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# Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

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# Oxovanadium(IV) and Niobium(V) Complexes with Some New Schiff Bases

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### OXOVANADIUM(IV) AND NIOBIUM(V) COMPLEXES WITH SOME NEW SCHIFF BASES

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### ABSTRACT

Complexes of the type  $[VO(LH)(H_2O)]$  and  $[Nb(LH)_2Cl_3]$ , where LH = a singly deprotonated Schiff base derived from condensation of 3-substituted-4-amino-5-mercapto-1,2,4-triazole with benzoin were synthesized in ethanol or dry chloroform, respectively. A coordination number of five for the oxovanadium(IV) and seven for the niobium(V) complexes have been proposed on the basis of analytical, molar conductance, magnetic, IR and <sup>1</sup>H NMR spectral data. Kinetic parameters were established by adopting Broido's method. All of the ligands and their oxovanadium(IV) complexes were screened for their antibacterial, antifungal and antituberculosis activity.

### **INTRODUCTION**

The coordination chemistry of  $oxovanadium(IV)^{1-4}$  and  $niobium(V)^{5-8}$ , in particular oxovandium(IV) has been studied well with various ligands. The complexes of niobium(V) with Schiff bases are of considerable interest because of the peculiarities of niobium(V) in forming complexes. However, the information on

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oxovanadium(IV) and niobium(V) complexes with Schiff bases derived from substituted 1,2,4-triazoles is scanty. The paucity of literature in this sphere and the important biological properties such as the antimicrobial<sup>9,10</sup>, antituberculosis<sup>11</sup> and antitumour<sup>12</sup> activities associated with the triazole moiety encouraged us to undertake a systematic study of the complexes of VO(IV) and Nb(V) with new tridentate Schiff bases<sup>13</sup>, obtained *via* the condensation of 3-substituted-4-amino-5-mercapto-1,2,4-triazole with benzoin (Fig. 1).

### **EXPERIMENTAL**

All the chemicals used were of reagent grade. Niobium(V) chloride (Fluka) and benzoin (BDH) were used. 3-Substituted-4-amino-5-mercapto-1,2,4-triazole<sup>14,15</sup> and their Schiff bases were prepared according to a method reported elsewhere<sup>13</sup>.

### Synthesis of Schiff Bases

The Schiff bases were prepared by refluxing a mixture of 3-substituted-4amino-5-mercapto-1,2,4-triazole (10 mmol) and benzoin (10 mmol) in 70 mL ethanol containing a few drops of concentrated HCl for about 3 h on a water bath. The product separated on evaporation of the yellow solution was filtered, washed with ethanol, recrystallzied from ethanol and dried under vacuum.

### Synthesis of Oxovanadium(IV) Complexes

To an 80 mL ethanolic solution of the ligand (10 mmol), vanadyl sulphate (1.81g, 10 mmol) in the minimum amount of water was added followed by 2 g of sodium acetate. The reaction mixture was refluxed for about 2 h. The complex thus obtained was filtered, washed thoroughly with alcohol and dried in *vacuo* over fused calcium chloride.

### Synthesis of Niobium(V) Complexes

Niobium pentachloride (2.68 g, 10 mmol) in 35 mL dry chloroform was treated with the ligand (20 mmol) in 40 mL of the same solvent. The reaction mixture



Fig. 1. Structure of the Ligands  $L^1H_2-L^4H_2$ 

was stirred under nitrogen atmosphere for 3 h. The precipitated complex was filtered, washed with chloroform and dried in *vacuo* over phosphorus pentoxide.

### Analyses of the Complexes and Physical Measurements

The metal content in the complexes was determined by standard methods<sup>16</sup>. Sulphur was determined gravimetrically as BaSO<sub>4</sub>. Nitrogen was determined by

Dumas' method. C, H and N content of the ligands were determined using an Heraeus-CHN-Rapid analyser. The conductance measurements of 10<sup>-3</sup> M DMF solutions of these complexes were carried out on an Elico CM82 conductivity bridge. The IR spectra were recorded on a Hitachi 170-50 IR spectrophotometer as KBr pellets. The electronic spectra were recorded on a Hitachi 150-20 spectrophotometer. The TG and DTG data were obtained using a Rigaku TAS-100 thermal analyser at the temperature range 25-800 °C in static air/nitrogen atmosphere at a heating rate of 10 °C/min. Magnetic moments were measured on a Gouy balance at room temperature. Melting/decomposition points of the ligands and their complexes were determined in open capillary tubes and are uncorrected.

