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Antifungal Activities of Oxovanadium (IV) Complexes With Schiff Bases Derived From Dicarboxylic Acids

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Abstract

In view of the interesting results obtained by the complexes of vanadium metal, a series of oxovanadium (IV) complexes have been synthesized by the reactions of Schiff bases, derived from tere-phthalic acid, succinic acid, adipic acid and salicylaldehyde and 2-hydroxyacetophenone with oxovanadium (IV) sulphate in absolute ethanol. Complexes were well characterized on the basis of analytical data, magnetic susceptibility, UV-Vis and IR data. The X-band EPR spectra of all the complexes have been recorded in room and liquid nitrogen temperature. Powder X-ray diffraction pattern shows the particles are in nano range. Tentative structures of the complexes have been proposed. All the oxovanadium (IV) complexes have also been asayed for their antifungal activities against three fungi, viz. Aspergillus niger, Curvularia pallescens and Colletotrichum capsici.

Keywords: Oxovanadium (IV); Schiffbase; IR; UV-Vis; EPR; Powder X-ray diffraction; Antifungal activity.

Introduction

Vanadium, a metal that exists in different oxidation states ranging from -1 to +5 in cationic and anionic forms is physiologically important. Recently, many oxovanadium (IV) complexes with a variety of ligands have been synthesized. Schiff base ligands have received more attention due to their extensive usage in synthesis and catalysis. Advancement of bioinorganic chemistry has amplified interest in Schiff base complexes as it has been understood that these complexes could serve as models for biologically important species.[1-8] Schiff base ligands and their applications indicated that comparatively less research has been conducted on transition metal complexes with Schiff base ligands derived from *bis* aminomercaptotriazoles.[9] For oxovanadium (IV), a large number of mononuclear complexes have been reported in the various fields of study, but reports involving dinuclear oxovanadium (IV) complexes are rare.[10-12] In light of the interesting results obtained during past investigations, metal complexes with several ligands were prepared and studied. This paper includes the preparation, characterization and antifungal activities of oxovanadium (IV) complexes of Schiff base ligands derived from *tere*-phthalic acid, succinic acid and adipic acid, and salicylaldehyde and 2-hydroxyacetophenone.

Materials and methods

The chemicals used in the present study were of pure analytical grade and were procured from Aldrich and Merck. Ethanol and hydrazine hydrate were

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obtained from BDH. The physical measurement and analytical methods were applied as per the methods given for different instruments. The room temperature magnetic susceptibilities were measured using $Hg[Co(NCS)_4]$ as calibrant by Guoy's method. Electronic spectra of the complexes were recorded on Varian Cary-100 Bio UV-Vis spectrophotometer using DMSO as solvent. Conductance measurements were recorded in DMSO (10^{-3} M) using Elico conductivity bridge type CM-82. X-ray powdered diffractometer (Rigaku Geigerflex) with Cu Kα 1 (λ = 1.54060 Å) source was used to calculate the size of the particle using Debye-Scherrer equation. The IR spectra were recorded on a Perkin Elmer 783 spectrophotometer in nujol in 4000–200 cm^{-1} and EPR spectra were obtained at room temperature and liquid nitrogen temperature from Indian Institute of Technology Bombay, Mumbai, India using TCNE as *g* marker.

The triazoles were prepared following a previously reported method.[13] The condensation reactions of bis-(4-amino-5-mercapto-4H-1, 2, 4- triazole-3-yl) of *tere*-phthalic acid/succinic acid / adipic acid and salicylaldehyde/ 2-hydroxyacetophenone in absolute ethanol in the presence of few drops of concentrated hydrochloric acid give rise to formation of Schiff base ligands. These compounds undergo thione ⇌ thiol tautomerism and exist in (a) and (b) forms:

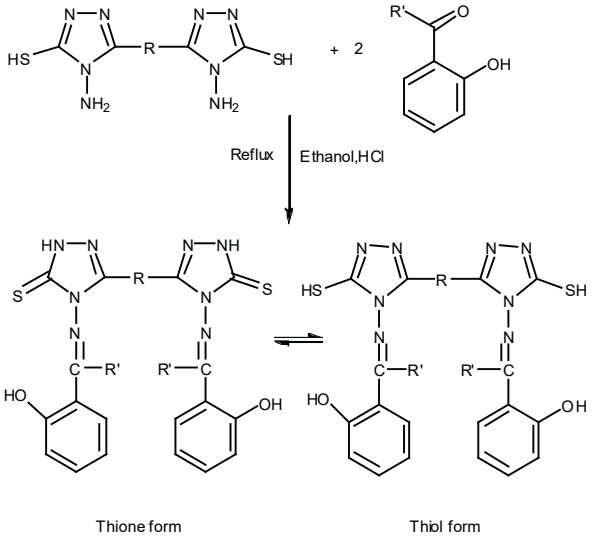

Fig. 1: Schiffbase ligands in tautomeric forms: (a) thione and (b) thiol.

R	R′	Abbreviation
$-(C_6H_4)-$	H	$PSTH_2$
$-(C_6H_4)-$	CH_3	$PATH_2$
$-(CH_2)_2-$	H	$SSTH_2$
$-(CH_2)_2-$	CH_3	$SATH_2$
$-(CH_2)_4-$	H	$ASTH_2$
$-(CH_2)_4-$	CH_3	$AATH_2$

Ethanolic solution of vanadyl sulphate and Schiff base ligand were mixed in a RB flask with 2:1 molar ratio and refluxed for about 10-12 hours till the formation of light green to green colored solution. The solution obtained was kept at 10^0C overnight. The crystalline precipitate formed was then filtered, washed with cold ethanol and ether and dried in *vacuu* and over fused $CaCl_2$. The $[(VO)_2(L)(H_2O)_2]$ type complexes were obtained according to the following equation:

$$2\ VOSO_4 + LH_2 \xrightarrow{\text{Ethanol, reflux}} [(VO)_2L(H_2O)_2] + 2\ H_2SO_4$$

(LH_2 = $PSTH_2$, $PATH_2$, $SSTH_2$, $SATH_2$, $ASTH_2$, $AATH_2$)

Where,

$PSTH_2$ = Schiff base derived from aminomercaptotriazole of *tere*-phthalic acid and salicylaldehyde

$PATH_2$ = Schiff base derived from aminomercaptotriazole of *tere*-phthalic acid and 2-hydroxyacetophenone

$SSTH_2$ = Schiff base derived from aminomercaptotriazole of succinic acid and salicylaldehyde

$SATH_2$ = Schiff base derived from aminomercaptotriazole of succinic acid and 2-hydroxyacetophenone

$ASTH_2$ = Schiff base derived from aminomercaptotriazole of adipic acid andsalicylaldehyde

$AATH_2$ = Schiff base derived from aminomercaptotriazole of adipic acid and 2-hydroxyacetophenone

Evaluation of fungicidal activity

(i) Test Fungi

The cultures of test fungi were obtained through the courtesy of Pathology Laboratory of Department of Botany, Deen Dayal Upadhyay Gorakhpur University, Gorakhpur. These fungi included *Aspergellus niger, Curvularia pallescence* and *Colletotrichum capsici*. The stock cultures were maintained on Czapek's agar.

(ii) Culture Medium

Czapek's agar medium[14] of following composition as adapted by Dox[15] was employed for the culture of test fungi throughout the present investigation:

Double Distilled Water	–	1000 ml
$NaNO_3$	–	3.0g
K_2HPO_4	–	1.0g
$MgSO_4.7H_2O$	–	0.5g
KCl	–	0.5g
$FeSO_4.7H_2O$	–	0.01g
Sucrose	–	30.0g
Agar	–	15.0g

The ingredients were taken in one 11 Erlenmeyer flask, plugged with non-absorbent cotton and sterilized at 15 lbs per sq. inch pressure for 30 minutes. 10 mg of streptopenicillin was added aseptically after cooling the medium to about 40^0C, in order to check bacterial contamination as recommended by Gupta and Banerjee.[16]

(iii) Preparation of Inoculum

The test fungi were grown in petriplate (80 mm diameter) containing 10 cm^3 of culture medium. Mycelial discs of 5 mm diameter along with the adhering agar, cut from the periphery of seven days old culture, served as inoculum throughout the present study. Care was taken to ensure a regular supply of uncontaminated, seven days old cultures until all *in vitro* experiments were over. The cultures were maintained at 28 ± 2^0C in a BOD incubator.

