Syntheses, characterization and biological applications of vanadium complexes derived from chalcone ligands.

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ABSTRACT

The Vanadyl (IV) complexes of substituted chalcones were prepared by refluxing vanadyl sulphate with different substituted chalcones in ethanoic medium. The chalcones were prepared with different aromatic aldehydes like Benzaldehyde, Hydroxy benzaldehyde, nitro benzaldehyde and Chloro benzaldehyde. The synthesized Vanadium complexes were characterized by different spectral techniques. The IR spectral studies revealed that the chalcone derivatives are bidentate ligand. Magnetic studies, electron spin resonance and UV studies suggest that the complexes are in square pyramidal geometry. Conductance measurements suggest that all complexes are non-electrolyte in DMF. The thermal study explained the stability of complex and its decomposition. The synthesized ligand and metal complexes were screened for their antibacterial activity against *E. coli* and *staphylococcus aureus* bacterial strains and for antifungal activity against *P. notatum.*

Keywords: Vanadyl sulphate, Chalcone Ligands, Complexes, Spectral Studies, TGA, Magnetic study, Antifungal and Antibacterial study.

1.Introduction

Chemically chalcones consist of open chain flavonoids in which the two aromatic ring joined by a three carbon. Chalcones are α, β-unsaturated ketones and contain a reactive keto-ethylenicgroup 2-hydroxychalcones and their heterocyclic analogues are also reported to form coordination complexes.

Chalcones are widely distributed in fruits, vegetables, tea, spices and also have applications in biological activities. These are abundant in edible plants and are considered to be the precursors of flavonoids and isoflavonoids[1]. Some chalcones has been employed for the gravimetric estimation of divalent ions of palladium, copper and nickel. Calcium determination by complexometric titration by using chalconemetanil as indicator also has been reported. Chalcones possesses several biological activities with wide ranging. Chalcones use for the the treatment of chronic diseases which involve inflammatory processes, for example, diabetes mellitus[2]. The study of chalcone derivatives has become of much interest in recent years on account of their antibacterial, antiviral activities[3]. Manychalcones based have beenrecognized in a number of screening assays for modulatingimportant pathways or molecular targets in cancer[4,5].

An increasing research interest of vanadium in coordination chemistry is not only due to its exhibiting a range of oxidation dates from +5 to -1 but also complexities exhibited by vanadium complexes and their industrial[6,7], biological[8,9] and medicinal[10,11]applications. Vanadium complexes have been reported to have interesting antibacterial activities[12-15]. It has been reported that V(IV) complexes high effect on anticancer activity[16].

2. Preparation of complexes

To a hot suspension of ligand (0.02M) in ethanol, ethanolic solution (0.01M) of the metal salt vanadyl sulphate ($VOSO_4$) was added drop wise with constant stirring and refluxed for 2-3 hrs. The resulting reaction mixture was cooled to room temperature and maintained upto pH 8.0 by adding ammonia then refluxed further for 30 min. The resultant product was filtered through Whatman filter paper no.1 and repeatedly washed with ethanol until the washing were free from the excess of ligand .These complexes were finally dried under vacuum in desiccator over fused $CaCl_2$.

3. Instrumental methods

The IR spectra of complexes were recorded on a Perkin-Elmer instrument in KBr pallets in the range of 4000-400cm^{-1}. TGA analysis of metal complexes were carried out in nitrogen atmosphere in the range 25-900^{0}C on Rigaku Thermo Plus-8120 TG-DTA instrument with a heating rate 10^{0}C min^{-1} using Alumina as a standard. UV-Visible spectra were recorded using DMF as solvent on Shimadzu UV-VIS spectrophotometer in the range 250-950nm. Electron spin resonance spectra complexes were recorded on E-112 ESR Spectrometer as ‘g’ marker (g = 2.00277) at room temperature. The conductance was measured in DMF solvent on Equiptronics Conductivity meter (EQ-664A).

