

Full Paper

Coordination properties and thermal studies of metal coordination polymers derived from 1,4-benzenedicarboxylate, imidazole or benzimidazole

Amna S. A. Zidan*, Aref A. M. Aly, Galal H. H. Ibrahim

Department of Chemistry, Faculty of Science, Assiut University, 71516 Assiut, (EGYPT).

E-mail: amna.zidan@yahoo.com

Article history: Received: 11/1/2015; Revised: - ; Accepted: 28/2/2015;
Available Online: 1/6/2015.

Abstract:

A number of new coordination polymers derived from Co(II), Cu(II) and Zn(II) with BDC=1,4-benzenedicarboxylate, Him = imidazole or Bimz = benzimidazole was prepared and characterized. The structure of the coordination polymers was assigned based on elemental analysis, FT-IR, electronic spectral studies, thermal analysis (TG, DTG and DTA), scanning electron microscope (SEM) and X-ray powder diffraction. The general formula of the complexes are $\{[M(\text{BDC})(\text{Him})(\text{H}_2\text{O})].x\text{H}_2\text{O}\}_n$ and $\{[M(\text{BDC})(\text{Bimz})_2].6\text{H}_2\text{O}\}_n$ where M = Co(II), Cu(II) or Zn(II), x= 5 or 7. During heating in dynamic air atmosphere, the complexes lose all water molecules in one step and the anhydrous compounds decompose stepwise to the corresponding oxides in the final step. The kinetic parameters were calculated making use of the Coats-Redfern and Horowitz-Metzger equations.

Keywords: Coordination polymers, Thermal studies, X-ray powder diffraction.

1. INTRODUCTION

In recent years, Metal-organic coordination polymers have attracted growing interest, due to their complicated molecular architectures and intriguing topology matrixes [1-3], as well as their potential applications in the areas of adsorption [4,5], electrochemistry [6] and catalysis [7]. 1,4-Benzenedicarboxylic acid is a versatile linear aromatic ligand, which can act as short bridges via one carboxylic group or long bridges via the benzene ring, leading

to abundant varieties of multidimensional coordination polymer [8]. A number of publications have dealt with the investigation of mixed ligand complexes comprising BDC and nitrogen donors [9]. Imidazoles are an important group of five-membered nitrogen heterocycles that have attracted much attention because of the participation in the structure of biological active molecule [10].

There are two nitrogen atoms in one imidazole molecule. The deprotonated nitrogen atom is suitable for binding to metal ions and a variety of metal complexes based on imidazole were reported [11-15]. On the other hand, the protonated nitrogen atom in imidazole molecule is a good hydrogen bonding donor and various superamolecular

assemblies could be obtained via hydrogen bonding interaction [16-21]. The aim of this investigation is to prepare some coordination polymers of Co(II), Cu(II) and Zn(II) with 1,4-benzenedicarboxylate, imidazole or benzimidazole and to study their spectroscopic and thermal decomposition behavior. The structures of the ligands are depicted in Figure 1.

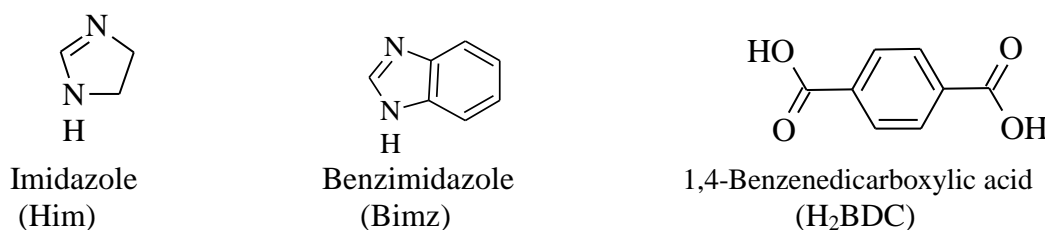


Fig. 1 Chemical structure of imidazole, benzimidazol and 1,4-benzenedicarboxylic acid.

