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## Sodium trihydrogen-1,4-benzenediphosphonate: an extended coordination network

Ayi A. Ayi,<sup>a,b</sup> Andrew D. Burrows,<sup>a\*</sup> Mary F. Mahon<sup>a</sup> and Viorica M. Pop<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, United Kingdom.

<sup>b</sup> Department of Pure and Applied Chemistry, University of Calabar, P.M.B. 1115, Calabar, Nigeria.

### Abstract

Crystals of sodium trihydrogen-1,4-benzenediphosphonate, Na[H<sub>3</sub>bdp], were prepared from the addition of aqueous sodium hydroxide to an acidified solution of 1,4-benzenediphosphonic acid (H<sub>4</sub>bdp). These were shown by X-ray crystallography to crystallize in the space group  $P\bar{1}$ , with cell parameters  $a = 5.7500(3)$  Å,  $b = 7.9180(5)$  Å,  $c = 10.4420(6)$  Å,  $\alpha = 80.398(3)^\circ$ ,  $\beta = 76.844(4)^\circ$  and  $\gamma = 81.389(4)^\circ$ . The crystal structure revealed that the title compound forms a coordination network in which sodium-phosphonate sheets are pillared by the benzene rings into a three-dimensional structure.

**Keywords:** Sodium salts, phosphonates, coordination networks, coordination polymers.

Running header: Sodium trihydrogen-1,4-benzenediphosphonate

## 1. Experimental section

### 1.1 Synthesis

1,4-benzenediphosphonic acid (0.024 g, 0.1 mmol) was dissolved in water (3.6 cm<sup>3</sup>, 200 mmol) and conc. hydrochloric acid (0.1 cm<sup>3</sup>, 0.4 mmol) added to adjust the pH to 2. Addition of 0.1M NaOH solution (1.0 cm<sup>3</sup>) afforded rectangular block crystals after 2 days.

### 1.2 Structural analysis

The structural data were collected on a Nonius KappaCCD diffractometer. Details of the X-ray crystallographic analysis are given in Table 1. Fractional coordinates for the refined atoms and equivalent isotropic thermal parameters are presented in Table 2. The crystal structure was solved using SHELXS-97 and refined using SHELXL-97.<sup>1</sup>

## 2. Results and discussion

Coordination networks, otherwise known as metal-organic frameworks (MOFs), are currently attracting considerable interest for a wide range of potential applications.<sup>2-6</sup> Metal phosphonates are a well-established class of extended porous structures.<sup>7</sup> The use of polyphosphonates containing organic spacers that lie between the phosphonate groups to generate network structures predates the routine use of polycarboxylates in MOF chemistry,<sup>8</sup> and has been used to generate materials with interesting properties.<sup>9-13</sup> 1,4-Benzenediphosphonic acid, H<sub>4</sub>bdp (Figure 1) has been used to prepare coordination polymers based on vanadium,<sup>14</sup> nickel, cobalt,<sup>15</sup> copper,<sup>16</sup> zinc,<sup>17</sup> tin<sup>18</sup> and uranium,<sup>19</sup> though its utility

to date is much less than that of the carboxylic acid analogue 1,4-benzenedicarboxylic acid, which has attracted widespread use in MOF chemistry.

\*\*\* Figure 1 \*\*\*

While investigating the use of H<sub>4</sub>bdp to prepare new coordination network structures, we isolated colourless crystals of the monosodium salt, Na[H<sub>3</sub>bdp] that were suitable for a single crystal X-ray analysis. The analysis revealed that the asymmetric unit consists of one sodium ion plus two crystallographically independent ligand halves (Figure 2). The phenyl ring fragments in both of the latter are located proximate to inversion centres implicit in the space group symmetry such that the full ligands are generated by symmetry. Hydrogen atoms H(1) and H(4) was readily located and refined subject to being 0.98 Å from O(1) and O(4), respectively. There is clearly an additional proton missing from the model presented, but this was not credibly identifiable, and hence was not included in the refinement. This is likely to reflect the disorder possibilities and consequent associated fractional occupancy resulting from the ligand symmetry. The most plausible location for this errant hydrogen lies between O(6) and O(2), as the short distance between these atoms suggests the presence of a hydrogen bond [O(6)⋯O(2) 2.498 Å].

