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Antimicrobial Studies of Schiff's Base Ligands and Their Oxovanadium (IV) Complexes

L. K. Mandal[1], S. K. Pandey[2] and M. L. Sharma[1*]

[1] Central Department of Chemistry, Tribhuvan University, Kirtipur, Kathmandu, Nepal
[2] Department of Chemistry, DDU Gorakhpur University,Gorakhpur-27009, India
Email: mlsharma.chem@gmail.com

Abstract

Some triazole derived Schiff's bases and their oxovanadium(IV) complexes have been synthesized. The Schiff's bases and the complexes were analyzed by different spectroscopic methods; UV-Vis, IR, EPR, magnetic susceptibility, X-ray, conductivity measurement and elemental analyses. The molar conductance values were relatively low, showing their non-electrolytic nature. The EPR spectra of the complexes shows the presence of single oxovanadium cation as metallic centre in the complex. The powder X-ray diffraction pattern shows the average size of particles in the range of 24-30nm. A square pyramidal geometry of complexes have been established. Antimicrobial sensitivity of the ligands and its metal complexes were assayed in vitro against four bacterial pathogens viz. S. aureus, P. aeruginosa, E. coli and K. pneumonia and two fungal pathogens namely C. albican and A.niger. The antimicrobial data show the oxovanadium(IV) complexes to be more antibacterial and antifungal than the patent Schiff's base against one or more bacterial and fungal strains.

Keywords: *Triazole Ligands, magnetic susceptibility, molar conductance, oxovanadium(IV) complexes, Schiff's base, pathogens, XRD*

Introduction

Vanadium is widely distributed in the biosphere and plays significant role in both plants and animals. It is bioessential element found in remarkably high concentration in marine ascidians, certain mushrooms and polychateworms[1]. Vanadium belongs to the first member of Group V having electronic configuration [Ar]$3d^3 4s^2$.It shows oxidation states from -3 to +5 with exception of -2.Under ordinary condition the most stable oxidation states are +4 and +5 [2]. The chemistry of vanadium metal is becoming significant due to its biological and industrial outcomes like antimicrobial spermicidal, anti-leukemia, antitumor and recently as insulin mimetic[3].

The chemistry of oxovanadium(IV) complex has received considerable attention as VO^{+2} unit can readily co-ordinate four, five or six donor atoms to form VOL_4, VOL_5 or VOL_6types of complexes respectively. The expanding role of Vanadium in biological system and the potential of the vanadium complexes as the therapeutic agents has led to the continuously increasing interest in the coordination

chemistry and the chemistry of this element [4].Within the spectrum of vanadium complexes that have been synthesized as a model compounds for understanding of Vanadium – controlled biological system or as a potential therapeutic agents within insulin mimetic properties , one finds a substantial number of oxovanadium(IV) chelate complexes with a variety of donor set[5]. On the other hand in the last decades Schiff's base ligands have received more attention because of their extensive application in the field of synthesis and catalysis [6].

The coordination chemistry of metal complexes has been advancing at a tremendous pace. Its various aspects *viz*., kinetic, photochemical, electrochemical, thermochemical etc. have been dealt with at length for studying the subtle aspects of interrelation between structure, configuration, stereochemistry and stereospecificity of metal complexes[7,8]. This remarkable progress in the field of metal complexes may be attributed to their diversified applications. These complexes have been finding use in the field of homogeneous catalysis, various biological systems, potential drugs and analytical chemistry[9,10,11].

The complexes of oxovanadium(IV) typically have square pyramidal or bipyramidal structure with vanadyl oxygen apical; the vanadium atom lying 0.035-0.055 Å above the plane defined by the equatorial ligands. There have been reports of five-coordinate trigonal bipyramidal complexes with structures determined by X-ray diffraction technique[12].

