Sal_2trien are stronger than free form Van_2trien. Table 9 also shows that Van_2trien and its zinc complex contains two more donor atoms (O3 and O4) compared to Sal_2trien and its zinc complex. Due to dipole moment of $ZnSal_2$trien (7.232 D) and $ZnVan_2$trien (5.5562 D), $ZnSal_2$trien can easier dissolve in polar organic solvent such as DMSO than $ZnVan_2$trien complex.

B3LYP/6-31G(d) optimized geometrical data of $ZnSal_2$trien and $ZnVan_2$trien were obtained and compared to X-ray crystallographic data. The B3LYP/6-31G(d) optimized structure of $ZnSal_2$trien and $ZnVan_2$trien are in good agreement with the X-ray crystallographic data as listed in Table 10.

4. Conclusions

$ZnSal_2$trien and $ZnVan_2$trien, have been synthesized and characterized. Structure determination of $ZnSal_2$trien and $ZnVan_2$trien by X-ray analysis show that both zinc complexes have a bent-shaped conformation with the slope-plane moieties that contain aromatic rings. The Zn atom is coordinated by two phenolic oxygen ligands and for amine ligands to form a distorted octahedral geometry. Protonation constants of the ligands Sal_2trien and Van_2trien and stability constants with their zinc complexes were determined by potentiometric titration. Structural optimization of Sal_2trien, Van_2trien, $ZnSal_2$trien and $ZnVan_2$trien were carried out and binding energies of $ZnSal_2$trien and $ZnVan_2$trien were obtained by quantum chemical calculations.

4. Supplementary material

The crystallographic data (excluding structure factors) of $ZnSal_2trien$ and $ZnVan_2trien$ has been deposited with the Cambridge Crystallographic Center as supplementary publication no. CCDC-203555 and CCDC-######, respectively.

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Table 10 Geometrical data for the structure of $ZnSal_2trien$ and $ZnVan_2trien$

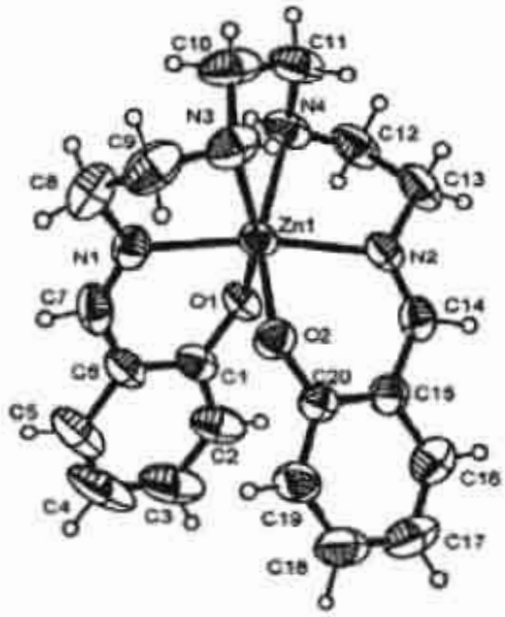


Fig. 1 An ORTEP diagram of $ZnSal_2trien$. Ellipsoids are drawn at 50% probability level.

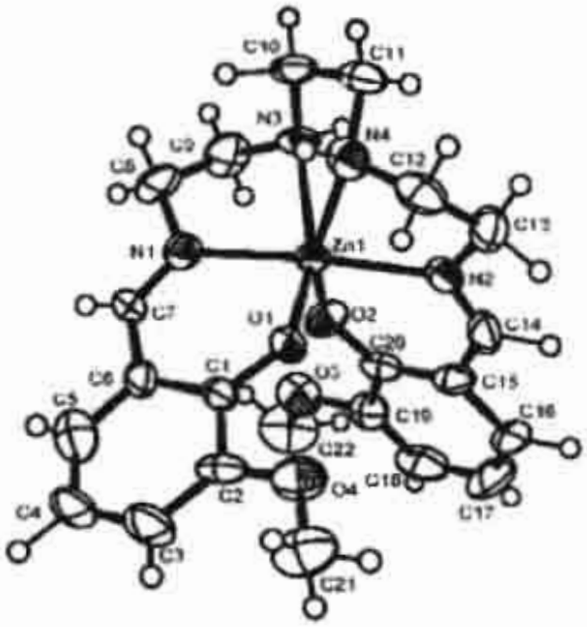


Fig. 2 An ORTEP diagram of $ZnVan_2trien$. Ellipsoids are drawn at 50% probability level.

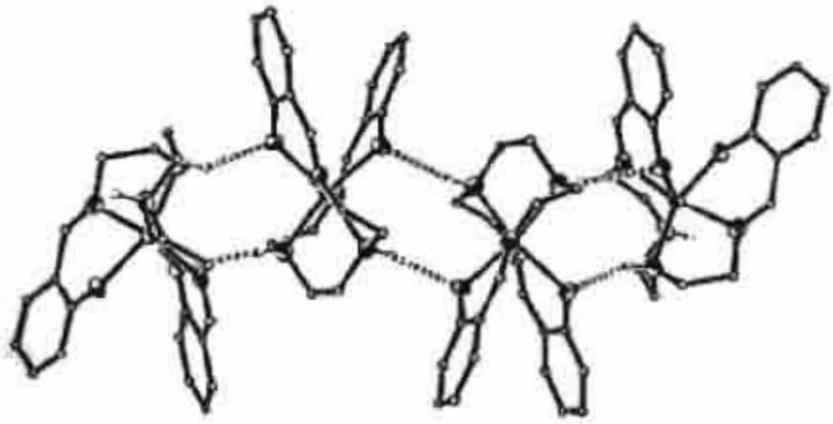


Fig. 3 Polymeric chain formed by N-H···O hydrogen bonding (d[N3···O2(*-x+1, y, -z+1/2*)] = 3.149(3)Å and d[N4···O1(*-x+1/2, -y+1/2, -z*)] = 3.136(3)Å).

