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Synthesis and spectral characterization of Macrocyclic Schiff bases with Vanadium(V) complexes and their antibacterial activities

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Abstract: Macrocyclic Schiff base ligands (HDAA) and (EDAA) have been synthesized by condensation of Hydrazinedihydrochloride and Ethylenediamine with acetyl acetone respectively in 1:1 molar ratio in ethanolic solution. Further the vanadium complexes were synthesized by refluxing ligands with $[VO(acac)_2]$ in1:1 molar ratio in ethanolic medium. The microanalytical analysis have been obtained and UV, IR, ^{1}HNMR spectral analysis have been carried out to suggest the tentative structures for the complexes. From the datas , it is evident that all complexes possess square planar geometry. The antibacterial activities of these compounds were also evaluated against various bacteria like Gram negative *E.coli,* Gram positive *S.aureus, M.luteus* and *B.licheniformis*.
Keywords: Macrocyclic ligands, Vanadium complexes, Antibacterial activities.

Introduction

Macrocyclic Schiff base are very important molecules in biological systems. They have wide range of applications in bioinorganic, coordination & catalysis field.[1] They have some interesting properties and biological functions such as being models for metalloproteins & oxygen carrier systems, in catalyzing organic oxidation ion reaction. These ligands found to be very versatile due to their capability of forming stable complexes.[2]

On the other hand vanadium found to be very important element as it exhibit variety of insulin mimetic properties. Vanadium possesses medicinal, pharmacalogical & biological application also in many enzymatic reactions. Recent advances in catalytic and medicinal properties of vanadium complexes have stimulated their design and synthesis. The biochemical aspects of vanadium complexes have further promoted the coordination chemistry of vanadium.[3] Its biological significance is further examplified by its incorporation in natural products and enzyme in potent inhibitor of phosphoryl transfer. Keeping all these facts in mind, we are presenting the synthesis, characterization and biological studies of macrocyclic Schiff bases with vanadium complexes in this paper.

Experimental

All the chemicals used in present investigation were of A.R. quality. All the solvents used were of high purity and distilled in the laboratory before use. Purity of the compounds was judged by using silica gel TLC plates and spots were visualized by iodine vapours. Molecular weights were determined by Rast Camphor method. Melting points were taken in open capillaries and are uncorrected. Conductivities of compounds were determined on Equiptronics model no. EQ-660A. Electronic spetra were determined on digital spectrophotometer.

IR spectra were recorded on Perkin-Elmer FT-IR spectrophotometer in range 4000- 500cm^{-1} using KBr pellets and ^{1}HNMR spectra in MeOD at 300 MHz using TMS as an internal standard. The ligands and complexes were analysed for C,H&N. All done at CDRI(Lucknow).

Synthesis of Macrocyclic Schiff bases

Ethanolic solutions of Hydrazinedihydrochloride (neutralized by dil.NaoH) and Ethylenediamine were mixed with acetyl acetone respectively in equimolar ratios with constant stirring. The resulting mixture was refluxed for 6-7 hours. The solid crystals were collected and dried over $CaCl_2$ in vaccum and were recrystallised by ethanol & Petroleum ether.

Synthesis of Vanadium(V) complexs

The complex of Vanadium (v) have been prepared by reacting an ethanolic solution of vanadium acetylacetone salt with ethanolic solution of prepared ligands (HDAA) and (EDAA) in 1:1 molar ratio. Resulting reaction mixture was refluxed on water bath for 5-6 hours. Brownish black powder was obtained & recrystallised by petroleum ether.

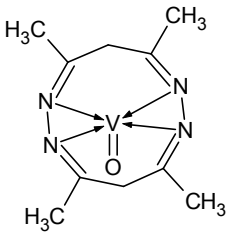

Fig 1: Oxovanadium complex of ligand HDAA

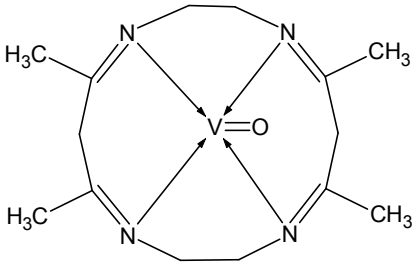

Fig 2: Oxovanadium complex of ligand EDAA

Antibacterial Activities

All the compounds were tested for antibacterial activities against *E.coli*(-), *S.aureus*(+), *M.luteus*(+) and *B.licheniformis*(+) (ATCC) at different concentration (100,500 and 1000ppm) following disc diffusion method. Compounds were dissolved in DMF. Muller Hinton agar medium was allowed to set and were uniformly seeded with the bacterium to be tested. Small sterile discs (having 6mm diameter) of Whatman no.1 filter paper, impregnated with standard solution of test compounds were placed on the plates of culture medium. Plates were immediately transferred to incubator. After one day of incubation, the degree of sensitivity is determined by measuring the zone of inhibition. The IC_{50} values were also determined.

Results and Discussion

The resulting macrocycic Schiff bases and their vanadium complexes are colored and soluble in methanol, ethanol, DMF& DMSO. They have sharp melting points and are stable at room temperature and are non-hygroscopic. Compounds are pure as both ligands and complexes moves as a single spot indicating the presence of only one component and hence their purity. The values of molar conductance in DMF (10^{-3}M) were found in the range 6-3-ohm^{-1}cm^{2}mol^{-1} suggesting a non-electrolytic nature of the compounds.

