Research Article

Characterization of Complexes Synthesized Using Schiff Base Ligands and Their Screening for Toxicity Two Fungal and One Bacterial Species on Rice Pathogens

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Coordination complexes with metal ions Cu(II), Ni(II), Co(II), Fe(III), Mn(II), Cr(III), and VO(II) with six ligands formed by condensation products using azides and aldehydes or ketones are characterized. Both the ligands and the complexes synthesized are characterized by C, H, N, Cl and metal analyses, IR, UV-Vis, TGA, and magnetic susceptibility for tentative structure proposal. Several of them are screened for their toxicity (i.e., physiological activity) against fungal species *Rhizoctonia solani* and *Acrocyndrium oryzae* and a bacterium, *Xanthomonas oryzae* on rice pathogens. The study shows that the observed physiological activity is enhanced for the metal complexes as compared to the simple metal salts or ligands, except in the case of L3 or HAEP ligand, where the free -OH and -NH₂ groups on the ligand seemed to have inhibited the activity. It is also observed that the order of activity has a dependence on the increased atomic weight of the metal ion in use. In some cases, especially the VO(II) complexes, they are found to be better than the standards in use, both for the fungicides and for the bactericide.

1. Introduction

Ever since the Italian chemist, Hugo Schiff used imines to make several “metallo-imines”, numbers of variants of the condensation products of imines and aldehydes or ketones such as $RCH=NR'$ —where R & R' are alkyl and/or aryl substituent's, are popularized. They are also known as Schiff bases (SBs), anils, imines or azomethines. They are also known as anils, imines, or azomethines. These have several applications in organic studies, such as for building new heterocyclic systems, for identification, detection, and determination of aldehydes and ketones, for purification of carbonyl or amino compounds, or for the protection of these groups during the complex formation or such sensitive reactions [1]. They have other side applications in various other fields, coordination chemistry [2–9], analytical chemistry [10–16], pigments and dyes [17], and polymer industries [18], in vitamins and enzymes [4] for model biomolecules. There is a special

mention of these complexes in agriculture [4] as fungicides, pesticides, and bacteriocides.

Survey of the literature for SB metal complexes and their applications showed excellent review articles [19, 20] for the detailed understanding of this class of compounds in all respects and one more especially dedicated to copper complexes [21]. They provide several details on number of metal complexes derived from SBs used widely for applications in food and dye industry, analytical chemistry, catalysis, polymers, antifertility, agrochemical, anti-inflammatory activity, antiradical activities, and biological systems as enzymatic agents. Several have reviewed them in light of their antimicrobial, antibacterial, antifungal, antitumor, and cytotoxic activities [19, 20]. There are some individual articles too not mentioned in them with studies on the above mentioned types of activities with some metals ions such as Cu(II), Ni(II), and Co(II) with SB derived from salicylaldehyde and 2-substituted aniline [22];

Cu(II), Ni(II), and Zn(II) complexes with SB from p-chlorobenzaldehyde with p-chloroaniline [23]; Mn(II), Fe(II), Ni(II), and Cu(II) complexes with SB from 5-acetamido-1,3,4-thiodiazole-2-sulphonamide and their biological activity [24]; Zn(II), Ni(II), and Cu(II) complexes with SB from dicinnamoylmethane and aromatic amines [25]; Zn(II), Mn(II), Ni(II), and Cu(II) complexes with SB from 2-hydroxy-1-naphthaldehyde and 5-amino-1-naphthol and their antibacterial activities [26]; Co(II), Ni(II), and Cu(II) complexes with SB from 1,4-dicarbonylphenyldihydrazide with 2,6-diformyl-4-methylphenol [27]; Co(II), Ni(II), and Cu(II) complexes with SB from 2-H/Cl/Br-6-(4-fluorophenyliminomethyl)phenol [28]; Co(II), Ni(II), and Cu(II) complexes with SB from pyrazolealdehyde with 2-aminophenol [29]; Co(II), Ni(II), Zn(II), Cd(II), Hg(II), and Cu(II) complexes with SB from benzofuran-2-carbohydrazide and 4-methyl-thio-benzaldehyde and their antifungal, antibacterial activities being screened [30]; Ni(II) and Cu(II) complexes of SB derived from 1-naphthylamine and 2-hydroxy-naphthalene-1-carbaldehyde [31]; Fe(III), Ni(II), Cu(II), Co(II), Zn(II), and UO₂(II) complexes of SB derived from 2-furancarboxaldehyde and o-phenylenediamine [32]; VO(II), Co(II), Rh(III), Pd(II), and Au(III) complexes of SB derived from 4-nitrobenzoic acid and thiosemicarbazide and their antibacterial activity [33]; VO(IV), Cu(II), and Ru(II) complexes of SB derived from 3-hydroxyquinoxaline-2-carboxaldehyde and several amines 1,8-diaminonaphthalene, 2,3-diamine maleonitrile, 1,2-diaminocyclohexane, 2-iminophenol, and 4-aminoantipyrine [34]; Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes of SB derived from 1, 10-phenanthroline and o-vanillidene-2-aminobenzothiazole and o-vanillidene-2-quinone-N-(2-pyridyl)-benzenesulfonamide [35]; Hg(II), Zn(II), and VO(IV) complexes of SB from S-aminosulfonyl-4-chloro-N-2,6-dimethylphenyl-2-hydroxybenzamide with salicylamide [36]; Co(II), Cu(II), Ni(II), and Zn(II) complexes of SB derived from several substituted pyridines with salicylaldehyde [37]. Recently new series of Co(II), Ni(II), Cu(II), Cd(II), and Hg(II) complexes were synthesized by the condensation of naphthofuran-2-carbohydrazide and diacetylmonoxime. The ligand along with its metal complexes has been characterized on the basis of analytical data, IR, electronic, mass, ¹HNMR, ESR spectral data, thermal studies, magnetic susceptibility, and molar conductance measurements. In order to evaluate the effect of metal ions upon chelation, both the ligand and its metal complexes were screened for their antibacterial and antifungal activities by minimum inhibitory concentration (MIC) method [38]. Metal chelates, [M(HL)₂(H₂O)₂]₂X₂ (where M = Mn(II), Co(II), Cu(II), Ni(II), or Zn(II), X = NO₃⁻ or Cl⁻, and HL = SB moiety), have been prepared and characterized by elemental analysis, magnetic and spectroscopic measurements (infrared, X-ray powder diffraction, and scanning electron microscopy). The SB and its metal chelates have been screened for their in vitro antibacterial activity against four bacteria, gram-positive (*Staphylococcus aureus*) and gram-negative (*Escherichia coli*), and two strains of fungus (*Aspergillus flavus* and *Candida albicans*). The metal chelates were shown to

possess more antibacterial activity than the free SB chelate [39].

Metal complexes of SBs derived from 2-furancarboxaldehyde and o-phenylenediamine (L1), and 2-thiophenecarboxaldehyde and 2-aminothiophenol (HL2) are reported and characterized based on elemental analyses, IR ¹H NMR, solid reflectance, magnetic moment, molar conductance, and thermal analysis (TGA). Consider M = Fe(III), Ni(II), Cu(II), Co(II), Zn(II), and UO₂(II). The synthesized ligands, in comparison to their metal complexes, were also screened for their antibacterial activity against bacterial species, *Escherichia coli*, *Pseudomonas aeruginosa*, and *Staphylococcus Pyogenes*, as well as fungi (Candida). The activity data show the metal complexes to be more potent antibacterials than the parent SB ligand against one or more bacterial species [32].

Synthesis and characterisation of new transition metal complexes of SBs derived from 3-hydroxyquinoxaline-2-carboxaldehyde and application of some of these complexes as hydrogenation and oxidation catalysts. The subnormal magnetic moment values substantiate a binuclear structure for all the Cu(II) complexes favouring square-planar geometry and those with magnetic moment of 1.76 BM favoured octahedral geometry with mononuclear complex formation with this SB ligand [34].

It is found that the SBs selected for synthesis for this study have not been found in the literature. It is also noticed that many of the tridentate ligands are found to show striking biochemical characters where the azomethine linkage are blended into stable structured inorganic metal chelates. In a delicately balanced living system, physiological activity is a result of several chemical and physical processes. In such processes, the metal complexes furnished useful drugs and other substances as described by selective toxicity in pharmacology [40–42]. They function by upsetting this delicate balance in two ways: (a) by reinforcing the toxicity of a heavy metal and/or (b) by withdrawing the essential metal content from the system. For example, in highly basic iron rich soils, the metal ion, not available to the rootlets of plants, is extracted by spraying Ethylenediaminetetraacetic acid—(edta) in the form of a soluble complex. Such a mechanism for many fungicides and bactericides is described as a partition effect or cooperative effect [43]. Thus, to evaluate the chemical substances as fungicides and bactericides, the following methods are used commonly: (1) slide germination method [44–46], (2) test-tube dilution method [47], (3) cell-volume assay method [48], (4) inhibition-zone or modified paper disc method [49–51], and (5) poisoned food technique [50].

