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Bidentate coordinating behaviour of chalcone based ligands towards oxocations: VO(IV) and Mo(V)

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HIGHLIGHTS

- Chalcon containg ligands are associated with biological activities.
- The VO(IV) and MoO(V) metal containing compounds are highly biological active materials.
- Such compounds are also used as catalyst.
- The main aim to synthesize such compounds as mesomesogens, due to shorter length of the ligands it will not exhibit mesomorphic property.
- The main findings are characterization of such compounds by spectroscopic, thermal and magnetic properties and determine the geometry.

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Introduction

G R A P H I C A L A B S T R A C T



ABSTRACT

We synthesized and studied the coordinating behaviour of chalcone based ligands derived from DHA and n-alkoxy benzaldehyde and their complexes of VO(IV) and MoO(V). The chalcone ligands are characterized by elemental analyses, UV-visible, IR, ¹H NMR, and mass spectra. The resulting oxocation complexes are also characterized by elemental analyses, IR, ¹H NMR, electronic, electron spin resonance spectra, magnetic susceptibility measurement and molar conductance studies. The IR and ¹H NMR spectral data suggest that the chalcone ligands behave as a monobasic bidentate with O:O donor sequence towards metal ion. The molar conductivity data show them to be non-electrolytes. From the electronic, magnetic and ESR spectral data suggest that all the chalcone ligand complexes of VO(IV) and MoO(V) have distorted octahedral geometry.

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Chalcones based ligands and their metal complexes play a prominent role in modern coordination chemistry. These compounds possessing novel structure features, interesting spectral and magnetic properties, have been the subject of intensive research due to their importance in medical, agriculture, analytical, biological and industrial fields. Chalcones are the condensation product of acetophenonne with aromatic aldehydes in the presence of strong base. In resent years a number of β -dicarbonyl compounds in which the carbonyl function(s) bonded to olefinic linkage(s) have gained considerable importance [1–3] mainly because of the fact that such compounds are structurally related to the active chemical constituents of several traditional medicinal plants. Chalcone is an aromatic ketone that forms the central core for a variety of important biological compounds, which are known

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collectively as chalcones. They show antibacterial, antifungal, antitumor and anti-inflammatory properties. Some chalcones demonstrated the ability to block voltage-dependent potassium channels [4].

The antimalarial activity of chalcones was first noted when licochalcone-A, a natural product isolated from Chinese liquorice roots, was reported to exhibit potent in vivo and in vitro antimalarial activity [5]. Subsequently, a synthetic analogue, 2,4 dimethoxy-4-butoxychalcone, was reported to have outstanding antimalarial activity [6].

The photo-alignment technique was introduced for the reduction of contamination that reduce the contrast ratio and the static electricity buildup that cause cross-track shorts or failure of thinfilm transistors [7]. For the application of photo-alignment technique to VA-LCD, polyimide film was used as an alignment layer, which is composed of DOCDA-DAP [5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylicanhydride1/1,4-diaminophenol]. Generally, polyimides exhibit high anchoring energy and good thermal stability. The chalcones derivatives were introduced on the surface of the PI film through chemical modification. The chalcone derivatives react fast with irradiation of UV light. The anisotropy of the PI film was induced by irradiating LP–UV light [8,9]. This study is designed for the elucidation of surface effects on liquid crystal alignment mechanism.

Makita et al. synthesized poly(4-methacryloyloxy chalcone) (PM4Ch) or poly(4'-methacryloyloxy chalcone) (PMCh) and investigated the photoreaction of their polymers. The authors also reported that PM_4Ch and PMCh would be employed as a photoalignment film. Hwang and Seo reported copolymers composed of a cholesteryl monomer and a chalcone monomer [10]. However, all the chalcone based polymers did not display mesomorphic properties. SLCPs with chalcone groups are little reported. Photosensitive polymers possess, with a combination of properties such as high photosensitivity, good solubility, good thermal stability, the ability to form films, resistance towards solvents after cross linking, as well as resistance towards plasmas and etching agents [11].

