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Structural, spectroscopic and thermal characterization of 2-tert-butylaminomethylpyridine-6-carboxylic acid methylester and its Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and UO₂(II) complexes

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Abstract

Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and UO₂(II) complexes with the ligand 2-tert-butylaminomethylpyridine-6-carboxylic acid methylester (HL²) have been prepared and characterized by elemental analyses, molar conductance, magnetic moment, thermal analysis and spectral data. 1:1 M:HL² complexes, with the general formula [M(HL²)X₂]·*n*H₂O (where M = Co(II) (X = Cl, *n* = 0), Ni(II) (X = Cl, *n* = 3), Cu(II) (grey colour, X = AcO, *n* = 1), Cu(II) (yellow colour, X = Cl, *n* = 0) and Zn(II) (X = Br, *n* = 0). In addition, the Fe(III) and UO₂(II) complexes of the type 1:2 M:HL² and with the formulae [Fe(L²)₂]Cl and [UO₂(HL²)₂](NO₃)₂ are prepared. From the IR data, it is seen that HL² ligand behaves as a terdentate ligand coordinated to the metal ions via the pyridyl N, carboxylate O and protonated NH group; except the Fe(III) complexes are non-electrolytes, while the Fe(III) and UO₂(II) complexes are 1:1 electrolytes. IR and ¹H-NMR spectral studies suggest a similar behaviour of the Zn(II) complex in solid and solution states. From the solid reflectance spectral data and magnetic moment measurements, the complexes have a trigonal bipyramidal (Co(II), Ni(II), Cu(II) and Zn(II) complexes) and octahedral (Fe(III), UO₂(II) complexes) geometrical structures. The thermal behaviour of the complexes is studied and the different dynamic parameters are calculated applying Coats–Redfern equation. © 2004 Elsevier B.V. All rights reserved.

Keywords: 2-tert-Butylaminomethylpyridine-6-carboxylic acid methylester (HL²) complexes; ¹H-NMR; IR; Molar conductance; Solid reflectance; Magnetic moment; Thermal analysis

1. Introduction

In many catalytic reactions, coordinatively unsaturated complexes appear as reactive intermediates at some stage. Such species initiate catalytic processes (catalytic precursor) and, of course, are part of catalytic cycles themselves. Thus, investigations of the factors controlling and affecting the reactivity and stability of unsaturated compounds are very important, not only for intrinsic reasons, but also for the understanding of virtually all homogeneously catalyzed processes. Recently, the pincer ligand class (1) has experienced a renaissance [1] from its earliest incarnations in mono-metal coordination chemistry. Here, E is a nitrogen or

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phosphorous donor and E' can be either a pyridine nitrogen or ring sp^2 carbon as shown in Fig. 1. This ligand is most often found as a meridional ligand (i.e., E' and two E will be approximately coplanar in the metal coordination sphere).

It is our purpose here to report progress on a related goal: pincer ligand chemistry of transition metals with a secondary amine donor at site E. Moreover, we have decided to make the donors E secondary (i.e., NH^tBu) rather than tertiary amines for the specific purpose of having a reactive hydrogen accompanied by a bulky but three-fold symmetric substituent [1]. This substitution pattern (ligand abbreviation N₂py when E' = N) will give rise to both mirror and C₂ asymmetric isomers **3**, which are not anticipated to interconvert on the synthetic time scale when the nitrogens are coordinated. It is shown from Fig. 2 that isomer **3** (m) clearly has a crowded ("up")

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Fig. 1. Pincer ligands with E=N or P and E'=pyridine N or sp^2 ring carbon.



Fig. 2. N₂Py ligands with mirror and C₂ asymmetric isomers.

and an uncrowded ("down") side, while in **3** (C₂), these are equivalent. The Ru(II)/Cl⁻, NCMe, PPh₃ chemistry of the related (but $C_{2\nu}$ symmetric) ligand 4 was recently reported [2,3].

The main idea of this article is to prepare an asymmetric pincer ligand type with E' is a nitrogen and E as NH^tBu in one arm and as COOMe in the second arm. The ligand and its complexes were characterized using different physico-chemical tools like elemental and thermal analyses, magnetic moment, molar conductance, IR, ¹H-NMR and solid reflectance spectral techniques.

