66.42 (66.78), N 6.53 (5.60), C 33.65 (33.60), H 4.61 (4.84)

2.2.2. Preparation of [Mg(H2O)4(4-clba)2] 2

Method I: A mixture of MgCO3 (0.168 g, 2 mmol) and 4-chlorobenzoic acid (4-clbaH) (0.6223 g, 4 mmol) was taken in water (20 ml) and heated on a steam bath. The insoluble starting materials slowly started dissolving accompanied with brisk effervescence. The heating of the reaction mixture was stopped when there was no more evolution of CO2. At this stage the reaction mixture was almost clear and the pH was close to neutral. The crystalline blocks that separated were filtered, washed thoroughly with ether and dried in vacuo. Yield: 0.528 g (65%)

Anal. Found (Calcd) for C14H16MgC12O8: Mg 5.86 (5.97), C 42.92 (41.24), H 3.63 (3.97)
**Method II:** A solution of sodium bicarbonate (0.84 g, 10 mmol) in water (10 ml) was added into 4-chlorobenzoic acid (1.565 g, 10 mmol) to obtain the sodium salt of the carboxylic acid. To this solution, anhydrous MgCl₂·6H₂O (1.015 g, 5 mmol) in water (30 ml) was slowly added. The resultant clear solution was filtered and filtrate was left undisturbed for crystallization. After 4-5 days the colourless blocks separated out. These were filtered, washed with cold water (5 ml) and dried in air. The product obtained in this method had an identical IR spectrum and analyzed satisfactorily as the product from method I. Yield: 1.60 g (79 %)

2.2.3. Preparation of [Ca(H₂O)₄(4-nba)₂] 3 [97] and [Ca(H₂O)₃(4-clba)₂] 4

**Method I:** A mixture of calcium carbonate (1.00 g, 10 mmol) and 4-nbaH (3.34 g, 20 mmol) was taken in water (50 ml) and heated on a steam bath. The insoluble starting materials slowly started dissolving accompanied with brisk effervescence. The heating of the reaction mixture was stopped when there was no more evolution of CO₂. At this stage, the reaction mixture was almost clear and the pH was close to neutral. The hot solution was filtered and left undisturbed for 3-4 days. The colourless crystalline blocks that separated were filtered, washed thoroughly with ether and dried in vacuum. The crystals obtained in this method were suitable for X-ray studies. Yield: 3.109 g (70 %). The use of 4-clbaH (3.12 g, 20 mmol) instead of 4-nbaH resulted in the formation of 4. Yield 1.6131 (80 %)

Anal. Found (Calcd) for C₁₄H₁₆CaN₂O₁₂ (444.24) 3: Ca 9.01 (9.02), 4-nbaH 74.32 (74.77), C 37.93 (38.07), H 3.58 (3.66), N 6.24 (6.34)

Anal. Found (Calcd) for C₁₄H₁₄CaC₁₂O₇ (404.20) 4: Ca 9.87 (9.92), C 42.94 (41.56), H 3.66 (3.50)

**Method II:** The sodium salt of 4-nba was first generated in situ by reacting 4-nbaH (3.34 g, 20 mmol) with NaHCO₃ (1.68 g, 20 mmol) in water. Into this, an aqueous solution of anhydrous CaCl₂ (1.11 g, 10 mmol) was added and the reaction mixture was filtered and left aside for crystallization. The crystals that separated after a few days were isolated. The IR spectrum of the product obtained in this method was identical to that of the spectrum of the product obtained using CaCO₃ as the Ca source. The product obtained in this method had an identical IR spectrum as the product from method I. Yield: 3.820 g (86 %). The use of 4-clbaH (3.12 g, 20 mmol) instead of 4-nbaH in the above reaction resulted in the formation of 4 in 78 % yield. The product analyzed satisfactorily.
2.2.4. Preparation of [Ca(4-nba)₂] 3a

A powdered sample of [Ca(H₂O)₄(4-nba)₂] (0.488 g) was heated in a temperature controlled furnace at 250 °C for ~20 min. This resulted in the formation of the anhydrous compound Ca(4-nba)₂ (0.408 g). The observed mass loss of 16.4% is in very good agreement with the expected value (16.2 %) for the loss of four moles of water.

2.2.5. Preparation of [Sr(H₂O)₇(4-nba)](4-nba).₂H₂O 5 [98] and [Sr(H₂O)(4-clba)₂] 6

**Method I:** A mixture of strontium carbonate (0.7381 g, 5 mmol) and 4-nbaH (1.67 g, 10 mmol) was taken in water (80 ml) and heated on a steam bath. The insoluble starting materials slowly started dissolving accompanied with brisk effervescence. The heating of the reaction mixture was stopped when there was no more evolution of CO₂. At this stage, the reaction mixture was almost clear and the pH was close to neutral. The hot solution was filtered and left undisturbed for a week. The colourless crystalline blocks that separated were filtered, washed thoroughly with water and air dried. The crystals are unstable in air. The crystals of 5 obtained in this method were suitable for X-ray studies. Yield: 2.0962 g (72%). The use of 4-clbaH instead (1.56 g, 10 mmol) of 4-nbaH in the above reaction resulted in the formation of 6 in 79% yield and analyzed satisfactorily.

Anal. Found (Calcd) for C₁₄H₂₆SrN₂O₁₇ (581.99): Sr 15.23 (15.06), 4-nbaH 56.28 (57.08), C 29.516 (28.86), H 3.677 (4.811), N 4.834 (4.512).

Anal. Found (Calcd) for C₁₄H₁₀SrCl₂O₅ (416.64): Sr 20.87 (20.2), C 41.48 (40.32), H 2.35 (2.42).

**Method II:** The sodium salt of 4-nba was first generated in situ by reacting 4-nbaH (1.67 g, 10 mmol) with NaHCO₃ (0.84 g, 10 mmol) in water. Into this, an aqueous solution of SrCl₂.6H₂O (0.793 g, 5 mmol) was added and the reaction mixture was filtered and left aside for crystallization. The crystals that separated after a week were isolated, washed with water and air dried. Compound is unstable in air. The IR spectrum and X-ray powder pattern of the product obtained in this method was identical to that of the spectrum of the product obtained using SrCO₃. The product obtained in this method was analyzed satisfactorily as the product from method I. Yield: 2.593 g (89 %). The similar reaction of 4-clbaH instead (1.56 g, 10 mmol) of 4-
nbaH with SrCl₂·6H₂O resulted in the formation of 6 in 77% (2.241 g) yield and analyzed satisfactorily.

