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# Metal-binding Motifs of Alkyl and Aryl Phosphinates; Versatile Mono and Polynucleating Ligands

Innis Carson, Mary R Healy, Euan D Doidge, Jason B Love, Carole A Morrison and Peter A Tasker\*

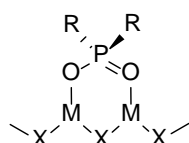
## Abstract

An analysis of 552 structures of metal complexes of alkyl and arylphosphinates in the Cambridge Crystallographic Database shows that the phosphinate ligating group is remarkably versatile and is able to adopt ten different binding motifs in both mono- and polynuclear complexes in which an individual phosphinate group can bind to up to five metal atoms. The majority of both homo- and heteroleptic complexes contain M-O-PR<sub>2</sub>-O-M units in oligomeric and polymeric structures. In many heteroleptic complexes ligands containing hydrogen bond donors form strong bonding interactions with the phosphinate, generating *pseudo*chelated structures. Similar *pseudo*chelates, <sup>-</sup>O-PR<sub>2</sub>=O<sup>-</sup>H-O-PR<sub>2</sub>=O, are formed when both a phosphinate and its parent phosphinic acid are coordinated to a single metal atom. Such structures feature also in the solution chemistry involved in metal extraction processes using phosphinate ligands. As might be expected, many of the binding motifs found in phosphinate complexes are similar to those in carboxylate complexes but there are fewer examples of phosphinates being used to form metal organic frameworks.

## Introduction & Background

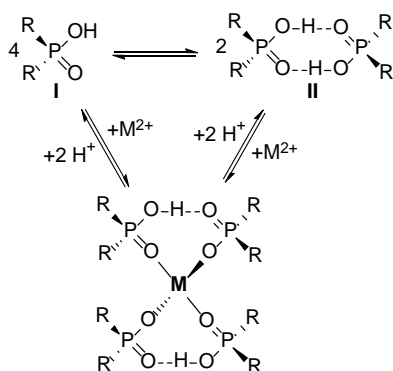
Dialkyl and diarylphosphinates (R<sub>2</sub>PO<sub>2</sub><sup>-</sup>) are versatile ligands which find applications in widely differing areas. The facility with which they form polynuclear complexes allows them to recognise and bind strongly to arrays of metal atoms in the *surfaces* of minerals or lightly corroded metals (Figure 1) and they have been used extensively in surface engineering as corrosion inhibitors [1,2], lubricant

additives [3–6], mineral flotation agents [7–10] and as adhesion promoters [11,12]. Dialkylphosphinates have also been used to obtain high loadings of metals into polymers to increase flame retardancy [13]. It is also possible to form metal organic frameworks (MOFs) from polyphosphinic acids [14,15].



**Figure 1.** A binding motif which allows phosphinate-attachment to a mineral surface.

Their ability to form stable complexes in *solution*, particularly with borderline or hard metal cations, is exploited in extractive hydrometallurgy using solvent extraction to achieve the concentration and separation of particular metals [16,17]. The propensity of phosphinic acid proligands to form dimers in the water-immiscible solvents used in these processes (usually high boiling hydrocarbons), retaining inter-ligand hydrogen bonding in metal complexes (Figure 1) [18,19] and their tendency to form polynuclear complexes [20] at high metal loadings makes the determination of the structures of the complexes formed challenging. It is even more difficult to determine the structures formed at the surfaces of metals and minerals. In order to define what structures are possible and to provide input structures for computational modelling of the complexes formed in solution and at interfaces, we have analysed the solid-state structures of phosphinates deposited in the Cambridge Structural Database [21].

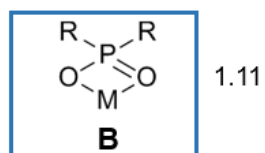
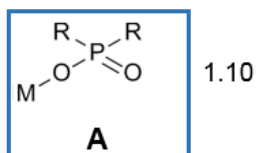


**Figure 2.** Monomeric and dimeric forms of phosphinic acid proligands, LH (see also Figure 27), showing the retention of interligand H-bonding on formation of a tetrahedral complex,  $[ML_2(LH)_2]$ , with a M(II) [18,19,22].

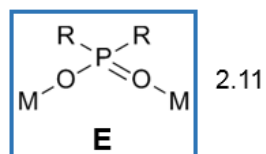
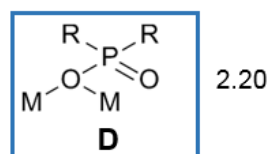
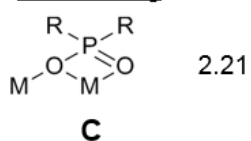
The aim of this review of solid-state structures is to identify the preferred types of coordination shown by *simple* phosphinates in which the metal-binding mode is not constrained by the group being present in chelating units containing other types of donor groups. For this reason complexes containing multidentate/macrocyclic ligands and polyphosphinic acids were not included in the structural analysis. In the discussion of the various structural motifs found in the CSD, we focus on complexes of phosphinates containing at least one P-C (alkyl or aryl) bonds. Complexes of mono alkyl or aryl phosphinates  $RXPO_2^-$  with X = H are included but not those where X is an electronegative atom because this is likely to influence the mode of coordination of the O=P-O<sup>-</sup> unit in “simple” organophosphinates.

Given the versatility of phosphinate ligands, a number of different binding modes might be expected. The more obvious motifs involving monomeric phosphinate ligands ( $R_2PO_2^-$ ) are shown in Figure 3 and those for the monoanionic dimeric form ( $R_2PO_2H$ ,  $R_2PO_2^-$  - see Figure 2) are displayed in Figure 4.

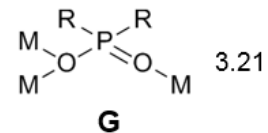
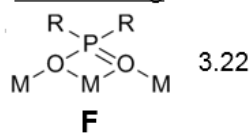
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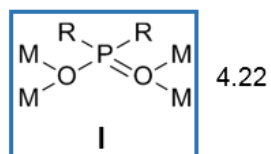
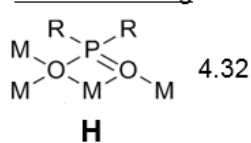
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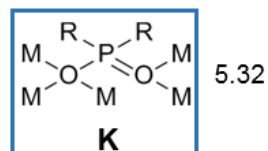
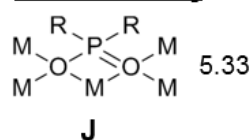
### Trinucleating



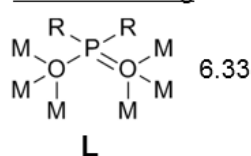
### Tetranucleating



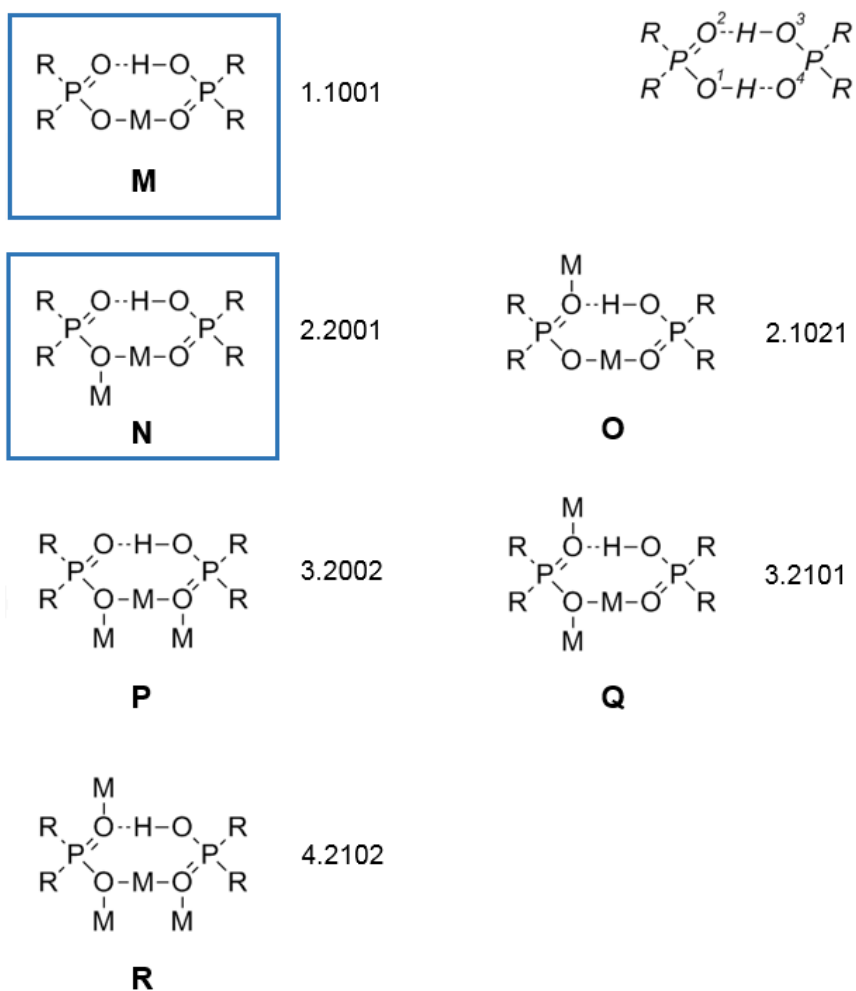
### Pentanucleating



### Hexanucleating

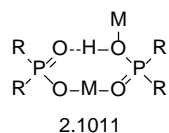


**Figure 3.** Twelve different coordination modes of phosphinate ligands classified using the Harris notation [23]: In “n.xy”, “n” defines the number of metals bound to each ligand and the subsequent two digits, “x” and “y”, indicate how many metal atoms are bonded to each of the two oxygen atoms.



**Figure 4.** Six different coordination modes of dimeric forms of phosphinate ligands in which an intraligand H-bond is retained (see Figure 2). In these motifs “n.wxyz” is used to define the total number of metals bound (“n”) and “w”, “x”, “y” and “z” indicate how many metal atoms are bonded to each of oxygen atoms labelled “1”, “2”, “3” and “4” in the proligand shown at the top-right of the figure.

Structural motifs in which a metal ion is bound to an oxygen atom carrying a proton (an example is shown in Figure 5) are not included in Figures 3 and 4. It is unlikely that a phosphinate oxygen atom can bond effectively to *both* a proton and a metal cation and indeed no example of such a motif is found in the CSD.

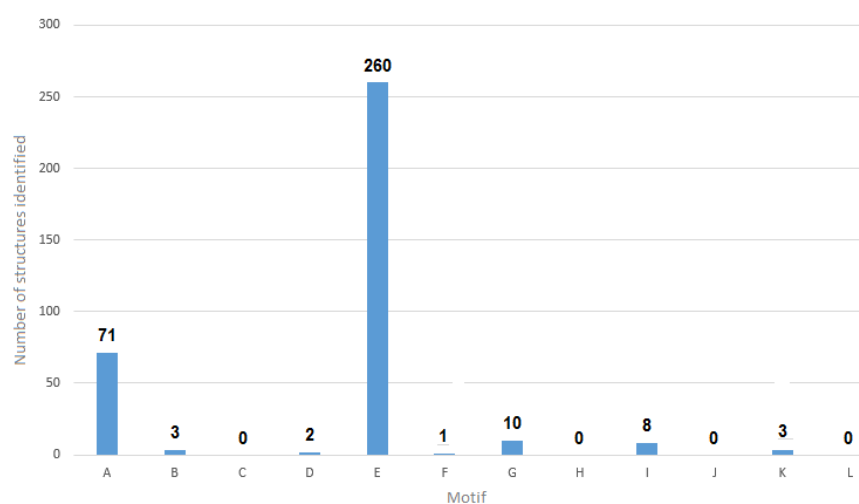


**Figure 5.** Motifs of this type, in which a metal ion is bound to an oxygen atom carrying a proton, are not found in the CSD.

#### Occurrences of the various motifs in the CSD

Ten of the eighteen possible modes of coordination shown in Figures 3 and 4, those enclosed in boxes, were found in the 552 metal phosphinate complexes retrieved from the Cambridge Structural Database (CSD).

By far the most common binding mode is the dinucleating form, 2.11, marked as motif **E** in Figure 3. This is present in both discrete molecular complexes and in oligomeric and polymeric structures. The number of occurrences of each motif is displayed in Figure 6 for simple complexes. As many complexes containing phosphinate ligands display more than one binding mode, the total number of occurrences (358) exceeds the number of complexes analysed or discussed in this review which is limited to “simple complexes” which do not contain the phosphinate group in a chelating unit or in a polyphosphinate (see introduction). A list showing which CSD entries contain the different binding motifs is provided in the appendix at the end of the review.



**Figure 6.** The number of occurrences in the CSD of the different phosphinate binding motifs **A** to **L** in “simple complexes” (see introduction) which do not contain the phosphinate group in a chelating unit or in a polyphosphinate. Motifs **M** and **N** involving dimeric forms of the ligand are included in counts of complexes containing their components, **A** and **D**.

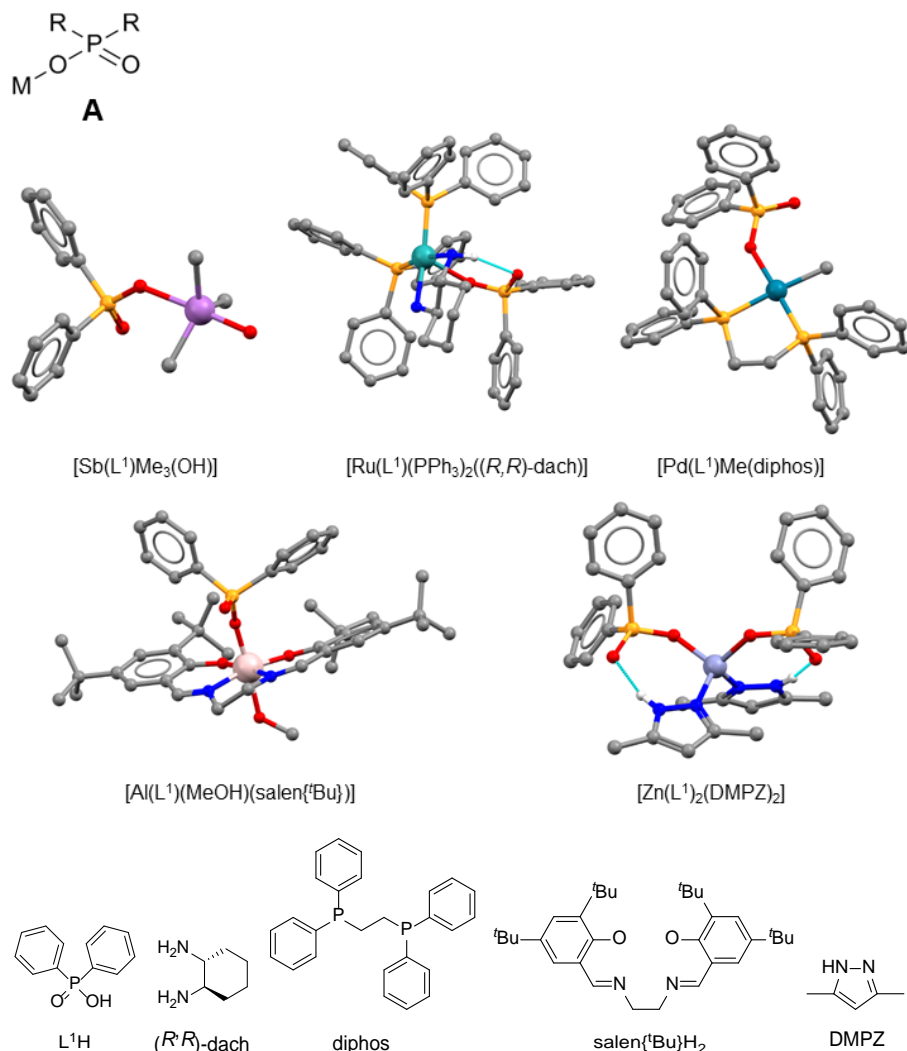
The binding mode 1.1001 (motif **M**, Figure 4) contains an 8-membered pseudochelate ring and is thought to be a common form in solution [18,19,22] when phosphinic acids are used in metal-recovery by solvent extraction. However, it is not a particularly common occurrence in the solid-state structures recorded in the CSD. This may in part be a consequence of the reagents most commonly used in solvent extraction, which have large multiply branched alkyl groups to enhance solubility in hydrocarbons, but which in turn militates against the isolation of crystalline solids needed for single crystal X-ray structure determination. Consequently, this motif may be under-represented in the data set.