2. EXPERIMENTAL

2.1 Materials and methods

High purity 1,4-benzenedicarboxylic acid, imidazole and benzimidazole were purchased from Sigma, Aldrich or Merck grade. All other chemicals were of AR grade.

2.2 Preparation of the coordination polymers

Preparation of the mixed ligand complexes of 1,4-benzenedicarboxylate and imidazole or benzimidazole with Co(II), Cu(II) and Zn(II) followed essentially the same procedure of [Co(BDC)(Him)(H₂O)].5H₂O is typical. Due to insolubility of 1,4-benzenedicarboxylic acid in water, the sodium salt was prepared (pH= 6.5) to obtain the soluble form of the ligand. The sodium salt (2.4ml) of the acid was added with stirring dropwise to an aqueous solution of CoCl₂.6H₂O(2.4ml). The auxiliary solution of imidazole (2.4 ml) was then added to the mixture. The mixture was refluxed and then cooled to room temperature. A pink precipitate separated which was filtered, washed with distilled water and dried over anhydrous CaCl₂.

2.3 Physical measurements

The stoichiometric analysis (C, H, N) were performed using Analyischer Funktionstest Vario El Fab- Nr.11982027 elemental analyzer. The IR spectra were recorded on a Shimadzu IR-470 spectrophotometer and the electronic spectra were obtained using a Shimadzu UV-2101 PC spectrophotometer. Thermal studies were carried out in dynamic air on a Shimadzu DTG 60-H thermal analyzer at a heating rate 10°C min⁻¹. The X-ray diffractometer was a Philips 1700 version with H.T. P.W1730 / 104KVA and the anode was Cu K α ($\lambda = 1.54180\text{\AA}$). The scanning electron microscope was a JEOLJFC-1100E ION SPUTTERING DEVICE; JEOLJSM-5400LV. SEM specimens were coated with gold to increase the conductivity.

3. RESULTS AND DISCUSSION

The complexes were prepared by the reaction of 1,4-benzenedicarboxylic acid (neutralized with NaOH) (pH=6.5), metal chlorides, and Him or Bimz (dissolved in EtOH). The prepared complexes were found to react in a molar ratio of 1:1:1 of metal ion, Na₂BDC and Him or in the molar ratio 1:1:2 of metal

ion, Na₂BDC and Bimz to yield the corresponding coordination polymers according to the following equations:



The different complexes which were prepared during the course of this investigation are

recorded in Table 1, along with their color, elemental analysis and melting points.

Table 1: Colors, elemental analysis and melting points of the compounds.

Compound	M. Wt	color	Found (calc.)			m.p. °C
			C%	H%	N%	
[Co(BDC)(Him)(H ₂ O)].5H ₂ O 1	398.90	Pink	33.79 (33.11)	4.84 (5.01)	7.26 (7.01)	207
[Cu(BDC)(Him)(H ₂ O)].7H ₂ O 2	439.53	Light-green	30.07 (30.05)	4.89 (5.46)	5.49 (6.37)	201
[Co(BDC)(Bimz) ₂].6H ₂ O 3	571.05	Pink	46.59 (46.26)	5.59 (5.60)	9.99 (9.80)	231
[Cu(BDC)(Bimz) ₂].6H ₂ O 4	575.66	Light-green	46.36 (45.89)	5.65 (5.55)	9.48 (9.72)	220
[Zn(BDC)(Bimz) ₂].6H ₂ O 5	571.81	White	46.35 (45.75)	5.55 (5.54)	9.25 (9.69)	241