2.2.6. Preparation of [Ba(H₂O)₅(4-nba)₂]₇ [63b] and [Ba(4-clba)₂] 8

**Method I:** A mixture of barium carbonate (1.98 g, 10 mmol) and 4-nbaH (3.34 g, 20 mmol) was taken in water (80 ml) and heated on a steam bath. The insoluble starting materials slowly started dissolving accompanied with brisk effervescence. The heating of the reaction mixture was stopped when there was no more evolution of CO₂. At this stage, the reaction mixture was almost clear and the pH was close to neutral. The hot solution was filtered and left undisturbed for 4-5 days. The colourless crystalline blocks that separated were filtered, washed thoroughly with ether and dried in vacuo. The crystals obtained in this method were suitable for X-ray studies. Yield: 4.653 g (83%). The use of 4-clbaH instead (1.6 g, 10 mmol) of 4-nbaH in the above reaction resulted in the formation of 8 in 72% (1.62 g) yield.

Anal. Found (Calcd) for C₁₄H₁₈BaN₂O₁₃ (559.64) 7: Ba 24.50 (24.53), 4-nbaH 60.99 (59.72), C 29.86 (30.00), H 3.114 (3.23), N 5.073 (5.00)

Anal. Found (Calcd) for C₁₄H₈BaCl₂O₄ (448.61) 8: Ba 29.55 (30.64), C 37.81 (37.45), H 1.746 (1.8)

**Method II:** The sodium salt of 4-nba was first generated in situ by reacting 4-nbaH (1.67 g, 20 mmol) with NaHCO₃ (0.84 g, 20 mmol) in water. Into this, an aqueous solution of BaCl₂·4H₂O (1.221 g) was added and the reaction mixture was filtered and left aside for crystallization. The crystals that separated after a few days were isolated washed with cold water, followed by ether and air dried. The IR spectrum and X-ray powder pattern of the product obtained in this method were identical to that of the spectrum of the product obtained using BaCO₃ as the Ba source. The product obtained in this method was analyzed satisfactorily as the product from method I. Yield: 2.378 g (85%). A use of 4-clbaH instead (1.56 g, 10 mmol) of 4-nbaH in above reaction resulted in the formation of 8 in 94% yield.

2.2.7 Preparation of [Li(4-nba)(H₂O)₃] 9

To an aqueous solution of lithium carbonate (1.4778 g, 10 mmol) in water (20 ml) 4-nbaH (3.34 g, 20 mmol) was added. The reaction mixture was heated on a water bath. Insoluble 4-nitrobenzoic acid slowly started dissolving. The clear solution obtained was kept for crystallization. The crystals separated were filtered, washed with ether and dried. Yield: 2.32 (51) %
Anal. Found (Calcd) for C$_7$H$_{10}$ LiN$_1$O$_7$ 2 (227): 4-nbaH 72.33 (73.21), C 36.87 (36.99), H 3.95 (4.45), N 6.53 (6.17).

2.2.8. Preparation of [Na(H$_2$O)$_2$(4-nba)] 10
To an aqueous solution of sodium carbonate (1.06 g, 10 mmol) in water (20 ml), 4-nitrobenzoic acid (3.34 g, 20 mmol) was added. The reaction mixture was heated on a water bath. Insoluble 4-nbaH slowly started dissolving. The clear solution obtained was kept for crystallization. The separated rectangular crystals separated were filtered, washed with ether and dried. Yield: 2.21 (91%)
Anal. Found (Calcd) for C$_7$H$_6$NaNO$_7$ 10 (243.26): 4-nbaH 67.0 (68.21), C 34.91 (34.53), H 3.69 (4.15), N 6.01 (5.76).

2.2.9. Preparation of [K(H$_2$O)$_2$(4-nba)] 11
To an aqueous solution of potassium carbonate (1.38 g, 10 mmol) in water (20 ml), 4-nbaH (3.34 g, 20 mmol) was added. The reaction mixture with 4-nbaH was heated on a water bath. Insoluble 4-nbaH slowly started dissolving. The clear solution obtained was kept for crystallization. The separated colourless crystals were filtered, washed with ether and dried. Yield: 3.55 (68.53 %)
Anal. Found (Calcd) for C$_7$H$_6$KNO$_6$ 11 (241.24): 4-nbaH 68.01 (68.89)

2.2.10. Preparation of [Rb(H$_2$O)$_2$(4-nba)] 12 and [Cs(H$_2$O)$_2$(4-nba)] 13

To the aqueous solution of rubidium carbonate (0.231 g, 1 mmol, 20 ml water), 4-nitrobenzoic acid (0.334 g, 2mmol) was added and solution was heated on water bath. Insoluble 4-nitrobenzoic acid slowly started dissolving. The clear solution obtained was kept for crystallization. The flat rectangular blocks that separated were filtered, washed with ether and dried. Yield: 0.466 g (78 %). A similar reaction of 4-nbaH with cesium carbonate (0.326 g, 1 mmol) resulted in the formation of 13 in 60% yield.
Anal. (Calc.) for C$_7$H$_8$RbNO$_6$ 12 (287.61): 4-nbaH 57.10 (57.77), C 29.06 (29.21), H 2.18 (2.81), N 4.75 (4.87)
Anal. Found (Calcd) for C$_7$H$_8$CsNO$_6$ 13 (335.05): 4-nbaH 48.87(49.60), C 25.22 (25.07), H 2.179(2.41), N 4.40 (4.18)
2.2.11. Preparation of $[\text{Mn(H}_2\text{O)}_4(\text{4-nba})_2]\cdot\text{2H}_2\text{O}$ \[\text{14} \{122\]
2.2.12. Preparation of $[\text{Mn-(4-nba)}_2] \ 14a$

The anhydrous yellow complex $[\text{Mn(4-nba)}_2]$ (0.390 g) can be obtained in near quantitative yield by heating a powdered sample of $[\text{Mn(H}_2\text{O)}_4(4\text{-nba)}_2]_{2\text{H}_2\text{O}}$ (0.500 g) in a temperature controlled oven for 25 min around 200°C. The complex thus obtained analyzed satisfactorily.

