

Synthesis, spectroscopic studies and crystal structure determination of a tetranuclear Zn(II) [2x2] square grid structure of 1,5-bis(1-(pyridin-2-yl)ethylidene)carbonohydrazide

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Abstract: The reported tetranuclear zinc(II) complex $[Zn_4(HL)_4](NO_3)_4 \cdot 2H_2O$ ($H_2L=1,5$ -bis(1-(pyridin-2-yl)ethylidene)carbonohydrazide) has been prepared by mixing a methanol solution of Zinc nitrate salt and a methanol solution of H_2L in 1:1 molar ratio. The suitable monocrystals afforded were analysed by X-ray diffraction. The title compound crystallizes in the tetragonal space group $I4_1/a$ with the following unit cell parameters: $a = 14.0254(2) \text{ \AA}$, $b = 14.0254(2) \text{ \AA}$, $c = 35.7967(8) \text{ \AA}$, $\alpha = 94.610(4)^\circ$, $V = 7041.6(3) \text{ \AA}^3$, $Z = 4$, $R1 = 0.048$ and $wR2 = 0.136$. The structures are [2x2] square grids of tetramers units in which the metal ions are joined in pairs by the oxygen atom of the deprotonated hydrazono moiety in μ_2 -mode. Each Zn(II) ion is in a distorted octahedral environment. The supramolecular structures are consolidated by multiple hydrogen bonds. The luminescence properties of the Schiff bases and his tetranuclear Zn(II) complex have been examined. The results of the measurements indicate that the complex exhibited higher luminescence intensity than the free Schiff base ligand.

Keywords: Schiff base, crystal, complex, grid, luminescence, octahedral.

Date of Submission: 03-12-2018

Date of acceptance: 20-12-2018

I. Introduction

Because of their enormous potential in different sectors, polynuclear complexes occupy more and more place in inorganic chemistry. The important development of this sector of inorganic chemistry is largely due to the possibilities of applications in diverse fields as molecular magnetism [1-3], luminescence [4], ion sensors [5][5], and the SMMs [6]. The strategy for the preparation of these complexes occupies an important place in the elaboration of these materials, self-assembly [7], solvothermal synthesis [8], or the control of parameters such as pH and temperature [9-10] are widely used in the literature. Self-assembly of metal ions with organic ligands with multiple coordination sites is one of the most common strategies. This well-controlled strategy makes it possible to obtain complexes with high nucleation such as grids [2x2] [11], [2x3] [12], [3x3] [13], [4x4] [14], and [5x5] [15]. The challenge is to prepare suitable ligands to generate such patterns. Symmetrical or asymmetric Schiff bases bearing the carbon or thiocarbonohydrazone unit are well suited for preparing compounds of this type. These Schiff bases are often deprotonable and generate an enoyl motif. Indeed the presence of two azomethine nitrogen atoms and an oxygen or sulfur atom in the enoyl or the thioenoyl unit combined with the geometry imposed by the presence of azo groups are favorable conditions for self-assembly. It is in this context that we prepared the Schiff H_2L base and reacted it with zinc nitrate (II) to obtain a [2x2] grid structure.

II. Materials and Methods

2.1 Starting materials and Instrumentations

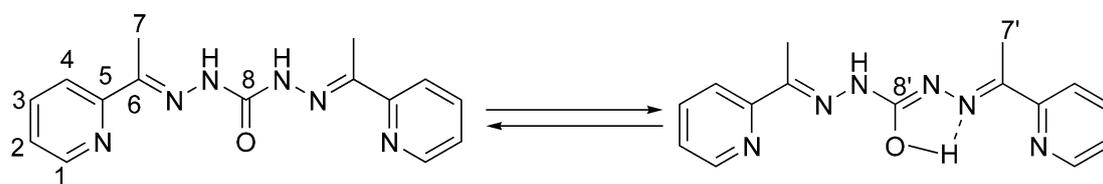
Commercially available 2-acetylpyridine, 2-carbonohydrazone and zinc nitrate were purchased from Aldrich and used without further purification. The IR spectra were recorded as KBr discs on a Perkin Elmer Spectrum Two spectrophotometer ($4000-400 \text{ cm}^{-1}$). Fluorescence spectra were recorded on a Perkin Elmer LS-55 spectrofluorimeter at room temperature (298 K). The molar conductance of 10^{-3} M solution of the metal complex in DMF was measured at 25°C using a WTW LF-330 conductivity meter with a WTW conductivity

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cell. Emission spectra were recorded on a Varian Cary Eclipse spectrofluorimeter. Samples in adequate solvent solutions were placed in 1 cm path length quartz cuvettes for room temperature measurements.