\*\*\* Figure 2 \*\*\*

Interactions between the oxygen atoms of the anion and the sodium cations give rise to a coordination network structure in which sodium-phosphonate sheets are pillared into a three-dimensional structure by the benzene rings.

The geometry around the sodium centre is distorted octahedral, as shown in Figure 3, with the *cis* angles ranging from 75.25(15) to 106.65(16)° and the *trans* angles ranging from 160.93(17) to 168.78(18)°. The distortion from a regular octahedron helps to accommodate an intramolecular hydrogen bond [O(4)⋯O(2) 2.541, H(4)⋯O(2) 1.59 Å, O(4)–H(4)⋯O(2) 161°] which involves an eight-membered ring and has the graph set S(8). A second intramolecular hydrogen bond [O(1)⋯O(3) 2.590, H(1)⋯O(3) 1.63 Å, O(1)–H(1)⋯O(3) 163°] is also present, but this involves a six-membered ring [graph set S(6)]. The presence of S(8) rings containing a coordination centre have been shown to widen bond angles in other systems.<sup>20</sup> The Na–O contacts lie between 2.263(5) and 2.493(5) Å, with the longest distances those to the protonated oxygen atoms, O(1) and O(4).

\*\*\* Figure 3 \*\*\*

The P–O distances in the hydrogenphosphonate groups range from 1.479(4) to 1.588(4) Å, with the lower values reflecting the multiple bond character in the bonds to the unprotonated oxygen atoms O(3) and O(5). Both hydrogenphosphonate groups are triply bridging, though they differ in their coordination modes. Thus, in the group containing P(2) each oxygen atom is coordinated to a different sodium ion. In contrast, for the group containing P(1), O(2) is uncoordinated, O(1) is coordinated to a single sodium ion whereas O(5) bridges between two sodium ions. In total, coordination generates layers (Figure 4) which contain both 4-membered (Na<sub>2</sub>O<sub>2</sub>) and 8-membered (Na<sub>2</sub>P<sub>2</sub>O<sub>4</sub>) rings. M<sub>2</sub>O<sub>2</sub> and M<sub>2</sub>P<sub>2</sub>O<sub>4</sub> rings are also present in the structure of [Cu<sub>2</sub>(bdp)(H<sub>2</sub>O)<sub>2</sub>], though in this case the ligand is fully deprotonated and the phosphonate groups bridge four metal centres.<sup>16</sup>

For Na[H<sub>3</sub>bdp], reduction of each hydrogenphosphonate group to a 3-connected node, reveals that the layers have a **kgd** topology.<sup>21</sup> The central benzene rings present in each of the ligands pillar the sodium-hydrogenphosphonate layers into a three-dimensional network structure (Figure 5), with the benzene rings adopting a herringbone structure.

\*\*\* Figure 4 \*\*\*

\*\*\* Figure 5 \*\*\*

### **Acknowledgement**

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## Figure Legends

Figure 1. 1,4-Benzenediphosphonic acid, H<sub>4</sub>bdp.

Figure 2. The asymmetric unit of Na[H<sub>3</sub>bdp]. Ellipsoids are represented at 30% probability.

Figure 3. The geometry around the sodium centre in the crystal structure of Na[H<sub>3</sub>bdp].

Figure 4. Part of one of the layers present in the crystal structure of Na[H<sub>3</sub>bdp].

Figure 5. The three-dimensional network observed in the crystal structure of Na[H<sub>3</sub>bdp].

