

## Synthesis and structural characterization of bis( $\mu_2$ -aqua)tetrakis(aqua)dilithium(I) bis(4-nitrobenzoate)

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Received 19 May 2011; revised and accepted 15 March 2012

Reaction of alkali metal carbonates  $M_2CO_3$  ( $M = Li$  or  $Na$ ) with 4-nitrobenzoic acid (4-nbaH) results in the formation of  $[(H_2O)_4Li_2(\mu-H_2O)_2](4-nba)_2$  (4-nba = 4-nitrobenzoate) (**1**) and  $[Na(4-nba)(H_2O)_3]$  (**2**). Compounds (**1**) and (**2**) have been characterized by analytical, spectral and thermal data. The structure of (**1**) consists of bis( $\mu_2$ -aqua)tetrakis(aqua)dilithium(I) dication situated on an inversion centre and a free 4-nba anion. In compound (**2**), one of the two independent 4-nba functions as a  $\mu_2$ -bridging bidentate ligand, bridging the two unique Na(I) ions via the oxygen atoms of the nitro functionality. Hydrogen bonding of coordinated water ligands in a dinuclear lithium cation with coordinated water molecules in an adjacent unit leads to the formation of a supramolecular chain of  $[(H_2O)_4Li_2(\mu-H_2O)_2]^{2+}$  cations. The cationic chain is further H-bonded to 4-nba anions resulting in alternating layers of  $[(H_2O)_4Li_2(\mu-H_2O)_2]^{2+}$  cations and 4-nba anions. Compounds (**1**) and (**2**) exhibit enhanced fluorescence emission. A study of the known *s*-block metal compounds containing 4-nba and coordinated water ligands reveals that the coordination number of the central metal varies from four in Li to nine in Ba.

**Keywords:** Coordination chemistry, Lithium, Sodium, Nitrobenzoates, Supramolecular chains

Recent years have witnessed a steady growth of publications describing the chemistry of *s*-block elements<sup>1-22</sup>. Non-toxic and water soluble nature, variable structural chemistry, affinity for O-donor ligands and relevance in biology are some factors responsible for the current interest in the chemistry of alkali and alkaline earths. The closed shell *s*-block metal cations lack properties like magnetism or variable oxidation states. Unlike the transition metals, no ligand field stabilization effects govern the bonding of *s*-block metal cations and hence the coordination numbers and geometries of alkali and alkaline earth metal cannot be accurately predicted. For example, the alkaline earth metal Ca adopts a range of coordination numbers from six to nine with eight coordination being the most preferred in several Ca(II) compounds<sup>23</sup>. An important property of *s*-block metals is their affinity for O-donor ligands, especially water. When synthesis is performed in aqueous media, the products invariably contain coordinated and lattice water molecules. In the case of Mg(II), coordination of six aqua ligands is a typical feature and several Mg(II) compounds possessing an

octahedral  $[Mg(H_2O)_6]^{2+}$  unit have been characterized<sup>24-31</sup>. Lighter elements like Li(I) in the alkali metal series or Be(II) in the alkaline earth series are known to prefer four coordination while cations like Na(I) and especially Mg(II) prefer a coordination number of six. As part of our research program we have developed an extensive structural chemistry of alkaline earth 4-nitrobenzoates<sup>32</sup>. In contrast, very few reports have appeared in the literature on the chemistry of alkali metal 4-nitrobenzoates<sup>33-35</sup>. Hence, we have extended our work to include the 4-nitrobenzoates of alkali metals. Herein, we describe the synthesis, spectral and structural characterization of the 4-nitrobenzoates of lithium and sodium.

### 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 are air stable and hence were prepared under normal laboratory conditions. Infrared (IR) spectra were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer in the range  $4000-400\text{ cm}^{-1}$ . The samples for the IR spectra

were diluted with KBr in the solid state and the signals referenced to polystyrene bands. UV-visible spectra of aqueous solutions were recorded on a Shimadzu UV-2450 double beam spectrophotometer using matched quartz cells. Photoluminescence of solid samples was studied using a Perkin Elmer LS55 fluorescence spectrometer.  $^1\text{H}$  NMR spectra were recorded on a 400 MHz Bruker Ultrashield spectrometer. X-ray powder pattern were recorded on a Rigaku Miniflex II powder diffractometer using  $\text{Cu-K}_\alpha$  radiation with a Ni filter. Thermal studies were performed in flowing air, in  $\text{Al}_2\text{O}_3$  crucibles on a STA-409PC simultaneous thermal analyzer from Netzsch. A heating rate of  $10\text{ K min}^{-1}$  was employed for all measurements. The insoluble 4-nbaH obtained on acid treatment of (1) and (2) was weighed as described earlier<sup>36</sup>.

