

# Spectroscopic, Structural Studies, Fluorescence and Optical Properties of Group VI Dinuclear Derivatives of N<sub>2</sub>O<sub>2</sub> Schiff Base

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**Abstract:** Reaction of  $M(CO)_6$  ( $M = Cr, Mo$  and  $W$ ) with 6, 6'([1,1'biphenyl]4, 4'diylbis (azaneylylidene)) bis (methaneylylidene)) bis(2,4-dichlorophenol)  $H_2L$  in THF were investigated. Under Sunlight irradiation, dinuclear carbonyl chromium complex  $[Cr_2(CO)_2L_2]$  and two dinuclear oxo complexes  $[Mo_2O_4L_2]$  and  $[W_2O_4L_2]$  were isolated. In air, the corresponding reaction with  $Mo(CO)_6$  produced the dinuclear carbonyl oxo complex  $[Mo_2O_5(CO)L]$ .  $H_2O$ . All complexes were characterized by elemental analysis, IR, mass and  $^1H$  NMR spectroscopy. Magnetic studies for  $[Mo_2O_4L_2]$ ,  $[W_2O_4L_2]$  and  $[Mo_2O_5(CO)L]$ .  $H_2O$  complexes showed diamagnetic characteristics. TG-DTG study was done to track the thermal behavior of the complexes and the thermodynamic parameters were computed from the thermal data using Coats-Redfern and Horowitz-Metzger methods. The ultraviolet-vis spectra of the complexes in DMSO showed broad bands due to ligand-to-metal charge transfer. The fluorescence spectra of these complexes indicate the luminescence characteristics of the complexes. The values of optical band gap energy ( $E_g$ ) of the synthesized complexes suggested that these compounds could be used as semiconductors.

**Keywords:** Benzidine; Carbonyl; Complexes; Fluorescence; Optical Properties

## 1. INTRODUCTION

Schiff bases metal complexes containing nitrogen and oxygen donor atoms play an important role in an enormous number of publications, ranging from pure synthetic work to physicochemical [1] and biochemically relevant studies of metal complexes [2]. They also use as photo-sensitizers, catalysts and conducting coordinating polymers [3,4,5] and found wide range of applications [6,7]. On the other hand, carbonyl complexes are useful intermediates in the synthesis of important coordination compounds [8,9,10]. In addition, metal carbonyl complexes are of considerable structural interest as well as of industrial, catalytical importance, epoxidation reactions, catalytic activity in hydrogenation of olefines and photochromic properties [11,12]. Schiff bases containing nitrogen and oxygen donor atoms such as bis-(salicylaldehyde)ethylenediimine (salenH<sub>2</sub>), bis (salicylaldehyde) phenylenediimine (salphenH<sub>2</sub>), salicylideneimine-2-anisole (salanH), N-salicylidene-2-hydroxyaniline (shaH<sub>2</sub>), 2,4-dichloro-5-Fluorophenyl and derivatives of benzimidazole, thiazole, pyridine, pyrazolone, hydrazine, p-fluorobezaldehyde are useful for the synthesis of transition metal complexes which play important role in biological systems [13,14,15,16,17,18].

Our interest in investigation of the reactions of metal carbonyls with Schiff bases has prompted us to investigate the reactions of  $M(CO)_6$  ( $M=Cr, Mo$  and  $W$ ) with Schiff base ( $H_2L$ ) derived from 3,5-dichlorosalicylaldehyde and benzidine.

## 2. EXPERIMENTAL

### 2.1. Materials

$M(CO)_6$ ,  $M=Cr, Mo$  and  $W$ ; 3,5-Dichlorosalicylaldehyde and benzidine were supplied from Aldrich. All the chemicals were of analytical reagent grade and used without purification

### 2.2. Instrumentation

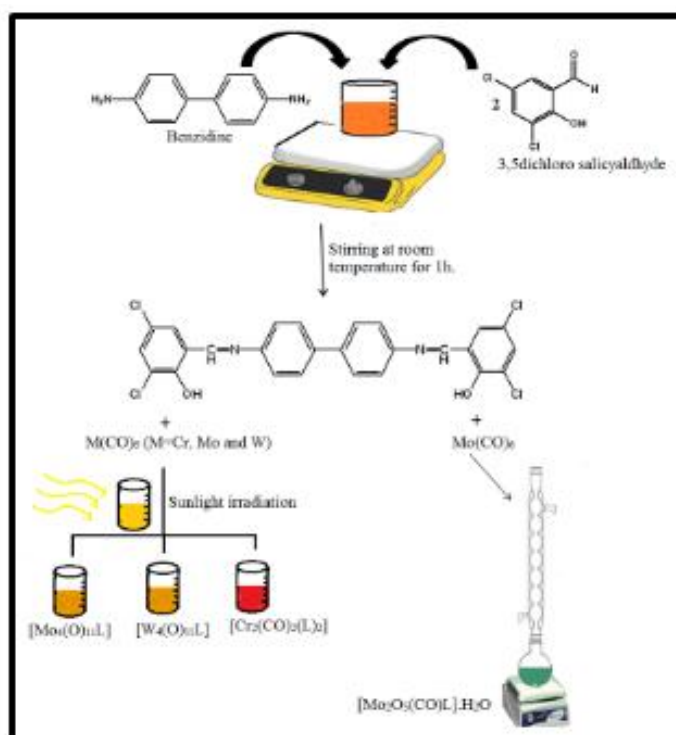
Carbon, hydrogen and nitrogen (C, H & N) analyses were carried out on a Perkin- Elmer 2400 mode instrument. IR spectra were recorded using KBr pellets in the region 4000-400  $cm^{-1}$  on FTIR spectrophotometer, Shimadzu 8201. The  $^1H$  NMR spectra was recorded by using DMSO as a solvent

and a BRUKER 500 MHz spectrophotometer using TMS as an internal reference. Mass spectrometry measurements of the solid ligand and its complexes were measured on a JEOL JMS-AX 500 spectrometer. The TG and DTG analysis were recorded with a heating rate of 10 °C/min under a nitrogen atmosphere using a Shimadzu DT-50 thermal analyzer. The ligand and its complexes spectra were measured on a Shimadzu 3101 pc spectrophotometer. The photoluminescent properties of all the compounds were studied using a LS50B Jenway 6270 Fluorimeter.

