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Oligo-*Ortho*-Chloroazomethinephenol and its Metal Complexes: Synthesis, Characterization, Antimicrobial and Thermal Properties

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The new Schiff base oligomer (oligo-ortho-chloroazomethinephenol) was synthesized by the condensation of ortho-chloroaniline with oligosalicylaldehyde (OSA). Oligomer-metal complexes of oligo-ortho-chloroazomethinephenol (OKAP) with Cu(II), Zn(II) and Co(II) were synthesized. The properties of OKAP and oligomer-metal complexes were studied by elemental, UV-Vis, ^{1}H-NMR, FT-IR, magnetic susceptibility analyses. The number average molecular weight and mass average molecular weight OKAP were found to be 1494 $g \cdot mol^{-1}$ and 5418 $g \cdot mol^{-1}$, respectively. Elemental analyses of oligomer-metal complexes suggest that the ratio of metal to oligomer is 1 : 2. The results indicate that the OKAP coordinate through azomethine nitrogen and phenolic oxygen to the metal ions. Antimicrobial activity of OKAP was tested against S. cerevisiae, B. subtilis, E. coli, K. pneumoniae, M. luteus and S. aureus. The thermal stabilities of the OKAP and oligomer-metal complexes were compared by thermogravimetric (TG) analyses. According to TG, OKAP, and oligomer-metal complexes were stable against temperature and thermooxidative decomposition. The weight losses of OKAP and oligomer-metal complexes were found to be at 400 and 800°C at 20.2 and 50.0 (OKAP), 17.1 and 41.1 (Cu(II)), 13.4 and 38.5 (Zn(II)), 18.3 and 68.2 (Co(II)), %, respectively. Based on half degradation temperature ($T_{50\%}$) parameters, Cu(II) and Zn(II) complexes were more resistant than the OKAP and Co(II) complex.

Keywords Schiff base oligomer, thermal properties, antimicrobial properties, metal complexes

Introduction

OKAP is Schiff base oligomers based on OSA and *ortho*-chloroaniline. Schiff base substitute oligophenols and their derivatives have been used in various fields because of their electron structure properties. They have useful properties such as paramagnetism, semi conductivity, electrochemical cell and resistance to high energy. Because of these properties they were used for graphite materials (1), photoresistors (2), antistatic materials (3, 4), semiconducting materials (5) and thermostabilizers (6). In addition, Schiff base substitute oligophenols have antimicrobial activity (7, 8). OKAP Schiff base oligomer has the capability of coordination with different metal ions, because of the

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groups of hydroxyl (—OH) and azomethine (—CH=N—) in its structure. So, OKAP Schiff base oligomer may be used for the cleaning of poisonous heavy metals in industrial wastewaters. Kaliyappan et al. sythesized poly(8-acryloloxy-quinoline) and polymer metal complexes (9). Thamizharasi et al. prepared poly Schiff base anilides and their Cu(II), Ni(II) complexes (10). Catalytic activity of polymer metal complexes was studied by Vinodkumar and Mathew (11). Antimicrobial activities of oligomer metal complexes was studied by Kaya et al. (12). Thermal properties of polymer metal complexes was studied by Gad et al. (13) and Sebastian et al. (14), and therefore, polychelates have a large range of applications. Besides, coordination compounds of salicylaldehyde Schiff base have proven to be an excellent model system with which to study the enzymatic reactions of pyridoxal phosphate because both of these systems effectively catalyze transamination and racemization reactions (15). For these reasons, the synthesis of the Schiff base oligomer and oligomer metal complexes are gaining much interest. In the present paper, the synthesis, characterization, antimicrobial and thermal stability studies of the OKAP and its metal complexes were described.

Experimental

Materials

Salicyaldehyde, o-chloro aniline, KOH, HCl, 1,4-dioxane, THF, methanol, DMF, ethanol, DMSO, chloroform, ethyl acetate, CCl_4, acetone, benzene, toluene, hexane $Zn(CH_3COO)_2 \cdot 2H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$, $Co(CH_3COO)_2 \cdot 4H_2O$, and H_2SO_4 were supplied from Merck Chemical Company as chromatographic grade and were used as received.

