Trigonal Bipyramidal Penta-aquazinc(II): Crystal Structure of Penta-aquazinc(II) Bis(3,3′,3″-phosphinetriyltripropionato)dizincate(II,II) Heptahydrate†

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Crystals of the title compound are hexagonal, space group $P6_1$ or $P6_5$. The crystal structure was determined by the heavy-atom method from 2 675 unique reflections and refined to $R = 0.059$. The structure can be best formulated as an ionic polymer with the composition $([Zn(H_2O)_5][Zn_2\{P(CH_2CH_2CO_2)_3\}_2]\cdot 7H_2O)_n$. It consists of a three-dimensional network of $[Zn\{P(CH_2CH_2CO_2)_3\}]^-$ anions, where the zinc atoms are each tetrahedrally co-ordinated by three carboxyl oxygen atoms belonging to three different 3,3′,3″-phosphinetriyltripropionate ligands [Zn–O, 1.950(12)—1.991(13) Å] and by one phosphorus atom from a fourth ligand [Zn–P, 2.405(4) and 2.429(4) Å; the first crystallographically documented zinc–phosphine bond]. Zinc cations are located in holes of the network as the hitherto unknown $[Zn(H_2O)_5]^{2+}$ moieties with trigonal bipyramidal arrangement. The structure is stabilized by hydrogen bonding in which carboxylate oxygen atoms and both co-ordinated and lattice water molecules are involved.

The investigation of chemical properties and crystal structures carried out in this laboratory on complexes of functionalized phosphines with the general formulae $R_{3-n}P(CH_2CO_2H)_n$ (R = Ph, n = 1—3; R = Me or Et, n = 2) or $[Ph_{2-m}(HO_2CCH_2)_mPCH_2-]_2$ (m = 1 or 2) revealed three types of ligand co-ordination to soft metal ions: *P*-monodentate (Pd,[1] Pt,[2] Hg,[3] or Rh[4]), *P,P*-chelating (Ni[5]), or *P,O*-chelating (Pd,[6] Pt,[2] or Rh[4]). Among further factors affecting the type of metal–ligand bonding, those of main interest are the influence of a hard metal ion and the distance between the phosphorus and oxygen donors in the ligand. The weak zinc(II) complex of 3,3′,3″-phosphinetriyltripropionic acid which was described previously in aqueous solution[7] seemed to be the obvious candidate for investigating the influence of both factors.

Experimental

Preparation.—Under an argon atmosphere, zinc(II) acetate dihydrate (0.88 g, 4.00 mmol) was dissolved in sodium acetate–acetic acid buffer (10 cm^3, 1 mol dm^{-3}; pH 5.5) and a solution of 3,3′,3″-phosphinetriyltripropionic acid hydrochloride[8] (0.57 g, 2.00 mmol) in the same buffer (10 cm^3) was added. The colourless crystals which developed on standing undisturbed for several days were filtered off, washed with water, and dried at room temperature affording 0.68 g (38%) of air-stable $[Zn_3\{P(CH_2CH_2CO_2)_3\}_2]\cdot 12H_2O$ [Found: P, 6.8; Zn, 21.6; H_2O, 23.5 (from weight loss at 140 °C under argon). $C_{18}H_{48}O_{24}P_2Zn_3$ requires P, 6.85; Zn, 21.6; H_2O, 23.8%); $\nu_{max.}$(OCO) at 1 565vs; $\nu_{max.}(H_2O)$ at 3 210vs and 3 320vs cm^{-1} (Nujol).

Crystal Data.—$C_{18}H_{48}O_{24}P_2Zn_3$, M = 906.6, hexagonal, $a = b$ = 11.441(4), c = 46.83(1) Å, U = 5 309(3) Å^3 (by least-squares refinement on diffractometer angles for 18 automatically centered reflections, λ = 0.710 69 Å), space group $P6_1$ (no.169) [alt. $P6_5$ (no.170)], D_m = 1.679(4), Z = 6, D_c = 1.70(1) g cm^{-3}, $F(000)$ = 2 808. Crystal dimensions 0.1 × 0.08 × 0.2 mm, μ(Mo-K_α) = 22.11 cm^{-1}.

