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Hirshfeld surface analysis, crystal structure and physicochemical studies of a new Zn(II) complex with the 2,6-dimethylpyrimidin-4-(1*H*)-one ligand

Kacem Klai¹, Christian Jelsch², Frédéric Lefebvre³, Valeria Ferretti⁴, Cherif Ben Nasr¹, Kamel Kaabi^{1*}

¹ Laboratoire de Chimie des Matériaux, Université de Carthage, Faculté des Sciences de Bizerte, 7021 Zarzouna, Tunisie.

² CRM², CNRS, Institut Jean Barriol, Université de Lorraine, Vandœuvre les Nancy Cedex, France.

³ Laboratoire de Chimie Organométallique de Surface (LCOMS), Ecole Supérieure de Chimie Physique Electronique, 69626 Villeurbanne Cedex, France.

⁴ Department of Chemical and Pharmaceutical Sciences and Center for Structural Diffraction, via Fossato di Mortara 17, I-44121 Ferrara, Italy

*Corresponding author Email address: kamel_kaabi@yahoo.fr

Abstract

A new Zn(II) complex with the monodentate ligand 2,6-dimethylpyrimidin-4-(1*H*)-one, $[\text{ZnCl}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{H}_2\text{O}]\text{NO}_3\cdot\text{H}_2\text{O}$, has been prepared and characterized by single crystal X-ray diffraction, elemental analysis, CP–MAS NMR and IR spectroscopy. The Zn(II) cation is tetra-coordinated, in a distorted tetrahedral fashion, by two nitrogen atoms of two organic ligands, one water oxygen atom and one chlorine atom. In the atomic arrangement, the $[\text{ZnCl}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{H}_2\text{O}]^+$ neighbor complexes are connected to each other via O–H...O, O–H...Cl and N–H...O hydrogen bonds to form a ribbon running along the **b**-axis direction. The ribbons are interconnected by the nitrate anions via O–H...O and N4–H...O hydrogen bonds to form layers parallel to (10 $\bar{2}$) plane. Intermolecular interactions were investigated by Hirshfeld surfaces. Globally, the structure is maintained primarily by the metal atom coordination as well as strong and weak (O,N,C)–H...O hydrogen bonds and C–H... π interactions. Besides a few strong electrostatic interactions (coordination and H-bonds), the nitrate and chloride anions are surrounded by many electropositive CH₃ groups. The ¹³C and ¹⁵N CP–MAS NMR spectra are discussed and the vibrational absorption bands were identified by infrared spectroscopy. Electronic properties such as HOMO and LUMO energies were derived.

Keywords: Zinc(II) complex; X-ray structure; Hirshfeld surface; Contact enrichment ratio; DFT calculations

1. Introduction

The properties of metal organic complexes do not simply result from the sum of the individual contributions of their components. Indeed, the strong energy created by a very extensive hybrid, organic and inorganic, interface plays also a preponderant role. A lot of properties such as optical properties, separation, catalysis, photoluminescence, magnetism, conductivity, and ferroelectricity are thus subject to modulation of [1–4]. In addition, these materials are rich in hydrogen-bonds which are of great importance for biological processes [5]; they are energetically weaker than the covalent bonds, but their cumulative effect reinforces and maintains the three-dimensional shape of the crystalline structures of these materials. The feebleness of these bonds is responsible for the flexibility and dynamics necessary for the biomolecules. Because of these important properties, metal–organic complexes have been extensively studied in the last years. Zinc, as one of the most commonly found metal ions in the human body, is an important bio-essential element that has been recognized as necessary in a large number of proteins and metallo-enzymes. In this paper, we present the synthesis and crystal structure of a new zinc complex with the 2,6-dimethylpyrimidin-4-(*1H*)-one ligand that belongs to N-heterocyclic derivatives that form an important class of bioactive compounds such as antioxidant [6], anticancer [7, 8], antidiabetic [9], anti-inflammatory [10, 11]. The Hirshfeld surface analysis has been performed to completely characterize the intermolecular interactions and explain the crystalline architecture. Furthermore, we seek to find a correlation between the crystallographic results and those of the Nuclear Magnetic Resonance of ^{13}C and ^{15}N in the solid state. Vibrational results were interpreted with the aid of DFT calculations.

