

## Synthesis and Characterization of Some New Coordination Polymers of Schiff Base Derived from Furfural

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**C** OORDINATION polymers of the Schiff base N,N bis-(Furan-2-ylmethylene)-1,4-phenylene diamine (BFMPDA) with zinc(II), cadmium(II) and cerium(III) have been prepared in dioxane medium. The optimal pH conditions for preparation the polymeric complexes were determined by potentiometry study. The stability constants of the complexes formed were calculated from the obtained potentiometric data. Polychelates polymers formed have been characterized on the basis of elemental analysis, infrared and electronic spectra. Glass transition temperature (T<sub>g</sub>) and thermal stabilities of the polymers have been investigated by carrying out differential scanning calorimetry and thermogravimetric analysis. Electrical conductivity measurements of the synthesized polychelated polymers showed that they are insulators. The metal contents in all polymers are found to be consistent with 1:1 metal : ligand stoichiometry. The solubility and viscosity of the polymer complexes were also determined. The surface of the synthesized polymers was examined by scanning electron microscopy.

**Keywords:** Polychelates, Zinc, Cadmium and cerium, Schiff base, Synthesis, Characterization and Potentiometric.

Coordination polymers are now of great interest <sup>(1-6)</sup>. The first example of the coordination polymer was reported by Arimato *et al.* <sup>(5)</sup> The formation of chelates by poly has widely been used for concentration, separation and extraction of metal ions <sup>(7-9)</sup>. The addition of metal ions to the polymers considerably improves the mechanical proportion and thermostability of the later. Many synthetic polymer-metal complexes exhibit high catalytic activity simulating the action of metal enzymes <sup>(10-12)</sup>. Organometalic and inorganic transition-metal compound have been used widely as flame retardant and smoke suppressants, dramatically increasing the resistance of various polymer to ignition and burning <sup>(13)</sup>. Much work has been done on the preparation of polychelates derived from poly Schiff bases <sup>(14-18)</sup>. Abd-El-Aziz <sup>(19-23)</sup> and other authors <sup>(24-27)</sup> presented reported several reviews on the syntheses and properties of metal containing and coordination polymers. Literature revealed that not any one have been reported the coordination polymers of the Schiff base ligand under investigation. Therefore, it was of interest to study the polymers of the

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Schiff base prepared from 1,4 phenylene diamine and furfural, because of its strong tendency to coordinate with the metal ions. Potentiometry being the classical and suitable method was used to search for the true equilibria, composition and the stability of the complex species in solution. This technique was used for determination the stability of coordination polymers<sup>(28,29)</sup>. Spectroscopic<sup>(30)</sup>, fluorescence spectra<sup>(31)</sup>, X-ray analysis<sup>(32)</sup>, ionic conductivity<sup>(33)</sup>, pH-effects on the complex formation<sup>(34)</sup>, thermogravimetry<sup>(35)</sup>..., etc have been used for the characterization of the coordination polymers and the system is apparently well known. The present paper describes the optimization of the complexation conditions reactions of N,N bis-(Furan-2-ylmethylene)-1,4-phenylene diamine (BFMPDA) towards Zn(II), Cd(II) and Ce(III) ions. The optimal pH values for the formation of the polymers were limited from potentiometric titrations<sup>(36,37)</sup>. The pH titration technique of Irving and Rossotti<sup>(38)</sup> was employed in this study. The measurements were carried out at 25°C, ionic strength of 0.1 mol dm<sup>-3</sup> (KNO<sub>3</sub>) in 50% (v/v) dioxane-water solution. The Schiff base acts as a tetradentate ligand bonding through the oxygen and nitrogen atoms. The resulting coordination polymers were characterized by elemental analysis, infrared and electronic spectra. Physical properties such as viscosity, solubility and electrical conductivity were also studied. High glass transition temperature indicated that the complexes in chain polymer. Electrical conductivity measurements proved that the complexes are non conducting polymers. The polymeric complexes examined by scanning electron microscopy (SEM).

## Experimental

### Materials

All chemicals were Analar chemically pure grade. The chemicals 1,4-phenylene diamine (para amino aniline), furfural (furaldehyde) which used for preparation the ligand N,N bis-(Furan-2-ylmethylene)-1,4-phenylene diamine (BFMPDA) were purchased from Sigma- Aldrich Chemicals Co., USA and were used as received. Different metal salts: zinc nitrate, cadmium nitrate tetrahydrate and cerium nitrate hexahydrate were purchased from Merck (Germany). HNO<sub>3</sub>, potassium nitrate, potassium hydroxide, potassium hydrophthalate, Borax, 1,4 dioxane, dimethylsulfoxide (DMSO) and dimethyl formamide (DMF) of Analar products were obtained from Sigma- Aldrich chem.Co., USA.

