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Synthesis, Characterization and Antimicrobial Studies of Mixed Ligand from Phthalic Acid and 1,10-Phenanthroline with Their Complexes

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Abstract. In the present work, the phthalic acid (phthH2) and 1.10 phenonthroline (phen), and their complexes were synthesized and isolated as [M(phth)(phen)2], Mn(II), Fe(II), Co(II), Ni(II) Cu(II), Zn(II), and Cd(II) ions. These complexes were characterized by elemental analysis, melting point, conductivity, percentage metal, UV–Vis, FT-IR, and magnetic moment measurements. The molar conductance indicates that all the metal complexes in DMSO are non-electrolytic.phthalic acid (phtha), and 1,10-Phenanthroline (phen), behaved as bidentate, coordinating to the metal ion through their two oxygen and two pyridinyl nitrogen atoms respectively, as corroborated by. Electronic spectra, FT-IR, spectroscopy amusement indicated that all the metal complexes adopted octahedral geometry. The in vitro antimicrobial activity of the mixed ligand complexes were tested against +ve Gram bacteria (Bacillus subtilis), –ve Gram bacteria (Escherichia coli), and (Candida albicans) fungus.

Keywords: 1,10-Phenanthroline, phthalic acid, mixed ligand,

INTRODUCTION

Numerous research papers have described the mixed ligand complexes of metal ions with ligands containing O and N as a donor ion, Saravanan et al, [1]. have synthesized and characterized ternary complexes of Cu (II) - 1,10-phenanthroline (Phen), Urea 2,2'-bipyridyl, and L-Valine. Susan et al, [2]. have synthesized and characterized and Photobiological Studies of Ru(II) Dyads- Derivatives of 1,10-Phenanthroline an important feature for their use as photosensitizers number of excited states that are accessible with near-infrared and visible light [1-4]. Selvakumaran et al. [5]. have reported synthesis many Nickel(II) complexes and fully characterized to predict their structures.

Phthalic acid $C6H4(COOH)2$ is an aromatic dicarboxylic acid, it has a role as a human xenobiotic metabolite. Razaet al have synthesized and characterized Phthalic Anhydride Ligand and Anthranilic Acid and their Metal Complexes [6]. preparing N-phthaloylglycinato complexes by reactions of phthalic anhydrides and glycine, of cobalt, nickel, copper, and zinc, [7],[8].

Phthalic acid derivatives are a class of important chemicals that are used as plasticizers and widely distributed as environmental ollutants. [9]. Three Cu(II) - Phthalic acid complexes were synthesized by the reaction of Cu(II) and Phthalic acid, complexes were obtained [10]. Complexes of Oxygen and Nitrogen donor atoms with transition metals have antimicrobial activities [11].

Literature survey shows that no studies on the synthesis and characterization of mixed ligand complexes of 1,10-phenanthroline and phthalic acid has been reported. Hence the present paper reports the synthesis, structure, and coordination of mixed ligand metal (II) complexes formed with phthalic acid and 1,10-phenanthroline.

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MATERIALS AND METHODS

All used chemicals were purchased from Merck and B.D.H. chemicals.

