

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/



CrossMark

Synthesis, Characterization, and X-ray Crystal Structure Analysis of

Zinc(II) Complex Based on 2-benzimidazolethiole

Karwan Omer Ali^{a*}, Hikmat Ali Mohamad^b, Eric Hosten^c, Thomas Gerber^c ^aDepartment of Physics, College of Science, University of Halabja, Halabja, Iraq ^bDepartment of Chemistry, College of Education, University of Salahaddin, Erbil, Iraq

^cDepartment of Chemistry, Faculty of Science, Nelson Mandela Metropolitan University, Port Elizabeth, South

Africa

Abstract

A novel mononuclear complex of the type $[Zn(S-2-BIT)_3(O-SO_3)(CH_3OH)_2]$ (where 2-BIT = 2-benzimidazolethiole) was synthesized and its structure was investigated by elemental analysis, FT-IR spectroscopy, UV-Vis spectroscopy, and single crystal X-ray diffraction. The crystal structure of the complex show that, crystallizes in the triclinic P1 space group, with a=9.2946(13) Å, b= 10.1997(13) Å, c= 17.345(3) Å, β =105.494(7)°, V= 1516.3(4) Å³, R1= 0.0316, wR₂= 0.0843. In this complex, the distorted tetrahedral arrangement around the Zinc(II) atom is formed by three sulfur atoms from the 2-MBI ligand and one oxygen atom from the sulfate ion, and the crystal lattice structure of the complex also contains two uncoordinated methanol molecules that formed N-H^{...}O and O-H^{...}O intermolecular hydrogen bonds.

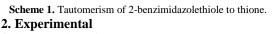
Keywords: Zn(II) complex; S-donor ligand; X-ray crystallography; Distorted tetrahedral coordination

1. Introduction

The design and synthesis of metal complexes of dblock with heterocyclic ligands containing a sulfur atom have been in perpetual interest in a variety of biological activities such as antitumor, antibacterial, antifungal and antiviral activity [1-3]. Also, a variety of dinuclear and polynuclear transition metal complexes of S-donor ligand have been widely used as powerful catalysts in the cycloaddition of alkyne derivatives to produce benzene derivatives [4]. Zinc(II) has adjustable coordination number and they can simply form different geometry, such as tetrahedral [5], trigonal bipyramidal [6], square planar [7], square pyramidal [8], and octahedral [9]. 2-benzi midazolethiole exists in a thiol and thione tautomers, but thione tautomer is more dominant over thiol isomer, as proved by X-ray crystallography structure analysis, and most spectroscopy identification (Scheme 1) [10,11]. 2-benzimidazolethiole behave as mono and bidentate ligand and coordinate to metals center through nitrogen and sulfur atoms [12]. For example, the trimeric copper and tetrameric zinc complexes of the form [N(CH₂CH₃)₄][Cu₃(MBD)₂] and $[Zn_4(\mu_4-O)(MBT)_6]$ have been prepared by solvothermal method and studied their luminescence properties [13]. In this paper, we have announced our

results in the synthesis, spectral analysis, elemental analysis, electronic spectra, and X-ray crystallography analysis of one novel Zn(II) complex containing 2-benzimidazolethiole ligand.





2.1 Materials and instrumentation

ZnSO₄.7H₂O and 2-benzimidazolethiole (2-BIT) we used for the synthesis of the complex were procured from Sigma Aldrich Company. The solvents such as methanol, dimethylsulfoxide (purchased from Alfa Aesar) and were directly used in the synthesis and analysis of the compound. X-ray crystallographic diffraction data of the complexes were received on a Bruker Kappa Apex II diffractometer with Mo-Ka radiation ($\lambda = 0.71073$ Å). IR spectra (as KBr discs) in the range 4000-400 cm⁻¹ was recorded on a Shimadzu FTIR-8400S spectrophotometer. The Electronic spectrum in DMSO was performed with a double-beam LTD Shimadzu spectrophotometer (AE-UV1609 (UK) CO.) at ambient temperature. The C, H,

*Corresponding author e-mail: <u>karwan.ali@uoh.edu.iq</u>.

