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Synthesis, Properties and Thermal Stability of Metal Complexes Derived from Polyvinyl Alcohol and 2-Aminobenzothiazole

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ABSTRACT

New mixed metal complexes with general formula [M (PVA)(ABZ)(H_2O)$_3$], were M is Cobalt (II), Nickel (II), Zinc (II) and Cadmium (II), PVA = polyvinyl alcohol and ABZ is 2-aminobenzothiazole have been achieved and characterized. The structure of hybrid complexes were fully confirmed by spectroscopic data of FT-IR, electronic spectral studies, elemental analysis, magnetic measurements, thermal analysis, X-ray powder diffraction and scanning electron microscope. Thermogravimetry TG, DTG and DTA analysis have been employed to study the thermal decomposition of novel complexes. The kinetic study was parameters have been calculated making use of the Coats-Redfern equation.

Keywords: Hybrid complexes, spectral studies, XRD, SEM, thermal stability, polyvinyl alcohol, 2-aminobenzothiazole.

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INTRODUCTION

The organometallic polymer structure which contains metal centers is bound by ligands which can be employed and extend to all domains. It can also be described as a polymer that includes repeating units as coordination complexes and also called organometallic structures (MOFs) and coordination networks, with some inconsistency in the distinctions between terms [1]. Polymers play a essential role in several scientific fields and have been extended to organic, inorganic chemistry, biology, materials science, electrochemistry and pharmacology with a variety potential applications [2, 3].

Polyvinyl alcohol PVA well known as water-soluble and ecological polymer [4]. PVA is at the forefront of mechanical properties, chemical stability, non-toxic effect, biocompatible, biodegradable, flexibility and low cost, film-forming ability, high hydrophilic behavior [5, 6].

Cyclic complexes azole ring derivatives connected by metal ions have beneficial properties as antifungal, anticancer, antibacterial, antiallergic and antibiotic [7-10].

On the other hand, 2-aminobenzothiazole (ABZ) is known for their various clinical applications. It is employed currently in the preparation of metal complexes and become increasingly important as biochemical, analytical and antimicrobial reagents in molecular model design and materials chemistry [11-13].

In this paper, gathering the two patterns in one molecule and combining their properties was our purpose and presents a new way to increase the efficiency of biologically active molecules. Herein, we designed a new synthetic route to novel hybrid complexes of cobalt (II), nickel (II), zinc (II) and cadmium (II) containing polyvinyl alcohol and 2-aminobenzothiazole as ligands described for the first time.

Experimental

All chemical were of analytical grades. Polyvinyl alcohol was supplied from Sigma Aldrich. 2-aminobenzothiazole was purchased from Merck and was used without further purification.

Preparation Complexes of **[Co (PVA)(ABZ)(H_2O)$_3$] (1)**

Polyvinyl alcohol PVA (1g) was dissolved in 35 mL distilled water by vigorously stirring at 45°C for 1 h. After cooling, solution of $CoCl_2.6H_2O$ (2.69 g) in 20 mL of distilled water was added drop wise under quickly stirring. Then 2-aminobenzothiazole (ABZ) solution (1.7 g) in 25 mL of ethanol was added. The obtained mixture was refluxed for 2h and then cooled to room temperature. A pink solid was produced and separated by filtration, washed with distilled water and ethanol and dried over anhydrous calcium chloride.

Anal. Calc. for $C_{10}H_{16}N_2SCoO_5$: C, 35.84; H, 4.77; N, 8.36; S, 9.56. Found: C, 34.52; H, 4.10; N, 8.03; S, 9.05. IR data: ν (cm^{-1}) = 3388 (m), 3266 (m), 3052 (m), 2908 (m), 2726 (m), 1637 (s), 1523 (s), 1440 (s), 1305 (m), 1099 (s), 884 (m), 841 (m), 714 (m), 632 (s), 569 (m), 476 (m). m.p. 229°C.

Preparation Complexes of **[Ni (PVA)(ABZ)(H_2O)$_3$] (2)**

To a solution of ethanolic nickel (II) chloride hexahydrates (2.69 g) in 25 mL of ethanol was added a solution of PVA (1g) in 35 mL of water dropwise with stirring. Then solution aminobenzimidazole (1.7 g) in 25 mL ethanol was added to the mixture and refluxed. At the end of the reaction, the mixture was cooled, light green precipitate separated by filtration, washed with distilled water and EtOH and dried over anhydrous $CaCl_2$.

Anal. Calc. for $C_{10}H_{16}N_2SNiO_5$: C, 35.86; H, 4.78; N, 8.36; S, 9.57. Found: C, 34.90; H, 4.19; N, 8.16; S, 9.14. IR data: ν(cm^{-1}) = 3567 (m), 3339 (m), 3145 (m), 3044 (m), 2720 (m), 1614 (s), 1520 (m), 1409 (m), 1245 (m),1051 (m), 880 (m), 830 (m), 710 (m), 661 (s), 550 (m), 430 (m). m.p. 233°C.

