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Synthesis, Characterization and Thermal Behavior of Some Novel Di-Oxomolybdenum (VI) Complexes

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Some novel dioxo-molybdenum (VI) hydrazone complexes of Schiff base ligands with the general formula cis-[MoO_2(L)(solv)] (where LH_2 = Schiff base ligand and solv=ethanol/H_2O) are synthesized and characterized by elemental, spectral analysis and their thermal behavior studied by TGA. Thermal behavior of the complexes studied in the temperature range 30-800°C, with increase of 10°C/min and the study of TGA curves have shown the thermal decomposition of the complexes in four steps corresponding to the release of solvent molecule, two stage decomposition of Schiff base ligands and finally the formation of molybdenum trioxide (MoO_3). Thermogravimetric data is studied using Freeman and Carroll method for evaluating kinetics of the reactions.

Keywords: Freeman and Carroll method, Hydrazone complexes, Schiff base ligands, Thermogravimetric (TGA)

1 Introduction

Schiff base metal complexes have gained great importance in the development of co-ordination chemistry. Complexes containing both transition and non-transition metals with multi-dentate ligand systems having significant stability have been synthesized as they occupy important position in coordination chemistry[1-2]. Further, these complexes are synthesized with interest to explore their catalytic properties, synthesis of drugs, biocides, ion-exchanger materials. They are also expected to help understanding enzymatic functions in bioinorganic chemistry [3-13].

In the present paper we report the synthesis of Schiff bases of salicylaldehyde (sal), o-hydroxyacetophenone (hap), o-hydroxypropiophenone (hpp) and o-hydroxybenzophenone (hbp) with nicotinic acid hydrazide (NAH). The corresponding Schiff bases (LH_2) are N'-salicylidene nicotinohydrazide (H_2sal-NAH), N'[(1Z)-1-(2-hydroxyphenyl) ethylidene] nicotinohydrazide (H_2hap-NAH), N'-[(1Z)-1-(2-hydroxyphenyl) propylidene] nicotinohydrazide (H_2hpp-NAH) and N'-[(1Z)-1-(2-hydroxyphenyl) phenylethylidene] nicotinohydrazide (H_2hbp-NAH). Their dioxo molybdenum complexes having a general formula MoO_2(L)(EtOH) were also synthesized. Both the ligands and the complexes were characterized by elemental analysis, FT-IR Spectra, UV-Visible absorption spectra, and NMR spectra.

Several authors have reported temperature induced oxidative degradation of various materials by thermo analytical methods[14-30]. The basis for calculating kinetic parameters for each succeeding step during progressive decomposition of these materials is often based on model for the kinetic analysis of a TG data. In view of this, thermogravimetric analysis was also performed, and the data were used for calculating activation energy (E_a), and reaction order (n) by applying Freeman-Carroll method.

2 Materials and Methods

Ammonium molybdate (VI) tetrahydrate was purchased from SRL, (Mumbai, India). Salicylaldehyde, o-hydroxyacetophenone, o-hydroxypropiophenone, o-hydroxybenzophenone and nicotinic acid hydrazide were purchased from Lancaster Synthesis Ltd (UK). $MoO_2(acac)_2$ was synthesized using the method previously[31].

2.1 Synthesis of Schiff base ligands (1a-4a)

An ethanolic solution of salicylaldehyde (1.06 ml, 10mmol) o-hydroxyacetophenone (1.36g, 10mmol), o-hydroxypropiophenone (1.50g, 10mmol) or o-hydroxybenzophenone (1.98g, 10mmol) was added to a hot ethanolic solution of nicotinic acid hydrazide (1.37g, 10mmol). The mixture was refluxed for 2-4 h and upon cooling in an ice bath, crystals of yellow

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*Corresponding author (E-mail: sumitarao2000@rediffmail.com) color were obtained which were filtered and washed with ethanol and then dried under vacuum. Yield: 2.45 g, 85% (1a), 2.32g, 85%; (2a) 2.61 g, 91% (3a) and 2.91 g, 87% (4a).

2.2 Synthesis of complexes (1b-4b)

A reaction mixture of hot ethanolic solution of the appropriate Schiff base ligand (1mmol, 1a- 0.241g, 2a-0.255 g, 3a- 0.269 g, 4a- 0.317 g) and [cis-$MoO_2(acac)_2$] (0.326, 1mmol) was refluxed for 6 h. The precipitates obtained were separated from their respective solutions followed by multiple washings with water and ethanol and then dried under vacuum. Yield: 0.50 g, 84% (1b); 0.47 g, 81% (2b); 0.50 g, 81 % (3b); 0.57g, 89% (4b).

