

Chromium and Molybdenum Carbonyl Derivatives of N₂O₂ Schiff Base and 2(2'-Pyridyl) Benzimidazole

Ramadan M. Ramadan¹, Omyma A. M. Ali^{2*}, Abeer S. S. Sayed³

¹Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt

²Chemistry Department, Faculty of Women, Ain Shams University, Cairo, Egypt

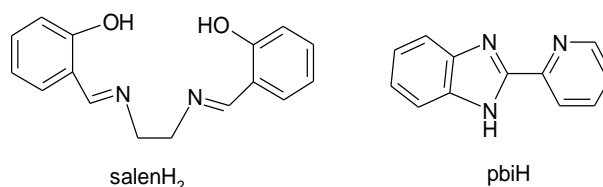
***Corresponding Author:** Omyma A. M. Ali, Chemistry Department, Faculty of Women, Ain Shams University, Cairo, Egypt

Abstract: Reactions of $M(\text{CO})_6$ ($M=\text{Cr}$ or Mo) with bis-(salicylaldehyde) ethylendiimine (salenH_2) Schiff base in the presence of 2(2'-pyridyl) benzimidazole (PbiH) in THF gave different complexes depending on the reaction conditions. Under reduced pressure, the binuclear complexes $\text{Cr}_2(\text{CO})_4(\text{salen})(\text{PbiH})$ and $\text{Mo}_2(\text{CO})_4(\text{salenH}_2)(\text{PbiH})$ were isolated. In air, the corresponding reactions gave the two complexes $\text{Cr}(\text{salenH}_2)(\text{pbiH})$ and $\text{Mo}_2(\text{CO})_4(\text{salen})(\text{PbiH})$. All complexes were characterized by elemental analysis as well as IR, UV-vis. and NMR spectroscopy. The thermal stabilities of some complexes were also investigated using the TG technique. The thermo gravimetric parameters E^* , H^* , S^* and G^* were also estimated from the DTG curves.

Keywords: Metal carbonyls; Schiff bases; Complexes; Spectra.

1. INTRODUCTION

The chemistry of Schiff bases is an area of increasing interest. Importance of these bases and their metal complexes is retained to their applications in biological, analytical and industrial fields as well as to their roles in catalysis and organic synthesis [1–9]. On the other hand, transition metal complexes having oxygen and nitrogen donor Schiff bases mostly possess unusual configuration, structural lability and are sensitive to molecular environment [10]. For example, the environment around the metal centre (such as coordination geometry, number of coordinated ligands and their donor groups) is the key factor for metalloproteins to carry out specific physiological functions [11]. The design and synthesis of symmetrical Schiff bases have been of interest due to their preparative accessibility, structural variability and tunable electronic properties allowing carrying out systematic reactivity studies based on ancillary ligand modifications [12]. Moreover, Schiff base ligands that are able to form binuclear transition metal complexes are useful to study the relation between structures and magnetic exchange interactions [13,14]. In addition, transition metal complexes with tetradentate Schiff bases have been extensively investigated as catalysts for a number of organic redox reactions and electrochemical reduction processes [15–17]. The chemistry of metal complexes containing salen-type (N₂O₂) Schiff base ligands derived from condensation of aldehydes and diamines are of enduring significance. These complexes have been used as synthetic oxygen carriers [18], catalysts for the asymmetric epoxidation [19–24] and the synthesis of optical and magnetic materials [25,26]. Salen complexes have also been recently used as catalytically active materials to develop surface-modified electrodes for sensing applications [27,28]. On the other hand, transition metal complexes with 2-substituted benzimidazole ligands are progressively used to model important bioinorganic systems [29,30] and act as cytotoxic [31], antiviral [32] and antiamebic [33] agents. Our interest in investigation of the reactions of metal carbonyls with Schiff bases [34–39] has prompted us to investigate the reactions of $M(\text{CO})_6$ ($M=\text{Cr}$ or Mo) with bis-(salicylaldehyde) ethylendiimine (salenH_2) in presence of 2(2'-pyridyl) benzimidazole (PbiH) (Scheme 1).



Scheme1. Structure of ligands

2. EXPERIMENTAL

2.1. Reagents

The hexacarbonyls of chromium and molybdenum were supplied by Aldrich. 2-(2-pyridyl) benzimidazole was purchased from British Drug House (BDH). Bis-(2-salicylaldehyde) ethylene diimine (salenH₂) was prepared as described in literature [40]. All solvents were purified by distillation before use.

