

Synthesis, characterization and properties of a water-rich calcium(II)-4-nitrobenzoate

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Solid state reaction of $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ (4-nba = 4-nitrobenzoate) with 2-aminopyridine (2-ap) at 100 °C results in the formation of an anhydrous compound, $[\text{Ca}(2\text{-ap})(4\text{-nba})_2]$, while in aqueous solution, the coordination sphere of Ca(II) in $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ reorganises in the presence of 2-ap resulting in the formation of a water-rich Ca(II) compound, $[\text{Ca}(\text{H}_2\text{O})_6(4\text{-nba})](4\text{-nba})(2\text{-ap})\cdot\text{H}_2\text{O}$. A comparative study of differently aquated 4-nitrobenzoates of Ca(II) is described.

Keywords: Coordination chemistry, Calcium, Nitrobenzoates, Aminopyridines, Water-rich compounds

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Non-toxic and water soluble nature, variable structural chemistry, affinity for O-donor ligands, relevance in biology are some factors responsible for the current interest in the chemistry of *s*-block elements¹. Of the *s*-block elements, calcium has received considerable attention in terms of development of its structural chemistry. The major structural features of interest are the interactions of calcium with O-donor ligands like water, carboxylate, carbonate, sulfate etc. The importance of the naturally occurring calcium carbonate, calcium sulfate and calcium phosphate is well documented² while the hydrates and carboxylates of Ca(II) are biologically relevant. Many research groups³⁻⁶ have analyzed the structural data in the Cambridge Structural Database (CSD) and Protein Data Bank (PDB) crystal structure databases in order to understand the structural chemistry of calcium and identify geometrical features of a general nature. In a pioneering study, Einspahr and Bugg³ examined the crystal structures of sixty two crystalline hydrates of calcium and showed that calcium-water interactions involve factors that impose significant constraints on the geometries of these compounds. Based on a study of protein crystal structures, Glusker and coworkers⁵ reported that calcium has less affinity for water as compared to magnesium. Of the 187 small molecular crystal

structures examined by the Glusker group⁵, only 16 compounds (8.5 %) had a Ca:water ratio of 1:5 and more. Of these, only one compound had a Ca:H₂O ratio of 1:8, while a 1:6 and 1:7 ratio for Ca:water was observed in six and two compounds respectively. A majority (73 %) of the Ca(II) compounds showed a Ca:water ratio of 1:3 or less, which is indicative of the low affinity of Ca(II) for water. To the best of our knowledge, the structures of the Ca(II) compounds $(\text{ImH})_4[\text{Ca}(\text{H}_2\text{O})_6][\text{Mo}_7\text{O}_{24}](\text{Im})\cdot 3\text{H}_2\text{O}$ ⁷ (Im = imidazole), $[\text{Ca}(\text{H}_2\text{O})_6(\text{C}_{16}\text{H}_{12}\text{O}_4)]\cdot 2\text{H}_2\text{O}$ ⁸ ($\text{C}_{16}\text{H}_{12}\text{O}_4$ = meso-2,3-diphenylsuccinate) and $[(\text{H}_2\text{O})_6\text{Ca}(\mu\text{-Hpdc})\text{Ca}(\text{H}_2\text{O})_3(\text{Hpdc})_2](\text{Hpdc})\cdot 2\text{H}_2\text{O}$ ⁸ (H_2pdc = pyridine-3,5-dicarboxylic acid) are the only known examples of Ca(II) containing six coordinated water molecules, after the study by Glusker⁵ and coworkers.

In small molecular weight compounds, many of which are normally crystallized from aqueous media, the affinity of Mg(II) for water can be evidenced by the structural characterization of many compounds which contain the octahedral $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ ion⁹⁻¹³. In contrast, several Ca(II) compounds prepared from aqueous reactions contain four or less than four coordinated water molecules¹³⁻²⁹ as can be evidenced by the synthesis and characterization of $[\text{Ca}(\text{H}_2\text{O})_2(4\text{-aba})_2]_n$, $[\text{Ca}(\text{H}_2\text{O})_3(2\text{-aba})_2]_n$, $[\text{Ca}(\text{H}_2\text{O})(\text{gly})_2]_n$, $[\text{Ca}(\text{H}_2\text{O})_2(3\text{-aba})_2]_n$, $[\text{Ca}(\text{H}_2\text{O})_4(\text{aip})_2]_n$,

[Ca(H₂O)₃(1,4-bdc)₂]_n, [Ca(H₂O)₂(mal)]_n, [Ca(H₂O)(OAc)₂]_n, [Ca(H₂O)₃(benz)₂]_n, [Ca(H₂O)(DMF)(benz)₂]_n, [Ca(H₂O)₃(4-fba)₂]_n, [Ca(H₂O)₂(2-fba)₂]_n, [Ca(H₂O)₃(dipic)₂]_n, [Ca(H₂O)₃(3,5-dnsa)₂]_n, [Ca(H₂O)₂(2-nba)₂]_n, [Ca(H₂O)₂(2-ca-4nba)₂]_n and [Ca(H₂O)₄(4-nba)₂] (4-aba = 4-aminobenzoate¹³; 2-aba = 2-aminobenzoate¹⁴; gly = glycinate¹⁵; 3-aba = 3-aminobenzoate¹⁶; aip = 5-aminoisophthalate¹⁷; 1,4-bdc = benzene-1,4-dicarboxylate¹⁸; mal = malonate¹⁹; OAc = acetate²⁰; benz = benzoate²¹; DMF = dimethylformamide²²; fba = fluorobenzoate^{23,24}; dipic = dipicolinate²⁵; 3,5-dnsa = 3,5-dinitrosalicylate²⁶; 2-nba = 2-nitrobenzoate²⁷; 2-ca-4nba = 2-carbamoyl-4-nitrobenzoate²⁸; 4-nba = 4-nitrobenzoate²⁹). The seven coordinated compound, [Ca(H₂O)₄(4-nba)₂]²⁹, differs from several other Ca-carboxylates in that the 4-nba ligand does not exhibit bridging coordination. We have shown in earlier reports³⁰⁻³³, that on reaction with N-donor ligands, the zero-dimensional compound [Ca(H₂O)₄(4-nba)₂], can be transformed into mixed ligand Ca(II) compounds containing less or no water as evidenced by the characterization of [Ca(Im)(H₂O)₃(4-nba)₂].Im³⁰, [Ca(Im)(4-nba)₂]³¹, [Ca(N-MeIm)(4-nba)₂]_n, [Ca(H₂O)(2-MeIm)(4-nba)₂]_n and [Ca(pyr)₂(4-nba)₂]_n (Im = imidazole^{30,31}; N-MeIm = N-methylimidazole³¹; 2-MeIm = 2-methylimidazole³²; pyr = pyrazole³³).

