

# Synthesis and Characterization of Water-Soluble Oligosalicylaldehyde-Sulfanilic Acid and Its Cu(II), Co(II), Pb(II) Complexes

Ersen Turac,<sup>1</sup> Yavuz Surme,<sup>1</sup> Ertugrul Sahmetlioglu,<sup>1</sup> Ramazan Varol,<sup>1</sup> Ibrahim Narin,<sup>2</sup> Levent Toppare<sup>3</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science and Arts, Nigde University, Nigde 51100, Turkey

<sup>2</sup>Faculty of Pharmacy, Erciyes University, Kayseri 38039, Turkey

<sup>3</sup>Department of Chemistry, Faculty of Science and Arts, Middle East Technical University, Ankara, Turkey

Received 30 July 2007; accepted 29 April 2008

DOI 10.1002/app.28650

Published online 9 July 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** This work presents the synthesis and characterization of a new water-soluble oligophenol derivative, 4-(2-hydroxybenzylideneamino)benzenesulfanilic acid (OSAL-SA) and its metal complexes. The chemical structure of the water-soluble polymer was characterized by nuclear magnetic resonance (<sup>1</sup>H NMR) and Fourier transform infrared (FTIR) spectroscopies and thermogravimetric analyses (TGAs). Pb(II), Cu(II), Co(II) complexes of the polymer were also synthesized in methanol. Characteriza-

tions of water insoluble polymer-metal complexes were performed by FTIR, flame atomic absorption spectroscopy, and TGA. The conductivity measurements of OSAL-SA and polymer-metal complexes were carried out by the four-probe technique. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 564–568, 2008

**Key words:** water-soluble polymers; metal-polymer complexes; thermogravimetric analysis (TGA); FTIR; NMR

## INTRODUCTION

Conjugated polymers are useful materials and they are of great interest because they have unique properties such as conductivity.<sup>1–4</sup> Water-soluble polymers (WSPs) can be synthesized via different routes. Important requirements for industrial application are good solubility in water, easy and cheap synthesis, chemical stability, and selectivity to one or more metal ions. Soluble and hydrophilic polymers have been prepared via addition polymerization and also by functionalizing various polymers.<sup>5</sup> They possess charged groups, or easily ionizable groups in aqueous solution. This charging or ionization is achieved by supplying water-soluble functional groups to water insoluble polymers.<sup>6</sup> The WSPs can give interactions with various analyte species present in the aqueous solutions.

WSPs have been developed for the complexation of various metals.<sup>7</sup> They are also used for preconcentration and determination of trace metal ions.<sup>8–11</sup> Synthesis of metal containing polymers has impor-

tant properties because the metal ions effectively change the thermal stability and the functional properties of the polymer backbone.<sup>12</sup> Metal-containing polymers have wide applications as catalysts for organic reactions, polymerizations, and also in superconducting materials, ultra-high strength materials, and liquid crystals.<sup>5</sup> The use of polymer-metal ion adducts may open new strategies also in biological applications.<sup>13</sup> In a previous study of Sahmetlioglu and coworkers, some oligosalicylaldehyde and its Schiff base oligomers were synthesized and thermal behaviors of these oligomers were also investigated.<sup>14</sup> In this study, we synthesized oligosalicylaldehyde (OSAL), oligosalicylaldehyde sulfanilic acid [4-(2-hydroxybenzylideneamino)benzenesulfanilic acid; OSAL-SA], and Pb(II), Cu(II), Co(II) complexes of OSAL-SA. Characterization and thermal behavior of these materials were also performed.

## EXPERIMENTAL

### Materials

Analytical reagent grade salicylaldehyde (SAL) and sulfanilic acid (SA) were purchased from Aldrich Chemical (Milwaukee, USA), Pb(CH<sub>3</sub>COO)<sub>2</sub>, Co(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, NaOCl, CH<sub>3</sub>OH, silicagel, KBr, and DMSO were purchased from Merck (Darmstadt, Germany); KOH was purchased

Correspondence to: E. Sahmetlioglu (sahmetlioglu@nigde.edu.tr).

