ELSEVIER

Journal of Organometallic Chemistry 624 (2001) 58–62

Journal of Organometallic Chemistry

www.elsevier.nl/locate/jorganchem

A single-strand polymer of hexacoordinated zinc(II) phosphodiester complex

Ariane Angeloff, Jean-Claude Daran* [1], Jean Bernadou* [2], Bernard Meunier

Laboratoire de Chimie de Coordination du CNRS, 205, route de Narbonne, F-31077 Toulouse cedex 4, France

Received 11 August 2000; accepted 10 November 2000

This article is dedicated to Professor Jean-François Normant in honor of his fruitful career

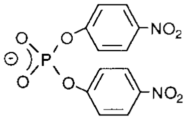
Abstract

The structure of the title compound **2**, *catena*-poly{aqua(dimethylformamide-*O*)bis{μ-[bis(*p*-nitrophenyl)phosphato]}zinc(II) mono(dimethylformamide)}, consists of linear polymers in which adjacent Zn^{2+} cations are joined by the oxygen atoms of two bidentate bridging phosphate diester ligands **1**. The metal shows an octahedral coordination geometry with the zinc connected to six O atoms, four belonging to four different surrounding phosphate groups, one to a water molecule and one to a DMF molecule. Each single-strand is built-up from Zn octahedrons having alternate configuration Δ or Λ. © 2001 Elsevier Science B.V. All rights reserved.

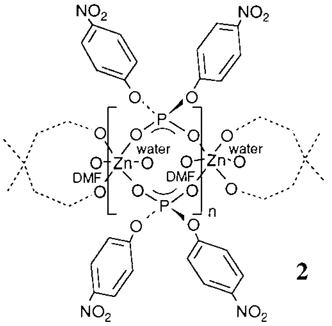
Keywords: Zinc; bis(*p*-Nitrophenyl)phosphate; Single-strand polymer

1. Introduction

The study of metal–nucleotide or metal–polynucleotide interactions has been a subject of continuing research interest since metal ions affect the secondary and tertiary structures, stabilities, and conformational states of nucleic acids. Furthermore, the importance of metal complexes lies on their potential use as models or biomimetic catalysts for metal-containing enzymes, mainly hydrolytic enzymes such as nucleases which are able to catalyze the hydrolysis of P–O bonds of phosphodiesters [1–3] (see Ref. [1] for a general review on zinc enzymology). During our recent studies on the search of new metal complexes able to catalyze the hydrolysis of phosphodiester linkages in nucleic acids [4], we have been able to isolate crystals of **2**, a complex of zinc(II) with the ligand bis(*p*-nitrophenyl)phosphate **1**, a phosphate diester frequently used as a model for metal–nucleic acid interaction studies [5–8]. It is therefore of interest to detail the crystallographic structure of this complex in order to document an original mode of interaction of the zinc(II) ion with a phosphate diester, and to improve our knowledge of such zinc(II) coordination polymers.



1



2

2. Results and discussion

We have been able to obtain the new zinc(II) coordination polymer **2** by treating a DMF solution of bis(*p*-nitrophenyl)phosphate **1** with an aqueous solution of zinc(II) acetate. Compound **2** crystallized as colorless needles by slow evaporation of the solution.

The structure of compound **2**, *catena*-poly{aqua(dimethylformamide-*O*) bis{μ-[bis(*p*-nitrophenyl)-

---

[1] *Corresponding author. E-mail: daran@lcc-toulouse.fr

[2] *Corresponding author. E-mail: bernadou@lcc-toulouse.fr

PII: S0022-328X(00)00892-5

phosphato]}zinc(II) mono(dimethylformamide)}, consists of polymeric chains with the phosphate groups forming double bridges between the zinc atoms. The coordination around the zinc atom is an almost regular octahedron with six oxygen atoms (Fig. 1, Table 1). Four of them belong to four different phosphate groups, whereas the last two oxygen *cis* to each other belong to a water molecule and a DMF molecule. The paired arrangement of the oxygen atoms on three edges leads to a chiral Zn octahedron which appeared to have a Λ configuration for the central Zn(1) on Fig. 1. However, as the space group is centrosymmetric, the two enantiomers Δ and Λ exist in the crystal.