The phosphinate binding mode found in solid-state structures depends greatly on the nature of the metal in the complex and on what other ligands are present. Structures are reviewed below in order of increasing size and complexity, considering differences between homo- and heteroleptic complexes and any unusual features imposed by having the phosphinate as part of a multidentate ligand.

#### **Mononucleating motifs:**

The simplest mode of binding, using the monodentate (mononucleating) 1.10 motif (**A** in Figure 3), is commonly found in complexes which also contain phosphinates with binding motifs that bridge metal ions, resulting in the formation of polynuclear complexes. This scenario, along with motif **A** H-bonding to another neutral phosphinic acid (motif 1.1001, **M** in Figure 4), are discussed below. Mononuclear complexes containing *only* motif **A** are found exclusively in heteroleptic complexes such as [Sb(L<sup>1</sup>)Me<sub>3</sub>(OH)] [24]<sup>-NEYWAP</sup>, [Ru(L<sup>1</sup>)<sub>2</sub>X] [25]<sup>-FIMMUK</sup>, [Pd(L<sup>1</sup>)Me(diphos)] [26]<sup>-IQEMIB</sup>, [Zn(L<sup>1</sup>)<sub>2</sub>(DMPZ)<sub>2</sub>] [27]<sup>XAXKAJ</sup> and [Al(L<sup>1</sup>)(MeOH)(salen<sup>t</sup>Bu))] [28]<sup>-YGRIM</sup> (Figure 7). The monodentate coordination expressed by motif **A** places minimal restrictions on the coordination geometry adopted by the metal, and consequently a wide range of geometries around the metal (including trigonal bipyramidal, square pyramidal, square planar, tetrahedral and octahedral structures, Figure 7) is observed.

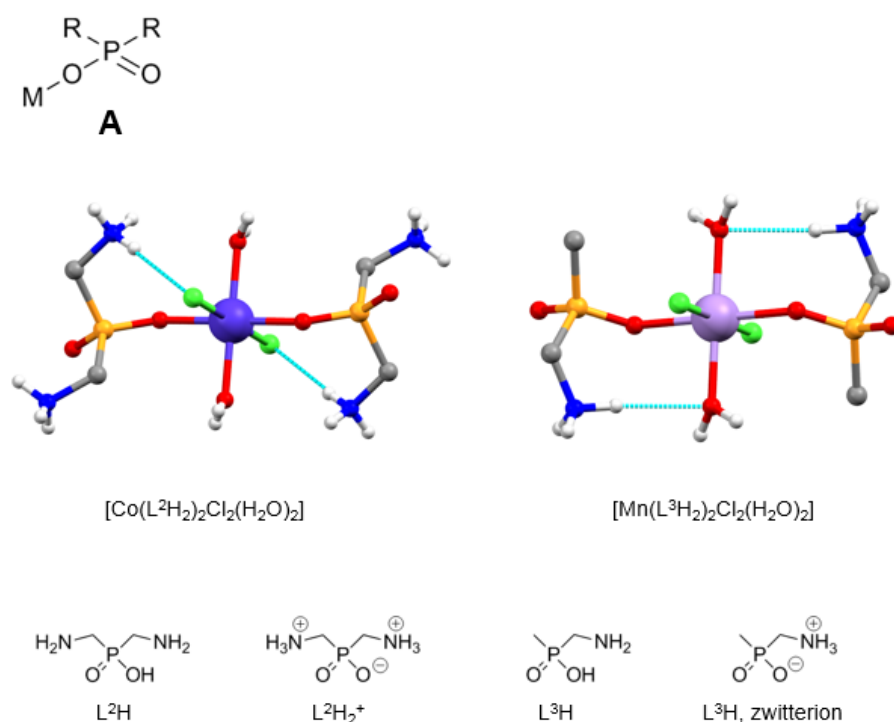




**Figure 7.** Heteroleptic complexes  $[\text{Sb}(\text{L}^1)\text{Me}_3(\text{OH})]$  [24]<sup>-NEYWAP</sup>,  $[\text{Ru}(\text{L}^1)(\text{Ph}_3\text{P})_2((R,R)\text{-dach})]$  [25]<sup>-FIMMUK $\alpha$</sup> ,  $[\text{Pd}(\text{L}^1)\text{Me}(\text{diphos})]$  [26]<sup>-IQEMIB</sup>,  $[\text{Zn}(\text{L}^1)_2(\text{DMPZ})_2]$  [27]<sup>-XAXKAJ</sup> and  $[\text{Al}(\text{L}^1)(\text{MeOH})(\text{salen}^{\text{tBu}})]$  [28]<sup>-YEGRIM</sup> containing the monodentate motif **A**. The structures of  $\text{L}^1\text{H}$ ,  $(R,R)\text{-dach}$ ,  $\text{diphos}$ ,  $\text{DMPZ}$  and  $\text{salen}^{\text{tBu}}\text{H}_2$  are also shown. <sup>a</sup>Only one of the two crystallographically independent complexes is shown.

The 1.10 motif (**A**) is also found in unusual heteroleptic complexes  $[\text{M}(\text{L}^2\text{H}_2)_2\text{Cl}_2(\text{H}_2\text{O})_2]\text{Cl}_2$  [29]<sup>-ALEJQQ</sup>, ALEJUW, ALEKAD, ALEKUX, ALELAE, ALELIM which contain a cationic form of the proligand  $\text{L}^2\text{H}$  in which the two pendant amine groups are protonated (see Figure 8). Complexes were isolated from the reaction of

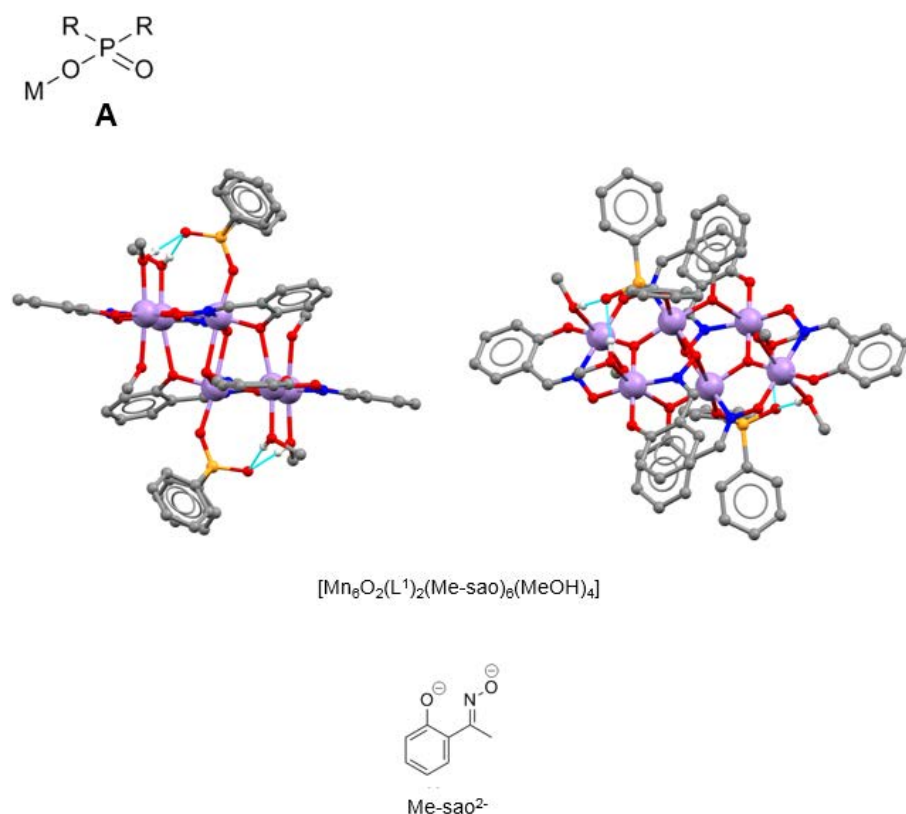
bis(aminomethyl)phosphinic acid hydrochloride with metal(II) chloride hydrate in 6 M HCl, and have chloride ions in both the inner- and outer-coordination spheres, charge-balancing the ammonium groups, see for example  $[\text{Co}(\text{L}^2\text{H}_2)_2\text{Cl}_2(\text{H}_2\text{O})_2]\text{Cl}_2$  (Figure 8). Similar structures are formed by Ca(II), Mn(II), Ni(II), Zn(II) and Cd(II). The complex  $[\text{Mn}(\text{L}^3\text{H})_2\text{Cl}_2(\text{H}_2\text{O})_2]$  [30]<sup>-AMP<sub>MNC</sub></sup> formed by the monoamino-substituted proligand (Figure 8) is charge-neutral because the ligand  $\text{L}^3\text{H}$  is present as a zwitterion.



**Figure 8.** The mononuclear octahedral complexes  $[\text{Co}(\text{L}^2\text{H}_2)_2\text{Cl}_2(\text{H}_2\text{O})_2]$  [29]<sup>-ALEKAD</sup> and  $[\text{Mn}(\text{L}^3\text{H})_2\text{Cl}_2(\text{H}_2\text{O})_2]$  [30]<sup>-AMP<sub>MNC</sub></sup> formed by the protonated zwitterionic form of  $\text{L}^2\text{H}$  ( $\text{L}^2\text{H}_2^+$  inset) and the zwitterionic form of  $\text{L}^3\text{H}$  (also inset) in which the phosphinate groups display motif **A**.

A feature of motif **A** binding is that an oxygen atom is available as a hydrogen-bond acceptor, providing a source of stability in heteroleptic complexes containing ligands with appropriately positioned H-bond donors. Examples are the amine N-H to phosphinate H-bond in  $[\text{Ru}(\text{L}^1)(\text{Ph}_3\text{P})_2(\text{dach})]$  [25]<sup>-FIMMUK</sup> and the pyrazole N-H to phosphinate H-bonds in  $[\text{Zn}(\text{L}^1)_2(\text{DMPZ})_2]$  [27]<sup>-XAXKAJ</sup> (Figure 7). The hexanuclear manganese cluster  $[\text{Mn}_6\text{O}_2(\text{L}^1)_2(\text{Me-sao})_6(\text{MeOH})_4]$  [31]<sup>-PUWKEY</sup> contains only two (motif **A**)

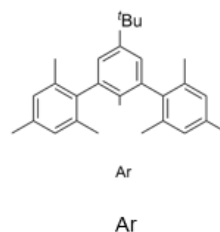
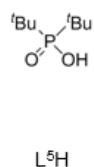
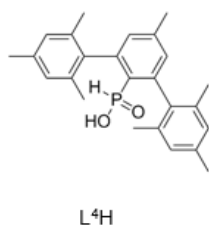
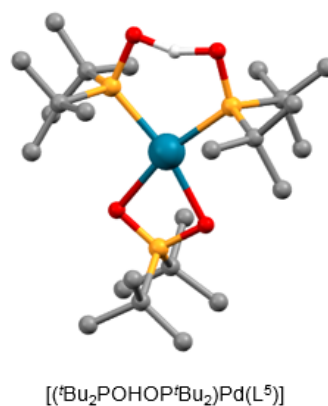
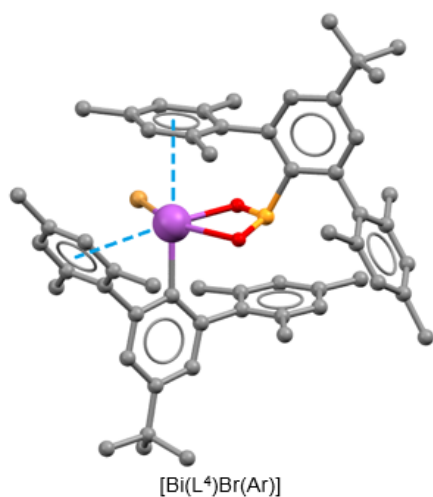
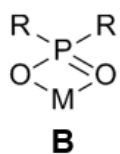
diphenyl phosphinate ligands (Figure 9), and these are each strongly H-bonded to two coordinated methanol molecules. Together these define the caps on the two  $Mn_3O$  triangles of the  $Mn_6$  cluster, which is otherwise typical of those showing single molecular magnetism [32,33]. Further examples of intracomplex H-bonding associated with other phosphinate binding motifs are shown below. These include the only examples of homoleptic complexes containing motif **A**.



**Figure 9.** The hexanuclear manganese complex  $[Mn_6O_2(L^1)_2(Me-sao)_6(MeOH)_4]$  [31]<sup>PUWKEY</sup> showing the H-bonding of the diphenyl phosphinate (motif **A**) to two capping methanol molecules. The complex is shown from two perspectives, and the structure of Me-sao<sup>2-</sup> is also defined.

The other possible mononucleating mode for phosphinate ligands is the chelating 1.11 motif, **B**. Only three examples of this binding mode are found in the CSD, suggesting that formation of 4-membered metal chelates is much less favourable than other modes of coordination. An unusual feature of

$[\text{Bi}(\text{L}^4)\text{Br}(\text{Ar})]$  [34]<sup>-DOXJAC</sup> (Figure 10), is that the bismuth achieves a coordination number of six by forming two  $\pi$  contacts with mesitylene groups present in both the phosphinate and aryl ligands. The complex  $[(^t\text{Bu}_2\text{POHOP}^t\text{Bu}_2)\text{Pd}(\text{L}^5)]$  [35]<sup>-LANSAU</sup> (Figure 10) was prepared by oxygenation of  $[\{\text{Pd}(\mu\text{-P}^t\text{Bu}_2)(\text{P}^t\text{Bu}_2\text{H})\}_2]$ , which resulted in formation of di(*t*-butyl)phosphinate and di(*t*-butyl)phosphinite ligands. The latter are bound to the palladium atom via their phosphorus atoms and their oxygen atoms are linked by a proton. The only other structure in the CSD containing the motif **B** is a very unusual Pd(II) complex in which the phosphinate is part of phosphacyclopentadienyl group which is also  $\pi$ -bonded to a  $\text{Mn}(\text{CO})_3$  unit [36]<sup>-HEFBID</sup>.