Contract grant sponsor: Scientific and Technological Research Council of Turkish; contract grant number: TUBITAK-104M406.

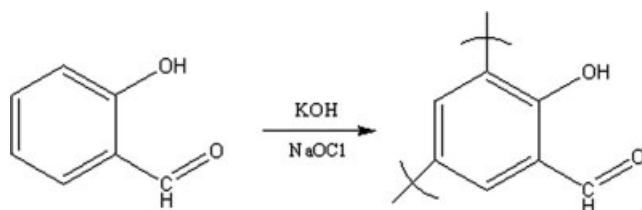


Figure 1 Synthesis of OSAL.

from Carlo Erba Reagenti (Rodano, Italy) and used without further purification.

### Instruments

WSP was characterized using  $^1\text{H}$  NMR spectra (Bruker-Instrument-NMR Spectrometer DPX-400) recorded at  $25^\circ\text{C}$  using deuterated DMSO as solvent. TMS was used as internal standard. The Fourier transform infrared (FTIR) spectra were recorded on JASCO FT/IR – 300E spectrometer. The FTIR spectra were recorded using KBr discs ( $4000\text{--}400\text{ cm}^{-1}$ ). Thermogravimetric analyses (TGAs) were performed from  $25$  to  $1000^\circ\text{C}$  under nitrogen with a heating rate of  $5^\circ\text{C min}^{-1}$  using Perkin-Elmer Pyrisdiamond 6.0 model TG/DTA. Metal contents of OSAL-SA/Pb, OSAL-SA/Co and OSAL-SA/Cu complexes were determined by Shimadzu AA 6501 F model flame atomic absorption spectrometer. The working conditions of flame atomic absorption spectrometer for Pb, Co, and Cu were in wavelengths of 217.0, 240.7, and 324.7 nm, slit widths of 1.0, 0.2, and 0.5 nm, lamp currents of 5, 7, and 4 mA, respectively. The conductivity measurements of OSAL-SA and polymer-metal complexes were carried out by four-probe technique. Compact thin pellets of WSP OSAL-SA and its metal complexes OSAL-SA/Pb, OSAL-SA/Co and OSAL-SA/Cu, were prepared under  $8\text{--}10\text{ tons/cm}^2$  to measure electrical conductivities.

### Synthesis of OSAL

About 0.05 mol SAL (6 g) were dissolved in aqueous solution of 0.05 mol KOH and placed into a 100-mL three-necked round-bottomed flask equipped with a condenser, a thermometer, and a stirrer. After heating to  $60^\circ\text{C}$ , NaOCl was added dropwise in 20 min. The reaction mixture was stirred at  $90^\circ\text{C}$  for 25 h. The mixture was neutralized with 3 mL HCl (37%) at room temperature. The unreacted SAL was removed by steam distillation. The crude product was washed with water.<sup>15</sup> Flash column chromatography ( $\text{SiO}_2$  column, elution with dichloromethane) afforded the desired compound. The reaction is given in Figure 1.

### Synthesis of OSAL-SA

A round-bottomed flask equipped with a magnetic stirrer was charged with sulfanilic acid (2.50 mmol), OSAL (4.34 mmol), NaOH (4.73 mmol), and methanol (20 mL). The resultant mixture was stirred and refluxed for 24 h at  $60^\circ\text{C}$ . Methanol was evaporated and the product was purified by flash column chromatography ( $\text{SiO}_2$  column, elution with dichloromethane).

### Synthesis of OSAL-SA/ $\text{M}^{2+}$ complexes

A round-bottomed flask equipped with a magnetic stirrer was charged with OSAL-SA dissolved in methanol (2.50 mmol), and Pb(II) acetate and Co(II), Cu(II) nitrates were dissolved in methanol (2.50 mmol each). Metal ion solutions were added dropwise into OSAL-SA solution. The resultant mixture including  $\text{Pb}^{2+}$  was stirred and refluxed for 6 h at  $60^\circ\text{C}$ . Those with  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  were stirred and refluxed for 12 h at  $60^\circ\text{C}$ . Methanol was evaporated. Products were washed three times with distilled