In this work, we have investigated the solid state and solution reactions of [Ca(H₂O)₄(4-nba)₂] with 2-aminopyridine (2-ap). In aqueous solution, reorganization of the coordination sphere of Ca(II) leading to the formation of an unusual water-rich Ca(II) compound, [Ca(H₂O)₆(4-nba)](4-nba)(2-ap)·H₂O, is observed, the details of which are reported herein.

Materials and Methods

All the chemicals used in this study were of reagent grade and were used as received. The starting materials and reaction products were air stable and hence were prepared under normal laboratory conditions. Infrared (IR) spectra of the solid samples diluted with KBr were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer in the range 4000-400 cm⁻¹. UV-visible spectra were recorded in water on a Shimadzu UV-2450 double beam spectrophotometer using matched quartz cells. TG-DTA studies were performed in flowing air, in Al₂O₃ crucibles on a STA-409 PC simultaneous thermal analyzer from Netzsch. A heating rate of

10 K min⁻¹ was employed for all measurements. Isothermal weight loss studies were performed in an electric furnace.

Modified method for rapid synthesis of [Ca(H₂O)₄(4-nba)₂] (1)

A modified method involving less reaction time is described for the rapid and bulk synthesis of the earlier reported [Ca(H₂O)₄(4-nba)₂]²⁹. The 4-nbaH (3.34 g, 20 mmol) was taken in water (20 mL) and the slurry was warmed on a water bath to expel dissolved CO₂. A freshly prepared sample of CaO obtained by heating commercial CaCO₃ (1 g, 10 mmol) in a muffle furnace at 800 °C for ~30 min, was added to the above slurry. The reaction mixture was stirred well for ~10 min, resulting in the immediate formation of a microcrystalline product. The reaction mixture was cooled to room temperature, filtered and the product was washed well with water, followed by ether and dried. Yield 3.9 g. The infrared spectrum and thermal properties of the product were identical to that of the reported compound²⁹.

Preparation of [Ca(2-ap)(4-nba)₂] (1-a)

A finely powdered solid mixture of [Ca(H₂O)₄(4-nba)₂] (1) (0.445 g, 1 mmol) and 2-aminopyridine (0.094 g, 1 mmol) was heated over a steam bath at 100 °C for 15-20 min., until the entire powder turned light yellow. The mixture was washed with ether and dried under vacuo. The observed weight loss of the product indicated the loss of four molecules of water resulting in the formation of an anhydrous compound (1-a). Alternatively (1-a) can be also prepared by first heating (1) at 100 °C for 15 min. and then adding 2-ap, followed by washing with ether and drying under vacuo. The use of 4-aminopyridine (4-ap) in the above reaction instead of 2-ap resulted in the formation of the monohydrate [Ca(H₂O)(4-nba)₂].

[Ca(2-ap)(4-nba)₂] (1-a): (Yield 0.458 g, 98 %); Anal.: Found (calc %) for CaC₁₉H₁₄N₄O₈: (466.41) = CaO 12.50 (12.02). IR (KBr cm⁻¹): 3458 (ν_{NH}), 3345 (ν_{NH}), 3082, 1620, 1566 ν_{as}(-COO), 1518 ν_{as}(-NO₂), 1487, 1440, 1416 ν_s(-COO), 1346 ν_s(-NO₂), 1317, 1153, 1107, 1014, 878, 841, 799, 775, 725, 513.

Preparation of [Ca(H₂O)₆(4-nba)](4-nba)(2-ap)·H₂O (2)

A mixture of [Ca(H₂O)₄(4-nba)₂] (1) (0.445 g, 1 mmol) and 2-aminopyridine (0.366 g, 4 mmol) was taken in water (~8 mL) and the reaction mixture was heated on a steam bath to obtain a clear yellow solution. The clear reaction mixture was left aside for crystallization. The pale yellow crystalline blocks

suitable for structure determination which separated after ~3 h were isolated by filtration, washed with a little ice cold water followed by ether and air dried. The use of stoichiometric amount of 2-ap (1 mmol) also resulted in the formation of a microcrystalline product which analyzed satisfactorily. The use of 4-ap instead of 2-ap in the above reaction under identical conditions resulted in the formation of the starting material (**1**).

[Ca(H₂O)₆(4-nba)](4-nba)(2-ap)·H₂O (**2**): (Yield 0.46 g, 77 %). Anal.: Found(calc.) (%) for CaC₁₉H₂₈N₄O₁₅ (592.52) = Ca 6.21 (6.76); C 38.13 (38.51); H 4.21 (4.76); N 8.74 (9.46); CaO 9.69 (9.46). IR (KBr cm⁻¹): 3475 (ν_{OH}), 3443, 3379 (ν_{NH}), 3347, 3217, 1678, 1620, 1572 ν_{as}(-COO), 1518 ν_{as}(-NO₂), 1445, 1422 ν_s(-COO), 1341 ν_s(-NO₂), 1319, 1258, 1155, 1105, 1044, 988, 876, 839, 797, 779, 771, 727, 623, 557, 515. DTA (in °C) : 117 (endo), 238 (endo), 421 (endo), 534 (exo). UV-Vis (λ_{max} in water) = 297 nm. ¹HNMR (DMSO-*d*₆) δ (in ppm): 5.85 (s, 2 H), 6.41 (m, 1 H), 6.40 (m, 1 H), 7.34 (m, 1 H), 7.88 (d, 1 H), 8.11 (d, 2 H), 8.20 (d, 2 H).

X-ray crystal structure determination

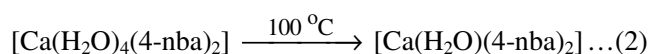
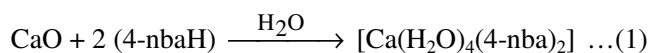
A single crystal of the title compound was selected using a Leica polarizing microscope and was used for intensity data-collection on an X'calibur (Oxford Diffraction System) X-ray diffractometer having CCD camera, using graphite-monochromated Mo-K_α radiation. CrysAlis^{Pro} program was used for data collection, reduction and space group determination. All non-hydrogen atoms were refined anisotropically. H atoms attached to the O and N atoms of water and 2-aminopyridine were located in the difference map and were refined isotropically using a riding model. Selected refinement data for (**2**) are listed in Table 1.