### 2.3. Synthesis of the Schiff base 6,6'-((1,1'-biphenyl)-4,4'-diylbis(azaneylylidene))bis(methaneylylidene))bis(2,4-dichlorophenol) (H<sub>2</sub>L)

Schiff base ligand (H<sub>2</sub>L) was prepared by dissolving 0.38 g (2 mmol) of 3,5-di-chlorosalicylaldehyde and 0.18 g (1 mmol) of benzidine in methyl alcohol. This mixture was stirring at room temperature for 1h. Orange precipitate was formed, filtrated off and washed several times with methanol and then left to dry at room temperature (Scheme 1).

### 2.4. Synthesis of Complexes



Scheme1. Synthesis of the ligand and its Cr, Mo and W complexes

#### 2.4.1. Synthesis of [Cr<sub>2</sub>(CO)<sub>2</sub>L<sub>2</sub>], [Mo<sub>2</sub>O<sub>4</sub>L<sub>2</sub>] and [W<sub>2</sub>O<sub>4</sub>L<sub>2</sub>] Complexes

A mixture of [M(CO)<sub>6</sub>], M=Cr, Mo and W, and ligand in equimolar ratio in 30 ml THF was exposed to sunlight irradiation for 24 h. The solvent was evaporated and the precipitate was isolated. The precipitate washed several times by hot petroleum ether (Scheme 1).

#### 2.4.2. Synthesis of [Mo<sub>2</sub>O<sub>5</sub>(CO)L].H<sub>2</sub>O complex

A mixture of Mo(CO)<sub>6</sub> (0.17 g, 0.2 mmol) and ligand (0.05 g, 0.1 mmol) in 30 ml THF was heated to reflux in air for 6 h. The color of the mixture was changed from orange to dark green with the formation of the precipitate. The solvent was evaporated. The isolated precipitate was washed several times by hot petroleum ether (Scheme 1).

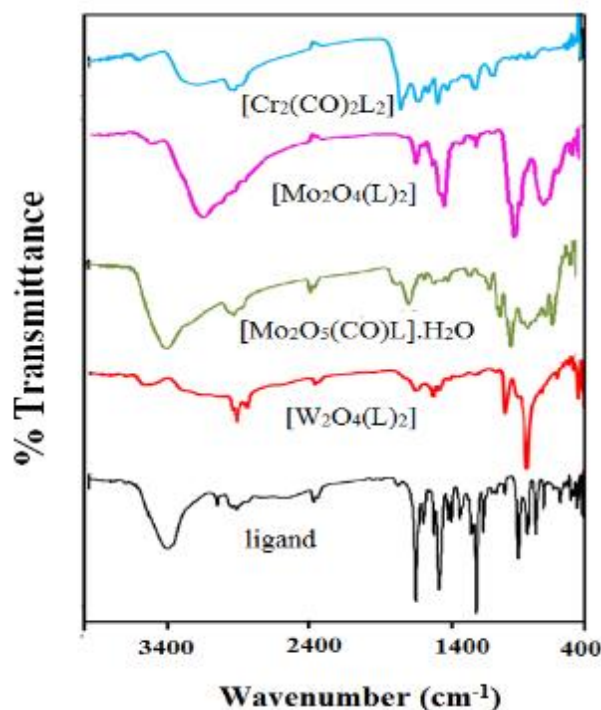
## 3. RESULTS AND DISCUSSION

Physicochemical, elemental analyses and mass spectrometry data of the prepared Cr, Mo and W solid complexes of the Schiff base (H<sub>2</sub>L) were summarized in Table 1. The data are in good agreement with the proposed structures of the complexes. The metal complexes were colored and stable towards air and moisture at room temperature. They were insoluble in common organic solvents (methanol, ethanol, acetone and chloroform), but soluble in dimethylformamide (DMF) and dimethylsulfoxide (DMSO).

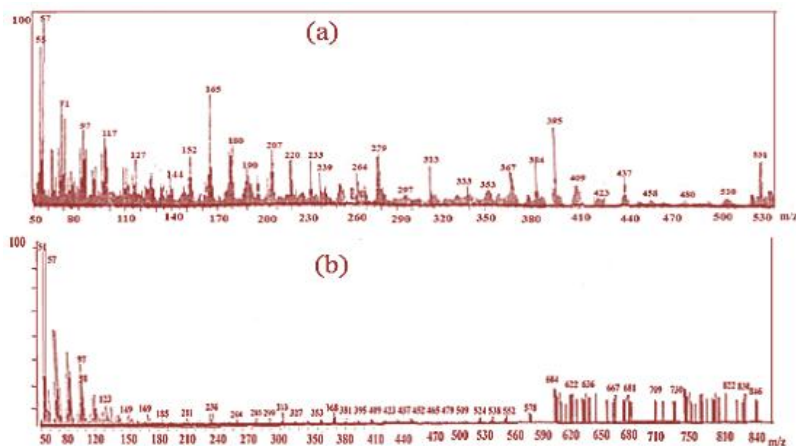
**Table1.** Physical properties and analytical data of the Schiff base ligand (H<sub>2</sub>L) and its metal carbonyl complexes.