2.2 Synthesis of the ligand

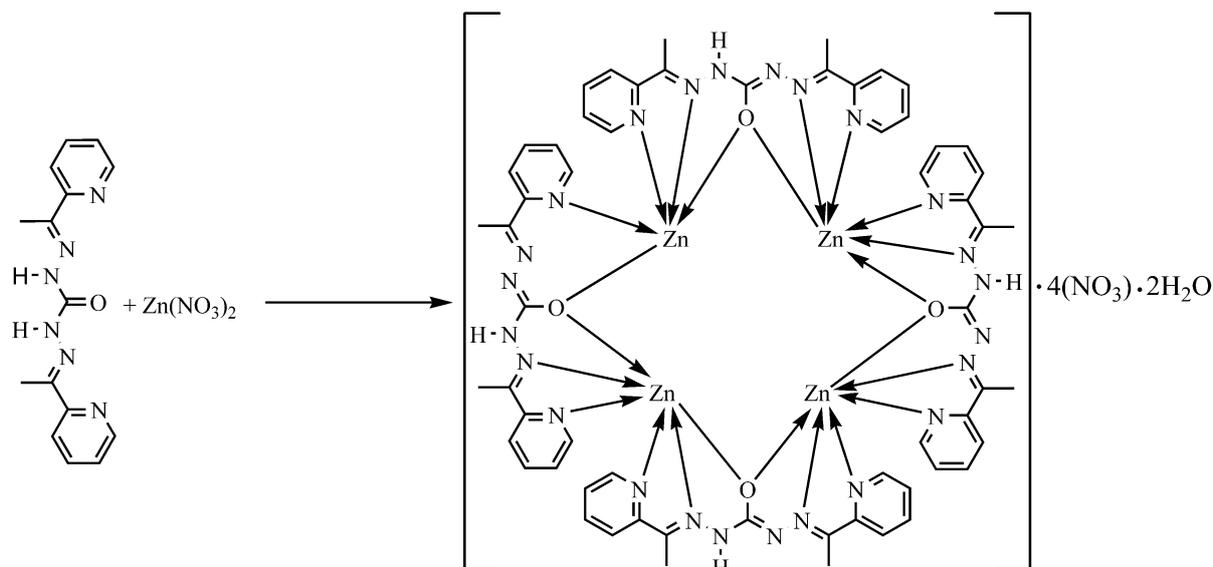
The Schiff base ligand 1,5-bis(1-(pyridin-2-yl)ethylidene)carbonohydrazide (H_2L) was synthesized as follows: carbonohydrazide (2 g, 22.2 mmol) in 20 mL of methanol was stirred under reflux during 30 min before addition of a solution of 2-acetylpyridine (10.75 g, 88.8 mmol) dissolved in 30 mL of methanol. The resulting mixture was stirred under reflux during 4 hours. On cooling a white precipitate appears from the uncoloured solution. After filtration the precipitate was thoroughly washed with cold ethanol and dried in desiccator over P_2O_5 . A slow evaporation of a methanol solution of the compound gave crystals suitable for X-ray analysis. Yield: 41.1%. M.p.: 195°C. 1H NMR δ_H (250 MHz, DMSO- d_6): 2.3 (s, 6H, CH_3), 7.3 – 8.6 (m, 8H, H_{py}), 8.7 (s, 2H, N-H); 10.1 (s, 1H, O-H iminol). ^{13}C NMR δ_C (250 MHz, DMSO- d_6): 155.4 (O-C=N), 153 (C=O), 152.1 (C_{py}), 120.4 (C_{py}), 137.0 (C_{py}), 124.2 (C_{py}), 149.1 (C_{py}), 147.9 (C=N), 11.9 (CH_3); 22.8 (CH_3). FT-IR (ν , cm^{-1}): 3415, 3206, 1681, 1612, 1558, 1466, 1429, 1207, 1104. Anal. calcd. for $C_{15}H_{16}N_6O$: C, 60.80; H, 5.44; N, 28.36%. Found: C, 60.83; H, 5.48; N, 28.32%.



Scheme 1. Iminolisation scheme for the ligand.

2.3 Synthesis of the Complexes

The synthesis of the complex $[Zn_4(HL)_4](NO_3)_4 \cdot 2H_2O$ is achieved as follows: a mixture of $Zn(NO_3)_2$ (0.25 mmol) and ligand H_2L (0.25 mmol) in methanol (15 mL) was stirred at room temperature during one hour. The yellow solution was filtered and the filtrate was kept at 298 K. After one week yellow crystals suitable for X-ray analysis appeared and were collected by filtration. Yield (%) = 85.7. FT-IR (cm^{-1}): 3459; 3152; 3089; 2916; 1627; 1573; 1547; 1466; 1353; 1310; 1262; 1213; 1158. UV-vis (solution, DMF, nm): 275; 310; 386; 475. Λ ($\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$): 414.4 (fresh solution) and 426.4 (two weeks after). Anal. calcd. for $C_{60}H_{64}Zn_4N_{28}O_{18}$: C, 41.73; H, 3.74; N, 22.71. Found: C, 41.74; H, 3.72; N, 22.68%.