2.2 Physical Measurements

Microanalysis of the ligands and their complexes were done on Carlo-Erba 1106 Elemental analyzer. IR spectra were recorded on Nicolet Impact 410 FTIR spectrophotometer. Proton NMR spectra were recorded on a Brucer–Variah 300 MHz instrument. The conductance measurements were done in DMF using a Toshniwal conductivity bridge and a dip type cell calibrated with potassium chloride solution. Electronic spectra were recorded on Perkin Elmer λ 900 UV- vis spectrophotometer. TGA and DTA of all complexes are conducted under nitrogen flow using Mettler Toledo (Star Switzerland SDTA/TGA 851), thermogravimetric Analyzer, at 10°C min^{-1} up to 800ºC.

3 Result and Discussions

The cis-MoO_2 complexes having general formula as [MoO_2 (L)(EtOH)] (where LH_2= Schiff base) are formed due to ligand exchange reaction between Bis(acetylacetonato) dioxo-molybdenum (VI) (MoO_2 $(acac)_2$) and the Schiff base ligands (1a-4a) as shown in Eq:

$$[cis - MoO_2(acac)_2] + LH_2 \xrightarrow{\substack{reflux \\ EtOH,6h}} cis - [MoO_2(L)(EtOH)] + 2acacH \; - - \qquad ...(1)$$

Based on the analytical reports of ligands & their cis-[MoO_2 (L)(EtOH)] complexes (Table 1), it was observed that Schiff base ligands are dibasic and tridentate which completely replace bidentate acetylacetone under the reaction conditions upon reaction with cis-MoO_2 $(acac)_2$ and the sixth coordination position in the complex is occupied by ethanol (Figure 1 ; structures of ligands 1a-4a and 1b-4b for complexes). The molar conductance values of the complexes in DMF were observed in the range 2.5 to 4.5 ohm^{-1} cm^{-2} mol^{-1}, suggesting that they are non-electrolytes.

3.1 IR Spectra

The Infra-Red spectra of the complexes (Table 1 & Fig. 2) displayed two bands in the regions 935-949 and 908-912 cm^{-1} that can be attributed to the *νsym*(O=Mo=O) and *νasym*(O=Mo=O) respectively, indicating the presence of cis MoO_2^{2+} moiety [32-33]. The IR spectra of the Schiff base ligands (1a-4a) exhibited a strong band in the regions 3026-3180 cm^{-1} and 1672-1679 cm^{-1} due to νNH and νC=O groups respectively, which were absent in the corresponding complexes suggesting the enolization of the –C=O of the aroyl keto group giving rise to the –C=N-N=C

Table 1 — Analytical and IR spectral data of ligands (1a-4a) and complexes (1b-4b)

		Elemental Analysis (%) Calculated (found %)			Infrared Data (cm^{-1})					
Sr. no.	Ligands/ complexes	C	H	N	ν (OH)	ν (NH)	ν (C=N)	ν (C=O)	ν (C-O)	ν (Mo=O)
1a	H_2-sal-NAH	64.73	4.56	17.42	3250.00	3100.00	1580.00	1608.00	-	-
	$C_{13}H_{11}N_3O_2$	(65.83)	(4.32)	(17.46)						
1b	MoO_2(sal-NAH)	43.58	3.63	10.17	3315.00	-	1560.00	-	1151.00	920.00
	$MoC_{15}H_{15}N_3O_5$	(43.97)	(3.65)	(10.20)			1535.00			913.00
2a	H_2-hap-NAH	65.88	5.09	16.40	3493.57	3179.55	1649.00	1672.00	-	-
	$C_{14}H_{13}N_3O_2$	(65.61)	(5.08)	(16.17)						
2b	MoO_2(hap-NAH)	44.97	3.98	9.83	3453.14	-	1598.91	-	1150.0	935.30
	$MoC_{16}H_{17}N_3O_5$	(45.10)	(3.74)	(9.70)			1556.60			908.20
3a	H_2-hpp-NAH	66.90	5.57	15.61	3226.00	3025.83	1651.50	1678.8	-	-
	$C_{15}H_{15}O_2N_3$	(66.40)	(5.60)	(15.36)						
3b	MoO_2(hpp-NAH)	42.76	2.37	9.60	3108.0	-	1605.50	-	1148.68	941.30
	$MoC_{17}H_{19}N_3O_5$	(42.26)	(2.30)	(9.52)			1555.70			910.00
4a	H_2-hbp-NAH	71.92	4.73	13.24	3172.90	3043.40	1653.70	1678.90	-	-
	$C_{19}H_{15}N_3O_2$	(71.90)	(4.75)	(13.25)						
4b	MoO_2(hbp-NAH)	51.54	3.88	8.89	3059.90	-	1600.11	-	1150.00	948.87
	$MoC_{21}H_{19}N_3O_5$	(51.24)	(4.02)	(8.79)			1553.0			912.34

