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A Study on Schiff Bases Containing Poly (Acryl Amide) In the Synthesis and Characterization.

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ABSTRACT

The aldehyde (Benzimidazole-2- Carboxyaldehyde) complex of Nickel (II) and Cobalt(II) were prepared by mixing aqueous solution of metal chloride with ethanolic solution of the aldehydes at 1:2 mol ratio. Then with a solution of polyacrylamide coordination polymers were prepared. IR study indicate that the aldehyde reacts with the polymer. Frequency shifts may be attributed to coordination of the metal ion with the azomethine nitrogen and imine oxygen of the carboxylate group. ¹H NMR studies suggests the existence of keto and enol forms even in the solution form. The thermal analysis reports the thermo-oxidative degradation of complexes. From the conductivity measurements it has been shown that the conductivity of the nickel complexes are higher than the cobalt complexes.

Keywords: Schiff base, acryl amide, characterization, aldehyde.

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INTRODUCTION

In the past decade, there has been much interest in the coordination chemistry of polymers due to their high thermal stability and semiconducting or conducting properties [1-3]. Metal–polymer complexes attracted the attention of researchers long ago and still hold a noteworthy place in modern chemistry [4,5]. Poly(acryl amide) (PAA) as a water–soluble synthetic polymer has found a significant role in many industrial applications as a coating in the textile and building industry. This significant role depends on the degree of amine and carboxyl group. PAA has the capability to change some of their behaviour, i.e., permeability and mechanical strength, with small changes in structure [6,7]. Developing the properties of individual polymers can be an important approach for to use in new fields. For this reason, we chose PAA and benzimidazole–2–carboxaldehyde (Figure 1) and attempted to prepare polymer–schiff bases by polycondensation.

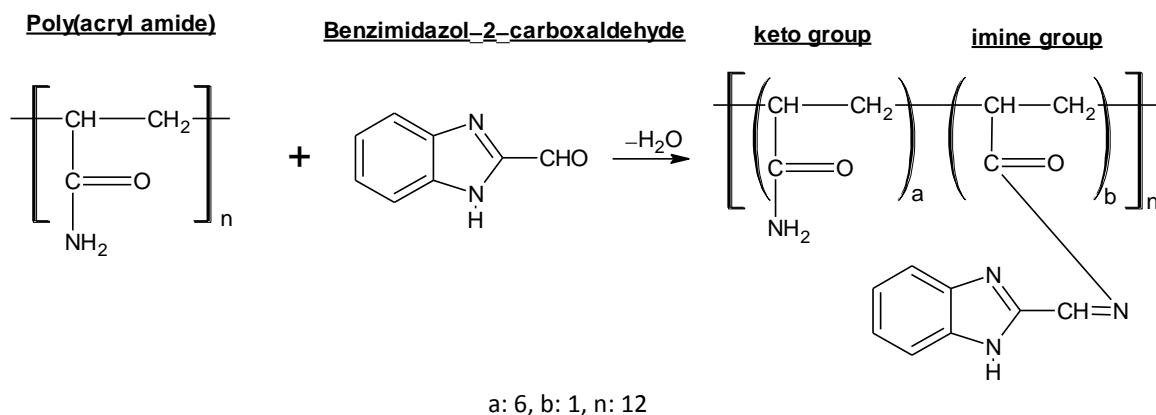


Figure 1: Structure of poly (acryl amide) and aldehyde.

In this way, derivatives new of PAA may be useful in the polymer network. PAA–Schiff bases may have conjugate bonding with a new active group, therefore, studied substances may have semi conductivity or conductivity [8,9], chemical sensors [10], corrosion protection [11,12], thermostabilizers.

EXPERIMENTAL

Materials

The solvents used in this study were analytical grade. All the other materials (poly(acryl amide), benzimidazole–2–carboxaldehyde, metal (II) salts and solvents) were reagent grade (Sigma Aldrich Company).