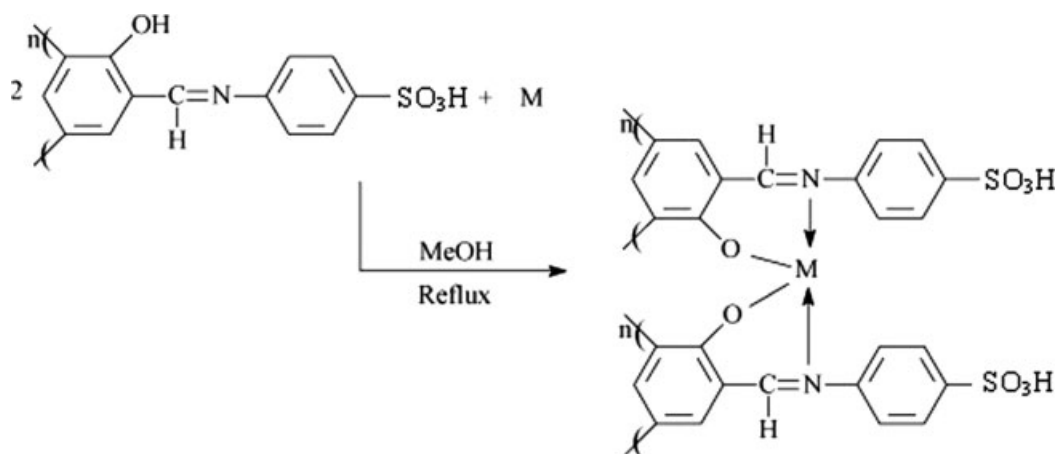
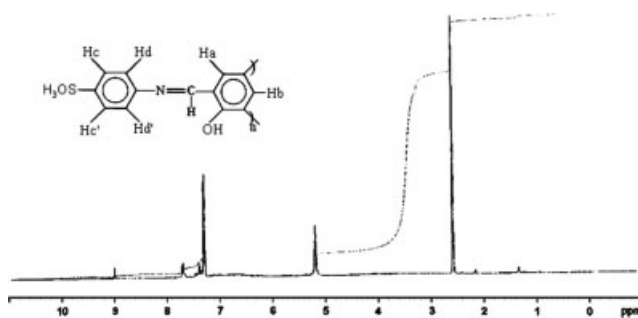


Figure 2 Reaction of OSAL-SA and M (II) ions.



**Figure 3**  $^1\text{H}$  NMR spectrum of water-soluble OSAL-SA.

water and filtered. Figure 2 shows the reaction between OSAL-SA and the metals.

#### Determination of Pb(II), Co(II), and Cu(II) in OSAL-SA/ $\text{M}^{2+}$ complexes

Approximately 0.025 g of each metal complex was taken into a glass beaker and 4 mL  $\text{HNO}_3$  and 8 mL  $\text{H}_2\text{O}_2$  were added. Samples were heated on an electrical heater and evaporated until dryness. This procedure was applied twice and clear solutions were diluted to 250 mL with 1M  $\text{HNO}_3$ .

### RESULTS AND DISCUSSIONS

#### $^1\text{H}$ NMR spectra of OSAL-SA

$^1\text{H}$  NMR spectrum was recorded in  $\text{DMSO}-d_6$ .  $^1\text{H}$  NMR spectrum of the polymer was given in Figure 3. In the  $^1\text{H}$  NMR spectrum of OSAL-SA, the signals of  $-\text{OH}$  and  $-\text{CH}=\text{N}$  groups were observed at 5.14 and 8.94 ppm, respectively. The existence of this signal at 8.94 ppm demonstrates that the aldehyde group of OSAL and amine group of SA were bounded to form the azomethine group of the polymer.

$^1\text{H}$  NMR spectrum of OSAL-SA,  $\delta\text{H}$  ( $\text{DMSO}-d_6$ ): 8.94 (1H, s,  $\text{HC}=\text{N}$ ), 7.69 (2H, d, Hc, Hc'), 7.53 (1H, s, Ha)–7.39 (2H, d, Hd, Hd<sup>1</sup>) 7.26 (1H, s, Hb), 5.14 (1H, s, OH), 2.53 (DMSO). 2.10 (1H, s,  $\text{SO}_3\text{H}$ ).