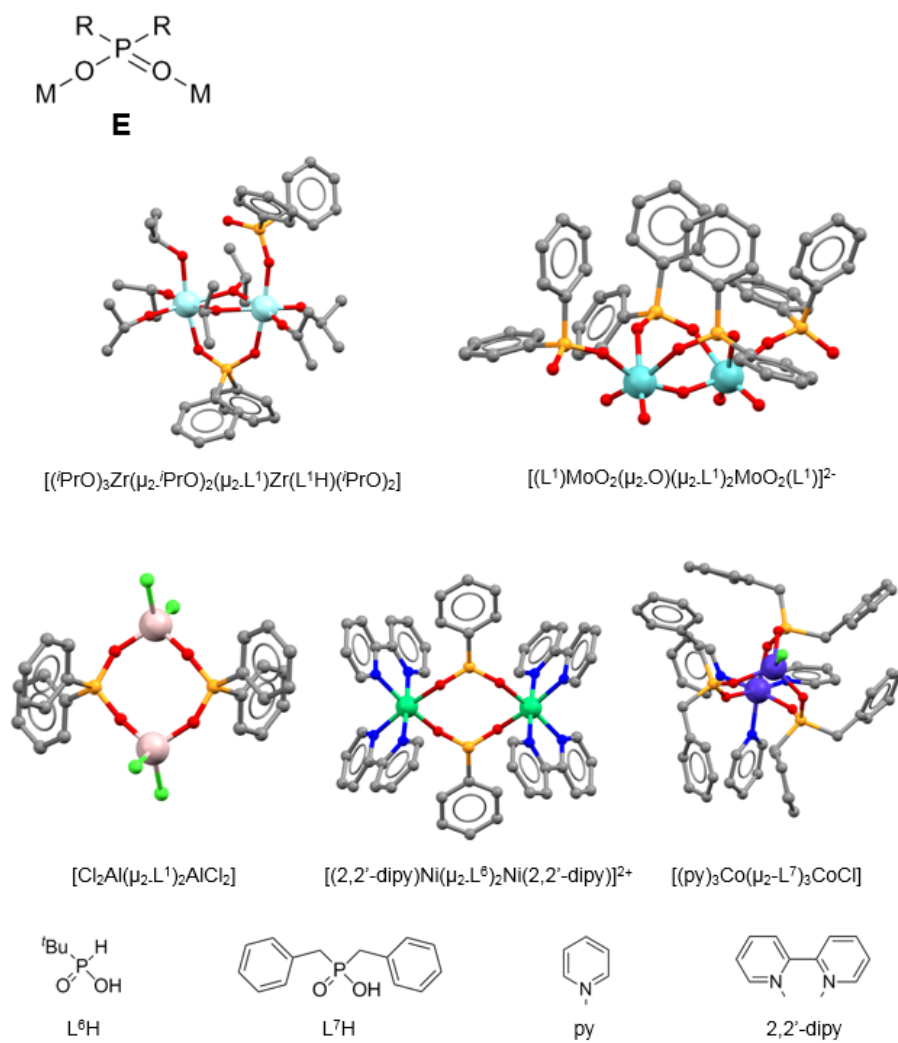
**Figure 10.** Structures of mononuclear complexes containing a motif **B** phosphinate:  $[\text{Bi}(\text{L}^4)\text{Br}(\text{Ar})]$  [34]<sup>DOXJAC</sup> showing the two  $\pi$ -contacts to mesitylene groups which lead to a coordination number of six and  $[(^t\text{Bu}_2\text{POHOP}^t\text{Bu}_2)\text{Pd}(\text{L}^5)]$  [35]<sup>LANSAU</sup> which contains an unusual phosphinite ligand. The structures of Ar, L<sup>4</sup>H and L<sup>5</sup>H are also shown.

#### Dinucleating motifs:

The only example of the 2.20 phosphinate motif (**D** in Figure 3) is part of the more complicated motif **N** (Figure 4) in which it is hydrogen-bonded to a neutral phosphinic acid ligand [37]<sup>KAMXUS</sup>. This structure and examples of the related motif **M** are discussed in more detail below.

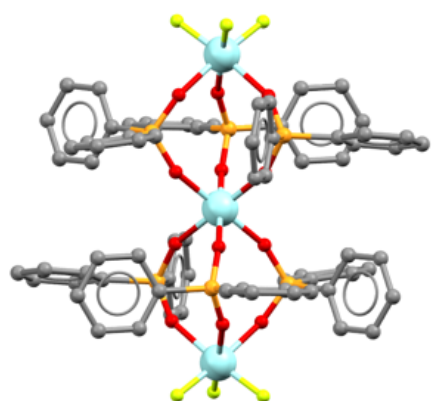
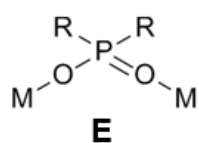
The symmetrical  $\mu_2$ -bridging motif 2.11 (**E** in Figure 3) is the most prevalent in the CSD and is present in many clusters and polymers and networks showing a wide range of structural forms.

The only dinuclear complex in the CSD which contains just *one* motif **E** bridge between two metal atoms is  $[(^t\text{PrO})_3\text{Zr}(\mu_2\text{-}^t\text{PrO})_2(\mu_2\text{-L}^1)\text{Zr}(\text{L}^1\text{H})(^t\text{PrO})_2]$  [38]<sup>QAXWOB</sup>. This is atypical of dinuclear structures, being unsymmetrical and having a neutral phosphinic acid coordinated to one of the zirconium atoms (L<sup>1</sup>H, in Figure 11). This allows both Zr(IV) atoms to have an octahedral O<sub>6</sub> donor set in a neutral complex. Figure 11 also provides examples of dinuclear complexes which contain *two* ( $[\text{Al}_2(\text{L}^1)_2\text{Cl}_4]$  [39]<sup>VELMEE</sup> and  $[\text{Ni}_2(\text{L}^5)_2(2,2'\text{-dipy})_2]^{2+}$  [40]<sup>ABEQUJ</sup>) and *three* ( $[\text{Co}_2(\text{L}^6)_3\text{Cl}]$  [41]<sup>GAWPEB</sup>) phosphinate bridges between the metal atoms. In  $[\text{Al}_2(\text{L}^1)_2\text{Cl}_4]$  [39]<sup>VELMEE</sup> and  $[\text{Ni}_2(\text{L}^5)_2(2,2'\text{-dipy})_2]^{2+}$  [40]<sup>ABEQUJ</sup>, the metal atoms show tetrahedral and octahedral geometry respectively, whilst  $[\text{Co}_2(\text{L}^6)_3\text{Cl}]$  [41]<sup>GAWPEB</sup>, is more unusual in having cobalt(II) atoms with different coordination numbers (six and four) at either end of the dinuclear complex. Octahedral O<sub>6</sub>-donor sets are present in the Mo(VI) complex  $[(\text{L}^1)\text{MoO}_2(\mu_2\text{-O})(\mu_2\text{-L}^1)_2\text{MoO}_2(\text{L}^1)]^{2-}$  [42]<sup>TIXKEQ</sup> which has an O<sup>2-</sup> and two diphenylphosphinate anions bridging the MoO<sub>2</sub><sup>2+</sup> units and a monodentate (motif **A**) phosphinate completing the coordination sphere of each metal.

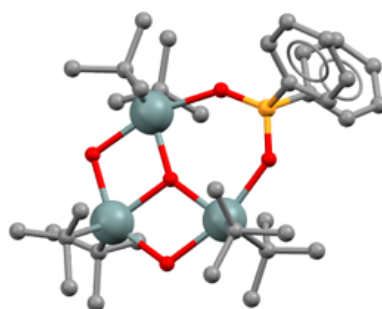


**Figure 11.** Examples of structures of dinuclear complexes which contain *one*,  $[(^i\text{PrO})_3\text{Zr}(\mu_2\text{-}^i\text{PrO})_2(\mu_2\text{-L}^1)\text{Zr}(\text{L}^1\text{H})(^i\text{PrO})_2]$  [38]<sup>-QAXWOB</sup>, *two*,  $[(\text{L}^1)\text{MoO}_2(\mu_2\text{-O})(\mu_2\text{-L}^1)_2\text{MoO}_2(\text{L}^1)]^{2-}$  [42]<sup>-TIXKEQ</sup> and  $[\text{Cl}_2\text{Al}(\mu_2\text{-L}^1)_2\text{AlCl}_2]$ , [39]<sup>-VELMEE</sup>  $[(2,2'\text{-dipy})\text{Ni}(\mu_2\text{-L}^6)_2\text{Ni}(2,2'\text{-dipy})]^{2+}$  [40]<sup>-ABEQI</sup>, and *three*,  $[(\text{py})_3\text{Co}(\mu_2\text{-L}^7)_3\text{CoCl}]$  [41]<sup>-GAWPEB</sup>, bridging, motif E, phosphinates.

The two trinuclear complexes shown in Figure 12 have very different structures. In  $[F_3Zr(\mu_2-L^1)_3Zr(\mu_2-L^1)_3ZrF_3]$  [43]<sup>-XEPRUF</sup>, the triple (motif E) phosphinate bridges between pairs of zirconium atoms defining a linear structure, whilst in  $[(\mu_3-O)(\mu_2-OH)_2(\mu_2-L^1)(^tBu_2Sn)_3]^+$  [44]<sup>-IPACUX</sup>, the single  $\mu_2-L^1$  unit fulfils a similar role to the two bridging hydroxides to complete a metallocycle.



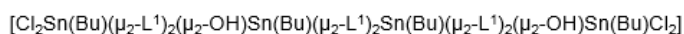
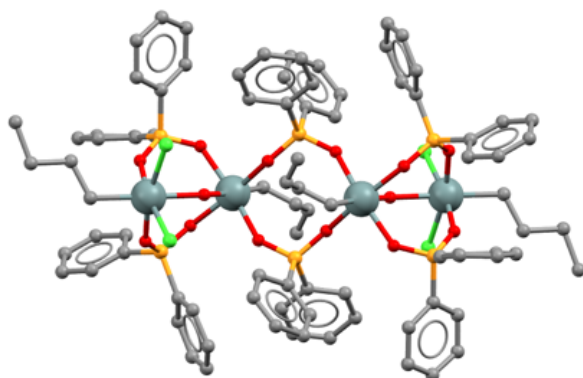
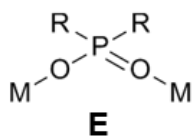
$[F_3Zr(\mu_2-L^1)_3Zr(\mu_2-L^1)_3ZrF_3]$



$[(\mu_3-O)(\mu_2-OH)_2(\mu_2-L^1)(^tBu_2Sn)_3]^+$

**Figure 12.** Linear and metallocyclic trinuclear complexes  $[F_3Zr(\mu_2-L^1)_3Zr(\mu_2-L^1)_3ZrF_3]$  [43]<sup>-XEPRUF</sup>, and  $[(\mu_3-O)(\mu_2-OH)_2(\mu_2-L^1)(^tBu_2Sn)_3]^+$  [44]<sup>-IPACUX</sup>, which contain bridging (motif E) phosphinate units, and in the tin complex also a  $\mu_3-O$  and two  $\mu_2-OH$  bridges.

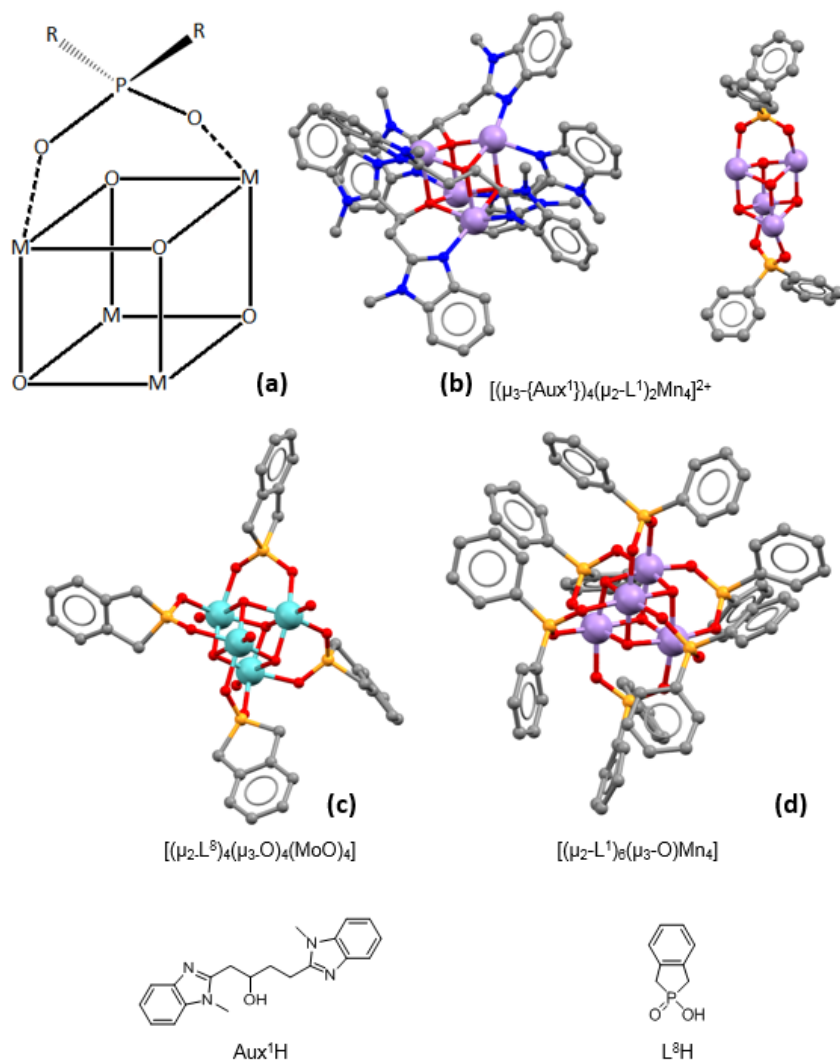
In the tetranuclear tin complex  $[Cl_2Sn(Bu)(\mu_2-L^1)_2(\mu_2-OH)Sn(Bu)(\mu_2-L^1)_2Sn(Bu)(\mu_2-L^1)_2(\mu_2-OH)Sn(Bu)Cl_2]$  [45]<sup>-JUMKOR</sup> (Figure 13) the outer pairs of *n*-butyltin units are linked by two motif E diphenyl phosphinates and a bridging hydroxide ion whilst the central pair has the just two motif E diphenyl phosphinate bridges. Such an arrangement allows all four tin atoms to adopt similarly distorted octahedral geometries.



