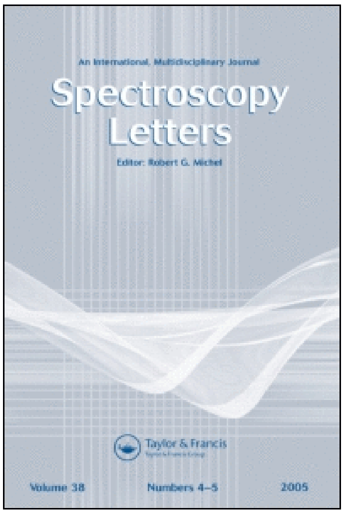

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Synthesis, magnetic and special studies of some novel metal complexes of Cu(II), Ni(II), Co(II), Zn(II), Nd(III), Th(IV), and UO_2(VI) with schiff bases derived from sulfa drugs, viz., Sulfanilamide/Sulfamerazine and o-vanillin.

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ABSTRACT

Keeping in view the chemotherapeutic value of the sulfa-drugs, two schiff base ligands viz *o*-vanillin-sulfanilamide (*o*VSaH) and *o*-vanillin-sulfamerazine (*o*VSmrzH) and their bipositive, tripositive tetrapositive and uranyl metal complexes have been synthesized and characterized by elemental analysis, IR spectra, thermal analysis, magnetic suceptibility measurements, diffuse reflectance spectra and ^{1}H NMR spectra and molar conductance measurements. The disappearance of phenolic proton signal at 12.6 ppm and the upfield shift of azomethine proton rignal (from 8.65 ppm against 8.96 ppm in the ligand) upon complexation indicate the coordination by phenolic oxygen (after deprotonation) and azomethine nitrogen respectively. Zn(II), Th(IV) and UO_2(VI). complexes are found to be diamagnetic as expected. The low molar conductance values suggest the non-electrolytic nature of these complexes. The general compositions of there complexes are found to be $[M(o\text{VSa})_2]$ where M=Cu(II), Ni(II), Zn(II), Co(II), $[Nd(o\text{VSa})(NO_3)_2(H_2O)_2]$ $[Th(o\text{VSa})(NO_3)_3(H_2O)]$ $[UO_2(o\text{VSa})(OAc)(H_2O)]$ and $[M'(o\text{VSmrz})_2(H_2O)_2]$ where M'=Cu(II), Ni(II), Co(II) and Zn(II) and $[UO_2(o\text{VSmrz})_2]$.

INTRODUCTION

The sulfa drugs, which are derivatives of a compound *p*-aminobenzenesulfonamide, commonly known as sulfanilamide, were the first effective chemotherapeutic agents to be widely used for the cure of bacterial infection in humans. They are termed as sulfonamides, due to the presence of sulfonamide group ($-SO_2NH_2$). *p*-Aminobenzene sulfonamide was first synthesized in the year 1908, but its therapeutic

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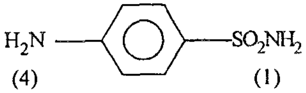
value was discovered even earlier.In 1932 a German firm prepared a red dye 4-(4'-Sulfamylphenylazo)-*m*-phenylenediamine and in 1935 Domagk reported remarkable curative effects of this compound and named it "prontosil". In the same year, a group of fresh investigators found that antibacterial property of the drug resided in the *p*-aminobenzenesulfonamide portion of the molecule.

The sulfanilamide are found to be active against several types of bacteria and hence used in the treatment of diseases eg. pneumonia, gonorrhea, meningitis, tonsillitis, sinus infections, etc. The sulfa drugs are white crystallline powder, mildly acidic in character and relatively insoluble in water. Some sulfonamides are amphoteric having both acidic and basic properties. The latter is due to the presence of an amino group in the aromatic ring. The basic structure of sulfonamide is shown below:



N_1 = Nitrogen of sulfonamide.
N_4 = Nitrogen of para amino group.

The work carried out by Woods clearly indicate the sulfanilamide to be antagonistic to *p*-aminobenzoic acid (PABA), a biological precursor of methionine.

Folic acid derived from PABA is important in bacterial metabolism. Sulfonamides inhibit the enzyme folic acid synthetase, which is involved in the conversion of PABA to folic acid. This causes folic acid deficiency resulting in injury to the bacterial cell. The antibacterial activity of sulfonamides is confined only to micro organisms which synthesize their own folic acid.[1-4]

The originally employed sulfonamide compounds like sulfanilamide, sulfapyridine and sulfathiazole are obsolete because of their high toxicity. The most frequently observed side effects are crystalluria, renal damage and hemecturia. Gastrointestinal side effects include nausia, vomiting, abdominal pain, diarrhea, etc. so the chelate type of metal complex is of great importance, especially in the pharmaceutical field. The complex so formed may result in precipitation of the metal or the formation of a stable, soluble compound. If the ligand forms a stable, water - soluble metal chelate, it is said to be a sequestering agent. Sequestration is the suppression of a property or reaction of a metal without removal of that metal from the system or phase by any process of precipitation or extraction. It has two important pharmaceutical uses, in analysis and the removal of deactivation of unwanted ions in solution. Certain theories have been advanced advocating that a major portion of drug action occurs through complexation.[5-7]

Studies have also been made to synthesise complexes formed by non - transition metal ions. Varshney *et al.*[8] Synthesized Lead(II) complexes of Schiff bases derived from sulfa drugs. They were tested against gram positive (S.aureus and S.subtilis) and gram negative (E.coli) bacteria and it was found that the metal complexes are much more active than the ligands. Interest was developed due to the synthetic flexibility, diverse stereochemistry as well as the unusual coordination numbers of main group IV elements, particularly of silicon, in the complexes with nitrogen and oxygen/sulfur donor ligands. Maurya *et al.*[9] have reported the synthesis of some ruthenium(II)complexes by the interactions of $K_2RuCl_5.H_2O$ with Schiff base derived from 4-benzoyl -3-methyl -1-phenyl -2-pyrazoline-5-one and sulfadrugs, *viz.*, sulfamerazine, and sulfadiazine. The complexes, which have been characterized on the basis of elemental analysis, molar conductance, cyclic - voltametry, IR, electronic and ^1H NMR spectral studies and have the general formula $[Ru(L—L)_2Cl_2]$.