### Apparatus

pH measurements were carried out using a Corning 215 pH meter with a combined glass electrode. The glass electrode was calibrated before each titration with two Merck standard buffer solutions, first with the pH 7.0 followed by a pH 4.0 at 25°C by coupling the titration cell with a thermostatic bath set at this temperature. The elemental analysis were carried on a Perkin-Elmer 240 C instrument. The electronic spectra of DMF solutions of the ligand (BFMPDA) and its different metal complexes were recorded on a Perkin-Elmer (Lambda 35) computerized spectrophotometer equipped with 1 cm matched quartz cells. The Infrared spectra were performed by a Fourier transform Infrared spectrometer (FT-IR) analysis in the region 400-4000 cm<sup>-1</sup> with Jasco 480 spectrometer using

potassium bromide disk technique. NMR spectra were recorded in DMSO on Varian EM-360 L, 60 MHz, NMR spectrometer and JEOL FX 90 Q Fourier transform NMR. Thermogravimetric analysis TGA and differential scanning calorimeter DSC were carried out with a Shimadzu Thermal Analyzer 50 H at heating rate of 10°C/min in nitrogen atmosphere up to 750 °C. The solubility of polymers was determined using 0.01 g in 3-5 ml of solvent at room temperature. The inherent viscosities of the polymers solutions (0.5% w/v) in DMF were determined at 30°C using Ubbelohde Suspended Level Viscometer. Conductivities were measured at 25°C using HIOKI 3532 – 50 LCR Hi TESTER computerized electrometer as pellets between two standard graphite electrodes. The isolated polymer systems were investigated by the scanning electron microscopy (SEM) with a JEOL JSM 5400 LV.

*Synthesis of N,N bis-(Furan-2-ylmethylene)-1,4-phenylenediamine (BFMPDA)*

To a 500 cm<sup>3</sup> round-bottom flask a 100 ml ethanolic solution of 1,4-phenylenediamine (0.01 M) treated with furaldehyde (0.02 M). The mixture was stirred at room temperature for one hour after that the mixture was refluxed at 70°C on a water bath for three hours. On cooling a black compound precipitated out. The formed black crystals of the Schiff base ligand were collected and observed that it dissolved only in dioxane solution. The product was filtered, washed with ethanol and dried in air, yield 82%, m.p. 170°C. <sup>1</sup>HNMR (in DMSO): δ 8.0 - 8.5 (s, 2H, CH=N); 7.25 (m, 4Hφ); 7.62 (s, 2H, 5H of Fu); 6.57 (s, 2H, 4H of Fu); 6.98 (s, 2H, 3H of Fu). Analysis calculated for C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: C, 72.23%; H, 4.54%; N, 10.61%; O, 12.12%. Found: C, 72.73%; H, 4.52%; N, 10.63%; O, 12.23%. Mass spectrum of the Schiff base ligand N,N bis-(Furan-2-ylmethylene)-1,4-phenylene diamine (BFMPDA) (Fig. 1) exhibited a molecular peak at m/z 187; with abase peak at 264.76 C100%.

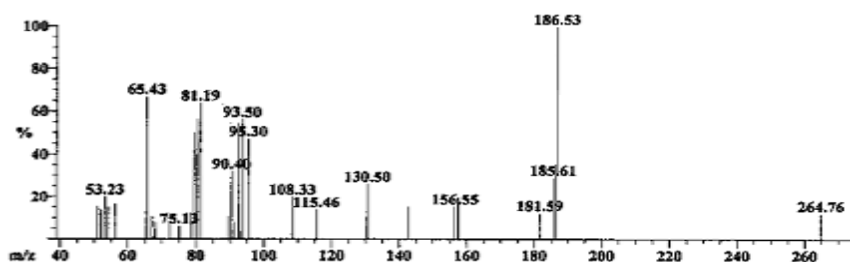
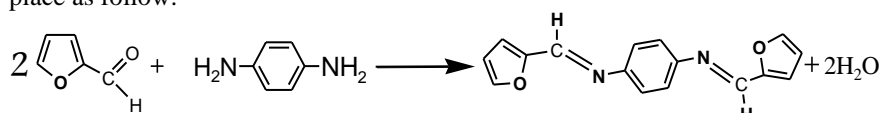


Fig. 1. Mass spectrum of BFMPDA.

The condensation involved in this study is the typical Schiff reaction take place as follow:



Figures 1,2. show <sup>1</sup>HNMR and FT-IR spectra of the product confirmed its regular linear structure.