2. Experimental

2.1. Chemical preparation

The title compound $[\text{ZnCl}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{H}_2\text{O}]\text{NO}_3\cdot\text{H}_2\text{O}$ was prepared at room temperature by mixing 68.15 mg (0.5 mmol) of ZnCl_2 and 148.75 mg (0.5 mmol) of $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ in 50 mL of water. A solution of 124.14 mg (1 mmol) of 4-hydroxy-2,6-dimethylpyrimidine in 20 mL of methanol was added drop by drop to this mixture under stirring. The resulting solution was slowly evaporated at room temperature until the formation of colorless crystals of the title compound (yield 63%). Anal. Calc.: C, 32.2; H, 4.4; N, 15.6 %. Found: C, 32.5; H, 4.5; N, 15.4 %.

2.2. Investigation techniques

The characterization of the investigated compounds was performed using X-ray diffraction, solid-state NMR and IR spectroscopy techniques.

2.2.1. X-ray single crystal structural analysis

A single crystal was carefully selected under polarizing microscope in order to perform the structural analysis by X-ray diffraction. Diffraction data were collected on a Nonius Kappa diffractometer equipped with a CCD detector with graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda=0.71069\text{\AA}$). Intensities were corrected for Lorentz polarization and absorption effects [12]. The structure was solved by direct methods with the SIR97 suite of programs [13] and refinements were performed on F^2 by full-matrix least-squares methods with all non-hydrogen

atoms anisotropic. Methyl hydrogen atoms were included at calculated positions, riding on their carrier atoms; all other hydrogen atoms were found in the difference Fourier map and refined isotropically. All calculations were performed using SHELXL-97 [14] implemented in the WINGX system of programs [15]. The crystal data are reported in Table 1. The drawings were made with Diamond [16] and Mercury [17].

2.2.2. NMR and IR measurements

The NMR spectra were recorded on a solid-state high-resolution Bruker DSX-300 spectrometer operating at 75.49 MHz for ^{13}C and 30.30 MHz for ^{15}N with a classical 4 mm probe head allowing spinning rates up to 10 kHz. ^{13}C and ^{15}N NMR chemical shifts are given relative to tetramethylsilane and neat nitromethane, respectively (precision 0.5 ppm). The spectra were recorded by use of cross polarization (CP) from protons (contact time 2 ms) and magic angle spinning (MAS). Sufficient delay between the scans was checked before recording the NMR spectra. The IR spectra were recorded in the range 4000–400 cm^{-1} using Perkin–Elmer FTIR spectrophotometer 1000 for samples dispersed in spectroscopically pure KBr pressed into a pellet.

NMR chemical shifts and infrared spectrum were calculated with the Gaussian 09 software [18]. All calculations were made at the B3LYP/6-31+G* level on the zinc complex with the chlorine, the water molecule and the two organic ligands. The positions of the atoms were those determined by the X-ray diffraction study, except for the hydrogen atoms, which were first optimized at the same level of theory. Indeed, the positions determined by X-ray do not correspond to the location of the proton but to that of the barycenter of electron density. The chemical shifts were then calculated by use of the GIAO method. The infrared spectrum

was also calculated and the absence of imaginary frequencies was checked. The same calculations were also performed after a full optimization of the complex.

3. Results and discussion

3.1. Structure description

The main geometrical features of the different chemical entities of the synthesized coordination compound are reported in Tables 2 and 3.

X-ray diffraction analysis of the compound $[\text{ZnCl}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{H}_2\text{O}]\text{NO}_3\cdot\text{H}_2\text{O}$ on a single crystal reveals that it crystallizes in a monoclinic system, with the $\text{P2}_1/\text{c}$ space group. The asymmetric unit of the title compound consists of one $\text{Zn}(\text{II})$ cationic complex, where the metal is linked to two organic ligands 2,6-dimethylpyrimidin-4-(1H)-one, one water molecules and one chloride anion, a nitrate counterion and a free water molecule. The $\text{Zn}(\text{II})$ atom is tetra-coordinated in a tetrahedral geometry to two nitrogen atoms, N1 and N3, belonging to the pyrimidine ligands, the chlorine atom Cl1 and the oxygen atom O1W of the coordinated water molecule (Fig. 1). In addition, there is a long-distance interaction ($d = 2.694(2), 2.767(1) \text{ \AA}$) with the oxygen atoms of carbonyl groups. Relevant bond lengths and angles concerning the ZnClON_2 tetrahedron, given in Table 2, are perfectly consistent with the corresponding distances found in similar compounds [19, 20]. The coordination bond distances and above all the bond angles, ranging from $100.70(6)^\circ$ to $125.31(6)^\circ$, deviate slightly from those of a regular tetrahedral geometry. In the structural arrangement, the neighboring complex cations $[\text{ZnCl}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{H}_2\text{O}]^+$ are connected to each other via $\text{O-H}\dots\text{O}$, $\text{O-H}\dots\text{Cl}$ and $\text{N-H}\dots\text{O}$ hydrogen bonds (Table 3), generated by the coordinated and the free water molecules and the N-H groups, to form ribbons running along the **b**-axis direction (Fig. 2). The nitrate anions are

