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Der Pharma Chemica, 2013, 5(4):43-50
(<http://derpharmachemica.com/archive.html>)



ISSN 0975-413X
CODEN (USA): PCHHAX

Synthesis, spectral and thermal studies of dimeric five coordinate oxovanadium (IV) complexes of tridentate ONO donor hydrazones

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ABSTRACT

The oxovanadium (IV) complexes of the hydrazones derived from 2-benzimidazolyl mercaptoaceto hydrazide and *o*-hydroxy aromatic aldehydes have been described. These complexes have been characterized by elemental analyses, molar conductance, magnetic susceptibilities, Infrared, EPR and electronic spectral measurements. The IR spectra suggest the presence of phenoxide bridging and the complexes are formulated as dimers, each unit having five coordinate distorted square pyramidal geometry. The electronic spectra have been interpreted in terms of energy level scheme delineated for distorted square pyramidal geometry. The low μ_{eff} values have been attributed to antiferromagnetic exchange coupling and the principal path for spin coupling is direct σ -metal-metal interaction. The EPR spectrum of the complex indicates a characteristic of dimers with spin-spin coupling between the two adjacent vanadium atoms. The thermal stabilities have been studied by TG and the kinetic parameters of these complexes are calculated using Coats-Redfern and MKN methods. The ligands and their oxovanadium (IV) complexes were screened for their antimicrobial activities.

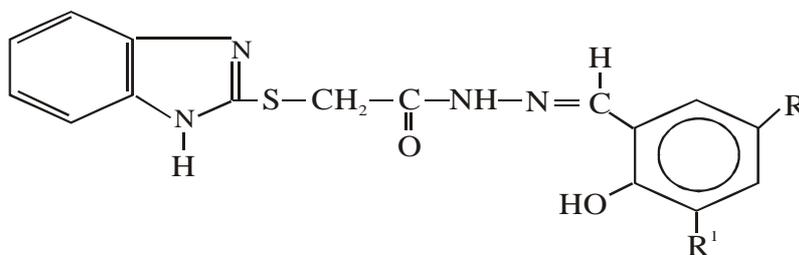
Keywords: Oxovanadium (IV), Tridentate, Distorted square pyramidal, Thermal studies, Kinetic parameters, Antimicrobial activities

INTRODUCTION

The chemistry of oxovanadium (IV) has received considerable attention as the VO^{2+} unit can readily coordinate four or five donor atoms to form the complexes. Among the oxymetal species, the oxovanadium (IV) ion, VO^{2+} is considered as the most stable oxidation of the first transition metal ions [1]. It forms stable anionic, cationic and neutral complexes with various types of ligands. Several generalizations [2-5] regarding the stereochemistry, spin-state and other characteristics such as monomeric and polymeric nature of the vanadyl complexes have been made on the basis of spectral and magnetic studies. However, the theoretical models presented to interpret magnetic and spectral properties of idealized or lower symmetries have often been found inadequate. Few communications deal with the limitations of various generalizations made so far [6,7]. Thus it is obvious that more intensive structural studies are essential in order to utilize vanadyl complexes in chemical reactivity [8] or as potential free-radical like activators of organic and inorganic molecules [7]. In continuation of our earlier work [9-11], this paper describes the synthesis and characterization of oxovanadium (IV) complexes with 2-benzimidazolyl mercaptoaceto hydrazones (structure 1).

