CHAPTER II

EXPERIMENTAL SECTION

2.1 Materials

All reagents and solvents were analytical grade quality. The solvents were obtained from Baker Chemical Company. Methylene chloride (CH_2Cl_2) was refluxed over calcium hydride (CaH_2) and distilled immediately before use. Zinc (II) acetate dihydrate, nickel (II) acetate tetrahydrate, salicylaldehyde, triethylenetetramine and *o*-vanillin were obtained from the Fluka. 3-Ethoxysalicylaldehyde, 3-*tert*-butyl-2-hydroxybenzaldehyde, 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, hexyl isocyanate, octyl isocyanate, 1,1,3,3-tetramethylbutyl isocyanate, phenyl isocyanate, benzyl isocyanate, 1-naphthyl isocyanate, hexamethylene diisocyanate and 4,4′-methylene-bis(phenyl isocyanate) were obtained from Aldrich. All chemicals were used without further purification.

2.2 Analytical Procedures

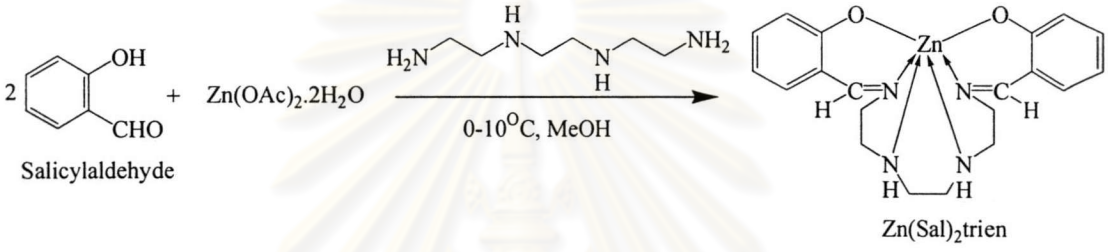
IR spectra were recorded on a Nicolet Impact 410 using KBr pellet method. NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 solution on an ACF 200 MHz Bruker instrument and a Varian Mercury-400 BB instrument. Chemical shifts are given in parts per million (ppm) using the proton residual as internal reference. Elemental analyses were carried out on a Perkin Elmer Elemental Analyzer 2400 CHN. X-ray crystallography was carried out using a Bruker Analytical SMART CCD X-ray system. FAB MS were obtained on a Finnigan MAT 90 mass spectrometer using glycerol as a matrix. Thermal properties were studied using a Netzsch DSC 200 differential scanning calorimeter and a Perkin-Elmer DSC 7 differential scanning calorimeter. All the samples were heated in DSC cell using a closed aluminium pan under air with the heating rate of 20°C/min. Thermogravimetric measurements were performed on a Netzsch thermogravimetric analyzer (STA 409C) at the heating rate 20°C/min under air/nitrogen (50/50) atmosphere. Initial decomposition temperature (IDT) was reported at the temperature where weight loss of the samples were observed. Inherent viscosities of the polymers were determined at a concentration of 0.5g/100ml in DMSO at 40°C using Cannon-Fenske viscometer. Limiting oxygen

index (LOI) data were obtained on an apparatus produced in accordance with ASTM-D2863-70 standard. The solubility of the polymers was tested in various polar and nonpolar solvents by addition of 10 mg samples to 2 ml of a solvent.

2.3 Synthetic Procedure

2.3.1 Synthesis of hexadentate Schiff base zinc complexes [$Zn(Sal)_2$trien and $Zn(XSal)_2$trien]

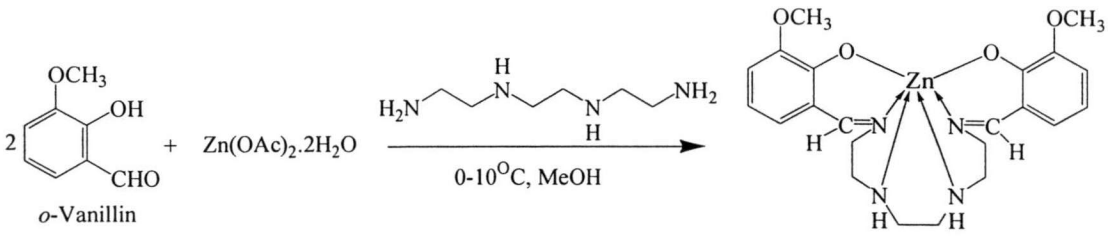
2.3.1.1 Synthesis of bis(salicylaldiminato)triethylenetetramine zinc(II) complex [$Zn(Sal)_2$trien]



$Zn(Sal)_2$trien

A cool (0-10°C) methanol solution (10 mL) of triethylenetetramine (0.149 mL, 1.0 mmol) was added dropwise to a stirred cool methanol solution (15 mL) of salicylaldehyde (0.244 g, 2.0 mmol) and zinc (II) acetate dihydrate (0.220 g, 1.0 mmol). The solution turned yellow slowly and was stirred for 15 min at cool temperature. This stirring solution was neutralized by 2M sodium hydroxide solution (1.0 mL, 2.0 mmol) and stirred for 1 hour. The yellow crystals of $Zn(Sal)_2$trien precipitated from the solution upon standing at room temperature for 10 hours. The yellow crystals were filtered and dried in vacuo to yield 0.387 g (93%) of $Zn(Sal)_2$trien. mp 220°C. IR (KBr, cm^{-1}); 3646 (NH), 3300, 3000, 2800, 1634(C=N), 1600, 1448, 1200, 930, 870. ^{1}H NMR (400 MHz, $CDCl_3$, ppm); δ 8.13 (2H, *s*, C<u>H</u>=N), 7.15 (2H, *t*, Ar-<u>H</u>, *J* = 7.2 Hz), 7.06 (2H, *d*, Ar-<u>H</u>, *J* = 7.2 Hz) 6.74 (2H, *d*, Ar-<u>H</u>, *J* = 8.0 Hz), 6.45 (2H, *t*, Ar-<u>H</u>, *J* = 7.6 Hz), 4.05-4.29 (2H, *m*, C<u>H</u>$_2$), 3.21-3.48 (4H, *m*, C<u>H</u>$_2$), 2.73-2.92 (2H, *m*, C<u>H</u>$_2$), 2.35-2.61 (4H, *m*, C<u>H</u>$_2$). ^{13}C NMR ($CDCl_3$, ppm); δ 172 (<u>C</u>=N), 168, 135, 133, 133, 124, 119, 112, 56, 47, 43. FAB MS (*m/z*) 417.3 ($C_{20}H_{24}N_4O_2Zn$). Anal. Calcd. for $C_{20}H_{24}N_4O_2Zn.H_2O$: C 55.12; H 6.01; N 12.79; found C 54.65; H 6.59; N 12.79.

2.3.1.2 Synthesis of bis(3-methoxysalicylaldiminato)triethylenetetramine zinc(II) complex [Zn(MeOSal)$_2$trien]



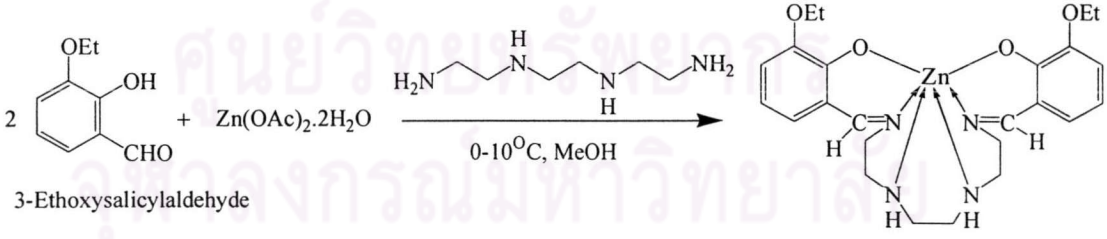
o-Vanillin

Zn(MeOSal)$_2$trien

The experiment was performed according to the procedure described in experiment 2.3.1.1 employing *o*-vanillin (0.304 g, 2.0 mmol) instead of salicylaldehyde. The yellow crystals were filtered and dried in vacuo to yield 0.289 g (61%) of Zn(MeOSal)$_2$trien. mp 293°C. IR (KBr, cm^{-1}); 3428 (NH), 3310, 2906, 2855, 1632(C=N), 1598, 1474, 1445, 1217, 1079, 973, 853. ^{1}H NMR (400 MHz, DMSO-*d*$_6$, ppm); δ 8.25 (2H, *s*, C<u>H</u>=N), 6.69 (2H, *dd*, Ar-<u>H</u>, *J* = 1.6, 8 Hz) 6.62 (2H, *dd*, Ar-<u>H</u>, *J* = 1.6, 8 Hz), 6.14 (2H, *t*, Ar-<u>H</u>, *J* = 7.6 Hz), 3.59 (6H, *s*, OC<u>H</u>$_3$). FAB MS (*m/z*) 477.1 ($C_{22}H_{28}N_4O_4Zn$). Anal. Calcd. For $C_{22}H_{28}N_4O_4Zn$: C 55.29; H 5.91; N 11.72; found C 55.05; H 5.94; N 11.74.