distributed between the ribbons. These anions, which act with their oxygen atoms O4 and O5 as hydrogen bond acceptors, link the adjacent ribbons O2W-H...O4 and N4-H...O5 hydrogen bonds to form layers parallel to the (10 $\bar{2}$) plane (Figs. 3 and 4). Moreover, the cohesion of the crystalline structure is also reinforced by intermolecular interactions of C-H... π type between the hydrogen atoms of the methyl group -CH₃ and the neighboring aromatic rings (Fig. 5) with H... π distances of 3.268 (3) and 3.848 (3) Å [21-23].

Due to the keto-enol tautomerism phenomenon, the organic cations could be found in their keto or enol forms. In this case, they are present as the keto tautomer 2,6-dimethylpyrimidin-4-(1*H*)-one, as confirmed by the C1-O1 and C7-O2 bond distances whose values, 1.245 (2) and 1.241 (2) Å respectively, are typical of a C=O double bond. This finding is in agreement with what is observed for all other compounds involving the 2-amino-6-methylpyrimidin-4-(1*H*)-one entity described so far [24-26].

3.2. Hirshfeld contacts analysis

The Hirshfeld surface is a region in space surrounding the molecules where the chemical nature of their intermolecular contacts can be analyzed. The contact enrichment, derived from the Hirshfeld surface, is computed from the ratio of the actual contacts C_{xy} in the crystal with those computed as if all types of contacts had the same probability to form [27, 28]. The contact enrichment ratio is a powerful tool to deduce which type of contacts are over or under-represented in the crystal packing. An enrichment ratio larger than unity for a given pair of chemical species X...Y indicates that these contacts are favored (over-represented) in the crystal. The analysis of contact types and their enrichment were computed with the program MoProViewer [29]. The fingerprint plots (Fig. 6) were obtained from software CrystalExplorer3.1 [30]. For both software, the Hirshfeld surface was computed on the

asymmetric unit made of moieties in the crystal packing not in contact with each other in order to obtain an integral Hirshfeld surface around each entity (organic and water molecules, chloride, metal and nitrate ions).

The fingerprint plot of molecular interactions (Fig. 6) show that the spikes at short distances originate from coordination bonds ($\text{Zn}\dots\text{N}$, $\text{Zn}\dots\text{O}$ and $\text{Zn}\dots\text{Cl}$) or strong hydrogen bonds ($\text{O}\dots\text{H}$ and $\text{Cl}\dots\text{H}$).

The weak H-bonds $\text{O}\dots\text{Hc}$ constitute the polar interactions with largest surface and are relatively enriched ($E=1.44$) while the strong $\text{O}\dots\text{Ho/n}$ hydrogen bonds are the second interaction in proportion and are significantly over-represented at $E=2.46$. The NO_3^- anion accepts two strong hydrogen bonds from a water molecule and a N-H group of the organic cation. Strikingly, the nitrate moiety is surrounded by as many as five CH_3 groups (Fig. 7) which are slightly electropositive [31]. Similarly, the chloride anion is surrounded by three methyl and one C-H groups. The $\text{Cl}^-\dots\text{Hc}$ weak H-bonds are therefore also favored at $E=1.35$ (Fig. Hb).

The $\text{N}\dots\text{Zn}^{++}$ coordination is the most enriched contact in the crystal packing while the $\text{Zn}^{++}\dots\text{Cl}^-$ and $\text{Zn}^{++}\dots\text{O}(\text{water})$ are also over-represented, but to a lesser extent. Self-interactions between charged chemical types (Zn^{++} , Cl^- , $\text{O}^{\delta-}$, $\text{Ho/n}^{\delta+}$) are all strongly avoided as unfavorable from an electrostatic point of view.