### **RESULTS AND DISCUSSION**

The characterization data of ligands and their oxovanadium(IV) and niobium(V) complexes are presented in Table I. The oxovanadium(IV) complexes are dark green, whereas, the niobium(V) complexes are yellow. They are insoluble in common organic solvents, however are sparingly soluble in DMF and DMSO. The elemental analyses (Table I) of the VO(IV) complexes agreed well with the 1:1 stoichiometry of [VO(LH)H<sub>2</sub>O], whereas, the Nb(V) complexes showed the 1:2 stoichiometry of [Nb(LH)<sub>2</sub>Cl<sub>3</sub>]. The low molar conductance values show that the complexes are non-electrolytes.

 $VOSO_4.H_2O + LH_2 \xrightarrow{CH_3COONa} VOLH.H_2O + Na^+HSO_4 + CH_3COO$ NbCl<sub>5</sub> + 2LH<sub>2</sub>  $\longrightarrow$  NbCl<sub>3</sub>(LH)<sub>2</sub> + 2HCl

### Magnetic Data

The oxovanadium(IV) ion belongs to the S =  $\frac{1}{2}$  system. The magnetically dilute oxovanadium(IV) complexes should exhibit magnetic moments close to the spin-only value of 1.73 B.M. as the sign of the spin-orbit coupling constants ( $\lambda$ ) is

positive and the orbital contribution is almost completely quenched in the oxovanadium(IV) complexes<sup>17-19</sup>. The room temperature magnetic moments of the present complexes are in the range 1.20-1.35 B.M. The subnormal magnetic moments arise due to the dimeric structure which is a consequence of an oxygen bridged structure. Since V=O bridging is ruled out on the basis of IR spectra, the subnormal magnetic moments may be due to spin coupling *via* super-exchange through the alcoholic oxygen atoms<sup>2,3</sup>.

The niobium(V) complexes are diamagnetic as expected for  $d^{\circ}$  Nb(V) state.

### Infrared Specta

The triazoles are reported to exhibit thiol-thione tautomerism<sup>20,21</sup>. Hence, the present Schiff bases can also exhibit thiol-thione tautomerism. These Schiff bases exhibit a broad, medium-intensity band around 3250 cm<sup>-1</sup> and a weak-intensity band observed around 2350 cm<sup>-1</sup> assignable to v(NH) and v(SH) vibrations, respectively, in analogy with 3-substituted-4-salicylideneimino-5-mercapto-1,2,4-triazole<sup>22,23</sup>. The presence of these two bands indicates thiol-thione tautomerism in these Schiff bases. A broad, weak band in the region 2600-2700 cm<sup>-1</sup> is attributed to the intramolecular H-bonded OH. As the ligands contain NCSH or NHCS groups, the bands observed around 1590, 1350 and 1040 cm<sup>-1</sup> are attributed to the thiamide-I, II and III vibrations, respectively<sup>24,25</sup>. In addition to the above, the medium-intensity bands due to the thiamide-IV vibration appeared around 750 cm<sup>-1</sup> which is mainly due to the v(C=S) group<sup>25</sup>. The strong-intensity band due to v(C=N) of the ligands appeared in the region 1660-1650 cm<sup>-1</sup>.

In the complexes the following changes were observed which emphasize the complex formation.