Scheme 2. Synthetic scheme for the Zn^{II} complex preparation.

2.4 X-ray data collection, structure determination and refinement

Details of the X-rays crystal structure solution and refinement are given in Table 1. Diffraction data were collected using an ENRAF NONIUS Kappa CCD diffractometer with graphite monochromatized $MoK\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Complex scattering factors were taken from the program package SHELXTL [16]. Structure

solution and refinement were performed using *SHELXT* [17] and *SHELXL-2014/7* [18]. All hydrogen atoms were added in calculated positions and refined in riding mode on the parent atom. Molecular graphics were generated using *ORTEP-3* [19].

Table-1. Crystallographic data and refinement parameter for the ligand and the complex.

Empirical formula	C ₁₅ H ₁₆ N ₆ O	C ₆₀ H ₆₀ N ₂₄ O ₄ Zn ₄ ·4(NO ₃)·2(H ₂ O)
Formula weight (g/mol)	296.34	1726.87
T (K)	293(2)	293
Crystal system	Monoclinic	Tetragonal
Space group	C2/C	I4 ₁ /a
Crystal size (mm ³)	0.342 x 0.192 x 0.078	0.09 x 0.07 x 0.06
Mo K α (Å)	0.71073	0.71073
a (Å)	21.2693(9)	14.0254(2)
b (Å)	7.3922(3)	14.0254(2)
c (Å)	20.5444(9)	35.7967(8)
β (°)	112.496(3)	90
V (Å ³)	2984.3(2)	7041.6(3)
Z	8	4
D _{cal} (g cm ⁻³)	1.319	1.629
F(000)	1248	3536
μ (mm ⁻¹)	0.09	1.44
θ_{max} (°)	26.367	29.155
h, k, l ranges	-26 ≤ h ≤ 25, -9 ≤ k ≤ 7, 25 ≤ l ≤ 24	-17 ≤ h ≤ 15, -15 ≤ k ≤ 17, -39 ≤ l ≤ 48
Measured reflections	11980	32421
Independent Reflections	7033	4265
Reflections [I > 2σ(I)]	3044	3282
R _{int}	0.08	0.73
R _i [I > 2σ(I)]	0.054	0.048
wR ₂	0.169	0.136
Data/parameters/restraints	3044/201	4265/283/31
Goodness-of-Fit	1.09	1.03
$\Delta\rho_{max, min}$ (e Å ⁻³)	0.23, -0.21	0.75, -0.75

III. Results and Discussion

3.1 General study

The acyclic tridentate ligand, 1,5-bis-((pyridin-2-yl)ethylidene)carbohydrazide, abbreviated as H₂L, was prepared by the 1: 2 condensation reaction of carbonohydrazide and 2-acetylpyridine in methanol. The reaction of Zn(NO₃)₂ with the solution of the prepared ligand, with a molar ratio of 1:1 in methanol, gives a yellow powder. The compound is thus formulated as [Zn₄(HL)₄](NO₃)₄·2H₂O using spectroscopy and physicochemical analysis. The structures are confirmed by ray diffraction. The ¹H and ¹³C NMR spectra of the 1,5-bis-((pyridin-2-yl)ethylidene) carbohydrazide ligand are recorded in DMSO-d₆ as shown in the experimental section. The ¹H NMR spectrum of the ligand reveals a partial iminolization of the ligand in solution (Scheme 1). A broad singlet appearing at 10.1 ppm is attributed to the H-O proton of the iminol function. The ¹³C NMR spectrum shows the presence of both forms of the ligand. A signal at 153 ppm is assigned to (N=C=O) and a signal at 155.4 (O=C=N) is assigned to the carbon atom carrying the iminol function. The IR spectrum of the ligand reveals bands at 3415 cm⁻¹, 3206 cm⁻¹, 1681 cm⁻¹ and 1612 cm⁻¹ which are respectively assigned to ν_{O-H} , ν_{N-H} , $\nu_{C=O}$ and $\nu_{C=N}$ [20]. The infrared spectrum of the compound obtained after complexation (Scheme 2) shows a shift of the bands $\nu_{C=O}$ and $\nu_{C=N}$ to low frequencies, indicating an involvement of the oxygen atom of the C=O function and the nitrogen atom of azomethine function in the coordination sphere of the zinc ion. The strong and intense band observed in the infrared spectrum of complex at about 1353 cm⁻¹ is characteristic of an ionic nitrate. The molar conductivity is measured for a freshly prepared solution of complex in acetonitrile and after two weeks. These values are respectively 414.4 and 426.4 $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ for the complex thus indicating electrolyte of type 4:1 [21] and good stability of these complexes in acetonitrile.