Keeping in view of the pharmacological properties of sulfadrugs, following Schiff base chelating ligands and their bipositive, tripositive tetrapositive and uranyl metal complexes were synthesized.

(I) *o*-vanillin -sulfanilamide (*o*VSaH).

(II) *o*-vanillin -sulfamerazine (*o*VSmrzH).

These metal complexes are synthesized and characterized by elemental analysis, IR spectra, thermal analysis, magnetic susceptibility measurements, diffuse reflectance spectra and ^1H NMR spectra and molar conductance mesurements.

EXPERIMENTAL

Materials: - *o*- Vanillin, dimethylformamide (Sisco. Chem., Bombay), Sulfanilamide, Sulfamerazine (Sigma. Chemical Co.U.S.A.), $Cu(CH_3COO)_2.H_2O$, $Co(CH_3COO)_2.4H_2O$, $Ni(CH_3COO)_2.4H_2O$, $UO_2(CH_3COO)_2.2H_2O$, $Zn(CH_3COO)_2.2H_2O$, $Th(NO_3)_4.4H_2O$ (E.Merck, Bombay), $Sm(CH_3COO)_3.3H_2O$ (Indian Rare Earth Ltd.) were used as supplied. Methanol, ethanol and other solvents employed were of A.R. grade.

Synthesis of Schiff base ligands

Ethanolic solution of *o*-Vanillin (0.05 mol, 7.60 g) was added to the methanolic solution of the following sulfadrugs :

(i) Sulfanilamide (0.05 mol, 8.61 g)

(ii) Sulfamerazine (0.05 mol, 13.21 g)

The resulting mixture was then refluxed on a water bath for 4-5 h. The coloured solid mass separated out on cooling, which was kept in a refrigerator for better crystallization. It was then filtered, washed with ethanol, ether and subsequently dried over anhydrous $CaCl_2$ in a des iccator. The purity of the ligands were checked by TLC. These ligands are insoluble in all common organic solvents, *viz.*, acetone, alcohal, benzene, etc. and soluble in polar solvents *viz.* DMF and DMSO. The microanalytical data, melting points, colours and other physical properties are given in Table I.

Synthesis of metal complexes

All complexes were synthesized in non - aqueous medium using ethanol - DMF mixture. Synthesis could not be carried out completely in the absence of water due to presence of lattice water in the hydrated metal salts.

Synthesis of metal complexes of *o*VSaH

Metal complexes of *o*VSaH were synthesized by mixing the hot solution of oVSaH (0.01 mol, 3.05 g) in minimum quantity of dimethylformamide (30 mL) and ethanolic solution (40 mL) of metal salts (0.005 mol) 0.99 g of $Cu(CH_3COO)_2.2H_2O$; 1.10 g of $Zn(CH_3COO)_2.4H_2O$; 1.24 g of $Co(CH_3COO)_2.4H_2O$; 1.24 g of $Ni(CH_3COO)_2.4H_2O$ / (0.01 mol 4.24 g of $UO_2(CH_3COO)_2.2H_2O$; 5.02 g of $Th(NO_3)_4.4H_2O$ and 4.38 g of $Nd(NO)_3.6H_2O$. The resulting mixture was then refluxed on a heating mantle at 80°C for 5 - 6 h. On Cooling coloured solid complex precipitated out which was suction filtered, washed with ethanol and finally with diethylether and dried over anhydrous $CaCl_2$ in *vacuo*. The micro-analytical data and other physical properties of the synthesized complexes are given in Table II. The yield was 55 - 65% in all the complexes with respect to the ligand.

Synthesis of metal complexes of *o*VSmrzH

Metal complexes of *o*-vanillinsulfamerazine (oVSmrzH) were synthesized by mixing the hot solution of *o*VSmrz (0.01 mol, 3.98 g) in minimum quantity (30 mL) of dimethylformamide and ethanolic solution of metal acetates (0.005 mol) 0.99 g of $Cu(CH_3COO)_2.H_2O$; 1.24 g of $Ni(CH_3COO)_2.4H_2O$; 1.10 g of $Zn(CH_3COO)_2.2H_2O$; 1.24 g of $Co(CH_3COO)_2.4H_2O$ and 2.12 g of $UO_2(CH_3COO)_2.2H_2O$. The resulting mixture was refluxed on a heating mantle at 80°C for 5 - 6 h. On cooling coloured solid complex precipitated, which was filtered, washed with ethanol and finally with diethylether and dried over $CaCl_2$ in *vacuo*. The microanalytical data and other physical properties of the synthesized complexes are given in Table II. The yields were 55 - 70% in all the complexes with respect to the ligand.

Table I. Microanalytical and some physical properties of the synthesized Schiff base ligands.

S.No.	Schiff base ligand (Emperical Formula)	Colour	M.P. (°C)	Yield (%)	Solubility	Elemental analysis(%) Found (calcd).		
						C	H	N
I.	*o*VSaH ($C_{14}H_{14}N_2O_4S$)	Yellow	220	70	Sol.in DMF & DMSO	54.58 (54.83)	4.70 (4.56)	8.94 (9.13)
II.	*o*VSmrzH ($C_{19}H_{18}N_4O_4S$)	Orangish yellow	230	60	Sol.in DMF & DMSO	56.98 (57.22)	4.35 (4.15)	14.23 (14.05)

Table II. Physical characterstics and microanalytical data of oVSaH's complexes.