2. Experimental

All reagents and solvents were obtained from commercial sources and used as received. Elemental analyses were

carried out at the Microanalytical Center at Cairo University. Infrared spectra were recorded on a Perkin-Elmer FT-IR type 1650 spectrophotometer in wave number region $4000-200 \text{ cm}^{-1}$. The spectra were recorded as KBr disc. The solid reflectance spectra were measured on a Shimadzu 3101pc spectrophotometer. The molar magnetic susceptibility was measured on powdered samples using the Faraday method. The thermogravimetric analysis (TGA and DrTG) was carried out in dynamic nitrogen atmosphere (20 mL min^{-1}) , with a heating rate of $10 \degree \text{C min}^{-1}$ using Shimadzu TGA-50H thermal analyzer. The ¹H-NMR spectra were recorded using a Bruker ARX-300 instrument. Chemical shifts are reported in parts per million downfield from tetramethylsilane. Deuterated chlorofirm and DMSO were used as a solvent in a concentric tube containing d₆acetone.

2.1. 2,6-Pyridinedicaboxylic acid dimethyl ester (C₉H₉NO₄)

2,6-pyridinedicarboxylic acid (26.0 g, 155.7 mmol) and H₂SO₄ concentrated (0.2 mL) in methanol (200 mL) were heated to reflux for 100 h. After evaporation of the solvent, the residue was redissolved in CH₂Cl₂ (200 mL), extracted twice with saturated aqueous solutions of NaHCO₃ (100 mL) followed by H₂O (100 mL). The organic layer was dried over Na₂SO₄, filtered and the solvent removed. The white product was dried in vacuo. Yield: 26.0 g (85%); IR (KBr disc): 1730 sh ($\nu_{C=O}$), 1595 sh ($\nu_{C=N}$), ¹H-NMR (25 °C, CDCl₃): $\delta = 8.33$ (d, 2H, J = 7.8 Hz), 8.02 (t, 1H, J = 7.8 Hz), 4.02 (s, 6H).

2.2. 2-Hydroxymethylpyridine-6-carboxylic acid methyl ester $(C_8H_9NO_3)$ (HL¹)

To 2,6-pyridinedicarboxylic acid dimethylester (20.9 g, 107.1 mmol) in MeOH (200 mL) was slowly added NaBH₄ (10.5 g, 55 mol), whereupon the exothermic reaction warmed the reaction mixture to reflux. The solution was then stirred at



Fig. 3. Preparation of HL² ligand.

room temperature for 12 h. After evaporation of the solvent, the residue was dissolved in saturated aqueous NaHCO₃ solution (200 mL) and extracted with CHCl₃ (300 mL) by continuous liquid–liquid extraction for 15 h. After evaporation of the solvent, the white product was washed with Et₂O and dried in vacuo. Yield: 15.0 g (72%); IR (KBr disc): 3384 br (ν_{OH}), 1732 sh ($\nu_{C=O}$), 1590 sh ($\nu_{C=N}$), ¹H-NMR (25 °C, DMSO-d₆): δ = 7.75 (t, 1H, *J* = 7.3 Hz), 7.35 (d, 2H, *J* = 7.3 Hz), 4.65 (s, 2H), 2.96 (bs, 1H), 3.94 (5, 3H).

2.3. 2-Toulenesulfonylmethylpyridine-6-carboxylic acid methyl ester ($C_{15}H_{15}NO_5S$)

A solution of HL¹ (2.24 g, 13.41 mmol) and KOH (2.58 g, 46.0 mmol) in 50 mL of THF was cooled in an ice bath and toluenesulfonyl chloride (3.5 g, 18.4 mmol) in 150 mL of THF was added dropwise. The temperature was not allowed to rise over 0 °C. The mixture was stirred for 5 h at 0 °C and then for another 12 h at room temperature. The white residue (KOH, KCl) was filtered off and washed twice with THF (30 mL). The THF fractions were combined, and after evaporation of the solvent, the product was dried in vacuo. Yield: 6.10 g (80%); IR (KBr disc): 1732 sh ($\nu_{C=O}$), 1593 m ($\nu_{C=N}$), ¹H-NMR (25 °C, CDCl₃): δ = 7.83 (m, 4H), 7.71 (t, 1H), 7.43 (d, 2H), 5.14 (s, 2H), 3.82 (5, 3H), 2.44 (s, 3H).

