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Binary zinc-oligophosphate complexes

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Abstract

Diorganodiphosphates (DPP^{2-}), triorganodiphosphates (TPP^{-}), a diorganotriphosphate ($DPPP^{3-}$), and a triorganomethylenediphosphonate ($TPCP^{-}$) were reacted with zinc perchlorate to form the complex compounds Zn(DPP), $Zn(TPP)_2$, $Zn_3(DPPP)_2$, and $Zn(TPCP)_2$. Spectroscopic investigations and the solubility properties allow to assign Zn(DPP) and $Zn_3(DPPP)_2$ as coordination polymers, while $Zn(TPP)_2$ and $Zn(TPCP)_2$ are molecular complexes.

Keywords: Zinc complexes; Diphosphate; Triphosphate; Spectra

1. Introduction

All enzymes transferring phosphate units from oligophosphates, e.g. ATPases, kinases, pyrophosphates, need metal ions for their function [1–5]. These are typically magnesium and calcium, but quite often zinc is also essential or can take the role of the former [6]. It suggests itself that during enzymatic action the oligophosphate unit which has to be interconverted is coordinated to the metal ion or ions in the active center. Support for this assumption comes from structure determinations of such enzymes containing metal-bound thiamine pyrophosphate (TPP) [7,8], ADP [9], or inorganic pyrophosphate [10].

The coordination chemistry associated with these phenomena, i.e. the study of metal-oligophosphate interactions, has attracted attention earlier on. The structural chemistry of metal oligophosphates is well developed [11], and interactions between metal ions and nucleotides or their constituents in solution have been studied extensively [4], with heavy emphasis on the omnipresent ATP.

We are interested in the biorelevant coordination chemistry of zinc and thus feel attracted also to systems containing zinc-bound oligophosphates. The earliest results in this field were the isolation and spectroscopic characterization of $Zn_3(ADP)_2$ and $Zn_2(ATP)$ [12]. Besides a number of zinc-pyrophosphate species [11] the structures of a triphosphate [13] and a cyclotetraphosphate [14] were determined, followed by the structures of zinc complexes with H_2ATP^{2-} [15] and $HATP^{3-}$ [16] ligands. No zinc enzyme containing metal-bound oligophosphate has been structurally characterized yet. We have already reported the cleavage of tetraorgano-diphosphates by Zn–OH complexes which are inorganic models of zinc enzymes [17].

We have now initiated a study of zinc-oligophosphate complexes, trying to contribute to an understanding of the binding and activation of biological oligophosphates by zinc. We are using organic oligophosphates instead of ATP, ADP or TPP, in order to simplify the systems and to reduce the functionality at the phosphate units. On the side of the zinc ion we control the number of available coordination sites by using chelate ligands of varying haptic-ity. This paper describes the simplest systems studied, i.e. the binary compounds containing only zinc and oligophosphate.

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2. Results and discussion

2.1. Anionic oligophosphates

The oligophosphates were chosen such that they bear not more than one negative charge per phosphorus atom. As a rule, but not throughout, aromatic substituents were used. Synthetic availability and, in the end, purity of the resulting products dictated the choice of the starting materials.

The simplest reagents were the diorganodiphosphates **1a**–**1c**. The preparation of **1c** from tetrabenzyl pyrophosphate by hydrolysis using NaI in acetone has been described before [18]. **1a** and **1b** are new. They were obtained in analogy to the described procedure [19] by condensation between the organophosphoric acid and the organo(n-butylcarbamoyl)phosphate.

$M_2[RO–PO_2–O–PO_2–OR]$

1a: M = Li, R = *p*-tolyl

1b: M = Li, R = *p*-tert-butylphenyl

1c: M = Na, R = benzyl

In order to use ligands with an even lower charge, two triorganodiphosphates were employed. The two benzyl derivatives **1d** and **1e** [18] resulted from the corresponding tetraorganopyrophosphates by hydrolysis like **1c**, using NaI in acetone.