Data Collection and Processing.[5]—Syntex $P2_1$ diffractometer, $\omega/2\theta$ mode, scan speed varied from 1.6 to 29.3° min^{-1} in 2θ, graphite-monochromated Mo-K_α radiation, 3 117 reflections measured ($0 \leqslant 2\theta \leqslant 58°$, $+hkl$), 2 675 unique (no absorption correction) giving 1 833 with $I > 1.96\sigma(I)$. Three standard reflections monitored every 47 reflections showed no significant intensity fluctuation.

Structure Analysis and Refinement.—Heavy-atom method, full-matrix least-squares refinement (in two blocks for final) with all non-hydrogen atoms anisotropic, methylene hydrogen atoms in calculated positions, water hydrogen atoms in positions found from difference map, and for all hydrogen atoms with one, overall, $U_{iso.}$ (0.063 Å^2). The weighting scheme $w = 1/\sigma^2(F_o)$ derived from counting statistics gave satisfactory agreement analyses. Final R and R' values were 0.059 and 0.061 respectively. A selection could not be made between the space groups $P6_1$ and $P6_5$ as, on changing from x,y,z to $-x,-y,-z$, the R value only increased by 0.0001. Programs and computers used and sources of scattering factor data are given in ref. 5.

Results and Discussion

The atomic co-ordinates of the non-hydrogen atoms are given in Table 1. Figure 1 shows a projection of the formula unit onto the xz plane together with the atomic numbering. Important bond distances and angles are summarized in Table 2.

The main feature of the structure is a three-dimensional network of $[Zn\{P(CH_2CH_2CO_2)_3\}]^-$ anions. The quadridentate ligand acts as a *P*-donor to one zinc atom and, by means of three propionate arms, as an *O*-donor to a further three zinc atoms, formally belonging to adjacent anions. Two zinc atoms [Zn(1), Zn(2)] of the formula unit have very similar environments but the third, Zn(3), is totally different. The environment of the Zn(1) atom is depicted in Figure 2. Bonds from zinc to three carboxyl oxygens and to one phosphorus point to the corners of a distorted tetrahedron. There is nothing unusual either in the Zn–O distances [1.950(12)—1.991(13) Å] or in the distortion of the O–Zn–O angles, which can be readily explained by the steric

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† *Supplementary data available* (No. SUP 56304, 10 pp.): H-atom co-ordinates, full list of bond distances and angles, thermal parameters, geometries of planar moieties and hydrogen bonds. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Atomic co-ordinates ($\times 10^4$) of non-hydrogen atoms with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Zn(1)	−186(2)	−44(2)	0
Zn(2)	6 485(2)	3 232(2)	796(1)
Zn(3)	5 288(2)	3 145(2)	−205(1)
P(1)	−206(4)	−56(4)	519(1)
P(2)	6 577(4)	3 192(4)	1 309(1)
C(11)	1 495(16)	809(18)	683(4)
C(12)	2 459(13)	409(14)	544(3)
C(13)	3 795(15)	1 098(16)	703(4)
O(1)	4 695(9)	2 282(10)	618(2)
O(2)	4 012(10)	504(12)	906(2)
C(14)	−1 008(15)	−1 741(14)	693(3)
C(15)	−2 316(16)	−2 779(15)	531(4)
C(16)	−2 955(14)	−4 117(15)	679(3)
O(3)	−2 719(10)	−5 028(9)	590(2)
O(4)	−3 680(10)	−4 292(11)	892(3)
C(17)	−1 094(16)	754(16)	682(4)
C(18)	−596(21)	2 165(20)	548(4)
C(19)	−1 387(18)	2 800(15)	683(4)
O(5)	−2 656(10)	2 258(10)	642(2)
O(6)	−745(11)	3 849(11)	829(2)
C(21)	7 776(14)	2 756(14)	1 467(3)
C(22)	7 450(14)	1 328(15)	1 416(3)
C(23)	8 445(16)	1 001(15)	1 548(4)
O(7)	8 374(9)	−113(10)	1 469(2)
O(8)	9 257(11)	1 737(10)	1 723(2)
C(24)	5 031(16)	2 016(16)	1 497(5)
C(25)	3 860(16)	2 311(15)	1 442(4)
C(26)	2 563(15)	1 295(16)	1 579(4)
O(9)	1 519(10)	1 309(10)	1 491(3)
O(10)	2 502(10)	415(10)	1 746(2)
C(27)	6 989(14)	4 754(14)	1 482(3)
C(28)	8 405(19)	5 863(16)	1 408(4)
C(29)	8 748(14)	7 213(15)	1 551(4)
O(11)	9 793(10)	8 264(10)	1 465(2)
O(12)	8 024(10)	7 251(10)	1 743(2)
O(13)	4 341(10)	3 385(10)	145(3)
O(14)	5 767(14)	1 712(15)	−160(4)
O(15)	5 732(12)	4 378(13)	−520(3)
O(16)	3 485(11)	1 919(11)	−422(2)
O(17)	7 232(12)	4 585(13)	−19(3)
O(18)	5 693(13)	341(13)	267(2)
O(19)	8 306(11)	6 376(13)	−480(3)
O(20)	7 713(13)	1 577(14)	−470(3)
O(21)	8 384(29)	3 565(24)	−885(6)
O(22)	6 195(24)	3 272(17)	−1 178(4)
O(23)	4 307(13)	1 047(13)	−872(3)
O(24)	6 326(24)	5 739(18)	−1 177(5)