Instruments

The infrared spectra were measured by a Shimadzu FT-IR 8300. The UV-Vis spectra was measured by a Shimadzu UV-160. Elemental analysis was carried out with a Carlo Erba 1106. OKAP oligomer was characterized using ^{1}H-NMR spectra (Bruker AC FT-NMR 200 MHz spectrometer) recorded at 25°C using deuterated DMSO as a solvent. TMS was used as an internal standard. The FT-IR spectra were recorded using KBr discs (4000–400 cm^{-1}). UV–Vis spectrum (200–800 nm) of OKAP oligomer was determined by using a THF solvent. The number average molecular weight (M_n), mass average molecular weight (M_w) and polydispersity index values (PDI) of OKAP was determined by size exclusion chromatography (SEC) from the Shimadzu Co. For SEC investigation, SGX (100 A° and 7 nm diameter loading material) 7.7 mm i.d. × 300 mm columns; eluent: DMF (0.4 $ml \cdot min^{-1}$), polystyrene standards was used. A refractive index detector (RID)(at 25°C) was used to analyze the oligomer. Thermo gravimetric analyses (TG) and differential thermal analyses (DTA) were performed with a Shimadzu TGA-50 and DTA-50 thermal analyzer, respectively. Magnetic measurements were made by the Gouy method using $Hg[Co(SCN)_4]$ as a calibrant. The thermogravimetric measurements were made between and 50 and 850°C (in air, rate 5°C min^{-1}). Metal analyses were determined by complexometric titration.

Preparation of Microbial Cultures

Saccharomyces cerevisae WET 136, *Echericha coli* DM, *Bacillus subtilis* IMG 22, *Klebsialle pneumoniea* DIG 1319, *S. aureus* COWAN 1 and *Micrococcus luteus* LA 2971 were used as the test organisms and yeast in an antimicrobial study. The bacteria and yeast strains were inoculated into nutrient broth (Difco) and malt extract broth (Difco) and incubated for 24 and 48 h, respectively. In the disc diffusion method, the sterile Mueller Hinton agar (oxoid) for bacteria and Sabouraud dextrose agar for yeast were separately inoculated with the test microorganisms (16). The OKAP dissolved in THF as 50 μg/disc disc solutions and absorbed on the sterile paper and an antibiotic disc were placed in wells (6 mm diameter) cut in the agar media and the plates were incubated at 32°C for bacteria (18–24 h) and 25°C for yeast (72 h). The resulting inhibition zones on the plates were measured after 48 h. The data reported in Table 6 are the average data of three experiments.

Synthesis of OKAP (17)

OSA-I (3.00 g, 0.025 mol unit^{-1}) and *o*-chlorooaniline (3.51 g, 0.0275 mol) were dissolved in 1,4-dioxane and placed into a 50 ml two-necked round-bottomed flask (Scheme 1) was 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 (4.19 g, 73% yield, mp.: >300°C).

Complexation of Metal Ions with OKAP

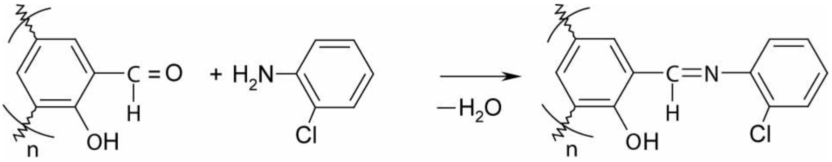
Copper(II) Complex. A solution of $Cu(AcO)_2 \cdot H_2O$ (0.5 mmol, 0.0998 g) in methanol (10 ml) was added to a solution of OKAP (1 mmol/unit, 0.229 g) in THF (50 ml). The mixture was stirred and heated at 80°C for 6 h. The precipitated complex was filtered and washed with cold THF/methanol (1 : 1), then dried in a vacuum oven (85.3% yield, mp.: >300°C).

Zinc(II) Complex

A solution of $Zn(AcO)_2 \cdot 2H_2O$ (0.5 mmol, 0.109 g) in methanol (10 ml) was added to a solution of OKAP (1 mmol/unit, 0.229 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 (87.1% yield, mp.: >300°C).

