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Full Paper

Coordination Polymers of Co(II), Cu(II) and Zn(II) Derived from 1,4-Naphthalenedicarboxylate and Certain Thiazoles, Characterization and Catalytic Activity

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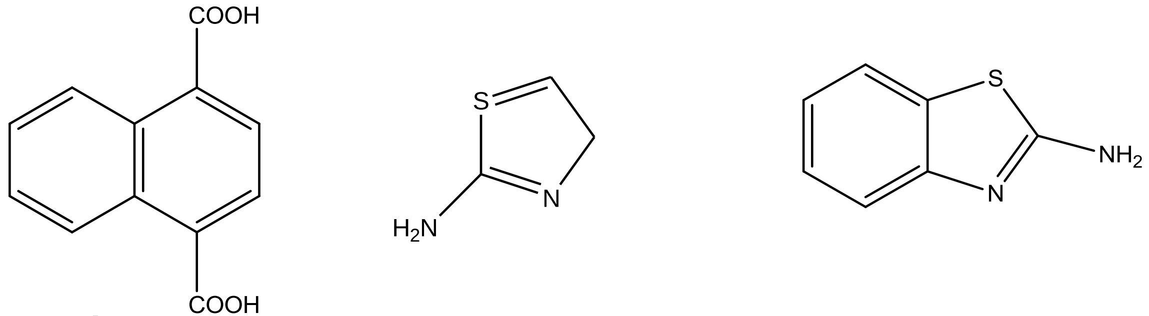
Abstract

A series of coordination polymers of the general formula $\{[M(ndc)(azoles)(H_2O)].XH_2O\}_n$ (where M =Co(II), Cu(II) and Zn(II), ndc = 1,4-naphthalenedicarboxylate, azoles = 2-aminothiazole and 2-aminobenzothiazole, x=0, 1 or 2) has been prepared and characterized. The coordination polymers have been characterized based on elemental analysis, FT-IR and electronic spectral studies magnetic measurements and thermal analysis. Thermogravimetry, derivative thermogravimetry, and differential thermal analysis were used to study the thermal decomposition of the complexes. Non isothermal kinetic parameters were calculated making use of the Coats-Redfern and Horowitz-Metzger equations. Catalytic performances of the two of the complexes for the degradation of methyl orange by sodium persulfate have been investigated.

Keywords: Coordination polymer, 1,4-naphthalenedicarboxylate, catalytic activity.

1. Introduction

Coordination polymers (CPs) or metal-organic frameworks (MOFs) are crystalline materials composed of organic linkers connecting metal ions. CPs have receiving great interest due to their vast potential applications as functional materials in a variety of technical areas such as gas storage[1-4], separation process[5-7], catalysis[8-13], molecular sensing[14-16] and carbon dioxide capture [17-19]. 1,4-Naphthalenedicarboxylic acid is a rigid linear bi-functional ligand. It is a good ligand for the preparation of a vast number of coordination polymers of interesting properties[20,21]. Thiazoles represents an important class of compounds owing to their pharmaceutical, analytical and industrial applications [22]. The present work describes the preparation and characterization of some mixed-ligand complexes of cobalt(II), copper(II) and zinc(II) containing 1,4-naphthalenedicarboxylate and azole ligands. The structures of the ligands are depicted in Fig.1.



H_2ndc AZ ABZ

Fig.1: Structures of the ligands

2. Materials and methods

2.1.Physical measurements

All reagents were of analytical grade. Naphthalenedicarboxylic acid was purchased from Alfa Aesar Company and azoles from Merck and were used as received. The elemental analysis (C, H, N) was performed using Analyischer Funktionstest Vario El Fab Nr. 11982027 Elemental analyzer. The IR spectra were recorded on a Shimadzu IR – 470 spectrophotometer using KBr disc technique and the electronic spectra were obtained using a Shimadzu UV- 2101 PC spectrophotometer . Magnetic susceptibility measurements of the prepared complexes were measured at room temperature using a magnetic susceptibility balance of the type MSB-Auto. Thermal studies were carried out in dynamic air on a Shimadzu DTG 60-H thermal analyzer at a heating rate 10^o C min^{-1}.