The occurrence of the double bridges leads to the formation of endless single-strand polymers which develop parallel to the *c* axis. Each chain is built-up from Zn octahedrons having alternate configuration Δ or Λ. A stereo view down the *c* axis (Fig. 2) shows the peculiar fan-shaped arrangement of the *p*-nitrophenyl substituents in one single-strand. This packing is certainly related to steric hindrance and tends to minimize intramolecular contacts between the nitrophenyl groups. These *p*-nitrophenyl substituents form an hydrophobic area which covers about 2/3 of the surface of the strand. Opposite to this part, there are the coordinated water and DMF molecules which complete the surface, defining an hydrophilic groove all along the strand (see also Scheme 1). At the outside of this groove, there is a solvent DMF molecule whose oxygen atom is connected through hydrogen bonding to the coordinated water molecule: Ow(1)–H(3A)···O(2) [(Ow(1)–H(3A) = 0.80(3) Å; H(3A)···O(2) = 1.90(3) Å; Ow(1)···O(2) = 2.687(3) Å; Ow(1)–H(3A)···O(2) = 169(5)°]. The second hydrogen H(3B) of the water molecule is also engaged in a bonding interaction with the O(1′) of the [$x, -y+1/2, z-1/2$] symmetry related DMF coordinated molecule: Ow(1)–H(3B) = 0.80(3) Å; H(3B)···O(1′) = 2.09(3) Å; Ow(1)···O(1′) = 2.893(3) Å; Ow(1)–H(3A)···O(1′) = 176(4)°. There is no direct connection between different single strands.

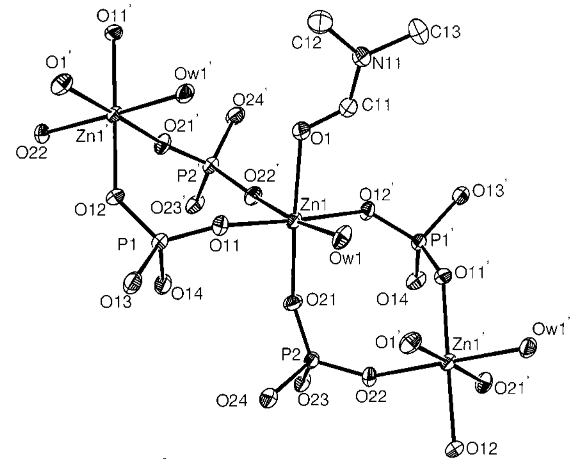


Fig. 1. An ORTEP drawing of **2** showing the metal ion with its octahedral geometry, the numbering of atoms and 50% probability thermal ellipsoids (the *p*-nitrophenyl groups of the phosphate diester ligands and the DMF solvate have been omitted for clarity).

The eight membered ring Zn(1)–O–P–O–Zn(1′)–O–P–O–Zn(1), resulting from the formation of the double bridges, has a boat conformation (Fig. 1). The Zn···Zn distance (4.964 Å) in this double bridge is longer than the 4.614 Å reported in the related complex bis(μ-methylphenylphosphinato)zinc(II) (structure C in Scheme 1) [9]. This lengthening of the Zn···Zn distance may be attributed to the octahedral surrounding of the Zn atoms (Zn has a tetrahedral coordination geometry in structure C) leading to a decrease in the value of the O–Zn–O angle which is close to 90°. The two bridges are slightly different as shown by the comparison of the distances and angles within the bridges. The main difference appears in the Zn–O–P angles, 137.6(1)° and 135.8(1)° for the Zn(1)–O–P(1)–O–Zn(1′) bridge compared to 155.5(1) and 151.5(1)° for the Zn(1)–O–P(2)–O–Zn(1′) bridge. The first type of bridge is coordinated to the metal in *trans* position to the symmetry related one thus building an infinite helicoïdal chain –Zn(1′)–O–P(1)–O–Zn(1)–O–P(1′)–O–Zn(1′)–, whereas the second type of bridge is coordinated to the metal in *trans* position alternatively to the water molecule or to the DMF molecule.