**Figure 13.** The linear zig-zag structure of the tetranuclear complex  $[\text{Cl}_2\text{Sn}(\text{Bu})(\mu_2\text{-L}^1)_2(\mu_2\text{-OH})\text{Sn}(\text{Bu})(\mu_2\text{-L}^1)_2\text{Sn}(\text{Bu})(\mu_2\text{-L}^1)_2(\mu_2\text{-OH})\text{Sn}(\text{Bu})\text{Cl}_2]$  [45]<sup>JUMKOR</sup>

The dinucleating motif **E** is also found in a large variety of cluster structures. These frequently contain single atom  $\mu_2\text{-O}$  and  $\mu_3\text{-O}$  linkages between the metal atoms. In cubane-like structures (**a** in Figure 14), examples can be found where two, four or six of the  $\text{O}\cdots\text{O}$  diagonals of the cube are bridged by phosphinates. There are only a few complexes containing just two diagonal-spanning phosphinates. These have complicated structures in which bulky bidentate or tridentate ligands compete with phosphinate for the diagonal sites as in  $[(\mu_3\text{-}\{\text{Aux}^1\})_4(\mu_2\text{-L}^1)_2\text{Mn}_4]^{2+}$  [46]<sup>NOJMUW</sup>. The occurrence of a variety of different ligands on the faces of the  $\text{M}_4\text{O}_4$  cubes makes it difficult to display such structures. In Figure 14 the two diphenylphosphinates are located on opposite faces of the  $\text{Mn}(\text{II})_4\text{O}_4$  cube (see **b**). The four tridentate 2-bis(1-methyl-1H-benzimidazol-2-yl)ethanol ligands provide the  $\mu_3\text{-O}$  corners of the cube and two of their imidazole nitrogen donor atoms form  $\text{Mn}\cdots\text{Mn}$  bridges of the faces of the cube (see **b**).



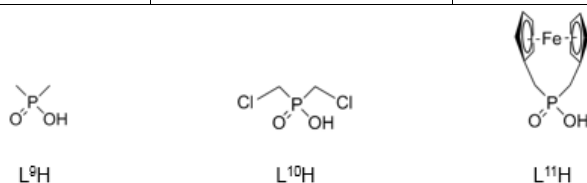


**Figure 14.** The  $M_4O_4$ -unit present in cubane-like structures (a) and examples of complexes in which *two, four* or *six* phosphinates (motif E) span the diagonals of the faces in  $[(\mu_2\text{-}L^1)_2(\mu_3\text{-}\{Aux^1\})_4Mn_4]^{2+}$  [46]<sup>-NOJMUW<sup>a</sup></sup>, (b)  $[(\mu_2\text{-}L^8)_4(\mu_3\text{-}O)_4(MoO)_4]$  [47]<sup>-AQOJAS</sup> (c) and  $[(\mu_2\text{-}L^1)_6(\mu_3\text{-}O)_4Mn_4]$  [48]<sup>-NAYSUB<sup>b</sup></sup> (d). <sup>a</sup>The dispositions of the four auxiliary ligands and the two phosphinates are shown separately (left and right). <sup>b</sup>Four crystallographically independent molecules have very similar structures.

The tetranuclear complex  $[(\mu_2\text{-}L^7)_4(\mu_3\text{-}O)_4(MoO)_4]$  [47]<sup>-AQOJAS</sup> shown in Figure 14 has four of the cubane faces occupied by the phosphinate anion, 2,3-dihydro-1H-isophosphindole-2,2-dioxidate. The two

“bare” faces have Mo...Mo distances (see Figure 15) consistent with metal-metal bonding and the presence of oxo groups on all the metal atoms allows these to be assigned as Mo(V). This feature is common to seven other phosphinato-Mo<sub>4</sub>O<sub>4</sub> clusters [47]<sup>a</sup>-AQOHUK, AQOJAS, [49]<sup>c</sup>-GACTAI, [50]<sup>c</sup>-KAPTOM, KAPTUS, [51]<sup>c</sup>-NOBZAG, [52]<sup>c</sup>-RAMXIN, RAXMIN01, [53]<sup>c</sup>-SEBLAM, [54]<sup>c</sup>-YAYXED. Despite having considerably different phosphinate ligands bridging the pairs of molybdenum atoms, the unbridged diagonals on the cubane unit have short Mo...Mo contacts distances falling in a fairly narrow range: 2.609 – 2.647 Å (see Figure 15).

CSD code	Composition	Short Mo...Mo contact distances/Å
AQOHUK	$[(\mu_2\text{-L}^9)_4(\mu_3\text{-O})_4(\text{MoO})_4]$	2.629(2) & 2.624(2)
AQOJAS	$[(\mu_2\text{-L}^8)_4(\mu_3\text{-O})_4(\text{MoO})_4]^c$	2.6433(7) & 2.6263(9)
GACTAI	$[(\mu_2\text{-L}^1)_4(\mu_3\text{-O})_4(\text{MoO})_4]^c$	2.6395(6) <sup>a</sup>
KAPTOM	$[(\mu_2\text{-L}^7)_4(\mu_3\text{-O})_4(\text{MoO})_4]^c$	2.6091(5) & 2.6158(5) <sup>b</sup> 2.6197(5) & 2.6266(5)
KAPTUS	$[(\mu_2\text{-L}^7)_4(\mu_3\text{-O})_4(\text{MoO})_4]^c$	2.6261(4)
NOBZAG	$[(\mu_2\text{-L}^{10})_4(\mu_3\text{-O})_4(\text{MoO})_4]$	2.6230(9) & 2.6237(9)
RAMXIN01	$[(\mu_2\text{-L}^1)_4(\mu_3\text{-O})_4(\text{MoO})_4]^c$	2.642(2) & 2.639(2) <sup>b</sup> 2.647(2) & 2.640(2)
SEBLAM	$[(\mu_2\text{-L}^1)_4(\mu_3\text{-O})_4(\text{MoO})_4]^c$	2.635(6) & 2.635(4)
YAYXED	$[(\mu_2\text{-L}^{11})_4(\mu_3\text{-O})_4(\text{MoO})_4]$	2.6110 & 2.6362



**Figure 15.** The two short Mo...Mo distances in the Mo<sub>4</sub>O<sub>4</sub> cubane tetraphosphinate complexes AQOHUK [47], AQOJAS [47], GACTAI [49], KAPTOM [50], KAPTUS [50], NOBZAG [51], RAMXIN [52], RAMXIN01 [52], SEBLAM [53], YAYXED [54] and the structures of the phosphinate ligands present.

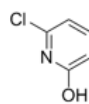
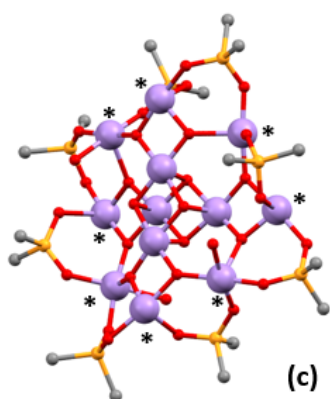
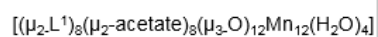
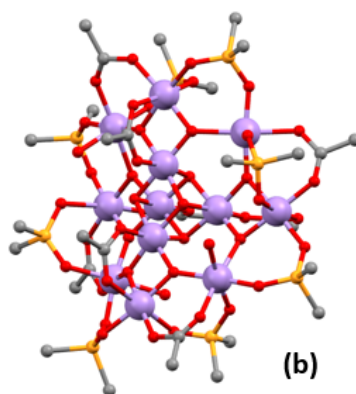
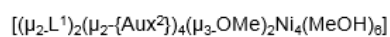
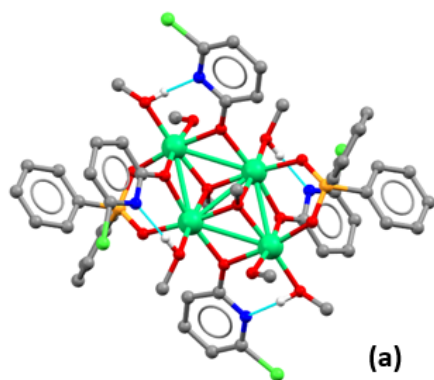
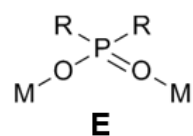
<sup>a</sup>The two Mo...Mo distances are symmetry related. <sup>b</sup>These structures have two cubane molecules per asymmetric unit. <sup>c</sup>Structures of L<sup>1</sup>H, L<sup>7</sup>H and L<sup>8</sup>H are given in Figures 7, 11 and 14.

In the tetranuclear manganese complex,  $[(\mu_2\text{-L}^1)_6(\mu_3\text{-O})_4\text{Mn}_4]$ , (**d** in Figure 14) the Mn...Mn distances are too long to be associated with any significant bonding interactions. An analysis of the structure led the authors to conclude that the compound is an example of a “mixed-valence Mn(III)/Mn(IV)

complex" [48]<sup>NAYSUB</sup>. Complexes of this type are of considerable interest as they have the potential to act as single molecule magnets (see below).

There are several other cubane-type and related phosphinate structures in the CSD and examples of some of the variations of structures of this type are shown in Figure 16. In the tetranuclear complex  $[(\mu_2\text{-L}^1)_2(\mu_2\text{-}\{\text{Aux}^2\})_4(\mu_3\text{-OME})_2\text{Ni}_4(\text{MeOH})_6]$  [21]<sup>FIQKUM</sup> (**a**) the Ni atoms lie in a plane. Two phosphinates provide motif **E** bridges between pairs of Ni atoms and the two methoxide groups provide  $\mu_3$ -linkages as in the cubane structures described above, but there are also four  $\mu_2$ -6-chloropyridin-2-olate units linking pairs of nickel atoms.

The  $\text{Mn}_{12}$  cluster  $[(\mu_2\text{-L}^1)_8(\mu_2\text{-acetate})_8(\mu_3\text{-O})_{12}\text{Mn}_{12}(\text{H}_2\text{O})_4]$  [55]<sup>VOQGAJ</sup> (**b**) is part of the family of Mn clusters which functions as single molecule magnets [56,57] and was studied to establish how replacement of carboxylate groups by phosphinate in previously well studied SMMs, e.g.  $[(\mu_2\text{-carboxylate})_8(\mu_3\text{-O})_{12}\text{Mn}_{12}(\text{H}_2\text{O})_4]$ , influence their structures and magnetic properties. The central  $\text{Mn}^{\text{IV}}_4\text{O}_4$  cubane core is retained and the remaining eight  $\text{Mn}^{\text{III}}$  atoms (marked with an asterisk in Figure 16) are attached *via*  $\mu_3$ -oxo bridges either to single Mn atoms on the vertices or to pairs of Mn atoms, spanning faces as shown in the diagram (c). The phosphinate and acetate ligands provide motif **E** bridges between pairs of Mn atoms but only the acetate ligands form bridges from the  $\text{Mn}^{\text{IV}}$  atoms of the cubane core to peripheral  $\text{Mn}^{\text{III}}$  atoms. The shorter  $\text{Mn}^{\text{IV}}\dots\text{Mn}^{\text{III}}$  distances (2.76 -2.78 Å) are presumably better suited to the O...O span (2.19 -2.29 Å) in the carboxylate than that in the phosphinate (3.38 – 3.62 Å). The eight peripheral Mn atoms are either linked by a single phosphinate bridge or by a phosphinate and acetate bridge (see c, Figure 14). The four water molecules in the cluster form stronger H-bonds to phosphinate oxygen atoms (O...O distances 2.64 - 2.90 Å) than to carboxylate oxygen atoms (O...O distances 3.36 – 3.40 Å). An analogous  $\text{Mn}_{12}$  cluster  $[(\mu_2\text{-L}^1)_9(\mu_2\text{-benzoate})_7(\mu_3\text{-O})_{12}\text{Mn}_{12}(\text{H}_2\text{O})_4]$  [58]<sup>AKIRAN</sup> with nine diphenylphosphinate and seven benzoate ligands has a very similar structure, suggesting that in general that dialkyl/arylphosphinates phosphinates are able to perform similar capping and bridging functions to carboxylates in metal cluster formation. When phenylphosphinic acid,  $\text{PhHPO}_2\text{H}$  ( $\text{L}^5\text{H}$ ), was used to displace propionate groups from  $[(\mu_2\text{-propionate})_{16}(\mu_3\text{-O})_{12}\text{Mn}_{12}(\text{H}_2\text{O})_4]$  it was oxidised *in situ* to phenylphosphonate and incorporated into a  $\text{Mn}_{22}$  cluster and a polymeric material containing  $\text{Mn}_{22}$  repeat units.[59]

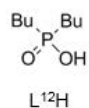
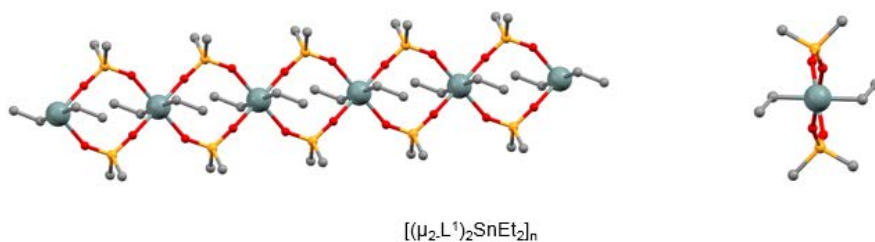
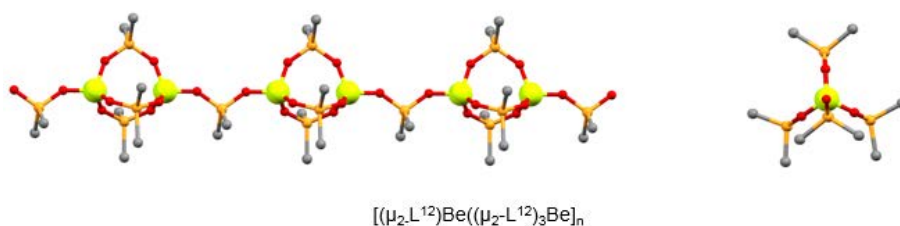
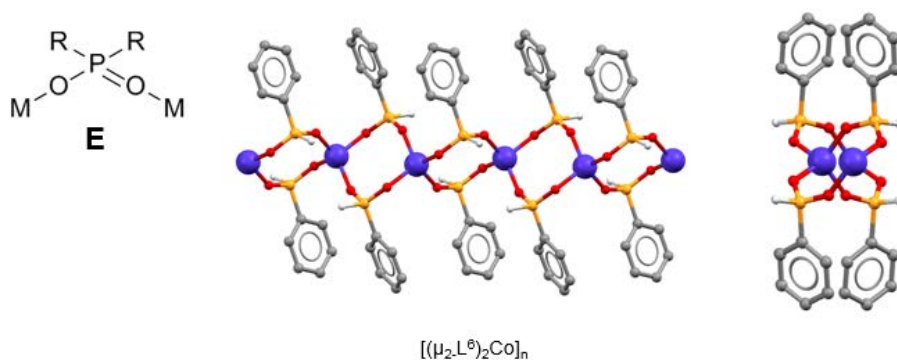


Aux<sup>2</sup>H

**Figure 16.** Tetranuclear,  $[(\mu_2\text{-L}^1)_2(\mu_2\text{-Aux}^2)_4(\mu_3\text{-OME})_2\text{Ni}_4(\text{MeOH})_6]$  [21]<sup>-FIQKUM</sup> (a) and dodecanuclear,  $[(\mu_2\text{-L}^1)_8(\mu_2\text{-acetate})_8(\mu_3\text{-O})_{12}\text{Mn}_{12}(\text{H}_2\text{O})_4]$  [55]<sup>-VOQGAJ</sup>, (b) clusters containing motif E phosphinate. Only the *ipso* carbon atoms of the phenyl rings in the latter are shown and in (c) the acetate ligands have been removed and the outer Mn atoms labelled with asterisks.