moiety[34] and consequent deprotonation upon coordination. Display of a new band in the spectra of the complexes due to νC-O, observed in the region 1149-1150 cm^{-1} further supports enolization. A strong band at 1649-1654 cm^{-1} due to νC=N shows a shift to lower frequency by 50 cm^{-1}, suggesting it's coordination to the metal center.

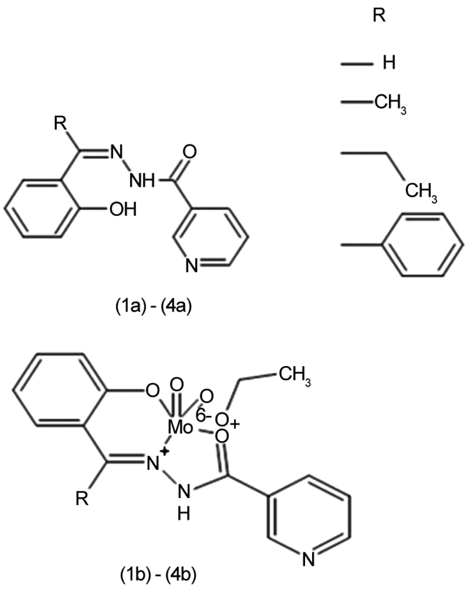

Fig. 1 — Structures of Schiff base ligands (1a-4a) and their complexes with cis-MoO_2 (1b-4b).

In the IR spectra (Table 1) of the complexes it is also seen that both symmetric and asymmetric stretching of cis-MoO_2 in the complex formed with (H_2hbp-NAH) (4b) occur at a comparatively higher energy (912 and 949 cm^{-1}) than the corresponding (H_2hpp-NAH) (3b) (910 and 941 cm^{-1}), (H_2hap-NAH) (2b) (908 and 935 cm^{-1}) and (H_2sal-NAH) (1b) (913 and 920 cm^{-1}) respectively. Also, the difference between sym and asym frequencies is small (Δν= 7, 27 and 31cm^{-1}) for complexes (1b), (2b) and (3b) and greater (Δν = 37 cm^{-1}) for complex (4b). The reason for these variations in stretching frequencies of the cis–MoO_2 moiety may be due to progressively decreasing steric and electron –withdrawing character of benzyl, ethyl, methyl and -H groups on azomethine carbon in the complexes (4b), (3b), (2b) and (1b), respectively.

3.2 Electronic Spectra

The electronic spectra of the complexes (Table 2) measured in DMF showed λmax in the range 390-400 nm which may be due to LMCT transitions which is also reported by another authors[35-38]. No d-d transitions were observed because of $4d^0$ system. As

