

SYNTHESIS AND CHARACTERIZATION OF THERMALLY STABLE OLIGOMER-METAL COMPLEXES OF COPPER(II), NICKEL(II), ZINC(II) AND COBALT(II) DERIVED FROM OLIGO-*p*-NITROPHENYLAZOMETHINEPHENOL

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ABSTRACT. Thermally stable metal complexes based on oligomers were prepared by the reaction between oligo-*p*-nitrophenylazomethinephenol (ONPAP) and Cu(II), Ni(II), Zn(II) and Co(II) ions. The properties of oligomer-metal complexes were studied by elemental, FT-IR and magnetic moments analyses. The thermal stabilities of the oligomer-metal complexes were compared by thermogravimetric (TG) and differential thermal (DTA) analyses. According to TG, oligomer-metal complexes were stable against to temperature and thermooxidative decomposition. The weight losses of oligomer-metal complexes were found to be 5 and 50 % at 200 and > 850 (Cu(II)), 172 and 600 (Ni(II)), 252 and > 850 (Zn(II)) and 174 and 510 (Co(II)), °C, respectively. Based on half degradation temperature parameters Cu(II) and Zn(II) complexes were more resistant than the others.

KEY WORDS: Oligomer metal complexes, Oligo-*p*-nitrophenylazomethinephenol, Cu(II) complex, Ni(II) complex, Zn(II) complex, Co(II) complex

INTRODUCTION

Polymer metal complexes can be prepared by the reaction of metal salts and polymers which contain electron donor groups such as, -CH=N-, -OH, -NH₂, -COOH and -CHO. Another approach for the preparation of such complexes is to use oligomers having electron donor groups. Oligo-*p*-nitrophenylazomethinephenol (ONPAP) has such groups and they can easily react with metal ions. The metal atoms reacted to the polymer backbone are found to exhibit characteristic catalytic behaviour which are distinctly different from their low molecular weight analogue. Polymer metal complexes have useful properties such as catalytic activity, thermal stability, ion selectivity and antimicrobial properties.

Several studies on polymer metal complexes have been reported in literature. Kaliyappan *et al.* synthesized poly(8-acryloxy-quinoline) and polymer metal complexes [1]. Thamizharasi *et al.* prepared poly(Schiff base anilides) and their Cu(II) and Ni(II) complexes [2]. Catalytic activity of polymer metal complexes was studied by Vinodkumar and Mathew [3]. Antimicrobial activities of Cu(II), Co(II), Zn (II) Pb (II) oligomer metal complexes was studied by Kaya *et al.* [4-6]. Thermal properties of polymer metal complexes was studied by Gad *et al.* [7, 8], Sebastian *et al.* [9] and Mart *et al.* [10]. The use of Sn(II), Cd(II) and Co(II) metal complexes as thermal stabilizers for rigid poly(vinyl chloride) was studied by Sabaa and Abdel-Naby [11]. Tsuchida and Nishide used Cu and Mn poly (4-vinylpyridine) complexes as initiator for the syntheses of phenolic polymers [12]. So polychelates have a large range of applications. Besides, coordination compounds of salicylaldehyde Schiff base have proven to be an excellent

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model system to study the enzymatic reactions of pyridoxal phosphate because both of these systems effectively catalyze transamination and racemization reactions [13]. In our earlier work [10], we investigated the thermal properties of oligomer metal complexes based on oligosalicylaldehyde. In that study, interestingly, we found that, although the prepared complexes were based on oligomers with low molecular weight, they had relatively better thermal stability than polymer metal complexes. Therefore, this study encouraged us to continue such investigations. For these reasons, in present paper, synthesis, characterization and thermal stabilities studies of the ONPAP and its metal complexes are described.

EXPERIMENTAL

Materials

Salicylaldehyde, *p*-nitroaniline, potassium hydroxide, hydrochloric acid, 1,4-dioxane, tetrahydrofuran, methanol, *N,N*-dimethylformamide, ethanol, dimethylsulfoxide, nitrobenzene, chloroform, ethyl acetate, carbontetrachloride, acetone, benzene, toluene, metal acetate's and sulfuric acid were supplied from Merck Chemical Company as chromatographic grade and were used as received.

