

Research Article

Complexation of Oxovanadium(IV) and Dioxouranium(VI) with Synthesized 1,2-(Diimino-4'-antipyrinyl)-1,2-diphenylethane Schiff Base: A Thermodynamic, Kinetic, and Bioactivity Investigation

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We report the comparative synthetic methodologies and characterization of a tetradentate Schiff base ligand 1,2-(diimino-4'-antipyrinyl)-1,2-diphenylethane (DE). The target synthesis of oxovanadium(IV) and dioxouranium(VI) complexes (vanadyl and uranyl) with the (DE) ligand was also attempted to envisage the effect of metal ion steric factor on complexation process through solution phase thermodynamic and kinetic studies. The thermodynamic stabilities of synthesized vanadyl and uranyl (DE) complexes are discussed in light of their solution phase thermodynamic stability constants obtained by electroanalytical method. A comparative kinetic profile of vanadyl and uranyl complexation with DE is also reported. The complexation reaction proceeds with an overall 2nd order kinetics with both metal ions. Temperature dependent studies of rate constants present an activation energy barrier of ca. 40.913 and 48.661 KJ mol⁻¹, for vanadyl and uranyl complexation, respectively, highlighting the metal ion steric and ligand preorganization effects. The synthesized Schiff base ligand and its vanadyl and uranyl complexes were screened for biocidal potential as antibacterial, antifungal, and anthelmintic agents with the results compared to corresponding reference drugs.

1. Introduction

Studies related to structure, reactivity, and applications of newly reported ligands and complexes form an imperative aspect of modern day inorganic chemistry. An insight into thermodynamic, kinetic, and biological property of compounds is always exciting and desirable from application point of view. Schiff bases are one of the most widely used organic compounds and their metal complexes have a variety of biological, analytical and material applications in addition to their important roles in catalysis and organic synthesis [1–6]. Schiff bases derived from the condensation of 4-aminoantipyrine with diketones represent an interesting class of biologically important chelating ligands; metal complexes of these ligands are of great interest owing to their pharmacological and analytical applications [7–11]. Conventional

Schiff base synthesis makes use of high boiling, toxic organic solvent as reaction media for refluxing the amine and the aldehyde mixtures, followed by lengthy chromatographic workup of purification and recrystallization. In addition, to keep the equilibrium in the direction of forward reaction, the water is usually removed, either azeotropically by distillation or with a suitable drying agent [12–14]. Environmentally benign synthetic methods have received considerable attention and some solvent-free protocols have been developed [15]. Microwave assisted organic synthesis (MAOS) are motivating for their low energy expense, very little solvent demand, enhanced yields, and shortened reaction times in a variety of reactions [16, 17]. In embracing the principles of green chemistry [18–20], herein we depict a comparative account of the conventional and nonconventional synthetic protocols for the synthesis of Schiff base (DE) obtained from

the condensation reaction of 4-aminoantipyrene with benzil. The target synthesis of oxovanadium(IV) and dioxouranium(VI) (vanadyl and uranyl) complexes with the Schiff base ligand (DE) was also attempted to envisage the effect of metal ion steric factor on complexation process through solution phase thermodynamic and kinetic studies. The thermodynamic stabilities of vanadyl and uranyl Schiff base (DE) complexes are discussed in light of their calculated solution phase stability constants using *Calvin-Bjerrum* and *Irwing-Rossotti* [21, 22] potentiometric method. The kinetic profile of the DE-uranyl and DE-vanadyl complexation through UV-Visible studies describes the effect of metal ion concentration and Steric effect on complexation reaction. Keeping in view the bioactive nature of the starting compounds and reported bioactivity of vanadium complexes [23–25], the synthesised ligand (DE) and its complexes were screened for biocidal potential using the standard protocols [26] with the results compared to corresponding reference drugs.

2. Materials and Methods

All chemicals and solvents were obtained from commercial sources as laboratory reagents and used without further purification in the syntheses. The metal salts used in complexation were analytical grade uranyl nitrate and vanadyl sulphate. The microwave assisted synthesis was carried out in Teflon reaction cells with SHARP 1000 W/R-21LCF commercial microwave oven fitted with a temperature relay, with circuit break at 145°C. The high performance liquid chromatography (HPLC) was carried on Shimadzu LC-20A with a SPD-M20A variable-wavelength UV detector. The mobile phase used consisted of water: methanol (10 : 90, v/v), flowing at rate of 0.5 mL min⁻¹. Electronic spectra of the complexes were recorded on a Shimadzu 3600 UV-Visible spectrophotometer with thermostatic control. CHN analyses of all the synthesized compounds were done on Vario EL III CHNS analyser. FT-IR spectra were recorded as KBr pellets with a Perkin Elmer FTIR Spectrum-2 in the 4000–400 cm⁻¹ range. The ¹H NMR spectrum was recorded in CDCl₃ on a Bruker Avance DRX 500 MHz NMR spectrometer. The mass spectra were taken on Micromass: Q-ToF micro YA-105. All instrumental measurements were done at room temperature (around 25°C) except in case of kinetic profile.

3. Synthesis of 1,2-(Diimino-4'-antipyrinyl)-1,2-diphenylethane (DE)

The tetradentate Schiff base ligand was synthesized by three different synthetic protocols (solvent refluxing, microwave assisted, and solvent free fusion method) for a comparative study aimed at environmentally benign procedure.

3.1. Solvent Refluxing Method. In this method an ethanolic solution of benzil (1.05 g, 5 mmol) and 4-aminoantipyrene (2.03 g, 10 mmol) was refluxed at 60°C for about 05 hrs. On cooling and solvent evaporation, the yellow solid of Schiff base ligand (DE) got separated which was filtered as crude product and recrystallized from ethanol.

3.2. Microwave Assisted Method. In this method the reactants in a molar ratio of 2 : 1 (2.03 g, 10 mmol of 4-aminoantipyrene and 1.05 g, 5 mmol of benzil) were thoroughly mixed with silica gel and put inside the Teflon tube for microwave irradiation under medium power for 05 minutes generating a maximum temperature up to 145°C. The solid product was dissolved in ethanol to separate the compound and silica gel; the Schiff base product got separated on evaporation of solvent.