2.2. Instruments

Infrared measurements were carried out on a Unicam-Mattson 1000 FT-IR spectrometer using KBr pellets. Nuclear magnetic resonance measurements were performed on a Varian Mercury 300 MHz NMR spectrometer. The samples were dissolved in DMSO, d₆ and tetramethylsilane (TMS) was used as an internal reference. Magnetic susceptibility measurements of the paramagnetic complexes in the solid state (Gouy method) were performed on a Sherwood Scientific Magnetic Susceptibility Balance. UV-vis spectra were measured on a Unicam UV2-300 spectrophotometer. Measurements of the thermo gravimetric analysis (TG) were carried out under nitrogen atmosphere with a heating rate of 10 °C/min. using a Shimadzu DT-50 thermal analyzer. The complexes were also characterized by elemental analysis (Perkin–Elmer 2400 CHN elemental analyzer) and mass spectroscopy (Finnigan MAT SSQ 7000). Table 1 gives the elemental analysis and mass spectrometry data for the complexes.

Table 1. Elemental analysis and mass spectrometry for the complexes

Complexes	Found (Calcd.) (%)			Mass spectrometry	
	C	H	N	Molecular weight	m/z
Cr(salenH ₂)(pbiH)	65.50 (65.24)	4.60 (4.88)	13.75 (13.58)	515.5	516 [P] ⁺
Cr ₂ (CO) ₄ (salen)(pbiH)	56.50 (56.73)	3.40 (3.42)	10.40 (10.34)	677.5	622 [P-2CO] ⁺
Mo ₂ (CO) ₄ (salenH ₂)(pbiH)	49.80 (50.00)	3.40 (3.54)	8.59 (8.57)	767.4	712 [P-2CO] ⁺
Mo ₂ (CO) ₄ (salen)(pbiH)	50.50 (50.22)	3.20 (3.03)	9.30 (9.15)	765.4	738 [P-CO] ⁺

2.3. Synthesis of Complexes

2.3.1. Synthesis of Cr (SalenH₂) (PbiH) Complex

A mixture of Cr (CO)₆ (0.15 g; 0.68 mmol), salenH₂ (0.18 g; 0.68 mmol) and pbiH (0.13 g; 0.68 mmol) in about 30 ml THF was heated to reflux in air for about 16h. The color of the reaction mixture changed from yellow to light brown. The reaction mixture was then cooled and the solvent was evaporated. The obtained residue was washed several times by hot petroleum ether and then recrystallized from hot THF to give light brown complex. The complex was left to dry in vacuo for several hours (yield 44%).

2.3.2. Synthesis of Cr₂(CO)₄(Salen)(Pbih) and Mo₂(CO)₄(SalenH₂)(Pbih) Complexes

Equal molar amounts of M(CO)₆, M = Cr or Mo, salenH₂ and pbiH were mixed together in about 30 ml THF. The reaction mixture was then degassed and then heated to reflux under the reduced pressure for about 3h. After the end of the reaction, the mixture was treated as described in the synthesis of Cr (salenH₂)(pbiH) complex. A brown solid was obtained for Cr₂(CO)₄(salen)(Pbih) with a yield of 90% and a dark-brown solid for Mo₂(CO)₄(salenH₂)(Pbih) with 36% yield.

2.3.3. Synthesis of Mo₂(CO)₄(Salen)(Pbih) Complex

A similar procedure was employed as in the synthesis of Cr₂(CO)₄(salen)(Pbih) complex. A brown solid complex was isolated with a yield of 81%.