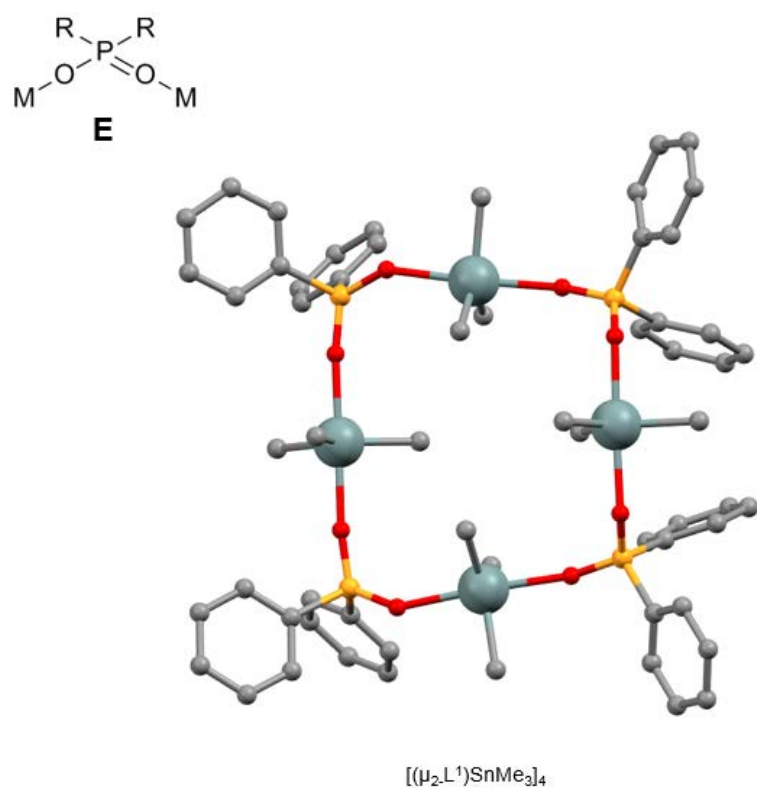
The versatility of the bridging motif E is manifest by numerous examples of it being present in polymeric and network structures. The double bridges between Co atoms in the  $[(\mu_2\text{-L}^6)_2\text{Co}]_n$  [21]<sup>-PATKUR</sup>

and the alternating sequence of single and triple bridges between Be atoms in  $[(\mu_2-L^9)Be((\mu_2-L^9)_3Be)_n][60]^{+HICZAU}$  (Figure 17) allows the metal atoms to achieve their preferred tetrahedral coordination geometry in these linear homoleptic polymeric complexes. There are many other examples of chain structures containing one or two bridging (motif E) phosphinates between pairs of metal atoms but none which involve triple bridging between all pairs of adjacent metal atoms in linear polymers.



**Figure 17.** The homoleptic linear polymers  $[(\mu_2\text{-L}^6)_2\text{Co}]_n$  [21]<sup>-PATKUR</sup> and  $[(\mu_2\text{-L}^{12})\text{Be}((\mu_2\text{-L}^{12})_3\text{Be})_n$  [60]<sup>-HICZAU</sup> and a heteroleptic analogue,  $[(\mu_2\text{-L}^1)_2\text{SnEt}_2]_n$  [61]<sup>-NAGKAH</sup> viewed perpendicular to and down the chains. All contain motif E phosphinate. Only the  $\alpha$ -carbon atom of the butyl groups in  $\text{L}^{12}\text{H}$  and the *ipso* carbon atom of the phenyl groups in  $\text{L}^1\text{H}$  are shown.

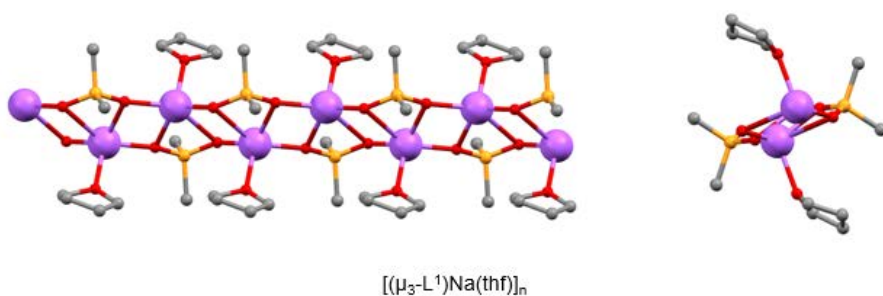
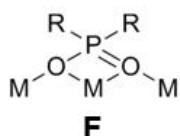
There are no examples of large “wheel-type” oligomeric complexes similar to those formed by carboxylates [62–66]. The largest cyclic phosphinate structure in the CSD is complex  $[(\mu_2\text{-L}^1)\text{SnMe}_3]_4$  [67]<sup>-PELZUB</sup>, shown in Figure 18, in which E-motif diphenylphosphinate bridges between pairs of tin atoms, occupying the axial sites in the metal's trigonal bipyramidal geometry.



**Figure 18.** The heteroleptic cyclic tetramer  $[(\mu_2\text{-L}^1)\text{SnMe}_3]_4$  [67]<sup>-PELZUB</sup>.

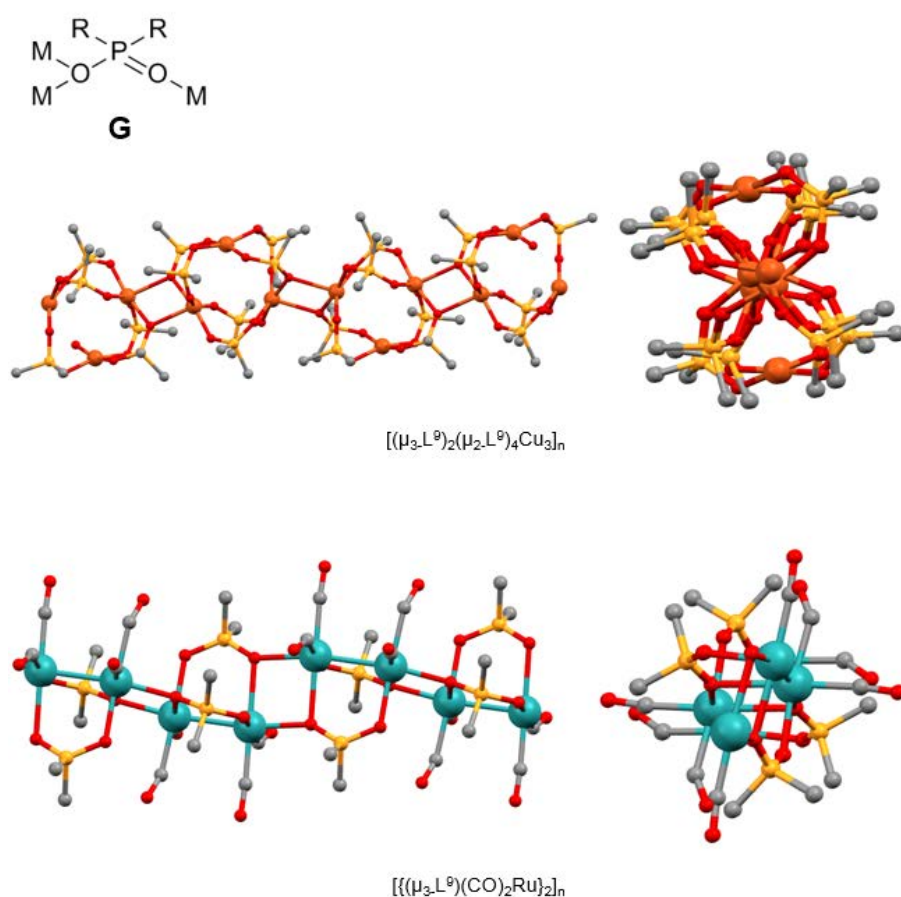
### Trinucleating motifs:

Eleven compounds in the CSD contain simple trinucleating phosphinates. Only one,  $[(\mu_3-L^1)Na(thf)]_n$  [68]<sup>-QAIDEK</sup>, has the symmetrical 3.22 coordination mode (motif **F**), forming the linear polymeric sodium complex shown in Figure 19.



**Figure 19.** The polymeric structure of  $[(\mu_3-L^1)Na(thf)]_n$  [68]<sup>-QAIDEK</sup>, viewed perpendicular to and down the chain, showing the trinucleating (motif **F**) mode of coordination of diphenylphosphinate,  $[L^1]$ . For clarity only the *ipso* C atoms of the phenyl rings are shown.

The unsymmetrical trinucleating motif **G** is more common. Examples of homo- and heteroleptic complexes,  $[(\mu_3-L^9)_2(\mu_2-L^9)_4Cu_3]_n$  [69]<sup>-RUQHUG</sup> and  $\{[(\mu_3-L^9)(CO)_2Ru]_2\}_n$  [70]<sup>-NULZOJ</sup>, formed by dimethylphosphinate are shown in Figure 20. The copper complex also contains dinucleating phosphinates. The compactness and multidenticity of the phosphinates, along with the plasticity [71] of the  $Cu^{2+}$  ions facilitates the formation of a “thick” linear polymer which contains both four and five coordinate copper atoms.

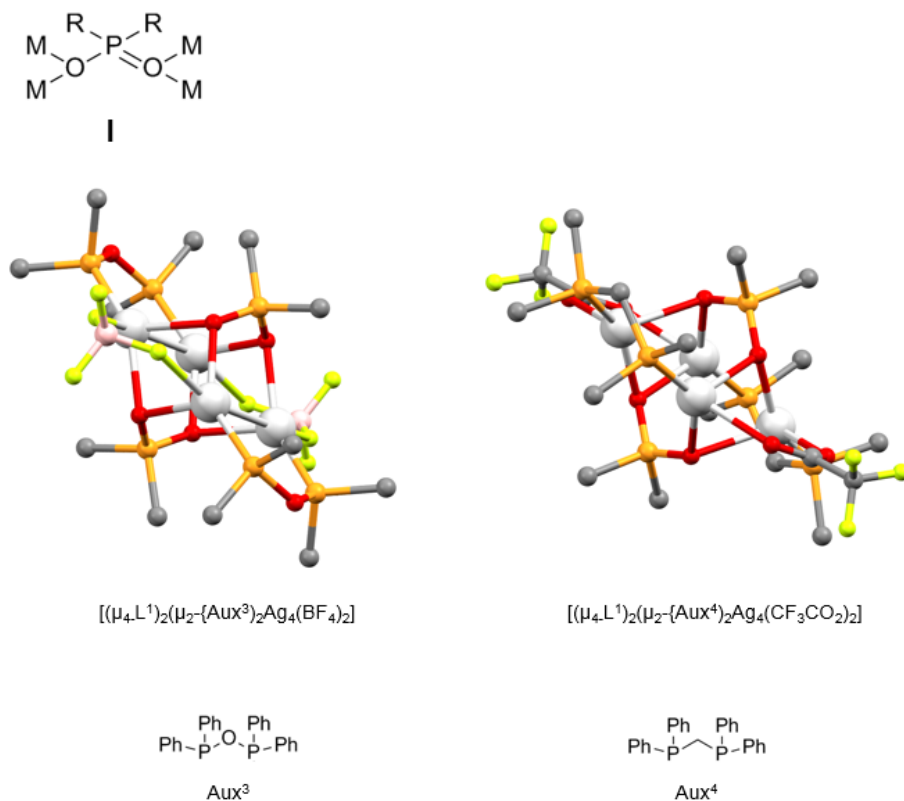


**Figure 20.** Homoleptic and heteroleptic complexes,  $[(\mu_3-L^9)_2(\mu_2-L^9)_4Cu_3]_n$  [69]<sup>-RUQHUG</sup> and  $[((\mu_3-L^9)(CO)_2Ru)_2]_n$  [70]<sup>-NULZOJ</sup> in which dimethylphosphinate acts as a trinucleating (motif **G**) ligand.

#### Tetranucleating motifs:

The only examples of phosphinates functioning as tetranucleating ligands are found in the silver(I) complexes  $[(\mu_4-L^1)_2(\mu_2-\{Aux^3\})_2Ag_4(BF_4)_2]$  [72]<sup>-ECESSAI</sup>, and  $[(\mu_4-L^1)_2(\mu_2-\{Aux^4\})_2Ag_4(CF_3CO_2)_2]$  [73]<sup>-IDATAK</sup>. These involve the symmetrical 4.22 motif (**I** in Figure 3) which allows each phosphinate to address two metal-metal bonded  $Ag_2^{2+}$  units (Figure 21), with Ag...Ag distances falling in the range 3.0670(2) – 3.523(1) Å. Different bisphosphines,  $Aux^3$  and  $Aux^4$ , and the anions,  $BF_4^-$  and  $CF_3CO_2^-$  also bridge the  $Ag_2^{2+}$  units in the two structures.

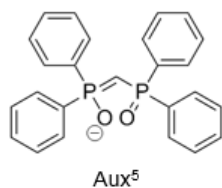
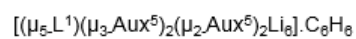
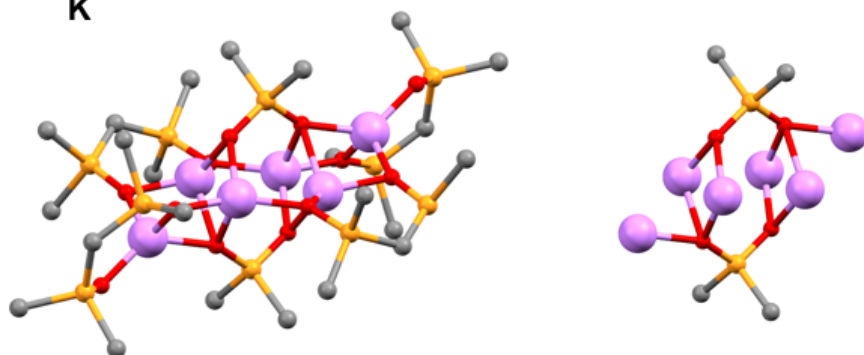
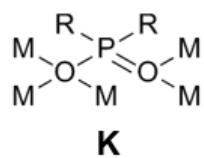




**Figure 21.** The tetranuclear silver(I) complexes  $[(\mu_4-L^1)_2(\mu_2-\{Aux^3\})_2Ag_4(BF_4)_2]$  [72]<sup>-ECESAI</sup>, and  $[(\mu_4-L^1)_2(\mu_2-\{Aux^4\})_2Ag_4(CF_3CO_2)_2]$  [73]<sup>-IDATAK</sup>, in which the deprotonated form of L<sup>1</sup>H exhibits motif I binding (only the *ipso* carbon atoms of its phenyl groups are shown).