Yeap et al. [12] has been synthesized a series of new chalcone derivatives with a general formula of $CH_3C_nH_{2n}COOC_6H_4$. CH:CHCOC₆H₄ where n = 10, 12, 14 and 16. All of the compounds except undecylcarbonyloxy analogue exhibit Cr_1-Cr_2 transition with smectic-like texture within the Cr_2 phase. Thaker et al. [13] have been synthesized and evaluation of thermal behaviour of two novel series of chalcone-based liquid–crystalline compounds. Rao et al. [14] synthesized the Co(II) complexes from chalcones i.e., 3-(2-pyridyl)-1-(2-hydroxy-phenyl)-2-propen-1-one (PHPO), 3-(1-naphthyl)-1-(2-hydroxy-phenyl)-2-propen-1-one (NHPO), 3-(3,4-dimethoxy-phenyl)-1-(2-hydroxy-phenyl)-2-propen-1-one (DMPHPO).

Experimental

Materials

For the synthesis of chalcone ligands and their metal complexes, solvents like acetone, methanol, petroleum ether, (AR grade), dehydroacetic acid (DHA) (Merk), 4-hydroxy benzaldehyde, alkyl bromides (Lancaster, England) were used. HCl, K_2CO_3 and KOH were made of Polypharm, Mumbai. The metal salts like VOSO₄·5H₂O (National chemicals) and MoCl₅ (Aldrich, USA) were used as received.

Instruments

Elemental analyses (C,H,N) were performed at RSIC, Lucknow. The vanadium metal was estimated gravimetrically as V_2O_5 . A

100 mg sample of VO(IV) complexes were placed in a silica crucible, decomposed by gentle heating and then treated with 2-3 ml of nitric acid, 2-3 times and igniting at 600 °C. Orange colored residues of V₂O₅ were obtained after decomposition and complete drying and weighing [15]. Similarly, Molybdenum was estimated gravimetrically as MoO₃, yellowish white colored residues of MoO₃ were obtained after decomposition and complete drying and weighing [16]. The conductance of oxo cation complexes were carried out on the Equip-Tronics conductivity meter, model No. EQ-664 with range 20 $\mu\Omega$ to 20 m Ω at 306 K temperature. IR spectrum of chalcone ligand and their complexes were recorded at Centre of Excellence, Quality Testing Facility & R & D Centre, GIDC, Vapi with a Perkin Elmer Spectrum-BX, IR spectrophotometer (4000–450 cm⁻¹) using KBr pellets. The electronic spectrum of complexes in the 200-800 nm were obtained in DMSO as a solvent on a SHIMADZU UV 160 A using quartz cell of 1 cm³ optical path. The magnetic measurement of metal complexes at room temperature was carried out on Gouy balance method [17] at M.S. University of Baroda, Vadodara. The mass spectrum were recorded by Electro impact mass spectrometer (GC-MS) at SAIF, Punjab University, Chandigarh. ESR spectrum of all VO(IV) and MoO(V) complexes were recorded by SAIF, IIT, Mumbai, at RT and LNT for polycrystalline state. TGA and DTG were performed on an Al₂O₃ crucible and samples under investigation decomposed in the N₂ atmosphere at a heating rate 10 °C/min at SAIF, Indian Institute of Technology - Madras, Chennai.

Synthesis of chalcone ligands

Synthesis of [A] 4-hydrxy-3[3-(4-η-tetradecyloxyphenyl)aery-loyl]6-methyl-2H-pyrane-2one.

[B] 4-hydrxy-3[3-(4-η-hexadecyloxyphenyl)aeryloyl]6methyl-2H-pyrane-2one.

Synthesis of 4-tetradecyloxy or 4-η-hexadecyloxy – benzaldehyde

4-hydroxy benzaldehyde (0.1 mol, 12.2 g), anhydrous K_2CO_3 (0.15 mol, 20.85 g) and corresponding η -tetradecyl bromide (0.12 mol, 33.24 g) or η -hexadcaylbromide (0.12 mol, 35.4 g) were added to dry acetone (60.00 mL) in a round-bottom flask fitted with a reflux condenser. The reaction mixture was heated on water bath for 12–14 h. The whole mass was then added to cold water and the aldehyde thus separated in the form of oily layer. It was extracted twice with ether. Ether extract was washed with dilute NaOH solution to remove unreacted 4-hydroxy benzaldehyde, followed by water and then dried. Ether was evaporated and the 4- η -alkoxy benzaldehyde thus obtained were purified by distillation under reduce pressure. Boiling points almost agreed with those reported in literature [18–21].

