Synthesis, crystal structure, infrared spectroscopy, thermal analysis and Hirshfeld surface analysis of a new hemihydrate of $[\text{Zn}(\text{H}_2\text{O})_6][\{(\text{CH}_2)_6\text{N}_4\}\text{ZnCl}_3]_2 \cdot 0.5\text{H}_2\text{O}$.

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Abstract

The new organic–inorganic hybrid material $[\text{Zn}(\text{H}_2\text{O})_6][\{(\text{CH}_2)_6\text{N}_4\}\text{ZnCl}_3]_2 \cdot 0.5\text{H}_2\text{O}$, is the second hydrate in this system, the first having been the hexahydrate. The new solid was prepared by slow evaporation of a solution of the reactants at room temperature and was structurally characterized by X-ray crystallography. This compound crystallizes in the trigonal system, space group $P\bar{3}c1$ with $a = 9.8303(2)\text{\AA}$, $c = 17.5460(2)\text{\AA}$, $V = 1468.38(4)\text{\AA}^3$ and with $Z = 2$. The complex was characterized by FT-IR, thermogravimetric analysis (TGA), differential thermal analysis (DTA) and with a detailed analysis of Hirshfeld surfaces and fingerprint plots. The structural unit of the title compound consists of a $[\text{Zn}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$ cation, two $[\text{Zn}^{\text{II}}\text{Cl}_3(\text{hmt})]^-$ anions and half of a water molecule, partially occupied and disordered [hmt is hexamethylenetetramine, $(\text{CH}_2)_6\text{N}_4$]. Crystal packing is mediated by O–H...N and O–H...Cl hydrogen bonds between the anions and cations, and to a lesser extent by O–H...O contacts, which are present only part of the time as a consequence of the partial occupancy of the isolated water molecules. The relationship between the packing in the new structure and that of the previous hexahydrate is described.

Keywords: hybrid compound; synthesis; X-ray diffraction; FTIR; thermal analysis; Hirshfeld surface analysis

1. Introduction

In the last decade, hybrid materials have attracted more attention because their properties combine the characteristics of both organic and inorganic components. When the interactions between the inorganic and organic components are significantly weaker than covalent or ionic bonds, they are sometimes called Class I hybrids. Some of these compounds are interesting due to the possibility of possessing new properties and multifunctional character. Potential applications have been described for such diverse fields as catalysis, optics, electronics, medicine, conductivity and biology [1–8].

Zinc is well suited for the construction of a diversity of coordination compounds, as its d^{10} electronic configuration allows a variety of coordination numbers and geometries which are not dependent on ligand-field stabilization but rather on ligand charge and size. The

zinc atom can accommodate different coordination geometries including tetrahedral (four-coordinate) [9-19], square-pyramidal (five coordinate) [20] and octahedral geometry (six-coordinate) [21, 22]. Zinc is involved in catalytic and structural functions of proteins; it is an essential element for all living organisms and it is the second most abundant metal in the human body [23-27].

Hexamethylenetetramine (HMTA; IUPAC name: 1,3,5,7-tetraazatricyclo[3.3.1.1]decane) is an important product obtained by condensation of formaldehyde and ammonia at room temperature and atmospheric pressure in aqueous acidic conditions. It has been known for over 130 years. It was the first organic crystal structure determined and it was found to have tetrahedral symmetry. It is a four-ring heterocycle and may act as an acceptor of two, three or four hydrogen bonds. HMTA is a tertiary amine, a colourless solid and a versatile reagent in organic synthesis [28-32].

Indeed, complexation of HMTA with zinc and numerous other metals was observed in early coordination chemistry studies [33]. Powder diffraction studies as early as 1954 yielded tentative cell constants for some complexes, [34] but clear structural analyses were not forthcoming until much later. In that regard, Mak *et al.* reported an accurate structure analysis of the hexahydrate $[\text{Zn}(\text{H}_2\text{O})_6][\{(\text{CH}_2)_6\text{N}_4\}\text{ZnCl}_3] \cdot 6\text{H}_2\text{O}$ [35].

In the present paper, we present the synthesis and characterization, including a single crystal structural study, of a new organic-inorganic Class I hybrid compound which is also a new, diminished hydrate of $[\text{Zn}(\text{H}_2\text{O})_6][\{(\text{CH}_2)_6\text{N}_4\}\text{ZnCl}_3]$, namely the hemihydrate. Its infrared spectroscopic properties, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) are discussed. Its Hirshfeld surfaces are also analyzed to clarify the nature of the intermolecular interactions. The new hybrid material has some structural similarities to the hexahydrate, but the two structures are clearly distinct.

2. Experimental

2.1 Synthesis

The hemihydrate $[\text{Zn}(\text{H}_2\text{O})_6][\{(\text{CH}_2)_6\text{N}_4\}\text{ZnCl}_3]_2 \cdot 0.5 \text{H}_2\text{O}$ was prepared by evaporation of an aqueous solution at room temperature. This solution was prepared from a mixture of hexamethylenetetramine (0.25g), $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (0.51g) and a few drops of concentrated HCl (37%) in water. The molar ratio is Zn: Cl: HMTA: H_2O = 1:1:1:50. After a few days of slow evaporation at room temperature, colourless single crystals were obtained.