Preparation Complexes of [Zn (PVA)(ABZ)$(H_2O)_3$] (3)

A solution of $ZnCl_2$ (1.54 g) in 20 mL of ethanol was added to a solution of PVA (1 g) in a distilled water 35 mL. Then a solution of 2-aminobenzothiazole (1.7 g) in 25 mL of ethanol was mixed and heated for 2 h, then gradually cooled to room temperature. A white precipitate was isolated.

Anal. Calc. for $C_{10}H_{16}N_2SZnO_5$: C, 35.16; H, 4.68; N, 8.20; S, 9.38. Found: C, 34.92; H, 4.85; N, 8.53; S, 9.06. IR data: ν (cm^{-1}) = 3344 (m), 3269 (m), 3078 (m), 2722 (m), 2360 (m), 1619 (s), 1524 (m), 1455 (s), 1343 (s), 1248 (m), 1128 (m), 1019 (m), 842 (m), 714 (s), 540 (m), 482 (m). m.p. 201°C.

Preparation Complexes of [Cd (PVA)(ABZ)$(H_2O)_3$] (4)

The procedure for the synthesis of complex **1** was adapted to the preparation of complexes **4** and $CoCl_2.6H_2O$ was replaced by $CdCl_2.H_2O$ (2.27 g). A white product was collected.

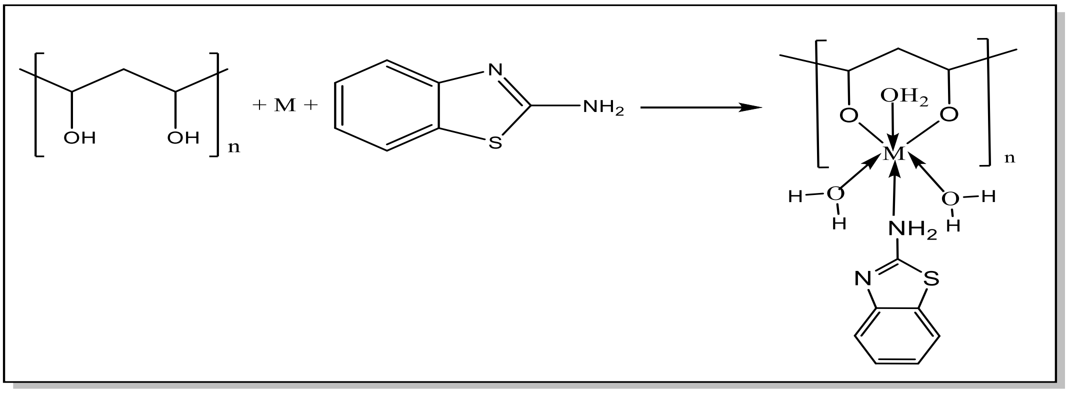
Anal. Calc. for $C_{10}H_{16}N_2SCdO_5$: C, 30.91; H, 4.12; N, 7.20; S, 8.25. Found: C, 30.32; H, 4.02; N, 7.01; S, 8.19. IR data: ν(cm^{-1})= 3433 (m), 3337(m), 3214 (m), 3022(m), 2710(m), 1615(s), 1526(s), 1456(s), 1338 (s), 1247(m), 1127(m), 1020(m), 841(m), 808(m), 717(s), 666(s), 545(m), 423(m). M.p. 190°C.

Physical measurements

The Measurements of ratio of carbon, hydrogen, nitrogen and sulfur contents of the solid complexes were accomplished by Elemental Analyzer system GmbhVario El analyzer. FT-IR spectra of the compounds were obtained by the KBr disc technique in the wavenumber range of 4000-400 cm^{-1}, using Thermo-Nicolet-6700 FT-IR spectrophotometer. The electronic absorption spectral measurements in the ultraviolet and visible regions were carried out in DMSO on a UV-2102 PC Shimadzu spectrophotometer using 1 cm matched quartz cell in the wavelength range 200-900 nm. The magnetic moments of the prepared cobalt (II) and nickel (II) complexes were measured at room temperature using a magnetic susceptibility balance of type MSB-Auto. The calibration of magnetic susceptibility balance was used with $Hg[Co(SCN)_4]$ as reference. Simultaneous TGA and DTA analyses were performed employing a Shimadzu DTG-60 instrument using a heating rate of 10 °C/min in air atmosphere. The average samples weight was 10 mg α-Al_2O_3 was used as a reference material in the DTA measurements. The X-ray powder diffraction patterns of the compounds were recorded an XRD diffractometer Model PW 1710 control unit the (Philips). The anode material was Cu Kα (λ = 1.54180 Å), 40 K.V 30 M.A Optics: Automatic divergence slit. The scanning electron microscope (SEM) was JEOL JFC-1100E ION SPUTTERING DEVICE, JEOL JSM-5400-LV SEM.

