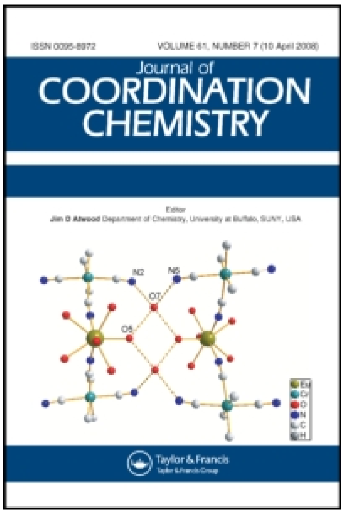

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Synthesis and characterization of tetradentate <i>bis</i>-Schiff base complexes of di- and tri-valent transition metals

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Synthesis and characterization of tetradentate *bis*-Schiff base complexes of di- and tri-valent transition metals

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The *bis*-Schiff bases of N_2O_2 dibasic ligands, H_2La and H_2Lb are synthesized by the condensation of ethylenediamine (a) and trimethylenediamine (b) with 6-formyl-7-hydroxy-5-methoxy-2-methylbenzo-pyran-4-one. The ligands are characterized using elemental analysis, IR, UV–Vis, ^{1}H-NMR and mass spectroscopy. The ionization constant pKa values are determined spectrophotometrically. The ^{1}H-NMR spectra of the ligands show the presence of phenolic coordinating groups. New complexes of H_2La and H_2Lb with metal ions Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) are synthesized. Elemental analyses, infrared, ultraviolet-visible, electron spin resonance and thermal analysis, as well as conductivity and magnetic susceptibility measurements, are used to elucidate the structures of the newly prepared metal complexes. Thermal degradation studies for some complexes show that the final product is the metal oxide. A square planar geometry is suggested for the Cu(II), Zn(II) (for H_2La and H_2Lb) and Ni(II) (for H_2La) complexes; an octahedral geometry for the Co(II), Cr(III), Fe(III) (for H_2La and H_2Lb), and Ni(II) (for H_2Lb) complexes. The coordination sites are two azomethine nitrogens and two phenolic oxygens in the tetradentate Schiff bases.

Keywords: *bis*-Schiff bases; Benzopyran-4-one; Di and trivalent transition metals; Complexes; Spectroscopy; Thermal analysis

1. Introduction

Schiff-base chelates [1–3] and their complexes have a variety of applications including biological [4], clinical [5] and analytical [6]. Some drugs show higher activity when administered as metal chelates rather than as organic compounds [4, 5]. Some Schiff-base chelates exhibit a catalytic activity in oxidation [7] and in ethylene oligomerization [8]. Novel oligomers viz. di-, tri-, tetra and pentamers of the furochromone visnagin, were isolated from the chloroform extract of fresh mature seeds of the plant *Pimpinella monoica* [9]. Reactions of flavones, isoflavones and

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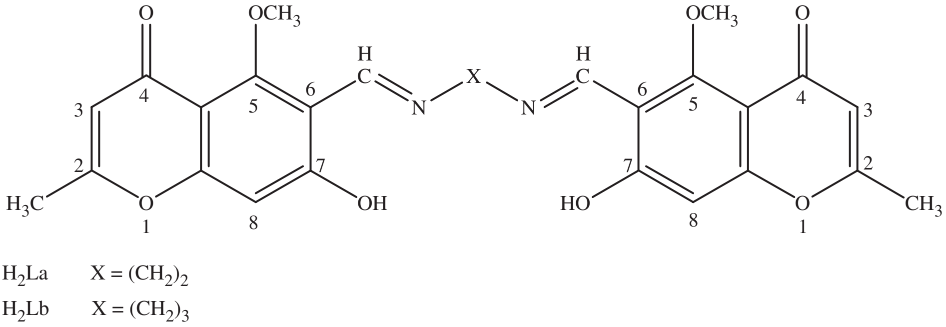


Scheme 1. Schematic of bis-Schiff bases H_2La and H_2Lb. For H_2La $X = (CH_2)_2$; For H_2Lb $X = (CH_2)_3$.

their analogs 2- and 3-hetaryl chromones with hydroxylamine have been reviewed [10]. The synthesis of dimeric coumarin and furanocoumarin models and their spectroscopic characterization have been reported [11].

