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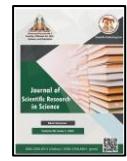
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Structural Characterization, thermal studies, fluorescence and optical properties of metal carbonyl derivatives of N₂O₂ Schiff Base

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Abstract

A series of four binuclear complexes [Cr₂(CO)₂L₂] (1), [Mo₂O₄(L)₂] (2), and [W₂O₄(L)₂] (3) [Mo₂O₅(CO)L].H₂O (4) were synthesized from the 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) H₂L in THF. The structures of the ligand and its complexes were characterized using elemental studies, IR, mass, UV-vis and ¹H NMR spectroscopy. Magnetic measurements showed diamagnetic properties for molybdenum and tungsten complexes and paramagnetic character for chromium complex. The thermal analyses for all metal complexes were also determined by the thermogravimetry technique. The thermodynamics parameters of complexes were calculated. Spectroscopic data revealed that H₂L was coordinated as a tetradentate ligand through two imine nitrogen and two deprotonated phenolic oxygen atoms. The Schiff base ligand (H₂L) and its complexes displayed fluorescence properties and can potentially serve as photoactive materials. The values of optical band gap energy (E_g) of the prepared complexes suggested that these compounds could be used as semiconductors.

Keywords

Benzidine; Metal Carbonyl Complexes; Fluorescence; Optical Properties

1. Introduction

Transition metal complexes containing NO play a significant role in a range of uses and applications, from types of synthetic work to physicochemical work [1] and biochemically related metal complex studies [2]. They're often used as photosensitizers, catalysts and coordinating polymers [3-5] and have established a broad variety of applications [6-7]. On the other hand, complexes containing C=O being essential

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intermediates in the combination of effective coordination compounds [8-10]. Also, these complexes are of great structural importance as well as commercial, catalytic, epoxidation, catalytic activity in olefin hydrogenation and photochromic effects. [11-12]. Also, transition complexes synthesized from Schiff bases including donor electrons, nitrogen and oxygen such as derivatives of benzimidazole, thiazole, pyridine, pyrazolone, hydrazine, p-fluorobezaldehyde play an essential part in biological systems [13-18]. Our attention in the investigation of metal carbonyl reactions with Schiff bases often brought us to research the reactions of $M(CO)_6$ ($M=Cr, Mo$ and W) to Schiff Base (H_2L).

2. Experimental

2.1. Materials

$M(CO)_6$ ($M=Cr, Mo$ and W), 3,5-Dichlorosalicylaldehyde and benzidine were purchased from Aldrich and used without purification.

2.2. Instrumentation

The ligand and its metal complexes were analyzed by elemental analysis (Perkin–Elmer-2400 CHN elemental analyzer) and mass spectrometry (JEOL JMS-AX 500 spectrometer). Infrared measurements were obtained as KBr plates using a Shimadzu 8000 FT–IR spectrometer. The 1H NMR spectra were registered by using d^6 -DMSO as a solvent and therefore, the BRUKER five hundred MHz photometer exploitation TMS as enclosed a reference. Magnetic measurements in the solid state (Gouy method) were carried out on a Sherwood magnetic susceptibility balance. The TG and DTG analysis techniques were recorded at a worming rate of ten $^0C/min$ underneath a gas atmosphere employing a Shimadzu DT-50 thermal analyzer. The luminescent characteristics of the ligand and its compounds analyzed using the 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_2L)

3,5-di-chlorosalicylaldehyde (0. 38 g, 2 mmol) was added to a solution of benzidine (0.18 g, 1 mmol) in methyl alcohol and the mixture was stirring at room temperature. After one-hour, an orange precipitate formed, filtrated off and washed several times with methanol and then left to dry over $CaCl_2$.

2.4. Synthesis of complexes

2.4.1. Synthesis of $[\text{Cr}_2(\text{CO})_2\text{L}_2]$ (1), $[\text{Mo}_2\text{O}_4\text{L}_2]$ (2) and $[\text{W}_2\text{O}_4\text{L}_2]$ (3) complex

A mixture of $\text{M}(\text{CO})_6$ ($\text{M}=\text{Mo}$ and W) and ligand, H_2L in 30 ml THF was exposed to sunlight irradiation. After 24 hours, the color of the mixture of (1) was changed from orange to red, While the color of (2) and (3) was changed from orange to brown the color of the reaction mixture. Then, the solvent was evaporated. The solid complexes were isolated and washed by petroleum ether.

2.4.2. Synthesis of $[\text{Mo}_2\text{O}_5(\text{CO})\text{L}]\cdot\text{H}_2\text{O}$ (4) complexes

A mixture of $\text{Mo}(\text{CO})_6$ and ligand, H_2L in 30 ml THF was refluxed in the air for 6 h. The color of the solution of was changed from orange to dark green. The solid complex was obtained by evaporation of the solvent then washed several times by petroleum ether.

3. Results and discussion

Elemental analyses, physical properties and mass spectrometry data of the ligand (H_2L) and its complexes were summarized in Table (1). The metal complexes were insoluble in common organic solvents (methanol, ethanol, acetone and chloroform), but soluble in dimethylformamide (DMF) and dimethylsulfoxide (DMSO).

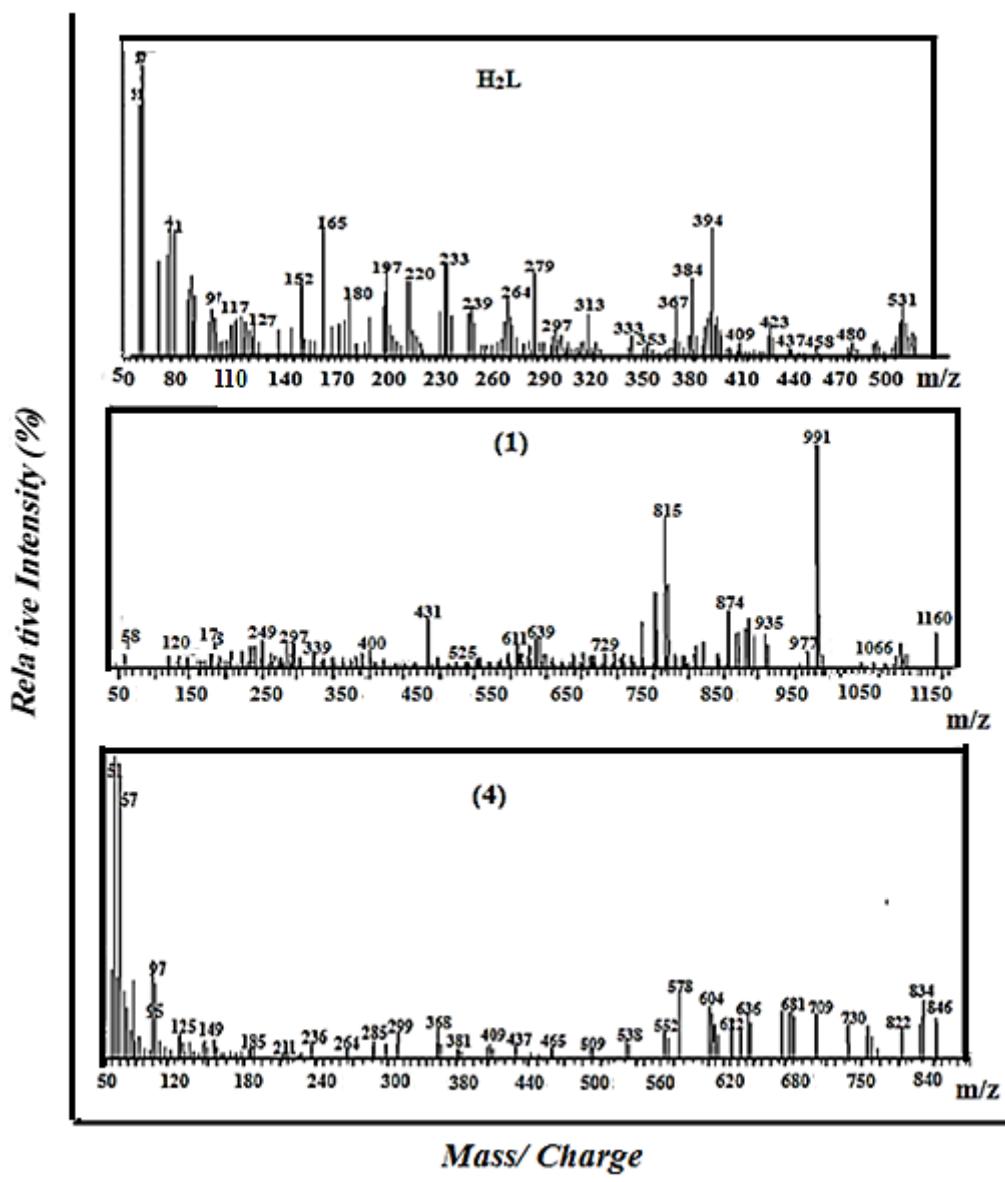
Table1. Physical properties and analytical data of the Schiff base ligand (H_2L) and its metal carbonyl complexes.

