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Research Article

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Synthesis and Characterization of Coordination Polymers of 1,3-Di(4-Pyridyl)-Propane And 2-Aminobenzothiazole with Mn(II), Co(II), Cu(II) and Ni(II) Ions

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ABSTRACT

A number of coordination polymers of the general formula $\{[M(DPP)(ABZ)Cl_2(H_2O)].xH_2O\}_n$*, (M = Mn(II), Co(II), Cu(II) and Ni(II), DPP = 1,3-di(4-pyridyl)-propane and ABZ=2-aminobenzothiazole, has been prepared and characterized. The structure of the compounds has been assigned based on elemental analysis, FT-IR and electronic spectral studies. Thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) have been used to study the thermal decomposition steps. The mechanism functions of the first decomposition step for Co(II) and Cu(II) complexes were determined. Meanwhile, the thermodynamic parameters (ΔH, ΔG and ΔS) and kinetic parameters (activation energy E) for the two complexes were also calculated. The antimicrobial activity of the synthesized compounds was tested against six fungal and five bacterial strains. The majority of compounds were effective against the tested microbes some of which are frequently reported from contaminated soil, water and food, or involved in human and animal diseases.*

Keywords: Coordination polymers; XRD; Thermal decomposition mechanism; Biological activity

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INTRODUCTION

The coordination polymer is an inorganic or organometallic polymer structure containing metal cation centers linked by ligands extending in an array. In recent years due to their potential applications in diverse areas such as electrical conductivity [1], magnetism [2], host-guest chemistry [3], molecular separation [4], gas storage [5], sensors [6] and catalysis [7]. The considerable interest in metal-organic supramolecular coordination polymers (MOSCPs) constructed through the deliberate selection of metal ions and multifunctional exodentate ligands, motivated by their intriguing structural diversity and potential functions as microporous solids for molecular adsorption, ion exchange, and heterogeneous catalysis [8-12]. Pyridyl groups are widely incorporated in compounds employed as antidepressant, insecticidal, pharmaceuticals, herbicidal and plant growth regulating agents [13-18]. Recent studies reveal that 1,3-di(4-pyridyl)-propane is a good candidate for the construction of extended inorganic-organic hybrid coordination polymers with special topologies and various structural features because of its length and flexibility [19,20]. The thiazole ring is very important in nature. Thiazole, thiazolamines are valuable medicines [21-23]. It is obvious that compounds with the thiazole ring have a potential biological activity. Thiazole derivatives are widely used in pharmacology [24]. 2-aminobenzothiazole is known as biologically active compounds with a broad range of activity and they are also used as intermediate products in the synthesis of antibiotics [25]. ABZ exhibits antimicrobial and antioxidant activity [26,27]. The manganese(II), cobalt(II), copper(II) and nickel(II) coordination polymers with DPP and ABZ were characterized by physiochemical and spectral studies. The structures of the ligands are presented in Figure 1.

