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SYNTHESIS, CHARACTERIZATION AND THERMAL INVESTIGATION OF SOME METAL COMPLEXES DERIVED FROM NEW SCHIFF BASE LIGANDS

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ABSTRACT

A new series of complexes of palladium(II), oxovanadium(IV) and zinc(II) ions with N-(3,4-dihydroxysalicylidene)-3,5-di(*tert*-butyl)-4-hydroxyaniline (HL) and N-(4,6-dihydroxysalicylidene-3,5-di(*tert*-butyl)-4-hydroxyaniline (HL^1) have been prepared and characterized by elemental analyses, electronic absorption spectral data, infrared, magnetic moment and molar conductance data. In order to determine the structures of the ligands with their palladium(II) and zinc(II) complexes, ^1H and ^{13}C NMR spectra were obtained. All compounds were found to be non-electrolytes in DMSO (~1 mM). The thermal behaviour of the ligands and their complexes have been investigated using thermogravimetric techniques (TG and DTA). The thermogravimetric data agree with the results of the analytical and spectral analyses. The degradation of the hydrated complexes occurs in several steps with the dehydration reaction followed by complete decomposition to the corresponding metal oxides.

INTRODUCTION

The ligands, derived by condensation of a primary amine and an active carbonyl group, contain the azomethine group. They form stable complexes with metal ions, especially if the amine and/or the carbonyl compounds contain a second functional group sufficiently near

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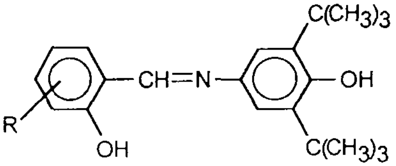


R = 3,4-$(OH)_2$ (HL), 4,6-$(OH)_2$ (HL^1)

Fig 1. General Structure of the Ligands

the site of condensation to form five- or six-membered chelate rings[1]. Metal chelation is involved in many important biological processes[2] where the coordination can occur between a variety of metal ions and a wide range of ligands. Many types of ligands are known and the properties of their derived metal chelates have been investigated[3,4].

The present paper reports the synthesis of two new Schiff base ligands (see Fig. 1) containing a sterically hindered phenol groups and their metal complexes. Spectral and magnetic studies have been used to characterize the structure of each of the complexes. ^1H and ^{13}C NMR spectra were obtained to determine the structures of the ligands and their Pd(II) and Zn(II) complexes. Thermogravimetric studies have been carried out to investigate the thermal behaviour of all compounds and to confirm the results of the other methods.

EXPERIMENTAL

Materials

The carbonyl compounds (3,4- and 4,6-dihydroxysalicylaldehyde) were obtained from Fluka. The metal salts ($Zn(AcO)_2.2H_2O$, $VO(SO_4).5H_2O$ and $Pd(AcO)_2$) were purchased from E. Merck and used as received. 3,5-Di(*tert*-butyl)-4-hydroxyaniline was synthesized according to the known procedure[5] and was used for ligand formation without further purification.

Preparation of Schiff Base Ligands

3,5-Di(*tert*-butyl)-4-hydroxyaniline (1 mmol, 0.221 g), dissolved in absolute ethanol (15 mL), was added with constant stirring to a solution of 3,4-dihydroxysalicylaldehyde

(1 mmol, 0.154 g for HL) or 4,6-dihydroxysalicylaldehyde (1 mmol, 0.154 g for HL^1) in absolute ethanol (10 mL). The mixture was allowed to stir magnetically at 50 °C on a water bath for 30 min. After cooling to room temperature, the resulting precipitate was collected on a filter, washed several times with ethanol and recrystallized from acetone/hexane (1:1 by volume).

HL (0.250 g, 80 % yield): ^1H NMR, in ppm ($CDCl_3$): δ 8.38 (s, 1H, CH=N), δ 6.40-7.19 (m, 4H, Ar-H), δ 1.48 (s, 18H, *t*-butyl). ^{13}C NMR, in ppm ($CDCl_3$): δ 166,7 (CH=N), δ 110.1-152.5 (aromatic), δ 32.0 (*t*-butyl).

HL^1 (0.247 g, 80 % yield): ^1H NMR, in ppm ($CDCl_3$): δ 8.61 (s, 1H, CH=N), δ 6.57-7.21 (m, 4H, Ar-H), δ 1.51 (s, 18H, *t*-butyl). ^{13}C NMR, in ppm ($CDCl_3$): δ 168.5 (CH=N), δ 113.5-156.1 (aromatic), δ 32.15 (*t*-butyl).