4. Results and discussion

All the vanadium chalcone complexes are insoluble in water and most common organic solvents but sparingly soluble in DMF. The complexes are stable at room temperature. The elemental analysis shown in Table 1 indicates that, all metal complexes have 1:2 (metal: ligand) stoichiometry for all the complexes.

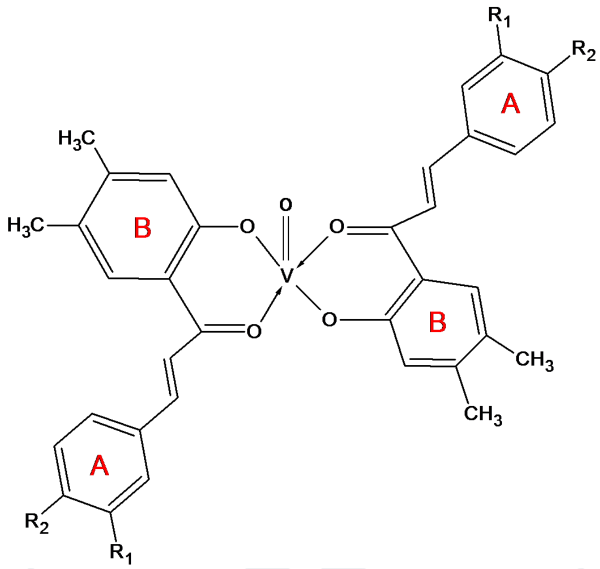

Fig.-1: Structure of Vanadium Complex

VL_1: R_1=H & R_2=H; VL_2: R_1=H & R_2=OH

VL_3: R_1=H & R_2=NO_2 and VL_4: R_1=Cl & R_2=H

All synthesized complexes are green in colour. All complexes are decomposed above 300°C. The molar conductance values obtained for these complexes at the concentration are in the range of 15-27mhos.cm^{2}mol^{-1} suggesting their non-electrolytic nature.

Table 1. Physical and analytical data of metal complexes

Complex	Empirical Formula	MolWt.	Yield %	% Elemental analysis Found (calculated)						Molar conductance mhos.cm^{2}mol^{-1}
				M	C	H	N	Cl	O	
V L_1	$C_{34}H_{30}O_5V$	569	62	9.10 (8.96)	71.52 (71.70)	5.15 (5.27)	-	-	14.13 (14.06)	18.21
V L_2	$C_{34}H_{30}O_7V$	601	59	8.55 (8.48)	67.94 (67.88)	4.91 (4.99)	-	-	18.58 (18.63)	23.46
VL_3	$C_{34}H_{28}N_2O_9V$	659	65	7.68 (7.74)	61.93 (61.91)	4.22 (4.25)	4.28 (4.25)	-	21.88 (21.85)	15.62
V L_4	$C_{34}H_{28}O_5Cl$ V	638	56	8.05 (7.99)	63.88 (63.95)	4.35 (4.39)	-	11.13 (11.1)	12.58 (12.54)	26.33

4.1 IR spectral studies

Some structurally significant IR bands for uncoordinated chalcones and complexes have been scanned in the 4000-400 cm^{-1} region and presented in Table-2. The complexes shows a band in the region 1162-1205 cm^{-1} which corresponds to strong band in the region 1185-1221 in free ligand of chalcones due to υ (C-O). The shifts of this band were observed to move to lower wave numbers indicates bonding of phenolic oxygen atom to metal center via deprotonation. The band in the region 552-573cm^{-1}can be assigned to the stretching modes of the metal to ligand bonds, ν (V-O)[17]. In addition the compound exhibit a strong band in the 952-983cm^{-1} range due to the terminal V=O stretching and this value is close to the majority of oxovanadium(IV) complexes[18]. In the IR spectra of all the ligands an intense band appearing around 1640 cm^{-1} is attributed[19] to (C=O) group. In the complexes this band is observed in the 1618-1626cm^{-1} range. The shifting of band to lower wave number indicating coordination through oxygen of (C=O) group. The band appear around 740 cm^{-1} in chloro complex indicating presence of C-Cl bond. The occurrence of band around 1500 cm^{-1} in VL_3 complex due to ν (C-NO_2) mode.