Three important rice pathogens were selected for the present study: two fungal species and a bacterium. The reasons for selecting these species are given in brief. (1) *Rhizoctonia solani* causes sheath blight [52, 53] which is a serious disease of the rice-crop. The symptoms are (a) grayish white patches and (b) yellowing of leaves. This spreads very quickly and causes enormous loss. It also causes several other diseases on many economically important commercial crops. (2) *Acrocyldrium oryzae* causes sheath rot of paddy decaying the sheath and was first reported [54–56] in India. A large number of fungicides are evaluated against this organism, in vitro and in vivo. A few of them are in use to

arrest the disease yet it is quite uncontrolled. (3) *Xanthomonas oryzae* causes bacterial-leaf-blight and is usually noticed [54–56] in the field at the heading stage. The young seedlings, after transplanting, are affected when the upper leaves are rolled along the mid-rib to wither away. Subsequently, the disease extends to the whole field giving a burnt appearance. Applications of heavy doses of nitrogenous fertilizers are said to be the cause of this disease.

In this paper we report the synthesis of new SBs and their metal complexes. They were characterized by C, H, N, Cl and metal analyses, Infra-red (IR), UV-Visible (UV-Vis), thermogravimetric analysis (TGA) for estimating coordinated water, and magnetic susceptibility measurements. By using the appropriate techniques or methods, these were screened for their toxicity against the chosen fungal and bacterial organisms. The results are summarized in the light of their observed physiological activity and a scope for future development.

2. Materials and Methods

2.1. Solvents and Reagents. Solvents were purified and distilled as per standard procedures [57]. Benzoic acid hydrazide or benzohydrazide [58, 59], 2-hydroxybenzohydrazide or salicylhydrazide [60, 61], and 1-(2,4-dihydroxyphenyl)ethanone or resacetophenone [62] were prepared as per reported procedures. Hydrazine carbothioamide or thiosemicarbazide was recrystallized from water. The sodium salt of dehydroacetic acid or 3-acetyl-2-hydroxy-6-methyl-4H-pyran-4-one [63] was used as a white solid after treating with dil HCl.

2.2. SBs Ligands Synthesized Are the Following (Scheme 1)

- (1) BHFH or Ligand 1 (L1) = N'-{[furan-2-yl] methyl-ene)-2-hydroxybenzohydrazide was obtained by condensing salicylhydrazide or 2-hydroxybenzohydrazide and furfuraldehyde or furan-2-carbaldehyde.
- (2) BHEH or Ligand 2 (L2) = 2-hydroxy-N'-(1-(2,4-dihydroxyphenyl)ethylidene) benzohydrazide) was obtained from salicylhydrazide or 2-hydroxybenzohydrazide and resacetophenone or 1-(2,4-dihydroxyphenyl)ethanone.
- (3) HAEP or Ligand 3 (L3) = 1-(1-(2, 4-dihydroxyphenyl) ethylidene thiosemicarbazide was obtained from hydrazinecarbothioamide or thiosemicarbazide and resacetophenone or 1-(2, 4-dihydroxy phenyl)ethanone.
- (4) BFH or Ligand 4 (L4) = N'-((furan-2-yl) methyl-ene)benzohydrazide was obtained from benzohydrazide and furfuraldehyde or furan-2-carbaldehyde.
- (5) BHDH or Ligand 5 (L5) = 2-hydroxyl-N'-(1-(2-hydroxy-6-methyl-4-oxo-4H-pyran-3-yl)ethylidene) benzohydrazide was obtained from salicylhydrazide or 2-hydroxybenzohydrazide and dehydroacetic acid or 3-acetyl-2-hydroxy-6-methyl-4H-pyran-4-one.
- (6) DHA or Ligand 6 (L6) = 3-acetyl-2-hydroxy-6-methyl-4H-pyran-4-one or dehydroacetic acid was used as it is.

2.3. Physical Measurements. C, H, and N analyses were done on Perkin-Elmer 240C analyzer. IR spectra were recorded on Perkin-Elmer grating spectrophotometer 577, near IR-Vis-UV spectra were recorded on DMR-21 in absorbance range of 300–2000 nm. Magnetic susceptibilities were determined at RT on Faraday's balance. The metal and chloride were estimated by gravimetry [64]. The TGA were analyzed in static air, using limiting temperature of 500°C and heating rate of 10°C/min.

2.4. Preparation of the Complexes. All the complexes were prepared by a very similar procedure: to the metal chloride (except VO(II) being a sulfate) in methanol, respective ligand dissolved in methanol is added slowly while stirring. This mixture was either refluxed for 30 min to 3 hrs or digested for 1-2 h for different complexes [52]. Some complexes were obtained at pH 5.5 and some around 8.5 depending on the basicity of the ligand in use. Quantitative precipitates were collected, washed, and dried.

The relevant physical data such as C, H, N, Cl, melting points or decomposition temperatures, colour, and metal analyses are compiled for each ligand and its complexes in Tables 1, 2, 3, 4, 5, and 6. For easy comparison and prediction of the complex formation with clarity on the denticity of the ligand, interpretation of the IR data of each ligand and its complexes are presented separately in Tables 7–12 with all the relevant explanation and references. The analysis of the magnetic susceptibility measurements, the bands obtained using the UV-Vis spectra, their transitions, the predicted geometries, and the interpreted molecular structures are discussed separately, for convenience, in Tables 13–19 for each metal ion forming complex with different ligands.

2.5. Physiological Activity. For the fungal species liquid broth method [52] was followed: peeled and cooked potato (350 g) was collected into which dextrose (35 g) was dissolved and made up to 1750 mL by distilled water (PDA medium). pH was adjusted to 7.0 by adding drops of NaOH solution. It was distributed as 100 mL each into seventeen 250 mL conical flasks containing 2 g of agar-agar and 100 mg metal complex for the organism *Rhizoctonia solani*. For the *Acrocyndrium oryzae*, it was distributed as 25 mL each into 70 (150 mL) conical flasks containing 25 mg of the metal complex (1000 ppm).

All the flasks were tightly plugged with cotton and paper. They were all sterilized in the autoclave at 15 lbs pressure and 121°C for 20 min. The sterilized molten PDA medium from each flask, with the metal complex suspended uniformly, was poured into five petri dishes (90 mm diameter and 20 mL each) and all the replicates were numbered and labeled immediately. All these specimens were inoculated and incubated along with a standard fungicide, Dithane M-45, for comparison. Control flasks without chemical were also inoculated and incubated simultaneously.

In the case of the bacterium well-zone or inhibition-zone technique [49, 51] was adopted. To hot 1L distilled water, Hayward's medium [49–52] was added while stirring. The solution was made up to 2 L and pH adjusted to 7.0 by adding drops of NaOH solution. It was distributed equally

SCHEME 1

TABLE 1: Elemental composition and physical data of BHFH ligand and its complexes.

S. number	Complex	Mpt °C	Colour	C	H	N	M	Cl	Mol Wt gm	Remarks
				Observed	(calculated)	%				
1	BHFH-L1 (C ₁₂ H ₈ N ₂ O ₃)	210	White	63.00 (63.18)	4.50 (4.38)	12.56 (12.27)	—	—	228.13	Loss of 2H
2	[Cu(BHFH)] ₂ -pH 5.5-7.0 Cu ₂ C ₂₄ H ₁₆ N ₄ O ₆	308	Grey	50.02 (50.10)	2.90 (2.78)	10.00 (9.73)	20.95 (22.09)	—	575.35	Loss of 8H
3	[Cu(BHFH)(H ₂ O)]-pH 8.5 CuC ₁₂ H ₁₀ N ₂ O ₄	280	Green	47.20 (47.44)	3.45 (3.29)	9.50 (9.22)	20.00 (20.94)	—	303.55	Loss of 8H
4	[Ni(BHFH)(H ₂ O)]-pH 5.5-7.0 NiC ₁₂ H ₁₀ N ₂ O ₄	265	Red	50.00 (50.25)	3.50 (3.49)	9.20 (9.76)	20.00 (20.47)	—	286.83	Loss of H ₂ O
5	[Ni(BHFH)] ₂ -pH 8.5 NiC ₂₄ H ₁₆ N ₄ O ₆	280	Green	56.00 (56.17)	4.00 (3.90)	11.00 (10.92)	11.50 (11.45)	—	512.70	Loss of 6H
6	[Co(BHFH)(H ₂ O)Cl] ₂ Co ₂ C ₂₄ H ₂₀ N ₄ O ₈ Cl ₂	260	Pink	42.55 (42.70)	3.30 (3.26)	8.51 (8.29)	17.50 (17.46)	10.50 (10.52)	675.12	Loss of 8H
7	[Fe(BHFH)Cl] ₂ Fe ₂ C ₂₄ H ₁₆ N ₄ O ₈ Cl ₄	320	Red	40.50 (40.58)	2.80 (2.82)	7.92 (7.89)	16.00 (15.74)	20.00 (20.01)	709.70	Loss of 4H
8	[Mn(BHFH)(H ₂ O)Cl] ₂ Mn ₂ C ₂₄ H ₂₀ N ₄ O ₈ Cl ₂	280	Yellow	44.50 (44.65)	2.98 (3.10)	8.12 (8.68)	17.00 (16.90)	10.00 (11.01)	645.00	Loss of 1.5H ₂ O
9	[VO(BHFH)Cl] ₂ V ₂ C ₂₄ H ₁₆ N ₄ O ₈ Cl ₂	285	Grey	44.00 (44.14)	3.00 (3.06)	8.50 (8.57)	15.00 (15.60)	10.74 (10.87)	653.14	Loss of 8H

TABLE 2: Elemental composition and physical data of BHEH ligand and its complexes.