2.2.13. Preparation of $[\text{Ni(H}_2\text{O)}_6(4\text{-nba)}_2].2\text{H}_2\text{O} \ 15 \ [50]$

**Method I:** A solution of NaOH (0.4 g, 10 mmol) in water (5 ml) was added to NiCl$_2.6\text{H}_2\text{O}$ (1.19 g, 5 mmol) in water (5 ml). Ni(OH)$_2$ thus generated *in situ* is reacted with 4-nbaH (1.67 g, 10 mmol) in aqueous ammonia (125 ml). The solution was stirred for 30 min. The blue solution thus obtained (pH ≈ 12) was filtered and left for crystallization. The blue product thus obtained after 1-2 days was filtered and washed with ammoniacal solution and air dried. The compound loses its water content on exposure to air. The complex was insoluble in water and CH$_3$CN, slightly soluble in methanol and soluble in DMSO. Yield: 1.326 g (50%) 

Anal. Found (Calcd) for C$_{14}$H$_{24}$NiN$_2$O$_{16}$ 15 (534.91): Ni 12.00 (11.00), 4-nbaH 63.91 (62.11)

**Method II:** An aqueous solution of NiCl$_2.6\text{H}_2\text{O}$ (1.19 g, 5 mmol) was reacted with Na$_2$CO$_3$ (0.53 g, 5 mmol) in 20 ml of water. To the NiCO$_3$ generated *in situ*, 4-nbaH (1.67 g, 10 mmol) was added in 100 ml water. The solution was stirred for 90 min to obtain a clear green colour solution. To the resultant solution 70 ml of aqueous NH$_3$ was added so that pH of the solution is ≈ 12. The green solution turned to blue, which was filtered and filtrate was kept for crystallization. After 3-4 days the blue crystals were filtered and washed with ammoniacal solution and dried in air. Yield: 1.05 g (38%) 

**Method III:** $[\text{Ni(H}_2\text{O)}_4(4\text{-nba)}_2].2\text{H}_2\text{O}$ (0.534 g) was dissolved in aqueous ammonia (15 ml). The resultant clear solution was filtered and kept for crystallization. Blue coloured crystals obtained were filtered, washed with ammoniacal solution and air dried. Yield: 0.229 g (40 %)
2.4.14. Preparation of \([\text{Cd}(H_2O)_2(4-nba)_2]\) \[16\] [92]
CdCl₂·H₂O (1.066 g, 5 mmol) was taken in water (5 ml). Into this, an aqueous solution of sodium 4-nitrobenzoate generated \textit{in situ} from 4-nbaH (1.67 g, 10 mmol), NaHCO₃ (0.84 g 10 mmol) in water (60 ml) was added. The clear solution thus obtained was filtered and kept for crystallization. The crystals obtained were filtered, washed with water followed by ether and air dried. Yield: 1.514 g (63%)
Anal. Found (Calcd) for C₁₄H₁₁CdN₂O₁₀ \[16\] (480.65): Cd 23.3 (23.4), 4-nbaH 69.44 (69.11)

2.3 Reactivity studies of bivalent metal 4-nitrobenzoate complexes with N-donor ligands

2.3.1. Preparation of \([\text{Mg}(H_2O)_2(Im)_2(4-nba)_2]\) \[17\] [127]
\textbf{Method I}: A mixture of magnesium carbonate (0.84 g, ~10 mmol) and 4-nbaH (3.34 g, 20 mmol) was taken in water (50 ml) and heated on a steam bath. The insoluble starting materials slowly started dissolving accompanied with brisk effervescence. The heating of the reaction mixture was stopped when there was no more evolution of CO₂. At this stage the reaction mixture was almost clear and the pH was close to neutral. The hot solution was filtered into a warm aqueous solution (5 ml) of imidazole (2.72 g, 40 mmol) and the filtrate was concentrated to half the volume and left undisturbed for 3-4 days. The crystalline blocks that separated were filtered, washed thoroughly with ether and dried in vacuo. The crystals obtained in this method were suitable for X-ray structure investigations. The complex was insoluble in methanol and slightly soluble in water, DMSO and CH₃CN. Yield 4.07 g (77%)
Anal. Found (Calcd) for C₂₀H₁₈MgN₂O₁₀ \[17\] (528.73): Mg 4.65 (4.62), 4-nbaH 62.08 (63.46), C 45.53(45.39), H 3.71(3.44), N 16.08 (15.89)

\textbf{Method II}: MgCl₂·6H₂O (2.03g, 10 mmol) was taken in water (5 ml). Into this, an aqueous solution of sodium 4-nitrobenzoate generated \textit{in situ} from 4-nbaH (3.34 g, 20 mmol), NaHCO₃ (1.68 g 20 mmol) and water (20 ml) was added. This resulted in the formation of a clear solution, which was filtered into an aqueous solution of imidazole (2.72 g, 40 mmol) in water (5 ml). The pale yellow solution was then concentrated to half its volume by heating on a water bath. The concentrated reaction mixture was kept aside for crystallization. The crystals that separated after 4-5 days were filtered,
washed with little ice-cold water (~2 ml), followed by ether and dried in air. The product obtained in this method analyzed satisfactorily and exhibited an identical IR spectrum as that of the product from method I. Yield: 3.331(63%)

**Method III:** A powdered sample of \([\text{Mg}(\text{H}_2\text{O})_6](4\text{-nba})_2\cdot 2\text{H}_2\text{O}\) (1 mmol, 0.500 g) was heated on a water bath for 15 min. The bright yellow coloured partially dehydrated compound thus obtained was reacted with an aqueous solution (~5 ml) of imidazole (4 mmol, 0.272 g). The clear solution thus obtained was left aside for crystallization. The product was isolated as described above (Method I). Yield: 0.418 g (85 %)

**Method IV:** Mechanical grinding of \([\text{Mg}(\text{H}_2\text{O})_6](4\text{-nba})_2\cdot 2\text{H}_2\text{O}\) (0.500 g) and Im (0.136 g ) for ~20 min, in a mortar and pestle resulted in the formation of \([\text{Mg}(\text{H}_2\text{O})_2(\text{Im})_2(4\text{-nba})_2]\). The compound analyzed satisfactorily and exhibited an identical IR spectrum as that of the product from Method I. Yield was quantitative.

### 2.3.2. Preparation of \([\text{Mg}(\text{Im})_2(4\text{-nba})_2]\) 17a

A powdered sample of \([\text{Mg}(\text{H}_2\text{O})_2(\text{Im})_2(4\text{-nba})_2]\) (0.488 g) was heated in a temperature controlled oven at 140 °C for ~20 min. This resulted in the formation of the anhydrous compound \([\text{Mg}(\text{Im})_2(4\text{-nba})_2]\) (0.451 g). The observed mass loss of 7.65 % is in very good agreement with the expected value (7.29 %) for the loss of two moles of water.

