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Preparation of Schiff's Base Complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) and Their Spectroscopic, Magnetic, Thermal, and Antifungal Studies[1]

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Abstract—The potassium salt of salicylidene-DL-alanine (KHL), bis(benzylidene)ethylenediamine (A^1), thiophene-*o*-carboxaldene-*p*-toluidine (A^2), and its metal complexes of the formula $[(M^{II}(L)(A)(H_2O)]$ (M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II); A = A^1 or A^2) are prepared. They are characterized by elemental analysis, magnetic susceptibility measurements, thermogravimetric analysis, and infrared and electronic spectral studies. The electronic spectral and magnetic moment data suggest an octahedral geometry for the complexes. All of these complexes, metal nitrates, fungicides (bavistin and emcarb), and ligands are screened for their antifungal activity against *Aspergillus niger*, *Fusarium oxysporum*, and *Aspergillus flavus* using a plate poison technique. The complexes show higher activity than those of the free ligands, metal nitrate, and the control (DMSO) and moderate activity against bavistin and emcarb.

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INTRODUCTION

Although numerous transition-metal complexes of Schiff's bases have been structurally characterized, relatively few free Schiff's bases have been similarly characterized [1]. A combination of distinctly different metal ion binding sites within one ligand can lead to materials with interesting new properties [2, 3], e.g., specific sensors, molecular wires, and magnetic and optical devices. Schiff's bases and their metal complexes have exhibited biological activity as antibiotics, antivirus, and antitumor agents because of their specific structure [4, 5]. Amino acid and sulfur-containing Schiff's base complexes derived from aldehyde are involved in a variety of biological processes, e.g., as catalysts of transamination, racemization, and carboxylation reactions [6, 7]. In some Schiff's base complexes, it has been observed that minor changes in the structure of the ligands containing hard/soft donor atoms, e.g., nitrogen, sulfur, and/or oxygen markedly affect the activity of the compounds [8, 9]. In continuation of earlier work [10], we report here the complexes of transition metal with Schiff's bases.

EXPERIMENTAL

All the chemicals and solutions used were of analytical grade. Metal nitrates, salicylaldehyde, benzaldehyde, DL-alanine, and *p*-toluidine were purchased from the E. Meark (India) Limited, Mumbai. Thiophene-*o*-carboxaldehyde was purchased from Lancaster (UK). Organic solvents were purified by recommended methods [11].

Potassium salt of salicylidene-DL-alanine. A solution of potassium hydroxide (10 mmol, 0.56 g) in 30 ml of absolute alcohol was added to (10 mmol, 0.8909 g) of DL-alanine. The mixture was stirred until it had completely dissolved in an ethanol–KOH solution. Then, an ethanolic solution of salicylaldehyde (10 mmol, 1.22 g) was added quickly. The reaction was allowed to come to completion by stirring at 60°C for an hour. The product was crystallized out by diffusion of excess absolute diethyl ether into the solution. The product was filtered off and dried in a vacuum desiccator. The yield was 64%; mp 224°C.

Thiophene-*o*-carboxaldene-*p*-toluidine. An ethanolic solution (100 ml) of thiophene-*o*-carboxaldehyde (10 mmol, 1.12 g) and an ethanolic solution (100 ml) of *p*-toluidine (10 mmol, 1.07 g) in a mole ratio of 1 : 1 were mixed with constant stirring. Refluxing was carried out for 6 h. The solution was cooled overnight at room temperature. The formed yellow crystals were collected and dried in air. The yield was 60%; mp > 360°C.

Bis(benzylidene)ethylenediamine. The preparation of bis(benzylidene)ethylenediamine was carried out by refluxing a solution of benzaldehyde (2 mmol, 0.212 g) in 100 ml of ethanol and a solution of ethylenediamine (1 mmol, 0.069 g) in 100 ml of ethanol for 2–3 h. The reaction mixture gave Schiff's base in the form of yellow crystals. The product was filtered off,

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[1] The text was submitted by the authors in English.