Coordination polymers with a –Zn–O–P–O–Zn sequence have been only previously described with available crystallographic data for polymeric chains of tetrahedral zinc atoms linked by simple phosphinate groups (structure A in Scheme 1) [10], alternating simple and triple phosphinate groups (structure B) [11] or double phosphinate groups (structure C) [9]. One example of a dinuclear octahedral Zn(II) complex with two bridging phosphate diesters has also been reported [12]. The present work on polymer **2** (structure D) shows that Zn(II) can also interact with phosphate diesters to give infinite chains of a double O–P–O bridged structure. This polymer is reminiscent of structure C in Scheme 1 but the coordination around the zinc atom is an almost regular octahedron including, in addition to the phosphate ligands, two ligated solvent molecules (one of water and one of DMF). Crystallization in the presence of these two types of *O*-donor solvent should explain the formation of this 6-coordinate zinc complex. A short comment on the presence and the possible role of the coordinated water molecule in biomimetic hydrolytic processes is provided hereafter.

Modeling of DNA and RNA hydrolytic enzymes is very challenging and since metals can facilitate the hydrolytic cleavage of phosphodiesters, we performed some preliminary experiments on the P–O bond cleavage with zinc(II) acetate [13]. No significant rate acceleration for hydrolyzing of bis(*p*-nitrophenyl)phosphate **1** could be observed. According to the present struc-

Table 1
Selected bond lengths (Å) and angles (°) for complex **1** [a]

Bond lengths			
Zn(1)–O(11)	2.0727(17)	Zn(1)–O(22) # 1	2.0513(17)
Zn(1)–O(21)	2.0581(17)	Zn(1)–O(12) # 2	2.0924(17)
Zn(1)–O(1)	2.1940(18)	Zn(1)–OW1	2.0866(18)
P(1)–O(11)	1.4794(18)	P(1)–O(12)	1.4837(18)
P(1)–O(14)	1.6018(18)	P(1)–O(13)	1.6105(19)
P(2)–O(21)	1.4683(18)	P(2)–O(22)	1.4786(17)
P(2)–O(23)	1.6139(18)	P(2)–O(24)	1.607(2)
O(13)–C(131)	1.387(3)	O(23)–C(231)	1.381(3)
O(14)–C(141)	1.379(3)	O(24)–C(241)	1.383(3)
O(131)–N(13)	1.222(4)	O(231)–N(23)	1.219(4)
O(132)–N(13)	1.222(4)	O(232)–N(23)	1.226(3)
O(141)–N(14)	1.232(4)	O(241)–N(24)	1.219(4)
O(142)–N(14)	1.222(4)	O(242)–N(24)	1.228(4)
O(1)–C(11)	1.241(3)	N(11)–C(12)	1.452(4)
N(11)–C(11)	1.322(3)	N(11)–C(13)	1.464(4)
Bond angles			
O(22) # 1–Zn(1)–O(21)	92.41(7)	O(22) # 1–Zn(1)–O(11)	93.04(7)
O(22) # 1–Zn(1)–OW1	173.02(8)	O(22) # 1–Zn(1)–O(12) # 2	89.61(7)
O(22) # 1–Zn(1)–O(1)	89.56(7)	O(11)–Zn(1)–O(12) # 2	174.78(7)
O(21)–Zn(1)–O(11)	95.70(7)	O(21)–Zn(1)–O(12) # 2	88.69(7)
O(21)–Zn(1)–OW1	94.21(7)	O(11)–Zn(1)–OW1	88.51(7)
O(21)–Zn(1)–O(1)	176.35(7)	OW1–Zn(1)–O(12) # 2	88.34(7)
O(11)–Zn(1)–O(1)	87.26(7)	O(12) # 2–Zn(1)–O(1)	88.26(7)
OW1–Zn(1)–O(1)	83.71(7)		
O(11)–P(1)–O(12)	120.78(10)	O(21)–P(2)–O(22)	121.97(11)
O(11)–P(1)–O(13)	111.10(10)	O(21)–P(2)–O(23)	111.13(10)
O(12)–P(1)–O(13)	103.27(10)	O(22)–P(2)–O(23)	103.19(10)
O(11)–P(1)–O(14)	105.68(10)	O(21)–P(2)–O(24)	105.54(11)
O(12)–P(1)–O(14)	112.28(10)	O(22)–P(2)–O(24)	111.05(10)
O(14)–P(1)–O(13)	102.28(11)	O(24)–P(2)–O(23)	102.34(10)
P(1)–O(11)–Zn(1)	137.55(10)	P(1)–O(12)–Zn(1) # 1	135.75(11)
P(2)–O(21)–Zn(1)	155.46(11)	P(2)–O(22)–Zn(1) # 2	151.49(12)
C(11)–O(1)–Zn(1)	119.29(17)	C(12)–N(11)–C(13)	117.3(2)
C(11)–N(11)–C(12)	121.7(2)	C(11)–N(11)–C(13)	121.0(3)