Synthesis of compounds [A] and [B]

Dehydroaceticacid (0.01 mol, 1.68 g) and 4- η -tetradecyloxy Or 4- η -hexadecyloxy – benzaldehyde (0.02 mol, 6.36 g or 7.92 g) were dissolved in the ethanol (80 mL). The ethanolic solution of dehydroacetic acid was added into the ethanolic solution of 4- η -alkoxy benzaldehyde. The reaction mixture made alkaline by adding chilled KOH solution to raise the P^H up to 12. The reaction mixture was heated at 80 °C for 6–7 h. After refluxing, the resulting solution poured into the 50% HCl in cooled ice water and stirred. The resulting mixture was allowed to stand overnight; the precipitate was collected by filtration. Crystallization was done with ethanol. The synthetic route is given in scheme 1 (Fig. 1).

Synthesis of binary metal complexes of VO(IV)

The metal salt VOSO₄·5H₂O (0.001 mol, 0.253 g) was dissolved in water (15 mL). The warmed methanolic solution (\sim 65 °C) of the



Where, $R = C_n H_{2n+1}$, n = 14 and 16, n = 14; A, n = 16; B

[A] 4-hydrxy-3[3-(4-η-tetradecyloxyphenyl)aeryloyl]6-methyl-2H-pyrane-2one

[B] 4-hydrxy-3[3-(4-η-hexadecyloxyphenyl)aeryloyl]6-methyl-2H-pyrane-2one

Fig. 1. Synthetic pathway of chalcone ligands: A and B.

corresponding chalcone ligand [A] (0.002 mol, 0.936 g) or ligand [B] (0.002 mol, 0.992 g) added into the metal solution. After addition was over, 2 g of sodium perchlorate was added to the reaction mixture for raising the P^{H} up to 5–6. It was refluxed for 3–4 h and then concentrated to half of its volume. It was cooled and kept for overnight. The resulting precipitates were filtered, washed with petroleum ether and dried. The purity of the compounds was checked by TLC. TLC shows only one spot indicating compounds are single and pure.

Synthesis of binary metal complexes of MoO(V)

Table 1

The warmed (50 mL) methanolic solution (\sim 65 °C) of the corresponding chalcone ligand [A] (0.002 mol, 0.936 g) or ligand [B]

(0.002 mol, 0.992 g) added into the (40 mL) methanolic solution (0.001 mol, 0.274 g) of MoCl₅. The pH of the reaction mixture was raised with NaOAc⁻ buffer up to six and stirred. The reaction mixture was refluxed for 3–3.5 h. During the refluxing the color of the reaction mixture was changed, the reaction mixture was concentrated up to half of its volume. It was cooled and kept for overnight. The resulting precipitates were filtered, washed with petroleum ether and dried. The purity of the compounds was checked by TLC. TLC shows only one spot indicating compounds are single and pure.

Result and discussion

Physical data and elemental analysis of chalcone ligands [A] and [B] and their metal complexes are shown in Table 1. The present VO(II) and MoO(V) are stable in air at room temperature for longer time. The elemental analyses are good agreement with expected stochiometry of complexes which indicate that the metal to ligand ratio in all VO(II) and MoO(V) complexes is 1:2.

Molar conductance measurements

The molar conductance of the oxovanadium(II) and oxomolybdenum(V) complexes in 10^{-3} M in DMSO as solvent obtained in the range 0.67–7.32 ohm⁻¹ cm² mol⁻¹. The molar conductance of VO(II) and MoO(V) complexes are shown in Table 1. The low conductivity values in DMSO reveal that all complexes are non-electrolytic in nature and there is no counter ion present outside the coordination sphere of oxocations complexes [15,22,23].