S. number	Complex	Mpt °C	Colour	C	H	N	M	Cl	Mol Wt gm	Remarks
				Observed	(calculated)	%				
1	BHEH-L2 (C ₁₅ H ₁₃ N ₂ O ₄)	215	Yellow	63.00 (63.18)	5.00 (4.91)	9.89 (9.82)	—	—	285.16	Loss of H
2	[Cu(BHEH)Cl] CuC ₁₅ H ₁₃ N ₂ O ₄ Cl	305	Green	47.05 (47.36)	3.50 (3.42)	7.50 (7.37)	16.00 (16.72)	9.50 (9.35)	380.10	Loss of 4H
3	[Ni(BHEH)] ₂ NiC ₃₀ H ₂₆ N ₄ O ₈	270	Red	57.00 (57.26)	4.20 (4.14)	8.77 (8.91)	9.50 (9.34)	—	628.70	Loss of 2H
4	[Co(BHEH)] ₂ CoC ₃₀ H ₂₈ N ₄ O ₈	260	Brown	57.50 (57.61)	4.35 (4.48)	9.01 (8.96)	10.00 (9.43)	—	630.93	—
5	[Fe(BHEH)(H ₂ O)Cl] ₂ Fe ₂ C ₃₀ H ₃₀ N ₄ O ₁₀ Cl ₂	305	Black	45.55 (45.64)	4.35 (3.80)	7.23 (7.10)	14.52 (14.16)	9.50 (9.00)	788.70	Loss of 2H
6	[Mn(BHEH)] ₂ MnC ₃₀ H ₂₆ N ₄ O ₈	285	Brown	58.00 (58.02)	3.93 (3.87)	9.00 (9.02)	10.00 (8.78)	—	620.50	Loss of 4H
7	[VO(BHEH)Cl] ₂ V ₂ C ₃₀ H ₂₆ N ₄ O ₁₀ Cl ₂	300	Grey	44.20 (44.28)	3.29 (3.34)	7.25 (7.38)	12.86 (13.43)	9.20 (9.46)	758.88	Loss of 2C and 2H

TABLE 3: Elemental composition and physical data of HAEP ligand and its complexes.

S. number	Complex	Mpt °C	Colour	C	H	N	M	Cl	Mol Wt gm	Remarks
				Observed	(calculated)	%				
1	HAEP-L3 (C ₉ H ₁₁ N ₂ O ₂ S)	193	Brown	52.00 (52.18)	5.40 (5.31)	13.30 (13.52)	—	—	207.16	Loss of NH ₂ and 2H
2	[Cu(HAEP)] ₂ Cu ₂ C ₁₈ H ₁₈ N ₆ O ₄ S ₂	310	Brown	40.00 (40.21)	3.50 (3.35)	15.50 (15.64)	24.00 (23.6)	—	537.22	Loss of 2NH ₂ and 2OH
3	[Ni(HAEP)] ₂ Ni ₂ C ₁₈ H ₁₈ N ₆ O ₄ S ₂	305	Brown	39.00 (39.31)	3.50 (3.28)	15.30 (15.29)	21.00 (21.36)	—	549.52	Loss of NH ₂
4	[Co(HAEP)(H ₂ O)] ₂ Co ₂ C ₁₈ H ₂₆ N ₄ O ₈ S ₂	295	Brown	35.70 (35.89)	4.30 (4.32)	9.30 (9.30)	20.00 (19.58)	—	601.86	Loss of NH ₂ and 4H
5	[Fe(HAEP)(H ₂ O)Cl] ₂ Fe ₂ C ₁₆ H ₂₂ N ₄ O ₆ Cl ₂ S ₂	300	Green	30.50 (30.88)	3.51 (3.54)	8.91 (9.01)	18.00 (17.97)	11.00 (11.42)	621.70	Loss of 2N, 2C; add 0.5H ₂ O
6	[Cr(HAEP)(H ₂ O)Cl] ₂ Cr ₂ C ₁₈ H ₂₂ N ₄ O ₆ Cl ₂ S ₂	265	Green	35.00 (35.23)	4.21 (3.59)	9.00 (9.13)	15.50 (16.96)	10.25 (11.58)	613.12	Loss of NH ₂
7	[VO(HAEP)(H ₂ O)] ₂ VC ₉ H ₁₃ N ₂ O ₅ S	310	Grey	34.50 (34.62)	3.20 (4.17)	8.99 (8.97)	15.74 (16.33)	—	312.00	Loss of NH ₂

TABLE 4: Elemental composition and physical data of BFH ligand and its complexes.

S. number	Complex	MPt °C	Colour	C	H	N	M	Cl	Mol Wt gm	Remarks
1	BFH-L4 (C ₁₂ H ₁₀ N ₂ O ₂)	182	Yellow	67.50 (67.63)	5.00 (4.69)	13.00 (13.14)	—	—	213.13	Loss of H
2	[Cr(BFH)(H ₂ O)Cl ₂] ₂ Cr ₂ C ₂₄ H ₂₀ N ₄ O ₆ Cl ₄ pH 5.5–7.0	270	Brown	42.00 (42.42)	3.25 (2.95)	8.10 (8.25)	13.50 (15.32)	19.52 (20.91)	679.00	Loss of 1.5H ₂ O
3	[Cr(BFH) ₂ (H ₂ O)]Cl ₂ CrC ₂₄ H ₂₀ N ₄ O ₅ Cl pH 8.5	310	Red	55.00 (55.38)	3.50 (3.85)	10.50 (10.77)	10.00 (10.00)	12.52 (13.65)	520.00	Loss of 2.5H ₂ O
4	[VO(BFH) ₂ (H ₂ O)] VC ₂₄ H ₁₈ N ₄ O ₆	300	Red	58.50 (58.42)	4.00 (4.06)	10.90 (11.36)	10.00 (10.33)	—	492.94	Loss of H ₂ O

TABLE 5: Elemental composition and physical data of BHDH ligand and its complexes.

S. number	Complex	MPt °C	Colour	C	H	N	M	Cl	Mo. Wt gm	Remarks
1	BHDH-L5 (C ₁₅ H ₁₄ N ₂ O ₅)	240	Yellow	60.00 (60.02)	5.00 (4.66)	9.40 (9.33)	—	—	300.16	Loss of 2H
2	[Cr(BHDH)Cl] ₂ Cr ₂ C ₃₀ H ₂₄ N ₄ O ₁₀ Cl ₂	300	Green	47.00 (47.06)	3.00 (3.14)	7.52 (7.32)	10.00 (13.59)	9.25 (9.28)	765.00	Loss of 2H
3	[VO(BHDH)(H ₂ O)] VC ₁₅ H ₁₄ N ₂ O ₇	305	Green	40.55 (40.63)	3.90 (3.91)	7.30 (7.29)	13.12 (13.27)	—	383.94	Loss of 2H, 2C; add H ₂ O, 4H

as 200 mL into 10 (500 mL) conical flasks containing 2 g of agar-agar each. All were inoculated and incubated. A set of plates with a standard bactericide, 2-bromo-2-nitro-1, 3-propanediol (Bronidiol), for comparison and another set of control plates with distilled water were kept for evaluation of results. All the data are consolidated in Table 20.

3. Results and Discussion

Five new ligands were synthesized by mixing the appropriate amine and the aldehyde condensation via a Schiff base reaction (Scheme 1). All of the SBs, thus formed, are crystalline powders white or pale-yellow in colour and are stable to air and moisture. They are found to be soluble in most of the polar solvents like ethanol, methanol, acetone, and so forth and also in bases. All of them were characterized by elemental analyses, melting points (Tables 1–6), and IR spectra (Tables 7–12). The elemental analyses of the ligands show that there is a loss of a few molecules during the CHN analyses, probably due to the low melting points of the synthesized ligands and the details are given in the remarks column of the Tables 1–6, while the IR spectra show all the expected structural peaks. From the IR data in Table 7, it was analyzed that L1 acts as a tridentate ligand by coordinating through –O of the deprotonated phenolic group, –O of another deprotonated –OH group formed due to enolization, and –N of the azomethine group. Table 8 shows that the L2 acts as a tridentate ligand similar to L1 and the –OH groups of the resacetophenone moiety do not participate in coordination. Table 9 gives the data for L3 which enolizes and acts as a tridentate ligand coordinating through the –O of the deprotonated phenolic group, –S of the –SH group after

deprotonation, and –N of the azomethine group. Thus it is found to remain in the “thione” form and not in the “thiol” form [65, 66] in the solid state. Table 10 gives details on L4 acting as a bidentate ligand with –O and –N donors. Table 11 shows the details of L5 acting as a tetradentate bound through three –O’s and one –N and L6, not a Schiff base but used directly for complexation, binds through carbonyl –O atom and –O of phenolic group as is shown in Table 12.