Experimental Methods

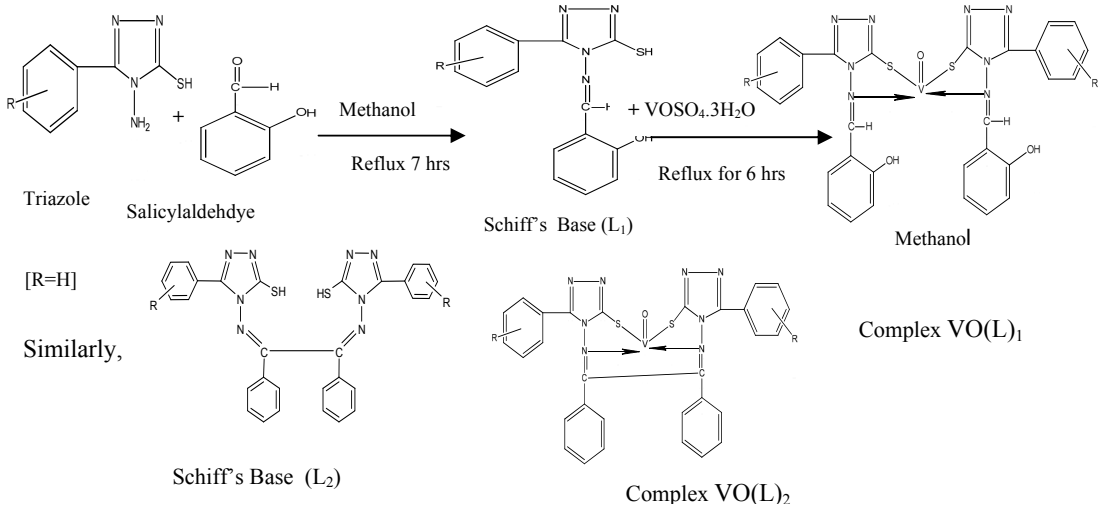
Synthesis of Schiff's bases and oxovanadium(IV) complexes

0.05 mole of aromatic carboxylic acid (benzoic acid) was taken in R.B. flask and methanol was added as a solvent till the benzoic acid was completely dissolved. 2-3 ml of concentrated $H_2SO_4$was added slowly and allowed to reflux for about 4-5 hours. Fruity smell indicates the formation of ester. The solution was cooled slowly and poured with stirring into crushed ice. Little amount of $NaHCO_3$ was added and ester formed is extracted by using separating funnel. The process was repeated to get sufficient amount of ester.

25 ml of ester (methyl benzoate) was taken in R.B. flask and was dissolved in methanol (solvent). 11.02 ml of hydrazine hydrate was added to it and allowed to reflux for 4 hours. The mixture was allowed to cool for 24 hours . White Crystal was formed. The crystal was re-crystallized in methanol and dried.

8.15 g of KOH in methanol was taken into R.B. flask and hydrazide was dissolved into it. Then1.6 mole CS_2 was added dropwise with constant stirring placing on plate with magnetic stirrer bar in an ice cold environment. Thick liquid was observed and excess hydrazine hydrate was added and allowed to reflux for about 4 hours. Formation of aminomercaptotriazole takes place. Then it was separated, recrystallized and dried [3,12]. 15.718 g of triazole and 8.277 ml of salicylaldehyde was taken in R.B. flask. Then methanol was added as solvent and reflux for 7 hours at 45^o C. Then yellowish white crystalline substance obtained was allowed to settle overnight. The crystal was separated and dried. Then it was re-crystallized and its melting point was determined**.** The melting point of Schiff's base$L_1$was found to be 112^{o}C.In the similar way Schiff's base L_2 (from benzil) was synthesized and melting point was found to be 120^{o}C.

Methanolic solution vanadyl sulphate (1 mmol) was added to a refluxing methanolic solution of appropriate Schiff's base (2 mmol) and sodium acetate (2 mmol). The reaction mixture was refluxed for 10 h. The compound separated in form of amorphous crystals from the clear solution of mixture was filtered, washed with ether and dried [3, 12]. The empirical formulae, color, percentage yield and elemental analysis values are listed in Table 1.



Scheme 1: *Synthetic route to Schiff's base and their corresponding complexes.*

Measurement

EDX were recorded on Horiba Model EMAX 7593-H at Nepal Custome, Tripureshwor, Kathmandu. UV-Vis electronic spectra were recorded on USB 2000, Photonics at Patan Multiple Campus, Lalitpur. XRD were recorded on X-ray diffractometer (Rigaku Geigerflex). FTIR were recorded on IR Tracer-100, SHIMADZU at Central Department of Chemistry, T. U., Kathmandu.The EPR spectra were on Bruker's ELEXSYS EPR spectrometer at Indian Institute of Technology, Bombay, India. The melting point were determined using melting point apparatus (Philips 500) and are uncorrected. The purity of synthesized compounds were checked with TLC.

