

Spectroscopic and Biological Studies of Cr (III), Co (III) And Zn (II) Metal Ion Complexes Derived from 2-Phenyl-4H-Benzo[D] [3,1]-Oxazin-4-One Ligand

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ABSTRACT

The preparation of Novel heterocyclic ligand PHBO (2-Phenyl-4H-benzo[d][3,1]-oxazin-4-one) is synthesized 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 antibacterial, antifungal, antiviral, antitumor and anticancer activities. A new PHBO complexes derived from 2-Phenyl-4H-benzo[d] [3,1]-oxazin-4-one with Cr (III), Zn (II) ions. The metal chelates were synthesized and characterized by IR, NMR, TGA-DTA, XRD, Elemental analysis and molar conductance measurements. The PHBO ligand and their metal chelates have been tested for their antimicrobial activity and anticancer activity.

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

INTRODUCTION

The chemistry of heterocyclic compounds gained lot of importance because their various medicinal and biological applications. The chemically, 2-Phenyl-4H-benzo[d] [3,1]-oxazin-4-one has six heterocyclic compounds containing one phenyl group, one nitrogen atom, a one oxygen atoms research interest in heterocyclic chemistry has been increased tremendously, due to their synthetic utility and biological applications [1]. A 2-Phenyl-4H-benzo[d] [3,1]-oxazin-4-one is heterocyclic compound that contain one heteroatom such as nitrogen and oxygen [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]. The Benz-oxazinone ring system is aromatic, contributing to the overall stability of the molecule. The oxygen and nitrogen atoms in the heterocyclic ring can act as potential sites for coordination to metal ions. The compound acts as starting materials for many organic syntheses as well as intermediate for many reactions because of nucleophilic nature of oxygen and nitrogen atom in the ring. The lone pairs of electrons on these heteroatoms make them capable of forming coordination bonds with metal centers [13]. 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 [14]. The review of literature did not reveal synthesis and characterization to explore the coordination chemistry of transition metal complexes with 2-Phenyl-4H-benzo[d] [3,1]-oxazin-4-one ligand. This has prompted us to synthesize and the structural studies of metal complexes involving this newly synthesized ligand.

Experimental

Materials

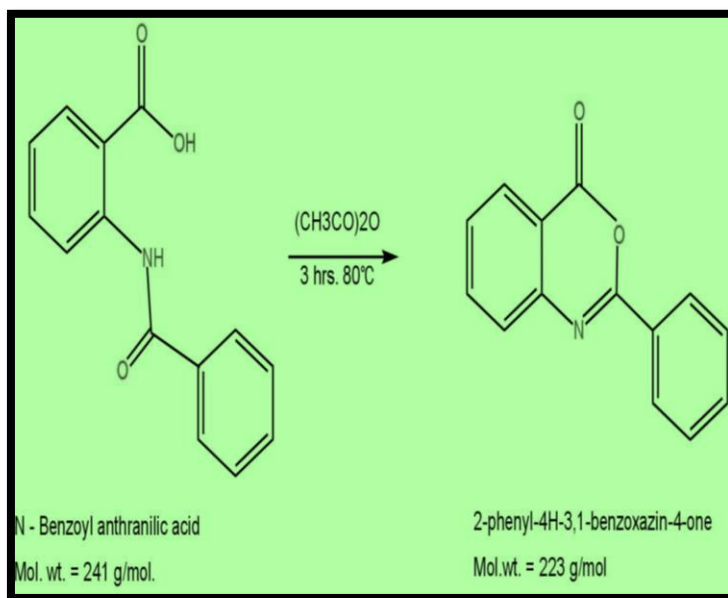
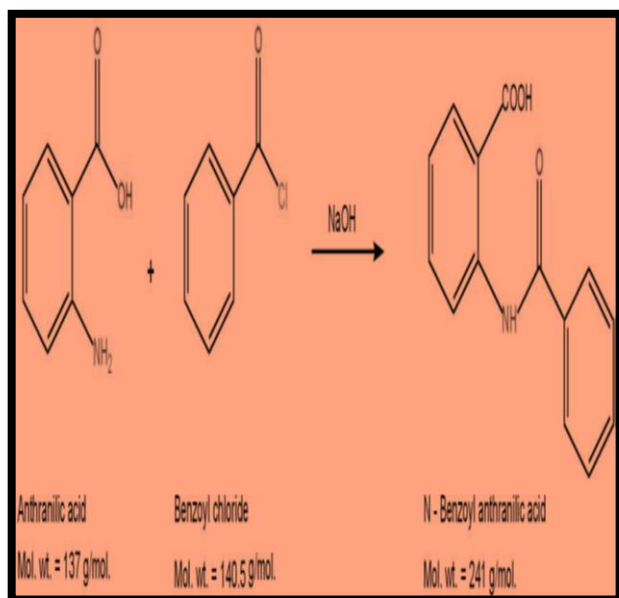
All the materials used for the preparation was AR grade and reactions were carried out under controlled condition. Ethanol, petroleum ether, toluene and n-hexane were distilled and dried before the use. The anthranilic

acid, benzoyl chloride, acetic anhydride, Nickel chloride, copper chloride was used and received for the synthesis. 2-Phenyl-4H-benzo[d][3,1]-oxazin-4-one was prepared by using anthranilic acid, benzoyl chloride and acetic anhydride.