RESULTS AND DISCUSSION

The polymer complexes were prepared by the reaction of polyvinyl alcohol PVA, metal chlorides and 2-aminobenzothiazole dissolved in ethanol in proportion 1: 1: 1 showed in scheme 1.



Scheme 1: Synthesis of complex

The obtained complexes are stable in air, insoluble in common organic solvents but partially soluble in DMF and DMSO. All new polymer complexes were fully characterized by spectroscopic data of FTIR, electronic spectral studies, elemental analysis, magnetic measurements, thermal analysis, X-ray powder diffraction and scanning electron microscope. Thermogravimetry TG, DTG and DTA analysis have been employed to study the thermal decomposition of novel complexes. The kinetic study was parameters have been calculated making use of the Coats-Redfern equation.

The main IR frequencies can be seen in Table 1. The IR spectra of the prepared compounds show an important absorption peak in the range of 1127-1150 cm^{-1}, This bands have been used as an assessment tool of polyvinyl alcohol structure because it is a semi-crystalline synthetic polymer able to form some domains depending on several process parameters [14]. Furthermore, it is found that the occurring of hydrogen bonded O-H stretching [15] and anti-symmetric stretching vibrations of both CH_2 and C-O-C at (2908-2940 cm^{-1}) and (1127-1145 cm^{-1}) for all complexes respectively. In addition, polyvinyl alcohol cross-linked by Co(II), Ni(II), Zn(II) and Cd(II), the band maximum corresponding to bonded OH group at (3430 cm^{-1}), was shifted to lower frequencies; 3388, 3339, 3344 and 3337 cm^{-1}respectively. The stretching vibration of the amino group in free ABZ observed at 3220 cm^{-1} is shifted to a wave number and appears at (3052-3145 cm^{-1}) in the complexes suggesting coordination of the amino nitrogen to the metals (II) ions [16]. The 2-aminobenzothiazoles (ABZ) ligand showed band at 1640 cm^{-1} for the imine ν(C=N) group which results from the schiff base condensation of ABZ was shifted to a lower frequency of (1614-1637 cm^{-1}) after complexation [17-18]. Moreover, the appearance of new bands at 423-482 cm^{-1}and 519-565 cm^{-1} corresponds to ν (M-N) and ν (M-O) respectively [19] (Fig.1).

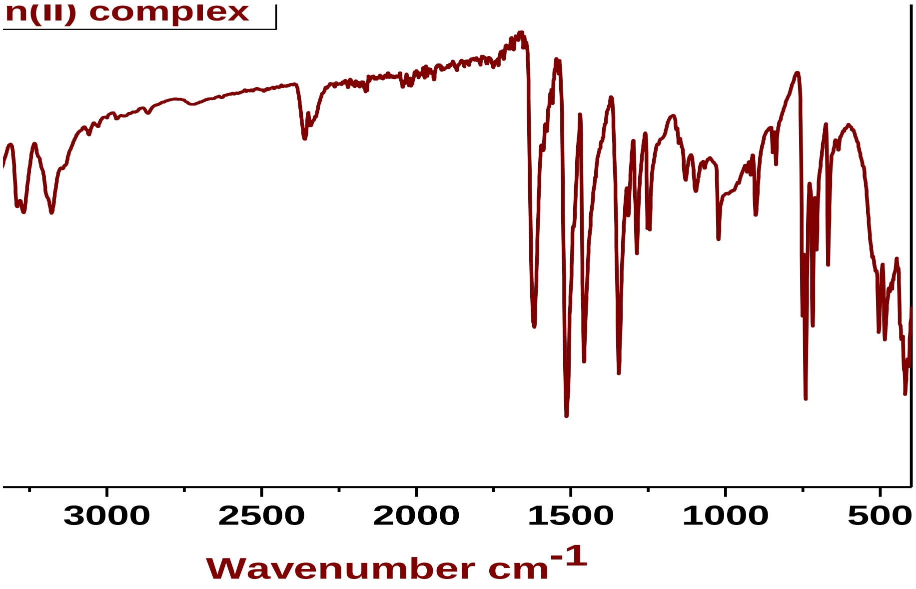


Figure 1: FTIR of Zn(II) complex.