Compound	Color	Yield %	M.P.	Elemental analysis Found (calc.)			Mass Spectrometry	
				C%	N%	H%	Mol.Wt.	m/z
H <sub>2</sub> L(C <sub>26</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> Cl <sub>4</sub> )	orange	87	260	58.96 (58.89)	5.39 (5.28)	3.12 (3.04)	530.21	531 (P <sup>+</sup> )
Cr <sub>2</sub> C <sub>54</sub> H <sub>28</sub> N <sub>4</sub> O <sub>6</sub> Cl <sub>8</sub>	red	46	>300	52.23 (52.32)	4.43 (4.60)	2.31 (2.32)	1216.41	1160 (P <sup>+</sup> - 2CO)
Mo <sub>2</sub> C <sub>52</sub> H <sub>28</sub> N <sub>4</sub> O <sub>8</sub> Cl <sub>8</sub>	brown	50	>300	47.76 (47.59)	4.67 (4.26)	2.21 (2.15)	1312.27	1312 (P <sup>+</sup> )
W <sub>2</sub> C <sub>52</sub> H <sub>28</sub> N <sub>4</sub> O <sub>8</sub> Cl <sub>8</sub>	brown	45	>300	41.71 (41.69)	3.82 (3.76)	1.86 (1.98)	1488.03	1488 (P <sup>+</sup> )
Mo <sub>2</sub> C <sub>27</sub> H <sub>16</sub> N <sub>2</sub> O <sub>9</sub> Cl <sub>4</sub>	Dark green	65	>300	38.84 (38.33)	3.21 (3.31)	1.89 (1.90)	846.01	846 (P <sup>+</sup> )

The significant infrared bands of the prepared Schiff base ligand and its metal complexes were summarized in Table 2& Figure 1. Infrared spectrum of the ligand showed a broad band at 3384 cm<sup>-1</sup> which can be attributed to phenolic OH group [19]. This band disappeared in all complexes, indicating the coordination of H<sub>2</sub>L oxidatively to metal with proton displacement. The free Schiff base ligand showed a strong band at 1615 cm<sup>-1</sup>, which was characteristic of the azomethine (-HC=N) group [20]. On complexation, this band was shifted to lower or higher frequencies indicating the coordination of the ligand to metal through azomethine nitrogen atoms [21,22]. Also, the C-O stretching band of the free H<sub>2</sub>L was shifted to a higher frequency range indicating coordination through the phenolic oxygen [23]. In the IR spectra of all complexes, the non-ligand bands observed in range from 574 to 590 cm<sup>-1</sup> due to M-O and from 473 to 493 cm<sup>-1</sup> for M-N bonds [24]. The IR spectrum of [Cr<sub>2</sub>(CO)<sub>2</sub>(L)<sub>2</sub>] complex showed strong band at 1718 cm<sup>-1</sup> due to bridging carbonyl group [25]. On the other hand, the IR spectrum of [Mo<sub>2</sub>O<sub>5</sub>(CO)L].H<sub>2</sub>O complex exhibited two bands at 1718 and 627 cm<sup>-1</sup> due to bridging carbonyl group and Mo-O-Mo bridged bond, respectively [26]. In addition, the IR spectrum of molybdenum complex displayed stretching vibrational band of hydrated water and symmetric and asymmetric stretching frequencies of terminal Mo=O bonds for a cis MO<sub>2</sub> fragment [27,28]. The IR spectra of the two oxo complexes [Mo<sub>2</sub>O<sub>4</sub>(L)<sub>2</sub>] and [W<sub>2</sub>O<sub>4</sub>(L)<sub>2</sub>] showed the two terminal Mo=O vibrations at 915-906 cm<sup>-1</sup> and 886-937 cm<sup>-1</sup> [29].



**Figure1.** IR spectra of the Schiff base ligand and its complexes



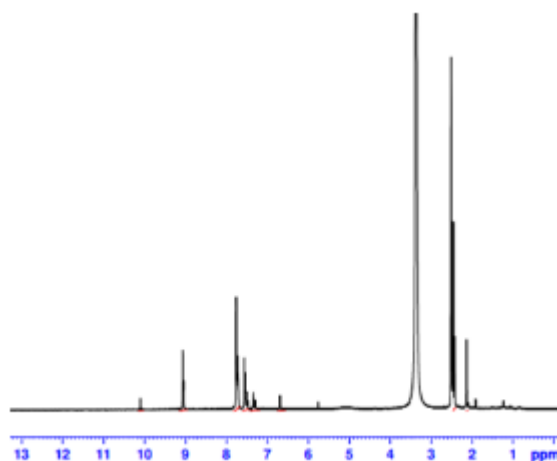
**Figure 2.** The mass spectra of (a) ligand (H<sub>2</sub>L) and (b) [Mo<sub>2</sub>O<sub>5</sub>(CO)L].H<sub>2</sub>O complex

**Table 2.** Most important IR spectral bands of the ligand and its complexes

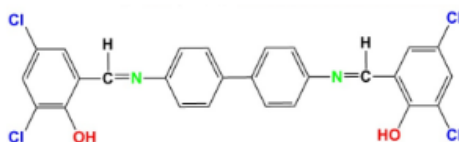
Compound	IR spectra (cm <sup>-1</sup> )							
	ν(OH)/(OH <sub>2</sub> )	ν(C=N)	ν(C-O)	νM=O	νM-O-M	νM-CO-M	νM-O	νM-N
H <sub>2</sub> L	3384	1615	1294	-	-	-	-	-
[Cr <sub>2</sub> (CO)L <sub>2</sub> ]	-	1599	1380	-	-	1718	590	492
[Mo <sub>2</sub> O <sub>4</sub> L <sub>2</sub> ]	-	1612	1402	890, 843	679	-	576	474
[Mo <sub>2</sub> O <sub>5</sub> (CO)L].H <sub>2</sub> O	3423	1636	1342	959, 880	627	1718	574	481
[W <sub>2</sub> O <sub>4</sub> L <sub>2</sub> ]	-	1620	1380	977, 813	699	-	587	473

The mass spectrum of the ligand and its complexes showed the molecular ion peak consistent with their proposed molecular formula (Table 1). The mass spectra of Schiff base and [Mo<sub>2</sub>O<sub>5</sub>(CO)L].H<sub>2</sub>O complex were shown in Figure 2.