^{13}C NMR spectrum of Zn(MeOSal)$_2$trien was not obtained due to the poor solubility of the metal complex in DMSO-*d*$_6$.

2.3.1.3 Synthesis of bis(3-ethoxysalicylaldiminato)triethylenetetramine zinc(II) complex [Zn(EtOSal)$_2$trien]



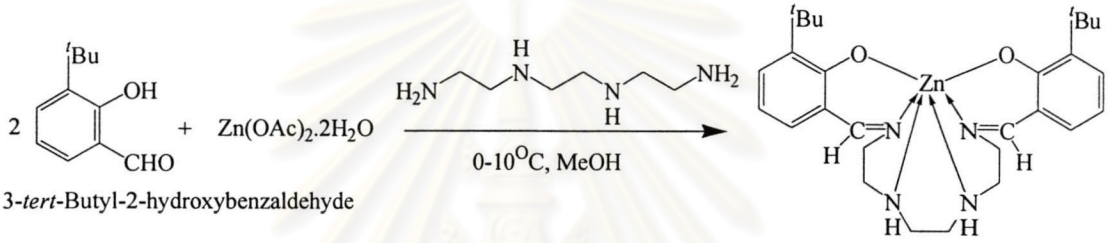
3-Ethoxysalicylaldehyde

Zn(EtOSal)$_2$trien

The experiment was performed according to the procedure described in experiment 2.3.1.1 employing 3-ethoxysalicylaldehyde (0.332 g, 2.0 mmol) instead of salicylaldehyde. The yellow crystals were filtered and dried in vacuo to yield 0.468 g (93%) of Zn(EtOSal)$_2$trien. mp 238°C. IR (KBr, cm^{-1}); 3446 (NH), 3297, 3048, 2969, 2861, 1642(C=N), 1596, 1442, 1219, 1071, 850. ^{1}H NMR (400 MHz, $CDCl_3$, ppm); δ

8.12 (2H, *s*, C<u>H</u>=N), 6.66 (2H, *d*, Ar-<u>H</u>, *J* = 8 Hz), 6.64 (2H, *d*, Ar-<u>H</u>, *J* = 8 Hz), 6.21 (2H, *t*, Ar-<u>H</u>, *J* = 7.6 Hz), 4.16-4.20 (2H, *m*, N<u>H</u>), 3.90-3.82 (2H, *m*, OC<u>H</u>$_2$), 3.74-3.78 (2H, *m*, OC<u>H</u>$_2$), 3.25-3.27 (4H, *m*, C<u>H</u>$_2$), 2.82-2.84 (2H, *m*, C<u>H</u>$_2$), 2.41-2.45 (4H, *m*, C<u>H</u>$_2$), 2.17 (2H, *m*, C<u>H</u>$_2$), 1.18-1.22 (6H, *t*, C<u>H</u>$_3$, *J* = 6.8 Hz). ^{13}C NMR ($CDCl_3$, ppm); δ 166(<u>C</u>=N), 164, 151, 127, 119, 117, 110, 64, 56, 47, 43, 15. FAB MS (*m/z*) 505.2 ($C_{24}H_{32}N_4O_4Zn$). Anal. Calcd. For $C_{24}H_{32}N_4O_4Zn$.MeOH: C 55.82; H 6.74; N 10.41; found C 55.58; H 6.85; N 10.83.

2.3.1.4 Synthesis of bis(3-*tert*-butyl-salicylaldiminato)triethylenetetramine zinc(II) complex [Zn(BuSal)$_2$trien]

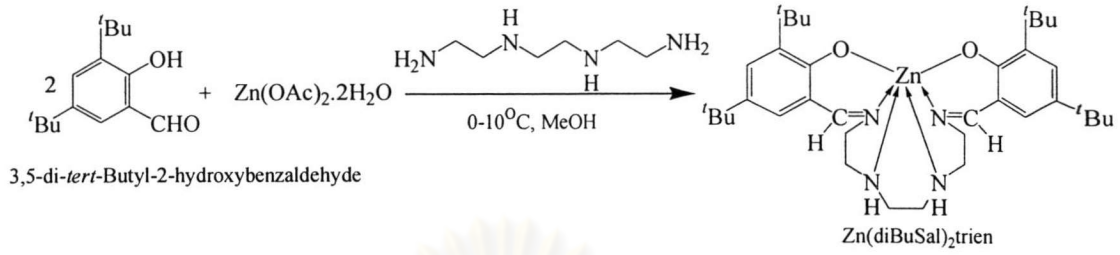


3-*tert*-Butyl-2-hydroxybenzaldehyde

Zn(BuSal)$_2$trien

The experiment was performed according to the procedure described in experiment 2.3.1.1 employing 3-*tert*-butyl-2-hydroxybenzaldehyde (0.356 g, 2.0 mmol) instead of salicylaldehyde. The yellow powder were filtered and dried in vacuo to yield 0.376 g (71%) of Zn(BuSal)$_2$trien. mp 296°C. IR (KBr, cm^{-1}); 3440 (NH), 3293, 3053, 2948, 2863, 1632(C=N), 1593, 1426, 1230, 903, 863. ^{1}H NMR (400 MHz, $CDCl_3$, ppm); δ 8.23 (2H, *s*, C<u>H</u>=N), 7.15 (2H, *dd*, Ar-<u>H</u>, *J* = 2 , 7.2 Hz), 6.91 (2H, *dd*, Ar-<u>H</u>, *J* = 1.6 , 7.6 Hz), 6.33 (2H, *t*, Ar-<u>H</u>, *J* = 7.2 Hz), 4.09-4.16 (2H, *m*, N<u>H</u>), 3.48-3.54 (2H, *m*, C<u>H</u>$_2$), 3.36-3.43 (2H, *m*, C<u>H</u>$_2$), 3.06-3.09 (2H, *m*, C<u>H</u>$_2$), 2.64-2.73 (4H, *m*, C<u>H</u>$_2$), 2.20 (2H, *s*, C<u>H</u>$_2$), 1.32 (18H, *s*, C<u>H</u>$_3$). ^{13}C NMR ($CDCl_3$, ppm); δ 171 (<u>C</u>=N), 167, 141, 133, 129, 119, 110, 55, 46, 43, 34, 29. FAB MS (*m/z*) 529.3 ($C_{28}H_{40}N_4O_2Zn$). Anal. Calcd. For $C_{28}H_{40}N_4O_2Zn$: C 63.45; H 7.61; N 10.57; found C 63.03; H 7.57; N 10.59.