3.1 IR spectra

The complexes were characterized by IR spectroscopy and the relevant bands are recorded in Table 2. The infrared spectrum of the Zn(II) complex **5** is depicted in Figure 2. The bands present in all complexes at 1560 - 1583 cm⁻¹ and 1386-1402 cm⁻¹ are assigned to the asymmetric and symmetric stretching vibrations of the carboxylate group and indicates that hydrogen was displaced by

the metal from the carboxylic group. Magnitudes of the separation (Δν) between the frequencies ν_{asym} (COO⁻) and ν_{sym} (COO⁻) in complexes are in the range 163 – 196 cm⁻¹, which suggest a bidentate mode of coordination for the carboxylate group [9]. The broad band around 3382-3566 cm⁻¹ in the IR spectra of all complexes is characteristic of ν (OH) of the water molecules [22] either coordinated or lattice water. The M-O and

M-N bonding are manifested by appearance of one band each at 510-580 and 420-431 cm^{-1} regions, respectively [23]. The infrared spectra

of the compounds show a band at 1600-1610 cm^{-1} corresponding to ν (C=N) [24] stretching frequency.

Table 2: Important IR bands of the complexes.

Complex	$\nu(\text{COO})_{\text{asym}}$	$\nu(\text{COO})_{\text{sym}}$	$\Delta\nu$	ν (C=N)	$\nu(\text{OH})$	ν (M-O)	ν (M-N)
1	1581	1402	179	1600	3416	517	430
2	1582	1386	196	1610	3560	580	420
3	1565	1397	168	1608	3414	510	423
4	1583	1400	183	1608	3566	553	431
5	1560	1397	163	1610	3382	510	425

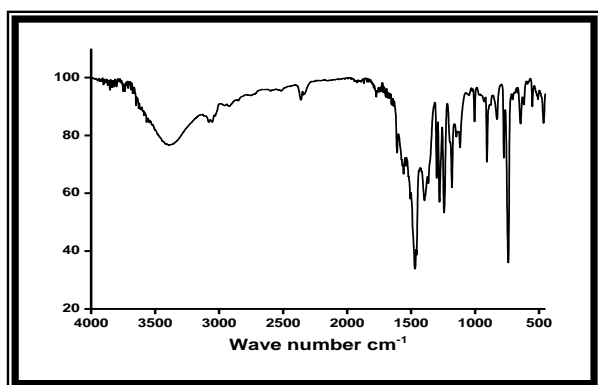


Fig. 2: FT-IR of $[\text{Zn}(\text{BDC})(\text{Bimz})_2] \cdot 6\text{H}_2\text{O}$.

3.2 Electronic spectra

The electronic spectral data of the prepared complexes in DMSO are summarized in Table 3. The Co(II) complexes **1** and **3** display a d-d transition at 15,417 and 17,825 cm^{-1} respectively. For the Cu(II) complexes **2** and **4** the d-d transition occurs at 14,417 and 16,132 cm^{-1} respectively. Moreover, the bands occurring in the two regions 36,363- 38,819 cm^{-1} and 25,473-28,573 cm^{-1} are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. The magnetic moment values for the two Co(II) complexes lie in the range 4.25-5.01 B.M and are closely related to the value expected for octahedral complexes [25]. The magnetic moment values found in the range 2.06-2.08 B.M for the Cu(II) complexes correspond to presence of one unpaired electron and typical for octahedral geometry around Cu(II)[26].

Table 3: Electronic spectral data of the complexes.

Complex	ν max (cm^{-1})	Assignment	μ_{eff} (B.M)
1	15,417 26,573 36,714	d - d $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	4.25
2	14,417 28,573 38,819	d - d $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	2.06
3	17,825 25,473 37,147	d - d $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	5.0
4	16,132 27,573 36,363	d - d $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	2.08
5	26,573 36,714	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	-

