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Synthetic, Structural, Thermal and Biological Studies of Zr(IV), Th(IV) and VO(IV) Chelates with *bis*-Bidentate Schiff Bases

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Zr(IV), Th(IV) and VO(IV) chelates with N,N'-*bis*-[2-hydroxynapthalidine]-4,4'-diaminodiphenylmethane [H_2-NaIDADPM](L_1) and N,N'-*bis*-[2-hydroxynapthalidine]benzidine [H_2-NaIBz](L_2), respectively have been synthesized and characterized by elemental analysis, magnetic susceptibility, spectral techniques like UV-Visible, IR, NMR, ESR and thermal studies. The molar conductivity data indicates that the chelates are non-electrolytes. Analytical data supports 1:1 (M:L) stoichiometry. The electronic spectra along with the magnetic data suggest octahedral geometry for VO(lV) chelates and revealed diamagnetic nature of the thorium and zirconium chelates. IR data shows the ligands function as *bis*-bidentate ligand coordinating through ON-NO donor system. The antimicrobial activities of the ligands and their metal chelates have been studied by screening the compounds against some selected microorganisms and the results have been compared.

Key Words: N,N'-*bis*-[2-Hydroxynapthalidine]-4,4'-diaminodiphenylmethane, N,N'-*bis*-[2-Hydroxynapthalidine]benzidine, *bis*-Bidentate coordination, Antimicrobial activity.

INTRODUCTION

Synthesis of dimeric or polymeric complexes using *bis*-bidentate Schiff base ligands aroused much interest in recent times particularly with a view to examine their structural diagnosis[1-3]. The present work deals with synthesis and characterization of complexes of Zr(lV), Th(lV) and VO(lV) with Schiff bases derived by condensation of 4,4'-diaminodiphenylmethane (DADPM) and benzidine with 2-hydroxynapthaldehyde. The compounds have been characterized by various physicochemical methods. The antimicrobial activity of the ligands as well as their chelates against *S. aureus, E. coli, S. typhi* and *B. subtilis*, have also been reported.

EXPERIMENTAL

All the chemicals used were of AR grade. 4,4'-Diaminodiphenylmethane and benzidine were obtained from M/s Fluka Chemicals. $ZrO(NO_3)_2$, $Th(NO_3)_4 \cdot 5H_2O$ and $VOSO_4 \cdot 5H_2O$ and 2-hydroxynapthaldehyde were purchased from Acros Organics. The solvents were purified and doubly distilled before use.

Preparation of Schiff base ligands: The required Schiff bases were obtained by reacting the (0.2 mol) 2-hydroxynapthaldehyde with corresponding diamine *i.e.*, 4,4'-diaminodiphenylmethane or benzidine (0.1 mol) in EtOH medium and the resultant mixture was refluxed on a waterbath for 3 h. The product was then filtered, repeatedly washed with EtOH and acetone and dried in air. The ligands so obtained were recrystallized from xylene as micro-crystalline compounds.

Preparation of Th(IV) chelates: To a hot suspension of the corresponding ligand (0.01 M) in chloroform, an ethanolic solution of $Th(NO_3)_4 \cdot 5H_2O$ (0.01 M) was added dropwise with constant stirring with the help of rotamental and refluxed for 3 h. The resultant coloured product was filtered, repeatedly washed with EtOH and dried *in vacuo*.

Preparation of VO(IV) chelates: To a hot suspension of the corresponding ligand (0.01 M) in DMF, an ethanolic solution (0.01 M) of $VOSO_4 \cdot 5H_2O$ was added dropwise with constant stirring with the help of rotamental and refluxed for 3 h. The resultant coloured product was filtered, repeatedly washed with EtOH and dried *in vacuo*.

Preparation of Zr(IV) chelates: In a typical reaction the corresponding ligand (0.01 M) suspended in EtOH was added to NaOH (0.02 M) and CH_3COONa (0.02 M) solution. The suspension was stirred with heating on rotamental whereupon a reddish brown solution produced. To this a hot aqueous solution (0.01 M) of zirconyl nitrate was added drop-wise. The resulting mixture was refluxed for 4 h. The coloured precipitate obtained was filtered by suction, repeatedly washed with EtOH followed by repeated washing with chloroform and acetone and dried at ambient temperature.

