

Synthesis, Characterization and Biocidal Properties of Oxovanadium Complexes

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VO(II) and VO(III) undergo complexation with tetradentate ligands viz. N,N'-bis(3-hydroxy quinoxaline-2-carboxalidene)-1,2-diaminocyclohexane (NQCH), N,N'-bis(3-hydroxyquinoxaline-2-carboxalidene)-1,8-diaminonaphthalene (NQAN) and N,N'-(3-hydroxy quinoxaline-2-carboxalidene)-2,3-diaminomaleonitrile (NQAM). On the basis of micro analytical data, the complexes are formulated as [VOL(H₂O)]SO₄, [VOL(H₂O)]Cl₂ and [VOL(H₂O)]Cl₃ where L is NQCH, NQAN or NQAM. These complexes have been characterized by infrared spectroscopy, molar conductivity, magnetic moment and electronic spectra. VO(II) complexes are found tetragonally distorted octahedral with -ve Dt value indicating compression along Z-axis. VO(III) complexes are diamagnetic in nature. The ligands as well as their oxovanadium complexes have been screened against some bacteria *E. coli* and *S. aureus* and plant pathogenic fungi, *A. niger* and *C. albicans*. All the complexes are found to be more active than the corresponding ligands against both bacteria and fungi.

Keywords: Tetragonally distorted octahedral, Antimicrobials activity, Tetradentate ligand.

INTRODUCTION

Vanadium is an essential trace element in plants and animals [1,2]. The complexes of vanadium have extensively been reported for their antimicrobial activities [3,4]. Vanadium in its +IV and +V oxidation states has strong affinity towards nitrogen and oxygen donor ligands due to its hard acidic nature [5-9]. The interest in exploring metal ion complexes with tetradentate *i.e.*, macrocyclic Schiff base ligands has been continuously increasing owing to their structure and potential applications [10-13]. The phenomenal growth in the coordination chemistry of Schiff bases over last three decades [14], this field has invited the attention of inorganic chemists. Further, the biological activities of Schiff base ligands often alter on coordination with suitable metal ions [15-19]. Keeping all these facts in consideration, we have further extended our work on vanadium complexes [20-22] and report here in the synthesis of VO²⁺ and VO³⁺ complexes with tetradentate Schiff base ligand and their biological effect against phytopathogenic fungi and bacteria.