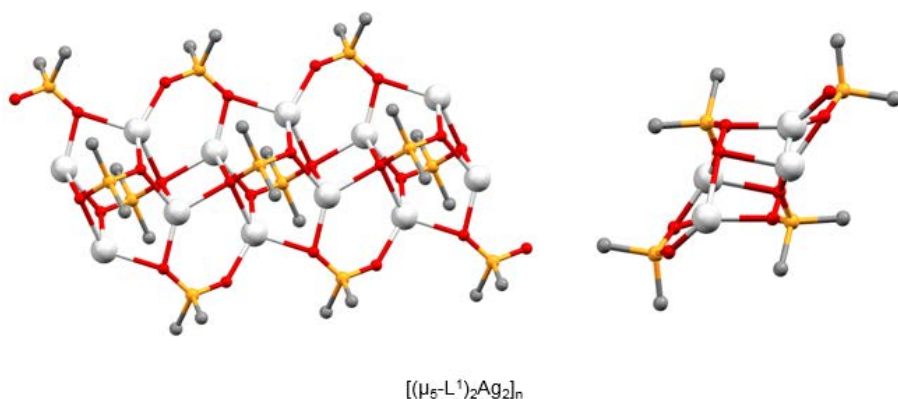
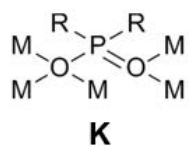
#### Pentanucleating motifs:

A phosphinate functioning as a pentanucleating ligand is found in three complexes [74]<sup>-FEQFEN</sup>, [75]<sup>-DUGHIV</sup>, [76]<sup>-YEGLON</sup> in the CSD. In  $[(\mu_5-L^1)(\mu_3-Aux^5)_2(\mu_2-Aux^5)_2Li_6]$  [74]<sup>-FEQFEN</sup> (Figure 22) the diphenylphosphinate displays the 5.32 motif (K in Figure 3). The complex was obtained when a Horner-Wittig reagent, the lithium derivative of  $(Ph_2P=O)_2CH_2$ , was exposed to oxygen. The diphenylphosphinate formed is bound to five lithium atoms in the centre of the cluster and the bis(diphenylphosphinoyl)methanido carbanions which were present in the parent Horner-Wittig reagent are attached to either three or two lithium atoms.



**Figure 22.** The hexalithium cluster in  $[(\mu_5\text{-L}^1)(\mu_3\text{-Aux}^5)_2(\mu_2\text{-Aux}^5)_2\text{Li}_6]\cdot\text{C}_6\text{H}_6$ . [74]<sup>FEQFEN</sup> For clarity only the *ipso*-carbon atoms of the phenyl groups in both the phosphinate and the bis(diphenylphosphino)l-methanido ligands ( $\text{Aux}^5$ ) are shown; on the right the latter have been removed to allow the pentanucleating (motif **K**) attachment of the phosphinate to be seen more clearly.

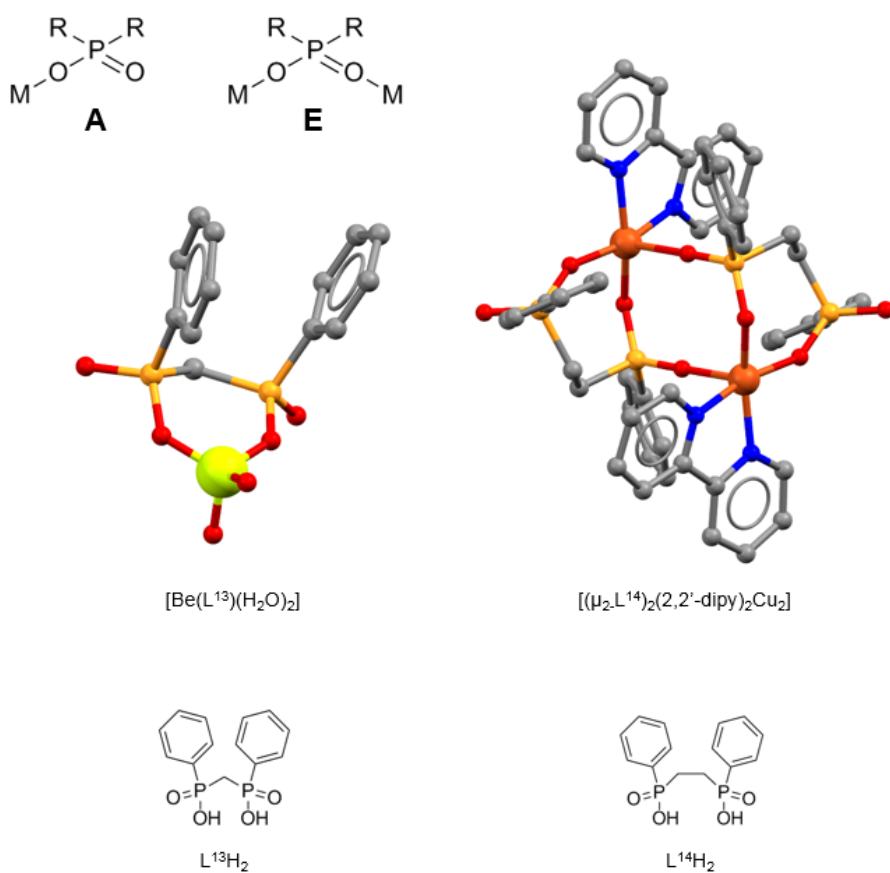
Diphenylphosphinate also displays motif **K** binding in the homoleptic polymer  $[(\mu_5\text{-L}^1)_2\text{Ag}_2]_n$  [75]<sup>DUGHYI</sup> shown in Figure 23.



**Figure 23.** The linear polymer  $[(\mu_5-L^1)_2Ag_2]_n$  [75]<sup>DUGHIV</sup> containing pentanuclear (motif **K**) diphenylphosphinate ligands. For clarity, only the *ipso*-carbon atoms of the phenyl groups are shown.

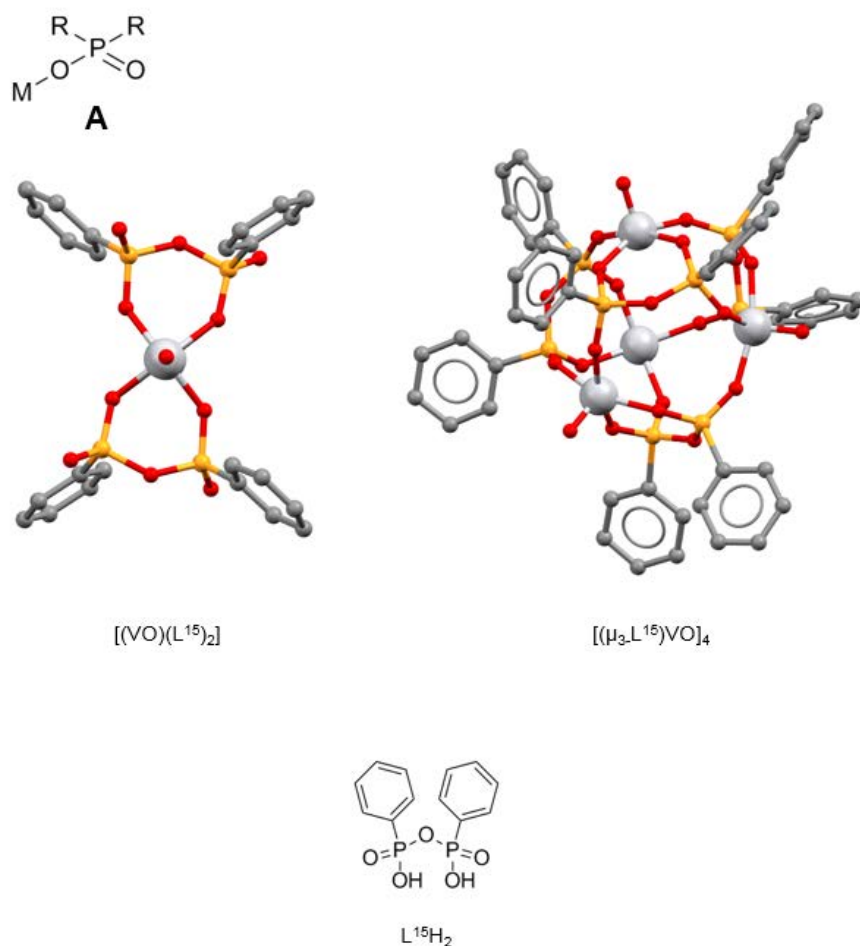
#### Complexes formed by polyphosphinic acids.

As mentioned earlier, we have chosen not to discuss at length the structures of complexes formed by potentially chelating diphosphinic acids such as  $L^{13}H_2$  and  $L^{14}H_2$  (Figure 24) because the mode of coordination of the phosphinate groups in these is likely to be constrained by the formation of chelate rings or by the strain induced in the ligand backbone by complexation of more than one phosphinate group. In many cases, the expected simple chelates are formed by diphosphinates which can form 6- or 7-membered rings. In  $[L^{13}Be(H_2O)_2]$  [77]<sup>AIOQEV</sup> both phosphinate groups display the simplest 1.10 binding motif **A** and do not make contacts with other Be atoms, whilst in  $[(\mu_2 L^{14})_2(2,2'-dipy)_2Cu_2]$  [78]<sup>BODVIA</sup> one of the phosphinate groups uses motif **E** binding to link to another Cu, forming the dinuclear complex shown in Figure 24.



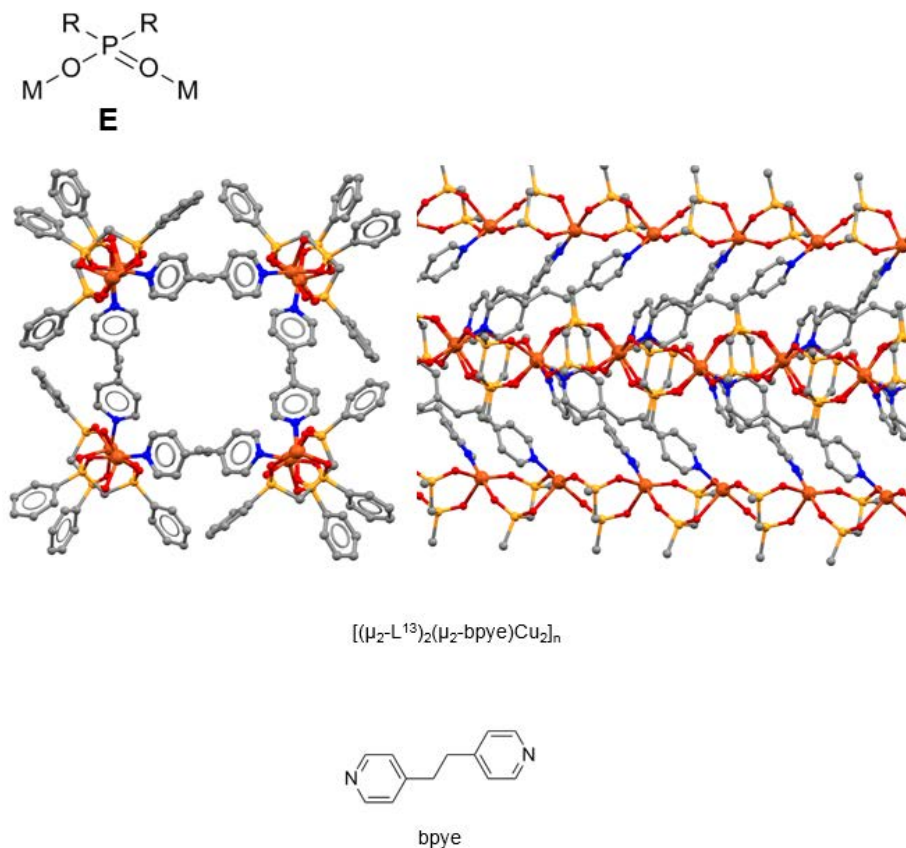
**Figure 24.** Diposphinic acids which form 6- and 7-membered chelate rings in the mononuclear  $[\text{Be}(\text{L}^{13})(\text{H}_2\text{O})_2]$  [77]<sup>-AJQEV</sup> and the dinuclear  $[(\mu_2\text{-L}^{14})_2(2,2'\text{-dipy})_2\text{Cu}_2]$  [78]<sup>-BODVIA</sup> complexes.

$\text{L}^{15}\text{H}_2$  (Figure 25) is a phosphonic acid anhydride analogue of  $\text{L}^{13}\text{H}_2$ . It forms both the conventional mononuclear vanadium(V) complex  $[\text{VO}(\text{L}^{15})_2]$  [79]<sup>-RARZIT</sup> in which all  $[\text{L}^{15}]^-$  units display a mononucleating binding motif (A), whereas in the unusual tetranuclear spherical cluster  $[(\mu_3\text{-L}^{15})\text{VO}]_4$  [80]<sup>-LICNOA</sup> they are dinucleating (motif E), creating the “ball-like structure”.



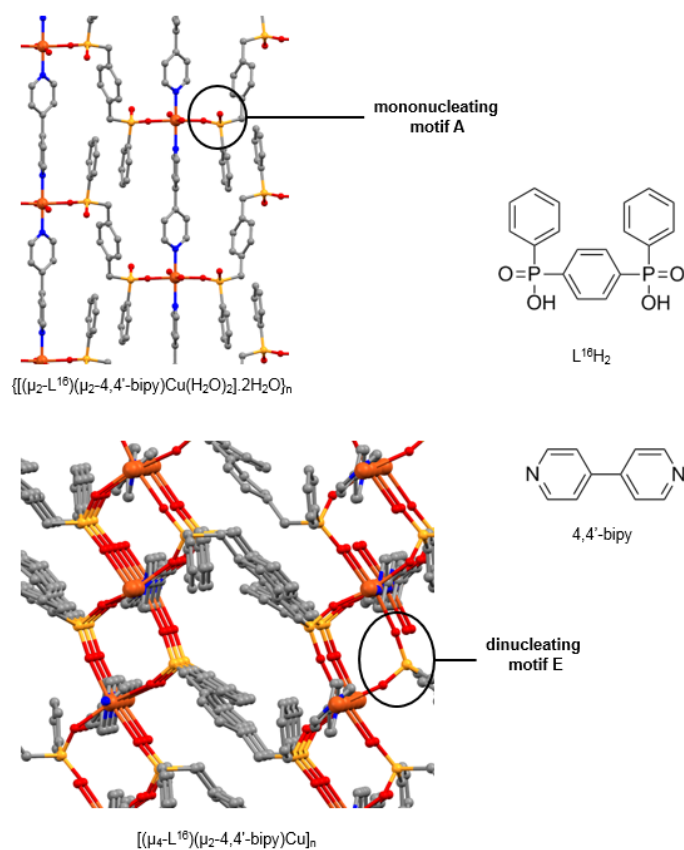
**Figure 25.** Mono- and tetra-nuclear complexes,  $[VO(L^{15})_2]^-$  [79]<sup>-RARZIT</sup> and  $[(\mu_3.L^{15})VO]_4$  [80]<sup>-LICNOA</sup> of the phosphonic anhydride  $L^{15}H_2$  analogous to the bisphosphonic acid  $L^{13}H_2$ .

