

Synthesis and Characterization of Homo Binuclear Macrocyclic Complexes of UO₂(VI), Th(IV), ZrO(IV) and VO(IV) with Schiff-Bases Derived from Ethylene diamine/Orthophenylene Diamine, Benzilmonohydrazone and Acetyl Acetone

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ABSTRACT. A series of homo binuclear complexes of the type [M₂(L/L')(NO₃)_n].mH₂O, [where M=UO₂²⁺, Th⁴⁺, ZrO²⁺] and [(VO)₂(L/L')(SO₄)₂].2H₂O, L=1,5,6,9,12,15,16,20 octaaza-7,813,14-tetraphenyl-2,4,17,19-tetramethyl-1,4,6,8,12,14,16,19-docosaoctene (OTTDO) or L'=10:11;21:22-dibenzo-1,5,6,9,12,15,16,20-octaaza-7,813,14-tetraphenyl-2,4,17,19-tetramethyl-1,4,6,8,12,14,16,19-docosaoctene (DOTTOT), n=4 for UO₂²⁺, ZrO²⁺ n=8 for Th⁴⁺ m=1,2,3 respectively, have been synthesized in template method from ethylenediamine/orthophenylene diamine, benzil monohydrazone and acetyl acetone and characterized on the basis of elemental analysis, thermal analysis, molar conductivity, magnetic moment, electronic, infrared, ¹H-NMR studies. The results indicate that the VO(IV) ion is penta co-ordinated yielding paramagnetic complexes; UO₂(VI), ZrO(IV) ions are hexa co-ordinated where as Th(IV) ion is octa co-ordinated yielding diamagnetic complexes of above composition. The fungi toxicity of the ZrO(IV) and VO(IV) complexes against some fungal pathogen has been studied.

Key words: Schiff base, Binuclear macrocyclic complexes, Template synthesis, Structure and spectral properties

INTRODUCTION

The metal complexes containing synthetic macrocyclic ligands have attracted a great deal of attention because they can be used as models for more intricate biological systems: metalloporphyrins (hemoglobin, myoglobin, cytochromes and chlorophylls), corrins (vitamin B₁₂) and antibiotics (valinomycin, nonactin).¹ In these macrocyclic complexes, both the metal ion and the size of the ring play an important role.² The Schiff base macrocyclic complexes which form neutral or cationic complexes with the metal of biological interest, fulfill these requirements because they are extremely rigid. Macrocyclic Schiff bases have been widely studied because they can selectively chelate certain metal ions depending on the number, type and position of their donor atoms, ionic radius of the metal centre and coordinating properties of counter ions. Ideally, the macrocyclic complex is formed by adding required metal ion to a preformed macrocycle. However, the direct synthesis of macrocycles often results in very low yield of the desired product with the combination of competing linear polymerization or other side reactions.

Schiff base compounds are widely studied and used, attracting wide range of applications in organic synthesis

and metal ion complexation.³ The conventional synthesis of such compounds is still very common along with modern synthetic approaches.⁴ Template condensation reactions lie at the heart of the macrocyclic chemistry.⁵ Therefore template reactions have been widely used for synthesis of macrocyclic complexes.⁶ The family of complexes with aza-macrocyclic ligands has remained a focus of scientific attention for many decades.⁷

In addition to above, increasing attention has been devoted to macrocyclic complexes involving Schiff base hydrazones in view of their potential applications in the field of pharmacology. Complexes of salicylaldehyde benzoylhydrazone were shown to be a potent inhibitor of DNA synthesis and cell growth.⁸ This hydrazone also has mild bacteriostatic activity and a range of analogues has been investigated as potential oral ion chelating drugs for genetic disorders such as thalasemia.^{9,10}

One major topic of interest is to develop homo-multi-metallic complexes because they exhibit distinct reactivity pattern as compared to corresponding monometallic complexes.¹¹ The magnetic interactions and coupling between the metal ions present in such complexes play key role in both natural and synthetic catalysts.¹² As a result, the synthesis and characterization of homo bimetallic complexes

continue to attract attention.¹³

Following all these observations and as a part of our continuing research on the coordination chemistry of multidentate ligands,¹⁴⁻¹⁷ we report here the synthesis and structural studies of some unknown homo binuclear macrocyclic complexes from the reaction of ethylenediamine/orthophenylene diamine, benzil monohydrazone and acetyl acetone in presence of UO₂²⁺, ZrO²⁺, Th⁴⁺ and VO²⁺ ions.