S.No	Compound	Colour	M.P. (°C)	Elemental analysis(%) Found (calcd).				C.N.	μ_{eff} (B.M.)	Λm *
				C	H	N	M			
1.	[CuL_2]	Nut brown	>280	49.89 (49.83)	3.49 (3.85)	8.18 (8.30)	9.20 (9.42)	4	2.01	8.21
2.	[$CoL]_2$	Green gold	>280	50.53 (50.17)	3.87 (3.88)	8.73 (8.36)	8.35 (8.80)	4	4.31	6.99
3.	[NiL_2]	Nut brown	>280	49.81 (50.19)	3.84 (3.88)	7.96 (8.46)	8.50 (8.77)	4	3.71	9.22
4.	[ZnL_2]	Greenish-yellow	>280	49.24 (49.69)	3.78 (3.84)	8.33 (8.28)	9.30 (9.66)	4	dia	7.81
5.	[$Nd(L)(NO_3)_2(H_2O)_2$	Rust-brown	>280	27.54 (27.55)	2.74 (2.78)	9.28 (9.18)	23.23 (23.66)	6	3.66	7.52
6.	[$Th(L)(NO_3)_3(H_2O)_2$]	Yellow-gold	>280	24.93 (24.09)	2.51 (2.43)	8.05 (8.03)	33.01 (33.27)	6	dia	10.67
7.	[$UO_2(L)(OAc)(H_2O)$]]	Reddish-brown	>280	29.81 (29.42)	3.10 (2.75)	4.15 (4.29)	36.17 (36.48)	6	dia	6.87

S.No.	Compound	Colour	M.P. (°C)	Elemental analysis(%) Found (calcd).				C.N.	μ_{eff} (B.M.)	Λm *
				C	H	N	M			
8.	$[CuL^1_2(H_2O)_2]$	Green gold	270	50.74 (50.98)	3.96 (4.24)	12.31 (12.52)	6.83 (7.10)	6	1.90	6.91
9.	$[NiL^1_2(H_2O)_2]$	Bottle green	280	51.01 (51.25)	3.92 (4.27)	12.37 (12.58)	6.33 (6.59)	6	3.22	8.50
10.	$[CoL^1_2(H_2O)_2]$	Black	260	51.07 (51.24)	4.09 (4.27)	12.29 (12.58)	6.20 (6.62)	6	5.10	9.81
11.	$[ZnL^1_2(H_2O)_2]$	Yellow gold	280	50.68 (50.87)	4.07 (4.23)	12.23 (12.49)	6.93 (7.29)	6	dia	11.32
12.	$[UO_2L^1_2]$	Rust brown	270	42.79 (42.81)	3.01 (3.19)	10.62 (10.51)	22.13 (22.34)	6	dia	10.20

L = *o*VSa, * (ohm^{-1} cm^2 $mole^{-1}$)

L_1H = *o*VSmrzH., * (ohm^{-1} cm^2 $mole^{-1}$)

RESULTS AND DISCUSSION

The Schiff base ligands *o*VSaH and *o*VSmrzH were prepared from *o*-vanillin and sulfadrugs, *viz*., sulfanilamide and sulfamerazine as follows :

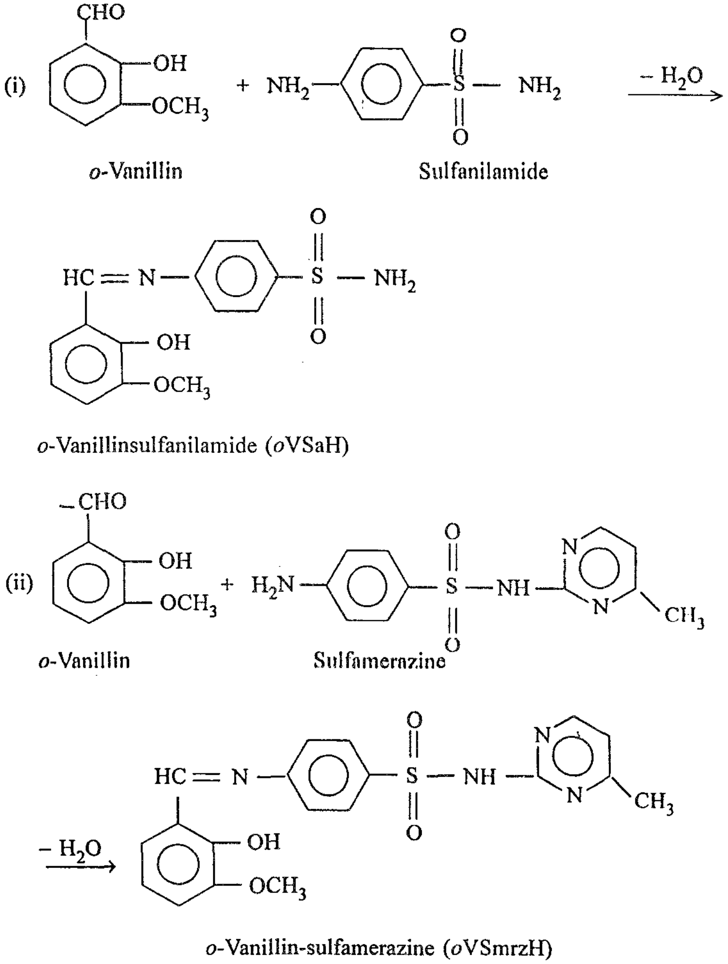


Fig. 1 Synthesis of Schiff base ligands *o*VSmrzH and *o*VSaH

The ^1H NMR spectra of the above two Schiff base ligands are given in Fig.2 and 3 along with indexing of various types of protons. The formation of Schiff base ligand is revealed by the appearance of –CH=N– proton signal at 8.99 and 8.96 pm in *o*VSaH and oVSmrzH, respectively.[10] This is further supported by the appearance of a band due to ν(C=N) (azomethine) at 1610 and 1615 cm^{-1} in *o*VSmrzH and *o*VSaH, respectively.[11] Both the ligands exhibits signals for aromatic protons, –OCH_3 group and phenolic –OH group at 6.0 - 8.3, 3.85 and 12.6 - 12.7 ppm, respectively.[12]

The metal complexes of oVSaH and oVSmrzH were prepared according to the following equations:

$$(1)\ M(CH_3COO)_2.nH_2O + 2LH \xrightarrow[\text{reflux}]{\text{Ethanol - DMF}} [M(L_2)] + 2CH_3COOH + nH_2O$$

where M = Cu(II), n = 1; Ni(II), n = 4; Co(II), n = 4; and Zn(II), n = 2, LH = *o*VSaH.