3.3. Solvent-Free Fusion Method. In an effort to introduce a novel eco-friendly synthetic procedure, solvent-free fusion method was attempted. In the solvent-free fusion reaction, the reactant with higher melting point, that is, 4-aminoantipyrene (M.P = 110°C), was melted and then the other reactant, benzil (M.P = 90°C), was added to the molten state of the former which served both as the reagent and as solvent, besides providing a high reaction temperature. The reaction mixture was kept at 100°C in a silicone oil bath under constant stirring for 2 hrs, over a magnetic stirrer. After stirring time the solid product was dissolved in ethanol and filtered; the filtrate on evaporation produced the Schiff base compound.

4. Synthesis of Complexes

The complexation of DE with metal salts was carried out by refluxing an equimolar (1:1) mixture of uranyl nitrate and vanadyl sulphate with Schiff base ligand DE, respectively, for about 5-6 hrs in ethanol. The progress of the reaction was followed by TLC. After completion of reaction time (6 hrs), the refluxed solution was concentrated to one-third of its initial volume on a water bath. The products were obtained on filtration, washed with ethanol, and dried under vacuum. A bright yellow compound of composition [UO₂(DE)](NO₃)₂ with melting point (M.P) 290–300°C and a grey compound of composition [VO(DE)]SO₄ with M.P 220–225°C were obtained for uranyl nitrate and vanadyl sulphate complexation with DE.

5. Results and Discussion

5.1. Comparative Synthetic Methodology. The Schiff base 1,2-(diimino-4'-antipyrinyl)-1,2-diphenylethane (DE) was synthesised by the condensation of 1-phenyl-2,3-dimethyl-4-aminopyrazol-5-one (4-aminoantipyrene) with 1,2-diphenylethane-1,2-dione (benzil) using three synthetic methodologies. The efficacy of these methods was compared in terms of reaction time, percent yield, and energy demand (Table 1).

The conventional solvent refluxing method was the least efficient of the three methodologies in terms of time and energy demand, besides being economically and environmentally less viable. The proposed fusion method is impressive in terms of product purity and appreciable yield in a smaller time. Thus relatively smaller reaction time, no solvent demand, and lower chemical and energy expense make this method meet green chemistry criteria [18]. Although microwave assisted synthesis required minimum reaction

TABLE 1: Comparative account of synthetic procedures in terms of yield and time.

	Solvent refluxing		Fusion method		Microwave			
	Time (min)	% yield	Time (min)	% yield	Solid support (silica gel)		Solvent (ethanol)	
					Time (min)	% yield	Time (min)	% yield
Schiff base	240	40	120	50	3	32	1	32.1
(DE)	300	45	150	70	5	60	5	78.1

TABLE 2: Characterization of Schiff base complexes.

Compound (formula)	Elemental analysis			Melting point (°C)	IR absorption (cm ⁻¹)				Λ_{\max} (nm)	Λ_m ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)
	% C	% H	% N		$\nu\text{C=O}$	$\nu\text{C=N}$	$\nu\text{M-N}$	$\nu\text{M-O}$		
[C ₃₆ H ₃₂ N ₆ O ₂] DE	72.86 (74.54)	5.40 (5.51)	12.77 (14.48)	179–185	1655 (vs)	1635 (vs)	—	—	410	20.0
[VO-(DE)]SO ₄	52.7 (53.07)	3.85 (3.93)	10.08 (10.32)	220–225	1630 (s)	1600 (ms)	400 (m)	540 (m)	502	160.6
[UO ₂ (DE)](NO ₃) ₂	51.06 (52.98)	4.98 (4.23)	10.52 (11.32)	290–300	1632 (s)	1615 (ms)	410 (m)	570 (m)	480	172.8

vs: very strong; s: strong; ms: medium to strong; m: medium.

time and also generated the best yield, the little need of solvent, product purification workup, and the need of microwave oven and microwave reaction vials put it next in choice over the fusion method.

In the synthetic procedures, apart from a sharp melting point of 180°C, formation of condensation product was also evidenced from UV-Visible spectral change and HPLC retention time (Figure 1). Reaction progress and completion and product purity were monitored by TLC (Ethyl acetate, n-hexane (1:1) developing solvent, and iodine vapour visualization). The Schiff base ligand was purified by chromatographic separation over a silica column using 1:1 ethyl acetate and n-hexane mobile phase. The compounds eluted from the column in the following order: Benzil, Schiff base (DE), and finally 4-aminoantipyrine with retention time 2.67, 2.88, and 3.97 minutes sequentially.

5.2. Spectroscopic Characterization of Ligand and Complexes.

The structural characterization of the ligand was done by the spectral (IR, NMR) mass and elemental (C, H, N) analysis. The Schiff base ligand was obtained as light yellow compound with M.P 179–185°C. The IR (KBr) displayed characteristic Carbonyl absorption (ν , cm⁻¹): 1650–1660, ν (cyclicketone C=O), 1630–1640 ν (CH=N). In the ¹H NMR, ¹H NMR (CDCl₃, 400 MHz, δ , ppm): (7.17–7.6 m for aromatic protons of C₆H₅), 3.3–3.4 (m, 6H for –N–CH₃ protons) 2.3 (m for methyl protons on double bonded ring carbon =C–CH₃). The high resolution electron impact mass spectrometry HRESIMS depicted the molecular ion peak at (m/z) 581.44 calcd. for C₃₆H₃₂N₆O₂ [M+H]⁺. The absorption spectra of 10⁻⁴ M solution of DE in ethanol at λ ranging from 300 to 700 nm, against the same solvent as a blank, give 2 bands at 330 nm ($\epsilon = 1.9 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$) and a sharp band (λ_{\max}) 410 nm with ($\epsilon = 2.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). The absorption can be

assigned to the intraligand transition bands corresponding to $n-\pi^*$ and $\pi-\pi^*$ transitions, respectively [27].