Table-2: Important IR spectral bands (cm^{-1}) of the complexes

Compound	OH group	C=O	C=C	C-O	C=CH(Aro)	V-O	-NO_2	C-Cl	V=O
L_1	2921	1640	1503	1221	2858	-			-
VL_1	3029	1626	-	1198	2964	552	-	-	963
L_2	3242	1639	1588	1221	2987	-			-
VL_2	3174	1621	1404	1205	3018	561	-	-	952
L_3	3390	1635	1513	1190	2921	-	1520		-
VL_3	3353	1623	1406	1168	3018	556	1490	-	983
L_4	3527	1635	1567	1185	2920	-		738	-
VL_4	3190	1618	1583	1162	3020	573	-	742	976

4.2 Magnetic susceptibility measurement

The magnetic susceptibility for all the Vanadium complexes at room temperature were recorded by the Gouy's method using $Hg[Co(SCN)_4]$ as a calibrant and reported in Table-3. The effective magnetic moments were calculated[13] after applying diamagnetic corrections for the ligand components using Pascal's constants**.** The room temperature μ_{eff} values for the Vanadium complexes were found in the range 1.71-1.76 B.M. The magnetic susceptibilities of the complexes are consistent with square pyramidal geometry around the central metal ion. The magnetic moments of the compounds investigated are in agreement with the findings of electronic absorption spectra.

Table-3: Magnetic moment values of the Vanadium (IV) Chalcone complexes.

Complexes	Magnetic moment(B.M.)
VL_1	1.73
VL_2	1.71
VL_3	1.76
VL_4	1.72

4.3 Thermal measurements

A plot of change in weight v/s temperature or time is known as Thermo gravimetric curve. It records the loss in weight as a function of temperature for transition that involves dehydration or decomposition. The TGA studies of the complexes was recorded in nitrogen atmosphere on Rigaku Thermo Plus-8120 instrument by increasing the temperature from room temperature upto 900°C at the heating rate of 10°C min^{-1}. The decomposition pattern obtained for VO(II) complexes of chalcone ligands follow two major stages (Fig.-2). The thermal dehydration of this complex in the first stage was attributed to the loss of water leaving behind the non hydrated complex takes place between 80^0C -120^0C. In the second stage the complex starts decomposing gradually which occurs in the temperature range corresponds to 220^0C -310^0C, this range correspond to the decomposition of part of chalcone ligand and the observed mass loss was recorded as 29.81% for VL_1, 32.41% for VL_2, 38.78% for VL_3 and 36.90% for VL_4 complex, which shows that at least unstable intermediate are also formed during this degradation stage. The third stage was decomposition of complete chalcone ligand in temperature range of 550^0C -700^0C. The overall total mass loss upto 700^0C is around 88% to 90% which show finally formation of VO. The residue left after 700^0C is around 9% to 11% which resemble the theoretical values. Hence from thermal analysis it is clear that the complexes under study contains two water molecules for VL_1, VL_3 and VL_4 complex and three water molecules for VL_2 complex which are present in the ionic sphere of the complex.

Table-4: Thermal data for Vanadium metal complexes

Complexes	Temperature Range (^{0}C)	% Weight loss		Decomposition product
		Found	Calculated	
VL_1	80-110	5.90	5.95	$2H_2O$
	235-290	29.81	29.75	$C_{14}H_{12}$
	550-680	53.26	53.20	$C_{20}H_{18}O_4$
	700-780	11.03	11.07	VO
VL_2	85-110	8.30	8.24	$3H_2O$
	230-300	32.41	32.36	$C_{14}H_{12}O_2$
	570-660	49.09	49.16	$C_{20}H_{18}O_4$
	700-750	10.16	10.22	VO
VL_3	80-115	5.12	5.17	$2H_2O$
	240-310	38.78	38.85	$C_{14}H_{10}O_4N_2$
	580-700	46.41	46.33	$C_{20}H_{18}O_4$
	720-780	9.70	9.64	VO
VL_4	90-120	5.27	5.34	$2H_2O$
	220-290	36.90	36.94	$C_{14}H_{10}Cl_2$
	550-660	47.85	47.77	$C_{20}H_{18}O_4$
	710-760	9.95	9.94	VO