The present work synthesizes and characterizes new metal chelates of salen like Schiff bases. The *bis*-Schiff bases of N_2O_2 dibasic ligands H_2La and H_2Lb are synthesized by condensation of ethylenediamine (a) or trimethylenediamine (b) with 6-formyl-7-hydroxy-5-methoxy-2-methylbenzopyran-4-one (scheme 1).

Several new complexes of H_2La and H_2Lb with Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) are synthesized.

2. Experimental

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

2.1. *Analysis and physical measurements*

Carbon, hydrogen, nitrogen and chlorine were analyzed by standard microanalysis methods at the Microanalytical Center, Cairo University, Giza, Egypt. UV-Vis spectra of the metal complexes in DMF were recorded on a UV/Vis-NIR 3101 PC Shimadzu spectrophotometer. 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 a Varian 300 MHz NMR spectrometer at room temperature using TMS as an internal standard. Mass spectra were recorded with the aid of a Q 1000 EX GC-MS Shimadzu spectrometer at 70 eV and 100 µA energy using a direct insertion probe at 90–110°C.

Magnetic susceptibilities of the complexes were measured at room temperature using a Cambridge England Sherwood Scientific magnetic susceptibility balance.

The effective magnetic moments were calculated from the expression $\mu_{eff} = 2.828(X_M \cdot T)^{1/2}$ B.M., where X_M is the molar susceptibility corrected using Pascal's constants for diamagnetism of all atoms in the compounds [12].

ESR spectra of the copper complexes were recorded on a JEOL X-band spectrophotometer equipped with an E 101 microwave bridge. The magnetic field was calibrated with diphenylpicrylhydrazyl free radical (DPPH) ($g = 2.0023$).

Molar conductivity of 10^{-3} M solutions of the complexes in DMF was measured on the ORION model 150 conductivity meter of 0.6 cell constant. Thermal analyses have been carried out using a Shimadzu-50 thermal analyzer from room temperature to 600°C at 10°C min^{-1}. Analyses of the metal ions were carried out by dissolving the complexes in concentrated nitric acid, neutralizing the diluted aqueous solutions with ammonia and titrating the metal solutions with standard EDTA.

The dissociation constants of H_2La and H_2Lb were determined spectrophotometrically at $\mu = 0.1$ ionic strength and 25°C. Stock solutions of Schiff bases were prepared containing 60% (v/v) ethanol–water mixture. The spectra of solutions at different pH values were recorded using the same solvent mixture as a blank.

2.2. *Synthesis of H_2La and H_2Lb*

H_2La and H_2Lb were prepared in two steps. The first step involved oxidation of visnagine $C_{13}H_{10}O_4$ (2.40 g, 10.4 mmole) 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 [13]. The product (2.34 g, 10 mmole) in ethanol (40 mL) was condensed with a solution of ethylenediamine (0.30 g, 5 mmole) or trimethylenediamine (0.37 g, 5 mmole). The solution was stirred at room temperature for at least 30 min; yellow solids were collected by filtration, washed, and recrystallized from ethanol (figure 1).

2.3. *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 dropwise to adjust the pH in the range 6–7. The resulting precipitates were filtered, washed with water, ethanol then diethylether, and finally air dried. The complexes are air stable in the solid state and soluble in DMF or DMSO.

3. Results and discussion

The analytical and physical data of metal complexes of H_2La and H_2Lb are shown in tables 1 and 2. Reaction of H_2La with salts of Ni(II), Cu(II), Zn(II) and reaction of H_2Lb with salts of Cu(II), Zn(II) in the molar ratio 1 : 1 give complexes $[ML] \cdot nH_2O$. Reaction of Ni(II) with H_2Lb and Co(II) with H_2La and H_2Lb in the molar ratio 1 : 1 gives complexes $[ML(H_2O)_2] \cdot nH_2O$. Reaction of H_2La with salts of Cr(III) and Fe(III) in the molar ratio 1:1 gives complexes $[ML(OH)(H_2O)] \cdot nH_2O$ and reaction of Cr(III) and Fe(III) in the molar ratio 1:1 with H_2Lb gives complexes $[ML(Cl)(H_2O)] \cdot nH_2O$.

