

Crystal structure and spectroscopic properties of [Zn(2-qmpe)Cl₂] containing diethyl (quinolin-2-ylmethyl)phosphonate ligand (2-qmpe)

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The crystal structure of [Zn(2-qmpe)Cl₂] (2-qmpe, diethyl (quinolin-2-ylmethyl) phosphonate) ligand) was determined by X-ray-diffraction. The compound was also characterized by IR, far-IR, ¹H and ³¹P NMR spectroscopy. In the molecule, 2-qmpe acts as a bidentate N,O-chelate ligand. Tetrahedral ZnNOC12 environment of Zn(II) atom is slightly distorted. The structure is stabilized by intermolecular H bond and $\pi\cdots\pi$ interactions. The spectral features are in agreement with the structural data.

Keywords: Zn(II); phosphonic acid ester N,O-donor ligand; crystal structure

1. Introduction

Zinc is one of the most important trace elements, playing a versatile role in biological systems due to its structural properties and catalytic role in enzymes [1–7]. On the other hand, various phosphonate derivatives are of interest because of their broad spectrum of biological properties [8–15]. In a previous study we demonstrated the reactivity of the N,O-donor (quinolin-2-ylmethyl)phosphonate ligand (2-qmpe) to various transition metal salts [16, 17]. The crystal structures of the compounds [M(2-qmpe)₄(H₂O)₂](ClO₄)₂ (with O bonded ligand), where M = Ni, Mn [16], and [Pd(2-qmpe)₂Cl₂] (with N bonded ligand) [18] were determined. For the Cu(II), the dimeric compound with a di- μ -hydroxo bridge having the formula [Cu(2-qmpe)₂(OH)(H₂O)₂]₂(ClO₄)₂ (with O-bonded ligand) was identified [16]. In solution, under atmospheric oxygen, this compound undergoes oxidative decomposition to [Cu(2-qca)₂·H₂O] (2-qca – quinoline-2-carboxylate) [19]. The biological relevance of the phosphonate derivatives to the heterocyclic system, and their reactivity to transition metal ions, was the motivation behind our investiga-

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tions into its zinc complexes. It is worth mentioning that in the interaction of the Zn(II) with (pyridyn-3-ylmethyl)phosphonate (3-pmpe), three interesting crystal forms were isolated [20].

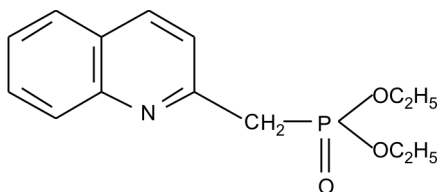


Fig. 1. A molecule of diethyl(quinolin-2-ylmethyl)phosphonate

In the paper, the synthesis, infrared spectra and crystal structure of the compound of the formula $[\text{Zn}(2\text{-qmpe})\text{Cl}_2]$ have been presented.

2. Experimental

Reagents and physical measurements: Starting materials and solvents were obtained commercially and used as-received. Elemental analyses were carried out using a Perkin-Elmer elemental analyzer 2400CHN. Infrared spectra ($100\text{--}4000\text{ cm}^{-1}$) were recorded using a Bruker IFS 113v spectrophotometer in KBr wafers. ^1H and ^{31}P NMR spectra were recorded on a Varian Mercury-300 spectrometer operating at the frequency of 300 MHz. Chemical shifts were reported using the standard (δ) notation in ppm with respect to TMS (1%) as an internal standard and H_3PO_4 (85%) as the external standard.

Determination of the crystal structure of $[\text{Zn}(2\text{-qmpe})\text{Cl}_2]$: X-Ray data were collected on a Kuma KM4CCD diffractometer (MoK_α radiation, $\lambda = 0.71073\text{ \AA}$). X-Ray data were collected at 100 K using an Oxford Cryosystem device. Data reduction and analysis were carried out with the CrysAlice 'RED' program [21].

Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by Clark and Reid was applied [22]. The space group was determined using the XPREP program. The structure was determined by direct methods, using the XS program, and refined using all the F^2 data, as implemented by the XL program [23]. Non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms were placed at the calculated positions. Before the last cycle of refinement, all H atoms were fixed and were allowed to ride on their parent atoms.

Synthesis of the diethyl (quinolin-2-ylmethyl)phosphonate ligand (2-qmpe). The ligand was prepared by phosphorylation of 2-chloromethylquinoline with diethyl phosphine according to the procedure described in detail elsewhere [16], and was checked for purity by spectroscopic and analytical methods.

^1H -NMR (300 MHz, CDCl_3): $\delta = 1.21$ (t, 6H, $^3J_{\text{HH}} = 6.8$, 2 CH_3), 3.57 (d, 2H, $^2J_{\text{HP}} = 22.02$; q- CH_2P), 4.05 (dq, 4H, $^3J_{\text{HH}} = 6.8$; 2 POCH_2), 7.12 (d, 1H, (q) H-C3), 7.46

(t, 1H, (q) H–C6), 7.64 (t, 1H, (q) H–C7), 7.73 (d, 1H, (q) H–C5), 8.01 (d, 1H, (q) H–C4), 8.05 (d, 1H, (q) H–C8); ³¹P–NMR (121 MHz, CDCl₃): δ = 24.53; IR (film) $\nu_{\max}$ (cm^{−1}): (py–ring) 1600(s), 1560(m), (P=O) 1254 (vs), (P–O–C) 1050–1030 (vs), (vs – very strong, s – strong, m – medium).

Synthesis of the Zn(2-qmpe)Cl₂ complex. The complex was prepared by dissolving the appropriate hydrated zinc nitrate (1 mmol) in ethanol (10 cm³) and adding it to a solution of the ligand (1 mmol) in ethanol (15 cm³). The resulting solution was filtered and left to evaporate slowly at room temperature. Pale yellow monocrystals of the Zn(II) compound, suitable for X-ray determination, were obtained after two weeks.

Anal. Calc. for C₁₄H₁₈Cl₂NO₃PZn: C, 40.46; H, 4.37; N, 3.37; Found: C, 40.05; H, 4.52; N, 3.17 ¹H–NMR (300 MHz, CDCl₃): δ = 1.34 (t, 6H, ³J_{HH} = 6.8, 2 CH₃), 4.07 (d, 2H, ²J_{HP} = 22.81; q–CH₂P), 4.35 (dq, 4H, ³J_{HH} = 6.8; 2 POCH₂), 7.49 (d, 1H, (q) H–C3), 7.73 (t, 1H, (q) H–C6), 7.96 (m, 2H, (q) H–C7, H–C5), 8.49 (d, 1H, (q) H–C4), 9.14 (d, 1H, (q) H–C8); ³¹P–NMR (121 MHz, CDCl₃): δ = 24.53.

3. Results and discussion

3.1. Description of the structure of [Zn(2-qmpe)Cl₂]

The crystallographic parameters of [Zn(2-qmpe)Cl₂] are summarized in Table 1. The selected bond lengths and angles are listed in Table 2. Figure 2 shows the structure and labelling scheme for the zinc(II) complex.

Table 1. Crystal data and structure refinement for [Zn(2-qmpe)Cl₂]

Empirical formula	C ₁₄ H ₁₈ Cl ₂ NO ₃ PZn	D_c [Mg·m ^{−3}]	1.618
Formula weight	415.53	Absorption coefficient [mm ^{−1}]	1.856
Temperature [K]	100(2)	$F(000)$	424
Wavelength [Å]	0.71073	Crystal size [mm]	0.15×0.13×0.12
Crystal system	triclinic	θ range for data collection [deg]	3.02–26.99
Space group	$\bar{P}1$	Ranges of h,k,l	−9÷9, −11÷11, −17÷17
a [Å]	7.505(3)	Reflections collected	8340
b [Å]	8.821(4)	Independent reflections (R_{int})	3700 (0.0315)
c [Å]	14.008(4)	Completeness to $2\theta = 28.00$	99.2%
α [°]	98.06(3)	Data/parameters	3700/199
β [°]	100.21(2)	Goodness-of-fit (F^2)	1.075
γ [°]	107.26(3)	Final R/wR indices ($I > 2\sigma$)	0.0362/0.0685
Volume [Å ³]	853.0(6)	Largest diff. peak/hole [Å ^{−3}]	0.346/−0.295
Z	2		