Table 1: ***Characteristic FTIR bands of the complexes (in cm^{-1})***

Compounds	υ (OH)	υ (NH)	υ (CH)	υ (CO)	υ (C=N)	υ (M-N)	υ (M-O)
1	3388	3052	2908	1145	1637	476	529
2	3339	3145	2912	1130	1614	440	519
3	3344	3098	2910	1128	1619	482	565
4	3337	3110	2940	1127	1615	423	535

The UV-Vis spectra of the compounds have been recorded in DMSO. The spectra display two distinct bands in the ranges 33,396-34,498 and 25,974-27,397 cm^{-1} which attributed to π→π* and n→π* transitions within polyvinyl alcohol and 2-aminobenzothiazole moieties [20,21], respectively. In the visible spectra, there are characteristic bands attributed to the d-d transitions in the Co (II) and Ni(II) complexes typical of octahedral structures (Fig.2). Thus, complexes **1** and **2** exhibit a d-d band in the range 17,241-19,230cm^{-1}. Additionally, the magnetic moments of the Co (II) and Ni (II) compounds were measured and it has been found that the cobalt (II) complex **1** has a magnetic moment value of 4.51 B.M typical for octahedral complex [22] whereas the nickel (II) complex **2** has a magnetic moment value of 2.82 B.M closely related to the value expected for octahedral complex [23]. The results are shown in Table (2).

Table 2: ***Electronic spectral data of the compounds***

Compounds	ν_{max} (cm^{-1})	Assignment	μ_{eff} B.M.
1	17.241	d→d	4.51
	26.315	n - π^* transition	
	33.369	π- π^* transition	
2	19,230	d→d	2.82
	26.315	n - π^* transition	
	33.369	π- π^* transition	
3	26.178	π - π^* transition	-
	34.498	π- π^* transition	
4	25.974	n - π^* transition	-
	34.098	π- π^* transition	

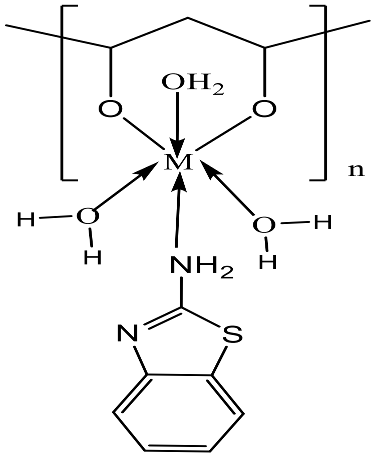


Figure 2: Structure of complexes [M(PVA)(ABZ)(H2O)3] and M (Co(II), Ni(II), Zn(II) and Cd(II))

The thermal decomposition of the complexes has been investigated in dynamic air from ambient temperature to 650 °C. As a representative the thermal behaviour of the cobalt complex will be described. The thermogram of the complex shows four decomposition stages. The first stage corresponds to the release of the three water molecules (calc. 16.11%, found 15.68 %). The DTG curve displays this step at 188°C and an endothermic peak appears at 190°C in the DTA trace. The second, third and forth steps correspond to the decomposition of ABZ and PVA. The final product was identified on the basis of mass loss consideration as CoO (calc. 22.36 %, found 20.12 %). As shown in Figure 3.

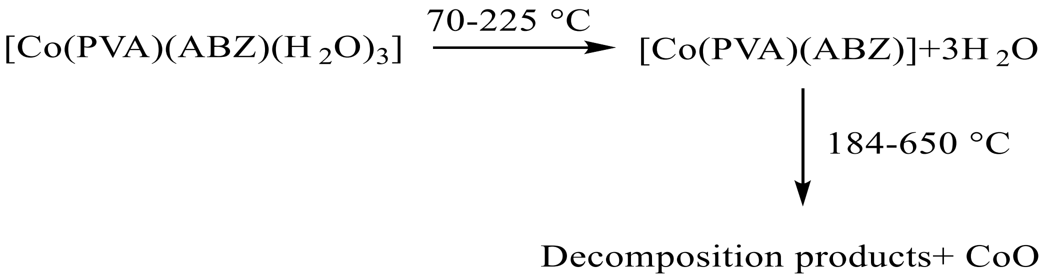


Figure 3: ***The thermal decomposition of the complexes***

The thermolysis of [Ni (PVA)(ABZ)(H_2O)$_3$] consists of four decomposition steps, In the first step the water molecules are released (calc. 16.12%, found 15.17 %). The corresponding DTG midpoint was seen at 165 °C and the corresponding endothermic effect appears at 168 °C. The second, third and fourth steps are related to decomposition of the rest of the compound. The DTG curve displays these three steps at 308, 420 and 523 °C with corresponding DTA exothermic peaks at 310, 422 and 525 °C respectively. The residue could be a nickel (II) oxide (NiO) (calc. 22.30 %, found 21.03 %). As shown in Figure 4.

Non-isothermal kinetic analysis of the complexes was carried out applying two different procedures: the Coats-Redfern [24] method.