A mixture of 4-nitrobenzoic acid (3.340 g, 20 mmol) and lithium carbonate (0.739 g, 10 mmol) in water (50 mL) was heated on a water bath till all the 4-nitrobenzoic acid dissolved completely to give a clear solution. The hot reaction mixture was filtered and left aside for crystallization. Pale yellow crystalline blocks of (1) that separated out were filtered, washed with ether and dried in air. Yield: 3.1 g (68 %). Use of sodium carbonate (1.06 g, 10 mmol) instead of lithium carbonate in the above reaction resulted in the formation of 3.6 g of (2) in 70% yield.

Anal. (%): Calcd for  $\text{Li}_2\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_{14}$  (1): 4-nbaH, 73.59; C, 37.02, H, 4.44; N, 6.17. Found: 4-nbaH, 73.03; C, 36.52; H, 3.82; N, 6.03. IR data ( $\text{cm}^{-1}$ ): 3582, 3400-2800 (br), 1641, 1566  $\nu_{\text{as}}(-\text{COO})$ , 1512  $\nu_{\text{as}}(-\text{NO}_2)$ , 1408  $\nu_{\text{s}}(-\text{COO})$ , 1369, 1344  $\nu_{\text{s}}(-\text{NO}_2)$ , 1323, 1161, 1105, 1011, 802, 723, 648, 517. UV-vis (in  $\text{H}_2\text{O}$ ): 299 nm.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ )  $\delta$  (in ppm): 8.05 (d,  $J = 8.8\text{ Hz}$ ,  $\text{H}_a$ ), 8.31 (d,  $J = 9.2\text{ Hz}$ ,  $\text{H}_b$ ). Thermal data (in  $^\circ\text{C}$ ): 105 (endo) and 389 (exo).

Anal. (%): Calcd for  $\text{NaC}_7\text{H}_{10}\text{NO}_7$  (2): 4-nbaH, 68.73; C, 34.58; H, 4.15; N, 5.76. Found: 4-nbaH, 68.39; C, 34.32; H, 4.11; N, 5.87. IR data ( $\text{cm}^{-1}$ ): 3578, 3500-2800 (br) 1678, 1572  $\nu_{\text{as}}(-\text{COO})$ , 1514  $\nu_{\text{as}}(-\text{NO}_2)$ , 1393  $\nu_{\text{s}}(-\text{COO})$ , 1350  $\nu_{\text{s}}(-\text{NO}_2)$ , 1319, 1107, 1011, 833, 804, 723, 511. UV-vis (in  $\text{H}_2\text{O}$ ): 299 nm.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ )  $\delta$  (in ppm): 8.03 (d,  $J = 8.8\text{ Hz}$ ,  $\text{H}_a$ ), 8.29 (d,  $J = 8.8\text{ Hz}$ ,  $\text{H}_b$ ). Thermal data (in  $^\circ\text{C}$ ): 105 (endo) and 368 (exo).

Intensity data were collected on a Nonius MACH3/CAD-4 single crystal diffractometer for (1) and on a Bruker Smart Apex Diffractometer for (2) using graphite-monochromated  $\text{Mo-K}_\alpha$  radiation. Structures

were solved with direct methods using SHELXS-97<sup>37</sup> and refinement was done against  $F^2$  using SHELXL-97<sup>37</sup>. All non-hydrogen atoms were refined using anisotropic displacement parameters. The C-H hydrogen atoms of 4-nba anion were positioned with idealized geometry and were refined using a riding model. H atoms attached to water oxygen were located in difference map, and were refined with fixed isotropic displacement parameters. The calculated bond valence sum from the crystallographic data for the central metal in both compounds is close to 1. Selected refinement results are listed in Table 1.