The hydrophobic atoms C and Hc constitute 45% of the Hirshfeld surface. The main contact $\text{Hc}\dots\text{C}$ is over-represented with an enrichment $E=1.5$ while the two other types $\text{C}\dots\text{C}$ and $\text{Hc}\dots\text{Hc}$ have enrichment ratios closer to unity (Table 4). The two aromatic rings of the two independent molecules show four different orientation planes in the crystal and are involved in extensive C-H... π interactions. More than 81% of the carbon surface is involved in these $\text{C}\dots\text{Hc}$ contacts. Globally, the interactions among charged atoms (C and Hc excluded) are slightly

enriched at $E=1.14$. The hydrophobic interactions represent only 19.2% of the surface as they are normally represented at $E=1.03$.

3.3. Quantum mechanical study

Quantum chemical calculation was performed from the crystal structure with DFT method at the 6-31+G* basis set, by using the Gaussian 09 program [18]. The HOMO and LUMO of the title compound are shown in Fig. 8. It is clear that the HOMO is localized mainly on the chlorine atom, while the LUMO is located on one of the two organic molecules. The gap energy value between the HOMO and LUMO orbitals is relatively large, $E_g = (E_{LUMO} - E_{HOMO}) = 4.6$ eV. This large HOMO-LUMO energy gap implies a high kinetic stability and a low chemical reactivity. The energy distribution of the different orbitals for the title compound is shown in Fig.9.

3.4. Molecular Electrostatic Potential analysis (MEP)

The Molecular Electrostatic Potential (MEP) surface is depicted on Figure 10. The MEP is used to determine the nuclear and electronic charge distribution of a given molecule. The maps were obtained at the B3LYP/6-31G* level of theory. As it can be seen, the electrostatic potential maps are color-coded and are subdivided into many regions where those various colors are used to identify different potentials. Blue and red colors indicate the positive and negative potentials, respectively. The most negative zones are on chlorine and zinc while the most positive ones are located at the NH protons and the water molecule.

3.5. Mulliken population analysis

The Mulliken charges distribution was obtained using the B3LYP method with the 6-31G* basis set. The charge distribution of all atoms in the title compound is shown in Table 5, the numbering of atoms being the following:

A calculation with the nitrate ion alone was also made and the results are included in the table. All hydrogen atoms carry positive charge in the range 0.219 to 0.448 e. The atomic charge distribution shows that, for the two organic ligands, the carbon atoms C1, C2 and C5 have negative charges while the other ones (C3, C4 and C6) have positive charges. The two independent ligands have a total Mulliken charge of $0.826 + 0.521 = 1.347$ e, while the total charge of the ZnClH_2O group is -0.346 e. This leads to a global charge of the cationic complex of 1.001 e, in agreement with the chemical formula.

3.6. Solid state NMR spectroscopy

The ^{13}C CP-MAS NMR spectrum of $[\text{ZnCl}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{H}_2\text{O}]\text{NO}_3 \cdot \text{H}_2\text{O}$ is shown in Fig. 11. It exhibits eight well-resolved resonances corresponding to the different crystallographic independent carbon atoms. This is in agreement with two organic molecules being present in the asymmetric unit cell, as revealed by the X-ray structure determination. In the resonance zone of the aliphatic carbons, the two lines at 18.3 ppm and 20.8 ppm correspond to the carbon

atoms of the methyl groups, while the other six resonances are related to the aromatic carbon atoms. The small peaks around 80 ppm correspond to the spinning bands of the aromatic carbon atoms.

The ^{15}N CP-MAS-NMR spectrum of $[\text{ZnCl}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{H}_2\text{O}]\text{NO}_3 \cdot \text{H}_2\text{O}$ is shown in Fig. 12. It has two resonance peaks in -238,1 and -235,9 ppm corresponding to the two N-H groups of two organic molecules. The other two nitrogen atoms that are linked to zinc are not observable because they have no proton nearby. This is also why we do not see the nitrate signal. This proves that there are two organic entities in the asymmetric unit of the compound.

Theoretical calculations were undertaken in order to assign the NMR resonances to the different crystallographic unequivalent carbon and nitrogen atoms of the unit cell. These calculations were made at the B3LYP/6-31+G*level. The different atoms are labeled as above. The results are listed on Table 6. Clearly, there is a very good agreement between the experimental and the theoretical values calculated after optimization of the position of the protons, allowing unambiguously the attribution of the different NMR signals, even though some calculated values for the isotropic chemical shifts are far away from the experimental ones.

