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Research Paper

Coordination polymers: synthesis, characterization and antimicrobial studies

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Abstract: A novel heteronuclear bisligand namely 5-(2-(4-(2-carboxybenzamido)-3-chloro phenyl)-2-oxoethylamino)-2-hydroxy benzoic acid (CSAPH) have been investigated. The synthesized bisligand CSAPH and its coordination polymers with Cu^{+2}, Co^{+2}, Ni^{+2}, Mn^{+2} and Zn^{+2} metal ions were prepared. The synthesized coordination polymers and its parent ligand have been characterized on the basis of elemental analyses, infrared spectra, electronic spectra, magnetic measurements and thermogravimetric analyses. All the coordination polymers are insoluble in acetone, ethanol, chloroform, methanol, benzene, DMF and DMSO. The thermal decomposition of the coordination polymers is studied and indicates that not only the coordinated water is lost but also that the decomposition of the ligand from the coordination polymers is necessary to interpret the successive mass loss. The synthesized ligand and its metal complexes were screened for their antimicrobial activity.

Introduction

The study of coordination polymers has made much progress [1]. These polymers are known for their semiconducting catalytic properties, waste water treatment for metal recovery, in protective coating, as antifouling paints and anti fungal agents [1-2]. Such coordination polymers are mostly derived from bi-chelating ligands in which metal ions and chelating agents arrayed alternatively. The joining segment of these two similar ligands are mainly –N=N-, SO_2, $-CH_2$ -, -O- [3-8]. Most of bichelating ligands are derived from well known chelating agents like, 8-hydroxy quinoline and salicylic acid etc [3, 6]. Salicylic acid and its bi-substituted derivatives are well known complexing agent. Salicylic acid forms water soluble complexes and used as analytical reagents [9-10]. Complexes of various 4-substituted salicylic acids have been investigated. Water insoluble metal complexes of 4-aminosalicylic acid (PAS) have been reported and investigated for tuberculolstatic effect [10-11]. Though 4-amino salicylic acid was an excellent anti T.B agent and act as a chelating ligand with better microbicidal activity. The area in which the coordination polymers having bis-azo dye containing ligands have not been developed so far. Such ligand may afford the coordination polymer with different properties. Hence, it was thought interesting to explore the field of coordination polymers based on hetronuclearting bisligands having

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salicylic acid and amic acid. Though the amic acid is generally derived by condensation of amines with anhydrides having carboxylic and amide group. Such amic acid may afford metal complex with metal ions. The metal complexation study of various amic acids has been reported recently from our Indian scientist [12-14], So the proposed present work is in connecting with the coordination polymers based on hetronuclearting bisligands. The synthetic route for the preparation of ligand and its coordination polymers are shown in Scheme-1.

Experimental Section

Material

All the chemicals used were of analytical pure grade. The precursor 4-amino salicylic acid, phthalic anhydride, acetone and metal salt were purchased from E. Merck Ltd. (India). The 4-chloro acetamido phenacyl chloride (APC) was prepared by known method [15].

Experimental procedure

Synthesis of 5-(2-(4-(2-carboxybenzamido)-3-chlorophenyl)-2-oxoethylamino)-2-hydroxy benzoic acid (CSAPH): Synthesis of 5-(2-(4-(2-carboxybenzamido)-3-chloro phenyl)-2-oxoethylamino)-2-hydroxy benzoic acid (CSAPH): 5-(2-(4-(2-carboxybenzamido)-3-chloro phenyl)-2-oxoethyl amino)-2-hydroxybenzoic acid (CSAPH) was synthesized in two steps as follows:

(i) Preparation of 5-(2-(4-amino-3-chlorophenyl)-2-oxoethylamino)-2-hydroxy benzoic acid (CSA): The solution of 2-chloro-N-(2-chloro-4-(2-chloroacetyl) phenyl) acetamide (CAPC) (27.8 *g*, 0.1 mole) in acetone was treated with 4-amino salicylic acid (ASA) (15.3 *g*, 0.1 mole) in acetone at room temperature. The resultant product was filtered and hydrolyzed by 1:1 HCl: ethanol mixture. The yield of CSAPH was 78% and m.p.126-128^{0}C (uncorrected). Anal. Theoretical. for $C_{15}H_{13}ClN_2O_4$ (%) C, 56.17; H, 4.09; Cl, 11.05; N, 8.73. Found C, 56.15; H, 4.08; Cl, 11.03; N, 8.71.