### 2.3.3. Preparation of \([\text{Mg}(\text{H}_2\text{O})(\text{N-MeIm})_2(4\text{-nba})_2]\) 18 [75]

**Method I:** A mixture of MgCO₃ (0.84 g, 10 mmol) and 4-nbaH (3.34 g, 20 mmol) was taken in water (50 ml) and heated on a steam bath. The insoluble starting materials slowly started dissolving as evidenced by the brisk effervescence. The heating of the reaction mixture was stopped when there was no more evolution of CO₂. At this stage the reaction mixture was almost clear and the pH was close to neutral. The reaction mixture was filtered and N-MeIm (3.19 ml, 40 mmol) was added to the hot filtrate. The solution was stirred and concentrated to around 10 ml and left undisturbed for a few days. The pale crystalline blocks that separated were filtered, washed thoroughly with ether and dried in air. The complex was insoluble in water and CH₃CN, slightly soluble in DMSO and insoluble methanol. Yield: 4.8 g (87 %).
Anal. Found (Calcd) for C_{44}H_{44}Mg_{2}N_{12}O_{18} \textbf{18} (1077.44): Mg 4.56 (4.51), 4-nbaH 60.25 (61.65), C 49.09 (49.01), H 4.201 (4.12), N 15.84 (15.59).

**Method II:** MgCl\textsubscript{2}.6H\textsubscript{2}O (2.03 g, 10 mmol) was dissolved in water (10 ml). Into this, an aqueous solution (40 ml) of sodium salt of 4-nbaH generated *in situ* from 4-nbaH (3.34 g, 20 mmol), NaHCO\textsubscript{3} (1.68 g, 20 mmol) was added, followed by the addition of N-Melm (3.19 ml, 40 mmol). The clear reaction mixture was filtered and kept aside for crystallization. The yellow crystalline blocks that separated after few days were filtered, washed with ice-cold water (2 ml), followed by ether and air dried. The IR spectra of the complexes obtained in both the methods are identical. Yield: 4.15 g (83%).

**Method III:** Mechanical grinding of \([\text{Mg(H}_2\text{O)}_6]\)\textsubscript{4-nba)}\textsubscript{2}.2H\textsubscript{2}O (0.500 g) and N-Melm (0.158 g) for ~15 min, in a mortar and pestle resulted in the formation of Mg dimmer \([\text{Mg(H}_2\text{O)}(\text{N-Melm)}\textsubscript{2}(4-nba)]\textsubscript{2}\) (0.537 g). The compound analyzed satisfactorily and exhibited an identical IR spectrum as that of the product from method I.

2.3.4. **Preparation of [Ca(H\textsubscript{2}O\textsubscript{3})(Im)(4-nba)]\textsubscript{2}.Im 19 [127]**

**Method I:** A mixture of CaCO\textsubscript{3} (1.08 g, ~10 mmol) and 4-nitrobenzoic acid (4-nbaH) (3.34 g, 20 mmol) was taken in water (50 ml) and heated on a steam bath. The insoluble starting materials slowly started dissolving accompanied with brisk effervescence. The heating of the reaction mixture was stopped when there was no more evolution of CO\textsubscript{2}. At this stage the reaction mixture was almost clear and the pH was close to neutral. The hot solution was filtered into a warm aqueous solution (5 ml) of imidazole (2.72 g, 40 mmol) and the filtrate was concentrated to half the volume and left undisturbed for 3-4 days. The crystalline blocks that separated were filtered, washed thoroughly with ether and dried in vacuo. The crystals obtained in this method were suitable for X-ray structure investigations. Yield: 4.39 (78%)

Anal. Found (Calcd) for C\textsubscript{20}H\textsubscript{22}CaN\textsubscript{6}O\textsubscript{11} \textbf{19} (562-52): Ca 7.32 (7.13), 4-nbaH 59.55 (59.06), C 42.771 (42.66), H 4.176 (3.95), N 15.773 (14.93)

**Method II:** CaCl\textsubscript{2} (1.11 g, 10 mmol) was taken in water (5 ml). Into this, an aqueous solution of sodium 4-nitrobenzoate generated *in situ* from 4-nbaH (3.34 g, 20 mmol), NaHCO\textsubscript{3} (1.68 g, 20 mmol) and water (20 ml) was added. This resulted in the formation of a clear solution, which was filtered into an aqueous solution of imidazole
(2.72 g, 40 mmol) in water (5 ml). The pale yellow solution was then concentrated to half its volume by heating on a water bath. The concentrated reaction mixture was kept aside for crystallization. The crystals that separated after 4-5 days were filtered, washed with little ice-cold water (~2 ml), followed by ether and dried in air. The product obtained in this method analyzed satisfactorily and exhibited an identical IR spectrum as that of the product from method I. Yield 3.488 (62 %).

2.3.5. Preparation of [Ca(Im)$_2$(4-nba)$_2$] $^{19a}$
The powdered sample of [Ca(H$_2$O)$_3$(Im)(4-nba)$_2$]·Im (0.464 g) was heated on a water bath for 15 min to obtain anhydrous complex [Ca(Im)$_2$(4-nba)$_2$] (0.420 g) in quantitative yield. The product obtained is analyzed satisfactorily and exhibited a different IR spectrum as well as X-ray powder pattern indicating the formation of new compound.

2.3.6. Preparation of [Ca(H$_2$O)(2-MeIm)(4-nba)$_2$] $^{20}$

**Method I:** Calcium carbonate (1.0 g, 10 mmol) was added to 4-nbaH (3.34 g, 20 mmol) in water (80 ml) and the solution was heated on waterbath to obtain clear solution. The solution was filtered and to the filtrate 2-MeIm (3.28 g, 40 mmol) in water (20 ml) was added. The clear yellow solution was filtered and left for crystallization. After 2-3 days pale crystals separated. These were filtered, washed with water followed by ether and air dried. Yield: 2.921 g (62 %).