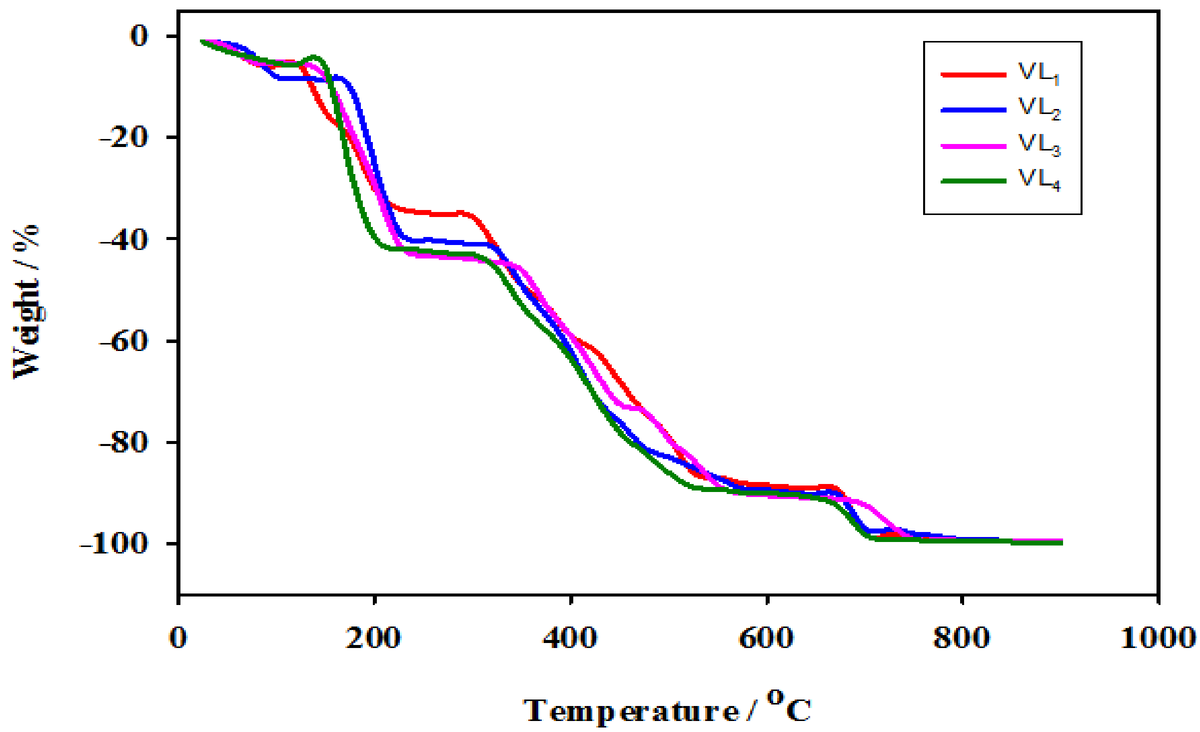

Fig.-2:Thermogravimetry spectra of V (IV) Complexes

4.4 Electronic spectra

The electronic spectra (Fig.-3) of the metal complexes in DMF (10^{-3}M) was recorded on Shimadzu UV-VIS spectrophotometer in the range 200-950nm. The Vanadium chalcone complexes show absorption band in 380-770nm region(Table-5). Most of the VO(II) complexes are green in colour. The electronic absorption spectra of VO(II) complexes showed three bands at 13,015-13,305cm^{-1}, 17.455-17,632 cm^{-1} and 25,755, -25,930cm^{-1}, with 17,455-17,632cm^{-1} representing 10Dq.These bands are assigned to the transitions $^2B_2 \rightarrow {}^2E(d_{xy} \rightarrow d_{xz},d_{yz})$,$^2B_2 \rightarrow {}^2B_1$ ($d_{xy} \rightarrow dx^2$-y^2), and $^2B_2 \rightarrow {}^2A_1$ ($d_{xy} \rightarrow d_z{}^2$) respectively. From these electronic absorption bands and paramagnetic nature, square pyramidal geometry suggested for VO(II) chalcone complexes. As these oxovanadium (IV) belong to the 3d^1 system, there is no interelectronic repulsion in the metal ion so B_0 value of V^{4+} is not available. Therefore calculation of Racah parameter is not possible for these vanadium complexes.

Table-5: Electronic spectral data for vanadium metal complexes

Complexes	(ν1)	(ν2)	(ν3)	Dq (cm^{-1})	CFSE (KJ/mol)
VL_1	13275	17455	25810	1745	-83.50
VL_2	13305	17585	25930	1758	-84.12
VL_3	13015	17632	25755	1763	-84.36
VL_4	13135	17490	25890	1749	-83.69