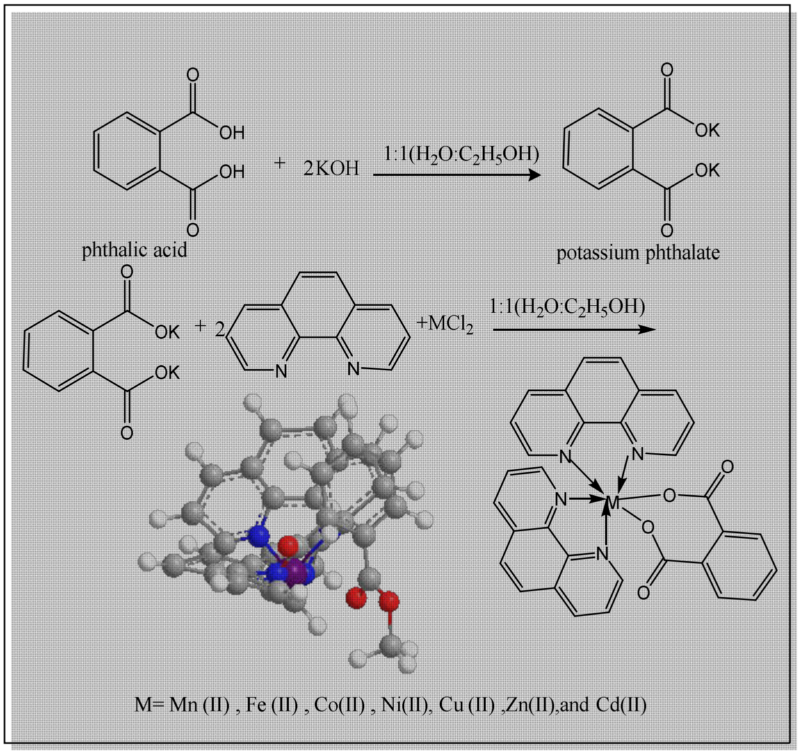
Synthesis of the Complexes

General procedure for the synthesis of mixed ligand metal complexes

A solution of the 1mmol potassium phthalate was prepared by neutered 1mmol phthalic acid with 2mmol potassium, hydroxide in (10 mL) H2O:C2H5OH (50 %)and a solution of -phena (0.36g, 2 m mol) in same solvent (10 mL) were added simultaneously to a solution of MCl2. nH2O (1 mmol) in aqueous ethanol 1:1 (10 mL) in the stoichiometric ratio. [phth: M 2phena]. Scheme 1 The solid products were filtered, washed with aqueous ethanol (1:1) and dried in air, and analyzed employing the standard method [11]. The metal contents were determined by atomic absorption. [12].

Biological Activities

The in vitro bacterial activity of the compounds were tested on Gram positive bacteria, and Gram negative and one fungal by the well-diffusion method. used dimethylsulphoxide as solvent and control. [13].



SCHEMA 1. Preparation of the [M(phth)2(phen)2] complexes

RESULTS AND DISCUSSION

The synthesis of mixed ligand Metal complexes [14]. may be represented as follows equations:

$$\mathrm{phthH2}\ + 2\mathrm{KOH} \rightarrow \mathrm{phth} -\ \mathrm{K} + 2\ \ + 2\mathrm{H2O} \ldots\ldots\ldots\ldots\ldots(1)$$

$$\mathrm{phth} -\ \mathrm{K} + 2\ \ + 2\mathrm{phen}\ + \mathrm{MCl2\,.nH2O} \rightarrow [\mathrm{M(phth)(Phen)2}] + 4\mathrm{H2O}\ \ + 2\ \mathrm{KCl} \ldots\ldots\ldots\ldots\ldots(2)$$

(where phth- is phthalate ion and,phen is 1,10-phenanthroline).

Melting points and the formula weightsare listed in Table1

TABLE 1. Analytical data for the compounds

Chemical Formula	**Color**	**M.wt**	**m.p °c**	**Λm**	**M% (Theor.)**	**M% Exp.**
Mn(Phth)(Phen)$_2$]	Olive	581.5	>260	12.65	9.45	9.00
[Fe (Phth)(Phen)$_2$]	Reddish Brown	580.4	>260	12.45	9.62.	9.00
[Co (Phth)(Phen) $_2$]	Reddish Orange	582.93	>260	10.01	10.10	10. 09
Ni(Phth)(Phen)$_2$]	Blue	583.2	>260	11.95	10.06	10. 0
[Cu(Phth)(Phen)$_2$]	Blue	587.55	239	9.39	10.81	10. 0
[Zn(Phth)(Phen)$_2$]	White	589.9	>260	12.09	11.08	10. 6
[Cd(Phth)(Phen)$_2$]	White	637.0	.>260	4.33	17.64	18. 4

M.wt = Molecular Weight, Λm=Molar Conductivity,(Phth) =(C8H6O4), (Phen)=(C12H8N2)

The complexes were insoluble in water, or slightly soluble in usual organic solvents (ethanol, methanol, benzene, acetone, and hexane). but soluble in in HCl acid ,DMSO . The values of (Λm) at 10-3 M concentration carried out in DMSO at range (4.33-12.65) Ω-1 cm2 mol, indicated that all complexes were nonelectrolyte, .and is no negative or positive ions outside the complexes. [14],[15]. The complexes were analyzed for their metal by atomic absorption and chloride contents by standard methods [16].