Biological activity

Antibacterial activity (in vitro)

All synthesized triazole Schiff bases (L_1 andL_2) and their oxovanadium(IV) complexes [$VO(L)_1$ and $VO(L)_2$]were screened *in vitro* for their antibacterial activity against three Gram-negative (*E. coli, k. pneumonia and P. aeruginosa*) and two Gram-positive (MRSA and MSSA) bacterial strains by the agar-well diffusion method. The wells (6 mm in diameter) were dug in the media with the help of a sterile metallic borer. Bacterial inocula (2-8 hrs old) containing approximately 10^4-10^6 colony-forming units (CFU/ml) were spread on the surface of the nutrient agar with the help of a sterile cotton swab. The recommended concentration of the test sample (4mg/ml,6mg/ml in DMSO) was introduced in the

respective wells. Other wells supplemented with DMSO and reference antibacterial drug gentamycin, served as negative and positive controls, respectively. The plates were incubated at 37^{o}C for 24 hrs. Activity was determined by measuring the diameter of zones showing complete inhibition (mm) (Table 3 and as figure 3 and 4). In order to evaluate the interfering effect of DMSO on the biological screening, alternate studies on DMSO solution showed no activity against any bacterial strains [3]. The percentage inhibition of the growth ofthe test organism was calculated by the following formula;

Inhibition (%) = Cd/Td x 100,where Cd is colony diameter of control and Td is colony diameter of treated set.

Minimum inhibitory concentration (MIC)

Compounds containing promising antibacterial (above 80%) activity were selected for minimum inhibitory concentration (MIC) studies. The minimum inhibitory concentration was determined using the disc diffusion technique by preparing discs containing 25, 50, 100 and 200 µg/ml concentrations of the compounds along with standards at the same concentrations[3].

Results and Discussion

Newly synthesized oxovanadium(IV) complexes with Schiff's bases derived from from 4-amino-3-phenyl-5-mercapto1,2,4-triazole and salicyaldehyde and benzil are colored, crystalline solids. The complexes are soluble in dimethylformamide and dimethylsulphoxide.

Table1: *Physical properties and elemental analysis data of oxovanadium(IV) complexes*

Complexes	**Molecular Formula**	**Formula Weight**	**Colour**	**Yield (%)**	**Analysis (%) Found (Calculated)**			
					V	**C**	**H**	**N**
$[VO(L)_1]$	$C_{30}H_{22}N_8S_2O_3V$	656.94	Yellowish Green	68	7.85 (7.90)	54.76 (54.79)	3.61 (3.65)	17.07 (17.04)
$[VO(L)_2]$	$C_{30}H_{20}N_8S_2OV$	622.94	Green	65	8.29 (8.34)	57.72 (57.79)	3.19 (3.21)	17.93 (17.97)

Characterization

Magnetic moment and electronic spectra

The magnetic moments of the oxovanadium(IV) complexes $VO(L)_1$and $VO(L)_2$ lie in the range 1.70–1.76 B.M at room temperature.. These values are well suited for oxovanadium(IV) complexes with one unpaired electron[22].The electronic spectra of the complexes recorded in DMSO show three bands in the regions of 833-800, 641-609 and 448-406 nm. In addition, one more band is obtained at 386-376 nm.

These transitions falls in the same range as reported for other five coordinated (C_{4v} symmetry) oxovanadium(IV) complexes [23]. These optical bands are observed in the visible region assigned to ($^2B_2 \rightarrow {}^2E$) i.e., $b_2 \rightarrow e^*_{II}$ (d_{xz}, d_{yz}), ($^2B_2 \rightarrow {}^2B_1$) i.e., $b_2 \rightarrow b^*_1(d_{x2-y2})$ and ($^2B_2 \rightarrow {}^2A_1$) i.e., $b_2 \rightarrow a^*_1(d^2_z)$, in increasing order of energy. The electronic spectral bands of two representative complexes [VO(L_1)]and [VO(L_2)] are represented in Figure 1 [3,12].