$$(2)\ Nd(NO_3)_3.6H_2O + LH \xrightarrow[\text{reflux}]{\text{Ethanol - DMF}} [Nd(L)(NO_3)_2(H_2O)_2] + HNO_3 + 4H_2O$$

$$(3)\ Th(NO_3)_4.4H_2O + LH \xrightarrow[\text{reflux}]{\text{Ethanol - DMF}} [Th(L)(NO_3)_3(H_2O)] + HNO_3 + 3H_2O$$

$$(4)\ UO_2(CH_3COO)_2.2H_2O + LH \xrightarrow[\text{reflux}]{\text{Ethanol - DMF}} [UO_2(CH_3COO)(H_2O)] + CH_3COOH + H_2O$$

$$(5)\ M(CH_3COO)_2.nH_2O + 2L^1H \xrightarrow[\text{reflux}]{\text{Ethanol - DMF}} [ML^1{}_2(H_2O_2)_2] + 2CH_3COOH + (n\text{-}2)H_2O$$

where M = Cu(II), n = 1; Ni(II), n = 4, CO(II), n = 4 and Zn(II), n = 2, L^1H = *o*VSmrzH.

$$(6)\ UO_2(CH_3COO)_2.2H_2O + 2L^1H \xrightarrow[\text{reflux}]{\text{Ethanol - DMF}} [UO_2L^1{}_2] + 2CH_3COOH + 2H_2O$$

Some physical properties such as % yields, colours, melting points, etc. of the synthesized complexes are given in table II. They are characterized by the following physicochemical studies.

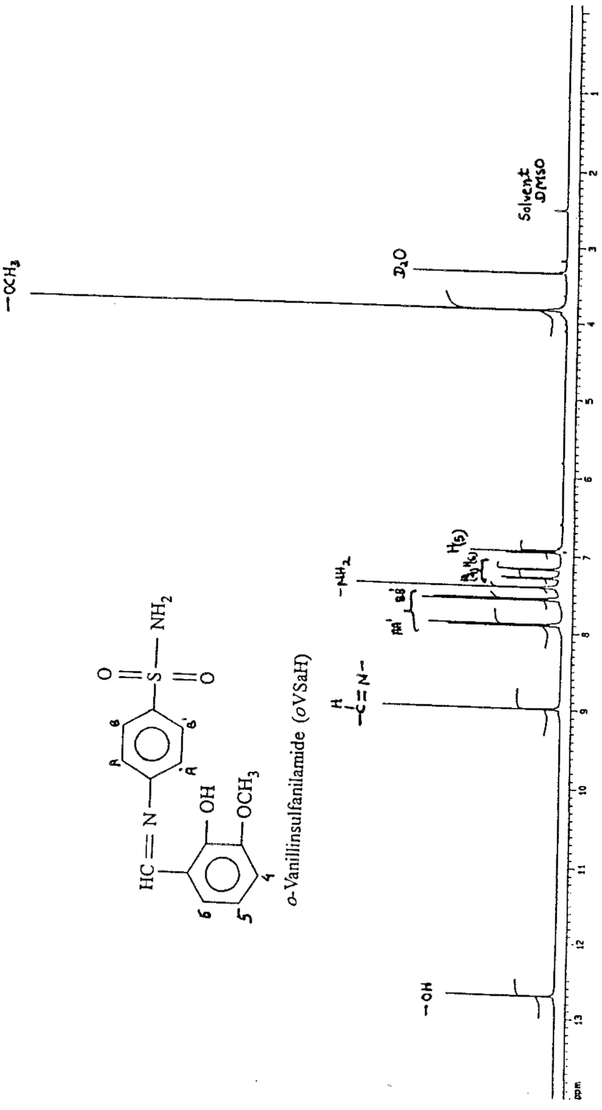


Fig 2 'H NMR spectrum of Schiff base *o*VSaH.

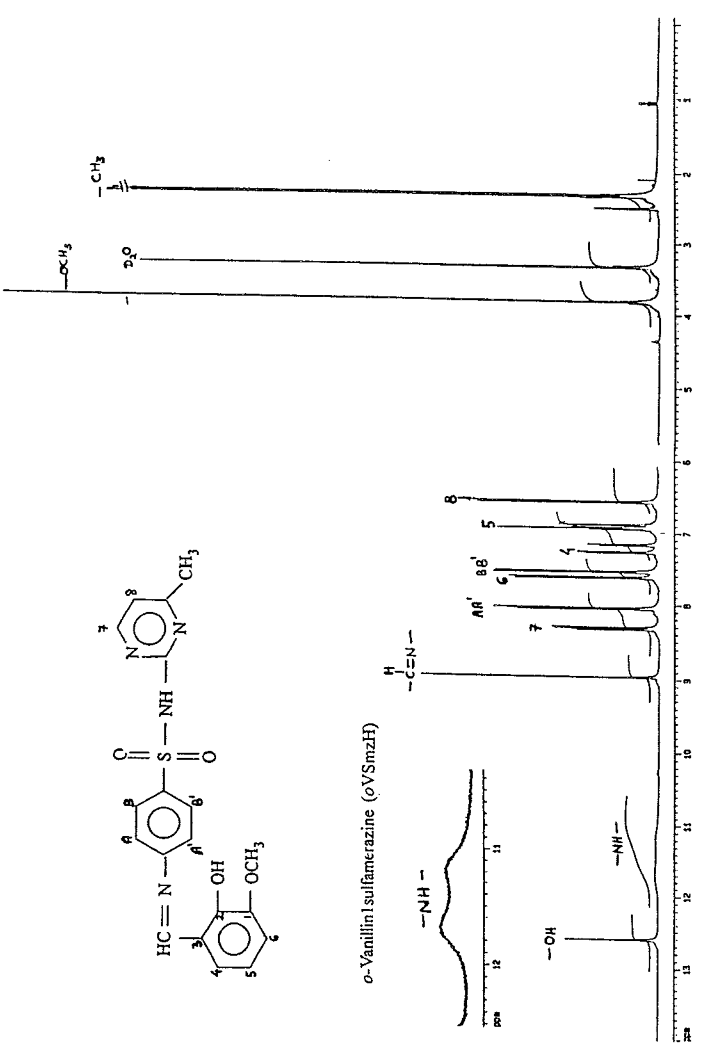


Fig 3 ¹H NMR spectrum of Schiff-base *o*VSmrzH.

Infrared Spectra.