Compound	Mass Spectrometry		Color	Yield %	M.P. (°C)	Elemental analysis					
	Mol.Wt.	m/z				Found (calc.)					
						C%	N%	H%			
$\text{H}_2\text{L}(\text{C}_{26}\text{H}_{16}\text{N}_2\text{O}_2\text{Cl}_4)$	(530.21)	531 (P+)	orange	87.8	260	58.96 (58.89)	5.39 (5.28)	3.12 (3.04)			
$\text{Cr}_2\text{C}_{54}\text{H}_{28}\text{N}_4\text{O}_6\text{Cl}_8$ (1)	(1216.41)	1160	red	46.2	>300	52.23 (52.32)	4.43 (4.60)	2.31 (2.32)			

Compound	Mass Spectrometry		Color	Yield %	M.P. (°C)	Elemental analysis					
	Mol.Wt.	m/z				Found (calc.)					
						C%	N%	H%			
Mo ₂ C ₅₂ H ₂₈ N ₄ O ₈ Cl ₈ (2)	(1312.27)	1312 (P+)	brown	50.5	>300	47.76 (47.59)	4.67 (4.26)	2.21 (2.15)			
W ₂ C ₅₂ H ₂₈ N ₄ O ₈ Cl ₈ (3)	(1488.03)	1488 (P+)	brown	45.7	>300	41.71 (41.69)	3.82 (3.76)	1.86 (1.98)			
Mo ₂ C ₂₇ H ₁₆ N ₂ O ₉ Cl ₄ (4)	(846.01)	846 (P+)	Dark green	65	>300	38.84 (38.33)	3.21 (3.31)	1.89 (1.90)			

3.1. Mass spectra

The mass spectra of the ligand and its complexes revealed that the molecular ion peak consistent with their proposed molecular formula (Table 1). The mass spectra of the Schiff base ligand and [Cr₂(CO)₂L₂] (**1**) and [Mo₂O₅(CO)L].H₂O, **4** complexes were shown in Fig.1.



a

Fig.1. The mass spectra of ligand (H_2L), $[\text{Cr}_2(\text{CO})_2\text{L}_2]$ (1) and $[\text{Mo}_2\text{O}_5(\text{CO})\text{L}]\cdot\text{H}_2\text{O}$ (4).

3.2. IR spectra

The infrared spectrum of the Schiff base ligand (H_2L) displayed broad band at 3384 cm^{-1} (Table 2) which can be attributed to the phenolic OH group or H_2O [19]. This band disappeared in all complexes except complex (4) (Fig.2). The IR spectrum of the ligand (H_2L) showed a band at 1615 cm^{-1} due to the azomethane ($-\text{HC}=\text{N}$) group [20]. The $\text{C}=\text{N}$ stretching vibration was shifted in the IR spectra of complexes indicating the coordination of ligand with metal throughout azomethine nitrogen atoms [21-22].

Also, the C-O stretching band of the H₂L was shifted to a higher frequency range indicating coordination through phenolic oxygen [23]. The non-ligand bands observed ranged from 574 to 590 cm⁻¹ due to M–O and from 473 to 493 cm⁻¹ due to M–N bonds in the infrared spectra of all complexes [24]. The IR spectrum of [Cr₂(CO)₂(L)₂], (1) complex observed band at 1718 cm⁻¹ due to carbonyl group bridging [25]. On the other hand, the IR spectrum of [Mo₂O₅(CO)L].H₂O, (4) complex displayed two bands at 1718 and 627 cm⁻¹ due to bridging carbonyl group and Mo–O–Mo bridged bond, respectively [26]. Also, the IR spectrum of complex (4) showed stretching frequencies of hydrated water and terminal Mo=O bonds for a cis MO₂ fragment [27-28]. Both oxo complexes (2) and (3) were showed in the IR spectra two-terminal Mo=O vibrations at 915-906 cm⁻¹ and 886-937 cm⁻¹, respectively [29].

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

Compound	IR spectra (cm ⁻¹)							
	v(OH)/(OH ₂)	v(C=N)	v(C-O)	vM=O	vM-O-M	vM-CO-M	vM-O	vM-N
H ₂ L	3384	1615	1294	-	-	-	-	-
1	-	1599	1380	-	-	1718	590	492
2	-	1612	1402	890, 843	679	-	576	474
3	-	1620	1380	977, 813	699	-	587	473
4	3423	1636	1342	959, 880	627	1718	574	481

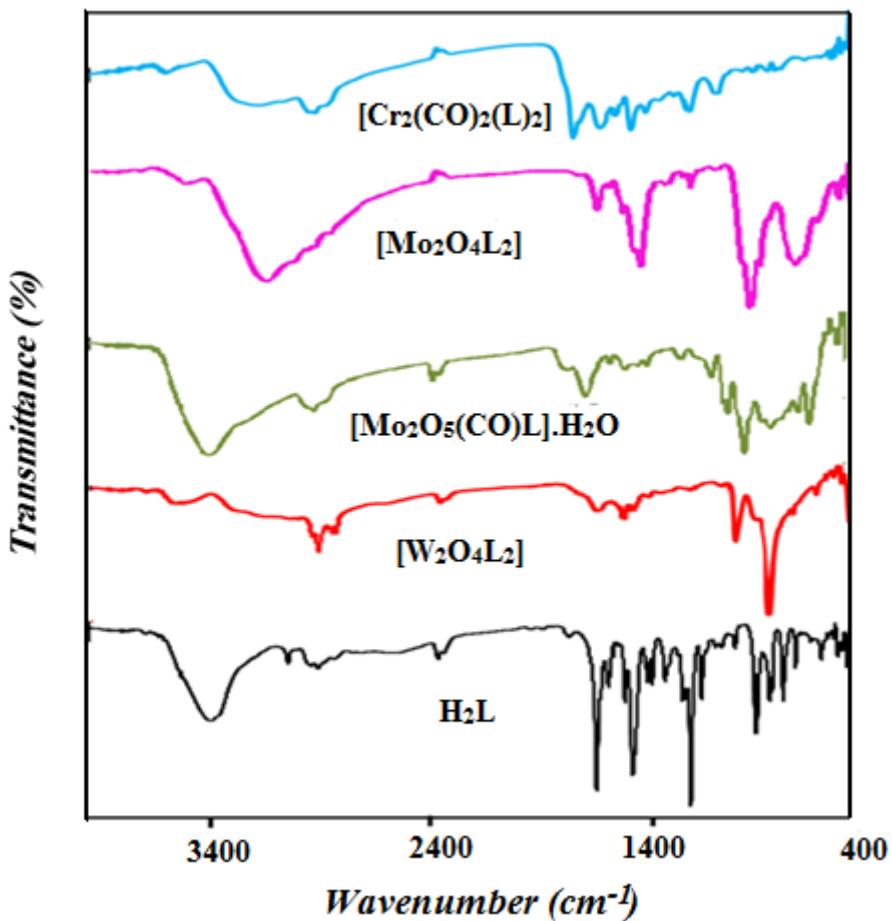


Fig.2. IR spectra of the Schiff base ligand and its complexes.