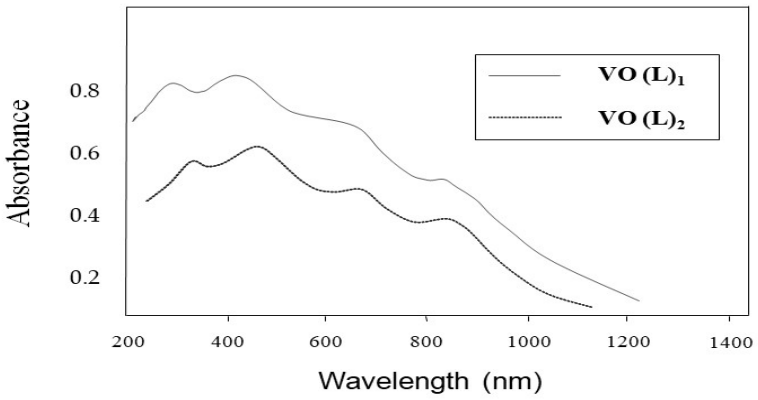


Figure 1: *Electronic spectra of the complexes [VO(L)$_1$] and [VO(L)$_2$].*

Infrared spectra

The qualitative aspects of IR spectroscopy are one of the most powerful attributes of this diverse and versatile analytical technique. The IR spectra provide valuable information regarding the nature of the functional group attached to the metal atom. IR spectra can be used as a finger print for identification by the comparison of the spectra from an unknown with previously recorded reference spectra. Schiff bases appear to exist in thiol form as suggested by broad band at 2700–2600 cm^{-1} assignable to ν(S-H). In complexes ν(S-H) band disappears indicating the deprotonation of thiol group and formation of bond between metal and sulphur. This is further confirmed by appearance of new band in complexes at 380-350 cm^{-1}, assignable to ν(V-S).Schiff bases exhibit strong band at 1650–1620 assigned ν(C=N). In complexes, this band shifts to lower frequency(1605–1600 cm^{-1}) indicating coordination of azomethine nitrogenwith VO^{+2} metal ion. New bands appear in metal complexes at 475–430 cm^{-1} due to ν(V-N) vibrations. The band due to ν (C=N) (triazole ring) appears at 1570–1550 cm^{-1} in the ligands which remains almost at the same position in the complexes indicating non-coordination to ring azomethine nitrogen in bond formation. All Schiff's base ligands and their respective VO(IV) complexes show bands at 3128–3050 cm^{-1} due to ν(Ar-H).The spectra of all oxovanadium(IV) complexes show a new characteristic band around 975–950 cm^{-1} due to ν(V=O) vibrations.Thus, the IR spectral studies indicate that the Schiff's baseligands, behave as dibasic, tetradentate chelating agents having coordination sites at two thiol sulphur atoms and two azomethine nitrogen atoms. The significant infrared spectral bands of the oxovanadium(IV) complexes are listed in Table 2 [12].

Table 2: *Significant IR spectral bands (cm^{-1}) of oxovanadium(IV) complexes*

Complexes	ν(C=N)Triazole ring	ν(C=N) Azomethine	ν(V=O)(m)	ν(V-S) (m)	ν (V-N) (m)	Ar-H
Complex $VO(L)_1$	1595-1570	1605	975	380 - 350	415 - 385	3050
Complex $VO(L)_2$	1590 - 1575	1610	970	385 - 350	410 - 385	3045

EPR spectra

The solid state X-band EPR spectrum for oxovanadium(IV) complex $VO(L)_1$ has been recorded at room temperature at field set 3200 G, microwave power 5 mW and microwave frequency 9.1 GHz. The room temperature spectra exhibits eight lines due to hyperfine splitting patterns due to coupling of d^1electron to the nucleus ^{51}V (I=7/2), which confirms the mononuclear oxovanadium(IV) units in the complex examined. The g average values determined from the spectra is 1.98, similar to the spin only values.

