Available online at **www.joac.info**

ISSN: 2278-1862

Journal of Applicable Chemistry

2020, 9 (5): 709-715

(International Peer Reviewed Journal)

Synthesis, Spectral and Structural Studies of (Z)-3-hydroxy-1-phenylbut-2-en-1-one Zn(II) Complex

S. Javaregowda[1]* and B. Pramodh[2]

1. Department of Physics, Bharathi College, Bharathi nagara, Mandya, Karnataka, **INDIA**
2. Department of Studies in Physics, University of Mysore, Manasagangotri, Mysuru, Karnataka, **INDIA**
Email: javaregowdas2013@gmail.com

Accepted on 3rd September, 2020

ABSTRACT

An important class of β-diketone derivative, (Z)-3-hydroxy-1-phenylbut-2-en-1-one show a wide range of pharmaceutical applications and they are found to be an excellent precursor for the metal complexes and crystal engineering. In the present work Zn(II) complex with (Z)-3-hydroxy-1-phenylbut-2-en-1-one was synthesized and crystallized by slow evaporation method using methanol solvent. The Zn(II) complex was characterized by Fourier transform infrared spectroscopy and UV-visible spectroscopy to confirm the formation of metal complex. The molecular structure was confirmed by the single crystal X-ray structural analysis. Slightly distorted trigonalpyramidal ZnO_5 *coordination polyhedral is observed around the central metal ion. Intermolecular hydrogen bond interactions leads to the formation of* $R_2^2(12)$ *and* $R_2^2(6)$ *supramolecular ring motif along with C-H...π and π... π intermolecular interactions, which plays a major role in the molecular stability.*

Highlights

- Zn(II) complex with (Z)-3-hydroxy-1-phenylbut-2-en-1-one was synthesized and crystallized by slow evaporation method.
- The Zn(II) complex was characterized by FTIR and UV-Visible spectroscopy.
- The crystal structure was confirmed by the single crystal X-ray structural analysis.
- Intermolecular hydrogen bond interactions revealed the supramolecular ring motif of $R_2^2(12)$ and $R_2^2(6)$.
- C-H...π and π... π intermolecular interactions also played a major role in the molecular stability.

Keywords: X-ray diffraction; Zn(II) complex, Supramolecular ring motif, Trigonalpyramidal.

INTRODUCTION

Metal complexes have engrossed researchers due to their versatile applications in the field of catalyst, sensors, luminescent devices [1, 2] and biological applications such as, antibacterial, anticancer and anti-inflammatory property [3, 4]. The synthesis and biological evaluation of new transition metal-based compounds are fields of growing interest. Among the various metal ions zinc, platinum, titanium, ruthenium, gold, copper and silver and their complexes showed potential application such as anti-tumor, anti-amoebic, anti-histaminic, anthelmintic, anti-ulcer, anti-bacterial, anti-fungal, anti-cancer and anti-hypertensive agents [1-4]. The Zinc metal complexes highly attracted by the researchers because of its significant biological activity as well as lower side effects along with higher lipophilicity or solubility compared to transition metals. Zinc (II) complexes are used as the catalytic centers in many enzymes (metallo-enzymes). Complexation with Zinc (II) metal center usually results in complexes with four-coordination number and a tetrahedral geometry. This is due to the fact that Zinc is a late transition metal with full d valence electrons, which means that a stable 18-electron complex can be formed through four-coordination number. Due to this reason, five-coordinate Zinc complex is considered unusual and expected to be unstable [5-9].

At the same time, selection of active ligands can induce the biologically important complex materials wherein, one such class of ligand is the β-diketone [10-13]. β-diketones possess a wide range of biological applications such as anti-microbial [10], anti-tumor [11, 12], anti-convulsants [13], anti-oxidant [14], anti-inflammatory [15], anti-ulcer [16] and antihypertensive[17]. Hence β-diketones play an significant role in inorganic chemistry, as it can easily form stable complexes with most transition metal ions due to their ability to form ketoenol tautomerism [18-21]. Herein, we study the synthesis, characterization, crystal structure, Hirshfeld surface analysis and molecular docking studies of five coordinated (Z)-3-hydroxy-1-phenylbut-2-en-1-one Zn(II) complex.