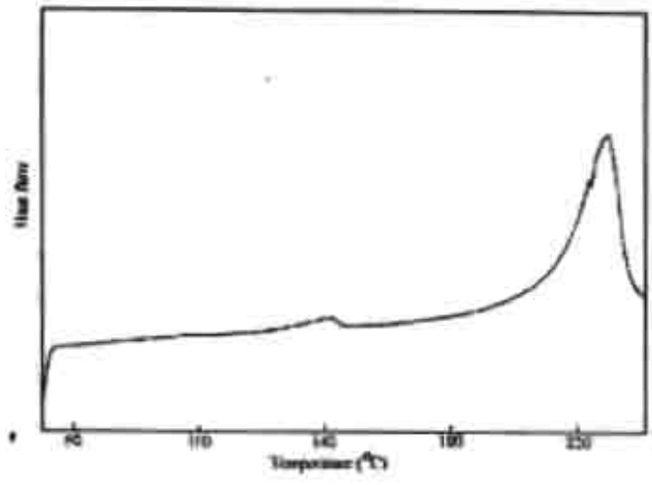


Fig. 4 DSC thermogram of $ZnSal_2$trien.

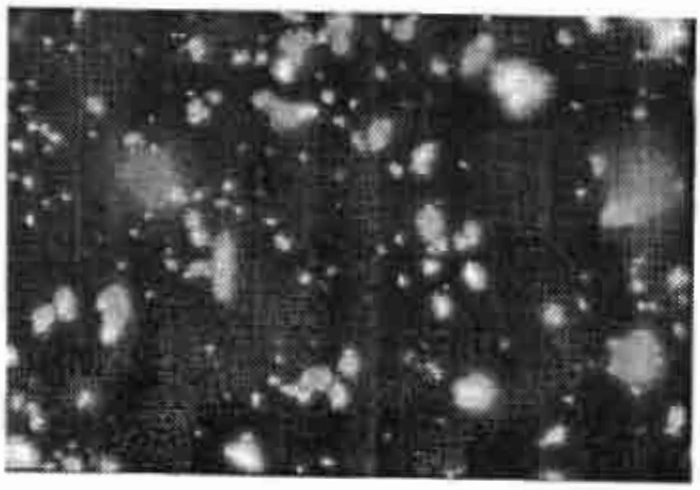
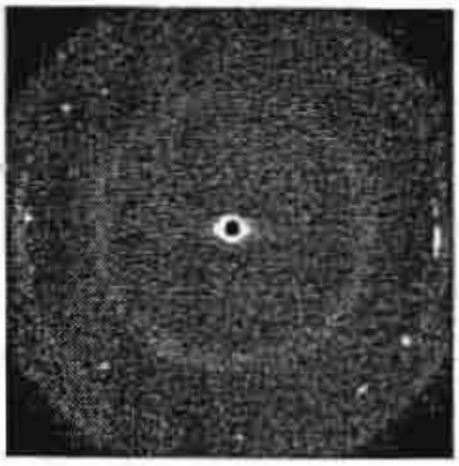
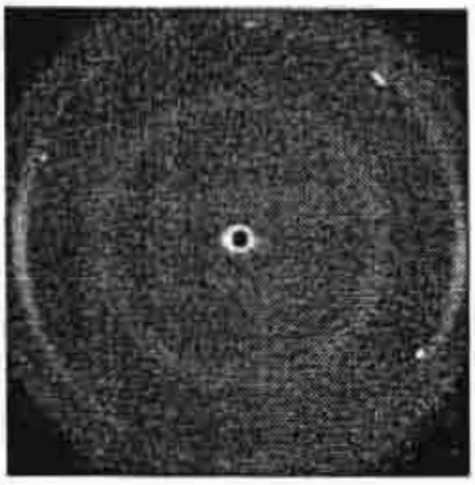


Fig. 5 Morphology of $ZnSal_2trien$ observed by POM at 213°C on heating.

(a)



(b)



(c)

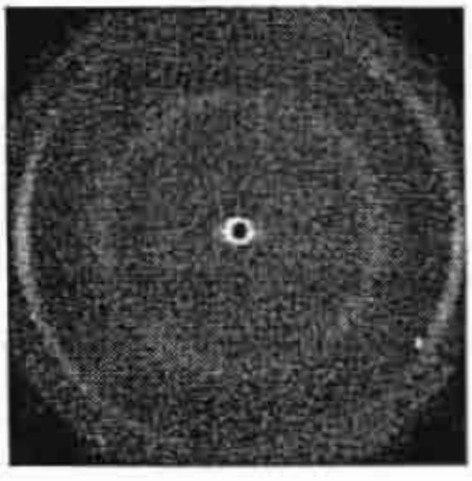


Fig. 6 X-ray diffractograms of $ZnSal_2trien$ at (a) room temperature, (b)210°C and (c) 220°C.