2.2. Physical measurements

The infrared (IR) spectra were collected on a Perkin-Elmer Spectrum 100 FT-IR Spectrophotometer with ATR accessory in the range of $4000\text{-}250 \text{ cm}^{-1}$ using pellets made from a pure crystalline sample. Thermal analysis by TGA and DTA was performed using a TA Instruments STD-2960 at a heating rate of 10°C per minute in a nitrogen atmosphere.

2.3 X-Ray crystallography

An irregular colourless crystal of $[\text{Zn}(\text{H}_2\text{O})_6][\{(\text{CH}_2)_6\text{N}_4\}\text{ZnCl}_3]_2 \cdot 0.5 \text{H}_2\text{O}$ was selected for X-ray diffraction analysis and was mounted on an Oxford Diffraction four-circle diffractometer equipped with graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Intensity data were collected at 100K using ω scans. A multi-scan absorption correction using spherical harmonics was applied.

The compound crystallizes in the trigonal system, space group $P(-3)c1$. The structure was solved by direct methods using SIR92 [36] and was refined by full matrix least squares based on F^2 using ShelXL-2014/7 [37].

The H-atoms of the cation and anion were located in difference Fourier maps. Their coordinates were refined freely, and their isotropic displacement parameters were constrained to $xU_{eq}(C,O)$ of their bonding partners, with $x = 1.2$ for C and $x = 1.5$ for O. The molecular graphics and crystallographic illustrations were prepared using Diamond [38]. The free water molecule at O2w is partially occupied and disordered about a special position of 32 symmetry at $(0,0,1/4)$. The hydrogen atoms of this water molecule were not located. The final refinement converged to the values of $R(F)=2.25\%$ and $wR(F^2)=5.93\%$. A summary of the crystallographic data and refinement parameters for $[Zn(H_2O)_6] \cdot [\{ (CH_2)_6N_4 \} ZnCl_3]_2 \cdot 0.5 H_2O$ is provided in Table 1.

3. Results and discussion

3.1 Structure description:

$[Zn(H_2O)_6][\{ (CH_2)_6N_4 \} ZnCl_3]_2 \cdot 0.5 H_2O$ crystallizes at room temperature, in the trigonal system, space group $P-3c1$ with $Z = 2$. The basic structural unit consists of one $[Zn^{II}(H_2O)_6]^{2+}$ cation, two $[Zn^{II}Cl_3(hmt)]^-$ anions and one-half formula unit of free water (fig 1), which is partially occupied and disordered. The different fragments are linked together via three types of hydrogen bonds, O–H...O, O–H...N and O–H...Cl.

Atom Zn1 of the cation occupies a special position (Wyckoff position b , symmetry -3) and it is located at the center of the $Zn1(O1WH_2)_6$ octahedron formed by six equivalent water molecules where the Zn1–O1W distance is 2.0705(10) Å. Bond distance and angle values are collected in Table 2. The octahedron $Zn1(O1WH_2)_6$ is only very slightly distorted from ideal geometry.

Zn2 also occupies a special position (Wyckoff position d , symmetry 3), and it is tetrahedrally coordinated by one nitrogen from the organic ligand and three chlorine atoms. The Zn2–N1 distance is 2.0852 (16) Å and Zn2–Cl1 is 2.2442 (3) Å. The values of the N–Zn2–Cl angles are $106.488(9)^\circ$ and the Cl–Zn2–Cl angles are $112.283(8)^\circ$. These values show that the tetrahedron is slightly distorted (Table 2).

To this point, despite having different space groups the present hemihydrate and the previously reported hexahydrate have in common the crystallographic symmetry elements on which the cation and anion reside. Moreover, both are trigonal and the a -axis repeat is similar (but not identical) in the two structures, differing by about 1 Å. The c -axis of the hemihydrate -- 17.5460 (2) Å -- is twice as long as that of the hexahydrate, 8.784 (1) Å.

In addition to the cation and anion, in the hemihydrate a disorder assembly composed of partially occupied, disordered free water sites occupies a space of volume 63 Å³ centered at $(0, 0, 1/4)$ and $(0, 0, 3/4)$ — that is, centered about a special position of symmetry 32. The previously known hexahydrate has an ordered, fully occupied hydrogen-bonded ring of six free water molecules related by the (-3) symmetry element about which they reside.

In the present structure the octahedral cations line up along the c -axis, at $x = y = 0$, with the central Zn1 atoms residing on sites of (-3) symmetry at elevations of $z = 0$ and $1/2$. The tetrahedral anions line up along the three-fold symmetry axes at $(1/3, 2/3, z)$ and $(2/3, 1/3, z)$, with the layers occupied by the anions centered at elevations of $z = 1/4$ and $z = 3/4$. The octahedral cations and tetrahedral anions are linked together via O–H...Cl hydrogen

bonding where the distance between the donor and acceptor atoms is 3.1759(11) Å and the value of D-H...A is 170(2)°.