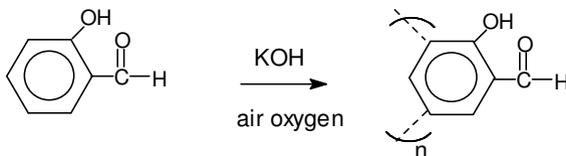
Instruments

Elemental analysis was carried out with a Carlo Erba 1106. The infrared spectra were recorded on Shimadzu FT-IR 8300. The FT-IR spectra were recorded using KBr discs ($4000\text{--}400\text{ cm}^{-1}$). OSA and ONPAP oligomer were characterized by using $^1\text{H-NMR}$ spectra (Bruker AC FT-NMR 200 MHz spectrometer) recorded at $25\text{ }^\circ\text{C}$ using deuterated DMSO as solvent. TMS was used as internal standard. UV-Vis spectrum ($200\text{--}800\text{ nm}$) of OSA and ONPAP oligomer were determined by using THF solvent. The number average molecular weight (M_n), mass average molecular weight (M_w) and polydispersity index values (PDI) of OSA and ONPAP were determined by size exclusion chromatography (SEC) of Shimadzu Co. For SEC investigation SGX (100 Å and 7 nm diameter loading material) 7.7 mm i.d. x 300 mm columns, eluent DMF ($0.4\text{ mL}\cdot\text{min}^{-1}$), and polystyrene standards were used. A refractive index detector (RID) (at $25\text{ }^\circ\text{C}$) was used to analyze the oligomer. Thermal data were obtained using a derivatograph MOM Q-1500D of Kovo Co. Magnetic measurements were made by Gouy method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. The thermogravimetric measurements were made between 50 and $850\text{ }^\circ\text{C}$ (in air, rate $5\text{ }^\circ\text{C min}^{-1}$). Metal analyses were determined by complexometric titration.

Synthesis of oligosalicylaldehyde (OSA) [14]

SA (3 g, 0.025 mol) was dissolved in an aqueous solution of KOH (10 %) (0.025 mol) and placed into a 50 mL three-necked round-bottomed flask. It was fitted with a condenser, a thermometer and a stirrer in addition to glass tubing over the condenser for sending air. The reaction mixture was stirred at $90\text{ }^\circ\text{C}$ for 25 h. The air was passed at a rate of 8.5 L h^{-1} during the course of the reaction. To prevent the loss of water in the reaction mixture and to deneutralize CO_2 in air with KOH, air was passed through 200 mL of an aqueous solution of KOH (20 %) before passing through the reaction mixture. It was cooled to room temperature, then 0.2 mol of HCl (37 %) was added to the reaction mixture. Unreacted SA was removed by steam distillation. The crude product was separated into two fractions by solubility differences in water. The first fraction (OSA-I, 75 % of product) was insoluble in water and the second fraction (OSA-II, 25 % of product) was soluble in water. The reaction product (OSA-I) was washed with water (50 mL

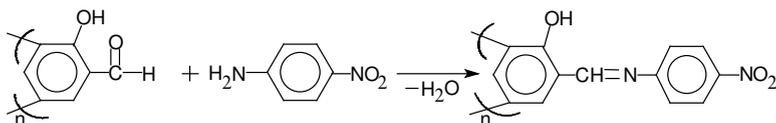
x 3), filtered and dried in the oven at 105 °C. Yield, 56 %, FT-IR (KBr; cm^{-1}): 3429 (phenol-OH); 1711 ($-\text{C}=\text{O}$); 3026 (aromatic $-\text{CH}$); 2932, 2863 (aldehyde $-\text{C}-\text{H}$). Anal. calcd. C: 70.00, H: 3.33. Found C: 69.21, H: 3.85. ^1H NMR (DMSO- d_6 ; δ , ppm, Me_4Si as internal standard): 10.75 ($-\text{OH}$, 1H, s); 10.30 ($-\text{CHO}-$, 1H, s); 7.72 (arom, 1H; s), 7.73 (arom, 1H; s). (Scheme 1).



