

A NEW SEVEN – COORDINATED COMPLEX OF Zn(II) WITH NICOTINAMIDO AND ACETATO LIGANDS: SYNTHESIS AND CHARACTERIZATION

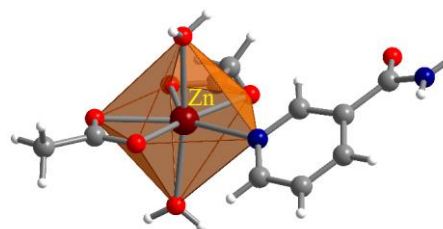
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A mononuclear Zn(II) coordination compound of formula $[Zn(ac)_2(H_2O)_2(na)].2H_2O$, where *ac* = acetate and *na* = nicotinamide, was synthesized and characterized by X – ray diffraction, IR, ¹³C and ¹H NMR spectra. The data obtained from X – ray diffraction revealed that the geometry of the central atom is a distorted pentagonal bipyramid, with the four oxygen atoms of the acetate groups and the heterocyclic nitrogen atom of the nicotinamide molecule making up the basal plane. The axial positions are occupied by the oxygen atoms of the water coordinated molecules.



INTRODUCTION

Nicotinamide, also named niacinamide, is a form of the well-known B3 vitamin, belonging to the water-soluble vitamin B group and being an essential nutrient found in a variety of foods, especially in meat and its derivatives. It fulfils its metabolic role by being incorporated into the NAD⁺/NADH coenzyme, which can be phosphorylated to form the NADP⁺/NADPH couple. The NAD⁺/NADH redox system takes part in about 400 biochemical reactions, such as the citric acid cycle or the ethanol metabolism, while the phosphorylated form is involved in other 30 reactions, like the cytochrome P450 metabolism of xenobiotics.^{1,2} In recent decades a lot of coordination compounds of various 3d metals with nicotinamide were synthesized and characterized,

interested sustained by their biological activity.³⁻⁸ Among them, there are several complexes of Zn(II) characterized by means of X – ray crystallography.⁹⁻¹⁵ On the other hand, zinc acetate is used as a medicine in the treatment of the Wilson disease, an inherited disorder of copper metabolism.^{16,17} Until now, the synthesis and characterization of some complexes with acetate and nicotinamide as mixed ligand for Cu(II)¹⁸ and Cr(III) were reported.¹⁹ Also, a Co(II) complex with nicotinamide, where acetate acts as counterion was synthesized.²⁰ Likewise, the literature mentions some Zn(II) complexes with nicotinamide and water or halogens as mixed ligands.²¹⁻²³ Besides this, it was reported a dinuclear complex of Zn(II) with nicotinamide, where four acetate ligands act as bridges between the metallic ions.²⁴

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RESULTS

IR (KBr), $\nu_{\max}/\text{cm}^{-1}$: 3600 – 2800 (ν O-H), 3350 (ν_{as} N-H), 3172 (ν_{s} N-H), 3070 (ν C-H), 3024 (ν C-H), 1681 (ν C=O), 1620 (ν C=N), 1597 (δ N-H), 1560 (ν_{as} COO⁻), 1479 (δ O-H), 1436 (ν_{s} COO), 1406 (ν C-C), 1199 (ν C-NH₂), 1151 (ν C-N), 1138 (δ C-H), 1112 (δ C-H), 1049 (δ C-H + ν C-C), 1014 (ρ_{r} CH₃), 972 (γ C-H), 941 (ν C-C), 837 (ν C-H), 788 (ν C-H), 673 (ρ_{w} NH₂), 650 (δ OCO), 580 (ρ_{w} H₂O), 522 (δ C-NH₂ + γ C=O).

¹H-NMR (500 MHz, DMSO-*d*₆, δ ppm, J Hz): 9.02 (d, 1H, H-1, 1.4), 8.70 (dd, 1H, H-5, 1.1, 4.7), 8.23 (m, 1H, H-3), 8.20 and 7.63 (s, 2H, NH₂), 7.52 (m, 1H, H-4), 1.83 (s, 6H, CH₃) ppm. The water resonance signal appears at 3.44 ppm.