$Na[(RO)_2PO–O–PO_2–OR]$

1d: R = benzyl

1e: R = *p*-bromobenzyl

As a representative of the triphosphates the new bis(*p*-tolyl) ester **1f** was chosen which is accessible by condensation between $POCl_3$ and two equivalents of *p*-tolylphosphoric acid. Finally a monoanionic methylenediphosphonate was employed: the triethyl ester **1g** [20] resulted from the commercially available tetraester by hydrolysis with NaOH.

$Na_3[RO–PO_2–O–PO_2–O–PO_2–OR]$

1f: R = *p*-tolyl

$Na[(RO)_2PO–CH_2–PO_2–OR]$

1g: R = ethyl

Of the organophosphates described here only the triorganodiphosphates are easily susceptible to hydrolytic cleavage into the monophosphates in the presence of water, even more so in the presence of divalent metal ions. They therefore were handled accordingly. It was observed, however, for all oligophosphates **1a**–**g** that in some cases their reactions with zinc salts produced hydrolysis products in the reaction mixtures.

2.2. Zinc complexes

When the three diorganodiphosphates **1a**–**1c** were treated with zinc perchlorate in boiling methanol or ethanol, they yielded the 1:1 complexes **2a**–**2c** upon cooling. **2a**–**2c** are soluble at room temperature (r.t.) only in very polar solvents like DMSO, but could be recrystallized from the hot alcohols.

$Zn[RO–PO_2–O–PO_2–OR]$

2a: R = *p*-tolyl

2b: R = *p*-tert-butylphenyl

2c: R = benzyl

1:2 complexes of much better solubility were obtained when the triorganodiphosphates **1d** and **1e** were reacted with zinc perchlorate. The resulting species **2d** and **2e** are soluble in ethyl acetate, and **2e** was susceptible to FAB mass spectrometry from solution.

$Zn[(RO)_2PO–O–PO_2–OR]_2$

2d: R = benzyl

2e: R = *p*-bromobenzyl

The formation and solubility properties of the diorganotriphosphate complex **2f**, resulting from **1f** and zinc perchlorate in water, resemble those of the diorganodiphosphate complexes **2a**–**2c**. **2f** has a good solubility only in water, in which the NMR data, however (see below) correspond to those of the free ligand **1f**.

$Zn_3[RO–PO_2–O–PO_2–O–PO_2–OR]_2$

2f: R = *p*-tolyl

The methylenediphosphonate **1g** turned out to be most easily hydrolyzed in the presence of zinc salts. The preparation of its zinc complex **2g** in methanol therefore required strictly anhydrous conditions, but still the product could not be obtained analytically pure. **2g** is soluble in most organic solvents, even in hydrocarbons.

$Zn[(RO)_2PO–CH_2–PO_2–OR]_2$

2g: R = ethyl

2.3. Product identifications

Although most of the products **2** were obtained as crystalline materials, none of them was suitable for X-ray diffraction. Hence indirect evidence had to be used for structural assignments. The simplest one is the solubility of the compounds: only the derivatives of the monoanionic triorganodiphosphates, **2d**, **2e,** and **2g**, are soluble in nonpolar organic solvents thereby pointing to their molecular nature. For **2e** and **2g** it was shown by mass spectrometry that they are monomolecular.

The low solubility of all other complexes, which are derived from dianionic oligophosphates, indicates that they are oligonuclear or polymeric.

NMR data of all complexes could be obtained from solutions in DMSO. It must be assumed that the polymers break up in this solvent and that the molecular complexes are partly dissociated. However, in all cases the spectra of the free ligands and of the complexes differ slightly. Table 1 lists the data. As a rule the ^{1}H NMR resonances shift to more positive δ values while the ^{31}P NMR resonances shift to more negative δ values upon coordination. In all cases the expected multiplet patterns are observed, proving the identity of the coordinated oligophosphates.