Scheme 1

Synthesis of ONPAP [14]

OSA-I (3.00 g, 0.025 mol unit $^{-1}$) and *p*-nitroaniline (3.80 g, 0.0275 mol) were dissolved in 1,4-dioxane and placed into a 50 mL two-necked round-bottomed flask fitted with a condenser and a thermometer. The mixture was stirred magnetically on a water bath at 80 °C for 5 h. Then 1,4-dioxane was separated from the condensation product by distillation. The condensation product was extracted by hot toluene for 15 h and dried in an oven at 105 °C. Yield, 70 %. FT-IR (KBr; cm^{-1}): 1629 ($\text{CH}=\text{N}$); 3362 (Ar-OH); 3076 (olefinic $-\text{CH}$). Anal. calcd. N, 11.70. Found for ONPAP: N, 8.98. (Scheme 2).



Scheme 2

Syntheses of oligomer-metal complexes

Copper(II) complex

A solution of $\text{Cu}(\text{AcO})_2 \cdot \text{H}_2\text{O}$ (0.5 mmol, 0.0998 g) in methanol (10 mL) was added to a solution of ONPAP (1 mmol/unit, 0.240 g) in THF (50 mL). The mixture was stirred and heated at 80 °C for 6 h. The precipitated complex was filtered and washed with cold THF/methanol (1:1), then dried in vacuum oven. Color: black; yield, 83.1 %; m.p. >250 °C.

Nickel(II) complex

A solution of $\text{Ni}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ (0.5 mmol, 0.124 g) in methanol (10 mL) was added to a solution of ONPAP (1 mmol/unit, 0.240 g) in THF (50 mL). The mixture was stirred and heated at 80 °C for 6 h. The precipitated complex was filtered and washed with cold THF/methanol (1:1), then dried in vacuum oven. Color: black; yield, 79.9 %; m.p. >250 °C.

Zinc(II) complex

A solution of $\text{Zn}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$ (0.5 mmol, 0.109 g) in methanol (10 mL) was added to a solution of ONPAP (1 mmol/unit, 0.240 g) in THF (50 mL). The mixture was stirred and heated at 80 °C

for 6 h. The precipitated complex was filtered and washed with cold THF/methanol (1:1), then dried in vacuum oven. Color: black; yield, 82.3 %; m.p. >250 °C.

Cobalt(II) complex

A solution of $\text{Co}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ (0.5 mmol, 0.124 g) in methanol (10 mL) was added to a solution of ONPAP (1 mmol/unit, 0.240 g) in THF (50 mL). The mixture was stirred and heated at 80 °C for 6 h. The precipitated complex was filtered and washed with cold THF/methanol (1:1), then dried in vacuum oven. Color: black; yield, 84.7 %; m.p. >250 °C.

RESULTS AND DISCUSSION

In this study OSA-I was synthesized from oxidative polycondensation of salicylaldehyde. OSA-I was soluble in aqueous alkaline medium, THF, DMF, DMSO and 1,4-dioxane. OSA-I was poorly soluble in acetone, ethyl acetate, and ethanol, and insoluble in water, aromatic solvents and chlorinated hydrocarbons such as chloroform and CCl_4 . ONPAP was synthesized from condensation reactions of OSA-I and *p*-nitro aniline. ONPAP was dark black powder. ONPAP was soluble in THF, DMF, and DMSO and insoluble in solvents like ethanol, CCl_4 and benzene. Besides ONPAP was partially soluble in nitrobenzene, acetone and chloroform. The ONPAP-metal complexes were stable at room temperature. They were insoluble in common organic solvents, such as THF, DMF, 1,4-dioxane, acetone, chloroform, benzene, and toluene. The insolubility of complexes indicates the oligomer-metal formation. Also, the insolubility of complexes is important for easy separation of the catalyst from the reaction mixture [15]. The analytical data for the ONPAP and its metal complexes are listed in Table 1. The results of the elemental analyses show that the metal to oligomer ratio in all the oligomer-metal complexes is 1:2.

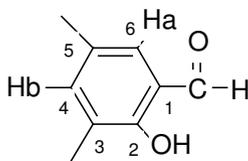
Table 1. Elemental analysis data of ONPAP and its oligomer-metal complexes.