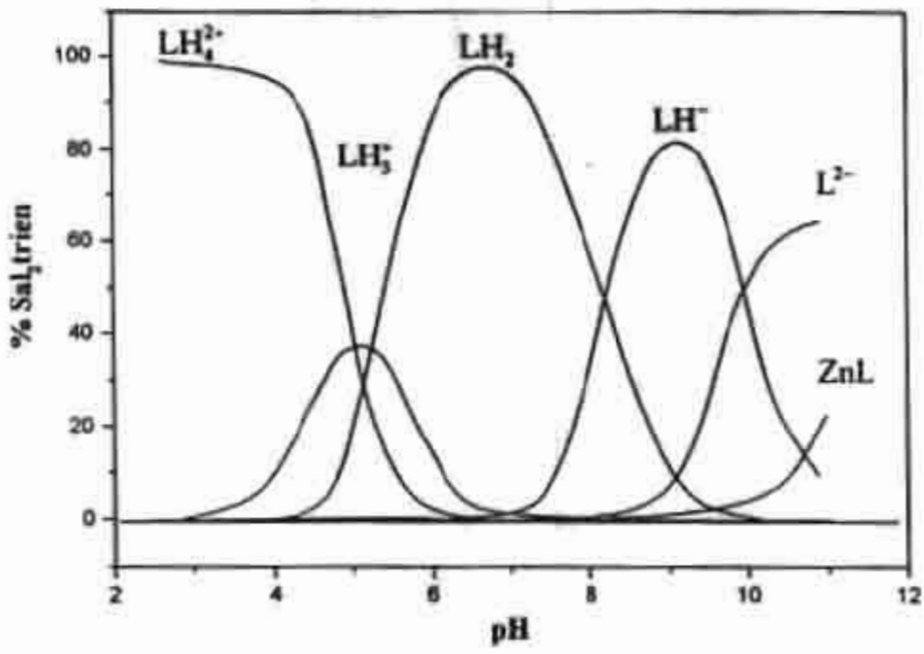


Fig. 7 Species distribution plot of Sal_2trien, denoted as L^{2-}, and $ZnSal_2trien$ in 1.00 x 10^{-2} M $Bu_4NCF_3SO_3$ in methanol at 25°C, C_{ZnL} = 7.685 x 10^{-4} M.

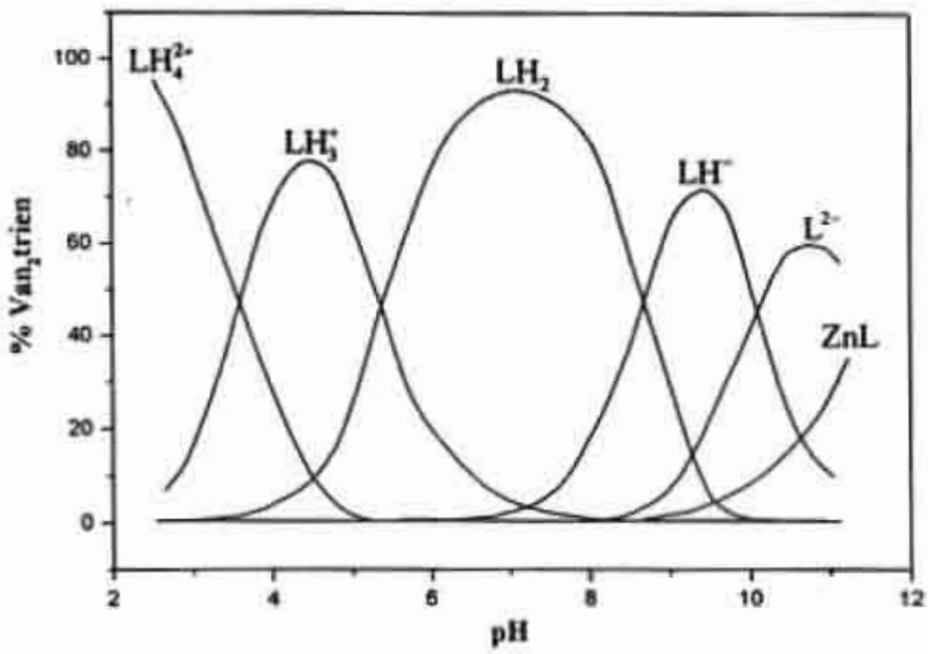


Fig. 8 Species distribution plot of Van_2trien, denoted as L^{2-}, and $ZnVan_2trien$ in 1.00 x 10^{-2} M $Bu_4NCF_3SO_3$ in methanol at 25°C, C_{ZnL} = 8.325 x 10^{-4} M.