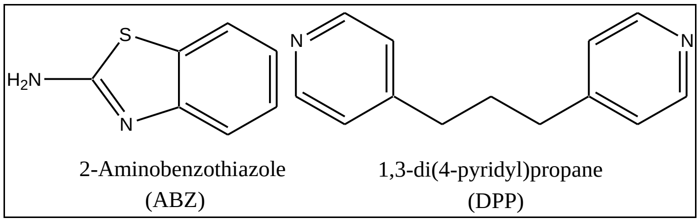

Figure 1: Chemical structure of DPP and ABZ

EXPERIMENTAL SECTION

Chemicals and Apparatus

All chemicals used were of analytical grade. High purity 1,3-di(4-pyridyl)propane and 2-Aminobenzothiazole were supplied from E. Merck grad. All other metal salts chemicals were of AR grade. They were purchased and used without purification. The contents of carbon, hydrogen, nitrogen and sulphur were performed using Analyischer Funktionstest Vario El Fab-Nr.11982027 elemental analyzer. The conductance was measured using a conductivity Meter model 4310 JENWAY. Infrared spectroscopy was conducted at room temperature from 4500 to 400 cm^{-1} using a Shimadzu IR-470 spectrophotometer with the KBr disc technique. The ultraviolet spectra were recorded on a Shimadzu UV-2101 PC spectrophotometer in DMSO. The TG-DTG experiments of the compounds were achieved using a Shimadzu DTG 60-H thermal analyzer at a heating rate 10°C min^{-1} from ambient to 750°C under a static air at mosphere. The X-ray diffractometer was a Philips 1700 version with H. T. P.W 1730 / 104 KVA and the anode was Cu Kα (λ=1.54180 Å). The scanning electron microscope was a JEOL JFC-1100E ION SPUTTERING DEVICE, JEOL JSM-5400LV. The antimicrobial activity of the complexes was tested against 5 bacterial and 6 fungal strains. These strains are common contaminants of the environment and some of which are involved in human and animal diseases (*Candida albicans, Geotrichum candidum, Scopulariopsis brevicaulis, Aspergillus flavus, T. rubrum, Staphylococcus aureus*), plant diseases (*Fusarium oxysporum*) or frequently reported from contaminated soil, water and food substances (*Escherichia coli, Bacillus cereus, Pseudomonas aeruginosa* and *Serratia marcescens*).

Synthesis of the Title Coordination Polymers

Synthesis of Mn(II), Co(II), Cu(II) and Ni(II) mixed ligand coordination polymers of 1,3-di(4-pyridyl)propane and 2-aminobenzothiazole follows essentially the same procedure. $[Cu(DPP)(ABZ)Cl_2(H_2O)]_n$ synthesis is typical. An ethanolic solution 25 mL of DPP (0.1 mmol) was slowly added into a hot ethanolic solution (20 mL) of $CuCl_2.2H_2O$ (0.1 mmol) and to an aqueous solution of ABZ (0.1 mmol) was added dropwise. The resultant mixture was stirred for 1 h and filtered. The Green precipitate was separated, washed with distilled water and EtOH and then dried over $CaCl_2$ in a vacuumed desiccator.

RESULTS AND DISCUSSION

Elemental Analysis

The contents of C, H, N, and S of the coordination polymers are shown in Table 1 together with the color and melting points.

Molar Conductance

The complexes were dissolved in DMSO solution with DMSO as a reference to determine their molar conductivity. The four complexes are air stable, insoluble in common organic solvents but partially soluble in DMSO.

FT-Infrared Spectra

Frequencies of characteristic absorption bands in The FT-infrared spectra (cm^{-1}) for the compounds are shown in Table 2. The Ft-IR spectra show a number of bands at 1618, 1614, 1620 and 1616 cm^{-1} corresponding to ν(C=N) 1,3-(4-pyridyl)propane for manganeas(II), cobalt(II), copper(II) and nickel(II) complexes respectively [28]. On the other hand show a series of bands at 816, 818, 820 and 822 cm^{-1} corresponding to the coordination of ν(C-N) ABZ moieties [29]. Moreover, the stretching vibration of the amino group in free ABZ observed at 3220 cm^{-1} is shifted to a lower wave number and appears in the range 3018-3190 cm^{-1} in the complexes suggesting coordination of the amino nitrogen to the metal(II) ions [30]. The M-O and M-N bonding are manifested by the appearance of two bands at 410-446 cm^{-1} and 508-538 cm^{-1} region, respectively [31]. The stretching vibration of νOH of coordinated water is located in the region 3180-3302 cm^{-1} [32] for all the complexes. For the cobalt(II) compound**,** νOH stretching vibration of lattice water was observed in the 3486 cm^{-1} [33]. The infrared spectra of Co(II) compound in Figure 2.