3.3. ^1H NMR spectra

The ^1H NMR spectra of Schiff base ligand (H_2L) and its molybdenum and tungsten complexes were shown in Fig.3 and all data are summarized in Table 3. The ^1H NMR spectra of the 2, 3 and 4 complexes showed a downfield shift of the azomethine proton ($-\text{HC}=\text{N}$) in comparison with that of the free ligand owing to its coordination only with the central metal atom via azomethane nitrogen [30]. The ^1H NMR spectra of the complexes showed an appropriate shift in phenyl protons compared with ligand [31]. ^1H NMR spectrum of complex 4 showed a signal consisting of two hydrogen protons allocated to a single water molecule [32]. In comparison, the ^1H NMR spectra of molybdenum and tungsten complexes revealed the absence of the hydroxyl proton signal suggesting that the ligand coordinated the metal with proton displacement [33].

Table 3. The ^1H NMR data (ppm) of the synthesized ligand and its complexes.

Compound	Chemical shift	Assignment
H_2L	9.06	s, $\text{CH}=\text{N}$
	7.76-6.68	m, 12Ar H
	10.10	s, OH
2	8.82	s, of $\text{CH}=\text{N}$
	8.29-6.67	m, 24Ar H
3	8.97	s, $\text{CH}=\text{N}$
	8.69-6.95	m, 24Ar H
4	8.15	s, $\text{CH}=\text{N}$
	7.9-6.9	m, 12ArH
	4.30-4.27	d, 2H, H_2O

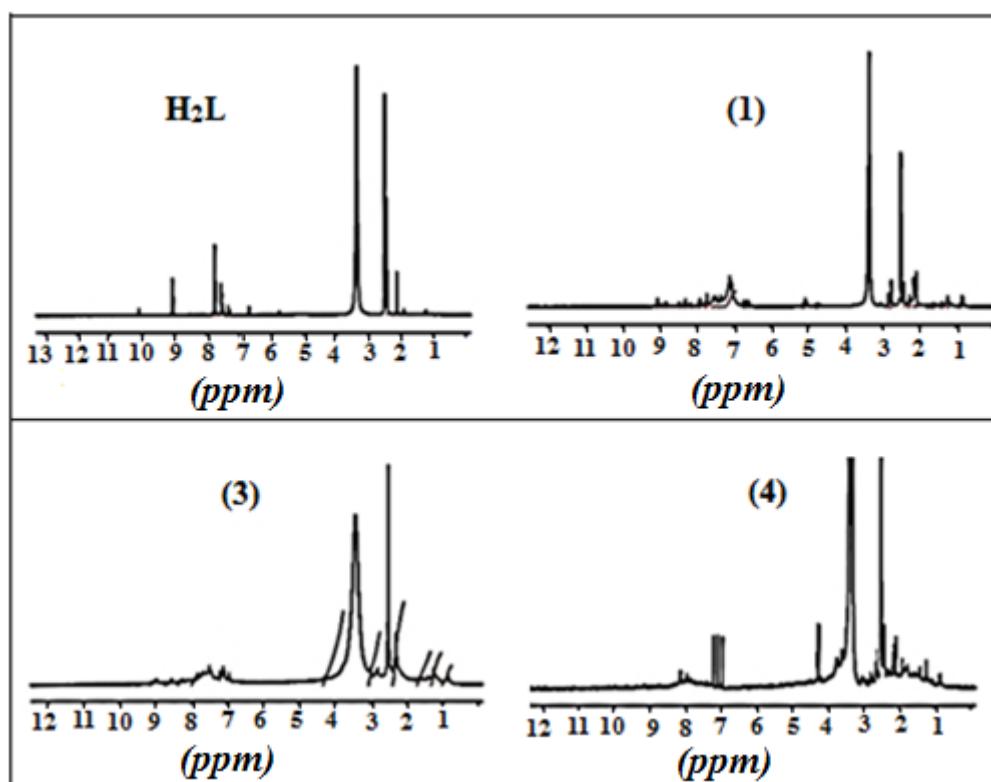


Fig.3. ^1H NMR spectra of ligand and its complexes.

3.4. Magnetic measurements

The magnetic study of the chromium complex revealed paramagnetic properties. The effective magnetic (μ_{eff}) value of 2.93 BM was close to the spin-only magnetic moment of two unpaired electrons (2.84 BM) in a low spin electronic configuration. Each chromium atom was existed in +2 oxidation state [34].

The results of the spectroscopic analysis were in full alignment with the suggested ligand and its complex structures (Figs. 4-5). The chromium complex, 1 was a binuclear complex with two Cr atoms bridged by two carbonyl groups. The complex $[\text{Mo}_2\text{O}_5(\text{CO})\text{L}]\cdot\text{H}_2\text{O}$ (4) could consist of two Mo atoms was bridged by one oxygen and one carbonyl group and each molybdenum may have +6 formal oxidation states[35]. The two complexes 2 and 3 were binuclear with two H_2L ligands bound to the metal by nitrogen and oxygen atoms. Each metal in 2 and 3 could have +6 formal oxidation states with d^0 electronic configuration.

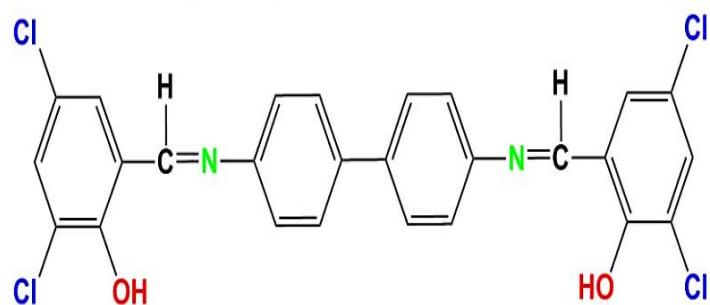
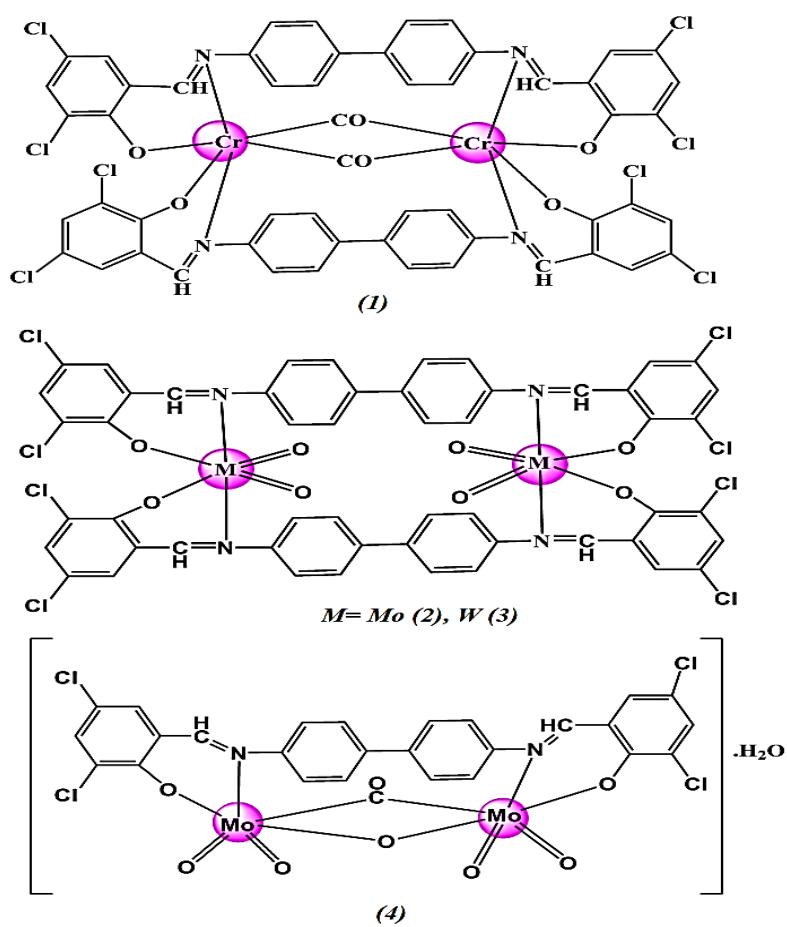
Fig.4. The proposed structure of the H_2L ligand.

Fig.5. The structure of metal carbonyl complexes.

