Eurasian Journal of Analytical Chemistry
ISSN: 1306-3057 OPEN ACCESS 2025 20 (2): 61-67

Thermogravimetric Analysis Of Metal Complexes Derived From 2-Phenyl-4H-Benzo[D] [3,1]-Oxazin-4-One Ligand.

Niteen Tarate[1*], Suraj B. Ade[2], Sarwade V.D[3]

[1*]Department of Chemistry, Jamkhed Mahavidyalaya, Jamkhed, Ahmednagar Pin-413201, India. tarate_niteen@rediffmail.com, niteentarate1986@gamil.com, SPPU, Pune.
[2]Department of Chemistry, Shri. Shivaji College, Parbhani, Pin-431401, India. adesb1975@gmail.com, SRTMU, Nanded,
[3]Department of Chemistry, Jamkhed Mahavidyalaya, Jamkhed, Ahmednagar Pin – 413201, India. vasusarwade@gmail.com, SPPU, Pune.

Abstract: Developments in the Synthesis of Certain Novel ligand PHBO (2-Phenyl-4H-benzo[d][3,1]-oxazin-4-one) is prepared from the condensation of anthranilic acid, benzoyl chloride and acetic anhydride. The heterocyclic classes which have drawn attention towards its synthesis because of their innumerable biological activities like antiviral, antitumor activity, A new complexes derived from 2-Phenyl-4H-benzo[d] [3,1]-oxazin-4-one with Ni (II), Cu (II), Cr (III), Co (III) ions. They are found to be soluble in organic solvents and characterized by IR, NMR, TGA-DTA, XRD, Elemental analysis and molar conductance measurements. The spectral data of synthesized complexes strongly support the stereochemistry of complexes and suggest the octahedral geometry for the metal ions. The thermogravimetric analysis (TGA) experiment is carried out to explore the thermal stability of the complexes. Thermal behavior of the complexes was checked in the range of temperature from 0 to 900^{0}C in a nitrogen atmosphere. The PHBO ligand and their metal chelates have been tested for their antimicrobial activity using Broth Dilution Method and the results were discussed.

Keywords: PHBO (2-Phenyl-4H-benzo[d] [3,1]-oxazin-4-one), Metal Chelates, TGA-DTA, XRD, elemental analysis and antimicrobial activity.

1.Introduction:

The 2-Phenyl-4H-benzo[d] [3,1]-oxazin-4-one is one of the important heterocyclic compounds because their various medicinal and biological applications. The colorless compound is insoluble in polar solvents but easily soluble in organic solvents such as dimethyl sulfoxide, dimethylformamide, chloroform, dichloromethane [1].
Heterocyclic compounds are the cyclic rings compounds that contain at least one heteroatom such as nitrogen, oxygen and sulfur [2,3]. Heterocycles are the most important traditional division of organic chemistry, and research interest on heterocycles are increasing because of their medicinal, anti-microbial, and industrial applications [4,5].
The 2-Phenyl-4H-benzo[d] [3,1]-oxazin-4-one is one of the heterocyclic compounds with potential applications as a ligand in coordination chemistry as they easily form stable complexes with most of the transition metal ions [6].
The many heterocyclic ligands have been reported in the literature possessing antibacterial [7], antifungal [8,9], herbicidal [10], antitubercular [11] and anticancer activities [12].
TGA-DSC is a technique, to know the effect of temperature on decomposition of metal complexes and also used to know the thermal behavior of materials (metal complexes). It is useful for the determining composition of materials, multicomponent, blended, thermal stabilities, estimation of product lifetime, decomposition of product etc.[13,14]. In TGA technique known weight of a substance is heated at a controlled atmosphere, measures the change in mass of a substance as a function of temperature. This technique can be used to evaluate thermal stability of material, in a desired temperature range, if a species is thermally stable, there will be no loss of mass change. If there is negligible loss of mass indicates no slope in the TGA trace [15-16].
X-ray diffraction (XRD) is a powerful technique used for analyzing the structure of crystalline materials at the atomic and molecular level. In X-ray diffraction technique, scattering of X-rays by solid crystals are studied. By this method we can identify the crystal structure, types dimensions of unit cell, sample purity of various solid compounds. When a beam of monochromatic X-ray radiation strikes on solid, the planes of atoms in a crystal gives interference phenomenon and beam is diffracted in a specific direction. The study revealed that synthesized complexes are of body centered cubic (BCC) unit cell [17].
The lone pairs of electrons on these heteroatoms make them capable of forming coordination bonds with metal centers [18]. The presence of the phenyl group introduces steric effects, which can influence the ligand's ability to bind to metal ions and affect the geometry of resulting coordination complexes [19].
The review of literature did not reveal synthesis and characterization to explore the coordination chemistry of transition metal complexes with PHBO ligand. This has prompted us to synthesize and the thermal studies of metal complexes involving this newly synthesized ligand.