Antimicrobial screening: The antimicrobial activity of ligands and their metal chelates has been studied by disc diffusion method[4]. The activity of the compounds was assessed by measuring the diameter of inhibited zone in millimeters. The culture of *E. coli, S. typhi, S. aureus* and *B. subtilis* were used as test organism, which were grown on nutrient agar medium. Solutions of the chelates (1 mg/10 cm^3) in DMF were used for the studies. In this method, 0.1 mL of inoculum of the test organism was spread uniformly on the surface of the agar medium in a Petri plate by using a spreader. The sterilized Whatmann filter paper discs of 5 mm diameter were dipped into the solution in DMF (10^{-3} M) and then were placed on the surface of the agar. Up to four discs in each plate were used. The plates were incubated at 37 ºC for 24 h. During incubation, the complex diffuses from the filter paper into the agar. The results were compared against reference compounds like streptomycin and penicillin, which was screened simultaneously. Solvent DMF, used as blank, was also run to know its activity.

The compounds were analyzed for C, H and N while the metal contents of the metal-chelates were estimated by standard methods. The molar conductance values at room temperature were measured in DMF (10^{-3} M) on an Elico digital direct reading conductivity meter model CM-180. Room temperature magnetic susceptibility measurements were made on solid samples, by a Gouy method using $Hg[Co(SCN)_4]$ as a calibrate. The electronic spectra of ligands and their metal-chelates were recorded on Shimadzu 160A spectrophotometer. Reflectance spectra of the solid complexes in the UV-Visible region were recorded against $BaSO_4$ as reference on V-570 solid state UV-Visible spectrophotometer. The Infrared spectra were recorded with a Perkin Elmer FTIR Spectrophotometer model 1600 using KBr pellets. The ^{1}H NMR spectra were recorded on Zeol-300 MHz high resolution instrument in $CDCl_3$ solvent using TMS as the internal reference. The ESR spectra of Cu(II) complexes were recorded on E-112 Varin-E line electron spin resonance spectrometer at room temperature in polycrystalline state and in DMSO solution using TCNE marker. TG and DTA data were made on Perkin-Elmer diamond instrument by recording the potential variations on increasing the temperature from room temperature at a heating rate of 10 ºC/min.

RESULTS AND DISCUSSION

The reaction of 4,4'-diaminodiphenylmethane and benzidine with 2-hydroxynaphthaldehyde, yields Schiff bases (H_2-NalDADPM)L_1 and (H_2-NalBz)L_2, the formulation of which is supported by analytical (Table-1) and spectral data. The reaction of Schiff bases with metal ions yielded chelates, which were found to be quite stable in atmosphere and non-hygroscopic in nature. The analytical and spectral data indicates that the metal ligand stoichiometry is 1:1 in all the metal-chelates. The resultant metal-chelates found to be highly coloured and insoluble in water and most of the organic solvent but were sparingly soluble in DMF and DMSO. Molar conductance values of the complexes in DMF (0.25×10^{-3} molar) at 27 ºC suggest their non-electrolytic nature (0.010-0.053 mhos cm^2 mol^{-1}).

The ^{1}H NMR Spectrum of the ligands in $CDCl_3$ exhibits the following data (δ ppm). The multiplet signals corresponding to aromatic protons occur in the range of 6.6-8.1ppm in case of L_1 and 7.00-8.2 ppm in case of L_2. The singlet resonance signals due to methylene ($-CH_2-$) protons in L_1 occurs at 3.5 ppm. The doublet at resonance signal 9.3 and 9.4 ppm in case of L_1 and L_2, respectively indicating that the associated hydrogen belongs to NH rather than to an OH group. This supports the condition may be an equilibrium mixture of the ketoenamine and enolimine forms[5].