2.2.Synthesis of the coordination polymers

Preparation of the mixed ligand coordination polymers of 1,4-naphthalenedicarboxylate and the azoles 2-aminobenzothiazole(ABZ) and 2-aminothiazole (AZ) with Co(II), Cu(II), and Zn(II) followed essentially the same procedure. $[Co(ndc)(ABZ)(H_2O)].2H_2O$ is typical.

To an ethanolic solution (15 mL) of Co(II) chloride (1.26 mmol), a solution of ndc (0.3g, 1.25mmol in 15 ml of 0.1 M NaOH, 2.4 mmol) was added dropwise with stirring, and then a solution of ABZ (0.16g in 15 mL of ethanol, 2.4 mmol) was added to the mixture. The mixture was refluxed and then cooled to room temperature. A light-pink precipitate separated, which was filtered, washed with distilled water and EtOH**,** and dried over anhydrous $CaCl_2$.

2.3.Catalytic degradation of the Cu(II) and Zn(II) coordination polymers for the degradation of methyl orange (MO)

50 mg of each of the two complexes, aqueous solution of methyl orange (150ml, 10mg/L) and 30mg of sodium persulfate were mixed shaken at different times. It was filtered and the dye concentration was determined spectrophotometrically at 463 nm. The same procedure was repeated in the absence of the complex as a blank comparison.

3. Results and discussion

The supramolecular coordination polymers were prepared by the reaction of 1,4-naphthalenedicarboxylic acid (neutralized with NaOH), metal salts and ABZ and AZ (dissolved in EtOH). The prepared complexes were found to react in a molar ratio of 1:1:1 of metal, ndc, and azoles to yield the corresponding coordination polymers according to equation 1:

$$MCl_2 + Na_2ndc + azole \rightarrow \{[M(ndc)(azole)(H_2O)].xH_2O\}_n + 2NaCl \qquad (1)$$

M=Co(II), Cu(II) and Zn(II); x = 0, 1or 2

The coordination polymers are air stable, insoluble in common organic solvents but partially soluble in DMF and DMSO. To establish the composition of complexes, the contents of carbon, hydrogen, nitrogen and sulfur were determined and the results are listed in Table 1 together with color and decomposition points of the complexes.

3.1. IR spectra

The most important infrared spectra of the compounds are given in Table 2 . Coordination of 1,4-naphthalenedicarboxylate is manifested by the appearance of a sharp band with a shoulder in the regions 1552-1609 and 1361-1413 cm^{-1} that corresponds to the asymmetric and symmetric stretching vibrations of the carboxylic groups of the ndc^{-2} coordinated to the metal center. The difference between the two bands (Δν) lies in the range 191-197 cm-1 and points to a bidentate mode of coordination for the carboxylate group[23]. All complexes exhibit a band in the range 3213-3310 cm^{-1}associated with the coordinated water molecules[24], whereas the υ OH stretching vibrations of the lattice water molecules were located in the range 3359-3400 cm^{-1} for complexes **1, 2** and **3** [25]. The IR spectra of the compounds display characteristic vibrations of υ(C=N) in the range 1614-1624 cm^{-1} [26]. Furthermore, the stretching vibration of the amino group in the free ABZ, observed at 3220 cm^{-1}, is shifted to a lower wavenumber, namely at 3180-3210 cm^{-1} in the complexes suggesting coordination of the amino nitrogen to the metal ions[27]. It is found that the CSC band of azoles at ~ 745 cm^{-1} is almost unchanged in the respective complexes, indicating that the thiazole-S is not involved in the bonding [28]. Metal-oxygen and metal-nitrogen bonding are manifested by the appearance of a band in the 520-524 cm^{-1} and 419-442 cm^{-1} ranges, respectively[24]. This is a further evidence for coordination of the metal ions through oxygen and nitrogen atoms of the ligands.