.

MATERIALS AND METHODS

Materials and instrumentation: All reactants and the general solvents of reagent grade for the experiment were purchased from Sigma-Aldrich. The Fourier transform infrared (FTIR) spectra of both the compounds were recorded using Perkin Elmer Spectrum Version 10.03.09 from 4000-400 cm^{-1}. The UV-Visible spectral analysis was performed using *Shimadzu-1800*.

Synthesis and crystallization: Zinc complex of (Z)-3-hydroxy-1-phenylbut-2-en-1-one was synthesized by following the procedure shown in scheme 1. (Z)-3-hydroxy-1-phenylbut-2-en-1-one dissolved in methanol and Zn(II) sulphate dissolved in distilled water was mixed and stirred for about 30 min. The catalytic amount of triethylamine was added to reaction mixture and heated upto 80°C for 15 min, followed by cooling in an ice bath. The formed precipitate was filtered, washed with distilled water and dried in hot air (90°C). Subsequently, the crystals of zinc complex were obtained by slow evaporation method.

Table 1. Crystal data and structure refinement parameters of Zn(II) complex.

Parameters	Complex	Parameters	Complex
Empirical formula	$C_{21}H_{23}O_5Zn$	F_{000}	438
Formula weight	420.81	θ range for data collection	3.15° to 27.56°
Temperature	293K	Crystal size	0.25x 0.26 x 0.27mm^3
Wavelength	0.71073Å	Index ranges	$-12 \le h \le 8$ $-12 \le k \le 12$ $-16 \le l \le 14$
Crystal system, space group	Triclinic, $P\bar{1}$	Reflections collected	5372
Unit cell dimensions		Unique reflections	4122 [R_{int} = 0.1479]
a	9.376(1)Å	Absorption correction	multi-scan
b	9.865(2)Å	Refinement method	Full matrix least-squares on F^2
c	12.394(2)Å		
α	103.37(1)°	Data/restraints/parameters	4122 / 3 / 250
β	101.94(1)°	Goodness-of-fit on F^2	1.013
γ	113.89(2)°		
Volume	966.5(2)$Å^3$	Final [$I > 2\sigma(I)$]	R_1 = 0.0778, wR_2 = 0.2021
Z	2	*R* indices (all data)	R_1 = 0.1039, wR_2 = 0.2502
Density(calculated)	1.446 Mg m^{-3}	Largest diff. peak and hole	1.405 and -1.509 e $Å^{-3}$
Absorption coefficient	1.300 mm^{-1}		

X-ray diffraction studies: X-ray quality crystal of the Zn(II) complex was selected for data collection. X-ray intensity data were collected on Rigaku XtaLAB mini diffractometer using graphite monochromated MoKα radiation (0.71073Å) at 293K. The data were collected at fixed χ with different angular settings of φ and ω with a scan width of 1° and the sample to detector distance of 50 mm. The crystal structure was solved by direct methods and refined using full-matrix least-squares against F^2 using *SHELXS* and *SHELXL* programs [22, 23]. All the non-hydrogen atoms were assigned anisotropically and refined without any positional constraints. Geometrical calculations were carried out using *PLATON* program [24] and the packing diagrams were generated using *MERCURY 4.2.0* software [25]. Crystal data and structure refinement parameters of Zn(II) complex are summarized in table 1.

RESULTS AND DISCUSSION

Synthesis and crystallization: The desired Zn(II) complex was prepared by mixing ZnSO4 with the (Z)-3-hydroxy-1- phenylbut-2-en-1-one ligand in [1:2] molar ratio, as shown in scheme 1. The reaction in methanol revealed complex with five coordination numbers with a distorted trigonal bipyramidal geometry. Interestingly, coordination number and the stereochemistry of the desired complex were affected by the coordinated solvent.