3.3 Thermogravimetric analysis

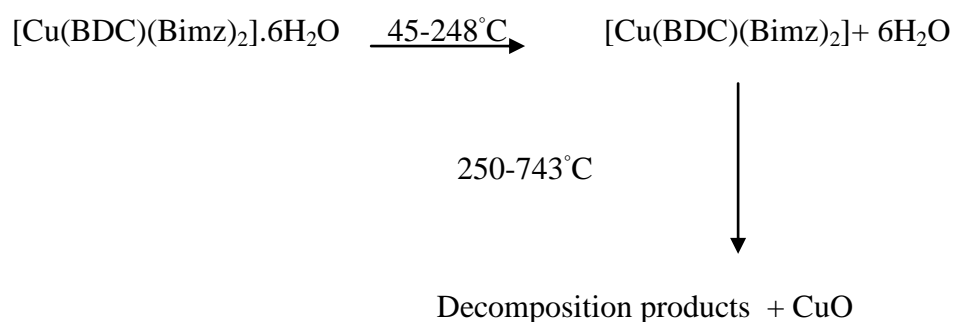
Thermogravimetric analysis of compounds **1** and **4** as representatives was performed. The thermal data are cited in Table 4. The results obtained from their thermal decomposition show them to be hydrated complexes. The thermal behavior of the copper complex **4** will be described. On heating in air atmosphere the complex loses all water molecules (calc. 18.9%, found 18.1%) (DTG peak at 192°C), for which a broad endothermic peak appears in the DTA curve at 194°C to form the anhy-

drous compound. The second and third steps correspond to the decomposition of Bimz and BDC ligands (calc.67.1%, found 66.9%) (DTG peaks at 316, 356°C). Their decomposition is characterized by a broad unsymmetric endothermic peak in the DTA curve at about 359°C. The final product was identified on the basis of mass loss consideration as CuO (calc.13.9%, found14.9%). Scheme 1 and Figure 3 illustrate the thermal behavior of this coordination polymer.

Table 4: Thermal decomposition data of compounds **1** and **4**.

Compound	Step	TG/DTG			Mass Loss (%)
		Ti	Tm	Tf	
1	1 st	30	259	302	25.9
	2 nd	304	620	745	56.7
4	1 st	45	192	248	18.1
	2 nd	250	316	344	24.1
	3 rd	346	356	743	42.8

Ti = Initial temperature, Tm = maximum temperature, Tf = final temperature



Scheme 1

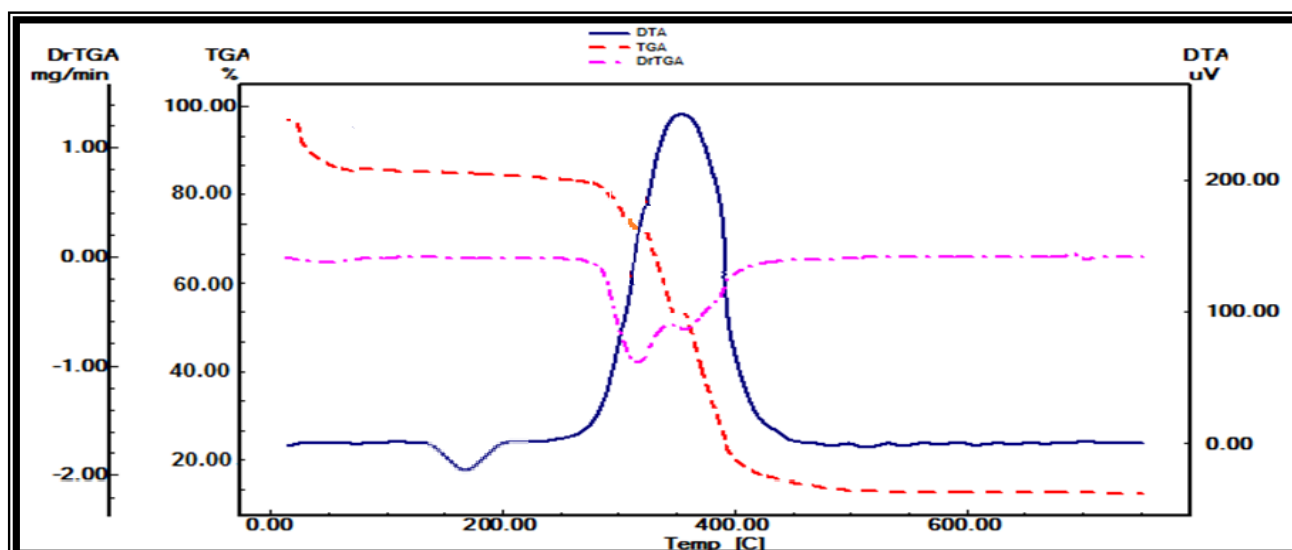


Fig. 3: TG, DTG, and DTA thermal analysis curves of compound 4.