Table 1: Colors, elemental analysis and decomposition points of the complexes

Compound	**color**		**Found (calc)**			**Dec.point.°C**
		C%	**H%**	**N%**	**S%**	
$\{[Co(ndc)(ABZ)(H_2O)].2H_2O\}_n$ **1**	Pink	47.7 (47.8)	3.6 (3.8)	5.5 (5.8)	5.2 (6.7)	360
$\{[Cu(ndc)(ABZ)(H_2O)].H_2O\}_n$ **2**	Light-blue	52.2 (52.2)	3.1 (3.0)	5.8 (6.4)	6.1 (7.3)	290
$\{[Cu(ndc)(AZ)(H_2O)].H_2O\}_n$ **3**	Greenish-blue	45.8 (44.4)	3.9 (3.4)	5.9 (6.7)	6.0 (7.2)	300
$\{[Zn(ndc)(ABZ)]. H_2O\}_n$ **4**	White	52.4 (51.1)	3.0 (3.1)	6.4 (6.2)	6.7 (7.1)	350

Table 2: Infrared spectral data of the complexes

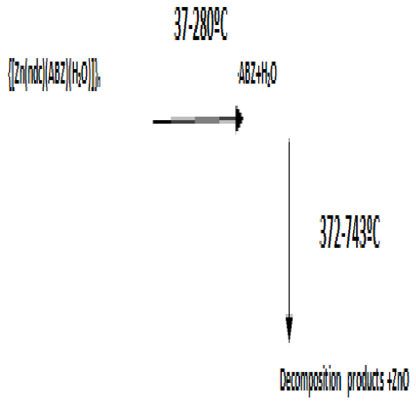
Complex	υ (NH_2)	υ (COO) asym	υ (COO) sym	Δ υ	υ (C=N)	υ(H_2O) Lattic (Coord)	υ (M-O)	υ (M-N)	υ (C-S)
1	3180	1552	1361	191	1618	3565 (3219)	521	439	744
2	3207	1557	1363	193	1616	3565(3253)	524	442	745
3	3210	1609	1412	197	1614	3547(3218)	522	419	740
4	182	106	1413	192	1624	3565(3218)	520	437	742

3.2. Electronic spectra and magnetic moments

The results of the ultraviolet spectra of the complexes have been recorded in dimethylsulphoxide (DMSO) and are shown in Table 3. The spectra exhibit two absorption maxima at 24,500-28,512 cm^{-1} and 35,418–38,515 cm^{-1} assigned to the intraligand n→π* and the the π→π* transitions in both ligands, namely the 1,4-naphthalenedicarboxylate and 2-aminothiazole or 2-aminobenzothiazole. In the visible spectra, there are characteristic bands attributed to the d-d transitions of the Co(II) and Cu(II) complexes. The Co(II) complex shows a d- d transition at 18,410 cm^{-1}. The copper complex displays the d-d band at 16,925 cm^{-1}. Additionally, the magnetic moment of the cobalt complex is of 4.25 B.M typical for octahedral ion complexes [29]. The magnetic moment value (2.06 B.M) of the Cu(II) complex indicates its octahedral structure[30].

3.3.Thermogravimetric analysis

Thermogravimetric analysis of compounds **3** and **4** was investigated in dynamic air from ambient temperature to 750ºC (Table 4). The thermal behavior of the zinc complex **4** is depicted as an example in Fig.2. Elimination of the one water molecule and the ABZ molecule occurs in the first and second steps (calc. 37.5%, found 33.5%) (DTG curve at 338°C). For these two steps a broad endothermic peak appears in the DTA at 340°C leading to the anhydrous $\{Zn(ndc)\}_n$ and indicating a change of coordination number and consequently in structure from octahedral to tetrahedral one. The third step is related to the decomposition of the 1,4-naphthalenedicarboxylate (calc. 48.3%, found 47.3%) with a DTG peak at 476°C associated with an exothermic peak at 479°C. The residue after the final decomposition is in agreement with the formation of ZnO (calc. 18.3%, found 19.0%)(scheme 1).



(Scheme 1)

Table 3: Electronic spectral data of 1,4-naphthalenedicarboxylate and 2-aminobenzothiazole mixed ligand complexes of Co(II), Cu(II) and Zn(II) (cm^{-1})

Complex	**υ max (cm^{-1})**	**Assignment**	**μ_{eff} (B.M)**
1	18,410 25,362 36,714	d-d n→ π* π →π*	4.25
2	16,925 24,520 35,418	d-d n→ π* π →π*	2.06
3	28,512 38,515	n→ π* π →π*	2.06
4	24,500 37,714	n→ π* π →π*	-