Scheme 1. Reaction pathway of (Z)-3-hydroxy-1- phenylbut-2-en-1-one Zn(II) complex.

FTIR: IR spectrum of Zn(II) complex was recorded and spectrum of complex is given in figure 1. In the spectrum of zinc complex weak to medium intensity absorption bands in the region 400-600 cm^{-1}, which confirms the absent in free ligands, may be attributed to M-O vibrations. Appearance of new bands in the regions of 489-560 cm^{-1} is assigned to Zn-O stretching modes, which confirms the formation of complex. In 1-phenyl-1, 3-butanedione bands due to C=O and C-O have been reported at 1708 and 1620 cm^{-1} respectively. The bands in the region 1600-1680 cm^{-1} are assigned to coordinated C=O and C-O. The C=O frequencies of the complexes are in the lower region as compared to those of the free ligands. The region 1420-1550 cm^{-1} is assigned to C=C stretching modes.

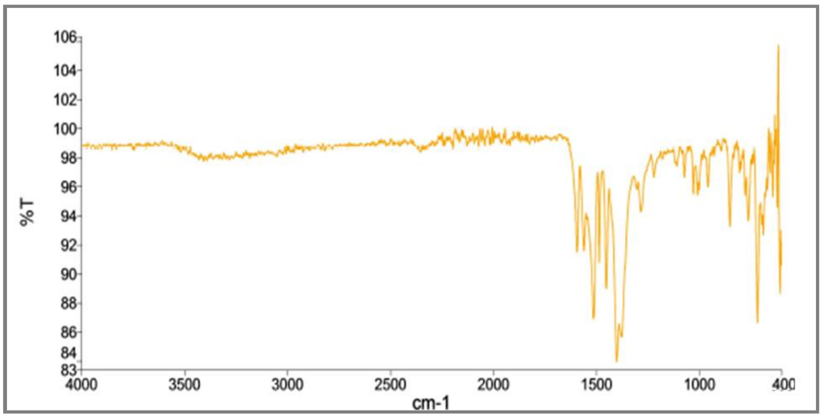

Figure 1. FTIR spectra of Zn(II) complex.

UV-Vis spectroscopy: Electronic absorption spectra of metal complexes are based on the excitation of π electrons to the π^* (excited) state which occurs in the UV-Visible region. The visible spectrum was recorded for the title compound in the range of 200 to 500 nm. The optical absorption spectrum of the Zn(II) complex is shown in the figure 2 and was recorded using acetonitrile solvent and the concentration of the solution is 27µg mL^{-1}. The spectrum evidences the strong absorption in the range 275-350 nm. The optical band gap energy (3.98 eV) of the title compound was calculated using lower cut off frequency (312.11 nm).

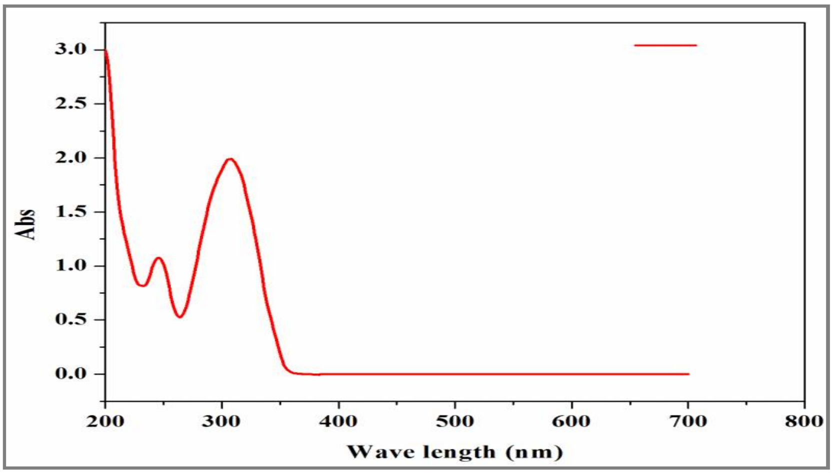

Figure 2. UV-Vis spectra of Zn(II) complex.