The important IR Spectral bands of the ligands *o*VSaH, *o*VSmrzH and their metal complexes are given in Table III respectively.

The *o*VSaH(I) used in the present investigation contains four possible donor sites: (i) phenolic oxygen (ii) azomethine nitrogen (iii) Sulfonamide nitrogen and (iv) Sulfonamide oxygen.

On the other hand the ligand *o*VSmrzH (II) has five possible donor sites, four of which are the same as in oVSaH and the fifth donor site is the ring nitrogen.

The $\nu(C{=}N)$ azomethine band occurs at 1610 and 1615 cm^{-1} in the Schiff base ligands *o*VSaH and *o*VSmrzH, respectively. This band shifts to lower frequency by 10-25 cm^{-1} after complexation, indicating the coordination of azomethine nitrogen to metal ion.[13] Both the ligands exhibit a band for $\nu(OH)$ phenolic at 3380 - 85 cm^{-1}. The disappearance of this band in all the complexes suggests the coordination of phenolic oxygen after deprotonation.[14] This is further substantiated by the appearance of $\nu(C{-}O)$ phenolic at lower frequencies (compared to 1455 - 1470 cm^{-1} in the ligands) in the range 1440-1450 cm^{-1}, after complexation. The coordination of phenolic oxygen and azomethine nitrogen is further supported by the appearance of two non ligand bands at 520 - 560 and 400 - 490 cm^{-1} due to $\nu(M{-}O)$[15] and $\nu(M{-}N)$[16] respectively in all the complexes.

The $\nu(NH)$ bands due to sulfonamide group in the ligands *o*VSaH and *o*VSmrzH appear at 3320, 3230 and 3050 cm^{-1}, respectively.[17] These bands either show upward shift or no change in their position in the complexes indicating the reluctance of sulfonamide nitrogen towards coordination.

The bands at 1340 and 1160 cm^{-1} are assigned to $\nu_{as}(SO_2)$[18] and $\nu_{sy}(SO_2)$[19], respectively, in both the Schiff base ligands I and II. These bands also show no significant change in all the complexes, and therebyindicatingthe non - participation of sulfonamide oxygen in the bonding. The same conclusion is also derived by no significant change in $\nu(S{-}N)$ and $\nu(C{-}S)$ (appearing at 960 - 970 and 835 - 840 cm^{-1}, respectively) in ligands after complexation.[20]

A band at 1570 cm^{-1} in *o*VSmrzH ligand remains almost at the same position in its complexes and hence indicates that ring nitrogen[21] does not take part in coordination with the metal centre. In complexes 6, 7, 8, 9, 10 and 11, the coordination of the water molecule is indicated by the appearance of a broad band in the region 3550 - 3400 cm^{-1}. A band at 1605 - 1660 cm^{-1} in the complexes 4, 9, and 11 is assigned to $\delta(H_2O)$ for coordinated water.[22]

Table III. Important IR spectral bands (cm^{-1}) of *o*VSaH and its complexes.

S.No. Compound	ν(O–H) phenolic	$\nu(NH_2)$	ν(C=N) azomethine	ν(C-O) phenolic	$\nu_{as}(SO_2)$	$\nu_s(SO_2)$	ν(S–N)	ν(C–S)	ν(M–O)	ν(M–N)
I. *o*VSaH	3380	3320 3230	1615	1455	1340	1160	960	840	–	–
1. $[CuL_2]$	–	3320 3220	1600	1440	1340	1160	965	840	540	410
2. $[CoL_2]$	–	3360 3230	1590	1440	1345	1160	965	840	540	460
3. $[NiL_2]$	–	3345 3260	1600	1440	1340	1160	960	840	540	490
4. $[ZnL_2]$	–	3340 3250	1600	1440	1340	1160	965	845	540	490
5. $[Nd(L)(NO_3)_2(H_2O)_2]$	–	3345 3260	1600	1445	1345	1155	960	840	560	460
6. $[Th(L)(NO_3)_3(H_2O)]$	–	3340 3250	1600	1440	1345	1155	960	850	540	460
7. $[UO_2(L)(OAc)(H_2O)]$	–	3300 – 3200 (broad)	1600	1440	1345	1155	960	850	530	440

(continued)

Table III. Continued

S.No.	Compound	ν(OH) pnenolic	ν(NH)	ν(C=N) azomethine	ν(=N–) Ring	ν(C-O) phenolic	$\nu_{as}(SO_2)$	$\nu_s(SO_2)$	ν(S–N)	ν(C–S)	ν(M–O)	ν(M–N)
II.	*o*VSmrzH	3385	3050	1610	1570	1470	1340	1160	970	835	–	–
8.	$[CuL^1_2(H_2O)_2]$	–	3060	1585	1565	1440	1330	1150	970	830	530	400
9.	$[NuL^1_2(H_2O)_2]$	–	3060	1590	1570	1450	1330	1150	965	835	520	425
10.	$[CoL^1_2(H_2O)_2]$	–	3080	1580	1570	1440	1330	1145	975	830	525	410
11.	$[ZnL^1_2(H_2O)_2]$	–	3100	1590	1570	1440	1340	1150	970	830	540	420
12.	$[UO_2L^1_2]$	–	3100	1580	1565	1445	1340	1145	970	830	520	420

L = *o*VSa.

L^1 = *o*VSmrz.

In the complexes 6 and 7 three additional bands, which are not present in the spectra of free ligand(I), are observed. Of these a band at 1030 is assigned to ν_2 mode of NO_3 group. The bands in the region 1410 - 1440 and 1330 - 1360 cm^{-1} in the complexes are assigned as ν_4 and ν_1 modes, respectively, of the coordinated nitrato group. The magnitude of $\Delta\nu((\nu_4\text{-}\nu_1) = \sim 80\ cm^{-1}$ indicates the unidentate coordination of nitrate ion to the metal centre.[23]

In the uranium complex (7), two additional bands at 1630 and 1390 cm^{-1} are assigned to ν_{as}(COO) and νs(COO) modes, respectively. The magnitude of $\Delta\nu(240\ cm^{-1})$ suggests the unidentate coordination for acetato group.[24]

In the IR Spectra of the uranium complexes 7 and 12 two additional bands are present at 940, 950 and 840, 835 cm^{-1}, which are assigned to $\nu_{as}(UO_2)$ and $\nu_s(UO_2)$ modes, respectively. This observation indicates that the O=U=O moiety is virtually linear in these complexes.[25]

Conductance measurements

The observed molar conductance ($\Lambda m = 6.8 - 11.3\ ohm^{-1}\ cm^2\ mole^{-1}$) of all the metal complexes in 10^{-3} M DMSO solutions are given in Table II which suggest the non - electrolytic nature of these complexes.[26]

Magnetic suceptibility measurements.