2.3.1.5 Synthesis of bis(3,5-di-*tert*-butyl-salicylaldiminato)triethylenetetra mine zinc(II) complex [Zn(diBuSal)$_2$trien]



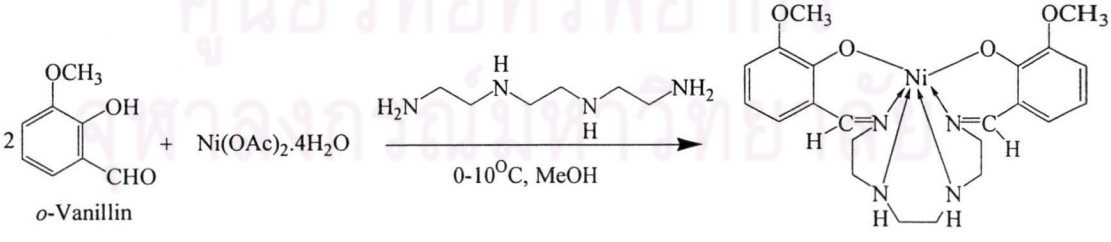
3,5-di-*tert*-Butyl-2-hydroxybenzaldehyde

Zn(diBuSal)$_2$trien

The experiment was performed according to the procedure described in experiment 2.3.1.1 employing 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (0.469 g, 2.0 mmol) instead of salicylaldehyde. The yellow powder were filtered and dried in vacuo to yield 0.540 g (84%) of Zn(diBuSal)$_2$trien. mp 292°C. IR (KBr, cm^{-1}); 3435 (NH), 3305, 3034, 2952, 2864, 1634(C=N), 1528, 1461, 1437, 1259, 899. ^{1}H NMR (400 MHz, $CDCl_3$, ppm); δ 8.23 (2H, *s*, C<u>H</u>=N), 7.25 (2H, *d*, Ar-<u>H</u>, *J* = 2.2 Hz), 6.84 (2H, *d*, Ar-<u>H</u>, *J* = 2.2 Hz), 4.29-4.35 (2H, *m*, N<u>H</u>), 3.32-3.39 (4H, *m*, C<u>H$_2$</u>), 2.99-3.01 (2H, *m*, C<u>H$_2$</u>), 2.54-2.64 (4H, *m*, C<u>H$_2$</u>), 2.11-2.14 (2H, *m*, C<u>H$_2$</u>), 1.37 (18H, *s*, C<u>H$_3$</u>), 1.28 (18H, *s*, C<u>H$_3$</u>). ^{13}C NMR ($CDCl_3$, ppm); δ 169 (<u>C</u>=N), 167, 140, 132, 128, 127, 117, 56, 46, 43, 35, 33, 31, 29. FAB MS (*m/z*) 641.4 ($C_{36}H_{56}N_4O_2Zn$). Anal. Calcd. For $C_{36}H_{56}N_4O_2Zn$: C 67.32; H 8.79; N 8.72; found C 66.90; H 8.76; N 8.72.

2.3.2 Synthesis of hexadentate Schiff base nickel complexes

2.3.2.1 Synthesis of bis(3-methoxysalicylaldiminato)triethylenetetramine nickel(II) complex [Ni(MeOSal)$_2$trien]



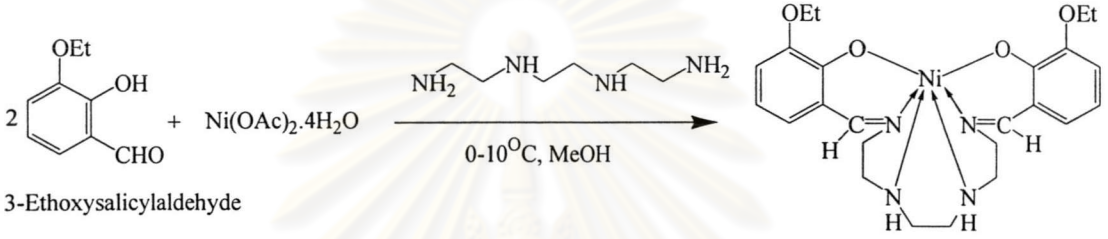
o-Vanillin

Ni(MeOSal)$_2$trien

The experiment was performed according to the procedure described in experiment 2.3.1.1 employing *o*-vanillin (0.304 g, 2.0 mmol) instead of salicylaldehyde and nickel (II) acetate tetrahydrate (0.249 g, 1.0 mmol) instead of zinc

(II) acetate dihydrate. The brown crystals were filtered and dried in vacuo to yield 0.210 g (45%) of $Ni(MeOSal)_2trien$. mp 301°C. IR (KBr, cm^{-1}); 3445 (NH), 3301, 3051, 2992, 2904, 2856, 1632, 1595, 1444, 1217, 1079, 977, 855, 740. FAB MS (*m/z*) 471.2 ($C_{22}H_{28}N_4O_4Ni$). Anal. Calcd. For $C_{22}H_{28}N_4O_4Ni.H_2O$: C 54.01; H 6.18; N 11.45; found C 54.53; H 6.31; N 11.57.

2.3.2.2 Synthesis of bis(3-ethoxysalicylaldiminato)triethylenetetramine nickel(II) complex [$Ni(EtOSal)_2trien$]

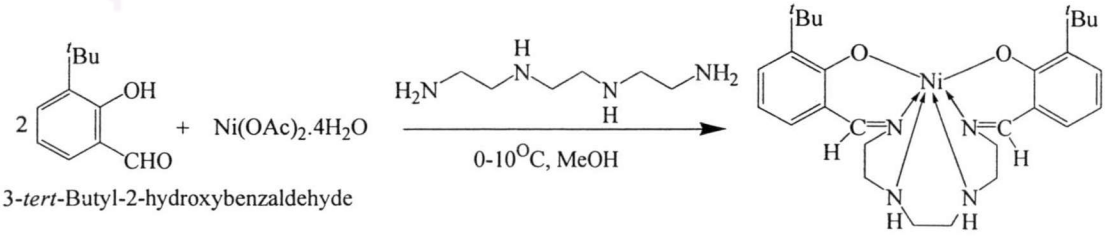


3-Ethoxysalicylaldehyde

$Ni(EtOSal)_2trien$

The experiment was performed according to the procedure described in experiment 2.3.1.1 employing 3-ethoxysalicylaldehyde (0.332 g, 2.0 mmol) instead of salicylaldehyde and nickel (II) acetate tetrahydrate (0.249 g, 1.0 mmol) instead of zinc (II) acetate dihydrate. The brown crystals were filtered and dried in vacuo to yield 0.490 g (98%) of $Ni(EtOSal)_2trien$. mp 235°C. Recrystallization from reflux methanol afforded crystal suitable for X-ray crystallographic analysis. IR (KBr, cm^{-1}); 3444 (NH), 3277, 3046, 2968, 2921, 2863, 1648, 1594, 1441, 1220, 1086, 1047, 990, 750. FAB MS (*m/z*) 499.2 ($C_{24}H_{32}N_4O_4Ni$). Anal. Calcd. For $C_{24}H_{32}N_4O_4Ni.3H_2O$: C 52.10; H 6.92; N 10.13; found C 52.76; H 7.20; N 10.73.