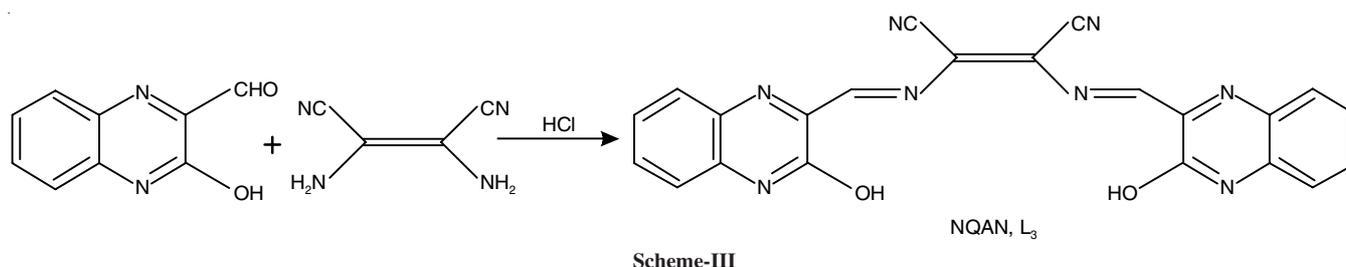
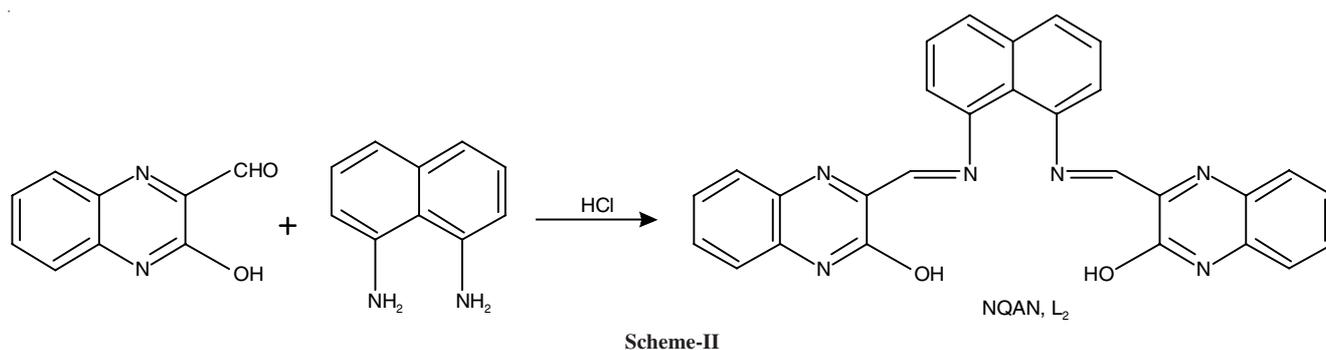
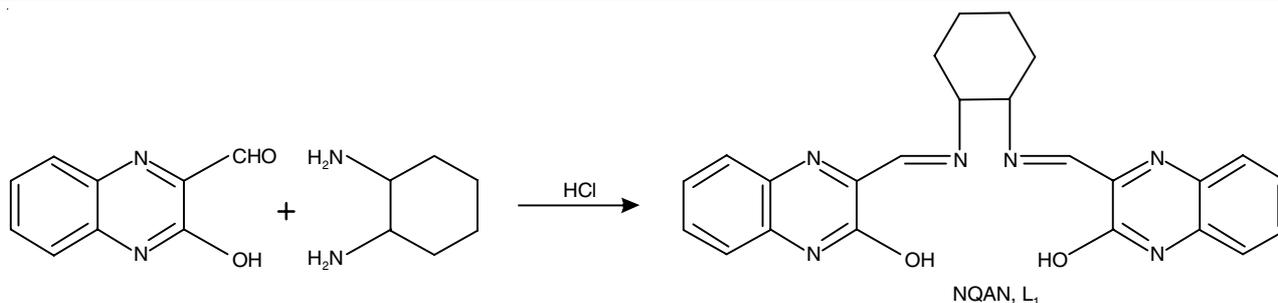
EXPERIMENTAL

All the reagents used were of AnalR grade. The precursor, 3-hydroxy quinoxaline-2-carboxaldehyde was procured from Merck and was used as received. The Schiff bases, N,N'-bis(3-hydroxy quinoxaline-2-carboxalidene)-1,2-diaminocyclo-

hexane (NQCH, L₁), N,N'-bis(3-hydroxyquinoxaline-2-carboxalidene)-1,8-diaminonaphthalene (NQAN, L₂) and N,N'-bis(3-hydroxyquinoxaline-2-carboxalidene)-2,3-diaminomaleonitrile (NQAM, L₃), were prepared by the condensation of 3-hydroxyquinoxaline-2-carboxaldehyde with 1,2-diaminocyclohexane, 1,8-diaminonaphthalene and 2,3-diaminomaleonitrile, respectively under slightly acidic condition as shown in **Schemes I-III**, respectively.

The yields were found 70-90 %. The three ligands were used for complexation with VO(IV) and VO(V) metal ions by usual method of refluxing the metal salts *i.e.* VOCl₂, VOSO₄ and VOCl₃ with alcoholic solutions of respective ligand taken in 1:1 molar ratio for 3-4 h. The coloured solid complexes were filtered on suction pump and dried in desiccator over anhydrous CaCl₂.

Physical and analytical measurements: The ligands as well as their VO(IV) and VO(V) complexes were microanalyzed for C, H and N by using micro analysis technique on Perkin-Elmer 2400 CHN elemental analyzer. IR spectra of ligands and complexes were recorded on Perkin-Elmer FTIR-spectrometer, spectrum two in range of 4000-400 cm⁻¹ using KBr pellets. The magnetic moment of complexes was determined by Gouy balance at room temperature using Hg[Co(CNS)₄] as calibrant. The electronic spectra of complexes were recorded on Perkin-Elmer UV/visible spectrometer Lambda-25 using DMSO solution. The molar conductivity of complexes was



measured on conductivity meter (CG 857 Schott-Grate Gambit) in DMSO solution of 10^{-3} M concentration.