MATERIALS AND METHODS

The chemicals used for the synthesis of ligands and complexes were of reagent grade, the solvents were dried and distilled before use according to standard procedures. 2-Mercapto benzimidazole was prepared using the standard method [12] and vanadyl chloride is prepared by using standard method [13]. Vanadium metal in all the complexes was estimated using EDTA and Eriochrome Black-T as indicator and confirmed by igniting the complexes in air and then estimating the metal as pentoxide. The elemental analysis of complexes was recorded on Heraeus Carlo Erba-1108 instrument. Conductance measurements were made using 10^{-3} M solutions of complexes in DMF using Elico conductivity bridge type CM-82 provided with a cell having cell constant 0.52 cm^{-1} . The electronic spectra of complexes in DMF were recorded on Hitachi 150-20 spectrophotometer and IR spectra were recorded on a Impact 410-Nicolet FTIR spectrophotometer in KBr pellets. Magnetic studies of the complexes on powder form were made on a Gouy balance using mercury (II) tetrathiocyanatocobaltate (II) as calibrant. The EPR spectra of the complexes at room temperature and liquid nitrogen temperature were recorded on Varian-E-4X band EPR spectrometer using TCNE as the g - marker. TG and DTG were carried out for a representative complex in the range of room temperature to about 800°C in dynamic air atmosphere on a Rigaku-TAS-100 model thermal analyzer maintaining a heating rate of $10^\circ\text{C}/\text{min}$. Kinetic parameters were computed from the thermal decomposition data. The ligands and their oxovanadium (IV) complexes were screened for their in-vitro antibacterial activity against *E.coli* and *S.aureus* and antifungal activity against *A.niger* and *C.albicans* by cup plate method at the concentration of $1 \text{ mg} / \text{ml}$ of DMSO.

 $L^1H_2 - L^5H_2$

Ligand	R	R ¹
L^1H_2	H	H
L^2H_2	Cl	H
L^3H_2	Br	H
L^4H_2	CH_3	H
L^5H_2	H	OCH_3

1. Structure of ligands

Preparation of 2-benzimidazolyl mercaptoaceto hydrazide [9,14]

To an absolute ethanolic solution (100 ml) containing sodium metal (2.8 g) was added with stirring 2-mercapto benzimidazole (18.7 g) and the resulting mercaptide was slowly treated with ethyl chloroacetate (35-40 ml). The solution turned turbid and in a few minute separation of sodium chloride was observed. The mixture was refluxed on a steam bath for about an hour and filtered hot in a dry Buckner funnel. The alcoholic solution was concentrated to about 50% of its original volume and hydrazine hydrate (15 ml) was added. The solution was refluxed for about 20 h on a steam bath and cooled in ice. The separated solid was filtered, washed with water and crystallized from alcohol.

Preparation of 2-benzimidazolyl mercaptoaceto hydrazone (LH_2)

To an ethanolic solution of 2-benzimidazolyl mercaptoaceto hydrazide (0.1mol) was added salicylaldehyde / substituted salicylaldehyde (0.1mol) and the mixture was refluxed on a steam bath for about 3 h. The solution was filtered hot from the suspended impurities, concentrated and cooled. The separated solid was filtered, washed with water and crystallized from alcohol.

Preparation of oxovanadium (IV) complexes

An ethanolic solution of a ligand (20 ml, 0.01mol) was added to ethanolic solution of vanadyl chloride (20 ml, 0.01mol). The mixture was refluxed in the presence of sodium acetate (1g) for about 3 h on a water bath. The green coloured complex thus obtained was filtered, washed with hot water and ethanol. The complexes were then dried and stored in vacuo over fused calcium chloride.

RESULTS AND DISCUSSION

All the complexes of oxovanadium (IV) are insoluble in common organic solvents such as methanol, ethanol, benzene, chloroform but soluble in DMF and DMSO. The elemental analysis (Table 1) show that all the complexes are of 1:1 metal to liquid stoichiometry then they can be represented by the general formulae [VO(L)]. The molar conductivity of the complexes measured in DMF at 10^{-3} M concentration fall in the range 1.8 - 7.5 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ reveal their non – electrolytic nature [15].

Table-1: Analytical and Physical data of oxovanadium (IV) complexes

Sl No	Complex formula [Abbreviation]	Found (Calcd) %				Molar conductance $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	μ_{eff} B.M
		V	C	H	N		
1	VO(C ₁₆ H ₁₂ N ₄ O ₂ S) [VO(L ¹)]	13.11 (13.02)	49.34 (49.12)	3.05 (3.07)	14.28 (14.30)	4.04	1.32
2	VO(C ₁₆ H ₁₁ N ₄ O ₂ SCl) [VO(L ²)]	12.03 (11.96)	45.18 (45.13)	2.58 (2.59)	13.20 (13.17)	7.21	1.37
3	VO(C ₁₆ H ₁₁ N ₄ O ₂ SBr) [VO(L ³)]	10.74 (10.83)	40.98 (40.87)	2.32 (2.35)	12.04 (11.91)	2.78	1.28
4	VO(C ₁₇ H ₁₄ N ₄ O ₂ S) [VO(L ⁴)]	12.75 (12.56)	50.50 (50.37)	3.42 (3.48)	13.68 (13.82)	1.82	1.21
5	VO(C ₁₇ H ₁₄ N ₄ O ₃ S) [VO(L ⁵)]	12.14 (12.10)	48.48 (48.45)	3.29 (3.32)	13.27 (13.30)	6.02	1.43