2.3.2.3 Synthesis of bis(3-*tert*-butyl-salicylaldiminato)triethylenetetramine nickel(II) complex [$Ni(BuSal)_2trien$]

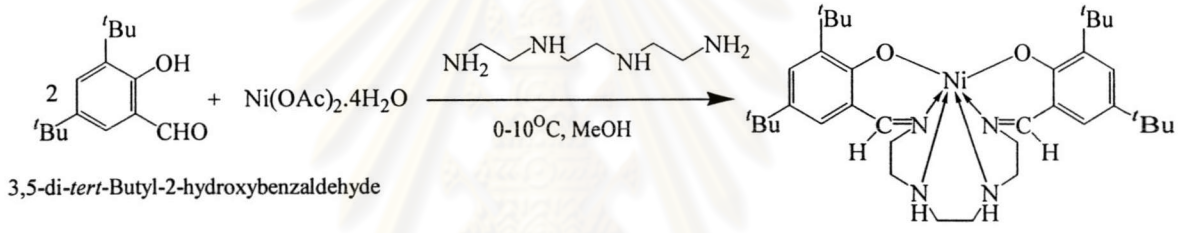


3-*tert*-Butyl-2-hydroxybenzaldehyde

$Ni(BuSal)_2trien$

The experiment was performed according to the procedure described in experiment 2.3.1.1 employing 3-*tert*-butyl-2-hydroxybenzaldehyde (0.356 g, 2.0 mmol) instead of salicylaldehyde and nickel (II) acetate tetrahydrate (0.249 g, 1.0 mmol) instead of zinc (II) acetate dihydrate. The green crystals were filtered and dried in vacuo to yield 0.276 g (53%) of Ni(BuSal)$_2$trien. Recrystallization from reflux methanol afforded crystal suitable for X-ray crystallographic analysis. mp 314°C. IR (KBr, cm^{-1}); 3429 (NH), 3293, 2946, 2904, 1633, 1593, 1533, 1457, 1426, 1139, 911, 863, 748. FAB MS (*m/z*) 523.3 ($C_{28}H_{40}N_4O_2Ni$). Anal. Calcd. For $C_{28}H_{40}N_4O_2Ni$: C 64.26; H 7.70; N 10.71; found C 64.24; H 7.72; N 10.78

2.3.2.4 Synthesis of bis(3,5-di-*tert*-butyl-salicylaldiminato)triethylenetetramine nickel(II) complex [Ni(diBuSal)$_2$trien]

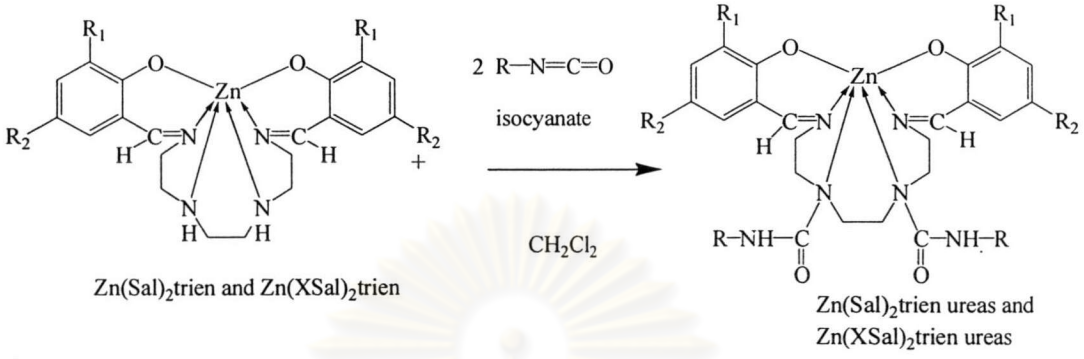


3,5-di-*tert*-Butyl-2-hydroxybenzaldehyde

NidiBuSal$_2$trien

The experiment was performed according to the procedure described in experiment 2.3.1.1 employing 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (0.469 g, 2.0 mmol) instead of salicylaldehyde and nickel (II) acetate tetrahydrate (0.249 g, 1.0 mmol) instead of zinc (II) acetate dihydrate. The brown powders were filtration and dried in vacuo to yield 0.451 g (71%) of Ni(diBuSal)$_2$trien. mp 338°C. IR (KBr, cm^{-1}); 3428 (NH), 3298, 2951, 2903, 1633 (C=N), 1523, 1462, 1437, 1156, 905, 793. FAB MS (*m/z*) 635.4 ($C_{36}H_{56}N_4O_2Ni$). Anal. Calcd. For $C_{36}H_{56}N_4O_2Ni$: C 68.03; H 8.88; N 8.82; found C 67.95; H 8.88; N 8.88.

2.3.3 Synthesis of hexadentate Schiff base zinc urea derivatives [Zn(Sal)$_2$trien ureas and Zn(XSal)$_2$trien ureas] from the reaction between zinc complexes and isocyanates



Zn(Sal)$_2$trien and Zn(XSal)$_2$trien

Zn(Sal)$_2$trien ureas and Zn(XSal)$_2$trien ureas

The isocyanates used were hexyl isocyanate, phenyl isocyanate, benzyl isocyanate and 1-naphthyl isocyanate. The general synthetic method was as follows: isocyanate was added dropwise to the solution of Zn(Sal)$_2$trien or Zn(XSal)$_2$trien in dried methylene chloride (30 mL). The mixture was stirred at room temperature. The progress of the reaction was followed by using IR spectroscopy. After stirring for 6 hours, the solution was evaporated under a reduced pressure to give Zn(Sal)$_2$trien or Zn(XSal)$_2$trien urea as a yellow powder. The residue was washed with hexane and then dried under vacuo for 48 hours to remove traces of the solvent.

Crude products of Zn(Sal)$_2$trien ureas and Zn(XSal)$_2$trien ureas could not be purified since it resulted in decomposition of the materials. Therefore, NMR spectra of these urea derivatives could not be obtained.

Table 2.1 Nomenclature of $Zn(Sal)_2$trien ureas and $Zn(XSal)_2$trien ureas

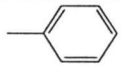
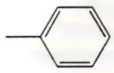
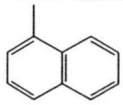
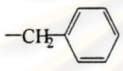
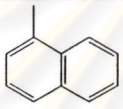
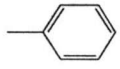
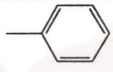
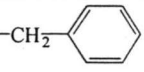
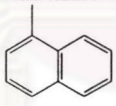
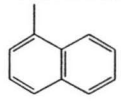
Metal complexes	R	R_1	R_2	Metal complexes	R	R_1	R_2
$Zn(Sal)_2$trien $urea_1$	$-(CH_2)_5CH_3$	H	H	$Zn(EtO)Sal_2$trien $urea_1$	$-(CH_2)_5CH_3$	OEt	H
$Zn(Sal)_2$trien $urea_2$	$-(CH_2)_7CH_3$	H	H	$Zn(EtO)Sal_2$trien $urea_2$	$-(CH_2)_7CH_3$	OEt	H
$Zn(Sal)_2$trien $urea_3$	$-C(CH_3)_2CH_2C(CH_3)_3$	H	H	$Zn(EtO)Sal_2$trien $urea_3$		OEt	H
$Zn(Sal)_2$trien $urea_4$		H	H	$Zn(EtO)Sal_2$trien $urea_4$		OEt	H
$Zn(Sal)_2$trien $urea_5$		H	H	$Zn(diBuSal)_2$trien $urea_5$	$-(CH_2)_5CH_3$	^{t}Bu	^{t}Bu
$Zn(Sal)_2$trien $urea_6$		H	H	$Zn(diBuSal)_2$trien $urea_6$	$-(CH_2)_7CH_3$	^{t}Bu	^{t}Bu
$Zn(MeO)Sal_2$trien $urea_1$	$-(CH_2)_5CH_3$	OMe	H	$Zn(diBuSal)_2$trien $urea_1$	$-C(CH_3)_2CH_2C(CH_3)_3$	^{t}Bu	^{t}Bu
$Zn(MeO)Sal_2$trien $urea_2$	$-(CH_2)_7CH_3$	OMe	H	$Zn(diBuSal)_2$trien $urea_2$		^{t}Bu	^{t}Bu
$Zn(MeO)Sal_2$trien $urea_3$		OMe	H	$Zn(diBuSal)_2$trien $urea_3$		^{t}Bu	^{t}Bu
$Zn(MeO)Sal_2$trien $urea_4$		OMe	H	$Zn(diBuSal)_2$trien $urea_4$		^{t}Bu	^{t}Bu

