

Hydrothermal synthesis, characterisation and
properties of new *s*-block metal-organic frameworks

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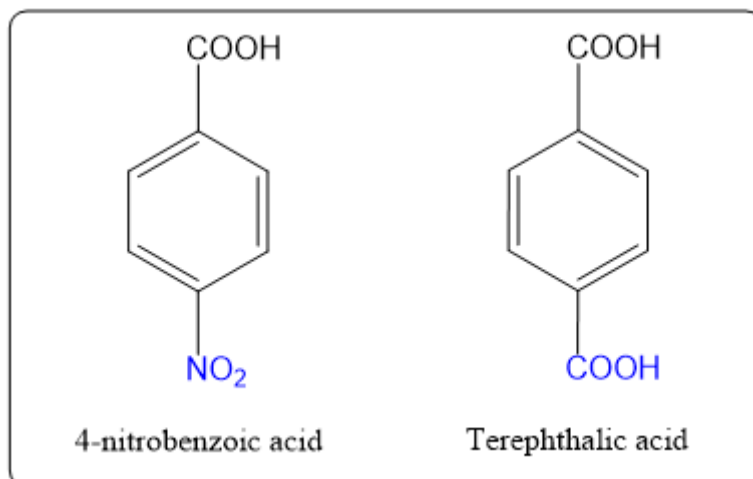
Final Report

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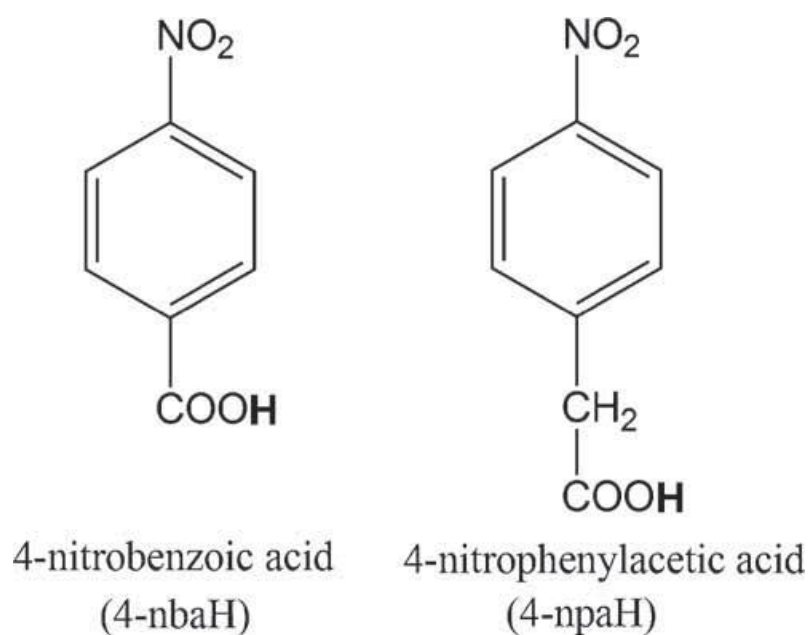
The chemistry of *s*-block (alkali and alkaline-earths) metals is a relatively less explored area of science unlike the *d*-block transition metals. The ready availability of *s*-block metal reagents, the aqueous solubility of *s*-block based materials, the diamagnetic nature of the closed shell *s*-block metal ions and the stereochemical flexibility of the heavier alkali as well as alkaline-earths (starting from Ca), are some reasons which attract the attention of several researchers including the Project Investigator (PI), who has a proven expertise in this area as he already developed the coordination chemistry of the *s*-block metals (especially the alkaline-earths) using nitrobenzoic acids as ligands. Hence, the main aim of the above titled project was to synthesize new *s*-block containing materials with a view to develop the chemistry of metal organic frameworks (MOF's) also known as coordination polymers (CPs), especially prepare new MOF's or CPs using multifunctional organic linkers and thus link the flexible alkali and alkaline earth metal ions (*s*-block) into framework materials exploiting their well-known structural flexibility. Coordination polymers (CP's) are inorganic structures containing metal centers linked by bridging ligands, extending in 1- (1-D), 2- (2-D) or 3-Dimensions (3-D). Metal-Organic Frameworks (MOF's) are crystalline compounds consisting of metal ions (clusters) coordinated to rigid organic molecules to form 2-D, or 3-D structures.

The key element for the construction of a CP or MOF which exhibit extended structure, is a bridging ligand and one of the first employed ligand for this purpose to prepare MOF-5 was terephthalic acid in which both -COOH groups are disposed *trans* to each other in a six membered ring. Since the -NO₂ group is isoelectronic with -COOH (Scheme 1) we have chosen 4-nitrobenzoic acid (4-nbaH) in which the -NO₂ group occupies the para position with respect to -COOH in the six membered ring. Unlike the -COOH group, the nitro group which is not known to involve in metal binding, but can participate in secondary interactions for example it can make H-acceptor bonds via the nitro O atom.



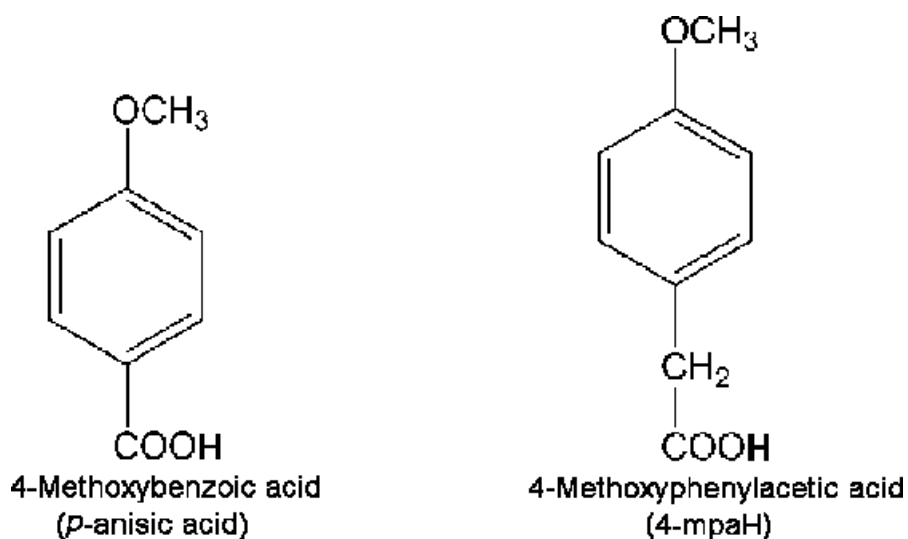
Scheme 1 - The isoelectronic 4-nitrobenzoic acid (4-nbaH) and terephthalic acid

In addition to using 4-nbaH as an organic linker to prepare the 4-nitrobenzoates (4-nba) of bivalent metals, we also used 4-nitrophenylacetic acid (Scheme 2) in some syntheses, which can be considered as a flexible linker since the -COOH group is not attached to the six membered but is attached to the -CH₂ (benzylic carbon).



