

Structural, Thermal, Biological and Semiconducting Properties of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and VO(IV) Complexes of Schiff Base Derived from Resdiacetophenone and S-Benzylidithiocarbazate

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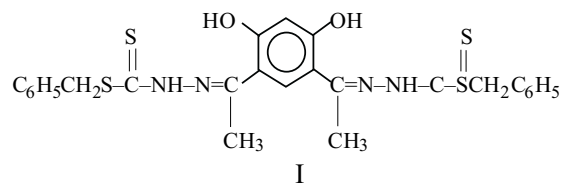
(Received June 26th, 2002; revised manuscript March 31st, 2003)

A series of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and VO(IV) complexes with Schiff base derived from resdiacetophenone and S-benzylidithiocarbazate have been synthesized and characterized by elemental analyses, magnetic moment, IR and electronic spectral studies and thermal analysis. The Schiff base functions as a binucleating tridentate chelating agent and coordinates *via* the deprotonated phenolic oxygen, azomethine nitrogen and thioenolate sulphur atoms to the metal ion favouring the formation of bimetallic complexes. From dynamic TG data, activation energy and other kinetic parameters have been computed using Freeman-Carroll, Sharp-Wentworth and Coats-Redfern methods. Electrical conductivity of the complexes have also been studied between 313–473 K in pellet forms and the complexes are found to exhibit semiconducting behaviour. The antimicrobial activity of the ligand and its complexes have been screened against various microorganisms and all of them were found to be moderately active against the organisms.

Key words: Schiff base, complexes, TGA, kinetics parameters, biological study

Sulphur containing ligands and their metal complexes have received considerable attention in recent years, due to their remarkable antitumour, antibacterial and antiviral properties [1–3]. The bimetallic complexes with no dimerization possibility may also be useful, in addition to above efficacy, in catalytic activity due to easy accessibility of two independent active metal centres. Such binucleating ligands and their metal complexes have been reported recently in literature [4]. Catalytic properties of some dioxomolybdenum (VI) complexes for the epoxidation of alkene using *t*-butyl hydroperoxide as an oxidant have also been reported [5–6]. Considering this, we have designed new class of ligand, BSBZRD (H₄L) (I) and studied its coordination behaviour with Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and VO(IV) ions. Characterization of these complexes using various physico-chemical methods along with thermogravimetric analyses constitutes part of this report. Dynamic TG data, activation energy and other kinetic parameters of these complexes give idea about stability and suitability of these complexes.

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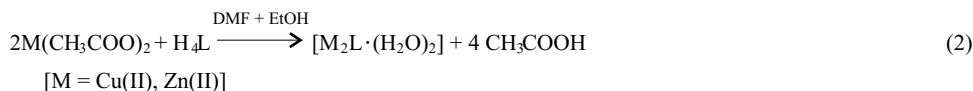
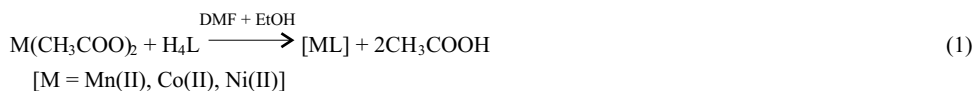


EXPERIMENTAL

All chemicals and metal salts (cupric acetate monohydrate, zinc acetate dihydrate, cobalt, manganese and nickel acetate tetrahydrate, cadmium chloride monohydrate, vanadyl sulphate pentahydrate, ferrous ammonium sulphate hexahydrate) used in the synthesis of Schiff base and complexes were of A.R. grade. Resdiacetophenone was prepared by Friedel-Craft's reaction. S-benzyl-dithiocarbamate was prepared by the method of Ali and Tarafder [7].