3.7. Vibrational studies

The infrared absorption spectrum of $[\text{ZnCl}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{H}_2\text{O}]\text{NO}_3 \cdot \text{H}_2\text{O}$ is shown in Fig.13-a. The most representative and characteristic vibrational modes of this compound can be compared to those of similar compounds [32-34]. The peaks between 3450 and 3050 cm^{-1} are assigned to the stretching vibrations of the O-H and N-H groups. The bands at 3000 and 2850 cm^{-1} are assigned to the C-H stretching modes. These groups are interconnected by a system of hydrogen bonds in the crystal. For this reason, the corresponding bands of these groups are very

broad. The intense band at 1680 cm^{-1} can be attributed to the C=O groups of the organic ligand [35, 36] confirming the presence of the 2-amino-6-methylpyrimidin-4-(*1H*)-one rather than the 2-amino-6-methyl-4-pyrimidinol starting material tautomer. The observed bands in the range $1600\text{--}1130\text{ cm}^{-1}$ can be attributed to the N–H, O–H and C–H bending vibrations and to the valence vibrations of the C=C, C=N, C–C, and N–O groups. The intense band at about 1350 cm^{-1} corresponds to the asymmetric NO_3 stretching mode [37]. Bands in the $100\text{--}500\text{ cm}^{-1}$ region correspond to the CH_3 rocking modes [38] and to the skeleton of the pyrimidinone rings (symmetric, asymmetric, stretching and deformation modes [39, 40]).

DFT calculations of the frequencies have been done on the geometry obtained after optimization of the protons. An additional calculation was also made on the nitrate anions and the water molecules and the contributions of the three components were summed to lead the full spectrum. The resulting IR spectrum between 4000 and 0 cm^{-1} is shown on Fig. 13-b and is very similar to the experimental one. A close agreement between the experimental and calculated wavenumbers is mostly achieved in the fingerprint region as shown in Fig. 14. Thus, the precision is well-sufficient to assign the experimental frequencies and to confirm the attributions proposed above.

4. Conclusions

A new Zn(II) complex with the 2,6-dimethylpyrimidin-4-(*1H*)-one ligand has been prepared at room temperature. In the title compound, the organic entity behaves as a monodentate ligand and Zn(II) adopts a slightly distorted tetrahedral coordination. In the atomic arrangement, the neighboring complex $[\text{ZnCl}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{H}_2\text{O}]^+$ cations are interconnected through multiple hydrogen bonds to form infinite ribbons. The contacts enrichment ratios derived from the Hirshfeld surface analysis shows that besides formation of the Zn(II) metal

coordination complex with N, O ligands and chloride anion, the crystal packing is mainly stabilized by strong N/O-H...O and weak C-O...O hydrogen bonds. There also well over-represented C-H... π hydrophobic interactions between the methyl groups and the two independent pyrimidine aromatic cycles.

The band gap energy between HOMO and LUMO indicates that the title compound is kinetically stable. NMR signals are in full agreement with the crystallographic data. DFT calculations allow the attribution of the experimental NMR lines.

Supplementary data

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC No 1960136. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK: fax: (+44) 01223-336-033; e-mail: deposit@ccdc.cam.ac.

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Figure captions

Fig. 1

Molecular structure of the title compound showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level.

Fig. 2

View of 1D ribbons $[\text{ZnCl}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{H}_2\text{O}]\cdot\text{H}_2\text{O}$ along the *b*-axis.

Fig. 3

Crystal packing arrangement of $[\text{ZnCl}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{H}_2\text{O}]\text{NO}_3\cdot\text{H}_2\text{O}$ viewed along *b*-axis. Dotted lines indicate hydrogen bonds.

Fig. 4

Crystal packing arrangement of $[\text{ZnCl}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{H}_2\text{O}]\text{NO}_3\cdot\text{H}_2\text{O}$. The dotted lines indicate hydrogen bonds.

Fig. 5

Intermolecular interactions C-H... π between hydrogen atoms of methyl group $-\text{CH}_3$ and the neighboring aromatic rings in $[\text{ZnCl}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{H}_2\text{O}]\text{NO}_3\cdot\text{H}_2\text{O}$.

Fig. 6.

Fingerprint plots of the main interactions in the crystal packing.

