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Synthesis and characterization of oxovanadium(IV) macrocyclic complexes with ligands derived by condensation of furil with 1,4-diaminobenzene or 3,4-diaminopyridine and their reactions with β-diketones

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Abstract: Oxovanadium(IV) complexes of the type $[VO(mac)]SO_4$, (where mac = tetraaza macrocyclic ligands derived by condensation of furil with 1,4-diaminobenzene or 3,4-diaminopyridine and their reaction with β-diketones) have been prepared using vanadyl ion as kinetic template. Tentative structures of the complexes have been proposed on the basis of elemental analysis, infrared, e.s.r. and electronic data . All the oxovanadium(IV) complexes are five coordinate.
Key words: oxovanadium(IV), kinetic template , macrocyclic complexes.

Introduction

The chemistry of vanadium has attracted attention due to its presence in biological system particularly its accumulation in sea squirts and in wild mushrooms like *Amanita muscaria* and others[1-3]. The literature contains several reports about oxovanadium(IV) complexes which show modulating activities of various enzymes[4-5]. Furil is a versatile chelating agent having two reactive carbonyl groups capable of undergoing Schiff-base condensation with a variety of di- and polyamines. The use of metals as templates in such reaction has led to the synthesis of metal complexes of macrocyclic ligands[6]. Thus, furil has played an important role in the development of macrocyclic complexes. Such complexes show unusual structure, stability and are known to have relevance to biological system. This provides an opportunity to design and study the model biological systems to understand the chemical changes taking place in such cases[7]. However, in most cases, the template effect of metal ions of the first transition series have been studied and the chemistry of metal complexes with macrocyclic ligands of oxovanadium(IV) incorporating four nitrogen donor atoms have received less attention[8-9]. With this aspect, some oxovanadium(IV) complexes with new denticity ligands derived from condensation of furil with 1,4-diaminobenzene or 3,4-diaminopyridine, capable of undergoing cyclization with β-diketones via the metal template effect have been prepared, characterized and their tentative structures are ascertained in this communication.

Experimental

Materials and Methods

All the chemicals and the solvents used were of the reagent grade. Oxovanadium(IV) sulfate was procured from Aldrich. The β-diketones viz. acetylacetone, benzoylacetone, thenoyltrifluoroacetone and dibenzoylmethane were SRL products and the diamines used were reagent grade products. Furil used was Aldrich product.

Analytical Methods and Physical Measurements

Vanadium was estimated gravimetrically after decomposing the complex with concentrated nitric acid by standard method[10]. Microanalysis of carbon and hydrogen for the complexes were done at central research facility, NERIST, nirjuli-791 109, Itanagar, Arunachal Pradesh. Standard method was employed to estimate nitrogen for the complexes. Sulfur was estimated as barium sulfate in the laboratory[11]. The standard technique of melting point (uncorrected) determination using sulfuric acid bath was employed. A Toshniwal conductivity bridge, Model No. CLO102A was used for conductance measurements at room temperature. The magnetic susceptibility of the oxovanadium(IV) complexes in powder form were carried out at room temperature using Gouy's balance. Mercury tetrathiocyanatocobaltate(II), Hg[Co(CNS)4], ($\chi g = 16.44 \times 10^{-6}$ c.g.s. unit at 20 ^{0}C), was used as calibrant. The suspension were kept in a closed glass chamber. Tube constant was checked from time to time to ensure the satisfactory working of the apparatus. The electronic spectra of the complexes were recorded on Beckmann DU-2 spectrophotometer and c Φ10 Russian spectrophotometer instrument in the ranges 2000-185 nm and 700-400 nm. The room temperature and liquid nitrogen temperature e.s.r. spectra were recorded at RSIC, IIT, Chennai, India. The infrared spectra of the complexes in the range 4000-200 cm^{-1}, were recorded in potassium bromide medium on Perkin-Elmer 621 and Beckmann Acculab-9 spectrophotometers.

In-situ preparation of oxovanadium(IV) complexes with ligands derived by condensation of furil with 1,4-diaminobenzene or 3,4-diaminopyridine

Vanadium sulfate (2 mmol) dissolved in methanol (25 mL) was added to a refluxing solution of furil (2 mmol) and 1,4-diaminobenzene (4 mmol) or 3,4-diaminopyridine (4 mmol) in ethanol (25 mL). The mixture was refluxed for 6 h, when the color of the solution turned green. The solvent was removed under vacuo at room temperature and the dark green color product was isolated. The complex was thoroughly washed with methanol/ethanol mixture. Yield 70%.