Anal. Found (Calcd) for CaC$_{18}$H$_{18}$N$_4$O$_{10}$ $^{20}$ (472.43): Ca 8.47(8.48), 4-nbaH 71.00 (70.30), C 45.65 (45.73), H 3.63 (3.84), N 12.537 (11.85)

**Method II:** The sodium salt of 4-nba was first generated *in situ* by reacting 4-nbaH (3.34 g, 20 mmol) with NaHCO$_3$ (1.68 g, 20 mmol) in water. Into this, an aqueous solution of anhydrous CaCl$_2$ (1.11 g) was added and the reaction mixture was filtered and to the filtrate 2-MeIm (3.24 g, 40 mmol) in water (20 ml) was added. The clear yellow solution was filtered and left for crystallization. After few days pale crystals separated were filtered and washed with water and then with ether and air dried. IR spectrum of the product obtained in this method was identical to that of the spectrum of the product obtained using freshly precipitated CaCO$_3$ as the Ca source. Yield: 2.971 g (63 %).
2.3.7. Preparation of \([\text{Ca(N-Melm)(4-nba) }_2]\) [21] [133]

A powdered sample of \([\text{Ca(H}_2\text{O})_4(4-\text{nba})_2]\) 3 (1.78 g, 4 mmol) was heated with N-Melm (1.4 ml, 17 mmol) on a steam bath for \(\sim 1\) h to obtain a light yellow solid. To this hot mass \(\sim 8\) ml of distilled water was added and the mixture reheated to obtain a pale yellow solution. The hot solution was quickly filtered and kept aside for crystallization. Fine colourless blocks of crystals suitable for X-ray study, which separated were washed with ether (5ml) and dried in air. Yield: 1.09 (60%) Anal. Found (Calcd) for \(\text{C}_{18}\text{H}_{14}\text{CaN}_4\text{Os}\) 21 (454.41): Ca 8.8 (8.8), 4-nbaH 73 (73.11)

2.3.8. Preparation of \([\text{Ca(H}_2\text{O})_2(N-\text{Melm})(4-\text{nba})_2]\) [22]

Calcium carbonate (0.50 g, 5 mmol) was added to 4-nbaH (1.67 g, 10 mmol) in water (80 ml) and the solution was heated on water bath to obtain clear solution. The solution was filtered and to the filtrate N-Melm (2.529 mL, 30 mmol) was added. The clear solution was filtered and left for crystallization. After few days white fine needle shape crystals separated were filtered and washed with cold water and air dried. Yield: 0.715 g (24.9 %).

Anal. Found (Calcd) for \(\text{C}_{18}\text{H}_{18}\text{CaN}_4\text{Os}\) 22 (490.28): Ca 7.7 (8.17), 4-nbaH 67.0 (67.8), C 45.42 (44.56), H 3.39 (3.71), N 11.56 (11.42)

2.3.9. Preparation of \([\text{Mn(H}_2\text{O})_2(\text{Im})_2(4-\text{nba})_2]\) [23] [123]

**Method I:** MnCO\(_3\) is generated \textit{in situ} by reaction between MnCl\(_2\) .4H\(_2\)O (0.99 g, 5 mmol), and Na\(_2\)CO\(_3\) (0.53 g, 5 mmol) in water (40 ml). To this solution 4-nbaH (1.67 g, 10 mmol) was added. The reaction mixture was refluxed in the heating mantle for 30 min to obtain a clear solution. The resulting clear solution was filtered and to the filtrate imidazole (0.68 g, 10 mmol) in water (10 ml) was added. The resultant pale yellow solution was filtered and kept for crystallization. The yellow crystalline blocks was separated within a day was filtered, washed with cold water then with ether and air dried. Yield: 2.55 g (91 %)

Anal. Found (Calcd) for \(\text{C}_{20}\text{H}_{20}\text{MnN}_6\text{O}_{10}\) 23 (559.36): Mn 9.82 (9.82), 4-nbaH 60.55 (59.39), C 42.93 (42.94), N 15.083 (15.027), H 3.67 (3.61)

**Method II:** A solution of sodium bicarbonate (0.84 g, 10 mmol) in water (10 ml) was added into 4-nbaH (1.69 g, 20 mmol) to obtain the sodium salt of the carboxylic acid. To this solution, MnCl\(_2\) .4H\(_2\)O (0.99 g, 5 mmol) in water (40 ml) was slowly added. The resultant clear solution was filtered. The reaction mixture was filtered and to the
filtrate imidazole (0.68 g, 10 mmol) in water (10 ml) was added. The yellow crystals were precipitated out within an hour was filtered, washed with cold water followed by ether and air dried. The product analyzed satisfactorily and exhibited an identical IR spectrum to that of the product obtained from the earlier method. Yield: 2.52 g (90%)

**Method III:** The [Mn(H2O)2(Im)2(4-nba)2] can be also prepared by single pot reaction from MnCl2.4H2O (0.99 g, 5 mmol), Imidazole (0.68 g, 10 mmol), 4-nbaH (1.67 g, 10 mmol), and NaHCO3 (0.84 g, 10 mmol) in water (70 ml) at room temperature in beaker. The reaction mixture was stirred for 1 hour till all effervescences ceases. The yellow crystalline product thus obtained was filtered, washed with cold water, followed by ether and air dried. The product obtained in near quantitative yield and exhibited an identical IR spectrum to that of the product obtained from the method. Yield: 1.99 g (80%)

**Method IV:** Mechanical grinding of [Mn(H2O)6](4-nba)2.2H2O (0.495 g) and Im (0.136 g) for ~15 min, in a mortar and pestle resulted in the formation of monomer [Mn(H2O)2(Im)2(4-nba)2]. The compound analyzed satisfactorily and exhibited an identical IR spectrum as that of the product from Method I. Yield: Quantitative.

2.3.10. Preparation of [Mn(Im)2(4-nba)2] 23a

The anhydrous pale yellow complex [Mn(Im)2(4-nba)2] (0.494 g) can be obtained in near quantitative yield by heating a powdered sample of Mn(H2O)2(Im)2(4-nba)2 (0.530 g) in a temperature controlled oven for 15 min around 150°C. The complex thus obtained analyzed satisfactorily.