RESULTS AND DISCUSSION

The physical and micro-analytical data of ligands and their complexes with VO^{2+} and VO^{3+} are presented in Table-1. On the basis of microanalytical data and molar conductivity the complexes have been formulated as $[\text{VOL}(\text{H}_2\text{O})]\text{Cl}_2$, $[\text{VOL}(\text{H}_2\text{O})]\text{SO}_4$ and $[\text{VOL}(\text{H}_2\text{O})]\text{Cl}_3$. The molar conductivity values of complexes **4**, **5** and **6** fall in the range of $88\text{--}97\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ which is really in the range of 1:1 electrolyte. Complexes **7**, **8**

and **9** record their molar conductivity values in the range of $148\text{--}168\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ which is indicative of 1:2 electrolytic nature of these complexes. The molar conductivity values in the range of $240\text{--}245\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ for the complexes **10**, **11** and **12** indicate their 1:3 electrolytic nature [23-26]. The IR spectra of free ligands as well as their complexes are very clumsy and it couldn't be possible to assign all the bands, particularly in the finger print region. Only the important bands have been assigned here. The broad band appearing at $3430\text{--}3410\text{ cm}^{-1}$ in the IR spectra of free ligand is assigned to the hydrogen bonded $\nu(\text{N-H})$ of the amide tautomers of free

TABLE-1
PHYSICAL AND MICROANALYTICAL DATA OF LIGAND AND COMPLEXES

Compound	Colour	m.p. (°C)	Elemental analysis (%): Calcd. (Found)				λ ($\text{ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$)	μ_{eff} (BM)
			V	C	H	N		
NQCH(L ₁)	Yellow	175.0	–	67.59 (67.88)	5.20 (5.11)	19.11 (19.00)	–	–
NQAN(L ₂)	Dark violet	179.0	–	62.86 (62.98)	2.88 (2.72)	26.66 (26.42)	–	–
NQAM(L ₃)	Red	185.0	–	71.48 (71.61)	3.86 (3.83)	17.86 (17.84)	–	–
$[\text{VO}(\text{L}_1)_2(\text{H}_2\text{O})]\text{SO}_4$	Brown	211.0	8.40 (8.21)	47.44 (47.64)	3.95 (3.72)	13.83 (13.66)	88	1.82
$[\text{VO}(\text{L}_2)_2(\text{H}_2\text{O})]\text{SO}_4$	Dull brown	214.0	8.51 (8.24)	44.70 (44.92)	2.00 (1.87)	18.64 (18.50)	97	1.79
$[\text{VO}(\text{L}_3)_2(\text{H}_2\text{O})]\text{SO}_4$	Brown	218.0	7.83 (7.77)	51.61 (51.86)	3.07 (3.00)	12.90 (12.78)	89	1.94
$[\text{VO}(\text{L}_1)_2(\text{H}_2\text{O})]\text{Cl}_2$	Magenta	213.0	8.76 (8.63)	49.48 (49.62)	4.12 (4.00)	14.43 (14.12)	148	1.82
$[\text{VO}(\text{L}_2)_2(\text{H}_2\text{O})]\text{Cl}_2$	Bright red	217.0	8.88 (8.57)	45.99 (46.28)	2.09 (1.92)	19.51 (19.40)	168	1.78
$[\text{VO}(\text{L}_3)_2(\text{H}_2\text{O})]\text{Cl}_2$	Dull red	220.0	8.14 (8.00)	53.67 (53.88)	3.19 (3.01)	13.41 (13.22)	–	1.96
$[\text{VO}(\text{L}_1)_2(\text{H}_2\text{O})]\text{Cl}_3$	White	213.8	8.26 (8.10)	46.67 (46.89)	3.88 (3.62)	13.61 (13.42)	240	Diamag.
$[\text{VO}(\text{L}_2)_2(\text{H}_2\text{O})]\text{Cl}_3$	Dull white	218.0	8.37 (8.18)	43.35 (43.69)	2.00 (1.90)	18.39 (18.21)	245	Diamag.
$[\text{VO}(\text{L}_3)_2(\text{H}_2\text{O})]\text{Cl}_3$	White	221.5	7.71 (7.61)	58.83 (58.68)	3.02 (2.91)	12.70 (12.61)	241	Diamag.