Preparation of the Zn(II) and VO(IV) Complexes

The complexes were prepared by the addition of metal salts (1 mmol in 5 mL absolute ethanol) to a hot solution of the ligand (1 mmol in 25 mL absolute ethanol) in a 1:2 (M:L) molar ratio. The reaction solution was heated to 80 °C for 45 min while stirring, then cooled to room temperature. The precipitated complexes were filtered and washed several times with cold ethanol and dried in the vacuum desiccator over $CaCl_2$. The physical data for the complexes are listed in Table I (the yield for the $[VO(L)_2].2H_2O$ complex: 0.297 g, 59 % and the $[VO(L^1)_2].H_2O$ complex: 0.218 g, 58 %).

$[Zn(L)_2].H_2O$ (0.273 g, 61 % yield): ^1H NMR, in ppm ($CDCl_3$): δ 8.69 (s, 2H, CH=N), δ 6.50-7.20 (m, 8H, Ar-H), δ 3.14 (s, 6H, H_2O), δ 1.60 (s, 36H, *t*-butyl). ^{13}C NMR, in ppm ($CDCl_3$): δ 171.7 (CH=N), δ 112.4-155.1 (aromatic), δ 32.90 (*t*-butyl).

$[Zn(L^1)_2(H_2O)_2]$ (0.260 g, 68 % yield): ^1H NMR, in ppm ($CDCl_3$): δ 8.90 (s, 2H, CH=N), δ 6.55-7.50 (m, 8H, Ar-H), δ 3.68 (s, 4H, H_2O), δ 1.57 (s, 36H, *t*-butyl). ^{13}C NMR, in ppm ($CDCl_3$): δ 172.4 (CH=N), δ 114.2-157.5 (aromatic), δ 33.15 (*t*-butyl).

Preparation of the Pd(II) Complexes

The calculated amount of the ligand (HL and HL^1, 1 mmol) was added to Pd(II) acetate (0.5 mmol, 0.112 g) in a 1:2 (M:L) molar ratio in acetic acid (15 mL) as

Table I. Anaytical and Physical Data for the Schiff Base Ligands and Their Complexes.

Compound	Empirical formula	Formula wt.	Colour	M. p. (°C)	Found (calc.) % C	H	N	Λ_M[a]
HL	$C_{21}H_{27}NO_4$	357	yellow	204	70.40 (70.54)	7.74 (7.51)	4.16 (3.92)	2.0
$[Pd(L)_2].2H_2O$	$C_{42}H_{56}PdN_2O_{10}$	854.4	green	>300	58.82 (58.99)	6.40 (6.55)	3.40 (3.28)	8.7
$[VO(L)_2].2H_2O$	$C_{42}H_{56}VON_2O_{10}$	815	dark brown	>300	61.93 (61.84)	6.71 (6.87)	3.37 (3.44)	8.0
$[Zn(L)_2].H_2O$	$C_{42}H_{54}ZnN_2O_9$	795.4	light yellow	293	63.45 (63.37)	7.10 (6.80)	3.61 (3.52)	7.4
HL^1	$C_{21}H_{27}NO_4$	357	orange	221	70.83 (70.59)	7.60 (7.56)	4.11 (3.92)	1.2
$[Pd(L^1)_2].2H_2O$	$C_{42}H_{56}PdN_2O_7$	854.4	green	>300	59.25 (58.99)	6.42 (6.55)	3.24 (3.28)	8.5
$[VO(L^1)_2].H_2O$	$C_{42}H_{54}VON_2O_9$	797	brown	>300	63.34 (63.24)	6.91 (6.80)	3.39 (3.51)	7.3
$[Zn(L^1)_2(H_2O)_2]$	$C_{42}H_{56}ZnN_2O_{10}$	813.4	orange	>300	61.83 (61.96)	7.01 (6.89)	3.30 (3.44)	6.7

a = $\Omega^{-1}\,cm^2\,mol^{-1}$

solvent. The solution was stirred for 3 h. The precipitated complexes were filtered and washed with warm water (45 °C), several times with cold ethanol and subsequently dried in a vacuum desiccator over $CaCl_2$. The physical data for the complexes are listed in Table I.