¹³C-NMR (125 MHz, DMSO-*d*₆, δ ppm): 178.3, 166.7, 152.2, 149.1, 135.9, 130.2, 123.9, 22.2 ppm.

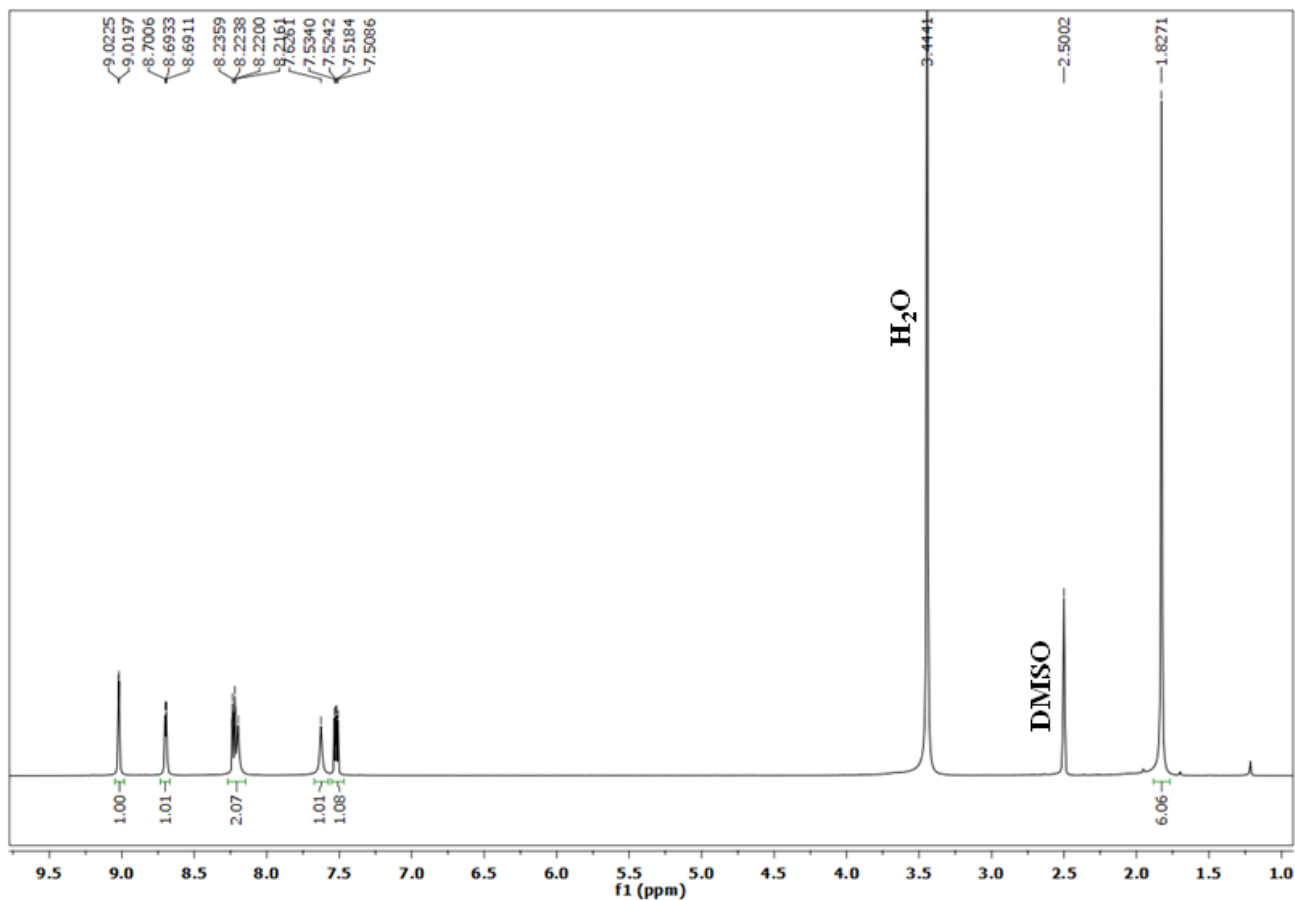
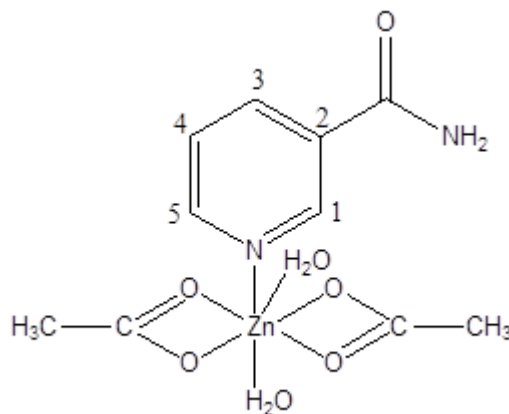