TABLE-2
 KEY IR BANDS (cm⁻¹) OF OXOVANADIUM COMPLEXES

Complexes	$\nu(\text{C}=\text{O})$	$\nu(\text{CH}=\text{N})$	$\nu(\text{V}=\text{O})$	$\nu(\text{V}-\text{N})$	$\nu(\text{V}-\text{O})$
[VO(NQCH)(H ₂ O)]SO ₄	1630	1655	960	420	470
[VO(NQAN)(H ₂ O)]SO ₄	1625	1660	960	430	470
[VO(NQAM)(H ₂ O)]SO ₄	1620	1665	955	420	465
[VO(NQCH)(H ₂ O)]Cl ₂	1630	1660	950	425	460
[VO(NQAN)(H ₂ O)]Cl ₂	1634	1655	940	425	465
[VO(NQAM)(H ₂ O)]Cl ₂	1635	1670	940	425	465
[VO(NQCH)(H ₂ O)]Cl ₂	1640	1665	945	425	460
[VO(NQAN)(H ₂ O)]Cl ₃	1640	1670	950	430	465
[VO(NQAN)(H ₂ O)]Cl ₃	1630	1660	950	420	460

ligands [27,28]. The medium intensity bands observed in 3160-2900 cm⁻¹ region in the IR spectra of free ligands are due to $\nu(\text{C}-\text{H})$ stretching vibration of phenyl group [29,30]. The amide, tautomeric form of these Schiff bases absorbs strongly in the range of 1670-1640 cm⁻¹ due to $\nu(\text{C}=\text{O})$ stretching [31-33]. The band appearing at 1620-1590 cm⁻¹ is well assigned to $\nu(\text{CH}=\text{N})$ (azomethine) stretching of the ligands [34,35] while the medium band appearing at 1580-1550 cm⁻¹ is assigned to $\nu(\text{C}=\text{N})$ of quinoxaline ring [36,37]. In the IR spectra of L₃ (NQAM) a medium band appears at 2250 cm⁻¹ which is safely assigned to $\nu(\text{C}\equiv\text{N})$ moiety of this ligand. The weak bands appearing at 1595, 1585, 1500 and 1450 cm⁻¹ may be assigned to benzene ring skeletal vibration which was further supported by the appearance of a band at 1180 cm⁻¹ due to in plane $\delta(\text{C}-\text{H})$ bending vibration and a band at 760 cm⁻¹ due to out of plane $\delta(\text{C}-\text{H})$ bending vibration of 1,2 substituted benzene ring [38].

The IR spectra of complexes on comparison with that of free ligands reveal the point of coordination of the ligands to VO(IV) and VO(V) ions. The important vibrational bands of complexes have been displayed in Table-2.

The band appearing at 1670-1640 cm⁻¹ in the IR spectra of free ligands due to $\nu(\text{C}=\text{O})$ gets shifted to lower frequencies, 1630-1620 cm⁻¹ in the IR spectra of complexes which is indicative of coordination through carbonyl oxygen of amide form of the ligands to metal ions [39,40]. The other major change in IR spectra of free ligands was found with azomethine frequency which shifts from 1620-1590 to 1675-1655 cm⁻¹ in the IR spectra of complexes. This is indicative of coordination through azomethine nitrogen of ligands to the metal ions [41,42]. The unexpected increase in azomethine stretching vibration may be due to the extensive delocalization of π electrons in fully conjugated Schiff base ligands. This was further supported by the appearance of two new bands at 470-460 and 430-420 cm⁻¹ due to stretching vibrations of $\nu(\text{V}-\text{O})$ and $\nu(\text{V}-\text{N})$, respectively in complexes [22]. The new band appearing at 960-948 cm⁻¹ in the IR spectra of complexes is attributed to $\nu(\text{V}=\text{O})$ stretching vibrations [43,44]. The presence of coordinated H₂O molecule in the coordination sphere of complexes is confirmed by the appearance of a new band at 3400-3300 cm⁻¹ in the IR spectra of complexes. Thus the ligands behave as neutral tetradentate coordinating through two amide carbonyl oxygen atoms and two azomethine nitrogen atoms.