The characterization of Schiff base (DE) complexes was done through changes in the diagnostic IR absorption bands, UV-Visible spectra, melting point, and CHN analysis which are summarized in Table 2. The 1:1 stoichiometry of vanadyl and uranyl complexes of DE was spectrophotometrically obtained using Jobs continuous variation and molar ratio methods (Figure 2). The monomeric nature of vanadyl DE complex was established from the characteristic metal-oxygen ν (V=O) stretching frequency in the region 965–960 cm⁻¹ [28]; the absence of a band below 900 cm⁻¹ due to bridging vanadyl group –V–O–V– rules out the possibility of polymeric vanadyl complexes [29]. The three IR bands corresponding to ionic sulphate group in [VO(DE)]SO₄ complex were observed at 900, 620, and 1110 cm⁻¹ [30]. The IR frequency of the O=U=O was observed at 908 cm⁻¹ and was in accordance with the expected value for a cationic uranyl complex [31]. The electronic spectra of the vanadyl and uranyl complexes depict slight splitting and shifting of the band positions to longer wavelength compared to that of the free ligand DE. The absorption bands at 502 nm and 795 nm (weak band) in case of [VO(DE)]²⁺ were assigned to the ²B₂ → ²A₁ and ²B₂ → ²E transitions of square pyramidal geometry [30]. The intense band at 480 nm in case [UO₂(DE)]²⁺ was assigned to the ligand to metal charge transfer (LMCT) transition of nonbonding electrons of ligand DE to the empty d orbitals of dioxouranium(VI) [32]. The high molar conductance of the DMF solution of vanadyl and uranyl DE complexes (Table 2) verify electrolytic nature of [VO(DE)](NO₃)₂ and uranyl [UO₂(DE)]SO₄. To get an insight of molecular geometry, we used density functional theory for structure optimization of Schiff base ligand (DE)

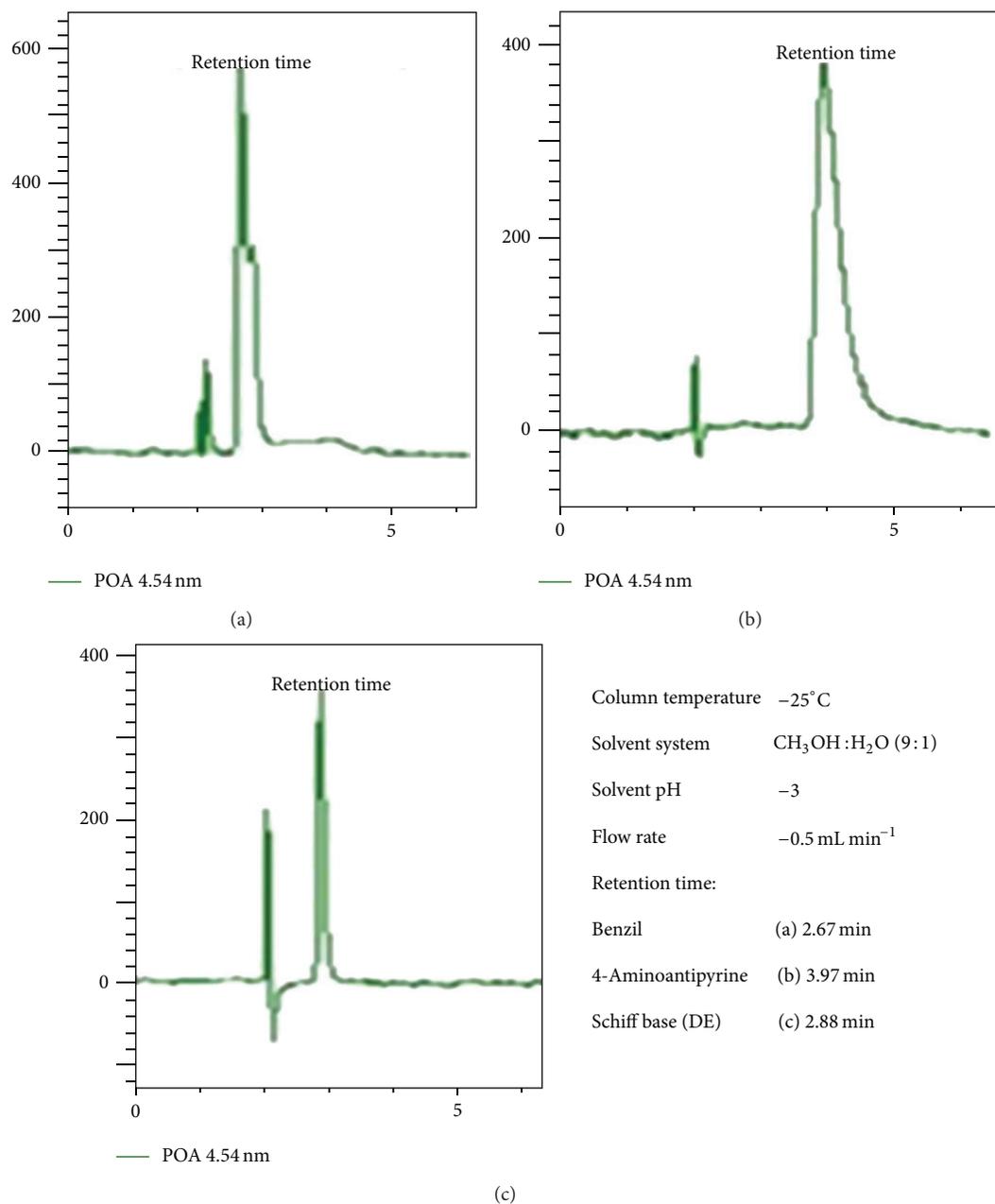


FIGURE 1: HPLC retention time of Schiff base (DE) and reagents.

and its uranyl and vanadyl complexes. The optimized geometries of vanadyl $[\text{VO}(\text{DE})]^{2+}$ and uranyl $[\text{UO}_2(\text{DE})]^{2+}$ complex ions were found to be square pyramidal and tetragonally compressed octahedron, respectively (Figure 3).

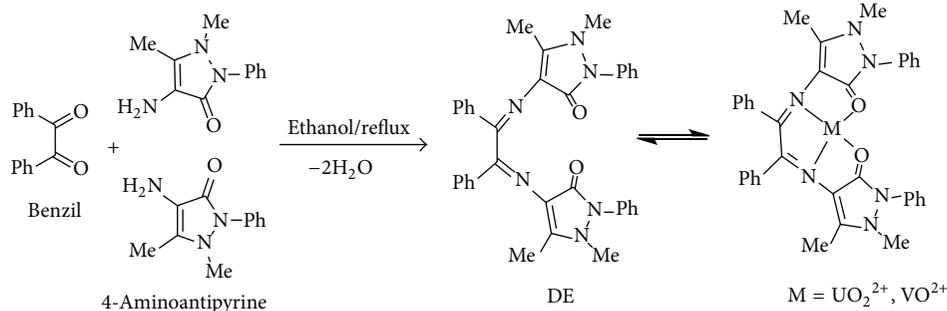
5.3. Thermodynamics of Complexation. The synthesis of the Schiff base and its complexation with vanadyl nitrate and uranyl sulphate was carried in two steps and is depicted in Scheme 1.