2.3.4. Determination of the Decomposition Reaction Order

The decomposition reaction order of the synthesized chromium and molybdenum complexes were calculated from their DTG plots. The weight fraction of the substance present at the DTG peak (C_s) was determined from the following relation:

$$C_s = (W_s - W_f) / (W_i - W_f) \quad (1)$$

where W_s is the weight remaining at T_s (the temperature of DTG peak), W_i and W_f are the initial and final weights of the substance. The order of the decomposition reaction (n) was calculated from the Horowitz-Metzger equation [41]:

$$C_s = (n)^{1/1-n} \quad (2)$$

Calculation of Kinetic and Thermodynamic Parameters

2.3.5. Integral Method Using the Coats-Redfern Equation

For a first order process, the Coats-Redfern (CR) equation [42] may be written in the form:

$$\log \left[\frac{\log(W_\infty / (W_\infty - W))}{T^2} \right] = \log \left[\frac{AR}{\phi E^*} \left(1 - \frac{2RT}{E^*} \right) \right] - \frac{E^*}{2.303RT} \quad (3)$$

where W_∞ is the mass loss at the completion of the decomposition reaction, W is the mass loss up to temperature T , R is the gas constant, E^* is the activation energy in J mol^{-1} and ϕ is the heating rate. Since $1 - (2RT/E^*) \cong 1$, the plot of the left-hand side of equation (3) against $1/T$ would give a straight line. Then, E^* could be calculated using the slope, and the Arrhenius constant, A , was obtained from the intercept.

2.3.6. Approximation Method using Horowitz-Metzger Equation

For the first order kinetic process, the Horowitz-Metzger (HM) equation [41] may be written in the form:

$$\log [W_\infty/W_r] = \theta E^* / 2.303 RT_s^2 \quad (4)$$

where T_s is the temperature of DTG peak and $\theta = T - T_s$. A plot of $\log[\log W_\infty/W_r]$ vs. θ will give a straight line and E^* can be calculated from the slope. The pre-exponential factor C was calculated from the following equation [41, 42]:

$$C = (\theta E^* / RT_s^2) \exp(E^* / RT_s) \quad (5)$$

The activation entropy S^* , the activation enthalpy H^* and the free energy of activation G^* were calculated using the following equations:

$$S^* = 2.303 (\log Ah / KT) R \quad (6)$$

$$H^* = E^* - RT \quad (7)$$

$$G^* = H^* - T_s S^* \quad (8)$$

where K and h are Boltzmann and Planck constants, respectively.

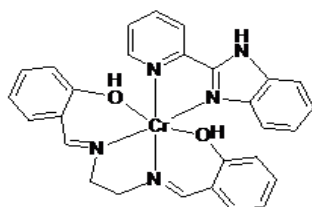
3. RESULTS AND DISCUSSION

Reaction of bis-(salicylaldehyde) ethylenediimine (salenH₂) with $M(\text{CO})_6$ ($M = \text{Cr}$ and Mo) in presence of 2(2'-pyridyl) benzimidazole (pbiH) resulted in the formation of four complexes depending on the reaction condition. Under reduced pressure, the two tetra carbonyl derivatives $\text{Cr}_2(\text{CO})_4(\text{salen})(\text{pbiH})$ and $\text{Mo}_2(\text{CO})_4(\text{salenH}_2)(\text{pbiH})$ were isolated. In air, the corresponding reaction with $\text{Cr}(\text{CO})_6$ gave the mononuclear complex $\text{Cr}(\text{salenH}_2)(\text{pbiH})$, while the reaction with $\text{Mo}(\text{CO})_6$ gave the binuclear $\text{Mo}_2(\text{CO})_4(\text{salen})(\text{pbiH})$ complex. The IR spectrum of salenH₂ showed characteristic bands corresponding to $\nu(\text{OH})$, $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{O})$ stretching's (Table 2). Interestingly, two $\nu(\text{C}=\text{N})$ were appearing in the spectrum which could be due to the presence of partial hydrogen bonding between the azomethine nitrogen and the hydrogen of the hydroxyl group. The IR spectrum of pbiH also exhibited characteristic bands due to the $\text{C}=\text{N}$ and NH groups (Table 2). On complexation, the bands due to $\nu(\text{C}=\text{N})$ stretching's of both salenH₂ and pbiH species were shifted to lower frequencies indicating the coordination of the nitrogen of these groups to the metal [43,44]. Also, the $\text{C}-\text{O}$ stretching band of the free salenH₂ was shifted to a higher frequency range indicating coordination through the phenolic oxygen. The coordination to nitrogen and oxygen donors was further supported by the appearance of two new bands at 470-543 and 406-434 cm^{-1} due to $\nu_{\text{M}-\text{O}}$ and $\nu_{\text{M}-\text{N}}$, respectively. In addition, the in-plane ring deformation bands of the pyridine moiety of pbiH were shifted to higher frequencies in all complexes due to coordination of the pyridyl nitrogen [45]. Also, the infrared spectrum of $\text{Cr}(\text{salenH}_2)(\text{pbiH})$ complex showed a broad band at 3413 cm^{-1} due to stretching OH frequency. The shift in the OH band relative to that of the free salenH₂ ligand was further indication for the participation of the OH in bonding [37]. The ¹H NMR spectrum of the complex displayed two signals at 13.06 and 13.35 ppm indicating the presence of both NH and OH groups of ligands (Table 3).