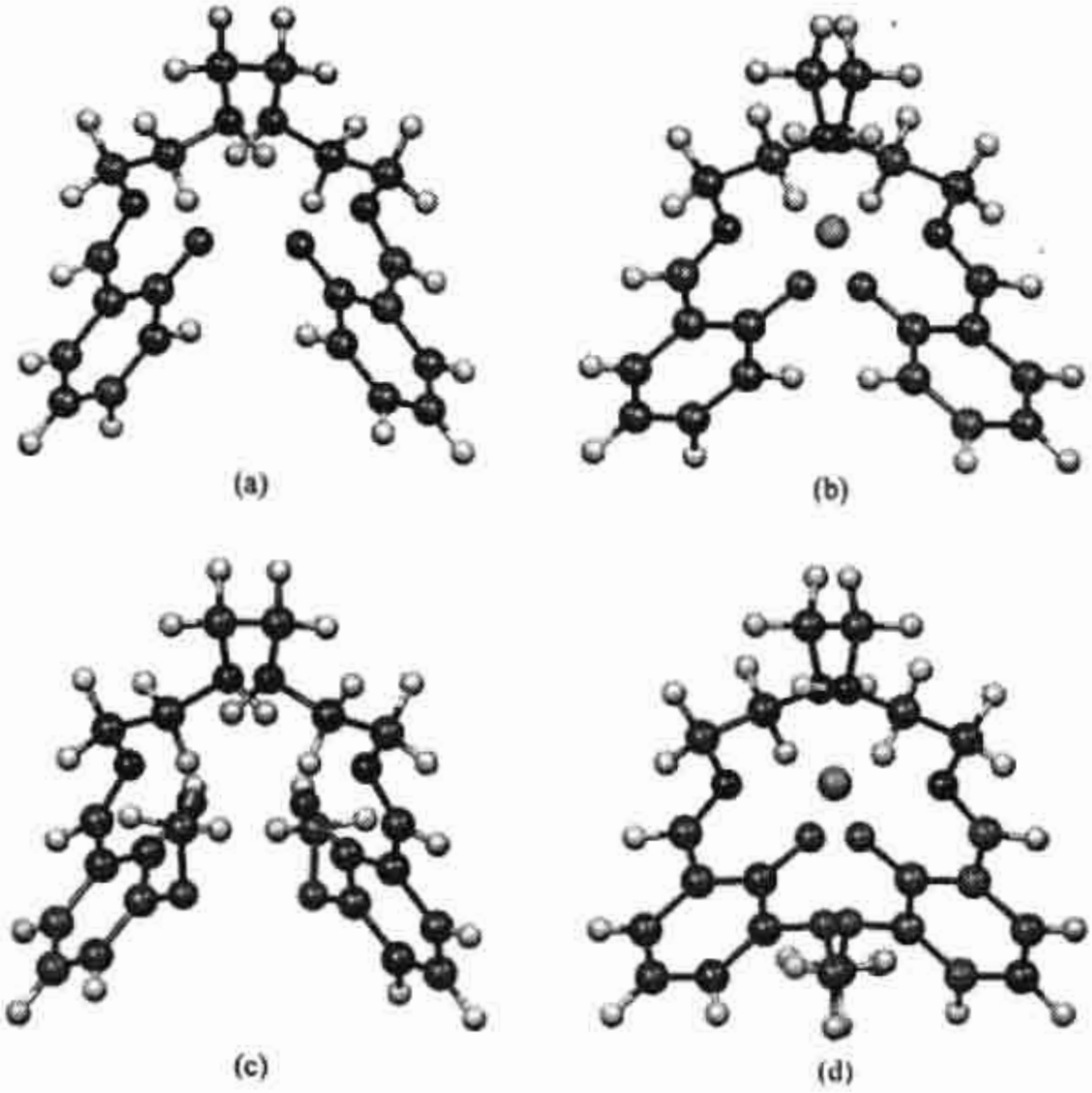
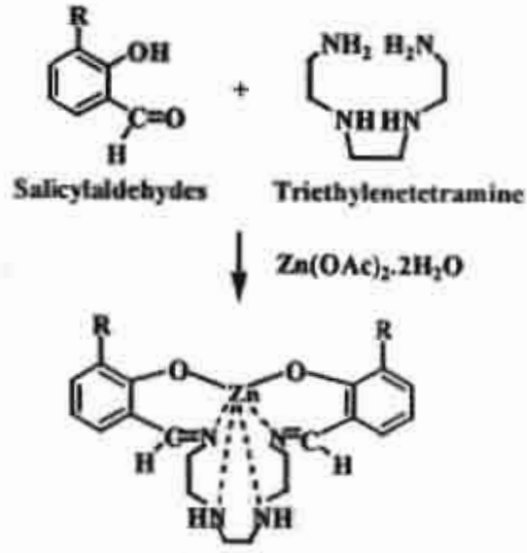


Fig. 9 B3LYP/6-31G(d)-optimized structures of (a) free form, (b) complex form of Sal_2trien, (c) free form and (d) complex form of Van_2trien



Scheme 1 Synthesis of $ZnSal_2trien$ and $ZnVan_2trien$

Table 1 Crystal data and structure refinement for $ZnSal_2trien$ and $ZnVan_2trien$ complexes

	$ZnSal_2trien$	$ZnVan_2trien$
Empirical formula	$C_{20}H_{24}N_4O_2Zn$	$C_{22}H_{28}N_4O_4Zn$
Color/shape	pale yellow/needle	pale yellow/prism
Formula weight	471.85	477.85
Space group	*C2/c*	*Cc*
Temperature	293(2) K	293(2) K
Cell constants	a = 15.6624(3) Å, b = 16.4014(3) Å c = 17.3847(4) Å, β = 102.167(1)	a = 18.8355(3) A, b = 7.551(1) c = 15.387(1), β=91.428(1)
Cell volume ($Å^3$)	4365.56(15)	2170.02(5)
Formula units/unit cell	8	4
F(000)	1984	1000
D_{calc}(Mg m^{-3})	1.436	1.463
μ_{calc}(mm^{-1})	1.164	1.168
Diffractometer/scan	Bruker SMART CCD	Bruker SMART CCD
Radiation used, graphite monochromator	Mo Kα (λ=0.71073 Å)	Mo Kα (λ=0.71073 Å)
Maximum crystal dimension (mm)		0.075×0.025×0.375
Reflections measured	15,969	7,755
Index ranges	-19 ≤ h ≤ 22, -23≤ k ≤ -23 -24 ≤ ≤ 13	-23 ≤ h ≤ 25, -8 ≤ k ≤ 10, -21 ≤ h 21
Data/parameters	6,293/387	4,910/380
GOF	1.048	1.018
R_1/wR_2 for observed reflection [$I>2\sigma(I)$]	0.0461/0.0802	0.0274/0.0641
$R1/Wr_2$ for all data	0.0890/0.0948	0.0370/0.0674
Largest resolution peak/hole (e $Å^3$)	0.292, -0.305	0.220, -0.416

