Zinc Complexes of Condensed Phosphates, 2[‡]

Diphosphate−Zinc Complexes with Chelating Coligands

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Zinc perchlorate, diorganodiphosphates (POP^{2-}), and chelating ligands L (L = 1,10-phenanthroline, neocuproine, 2,2′-bipyridine, oxinate) yield three types of ternary complexes. Type 1 ($L_2Zn{\cdot}POP$) contains octahedral zinc bound by the diphosphate as an OPOPO chelate ligand. Type 2 (LZn·POP) consists of dimeric complexes containing five-coordinate zinc, with the diphosphates acting as OPOPO chelate ligands for one zinc ion and as OPO bridges between two zinc ions. Type 3 ($L_2Zn_2{\cdot}POP$), observed only for oxinate, is proposed to contain two five-coordinate zinc ions bridged by the diphosphate as a tetradentate ligand.

Introduction

In the chemistry of condensed phosphates, metal ions play an important role with regard to both the stabilization of the phosphate structures in the solid state[2] and in solution[3] and the activation of the phosphates for hydrolytic cleavage, as exemplified by the many enzymes that transfer phosphate units from oligophosphates, e.g. ATPases, kinases, and pyrophosphatases.[4−7] While the typical metal ions for this purpose are magnesium, calcium, and manganese, zinc can also fulfil the role of the former and may be essential in certain enzymes.[8]

This clearly provides a motivation to study the coordination chemistry of oligophosphates, both from a structural and mechanistic standpoint as well as with regard to modeling of the bonding and reactivity patterns of enzymes that act on oligophosphates. Numerous studies have been published in this field, with a considerable emphasis on metal complexes of ATP and cyclic triphosphate.[3,9] There has been comparatively little work on soluble coordination compounds of pyrophosphate,[10−12] although a copper complex of thiamine pyrophosphate has been described.[13] In addition, structure determinations of several enzymes containing metal-bound oligophosphates, e.g. inorganic pyrophosphate,[14] ADP,[15] and thiamine pyrophosphate,[16] have been reported.

In our field, namely the biorelevant coordination chemistry of zinc, information on condensed phosphates as ligands is still scarce. We are not aware of any solution studies or syntheses of species containing zinc coordinated by simple inorganic or organic pyrophosphates or triphosphates. However, the interactions between zinc and nucleotides have been investigated in solution,[2] the species $Zn_3(ADP)_2$ and $Zn_2(ATP)$ have been isolated,[17] and the structures of zinc complexes with H_2ATP^{2-} [18] and $HATP^{3-}$ [19] have been reported. Among the many metal−oligophosphate solid-state compounds, several zinc pyrophosphate species,[2] a zinc triphosphate,[20] and a zinc tetraphosphate[21] have been obtained and structurally characterized.

Our interest in the coordination chemistry of zinc with oligophosphates stems from our observation that our "enzyme models", the pyrazolylborate−zinc hydroxide complexes, are well suited to effect hydrolytic cleavage of tetraorganopyrophosphates.[22] Our mechanistic implications for these and similar hydrolytic reactions with Zn−OH species[23,24] require that the substrate (e.g. the pyrophosphate) is attached to only one zinc ion through only one oxygen donor during the activation step, which is in contrast to common schemes for phosphate hydrolyses[3,8] that imply attachment of zinc to two P−O units or the attachment of two metal ions to one phosphate entity. We therefore embarked on a comprehensive study of the coordination chemistry of zinc with condensed phosphates.

The aim of this study was to gain an understanding of the factors that control the bonding modes (terminal, chelating, bridging) and the hapticity (monodentate to polydentate) of oligophosphates towards zinc. The measures taken to achieve this were a control of the number of available coordination sites on the zinc ion and influence on the number of donor sites on the oligophosphates. The former was accomplished by using nitrogen-containing coligands with varying donor numbers, the latter by using partially esterified oligophosphates. Thus, we used neither inorganic pyrophosphate or triphosphates nor ADP, ATP, or analogues thereof. Our "substrates" were triorgano- or diorgano-diphosphates, -triphosphates, and -methylenediphosphonates. Our coligands were bidentate and tridentate chelators or tridentate and tetradentate tripods. In accordance with the aims of this investigation, conditions favoring

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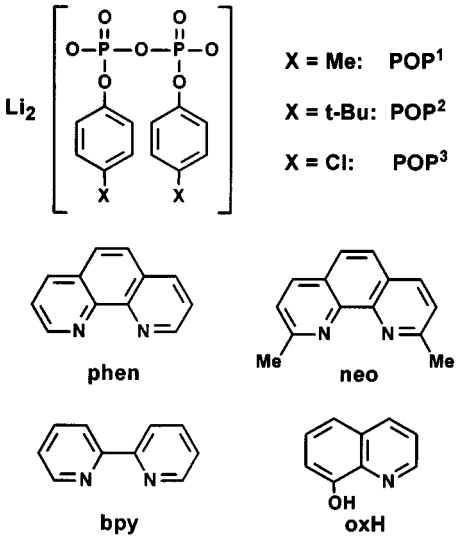
the stoichiometric or catalytic hydrolysis of the oligophosphates were carefully avoided.