Coats-Redfern equation

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

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

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

The correlation coefficient *r* is computed using the least squares method for equations (1) and (2). Linear curves were drawn for different values of n ranging from 0 to 2. The value of n, which gave the best fit, was chosen as the order parameter for the decomposition stage of interest. The kinetic parameters were calculated from the plots of the left hand side of equations (1) and (2) against 1/T (Fig.5).The kinetic parameters were calculated according to the above coats-redfern method and are cited in Table 3.

Table 3: ***Kinetic parameters for the first step thermal decomposition of the Co (II) and Ni (II) complexes***

Compound	Step	**Coats-Redfern equation**		
		r	n	E
1	1st	0.9998	0.00	24.72
		1.0000	0.33	32.80
		1.0000	0.50	37.08
		1.0000	0.66	41.84
		0.9999	1.00	53.25
		0.9996	2.00	94.14
2	1st	0.9994	0.00	20.27
		1.0000	0.33	24.40
		0.9999	0.50	29.79
		0.9998	0.66	35.50
		0.9992	1.00	50.40
		0.9973	2.00	110.31

E in kJ mol^{-1}.

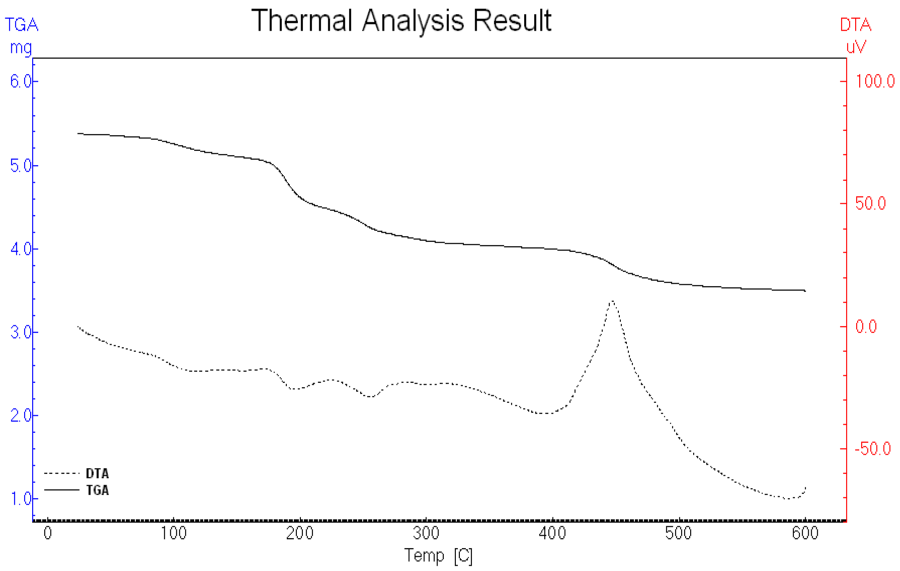


Figure 4: ***TG, DTG and DTA thermograms of Co(II) compound (in dynamic air).***

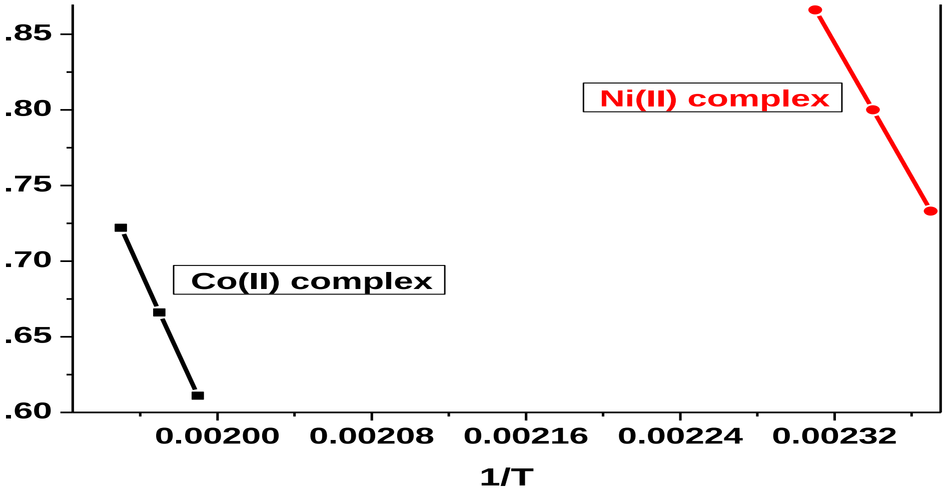


Figure 5: ***Coats-Redfern plots for Co(II) and Ni(II) complexes first step in dynamic air where Y=ln[1-(1-α)1-n /(1-α) T2] for n≠ 1 or Y=ln[-ln (1- α) / T2] for n=1.***

The X-ray powder diffraction patterns of complexes were recorded (Fig. 6). The crystal lattice parameters were computed with the aid of the computer program TREOR. The crystal data of the Ni (II) and Zn (II) mixed-ligand complexes belong to the crystal system Orthorhombic.