2.4. 2-tert-Butylaminomethylpyridine-6-carboxylic acid methylester ($C_{12}H_{18}N_2O_2$) (HL^2)

2-Toluenesulphonylmethylpyridine-6-carboylic acid methylester (5.19 g, 16.17 mmol) and tert-butylamine (36 mL, 350 mmol) were dissolved in benzene and heated to reflux for 15 h. After evaporation of the solvent, the residue was redissolved in CH₂Cl₂, extracted twice with saturated aqueous Na₂CO₃ (100 mL) and H₂O (100 mL), and dried over Na₂SO₄. The solvent was removed and the product dried in vacuo. Yield: 2.86 g (93%); IR (KBr disc): 3269 sh (ν_{NH}), 1726 sh ($\nu_{\text{C=O}}$), 1591 sh ($\nu_{\text{C=N}}$), ¹H-NMR (25 °C, CDCl₃): δ = 7.67 (t, 1H, *J* = 8.1 Hz), 7.26 (d, 2H, *J* = 8.1 Hz), 3.99 (s, 3H), 1.85 (bs, 1H), 1.45 (5, 9H).

3. Results and discussion

The pincer ligand class (1) is found as a meridional ligand where the ^tBuNH and ester groups are approximately coplanar in the metal coordination sphere. HL^2 can be synthesized according to the reaction given below in Fig. 3.

The purpose of preparing such ligand is to have a reactive hydrogen accompanied by a bulky but three-fold symmetric ^tBu-NH group in one arm of pyridine and a C=O group in the second arm. The analytical and physical data for the metal complexes are listed in Table 1. The complexes are coloured, quite stable in air and insoluble in common organic solvents, but soluble in DMF and DMSO. Analyses reveal the metal to ligand ratio to be 1:2 in case of UO₂(II)

Table 1	-							
Analyucal and physical data of HL ⁻ and its	complexes							
Compound	Colour (% yield)	M.p. (°C)	Found (calculated	(%) (f			$\mu_{\rm eff.}$ (B.M.)	$A_{ m m}~(\Omega^{-1}~{ m cm}^2~{ m mol}^{-1})$
			U	Н	Z	M		
HL ² C ₁₂ H ₁₈ N ₂ O ₂	White (80)	68 ± 2	64.56 (64.86)	7.99 (8.11)	12.74 (12.61)	I	I	1
$[Fe(L^2)_2]CI C_{24}H_{34}CIFeN_4O_4$	Yellow (73)	225 (decomp.)	53.57 (53.98)	5.66(6.00)	10.17 (10.50)	(10.50)	5.63	0.69
$[Co(HL^2)Cl_2] C_{12}H_{18}Cl_2CoN_2O_2$	Blue (82)	>300	41.18(40.91)	5.43 (5.11)	7.82 (7.96)	(16.76)	4.30	13.40
[Ni(HL ²)Cl ₂].3H ₂ O C ₁₂ H ₂₄ Cl ₂ NiN ₂ O ₅	Green (80)	>300	35.64 (35.38)	6.23 (5.90)	6.55 (6.88)	(14.74)	2.98	11.60
$[Cu(HL^2)Cl_2] C_{12}H_{18}Cl_2CuN_2O_2$	Yellow (62)	230 (decomp.)	40.62 (40.39)	5.45 (5.05)	7.56 (7.85)	(17.81)	2.10	16.30
[Cu(HL ²)(AcO) ₂]·H ₂ O C ₁₆ H ₂₆ CuN ₂ O ₇	Grey (69)	>300	45.45 (45.55)	5.92 (6.17)	6.80 (6.64)	(15.07)	2.03	15.50
$[Zn(HL^2)Br_2] C_{12}H_{18}Br_2ZnN_2O_2$	White (80)	300 (decomp.)	32.52 (32.21)	4.43 (4.03)	6.52 (6.26)	(14.54)	Diam.	15.31
$[UO_2(HL^2)_2](NO_3)_2 C_{24}H_{36}UN_6O_{12}$	Yellow (76)	218 (decomp.)	34.81 (34.53)	4.61 (4.32)	6.35 (6.72)	I	Diam.	120