Table 1
NMR data (in DMSO-d_6, data given as δ [ppm]/J [Hz])

No.	^{1}H NMR	^{31}P NMR
1a	6.98m (C_6H_4), 2.21 (CH_3)	−15.2
2a	7.02m (C_6H_4), 2.23 (CH_3)	−17.6
1b	7.05m, 7.18m (C_6H_4), 1.25 (t-Bu)	−15.5
2b	7.05m, 7.25m (C_6H_4), 1.25 (t-Bu)	−17.5
1c	7.29m (C_6H_5), 4.79m (CH_2)	−8.5
2c	7.31m (C_6H_5), 4.90m (CH_2)	−11.8
1d	($P(OR)_2$): 7.32m (C_6H_5), 5.03/7.6	−10.7/22.4
2d	($P(OR)_2$): 7.30m (C_6H_5), 5.06/8.0	−11.4/28.9
1d	(P–OR): 7.32m (C_6H_5), 4.83/7.8	−11.4/22.4
2d	(P–OR): 7.30m (C_6H_5), 4.89/8.0	−12.2/18.9
1e	($P(OR)_2$): 7.35m (C_6H_5), 5.00/7.6	−10.6/21.1
2e	($P(OR)_2$): 7.28m (C_6H_5), 5.03/7.3	−11.1/19.0
1e	(P–OR): 7.35m (C_6H_5), 4.77/7.6	−11.0/21.1
2e	(P–OR): 7.49m (C_6H_5), 4.85m	−11.8/19.0
1f	7.05m (C_6H_4), 2.20 (CH_3)	−23.2t, −15.8d/18.4
2f	7.01m (C_6H_4), 2.20 (CH_3)	−22.2t, −15.8d/16.0
1g [a]	($P(OR)_2$): 1.20/7.1(CH_3), 4.01/7.1, 7.2 (OCH_2)	12.2/10.3
2g [b]	($P(OR)_2$): 1.35m (CH_3), 4.06/7.2, 7.6 (OCH_2)	12.2/9.7
1g [a]	(P–OR): 1.09/7.1 (CH_3), 3.70/7.0, 7.1 (OCH_2)	26.7/10.3
2g [b]	(P–OR): 1.35m (CH_3), 3.87/7.2, 7.2 (OCH_2)	26.7/9.7

[a] $P–CH_2–P$: 2.09t/20.1.
[b] $P–CH_2–P$: 2.34t/19.6.

Table 2
IR data (in KBr, $\tilde{\nu}$ in cm^{-1})

No.	P=O	PO_2		P–O–P
1a		1270	1140	963
2a		1216	1148	
1b		12498	1141	927
2b		1230	1137	
1c		1239	1141	936
2c		1258	1140	
1d	1291	1136		968
2d	1259	1128		
1e	1273	1133		974
2e	1260	1129		
1f		1259	1151	967
2f		1233	1165	
1g	1237	1168		968
2g	1213	1146		

The IR spectra of oligophosphates are well investigated [21], and some data for their zinc complexes have been published [22,23]. The observations for the organic oligophosphates **1** and their complexes **2** are in accord with these findings, cf. Table 2. The spectra are dominated by intense bands due to P–O functions in the 950–1300 cm^{-1} range. The two most intense of these can be assigned to the terminal P–O units as given in the table. As discussed previously [21–23], unambiguous assignments like the assignment for the $(RO)_2P=O$ units in **d**, **e**, and **g** or for the symmetrical and antisymmetrical stretch of the $RO–PO_2$ units in all ligands and complexes, cannot be made and superpositions of the bands for the various P–O functions, especially in the triphosphate derivatives **f**, must be assumed. Nevertheless a consistent picture emerges from the comparison of the data. In all but one cases the highest frequency P–O band is shifted significantly to lower frequencies while the position of the other band varies irregularly and only by small amounts. In all cases the P–O–P band loses so much intensity upon coordination that it can no longer be assigned among other bands of equally low intensity. This, in accordance with the literature data [21–23], allows the conclusion that two neighbouring phosphate units of all seven phosphate ligands are coordinated to zinc in the solid state compounds, and it does not rule out the possibility that more than two oxygen atoms of each oligophosphate are coordinated.