#### FTIR spectra

The strong and sharp band at  $1609\text{ cm}^{-1}$  is attributed to the stretching of azomethine group ( $\text{C}=\text{N}$ ) in the OSAL-SA molecule. This band is shifted to

$1616$ ,  $1614$ , and  $1616\text{ cm}^{-1}$  in the presence of Co, Cu, and Pb, respectively. This shift suggests that in the metal complexes the azomethine group is involved in binding to the metal ions.<sup>16</sup> The aromatic CH out-of-plane bands appeared at  $846\text{ cm}^{-1}$  while the aromatic CH in-plane showed up at 1011 and  $1018\text{ cm}^{-1}$ <sup>17</sup> for OSAL-SA and its metal complexes. The peaks of metal–oxygen and metal–nitrogen bonds observed between  $555$  and  $595\text{ cm}^{-1}$  and  $610$ – $650\text{ cm}^{-1}$ , respectively, for metal complexes of polymer. These FTIR results demonstrate that the syntheses of metal complexes were achieved. The main FTIR absorption bands of OSAL-SA and its metal complexes were summarized in Table I.

#### Pb(II), Co(II), and Cu(II) contents in OSAL-SA/ $\text{M}^{2+}$ complexes

Flame atomic absorption studies have revealed the ligand/metal ratio of complexes. Table II shows the FAAS results of Pb(II), Co(II), and Cu(II) complexes.

The results indicate that one metal ion was coordinated to two OSAL-SA molecules for each complex because Co, Cu, and Pb metals are possibly bonded to two nitrogen atoms of different OSAL-SA molecules. Molecular structure estimated from FAAS data of  $(\text{OSAL-SA})_2\text{M}$  is shown in Figure 2.

#### Conductivity studies of OSAL-SA and its metal complexes

Compact thin pellets of WSP OSAL-SA and its metal complexes OSAL-SA/Pb, OSAL-SA/Co, and OSAL-SA/Cu were prepared under  $8$ – $10\text{ tons/cm}^2$  to measure electrical conductivities. A typical sample dimensions were 13 mm diameter and 0.5 mm thickness. Conductivity measurements of polymer and metal complexes were performed by the four probe technique and calculated from the following equation:  $\sigma = V^{-1} I (\ln 2/\pi dn)$ , where  $V$  is the potential in volts,  $I$  is the current in amperes, and  $dn$  is the thickness of the samples in centimeters.

The electrical conductivities of Pb(II), Co(II), and Cu(II) polymer complexes were found as  $3 \times 10^{-4}$ ,  $3 \times 10^{-4}$ , and  $4 \times 10^{-4}$  while the OSAL-SA polymer has a conductivity of  $3 \times 10^{-6}\text{ S cm}^{-1}$ . Conductivity

**TABLE I**  
The Main FTIR Absorption Bands for the Mixed Metal Complexes

Compound	OH ( $\text{cm}^{-1}$ )	C=N ( $\text{cm}^{-1}$ )	C=C ( $\text{cm}^{-1}$ )	$\text{CH}_{\text{OOP}}$ ( $\text{cm}^{-1}$ )	$\text{CH}_{\text{IP}}$ ( $\text{cm}^{-1}$ )	M–O ( $\text{cm}^{-1}$ )	M–N ( $\text{cm}^{-1}$ )
OSAL-SA	3401	1609	1581	846	1011	–	–
OSAL-SA/Co	3409	1616	1581	846	1018	557	659
OSAL-SA/Cu	3406	1614	1588	846	1018	584	623
OSAL-SA/Pb	3416	1616	1581	846	1011	598	627

OOP, out of plane; IP, in plane; M, metal.