3.5. Electronic spectra

Electronic absorption studies of Schiff base (H_2L) and its complexes were studied in DMSO (Table 4). The UV–Vis absorption spectrum of the H_2L ligand showed three absorption bands at 296 nm corresponding to $\pi\text{--}\pi^*$ and 386, 454 nm corresponding to $\text{n}\text{--}\pi^*$ electronic transitions [36]. Hypsochromic shifts were carried out in the $\pi\rightarrow\pi^*$ and $\text{n}\rightarrow\pi^*$ electronic transitions in the spectra of 1 and 3. In the spectra of complexes 2 and 4, a bathochromic shift in electronic transitions in the $\pi\rightarrow\pi^*$ was detected. while the $\text{n}\rightarrow\pi^*$ bands observed hypsochromic shift with a significant change in absorbance [37].

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

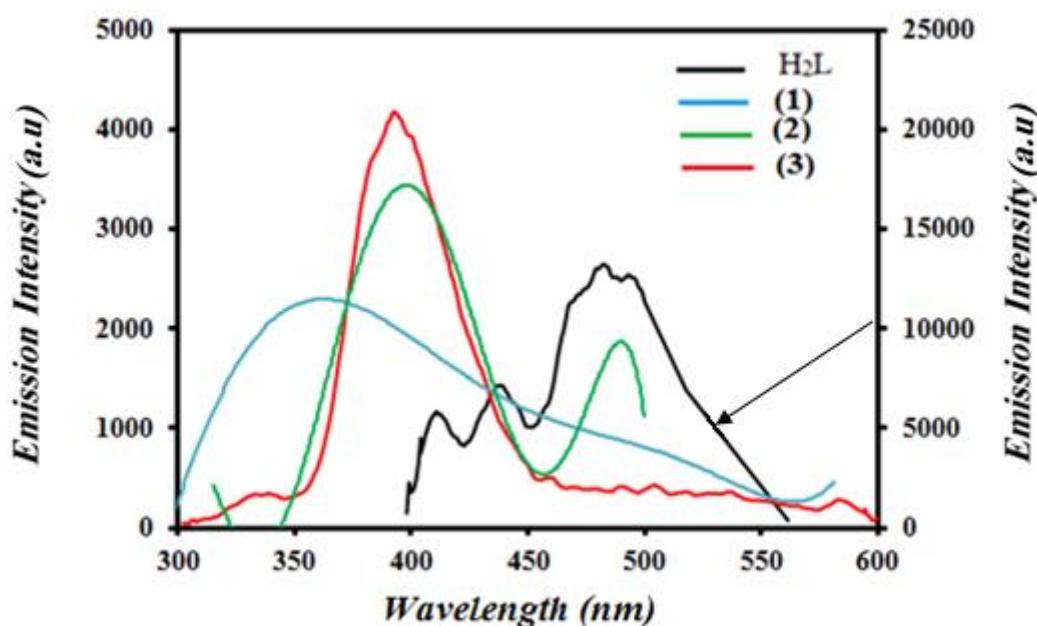
Compound	UV – Vis data	
	λ_{max} (nm)	
	$\pi\rightarrow\pi^*$	$\text{n}\rightarrow\pi^*$
H_2L	296	386, 454
1	280	290
2	294	366
3	286	292
4	294	320

3.6. Fluorescence spectra

At room temperature, the photoluminescence examination of ligand and its complexes in DMSO was evaluated (Table 5 & Fig. 6). Upon excitation at 386 nm, the ligand showed maximum emission bands at 442 and 479 nm. The emission bands of all complexes displayed a blue shift compared to that of the free ligand, in which, when excited at 292 nm, both 2 and 3 showed maximum emission bands at 396 and 391 nm. On the other hand, on excitation at 290 nm, complex (1) exhibited an emission band at 352 nm. The $[\text{Mo}_2\text{O}_5(\text{CO})\text{L}]\cdot\text{H}_2\text{O}$ (4) complex showed no emission at 294 nm upon excitation.

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

Compound	Fluorescence data	
	Excitation	λ_{max} (nm) Emission
H ₂ L	386	410, 442, 479
1	290	362
2	292	396
3	292	391
4	294	-

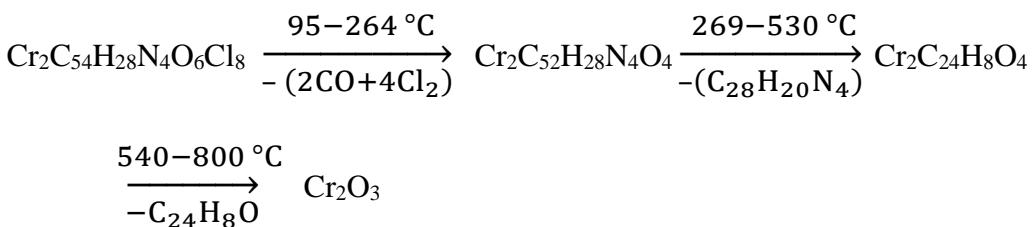
Fig.6. Fluorescence spectra of the ligand (H₂L) and its complexes.

3.7. Thermal analysis

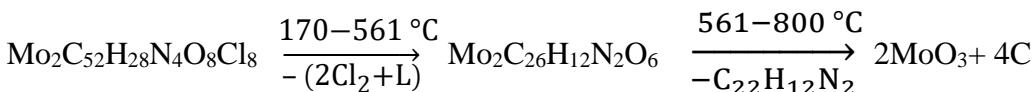
The thermal decompositions of the [Cr₂(CO)₂L₂] (1), [Mo₂O₄(L)₂] (2), [W₂O₄(L)₂] (3) and [Mo₂O₅(CO)L].H₂O (4) complexes were performed within a

temperature range from room temperature to 800 °C Fig. (7). The detailed thermal decomposition data for complexes gave in Table (6).

The complex (1) was decomposed thermally in three stages. The first decomposition step resulted at 95-264 °C with the elimination of (2CO+4Cl₂) moieties. At 269-530 °C, the second peak of decomposition occurred with a weight loss of 33.89 % (33.91 % calc.). The third decomposition stage occurred in the temperature range 540-800 °C with a net weight loss of 25.71 % (25.68 % calc.) referred to the elimination of C₂₄H₈O species to give finally Cr₂O₃ as residue.



The TGA curve of complex, 2 showed two thermal steps in the temperature range of 170-800 °C. The first stage of decomposition at 170-561 °C with a net weight loss of 51.31 % (51.05 % calc.) corresponded to the removal of – (2Cl₂+L) species. The second step of decomposition resulted in a weight loss of 23.24 % (23.35 % calc.) due to the elimination of C₂₂H₁₂N₂ species, leaving finally a residue of 2MoO₃+ 4C with a net weight of 25.45 percent (25.60 percent calc.).



The TGA plot of complex, 3 showed two resolved well-defined decomposition steps within temperature range 150–798 °C. The first decomposition step occurred in the temperature range 150–489 °C with a net weight loss of 35.13 % (35.49 % calc.) which corresponds to the loss of 2Cl₂+L species. The second decomposition stage occurred in the temperature range 490- 798 °C with a weight loss of 36.45 % (36.57% calc.) to give finally a solid residue W₂O₃ with a net weight of 28.42 % (27.93 % calc.).



The complex (4) decomposed in three stages within the temperature ranges 25-800 °C. The first step occurred in the range 25-262°C of temperature with a net loss of

weight (Found = 13.78 %, Calc. = 13.82 %), which corresponds to the loss of (CO+H₂O+Cl₂) species. The second and third decomposition steps occurred in the temperature range 265-572 °C and 610-800 °C, respectively, to give finally a residue 2MoO₃.

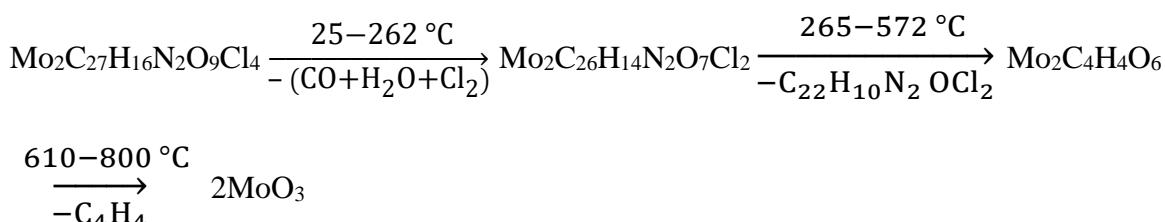


Table 6. Thermogravimetric data of Schiff base metal complexes.