(ii) Preparation of 5-(2-(4-(2-carboxybenzamido)-3-chlorophenyl)-2-oxoethyl amino) -2-hydroxy benzoic acid (CSAPH): The CSAPH was prepared by the solution of 5-(2-(4-amino-3-chlorophenyl)-2-oxoethylamino)-2-hydroxybenzoic acid(CSA) (32*g*,0.1mole) in acetone was cooled to 10^{o}C, to this solution the phthalic anhydride (29.6*g*,0.2mole) was added with stirring, the resulting product was filtered and air-dried. The yield of CSAPH was 64% and m.p.186-189^{0}C (uncorrected).Anal. Theoretical for $C_{23}H_{17}N_2O_7$ (%):C, 58.92; H, 3.65; N, 5.98. Found C, 58.90; H, 3.63; N, 5.96. IR (cm^{-1}): 3340(OH stretching),2862,2945 (CH_2 stretching), 3400(Sec. NH stretching),1710(CO stretching),1690(COOH stretching);^{1}HNMR (δ,ppm):4.7(s,2H,CH_2),4.6 and 9.4(s,2H,NH),5.7(s,1H,OH),8.5-6.9(m,10H,Ar-H),11.3(s,2H, COOH).^{13}C NMR (δ,ppm): 60.8(-CH_2),168-196(-CO), 113.5-158(Ar-C). The predicted structure and formation of polymeric ligand is shown in Scheme-1.

Preparation of coordination polymers

All coordination polymers were synthesized by using metal acetates. A warm and clear solution of CSAPH (4.68gm, 0.01mole) in 20% aqueous formic acid (200ml) was added to a solution of metal acetate (0.01mole) in 50% aqueous formic acid (50ml) with constant stirring. After complete addition of metal salt solution, the pH of reaction mixture was adjusted to about (~5) with dilute ammonia solution. The polymer chelate was separated out in the form of suspension and digested on a water bath for one hour. Eventually filtered, washed with hot water followed by acetone and dimethyl formamide (DMF) and then dried in air at room temp. The yields of all coordination polymers were almost quantitative. The obtained solid metal complexes and their colors are shown in Table 1. The complexes are stable solids, decomposing above 258^0C without melting and insoluble in ether, acetone, ethanol, methanol and chloroform; however, they are soluble in DMSO and DMF.

Physical measurements and analyses

Elemental analysis of CSAPH and its coordination polymers were carried out on a C, H, N elemental analyzer (Italy). IR spectra of the ligand and the polymeric chelates were scanned on a Nicolet-760D FTIR spectrophotometer in KBr. ^{1}H-NMR spectra were carried out at room temperature in DMSO-d_6 and tetramethylsilane (TMS) as an internal reference using a Brucker spectrophotometers (400 MHz and 100 MHz).

The metal content analyses of the polymeric chelates were performed by decomposing a weighed amount of each polymeric chelates followed by EDTA (disodium ethylene diamine tetra acetate) titration as reported in the literature [8]. Magnetic susceptibility measurements of all the polymeric chelates were carried out at room temperature by the Gouy method. Mercury tetrathiocynatocobaltate (II) was used as a calibrant. Molar Susceptibilities were corrected for diamagnetism of component atoms using Pascal’s constant. The diffuse reflectance spectra of the solid polymeric chelates were recorded on a Beckman DK-2A spectrophotometer with a solid reflectance attachment. MgO was employed as the reference compound. The number average molecular weight $(\overline{Mn})$ of all the coordination polymers were determined by method reported in earlier communications [16]. Thermogravimetric analysis of coordination polymers were carried on DuPont 950 TGA analyzer in air at a heating rate of 20^oC/min.

Screening of antibacterial and antifungal activities

Antibacterial activities

The *in vitro* antibacterial screening of CSAPH ligand and its coordination polymers were studied against gram-positive bacteria (*Bacillus subtilis and staphylococcus aureus*) and gram-negative bacteria (*E.coli and salmonella typhi)* by cup-plate method [17] using nutrient agar as medium. In a typical procedure, molten nutrient agar kept at 45^oC was then poured into Petri dishes and allowed to solidify. Then holes of 5mm diameter were punched carefully using a sterile cork borer and completely filed with test solutions (1mg/ml) in DMF). The diameter of the zone of inhibition for all the compounds was measured and the results were compared with the standard drug streptomycin of the same concentration as that of the test compound under identical conditions [18].