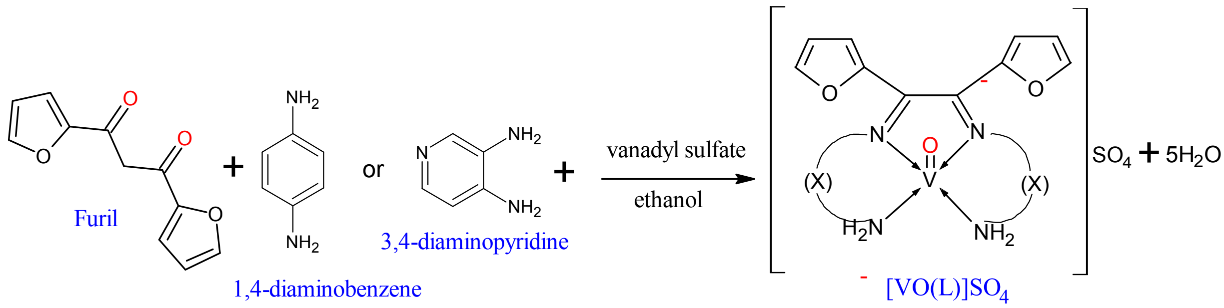
In-situ preparation of macrocyclic complexes of oxovanadium(IV)

Vanadium sulfate (2 mmol) dissolved in methanol (25 mL) was added to a refluxing solution of furil (2 mmol) and 1,4-diaminobenzene or 3,4-diaminopyridine (4 mmol) in ethanol (25 mL). The mixture was refluxed for 5 h, when the color of the solution intensified and turned green. To this reaction mixture, an ethanolic solution (10 mL) of acetylacetone (2 mmol) and glacial acetic acid (5 mL) were added. The reaction mixture was refluxed for about 5 h then green precipitate was obtained. The complex was purified by washing with the mixture (10 mL) of methanol/ethanol (1:1). Yield 60%. The same procedure was adopted for the synthesis of other oxovanadium(IV) macrocyclic complexes using benzoylacetone, thenoyltrifluroacetone and dibenzolylmethane. The physical and analytical data of the complexes are presented in **Table 1.**

Result and Discussion

The oxovanadium(IV) complexes were synthesized using in-situ method by refluxing the reaction mixture of furil, diamines and vanadylsulfate in 1:2:1 molar ratio in aqueous ethanol. The reaction appears to proceed according to the scheme I and II given in the figure.

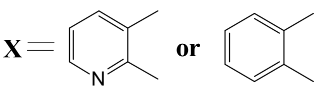
The elemental analysis (**Table 1)** of complexes show 1:1 metal to ligand stoichiometry. The molar conductivity of oxovanadium(IV) complexes in dimethylformamide showed values of Λ_M between 120-138 ohm^{-1} cm^{2} mol^{-1} which indicate their electrolytic nature.



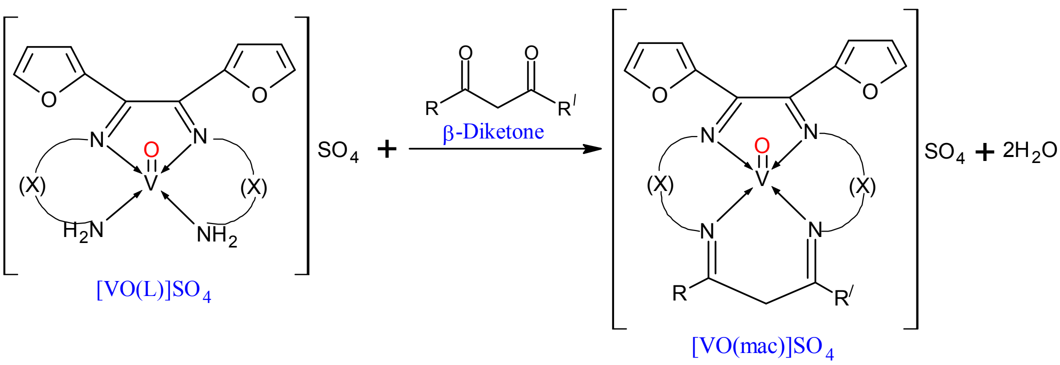
Type I

Scheme I

Where, L^1 = Furil + 1,4-diaminobenzene; L^2 = Furil + 3,4-diaminopyridine



The parent complexes $[VO(L)]SO_4$ react with β-diketones to yield $[VO(mac)]SO_4$ as given below:



Scheme II

Type II

R	R'	β-Diketone
CH_3	CH_3	Acetylacetone
C_6H_5	CH_3	Benzoylacetone
C_4H_3S	CF_3	Thenoyltrifluroacetone
C_6H_5	C_6H_5	Dibenzoylmethane

Where, mac = tetraaza macrocyclic ligands derived by condensation of L^1 or L^2 with β-diketones in presence of oxovanadium(IV) cation.