In many complexes of polyphosphinates the individual phosphinate groups also fulfil bridging roles and display many of the polynucleating motifs listed in Figure 3. Unusual networks and metal organic frameworks (MOFs) can result. When  $L^{13}H_2$  is used in conjunction with the non-chelating auxiliary ligand bpye (see Figure 26) a tubular 1D MOF,  $[(\mu_2-L^{13})_2(\mu_2-bpye)Cu_2]_n$  [81]<sup>-CEKHEH</sup> results which can be obtained in both micro- and nano-crystalline forms. The rate of  $CO_2$  uptake is much greater in the latter.



**Figure 26.** Views of  $[(\mu_2-L^{13})_2(\mu_2\text{-bpye})\text{Cu}_2]_n$  [81]<sup>-CEKHEH</sup> showing the tubular 1D MOF and the dinucleating (motif **E**) binding of each phosphinate in  $[L^{13}]^{2-}$  (right). In the latter, only the *ipso*-carbon atoms of the phenyl groups in  $L^{13}$  are shown.

The incorporation of two phosphinic acid groups in the *non-chelating* framework of  $L^{16}\text{H}_2$  (Figure 27) is more interesting because, when used in conjunction with the non-chelating 4,4'-dipyridyl ligand, it generates polymeric complexes with 2-D and 3-D networks. In the copper complexes shown, the phosphinate groups are mononucleating (motif **A**) in  $\{[(\mu_2-L^{16})(\mu_2\text{-4,4'-bipy})\text{Cu}(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$  [15]<sup>-QUTXIN</sup>, resulting in a two dimensional network, whilst in  $[(\mu_4-L^{16})(\mu_2\text{-4,4'-bipy})\text{Cu}]_n$  [15]<sup>-QUTXOT</sup> they are dinucleating (motif **E**) and crosslink sheets to generate a three dimensional structure. The latter resembles a metal organic framework [82–84] but the pores are not large enough to incorporate guest molecules.

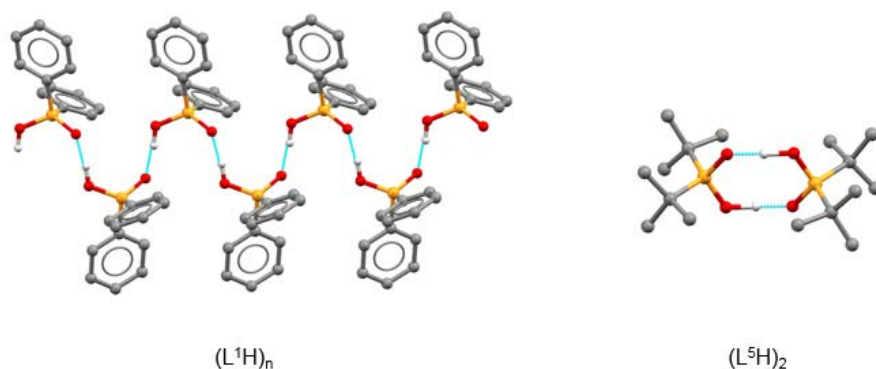


**Figure 27.** The two- and three-dimensional network structures  $\{[(\mu_2-L^{16})(\mu_2-4,4'\text{-bipy})\text{Cu}(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$  [15]<sup>-QUTXIN</sup> and  $[(\mu_4-L^{16})(\mu_2-4,4'\text{-bipy})\text{Cu}]_n$  [15]<sup>-QUTXOT</sup> with the motif A coordination of the phosphinate marked in the former and the motif E (bridging mode) in the latter. For clarity, the waters of crystallisation are omitted from the former.

#### Complexes of H-bonded phosphinic acid/phosphinate units.

The 1.1001 motif (**M** in Figure 4) allows phosphinic acid dimers to retain an intermolecular hydrogen bond when one of the acidic hydrogen atoms is replaced by a metal cation (see Figure 2). Phosphinic acids form one of the most stable types of organic acid dimers [85], both in solution [86] and the gas phase [87,88]. The high dimerization enthalpy determined for dimethyl phosphinic acid ( $100 \text{ kJ mol}^{-1}$ ) has been reproduced using DFT calculations with large basis sets,<sup>3</sup> and helps to account for the

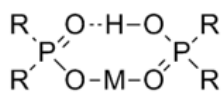
retention of a H-bond on formation of metal complexes (see Figure 2). In the solid state, metal-free phosphinic acids exist in polymeric H-bonded forms such as  $(L^1H)_n$  [89]<sup>-DPPHINO1</sup>, see Figure 28, as well as 8-membered ring dimers such as  $(L^5H)_2$  [90]<sup>-DTBUPA01</sup>.



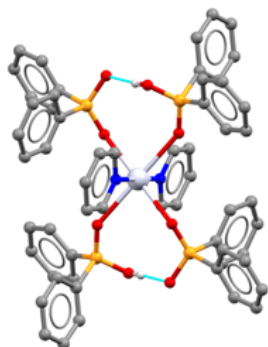
**Figure 28.** Examples of the two structural types, polymers and dimers, shown by phosphinic acid proligands:  $(L^1H)_n$  [89]<sup>-DPPHINO1</sup>, and  $(L^5H)_2$  [90]<sup>-DTBUPA01</sup>.

Whilst motif **M** is relatively uncommon in the solid-state structures (there are 7 occurrences in the CSD), it is thought to be an important form in the hydrocarbon solvents used in commercial metal solvent extraction processes [16,17]. Three examples of heteroleptic complexes  $[Hg(L^1.L^1H)_2py_2]$  [91]<sup>-UDAKEQ</sup>,  $[Co(L^1.L^1H)_2(DMF)_2]$  [92]<sup>-GEPBEI</sup> and  $[Ni(L^1.L^1H)_2(DMF)_2]$  [93]<sup>-SAXPEN</sup> are shown in Figure 29. These have the two monodentate ligands in a *trans* arrangement with the two  $(L^1.L^1H)^-$  anions defining an approximately planar  $MO_4$  unit in which the disposition of the four oxygen atoms deviates considerably from a square. The bite angles defined by the  $(L^1.L^1H)^-$  chelating units are 85.0° [91]<sup>-UDAKEQ</sup>, 91.6° [92]<sup>-GEPBEI</sup> and 91.5° [93]<sup>-SAXPEN</sup> in  $[Hg(L^1.L^1H)_2py_2]$ ,  $[Co(L^1.L^1H)_2(DMF)_2]$  and  $[Ni(L^1.L^1H)_2(DMF)_2]$  respectively.

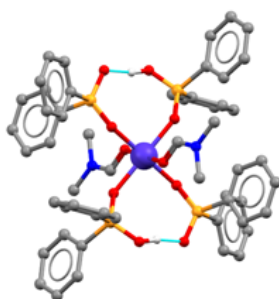




**M**



[Hg(L<sup>1</sup>.L<sup>1</sup>H)<sub>2</sub>py<sub>2</sub>]



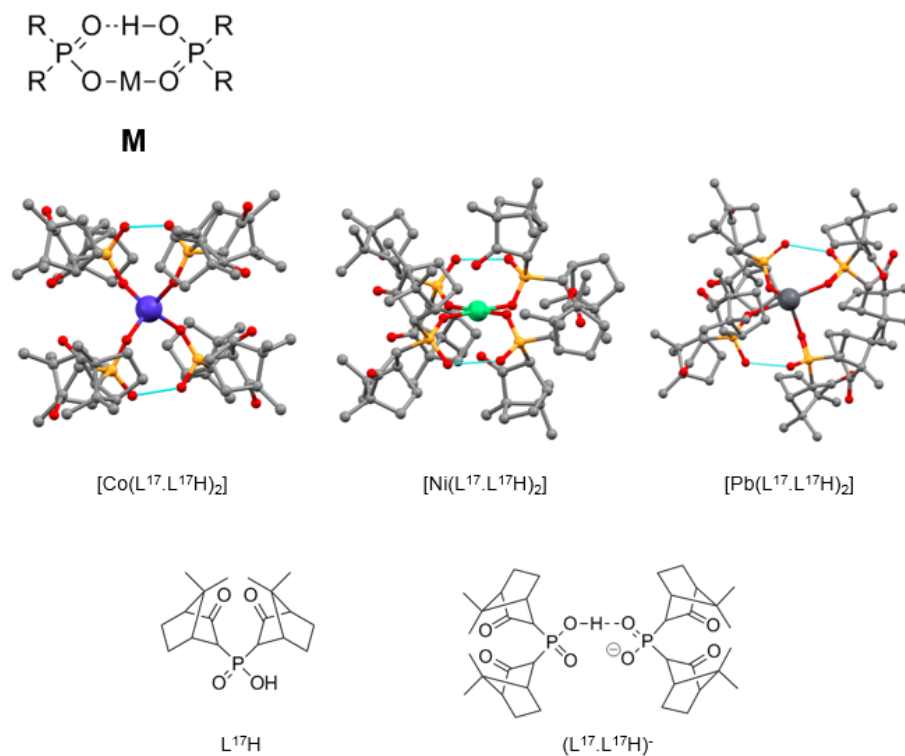
[Co(L<sup>1</sup>.L<sup>1</sup>H)<sub>2</sub>(DMF)<sub>2</sub>]



[Ni(L<sup>1</sup>.L<sup>1</sup>H)<sub>2</sub>(DMF)<sub>2</sub>]

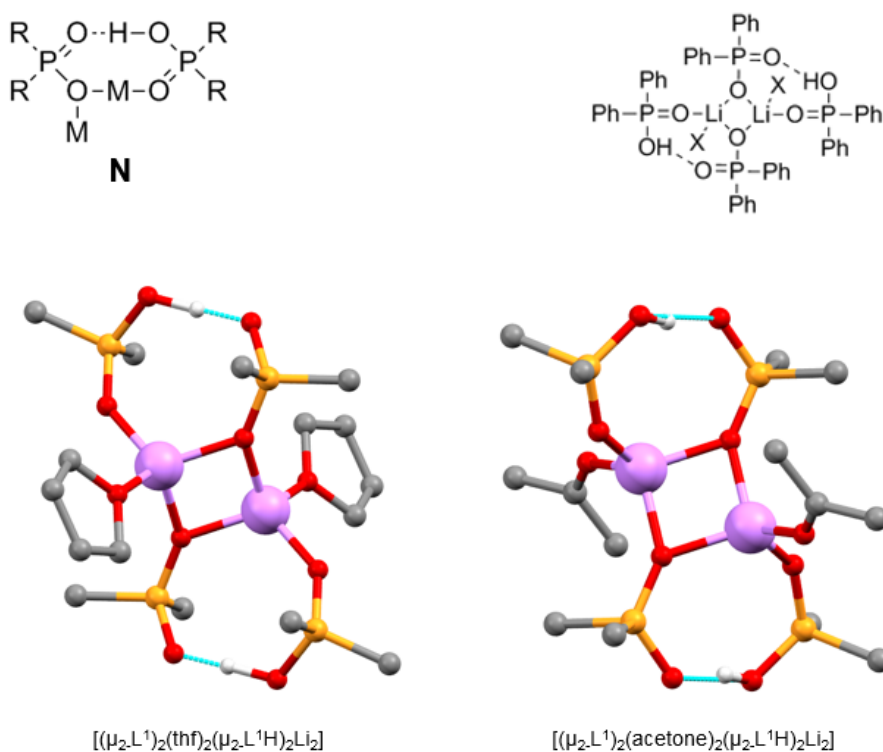
**Figure 29.** Mononuclear heteroleptic complexes [Hg(L<sup>1</sup>.L<sup>1</sup>H)<sub>2</sub>py<sub>2</sub>] [91]<sup>-UDAKEQ</sup>, [Co(L<sup>1</sup>.L<sup>1</sup>H)<sub>2</sub>(DMF)<sub>2</sub>] [92]<sup>-GEPBEI</sup> and [Ni(L<sup>1</sup>.L<sup>1</sup>H)<sub>2</sub>(DMF)<sub>2</sub>] [93]<sup>-SAXPEN</sup> containing the 1.1001 motif (**M** in Figure 4) with an intermolecular H-bond between coordinated ligands.

Homoleptic complexes containing the 1.1001 (motif **M**) are formed by the bulky proligand biscamphorylphosphinic acid, L<sup>17</sup>H. Three examples are shown in Figure 30. The cobalt(II) complex, [Co(L<sup>17</sup>.L<sup>17</sup>H)<sub>2</sub>] [94]<sup>-IHAJUX</sup>, is tetrahedral with O-Co-O angles falling in the range 99.2-115.7°. In the pseudo-octahedral nickel(II) complex [Ni(L<sup>17</sup>.L<sup>17</sup>H)<sub>2</sub>] [94]<sup>-IHAKEI</sup> the two **M** motif units define an NiO<sub>4</sub> plane with mean Ni-O lengths 2.033 ± 0.008 Å and camphoryl oxygen atoms lie in axial sites with Ni-O distances of 2.153 Å. A much less regular geometry is observed in the complex [[Pb(L<sup>17</sup>.L<sup>17</sup>H)<sub>2</sub>] [94]<sup>-IHAKEI</sup> with O-Pb-O angles falling in the range 80.7-92.7°.



**Figure 30.** Mononuclear homoleptic complexes  $[\text{Co}(\text{L}^{17}.\text{L}^{17}\text{H})_2]$  [94]<sup>-IHAIJX</sup> (upper left),  $[\text{Ni}(\text{L}^{17}.\text{L}^{17}\text{H})_2]$  [94]<sup>-IHAKAE</sup> (upper middle) and  $[\text{Pb}(\text{L}^{17}.\text{L}^{17}\text{H})_2]$  [94]<sup>-IHAKEL</sup> (upper right) containing the 1.1001 motif (**M** in Figure 4) with an intermolecular H-bond between coordinated ligands. The structures of  $\text{L}^{17}\text{H}$  (lower left) and  $(\text{L}^{17}.\text{L}^{17}\text{H})^-$  (lower right) are also shown.

