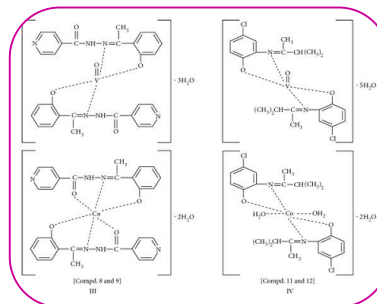




SYNTHESIS, STRUCTURAL AND BIOLOGICAL ACTIVITY STUDIES OF THEIR METAL COMPLEXES WITH SOME SCHIFF BASES

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ABSTRACT

Nicotinamide (*mna*)/2-amino-4-chlorophenol (*map*) and nicotinamide (*han* / isoniazide)-2-hydroxy acetophenone (*hair*) are newly bident or trident schiff bases with VO(IV) and Co(II) complexes formed by methyl Isobutyl Ketone condensation. In order to describe the composition of the complexes, physicochemical characterisation was carried out. The FAB weight and the thermal data display the complexes' degrading trend. XRD analysis indicates that the complexes under study crystallise as a crystal system tetragonal.

KEYWORDS: Biological Activity, Schiff Bases, Metal Complexes, Thermal Analysis, Oxovanadium (IV) Complexes, X-Ray Studies.

INTRODUCTION

V / O chemistry research is focused on its usefulness in many biological and industrial processes [1]. Since vanadium has been identified as a co-factor for vanadium-dependent haloperoxidases and vanadium nitrogenase [2], the co-ordinating chemistry of vanadium has acquired renewed interest. Recent development has stimulated their design and synthesis with the catalytic and medicinal properties of vanadium complexes. Vanadium complexes were further promoted by biochemical aspects to the coordination of vanadium chemistry [3]. Further examples of its biological significance are its incorporation into natural products and enzymes into a powerful phosphoryl transfer inhibitor. As an insulin mimetic and antiameobial agent, vanadium-containing compounds are useful. So far only slightly exploring the potentials of vanadium (V) complexes as antiameobial agents [4]. Vanadium can also be considered a representative of a new class of antitumor anti-platinum metal agents.

The schiff base and its complexes are used in various applications for clinical and analytical biological applications [5]. Recently, due to their possible pharmacological uses, significant interest has been shown in the chemical of hydrazine and hydrazone compounds [6]. Based on potential biomimetic applications, the remarkably biological activity of the R-CO-NH-NH₂, their respective CO-NH-N=CHR arylhydrazones and even their chelation modes with transit metal ions have been of interest in the past. Arylhydrazone coordination compounds acting as enzyme inhibitors have been documented to be useful for pharmacologic use [7]. This paper describes the synthesis, characterisation and biological activity of some Schiff base complexes of Oxovanadium (IV) and Cobalt (II), complexes of Schiff bases, namely, *mna*, *map*, *han*, and *hai*.

EXPERIMENT

1. Synthesis of Schiff Bases (Ligands) and Complexes

Schiff bases (*mna*, *han*, *hai*, *map*) have been synthesized by condensing the methanolic solution of methyl isobutyl ketone (0.08 mol) to the methanolic solution of nicotinamide/2-amino-4-chlorophenol (0.08 mol) and The methanolic solution for nicotinamide / isoniazide (0.08 mol) is 2-hydroxy acetophenone (0.08 mol) in an equimolar relationship. The condensation product was filtered, ethanol and ether washed,

ethanol recrystallized and the anhydrous CaCl_2 was dried under reduced pressure. TLC has controlled the purity of the compounds with silica gel G. Elemental and IR spectrums characterised Schiff bases.

Mixing the VO(II) and Co(II) methanol of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}/\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.08 mol) to the methanol solution of the Schiff bases (mna, han, hai, map) (0.016 mol) in 1:2 molar ratio, was the result of the development of VO(II) and Co(II) composites. In the water bath for 10–12 hours, the resulting mixture was refluxed. Due to the precipitation complexes, the oil ether washed with ethanol twice (60 to 80°C) and the CaCl_2 washed in an anhydrous desiccator under reduced pressure.