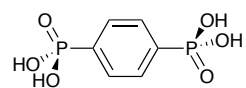
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**Figure 1**



**Figure 2**

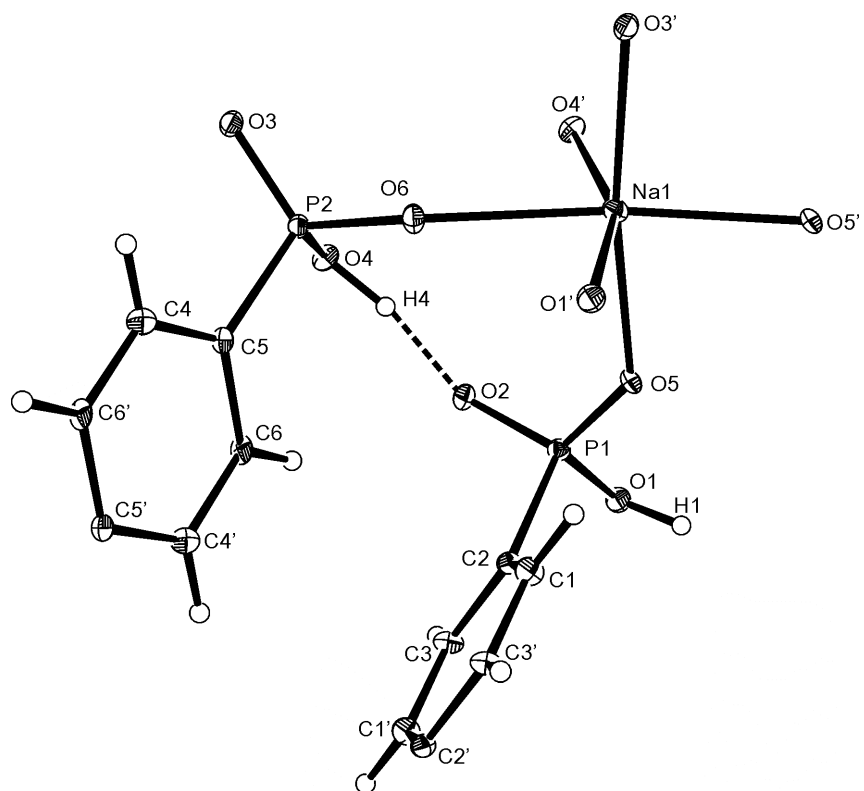