2. Experimental

2.1. Materials

All the materials used were of AR grade and reactions were carried out under controlled condition. Ethanol, petroleum ether, toluene and n-hexane were distilled and dried before the use as per standard procedure. The anthranilic acid, benzoyl chloride, acetic anhydride, Nickel chloride, copper chloride, cobalt chloride was used and received for the synthesis from the Merck. 2-Phenyl-4H-benzo[d] [3,1]-oxazin-4-one was prepared by using anthranilic acid, benzoyl chloride and acetic anhydride.

2.1.1 Synthesis of N-Benzoyl anthranilic acid

A 6.85 g (0.05 moles) of anthranilic acid was dissolved in 20 cm^3 (7.03g) of 15% NaOH solution. To this solution, 5.6 cm^3 (0.05 moles) of benzoyl chloride was added in small portions with frequent shaking. After complete addition, the reaction mixture was shaken for about 0.5 hrs. till there was no smell of benzoyl chloride. The reaction mixture was taken in 250 ml beaker and was acidified with conc. HCl. The solid was separated out. This separated solid was washed with water, dried and recrystallized from 20% ethanol to remove the unreacted benzoyl chloride [20].

2.1.2 Synthesis of 2-Phenyl-4H-benzo[d] [3,1]-oxazin-4-one *from N-benzoyl anthranilic acid*

A 4.82g (0.02 mol) of N-benzoyl anthranilic acid and 20 cm^3 (0.02 mol) of Acetic anhydride was refluxed for 3 hours at 80°C with frequent shaking. The progress of reaction was checked by TLC and unreacted acetic anhydride was evaporated under reduce pressure. The obtained solid was recrystallized with petroleum ether [21].

2.1.3 Synthesis of Ni (II), Cu (II), Cr (III) and Co (III) Chelates of 2-Phenyl-4H-benzo[d] [3,1]-oxazin-4-one complexes:

To an ethanolic solution of PHBO (0.01M) was added to the hot ethanolic solution of metal chloride salt (0.01M) in the ratio of 1:1 drop wise with constant stirring using magnetic stirrer. The resulting mixture was refluxed for 3 hours. The P^H of solution was adjusted in the range of 7 to 8 by adding alcoholic ammonia. The reaction mixture was further refluxed for $1^{1/2}$ to 2 hours in water bath. Then reaction mixture was poured in crushed ice pieces, the colored solids were suspended at the end. The solids were digested and separated by filtration and washed using alcohol and water for the drying. The complex was dried in vacuum at room temperature and stored in glass bottle [22-23].

2.1.4 Result and Discussion

The physical properties of ligand and their metal complexes are given in Table No. 1. The synthesized metal complexes were intense colored and solid in nature, stable at room temperature. They are insoluble in polar solvents but soluble in DMF, DMSO. For the estimation of chloride Volhard's method were used [24]. For the estimation of water molecule gravimetric and TGA-DTA methods were used. Metal ion percentage is determined by standard method. Thermogravimetric analysis suggests that the stability of complexes [25]. The prepared complexes were screened for the elemental analysis. The result of elemental analysis was indicated that the values are very close to the theoretical values calculated using molecular formulas of ligand and metal complexes. The probable structure can be confirmed using IR, TGA-DTA and XRD studies of ligand and complexes. This suggesting that there is 1:2 ratios and the octahedral geometry for the Ni (II), Cu (II), Cr (III) and Co (III) complexes [26].

Table No. 1st: Analytical data and physical properties of 2-Phenyl-4H-benzo[d] [3,1]-oxazin-4-one and their Ni (II), Cu (II), Cr (III) and Co (III) ions chelates.