[a] Symmetry transformations used to generate equivalent atoms: # 1 x, $-y+1/2$, $z+1/2$; # 2 x, $-y+1/2$, $z-1/2$.

tural data on the complex **2**, this absence of reactivity is likely to be due to at least one of the following reasons: (i) since the zinc(II) cation is connected to four different phosphates, the neutralization of the initial phosphate charge may not be sufficient, the pK_a value of the bound water may not be low enough to generate a strong OH^- nucleophile and/or the stabilization of the *O*-leaving group fails; (ii) geometric factors such as the O(bound water)–P distances may be inappropriate for an efficient nucleophilic attack on the phosphorus atom: Ow(1)–P distances in Fig. 1 are 3.48, 3.86, 4.32 and 5.46 Å for Ow(1)–P(1′), Ow(1)–P(2), Ow(1)–P(1) and Ow(1)–P(2′), respectively; examples of efficient hydrolysis were previously observed for a distance ranging from 2.8 to 3.2 Å [5,14,15]; (iii) in addition, the rigidity of the system is probably too high to allow inversion of configuration during P–O hydrolysis.

In conclusion, the new stable zinc(II) phosphodiester complex **2** shows some structural features of the previously known zinc polymers connected by phosphinate bridges but, in the present case, the octahedral coordination of the Zn^{2+} cation, the double phosphate bridges, the fan-shaped arrangement of the hydrophobic *p*-nitrophenyl substituents and the presence of two solvent molecules as ligands giving an hydrophilic groove at the surface of the strand result in an original single-strand coordination polymer. In addition, such a structure indicates that the metal-catalyzed hydrolysis of P–O bonds of phosphate diesters is not a simple process only related to the coordination of a metal ion to the phosphate group but a more complex processes involving probably more than one metal ion by phosphate site.

3. Experimental

Elemental analyses were carried out by the 'Service de Microanalyse du Laboratoire de Chimie de Coordination'. ^{1}H-NMR spectra were recorded with a Brucker AM 250 (250 MHz), DMSO-d_6 was used as a solvent, $\delta_H = 2.6$. MS spectra were recorded with a Nermag R10-10, 70 eV (FAB$^+$/*meta*-nitrobenzyl alcohol) or a Perkin–Elmer SCIEX API 365 (electrospray) by the 'Service de Spectrométrie de Masse de Chimie UPS-CNRS de Toulouse'.

3.1. Synthesis of complex 2

The complex **2** was obtained by mixing a solution of bis(*p*-nitrophenyl)phosphate (50 mg, 147 μmol, 1.7 equivalent) in 2 ml of DMF with a solution of $Zn(AcO)_2$ (16 mg, 87 μmol, one equivalent) in 2 ml H_2O. Colorless needles suitable for X-ray analysis were obtained by slow evaporation of the solvent at 4°C.