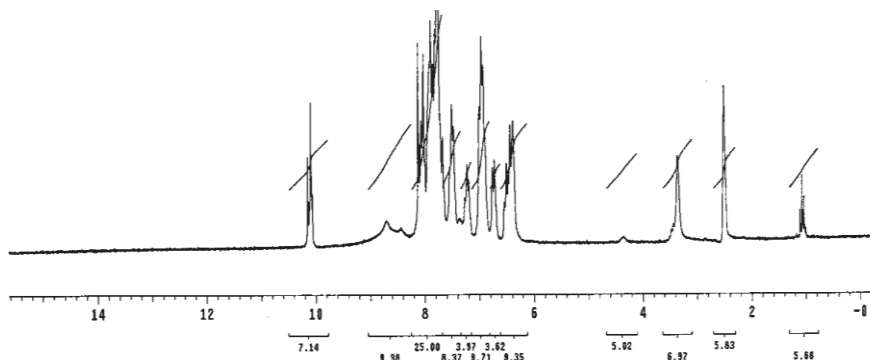


Fig. 2.  $^1\text{H-NMR}$  spectrum (in DMSO) of BFMPDA.

#### Potentiometric titrations

Dioxane and doubly distilled water were used for the preparation of the solutions. Potassium nitrate (1.0 M) and standard solutions (0.01 M) of potassium hydroxide and nitric acid were prepared. Standard stock solutions of Zn(II), Cd(II) or Ce(II) 0.02 M were prepared<sup>(39)</sup>. Each solution was diluted so as to prepare the standard solution. The ligand BFMPDA solution was prepared in dioxane, the ligand and the metal salt concentration was  $2.5 \times 10^{-3}$  M. The potentiometric equilibrium measurements were made on  $5.00 \text{ cm}^3$  of the ligand solutions diluted to a final volume of  $50.00 \text{ cm}^3$ , in the presence and absence of metal ion for which the  $C_M:C_L$  ratio were 1:1 and 1:2 in 50% (v/v) dioxane-water solution, at  $25^\circ\text{C}$  and the ionic strength was adjusted with  $0.1 \text{ mol dm}^{-3}$  ( $\text{KNO}_3$ ) in each case. The pH titration technique of Irving and Rossotti<sup>(38)</sup> was applied. The pH values in the partially aqueous solutions were corrected by using the equation which described previously<sup>(40)</sup>. All the dissociation and the complex formation constants were determined using the SUPERQUAD program<sup>(41)</sup>. The program has been used to calculate acidity constants in systems previously studied<sup>(42-44)</sup>. The protons association constants  $\text{p}K_1$  and  $\text{p}K_2$  were determined by potentiometric titration of 50 ml of 0.30 mmol  $\text{HNO}_3$  and  $\text{KNO}_3$  ( $I=0.1 \text{ M}$ ) with carbonate free potassium hydroxide. The stability constants for the binary Zn(II), Cd(II) or Ce(III)-BFMPDA complexes were computed from titration curves in which the metal concentration was  $8 \times 10^{-5}$  M. Multiple titrations were carried out for each system.

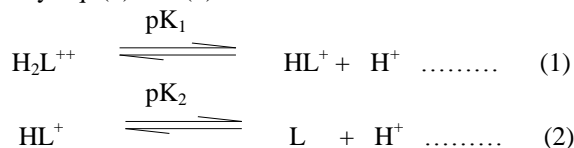
#### Syntheses of Zn(II), Cd(II) and Ce(III)-(BFMPDA) binary system

All the coordination complexes were prepared by a condensation between equimolar amounts of the ligand (BFMPDA) in dioxane solution with nitrate salt of zinc(II), cadmium(II) or cerium(III) in 2.0 mmol in of doubly distilled water for 24hr, with adjusted pH degree at 6.30, 7.9 and 6.10, respectively by adding aqueous potassium hydroxide. Every mixture was stirred under with heating on a water bath at a constant temperature of  $70^\circ\text{C}$  then concentrated by evaporation to its half volume and left to cool to room temperature overnight. Each complex was filtered off on a water pump and the obtained metal chelates washed several times with doubly distilled water,  $\text{Et}_2\text{O}$ , and ethanol and finally dried in vacuum over  $\text{P}_4\text{O}_{10}$ .

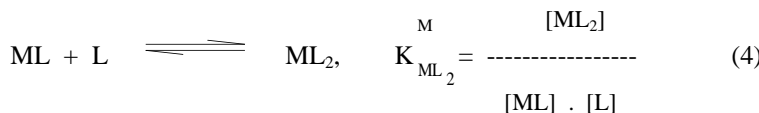
**Results and Discussion**

*Potentiometric titrations*

The acid-base properties of the Schiff base ligand N,N bis-(Furan-2-ylmethylene)-1,4-phenylene diamine (BFMPDA) in 50% dioxane-water mixture solution, Temp. 25°C, I=0.1M (KNO<sub>3</sub>); yield three forms, H<sub>2</sub>L<sup>2+</sup>, HL<sup>+</sup> and L. The predominant form of the ligand is the dicationic species, which undergoes stepwise ionization on increasing the pH of solution. pK<sub>1</sub> and pK<sub>2</sub> values for (BFMPDA) are 5.9 and 10.77, respectively. The protonation equilibria of ligand (L) can be represented by Eq. (1) and (2).