Apparatus

¹H and ¹³C–NMR spectra of the ligands were recorded with a Bruker Spectrospin Advance DPX–400 using TMS as internal standard and DMSO–d₆ as solvent. IR spectra in the 4000–400 cm^{–1} ranges were recorded using KBr discs on a Mattson 1000 FTIR spectrophotometer. Carbon, hydrogen and nitrogen values were obtained using a LECO–9320 analyzer. Metals were determined with a Philips PU 9285 model AAS spectrophotometer. Chlorine was determined titrimetrically by the Mohr method. The weight average molecular weight (M_w) was suggested from this element analyses. The number average molecular weight (M_n) was determined with a vapor pressure osmometer using Vescor 5520X. The TGA curves were obtained on a General V4.1C Du Pont 2000 between 30–600°C at a heating rate of 10°C min^{–1} in nitrogen atmosphere. Conductivity measurements were carried out at 20°C in 10^{–3} M DMF using a Siemens WPA CM 35 apparatus. The room temperature magnetic moments were measured with a MK–1 model Gouy Balance (Christon Scientific Equipments Ltd.).

Preparation of the Polymeric–Schiff Bases

A solution of poly(acryl amide) (0.001 mol) in hot water (15 mL) was added drop wise to a solution of the benzimidazole–2–carboxaldehyde (0.012 mol) dissolved in CH₃OH solution (20 mL). The stirring was

continued until the solution was dense ca 4 d. The mixture was evaporated until about the ratio 1:3 of its original volume and cooled.

A crystalline yellow precipitate was obtained. Then the crystalline solids were filtered, washed with a mixture of water–methanol (1:1) and methanol–ether (1:1). Finally, it was dried in vacuo (over P₄O₁₀).

Anal. Calcd for [C₂₉H₃₉N₉O₇] in the main unit: Calcd: C: 55.68; H: 6.24; N: 20.16; Found: C, 54.23; H: 6.04; N: 19.61 UV–Vis (λ_{max}); 221, 264, 230 and 336 nm. FT–IR (major I.R. absorption; KBr cm⁻¹); $\nu(\text{NH})_{\text{ring}}$, 2937 m; $\nu(\text{NH}_2)_{\text{asym}}$, 3201 $\nu(\text{NH}_2)_{\text{sym}}$, 3423; $\nu(\text{CN})+\delta(\text{NH})$, 1518; $\delta(\text{NH})$, 1256; $\nu(\text{C=O})_{(\text{out-of-planes})}$, 483; ¹H NMR (DMSO–d₆); $\delta(\text{ppm})$; [–C–NH₂, 7.62(s, 2H), –CH, 2.93 (m, 1H), –CH₂, 2.67 (t, 2H)]_{keto}; [–C–NH, 7.27(s, 2H), –CH, 2.44 (m, 1H), –CH₂, 2.31 (t, 2H)]_{enol}; N=CH, 9.56(s, 1H), CH_(arom), 7.92–7.80(s, 2H) and 6.45–6.28 (m, 4H), NH_{ring}, 8.16 (s, 1H), –CH₂(min group), 3.23 (m, 2H), –CH_(imin group), 3.52(m, 1H), ¹³C NMR (DMSO–d₆); $\delta(\text{ppm})$; –C=O, 165.01, –C=O(imin group), 196.30, –CH_(keto and enol), 40–45, –CH₂(keto and enol), 33–38, –N=CH, 196.30, C_(arom), 112.72, 125.90, 123.40, 122.54, 132.77, 120.84, 138.34, 113.26.

Synthesis and Isolation of Complexes

First Step: Preparation of Metal–Aldehyde Complexes

The aldehyde (Benzimidazole–2–carboxaldehyde) complexes of Nickel(II) and Cobalt(II) were prepared by mixing aqueous solutions of metal chloride with ethanolic solutions of the aldehydes at 1:2 mol ratio [13]. The resulting solutions was stirred for ca. 1 h, filtered, and allowed to stand. On standing for further 8 h, the golden–yellow solid complexes formed was collected by filtration, washed with a small volume, then dried in a desiccators over CaCl₂ (Figure 2).