Fig.7

View of the Hirshfeld surface around (a) the nitrate group, (b) the chloride anion. The surfaces are colored according to the contact types.

Fig. 8

Frontier orbitals of $[\text{ZnCl}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{H}_2\text{O}]\text{NO}_3\cdot\text{H}_2\text{O}$.

Fig. 9

Energy distribution of the different orbitals for $[\text{ZnCl}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{H}_2\text{O}]\text{NO}_3\cdot\text{H}_2\text{O}$.

Fig. 10

MEP surface of $[\text{ZnCl}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{H}_2\text{O}]\text{NO}_3\cdot\text{H}_2\text{O}$.

Fig. 11

^{13}C CP-MAS NMR spectrum of $[\text{ZnCl}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{H}_2\text{O}]\text{NO}_3\cdot\text{H}_2\text{O}$. *Spinning sidebands.

Fig. 12

^{15}N CP-MAS NMR spectrum of $[\text{ZnCl}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{H}_2\text{O}]\text{NO}_3\cdot\text{H}_2\text{O}$.

Fig. 13

Infrared absorption spectrum experimental of $[\text{ZnCl}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{H}_2\text{O}]\text{NO}_3\cdot\text{H}_2\text{O}$.

Fig. 14

Comparison between experimental and calculated IR frequencies of $[\text{ZnCl}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{H}_2\text{O}]\text{NO}_3\cdot\text{H}_2\text{O}$.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

(a)

(b)

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12

Fig. 13

Fig. 14

Table 1 Experimental details of $\text{ZnC}_{12}\text{H}_{18}\text{ClN}_4\text{O}_3 \cdot \text{NO}_3 \cdot \text{H}_2\text{O}$.

Crystal data	
Chemical formula	$\text{ZnC}_{12}\text{H}_{18}\text{ClN}_4\text{O}_3 \cdot \text{NO}_3 \cdot \text{H}_2\text{O}$
M_r	447.15
Crystal system, space group	Monoclinic, P 2 ₁ /c
Temperature (K)	295
a, b, c (Å)	7.0956 (3), 7.1686 (3), 35.1680 (13)
β (°)	97.559 (1)
V (Å ³)	1773.29 (12)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	1.58
Crystal size (mm)	0.44 × 0.30 × 0.29
Data collection	
Diffractometer	Nonius Kappa CCD
Absorption correction	Multi-scan
$T_{\min}, T_{\max}$	0.603, 0.665
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16483, 5108, 4024
R_{int}	0.034
$(\sin \theta/\lambda)_{\max}$ (Å ⁻¹)	0.705
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.037, 0.092, 1.00
No. of reflections	5108
No. of parameters	259
No. of restraints	6
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	0.41, -0.54

Table 2. Selected bond distances and angles (Å,°) in [ZnCl(C₆H₈N₂O)₂H₂O]NO₃.H₂O.

Zn1—O1W	1.9742 (15)	O1W—Zn1—N1	125.31 (6)
Zn1—N1	2.0461 (15)	O1W—Zn1—N3	100.70 (6)
Zn1—N3	2.0859 (14)	N1—Zn1—N3	114.29 (6)
Zn1—Cl1	2.2876 (6)	O1W—Zn1—Cl1	104.68 (5)
N1—Zn1—Cl1	101.56 (5)	N3—Zn1—Cl1	109.51 (5)

Table 3. Hydrogen-bond geometry (Å,°) in [ZnCl(C₆H₈N₂O)₂H₂O]NO₃.H₂O.

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C2—H2 $\cdots$ Cl1 ⁱ	0.93	2.95	3.763 (2)	148
C5—H5A $\cdots$ Cl1 ⁱ	0.96	2.72	3.649 (2)	162
C6—H6A $\cdots$ O4	0.96	2.35	3.235 (3)	153
C8—H8 $\cdots$ O3 ⁱⁱ	0.93	2.39	3.281 (3)	160
C11—H11C $\cdots$ O3 ⁱⁱⁱ	0.96	2.65	3.405 (4)	136
C12—H12A $\cdots$ Cl1	0.96	2.85	3.404 (2)	117
C12—H12B $\cdots$ O5 ⁱⁱⁱ	0.96	2.61	3.417 (3)	142
C12—H12C $\cdots$ O2 ^{iv}	0.96	2.63	3.466 (3)	146
N4—H1N $\cdots$ O5 ⁱⁱⁱ	0.85 (2)	1.97 (2)	2.819 (2)	173 (3)
N2—H2N $\cdots$ O2 ^v	0.86 (2)	2.12 (2)	2.881 (2)	148 (2)
O1W—H1W $\cdots$ O1 ^{vi}	0.83 (2)	1.89 (2)	2.713 (2)	178 (3)
O1W—H2W $\cdots$ O2W ^{vii}	0.83 (2)	1.87 (2)	2.672 (3)	163 (3)
O2W—H3W $\cdots$ O4	0.85 (1)	2.05 (2)	2.884 (3)	167 (4)
O2W—H4W $\cdots$ Cl1	0.81 (4)	2.32 (4)	3.127 (2)	175 (4)