Ligand/Metal Chelates	D.P ^0C	M:L ratio	Yield %	Color	% Cl, Cal.	Molar Conductance S cm2 mol-1	Magnetic Moment. μ B.M.
PHBO ($C_{14}H_9NO_2$)	105	-	*80.5*	*White*		-	
[Ni $(PHBO)_2ClH_2O$] Cl	>300	1:2	*69.56*	*Yellowish*	*11.95*	*19.4*	*paramagnetic*
[Cu $(PHBO)_2Cl_2$] H_2O	240	1:2	*72.53*	*Blue*	*11.86*	*12.2*	*paramagnetic*
[Cr $(PHBO)_2Cl_2$] H_2O	>300	1:2	*75.2*	*Grey*	*17.11*	*14.48*	*paramagnetic*
[Co $(PHBO)_2Cl_2$] $Cl.H_2O$	216	1:2	*69.56*	*Cream*	*16.92*	*34.4*	*Paramagnetic*

Table No. 2nd: Analytical and Physical data of ligand and metal complexes.

Ligand/Metal Chelates	Mol. Weight	Empirical Formula	Elemental Analysis				
			C	H	O	N	Cl
PHBO	223.23	$C_{14}H_9NO_2$	*75.33*	*4.03*	*14.35*	*6.28*	-
[Ni (PHBO)$_2$ClH$_2$O] Cl	593.69	[Ni($C_{14}H_9NO_2$)$_2$ClH$_2$O] Cl	*56.59*	3.3	*13.47*	*4.72*	*11.95*
			56.6	3.3	*13.3*	*4.7*	*11.9*
Cu (PHBO)$_2$Cl$_2$] H$_2$O	598.5	[Cu($C_{14}H_9NO_2$)$_2$Cl$_2$] H$_2$O	*56.14*	*3.34*	*13.36*	*4.68*	*11.86*
			56.1	*3.3*	*13.3*	*4.6*	*11.8*
[Cr (PHBO)$_2$Cl$_2$] H$_2$O	622.49	[Cr($C_{14}H_9NO_2$)$_2$Cl$_2$] H$_2$O	*53.97*	*3.21*	*12.85*	*4.49*	*17.11*
			53.8	*3.2*	*12.7*	*4.4*	*17.1*
[Co (PHBO)$_2$Cl$_2$] Cl, H$_2$O	629.43	[Co($C_{14}H_9NO_2$)$_2$Cl$_2$] Cl, H$_2$O	*53.38*	*3.17*	*12.7*	*4.45*	*16.92*
			53.3	*3.1*	*12.6*	*4.4*	*16.8*

Infrared Spectra

A ligand PHBO contains cyclic ester -COO- group, azomethine (C=N) group, one monosubstituted and one disubstituted benzene ring. The IR spectrum of ligand PHBO exhibits bands in the 3034 cm^{-1} indicates **υ** (-C-H) aromatic stretching frequency. A band at 1757 cm^{-1} can be assigned to υ (-COO) stretching frequency due to cyclic ester functional group. A ligand shows band at 1603 cm^{-1} is due to the azomethine group υ (-C=N) stretching frequency. Along with this ligand also shows peak at 1221 cm^{-1} can be assigned to υ (-C-O) stretching frequency of ester group. There was a significant change in the IR stretching frequencies of ligand on complexation [27-28].

IR Spectra of Ni (II) PHBO complex

The IR spectrum of Ni (II) PHBO complex, the band observed at 1757 cm^{-1} due to cyclic ester υ (-COO) functional group in ligand is decreased in the complex and appeared at 1730 cm^{-1} and this is because of involvement of group in metal coordinate bond [29-31]. This has been further indicated by the ester υ (C-O) at 1221 cm^{-1}, such band shifted to longer wavelength at 1251 cm^{-1} in the complex, indicates that ester oxygen atom has been coordinated to the metal ion [32]. Further, the band observed at 1603 cm^{-1} due to the azomethine group υ (-C=N) stretching frequency in ligand and shifted in complex towards longer frequency at 1665 cm^{-1}. The increased frequency of azomethine group indicates that it does not involve in bond formation [33]. The appearance of new band in the Ni (II) PHBO complex at 689 cm^{-1} is due to metal oxygen coordinate bond υ (M-O) [31]. Further a one new band is appeared in the complex at 3302 cm^{-1} is due to the presence of coordinated water molecule υ (H_2O) this frequency is not present in the ligand [34]. The new band appeared at 808 cm^{-1} is due to metal chlorine bond υ (M-Cl).