Compound	Stage	Temp. °C	Mass loss (%)		Evolved moiety	Residue (%) Found (Calc.)
			found	(Calc.)		
(1)	I	95-264	27.95	27.92	2CO+4Cl ₂	Cr ₂ O ₃
	II	269-530	33.89	33.91	C ₂₈ H ₂₀ N ₄	12.45 (12.49)
	III	540-800	25.71	25.68	C ₂₄ H ₈ O	
(2)	I	170-561	51.31	51.05	2Cl ₂ +L	2MoO ₃ + 4C
	II	561-800	23.24	23.35	C ₂₂ H ₁₂ N ₂	25.45 (25.60)
(3)	I	150-489	35.13	35.49	2Cl ₂ +L	W ₂ O ₃
	II	490-798	36.45	36.57	C ₂₆ H ₁₄ N ₂ O ₃ Cl ₂	28.42 (27.93)
(4)	I	25-262	13.78	13.82	CO+H ₂ O+Cl ₂	2MoO ₃
	II	265-572	46.02	46.00	C ₂₂ H ₁₀ N ₂ OCl ₂	34.04 (34.03)
	III	610-800	6.16	6.15	C ₄ H ₄	

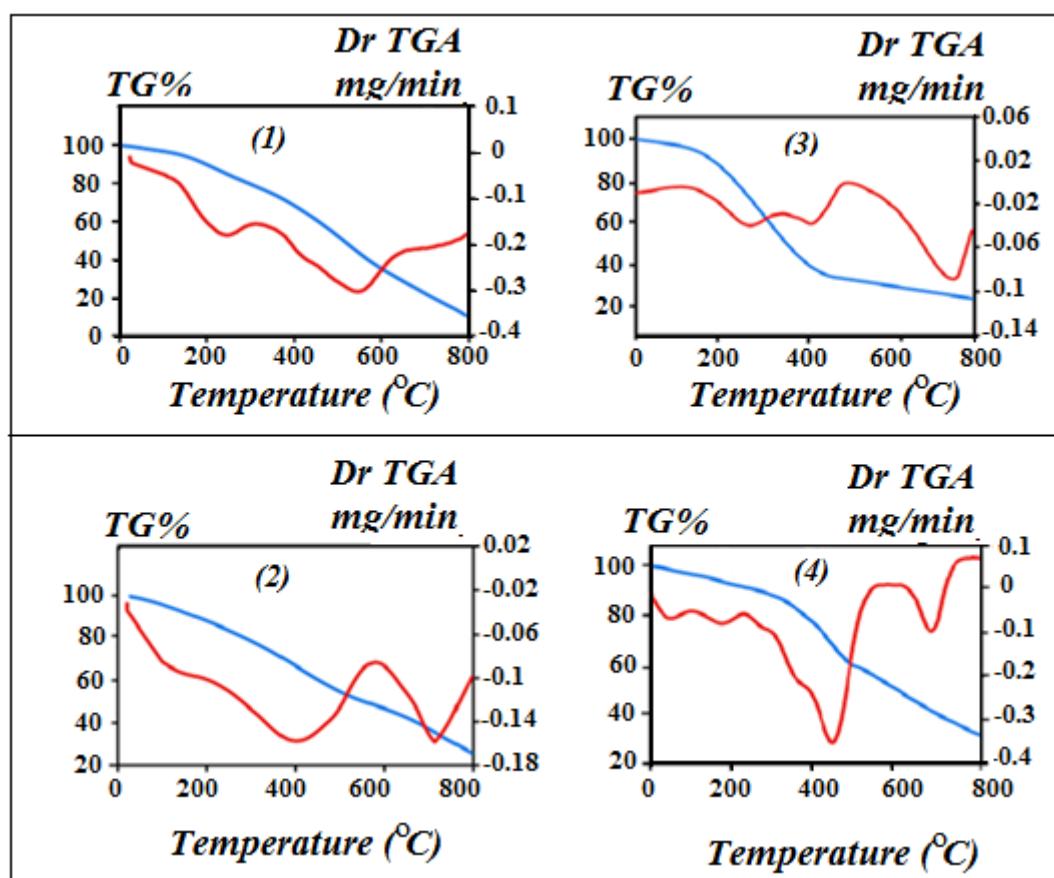


Fig.7. TG-DT thermograms of metal carbonyl complexes.

3.7.1 Kinetic data

The kinetic analysis parameters such as activation energy (E^*), enthalpy of activation (ΔH^*), the entropy of activation (ΔS^*) and Gibbs free energy change of decomposition (ΔG^*) for the thermal degradation of all complexes have been tested using Coats–Redfern (CR) [38] and Horowitz–Metzger (HM) [39] relationships (Figs 8-9). The data are summarized in Table (8). The entropy of activation was found to have negative values for all metal complexes which denoting that decomposition reactions proceed with a lower rate than normal ones [40-41]. The activation energies of decomposition were found to be in the range of 3.53-74.32 kJ mol⁻¹. The high values of the activation energies reflect the thermal stability of the complexes [42].

Table 7: Kinetic thermodynamic data of Schiff base metal complexes.

Compound	Stage	Ts °C	Decomposition range. °C	Method	A (S ⁻¹)	ΔH [#] (KJ/mol)	ΔS [#] (KJ/mol)	ΔG [#] (KJ/mol)	Ea (KJ/mol)	R ²
1	I	211	95-264	CR	8.4x10 ⁻⁴	17.13	-243.52	68.51	18.89	0.991
				HM	7.48	38.03	-174.81	122.64	42.06	0.958
	II	464	269-530	CR	2x10 ⁻⁴	27.35	-262.03	195.89	18.30	0.955
				HM	2.3x10 ⁻³	9.41	-241.66	121.54	13.27	0.999
	III	664	540-730	CR	8.4x10 ⁻⁴	13.36	-253.05	181.39	18.89	0.988
				HM	1.3x10 ⁻³	12.63	-249.25	178.14	18.15	0.999
2	I	379	170-561	CR	1.2x10 ⁻⁶	0.62	-302.71	114.11	2.532	0.996
				HM	2.5x10 ⁻³	6.91	-240.96	98.23	10.063	0.985
	II	715	560-795	CR	1.2x10 ⁻⁶	2.89	-307.22	197.41	2.53	0.994
				HM	1.6x10 ⁻³	14.92	-248.09	192.31	20.87	0.999
3	I	450	308-493	CR	4x10 ⁻⁶	51.78	-298.23	220.81	11.20	0.976
				HM	2.4x10 ⁻²	28.37	-225.84	191.66	28.37	0.972
	II	540	494-660	CR	1.2x10 ⁻⁵	78.71	-291.39	244.77	14.63	0.987
				HM	3.4x10 ⁻³	20.94	-244.05	219.36	27.71	0.994
	III	560	662-798	CR	2.3x10 ⁻⁵	14.91	-282.86	250.52	21.83	0.972
				HM	1.3x10 ⁻³	16.82	-251.51	226.33	23.75	0.985
4	I	117	25-262	CR	1.5x10 ⁻⁵	4.97	-281.63	111.71	8.123	0.962
				HM	2.1x10 ⁻³	6.91	-240.96	98.23	10.06	0.968
	II	455	265-572	CR	4.5x10 ⁻⁶	23.275	-67.46	57.21	14.15	0.972
				HM	8.4x10 ⁻³	8.09	-234.61	194.07	29.32	0.993
	III	757	720-798	CR	1.2x10 ⁻⁶	0.31	-311.33	320.98	8.87	0.981
				HM	0.5x10 ⁻²	65.76	-203.65	275.53	74.32	0.971