Table 1: Data of elemental analysis for the compounds

Compound	M. F (M.Wt)	Color	Found (Calcd. %)				m.p.°C (Decom.)	Λm Scm^2 mol^{-1}
			C	H	N	S		
$[Mn(DPP)(ABZ)Cl_2(H_2O)]_n$ **1**	$C_{20}H_{22}N_4SMnCl_2O$	Light-	47.2	4.42	11.35	6.39	210	54
	-492.48	brown	-48.77	-4.49	-11.41	-6.5		
$\{[Co(DPP)(ABZ)Cl_2(H_2O)].2H_2O\}_n$ **2**	$C_{20}H_{26}N_4SCoCl_2O_3$	Blue	44.98	4.71	10.32	5.99	235	45
	-532.48		-45.1	-4.88	-10.56	-6.02		
$[Cu(DPP)(ABZ)Cl_2(H_2O)]_n$ **3**	$C_{20}H_{22}N_4SCuCl_2O$	Green	47.22	4.29	10.96	6.1	204	37
	-501.09		-47.93	-4.42	-11.22	-6.39		
$[Ni(DPP)(ABZ)Cl_2(H_2O)]_n$ **4**	$C_{20}H_{22}N_4SNiCl_2O$	Light- green	47.97	4.33	11.08	6.39	207	35
	-496.24		-48.4	-4.46	-11.33	-6.46		

Table 2: FT-IR absorption for the coordination polymers (cm^{-1})

Compounds	υ(OH)	υ(NH_2)	υ(C=N)	υ(C-N)	υ(C-S)	υ(M-N)	υ(M-O)
1	3180	3018	1618	816	746	410	508
2	3284	3088	1614	818	794	432	522
3	3238	3126	1620	820	782	418	538
4	3302	3190	1616	822	750	446	516

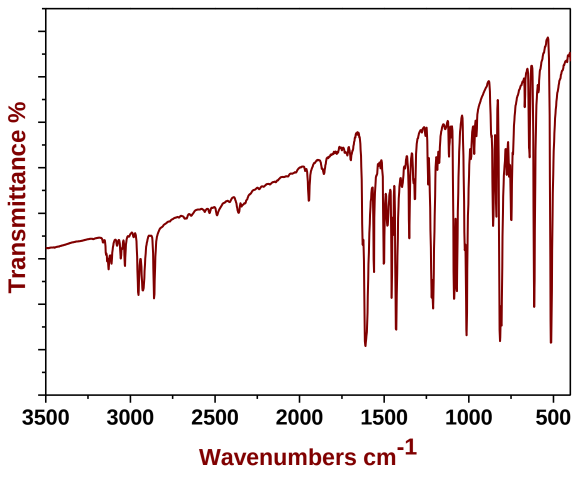

Figure 2: FT-IR of compound Co(II) coordination polymer

Ultraviolet Spectra

The UV spectral data of the complexes in DMSO solution are listed in Table 3. The band observed in the electronic spectra in DMSO of the Mn(II), Co(II), Cu(II) and Ni(II) ternary coordination polymers of 1,3-di(4-pyridyl)propane and 2-aminobenzothiazole which located in the region 35,644 - 39,262 cm^{-1} assigned to a $\pi \rightarrow \pi^*$ transition due to molecular orbital energy levels originating in the DPP moiety [28]. For all the compounds another band is recorded in the region 24,498 - 33,672 cm^{-1} is ascribed to an intraligand transition for the ABZ [29].

Magnetic Measurements

For manganese complex the electronic spectra exhibit a band in the 19,420 cm^{-1} reflecting the octahedral arrangement around the Mn(II) ion which is confirmed by the value of the magnetic moment 5.34 BM [34]. Cobalt(II) compound a d-d band observed in the 20,802 cm^{-1}. The corresponding magnetic moment value for this compound was found to be 4.30 BM, which is in agreement with the octahedral environment around Co(II) ion [35]. The magnetic moment value of 1.83 B.M for the Cu(II) complex indicates a octacoordination around copper(II) and a d-d band showed in the 19,733 cm^{-1} [36]. However, the magnetic moment value of 2.98 B.M. confirms the paramagnetic nature of the Ni(II) complex and the octahedral geometry around Ni(II) ion [36,37] with a d-d band observed in the 18,167 cm^{-1}. The electronic spectral data and magnetic moment values are shown in Table 3.