5.4. Determination of Stability Constant. The protonation constant of DE was determined by adopting the method suggested by *Irwing and Rossetti*. The plots of pH versus

volume of alkali added were drawn (Figure 4) and used for evaluation of nA , using

$$nA = \frac{(E_0 + N)(V_2 - V_1)}{(V_0 + V_1)T_{L_0}}, \quad (1)$$

where N stands for concentration of KOH (100 mM) and $(V_2 - V_1)$ is the displacement (mL) of the ligand curve relative to acid curve (Figure 4), where V_2 and V_1 are the volume of alkali added to reach the same pH value as for free acid. E_0 and T_{L_0} are the resultant concentrations of HCl and Ligand (DE), respectively. V_0 is the initial volume of reaction mixture (20 mL). Proton-ligand stability constant $\log K_a$ value of



SCHEME 1: Synthesis of Schiff base (DE) and its metal ion complexation.

ligand was calculated from formation curve (nA versus pH) by half integral method, pH at which nA = 0.5 (Figure 5(a)). From the shift in equivalence point values and corresponding pH values, the value of pK_a for DE was calculated to be 7.83. Stability constants of metal-DE complexes ([VO(DE)]²⁺ and [UO₂(DE)]²⁺ complex) were determined using Bjerrum pH metric method. In this regard three sets of solutions were titrated pH metrically against standard potassium hydroxide solution at constant temperature (298 K).

- (1) Free acid titration (A): HCl (100 mM).
- (2) Free acid + ligand titration (A + DE): HCl + Schiff base (DE).
- (3) Free acid + ligand + metal titration (A + DE + M): HCl + ligand (DE) + Metal ion solution (M) [M = (Vanadyl sulphate, Uranyl nitrate)].

Metal-ligand stability constants (log K) were determined by the half integral method by plotting nL versus pL (Figure 5(b)). The experimental nL values were determined using

$$nL = \frac{(E_0 + N)(V_3 - V_2)}{(V_0 + V_2)T_{M_0}}, \quad (2)$$

where N, E₀, V₀, and V₂ have same significance as in (1), V₃ is the volume of KOH added in the metal ion titration to attain the same pH reading, and T_{M₀} (10 mM) is the concentration of metal ion in reaction mixture. Plots of nL versus pL allowed calculation of the stability constants by the Bjerrum method (Figure 5(c)). The calculated stability constant values of metal-DE complexes are 5.01 × 10³ and 2.82 × 10³ (log K = 3.70 and 3.45) for vanadyl and uranyl complexes, respectively. The relatively higher stability constant of the vanadyl complex than uranyl complex can be attributed to the preorganization energies needed for the metal ion to get into the planar Schiff base ligand (DE) [27, 33, 34].

6. Kinetics of Complexation

Kinetic investigation of complexation reaction was carried out by absorbance measurements at 410 nm (λ_{max} of DE). The absorbance at 410 nm showed remarkable changes (decrease) in a time dependent manner upon addition of metal ions,

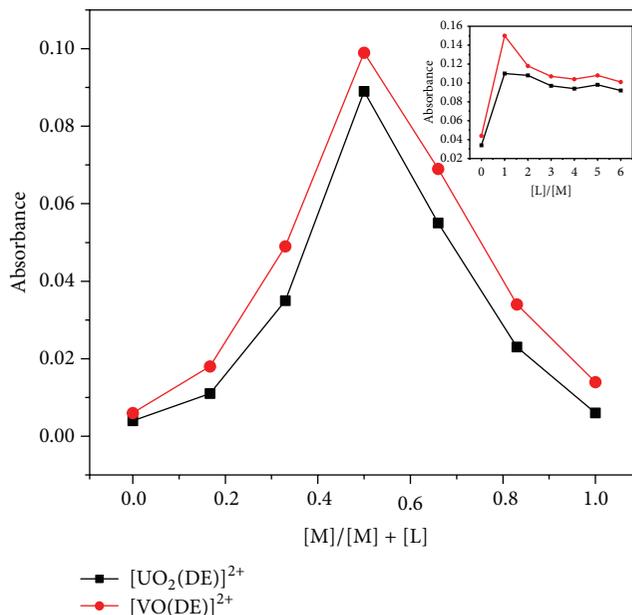


FIGURE 2: Stoichiometry of DE-vanadyl and DE-uranyl complexation by Jobs method. Insert: mole ratio plot.

which we ascribed to the slowness of the complexation reaction. The decreases in absorbance were relatively slower in case of uranyl system than vanadyl system. It was this slowness which prompted us to undertake the kinetic studies of this complexation reaction. The reaction of metal ions with DE can be expressed by the following equation:



where M = UO₂²⁺ and VO²⁺. The rate equation for the complexation reaction was established as under

$$\text{Rate } (\nu) \propto [M]^X [DE]^Y \quad (4)$$

$$\nu = k [M]^X [DE]^Y$$

under pseudo first order conditions:

$$\nu_1 = k' [M]^X, \quad (5)$$

$$\nu_2 = k'' [DE]^Y \quad \left\{ \text{where } k' = k [DE], k'' = k [M] \right\}.$$