Elemental analyses of metal–aldehyde complexes: found (calcd) %: [Co(L)₂Cl₂]; C: 48.60 (48.73), H: 2.97 (3.04); N, 7.0 (7.10), Co: 13.79 (14.96); decomp. > 200°C. UV–vis (λ_{max}); 221, 264, 332 and 552 nm. FT–IR (KBr, cm⁻¹); $\nu(\text{NH})$ 3142 m, $\nu(\text{CHO})$ 1728 s, $\nu(\text{M–O})$ 412 m, $\nu(\text{M–N})$ 507 m, [Ni(L)₂Cl₂]; C: 47.82 (48.76), H: 2.88 (3.04), N, 6.94 (7.11); Ni: 14.80 (14.91); decomp. > 200°C. UV–Vis (λ_{max}): 221, 263, 338 and 447 nm. FT–IR (KBr, cm⁻¹): $\nu(\text{NH})$ 3140 m, $\nu(\text{CHO})$ 1721, $\nu(\text{M–O})$ 417 m, $\nu(\text{M–N})$ 512 m.

Second Step: Preparation of Coordination Polymers

A solution of poly(acryl amide) (4 mL, 0.001 mol) in water (25 mL) was added to a solution of metal–aldehyde complexes (0.006 mmol) in methanol (25 mL). These solutions were stirred until viscous and the solution changed colour, ca 4 d. After cooling, the complexes were washed repeatedly with a mixture of ether–methanol (1:1) and then dried in vacuo (over P₄O₁₀). The coordination polymers were coloured, crystalline solids, soluble in water, DMSO and DMF (Table 5.1).

Elemental analyses of (PAA–SB) complexes: found (calcd) %: Co(PAA–SB); C:50.0 (50.40), H: 4.70 (5.49), N: 18.70 (18.09), Co: 3.80 (4.26), Cl: 5.69 (5.73), UV–Vis (λ_{max}): 221, 264, 330, 337 and 672 nm. FT–IR (KBr, cm⁻¹); $\nu(\text{NH})_{\text{ring}}$ 2939 m, $\nu(\text{NH}_2)_{\text{asym}}$ 3203 m, $\nu(\text{NH})_{\text{sym}}$ 3426 m, $\nu(\text{M–O})$ 448m, $\nu(\text{M–N})$ 521m.

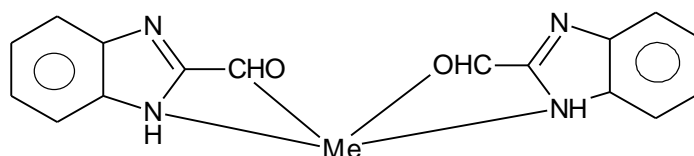


Figure 2: Reaction of metal–aldehyde complexes (Me: Ni(II), Co(II)).

Ni(PAA–SB); C: 50.81 (50.41), H: 5.36 (5.49); N: 17.84 (18.09); Ni: 3.78 (4.74); Cl: 5.61 (5.73); UV–Vis (λ_{max}): 221, 263, 338 and 448 nm. FT–IR (KBr, cm⁻¹); $\nu(\text{NH})_{\text{ring}}$ 2941 m, $\nu(\text{NH}_2)_{\text{asym}}$ 3206 m, $\nu(\text{NH}_2)_{\text{sym}}$ 3421 m, $\nu(\text{M–O})$ 439 m, $\nu(\text{M–N})$ 541 m.

Solid State Conductivity Measurements

Solid state electrical conductivities (σ) were measured with a Nippon NP-900 multimeter using a four-probe technique. The four-probe technique used for measuring the solid-state conductivity of pressed pellets was developed by van der Pauw (14). The pellets of the Schiff bases and the complexes were prepared at a loading of ca 9 tons and thickness of ca. 0.04 cm.

Table 1: M_n, M_w and terminal unit of PAA-Schiff bases and their metal complexes