Scherrer's equation (3) was applied to estimate the particle size of the polymers:

$$D = K \lambda / \beta \cos\theta$$

where $\boldsymbol{K}$ is the shape factor, $\boldsymbol{\lambda}$ is the X-ray wavelength typically 1.54 Å, $\boldsymbol{\beta}$ is the line broadening at half the maximum intensity in radians and $\boldsymbol{\vartheta}$ is Bragg angle, $\boldsymbol{D}$ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size. The crystal data of compounds are recorded in Table (4).

Table 4: X-ray powder diffraction crystal data of the compounds

Parameters	Compound 2	Compound 3
Empirical formula	$C_{10}H_{16}N_2SNiO_5$	$C_{10}H_{16}N_2SZnO_5$
Crystal system	Orthorhombic	Orthorhombic
a (Å)	5.474	3.383
b (Å)	5.496	4.322
c (Å)	7.749	11.811
α (°)	90.00	90.00
β (°)	90.00	90.00
γ (°)	90.00	90.00
Volume of unit cell(Å3)	233.17	172.77

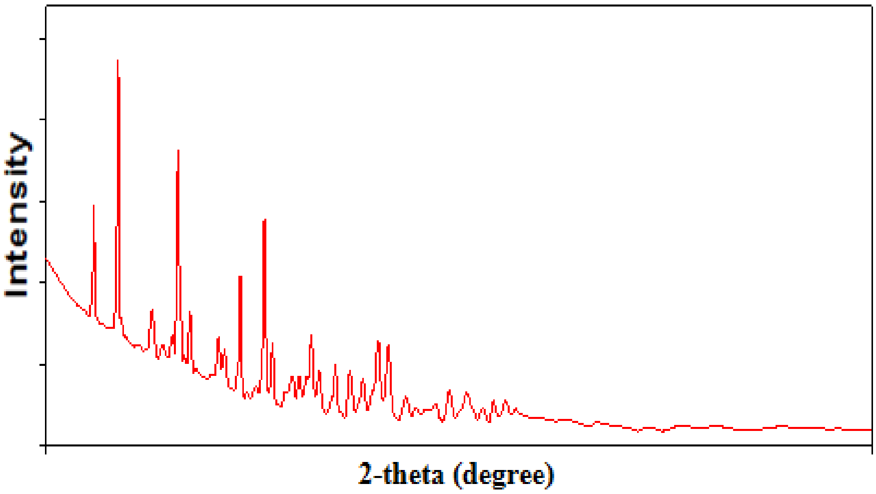


Figure 6: X-ray powder diffraction of Zn (II) compound

The scanning electron micrographs of Co(II),Ni(II), Zn(II) and Cd(II) mixed ligand complexes as representatives are given in Figures (7- 10).

These compounds are crystalline and the size of the particles is indicated under each figure in µm. The figures show the different morphologies of the complexes.

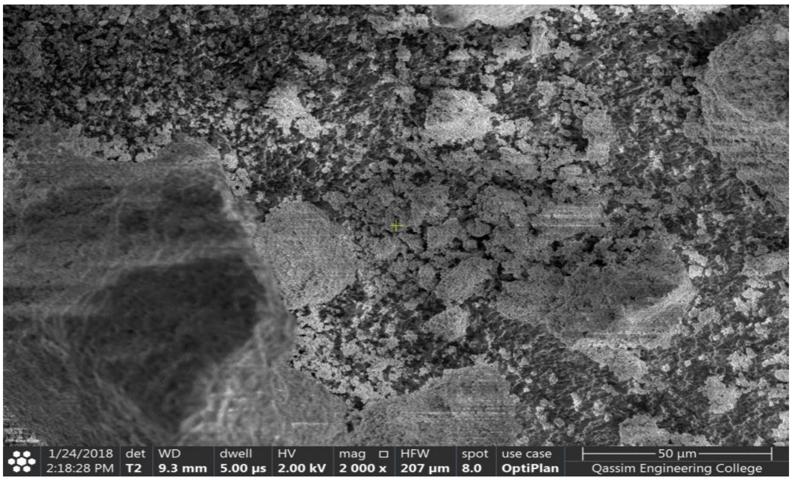


Figure 7: S.E.M of Co(II) compound.