Table1: Physical and Analytical data of the complexes:

Complex	Empirical Formula	Decomp. Temp.(^{O}C)	C% calcd. (found)	H% calcd. (found)	N% calcd. (found)	V% calcd. (found)	S% calcd. (found)	µeff. BM ($300^{0}C$)
$[VO(L^1)]SO_4$	$C_{22}H_{18}N_4VSO_7$	212	49.5 (49.4)	3.4 (3.3)	10.5 (10.4)	9.6 (99.6)	6.0 (5.9)	1.72
$[VO(L^2)]SO_4$	$C_{20}H_{16}N_6VSO_7$	218	44.9 (44.8)	3.0 (3.9)	15.7 (15.7)	9.5 (9.5)	6.0 (5.9)	1.75
$[VO(mac^1)]SO_4$	$C_{27}H_{22}N_4VSO_7$	214	54.3 (54.2)	3.7 (3.6)	9.4 (9.3)	8.5 (8.5)	5.4 (5.3)	1.74
$[VO(mac^2)]SO_4$	$C_{32}H_{24}N_4VSO_7$	216	58.3 (58.2)	3.6 (3.5)	8.5 (8.4)	7.7 (7.6)	4.9 (4.8)	1.75
$[VO(mac^3)]SO_4$	$C_{30}H_{19}N_4VS_2O_7F_3$	217	50.1 (50.0)	2.6 (2.5)	7.8 (7.8)	7.1 (7.1)	8.9 (8.8)	1.76
$[VO(mac^4)]SO_4$	$C_{37}H_{26}N_4VSO_7$	214	61.6 (61.5)	3.6 (3.5)	7.8 (7.7)	7.1 (7.1)	4.4 (4.3)	1.73
$[VO(mac^5)]SO_4$	$C_{25}H_{20}N_6VSO_7$	220	50.1 (50.0)	3.3 (3.2)	14.0 (13.9)	8.5 (8.4)	5.3 (5.2)	1.74
$[VO(mac^6)]SO_4$	$C_{30}H_{22}N_6VSO_7$	221	54.5 (54.3)	3.3 (3.2)	12.7 (12.6)	7.7 (7.7)	4.8 (4.7)	1.73
$[VO(mac^7)]SO_4$	$C_{28}H_{17}N_6VS_2O_7F_3$	218	44.6 (44.5)	2.4 (2.3)	11.7 (11.6)	7.1 (7.0)	8.9 (8.8)	1.75
$[VO(mac^8)]SO_4$	$C_{35}H_{24}N_6VSO_7$	215	58.1 (58.0)	3.3 (3.2)	11.6 (11.5)	7.0 (6.9)	4.4 (4.3)	1.74

L^1 = Ligand derived by condensation of furil with 1,4-diaminobenzene (1:2); L^2 = Ligand derived by condensation of furil with 3,4-diaminopyridine (1:2); Mac^1 = macrocyclic ligand derived by condensation of L^1 with acetylacetone; Mac^2 = macrocyclic ligand derived by condensation of L^1 with benzoylacetone; Mac^3 = macrocyclic ligand derived by condensation of L^1 with thenoyltrifluoroacetone; Mac^4 = macrocyclic ligand derived by condensation of L^1 with dibenzoylmethane; Mac^5 = macrocyclic ligand derived by condensation of L^2 with acetylacetone; Mac^6= macrocyclic ligand derived by condensation of L^2 with benzoylacetone; Mac^7 = macrocyclic ligand derived by condensation of L^2 with thenoyltrifluoroacetone; Mac^8 = macrocyclic ligand derived by condensation of L^2 with dibenzoylmethane.

Infrared spectra

The important bands of the infrared spectra for the complexes are listed in Table 2. The macrocyclic complexes of oxovanadium(IV) exhibit >C=N absorption around 1625-1610 cm^{-1}, which normally appears at 1660 cm^{-1} in free ligands[12-15]. The lowering of this band in the complexes (Type - I) indicates the coordination of nitrogen atoms of the azomethine groups to the vanadium[16-17]. The presence of a band at around 300 cm^{-1} may be assigned to ν(V-N) vibration[18]. The appearance of >C=N band and the absence of the >c=O band around 1700 cm^{-1} is a conclusive evidence for condensation of the diamines with the two keto group of furil[15]. The bands appearing at 3350 and 3180 cm^{-1} may be assigned to asymmetrical and symmetrical N-H stretching modes of the coordinated terminal amino group[18]. The oxovanadium(IV) complexes show a band at around 980 cm^{-1}, which is assigned to ν(V=O) vibration[19]. The presence of an ionic sulfate group in the complexes is confirmed by the appearance of three bands at ca. 1130-1135 cm^{-1} (ν_3), 955-960 cm^{-1} (ν_1) and 600-610 cm^{-1} (ν_4). The absence of a ν_2 band and non-splitting band of ν_3 band indicate that Td symmetry is retained[20-21]. The infrared spectra of macrocyclic complexes of type-II show the same pattern of bands but the asymmetrical and symmetrical N-H stretching modes of terminal amino groups disappear due to condensation of these amino groups with carbonyl group of β-diketones in cyclization reactions.

