

SYNTHESIS AND CRYSTAL STRUCTURE OF NEW Zn(II) COMPLEX WITH *N*-[BIS(BENZYLAMINO)PHOSPHORYL]-2,2,2-TRICHLOROACETAMIDE

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Abstract. The novel binuclear Zn(II) complex of general formula $[Zn_2(L)_4(CH_3OH)_2]$, where $L = \{Cl_3C(O)NP(O)(NHCH_2Ph)_2\}^-$ (*N*-[bis(benzylamino)phosphoryl]-2,2,2-trichloroacetamide), has been synthesized from a non-aqueous solution and characterized by elemental analysis, FTIR and NMR spectroscopies as well by the X-ray single crystal diffraction technique. This complex represents the third example of binuclear complexes with this ligand. It crystallizes in the triclinic *P*-1 space group $a = 11.1197(2)$ Å, $b = 13.3545(2)$ Å, $c = 15.4398(3)$ Å, $\alpha = 106.9280(9)^\circ$, $\beta = 90.8146(9)^\circ$, $\gamma = 113.5503(9)^\circ$. The metal ion has distorted octahedral geometry; two deprotonated phosphoryl ligands in independent part are coordinated in bidentate chelate manner and joined in a dimer by the bridging oxygen atoms of the phosphoryl groups of the ligand molecules, the coordinated methanol molecule complete the coordination sphere of the central atom to six.

Keywords: carbacylamidophosphate, synthesis, zinc, complex, crystal structure.

Received: 24 September 2021/ Revised final: 23 November 2021/ Accepted: 27 November 2021

Introduction

The design of new ligand systems for the synthesis of the complexes with given structure and useful properties (optical, conductive, biologically active, catalytic *etc.*) remains one of the priority tasks of modern coordination chemistry. From this point of view polydentate carbacylamidophosphate (CAPH) ligands and their complexes present a very promising and intensively studied class of compounds. Such O,O'-donor ligands of the general formula $RC(O)NHP(O)R_2$ [1] can be considered as *P,N*-substituted analogues of β -diketones – widely studied and practically used chelate ligands. Simultaneous presence in the same molecule of both phosphoryl and carbonyl bonds promoted unique physicochemical properties of the ligands and their complexes. Many compounds of this type are biologically active (*e.g.* antiviral [2] and anticancer [3] properties). The presence of the phosphoryl group in carbacylamidophosphates, which shows high affinity to lanthanide ions, makes them particularly interesting for the coordination chemistry of rare earth metal. One of the most interesting features of these compounds is CAPH complexation modes - in the

deprotonated form (L^-) that behaves as a powerful chelating agent for various metal ions [4], while in the neutral form (HL) - as coordinated *via* the phosphoryl oxygen [5].

This work is a result of ongoing research into the coordination chemistry of carbacylamidophosphate compounds: types of their coordination with different metals ions (3d, 4f metals), the influence of substituents nature near the $-C(O)N(H)P(O)<$ functional fragment on the structural parameters of compounds and on the peculiarity of the intramolecular interactions in the crystal state of CAPH compounds. The structure of CAPH ligands offers rich and versatile possibilities for their further functionalization.

Herein, the goal of the study was set to the synthesis, spectral characterisation and X-ray diffraction analysis of the structure of the new binuclear Zn complex based on *N*-[bis(benzylamino)phosphoryl]-2,2,2-trichloroacetamide. To the best knowledge, another two examples of the Cu and Ni binuclear complexes based on above mentioned ligand, having dimeric structure due to bridging function of the phosphorylic oxygen atoms only, have been reported previously by us [6] and one more Zn

complex with carbacylamidophosphate-type ligand was reported by Gholivand, K. *et al.* [7]. The crystal structure of the *N*-[bis(benzylamino)phosphoryl]-2,2,2-trichloroacetamide was previously described by Ovchynnikov, V.A. [8].

Experimental

Materials

All reagents (phosphorus pentachloride, trichloroacetamide, benzylamine, zinc nitrate hexahydrate) were purchased from commercial sources and used as received unless otherwise stated.