This paper describes the results obtained with bidentate coligands. The first paper in this series[1] dealt with oligophosphate complexes of zinc without coligands. The two succeeding papers[25,26] will deal with complexes incorporating coligands of higher donor numbers.

Phosphates and Coligands

The three dilithium diorganodiphosphates $Li_2[POP^1]$, $Li_2[POP^2]$, and $Li_2[POP^3]$ have been described previously by both ourselves[1] and others.[27] They are obtained by condensation of the appropriate organophosphoric acid with the organo(*n*-butylcarbamoyl)phosphate. They undergo hydrolytic cleavage in water only very slowly, but in some cases their reactions with zinc salts give rise to hydrolysis products in the reaction mixtures.

As coligands, we chose the classical examples listed below. Of these, neocuproine could be expected to favor lower coordination numbers than six for zinc, while oxinate, as a negatively charged O,N donor, was likely to produce complexes of a different type compared to the other three coligands.



In the following discussion, the resulting complexes are classified according to product types. Three different stoichiometries corresponding to three different structural types were observed.

Type 1 Complexes: $L_2Zn(POP)$

The complexes of this type, **1** and **2**, were obtained when the *p*-chlorophenyl-substituted diphosphate POP^3 was combined with zinc perchlorate and the coligands phen and bpy. They are the only products in this series for which the octahedral coordination of zinc and the chelating nature of the diphosphate ligands could be predicted from their compositions coupled with the mirror symmetry of the diphosphates and coligands as evidenced by NMR.

$(phen)_2Zn(POP^3)$ **1**

$(bpy)_2Zn(POP^3)$ **2**

X-ray structure determinations of **1** and **2** verified their octahedral nature. Inspection of Figure 1 and 2 reveals the similarity of the two structures. Table 1 summarizes the relevant structural features. It is noticeable that the Zn−O bonds are shorter than the Zn−N bonds, indicating good zinc−phosphate bonding, and that the P=O and P−O(Zn) bond lengths are similar, pointing to a highly ionic nature of the zinc−phosphate interactions. The other structural features are normal for these types of ligands, as observed for instance in $(bpy)_2Zn(NO_3)_2$,[28] $[(phen)_2Zn(H_2O)_2]SO_4$,[29] $(NH_3)_4Co(HP_2O_7)$,[30] and $(bpy)Zn(H_2ATP)$.[18] Both structures demonstrate the stress-free attachment of the organodiphosphates as bidentate ligands forming six-membered chelate rings.