Compound	Empirical formula	Calculated (Found) (%)			
		C	H	N	Metal
ONPAP	$\text{C}_{12}\text{H}_8\text{N}_2\text{O}_3$	65.0 (64.2)	3.33 (3.20)	11.70 (9.0)	---
ONPAP-Cu(II)	$(\text{C}_{12}\text{H}_7\text{N}_2\text{O}_3)_x \cdot \text{Cu}$	57.6 (56.9)	2.58 (2.49)	10.34 (10.1)	11.73 (11.58)
ONPAP-Ni(II)	$(\text{C}_{12}\text{H}_7\text{N}_2\text{O}_3)_x \cdot \text{Ni}$	58.1 (57.2)	2.61 (2.51)	10.43 (9.9)	10.94 (10.49)
ONPAP-Zn(II)	$(\text{C}_{12}\text{H}_7\text{N}_2\text{O}_3)_x \cdot \text{Zn}$	57.4 (57.1)	2.28 (2.53)	10.31 (10.2)	12.03 (11.51)
ONPAP-Co(II)	$(\text{C}_{12}\text{H}_7\text{N}_2\text{O}_3)_x \cdot \text{Co}$	58.1 (56.8)	2.61 (2.55)	10.43 (10.3)	10.97 (10.71)

Calculated percentage of Cu, Ni, Zn and Co for oligomer metal complexes are based on value of $x = 2$.

The M_n , M_w and PDI values of oligomers were found to be 1690 $\text{g}\cdot\text{mol}^{-1}$, 5150 $\text{g}\cdot\text{mol}^{-1}$ and 3.05 for OSA-I and 1280 $\text{g}\cdot\text{mol}^{-1}$, 5510 $\text{g}\cdot\text{mol}^{-1}$ and 4.30 for ONPAP. M_n , M_w and PDI values of ONPAP were different from the same parameters of OSA-I. The fact that ONPAP oligomers have different M_n , M_w and PDI values proves that OSA-I can enter into reaction with the *p*-nitroaniline. UV-Vis spectra of salicylaldehyde and OSA-I showed high intensive K, less intensive B and less intensive R bands at 210, 254 and 331 nm, respectively. R band of OSA-I was observed at a shorter wavelength of about 5 nm than the same band of salicylaldehyde. The difference in visible region (400-740 nm) of spectrum between salicylaldehyde and OSA-I depends on shifting of B band. In the IR spectrum of OSA-I, vibration band of phenol was observed to be an intense and broad band at 3429 cm^{-1} . The weak vibration bands of the aromatic C-H and aldehyde C-H were observed at 3026 cm^{-1} and 2932, 2683 cm^{-1} , respectively. The $\text{C}=\text{O}$ band has strong infrared absorbances at 1711 cm^{-1} . The $\text{C}=\text{C}$ band was observed at

1608 cm^{-1} for OSA-I. In order to identify the structures of OSA-I, the ^1H NMR spectrum was recorded in DMSO-d_6 . Ar-OH proton resonates at δ 10.75 (singlet), and Ar-CHO proton at δ 10.3 (singlet) and phenyl protons at δ 7.72 (singlet, Ar-H_a) and δ 7.73 (singlet, Ar-H_b) for OSA-I. ^1H NMR results showed the formation of OSA-I macromolecules from salicylaldehyde unit by the polymerization on C₃ and C₅ positions (Scheme 3).



Scheme 3

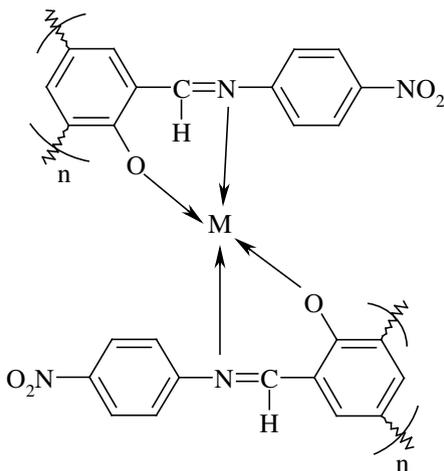
The UV-Vis spectrum of ONPAP oligomer was recorded in THF. The K band of the ONPAP was divided into two peaks (208 and 222 nm). The reason for this is the conjugation between the benzene ring and the nonbonding electrons of nitrogen in the azomethine group. The B and R bands of the azomethine groups were observed at 265 nm and 331 nm, respectively, in the UV-Vis spectrum of ONPAP. The FT-IR spectral data of the ONPAP and its metal complexes are given in Table 2.