Table2: Infrared spectral bands of complexes:

Complex	Bands (cm^{-1})							
	ν (C=N)	ν (V-N)	ν (V=0)	$ν_3$ SO_4^{--}	$ν_1$ SO_4^{--}	$ν_4$ SO_4^{--}	$ν_{as}$ (N-H)	$ν_s$ (N-H)
$[VO(L^1)]SO_4$	1622	302	982	1132	960	604	3355	3182
$[VO(L^2)]SO_4$	1622	303	981	1130	956	602	3352	3184
$[VO(mac^1)]SO_4$	1624	304	982	1134	955	604		
$[VO(mac^2)]SO_4$	1616	300	981	1135	955	608		
$[VO(mac^3)]SO_4$	1622	302	980	1132	958	604		
$[VO(mac^4)]SO_4$	1618	301	980	1134	960	604		
$[VO(mac^5)]SO_4$	1620	301	981	1132	958	602		
$[VO(mac^6)]SO_4$	1622	302	980	1135	955	604		
$[VO(mac^7)]SO_4$	1618	304	981	1132	960	608		
$[VO(mac^8)]SO_4$	1620	302	980	1134	956	604		

Magnetic moments and Electronic Spectra

Oxovanadium(IV) complexes show magnetic moment values in the range 1.71 – 1.76 B.M. at room temperature. These values are in the range reported for oxovanadium(IV) complexes with one unpaired electron[19]. The electronic spectra show bands in the regions 11,040 – 11,980 cm^{-1} and 21,080 – 22,380 cm^{-1}. These spectra are similar to other five coordinate oxovanadium(IV) complexes involving nitrogen donor atoms. These spectral bands are interpreted according to an energy level scheme reported by Wason et.el[20] for distorted, five coordinate square pyramidal oxovanadium(IV) complexes[21]. Accordingly, the observed bands can be assigned to $^2B_2 \rightarrow {}^2E$, $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2A_2$ transitions, respectively. One more band is observed in the region 35,260 – 35,760 cm^{-1}, which may be due to transition of the azomethine linkages[22].

ESR spectra

The X-band ESR spectra of an oxovanadium(IV) complex was recorded in DMSO at room temperature and at nitrogen temperature(177K). ESR spectra of the complexes were analyzed by the standard method[23-25].The room temperature ESR spectra show eight lines, which are due to hyperfine splitting arising from the interaction of the unpaired electron with a ^{51}V nucleus having the nuclear spin I=7/2. This confirms the presence of a single oxovanadium(IV) cation as the metallic centre in the complex. The anisotropy is not observed due to rapid tumbling of molecules in solution at room temperature and only g-average values are obtained. The anisotropy is clearly visible in the spectra at liquid nitrogen temperature and eight bands each due to $g_{\parallel}$ and $g_{\perp}$ are observed separately. The $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$ and $A_{\perp}$ values (RT/LNT) are measured from the spectra, which are in good agreement for a square-pyramidal structure[26-28]. The g_{iso} value from mobile solution at room temperature and g_{av} from frozen solution at liquid nitrogen temperature do not agree very closely since the g and A tensors are corrected for second-order. Further, g values are all very close to the spin-only value (free electron value) of 2.0023, suggesting little spin-orbit coupling. On the basis of the above studies, the tentative structures may be proposed for these oxovanadium(IV) complexes of the type **(I)** and macrocyclic complexes of the type (**II**) are shown in figure.

Conclusion

The spectral data show that the furil is a versatile chelating agent having two reactive carbonyl groups capable of undergoing Schiff base condensation with a variety of diamines. Schiff bases behave as tetradentate ligands by bonding to the metal ion through the azomethine nitrogen and amine nitrogen. The analytical data show the presence of one metal ion per ligand molecule and suggest a mononuclear structure for complexes. The magnetic moment values and electronic data are in the favour of square pyramidal structure for VO(IV) complexes.

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