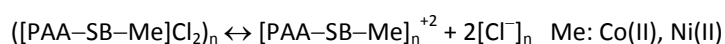
S.No.	Abbreviation ^a M_n ; M_w , chemical formula	Heterojenic index	Main unit (a: ^a 6,10 n:1) λ_M ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)	Colour Yield % μ_{eff} BM
1.	(PAA-SB) 6820; 7500, a: 6, n:12 [(C ₃ H ₅ ON)a(C ₁₁ H ₉ ON ₃)] _n	1.1	a[(C ₃ H ₅ OH) _a (C ₁₁ H ₉ ON ₃)] _n [625] _n	Yellow 63 42
2.	Co(PAA-SB) 4367, 7427.64, a: 10, n:6 [(C ₃ H ₅ ON) _a (C ₂₂ H ₁₈ O ₂ N ₆ Co)] _n .2nCl	1.7	[(C ₃ H ₅ ON) _a (C ₂₂ H ₁₈ O ₂ N ₆ Co)] _n 2nCl [1237.94] _n 128	Deep blue 74
3.	Ni(PAA-SB) 4126, 7426.26; a: 10, n:6 [(C ₃ H ₅ ON) _a (C ₂₂ H ₁₈ O ₂ N ₆ Ni)] _n .2nCl	1.8	[(C ₃ H ₅ ON) _a (C ₂₂ H ₁₈ O ₂ N ₆ Ni)] _n 2nCl [1237.71] _n 125	Green 64 3.18

^aMeasurements are according to vapor pressure osmometer.

RESULTS AND DISCUSSION

PAA-Schiff bases and their metal complexes are prepared by a condensation reaction. Deviation from the theoretical values in the case of polymeric ligand may be due to the polymeric nature of the acryl amide. It is very well possible that the polydispersity of the ligand is not in a narrow range. The polymer-metal complexes were prepared from the reaction in PAA-Schiff bases with the corresponding metal salts also in methanol. The good solubility of metal complexes suggests their poly(acryl) amide nature in water and common organic solvents. Furthermore, the molar conductance values of the complexes were found to be 125–139.

$\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ in a DMF solution (10^{-3} M), indicates the 1:2 electrolytic behaviour and suggests dissociations of main units according to the equilibrium [15].



The number average molecular weight (M_n) of the PAA-Schiff bases and their complexes were determined with a vapour pressure osmometer to be 6820, 4367 and 4126, respectively (PAA-SB), Co(PAA-SB) and Ni(PAA-SB). The number average and weight average molecular weights (M_w and M_n) of PAA-Schiff bases and polydispersity index (M_w/M_n) were given in Table 5.1. The polydispersity index of studied substances varied in the range of 1.01–1.80. These data clearly indicates that as metal(II) content in the main units increases, the molecular weight and polydispersity also increases.

Figure 3 was assumed for the polymeric-Schiff bases. Elemental analyses are consistent with a polymeric-Schiff base-to-metal ratio of 2:1 where $a = 10$ and $b = 1$. However, deviations from these values should be noted, and may be attributed to the polymeric nature of coordination polymers [16].

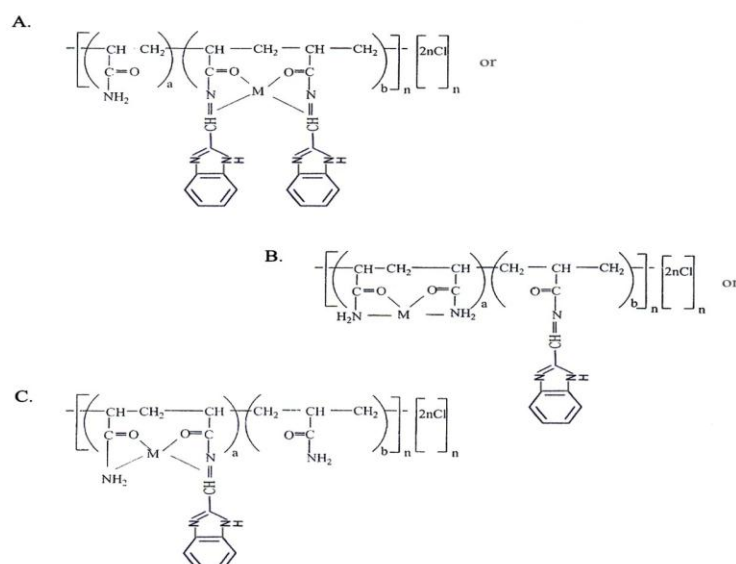


Figure 3. Suggested structures for (PAA-SB)—metal (II) complexes.