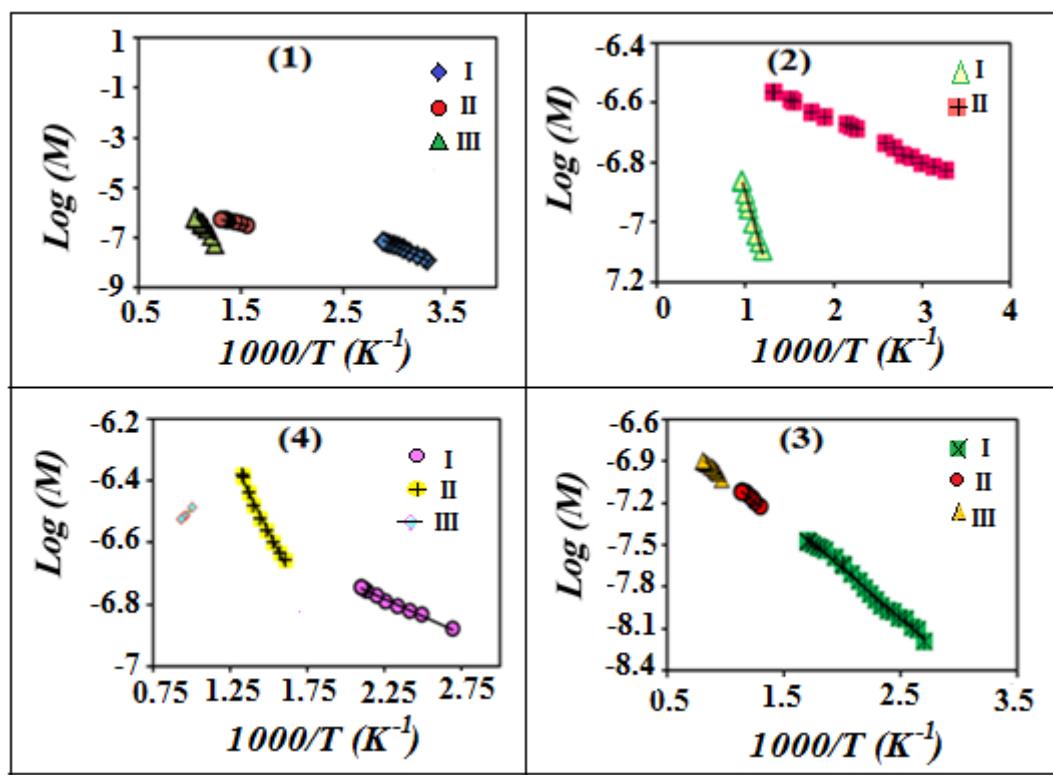


Fig.8. Coats-Redfern plots of complexes. $\log M = \log[\log\{W_\infty(W_\infty - W)^{-1}\}T^{-2}]$.

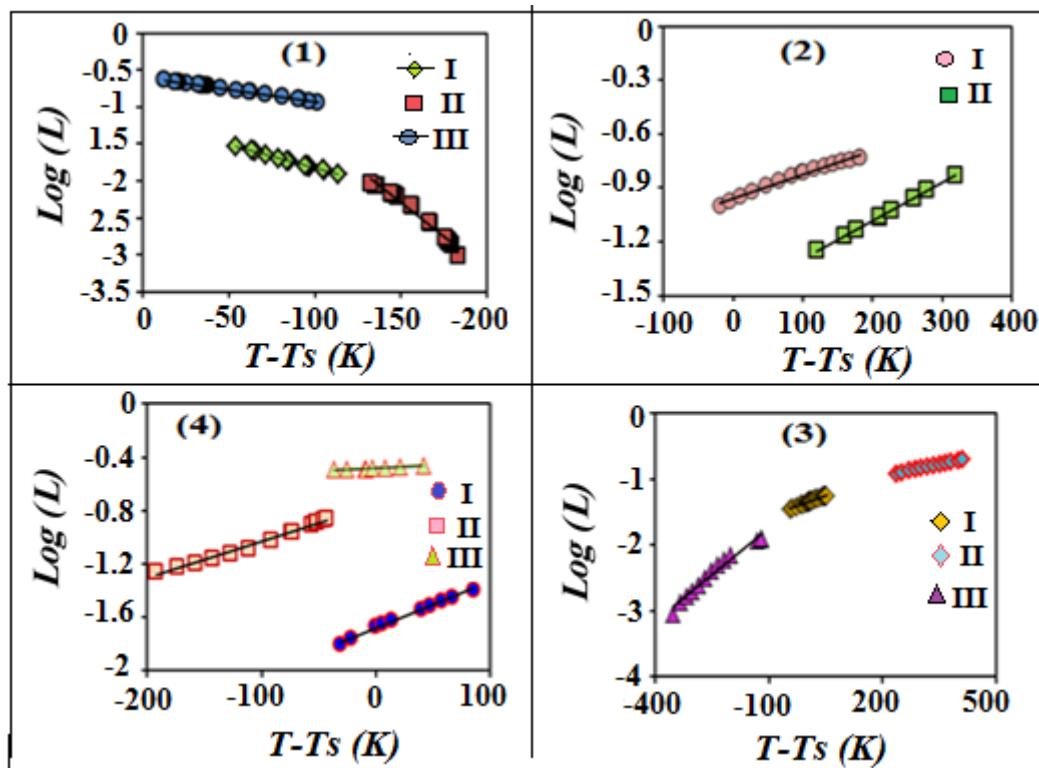


Fig.9. Horowitz-Metzger plots of complexes. $\log L = \log[\log\{W_\infty(W_\infty - W)^{-1}\}]$.

3.8. Optical properties

From the electronic spectra of the complexes, the optical band gap (E_g) was estimated using the relationship below:

$\alpha h\nu = A (h\nu - E_g)^m$, where m is equal to 1/2 and 2 for indirect and direct transition respectively, A is energy independent constant and from the relation $\alpha = 1/d \ln A$ (where A is the absorbance and d is the width of the cell), α was determined [43]. The plot $(\alpha h\nu)^2$ vs. $h\nu$ indicated that the type of electronic transition was direct (Fig.10). The values of band gap (E_g) equal to 3.51, 2.91, 3.52 and 3.49 eV for complexes (1), (2), (3) and (4), respectively. This reveals that these complexes could be used as promising materials for optoelectronic devices [44].

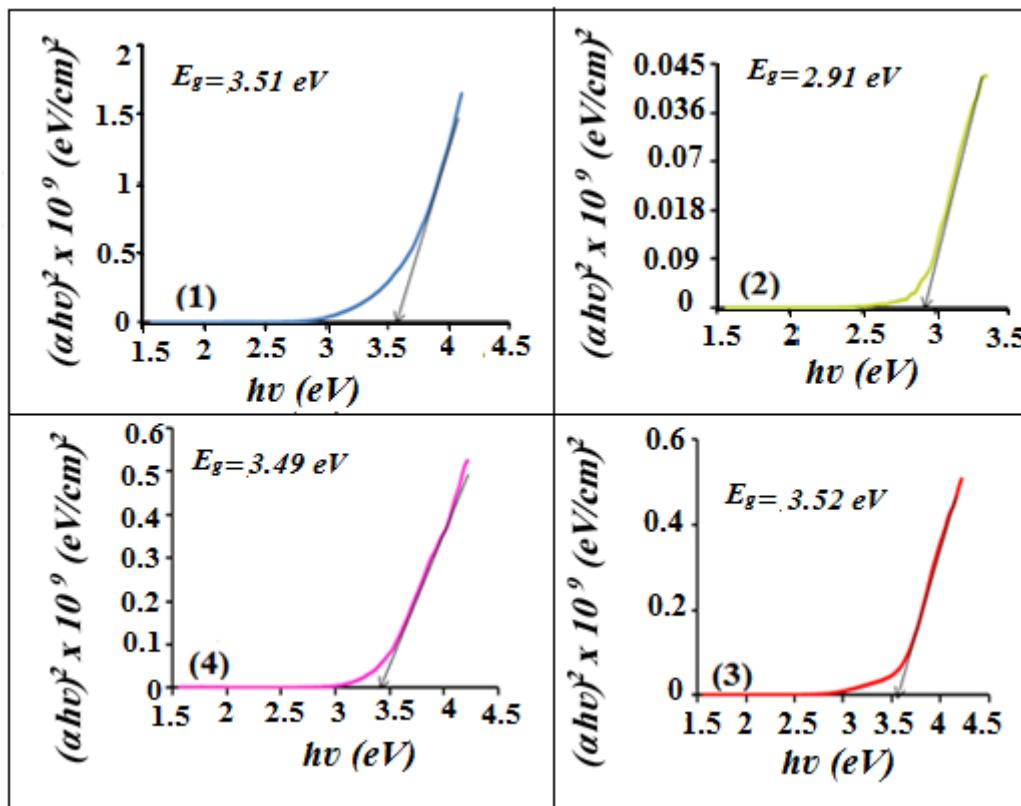


Fig.10. The optical band gap of complexes.