Figure 3

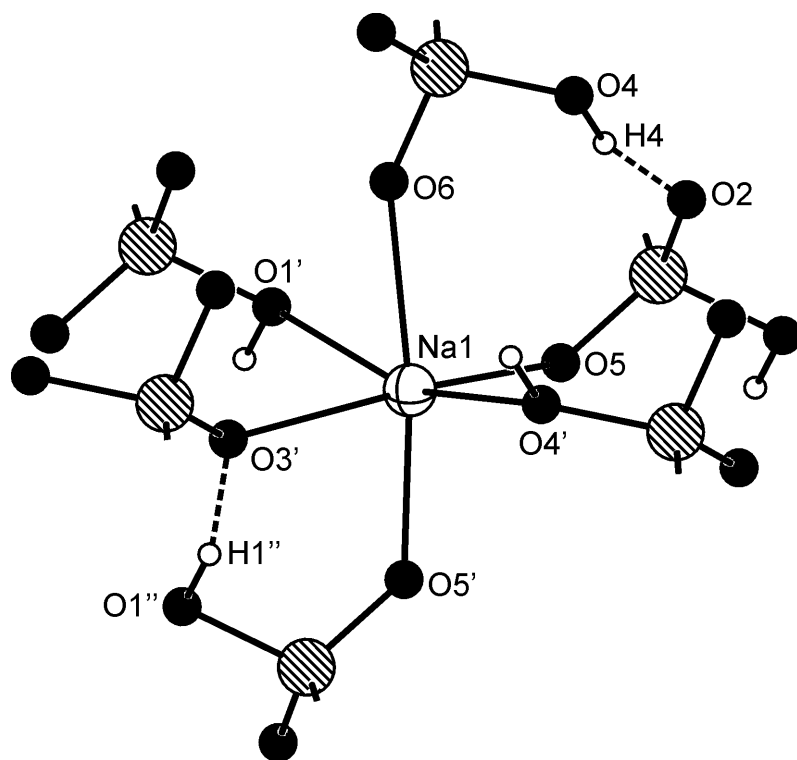


Figure 4

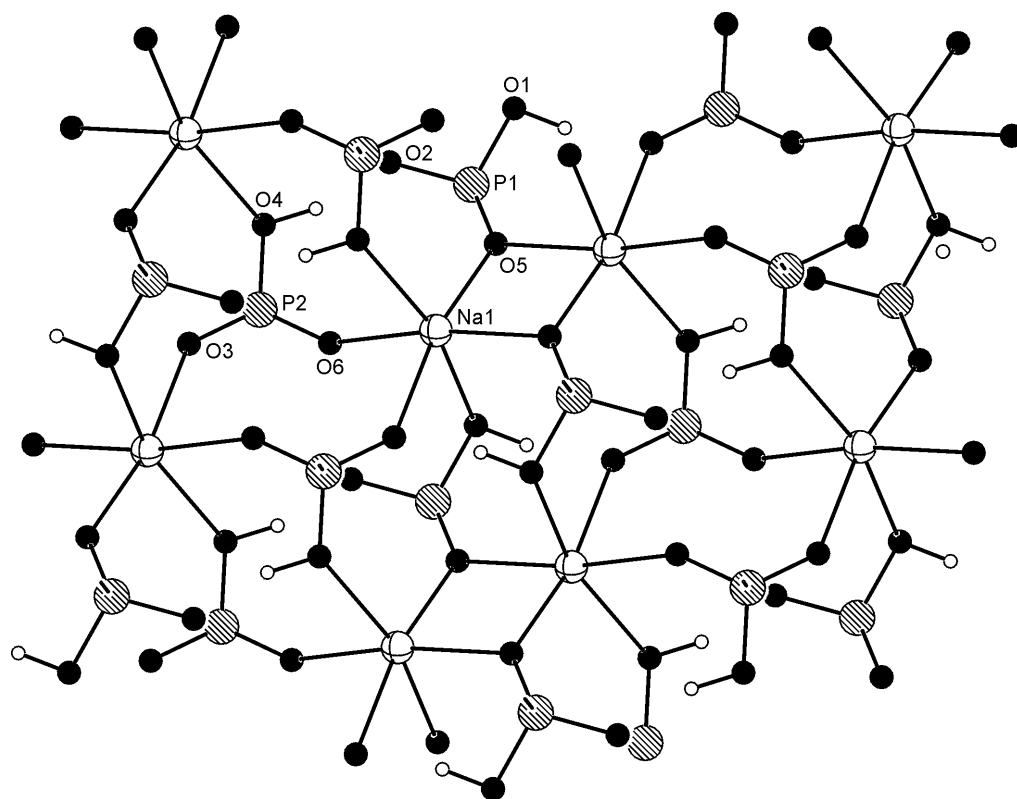
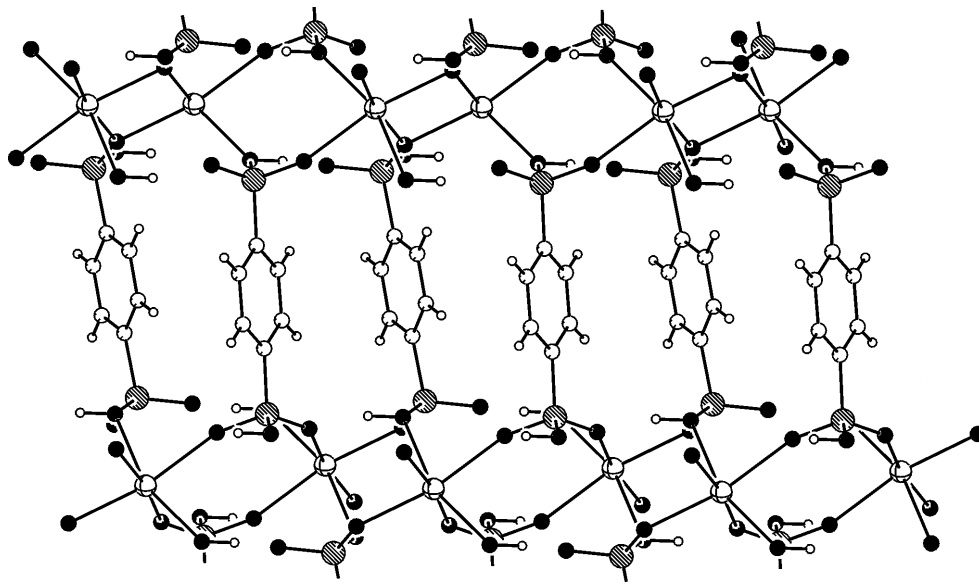