Synthesis of Schiff base (BSBZRD): An ethanolic solution of resdiacetophenone (1.94 g, 0.01 mol in 10 ml) was added to S-benzyl-dithiocarbamate (3.96 g, 0.02 mol) dissolved in 20 ml of ethanol and the reaction mixture was refluxed on a water bath for about 4 h. A greenish yellow solid, which separated on cooling the flask, was filtered and washed with ethanol. Finally it was recrystallized from DMF and dried *in vacuo*. Purity of ligand was checked by TLC, (yield 62%, m.p. 185°C).

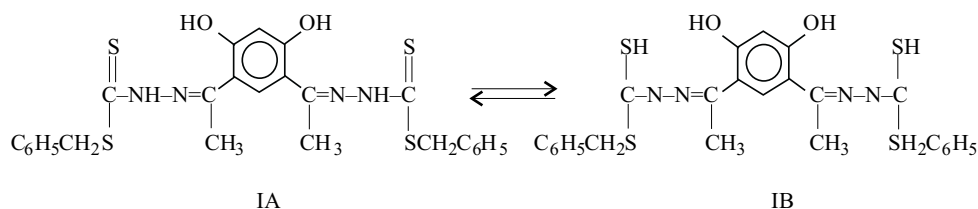
Synthesis of metal complexes: The complexes of Mn(II), Fe(II), Co(II) and Ni(II) were prepared by treating DMF solution (20 ml) containing Schiff base (0.5 mmol) with hot ethanolic solution of corresponding metal salts (0.5 mmol, 20 ml), while in case of Cu(II), Zn(II), Cd(II) and VO(IV) complexes 2:1 (M:L) ratio have been taken and the reaction mixture was refluxed on water bath for about 4 h. The coloured products thus separated during reaction were filtered after cooling the reaction flask at ambient temperature, washed thoroughly with DMF followed by ethanol and dried *in vacuo* over fused calcium chloride. An ethanolic solution of appropriate metal salt reacted with ligand in DMF and formed metal complexes of compositions [ML] and [M₂L·(H₂O)₂]. Synthetic strategy of the chelates may be given by



Elemental analysis of ligand and complexes were carried out at microanalytical laboratory of RSIC, Punjab University, Chandigarh (India). The ¹H NMR spectrum of the Schiff base was recorded in a mixed solvent (CDCl₃ + DMSO-d₆) on 90 MHz Perkin-Elmer R-32 instrument. Infrared spectra were recorded on a Perkin-Elmer 842 spectrometer, while the diffuse reflectance spectra on a Cary 2390 spectrophotometer at RSIC, IIT Chennai, India. Magnetic susceptibility was measured at room temperature by the Gouy balance. Thermal decomposition of complexes were studied on a laboratory set up apparatus using a heating rate of 10°C min⁻¹ in static air atmosphere. Instrument was calibrated with recrystallized CuSO₄·5H₂O. Solid state electrical conductance of ligand and its complexes have been measured in their pellet forms over 313–473 K range using a digital instrument. The antibacterial activities of ligand and its metal complexes were tested against *S. aureus*, *E. coli*, *Pr. mirabilis* and *S. typhi* using agar diffusion method.

RESULTS AND DISCUSSION

The reaction of resdiacetophenone and S-benzylthiocarbamate in absolute ethanol yields the Schiff base (BSBZRD) (I), the formulation of which is supported by analytical and spectral data. Its ^1H NMR spectrum shows signals at 2.49, 4.59 and 10.80 ppm (δ) corresponding to methyl, methylene and -NH protons, respectively. The signals due to thiol (-S-H) and phenolic protons were observed at 1.10 and 12.70 ppm (δ). The multiplet signals in the range 7.3–7.9 ppm (δ) are due to characteristics feature of aromatic protons [8]. The IR spectrum of the Schiff base displays the $\nu(\text{C}=\text{N})$ and $\nu(\text{N}-\text{N})$ bands at 1633 and 930 cm^{-1} , respectively. The IR spectrum does not display the $\nu(\text{S}-\text{H})$ at 2600 cm^{-1} suggesting that in the solid state Schiff base remains in the thioketo form IA but in solution it may remain as an equilibrium mixture of both the thioketo IA and thiol IB tautomeric forms:



The reaction of Schiff base (BSBZRD) with metal ions yielded complexes, which are found to be quite stable in the atmosphere and non-hygroscopic in nature. The Mn(II), Fe(II), Co(II) and Ni(II) complexes are insoluble in water and common organic solvents. While Cu(II), Zn(II), Cd(II) and VO(IV) complexes are partly soluble in DMSO. The physical data of the complexes are presented in Table 1. All the compounds gave satisfactory C, H, N and S analysis and agree well with the stoichiometry and proposed chemical formulae of the complexes.

Table 1. Physical and electrical conductivity data of metal complexes.

Sr. No.	Compound	Colour	Electrical Conductivity (σ) ($\text{ohm}^{-1} \text{cm}^{-1}$)	Ea (eV)
1.	BSBZRD $\text{C}_{26}\text{H}_{26}\text{O}_2\text{N}_4\text{S}_4$	Greenish yellow	3.11×10^{-9}	0.275
2.	$[(\text{VO})_2(\text{BSBZRD}) \cdot (\text{H}_2\text{O})_2]$	Coffee	6.10×10^{-12}	0.375
3.	$[\text{Mn}(\text{BSBZRD})]_n$	Pale rose	1.26×10^{-11}	0.571
4.	$[\text{Fe}(\text{BSBZRD})]_n$	Light green	3.30×10^{-12}	0.403
5.	$[\text{Co}(\text{BSBZRD})]_n$	Candy	1.43×10^{-11}	0.736
6.	$[\text{Ni}(\text{BSBZRD})]_n$	Pale green	2.73×10^{-11}	0.700
7.	$[\text{Cu}_2(\text{BSBZRD}) \cdot (\text{H}_2\text{O})_2]$	Olive green	2.10×10^{-11}	0.695
8.	$[\text{Zn}_2(\text{BSBZRD}) \cdot (\text{H}_2\text{O})_2]$	Light brown	3.22×10^{-11}	0.530
9.	$[\text{Cd}_2(\text{BSBZRD}) \cdot (\text{H}_2\text{O})_2]$	Pale orange	4.85×10^{-10}	0.433

The strong band at 1633 cm^{-1} in the IR spectrum of ligand is assigned to $\nu(\text{C}=\text{N})$ stretch. This band is shifted to lower frequency by $15\text{--}50\text{ cm}^{-1}$ in complexes, indicating the coordination of azomethine nitrogen to the metal ion [9]. The increase in $\nu(\text{N}-\text{N})$ frequency from 930 cm^{-1} in the ligand to $935\text{--}945\text{ cm}^{-1}$ in the complexes provides further support for the participation of the azomethine nitrogen in coordination [10]. The new bands in the region $475\text{--}525\text{ cm}^{-1}$ in the complexes are attributable to $\nu(\text{M}-\text{N})$ vibration [11]. The ligand also exhibits a medium intensity band at 2920 cm^{-1} and this may be due to intramolecular hydrogen bonding of hydroxyl group [12]. Absence of this band in the complexes indicates the breaking of hydrogen bond followed by deprotonation and coordination of phenolic oxygen to metal ions [13]. This is further supported by the positive shift of C-O (phenolic) band from 1277 cm^{-1} to 1317 cm^{-1} in the spectra of complexes. This shift to higher energy is expected due to the maintenance of ring currents arising from the electron delocalization in the chelate ring. The appearance of a medium sharp band in the region $550\text{--}605\text{ cm}^{-1}$ is assignable to $\nu(\text{M}-\text{O})$ vibration [14]. The Schiff base displays a broad band at about 3040 cm^{-1} assignable to $\nu(\text{N}-\text{H})$ stretching frequency [15]. The ligand spectrum exhibits a band at 850 cm^{-1} attributable to thioamide ($\text{NHC}=\text{S}$) vibration [16].