Fig. 1 – ¹H-NMR spectrum of the compound $[\text{Zn}(\text{ac})_2(\text{H}_2\text{O})_2(\text{na})].2\text{H}_2\text{O}$.

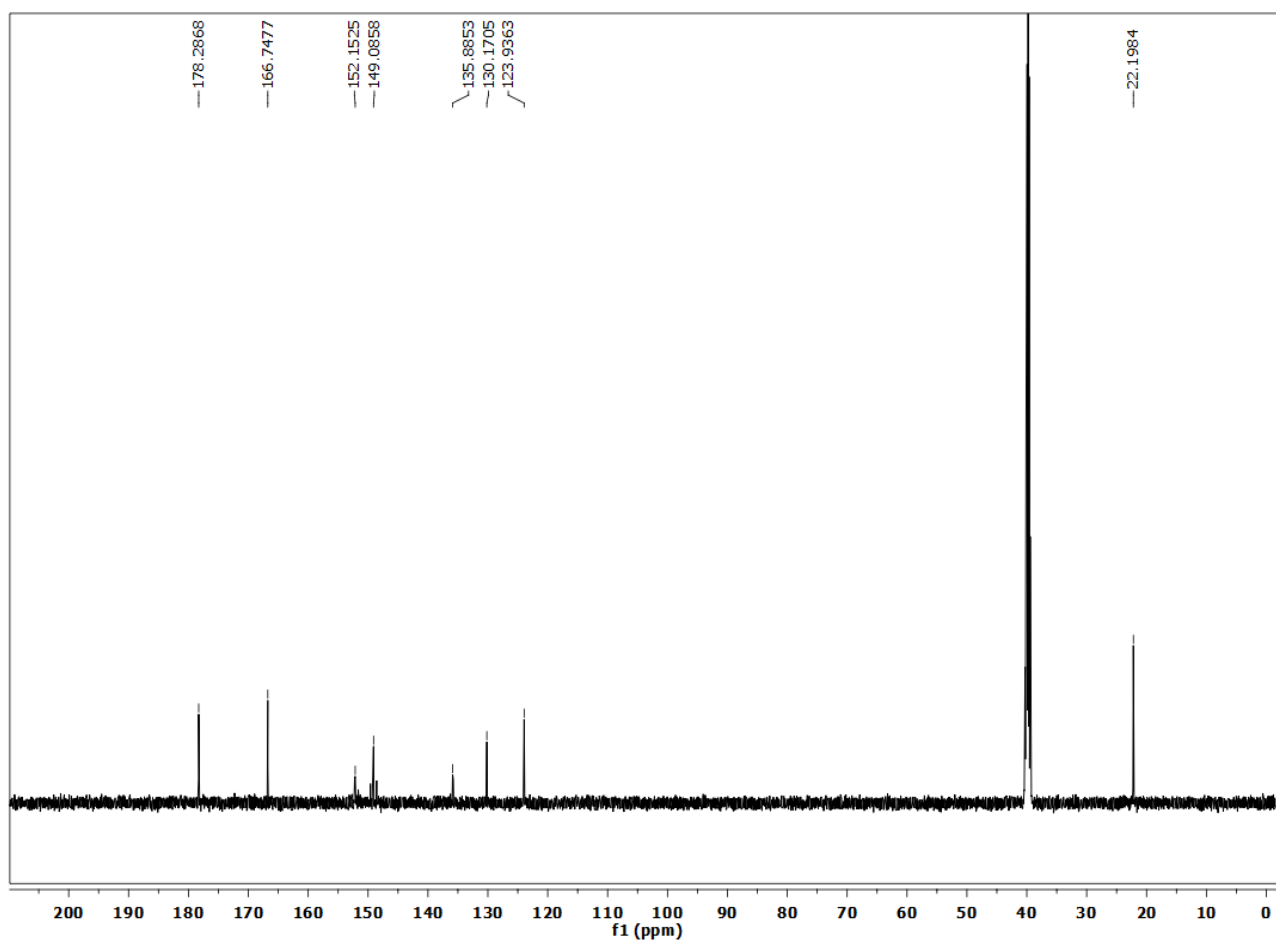
Fig. 2 – ^{13}C -NMR spectrum of the compound $[\text{Zn}(\text{ac})_2(\text{H}_2\text{O})_2(\text{na})].2\text{H}_2\text{O}$