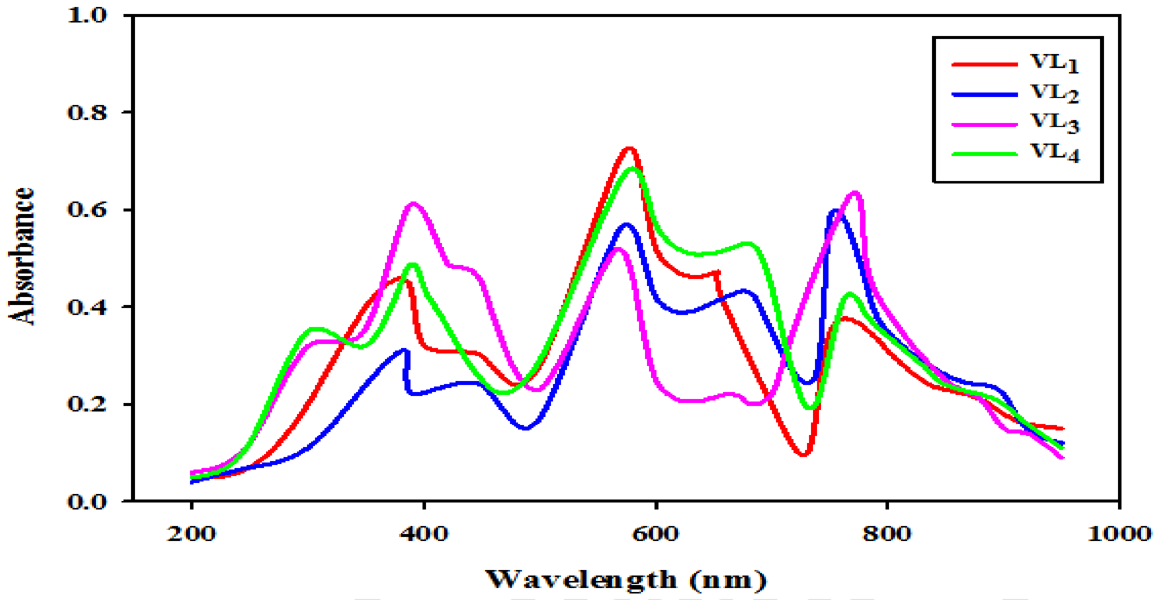

Fig. -3: Electronic spectra of V (IV) Complexes

4.5 Electron spin resonance study

ESR spectrum of VO(II) complexes was recorded at room temperature as polycrystalline sample, on x-band at 9.1GHz, under the magnetic field strength 3000G using TCNE as marker. The value of $g_{||}$ and $g_{\perp}$ shown in Table-6. Paramagnetism of Vanadyl ion arises from the single unpaired electron, its paramagnetism is due to spin angular momentum and $VO^{2+}$is most stable diatomic cation. In V(IV) complexes value of g is below value of free electron. The trend 2.0023 > $g_{\perp}$ > $g_{||}$, observed for the complexes. The EPR signal are split into eight lines suggested that V(IV) complexes are mononuclear. The oxovanadium(IV) ion belong to the $3d^1$ system. Because of strong multiple covalent vanadium oxo-bond, a tetragonal compression occurs and therefore square pyramidal geometry proposed for VO(II) complex. The d orbital split into different level, dx^2-y^2 orbital is least stable as it is face to face with all four equatorial ligands. dxy being most stabilized orbital therefore d^1 electron lies in dxy orbital. As G values of present complexes are lower than 4 indicates, the ligands involve in the complex formation are the strong field ligands.

Table-6: ESR Spectral data of Vanadium (IV) metal complexes

Complex	$g_{\|\|}$	$g_{\perp}$	g_{av}	G axial Symmetry Parameter
VL_1	1.981	1.986	1.984	1.31
VL_2	1.958	1.983	1.975	2.29
VL_3	1.973	1.987	1.982	1.91
VL_4	1.949	1.987	1.974	3.48

4.6 NMR and X-ray: Allcomplexes are paramagnetic in nature, due to this and less solubility in $CDCl_3$, well resolved spectra does not obtained. The XRD pattern do not show good peaks may be due to amorphous nature of the complexes.

5. Antibacterial activity

It is known that killing of bacteria by chelated ligand is more powerful than non-chelated ligand, therefore chelated ligand acts as potent bactericidal agents. It was observed that due to delocalization of the π electrons over whole ligand and partial sharing of its positive charge with donor groups reduce the polarity of a metal ion in a complex. Thus, chelation increases the lipophilic character in complexes and results in an enhancement of activity.[20, 21].The antibacterial results, Table-7, showed that the complexes shows moderate activity against the bacteria E. coli and S. aureus.