Table 2 Bond lengths (Å) for $ZnSal_2trien$ and $ZnVan_2trien$ complexes

$ZnSal_2trien$	Å	$ZnVan_2trien$	Å
Zn(1)-O(1)	2.087(1)	Zn(1)-O(1)	2.063(4)
Zn(1)-O(2)	2.091(1)	Zn(1)-O(2)	2.055(4)
Zn(1)-N(1)	2.125(2)	Zn(1)-N(1)	2.147(5)
Zn(1)-N(2)	2.149(2)	Zn(1)-N(2)	2.146(5)
Zn(1)-N(3)	2.224(2)	Zn(1)-N(3)	2.295(5)
Zn(1)-N(4)	2.222(2)	Zn(1)-N(4)	2.228(6)
C(1)-O(1)	1.318(3)	C(1)-O(1)	1.308(6)
C(1)-C(2)	1.414(4)	C(1)-C(2)	1.455(9)
C(1)-C(6)	1.415(4)	C(1)-C(6)	1.492(8)
C(2)-C(3)	1.373(5)	C(2)-O(4)	1.340(8)
C(3)-C(4)	1.380(6)	C(2)-C(3)	1.388(8)
C(4)-C(5)	1.345(6)	C(3)-C(4)	1.420(12)
C(5)-C(6)	1.407(4)	C(4)-C(5)	1.419(11)
C(6)-C(7)	1.440(4)	C(5)-C(6)	1.371(9)
C(7)-N(1)	1.270(3)	C(6)-C(7)	1.441(8)
C(8)-N(1)	1.467(4)	C(7)-N(1)	1.290(7)
C(8)-C(9)	1.517(5)	C(8)-C(9)	1.501(10)
C(9)-N(3)	1.460(4)	C(8)-N(1)	1.503(7)
C(10)-N(3)	1.484(4)	C(9)-N(3)	1.485(9)
C(10)-C(11)	1.500(5)	C(10)-C(11)	1.511(4)
C(11)-N(4)	1.473(4)	C(10)-N(3)	1.519(9)
C(12)-N(4)	1.469(4)	C(11)-N(4)	1.458(9)
C(12)-C(13)	1.526(4)	C(12)-N(4)	1.464(10)
C(13)-N(2)	1.467(3)	C(12)-C(13)	1.566(9)
C(14)-N(2)	1.276(3)	C(13)-N(2)	1.433(8)
C(14)-C(15)	1.441(3)	C(14)-N(2)	1.288(7)
C(15)-C(16)	1.406(4)	C(14)-C(15)	1.458(9)
C(15)-C(20)	1.426(3)	C(15)-C(20)	1.367(9)
C(16)-C(17)	1.365(4)	C(15)-C(16)	1.473(7)
C(17)-C(18)	1.376(5)	C(16)-C(17)	1.299(12)
C(18)-C(19)	1.369(4)	C(17)-C(18)	1.402(13)

Table 2 (cont.)

$ZnSal_2$trien	Å	$ZnVan_2$trien	Å
C(19)-C(20)	1.418(3)	C(18)-C(19)	1.397(9)
C(20)-O(2)	1.307(3)	C(19)-O(3)	1.427(8)
		C(19)-C(20)	1.439(9)
		C(20)-O(2)	1.291(7)
		C(21)-O(4)	1.417(9)
		C(22)-O(3)	1.427(8)

Table 3 Bond angles (°) for $ZnSal_2trien$ and $ZnVan_2trien$ complexes

$ZnSal_2trien$	(°)	$ZnVan_2trien$	(°)
N(1)-C(8)-C(9)	108.9(2)	C(7)-C(6)-C(1)	122.8(5)
N(3)-C(9)-C(8)	110.9(3)	N(1)-C(7)-C(6)	126.8(5)
N(3)-C(10)-C(11)	110.3(3)	C(9)-C(8)-N(1)	111.1(5)
N(4)-C(11)-C(10)	109.3(3)	N(3)-C(9)-C(8)	110.7(6)
N(4)-C(12)-C(13)	110.6(3)	C(11)-C(10)-N(3)	110.0(6)
N(2)-C(13)-C(12)	108.6(2)	N(4)-C(11)-C(10)	105.6(6)
N(2)-C(14)-C(15)	126.1(2)	N(4)-C(12)-C(13)	108.7(6)
C(16)-C(15)-C(20)	119.4(2)	N(2)-C(13)-C(12)	108.8(5)
C(16)-C(15)-C(14)	116.7(2)	N(2)-C(14)-C(15)	127.1(6)
C(20)-C(15)-C(14)	123.9(2)	C(20)-C(15)-C(14)	123.2(5)
C(17)-C(16)-C(15)	122.3(3)	C(20)-C(15)-C(16)	121.8(6)
C(16)-C(17)-C(18)	118.5(3)	C(14)-C(15)-C(16)	114.9(6)
C(19)-C(18)-C(17)	121.6(3)	C(17)-C(16)-C(15)	119.8(7)
C(18)-C(19)-C(20)	121.8(3)	C(16)-C(17)-C(18)	121.5(6)
O(2)-C(20)-C(19)	120.2(2)	C(19)-C(18)-C(17)	118.9(7)
O(2)-C(20)-C(15)	123.4(2)	C(18)-C(19)-O(3)	123.0(7)
C(19)-C(20)-C(15)	116.3(2)	C(18)-C(19)-C(20)	122.1(7)
C(1)-O(1)-Zn(1)	120.47(14)	O(3)-C(19)-C(20)	114.8(5)
C(20)-O(2)-Zn(1)	121.67(14)	O(2)-C(20)-C(15)	126.5(5)
O(1)-Zn(1)-O(2)	96.05(6)	O(2)-C(20)-C(19)	118.0(6)
O(1)-Zn(1)-N(1)	84.99(7)	C(15)-C(20)-C(19)	115.4(5)
O(2)-Zn(1)-N(1)	89.80(7)	C(7)-N(1)-C(8)	119.2(5)
O(1)-Zn(1)-N(2)	87.94(7)	C(7)-N(1)-Zn(1)	126.1(4)
O(2)-Zn(1)-N(2)	83.94(7)	C(8)-N(1)-Zn(1)	114.1(4)
N(1)-Zn(1)-N(2)	170.02(8)	C(14)-N(2)-C(13)	118.1(6)
O(1)-Zn(1)-N(4)	94.73(7)	C(14)-N(2)-Zn(1)	123.5(4)
O(2)-Zn(1)-N(4)	158.44(8)	C(13)-N(2)-Zn(1)	117.4(4)
N(1)-Zn(1)-N(4)	109.74(9)	C(9)-N(3)-C(10)	116.7(5)
N(2)-Zn(1)-N(4)	77.83(9)	C(9)-N(3)-Zn(1)	104.3(4)
O(1)-Zn(1)-N(3)	159.02(8)	C(10)-N(3)-Zn(1)	104.4(4)
O(2)-Zn(1)-N(3)	96.27(7)	C(11)-N(4)-C(12)	115.4(5)