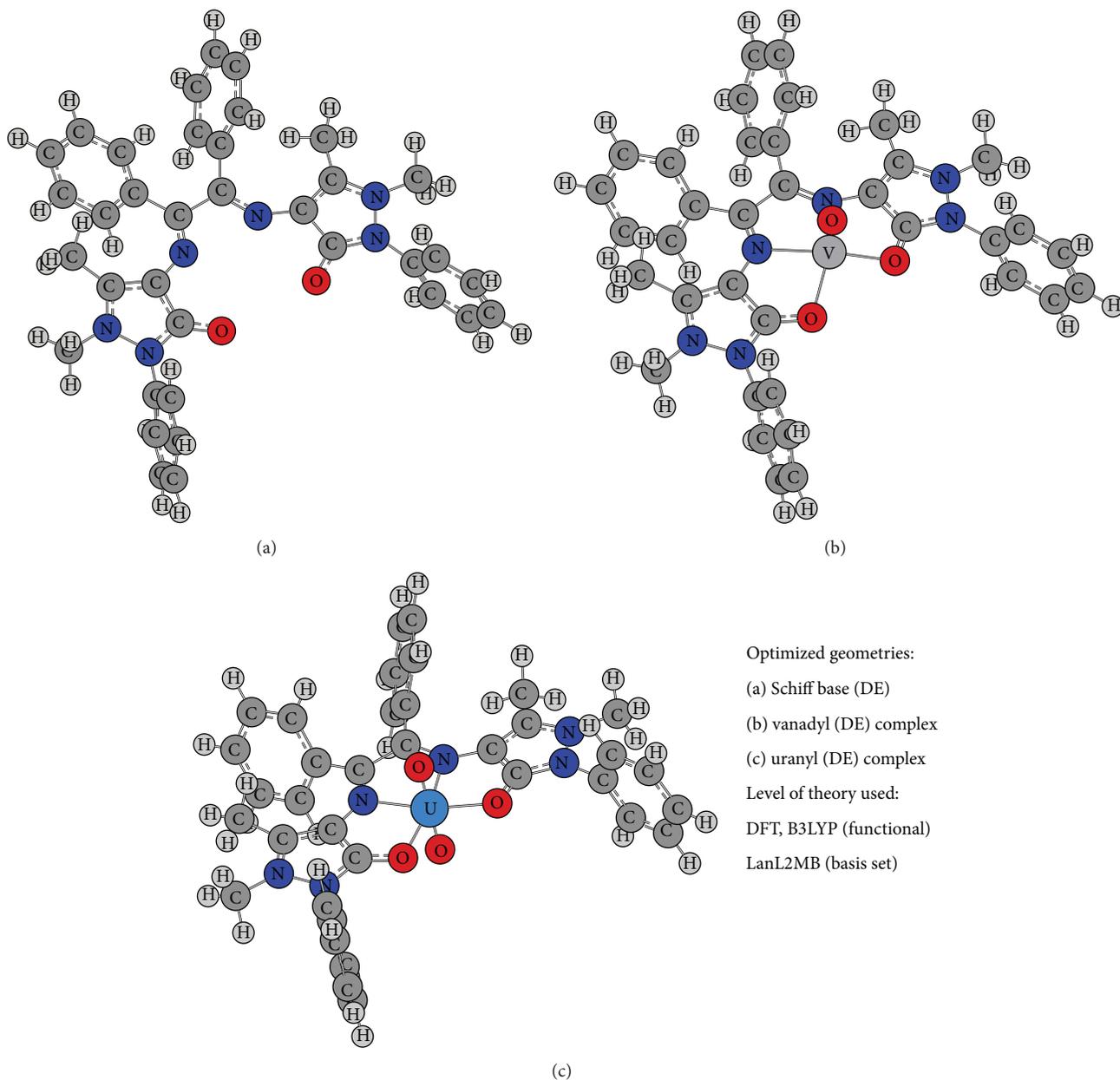


FIGURE 3: Optimized geometries of Schiff base (DE), vanadyl-DE, and uranyl-DE complex.

The absorbance changes at varying concentrations of one reactant and fixed (excess) concentration of other in logarithmic scale was observed as a straight line with slopes equal to x and y , respectively, and the intercepts equal to k' and k'' , respectively. Value of actual rate constant (k) was then determined from the intercept values after substituting for the concentration values used for the studies. The plots of $\ln(\text{Rate})$ versus metal ion concentration were observed to be a straight line with slope of 0.980 indicative of first order kinetics with respect to metal ion concentration (Figure 6). Similar studies, keeping DE concentration as limiting and metal ion concentration in excess, again showed a straight line predicting first order kinetics with respect to DE as well. Thus, from concentration profile kinetic study, the

complexation reaction was observed to follow first order kinetics with respect to metal ions and DE with an overall 2nd order kinetics. However, the pseudo first order kinetics with respect to both reactants was further verified by using the 1st order integrated rate equation

$$t = \frac{2.303}{k} \log \frac{A_0}{A_t} \quad (6)$$

The plot of t versus $\log(A_0/A_t)$ was observed as a straight line with slope equal to $k/2.303$ (Figure 7). The rate constant values from both the initial rate method and integrated rate law calculations were in close agreement with each other confirming 1st order kinetics for both reactants and an overall

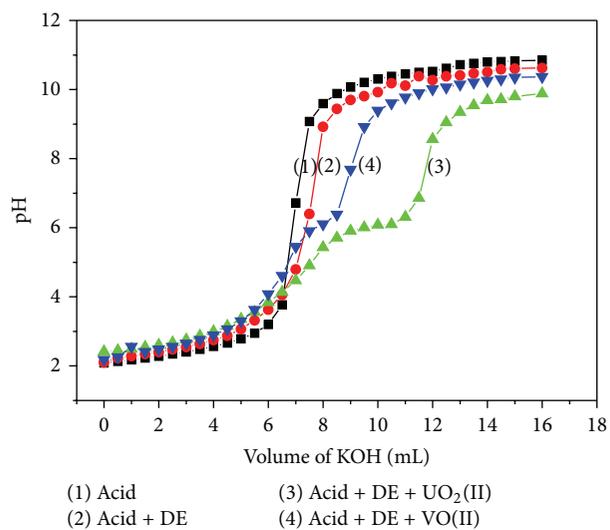


FIGURE 4: Plot depicting pH titration of ligand (DE) in presence of vanadyl and uranyl metal ions.