Table 2. FT-IR spectral data of the ONPAP and its oligomer-metal complexes.

Compound	Wavenumber (cm^{-1})				
	OH	CH=N	Arom. C=C	M-O	M-N
ONPAP	3363	1629	1486-1600
ONPAP-Cu(II)	3372	1602	1460-1526	420	624
ONPAP-Ni(II)	3369	1600	1462-1558	432	622
ONPAP-Zn(II)	3382	1603	1452-1568	428	620
ONPAP-Co(II)	3379	1605	1458-1550	430	621

The ONPAP oligomer showed band at 3363 cm^{-1} which is attributed to the vibration of the OH group. In the oligomer-metal complexes, this band was observed between at 3369-3379 cm^{-1} ranges. This higher frequency indicated that the phenolic OH group was coordinated with metal ion. When the spectra of the oligomer-metal complexes were compared with that of ONPAP, the azomethine (-CH=N-) band shifted to lower frequency. At the FT-IR spectra of ONPAP and oligomer-metal complexes, vibration bands of azomethine were observed at 1629 cm^{-1} and 1600-1605 cm^{-1} respectively. As a result of coordination of the azomethine nitrogen atom with metal ion, the shifts in the complexes are towards to lower values [4]. In the oligomer metal complexes, the bands in the 624-620 cm^{-1} and 432-420 cm^{-1} ranges can be attributed to the M-N and M-O stretching [5]. The ^1H NMR spectrum of ONPAP, azomethine proton was observed 9.10 ppm as a singlet. The hydroxyl group proton was observed 12.72 ppm as a singlet. Besides, aromatic ring protons were observed between 6.53-7.90 ppm as a multiplet. The magnetic susceptibilities of oligomer metal complexes were measured at room temperature. The copper(II) complex exhibited the 1.78 B.M. value. The nickel(II) complex is diamagnetic, which strongly suggests a square planar geometry at the metal center. Zinc(II) complex is diamagnetic. The cobalt(II) complex was found with paramagnetic character (4.11 B.M.). Also, in the FT-IR spectra of oligomer-metal complexes, there was no evidence associated with coordinated water molecules. Because this band generally was observed at 3700-3500 cm^{-1} region as a broad band. These data suggest that the oligomer metal complexes may have

tetrahedral or squar planar geometry. From the observations above, the structures of the oligomer-metal complexes may be suggested as shown in Scheme 4.



Scheme 4

Thermal stabilities of oligomer-metal complexes were compared by TG analyses at the air medium. The results of these analyses are given in Table 3 and 4.

Table 3. 5 % and 50 % weight losses temperature and % char residue values of ONPAP and its oligomer-metal complexes.

Compound	5 % (weight loss) °C	50 % (weight loss) °C	Char residue, % (at 850 °C)
ONPAP	250	670	27
ONPAP-Cu(II)	200	>850	55.9
ONPAP-Ni(II)	172	600	34.5
ONPAP-Zn (II)	252	>850	63.1
ONPAP-Co(II)	174	510	29.2

Table 4. The weight losses (%) at temperature chosen values of oligomer-metal complexes.

Compound	200 °C	400 °C	600 °C	800 °C
ONPAP-Zn(II)	4.8	18.2	34.3	43.8
ONPAP-Cu(II)	4.9	21.5	33.2	43.6
ONPAP-Ni(II)	8.3	24.9	48.2	66.5
ONPAP-Co(II)	6.7	25.1	64.8	76.4

The results of TG analyses indicate that 5 % of the mass of the oligomer-metal complexes were lost at 200 (Cu(II)), 172 (Ni(II)), 252 (Zn(II)) and 174 (Co(II)), °C, respectively (Figure 1).