## Results and Discussion

An aqueous solution containing a mixture of 4-nbaH and alkali metal carbonate  $\text{M}_2\text{CO}_3$  ( $\text{M} = \text{Li}$  or  $\text{Na}$ ) in 2:1 mole ratio was heated till the 4-nbaH dissolved. Filtration of the reaction mixture followed by slow evaporation afforded in good yields the alkali metal 4-nitrobenzoates  $[(\text{H}_2\text{O})_4\text{Li}_2(\mu\text{-H}_2\text{O})_2](4\text{-nba})_2$  (1) or  $[\text{Na}(4\text{-nba})(\text{H}_2\text{O})_3]$  (2) respectively. The unit cell parameters of a trihydrate of Li(I) charge balanced by 4-nba, with no details on compound synthesis, have been reported by Prabhakar *et al.*<sup>35</sup> More recently, the synthesis of anhydrous  $[\text{M}(4\text{-nba})]$  ( $\text{M} = \text{Li}$  or  $\text{Na}$ ) by an aqueous reaction of MOH with 4-nbaH followed by removal of solvent under reduced pressure, has been reported by Regulska *et al.*<sup>38</sup> For synthesis of compound (2),  $\text{NaHCO}_3$  can also be used instead of  $\text{Na}_2\text{CO}_3$ . Compounds (1) and (2), which were isolated from a neutral reaction mixture, are freely soluble in water but unstable in acidic medium. On reaction with dilute HCl, (1) and (2) decompose forming quantitatively 4-nbaH, the insoluble nature of which provides a convenient method for the gravimetric analysis of (1) and (2). The composition of (1) and (2) was arrived at based on elemental analysis, and the 4-nbaH content obtained by acidification. Analytical data of (1) and (2) reveals the presence of three moles of water per mole of alkali metal. Despite this similarity, both compounds adopt different structures (*vide infra*). The presence of water in both compounds was also confirmed based on their characteristic infrared spectra in the O-H region and weight loss studies on heating at  $130\text{ }^\circ\text{C}$ . Presence of three moles of water in (1) and (2) is evidenced by mass loss of 24.0 and 22.0 % respectively.

The UV-visible spectra of both compounds in water are identical (Supplementary Data Fig. S1) and the observed  $\lambda_{\text{max}}$  at 299 nm can be assigned to the

Table 1—Selected refinement data for [(H<sub>2</sub>O)<sub>4</sub>Li<sub>2</sub>(μ-H<sub>2</sub>O)<sub>2</sub>](4-nba)<sub>2</sub> (**1**) and [Na(4-nba)(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub> (**2**)

Empirical formula	C <sub>14</sub> H <sub>20</sub> Li <sub>2</sub> N <sub>2</sub> O <sub>14</sub>	C <sub>7</sub> H <sub>10</sub> NaNO <sub>7</sub>
Formula weight (g mol <sup>-1</sup> )	454.20	243.15
Temp. (K)	293(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$
Unit cell dimensions	<i>a</i> = 12.324(4) Å; $\alpha$ = 90° <i>b</i> = 6.719(5) Å; $\beta$ = 104.29(3)° <i>c</i> = 12.402(3) Å; $\gamma$ = 90°	<i>a</i> = 7.2109(14) Å; $\alpha$ = 96.42(3)° <i>b</i> = 12.033(2) Å; $\beta$ = 91.65(3)° <i>c</i> = 12.382(3) Å; $\gamma$ = 104.43(3)°
Volume (Å <sup>3</sup> )	995.2(8)	1032.2(4)
Z	2	4
Density (calc.) (mg/m <sup>3</sup> )	1.516	1.565
Abs. coeff. (mm <sup>-1</sup> )	0.135	0.174
F(000)	472	504
Crystal size (mm <sup>3</sup> )	0.25 × 0.19 × 0.17	0.12 × 0.10 × 0.08
Theta range for data collection (°)	3.39 to 24.96	1.76 to 25.98
Completeness to theta	99.9 %	98.8%
Index ranges	0 ≤ <i>h</i> ≤ 14, -1 ≤ <i>k</i> ≤ 7, -14 ≤ <i>l</i> ≤ 14	-8 ≤ <i>h</i> ≤ 8, -14 ≤ <i>k</i> ≤ 14, -15 ≤ <i>l</i> ≤ 15
Reflections collected	2170	10532
Independent reflections	1741 [ <i>R</i> (int) = 0.0364]	3990 [ <i>R</i> (int) = 0.0228]
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	1741/ 0 / 164	3990/ 0 / 290
Goodness-of-fit on F <sup>2</sup>	1.194	0.948
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0377, w <i>R</i> 2 = 0.1112	<i>R</i> 1 = 0.0390, w <i>R</i> 2 = 0.1044
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0437, w <i>R</i> 2 = 0.1154	<i>R</i> 1 = 0.0458, w <i>R</i> 2 = 0.1105
Extinction coefficient	0.203(9)	0.022(2)
Largest diff. peak and hole (e.Å <sup>-3</sup> )	0.219 and -0.173	0.411 and -0.256
Bond valence sum of central metal <sup>a</sup>	1.059, 1.058	1.117, 0.999

<sup>a</sup>Bond valence sums were determined from the crystallographic data using Valist. A.S. Wills, VaList, Program available from [www.ccp14.ac.uk](http://www.ccp14.ac.uk).