Table 3 (cont.)

$ZnSal_2$trien	(°)	$ZnVan_2$trien	(°)
N(1)-Zn(1)-N(3)	78.14(9)	C(11)-N(4)-Zn(1)	111.7(5)
N(2)-Zn(1)-N(3)	110.21(9)	C(12)-N(4)-Zn(1)	106.6(4)
N(4)-Zn(1)-N(3)	79.57(9)	C(1)-O(1)-Zn(1)	129.7(4)
C(7)-N(1)-C(8)	119.2(3)	C(20)-O(2)-Zn(1)	128.4(4)
C(7)-N(1)-Zn(1)	121.88(19)	C(22)-O(3)-C(19)	117.2(6)
C(8)-N(1)-Zn(1)	115.4(2)	C(2)-O(4)-C(21)	116.4(6)
C(14)-N(2)-C(13)	117.5(2)	O(2)-Zn(1)-O(1)	108.21(5)
C(14)-N(2)-Zn(1)	121.67(16)	O(2)-Zn(1)-N(1)	91.11(18)
C(13)-N(2)-Zn(1)	115.49(18)	O(1)-Zn(1)-N(1)	86.21(18)
C(9)-N(3)-C(10)	113.3(3)	O(2)-Zn(1)-N(2)	86.04(17)
C(9)-N(3)-Zn(1)	107.46(19)	O(1)-Zn(1)-N(2)	90.92(17)
C(10)-N(3)-Zn(1)	107.11(19)	N(1)-Zn(1)-N(2)	175.12(6)
C(12)-N(4)-C(11)	113.7(3)	O(2)-Zn(1)-N(4)	154.33(17)
C(12)-N(4)-Zn(1)	107.42(17)	O(1)-Zn(1)-N(4)	90.9(2)
C(11)-N(4)-Zn(1)	107.92(19)	N(1)-Zn(1)-N(4)	107.52(19)
		N(2)-Zn(1)-N(4)	76.43(18)
		O(2)-Zn(1)-N(3)	89.54(18)
		O(1)-Zn(1)-N(3)	156.63(16)
		N(1)-Zn(1)-N(3)	78.17(19)
		N(2)-Zn(1)-N(3)	105.74(18)
		N(4)-Zn(1)-N(3)	77.59(8)

Table 4 Atomic coordinates and equivalent isotropic displacement parameters with e.s.d's in parentheses for $ZnSal_2trien$ and $ZnVan_2trien$ complexes.

	x	y	z	$B(Å)$
$ZnSal_2trien$				
Zn(1)	115(1)	1300(1)	813(1)	30(1)
N(1)	651(3)	1153(6)	2130(3)	38(1)
N(2)	-420(3)	1205(6)	-505(3)	37(1)
N(3)	-380(3)	3647(6)	1465(4)	37(1)
N(4)	562(3)	3618(7)	171(4)	44(1)
O(1)	925(2)	-301(5)	477(2)	39(1)
O(2)	-697(2)	-297(5)	1129(2)	42(1)
O(3)	-1472(3)	-2515(6)	1952(3)	53(1)
O(4)	1708(3)	-2501(6)	-325(3)	52(1)
C(9)	-353(4)	3114(11)	2398(4)	55(2)
C(10)	75(4)	5225(8)	1274(6)	52(2)
C(11)	176(4)	5244(8)	316(5)	46(2)
C(12)	574(4)	3134(9)	-748(4)	51(2)
C(13)	-181(4)	2405(9)	-1128(4)	52(2)
C(14)	-858(3)	-35(8)	-795(4)	47(2)
C(15)	-1202(3)	-1315(7)	-276(4)	38(1)
C(16)	-1681(3)	-2580(7)	-791(5)	50(2)
C(17)	-2021(5)	-3765(10)	-392(6)	68(2)
C(18)	-2001(4)	-3765(8)	522(6)	58(2)
C(19)	-1546(3)	-2578(8)	1018(4)	42(2)
C(20)	-1118(3)	-1309(7)	620(4)	34(1)
C(21)	2155(4)	-3597(10)	-769(6)	69(2)
C(22)	-1939(5)	-3610(11)	2378(6)	74(3)
$ZnVan_2trien$				
Zn(1)	3470(1)	3175(1)	1414(1)	39(1)
N(1)	3185(1)	4266(1)	750(1)	50(1)
N(2)	3574(1)	2134(1)	2178(1)	46(1)

Table 4 (cont.)