The bands due to $\nu(\text{N}-\text{H})$ and $\nu(\text{C}=\text{S})$ disappear in the complexes, suggesting coordination through the thioenolate sulphur [17]. This may result from the thioenolization and deprotonation of the thioamide group ($-\text{NHC}=\text{S} \rightleftharpoons -\text{N}=\text{C}-\text{SH}$). The mode of coordination *via* thioenolate sulphur is manifested by the appearance of new bands in the region $320\text{--}355\text{ cm}^{-1}$ due to $\nu(\text{M}-\text{S})$ vibrations [18]. In the oxovanadium(IV) complex band due to $\nu(\text{V}=\text{O})$ mode [19] occurs at 997 cm^{-1} , which is in agreement with the usual range and rules out the presence of $\dots\text{V}=\text{O}\dots\text{V}=\text{O}\dots$ interactions [20]. The Cu(II), Zn(II), Cd(II) and VO(IV) complexes exhibit broad bands in the region $3400\text{--}3600\text{ cm}^{-1}$ together with weak but sharp bands around at $1500\text{--}1600\text{ cm}^{-1}$ indicating the presence of coordinated water molecules in these complexes [21] (Fig. 1).

The electronic spectrum of the VO(IV) complex shows three bands at 14285 , 16530 and 25000 cm^{-1} , which may be attributed to ${}^2\text{B}_2 \rightarrow {}^2\text{E}_1$, ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$ and ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$ transitions, respectively. Its magnetic moment value of 1.72 B.M. together with the electronic spectral features are consistent with a five-coordinate square pyramidal geometry [22]. The Mn(II) complex exhibits three weak absorption bands at 15486 , 18996 and 25941 cm^{-1} assignable to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g} ({}^4\text{G})$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g} ({}^4\text{G})$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g} {}^4\text{E}_g ({}^4\text{G})$ transitions, respectively for an octahedral stereo-chemistry. Its magnetic moment value of 5.17 B.M. indicates a high-spin six-coordinated structure [23]. The lower magnetic moment value than expected (5.92 B.M.) for five unpaired electrons may be due to partial air oxidation of Mn(II) \rightarrow Mn(III) during synthesis. The ligand field parameters like ligand field splitting energy (10 Dq), Racah inter-electronic repulsion parameter (B) and nephelauxetic ratio (β) have been calculated for the Mn(II) complex and values are given in Table 2. The B value is lower than the free ion value of Mn(II) (960 cm^{-1}) thereby indicating the orbital overlap and delocalization of d-orbitals. The β value is less than unity suggesting considerable amount of covalent character of the metal-ligand bond. The electronic spectrum of Fe(II) complex