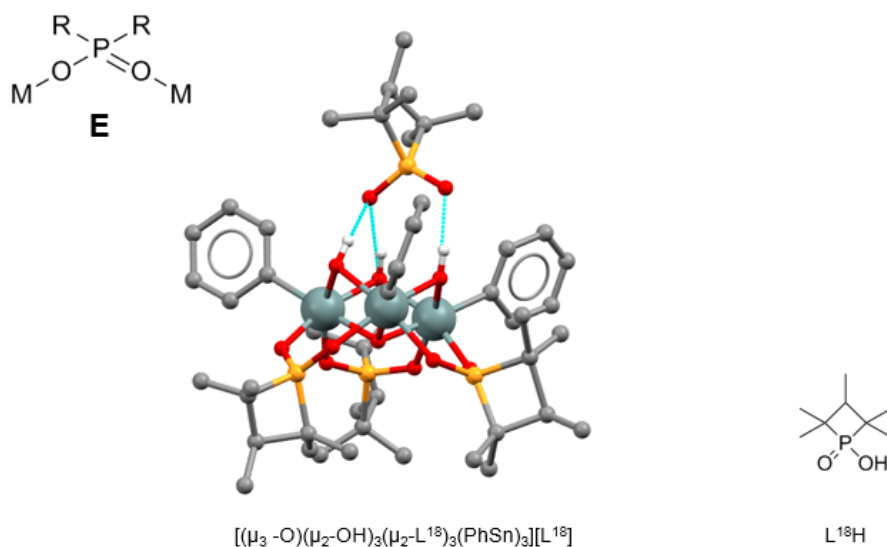
There is one other binding motif which can be found in the CSD for a dimeric form of a phosphinic acid. As in the 1.1001 motif discussed above, the 2.2001 motif (**N** in Figure 4), has a phosphinate H-bonded to phosphinic acid, but in this case the phosphinate is dinucleating. There are only two examples in the CSD, both of which are dilithium complexes,  $[(\mu_2\text{-L}^1)_2(\text{thf})_2(\mu_2\text{-L}^1\text{H})_2\text{Li}_2]$  [95]<sup>-ALUGEJ</sup>, and  $[(\mu_2\text{-L}^1)_2(\text{acetone})_2(\mu_2\text{-L}^1\text{H})_2\text{Li}_2]$  [37]<sup>-KAMXUS</sup>, differing only in the nature of a monodentate neutral ligand, thf or acetone (X in the connectivity diagram shown on the top right of Figure 31).



**Figure 31.** The dilithium complexes  $[(\mu_2-L^1)_2(\text{thf})_2(\mu_2-L^1H)_2Li_2]$  [95]<sup>-ALUGEU</sup>, and  $[(\mu_2-L^1)_2(\text{acetone})_2(\mu_2-L^1H)_2Li_2]$  [37]<sup>-KAMXUS</sup>, showing the H-bonds between the phosphonic acid and phosphinate ligands (motif **N**). Only the *ipso*-carbon atoms of the phenyl groups in  $L^1$  are shown.

The association of coordinated phosphonic acid and phosphinate molecules in metal complexes is favoured by the strong H-bond donor/acceptor capabilities of the former/latter. As mentioned earlier, many heteroleptic complexes which contain ligands with appropriately positioned H-bond donor groups, are stabilised by these bonding to phosphinate oxygen atoms (see for example  $[Ru(L^1)(Ph_3P)_2((R,R)\text{-dach})]$ , and  $[Zn(L^1)_2(\text{DMPZ})_2]$ , in Figure 7).

The strong H-bond acceptor capability of phosphinates also allows them to act as “outer sphere” ligands. An example [96]<sup>-BUNFAS</sup> is shown in Figure 32 in which the three  $\mu_2$ -hydroxy groups in the cationic  $[(\mu_3-O)(\mu_2-OH)_3(\mu_2-L^{18})(PhSn)_3]^+$  molecule all form hydrogen bonds with the phosphinate counter anion,  $[L^{18}]^-$ .

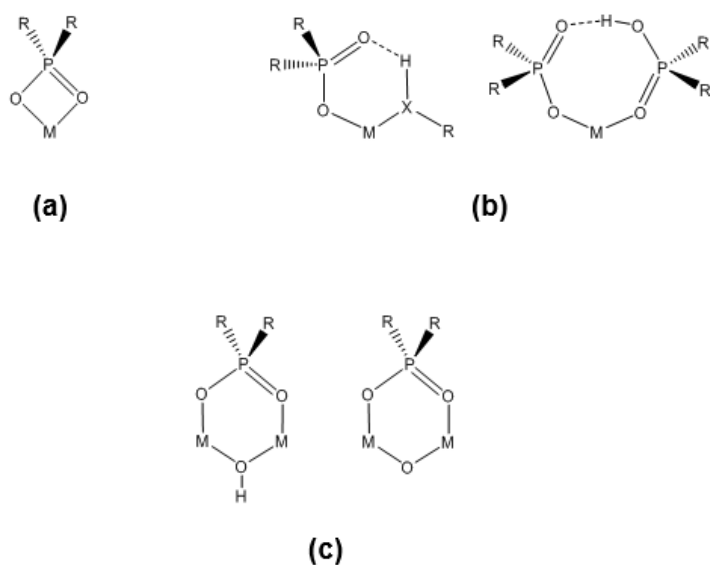


**Figure 32.**  $[(\mu_3\text{-O})(\mu_2\text{-OH})_3(\mu_2\text{-L}^{18})_3(\text{PhSn})_3][\text{L}^{18}]$  [96]<sup>-BUNFAS</sup>, showing the “outer sphere coordination” of the phosphinate counter anion  $[\text{L}^{18}]^-$  via H-bonding to three  $\mu_2$ -hydroxy ligands. The inner sphere phosphinates all display motif **E** binding.

### Conclusions

An analysis of the 552 structures of complexes in the CSD has revealed that phosphinate ligands show 10 different modes of coordination to metal ions. Their versatility is manifest by their ability to form complexes with metal cations from all regions of the periodic table. High nuclearity complexes are more prevalent with “hard” *s*- and *p*-block metals but pentanuclear Ag(I) complexes are also known.

Bridging to generate oligomeric or polymeric complexes is more common than the formation of mononuclear complexes. There are only 3 examples of the latter in which a phosphinate forms a 4-membered chelate (**a** in Figure 33). Non-chelating monodentate binding is more common and this is often stabilised by the uncoordinated oxygen atom of a phosphinate interacting with a H-bond donor group in an adjacent ligand as illustrated in (**b**) in Figure 33. Examples of such behaviour include neutral phosphonic acid molecules, and this is thought to facilitate transport into a water-immiscible solvent in liquid:liquid extraction processes by generating hydrophobic complexes in which the outer sphere is largely composed of the alkyl or aryl groups on the ligands.



**Figure 33.** Mononucleating motifs in which the phosphinate ligand is chelated to the metal ion **(a)** or is monodentate and accepts a H-bond donor from an adjacent ligand **(b)**. Also shown is the most common dinucleating motif **(E)** in which the metal atoms are also bridged by a  $\mu_2$ -hydroxy or  $\mu_2$ -oxo group **(c)**.

The most common binding mode, motif E, is frequently found in phosphinate complexes that also have a  $\mu$ -hydroxy or oxo group bridging the metal centres (see **(c)** in Figure 33, examples of which can be found in Figures 11, 12, 13, 14, 16 and 32 above). Such subunits provide very plausible models for the attachment of phosphinates to oxidised metal surfaces or to metal oxides, accounting for their uses as corrosion inhibitors, lubricant additives, adhesion promoters and pigment dispersants.

The structural motifs of phosphinate ligands listed in Figures 3 and 4 are very similar to those which are possible for carboxylate ligands [97,98] and consequently there are similarities in their coordination chemistry. However, based on the occurrence of structures in the CSD, the propensity to form polymeric complexes using M-O-X-O-M links (based on motif E etc.) appears to be more pronounced for phosphinates. It is possible that the tendency to form “high density” polynuclear clusters partly accounts for the relatively few examples of “open” polynuclear (MOF-type) structures, but it is also possible that there have been fewer attempts to synthesise phosphinate-containing MOFs than carboxylate analogues.

### **Acknowledgements.**

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**Appendix.** A listing of the CSD codes of complexes containing phosphinates with the binding motifs **A** – **L** shown in Figure 3. Structures containing motifs **M** and **N** involving dimeric ligands (Figure 4) are included in the counts of complexes containing their components, **A** and **D**. Some CSD codes appear more than once in the table because these structures contain phosphinates with more than one binding motif.

A	B	D	E	F	G	I	K	M	N			
ADIZEU	DOXJAC	ALUGEU	ABEQAB	GACTAI	MEPBEP	TIXKEQ	QAJDEK	DUGHY	AWOWIT	DUGHY	GABVAG	ALUGEU
AJOQEV	HEFBID	KAMXUS	ABEQEF	GAFOIQ	MEPBIT	TONJAJ		HUMCAT	ECESAI	FEQFEN	GEPBAE	KAMXUS
ALEJOQ	LANSAU		ABEQU	GAWNUP	MEPBOZ	TONJEN		JOSPUC	ECIGOM	YEGLON	GEPBEI	
ALEJUW			ABOXAR	GAWPEB	MIGJET	TONJIR		JUWFEO	ECIGUS		IHAJUX	
ALEKAD			ACAVUV	GAWPIF	MPCTRE	TONJOX		NULZID	IDATAK		IHAKEA	
ALEKIL			ACAWEG	GAWZAF	MUBWOX	TONJUD		NULZDJ	KECWAR		IHAKEA	
ALEKUX			ADIBUK	GENZUU	NAGKAH	UCEBIP		OJUZUP	LEZGON		JICCAZ	
ALELAE			ADICAR	GEYGIC	NAYSUB	UDALIU		OLOBIB	OKABUY			
ALELIM			ADICEV	GEYGOI	NECJAH	UDALUG		RAKQIE				
ALIKUB			ADICIZ	GEYGUO	NELLUM	UFAQEX		RUQHUG				
ALUGEU			AHAVEK	GEYHAV	NETCUK	UFEPUS						
AMPMNC			AKIRAN	GBPIQ	NIMWAH	ULUYU						
BEQCUX			AMEPZN	GIRPOM	NIMWOV	ULUYOP						
BEQDAE			AMPMN	GIRPUS	NOBZAG	VABSAS						
BODVIA			AQOHUK	GIRRAA	NOBZEK	VACJAK						
CEYVEJ			AQOJAS	GOMPH	NOJLOP	VACJEO						
CEYVIN			AWUGAA	GOPPAC	NOJMOQ	VACJIS						
FASCIN			BAPDOM	GOXMUB	NOJMUW	VACJOY						
FEDYX			BAPDUS	GUNCOH	NUBCUI	VACJUE						
FIMMUK			BEQCIL	HEGBOL	OCOREF	VACKAL						
GABVAG			BEQQOR	HEQNAS	OCORU	VANLOM						
GEPBAE			BICHUS	HICZAU	OCOROP	VAQNAC						
GEPBEI			BIRFAJ	HILPOH	OGEWAZ	VEGXIP						
GUFZIQ			BISCEL	HIRDIV	OHEYAC	VEGXOV						
HAZRUV			BODVIA	HOCGEN	OMOQEO	VEHMOK						
HAZSAC			BOWBYI	ICEYOG	PAMYOR	VEHNAX						
HEGBOL			BOXBIZ	ICEYUM	PATKUR	VELMEE						
IGOSAA			BUNFAS	ICINAK	PATLAY	VEPNEJ						
IHAJUX			CAJTOW	IDASOX	PELZUB	VEPNIN						
IHAKEA			CEKHAD	IJAYIB	PHACCR	VEPNOT						
IHAKEI			CEKHEH	IPACUX	PIMTEK	VOBISOV						
ILUBAT			CEVKIV	JEGJOU	QAXWOB	VOQGAJ						
IQEMIB			CEVKOE	JIBVEV	QOPSUJ	VOQGEN						
IRERED			CEYVIN	JIRNON	QOPTAQ	WABSIC						
JICCAZ			CLPSSB	JIRNUT	QOPTEU	WACRIB						
KAMXUS			COBZAU	JOLSEK	QUTXOT	WACROH						
KUDPAA			CODTAR	JOLSIO	QUVXOW	WIGGEZ						
KUNTW			COLCEN	JORXUJ	QUVXUC	XAHHET						
MUDHOJ			COTQEI	JORYAQ	RAKTIG	XAHHIK						
NEYWAP			DACHUK	JOSBOI	REGPUO	XAPREL						
NOWBEG			DBURCU	JUMKEH	REGQAV	XAWQAN						
PZMIV			DEFDID	JUMKIL	RELLOJ	XEPRUF						
PUWKEY			DEFDOJ	JUMKOR	RELLUP	XIKSIF						
PUWKIC			DPINRE	KACQIQ	REQQUZ	YAYXED						
PUWKOI			DRPOP	KAMXUS	RHYVUQ	YEFTTEK						
PUWKUO			EHUYAH	KAPTOM	RUQHUG	YEFTIO						
PUWLAV			EHUYEL	KAPTUS	SAKYUZ	YEFTOU						
PUWLEZ			EMAVET	KAPVAA	SAKZAG	YEYJIV						
QAXWOB			EQUVIV	KAPWU	SAXNUB	YEYJOB						
QEVGEE			EWUMIOY	KECWAR	SAXYAT	YMYIO						
QUTXIN			EWUMUE	KEGHAF	SAXYEX	YMYOU						
RARZIT			EXOKOS	KUNTES	SEBLAM	YMWZEL						
RFTL			EXOKUY	KUNTW	SOGMEI	YXHEU						
SAXPEN			FAMFEF	LAHKEY	SOGMIM	YUMQAZ						
TENRIN			FAMFU	LAHXIC	SOGMOS	YUMQED						
TIXKEQ			FEFDOJ	LAHXOI	SOGMUY	ZAZZUV						
TOXKOG			FEPBEH	LECLUC	SOSWIG	ZBPPHN						
TUPXEH			FIQKOG	LECMUD	SUMYAB	ZESTUM						
UCAGEK			FIQKUM	LEHLOZ	SUPKAQ	ZIRMES						
UDAKEQ			FIRFAN	LICNOA	TATYES	ZOWMON						
VACJIS			FISGEV	LILVAD	TAVYOE	ZOZJUT						
VOBRUA			FISGIZ	LILWAE	TAVYUK	ZUHCUA						
VOBSAH			FOBGOS	LIZXOI	TAVZAR	ZULGUK						
WIGGID			FOMNEA	LUTCUY	TENRAF	ZUXVOF						
WIZPOK			GABXEM	LUTDAF	TENREJ	ZUXVUL						

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I will check through all refs just before submission but a casual scan indicated...

Refs 1&2 have details missing – need inventors?

Ref 2 needs lower case unlauded “oh”

Ref 3 needs publisher

Ref 7 I’ve made several initials uc

Ref 84 – I removed some extra full stops