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Thermal and spectral studies on complexes derived from tetradentate Schiff bases

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Abstract Several new complexes of Schiff bases ligands H_4La and H_4Lb with transition metal ions such as Cr(III), Fe(III), Co(II) and Zn(II) are synthesized. Elemental analysis, infrared, UV–Vis and thermal analysis, as well as conductivity and magnetic susceptibility measurements are used to elucidate the structure of the newly prepared metal complexes. A square planar geometry is suggested for Zn(II) complexes, while an octahedral geometry suggested for the Cr(III), Fe(III) and Co(II) complexes. The thermal decomposition of complexes was found to be first order reaction and the thermodynamic parameters corresponding to the different decomposition steps were reported.

Keywords Schiff bases · Thermal analysis · Transition metal chelates · IR · UV–Vis · Magnetic measurements

Introduction

The transition metal complexes with Schiff bases derived from aliphatic amines and salicylaldehyde drew the interest of many workers based on their similarity to biological oxygen carrier [1–3] and their ability to insert oxygen into organic substances [4, 5]. Some Schiff bases complexes show catalytic properties [6] or act as oxygen carriers [7] and antifungal agents; the activity increases by the presence of hydroxyl groups in the ligands [8–12]. The interaction of DNA with complexes $[Cr(Schiff\ base)(H_2O)_2] \cdot ClO_4$ [13, 14] was reported.

The thermal decomposition of the complexes of Cr and Mo with salicylidene aniline derivatives was found to be first order reaction and the thermodynamic parameters corresponding to different decomposition steps were reported [15]. Many authors determined the thermodynamic parameters of metal complexes from the TG data [16–18]. Recently, the thermal decomposition pathways of some transition metal complexes are reported [19, 20]. Despite the fact that Schiff base complexes were the subject of several interesting studies, yet the chromone Schiff bases were included in few studies [21–24]. This work aims to synthesize and characterize new Cr(III), Fe(III), Co(II) and Zn(II) complexes of Schiff base ligands, H_4La and H_4Lb derived from the condensation of 6-formyl-5,7-dihydroxy-2-methylbenzopyran-4-one with ethylenediamine or trimethylenediamine (Scheme 1). The complexes are characterized by elemental analysis, IR, UV–Visible, ^1H-NMR spectroscopy, and studied using thermal analysis. The thermal stability and the thermodynamic parameters of the different decomposition steps of the complexes are calculated.

Experimental

The chloride salts of Cr(III), Fe(III), Co(II) and acetate salts of Co(II), Zn(II) and perchlorate salts of Co(II), potassium dichromate, ethylenediamine, trimethylenediamine, visnagine are Aldrich Chemicals. The organic solvents are reagent grade chemicals and used as received.

Analysis and physical measurements

Carbon, hydrogen, nitrogen and chlorine were analyzed by standard microanalysis methods at Microanalytical center,

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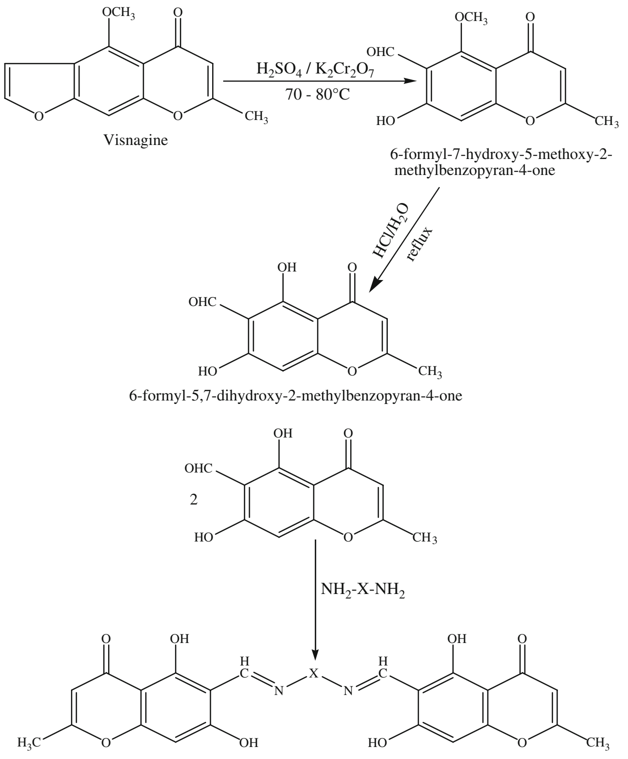