Results and Discussion

Synthetic aspects, spectral and thermal studies

The zero-dimensional compound, [Ca(H₂O)₄(4-nba)₂] (**1**) used earlier as a starting material for the synthesis of new Ca(II) coordination polymers³¹⁻³³ has been used in this study for the synthesis of new compounds using aminopyridines. We have developed a facile method for the synthesis of [Ca(H₂O)₄(4-nba)₂] in this work. The modified method of preparation involves direct reaction of a slurry of 4-nbaH in water with freshly prepared CaO (Eq. 1). Use of CaO affords the synthesis of (**1**) in high yields in a very short time period, unlike the

earlier reported method²⁹ using CaCO₃ where the reaction of commercial CaCO₃ with aqueous 4-nbaH as well as crystallization of (**1**) required longer time duration. Thermal behaviour of (**1**) (Eq. 2) to form [Ca(H₂O)(4-nba)₂] with loss of three moles of water (weight loss = 12.16 %) on heating at 100 °C, serves as a sensitive and useful method for the convenient identification of (**1**).



In earlier works^{31,32} we have shown that N-donor ligands like N-methylimidazole (N-MeIm) or 2-methylimidazole (2-MeIm) can be incorporated into the coordination sphere of Ca(II) by reaction of solid

Table 1 — Selected refinement data for compound **2**

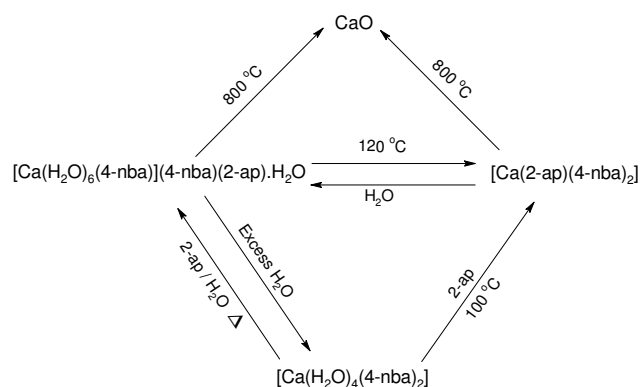
Empirical formula	C ₁₉ H ₂₈ CaN ₄ O ₁₅
Formula weight (g mol ⁻¹)	592.52
Temperature (K)	293 (2)
Wavelength (Å)	0.71073
Crystal system/Space group	Triclinic / <i>P</i> $\bar{1}$
Unit cell dimensions	
<i>a</i> (Å)	6.8667(4)
<i>b</i> (Å)	10.1174(4)
<i>c</i> (Å)	19.4741(8)
α (°)	75.700(4)
β (°)	87.453(4)
γ (°)	84.675(4)
Volume (Å ³) / Z	1305.03(11) / 2
Density (calc.) (mg/m ³)	1.508
Abs. coeff. (mm ⁻¹)	0.321
F (000)	620
Crystal size (mm ³)	0.15 × 0.2 × 0.30
θ range for data collection (°)	3.15 to 32.35
Completeness to θ (32.35°)	90.0 %
Index ranges	-10 ≤ <i>h</i> ≤ 10, -15 ≤ <i>k</i> ≤ 15, -28 ≤ <i>l</i> ≤ 28
Reflections collected	19968
Independent reflections	8439 [<i>R</i> (int) = 0.0201]
Refinement method	Full-matrix least-square on <i>F</i> ²
Data/restraints/parameters	8439 / 0 / 465
Goodness-of-fit on <i>F</i> ²	0.936
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0373 <i>wR</i> 2 = 0.0961
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0556 <i>wR</i> 2 = 0.1008
Extinction coefficient	0.0060(19)
Largest diff. peak and hole (e. Å ⁻³)	0.325 and -0.276

$[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ with N-MeIm or 2-MeIm. Further, the same reaction using excess methylimidazoles when performed in minimum quantity of water can give rise to the formation of the same product obtained in the solid state reaction as crystalline material suitable for structure determination. It is to be noted that use of excess N-donor ligand is essential to suppress the hydrolysis of mixed ligand compounds into the starting tetraqua compound $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$. In addition, N-donor ligands which are soluble in water as well as organic solvents are desirable for the synthesis of new mixed ligand compounds of Ca(II) from (1). The aminopyridines are both water and organic soluble and hence, were employed for the formation of new compounds in this study by reaction with $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ (1) in the solid state or in aqueous solution.

Reaction of a solid 1:1 mixture of (1) and 2-aminopyridine at 100 °C resulted in the formation of the anhydrous compound $[\text{Ca}(2\text{-ap})(4\text{-nba})_2]$ (1-a) in near quantitative yields (Scheme 1). The presence of free or unreacted 2-ap can be easily ruled out as no free 2-ap was recovered on washing of compound (1-a) with ether. Alternatively, (1-a) was prepared by first heating (1) at 100 °C for 15 min to form the reactive monohydrate $[\text{Ca}(\text{H}_2\text{O})(4\text{-nba})_2]$ and then adding 2-ap. However, under identical conditions, reaction of 4-ap with $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ resulted in the formation of $[\text{Ca}(\text{H}_2\text{O})(4\text{-nba})_2]$ and unreacted 4-ap which could be separated from the monohydrate by washing with ether in which 4-ap dissolves while the monohydrate remains insoluble. The reaction of $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ (1) was investigated in aqueous solution in the presence of excess 2-ap and 4-ap (Ca:aminopyridine = 1:4). With 4-ap, only the starting material $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ could be recovered as evidenced by the IR spectrum and weight loss study of the product at 100 °C. Interestingly, the aqueous reaction of (1) with 2-ap resulted in the formation of a crystalline material (2) which is quite different from that of the product of the solid state reaction, namely, (1-a). The different nature of (1-a) and (2) can be readily evidenced from the spectral, analytical and thermal data. The crystalline material (2) exhibits a weight loss of 16.2 % at 100 °C indicating that was not the starting material (1). Further, the large weight loss is indicative of the probable presence of more water in (2) than in (1). Analytical data of (2) reveals a Ca:4-nba:2-ap:water ratio of 1:2:1:7 ratio. The

presence of seven moles of water in (2) can be accounted for by six coordinated water molecules and a lattice water based on the single crystal data (vide infra). Compound (2) can be fully dehydrated by heating at 120 °C leading to the formation of (1-a), while (1-a) can be converted to (2) on exposure to moisture under controlled conditions. Both (1-a) and (2) can be converted to (1) by stirring in excess water (Scheme 1). Such a hydrolysis reaction of mixed ligand Ca(II) complexes has been reported by us earlier^{31,32}. Pyrolysis of (2) or (1-a) results in the formation of calcium oxide. Reaction of (2) or (1-a) with dilute HCl results in decomposition leading to the quantitative formation of insoluble 4-nbaH, which can be filtered and weighed.