FT-IR spectra of chalcone ligand and their oxocation complexes

In the IR spectral studies of ligands only few important absorption frequencies related to groups involved in the complex formation like enolic O—H, aromatic C=C, olefinic C=C, lactone C=O and acetyl C=O in ligands are discussed. The O—H stretching frequency is not observed as broad band and sharp band in the 3600-3200 cm⁻¹ region. This result indicates that chalcone ligand in the solid state remain in keto form (Fig. 1). The lactone carbonyl band observed in the ligand at 1716 cm⁻¹ and 1720 cm⁻¹ in the ligand [A] and [B], respectively. These bands remain unchanged in complex formation, indicating non participation of this group during the complex formation. In the present investigation, in ligands, the bands observed at 1638 cm⁻¹ are assigned to C=O stretching vibration of acetyl carbonyl group [24,25]. A prominent band at 985 cm⁻¹ and 995 cm⁻¹ typical of trans -CH=CH—absorption [26].

The IR spectrum of the metal complexes, the broad band observed at 3420 cm^{-1} [VO(A)₂ (H₂O)] and 3423 cm^{-1} [VO(B)₂ (H₂O)] due to the coordinated water [27]. The sharp band observed at 1659–1653 cm⁻¹ due to v(C=O) of acetyl group of DHA moiety. A band ~40 cm⁻¹ down field of the acetyl group v(C=O) has been observed in the complexes as coordinated to ligands, suggesting

Elemental analysis and some physical data of chalcone ligand and their oxocation complexes.

				Elemental anal	ysis found % (o	calculated %)		
Compounds	Color	Yield (%)	Melting point (°C)	С	Н	М	Molar conductivity $(ohm^{-1} cm^2 mol^{-1})$	$u_{eff}(BM)$
Ligand-A	Bright yellow	65	66	74.48(74.17)	8.46(8.37)	-	_	-
Ligand-B	Bright yellow	67	50	75.59(75.27)	8.63(8.55)	-	-	-
$[VO(A)_2 (H_2O)]$	Green	72	>250	68.53(68.32)	8.01(7.90)	4.95(4.90)	0.67	1.77
$[VO(B)_2 (H_2O)]$	Green	71	>250	69.42(69.23)	8.45(8.24)	4.92(4.73)	2.24	1.78
$[MoO(A)_2Cl]$	Brown	67	>250	64.56(64.35)	7.48(7.26)	8.97(8.86)	7.34	1.75
[MoO(B) ₂ Cl]	Brown	60	>250	65.74(65.53)	7.83(7.61)	8.63(8.42)	7.02	1.74

Table 2

FT-IR spectral data of chalcone ligand and their oxocation complexes.

Functional group and IR frequencies (cm ⁻¹)									
Compounds	v(OH) coord.	v(C=O) lactone	v(C=O) acetyl carbonyl	v(C=0) coord.	—CH=CH— Trans	v(M=0)	v(M—O) stra.	v(M—N) stra.	
Ligand-A	-	1716	1638	-	985	-	-	-	
Ligand-B	-	1720	1638	-	995	-	-	-	
$[VO(A)_2 (H_2O)]$	3420	1719	1659	1281	1008	975	553	471	
$[VO(B)_2 (H_2O)]$	3423	1722	1654	1279	1006	974	551	469	
[MoO(A) ₂ Cl]	-	1719	1656	1280	1001	958	509	485	
[MoO(B) ₂ Cl]		1717	1653	1278	1009	955	504	483	

Table 3

¹H NMR spectral data of chalcone ligand and their oxocation complexes.

Functional gro	Functional group and chemical shifts δ in ppm									
Compounds	a —CH₃ alkoxy chain	b —CH2 alkoxy chain	c ─CH₃ DHA	d OCH ₂	e Hα proton chalcone	f Phenyl proton multiplets	g H _β proton aldehydic	h (─OH···O─) enolic		
Ligand-A	0.84-0.88	1.27-1.89	2.27	2.68	5.92	6.97-8.0	9.88	16.70		
Ligand-B	0.86-0.89	1.25-1.88	2.27	2.66	5.93	6.82-8.01	9.87	16.69		
[VO(A) ₂ (H ₂ O)]	0.85-0.87	1.23-1.89	2.27	2.46	5.92	6.88-7.84	9.87	-		
[VO(B) ₂ (H ₂ O)]	0.85-0.89	1.25-1.90	2.29	2.47	5.95	6.91-7.94	9.86	-		
[MoO(A) ₂ Cl]	0.85-0.87	1.25-1.98	2.16	2.58	5.92	6.65-7.71	9.78	-		
[MoO(B) ₂ Cl]	0.88-0.90	1.26-2.0	2.17	2.57	5.96	6.67-7.80	9.81	-		
H ₃ C O	$\begin{array}{c} (MOO(B)_2(1) & 0.38-0.90 \\ & 1.26-2.0$									