Scheme 1 Preparation of the Schiff bases H_4La and H_4Lb, where $X = (CH_2)_2$ or $(CH_2)_3$

Cairo University, Giza, Egypt. IR spectra of the ligands and their metal complexes, as KBr discs, were recorded on a Shimadzu FTIR spectrometer. ^{1}H-NMR spectra of the ligands and their Zn(II) complexes, in DMSO-d6, were recorded on Varian 300 MHz NMR spectrometer at room temperature using TMS as an internal standard. UV–Vis spectra of the metal complexes in DMF were recorded on UV–Vis-NIR 3101 PC Shimadzu spectrophotometer.

Magnetic susceptibilities of the complexes were measured at room temperature using Cambridge, England Sherwood Scientific magnetic susceptibility balance. The effective magnetic moments were calculated from the expression:

$$\mu\mathrm{eff} = 2.828(X_M \cdot T)^{1/2}\mathrm{B.M.}$$

where X_M is the molar susceptibility corrected using Parcel's constants for diamagnetism of all atoms in the compounds [25].

Molar conductivity of 10^{-3} M solutions of the complexes in DMF was measured on the conductivity meter ORION model 150 of 0.6 Pascal's constant.

Thermal analyses have been carried out using Shimadzu-50 Thermal Analyzer from room temperature to 600 °C with heating rate of 10 °C min^{-1}.

Synthesis of the Schiff-bases H_4La and H_4Lb

The ligands H_4La and H_4Lb were prepared in two steps. The first step involved the oxidation of visnagine $C_{13}H_{10}O_4$ (2.40 g, 10.4 mmol) with chromic acid (60 mL of 10% H_2SO_4 and 40 mL of 10% $K_2Cr_2O_7$) at 70–80 °C with constant stirring [26]. The product (1 g, 4.27 mmol) was hydrolyzed by refluxing with 25 mL 1:1 HCl to produce 6-formyl-5,7-dihydroxy-2-methylbenzopyran-4-one. The second step involved the addition of a solution of ethylenediamine (0.30 g, 5 mmol) or trimethylenediamine (0.37 g, 5 mmol) to 6-formyl-5,7-dihydroxy-2-methylbenzopyran-4-one (2.20 g, 10 mmol) according to a method described previously [27] (Scheme 1).

Synthesis of the metal complexes

A hot ethanolic solution of the metal salt (10 mL) was gradually added to (20 mL) solution of the ligand in 1:1 molar ratio and the solution was stirred on a water bath for 2 h during which the metal complex precipitated. If the complex did not precipitate, ammonia solution was added dropwisely to adjust the pH value in the range 6–7. The resulting precipitates were filtered off, washed with water, ethanol then diethyl ether, and finally air-dried. The complexes are air stable in the solid state and soluble in DMF or DMSO. The obtained complexes were subjected to CHN elemental analysis at the Micro Analytical center, Faculty of Science, Cairo University. The metal content was determined by recommended methods [28].

Determination of reaction order n of decomposition

We used the Horowitz and Metzger [29] equation, $C_s = n^{1/1-n}$ which is given by:

$$C_s = (W_s - W_f)/(W_o - W_f)$$

Where C_s is the mass fraction of the complex present at DTG peak temperature T_s, W_s is the mass remaining at T_s, W_o and W_f are the initial and final masses respectively.

Coats-Redfern method [30]

For a first order process, the Coats-Redfern equation is written after approximation in the form:

$$\log\left[\log(W_f/W_r)/T^2\right] = \log[AR/\theta E^*] - E^*/2.303\,RT$$

where W_f is the mass loss at the completion of the reaction, W_r is the remaining mass at temperature T, R is the gas constant, E^* is the activation energy, θ is the heating rate. Plots of the left-hand side of the last equation versus $1/T$

give straight lines, where E^* and A (Arrhenius constant) are calculated from the slope and the intercept, respectively.