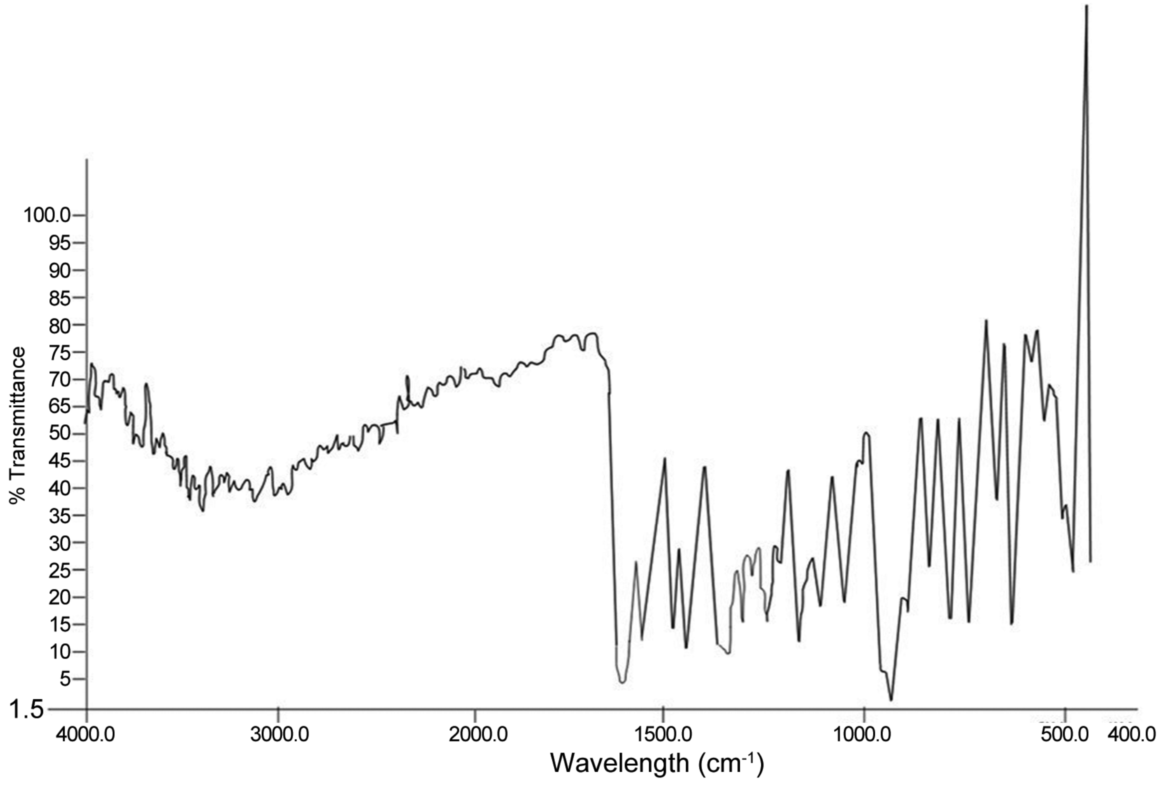

Fig. 2 — IR spectra of complex MoO_2 (hpp-NAH) (C_2H_5OH) (3b).

Table 2 — UV-VIS and ^{1}H NMR spectral data of complexes

Sr.No.	*Ligands/ complexes*	^{1}H NMR , ppm	UV λ (ε $M^{-1}cm^{-1}$)
1b	MoO_2(sal-NAH) $MoC_{15}H_{15}N_3O_5$	8.34 (s, -CH,1H); 1.06-1.17(q,-CH_3,3H); 3.16-3.31(t,-CH_2 ,2H); 6.87-8.75 (m, -ArH,8H); 12.91(s, -OH,1H)	410 (0.3 x10^4)
2b	MoO_2(hap-NAH) $MoC_{16}H_{17}N_3O_5$	1.06-1.17 (t, -CH_3, 3H);1.25(s,-CH_3,3H); 3.16-3.31(q,-CH_2 ,2H); 6.94-9.39(-ArH,7H); 12.91(s, -OH,1H)	375 (1.3x10^4)
3b	MoO_2(hpp-NAH) $MoC_{17}H_{19}N_3O_5$	1.17-1.28(t, -CH_3,3H); 2.90-3.61(q,-CH_2,4H); 6.9-8.3(ArH-6H);12.92(sOH,1H)	390 (8.0x10^3)
4b	MoO_2(hbp-NAH) $MoC_{21}H_{19}N_3O_5$	1.19-1.30(t,-CH_3,3H);3.41-3.70(q,-CH_2,2H); 7.50-8.60(m,-ArH,13H);12.93(s,-OH,1H)	405 (7.5x10^3)