EXPERIMENTAL

Materials

All the chemicals used of AR grade. The solvents were purified before use by standard procedures.

Preparation of benzilmonohydrazone/diacetylmonohydrazone

The analytical monohydrazones were synthesized according to literature method.¹⁸ As the isolation of Schiff base ligand proved futile, all the metal complexes were synthesized (in an identical method) in situ by taking different amount of metal salts, ethylene diamine/orthophenylene diamine, benzilmonohydrazone and acetyl acetone.

Preparation of the complexes of the type [M₂(OTTDO)(NO₃)_n]mH₂O, M=UO₂²⁺, ZrO²⁺, Th⁴⁺ and [(VO)₂(OTTDO)(SO₄)₂]2H₂O

An ethanolic solution of hydrated UO₂(VI)/Th(IV)/ZrO(IV) nitrates /vanadyl sulphate (1 mmol in 10 mL) was added to a hot ethanolic solution of the mixture of ethylene diamine (1 mmol in 10 mL), benzil monohydrazone (2 mmol in 20 mL) and acetyl acetone (2 mmol in 20 mL). The resulting mixture was refluxed on a water bath for 2-3 hours during which a coloured complex was precipitated out in each case. The ethanolic suspension of the complexes were treated with ethylene diamine (1 mmol in 10 mL), which is followed by the corresponding metal salts (1 mmol in 10 mL EtOH). The mixture was again refluxed for 3-4 hours on a water bath during which the metal complexes of different colour than the precursor complexes were obtained (*Table 1*). The progress of the reaction was signaled by colour change of the resulting solution. These were filtered off, washed several times with ethanol followed by ether and finally dried in vacuo over anhydrous CaCl₂(fused).

Preparation of the complexes of the type [M₂(DOTTDO)(NO₃)_n]mH₂O, M=UO₂²⁺, ZrO²⁺, Th⁴⁺ and [(VO)₂(DOTTDO)(SO₄)₂]2H₂O

Same procedure was adopted for preparation of [M₂(DOTTOD)(NO₃)_n]mH₂O and [(VO)₂(DOTTOD)(SO₄)₂]2H₂O by taking orthophenylene diamine instead of ethylene diamine.

Analysis and Physical Measurements

The metal contents in the complexes were determined gravimetrically following standard procedures.¹⁹ A weighed quantity of the compound (0.2-0.3 g) was treated with a few drops of concentrated H₂SO₄ and 1 cc. of concentrated HNO₃. It was heated till all the organic matter decomposed and sulphur trioxide fumes came out. The same process was repeated two to three times to decompose the substance completely. Then it was dissolved in water and the resulting solution was used for analysis of metal ions. Uranium, thorium, zirconium and vanadium were precipitated as ammonium diuranate, thorium oxalate, zirconium mandelate and ammonium vanadate followed by subsequent ignition to their respective oxides as U₃O₈, thoria (ThO₂), zirconia (ZrO₂) and V₂O₅. Sulphur was determined as BaSO₄. Room temperature magnetic susceptibilities were measured by Gouy method using Hg [Co(NCS)₄] as the calibrant. The molar conductance measurements were carried out at room temperature with a Toshniwal conductivity Bridge (Model CL-01-06, cell constant 0.5 cm⁻¹) using 1×10⁻³ M solution of the complexes in DMSO. Carbon, hydrogen and nitrogen contents of the complexes were determined by using a MLW-CHN microanalyser. FTIR spectra in KBr pellets were recorded on a varian FTIR spectrophotometer, Australia. The electronic spectra of the complexes in DMSO were recorded on a PerkinElmer* spectrophotometer. Thermogravimetric analysis was done by Netzsch-429 thermoanalyser. The ¹H-NMR spectra of the complexes were recorded in DMSO-d₆ medium on JEOL GSX-400 model equipment.