The activation entropy ΔS^*, activation enthalpy ΔH^* and free energy of activation ΔG^* were calculated using the following equations:

$$\Delta S^* = 2.303(\log A\, h/kT)R$$

$$\Delta H^* = E^* - RT$$

$$\Delta G^* = \Delta H^* - T_s\,\Delta S^*$$

where k and h are the Boltzman and Planck constants, respectively.

Results and discussion

The formulae of the complexes, together with the physical properties, elemental analyses and formula masses are listed in Table 1. The isolated solid complexes are stable at room temperature (25 °C), non-hygroscopic and almost insoluble in water and most organic solvents but are soluble in DMF and DMSO. Most of the complexes decomposed on heating at >300 °C.

IR spectra

The most important infrared bands of the ligands and the metal complexes with their probable assignments are given in Table 2. The IR spectra of the ligands (H_4La and H_4Lb) exhibit bands at 3429–3433, 1110–1113, 1222 cm^{-1} attributed to νOH, δOH def. and δC–OH, respectively. The C=O group in position four shows stretching band at 1658 and 1651 cm^{-1} for ligands H_4La and H_4Lb. The azomethine νC=N band overlaps with νC=C as a strong band at 1620 for H_4La and 1612 for H_4Lb.

The existence of numerous coordination sites in the ligands gives variable bonding modes; however comparison of the IR spectra of the ligands and their complexes reveal that the ligands are bonded to metal ions in one coordination mode. The ligands are quadridentate dibasic (N_2O_2) donors in the complexes. The spectra proved that the C=N and C_7–OH groups are the coordination centers. Strong evidence is (i) The band assigned to the stretching vibration of the azomethine groups of the ligands at (1620, 1612 cm^{-1}) is shifted to lower frequency or higher frequency in metal complexes suggesting that one of the coordination sites of the ligand to the central metal atom is through nitrogen atom of azomethine groups. (ii) The existence of stretching C=O in position 4 which is more or less invariant; indicates that this group is not taking part in coordination. (iii) The band at 1218–1222 cm^{-1} is ascribed to the stretching vibration of the phenolic υC–O [31], this band is shifted to higher frequency (1222–1272 cm^{-1}) in

Table 1 Analytical and physical data of the metal complexes of Schiff base H_4La and H_4Lb

Ligand or complexes	Formula	Color	M. W.	Yield (%)	M:L	C% Calc. (found)	H% Calc. (found)	N% Calc. (found)	M% Calc. (found)	Cl% Calc. (found)
H_4La	$C_{24}H_{20}N_2O_8$	Reddish yellow	464.43	90	–	62.06 (62.00)	4.34 (4.35)	6.03 (6.02)	–	–
$[CrH_2LaOH(H_2O)] \cdot 3H_2O$	$C_{24}H_{27}CrN_2O_{13}$	Yellowish-green	603.47	70	1:1	47.76 (47.78)	4.51 (4.52)	4.64 (4.60)	8.62 (8.60)	–
$[FeH_2LaOH(H_2O)] \cdot 3H_2O$	$C_{24}H_{27}FeN_2O_{13}$	Reddish-brown	607.32	65	1:1	47.46 (47.43)	4.48 (4.46)	4.61 (4.60)	9.20 (9.21)	–
$[Co_aH_2La(H_2O)_2] \cdot H_2O$	$C_{24}H_{24}Co_aN_2O_{11}$	Brown	575.39	71	1:1	50.10 (50.09)	4.20 (4.21)	4.87 (4.86)	10.24 (10.28)	–
$[Co_pH_2La(H_2O)_2] \cdot 4H_2O$	$C_{24}H_{30}Co_pN_2O_{14}$	Brown	629.43	60	1:1	45.80 (45.83)	4.80 (4.80)	4.45 (4.48)	9.36 (9.34)	–
$[Co_cH_2La(H_2O)_2] \cdot 3H_2O$	$C_{24}H_{28}Co_cN_2O_{13}$	Deep brown	611.42	63	1:1	47.15 (47.16)	4.61 (4.62)	4.58 (4.52)	9.64 (9.65)	–
$[ZnH_2La] \cdot H_2O$	$C_{24}H_{20}ZnN_2O_9$	Reddish yellow	545.81	90	1:1	52.81 (52.79)	3.70 (3.72)	5.13 (5.10)	11.98 (11.95)	–
H_4Lb	$C_{25}H_{22}N_2O_8$	Reddish yellow	478.45	90	–	62.76 (62.74)	4.63 (4.61)	5.85 (5.89)	–	–
$[CrH_2LbCl(H_2O)] \cdot 3H_2O$	$C_{25}H_{28}CrClN_2O_{12}$	Orange	635.95	75	1:1	47.22 (47.20)	4.44 (4.42)	4.41 (4.45)	8.18 (8.08)	5.57 (5.53)
$[FeH_2LbOH(H_2O)] \cdot 5H_2O$	$C_{25}H_{33}FeN_2O_{15}$	Orange	657.38	76	1:1	45.68 (45.63)	5.06 (5.03)	4.26 (4.22)	8.49 (8.47)	–
$[Co_aH_2Lb(H_2O)_2] \cdot 3H_2O$	$C_{25}H_{30}Co_aN_2O_{13}$	Violet-blue	625.45	75	1:1	48.01 (47.99)	4.83 (4.81)	4.48 (4.43)	9.42 (9.39)	–
$[Co_pH_2Lb(H_2O)_2] \cdot 2H_2O \cdot ClO_4$	$C_{25}H_{28}Co_pClN_2O_{16}$	Violet-blue	706.88	80	1:1	42.48 (42.43)	3.99 (3.98)	3.96 (3.94)	8.34 (8.30)	5.02 (5.05)
$[Co_cH_2Lb(H_2O)_2] \cdot 3H_2O$	$C_{25}H_{30}Co_cN_2O_{13}$	Yellow	625.45	78	1:1	48.01 (48.00)	4.83 (4.80)	4.48 (4.45)	9.42 (9.39)	–
$[ZnH_2Lb] \cdot H_2O$	$C_{25}H_{22}ZnN_2O_9$	Yellow	559.84	78	1:1	53.63 (53.60)	3.96 (3.98)	5.00 (4.96)	11.68 (11.69)	–