The presence of 4-nba and 2-ap in (2) can be readily evidenced from the ¹H NMR spectrum, which exhibits characteristic signals of both moieties. The electronic spectrum of (2) exhibits a strong absorption at 297 nm and the peak position is the same as that of a dilute aqueous solution of (1) containing 2-ap in a Ca:2-ap ratio of 1:1. The observed signal can be attributed to an internal charge transfer of the aromatic 4-nba anion. In addition to a change in profile of the IR spectrum of (2) as compared to that of $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ (1) in the 3000-3500 cm⁻¹ region, additional signals are observed in the spectrum of (2) at 1258, 1155, 1044, 988, 876, 779 cm⁻¹ indicating the presence of 2-ap in (2). A broad and strong absorption in the O-H and N-H region of the IR spectrum with signals centered around 3475 cm⁻¹ and 3345 cm⁻¹ may be assigned for the O-H and N-H stretching vibrations of water and amine of 2-ap respectively in (2). The symmetric and asymmetric stretching vibrations of carboxylate are observed at 1572 and 1421 cm⁻¹ respectively, while



Scheme 1

those of the nitro group are observed at around 1517 and 1341 cm^{-1} respectively.

The TG-DTA thermogram of (2) (Fig. 1) exhibits first an endothermic process at 117 °C which is not observed for (1-a). The observed weight loss and the profile of the dropping TG curve of (2) can be attributed to the loss of the neutral water followed by 2-ap. The profile of the TG curve of (1-a) which is initially a straight line parallel to X-axis until about 150 °C drops down, indicating the loss of 2-ap. The exothermic events at temperatures above 400 °C in both compounds can be attributed to the decomposition of 4-nba³¹. In both cases CaO is

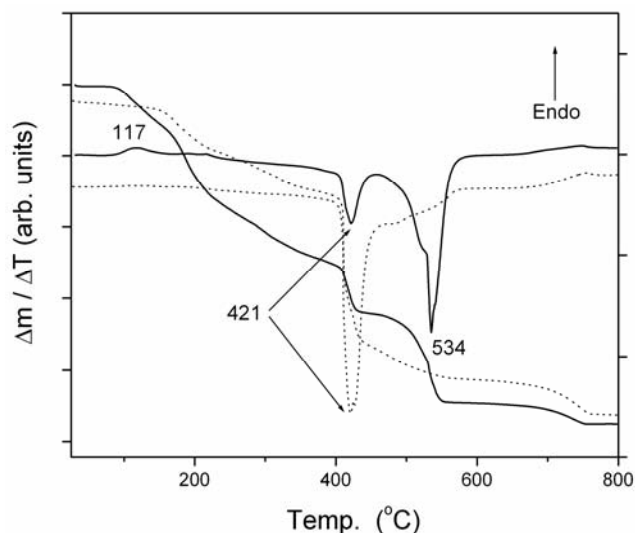


Fig. 1 — TG-DTA thermograms of $[\text{Ca}(\text{H}_2\text{O})_6(4\text{-nba})](4\text{-nba})(2\text{-ap})\cdot\text{H}_2\text{O}$ (2) (solid line) and $[\text{Ca}(4\text{-nba})_2(2\text{-ap})]$ (1-a) (dotted line).

formed as the final residue. The observed mass loss of 20.6 %, on heating (2) at 120 °C is in agreement with the expected value (21.28 %) for the loss of seven moles of water. The formation of CaO as the final residue was further confirmed based on isothermal weight loss studies by heating compounds (2) or (1-a) at 800 °C in a temperature controlled furnace. Thus the weight loss studies add credence to the thermal behavior of both compounds.

Crystal structure of $[\text{Ca}(\text{H}_2\text{O})_6(4\text{-nba})](4\text{-nba})(2\text{-ap})\cdot\text{H}_2\text{O}$ (2)

The water-rich Ca(II) compound (2), crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with all atoms situated in general positions. The crystal structure consists of a $[\text{Ca}(\text{H}_2\text{O})_6(4\text{-nba})]^+$ complex cation, a free 4-nitrobenzoate anion, a solvent 2-aminopyridine (2-ap) and a lattice water (Fig. 2). In the complex cation, the central Ca(II) is seven coordinated and is bonded to six terminal water molecules and a monodentate 4-nitrobenzoate resulting in a distorted pentagonal bipyramidal $\{\text{CaO}_7\}$ polyhedron (Fig. 2). The water-rich Ca(II) compound differs from the known structurally characterized Ca(II)-4-nitrobenzoates²⁹⁻³³ in that the central metal is coordinated to a single 4-nba ligand with the second unique 4-nba remaining uncoordinated. In all other structurally characterized 4-nitrobenzoates of Ca(II), the central metal is bonded to at least two 4-nba anions as in $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ ²⁹ or to more than two 4-nba ligands as observed in the one-dimensional polymers³¹⁻³³. The coordination of six water molecules to Ca(II) and the presence of free

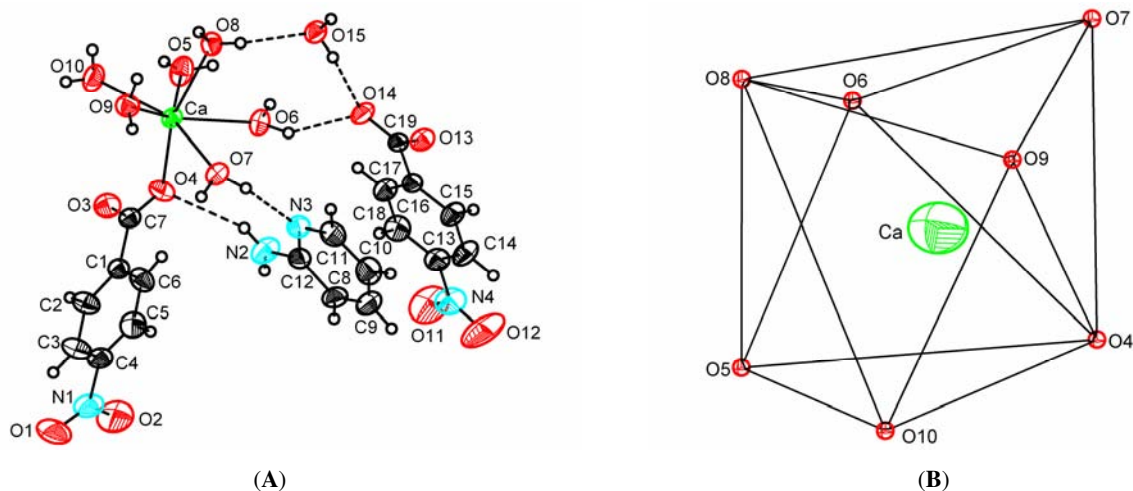


Fig. 2 — (A) Crystal structure of $[\text{Ca}(\text{H}_2\text{O})_6(4\text{-nba})](4\text{-nba})(2\text{-ap})\cdot\text{H}_2\text{O}$ showing the atom labeling scheme. Displacement ellipsoids are drawn at 50% probability level except for the H atoms, which are shown as circles of arbitrary radius. Intramolecular H-bonding is shown as broken lines. (B) The distorted pentagonal bipyramidal $\{\text{CaO}_7\}$ coordination polyhedron around Ca.