The observed magnetic moments of Cu(II) complexes 1 and 8 are 2.01 and 1.90 B.M., respectively. These values suggest tetracoordinated[27] and hexacoordinated[28] stereochemistry for complexes 1 and 8 respectively. The nickel(II) complexes 3 and 9 of the present study display magnetic moment values 3.71 and 3.22 B.M., respectively. These data suggest a tetrahedral[29] geometry for the complex 3 and an octahedral[30] geometry for the complex 9.

The cobalt(II) complexes 2 and 10 of this investigation exhibits magnetic moments 4.31 and 5.10 B.M., respectively. These values are consistent with a tetrahedral[31] geometry for the former and an octahedral[32] geometry for the latter. The paramagnetic behaviour of this complex(5) is consistent with the presence of three unpaired electrons. The observed magnetic moment 3.66 B.M. of this complex is closed to that given by Van Vleck equation[33], indicating that the neodymium in the complex remains in the (+3) oxidation state and the 4f electrons are little influenced by the ligand. (Table II). Zink(II), Thorium(IV) and UO_2(VI) complexes are found to be diamagnetic as expected.

Electronic Spectra.

The drs spectra of few representative compounds were recorded in the range 260 - 800 nm. The compound 9 displays five absorption peaks at 270, 301, 339, 409 and 590 nm. The first three peaks are most probably due to ligand → Metal charge - transfer transitions. The last two peaks are due to d - d transitions and these are assigned as $^3A_2g(F)\rightarrow{}^3T_{1g}(P)$ and $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$ respectively. This suggests an Octahedral geometry[34-36] around Ni(II) ion. (Fig. 4) The drs spectra of the complex(3) shows three absorption bands at 37,593 (ε = 2.334 Lmole^{-1} cm^{-1}), 29,762 (ε =1.116) and 24,450 cm^{-1} (ε = 0.386). The first two bands which are of relatively high intencity are attributed to L→M charge transfer transitions. The third broad band is assigned to $^3T_1(P)\leftarrow{}^3T_1(F)$ transition. This is reasonably anticipated in a tetrahedral[18] complex of much lower field as compared with octahedral complex. The magnetic moment value also ruled out the possibility of octahedral complex. Cu(II)-*o*VSa complex displays four bands at 265 nm/37,735 cm^{-1}, 317 nm/31,545 cm^{-1}, 333 nm / 30,030 cm^{-1} and 409 nm/24,450 cm^{-1}. The first three bands of relatively high intensity are due to $\sigma\rightarrow\sigma^*$, $n\rightarrow\sigma^*$ and $\pi\rightarrow\pi^*$ intra ligand transitions, respectively of the ligand moiety.[12] The fourth broad band at 409 nm is indicative of a modified stereochemistry due to Jahn Teller distortions, as is mostly observed in all Cu(II) complexes. This result coupled with the magnetic moment value (vide supra) for this complex indicate tetracoordinated stereochemistry around the metal ion.[37] Co(II) - *o*VSmrz complex exhibits four absorption bands at 265, 333, 526 and 552 nm. The first two intense maxima are due to intraligand $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions respectively of the organic moiety. The other two transitions in the visible region at 526 and 552 nm may be assigned to $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ and $^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$ respectively, suggesting an octahedral[38] geometry for this complex.

Thermogravimetric analysis

TG. curves of four representative compounds were recorded in the temperature range 90 - 910°C in N_2 gas atmosphere, at a heating rate of 15°C/min.

The TGA - curve (Fig. 5) of the compund 8 does not show any weight loss upto 190°C. Thereafter, it starts losing weight and the first weight loss completes at 290°C, which is observed to be 4.0% against theoretical wt. loss of 4.02%. This wt. loss confirms the presence of two coordinated water moleculesin the complex.[39] Beyond 290°C a sudden wt. loss was observed which seems to be completed at 649°C (observed wt. loss = 92.0%) calcd wt. loss 92.5%). This weight loss corresponds to the elimination of two molecules of *o*VSmrz (ligand). Finally it attains a constant composition corresponding to CuO at 690°C. (theot. mass retained = 8.9% and observed 11.5%).

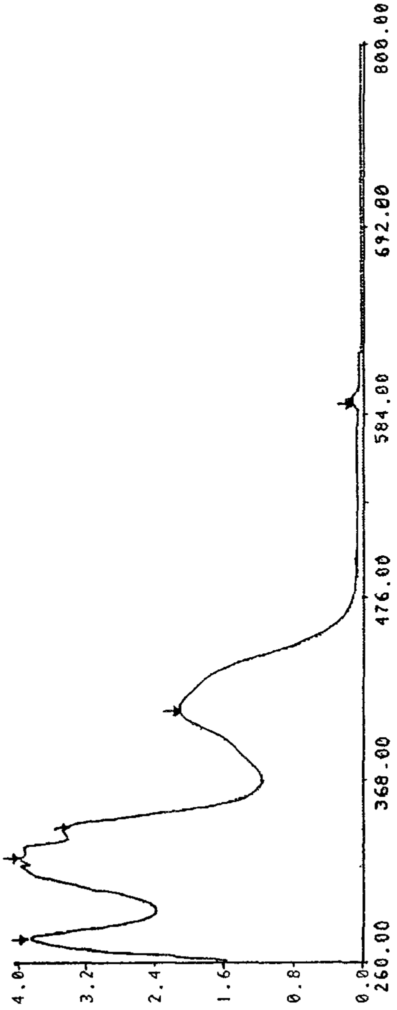


Fig 4 DRS spectrum of [Ni(*o*VSmrz)$_2$(H$_2$O)$_2$] complex.