Fig. 2. Mass spectra of chalcone ligand B.

 Table 4

 Electronic spectral data of chalcone ligand and their oxocation complexes.

Complexes	d-d transition (cm	$(n^{-1})/(m)$	Charge transfer band (cm ⁻¹)/(nm)			<i>d-d</i> transition (cm ⁻¹)/(nm)			
	$d_{xy} \rightarrow d_{xy}, d_{yz}, (v_1)$	$d_{xy} \rightarrow d_{x^2-y^2}, (v_2)$	$d_{xy} \rightarrow d_{z^2}(v_3)$				$^2B_2 \rightarrow {}^2E$	$^2B_2 \rightarrow {}^2B_1$	$^{2}B_{2} \rightarrow ^{2}A_{1}$ O(π) \rightarrow d(Mo)
[VO(A) ₂ (H ₂ O)] [VO(B) ₂ (H ₂ O)] [MoO(A) ₂ Cl] [MoO(B) ₂ Cl]	12,787(782) 13,793(725) - -	17,985(556) 16,722(598) - -	20,080(498) 19,880(500) - -	23,360(428) 32,809(305) 28,409(352) 27,624(362)	32,786(305) 32,776(305) 28,735(348) 28,985(345)	37,740(262) 39,215(255) 32,680(306) 32,470(308)	- - 14,388(695) 13,888(720)	- - 18,867(530) 18,518(540)	- 23,255(430) 22,883(437)



Fig. 3. The power ESR spectra of $[VO(A)_2 (H_2O)]$ complex at (a) RT and (b) LNT.



Fig. 4. The power ESR spectra of [MoO(A)₂Cl]complex at (a) RT and (b) LNT.

the participation of acetyl C=O in complex formation. The shift is mainly due to weakening of double bond between carbon and oxygen and also, the pair of electrons from oxygen is involved in the formation of coordinate bond with metal ion [28,29]. The medium but sharp band appeared at 1281–1279 cm⁻¹ in complexes is due to enolic v(C–O) after removing the proton during complexation. This band is shifted towards higher wave number ~27 cm⁻¹ [27,30,31]. The spectrum of all VO(IV) complexes show sharp intense band at 975 cm⁻¹ and 974 cm⁻¹ is indicative of the v(V=O) grouping in complexes [32]. All MoO(V) complexes spectrum shows sharp intense band at 958 cm⁻¹ and 955 cm⁻¹ is indicative of the v(Mo=0) grouping in complexes [33]. The bands in the region 553–504 cm⁻¹ and 485–469 cm⁻¹ which may be due to the formation of M–O and M–N respectively [34]. The FT-IR spectral data of [A]and [B] chalcone ligands and their complexes presented in the Table 2.

¹*H* NMR spectra of chalcone ligands [A] and [B] and their oxocation complexes

¹H NMR spectrum of chalcone ligand exhibits signals at δ 0.84–0.89 ppm as a triplet and δ 1.25–1.89 ppm as a multiplet which are

Table 5

Thermal behaviour and thermodynamic parameters of $\left[\text{VODC}_{16} \ (\text{H}_2\text{O})\right]$ and $\left[\text{MoODC}_{16}\text{Cl}\right]$ complexes.