Synthesis of HL

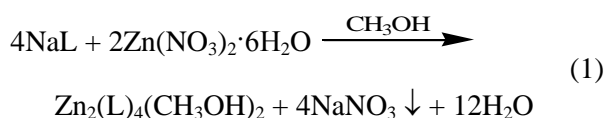
The *N*-[bis(benzylamino)phosphoryl]-2,2,2-trichloroacetamide was prepared *via* the three-step procedure based on the Kirsanov's reaction [9] according to the previously described procedure [7,8]. The identification of the ligand and its sodium salt was performed by measuring melting point values and by registering the FTIR and NMR spectra, which were in agreement with literature data [8,10].

HL (C₁₆H₁₇C₁₃N₃O₂P) (m.p.= 144°C; M= 420.66). Anal. calcd.: C 45.68, H 4.07, N 9.99; found: C 45.73, H 3.95, N 9.85. FTIR: 3365 [ν(N-H)], 3030 [s, ν(CH)], 1708 [w, ν(C=O)], 1454 [s, ν(amide II)], 1251 [vs, ν(P=O)], 873 s [w, ν(PN)], 679 s [s, ν(CCl)]. ¹H NMR: δ= 4.04 (m, 4H, CH₂), 5.3 (m, 2H, NH), 7.18 - 7.33 (m, 10H, Ph), 9.74 (s, 1H, NH). ¹³C NMR: 43.72 s, 93.08 d (CCl); 126.65 s, 127.26 s, 128.09 s, 140.74 d – aromatic; 161.47 [s, NH-C=O]. ³¹P NMR: 7.68 [s, PO] (Figures S1-S4, Supplementary material).

NaL (C₁₆H₁₆Cl₃N₃O₂PNa) FTIR: 3404 [w, OH (from MeOH)], 3030 [w, ν(CH)], 1620 [vs, ν(C=O)], 1338 [vs, ν(amide II)], 1208 m [s, ν(P=O)], 1098 m, 1072m [w, ν(PO)], 873 s [w, ν(PN)], 678 s [s, ν(CCl)], 482 s. ¹H NMR: δ= 3.4 (m, 4H, CH₂), 4.04 (m, 2H, NH), 7.14 - 7.33 (m, 10H, Ph) [Solv(CH₃OH) - 3.15 (d, 1.5H, CH₃), 4.1 (d, 1H, OH)]. ¹³C NMR: 44.35 [s, CH₂], 48.64 wv [res. CH₃OH]; 126.20 s, 127.47 s, 127.93 s, 142.28 d – aromatic; 165.03 [s, NH-C=O]. ³¹P NMR: 7.68 [s, PO] (Figures S5-S8 from Supplementary material).

Synthesis of [Zn₂L₄(CH₃OH)₂]

The Zn₂L₄(CH₃OH)₂ complex was synthesized according to the reaction described in Eq.(1).



For this, the methanol solution of Zn(NO₃)₂·6H₂O (1 mmol) was added to a solution of NaL (2 mmol) in methanol according to literature procedures [6,10,11]. The solution was evaporated and the residue was triturated with acetone- methanol mixture (9:1v/v). The solid that precipitated within an hour (NaNO₃) was filtered off and the clear solution was placed in a vacuum desiccator over CaCl₂. Colourless crystals of the complexes suitable for X-ray analysis were formed within 1-2 days. Afterwards, these were filtered off, washed with cooled 2-propanol, and air-dried at room temperature (yield 78-82%). The obtained complex was soluble in acetone, acetonitrile, alcohols and toluene; and insoluble in water, hexane and cyclohexane.