Table 1. Analytical data of the ligands and complexes

Compound* (empirical formula)	Mol. wt.	Content (found/calcd), %					Mp, °C	Yield, %
		C	H	N	S	metal		
KHL ($C_{10}H_{10}KNO_3$)	231.19	51.99/51.94	4.42/4.32	6.23/6.05			224	64
A^1 ($C_{16}H_{16}N_2$)	236.16	81.32/81.36	6.78/6.77	11.83/11.85			235	72
A^2 ($C_{12}H_{11}NS$)	201.20	71.66/71.63	5.43/5.46	6.91/6.95	15.92/15.94		>360	58
$[Mn^{II}(L)(A^1)(H_2O)]$ ($C_{26}H_{27}N_3O_4Mn$)	500.20	62.46/62.42	5.33/5.39	8.40/8.39		10.96/10.98	>360	59
$[Co^{II}(L)(A^1)(H_2O)]$ ($C_{26}H_{27}N_3O_4Co$)	504.18	61.96/61.93	5.34/5.35	8.36/8.33		11.62/11.68	>360	64
$[Ni^{II}(L)(A^1)(H_2O)]$ ($C_{26}H_{27}N_3O_4Ni$)	503.95	61.93/61.96	5.37/5.35	8.32/8.33		11.61/11.64	>360	53
$[Cu^{II}(L)(A^1)(H_2O)]$ ($C_{26}H_{27}N_3O_4Cu$)	508.80	61.32/61.37	5.36/5.30	8.27/8.25		12.49/12.48	>360	55
$[Zn^{II}(L)(A^1)(H_2O)]$ ($C_{26}H_{27}N_3O_4Zn$)	510.65	61.11/61.14	5.26/5.28	8.26/8.22		12.79/12.80	>360	60
$[Cd^{II}(L)(A^1)(H_2O)]$ ($C_{26}H_{27}N_3O_4Cd$)	557.67	55.91/55.99	4.87/4.84	7.52/7.53		20.20/20.15	>360	61
$[Mn^{II}(L)(A^2)(H_2O)]$ ($C_{22}H_{22}N_2O_4SMn$)	465.22	56.71/56.79	4.76/4.72	6.08/6.01	6.82/6.89	11.76/11.80	>360	54
$[Co^{II}(L)(A^2)(H_2O)]$ ($C_{22}H_{22}N_2O_4SCo$)	469.21	56.34/56.31	4.62/4.68	5.92/5.96	6.84/6.83	12.59/12.55	>360	61
$[Ni^{II}(L)(A^2)(H_2O)]$ ($C_{22}H_{22}N_2O_4SNi$)	468.97	56.30/56.34	4.62/4.69	5.99/5.97	6.86/6.83	12.52/12.51	>360	60
$[Cu^{II}(L)(A^2)(H_2O)]$ ($C_{22}H_{22}N_2O_4SCu$)	473.82	55.78/55.76	4.65/4.64	5.95/5.90	6.74/6.76	13.46/13.41	>360	55
$[Zn^{II}(L)(A^2)(H_2O)]$ ($C_{22}H_{22}N_2O_4SZn$)	475.67	55.62/55.54	4.60/4.62	5.84/5.88	6.75/6.73	13.77/13.74	>360	59
$[Cd^{II}(L)(A^2)(H_2O)]$ ($C_{22}H_{22}N_2O_4SCd$)	522.69	50.45/50.55	4.22/4.20	5.33/5.35	6.11/6.13	21.58/21.50	>360	49

* KHL is potassium salt of salicylidene-DL-alanine; A^1 is bis(benzylidene)ethylenediamine; A^2 is thiophene-*o*-carboxaldene-*p*-toluidine (the same in Tables 2–4).

washed with ether, and dried in air. The yield was 72%; mp 235°C.

Synthesis of the complexes. The preparation of mixed-ligand complexes was carried out by mixing aqueous solutions (100 ml) of metal nitrate (10 mmol) and a hot methanolic solution of the potassium salt of salicylidene-DL-alanine (10 mmol, 2.31 g) and bis(benzylidene)ethylenediamine (10 mmol, 2.36 g) or thiophene-*o*-carboxaldene-*p*-toluidine (10 mmol, 2.01 g). The complexes were formed by heating the mixture in a water bath for 2 h at 60°C. The mixture was kept overnight at room temperature. Finally, the obtained colored crystals were collected by filtration, washed with water and ethanol, and dried in air.

Physical measurements. Infrared spectra were recorded on a FT-IR Nicolet 400D spectrophotometer as KBr pellets in the range 4000–400 cm^{-1}. Carbon, hydrogen, nitrogen, and/or sulfur elemental analyses were performed with a model 240 Perkin-Elmer elemental analyzer. The metal contents of the complexes were analyzed by EDTA titration [12] after decomposing the organic matter with a mixture of $HClO_4$, H_2SO_4, and HNO_3 (1 : 1.5 : 2.5). Thermogravimetric analyses were obtained with a model 5000/2960 SDTA, TA Instrument (USA). The reflectance spectra of the complexes were recorded in the range 1700–350 nm (as MgO discs) on a Beckman DK-2A spectrophotometer. The magnetic moments were measured by Gouy's method using mercury tetrathiocyanatocobaltate(II) as the calibrant ($\chi_g = 16.44 \times 10^{-6}$ cgs units at 20°C). The diamagnetic correction was made using Pascal's constant.