Receive Date: 25 December 2020, Revise Date: 13 January 2021, Accept Date: 03 February 2021 DOI: 10.21608/EJCHEM.2021.55124.3155

^{©2021} National Information and Documentation Center (NIDOC)

N, and S contents were determined using a EURO EA 300 CHNS analyzer. Molar conductivity was measured in DMF solutions (10^{-3} M) at 25 °C by using Meter CON 700 Benchtop conductivity meter. The melting point was measured with a Stuart SMP3 melting point apparatus.

2.2 Synthesis of $[Zn(S-2-BIT)_3(O-SO_3)(CH_3OH)_2]$ (1)

To a MeOH (25 ml) solution of 2-benzimidazole thiole (0.090 g, 0.6 mmol), an equivalent MeOH (25 ml) solution of ZnSO₄.7H₂O (0.057 g, 0.2 mmol) was added in dropwise. In addition, the white precipitate was formed immediately. 3h stirred at room temperature was required to complete the reaction mixture. The resulting white mixture was filtered, the white crystals for X-ray analysis were obtained by evaporation of the filtrate after seven days. Yield: 0.134 g (91%), m.p. 297-299 °C. Anal. Calc. for C₂₁H₁₈N₆O₄S₄Zn,2(CH₄O) (676.13): C, 40.85; H, 3.87; N, 12.43; S, 18.97. Found: C, 40.61; H, 3.89; N, 12.48; S, 19.15 %. Molar conductivity (DMF, 10⁻³M): 65 (Ω^{-1} cm² mol⁻¹) indicates that it is an electrolyte. IR (cm⁻¹): 3530 (CH₃OH), 3247 v(N-H), 3117 v(ArC-H), 1462 v(ArC=C), 1354 v(C-N). UV-Vis (DMSO, λ_{max} nm): 320, 290.

2.3 X-ray crystal structure determination

White single crystals with a suitable quality of [Zn(S-2-BIT)₃(O-SO₃)(CH₃OH)₂] (1) (0.13 x 0.34 x 0.50 mm) were produced by slow evaporation of methanol solution under normal condition. Crystal data of 1 was received on a Burker Kappa Apex II diffractometer equipped with Mo Ka radiation $(\lambda=0.71073 \text{ Å})$ at 296K. The SHELXS was used to manipulate the complex structure and least-squares procedures on the SHELXL program was used to refine the structure [14,15]. Non-hydrogen atoms were refined anisotropic parameters. Hydrogen atoms bonded to carbon and nitrogen atoms in the models were calculated by (HFIX 147 of SHELX program) [14]. APEX-II and SAINT were used for data collection, data reduction, and cell refinement [16]. Crystallographic data and structure refinement details of **1** are summarized in Table 1. Table 1: Crystal data and structure refinement for complex 1

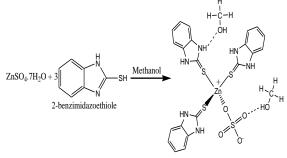
Empirical Formula	$C_{21}H_{18}N_6O_4S_4Zn, 2(CH_4O)$	
Formula weight	676.13	
T/K	296	
Wavelength λ/Å	0.71073	
Crystal system	triclinic	
Space group	ΡĪ	
Crystal size/mm	0.13 x 0.34 x 0.50	
a/Å	9.2946(13)	
b/Å	10.1997(13)	
c/Å	17.345(3)	
α/°	99.673(6)	
β/°	105.494(7)	
γ/°	100.564(6)	
V/Å ³	1516.3(4)	
Z	2	

Egypt. J. Chem. 64, No. 5 (2021)

Density(calc.)/g cm ⁻¹	1.481
Absorption coefficient (mm ⁻¹⁾	1.132
θ ranges for data collection (°)	1.3-28.3
Dataset	-12:12; -13:13; -23:23
Tot., Uniq. Data	53641,7553
F(000)	696
Nref	7553
Npar	365
R _{int}	0.027
R1, wR ₂	0.0316,0.0843
S	1.05
(I>26(I))	6057
Largest diff peak and hole/e ⁻ ,Å ⁻³	-0.38,0.52

3. Result and Discussion

The Zn(II) complex was synthesized by reactions of the ligand (2-BIT) with ZnSO₄.7H₂O in Methanol at room temperature (Scheme 2). Complex 1 was produced as white crystals in good yield suitable for single crystal X-ray structure analysis.



Scheme 2. Synthesis of Zn(II) complex.