- 1. All of the complexes exhibited a broad, medium-intensity band around 3250 cm<sup>-1</sup> and a broad band of weak intensity at 2350 cm<sup>-1</sup> attributable to v(NH) and v(SH) vibrations, respectively.
- 2. The band due to v(C=S) in the ligands around 750 cm<sup>-1</sup> is unaffected in the

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	Molar conductance	mhos cm <sup>2</sup> mol <sup>-1</sup>		1		1	25	17	10
Table 1 aracterization Data of Ligands and their Oxovanadium(1V) and Niobium(V) Complexes.	Heff.			1	I		1.20	1.30	1.25
		ច				ł	1	I	1
		M		1		· .	12.00 (12.94)	11.75 (12.50)	12.00 (12.08)
	aic.) %	s	10.35 (10.32)	9.89 (9.87)	9.42 (9.46)	9.10 (9.09)	8.10 (8.12)	7.15 (7.84)	7.45 (7.58)
	Found (C	z	18.05 (18.06)	17.26 (17.28)	16.54 (16.56)	15.91 (15.90)	14.00 (14.21)	13.75 (13.72)	13.10 (13.27)
		Н	4.49 (4.51)	4.90 (4.93)	5.35 (5.32)	5.70 (5.68)		ł	1
		ပ	61.95 (61.93)	62.95 (62.96)	63.91 (63.90)	64.76 (64.77)	I	1	1
	M.p./dec. pt. °C		150	110	125	120	110 đ	100 d	120 d
	% Yield		85	80	06	83	60	65	63
	Formula wt.		310	324	338	352	394	408	422
Ċ	Empirical formula		C <sub>16</sub> H <sub>14</sub> N4OS	C <sub>17</sub> H <sub>16</sub> N₄OS	C <sub>18</sub> H <sub>18</sub> N₄OS	CI9H20N4OS	C <sub>16</sub> H <sub>15</sub> N <sub>4</sub> VO <sub>3</sub> S	C <sub>17</sub> H <sub>17</sub> N₄VO <sub>3</sub> S	C <sub>18</sub> H <sub>19</sub> N₄VO <sub>3</sub> S
	No.		L'H <sub>2</sub>	L <sup>2</sup> H <sub>2</sub>	L <sup>3</sup> H <sub>2</sub>	L <sup>4</sup> H <sub>2</sub>	(1)	(2)	(3)

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(4)	C <sub>19</sub> H <sub>21</sub> N₄VO <sub>3</sub> S	436	20	115 d			12.80 (12.84)	7.20 (7.33)	11.55 (11.69)	ł	1.35	80
(5)	C32H26CI3N8NbO2S2	816	67	80 d	ł	ł	13.60 (13.74)	7.31 (7.85)	11.20 (11.28)	12.50 (12.88)	Dia	S
(9)	C <sub>34</sub> H <sub>30</sub> Cl <sub>3</sub> N <sub>8</sub> NbO <sub>2</sub> S <sub>2</sub>	844	68	45 d	ŀ		12.98 (13.51)	7.45 (7.72)	11.00 (11.09)	12.66 (12.66)	Dia	18
6	C <sub>36</sub> H <sub>14</sub> Cl <sub>3</sub> N <sub>8</sub> NbO <sub>2</sub> S <sub>2</sub>	872	62	50 đ		****	13.20 (13.28)	7.58 (7.59)	10.80 (10.91)	12.41 (12.45)	Dia	10
(8)	C <sub>38</sub> H <sub>38</sub> Cl <sub>3</sub> N <sub>8</sub> NbO <sub>2</sub> S <sub>2</sub>	006	66	70 d		ļ	12.95 (13.06)	6.99 (7.46)	10.70 (10.73)	12.20 (12.25)	Dia	20
d = d	composition											

corresponding complexes indicating the non-involvement of the sulphur atom of the SH group in coordination to the metal ion.