The obtained curves showed the potentiometric pH profiles of a solution of 2.5X10<sup>-4</sup>M of BFMPDA in the absence and in the presence of various metal ions. The potentiometric titration curve for BFMPDA in the cationic form H<sub>2</sub>L<sup>2+</sup> shows a two inflections at a = 1 followed by a moderate inflection at a = 2 (a = moles of base added per mole of ligand ) corresponding the stepwise dissociation constants of the ligand. The titration curve for a system containing 1:1 or 1:2 molar ratio of Zn(II), Cd(II) or Ce(III) and dicationic BFMPDA exhibits two inflections at m = 1 and m = 2 ( m = moles of base added per mole of metal ion) indicating the formation of mono and bis-binary complexes. But the ligand BFMPDA containing two centers of binding groups each one has O and N atoms, this means that every ligand molecule bonded with two metal ions gives two five member rings. This proves that the composition of the polychelates confirmed as 1:1 (M : L) complex. The study revealed the optimal pH conditions for formation of a complex with Zn(II), Cd(II) or Ce(III): BFMPDA ratio of 1 : 1 is 6.30, 7.9 and 6.10, respectively. The stability constants for binary complexes, as depicted from the titration curves are given in Table 1. The complexed species found in this work for BFMPDA and the studied metal ions can be represented by the following Eqs. 3 and 4:



*Absorption spectra*

The absorption spectra of 2.5X10<sup>-4</sup>M solution of the reagent (BFMPDA) were recorded as the dependence of A = F(λ) for various pH in the presence of 50% dioxane. The spectra showed two absorption bands with the pH range 3–11.5. The first band observed at pH range 3-8.3 at λ=340 nm and is presumably due to the absorption of dicationic molecules of the compound. At higher pH values > 8.4 the absorption decreases in intensity and a new band appears at 360 nm. This

band corresponding to absorption by the monocationic form of BFMPDA. The wavelength U.V.-visible region spectra suggests that the contribution to conjugation, and this to the reduction of the energy association with the lowest  $\pi$ - $\pi^*$  transition. The absorption spectra of M-BFMPDA in 1: 1 molar ratio ( $2.5 \times 10^{-4} \text{M}$ ) complex with the reagent as reference in dioxane are characterized by an absorption maxima at 420 nm for Zn(II), Cd(II) and Ce(III) complexes. On comparison the electronic absorption spectra of the free ligand BFMPDA with those of the chelates of Zn(II) or Cd(II) or Ce(III) proved shifted of the ligand spectrum band at 360 nm to longer wavelength showed that coordination of the metal ions to the ligand.

**TABLE 1. Logarithms of the stability constants of binary complexes containing 1:1 ratio of metal ions with the schiff base N,N bis-(furan-2-ylmethylene)-1,4-phenylenediamine(BFMPDA).**

Metal ion	$\log k_{ML}^M$	$\log k_{ML_2}^{ML}$	$\log \beta_{ML_2}^{ML}$
Zn(II)	8.85	8.34	17.19
Cd(II)	6.52	6.26	12.78
Ce(III)	8.58	8.25	16.83

#### *Microchemical analysis and electrical conductivity*

The molar conductance values of  $10^{-3} \text{M}$  of 1:1 (M:L) ratio of zinc(II), cadmium(II) and cerium(III)-(BFMPDA) in dioxane solution, at room temperature were found 4.1, 3.98 and 4.04  $\text{ohm}^{-1} \text{mol}^{-1} \text{cm}^{-1}$ , respectively. This indicates that all polychelates are insulator.

The electrical conductivities of the various complexes at room temperature are summarized in Table 2. The electrical conductivity of the divalent Zn(II) and Cd(II) and the trivalent Ce(III) metal ion complexes lies in the range  $6.555 \times 10^{-12}$  and  $6.784 \times 10^{-10} \Omega^{-1} \text{cm}^{-1}$ . The data reveals that the coordination polymers are poor electrical conductors. The Microchemical analysis data are listed in Table 2, and help for suggested the structure formula of the poly chelates. The data reveals that the coordination polymers are poor electrical conductors.

#### *FT-IR Spectrum*

The FT-IR spectrum of the ligand BFMPDA (Fig. 3) shows the important peaks at 3100, 1509, 1013, 824,  $750 \text{cm}^{-1}$  which attributed to the stretching of the five heterocycle ring (furan ring breathing mode)<sup>(45)</sup>. The weak peaks at 2924 and  $2900 \text{cm}^{-1}$  were attributed to the asymmetrical and symmetrical C-H stretching of methylene groups. Another important peak occurs at  $1617 \text{cm}^{-1}$  attributed to  $\nu_{(\text{C}=\text{N})}$  stretching mode<sup>(46)</sup>. The ligand BFMPDA is expected to act as a tetradentate with possible coordination sites being azomethinic-nitrogen and heterocyclic oxygen. By a comparison of its spectra with those of the polychelates (Fig. 4-6), the band occurs at  $1617 \text{cm}^{-1}$  which attributed to  $\nu_{(\text{C}=\text{N})}$  stretching mode, this band is shifted to a lower wave number and appears at 1607, 1600 and  $1590 \text{cm}^{-1}$  in the IR spectrum of Zn(II), Cd(II) and Ce(III) complex, respectively. This indicates the involvement of the N-atom of the azomethine in coordination<sup>(47)</sup>. The peaks at *Egypt. J. Chem.* **54**, No.3 (2011)