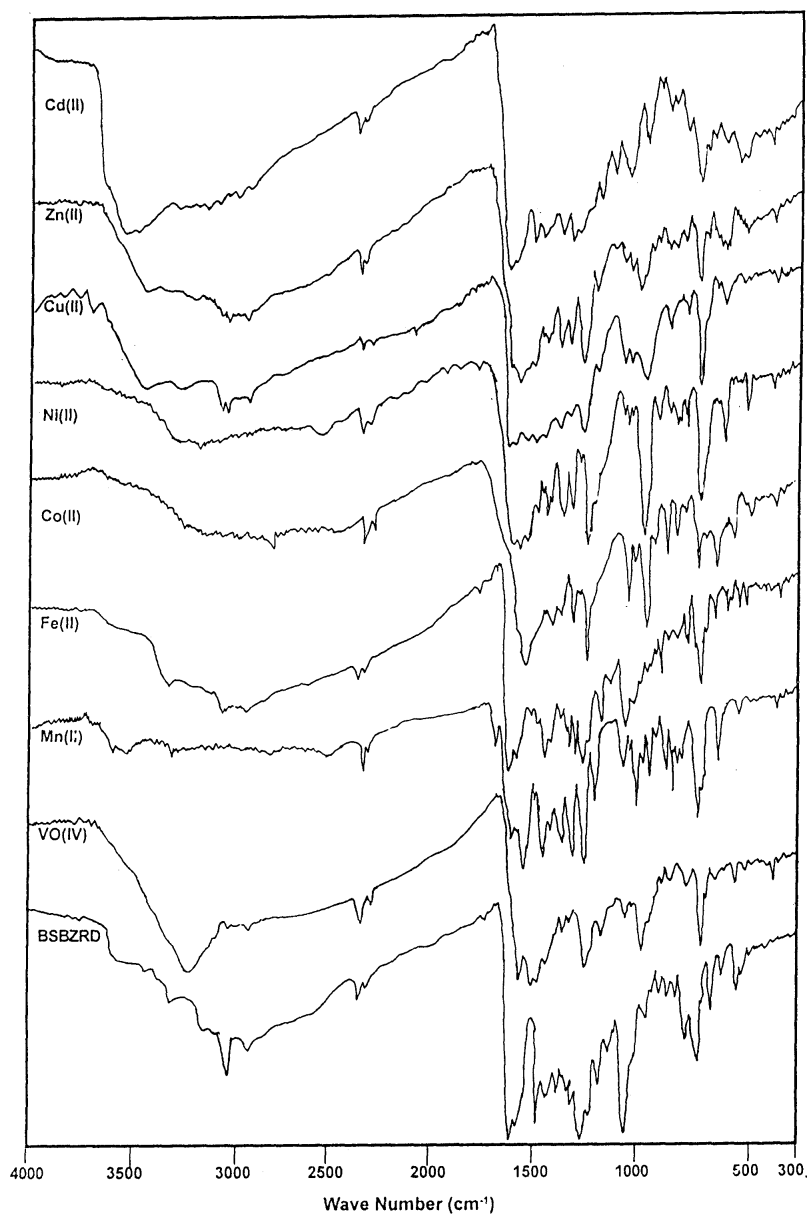


Figure 1. IR spectra of BSBZRD and its chelates.

exhibits bands at 10789, 15820 and 26259 cm^{-1} , which may be assigned to octahedral geometry. The first band may be due to ${}^5T_{2g} \rightarrow {}^5E_g$ transition [24], while other two bands may be of charge transfer transitions origin. The magnetic moment of 5.67 B.M. is found to be characteristic of high-spin octahedral geometry [25]. The crystal field parameters Dq , B , β and LFSE have been calculated for Fe(II) complex by using standard equations and are listed in Table 2. The electronic spectrum of Co(II) com-

plex shows three bands at 9010, 17990 and 19300 cm^{-1} corresponding to the transitions ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$, respectively, favouring an octahedral geometry [26]. Its magnetic moment value (4.60 B.M.) suggests the high-spin octahedral structure. The calculated values of ligand field parameters agreed with the values for octahedral Co(II) complexes. In case of Ni(II) complex three broad bands are observed at 10215, 16843 and 26661 cm^{-1} and may be assigned to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ transitions respectively, diagnostic of an octahedral field around Ni(II) ion. The magnetic moment value 2.90 B.M. for Ni(II) chelate falls in the range for an octahedral geometry [27]. The various ligands parameters are calculated from the observed electronic transitions and are reported in Table 2. Their values are in good agreement with reported values for octahedral Ni(II) complexes. The spectrum of Cu(II) complex shows three bands at 17690, 19210 and 24830 cm^{-1} , which can be assigned to ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$, ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ and charge transfer transitions respectively. The position of these bands indicates the square planar geometry for Cu(II) complex [28]. The observed magnetic moment value 1.70 B.M. of Cu(II) complex lies within the range of Cu(II) ions in a d^9 system. The Zn(II) and Cd(II) complexes being d^{10} ions are diamagnetic and do not show d-d transitions and may have tetrahedral geometry [29].