Cobalt(II) Complex

A solution of $Co(AcO)_2 \cdot 4H_2O$ (0.5 mmol, 0.124 g) in methanol (10 ml) was added to a solution of OKAP (1 mmol/unit, 0.229 g) in THF (50 ml). The mixture was stirred and



Scheme 1.

heated at 80°C for 6 h. The precipitated complex was filtered and washed with cold THF/methanol (1 : 1), then dried in a vacuum oven (83.7 yield, mp.: >300°C).

Results and Discussion

In this study, OSA-I was synthesized from oxidative polycondensation of salicylaldehyde. OSA-I was soluble in an aqueous alkaline medium, THF, DMF, DMSO, and 1-4 dioxane. OSA-I was poorly soluble in acetone, ethyl acetate, ethyl alcohol and insoluble in water, chloro organic solvents, such as chloroform and CCl_4. OKAP was synthesized from condensation reactions of OSA-I and *o*-chloro aniline. The OKAP was black in color, and it was stable at room temperature. OKAP was completely soluble in THF, DMSO, DMF, and aqueous NaOH solvents. In addition, it was poorly soluble in 1,4-dioxane and acetone and was insoluble in water, chloroform, ethyl alcohole and some apolar solvents such as benzene, toluene and hexane. The oligomer-metal complexes were black in color and they were stable at room temperature. The solubulities of oligomer metal complexes were completely different from than that of OKAP. The oligomer metal complexes were insoluble in chosen solvents such as THF, DMF, 1,4-dioxane, ethylalcohol, acetone, benzene, chloroform, toluene, water and hexane. The insolubility of oligomer metal complexes were in relation with the formation of metal oxygen and metal nitrogen bonds between oligomer-metal ions. Insolubulity of complexes could be due to the intrapolymer crosslinking. Also, the insolubilities of complexes are important for easy separation of the catalyst from the reaction mixture (18).

The elemental analysis data for OKAP and its metal complexes were presented in Table 1. The elemental analysis data reveal that the metal to ligand ratio in all oligomer metal complexes is 1 : 2 and is in good agreement with the calculated values.

UV-Vis spectra of salicylaldehyde and OSA-I high intensive K, less intensive B and less intensive R bands were observed in 210, 254, and 331 nm, respectively. R band of OSA-I was observed in a lower field such as 5 nm than the same band of salicylaldeyhde. The difference in a visible region (400–740 nm) of spectrum between salicylaldehyde and OSA-I depends on shifting of B band.

In the structure of OSA-I, a vibration band of phenol was observed to be an intense and wide band 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 —C═O band has strong infrared absorbances at 1711 cm^{-1}. The —C═C— band was observed at 1608 cm^{-1} for OSA-I. In order to identify the structures of OSA-I, the ^{1}H-NMR spectra was recorded in DMSO-d_6. Ar-OH proton resonance at $\delta = 10.75$ (singlet), and Ar-CHO

Table 1
The elemental analysis data of OKAP and its metal complexes

	Calculated (% found)			
Compound	C	H	N	Metal
OKAP	68 (67.3)	3.49 (3.41)	6.1 (5.8)	—
OKAP-Cu(II)	59.94 (59.1)	2.69 (2.6)	5.38 (5.2)	12.2 (12.1)
OKAP-Zn(II)	59.72 (59.2)	2.68 (2.5)	5.36 (5.1)	12.52 (12.2)
OKAP-Co(II)	60.48 (60.2)	2.71 (2.6)	5.43 (5.3)	11.42 (11.3)

proton at $\delta = 10.3$ (singlet) and phenyl protons at $\delta = 7.72$ (singlet, Ar-H_a) and $\delta = 7.73$ (singlet, Ar-H_b) for OSA-I. ^{1}H-NMR results showed the formation of OSA-I macromolecules from a salicylaldeyhde unit by the polymerization on C_3 and C_5 positions. Thin layer chromotography (TLC) results showed only one isomer.