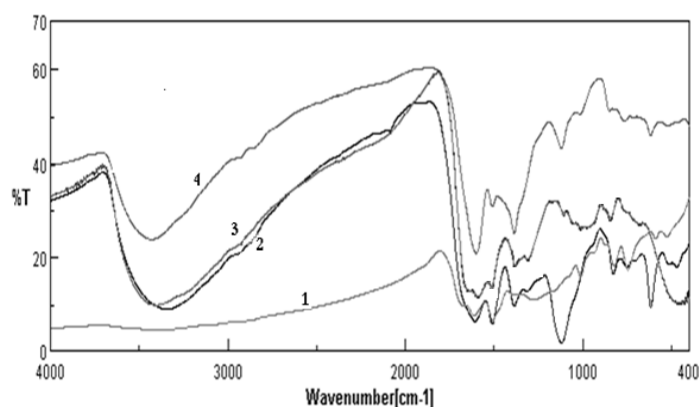
3100, 1509, 1013, 824, 750  $\text{cm}^{-1}$  assigned to the ring stretching of the five membered ring undergoes, the peak at 3100  $\text{cm}^{-1}$  disappeared in the spectra of all coordination polymers, while the peak at 1509  $\text{cm}^{-1}$  is found in the same region due to a decrease in electron density of the ring on complexation. The appearance of new strong band in the spectra of the complexes at 1385  $\text{cm}^{-1}$  is attributed to the free nitrate ion. The absorption bands occurring in the regions 1130 – 1115 and 850 – 828  $\text{cm}^{-1}$  which are not present in the spectra of free ligand, suggest the nitrate groups are coordinated mono dentately in the subject complexes. The presence of water can be detected by the characteristic band in the 3562 – 3360  $\text{cm}^{-1}$  region in the spectra of the three complexes. The stretching vibrations  $\nu_{(M-N)}$  are observed around 500 and the bands in the far infrared region in the 468 – 400 range are assigned to  $\nu_{(M-O)}$  modes. All the complexes have similar IR spectra (Table 3), indicating that they have similar structures.

**TABLE 2. Some physical and electrical conductivity of the ligand BFYMDA and Its Zn(II), Cd(II) and Ce(III) polychelates.**

Chelate Empirical Formula	Colour	Yield %	M.P (°C)	Found (Calc.) %			<sup>a</sup> $\eta_{inh}$ (dl/g)	Electrical Conductivity (ohm $\text{cm}^{-1}$ )	<sup>b</sup> M.W.
				C	H	N			
$\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2$	black	82	170	72.72 75.88	4.54 5.10	10.60 8.90	0.89	$7.82 \times 10^{-13}$	264
$[\text{ZnC}_{16}\text{H}_{10}\text{N}_2\text{O}_2 \cdot \text{H}_2\text{O}]_n$	black	85	>360	55.59 60.81	3.47 4.08	8.11 7.09	0.54	$7.112 \times 10^{-11}$	345.39
$[\text{CdC}_{16}\text{H}_{10}\text{N}_2\text{O}_2 \cdot \text{H}_2\text{O}]_n$	dark brown	89	>360	48.93 53.99 53.97	3.06 3.57 3.62	7.14 6.27 6.3	0.46	$6.555 \times 10^{-12}$	392.41
$[\text{CeNO}_3\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2 \cdot \text{H}_2\text{O}]_n$	dark brown	87	>360	42.14 44.33 44.49	2.63 2.94 2.98	9.22 5.1 5.1	0.47	$6.784 \times 10^{-10}$	455.65

<sup>a</sup> $\eta$  = inherent viscosity

<sup>b</sup>M.W. = molecular weight of repeat unit.



**Fig. 3. FT-IR absorption spectra of (1) the ligand BFMPDA, (2)  $\text{Zn}^{\text{II}}$ -BFMPDA, (3)  $\text{Ce}^{\text{III}}$ -BFMPDA and (4)  $\text{Cd}^{\text{II}}$ -BFMPDA.**

