Sodiated β-Diphosphonate Carbanions: Characterization of the Tetrameric Cubane and the Hexameric Ladder Complexes $[\{(i\mathrm{PrO})_2\mathrm{P(O)}\}_2\mathrm{CHNa}]_4$ and $[\{(\mathrm{EtO})_2\mathrm{P(O)}\}_2\mathrm{CHNa}]_6$

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In memory of the late Dr. Ron Snaith, an independent thinker and spirit

Keywords: Alkali metals / Sodium / Cage compounds / Chelates / O Ligands

Reaction of the methylene diphosphonates $[(\mathrm{RO})_2\mathrm{P(O)}]_2\mathrm{CH}_2$, where R = *i*Pr or Et, with the metalating reagents NaH, *n*BuNa or the superbasic mixture *t*BuONa/*n*BuLi leads to monodeprotonation, and formation of the complexes $[\{(i\mathrm{PrO})_2\mathrm{P(O)}\}_2\mathrm{CHNa}]_4$ (**1**) and $[\{(\mathrm{EtO})_2\mathrm{P(O)}\}_2\mathrm{CHNa}]_6$ (**2**). Single-crystal X-ray diffraction studies revealed that **1** is tetrameric in the solid state, with a central $\mathrm{Na_4O_4}$ cubane core. Each metal in **1** is rendered pentacoordinate by binding to three μ_3-O phosphoryl bridges within the cubane, a chelating phosphoryl unit, and also a single *i*PrO group. In contrast, the structure of **2** is hexameric, and is composed of an unusual six-rung $\mathrm{Na_6O_6}$ ladder core. Three distinct sodium environments as well as μ_1-, μ_2- and μ_3-O phosphoryl units are present within the ladder framework. No Na–C interactions are present in either **1** or **2**. All of the six-membered NaOPCPO chelate rings display localized P=O double bonds and partial multiple bonding on the P–C–P linkages (mean P–O: 1.49 Å, and mean P–C: 1.69 Å). Ab initio molecular orbital calculations (HF/6–31G*) on model complexes indicate that the hexameric arrangement found for **2** is thermodynamically more stable than the cubane structure of **1**, in the absence of steric effects.

Introduction

Metallated β-diphosphonates, $[\{(\mathrm{RO})_2\mathrm{P(O)}\}_2\mathrm{CH}]^- \ \mathrm{M}^+$, have been receiving continuous attention since their first reported synthesis and subsequent usage in 1953 by Kosolapoff.[1] The presence of two stabilizing groups adjacent to a methylene unit of the parent neutral diphosphonate allows straightforward access to the carbanion by deprotonation using a variety of bases. In turn, these carbanions have proven highly useful in the formation of new carbon-carbon bonds, in particular via alkylation and also Horner−Wadsworth−Emmons-type reactions.[2−4] Interest in β-diphosphonates has resulted from their potent biological activity,[5] and they have found applications as agrochemicals,[6] and in medicinal chemistry.[7] In addition, they are used in several industrial processes including as detergents,[8] sequestrates[9] and as fixing agents in photography.[10]

From a coordination chemistry perspective, there are clear parallels between β-diphosphonates and the widely studied β-diketonates,[11] β-enaminoketonates[12] and β-diketiminates,[13] as metal binding ligands (Figure 1). However, relatively few solid-state studies of metallated β-diphosphonates have been reported, and these have generally been limited to transition metal complexes.[14,15] This is somewhat surprising considering that the vast majority of the reaction chemistry involving these ligands has been developed using their alkali metal salts as reactive intermediates.

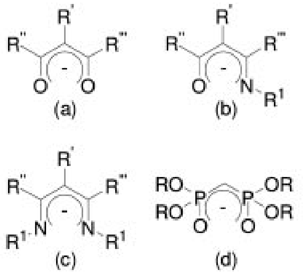

Figure 1. Generalized (a) β-diketonato, (b) β-enaminoketonato, (c) β-diketiminato, and (d) β-diphosphonato ligand frameworks

Of particular relevance to this study is the finding that the nature of the alkoxyl sidearms can strongly influence the reactivity of the β-diphosphonates.[3a] For example, whereas the tetraisopropyl esters react to give almost quantitative yields of *C*-alkylated esters, the methyl and ethyl esters give very low yields (>20%) under similar conditions.

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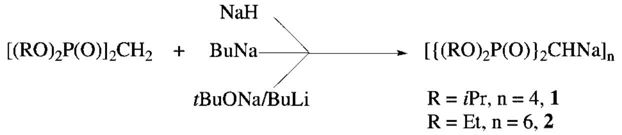
Moreover, the rates of alkylation are higher and less side products are formed when the larger alkoxy groups are used in these reactions. Such large and unexpected discrepancies between apparently very similar types of ligands still remains to be fully explained.[3b] In an effort to shed light on some of these issues we wish to report the single-crystal X-ray diffraction studies of the two sodium β-diphosphonate complexes $[\{(RO)_2P(O)\}_2CHNa]_n$, where R = *i*Pr and *n* = 4 (**1**) and where R = Et and *n* = 6 (**2**).