intra ligand charge transfer of 4-nba. The fluorescence emission spectra of compounds (**1**) and (**2**) exhibit an enhanced emission as compared to that of free 4-nitrobenzoic acid (Supplementary Data Fig. S2). A similar enhancement of fluorescence has been recently reported by us in a Ca(II) coordination polymer based on 4-nitrobenzoate<sup>39</sup> and as in the case of the Ca compound, the emissions can be assigned to the intraligand fluorescent emission. The luminescent property of (**1**) and (**2**) can be assigned for ligand centered orbital transitions since similar emissions are also observed for the free ligand. The <sup>1</sup>H NMR spectra of both compounds exhibit a typical AB quartet for the two sets of aromatic protons in the 4-nba anion (Supplementary Data Fig. S3) and the observed chemical shifts of (**1**) and (**2**) are nearly identical and in agreement with the reported values<sup>36</sup> for [Mg(H<sub>2</sub>O)<sub>6</sub>](4-nba)<sub>2</sub>·2H<sub>2</sub>O. The presence of 4-nba in both compounds can be further confirmed based on the several signals in the mid IR region. It is interesting to note that the infrared spectra of both compounds are nearly similar excepting for a change

in the profile of the spectra in the 3500-3000 cm<sup>-1</sup> region (Supplementary Data Fig. S4). The broad signal in this region assignable for the ν<sub>O-H</sub> vibration disappears in the spectra of samples obtained on heating (**1**) and (**2**) at 130 °C. The values of the symmetric (ν<sub>s</sub>) and asymmetric (ν<sub>as</sub>) stretching vibrations of the carboxylate and the nitro groups are in the expected range (for assignment see Experimental section). Both compounds exhibit characteristic signals assignable to the vibrations of the carboxylate and nitro groups. The crystalline nature of both compounds (Supplementary Data Fig. S5) can be evidenced from the sharp signals in their powder diffractograms. A comparison of the powder patterns reveals that the phases are different indicating that the structure of the Li compound is different from that of the sodium compound.

Thermal studies reveal that both compounds exhibit an initial endothermic event centered at 105 °C followed by a strong exothermic signal at 368 and 389 °C for (**1**) and (**2**) respectively. The endothermic signal can be assigned for the removal of three moles

of water in both compounds while the exothermic event can be attributed to the decomposition of 4-nba. It is to be noted that the decomposition of 4-nba occurs at lower temperatures in the alkali metal compounds unlike in alkaline earth 4-nba compounds which exhibit exothermic decomposition above 400 °C. The results of the isothermal weight loss studies at 130 °C and the characteristic IR spectra of the anhydrous compounds (Supplementary Data Fig. S6) obtained on heating add credence to the thermal data.

Compound (1) crystallizes in the centrosymmetric monoclinic space group  $P2_1/c$  and its structure consists of a bis( $\mu$ -aqua)bridged tetraaquadilithium unit situated on an inversion centre and a free uncoordinated 4-nitrobenzoate anion located in general positions (Fig. 1). Each Li(I) in the dimeric unit is four coordinated and is bonded to two terminal water ligands and two bridging water molecules. In view of the presence of an inversion centre at the mid point of the  $\text{Li}_2\text{O}_2$  ring, the asymmetric unit is a half

of the formula unit. The metric parameters of the centrosymmetric dimeric cation are in agreement with reported data for  $[(\text{H}_2\text{O})_4\text{Li}_2(\mu\text{-H}_2\text{O})_2][\text{Li}(\text{SR})_2]$  [ $\text{R} = \text{bis}(\text{tri-tert-butoxysilanethiolato})$ ]<sup>40</sup>. The O-Li-O angles ranging from 89.69(15) to 126.57(19)° (Table 2)

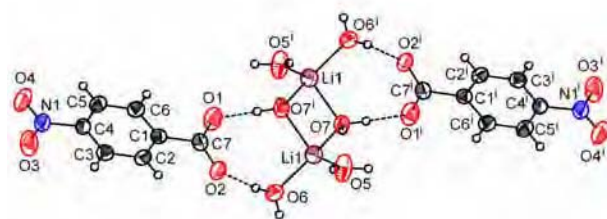


Fig. 1—Crystal structure of  $[(\text{H}_2\text{O})_4\text{Li}_2(\mu\text{-H}_2\text{O})_2](4\text{-nba})_2$  (1) showing the coordination sphere of Li(I) and atom-labeling scheme. Displacement ellipsoids are drawn at 50 % probability level except for the H atoms, which are shown as circles of arbitrary radius. Intramolecular H-bonding is shown as broken lines. [Symmetry code: (i)  $-x+1, -y+1, -z$ ].