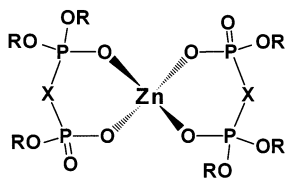
3. Conclusions

In the purely inorganic zinc oligophosphates the zinc ion is almost exclusively in a octahedral ZnO_6 environment [11–16]. It seems unlikely to us that this is also the case in all complexes described here. Our assumption is based on the fact that almost always less than six terminal P–O functions are available per zinc ion. Furthermore we have crystallized a series of zinc complexes bearing tridentate nitrogen donors and organodiphosphates as ligands, which contain five-coordinate or tetrahedral zinc [24]. We therefore propose that the species described here contain four- or five-coordinate zinc and that the principal coordination pattern is that of a chelating O=P–O–P=O attachment.

Applied to the polymeric complexes **2a**, **b**, and **c** this means that one such chelating pattern per diphosphate ligand as well as per zinc ion is possible and that the two remaining P–O functions are used to bind to neighbouring zinc ions thereby establishing the poly-

meric network. Additional Zn–O bonds are possible if some of the P–O functions are used to bridge two zinc ions. Likewise in the triphosphate derivative **2f** two chelating patterns are provided by each triphosphate anion which may be used for the same or for two different zinc ions, the remaining P–O functions being available for linking up the polymeric network again.

Complexes **2d**, **e**, and **g** which are likely to be molecular allow a much simpler formulation which is given below. Taking the monoanionic diphosphates as only bidentate ligands we get tetrahedral coordination in monomolecular species. Including the remaining terminal P–O function as a donor would produce five or six-coordinate zinc, most likely in the form of dinuclear complexes. Again it must be said that we have proved the bidentate coordination of the diphosphates for LZn(diphosphate) complexes where L is a tridentate nitrogen donor [24]. The bonding alternatives for **2d**, **e**, and **g** can be realized strain-free and correspond to molecular entities with a predominantly organic exterior, in accord with the observed solubility of the complexes and their susceptibility to mass spectrometry.



2d, 2e: X = O **2g**: X = CH_2

The present investigation has shown that binary zinc complexes of organic oligophosphates can be obtained. However, even the diorganodiphosphates which bear only two negative charges are still too 'inorganic' to allow the formation of simple (i.e. soluble or molecular) compounds. In order to obtain complexes which are better suited for NMR spectroscopy or crystallization the organic content of the phosphates has to be increased or the available coordination sites at the zinc ions have to be decreased. We have been successful with the latter approach, and subsequent papers in this series will report on molecular (ligand)zinc(pyrophosphate) complexes.

4. Experimental

The general experimental methods and measuring techniques were as in Ref. [25]. The precursors *p*-tolyl-O–$PO(OH)_2$ [26,27], *p*-t-butylphenyl–O–$PO(OH)_2$ [28,29], triethylammonium-(*N*-n-butylcarbamoyl)-OPO_2OR (R = *p*-tolyl, *p*-t-butylphenyl) [19] as well as the known organo-oligophosphates **1c** [18], **1d** [18], **1e** [18] and **1g** [20] were prepared according to the published procedure.