a the metal salt used in the preparation was metal acetate, *c* the metal salt was metal chloride, *p* the metal salt was metal perchlorate

Table 2 Assignment of IR-bands of metal chelates of bis-Schiff bases H_4La and H_4Lb

Metal chelates	ν cm^{-1}								
	M:L	νC=O	νC=N	νC–N	νC–O	δOH	γOH	νM–N	νM–O
Free ligand H_4La	–	1658	1620	1357	1218	1112	925	–	–
Zn(II)–H_4La	1:1	1651	1614	1350	1222	–	–	586	412
Co_a(II)–H_4La	1:1	1655	1612	1353	1226	1133	956	586	420
Co_p(II)–H_4La	1:1	1647	1600	1350	1230	1133	960	547	420
Co_c(II)–H_4La	1:1	1647	1612	1342	1226	1134	960	547	420
Cr(III)–H_2La	1:1	1651	1614	1350	1230	1133	960	586	422
Fe(III)–H_2La	1:1	1643	1581	1353	1222	1103	964	509	435
Free ligand H_4Lb	–	1651	1612	1346	1222	1110	952	–	–
Zn(II)–H_4Lb	1:1	1651	1620	1307	1272	–	–	509	408
Co_a(II)–H_4La	1:1	1654	1616	1307	1226	1110	952	509	486
Co_p(III)–H_4La	1:1	1651	1589	1334	1233	1130	960	543	443
Co_c(II)–H_4La	1:1	1644	1616	1315	1230	1111	941	505	466
Cr(III)–H_4Lb	1:1	1647	1593	1311	1234	1130	968	513	424
Fe(III)–H_4Lb	1:1	1643	1585	1303	1230	1110	964	509	428

The band of ClO_4 in Co(III)-H_4Lb at 1097 cm^{-1}

the IR spectra of the metal complexes indicating that the metal ions are coordinated through the oxygen atoms of the phenolic groups after deprotonation. (iv) The new band in the spectra of all complexes in the frequency range 408–466 and 509–586 cm^{-1} can be assigned to the stretching frequencies υM–N and υM–O, respectively, which are absent in the IR spectra of the free ligands [32]. The presence of the bands at 1097 and 624 cm^{-1} in the IR spectrum of Co(II) perchlorate complex with H_4Lb are indicative of the presence of non-coordinated perchlorate ion [34].