Table 2.2 Synthesis data of $Zn(Sal)_2$trien ureas and $Zn(XSal)_2$trien ureas

Metal complexes	Weight of starting materials							Yield (%)
	Zn-complexes	Isocyanates						
	(g)	HI (ml)	OI (ml)	TI (ml)	PI (ml)	BI (ml)	NI (ml)	
$Zn(Sal)_2$trien $urea_1$	0.150 g, 0.36 mmol	0.105 mL, 0.72 mmol	-	-	-	-	-	92
$Zn(Sal)_2$trien $urea_2$	0.150 g, 0.36 mmol	-	0.125 mL, 0.72 mmol	-	-	-	-	54
$Zn(Sal)_2$trien $urea_3$	0.150 g, 0.36 mmol	-	-	0.130 mL, 0.72 mmol	-	-	-	61
$Zn(Sal)_2$trien $urea_4$	0.150 g, 0.36 mmol	-	-	-	0.079 mL, 0.72 mmol	-	-	91
$Zn(Sal)_2$trien $urea_5$	0.150 g, 0.36 mmol	-	-	-	-	0.089 mL, 0.72 mmol	-	34
$Zn(Sal)_2$trien $urea_6$	0.150 g, 0.36 mmol	-	-	-	-	-	0.104 mL, 0.72 mmol	83
$Zn(MeO)Sal_2$trien $urea_1$	0.200 g, 0.418 mmol	0.122 mL, 0.84 mmol	-	-	-	-	-	43
$Zn(MeO)Sal_2$trien $urea_2$	0.200 g, 0.418 mmol	-	0.147 mL, 0.84 mmol	-	-	-	-	69
$Zn(MeO)Sal_2$trien $urea_3$	0.200 g, 0.418 mmol	-	-	-	0.092 mL, 0.84 mmol	-	-	78
$Zn(MeO)Sal_2$trien $urea_4$	0.200 g, 0.418 mmol	-	-	-	-	-	0.120 mL, 0.84 mmol	55
$Zn(EtO)Sal_2$trien $urea_1$	0.200 g, 0.395 mmol	0.115 mL, 0.79 mmol	-	-	-	-	-	49
$Zn(EtO)Sal_2$trien $urea_2$	0.200 g, 0.395 mmol	-	0.139 mL, 0.79 mmol	-	-	-	-	40
$Zn(EtO)Sal_2$trien $urea_3$	0.200 g, 0.395 mmol	-	-	-	0.086 mL, 0.79 mmol	-	-	25
$Zn(EtO)Sal_2$trien $urea_4$	0.200 g, 0.395 mmol	-	-	-	-	-	0.114 mL, 0.79 mmol	32
$Zn(diBuSal)_2$trien $urea_1$	0.250 g, 0.39 mmol	0.114 mL, 0.78 mmol	-	-	-	-	-	62

Table 2.2 (cont.) Synthesis data of $Zn(Sal)_2$trien ureas and $Zn(XSal)_2$trien ureas

Metal complexes	Weight of starting materials							Yield (%)
	Zn-complexes	Isocyanates						
	(g)	HI (ml)	OI (ml)	TI (ml)	PI (ml)	BI (ml)	NI (ml)	
$Zn(diBuSal)_2$trien $urea_2$	0.250 g, 0.39 mmol	-	0.137 mL, 0.78 mmol	-	-	-	-	86
$Zn(diBuSal)_2$trien $urea_3$	0.250 g, 0.39 mmol	-	-	0.141 mL, 0.78 mmol	-	-	-	48
$Zn(diBuSal)_2$trien $urea_4$	0.250 g, 0.39 mmol	-	-	-	0.085 mL, 0.78 mmol	-	-	56
$Zn(diBuSal)_2$trien $urea_5$	0.250 g, 0.39 mmol	-	-	-	-	0.096 mL, 0.78 mmol	-	27
$Zn(diBuSal)_2$trien $urea_6$	0.250 g, 0.39 mmol	-	-	-	-	-	0.112 mL, 0.78 mmol	93

HI = hexyl isocyanate, OI = octyl isocyanate, TI = 1,1,3,3-tetramethylbutylisocyanate, PI = phenyl isocyanate, BI = benzyl isocyanate, NI = 1-naphthyl isocyanate

$Zn(Sal)_2$trien $urea_1$: IR (KBr, cm^{-1}); 3331 (NH), 2955, 2928, 2850, 1621 (C=N), 1576, 1465, 1342, 1254, 1190, 1149, 1068, 758. Anal. Calcd. For $C_{34}H_{50}N_6O_4Zn$: C 60.75; H 7.50; N 12.50; found C 60.73; H 7.58; N 12.43.

$Zn(Sal)_2$trien $urea_2$: IR (KBr, cm^{-1}); 3332 (NH), 2925, 2854, 1627 (C=N), 1574, 1465, 1404, 1342, 1272, 1190, 1148, 909, 754. Anal. Calcd. For $C_{38}H_{58}N_6O_4Zn$: C 62.67; H 8.03; N 11.54; found C 63.13; H 8.34; N 11.17.

$Zn(Sal)_2$trien $urea_3$: IR (KBr, cm^{-1}); 3366 (NH), 3075, 2954, 2897, 1634 (C=N), 1555, 1467, 1397, 1277, 1220, 1148, 1069, 1033, 905, 757. Anal. Calcd. For $C_{38}H_{58}N_6O_4Zn.MeOH$: C 62.67; H 8.03; N 11.54; found C 62.63; H 8.06; N 11.78.

$Zn(Sal)_2$trien $urea_4$: IR (KBr, cm^{-1}); 3426 (NH), 3042, 2934, 1623 (C=N), 1600, 1539, 1446, 1402, 1245, 1066, 909, 755. Anal. Calcd. For $C_{34}H_{34}N_6O_4Zn$: C 62.24; H 5.22; N 12.81; found C 61.93; H 5.27; N 12.85.

$Zn(Sal)_2$trien $urea_5$: IR (KBr, cm^{-1}); 3319 (NH), 3029, 2920, 2863, 1705 (C=O), 1629 (C=N), 1569, 1451, 1268, 1341, 1268, 1190, 905, 754.

$Zn(Sal)_2$trien $urea_6$: IR (KBr, cm^{-1}); 3429 (NH), 3273, 3049, 1633 (C=N), 1553, 1503, 1465, 1397, 1343, 1250, 1215, 1151, 769.

$Zn(MeOSal)_2$trien $urea_1$: IR (KBr, cm^{-1}); 3333 (NH), 3054, 2925, 2853, 1626 (C=N), 1572, 1472, 1445, 1403, 1336, 1216, 1078, 973, 739.

Zn(MeOSal)$_2$trien urea$_2$: IR (KBr, cm^{-1}); 3333 (NH), 2925, 2853, 1620 (C=N), 1576, 1470, 1336, 1269, 1215, 1078, 973, 737.

Zn(MeOSal)$_2$trien urea$_3$: IR (KBr, cm^{-1}); 3294 (NH), 3052, 2931, 2821, 1625 (C=N), 1544, 1445, 1404, 1313, 1240, 1216, 1077, 971, 855, 746.

Zn(MeOSal)$_2$trien urea$_4$: IR (KBr, cm^{-1}); 3312 (NH), 3049, 2906, 1632 (C=N), 1538, 1470, 1445, 1403, 1333, 1215, 1079, 971, 854, 774, 739.

Zn(EtOSal)$_2$trien urea$_1$: IR (KBr, cm^{-1}); 3332 (NH), 2928, 2858, 1621 (C=N), 1576, 1464, 1403, 1216, 1074, 895, 739.

Zn(EtOSal)$_2$trien urea$_2$: IR (KBr, cm^{-1}); 3333 (NH), 3044, 2925, 2825, 1633 (C=N), 1567, 1464, 1396, 1324, 1217, 1075, 739.

Zn(EtOSal)$_2$trien urea$_3$: IR (KBr, cm^{-1}); 3324 (NH), 3034, 1648 (C=N), 1597, 1551, 1495, 1443, 1310, 1232, 894, 753.

Zn(EtOSal)$_2$trien urea$_4$: IR (KBr, cm^{-1}); 3275 (NH), 3051, 1637 (C=N), 1556, 1504, 1397, 1344, 1248, 1214, 785.