Table-7: Antibacterial and antifungal activities (inhibition zone of bacterial growth, mm) of the ligand and metal complexes

	Antibacterial activity		Antifungal activity
Compound	*E. coli*	*S. aureus*	*P. notatum*
	1.0 mg ml^{-1}	1.0 mg ml^{-1}	250 µg disc^{-1}
L_1	6	5	8
VL_1	9	8	9
L_2	8	9	11
VL_2	11	13	13
L_3	5	4	6
VL_3	7	6	7
L_4	7	8	10
VL_4	9	11	12
Neomycin	26	27	-

Antifungal activity

Table-7 showed that metal complexes exhibited significant antifungal activity than chalcones at the same concentration against the fungi *P. notatum*. The order of inhibition with respect to metal complexes was $VL_2 > VL_4 > VL_1 > VL_3$.

It was concluded from above data that electron withdrawing substituents like nitro, cyno at para position in ring A decreases the antibacterial and antifungal activity. Electron donating group like hydroxyl, methoxy at para position increases the activity. Presence of halogen group at meta position in ring A shows good activity than the unsubstituted ring. The increased activity of the chelates can be explained based on the overtone concept and the Tweedy chelation theory[22]. According to the overtone concept of cell permeability, the lipid membrane that surrounds the cell favors the passage of only lipid-soluble material.

6. Conclusion

Based on the results the following conclusion maybe drawn. The higher decomposition temperature and electrical conductance studies show the presence of strong metal-ligand bonding and non-electrolytic nature of the complexes, respectively. Room temperature magnetic studies are indicative of paramagnetic nature and square pyramidal geometry of the VO(II) complexes which is supported by the electronic spectra.The IR spectra shows bonding of the metal through O-donor atoms of the ligands.

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