Crude complex **2**: m.p: 93°C. Anal. Calc. for $[C_{27}H_{25}O_{18}N_5P_2Zn, 0.5DMF, 0.5{\cdot}H_2O]_n$: C, 38.90; H, 3.02; N, 8.41. Found: C, 38.34; H, 2.88; N, 9.11%. ^{1}H NMR (DMSO-d_6): δ 2.84 (s, 1.5×3H, N(CH_3)$_2$), 3.00 (s, 1.5×3H, N(CH_3)$_2$), 7.51 (d, $J = 7.2$ Hz, 8H, aromatic protons), 8.07 (s, 1.5×1H, NC*H*O), (d, $J = 7.2$ Hz, 8H, aromatic protons). MS data: ES–MS (DMSO–H_2O) *m*/*z*: 480.9 $[\mathbf{1} + Zn^{II} + DMSO]^+$, 558.9 $[\mathbf{1} + Zn^{II} + 2 \times DMSO]^+$, 498.9 $[\mathbf{1} + Zn^{II} + DMSO + H_2O]^+$. FAB-MS (MNBA–DMSO–$H_2O$) *m*/*z*: 481 $[\mathbf{1} + Zn^{II} + DMSO]^+$, 559 $[\mathbf{1} + Zn^{II} + 2 \times DMSO]^+$, 637 $[\mathbf{1} + Zn^{II} + 3 \times DMSO + H_2O]^+$, 899 $[2 \times \mathbf{1} + Zn^{II} + 2 \times DMSO + H^+]^+$.

3.2. X-ray crystallographic study

Data were collected on a Stoe IPDS diffractometer. The final unit cell parameters were obtained by the least-squares refinement of 5000 reflections. Only statistical fluctuations were observed in the intensity monitors over the course of the data collections.

The structure was solved by direct methods (SIR97 [16]) and refined by least-squares procedures on F^2. All H atoms attached to carbon were introduced in calculation in idealized positions [d(CH) = 0.96 Å] and treated as riding models. H atoms attached to water molecules were refined with an equivalent isotropic thermal parameter. Least-squares refinements were carried out by minimizing the function $\Sigma\, w(F_o^2 - F_c^2)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Models reached convergence with $R = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$ and $wR_2 = \{\Sigma\, w(F_o^2 - F_c^2)^2/\Sigma\, w(F_o^2)^2)^{1/2}\}$, having values in Table 2.

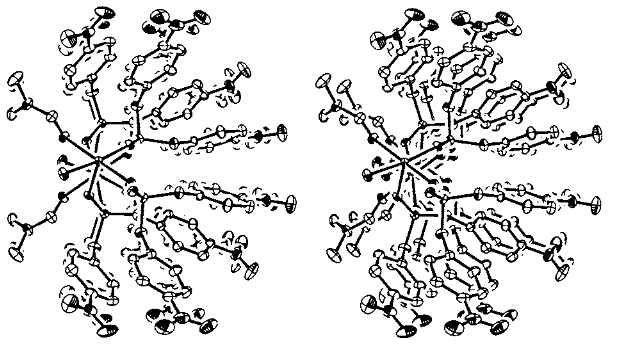
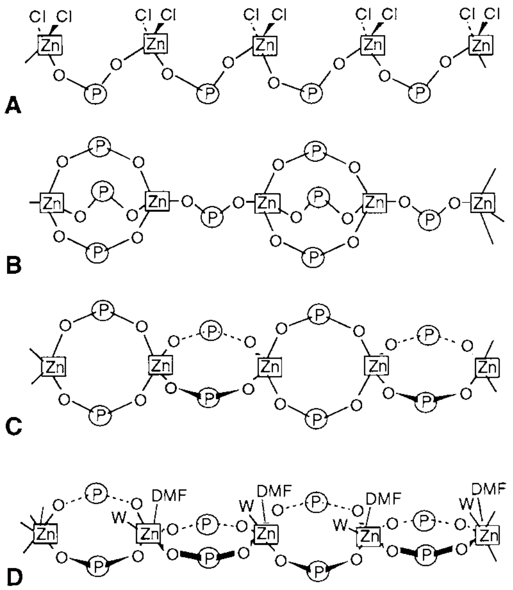


Fig. 2. Stereo view of the structure of **2**, down the crystallographic *c* axis.