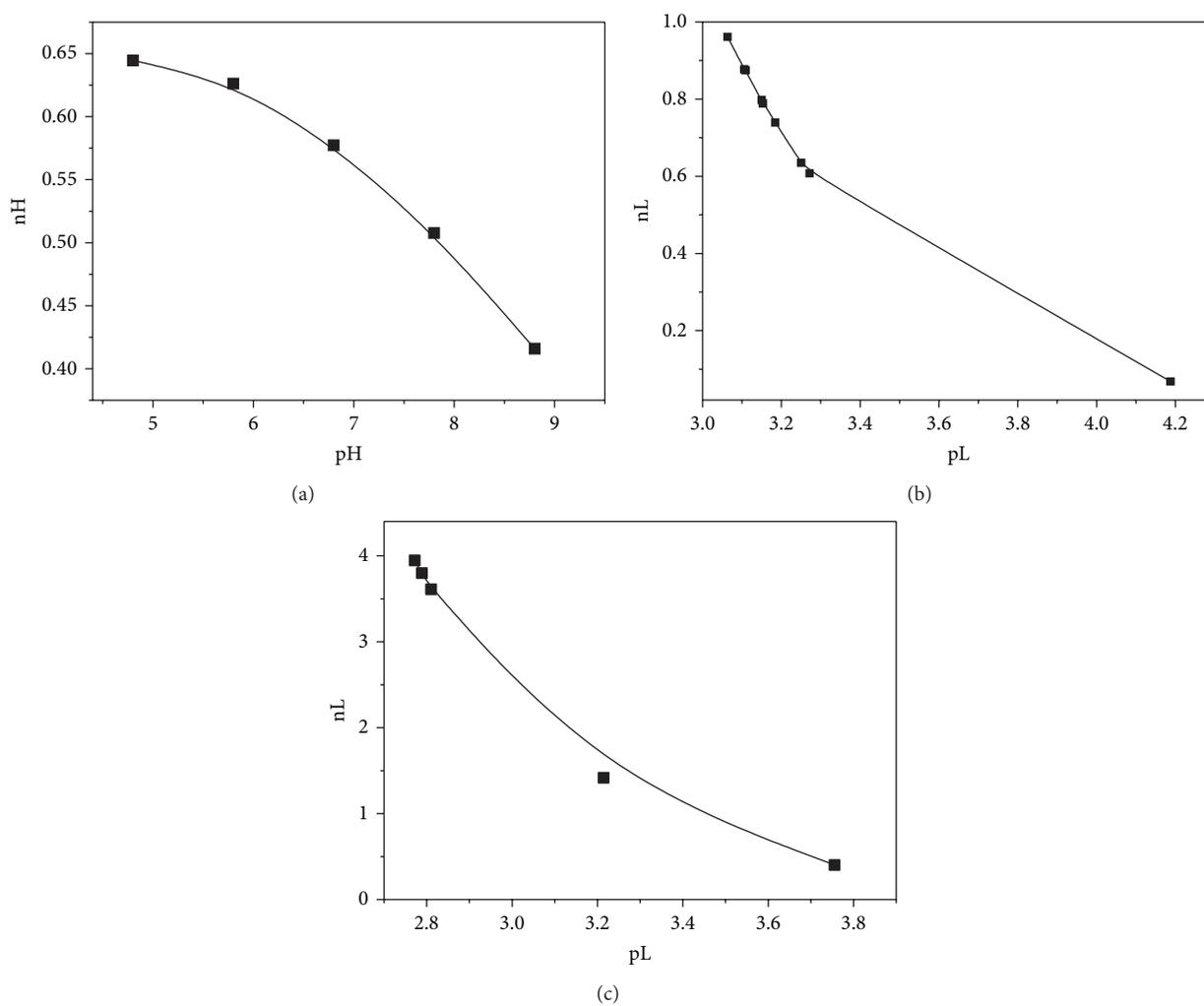


FIGURE 5: (a) Plot depicting variation of nH with pH; (b) nL as a function of pL for vanadyl-DE; (c) nL as a function of pL for uranyl-DE complexation reactions.

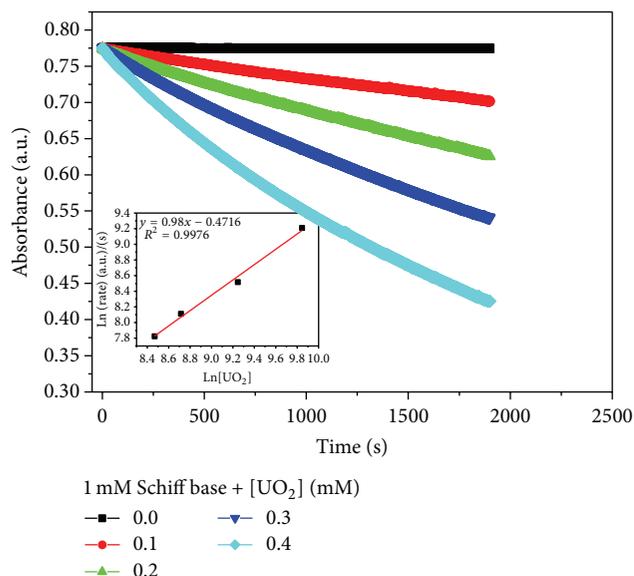


FIGURE 6: Pseudo first order kinetic profile of uranyl-DE complexation reaction.

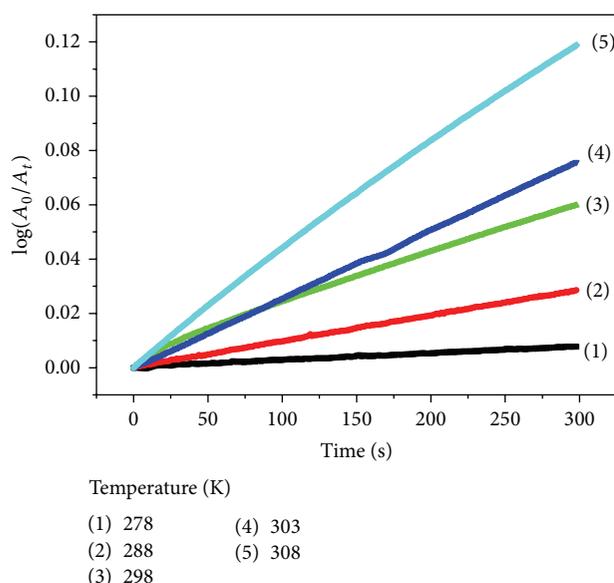


FIGURE 7: Plot of integrated rate law for uranyl-DE complexation reaction.

order of two. The value of rate constant k at 25°C from an average of three sets of experiments was calculated to be $5.25 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$ for vanadyl DE and $3.47 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ for uranyl DE complexation. Temperature dependent kinetic studies were carried to calculate the activation energy (E_a) for the said complexation reactions. Rate constants determined at the studied temperatures are tabulated in Table 3. From the plot of individual rate constant values at different temperatures ($\ln k$ vs. $1/T$) (Figure 8), activation energy barrier (E_a) of ca. 40.913 and 48.661 KJ mol^{-1} was calculated for vanadyl and uranyl DE complexation, respectively, from the slope = $-E_a/R$ (where R stands for gas constant).