Table 4: Thermal decomposition data of 3 and 4

Compound	**Step**	**T /DTG**			**Mass Loss (%)**
		T_i	**T_m**	**T_f**	
3	1st	23	59	132	3.68
	2nd	133	285	382	54.7
	3rd	383	693	750	19.09
4	1st	37	150	280	1.17
	2nd	282	338	371	32.33
	3rd	372	476	743	47.30

T_i=initial temperature,T_m=maximum temperature ,T_f= final temperature

3.4. kinetic analysis

Non-isothermal kinetic analysis for the thermal decomposition of the prepared complexes was carried out using two different equations, namely the Coats-Redfern[31] and Horowitz-Metzger[32] equations(2,3,4,5).

(a) The Coats-Redfern equation

where α is the fraction of material decomposed, n is the order of the decomposition reaction and M=E/R and B=ZR/ΦE; E, R, Z and Φ are the activation energy, gas constant, pre-exponential factor and heating rate, respectively.

(b) The Horowitz-Metzger equation

where θ = T-Ts and Ts is the temperature at the DTG peak. The correlation coefficient r is computed using the least squares method for equations (2), (3), (4) and (5) . The kinetic parameters for compounds **3** and **4** were calculated according to the above two methods and are cited in Table 5 . The thermodynamic parameters, entropy (ΔS*), enthalpy(ΔH*) and free energy(ΔG*) for the two complexes were computed (Table 6) using equations 6,7,8where h, Planck's constant, k, Boltzmann constant and R, gas constant. The negative ΔS* value for the dehydration step of decomposition suggests that the activated complex is more ordered than the reactants and that the reactions are slower than normal [33,34]. The more ordered nature may be due to the polarization of the bonds in the activated state, which might happen through charge transfer electronic transition [35]. The different values of ΔH*and ΔG*of the complexes refer to the effect of the nature of the metal ion on the thermal stability of the complexes [36] . The positive values of ΔG* indicate that the decomposition reaction is not spontaneous.

$$\ln[1-(1-\alpha)1-n/(1-n)T2]=M/T+B \qquad \text{for } n\neq 1 \qquad (2)$$

$$\ln[-\ln(1-\alpha)/T2]=M/T+B \qquad \text{for } n=1 \qquad (3)$$

$$\ln[1-(1-\alpha)1-n/1-n]=\ln ZR\,Ts2/\Phi E - E/RTs+E\theta/RTs2 \qquad \text{for } n\neq 1 \qquad (4)$$

$$\ln[-\ln(1-\alpha)] = E\theta/RTs2 \qquad \text{for } n=1 \qquad (5)$$

$$\Delta S^{*}= R\,[\ln Zh / kTs] \qquad (6)$$

$$\Delta H^{*} = \Delta E-\Delta RTs \qquad (7)$$

$$\Delta G^{*}=\Delta H^{*}-\Delta Ts\Delta S^{*} \qquad (8)$$

Table 5 : Kinetic parameters for the thermal decomposition of the compounds 3 and 4

compound	**Step**	**Coats–Redfern equation**				**Horowitz- Metzger equation**			
			n	**E**	**Z**	***r***	**n**	**E**	**Z**
3	1^{st}	0.9745	0.00	90.98	1.63×10^{3}	0.9906	0.00	104.93	1.843×10^{3}
		0.9747	0.33	94.86	1.66×10^{3}	0.9910	0.33	106.80	1.850×10^{3}
		0.9750	0.50	96.04	1.68×10^{3}	0.9912	0.50	107.64	1.854×10^{3}
		0.9758	0.66	104.04	1.69×10^{3}	0.9914	0.66	109.67	1.857×10^{3}
		0.9759	1.00	106.16	1.73×10^{3}	0.9925	1.00	111.54	1.865×10^{3}
		0.9757	2.00	110.14	1.81×10^{3}	0.9916	2.00	122.74	1.891×10^{3}
4	2^{nd}	0.9887	0.00	54.04	8.75×10^{2}	0.9996	0.00	72.60	4.03×10^{4}
		0.9870	0.33	62.08	1.01×10^{3}	0.9997	0.33	82.49	3.97×10^{4}
		0.9866	0.50	66.97	1.07×10^{3}	0.9998	0.50	87.74	3.96×10^{4}
		0.9863	0.66	71.86	1.15×10^{3}	0.9999	0.66	93.01	3.96×10^{4}
		0.9888	1.00	82.18	1.32×10^{3}	0.9999	1.00	104.74	3.95×10^{4}
		0.9820	2.00	116.1	1.85×10^{3}	0.9999	2.00	123.59	3.92×10^{4}