The 2-qmpe ligand chelates to the zinc ion, forming a six-membered ring. Zn(II) ion is surrounded by the nitrogen atom of pyridine, oxygen atom of the phosphoryl group of the 2-qmpe ligand, and two chloride atoms. A distorted tetrahedral environ-

ment (ZnONC_2) reveals around the metal cation, with angles deviate from 109.5° . The $\text{Zn}-\text{O}(1)$, $\text{Zn}-\text{N}(1)$ bond lengths are equal to $2.0114(19)$ and $2.087(2)$ Å, respectively. However, the $\text{Zn}-\text{Cl}(1)$ and $\text{Zn}-\text{Cl}(2)$ distances are equal to $2.2270(11)$ and $2.2249(13)$ Å, respectively (Table 2), being similar to those described previously in the literature [20].

Table 2. Bond lengths [Å] and angles [deg] for $[\text{Zn}(\text{2-qmpe})\text{Cl}_2]$

$\text{Zn}-\text{O}(1)$ 2.0114(19)	$\text{C}(14)-\text{C}(15)$ 1.490(4)
$\text{Zn}-\text{N}(1)$ 2.087(2)	$\text{N}(1)-\text{C}(2)$ 1.336(3)
$\text{Zn}-\text{Cl}(2)$ 2.2249(13)	$\text{N}(1)-\text{C}(10)$ 1.383(3)
$\text{Zn}-\text{Cl}(1)$ 2.2270(11)	$\text{O}(1)-\text{Zn}-\text{N}(1)$ 97.34(8)
$\text{P}-\text{O}(1)$ 1.4902(19)	$\text{O}(1)-\text{Zn}-\text{Cl}(2)$ 101.56(6)
$\text{P}-\text{O}(2)$ 1.5523(19)	$\text{N}(1)-\text{Zn}-\text{Cl}(2)$ 120.43(7)
$\text{P}-\text{O}(3)$ 1.5631(18)	$\text{O}(1)-\text{Zn}-\text{Cl}(1)$ 112.14(6)
$\text{P}-\text{C}(11)$ 1.794(2)	$\text{N}(1)-\text{Zn}-\text{Cl}(1)$ 103.45(6)
$\text{O}(2)-\text{C}(12)$ 1.485(3)	$\text{Cl}(2)-\text{Zn}-\text{Cl}(1)$ 119.71(4)
$\text{O}(3)-\text{C}(14)$ 1.475(3)	$\text{O}(1)-\text{Zn}-\text{Cl}(2)$ 101.56(6)
$\text{C}(12)-\text{C}(13)$ 1.479(4)	

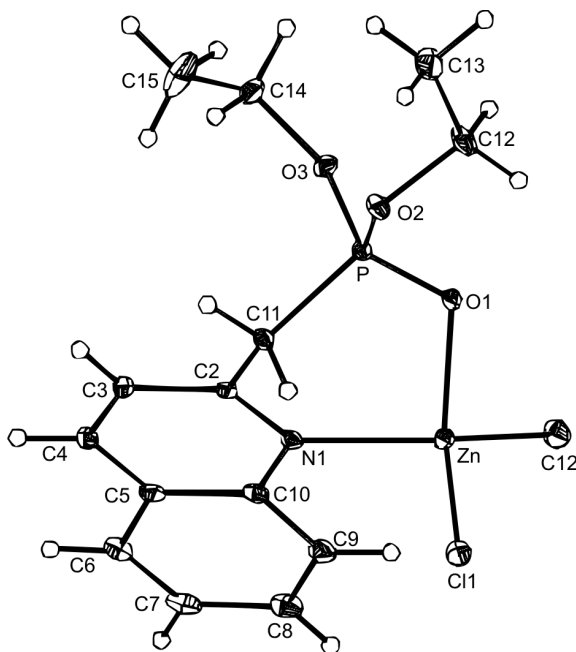


Fig. 2. Diagram of a molecule of $[\text{Zn}(\text{2-qmpe})\text{Cl}_2]$ showing the atomic numbering