The important IR frequencies of the ligands and their complexes are given in Table 2. The infrared spectra of the ligands show a broad band around 3445–3420 cm^{-1} due to the intramolecular hydrogen bonded –OH. The ligands show bands in the regions 3240–3200, 3050–3070 and 1705–1685 cm^{-1} assigned to $\nu(\text{N-H})$ of hydrazide, $\nu(\text{N-H})$ of imidazole moiety and $\nu(\text{C=O})$ respectively. The bands due to $\nu(\text{C-O})$ and $\nu(\text{C=N})$ are located in the regions 1504–1518 and 1654–1648 cm^{-1} respectively [9,12,16]. In spectra of oxovanadium (IV) complexes the band due to $\nu(\text{-OH})$ disappear indicating the involvement of phenolic oxygen atom in coordination through deprotonation [17]. The bands due to $\nu(\text{N-H})$ hydrazide and $\nu(\text{C=O})$ also disappear due to enolization of the ligand followed by coordination of carboxyl oxygen to the metal ion via deprotonation. This is further supported by the appearance of a new band around 1620–1606 cm^{-1} due to $>\text{C=N-N=C}<$. The $\nu(\text{C=N})$ of hydrazide) modes of ligands are found to lower wave number ($\Delta\nu=18-25\text{ cm}^{-1}$) suggesting coordination of the azomethine nitrogen to the central metal ion. A noticeable change in the spectra of the complexes is the shift of $\nu(\text{C-O})$ phenolic to higher energy side by 20–30 cm^{-1} is probably due to the increase in C–O bond strength by extended delocalisation of the π -system of the azine moiety and also the existence of phenoxide bridging in the complexes. The dimeric nature of the complexes is also supported by the appearance of a number of bands between 475–425 cm^{-1} . The present oxovanadium (IV) complexes exhibit the characteristic metal–oxygen multiple band $\nu(\text{V=O})$ stretching frequency in the region 975–960 cm^{-1} , ruling out the possibility of polymeric nature of the complexes as the polymeric oxovanadium (IV) complexes exhibit one or more broad absorption bands below 900 cm^{-1} due to bridging vanadyl group –V-O-V- [18]. The present complexes exhibit broad but medium intense band in the region 975–960 cm^{-1} as against the monomeric species having a fairly strong band $\sim 990\text{ cm}^{-1}$ [19]. The spread of about 10–15 cm^{-1} frequency range is considered as due to the dimeric nature of the complexes.

The non–ligand bands observed in the region 560–498 cm^{-1} and 455–427 cm^{-1} are assigned to $\nu(\text{V-O})$ and $\nu(\text{V-N})$ modes respectively [20,21]. On the basis of IR spectral studies, it appears that the complexes are dimeric in nature with each unit having a five–coordinate square pyramidal geometry. The units are stacked together through phenolic oxygen atom bridges.

Table-2: Important IR frequencies of the ligands and their oxovanadium (IV) complexes

Ligand / Complex	$\nu(\text{C}=\text{N})$ azomethine	$\nu(\text{C}-\text{O})$ phenolic	$\nu(>\text{C}=\text{N}-\text{N}=\text{C}<)$	$\nu(\text{V}-\text{N})$	$\nu(\text{V}-\text{O})$	$\nu(\text{V}=\text{O})$
$\text{C}_{16}\text{H}_{13}\text{N}_4\text{O}_2\text{S}$	1652	1514	-	-	-	-
$\text{VO}(\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}_2\text{S})$	1627	1542	1608	455	542	962
$\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}_2\text{SCL}$	1654	1518	-	-	-	-
$\text{VO}(\text{C}_{16}\text{H}_{11}\text{N}_4\text{O}_2\text{SCL})$	1629	1547	1610	440	540	975
$\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}_2\text{SBr}$	1648	1511	-	-	-	-
$\text{VO}(\text{C}_{16}\text{H}_{11}\text{N}_4\text{O}_2\text{SBr})$	1630	1532	1608	427	560	968
$\text{C}_{17}\text{H}_{15}\text{N}_4\text{O}_2\text{S}$	1653	1509	-	-	-	-
$\text{VO}(\text{C}_{17}\text{H}_{14}\text{N}_4\text{O}_2\text{S})$	1635	1529	1618	436	525	965
$\text{C}_{17}\text{H}_{15}\text{N}_4\text{O}_3\text{S}$	1649	1504	-	-	--	-
$\text{VO}(\text{C}_{17}\text{H}_{14}\text{N}_4\text{O}_3\text{S})$	1628	1533	1607	448	496	970