	x	y	z	B(Å)
N(3)	4786(2)	3544(2)	1247(1)	58(1)
N(4)	3744(1)	2175(2)	639(1)	55(1)
O(1)	2120(1)	2998(1)	1154(1)	43(1)
O(2)	3513(1)	3836(1)	2450(1)	44(1)
C(1)	1587(1)	3603(2)	1221(1)	44(1)
C(2)	817(2)	3449(2)	1500(2)	68(1)
C(3)	217(2)	4053(3)	1527(3)	93(1)
C(4)	351(3)	4833(3)	1281(3)	108(2)
C(5)	1089(3)	5009(2)	1035(2)	83(1)
C(6)	1731(2)	4416(2)	1006(2)	50(1)
C(7)	2508(2)	4687(2)	764(2)	55(1)
C(8)	3934(2)	4656(2)	516(2)	71(1)
C(9)	4761(2)	4421(2)	1099(2)	74(1)
C(10)	4971(2)	3057(3)	582(2)	74(1)
C(11)	4685(2)	2190(2)	639(2)	70(1)
C(12)	3451(2)	1410(2)	939(2)	63(1)
C(13)	3764(2)	1357(2)	1831(2)	63(1)
C(14)	3180(2)	2105(2)	2750(2)	47(1)
C(15)	2893(2)	2796(2)	3142(1)	44(1)
C(16)	2420(2)	2624(2)	3726(2)	63(1)
C(17)	2090(2)	3224(2)	4123(2)	73(1)
C(18)	2225(2)	4024(2)	3941(2)	68(1)
C(19)	2693(2)	4226(2)	3386(2)	54(1)
C(20)	3050(1)	3623(1)	2961(1)	41(1)
O(1W)	1341(2)	1458(2)	1333(2)	82(1)
O(2W)	3534(2)	5583(2)	2261(2)	99(1)
O(3W)	449(2)	1589(2)	3533(3)	152(1)

Table 5 Hydrogen bond lengths (Å) and bond angles (°) for $ZnSal_2trien$ complex

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1W)-H(1W)...O(1)	0.83(5)	2.03(5)	2.850(3)	173(5)
N(3)-H(3N)...O(2)#1	0.86(3)	2.41(3)	3.149(3)	146(2)
N(4)-H(4N)...O(1)#2	0.80(3)	2.37(3)	3.138(3)	159(3)
O(2W)-H(2W)...O(2)	1.05(6)	1.84(6)	2.886(3)	172(5)
O(1W)-H(4W)...O(2W)#3	0.97(8)	1.86(8)	2.805(4)	164(6)
O(2W)-H(12W)...O(3W)#4	0.92(3)	2.64(3)	2.844(5)	93(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2 #2 -x+1/2,-y+1/2,-z #3 -x+1/2,y-1/2,-z+1/2
#4 -x+1/2,y+1/2,-z+1/2

Table 6 Protonation constants of Sal_2trien, Van_2trien and their stability constant with zinc cations, in terms of log K, in 1.00×10^{-2} M $Bu_4NCF_3SO_3$ in methanol at 25°C.

Reactions					Log K	
					Sal_2trien	Van_2trien
L^{2-}	+	H^+	⇌	LH^-	12.74 ± 0.08	11.14 ± 0.05
LH^-	+	H^+	⇌	LH_2	12.12 ± 0.09	8.61 ± 0.03
LH_2	+	H^+	⇌	LH_3^+	9.10 ± 0.09	5.50 ± 0.05
LH_3^+	+	H^+	⇌	LH_4^{2+}	6.79 ± 0.10	3.81 ± 0.05
L^{2-}	+	Zn^{2+}	⇌	LZn	4.25 ± 0.16	4.30 ± 0.11

Table 7 Total energies of Sal_2trien and Van_2trien, free forms and their Zn^{2+} complexes

Species	HF/6-31G(d)//AM1*	HF/6-31G (d)//HF/6-31G(d)*	HF/6-31G(d, p)// HF/6-31G(d)*	B3LYP/6-31G(d)*
$ZnSal_2trien$	-2916.41720003	-2916.45886787	-2916.49951104	-2925.25929533
Sal_2trien	-1138.58835144	-1138.60758524	-1138.65144083	-1145.86961888
Sal_2trien(free)	-1138.68738444	-1138.71911150	-1138.76244570	-1145.96932343
$ZnVan_2trien$	-3144.15257814	-3144.20392997	-3144.25111190	-3154.29409379
Van_2trien	-1366.32511534	-1366.34981458	-1366.39966510	-1374.90185221
Van_2trien(free)	-1366.44150424	-1366.50437987	-1366.55355383	-1374.53792408

* in hartree.

Table 8 Preorganization energies of Sal_2trien and Val_2trien, binding and complexation energies of their zinc complexes, derived from different energy levels.

System/method	$\Delta E_{binding}$ [a]	$\Delta E_{preorg.}$ [a]	$\Delta E_{complex}$ [a]
Zn: Sal_2trien			
HF/6-31G(d, p)//HF/6-31G(d)	-705.94	69.66	-775.60
HF/6-31G(d)//HF/6-31G(d)	-707.63	69.98	-777.62
HF/6-31G(d)//AM1	-763.54	62.14	-701.39
B3LYP/6-31G(d)	-742.32	62.57	-804.88
Zn: Van_2trien			
HF/6-31G(d, p)//HF/6-31G(d)	-681.15	96.57	-777.72
HF/6-31G(d)//HF/6-31G(d)	-682.40	96.99	-779.39
HF/6-31G(d)//AM1	-689.63	73.04	-762.67
B3LYP/6-31G(d)	-735.62	70.87	-806.49

[a] in kcal/mol. [b] method of calculations.

Table 9 Atomic charges of binding atoms in free forms of Sal_2trien and Van_2trien and their complexing forms with Zn^{2+} ions.