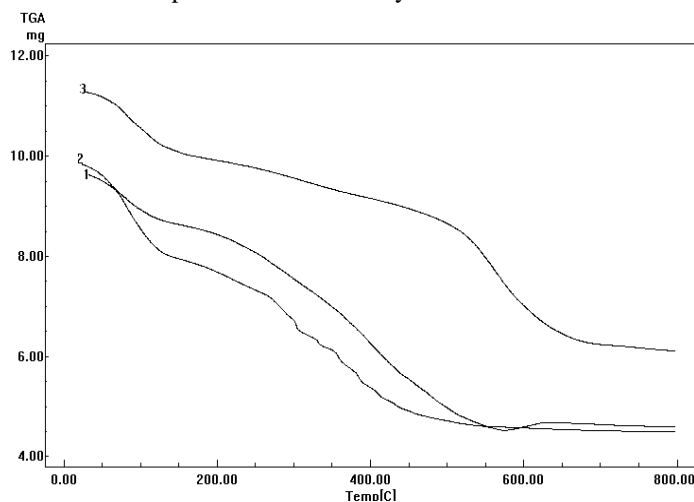
TABLE 3. IR bands ( $\text{cm}^{-1}$ ) of ligand BFYMDA, Zn(II)-BFYMDA, Cd(II)-BFYMDA and Ce(III)-BFYMDA.

Compound	$\nu$ (ring stretching of the five membered ring )					$\nu(\text{C}=\text{N})$	$\nu(\text{HOH})$	$\nu(\text{NO}_3)^-$	$\nu_a(\text{NO}_2)$	$\nu_s(\text{NO}_2)$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
BFYMDA	3100	1509	1013	824	750	1617	-	-	-	-	-	-
Zn(II)-BFYMDA	-	1509	-	-	750	1607	3341	1387	1116	828	513	468
Cd(II)-BFYMDA	-	1509	-	-	763	1600	3428	1386	1119	851	510	410
Ce(III)-BFYMDA	-	-	1013	-	750	1591	3407	1383	1118	846	530	469



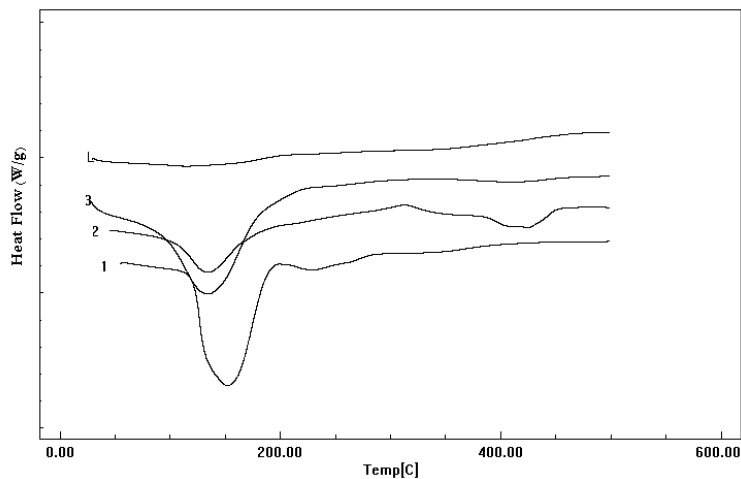
*Thermal analysis and differential scanning calorimeter*

In order to obtain convincing evidence for suggested formula of synthesized complexes, thermogravimetric analysis TGA of these complexes have been carried out under nitrogen atmosphere. Thermogravimetry of three polychelates reveals the variation of thermal stability. The obtained TG curves (Fig.4) show that the three polychelates of BFMPDA decompose in a similar way, the weight loss corresponds to amounts 3.7%, 3.5% and 5.32% can be attributed to elimination of one, one and two crystallization water molecules for Zn(II), Cd(II) and Ce(III) complex, respectively. The weight loss in the temperature 120-190°C can be attributed to the removal of one coordinated water molecule. The thermal decomposition of these curves suggests that above 200 °C the compounds start to loss mass with partial evaporation of the organic ligand. The TG thermograms indicate that the polychelates decompose in two stages, and that the rate of degradation in the second stage is fast compared to the first stage. The other decomposition step, the weight loss can be attributed to the removal of NO<sub>2</sub> molecules of the two and three coordinated nitrate groups for Zn(II), Cd(II) and Ce(III) complex, respectively. The metal oxide is the finally product and the TG data shows that the complex Ce-BFYMDA system is the most thermal stability.



**Fig. 4. Thermogravimetric curves of polychelates: 1) Zn(BFYMDA)(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O), 2) Cd(BFYMDA)(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O), 3) Ce(BFYMDA)(NO<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O).**