RESULTS AND DISCUSSION

The complexes were formulated from the analytical data and molar conductance data support the suggested formulae (*Table 1*). The complexes are highly coloured and insoluble in water and common organic solvents such as ethanol, methanol, acetone, CCl₄, CHCl₃, benzene and ether but moderately soluble in highly coordinating solvents such as DMF and DMSO. They are non-hygroscopic, highly stable under normal conditions and all of them decompose above 250 °C. The molar conductance data in DMSO for the complexes indicate them to be non-elec-

Table 1. Analytical and physical data of the complexes

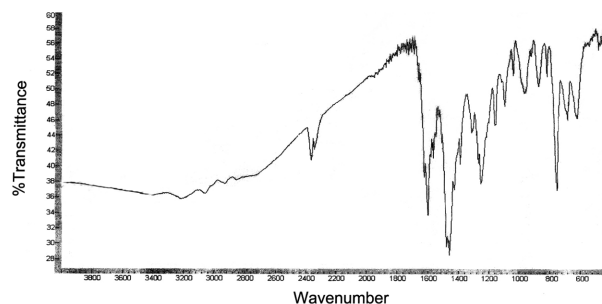
Sl. no.	Compounds	Colour	Yield (%)	Λ_m^a	Found (calc.)%				
					C	H	N	S	M
1	$[(\text{UO}_2)_2(\text{L})(\text{NO}_3)_2] \cdot 3\text{H}_2\text{O}$	Canary yellow	71.5	24.12	34.91(34.95)	2.88(2.91)	11.63(11.65)	-	32.98(33.00)
2	$[(\text{UO}_2)_2(\text{L}')(\text{NO}_3)_2] \cdot 3\text{H}_2\text{O}$	Brownish yellow	69.3	22.24	38.38(38.41)	2.91(2.94)	10.73(10.75)	-	30.43(30.47)
3	$[(\text{Th})_2(\text{L})(\text{NO}_3)_4] \cdot \text{H}_2\text{O}$	Lemon yellow	72.6	36.82	30.47(30.50)	2.62(2.66)	13.51(13.55)	-	28.05(28.08)
4	$[(\text{Th})_2(\text{L}')(\text{NO}_3)_4] \cdot \text{H}_2\text{O}$	Red oxide	73.1	32.66	34.20(34.24)	2.71(2.73)	12.74(12.78)	-	27.23(27.28)
5	$[(\text{ZrO})_2(\text{L})(\text{NO}_3)_2] \cdot 2\text{H}_2\text{O}$	Cream	75.3	38.52	46.96(47.02)	4.22(4.25)	14.25(14.28)	-	15.44(15.47)
6	$[(\text{ZrO})_2(\text{L}')(\text{NO}_3)_2] \cdot 2\text{H}_2\text{O}$	Golden Brown	76	33.82	42.81(42.85)	4.22(4.25)	13.11(13.16)	-	14.22(14.26)
7	$[(\text{VO})_2(\text{L})(\text{SO}_4)_2] \cdot 2\text{H}_2\text{O}$	black	72.3	20.36	49.28(49.31)	4.66(4.69)	10.91(10.95)	6.23(6.26)	9.92(9.98)
8	$[(\text{VO})_2(\text{L}')(\text{SO}_4)_2] \cdot 2\text{H}_2\text{O}$	brown	74.1	18.25	53.42(53.47)	4.59(4.63)	9.95(9.98)	5.65(5.70)	9.05(9.09)

trolyte in nature. However, the conductivity value is higher than as expected for non-electrolytes probably due to partial solvolysis of the complexes in DMSO medium.²⁰

IR spectra

As the Schiff base ligands could not be isolated, the spectra of the complexes were compared with spectra of the starting materials and other related compounds. The IR spectra of the ligand show strong bands appearing at 1590 and $\sim 1070 \text{ cm}^{-1}$ assignable to azomethine $\nu\text{C}=\text{N}$ and $\nu\text{N}-\text{N}$. The position of former band at comparatively lower frequency region than usual free $\nu\text{C}=\text{N}$ value²¹ and that of later band at comparatively higher frequency region than that of free $\text{N}-\text{N}$ ²² leads us to suggest that azomethine nitrogen atom has taken part in complexation as evidenced from the appearance of band in the region $\sim 480 \text{ cm}^{-1}$ due to $\nu(\text{M}-\text{N})$.²³ The occurrence of $\text{N}-\text{N}$ band at higher frequency in the IR spectra of the complex is due to reduction of the repulsion between the lone pair of nitrogen atoms as a result of coordination via azomethine nitrogen atoms.