4. Conclusion

Four new complexes were synthesized from the reactions of $M(CO)_6$ ($M= Cr, Mo, W$) with the 6,6'(([1,1'biphenyl]4,4'diylbis(azaneylylidene)) bis(methaneylylidene))bis(2,4dichlorophenol) (H_2L) Schiff base in THF. The binuclear carbonyl complex $[Cr_2(CO)_2(L)_2]$ and three oxo complexes $[Mo_2O_4(L)_2]$, $[W_2O_4(L)_2]$ and $[Mo_2O_5(CO)L].H_2O$ were characterized. Analytical and spectral data showed that H_2L was co-ordinated as a dibasic ligand via two imine nitrogen and two deprotonated phenolic oxygen atoms. The magnetic measurements of the synthesized complexes showed all the complexes were diamagnetic except $[Cr_2(CO)_2(L)_2]$ complex was paramagnetic. Activation thermodynamic parameters, such as activation energy, enthalpy, entropy and Gibbs free energy change of complex decomposition, have been determined from the TG curves. Furthermore, these complexes exhibited fluorescence properties and could be used as photoactive materials. The optical band gap values of all complexes illustrate the semi-conductivity properties of these compounds.

References

- [1] X. F. Luo, X. Hu, X. Y. Zhao, S. H. Goh, X. D. Li, Miscibility and interactions in blends and complexes of poly(4-methyl-5-vinylthiazole) with proton-donating polymers, *Polymer*, 44: (2003) 5285-5291.
- [2] R. Baumgrass, M. Weiwad, F. Erdmann, J. O. Liu, D. Wunderlich, S. Grabley, G. Fischer, Reversible inhibition of calcineurin by the polyphenolic aldehyde gossypol, *J Bio Chem.*, 276:(2001) 47914-47921.
- [3] C. A. Hunter, Self-Assembly of Molecular-Sized Boxes, *Angew Chem Int Ed Engl.*, 34:(1995) 1079–1081.
- [4] P. J. Stang, D. H. Cao, S. Saito, A. M. Arif, Self-Assembly of Cationic, Tetranuclear, Pt (II) and Pd (II) Macroyclic Squares. x-ray Crystal Structure of $[Pt^{2+}(dppp)(4, 4'\text{-bipyridyl})\cdot cntdot\cdot 2-OSO_2CF_3]_4$, *J Am Chem Soc.*, 117: (1995) 6273–6283.
- [5] I. Y. Wu, J. T. Lin, J. Luo, S. S. Sun, C. S. Li, K. J. Lin, C. Tsai, C. C. Hsu, J. L. Lin, Syntheses and Reactivity of Ruthenium σ -Pyridylacetylides, *Organometallics*, 16: (1997) 2038–2048.
- [6] A. A. Abu-Hussen, Synthesis and spectroscopic studies on ternary bis-Schiff-base complexes having oxygen and/or nitrogen donors, *J Coord Chem.*, 59: (2006) 157–176.
- [7] M. S. Karthikeyan, D. J. Parsad, B. Poojary, K. S. Bhat, B. S. Holla, N. S. Kumari, Synthesis and biological activity of Schiff and Mannich bases bearing 2, 4-dichloro-5-fluorophenyl moiety, *Bioorg Med Chem.*, 14: (2006) 7482–7489.

- [8] S. M. El-Medani, Structural studies of some chromium, molybdenum and tungsten complexes of N-salicylidene-2-hydroxyaniline, *J Coord Chem.*, 57: (2004) 115–122.
- [9] S. M. El-Medani, Reactions of chromium, molybdenum and tungsten carbonyls with a tetradentate Schiff base, *J Coord Chem.*, 57: (2004) 497–507.
- [10] S. M. El-Medani, M. M. Aboaly, H. H. Abdalla, R. M. Ramadan, Reactions of group 6 metal carbonyls with salicylaldehyde hydrazone, *Spectroscopy Lett.*, 37: (2004) 619–632.
- [11] J. Collman L. S. Hegedus, *Principles and Application of Organotransition Metal Chemistry*, University Science Book, CA, 1980.
- [12] J. Zhao, B. Zhao, J. Liu, W. Xu, Z. Wang, Spectroscopy study on the photochromism of Schiff Bases *N,N'-bis(salicylidene)-1,2-diaminoethane* and *N,N'-bis(salicylidene)-1,6 hexanediamine*, *Spectrochim Acta A.*, 57: (2001) 149–154.
- [13] S. A. Ali, A. A. Soliman, M. M. Aboaly, R. M. Ramdan, chromium, molybdenum and ruthenium complexes of 2-Hydroxyacetophenone Schiff bases, *J Coord Chem.*, 55: (2002) 1161–1170.
- [14] A. A. Soliman, S. M. El-Medani, O. A. M. Ali, Thermal study of chromium and molybdenum complexes with some nitrogen and nitrogen-oxygen donors ligands, *J Ther Analy and Calor.*, 83: (2006) 385–392.
- [15] S. M. El-Medani, , O. A. M. Ali, R. M. Ramadan, Photochemical reactions of group 6 metal carbonyls with N-salicylidene-2-hydroxyaniline and bis(salicylaldehyde)phenylenediimine, *J Mol Struct.*, 738: (2005) 171–177.
- [16] C. Silva da, D. Silva da, L. Modolo, R. Alves, Schiff bases: A short review of their antimicrobial activities, *J Ad Res.*, 2: (2011) 1–8.
- [17] X. Yang, Q. Wang, Y. Huang, P. Fu, J. Zhang, R. Zeng, Synthesis, DNA interaction and antimicrobial activities of copper (II) complexes with Schiff base ligands derived from kaempferol and polyamines, *Inorg Chem Com.*, 25: (2012) 55–59.
- [18] S. Kumar, D. N. Dhar, P. N. Saxena, Applications of metal complexes of Schiff bases – a review, *J Sci Ind Res.*, 68: (2009) 181–187.
- [19] T. H. Sanatkaran, A. Khorshidi, E. Sohouli, and J. Janczak, Synthesis, Crystal Structure, and Characterization of Two Cu(II) and Ni(II) Complexes of a Tetradentate N_2O_2 Schiff Base Ligand and Their Application in Fabrication of a Hydrazine Electrochemical Sensor, *Inorg Chim Acta.*, 506: (2020) 119537–119548.
- [20] S. E. Abd El-Razek, S. M. El-Gamasy, M. Hassan, M. S. Abdel-Aziz, S. M. Nasr, Transition Metal Complexes of a Multidentate Schiff Base Ligand Containing Guanidine Moiety: Synthesis, Characterization, Anti-Cancer Effect, and Anti-Microbial Activity, *J Mol Struct.*, 1203: (2020) 127381–127390.
- [21] O. A. M. Ali, M. M. H. Khalil, G. M. Attia, R. M. Ramadan, Group VI Dinuclear Oxo Metal Complexes of Salicylideneimine-2-Anisole Schiff Base, *Spectroscopy Lett.*, 36: (2003) 71–82.