ZnL₄(CH₃OH)₂ (C₆₆H₇₂Cl₁₂N₁₂O₁₀P₄Zn₂) (M= 1860.49 g/mol) (m.p.= 175-188°C). Anal. calcd.: Zn, 6.98; C, 42.31; H, 3.87; N, 8.97%; found: Zn, 6.96; C, 41.94; H, 4.11; N, 8.89%. FTIR: 3345 d [s, ν(N-H)], 3030, 2929 [w, ν(CH)], 1601 [vs, ν(C=O)], 1496 [s, ν(CC)_{aromatics}], 1344 [vs, ν(amide II)], 1209 m [vs, ν(P=O)], 1098 m, 1071m [w, ν(PO)], 874 s [w, ν(PN)], 679 s [s, ν(CCl)], 488 s. ¹H NMR: δ= 3.18 (d, 6H, CH₃), 4.13 (m, 16H, CH₂), 4.77 (m, 8H, NH), 7.16 - 7.34 (m, 40H, Ph). ¹³C NMR: 44.35 [s, CH₂], 48.64 wv [res. CH₃OH]; 99.04 d, 126.20 s, 127.47 s, 127.93 s, 148.28 s – aromatic; 165.03 [s, NH-C=O]. (Figures S9-S11 from Supplementary material).

Physical measurements

The composition of the complex was determined by the *elemental analysis*(C,H,N) using EL III Universal CHNOS Elemental Analyzer.

Quantitative determination of the metal was performed by *atomic absorption spectroscopy* using a Perkin-Elmer flame atomic absorption spectrometer 3300 (Connecticut, U.S.A.).

Melting point values were measured by using simultaneous TGA–DTA Shimadzu DTG-60H thermal analyzer apparatus.

¹H, ¹³C and ³¹P NMR spectra in DMSO-*d*₆ solution were recorded on a Varian 400 NMR 64 spectrometer, at room temperature. ¹H chemical shifts were determined relative to the internal TMS; ³¹P chemical shift were determined relative to 85% H₃PO₄ as an external standard. NMR data are given in ppm.

FTIR measurements were performed on a Perkin Elmer Spectrum BX spectrometer on samples in the form of KBr pellets in the spectral range 4000–400 cm⁻¹.

Single crystal X-ray diffraction (XRD) data for [Zn₂(L)₄(CH₃OH)₂] were collected at 20°C

using Bruker SMART APEXII diffractometer (Mo-K α radiation, CCD-detector, graphite monochromator, ω -scan). The crystal data collection and structure refinement details are summarized in Table 1. The structure was solved by direct method and refined against F^2 by full-matrix least-squares method using the SHELXTL package [12-14]. All non-hydrogen atoms were refined within anisotropic approximation. The hydrogen atoms (except H₆N and H₅N which were refined within isotropic approximation) were added geometrically and refined as riding, with Uiso= 1.2Ueq(C) for carbon atoms of the ligand and Uiso= 1.5Ueq(C) for methyl atoms of coordinated solvate (CH₃OH) molecules. One of the NH-CH₂-Ph fragments (N3 C10 C11-C16) is *disordered* over two sets of sites with *refined* occupancies 0.66788 and 0.33212. The *disordered phenyl group* (C11-C16) was constrained to a rigid hexagon with bond lengths of 1.39 Å, performing rigid group refinements for phenyl rings (AFIX 66).

Program used to solve the structure: SHELXT [12]; program used to refine structure: SHELXL-2016/4 [13]; molecular graphics: SHELXTL [14]. Crystallographic

data for the structure have been deposited to the Cambridge Crystallographic Data Centre with CCDC number 2094403. Copies of the data can be obtained free of charge by an application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(122) 333-6033; e-mail: deposit@ccdc.cam.ac.uk; website: <http://www.ccdc.cam.ac.uk>).

Results and discussion

FTIR and NMR spectral results

The FTIR investigations are very useful for preliminary analysis of the coordination mode of the carbacylamidophosphates ligands due to the sensitivity of the characteristic bands corresponding to vibrations of the phosphoryl and carbonyl groups to the coordination method. As it was noted in previous studies [15], the carbacylamidophosphates in the neutral form are coordinated mainly in a monodentate manner [16,17] *via* the oxygen atom of the phosphoryl group, whereas in the deprotonated forms – in a bidentate manner *via* the oxygen atoms of the phosphoryl and carbonyl groups with 6-membered chelating cycle formation.