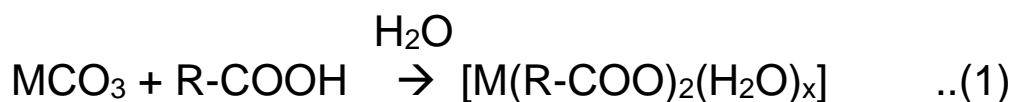
Scheme 2 Rigid versus flexible -COOH group in 4-nbaH and 4-npaH.
 (Srinivasan et al *J. Chem. Sciences* **128** (2016) 1765-1774.)

Similarly, we have also employed the rigid 4-methoxybenzoic acid (*p*-anisic acid) and the flexible 4-methoxyphenylacetic acid as organic linkers in some experiments (Scheme 3).



Scheme 3. Rigid versus flexible –COOH group in *p*-anisic acid and 4-mpaH

For compound synthesis we employed a well-known acid-base reaction (see equation 1) wherein the carboxylic acid (R-COOH which can be any of the acids in Scheme 1 to 3) and metal carbonate (MCO₃ where M=Mg, Ca, Sr or Ba) were reacted in an aqueous solution. The solubilization of the insoluble carbonate could be evidenced by the brisk effervescence. The use of freshly precipitated metal carbonates (instead of commercial carbonate sample) by reaction of bivalent metal chloride with sodium carbonate, resulted in less reaction times.



The chemistry of the alkaline-earth metals with 4-nitrophenylacetic acid (4-npaH) has been investigated by following the synthetic protocol as per equation 1, which resulted in the structural characterization of two new 1-D coordination polymers each of Ca and Sr (see Figures 1-3) and a monomeric Mg compound. In both cases the extended structure is due to a μ_2 -bridging tridentate binding mode of the 4-nitrophenylacetate ligand. These results were published in Journal of Chemical Sciences.

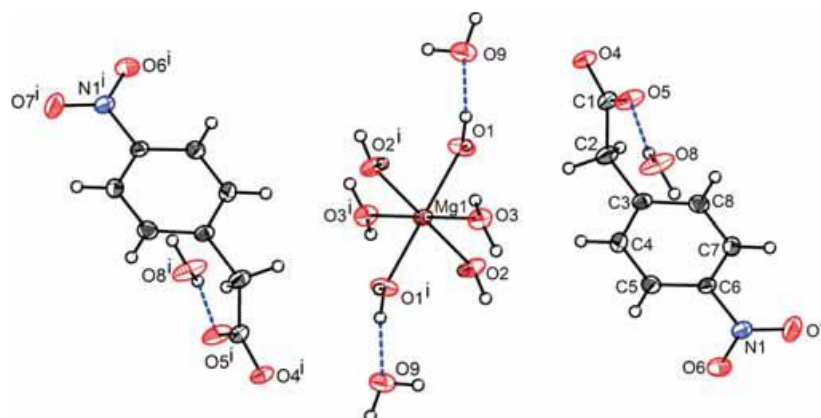


Fig 1. The crystal structure of $[\text{Mg}(\text{H}_2\text{O})_6](4\text{-npa})_2 \cdot 4\text{H}_2\text{O}$ (4-npa = 4-nitrophenylacetate) showing atom labelling scheme and coordination sphere of Mg(II). Symmetry code i) $-x, -y-1, -z+1$ (Reproduced from Srinivasan et al *J. Chem. Sciences* **128** (2016) 1765-1774.)

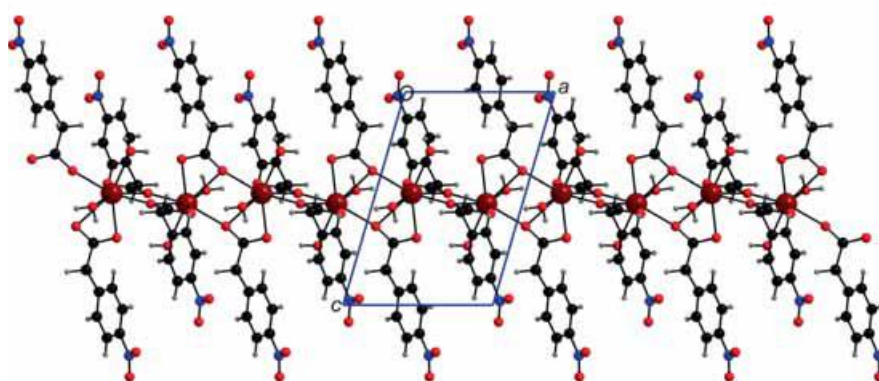
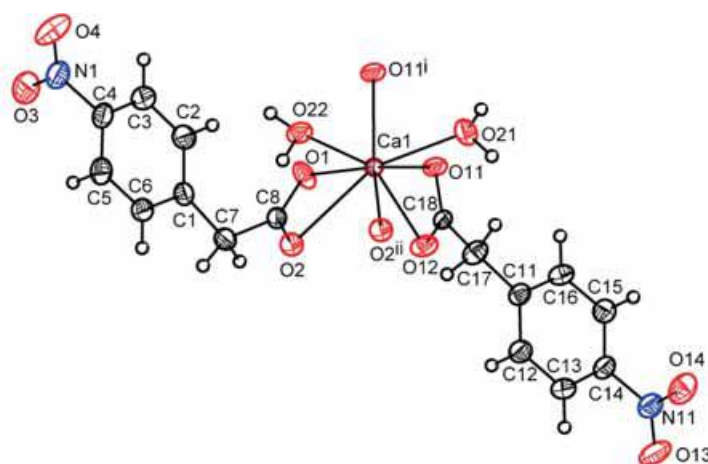


Figure 2. The crystal structure of $[\text{Ca}(\text{H}_2\text{O})_2(4\text{-npa})_2]$ showing the atom labelling scheme and the eight coordination around Ca(II). Displacement ellipsoids are drawn at the 50% probability level for all non hydrogen atoms. Symmetry code: i) $-x+1, y+1, -z+1$; ii) $-x+2, y+1, -z+1$ (**top**); A portion of the 1-D chain along a-axis due to the μ_2 -bridging tridentate coordination modes of the unique ligands (**bottom**). (Srinivasan et al *J. Chem. Sciences* **128** (2016) 1765-1774.)