**TABLE II**  
FAAS Results of Metal Complexes  
(mmol Metal/g Complex)

Form of complex	Theoretical metal weight (mmol/g)	Found metal weight (mmol/g)
(OSAL-SA) <sub>2</sub> Pb	1.31	1.36
(OSAL-SA) <sub>2</sub> Co	1.63	1.67
(OSAL-SA) <sub>2</sub> Cu	1.61	1.63

of Pb(II), Co(II), and Cu(II) polymer complexes were increased from  $3 \times 10^{-6}$  to  $3 \times 10^{-4}$  S cm<sup>-1</sup> (Table III). The conductivity value of OSAL-SA/Cu complex was slightly higher than the OSAL-SA/Pb and OSAL-SA/Co and the conductivity of all three metal complexes were much higher than the polymer itself.

### Thermal analyses of OSAL-SA and its metal complexes

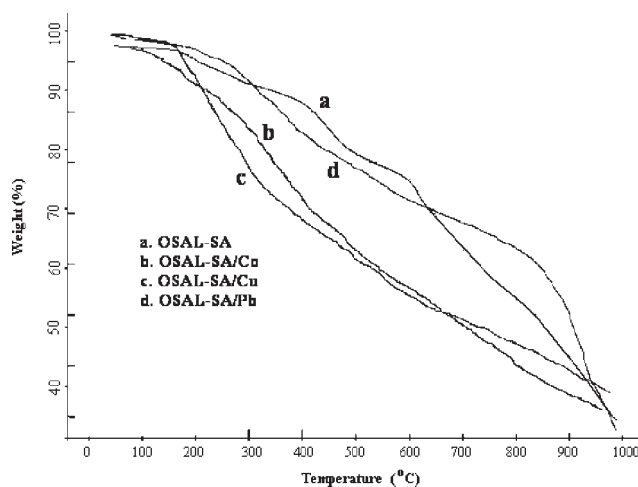
Thermal methods are interesting tools for investigation of the thermal stability and determination of disintegration energy of polymer-metal complexes. Heating the polymer and polymer-metal complexes causes chemical and physical transformations, accompanied with endothermic or exothermic processes.<sup>17</sup> These reactions are determined accurately by the TGA. To understand the thermal stability of the polymer and its metal complexes, TGA were performed.

TGA of OSAL-SA and its metal complexes were measured under nitrogen atmosphere in the temperature range 25–1000°C to investigate the thermal stability. Figure 4 shows the results of OSAL-SA, and its Co, Cu, Pb complexes for the TGAs. The results of thermal analyses were summarized in Table IV. The polymers were kept at 150°C about 3 h to remove unreacted monomer and humidity before carrying out the analyses.

The polymer and metal complexes were revealed 50% weight loss at 860, 680, 800, and 920°C. These results significantly indicate that the OSAL-SA/Pb complex is thermally more stable while the OSAL-SA/Co reveals the minimum thermal stability. This may be due to the stronger covalent bonding of Pb atoms to the OSAL-SA. The residue of OSAL-SA was supposed to be carbonized polymer.

**TABLE III**  
The Conductivities of Water-Soluble Polymer OSAL-SA and Its Metal Complexes

Polymer and complexes	Conductivity (S/cm)
OSAL-SA	$3 \times 10^{-6}$
OSAL-SA/Pb	$3 \times 10^{-4}$
OSAL-SA/Co	$3 \times 10^{-4}$
OSAL-SA/Cu	$4 \times 10^{-4}$



**Figure 4** TGA curves of OSAL-SA, OSAL-SA/Co, OSAL-SA/Cu, and OSAL-SA/Pb.

The thermal stability of polymer-metal complexes depends on the nature of the polymer main chain, coordination bonds, and crosslinking. When the polymer interacts with metal ions, the thermal energy supplied to the polymer-metal complex may result in a catalytic role of metal ion to the thermal decomposition of the polymer-metal complex.<sup>18</sup> By the way the thermal stability of functional polymers with metal will generally be enhanced.<sup>19–21</sup>

### CONCLUSIONS

The synthesis of a new WSP: OSAL-SA and its three different metal complexes with Pb(II), Co(II), Cu(II) were successfully achieved. Characterization studies were performed by using spectral techniques such as FTIR, <sup>1</sup>H NMR, and TGA. The molar composition of the polymer and its metal complexes were determined by flame atomic absorption spectrometry (FAAS).