Table 1

Crystal data and structure refinement for [Zn₂(L)₄(CH₃OH)₂].

Parameters	Value
Empirical formula	C ₆₆ H ₇₂ Cl ₁₂ N ₁₂ O ₁₀ P ₄ Zn ₂
Formula weight, M	1873.37
Temperature, K	293(2)
Wavelength, Å	0.71073
Crystal system, space group	Triclinic, <i>P</i> -1
Unit cell dimensions	<i>a</i> = 11.1197(2) Å, α = 106.9280(9)° <i>b</i> = 13.3545(2) Å, β = 90.8146(9)° <i>c</i> = 15.4398(3) Å, γ = 113.5503(9)°
Volume, Å ³	1988.34(6)
Z, Calculated density, g/cm ³	1, 1.565
Absorption coefficient, mm ⁻¹	1.150
<i>F</i> (000)	956
Crystal size, mm	0.290 x 0.290 x 0.140
Theta range for data collection	2.020 to 26.462 deg.
Limiting indices	-13 ≤ <i>h</i> ≤ 13, -16 ≤ <i>k</i> ≤ 16, -19 ≤ <i>l</i> ≤ 13
Reflections collected / unique	34283 / 8183 (<i>R</i> _{int} = 0.0303)
Completeness to	θ = 25.242 100.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.6739
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8183 / 6 / 536
Goodness-of-fit on F^2	1.019
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0415, <i>wR</i> ₂ = 0.1057
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0622, <i>wR</i> ₂ = 0.1197
Extinction coefficient	n/a
Largest diff. peak and hole, e ⁻ Å ⁻³	0.584 and -0.395

In the registered FTIR spectrum, the bidentate coordination manner comes out in a bathochromic shift of the valence vibrations of the phosphoryl $\nu(\text{P}=\text{O})$ and carbonyl $\nu(\text{C}=\text{O})$ groups ($\Delta\nu(\text{P}=\text{O})=72\text{--}86\text{ cm}^{-1}$, $\Delta\nu(\text{C}=\text{O})=119\text{--}126\text{ cm}^{-1}$) compared with the spectrum of the “free” ligand [18].

The FTIR spectra of HL (Figure S1) and the complex (Figure S9) contains all characteristic bands $\nu(\text{C}=\text{O})$, $\nu(\text{P}=\text{O})$, $\nu(\text{NH})$, $\nu(\text{amide II})$ and $\rho(\text{PNC})$ (Table 2). The IR-spectroscopic study of the ligand and title complex revealed the bidentate coordination manner of the ligand. It is reflected in lowering frequencies of $\nu(\text{P}=\text{O})$ and $\nu(\text{C}=\text{O})$ in IR spectrum of the complex compared with corresponding data for the free ligand ($\Delta\nu(\text{P}=\text{O})\sim 40\text{ cm}^{-1}$, $\Delta\nu(\text{C}=\text{O})\sim 107\text{ cm}^{-1}$). The FTIR spectrum of the complexes contains two adsorption bands around 1100 cm^{-1} which differ in approximately 20 cm^{-1} and which can be assigned to two unequal phosphorylic groups

existent in the complex, as shown in Table 2, Figure 1. The adsorption band at 3365 cm^{-1} in the FTIR spectrum of the free ligand can be assigned to the NH group’s vibrations. Coordination of the metal atom by deprotonated ligand leads to the shift in position of this vibration to 3345 cm^{-1} in the FTIR spectrum of the complex.