Antifungal activities

The antifungicidal activity of all the compounds was evaluated against *penicillium expansum, Nigrospora Sp., Trichothesium Sp., and Rhizopus nigricum* by cup-plate method cultured on potato-dextrose agar medium adapting similar procedure describe above. The plates were incubated at 37^o C for 48 hours. The diameter of the zone of inhibition for all the compounds was measured and the results was compared with the standard drug Chlotrimazole of the same concentration as that of the test compound under identical conditions [19].

Results and Discussion

The synthesis of the bisbidentate ligand, 5-(2-(4-(2-carboxybenzamido)-3-chlorophenyl)-2-oxoethylamino)-2-hydroxybenzoic acid(CSAPH) has not

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been reported in the literature. All the complexes were sparingly soluble in common organic solvents but soluble in DMF, DMSO and acetonitirle. The results of elemental analyses of ligand CSAPH and its coordination polymers are agreed with those predicted on the basis of formula (Table 1). The analytical data indicates that the complexes are agreed well with 1:1 metal to ligand (M:L) stoichiometry. The structure of CSAPH and its coordination polymers are confirmed by the elemental analysis, FTIR, ^{1}H-NMR and ^{13}C-NMR, reflectance spectra, magnetic susceptibility measurements and TGA. Elemental (CHN) analysis, physical properties and IR data provided good evidence that the chelates are polymeric in nature [20]. The recommended structure of the coordination polymers is shown in Scheme 1.

IR spectral studies

The IR spectrum of CSAPH shows a broad band at 3340 cm^{-1} attributed to the -OH stretching vibrations. The weak bands around 2862 and 2945 cm^{-1} may be due to asymmetric and symmetric stretching vibrations of methylene groups. The bands at 3400cm^{-1} and at 1710cm^{-1} are respectively due to NH (Sec) and CO group respectively. The bands around 1634, 1575, 1500 and 1440 cm^{-1} are attributed to the salicylic acid nucleus [21]. The band at 1690 cm^{-1} due to COOH group. The band around 1650, 1610 and 1520 are attributed to amide group. Comparison of the IR spectrum of the ligand CSAPH and those of the coordination polymers reveals certain characteristic differences. The broad band at 3340 cm^{-1} for CSAPH has almost disappeared for the spectra of polymers. However, the weak bands around 3200cm^{-1} in the spectra of CSAPH-Co^{2+}, CSAPH-Ni^{2+}, CSAPH-Mn^{2+} indicate the presence of water molecules which may have been strongly absorbed by the polymer sample. The C-O stretching in the ligand may be suggested due to the absorptions at 1366 and 1252 cm^{-1}. In the complexes this peaks are shifted to 1347 and 1245 cm^{-1} respectively. This indicating the formation of C-O-M bond. The peak at 1234 cm^{-1} in the ligand is assigned to OH-bending of the phenolic moiety, this is absent in the coordination polymers. In addition to these bands, the spectrum of CSAPH has many characteristic absorption bands, which are identical to those that occur in 5-amino salicylic acid (PSA) and phthalic anhydride. The new bands observed in the region 470-440 cm^{-1} and 430 cm^{-1} are probably due to the formation of M-O and M-N bonds respectively [22]. Thus, it believed that the oxygen atoms of 5-amino salicylic acid groups are coordinated to the metal [23-24]. From the above data the following structure has been proposed for the coordination polymers shown in Scheme 1.

^{1}H NMR and ^{13}C NMR spectra of the ligand (CSAPH)

The ^{1}H NMR spectrum of CSAPH also shows the signal at δ 4.7 ppm (2H, s) which is due to -CH$_2$ protons. Single at δ 4.6, 9.4 ppm (2H,s) due to –NH proton and δ 5.7 ppm(1H,s) due to –OH proton. The single at δ 8.5-6.9 ppm (10H, m) are assign to aromatic protons of phenyl moieties. A sharp peak at δ 11.3 ppm (2H, s) is assign to –COOH. These all features confirm the proposed structure of ligand CSAPH. The NMR Data of CSAPH shown in experimental part are also confirming the structure of CSAPH.