Single crystal XRD: The asymmetric unit of (Z)-3-hydroxy-1-phenylbut-2-en-1-one zinc(II) complex consists of the mononuclear [Zn($C_{10}H_9O_2$)$_2$(CH_4O)]. The central metal Zinc atom is five coordinated with two bidentate 3-hydroxy-1-phenylbut-2-en-1-one ligands via O1, O2, O3 and O4 atoms with metal-oxygen bond distance of 2.013(4), 2.007(4), 2.025(4) and 1.970(4) Å respectively together with O5 (MeOH solvent) at 2.022(4) Å. Both (Z)-3- hydroxy-1-phenylbut-2-en-1-one chelate to the zinc ion *cis* to each other (Figure 3) as this isomer is sterically favored to the *trans* isomer. The presence of MeOH solvent ligand forced the coordination geometry around the metal centre to be slightly distorted trigonal bipyramidal. The geometry of four and five coordinate transition metal complexes can be systematically described using the values of angular structural parameters τ_4= [360°-(α+β)]/141° and τ_5= (α-β)/60° Parameter used to assess molecular shape of five coordinate transition metal complexes. Where α and β are the largest angles in the complex ($\alpha > \beta$). Parameter τ_5 is calculated for Zn(II) complex, which is equal to 0.749166, confirms distorted trigonal pyramidal geometry around the ion.

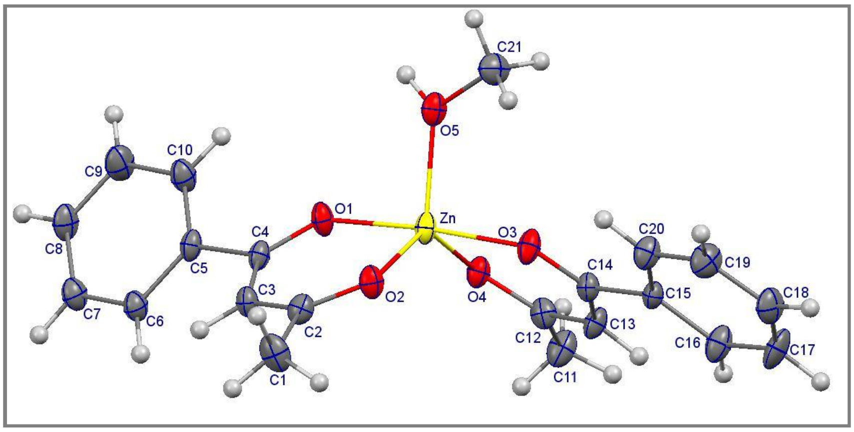

Figure 3. ORTEP of (Z)-3-hydroxy-1-phenylbut-2-en-1-one Zn(II) complex.

The molecular structure of (Z)-3-hydroxy-1-phenylbut-2-en-1-one Zn(II) complex is stabilized by inter and intra-molecular hydrogen bond, C-H...π and π... π interactions. Inter molecular hydrogen bond interaction of type C(1)-H(1)...O(4) is forming $R_2^2(12)$ ring motif whereas short interaction between O(4) and O(5) atoms of adjacent molecules forms $R_2^2(6)$. These interactions are combining to form two dimensional supramolecular architecture of $[Zn(C_{10}H_9O_2)_2(CH_4O)]$ along the *a*-axis (Figure 4). Apart from these interactions C(1) H(1a)...C(19) and C(18)...C(18) interactions between neighboring complexes contributing to stabilize the crystal with an inter-atomic distance of 2.781 and 3.355 Å respectively. Molecular packing of Zn(II) complex along *b* and *c* axis are shown in figure 5 and 6, respectively.