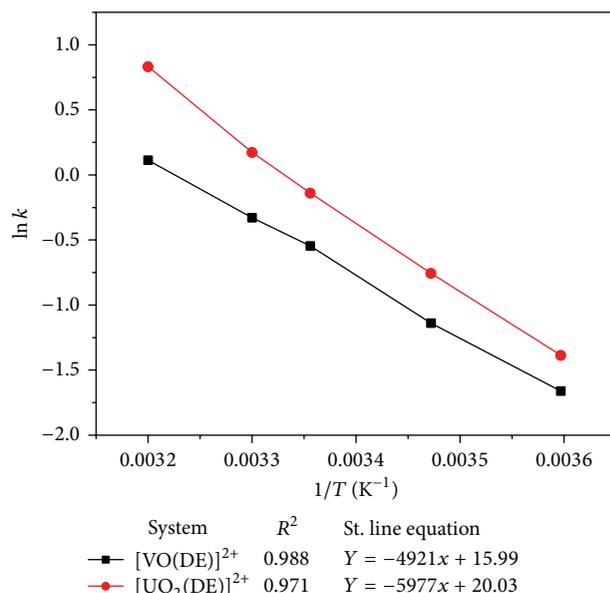


FIGURE 8: Arrhenius plot for the determination of activation energy barrier of vanadyl-DE and uranyl-DE complexation.

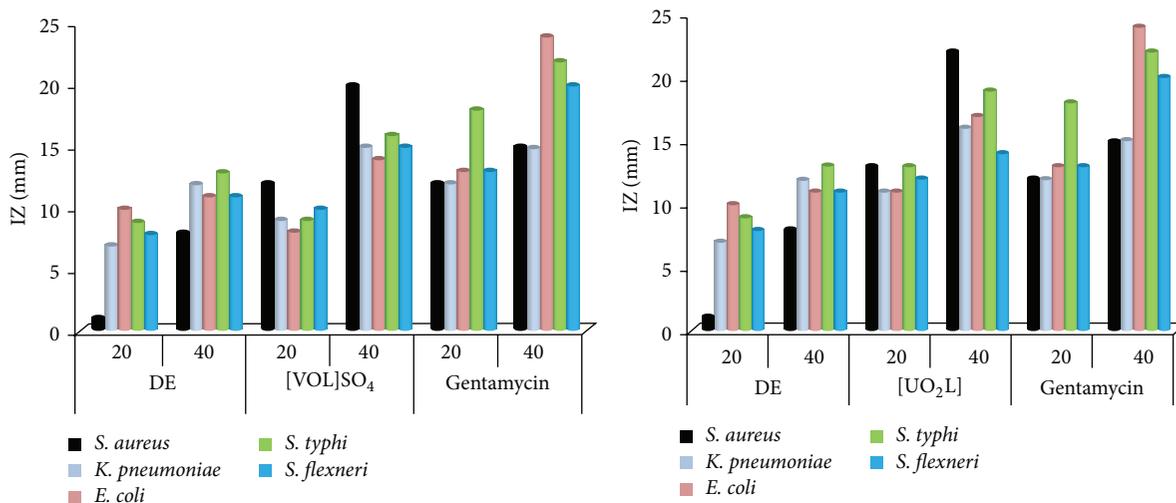
From the kinetic investigations it was concluded that complexation of both vanadyl and uranyl ions with Schiff base ligand DE is a slow reaction; however the complexation reaction is more slow in case of uranyl than vanadyl ion. This difference in the kinetics of two complexation reactions highlighted the influence of metal ion steric factors and anticipated ligand preorganization on complexation process [35]. The presence of two axial oxygen atoms on uranium in case of uranyl poses a double steric restriction for approach of the ligand to the metal ion in comparison to single axial oxygen on vanadium in vanadyl. Accordingly the complexation reaction is slower in uranyl than vanadyl. Moreover DE as a tetradentate ligand has a rigid frame work due to the presence of four phenyl rings on its outer periphery nearly perpendicular to the N_2O_2 plane (Figure 2). Presence of two axial oxygens on uranyl ion causes DE to make more adjustments so as to occupy four planar positions. This rigidity of DE coupled with the preoccupation of two axial sites by oxygen atoms result in a very slow DE complexation with uranyl due to ligand preorganization barriers [36].

7. Bioactivity Evaluation

The *in vitro* screening of biocidal potential of the Schiff base ligand (DE) and its vanadyl and uranyl complexes as antibacterial, antifungal, and antihelminthic was carried out. The antibacterial activities of synthesised ligand (DE) and its metal complexes towards the Gram-positive bacteria, *S. aureus*, and the Gram-negative bacteria, *K. pneumoniae*, *S. typhi*, *E.coli*, and *S. flexneri*, were compared through the radius of zones of inhibition against *Gentamycin* (Control). The antibacterial study was done by *Well diffusion method* [37], Figure 9. The antifungal activities of Schiff base ligand DE and its vanadyl and uranyl complex were evaluated by the

TABLE 3: Rate constants of vanadyl and uranyl (DE) complexation at different temperatures.

Temperature ($^{\circ}\text{C}$)	$1/T$ (K^{-1})	VO (DE) rate constant (k_1) $k \pm 0.05$ (s^{-1})	UO ₂ (DE) rate constant (k_2) $k \pm 0.05$ (s^{-1})	$\ln(k_1)$	$\ln(k_2)$
5	0.003597	0.19	0.25	-1.66	-1.34
15	0.003472	0.32	0.47	-1.14	-0.76
25	0.003356	0.58	0.87	-0.54	-0.14
30	0.0033	1.72	1.19	-0.32	0.17
35	0.003247	1.12	2.30	0.113	0.83

FIGURE 9: Antibacterial activities of Schiff base (DE), vanadyl-DE, and uranyl-DE complex and Gentamycin (Control) at 20 and 40 $\mu\text{g mL}^{-1}$.

Agar Well Diffusion method [37] against the two types of fungi *A. niger* and "*R. bataticola*." The comparison of antifungal activity was done in terms of zones of inhibition (in mm) measured against *Amphotericin* (Control) Figure 10.