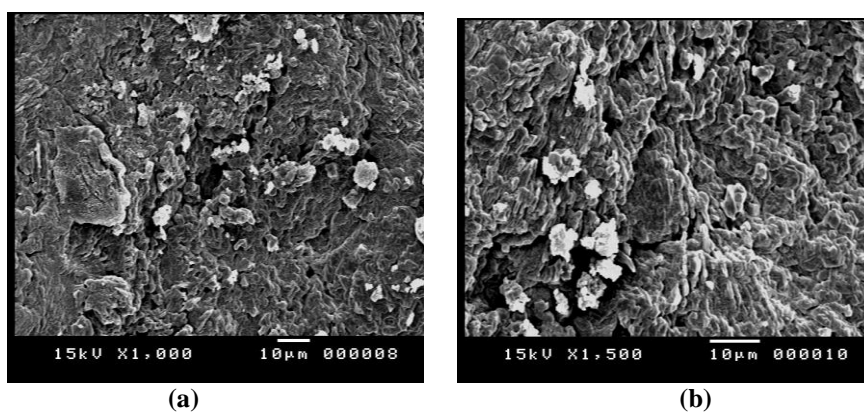
In the DSC curves the glass transition zone was determined as the temperature range between two intersection points of the base line with the extrapolated sloping portion of the thermogram, which resulted from a heat capacity change. Tg was defined as the inflection point of the curve. The DSC thermogram of the resulting polychelates Zn-BFMPDA, Cd-BFMPDA and Ce-BFMPDA samples is shown in Fig. 5. The values of their glass transition temperature (T<sub>g</sub>) are 135, 125 and 110 for Zn(II), Cd(II) and Ce(III) polychelates, respectively. The synthesized coordination polymers show a single T<sub>g</sub>, showing the absence of formation of mixture of homopolymer.



**Fig. 5. DSC Thermograms of Coordination polymers: 1)  $\text{Zn}(\text{BFYMDA})(\text{NO}_3)_2(\text{H}_2\text{O})$ , 2)  $\text{Cd}(\text{BFYMDA})(\text{NO}_3)_2(\text{H}_2\text{O})$ , 3)  $\text{Ce}(\text{BFYMDA})(\text{NO}_3)_3(\text{H}_2\text{O})$ .**

Scanning electron microscopic (SEM) images of the resulting polychelates Zn-BFMPDA, Cd-BFMPDA and Ce-BFMPDA samples are shown in Fig. 6-8. Hence, the morphological features of the surface are another convincing evidence proved that the above complexes are coordination polymers.

The analytical results indicate that the synthesized coordination polymers possess the general formulas  $[\text{Zn}(\text{BFYMDA})(\text{NO}_3)_2(\text{H}_2\text{O})]_n$ ,  $[\text{Cd}(\text{BFYMDA})(\text{NO}_3)_2(\text{H}_2\text{O})]_n$  and  $[\text{Ce}(\text{BFYMDA})(\text{NO}_3)_3(\text{H}_2\text{O})]_n$ .



**Fig. 6. SEM micrograph of  $(\text{Zn-BFYMDA})_n$  coordination polymer film = a) electrode side, magnification 1000x, bar =10  $\mu\text{m}$ ; b) electrode side, magnification 1500x, bar =10  $\mu\text{m}$ .**

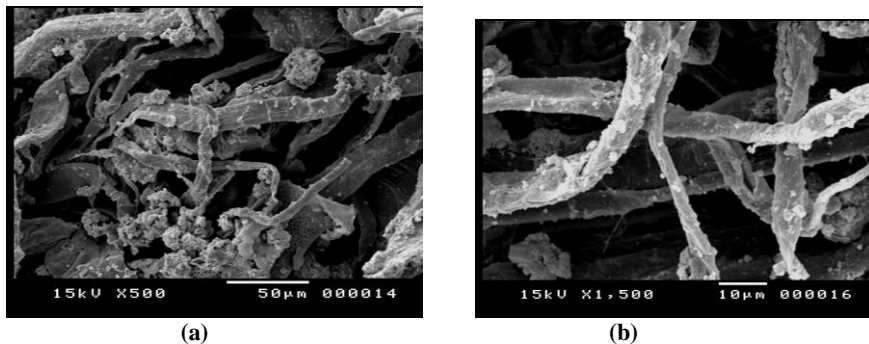


Fig. 7. SEM micrograph of  $(\text{Cd-BFYMDA})_n$  coordination polymer film = a) electrode side, magnification 1000x, bar =10  $\mu\text{m}$ ; b) electrode side, magnification 1500x, bar=10  $\mu\text{m}$ .