Synthesis of N-Benzoyl anthranilic acid

A 6.85 g (0.05 moles) of anthranilic acid was dissolved in 20 cm³ (7.03g) of 15% NaOH solution. To this solution, 5.6 cm³ (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 [15].

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 cm³ (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 [16].

Synthesis of Cr (III), Co (III) and Zn (II) Chelates of 2-Phenyl-4H-benzo[d][3,1]-oxazin-4-one.

Synthesis of Complexes:

To an ethanolic solution of metal chloride salts of *Cr (III)*, *Co (III)* and *Zn (II)* ions (0.01M) was added to the hot ethanolic solution PHBO (0.01M) in the ratio of 1:1 drop wise with constant stirring. The resulting mixture was refluxed for 3 hours after that P^H of solution was adjusted in the range of 7 to 9 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 bright 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 [17-18].

RESULT AND DISCUSSION

The physical properties of ligand and their metal complexes are given in Table No. 1. The metal complexes were intense colored, insoluble in water, DMF, DMSO. For the estimation of chloride Volhard's method were used [19]. The estimation of water molecule was done by gravimetric and TGA-DTA methods. Metal ion percentage is determined by standard method [20]. 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. XRD patterns proved that increasing the crystallinity of the samples and the particles is in nano size range before gamma radiation. This suggesting that there is 1:2 ratios and the octahedral geometry for the Cr (III), Co (III) and Zn (II) complexes [21].

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

Ligand/Metal Chelates	D.P °C	M:L ratio	% Yield	Color	% Cl, Cal.	Molar Cond. S Cm ² mol ⁻¹	Magnetic Moment. μ BM
PHBO (C ₁₄ H ₉ NO ₂)	105	-	80.5	White		-	
[Cr (PHBO) ₂ Cl ₂] H ₂ O	>300	1:2	75.2	Grey	17.11	14.5	Paramagnetic
[Co (PHBO) ₂ Cl ₂] Cl, H ₂ O	216	1:2	69.56	Cream	16.92	12.98	Paramagnetic
[Zn (PHBO) ₂ Cl, H ₂ O] Cl	220	1:2	70.35	Whitish	11.83	34.4	Diamagnetic

Electronic Spectra:

“The electronic spectra suggesting that transition in UV and Visible region. The ligand exhibits strong absorption band around “30120 and 24557 cm⁻¹ assigned to π-π* and n-π* transition respectively”. The various absorption bands and the corresponding transition of “ligands and their metal complexes are given in the table 2. The UV-Visible spectra of Ni (II), Cu (II), Cr (III), Co (III) and Zn (II) complexes show the electronic transition shifted towards the longer and shorter frequencies which indicates the coordination of ligand to the central metal ions. Also, electronic spectra of all the complexes, shows the absorption band between 21853 to 24557 cm⁻¹, assigned that ligand to metal charge transfer band”

“Table 2: Electronic Spectral Data of PHBO and its metal complexes

Compounds	Absorption band cm ⁻¹	Molar Absorptivity 10 ⁴	Transition
PHBO	30120	2.803	π-π*, n-π*
	24557		
[Cr (PHBO) ₂ Cl.H ₂ O] Cl ₂	28328	7.788	π-π*, n-π*, C→Γ
	22084		
[Co (PHBO) ₂ Cl ₂] Cl.H ₂ O	28571	3.484	π-π*, n-π*, C→Γ
	23320		
[Zn (PHBO) ₂ Cl.H ₂ O] Cl	30769	7.184	π-π*, n-π*, C→Γ
	21853		

Infrared Spectra

The IR spectra of 2-Phenyl-4H-benzo[d] [3,1]-oxazin-4-one (PHBO) ligand exhibit a band in the region at 3034 cm⁻¹ due to ν(C-H), this band is disappeared in the complexes and new band at 3122 cm⁻¹ is appears which indicated the presence of ν(C=N) [22]. Similarly, band observed around 1757 cm⁻¹ is due to ν(-COO-), this band is disappearing in the complexes suggesting the involvement in metal ligand bond coordination. The band in the region at 1568 cm⁻¹ is due to aromatic ν(-C=C-) and at 1603 cm⁻¹ is due to bending vibration of ν(-C=N) azomethine group. the frequency of both ν(-C=C-) and ν(-C=N) is increased in the complexes due to influence of coordination. Similarly, a band observed around 1221 cm⁻¹ is due to bond bending vibration of ν(-C-O) of ester group is shifted towards longer wavelength between 1229-1291 cm⁻¹ in metal complexes suggesting that the involvement of group in coordination [23].