Order (n), Z(s^{-1}), E ($kJmol^{-1}$), underlined *r* in all tables represented the best fit values of n, E and Z

Table 6 : Thermodynamic parameters of compounds 3 and 4

compound	**Step**	**n**	**ΔS***	**ΔH***	**ΔG***
3	1st	0.00	-184.40	88.18	150.13
		0.33	-184.25	91.88	153.77
		0.50	-183.15	93.24	155.09
		0.66	-183.02	101.21	163.03
		1.00	-181.39	103.36	165.15
		2.00	-180.73	107.34	168.52
4	2nd	0.00	-194.55	48.96	167.83
		0.33	-192.64	57.01	174.71
		0.5	-192.57	61.89	179.55
		0.66	-192.23	66.78	184.23
		1.00	-191.13	77.10	193.88
		2.00	-188.32	111.07	226.13

$\Delta H^*$and ΔG *in $kJmol^{-1}$, ΔS^*in $kJmol^{-1}K^{-1}$

From the foregoing discussion , the general structure of the complexes is suggested as illustrated in Fig.3.

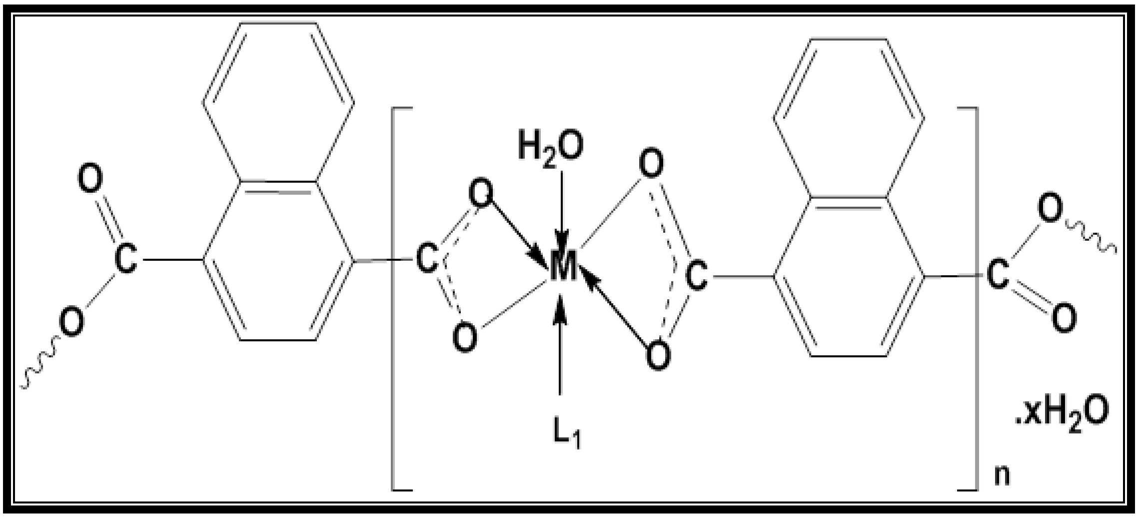


Fig.3: Structure of the complexes

M = Co(II), Cu(II) or Zn(II), L_1 = AZ or ABZ, x = 0, 1 or 2

3.5. Catalytic activity of complexes 3 and 4 for the degradation of methyl orange (MO)

The degradation experiment of MO was followed using visible electronic spectra and the results are depicted in Fig. 4 . When complex **3** or **4** as heterogeneous catalyst is introduced to the system, a catalytic oxidation process is immediately initiated, but degradation efficiencies are distinctively different under the same conditions.