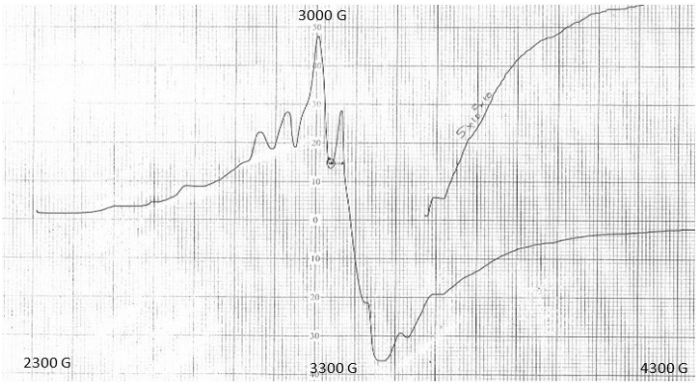


Figure 2: *The solid state EPR spectrum of complex $VO(L)_1$ at room temperature.*

XRD Diffraction study

X-Ray powder diffraction pattern of one representative oxovanadium(IV) complex $VO(L)_1$ is given in the Figure3. The structural characterization of the complex was carried out from the analysis of X-ray powder diffraction (XRD) pattern obtained using an X-ray powder diffractometer (Bruker AXS D8 Advance) with CuKa (k = 1.54056 Å) source. The XRD pattern clearly indicates the formation of nano-crystal. The crystallite size have been calculated by using Debye-Scherer formula given as $D=0.94\ \lambda / \beta \cos\theta$ **;**WhereD is the crystallite size, λ is the wavelength of X-ray used, β is the full width at half maximum (FWHM) and h is the Bragg's angle of diffraction. The average crystalline size of the oxovanadium(IV) complexes were found to be 18.3 nm to 22.2 nm range[3,12].

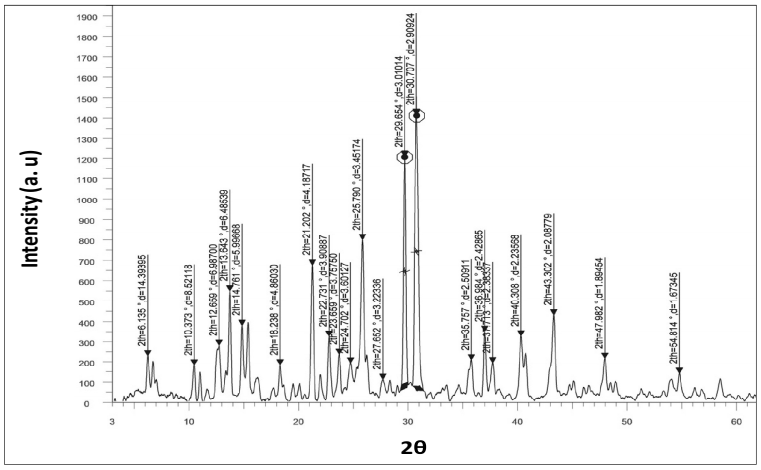


Figure 3: *XRD of complexVO(L)$_1$*

Biological activity

Antibacterial bioassay (in vitro)

The synthesized triazole Schiff's bases and their oxovanadium(IV) complexes$VO(L)_1$ and $VO(L)_2$ were screened for in vitro antibacterial activity against three Gram-negative (*E. coli, k. pneumonia and P. aeruginosa*) and two Gram-positive (MRSA and MSSA) bacterial strains by the agar-well diffusion method (concentration 4mg/ml). The results obtained were compared with that of the standard drug Gentamycin and are reported in Table 3 and as Figure 4. The activity of synthesized compounds (in % age) was compared with the activity of the standard drug considering its activity as 100%. The synthesized compounds showed varying degree of inhibitory effects: low (up to 33%), moderate (up to 53%) and significant (above 53%). The ligand (L_1) possessed a significant (53-84%) activity against (b), (c), and (d) bacterial strain and moderate (50%) activity against (a). Similarly, the ligand (L_2) exhibited significant (59-75%) activity against (a), (b), (c), (d), and (e). Complex $VO(L)_1$, showed significant (56-83%) activity against (a), (b), (c), (d), and (e). Similarly, Complex C_2 possessed significant (70-80%) activity against (a), (b), (c), (d), and (e).Similar results were obtained at concentration 6mg/ml. It is interesting to note that antibacterial activity of simple ligands is increased upon coordination (Figure 3) that confirmed our previous studies 12]. It is, therefore evident that coordination makes the ligands strongly antibacterial agent and inhibits the growth of bacteria more than the parent Schiff's base ligands. The antibacterial results of the oxovanadium(IV) complexes $VO(L)_1$and $VO(L)_2$ were considered the most active compounds due to the presence of more number of nitrogen atoms, hence carried out their MIC screening (Table 4).