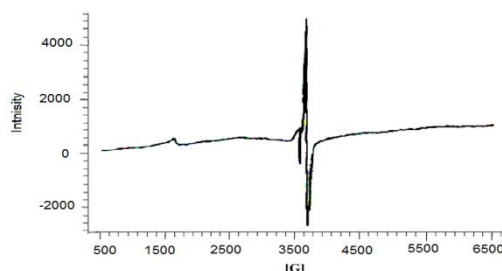
Table2. Important IR data for salenH₂, pbiH and their complexes.

Compound	IR data (cm ⁻¹)							
	$\nu(\text{OH})$	$\nu(\text{N-H})$	$\nu(\text{CO})$	$\nu(\text{C=N})$	$\nu(\text{C-O})$	$\delta(\text{py})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
salenH ₂	3425(b)		-	1634(s) 1577(m)	1285(s)		-	-
pbiH	-	3055(s)	-	1594(m) 1566(w)	-	616(m) 542(m) 500(w)	-	-
Cr(salenH ₂)(pbiH)	3413(b)	3056(m)	-	1630(s) 1535(w)	1315(m) 1280(m)	649(w) 615(w) 570(w)	543(w)	434(w)
Cr ₂ (CO) ₄ (salen)(pbiH)	-	3056(w)	2009(m) 1895(s) 1817(s) 1800(sh)	1631(w) 1537(w)	1320(w) 1281(m)	646(m) 592(m) 555(m)	470(w)	430(w)
Mo ₂ (CO) ₄ (salenH ₂)(pbiH)	3416(b)	3056(w)	2014(m) 1898(s) 1868(sh) 1786(s)	1620(m)	1316(w) 1285(w)	621(w) 607(w) 560(w)	470(w)	430(w)
Mo ₂ (CO) ₄ (salen)(pbiH)	-	3057(w)	2003(s) 1889(s) 1816(s) 1750(m)	1617(vs) 1528(m)	1311(sh) 1277(m)	633(w) 612(m) 527(w)	450(w)	406(w)

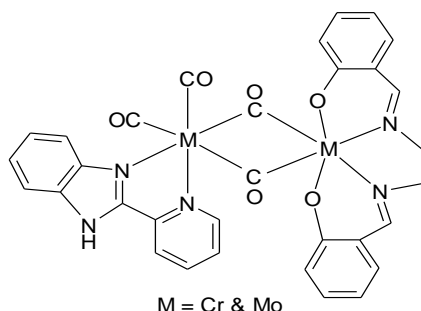
According to the elemental and spectroscopic data, a proposed structure for the chromium complex with zero oxidation state (d⁶ electronic configuration) is given in Scheme 2.

**Scheme2.** Structure of Cr (salenH₂) (pbiH) complex

The IR spectra of the two complexes Cr₂(CO)₄(salen)(pbiH) and Mo₂(CO)₄(salen)(pbiH) showed the disappearance of the OH bands of the salenH₂ moiety indicating that the ligand coordinated to the metal oxidatively with the displacement of the OH protons [46,47]. In addition, the IR spectra exhibited two CO bands due to asymmetric and symmetric stretching frequencies in the terminal metal carbonyl region. Furthermore, the spectra of complexes displayed two bands in the range 1816-1817 and 1750-1800 cm⁻¹ due to bridging carbonyl groups [44]. The appearance of the bands of the bridged CO groups at higher values than normal could be retained to their existence trans to nitrogen atoms of both two ligands which would consequently increase the bond order of the CO bond. The magnetic studies of the chromium and molybdenum complexes showed paramagnetic characteristics. Magnetic measurements at 298 K gave effective magnetic (μ_{eff}) values of 3.01 and 2.93 BM, respectively. These values are close to the spin-only moment of two unpaired electrons (2.84 BM). The ESR spectrum of [Cr₂(CO)₄(salen)(PbiH)] complex (**Fig. 1**) exhibited two sharp signals with relative intensity 2:1 at $\langle g \rangle$ value of 2.0035 and 1.9645. The smaller signal could be assigned for salen moiety and the other signal was due to the two unpaired electrons located on the Cr atom. No hyperfine structure was observed in the spectrum indicating that there was no magnetic interaction of the paramagnetic centers with the surrounded nuclei.