Complexes	Step	Step analysis temperature °C		ΔE^* (kcal mol ⁻¹)	$C_s = W_s - W_f / W_0 - W_f$	Order of reaction	
		Ti	$T_{\rm max}$	$T_{\rm f}$			
	Ι	120	150	170	15.10	0.291	1
$[VO(B)_2(H_2O)]$	II	255	275	315	10.01	0.345	1
	III	410	425	565	5.38	0.333	1
	Ι	195	205	235	12.13	0.314	1
[MoO(B) ₂ Cl]	II	270	310	330	9.97	0.408	1
	III	405	425	600	4.72	0.397	1

 T_i = Initial decomposition temperature.

 T_{max} = Temperature for maximum rate of decompositions.

 $T_{\rm f}$ = Final decomposition temperature.

attributed to the methyl and methylene protons of alkoxy chain, respectively. The doublet signal appeared at δ 2.27 ppm due to the methyl proton of dehydroacetic acid. A singlet observed at δ 5.92–5.93 ppm can be assigned to the olefinic protons of H $_{\alpha}$ proton of chalcone group. The phenyl multiplets observed at δ 6.97–8.01 ppm. The aldehydic (H $_{\beta}$) proton gives singlet at δ 9.88–9.87 ppm. The 1H NMR spectrum shows the singlet at δ 16.70–16.69 ppm due to the presence of strong intramolecular hydrogen bonding between the phenolic hydrogen and acetyl carbonyl group of the ligands [35], which indicates the chalcone ligand in solution state converted into enolic form.

In the spectrum of VO(IV) and MoO(V) complexes, weak singlet observed up field at δ 2.16–2.29 ppm due to the –CH₃ protons of DHA. The proton of the coordinated water molecule did not observed in solution spectrum of VO(IV) complexes, this coordinated water molecule is further confirmed by thermal analysis. A weak singlet observed at δ 5.92–5.96 ppm can be assigned to H_{α} – protons of –CHa_{β}=CHb_{α}– group. The phenyl multiplets observed at δ 6.65–7.94 ppm. The H_{β} chalcone proton gives singlet at δ 9.78–9.87 ppm. In the ¹H NMR spectrum of VO(IV) and MoO(V) complexes, the peak disappeared at δ ~16.70 ppm of enolic –OH proton of DHA moiety, we concluded that the coordination occur through the oxygen atom of —OH group of dehydroacetic acid, after deprotanation. Their spectral data are presented in Table 3.

Mass spectral study

The mass spectrum of chalcone ligand [B] is represented in (Fig. 2), which also gives molecular ion peak at 497.5 (M^+ + 1), which are also agreement with molecular masses of the ligand [B] ($C_{31}H_{44}O_5 = 496.66$).

UV/visible spectra of chalcone ligand and their oxocation complexes

The electronic spectrum of ligands [A] and [B] have been taken in methanol solvent in the range of 200–400 nm. The high intensity band observed at 246 nm (ε = 4000) and 305 nm (ε = 3900) are due to $\pi \rightarrow \pi^*$ of >C=O group in the ligands [A] and [B], respectively. The low intensity band observed at 383 nm (ε = 3600) and 410 nm (ε = 3600) are due to (–CH=CH–) chalcone group of ligands [A] and [B], respectively.

The electronic spectral results for the coordinate complexes of VO(IV) and MoO(V) in solution are characteristic of an octahedral geometry around the central metal ion [36,37]. From electronic spectrum of VO(IV), three expected low-energy ligand field bands observed at 12,789-13,793 cm⁻¹ (781.9-725.0 nm), 16,722-17,985 cm⁻¹ (598.0–556.0 nm) and 19,880–20,080 cm⁻¹ (503.0– 498.0 nm) range are assigned as ${}^{2}B_{2g} \rightarrow {}^{2}E_{2g}$, ${}^{2}B_{2g} \rightarrow {}^{2}B_{1g}$, and ${}^{2}B_{2g} \rightarrow {}^{2}A_{1g}$ transitions, respectively. According to Ballhausen [38,39], these bands are assigned to ligand field transitions: $d_{xy} \rightarrow (d_{xz}, d_{yz}), d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{z^2}$ corresponding to $b^2 \rightarrow e^*(v_1), b^2 \rightarrow b_1^*(v_2)$, and $b^2 \rightarrow a_1^*(v_3)$ transitions, respectively [40]. In the UV region, bands appeared at 23,360-32,809 cm⁻¹ $(428.1-304.8 \text{ nm}), 32,786-28,735 \text{ cm}^{-1}$ (305.0-348.0 nm) and 39,215–32,470 cm⁻¹ (254.8–307.9 nm). The three bands can be due to the inter ligand transition, whereas the last band can be due to the charge transfer [41]. Similarly, electronic spectrum of MoO(V) exhibits, three expected low-energy ligand field bands observed at 13,888-14,388 cm⁻¹ (746.9-695.0 nm), 18,518-18,867 cm⁻¹ (540.0–530.0 nm) and 22,883–23,255 cm⁻¹ (437.0–