Results and Discussion

Synthetic and Solid-State Studies

Three alternative metalating reagents, NaH, *n*BuNa and *t*BuONa/*n*BuLi,[16] were reacted with hexane solutions of the parent phosphonates $[(RO)_2P(O)]_2CH_2$ [R = *i*Pr (**3**), Et (**4**)] in stoichiometries varying from 1:1 to 3.5:1 (Scheme 1). In all instances, the only crystalline material precipitated from the resulting solutions (or filtrates) was the monosodiated complex **1** or **2**, as determined by NMR spectroscopy. Previous spectroscopic studies of both **1** and **2** have been reported and will not be elaborated upon here.[3b,15] Single crystals suitable for X-ray diffraction were prepared for both complexes and their structures elucidated.



Scheme 1

The core of cage complex **1** is composed of four sodium and four oxygen centers arranged in an approximate cubane structure (Figure 2 and 3). In addition to the three Na−O contacts associated with the Na_4O_4 unit, each metal binds to one chelating phosphoryl group and also to a single *i*PrO group, rendering the sodium centers pentacoordinate. Hence, within **1**, each phosphonate forms five Na−O bonds and bridges between three different metal centers. Tetrameric cubane aggregates are comparatively common for sodium complexes, in particular when alkoxy or aryloxy ligands are employed.[17] The closest structural analog to **1** is the complex $[4\text{-Me-}2,6\text{-}(Me_2NCH_2)_2C_6H_2ONa]_4$, in which the "pincer phenolate" ligands coordinate to three sodium centers of a Na_4O_4 cubane.[18] However, the phenolate possesses approximate D_2 symmetry, whereas **1** is rendered closer to C_2 symmetry due to the "secondary" chelation of the *i*PrO groups.

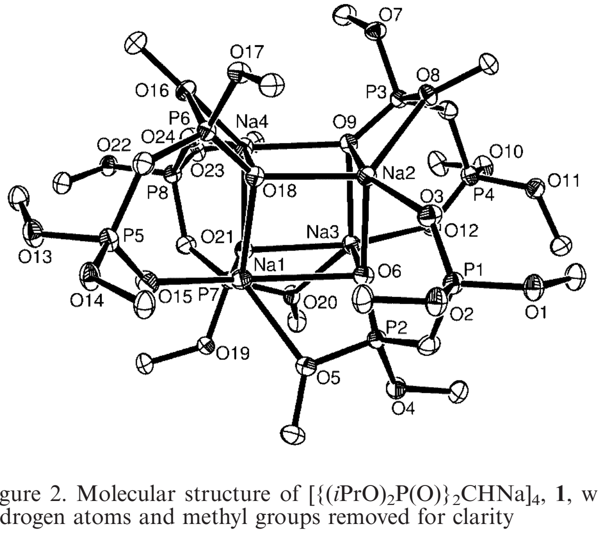


Figure 2. Molecular structure of $[\{(iPrO)_2P(O)\}_2CHNa]_4$, **1**, with hydrogen atoms and methyl groups removed for clarity

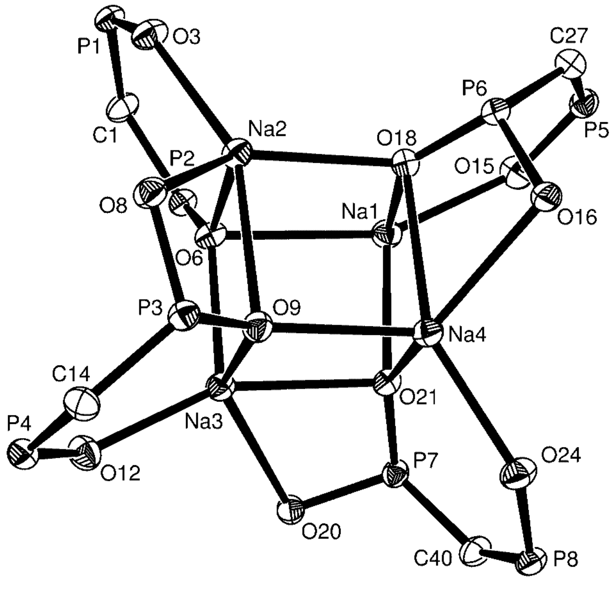


Figure 3. Core of the molecular structure of **1**, showing only the atoms involved with binding to the metal centers