$[Pd(L)_2].2H_2O$ (0.341 g, 77 % yield): ^1H NMR, in ppm ($CDCl_3$): δ 8.60 (s, 2H, CH=N), δ 6.47-7.25 (m, 8H, Ar-H), δ 3.08 (s, 4H, H_2O), δ 1.57 (s, 36H, *t*-butyl). ^{13}C NMR, in ppm ($CDCl_3$): δ 170.1 (CH=N), δ 111.7-154.5 (aromatic), δ 32.85 (*t*-butyl).

$[Pd(L^1)_2].2H_2O$ (0.338 g, 64 % yield): ^1H NMR, in ppm ($CDCl_3$): δ 8.79 (s, 2H, CH=N), δ 6.62-7.43 (m, 8H, Ar-H), δ 3.03 (s, 4H, H_2O), δ 1.53 (s, 36H, *t*-butyl). ^{13}C NMR, in ppm ($CDCl_3$): δ 173.5 (CH=N), δ 115.6-159.4 (aromatic), δ 33.2 (*t*-butyl).

Physical Measurements

Elemental analyses (C, H, N) were performed using a Carlo Erba 1106 elemental analyser. The infrared spectra were obtained using KBr discs (4000-400 cm^{-1}) on a Shimadzu 435 A spectrophotometer. The electronic spectra in the 200-900 nm range were obtained in $CHCl_3$ on a Shimadzu UV-160 A spectrophotometer. Magnetic measurements were carried out by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. Molar conductances of the Schiff base ligands and their transition metal complexes were determined in DMSO ($\sim 10^{-3}$ M) at room temperature using a Jenway Model 4070 conductivity meter. The thermal analyses were performed on a Rigaku Thermal Analyzer using 10 mg samples. The DTA and TG curves were obtained at a heating rate of 10 °C min^{-1}. In all cases the 25-800 °C temperature range was studied in air atmosphere. The ^1H and ^{13}C NMR spectra of the Schiff bases, Pd(II) and Zn(II) complexes were recorded with a Varian XL-200 NMR instrument in $CDCl_3$ using TMS as internal standard.

RESULTS AND DISCUSSION

The analytical data for the ligands HL and HL^1 and their metal complexes are listed in Table I. These show that the 1:2 molar ratio reactions of the metal acetates with HL and HL^1 produce complexes of the general formula $[M(L)_2].nH_2O$ or $[M(L^1)_2].nH_2O$ where M is VO(IV) and Zn(II) for the complexes of the ligand HL and Pd(II) and VO(IV) for the ligand HL^1. For the Zn(II) complex of the ligand HL^1 the general formula is

$[Zn(L^1)_2(H_2O)_2]$. The ligands are soluble in polar and non-polar organic solvents and their complexes are soluble in $CHCl_3$, EtOH, THF, DMSO and DMF. The molar conductances of the solutions of the compounds in DMSO (~1 mM) were in the range 1.2-8.7 $\Omega^{-1}cm^2mol^{-1}$. These values are lower than those expected for an electrolyte[5]. The conductance of all compounds in DMF (Λ_M = 0.3-5.7 $\Omega^{-1}cm^2mol^{-1}$ range at 1 mM concentration) is lower than in DMSO. However, the Pd(II) complexes exhibit weak conductance in DMF due to solvolysis. The molar conductivity values of the Pd(II) complexes in DMF (in the range 25-35 Ω^{-1} cm^2 mol^{-1}) suggest partial solvolysis by DMF. These observations suggest that the ligands and their complexes are non-electrolytes. Although the Schiff base ligands were obtained in high yields (80 %), their complexes were obtained in lower yields, about 58-77 %. Heating and stirring for longer periods of time did not improve the yields for these complexes. The relatively lower yields for the complexes may be due to steric hindrance around the coordination center in the compounds containing *tert*-butyl groups.