2. Characterization of the Complexes

Perkin Elmer RX-I spectrophotometer (Perkin RX-I) from Lucknow is an assessment of percent microanalysis % C, N, and H (on Heraeus elemental analyzer) and IR spectrum. Molar conductivity at room temperature and electronic (on Perkin Elmer Lambda-2B spectrophotometer) tests of absorption were made in Sagar. (on Elico-CM82 Conductivity Bridge) Chandigarh, Nagpur X-ray, FAB mass (on JEOL SX102/DA-6000 mass spectrometer/data system using argon/xenon (accelerating voltage 10 kV), from Lucknow was used as TGA (on Metler Toledo star e system). Spectrophotometer Varian E112 (TCNA (= 2 . 0 0 2 7) as the standard) from Mumbai have registered X-band EPR spectra at room temperature.

RESULTS AND DISCUSSION

Table 1 offers analytical and physical data on the metal complexes. The stoichiometry to be 1:2 metal: ligand (Schiff base) is suggested by an elemental study of complexes. For the complexes of Co(II) and VO(II) (mna) molar conductance values in methanol (10^{-3} M) are 124.5 and 53.8 $\text{S cm}^2 \text{mol}^{-1}$ which display the unicomplex electrolytic characteristics of those complexes. The observed Co(II) and VO(II)(han), (hai) and (map) compounds conductivity values fell within 6 . 5 - 2 0 . 1 $\text{S cm}^2 \text{mol}^{-1}$ showing the complex's nonelectrolytic nature.

Table 1: Ligand and metal complex analytical and physical data.

Compound number	Compounds/Molecular Formulae		Elemental analysis % found/(Cal.)					
	Molecular wt/colour	Dec.temp./ M.Pt. (°C)	C %	H %	N %	Yield %	μ_{eff} B.M	Cond. $\text{S cm}^2 \text{mol}^{-1}$
(1)	$\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}$ (mna)	120–125	69.5	7.1	14.5	62.0	—	—
	(Pinkish Cream)		(69.4)	(7.3)	(14.7)			
(2)	$[\text{VO}(\text{mna})_2]\text{SO}_4 \cdot 2\text{H}_2\text{O}$	230–239	45.9	4.5	12.7	70.7	1.76	53.8
	(Dark Green)		(45.6)	(4.8)	(9.6)			
(3)	$[\text{Co}(\text{mna})_2(\text{H}_2\text{O})_2]\text{Cl}_2$	>300	48.0	5.2	12.7	54.5	5.07	124.5
	(Purple)		(48.3)	(5.1)	(10.2)			
(4)	$\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$ (han)	123	70.1	5.2	11.9	91.2	—	—
	(Cream)		(70.0)	(5.0)	(11.6)			
(5)	$[\text{VO}(\text{han})_2]\text{H}_2\text{O}$	205–207	59.5	3.5	14.3	85.9	1.78	20.1
	(Dark Green)		(59.4)	(3.8)	(9.9)			

(6)	[Co(han) ₂] (Purple)	276–278	62.4 (62.3)	4.1 (4.0)	14.3 (10.3)	55.3	5.12	16.9
(7)	C ₁₄ H ₁₃ N ₃ O ₂ (hai) (Cream)	240	65.6 (65.8)	5.2 (5.0)	16.3 (16.4)	86.4	—	—
(8)	[VO(hai) ₂]3H ₂ O (Dark Brown)	120–125	53.4 (53.2)	3.5 (3.8)	13.1 (13.3)	54.2	1.79	7.1
(9)	[Co(hai) ₂]2H ₂ O (Light Brown)	>300	55.7 (55.5)	3.7 (3.9)	13.1 (13.8)	73.4	5.10	13.3
(10)	C ₁₁ H ₁₄ NOCl (map) (Light Coffee)	140	62.8 (62.5)	6.5 (6.6)	6.4 (6.6)	44.4	—	—
(11)	[VO(map) ₂]5H ₂ O (Black)	>300	45.0 (45.5)	4.1 (4.4)	5.0 (4.8)	88.3	1.76	6.5
(12)	[Co(map) ₂ (H ₂ O) ₂] 2H ₂ O (Black)	>300	47.3 (47.6)	4.8 (4.6)	5.0 (5.0)	60.8	5.08	18.8

Table 2: Spectral electronic data and metal complex ligand field parameters [8–11].