**Figure1.** The ESR spectrum of [Cr₂(CO)₄(salen)(PbiH)] complex

According to the spectroscopic data, the two complexes may have two different atomic species, one with zero valent bound to the pbiH ligand and the other has +2 oxidation state which bound to the salen moiety. As the magnetic measurements showed μ_{eff} of two unpaired electrons, it may indicate that the +2 metal species existed in low spin electronic configuration with the further splitting of the t_{2g} orbitals, i.e., the electronic structure would be $d_{xy}^2, d_{xz}^1, d_{yz}^1, e_g^0$. Scheme 3 gives the proposed structure of the two complexes.



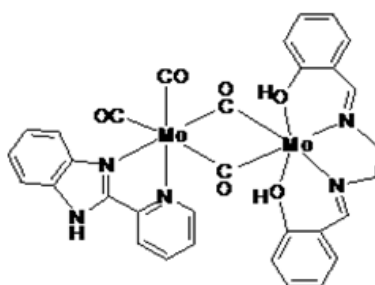
Scheme3. Structure of the $\text{Cr}_2(\text{CO})_4(\text{salen})(\text{pbiH})$ and $\text{Mo}_2(\text{CO})_4(\text{salen})(\text{pbiH})$ complexes

Table3. Important ^1H NMR data for salenH₂, pbiH and their complexes

Compound	^1H NMR (ppm)
salenH ₂	2.50(t, CH ₂), 6.84-7.42(m, Ph), 8.59(s, CH), 13.32(s, OH)
pbiH	7.22(m, Ph), 7.66(m, Ph), 8.32(d, Ph), 8.72(d, Ph), 13.06(s, NH)
Cr(salenH ₂)(pbiH)	2.49(t, CH ₂), 6.86-8.33(m, Ph), 8.58(s, CH), 13.06(s, NH), 13.35(s, OH)
Mo ₂ (CO) ₄ (salenH ₂)(pbiH)	2.50(t, CH ₂), 8.58(s, CH), 7.2-8.43(m, Ph), 13.07(s, NH), 13.36(s, OH)

s, singlet; d, doublet; t, triplet; m, multiplet.

Under reduced pressure, interaction of Mo(CO)₆ with salenH₂ in presence of PbiH gave the tetracarbonyl derivative Mo₂(CO)₄(salenH₂)(pbiH). The IR spectrum of the complex showed two bands in the terminal metal carbonyl region due to two CO groups. Also, the spectrum showed two CO stretching frequencies in the bridged metal carbonyl range (Table 2) [44]. In addition, the complex exhibited characteristic bands due to the OH and NH groups of the ligands with the corresponding shifts. Furthermore, the ^1H NMR spectrum of the complex displayed a signal at 13.36 ppm indicating the presence of OH groups of salenH₂ part (Table 3). The signal showed lower field shift and indicated that the ligand coordinated to the molybdenum atom through the OH groups. Also, the diamagnetism characteristics of the binuclear complex suggested the existence of molybdenum in zero oxidation state with low spin d⁶ electronic structure, Scheme 4.



Scheme4. Structure of the $\text{Mo}_2(\text{CO})_4(\text{salenH}_2)(\text{pbiH})$ complex

3.1. Electronic Absorption Spectra

The electronic absorption spectra of salenH₂, pbiH and its complexes were investigated in DMF. Two absorption bands were observed for the free ligands (salenH₂ and pbiH) due to $\pi-\pi^*$ and $n-\pi^*$ transitions (Table 4). These two transitions were shifted in the spectra of all complexes with appropriate shifts. The UV-vis spectra of complexes showed a band at 300-306 nm due to $\pi-\pi^*$ transition and a band at 310-323 nm with a shoulder at 332-360 nm corresponding to the $n-\pi^*$ transition. In addition, the two complexes Cr₂(CO)₄(salen)(pbiH) and Mo₂(CO)₄(salenH₂)(PbiH) displayed a new absorption band around 510 nm which may be assigned as metal-to-ligand charge transfer transition.