There are no significant interactions present between the carbanionic carbons and the sodium centers, with all Na−C distances greater than 3.8 Å (see Table 1 for a list of pertinent bond lengths and angles). This bonding arrangement is commonly found for alkali metal complexes of α-stabilized carbanions, where the highly electropositive cations preferentially bind to the electronegative groups of the anion.[19,20] In fact, the phosphoryl unit has proved to be an excellent bridge for group 1 metals even when present as part of a neutral ligand.[21] For example, the crystal structure of the dimeric lithium chloride complex $[\{(iPrO)_2P(O)\}_2CH_2{\cdot}LiCl]_2$ contains a central Li_2O_2 ring and terminal chloride anions.[22]

Complex **2** was the focus of an early ^1H NMR spectroscopic study by Cotton in 1962.[15a] As part of these investigations cryoscopic measurements indicated that **2** is hexameric in benzene solution. However, at that time he did not speculate on the structure of the complex. Our X-ray diffraction studies of **2** confirm that it is indeed hexameric in the solid state and that it adopts a highly unusual centrosymmetric six-rung ladder framework (Figure 4 and 5, and Table 2). Each sodium is bound to five oxygen centers, however, three distinct metal and ligand environments are present within the structure. The three different types of sodium centers present can be related to their position within the ladder framework, i.e. rung-one, rung-two or rung-three. The three crystallographically unique phosphonate li-

Table 1. Selected bond lengths (Å) and angles (°) within **1**

Na(1)−O(15)	2.222 (1)	Na(1)−O(21)	2.286 (1)
Na(1)−O(18)	2.296 (1)	Na(1)−O(5)	2.344 (1)
Na(1)−O(6)	2.623 (1)	Na(2)−O(3)	2.235 (1)
Na(2)−O(6)	2.270 (1)	Na(2)−O(18)	2.346 (1)
Na(2)−O(8)	2.396 (1)	Na(2)−O(9)	2.534 (1)
Na(3)−O(12)	2.202 (1)	Na(3)−O(6)	2.298 (1)
Na(3)−O(9)	2.340 (1)	Na(3)−O(20)	2.424 (1)
Na(3)−O(21)	2.434 (1)	Na(4)−O(24)	2.221 (1)
Na(4)−O(9)	2.329 (1)	Na(4)−O(21)	2.333 (1)
Na(4)−O(16)	2.436 (1)	Na(4)−O(18)	2.480 (1)
P(1)−O(3)	1.485 (1)	P(2)−O(5)	1.612 (1)
P(2)−O(6)	1.490 (1)	P(3)−O(8)	1.608 (1)
P(3)−O(9)	1.500 (1)	P(4)−O(12)	1.484 (1)
P(5)−O(15)	1.480 (1)	P(6)−O(16)	1.617 (1)
P(6)−O(18)	1.502 (1)	P(7)−O(20)	1.616 (1)
P(7)−O(21)	1.495 (1)	P(8)−O(24)	1.482 (1)
P(2)−O(6)−Na(2)	131.22 (6)	P(2)−O(6)−Na(3)	131.79 (6)
Na(2)−O(6)−Na(3)	96.23 (4)	P(2)−O(6)−Na(1)	95.89 (5)
Na(2)−O(6)−Na(1)	90.24 (4)	Na(3)−O(6)−Na(1)	91.23 (4)
P(3)−O(9)−Na(4)	140.52 (6)	P(3)−O(9)−Na(3)	127.37 (6)
Na(4)−O(9)−Na(3)	90.60 (4)	P(3)−O(9)−Na(2)	97.59 (5)
Na(4)−O(9)−Na(2)	93.33 (4)	Na(3)−O(9)−Na(2)	88.41 (4)
P(6)−O(18)−Na(1)	128.43 (6)	P(6)−O(18)−Na(2)	132.38 (6)
Na(1)−O(18)−Na(2)	96.99 (4)	P(6)−O(18)−Na(4)	100.16 (5)
Na(1)−O(18)−Na(4)	87.83 (4)	Na(2)−O(18)−Na(4)	94.34 (4)
P(7)−O(21)−Na(1)	133.90 (6)	P(7)−O(21)−Na(4)	131.02 (6)
Na(1)−O(21)−Na(4)	91.71 (4)	P(7)−O(21)−Na(3)	100.58 (5)
Na(1)−O(21)−Na(3)	96.57 (4)	Na(4)−O(21)−Na(3)	88.20 (4)
O(15)−Na(1)−O(21)	118.87 (4)	O(15)−Na(1)−O(18)	88.65 (4)
O(21)−Na(1)−O(18)	92.67 (4)	O(15)−Na(1)−O(5)	111.65 (4)
O(21)−Na(1)−O(5)	116.66 (4)	O(18)−Na(1)−O(5)	124.90 (4)
O(15)−Na(1)−O(6)	156.01 (4)	O(21)−Na(1)−O(6)	83.98 (4)
O(18)−Na(1)−O(6)	82.69 (4)	O(5)−Na(1)−O(6)	57.79 (3)
O(3)−Na(2)−O(6)	87.08 (4)	O(3)−Na(2)−O(18)	120.46 (4)
O(6)−Na(2)−O(18)	89.80 (4)	O(3)−Na(2)−O(8)	104.85 (4)
O(6)−Na(2)−O(8)	122.96 (4)	O(18)−Na(2)−O(8)	125.53 (4)
O(3)−Na(2)−O(9)	153.15 (4)	O(6)−Na(2)−O(9)	85.59 (4)
O(18)−Na(2)−O(9)	85.32 (4)	O(8)−Na(2)−O(9)	59.04 (3)
O(12)−Na(3)−O(6)	116.61 (4)	O(12)−Na(3)−O(9)	89.11 (4)
O(6)−Na(3)−O(9)	89.68 (4)	O(12)−Na(3)−O(20)	103.88 (4)
O(6)−Na(3)−O(20)	123.49 (4)	O(9)−Na(3)−O(20)	130.19 (4)
O(12)−Na(3)−O(21)	155.12 (4)	O(6)−Na(3)−O(21)	88.19 (4)
O(9)−Na(3)−O(21)	89.14 (4)	O(20)−Na(3)−O(21)	59.69 (3)
O(24)−Na(4)−O(9)	121.50 (4)	O(24)−Na(4)−O(21)	86.72 (4)
O(9)−Na(4)−O(21)	91.89 (4)	O(24)−Na(4)−O(16)	104.48 (4)
O(9)−Na(4)−O(16)	120.73 (4)	O(21)−Na(4)−O(16)	128.30 (4)
O(24)−Na(4)−O(18)	151.03 (4)	O(9)−Na(4)−O(18)	86.96 (4)
O(21)−Na(4)−O(18)	87.00 (4)	O(16)−Na(4)−O(18)	59.08 (3)