The values of μ_{eff} at room temperature for these complexes lie in the range 1.21–1.49 B.M. These magnetic moments for vanadyl (IV) complexes are appreciably lower than the spin only value of 1.73 B.M. when the orbital contribution is completely quenched [22]. The results indicate the existence of exchange interactions. The presence of phenoxide bridges giving rise to dimeric structure for these complexes has been supported by infrared spectral studies. A slight lowering may also be attributed to the presence of lower symmetry components and distortion from the idealized symmetry [6]. The mode of exchange coupling is different in VO (IV) complexes than those of other metal ions, particularly copper (II). In the copper (II) complexes, spin-coupling takes place by super-exchange through the bridging oxygen atom and the magnitude of the exchange integral depends on the overlap between the metal atom magnetic orbital ($3d_{x^2-y^2}$) and the orbitals of the bridging atoms, whereas in the oxovanadium (IV) complexes the σ -metal–metal interaction appears to be the principal path for spin–coupling. In the present oxovanadium (IV) complexes having a distorted square pyramidal geometry, the unpaired spin is expected to be in the $3d_{xy}$ orbital, further both the p_x and p_y orbitals of the oxygen atoms acting as phenoxide bridges are involved in σ -bonding with carbon atoms and therefore do not π -donate to the vanadium $3d_{xy}$ orbital. The $3d_{xy}$ orbital is therefore lowered in energy with respect to $3d_{xz}$ and $3d_{yz}$ orbitals. Thus in the binuclear complexes the $3d_{xy}$ orbitals have appropriate symmetry to form σ -bond with each other [5] and as such this σ -metal interaction should be the principal path for spin coupling.

The electronic spectra of complexes were recorded in DMF show bands in the regions $16986\text{--}16297\text{ cm}^{-1}$ and $26214\text{--}25105\text{ cm}^{-1}$. Several methods are available to interpret the electronic spectra of vanadyl complexes of idealized or distorted square–pyramidal geometry. Ballhausen and Gray [23] delineated an energy level scheme for complexes with C_{4v} micro-symmetry (five coordinate square pyramidal) as; $d_{xy} < d_{xz}$, $d_{yz} < d_{x^2-y^2} < d_z^2$, a similar scheme was proposed by Selbin et al [24] to explain the electronic spectra of lower symmetry complexes and those recorded at low temperature. Wood et al [25] suggested the energy level sequence; $a_2(xy) < b_1(xz) < b_2(yz) < a_1(x^2-y^2) < a_1(z^2)$ to account for the electronic spectra of $\text{VO}[\text{N}(\text{CH}_3)_3]_2\text{Cl}_2$ (C_{2v} symmetry) and Kuska and Yang [26] proposed the order; $a_2(xy) < b_1(xz) \approx b_2(yz) < a_1(x^2-y^2) < a_1(z^2)$. According to Wasson et al [27] model the energy level order is $d_{xy} < d_{yz} < d_{xz} < d_{x^2-y^2} < d_z^2$. Except for the splitting of d_{yz} and d_{xz} levels, the scheme is similar to one reported by Ballhausen and Gray.

The electronic spectra of the present complexes have been interpreted on the basis of energy level scheme delineated by Ballhausen and Gray [23] and accordingly the bands $16986\text{--}16297$ and $26214\text{--}25106\text{ cm}^{-1}$ may be assigned to $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_z^2$ respectively. These observations suggest the square pyramidal geometry for the complexes [27].