Scheme 1. Examples of polymeric chains in which single phosphinate groups (A) [10], single and triple phosphinate groups (B) [11], double phosphinate groups(C) [9] and double phosphate groups (D) [this work] alternate between tetrahedral (A–C) or octahedral (D) zinc atoms. P = phosphinate or phosphate group; W = water molecule.

Table 2
Crystal data

Empirical formula	$C_{30}H_{32}N_6O_{19}P_2Zn$
Formula weight	907.93
Temperature (K)	160(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	16.3816(19)
b (Å)	23.534(3)
c (Å)	9.8549(11)
α (°)	90.0
β(°)	106.590(13)
γ (°)	90.0
V (Å$^{3)}$	3641.1(7)
Z	4
Crystal size (mm^3)	0.32 × 0.30 × 0.08
θ range for data collection (°)	3.67–29.13
Reflections collected	40818
Independent reflections	9736 [$R_{int} = 0.0590$]
Completeness to $\theta = 29.13°$	99.2 %
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9736/1/534
Goodness-of-fit on F^2	1.041
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0443$, $wR_2 = 0.1060$
R indices (all data)	$R_1 = 0.0674$, $wR_2 = 0.1193$
Largest difference peak and hole (e Å^{-3})	0.517 and −0.726

The calculations were carried out with the SHELXL-97 program [17] using the integrated system WINGX (1.63) [18]. Molecular view was realized with the help of ORTEP [19].

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147765. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank Bruno Donnadieu for X-ray data.

References

[1] W.N. Lipscomb, N. Sträter, Chem. Rev. 96 (1996) 2375.

[2] E. Kimura, T. Koike, Adv. Inorg. Chem. 44 (1997) 229.

[3] G. Pratviel, J. Bernadou, B. Meunier, Adv. Inorg. Chem. 45 (1998) 251.

[4] A. Angeloff, J.-C. Daran, J. Bernadou, B. Meunier, Eur. J. Inorg. Chem. (2000) 1985.

[5] E. Kövari, R. Krämer, J. Am. Chem. Soc. 118 (1996) 12704.

[6] E. Kimura, Y. Kodama, T. Koike, M. Shiro, J. Am. Chem. Soc. 117 (1995) 8304.

[7] M. Wall, B. Linkletter, D. Williams, A.-M. Lebuis, R. Hynes, J. Chin. J. Am. Chem. Soc. 121 (1999) 4710.

[8] P. Hendry, A.M. Sargeson, J. Am. Chem. Soc. 111 (1989) 2521.

[9] R. Cini, P. Orioli, M. Sabat, H.D. Gillman, Inorg. Chim. Acta 59 (1982) 225.

[10] Z. Zak, J. Kozisek, T. Glowiak, Z. Anorg. Allg. Chem. 477 (1981) 221.

[11] F. Giordano, L. Randaccio, A. Ripamonti, Acta Crystallogr. Sect. B 25 (1969) 1057.

[12] C. Bazzicalupi, A. Bencini, A. Bianchi, V. Fusi, C. Giorgi, P. Paoletti, B. Valtancoli, D. Zanchi, Inorg. Chem. 36 (1997) 2784.

[13] A. Angeloff, Toulouse University, Ph.D. Thesis, 1999.

[14] T.C. Bruice, A. Tsubouchi, R.O. Dempcy, L.P. Olson, J. Am. Chem. Soc. 118 (1996) 9867.

[15] J.S. Seo, N.-D. Sung, R.C. Hynes, J. Chin, Inorg. Chem. 35 (1996) 7472.

[16] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagn, J. Appl. Cryst. 32 (1999) 115.

[17] G.M. Sheldrick, SHELX97, Programs for Crystal Structure Analysis (Release 97-2), lnstitüt für Anorganische Chemie der Universitat, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.

[18] L.J. Farrugia, J. Appl. Cryst. 32 (1999) 837.

[19] M.N. Burnett, C.K. Johnson, ORTEP-III, Report ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, TN, 1996.