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF LIGANDS AND THEIR Th(IV), VO(IV) AND Zr(IV) CHELATES

Compound (colour)	Equivalent weight	m.p./Dcomp. Temp. ºC	Elemental analysis: Calcd. (Found) %				Molar conductance (mhos cm^2 mol^{-1})
			M	C	H	N	
H_2-NalDADPM (Yellow)	506.6	230*	–	82.98 (83.00)	5.53 (5.60)	5.17 (5.20)	–
$[Th(NalDADPM)(H_2O)_2(NO_3)_2]_n$ (Yellowish orange)	896.6	>360	26.99 (25.87)	47.25 (46.88)	3.32 (3.14)	6.45 (6.24)	0.052
$[VO(NalDADPM)(H_2O)]_2$ (Lemon yellow)	589.5	>360	8.85 (8.38)	72.45 (71.31)	4.76 (4.44)	5.00 (4.75)	0.010
$Zr(OH)_2(NalDADPM)(H_2O)(NO_3)]$ (Reddish brown)	704.7	>360	13.50 (12.94)	60.64 (59.65)	4.65 (4.00)	6.87 (5.96)	0.011
H_2-NalBz (Red)	492.6	270*	–	83.5 (82.91)	5.70 (5.68)	5.05 (4.91)	–
$[Th(NalBz)(H_2O)(NO_3)]_n$ (Blood red)	802.5	>360	30.05 (28.91)	51.08 (50.88)	3.50 (3.01)	5.50 (5.23)	0.050
$[VO(NalBz)(H_2O)]_2$ (Brownish red)	575.5	>360	9.00 (8.85)	71.5 (70.95)	4.50 (4.20)	5.25 (4.86)	0.014
$Zr(OH)_2(NalBz)(H_2O)_2]_n$ (Brownish red)	644.7	>360	14.20 (14.14)	63.85 (63.34)	4.85 (4.69)	4.47 (4.34)	0.015

*Melting point.

A careful comparison of the spectra of ligands and their metal-chelates shows the following observations: The ligands L_1 and L_2 show a medium broad band at 3041 and 3037 cm^{-1}, respectively; which may be assigned to the phenolic ν(OH) stretching vibration. The observed shifts to lower frequency indicating the presence of intramolucular hydrogen bonding as part of resonating ring system[6]. This band is being disappeared in spectra of all metal-chelates indicating the dissociation of phenolic hydrogen with bond formation between metal and oxygen[7].

The ν(C-O) bonding frequency is observed at 1324 and 1311 cm^{-1} in case of Schiff base ligands L_1 and L_2, respectively. It is shifted to higher frequency (24-53 cm^{-1}) in their metal-chelates, which is supported by the appearance of a new low intensity band in the region around 647-581 cm^{-1} in the spectra of the chelates due to ν(M-O) vibrations[7].

In both the Schiff bases L_1 and L_2 an intense band at 1624 and 1620 cm^{-1}, respectively are assigned to ν(C=N). This band is observed to be shifted to a higher wavenumber by 7-12 cm^{-1} in case of thorium and zirconium complexes. It may be due to the increase in C-N bond order due increase in the electron density on the metal and formation of the bond between the oxygen of the OH group and the metal[8]. In case of oxovanadyl chelates ν(C=N) frequency shift to lower wavenumber by 7-8 cm^{-1}. This lowering in frequency is indicative of the fact that the lone pair of electrons on the azomethine nitrogen are withdrawl and compensate for the decrease in the electron density on the metal, indicating coordination of the azomethine nitrogen with the metal ion[9]. It is further reflected by the appearance of new bands due to ν(M-N) in the low wavnumber region at around 431-410 cm^{-1} (Table-2).

The spectra of the oxovanadium(IV) chelates of L_1 and L_2, display a strong band at 983 and 968 cm^{-1}, respectively, assigned to the vanadium-oxygen stretching frequency, which is diagnostic of the presence of the V-O multiple bond in a complex[10]. In case of zirconium chelates, the absence of a band in the region of 850-950 cm^{-1} due to ν(Zr=O)[11] and the appearance of a new band[12] around 1140 cm^{-1} due to the (Zr-OH).