3.2 X-ray structure of the ligand

The crystallographic parameters are shown in Table 1. The lengths and binding angles are given in Table 2. The compound crystallizes in the monoclinic system and in the C2/c space group. The asymmetric unit contains a molecule of C₁₅H₁₆N₆O ligand. Figure 1 shows the ORTEP diagram. The lengths and binding angles are normal and comparable to those observed in 1,5-bis(1-(pyridin-2-yl)ethylidene)carbonohydrazide. The bond lengths values of C-N are 1.291(2) Å and 1.2816(18) Å (C6-N2 and C9-N5 respectively) and are compatible with double bond character. The lengths of the bonds C8-N4 = 1.3634(19) Å, C8-N3 = 1.3598(18) Å indicate their simple bonding character and the length of the bond C8-O1 (1.2246 (16) Å) shows that it is a double bond. Consequently, in the solid state, an iminolization is not observed, contrary to what has been observed with ¹H

NMR in solution in DMSO-d₆. The stability of the crystalline structure is ensured by the existence of intermolecular hydrogen bonds of the N4-H ... O1 and intramolecular type N3-H ... N1 type.

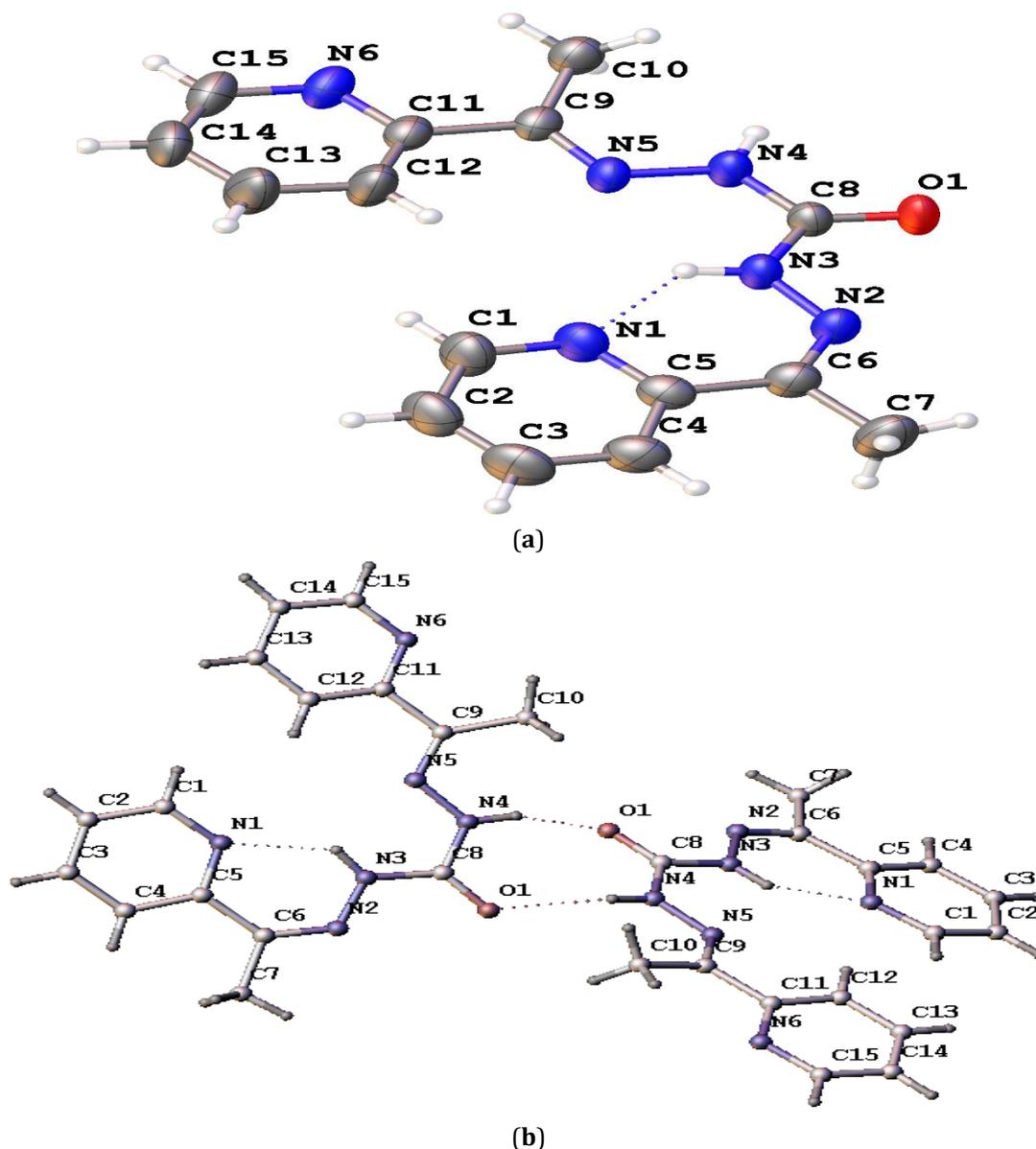


Figure 1: ORTEP plot (30% probability ellipsoids) showing the molecule structure of the ligand (a) and the intramolecular and intermolecular hydrogen bonds (b) in the ligand.