- 3. A broad band with fine structure in the region 2600-2700 cm<sup>-1</sup>, assignable to the H-bonded OH in ligands, is absent in the spectra of the complexes suggesting the involvement of the OH group in complex formation *via* deprotonation, which is further confirmed by the presence of a new band in the region 435-450 cm<sup>-1</sup> due to v(M-O) vibrations<sup>7,8</sup>. The v(C-O) frequency of the enolic band of the Schiff bases shifted to higher frequency and appeared in the vicinity of 1330 cm<sup>-1</sup> on complexation, suggesting the involvement of the OH group in complex formation *via* deprotonation.
- 4. The strong-intensity band due to (C=N) of the ligand (1660-1650 cm<sup>-1</sup>) is shifted to lower frequency to around 1625 cm<sup>-1</sup> in the case of the complexes indicating the coordination of the azomethine group through its nitrogen. The mode of coordination is further supported by the presence of new bands in the region 520-510 cm<sup>-1</sup> due to v(M-N) vibrations<sup>7.8</sup>.
- 5. The usual range for the v(V=O) mode is 960 ± 50 cm<sup>-1</sup> and is observed for the majority of oxovanadium(IV) complexes<sup>26,27</sup>. It is documented in the literature<sup>2,3</sup> that, in the oxovanadium(IV) complexes with V=O·····V=O····· interactions, the band due to this bonding occurs at a much lower frequency (~ 850 cm<sup>-1</sup>). In the present complexes the band due to the v(V=O) mode occurs in the region 998-1005 cm<sup>-1</sup> and this is in agreement with the usual range and rules out the presence of ·····V=O····· interactions<sup>26,27</sup>.
- 6. In addition to the above bands we observed a new non-ligand band around  $3400 \text{ cm}^{-1}$  in the oxovanadium complexes which is assigned to v(OH) of coordinated water.
- The new non-ligand bands observed in the region 340-345 cm<sup>-1</sup> for the niobium(V) complexes are assigned to v(Nb-Cl) vibrations<sup>5</sup>.

### Electronic Spectra

The electronic spectra of the present oxovanadium complexes exhibited two bands in the ranges 17,850-15,380 cm<sup>-1</sup> and 25,310-25,000 cm<sup>-1</sup> which may be attributed to the transitions  $b_2 \rightarrow b_1$  and  $b_2 \rightarrow a_1$ , respectively. These observations suggest square-pyramidal geometry for the complexes<sup>26,27</sup>.

The electronic spectra of the ligands exhibit a medium-intensity band in the region 38,461-37,037 cm<sup>-1</sup> assigned to  $n \rightarrow \pi^{\bullet}$  and a medium intensity broad band in the region 33,333-26,315 cm<sup>-1</sup> assigned to  $\pi \rightarrow \pi^{\bullet}$  transitions. The band in the region 33,333-26,315 cm<sup>-1</sup> involves hydrogen bonded chelate rings and also indicates thiol-thione tautomerism<sup>22</sup>.

In the electronic spectrum of the niobium(V) complexes with these ligands, the bands are modified and are broad and more intense. The band in the region 38,461-37,037 cm<sup>-1</sup> in the ligand is much broadened and covers the region 37,037-33,333 cm<sup>-1</sup> in the complex and there is a more intense and broad band in the region 29,411-25,641 cm<sup>-1</sup>. This can be taken as a proof for complex formation.

### EPR Spectra

The EPR spectra of the oxovanadium(IV) complex (2) were recorded in the polycrystalline state at room temperature and at liquid nitrogen temperature. The spectra are quite different from the EPR spectra of magnetically dilute oxovanadium(IV) complexes and are similar to those of magnetically concentrated oxovanadium(IV) complexes<sup>17</sup>. The EPR spectra exhibit a band at 1600 Gauss due to the spin-forbidden  $\Delta M = \pm 2$  transition and this indicated the presence of a triplet state dimeric species. The EPR parameters are  $g_{\perp} = 1.98$ ,  $g_{\parallel} = 1.96$   $g_{av} = 1.97$  (at RT) and  $g_{\perp} = 1.99$ ,  $g_{\parallel} = 1.95$ ,  $g_{av} = 1.975$  (at LNT). The above observations suggest a penta-coordinated complex with square-pyramidal geometry<sup>2, 27</sup>.

### <sup>1</sup>H NMR Spectrum of Niobium(V) Complex

The <sup>1</sup>H NMR spectrum of a representative niobium(V) complex, (6) of the corresponding ligand  $L^{2}H_{2}$ , has been studied.