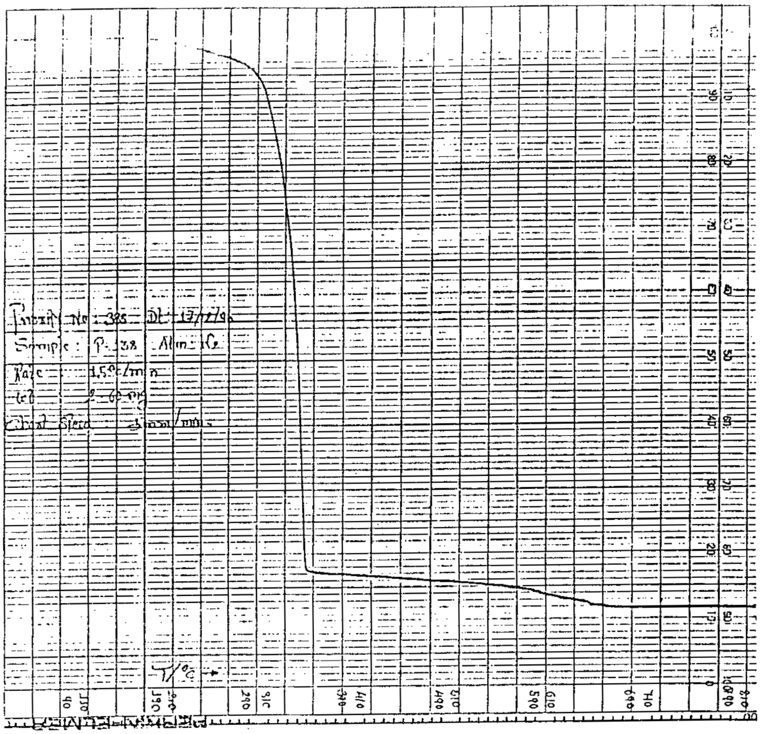


Fig 5 TGA curve of [Cu(*o*VSmrz)$_2$(H$_2$O)$_2$] complex.

The thermogram of the compound 11 shows a weight loss of 4.0% (theot. wt. loss 4.01%) at 150° C, which corresponds to two coordinated water molecules[39]. The second, third and fourth wt. losses were noticed in the temperature ranges 150 - 376°, 376-490° and 490 - 661° C respectively. However these wt. losses could not be correlated with the eliminated species from the complex. Thereafter it attains a constant composition corresponding to impure Zinc oxide. (Observed retained mass = 11.0%; theoretical retained mass = 9.07%).

The TG curve of the compound 5 shows a weight loss of 6.0% (theot. 5.9%) at 228° C. This is consistent with the elimination of two coordinated water molecules[39] from the complex. The second wt. loss (observed 26.0%, calcd 26.2%) shown by this compound at 405°C corresponds to the removal of two nitrate groups from the complex. The wt. loss continues beyond this temperature and finally attains a constant mass corresponding to Nd_2O_3. (observed 55.0%, calcd. 55.1%).

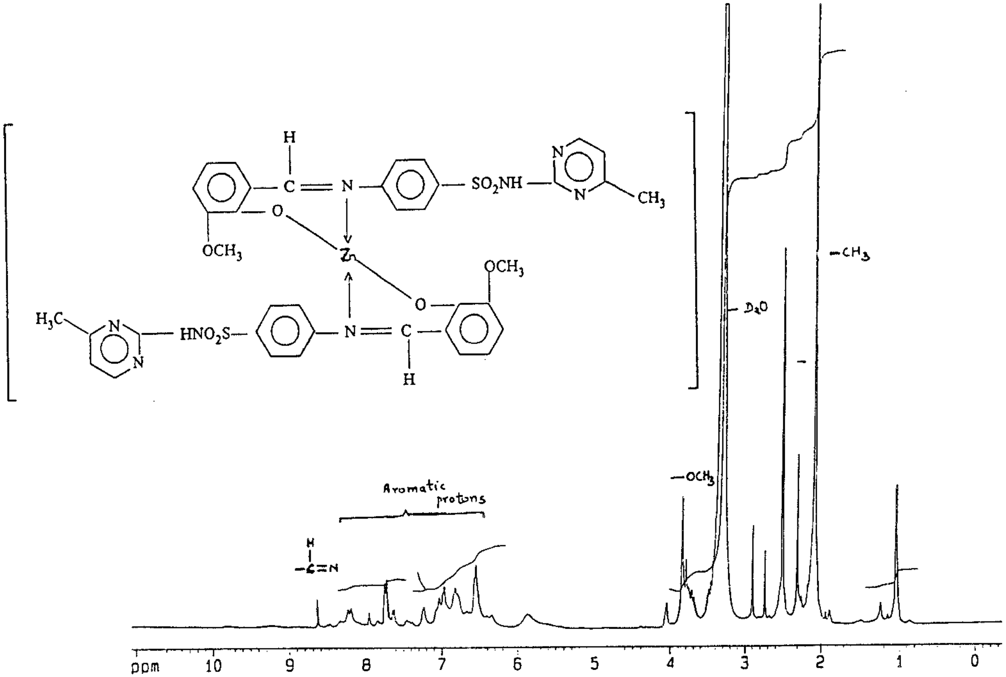


Fig 6. ^1H NMR spectrum of [Zn(*o*VSmrz)$_2$(H$_2$O)$_2$] complex.

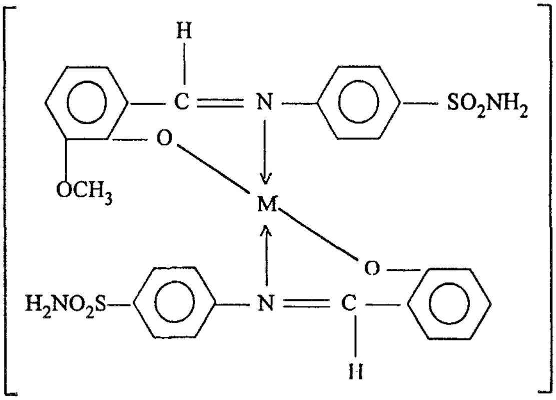


Fig. 7 Proposed tetrahedral structure of [M(*o*VSa)$_2$] complex.
[Where, M = Cu(II), Ni(II), Zn(II), Co(II)]

The thermogram of the complex 6 exhibit a weight loss of 3.5% (theot. wt. loss = 2.5%) at 117° C, which may be due to one coordinated water molecule.[40] This curve shows another wt. loss (observed 11%, calcd. 10.8%) at 190°C and this corresponds to the elimination of one nitrate group from the complex. The removal of a second nitrate group was observed at 291°C as the third wt. loss (observed = 19.0%, calcd = 19.15%). Beyond this temperature weight loss continues and it finally attains a constant mass at 900°C corresponding to ThO_2 (observed retained mass 35.0%, calcd = 35.0%).