The magnetic moment of VO(IV) complexes falls in the range of 1.78-1.96 BM at room temperature. The values correspond to the presence of one unpaired electron and show that

complexes are magnetically dilute [44,45]. The electronic spectra of VO(IV) complexes display three bands in the range of 12,250-12,340, 18,100-18,340 and 19,880-19,900 cm⁻¹, which may be assigned to ${}^2\text{B}_{2g} \rightarrow {}^2\text{E}_g$, ${}^2\text{B}_{2g} \rightarrow {}^2\text{B}_{1g}$ and ${}^2\text{B}_{2g} \rightarrow {}^2\text{A}_{1g}$ spin allowed transitions for a d^1 system. The energy associated with the different transitions are given as: $\nu_1 = {}^2\text{B}_{2g} \rightarrow {}^2\text{E}_g = 3\text{Ds} - 5\text{Dt}$, $\nu_2 = {}^2\text{B}_{2g} \rightarrow {}^2\text{E}_{1g} = 10\text{Dq} - 4\text{Ds} - 5\text{Dt}$ and $\nu_3 = {}^2\text{B}_{2g} \rightarrow {}^2\text{A}_{1g} = 10\text{Dq}$ [45]. So, ν_3 is the measure of 10Dq while $\nu_2 - \nu_1 = 10\text{Dq} - 7\text{Ds}$. Thus getting the value of Ds from $\nu_2 - \nu_1$ and putting its value in $\nu_1 = 3\text{Ds} - 5\text{Dt}$, the value of Dt. *i.e.* distortion in O_h symmetry has been derived. The values of different crystal field parameter of VO(IV) complexes have been presented in Table-3.

TABLE-3

Complexes	10Dq	Ds	Dt.
[VO(NQCH)(H ₂ O)]SO ₄	19,875	1982	1278
[VO(NQAN)(H ₂ O)]SO ₄	19,900	2014	1251
[VO(NQAM)(H ₂ O)]SO ₄	19,890	2263	1092
[VO(NQCH)(H ₂ O)]Cl ₂	19,880	1982	1274
[VO(NQAN)(H ₂ O)]Cl ₂	19,895	1984	1275
[VO(NQAM)(H ₂ O)]Cl ₂	19,885	1980	1271

These values are in good agreement with the values reported for distorted octahedral complexes of VO(IV) [4]. The VO(V) complexes are diamagnetic which is in accordance with the d^0 system of V⁵⁺. Also due to this, these complexes don't display any band in their electronic spectra. On the basis of their elemental analysis and diamagnetic character, their six coordinated complexes have been assigned octahedral geometry.

Biological profile of ligands and their complexes with VO(IV) and VO(V): The ligands NQCH (L₁), NQAN (L₂) and NQAM (L₃) and their metal complexes with VO(IV) and VO(V) were screened for their *in vitro* antibacterial activity against bacteria *Staphylococcus aureus* and *Escherichia coli* by disc diffusion method using nutrient Agar as medium and streptomycin as control. The *in vitro* antifungal activities of ligands as well as complexes were tested against the fungi *Aspergillus niger* and *Candida albicans* by well diffusion method on potato dextrose agar as the medium and miconazole as control. The compounds were dissolved in DMSO and solution of different concentration (25, 50 and 100 ppm) were prepared separately. The procedure involves a well made on agar medium inoculated with microorganism. The well was filled with the test solution using a micropipette and the plate