Zn(diBuSal)$_2$trien urea$_1$: IR (KBr, cm^{-1}); 3332 (NH), 2954, 2860, 1622 (C=N), 1577, 1529, 1463, 1256, 1159, 1075, 899, 793, 738.

Zn(diBuSal)$_2$trien urea$_2$: IR (KBr, cm^{-1}); 3332 (NH), 2925, 2853, 1616 (C=N), 1576, 1466, 1270, 1237, 1083, 890, 726.

Zn(diBuSal)$_2$trien urea$_3$: IR (KBr, cm^{-1}); 3370 (NH), 2955, 2901, 2865, 1630 (C=N), 1549, 1467, 1389, 1363, 1272, 1164, 1070, 834.

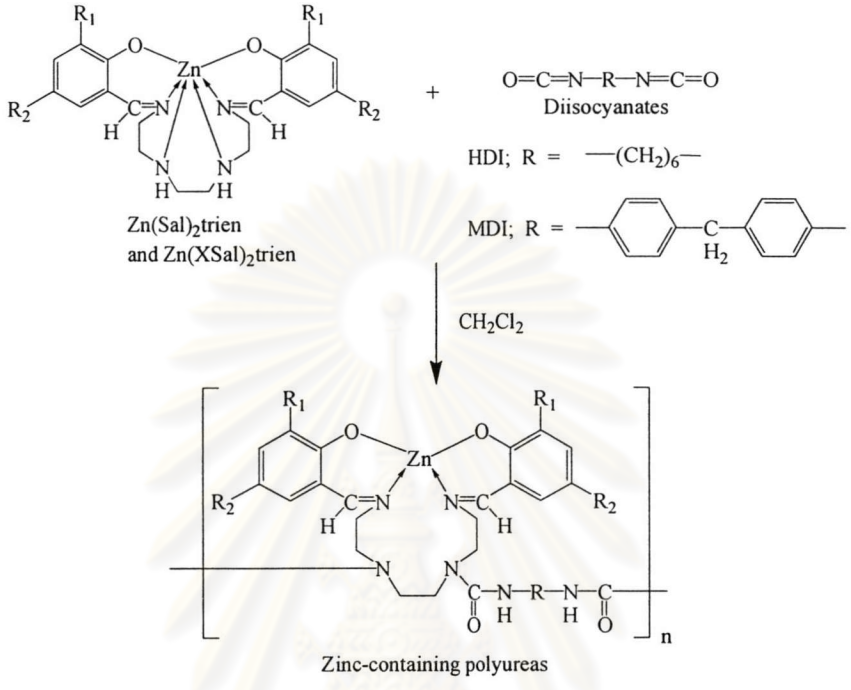
Zn(diBuSal)$_2$trien urea$_4$: IR (KBr, cm^{-1}); 3302 (NH), 3044, 2955, 2901, 2899, 1706 (C=O), 1625 (C=N), 1540, 1443, 1312, 1246, 1168, 1071, 879, 753.

Zn(diBuSal)$_2$trien urea$_5$: IR (KBr, cm^{-1}); 3325 (NH), 3030, 2922, 2872, 1626 (C=N), 1573, 1452, 1365, 1253, 1078, 732.

Zn(diBuSal)$_2$trien urea$_6$: IR (KBr, cm^{-1}); 3426 (NH), 3278, 3050, 2954, 2901, 2865, 1629 (C=N), 1534, 1437, 1394, 1256, 1165, 1064, 790, 772.

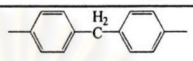
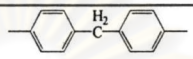
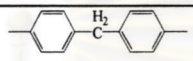
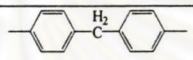
2.3.4 Synthesis of metal-containing polyureas

2.3.4.1 Synthesis of zinc-containing polyureas from the reaction between zinc complexes and diisocyanates



Diisocyanates employed were hexamethylene diisocyanate (HDI) and 4,4′-diphenylmethane diisocyanate (MDI). The general polymerization reaction was as follows: diisocyanate was added dropwise to the stirred solution of $ZnSal_2trien$ or $Zn(XSal)_2trien$ in dried methylene chloride (30 mL) at room temperature. The progress of the reaction was followed by using IR spectroscopy. The precipitated polyurea was filtered and dried in vacuo.

Table 2.3 Nomenclature of zinc-containing polyureas

Polyureas	R	R_1	R_2
$Zn(Sal)_2$trien-HDI	$-(CH_2)_6-$	H	H
$Zn(MeOSal)_2$trien-HDI	$-(CH_2)_6-$	OMe	H
$Zn(EtOSal)_2$trien-HDI	$-(CH_2)_6-$	OEt	H
$Zn(diBuSal)_2$trien-HDI	$-(CH_2)_6-$	^{t}Bu	^{t}Bu
$Zn(Sal)_2$trien-MDI		H	H
$Zn(MeOSal)_2$trien-MDI		OMe	H
$Zn(EtOSal)_2$trien-MDI		OEt	H
$Zn(diBuSal)_2$trien-MDI		^{t}Bu	^{t}Bu

HDI = hexamethylene diisocyanate, MDI = 4,4′-diphenylmethane diisocyanate

Table 2.4 Synthesis data of zinc-containing polyureas

Polymer	Weight of starting materials			Reaction Time (hr)	Yield (%)
	Zinc complexes (g)	Isocyanate (ml)			
		HDI	MDI		
$Zn(Sal)_2$trien-HDI	0.628 g, 1.50 mmol	0.242 mL, 1.50 mmol	-	6	61
$Zn(MeOSal)_2$trien-HDI	0.717 g, 1.50 mmol	0.242 mL, 1.50 mmol	-	6	75
$Zn(EtOSal)_2$trien-HDI	0.759 g, 1.50 mmol	0.242 mL, 1.50 mmol	-	6	55
$Zn(diBuSal)_2$trien-HDI	0.482 g, 0.75 mmol	0.121 mL, 0.75 mmol	-	6	86
$Zn(Sal)_2$trien-MDI	1.160 g, 2.78 mmol	-	0.695 g, 2.78 mmol	4	80
$Zn(MeOSal)_2$trien-MDI	0.717 g, 1.50 mmol	-	0.375 g, 1.50 mmol	4	75
$Zn(EtOSal)_2$trien-MDI	0.759 g, 1.50 mmol	-	0.375 g, 1.50 mmol	4	49
$Zn(diBuSal)_2$trien-MDI	0.318 g, 0.49 mmol	-	0.124 g, 0.49 mmol	4	85

$Zn(Sal)_2$trien-HDI; IR (KBr, cm^{-1}); 3348 (NH), 3048, 2950, 2929, 2857, 1720 (C=O), 1629 (C=N), 1544, 1467, 1341, 1150, 930, 759. ^{1}H NMR (400 MHz, DMSO-d_6, ppm); δ 8.25 (2H, *s*, C<u>H</u>=N), 7.03 (2H, *d*, Ar-<u>H</u>, *J* = 7.6 Hz), 6.95 (2H, *t*, Ar-<u>H</u>, *J* = 8.0 Hz), 6.32 (2H, *d*, Ar-<u>H</u>, *J* = 8 Hz), 6.23 (2H, *t*, Ar-<u>H</u>, *J* = 7.6 Hz), 5.81 (2H, *m*, N<u>H</u>), 1.36 (4H, *br*, C<u>H</u>$_2$), 1.24 (4H, *br*, C<u>H</u>$_2$). Anal. Calcd. For $C_{28}H_{36}N_6O_4Zn$: C 57.39; H 6.19; N 14.34; found C 54.37; H 6.53; N 14.48.