Table 3: Electronic spectral data and magnetic moments of the compounds

Compound	ν_{max} (cm^{-1})	Assignment	$\mu_{eff\ B.M}$
1	19,420	d-d transition	5.34
	24,498	n → π* transition	
	35,644	π→ π* transition	
2	20,802	d-d transition	4.3
	26,134	n → π* transition	
	39,262	π → π* transition	
	19,733	d-d transition	
3	25,386	n→ π* transition	1.83
	38,120	π → π* transition	
	18,167	d-d transition	
4	31,058	n→ π* transition	2.98
	37,636	π → π* transition	

The suggested structures for DPP mixed ligand coordination polymers are shown in Figure 3. It is to be noted that in all the published results of 1,3-di(4-pyridyl)propane the two pyridyl moieties stand almost cis to each other with different conformations and certain angle [38,39].

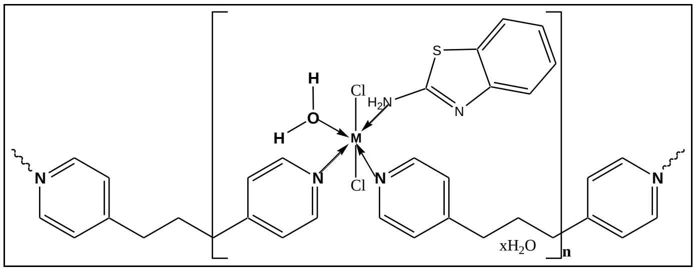

Figure 3: Structure of {[M(DPP)(ABZ)Cl_2(H_2O)].xH_2O}$_n$, (M = Mn(II), Co(II), Cu(II) and Ni(II), x = 0 or 2)

Thermal Decomposition Mechanism

The TG, DTG and DTA curves of cobalt(II) complex are shown in Figure 4. They show that the thermal decomposition processes of the complex involve three stages. The first stage is a dehydration process occurring in the temperature range from 32 to 198°C. The mass loss (calc. 10.14%, found 10.02%) indicates the loss of $3H_2O$ molecules and formation of the complex [Co(DPP)(ABZ)Cl_2]. For this step (DTG minimum at 72°C) an endothermic broad peak is observed in the DTA at 74°C in the curve.

$$[Co(DPP)(ABZ)Cl_2(H_2O)].2H_2O \xrightarrow{32\text{-}198\ ^{o}C} [Co(DPP)(ABZ)Cl_2] + 3H_2O$$

The observed mass losses of the second step (199-302°C) in the TG curve agree with the decomposition of the 2-aminobenzothaizole ligand (calc. 28.20%, found 27.85%). This step is marked on the DTG peak at (250°C) corresponding to exothermic peak in the DTA curve at 252°C. The third step shows a mass loss corresponding to the decomposition of DPP and chlorine (calc. 50.55%, found 50.14%). The DTG curve displays a midpoint at 365, 436 °C and an exothermic effect at 367, 438°C in the DTA trace respectively. The ultimate product at 750°C is consistent with the formation of CoO (calc.14.07%, found 13.92%).

$$[Co(DPP)(ABZ)Cl_2] \xrightarrow{199\text{-}750^{o}C} \text{Decomposition products} + CoO$$

Kinetic Analysis

Non-isothermal kinetic analysis of the coordination polymers was carried out applying two different procedures: the Coats-Redfern [40] method (Figures 5 and 6). The kinetic and thermodynamic parameters for Mn(II) and Co(II) compounds are calculated for the first step according to the above this method and are cited in Table 4. The Thermodynamic parameters, namely entropy (ΔS^*), enthalpy (ΔH^*) and free energy (ΔG^*) of activation were calculated.