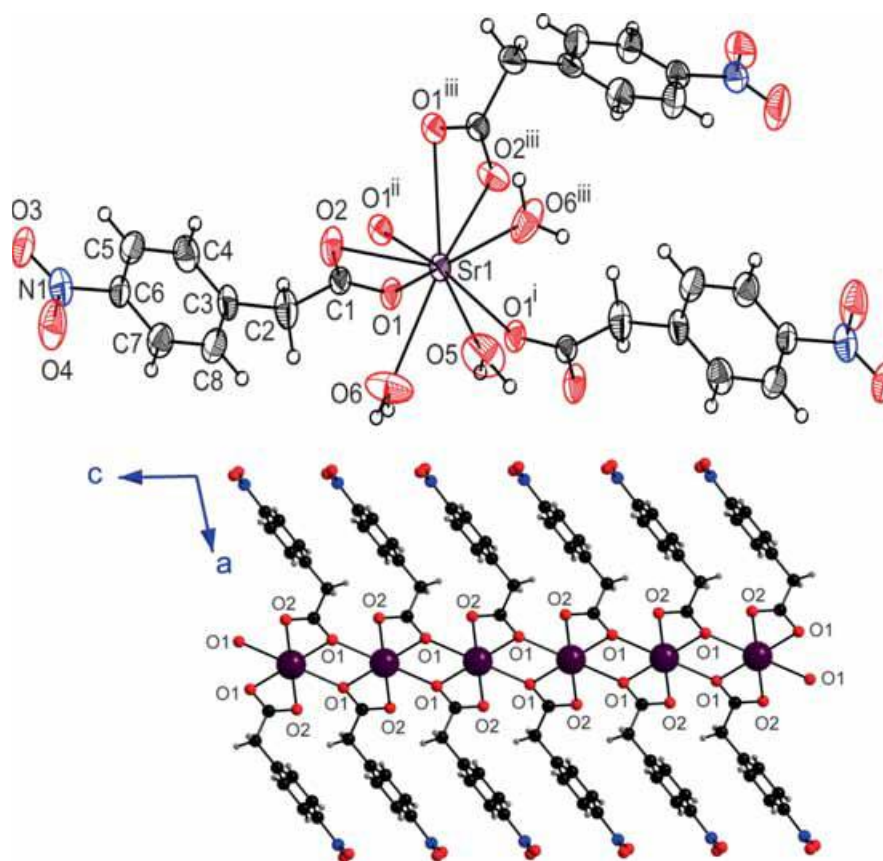


Figure 3. The crystal structure of $[\text{Sr}(\text{H}_2\text{O})_3(4\text{-npa})_2] \cdot 4.5\text{H}_2\text{O}$ showing the atom labelling scheme and the coordination around Sr(II). Displacement ellipsoids are drawn at 50% probability level for all non hydrogen atoms. For clarity the lattice water molecules are not shown. Symmetry code: i) $-x+1, -y, -z$; ii) $x, -y, z+1/2$; iii) $-x+1, y, -z+1/2$ (**top**); A portion of the 1-D coordination polymer extending along c axis due to the μ_2 -bridging tridentate coordination of the unique 4-npa ligand. For clarity the three coordinated water molecules are not displayed (**bottom**). (Srinivasan et al *J. Chem. Sciences* **128** (2016) 1765-1774.)

In addition to the structures of the 4-npa compounds of Mg, Ca and Sr given above, the spectral and thermal properties were also studied and reported. In this study of alkaline-earth metal salts of 4-npaH, a Ba compound of composition $[\text{Ba}(4\text{-npa})_2(\text{H}_2\text{O})]$ was also synthesized but could not be structurally characterized.

The reactions of metal carbonate with p-anisic acid and 4-npaH afforded interesting results namely a tetraaquaMg(II) compound of Mg(II) with 4-npaH (Fig 4) and a two-dimensional coordination polymer of Ca with p-anisic acid (Fig 5 and 6).

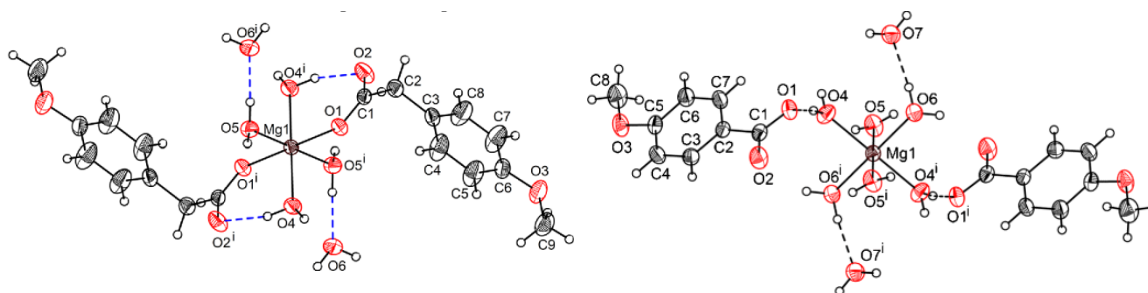


Fig 4. Crystal structure of $[\text{Mg}(\text{H}_2\text{O})_4(4\text{-mpa})_2] \cdot 2\text{H}_2\text{O}$ showing the mpa bound to Mg(II) (**left**) (Dhavskar & Srinivasan *Indian J Chem* **55A** (2016) 170-176). The structure of $[\text{Mg}(\text{H}_2\text{O})_6](\text{p-anisate})_2 \cdot 2\text{H}_2\text{O}$ showing the coordination sphere of Mg(II) with the p-anisate functioning as anion (**right**).