The ligand exhibits signals due to NH and SH protons at 13.54 and 2.50 ppm indicating the thione thiol tautomerism in the ligands. The characteristic resonance due to OH of an alcoholic group appeared at 6.00 ppm. In addition to the above signals, we observed a multiplet in the region 7.20-8.00 ppm due to aromatic protons and a signal at 2.24 ppm due to methyl protons.

In the <sup>1</sup>H NMR spectrum of the niobium(V) complex all the signals appeared almost in the same region as in the case of the ligand except the signal due to the alcoholic OH which was absent, indicating the coordination of the oxygen atom of the OH group *via* deprotonation and non-involvement of the sulphur of the mercapto group in coordination.

### **Thermal Studies**

The TG curves of the oxovanadium(IV) complexes show a stable pleateau upto 100 °C indicating that the complexes are stable upto this temperature. The complexes then undergo a single-stage decomposition as represented by a DTG peak around 280 °C. The weight loss corresponds to coordinated water and ligand. The TG curve shows that the decomposition is completed at 560 °C, after which temperature stable oxide  $V_2O_5$  is formed (Table II).

Niobium(V) complexes decompose in three steps as denoted by three DTG peaks around 85, 220 and 440 °C. The first step in the temperature range 45-130 °C with a weight loss ranging between 11.47-11.89% corresponds to loss of chloride as HCl. In the second step of decomposition, a weight loss of 36.96-37.00% in the temperature range 110-320 °C corresponds to one ligand molecule detached from the complex. A weight loss of 37.57-37.83% indicates the loss of another ligand molecule. Beyond 570 °C a pleateau is seen, which indicates the formation of stable Nb<sub>2</sub>O<sub>5</sub>. The weight of Nb<sub>2</sub>O<sub>5</sub> agrees with the analytical result for the metal content.

### Reaction Kinetics of Decomposition

The thermodynamic parameters were calculated by adopting Broido's method<sup>28</sup>. In niobium(V) complexes, the energy of activation values for the second

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Table II.

Thermogravimetric Characterisites of Some of the Complexes Under Study

		2	×0	<b>S</b>	0
s/Nb2O5	Calc	44.9	43.4	15.80	15.6(
0²V	Obs.	43.25	42.95	13.35	14.79
No. of	moles			€ – –	n
Product		Н <sub>2</sub> О & L <sup>2</sup> Н	Н <sub>2</sub> О & L <sup>3</sup> H	CI L <sup>2</sup> H L <sup>2</sup> H	CI L <sup>3</sup> H L <sup>3</sup> H
t. loss	Cal.	83.53	84.38	12.62 38.18 38.18	12.04 38.64 38.64
W %	Obs.	81.75	84.00	19.89 37.00 37.57	11.47 36.96 37.83
Peak in	° Su Su	290	280	85 220 440	90 215 430
Temperature	range, 'C	100-540	120-560	45-110 110-300 300-560	50-130 130-320 320-570
Process		Dehydration and decompo- sition of coor- dination sphere	Dehydration and decompos- ition of coord- ination sphere	Decomposition of coordination sphere	Decomposition of coordination sphere
Complex		[Vo(L <sup>2</sup> H)H <sub>2</sub> O]	[V0(L <sup>±</sup> H)H <sub>2</sub> O]	$[Nb(L^{2}H)_{2}Cl_{3}]$	[Nb(L <sup>3</sup> H) <sub>2</sub> Cl <sub>3</sub> ]
Complex		(2)	(3)	(9)	E

Complex No.	Complex	<sup>™</sup> ℃	<sup>T</sup> ‰C	T <sub>Max</sub> /C	Stages	Ea kJ mol <sup>-1</sup>	ln A min <sup>-l</sup>
(2)	[VO(L <sup>2</sup> H)H <sub>2</sub> O]	100	220	540	I	5.55	7.54
(3)	$[VO(L^{3}H).H_{2}O]$	120	230	560	1	9.76	9.30
(6)	[Nb(L <sup>2</sup> H) <sub>2</sub> .H2O]	45	230	560	1 11 111	1.91 5.74 19.14	5.40 7.32 10.81
(7)	[Nb(L <sup>3</sup> H) <sub>2</sub> .H <sub>2</sub> O]	50	250	570	I II III	2.29 7.65 23.16	5.70 8.07 11.65