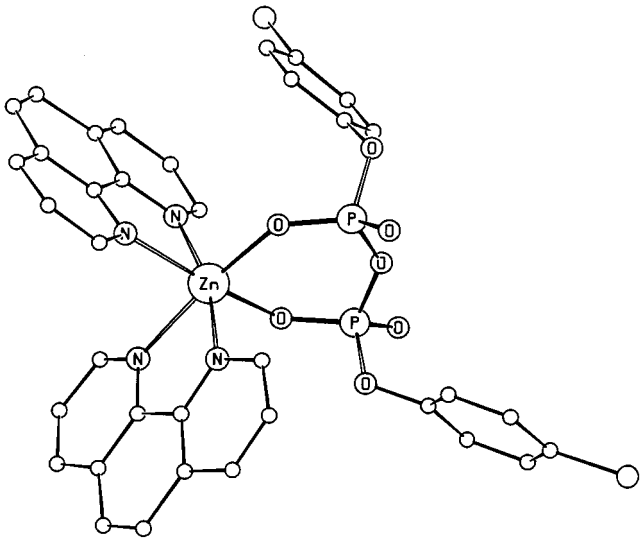


Figure 1. Molecular structure of **1**

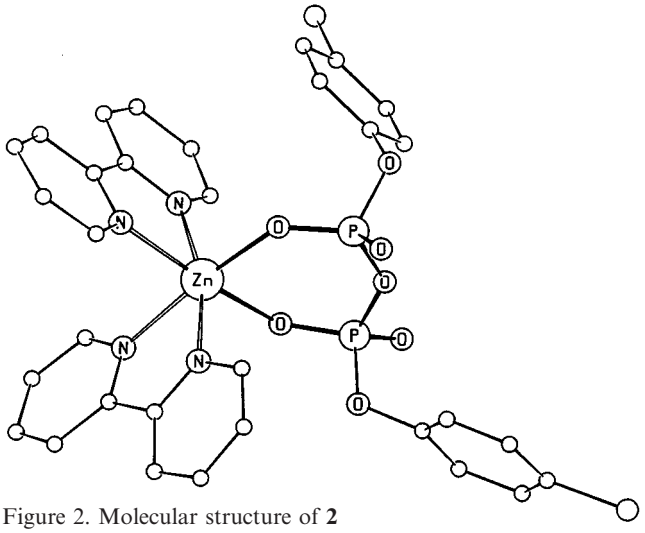


Figure 2. Molecular structure of **2**

Table 1. Bond lengths [Å] and angles [°] in **1** and **2**

	1	**2**
Zn−N	2.12−2.22(1)	2.130−2.214(2)
Zn−O	2.05−2.07(1)	2.057−2.098(2)
P−O(Zn)	1.48−1.49(1)	1.484−1.491(2)
P=O	1.45−1.49(1)	1.468−1.469(2)
P−O(P)	1.59−1.62(1)	1.584−1.615(2)
P−O(C)	1.59−1.62(1)	1.593−1.599(2)
Zn−O−P	130.4−136.0(5)	132.1−137.2(1)
P−O−P	135.5(5)	136.3(1)
O−Zn−O	90.6(3)	89.0(1)

Type 2 Complexes: LZn(POP)

Irrespective of the reaction stoichiometry, all three N,N coligands (phen, neo, bpy) formed 1:1:1 complexes of type 2 with zinc perchlorate and the diphosphates POP^1 and POP^2. In addition, neo also yielded a complex of this type with POP^3. The ^1H NMR data (see Experimental Section) allow a distinction to be made between types 1 and 2, cf. **1**/**3** or **2**/**8**, but they yield no structural information other than that both the diphosphates and the coligands have mirror symmetry. The ^{31}P NMR spectra give the same indications, thereby pointing to a symmetrical bidentate coordination of the diphosphates. This would imply that in solution complex type 2 contains zinc in a tetrahedral ZnN_2O_2 environment.

L·Zn(POP)

L	POP^1	POP^2	POP^3
phen	**3**	**4**	
neo	**5**	**6**	**7**
bpy	**8**	**9**	

Structure determinations of **5** and **6** yielded the surprising information that the compounds are dimeric in the solid state. Figure 3 and 4 show that zinc is five-coordinate in the solid state, its coordination geometry being distorted trigonal-bipyramidal. In both compounds, the two mononuclear fragments are related to each other by an inversion center. Each diphosphate ligand uses two of its terminal oxygen atoms for chelate bonding to one zinc ion and another one to form the bridge linking the two complex halves.

The bonding details (see Table 2) of the coligands and of the chelating diphosphates resemble those of complexes **1** and **2** and may be compared to the same reference compounds (see above). There is, however, a wider spread of bond lengths and angles between **5** and **6** than between **1** and **2**. Overall, the Zn−O and Zn−N bonds in **5** and **6** are shorter, in agreement with the lower coordination number. A notable feature concerns the Zn−O bond lengths in the bridging vs. the chelating mode of the diphosphates. One of the two Zn−O (chelate) bonds is short while the other is 0.10−0.13 Å longer. The latter involves the monophosphate fragment that also provides the bridge bond, thus indicating a weakening of the Zn−O interaction due to the attach-