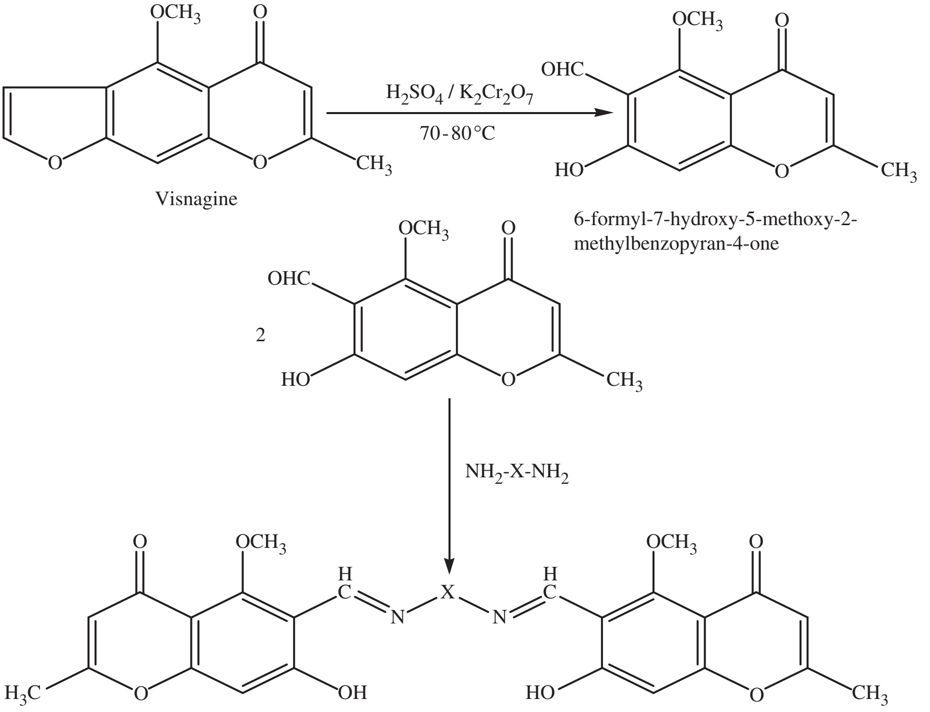


Figure 1. Preparation of H_2La and H_2Lb where X = $(CH_2)_2$ or $(CH_2)_3$.

These metal complexes are stable, non-hygroscopic, partially soluble in most organic solvents and soluble in DMF and DMSO.

3.1. *Characterization of H_2La and H_2Lb*

3.1.1. Mass spectra and ^{1}H-NMR. Mass spectra of H_2La and H_2Lb exhibit the molecular ion peaks at m/e = 493 (M + 1) and 506 (M) for H_2La and H_2Lb confirming their formula weights are equal to their molecular weights. Fragmentation was proposed for H_2La and H_2Lb in the Supplementary Data.

The ^{1}H-NMR spectra of H_2La and H_2Lb in DMSO-d6 display resonances at $\delta = 15.19$ and 15.30 assignable to phenolic OH groups, a resonance for H–C=N at $\delta = 8.8$ ppm, signals at 5.8 and 6.3 ppm for C_3 and C_8 aromatic protons, respectively [14] and resonances at $\delta = 3.8$, 2.6 and 2.2 ppm assigned to OCH_3, CH_2 and CH_3, respectively (J_{H-H} for $CH_2 = 6.7$ Hz). The signal due to phenolic OH protons disappeared on adding D_2O while the other signals remain at their expected positions.

3.1.2. IR spectra. The IR spectra of H_2La and H_2Lb show a broad band at 3398–3386 cm^{-1} due to phenolic OH stretching. The broadness is due to intramolecular hydrogen bonding between the phenolic groups and the azomethine groups. Bands at 1662–1654, 1620, 1396 and 1076 cm^{-1} are assigned to ν(C=O) of the pyrone ring, ν(C=N) (azomethine), ν(C–N) and ν(C–O–C) respectively.

Table 1. Analytical and physical data of the metal complexes of Schiff base La.