Table 2—Selected bond distances (Å) and bond angles (°) of (1) and (2)

$[(\text{H}_2\text{O})_4\text{Li}_2(\mu\text{-H}_2\text{O})_2](4\text{-nba})_2$ (1)			
Li(1)-O(5)	1.901(4)	O(5)-Li(1)-O(6)	110.1(2)
Li(1)-O(6)	1.934(4)	O(5)-Li(1)-O(7)	115.28(18)
Li(1)-O(7)	1.989(4)	O(6)-Li(1)-O(7)	126.57(19)
Li(1)-O(7) <sup>i</sup>	2.018(4)	O(5)-Li(1)-O(7) <sup>i</sup>	109.37(18)
Li(1)···Li(1) <sup>i</sup>	2.842(7)	O(6)-Li(1)-O(7) <sup>i</sup>	100.81(17)
		O(7)-Li(1)-O(7) <sup>i</sup>	89.69(15)
$[\text{Na}(4\text{-nba})(\text{H}_2\text{O})_3]_n$ (2)			
Na(1)-O(22)	2.3655(15)	O(23)-Na(1)-O(24)	96.38(5)
Na(1)-O(23)	2.3728(16)	O(21)-Na(1)-O(24)	173.77(5)
Na(1)-O(21)	2.4283(15)	O(22) <sup>ii</sup> -Na(1)-O(24)	90.24(5)
Na(1)-O(22) <sup>ii</sup>	2.4327(16)	O(22)-Na(1)-O(3)	166.40(6)
Na(1)-O(24)	2.4391(14)	O(23)-Na(1)-O(3)	96.30(7)
Na(1)-O(3)	2.5365(18)	O(21)-Na(1)-O(3)	79.95(6)
Na(2)-O(24)	2.4041(15)	O(22) <sup>ii</sup> -Na(1)-O(3)	80.97(6)
Na(2)-O(25) <sup>iii</sup>	2.4120(17)	O(24)-Na(1)-O(3)	93.82(6)
Na(2)-O(26)	2.4317(17)	O(24)-Na(2)-O(26)	149.90(6)
Na(2)-O(25)	2.4359(16)	O(25) <sup>iii</sup> -Na(2)-O(26)	118.45(6)
Na(2)-O(26) <sup>iv</sup>	2.4749(16)	O(24)-Na(2)-O(25)	89.62(6)
Na(2)-O(4)	2.729(2)	O(25) <sup>iii</sup> -Na(2)-O(25)	77.39(5)
Na(1)···Na(1) <sup>ii</sup>	3.5221(18)	O(26)-Na(2)-O(25)	101.85(5)
Na(1)···Na(2)	4.1500(13)	O(24)-Na(2)-O(26) <sup>iv</sup>	91.63(5)
Na(2)···Na(2) <sup>iii</sup>	3.7836(16)	O(25) <sup>iii</sup> -Na(2)-O(26) <sup>iv</sup>	103.52(5)
Na(2)···Na(2) <sup>iv</sup>	3.8500(17)	O(26)-Na(2)-O(26) <sup>iv</sup>	76.60(5)
O(22)-Na(1)-O(23)	96.87(6)	O(25)-Na(2)-O(26) <sup>iv</sup>	178.43(5)
O(22)-Na(1)-O(21)	98.01(5)	O(24)-Na(2)-O(4)	73.68(6)
O(23)-Na(1)-O(21)	84.32(5)	O(25) <sup>iii</sup> -Na(2)-O(4)	154.69(6)
O(22)-Na(1)-O(22) <sup>ii</sup>	85.56(5)	O(26)-Na(2)-O(4)	80.33(6)
O(23)-Na(1)-O(22) <sup>ii</sup>	173.01(5)	O(25)-Na(2)-O(4)	82.33(6)
O(21)-Na(1)-O(22) <sup>ii</sup>	88.86(5)	O(26) <sup>iv</sup> -Na(2)-O(4)	97.12(6)
O(22)-Na(1)-O(24)	88.07(5)		

Symmetry transformations used to generate equivalent atoms.