(iv) Screening of Chemicals for Fungitoxicity

The concentrations (10 ppm, 100 ppm, 1000 ppm) of each compound in acetone were tested against all the test fungi by poisoned food technique of Grover and Moore.[17]

(v) Assessment of Fungitoxicity

The fungitoxicity of the newly synthesized oxovanadium(IV) complexes were assessed in terms of percent inhibition of mycelial growth of test fungi using poisoned food technique[18] with some modifications as follows. Each assay was replicated thrice and the average of observations was recorded.

(iv) Poisoned Food Technique

The desired amount of test material, *e.g.* chemical is taken with acetone to make a final volume of 0.5 cm^3 in presterilized cooled petriplate (80 mm diameter). Melted culture medium (9.5 $cm^{3)}$ is poured in the plate, which is gently swirled to mix the content thoroughly. In the control set, the mixture of chemicals is replaced by an equal amount of solvent. After the medium solidifies, one mycelial inoculum disc of the test fungus i.e., aseptically inoculates upside down on the medium in the center of each plate. The inoculate disc (5 mm diameter) is cut from the periphery of the mycelial colony of a seven days old culture of the test fungus, with the help of sterilized cork borer of appropriate bore size.

The assay plates were incubated at 28 ± 2^0C for six days. On the seventh day, the colony diameter of the text fungus was noted in mutually perpendicular directions and average of observation recorded. Mycelial growth was calculated by subtracting the diameter inoculation disc (0.5 mm) from the final colony diameter. The percent inhibition of mycelial growth was calculated using the following formula:

$$\text{Percent (\%) inhibition of mycelial growth} = \frac{g_c - g_t}{g_c} \times 100$$

Where, g_c = mycelial growth in term of colony diameter in control set

g_t = mycelial growth in term of colony diameter in the treatment

Results and Discussion

The analytical data are compatible with a 2:1 metal to ligand stoichiometry. The complexes are green /dark green in colour, soluble in DMF, DMSO and sparingly soluble in nitrobenzene. Electrical conductance measurements in DMF reveal that they are non electrolyte in nature.

Magnetic moment and electronic spectra

Room temperature magnetic moments of oxovanadium (IV) complexes found *ca.*1.73 per vanadium (IV) centre.[19] The electronic spectra of the oxovanadium (IV) complexes are most often interpreted by in terms of energy level scheme proposed by Ballhausen and Gray model.[20] Usually three bands are observed in the visible region assigned to $^2B_2(d_{xy}) \rightarrow {}^2E(d_{xz}, d_{yz})$, $^2B_2(d_{xy}) \rightarrow {}^2B_1(d_{x^2-y^2})$ and $^2B_2(d_{xy}) \rightarrow {}^2A_1(d_{z^2})$, respectively.[21] The electronic spectra of these complexes recorded in DMSO show bands in the regions 12195-12350 cm^{-1}, 15300–15500 cm^{-1} and 18300–18400 cm^{-1}.

Infrared spectra

IR spectra of the Schiff base ligands and their corresponding oxovanadium (IV) complexes give

several bands.[22] Schiff bases exhibit strong band at *ca.* 1620 cm^{-1} assigned to ν(C=N). In complexes, this band shifts to lower frequency (*ca.* 10–15 cm^{-1}) indicating the participation of azomethine nitrogen in bond formation with VO^{2+} ion. New bands appear in metal complexes at *ca.* 475–430 cm^{-1} due to ν(V–N) vibrations. The band due to ν(C=N) (triazole ring) appears at *ca.* 1575 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 bases and their oxovanadium(IV) complexes show bands at *ca.* 3128–3050 cm^{-1} due to ν(Ar-H). The presence of coordinated water molecule in the complexes is indicated by a broad band at 3400 cm^{-1} due to ν(-OH) and weak bands in the region 820–780 cm^{-1} and 720–680 cm^{-1} due to ν(-OH) rocking and wagging modes of vibration.[13]