RESULTS AND DISCUSSION

The complexes were synthesized following the general procedures outlined by the following equations:

$$M(NO_3)_2 \cdot nH_2O + KHL + A \longrightarrow [M^{II}(L)(A)(H_2O)] + KNO_3 + HNO_3 + (n-1)H_2O.$$

The elemental analysis data and some physical properties of the complexes are listed in Table 1. The elemental analyses indicate that the complexes have the general formula $[M^{II}(L)(A)(H_2O)]$. All the complexes are insoluble in methanol, diethyl ether, ethanol, and DMF but soluble in DMSO.

IR spectra. The FT-IR spectra of the mixed-ligand complexes are quite complex owing to the presence of numerous bands of varying intensities, making the task of their assignment quite difficult. However, an attempt has been made to assign some of the important bands. The presence of coordinated water in the complexes is indicated in the range 3300–3450 cm^{-1} and bands at 690, 680, and 920 cm^{-1} assigned to the M–OH_2 band [13]. The strong band at 1635 cm^{-1} attributable to the C=N stretching vibration of ligands is shifted to a

Table 2. Electronic parameters of the cobalt(II) and nickel(II) complexes*

Complexes	Observed bands (cm^{-1})			ν_2/ν_1	B	β	β, deg	10Dq
	ν_1	ν_2	ν_3					
$[Co^{II}(L)(A^1)(H_2O)]$	9200	18050	19080	1.96	756	0.77	22	10665
$[Ni^{II}(L)(A^1)(H_2O)]$	10430	18000	23980	1.72	713	0.69	30	10430
$[Co^{II}(L)(A^2)(H_2O)]$	9130	18200	18970	1.99	754	0.77	22	10603
$[Ni^{II}(L)(A^2)(H_2O)]$	10270	18040	24600	1.75	788	0.76	24	10270

* The ligand-field splitting energy (10Dq), interelectronic repulsion parameter (B), and covalency factor (nephelauxetic ratio) (β) for the Co(II) and Ni(II) complexes were calculated using the secular equations given by E. König [28]:

for the Co(II) complexes

$$10Dq = 1/2\,[(2\nu_1 - \nu_3) + (\nu_3^2 + \nu_1\nu_3 - \nu_1^2)^{1/2}]$$

$$15B = \nu_3 - 2\nu_1 + 10Dq$$

$$\beta = B/B_0\ (B_0(\text{free ion}) = 971)$$

$$\beta,\ \text{deg} = (1 - \beta) \times 100$$

for the Ni(II) complexes

$$10Dq = \nu_1$$

$$15B = (\nu_2 + \nu_3) - 3\nu_1$$

$$\beta = B/B_0\ (B_0\ (\text{free ion}) = 1030)$$

$$\beta,\ \text{deg} = (1 - \beta) \times 100$$

region of 1605–1620 cm^{-1} in the complexes, indicating the coordination of the azomethine nitrogen [14]. In the free ligand, a strong band at 1525–1540 cm^{-1} due to ν(C–O)(phenolic) shifts to higher energy by 5–10 cm^{-1} in the complexes indicating the coordination of the phenolic oxygen atom to the metal ion [15]. Two strong and broad bands in the 1400–1600 cm^{-1} region in all the complexes are attributed to the $\nu_{as}(COO^-)$ (~1585 cm^{-1}) and $\nu_s(COO^-)$ (~1390 cm^{-1}) stretching vibrations of the coordinated carboxylate group [16].

The mode of coordination is further supported by the presence of a new band at ~425 cm^{-1} due to the $\nu(M–O)_{carbo}$ vibration [17]. The aromatic ν(C–H) and ν(C=C) bands are observed in a range of 750–780 and 1525–1535 cm^{-1}, respectively. The band in the range 1370–1380 cm^{-1} is due to $\nu(C–CH_3)$. In all the complexes, a new band is seen in the 460–485 cm^{-1} region, which is probably due to the formation of the M–N bond [18]. In all of the complexes, a medium and/or weak band observed in the 415–470 cm^{-1} range can be attributed to ν(M–O)[19]. The ν(C–S) [20–22] band of the thiophene-*o*-carboxaldene-*p*-toluidine observed at 765 cm^{-1} is shifted to lower frequency about 750 cm^{-1} in the spectra of the mixed-ligand complexes, indicating the participation of the sulfur atom of the thiophene ring in coordination. The new band in the region of 430–420 cm^{-1} can be assigned to the ν(M–S) mode [23].