4-nba in (2) clearly indicate the reorganization of the coordination sphere of Ca(II) in $[\text{Ca}(\text{H}_2\text{O})_4(4\text{nba})_2]$ (1) on reaction with 2-ap. The geometric parameters of the coordinated and the free 4-nba and the 2-ap solvent are in the normal range. The Ca-O distances range from 2.3595(9) to 2.5315(10) Å (Table 2) and are in good agreement with reported values for several Ca(II) compounds. The O-Ca-O angles range from 47.91(3) to 159.89(4)°.

Table 2 — Selected bond lengths and bond angles for (2)

Bond lengths (Å)			
Ca-O(4)	2.3595(9)	Ca-O(7)	2.4367(9)
Ca-O(8)	2.4379(9)	Ca-O(6)	2.4493(10)
Ca-O(9)	2.5315(10)	Ca-O(10)	2.3900(10)
Ca-O(5)	2.4881(11)		
Bond angles (°)			
O(4)-Ca-O(7)	84.30(3)	O(4)-Ca-O(10)	98.76(4)
O(4)-Ca-O(8)	159.89(4)	O(10)-Ca-O(7)	145.92(4)
O(7)-Ca-O(8)	91.49(3)	O(10)-Ca-O(8)	95.71(4)
O(10)-Ca-O(6)	141.87(4)	O(4)-Ca-O(6)	83.71(3)
O(8)-Ca-O(6)	76.29(3)	O(7)-Ca-O(6)	72.17(4)
O(10)-Ca-O(5)	71.83(4)	O(4)-Ca-O(5)	86.86(4)
O(8)-Ca-O(5)	84.46(4)	O(7)-Ca-O(5)	142.(4)
O(4)-Ca-O(9)	122.74(3)	O(6)-Ca-O(5)	70.32(4)
O(7)-Ca-O(9)	76.31(3)	O(10)-Ca-O(9)	73.59(4)
O(6)-Ca-O(9)	136.14(3)	O(8)-Ca-O(9)	74.83(3)
O(4)-Ca-O(3)	47.91(3)	O(5)-Ca-O(9)	137.31(4)
O(7)-Ca-O(3)	74.70(3)	O(10)-Ca-O(3)	82.33(4)
O(6)-Ca-O(3)	123.11(3)	O(8)-Ca-O(3)	148.99(3)
O(9)-Ca-O(3)	74.96(3)	O(5)-Ca-O(3)	123.36(4)

A scrutiny of the crystal structure of (2) reveals that the $[\text{Ca}(\text{H}_2\text{O})_6(4\text{nba})]^+$ cation, the free 4-nba anion, lattice water and solvent 2-aminopyridine are involved in four varieties of H-bonding interactions, comprising of thirteen O-H...O, two N-H...O, one O-H...N and four C-H...O bonds (Table 3). The O...H distances ranging from 1.772 to 2.674 Å are accompanied by DHA angles ranging from 125° – 174°. All the H atoms of the coordinated and lattice water molecules, the amino group of 2-ap, H atoms attached to two of the carbon atoms (C2 and C5) of the monodentate 4-nba and H atoms bonded to C8 and C10 of 2-ap function as H-donors. All oxygen atoms of the coordinated and lattice water molecules and the N3 nitrogen atom of 2-ap, function as H-acceptors. The oxygen atom (O1) of the nitro group of coordinated 4-nba is not involved in H-bonding. The O11 and O12 atoms of the nitro group of free 4-nba are involved in weak C-H...O interactions, a feature observed in several metal 4-nitrobenzoates^{29-33,36}.

The H-acceptor characteristics of the lattice water (O15) results in tetra coordination around O15 (Fig. 3). In addition, O15 functions as H-donor, which results in the lattice water being linked to three different $[\text{Ca}(\text{H}_2\text{O})_6(4\text{nba})]^+$ cations and a free 4-nba anion. The solvent, 2-aminopyridine, serves to link three different $[\text{Ca}(\text{H}_2\text{O})_6(4\text{nba})]^+$ cations and a free anion with the aid of two O-H...N, two C-H...O and one N-H...O interaction (Fig. 3). The secondary interactions of 2-ap with the cations and free

Table 3 — Hydrogen-bonding geometry for $[\text{Ca}(\text{H}_2\text{O})_6(4\text{nba})](4\text{nba})(2\text{-ap})\cdot\text{H}_2\text{O}$ (2)

D-H...A	D(D-H) (Å)	D(H...A) (Å)	D(D...A) (Å)	<DHA (°)	Symmetry code
O8-H8B...O15	0.772	2.022	2.785	169	x, y, z
O6-H6A...O14	0.916	2.050	2.826	142	x, y, z
O15-H16A...O14	0.824	1.909	2.713	165	x, y, z
O8-H8A...O13	0.960	1.773	2.713	166	-x+1, -y+1, -z
O9-H9B...O13	0.878	1.958	2.821	167	-x+1, -y+1, -z
O15-H16...O7	0.802	2.014	2.809	172	-x+1, -y+1, -z
O9-H9A...O15	0.881	1.914	2.792	174	x-1, y, z
O7-H7A...O14	0.890	2.023	2.886	163	x-1, y, z
O5-H5A...O3	0.898	1.957	2.846	170	x+1, y, z
O6-H6B...O3	0.835	1.986	2.812	170	x+1, y, z
O5-H5B...O13	0.740	2.167	2.891	166	x, y-1, z
O10-H10A...O8	0.857	2.025	2.873	170	-x+1, -y, -z
O10-H10B...O9	0.805	2.202	2.961	157	-x, -y, -z
N2-H34...O4	0.821	2.399	3.174	158	x, y, z
N2-H33...O2	0.830	2.241	3.057	168	-x, -y, -z+1
O7-H7B...N3	0.911	1.772	2.671	169	x, y, z
C2-H2...O6	0.971	2.666	3.505	145	x-1, y, z
C5-H5...O11	0.997	2.526	3.204	125	x-1, y, z
C8-H8...O12	0.899	2.563	3.397	154	-x+1, -y+1, -z+1
C10-H10...O4	0.915	2.674	3.555	162	x, y+1, z

4-nba appears to be an important factor for the formation of the water-rich compound starting from $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ (**1**) since the reaction of 4-ap with (**1**) does not give rise to any new compound. It is interesting to note that the H-bonding surrounding of 2-ap is identical to that of the lattice water. An analysis of the crystal structure reveals that each seven coordinated $\text{Ca}(\text{II})$ complex cation is H-bonded to two symmetry related lattice water molecules, two different 2-ap molecules, five different uncoordinated 4-nba anions and four symmetry related $[\text{Ca}(\text{H}_2\text{O})_6(4\text{nba})]^+$ ions with the aid of eleven $\text{O}\cdots\text{O}$ bonds, one $\text{N}\cdots\text{O}$ bond, one $\text{O}\cdots\text{N}$ bond and three weak $\text{C}\cdots\text{O}$ interactions (Fig. 4). The free uncoordinated 4-nba anion is linked to a lattice water, a solvent 2-ap and five different complex cations with the aid of seven $\text{O}\cdots\text{H}$ contacts (Fig. 4). The net result of the several H-bonding

interactions in (**2**) is the organization of cations and anions into alternating layers with the lattice water and solvent 2-aminopyridine serving as links between layers (Fig. 5).