	$\nu(\rm NH)$	$v_{asym}(COO)$	$v_{sym}(COO)$	δ(NH)	ν (C–N)	ν (C=N)	ν (C=O)	ν(M–O)	ν(M–N) (NH)	ν(M–N) (py)
HL ²	3269 sh	1555 sh	1392 m	765 s	1138 sh	1591 sh	1726 sh	_	_	_
$[Fe(L^2)_2]Cl$	3269 sh	1598 sh	1369 sh	767 m	1140 sh	1658 sh	1737 m	590 m	493 m	553 m
$[Co(HL^2)Cl_2]$	3163 sh	1565 s	1373 sh	770 sh	1145 m	1605 sh	1713 sh	520 s	450 w	480 m
[Ni(HL ²)Cl ₂]·3H ₂ O	3087 m	1597 sh	1381sh	761 m	1150 m	1630 m	1674 sh	596 s	472 w	500 s
$[Cu(HL^2)Cl_2]$	3089 sh	1560 m	1375 m	772 sh	1145 m	1607 sh	1688 sh	530 s	470 w	505 s
[Cu(HL ²)(AcO) ₂]·H ₂ O	3269 sh	1598 m	1390 m	769 sh	1140 sh	1657 m	1703 m	590 sh	494 m	554 m
$[Zn(HL^2)Br_2]$	3173 sh	1565 s	1371 sh	769 sh	1148 m	1605 sh	1732 sh	530 s	640 s	510 s
$[UO_2(HL^2)_2](NO_3)_2$	3569 sh	1598 sh	1370 sh	770 m	1140 sh	1624 m	1666 m	553 sh	423 m	492 m

Table 2 IR assignment $(4000-200 \text{ cm}^{-1})$ of HL² and its complexes

s = small; w = weak; m = medium; br = broad, sh = sharp.

and Fe(III) complexes and 1:1 in all other complexes. The Co(II), Ni(II) and Zn(II) complexes were found to have the formula $[M(HL^2)X_2] \cdot yH_2O$, where M = Co(II) (X = Cl, y = 0), Ni(II) (X = Cl, y = 3), Zn(II) (X = Br, y = 0). The Fe(III) complex has the formula $[Fe(L_2)_2]Cl$ while UO₂(II) complex has the formula $[UO_2(HL^2)_2](NO_3)_2$. The grey Cu(II) complex has the formula $[Cu(HL^2)(ACO)_2] \cdot H_2O$, while the yellow Cu(II) complex has the formula $[Cu(HL^2)Cl_2]$.

3.1. IR spectra

The IR spectra of the ligand as well as its complexes with Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) and $UO_2(II)$ are listed in Table 2, together with assignments for most of the major peaks.

The absorption bands in the region $3269-3087 \text{ cm}^{-1}$ in the free ligand and its complexes are assigned to the NH stretching frequencies. The IR spectrum of the ligand shows two bands at 765 and 1138 cm⁻¹, which are assigned to the out-of-plane δ (NH) and ν (C–N) aliphatic secondary amine stretching frequencies. The coordination of the NH group to the metal ions is confirmed by the blue shift (4 cm⁻¹) or red shift (2–12 cm⁻¹) in the frequencies of out-of-plane δ (NH) and ν (C–N) bands [4].

The band located at 1591 cm^{-1} is assigned to the ν (C=N) stretching vibration of pyridyl nitrogen. Coordination of the pyridyl nitrogen is indicated by a 14–66 cm⁻¹ shift to longer wave numbers in all complexes [5,6]. In the wave number region 1726 cm^{-1} range, some of the most characteristic bands of these systems are found. The so-called amide I band, which represents mainly the ν (C=O) stretching mode in the chelates. This band is shifted to higher (6–11 cm⁻¹) or lower (23–60 cm⁻¹) frequencies, supporting the participation of the carbonyl group of this ligand in the metal coordination [7]. The bands at the wave number 1555 and 1392 cm⁻¹

Table 3		
The solid refle	ctance spectra of HL ²	complexes

Complex	Absorption	n maximum (c	$m^{-1})$	
Fe(III)	15,552	17,482	25,000	_
Co(II)	12,870	15,873	20,000	22,779
Ni(II)	12,903	15,923	21,786	27,777
Cu(II) (yellow)	12,850	15,600	20,161	_
Cu(II) (green)	12,500	15,037	21,276	-

regions in the free ligand are assigned to the asymmetric and symmetric stretching vibrations of the carboxylate group, respectively. The ν_{as} (COO) band is shifted to higher wavelengths (1598–1560 cm⁻¹), while ν_{sym} (COO) band is shifted to lower wavelengths (1390–1369 cm⁻¹). The shift of these two bands to higher or lower frequencies suggest the participation of –COOMe group in complex formation [8,9]. New bands observed in the complexes at 596–520, 510–480 and 494–423 cm⁻¹ are tentatively assigned to the ν (M–O) [10], ν (M–N) of the pyridine [10] and ν (M–N) of the secondary amine [11].