Compound number	Complexes	Transitions	Bands (cm ⁻¹)	Parameters 10Dq, B, β, β%, ν ₁ /ν ₂ , LFSE, λ	Geometry of the complexes
(2)	VO(II)(mna)	² B ₂ - ² E (ν ₁) ² B ₂ - ² B ₁ (ν ₂) ² B ₂ - ² A ₁ (ν ₃)	12722 19567 —	—	Square pyramidal/trigonal bipyramidal
(3)	Co(II) (mna)	⁴ T _{1g} (F)- ⁴ A _{2g} (F) (ν ₂) ⁴ T _{1g} (F)- ⁴ T _{1g} (P) (ν ₃)	12484 19607	6935, 1029, 0.91, 8.12, 2.2, 66.2, -525	Octahedral
(5)	VO(II) (han)	² B ₂ - ² E (ν ₁) ² B ₂ - ² B ₁ (ν ₂) ² B ₂ - ² A ₁ (ν ₃)	12500 22311 —	—	Square pyramidal/trigonal bipyramidal
(6)	Co(II) (han)	⁴ T _{1g} (F)- ⁴ A _{2g} (F) (ν ₂) ⁴ T _{1g} (F)- ⁴ T _{1g} (P) (ν ₃)	12363 19168	6868, 1003, 0.89, 10.4, 2.2, 65.6, -542	Octahedral
(8)	VO(II) (hai)	² B ₂ - ² E (ν ₁) ² B ₂ - ² B ₁ (ν ₂) ² B ₂ - ² A ₁ (ν ₃)	13000 — 24271	—	Square pyramidal/Trigonal bipyramidal
(9)	Co(II) (hai)	⁴ T _{1g} (F)- ⁴ A _{2g} (F) (ν ₂) ⁴ T _{1g} (F)- ⁴ T _{1g} (P) (ν ₃)	16531 20584	9183, 1004, 0.89, 10.3, 2.2, 87.7, -714	Octahedral
(11)	VO(II) (map)	² B ₂ - ² E (ν ₁) ² B ₂ - ² B ₁ (ν ₂) ² B ₂ - ² A ₁ (ν ₃)	13200 — 24218	—	Square pyramidal/Trigonal bipyramidal
(12)	Co(II) (map)	⁴ T _{1g} (F)- ⁴ A _{2g} (F) (ν ₂) ⁴ T _{1g} (F)- ⁴ T _{1g} (P) (ν ₃)	16894 19912	9385, 951, 0.84, 15.0, 2.2, 89.7, -717	Octahedral

Thermal Analysis

1. Thermal Decomposition of $[\text{VO}(\text{mna})_2] \text{SO}_4 \cdot 2\text{H}_2\text{O}$ [2]

The complex's TG curve suggests that the complex begins to decay at 60°C. Elimination of water grinding molecules on the temperature rise up to 130°C was observed (Re. wt%, obs./cal., 95/93.7). A gradual (but slow) loss of weight over this temperature continues to 450°C, which is similar to Schiff base decomposition and sulphate movement of metal chelate [12]. The thermal curve was observed nearly horizontally after 450°C. A combination of metal oxide and ashes in nitrogen atmosphere is the remaining weight (obs./cal. 29/24.6) as the final pyrolysis product.

FAB Mass Spectra

The FAB mass spectrum of $[\text{Co}(\text{han})_2]$ [6] displays a molecular ion limit (M^+) at m/z 545 indicating monomeric complex. A sequence of tops in m/z 513, 460, 391, 338, 276, 107, corresponding to different fragments [2, 13], is also showing the spectrum of the complex. Its density gives an indication of the fragments' richness and stability. The following molecular formula can be suggested for this complex on the basis of the above spectral studies (see Table 1 [6]).