3.1 FTIR Studies

In the IR spectrum of the ligand (2-BIT), the medium intensity peak at 3153 cm⁻¹ can be related to the stretching vibration of the NH group which is shifted by 97 cm⁻¹ to a higher frequency, is indicative of the formation of (N-H....O) intermolecular hydrogen bonding in the crystallized complex [17,18]. The absence of the stretching vibration of the thiol (SH) group at 2561 cm⁻¹ in the IR spectrum of the complex, confirms that the thione tautomer to be more dominant over thiol Tautomer in the solid complex [19]. The broad medium intensity band for the complex at 3533 cm⁻¹ could be assigned to the v(O-H)vibration of the methanol molecule that crystallized in the complex [20]. In the IR spectrum of complex, the band at 538 cm⁻¹ may be attributed to Zn-O vibration while the band at 459 cm⁻¹ is ascribed to Zn-S vibrations [21,22].

3.2 UV-Vis Studies

The UV-Vis spectra of the free ligand and the complex were investigated in dimethyl sulfoxide (10^{-3} mol. L⁻¹) at room temperature. As shown in Fig. 1, the free 2-BIT ligand shows two bands at 324 nm and 300 nm, while the absorption spectra of the Zn-

coordination complex were blue-shifted by 4 nm and 10 nm respectively which is an indication of C=S coordination to the Zn(II) center [23]. These bands of complex are assigned to intraligand charge transitions of 2-BIT. Zn(II) metal complexes have filled d orbital and form a diamagnetic complex [24]. The diamagnetic property of this zinc complex upholds in the presence of intraligand charge transfer and no d-d transition proposing its distorted tetrahedral geometry [25].

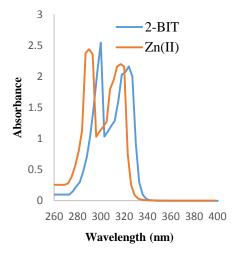
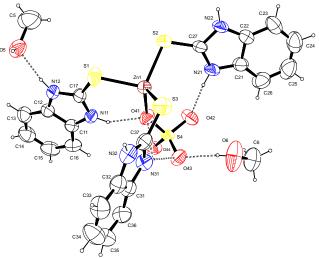


Fig.1. Electronic spectra of 2-MBI ligand and complex 1.3.3 X-ray crystal structures description

The molecular structure of the complex with the atomic numbering scheme is shown in Fig. 2 and selected bond angles and bond distances are collected in Table 2. Single crystal X-ray analysis reveals that complex 1 crystallizes in the triclinic system with a space group $P\overline{1}$. The asymmetric unit of complex 1 contains one Zn(II) ion, three 2-BIT ligands, one coordinated Sulfate ion, and two lattice methanol molecules. Zn(II) ion is surrounded by three sulfur atoms from the 2-BIT ligands and one oxygen atom from the Sulfate ion, and exhibits distorted tetrahedral geometry. The Zn1-S1, Zn1-S2, Zn1-S3, and Zn1-O41 bond distances of 2.3367(8), 2.3156(8), 2.3246(8), and 1.9654(17) Å are close to those described in other zinc complexes [26-28]. As presented in Table 2, the bond angles about the Zn(II) metal ion deflect from the standard value of 109° predicted for tetrahedral geometry, as demonstrated by the angles S1-Zn1-S2, S1-Zn1-S3, S1-Zn1-O41, and S2-Zn1-O41 (102.98(3), 111.97(3), 103.34(5), and 117.08(5)° respectively). In this complex, the 2-BIT ligand acts as a monodentate ligand and is coordinated to the Zn(II) ion through the sulfur atom. In the crystal structure of 1, there are intermolecular N-H...O, and O-H...O hydrogen bonds the nitrogen atoms of 2-BIT ligand acts as proton donors, whereas the oxygen of sulfate ion acts as proton acceptors. Lattice methanol molecules also act as a proton donor and an acceptor at the same time and



forming O-H...O and N-H...O hydrogen bonds as shown in Table 3.

Fig. 2. Single crystal x-ray molecular structure of [Zn(S-2MBI)₃ (O-SO₃)] (CH₃OH)₂

Table 2. Selected bond distances (Å) and bond angles (°).