The <sup>1</sup>H NMR spectrum of ligand, H<sub>2</sub>L (Figure 3) showed azomethine proton signal (s, CH=N) at 9.06 ppm [30] and singlet signal at 10.1 ppm due to O-H group [31]. The multiplies aromatic ring protons appeared in the region 6.68- 7.76 ppm (m, 12H, ArH) [32]. Scheme 2 gave the proposed structure of H<sub>2</sub>L ligand. The <sup>1</sup>H NMR spectra of the [Mo<sub>2</sub>O<sub>4</sub>(L)<sub>2</sub>], [Mo<sub>2</sub>O<sub>5</sub>(CO)L].H<sub>2</sub>O and [W<sub>2</sub>O<sub>4</sub>(L)<sub>2</sub>] complexes showed downfield shift in the position of the azomethine proton (-HC=N) in comparison with that of the free ligand due to its coordination to metal atom through the azomethine nitrogen [33]. The <sup>1</sup>H NMR spectra of the complexes showed appropriate shift in phenyl protons compared with ligand as a result of complexation (Table 3) [34]. The <sup>1</sup>H NMR spectrum of [Mo<sub>2</sub>O<sub>5</sub>(CO)L].H<sub>2</sub>O complex showed signal attributed to two protons of hydrogen which assigned to one molecule of water [35]. In addition, the <sup>1</sup>H NMR spectra of the molybdenum and tungsten complexes showed the disappearance of the hydroxyl proton signal indicating that the ligand coordinated to the metal with proton displacement [36].



**Figure 3.** <sup>1</sup>H NMR spectrum of ligand



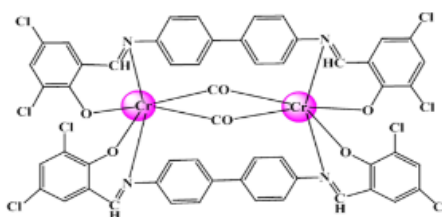
**Scheme 2.** The proposed structure of H<sub>2</sub>L ligand

**Table 3.** The <sup>1</sup>H NMR data of the synthesized ligand and its complexes

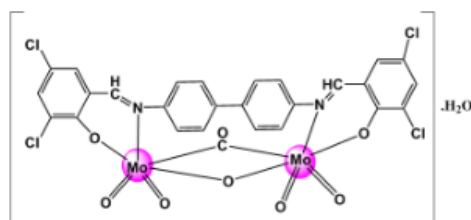
Compound	Chemical shift	Assignment
C <sub>26</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> Cl <sub>4</sub>	9.06	s, CH=N
	7.76-6.68	m, 12Ar H
	10.10	s, OH
Mo <sub>2</sub> C <sub>52</sub> H <sub>28</sub> N <sub>4</sub> O <sub>8</sub> Cl <sub>8</sub>	8.82	s, of CH=N
	8.29-6.67	m, 24Ar H
	4.30-4.27	d, 2H, H <sub>2</sub> O
Mo <sub>2</sub> C <sub>27</sub> H <sub>16</sub> N <sub>2</sub> O <sub>9</sub> Cl <sub>4</sub>	8.15	s, CH=N
	7.9-6.9	m, 12ArH
W <sub>2</sub> C <sub>52</sub> H <sub>28</sub> N <sub>4</sub> O <sub>8</sub> Cl <sub>8</sub>	8.97	s, CH=N
	8.69-6.95	m, 24Ar H

The magnetic study of the chromium complex showed paramagnetic characteristics. Magnetic measurements at 298 K gave effective magnetic ( $\mu_{\text{eff}}$ ) values of 2.93 BM. This value was close to the spin-only magnetic moment of two unpaired electrons (2.84 BM) in low spin electronic configuration and each chromium atom existed in +2 oxidation states [37].

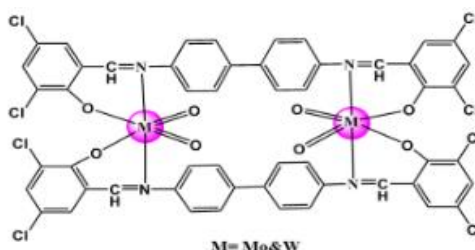
From spectroscopic studies and elemental analysis, it can be suggested that the [Cr<sub>2</sub>(CO)<sub>2</sub>(L)<sub>2</sub>] was a dinuclear complex with two Cr atoms were bridged by two carbonyl groups (Scheme 3). The dinuclear complex [Mo<sub>2</sub>O<sub>5</sub>(CO)L].H<sub>2</sub>O might consist of two Mo atoms were bridged by one oxygen and one carbonyl group in addition to two terminal oxo groups and each molybdenum may have +6 formal oxidation states with d<sup>0</sup> electronic configuration (Scheme 4) [38]. The two complexes [Mo<sub>2</sub>O<sub>4</sub>L<sub>2</sub>] and [W<sub>2</sub>O<sub>4</sub>L<sub>2</sub>] are dinuclear with the two H<sub>2</sub>L moieties bound to the metal through nitrogen and oxygen atoms and each metal may have +6 formal oxidation states with d<sup>0</sup> electronic configuration (Scheme 5).