The FAB mass spectrum of $[\text{VO}(\text{map})_2] \cdot 5\text{H}_2\text{O}$ [14] shows a molecular ion peak (M^+) at m/z 579, That indicates the complex's monomeric and confirms the formula proposed [14]. The maximum strength was significantly high, with the fragmentation pattern showing m/z values 560, 519, 503, 487, 276, and 107. The value of m/z is 560 corresponds to $[\text{VO}(\text{map})_2] \cdot 4\text{H}_2\text{O}$, 519 to $[\text{VO}(\text{map})_2]2\text{H}_2\text{O}$, 503 to $[\text{VO}(\text{map})_2] \cdot \text{H}_2\text{O}$, 487 to $[\text{VO}(\text{map})_2]$, 276 to $[\text{VO}(\text{map})]$. VO with chelated O and N as a ligand moiety corresponds to the value 107. [2, 11, 13].

ESR Spectra of the Oxovanadium (IV) Complexes

The X-band EPR oxovanadium spectra (IV) (d^1 , ^{51}V , $I = 7/2$) Complexes are not solved to show all eight-hyperfine lines at room temperature. The values calculated g_{\parallel} , g_{\perp} , g_{av} , and Δg Table 3 points out these two complexes. Here, $g_{av} = 1/3 [2g_{\perp} + g_{\parallel}]$. Typical for the spectra shown in the orbit of mainly d_{xy} character are the values shown in the trigonalbipyramidal or pyramidal complexes VO(II). A two-g spectrum anisotropic EPR is expected to demonstrate ($z = g_{\parallel} < g_{\perp} = g_x = g_y$) [2, 11, 20, 24, 25].

Table 3: Oxovanadium complex ESR parameters (IV).

Compound number	Complexes	g_{\parallel}	g_{\perp}	g_{av}	Δg
(2)	$[\text{VO}(\text{mna})_2] \text{SO}_4 \cdot 2\text{H}_2\text{O}$	1.9032	1.9664	1.9453	0.0632
(8)	$[\text{VO}(\text{hai})_2] \cdot 3\text{H}_2\text{O}$	1.9429	1.9724	1.9625	0.0295

X-Ray Studies

X-ray diffractogram powder $[\text{Co}(\text{hai})_2] \cdot 2\text{H}_2\text{O}$ [13] and $[\text{VO}(\text{map})_2] \cdot 5\text{H}_2\text{O}$ [14] The $\text{CuK}\alpha$ source is reported at $5.50\text{--}80^\circ$ (2θ) with differentiate. In order to find the best match between observed and measured $\sin^2 2\theta$ values [2], X-ray crystal system has been developed by test and error methods. Parameters of crystal for $[\text{Co}(\text{hai})_2] \cdot 2\text{H}_2\text{O}$ [13] Complex is like $a = b = 17.2238 \text{ \AA}$, $c = 30.4478 \text{ \AA}$, $V = 9032.62 \text{ \AA}^3$, $Z = 9$, $D_{obs} = 1.000 \text{ g/cm}^3$, $D_{cal} = 1.030 \text{ g/cm}^3$, particle size = 21.87 nm, and crystal parameters for $[\text{VO}(\text{map})_2] \cdot 5\text{H}_2\text{O}$ [14] complex are as $a = b = 11.2836 \text{ \AA}$, $c = 34.4447 \text{ \AA}$, $V = 4385.86 \text{ \AA}^3$, $Z = 7$, $D_{obs} = 1.5367 \text{ g/cm}^3$, $D_{cal} = 1.6951 \text{ g/cm}^3$, particle size = 12.01 nm. This represents the crystallisation of these complexes in a tetragonal system.

Biological Activity:

Tables 4 and 5 include the results of the *in vitro* biological [26] screening.

Table 4. Schiff bases and their metal complexes are anti-bacterial screening data. Standard = Gentamycin.

Compound number	Diameter of inhibition zone (mm) (concentrate in ppm)								
	<i>E.coli</i>			<i>S. aureus</i>			<i>S. fecalis</i>		
	25	50	100	25	50	100	25	50	100
7(S.B)	12	12	16	—	10	20	—	—	—
8(Complex)	27	31	34	11	12	13	13	13	15
10(S.B)	12	13	15	12	12	14	12	—	13
11(Complex)	12	13	16	11	12	15	15	14	15
Standard	20	23	20	10	10	12	18	20	19
DMSO	—	—	—	—	—	—	—	—	—

(—) = not measurable.