They were used to make complexes with Cu(II), Ni(II), Co(II), Fe(III), Mn(II), Cr(III), and VO(II) metal ions. Generally all the metal complexes were synthesized in alcoholic solutions at room temperature or by reflux at pH 5.5 or 8.5. These were characterized by the usual analytical and spectroscopic methods. All the complexes formed with the respective ligands have been shown to coordinate with the denticity mentioned above and the shift of the coordinating atoms is also shown in Tables 7–12, thus confirming the formation of stable metal chelates with the new Schiff bases and DHA, L6. The physical data, elemental analyses are also given in Tables 1–6 for all the complexes synthesized. These data for all the complexes also show a loss of a few molecules during the analysis of CHN, probably due to the lower decomposition temperature, while the IR spectra show all the expected structural peaks. Some of the complexes have one, two, or four coordinated water molecules which were analysed by TGA analyses. The variable temperature data of these complexes from room temperature to decomposition of the complex and the loss in weight of the material taken confirm the percentage of coordinated water which is present in the complex composition predicted.

The chemistry of ligands upon binding to different metal atoms leads to the formation of expected four and/or six coordinate complexes and the salient features are discussed

TABLE 6: Elemental composition and physical data of DHA ligand and its complexes.

S. number	Complex	MPt °C	Colour	C Observed (calculated) %	H Observed (calculated) %	M	Mol Wt gm	Remarks
1	DHA-L6 $C_8H_8O_4$	109	Colorless	57.00 (57.17)	5.00 (4.76)	—	168.08	—
2	$[Cr(DHA)_3]$ $CrC_{24}H_{24}O_{12}$	285	Green	55.00 (55.41)	4.25 (4.61)	10.00 (10.00)	520.26	Loss of two H_2O
3	$[VO(DHA)_2(H_2O)]$ $VC_{16}H_{18}O_{10}$	305	Green	45.50 (45.61)	—	11.75 (12.10)	420.94	—

FIGURE 1: Electronic (MULL) spectra of OXOVANADIUM(N) complexes of (a) BHFH-[Vo(BHFH)(Cl)]₂; (b) BHEH-[Vo(BHDH)(Cl)]₂; (c) DHA-[Vo(DHA)₂(H₂O)]. FIGURE 2: Electronic (MULL) spectra of OXOVANADIUM(II) complexes of (a) BHDH-[Vo(BHDH)(H₂O)]; (b) HAEP-[Vo(HAEP)(H₂O)₂]; (c) BFH-[Vo(BFH)₂(H₂O)].

below based on the collected electronic and magnetic data. The data are presented in Tables 13–19 and Figures 1–8 for different metal ions.

3.1. VO(II) Complexes. All the OXOVANADIUM complexes are highly coloured, fine amorphous powders. They are stable to air, moisture and insoluble in water and other common organic polar and nonpolar solvents. They all decompose above 300°C (except complex of L1 at 285°C). V complex with L4 showed loss of weight starting at 52°C (0.0006 gm) and decomposed at 300°C (0.0090 gm), complex with L3 at 50°C (0.0004 gm) and decomposed at 310°C (0.0088 gm), complex with L5 at 50°C (0.0008 gm) and decomposed at 305°C (0.0096 gm), and complex with L6 at 50°C (0.0009 gm) and decomposed at 305°C (0.0099 gm) in the thermal analysis, thus confirming one or two molecules of water coordination in the complexes as per the composition predicted.

All the VO(II) complexes are paramagnetic as shown in Table 13; Figures 1 and 2. The values of L6, L3, and L5 based complexes are in agreement with the expected spin-only value of 1.73 BM at RT. However, the complexes with L1 and L2 have shown lower values 1.5–1.6 BM may be due to low symmetry expected at 1.73 BM when the orbital angular contribution is almost quenched [67] and may occur due to

the presence of exchange coupled antiferromagnetism [68]. Several reports indicate such behavior [69–71]. Hence, they are assigned binuclear structures.

Electronic spectra show three bands below 30,000 cm⁻¹ at RT in diffuse reflectance mull data as given in Table 13 corresponding to octahedral symmetry (Oh) with tetragonal distortion. The bands, transitions, molecular structure, and the predicted geometry are given in Table 13. A few complexes may also show a vibrational structure with a spacing of 700 cm⁻¹ at the 2B₂ → 2E transition band, corresponding to the V=O stretching frequency in the excited state, which is not clearly observed.

3.2. Cr(III) Complexes. All the Cr(III) complexes are coloured solids and they are stable to air and moisture. They are insoluble in water and in most of the common organic solvents like methanol, ethanol, benzene, acetone, and so forth. Hence, conductivity could not be measured due to the insolubility. Cr complex with L4 at lower pH showed loss of weight starting at 110°C (0.0005 gm) and decomposed at 270°C (0.0091 gm), complex with L4 at higher pH at 52°C (0.0005 gm) and decomposed at 310°C (0.0091 gm), and complex with L3 at 52°C (0.0005 gm) and decomposed at 265°C (0.0091 gm) in the thermal analysis. Thus, confirming

TABLE 7: Characteristic IR data for the L1-BHFFH (tridentate -O, -O, and -N) and its participation in complex formation with metal ions.

S. number	Complex	Coord water ^e	IR cm ⁻¹ (s = sharp; b = broad; d = doublet; w = weak; vw = very weak) vO-H and vN-H ^e	vC=O ^e	vC=N ^e	vC=O phenolic ^e	M-O, M-N, or M-Cl ^e
1	BHFFH-L1 ^{c,d,e}	—	3260 ^a	1640 (s)	1610 (s)	1220 (s) ^b	—
2	[Cu(BHFFH)] ₂	—	Absent	Absent	1590 (d)	1250 (s)	490, 475, 430
3	[Cu(BHFFH)(H ₂ O)]	3420–3220 (b)	Absent	Absent	1590 (s)	1190	830 (s), 485, 430, 410
4	[Ni(BHFFH)(H ₂ O)]	3500–3400 (b)	Absent	Absent	1620 (s), 1590 (s)	1255 (s)	830 (s), 580, 560
5	[Ni(BHFFH)] ₂	—	3210 (s)	Absent	1610 (d)	1250 (s)	450, 370
6	[Co(BHFFH)(H ₂ O)Cl] ₂	3500–3400 (b)	3210 (s)	Absent	1615 (s) 1580 (s)	1255 (s)	870 (s), 550, 440, 360
7	[Fe(BHFFH)Cl] ₂	—	3220 (s)	Absent	1615 (s), 1585 (s)	1250 (s)	550, 440, 360
8	[Mn(BHFFH)(H ₂ O)Cl] ₂	3500–3400 (b)	3220 (s)	Absent	1610 (s), 1575 (s)	1245 (s)	845–835 (d), 440, 390, 350
9	[VO(BHFFH)Cl] ₂	—	3175 (s)	Absent	1610 (s), 1585 (s)	1250 (s)	970 (V=O) ^f , 550, 420, 370

^aOverlap of hydrogen bonded O-H and N-H; ^bStretching frequency; ^cNo change in vN=N at 1075 cm⁻¹, Shyamal and Kale [88]; ^dNo change in symmetric and asymmetric frequencies of furfural ring vC-O-C at 1020 (s); 895 (s) cm⁻¹ indicates noninvolvement of O of furfural ring in complexation; ^eThe enolization of the hydrazide residue and the subsequent deprotonation of both the hydroxyl groups or cleavage of hydrogen bond forming M-O bonds confirmed by vC-O phenolic shift, doublet for two vC=N groups (one azomethine participating in complex formation and one formed due to enolization of ligand), absence of vC=O, and new bands for vN-H, vC=N, M-O, and M-N vibrations; Nakamoto [91], Ueno and Martell [92, 93]; ^fSelbin [94].

TABLE 8: Characteristic IR data for the L2-BHEH (tridentate -O, -O, and -N) and its participation in complex formation with metal ions.

S. number	Complex	IR cm^{-1} (s = sharp; b = broad; d = doublet; w = weak; vw = very weak)						
		Coord water	$\nu\text{O-H}^c$	$\nu\text{N-H}^c$	$\nu\text{C=O}^d$	$\nu\text{C=N}^d$	$\nu\text{C=O phenolic}^e$	M-O or M-N or M-Cl ^f
1	BHEH-L2 ^g	—	3330 (b) ^a	3260 (b) ^b	1650 (s)	1610 (s)	1240 (s)	—
2	[Cu(BHEH)Cl]	—	3460 (b)	3340 (b)	1600 (s)	1585 (s)	1255 (s)	690, 510, 270
3	[Ni(BHEH) ₂]	—	3600 (b)	3340 (b)	1620 (s)	1600 (s)	1255 (s)	500, 380
4	[Co(BHEH) ₂]	—	3450 (b)	3280 (s)	1620 (s)	1600 (s)	1255 (s)	650–400
5	[Fe(BHEH)(H ₂ O)Cl] ₂	3500–3450 (b)	—	3340 (b)	1605 (s)	1580 (s)	1255 (s)	840 (s), 620, 580, 490
6	[Mn(BHEH) ₂]	—	3460 (b)	3280 (s)	1620 (d)	1600 (s)	1255 (s)	650–400
7	[VO(BHEH)Cl] ₂	—	3500 (w)	3260 (b)	1600 (s)	1590 (s)	1260 (s)	970 (V=O), 570, 520, 340

^aIntramolecular hydrogen bonding; ^bHydrogen bonding; ^cShift indicates cleavage of intramolecular H bonds after complex formation; ^dInvolvement of O of carbonyl group and N of azomethine group in complex formation, Watt and Dowes [95]; Truter and Rutherford [96]; Cotton and Wilkinson [97]; ^eDavison and Christie [98]; Kubo et al. [99]; indicates deprotonation of phenolic OH and binding to M; ^fNakamoto [91, 100] and Selbin [94]; ^gNo change in $\nu\text{N-N}$ at 1040 (w) cm^{-1} .