Symmetry codes: (i)  $-x+1, -y-1, -z$  (ii)  $-x+1, -y+1, -z+2$  (iii)  $-x+1, -y+2, -z+2$  (iv)  $-x+2, -y+2, -z+2$

indicate a distortion of the  $\{\text{LiO}_4\}$  tetrahedron. The Li-O distances range from 1.901(4) to 2.018(4) Å. The two shorter Li-O distances at 1.901(4) and 1.934(4) Å are associated with the terminal water molecules O5 and O6 respectively. The coordinated water (O7) functions as a  $\mu_2$ -bridging ligand and is bonded to Li at a longer distance of 1.989(4) Å and the O7 is further linked to a symmetry related Li with a very long Li-O bond length of 2.018(4) Å. This  $\mu_2$ -bridging bidentate mode of O7 results in a Li...Li separation of 2.842(7) Å in the dimeric unit which is slightly shorter than the reported value of 2.876(7) Å for  $[(\text{H}_2\text{O})_4\text{Li}_2(\mu\text{-H}_2\text{O})_2][\text{Li}(\text{SR})_2]^{40}$ .

In the crystal structure of (1) the dimeric cation and the free 4-nba anion are linked by two varieties of H-bonding interactions comprising of six O-H...O bonds and a C-H...O interaction. All these O...H contacts (Table 3) are shorter than the sum of their van der Waals radii. All the H atoms of the coordinated water molecules and one hydrogen atom (H3) attached to a carbon (C3) function as H-donors. Each 4-nba unit is H-bonded to three different dimers with the aid of five O-H...O interactions and to one anion via the C3-H3...O3 interaction (Supplementary Data Fig. S7). In contrast, each dimeric cation is linked by H-bonding to two adjacent dimers and eight

symmetry related 4-nba anions with the aid of six O-H...O interaction (Supplementary Data Fig. S8). The O5-H1W...O6 interaction at 2.09(4) Å accompanied by a DHA angle of 168(3)° between the H atom of a coordinated water in a dimeric unit and the coordinated water O6 of an adjacent dimer results in the formation of an infinite supramolecular chain of  $[(\text{H}_2\text{O})_4\text{Li}_2(\mu\text{-H}_2\text{O})_2]^{2+}$  cations extending along *b* axis (Supplementary Data Fig. S9). The chain is further H-bonded to 4-nba anions on either side resulting in the formation of alternating layers of cations and 4-nba anions (Fig. 2).

Compound (2) crystallizes in the centrosymmetric triclinic space group  $P\bar{1}$  and the observed unit cell parameters are in excellent agreement with reported data<sup>34</sup>. The structure consists of two crystallographically independent Na(I) ions, six unique water molecules and two independent 4-nba anions (Supplementary Data Fig. S10). Of the six water molecules, two aqua ligands (O21 and O23) attached to Na1 are terminal in nature while the remaining four function as  $\mu_2$ -bridging bidentate aqua ligands (Fig. 3). One of the two unique 4-nba anions functions as a free anion as in compound (1), while the second 4-nba anion functions as a  $\mu_2$ -bridging bidentate ligand attached to the unique Na(I) ions Na1

Table 3—Hydrogen-bonding geometry for  $[(\text{H}_2\text{O})_4\text{Li}_2(\mu\text{-H}_2\text{O})_2](4\text{-nba})_2$  (1) and  $[\text{Na}(4\text{-nba})(\text{H}_2\text{O})_3]_n$  (2)

D-H...A	<i>D</i> (D-H) (Å)	<i>D</i> (H...A) (Å)	<i>D</i> (D...A) (Å)	<DHA (°)	Symmetry code
$[(\text{H}_2\text{O})_4\text{Li}_2(\mu\text{-H}_2\text{O})_2](4\text{-nba})_2$ (1)					
O5-H1W...O6	0.79(4)	2.09(4)	2.876(3)	168(3)	-x+1, -y, -z
O5-H2W...O3	0.89(4)	2.16(4)	3.028(2)	165(3)	x+1, -y+1/2, z-1/2
O6-H3W...O2	0.79(3)	2.11(3)	2.855(2)	159(3)	-x+1, y-1/2, -z+1/2
O6-H4W...O2	0.92(3)	1.81(3)	2.721(2)	171(2)	x, y, z
O7-H5W...O1	0.92(3)	1.75(3)	2.663(2)	172(2)	-x+1, -y+1, -z
O7-H6W...O2	0.82(3)	2.06(3)	2.869(3)	172(2)	-x+1, y-1/2, -z+1/2
C3-H3...O3	0.93	2.60	3.323(3)	135	-x, -y+1, -z+1
$[\text{Na}(4\text{-nba})(\text{H}_2\text{O})_3]_n$ (2)					
O21-H1O...O1	0.820	2.031	2.785	153	-x+1, -y+1, -z+1
O21-H2O...O11	0.820	2.105	2.924	178	x+1, y, z
O22-H3O...O1	0.820	1.984	2.780	164	x, y, z+1
O22-H4O...O11	0.820	1.957	2.777	178	-x+1, -y+1, -z+2
O23-H5O...O21	0.820	2.012	2.832	178	-x+2, -y+1, -z+2
O23-H6O...O12	0.820	2.001	2.800	164	x+1, y, z
O24-H7O...O12	0.820	2.108	2.908	165	x, y, z
O24-H8O...O1	0.820	2.013	2.802	161	x, y, z+1
O25-H9O...O12	0.820	1.983	2.765	159	x, y, z
O25-H10O...O2	0.820	1.888	2.707	176	-x+1, -y+2, -z+1
O26-H11O...O14	0.820	2.281	3.097	174	-x+1, -y+2, -z+1
O26-H11O...O13	0.820	2.633	3.181	126	-x+1, -y+2, -z+1
O26-H12O...O23	0.820	1.956	2.773	175	-x+2, -y+2, -z+2
C15-H15...O14	0.931	2.596	3.318	135	-x, 2-y, 1-z