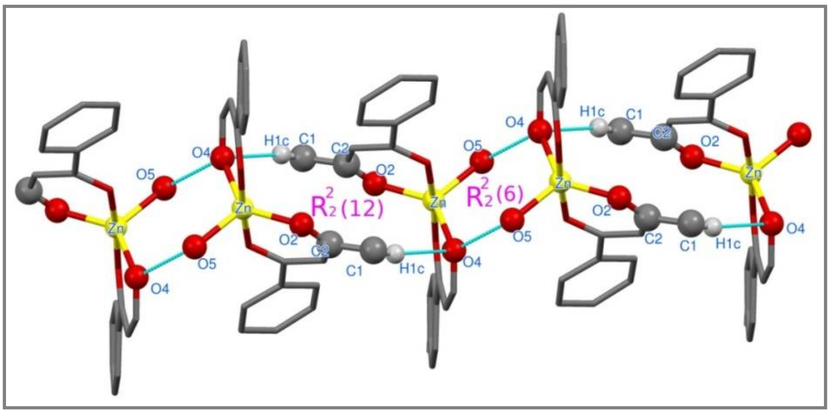

Figure 4. Supramolecular architecture of Zn(II) complex when viewed along *a*-axis.

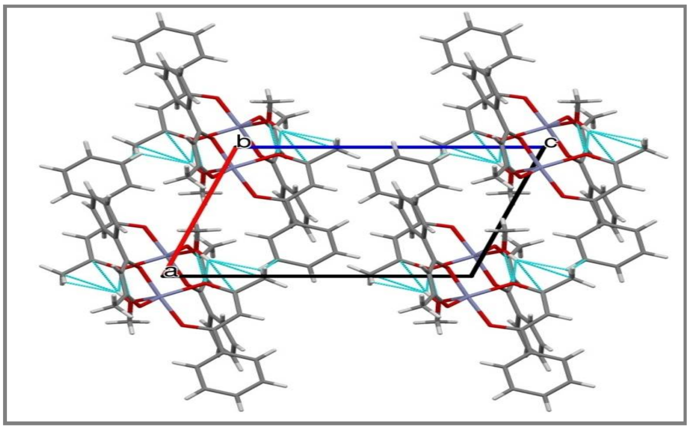

Figure 5. Packing of Zn(II) complex when viewed along *b*-axis.

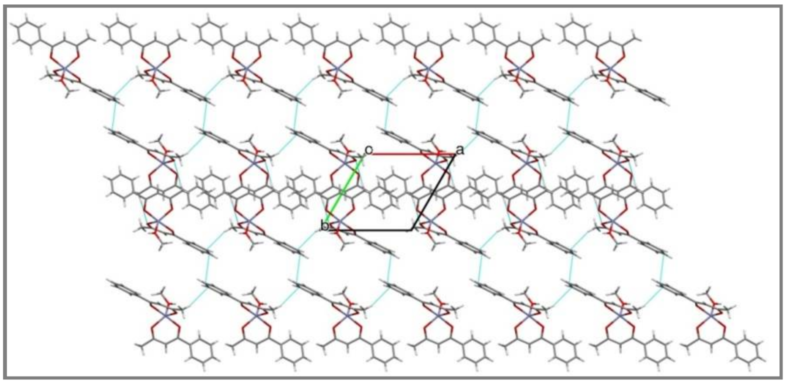

Figure 6. Packing of Zn(II) complex when viewed along *c*-axis.

APPLICATION

Zinc complexes were used for therapeutic agents. Zinc coordination compounds have been effectively tested for healing of diabetes. These complexes also exhibit, antibacterial, antifungal, anti-inflammatory and antioxidant properties. This complex, could be tested against deadly bacterial cell, life threatening cancer cells, inflammation and cytotoxicity studies, which leads to the multicomponent antibacterial, anticancer and anti-inflammatory drug discovery.