Bond distance		Bond angle	
Zn1-S1	2.3367(8)	S1-Zn1-S2	102.98(3)
Zn1-S2	2.3156(8)	S1-Zn1-S3	111.97(3)
Zn1-S3	2.3246(8)	S1-Zn1-O41	103.34(5)
Zn1-O41	1.9654(17)	S2-Zn1-S3	110.80(3)
S1-C17	1.706(2)	S2-Zn1-O41	117.08(5)
S2-C27	1.709(2)	S3-Zn1-O41	110.23(5)
S3-C37	1.714(3)	Zn1-S1-C17	108.34(7)
S4-O41	1.4944(16)	Zn1-S2-C27	107.86(7)
S4-O42	1.4525(17)	Zn1-S3-C37	100.95(8)
N11-C11	1.390(3)	Zn1-O41-S4	141.35(10)
N12-C12	1.387(3)	S1-C17-N11	128.78(15)

Table 3. Hydrogen bonds (Å, °) for complex 1.

D-H A	D-H	H A	D A	D-H A
O5H5O42	0.8200	1.9300	2.748(3)	173.00
O6H6O43	0.8200	1.9400	2.753(3)	173.00
N11H11O41	0.8600	1.9700	2.748(2)	150.00
N12H12O5	0.8600	1.8500	2.709(3)	172.00
N21H21O42	0.8600	1.8800	2.732(2)	168.00
N22H22O44	0.8600	1.9100	2.721(2)	157.00
N31H31O41	0.8600	2.5600	3.178(2)	129.00
N31H31O43	0.8600	1.9400	2.785(2)	165.00
N32H32O6	0.8600	1.9200	2.754(4)	162.0

4. Conclusions

In conclusion novel complex of zinc(II) metal derived from 2-benzimidazolethiole (2-BIT) ligand has been synthesized and structurally characterized. The metal atom in the complex was tetrahedrally coordinated by three S-donor 2-BIT ligands and one O-SO₃. The geometry of the resulting complex was found to be a distorted tetrahedral. The UV-Vis spectrum of the complex display's bands at 320 nm

and 290 nm, which are corresponding to intraligand charge transfer transition.

5. Supplementary Data

Crystallographic data for the analysis have been deposited with the Cambridge Crystallographic data center, CCDC deposit number is 1991209 (1). This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

6. Conflicts of interest

There are no conflicts to interest.

7. Acknowledgements

The authors are thankful to the Physics Department College of Science, at Halabja University for accomplishing this research.

8. References

- Sousa-Pedrares, A., Romero, J., García-Vázquez, J. A., Durán, M. L., Casanova, I. & Sousa, A. (2003). Electrochemical synthesis and structural characterisation of zinc, cadmium and mercury complexes of heterocyclic bidentate ligands (N, S). Dalton Trans., 7, 1379-1388. <u>doi.org/10.1039/B30013</u> <u>3B.</u>
- [2] Ekegren, J. K., Roth, P., Källström, K., Tarnai, T. & Andersson, P. G. (2003). Synthesis and evaluation of N, S-compounds as chiral ligands for transfer hydrogenation of acetophenone. *Org. biomol. Chem.*, 1(2), <u>doi.org/10.1039/B208907F</u>.
- [3] Mévellec, F., Tisato, F., Refosco, F., Roucoux, A., Noiret, N., Patin, H. & Bandoli, G. (2002). Synthesis and characterization of the "sulfur-rich" bis (perthiobenzoato)(dithiobenzoato) technetium (III) heterocomplex. Inorg. Chem., 41(3), 598-601. doi.org/10.1021/ic0107577.
- [4] Mori, N., Ikeda, S. I. & Odashima, K. (2001). Chemoand regioselective cyclotrimerization of monoynes catalyzed by a nickel(0) and zinc(II) phenoxide system. Chem. Commun., (2), 181-182. <u>doi.org/10.1039/B008</u> <u>882J.</u>
- [5] Chamayou, A. C., Lüdeke, S., Brecht, V., Freedman, T. B., Nafie, L. A. & Janiak, C. (2011). Chirality and diastereoselection of Δ/Λ-configured tetrahedral zinc complexes through enantiopure Schiff base complexes: combined vibrational circular dichroism, density functional theory, 1H NMR, and X-ray structural studies. Inorg. Chem., 50(22), 11363-11374. doi.org/1 0.1021/ic2009557.
- [6] Bhattacharyya, A., Sen, S., Harms, K. & Chattopadhyay, S. (2015). Formation of three photoluminescent zinc(II)

complexes with Zn₂O₂ cores: Examples of bi-dentate bonding modes of potentially tri-and tetra-dentate Schiff bases. Polyhedron, 88:156-163. <u>doi.org/10.1016/j.pol</u> <u>y.2014.12.018.</u>