Association of water molecules in the complexes is confirmed by the appearance of new band in the region 3400-2500 cm^{-1} and sharp band near 830 cm^{-1} assigned to O-H stretching and rocking mode[13] of coordinated water molecule, respectively.

The coordination of NO_3 can be conformed by the appearance of band around ν_1(1297-1267 cm^{-1}), ν_2(1029-1013 cm^{-1}), ν_3(749-735 cm^{-1}) and ν_4(1492-1468 cm^{-1}) frequencies[15] in case of ZrL_2 and Th(IV) complexes. Thus, the IR data suggest that the Schiff bases are dibasic *bis*-bidentate ON-NO donor type (Figs. 1 and 2).

TABLE-2

CHARACTERISTIC IR BANDS (cm^{-1}) OF LIGANDS AND THEIR Th(IV), VO(IV) AND Zr(IV) CHELATES

Compounds	ν(C=N)	ν(C-O)	ν(M-N)	ν(M-O)	ν(OH····N)	$\nu(M\text{-}OH)^{Zr(IV)}$ $\nu(M{=}O)^{VO(IV)}$	$\nu(O\text{-}NO_2)$	$\nu(H_2O)$
H_2-NalDADPM	1624s	1324s	-	-	3041b	-	-	-
$[Th(NalDADPM)(H_2O)_2(NO_3)_2]_n$	1631s	1367s	492m	639m	-	-	1468s, 267s, 1013m, 735m	3193b 838s
$[VO(NalDADPM)(H_2O)]_2$	1617s	1358s	462m	614m	-	983s	-	3055b 830s
$[Zr(OH)_2(NalDADPM)(H_2O)(NO_3)]_n$	1632s	1358s	452m	581m	-	1142s	1492s, 1297s, 1029m, 749m	2890b 826s
H_2-NalBz	1620s	1311s			3037b	-		-
$[Th(NalBz)(H_2O)(NO_3)]_n$	1627s	1374s	446m	648m	-	-	1473s,1282s, 1027m, 746m	3209b 844s
$[VO(NalBz)(H_2O)]_2$	1612s	1358s	432m	608m	-	968s	-	3414b 812s
$Zr(OH)_2(NalBz)(H_2O)_2]_n$	1632s	1354s	432m	647m	-	1135s	-	3402b 812s

TABLE-3

MAGNETIC, ELECTRONIC AND EPR SPECTRAL DATA OF THE VANADYL CHELATES

Complex	Characteristic *d-d* transitions (cm^{-1})			μ_{eff} (BM)	$g_{\parallel}$	$g_{\perp}$	g_0	$A_{\parallel}$	$A_{\perp}$	A_0
	$d_{xy}(b_2) \rightarrow d_{xz}d_{yz}(e^*)$	$d_{xy}(b_2) \rightarrow d_{x^2 y^2}(b_1^*)$	$d_{xy}(b_2) \rightarrow d_{z^2}(a_1^*)$							
$[VONalDADPM)(H_2O)]_2$	22624	19230	13850	1.80^a	1.960	2.0095	1.993	172	61	98
$[VO(NalBz)(H_2O)]_2$	18867	15673	13333	1.76^a	1.962	2.0070	1.992	175	60	98

[a] Per metal ion.

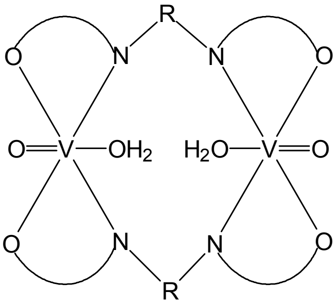

Fig. 1. Proposed dimeric structure of vanadyl chelates; R = 4'4-Diaminodiphenylmethane in case of L_1 and Benzidine in case of L_2