2.3.11. Preparation of [Mn(H2O)(N-MeIm)2(4-nba)2] 24

**Method I:** Sodium salt of 4-nitrobenzoic acid is generated in situ from the reaction between 4-nbaH (0.334 g, 2 mmol) and sodium bicarbonate (0.168 g, 2 mmol) in water (30 ml) and MnCl2.4H2O (0.198 g, 1 mmol) solution. To the cold solution N-MeIm (0.158 ml, 2 mmol) solution in water (5 ml) was added with constant stirring. The solution was filtered and kept for crystallization. The yellow crystals obtained after a week were filtered and washed with water followed by ether and air dried. Yield: 0.3183 (55.55%)

Anal. Found (Calcd) for C44H44Mn2N12O18 24 (1138.44): Mn 9.965 (9.59), 4-nbaH 58.2 (57.96), C 45.938 (46.37), N 14.61 (14.76), H 3.83 (3.90)

42
Method II: Mechanical grinding of \([\operatorname{Mn}(\text{H}_2\text{O})_4(4\text{-nba})_2]\cdot 2\text{H}_2\text{O} \ (0.495 \text{ g, } 1 \text{ mmol})\) and N-Melm (0.158 ml, 2 mmol ) for ~15 min, in a mortar and pestle resulted in the formation of Mg dimmer \([\operatorname{Mn}(\text{H}_2\text{O})(\text{N-Melm})_2(4\text{-nba})_2]\). The compound analyzed satisfactorily and exhibited an identical IR spectrum as that of the product from Method I. Yield: Quantitative

2.3.12. Preparation of \([\operatorname{Mn}(\text{H}_2\text{O})_4(\text{benzim})_2](4\text{-nba})_2\) 25

Sodium salt of 4-nbaH is generated in situ from the reaction between 4-nbaH (1.67 g, 10 mmol) and sodium bicarbonate (0.84 g, 10 mmol) in water (30 ml) was reacted with MnCl\(_2\cdot 4\text{H}_2\text{O} \ (0.99 \text{ g, } 5 \text{ mmol})\) solution. The resultant clear solution was diluted to approximately 250 ml. To this solution benzimidazole (1.1813 g, 10 mmol) solution in methanol (5 ml) was added with constant stirring. The solution was filtered and kept for crystallization. The colourless crystals obtained after 3 days were filtered and washed with water followed by ether and air dried. Yield: 2.58 g (74.1 %)

Anal. Found (Calcd) for C\(_{28}\)H\(_{28}\)MnN\(_6\)O\(_{12}\) 25 (695.5): Mn 7.90 (7.90), 4-nbaH 47.17 (47.76), C 48.50 (48.31), H 4.25 (4.07), N 12.87 (12.08).

2.3.13. Preparation of \([\operatorname{Mn}(\text{benzim})_2(4\text{-nba})_2]\) 25a

A powdered sample of \([\operatorname{Mn}(\text{H}_2\text{O})_4(\text{benzim})_2](4\text{-nba})_2 \ (0.659 \text{ g})\) was heated in the temperature controlled oven at 114 °C for about 15 min resulting in the formation of a yellow coloured compound. The sample was then cooled in a desiccator and weighed. The resultant weight of the sample was 0.595 g. The observed mass loss of 9.71 % is in good agreement with the expected value (10.36 %) for the loss of four moles of water.

2.3.14. Preparation of \([\operatorname{Co}(\text{H}_2\text{O})_2(\text{Im})_2(4\text{-nba})_2]\) 26 [79]

Method I: Sodium salt of 4-nbaH obtained from the reaction between NaHCO\(_3\) (1.68 g, 20 mmol) and 4-nbaH (3.34 g, 20 mmol) in water (60 ml) was reacted with CoCl\(_2\cdot 6\text{H}_2\text{O} \ (2.38 \text{ g, } 10 \text{ mmol})\) in water (10 ml). To the resultant red coloured solution, Im (1.36 ml, 20 mmol) was added with continuous stirring. The reaction mixture thus obtained was filtered and kept for crystallization. After few weeks crystals slowly separated, which were filtered, washed with water (5 mL) and air dried. Yield: 4.77 g (85 %).
Method II: CoCO₃ is generated in situ by reaction between CoCl₂ .6H₂O (1.19 g, 5 mmol), and Na₂CO₃ (0.53 g, 5 mmol) in water (40 ml). To this solution 4-nbaH (1.67 g, 10 mmol) was added. The reaction mixture was stirred for 20 min to obtain clear solution at room temperature or below 50 °C. The resulting clear solution was filtered and to the filtrate imidazole (0.68 g, 10 mmol) in water (10 ml) was added with constant stirring. The resultant coloured solution was filtered and kept for crystallization. The crystals was separated within a day was filtered, washed with cold water then with ether and air dried. Yield: 1.737 (61 %)

2.3.15. Preparation of anhydrous [Co(Im)₂(4-nba)₂] 26a

A powdered sample of [Co(H₂O)₂(Im)₂(4-nba)₂] (0.550 g) was heated in the temperature controlled oven at 128 °C for about 20 min. The sample was then cooled in a desiccator and weighed. The resultant weight of the sample was 0.496 g. The observed mass loss of 6.41 % is in good agreement with the expected value (6.4 %) for the loss of two moles of water. The infrared spectrum of the heat treated sample clearly indicates the anhydrous nature of the compound. The X-ray powder pattern of the compound was quite different from the pristine complex, indicating the formation of a new compound.

2.3.16. Preparation of [Co(N-MeIm)₂(4-nba)₂] 27 and [Co(2-MeIm)₂(4-nba)₂] 28

Sodium salt of carboxylic acid obtained from the reaction between NaHCO₃ (0.168 g, 2mmol) and 4-nbaH (0.334 g, 2 mmol) in water (50 ml) was reacted with CoCl₂.6H₂O (0.238 g, ≈ 1 mmol) in water (10 ml). To the resultant red coloured solution, N-MeIm (0.16 ml, ≈ 2 mmol) was added with continuous stirring. Initially blue coloured solution formed is turns to purple on stirring for 10 min. The purple coloured solution thus obtained was kept for crystallization. After few weeks big crystals obtained was filtered, washed with water (5 ml) and air dried. The complex was insoluble in water, slightly soluble in DMSO and insoluble in methanol, and CH₃OH. Yield: 0.461 g (83 %). The use of 2-MeIm (0.164 g, 2 mmol) instead of N-MeIm in the above reaction resulted in 28 in 86% yield. The complex was partially soluble in DMSO, CH₃CN, methanol.
2.3.17 Preparation of $[\text{Co(phen)}_2(\text{HCO}_3)(4\text{-nba})]4.5\text{H}_2\text{O}$ 29