The disordered molecules of unligated water and the $\text{Zn1}(\text{O1WH}_2)_6$ octahedra alternate along the c axis, with the O1W-H...O2W hydrogen bonds providing at least some degree of stabilization (fig.2; fig.3).

A three dimensional-network is mediated by three types of hydrogen bonds O-H...Cl, O-H...O (where present, since as mentioned the receptor O2W has partial occupancy) and O-H...N involving the cations, anions and uncoordinated water molecules; these interactions stabilize the crystal packing (fig.4).

Each octahedron $\text{Zn1}(\text{O1W})_6$ is connected to one of six disordered, partially occupied free water sites via O-H...O hydrogen bonding (fig.5a), to six anionic complexes via O-H...N hydrogen bonding (fig.5b) and another six anionic complexes via O-H...Cl hydrogen bonding (fig.5c). Each anionic complex is surrounded by six $\text{Zn1}(\text{O1WH}_2)_6$ octahedra, connected via O-H...Cl and O-H...N hydrogen bonding (fig.6). The details of all hydrogen bond interactions are collected in table 3.

By way of comparison, the hexahydrate structure has a similar arrangement of cations and anions; that is, $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ cations line up along the c-axis at $x = y = 0$, while the anions form columns along the central 3-fold crystallographic symmetry elements at $(2/3, 1/3, z)$ and $(1/3, 2/3, z)$.

The free water substructures mark the only significant qualitative difference between the hexahydrate and the present hemihydrate. While in the former an ordered, H-bonded ring of water molecules resides around (-3) sites at $(0, 0, 1/2)$ and its symmetry equivalents, in the present structure a scant presence of water, stoichiometrically just one-half unit in the overall formula, is disordered about a site of symmetry 32. As in the hexahydrate, this water area lines up between cations in their columns along $(0, 0, z)$.

The relationships between anion and cation columns, as regards their displacement along the c-axis, mark the difference between the two structures. In both structures, Zn1 of the cation is situated on a site of (-3) symmetry, and six nearest-neighbor anions (Zn2) are located on 3-fold axes around the cation. In the hexahydrate the relative elevations along the c-axis of Zn1 and Zn2 differ by 1.278 Å, while in the present structure the elevations differ by 3.494 Å. The nearest Zn1...Zn2 distances are 6.4126 (6) Å in the hexahydrate and 6.6651 (2) Å in the new hemihydrate. More telling are the Zn2...Zn2 distances around the cycle of anions related by the (-3) axis. For the hemihydrate these are 9.0028 (4) Å, consistent with the larger difference in elevation between Zn1 and Zn2 in comparison with that in the hexahydrate, where the corresponding Zn2...Zn2 distances are 6.7841 (5) Å (Figure 7a, Figure 7b).

3.2 FT_IR spectral analysis:

To gain more information on the crystal structure of the title compound, infrared spectroscopy is used to identify the functional groups; the infrared spectrum of $[\text{Zn}(\text{H}_2\text{O})_6]\text{-}[\{(\text{CH}_2)_6\text{N}_4\}\text{ZnCl}_3]_2 \cdot 0.5 \text{ H}_2\text{O}$ performed at room temperature is shown in fig.8. Our assignment of the vibrational bands, listed in table 4, is based on comparison with studies of similar compounds [23, 25]. The higher frequency region 3443 and 3087 cm^{-1} is assigned to the asymmetric and symmetric stretching of (OH). The (OH) deformation band is observed at 1643 cm^{-1} . The band attributed to the (CH) scissoring is probably observed at 1469 cm^{-1} 1383 cm^{-1} . The assignment of the bands observed at 1230 and 1007 cm^{-1} are

associated with CN stretching. The deformation of the (CN) group is located experimentally at 825 cm⁻¹ and 675 cm⁻¹ in all likelihood. Concerning the bands found at 496 and 292 cm⁻¹ in the IR spectrum, they are attributed to the ZnN and ZnCl groups, respectively.

3.3 DTA and TGA analysis:

The thermal properties of the compound were investigated by TGA and DTA methods in the temperature range (0 - 400) °C (Fig.9).

It is clear from the TGA and DTA curves that the compound decomposes in two weight loss stages, in the experiment temperature range from 0 to 400 °C. The first one lies in the temperature range of 85 - 170°C and it is divided as a result of two successive losses related to the two exothermic peaks of the DTA curve. These can be assigned to the loss of the half free water molecule and the six coordinated water molecules, respectively (experimental weight loss: 13.5% and calculated weight loss is 14.6%) [25]. The corresponding probable equations are:

The second signal, in the temperature range of 200 - 300 °C can be assigned to the release of one molecule of Cl₂ (experiment weight loss: 10.78% and calculated weight loss is 8,79%) [39]. the corresponding probable equation is:

3.4 Hirshfeld surface analysis:

The Hirshfeld surfaces and the associated 2D fingerprint plots were calculated using Crystal Explorer. [40] The Hirshfeld surfaces and the fingerprint analysis provide convenient graphical representations of intermolecular contacts and have been used to study assorted phenomena including polymorphism, solvatomorphism, and other aspect or consequences of supramolecular arrangement. The Hirshfeld surface is unique for a given crystal structure and set of spherical atomic electron densities [41]. The normalized contact distance (d_{norm}) is based on both d_e and d_i and the van der Waals (vdw) radii of the atoms, where d_e is the distance from a point on the surface to the nearest nucleus external to the surface, and d_i is the distance from a point on the surface to the nearest nucleus internal to the surface; it is given by equation (1). The d_{norm} values are represented on the Hirshfeld surface by using red-blue-white coloring. The red regions correspond to negative d_{norm} values for which the intermolecular contacts are shorter than the van der Waals separations and are representative of significant hydrogen bonding contacts. The blue regions correspond to positive d_{norm} values where the intermolecular contacts are longer than the van der Waals separations and the white areas correspond to intermolecular contacts near the van der Waals separations and d_{norm} values near zero [42-47].

$$d_{\text{norm}} = \frac{d_i - r_i^{\text{vdw}}}{r_i^{\text{vdw}}} + \frac{d_e - r_e^{\text{vdw}}}{r_e^{\text{vdw}}} \quad (1)$$

The Hirshfeld surface of the cationic fragment $[\text{Zn}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$ in the present compound is shown in (fig. 10), representing the surfaces that have been mapped around the molecule by d_{norm} mapping. The 2D fingerprint plots for $[\text{Zn}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$ are illustrated in (fig. 11).

The 2D fingerprint plots reveal that the H...N contacts cover 16% of the total surface; this interaction appears as a spike in the top area and can be attributed to O-H...N hydrogen bond interactions. The O...H/H...O contacts comprise 21.1% of the total Hirshfeld surface; these can be attributed to O-H...O hydrogen bonds. The H...Cl short contacts comprise 16.6% of the total surface and are represented as a spike in the top part of fingerprint plot; these can be attributed to O-H...Cl hydrogen bonding interactions. Additionally, the H...H contacts cover 44.1% of the surface and is predominant compared to the other interactions. These are van der Waals' interactions.

The Hirshfeld surface d_{norm} maps of the anionic complex of the hemihydrate compound is illustrated in (fig. 12) and the associated fingerprint plots are shown in (fig. 13). The H...Cl/Cl...H play a dominant role with a percentage contribution of 49.8% of the total surface, which is attributed to the O-H...Cl hydrogen bonding. The H...O and N...H contacts comprise 6.3% and 6.1%, respectively, of the total surface. These interactions make a small contribution if compared with the H...Cl/Cl...H interactions. They can be attributed to the O-H...O and O-H...N hydrogen bonds, respectively; and the O-H...O interactions are even less important when one considers that the receptor O2W is only partially occupied. The existence of other weak intermolecular interactions is also shown by the Hirshfeld surface analysis, their percentage contributions to the surface are presented in the fingerprint plots (fig. 13).

For the purpose of comparison, the Hirshfeld surfaces for the cation and anion of the hexahydrate are shown in Figure 14 and 15. It can be seen that the different hydration levels coincide with different proportions of the various interactions that take place. For example, considering the Hirshfeld surface and fingerprint plots of the cations in both structures (Figures 10 and 11 for the hemihydrate, Figures 14 and 15 for the hexahydrate), we see that the lower hydration level in the present compound reduces the prominence of O...H contacts to the extent that they are 21.1% as compared to 39.4% in the hexahydrate. Moreover, the lower hydration level permits the H...N interactions to have more relative prominence, 16% of all interactions in the cation surface analysis as opposed to an inappreciable extent in the hexahydrate.

4. Conclusion

A novel Class I organic-inorganic hybrid compound of Zn(II) has been synthesized. Its structure was determined using single crystal X-ray diffraction and it was characterized by FTIR, DTA and TGA studies. The structure of the title compound can be described as consisting of stacks parallel to the crystallographic *c* axis: Firstly, cationic $\text{Zn}(\text{O}1\text{WH}_2)_6$ octahedra and disordered unligated water molecules line up along the three-fold symmetry axis at $x = 0, y = 0$; secondly, the anionic complexes are arranged along the three-fold axes at $(1/3, 2/3, z)$ and $(2/3, 1/3, z)$. The stability of this arrangement is governed by O-H...N and O-H...Cl hydrogen bonding interactions between cation and anion chains, with a lesser contribution within the cation/water chains from O-H...O H-bonds with the partially occupied free water as receptor. Thermal analysis characterized the stability of this compound. The Hirshfeld surface analysis and the fingerprint plots were applied to confirm the existence of weaker intermolecular interactions in the crystal.