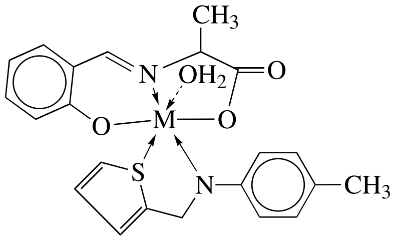
Magnetic measurements and electronic spectra. In order to obtain further structural information, the magnetic moments and electronic reflection spectra of the complexes were measured. The solid reflectance spectra of the Ni(II) complexes are consistent with the formation of an octahedral geometry with the appearance of three bands at ~23900, ~18000, and ~10400 cm^{-1} corresponding to the transitions $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)(\nu_3)$, $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)(\nu_2)$, and $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)(\nu_1)$. The magnetic moment values for Ni(II) are 2.91 and 2.88 μ_B and support the hexacoordinate configuration [24]. For the Co(II) complexes, the reflectance spectra exhibit the bands of medium intensity at ~19 000, ~18 050, and ~9200 cm^{-1}, which are assigned to the transitions $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)(\nu_3)$, $^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)(\nu_2)$, and $^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)(\nu_1)$, respectively, of an octahedral cobalt(II) complexes [25] and the magnetic moment values are 4.10 and 4.18 μ_B.

The electronic spectra of the Mn(II) complexes exhibit three weak absorption bands for the transitions $^6A_{1g} \longrightarrow {}^4T_{1g}\ (\nu_1)$ (~14.534 cm^{-1}), $^6A_{1g} \longrightarrow {}^4T_{2g}\ (\nu_2)$ (~19.600 cm^{-1}), and $^6A_{1g} \longrightarrow {}^4A_{1g}$, $^4E_g(\nu_3)$ (24.471 cm^{-1}). These absorptions are consistent with an octahedral geometry around Mn(II) in all of the complexes. The magnetic moment values of the Mn(II) complexes are 6.09 and 6.01 μ_B, suggesting an octahedral geometry [26]. The Cu(II) complexes display a broad band at ~15520 cm^{-1} due to the $^2E_g \longrightarrow {}^2T_{2g}$ transition. The Cu(II) complexes exhibit magnetic moments of 1.83 and 1.79 μ_B, respectively. These values are close to the spin-allowed values expected for a $S = 1/2$ system (1.73 μ_B) and may be indicative of an octahedral geometry around the Cu^{2+} ions [27]. The values of the electronic parameters, such as the ligand-field splitting energy (10Dq), Racah interelectronic repulsion parameter ($\boldsymbol{B}$), nephelauxetic ratio ($\boldsymbol{\beta}$), and ratio ν_2/ν_1, are presented in Table 2. The Zn(II) and Cd(II) complexes are diamagnetic and are likely to be

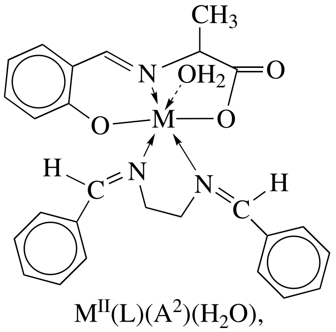
Table 3. Thermogravimetric data of the complexes