Table4. The UV-vis. data for salenH₂, PbiH and their complexes

Compound	λ_{\max} (nm)
salenH ₂	265, 314
pbiH	298, 324
Cr(salenH ₂)(pbiH)	301, 322, 360(sh)
Cr ₂ (CO) ₄ (salen)(pbiH)	300, 322, 360(sh), 511(b)
Mo ₂ (CO) ₄ (salenH ₂)(pbiH)	303, 310, 332(sh), 512(b)
Mo ₂ (CO) ₄ (salen)(pbiH)	306, 323, 338(sh)

sh, shoulder; b, broad.

3.2. Thermo gravimetric Analysis

In order to give more insight into the structure of the complexes, the thermal studies of some complexes were carried out using the thermo gravimetric (TG) technique. The TG plot of [Cr(salenH₂)(PbiH)] showed one resolved peak in the range 349.62-709.7 K with a loss of 83.45%. This percentage loss could be attributed to the loss of PbiH+C₁₆H₁₆N₂ species leaving CrO₂ as metallic residue (Table 5). The complex [Cr₂(CO)₄(salen)(PbiH)] was decomposed in two unresolved and one resolved steps. The first two unresolved peaks were found in the range 337.76-497.6 K and 497.6-647.8 K, respectively. The third decomposition peak was found at the temperature range 927.7-1237.7 K with loss of 46.09%. This percentage loss could be probably due to elimination of PbiH+C₉H₉ species to give finally the residue 2CrO (Table 5). The TG plot of the [Mo₂(CO)₄(salen)(PbiH)] displayed four decomposition steps in the temperature range 424.9-1254.1 K. The mass losses for the four decomposition steps with the corresponding mass losses and the suggested species eliminated are tabulated in Table 5.

Table5. Thermal analysis data for the complexes.

Molecular formula	Molecular weight	Decomposition temperature (K)	% Weight loss		Eliminated species	% Solid residue (found)
			Found	Calculated		
Cr(C ₁₆ H ₁₆ N ₂ O ₂)(C ₁₂ H ₉ N ₃)	515.5	349.62-709.7	83.45	83.70	PbiH+C ₁₆ H ₁₆ N ₂	CrO ₂ (16.55)
Cr ₂ (CO) ₄ (C ₁₆ H ₁₄ N ₂ O ₂)(C ₁₂ H ₉ N ₃)	677.5	337.76-497.6	16.35	16.52	4CO	2CrO (20.46)
		497.6-647.8	17.10	17.29	C ₇ H ₅ N ₂	
		927.7-1237.7	46.09	46.11	PbiH + C ₉ H ₉	
Mo ₂ (CO) ₄ (C ₁₆ H ₁₄ N ₂ O ₂)(C ₁₂ H ₉ N ₃)	765.4	424.9-624.8	14.36	14.63	4CO	2MoO (38.12)
		624.9-914.9	20.25	20.54	C ₁₀ H ₉ N ₂	
		914.9-1114.4	18.43	18.70	C ₉ H ₇ N ₂	
		1114.4-1254.1	16.44	16.87	C ₉ H ₇ N	

3.3. Kinetics Of Thermal Decomposition

The thermodynamic activation parameters of decomposition processes of complexes namely activation energy E*, enthalpy H*, entropy S* and Gibbs free energy change of the decomposition G* were evaluated graphically by employing the Coats-Redfern relation method [42] and Horowitz-Metzger relation method [41] (Table 6). According to the kinetic data obtained from DTG curves, the C_s for the decomposition steps agreed with first order kinetics [48, 49]. Also, all the complexes have -ve entropy, which indicates that activated complexes have more ordered systems than reactants [50, 51]. From Table 6, it is obvious that, the molybdenum complex was found to be more stable than chromium complexes based on the sum of the activation energies of the different decomposition steps. The order of thermal stability was found to be [Mo₂(CO)₄(salen)(PbiH)] > [Cr₂(CO)₄(salen)(PbiH)] > [Cr(salenH₂)(PbiH)]. Similar trend was found for the complexes of chromium and molybdenum with salicylidene-2-aminophenol, salicylidene-2-aminoanisole, salicylidene-2-aminoaniline and biquionline [52]. On the other hand, the carbonyl groups in the complexes [M(CO)₄(salen)(PbiH)] are more easily lost on heating.