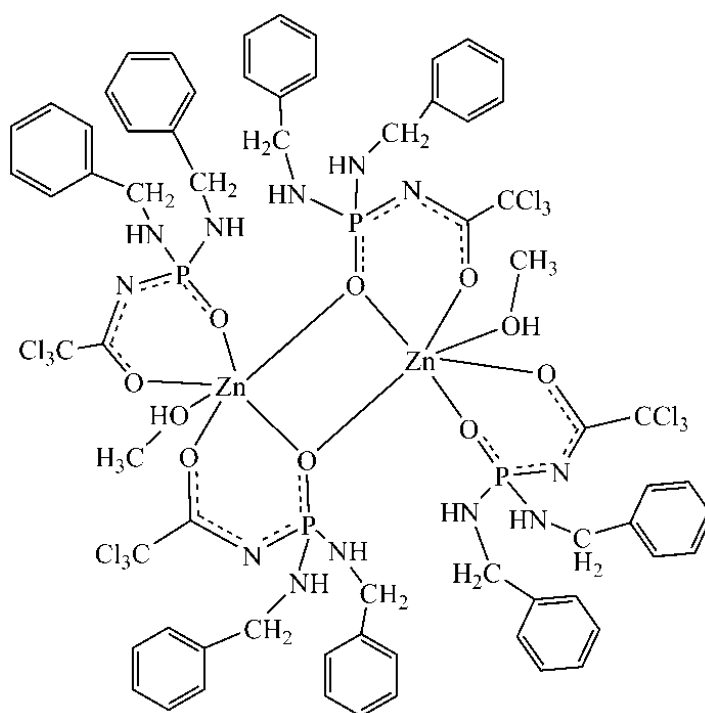
The ^1H NMR spectra of the ligand, its sodium salt and Zn complex displayed the expected multiplicity of signals, and integrated proton ratios corresponding to the stoichiometric formulae of the compounds. A comparison of the ^1H NMR spectra of ligand (Figure S2 from Supplementary material) with corresponding spectra of the sodium salt and Zn complex (Figures S6, S10 from Supplementary material) revealed the (i) absence of a signal assignable to amid NH at 9.72 ppm; (ii) appearance of signals from OH and CH_3 protons of the methanol observed at 4.1 ppm and 3.15 ppm, respectively.

Table 2

FTIR data (cm^{-1}) of the HL and its coordination compound $[\text{Zn}_2(\text{L})_4(\text{CH}_3\text{OH})_2]$.

Compound	$\nu(\text{NH})$	$\nu(\text{CO})$	$\nu(\text{Amid-II})$	$\nu(\text{P}=\text{O})$	$\nu(\text{P}-\text{O})$	$\nu(\text{P}-\text{N})$	$\nu(\text{C-Cl})$
HL	3365	1708	1454	1252	1094	878	676
$\text{Zn}_2(\text{L})_4(\text{CH}_3\text{OH})_2$	3345	1601	1344	1209	1071	874	679

$\Delta\nu=107\text{ cm}^{-1}$ $\Delta\nu=40\text{ cm}^{-1}$

Figure 1. Representation of CAPH-ligand coordination mode in $[\text{Zn}_2(\text{L})_4(\text{CH}_3\text{OH})_2]$.

X-ray diffraction results on $[\text{Zn}_2(\text{L})_4(\text{CH}_3\text{OH})_2]$

The X-ray investigations confirmed the conclusions regarding the coordination mode of the ligand in the obtained complex. Selected bond lengths (Å) and angles (°) are listed in Table 3, the hydrogen bonds parameters are given in Table 4. The obtained complex (Figure 2)

crystallizes in the triclinic *P*-1 space group, furthermore, the centrosymmetric dimeric unit consists of two Zn metal ions, four CAPH ligand molecules (*N,N'*-dibenzyl-*N''*-trichloroacetylphosphortriamide) and two coordinated methanol molecules.