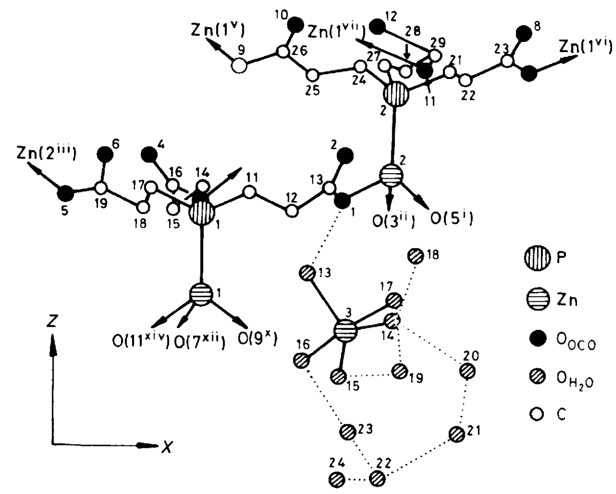

Figure 1. Projection of the formula unit onto the *xz* plane. Hydrogen atoms are omitted for clarity

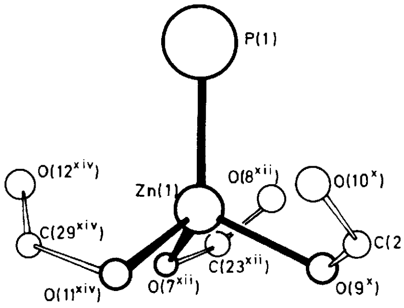

Figure 2. View of the Zn(1) environment

bulk of phosphorus. The direct Zn–P bonding is, however, unique in that it represents, to our knowledge, the first direct zinc–tertiary phosphine bond established by a crystal-structure determination. It follows from a survey of zinc complexes of tertiary phosphines that, in complexes of the type $[ZnX_2(PR_3)_2]$, the presence of Zn–P bonding has been assumed on the basis of indirect spectral evidence;[9] the structure determination of complexes of functionalized phosphines[10] (*i.e.*, bearing further donor atoms besides phosphorus) revealed a strong preference of zinc for hard ligand donors, leaving its P atom(s) unco-ordinated. As the present complex also contains a functionalized phosphine ligand with hard donors, the direct Zn–P bonding is somewhat unexpected and may be related to the steric ability of the ligand to be *P*,*O*-bridging. Zn–P distances of *ca.* 2.41 Å are, of course, typical for a bivalent first-row transition-metal ion and indicate a surprisingly strong P→Zn σ-donation.