IR Spectra of Cu (II) PHBO complex

The band observed at 1757 cm^{-1} due to cyclic ester in the ligands was slightly decreased in the Cu (II) PHBO complex and appeared at 1750 cm^{-1} this was suggested that the ester group strongly involved in the metal coordination. The band observed at 1221 cm^{-1} due ester υ (-C-O) group was shifted to longer wavelength at 1256 cm^{-1}, indicates that oxygen atom strongly coordinated with the central metal ion. This has been further indicated that the band observed in ligand at 1603 cm^{-1} due to azomethine group υ (-C=N) was shifted in the complex at longer frequency at 1655 cm^{-1} and in complex υ (M-N) band is not present which indicates that it was not involved in bond formation [41]. The appearance of new band in the Cu (II) PHBO complex at 591 cm^{-1} is due to metal oxygen coordinate bond υ (M-O) [35]. Further a one new band is appeared in the complex at 811 cm^{-1} is due to the presence of υ (M-Cl) bond this frequency is not present in the ligand [36].

IR Spectra of Cr (III) PHBO complex

The IR spectrum of Cr (III) PHBO complex reveals that, the band observed at the 1757 cm^{-1} due to stretching vibration of cyclic ester υ (-COO) in ligand is appeared in the complex at 1740 cm^{-1}. The decrease of this frequency in complex indicating that ester group involved in metal coordination. The stretching frequency observed in the ligand at 1221 cm^{-1} due ester υ (-C-O) group was shifted to longer wavelength at 1291 cm^{-1}, indicates that oxygen atom coordinated to metal ion. Further the band observed at 1603 cm^{-1} due to azomethine group υ (-C=N) in the ligand, shifted to longer wavelength at 1658 cm^{-1} [37]. This longer shift observed due to the closeness of coordinate bond and azomethine group does not involved in metal bond formation. A new IR stretching frequency is appeared at 3462 cm^{-1} is due to presence of coordinated water molecule. Further the conclusive evidence of the coordination of this PHBO ligand with the Cr (III) ion was shown by appearance of new band at 534 cm^{-1} were assigned to the metal- oxygen coordinate bond υ (M-O). The band observed at 807 cm^{-1} indicates that presence of υ (M-Cl) bond this frequency was not present in the ligand.

IR Spectra of Co (III) PHBO complex

The band observed at 1757 cm^{-1} due to stretching vibration of cyclic ester υ (-COO) in ligand is observed in the complex at 1750 cm^{-1}. The slight decrease of this frequency suggesting that ester group is strongly involved in the metal coordination. This has been further supported that 1221 cm^{-1} due ester υ (-C-O) group was shifted towards longer wavelength at 1229 cm^{-1} in metal complex indicates that υ (-C-O) group coordinated to the central metal ion. Further the band observed at 1603 cm^{-1} due to azomethine group υ (-C=N) in the ligand, is shifted to longer wavelength at 1681 cm^{-1} indicates that azomethine group does not involved in bond formation. The additional new band is appeared at 806 cm^{-1} is

due to presence of (M-Cl) bond. A new sharp band appeared at 535 cm^{-1} cans be assigned to υ (M-O) stretching frequency [38-41].

Table No. 3rd: Infrared spectral data of ligand (PHBO) and their metal Chelates

Compound	υ (H_2O)	υ (-COO)	υ (C=N)	υ (C-O)	υ (M-O)	υ (M-Cl)
PHBO	-	1757	1603	1221	-	-
Ni (II)	3302	1730	1665	1251	689	808
Cu (II)	-	1750	1655	1256	591	811
Cr (III)	3462	1740	1658	1291	534	807
Co (III)	-	1750	1681	1229	535	806

^{1}H-NMR Spectra:

The ^{1}H-NMR Spectrum of the ligand PHBO indicated signals at δ7.2-8.4 ppm (m, 5H) due to aromatic proton of phenyl ring at position 2 of Benz-oxazinone ring, δ7.2-7.7 ppm (m, 4H) due to aromatic ring of Benz-oxazinone ring. Its values can be shielded due electron withdrawing effect of heterocyclic ring.