FIGURE 3: Electronic (MULL) spectra of CHROMIUM(III) complexes of (a) DHA-[Cr(DHA)₃]; (b) BFH-[Cr(BFH)₂(Cl)(H₂O)]; (c) HAEP-[Cr(HAEP)(Cl)(H₂O)₂]; (d) BHDH-[Cr(BHDH)(Cl)]₂. FIGURE 5: Electronic (MULL) spectra of IRON(III) complex of (a) BHFH-[Fe(BHFH)(Cl)₂]₂; (b) BHEH-[Fe(BHEH)(Cl)(H₂O)₂]; (c) HAEP-[Fe(HAEP)(Cl)(H₂O)₂]₂. FIGURE 4: Electronic (MULL) spectra of MANGANESE(II) complexes of (a) BHFH-[Mn(BHFH)(Cl)(H₂O)₂]; (b) BHEH-[Mn(BHEH)₂]. FIGURE 6: Electronic (MULL) spectra of COBALT(II) complexes of (a) BHFH [Co(BHFH)(Cl)(H₂O)₂]₂; (b) HAEP [Co(HAEP)(H₂O)₂]₂.

TABLE 9: Characteristic IR data for the L3-HAEP (tridentate -O, -N, and -S) and its participation in complex formation with metal ions.

S. number	Complex	Coord water	$\nu\text{O}-\text{H}^a$	IR cm^{-1} (s = sharp; b = broad; d = doublet; w = weak; vw = very weak)				$\nu\text{C}=\text{O}$ phenolic ^c	$\nu\text{C}=\text{S}^{**}$	M-O, M-N, and M-S ^{**}
1	HAEP-L3	—	3400 (b)	$\nu\text{N}-\text{H}_2^b$	3320 (s), 3280 (s)	1630 (s)	1270 (s)	1280 (s)	—	—
2	$[\text{Cu}(\text{HAEP})]_2$	—	3440 (s) ^c		3320 (s), 3280 (s)	1640, 1610 (s)	1295 (s)	1225 (s)	850, 500, 400	
3	$[\text{Ni}(\text{HAEP})_2]$	—	3460 (s)		3320–3280 (s)	1640, 1610 (s)	1295 (s)	1220 (w)	850, 600–400	
4	$[\text{Co}(\text{HAEP})(\text{H}_2\text{O})_2]_2$	3560 (b)	3480 (b)		3320 (b), 3280 (b)	1610–1620 (b)	1280 (s)	1220 (w)	850, 570, 470, 410, 400	
5	$[\text{Fe}(\text{HAEP})(\text{H}_2\text{O})\text{Cl}]_2$	3560 (b)	3480 (b)		3320 (s), 3280 (s)	1640, 1620 (d)	1295 (s)	1220 (w)	850, 575, 480, 400	
6	$[\text{Cr}(\text{HAEP})(\text{H}_2\text{O})\text{Cl}]_2$	3500–3450 (b)	3480 (b)		3320 (s), 3280 (s)	1605, 1595 (d)	1280 (s)	1010 (w)	850, 520, 440, 295	
7	$[\text{VO}(\text{HAEP})(\text{H}_2\text{O})_2]$	3560 (b)	3460 (s)		3320 (s), 3280 (s)	1600–1610	1290 (s)	—	970 (V=O), 850, 310, 300	

^{**} Ligand exists in “thione” form and not “thiol” form in the solid state as the expected $\nu\text{S}-\text{H}$ band at 2570 cm^{-1} for “thiol” form is not observed and $\nu\text{C}=\text{S}$ is present, Pradhan and Rao [65]; Saha and Deepak [66] and other references therein, Suzuki [101]; Pradhan and Rao [102]; ^aOverlap of two hydroxyl groups of resacetophenone moiety and hydrogen bonding to some extent; ^bSymmetric and asymmetric frequencies of NH_2 group not participated in complexation; ^cNew sharp band of free -OH indicates deprotonation and coordination; ^dNew $\nu\text{C}=\text{N}$ group due to enolization and shift in original $\nu\text{C}=\text{N}$ group of azomethine.

TABLE 10: Characteristic IR data for the L4-BFH (bidentate -O, -N) and its participation in complex formation with metal ions.

S. number	Complex	IR cm ⁻¹ (s = sharp; b = broad; d = doublet; w = weak; vw = very weak)				
		Coord water	ν N-H	ν C=O	ν C=N ^d	M-O, M-N, M-Cl ^e
1	BFH-L4 ^b	—	3240 (s) ^a	1650 (s)	1620 (s)	—
2	[Cr(BFH)(H ₂ O)Cl ₂] ₂	3550–3450	Absent ^c	—	1610 (s), 1590 (s)	830, 570, 400 (s), 300 (vw)
3	[Cr(BFH) ₂ (H ₂ O)Cl]	3550–3450	Absent ^c	—	1610 (s) 1590 (s)	840, 575, 395 (s), 300 (vw)
4	[VO(BFH) ₂ (H ₂ O)]	3550–3450 (b)	Absent ^c	—	1600–1610 (s)	970 (V=O), 810, 440, 350

^aHydrazone moiety; ^bNo shift in symmetric and asymmetric stretching frequencies of furfural ring oxygen at 1020 (s), 895 (s) cm⁻¹ and N-N at 1040 (w) indicates no involvement in complex formation; ^cAbsence of ν N-H band suggests enolization of the ligand which is confirmed by disappearance of strong ν C=O band; ^dShift indicates participation of -N of azomethine group in coordination; ^eNakamoto [91, 100] and Selbin [94].

TABLE 11: Characteristic IR data for the L5-BHDH (tetradentate -O, -O, -N, and -O) and its participation in complex formation with metal ions.

S. number	Complex	IR cm ⁻¹ (s = sharp; b = broad; d = doublet; w = weak; vw = very weak)						
		Coord water	ν O-H	ν N-H	ν C=O	ν C=N	ν C-O phenolic	M-O, M-N, or M-Cl
1	BHDH-L5 ^c	—	3350–3400 (b) ^a	3280 (s)	1655 (s)	1600 (s)	1260 (s)	—
2	[Cr(BHDH)Cl] ₂	—	Absent ^b	3280 (s)	1635 (s)	1580 (s)	1300–1310 (d)	550 (w), 435, 310, 295 (w)
3	[VO(BHDH)(H ₂ O)]	3500–3450 (b)	Absent ^b	3280 (s)	1610 (s)	1575 (s)	1270 (s)	970 (V=O), 820 (s), 520, 470, 440, 340

^aInter and intramolecular hydrogen bonding; ^bThe breakage of hydrogen bonding and the deprotonation of both the hydroxyl groups (phenolic), that is, hydrazide -OH and pyrone -OH and their M-O coordination; ^cNo shift of lactone ν C=O at 1710 (s) cm⁻¹; and ν C-O-C at 1010 (s) cm⁻¹ suggests noninvolvement in complex formation; shift of hydrazide, phenolic ν C-O and ν C=N indicate participation in complexation.

FIGURE 7: Electronic (MULL) spectra of NICKEL(II) complexes of (a) BHFH (AT ph 8.5) [Ni(BHFH)]₂; (b) BHFH (AT ph 5.5–7.0) [Ni(BHFH)(H₂O)]; (c) BHEH [Ni(BHEH)]₂; (d) HAEP [Ni(HAEP)]₂.

FIGURE 8: Electronic (MULL) spectra of Copper(II) complexes of (a) BHFH (AT ph 5.5–7.0)-[Cu(BHFH)]₂; (b) BHFH (AT ph 8.5)-[Cu(BHFH)(H₂O)]; (c) BHEH-[Cu(BHEH)(Cl)]; (d) HAEP-[Cu(HAEP)]₂.

one or two molecules of water coordination in the complexes as per the composition predicted.

The Cr(III) complexes are synthesized with L3, L4, L5, and L6 and are characterized [72, 73] as having Oh geometry as shown in Table 14; Figure 3. The magnetic moments of L6 and L4 (prepared at pH 8.5) at RT are close to the expected spin-only value for Oh complexes of Cr(III) [72–75]. The other complexes show lower values and so may be due to metal-metal interactions with binuclear bridge structures. All the electronic spectra for several greenish Cr(III) complexes

fit with very large number of such complexes studied and surveyed. However in the present case, the highest energy band is found to be obscured due to the dark colour of all the complexes.

3.3. Mn(II) Complexes. The Mn(II) complex of L1 is a fine powder, light-yellow in colour and decomposed at 280°C without melting. The Mn(II) complex of L2 is a dark-brown powder decomposed at 286°C. Both the compounds are very stable in air and moisture and are insoluble in water and

TABLE 12: Characteristic IR data for the ligand DHA (bidentate -O, -O) and its participation in complex formation with metal ions.