Ligand or complexes	Formula	Color	M.W.	Yield%	Calc. (Found)				
					C%	H%	N%	M%	Cl%
La	$C_{26}H_{24}N_2O_8$	Yellow	492.48	90	63.34 (63.14)	4.91 (4.91)	5.69 (5.59)	–	–
1 $[CrLaCl(H_2O)] \cdot 6H_2O$	$C_{26}H_{36}ClCrN_2O_{15}$	Yellowish-green	704.024	55	44.36 (43.28)	5.10 (4.57)	4.00 (4.28)	7.38 (7.18)	5.10 (5.28)
2 $[FeLaCl(H_2O)] \cdot H_2O$	$C_{26}H_{26}ClFeN_2O_{10}$	Reddish-brown	617.79	65	50.60 (51.12)	4.24 (4.32)	4.50 (4.27)	9.04 (9.10)	5.70 (5.21)
3 $[Co_aLa(H_2O)_2] \cdot 6H_2O$	$C_{26}H_{38}Co_aN_2O_{16}$	Brown	693.52	71	45.03 (45.21)	5.52 (5.63)	4.08 (4.05)	8.49 (8.60)	–
4 $[Co_pLa(H_2O)_2] \cdot 7H_2O$	$C_{26}H_{40}Co_pN_2O_{17}$	Brown	711.54	60	43.88 (43.87)	5.67 (4.88)	3.90 (4.93)	8.28 (8.70)	–
5 $[Co_cLa(H_2O)_2] \cdot 6H_2O$	$C_{26}H_{38}Co_cN_2O_{16}$	Deep brown	693.52	63	45.03 (45.12)	5.52 (5.30)	4.04 (4.05)	8.49 (8.60)	–
6 $[Ni_pLa] \cdot 2H_2O$	$C_{26}H_{26}Ni_pN_2O_{10}$	Orange	585.19	75	53.37 (53.08)	4.47 (4.39)	4.78 (4.65)	10.10 (9.95)	–
7 $[Ni_cLa] \cdot 2H_2O$	$C_{26}H_{26}Ni_cN_2O_{10}$	Orange	585.19	76	53.36 (53.83)	4.47 (4.45)	4.78 (4.79)	10.10 (10.00)	–
8 $[Cu_aLa] \cdot 2H_2O$	$C_{26}H_{26}Cu_aN_2O_{10}$	Violet-blue	590.05	75	52.93 (53.27)	4.44 (4.39)	4.75 (4.68)	10.89 (11.30)	–
9 $[Cu_cLa] \cdot 2H_2O$	$C_{26}H_{26}Cu_cN_2O_{10}$	Violet-blue	590.05	80	52.93 (53.45)	4.44 (4.26)	4.75 (4.76)	10.80 (11.00)	–
10 $[ZnLa] \cdot 3H_2O$	$C_{26}H_{28}ZnN_2O_{11}$	Yellow	609.89	78	51.20 (51.73)	4.63 (4.68)	4.59 (4.58)	10.71 (10.20)	–

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. Analytical and physical data of the metal complexes of Schiff base Lb.

Ligand or complexes	Formula	Color	M.W.	Yield%	Calc. (Found)				
					C%	H%	N%	M%	Cl%
Lb	$C_{27}H_{26}N_2O_8$	Yellow	506.51	90	64.02 (63.92)	5.17 (5.10)	5.53 (5.19)	–	–
11 $[CrLb(OH)(H_2O)]\cdot 4H_2O$	$C_{27}H_{35}$ Cr N_2O_{14}	Green	663.57	65	48.87 (48.80)	5.30 (4.80)	4.20 (4.00)	7.84 (7.89)	–
12 $[FeLb(OH)(H_2O)]\cdot H_2O$	$C_{27}H_{29}FeN_2O_{11}$	Reddish-brown	613.37	70	52.90 (53.28)	4.76 (4.63)	4.57 (4.47)	9.10 (9.11)	–
13 $[Co_aLb(H_2O)_2]\cdot 5H_2O$	$C_{27}H_{38}Co_aN_2O_{15}$	Brown	689.53	60	47.03 (46.51)	5.55 (5.50)	4.06 (4.05)	8.54 (8.06)	–
14 $[Co_pLb(H_2O)_2]\cdot H_2O\cdot ClO_4$	$C_{27}H_{30}ClCo_pN_2O_{15}$	Brown	716.92	62	45.24 (45.49)	4.22 (4.32)	3.90 (4.00)	8.22 (8.49)	5.00 (5.30)
15 $[Co_cLb(H_2O)_2]\cdot 5H_2O$	$C_{27}H_{38}Co_cN_2O_{15}$	Brown	689.53	75	47.03 (46.89)	5.55 (5.43)	4.06 (4.05)	8.54 (8.60)	–
16 $[Ni_pLb(H_2O)_2]\cdot 3H_2O$	$C_{27}H_{34}Ni_pN_2O_{13}$	Pale green	653.27	80	49.60 (49.56)	5.20 (4.99)	4.30 (4.60)	8.98 (8.70)	–
17 $[Ni_cLb(H_2O)_2]\cdot 2H_2O$	$C_{27}H_{32}Ni_cN_2O_{12}$	Pale green	635.25	82	51.20 (51.42)	5.08 (5.05)	4.41 (4.64)	9.20 (9.00)	–
18 $[Cu_aLb]\cdot 2H_2O$	$C_{27}H_{28}Cu_aN_2O_{10}$	green	604.07	86	53.70 (54.00)	4.70 (4.55)	4.60 (4.17)	10.50 (10.20)	–
19 $[Cu_cLb]\cdot 3H_2O$	$C_{27}H_{30}Cu_cN_2O_{11}$	green	586.05	79	52.13 (51.31)	4.86 (4.46)	4.50 (4.15)	10.20 (10.23)	–
20 $[ZnLb]\cdot H_2O$	$C_{27}H_{26}ZnN_2O_9$	Yellowish white	587.89	85	55.10 (55.02)	4.50 (4.64)	4.70 (4.69)	11.12 (11.10)	–