Thermogravimetric Analysis (TGA):

Thermogravimetric analysis (TGA) is one of the important techniques to study the thermal stability, nature of water molecules presents and the how the synthesized metal complexes can be decomposed i.e. decomposition pattern of the complexes. During the heating the lattice water molecule present in the complexes was lost at the temperature range of 60-120^{0}C, while the coordinated water molecules can be decomposed at high temperature in the range of 150-350^{0}C. the whole decomposition of ligands occurs at about 750-800^{0}C and observed the corresponding metal oxide residue. All synthesized metal complexes were scanned in the range of room temperature to 900^{0}C [42-44].

The percent losses of material as obtained from the TGA curves are the good agreement with calculated percent loss in mass by gravimetric analysis.

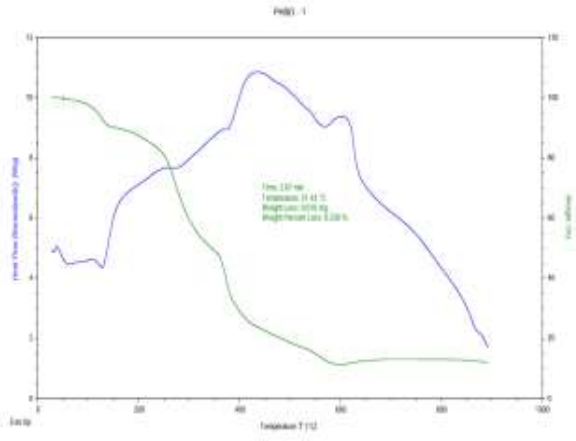

Fig. 1st. TGA of Ni-Complex

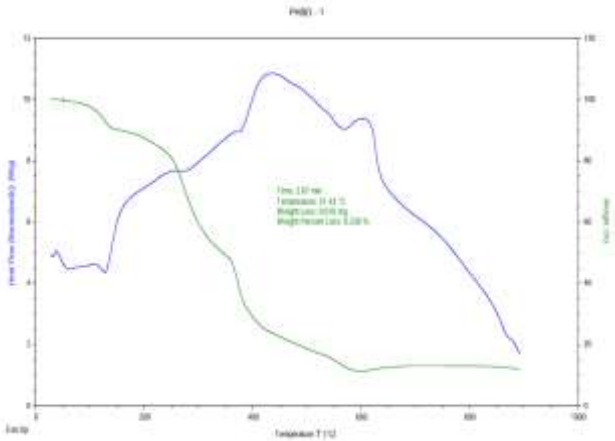

Fig. 2nd. TGA of Cu-Complex

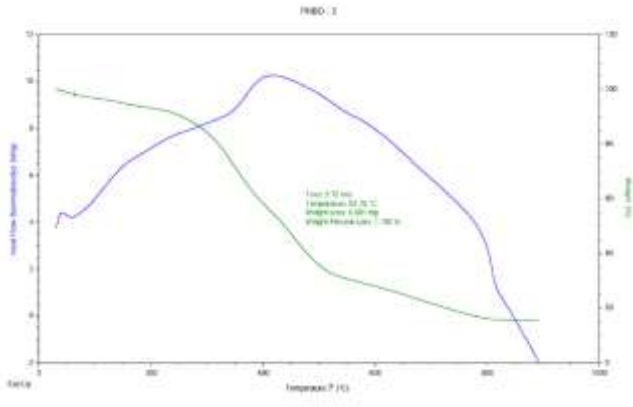

Fig. 3rd. TGA of Cr-Complex

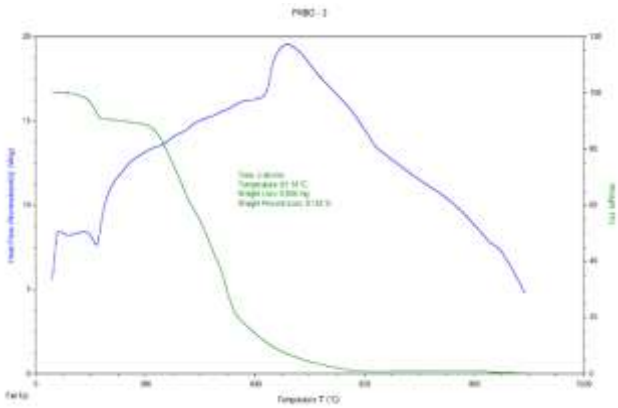

Fig. 4th: TGA of Co-Complex

By TGA we study the thermal stability range of the complexes, percent loss of weight, percentage of residue remain after the decomposition and the decomposition pattern and number of steps involved in the decomposition process. Thermogravimetric curve of the complexes was recorded at the temperature range of 50 to 900^{O}C, in an inert