CONCLUSION

(Z)-3-hydroxy-1-phenylbut-2-en-1-one Zn(II) complex was synthesized and single crystal were obtained by slow evaporation method using methanol solvent. FTIR experiment confirmed the absorption peaks in the region of 489-560 nm belongs to Zn-O stretching modes, which confirms the presence of keto (C=O) group. UV-Vis spectrum exhibits the peak and the energy gap was found to be 3.98 eV. Single crystal X-ray diffraction experiment reveals that the zinc(II) complex adopts trigonal distorted pyramidal coordination environment around its central metal ion. Intermolecular interaction of type C-H…O is dominating in the stabilization of molecular crystal packing by forming supramolecular architecture of (Z)-3-hydroxy-1-phenylbut-2-en-1-one zinc(II) complex along *bc* plane.

REFERENCES

[1]. A. A. Nazarov, C. G. Hartinger, P. J. Dyson, Opening the lid on piano-stool complexes: an account of ruthenium (II) arene complexes with medicinal applications, *Journal of Organometallic Chemistry*, **2014**, 751, 251-260.

[2]. N. Muhammad, Z. Guo, Metal-based anticancer chemotherapeutic agents, *Current Opinion in Chemical Biology*, **2014**, 19, 144-153.

[3]. N. Charef, F. Sebti, L. Arrar, M. Djarmouni, N. Boussoualim, A. Baghiani, D. G. Peters, Synthesis, characterization, X-ray structures, and biological activity of some metal complexes of the Schiff base 2, 2-(((azanediylbis (propane-3, 1-diyl)) bis (azanylylidene)) bis (methanylylidene)) diphenol, *Polyhedron*, **2015**, 85, 450-456.

[4]. M. Wehbe, A. W. Leung, M. J. Abrams, C. Orvig, M. B. Bally, A Perspective can copper complexes be developed as a novel class of therapeutics?, *Dalton Transactions*, **2017**, 46(33), 10758-10773.

[5]. M. Franks, A. Gadzhieva, L. Ghandhi, D. Murrell, A. J. Blake, E. S. Davies, M. Schroder, Five coordinate M (II)-diphenolate [M=Zn(II), Ni(II), and Cu(II)]Schiff base complexes exhibiting metal-and ligand-based redox chemistry, *Inorganic chemistry*, **2013**, 52(2), 660-670.

[6]. E. Szyk, A. Wojtczak, A. Surdykowski, M. Godzikiewicz, Five-coordinate zinc (II) complexes with optically active Schiff bases derived from (1R, 2R)-cyclohexane diamine: X-ray structure and CP MAS NMR characterization of [cyclohexylenebis (5-chlorosalicylideneiminato) zinc (II) pyridine] and [cyclohexylenebis (5-bromosalicylideneiminato) zinc (II) pyridine], *Inorganica chimica acta*, **2005**, 358(3), 467-475.

[7]. J. M. Newman, B. C. A.ear, T. W. Hambley, H. C. Freeman, Structure of bis(glycinato) zinc (II) monohydrate, a five-coordinate zinc (II) complex, *Acta Crystallographica Section C: Crystal Structure Communications*, 1990, 46(1), 44-48.

[8]. X. W. Song, X. J. Gao, H. X. Liu, H. Chen, C. N. Chen, Synthesis and characterization of a supramolecular assembly based on a pyridyl-functionalized [FeFe]-hydrogenase mimic and zinc tetraphenylporphyrin, *Inorganic Chemistry Communications*, **2016**, 70, 1-3.

[9]. W. Che, T. Yu, D. Jin, X. Ren, D. Zhu, Z. Su, M. R. Bryce, A simple oxazoline as fluorescent sensor for Zn^{2+} in aqueous media, *Inorganic Chemistry Communications*, **2016**, 69, 89-93.

[10]. M. Kawase, N. Motohashi, H. Sakagami, T. Kanamoto, H. Nakashima, L. Ferenczy, J. Molnr, Antimicrobial activity of trifluoromethyl ketones and their synergism with promethazine. *International journal of antimicrobial agents*, **2001**, 18(2), 161-165.

[11]. J .Kljun, I. Turel, Diketones as scaffolds for anticancer drug design from organic building blocks to natural products and metallodrug components, *European Journal of Inorganic Chemistry*, **2017**, (12), 1655-1666.