Therefore, from the IR spectra, it is obvious that HL^2 ligand behaves as a neutral terdentate ligand coordinated to the metal ions through C=O, pyridyl-N and protonated secondary aliphatic amine-NH groups; in case of UO₂(II), CO(II), Ni(II), Cu(II) and Zn(II) complexes, except Fe(III) complex, it behaves as a uni-negative terdentate ligand where deprotonation of NH proton takes place. This is supported by the conductance and ¹H-NMR spectral data.

3.2. Molar conductance data

The conductance data of the complexes discussed herein indicate that Co(II), Ni(II), Cu(II) and Zn(II) complexes are non-electrloytes suggesting that the anions [Cl or Br] are covalenty bonded to the metal ions. While Fe(III) and UO₂(II) complexes have conductance values of 69 and $120 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, respectively. This indicates that Fe(III) and UO₂(II) complexes are 1:1 electrolytes.

Table 4		
¹ H-NMR data of	f HL ² and its	Zn complex

Compound	Chemical shift (δ) (ppm)	Assignment
HL ²	7.67	(t, 1H, py)
	7.26	(d, 2H, py)
	5.05	(s, 2H, –CH ₂)
	3.99	(s, 3H, –COOH ₃)
	1.90	(bs, 1H, -NH)
	1.15	(s, 9H, –C(CH ₃) ₃)
$[Zn(H L^2)Br_2]$	8.17	(t, 1H, py)
	7.89	(d, 2H, py)
	4.15	(s, 2H, –CH ₂)
	3.93	(s, 3H, -COOCH ₃)
	2.10	(s, 1H, –NH)
	1.28	(s, 9H, –C(CH ₃) ₃)

3.3. Electronic spectra and magnetic moment data

The solid reflectance spectra of the complexes show bands in the range 35,714–40,160 cm⁻¹, which may be attributed to π – π * or n– π * transition within the HL² ligand.

In the high spin octahedral Fe(III) complexes, the magnetic moments are always very close to spin-only value of 5.9 B.M. because the ground state has no orbital angular momentum. The complex under study has a magnetic moment of 5.69 B.M., where Fe(III) has the ground state ⁶S. Reflectance spectrum shows three bands at 25,000, 17,482 and 15,552 cm⁻¹, which may be assigned to ${}^{6}A_{1g} \rightarrow {}^{5}T_{2g}$ (G) transition in octahedral geometry [12]. The ${}^{6}A_{1g} \rightarrow {}^{5}T_{1g}$ transition appears to be split into two bands at 15,552 and 17.482 cm⁻¹ [13].

As the result of failure to obtain a single crystal for X-ray analyses to confirm the trigonal bipyramidal structure for these complexes, solid reflectance spectra



Fig. 4. ¹H-NMR spectra of HL² and its Zn(II) complex.

and magnetic moment measurements are used for this purpose.

The spectra of Ni(II) and Co(II) complexes (Table 3) appear to be five coordinate as do the corresponding NS₂ and N₃ complexes [14–16], for which similar arguments apply. The Ni(II) complex shows bands at 15,923 and 21,786 cm⁻¹, which correspond to the ${}^{1}A_{1} \rightarrow {}^{1}E$ transitions from the two e levels to the a_{1} level [17]. The spectrum of Co(II) complex resembles those of other five coordinate Co(II) complexes [15,16], where three bands are observed at 12,870, 15,873 and 20,000 cm⁻¹. The relatively low values of μ_{eff} of Co(II) and Ni(II) complexes compared with those of octahedral or tetrahedral geometry may support the five-coordinate geometry of these complexes. The bands observed at 27,777 and 22,779 cm⁻¹ are attributed to $L \rightarrow Ni$ and $L \rightarrow Co$ charge transfer bands, respectively.