Comparative study of differently hydrated 4-nitrobenzoates of $\text{Ca}(\text{II})$

During the course of our studies on alkaline earth 4-nitrobenzoates³⁷, we have synthesized and characterized several 4-nitrobenzoates of $\text{Ca}(\text{II})$ which differ in their water content (Table 4). The mixed ligand compounds containing both 4-nba and N-donor ligands like Im, N-MeIm, 2-MeIm, pyr, 2-ap (for ligand abbreviation see Table 4) have been prepared starting from the zero-dimensional compound $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$. All compounds listed in Table 4 exhibit a 1:2 ratio of Ca:4-nitrobenzoate and the structurally characterized compounds crystallize in

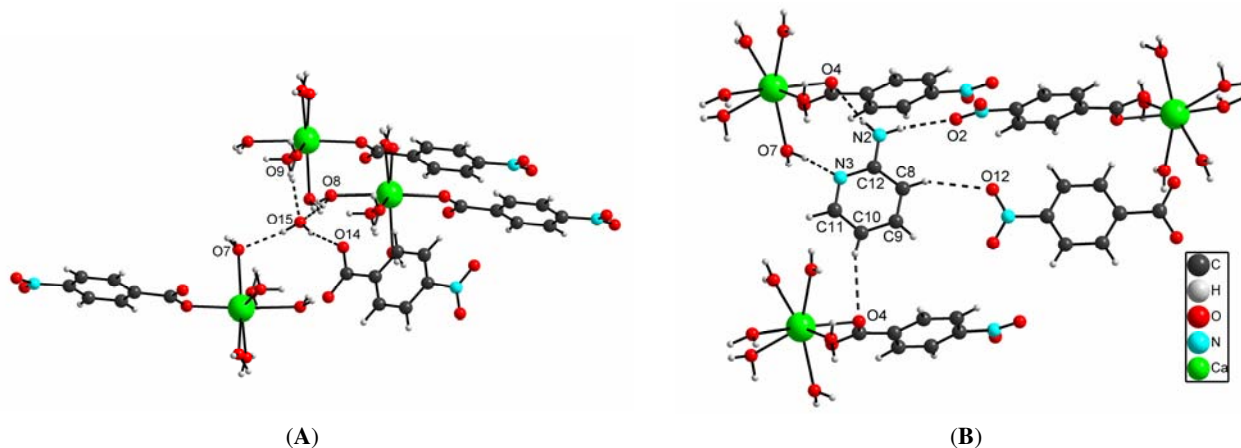


Fig. 3 — H-bonding surroundings of (A) lattice water (O15) and (B) 2-aminopyridine.

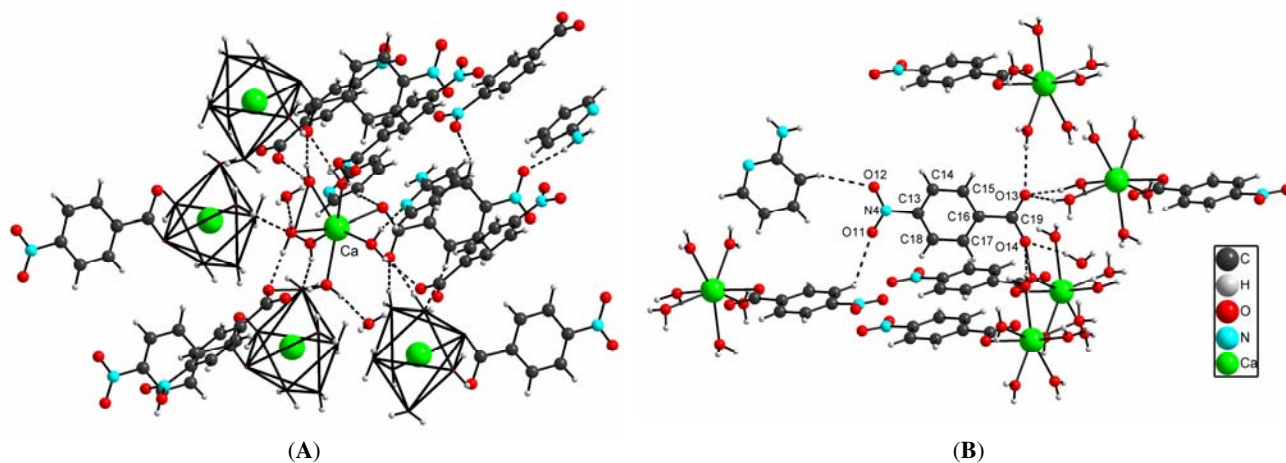


Fig. 4 — (A) H-bonding surroundings of the $[\text{Ca}(\text{H}_2\text{O})_6(4\text{nba})]^+$ cation showing the Ca cation bonded to two lattice waters, two 2-ap molecules, five free 4-nba anions and four different cations (open polyhedra). (B) H-bonding surroundings of free uncoordinated 4-nba.

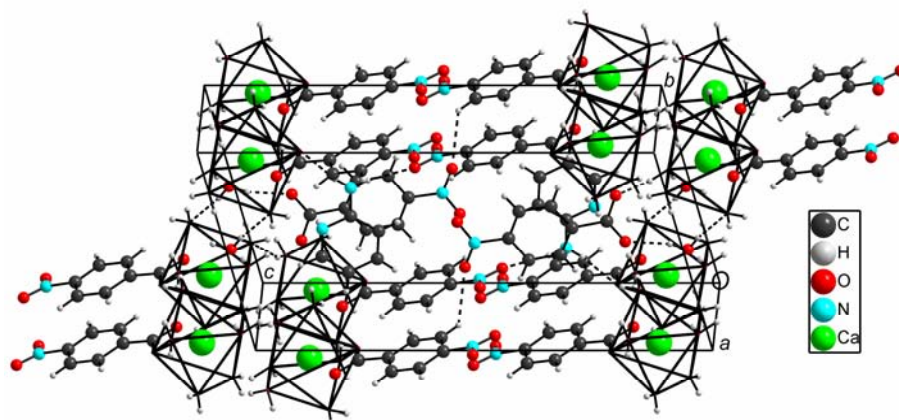


Fig. 5 — A view of the crystallographic packing of $[\text{Ca}(\text{H}_2\text{O})_6(4\text{-nba})](4\text{-nba})(2\text{-ap})\cdot\text{H}_2\text{O}$ (**2**). [H-bonding is shown in broken lines. $\{\text{CaO}_7\}^+$ units are shown as open polyhedra].