The carboxylate groups adopt an unusual conformation which forces the carbonyl oxygens close to the zinc atom to which the appropriate carboxyl oxygens are co-ordinated. The zinc–carbonyl oxygen distances vary from 2.627(11) to 2.771(11) Å for Zn(1) and from 2.880(9) to 3.034(12) Å for Zn(2), which is the main difference between Zn(1) and Zn(2). From a geometrical point of view, the resulting O_6P polyhedron around zinc can be described as a monocapped twisted trigonal prism (local C_3 pseudosymmetry) composed of the lower trigonal face of the carboxyl oxygens, the almost parallel upper trigonal face of the carbonyl oxygens which is twisted by some 50° relative to the lower face, and with the P atom as the cap over the upper face. The zinc atom is located approximately 0.35 Å under the upper face, *i.e.* well inside the O_6P cage. It should be pointed out that ZnOCO moieties of the geometry very similar to that in the present complex occur, though rarely, in other zinc carboxylates and have been either interpreted as chelate bonding,[11] ignored,[12] or possibly overlooked.[13] Despite the remarkable planarity of the ZnOCO moieties we believe that there is no reason to suggest donor–acceptor bonding of the carbonyl oxygens to zinc, mainly because it should involve antibonding orbitals (see ref. 14 for discussion).

The third zinc atom, Zn(3), forms an unprecedented penta-aquazinc(II) cation which is located in holes of the polymeric network. Its geometry (Figure 3) is somewhat distorted but much closer to trigonal bipyramidal (tbp) than to square pyramidal (sp). This is documented, *e.g.*, by the average difference of the actual angles from the ideal ones, which amounts to 3.9° for tbp but 14.4° for sp. In accordance with theoretical calculations,[15] the average axial distance in tbp [2.313(12) Å in the present case] is longer than the average equatorial one [1.990(18) Å]. The Zn(3) atom is located 0.05 Å out of the plane of the equatorial oxygens. The tbp co-

Table 2. Selected distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Zn(1) environment					
Zn(1)–P(1)	2.429(4)	P(1)–Zn(1)–O(11^{xiv})	118.1(3)	O(7^{xii})–Zn(1)–O(9^{x})	104.0(5)
Zn(1)–O(7^{xii})	1.970(10)	P(1)–Zn(1)–O(7^{xii})	118.2(3)	O(7^{xii})–Zn(1)–O(11^{xiv})	99.5(4)
Zn(1)–O(9^{x})	1.991(13)	P(1)–Zn(1)–O(9^{x})	114.7(4)	O(9^{x})–Zn(1)–O(11^{xiv})	99.6(5)
Zn(1)–O(11^{xiv})	1.981(11)				
(*b*) Zn(2) environment					
Zn(2)–P(2)	2.405(4)	P(2)–Zn(2)–O(1)	117.2(3)	O(1)–Zn(2)–O(3^{ii})	100.3(5)
Zn(2)–O(1)	1.961(11)	P(2)–Zn(2)–O(3^{ii})	120.2(3)	O(1)–Zn(2)–O(5^{i})	102.0(5)
Zn(2)–O(3^{ii})	1.977(9)	P(2)–Zn(2)–O(5^{i})	108.6(3)	O(3^{ii})–Zn(2)–O(5^{i})	106.5(5)
Zn(2)–O(5^{i})	1.950(12)				
(*c*) Zn(3) environment					
Zn(3)–O(13)	2.057(14)	O(13)–Zn(3)–O(14)	113.9(6)	O(14)–Zn(3)–O(16)	95.1(6)
Zn(3)–O(14)	1.987(18)	O(13)–Zn(3)–O(15)	118.5(5)	O(14)–Zn(3)–O(17)	88.9(6)
Zn(3)–O(15)	1.926(13)	O(14)–Zn(3)–O(15)	127.5(7)	O(15)–Zn(3)–O(16)	85.9(5)
Zn(3)–O(16)	2.091(11)	O(13)–Zn(3)–O(16)	93.7(5)	O(15)–Zn(3)–O(17)	87.6(5)
Zn(3)–O(17)	2.178(12)	O(13)–Zn(3)–O(17)	89.3(5)	O(16)–Zn(3)–O(17)	173.6(4)