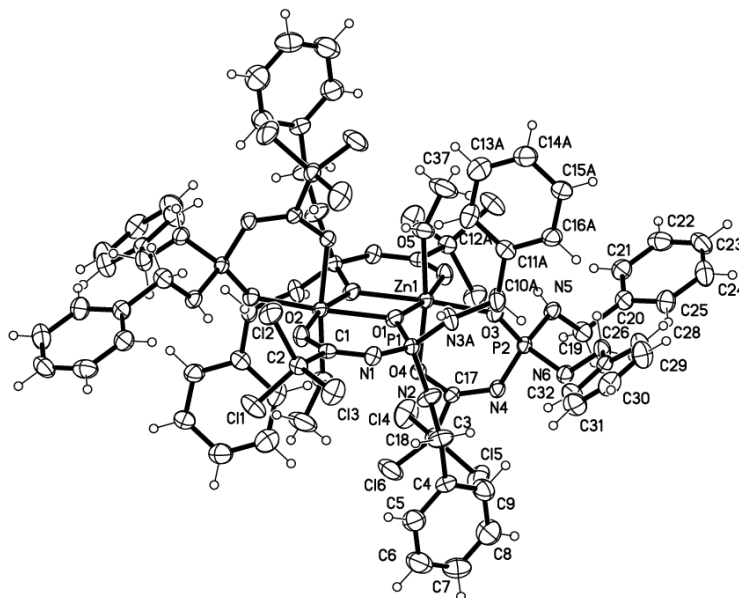


Figure 2. The molecular structure of the $[\text{Zn}_2(\text{L})_4(\text{CH}_3\text{OH})_2]$, showing the atom numbering scheme. (50% probability displacement ellipsoids)

Table 3

Selected bond lengths (Å) and angles for $[\text{Zn}_2(\text{L})_4(\text{CH}_3\text{OH})_2]$.

Bond length	<i>d</i> (Å)	Bond length	<i>d</i> (Å)
ZN1—O1	2.092 (2)	N2—P1	1.624 (3)
ZN1—O1 ⁱ	2.147 (2)	N4—P2	1.633 (2)
O2—ZN1 ⁱ	2.050 (2)	N5—P2	1.631 (3)
O3—ZN1	2.0257 (18)	N6—P2	1.638 (3)
O4—ZN1	2.1135 (19)	O1—P1	1.515 (2)
O5—ZN1	2.132 (2)	O3—P2	1.5063 (18)
C17—O4	1.266 (3)	C18—CL5	1.749 (3)
C17—N4	1.286 (3)	C18—CL4	1.762 (3)
N1—P1	1.620 (3)	C18—CL6	1.771 (3)
Angle	ω (°)	Angle	ω (°)
O3—ZN1—O2 ⁱ	90.64 (8)	O1—P1—N3B	105.6 (4)
O3—ZN1—O1	99.43 (8)	O1—P1—N1	117.00 (12)
O2 ⁱ —ZN1—O1	168.69 (8)	N3B—P1—N1	120.8 (3)
O3—ZN1—O4	90.05 (7)	O1—P1—N2	105.66 (14)
O2 ⁱ —ZN1—O4	93.85 (9)	N3B—P1—N2	95.9 (4)
O1—ZN1—O4	91.29 (8)	N1—P1—N2	108.92 (14)
O3—ZN1—O5	96.12 (8)	O1—P1—N3A	116.1 (2)
O2 ⁱ —ZN1—O5	91.61 (9)	N1—P1—N3A	94.2 (2)
O1—ZN1—O5	82.27 (8)	N2—P1—N3A	115.0 (2)
O4—ZN1—O5	171.72 (8)	O3—P2—N5	107.57 (12)
O3—ZN1—O1 ⁱ	176.37 (7)	O3—P2—N4	117.91 (11)
O2 ⁱ —ZN1—O1 ⁱ	90.64 (8)	N5—P2—N4	111.00 (13)
O1—ZN1—O1 ⁱ	79.61 (9)	O3—P2—N6	111.94 (13)
O4—ZN1—O1 ⁱ	86.48 (8)	N5—P2—N6	106.88 (14)
O5—ZN1—O1 ⁱ	87.24 (9)	N4—P2—N6	101.01 (13)

Symmetry transformations used to generate equivalent atoms: (i) $-x+1, -y, -z+1$

Table 4
Hydrogen geometric parameters (Å, °) of
[Zn₂(L)₄(CH₃OH)₂].