The uranyl complexes exhibit a strong band at $\sim 940-900 \text{ cm}^{-1}$ and the medium intensity band at $\sim 845-830 \text{ cm}^{-1}$ assignable to $\nu_{\text{as}}(\text{O}=\text{U}=\text{O})$ and $\nu_{\text{s}}(\text{O}=\text{U}=\text{O})$ mode respectively.²⁴ The co-ordination of nitrate ions in unidentate manner has been indicated by the appearance of additional band at the region $\sim 1385 \text{ cm}^{-1}$ and $\sim 1050 \text{ cm}^{-1}$ corresponding to the ν_2 and ν_4 modes of the vibration of coordinating nitrate ion under C_{2v} symmetry.²⁵ The zirconyl complexes exhibit one strong band in the region $910-865 \text{ cm}^{-1}$ which can be attributed to the $\nu(\text{Zr}=\text{O})$ as reported earlier²⁶ indicating the presence of $(\text{Zr}=\text{O})^{2+}$ moiety in these complexes. In the oxovanadium polychelates strong bands at $\sim 955 \text{ cm}^{-1}$ are assigned to $\nu(\text{V}=\text{O})$ modes.^{27,28} However, these bands are absent in the complexes of Th(IV). However in vanadyl complexes, an additional series of four bands appeared at ~ 1110 , ~ 1040 , ~ 970 &

**Fig. 1.** IR Spectra of $[(\text{Th})_2(\text{L})(\text{NO}_3)_4] \cdot \text{H}_2\text{O}$.

$\sim 645 \text{ cm}^{-1}$ indicating the coordination of sulphate group in unidentate manner through oxygen atom;²⁹ the symmetry being lowered from T_D to C_{3v} upon coordination. Besides the bands observed at $\sim 3500 \text{ cm}^{-1}$ may be assigned to $\nu(\text{O}-\text{H})$ of coordinated or lattice water. However all the complexes lost water when heated to $\sim 100^\circ\text{C}$ indicating the presence of lattice water molecules which has been confirmed by thermal analysis. The representative spectrum of $[(\text{Th})_2(\text{L})(\text{NO}_3)_4] \cdot \text{H}_2\text{O}$ complex is shown in Fig. 1.

Thermal analysis

All these complexes follow the same pattern of thermal decomposition. The complexes remain almost unaffected upto $\sim 40^\circ\text{C}$. After this a slight depression upto $\sim 100^\circ\text{C}$ is observed. The weight loss at this temperature range is equivalent to one water molecule for the complexes (3) and (4), two water molecule for the complexes (5), (6), (7) and (8) three water molecule for the complexes (1) and (2) indicating them to be lattice water in conformity with our earlier observations from analytical and IR spectral investigations. The anhydrous complexes remain stable upto $\sim 340^\circ\text{C}$ then the complexes show rapid degradation presumably due to decomposition of organic constituents of the complex molecules as indicated by the steep fall in the percentage weight loss. The decomposition continues upto $\sim 670^\circ\text{C}$ and reaches to a stable product in each complex

Table 2. Important features of thermo gravimetric analysis (TGA)

Sl. no.	Total wt. for TG (mg)	Temp. range of water loss (°C)	% of water loss Found (calcd.)	Decomposition temperature (°C)	% weight of residue Found (calcd.)	Composition of the residue
1	104	70-100	1.21(1.24)	385-615	38.42(38.46)	U ₃ O ₈
2	98	70-100	1.11(1.15)	375-630	35.48(35.51)	U ₃ O ₈
3	107	50-85	2.14(2.17)	370-620	31.92(31.96)	ThO ₂
4	102	40-90	2.01(2.05)	380-640	30.09(30.13)	ThO ₂
5	96	50-90	4.54(4.59)	365-635	20.87(20.91)	ZrO ₂
6	92	40-100	4.20(4.23)	370-615	19.24(19.27)	ZrO ₂
7	88	40-80	3.48(3.51)	360-660	17.75(17.80)	V ₂ O ₅
8	86	50-90	3.16(3.20)	350-670	16.18(16.22)	V ₂ O ₅

as indicated by the consistency in weight in the plateau of the thermogram. The decomposition temperature varies for different complexes as shown in Table 2. The thermal stability of the complexes decreases in the order:

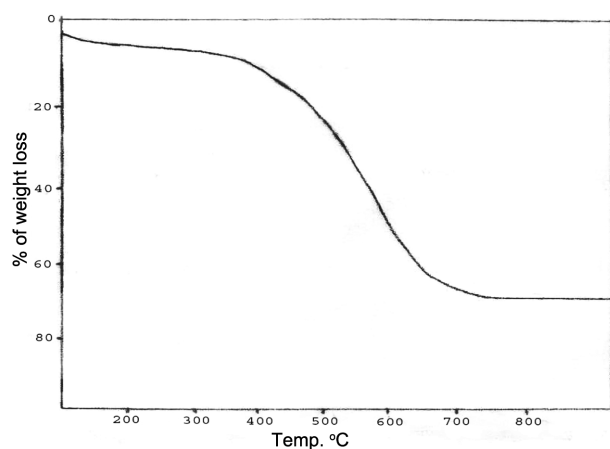
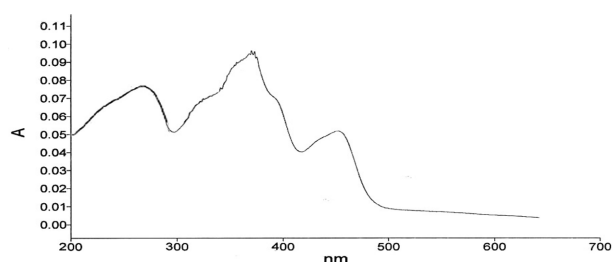
(L) complexes: UO₂(VI) > Th(IV) > ZrO(IV) > VO(IV)

(L') complexes: Th(IV) > UO₂(VI) > ZrO(IV) > VO(IV)

In the complexes, weight loss was encountered at ~40 °C to ~100 °C with a broad endothermic peak at the same temperature corresponding to one, two and three molecules of water of crystallization.³⁰ The representative thermogram of [(Th)₂(L')(NO₃)₄]H₂O complex is shown in Fig. 2.

Electronic spectra

The electronic spectra of the UO₂(VI) complexes are quite similar. The complexes display mainly one weak band at ~470 nm and a highly intense band at ~280-290 nm, which may be due to ¹Σ_g⁺ → ³Π_u transitions and charge transfer transitions respectively.³¹ It may be noted that the band occurring at 370 nm is due to uranyl moiety because of apical oxygen → f⁰(U) transition³¹ is being merged with

**Fig. 2.** Thermogram of [(Th)₂(L')(NO₃)₄]H₂O.**Fig. 3.** Electronic spectrum of [(UO₂)₂(L)(NO₃)₂]3H₂O.

the ligand band due to n → Π* transition as evident from broadness and intensity. The electronic spectra of Th(IV) and ZrO(IV) exhibit only one extra highly intensive band in the region 360-385 nm which may be due to charge transfer band besides the ligand bands. However the electronic spectra could not provide structural details of these complexes. The electronic spectra of VO(IV) complexes show three bands at ~12400, ~18800 and ~25900 cm⁻¹ corresponds to transitions, d_{xy}(b₂) → d_{xz}d_{yz}(e), d_{xy}(b₂) → d_{x²-y²}(b₁) and d_{xy}(b₂) → d_{z²}(a₁) respectively, indicating the complexes to be in distorted octahedral environment under C_{4v} symmetry.³² The representative spectrum of the [(UO₂)₂(L)(NO₃)₂]3H₂O complex is shown in Fig. 3.

Magnetic moment

All the complexes except VO(IV), are diamagnetic consistent with their d⁰ and f⁰ electronic configuration. The magnetic moment values for the oxovanadium(IV) complexes (7) and (8) lie in the range 2.50-2.65 BM. These values are less than spin-only value required for two unpaired electrons indicating spin-spin coupling in the solid state between unpaired electrons belonging to different VO(IV) ions in the same structural unit.

¹H NMR spectra

The ¹H-NMR spectra of the diamagnetic complexes are recorded in DMSO-d₆ medium. The complexes show a

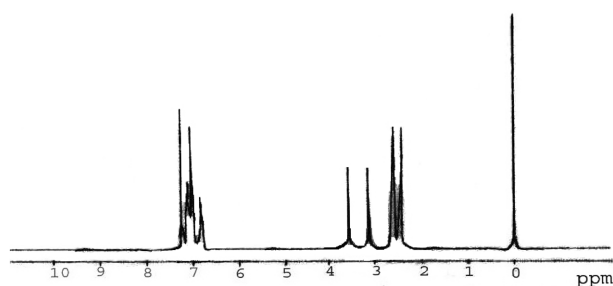


Fig. 4. ^1H NMR spectrum of $[(\text{UO}_2)_2(\text{L})(\text{NO}_3)_2]3\text{H}_2\text{O}$.