The thermal analysis of the prepared complexes were carried out in the temperature range 40–700°C in air atmosphere. All the complexes show a gradual weight-loss indicating decomposition by fragmentation with increasing temperature. The thermograms of the complexes show nearly the same pattern of decomposition reflecting their isostructural characteristics. The Cu(II), Zn(II), Cd(II) and oxovanadium(IV) complexes exhibit the weight-loss between 160–230°C corresponding to about 5.04, 5.00, 4.43 and 5.20% respectively. This value fits midway with the loss of two coordinated water [30] molecules in these complexes. Mn(II), Fe(II), Co(II), and Ni(II) complexes are stable up to 230°C indicating the absence of any water molecules. The complete decomposition of metal complexes takes place in two steps. The first step starts at about 250°C and complete at about 450°C, while second and major mass loss occurs between 450–650°C. The remaining residue of the complexes at ~700°C corresponds to the respective metal oxides (Fig. 2).

From the thermal decomposition data of the complexes, the kinetic and thermodynamic parameters such as activation energy (Ea), free energy change (ΔF), entropy of activation (S^*) and frequency factor (Z) were calculated by adopting Freeman-Carroll, Sharp-Wentworth and Coats-Redfern methods [31–33]. The results with an accuracy of ± 0.05 are summarized in Table 3. On the basis of experimental findings, the relative stability can be recognized as: VO(IV) > Cd(II) > Zn(II) > Ni(II) > Mn(II) > Co(II) > Fe(II) > Cu(II) > BSBZRD. The negative values of entropy of activation (S^*) for the complexes suggest that the activated complex has more ordered structure than the reactants and the reactions are slower than normal [34].

Table 2. Magnetic and electronic spectral data of metal complexes.

Sr. No.	Complex	μ_{eff} (B.M.)	Absorption bands (cm^{-1})	Assignments	Ligand field parameters					
					Dq (cm^{-1})	B (cm^{-1})	β	β %	ν_2/ν_1	LFSE (kJ mol^{-1})
1.	[(VO) ₂ (BSBZRD)·(H ₂ O) ₂]	1.72	14285	² B ₂ → ² E	–	–	–	–	–	–
			16530	² B ₂ → ² B ₁	–	–	–	–	–	–
			25000	² B ₂ → ² A ₁	–	–	–	–	–	–
2.	[Mn(BSBZRD)] _n	5.17	15486	⁶ A _{1g} → ⁴ T _{1g} (⁴ G)	1548.6	501	0.521	–	1.17	–
			18996	⁶ A _{1g} → ⁴ T _{2g} (⁴ G)						
			25941	⁶ A _{1g} → ⁴ A _{1g} ⁴ E _g (⁴ G)						
3.	[Fe(BSBZRD)] _n	5.67	10789	⁵ T _{2g} → ⁵ E _g	1078.9	583.2	0.566	–	–	51.79
			15820	C.T.						
			26259	C.T.						
4.	[Co(BSBZRD)] _n	4.60	9010	⁴ T _{1g} (F) → ⁴ T _{2g} (F)	1013.4	760	0.678	32.14	2.12	72.96
			17990	⁴ T _{1g} (F) → ⁴ A _{2g} (F)						
			19300	⁴ T _{1g} (F) → ⁴ T _{1g} (P)						
5.	[Ni(BSBZRD)] _n	2.90	10215	³ A _{2g} (F) → ³ T _{2g} (F)	1021.5	857.3	0.793	26.57	1.65	147.1
			16843	³ A _{2g} (F) → ³ T _{1g} (F)						
			26661	³ A _{2g} (F) → ³ T _{1g} (P)						
6.	[Cu ₂ (BSBZRD)·(H ₂ O) ₂]	1.70	17690	² B _{1g} → ² A _{1g}	–	–	–	–	–	–
			19210	² B _{1g} → ² E _g						
			24830	C.T.						