The structure reveals the ligand to have a short $\text{P}=\text{O}$ distance for the phosphoryl group ($\text{P}-\text{O}(1)$ of $1.4902(19)$ Å), and longer distances between the $\text{P}-\text{O}$ atoms of the phosphonate groups ($\text{P}-\text{O}(2)$ and $\text{P}-\text{O}(3)$ of $1.5523(19)$ and $1.5631(18)$ Å, respective-

ly). The geometry of the phosphonate groups deviates significantly from an ideal tetrahedron (Table 2), as is observed for phosphonate diesters [16, 18, 24]. The structure of the monomer (Table 3) is stabilized by the intramolecular hydrogen interaction, in which the quinolil group is involved: C(9)–H(9)⋯Cl(2).

Table 3. Hydrogen bonds [$\text{\AA}$] and contacts [deg] for [Zn(2-qmpe)Cl₂]

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	Angle (DHA)
C(4)–H(4)...Cl(1) ⁱ	0.95	2.96	3.758(3)	143
C(8)–H(8)...Cl(1) ⁱⁱ	0.95	2.94	3.824(3)	155
C(13)–H(13A)...Cl(1) ⁱⁱⁱ	0.98	2.91	3.669(3)	136
C(3)–H(3)...Cl(2) ^{iv}	0.95	2.80	3.698(3)	158
C(9)–H(9)...Cl(2)	0.95	2.77	3.576(3)	144
C(11)–H(11B)...Cl(2) ^{iv}	0.99	2.91	3.862(3)	161
C(14)–H(14B)...Cl(2) ^{iv}	0.99	2.96	3.773(3)	140
C(14)–H(14A)...O(1) ^v	0.99	2.66	3.299(3)	122
C(12)–H(12B)...O(3) ^v	0.99	2.52	3.470(4)	162

Symmetry transformations used to generate equivalent atoms are: (i) $-x + 2$, $-y + 1$, $-z + 1$; (ii) $-x + 2$, $-y + 2$, $-z + 1$; (iii) $-x + 1$, $-y + 1$, $-z$; (iv) x , $y - 1$, z ; (v) $-x + 2$, $-y + 1$, $-z$.

The crystal structure of the compound is additionally stabilized by intermolecular C–H⋯Cl hydrogen interactions, in which the C(4), C(8), C(3) quinolil, C(11) methylene and the C(13), C(14) etoxy atoms are involved. Additionally, the structure is stabilized by the C–H⋯O interactions between the C(12) atom of the etoxy group and the phosphoryl oxygen atom O(3)^v of the ester group OC₂H₅. With regard to the observed weak C–H⋯O hydrogen bonds, the D⋯A bond distance and the D–H⋯A angle are well within the accepted range reported for similar C–H⋯O hydrogen bonds [25].

Table 4. π – π interactions in [Zn(2-qmpe)Cl₂]

Interaction	C1G...C1G	Interplanar angle	C1g(perp)	Slippage
C1G...C1G ^a	3.588	0.00(13)	3.440(2)	1.02

Symmetry transformations used to generate equivalent atoms: (i) $-x + 2$, $-y + 1$, $-z + 1$. C1g represents the centroid of the ring N(1) C(2) C(3) C(4) C(5) C(10). C1g(perp) is the perpendicular distance of the C1gⁱ centroid from the ring N(1) C(2) C(3) C(4) C(5) C(10).