In the ^{13}C NMR spectrum of CSAPH shows a signal at δ 60.8 ppm is assigned to methylene carbons. Signal at δ 168-196 ppm is assigned to carbonyl carbon and the signals observed between δ 113.5-158.6 ppm were assigned to aromatic carbons of the ligand.

Magnetic susceptibility

The magnetic susceptibility measurements of the complexes were performed at room temperature (Table 1). The magnetic susceptibility value for Cu^{+2} complexes of the ligand CSAPH is 1.92 B.M. The copper atom is less than the normal value [24] (1.86-2.24B.M.). The lowered magnetic moment value observed for Cu^{+2} complexes under present study is due to distorted octahedral geometry [25-26]. On the other hand Co^{+2} and Ni^{+2} complex have shown magnetic moment value 4.87 and 3.24 B.M. respectively. This indicates octahedral geometry [27] for their Co^{+2} and Ni^{+2} complexes. The complex of Mn^{+2} exhibited the magnetic moments values 5.46 B.M. These values indicates that the complexes are high-spin type paramagnetic, it lies within the octahedral range which very close to spin value 5.90 B.M. as the ground term is $^6A_{1g}$ and thus supports the octahedral geometry[28].

Electronic spectral studies

The diffusion electronic spectrum of Cu^{+2}, Co^{+2}, Ni^{+2}, Mn^{+2} and Zn^{+2} complexes were recorded in DMF. They have been studied with the view to obtain information on stereochemistry of the complexes and to procure more support for the conclusion, deduced with the help of magnetic data. The diffusion electronic spectrum of CSAPH-Cu^{2+} coordination polymers shows two broad bands around 15,382 cm^{-1} and 22,734 cm^{-1}. The first bands may be due to $^2T_{2g} \rightarrow {}^2E_g$ transition, while the second may be due to charge transfer. The first band shows structure suggestion a distorted octahedral structure for the CSAPH-Co^{2+} polymers. The higher value of μ_{eff} of the CSAPH-Cu^{2+} polymer supports this view [29-30]. The CSAPH-Ni^{2+} and CSAPH-Co^{2+} polymers give two absorption bands respectively at 17,257 and 24,009 cm^{-1} and at 17,242 and 23736 cm^{-1} which can be assigned respectively to $^4T_{1g} \rightarrow {}^2T_{2g}$, $^4T_{1g} \rightarrow {}^4T_{1g(P)}$ transitions. These absorption bands and the values of μ_{eff} indicate an octahedral configuration for the CSAPH-Ni^{2+} and CSAPH-Co^{2+} polymers [31-32]. The spectrum of CSAPH-Mn^{2+} show weak bands at 16,475, 17,691 and 23,166 cm^{-1} assigned to the transitions $6_{A1g} \rightarrow 4_{T1g9}$(4G), $6_{A1g} \rightarrow {}_{4T2g}$(4G) and $6_{A1g} \rightarrow 4_{A1g}, 4_{Eg}$ respectively, suggesting an octahedral structure for the Mn [II] ions [32]. The spectrum of the Zn [II] polymer is not well resolved, so it is not interpreted, but its μ_{eff} value shows that it is diamagnetic as expected.

Thermal analyses

Thermal behavior of coordination polymers and parent bisligand was investigated by TGA. The TGA of all the samples are presented in Table 2. The weight loss of the polymer samples at different temperature indicates that the degradation of the polymers is noticeable beyond 300°C.

A very slight decrease in weight loss (1.5 to 5%) depicted from the thermogram in the temperature range 50-150°C for the parent ligand may be attributed to loosely bonded moisture. However, the initial slow weight loss occurring below 150°C in all of the coordination polymers may be attributed to the removal of water molecules.

Inspection of the thermograms of all coordinated polymer samples reveals appreciable weight loss in the range 150 to 270°C which might be due to metal-coordinated water molecules [16]. It is recommended that the water molecules are coordinated to the metal ions [33]. The rate of degradation becomes maximum at temperature between 400°C to 500°C and upto this temperature coordination polymers are most stable and each coordination polymers loses about 55% of its weight when heated up to 700°C and its form a metal oxides.