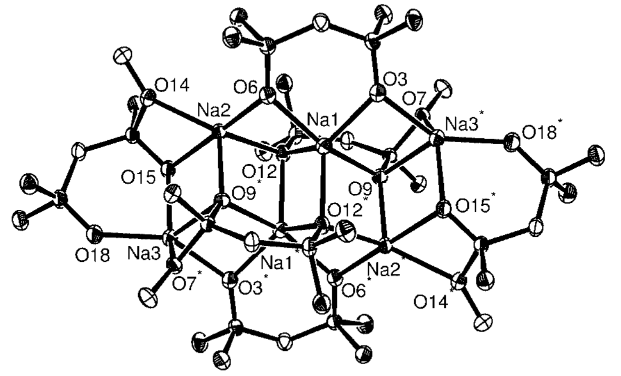


Figure 4. Molecular structure of $[\{(EtO)_2P(O)\}_2CHNa]_6$, **2**, with hydrogen atoms and ethyl groups (except for the α-Cs of the ethoxy groups involved in metal binding) removed for clarity

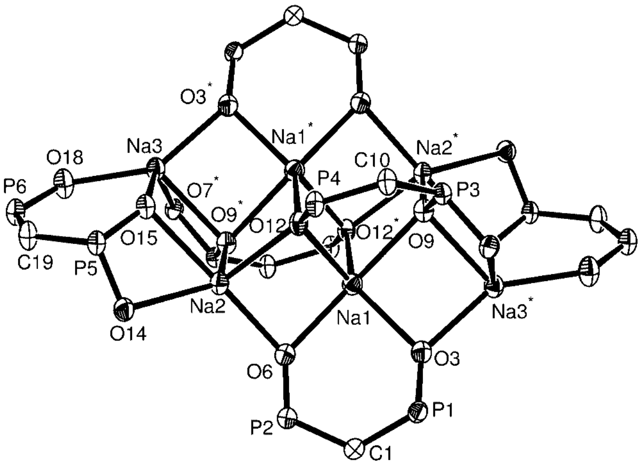


Figure 5. Alternative view of **2** showing the six-rung step ladder core, with only the atoms involved with binding to the metal centers displayed

gands within **2** can be distinguished by the number of Na−O contacts they make and the number of metals they bind to, i.e. (i) four Na−O contacts, and bridging two metals [terminal ligand carrying P(5) and P(6)]; (ii) four Na−O contacts, and bridging three metals [central ligand carrying P(1) and P(2)]; and (iii) seven Na−O contacts, and bridging five metals [central ligand carrying P(3) and P(4)]. The remarkable coordination flexibility of the β-diphosphonate ligands found within **1** and **2** is illustrated in Figure 6.