$Zn(MeOSal)_2$trien-HDI; IR (KBr, cm^{-1}); 3312 (NH), 3044, 2928, 2856, 1632 (C=N), 1565, 1473, 1446, 1335, 1217, 1078, 972, 854, 741. ^{1}H NMR (400 MHz, DMSO-d_6,

ppm); δ 8.25 (2H, *s*, C<u>H</u>=N), 6.69 (2H, *dd*, Ar-<u>H</u>, *J* = 1.6, 8.0 Hz), 6.61 (2H, *dd*, Ar-<u>H</u>, *J* = 1.2, 7.6 Hz) 6.13 (2H, *t*, Ar-<u>H</u>, *J* = 7.6 Hz) 5.80 (2H, *m*, N<u>H</u>), 3.59 (6H, *s*, OC<u>H</u>$_3$), 1.37 (4H, *br*, C<u>H</u>$_2$), 1.24 (4H, *br*, C<u>H</u>$_2$). Anal. Calcd. For $C_{30}H_{40}N_6O_6Zn$: C 55.77; H 6.24; N 13.01; found C 55.60; H 6.36; N 13.04.

Zn(EtOSal)$_2$trien-HDI; IR (KBr, cm^{-1}); 3346 (NH), 3039, 2927, 2859, 1719 (C=O), 1634 (C=N), 1550, 1463, 1398, 1214, 1071, 850, 741. ^{1}H NMR (400 MHz, DMSO-d_6, ppm); δ 8.25 (2H, *s*, C<u>H</u>=N), 6.71 (2H, *dd*, Ar-<u>H</u>, *J* = 1.6, 8.0 Hz), 6.61(2H, *dd*, Ar-<u>H</u>, *J* = 1.6, 8.0 Hz), 6.09 (2H, *t*, Ar-<u>H</u>, *J* = 7.6 Hz), 5.82 (2H, *m*, N<u>H</u>), 3.74-3.89 (4H, *m*, OC<u>H</u>$_2$), 1.35 (4H, *br*, C<u>H</u>$_2$), 1.24 (4H, *br*, C<u>H</u>$_2$), 1.10 (6H, *t*, C<u>H</u>$_3$, *J* = 6.8 Hz). Anal. Calcd. For $C_{32}H_{44}N_6O_6Zn$: C 57.01; H 6.58; N 12.47; found C 54.48; H 7.61; N 14.44.

Zn(diBuSal)$_2$trien-HDI; IR (KBr, cm^{-1}); 3337 (NH), 3034, 2951, 2863, 1624(C=N), 1531, 1457, 1437, 1257, 1162, 834, 789, 741, 636. ^{1}H NMR (400 MHz, DMSO-d_6, ppm); δ 8.21 (2H, *s*, C<u>H</u>=N), 6.99 (2H, *d*, Ar-<u>H</u>, *J* = 2.8 Hz), 6.76 (2H, *d*, Ar-<u>H</u>, *J* = 2.4 Hz), 5.81 (2H, *m*, N<u>H</u>), 1.37-1.31 (8H, *m*, C<u>H</u>$_2$), 1.22 (9H, *s*, C<u>H</u>$_3$), 1.80 (9H, *s*, C<u>H</u>$_3$). Anal. Calcd. For $C_{44}H_{68}N_6O_4Zn$: C 65.21; H 8.46; N 10.37; found C 63.63; H 8.76; N 10.23.

Zn(Sal)$_2$trien-MDI; IR (KBr, cm^{-1}); 3339(NH), 3027, 2914, 1703(C=O), 1632(C=N), 1514, 1466, 1238, 1150, 903, 760. ^{1}H NMR (400 MHz, DMSO-d_6, ppm); δ 8.25 (2H, *s*, C<u>H</u>=N), 7.33-7.36 (2H, *m*, Ar-<u>H</u>), 7.05-7.12 (2H, *m*, Ar-<u>H</u>), 7.03 (2H, *d*, Ar-<u>H</u>, *J* = 7.2 Hz), 6.95 (2H, *t*, Ar-<u>H</u>, *J* = 7.6 Hz), 6.86-6.88 (2H, *m*, Ar-<u>H</u>), 6.48-6.50 (2H, *m*, Ar-<u>H</u>), 6.32 (2H, *d*, Ar-<u>H</u>, *J* = 8.8 Hz), 6.23 (2H, *t*, Ar-<u>H</u>, *J* = 6.4 Hz). Anal. Calcd. For $C_{35}H_{34}N_6O_4Zn$: C 62.92; H 5.13; N 12.58; found C 61.13; H 5.23; N 12.45.

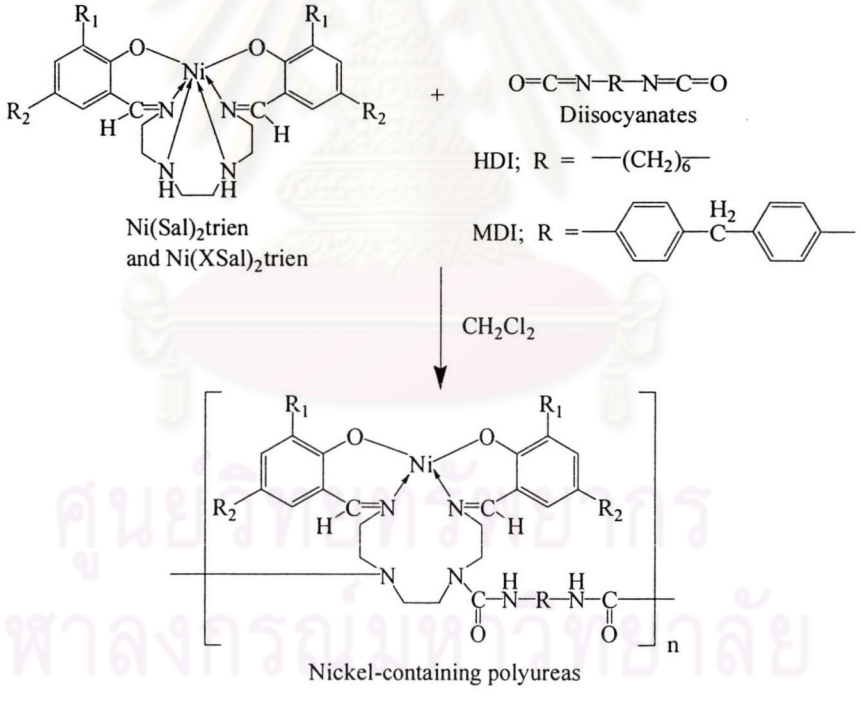
Zn(MeOSal)$_2$trien-MDI; IR (KBr, cm^{-1}); 3310 (NH), 3039, 2982, 2906, 2823, 1630 (C=N), 1513, 1470, 1445, 1312, 1216, 1078, 972, 853, 741. ^{1}H NMR (400 MHz, DMSO-d_6, ppm); δ 8.25 (2H, *s*, C<u>H</u>=N), 7.32-7.36 (2H, *m*, Ar-<u>H</u>), 7.06-7.12 (2H, *m*, Ar-<u>H</u>), 6.81-6.87 (2H, *m*, Ar-<u>H</u>), 6.69 (2H, *dd*, Ar-<u>H</u>, *J* = 1.6, 7.6 Hz), 6.61 (2H, *dd*, Ar-<u>H</u>, *J* = 1.6, 7.2 Hz), 6.48-6.50 (2H, *m*, Ar-<u>H</u>), 6.14 (2H, *t*, Ar-<u>H</u>, *J* = 7.6 Hz), 3.59 (6H, *s*, OC<u>H</u>$_3$). Anal. Calcd. For $C_{37}H_{38}N_6O_6Zn$: C 61.03; H 5.26; N 11.54; found C 59.32; H 5.37; N 11.11.