3.4 Kinetic analysis

Nonisothermal kinetic analysis of the complexes were carried out by application of two different procedures:

(a) The Coats-Redfern equation

$$\ln[1 - (1 - \alpha)^{1-n} / (1 - n)T^2] = M/T + B \quad \text{for } n \neq 1 \quad (3)$$

$$\ln[-\ln(1 - \alpha)/T^2] = M/T + B \quad \text{for } n = 1 \quad (4)$$

where, α is the fraction of material decomposed, n is the order of the decomposition reaction, and $M = E/R$ and $B = ZR/\Phi E$, where E , R , Z , and Φ are the

The Coats-Redfern [27] and the Horowitz-Metzger [28] methods.

activation energy, gas constant, pre exponential factor, and heating rate, respectively.

(b) The Horowitz-Metzger equation

$$\ln[1 - (1 - \alpha)^{1-n} / 1 - n] = \ln ZRT_s^2 / \Phi E - E/RT_s + E\theta/R T_s^2 \quad \text{for } n \neq 1 \quad (5)$$

$$\ln[-\ln(1 - \alpha)] = E\theta/R T_s^2 \quad \text{for } n = 1 \quad (6)$$

where, $\theta = T - T_s$, and T_s is the temperature at the DTG peak. The kinetic and thermodynamic parameters for compounds **1** and **4** are calculated for the first step according to the above two

methods and cited in Tables 5 and 6. The thermodynamic parameters, namely entropy (ΔS^*), enthalpy (ΔH^*) and free energy (ΔG^*) of activation were calculated using the following standard relations:

$$\Delta S^* = R [\ln Zh / kT_s] \quad (7)$$

$$\Delta H^* = \Delta E - \Delta RT_s \quad (8)$$

$$\Delta G^* = \Delta H^* - \Delta T_s \Delta S^* \quad (9)$$

where h , Planck's constant, k , Boltzmann constant and R , gas constant.

Table 5: Kinetic parameters for the thermal decomposition of the compounds **1** and **4**.

compound	step	Coats–Redfern equation				Horowitz- Metzger equation			
		r	n	E	z	r	n	E	z
1	1 st	1.000	0.00	16.66	2.72×10^{-2}	0.998	0.00	21.65	21.79×10^4
		0.999	0.33	19.83	3.17×10^{-2}	0.999	0.33	31.45	15.13×10^4
		0.999	0.50	25.40	4.06×10^{-2}	1.000	0.50	37.89	12.63×10^4
		0.999	0.66	31.65	5.06×10^{-2}	0.998	0.66	44.56	10.80×10^4
		1.000	1.00	47.14	7.57×10^{-2}	1.000	1.00	61.86	83.63×10^3
		0.998	2.00	110.71	17.60×10^{-2}	0.998	2.00	128.89	40.23×10^3
4	1 st	1.000	0.00	76.07	12.22×10^{-2}	0.999	0.00	75.07	77.65×10^3
		0.999	0.33	94.14	15.07×10^{-2}	0.999	0.33	91.55	64.55×10^3
		0.999	0.50	105.55	16.86×10^{-2}	1.000	0.50	100.00	59.46×10^3
		0.999	0.66	116.96	18.64×10^{-2}	0.998	0.66	110.05	54.34×10^3
		0.998	1.00	141.69	22.49×10^{-2}	0.998	1.00	133.05	45.97×10^3
		1.000	2.00	156.81	24.82×10^{-2}	0.997	2.00	152.89	40.69×10^3

order (n), Z(s⁻¹), E (kJmol⁻¹).