Symmetry codes: (i) $-x, -y, -z+2$; (ii) $x+1, y+1, z$; (iii) $-x-1, y+1/2, -z+3/2$; (iv) $x-1, y, z$; (v) $x, y-1, z$; (vi) $-x, -y+1, -z+2$; (vii) $x, y+1, z$.

Table 4. Statistical analysis of intermolecular contacts on the Hirshfeld surface. The second row shows the chemical content on the Hirshfeld surface. C_{xy} represent the actual contact types and E_{xy} their enrichment ratios. Reciprocal contacts (X..Y and Y...X) are merged. The main contacts and the most enriched ones are highlighted in bold. The more hydrophobic Hc hydrogen atoms bound to carbon were distinguished from those bound to nitrogen or oxygen (Ho/n).

atom	Zn	Cl	O	Ho/n	N	Hc	C
Surface %	6.5	7.9	22.2	13.0	6.0	30.1	14.3
Zn	0.0						
Cl	3.9	0.0				C_{xy}	
O	5.3	0.4	0.7				
Ho/n	0.7	2.2	14.1	0.3			
N	5.2	0.5	0.3	1.3	0.4		
Hc	1.8	6.2	18.6	3.9	2.1	6.5	
C	0.8	2.8	4.3	2.8	0.5	11.7	2.1
Zn	0						
Cl	2.77	0				E_{xy}	
O	1.34	0.1	0.13				
Ho/n	0.3	1.08	2.46	0.17			
N	5.09	0.55	0.37	0.9	1.22		
Hc	0.35	1.35	1.44	0.53	0.65	0.8	
C	0.34	1.3	0.71	0.81	0.33	1.5	1.15

Table 5. Mulliken charges (e) distribution in $[\text{ZnCl}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{H}_2\text{O}]^+$ and nitrate moieties.

Atoms	Charge	
Zn	-0.437	
Cl	-0.217	
O	-0.830	
H(O)	0.563 0.575	
Sum of ZnClH ₂ O	-0.346	
N(Zn)	-0.012	0.056
N(H)	-0.418	-0.469
H(N)	0.459	0.448
O(C6)	-0.477	-0.453
C1	-0.784	-0.916
H(C1)	0.293 0.219 0.287	0.263 0.228 0.279
C2	-0.784	-0.839
H(C2)	0.251 0.253 0.249	0.252 0.245 0.251
C3	0.320	0.443
C4	0.440	0.586
C5	-0.280	-0.178
H(C5)	0.236	0.237
C6	0.269	0.393
Sum for the ligands	0.521	0.826
Global Charge	1.001	
Nitrate ion		
N	-0.006	
O	-0.318	
O	-0.336	
O	-0.340	
Sum for nitrate	-1.000	

Table 6. Comparison of calculated and experimental chemical shift values (ppm) of carbon and nitrogen atoms in $[\text{ZnCl}(\text{C}_6\text{H}_8\text{N}_2\text{O})_2\text{H}_2\text{O}]\text{NO}_3\cdot\text{H}_2\text{O}$.

Atoms	Ligand 1	Ligand 2	Experiment
C1	24.6	22.4	20.7
C2	20.0	19.3	18.3
C3	160.6	151.8	169.6 161.9
C4	144.0	143.6	157.1
C5	106.1	107.7	108.9
C6	162.6	160.0	170.7 166.5
N(Zn)	-135.7	-136.3	not observed
N(H)	-211.8	-213.3	-235.9 -238
NO ₃	-11.4		not observed

Supplementary data

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC No 1960136. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK: fax: (+44) 01223-336-033; e-mail: deposit@ccdc.cam.ac.