The coordination modes labeled (a), (b) and (d) in Figure 6 have not previously been observed for either neutral or anionic complexes of β-diphosphonates.[14] In fact, to the best of our knowledge, there are no reported examples of ester phosphonates that utilize an attached alkoxy unit as a ligating site to a metal center.[23] However, simple chelation by the phosphoryl units and also binding mode (c) in Figure 6 have previously been found for several transition metal and lanthanide complexes of β-diphosphonates.[14,24,25]

Although hexameric aggregates for sodium complexes have previously been characterized,[26] the six-rung ladder arrangement found in **2** is unusual. Most commonly, sodium hexamers adopt either double-stacked trimeric[27] or triple-stacked dimeric[28] structures (Figure 7). The closest structural analog to **2** is the imidophosphate complex $[\{(PhO)_2P(O)\}_2NNa]_6$, which has a similar Na_6O_6 ladder core but has only very long range interactions between the metals and the phenoxy groups (>2.8 Å).[29] A simple six-rung ladder aggregate of a group 1 complex has also been characterized, the lithium phosphane $[(Me_3Si)_2PLi]_6$.[30] Most commonly, four-rung (association of two dimers) or polymeric ladders are formed for these metal complexes.[31] The seminal work of Snaith and others in developing the ring-laddering and ring-stacking principles has been essential to our understanding of such systems.[32,33]

Looking in detail at the key geometric parameters within the cages **1** and **2**, the Na−O bond lengths vary over a

Table 2. Selected bond lengths (Å) and angles (°) within **2**

Na(1)−O(3)	2.268 (2)	Na(1)−O(6)	2.291 (2)
Na(1)−O(12)	2.374 (2)	Na(1)−O(12*)	2.386 (2)
Na(1)−O(9)	2.441 (2)	Na(2)−O(9*)	2.244 (2)
Na(2)−O(6)	2.291 (2)	Na(2)−O(12)	2.347 (2)
Na(2)−O(14)	2.396 (2)	Na(2)−O(15)	2.450 (2)
Na(3)−O(18)	2.225 (2)	Na(3)−O(15)	2.267 (2)
Na(3)−O(3*)	2.296 (2)	Na(3)−O(7*)	2.437 (2)
Na(3)−O(9*)	2.451 (2)	P(1)−O(3)	1.493 (2)
P(2)−O(6)	1.489 (2)	P(3)−O(7)	1.613 (2)
P(3)−O(9)	1.496 (2)	P(4)−O(12)	1.504 (1)
P(5)−O(14)	1.615 (2)	P(5)−O(15)	1.489 (2)
P(6)−O(18)	1.489 (2)		
P(3)−O(9)−Na(2*)	139.16 (9)	P(3)−O(9)−Na(1)	123.63 (8)
Na(2*)−O(9)−Na(1)	94.77 (6)	P(3)−O(9)−Na(3)*	100.65 (7)
Na(2*)−O(9)−Na(3*)	95.91 (6)	Na(1)−O(9)−Na(3)*	84.57 (5)
P(4)−O(12)−Na(2)	125.44 (8)	P(4)−O(12)−Na(1)	126.83 (8)
Na(2)−O(12)−Na(1)	85.02 (5)	P(4)−O(12)−Na(1)*	130.79 (9)
Na(2)−O(12)−Na(1)*	93.62 (6)	Na(1)−O(12)−Na(1)*	79.76 (5)
P(5)−O(15)−Na(3)	130.96 (9)	P(5)−O(15)−Na(2)	99.57 (8)
Na(3)−O(15)−Na(2)	95.37 (6)	O(10)−C(15)−C(16)	109.1 (3)
O(3)−Na(1)−O(6)	87.79 (6)	O(3)−Na(1)−O(12)	131.70 (7)
O(6)−Na(1)−O(12)	87.49 (6)	O(3)−Na(1)−O(12*)	123.61 (6)
O(6)−Na(1)−O(12)*	119.09 (6)	O(12)−Na(1)−O(12*)	100.24 (5)
O(3)−Na(1)−O(9)	88.22 (6)	O(6)−Na(1)−O(9)	155.94 (7)
O(12)−Na(1)−O(9)	77.60 (5)	O(12*)−Na(1)−O(9)	82.50 (5)
O(9*)−Na(2)−O(6)	94.75 (6)	O(9*)−Na(2)−O(12)	87.76 (6)
O(6)−Na(2)−O(12)	88.13 (6)	O(9*)−Na(2)−O(14)	120.65 (6)
O(6)−Na(2)−O(14)	119.21 (6)	O(12)−Na(2)−O(14)	135.57 (6)
O(9*)−Na(2)−O(15)	84.62 (6)	O(6)−Na(2)−O(15)	178.19 (7)
O(12)−Na(2)−O(15)	93.55 (6)	O(14)−Na(2)−O(15)	59.88 (5)
O(18)−Na(3)−O(15)	87.84 (6)	O(18)−Na(3)−O(3*)	145.54 (7)
O(15)−Na(3)−O(3*)	113.41 (6)	O(18)−Na(3)−O(7*)	90.11 (6)
O(15)−Na(3)−O(7*)	133.60 (6)	O(3*)−Na(3)−O(7*)	93.31 (6)
O(18)−Na(3)−O(9*)	122.99 (7)	O(15)−Na(3)−O(9*)	84.10 (6)
O(3*)−Na(3)−O(9*)	87.36 (6)	O(7*)−Na(3)−O(9*)	58.91 (5)