Table 6: Thermodynamic parameters of compounds **1** and **4**.

compound	ΔS^*	ΔH^*	ΔG^*
1	-203.49	12.44	126.00
	-202.24	15.18	128.05
	-200.12	20.74	132.42
	-198.34	27.00	137.69
	-195.00	63.00	151.82
	-187.99	106.06	210.20
4	-191.72	71.02	187.44
	-189.98	89.09	204.45
	-189.05	100.50	215.29
	-188.21	111.91	226.16
	-186.60	136.64	249.94
	-185.83	151.76	298.67

ΔH^* and ΔG^* in kJmol⁻¹, ΔS^* in kJmol⁻¹K⁻¹.

Negative ΔS^* values for the first stage of decomposition of the coordination polymers suggest that the activated complex is more ordered than the reactants and the reactions are normal [29,30].

3.5 Calcination of [Co(BDC)(Bimz)₂].6H₂O

[Co(BDC)(Bimz)₂].6H₂O was subjected to calcination at 750°C for 2 hours. The oxide residue Co₃O₄ was confirmed by IR spectra and X-ray.

3.6 X-ray powder diffraction of the coordination polymers **1**, **4** and Co₃O₄

The X-ray powder diffraction patterns were recorded for the two coordination polymers [Co(BDC)(Him)(H₂O)].5H₂O and [Cu(BDC)(Bimz)₂].6H₂O and the oxide Co₃O₄ in Table 7 and Figures 4 and 5. The diffraction patterns indicate that the compounds are crystalline. The crystal lattice parameters were computed with

the aid of the computer program TREOR. The crystal data for the two compounds belong to crystal system triclinic and cubic for Co_3O_4 . Based on the XRD pattern, the peaks in the diffractogram can be indexed as (220), (311), (222), (400), (422), (511), (440), (531), (533) and (622). The phase purity of the cubic

$$D = K\lambda/\beta \cos \theta \quad (10)$$

where K is the shape factor, λ is the X-ray wavelength (typically 1.54 \AA), β is the line broadening at half the maximum intensity in radians, θ is the Bragg angle, and D is the

Co_3O_4 nanoparticles is thus obvious and no peaks of impurities are detected. The phase significant broadening of the peaks indicates that the particles are of a nanometer dimension. The particle size of compounds **1** and **4** as well as Co_3O_4 was calculated according to the Scherrer's equation:

mean size of the ordered (crystalline) domains, which may be smaller than or equal to the grain size.

Table 7: X-ray powder diffraction crystal data of the compounds.

Parameter	Compound 1	compound 4	Co_3O_4
Empirical formula	$[\text{Co}(\text{BDC})(\text{Him})(\text{H}_2\text{O})].5\text{H}_2\text{O}$	$[\text{Cu}(\text{BDC})(\text{Bimz})_2].6\text{H}_2\text{O}$	Co_3O_4
Formula Weight	398.90	575.66	240.79
Crystal System	Triclinic	Triclinic	Cubic
a (Å)	6.685	5.141	8.083
b (Å)	9.035	14.345	8.083
c (Å)	12.668	86.997	8.083
α	68.072	104.96	90.000
β	67.953	47.037	90.000
γ	100.814	80.555	90.000
Volume of unit cell(Å ³)	656.85	568.80	528.14
Particle size(nm)	18	12	22

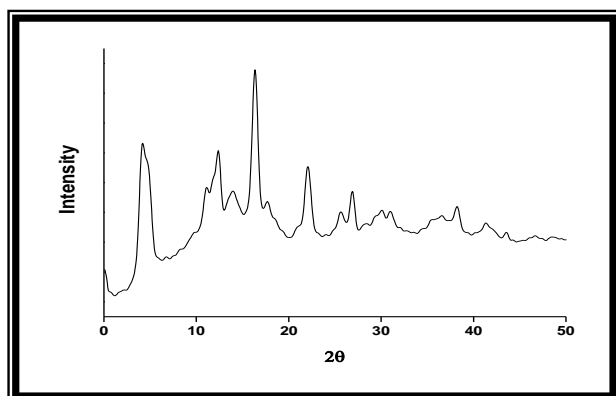


Fig. 4: X-ray diffraction pattern of $[\text{Cu}(\text{BDC})(\text{Bimz})_2].6\text{H}_2\text{O}$