The number average molecular weight and mass average molecular weight OKAP were found to be 1494 g mol^{-1} and 5418 g mol^{-1}, respectively. The UV-Vis spectrum of OKAP oligomer was recorded in THF solvent. In the spectrum of OKAP, the aromatic band at 260 nm was attributed to benzene $\pi \rightarrow \pi^*$ transition. The bands at 305–324 nm were assigned to azomethine (—CH=N—) $\pi \rightarrow \pi^*$ transition. The FT-IR spectra of OKAP and its metal complexes are shown in Figure 1. In the structures of OKAP, the stretching vibration band of phenol OH group was observed at 3450 cm^{-1}. The —CH=N— absorption band was observed at 1617 cm^{-1} for OKAP. The FT-IR spectra of OKAP, aromatic ring and —C=C— double bands were observed at the 1460–1475 cm^{-1} and 1579–1479 cm^{-1} range, respectively. In addition, the FT-IR spectra of OKAP show absorption bands in the region of 764 cm^{-1}, corresponding to out-of-plane deformation vibrations of aromatic C—H bonds. The weak band at 764 cm^{-1} is due to four neighboring C—H groups of the aromatic ring (19). The ^{1}H-NMR spectrum of OKAP, azomethine proton, was observed 9.17 ppm as a singlet. The hydroxyl group proton was observed 13.21 as a singlet. Besides, aromatic ring protons were observed between the 6.78–7.61 ppm range as a multiplet. The FT-IR spectral data of the OKAP and it's metal complexes are given in Table 2. In the FT-IR spectra of oligomer-metal complexes, a phenol OH band was observed between the 3425–3437 cm $^{-1}$ range (Figure 1). These values are lower than that of the OKAP oligomer. This lower frequency indicated that the phenol OH group was coordinated

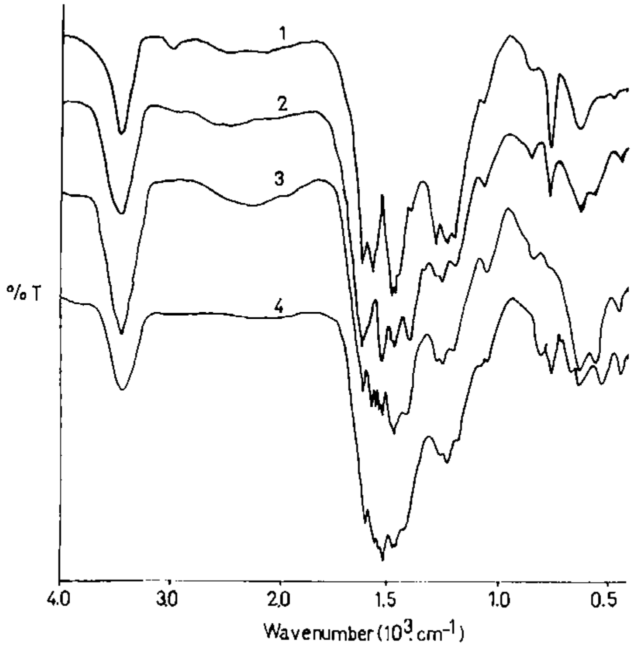


Figure 1. FT-IR spectra of OKAP (1) and its oligomer metal complexes [Cu(II), 2, Zn(II), 3 and Co(II), 4].

Table 2

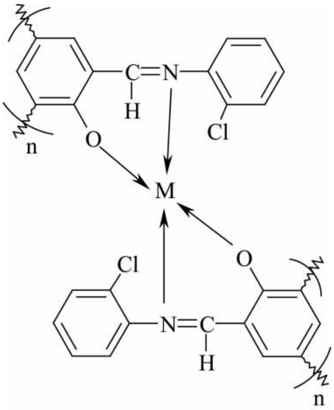
The FT-IR spectral data of the OKAP and its metal complexes

Compound	Wavenumber (cm^{-1})				
	OH	CH=N	Arm, C=C	M—N	M—O
OKAP	3450	1617	1460–1579	—	—
OKAP-Cu(II)	3425	1607	1478–1525	542	418
OKAP-Zn(II)	3436	1611	1472–1569	539	428
OKAP-Co(II)	3429	1613	1478–1550	533	417

with a metal ion. When the spectra of the oligomer-metal complexes were compared with that of OKAP, the azomethine (—CH=N—) band shifted to a lower frequency. At the FT-IR spectra, oligomer-metal complexes, vibration bands of azomethine, 1607–1613 cm^{-1}, were observed respectively. As a result of coordination of the azomethine nitrogen atom to metal ion, the –CH=N– bonds of the complexes shift towards lower values (7). In addition, in the oligomer metal complexes, the bands in the 542–530 cm^{-1} and 431–417 cm^{-1} range can be related with the M-N and M-O stretching.