Table-2. Selected bond distances [Å] and angles [deg] for the H₂L and Zn^{II} complexes.

H ₂ L			
O1—C8	1.2246 (16)	N1—C5	1.346 (2)
N3—N2	1.3624 (17)	N1—C1	1.334 (2)
N3—C8	1.3598 (18)	C9—C11	1.486 (2)
N5—N4	1.3712 (16)	C9—C10	1.498 (2)
N5—C9	1.2816 (18)	C11—C12	1.381 (2)
N4—C8	1.3634 (19)	C5—C6	1.481 (2)
N2—C6	1.291 (2)	C5—C4	1.390 (2)
N6—C11	1.341 (2)	C6—C7	1.505 (2)
N6—C15	1.337 (2)	C15—C14	1.363 (3)
[Zn ₄ (HL) ₄](NO ₃) ₄ ·2H ₂ O			
Zn1—N5 ⁱ	2.072 (2)	Zn1—N1	2.151 (2)
Zn1—N2	2.076 (2)	Zn1—O1	2.1534 (17)
Zn1—O1 ⁱ	2.1366 (17)	Zn1—N6 ⁱ	2.191 (2)
N5 ⁱ —Zn1—N2	174.47 (9)	O1 ⁱ —Zn1—O1	92.63 (9)
N5 ⁱ —Zn1—O1 ⁱ	75.28 (8)	N1—Zn1—O1	150.02 (9)

N2—Zn1—O1 ⁱ	110.04 (8)	N5 ⁱ —Zn1—N6 ⁱ	74.91 (9)
N5 ⁱ —Zn1—N1	105.85 (10)	O1 ⁱ —Zn1—N6 ⁱ	150.13 (8)
N2—Zn1—N1	75.82 (10)	N1—Zn1—N6 ⁱ	97.00 (9)
O1 ⁱ —Zn1—N1	92.88 (8)	O1 ⁱ —Zn1—N6 ⁱ	92.70 (8)
N5 ⁱ —Zn1—O1	104.06 (8)	Zn1 ⁱⁱ —O1—Zn1	134.98 (8)
N2—Zn1—O1	74.61 (8)		

Symmetry codes: (i) $-y+7/4, x-1/4, -z+7/4$; (ii) $y+1/4, -x+7/4, -z+7/4$.

3.3 X-ray Structure of the complex $[\text{Zn}_4(\text{HL})_4](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$

The reaction between the synthesized H₂L ligand and zinc nitrate in a molar ratio 1: 1 made it possible to prepare the tetranuclear complexes $[\text{Zn}_4(\text{HL})_4](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ as yellow crystals by self-assembly. The carbonohydrazone ligand used may exist as two keto and enol tautomers. The latter is known to have two modes of coordination according to its two types of conformation. In its syn-conformation it coordinates in pentadentate form and gives by self-assembly square complexes in which the single oxygen atom of the molecule acts as a bridge between two metallic centers [22]. In some complexes there is the presence of the *syn-form* and the *anti-form* that coordinates in a hexadentate way to self-assemble rectangular-type complexes in which there are μ -O bridges and μ -N-N bridges [23]. In the case of our complexes the ligand acts in its *syn-form* and gives square complexes.

Compound $[\text{Zn}_4(\text{HL})_4](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ crystallizes in the tetragonal system with space group I41/a. In the asymmetric unit there are four crystallographically equivalent Zn(II) centers, four deprotonated mono ligands that have the same coordination mode, four free nitrate ions and two uncoordinated water molecules. The ORTEP diagram is shown in figure 2 and the coordination sphere is shown in figure 3. Each Zn atom is bound to two tridentate ligands. Both Zn atoms are in a distorted octahedral site consisting of two nitrogen atoms of pyridine, two nitrogen atoms of the N-N group and two enol oxygen atoms thus giving ZnN_4O_2 . The adjacent Zn(II) ions are bridged by the oxygen atom of their shared ligand. The Zn-O binding lengths vary between 2.1366(17)° and 2.1534(17)° and are comparable to the values found for a similar complex [24]. The lengths Zn-N_{py} are in the range 2.151(2)° and 2.191(2)° and are longer than the distances Zn-N which are between 2.072(2)° and 2.076(2)°. These observations are consistent with values found in Zn complexes with the same ligand [24,25]. The binding angles around Zn indicate that the environment is octahedral. The equatorial plane is occupied by the N1, N6, O1 and O1ⁱ atoms while the N2 and N5 atoms occupy the apical positions. The values of the *cisoids* angles in the equatorial plane vary between 92.63(9)° and 97.00(9)° while the *transoids* angles are 150.02(9)° and 150.13(8)°. The angle between the atoms occupying the axial positions is 174.47(9)°. All these angles values are very different from the ideal values of an octahedral environment and confirm the strong deformation of the octahedron around the zinc atom. These observations are consistent with the reported results in the literature [23]. The angle Zn-O-Zn is 134.99(9)° and the angle O-Zn-O is 92.63(7)°. All the Zn(II)---Zn(II) angles are ~89.70(1)°. The four nearby Zn(II)---Zn(II) distances values are equal to 3.9633(4) Å and both Zn(II)---Zn(II) distances along the corners of the square are 5.5901(4) Å. Two of the oxygen atoms forming the Zn-O-Zn bridges are located above the average plane of the four Zn atoms (0.8705 Å for O1 and 0.6631 Å for O1_{\$3}), while the two others are located below this average plane (-0.6953 Å O1_{\$1} for O1 and 0.6631 Å for O1_{\$2}), thus leading to an arrangement similar to a deformed boat as shown in figure 3.