$$Zn(AcO)_2.2H_2O + 2HL \xrightarrow[80\ ^\circ C]{EtOH} [Zn(L)_2].H_2O + 2AcOH + H_2O \quad (1)$$

$$Zn(AcO)_2.2H_2O + 2HL^1 \xrightarrow[80\ ^\circ C]{EtOH} [Zn(L^1)_2(H_2O)_2] + 2AcOH \quad (2)$$

$$VO(SO_4).5H_2O + 2HL^x \xrightarrow[80\ ^\circ C]{EtOH} [VO(L^x)_2].nH_2O + H_2SO_4 + mH_2O \quad (3)$$

$$n = 1\ (m = 4)\ \text{or}\ 2\ (m = 3)$$

$$Pd(AcO)_2 + 2HL^x \xrightarrow[45\ ^\circ C]{AcOH} [Pd(L^x)_2].2H_2O + 2AcOH \quad (4)$$

$$HL^x = HL\ \text{or}\ HL^1$$

Infrared Spectra

The infrared absorption spectra of the isolated imine products were measured in order to assist in the identification of all complexes and to confirm the identity of the imines. A partial list of the infrared absorptions for the ligands and their complexes is given in Table II. The spectra of the ligands HL and HL^1 exhibit sharp bands at 1620 and 1605 cm^{-1} due to the ν(C=N) vibration of the azomethine groups, respectively[7]. In the spectra of the complexes, these bands are shifted to lower frequencies indicating that the nitrogen atom of the azomethine group takes part in complex formation[8]. The IR spectrum of the ligand

Table II. The Infrared Absorption Spectral Data of the Schiff Base Ligands and Their Complexes (cm^{-1}).

Compound	ν(OH)/(H_2O)	ν(CH=N)	ν(V=O)	ν(M-N)	ν(M-O)
HL	-	1620 s	-	-	-
$[Pd(L)_2].2H_2O$	3402 w	1615 m		490 w	430 w
$[VO(L)_2].2H_2O$	3375 m,br	1615 s	980	495 m	415 m
$[Zn(L)_2].H_2O$	3350 w,br	1610 m	-	470 w	420 w
HL^1	-	1605 s	-	-	-
$[Pd(L^1)_2].2H_2O$	3270 m	1597 m	-	500 m	430 m
$[VO(L^1)_2].H_2O$	3240 m,br	1590 m	975	490 w	435 w
$[Zn(L^1)_2(H_2O)_2]$	3420 m,br	1580 m	-	490 w	440 w

Key: s (strong), m (medium), w (weak), br (broad)

HL exhibits three phenolic ν(C-OH) group frequencies at 1360, 1335 and 1280 cm^{-1} for the ortho, meta and para positions, and the spectrum of the ligand HL^1 shows two phenolic ν(C-OH) group frequencies at 1365 and 1295 cm^{-1} for the ortho and para positions. In the spectra of all the complexes, the bands at 1365, 1360 and 1335 cm^{-1} did not shift, suggesting that these oxygen atoms of the phenolic C-OH groups are not coordinated to the metal ions. However, the band at 1280 cm^{-1} is shifted to lower frequency (about 10-25 cm^{-1}). It is suggested that the oxygen atom of this phenolic C-OH group is coordinated to the metal ions[9]. Although the band at 1295 cm^{-1} does not undergo any shift in the complexes, its intensity decreases and this indicates that the oxygen atom of one of the two phenolic C-OH groups in the ortho and ortho' positions of the ligand HL^1 is coordinated to the metal ion. A weak and broad band occuring around 3420-3405 cm^{-1} may be attributed to the ν(OH) vibration of the coordinated water molecules in the Zn(II) complex[10]. Broad bands in the 3350-3240 cm^{-1} region are assigned to the ν(OH) vibration of the water molecules[11]. Oxovanadium (V=O) stretching frequencies are normally intense absorptions[12] between 900 and 1000 cm^{-1} and are observed at 980 and 975 cm^{-1} for the $[VO(L)_2].2H_2O$ and $[VO(L^1)_2].H_2O$ complexes, respectively. In the spectra of the complexes, the bands observed in the 500-470 and 440-415 cm^{-1} regions may be due to ν(M-N) and ν(M-O), respectively[13].

Electronic Spectra

The electronic absorption spectral data of the compounds are given in Table III. Because the complexes are soluble in polar organic solvents, the spectra were recorded in $CHCl_3$ as solvent. In the spectra of the ligands, the bands in the 425-348 nm range are assigned to the n-π* transitions of the imine group[14]. During the formation of the complexes, these bands are shifted to lower wavelength, suggesting that the nitrogen atom of the imine group is coordinated to the metal ion[15]. The values in the 294-249 nm range are attributed to the π-π* transitions of the benzenoid rings[16]. In the spectra of the complexes, these bands are slightly shifted to lower wavelength. The electronic spectra of the oxovanadium complexes displayed bands at 825 and 716 nm which are assigned to the d-d transitions. The electronic spectra of the Zn(II) and Pd(II) complexes, which are diamagnetic, have bands in the 283-249 nm range, and these bands may be due to the n-π* and π-π* transitions of the benzene rings and azomethine group. In the spectra of the complexes, the less intense and broad bands in the 443-244 nm range result from the overlap of the low energy π-π* transitions mainly localized within the imine chromophore[17] and the LMCT (ligand to metal charge-transfer bands) transitions from the lone pairs of the phenolate oxygen donor to the M(II) ions[18].