Table 1

Crystallographic data for the complex $[\text{Zn}(\text{ac})_2(\text{H}_2\text{O})_2(\text{na})].2\text{H}_2\text{O}$

Compound	$[\text{Zn}(\text{ac})_2(\text{H}_2\text{O})_2(\text{na})].2\text{H}_2\text{O}$
Chemical formula	$\text{C}_{10}\text{H}_{20}\text{N}_2\text{O}_9\text{Zn}$
M (g mol^{-1})	377.65
Temperature, (K)	293(2)
Wavelength, (\AA)	0.71073
Crystal system	<i>Triclinic</i>
Space group	<i>P-1</i>
<i>a</i> (\AA)	8.0829(2)
<i>b</i> (\AA)	8.2546(2)
<i>c</i> (\AA)	13.5618(3)
α ($^\circ$)	76.301(2)
β ($^\circ$)	86.402(2)
γ ($^\circ$)	66.025(2)
V (\AA^3)	802.70(4)
Z	2
D_c (g cm^{-3})	1.562
μ (mm^{-1})	1.574
$F(000)$	392
Goodness-of-fit on F^2	1.101
Final R_1 , wR_2 [$I > 2\sigma(I)$]	0.0501, 0.1465
R_1 , wR_2 (all data)	0.0526, 0.1495

DISCUSSION

FT – IR spectrum

The spectrum exhibits a broad band, situated between 3600 and 2800 cm^{-1} which is due to O – H stretching from the lattice and coordinated water molecules. The existence of the coordinated water molecules is sustained by the additional band, observed at 580 cm^{-1} , due to the wagging vibrational mode, $\rho_w(\text{H}_2\text{O})$. The bands observed at 3350 and 3172 cm^{-1} can be assigned to asymmetrical and symmetrical N – H stretching vibrations from the amido group of the nicotinamide molecule, while the N – H in-plane bending vibration appears at 1597 cm^{-1} . The strong absorption from 1620 cm^{-1} is due to $\nu(\text{C}=\text{N})$ from the pyridinic ring, while the band from 1151 cm^{-1} is due to $\nu(\text{C}-\text{N})$ vibration. Also, the band from 1199 cm^{-1} was assigned to C–NH₂ stretching vibration. Finally, the $\nu(\text{C}=\text{O})$ from the amido group of the nicotinamide fragment is observed at 1681 cm^{-1} .²⁵ Regarding the acetate groups, the strong bands which appear at 1560 cm^{-1} and 1436 cm^{-1} were assigned to $\nu_{\text{as}}(\text{COO}^-)$, irrespective $\nu_{\text{s}}(\text{COO}^-)$ vibrations. The Δ value = $\nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$ is a parameter which allows to distinguish between various coordination modes of the acetate groups. In this case, $\Delta = 124 \text{ cm}^{-1}$, indicating a bidentate chelating coordination mode. On top of that, the bands from 1014 cm^{-1} and 650 cm^{-1} were assigned to $\rho_r(\text{CH}_3)$ and $\delta(\text{OCO})$ vibrations of the acetate fragments.²⁶

X – ray crystallography

The structure of the compound $[\text{Zn}(\text{ac})_2(\text{H}_2\text{O})_2(\text{na})].2\text{H}_2\text{O}$ was determined by