IR spectra of the ligands have prominent bands appearing at *ca.* 3380, 3200 and 1250 cm^{-1} due to ν(O-H), ν(N-H) and ν(C=S) stretching modes of vibration, respectively.[22] These bands are missing in the complexes. Further, a weak band is observed at 2570–2490 cm^{-1} in the spectra of ligand (in solution) assignable to ν(S-H). In complexes the band disappears indicating the deprotonation of thiol group and formation of bond between VO^{2+} and sulphur. Careful screening of the spectra reveals the appearance of a new band in the complexes at *ca.* 380 cm^{-1} assignable to ν(V-S). The complexes show bands at *ca.* 490–470 cm^{-1}, which correspond ν(V-O) vibration.[23] In addition, all complexes show a band at *ca.* 980–970 cm^{-124} due to ν(V = O).

On the basis of IR data, it is inferred that the oxovanadium(IV) ion is bonded with azomethine nitrogens, thiol sulphurs and coordinated water oxygens. All these data indicate that ligands are dibasic, tetradentate chelating agents.

Electron paramagnetic resonance (EPR) spectra

EPR spectra of VO^{2+} polycrystalline sample at room temperature (298K) and at liquid nitrogen temperature (77K) exhibit an eight line pattern corresponding to the usual parallel and perpendicular components of g and hyperfine A-tensor.[25] In the frozen state, the same solution displays well resolved axial anisotropy with two sets of eight line pattern. At room temperature the dinuclear vanadium (IV) complexes exhibit a similar eight line pattern as observed with the mononuclear complexes. The spin-spin interactions in these compounds are so insignificant that each unpaired electron virtually interacts with only one vanadium centre.[26]

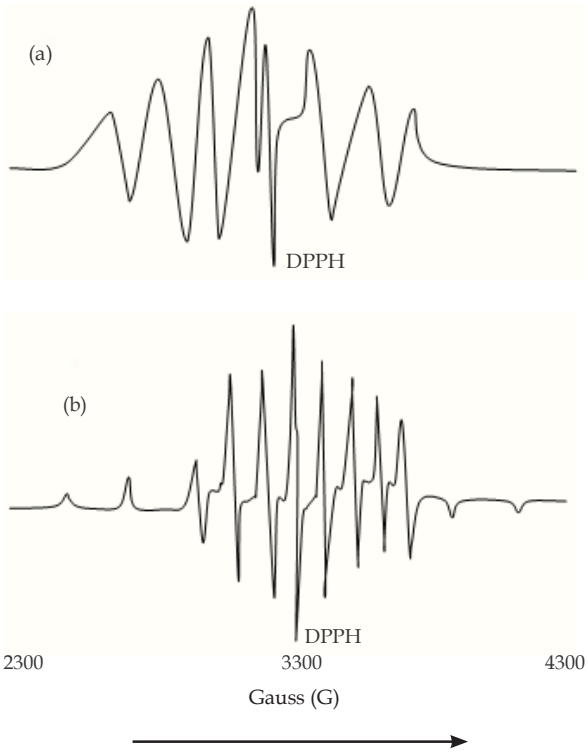

Fig. 2: EPR spectra of $[(VO)_2(SST)(H_2O)_2]$ in DMSO at (a) RT and (b) LNT.

X-ray powder diffraction pattern

X-ray powder diffraction pattern is a rapid analytical technique. This technique is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation to concentrate and directed toward sample.

X-ray powder diffraction pattern of one representative complex $[(VO)_2(SST)(H_2O)_2]$ has been carried. The size of the particles has been calculated using Debye-Scherrer formula [27]. which is given by $D=0.94\ \lambda / \beta \cos\theta$; Where D is the size of the particle, λ is the wavelength of X-ray, β (expressed in radian) is the full width at half maximum (FWHM) after correcting the instrument peak broadening and θ is the Bragg's angle. The size of the particles is found in the range 32-45 nm which falls in the nano range.