The Cu chelates $[Cu(HL^2)Cl_2]$ and $[Cu(HL^2)(AcO)_2]$ H_2O exhibit broad bands at 12,820–12,500, 15,037–15,600 and 21,276–20,161 cm⁻¹. These bands are generally consistent with five coordinate geometry for Cu(II) complexes [14,16,18]. The reflectance spectra also show a band at 30.769–30.487 cm⁻¹, which may be attributed to L \rightarrow Cu charge transfer band. The magnetic moment values of 2.03–2.1 B.M. are indicative of the existence of Cu(II) complexes in trigonal bipyramidal structure [14,16,18–20].

According to the previously reported data of Zn complex with similar N_3 or NS_2 ligand [14–16], the Zn complex reported herein is considered to be trigonal bipyramidal.

3.4. ¹H-NMR spectra

The ¹H-NMR spectra of the diamagnetic Zn (1:1) complex was compared with that of the free ligand as shown in Fig. 4 (Table 4). The NH singlet, which appears at 1.90 ppm in the free ligand, is deshielded at 2.1 ppm in the Zn complex, indicating the participation of the NH group in chelation without proton displacement. Therefore, the ¹H-NMR data are consistent with IR and molar conductance data.

3.5. Thermogravimetric analysis

Thermal analysis (TGA) data of the complexes are given in Table 5 and the activation thermodynamic data are listed in Table 6.

The Fe(III), Cu(II) and UO₂(II) complexes give pattern one step of decomposition within the temperature range 100–400 °C. The found mass losses of 86.0% (calculated mass loss 85.0%), 78.24% (calculated mass loss 77.70%) and 70.24% (calculated mass loss 69.69%) for Fe(III), Cu(II) and UO₂(II) complexes, respectively, are attributed to the decomposition of the anions and ligand molecules leaving 1/2Fe₂O₃, CuO and UO as a residue. The energy of activation of the thermal decomposition of the complexes was 98.35, 39.39 and 56.13 kJ mol⁻¹ for the Fe(III), Cu(II) and UO₂(II) complexes (Table 6), respectively.

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Complex	Temperature	Peak temperature (°C)	Number of	% Found (calculat	ed)	Assignment	Metallic residue
	range (°C)		decomposition steps	Mass loss	Total mass loss		
Fe(L ²) ₂]Cl	130-400	225	1.0		86.00 (85.00)	Loss of two ligand molecules	1/2 Fe ₂ O ₃
$Ni(HL^2)Cl_2] \cdot 3H_2O$	50 - 110	83	1.0	13.40 (13.27)		Loss of 3H ₂ O	NiO
	110-650	240, 370, 550	3.0	68.60 (68.06)	82.00 (81.23)	Loss of 2HCl and ligand molecules	
$Cu(HL^2)Cl_2$]	130-350	230	1.0		78.42 (77.70)	Loss of 2HCl and ligand molecules	CuO
$Zn(HL^2)Br_2]$	220-350	270	1.0	36.65 (36.24)		Loss of 2HBr	
	350-660	470, 630	2.0	46.20 (45.64)	82.85 (81.88)	Loss of ligand molecule	ZnO
UO ₂ (HL ²) ₂](NO ₃) ₂	100-350	218	1.0		70.25 (69.69)	Loss of N_2O_7 and two ligand molecules	NO

Table 6 Thermodynamic data of the thermal decomposition of HL^2 chelates

Complex	Decomposition range (°C)	E^* (kJ mol ⁻¹)	$A(S^{-1})$	$\Delta S^* (\mathrm{J} \mathrm{K}^{-1} \mathrm{mol}^{-1})$	$\Delta H^* (\mathrm{kJ}\mathrm{mol}^{-1})$	$\Delta G^* (\mathrm{kJmol^{-1}})$	r^2
[Fe(L ²) ₂]Cl	130-400	98.35	2.15×10^{6}	-39.14	43.92	43.92	0.973
$[Ni(HL^2)Cl_2]\cdot 3H_2O$	50-110	144.8	4.01×10^{8}	-26.85	56.06	59.38	0.929
	110-240	114.2	5.08×10^{4}	-14.93	118.7	164.80	0.993
	240-320	132.20	2.28×10^{10}	-36.25	81.55	119.60	0.992
	320-650	109.60	3.88×10^{11}	-68.16	135.7	87.62	0.974
$[Cu(HL^2)Cl_2]$	130-350	39.39	2.85×10^{6}	-22.05	43.17	49.10	0.968
$[Zn(HL^2)Br_2]$	220-350	23.82	1.14×10^{5}	-19.93	89.54	64.94	0.993
	350-660	90.10	2.07×10^{9}	-28.11	64.80	106.20	0.994
$[UO_2(HL^2)_2](NO_3)_2$	100–350	56.13	1.09×10^8	-42.65	88.31	93.17	0.987