X-ray diffraction on single crystal. The compound crystallises in the triclinic $P-1$ space group and the structure comprises neutral mononuclear $[\text{Zn}(\text{ac})_2(\text{H}_2\text{O})_2(\text{na})]$ molecules and crystallization water molecules. The Zn(II) ions are heptacoordinated by one nicotinamide ligand, two acetate ions acting in a bidentate chelating manner and two water molecules (Figure 3a). The coordination geometry of the metal ions is a distorted pentagonal bipyramid, where the coordination positions of the basal plan are occupied by the oxygen atoms of the acetate groups and the pyridine nitrogen atom of the nicotinamide fragment, while in the axial ones there are the oxygen atoms of the coordinated water molecules. The bond lengths Zn–O with the chelate acetate ligands are significantly longer, 2.326(5) – 2.469(5) Å, in comparison with those encountered in the acetate zinc dihydrate, $\text{Zn}(\text{CH}_3\text{COO})_2.2\text{H}_2\text{O}$ (2.17 and 2.18 Å) and in other complexes where acetate groups act in a bidentate chelating manner.^{20,27,28} The same situation is valid for the Zn–N bond length (2.336(5) Å) which is longer than in other complexes of 3d metals with nicotinamide.¹⁸⁻²⁰ The distortion from the bipyramidal pentagonal regular geometry is shown by the basal plane angles, which are significantly different from the theoretical value of 72°. As it can be observed, the angles O–Zn–O of the acetate groups have 52.70(19)°, respective 54.15(16)°, while those N1–Zn1–O2 and N1–Zn1–O6 are greater than 80°. The distortion is also shown by the value of the angle O6–Zn–O7, 171.55(18)°, which is deviated from the theoretical value of 180°. Selected bond distances and angles concerning metal ions surroundings are presented in Table 2.

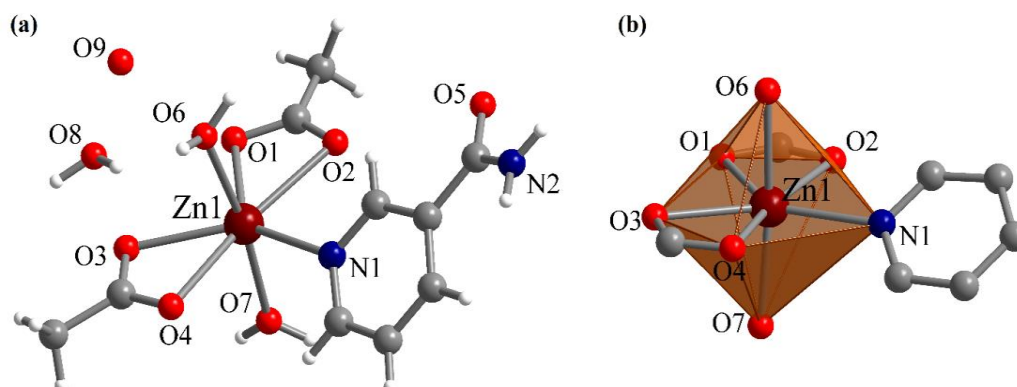
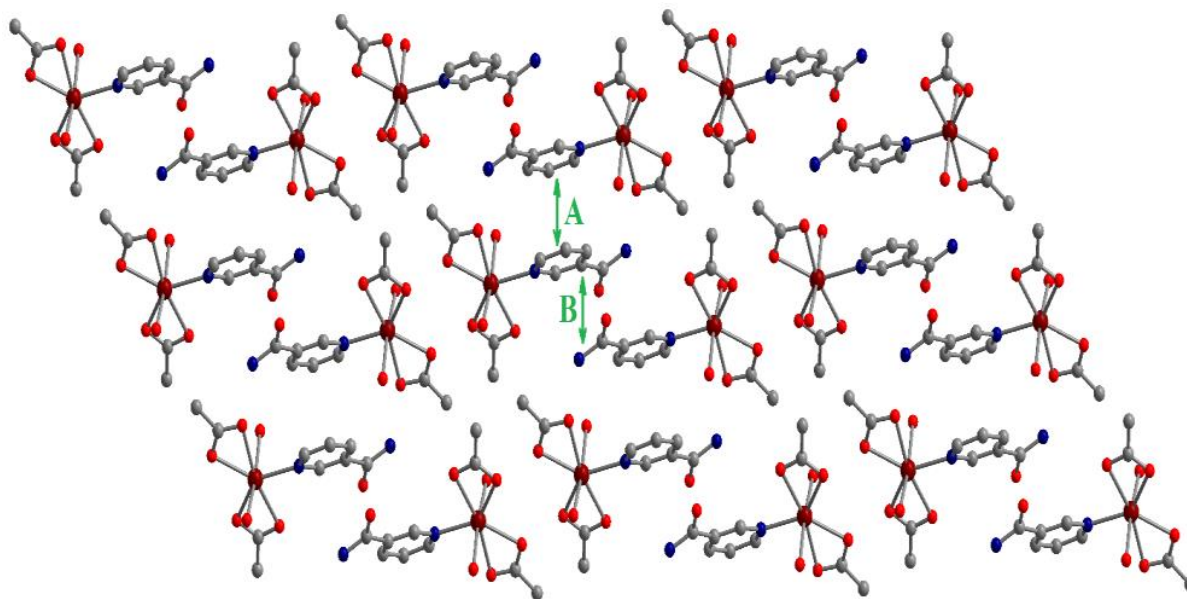