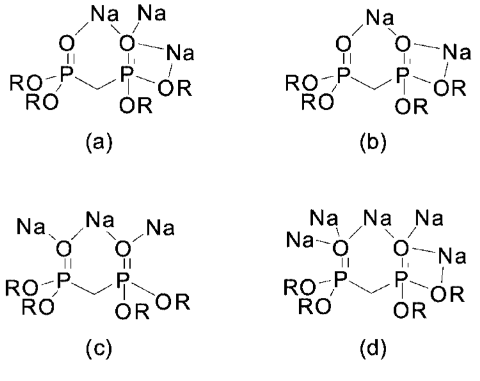


Figure 6. The different bonding modes found for the ligands in **1** (a), and **2** (b-d)

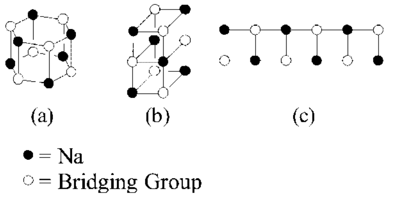


Figure 7. Hexameric aggregation states of sodium complexes: (a) double-stacked trimeric, (b) triple-stacked dimeric, (c) six-rung ladder

relatively wide range, from 2.202(1) to 2.623(1) Å. The shortest Na−O distances are associated with the chelating phosphoryl units, which ligate to a single sodium center [mean 2.220 Å in **1** and Na(3)−O(18): 2.225(2) Å in **2**]. Within the cubane framework of **1** each metal has two relatively short Na−O contacts (mean 2.312 Å) and a third longer contact (mean 2.518 Å) along the edges of the cube containing the chelating *i*PrO groups. The Na−O distance involving the *i*PrO groups lies in between these values at 2.400 Å (mean). A similar pattern is observed in **2**, where the Na−O distances lengthen, as expected, as the number of metals bridged by the phosphoryl increases (μ_1 to μ_3). The exceptions are the phosphoryl to sodium bonds Na(2)−O(15) at 2.450(2) and Na(3)−O(9*) at 2.451(2) Å, which are longer than expected. These elongated bonds are again associated with the four-membered NaOPO rings formed by the chelating OEt groups. Hence, the alkoxy-to-metal interactions in both **1** and **2** are relatively strong, and in fact the structures are significantly distorted in order to accommodated this mode of bonding.

The P=O distances lie in a relatively narrow range from 1.480(1) to 1.504(1) Å (mean 1.491 Å) over the two complexes, with the bonds lengthening as the number of metals bridged increases, i.e. μ_1, μ_2 and μ_3. These distances correspond well with those of previously characterized transition metal complexes of neutral β-diphosphonates,[14a,14b] and are consistent with localized P=O double bonds. The P−C distances in **1** and **2** range between 1.679(2) and 1.705(2) Å (mean 1.692 Å), and are substantially shorter than single P−C bonds in neutral β-diphosphonates (approximately 1.79 Å).[14] The shorter P−C bonds are associated with phosphoryl units that are involved in bridging multiple sodium centers. However, for the set of symmetrically bound ligands in **2** the P−C distances are identical, i.e. where P(1)−C(1) and P(2)−C(1) are both 1.694(2) Å. For comparison, the P−C distances in the ylides $Ph_3P=CH_2$ and mesityl$P=CPh_2$ are 1.67 and 1.69 Å respectively.[34] Overall, the bonding within the ligand backbone is best described as localized double bonding for the P=O units and delocalized partial multiple bonding over the P−C−P fragment.

It is also worth noting that although there are four different modes of ligation found for the β-diphosphonates in **1** and **2** (Figure 6), all the ligands contain synperiplanar phosphoryl units that chelate a metal center. It has previously been speculated that the reactivity differences between the anions of **3** and **4** may be due to the steric bulk of the isopropyl groups prohibiting coplanarity of the phosphoryl and carbanion groups.[3a] However, the six-membered OPCPONa chelate rings in both complexes are all similarly non-planar, with the range of the rms deviations from the planes being between 0.077 and 0.277 Å (mean 0.117). Again, these results are in agreement with the mostly localized bonding model described above.