TABLE-4
ANTIBACTERIAL SCREENING OF LIGANDS AS WELL AS THEIR VO(IV) AND VO(V) COMPLEXES

Compound	<i>E. coli</i>						<i>S. aureus</i>					
	Diameter of inhibition zone (mm)			Activity index (%)			Diameter of inhibition zone (mm)			Activity index (%)		
Concentration	25	50	100	25	50	100	25	50	100	25	50	100
L ₁	10	12	13	48	52	46	12	13	14	67	57	56
L ₂	14	15	16	67	65	57	12	14	15	67	61	60
L ₃	13	15	17	62	51	61	13	15	16	72	65	64
[VOL ₁ H ₂ O]SO ₄	15	18	19	65	78	68	14	16	20	78	70	80
[VOL ₂ H ₂ O]SO ₄	15	17	19	71	74	68	15	18	21	83	78	84
[VOL ₃ H ₂ O]SO ₄	16	17	19	76	74	68	15	16	20	83	70	80
[VO L ₁ H ₂ O]Cl ₂	18	19	22	86	83	79	17	20	22	94	95	88
[VOL ₂ H ₂ O]Cl ₂	18	19	21	86	83	75	16	21	22	89	91	88
[VOL ₃ H ₂ O]Cl ₂	18	20	23	86	87	82	17	21	23	94	91	92
[VO L ₁ H ₂ O]Cl ₃	17	18	20	81	78	71	16	20	21	83	96	84
[VOL ₂ H ₂ O]Cl ₃	17	19	21	81	83	75	16	19	20	89	83	80
[VOL ₃ H ₂ O]Cl ₃	17	18	20	81	78	71	16	20	22	89	96	88
Streptomycin	21	23	28	100	100	100	18	23	25	100	100	100

TABLE-5
ANTIFUNGAL SCREENING OF LIGANDS AND THEIR COMPLEXES WITH VO(IV) AND VO(V) COMPLEXES

Compound	<i>A. niger</i>						<i>C. albicans</i>					
	Diameter of inhibition zone (mm)			Activity index (%)			Diameter of inhibition zone (mm)			Activity index (%)		
Concentration	25	50	100	25	50	100	25	50	100	25	50	100
L ₁	12	15	20	55	60	67	14	16	17	58	67	61
L ₂	13	15	20	59	60	67	16	16	18	67	67	64
L ₃	13	14	21	59	56	70	15	14	18	63	58	64
[VOL ₁ H ₂ O]SO ₄	14	16	22	64	64	73	17	18	19	71	75	68
[VOL ₂ H ₂ O]SO ₄	14	17	22	64	68	73	17	17	20	71	71	71
[VOL ₃ H ₂ O]SO ₄	15	16	22	68	64	73	18	18	19	75	75	68
[VO L ₁ H ₂ O]Cl ₂	19	21	26	86	84	87	20	21	25	83	88	89
[VOL ₂ H ₂ O]Cl ₂	18	20	25	82	80	83	20	20	26	83	83	93
[VOL ₃ H ₂ O]Cl ₂	18	22	25	82	88	83	21	22	26	88	92	93
[VO L ₁ H ₂ O]Cl ₂	16	18	23	73	72	77	19	19	21	79	79	75
[VOL ₂ H ₂ O]Cl ₃	17	19	24	77	76	80	19	19	22	79	79	79
[VOL ₃ H ₂ O]Cl ₃	17	18	23	77	72	77	18	20	22	75	83	79
Miconazole	22	25	30	100	100	100	24	24	28	100	100	100

was incubated 24 h for bacteria at 35 °C and 72 h for fungi at 30 °C. During this period the test solution got diffused and the growth of inoculated microorganism was affected. The inhibition zone was developed at which the concentration was noted down. All the determinations were performed thrice. The results have been summarized in Tables 4 and 5 for antibacterial screening and antifungal screening, respectively.

The activity index of compounds was determined by using the expression given below:

$$\text{Activity index (\%)} = \frac{\text{Inhibition zone by test comp. (diameter)}}{\text{Inhibition zone by control (diameter)}} \times 100$$

Tables 4 and 5 clearly reveals that all the ligands are active against both the bacteria and both the fungi. On complexation their activities enhance considerably. The increased activity of metal chelates in respect of ligands can be explained on the basis of chelation theory. On chelation the polarity of the metal ion gets reduced to a greater extent due to the overlap of ligand orbitals and partial sharing of the positive charge of the metal ion with donor ligands [46].

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