nitrogen atmosphere. Complexes undergo decomposition at 3 to 5 stages, which shows 88 to 90 % decomposition of complex [45-46]. The final loss observed agreed with the theoretical percentage of conversion of complex in to corresponding metal oxide. The percentage of metal oxide obtained from the TG curve has good agreement with theoretical values [47].

Probable Structure-

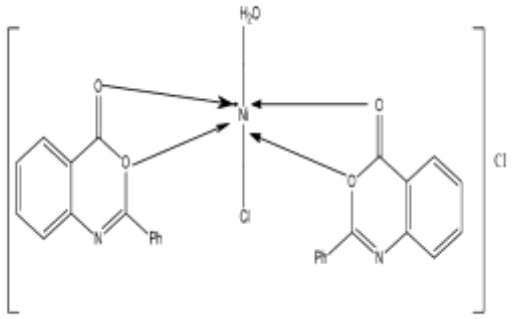

Fig. 5th: Ni-PHBO Complex

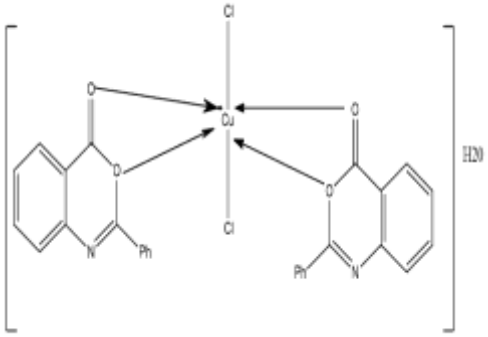

Fig. 6th: Cu-PHBO Complex

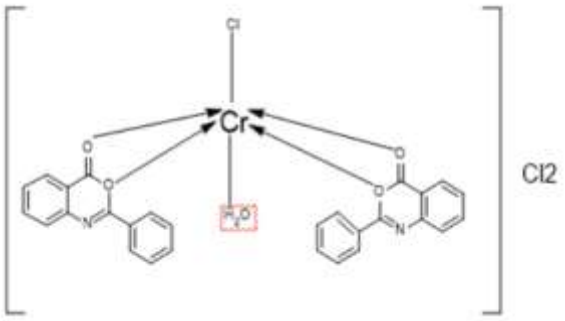

Fig. 7th: Cr-PHBO Complex

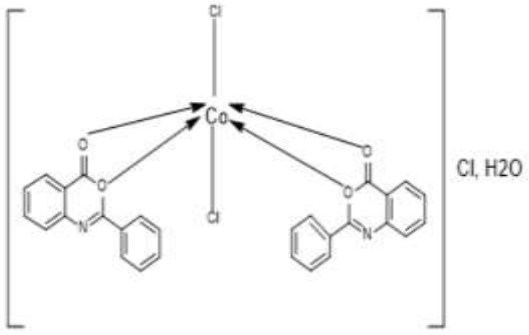

Fig. 8th: Co-PHBO Complex

Antimicrobial Activity:

The PHBO ligand and their metal complexes were screened against Escherichia coli, Aeruginosa, Aureus and S. Pyogenus to assess their potential as antimicrobial agents by **Broth Dilution Method** [38]. The zone of inhibition based upon zone size around discs were measured. The measured zone of inhibition against the growth of various microorganism. The highest dilution showing at least 99 % inhibition zone is taken as MIC. The result of this is much affected by the size of the inoculum. The test mixture should contain 10^8 organism/ml [48-49].

The synthesized heterocyclic ligand (PHBO) and their metal complexes were screened against C. Albicans and A. Niger to assess their potential activity as antifungal agents. The measured zone indicates both the complex has little antifungal activity [50-52].