TABLE 2. Relevant infrared and electronic spectra data of the e [phth-M-phen] complexes

Compound	**(C-H) aromatic**	**(C=O)**	**COO$^-$ Asym**	**COO$^-$ sym**	**Δ-COO$^-$ asy COO$^-$ sy**	**(C=N)**	**(C-O-C**	**(M-N)**	**(M-O)**
Phen	3059		-	-	-	1573	-	-	-
phthH2	3073	1687	1585	1404	-	--	1280	-	-
[Mn(phth)(phen)2]	3047	1620	1570	1342	228	1577	1219	551	478
[Fe (phth)(phen)2]	3066	1612	1566	1415	151	1543	1265	567	478
[Co(phth)phen)2]	3093	1616	1585	142	159	1423	1273	578	439
[Ni(phth)(phen)2]	3069	1627	1560	140	160	1516	1265	555	478
[Cu(phth)(phen)2]	3074	1612	1585	139	187	1519	1261	570	434
[Zn(phth)(phen)2]	3062	1620	1570	138	182	1570	1222	587	462
[Cd(phth)(phen)2]	3047	1620	1508	134	166	1570	1222	551	489

3059 cm-1 due to νCH stretching.,The spectra of 1:10-phenanthroline (phen) and phthalic acid at there complexes in general were complicated. The absence of a strong band near 1500 cm-1 suggests that this particular ring frequency in the (phen) compound is associated with the carbocyclic ring. The strong two bands at 735 cm-1 plane motion of the (H) atoms on the heterocyclic rings and 852 cm-1 hydrogen on the centre ring, respectively. largest shift in frequency is found with the ν C— C and νC — N involving stretching modes. All of these bands involve at range(1423- 1427) cm – 1 ,ν C — N and (1581- 1593) c m – 1 C=C] respectively in complexes . In the infrared spectra of the complexes, the band due toυ (C=N) ring vibrations of the uncoordinated (phen) at 1573 cm-1 was shifted to 1588 cm-1 in the complexes. This shift by 33 cm-1 to a lower frequency shows that (phen)is coordinated to the metal centres [14].In the FTIR spectra of the complexes, the C-H and C=C stretching bands undergo a coordination-induced lower frequency [14],[15].

Phthalic acid exhibited peaks at 1687 cm−1 for the (C=O) stretching and at 1404 and 1280 cm−1 for the coupling mode of the(C−O) stretching and (O−H) in-plane bending 1585 cm−1and 1404 cm−1 for the antisymmetry (νas(COO−) and symmetry (νs(COO) stretching bands, respectively [15,18]. and 1593 cm-1 (νC=C). The FT-IR peaks of the phthalate were located at 3005-2893, 1685, and 1285 cm−1 assigned to the CH2/CH antisymmetry stretching, the C=O stretching, and C−O−C antisymmetry stretching vibrations.(δCOH) and bands associated with C=C and C-H vibrations (1072 and1006 cm-1). This is in good agreement with published data [15].

[M(phth)(phena)2] , Fe(II) ,Co(II) , Ni(II) Cu(II), Zn(II), and Cd(II)The (COO) νas vibration band appeared in the domain 1508–1585 cm–1 in the spectra of the complexes while those characteristic of the νsym(COO) appeared in the (1342–1426) cm–1 range. Δν -COO- asy COO- sy was (>150)cm–1 which leads to the conclusion that the carbonyl group (COO) in these complexes was in a chelating binding mode[16-18] .