S. number	Complex	IR cm ⁻¹ (s = sharp; b = broad; d = doublet; w = weak; vw = very weak)					M-O
		Coord water	vO-H	vC=O (lactone)	vC=O	vC-O phenolic	
1	DHA-L6 ^b	—	3030 (s) ^a	1710 (s)	1655 (s)	1265 (s)	—
2	[Cr(DHA) ₃]	—	Absent ^c	1740 (s)	1635 (s)	1280 (s)	480, 440
3	[VO(DHA) ₂ (H ₂ O)]	3500–3400 (b)	Absent ^c	1740 (s)	1640 (s)	1290 (s)	910 (V=O) ^d , 850, 480, 440

^aIntramolecular hydrogen bonded; ^bNo shift in vC–O–C indicates noninvolvement in complex formation, Mahesh and Gupta [103]; ^cCleavage of hydrogen bonding due to complexation, ^dSelbin [94].

in common organic solvents like methanol, ethanol, chloroform, benzene, and so forth. Mn complex with L1 at lower pH showed loss of weight starting at 56°C (0.0014 gm) and decomposed at 280°C (0.0205 gm) in the thermal analysis, thus confirming a molecule of water coordination in the complex as per the composition predicted.

As can be seen from Table 15; Figure 4, Mn(II) complex of L1 shows subnormal magnetic moment which may be due to metal-metal interactions or due to spin-exchange or superexchange in the solid state [76, 77]. The Mn(II) complex of L2 is 5.92 BM expected region for high-spin Oh Mn(II) complexes [72, 73]. The electronic spectra are consistent with the Oh symmetry in both the cases.

3.4. Fe(III) Complexes. All the complexes are dark coloured and fine amorphous powders. All decomposed above 300°C are very stable to air, moisture and insoluble in most of the common organic solvents like acetone, methanol, ethanol, and so forth. They are soluble to some extent in solvents like 1-4 dioxane, dimethylformamide, and dimethyl sulfoxide. Their conductivity could not be measured owing to their insoluble nature. Fe complex with L2 showed loss of weight starting at 68°C (0.0012 gm) and decomposed at 305°C (0.0057 gm) and complex with L3 at 66°C (0.0018 gm) and decomposed at 300°C (0.0055 gm) in the thermal analysis. Thus, confirming two molecules of water coordination in the complexes as per the composition predicted.

All the Fe(III) complexes formed with L1–L3 ligands have subnormal magnetic moments which may be due to the fact that metal-metal interactions or superexchange is anticipated [76, 78, 79], as all the complexes may be binuclear in nature as shown in Table 16; Figure 5. The electronic spectra have very weak transitions and could not be concluded decisively and, however, are close to Oh symmetry with some tetragonal distortion.

3.5. Co Complexes. All Co(II) complexes are coloured, fine amorphous powders and decompose above 260°C without melting. They are all very stable to air, moisture and insoluble in most of the common organic solvents and to a small extent in 1-4 dioxane, dimethylformamide, and dimethyl sulfoxide. The conductivity of the compounds could not be determined owing to their insoluble nature. Co complex with L1 showed loss of weight starting at 52°C (0.0020 gm) and decomposed at 260°C (0.0555 gm) and complex with L3 at 54°C (0.0007 gm) and decomposed at 295°C (0.0089 gm) in the thermal analysis, thus confirming two molecules of

water coordination in the complexes as per the composition predicted.

The observed magnetic moments of all the three Co(II) complexes formed with L1–L3 ligands are slightly lower than the expected 4.7–5.2 BM for high-spin octahedral Co(II) complexes as given in Table 17; Figure 6. The lower moments may be due to the metal-metal interactions [80].

In the Oh Co(II) complexes 4T_{1g} and E_g are the spin-free and spin-paired ground states. Broad band in lower energies and a multiple band in slightly higher energy in admixtures with spin-forbidden transition to doublet state are expected [72]. The asymmetric visible band is typical of Oh Co(II) complexes, the shoulder on the high energy side being assigned to spin-forbidden transitions [74].

3.6. Ni(II) Complexes. Ni(II) complexes are bright-red, green, and dark-brown in colour. These are insoluble in water and sparingly soluble in common organic solvents and also in 1-4 dioxane, dimethylformamide, and dimethyl sulfoxide. The conductivity could not be measured owing to very low solubility of the complexes. Ni complex with L1 at lower pH showed loss of weight starting at 68°C (0.0010 gm) and decomposed at 265°C (0.0053 gm) in the thermal analysis, thus confirming a molecule of water coordination in the complex as per the composition predicted.

The L1 complex at pH 5.5–7.0 and the L3 complexes are diamagnetic [81] and the other two with L1 at pH 8.5 and L2 have magnetic moment around 2.91–3.40 BM as expected for six-coordinated spin-free Ni(II) complexes as seen in Table 18; Figure 7. In regular Oh complexes of Ni(II) consideration of spin-orbit coupling and contribution from the 3A_{2g} and the next higher 3T_{2g} states give a somewhat higher magnetic moment than the spin-only moment of 2.83 BM [72, 82, 83].

The electronic spectra of the diamagnetic complex with L1 at pH 5.5–7.0 show two bands assigned to strong charge-transfer d-pi* transition [84] and the lower energy band to 1A_{1g} → 1A_{2g} transition [74, 84–87] as expected for square-planar complexes. The other two complexes show three intense bands expected for regular octahedral geometry.

3.7. Cu(II) Complexes. All the complexes are coloured, fine amorphous powders and decompose above 250°C without melting. They are all very stable to air, moisture and are insoluble in most of the common organic solvents, except to a small extent in 1-4 dioxane, dimethylformamide, and dimethyl sulfoxide. The conductivity could not be measured

TABLE 13: Electronic spectra and magnetic moment data for VO(II) complexes with L1–L6 ligands predicted molecular formula, structure, and geometry.

S. number	Molecular formula-electronic spectra ^b bands, transitions ^a , predicted structure (a rough M–L sketch given), and geometry ^a			μ_{eff} BM
1	$[\text{VO}(\text{BHFH})\text{Cl}]_2$ M–M complex with Cl bridges, V=O and two L1 with –O, –O, and –N coordination	28,006 18,270 13,330		1.54 M–M
2	$[\text{VO}(\text{BHEH})\text{Cl}]_2$ M–M complex with Cl bridges, V=O and two L2 with –O, –O, and –N coordination	25,000 14,920 13,000		1.63 M–M
3	$[\text{VO}(\text{HAEP})(\text{H}_2\text{O})_2]$ Distorted Oh complex, V=O, two –OH ₂ , and L3 with –N, –O, and –S coordination on the equatorial plane	25,000 22,200 13,560		1.72
4	$[\text{VO}(\text{BFH})_2(\text{H}_2\text{O})]$ Distorted Oh complex, V=O, –OH ₂ , and two L4 with –N, –O coordination	25,000– 22,200 16,100		1.74
5	$[\text{VO}(\text{BHDH})(\text{H}_2\text{O})]$ Distorted Oh complex, V=O, –OH ₂ , and L5 with –N, –O, –O, and –O coordination on the equatorial plane	25,800 15,380 13,150		1.71
6	$[\text{VO}(\text{DHA})_2(\text{H}_2\text{O})]$ Distorted Oh complex, V=O, –OH ₂ , and two L6 with –O, –O coordination on the equatorial plane	30,000 25,500 18,180		1.72

2B2–2A1
2B2–2B1
2B2–2E
Correspond to Oh
symmetry with
tetragonal distortion.

^aLever [73]; Rana et al. [104]; ^bRecorded for solid compounds (mull-diffuse reflectance) at room temperature—Figures 1 and 2.

owing to their insoluble nature and their stoichiometry is deduced from the analytical data and geometry from the diffuse reflectance data in conjunction with magnetic moments. Cu complex with L1 at higher pH showed loss of weight starting at 73°C (0.0010 gm) and decomposed at

280°C (0.0300 gm) in the thermal analysis, thus confirming a molecule of water coordination in the complex as per the composition predicted.

The subnormal magnetic moments of Cu L1 at lower pH and Cu L3 indicate some metal-metal interactions in the solid

TABLE 14: Predicted molecular formula, structure and geometry from electronic spectra and magnetic moment data for Cr(III) complexes with L3–L6 ligands.