Table6. The thermodynamic data of the thermal decompositions of Cr(salenH₂)(pbiH) and Cr₂(CO)₄(salen)(pbiH)

Complex	Decomposition Temperature/K	Ts	Method	E*/kJmol ⁻¹	R ²	A*/s ⁻¹	S*/kJmol ⁻¹	H*/kJmol ⁻¹	G*/kJmol ⁻¹	Cs
Cr(salenH ₂)(pbiH)	349.62-709.7	539.9	CR	52.06	0.995	1.21×10 ⁴	-171.75	47.56	140.29	0.30
			HM	80.12	0.994	1.87×10 ⁷	-110.66	75.64	135.38	

Cr ₂ (CO) ₄ (salen)(pbiH)	337.76-497.6	467.9	CR	1025	0.998	2.22	-	6.36	119.62	0.30
			HM	36.08	0.995	2.11×10 ³	-	32.19	118.77	
	497.6-647.8	557.5	CR	14.62	0.997	0.73	-	9.98	150.91	0.37
			HM	23.17	0.999	13.30	-	18.54	146.00	
	927.7-1237.7	987.8	CR	32.54	0.991	0.83	-	24.32	277.66	0.33
			HM	42.39	0.994	9.12	-	34.18	267.83	
Mo ₂ (CO) ₄ (salen)(pbiH)	424.9-624.8	484.8	CR	17.71	0.998	1.21	-	13.68	133.62	0.30
			HM	23.09	0.993	0.133	-	19.06	147.89	
	624.8-914.9	654.6	CR	17.06	0.993	0.27	-	11.61	183.43	0.29
			HM	22.11	0.999	3.61	-	16.67	195.77	
	914.9-1114.4	1024.5	CR	30.55	0.962	0.93	-	22.03	284.14	0.31
			HM	49.06	0.991	17.82	-	40.54	325.51	
	1114.4-1254.1	1194.3	CR	70.42	0.962	82.18	-	60.48	323.03	0.28
			HM	90.18	0.981	6.68×10 ²	-	80.25	410.97	

Table 7. The thermodynamic data of the thermal decompositions of Mo₂(CO)₄(salen)(pbiH)

Complex	Decomposition Temperature/K	Ts	Method	E*/kJ mol ⁻¹	R ²	A*/s ⁻¹	S*/K ⁻¹ Jm ^{ol} ⁻¹	H*/kJ mol ⁻¹	G*/kJ mol ⁻¹	Cs
Mo ₂ (CO) ₄ (salen)(pbiH)	424.9-624.8	484.8	CR	17.71	0.998	1.21	-	13.68	133.62	0.30
			HM	23.09	0.993	0.133	-	19.06	147.89	
	624.8-914.9	654.6	CR	17.06	0.993	0.27	-	11.61	183.43	0.29
			HM	22.11	0.999	3.61	-	16.67	195.77	
	914.9-1114.4	1024.5	CR	30.55	0.962	0.93	-	22.03	284.14	0.31
			HM	49.06	0.991	17.82	-	40.54	325.51	
	1114.4-1254.1	1194.3	CR	70.42	0.962	82.18	-	60.48	323.03	0.28
			HM	90.18	0.981	6.68×10 ²	-	80.25	410.97	

4. CONCLUSION

The tetra carbonyl complexes Cr₂(CO)₄(salen)(PbiH) and Mo₂(CO)₄(salenH₂)(PbiH) have been synthesized from the reactions of M(CO)₆ (M=Cr or Mo) with salenH₂ Schiff base in presence of PbiH under reduced pressure. IR spectroscopy revealed the presence of terminal and bridge M-CO bonds. The same synthetic procedure gives the two complexes Cr(salenH₂)(pbiH) and

Mo₂(CO)₄(salen)(PbiH) in air. Magnetic studies showed that the two complexes Cr(salenH₂)(pbiH) and Mo₂(CO)₄(salenH₂)(PbiH) were diamagnetic. The activation thermodynamic Parameters E*, H*, S* and G* are calculated from the TG curves.

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