The EPR spectra of the oxovanadium (IV) complexes have been recorded in polycrystalline state at room temperature. The spectra are quite different from the EPR spectra of magnetically dilute oxovanadium (IV) complexes [5] and are similar to those of magnetically concentrated oxovanadium (IV) complexes [28]. The ESR spectra of the prepared complexes exhibit a band at 1600 gauss due to the spin-forbidden $\Delta m \pm 2$ transition is another criteria for the dimer formulation [29, 30], the high field EPR spectra of powder sample at room temperature of the present oxovanadium (IV) complexes give five spectral lines whereas at liquid nitrogen temperatures a fifteen line spectra, which is a characteristic of dimers with spin-spin coupling between the two adjacent vanadium atoms is obtained. The EPR parameters viz., g_{\perp} and g_{\parallel} for complexes are 2.01 ± 0.02 and 1.99 ± 0.02 respectively with g_{av} value of 1.99. These g -tensors are very close to those reported for similar type of tridentate dibasic Schiff base complexes of oxovanadium (IV) with subnormal magnetic moments [29, 30].

The thermal behaviour of the representative oxovanadium complex $[\text{VO}(\text{L}^2)]$ including stability ranges, peak temperatures, percentage of weight loss and percentage of residue obtained after decomposition process has been studied. The complex undergoes decomposition in two stages. The TG curves of the complex do not show the presence of water molecules either in or out of the coordination sphere. In the complex the first step of decomposition occurs between 105–295°C and the second step of decomposition occurs between 295–545°C. The total loss of weight at the end of second stage is 82.57% (Calcd. 84.27%), which corresponds to the loss of two molecules of ligands. Beyond 545°C a plateau is obtained, which indicates the formation of stable V_2O_5 . The weight of the residue V_2O_5 (41.46%) agrees well with the calculated value (42.72%). The parameters such as energy of activation, entropy of activation and pre-exponential factor calculated using Coats – Redfern and MKN equations are presented in Table 3.

Table 3- Kinetic parameters of $\text{VO}(\text{L}^2)$ complex using Coats – Redfern (MKN) equation

Decomposition stage	Energy of activation (E_a) (kJ mol^{-1})	Arrhenius factor (A) (S^{-1})	Energy of activation (ΔS^*) ($\text{JK}^{-1}\text{mol}^{-1}$)	Correlation coefficient (r)
I	38.8290 (39.0293)	9.9303×10^4 (4.1838×10^4)	-153 (-160)	0.9979 (0.9983)
II	16.4434 (16.7757)	51.3502 (34.4589)	-219 (-222)	0.9968 (0.9986)

The thermal decomposition reactions of the complex were studied using non-isothermal method. In the present complex the kinetic parameters for the decomposition stages of the complex have been calculated using Coats – Redfern and MKN equations by graphical as well as least square method (Fig. 1a and 1b).