S. number	Molecular formula-electronic spectra ^b bands, transitions ^a , predicted structure (a rough M–L sketch given), and geometry ^a	μ_{eff} BM
1	<p>$[\text{Cr}(\text{HAEP})(\text{H}_2\text{O})\text{Cl}]_2$ Distorted Oh complex with Cl bridges, two $-\text{OH}_2$, and two L3 with $-\text{O}$, $-\text{N}$, and $-\text{S}$ coordination on the equatorial plane</p> <p>27,930 17,390</p>	3.49 M–M
2	<p>$[\text{Cr}(\text{BFH})(\text{H}_2\text{O})\text{Cl}_2]_2$ Distorted Oh complex with Cl bridges, two $-\text{Cl}$, two $-\text{OH}_2$, and two L3 with $-\text{O}$, $-\text{N}$ coordination on the equatorial plane</p> <p>27,878 17,420</p>	3.55 M–M
3	<p>$[\text{Cr}(\text{BFH})_2(\text{H}_2\text{O})\text{Cl}]$ Distorted Oh complex with $-\text{OH}_2$, Cl, and two L3 with $-\text{O}$, $-\text{N}$ coordination on the equatorial plane</p> <p>26,670 17,500</p> <p>4A2g–4T1g (F) 4A2g–4T2g Charge transfer transition 4A2g–4T1g (P) is obscured due to dark colour Octahedral symmetry high-spin complex</p>	3.88
4	<p>$[\text{Cr}(\text{BHDH})\text{Cl}]_2$ Distorted Oh complex with Cl bridges and two L5 with $-\text{O}$, $-\text{N}$, $-\text{O}$, and $-\text{O}$ coordination on the equatorial plane</p> <p>28,980 17,390</p>	3.74 M–M
5	<p>$[\text{Cr}(\text{DHA})_3]$ Distorted Oh complex with three L6 with $-\text{O}$, $-\text{O}$ coordination</p> <p>26,670 18,200</p>	3.89

^aLever [73]; ^bRecorded for solid compounds (mull-diffuse reflectance) at room temperature—Figure 3.

state. The dimeric nature of the complexes predicted with $-\text{O}$ and $-\text{S}$ as bridges supports this [88, 89]. All the data in the references cited show that magnetic moments of square-planar Cu(II) complexes lie in the range of 1.7–1.9 BM. While slightly higher values of the other two complexes suggest presence of one unpaired electron with spin-orbit coupling [90]. Thus, all of the Cu(II) complexes are assigned [72] square-planar geometry as shown in Table 19; Figure 8. Two of them indicate metal-metal interactions due to slightly lower magnetic moments; one of them shows a loss of weight

corresponding to one molecule of water from the TGA at variable temperature and one another with the chloride estimation.

3.8. Physiological Activity. The effect of the metal complex on fungal growth is measured by poisoning the nutrient (a solid like an agar-agar or a liquid medium) with a fungi toxicant. Then, it is allowed to grow as a test fungus.

TABLE 15: Predicted molecular formula, structure, and geometry from electronic spectra and magnetic moment data for Mn(II) complexes with L1-L2 ligands.

S. number	Molecular formula-electronic spectra ^b bands, transitions ^a , predicted structure (a rough M–L sketch given), and geometry ^a				μ_{eff} BM
1	<p>[Mn(BHFH)(H₂O)Cl]₂ Distorted Oh complex with Cl bridges, two –OH₂, and two L1 with –O, –O, and –N coordination on the equatorial plane</p>	<p>27,030 21,270 19,610 18,180</p>	<p>6A_{1g}-4E_g, 4A_{1g} (G) 6A_{1g} · 4T_{2g} (G) 6A_{1g} · T_{1g} (G)</p>		<p>5.44 M–M</p>
2	<p>[Mn(BHEH)₂] Oh complex with two L2 with –O, –O, and –N coordination</p>	<p>26,670 17,240</p>	<p>Oh high-spin geometry is predicted</p>		<p>5.92</p>

^aPappalardo [105]; ^brecorded for solid compounds (mull-diffuse reflectance) at room temperature—Figure 4.

TABLE 16: Predicted molecular formula, structure, and geometry from electronic spectra and magnetic moment data for Fe(III) complexes with L1-L3.

S. number	Molecular formula-electronic spectra ^b bands, transitions ^a , predicted structure (a rough M-L sketch given), and geometry ^a			μ_{eff} BM
1	<p>[Fe(BHFH)Cl₂]₂ Distorted Oh complex with Cl bridges, two -Cl, and two L1 with -O, -O, and -N coordination on the equatorial plane</p>	23,260 21,740 19,040 17,540		5.70 M-M
2	<p>[Fe(BHEH)(H₂O)Cl]₂ Distorted Oh complex with Cl bridges, two -OH₂, and two L2 with -O, -O, and -N coordination on the equatorial plane</p>	26,670 22,220 18,520 17,390 15,600		5.73 M-M
3	<p>[Fe(HAEP)(H₂O)Cl]₂ Distorted Oh complex with S bridges, two -OH₂, two -Cl, and two L3 with -O, -N, and -S (used in bridging) coordination on the equatorial plane</p>	Extremely weak transitions		5.88 M-M

^aOh geometry with metal-metal interactions; ^bRecorded for solid compounds (mull-diffuse reflectance) at room temperature—Figure 5.

3.9. For the Organism *Rhizoctonia Solani*

(i) L1 has shown 30% inhibition at 1000 ppm, 17% at 500 ppm, and nil effect at 250 ppm (Table 20). Hence, all the newly synthesized complexes were tested for activity at 1000 ppm (observe carefully Figure 9). It was found that the VO(II) complex is 100% effective,

Mn(II) 95%, Fe(III) 62%, Co(II) nil effect, Ni(II) 45% and Cu(II) nil effect. Thus, the activity order may be evaluated as VO > Mn > Fe > Ni > L1 > Co = Cu.

(ii) L2 shows the following trend VO > Mn > Ni > Cu > L2 > Co.

TABLE 17: Predicted molecular formula, structure, and geometry from electronic spectra and magnetic moment data for Co(II) complexes with L1-L3 ligands.

S. number	Molecular formula-electronic spectra ^b bands, transitions ^a , predicted structure (a rough M-L sketch given), and geometry ^a			μ_{eff} BM
1	$[\text{Co}(\text{BHFH})(\text{H}_2\text{O})\text{Cl}]_2$ Distorted Oh complex with Cl bridges, two $-\text{OH}_2$, and two L1 with $-\text{O}$, $-\text{O}$, and $-\text{N}$ coordination on the equatorial plane	31,250 20,000 18,520 15,400		4.58 M-M
2	$[\text{Co}(\text{BHEH})_2]$ Oh complex with two L2 with $-\text{O}$, $-\text{O}$, and $-\text{N}$ coordination on the equatorial plane	19,750 18,450 15,700 8,430		3.92
3	$[\text{Co}(\text{HAEP})(\text{H}_2\text{O})_2]_2$ Distorted Oh complex with S bridges, two $-\text{OH}_2$, two $-\text{Cl}$, and two L3 with $-\text{O}$, $-\text{N}$, and $-\text{S}$ (used in bridging) coordination on the equatorial plane	27,030 17,700 15,630 8,330		4.53 M-M

^aLever [73]; the asymmetric visible band is typical of Oh Co(II) complexes and the shoulder on the high energy side being assigned to spin-forbidden transitions, Drago [74]; ^bRecorded for solid compounds (mull-diffuse reflectance) at room temperature—Figure 6.

FIGURE 9: Activity observed for the following: 1—Dithane M45-500 ppm; 2—VO(II)-250 ppm; 3—VO(II)-500 ppm; 4—VO(II)-750 ppm; 5—VO(II)-1000 ppm and 6—Blank.

FIGURE 10: Complexes with VO(II)-100% effective, Mn(II)-95% effective, Fe(III)-62% effective, Ni(II)-45% effective, and Co(II), Cu(II)-nil effect are observed in this photo.

(iii) quite unexpectedly, L3 upon complexation completely subsides the activity. This may be due to the presence of two free $-\text{OH}$ groups and one free $-\text{NH}_2$ group in the ligand, the structure of which is comparable to the antidotes used for the expulsion of food poisoning in hospitals.

(iv) L4 trend shows $\text{VO} > \text{Cr} > \text{L4}$.

(v) L5, L6 show $\text{VO} > \text{Cr}$.

Thus the complexes with L1, L2, and L4 are as effective as the commercially used Dithane M-45 (Table 20). The VO complexes with L1 and L2 are dimeric in nature and probably in solution dissociate to monomeric units due to the $\text{V}=\text{O}$

TABLE 18: Predicted molecular formula, structure, and geometry from electronic spectra and magnetic moment data for Ni(II) complexes with L1–L3 ligands.

S. number	Molecular formula-electronic spectra ^b bands, transitions ^a , predicted structure (a rough M–L sketch given), and geometry ^a			μ_{eff} BM	
1	<p>[Ni(BHFH)H₂O]</p> <p>Square-planar complex with –OH₂ and L1 with –O, –O, and –N coordination on the equatorial plane</p>	<p>26,130</p> <p>18,100</p>	<p>Charge-transfer band d-pi* transition</p> <p>1A_{1g} · 1A_{2g}</p> <p>Square-planar geometry</p>		Dia
2	<p>[Ni(BHFH)₂]</p> <p>Regular Oh complex with two L1 with –O, –O, and –N coordination</p>	<p>26,300</p> <p>15,000</p> <p>9,520 (w)</p>	<p>3A_{2g}-3T_{1g} (P)</p> <p>3A_{2g}-3T_{1g} (G)</p> <p>3A_{2g}-3T_{2g}</p> <p>Regular Oh geometry</p>		3.24
3	<p>[Ni(BHEH)₂]</p> <p>Regular Oh complex with two L1 with –O, –O, and –N coordination</p>	<p>26,670 (s)</p> <p>20,000</p> <p>13,100</p> <p>8,200 (w)</p>	<p>Strong charge-transfer band-d-pi* transition</p> <p>3A_{2g}-3T_{1g} (P)</p> <p>3A_{2g}-2T_{1g}, 3T_{1g} (F)</p> <p>3A_{2g}-3T_{2g}</p> <p>Regular Oh geometry</p>		2.91
4	<p>[Ni(HAEP)₂]</p> <p>Distorted square-planar complex with S bridges and two L3 with –O, –N, –S (used in bridging) coordination on the equatorial plane</p>	<p>27,030</p> <p>16,600</p>	<p>Charge-transfer band d-pi* transition</p> <p>1A_{1g}-1A_{2g}</p> <p>Diamagnetic tetragonal or square planar complex with high intensity band in 14000–18000 cm^{–1}</p>		Dia M–M

^aHolm et al. [77]; Shaw and Dudek [106]; Drago [74]; ^bRecorded for solid compounds (mull-diffuse reflectance) at room temperature—Figure 7.

group unlike the other dimeric complexes synthesized. The $-\text{O}$ of $\text{V}=\text{O}$ might bind in such a way that the activity order is tremendously increased and the growth of fungus is completely inhibited making it 100% effective. And probably the ligands are bound to metal atoms by rearrangement caused by enolization, thus making them more viable for dissociation, unlike the first deceptive appearance they give as if they are coordinately more saturated.