Molecular weights determined by Rast Camphor method and were found in accordance with calculated value thus the monomeric nature of these ligands and complexes is also confirmed. The micro analytical datas are given in table 1.

Electronic spectra of ligand (HDAA) shows weak band at 300nm and 360nm attributable to п- п* and n-п* transition respectively, in its complex first remains unchanged while second shows blue shift and a band appear at 320nm due to donation of lone pair of C=N group to vanadium atom. Ligand (EDAA) shows the same weak band at 310nm and 365nm while second appears at 325nm. The IR spectra of ligands shows strong band in the region1590-1640cm-1 due to C=N which is assignable to macrocyclic Schiff bases. In spectra of vanadium complexes, very sharp peak in region 970-990cm^{-1} suggests the presence of V=O bond. The band due to C=N has shifted to lower frequency in the complexes, indicating the coordination through azomethine nitrogen.

The ^{1}HNMR spectra of ligands (HDAA) and (EDAA) shows signal between δ7.169-7.463 due to aromatic ring which gets shifted downfield and appears between δ7.180-8.006 in their vanadium complexes. The proton signal for methylene group in both ligands appears between δ3.690-3.783 also get shifted downfield and appears between δ3.900-3.982 in the complexes.

All the compounds were evaluated for their antibacterial activity [4-6] *in vitro* by using zone inhibition technique[7-10] against *E.coli*(-) *S.aureus*(+) *M.luteus*(+) and *B.licheniformis* (+) at different concentration (100,500 and 1000ppm). Experiments were repeated three times and the results were expressed as (Mean±SEM) values in table 2. The results obtained were compared with the standard drug Ofloxacin. The IC_{50} values are shown in table 3. All compounds were found to be potent towards all bacteria. Ligand(HDAA) was more potent towards *M.luteus*(+) and *B.licheniformis*(+) with having 0.50mg/ml IC_{50} values while ligand (EDAA) was equally potent towards all bacteria except *M.luteus*(+). All metal complexes showed enhanced activity as their IC_{50} values ranged from 0.20mg/ml to 0.35mg/ml.

Table 1: The micro analytical datas

COMPOUND	YIELD IN %	COLOUR	MW F (C)	MP IN °C	ELEMENT ANALYSIS IN % FOUND (CALCD)				
					C	H	N	V	O
LIGAND (HDAA)	65	PALE YELLOW	190 (192)	85	61.2 (62.5)	8.5 (8.3)	30.2 (29.1)	-	-
VANADIUM COMPLEX OF (HDAA)	70	BROWNISH BLACK	258 (260)	200	45.8 (46.1)	6.9 (6.1)	22.1 (21.5)	19.3 (20.0)	5.8 (6.1)
LIGAND (EDAA)	68	PALE BROWN	246 (248)	80	68.7 (67.7)	10.1 (9.6)	21.0 (22.5)	_	-
VANADIUM COMPLEX OF(EDAA)	75	BROWNISH BLACK	(318) 316	85	52.6 (53.1)	8.1 (7.5)	18.1 (17.7)	15.9 (16.4)	5.2 (5.0)

Table 2 – Antibacterial activities of ligands and their Oxovanadium complexes (in mm).

Bacteria	Conc In ppm	Ligand HDAA (Mean±SEM)	Complex of HDAA (Mean±SEM)	Ligand EDAA (Mean±SEM)	Complex of EDAA (Mean±SEM)
E. coli(-)	100	15±0.625*	17±0.289	15±0.557	18±0.755*
	500	22±0.710*	26±0.437	23±0.451	29±0.803
	1000	28±0.404	30±0.321	28±0.503	31±0.204
S.aureus(+)	100	14±0.513*	17±0.513	14±0.404	17±0.173
	500	22±0.462	25±0.625	23±0.208	28±0.231
	1000	28±0.115	31±0.458	28±0.351	32±0.404
M.luteus(+)	100	15± 0.586*	18±0.603*	14±0.440	17±0.710*
	500	23± 0.666	26±0.551	22±0.493	28±0.755
	1000	29±0.625	32±0.332	29±0.683	32±0.803
B.licheniforms (+)	100	16±0.851	18±0.607*	15±0.529*	17±0.493
	500	23±0.569	27±0.901*	23±0.416	29±0.656
	1000	29±0.529	32±0.404	29±0.305	31±0.703

Significance level P< 0.001, *P< 0.01. Each value represents Mean±SEM (n=3)

Table 3 – IC_{50} values of ligands and their Oxovanadium complexes

Compound	IC_{50}values (in mg/ml) against			
	E. coli(-)	S.aureus(+)	*M.luteus* (+)	*B.licheniforms* (+)
Ligand HDAA	0.58	0.56	0.50	0.50
Complex of HDAA	0.31	0.35	0.25	0.23
Ligand EDAA	0.50	0.50	0.56	0.50
Complex of EDAA	0.20	0.26	0.26	0.24

Conclusions

On the basis of above evidences the tentative structure with possibly four coordinated oxo-vanadium (V) complexes can be proposed with having square planar geometry of both ligands (HDAA) and (EDAA) as shown in fig. 1 & 2 respectively. The results of biological activities showed that metal complexes are more potent in comparison to their respective ligands as chelation tends to make them more powerful. Further, it is observed that the activity increases with increase in concentration.

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