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References:

- [1] H. El Hamdani , M. El Amane, C. Duhayon, Synthesis, structure, spectral characterization and thermal analysis of the tetraaquabis (isothiocyanato-kN) Cobalt (II)-bis(caffeine)-tetrahydrate complex, J. Mol. Struct. 1157 (2018) 1-7 **10.1016/j.molstruc.2017.12.033**
- [2] R. Mesbeh, B. Hamdi, R. Zouari, Crystal structure, thermal studies, Hirshfeld surface analysis, vibrational and DFT investigation of organic-inorganic hybrid compound $[C_9H_6NOBr_2]_2CuBr_4 \cdot 2H_2O$, J. Mol. Struct. 1125 (2016) 217-226 **10.1016/j.molstruc.2016.06.069**
- [3] R. Mesbeh, B. Hamdi, R. Zouari, Elaboration, structural, spectroscopy, DSC investigation and Hirshfeld surface analysis of a one-dimensional self-assembled organic-inorganic hybrid compound, J. Mol. Struct. 1128 (2017) 205-214 **10.1016/j.molstruc.2016.08.068**
- [4] M. Ben Nasr, E. Aubert, E. Espinosa, F. Lefebvre, Synthesis and physico-chemical studies of a novel organo-metallic compound $CdCl_2(C_6H_4FNH_2)_2$, C. Ben Nasr, J. Mol. Struct, (2014) **10.1016/j.molstruc.2014.10.075**
- [5] R. Mesbeh, A. B. Ahmed, B. Hamdi, R. Zouari, Synthesis, crystal structure, Hirshfeld surface analysis and vibrational and DFT investigation of $[C_6H_{10}(NH_3)_2]_3CuBr_4 \cdot 3Br$, J. Ionics **10.1007/s11581-016-1757-3**
- [6] R. Mesbeh, B. Hamdi, R. Zouari, Elaboration, structural, Vibrational, DSC Investigation and Hirshfeld Surface Analysis of New Organic-Inorganic Hybrid Compound: $[H_2mela]Cu_2Br_6$, J. Clust. Sci. **10.1007/s10876-016-1041-8**
- [7] R. Mesbeh, B. Hamdi, R. Zouari, $(H_2pdcCuBr_2)_2 \cdot 2(MH^+) \cdot 2Br^-$ (M = Melamine, H_2pdc = Pyridine-2,6-Dicarboxylic Acid): Crystal structure, Hirshfeld Surface Analysis, Vibrational and Thermal Studies, J. Inorg. Organomet. Polym. 26 (2016) 744-755 **10.1007/s10904-016-0371-1**
- [8] R. Pardo, M. Zayat, D. Levy, Photochromic organic-inorganic hybrid materials, Chem. Soc. Rev. 40 (2011) 672-687 **10.1039/c0cs00065e**
- [9] M. Ben Nasr, S. Soudani, F. Lefebvre, C. Jelsch, C. Ben Nasr, Crystal structure, Hirshfeld surface analysis, quantum mechanical study and spectroscopic characterization of the non-centrosymmetric coordination compound bis(4-fluoroaniline)dichloridozincate, J. Mol. Struct. 1138 (2017) 71-80 **10.1016/j.molstruc.2017.02.098**
- [10] W. Nbili, M. Zeller, F. Lefebvre, C. Ben Nasr, Synthesis, structure and characterization of two new Zn(II) and Cd(II) complexes with the bidentate ligand 2[(2-aminoethyl)amino]ethanaminium(AEEA), J. Mol. Struct. (2014) **10.1016/j.molstruc.2014.12.059**