The Schiff base (DE) and its vanadyl and uranyl complexes were tested for *in vitro* antihelminthic activity by Ghosh et al. method [38] wherein the adult *Pheretima posthuma* (earth worms) were exposed to different concentrations of Schiff base (DE) and its complexes. The dose dependent antihelminthic activity was compared on the basis of time taken for paralysis and death of individual earthworm against *Albendazole* as control drug, Figure 11.

It was observed from the inhibition zone radii and time taken for death of earth worm that the biocidal potential of DE increases on complexation with the studied metal ions. This can be well explained by Overtones concept and Tweedy chelation theory [39–41]. The lipophilicity of free ligand increases and polarity of metal ion gets reduced due to overlap of ligand and metal orbitals on complexation. According to the Overtones concept of cell permeability, an increase in the hydrophobicity increases the antimicrobial activity due to enhanced bioavailability. Moreover due to increased delocalization of electrons over the whole chelate ring, the lipophilicity of the complexes is boosted. This increased lipophilicity enhances the biocidal potential of bioactive compounds by their penetration into the lipid membrane

and cytoplasm. In our study the antimicrobial, antifungal, and antihelminthic activity were found to be in the order $[\text{VODE}]\text{SO}_4 > [\text{UO}_2\text{DE}](\text{NO}_3)_2 > [\text{DE}]$. The maximum biocidal potential of vanadyl complex can be attributed to its maximum lipophilicity and relatively lower polarity (due to single oxygen attached to metal), in light of Overtones concept, and better ability to bind with cellular components due to coordinatively unsaturated pentacoordinate nature of trigonal bipyramidal geometry.

8. Conclusion

In summary, this work describes the synthesis and structure elucidation of a tetradentate Schiff base ligand (DE) and its target complexation with oxovanadium(IV) and dioxouranium(VI) metal ions. The solution phase thermodynamic stability constants of $\log K = 3.70$ and 3.45 were calculated for $[\text{VO}(\text{DE})]\text{SO}_4$ and $[\text{UO}_2\text{DE}](\text{NO}_3)_2$ complexes, respectively. An extensive kinetic investigation of DE complexation reaction with oxovanadium(IV) and dioxouranium(VI) predicts overall 2nd order kinetics with rate constants of 5.25×10^{-2} for vanadyl and $3.47 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ for uranyl DE complex. The different complexation rates under identical conditions in case of oxovanadium(IV) and dioxouranium(VI) were corroborated with the ligand preorganization and metal ion steric effects. The presence of one and two axial oxygen

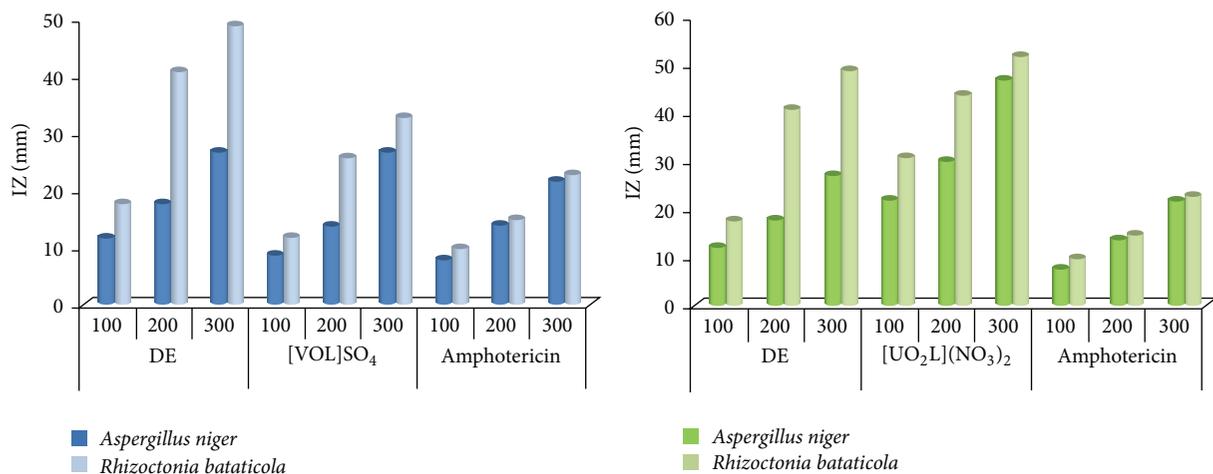


FIGURE 10: Antifungal activities of Schiff base (DE), vanadyl-DE, and uranyl-DE complex and Amphotericin (Control) at 100, 200, and 300 $\mu\text{g mL}^{-1}$.

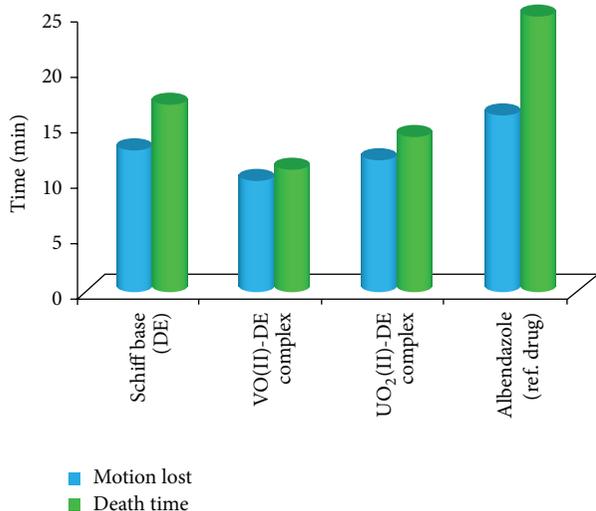


FIGURE 11: Antihelminthic activity of Schiff base (DE), vanadyl-DE, and uranyl-DE complex and Albendazole (Control) at 25 $\mu\text{g mL}^{-1}$.

atoms in case of oxovanadium(IV) and dioxouranium(VI), respectively, creates less steric restriction in case of oxovanadium(IV) than dioxouranium(VI). The biological screening (antibacterial, antifungal, and antihelminthic) of the Schiff base ligand DE its oxovanadium(IV) and dioxouranium(VI) complex were found to be in the order $[\text{VODE}]\text{SO}_4 > [\text{UO}_2\text{DE}](\text{NO}_3)_2 > [\text{DE}]$. Further studies aimed at the mode of action of the screened compounds are underway and efforts are continued towards synthesizing compounds of possible therapeutic significance.

Conflict of Interests

The authors declare that they have no competing financial interest and there is no conflict of interests regarding the publication of this paper.

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