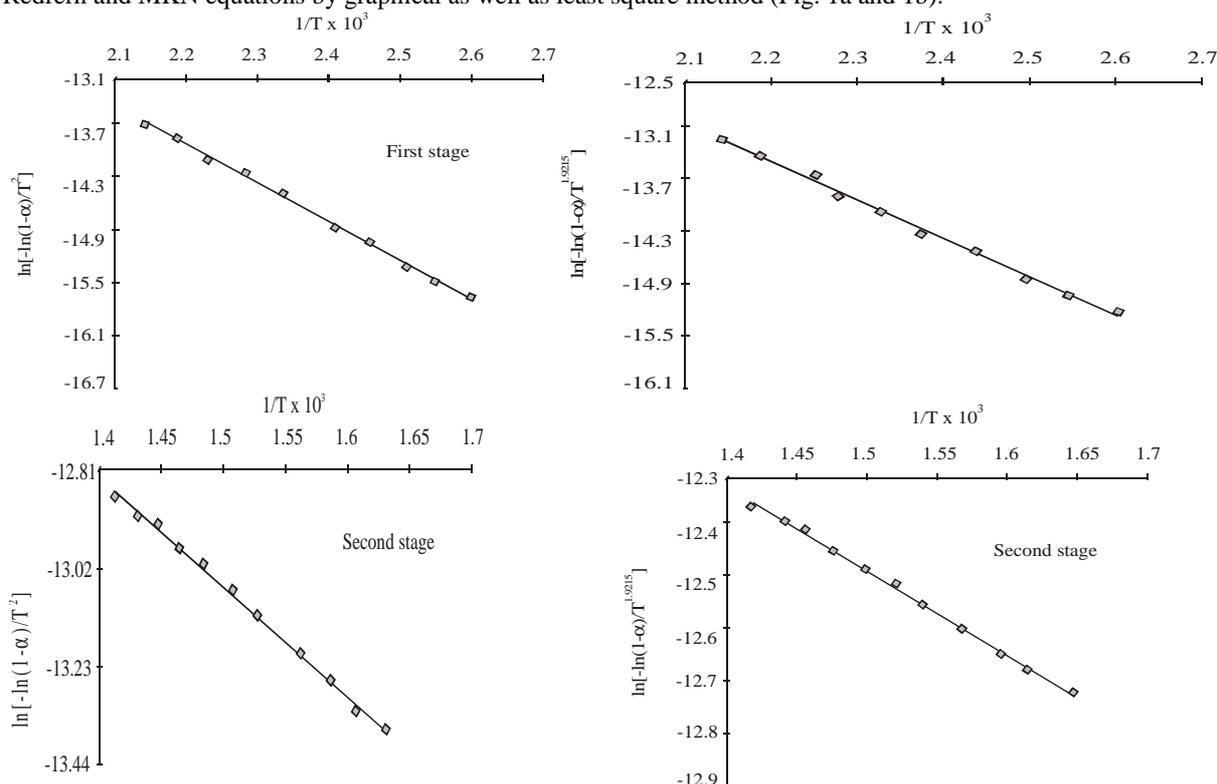


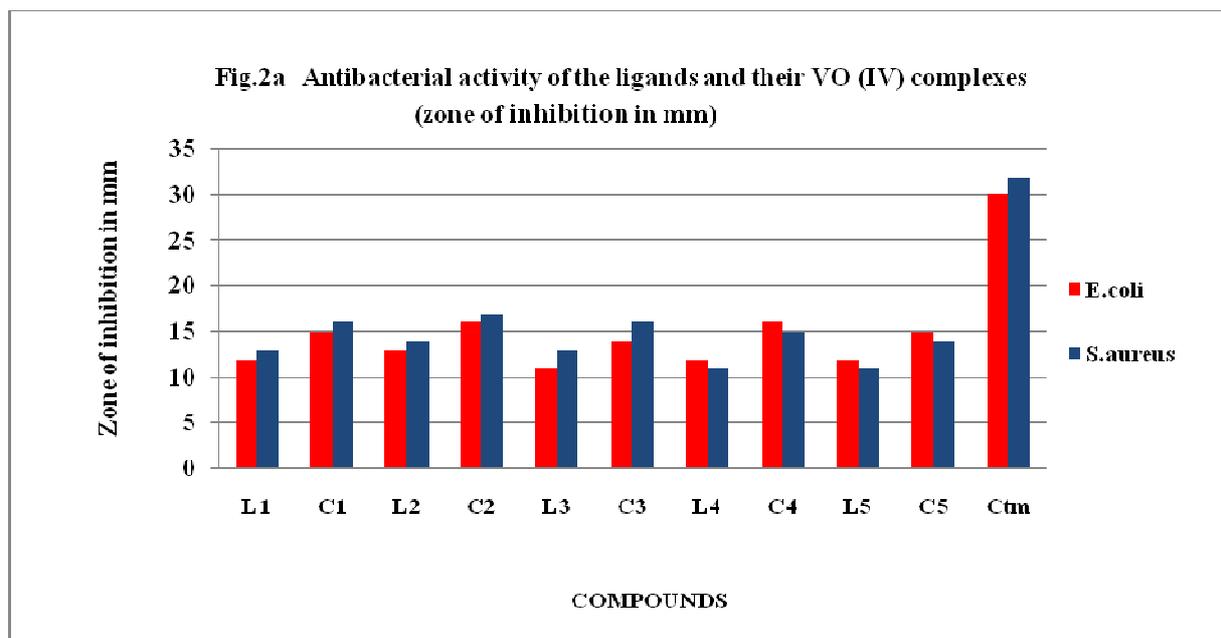
Fig. 1a - Coats-Redfern plots for the two decomposition steps of $\text{VO}(\text{L}^2)$ Fig. 1b - MKN plots for the two decomposition steps of $\text{VO}(\text{L}^2)$.