[12]. K. Nakano, T. Nakyachi, E. Yasumoto, S. R. M. Morshed, K. E. N. Hashimoto, H. Kikuchi, H. Sakagami, Induction of apoptosis by β-diketones in human tumor cells, *Anticancer research*, **2004**, 24(2B), 711-718.

[13]. F. D. Popp, H. Pajouhesh, Potential anticonvulsants IV: Condensation of isatin with benzoylacetone and isopropyl methyl ketone, *Journal of pharmaceutical sciences*, **1982**, 71(9), 1052-1054.

[14]. D. Bagchi, S. Chaudhuri, S. Sardar, S. Choudhury, N. Polley, P. Lemmens, S. K. Pal, Modulation of stability and functionality of a phyto-antioxidant by weakly interacting metal ions: curcumin in aqueous solution, *RSC Advances*, **2015**, 5(124), 102516-102524.

[15]. T. S. Rao, N. Basu, H. H. Siddiqui, Anti-inflammatory activity of curcumin analogues, *Indian Journal of Medical Research*, **1982**, 75, 574-578.

[16]. P. He, R. Zhou, G. Hu, Z. Liu, Y. Jin, G. Yang, Q. Lin, Curcumin-induced histone acetylation inhibition improves stress-induced gastric ulcer disease in rats, *Molecular medicine reports*, **2015**, 11(3), 1911-1916.

[17]. S. Singh, A. K. Singh, G. Wadhwa, D. B. Singh, S. Dwivedi, B. Gautam, P. W. Ramteke, A quantitative measure of conformational changes in apo, holo and ligand-bound forms of enzymes, *Interdisciplinary Sciences: Computational Life Sciences*, **2016**, 8(2), 192-201.

[18]. G. Dutkiewicz, B. Narayana, S. Samshuddin, H. S. Yathirajan, M. Kubicki, Synthesis and crystal structures of two new Schiff base hydrazones derived from biphenyl-4-carbohydrazide, *Journal of Chemical Crystallography*, **2011**, 41(10), 1442-1446.

[19]. P. Fita, E. Luzina, T. Dziembowska, D. Kope, P. Pitkowski, C. Radzewicz, A. Grabowska, Ketoenol tautomerism of two structurally related Schiff bases: Direct and indirect way of creation of the excited keto tautomer, *Chemical physics letters*, **2005**, 416(4-6), 305-310.

[20]. S. R. Kelode, P. R. Mandlik, Synthesis, characterization, thermal and antibacterial studies of cobalt(II), nickel(II), copper(II) and zinc(II) complexes of hydrazone Schiff base, *International Journal of Chemical and Pharmaceutical Sciences*, **2012**, 39(3), 3033.

[21]. H. H. Monfared, O. Pouralimardan, C. Janiak, Synthesis and spectral characterization of hydrazone schiff bases derived from 2, 4-dinitrophenylhydrazine. Crystal structure of salicylaldehyde-2, 4-dinitrophenylhydrazone, *Zeitschriftfr Natur for schung B*, **2007**, 62(5), 717-720.

[22]. G. M. Sheldrick, Phase annealing in SHELX-90: direct methods for larger structures, *Acta Crystallographica Section A: Foundations of Crystallography*, **1990**, 46(6), 467-473.

[23]. G. M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Crystallographica Section C: Structural Chemistry*, **2015**, 71(1), 3-8.

[24]. A. L. Spek, PLATON, an integrated tool for the analysis of the results of a single crystal structure determination, *Acta Crystallographica Section A: Foundations of Crystallography*, **1990**, 46(s1), c34-c34.

[25]. C. F.Macrae, I. Sovago, S. J. Cottrell, P. T. Galek, P. McCabe, E. Pidcock, P. A. Wood, Mercury 4.0: from visualization to analysis, design and prediction, *Journal of Applied Crystallography*, **2020**, 53, 226-235.