Proton nuclear magnetic resonance (^{1}H-NMR) spectra

The ^{1}H-NMR spectra of ligand recorded in d6-DMSO show that the phenolic OH proton signals appear at 14.35 and 14.43 ppm (s, 4H) for H_4La and H_4Lb, respectively, this may be due to that the molecule is planar [33]. In the ^{1}H-NMR spectra of Zn(II) complexes no signals are observed at 14.00–14.50 region, meanwhile a new signal appeared at 7.95 ppm (s, 2H) equivalent to two hydrogens. This signal indicates that two phenolic protons are participated in complex formation and the other two protons are shifted to high field after chelation.

Electronic spectra, magnetic moment studies and molar conductivity

The electronic spectra of both ligands showed a band at 402 nm (24876 cm^{-1}) assigned to n–π* transition, which is shifted to lower wave number on coordination, as a result of the participation of the two azomethine nitrogens in coordination (Table 3).

Table 3 Electronic absorption bands and magnetic moments of the metal chelates of Schiff bases H_4La and H_4Lb

Compound	ν cm^{-1}	B. M.
H_4La	24876	–
$[CrH_2LaOH(H_2O)] \cdot 3H_2O$	25000	3.85
$[FeH_2LaOH(H_2O)] \cdot 3H_2O$	34247, 21142	5.80
$[Co_aH_2La(H_2O)_2] \cdot H_2O$	20000	4.09
$[Co_pH_2La(H_2O)_2] \cdot 4H_2O$	20366	4.15
$[Co_cH_2La(H_2O)_2] \cdot 3H_2O$	20408	4.06
$[ZnH_2La] \cdot H_2O$	27548	0.00
H_4Lb	24876	–
$[CrH_2LbCl(H_2O)] \cdot 3H_2O$	27027	3.65
$[FeH_2LbOH(H_2O)] \cdot 5H_2O$	34014, 20202	5.85
$[Co_aH_2Lb(H_2O)_2] \cdot 3H_2O$	26954	4.05
$[Co_pH_2Lb(H_2O)_2] \cdot 2H_2O \cdot ClO_4$	26666	0.00
$[Co_cH_2Lb(H_2O)_2] \cdot 3H_2O$	26525	5.01
$[ZnH_2Lb] \cdot H_2O$	27397	0.00

The electronic spectra of the 1:1 (M:L) Cr(III) complexes display charge-transfer band at 25000 and 27027 cm^{-1} for H_4La and H_4Lb, attributed to ligand-to-metal charge-transfer bands. These charge-transfer transitions probably occur from π-orbitals of the Schiff base to the d-orbitals of chromium. The magnetic moment values are 3.85 and 3.65 B.M. indicating the presence of three unpaired electrons (3d^3) in Cr(III) ion. These values of magnetic moments are consistent with the octahedral geometry [35, 36].

The visible spectra of Fe(III) complexes show two bands for each complex. The first band occurred at 34247 and 34014 cm^{-1} for H_4La and H_4Lb complexes. These bands may be attributed to LMCT transition. The second band at 21142 and 20202 cm^{-1} for these complexes is due to ligand field (d–d) transitions, this band can be assigned to the transition $^2T_{2g} - {}^2T_{1g}$ [37]. The magnetic moment values are 5.80 and 5.85 B.M. for these complexes. The calculated μ_{eff} value 5.91 B.M. of the magnetic moments are evidence for the octahedral geometry for these chelates [38].

The visible spectra of Schiff bases complexes with cobalt (II) acetate, chloride and perchlorate with ligands H_4La and H_4Lb are studied. The spectra of the complexes with H_4Lb show band in the range of 26525–26954 cm^{-1} that may be due to a LMCT transition, whereas the complexes with H_4La show band in the range 20000–20408 cm^{-1} assigned to d–d transition and may be attributed to $^4T_{1g} \rightarrow {}^4T_{1g}(p)$ [37] transition. The magnetic moments of these cobalt complexes are in the range 4.05–5.01 B.M. which are in good agreement with ($3d^7$) high spin octahedral geometry [37]. On the other hand, the diamagnetic nature of cobalt-H_4Lb complex (prepared from Co(II) perchlorate) is taken as a good evidence for oxidation of Co(II) to Co (III) [39].