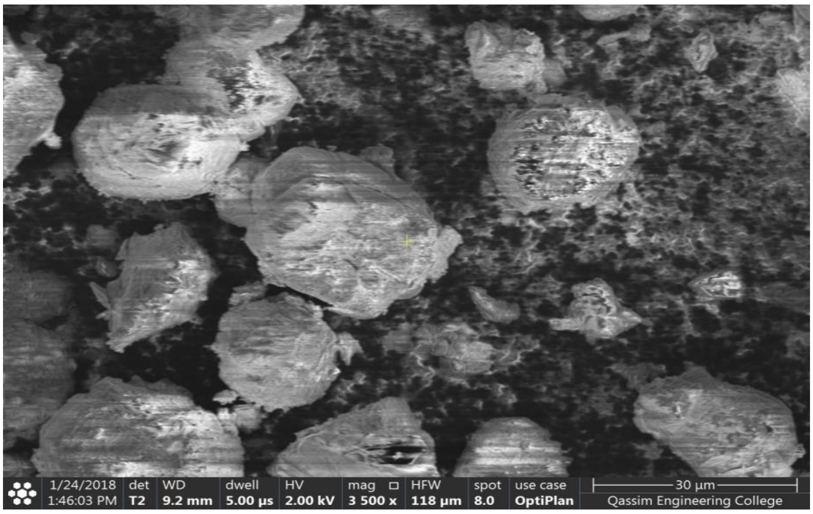


Figure 8: S.E.M of Ni(II) compound.

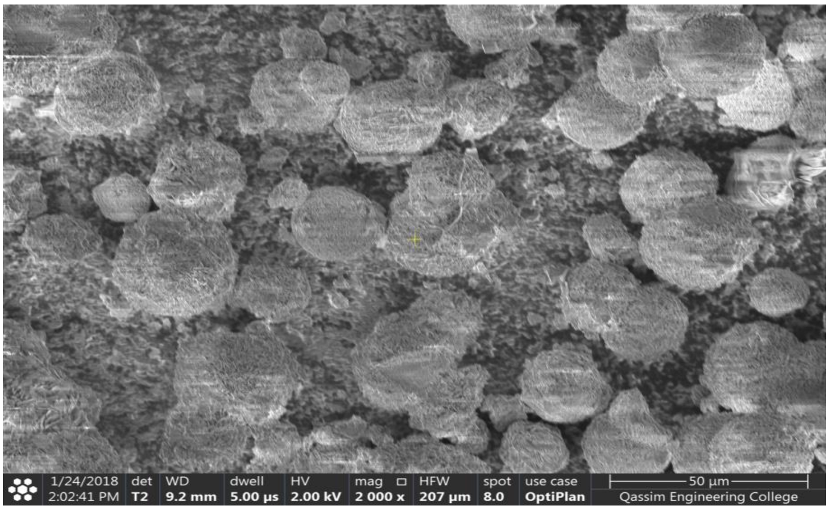


Figure 9: S.E.M of Zn(II) compound.

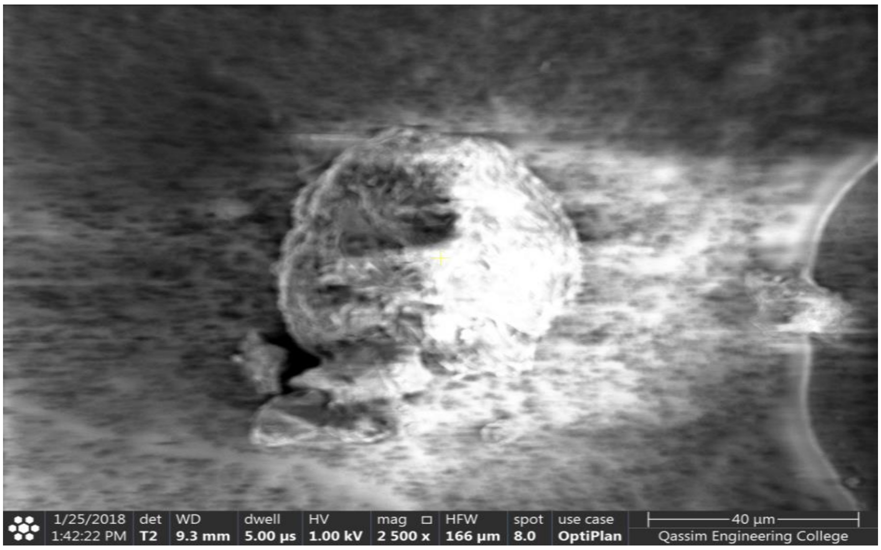


Figure 10: S. E. M of Cd(II) compound.

CONCLUSION

The present work synthesized and characterized mixed ligand complexes containing polyvinyl alcohol and 2-aminobenzothiazole with the metal ions Co (II), Ni (II), Zn(II) and Cd(II). The results show the formation of 1:1: 1 complex. The compounds are exhibit high thermal stabilities.