- According to FAAS data, the ratio of metal to polymer chelate was approximately 1 : 2, which confirmed that one metal ion is coordinated through two OSAL-SA molecules.

**TABLE IV**  
Thermal Stability from TGA (% wt loss at °C) of Water-Soluble Polymer and Its Complexes

Polymer and complexes	T <sub>5%</sub> (°C)	T <sub>50%</sub> (°C)	Residue at 990°C (%)
OSAL-SA	200	860	33
OSAL-SA/Co	150	680	32
OSAL-SA/Cu	190	800	41
OSAL-SA/Pb	290	920	30

T<sub>5%</sub>: 5% weight loss; T<sub>50%</sub>: 50% weight loss.

- $^1\text{H}$  NMR spectrum clearly indicates that the OSAL-SA was successfully synthesized.
- The results of thermal analyses showed that OSAL-SA/Pb complex has higher thermal stability than the pristine polymer and other polymer-metal complexes.
- According to the conductivity measurements, OSAL-SA/Cu, OSAL-SA/Co, OSAL-SA/Pb complexes have higher conductivity than OSAL-SA polymer. These results indicated that the complexes have semiconductor characteristics.
- Many applications of WSPs, such as removal of target metal ions from different water samples, will be performed by using OSAL-SA polymer due to its solubility properties.

## References

1. Aoki, T.; Kaneko, T.; Teraguchi, M. *Polymer* 2006, 47, 4867.
2. John, A.; Palaniappan, S. *Polymer* 2005, 46, 12037.
3. Wu, T. Y.; Lee, N. C.; Chen, Y. *Synth Met* 2003, 139, 263.
4. Xuea, C.; Luob, T.; Chenc, J.; Liu, H. *Anal Chim Acta* 2006, 569, 27.
5. Rivas, B. L.; Pereira, E. D.; Moreno-Villoslada, I. *Prog Polym Sci* 2003, 28, 173.
6. Rivas, B. L.; Geckeler, K. E. *Adv Polym Sci* 1992, 102, 171.
7. Pizarro, G. C.; Marambio, O. G.; Jeria, M.; Huerta, M.; Rivas, B. L. *J Appl Polym Sci* 2006, 100, 178.
8. Mohammad, F. S.; Taher, A. *Anal Chim Acta* 2006, 565, 152.
9. Canizares, P.; Perez, A.; Camarillo, R. *Desalination* 2002, 144, 279.
10. Osipova, E. A.; Sladkov, V. E.; Kamenev, A. I.; Shkinev, V. M.; Geckeler, K. E. *Anal Chim Acta* 2000, 404, 231.
11. Dzherayan, T. G.; Shkinev, V. M.; Shpigun, L. K.; Kamilova, P. M.; Geckeler, K. E. *Talanta* 2002, 57, 7.
12. Nanjundan, S.; Selvamalar, C. S.; Jayakumar, R. *Eur Polym Mater* 2004, 40, 2313.
13. Lee, V. A.; Rashidova, S. In *Proceedings of the 36th IUPAC International Symposium on Macromolecules*, Seoul, Korea, 1996; p 513.
14. Mart, H.; Sacak, M.; Yuruk, H.; Sahmetioglu, E.; Vilayetoglu, A. R. *J Polym Sci Part A: Polym Chem* 2004, 42, 1120.
15. Kaya, I.; Vilayetoglu, A. R.; Mart, H. *Polymer* 2001, 42, 4859.
16. Mohamed, G. G. *Spectrochim Acta Part A* 2006, 64, 188.
17. Shekeil, A. E.; Khader, M. A.; Abu-Bakr, A. O. *Synth Met* 2004, 143, 147.
18. Choi, S. J.; Geckeler, K. E. *Polym Int* 2000, 49, 1519.
19. Kaliyappan, T.; Swaminathan, C. S.; Kanan, P. *Polymer* 1996, 37, 2865.
20. Kaliyappan, T.; Kanan, P. *J Polym Sci Part A: Polym Chem* 1996, 34, 3551.
21. Bajpai, U. D. N.; Rai, S. *J Appl Polym Sci* 1988, 35, 1169.