In the Case of *Acrocylindrium oryzae*, a nominal activity for the L4–L6 Cr(III) complexes and maximum activity for all VO(II) complexes were observed. Hence, screening of VO(II) complex of L1 was done at lower concentrations and compared with the commercially used fungicide Dithane M-45 (observe carefully Figure 10). From the average of four replications in each case, the dry-weight of the fungal

mycelium was recorded in milligrams and was shown in Table 20. It was observed that L1–L3 has totally inhibited the growth at 1000, 500, and 250 ppm. Nominal growth of the organism on the disc of the inoculums was observed to be about 2–5 mg. but L4 showed nominal activity at 1000 ppm with decreased activity at lower concentrations. So the activity order for all these is given as follows. $\text{L1} > \text{VO} > \text{Ni} > \text{Mn} > \text{Fe} > \text{Co} > \text{Cu}$ and $\text{L2} > \text{Ni} > \text{VO} > \text{Mn} > \text{Fe} > \text{Cu} > \text{Co}$. Cr(III) complexes of L3–L6 were found less toxic than VO(II) complexes. The activity of these was found to be marginal when compared to that of the commercial Dithane M-45. Interestingly, it was found that the VO(II) complex at 250 ppm is more effective compared to Dithane M-45 at 500 ppm and may be more useful. It is interesting to note from the above data that L1 and L2 are very toxic to this organism

TABLE 19: Predicted molecular formula, structure, and geometry from electronic and magnetic moment data for Cu(II) complexes with L1-L3 ligands.

S. number	Molecular formula-electronic spectra ^b bands, transitions ^a , predicted structure (a rough M-L sketch given), and geometry ^a	μ_{eff} BM
1	<p>[Cu(BHFH)]₂ Distorted square-planar complex with M-M complex with -O of L1 bridges and L1 with the rest of -O, -N coordination</p> <p>28,570 (sm) 14,300 (b)</p>	1.50 M-M
2	<p>[Cu(BHFH)H₂O]</p> <p>Distorted square-planar complex with -OH₂ and L1 with -O, -O, and -N coordination</p> <p>27,030 (s) 18,180 (b)</p> <p>Strong charge-transfer band d-pi* transition 2B2g-Eg 2B2g-2A1g 2B2g-2B1g Normally Cu(II) show broad bands around 16670-1110 cm⁻¹. The observed spectra resemble Cu(II)-SB complexes whose geometry is considered square planar</p>	2.04
3	<p>[Cu(BHEH)Cl]</p> <p>Distorted square-planar complex with -Cl and L1 with -O, -O, and -N coordination</p> <p>26,650 17,540</p>	1.91
4	<p>[Cu(HAEP)]₂ Distorted square-planar complex with S bridges and two L3 with -O, -N, and -S (used in bridging) coordination on the equatorial plane</p> <p>25,640 15,380 13,330</p>	1.40 M-M

^aLever [73]; Sutton [107]; Satyanarayana and Mohapatra [108]; Sacconi and Ciampolini [109]; Muzundar and Bhattacharya [110]; Sheela [111]; ^bRecorded for solid compounds (mull-diffuse reflectance) at room temperature—Figure 8.

compared to *Rhizoctonia solani* and also VO(II) complexes show more activity.

After 48 hrs of inoculation of the bacterium *Xanthomonas oryzae*, percentage inhibition growth was calculated from each plate and average readings from fine replicas are shown in Table 20. It was observed that neither the ligands nor the complexes could control the growth of this bacterium fully. None of the complexes showed considerable percentage inhibition at the 1000 ppm concentration and, hence, they were not screened at lower concentrations. The saturated bactericide, Branidiol, was also found to be effective only to the extent of 50% but its effect so persists in the system that the growth is arrested at that stage and never continues. The order of activity of complexes of L1 is as follows: VO > Mn > Fe > L1 > Ni > Co > Cu and that in the complexes of L2 is Ni

> Mn > VO > Co > Fe > Cu > L2. L3 and all its complexes have shown nil activity on this bacterium. L4-L6 and their Cr(III), VO(II) complexes were screened and the order of activity in them was as follows: VO > Cr > L4 > L5 > L6. Thus it was observed that the complexation increases the activity of ligand, but it was less than the standard bactericide, Bronidiol.

4. Conclusions

Synthesis of Schiff bases L1-L5 and L6 and their use as ligands for coordination with VO(II), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), and Cu(II) form a major study. All the prepared complexes were analyzed by C, H, N, Cl, and metal analyses. They were assigned molecular structures and geometries using information obtained from IR, UV-Vis,

TABLE 20: Evaluation of fungicidal property of Schiff bases and metal complexes in vitro.

S. number	Chemical complex	<i>Rhizoctonia solani</i> (PDA medium), average % inhibition of growth after 72 hrs; poisoned food technique concentration in ppm			<i>Acrocyndrium oryzae</i> (PA liquid) average % inhibition of growth after 48 hrs; liquid broth method concentration in ppm			<i>Xanthomonas oryzae</i> (Hayward's medium) average % inhibition of growth after 8 days; inhibition zone technique concentration in ppm		
		1000	500	250	1000	500	250	1000	500	250
1	BLANK	-	-	-	246	245	246	-	-	-
2	DITHANE-M-45	100	100	80	nil	200	240	55	50	48
3	L1-BHFH	30	16.66	-	nil	nil	2	12	--	--
4	[Cu(BHFH)] ₂	-	--	--	190	200	240	5	--	--
5	[Co(BHFH)(H ₂ O)Cl] ₂	-	--	--	170	150	240	8	--	--
6	[Ni(BHFH)] ₂	45.5	15	-	5	28	130	11.2	--	--
7	[Fe(BHFH)Cl ₂] ₂	62.2	34.4	10	55	100	220	22.3	--	--
8	[Mn(BHFH)(H ₂ O)Cl] ₂	95.2	67.2	40	25	76	130	23	--	--
9	[VO(BHFH)Cl] ₂	100	69.66	50	nil	nil	12	20	--	--
10	L2-BHEH	20	6.6	-	nil	nil	2	3	--	--
11	[Cu(BHEH)Cl]	25	21.1	10	150	200	245	8	--	--
12	[Co(BHEH)] ₂	-	--	--	175	190	225	16.7	--	--
13	[Ni(BHEH)] ₂	27	--	--	nil	nil	nil	30	--	--
14	[Fe(BHEH)(H ₂ O)Cl] ₂	35	20	-	100	155	200	15	--	--
15	[Mn(BHEH)] ₂	82	50	50	96	100	150	19	--	--
16	[VO(BHEH)Cl] ₂	100	45	40	nil	nil	50	20	--	--
17	L3-HAEP	50	20	-	5	5	5	10	--	--
18	[Cu(HAEP)] ₂	-	--	--	245	--	--	--	--	--
19	[Co(HAEP)(H ₂ O)] ₂	-	--	--	240	--	--	--	--	--
20	[Ni(HAEP)] ₂	-	--	--	185	--	--	--	--	--
21	[Fe(HAEP)(H ₂ O)Cl] ₂	-	--	--	200	--	--	--	--	--
22	[Cr(HAEP)(H ₂ O)Cl] ₂	-	--	--	242	--	--	--	--	--
23	[VO(HAEP)(H ₂ O)] ₂	-	--	--	245	--	--	2	--	--
24	L4-BFH	32	20	-	70	100	240	20	--	--
25	[Cr(BFH)(H ₂ O)Cl] ₂	-	--	--	150	200	240	22	--	--
26	[VO(BFH) ₂ (H ₂ O)]	98	69.66	50	125	150	200	25	--	--
27	[Cr(BHDH)Cl] ₂	15.5	5.12	5	190	--	--	15	--	--
28	[VO(BHDH)(H ₂ O)]	32.2	15	-	150	198	240	20	--	--
29	[Cr(DHA)] ₃	28.5	--	--	200	240	245	15	--	--
30	[VO(DHA) ₂ (H ₂ O)]	50	30	15	170	200	238	18	--	--

- indicates negative effect; -- indicates that the compound is not screened.

magnetic susceptibility, and TGA analysis. The physiological activity studies with ligands L1–L4 along with some results of metal complexes with L1–L6 ligands are tabulated, suggesting them to be toxic to the organisms studied and, hence, may be useful as fungicides and bactericides. The VO(II) complexes are found to be more active compared to the activity of the commercial standard.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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