The C–H⋯O, C–H⋯Cl hydrogen bonds and π – π interactions (symmetry codes are given in Tables 3 and 4) stabilize the structure and lead to a three-dimensional (3D) network. The crystal packing is shown in Figs. 3 and 4.

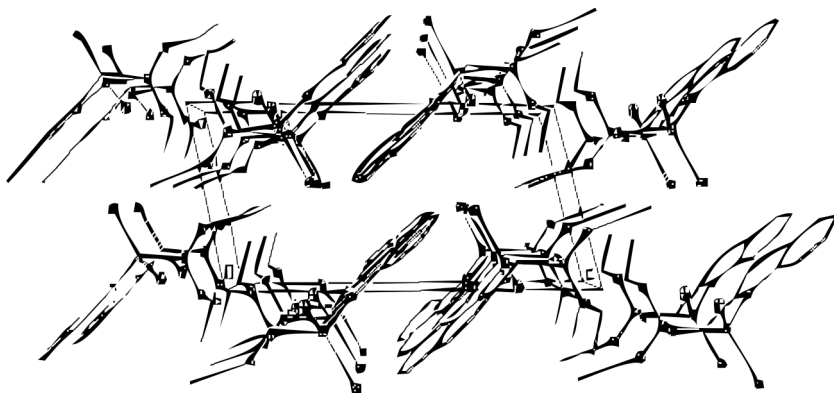


Fig. 3. Crystal packing of $[\text{Zn}(\text{2-qmpe})\text{Cl}_2]$ along the b axis

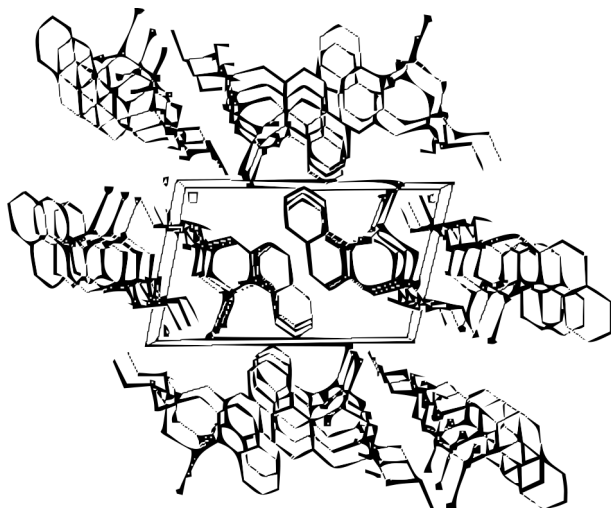


Fig. 4. Crystal packing of $[\text{Zn}(\text{2-qmpe})\text{Cl}_2]$ along the a axis

3.2. ^1H and ^{31}P NMR spectroscopy

The ^1H -NMR spectrum of 2-qmpe shows that the two ester groups, POCH_2CH_3 , are equivalent. Only one triplet at 1.21 ppm is found for the methyl protons, and only one double quartet at 4.05 ppm is found for methylene protons. The two methylene protons of the CH_2P group give rise to a doublet at $\delta = 3.57$ ppm and $^2J_{\text{HP}} = 22.02$ Hz. The multiplets above 7 ppm are attributed to the quinoline ring, i.e. $\delta = 7.12$ ppm (d) is attributed to the C-3 proton, $\delta = 7.46$ ppm (t) to the C-6 proton, $\delta = 7.64$ ppm (t) to the C-7 proton, $\delta = 7.73$ ppm (d) to the C-5 proton, $\delta = 8.01$ ppm (d) to the C-4 proton, and $\delta = 8.05$ ppm (d) to the C-8 proton.

In the spectra of the complex a shift to lower fields exists for the protons adjacent to the coordination site with respect to the free ligand. The greatest shifts are observed

for the protons of the q-CH₂-P group ($\Delta\delta = 0.50$ ppm) and H(8) of the quinoline ring ($\Delta\delta = 1.09$ ppm) which indicates that the nitrogen atom is coordinated to the zinc. These shifts may be explained by the lowering of the electron density in the quinoline ring caused by the coordination to the zinc ion.