A series of novel oxovanadium(IV) complexes with Schiff bases derived from aminomercaptotriazoles of dicarboxylic acids have been prepared and fully characterized. Thus, on the basis of above studies, the following structure be tentatively assigned for the $[(VO)_2\ L(H_2O)_2]$ complexes.

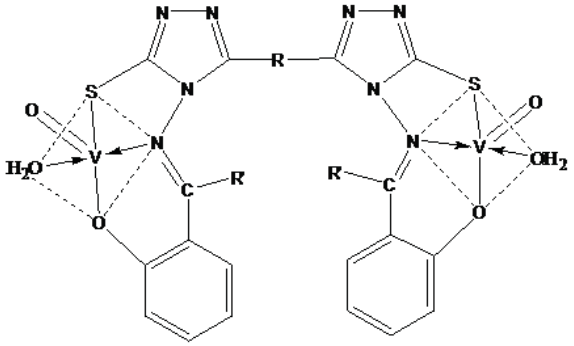

Fig. 3: Proposed structure of dinuclear oxovanadium (IV) complexes.

Fungicidal activity

Fungicides disrupt the metabolism of fungal pathogens, inhibiting their development or killing them off. However, the various active substances act at different points (targets) in the metabolic pathways of the fungi. Some substances act very specifically, as they block the activity of individual enzymes or groups of enzymes. Other active substances inhibit several metabolic steps, meaning that they are less selective. The path and extent of distribution on the plant surface and uptake into plant tissues are characteristics that allow for a differentiation among fungicidal active substances. Non-systemic active substances do not penetrate into plant tissues, and are therefore unable to reach fungal structures that have already developed within the plant.[28] So these active substances can only be applied to obtain protective activity. Fungicides with systemic properties can be applied after the pathogen has succeeded in penetrating into the plant's tissues, as the internal transport of the active substance allows it to reach the fungal structures in order to kill them off. However, curative activity is only possible up to a certain point. Fungicides are active substances that are taken up extensively at the plant surface. They tend to form a depot of active substance from which a continuous transfer takes place, either into the plant, or across its surface.[29]

The result is a much-extended duration of activity. Only a few groups of active substances are available for controlling the most important fungal diseases of cereal crops. The repeated use of fungicides from the same class of active substance encourages the development of resistance, which can quickly become a fixed genetic feature, spreading rapidly within the fungal population. Eventually, the resistant variant of the pathogen predominates, and all fungicides with the same mode-of-action are equally useless against it. In order to prevent the development of resistance to fungicides, spraying programmes should include active substances with different modes of action. Unnecessary applications and treatments with reduced application rates should also be avoided; these not only increase the risk of resistance development, they also represent a false economy if they fail to check the progress of the disease. Different chemical compounds have been used as chemotherapeutants to control different diseases. However, several chemical compounds are dangerous to human beings and host plants. The increasing consciousness of the hazards involved in the use of such fungicides has reinforced the need to search for more potent and eco-friendly compounds.[30,31]

Activities of the complexes (Table 1) reveal that the activity of the complexes is affected by the nature of substituent (s) and donor site of the ligands, this in relation to their membrane permeability, a key factor in determining their entry inside the cell. In each table, activities of the complexes with respect to different fungi at different concentrations have been compared with standard drug fluconazole. The most active complex (es) of each series against different fungi at 1000 ppm concentrations have also been compared and illustrated (Figure 4).