Table 4 — Comparative structural features of some Ca(II) 4-nitrobenzoates^a

Compound	S. G.	Ca:H ₂ O ^b	Coord. sphere	No. of 4-nba	Binding mode ^c	D	Ref.
$[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ (1)	$P2_1/c$	1:4	$\{\text{CaO}_7\}$	2	(d), (e)	0-D	29
$[\text{Ca}(\text{H}_2\text{O})_3(\text{Im})(4\text{-nba})_2]\cdot\text{Im}$	$P2_1/c$	1:3	$\{\text{CaNO}_5\}$	2	(d), (d)	0-D	30
$[\text{Ca}(\text{N-MeIm})(4\text{-nba})_2]_n$	$P\bar{1}$	1:0	$\{\text{CaNO}_5\}$	5	(a), (b)	1-D	31
$[\text{Ca}(\text{pyr})_2(4\text{-nba})_2]_n$	$P\bar{1}$	1:0	$\{\text{CaN}_2\text{O}_4\}$	4	(a)	1-D	33
$[\text{Ca}(\text{H}_2\text{O})(2\text{-MeIm})(4\text{-nba})_2]_n$	$P2_1/n$	1:1 ^d	$\{\text{CaNO}_6\}$	4	(a), (c)	1-D	32
$[\text{Ca}(\text{H}_2\text{O})_6(4\text{-nba})](4\text{-nba})(2\text{-ap})\cdot\text{H}_2\text{O}$ (2)	$P\bar{1}$	1:6	$\{\text{CaO}_7\}$	1	(e), (f)	0-D	This work
$[\text{Ca}(4\text{-nba})_2]^\#$	---	1:0	---	---	---	---	29
$[\text{Ca}(\text{H}_2\text{O})(4\text{-nba})_2]^\#$	---	1:1	---	---	---	---	29, 31
$[\text{Ca}(\text{Im})(4\text{-nba})_2]^\#$	---	1:0	---	---	---	---	31
$[\text{Ca}(2\text{-ap})(4\text{-nba})_2]^\#$ (1-a)	---	1:0	---	---	---	---	This work

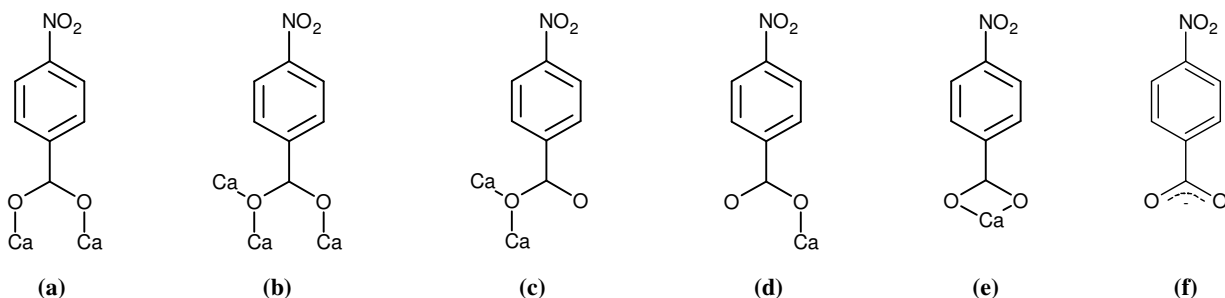
^aAll Ca(II) compounds excepting $[\text{Ca}(\text{pyr})_2(4\text{-nba})_2]_n$ contain two unique 4-nitrobenzoates;

^bOnly coordinated water molecules are considered;

^cfor the binding mode of 4-nba see Scheme 2;

^d μ_2 -bridging water; [#] characterized by analytical, spectral and thermal data.

Abbreviations used: S.G. = Space group; Coord sphere = Coordination sphere of Ca; No. of 4-nba = Number of 4-nitrobenzoates linked to each Ca; D = Dimensionality; 4-nba = 4-nitrobenzoate; Im = imidazole; N-MeIm = N-methylimidazole; pyr = pyrazole; 2-MeIm = 2-methylimidazole; 2-ap = 2-aminopyridine.



Scheme 2

centrosymmetric space groups. The 4-nba ligand exhibits six different modes of binding in these compounds (Scheme 2). The three different bridging modes of ligation, namely, symmetrical bridging, tridentate bridging and monoatomic bridging are observed in the one-dimensional mixed ligand polymers³¹⁻³³, while the monodentate and bidentate modes of ligation and free uncoordinated form are observed in the zero-dimensional compounds. In the polymeric compounds, each Ca(II) is coordinated to oxygen atoms from at least four different 4-nba ligands with five carboxylates surrounding the Ca(II) in the one-dimensional ladder polymer $[\text{Ca}(\text{N-MeIm})(4\text{-nba})_2]_n$. It is interesting to note that five of the compounds listed in Table 4 are anhydrous (water deficient), while two compounds $[\text{Ca}(\text{H}_2\text{O})(4\text{-nba})_2]$ and $[\text{Ca}(\text{H}_2\text{O})(2\text{-MeIm})(4\text{-nba})_2]_n$ exhibit a Ca:water ratio of 1:1. The mixed ligand compounds, $[\text{Ca}(\text{H}_2\text{O})_3(\text{Im})(4\text{-nba})_2]\cdot\text{Im}$ and $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$, show a Ca:water ratio of 1:3 and 1:4 respectively. The title compound, $[\text{Ca}(\text{H}_2\text{O})_6(4\text{-nba})](4\text{-nba})(2\text{-ap})\cdot\text{H}_2\text{O}$, referred to as water-rich Ca(II) 4-nitrobenzoate, contains the maximum water and is unique in that it contains six water molecules coordinated to Ca(II) and a lattice water and a solvent 2-aminopyridine. In the water-rich compound, each Ca(II) is linked to a single 4-nba ligand in a monodentate fashion, while the second unique 4-nba functions as a free anion for charge balance. It is to be noted that compounds which contain less or no water exhibit bridging 4-nba ligation, while compounds with a higher water content exhibit monodentate or bidentate binding modes of 4-nba.