Magnetic Moments

The Pd(II) complexes were found to be diamagnetic and have square-planar structure. The VO(IV) complexes show μ_{eff} values of 1.81 and 1.79 B.M., which may be attributed to square-pyramidal geometry. While the Zn(II) complex of the ligand HL has a tetrahedral structure, the Zn(II) complex of the ligand HL^1 has an octahedral structure.

^1H and ^{13}C NMR Spectra

The conclusions drawn from ^1H and ^{13}C NMR spectral studies of these compounds lend further support to the mode of bonding discussed above. The ^1H and ^{13}C NMR spectra of the ligands HL and HL^1 and the complexes $[Zn(L)_2].H_2O$, $[Pd(L)_2].2H_2O$, $[Pd(L^1)_2].2H_2O$ and $[Zn(L^1)_2(H_2O)_2]$ were recorded using $CDCl_3$ as solvent. In the ^1H NMR spectra of the ligands, the singlets at 1.51 and 1.48 ppm with the multiplets in the 6.68-7.25 ppm range are assigned the protons of the *tert*-butyl groups and aromatic rings[19], respectively. The spectra of the complexes show that the protons of the *tert*-butyl groups and aromatic rings

Table III. The Electronic Absorption Spectral Data and Magnetic Moments of the Compounds.

Compound	μ_{eff} (B.M.)	λ_{max} (ε_{max}, M^{-1} cm^{-1})
HL	-	425 (892), 348 (3.3×10^3), 294 (1.7×10^4), 255 (9.9×10^5)
$[Pd(L)_2].2H_2O$	diamag.	377 (1×10^4), 283 (5.2×10^3), 260 (9×10^4)
$[VO(L)_2].2H_2O$	1.81	716 (424), 583 (1×10^3), 390 (2.2×10^3), 344 (2.3×10^3), 271 (1.6×10^3)
$[Zn(L)_2].H_2O$	diamag.	379 (6.4×10^3), 249 (5.2×10^3)
HL^1	-	393 (4.2×10^3), 260 (1.9×10^3)
$[Pd(L^1)_2].2H_2O$	diamag.	443 (6×10^3), 348 (7×10^3), 250 (6×10^3)
$[VO(L^1)_2].H_2O$	1.79	825 (231), 385 (7×10^3), 256 (4×10^3)
$[Zn(L^1)_2(H_2O)_2]$	diamag.	379 (6.4×10^3), 249 (4.2×10^3)

have undergone downfield shifts, relative to the protons of the free ligands. The singlets observed at 8.59 and 8.61 ppm for the ligands are attributed to the protons of the imine groups. In the spectra of the diamagnetic Pd(II) and Zn(II) complexes, these signals appear downfield compared to the corresponding signals of the ligands, indicating coordination of the ligands to the metal ion via the azomethine nitrogen. For the complexes, the largest shift is that undergone by the methine proton on the imine nitrogen donor. For the Zn(II) complexes the signal of the imine group appears shifted slightly downfield, while the signals of the imine groups of the Pd(II) complexes seem little affected. These differences in chemical shifts probably reflect different interactions between the central ion and the donor atoms in the complexes: the softer acid Pd(II) interacts more weakly with the azomethine nitrogen, while the harder acid Zn(II) is more strongly bound to the harder nitrogen base -CH=N-[20]. The spectra of the Zn(II) and Pd(II) complexes show singlets in the 3.03-3.14 ppm range, and these are assigned to protons of the water molecules[21]. In the spectrum of the Zn(II) complex of the ligand HL^1, the singlet at 3.68 ppm may be due to the protons of the coordinated water molecules[22]. These protons have been easily identified by their disappearance upon D_2O exchange.

In the ^{13}C NMR spectra of the ligands, the presence of signals at 166.75 and 167.6 ppm may be due to the carbon atoms of the azomethine groups. In the spectra of the diamagnetic Pd(II) and Zn(II) complexes, these signals shift downfield to the 170.1-172.4 ppm range,

Table IV. Thermal Degradation of the Metal Complexes.