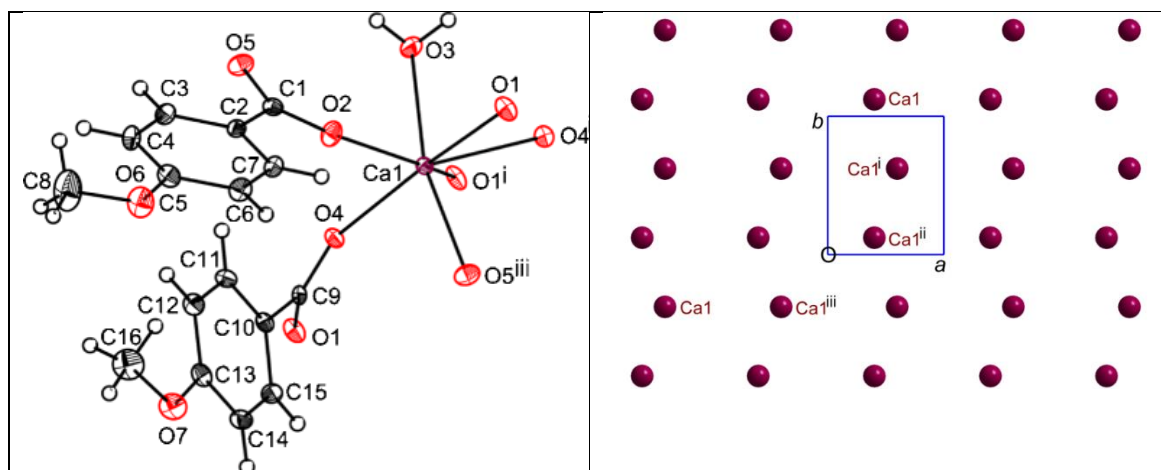


Fig. 5 The crystal structure of $[\text{Ca}(\text{H}_2\text{O})(\text{p-anisate})_2]$ showing the the coordination sphere of Ca(II) (**left**). The layer of Ca(II) ions in $[\text{Ca}(\text{H}_2\text{O})(\text{p-anisate})_2]$ (**right**) (Dhavskar, Bhargao & Srinivasan *J. Chem. Sciences* **128** (2016) 421-428.)

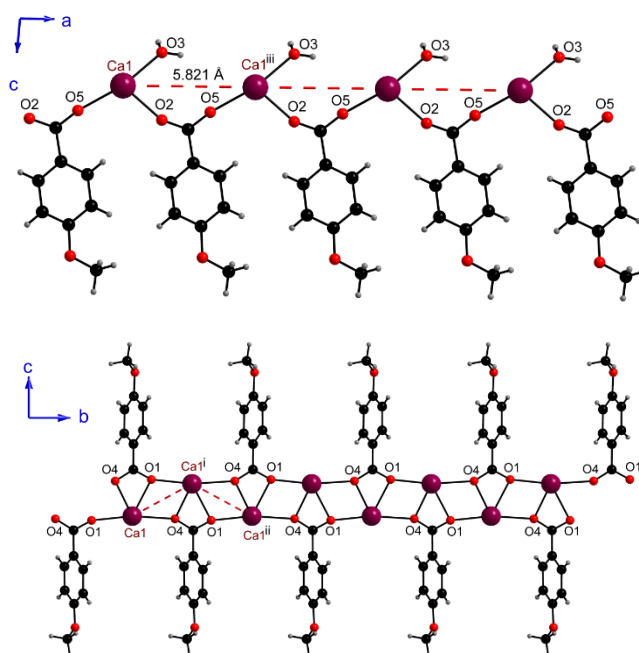


Fig 6. A portion of an infinite chain extending along a-axis due to the first unique p-anisate (O2, O5); For clarity the p-anisates (O1, O4) around each Ca(II) are not shown (**top**). A view of an infinite double chain along b-axis due to the second unique p-anisate (O1, O4). For clarity, the monodentate water ligand and the p-anisates (O2, O5) on each Ca(II) are not shown (**bottom**). (Dhavskar, Bhargao & Srinivasan *J. Chem. Sciences* **128** (2016) 421-428.)

The aqueous reaction of alkaline-earth metal carbonate with 4-nbaH (4-nitrobenzoic acid) has been well investigated by our group and we reported the formation of a 1D coordination polymer only in the case of Ba namely $[\text{Ba}(\text{H}_2\text{O})_5(4\text{-nba})](4\text{-nba})$ while monomeric compounds viz. $[\text{Mg}(\text{H}_2\text{O})_6](4\text{-nba})_2 \cdot 2\text{H}_2\text{O}$, $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ and the water-rich $[\text{Sr}(\text{H}_2\text{O})_7(4\text{-nba})](4\text{-nba}) \cdot 2\text{H}_2\text{O}$. We have also reported that the monomeric tetraaqua Ca(II) compound can be converted to a polymer by dehydration followed by reaction with neutral N-donor ligands. In view of the oxophilic nature of the alkaline-earths, we investigated these reactions with readily available neutral O-donor amide ligands.

A continuation of the chemistry of the 4-nitrobenzoates (4-nba) of Ca(II) resulted in the structural characterization of two new 1-D coordination polymers containing terminal amide ligands. The 1-D structure of both these compounds is due to a μ_2 -bridging bidentate binding mode of the 4-nba ligand (Fig. 7). These results have been published in Indian J Chemistry Section A. A comparative study (Table 1) of several 4-nitrobenzoates of Ca(II) reveals a rich and variable coordination chemistry of Ca(II).

Table 1 Structure features of 4-nitrobenzoates of Ca(II)