To explain the structures of oligomer metal complexes, magnetic susceptibilities and diffuse reflectance spectra were measured. The magnetic susceptibilities of oligomer metal complexes were measured at room temperature. The values of magnetic susceptibilities of complexes were found to be 1.83 B.M and 4.12 B.M for Cu(II) and Co(II), respectively. The Zn(II) complex is diamagnetic. The Cu(II) complex of OKAP exhibited three absorption bands: 10,918, 13,125 and 15,377 cm^{-1}. Tetrahedral systems exhibit the absorbtion band below 10,000 cm^{-1}. Also, the octahedral complexes usually exhibit bands in the 15,000–39,000 cm^{-1} region. For this reason, it can be said that the Cu(II) complex has square planar geometry. The Zn(II) and Co(II) complexes of OKAP showed absorption at 7815, 11,599, 16,318 and 6981, 10,897, 15,985 cm^{-1}, respectively. As both complexes have the bands below 10,000 cm^{-1} and don't have bands in the 15,000–39,000 cm^{-1}region, they have tetrahedral geometry.

From the observations above, the structures of the oligomer-metal complexes may be suggested as shown in Scheme 2.



Scheme 2.

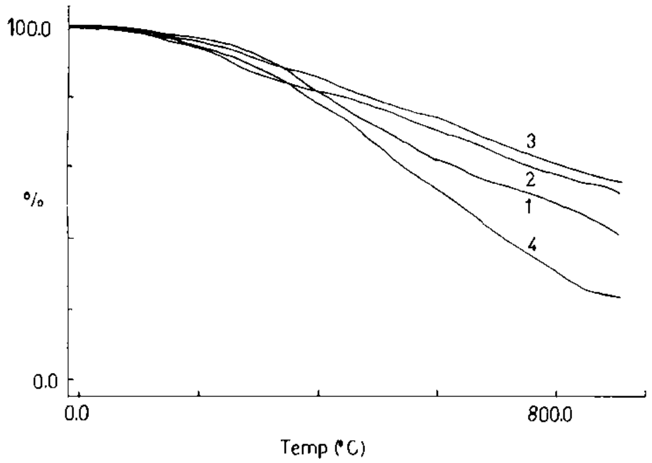


Figure 2. TG curves of OKAP (1) and its oligomer metal complexes [Cu(II), 2, Zn(II), 3 and Co(II), 4].

Thermal stabilities of OKAP and oligomer metal complexes were compared by TGA (Figure 2) and DTA analyses at the air medium. The results of these analyses are given in between Tables 3, 4 and 5. As is seen in Table 3, the half degradation temperature ($T_{50\%}$) of OKAP was 800°C. This value is higher than that of OSA and those of Schiff base oligomers based on OSA (17), which are 587°C and 666–677°C, 50% wt losses. Furthermore, this value is again higher than the value of oligo-*ortho*-azomethinephenol (OPAP) (8) and oligo-2-*p*-tolylazomethinephenol (OTAP) (7) oligomers which are 541 and 677°C for the 50% weight losses. These higher half degradation temperatures may be related with –Cl groups in its structure. At 850°C, the level of carboneous residue quantity of OKAP is 43%. This property is important for its usage of graphite materials, which is very useful for technological purposes (1). In addition, 5% wt loss temperature and carboneous residue of OKAP were 251°C and 43% (at 850°C), respectively. The half dedradation temperatures ($T_{50\%}$) of oligomer metal complexes were >850 (Cu(II)), >850 (Zn(II)) and 621 (Co(II)), °C, respectively (Figure 2). Based on half degradation temperature parameters, Cu(II) and Zn(II) complexes were more resistant than a Co(II) complex. Besides, the half degradation temperatures of Cu(II) and Zn(II) complexes

Table 3

5% and 50% w losses temperature and % char residue values of OKAP and its oligomer-metal complexes

Compound	5%, °C (wt loss)	50%, °C (wt loss)	Char residue, % (at 850°C)
OKAP	251	800	43
ONPAP-Cu(II)	188	>850	54
ONPAP-Zn(II)	226	>850	58
ONPAP-Co(II)	178	621	27