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.

The elemental analyses (tables 1 and 2), IR, ^{1}H-NMR and mass spectra verified the molecular structure shown in scheme 1. Infrared spectral bands, which are most useful for determination of the mode of chelation, are listed in table 3.

3.1.3. Dissociation constants. The acidity constants pKa of the hydroxyl groups in position 7 of H_2La and H_2Lb were determined by considering the spectral shifts of these compounds with pH change of solutions containing 60% (v/v) ethanol to ensure complete solubility of the compounds (figure 2). The absorbance-pH curves (see online

Table 3. Assignment of IR–bands of metal chelates of La and Lb.

	ν cm^{-1}							
Metal chelates	νC=O	νC=N	νC–N	νC–O	δOH	γOH	νM–N	νM–O
Free ligand La	1654	1620	1396	1218	1110	941	–	–
Zn(II)–La	1647	1581	1388	1222	–	–	547	422
Cu(II)–La	1639	1639	1392	1222	–	–	567	416
Ni(II)–La	1631	1631	1388	1230	–	–	547	462
Co(II)–La	1651	1577	1392	1226	1126	902	543	459
Cr(III)–La	1651	1581	1392	1230	1130	902	543	428
Fe(III)–La	1651	1614	1392	1222	1122	902	582	422
Free ligand Lb	1662	1620	1396	1222	1110	937	–	–
Zn(II)–Lb	1658	1614	1388	1226	–	–	532	478
Cu(II)–Lb	1608	1577	1392	1226	–	–	536	420
Ni(II)–Lb	1651	1651	1392	1226	1122	952	532	443
Co(II)–Lb	1658	1658	1392	1230	1126	945	505	466
Co(III)–Lb	1651	1573	1392	1230	1122	941	505	466
Cr(III)–Lb	1651	1585	1392	1226	1114	941	501	433
Fe(III)–Lb	1662	1585	1392	1226	1118	945	501	416

The band of ClO_4 in Co(III)–Lb at 1090 cm^{-1}.

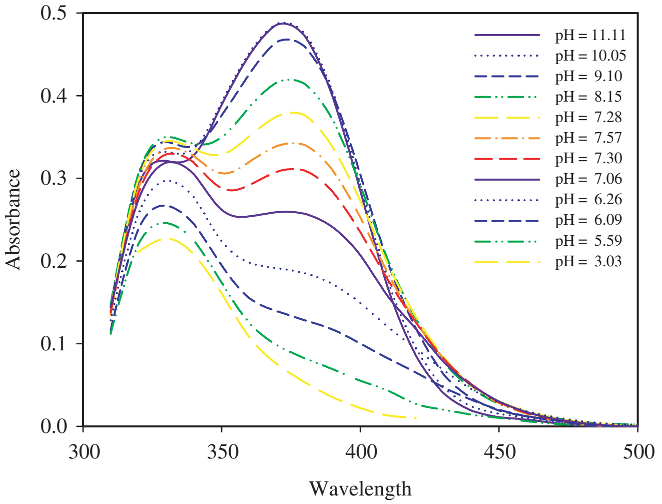


Figure 2. Absorption spectra of bis-Schiff base H_2La in ethanol–water mixtures of varying pH values.

supplementary material) give pKa values 7.08 for H_2La and 7.09 for H_2Lb [15]. The presence of one inflection can be considered as evidence for simultaneous ionization of the hydroxyl groups.