For the All complexes the magnetic moments were indicating paramagnetic for all complexes except for Cd(II) ad Zn(II) complexes diamagnetic nature respectively. Table 3 listed calculated from the measured magnetic susceptibilities for [Ni(phth)(phen)2]. [19]

The UV-Vis spectrum for the phthalic acid (phthH2) shows tow peaks at λmax 274 nm (36231cm-1), and 374nm (28653cm-1) appointed to (π-π* & (n-π *) transition respectively . The (UV-Vis) for the (1.10 phenonthroline) exhibits one absorption peak at (289 nm) 34602 cm-1 is assigned to (π-π*), transitions. The electronic spectra of mixed metal ligand complexes the absorption band at range 374nm (28653cm-1) appointed to (π-π* & (n-π *) transition respectively. The (UV-Vis) for the (1.10 phenonthroline) exhibits one absorption peak at (289 nm) 34602 cm-1 is assigned to (π-π*), transitions. The electronic spectra of mixed metal ligand complexes the absorption band at range 276-301 nm were assigned it indicates the complex containing (C=C) in benzene ring such as phthalic acid and all the complexes showed the charge transfer transitions which can be assigned to ligand to metal (LMCT),and d-d transition in the range around (19417- 36231) and (10582 -23752) cm-1 respectively , as listed in table 3. [18-20]

TABLE 3. Electronic spectra data of the complexes

Comp.	nm	υ' cm^{-1}	Є max mol^{-1}. L.cm^{-1}	Assignments	μ_{eff} B.M
[Mn (Phth)(Phen)$_2$]	299	33444	1901	Charge transfer	1.73
	722	13850	64	$^{6}A_{1}g^{(S)}$ …$^{4}T_{1}g$	
[Fe (Phth)(Phen)$_2$]	289	34602	1404	Charge transfer	6.01
	760	13157	71	$^{6}A_{1}g^{(S)}$ ….$^{4}T_{1}g$	
	827	12091	64	$^{6}A_{1}g^{(S)}$ …$^{4}T_{2}g$	
	945	10582	63	$^{5}T_{2}g$…^{5}Eg	
[Co(Phth)(Phen)$_2$	276	36231	1033	Charge transfer	4.77
	349	28653	332	Charge transfer	
	467	21413	227	$^{3}A_{2}g^{(F)}$ …$^{3}T_{1}g^{(F)}$	
	760	13157	141	$^{3}A_{2}g^{(F)}$ …$^{3}T_{1}g^{(p)}$	
	826	12106	136	$^{3}{}_{2}g^{(F)}$ …$^{3}T_{2}g^{(f)}$	
[Ni(Phth)(Phen)$_2$]	298	33557	1813	Charge transfer	3.64
	421	23752	37	$^{3}A_{2}g^{(F)}$ …$^{3}T_{1}g^{(p3}$	
	515	19417	26	$A_{2}g^{(F)}$ …$^{3}T_{1}g^{(F)}$	
	737	13568	26	$^{3}A_{2}g^{(F)}$ …$^{3}T_{2}g^{(F}$	
[Cu(Phth)(Phen)$_2$]	301	33222	2045	Charge transfer **(**CT**)**	1.65
	721	13869	115	$^{2}B_{1}g$ …$^{2}B_{2}g$	
[Zn(Phth)(Phen)$_2$]	299	33444	1805	CT	Diamag.
	515	19417	20	CT	
[Cd(Phth)(Phen)$_2$]	300	3 3333	1855	CT	Diamag.
	443	22573	19	CT	

TABLE 4. The (μeff) for [Ni(phth)(phen)2]

Complexes	X_{gm} **.10⁻⁶**	X_m **.10⁻⁶**	X_A **.10⁻⁶**	μ_{eff}
[Ni(phth)(phen)$_2$]	3.960	3963	4139	3.64

Biological Activity

Data obtained from the measured of inhibition zone size(IZ) around the discs are tabulated in Table 5 and Shows in Fig. 1 whole chelate ring and inhibits the penetration of the chelates into lipid membranes and blocking of the Metal (II) binding sites Improving the activity by Tweedy's chelation theory. [21]. and increases the delocalization of (π-electron) and partial sharing of (+) charge of the Metal (II) with donor groups. Furthermore [Cd(phth)(phen)2] and [Mn(phth)(phen)2] complexes have shown highest bactericidal activity (ZI) against both bacterial strains and fungicidal may be attributed to the grater number of d-electron

The antimicrobial studies carried the [Cd(phth)(phen)2] and [Mn(phth)(phen)2] complexes presented better results against bacterial strains while comparing with fungal pathogens. [22].