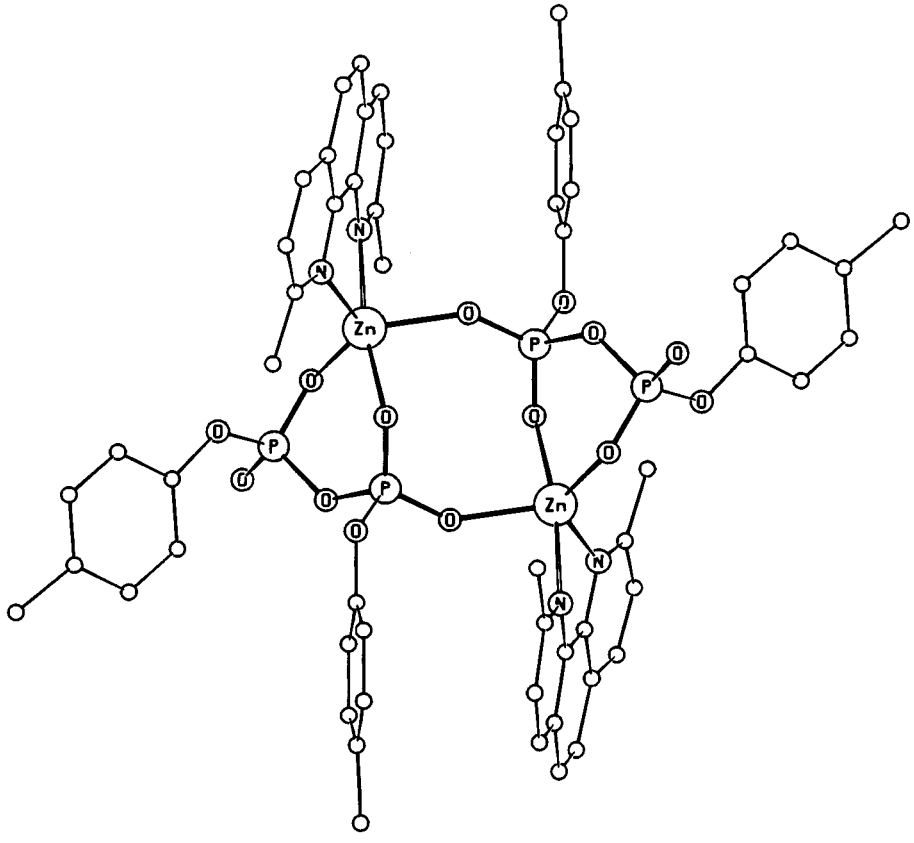


Figure 3. Molecular structure of dimeric **5**

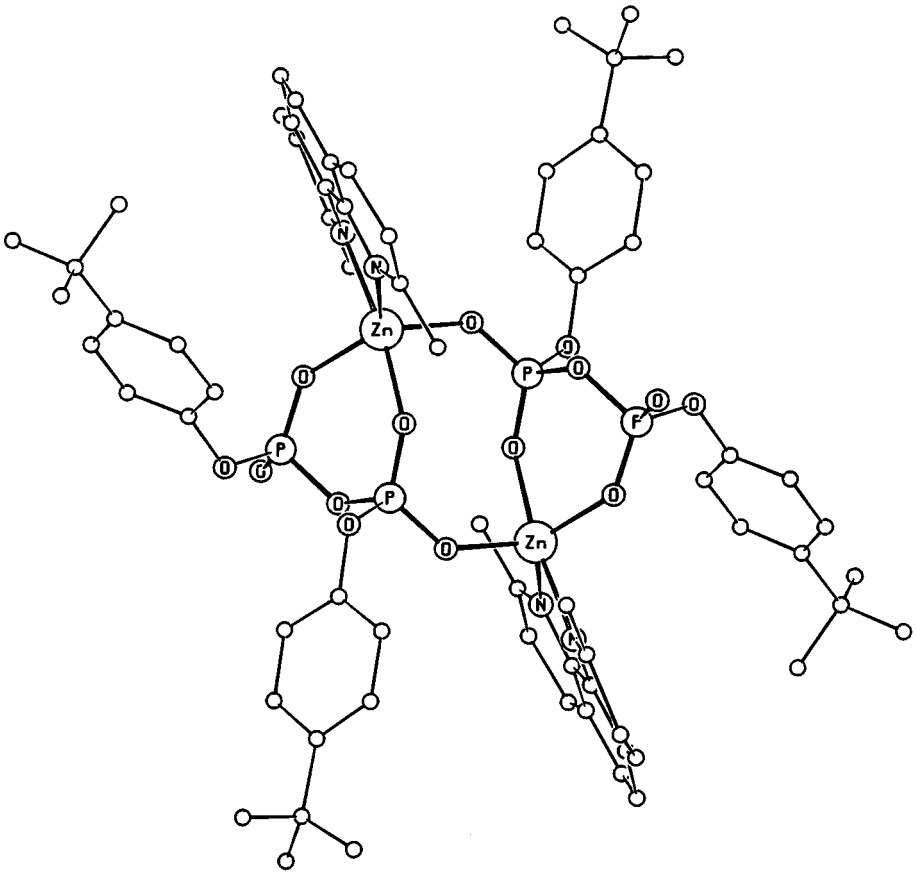


Figure 4. Molecular structure of dimeric **6**

Table 2. Bond lengths [Å] and angles [°] in **5** and **6**

	5	**6**
Zn−N	2.104, 2.141(2)	2.158, 2.173(4)
Zn−O(br)	2.018(2)	1.974(3)
Zn−O(chel)	1.981, 2.078(2)	1.951, 2.082(3)
P−O(br)	1.482(2)	1.530(3)
P−O(chel)	1.478, 1.484(2)	1.534, 1538(3)
P=O	1.470(2)	1.518(4)
P−O(P)	1.601, 1.610(2)	1.602, 1.601(4)
P−O(C)	1.594, 1.600(2)	1.579, 1.587(4)
Zn−O−P(br)	141.9(2)	133.4(2)
Zn−O−P(chel)	128.9, 130.9(2)	137.2, 139.9(2)
P−O−P	129.7(1)	125.8(2)
O−Zn−O(chel)	90.1(7)	83.2(2)
O−Zn−O(br)	87.7, 122.7(8)	93.3, 120.3(2)

ment of a second zinc ion. In contrast, the bridging Zn−O interaction is strong, as indicated by the short bond length. Again, the P−O bond lengths, which are virtually identical for the terminal, bridging, and chelating situations, do not reflect the varying Zn−O interactions in which these P−O functions are involved.