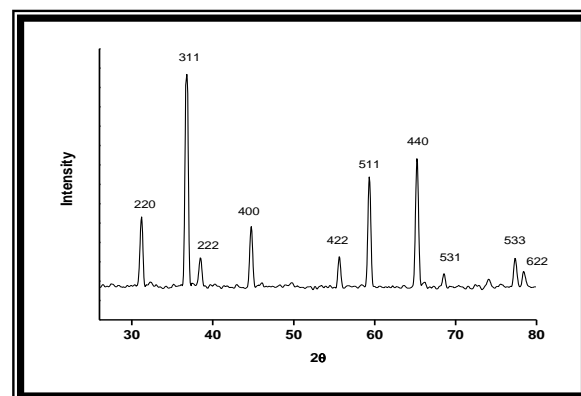
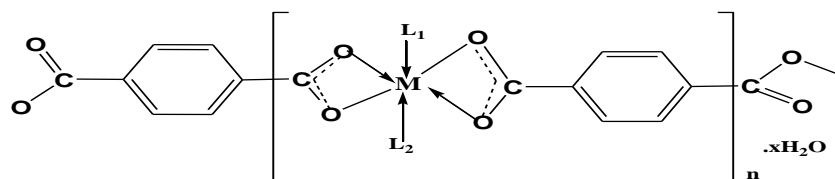


Fig. 5: X-ray diffraction pattern of Co_3O_4 nanoparticles.

From the foregoing discussion the general structure of the complexes can be illustrated in Figure 6.



M= Co(II), Cu(II) or Zn(II), L₁= H₂O or Bimz, L₂= Him or Bimz, x= 5, 6 or 7

Fig. 6: Structure of the complexes.

3.7 Scanning electron microscope (SEM)

The scanning electron microscope photograph of Co₃O₄ which was prepared by calcination of compound **3** is given in Figure 7. The particles are nearly spherical with some aggregation based on the SEM photograph and the average size of the particles is about ~80 nm.

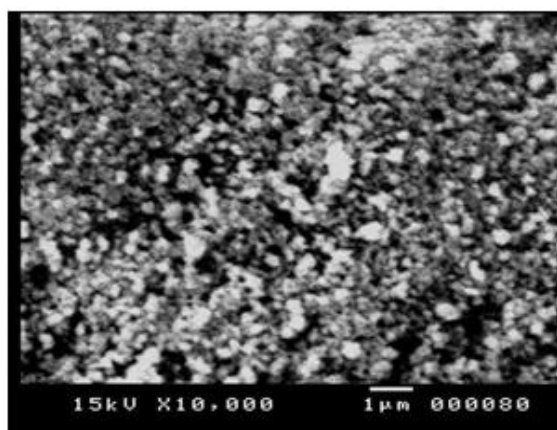


Fig.7: SEM of Co₃O₄ nanoparticles.

4. CONCLUSION

The prepared complexes comprise the metal ions Co(II), Cu(II) and Zn(II), 1,4-benzendicarboxylate, imidazole and benzimidazole. These mixed ligand coordination polymers constitute a complete series together with other mixed ligand complexes containing thiazoles reported in the literature. The compounds were fully characterized using spectroscopy methods, X-ray diffraction and thermal analysis, besides scanning electron microscopy.