**Scheme 3.** The structure of [Cr<sub>2</sub>(CO)<sub>2</sub>(L)<sub>2</sub>]



**Scheme 4.** The structure of [Mo<sub>2</sub>O<sub>5</sub>(CO)L].H<sub>2</sub>O



**Scheme 5.** The structure of [Mo<sub>2</sub>O<sub>4</sub>(L)<sub>2</sub>] and [W<sub>2</sub>O<sub>4</sub>(L)<sub>2</sub>]

#### 4. ELECTRONIC SPECTRA

The electronic absorption studies of H<sub>2</sub>L and its complexes were studied in DMSO solvent (Table 4). The UV-vis spectrum of the H<sub>2</sub>L ligand displayed three absorption bands at 292 nm corresponded to  $\pi-\pi^*$  and 378, 460 nm corresponded to  $n-\pi^*$  electronic transitions [39]. Upon complexation with chromium and tungsten a hypsochromic shifts were exerted in the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  electronic transitions. But in the spectra of the complexes [Mo<sub>2</sub>O<sub>4</sub>(L)<sub>2</sub>] and [Mo<sub>2</sub>O<sub>5</sub>(CO)L].H<sub>2</sub>O, a bathochromic shift in the  $\pi \rightarrow \pi^*$  electronic transitions was observed, while the  $n \rightarrow \pi^*$  bands exhibited hypsochromic shift with a considerable change in absorbance [40].

**Table 4.** The UV-Vis data of synthesized ligand and its complexes

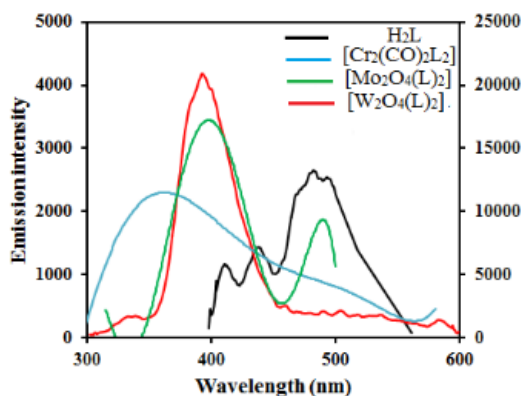
Compound	UV – Vis data $\lambda_{\max}$ (nm)	
	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$
H <sub>2</sub> L	292	378, 460
[Cr <sub>2</sub> (CO) <sub>2</sub> L <sub>2</sub> ]	280	290
[Mo <sub>2</sub> O <sub>4</sub> (L) <sub>2</sub> ]	294	366
[Mo <sub>2</sub> O <sub>5</sub> (CO)L].H <sub>2</sub> O	294	320
[W <sub>2</sub> O <sub>4</sub> (L) <sub>2</sub> ]	286	292

#### 5. FLUORESCENCE SPECTRA

Photoluminescence study of the ligand and its complexes were measured at room temperature in DMSO (Table 5 & Figure 4). The ligand exhibited the maximum emission bands at 442 and 479 nm upon excitation at 386 nm. The emission bands of all complexes showed blue shift than that of the ligand, in which, both [Mo<sub>2</sub>O<sub>4</sub>(L)<sub>2</sub>] and [W<sub>2</sub>O<sub>4</sub>(L)<sub>2</sub>] displayed the maximum emission bands at 396 and 391 nm when excited at 292 nm. On the other hand, [Cr<sub>2</sub>(CO)<sub>2</sub>(L)<sub>2</sub>] complex exhibited emission band at 352 nm upon excitation at 290 nm. The complex Mo<sub>2</sub>O<sub>5</sub>(CO)L].H<sub>2</sub>O showed no emission upon excitation at 294 nm.

**Table 5.** The fluorescence data of the synthesized ligand and its complexes

Compound	Fluorescence data $\lambda_{\max}$ (nm)	
	Excitation	Emission
H <sub>2</sub> L	386	410, 442, 479
[Cr <sub>2</sub> (CO) <sub>2</sub> L <sub>2</sub> ]	290	362
[Mo <sub>2</sub> O <sub>4</sub> (L) <sub>2</sub> ]	292	396
[Mo <sub>2</sub> O <sub>5</sub> (CO)L].H <sub>2</sub> O	294	-
[W <sub>2</sub> O <sub>4</sub> (L) <sub>2</sub> ]	292	391



**Figure 4.** Fluorescence spectra of the ligand (H<sub>2</sub>L) and its complexes

#### 6. THERMAL ANALYSIS

The thermal studies of the reported chromium, molybdenum and tungsten complexes provided further insight into the proposed structures. The detailed thermal decomposition data for complexes gave in Table 6. In addition, the structures of the investigated complexes were undertaken using thermogravimetry (T.G.) and derivative thermogravimetry (DTG) techniques (Figure 5).

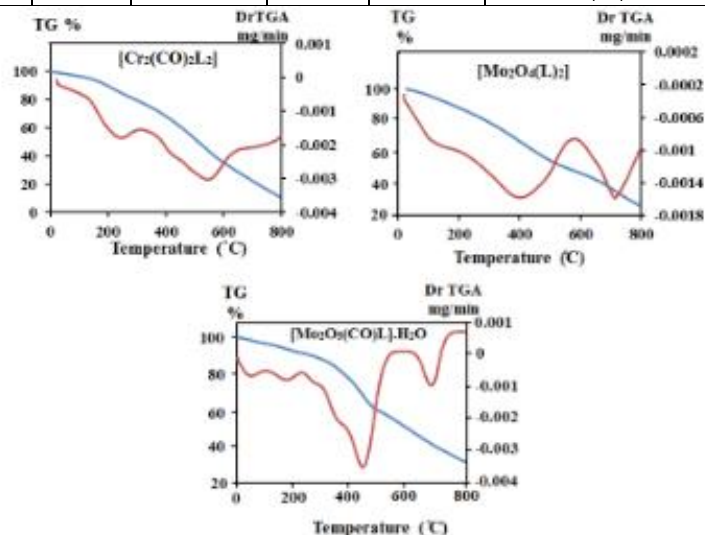
The TGA plot of [Cr<sub>2</sub>(CO)<sub>2</sub>L<sub>2</sub>] complex decomposed in three thermal steps. The first decomposition step occurred at 95-264 °C with a weight loss of 27.95% (27.92% calc.) was probably due to the elimination of (2CO+4Cl<sub>2</sub>) moieties. The second decomposition peak occurred at 269-530 °C with a weight loss of 33.89% (33.91% calc.), corresponding to the elimination of C<sub>28</sub>H<sub>20</sub>N<sub>4</sub> species. The third decomposition step occurred in the temperature range 540-800 °C with a net weight loss of 25.71% (25.68% calc.) attributed to the elimination of C<sub>24</sub>H<sub>8</sub>O species to give finally Cr<sub>2</sub>O<sub>3</sub> as residue.