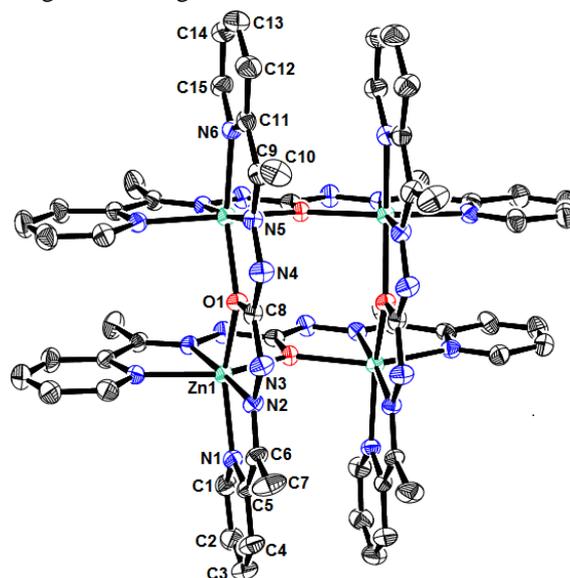


Figure 2: ORTEP plot (30% probability ellipsoids) showing the molecule structure of the Zn^{II}.

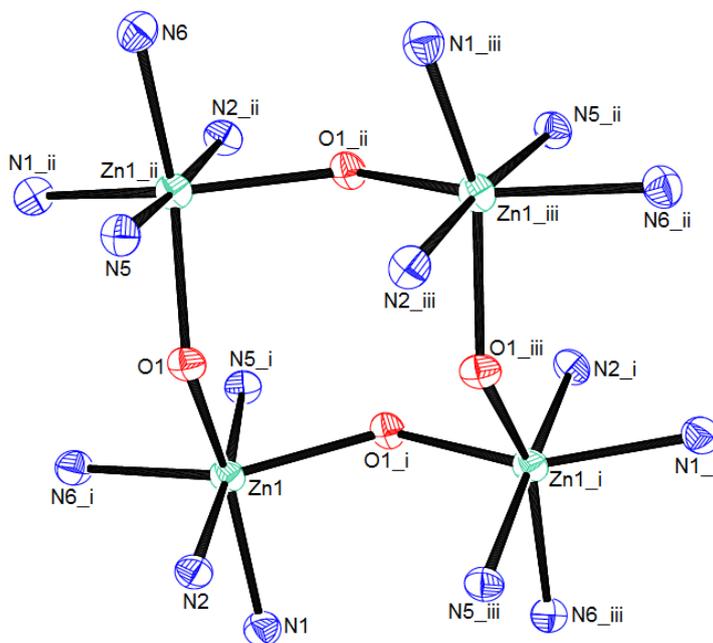


Figure 3:Plot showing the coordination sphere of Zn²⁺ and the boatlike arrangement.

Table-3.Hydrogen-bond geometry (Å, °) for the ligand and Zn^{II} complex.

D—H...A	D—H	H...A	D...A	D—H...A
O2W—H2W...O3	0.91 (2)	2.15 (3)	3.037 (17)	165 (7)
O2W—H2W...O4 ⁱ	0.91 (2)	2.09 (4)	2.944 (15)	155 (7)
N4—H4...O6	0.86	2.23	2.960 (9)	142.6
N4—H4...O7 ⁱⁱ	0.86	2.19	2.951 (11)	147.2
C1—H1...O6 ⁱⁱⁱ	0.93	2.60	3.406 (11)	145.9
C1—H1...O7 ^{iv}	0.93	2.49	3.327 (12)	150.1
C2—H2...O8 ^v	0.93	2.51	3.155 (8)	126.9
C4—H4A...O3 ^v	0.93	2.57	3.326 (9)	138.2
C4—H4A...O4 ^{vi}	0.93	2.45	3.303 (8)	152.6
C7—H7C...O6 ⁱⁱ	0.96	2.58	3.360 (10)	138.6
C7—H7C...O8	0.96	2.53	3.478(8)	170.6
C10—H10A...N3 ^{vii}	0.96	2.61	3.477 (5)	150.9
C10—H10B...O5 ^{viii}	0.96	2.53	3.456 (10)	162.3
C10—H10C...O6	0.96	2.61	3.556 (7)	170.3
C12—H12...O3 ^{ix}	0.93	2.57	3.404 (10)	149.8
C14—H14...O4 ^x	0.93	2.64	3.320 (11)	130.5