Fig. 3 – (a) Perspective view of the asymmetric unit of complex $[\text{Zn}(\text{ac})_2(\text{H}_2\text{O})_2(\text{na})].2\text{H}_2\text{O}$ and (b) details of the metal ion stereochemistry.

Table 2

Selected bond distances (Å) and angles (°) for the complex $[Zn(ac)_2(H_2O)_2(na)].2H_2O$

Atoms	Bond distance	Atoms	Angle
Zn1–O1	2.343(5)	O1–Zn1–O2	52.70(19)
Zn1–O2	2.469(5)	O3–Zn1–O4	54.15(16)
Zn1–O3	2.326(5)	O6–Zn1–O7	171.55(18)
Zn1–O4	2.462(5)	N1–Zn1–O2	81.77(17)
Zn1–O6	2.364(3)	N1–Zn1–O4	84.89(16)
Zn1–O7	2.318(3)	N1–Zn1–O6	89.11(17)
Zn1–N1	2.336(5)	N1–Zn1–O7	92.54(18)

Fig. 4 – View of the packing diagram showing the π - π interactions established between the nicotinamide ligands.

The examination of the packing diagrams shows a pile organization of the molecules through π - π interactions established between the nicotinamide ligands. There are two types of interactions: type A involving the pyridine rings of neighbouring complexes with separations of 3.38–3.62 Å and type B involving the amido group of one complex and pyridine ring of another complex, with separations of 3.32–3.77 Å (Figure 4).

The oxygen atoms of the complex and the nitrogen atom of the amido group are involved in a network of intermolecular hydrogen bonds with the crystallization water molecules generating a supramolecular 3D architecture. Some data regarding these supramolecular interactions are presented in Table 3.

Table 3

Geometrical details of the hydrogen interactions (the hydrogen atoms of the crystallization O9 water molecule were not observed)

D–H...A	d(H...A)(Å)	d(D...A)(Å)	$\angle(DHA)$ (°)
O6–H1W...O5 ⁱ	1.870	2.720	169.1
O6–H2W...O8	1.959	2.721	147.4
O7–H3W...O9 ⁱⁱ	2.038	2.775	143.1
O7–H4W...O3 ⁱⁱⁱ	1.949	2.761	156.6
O8–H5W...O2 ^{iv}	1.936	2.761	160.3
O8–H6W...O5 ^v	2.080	2.833	145.1
O9...O6		3.033	
N2–H2E...O4 ^v	2.029	2.852	160.0

Symmetry codes: ⁱ = -x, 2-y, 1-z; ⁱⁱ = x, -1+y, z; ⁱⁱⁱ = 1-x, 1-y, 2-z; ^{iv} = 1+x, y, z; ^v = 1-x, 1-y, 1-z.