<i>D</i> – <i>H</i> ⋯ <i>A</i>	<i>D</i> – <i>H</i>	<i>H</i> ⋯ <i>A</i>	<i>D</i> ⋯ <i>A</i>	<i>D</i> – <i>H</i> ⋯ <i>A</i>
O5–H5A⋯O4 ⁱ	0.93	2.25	2.950(3)	131.2

The dimeric structure of the compound is supported by the bridging function of only the phosphorylic oxygen atom. Each metal centre is coordinated by the oxygen atoms of the one methanol molecule and two ligands. X-ray investigations (Figures 3 and 4) reveal the presence of two unequal phosphorylic groups in the complex. Two of the four PO groups presented in the complex provide the dimeric structure of the complex by bridging function of their oxygen atoms, which are bridging the neighbouring zinc centres; whereas another two are chelating metal atoms together with carbonyl oxygen atom. As in the previously studied binuclear Co and Ni complexes [9], all phosphorylic oxygen atoms are situated in the equatorial plane of the dimer and all of them are involved into a six membered chelate metallacycles. The coordination geometry around each Zn(II) ion of the complex unit can be

described as distorted octahedral with an O6 coordination sphere (Figure 3) – in equatorial plane there are two bridging and one non-bridging phosphoryl oxygen atoms, as well one carbonyl oxygen atom; the apical positions are occupied by the carbonyl oxygen of the “second” ligand molecule and oxygen from the methanol molecule. The Zn–O distances are within the range 2.093(2)–2.147(2) Å.

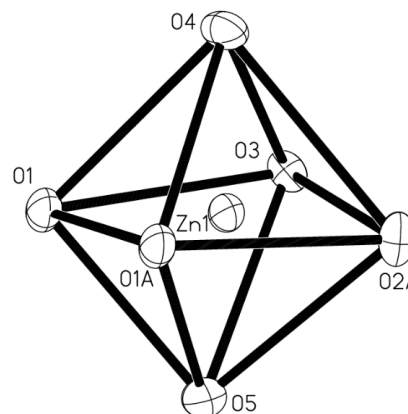


Figure 3. The coordination polyhedron around the Zn(II) central atom in the complex [Zn₂(L)₄(CH₃OH)₂].