On the other hand, the TGA plot of [Mo<sub>2</sub>O<sub>4</sub>(L)<sub>2</sub>] complex displayed two thermal steps in the temperature range 170-800 °C. The first decomposition step at 170-561 °C with a net weight loss of 51.31% (51.05% calc.) corresponded to the elimination of 2Cl<sub>2</sub>+L species. The second decomposition step occurred in the range 561-800 °C with a net weight loss of 23.24% (23.35% calc.) consistent with elimination of C<sub>22</sub>H<sub>14</sub>N<sub>2</sub> species, leaving finally a residue of 2MoO<sub>3</sub>+ 4C with a net weight of 25.45% (25.60% calc.).

The TG/DTG curves of [Mo<sub>2</sub>O<sub>5</sub>(CO)L].H<sub>2</sub>O showed three decomposition steps within the temperature ranges 25-262 °C, 265-572 °C and 610-800 °C. The weight loss of first step (Found = 13.78%, Calc. = 13.82%), the second step (Found = 46.02%, Calc. = 46.00%) and third step (Found = 6.16%, Calc. = 6.15%) were assigned to the loss of (CO+H<sub>2</sub>O+Cl<sub>2</sub>), C<sub>22</sub>H<sub>10</sub>N<sub>2</sub>OCl<sub>2</sub> and C<sub>4</sub>H<sub>4</sub>, respectively.

**Table 6.** Thermogravimetric data of Schiff base metal complexes

Compound	Stage	Temp. °C	Mass loss (%)		Evolved moiety	Residue (%)	
			found	(Calc.)		Found	(Calc.)
[Cr <sub>2</sub> (CO) <sub>2</sub> L <sub>2</sub> ]	I	95-264	27.95	27.92	2CO+4Cl <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	
	II	269-530	33.89	33.91	C <sub>28</sub> H <sub>20</sub> N <sub>4</sub>	12.45 (12.49)	
	III	540-800	25.71	25.68	C <sub>24</sub> H <sub>8</sub> O		
[Mo <sub>2</sub> O <sub>4</sub> (L) <sub>2</sub> ]	I	97-560	51.31	51.05	2Cl <sub>2</sub> +L	2MoO <sub>3</sub> + 4C	
	II	562-800	23.24	23.35	C <sub>22</sub> H <sub>14</sub> N <sub>2</sub>	25.45 (25.60)	
[Mo <sub>2</sub> O <sub>5</sub> (CO)L].H <sub>2</sub> O	I	25-262	13.78	13.82	CO+H <sub>2</sub> O+Cl <sub>2</sub>	2MoO <sub>3</sub>	
	II	265-572	46.02	46.00	C <sub>22</sub> H <sub>10</sub> N <sub>2</sub> OCl <sub>2</sub>	34.04 (34.03)	
	III	610-800	6.16	6.15	C <sub>4</sub> H <sub>4</sub>		



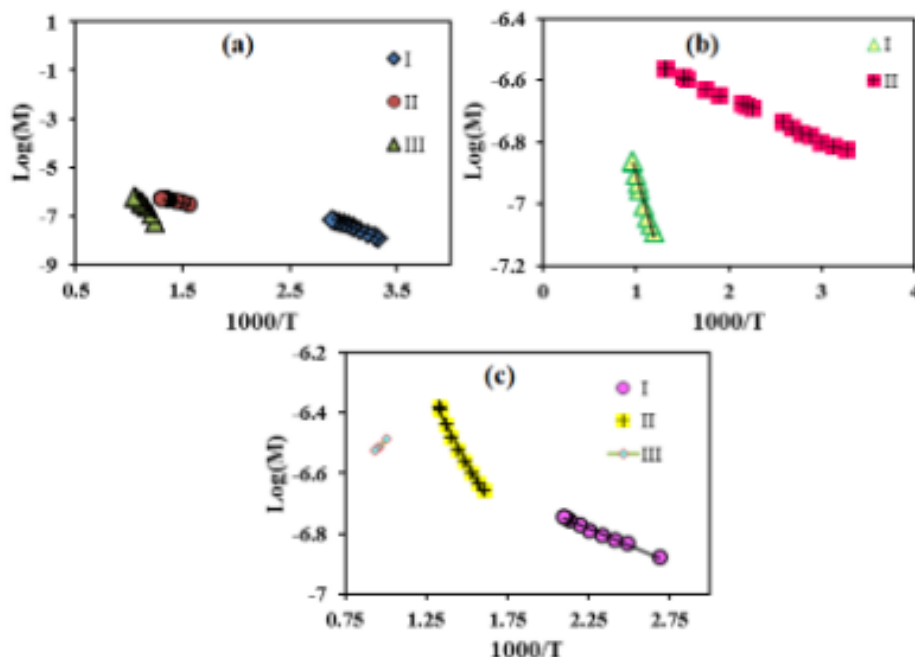
**Figure 5.** TG-DTG thermograms of [Cr<sub>2</sub>(CO)<sub>2</sub>(L)<sub>2</sub>], [Mo<sub>2</sub>O<sub>4</sub>(L)<sub>2</sub>] and [Mo<sub>2</sub>O<sub>5</sub>(CO)L].H<sub>2</sub>O complexes

## 7. KINETIC DATA

The kinetic parameters for the thermal degradation of Cr, Mo and W complexes of the Schiff base H<sub>2</sub>L were summarized in Table 7. The kinetic analysis parameters such as activation energy (E\*), enthalpy of activation (ΔH\*), entropy of activation (ΔS\*) and Gibbs free energy change of decomposition (ΔG\*) were evaluated using Coats–Redfern (CR) [41] and Horowitz–Metzger (HM) [42,43] relationships (Figs 6-7). The entropy of activation was found to have negative values for all metal complexes which indicate that decomposition reactions proceed with a lower rate than normal ones [44,45,46]. The activation energies of decomposition were found to be in the range 3.53-74.32 kJ mol<sup>-1</sup>. The high values of the activation energies reflect the thermal stability of the complexes [43].