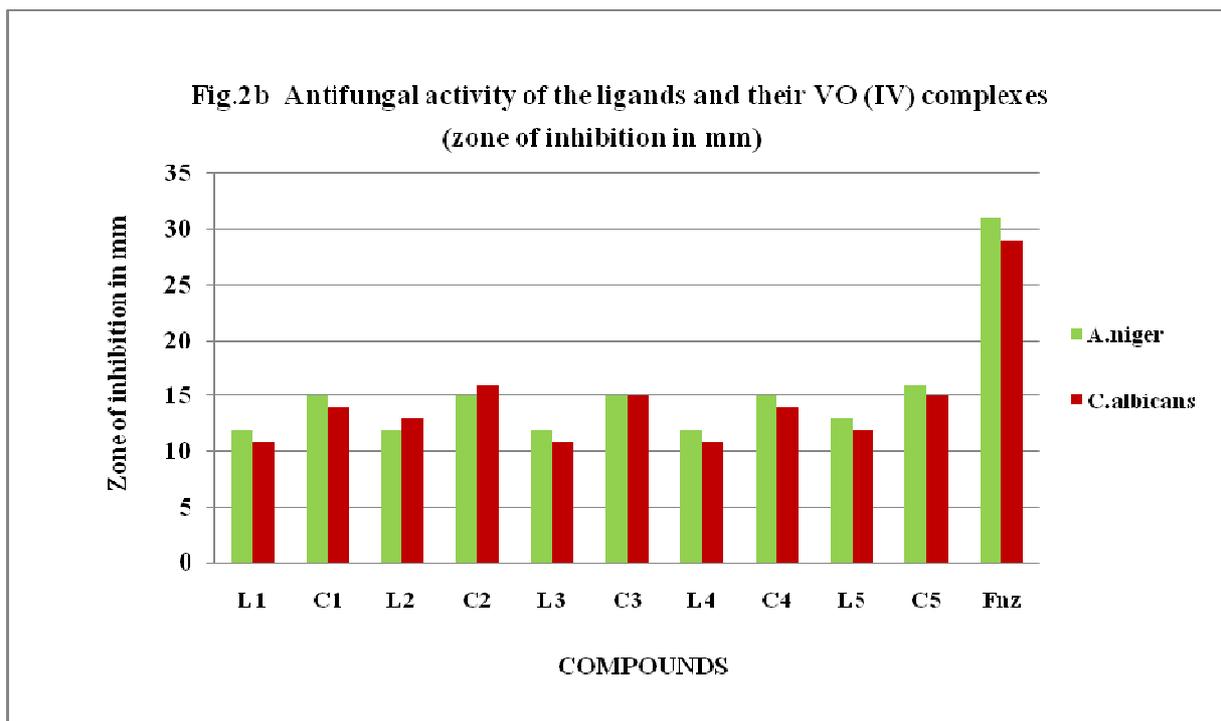
The energy of activation value for the second stage decomposition of the complex is found to be lower than the first stage decomposition. The lower value of energy of activation indicates an increased rate at this stage [25, 31]. The negative entropy of activation values are compensated by the values of the energies of activation. The entropy of activation value decreases from first step to second step indicates that the rate of decomposition increases in stepwise reactions.

Antimicrobial activities were carried out using the cup-plate method [32]. The ligands and their oxovanadium (IV) complexes were screened for their in-vitro antibacterial activity against *E.coli* and *S.aureus* and antifungal activity against *A.niger* and *C.albicans* by cup plate method at the concentration of 1mg / ml of DMSO. The standard drugs contrimoxazole and flucanazole were also tested for their antibacterial and antifungal activities at the same concentration under the conditions similar to that of the test compounds. The antimicrobial activity was measured by measuring the diameter of the inhibited zone in millimeter and the results of the screened compounds are given in the Table 4. The data show that the antibacterial and antifungal activity of the ligand was enhanced on complexation, but less than standard used. The higher inhibition zone of metal complexes than those of the ligands can be explained on the basis of overtone concept and chelation theory.