Ab Initio Calculations

In an effort to determine the relative stabilities of the tetrameric and hexameric aggregations states found for **1** and **2** a set of ab initio calculations performed at the HF/

6−31G* level were undertaken on model systems.[35,36] The tetramethoxy complexes $[\{(MeO)_2P(O)\}_2CHNa]_4$ (**I**) and $[\{(MeO)_2P(O)\}_2CHNa]_6$ (**II**) were geometry optimized using the relevant crystal structure data for **1** and **2** as starting positions. The geometries of the calculated and experimentally determined structures are in excellent agreement, with differences of less than 0.01 Å (mean) for the bonds involving the metals. The key finding from these calculations was that the hexamer is more stable than the tetramer by 12.08 kcal mol^{-1} according to Equation (1) (or by 2.01 kcal mol^{-1} on a per-monomer basis).

$$3/2\ [\{(MeO)_2P(O)\}_2CHNa]_4 \xrightarrow{-12.08\ \mathrm{kcal\ mol^{-1}}} [\{(MeO)_2P(O)\}_2CHNa]_6 \qquad (1)$$

Considering that all the metals are pentacoordinate, and in the absence of any significant steric effects, the stability of the aggregates is most likely related to differences in the types of metal-to-ligand interactions present. In **I** each metal binds to four phosphoryl oxygen centers and a single *i*PrO group. Two of the metals in **II** also have this bonding pattern but the third metal bonds solely to five phosphoryl units. The increased coulombic component resulting from this bonding mode may, in turn, favor the formation of the hexamer. Furthermore, formation of the more open ladder framework will result in a decrease in ring strain compared with the cubane but without necessitating a reduction in the coordination number at the metals.

Conclusions

The main findings from this work are: (i) complexes **1** and **2** are the first examples of simple alkali metal derivatives of β-diphosphonates to be crystallographically characterized, and were found to form tetrameric cubane and hexameric ladder structures respectively, (ii) the β-diphosphonate ligands display four distinct ligation modes, three of which have not been described previously, (iii) the bonding within the β-diphosphonate backbones in both complexes are similar, and are composed of localized P=O double bonds and partial delocalization of the charge over the P−C−P units, and (iv) the hexameric six-rung ladder structure has been determined by calculations to be thermodynamically preferred over the tetrameric cubane structure for the model complexes **I** and **II**.

In summary, formation of the cubane **1** is most likely a consequence of the increased steric encumbrance of the attached alkoxy sidearms precluding the multiple bridging ligand environments required for construction of the hexameric framework found for **2**. Nevertheless, each individual β-diphosphonate ligand within **1** and **2** still adopts relatively similar local geometries, with synperiplanar phosphoryl units. Finally, in view of the different aggregation states found for **1** and **2**, it is unsurprising that there are differences in the reactivity of the β-diphosphonates. While it is true that the smaller tetrameric aggregate **1** has increased reactivity compared to the larger hexameric **2**, it may be too simplistic to attribute the reactivity differences solely to aggregate size.[37] Rather, the ability of the electrophile to approach the carbanion has to be considered. Also, the increased strain within the cubane compared to the ladder may lead to an attenuation in its reactivity.[38]

Experimental Section

General Procedures: All manipulations were carried out under a protective dinitrogen atmosphere using standard Schlenk techniques.[39] All glassware was flame-dried under vacuum before use. Hexane was purified by passage through copper-based catalyst and molecular sieves columns (Innovative Technology). The sodium hydride was supplied by Alfa Aesar as an oil dispersion, and was washed with dry hexane prior to use. The sodium butoxide was used as supplied by Acros Organics. *n*BuLi was purchased from Aldrich as a 1.6 M solution in hexane and was standardized by titration with salicylaldehyde phenylhydrazone directly before use.[40] Butylsodium (*n*BuNa) was prepared according to modified literature procedures and stored in an argon-filled glove box before use.[41] The phosphonate ligands $[(RO)_2P(O)]_2CH_2$ (R = *i*Pr, Et), **1** and **2**, were supplied by Lancaster and were purified by distillation from over calcium hydride and stored over 4 Å molecular sieves.

Although reactions using stoichiometries ranging between 1:1 and 3.5:1 of the three metalating reagents — NaH, *n*BuNa and *t*BuONa/*n*BuLi — and the parent phosphonates **3** and **4** were conducted, the only single crystals gleaned were the monodeprotonated complexes **1** or **2**. It has been reported previously that these ligands undergo cleavage in the presence of excess base and at elevated temperatures.[3g] Complexes **1** and **2** could be prepared in a rational manner as described below.