Symmetry codes: (i) $-x+1/2, -y+1/2, -z+3/2$; (ii) $-x+2, -y+3/2, z$; (iii) $y-1/4, -x+7/4, z-1/4$; (iv) $-y+5/4, x-1/4, z-1/4$; (v) $-y+3/4, x+1/4, z+1/4$; (vi) $y+1/4, -x+3/4, -z+7/4$; (vii) $-x+2, -y+2, -z+2$; (viii) $y+5/4, -x+5/4, z+1/4$; (ix) $-y+7/4, x+3/4, -z+7/4$; (x) $-x+3/2, -y+3/2, -z+3/2$.

3.4 Fluorescence properties

The emission spectra of the ligand and the complex of Zn(II) have been investigated at room temperature in the present work. As shown in figure 4 and figure 5, the emission spectra of the ligand and his Zn complex in ultrapure water are very different both in emission waves length and emission intensities. These facts are indicative that the fluorescence of the complex is not based on the ligand but on the coordination of the ligand with the metal ion. The emission peak appears at 447 nm ($\lambda_{ex}=340$ nm) for the complex and 390 nm ($\lambda_{ex}=340$ nm) for the ligand, respectively. The intensity of the emission spectrum of the complex is much higher than that of the free ligand. The decrease in fluorescence after complexation with a transition metal is a widespread phenomenon that is explained by factors such as redox activity, magnetic perturbation, and electronic energy transfer [26]. On the other hand, the increase of the fluorescence of the complex relative to the free ligand is explained by factors related to the restriction of the photoinduced electron transfer consequence of the rigidity of the structure of the complex molecule [27]. In the case of our study, the increase of the fluorescence of the complex relative to the free ligand seems to be due to these last two factors. As the crystallographic structure has shown, the reaction of the ligand with Zn (II) ion generates a rigid 2x2 grid structure. The conformation of the structure of the complex is more rigid than that of the free ligand. This rigidity will contribute to reducing the possibilities of vibration of the complex molecule and consequently the possibilities of energy loss by vibration. Thus, the enhanced fluorescent intensity of the complex is

observed. When comparing the spectra of the complex at 2.10^{-5} mol/L, in ultrapure water and methanol, it appears a significant enhancement of the fluorescence in methanol relative to water. Because of the coordination possibilities of these two solvents, the oxygen atom of methanol is better coordinated to the zinc atom than the oxygen atom of the water molecule because of the inductive donor effect of methyl group (figure 6). Indeed, it has been shown that the more the ligand is electro-donors, the more the fluorescence is enhanced and the more the ligand is electro-attractor the more the fluorescence decreases. On varying the concentration of the complex and the ligand in ultrapure water, no shift of λ_{em} is observed only the fluorescence intensity is concentration dependent (figure 4 and figure 5).

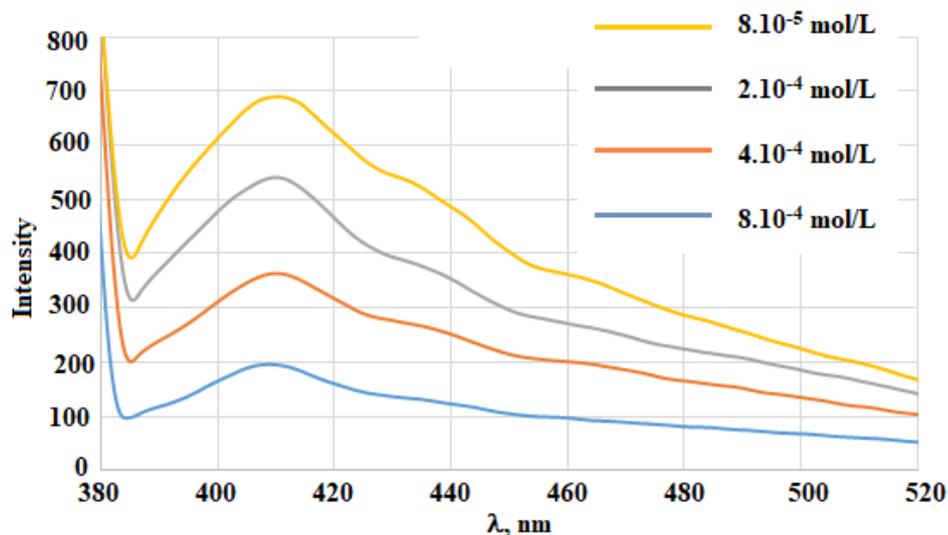


Figure 4: Fluorescence spectra of the Schiff base recorded at room temperature in ultra-pure water at different concentration..