Fig. 5. TGA/DTG curve of [VO(B)₂ (H₂O)] complex.



Fig. 6. TGA/DTG curve of [MoO(B)₂Cl]complex.

430.0 nm) range are assigned as ${}^{2}B_{2} \rightarrow {}^{2}E_{2} (v_{1}), {}^{2}B_{2} \rightarrow {}^{2}B_{1} (v_{2})$, and $O(\pi) \rightarrow d(Mo)(v_{3})$ transitions, respectively [17,42]. In the UV region, bands appeared at 27,624–28,409 cm⁻¹ (362.0–352.0 nm), 28,735–28,985 cm⁻¹ (380.0–345.0 nm) and 32,470–32,680 cm⁻¹ (307.9–305.9 nm). The bands can be due to the inter ligand transition, whereas the last band can be due to charge transfer. These spectral data are consistent with those predicted for six-coordinate VO(IV) and MoO(V) complexes, whose structures are distorted octahedral in C_{4v} symmetry. The electronic spectral data of complexes are presented in Table 4.

Magnetic susceptibility

The magnetic susceptibility measurement of $[VO(A)_2 (H_2O)]$ and $[VO(B)_2 (H_2O)]$ complexes were carried out by Gouy method at room temperature. The observed magnetic moment (μ_{eff}) values are 1.77 BM and 1.78 BM, indicating the VO(IV) compounds in d^1 configuration are normal paramagnetic behaviour having one unpaired electron, s = 1/2. There is no reduced magnetic moment for these compounds, ruling out any antiferromagnetic interaction present in these molecules. Therefore, VO(IV) complexes are mono nuclear. All the two complexes of $[MO(A)_2CI]$ and $[MO(B)_2CI]$ are paramagnetic with effective magnetic moments are 1.75 and 1.74 BM respectively, (shown in Table 1) with no significant magnetic interactions between the neighboring oxomolybdenum(V) ions, indicating mononuclear nature of chalcone ligand complexes [42]. The ESR spectral studies indicate that the MoO(V)compounds are magnetically dilute in nature.

ESR spectra

EPR (ESR) spectroscopy has proven to be a powerful technique revealing three important types of information about: (i) the environment of the oxocations, (ii) the nature of the ligand types, and (iii) the distortion of the complexes and degree of association within the system [43]. The EPR spectrum of $[VO(A)_2 (H_2O)]$ complex in polycrystalline form at RT and LNT shown in (Fig. 3). The EPR spec-

trum of $[VO(A)_2 (H_2O)]$ complex consists of one signal line with shape of the signals in polycrystalline state is lorentzian. The *g* values, |g| or $g_0 = 1.96$ and 1.97, $g_{\perp} = 1.98$ and 1.99 and $g_{\parallel} = 1.94$ at RT and LNT respectively, are essentially the same for the entire complex examined. The $g_{\parallel} < g_{\perp}$ relations are consistent with octahedral geometry in complexes with C_{4v} symmetry with the unpaired electron in the d_{xy} orbital [44]. As expected, the g values are invariably lower than the free electron value ($g_e = 2.0023$). This lowering is related to the spin–orbit interaction of the ground state d_{xy} level, with the low lying excited states.