Table III. Data Obtained by TG Analysis: Temperature Characteristics, Activation Energies and Frequency Factors of Decomposition Process.

stage of decomposition were found to be much lower than that of the third stage decomposition (Table III). The lower value of  $E_a$  indicates an increased rate at this stage, and might be due to the catalytic effect of the metal complexes on the oxidation of the ligands and other decomposition products<sup>29</sup>.

The energy of activation for the third stage of decomposition of the niobium(V) complexes was found to be much higher than those for the other stages, indicating that the rate of decomposition for this stage is lower than for the other stages. It is generally observed that step-wise formation constants decrease with an increase in the number of ligands attached to the metal ion<sup>30</sup>. The negative  $\Delta S^{\#}$  values (Table IV) suggest a more ordered activated state through the chemisorption of oxygen and other decomposition products<sup>31</sup>.

From the foregoing discussion it is concluded that the ligands react with Nb(V) and VO(IV) through the nitrogen of azomethine and oxygen of the alcoholic OH group. Based on analytical and spectral studies the structures in Figs. 2 and 3 have been proposed.

	2		-	-	
Complex No.	Complex	Stages	ΔH <sup>#</sup> kJ mol <sup>-1</sup>	ΔS <sup>#</sup> JK <sup>-1</sup> mol <sup>-1</sup>	∆G <sup>#</sup> kJ mol <sup>-1</sup>
(2)	[VO(L <sup>2</sup> H)H <sub>2</sub> O]	I	1.99	-233.80	102.06
(3)	[VO(L <sup>3</sup> H)H <sub>2</sub> O]	I	6.24	-191.20	87.12
(6)	$[Nb(L^2H)_2Cl_3]$	I II III	-0.79 1.47 13.34	-260.98 -242.10 -184.40	113.33 125.67 142.06
(7)	$[Nb(L^{3}H)_{2}Cl_{3}]$	I	-0.6994	-257.47	92.85

3.47

17.28

-224.88

-125.47

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Thermodynamic Parameters for the Thermal Degradation of the Complexes.



Fig. 2. Suggested Structure of the Oxovanadium(IV) Complexes.

116.59

106.11



Fig. 3. Suggested Structure of the Niobium(V) Complexes.

### **Biological Activity**

The biological and medicinal potency of coordination compounds has been established by their antitumour<sup>32</sup>, antiviral<sup>33</sup> and antimalarial<sup>34</sup> activity observed for some derivatives. This characteristic property has been related to the ability of the metal ion to form complexes<sup>35</sup> with ligands containing sulphur, nitrogen and oxygen donor atoms. It has been demonstrated<sup>36</sup> that, chelation in compounds is to a large extent responsible for the antibacterial and antifungal activity. Recently, it has been shown that 6-methyl-2-acetylyridin-3-hexamethyleneiminylthiosemicarbazone and its copper(II) complex are potent cytotoxic agents in murine and tumour cell lines<sup>37</sup>. In view of the biological and medicinal potency of sulphur-containing ligands and their metal complexes, we are allured towards the evaluation of the antibacterial and antifungal activity of these ligands and their oxovanadium(IV) complexes by the cup plate method<sup>38</sup> (Table V) with two different bacteria, Escherichia coli and Bacillus cirroflagellosus, and two fungal species, Aspergillus niger and Candida albicans, on base layer medium. The base layer medium for antibacterial testing was prepared by dissolving definite volumes of peptone (0.6%), yeast extract (0.3%), beef extract (0.13%) and agar (2.5%) in distilled water. The pH of the medium was adjusted to