No	Compound	Space group	Ca:H ₂ O [@]	C.N (*)	C.S	binding mode of unique 4-nba ligand	D
1	$[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ 1a	<i>P2₁/c</i>	1:4	7 (2)	{CaO ₇ }	η^1, η^2	0
2	$[\text{Ca}(\text{H}_2\text{O})_6(4\text{-nba})](4\text{-nba})(2\text{-ap}) \cdot \text{H}_2\text{O}$	<i>P$\bar{1}$</i>	1:6	7 (1)	{CaO ₇ }	η^1 , anion	0
3	$[\text{Ca}(\text{H}_2\text{O})_3(\text{Im})(4\text{-nba})_2] \cdot \text{Im}$	<i>P2₁/c</i>	1:3	6 (2)	{CaO ₅ N}	η^1, η^1	0
4	$[\text{Ca}(\text{NMF})_2(4\text{-nba})_2]$ 1	<i>P$\bar{1}$</i>	1:0	6 (4)	{CaO ₆ }	$\mu_2\text{-}\eta^1\text{:}\eta^1$ #	1
5	$[\text{Ca}(\text{BA})_2(4\text{-nba})_2]$ 2	<i>C2/c</i>	1:0	6 (4)	{CaO ₆ }	$\mu_2\text{-}\eta^1\text{:}\eta^1$ #	1
6	$[\text{Ca}(\text{pyr})_2(4\text{-nba})_2]$	<i>P$\bar{1}$</i>	1:0	6 (4)	{CaO ₄ N ₂ }	$\mu_2\text{-}\eta^1\text{:}\eta^1$ #	1
7	$[\text{Ca}(\text{L}^1)(4\text{-nba})_2]$	<i>P$\bar{1}$</i>	1:0	6 (5)	{CaO ₅ N}	$\mu_2\text{-}\eta^1\text{:}\eta^1, \mu_3\text{-}\eta^2\text{:}\eta^1$	1 ^{\$}
8	$[\text{Ca}(\text{H}_2\text{O})(\text{L}^2)(4\text{-nba})_2]$	<i>P2₁/n</i>	1:1	7 (4)	{CaO ₆ N}	$\mu_2\text{-}\eta^1\text{:}\eta^1, \mu_2\text{-}\eta^2$	1
9	$[\text{Ca}(\text{H}_2\text{O})_2(4\text{-nba})_2] \cdot 2 \text{ dmp}$	<i>P$\bar{1}$</i>	1:2	8 (4)	{CaO ₈ }	$\mu_2\text{-}\eta^2\text{:}\eta^1, \mu_2\text{-}\eta^2\text{:}\eta^1$	1
10	$[\text{Ca}(4\text{-nba})_2]$	--	1:0	--	--	--	--
11	$[\text{Ca}(\text{Im})(4\text{-nba})_2]$	--	1:0	--	--	--	--
12	$[\text{Ca}(\text{H}_2\text{O})(4\text{-nba})_2]$	--	1:1	--	--	--	--

Abbreviations: [@] - Number of coordinated water; C.N (*) = Coordination No. The number in parentheses is the number of carboxylates linked to each Ca; C.S= coordination sphere; D = Dimensionality; 4-nba = 4-nitrobenzoate; 2-ap = 2-aminopyridine; Im = imidazole; NMF = N-methylformamide; BA = benzamide; L¹ = N-methylimidazole; L² = 2-methylimidazole; pyr = pyrazole; dmp = 3,5-dimethylpyrazole; #an unique 4-nba ligand; ^{\$}1-D ladder.

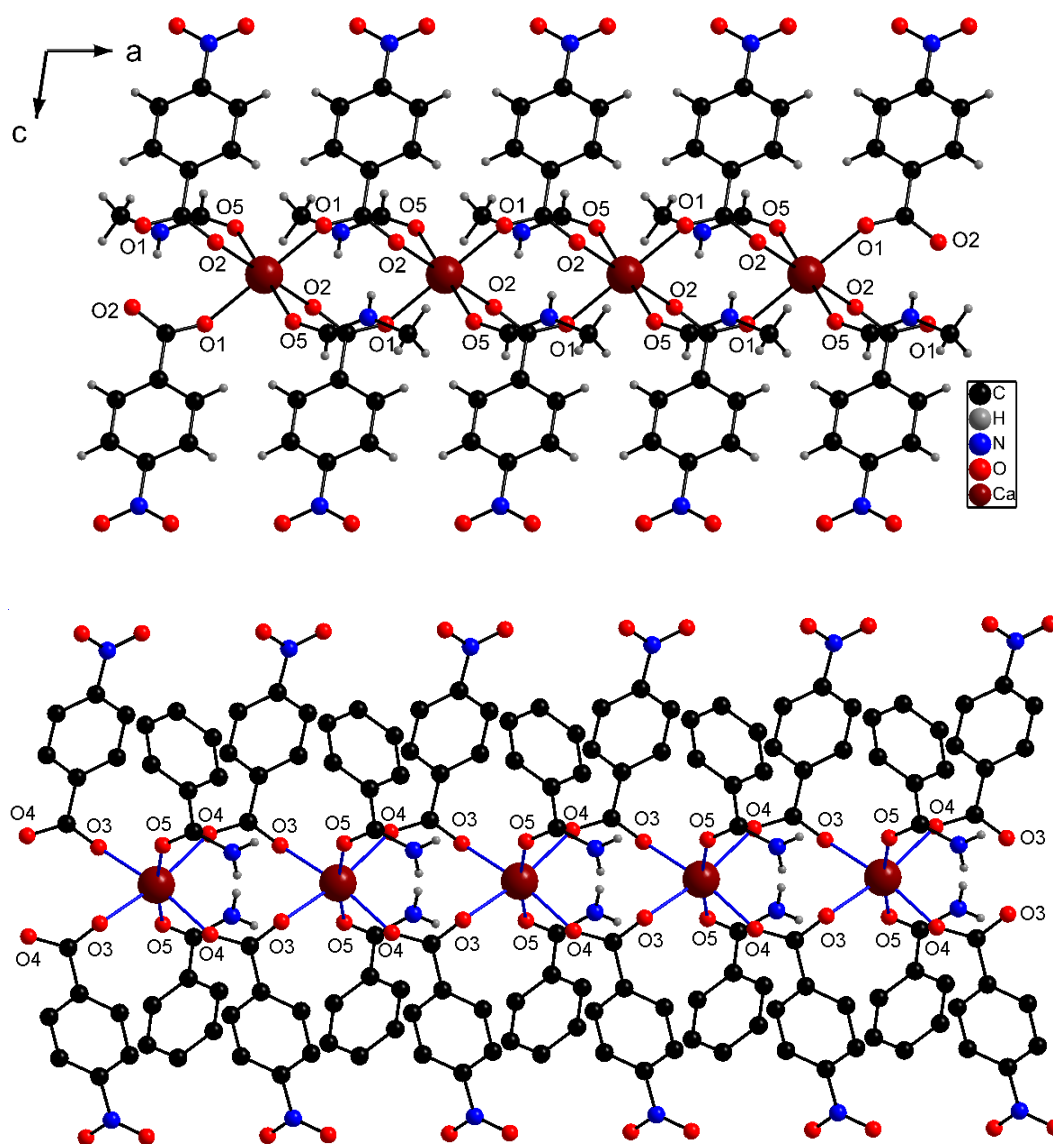


Fig. 7 – The μ_2 - η^1 : η^1 bridging binding mode of the 4-nba ligand (O1, O2) links the Ca(II) ions into a 1-D chain extending along *a* axis. O5 is the binding site for the terminal NMF ligand in $[\text{Ca}(\text{NMF})_2(4\text{-nba})_2]$ (4-nba = 4-nitrobenzoate; NMF=N-methylformamide) (**top**) The μ_2 - η^1 : η^1 bridging binding mode of the 4-nba ligand (O3, O4) links the Ca(II) ions into a 1-D chain extending along *a* axis. O5 is from the terminal benzamide (BA) ligand in $[\text{Ca}(\text{BA})_2(4\text{-nba})_2]$. For clarity H atoms of the aromatic rings are not shown (**bottom**). (Taken from Srinivasan & Dhavskar, *Indian J Chem.* **56A** (2017) 387-393).