Table 3: *Antibacterial activity of compounds at concentration (4 mg/ml in DMSO)*

ZONE OF INHIBITION (mm) Concentration (4 mg/ml in DMSO)/(6mg/ml in DMSO)										
	BACTERIA									
Compounds	**MRSA**		**MSSA**		***P. aeruginosa***		***K. pneumoniae***		***E. coli***	
L_1	16	15	17	16	21	22	20	22	19	21
L_2	18	20	19	20	17	18	19	20	21	23
$VO(L)_1$	18	17	20	18	18	19	21	22	23	25
$VO(L)_2$	19	20	19	21	18	20	20	21	22	24
STANDARD (Gentamycin)	30	30	30	30	26	26	30	30	30	30

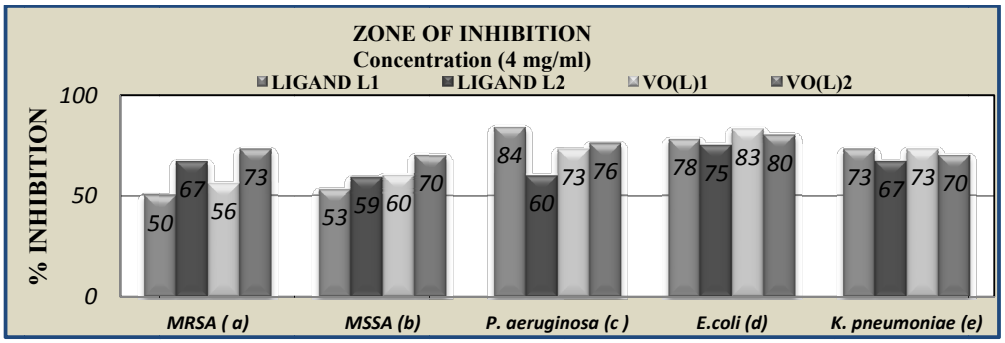


Figure 4: *Comparison of antibacterial activity of free Schiff's base ligands(L_1 and L_2) and complexes $VO(L)_1$ and $VO(L)_2$ at concentration (4 mg/ml in DMSO)*

Minimum inhibitory concentration (MIC)

The data of preliminary antibacterial screening showed that the oxovanadium(IV) complexes $VO(L)_1$ and $VO(L)_2$ against *MRSA, P. aeruginosa, E. coli* and *K. pneumonia* were the most active compounds. Therefore, these compounds were selected for the MIC studies. The results obtained were compared with that of the standard drug Gentamycin and are reported in Table 4 and as Figure 5. The activity of synthesized compounds (in % age) was compared with the activity of the standard drug considering its activity as 100%. The synthesized complex $VO(L)_1$ showed varying degree of inhibitory effects: low (up to 33%), moderate (up to 53%) and significant (above 53%). The complex $VO(L)_1$ possessed a significant (53-61%) activity against (a), (b), (c), and (d) bacterial strain at 200 µg/ml; moderate (46%) against (a)

and significant (61-66%) activity against (b), (c), and (d) at 100 µg/ml; moderate (47%) against (a) and significant (56-75%) activity against (b), (c), and (d) at 50 µg/ml; moderate (45%) against (a) and significant (57-70%) activity against (b), (c), and (d) at 25 µg/ml. Similar results were obtained for complex $VO(L)_2$ at four different concentrations[3,12].

Table. 4:*Minimum inhibitory concentration (MIC) of the selected compounds against selected bacteria*

	MIC (mm) Concentration (µg/ml in DMSO) COMPLEX $VO(L)_1$				**MIC (mm) Concentration (µg/ml in DMSO) COMPLEX $VO(L)_2$**				
Bacteria	**200**	**100**	**50**	**25**	**200**	**100**	**50**	**25**	**Control**
Mrsa	16	14	14	13.5	14	11.5	11	11.5	26
P. aeruginosa	16	16	17	15	14	16	16	17	24
K. pneumonia	17	20	17	18	17	18	19	17	26
E. coli	17	19	21	21	18	16	17	19	26