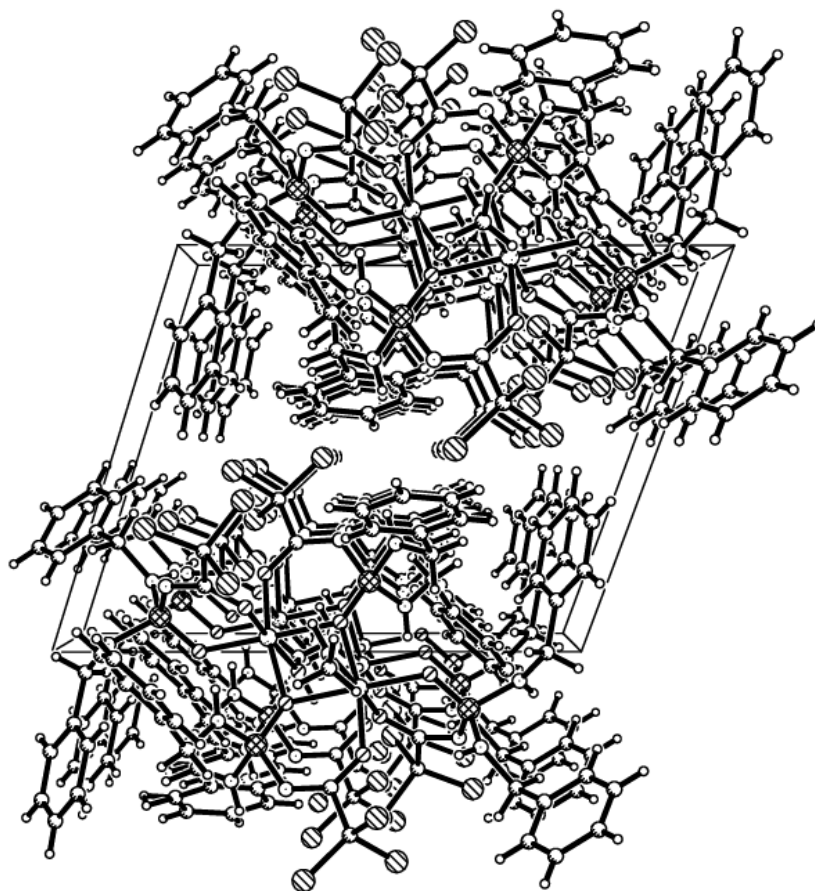


Figure 4. The crystal packing of the [Zn₂(L)₄(CH₃OH)₂] (along *a* axis).

Due to a higher affinity of the metal ions to the phosphorylic ligands the monodentate Zn—O(P) bond distance is a bit shorter in comparison with Zn—O(C) (2.026 Å vs. 2.050 Å, Table 3). The O—Zn1—O angles values for the nearest and for the opposite O atoms are within the ranges 86.26(8)°–96.13(8)° and 168.68(8)°–176.36(7)°, respectively.

The chelating 6-membered ring (Zn1/O3/P2/N4/C17/O4) is non-planar - maximum deviations from the least-squares plane are in average 0.222 Å for oxygen atoms and 0.239 Å for Zn atom. Whereas the non-chelating 6-membered ring (Zn1/O1/P1/N1/C1/O2) with bridging phosphoryl oxygen atom is almost planar - maximum deviation from the least-squares plane is 0.106 Å for the phosphorus atom.

The coordination environment of the phosphorus atoms of the ligands is typical for the CAPH ligands and could be described as distorted tetrahedron. The bond angles around phosphorus atoms differ from the ideal tetrahedral angle of 109.28° and are within the range 101.03°–111.01° and 94.18°–117.0° for the chelating ligand and non-chelating ligand, respectively. The P=O and C=O bond lengths in the title compound have typical values and expectably just a little bit longer in comparison with free ligand - the average values are 1.51 Å and 1.26 Å, respectively [8,19]. In the crystal (Figure 4), the intramolecular OH—O hydrogen bonding [O5H5A - O4 2.950(3) Å] is present (Table 4). In general, all bonding parameters and the dimensions of the angles in the title complex are in good agreement with those encountered in related complexes.

As a concluding remark to the study presented in this paper, to the authors knowledge and Cambridge structural database, the complex reported in this study is only the third known example of binuclear complex with *N*-[bis(benzylamino)phosphoryl]-2,2,2-trichloroacetamide. In general, only the four complexes with this ligand have been reported to this date [9,20,21].

Conclusions

A novel binuclear Zn complex with carbacylamidophosphate ligand $\{Cl_3C(O)NP(O)(NHCH_2Ph)_2\}^-$ was synthesized and characterized by means of X-ray diffraction technique, FTIR and NMR spectroscopies.

FTIR spectroscopic analysis revealed that the bidentate chelating coordination manner of the ligand reflecting in lowering frequencies of $\nu(P=O)$ and $\nu(C=O)$ and with adsorption bands at 1093 cm^{-1} and 1072 cm^{-1} from two unequal

phosphorylic groups. The NMR study confirmed the stoichiometric formula of the synthesized compound and indicated on the coordination of the methanol molecules to the metal complex.

The X-ray diffraction data confirmed the bidentate coordination mode of the ligand. The dimeric structure of the central centrosymmetric unit of the complex is supported by the bridging function of only the phosphorylic oxygen atom. The coordination polyhedron around the Zn(II) central atom in the title complex is a distorted octahedron. The bidentate chelate coordination of the ligand *via* the O atoms of the phosphorylic and carboxylic groups leads to the increasing of the OPN_{imide} and OCN_{imide} angles (117.00° and 131.95° respectively in comparison with 106.89° and 124.94° for the free ligand).

Funding

This work was supported by the Ministry of Education and Science of Ukraine (project no. 19BF037-05).

Supplementary information

Supplementary data are available free of charge at <http://cjm.asm.md> as PDF file.

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