Table 4- Antimicrobial activity of the ligands and their VO (IV) complexes (zone of inhibition in mm)

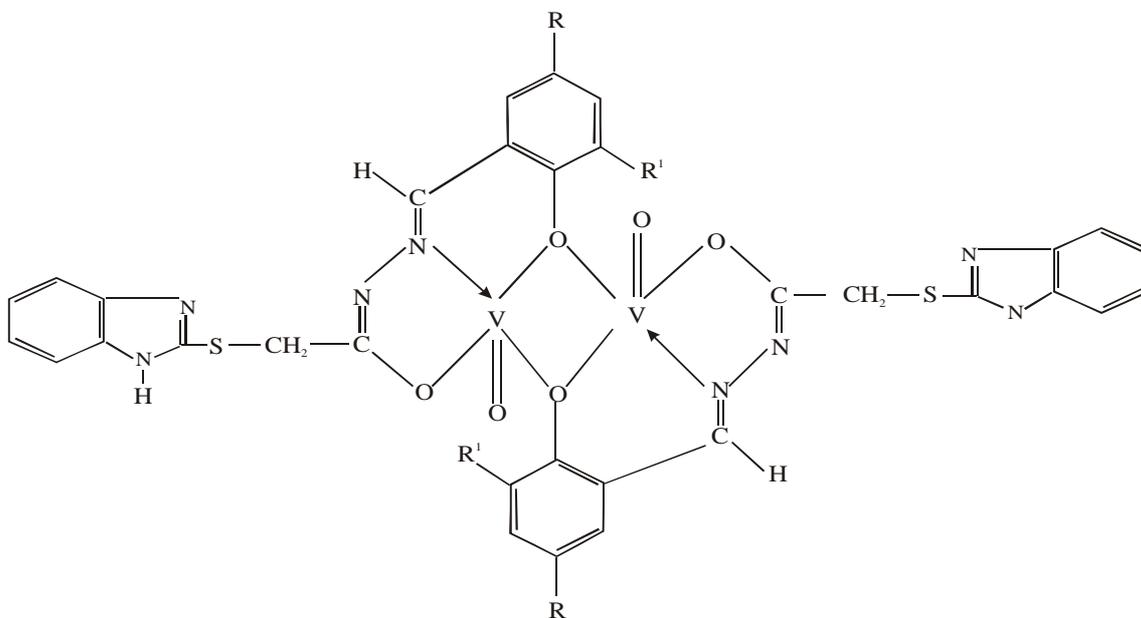
Code	Compound	Antibacterial activity		Antifungal activity	
		<i>E.coli</i>	<i>S.aureus</i>	<i>A.niger</i>	<i>C.albicans</i>
L ₁	C ₁₆ H ₁₃ N ₄ O ₂ S	12	13	12	11
C ₁	VO(C ₁₆ H ₁₂ N ₄ O ₂ S)	15	16	15	14
L ₂	C ₁₆ H ₁₂ N ₄ O ₂ SCl	13	14	12	13
C ₂	VO(C ₁₆ H ₁₁ N ₄ O ₂ SCl)	16	17	15	16
L ₃	C ₁₆ H ₁₂ N ₄ O ₂ SBr	11	13	12	11
C ₃	VO(C ₁₆ H ₁₁ N ₄ O ₂ SBr)	14	16	15	15
L ₄	C ₁₇ H ₁₅ N ₄ O ₂ S	12	11	12	11
C ₄	VO(C ₁₇ H ₁₄ N ₄ O ₂ S)	16	15	15	14
L ₅	C ₁₇ H ₁₅ N ₄ O ₃ S	12	11	13	12
C ₅	VO(C ₁₇ H ₁₄ N ₄ O ₃ S)	15	14	16	15
Ctm	Contrimoxazole	30	32	-	-
Fnz	Flucanazole	-	-	31	29





CONCLUSION

On the basis of subnormal values of magnetic moment, elemental analyses and spectral studies the phenoxide bridged 5-coordinated dimeric square pyramidal structure may be proposed for the present complexes (structure 2) and in which hydrazone ligands act as dibasic tridentate nature, exist in enol form.



2. Proposed structure of VO(IV) complexes

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