The electronic spectra of metal chelated of Zn(II) exhibit bands at 27397–27548 cm^{-1}.

The molar conductance value of H_4La and H_4Lb complexes in DMF (10^{-3} M) range from 5.0-58.8 ohm^{-1} cm^2 mol^{-1} suggested non electrolytic nature of these complexes [40, 41]. These values indicate that no anions (OH^- and Cl^-) are present outside the coordination sphere. The high observed value of cobalt perchlorate complex with H_4Lb 149 ohm^{-1} cm^2 mol^{-1} indicates that this complex is 1:1 ionic compound [41].

TG analysis of solid complexes

For elucidating the molecular structure and thermal stability of the prepared complexes, the TG study is proved successful [42, 43]. The TG analysis was measured for six solid complexes of H_4La and H_4Lb with Cr(III), Fe(III) and Co(II) ions.

A typical TG plot for the Schiff base H_4Lb with Co(II) is shown in Fig. 1.

The initial mass loss up to 200 °C corresponds to the elimination of the hydrated H_2O from the complex. Then an inflection is shown indicating the beginning of removal of the more strongly bound (coordinated) H_2O molecules which occupy some positions in the coordination sphere. Further heating of the anhydrous complex [ML] results in a continuous mass-loss till a constant mass where the MO or M_2O_3 residue is formed as a final product. The following mechanism can be proposed for the thermal decomposition of these Schiff base complexes.

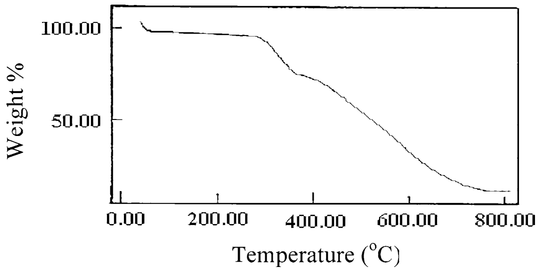

Fig. 1 TG plot of the Schiff base H_4Lb complex with Co(III) ion

(a) For divalent Co(II) complex

$$\begin{array}{ccc} [CoL(H_2O)_2]\cdot 4H_2O & \xrightarrow{25-200\,^{\circ}C} & [CoL(H_2O)_2] \\ [CoL(H_2O)_2] & \xrightarrow{200-300\,^{\circ}C} & [CoL] \\ [CoL] & \xrightarrow{300-720\,^{\circ}C} & \text{Intermediate} \\ \text{Intermediate} & \xrightarrow{800\,^{\circ}C} & CoO \end{array}$$

(b) For trivalent M(III) complexes.

$$\begin{array}{ccc} [ML(H_2O)_n]\cdot mH_2O & \xrightarrow{25-200\,^{\circ}C} & [ML(H_2O)_n] \\ [ML(H_2O)_n] & \xrightarrow{200-300\,^{\circ}C} & [ML] \\ [ML] & \xrightarrow{300-700\,^{\circ}C} & \text{Intermediate} \\ \text{Intermediate} & \xrightarrow{800\,^{\circ}C} & M_2O_3 \end{array}$$

$[CrH_2La(OH)(H_2O)]\cdot 3H_2O$ complex

The TG plot of the complex displayed several decomposition steps. The first two steps were due to elimination of both lattice and coordinated water molecules. The decomposition of the anhydrous complex starts at temperature range 300–420 °C with mass loss of 41.43%, this decomposition follows a first order kinetic and the E^* was calculated (Table 5). The mass loss in the temperature range 420–480 °C was 34.55% due to complete decomposition of the organic part, the Coats-Redfern relation was not verified and E^* can not be calculated. The final product was found to confirm the formation of metal oxide residue Cr_2O_3.

$[FeH_2La(OH)(H_2O)]\cdot 3H_2O$ complex

The anhydrous iron complex $[FeH_2La(OH)]$ decomposes in two main steps. The first decomposition step occurs in the temperature range 300–600 °C with a mass loss of 54.57% while the second step exists over temperature range 600–790 °C with a mass loss of 20.42% corresponding to the elimination of the rest of the Schiff base molecule with the formation of Fe_2O_3 as a metallic residue (13.14%).