IR—Spectral Studies

The assigned absorption bands are consistent with suggested structure polymeric—Schiff bases and their complexes. Bands in the region of $2937\text{--}2941\text{cm}^{-1}$, $3202\text{--}3206\text{cm}^{-1}$ and $3423\text{--}3426\text{cm}^{-1}$ may be due to $\nu(\text{NH})$, $\nu(\text{NH}_2)_{\text{asym}}$ and $\nu(\text{NH}_2)_{\text{sym}}$ modes, respectively [17].

The observation of a medium new band at 1647cm^{-1} may be attributed to the $\nu(-\text{CH}=\text{N}-)$ stretching vibration⁽¹⁷⁾. Bands appearing at 1515cm^{-1} , 1255cm^{-1} and 485cm^{-1} are assigned to $\nu(\text{CN}) + \delta(\text{NH})$, $\delta(\text{NH})$ and $\nu(\text{C}=\text{O})$ vibrations, respectively, for the polymeric—Schiff bases [17]. These observations indicate that the aldehyde reacts with the polymer. On complexing, the $\nu(\text{CN}) + \delta(\text{NH})$, $\delta(\text{NH})$, and $\nu(\text{C}=\text{O})$ frequencies generally increase. Such frequency shifts, when compared to those of the polymeric—Schiff bases, may be attributed to coordination of the metal ion with the azomethine nitrogen and the imine oxygen of the carboxylate group. Furthermore, the appearance of new bands in the $410\text{--}420\text{cm}^{-1}$ and $495\text{--}520\text{cm}^{-1}$ can be assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$, respectively [18,19].

¹H—NMR Spectral Studies

The ¹H—NMR spectra of the polymeric—Schiff bases exhibit three signals at 7.72 ppm, 7.62 ppm and 6.89 ppm, which are assigned to the —OH, —NH and —NH₂ protons respectively (Figure 4). The spectra strongly suggest that even in solution the keto and enol forms remain as two dominant species in polymeric—Schiff bases. Similar keto—enol tautomerism has been previously reported for other Schiff bases studies [20].

The ¹H—NMR spectra of the polymeric—Schiff bases exhibits a signals at 8.15 and 9.56 ppm due to the —NH protons in benzimidazole ring and imine protons (—N=CH—), respectively. The ring proton signals appear at 7.92, 7.81, 6.68 and 6.28–6.45 ppm in the (PAA—SB). Most polydispersed polymers exhibit broad and multiple peaks in the NMR spectra [21]. Multiple peaks are shown in (PAA—SB). Therefore, the δ values were reported in terms of data in the midpoint of multiple peaks. For (PAA—SB), signals at 3.68 ppm/3.52 ppm, 2.93/–2.67 and 2.44, 2.31 ppm are assigned to the —CH/—CH₂ of imine group and —CH/—CH₂ of keto and —CH/—CH₂ of enol group, respectively. These data strongly support the presence of keto and enol forms in polymeric—Schiff bases. Peak high (one unit) of imine proton (—CH=N) and total peak high (six unit) —CH of keto—enol group were compared in the polymeric—Schiff base. From the ¹H—NMR spectrum it can be concluded that imine (—CH=N)/acryl amide (keto group + enol group) can be 1/6 in the unit structure (Figure 4).

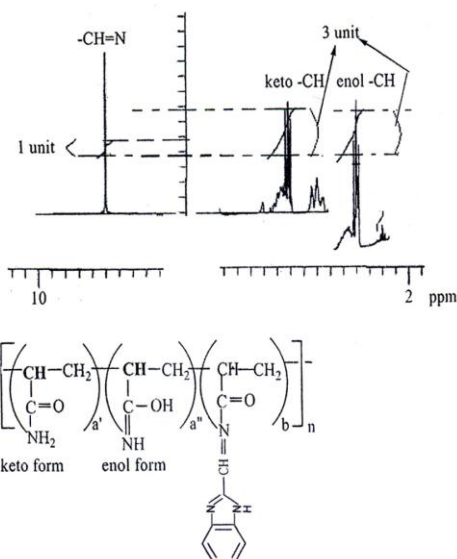


Figure 4. Evaluation of peak high in $^1\text{H-NMR}$ spectrum according to suggested unit.