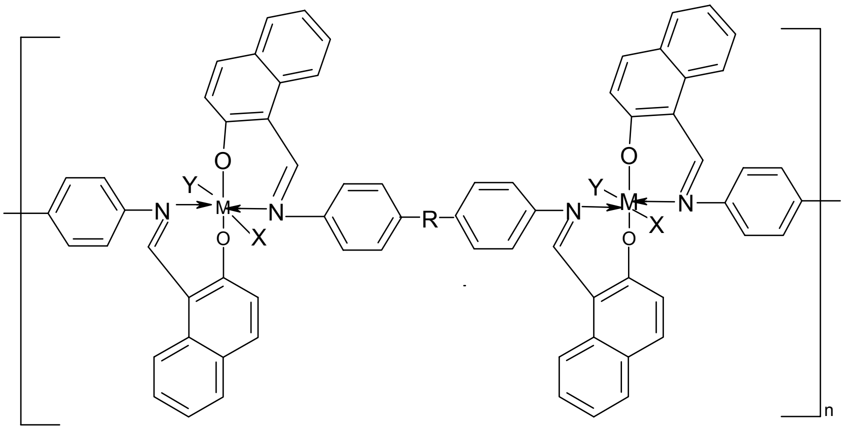

Fig. 2. Proposed polymeric structure of the chelates,
R = CH_2 in case of L_1 R = Nil in case of L_2
M = Zr(IV), X = $(OH)_2$, Y = H_2O and NO_3 M = Zr, X = $(OH)_2$, Y= $2H_2O$,
M = Th(IV), X = $2H_2O$, Y = $2NO_3$, M = Th(IV), X = H_2O, Y = NO_3

Magnetic and electronic studies: The chelates of Zr(IV) and Th(IV) shows only charge transfer transitions between metal and ligand and intraligand transition bands which is as according with the results revealed by magnetic susceptibility as diamagnetic nature of the complexes. The electronic spectra of the Zr(IV) and Th(IV) complexes on comparison with the spectra of the ligands shows that the peaks of the complexes are deep and intense which support the complex formation.

Electronic spectral data along with magnetic moments of vanadyl chelates are listed in Table-3. Room temperature magnetic moment values of VO(IV) chelates lie in the range 1.70-1.80 BM suited for oxovanadium(IV) dimeric complexes with one unpaired electron. The electronic spectra of VO(IV) complexes show *d-d* bands in the visible region which according to the scheme of Balhusen and Gray[15] ($d_{xy} < d_{xz}$, $d_{yz} < d_{x^2y^2} < d_{z^2}$) are assigned to [$d_{xy}(b_2) \rightarrow d_{xz}d_{yz}(e^*)$, $d_{xy}(b_2) \rightarrow d_{x^2y^2}(b_1^*)$ and $d_{xy}(b_2) \rightarrow d_{z^2}(a_1^*)$] transitions. From the electronic spectral data a six coordinate octahedral structure can be assigned to the VO(IV) chelates[16].

EPR Spectroscopy: The X-band EPR spectra of the oxovanadium(IV) Schiff base complexes in dilute DMSO solution and in solid state at room temperature were recorded. The solid state spectra of the oxovanadium(IV) complexes show single isotropic signal centered at $g = 1.995$ corresponding $\Delta M_S = \pm 1$. There were no absorption recorded at half field corresponding to $\Delta M_S = \pm 2$ which supports the absence of strong antiferromagnetic interaction[17]. ESR spectra of polycrystalline complexes differ from the dimers having antiferromagnetic interaction by the several respects. (i) The main signal corresponding to $\Delta M_S = \pm 1$ is comparatively broader than the signal obtained in case of antiferromagnetic compounds. (ii) The signal is centered at higher g-value (> 1.971). (iii) The complexes don't show stronger half field signal at room temperature.

These observations are suggestive of absence of antiferromagnetic interactions and thus deny the V-O-V-O chain structure for these compounds. Broad lines observed for the complexes may be due to weak exchange interaction between the individual complex molecules. In case of compounds having a strong exchange interaction through V-O-V-O bridge, the electrons are free to move throughout the crystal resulting into exchange narrowing.