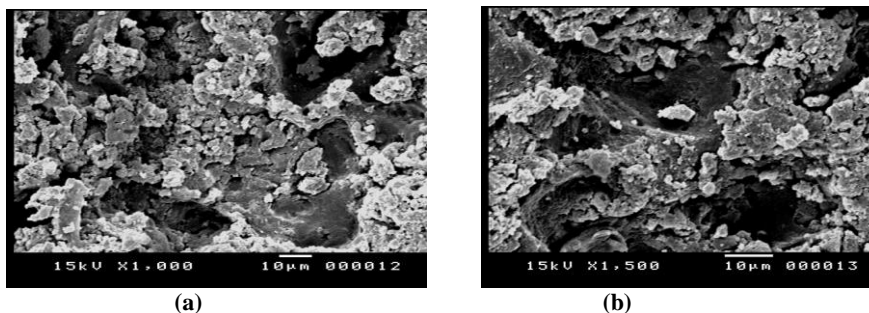
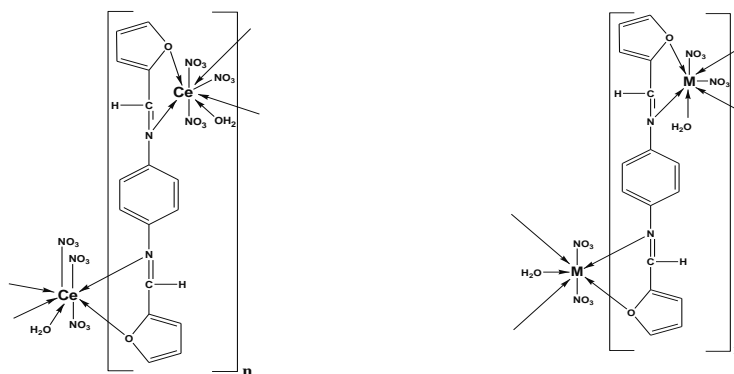


Fig. 8. SEM micrograph of  $(\text{Zn-BFYMDA})_n$  coordination polymer film= a)electrode side, magnification 1000x, bar =10  $\mu\text{m}$ ; b) electrode side, magnification 1500x, bar=10 $\mu\text{m}$ .

The polymeric metal complexes structure are:



where  $\text{M} = \text{Zn(II)}$  or  $\text{Cd(II)}$  in the right-hand structure.

### Conclusion

Coordination polymers of the Schiff base N, N bis-(Furan-2-ylmethylene)-1,4-phenylene diamine (BFMPDA) with zinc(II), cadmium(II) and cerium(III) have been prepared in dioxane medium. The optimal pH conditions for preparation the polymeric complexes were determined by potentiometry study. The stability constants of the complexes formed were calculated from the obtained potentiometric data. Polychelates polymers formed have been characterized using elemental analysis, infrared and electronic spectra. The polymers have high glass transition temperature (T<sub>g</sub>) and thermal stabilities. Electrical conductivity measurements of the synthesized polychelated polymers showed that they are insulators. The metal contents in all polymers are found to be consistent with 1:1 metal:ligand stoichiometry. The solubility and viscosity of the polymer complexes were also determined. Scanning electron microscopy (SEM) on the surface of the synthesized samples supported the structural studies of these polymeric complexes. The analytical results indicate that the synthesized coordination polymers possess the general formulas [Zn (BFMPDA) (NO<sub>3</sub>)<sub>2</sub> (H<sub>2</sub>O)]<sub>n</sub>, [Cd (BFMPDA) (NO<sub>3</sub>)<sub>2</sub> (H<sub>2</sub>O)]<sub>n</sub> and [Ce (BFMPDA) (NO<sub>3</sub>)<sub>3</sub> (H<sub>2</sub>O)]<sub>n</sub>.

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## تحضير وتوصيف بعض البوليمرات التناسقية الجديدة مع قاعدة شيف مشتقة من فيورفيرال

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يشتمل هذا البحث علي دراسات فيزيوكيميائية علي متراكبات بوليمرية جديدة تم تحضيرها من تفاعل بعض أيونات العناصر الانتقالية وهي  $Cd^{2+}$  و  $Zn^{2+}$  ومن عناصر الانتثيدات  $Ce^{3+}$  مع قواعد شيف ( ن ، ن بيس ٣ فيوران-٢- يل ميثيلين ٤،١ فينيلين داى أمين). ويتضمن دراسات جهدية تفصيلية عن حالات الإتران القائمة فى المحلول عند تكوين المتراكبات المذكورة وذلك بهدف تحديد حالات إترانات التراكب الممكن تواجدها بالمحلول ونسب تكوينها وتدرج ثبات نظم التراكب المختلفة على ضوء طبيعة الكاشف الداخلى فى التفاعل ومقارنة ثبات هذه النظم التراكبية المختلفة فى المعايير عند تغير درجة تركيز أيون الهيدروجين بالمحلول وذلك لمعرفة الظروف المثلى لتصنيع المتراكبات موضع الدراسة وكذلك استخدمت فى هذه الدراسات قياسات أطيف الإمتصاص المرئية وال فوق بنفسجية خلال معايير تتبع تغير درجة تركيز أيون الهيدروجين بالمحلول عند ظروف تجريبية محددة. كما تم تحضير المتراكبات الصلبة فى الظروف التجريبية المناسبة والمحددة ليتم التعرف على شكل وتركيب هذه المتراكبات بالتحليل العنصرى وطيف الأشعة تحت الحمراء وطيف الإمتصاص الإلكتروني وقياسات التوصيل الجزئية والكهربية والتحليل الحرارى الوزنى والمسح الميكروسكوبى الإلكتروني.

وقد بينت دراسة المتراكبات الصلبة أن هذه المركبات هى سلاسل بوليمرات تناسقية.