The thermodynamic activation parameter of the decomposition process of the

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coordination polymers such as energy of activation (Ea) and order of reaction (n) were evaluated graphically by employing the Freeman–Carroll method [15]. Using the following relation: $[(-Ea/2.303R)\ \Delta\ (1/T)]\ \Delta\ \log Wr = -n + \Delta\log\ (dW/dt)\ \Delta\log\ Wr$

where T is the temperature in K, R is gas constant, Wr = Wc-W; Wc is the weight loss at the completion of the reaction and w is the total mass loss up to time t. Ea and n are the energy of activation and order of reaction, respectively. A typical curve of $[\Delta\log(dw/dt)/\Delta\log wr]$ vs $[\Delta(1/T)/\ \Delta\log wr]$ for the Co(II) coordination polymer is shown in Figure 1. The slope of the plot gave the value of Ea/2.303R and the order of reaction (n) was determined from the intercept.

The kinetic parameter, especially activation energy (Ea) is helpful in assigning the strength of the coordination polymers. The calculated Ea values of the investigated coordination polymers are formation of volatile gas products are in the range of 6.5-9.2 kcal mol^{-1}. The relatively high value of Ea (Table 2) indicates that the ligand is strongly bonded to the metal ion [34-35]. Based on the activation energy values, the thermal stability of the coordination polymers in the increasing order is: Cu< Zn < Ni < Co < Mn [36].

Antimicrobial activity of ligand and its coordination polymers

All the test compounds and standard drugs were prepared in freshly distilled DMF; its zone of inhibition was found to be very negligible and taken as zero mm. The antibacterial activity results revealed that the ligand CSAPH and its coordination polymers shows weak to good activity are presented in Table 3.

The ligand and its Cu (II) and Co (II) complexes shows weakly active with the zone of inhibition 14-16 mm against the both organisms when compared to the standard drug streptomycin. The Ni (II) and Mn (II) complexes shows active and moderate activity as compared to its ligand with zone of inhibition 15-17 mm and Zn (II) complexes have exhibited good activity with the zone of inhibition 20-23 mm against the both organisms when compared to the standard drug streptomycin.

The antifungal activity results revealed that the ligand CSAPH and its Coordination polymers shows weak to good activity are presented in Table-4.

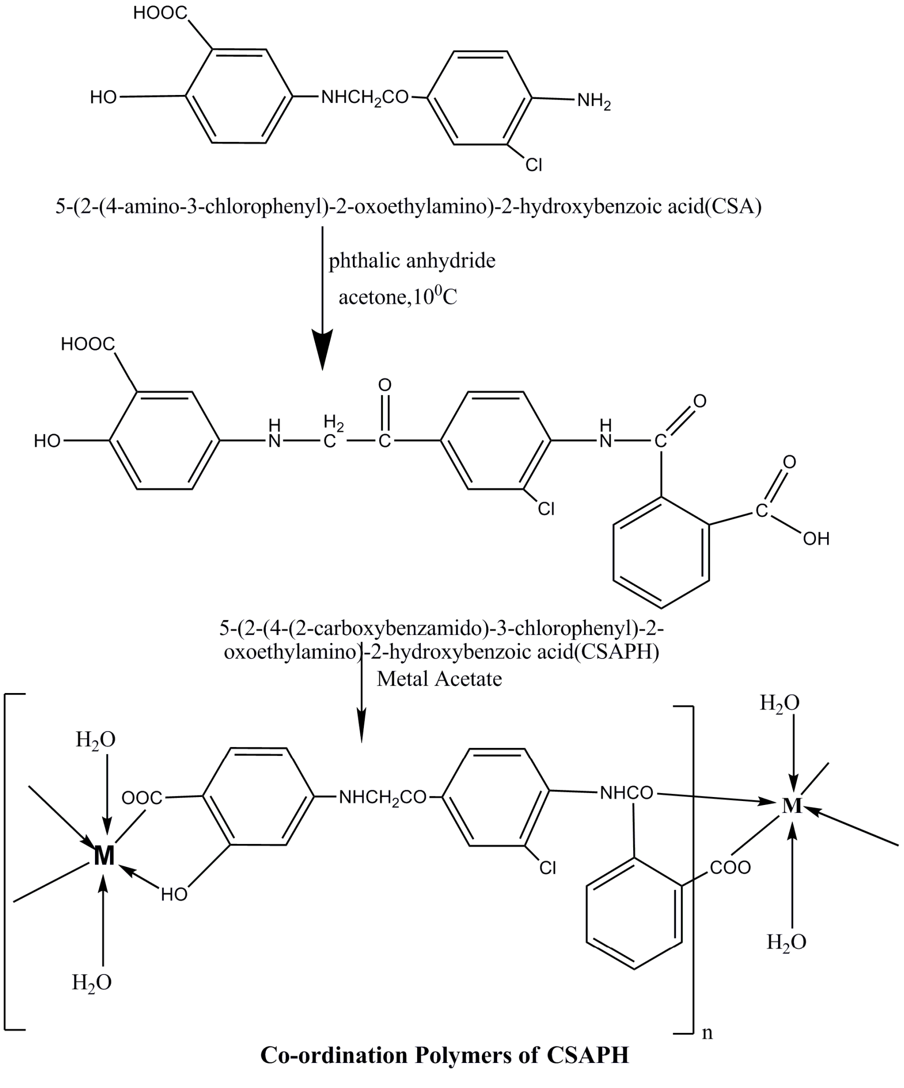
The ligand and its Cu (II) and Co(II) complexes shows weak active with the zone of inhibition 14-16 mm against the both organisms when compared to the standard drug chlotrimazole. The Ni (II) and Zn(II) complexes shows active and moderate activity as compared to its ligand with zone of inhibition 17-19 mm and Mn(II) complexes have exhibited good activity with the zone of inhibition 20-23 mm against the both organisms when compared to the standard drug chlotrimazole.