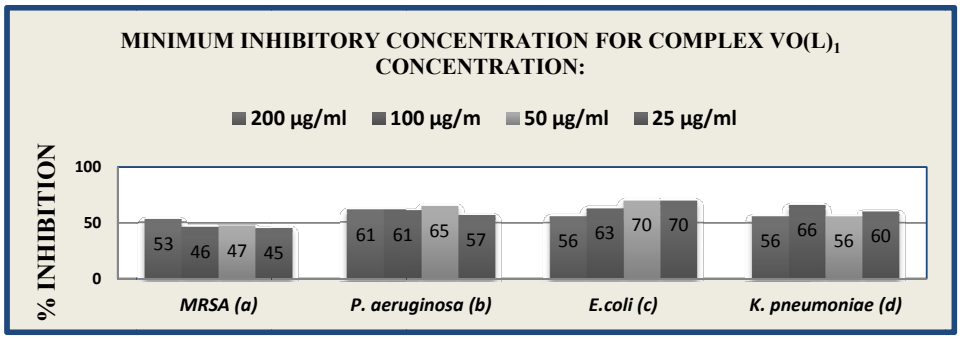
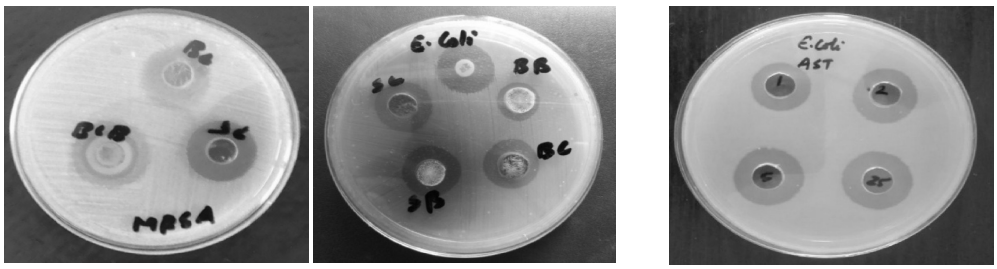


Figure 5: *Minimum Inhibitory Concentration (MIC) of complex $VO(L)_1$ against selected bacteria.*



ZONE OF INHIBITION (4mg/ml) **MIC at four different concentration (µg/ml in DMSO)**

Figure 6: *Antibacterial activity of synthesized compounds [Zone of Inhibition (mm)].*

All complexes show higher activity against bacteria as compared to Schiff's base. Such increased activity of the metal complexes can be explained on the basis of oxidation state of the metal ion,

Overtone's concept and Tweedy's chelation theory[12]. It has been suggested that the ligands with N and S donor system might have inhibited enzyme production, since enzyme which requires a free hydroxyl group for their activity appears to be especially susceptible to deactivation by the ions of the complexes. Chelation reduces the polarity of central ion mainly because of partial sharing of its positive charge with donor groups and possible p-electron delocalization within the whole chelating ring. This chelation increases the lipophylic nature of the central atom which favours its permeation through lipid layer of cell membrane.

Furthermore, the mode of action of compounds may involves the formation of hydrogen bonds through the azomethine (C=N) group of complexes with the active centers of cell constituents resulting in the interference with normal cell process. Though the complexes possess activity, it could hardly reach the effectiveness of the standard drug such as Gentamycin. Some compounds are less effective, the variation in effectiveness depends on either on the impermeability of the cells of the microbes or on differences in the ribosome of microbial cells. It is also well known fact that heterocyclic ring has cell wall damaged capacity. The newly synthesized complexes have triazole ring which on contact with the microbes, damages cell wall and also disturb the respiration process of the cell and thus block the synthesis of proteins, whichrestricts further growth of microorganism. The toxicity of compounds is directly proportional to the concentration.

Conclusion

The Schiff's bases were synthesized from 4-amino-3-phenyl-5-mercapto-1, 2, 4–triazole with salicylaldehyde and benzil. These Schiff's bases form stable complexes with VO^{+2} ion. Schiff bases act as dibasic, tetradentate chelating agents and coordination takes place through azomethine nitrogen and thiol sulphur via deprotonation. A square-pyramidal geometry of complexes has been established by spectral studies. Oxovanadium(IV) complexes $VO(L)_1$and $VO(L)_2$ synthesized in the laboratory have been studied against three Gram-negative (*E. coli, K. pneumonia and P. aeruginosa*) and two Gram-positive (MRSA and MSSA) bacteria. The complexes $VO(L)_1$ and $VO(L)_2$ show significant activity with the change in the nature of the ligand attached to VO^{+2} ion. The complexes show higher antimicrobial activity as compared to free ligands.

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