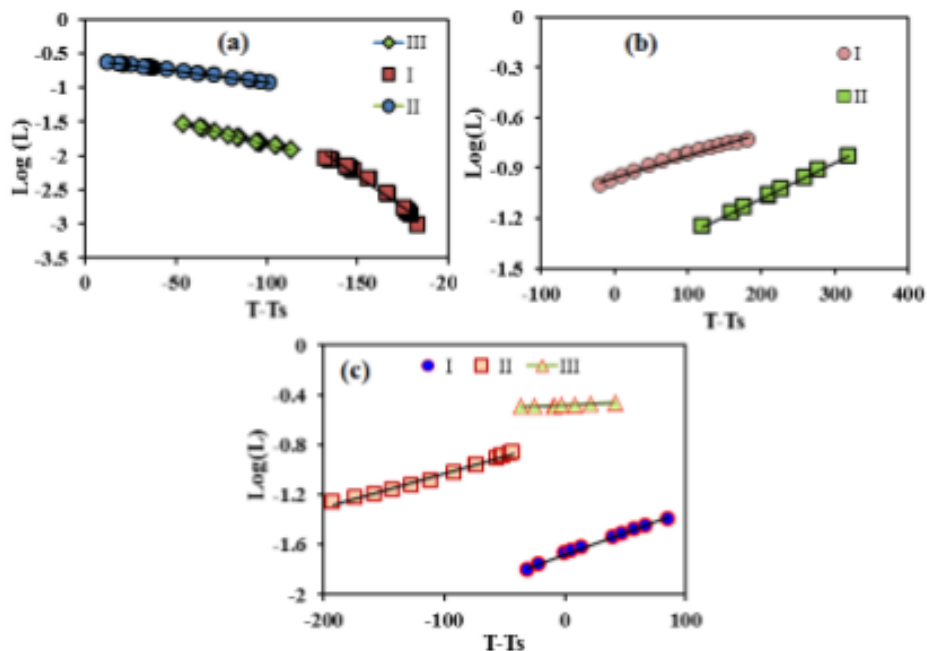
**Table7.** Kinetic thermodynamic data of Schiff base metal complexes

Compound	Stage	Ts °C	Decomposition range. °C	Method	A (S <sup>-1</sup> )	ΔH <sup>#</sup> (KJ/mol)	ΔS <sup>#</sup> (KJ/mol)	ΔG <sup>#</sup> (KJ/mol)	Ea (KJ/mol)	R <sup>2</sup>
[Cr <sub>2</sub> (CO) <sub>2</sub> L <sub>2</sub> ]	I	21	95-264	CR HM	8.41x 10 <sup>-4</sup> 7.48	17.13 38.03	- 243.52 - 174.81	68.518 122.64	18.89 42.06	0.99 1 0.95 8
	II	46	269-530	CR HM	2x10 <sup>-4</sup> 2.3x10 <sup>-3</sup>	27.35 9.41	- 262.03 - 241.66	195.89 121.54	18.304 13.27	0.95 5 0.99 9
	III	66	540-730	CR HM	8.4x10 <sup>-4</sup> 1.33x10 <sup>-3</sup>	13.36 12.63	- 253.05 - 249.25	181.39 178.14	18.89 18.15	0.98 8 0.99 9
[Mo <sub>2</sub> O <sub>4</sub> (L) <sub>2</sub> ]	I	37	170-561	CR HM	1.22x10 <sup>-6</sup> 2.05x10 <sup>-3</sup>	0.62 6.91	- 302.71 - 240.96	114.11 98.23	2.532 10.063	0.99 6 0.98 5
	II	71	560-795	CR HM	1.22x10 <sup>-6</sup> 1.64x10 <sup>-3</sup>	2.89 14.92	- 307.22 - 248.09	197.41 192.31	2.53 20.87	0.99 4 0.99 9
[Mo <sub>2</sub> O <sub>5</sub> (CO)L].H <sub>2</sub> O	I	11	25-262	CR HM	1.54x10 <sup>-5</sup> 2.05x10 <sup>-3</sup>	4.97 6.91	- 281.63 - 240.96	111.71 98.23	8.123 10.06	0.96 2 0.96 8
	II	45	265-572	CR HM	4.54x10 <sup>-6</sup> 8.46x10 <sup>-3</sup>	23.275 8.09	-67.46 - 234.61	57.21 194.07	14.15 29.32	0.97 2 0.99 3
	III	75	720-798	CR HM	1.18x10 <sup>-6</sup> 0.49x10 <sup>-2</sup>	0.31 65.76	- 311.33 - 203.65	320.98 275.53	8.87 74.32	0.98 1 0.97 1



**Figure6.** Coats-Redfern plots of (a) [Cr<sub>2</sub>(CO)<sub>2</sub>L<sub>2</sub>], (b) [Mo<sub>2</sub>O<sub>4</sub>(L)<sub>2</sub>] and (c) [Mo<sub>2</sub>O<sub>5</sub>(CO)L].H<sub>2</sub>O complexes ( $\log M = \log[\log\{W_{\infty}(W_{\infty}-W)^{-1}\}T^2]$ ).