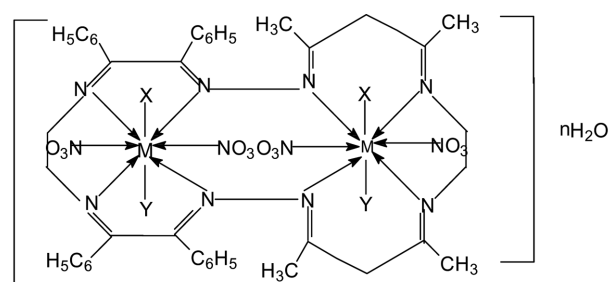


Fig. 5. $[\text{M}_2(\text{L}')(\text{NO}_3)_n]m\text{H}_2\text{O}$.

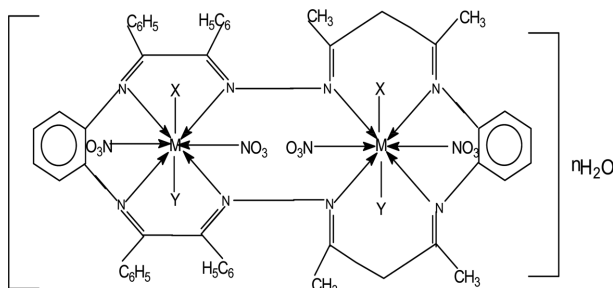


Fig. 6. $[\text{M}_2(\text{L}')(\text{NO}_3)_n]m\text{H}_2\text{O}$ where $\text{M}=\text{UO}_2^{2+}$, Th^{4+} , ZrO^{2+} .

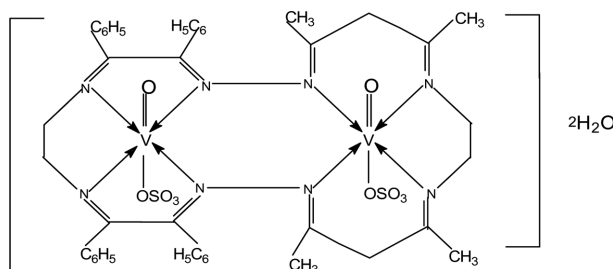


Fig. 7. $[(\text{VO})_2(\text{L})(\text{SO}_4)_2]2\text{H}_2\text{O}$.

sharp signal at δ 2.26-2.35 ppm corresponding to imine methyl ($\text{CH}_3\text{-C}=\text{N}$; 12H) protons.^{33,34} A singlet is also observed in the region δ 2.51-2.98 ppm which may be assigned to methylene ($=\text{C-CH}_2\text{-C}=\text{C}$; 4H) protons.³⁵ In L complexes an additional peak at 3.85 ppm is observed corresponding to 8 protons ($\text{NCH}_2\text{CH}_2\text{N}$).³⁶ Besides, a broad multiplet at δ 7.2-7.9 ppm is observed corresponding to 28 aromatic protons for L' complexes and 20 aromatic pro-

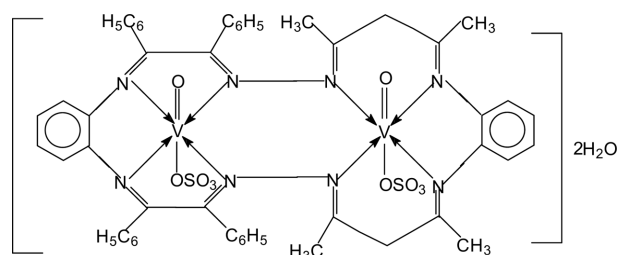


Fig. 8. $[(\text{VO})_2(\text{L})(\text{SO}_4)_2]2\text{H}_2\text{O}$.

tons for OTTDO complexes. The representative spectrum of the $[(\text{UO}_2)_2(\text{L})(\text{NO}_3)_2]3\text{H}_2\text{O}$ complex is shown in Fig. 4.

Based on the foregoing observations the following tentative structures have been proposed for the present complexes.

Fungicidal Screening

The antifungal activity of ZrO(IV) and VO(IV) complexes have been studied by potato dextrose agar diffusion method in DMSO solvent against *A. niger* and *A. flavus*. The complexes showed good antifungal activity against the species. This may be explained on the basis that their structures mainly possess $\text{C}=\text{N}$ bonds. Moreover, coordination reduces the polarity^{37,38} of the metal ion mainly because of the partial sharing of its positive charge within the chelate ring formed during coordination. This process increases the lipophilic nature of the central metal atom, which favors its permeation more efficiently through the lipid layer of the micro-organism^{39,40} thus destroying them more aggressively.

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