Symmetry code: i: $x + 1, y, z$; ii: $x + 1, y + 1, z$; iii: $x - 1, y, z$; iv: $x - 1, y - 1, z$; v: $x - y, x, z + \frac{1}{6}$; vi: $x - y + 1, x, z + \frac{1}{6}$; vii: $x - y + 1, x + 1, z + \frac{1}{6}$; viii: $x - y, x - 1, z + \frac{1}{6}$; ix: $x - y - 1, x - 1, z + \frac{1}{6}$; x: $y, y - x, z - \frac{1}{6}$; xi: $y + 1, y - x, z - \frac{1}{6}$; xii: $y, y - x + 1, z - \frac{1}{6}$; xiii: $y + 1, y - x + 1, z - \frac{1}{6}$; xiv: $y - 1, y - x, z - \frac{1}{6}$; xv: $1 - y, x - y, z + \frac{1}{3}$; xvi: $y - x + 1, 1 - x, z - \frac{1}{3}$.

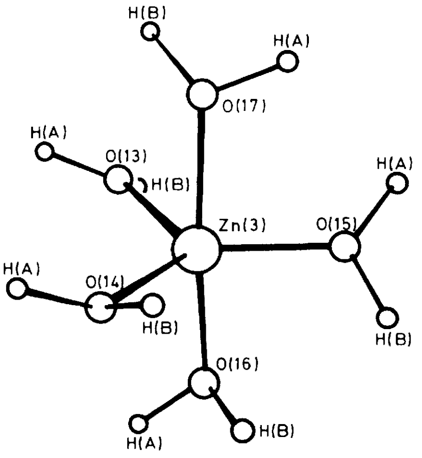

Figure 3. View of the Zn(3) environment

ordination of zinc by chelating nitrogen and oxygen ligands is relatively common,[16] being usually considered as a consequence of the steric requirements of the ligands. With unidentate oxygen donors, only two examples of a tbp ZnO_5 core are known;[13,17] the overall geometry in both is very close to that of Zn(3) in the complex studied. As no strain can be imposed by the unidentate water molecules, the existence of the $[Zn(H_2O)_5]^{2+}$ cation in the present special case must reflect a preference of the metal ion for this co-ordination. Detailed inspection of hydrogen bonding (see later), a factor which might be suspected to be responsible, at least to some extent, for this unusual cation, clearly shows, however, that Zn(3) could be readily accommodated into the accessible system of hydrogen-bonding acceptors as the more familiar tetrahedral tetra-aqua ion and even as the octahedral hexa-aqua ion.

The bond lengths and angles within the ligand are quite normal. They compare fairly well with those of the closely related 3-(diphenylphosphino)propionate anion.[18] Small differences between the ligands bonded to Zn(1) and to Zn(2) are evidently caused by crystal-packing requirements and reflect various distances of the propionate chains from the Zn(3) atom. For instance, the chains belonging to P(1) are slightly more strained than those at P(2), but their carbonyl oxygen contacts to Zn(2) are distinctly longer than the analogous contacts to Zn(1), and *vice versa*. Small differences also apply to the C–P–Zn angles. Such relations are in agreement with the assumption that no donor–acceptor bonding occurs between carbonyl oxygens and zinc.

The whole structure is stabilized by extensive hydrogen bonding. The 'intramolecular' contacts are depicted by dashed lines in Figure 1 and a complete list of all O • • • O distances and the appropriate O–H • • • O geometries which satisfy the criteria for hydrogen bonding[19] is presented in SUP No. 56304. In general, each carboxylate oxygen takes part in one hydrogen bond as a proton acceptor from a water molecule [except O(4) and O(6) which form two such bonds]. In addition to bonding to carboxylate oxygens, the water molecules are also mutually hydrogen bonded, resulting in an approximately tetrahedral geometry at O(19) and O(20) and an approximately trigonal one at the remaining water oxygens. All 12 water molecules in the formula unit are located near to Zn(3). Five of them are co-ordinated to zinc; the remaining seven 'lattice' water molecules are hydrogen bonded to the co-ordinated water molecules either directly [as the one-proton acceptor, O(18), and the two-proton acceptor from the adjacent water molecules, O(19)], or as an unusual 'bidentate' branched chain of water molecules comprising O(20), O(21), O(22), O(23), O(24) in which the first four oxygen atoms are very nearly coplanar.

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