The percent removal of dye from the solution can be calculated by equation 9:

% Removal efficiency= $C_0 - C_i/C_0*100$ (9)

Where C_0 is the initial concentration of the dye and C_i is the final concentration of the dye after treatment with the complex. It can be observed that the degradation efficiency for MO after 110 min is about 80 % using compound **3** as a catalyst,while for compound **4**, the degradation efficiency can only reach about 50%. The two complexes activate the persulfate to produce more strongly oxidizing sulfate radicals ($SO_4^{\cdot-}$). The different catalytic performances of the two complexes may be due to the distinct coordination environments around the metal centers [37]. Overall, both complexes show positive activity as catalysts for the Fenton-like reaction to degrade methyl orange. However, the uncatalyzed reaction rate is extremely slow. We proposed a mechanism for the Cu(II) complex **3** as a heterogeneous catalyst to activate the persulfate anions and generate $SO_4^{\cdot-}$**.** The mechanism is illustrated by equations 10 and 11. For the Zn(II) complex **4** another mechanism can illustrate its catalytic action, but certainly involves the production of sulphate radical.

$$Cu^{II}\text{-MOF} + S_2O_8^{-2} \longrightarrow Cu^{III}\text{-MOF} + SO_4^{-2} + SO_4^{\cdot-} \qquad (10)$$

Cu^{III}-MOF reacts then with another $S_2O_8^{-2}$ to produce Cu^{II}-MOF and $SO_4^{\cdot-}$.

$$\text{Azo dye} + SO_4^{\cdot-} \longrightarrow \text{Oxidation products} \qquad (11)$$

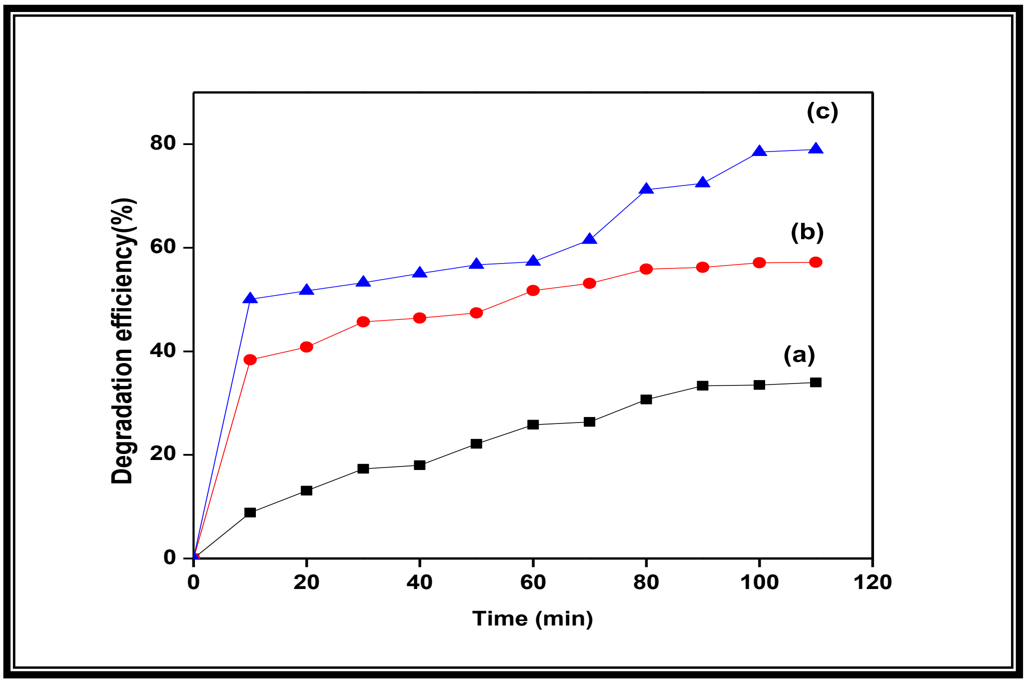


Fig.4 : Degradation efficiency of methyl orange as a function of time
(a) No catalyst, (b) In presence of complex 4
(c) In presence of complex 3

Conclusion

A number of mixed ligand coordination polymers were prepared from the reaction of some metal ions with 1,4-naphthalene dicarboxylate and two thiazoles. The coordination polymers were proved from the thermal decomposition that they possess a relative high stability. The catalytic behavior of the Cu(II) and Zn(II) compounds was tested and they exhibit high catalytic activities towards the degradation of methyl orange from 50-80%. Thus, these coordination polymers are good candidates as catalysts for dye degradation.

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