3.2. *Characterization of the complexes*

3.2.1. Infrared spectroscopy. Infrared spectra of the complexes exhibit a broad band around 3363–3560 cm^{-1} which is assignable to ν(OH) of water molecules associated with the complex; this is confirmed by elemental and thermal analysis. Upon complexation, the C=O stretching vibration in position four of the benzopyrone moiety does not change, indicating that it does not participate in chelation. Supplementary data show IR spectra of H_2La chelates. A shift of the ν(C=N) bands towards lower or higher wavenumbers compared with free ligands indicates coordination of the two azomethine groups to the metal ions [16]. Coordination through the phenolic oxygen after deprotonation is revealed by a band due to ν(C–O) at higher frequencies (1222–1230 cm^{-1}) in all the complexes compared to that of H_2La and H_2Lb (table 3), suggesting that hydroxyl groups of the Schiff base coordinate with M [17, 18]. The band at 1346–1396 cm^{-1} due to C–N stretching [19] in the IR spectra of ligands shifts to lower wavenumber in the spectra of complexes confirming participation of azomethine in chelation. New bands in the 411–480 and 500–580 cm^{-1} range are assigned to ν(M–N) and ν(M–O), respectively.

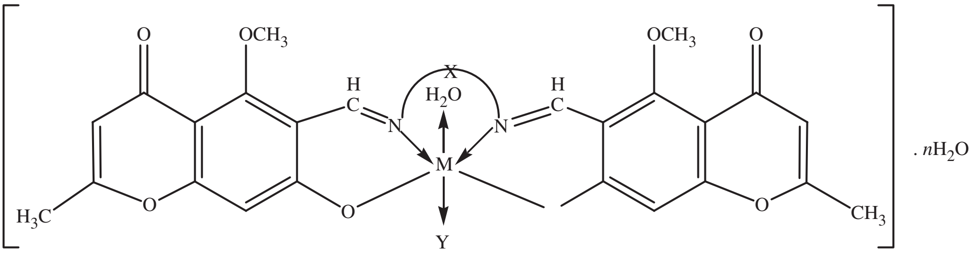
The infrared spectrum of cobalt perchlorate complex with H_2Lb exhibits bands at 1090 and 1097 cm^{-1} with a band at 624 cm^{-1}, suggesting non-coordinated perchlorate [16].

3.2.2. Spectroscopic, magnetic moment studies and molar conductivity. The electronic spectra of the ligands show a shoulder at 364 nm and 360 nm for H_2La and H_2Lb, respectively, assigned to π–π* transition of the benzopyrone ring [20]. Absorption bands at 402 nm for both ligands were assigned to the π–π* transition within the azomethine group [21], which is shifted to lower wavelength, as a result of participation of the two azomethine nitrogens in coordination.

The electronic spectra of the complexes showed several absorption bands, including absorption bands of the ligands, charge transfer bands and d-d transition of the metal ions. The electronic absorption spectra of complexes **1** and **11** display charge transfer bands at 391 and 375 nm, respectively, attributed to the $^4A_{2g}$ (F) $\rightarrow$ $^4T_{1g}$ (F) [22] transition in octahedral complexes. The magnetic moments of these complexes are 3.7 and 3.9 B.M., respectively, indicating three unpaired electrons in Cr(III), consistent with octahedral geometry [23, 24].

The visible spectra of **2** and **12** show two bands, the first at 291 and 293 nm, respectively, attributed to LMCT transition, and the second at 442 and 438 nm due to d-d transitions, assigned to $^2T_{2g} \rightarrow {}^2T_{1g}$ [26]. The magnetic moment values are 5.70 and 5.71 B.M., evidence for the octahedral geometry [25].

The visible spectra of the brown Co(II) complexes **3**, **4**, **5**, **13** and **15** are consistent with octahedral geometry, showing two bands. The first in the 372–391 nm range may be attributed to an LMCT transition and the second in the 466–470 nm range may be assigned to d–d transition $^4T_{1g} \rightarrow {}^4T_{1g}$ (P) [26]. The magnetic moments



M	X	Y	n
Co(II)	$(CH_2)_2$ or $(CH_2)_3$	H_2O	5, 6, 7
Cr(III), Fe(III)	$(CH_2)_2$	Cl	6, 1
Cr(III), Fe(III)	$(CH_2)_3$	OH	4, 1
Ni(II)	$(CH_2)_3$	H_2O	2, 3

Figure 3. Structures of octahedral complexes.

of the cobalt complexes are in the range 4.32–5.02 B.M. in good agreement with high spin octahedral geometry [26]. The diamagnetic nature of **14** is good evidence for oxidation of Co(II) to Co(III) [22]. The octahedral structures are represented in figure 3.