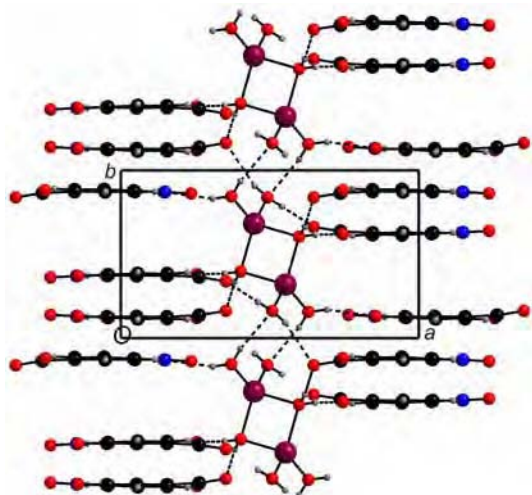


Fig. 2—A portion of the supramolecular chain of  $[(\text{H}_2\text{O})_4\text{Li}_2(\mu\text{-H}_2\text{O})_2]^{2+}$  cations in (1) extending along *b* axis and flanked by 4-nitrobenzoate anions on either side.

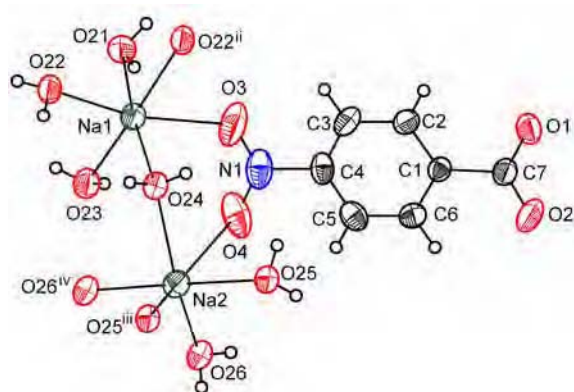


Fig. 3—Crystal structure of  $[\text{Na}(4\text{-nba})(\text{H}_2\text{O})_3]_n$  (2) showing the coordination sphere of the unique Na(I) ions and atom-labeling scheme. Displacement ellipsoids are drawn at 50 % probability level except for the H atoms, which are shown as circles of arbitrary radius. For clarity, the free uncoordinated 4-nba anion in (2) is not shown. [Symmetry codes: (ii)  $-x+1, -y+1, -z+2$ ; (iii)  $-x+1, -y+2, -z+2$ ; (iv)  $-x+2, -y+2, -z+2$ ].

and Na2 via the oxygen atoms O3 and O4 of the nitro functionality. The  $\mu_2$ -bridging binding modes of the four aqua ligands results in a two-dimensional structure (Fig. 4). Although one of the 4-nba anions functions as a  $\mu_2$ -bridging ligand, this binding mode alone does not lead to an extended structure (Supplementary Data Fig. S11). Each Na(I) in (2) is six coordinated and the observed Na-O distances and O-Na-O angles (Table 2) are in agreement with reported data<sup>34</sup>. Like in (1), two varieties of H-bonding interactions are observed (Table 3).