References

- [1] P. Cui, M. YG, H. Li, B. Zhao, J. Li, P. Cheng, P. Balbuena, H. Zhou; *J Am Chem Soc* 134(2012)18892.
- [2] Y. He, Y. Tan, J. Zhang; *J Cryst Growth Des* 13(2013) 6.
- [3] H. Tsai, C. Yang, W. Wernsdorfer, S. Huang, S. Jhan, M. Liu, G. Lee ; *Inorg Chem* 51(2012)13171.
- [4] M. Mohamed, S. El saidi, L. Wojtas, T. Pham, K. Forrest, B. Tudor, M. Zaworotko; *J Am Chem Soc* 134(2012) 19556.
- [5] R. Yun, J. Duan, J. Bai, Y. Li; *Cryst Growth Des*13(2013) 24.
- [6] X. Wang, B. Mu, H. Lin, G. Liu, A. Tian, S. Yang; *CrystEngComm* 14(2012) 1001.
- [7] A. Bhunia, M. Gotthardt, M. Yadav, M. Gamer, A. fer, W. Kleist W, P. Roesky; *PW Chem Eur J* 19(2013) 1986.
- [8] J. Yao, X. Cao, L. Zhang, Y. Wang, J. Guo , C. Fan; *J Chem Crystallogr* 41(2011) 1400.
- [9] A. A. M. Aly, M. A. Ghandour, M. S. Al-fakeh; *J Turk Chem* 36 (2012)69.
- [10] J. Safari, S. Gandomi-Ravandi, Z. Akbari; *J of Advanced Research* 4 (2013)509.
- [11] N. Masciocchi, G. A. Ardizzoi, S. Brenna; *Chem.Commun.*16 (2000)2018.
- [12] F. Lambert, J. Renault, C. Policar; *Chem.Commun.*1 (2000)35.
- [13] X.C. Huang, J. Zhang, Y. Y. Lin; *Chem. Commune.*9 (2004)1100.
- [14] O. Sanchiz, Y. R. Martin, C. R. Perrez; *New J, Chem.* 11(2002)1624.
- [15] B. H. Ye, T. Mak, I D, Williams, and X.Y. Li; *J Chem. Soc., Dalton Trans., No. 12* (1998)1935.

- [16] A. M. Atria, P. Cortes, M. T. Garland, and R. Baggio; *Acta Crystalllogr., Sect. C59*, m396 (2003).
- [17] G. J. M. Ivarsson, W. Forsling; *Acta Crystalllogr., Sect. B 35* (1979)1896.
- [18] F. F. Jian, P. S. Zhao, H. L. Xiao, and S. S. Zhang; *Chin. J Chem.* 20 (2002)1134.
- [19] K. B. Shiu, C. H. Yen, F. L. Liao, and S.L. Wang; *Acta Crystallogr., Sec, E59*, m1189 (2003).
- [20] S. Y. Niu and Z. Z. Yan, *Chem; J. Chin, Univ*, 20(1999)1671.
- [21] P. S. Zhao, F. F. Jian, L. D. Lu; *Chin. J, Inorg. Chem.* 16 (2000)964.
- [22] G. B. Deacon and R. Philips; *Coord. Chem., Rev.*88 (1980) 227.
- [23] T. Rakha; *Synth. React. Inorg. Met. Org. Chem.*, 30(2000)205.
- [24] J. Q. Liu, W.P. Wu, Y.Y. Wang, W.H. Huang, W.H. Zhang, Q. Z. Shi, J.S. Miller; *Inorg. Chim. Acta*, 362 (2009)1291.
- [25] A. B. P. Lever; *Inorganic electronic conductivity*, (2nd Edition) Elsevier Amsterdam, (1986).
- [26] J. R. Anacona and C. Toledo, *Transition Met. Chem*, 26(2001)228.
- [27] A. Coats, J. Redfern; *Nature*, 20 (1964)68.
- [28] H. Horowitz, G. Metzger; *Anal. Chem.*, 35 (1963)1464.
- [29] G. G. Mohamed, W.M. Hosny, M. A. Abd El-Rahim; *Synth. React. Inorg. Met. Org. Chem.*, 32(2000)1501.
- [30] M. A. A. Beg, M. A. Qaiser; *Thermochim. Acta.*, 210 (1998)123.