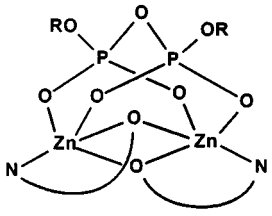
Type 3 Complexes: $L_2Zn_2(POP)$

Only one complex of this type was obtained, and it was also the only complex that could be isolated in a pure state from reactions with oxine. Compound **10** was found to be readily soluble in methanol and hence is unlikely to be a coordination polymer.

$$(ox)_2Zn_2(POP^2)$$

10

The spectra of **10** (see below) again give no information other than that the diphosphate is bound symmetrically. It seems likely that the oxinate oxygen serves as a bridging ligand, as observed for tetrameric bis(oxinato)zinc,[31] and that zinc with oxinate ligands is five- or six-coordinate.[31,32] If one also excludes coordination polymers or solvated species, the number of possible constitutions for **10** becomes small. That depicted below is one of the possibilities, but in view of the lack of spectroscopic support, it can only be regarded as a proposal.



Spectroscopy

The ^{1}H NMR data (see Experimental Section) serve no other purpose than to confirm the compositions of the complexes. In all cases, they indicate that the diphosphates are bound in a symmetrical fashion. As has been shown for **5** and **6**, this is not the case in the solid state. Thus, it must be concluded that the complexes are labile, being characterized by the solution phenomena of solvation and/or fluxionality.

Table 3 lists the IR and ^{31}P NMR spectroscopic data. Coordination of the diphosphates leads to typical features for the very strong IR bands of the PO_2 stretches. In all cases, the two bands due to $\nu_{as}(PO_2)$ are significantly shifted to higher wavenumbers, while the band for $\nu_s(PO_2)$ is shifted by a similar amount to lower wavenumbers. However, as shown by the arrangement in Table 3, similarities within groups of the same POP ligand are more typical than similarities within groups representing the same complex type. Similar conclusions can be drawn from the ^{31}P NMR data. Coordination of the diphosphates is evident from a shift of about 2 ppm to higher field in all cases. However, there are no group trends, and the unsymmetrical nature of the diphosphates in complex type 2 is not reflected in the spectra.

Table 3. IR and ^{31}P NMR data

	$\nu_{as}(PO_2)$[a]	$\nu_s(PO_2)$[a]	$\delta(^{31}P)$[b]
$Li_2[POP^1]$	1270/1230	1140	−15.3
(phen)Zn(POP^1) (**3**)	1288/1228	1115	−17.2
(neo)Zn(POP^1) (**5**)	1289/1241	1118	−17.5
(bpy)Zn(POP^1) (**8**)	1293/1235	1117	−17.2
$Li_2[POP^2]$	1249/1220	1138	−15.5
(phen)Zn(POP^2) (**4**)	1282/1240	1121	−17.2
(neo)Zn(POP^2) (**6**)	1281/1240	1121	−17.4
(bpy)Zn(POP^2) (**9**)	1291/1234	1119	−17.1
$(ox)_2Zn_2(POP^2)$ (**10**)	1274/1230	1119	−17.4
$Li_2[POP^3]$	1254/1223	1155	−16.0
$(phen)_2Zn(POP^3)$ (**1**)	1275/1238	1120	−17.5
(neo)Zn(POP^3) (**7**)	1279/1241	1132	−18.0
$(bpy)_2Zn(POP^3)$ (**2**)	1274/1250	1119	−17.8

[a] In KBr, cm^{-1}. − [b] In DMSO, ppm rel. to H_3PO_4.

Conclusions

In the preceding paper[1] it was shown that reducing the donor capacity of oligophosphates by esterification is not sufficient to produce low molecular weight zinc−oligophosphate complexes. In the present work, we have shown that this can be achieved by reducing the number of coordination sites on zinc through the use of chelating coligands. Complex types **1** and **2**, for which structural information has been obtained, contain one diphosphate ligand per zinc ion, which is bound as an O,O chelate ligand with a six-membered chelate ring. With two N,N coligands, zinc achieves octahedral ZnO_2N_4 coordination. When only one N,N coligand is attached, the diphosphates become tridentate, using one of their P=O functions as a bridging donor. The resulting dinuclear complexes contain zinc in a trigonal-bipyramidal ZnO_3N_2 coordination. Neither a monodentate attachment to one zinc ion nor a bis-monodentate bridging of two zinc ions has been observed. This has prompted us to increase the hapticity of the coligands, leading to the results presented in the two succeeding papers.

Experimental Section

General: For general working and measuring procedures, see ref.[33] The lithium salts of the diphosphates[1,27] were stored under anhydrous conditions. During the course of the reactions, no precautions were taken to prevent the access of moisture. All organic phosphates are potentially toxic and were handled accordingly.