Extending this study by reaction of the water-rich $[\text{Sr}(\text{H}_2\text{O})_7(4\text{-nba})](4\text{-nba})\cdot 2\text{H}_2\text{O}$ with amides afforded three new strontium coordination polymers. In this case 4-nba functions as a μ_3 -tetradentate bridging ligand. Three Sr(II) compounds based on this binding mode of 4-nba were structurally characterized. A representative structure is shown in Fig. 8.

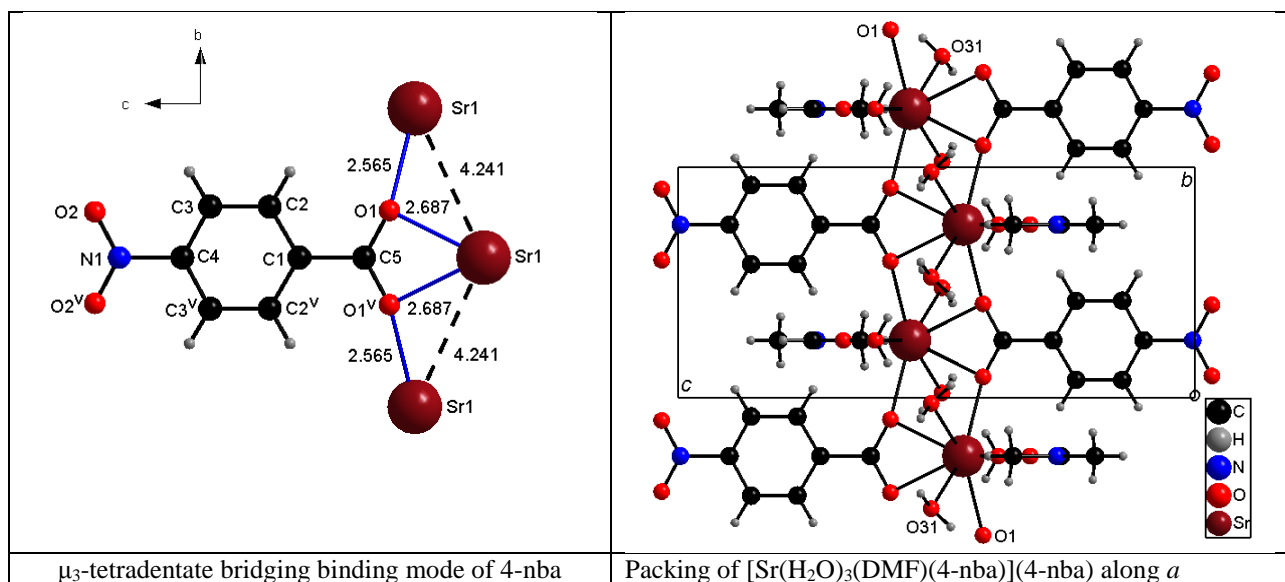
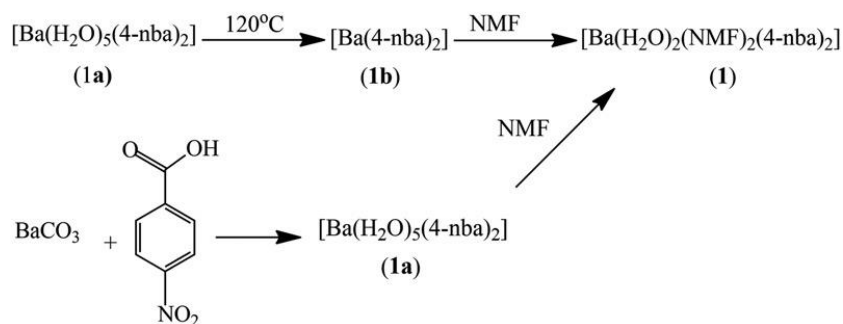


Fig. 8 A one dimensional Sr(II) coordination polymer based on a μ_3 -tetradentate bridging 4-nba.

A further extension of amide incorporation *viz.* reaction of $[\text{Ba}(\text{H}_2\text{O})_5(4\text{-nba})](4\text{-nba})$ **1a** with NMF (N-methylformamide) (Scheme 4) afforded $[\text{Ba}(\text{H}_2\text{O})_2(\text{NMF})_2(4\text{-nba})_2]$, which is a new Ba coordination polymer, exhibiting a characteristic IR spectrum (Fig. 9)



Scheme 4: Synthesis of $[\text{Ba}(\text{H}_2\text{O})_2(\text{NMF})_2(4\text{-nba})_2]$ (Bhargao & Srinivasan, *J Coord Chem* **72** (2019) 2599-2615)

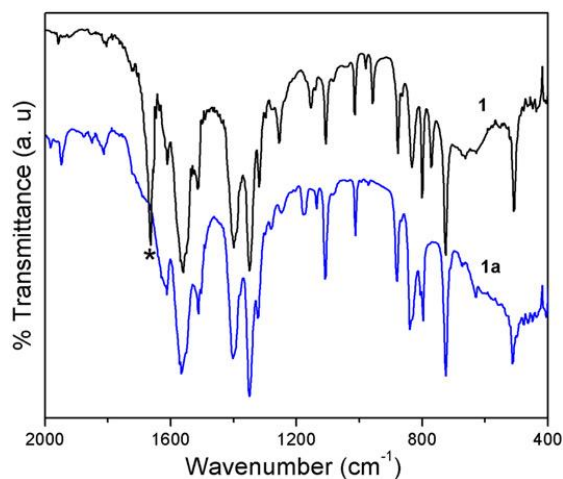


Fig. 9 Infrared spectra of **1** & **1a**. *Signal of amide carbonyl (Bhargao & Srinivasan, *J Coord Chem* **72** (2019) 2599-2615)