Since Co(II) complexes and Ni(II) complexes are paramagnetic, the $^1\text{H-NMR}$ spectra could not be obtained.

In the $^{13}\text{C-NMR}$ spectra of the polymeric-Schiff base, a new peak appears at 165.01 ppm. This behaviour can be due to a change in the chemical state of C-atom in the $-\text{C}=\text{O}$ (carbonyl) in (PAA-SB). Furthermore, C atoms of the $-\text{CH}=\text{N}$ (imine) group are observed of 196.30 ppm in PAA-Schiff base. The $^{13}\text{C-NMR}$ spectra data of the poly-Schiff base is also in agreement with the proposed structures (Figure 4).

Mass Spectral Studies

LC mass spectra for the given $[\text{M}]^+$ 79.1 ($m/z = \%38$) and $[\text{M}]^+$ 195.1 ($m/z = \%37$) for (PAA-SB), $[\text{M}]^+$ 79.1 ($m/z = \%32$), $[\text{M}]^+$ 195.1 ($m/z = \%21$) $[\text{M}]^+$ 465.7 ($m/z = \%12$), for Co(PAA-SB); $[\text{M}]^+$ 79.1 ($m/z = \%31$), $[\text{M}]^+$ 195.1 ($m/z = \%19$) $[\text{M}]^+$ 465.2 ($m/z = \%11$), for Ni(PAA-SB). These results indicate that (PAA-SB) and their complexes have been synthesized according to the suggested structure (Figure 5).

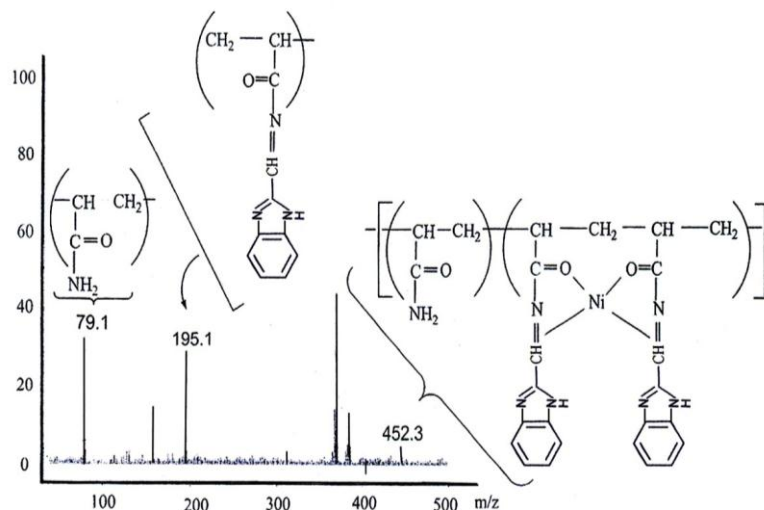


Figure 5. LC-MS spectrum for Ni(PAA-SB).

Electronic Spectral Studies

The electronic spectra of the (PAA-SB) in water were recorded in the range of 200–800 nm. The strong absorption bands which appeared in the range of 221nm, 264nm, and 230 nm are due to intra-ligand electronic transition. The magnetic moment 4.34 BM is commensurate with tetrahedral geometry about Co(II) in the complexes [22]. Electronic spectra of Co(II) complexes shows a medium intense assigned to $^4A_2 \rightarrow ^4T_1(P)$ (448 nm) transition for tetrahedral coordination about Cobalt(II). The magnetic moment 3.18 B.M. is commensurate with octahedral geometry around Ni(II) ion [22,23]. Nickel(II) complexes show two d-d bands between 693 nm and 397 nm, indicating an octahedral structure.