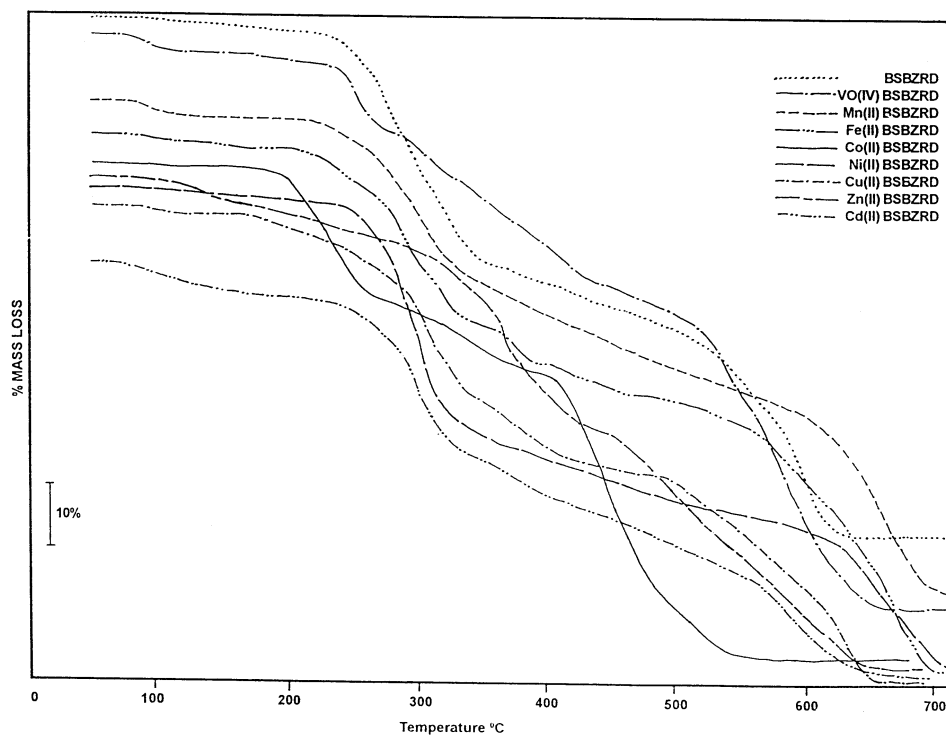


Figure 2. Thermogravimetric analysis of BSBZRD and its chelates.

Table 3. Thermal data of BSBZRD complexes.

Sr. No.	Compound	Dec. Temp. (°C)	Method	Ea (kJ mol ⁻¹)	ΔF (kJ mol ⁻¹)	S* (JK ⁻¹ mol ⁻¹)	Z (S ⁻¹)
1.	BSBZRD C ₂₆ H ₂₆ O ₂ N ₄ S ₄	185	FC	15.1	112.5	282.0	2.5 × 10 ⁻²
			SW	17.0	85.6	283.4	2.2 × 10 ⁻²
			CR	19.1	97.8	280.1	3.1 × 10 ⁻²
2.	[(VO) ₂ (BSBZRD) · (H ₂ O) ₂]	240	FC	21.9	117.6	286.4	1.7 × 10 ⁻²
			SW	21.5	88.8	286.4	1.7 × 10 ⁻²
			CR	17.4	95.6	278.4	4.6 × 10 ⁻²
3.	[Mn(BSBZRD)] _n	250	FC	18.7	116.0	279.8	3.6 × 10 ⁻²
			SW	18.0	87.9	279.7	3.6 × 10 ⁻²
			CR	16.0	95.7	284.2	2.1 × 10 ⁻²
4.	[Fe(BSBZRD)] _n	195	FC	15.1	112.5	286.4	1.7 × 10 ⁻²
			SW	23.9	91.4	271.5	1.3 × 10 ⁻²
			CR	21.3	99.2	270.6	1.2 × 10 ⁻²

Table 3 (continuation)