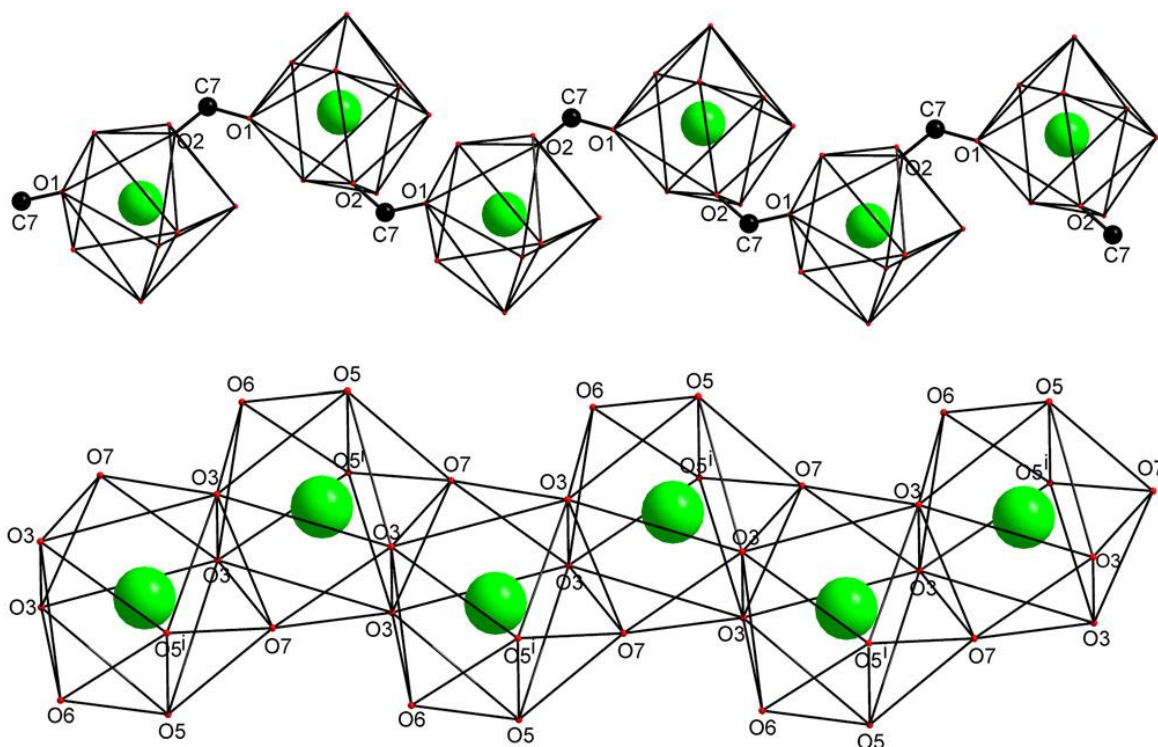


Fig. 10 A portion of the 1-D chain showing discrete versus face sharing $\{BaO_9\}$ polyhedra in $[Ba(H_2O)_5(4-nba)_2]$ **1a** (top) and $[Ba(H_2O)_2(NMF)_2(4-nba)_2]$ **1** (bottom). In **1a**, the O1 and O2 are attached to C7 of the symmetrical bridging 4-nba. In **1**, O5, O5ⁱ and O6 are the terminal ligands and the O3, O3 and O7 face is shared between adjacent Ba(II) ions in the chain. Symmetry code: (i) x, -y+1/2, z. (Bhargao & Srinivasan, *J Coord Chem* **72** (2019) 2599-2615)

Although both the precursor $[Ba(H_2O)_5(4-nba)](4-nba)$ **1a** and $[Ba(H_2O)_2(NMF)_2(4-nba)_2]$ **1** exhibit nine coordination namely $\{BaO_9\}$ coordination sphere, the unique 4-nba ligands in **1a** exhibit symmetric bridging and bidentate modes respectively while in the centrosymmetric **1**, the unique 4-nba ligand functions as a monoatomic bridge ($\mu_2-\eta^2$) and the unique NMF as a terminal ligand. In **1a** all the five aqua ligands are terminal while in **1** one water is a bridging ligand, the other being terminal. As a result, the $\{BaO_9\}$ polyhedra in **1** exhibit a face-sharing arrangement (Fig. 10), while the $\{BaO_9\}$ polyhedra in **1a** are discrete with the carboxylate carbon (C7) acting as a link between adjacent polyhedra in the chain. The extensive chemistry developed by our group in the area of alkaline-earth 4-nitrobenzoates before and during this project demonstrates the rich and variable coordination behaviour of the 4-nba ligand (Table 2). This project work has resulted in the structural characterization of monomeric as well as coordination polymeric compounds.