Conclusion

Polycondensation of 5-(2-(4-amino-3-chlorophenyl)-2-oxoethylamino)-2-hydroxy benzoic acid (CSA) with phthalic anhydride in the presence of a base catalysed yielded a novel 5-(2-(4-(2-carboxybenzamido)-3-chlorophenyl)-2-oxoethylamino)-2-hydroxybenzoic acid (CSAPH) polymeric ligand. The applicability of the polymeric ligand was explored by preparing polymeric chelates using different divalent metal ion indicating that the CSAPH polymeric ligand has good chelating property. Further, the coordination polymers are thermally stable then ligand. All the coordination polymers have good antimicrobial activity relative to the ligand due to the insertion of metal ions.

A comparison of the thermal stability of the present polymeric chelates with those of 5-(2-(4-amino-3-chlorophenyl)-2-oxoethylamino)-2-hydroxy benzoic acid (CSA) with phthalic anhydride as a pendent groups of polymeric chelates revels that the CSAPH polymeric chelates are thermally more stable. Finally, the maganetic susceptibility results indicate that polymeric chelates of Cu^{+2}, Ni^{+2}, and Co^{+2} are paramagnetic, whereas that of Zn^{+2} is diamagnetic in nature.

All the coordination polymers have good microbicidal activity relative to the ligand because of the insertion of the metal ions.



Where M=Cu^{+2},Ni^{+2},CO^{+2},Mn^{+2},Zn^{+2}

Scheme 1 Synthesis of Ligand (CSAPH) and its coordination polymer

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TABLE 1 Analytical and spectral data of the coordination polymers of CSAPH

Ligand/ Coordination polymers	**Empirical Formula**	**Yield (%)**	**Color**	**Formula Weight**	**Analyses %Found (Theoretical)**				**$\mu_{eff.}$ (B.M.)**	**$(\overline{Mn})$ ± 60**	**$\overline{Dp}$**
					%M	**%C**	**%H**	**%N**			
CSAPH	$C_{23}H_{17}N_2O_7Cl$	69	pale yellow	468	-	58.91 (58.92)	3.64 (3.65)	5.96 (5.98)	-	-	-
$[Cu(CSAPH)(H_2O)_2]_n$	$Cu.C_{23}H_{15}N_2O_7Cl.2H_2O$	81	Light blue	566.04	11.20 (11.22)	48.73 (48.75)	3.33 (3.35)	4.92 (4.94)	1.93	3462	6
$[Co(CSAPH)(H_2O)_2]_n$	$Co.C_{23}H_{15}N_2O_7Cl.2H_2O$	76	Light red	561.44	10.48 (10.49)	49.14 (49.15)	3.36 (3.38)	4.97 (4.98)	4.87	2876	5
$[Ni(CSAPH)(H_2O)_2]_n$	$Ni.C_{23}H_{15}N_2O_7Cl.2H_2O$	83	Green	561.21	10.45 (10.46)	49.16 (49.17)	3.37 (3.38)	4.97 (4.98)	3.23	3430	6
$[Mn(CSAPH)(H_2O)_2]_n$	$Mn.C_{23}H_{15}N_2O_7Cl.2H_2O$	78	Dule white	557.44	9.83 (9.85)	49.50 (49.51)	3.39 (3.40)	5.01 (5.02)	5.46	2858	5
$[Zn(CSAPH)(H_2O)_2]_n$	$Zn.C_{23}H_{15}N_2O_7Cl.2H_2O$	82	Yellow	567.88	11.49 (11.51)	48.58 (48.60)	3.32 (3.34)	4.91 (4.93)	Diamagnetic	2810	5