Synthesis of 1 and 2: The parent phosphonate (**3** or **4**, 10 mmol) was dissolved in 5 mL of hexane and the solution cooled to 0 °C. *n*BuNa (10 mmol) was added to the reaction mixture via a solids addition tube over several minutes, and the resulting mixture was slowly warmed to room temperature. The mixture was heated gently, filtered and the filtrate was stored at −45 °C. After one day, small colorless blocks of the complexes **1** or **2** were precipitated. Formation of **1** and **2** was confirmed by their ^1H and ^{13}C NMR spectra, which were in agreement with previously published data.[3b,15a]

1: Yield = 52%. ^1H NMR (300 MHz, [D$_5$]pyridine, 25 °C): δ = 1.05 (t, $^2J_{H,P}$ = 6.3 Hz, 1 H, PCH), 1.33 (d, $^3J_{H,H}$ = 6.0 Hz, 12 H, CH_3), 1.37 (d, $^3J_{H,H}$ = 6.0 Hz, 12 H, CH_3), 4.80 (m, 4 H, CH) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, [D$_5$]pyridine, 25 °C): δ = 12.8 (t, $^1J_{C,P}$ = 213.4 Hz, CP), 24.7 (t, $J_{C,P}$ = 4.5 Hz, CH_3), 24.9 (t, $J_{C,P}$ = 4.5 Hz, CH_3), 67.7 (s, CH) ppm.

2: Yield = 46%. ^1H NMR (300 MHz, [D$_5$]pyridine, 25 °C): δ = 1.13 (t, $^2J_{H,P}$ = 6.4 Hz, 1 H, PCH), 1.28 (t, $^3J_{H,H}$ = 7.0 Hz, 12 H, CH_3), 4.16 (m, 8 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, [D$_5$]pyridine, 25 °C): δ = 10.2 (t, $^1J_{C,P}$ = 217.1 Hz, CP), 17.1 (t, $J_{C,P}$ = 3.7 Hz, CH_3), 60.4 (s, CH_2) ppm.

X-ray Structure Determination: Table 3 contains details of the data collection. In both cases the crystalline sample was placed in inert oil, mounted on a glass pin, and transferred to the cold N_2 gas stream of the diffractometer. Crystal data were collected and integrated using a Bruker Apex system, with graphite monochromated Mo-K_α (λ = 0.71073 Å) radiation at 100 K. The structures were solved by direct methods using SHELXS-97 and refined using SHELXL-97.[42] Non-hydrogen atoms were found by successive full-matrix least-squares refinement on F^2 and refined with anisotropic thermal parameters. All hydrogen atoms were placed at idealized positions and a riding model was applied, with fixed thermal parameters [uij = $1.2U$ij(eq) for the atom to which they are bonded]. The asymmetric unit contains one tetrameric cage for **1** and one half of a hexameric cage for **2**.

Table 3. Crystallographic data for **1** and **2**

Compound	**1**	**2**
Formula	$C_{52}H_{116}Na_4O_{24}P_8$	$C_{54}H_{126}Na_6O_{36}P_{12}$
Molecular weight	1465.17	1861.13
Temperature (K)	100 (2)	100 (2)
Crystal System	Monoclinic	Triclinic
Space Group	$P2_1/c$	$P\bar{1}$
a (Å)	7.5772 (10)	12.4357 (9)
b (Å)	21.6203 (13)	13.9757 (11)
c (Å)	12.8075 (15)	14.1637 (11)
α (°)	90	73.5970 (10)
β (°)	90.8460 (10)	73.3650 (10)
γ (°)	90	83.0830 (10)
Volume (Å^3)	7812.9 (8)	2260.5 (3)
Z	4	1
Density (calcd.) (Mg/m^3)	1.246	1.367
Absorption Coefficient (mm^{-1})	0.266	0.331
F(000)	3136	984
Crystal Size (mm)	0.3 × 0.1 × 0.1	0.4 × 0.3 × 0.3
Reflections Collected/ unique	82239/19424 [*R*(int) = 0.0559]	24137/11236 [*R*(int) = 0.0244]
Data/Restraints/Parameters	5574/0/277	11236/0/487
Goodness-of-fit on F^2	1.023	1.043
R_1	0.0345	0.0503
wR_1	0.0967	0.1467

CCDC-209651 (**1**) and -209652 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1233/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Computational Details: The Gaussian 98 series of programs were used for the calculations.[35] No symmetry constraints were imposed and the molecules were allowed to freely optimize at the HF/6−31G* level using the relevant crystal structure data for **1** and **2** as starting geometries.[36] Frequency analysis was used to ensure that true minima were located. The total energies for **I** and **II** are 5958.4381 and 8937.6764 Hartrees respectively.

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