1a: 877 mg (4.61 mmol) of *p*-tolyl-O–$PO(OH)_2$ were dissolved in a nitrogen atmosphere in 6 ml of anhydrous acetonitrile and 2 ml of pyridine. 1.800 g (4.61 mmol) of triethylammonium-*N*-butylcarbamoyl-O-*p*-tolyl-phosphate were added and the mixture stirred at 40°C for 20 h. Then a solution of 391 mg (9.22 mmol) of LiCl in 1.4 ml of water was added with stirring. The precipitate which resulted after a few minutes was filtered off and washed several times with small portions of warm 1:1 acetone/ethanol and once with cold acetonitrile. After drying in vacuo 1.07 g (52%) of **1a**·pyridine remained which melts above 300°C. *Anal.* Calc. for $C_{14}H_{14}Li_2O_7P_2 \cdot C_5H_5N$ (370.1 + 79.1): C, 50.80; H, 4.26; N, 3.12. Found: C, 49.83; H, 4.12; N, 3.10%.

1b: Like **1a** from 2.41 g (10.45 mmol) *p*-t-butylphenyl-O–$PO(OH)_2$ and 4.50 g (10.45 mmol) of triethylammonium-*N*-butylcarbamoyl-O-*p*-t-butylphenyl-phosphate in 7 ml of anhydrous acetonitrile and 5.5 ml of pyridine. Addition of 886 mg (20.90 mmol) of LiCl and workup yielded 3.45 g (70%) of **1b** which according to NMR contained less than one equivalent of pyridine per formula unit. In order to free the product from pyridine 205 mg of it were dissolved in 100 ml of boiling ethanol. The solution was reduced to 30 ml in a rotary evaporator when **1b** began to precipitate. Cooling to −24°C, filtration and drying in vacuo left 39 mg (19%) of analytically pure **1b**·H_2O, melting above 300°C. *Anal.* Calc. for $C_{20}H_{26}Li_2O_7P_2 \cdot H_2O$ (454.3 + 18.0): C, 50.87; H, 5.98. Found: C, 49.22; H, 5.67%.

1f: A suspension of 1.13 g (5.92 mmol) of *p*-tolyl-O-$PO(OH)_2$ in 20 ml of toluene was cooled to 0°C and treated dropwise with stirring with 0.60 g (0.82 ml, 5.92 mmol) of triethylamine and 0.91 g (0.54 ml, 5.92 mmol) of $POCl_3$. After stirring for 1 day at r.t. another 0.60 g (0.82 ml, 5.92 mmol) of triethylamine were added and the mixture stirred for another 12 h. After filtration and washing of the precipitate with toluene the filtrates were hydrolyzed by stirring with 0.71 g (17.7 mmol) NaOH in a few millilitres of water. After decanting the solution the remaining precipitate was dissolved in 10 ml of boiling water. Layering with 40 ml of methanol produced 0.12 g of a precipitate which according to ^{31}P NMR contained four different phosphate derivatives. The filtrate was concentrated in vacuo to 10 ml yielding a second fraction (204 mg) of colourless crystals, consisting mainly of Na_2 (**1a**). Further concentration to 5 ml and layering with 20 ml of methanol resulting in the precipitation of **1f**. Recrystallization from 6 ml of water and 42 ml of methanol yielded 0.56 g (36%) of **1f**·H_2O which melts above 300°C. *Anal.* Calc. for $C_{14}H_{14}O_{10}P_3Na_3 \cdot H_2O$ (504.2 + 18.0): C, 32.20; H, 3.09. Found: C, 32.50; H, 2.69%.

2a: A suspension of 100 mg (0.22 mmol) of **1a**·py in 90 ml of boiling ethanol was treated with stirring with

a solution of 83 mg (0.22 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$ in 10 ml of boiling ethanol. After cooling to r.t. and filtration the filtrate was slowly concentrated to about one third in vacuo. The precipitate of **2a** was filtered off, washed with ethanol and recrystallized from 50 ml of hot ethanol, yielding 40 mg (42%) of **2a**, m.p. 270°C (dec.). *Anal.* Calc. for $C_{14}H_{14}O_7P_2Zn$ (421.6): C, 39.89; H, 3.35; Zn 15.51. Found: C, 39.25; H, 3.88; Zn, 14.95%.