Acknowledgements:

The author would like to thanks the Head Department of Central Instrumentation Laboratory, Savitribai Phule Pune University, Pune for providing all necessary facilities for the interpretation of IR, ^{1}H-NMR, TGA-DTA and XRD. I would like to thanks research guide Department of Analytical Chemistry, Shri Shivaji College Parbhani and also, would like to thanks Principal of Jamkhed Mahavidyalaya Jamkhed for giving opportunities for doing research activities.

Reference:

1. Emranul Kabir., Monir Uzzaman, Result in Chemistry, (4), 2022, 100606.
2. J. Alv´ arez-Builla, J. Barluenga, Mod. Heterocycl. Chem. 1 (2011) 1–9.
3. D. Barton, W.D. Ollis, Compr. Org. Chem. (1979) 357.
4. R. Mahdi Ubaid Mahmood, N. Mahmood Aljamali, 7 (2020) 2020.
5. Y. Ogawa, E. Tokunaga, O. Kobayashi, K. Hirai, N. Shibata, IScience 23 (2020),101467.
6. Adejoke D. Osinubi., Josephat U. Izunobi, Research Gate, CT, 2021.
7. Sakiyan I., Logoglu E., Arslan S., Sari N. and Sakiyan N., Biometals, 2004, 17, 115.
8. Pandeya S.N., Sriram D., Nath G. and DeCleeq E., European J. Pharm., 1999, 9, 25.
9. Chen H. and Rhodes J., J. Mol. Med., 1996, 74, 497.
10. Molla B.S., Rao B.S., Shridhara K. and Akberali P.M., Farmaco, 2000, 55, 338.
11. Islam M.R., Mirza A.H., Huda Q.M.N. and Khan B.R., J. Bang. Chem. Soc., 1989,2,87.
12. Ali M.M., Jesmin M., Sarkar M.K., Salahuddin M.S., Habib M.R. and Khanam J.A., Int. J. Biol. Chem. Sci., 2008, 2, 292.
13. K. Mészáros Szécsényi, V. M. Leovac., K. Jaæimoviæ et.al., Journal of Thermal Analysis and Calorimetry, Vol. 63 (2001), p.723–732.
14. Gamze Koz, Hale Kaya, Demet Astley, Ishan Yasa, Stephen T. Astley; Guj. Sci., 24(3), 2011, p.407.
15. Abu Shama, Oriental Journal of Chemistry, 26 (4), 2010, p. 1497.
16. Mahmoud M. Mashaly., Zinab H. Abd-Elwahab and Abeer A. Faheim., Journal of Chinese Chem. Soc., 51, 2004, p. 901.
17. Tadewos Damena., MamaruBitewAlem., Digafie Zeleke., Frontiers in Chemistry, Nov-2022.
18. H.M.F. Madkour., ARKIVOC, 2004 (i), 36-54.
19. H. Annita Zhong., Jay A. Labinger., and John E. Bercaw, J. AM. CHEM. SOC. 9, VOL. 124, NO. 7, 2002, p. 1399.
20. ALI HAMMADI SAMIR., Oriental Journal of Chemistry, Vol.33, No. (3), 2017, p. 1422-1432.
21. Bipransh Kumar Tiwary., Ravindra Kailasrao Zirmire., Kiran Pradhan., Ashis Kumar Nanda., international journal of Pharmacy and Pharmaceutical Sciences, Vol 6, Issue 3, 2014. P. 176-179.
22. Suraj B. Ade., M.N. Deshpande and J.H. Deshmukh, Rasayan. J. Chem, Vol. 5, No.1 2012, p. 10-15.
23. Shobhana Sharma., Poonam Yadav., Seema., and Suman Kumari, Rasayan. J. Chem, Vol. 15, No.2 2022, p. 836-841.
24. C, Gh, Macarovici analiza., Chimica. Cantitativa Anorganica, Inorganic Quantitative Chemical Analysis, Editura, Academiei, R.S.R. Bucuresti, 1979, p. 364.
25. SURAJ B. ADE., D.G. KOLHATKAR., AND M.N. DESHPANDE, International Journal of Pharma and Bio Sciences, Vol 3, Issue 2, 2012.
26. Samar A. Aly., Safaa S. Hassan., HanaaA.El-Boraey., Ayman Eldourghamy., Ehab M. Abdalla., et.al, Arabian Journal for Science and Engineering, 49: 2024, p.361–379.
27. Pingalkar S.R. and Deshpande M.N., Orient. J. Chem., 23(1), 2007, p. 265.
28. Chandra Sekhara Rao G M et al, Int Jou Phar Chem 4(2), 2023, p. 7-11.
29. Dixit, B. C. and Patel, H.M.., E-Journal of Chemistry, 8(2), 2011, p. 615.
30. Mapari, A.K. and Mangaokar, K.V.., International Journal Chem. Tech, Res., Vol, 3(2), 2011, p. 636.
31. Md. Kudrat-E-Zahan., Md. Masuqul Haque., Lokonuzzaman Ahmmed., M. Sher Ali., International Journal of Materials Science and Applications, 4(2), 2015, p. 120-123.
32. Chioma Festus., International Journal of Chemistry, Pharmacy & Technology, Vol. 2, No.5, 2017, p. 202-211.
33. Thakur, G.A. and Shaikh, M.M., Acta Poloniae Pharmaceutical Drug Res., Vol. 63(2), 2006, p.95.
34. Ebd EI Wahed, M.G., Thermo. Chimica Acta., Vol 182 (2), 1991, p. 181.
35. Thakor, Y, J., Patel S.G and Patel, K. N., Der Chimica Sinica., vol 2(1), 2011, p. 43.
36. D. A. Köse and H. Necefo lu., Journal of Thermal Analysis and Calorimetry, Vol. 93(2), 2008, p. 509-514.
37. Saleh A. Ahmed., J. of university of Anbar for pure science, Vol.4, 2010, p.1.
38. El-Tabi., A.S., Shakofa., M.M.E., El-SZeidy., A.M.A. and Al-Hakimi A.N., J. Korean Chem. Soc., Vol. 55(1).
39. Modi, C.K., Patel A. S, and Thaker, B, T., E- Journal of Chemistry, Vol.2 (6), 2005, p.21.
40. Adesoji A. Olanrewaj, Collins U. Ibeji, Festus S. Fabiyi., Indian Journal of Heterocyclic Chemistry, Vol. 28. (03), 2018, p. 351-361.
41. V. Mukil Meenakshi, S. Balasubramaniyan, R. Govindharaju and M. Marlin Risana., Indian Journal of Natural Sciences, Vol.13, Issue 71, 2022.