**Method I:** The solution of $\text{Na}_2\text{CO}_3$ (0.53 g, 5 mmol) in 5 ml water was added to $\text{CoCl}_2\cdot6\text{H}_2\text{O}$ (1.19 g, 5 mmol). $\text{CoCO}_3$ generated in situ from above reaction was treated with 4-nbaH (1.67 g, 10 mmol) in 70 ml water. The solution was stirred for an half an hour to obtain clear solution at room temperature. The resultant clear solution with small quantity of precipitate was filtered. In to this 20 ml of the methanolic solution of 1, 10 phenanthroline (1.98 g, 10 mmol) was added. The brownish red solution was stirred for 15 min and filtered and kept for crystallization. The reddish big blocks obtained after a few weeks were filtered, washed with little cold water and dried in air. The compound was soluble in water, CH$_3$CN, DMSO and freely soluble in methanol. Yield: 38%

Anal. Found (Calcd) for C$_{32}$H$_{30}$CoN$_5$O$_{11.50}$ 29 (726.94): Co 8.7 (8.08), 4-nbaH 21.1 (22.94), C 52.547 (52.82), H 3.927 (4.17), N 9.44 (9.63)

2.3.18. Preparation of $[\text{Ni(H}_2\text{O})_2(\text{Im})_2(4\text{-nba})_2]$ 30 [84]

**Method I:** The solution of $\text{Na}_2\text{CO}_3$ (0.53 g, 5 mmol) in water (5 ml) was added to $\text{NiCl}_2\cdot6\text{H}_2\text{O}$ (1.19 g, 5 mmol). $\text{NiCO}_3$ generated in situ from above reaction was treated with 4-nbaH (1.67 g, 10 mmol) in water ($\approx$ 90 ml) and refluxed in heating mantle to obtain clear solution for 1 h. The green coloured solution obtained was filtered into imidazole (0.68 g, 10 mmol) in 5 ml water. Bluish green solution obtained was kept for crystallization. After a day bluish green crystalline product was filtered and washed with water and then with ether and dried in air. Yield: 2.548 g (90.45 %)

Anal. Found (Calcd) for NiC$_{20}$H$_{20}$N$_6$O$_{10}$ 30 (563.13): Ni 10.76 (10.4), 4-nbaH 58.88 (58.99), C 43.00 (42.62), H 3.40 (3.58), N 14.36 (14.91)

**Method II:** Sodium salt of 4-nbaH generated in situ from the reaction between 4-nbaH (1.67 g, 10 mmol) and $\text{NaHCO}_3$ (0.84 g, 10 mmol) in water (30 ml) and added to $\text{NiCl}_2\cdot6\text{H}_2\text{O}$ (1.19 g, 5 mmol) solution in 20 ml water. The resultant green solution,
imidazole (0.68 g, 10 mmol) in 5 ml water was added with constant stirring. The resultant bluish green solution was kept for crystallization. After a day bluish green crystals obtained were isolated as that of the method I and analyzed satisfactorily. Yield: 2.08 g (74 %)

**Method III:** A solution of NaOH (0.4 g, 10 mmol) in water (5 ml) was added to NiCl₂₆H₂O (1.19 g, 5 mmol) in water (5 ml). Ni(OH)₂ generated in situ is reacted with 4-nbaH (1.67 g, 10 mmol) in aqueous ammonia (125 ml). The solution was stirred for 30 min. The blue solution thus obtained (pH ≈ 12) was filtered into aqueous solution of imidazole (0.681 g, 10 mmol) and the resultant blue solution heated on water bath to expel excess of ammonia and then kept for crystallization. The bluish green crystals obtained after a week were filtered, washed with water followed by ether and air dried. Yield: 1.31 g (47 %)

2.3.19. Preparation of anhydrous [Ni(Im)₂(4-nba)₂] 30a

A powdered sample of [Ni(H₂O)₂(Im)₂](4-nba)₂ (0.550 g) was heated in the temperature controlled oven at 200 °C for about 20 min. The sample was then cooled in a desiccator and weighed. The resultant weight of the sample was 0.496 g. The observed mass loss of 6.27 % is in good agreement with the expected value (6.4 %) for the loss of two moles of water.

2.3.20. Preparation of [Ni(Im)₆]4-nba₂·2H₂O 31

**Method I:** 1.19 g of NiCl₂₆H₂O solution in water (60 ml) was added to in situ generated sodium salt of 4-nitrobenzoate obtained from the reaction of 4-nbaH (1.67 g, 10 mmol) and NaHCO₃ (0.84 g, 10 mmol) in 40 ml of water. To this clear solution imidazole (2.042 g, 30 mmol) was added in 30 ml of water. The clear blue coloured crystals separated. These were filtered and kept for crystallization. After 3-4 days blue colour solution obtained was filtered, washed with water and air dried. Yield: 3.35 (80 %)

Anal. Found (Calcd) for C₃₂H₃₄NiN₁₄O₁₀ 31 (837.43): Ni 7.46 (7.03), 4-nbaH 40.4 (39.76), C 45.70 (45.85), H 4.30 (4.1), N 23.59 (23.40)

**Method II:** A solution of Na₂CO₃ (0.265 g, 2.5 mmol) in 5 ml water was added to NiCl₂ .6H₂O (0.595 g, 2.5 mmol). NiCO₃ thus generated in situ from above reaction was treated with 4-nbaH (0.835 g, 5 mmol) in 50 ml water. The solution was heated
was filtered and to the filtrate a solution of imidazole (1.02 g, 15 mmol) was added. The blue solution was stirred and filtered and kept for crystallization. Blue crystals were obtained after 3-5 days. These were filtered washed with water and air dried. Yield 0.937 g (67 %)

**Method III:** A solution of NaOH (0.4 g, 10 mmol) in water (5 ml) was added to NiCl₂·6H₂O (1.19 g, 5 mmol) in water (5 ml). Ni(OH)₂ generated *in situ* is reacted with 4-nbaH (1.67 g, 10 mmol) in aqueous ammonia (125 ml). The solution was stirred for 30 min. The blue solution thus obtained (pH ≈ 12) was filtered into aqueous solution of imidazole (2.042 g, 10 mmol) and the resultant blue solution heated on water bath to expel excess of ammonia and then kept for crystallization. The blue crystals obtained after 2-3 days were filtered, washed with water and air dried. Yield: 1.40 g (66 %)

**Method IV:** A solution of imidazole (0.4042 g, 6 mmol) was added to NiCl₂·6H₂O (0.238 g, 1 mmol) in 10 ml water. To the resultant blue solution sodium salt of 4-nba generated *in situ* from the reaction of 4-nbaH (0.334 g, 2 mmol) and NaHCO₃ (0.168 g, 2 mmol) was added. The resultant solution was filtered and kept for crystallization. After a day blue coloured crystals separated. These were isolated by similar procedure as above. Yield: 0.379 g (45 %)

2.3.20. **Preparation of [Ni(Im)₆]4-nba₂·31a**

A powdered sample of [Ni(Im)₆](4-nba)₂·2H₂O (0.315 g) was heated on a water bath for 30 min. The hot mass was cooled in a desiccator and weighed. The observed mass loss of 3.97 % is in good agreement with the expected value (4.3 %) for the loss of two moles of water.