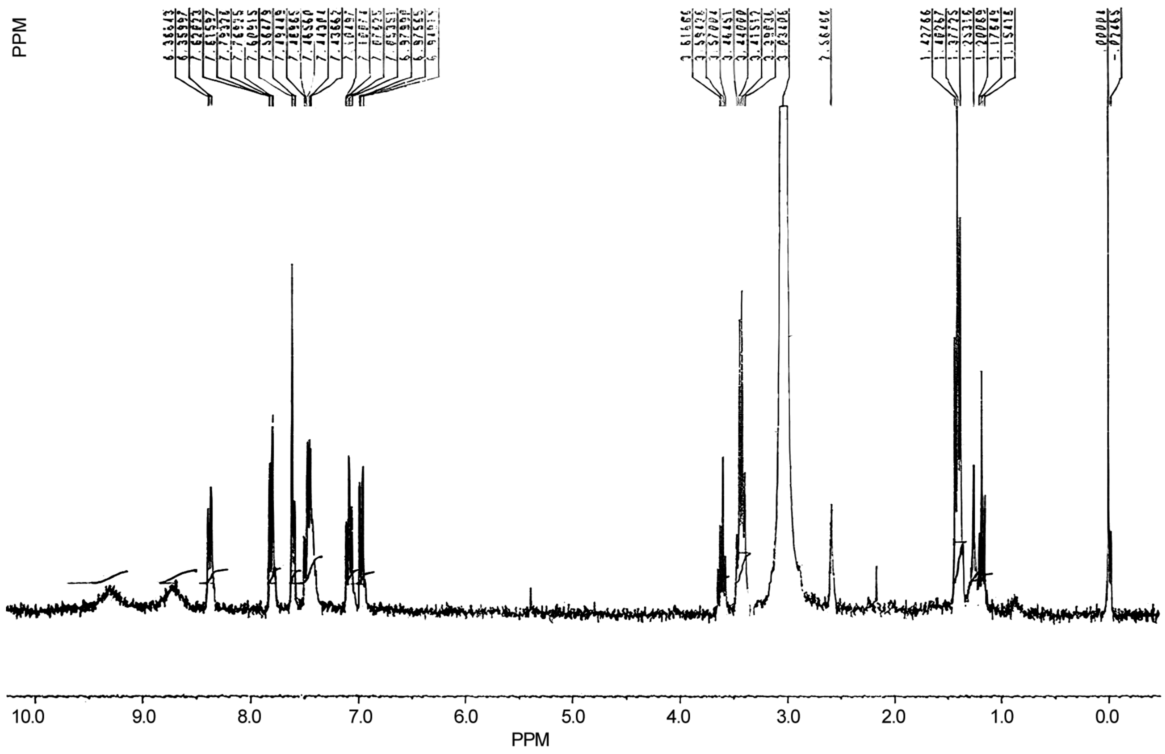

Fig. 3 — ^{1}H NMR spectra of complex MoO_2 (hpp-NAH) (C_2H_5OH) (3b).

expected for a d^0 system, these dioxomolybdenum (VI) complexes are found to be diamagnetic.

3.3 1H NMR Spectra

The ^{1}H NMR spectra (Table 2 & Fig. 3) of the ligands exhibit two signals in the range 11.20-11.80 ppm (s,1H each) and 12.20-13.20ppm (s,1H) due to NH and phenolic OH protons, respectively. These signals were not seen in the spectra of the complexes suggesting that coordination of the ligand with metal center was through phenolic oxygen and enolization of the –C=O of the aroyl keto group and subsequent deprotonation. A multiplet in the range 6.65-9.3 ppm was seen in spectra of ligands which can be attributed to the aromatic protons and did not undergo any significant change after coordination. The presence of the singlet, triplet, and quartet of OH, CH_3 and CH_2 respectively at 12.91-12.93, 1.06-1.30 and 3.16-3.70 ppm, indicate that ethanol is coordinated to metal center.

Based on the FT-IR data, electronic spectral data and NMR it is inferred that these Schiff base ligands behave as tridentate and form six-coordinate MoO_2 complexes with the sixth site being occupied by ethanol molecule.

3.4 Thermogravimetric Analysis of Complexes

The thermograms were interpreted and analysed for calculating the % weight loss at different temperatures. The calculated and observed thermal decomposition values for all the complexes (1b-4b) are shown in Tables 3.

Table 3 — Thermal decomposition data of complexes (1b-4b)

Sr. No.	T_d (°C)	% Weight Loss						Ea (KJ/mol)	n
		80-102°C		296-420°C		420-770°C			
		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.		
1	1b MoO_2(sal-NAH) $MoC_{15}H_{15}N_3O_5$	10.77	10.70	34.91	34.50	48.39	48.00	19.91	0.98
2	2b MoO_2(hap-NAH) $MoC_{16}H_{17}N_3O_5$	10.43	10.45	37.22	36.89	48.39	47.58	16.66	1.08
3	3b MoO_2(hpp-NAH) $MoC_{17}H_{19}N_3O_5$	9.40	9.25	44.02	43.82	48.39	47.71	21.14	0.99
4	4b MoO_2(hbp-NAH) $MoC_{21}H_{19}N_3O_5$	11.39	11.20	32.43	31.90	48.39	47.62	21.85	0.85