42. Ghosh, S., and Malik, S., E-Journal of Chemistry,7(4), 2010, p.1391.
43. Baluja, S., Solanki, A., and Kachhadia, N., Journal of the Iranian Chemical Society, Vol. 3(4), 2006, p. 312.
44. Pingalkar S.R. and Deshpande M.N., Orient. J. Chem., 23(1), 2007, p. 265.
45. Mohammed H. A. Al-Amery, Journal of Al-Nahrain University, Vol.15 (3),2012, p.55-61.
46. SURAJ B. ADE., D.G. KOLHATKAR AND M.N. DESHPANDE, International Journal of Pharma and Bio Sciences, Vol 3, Issue 2, 2012.
47. Suraj B. Ade., M.N. Deshpande and J.H. Deshmukh, Rasayan Journal of Chemistry, Vol. 5, No.1, 2012, p. 10-15.
48. Tabot, P.C., and Mackinnon, I.D.R., Journal of Material Science Letter, Vol. 13 (18), 1994, p. 1377.
49. Clinical microbiology procedure handbook, vol.2, chapter 5 page no 5.0.1 Henry d. Isenberg, 2nd edition, National Committee for Clinical Laboratory Standards, Methods for Dilution, Antimicrobial Susceptibility Tests for Bacteria, that Grow Aerobically Approved Standard, (M7A5), 9th ed.; National, Committee for Clinical Laboratory Standards: Wayne, PA, 2010.
50. Shadowy, S. In Manual of Clinical Microbiology; Albert., Ed.; ASM Press: Washington, DC, 1991; p 1173.
51. Rattan, A. Antimicrobials in Laboratory Medicine; BI, Churchill Livingstone: India, 2000; p 85.