TABLE 5. Zones of inhibition (in mm) of the compounds against various microbes after24 hour incubation paid and 37°C for compounds

Compounds	**Staphylococcus staph aureus Gram+)(**	**Bacillus cerus (Gram+)**	**Esherichia Coli (Gram-)**	**Pseudomonas-**	**Candida albican**
Control (DMSO)	7	6	4	4	4
[Mn(Phth(Phen)$_2$]	33	35	23	34	27
[Fe(Phth) (Phen)$_2$]	24	17	18	-	19
[Ni(Phth) (Phen)$_2$]	11	-	11	-	18
[Cu(Phth) (Phen)$_2$]	12	19	18	12	25
[Zn(Phth) (Phen)$_2$]	-	-	-	12	28
[Cd(phth) (Phen)$_2$]	25	28	26	27	26

CONCLUSIONS

A series of mixed ligand complexes were synthesized by a simple reactionthey were characterized by different techniques (Melting points ,elemental analysis, and conductivity measurements, percentage metal ,UV–Vis, , FTIR, and magnetic moment measurements).The Ft-IR spectral data suggested that the two ligands behaves as bidentate ligand coordinated to the metal (II) ions From the elemental analysis data, the Stoichiometry of the all complexes reacts with metal (II) ions , by molar ratios (1: 1:2) ((Phthalate : metal ion: 1,10-Phenanthroline). The compounds were screened against both of antibacterial and fungicidal activities.

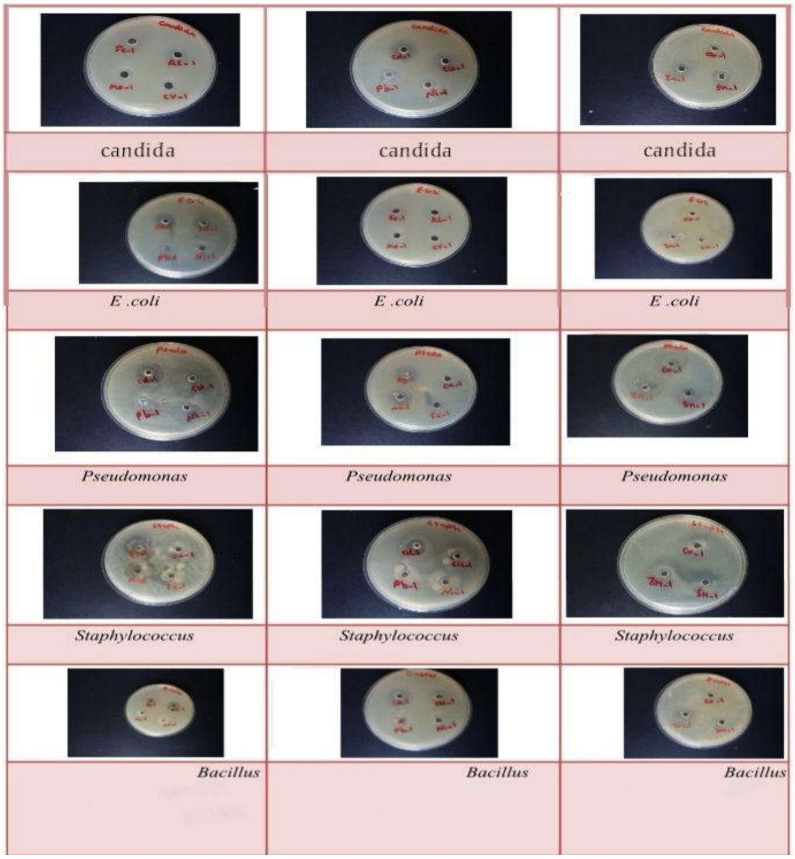


FIGURE 1. Shows Antibacterial and activity of compounds

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