3.3. Infrared spectrum

In the IR spectrum of the compound under investigation, the band corresponding to the C=C and C=N stretching modes of the pyridine molecule in the range 1600–1500 cm⁻¹ are not shifted appreciably, whereas the characteristic out-of-plane and in-plane deformation bands of the 2-substituted pyridine ring (at 396 and 620 cm⁻¹ in free ligand, respectively) are shifted to higher frequencies (406 and 635 cm⁻¹, respectively), suggesting coordination of the quinolil nitrogen donor atom. The band at 967 cm⁻¹ is associated with a pyridine ring breathing mode, and is characteristically shifted to higher energy on coordination. Thus, the band observed at 974 cm⁻¹ indicates the coordination of pyridine residues. A very strong band at 1254 cm⁻¹ corresponding to P=O stretching frequencies of the free ligand in the spectrum of the compound, is shifted towards lower frequencies (1192 cm⁻¹), indicating the coordination of the phosphoryl oxygen to the metal ion. Other ligand bands characteristic of the phosphonate moiety, namely $\delta(PO-C)$ at 1130–1170 cm⁻¹ and $\nu(P-OC)$ at 1030–1050 cm⁻¹, do not display any significant shifts upon the formation of the Zn(II) complex. In the far IR region one band attributed to the $\nu(Zn-N)$ stretching vibration was found. The $\nu(Zn-Cl)$ symmetric and asymmetric frequencies (302 and 328 cm⁻¹, respectively) are consistent with a pseudotetrahedral environment [26].

4. Conclusions

Zn(II) compound with diethyl quinolin-2-ylmethyl)phosphonate ester (2-qmpe) has been successfully synthesized. The presented results demonstrate that ZnCl₂ reacts with 2-qmpe ligand in a 1:1 molar metal/ligand ratio, forming the compound of the empirical formula $[Zn(2-qmpe)Cl_2]$. X-ray analysis of the crystal structure indicates that the Zn(II) displays tetrahedral coordination (most common for zinc), which is in agreement with the spectroscopic data. The earlier works [16, 17] and the results presented in this paper indicate that 2-qmpe ligand in reaction with metal salts can act as a monodentate ligand coordinated through the nitrogen or oxygen atoms.

Thereby, the 2-qmpe ligand engagement into monodentate coordination favours coordination by O donor atom (perchlorate metal compounds [16], chloride cobalt [17] and copper compounds [16,19]) in contrast to a compound with PdCl₂ [18]. In this compound Pd(II) is bound in a N-monodentate fashion to the nitrogen pyridine atom according to the known strong preference of the pallad ion as a soft metal toward nitrogen atom. 2-qmpe ligand coordinated in bidentate chelate manner via the quinoline nitrogen and the phosphoryl oxygen donor atoms [17] with nitrate and chloride metal

salts. The non-coordinating behaviour of the pyridine nitrogen atom in perchlorate compounds is probably due to poor donor properties in combination with possible steric constraints and/or crystal packing effects.

In summary, Zn(II) ions are recognized to be essential for life, being present in several naturally occurring metalloenzymes. On the other hand, it is well known that some organophosphorous compounds, in particular various derivatives of phosphonic acid and esters, can exhibit antibiotic, antibacterial, and antiviral and cytostatic activity [27–32]. However, some of their palladium and platinum halide complexes have been found to be cytostatic to various animal and human tumor cells [18, 24–35]. Similar behaviour may be expected in Zn(II) complexes having been synthesised and studied also for this purpose; then its metal complexes should be investigated as potential cytotoxic agents. It is expected that Zn(II) complexes will exhibit similar behaviour. In particular, the question of whether the metal complexes of Zn(II) can potentially be used as cytotoxic agents is one which deserves further investigation*.

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*Crystallographic data for the structure have been sent to the Cambridge Crystallographic Data Centre, CCDC-672232. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

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