5.	[Co(BSBZRD)] _n	280	FC	15.7	111.1	281.0	3.0×10 ⁻²
			SW	16.0	86.2	280.9	3.0×10 ⁻²
			CR	12.8	93.4	283.1	2.3×10 ⁻²
6.	[Ni(BSBZRD)] _n	210	FC	19.1	114.9	277.7	3.8×10 ⁻²
			SW	21.5	89.9	250.7	5.4×10 ⁻²
			CR	17.1	98.3	277.6	3.8×10 ⁻²
7.	[Cu ₂ (BSBZRD)·(H ₂ O) ₂]	205	FC	15.1	110.6	277.8	4.3×10 ⁻²
			SW	12.8	82.9	277.8	4.3×10 ⁻²
			CR	16.0	102.7	270.4	1.1×10 ⁻²
8.	[Zn ₂ (BSBZRD)·(H ₂ O) ₂]	260	FC	19.1	115.2	278.2	4.2×10 ⁻²
			SW	23.4	87.8	272.2	8.7×10 ⁻²
			CR	21.3	99.0	273.3	7.6×10 ⁻²
9.	[Cd ₂ (BSBZRD)·(H ₂ O) ₂]	300	FC	19.2	135.5	275.6	5.3×10 ⁻²
			SW	17.2	88.2	275.6	5.3×10 ⁻²
			CR	15.5	96.2	271.6	5.3×10 ⁻²

FC = Freeman-Carroll, SW = Sharp-Wentworth, CR = Coats-Redfern.

The measurements of d.c. electrical conductivity of the Schiff base ligand and its metal complexes were carried out from room temperature to about 473 K. The results of electrical conductivity and activation energy are incorporated in Table 1. The general behaviour of electrical conductivity (σ) obeys the relation $\sigma = \sigma_0 \exp(-E_a/kT)$, where σ_0 is a constant, E_a is the activation energy of conduction process, T is the absolute temperature and k is the Boltzmann constant. The plots of $\log \sigma$ versus $1/T$ for all the complexes are found to be linear over a studied temperature range indicating the semiconducting nature of complexes [35]. The room temperature electrical conductivity of all the compounds lies in the range 3.11×10^{-9} to $6.10 \times 10^{-12} \text{ ohm}^{-1} \text{ cm}^{-1}$ also indicating their semiconducting behaviour [36]. The room temperature electrical conductivity decreases in the order BSBZRD > Cd > Zn > Ni > Cu > Co > Mn > VO > Fe, respectively, while the activation energy of electrical conduction lies in the range 0.275 to 0.736 eV. The higher value of electrical conductivity of the ligand as compared to its metal complexes may be attributed to the large number of delocalized π electrons, which may be responsible for carrying the current.

The ligand BSBZRD and its metal complexes have been tested for their effect on the growth of microbial cultures and studies for their interactive role with *Staphylococcus aureus*, *Escherichia coli*, *Proteus mirabilis* and *Salmonella typhi* using the "Agar Diffusion Method" [37]. The results are interpreted by measuring the zones of inhibition of growth of the bacterial culture used. The ligand shows sensitivity towards all the species except *E. coli*. Complexes of oxovanadium(IV) and Zn(II) are found to be resistant to all microorganisms except *S. typhi*. Only Ni(II) complex shows good activity against all the microorganisms, whereas Mn(II) and Cd(II) complexes are active against *S. aureus* and *S. typhi* but other strains are resistant. Similar-

ly Fe(II) and Cu(II) complexes show good activity towards all the microorganisms except *S. aureus*. Only Co(II) complex seems to be more active against *S. aureus*, while other strains are resistant to it. All the compounds show good activity against *Pr. mirabilis* and *S. typhi*. The variation in the effectiveness of different compounds against different organisms depends either on the impermeability of the cells of the microbes or differences in ribosomes of microbial cells. Normally, the inhibition activity of the compounds increases with increase in the concentration of the solution.

Acknowledgment

The authors thank the RSIC, IIT, Chennai and Punjab University, Chandigarh, India for spectral and analytical data. One of us (JTM) is thankful to UGC, New Delhi, India for the award of Teacher Fellowship.

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