Atom	Mulliken [a]			
	Sal_2trien	$ZnSal_2trien$	Van_2trien	$ZnVan_2trien$
O1	-0.6134	-0.6997	-0.6136	-0.6889
O2	-0.6134	-0.6997	-0.6136	-0.6889
O3 [b]	-	-	-0.5356	-0.4885
O4 [b]	-	-	-0.5356	-0.4885
N1	-0.3668	-0.4873	-0.3672	-0.4858
N2	-0.3668	-0.4873	-0.3672	-0.4858
N3	-0.5929	-0.6077	-0.5956	-0.6122
N4	-0.5929	-0.6077	-0.5956	-0.6122
Dipole moment, D	1.4968	7.2320	2.2294	5.5562

[a] in hartree based on the B3LYP/6-31G(d) level. [b] methoxy oxygen.

Table 10 Geometrical data for the structure of $ZnSal_2trien$ and $ZnVan_2trien$.

	$ZnSal_2trien$.		$ZnVan_2trien$.	
	B3LYP/6-31G(d)	Exp.	B3LYP/6-31G(d)	Exp.
Bond length (Å)				
C1-C2	1.530	1.503	1.536	1.511
C2-N3	1.460	1.480	1.460	1.455
N3-C3	1.470	1.450	1.470	1.462
C3-C4	1.530	1.510	1.530	1.565
C4-N1	1.450	1.460	1.450	1.432
N1-C5	1.290	1.260	1.290	1.288
C5-C6	1.430	1.430	1.430	1.461
C6-C7	1.410	1.410	1.420	1.473
C7-C8	1.380	1.410	1.370	1.300
C8-C9	1.410	1.340	1.410	1.402
C9-C10	1.380	1.380	1.380	1.395
C10-C11	1.430	1.410	1.430	1.434
C11-O2	1.290	1.318	1.290	1.289
C10-O4	-	-	1.360	1.432
O4-C12	-	-	1.410	1.430
N1-Zn	2.138	2.110	2.130	2.140
N3-ZN	2.310	2.200	2.290	2.229
O2-Zn	2.000	2.080	2.010	2.055
Bond angles (°)				
C1-C2-N3	109.910	110.340	109.690	105.818
C2-N3-C3	117.080	112.960	117.450	115.548
N3-C3-C4	110.490	111.000	110.590	108.813
C3-C4-N1	110.370	108.990	110.160	108.657
C4-N1-C5	118.700	119.280	118.640	118.03
N1-C5-C6	127.480	126.780	127.400	126.894
C5-C6-C11	122.410	124.160	117.900	114.674
C6-C11-O2	124.000	123.060	121.390	119.677
N1-Zn-N3	76.360	78.580	77.050	76.387
N1-Zn-O2	86.400	85.250	85.730	86.058
N1-Zn-N4	103.400	109.980	104.310	105.698
N1-Zn-N2	179.870	169.470	178.570	175.138
Dihedral angles (°)				
N3-C2-C1-N4	55.130	58.580	55.100	162.493
C1-C2-N3-C3	-138.700	-160.350	159.110	166.086
C2-N3-C3-C4	71.100	73.800	71.520	74.235
N3-C3-C4-N1	46.320	46.810	44.990	45.018
C3-C4-N1-C5	152.500	133.520	153.150	152.851
C4-N1-C5-C6	177.120	-177.460	176.370	175.611
C11-C10-O4-C12	-	-	178.090	173.591

ภาคผนวก 2 manuscript เรื่อง "Thermally stable metal-containing polyureas from hexadentate Schiff base metal complexes and diisocyanates"

Thermally stable metal-containing polyureas from hexadentate Schiff base metal complexes and diisocyanates

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Abstract

Hexadentate Schiff base metal complexes were synthesized and used in the preparation of metal-containing polyureas. Polycondensation reactions of hexadentate Schiff base metal complexes with diisocyanates, namely hexamethylene diisocyanate (HDI) and 4,4'-diphenylmethane diisocyanate (MDI) were performed in dichloromethane without use of catalyst. The reaction proceeded with good yield and the polymers could be isolated by precipitation from the reaction mixture. The polymers were characterized by IR, NMR, elemental analysis, solubility and viscosity. Thermal stability and flame retardant property of

the polymers were investigated by thermogravimetric analysis in air and by measuring limiting oxygen index values.

1. Introduction

Polyureas are very tough materials with high hardness and good chemical resistance. They can be tailor-made to obtain the properties which leads to versatile applications such as coating systems for waterproof and corrosion protection.

Attempts to synthesized new types of thermally stable polyureas such as phosphorus-containing polyureas and heterocyclic polyureas to obtain different properties have been reported [1-4]. The synthesis of metal-containing polyureas has also received interest since it is known that the introduction of metal into a polymer chain can increase thermal stability of the materials. Metal-containing polyureas having ionic link in the main chain were synthesized by the polymerization of 2,4-tolylene diisocyanate with mixtures of 4,4'-diaminodiphenylmethane and divalent metal salts of *p*-aminobenzoic acid [5] and *p*-aniline sulfonic acid [6]. It was found that polyureas containing salts of *p*-aniline sulfonic acid showed an increase thermal stability.

In our previous study, metal-containing epoxy polymers containing hexadentate Schiff base metal complexes in the polymer chain have been studied [7,8]. Polymerization of these metal complexes with DGEBA epoxy resin gave polymers with good thermal stability. Therefore, we became interested in the application of Schiff base metal complexes in the preparation of metal-containing polyureas. In this papers, we describe the synthesis and characterization of metal-containing polyureas from the polycondensation between the metal complexes and diisocyanates.