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Table 2 Thermogravimetric analysis of ligand (CSAPH) and it's coordination polymers

Ligand/ Coordination polymers	**% Weight loss at different temperature (°C)**							**Activation energy (Ea) kcal/mol^{-1}**
	100	**200**	**300**	**400**	**500**	**600**	**700**	
CSAPH	1.1	6.4	40.0	56.4	60.1	62.7	65.6	9.4
[Cu CSAPH $(H_2O)_2]_n$	1.0	4.7	11.3	26.0	30.2	33.1	36.7	6.3
[Co CSAPH $(H_2O)_2]_n$	5.4	6.5	12.5	25.9	37.6	42.7	49.6	8.2
[Ni CSAPH $(H_2O)_2]_n$	4.2	8.2	13.4	24.1	38.7	42.0	49.2	8.4
[Mn CSAPH $(H_2O)_2]_n$	3.4	5.9	11.7	22.1	31.1	34.1	36.0	8.1
[Zn CSAPH $(H_2O)_2]_n$	3.4	7.1	17.2	33.4	41.4	48.6	52.1	9.2

TABLE 3 Antibacterial activities of coordination polymers

	Zone of Inhibition (mm)			
	Gram +Ve		**Gram –Ve**	
Compounds	***Bacillus subtilis***	***Staphylococcus aureus***	***Salmonella typhi***	***E.coli***
CSAPH	12	10	11	11
[CuCSAPH(H_2O)$_2$]$_n$	13	14	15	14
[CoCSAPH(H_2O)$_2$]$_n$	14	13	14	15
[NiCSAPH(H_2O)$_2$]$_n$	17	16	18	17
[MnCSAPH(H_2O)$_2$]$_n$	18	17	17	16
[ZnCSAPH(H_2O)$_2$]$_n$	20	21	19	21
Streptomycin	23	24	24	25
DMF (Control)	00	00	00	00
Bore size	08	08	08	08

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TABLE 4 Antifungal activities of coordination polymers

	Zone of Inhibition at 1000 ppm (%)			
Compounds	***Penicillium Expansum***	***Nigrospora Sp.***	***Trichothesium Sp.***	***Rhizopus Nigricum***
CSAPH	09	09	10	11
$[CuCSAPH(H_2O)_2]_n$	15	14	14	13
$[CoCSAPH(H_2O)_2]_n$	13	13	15	14
$[NiCSAPH(H_2O)_2]_n$	17	16	18	17
$[MnCSAPH(H_2O)_2]_n$	20	19	21	20
$[ZnCSAPH(H_2O)_2]_n$	16	18	17	16
Chlotrimazole	24	26	24	25
DMF(Control)	00	00	00	00
Bore size	08	08	08	08

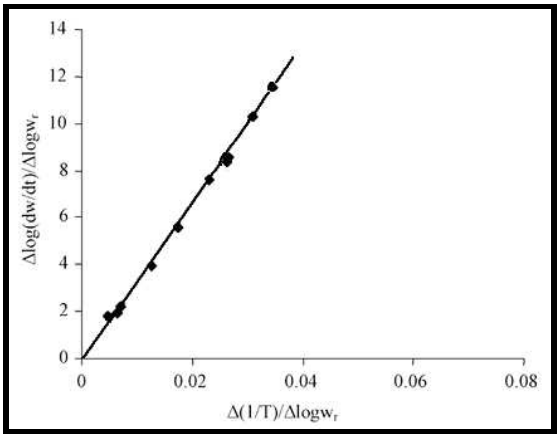

Figure 1. Freeman- Carroll plot for thermal degradation of [CuCSAPH$(H_2O)_2$]n

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