[$CoH_2La(H_2O)_2$] · $4H_2O$ complex

For the anhydrous complex [CoH_2La], two decomposition steps are considered. The first step occurs over temperature range 300–480 °C and the second step exists in the range 480–720 °C. Both successive steps produce intermediates which decompose by further heating to give metal residue CoO as a final product.

[$CrH_2LbCl(H_2O)$] · $3H_2O$ complex

The TG plot of the above hydrated complex displays four steps. The first two steps occur due to removal of hydrated $3H_2O$ and coordinated H_2O molecules in the range 25–200 and 200–300 °C. The next two decomposition steps occurring at 300–645 °C and at 645–750 °C with mass losses 41.11% and 35.62% represent the decomposition of the anhydrous complex to intermediate and to oxide.

[$FeH_2Lb(OH)(H_2O)$] · $5H_2O$

The Fe(III) complex [$FeH_2Lb(OH)(H_2O)$] · $5H_2O$ decomposes in three main steps. Two steps of dehydration occur in the range up to 300 °C with mass losses 13.69% and 2.74%. The next step occurs over a range 300–625 °C with a mass loss of 71.43% followed by metal oxide formation.

[$CoH_2Lb(H_2O)_2$]ClO_4 · $2H_2O$ complexes

For the anhydrous complex formed at 220 °C, there are three decomposition steps shown in Table 4. One step occurs at 300–360 °C with mass loss 14.07%. The next steps of partial decomposition occur at 360–550 °C and 550–790 °C with mass loss 28.37% and 35.65%, respectively, with the formation of metallic residue 11.73% of Co_2O_3.

Kinetics and thermodynamic parameters

The C_s values (mass fraction at T_s) of thermal decomposition of the complexes are in the range 0.28–0.37 (Table 5). This indicates that the decomposition follows first order kinetics [44]. The calculated values of E^*, A, ΔS^*, ΔH^* and ΔG^* for the decomposition steps are given in Table 5. For the chromium complexes, [$CrH_2La(OH)(H_2O)$] · $3H_2O$ complex showed considerable thermal stability as reflected from the high value of activation energy averaged to 81 KJ mol^{-1}. While [$CrH_2LbCl(H_2O)$] · $3H_2O$ complex

Table 4 TG data for the solid complexes of the Schiff bases H_4La and H_4Lb

Complex	Temperature range	Mass loss (%)	Removed species	Residue %/800 °C
[$CrH_2La(OH)(H_2O)$] · $3H_2O$	25–150	8.94	$3H_2O$	12.59
	150–300	2.98	H_2O	
	300–420	41.43	$C_{14}H_6NO_4$	
	420–480	34.55	$C_{10}H_{10}NO_4$	
[$FeH_2La(OH)(H_2O)$] · $3H_2O$	25–180	8.89	$3H_2O$	13.14
	180–250	2.96	H_2O	
	300–600	54.57	$C_{19}H_9NO_5$	
	600–790	20.42	$C_5H_2NO_3$	
[$CoH_2La(H_2O)_2$] · $4H_2O$	25–200	11.44	$4H_2O$	11.90
	200–300	5.72	$2H_2O$	
	300–480	38.56	$C_{13}H_8NO_4$	
	480–720	32.38	$C_{11}H_9NO_3$	
[$CrH_2LbCl(H_2O)$] · $3H_2O$	25–200	8.49	$3H_2O$	11.95
	200–300	2.83	H_2O	
	300–645	41.11	$C_{12}H_4NO_4Cl$	
	645–750	35.62	$C_{11}H_{16}NO_4$	
[$FeH_2Lb(OH)(H_2O)$] · $5H_2O$	25–200	13.69	$5H_2O$	12.14
	200–300	2.74	H_2O	
	300–625	71.43	$C_{23}H_{21}N_2O_9$	
[$CoH_2Lb(H_2O)_2$] · ClO_4 · $2H_2O$	25–120	5.09	$2H_2O$	11.73
	120–220	5.09	$2H_2O$	
	300–360	14.07	ClO_4	
	360–550	28.37	$C_9H_{14}NO_4$	
	550–790	35.65	$C_{14}H_5NO_4$	