1: A solution of $Li_2[POP^3]$ (100 mg, 0.23 mmol) in boiling methanol (80 mL) was added to a solution of phen (42 mg, 0.23 mmol) and $Zn(ClO_4)_2{\cdot}6H_2O$ (87 mg, 0.23 mmol) in boiling methanol (50 mL). The mixture was filtered while hot, slowly allowed to cool to room temp., and then slowly concentrated to a volume of 20 mL in a desiccator. 30 mg (30%) of **1**, m.p. 168 °C, was precipitated. − $C_{36}H_{24}Cl_2N_4O_7P_2Zn{\cdot}3\,H_2O$ (822.8 + 54.1): calcd. C 49.31, H 3.45, N 6.39, Zn 7.46; found C 48.86, H 3.10, N 6.70, Zn 7.85. − ^{1}H NMR ([D$_6$]DMSO): δ = 6.69 (d, *J* = 8.2 Hz, 4 H, Ph), 6.90 (d, *J* = 8.2 Hz, 4 H, Ph), 7.97 (s, 6 H, phen), 8.25 (s, 6 H, phen), 8.84 (d, *J* = 7.8 Hz, 12 H, phen).

2: Prepared in the same manner as **1** from $Li_2[POP^3]$ (100 mg, 0.23 mmol), bpy (36 mg, 0.23 mmol), and $Zn(ClO_4)_2{\cdot}6H_2O$ (87 mg, 0.23 mmol). After cooling, the mixture was filtered and the filtrate was slowly concentrated to a volume of 8 mL, yielding 35 mg (39%) of **2**; m.p. 261 °C. Water of crystallization (5 H_2O) could be removed by prolonged pumping. − $C_{32}H_{24}Cl_2N_4O_7P_2Zn$ (774.8): calcd. C 49.61, H 3.12, N 7.23, Zn 8.44; found C 48.55, H 2.91, N 6.89, Zn 8.25. − ^{1}H NMR ([D$_6$]DMSO): δ = 7.05 (d, *J* = 8.8 Hz, 4 H, Ph), 7.20 (d, *J* = 8.8 Hz, 4 H, Ph), 7.55 (m, 4 H, bpy), 8.06 (m, 4 H, bpy), 8.45 (m, 4 H, bpy), 8.71 (m, 4 H, bpy).

3: Prepared in the same manner as **1** from $Li_2[POP^1]$ (124 mg, 0.28 mmol) in methanol (25 mL) and phen (50 mg, 0.28 mmol) and $Zn(ClO_4)_2{\cdot}6H_2O$ (103 mg, 0.28 mmol) in methanol (95 mL). Upon cooling, 72 mg (43%) of **3**, m.p. 284 °C, was precipitated. − $C_{26}H_{22}N_2O_7P_2Zn$ (601.8): calcd. C 51.89, H 3.68, N 4.65, Zn 10.86; found C 51.12, H 3.66, N 4.61, Zn 10.76. − ^{1}H NMR ([D$_6$]DMSO): δ = 2.10 (s, 6 H, Me), 6.80 (m, 8 H, Ph), 8.02 (dd, *J* = 6.4, 6.4 Hz, 2 H, phen), 8.19 (s, 2 H, phen), 8.81 (d, *J* = 8.0 Hz, 2 H, phen), 9.11 (d, *J* = 4.2 Hz, 2 H, phen).

4: Prepared in the same manner as **1** from $Li_2[POP^2]$ (92 mg, 0.19 mmol) in methanol (30 mL) and phen (35 mg, 0.19 mmol) and $Zn(ClO_4)_2{\cdot}6H_2O$ (72 mg, 0.19 mmol). Yield 30 mg (23%) of **4**; m.p. 296 °C. − $C_{32}H_{34}N_2O_7P_2Zn$ (686.0): calcd. C 56.03, H 5.00, N 4.08, Zn 9.53; found C 55.43, H 5.01, N 3.89, Zn 9.65. − ^{1}H NMR ([D$_6$]DMSO): δ = 1.19 (s, 18 H, *t*Bu), 6.94 (d, *J* = 8.4 Hz, 4 H, Ph), 7.12 (d, *J* = 8.4 Hz, 4 H, Ph), 8.08 (dd, *J* = 6.4, 6.4 Hz, 2 H, phen), 8.21 (s, 2 H, phen), 8.83 (d, *J* = 8.1 Hz, 2 H, phen), 9.23 (d, *J* = 3.5 Hz, 2 H, phen).

5: Prepared in the same manner as **1** from $Li_2[POP^1]$ (148 mg, 0.33 mmol) in methanol (20 mL) and neo·H_2O (74 mg, 0.33 mmol) and $Zn(ClO_4)_2{\cdot}6H_2O$ (123 mg, 0.33 mmol) in methanol (20 mL). After cooling, the mixture was filtered and the filtrate was slowly concentrated to a volume of 35 mL, yielding 50 mg (24%) of **5**;

m.p. 282 °C. – $C_{28}H_{26}N_2O_7P_2Zn$ (629.9): calcd. C 53.39, H 4.16, N 4.45, Zn 10.38; found C 53.19, H 4.14, N 4.39, Zn 10.40. – ^{1}H NMR ([D$_6$]DMSO): δ = 2.20 (s, 6 H, Me), 2.98 (s, 6 H, Me), 6.91 (m, 8 H, Ph), 7.96 (d, J = 8.6 Hz, 2 H, neo), 8.15 (s, 2 H, neo), 8.80 (d, J = 7.6 Hz, 2 H, neo).