Table 5. Schiff bases and their metal complexes have antifungal screening data.

Compound number	Diameter of inhibition zone (mm) (concentrate in ppm)					
	<i>A. niger</i>			<i>T. polysporum</i>		
	25	50	100	25	50	100
7(S.B)	13	13	15	—	15	19
8(Complex)	—	—	—	11	15	17
10(S.B)	—	—	—	10	19	19
11(Complex)	—	—	—	12	13	20
Standard	—	—	—	—	—	—
DMSO	—	—	—	—	—	—

(—) = not measurable.

These observations indicate that most compounds are more active than the Schiff base. Schiff bases and their complexes, in some cases, have similar bacteria and fungi activity. Biochemical ability of bioactive

organic species can be enhanced or suppressed by chelation. In the normal cell membrane, the increased activity of the metal complexes may be due to the influence of metal ions. Metal chelates together have polar and non-polar properties, making them ideal for cell and tissue permeation. The improvements in hydrophilicity and lipophilicity are likely to result in lowering the solubility and permeability of cells, which in turn increase chemotherapeutic bioavailability on the one hand and other potential [27].

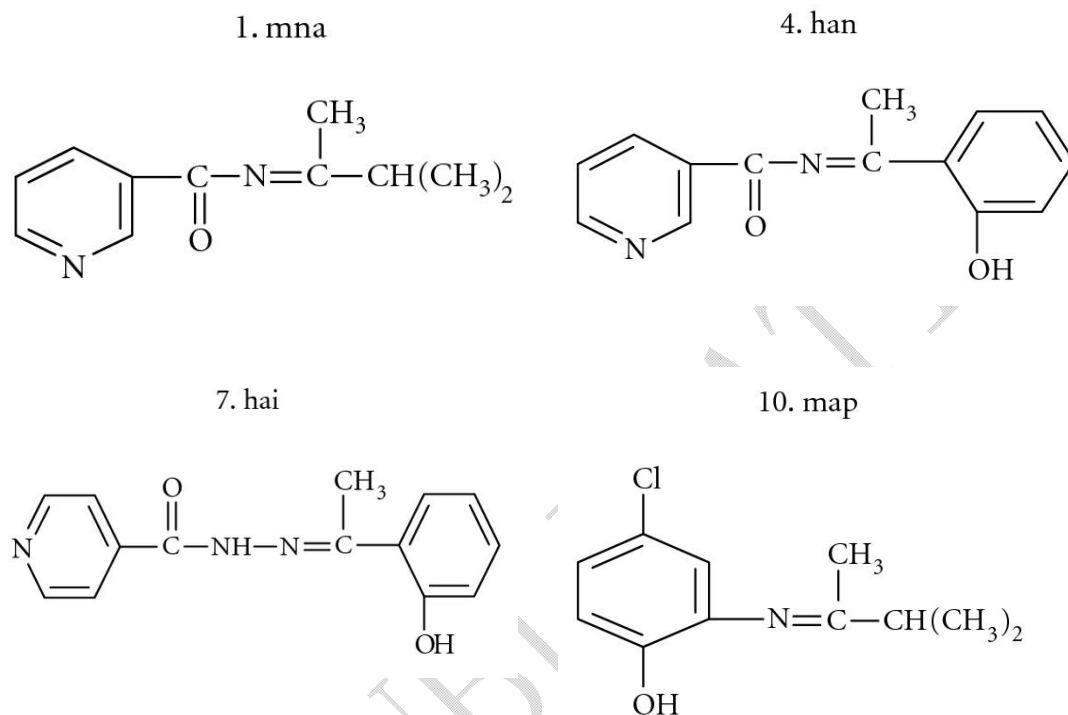
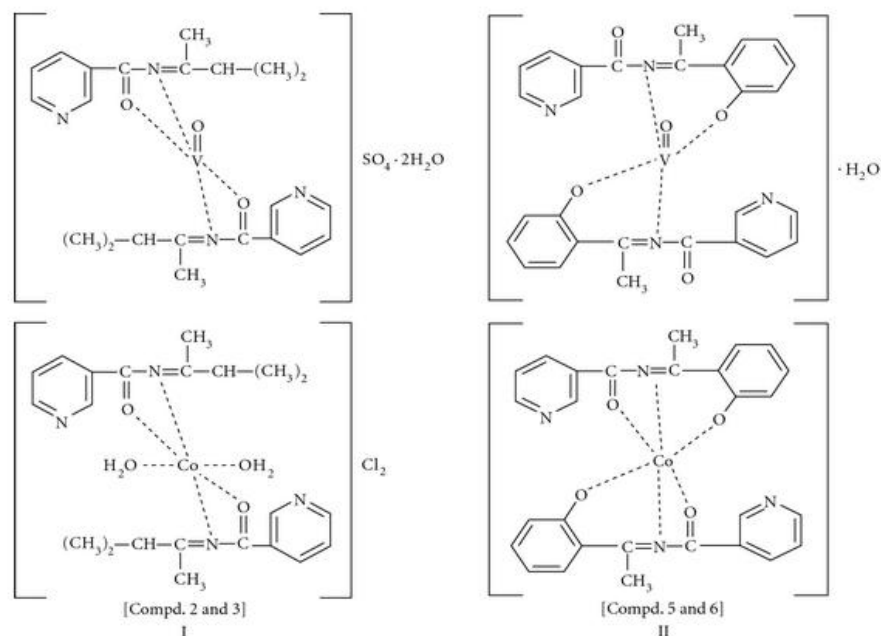
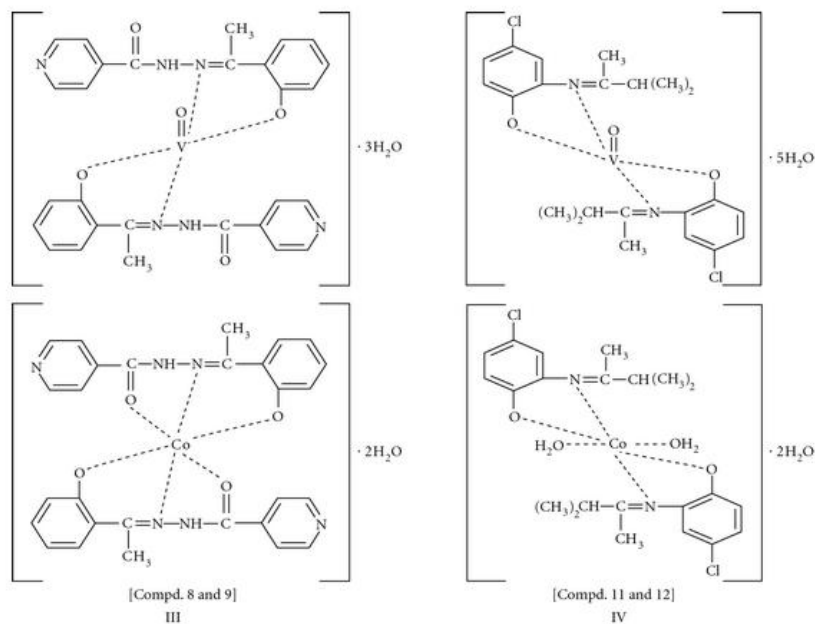


Figure 1 :Schiff Base structures (Ligands).



(a) I schiff base complexes (mna) of (I) oxovanadium (IV), and cobalt(II). (II) Schiff-base complexes of oxovanadium(IV) and cobalt(II)



(b) (III) schiff base complexes (hai) of oxovanadium(IV) and cobalt(II). (IV) Schiff base complexes (map) of oxovanadium(IV) and cobalt(II)

Figure 2: The metal complexes proposed structures.

CONCLUSION:

The well diffusion technique using DMSO as a solvent on various pathogenic bacteria / fungi species has tested such complexes for their antimicrobial activities *E. coli*, *S. aureus*, *S. fecalis*, *A. niger*, *T. polysporum*, They discussed and discussed their antimicrobial ability. All the complexes have been found to be antimicrobially active and to be more active than the free ligand. The antimicrobial / bioactive behaviour of organic ligands is influenced by metal chelation.

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