Table 4
The wt losses (%) values of OKAP and its oligomer metal complexes at chosen temperatures

Compound	200°C	400°C	600°C	800°C
OKAP	2.1	20.2	37.3	50.0
OKAP-Cu(II)	4.2	17.1	28.1	41.1
OKAP-Zn(II)	3.8	13.4	24.8	38.5
OKAP-Co(II)	4.0	18.3	44.6	68.2

were higher than that of OKAP. These higher thermal stabilities may be attributed to their coordination geometry type. Likewise, $T_{\%50}$ of OKAP- Cu(II) complex and Zn(II) complex were higher than those of OTAP – Cu(II), OTAP–Zn(II) (7) and OPAP-Cu(II), OPAP- Zn(II) (8) complexes. This may be due to the chloro groups in the OKAP structure. The 5% wt loss temperatures of oligomer metal complexes were 188 (Cu(II)), 226 (Zn(II)), and 178 (Co(II)), °C, respectively. The DTA curves of the OKAP and its metal complexes exothermic reactions were started at 534°C for OKAP and ended at 570°C. In addition, DTA curve of OKAP, endothermic reaction was not observed. In the oligomer metal complexes exothermic reactions were started at 304–427°C range and ended at the 443–583°C range. Besides the DTA curve of oligomer-metal complexes, endothermic reactions were not observed.

In addition, the thermal stabilities of OKAP and oligomer-metal complexes were higher than those of some polymeric Schiff base and polymer metal complexes (9–14). Therefore, for these reasons, the syntheses of Schiff base substitute oligophenol and oligomer are very important to prepare new thermally stable materials.

Antimicrobial activity of starting compounds (salicylaldehyde, *o*-chloroaniline and OSA-I) and OKAP against bacteria and yeast is given Table 6. As seen in Table 6, the antimicrobial activities of starting compounds and OKAP were clearly different. Salicylaldehyde and *o*-chloroaniline demonstrated higher activity than OKAP. However, OSA-I, which is oligomer based on salicylaldehyde affected no organisms. Like OSA-I, other Schiff base oligomers based on OSA-I (17) had no activity against bacteria and yeast. However, OKAP has activity against five types of organisms. This result indicates that it is very important to synthesize Schiff base substitute oligophenols to prepare new active materials.

Table 5
DTA analyses of OKAP and its oligomer-metal complexes

Compound	TDP[a]	Onset	End set	Heat (kj/g)
OKAP	570	221	652	12.29
OKAP-Cu(II)	444	376	669	4.11
OKAP-Zn(II)	583	453	724	3.63
OKAP-Co(II)	506	395	623	6.16

[a] Thermal decomposition peak with a heating rate 5°C min^{-1} in air atmosphere.

Table 6
Antimicrobial effects of the starting compounds and OKAP microorganism (inhibition zone[b])

Compound[a]	*S. cerevisiae*	*B. subtilis*	*E. coli*	*K.pneumoniea*	*M.luteus*	*S. aureus*
Salicylaldehyde	15	18	12	19	15	13
o-chloroaniline	34	29	36	28	27	25
OSA-I	—	—	—	—	—	—
OKAP	10	7	—	8	6	9

[a] Compounds concentration 50 μg/disc.

[b] Including disc diameter 86 mm. The symbol '—'reveals that the compound has no activity against the microorganism.

Conclusions

The new Schiff base oligomer (oligo-*ortho*-chloroazomethinephenol) was synthesized by the condensation of *ortho*-chloroaniline with oligosalicylaldehyde (OSA). Oligomer-metal complexes were synthesized from OKAP with Cu(II), Zn(II) and Co(II) and their structure and properties were determined. OKAP has activity against five types of organisms. Thermal stabilities of OKAP and its metal complexes were compared by TG analyses. TG analyses showed that the half degradation temperature of Cu(II) and Zn(II) complexes is higher than that of OKAP. The char residue of OKAP and oligomer-metal complexes was 27–58% at 850°C. The half degradation temperature of OKAP and its metal complexes decreased in the order: Cu(II) = Zn(II) > OKAP > Cu(II). As might be expected, OKAP and its metal complexes were showed thermal stability and graphite materials properties. These properties are important for technological usage.

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