^{1}H NMR Spectra

The ^{1}H NMR spectra of Zn - oVSmrz complex (11) (Fig.6) apparently gives following two informations, regarding complexation :

(i) The disappearance of phenolic (–OH) proton signal at 12.6 ppm, which confirms the coordination by phenolic oxygen to metal ion after deprotonation.[37] (ii) The azomethine proton (–CH=N–) signal shifts upfield (8.65 ppm against 8.96 ppm in the ligand) upon complexation. This also confirms the coordination by azomethine nitrogen.[12], which has already been shown by the IR spectral data.

CONCLUSION

From the satisfactory microanalytical, magnetic and various spectral data, it is concluded that ligand *o*VSaH and *o*VSmrzH act as monobasic bidentate manner and

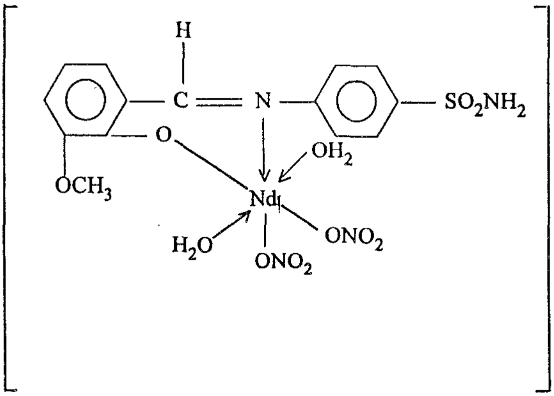


Fig. 8 Structure of $[\mathrm{Nd}(o\mathrm{VSa})(\mathrm{NO_3})_2(\mathrm{H_2O})_2]$ complex.

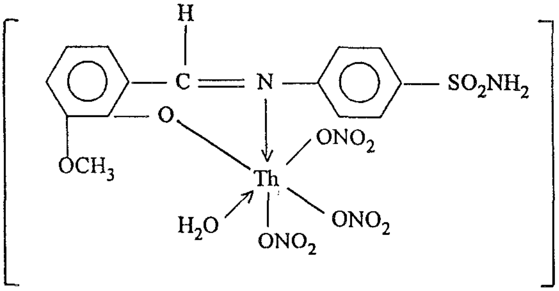


Fig. 9 Structure of $[\mathrm{Th}(o\mathrm{VSa})(\mathrm{NO_3})_3(\mathrm{H_2O})]$ complex.

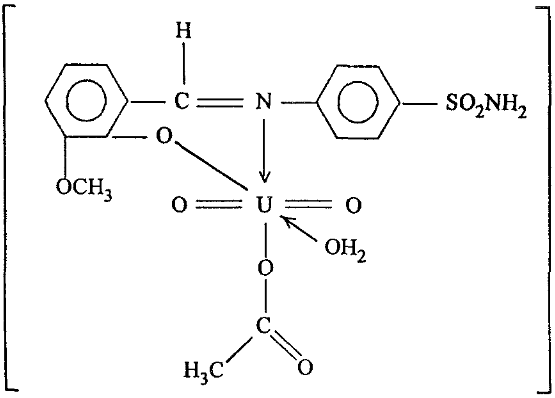


Fig. 10 Structure of $[\mathrm{UO_2}(o\mathrm{VSa})(\mathrm{OAc})(\mathrm{H_2O})]$ complex.

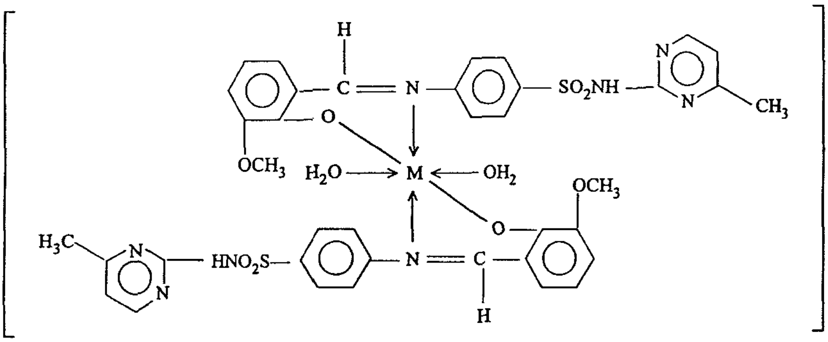


Fig. 11 Structure of $[M(oVSmrz)_2(H_2O)_2]$ complex.
[Where, M = Cu(II), Ni(II), Co(II) and Zn(II)].

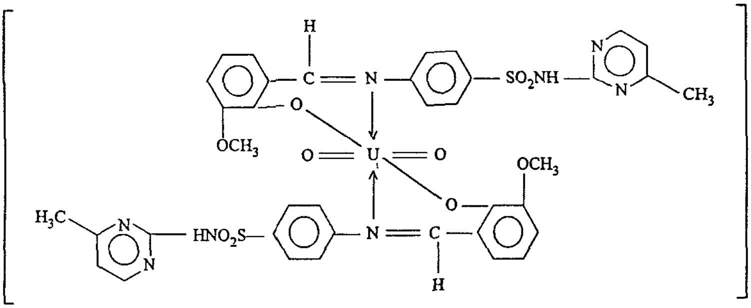


Fig. 12 Structure of $[UO_2(oVSmrz)_2]$ complex.

coordinate through their phenolic oxygen and azomethine nitrogen to yield four - and six - coordinate metal complexes. The proposed structures of the complexes are shown in Fig.7, 8, 9, 10, 11 and 12.

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