6: Prepared in the same manner as **1** from $Li_2[POP^2]$ (257 mg, 0.54 mmol) in ethanol (150 mL) and neo·H_2O (123 mg, 0.54 mmol) and $Zn(ClO_4)_2$·$6H_2O$ (220 mg, 0.54 mmol) in ethanol (50 mL). After cooling, the mixture was filtered and the filtrate was slowly concentrated to a volume of 150 mL, yielding 171 mg (40%) of **6**; m.p. 294 °C. – $C_{34}H_{38}N_2O_7P_2Zn$·EtOH·H_2O (714.0 + 46.1 + 18.0): calcd. C 55.57, H 5.96, N 3.60, Zn 8.40; found C 55.29, H 5.50, N 3.68, Zn 8.90. – ^{1}H NMR ([D$_6$]DMSO): δ = 1.05 (t, J = 6.9 Hz, 3 H, EtOH), 1.23 (s, 18 H, *t*Bu), 2.99 (s, 6 H, Me), 3.17 (s, 2 H, H_2O), 3.43 (q, J = 6.9 Hz, 2 H, EtOH), 6.95 (d, J = 8.7 Hz, 4 H, Ph), 7.18 (d, J = 8.7 Hz, 4 H, Ph), 7.93 (d, J = 8.1 Hz, 2 H, neo), 8.22 (s, 2 H, neo), 8.73 (d, J = 8.9 Hz, 2 H, neo).

7: Prepared in the same manner as **1** from $Li_2[POP^3]$ (138 mg, 0.32 mmol) in ethanol (100 mL) and neo·H_2O (73 mg, 0.32 mmol) and $Zn(ClO_4)_2$·$6H_2O$ (120 mg, 0.32 mmol) in ethanol (100 mL). Yield 46 mg (21%) of **7**; m.p. 235 °C. – $C_{26}H_{20}Cl_2N_2O_7P_2Zn$ (670.7): calcd. C 46.56, H 3.01, N 4.18, Zn 9.75; found C 47.00, H 3.56, N 3.98, Zn 9.60. – ^{1}H NMR ([D$_6$]DMSO): δ = 3.00 (s, 6 H, Me), 7.04 (d, J = 8.8 Hz, 4 H, Ph), 7.21 (d, J = 8.8 Hz, 4 H, Ph), 7.97 (m, 2 H, neo), 8.16 (s, 2 H, neo), 8.77 (m, 2 H, neo).

8: Prepared in the same manner as **1** from $Li_2[POP^1]$ (105 mg, 0.23 mmol) in methanol (90 mL) and bpy (36 mg, 0.23 mmol) and $Zn(ClO_4)_2$·$6H_2O$ (87 mg, 0.23 mmol) in methanol (10 mL). The mixture was filtered while hot and the filtrate was slowly concentrated to a volume of 50 mL at room temp., yielding 21 mg (16%) of **8**; m.p. 266 °C. – $C_{24}H_{22}N_2O_7P_2Zn$ (577.8): calcd. C 49.89, H 3.84, N 4.85, Zn 11.32; found C 48.82, H 3.64, N 4.76, Zn 11.14. – ^{1}H NMR ([D$_6$]DMSO): δ = 2.18 (s, 6 H, Me), 6.91 (m, 8 H, Ph), 7.71 (m, 2 H, bpy), 8.23 (m, 2 H, bpy), 8.57 (d, J = 7.5 Hz, 2 H, bpy), 8.74 (s, 2 H, bpy).

9: Prepared in the same manner as **1** from $Li_2[POP^2]$ (100 mg, 0.21 mmol) in methanol (90 mL) and bpy (33 mg, 0.21 mmol) and $Zn(ClO_4)_2$·$6H_2O$ (79 mg, 0.21 mmol) in methanol (10 mL). The mixture was filtered while hot and then slowly concentrated to a volume of 50 mL at room temp., yielding 29 mg (20%) of **9**; m.p. 296 °C. – $C_{30}H_{34}N_2O_7P_2Zn$·H_2O (661.9 + 18.0): calcd. C 52.99, H 5.34, N 4.12, Zn 9.62; found C 52.79, H 5.07, N 4.03, Zn 9.45. – ^{1}H NMR ([D$_6$]DMSO): δ = 1.22 (s, 18 H, *t*Bu), 3.17 (s, 2 H, H_2O), 6.97 (d, J = 8.7 Hz, 4 H, Ph), 7.16 (d, J = 8.7 Hz, 4 H, Ph), 7.72 (m, 2 H, bpy), 8.23 (m, 2 H, bpy), 8.58 (d, J = 7.9 Hz, 2 H, bpy), 8.78 (m, 2 H, bpy).