- [11] J. Govindaraj, S. Thirumurugan, D. Snehalatha Reddy, K. Anbalagan, A. SubbiahPandi, Crystal structure of dichloridobis (4-ethylaniline- κ N)zinc, *Acta. Cryst.* (2015). E71, m21-m22 **10.1107/S2056989014027832**
- [12] C-Y. Wang, Dichlorido[2-(((3-(cyclohexylazaniumyl)propyl)imino)methyl)-5-methoxyphenolate]zinc, *Acta. Cryst.* (2011). E67, m1085-m1086 **10.1107/S1600536811027085**
- [13] A. D. Khalaji, S. Jalali Akerdi, G. Grivani, H. Stoeckli-Evans, D. Das, Synthesis, Spectral and Thermal Studies of Zinc(II) and Mercury(II) Complexes with Bidentate Schiff-Base Ligand (234-MeO-Ba)₂En: the Crystal Structure of Zn(234-MeO-Ba)₂EnI₂, *Russ. J. Coord. Chem.* 2011, 37, 578-584 **10.1134/s1070328411080045**
- [14] M. Zhu, L. Lu, X. Jin, P. Yang, Trichloro(1,1-dimethylbiguanidium- κ N³)zinc(II), *Acta. Cryst.* (2002). C58, m158-m159
- [15] Y-Q. Cheng, L-P. Lv, J-W. Xie, H-B. Wang, Z-M. Jin, Ammonium trichloro(hexamethylene-tetramine)zincate(II) sesquihydrate, *Acta. Cryst.* (2006), E62, m3591-3593 **10.1107/S1600536806050550**
- [16] J. H. Jeong, Y. D. Park, S-G. Roh, Synthesis and X-ray structure of Zn(bpeae)ZnCl₃ (bpeae = 2-(Bis-[2-(3,5-dimethyl-pyrazol-1-yl)-ethyl]amino)ethoxy), *Bull. Korean. Chem. Soc.* (2003). 24, 4 **10.5012/bkcs.2003.24.4.521**
- [17] Y-F. Shi, Q-H. Feng, W-J. Zhao, Y-B. Shi, P. Zhan, Dichlorido[N-(2-pyridylmethylidene)-benzene-1,4-diamine]zinc(II), *Acta. Cryst.* (2010). E66, m593 **10.1107/S1600536810015138**
- [18] J. Kang, H. Yun, J. Do, Crystal structure of quininium-trichloro-zinc(II), ZnCl₃(C₂₀H₂₅N₂O₂), C₂₀H₂₅Cl₃N₂O₂Zn, *Z. Kristallogr. –New Cryst. Struct.* (2013). 228, 57-58 **10.1524/ncrs.2013.0035**
- [19] C-Y. Wang, Dichlorido[2-[[[3-(cyclohexylazaniumyl)-propyl]imino}methyl)-5-methoxyphenolate]zinc, *Acta. Cryst.* (2011). E67, m1085-m1086 **10.1107/S1600536811027085**
- [20] Abdul-Razak H. Al-Sudani, Dichlorido{8-[2-(dimethylamino)ethyl-amino]quinolone- κ^3 N,N',N''}zinc, *Acta. Cryst.* (2014). E70, m1
- [21] S. Saha, A. Sasmal, C. R. Choudhury, G. Pilet, A. Bauzá, A. Frontera, S. Chakraborty, S. Mitra, Synthesis, crystal structure, antimicrobial screening and density functional theory calculation of Nickel(II), Cobalt(II) and Zinc(II) mononuclear Schiff base, *Inorg. Chim. Acta* **10.1016/j.ica.2014.10.007**
- [22] T. Arumuganathan, A. Srinivasarao, T. V. Kumar, S. K. Das, Two different zinc(II)-aqua complexes held up by a metal-oxide based support: Synthesis, crystal structure and catalytic activity of [HMTAH]₂[{Zn(H₂O)₅}{Zn(H₂O)₄}{Mo₇O₂₄}.2H₂O, *J. Chem. Sci.* (2008). 120, 95-103 **10.1007/s12039-008-0012-5**
- [23] S. Hazra, B. Sarkar, S. Naiya, M.G.B Drew, A. Ghosh, Structural variations in self-assembled coordination complexes of Zn(II) with hexamethylenetetramine and isomeric 2-, 3- and 4- nitrobenzoates, *j.poly.* 46 (2012) 8-5 **10.1016/j.poly.2012.07.068**
- [24] A. Adach, M. Daszkiewicz, B. Barszcz, M.C. Golonka, G. Maciejewska, Redox processes as a route for the formation of an unusual structure of the Co(II)/Zn(II) complex isolated from

the system: [Co(0)/Zn(II)-1-hydroxylmethyl-3,5-dimethylpyrazole], *j.inorg.Chem.Commun.* 13 (2010) 361-364 **10.1016/j.inoche.2009.12.022**

[25] R. Kruszynski, T. Sierański, M. Świątkowski, M. Zielak, J. Wojciechowski, M. Dzierżawska, B. Lewiński, on the coordination behavior of the hmta toward zinc and cadmium cations in presence of sulfate(VI) and nitrate(V) anions, *j.Coord.Chem.* 67 (2014) 1332-1352 **10.1080/00958972.2014.915524**

[26] A. I. Anzellotti, N. P. Farrell, Zinc metalloproteins as medicinal targets, *j.Chem.Soc.Rev.* 37 (2008) 1629-1651 **10.1039/b617121b**

[27] G. Parkin, Synthetic Analogues Relevant to the Structure and Function of Zinc Enzymes, *j.Chem.Rev.* 104 (2004) 699-767 **10.1021/cr0206263**

[28] V. Vinogradoff, A. Rimola, F. Duvernay, G. Danger, P. Theulé, T. Chiavassa, The mechanism of hexamethylenetetramine (HMT) formation in the solid state at low temperature, *Phys. Chem. Chem. Phys.* 14 (2012) 12309-12320 **10.1039/C2CP41963G**

[29] M. P. Bernstein, S. A. Sandford, L. J. Allamandola, S. Chang, Infrared Spectrum of Matrix-Isolated Hexamethylenetetramine in Ar and H₂O at Cryogenic, *J. Phys. Chem.* 98 (1994) 12206-12210 **10.1021/j100098a014**

[30] L. H. Blanco, N. R. Sanabria, M. T. Dávila, Solubility of 1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane (HMT) in water from 275.15K to 313.15K, *Thermochim. Acta*, 450 (2006) 73-75 **10.1016/j.tca.2006.08.010**

[31] T. Takagishi, N. Kuroki, Thermodynamics of Binding Methyl Orange and its Homologs by Polyvinylpyrrolidone: The effect of Hexamethylenetetramine, *J. Polym. Sci.* 18 (1980) 259-264 **10.1002/pol.1980.170180124**

[32] W. Li, J-P. Zhang, M-L. Tong, X-M. Chen, Cocrystallization of Hexamethylenetetramine (hmt) with Dicarboxylic Acids. Crystal Structures of Molecular Adducts of hmt with Three Different Dicarboxylic Acids, *Aust. J. Chem.* 54 (2001) 213-217 **10.1071/CH01035**

[33] J. C. Duff and E. J. Bills, *J. Chem. Soc.* 1929, 411-419. **10.1039/JR9290000411**

[34] G. Giuseppetti, *Period. Mineral.* 1954, 23, 177-94

[35] Thomas C. W. Mak and Sheng-Hua Huang, *Polyhedron* 6, 1111-1114, 1987.