Conclusions

In the present work we have described a simple method of synthesis of the compound $[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$ (**1**) which can be used as a convenient source for the synthesis of new mixed ligand compounds of Ca(II) on reaction with N-donor ligands. The reaction of (**1**) with 2-ap resulted in the formation of a water-rich compound (**2**) in aqueous conditions and an anhydrous compound (**1-a**) in a solid state reaction. The water-rich Ca(II) compound, $[\text{Ca}(\text{H}_2\text{O})_6(4\text{-nba})](4\text{-nba})(2\text{-ap})\cdot\text{H}_2\text{O}$, is a rare example of a structurally characterized Ca(II) compound containing six coordinated water molecules. A comparative study of differently hydrated Ca(II) 4-nitrobenzoates reveals a rich structural chemistry.

Supplementary Data

Crystallographic data (excluding structure factors) for the structure of $[\text{Ca}(\text{H}_2\text{O})_6(4\text{-nba})](4\text{-nba})(2\text{-ap})\cdot\text{H}_2\text{O}$ reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 793917. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK; Fax: +44-(0)1223-336033; Email: deposit@ccdc.cam.ac.uk

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References

- 1 Fromm K M, *Coord Chem Rev*, 252 (2008) 856.
- 2 Cotton F A, Wilkinson G, Murillo C A & Bochmann M, *Advanced Inorganic Chemistry*, 6th Edn, (Wiley, New York), 1999, Chap. 4, pp. 111-130.
- 3 Einspahr H & Bugg C E, *Acta Crystallogr*, 36B (1980) 264.
- 4 Einspahr H & Bugg C E, *Acta Crystallogr*, 37B (1981) 1044.
- 5 Katz A K, Glusker J P, Beebe S A & Bock C W, *J Am Chem Soc*, 118 (1996) 5752.
- 6 Murugavel R & Korah R, *Inorg Chem*, 46 (2007) 11048.
- 7 Gili P, Lorenzo-Luis P A, Mederos A, Arrieta J M, Germain G, Castiñeiras A & Carballo R, *Inorg Chim Acta*, 295 (1999) 106.
- 8 Morin G, Shang M & Smith B D, *Acta Crystallogr*, 56C (2000) 544; Starosta W, Ptasiwicz-Bak H & Leciejewicz J, *J Coord Chem*, 56 (2003) 33.
- 9 Srinivasan B R, Shetgaonkar S Y & Raghavaiah P, *Indian J Chem*, 48A (2009) 1662.
- 10 Dale S H, Elsegood M R J & Kainth S, *Acta Crystallogr*, 59C (2003) m505; Morgant G, Angelo J, Desmaele D, Dichi E, Sghaier M, Fraisse B, Retailleau P, Brumas V, Fiallo M M L, Tomas A, *Polyhedron*, 27 (2008) 2097.
- 11 Srinivasan B R, Sawant J V, Näther C & Bensch W, *J Chem Sci*, 119 (2007) 243; Srinivasan B R & Sawant S C, *Thermochim Acta*, 402 (2003) 45.
- 12 Wiesbrock F, Schier A & Schmidbaur H, *Z Naturforsch*, B57 (2002) 251; Srinivasan B R, Sawant S C & Dhuri S N, *Indian J Chem*, 41A (2002) 290.
- 13 Murugavel R, Karambelkar V V & Anantharaman G, *Indian J Chem*, 39A (2000) 843.
- 14 Murugavel R, Karambelkar V V, Anantharaman G & Walawalkar M G, *Inorg Chem*, 39 (2000) 1381.
- 15 Fox S, Busching I, Barklage W & Strasdeit H, *Inorg Chem*, 46 (2007) 818.
- 16 Murugavel R & Banerjee S, *Inorg Chem Commun*, 6 (2003) 810.
- 17 Murugavel R, Kumar P, Walawalkar M G & Mathialagan R, *Inorg Chem*, 46 (2007) 6828.
- 18 Groneman R H & Atwood J L, *Cryst Eng*, 2 (1999) 241.
- 19 Karipides A, Ault J & Reed A T, *Inorg Chem*, 16 (1977) 3299.

- 20 van Der Sluis P, Schouten A & Spek A L, *Acta Crystallogr*, 43C (1987) 1922.
- 21 Senkovska I & Thewalt U, *Acta Crystallogr*, 61C (2005) m448.
- 22 Yano S, Numata M, Kato M, Motoo S & Nishimura T, *Acta Crystallogr*, 57E (2001) m488.
- 23 Karipides A, McKinney C & Peiffer K, *Acta Crystallogr*, 44C (1988) 46.
- 24 Karipides A & Miller C, *J Am Chem Soc*, 106 (1984) 1494.
- 25 Strahs G & Dickerson R E, *Acta Crystallogr*, 24B (1968) 571.
- 26 Song W D, Guo X & Zhang C H, *Acta Crystallogr*, 63E (2007) m399.
- 27 Srinivasan B R, Shetgaonkar S Y & Raghavaiah P, *Polyhedron*, 28 (2009) 2879.
- 28 Srinivasan B R & Shetgaonkar S Y, *J Coord Chem*, 63 (2010) 3403.
- 29 Srinivasan B R, Sawant J V & Raghavaiah P, *Indian J Chem*, 45A (2006) 2392.
- 30 Srinivasan B R, Sawant J V & Raghavaiah P, *J Chem Sci*, 119 (2007) 11.
- 31 Srinivasan B R, Shetgaonkar S Y, Sawant J V & Raghavaiah P, *Polyhedron*, 27 (2008) 3299.
- 32 Srinivasan B R, Shetgaonkar S Y, Näther C & Bensch W, *Polyhedron*, 28 (2009) 534.
- 33 Srinivasan B R, Shetgaonkar S Y & Näther C, *Z Anorg Allg Chem*, 636 (2010) (in press). <http://onlinelibrary.wiley.com/doi/10.1002/zaac.201000214/abstract>.
- 34 Sheldrick G M, *Acta Crystallogr*, 64A (2008) 112.
- 35 Srinivasan B R, Sawant S C & Das S K, *Indian J Chem*, 43A (2004) 1066; Srinivasan B R, Sawant J V & Raghavaiah P, *Indian J Chem*, 48A (2009) 181; Srinivasan B R & Rane G K, *J Chem Sci*, 121 (2009) 145.
- 36 Srinivasan B R, Sawant J V, Sawant S C & Raghavaiah P *J Chem Sci*, 119 (2007) 593; Srinivasan B R, Raghavaiah P & Sawant J V, *Acta Crystallogr*, 63E (2007) m2251.