- [7] Parkin, G. (2004). Synthetic analogues relevant to the structure and function of zinc enzymes. *Chem. Rev.*, 104(2):699-768. doi.org/10.1021/cr0206263.
- [8] Majumder, A., Rosair, G.M., Mallick, A., Chattopadhyay, N. & Mitra, S. (2006). Synthesis, structures and fluorescence of nickel, zinc and cadmium complexes with the N, N, O-tridentate Schiff base N-2pyridylmethylidene-2-hydroxyphenylamine. Polyhedro n, 25(8), pp. 1753-1762. <u>doi.org/10.1016/j.poly.2005.11</u> .029.
- [9] Sakiyama, H., Mochizuki, R., Sugawara, A., Sakamoto, M., Nishida, Y. & Yamasaki, M. (1999). Dinuclear zinc(II) complex of a new acyclic phenol-based dinucleating ligand with four methoxyethyl chelating arms: first dizinc model with aminopeptidase function. J. Chem. Soc., Dalton Trans., (6), 997-1000. <u>doi.org/</u> 10.1039/A808055K.
- [10] Kotera, M. & Suzuki, T. (2010). Syntheses and crystal structures of mononuclear and dinuclear (pentamethyl cyclopentadienyl)iridium(III) complexes containing 2mercaptobenzimidazole. Inorganica Chim. Acta, 36 3(13), 3602-3605. <u>doi.org/10.1016/j.ica.2010.05.05 3</u>.
- [11] Mohamed, T. A., Mustafa, A. M., Zoghaib, W. M., Afifi, M. S., Farag, R. S. & Badr, Y. (2008). Reinvestigation of benzothiazoline-2-thione and 2mercaptobenzo thiazole tautomers: Conformational stability, barriers to internal rotation and DFT calculations. J. Mol. Struct. THEOCHEM, 868(1-3), 27-36. doi.org/10.1016/j.theochem.2008.07.037.
- [12] Abedin, T. S., Moni, M. R., Ghosh, S., Tocher, D. A., Hossain, G. G., Mobin, S. M. & Kabir, S. E. (2018). Mn₂(CO)₆(μ-mbi)₂ as a precursor for mono-and polynuclear complexes containing the 2-mercapto benzimidazolate (mbi) ligand. Polyhedron, 152, 164-171. doi.org/10.1016/j.poly.2018.06.039.
- [13] Chen, S. C., Yu, R. M., Zhao, Z. G., Chen, S. M., Zhang, Q. S., Wu, X.Y., Wang, F. & Lu, C.Z. (2010). A series of polynuclear complexes of d¹⁰ metals with interesting luminescent properties. Cryst. growth des., 10(3), 1155-1160. <u>doi.org/10.1021/cg901031x.</u>
- [14] Sheldrick, G. M. (2008). A short history of SHELX. Acta Crystallogr. Sect. A: Found. Crystallogr., A64(1), 112-122. <u>doi.org/10.1107/S0108767307043930.</u>
- [15] Hübschle, C. B., Sheldrick, G. M. & Dittrich, B. (2011). ShelXle: a Qt graphical user interface for SHELXL. J. appl. Cryst., 44(6), 1281-1284. <u>doi.org/10.1107/S0021</u> <u>889811043202.</u>
- [16] Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure

Egypt. J. Chem. 64, No. 5 (2021)

determination. J. appl. Cryst., 48(1) 3-10. <u>doi.org/10.11</u> 07/S1600576714022985.