Zn(EtOSal)$_2$trien-MDI; IR (KBr, cm^{-1}); 3308 (NH), 3042, 2924, 2854, 1631 (C=N), 1536, 1446, 1316, 1219, 1072, 970, 853, 739. ^{1}H NMR (400 MHz, DMSO-d_6, ppm);

δ 8.25 (2H, *s*, C<u>H</u>=N), 7.32-7.36 (2H, *m*, Ar-<u>H</u>), 7.06-7.12 (2H, *m*, Ar-<u>H</u>), 6.79-6.86 (2H, *m*, Ar-<u>H</u>), 6.71 (2H, *dd*, Ar-<u>H</u>, *J* = 1.6, 8.0 Hz), 6.61 (2H, *dd*, Ar-<u>H</u>, *J* = 1.6, 6.8 Hz), 6.48-6.50 (2H, *m*, Ar-<u>H</u>), 6.09 (2H, *t*, Ar-<u>H</u>, *J* = 7.6 Hz), 3.74-3.89 (4H, *m*, OC<u>H</u>$_2$), 1.10 (6H, *t*, C<u>H</u>$_3$, *J* = 6.8 Hz). Anal. Calcd. For $C_{39}H_{42}N_6O_6Zn$: C 61.95; H 5.60; N 11.11; found C 58.07; H 5.61; N 11.03.

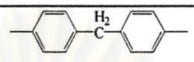
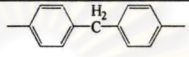
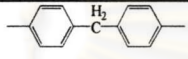
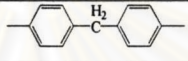
Zn(diBuSal)$_2$trien-MDI; IR (KBr, cm^{-1}); 3362 (NH), 3027, 2953, 2895, 2853, 1617 (C=N), 1518, 1464, 1414, 1311, 1250, 1165, 831. ^{1}H NMR (400 MHz, DMSO-d_6, ppm); δ 8.43 (1H, *s*, C<u>H</u>=N), 8.29 (1H, *s*, C<u>H</u>=N), 6.70-7.46 (10H, *m*, Ar-<u>H</u>), 6.50-6.54(2H, *m*, Ar-<u>H</u>), 1.22-1.32 (18H, *s*, C<u>H</u>$_3$). Anal. Calcd. For $C_{51}H_{66}N_6O_4Zn$: C 68.63; H 7.45; N 9.42; found C 67.16; H 7.54; N 9.23.

2.3.4.2 Synthesis of nickel-containing polyureas from the reaction between nickel complexes and diisocyanates



Disocyanate was added dropwise to the stirred solution of Ni(Sal)$_2$trien or Ni(XSal)$_2$trien in dried methylene chloride (30 mL) at reflux under N_2 atmosphere. The progress of the reaction was followed by using IR spectroscopy. The precipitated product was filtered and dried in vacuo.

Table 2.5 Nomenclature of nickel-containing polyureas

Polyureas	R	R_1	R_2
Ni(Sal)$_2$trien-HDI	-$(CH_2)_6$-	H	H
Ni(MeOSal)$_2$trien-HDI	-$(CH_2)_6$-	OMe	H
Ni(EtOSal)$_2$trien-HDI	-$(CH_2)_6$-	OEt	H
Ni(diBuSal)$_2$trien-HDI	-$(CH_2)_6$-	^{t}Bu	^{t}Bu
Ni(Sal)$_2$trien-MDI		H	H
Ni(MeOSal)$_2$trien-MDI		OMe	H
Ni(EtOSal)$_2$trien-MDI		OEt	H
Ni(diBuSal)$_2$trien-MDI		^{t}Bu	^{t}Bu

HDI = hexamethylene diisocyanate, MDI = 4,4′-diphenylmethane diisocyanate

Table 2.6 Synthesis data of nickel-containing polyureas

Polymer	Weight of starting materials			Reaction Time (hr)	Yield (%)
	Nickel complexes (g)	Isocyanate (ml)			
		HDI	MDI		
Ni(Sal)$_2$trien-HDI	2.156 g, 4.98 mmol	0.806 mL, 4.98 mmol	-	6	70
Ni(MeOSal)$_2$trien-HDI	0.354 g, 0.75 mmol	0.121 mL, 0.75 mmol	-	6	61
Ni(EtOSal)$_2$trien-HDI	0.337 g, 0.75 mmol	0.121 mL, 0.75 mmol	-	6	70
Ni(diBuSal)$_2$trien-HDI	0.477 g, 0.75 mmol	0.121 mL, 0.75 mmol	-	8	57
Ni(Sal)$_2$trien-MDI	2.156 g, 4.98 mmol	-	1.246 g, 4.98 mmol	4	72
Ni(MeOSal)$_2$trien-MDI	0.533 g, 0.885 mmol	-	0.221 g, 0.88 mmol	4	70
Ni(EtOSal)$_2$trien-MDI	1.00 g, 2.23 mmol	-	0.558 g, 2.23 mmol	4	79
Ni(diBuSal)$_2$trien-MDI	0.477 g, 0.75 mmol	-	0.187 g, 0.75 mmol	4	64

Ni(Sal)$_2$trien-HDI; IR (KBr, cm^{-1}); 3333 (NH), 2930, 2857, 1628 (C=N), 1573, 1466, 1258, 1158, 1079, 912, 761, 731, 644. Anal. Calcd. For $C_{28}H_{36}N_6O_4Ni$: C 58.05; H 6.26; N 14.51; found C 56.49; H 6.42; N 14.42.

Ni(MeOSal)$_2$trien-HDI; IR (KBr, cm^{-1}); 3423 (NH), 2930, 2847, 1632 (C=N), 1564, 1473, 1442, 1337, 1216, 1079, 976, 853, 740, 643. Anal. Calcd. For $C_{30}H_{40}N_6O_6Ni$: C 56.36; H 6.31; N 13.14; found C 57.35; H 5.81; N 9.65.

Ni(EtOSal)$_2$trien-HDI; IR (KBr, cm^{-1}); 3337 (NH), 3044, 2930, 2853, 1701 (C=O), 1628 (C=N), 1570, 1465, 1324, 1217, 1078, 894, 740. Anal. Calcd. For $C_{32}H_{44}N_6O_6Ni$: C 57.59; H 6.64; N 12.59; found C 53.68; H 7.34; N 12.65.

Ni(diBuSal)$_2$trien-HDI; IR (KBr, cm^{-1}); 3310 (NH), 2949, 2862, 1687 (C=O), 1630 (C=N), 1530, 1462, 1436, 1259, 1160, 1090, 877, 793, 739. Anal. Calcd. For $C_{44}H_{68}N_6O_4Ni$: C 65.75; H 8.53; N 10.46; found C 64.31; H 10.41; N 9.09.

Ni(Sal)$_2$trien-MDI; IR (KBr, cm^{-1}); 3309 (NH), 3019, 2903, 1693 (C=O), 1639 (C=N), 1598, 1536, 1511, 1449, 1407, 1310, 1233, 1188, 1149, 1121, 907, 813, 757. Anal. Calcd. For $C_{35}H_{34}N_6O_4Ni$: C 63.56; H 5.18; N 12.71; found C 61.32; H 5.96; N 12.87.

Ni(MeOSal)$_2$trien-MDI; IR (KBr, cm^{-1}); 3417 (NH), 2901, 1633 (C=N), 1601, 1544, 1512, 1442, 1411, 1311, 1219, 1079, 971, 740. Anal. Calcd. For $C_{37}H_{38}N_6O_6Ni$: C 61.60; H 5.31; N 11.65; found C 59.18; H 5.10; N 11.09.

Ni(EtOSal)$_2$trien-MDI; IR (KBr, cm^{-1}); 3308 (NH), 3034, 2962, 2902, 1709 (C=O), 1640 (C=N), 1599, 1540, 1513, 1442, 1407, 1311, 1217, 1071, 903, 741. Anal. Calcd. For $C_{39}H_{42}N_6O_6Ni$: C 62.50; H 5.65; N 11.21; found C 60.20; H 6.60; N 10.50.

Ni(diBuSal)$_2$trien-MDI; IR (KBr, cm^{-1}); 3431, 3333 (NH), 3029, 2952, 2904, 2867, 1707 (C=O), 1631(C=N), 1528, 1461, 1437, 1314, 1234, 1158, 1072, 909, 791. Anal. Calcd. For $C_{51}H_{66}N_6O_4Ni$: C 69.15; H 7.51; N 9.49; found C 65.38; H 8.05; N 8.78.