Complex	Dehydration		Total Decomp.		Final
	Mass loss	T/ °C	Mass loss	T/ °C	product
	Found (calc.[a]) %		Found (calc.[b]) %		
$[Pd(L)_2].2H_2O$	4.2 (4.7)	43-47	87.0 (87.3)	329-593	PdO
$[VO(L)_2].2H_2O$	4.2 (4.3)	70-80	87.0 (87.1)	358-607	V_2O_5
$[Zn(L)_2].H_2O$	2.3 (2.3)	47-53	89.5 (90.0)	298-478	ZnO
$[Pd(L^1)_2].2H_2O$	4.2 (4.3)	55-60	87.0 (87.3)	318-622	PdO
$[VO(L^1)_2].H_2O$	2.3 (2.0)	75-80	89.6 (89.8)	350-637	V_2O_5
$[Zn(L^1)_2(H_2O)_2]$	4.4 (4.7)	130-135	87.6 (87.5)	249-494	ZnO

a : Calculated for the loss of all water molecules

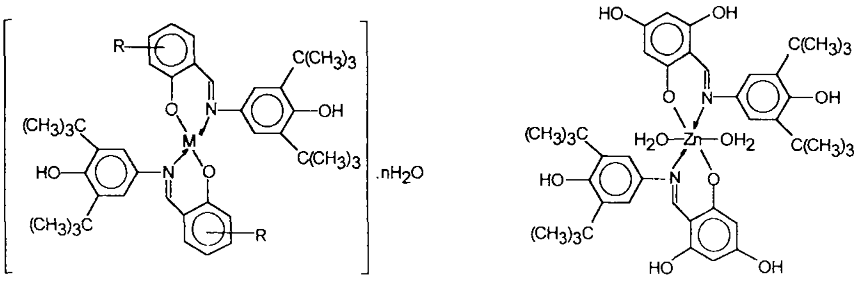
b : Calculated for the weight loss based on the dehydrated complexes

indicating that the nitrogen atom of the azomethine group is coordinated to the metal ion. The spectra of the ligands HL and HL[1] show signals at 32.0 and 32.15 ppm, respectively, and these signals can be attributed to the carbon atoms of the *tert*-butyl groups. During the formation of the complexes, the signals shift to the 32.15-33.20 ppm range. The signals observed in the 110.1-156.75 ppm range are assigned to the carbon atoms of the aromatic rings. In the spectra of the complexes, these signals shifted to the 113.8-159.4 ppm range. These observations further support the above mode of coordination.

Thermal Studies

The results of the thermal analyses are in good agreement with the analytical and spectral data. The melting points of all the compounds were also confirmed by the DTA method. When the TG and DTA curves of the ligands are examined, it is shown that the ligand HL[1] has higher thermal stability than the ligand HL. The metal complexes of the ligands exhibit a uniform decomposition behaviour including a dehydration reaction followed by complete decomposition to the corresponding metal oxides.

The temperature ranges of the dehydration processes show a strong relationship to the binding mode of the water molecules of the respective metal complexes. The elimination of the water molecules of the complexes occurs in two steps. The first step can be attributed to the release of the hydration water molecules (in the range 40-80 °C)[23]. In the second step,



R 3,4-(OH)$_2$ (HL), 4,6-(OH)$_2$ (HL^1)
M = Pd(II),VO(IV) and Zn(II) for HL only.
n = 1 or 2

Fig. 2. Suggested Structure of the Complexes

the Zn(II) complex of the ligand HL^1 looses the coordinated water molecules[24] at 135-140 °C. The thermal decomposition of the anhydrous complexes starts in the range 316-350 °C and is complete in the range 590-637 °C. The final decomposition products are metal oxides. As a result of the dehydration and decomposition processes, the observed weight losses for all complexes are in good agreement with the calculated values (Table IV).

The TG curves of all complexes show that the thermal decomposition of the anhydrous product takes place in several steps. It is possible to suggest that the *tert*-butyl groups in the ligands decrease the stability of all complexes. Furthermore, it is known that the electronegativity and atomic radius of the central metal atom effect also the thermal stability.

Single crystals of the complexes could not be isolated from any solutions, thus no definite structure can be described. However, the analytical, spectroscopic and magnetic data enable us to predict possible structures as shown in Fig. 2.

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