[36] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, Completion and Refinement of Crystal Structures with SIR92, *J. Appl. Cryst.* 26 (1993) 343-350 **10.1107/S0021889892010331**

[37] G. Sheldrick, *Acta Cryst. Section C: Struct. Chem.* 71 (2015) 3-8 **10.1107/S2053229614024218**

[38] Branderburg, K & Putz, H. (2005). DIAMOND. Version 3. Crystal Impact GbR, Bonn, Germany

[39] R. Kefi, C. Ben Nasr, F. Lefebvre, A. Durif, Hydrothermal synthesis and characterization of a new inorganic-organic hybrid compound AMP[ZnCl₃], *Inorg. Chim. Acta.* 358 (2005) 4075-4080 **10.1016/j.ica.2005.06.042**

- [40] S.K.Wolff, D.J.Grimwood, J.J.McKinnon, M.J.Turner, D.Jayatilaka and M.a. Spackman, CrystalExplorer 3.1, University of Western Australia, 2012.
- [41] J.J. Mckinnon, M.A. Spackman, A.S. Mitchell, Novel tools for visualizing and exploring intermolecular interactions in molecular crystals, Acta. Cryst. B60 (2004) 627-668 **10.1107/S0108768104020300**
- [42] M.A. Spackman, J.J. Mckinnon, Fingerprinting intermolecular interactions in molecular crystals, Cryst. Eng. Comm. 4(66) (2002) 378_ 392 **10.1039/B203191B**
- [43] J.J. Mckinnon, A.S. Mitchell, M.A. Spackman, Hirshfeld Surfaces: A New Tool for visualizing and Exploring Molecular Crystals, Chem. Eur. J. 4, No. 11 (1998) **10.1002/(SICI)1521-3765(19981102)4:11<2136::AID-CHEM2136>3.0.CO;2-G**
- [44] J.J. Mckinnon, D. Jayatilaka, M.A. Spackman, Towards quantitative analysis of intermolecular interactions with Hirshfeld surfaces, Chem. Commun (2007) 3814-3816 **10.1039/B704980C**
- [45] M.A. Spackman, J.J. Mckinnon, D. Jayatilaka, Electrostatic potentials mapped on Hirshfeld surfaces provide direct insight into intermolecular interactions in crystals, Cryst. Eng. Comm. 10 (2008) 377-388 **10.1039/B715227B**
- [46] M.A. Spackman, J. Jayatilaka, Hirshfeld surface analysis, Cryst. Eng. Comm. 11 (2009) 19-32 **10.1039/B818330A**
- [47] H.F. Clausen, M.S. Chevallier, M.A. Spackman, B.B. Iversen, Three new co-crystals of hydroquinone: crystal structures and Hirshfeld surface analysis of intermolecular interactions, New. J. Chem. 34 (2010) 193-199 **10.1039/B9NJ00463G**

FIGURE CAPTIONS

Fig. 1. Molecular structure of $[\text{Zn}(\text{H}_2\text{O})_6][\{(\text{CH}_2)_6\text{N}_4\}\text{ZnCl}_3]_2 \cdot 0.5 \text{H}_2\text{O}$.

Fig. 2. Projection of the crystal structure along the a-axis.

Fig. 3. Projection of the crystal structure along the c-axis.

Fig.4. Projection of the crystal structure showing hydrogen bonding interactions.

Fig.5a. Environment of the octahedral cation showing one of the possible O-H...O hydrogen bonds. **(b)** O-H...N hydrogen bonds around the octahedral cation. **(c)** O-H...Cl hydrogen bonds around the octahedral cation.

Fig.6. Environment of the anionic complex.

Fig.7a. $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ cation environment showing Zn²⁺-Zn²⁺ distance for **(a)** the hemihydrate and **(b)** the hexahydrate.

Fig.8. FTIR spectrum of $[\text{Zn}(\text{H}_2\text{O})_6][\{(\text{CH}_2)_6\text{N}_4\}\text{ZnCl}_3]_2 \cdot 0.5 \text{H}_2\text{O}$.

Fig.9. the TGA-DTA thermograms of $[\text{Zn}(\text{H}_2\text{O})_6][\{(\text{CH}_2)_6\text{N}_4\}\text{ZnCl}_3]_2 \cdot 0.5 \text{H}_2\text{O}$.

Fig. 10. 3D *dnorm* surface of the cationic fragment of the hemihydrate compound.

Fig. 11. Fingerprint plots analysis of the cationic fragment of the hemihydrate.

Fig. 12. 3D *dnorm* surface of the anionic complex in the hemihydrate.

Fig. 13. Fingerprint plots analysis of the anionic complex in the hemihydrate.