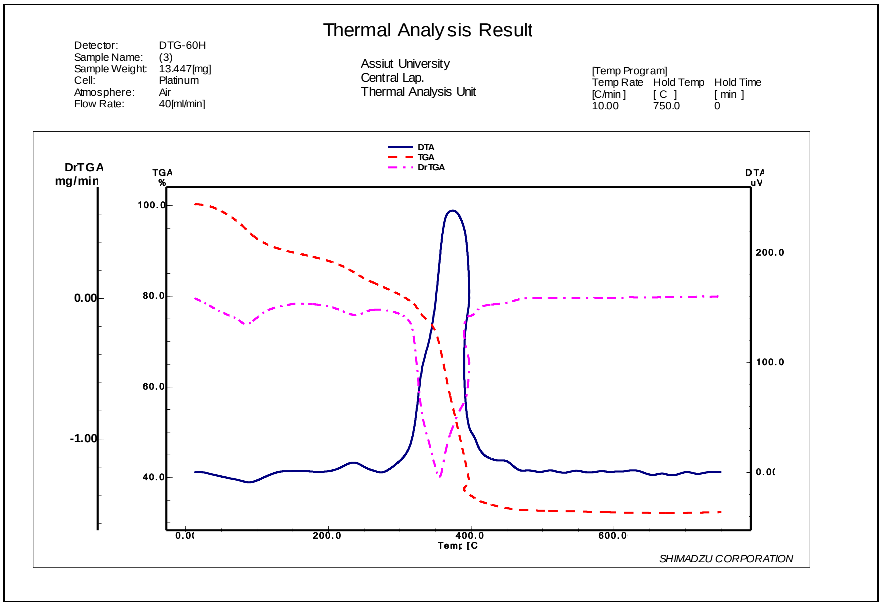

Figure 4: TG, DTG and DTA curves of [Co(DPP)(ABZ)Cl_2(H_2O)].$2H_2O$

Table 4: Kinetic and thermodynamic parameters for the Mn(II) and Co(II) compounds

Compound	Step	*r*	n	E	Z	$S^{*}\Delta$	$H^{*}\ \Delta$	$G^{*}\ \Delta$
Mn(II) 1	1^{st}	0.9996	0	17.95	3.32 x 10^2	-202.34	14.6	66.74
		0.9995	0.33	23.17	x 10^2 5.83	-198.12	19.82	59.82
		0.9998	0.5	29.28	x 10^2 6.12	-196.65	25.93	53.12
		0.9994	0.66	34.79	6.95 x 10^2	-195.16	31.44	47.01
		0.9999	1	39.05	7.84 x 10^2	-194.28	35.7	42.4
		0.9997	2	48.54	8.19 x 10^2	-192.42	45.19	32.16
Co(II) 2	1^{st}	0.9994	0	40.16	8.94 x 10^2	-206.73	36.83	45.86
		0.998	0.33	43.85	9.82 x10^2	-205.52	40.52	41.68
		0.9989	0.5	49.29	10.28 x10^2	-204.1	45.96	35.68
		0.9999	0.66	56.03	10.89 x10^2	-203.93	52.7	28.87
		0.9995	1	60.27	12.52 x10^2	-202.38	56.94	24.01
		0.9973	2	72.48	14.34 x10^2	-200.73	69.15	11.14

E in KJ mol^{-1}, underlined *r* in all tables represents the best fit values of n and E; ΔH^{*} and ΔG^{*} in kJmol^{-1} & ΔS^{*} in kJmol^{-1}K^{-1}

Negative ΔS* values for the first stage of decomposition of the three coordination polymers suggest that the activated complexes is more ordered than the reactants and that the reactions are slower than normal [41]. The different values of ΔH* and ΔG* of the complexes refer to the effect of the type of the metal ion on the thermal stability of the complexes [42].

X-ray Powder Diffraction of the Coordination Polymers

The cobalt(II) and copper(II) complexes were chosen for X-ray powder diffraction studies (Figure 6). The crystal data of the Co(II) or Cu(II) mixed-ligand compounds belong to the crystal system triclinic. The crystal data are recorded in Table 5.