Thermal Analyses

The thermal analysis data of the three studied substances are given in Table-5.2. (PAA-SB), Co(PAA-SB) and Ni(PAA-SB) are thermally stable up to 115, 60 and 55, respectively. Polymeric Schiff base is thermally decomposed in two steps. The first one is consistent with the loss (ca 10%) of imine in the 'b' group molecules in the temperature range ca 115–230°C. The second one occurs in a wide temperature range (235–600°C) and corresponds to decomposition of $-\text{CH}(\text{CONH}_2)\text{-CH}_2-$ 'a' group molecules due to the polydispersity. In the decomposition process of the Co(PAA-SB), and Ni(PAA-SB) the mass losses corresponded to Cl, imine group and organic moieties leaving in the first, second and third stages of the decomposition, respectively [24]. In the first step, 5% weight loss was observed at 65°C and 50°C, respectively, Co(PAA-SB) and Ni(PAA-SB). This result shows that the polymer-complexes contain 12 mol Cl. The second step, 16% weight loss was observed in the temperature range 200–260°C due to loss of imine group with the aromatic ring.

The third step, the decomposition continued up to 310–600°C with weight loss corresponding to the loss of poly(acryl amide) group. The half degradation temperature of PAA-Schiff bases was higher than the complexes. There is no further weight loss beyond 600°C, which indicates thermo-oxidative degradation with the formation of stable NiO/CoO and carbon residue (Figure 6).

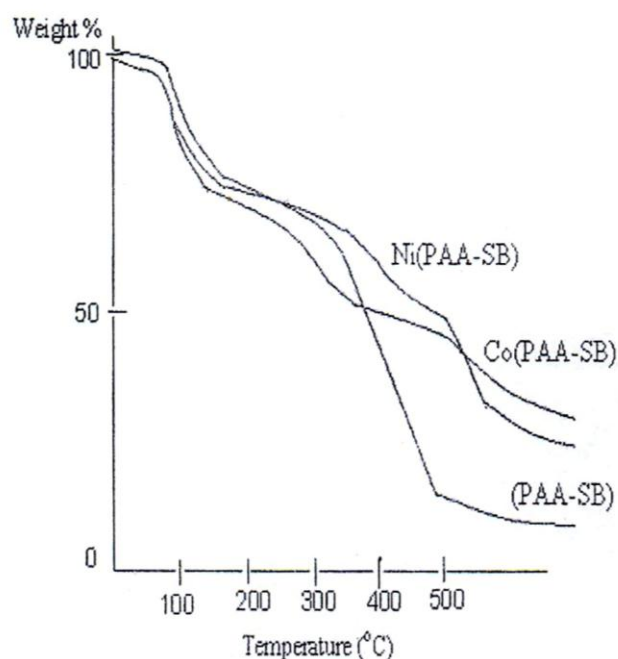


Figure 6. TG curves of (PAA-SB) and their complexes.

Table 2: Solid state conductivity measurements and thermal analysis data of the polymeric–Schiff base and it's complexes

Compound	σ (S cm ⁻¹) at 25±0.1°C	Thermal analysis (°C)				NiO/CoO–carbon residue
		T _{start}	Weight loss 5%	Weight loss 16%	Weight loss 50%	
PAA	Nonconductivity					
(PAA–SB)	3.21×10 ⁻⁶	115	235, 9.7		330	18
Co(PAA–SB)	6.80×10 ⁻⁶	65	193	285	370	47
Ni(PAA–SB)	9.91×10 ⁻⁶	50	211	275	350	42

Solid State Conductivity Measurements

Solid state electrical conductivity of the studied compounds is given in Table 2. On the contrary, PAA is nonconductive, the complexes and polymeric–Schiff bases are semiconductive. The conductivity range for semi-conducting materials is known to be 10⁻⁷–10⁻² S cm⁻¹ [25–28]. The conductivities of the (PAA–SB) is higher than the complexes. This may be ascribed to the conjugation length in the complexes arising from delocalization of π –electrons in the chelate ring. The conjugation length in the complexes may lead to higher conductivity [29–32]. The conductivities of the nickel complexes are higher than the cobalt complexes. This may be ascribed to the conjugation ease in nickel complexes due to octahedral structure.

CONCLUSION

The Schiff Bases Containing Poly(acryl amide) has been derived from the condensation reaction. Then, Ni(II) and Co(II) complexes of this PAA–Schiff bases have been synthesized. Chemical structures were investigated and solid state conductivities were compared. PAA do not conduct, but PAA–Schiff bases and their metal complexes have conductivity. This may be attributed to delocalization of π –electrons in the chelate ring. The conjugation length in complexes may lead to higher conductivity. So this study may be useful for various applications.

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