REFERENCES

[1] L. Carlucci, C. Gianfranco, M. Davide. Coordination polymers and supramolecular architectures book. (1999).

[2] K. Fromm, Coord. Chem. Rev. 252 (2008) 856.

[3] X. You, Coord. Chem. Rev. 359 (2006) 3257.

[4] A. Sinha, S.K. Das, V. Rao, P. Ramachandrarao, J. Mater. Res. 16 (2001) 1354–1357.

[5] Lebrun L., Silva A. D., Metayer M.: Elaboration ofion-exchange membranes with semi-interpenetratingpolymer networks containing poly(vinyl alcohol) as polymer matrix. Journal of Applied Polymer Science,84 (2002)1572–1580.

[6] Hirankumar G., Selvasekarapandian S., BhuvaneswariM. S., Baskaran R., Vijayakumar M.: AC impedancestudies on proton conducting polymer electrolyte complexes(PVA + CH3COONH4). Ionics, 10(2004)135–138.

[7] Rai, B.K. & Kumar, A. Synthesis, characterization and biocidal activity of some some schiff base and itsmetal complexes of Co(II), Cu(II) and Ni(II). Orient. J. Chem., 29(3) (2013) 1187-1191.

[8] Fugui, M.B., Ndahi, N.P. & Paul, B.B. & Mustapha, A.N. Synthesis, characterization, and antimicrobialstudies of some vanillin schiff base metal (II) complexes. J. Chem. Pharm. Res., 5(4)(2013) 22-28.

[9] Choudhary, A., Sharma, R. & Nagar, M. Synthesis, characterization and antimicrobial activity of mixedligand complexes of Co (II) and Cu (II) with N, O/S donor ligands and amino acids. Int. Res. J. Pharm. Pharmacol.,1(6)(2011) 172-187.

[10] Prakasha, R., Sharma, N., & Chaturvedi, K. Spectroscopic and antimicrobial studies of mixed ligandcomplexes of transition metal (II) ions with nitro quinoline and dibenzoyl methan. Sci. Revs. Chem. Commun.,2(2).(2012) 108-114.

[11] N. Raman, S.J. Raja, J. Joseph and J.D. Raja, J. Chil. Chem. Soc., 52(2) (2007) 1138-1141.

[12] R.R. Coombs, M.K. Ringer, J.M. Blacquiere, J.C. Smith, J.S. Neilsen, Yoon-Seo Uh, J.B. Gilbert, L.J. Leger, H. Zhang, A.M. Irving, S.L. Wheaton, C.M. Vogles, S.A. Westcott, A. Decken and F.J. Baerlocher, Trans. Met. Chem., 30 (2005) 411-418.

[13] M. A. Neelakantan, S.S. Marriappan, J. Dharmaraja, T. Jeyakumar and K. Muthukumaran, Spectrochim. Acta part A., 71 (2008) 628-635.

[14] Mansur HS, Oréfice RL, Mansur AAP. Characterization of poly(vinyl alcohol)/poly(ethylene glycol) hydrogels and PVA-derived hybrids by small-angle X-ray scattering and FTIR spectroscopy, Polymer. 45, 21 (2004) 7193-7202

[15] Z.M. Zaki, G.G. Mohamed, Spectrochimica Acta- Part A 26 (2000) 1245-1250.

[16] Maged S. Al-Fakeh, Synthesis and Characterization of Nanosized Uranyl Coordination Polymers derived from Terephthalic acid and Azoles, Orient. J. Chem., Vol. 32, 2(2016) 1155-1162.

[17] Neelakantan MA., Esakkiammal M., Marriappan SS., Dharmaraja J., Jeyakumar T. Indian J Pharm Sci. 72 (2010) 216.

[18] J. Joseph, G. Boomadevi Janaki, Synthesis, structural characterization and biological studies of copper complexeswith 2-aminobenzothiazole derivatives, J. Mater. Environ. Sci. 5 (3) (2014) 693-704.

[19] Raman N., Joseph J. Russian J. Inorg.Chem. 55 (2010) 1064.

[20] Kai-Ling Liang, Ya-Chi Wang, Wei-Li Lin and Jiang-Jen Lin, RSC Adv., 4 (2014) 15098.

[21] R. C. Maurya, R. Verma, H. Singh,Synth. React. in Inorg. and Metal-Org. Chem. 33:(2003)1063.

[22] A.B.P.Lever; Inorganic electronic conductivity, (2nd Edition)ElsevierAmsterdam, (1986).

[23] A. A. El-Asmy, M. Mounir, Transition Met. Chem., 13 (1988) 143.

[24] A. W. Coats and J. P. Redfern, Nature, 20 (1964) 68.