Figure 5



**Table 1** – Crystal data and structure refinement for Na[H<sub>3</sub>bdp]

Empirical formula	C <sub>6</sub> H <sub>7</sub> NaO <sub>6</sub> P <sub>2</sub>
Formula weight	260.05
Temperature / K	150(2)
Wavelength / Å	0.71073
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> / Å	5.7500(3)
<i>b</i> / Å	7.9180(5)
<i>c</i> / Å	10.4420(6)
$\alpha$ / °	80.398(3)
$\beta$ / °	76.844(4)
$\gamma$ / °	81.389(4)
Volume / Å <sup>3</sup>	453.34(5)
<i>Z</i>	2
Density (calculated)	1.905 g cm <sup>-3</sup>
Absorption coefficient / mm <sup>-1</sup>	0.531
Absorption correction	Multi-scan
<i>F</i> (000)	264
Crystal size / mm	0.30 × 0.25 × 0.20
Theta range for data collection / °	3.53 to 27.55
Index ranges	-7 ≤ <i>h</i> ≤ 7; -10 ≤ <i>k</i> ≤ 10; -13 ≤ <i>l</i> ≤ 13
Reflections collected	5552
Independent reflections	2011 [R(int) = 0.0798]
Reflections observed (>2σ)	1275
Data Completeness	0.958
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.905 and 0.814
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	2011 / 2 / 143
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.093
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0658 <i>wR</i> <sub>2</sub> = 0.1445
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1225 <i>wR</i> <sub>2</sub> = 0.1692
Largest diff. peak and hole / e Å <sup>-3</sup>	0.676 and -0.647

**Table 2** – Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for Na[H<sub>3</sub>bdp].

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Na(1)	−1931(4)	16880(3)	4897(2)	18(1)
P(1)	2175(3)	16267(2)	6943(2)	14(1)
P(2)	−3388(3)	20773(2)	6837(2)	14(1)
O(1)	4942(7)	15532(5)	6677(4)	18(1)
O(2)	2223(7)	18213(5)	6803(4)	17(1)
O(3)	−4856(7)	22345(5)	6333(4)	17(1)
O(4)	−643(7)	20946(5)	6475(4)	17(1)
O(5)	841(7)	15633(5)	6100(4)	16(1)
O(6)	−3649(7)	19120(5)	6289(4)	18(1)
C(1)	−1109(11)	14704(8)	9011(6)	19(1)
C(2)	966(11)	15534(8)	8668(6)	15(1)
C(3)	2068(11)	15832(8)	9658(6)	18(1)
C(4)	−6607(12)	20881(8)	9239(6)	21(1)
C(5)	−4255(11)	20365(7)	8617(6)	16(1)
C(6)	−2643(10)	19486(8)	9394(6)	17(1)