In DMSO solution, normal eight line spectra showing hyperfine splitting for the ^{51}V nucleus ($I = 7/2$) are obtained in both cases. The go values and vanadium nuclear hyperfine splitting constants are recorded in Table-3. The A_o values are remarkably constant for both the complexes. The ligand nitrogen or hydrogen superhyperfine splitting is not observed on the vanadium line. This indicates the unpaired electron to be in b_2g orbital localized on metal. Thus excluding the possibility of its direct interaction with the ligand[17].

Thermal study: Thermal study indicates that there is no weight loss up to 150 ºC suggest the absence of any lattice water molecule in all the present metal-chelates. Further decomposition shows the following observations.

The thermogram of thorium chelates show the weight loss corresponding to decomposition of coordinated water around the temperature *ca.* 200 ºC, followed by loss in weight due to nitrate molecule *ca.* 270 ºC. The DTA graph shows endothermic and exothermic peaks sign at the respective temperature range. The TG-DTA thermograms of oxovanadium chelates show weight loss corresponding to decomposition of two molecules of coordinated water molecule around the temperature *ca.* 200 ºC accompanied with two endothermic peaks.

The TG-DTA thermogram of the ZrL_1 chelate, shows weight loss corresponding to decomposition of one coordinated water molecule accompanied with one endothermic peak and one nitrate molecule accompanied one exothermic peak with in the temperature range of 151-245 ºC. On further decomposition two -OH species detaches in between the temperature range of 245-320 ºC accompanied with two small endothermic peaks. In case of ZrL_2 chelate the thermogram in first step decomposition shows the loss of two coordinated water molecule accompanied with one endothermic peak in the temperature range of 148-225 ºC followed by loss of two coordinated -OH species in the temperature range of 225-300 ºC accompanied with the two endothermic peaks. The half thermal decomposition temperature decreases in order Zr(IV) > Th(IV) > VO(IV) in case of chelates of L_1 and Th(IV) > Zr(IV) > VO(IV) in case of L_2.

Biological activity: The results of the preliminary study on antimicrobial activity through disc diffusion method against the present bacterial strain indicate that most of the compounds are less to highly active (Table-4). The free ligand L_1 shows moderate activity towards *E. coli* (growth inhibiter zone 10 mm) species than rest of chelates, it seems to have negative effect on the activity of the parent ligand on chelation. All the complexes are moderately active against *B. subtilis* and *S. aureus* except Zr-L_2 (7-8 mm). The present compounds are quite less active compared to standard compound like streptomycin and penicillin. Normally the inhibition activity of the compound increases with increase in the concentration of the solution.

TABLE-4
ANTIBACTERIAL ACTIVITY OF COMPOUND (1 mg/10 cm^3)

Compound	Inhibition zone of diameter in mm				
	ST	EC		BS	SA
Streptomycin	16	14	Penicillin	12	10
H_2-NalDADPM	–	10		–	–
$[Th(NalDADPM)(H_2O)_2(NO_3)_2]_n$	–	–		8.0	7.0
$[VO(NalDADPM)(H_2O)]_2$	–	–		8.0	7.0
$Zr(OH)_2(NalADPM)(H_2O)(NO_3)]$	–	–		7.0	8.0
H_2-NalBz	–	–		8.0	7.0
$[Th(NalBz)(H_2O)(NO_3)]_n$	–	–		7.0	7.0
$[VO(NalBz)(H_2O)]_2$	–	–		7.0	7.0
$Zr(OH)_2(NalBz)(H_2O)_2]_n$	–	–		–	–

ST = *S. typhi*; EC = *E. coli*; BS = *B. subtilis*; SA = *S. aureus*.

Conclusion

On the basis of analytical, conductivity, magnetic susceptibility, TG and DT analyses, IR, electronic and ESR spectral data, the metal:ligand, (1:1) composition, insolubility and high thermal stability (> 250 ºC) of the complexes indicates dimeric (Fig. 1) in case of VO(IV) chelates[17,18] and polymeric (Fig. 2) in nature in rest of the cases[2,16]. The antibacterial studies show mild antibacterial activity of the compounds against selected strains of *E. coli, S. typhi, S. aureus* and *B. subtilis* compared to standard antibacterial compound (streptomycin and penicillin). The present complexes are less active against the selected strains of microorganisms.

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