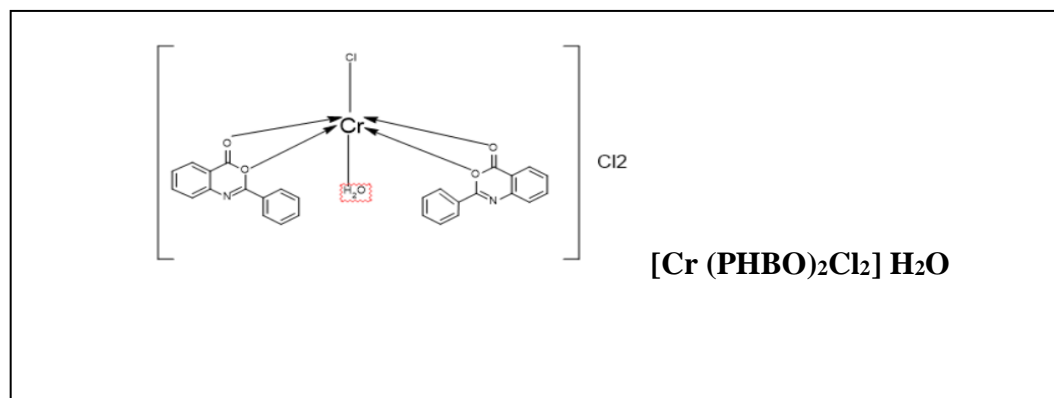
The bands appear at the 806-809 cm^{-1} indicates that the presence of metal chlorine bond in both the complexes. The additional band appears at 3462 cm^{-1} in Cr (III) complex suggesting that the presence of coordinated water molecules. Such type of band is appearing in Co (III) complex at 3326 cm^{-1} which indicates there is also presence of coordinated water molecules. This band Zn (II) complex is found at 3299 cm^{-1} [24]. The appearance of new band at 534 cm^{-1} in the Cr (III), 535 cm^{-1} in the Co (III) complex and 523 cm^{-1} in the Zn (II) metal ion complexes is due to new bonding i.e. $\nu(-\text{M}-\text{O})$ [25].

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

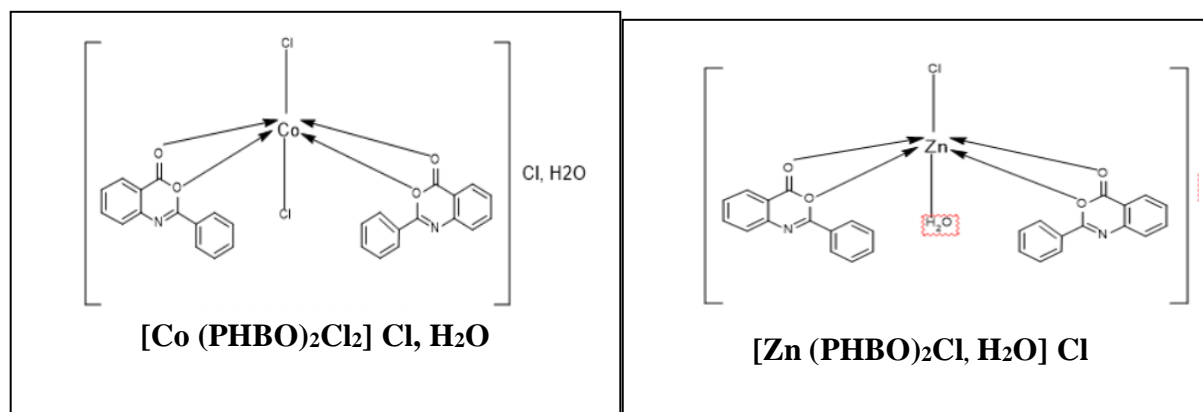
Compound	$\nu (\text{H}_2\text{O})$	$\nu (-\text{COO}-)$	$\nu (\text{C}=\text{N})$	$\nu (\text{C}-\text{O})$	$\nu (\text{M}-\text{O})$	$\nu (\text{M}-\text{Cl})$
PHBO		1757	1603	1221		
Cr (III)	3462	1757	1681	1291	534	807
Co (IV)	3326	1760	1662	1229	535	806
Zn (II)	3299	1757	1658	1250	523	809

¹H-NMR Spectra:

The ¹H-NMR Spectrum of the ligand PHBO indicated signals at $\delta 7.2-8.4$ ppm (m, 5H) due to aromatic proton of phenyl ring at position 2 of Benz-oxazinone ring, $\delta 7.2-7.7$ ppm (m, 4H) due to aromatic ring of Benz-oxazinone ring. Its values can be shielded due electron withdrawing effect of heterocyclic ring.