On the other hand, the Ni(II) complex of the general formula [Ni($C_{12}H_{18}N_2O_2$)Cl₂]·3H₂O exhibits four successive decomposition steps. The first decomposition step in the temperature range 50–110 °C, with an estimated mass loss of 13.40% (calculated mass loss 13.27%), may be attributed to the loss of three water molecules of hydration. The activation energy of the thermal dehydration of the complex was 144.8 kJ mol⁻¹. The 2nd, 3rd and 4th steps within the temperature range of 110–650 °C correspond to the removal of 2HCl and ligand molecules as deduced from mass loss calculations (estimated mass loss 68.60%, calculated mass loss 68.06%), leaving NiO residue. The activation energies of these steps were 114.2, 132.2 and 109.6 kJ mol⁻¹ for the 2nd, 3rd and 4th steps, respectively.

The Zn(II) complex, $[Zn(C_{12}H_{18}N_2O_2)Br_2]$, was thermally decomposed in two successive decomposition steps.

The first estimated mass loss of 36.65% within the temperature range 220–350 °C may be attributed to the liberation of 2HBr gases (calculated mass loss 36.24%). The energy of activation of this step was $32.82 \text{ kJ} \text{ mol}^{-1}$. The second step occurs within the temperature range 280-650 °C with an estimated mass loss 46.20% (calculated mass loss 45.65%) might be reasonably accounted for the decomposition of the ligand molecule as CO, CO₂, NO gases leaving ZnO residue. The activation energy of this step was 90.10 kJ mol⁻¹.

3.6. Kinetic data

The kinetic parameters namely activation energy (E^*) , enthalpy (ΔH^*) , entropy (ΔS^*) and free energy change of decomposition (ΔG^*) were evaluated graphically by employing

MeO -MeO .Cl . nH₂O (CH_2) C(CH,), OMe M = Co(II), X = Cl, n = 0Ni(II), X = Cl, n = 3Cu(II), X = AcO, n = 1Cu(II), X = Cl, n = 0Zn(II), X = Br, n = 0MeO $(NO_3)_2$ (CH.) -C(CH₃)₃ ΗN MeC

Fig. 5. Suggested formulas of HL² complexes.

the Coats-Redfern relation [21]

$$\log\left[\log\frac{[W_f/(W_f - W)]}{T^2}\right] = \log\left[\frac{AR}{\theta E^*(1 - 2RT/E^*)}\right] - \frac{E^*}{2.303RT}$$
(1)

where W_f is the mass loss at the completion of the reaction, W is the mass loss up to the temperature T, R is the gas constant, E^* is the activation energy in kJ mol⁻¹, θ is the heating rate and $(1-(2RT)E^*)) \cong 1$. A plot of the left-hand side of Eq. (1) against 1/T gives a slope from which E^* was calculated and A (Arrhenius constant) was determined from the intercept. The entropy of activation (ΔS^*), enthalpy of activation (ΔH^*) and free energy change of activation (ΔG^*) were calculated using the following equations

$$\Delta S^* = 2.303 \left[log \left(\frac{Ah}{kT} \right) \right] R \tag{2}$$

$$\Delta H^* = E^* - RT \tag{3}$$

$$\Delta G^* = \Delta H^* - T \Delta S^* \tag{4}$$

where k and h are the Boltzman and Plank constants, respectively. The thermodynamic parameter data are listed in Table 6, from which it is obvious that all the complexes have negative entropy values, which indicates that the activated complexes are formed spontaneously.

3.7. Structural interpretation

From the elemental analyses, molar conductance, magnetic moment and spectral studies, the structure of HL^2 complexes is shown below in Fig. 5.

4. Conclusion

As a general conclusion, HL² ligand behaves as neutral terdentate ligand through ester C=O, pyridyl-N and protonated secondary aliphatic amine-NH groups in case of UO₂(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes, while in case of Fe(III) complex, it behaves as a uni-negative terdentate ligand, where deprotonation of NH proton takes place. From the reflectance spectra and magnetic moment measurements, the geometrical structure of the chelates were proposed and found to be octahedral or trigonal bipyramidal.

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