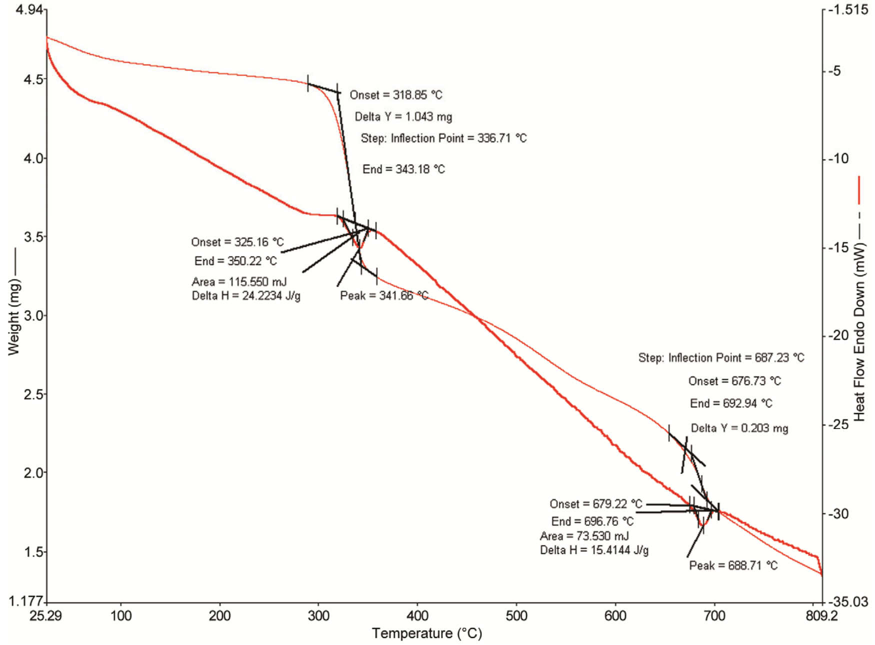

Fig. 4 — TG curve for the Complex MoO_2 (hap-NAH) (C_2H_5OH) (1b).

The TG curves exhibit weight loss in four steps corresponding to the release of solvent molecule, two stage decomposition of Schiff base ligands and finally the formation of molybdenum trioxide The TG curves of 1b complex are shown in Fig. 4.

Complexes (1b-4b) undergo a rapid weight loss of 9.25-11.20% from 80-102°C due to release of coordinated C_2H_5OH molecule. The total weight loss of 47.62-48.0% by two step decomposition, which are significant weight loss of 31.90-43.82% from 296-420°C and gradual weight loss of 3.89-15.72% between 420-770°C, is attributable to the concomitant release of hap-NAH, hpp-NAH, hbp-NAH and sal-NAH organic ligands.

The kinetic parameters and activation energy (Ea) was calculated to know the thermal stability of complexes based on the observed thermograms. The following equation of Freeman-Carroll was applied to obtain the kinetic terms of complexes 1b-4b,

$$\frac{(\Delta \log dw/dt)}{(\Delta \log Wr)} = \left(-\frac{Ea}{2.303R}\right) - \frac{\Delta(1/T)}{\Delta \log Wr} + n$$

where, dw/dt = rate of change of weight of complex with respect to time, $Wr = Wc\text{-}W$, where Wc is the weight loss at the completion of the reaction or at definite time and W is the total weight loss up to time

t. T is the temperature, R is the gas constant and n is the order of reaction. On plotting a graph between

$$\frac{(\Delta \log dw/dt)}{(\Delta \log Wr)} \; verses \; \frac{\Delta(1/T)}{\Delta \log Wr}$$

order of reaction (n) and Ea is calculated using the values of intercept and slope, respectively. The Ea values for the complexes are found to be in the range of 16-22 k J mol^{-1}, indicating that they are thermally labile complexes. The thermal decomposition reactions follow pseudo first order kinetics (Table 4)

4 Conclusion

The Schiff base ligands(1a-4a) described above contain three donor atoms and co-ordinate with di-oxo molybdenum using phenolic oxygen, azomethine nitrogen and enolic oxygen atoms. Their corresponding cis-MoO_2^{2+} (1b-4b) complexes are monomers, non-electrolytes, diamagnetic and six coordinated. Solvent molecule (C_2H_5OH) is also coordinated with metal center and is present in the sixth coordination site of the complex. Kinetic studies done using Freeman and Carroll method show that these complexes decompose following pseudo first order reaction.

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