Probable Structure-



Antimicrobial Activity:

The synthesized heterocyclic ligand 2-Phenyl-4H-benzo[d][3,1]-oxazin-4-one (PHBO) 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 [26-27]. The zone of inhibition based upon zone size around discs were measured. 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.

Table No. 4: Results of Antibacterial activity testing

Sr. No	Compounds	E. coli	Aeruginosa	Aureus	S. Pyogenus
1	PHBO (C ₁₄ H ₉ NO ₂)	6 mm	5 mm	4 mm	8 mm
2	[Cr (PHBO) ₂ Cl.H ₂ O] Cl ₂	15 mm	16 mm	18 mm	14 mm
3	[Co (PHBO) ₂ Cl ₂] Cl.H ₂ O	7 mm	9 mm	11 mm	12 mm
4	[Zn (PHBO) ₂ Cl.H ₂ O] Cl	-ve	-ve	-ve	-ve

From the table it was clear that ligand PHBO and its metal complexes with Co (III), Cr (III) and Zn (II) metal ions shows an antibacterial activity.

Table No. 5: Result of Antifungal activity

Sr. No	Compounds	C.Albicans	Aspergillus Niger
1	PHBO (C ₁₄ H ₉ NO ₂)	250	500
2	[Cr (PHBO) ₂ Cl.H ₂ O] Cl ₂	500	100
3	[Co (PHBO) ₂ Cl ₂] Cl.H ₂ O	1000	500
4	[Zn (PHBO) ₂ Cl.H ₂ O] Cl	500	100
5	Nystatin	100	100
6	Greseofulvin	500	100

A Cr (III), Co (III) and Zn (II) metal ion forms different types of metal chelate complexes with di ligands PHBO. These metal complexes were introduced to antifungal activity studies. The result was given in table. The results indicate that [Cr (PHBO)₂Cl.H₂O] Cl₂ and [Zn (PHBO)₂Cl.H₂O] Cl metal ion complexes have positive zone of inhibition towards C. Albicans and their minimal inhibition concentration for all complexes is 500 ppm which is similar to the standard drug Greseofulvin and for Aspergillus Niger it is 100 ppm which is similar to the Nystatin. The zone of inhibition indicating that both have positive antifungal activity.

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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. H.M.F. Madkour., ARKIVOC, 2004 (i), 36-54.
14. H. Annita Zhong., Jay A. Labinger., and John E. Bercaw, J. AM. CHEM. SOC. 9, VOL. 124, NO. 7, 2002, p. 1399.
15. ALI HAMMADI SAMIR., Oriental Journal of Chemistry, Vol.33, No. (3), 2017, p. 1422-1432.
16. Bipranch 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.
17. Suraj B. Ade., M.N. Deshpande and J.H. Deshmukh, Rasayan. J. Chem, Vol. 5, No.1 2012, p. 10-15.
18. Shobhana Sharma., Poonam Yadav., Seema., and Suman Kumari, Rasayan. J. Chem, Vol. 15, No.2 2022, p. 836-841.
19. C, Gh, Macarovici analiza., Chimica. Cantitativa Anorganica, Inorganic Quantitative Chemical Analysis, Editura, Academiei, R.S.R. Bucuresti, 1979, p. 364.
20. SURAJ B. ADE., D.G. KOLHATKAR., AND M.N. DESHPANDE, International Journal of Pharma and Bio Sciences, Vol 3, Issue 2, 2012.
21. 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.
22. Pingalkar S.R. and Deshpande M.N., Orient. J. Chem., 23(1), 2007, p. 265.
23. Mohammed H. A. Al-Amery, Journal of Al-Nahrain University, Vol.15 (3),2012, p.55-61.
24. SURAJ B. ADE., D.G. KOLHATKAR AND M.N. DESHPANDE, International Journal of Pharma and Bio Sciences, Vol 3, Issue 2, 2012.
25. Suraj B. Ade., M.N. Deshpande and J.H. Deshmukh, Rasayan Journal of Chemistry, Vol. 5, No.1, 2012, p. 10-15.
26. Clinical microbiology procedure handbook, vol.2, chapter 5 page no 5.0.1
27. Henry d. Isenberg, 2nd edition,
28. 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.