10: Prepared in the same manner as **1** from $Zn(ClO_4)_2$·$6H_2O$ (81 mg, 0.22 mmol) and $Li_2[POP^2]$ (103 mg, 0.22 mmol) in methanol (30 mL) and oxH (32 mg, 0.22 mmol) in methanol (5 mL). The mixture was refluxed for 15 min., filtered while hot, allowed to cool, and then slowly concentrated to a volume of 15 mL, yielding 40 mg (21%) of **10**; m.p. 206 °C. – $C_{38}H_{38}N_2O_9P_2Zn_2$ (859.5): calcd. C 53.11, H 4.46, N 3.26, Zn 15.21; found C 54.27, H 4.87, N 3.20, Zn 14.89. – ^{1}H NMR ([D$_6$]DMSO): δ = 1.23 (s, 18 H, *t*Bu), 7.03 (d, J = 8.5 Hz, 4 H, Ph), 7.08 (s, 2 H, ox), 7.22 (d, J = 8.5 Hz, 4 H, Ph), 7.41 (m, 4 H, ox), 7.56 (dd, J = 6.2, 6.2 Hz, 2 H, ox), 8.35 (d, J = 8.2 Hz, 2 H, ox), 8.83 (s, 2 H, ox).

Structure Determinations:[34] The selected crystals were taken directly from the reaction solutions and used without drying in vacuo. They were immersed in fluorinated polyether oil and immediately placed in the nitrogen stream of the diffractometer's cooling system. Diffraction data were recorded at ca. −100 °C using the ω/2θ technique with a Nonius CAD4 diffractometer fitted with a molybdenum tube (K_α, λ = 0.7107 Å) and a graphite monochromator. Empirical absorption corrections based on ψ scans were applied. The structures were solved by direct methods and refined anisotropically with the SHELX program suite.[35] Hydrogen atoms were included with fixed distances and isotropic temperature factors 1.5 times those of their attached atoms. Parameters were refined against F^2. The R values are defined as $R_1 = \Sigma|F_o - F_c|/\Sigma F_o$ and

Table 4. Crystallographic details

	1	**2**	**5**	**6**
Empirical formula	$C_{36}H_{24}Cl_2N_4O_7P_2Zn$·$3H_2O$	$C_{32}H_{24}Cl_2N_4O_7P_2Zn$·$5H_2O$	$C_{28}H_{26}N_2O_7P_2Zn$·MeOH	$C_{34}H_{38}N_2O_7P_2Zn$·EtOH·H_2O
Molecular mass	822.8 + 36.0	774.8 + 90.1	629.9 + 32.0	714.0 + 46.1 + 18.0
Crystal size [mm]	0.4 × 0.4 × 0.4	0.5 × 0.5 × 0.5	0.5 × 0.4 × 0.3	0.3 × 0.2 × 0.2
Space group	$P2_1$	$P2_1/n$	P-1	$P2_1/c$
Z	4	4	2	4
a [Å]	15.655(1)	15.029(1)	9.868(2)	11.648(2)
b [Å]	15.151(1)	15.499(1)	10.013(2)	29.480(6)
c [Å]	16.737(1)	16.607(1)	15.929(3)	12.255(2)
α [°]	90	90	88.42(3)	90
β [°]	105.54(1)	99.53(1)	72.13(3)	113.70(3)
γ [°]	90	90	75.79(3)	90
V [Å^3]	3824.9(2)	3815.0(1)	1450.2(5)	3853.3(12)
d(calcd.) [gcm^{-3}]	1.43	1.51	1.52	1.29
μ(Mo-K_α) [mm^{-1}]	0.92	0.93	1.01	2.08 (Cu-K_α)
hkl range	h: −20 to 21	h: 0 to 21	h: −12 to 11	h: −13 to 15
	k: −20 to 21	k: 0 to 21	k: −12 to 0	k: −36 to 0
	l: −23 to 21	l: −23 to 23	l: −19 to 19	l: −14 to 0
Measured reflections	12090	11151	6020	8239
Independent reflections	10154	11151	5679	7847
Observed refl. [$I > 2\sigma(I)$]	6493	6325	5120	5542
Parameters	961	478	408	448
Refined reflections	10154	11151	5679	7847
R_1 (obsd. refl.)	0.073	0.040	0.033	0.067
wR_2 (all refl.)	0.206	0.123	0.095	0.220
Residual electron density [e/Å^3]	+0.5	+0.6	+0.8	+0.5
	−0.3	−0.3	−0.5	−0.5

$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]\Sigma[w(F_o^2)^2]\}^{1/2}$. Drawings were produced with SCHAKAL.[36] The crystallographic data are collected in Table 4.

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