Recently we had shown that the charge balancing 4-nba anion is a versatile ligand and exhibits several

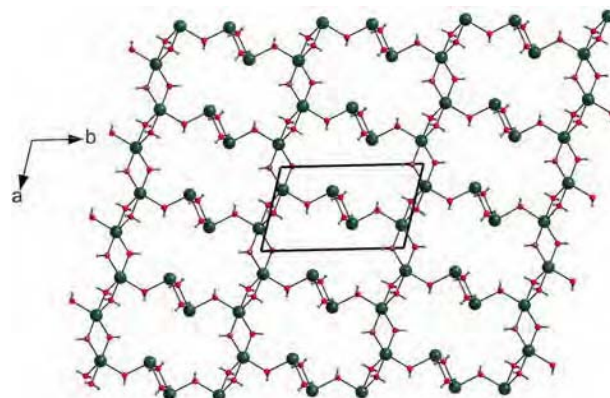


Fig. 4—A portion of the polymeric structure of  $[\text{Na}(4\text{-nba})(\text{H}_2\text{O})_3]_n$  (2) due to bridging water ligands showing the 2-D architecture. For clarity the terminal water ligands on Na and the two unique 4-nba anions are not shown.

Table 4—Varying coordination number (C.N) of *s*-block metals

Compound	C.N.	Nuclearity	Ref.
$[(\text{H}_2\text{O})_4\text{Li}_2(\mu\text{-H}_2\text{O})_2](4\text{-nba})_2$	4	Dimer	This work
$[\text{Na}(\text{H}_2\text{O})_3(4\text{-nba})]_n$	6, 6	Polymer	34 & this work
$[\text{Rb}(\text{H}_2\text{O})_2(4\text{-nba})]_n$	9	Polymer	CCDC 717713
$[\text{Cs}(\text{H}_2\text{O})_2(4\text{-nba})]_n$	9	Polymer	CCDC 717712
$[\text{Mg}(\text{H}_2\text{O})_6(4\text{-nba})_2 \cdot 2\text{H}_2\text{O}]$	6	Monomer	30
$[\text{Ca}(\text{H}_2\text{O})_4(4\text{-nba})_2]$	7	Monomer	41
$[\text{Sr}(\text{H}_2\text{O})_7(4\text{-nba})](4\text{-nba}) \cdot 2\text{H}_2\text{O}$	9	Monomer	42
$[\text{Ba}(\text{H}_2\text{O})_5(4\text{-nba})_2]_n$	9	Polymer	43

bridging binding modes<sup>39</sup>, in addition to binding in a monodentate or a bidentate fashion through the carboxylate oxygen atoms. A study of the 4-nba compounds of Li and Na reported in this work and earlier reported compounds<sup>30,34,41-43</sup> reveals some useful trends in terms of the coordination number of the *s*-block metals. All compounds listed in Table 4 contain coordinated water ligands and can be synthesized by an aqueous reaction of the *s*-block metal carbonate with 4-nbaH. In the alkali metal series, the lighter element Li exhibits a coordination number of four which increases to six on going to Na and a maximum value of nine is observed for the Rb and Cs compounds. In this series, the Li compound is a dimer, while all others are polymers. In the 4-nba compounds of Na, K, Rb and Cs, coordination of the central metal to the oxygen atom of the nitro functionality is observed. In contrast, for the alkaline earths, Mg exhibits a coordination number of six<sup>30</sup> which increases to seven on going to Ca<sup>41</sup> and attains the maximum value of nine for Sr<sup>42</sup> and Ba<sup>43</sup>. In the alkaline earth series excepting the Ba compound which is a one-dimensional polymer, all other compounds are zero-dimensional. A study of the known *s*-block metal compounds containing 4-nba



and coordinated water ligands reveals that the coordination number of the central metal varies from four in Li to nine in Ba. The hydrated 4-nba compounds of K and Be are not yet known and efforts are underway to characterize these compounds.

### Supplementary Data

Crystallographic data (excluding structure factors) for the structures of  $[(\text{H}_2\text{O})_4\text{Li}_2(\mu\text{-H}_2\text{O})_2](4\text{-nba})_2$  (4-nba = 4-nitrobenzoate) (1) and  $[\text{Na}(4\text{-nba})(\text{H}_2\text{O})_3]$  (2) reported herein have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 822969 (1) and CCDC 822970 (2). 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 or Email: deposit@ccdc.cam.ac.uk). Other supplementary data associated with this article, viz., (Figs S1-S11) are available in electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA 51A\(04\) 564-570\\_Suppl Data.PDF](http://www.niscair.res.in/jinfo/ijca/IJCA 51A(04) 564-570_Suppl Data.PDF).

### Acknowledgement

BRS thanks Dr. N N Ghosh, BITS-Pilani (Goa Campus) for the X-ray powder data and Shri M. Saxena, Department of Chemistry, IIT Kanpur for recording the luminescence spectra. Financial support under Nanomission program (SR/NM/NS-86, 2009) of Department of Science and Technology, New Delhi, India, and the Special Assistance Programme [F.540/25/DRS/2007/(SAP-I)] of University Grants Commission, New Delhi, India, is gratefully acknowledged.

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