Diamagnetic Ni(II) complexes **6** and **7** indicate square planar geometry, while **16** and **17** have magnetic moment values of 3.3 B.M. which could be attributed to high spin octahedral Ni(II) [26, 27]. The spectrum of **6** and **7** exhibit a band at 400 nm attributed to $^1A_{1g} \rightarrow {}^1B_{1g}$ [28], indicating square planar geometry. **16** and **17** show broad and strong bands at 365 nm corresponding to $^3A_{2g}$ (F) $\rightarrow {}^3T_{1g}$ (P) in approximately octahedral field [27].

The copper complexes **8**, **9**, **18** and **19** exhibit magnetic moment values close to the spin only value at 2.07 B.M. The electronic spectra of **8** and **9** exhibit a symmetric d-d band with a maximum at 569 nm usually found in square-planar Cu(II) complexes (assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$) [29]. The spectra of **18** and **19** show bands at 362 nm assigned as charge transfer with the position supporting square planar geometry [29].

The ESR spectrum of Cu(II) complex **9** (see online supplementary material) exhibits g_{eff} 2.1154; the value of g_{eff} and the shape of the ESR signal suggests square-planar coordination [30].

The electronic spectra of complexes **10** and **20** exhibit a band at 27624 cm^{-1}; square planar geometry is suggested.

The molar conductance values of the complexes in DMF (10^{-3} M) range from 7.2–65.7 $Ohm^{-1}\,cm^2\,mole^{-1}$ suggesting non electrolytic nature of these complexes [31, 32]. The higher observed value of **14** (149 $Ohm^{-1}\,cm^2\,mole^{-1}$) indicates a monocation [33], in agreement with IR studies.

3.2.3. Thermogravimetric analysis. Thermal studies of **1**, **3**, **4**, **5**, **11**, **12**, **15** and **16** were carried out using TGA and DTA techniques. The TGA-curves of the divalent metal ions complexes $[ML \cdot nH_2O] \cdot mH_2O$ show a first step at 50–300°C corresponding to loss of lattice and coordinated water (table 4). The second step due to decomposition of the complex and formation of metal oxides or carbonates occurs

Table 4. Thermogravimetric analysis data of some metal complexes.

	Water weight loss %				Metal oxide residual %	
Chelates	Calc.	Found	No. of water molecules	Temp. (°C)	Calc.	Found
$[Cr(La) \cdot Cl \cdot H_2O] \cdot 6H_2O$	17.90	18.12	7	250	21.58	21.00
$[Co_a(La) \cdot 2H_2O] \cdot 6H_2O$	20.78	22.00	8	300	10.80	11.00
$[Co_p(La) \cdot 2H_2O] \cdot 7H_2O$	22.80	23.40	9	300	10.53	11.12
$[Cr(Lb) \cdot OH \cdot H_2O] \cdot 4H_2O$	13.57	12.00	5	300	42.80*	43.12*
$[Fe(Lb) \cdot OH \cdot H_2O] \cdot H_2O$	5.87	5.34	2	288	47.55*	47.50*
$[Co_c(Lb) \cdot 2H_2O] \cdot 5H_2O$	18.29	17.93	7	275	10.80	10.81
$[Ni_p(Lb) \cdot 2H_2O] \cdot 3H_2O$	13.78	12.87	5	300	18.17*	17.60*

* = Metal carbonate residual %.

at temperatures greater than 500°C. The thermal decomposition is suggested to proceed as follows:

$$[ML \cdot nH_2O] \cdot mH_2O \xrightarrow{25-300^\circ C} [ML]$$

$$[ML] \xrightarrow{\text{up to } 400^\circ C} \text{Intermediate (Unstable)}$$

$$\text{Intermediate} \xrightarrow{>500^\circ C} \text{Metallic residue}$$

Thermal decomposition of the trivalent metal complexes $[ML \cdot X \cdot nH_2O] \cdot mH_2O$ proceed by similar steps. All DTA curves display two peaks, the first endothermic peak below 300°C representing elimination of lattice and coordinated water and the second exothermic peak at temperatures above 300°C representing decomposition of the complexes.

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