Table 2. Binding mode of 4-nba ligand in alkaline-earth metal 4-nitrobenzoates

Compound	S.G.	C.N. ^a	C.S	4-nba binding mode	D
[Ba(H ₂ O) ₅ (4-nba)](4-nba) 1a	<i>P2₁/c</i>	9 (3)	{BaO ₉ }	$\mu_2-\eta^1:\eta^1, \eta^2$	1
[Ba(H ₂ O) ₂ (NMF) ₂ (4-nba) ₂] ^b 1	<i>Pnma</i>	9 (4)	{BaO ₉ }	$\mu_2-\eta^2$	1
[Sr(H ₂ O) ₃ (DMF)(4-nba)](4-nba)	<i>P2₁/m</i>	8 (3)	{SrO ₈ }	$\mu_3-\eta^2:\eta^2, \text{anion}$	1
[Sr ₂ (H ₂ O) ₂ (NMF) ₃ (4-nba) ₄]	<i>C2/c</i>	8 (4)	{SrO ₈ }	$\mu_3-\eta^2:\eta^2, \eta^1$	1
[Sr(Pyr) ₂ (4-nba) ₂] ^b	<i>C2/c</i>	8 (4)	{SrN ₂ O ₆ }	$\mu_2-\eta^1:\eta^2$	1
[Ca(NMF) ₂ (4-nba) ₂] ^b	<i>P$\bar{1}$</i>	6 (4)	{CaO ₆ }	$\mu_2-\eta^1:\eta^1$	1
[Ca(BA) ₂ (4-nba) ₂] ^b	<i>C2/c</i>	6 (4)	{CaO ₆ }	$\mu_2-\eta^1:\eta^1$	1
[Ca(pyr) ₂ (4-nba) ₂] ^b	<i>P$\bar{1}$</i>	6 (4)	{CaO ₄ N ₂ }	$\mu_2-\eta^1:\eta^1$	1
[Ca(L ¹)(4-nba) ₂]	<i>P$\bar{1}$</i>	6 (5)	{CaO ₅ N}	$\mu_2-\eta^1:\eta^1, \mu_3-\eta^2:\eta^1$	1
[Ca(H ₂ O)(L ²)(4-nba) ₂]	<i>P2₁/n</i>	7 (4)	{CaO ₆ N}	$\mu_2-\eta^1:\eta^1, \mu_2-\eta^2$	1
[Ca(H ₂ O) ₂ (4-nba) ₂] \cdot 2dmp	<i>P$\bar{1}$</i>	8 (4)	{CaO ₈ }	$\mu_2-\eta^2:\eta^1, \mu_2-\eta^2:\eta^1$	1
[Ca(H ₂ O) ₂ (4-nba) ₂] \cdot (4,4'-bipyridine)	<i>P$\bar{1}$</i>	8 (4)	{CaO ₈ }	$\mu_2-\eta^2:\eta^1, \mu_2-\eta^2:\eta^1$	1
[Ca(H ₂ O) ₂ (4-nba) ₂] \cdot (1H-1,2,4-triazole)	<i>C2/c</i>	8 (4)	{CaO ₈ } ^c , {CaO ₈ }	$\mu_2-\eta^2:\eta^1, \mu_2-\eta^2:\eta^1$	1
[Mg(H ₂ O)(N-MeIm) ₂ (4-nba) ₂] ₂	<i>P$\bar{1}$</i>	6 (3)	{MgO ₄ N ₂ }	$\eta^1, \mu_2-\eta^1:\eta^1$	0 ^d
[Sr(H ₂ O) ₇ (4-nba)](4-nba) \cdot 2H ₂ O	<i>P2₁/c</i>	9 (1)	{SrO ₉ }	η^2, anion	0
[Ca(H ₂ O) ₄ (4-nba) ₂]	<i>P2₁/c</i>	7 (2)	{CaO ₇ }	η^1, η^2	0
[Ca(H ₂ O) ₆ (4-nba)](4-nba) \cdot (2-ap)H ₂ O	<i>P$\bar{1}$</i>	7 (1)	{CaO ₇ }	η^1, anion	0
[Ca(H ₂ O) ₃ (Im)(4-nba) ₂] \cdot Im	<i>P2₁/c</i>	6 (2)	{CaO ₅ N}	η^1, η^1	0
[(Ca(H ₂ O) ₄ (4-nba) ₂)(μ_2 -H ₂ O) ₂](4-nba) ₂ \cdot 8H ₂ O	<i>P2₁</i>	8 (1)	{CaO ₈ } ^c , {CaO ₈ }	η^2, anion , η^2, anion	0
[Mg(H ₂ O) ₂ (Im) ₂ (4-nba) ₂] ^b	<i>P$\bar{1}$</i>	6 (2)	{MgO ₄ N ₂ }	η^1	0
[Mg(CH ₃ OH) ₄ (4-nba) ₂] ^b	<i>P2₁/c</i>	6 (2)	{MgO ₆ }	η^1	0
[Mg(H ₂ O) ₆](4-nba) ₂ \cdot 2H ₂ O ^b	<i>P$\bar{1}$</i>	6 (0)	{MgO ₆ }	Anion	0
[Mg(H ₂ O) ₆](4-nba) ₂ (DMF) ₂ ^b	<i>P$\bar{1}$</i>	6 (0)	{MgO ₆ }	Anion	0
[Mg(H ₂ O) ₆](3-nba) ₂ (Acet) ₂	<i>P2₁/c</i>	6 (0)	{MgO ₆ }	Anion	0

Abbreviations used: S.G.= space group; C.N. =Coordination number ^aNumber in parentheses is the number of 4-nba linked to each unique M(II); C.S = Coordination sphere; D=Dimensionality; ^bunique 4-nba ligand; ^ctwo unique Ca(II); ^dmolecular solid (note- all OD compounds are molecular solids); NMF = N-methyl-formamide; DMF = Dimethylformamide; Pyr = Pyrazole; BA = benzamide; L¹ = N-methylimidazole; L² = 2-methylimidazole; dmp = 3,5-dimethylpyrazole; N-Me-Im = N-methylimidazole; 2-ap = 2-aminopyridine; Im = imidazole; aceta = acetamide

Results at a glance

- A rich structural chemistry of alkaline-earth 4-nitrobenzoate (Table 2) is unravelled
- Oxophilicity of the alkaline-earths can be evidenced from structure characterization
- Mg(II) compounds exhibit 6 coordination with a {MgO₆} coordination sphere
- The octahedral [Mg(H₂O)₆]⁺² ion is found in many Mg(II) compounds
- Ca, Sr, Ba are structurally flexible and exhibit a range of coordination numbers
- Ca, Sr, Ba normally bind to fewer water molecules unlike Mg(II)

Outcome

- The project assistant registered for her Ph.D, is awarded PhD degree resulting in human resource development
- 04 Publications in peer review Journals:
 1. K. T. Dhavskar, P. H. Bhargao, B. R. Srinivasan, Synthesis, crystal structure and properties of magnesium and calcium salts of *p*-anisic acid, *J. Chem. Sciences* **128** (2016) 421-428. <http://dx.doi.org/10.1007/s12039-016-1037-9>
 2. B. R. Srinivasan, K.T. Dhavskar, C. Näther, Syntheses, structures and properties of alkaline-earth metal salts of 4-nitrophenylacetic acid, *J Chem Sci* **128** (2016) 1765-1774. <http://dx.doi.org/10.1007/s12039-016-1182-1>
 3. B. R. Srinivasan, K.T. Dhavskar, On the syntheses and structures of two calcium coordination polymers containing terminal amide ligands, *Indian J Chem*, **56A** (2017) 387-393. <http://nopr.niscair.res.in/handle/123456789/41203>
 4. P. H. Bhargao, B. R. Srinivasan, Synthesis and structural characterization of a barium coordination polymer based on a μ_2 -monoatomic bridging 4-nitrobenzoate, *J Coord Chem*, **72** (2019) 2599-2615. <https://doi.org/10.1080/00958972.2019.1666980>