The EPR spectrum of oxomolybednum complex consists of six ESR line signals arising from the interaction of a single unpaired electron ($S = \frac{1}{2}$) with the quenched orbital angular momentum of molybdenum nucleus of spin I = 5/2. But 75% of molybdenum atoms are isotopes ⁹⁴Mo and ⁹⁶Mo with the nuclear spin quantum number I = 0 and these isotopes give $2I + 1 = 2 \times 0 + 1 = 1$ ESR line. The polycrystalline ESR spectrum of [MoO(A)₂Cl] complex show one typical ESR line at RT and LNT (Fig. 4). The |g| = 1.91 and 1.99, $g_{\perp} = 1.89$ and 1.98, $g_{\parallel} = 1.95$ and 2.02 at RT and LNT respectively. The $g_{\parallel} > g_{\perp}$ relation is consistent with distorted octahedral geometry in complexes with $C_{4\nu}$ symmetry with the unpaired electron in the d_{xy} orbital [17,32].

Thermal study

From the TGA and DTG curves $[VO(B)_2 (H_2O)]$ complex, it has been observed that there are main three steps in the decomposition of $[VO(B)_2 (H_2O)]$ complex. In complex, decomposition starts from 120–170 °C, the first mass loss 1.75% (1.67% cal.) up to 170 °C is in good agreement with loss of one coordinated water molecule. The second step and third step start from 255 to 315 °C and 410 to 565 °C respectively, which is due to the pyrolysis of organic molecule into two steps. After 850 °C, the stable metal oxide V₂O₅ was formed. From TGA and DTG curves of [MoO(B)₂Cl] complex, it has been also observed that there are mainly three steps in decomposition of [MoO(B)₂Cl] complex. The curves of



Fig. 8. Broido plots of $[MOO(B)_2CI]$ complex. Where M = V(IV); X = H₂O and M = MO(V); X = Cl, R = C_nH_{2n+1}, n = 14 and 16, n = 14; A, n = 16; B.

TGA show no loss up to 190 °C, which indicate that neither crystalline nor coordinated water molecule present in $[MoO(B)_2Cl]$ complex. The curves exhibit the first step starts at 195–235 °C, is due to the completely remove of the chlorine atom, found percentage is 3.25% (calc. 3.11%), which is coordinated with the Mo atom. Decomposition of organic ligand begins after 250–600 °C. The DTG curve also shows endothermic peak at 195–235 °C. This is followed by exothermic process with the mass loss 87.5–80.0%, due to the pyrolysis of organic molecule into two steps. After 800 °C the stable metallic oxide MoO₃ formed.

The thermal behaviour and thermodynamic parameters presented in the Table 5. The TGA/DTG curves of $[VO(B)_2 (H_2O)]$ and $[MoO(B)_2Cl]$ of binary complexes also shown in Figs. 5 and 6, respectively. The plot of lnln(1/y) vs 1/T, results in straight line are shown in Figs. 7 and 8. From these plots we calculated the activation energy ΔE^* and also calculated order of reaction. Application of Broido's [45] method used to determine the kinetic parameter for complexes.

The Horowitz–Metzger equation [46,47].

$$C_s = n^{1/(1-n)},$$

$$C_s = W_s - W_f/W_0 - W_f.$$

The above equation is used for the determination of the reaction order, where C_s is the mass fraction of the substance, here W_s stands for the mass remaining at a given temperature, W_0 and W_f are the initial and final masses of the substance, respectively. On the basis of above studies the probable structure of the chalcone ligand complexes of oxovanadium (IV) and oxomolybdenum (V) have distorted octahedral geometry as shown in Fig. 9.



Where M = V(IV); $X = H_2O$ and M = MO(V); $X = CI, R = C_nH_{2n+4}, n = 14$ and 16, n = 14; A, n = 16; B

Fig. 9. Probable structures of chalcone ligand complexes of oxovanadium(IV) and oxomolybednum(V).

Conclusion

The IR and ¹H NMR spectral data suggest that the chalcone ligands behave as a monobasic bidentate with O:O donor sequence towards metal ion. The molar conductivity data show them to be non-electrolytes. From the magnetic measurement, electronic and ESR spectral data suggest that all the oxovanadium(IV) and oxomolybdenum(V) complexes have distorted octahedral geometry. The presence of one coordinated water molecule in the oxovanadium(IV) complexes and one coordinated chlorine atom in the oxomolybdenum(V) complexes are confirmed by thermal study such as TGA and DTG.

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