- [22] R. G. Mohamed, F. M. Elantabli, N. H. Helal, S. M. El-Medani, New Group 6 Metal Carbonyl Complexes with 4,5-Dimethyl-N,N-Bis(Pyridine-2-Ylmethylene)Benzene-1,2-Diimine Schiff Base: Synthesis, Spectral, Cyclic Voltammetry and Biological Activity Studies, *Spectrochim Acta A Mol Biomol Spectrosc.*, 141: (2015) 316–326.
- [23] Y. Guo, X. Hu, X. Zhang, X. Pu, Y. Wang, The Synthesis of a Cu(Ii) Schiff Base Complex Using a Bidentate N₂O₂ Donor Ligand: Crystal Structure, Photophysical Properties, and Antibacterial Activities, *RSC Adv.*, 9: (2019) 41737–41744.
- [24] A. A. Soliman, S. A. Ali, A. H. Marei, D. H. Nassar, Synthesis, characterization and biological activities of some new chromium, molybdenum and tungsten complexes with 2,6-diaminopyridine, *Spectrochim Acta A.*, 89: (2012) 329–332.
- [25] M. M. H. Khalil, H. A. Mohamed, S. M. El-Medani R. M. Ramadan, New group 6 metal carbonyl derivatives of 2-(2-pyridyl) benzimidazole: synthesis and spectroscopic studies, *Spectrochim Acta A.*, 59: (2003) 1341–1347.
- [26] M. A. Taher, S. E. Jarelnabbi, B. E. Bayoumy, S. M. El-Medani, R. M. Ramadan, "Synthesis and Spectroscopic Studies of Some New Molybdenum, Tungsten, and Ruthenium Carbonyl Derivatives of 2-Hydroxymethylpyridine, *Inter J Inorg Chem.*, 2010: (2010) 1–6.
- [27] A. B. Garin, D. Rakarić, E. K. Andrić, M. M. Kosanović, T. Balić, F. Perdih, Synthesis of Monosubstituted Dipicolinic Acid Hydrazide Derivative and Structural Characterization of Novel Co(III) and Cr(III) Complexes, *Polyhedron.*, 166: (2019) 226–232.
- [28] O. A. M. Ali, S. M. El-Medani, D. A. Ahmed, D. A. Nassar, Metal carbonyl complexes with Schiff bases derived from 2-pyridinecarboxaldehyde: Syntheses, spectral, catalytic activity and antimicrobial activity studies, *J Mol Struct.*, 1074: (2014) 713–722.
- [29] S. A. Ali, A. A. Soliman, A. H. Marei, D. H. Nassar, Synthesis and characterization of new chromium, molybdenum and tungsten complexes of 2-[2-(methylaminoethyl)] pyridine, *Spectrochim Acta A.*, 94: (2012) 164–168.
- [30] P. Datta, D. Sardar, A. P. Mukhopadhyay, E. López-Torres, C. J. Pastor, C. Sinha, Group-6 Metal Carbonyl Complexes of Pyridylbenzoxazole and Pyridylbenzothiazole: Synthesis", Structure, Electrochemistry, Photophysical Property and DFT Calculations, *J Organomet Chem.*, 696: (2011) 488–495.
- [31] M. M. H. Khalil F. A. Al-Seif, Group 6 Metal Carbonyl Complexes of 3'H-Spiro[Indole-3,2'-(1,3]Benzothiazole-2(1H)]-One, *J Saudi Chem Soc.*, 14: (2010) 33–39.
- [32] S. M. Abdallah, M. A. Zayed, G. G. Mohamed, Synthesis and Spectroscopic Studies of New tetradentate Schiff base and its coordination compounds of NOON donor atoms and their antibacterial and antifungal activity, *Arabian J Chem.*, 3: (2010) 103–113.
- [33] L. H. Abdel-Rahman, A. M. Abu-Dief, R. M. El-Khatib, S. M. Abdel-Fatah, Some New Nano-Sized Fe(II), Cd(II) and Zn(II) Schiff Base Complexes as Precursor for

- Metal Oxides: Sonochemical Synthesis, Characterization, DNA Interaction, in Vitro Antimicrobial and Anticancer Activities, *Bioorg Chem.*, 69: (2016) 140–152.
- [34] H. A. Mohamed, Photochemical reactions of chromium, molybdenum and tungsten hexacarbonyls with dimethylglyoxime, *J Mol Struct.*, 784: (2006) 254–258.
- [35] O. A. M. Ali, Synthesis and characterization of molybdenum complexes with salicylideneimine-2-anisole and certain heterocyclic nitrogen ligands, *J Coord Chem.* 60: (2007) 1213–1221.
- [36] Y. Salman, F. B. Barlas, M. Yavuz, K. Kaya, S. Timur, F. Ç. Telli, Synthesis, characterization and biological application of dinuclear Cu(II) complexes of Schiff base ligands of galactochloralose and α -chloralose, *Inorg Chim Acta.*, 483: (2018) 98–105.
- [37] O. A. M. Ali, A. K. Abu Al-Nasr, R. M. Ramadan, "Synthesis and spectroscopic and structural studies of ruthenium carbonyl derivatives of N-salicylidene-2-hydroxyaniline Schiff base, *J Taibah Uni Sci.*, 8: (2014) 258–264.
- [38] A. W. Coats J. P. Redfern, Kinetic Parameters from Thermogravimetric Data, *Nature.* 201: (1964) 68-69.
- [39] H. W. Horowitz, G. A. Metzger, A New Analysis of Thermogravimetric Traces, *Analy Chem.*, 35: (1963) 1464-1468.
- [40] A. A. Frost, R. G. Pearson, Kinetics and Mechanism – A Study of Homogeneous Chemical Reactions, John Wiley, New York., 73: (1961) 719-719.
- [41]. W. H. Mahmoud, G. G. Mohamed, M. M. I. El-Dessouky, Synthesis, structural characterization, in vitro antimicrobial and anticancer activity studies of ternary metal complexes containing glycine amino acid and the anti-inflammatory drug lornoxicam, *J Mol Struct..* 1082: (2015) 12–22.
- [42] S. Shukla, A. P. Mishra, Non-isothermal degradation-based solid state kinetics study of copper (II) Schiff base complex, at different heating rates, *J Therm Anal Calorim.*, 107: (2012) 111-117.
- [43] F. Karipcin, B. Dede, Y. Caglar, D. Hur, S. Ilcian, M. Caglar, Y. Sahin, A new dioxime ligand and its trinuclear copper (II) complex: Synthesis, characterization and optical properties, *Opt Commu.*, 272: (2007) 131–137.
- [44] M. M. Rashad, A. M. Hassan, A. M. Nassar, N. M. Ibrahim, A. Mourtada, A new nano-structured Ni (II) Schiff base complex: synthesis, characterization, optical band gaps, and biological activity, *Apply Phys A.*, 117: (2014) 877–890.

المُلْخَصُ الْعَرَبِيُّ

الوصف الهيكلي ، الدراسات الحرارية ، الفلورسينس والخصائص الضوئية لمشتقات الكربونيل المعدنية



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تم تحضير سلسلة من المتراكبات $[Cr_2(CO)_2L_2]$ (1)، $[Mo_2O_4L_2]$ (2)، $[W_2O_4L_2]$ (3) و $[Mo_2O_5(CO)L \cdot H_2O]$ (4) ناتجة من تفاعل سداسي كربونيلات الكروم والموليبدينوم والتنجستن مع اللحامنة

6,6'-(([1,1'-biphenyl]-4,4'diylbis(azaneylylidene))bis(methaneylylidene))bis(2,4-dichloro- phenol) H₂L .

لقد تم توصيف قواعد شيف ومتراكماتها بواسطه قياس التحليل العنصري، طيف الاشعه تحت الحمراء، طيف الرنين النووي المغناطيسي ، طيف الكتله. أظهرت الدراسات المغناطيسية للمترامكبات الموليدننيوم والتجستان خصائص ديماغناطيسية و متراكب الكروم له خاصيه بارامغناطيسية. وايضاً أجريت دراسة التحليل الوزني الحراري للمترامكبات. وتم حساب القيم الكيناتيكية و الترموديناميكية بيانياً للفاقيده شيف ومتراكماتها. كشفت البيانات الطيفية أن الليجند رباعي التنساق حيث يرتبط من خلال اثنين من النيتروجين الإيمين واثنين من ذرات الأكسجين. وأوضحت نتائج طيف الفلورسنس امكانيه استخدام هذه المترامكبات كمواد حساسه للضوء. أظهرت قيم طاقة فجوة (E_g) النطاق البصري للمترامكبات أنه يمكن استخدام هذه المركبات كأشباه موصلات.