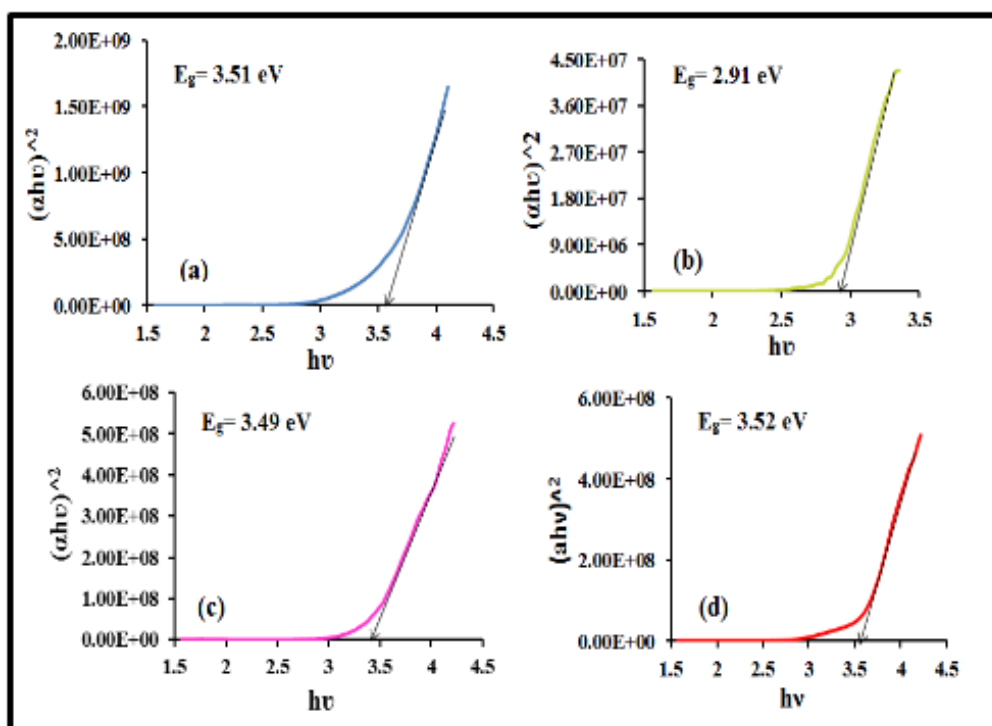




**Figure 7.** Horowitz–Metzger plots of (a)  $[\text{Cr}_2(\text{CO})_2(\text{L})_2]$ , (b)  $[\text{Mo}_2\text{O}_4(\text{L})_2]$  and (c)  $[\text{Mo}_2\text{O}_5(\text{CO})\text{L}]\cdot\text{H}_2\text{O}$  complexes ( $\log L = \log[\log\{W\infty(W\infty-W)-1\}]$ )

## 8. OPTICAL PROPERTIES

The optical band gap ( $E_g$ ) was determined from the electronic spectra of the complexes by using the following relation  $\alpha h\nu = A(h\nu - E_g)^m$ , where  $m$  is equal to  $1/2$  and  $2$  for indirect and direct transition respectively,  $A$  is an energy independent constant and  $\alpha$  was calculated from the relation  $\alpha = 1/d \ln A$  (where,  $A$  is the absorbance and  $d$  is the width of the cell) [47]. The plot  $(\alpha h\nu)^2$  vs.  $h\nu$  indicated that the type of electronic transition was direct (Figure 8). The values of band gap ( $E_g$ ) for  $[\text{Cr}_2(\text{CO})_2(\text{L})_2]$ ,  $[\text{Mo}_2\text{O}_4(\text{L})_2]$ ,  $[\text{Mo}_2\text{O}_5(\text{CO})\text{L}]\cdot\text{H}_2\text{O}$  and  $[\text{W}_2\text{O}_4(\text{L})_2]$  were found to be 3.51, 2.91, 3.49 and 3.52, respectively. This indicated that these complexes could be used as promising materials for optoelectronic devices [48].



**Figure 8.** Optical band gap of (a)  $[\text{Cr}_2(\text{CO})_2(\text{L})_2]$ , (b)  $[\text{Mo}_2\text{O}_4(\text{L})_2]$ , (c)  $[\text{Mo}_2\text{O}_5(\text{CO})\text{L}]\cdot\text{H}_2\text{O}$ , (d)  $[\text{W}_2\text{O}_4(\text{L})_2]$ .

## 9. CONCLUSION

Four new complexes were synthesized from the reactions of M(CO)<sub>6</sub> (M= Cr, Mo, W) with the 6,6'([1,1'biphenyl]4,4'diylbis(azaneylylidene))bis(methaneylylidene))bis(2,4dichlorophenol) (H<sub>2</sub>L) Schiff base in THF. The dinuclear carbonyl complex [Cr<sub>2</sub>(CO)<sub>2</sub>(L)<sub>2</sub>] and two oxo complexes [Mo<sub>2</sub>O<sub>4</sub>(L)<sub>2</sub>] and [W<sub>2</sub>O<sub>4</sub>(L)<sub>2</sub>] formed under sunlight irradiation. In air, the corresponding reaction gave the oxocarbonyl complex [Mo<sub>2</sub>O<sub>5</sub>(CO)L].H<sub>2</sub>O. Analytical and spectral data revealed that H<sub>2</sub>L was coordinated as tetradentate ligand through two imine nitrogen and two deprotonated phenolic oxygen atoms with 2:2 stoichiometries. The magnetic measurements of the synthesized complexes showed all the complexes were diamagnetic except [Cr<sub>2</sub>(CO)<sub>2</sub>(L)<sub>2</sub>] complex was paramagnetic. The activation thermodynamic parameters, such as activation energy, enthalpy, entropy and Gibbs free energy change of complexes decomposition were calculated from TG curves. Furthermore, these complexes exhibited fluorescence properties and could be used as photoactive materials. The optical band gap of the isolated complexes indicated semi-conductivity nature of these compounds.

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