Table 5 Thermodynamic and kinetic data of the thermal decomposition

Complex	Temperature range (°C)	E^* KJ mol^{-1}	A (s^{-1})	ΔS^*	ΔH^*	ΔG^*	T_s (°C)	C_s
Cr–La	320–400	81	2.5×10^5	−0.15	76	172	377	0.36
Fe–La	200–310	81.2	2.2×10^6	−0.13	76	153	320	0.28
	350–600	47.8	81	−0.22	41	219	550	0.35
Co–La	300–450	73	1.5×10^4	−0.17	67	192	455	0.30
	500–670	42.5	4.0	−0.24	37	206	430	0.35
Cr–Lb	300–615	41.5	11.8	−0.23	34	239	606	0.37
Fe–Lb	47–230	33.7	1.1×10^3	−0.19	30	112	157	0.35
	277–566	20.4	0.74	−0.25	15	197	443	0.37
Co–Lb	270–350	107	4×10^8	−0.09	102	154	330	0.30
	400–750	38.8	3.88	−0.24	32	224	520	0.37

showed moderate thermal stability as reflected from the activation energy value 41.5. For iron complexes $[FeH_2La(OH)] \cdot 3H_2O$ and $[FeH_2Lb(OH)(H_2O)] \cdot 5H_2O$ showed moderate thermal stability as shown in Table 5, E^* ranging from 20.4 to 81.2 KJ mol^{-1}. With respect to cobalt complexes the Co(II) complex $[CoH_2La(H_2O)_2] \cdot 4H_2O$ the E^* ranging from 42.5 to 73 KJ mol^{-1} reflects moderate stability while Co(III) complex $[CoH_2Lb\,(H_2O)_2]ClO_4 \cdot 2H_2O$ showed high thermal stability which reflected from the energies of activation ranging from 38.8 to 107 KJ mol^{-1}.

In general and based on the sum of the energies of activation, the H_4La complexes are thermally more stable than the H_4Lb complexes; this may be due to that the aliphatic chain $(CH_2)_2$ in H_4La is shorter than chain $(CH_2)_3$ in H_4Lb. It is well known that Co(III) complexes are inert and stable, so the E^* of $[CoH_2Lb(H_2O)_2]ClO_4 \cdot 2H_2O$ complex is higher than that of the other studied complexes.

The entropy change ΔS^* for the complex formation from the starting reactants is negative for all the studied complexes. This means that the decomposition reactions are slow [45].

Considering the TG results, some remarks and conclusions can be drawn as follows:

1. There are two kinds of H_2O molecules i.e. hydrated and coordinated.
2. The thermal decomposition of complexes includes several steps.
3. A coordination number 6 is proposed for these metal ions considering the $H_4L(a)$ and $H_4L(b)$ as tetradentate ligands.

Geometrical structure of the complexes

Concerning the ligating properties of the Schiff bases and the geometry of their metal complexes, the following conclusions can be drawn:

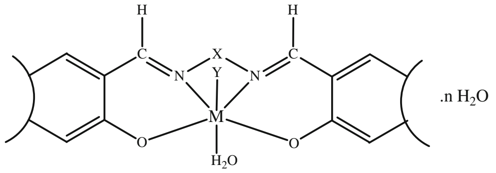

Fig. 2 Octahedral structure of 1:1 chelates $[M(H_2L)(H_2O)Y] \cdot nH_2O$, where Y = OH or Cl anion as shown in Table 1

(a) The IR spectral data indicate that the Schiff bases H_4La and H_4Lb act as dinegative N_2O_2 tetradentate ligands. The bonding occur via two azomethine N atoms and two phenolic O atoms in position 7 (and not in position 5) to form 1:1 M/L complex.

(b) From the electronic spectral data and magnetic moment values, a square planar structure has been proposed for [Zn L]. Whereas, the results of the electronic absorption spectra of the chelates of the type $[ML(H_2O)_2]$ and $[MLX(H_2O)]$ (M = Cr(III), Fe(III), Co(III)) agree with an octahedral environment around the metal ion as in Fig. 2. The dinegative tetradentate Schiff base lies in the equatorial plane while 2 H_2O (or H_2O + anion Y) occupy the two axial positions. Moreover, the Co(III)–H_2Lb complex behaves as a cationic complex and its molar conductance is in agreement with the 1:1 electrolyte. Based on the above discussion, the structure of the octahedral complexes may be represented in Fig. 2

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