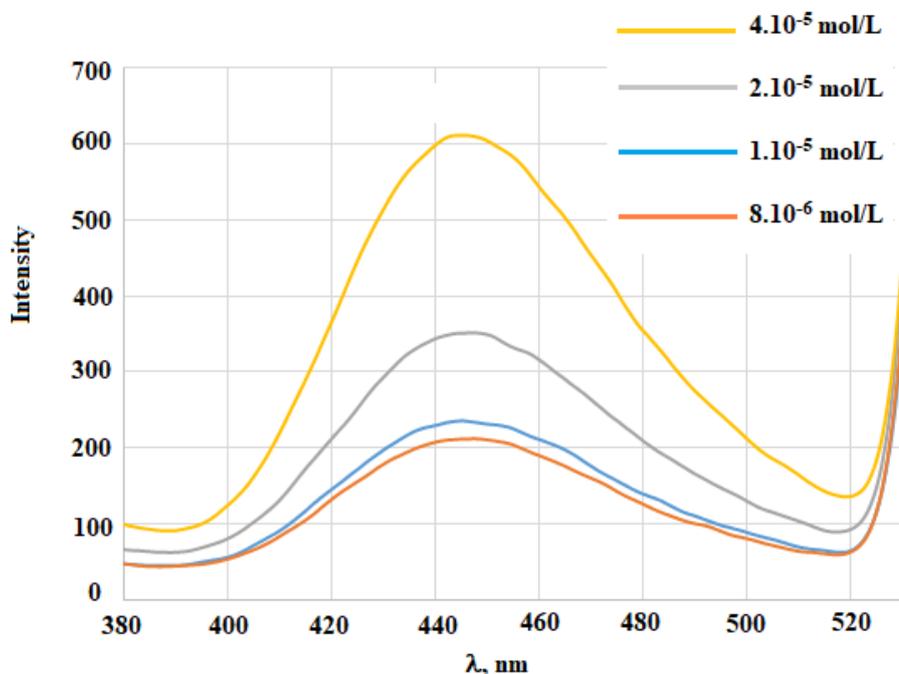


Figure 5: Fluorescence spectra of the complex recorded at room temperature in ultra-pure water at different concentration.

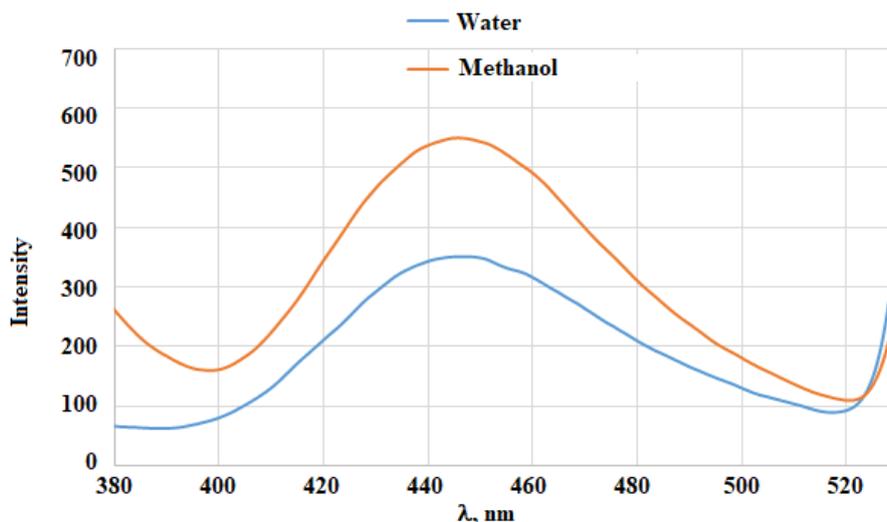


Figure 6: Fluorescence spectrum of the complex in two different solvents.

IV. Concluding remarks

The use of carbonohydronepolyfunctional ligands has made it possible to synthesize a large number of complexes with a grid structure as well with transition metal ions as with lanthanides. The polytopic nature of the ligands, having suitable coordination chambers, can be controlled to accommodate ions of different sizes. In this work, we report the synthesis, the spectroscopic study and the structural determination of a tetranuclear complex derived from the organic molecular ligand, N,N'-1,2-phenylene-bis-(3-methoxysalicylaldehyde) and Zn²⁺ ion. The structure of this complex is in the form of a 2 x 2 grid and all zinc atoms are hexacoordinate in a highly deformed octahedral environment. Two adjacent zinc atoms are bridged by an oxygen atom of the hydrazono group in μ_2 mode. An increase in the intensity of the luminescence of the complex relative to the ligand is observed.

V. Supporting information

CCDC-1882047 (ligand) and 1880831 (complex) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Acknowledgements

The authors thank the FONDATION SONATEL for his financial support, <http://fondationsonatel.sn/>.

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