Table 1: Fungicidal screening data of oxovanadium (IV) complexes with Schiff bases derived from bis-(4-amino-5-mercapto-4H-1,2,4-triazol-3-yl) arene/alkanes and salicylaldehyde / 2-hydroxyacetophenone

Compound	Fungicidal Inhibition (%) Compound dose (ppm)								
	Aspergillus niger			Curvularia pallescens			Colletotrichum capsici		
	10	100	1000	10	100	1000	10	100	1000
$[(VO)_2(PST)(H_2O)_2]$	42.6	64.3	80.8	39.6	50.4	79.0	38.0	58.2	76.8
$[(VO)_2(PAT)(H_2O)_2]$	35.0	52.6	80.4	33.6	50.2	77.6	36.5	56.2	75.5
$[(VO)_2(SST)(H_2O)_2]$	36.7	54.2	78.2	35.8	49.0	77.0	35.4	54.0	74.6
$[(VO)_2(SAT)(H_2O)_2]$	38.6	56.8	76.2	37.6	48.6	75.4	37.8	55.8	71.0
$[(VO)_2(AST)(H_2O)_2]$	40.3	62.2	76.4	38.1	46.8	78.2	35.0	58.0	74.5
$[(VO)_2(AAT)(H_2O)_2]$	40.5	60.4	76.0	38.8	47.2	76.0	35.2	57.4	72.4
Fluconazole	100	100	100	100	100	100	100	100	100

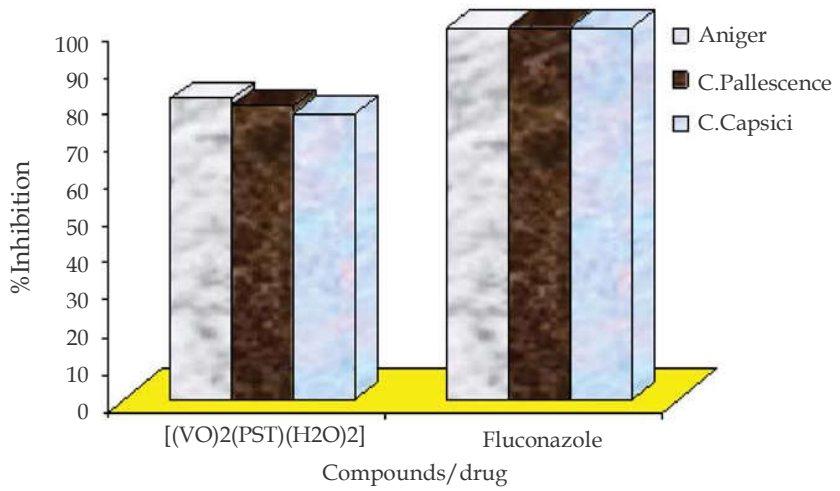

Fig. 4: The most active complex of against different fungi at 1000 ppm.

Where,

$PSTH_2$ = Schiff base derived from bis-(4-amino-5-mercapto-4H-1,2,4- triazol-3-yl) arene and salicylaldehyde

$PATH_2$ = Schiff base derived from bis-(4-amino-5-mercapto-4H-1,2,4- triazol-3-yl) arene and 2-hydroxyacetophenone

$SSTH_2$ = Schiff base derived from bis-(4-amino-5-mercapto-4H-1,2,4- triazol-3-yl) ethane and salicylaldehyde

$SATH_2$ = Schiff base derived from bis-(4-amino-5-mercapto-4H-1,2,4- triazol-3-yl) ethane and 2-hydroxyacetophenone

$ASTH_2$ = Schiff base derived from bis-(4-amino-5-mercapto-4H-1,2,4- triazol-3-yl) butane and salicylaldehyde

$AATH_2$ = Schiff base derived from bis-(4-amino-5-mercapto-4H-1,2,4- triazol-3-yl) butane and 2-hydroxyacetophenone

Conclusion

The Schiff bases were derived from three dicarboxylic acids: *tere*-pthalic acid, succinic acid, adipic acid with salicylaldehyde and 2-hydroxyacetophenone in order to prepare binuclear oxovanadium (IV) complexes. These Schiff bases form stable complexes with VO^{2+} ions. The EPR spectrum of oxovanadium (IV) complexes gives the expected splitting pattern at room and liquid nitrogen temperature. Study of X-ray powder diffraction pattern reveal that the size of the particles is in the nano range. The complexes show significant antifungal activity as compared to standard drug.

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