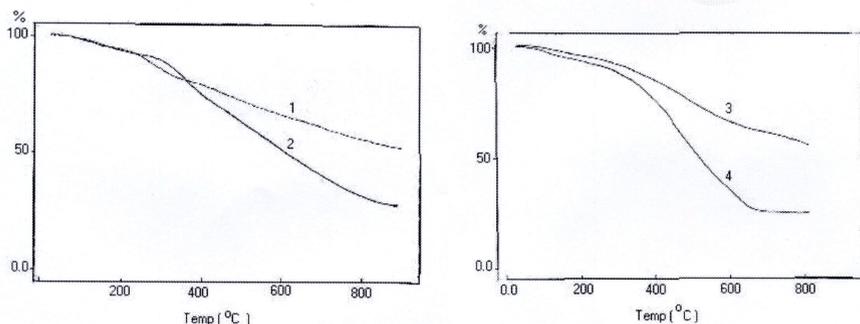


Figure 1. TG curves of oligomer-metal complexes [1, Cu(II); 2, Ni(II); 3, Zn (II); and 4, Co(II)].

The half degradation temperatures ($T_{50\%}$) of oligomer-metal complexes were >850 (Cu(II)), 600 (Ni(II)), >850 (Zn(II)) and 510 (Co(II)), $^{\circ}\text{C}$, respectively. Based on half degradation temperature parameters Cu(II) and Zn(II) complexes were more resistant than the Ni(II), Co(II) complexes and corresponding complexes of OSA [10]. Besides, the half degradation temperatures of Cu(II) and Zn(II) complexes were higher than that of ONPAP oligomer. These higher thermal stabilities may be related with their coordination geometry type. Likewise, $T_{50\%}$ of ONPAP-Cu(II) complex and Zn(II) complex were higher than oligo-2-*para*-tolylazomethinephenol (OTAP)-Cu(II), OTAP-Zn(II) [5] and oligo-*ortho*-azomethinephenol (OPAP)-Cu(II), OPAP-Zn(II) [4] complexes. This may be due to the nitro groups in ONPAP structure. The char residues of oligomer-metal complexes were 29.2-63.1 % at 850°C . DTA curves of oligomer metal complexes were similar. The exothermic process of oligomer-metal complexes started between in the range $304\text{-}363^{\circ}\text{C}$ and ended in the range $424\text{-}586^{\circ}\text{C}$. Endothermic processes were not observed in the curve of oligomer-metal complexes.

In addition the thermal stabilities of ONPAP and oligomer-metal complexes were higher than those of some polymeric Schiff base and polymer metal complexes [1-3, 7-9]. For these reasons, the syntheses of Schiff base substitute oligophenol and oligomer metal complexes are very important to prepare new thermally stable materials.

CONCLUSIONS

Oligo-*p*-nitrophenilazomethinephenol (ONPAP) was synthesized from the condensation of oligosalicylaldehyde (OSA) and *p*-nitroaniline. The number average molecular weight, mass average molecular weight and polydispersity index values of ONPAP were found to be $1280\text{ g}\cdot\text{mol}^{-1}$, $5510\text{ g}\cdot\text{mol}^{-1}$ and 4.30, respectively. Thermally stable oligomer-metal complexes were synthesized from ONPAP with Cu(II), Ni(II), Zn(II) and Co(II) and their structure and properties were determined. Thermal stabilities of ONPAP and its metal complexes were compared by TG analyses. According to TG curves, oligomer-metal complexes demonstrated high stability against thermooxidative degradation and showed that the half degradation temperature of Cu(II) and Zn(II) complexes is higher than that of ONPAP. The carbon residue of oligomer-metal complexes was 29.2-63.1 % at 850°C . The half degradation temperature of ONPAP and its metal complexes decreased in the order: Cu(II) = Zn (II) $>$ ONPAP $>$ Ni(II) $>$ Cu (II). As might

be expected, prepared oligomer metal complexes showed thermal stability and insolubility properties. We assume that these properties of complexes are important for technological usage such as catalyst and thermal resistant agent.

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