2b: Like **2a** from 88 mg (0.19 mmol) of **1b**·H_2O in 50 ml of boiling methanol and 70 mg (0.19 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$ in 10 ml of boiling methanol. Workup and recrystallization from 30 ml of hot methanol yielded 37 mg (39%) of **2b**, m.p. 280°C (dec.). *Anal.* Calc. for $C_{20}H_{26}O_7P_2Zn$ (505.8): C, 47.50; H, 5.18; Zn, 12.93. Found: C, 46.63; H, 5.11; Zn, 12.72%.

2c: Like **2a** from 100 mg (0.25 mmol) of **1c** in 50 ml of boiling methanol and 92 mg (0.25 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$ in 10 ml of boiling methanol. After heating for 15 min and cooling to r.t. the resulting precipitate was filtered off and washed with cold methanol and a few millilitres of hot water. Drying in vacuo yielded 60 mg (54%) of **2c**·H_2O, m.p. 178°C. *Anal.* Calc. for $C_{14}H_{14}O_7P_2Zn \cdot H_2O$ (421.6 + 18.0): C, 38.25; H, 3.67; Zn, 14.87. Found: C, 37.54; H, 3.57; Zn, 14.94%.

2d: A solution of 75 mg (0.16 mmol) of **1d** in 30 ml of boiling ethanol was treated with a solution of 30 mg (0.08 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$ in 30 ml of ethanol. Upon cooling to r.t. the product precipitated which was filtered off, washed several times with ethanol and dried in vacuo, yielding 30 mg (39%) of **2d**, m.p. 134°C. *Anal.* Calc. for $C_{42}H_{42}O_{14}P_4Zn$ (960.1): C, 52.54; H, 4.41; Zn, 6.81. Found: C, 52.18; H, 4.41; Zn, 6.57%.

2e: Like **2d** from 114 mg (0.16 mmol) **1e** and 30 mg (0.08 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$. Yield 64 mg (55%) of **2e**, m.p. 140°C. *Anal.* Calc. for $C_{42}H_{36}Br_6O_{14}P_4Zn$ (1433.5): C, 35.19; H, 2.53; Zn, 4.56. Found: C, 35.17; H, 2.52; Zn, 4.13%; FAB-MS (*p*-nitrobenzylalcohol): $m/z = 1433$.

2f: A solution of 100 mg (0.20 mmol) of **1f** in 8 ml of water was treated dropwise with stirring with a solution of 111 mg (0.30 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$ in 2 ml of water. Slow diffusion of acetone into this solution produced a precipitate which was filtered off, washed several times with small amounts of methanol and dried in vacuo, yielding 60 mg (57%) of **2f**, which decomposes without melting above 225°C. *Anal* Calc. for $C_{28}H_{28}O_{20}P_6Zn_3$ (1066.5): C, 31.53; H, 2.65; Zn, 18.39. Found: C, 31.40; H, 2.67; Zn, 18.03%.

2g: 38 mg (0.13 mmol) of carefully dried **1g** were dissolved in 1 ml of anhydrous methanol in a nitrogen atmosphere. A solution of 36 mg (0.067 mmol) of $Zn(ClO_4)_2 \cdot 6H_2O$ in 1.5 ml of anhydrous methanol was added dropwise. After addition of 1 ml of hexane the precipitate (mainly $NaClO_4$) was filtered off. The filtrate was evaporated to dryness and the residue washed with a small amount of hexane, leaving behind 29 mg (74%) of **2g**, m.p. 45.50°C, which is highly hygroscopic and was not analytically pure. *Anal.* Calc. for $C_{14}H_{34}O_{12}P_4Zn$ (583.7): C, 28.81; H, 5.87; Zn, 11.20. Found: C, 26.55; H, 4.95; Zn, 10.66%. ESI-MS: $m/z = 583$.

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