1595

	Zo	one of inhib	oition in m		
Compound	Antib	acterial	Antif	ungal	- % inhibition
No.	E	F	G	H.	- Antituberculosis
Ligands			· · · · · · · ·		
$L^{1}H_{2}$	12	11	10	13	57
$L^2H_2$	10	12	11	12	53
$L^{3}H_{2}$	11	14	12	12	52
$L^4H_2$	13	10	11	12	61
VO(IV) complexes					
(1)	14	16	11	12	64
(2)	12	16	13	14	14
(3)	13	14	13	13	44
(4)	15	14	14	11	48
Standards					
Cotrimoxazole	20	20			
Flucanzole			25	25	

Та	bl	e	v	

Antibacterial, Antifungal and Antituberculosis Activity Results of Ligands and their Complexes

E = Escherichia coli, F = Bacillus cirroflagellosus

G = Aspergillus niger, H = Candida albicans

Key for interpretation : Less than	10 mm	_	Inactive
	10 <i>–</i> 12 mm	-	Weakly active
	13 – 15 mm	-	Moderately active
	16 – 18 mm	-	Highly active

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7.2 and sterilised by autoclaving at 15 p.s.i. for 20 minutes. For the antifungal activity testing the base layer medium was prepared by dissolving definite volumes of peptone (0.4%), yeast extract (0.6%), sodium chloride (0.5%), potassium dihydrogen phosphate (0.3%), glucose (1%) and agar (2.5%) in distilled water. The pH of the medium was adjusted to 6.0 and sterilised by autoclaving at 15 p.s.i. for 20 minutes. The cups were made by scooping out nutrient agar with a sterilized cork bore. The solution of the test compounds (0.1 mL) were added to the cups by using sterile pipettes and the plates were subsequently incubated at 37 °C for 48 h. The antimicrobial activity was estimated on the basis of the size of the inhibition zone in mm formed around the holes on the seeded agar plates.

From Table V it is clear that all of the ligands and complexes are active towards all the organisms used. The results also suggest that metal chelates exhibit higher antimicrobial activity than their free ligand molecule in most of the cases. All the ligands are weakly active against all the organisms except  $L^1H_2$ ,  $L^3H_2$  and  $L^4H_2$  which are moderately active against *C. albicans*, *B. cirroflagellosus* and *E. coli*, respectively. In the case of the VO(IV) complexes, (1) is highly active against bacteria, *B. cirroflagellosus*, moderately against *E. coli* and weakely against both fungi, *C. albicans* and *A. niger*. Complex (3) is moderately active against all the organisms used. Complex (4) is weakly active against fungi, *C. albicans*, and moderately active against other organisms.

Overall, the ligands and complexes are less active as compared to the standards cotrimoxazole and flucanazole used in the present study.

All of the ligands and their oxovanadium(IV) complexes were tested for their antituberculosis activity at 6.25  $\mu$ g/mL (MIC) against *Mycobacterium tuberculosis*  $H_{37}$  *Rv(ATCC 27294)* in BACTEC 12B medium using a broth microdilution assay, the Microplate Almar Blue Assay (MABA)<sup>39</sup> at Southern Research Institute, Alabama, USA. The ligand L<sup>2</sup>H<sub>2</sub> and the oxovanadium(IV) complex (1) have exhibited significant antituberculosis activity.

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### **REFERENCES**

- 1. C. C. Lee, A. Syamal and L. J. Theriot, Inorg. Chem., 10, 1669 (1971).
- 2. A. Symal and K. S. Kale, Indian J. Chem., 19A, 486 (1980).
- 3. A. Symal and K. S. Kale, Indian J. Chem., 19A, 225 (1980).
- P. R. Athapan, P. Shantha and C. Natarajan, Indian J. Chem., <u>37A</u>, 136 (1998).
- 5. N. S. Biradar and T. R. Goudar, Curr. Sci., <u>43</u>, 740 (1974).
- 6. D. D. Agarwal, A. Kaul and A. Chaturvedi, Indian J. Chem., <u>34A</u>, 743 (1995).
- 7. T. R. Goudar and P. B. Maravalli, Indian J. Chem., <u>37A</u>, 83 (1998).
- 8. P. B. Maravalli and T. R. Goudar, Polish J. Chem., 71, 1631 (1997).
- 9. M. S. Yadawe and S. A. Patil, Trans. Met. Chem., 22, 220 (1997).
- M. C. Hosur, M. B. Talwar and S. C. Bennur, Indian J. Chem., <u>34B</u>, 707 (1995).
- 11. L. Muslin, W. Roth and H. Erlenmeyer, Helv. Chim. Acta., 36, 886 (1951).
- 12. L. Mishra and M. Kamil Said, Indian J. Chem., 35A, 304 (1996).
- 13. G. M. Shashidhara, M. Phil. Dissertation, Gulbarga University (1996).
- 14. D. N. Dhar, J. Org. Chem., 25, 1247 (1960).
- K. S. Dhaka, J. Mohan, V. K. Chadha and H. K. Pujari, *Indian J. Chem.*, <u>12</u>, 288 (1974).