- [17] Ali, K. O. & Mohammad, H.A. (2020). Synthesis, Characterization, and Antibacterial Activity of Ni (II), Pd (II), and Pt (II) Complexes with 2benzoylthiobenzimidazole. ZJPAS., 32(2):15-23. doi .org/10.21271/ZJPAS.32.2.3.
- [18] Mardani, Z., Dorjani, S., Moeini, K., Darroudi, M., Carpenter-Warren, C., MZ Slawin A. & Woollins, J.D. (2019). A novel ligand transfer reaction: Transferring an N₃-donor amine ligand from Ni(II) to Cu(II) structural, spectral, theoretical, and docking studies. J. Chem. Res., 43(9-10), 330-339. <u>doi.org/10.1177/1747</u> <u>519819863134.</u>
- [19] Mohammed, L. A., Mahdi, N. I. & Aldujaili, R. A. B. (2020). Preparation, Characterization and The Biological Activity Study of A new heterocyclic (Azo-Schiff base) ligand and Their Complexation with {Co, Ni, Cu, Zn(II)} Ions. Egypt. J. Chem., 63(1), 289-300. 10.21608/ejchem.2019.19821.2195.
- [20] Berreau, L. M., Makowska-Grzyska, M. M. & Arif, A. M. (2001). Modeling the active site chemistry of liver alcohol dehydrogenase: mononuclear zinc methanol and N,N-dimethylformamide complexes of a nitrogen/sulfur ligand possessing an internal hydrogen bond donor. Inorg. Chem., 40(10), 2212-2213. doi.org/10.1021/ic001190h.
- [21] M Hassan, A., Heakal, B. H., Said, A. O., Aboulthana, W. M. & Abdelmoaz, M. A. (2020). Comparative study for synthesis of novel Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Zr(IV) complexes under conventional methods and microwave irradiation and evaluation of their antimicrobial and Anticancer activity. Egypt. J. Chem., 63(7), 26-27. <u>10.21608/</u> <u>ejchem.2020.21048.2255.</u>
- [22] Rodríguez, A., Sousa-Pedrares, A., García-Vázquez, J. A., Romero, J. & Sousa, A. (2009). Electrochemical synthesis and characterization of zinc(II) complexes with pyrimidine-2-thionato ligands and their adducts with N, N donors. Polyhedron, 28(11), 2240-2248. doi.org/10.1016/j.poly.2009.03.029.
- [23] Xiao, Y., Hossain, A. M., Yu, Z., Su-Ci, M., Chang-Kun, X. & Ji-Min, X. (2014). Syntheses, Crystal Structure, Properties of Cobalt and Zinc Complexes Based on N, N'-Diisobutyl-2, 3-diaminoquinoxaline. Chinese J. Inorg. Chem., 30(5), 1160-1166. <u>doi.</u> org/10.11862/CJIC.2014.176.
- [24] Hong-Hong, L., Xiao-Tong, L., Wen-Juan, C., Chun-Ying, X. & Bao-Ming, J. (2019). Syntheses, Crystal Structures and Luminescence Properties of Two Zn(II) Coordination Polymers Based on Flexible Bisbenzimidazole Ligand. Chinese J. Inorg. Chem., 35(10), 1896-1902.
- [25] Farooq, A., Imran, M., Iqbal, Z., Bokhari, T. H., Latif, S., Liaqat, M. & Mitu, L. (2018). Synthesis, structural and photo-physical studies of transition metal

Egypt. J. Chem. 64, No. 5 (2021)

complexes with Mannich bases derived from 2mercaptobenzimidazole. Bull. Chem. Soc. Ethiop., 32(3), 481-490. doi.org/10.4314/bcse.v32i3.7.

- [26] Chen, S. C., Yu, R. M., Zhao, Z. G., Chen, S. M., Zhang, Q. S., Wu, X. Y., Wang, F. & Lu, C. Z. (2010). A series of polynuclear complexes of d¹⁰ metals with interesting luminescent properties. Cryst. growth des., 10(3), 1155-1160. doi.org/10.1021/cg901031x.
- [27] Cheng, D., Zhang, Y. P., Wang, K., Meng, X. R. & Li, X.F. (2018). Three-dimensional Zn (II) complex based on 2-[(1H-imidazol-1-yl)methyl]-6-methyl-1Hbenzimidaz ole and aliphatic carboxylate. J. Chem. Res., 42(11), 575-578. doi.org/10.3184/174751918 X15404082426894.
- [28] Ali, K. O., Ali, H. M., Gerber, T. & Hosten, E. (2017). Mixed Ligand, Palladium (II) and Platinum (II) Complexes of Tertiary DiphosphineswithS-1H Benzo [d] Imidazole-2-yl Benzothioate. Orient. J. Chem., 33 (2), 584-592. doi.org/10.13005/ojc/330205.