Fig. 14. 3D *dnorm* surface of the cationic fragment of the hexahydrate.

Fig. 15. Fingerprint plots analysis of the cationic fragment in the hexahydrate.

Fig. 16. 3D *dnorm* surface of the anionic complex in the hexahydrate.

Fig. 17. Fingerprint plots analysis of the anionic complex in the hexahydrate.

Table 1

Crystal data and structure refinement of $[\text{Zn}(\text{H}_2\text{O})_6][\{(\text{CH}_2)_6\text{N}_4\}\text{ZnCl}_3]_2 \cdot 0.5 \text{H}_2\text{O}$. CCDC 1823072 contains the supplementary crystallographic data for this structure.

Crystal data	
Chemical formula	$[\text{Zn}(\text{H}_2\text{O})_6][\{(\text{CH}_2)_6\text{N}_4\}\text{ZnCl}_3]_2 \cdot 0.5 \text{H}_2\text{O}$
Mr (g.mol ⁻¹)	806.3
Crystal system, space group	Trigonal, P-3c1
Temperature (K)	100 (1)
a, c (Å)	9.8303 (2), 17.5460 (2)
V (Å ³)	1468.38 (4)
Z	2
Radiation type	Mo K α
μ (mm ⁻¹)	3.02
Crystal size (mm)	0.56 × 0.38 × 0.31
Data collection	
Diffractometer	Xcalibur, Sapphire3
Absorption correction	Multi-scan
$T_{\min}$, $T_{\max}$	0.686, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	68418, 1756, 1629
R_{int}	0.037
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.753
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.023, 0.059, 1.11
No. of reflections	1756
No. of parameters	81
H-atom treatment	Only H-atom coordinates refined
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.47, -0.66
CCDC ID	1823072

Table 2: Selected bond distances and angles along with distortion indexes ID (Å, °, %) for $[\text{Zn}(\text{H}_2\text{O})_6][\{(\text{CH}_2)_6\text{N}_4\}\text{ZnCl}_3]_2 \cdot 0.5 \text{H}_2\text{O}$

Bond lengths (Å)		Bond angles (°)	
Octahedron [Zn1(H ₂ O1W) ₆]			
Zn1—O1W	2.0705 (10)	O1W—Zn1—O1W ⁱ	180.0
		O1W—Zn1—O1W ⁱⁱ	89.50 (5)
DI Zn-O = 0		DI O-Zn-O = 0.31	
Tetrahedron [Zn2NCl ₃]			
Zn2—N1	2.0852 (16)	N1—Zn2—Cl1	106.488 (9)
Zn2—Cl1	2.2442 (3)	Cl1 ^{vi} —Zn2—Cl1	112.283 (8)
DI Zn-X 0.0268		DI X-Zn-X = 0.0264	
$DIb = \frac{\sum_1^i di - dm }{v * dm}$		$DIa = \frac{\sum_1^i ai - am }{u * am}$	

With:

d_i: value of the distance Zn-X (X=O, N, Cl)

d_m: the average value of the distance

a_i: value of the angle X-Zn-X

a_m: the average angle

v: zinc coordination number

u: angles number in the polyhedron

Table 3: Hydrogen-bond geometry (Å, °) for $[\text{Zn}(\text{H}_2\text{O})_6][\{(\text{CH}_2)_6\text{N}_4\}\text{ZnCl}_3]_2 \cdot 0.5 \text{H}_2\text{O}$

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1W—H1WA...Cl1 ^{vii}	0.76 (2)	2.42 (3)	3.1759 (11)	170 (2)
O1W—H1WA...O2W	0.76 (2)	2.41 (3)	2.777 (19)	111 (2)
O1W—H1WB...N2 ^{viii}	0.85 (2)	2.00 (2)	2.8239 (14)	163 (2)

Symmetry codes:(vi) $-x+y+1, -x+1, z$; (vii) $-y+1, x-y, z$; (viii) $-x+1, -x+y+1, -z+1/2$; (ix) $-x+1, -x+y, -z+1/2$

Table 4: Tentative of assignments of IR wavenumbers for $[\text{Zn}(\text{H}_2\text{O})_6][\{(\text{CH}_2)_6\text{N}_4\}\text{ZnCl}_3]_2 \cdot 0.5 \text{H}_2\text{O}$

Wavenumbers (cm^{-1})	Band assignment
3443-3087	$\nu_{\text{as}}(\text{OH})$ - $\nu_{\text{s}}(\text{OH})$
1643	$\delta(\text{OH})$
1469-1383	$\sigma(\text{CH})$
1230-1007	$\nu(\text{CN})$
825-681	$\delta(\text{CN})$
496-292	$\nu(\text{Zn-O})$; $\nu(\text{Zn-Cl})$

Abbreviations: ν : stretching, δ : deformation, σ : scissoring

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Fig.8. FTIR spectrum of $[\text{Zn}(\text{H}_2\text{O})_6][\{(\text{CH}_2)_6\text{N}_4\}\text{ZnCl}_3]_2 \cdot 0.5 \text{H}_2\text{O}$.

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