# A Planar $Zn_4P_4$ Ring in the First Structurally Characterised Zinc Diorganophosphide: $[Zn_2(Bu^t{}_2P)_2(OH)(\mu\text{-}OH)]_2$

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The first structurally characterised zinc diorganophosphide, $[Zn_2(Bu^t{}_2P)_2(OH)(\mu\text{-}OH)]_2$, is a tetramer with a novel eight-membered planar ring structure.

Although diorganophosphide derivatives of zinc of composition $(R_2PZnR)_x$[1] and $(R_2P)_2Zn$[2] have been known for some time they are poorly characterised materials which appear to be polymeric in many cases. Since we have been successful in isolating and characterising diorganophido and arsenido derivatives of the s, p, and d block elements using bulky phosphido and arsenido ligands,[3] we attempted the synthesis of zinc derivatives *via* the interaction of $ZnCl_2$ with 2 equiv. of $Bu^t{}_2PLi$.[4] Under strictly anhydrous conditions we were unable to isolate a pure compound using either toluene or tetrahydrofuran (THF) as the solvent. However, the presence of adventitious $H_2O$ in our hexane during work-up permitted the isolation and structural characterisation of $[Zn_2(Bu^t{}_2P)_2(OH)(\mu\text{-}OH)]_2$ (**1**) in low yield. To our knowledge (**1**) is the first structurally characterised diorganophosphide of zinc.

The interaction of anhydrous zinc(II) chloride with 2 equiv. of $LiBu^t{}_2P$ in toluene at −78 °C produces no apparent change. However, subsequent work-up of the off-white suspension at room temperature by evaporation to dryness, extraction into hexane, and crystallisation from toluene at −20 °C yields large clear prisms of (**1**) in variable yield. We have so far only been able to prepare (**1**) in low yield *via* this somewhat serendipitous route. Characterisation of (**1**) is also hampered since, once crystallized, it is either insoluble or decomposes rapidly in more polar solvents such as $CH_2Cl_2$ or MeOH. The molecular structure of (**1**) was therefore determined unequivocally by a single crystal *X*-ray diffraction study.†

A view of the molecule is shown in Figure 1. The molecular geometry consists of tetrameric units in which the $Zn_4P_4$ framework is essentially planar and forms an eight-membered ring. Two central zinc atoms [Zn(1)–Zn(1′)] are four-co-ordinate and bridged by two OH units [O(1)–O(1′)] which lie above and below the $Zn_4P_4$ plane. There is a crystallographically imposed centre of inversion at the midpoint of Zn(1)–Zn(1′). The remaining two zinc atoms, Zn(2) and Zn(2′), each bear a terminal OH unit and are examples of rarely found three-co-ordinate zinc.[5]

The Zn(1)–O(1) and Zn(1)–O(1′) distances are notably longer than analogous distances reported recently for the interesting zinc(II) hydroxide dimer $[(tpsi)Zn(OH)]_2$[5] [1.899(9) Å] [tpsi = tris(dimethylphenylsilyl)methyl]. The reasons for the anomalous Zn–O distances may be steric in

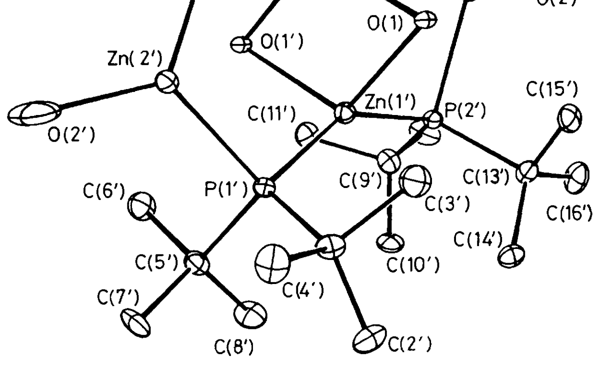

**Figure 1.** ORTEP view of (**1**); key bond lengths (Å) and angles (°) not found in text: Zn(1)–P(1) 2.368(4), Zn(1)–P(2) 2.369(3), Zn(1)–O(1) 2.32(2), Zn(2)–P(1) 2.424(4), Zn(2)–O(2) 2.30(2), Zn(2)–P(2′) 2.428(2), Zn(1)–O(1′) 2.33(2), P(1)–Zn(1)–P(2) 147.2(2), P(1)–Zn(1)–O(1) 97.8(4), P(2)–Zn(1)–O(1) 101.3(3), P(1)–Zn(2)–O(2) 123.6(7), Zn(1)–P(1)–Zn(2) 105.6(2), Zn(1)–O(1′)–Zn(1′) 71.4(4), O(1′)–Zn(1′)–O(1) 108.6(4).

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† *Crystal data* for (**1**): $C_{46}H_{92}O_4P_4Zn_4$, $M$ = 1094.62, triclinic, space group $P\bar{1}$ (No. 2), $a$ = 12.072(3), $b$ = 15.812(3), $c$ = 8.884(4) Å, $\alpha$ = 91.53(2), $\beta$ = 111.01(3), $\gamma$ = 110.73(2)°, $U$ = 1457.5(5) Å$^3$, $D_c$ = 1.247 g cm$^{-3}$, $Z$ = 1, $\mu$ = 18.10 cm$^{-1}$, $\lambda(\text{Mo-}K_\alpha)$ = 0.71073 Å. Refinement of 2024 reflections [$I > 3\sigma(I)$] out of 4556 unique measured gave final $R$ and $R_w$ values of 0.071 and 0.079 respectively. Data/parameter ratio = 9.076. Data were collected on an Enraf-Nonius CAD-4 diffractometer at 23 ± 2 °C. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

nature. The Zn–P distances (av. 2.397 Å) compare favourably with the sum of the covalent radii of $Zn^{II}$ and $P^{II}$ (2.30 Å).[6] The planar structure of (**1**) is in distinct contrast to those of other Zn tetrameric species which have been structurally characterised. It seems reasonable to assume that the planarity is due at least in part to the presence of the bulky $Bu^t$ groups of the phosphido ligands. Lastly, an intriguing structural feature is the close approach of the two central zinc atoms [Zn(1) · · · Zn(1′) = 2.713(5) Å]. Although one cannot view this formally as a normal bond, it suggests a weak van der Waals attraction between the two Zn atoms. It can be compared with the Zn–Zn distance found in zinc metal (2.665 Å).[7]

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