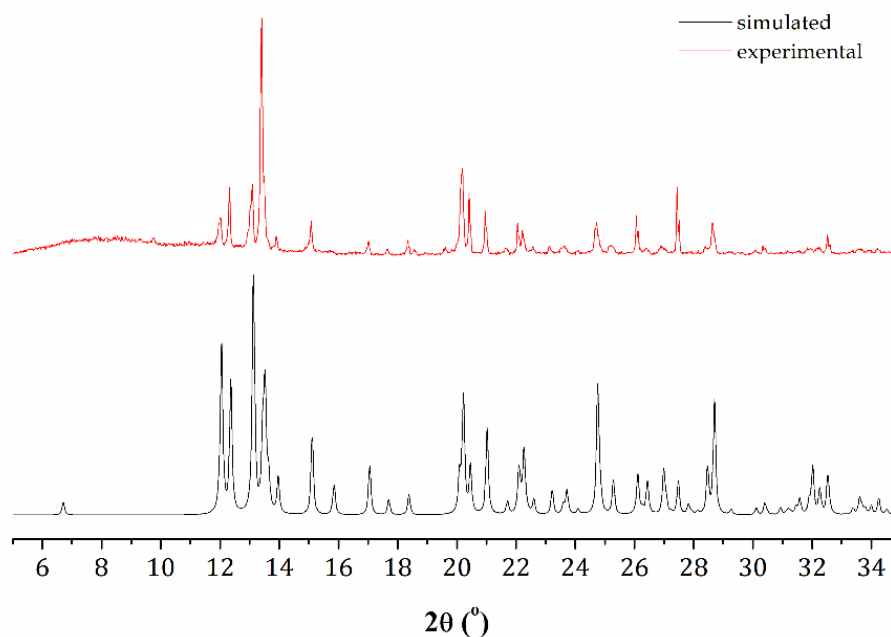


Fig. 5 – Measured (red) and calculated (black) powder X-ray diffraction patterns of $[\text{Zn}(\text{ac})_2(\text{H}_2\text{O})_2(\text{na})] \cdot 2\text{H}_2\text{O}$.

EXPERIMENTAL

Materials

The metal salts and the ligands were purchased from local suppliers (Merck). All solvents and reagents were reagent grade and used as received without further purification.

Synthesis of the complex $[\text{Zn}(\text{ac})_2(\text{H}_2\text{O})_2(\text{na})] \cdot 2\text{H}_2\text{O}$

The complex was synthesized as follows: the solution (20 mL) obtained by dissolving 1 mmol of nicotinamide in a mixed water – ethanol solvent (1:1) was added to a solution (20 mL) of 1 mmol zinc acetate which was prepared using the same solvent. The mixture was refluxed for 1 h and left to slow evaporation at room temperature. After several days, colourless crystals were separated from the solution. The powder X-ray diffraction shows that the sample contains only one crystalline phase (Figure 5).

FT - IR spectrum was recorded with a Varian 3100 Excalibur spectrophotometer using ATR Pyke MIRacle (SeZn crystal), in the range $4000 - 400 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ spectrum was recorded on a Bruker Avance III Ultrashield Plus 500 MHz spectrometer, operating at 11.74 T, corresponding to the resonance frequency of 500.13 MHz for the ^1H nucleus, equipped with a direct detection four nuclei probe head and field gradients on z axis.

X – ray crystallography. X-ray diffraction measurements were performed on a Rigaku XtaLAB Synergy-S diffractometer operating with Mo-K α ($\lambda = 0.71073 \text{ \AA}$) micro-focus sealed X-ray tube. The structure was solved by direct methods and refined by full-matrix least squares techniques based on F^2 . The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-2014 or SHELX-2018 crystallographic software package. A summary of the crystallographic data and the structure refinement are given in Table 1. CCDC reference number: 2173880.

The X-ray powder diffraction measurements (XRPD) were carried out on a Proto AXRD Benchtop using the Cu-K α radiation with a wavelength of 1.54059 \AA in the 2θ range of $5\text{-}35^\circ$.

CONCLUSIONS

The present work describes the synthesis and characterization of a new complex of Zn(II) with acetato and nicotinamido ligands. The product of the reaction between zinc acetate dihydrate and nicotinamide is a mononuclear complex, with an unusual pentagonal bipyramidal geometry. The X – ray crystallographic data reveals the bidentate chelating coordination mode of the acetate fragments and the coordination of the nicotinamide molecule through the pyridinic nitrogen. This data is sustained by the IR spectrum of the complex, while the ^1H NMR and ^{13}C NMR spectra confirm the presence of these ligands in the coordination compound.

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