- A. I. Vogel "A Text Book of Quantitative Inorganic Analysis" ELBS, London 4<sup>th</sup> Edn. (1978)
- 17. J. Selbin, Chem. Rev., 65, 153 (1965).
- 18. A. Pasini and M. Gulloti, J. Coord. Chem., <u>3</u>, 319 (1974).
- 19. R. L. Dutta and G. P. Sengupta, J. Indian Chem. Soc., 49, 919 (1972).
- 20. R.V. Gadag and M. R. Gajendragad, Talanta, 25, 418 (1978).
- B. K. Sinha, R. Singh and J. P. Srivastava, J. Inorg. Nucl. Chem., <u>39</u>, 1797 (1977).
- 22. S. A. Patil, B. M. Badiger, S. M. Kudari and V. H. Kulkarni, *Trans. Met. Chem.*, **8**, 238 (1983).
- B. M. Badiger, S. A. Patil, S. M. Kudari and V. H. Kulkarni, *Rev. Roum. Chim.*, <u>31</u>, 849 (1986).
- 24. N. K. Singh, S. Agarwal and R. C. Agarwal, Indian J. Chem., 21, 973 (1982).
- 25. R. V. Gadag and M. R. Gajendragad, Curr. Sci., 48, 839 (1979).
- 26. B. R. Havinale and I. B. Pujar, J. Inorg. Nucl. Chem., 43, 2689 (1981).
- 27. L. N. Sharada and M. C. Ganorkar, Indian J. Chem., 27A, 617 (1988).
- 28. A. Broido, J. Polym. Sci., Part A-2, 7, 1761 (1969).
- 29. P. B. Maravalli and T. R. Goudar, Thermochim. Acta, <u>325</u>, 35 (1999).
- F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry" 3rd Edn. (1980).
- P. B. Maravalli, S. D. Dhumwad and T. R. Goudar, Synth. React. Inorg. Met-Org. Chem., 29, 525 (1999).
- W. E. Antholine, J. M. Knight and D. H. Petering, *Inorg. Chem.*, <u>16</u>, 569 (1977).
- D. H. Jones, R. Slack, S. Squires and K. R. H. Wooldrige, J. Med. Chem., <u>8</u>, 676 (1965).
- D. L. Klayman, J. P. Scorill, J. F. Bafosevich and J. Bruce, J. Med. Chem., <u>26</u>, 35(1983).

### OXOVANADIUM(IV) AND NIOBIUM(V)

- 35. K. C. Agarwal and A. C. Santoelli, Prog. Med. Chem., 15, 349 (1978).
- 36. S. Albert, "Selective Toxicity", Methuen and Co. Ltd. (1960).
- M. C. Miller, K. H. Bastow, C. N. Seneman, J. R. Vank, S. C. Song, D. X. West and L. H. Hall, *Arch. Pharm. Pharm. Med. Chem.*, <u>331</u>, 121 (1998).
- H. W. Seeley and P. J. Denmark, "Microbes in Action" A Laboratory Manual of Microbiology, 2<sup>nd</sup> Edn. (1975).
- 39. L. Collins and S. G. Franzblau, Antimicrob. Agents Chemother., <u>41</u>, 1004 (1997).

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