2.3.21. **Preparation of [Ni(H₂O)₂(2-Melm)₂(4-nba)₂] 32**

**Method I:** Sodium salt of 4-nbaH generated *in situ* from reaction between 4-nbaH (0.334 g, 2 mmol) and NaHCO₃ (0.168 g, 2 mmol) in water (30 ml) was added to NiCl₂·6H₂O (0.238 g, 1 mmol) in water (10 ml). The addition of 2-Melm (0.164 g, 2 mmol) in water (3 ml) to the solution resulted in bountiful amount of light green precipitate, which was dissolved in minimum quantity of aqueous ammonia. The solution was filtered and kept for crystallization. After few days bluish green crystals obtained were filtered, washed with water, followed by ether and air dried. The
compound was partially soluble in water and CH$_3$CN and soluble in DMSO and, methanol. Yield: 0.272 (46 %)

Anal. Found (Calcd) for C$_{22}$H$_{24}$NiN$_6$O$_{10}$ (591.16): Ni 9.94 (9.92), 4-nbaH 55.92 (56.19), C 44.71 (44.69), H 4.26 (4.1), N 14.15 (14.21).

*Method II:* A solution of NaOH (0.08 g, 2 mmol) in water (5 ml) was added to NiCl$_2$·6H$_2$O (0.238 g, 1 mmol) in water (5 ml). Ni(OH)$_2$ generated in situ is reacted with 4-nbaH (0.334 g, 2 mmol) in aqueous ammonia (12 ml). The solution was stirred for 30 min. To the clear blue solution 2-MeIm (0.164 g, 2 mmol) was added. The resultant solution was heated on a water bath for few min to expel ammonia, and was filtered and left for crystallization. The bluish green product thus obtained after few days was filtered and washed with water followed by ether and air dried. Yield: 0.4211 g (71 %)

2.3.22. Preparation of [Ni(H$_2$O)(N-MeIm)$_2$(4-nba)$_2$]

Ni(4-nba)$_2$·6H$_2$O generated in situ from the reaction between NiCl$_2$·6H$_2$O (0.238 g, 1 mmol) in water with sodium salt of 4-nba generated in situ from reaction between 4-nbaH (0.334 g, 2 mmol) and NaHCO$_3$ (0.168 g, 2 mmol) in water (30 ml). To this solution, N-MeIm (0.164 g, 2 mmol) was added. The clear solution thus obtained was filtered and left for crystallization after few weeks green crystals obtained were filtered and washed with cold water and air dried. Yield: 0.404 g (70 %).

Anal. Found (Calcd) for NiC$_{22}$H$_{22}$N$_6$O$_9$ (573.16): Ni 10.18 (10.23), 4-nbaH 56.44 (57.88), C 47.27 (46.06), H 3.64 (3.88), N 13.93 (14.60)

*Method II:* A solution of NaOH (0.08 g, 2 mmol) in water (5 ml) was added to NiCl$_2$·6H$_2$O (0.238 g, 1 mmol) in water (5 ml). Ni(OH)$_2$ generated in situ is reacted with 4-nbaH (0.334 g, 2 mmol) in aqueous ammonia (12 ml). The solution was stirred for 30 min. To the clear blue solution N-MeIm (0.16 ml, 2 mmol) was added. The resultant solution was heated on a water bath to expel ammonia, filtered and left for crystallization. The green product thus obtained after few days were filtered and washed with ammoniacal solution followed by ether and air dried. Yield: 0.408 g (71 %)
2.3.23. Preparation of $[\text{Cd}(\text{H}_2\text{O})_2(\text{Im})_2(4\text{-nba})_2]$ \[34\]

**Method I:** CdCl$_2$·H$_2$O (1.066 g, 5 mmol) was taken in water (5 ml). Into this, an aqueous solution of sodium 4-nitrobenzoate generated *in situ* from 4-nbaH (1.67 g, 10 mmol), NaHCO$_3$ (0.84 g 10 mmol) in water (60 ml) was added. This resulted in the formation of a clear solution, which was filtered into an aqueous solution of imidazole (1.36 g, 10 mmol) in water (10 ml). The colourless solution was kept aside for crystallization. The crystals that separated after 4-5 days were filtered, washed with little ice-cold water (~2 ml), followed by ether and dried in air. Yield: 2.568g (83 %)

*Anal. Found (Calcd) for C$_{20}$H$_{20}$CdN$_6$O$_{10}$ \[34\] (616.48): Cd 18.22(18.23), 4-nbaH 52.38(53.8), C 38.65 (38.92), H 3.10 (3.27), N 13.62 (13.62)*

**Method II:** To a solution of CdCl$_2$·H$_2$O (0.503 g, 2.5 mmol) in water (20 ml), Na$_2$CO$_3$ (0.265 g, 2.5 mmol) in water (5 ml) was added. The CdCO$_3$ generated *in situ* was treated with 4-nbaH (0.835 g, 5 mmol) and reflux in the heating mantle for 30 min to obtain a clear solution. The volume of the resultant solution was maintained around 60 ml and filtered directly into an aqueous imidazole solution (0.3404 g, 5mmol). The crystals obtained immediately were filtered, washed with ether and dried in air. Yield: 1.37 g (89 %)

2.3.24. Preparation of $[\text{Cd}(\text{Im})_2(4\text{-nba})_2]$ \[34a\]

The powdered sample of $[\text{Cd}(\text{H}_2\text{O})_2(\text{Im})_2(4\text{-nba})_2]$ (0.464 g) was heated on a water bath for 15 min to obtain the anhydrous complex $[\text{Cd}(\text{Im})_2(4\text{-nba})_2]$ (0.437 g) in quantitative yield. The observed mass loss of 5.87 % is in good agreement with the loss for two moles of water (5.82 %). The product obtained analyzed satisfactorily.