Table 5: X-ray powder diffraction crystal data of the Co(II) and Cu(II) compounds

Parameters	Co(II) compound	Cu(II) compound
Empirical formula	$C_{20}H_{26}N_4SCoCl_2O_3$	$C_{20}H_{22}N_4SCuCl_2O$
Formula weight	532.48	501.09
Crystal system	triclinic	triclinic
a (Å)	2.74	6.11
b (Å)	8	8.89
c (Å)	11.45	3.53
α (°)	60.601	91.916
β(°)	100.556	90.623
γ(°)	99.21	82.016
Volume of unit cell(Å3)	214.83	190.37

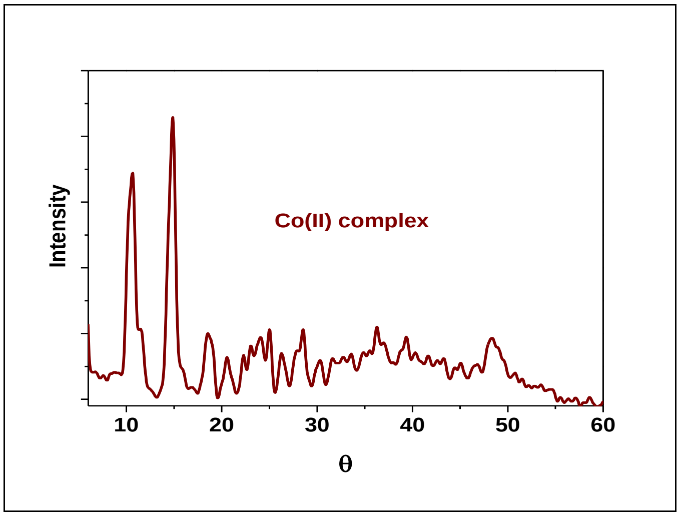

Figure 5: X-ray of [Co(DPP)(ABZ)Cl_2(H_2O)].$2H_2O$

Microbiological Screening

The antimicrobial activity of compounds Mn(II), Co(II), Cu(II) and Ni(II) was tested against 5 bacterial and 6 fungal strain (Figure 6). Mn(II) compound exhibited a broad spectrum of the antibacterial action with the highest activity observed against *Pseudomonas aeruginosa* (Gram-ve). Concerning the antifungal activity, Mn(II) and Ni(II) compounds were effective against *Geotrichum Candidum* (a yeast like human pathogen fungus) with the highest inhibitory activity exerted by Mn(II) compound. *Candida albicans* (also yeast like human pathogen fungus) was inhibited by three compounds (Figure 6).

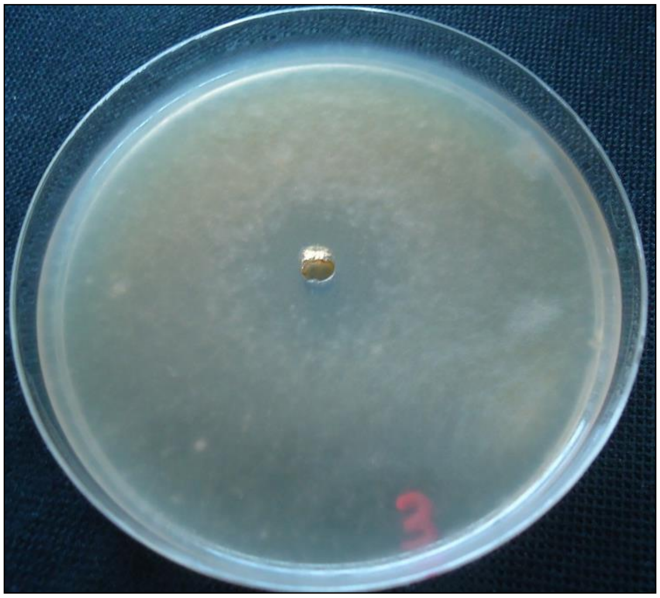

Figure 6: Microbiological screenning of Mn(II) compound against *G. candidum*

CONCLUSION

In conclusions, new compounds containing from Mn(II), Co(II), Cu(II) and Ni(II), 1,3-di(4-pyridyl)-propane and 2-aminobenzothiazole were prepared and characterized. The Co(II) and Cu(II) compounds were structurally characterized by X-ray powder diffraction. In testing the antibacterial and antifungal activity of these compounds we used more than one test organism to increase the chance of detecting antibiotic principles in tested materials. The complexes of certain metal ions enhanced the antimicrobial activity and in some case a higher or similar activity than the selected standards.

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