Complexes	*TG* range, °C	Mass loss (found/calcd), %		Assignment
$[Mn^{II}(L)(A^1)(H_2O)]$	150–180	3.52/3.59		Loss of coordinated water molecule
	180–800	82.27/82.22	14.12/14.18	Loss of ligand and leaving metal oxide residue
$[Co^{II}(L)(A^1)(H_2O)]$	150–180	3.50/3.57		Loss of coordinated water molecule
	180–800	79.93/79.98	16.40/16.44	Loss of ligand and leaving metal oxide residue
$[Ni^{II}(L)(A^1)(H_2O)]$	150–180	3.59/3.57		Loss of coordinated water molecule
	180–800	81.66/81.60	14.84/14.82	Loss of ligand and leaving metal oxide residue
$[Cu^{II}(L)(A^1)(H_2O)]$	150–180	3.51/3.53		Loss of coordinated water molecule
	180–800	80.83/80.82	15.68/15.63	Loss of ligand and leaving metal oxide residue
$[Zn^{II}(L)(A^1)(H_2O)]$	150–180	3.57/3.52		Loss of coordinated water molecule
	180–800	80.50/80.53	15.90/15.93	Loss of ligand and leaving metal oxide residue
$[Cd^{II}(L)(A^1)(H_2O)]$	150–180	3.26/3.22		Loss of coordinated water molecule
	180–800	73.77/73.74	23.06/23.02	Loss of ligand and leaving metal oxide residue
$[Mn^{II}(L)(A^2)(H_2O)]$	150–180	3.88/3.86		Loss of coordinated water molecule
	180–800	80.85/80.88	15.25/15.24	Loss of ligand and leaving metal oxide residue
$[Co^{II}(L)(A^2)(H_2O)]$	150–180	3.81/3.83		Loss of coordinated water molecule
	180–800	78.42/78.48	17.69/17.67	Loss of ligand and leaving metal oxide residue
$[Ni^{II}(L)(A^2)(H_2O)]$	150–180	3.84/3.83		Loss of coordinated water molecule
	180–800	80.23/80.23	15.91/15.92	Loss of ligand and leaving metal oxide residue
$[Cu^{II}(L)(A^2)(H_2O)]$	150–180	3.80/3.79		Loss of coordinated water molecule
	180–800	79.46/79.41	16.72/16.78	Loss of ligand and leaving metal oxide residue
$[Zn^{II}(L)(A^2)(H_2O)]$	150–180	3.71/3.78		Loss of coordinated water molecule
	180–800	79.18/79.10	17.17/17.11	Loss of ligand and leaving metal oxide residue
$[Cd^{II}(L)(A^2)(H_2O)]$	150–180	3.47/3.44		Loss of coordinated water molecule
	180–800	71.72/71.78	24.54/24.56	Loss of ligand and leaving metal oxide residue

of octahedral structure. The suggested structures of the complexes are the following:



$M^{II}(L)(A^1)(H_2O)$



$M^{II}(L)(A^2)(H_2O)$,

where M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II).

Thermogravimetric analyses. Thermogravimetric analyses of the prepared complexes were made in a N_2 in the temperature range of 50–800°C to establish their compositional differences, as well as to ascertain the nature of associated water molecules [29]. Thermogravimetric data are summarized in Table 3.

The *TG* curves of the Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) complexes show two decomposition steps within temperature ranges of 150–180 and 180–800°C, respectively, for Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) complexes. The first estimated mass losses for the $[M^{II}(L)(A^1)(H_2O)]$ complexes are (%): 3.52 (calcd. 3.59), 3.50 (3.57), 3.59 (3.57), 3.51 (3.53), 3.57 (3.52), and 3.26 (3.22) within temperature range of 150–180°C and can be attributed to the loss of coordinated water molecules [30] of the Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) complexes, respectively. The second estimated mass losses for the $[M^{II}(L)(A^1)(H_2O)]$ complexes are (%): 82.27 (calcd. 82.22), 79.93 (79.98), 81.66 (81.60), 80.83 (80.82), 80.50 (80.53), and 73.77 (73.74) within a temperature range of 180–800°C and can be attributed to the loss of ligand molecules of the Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) complexes, respectively. The masses of the remaining residue are (%): 14.12 (calcd. 14.18),

Table 4. Antifungal activities data of the complexes

Compounds	Growth diameter, mm/Inhibition, %		
	A. niger	*F. oxysporum*	*A. flavus*
DMSO (control)	29	46	39
Bavistin	00/100	00/100	00/100
Emcarb	00/100	00/100	00/100
KHL	19/34	31/32	27/30
A^1	22/23	34/27	26/32
A^2	20/31	31/32	29/25
$Mn(NO_3)_2 \cdot 4H_2O$	18/38	28/40	29/25
$Co(NO_3)_2 \cdot 6H_2O$	20/31	29/37	27/30
$Ni(NO_3)_2 \cdot 6H_2O$	22/23	31/32	29/25
$Cu(NO_3)_2 \cdot 3H_2O$	19/34	28/40	28/28
$Zn(NO_3)_2 \cdot 6H_2O$	22/23	30/35	27/30
$Cd(NO_3)_2 \cdot 4H_2O$	20/31	31/32	27/30
$[Mn^{II}(L)(A^1)(H_2O)]$	16/45	24/48	19/51
$[Co^{II}(L)(A^1)(H_2O)]$	11/62	20/57	19/51
$[Ni^{II}(L)(A^1)(H_2O)]$	11/62	25/46	20/49
$[Cu^{II}(L)(A^1)(H_2O)]$	12/59	21/54	19/51
$[Zn^{II}(L)(A^1)(H_2O)]$	13/55	20/57	18/54
$[Cd^{II}(L)(A^1)(H_2O)]$	15/48	25/46	20/49
$[Mn^{II}(L)(A^2)(H_2O)]$	14/52	20/57	18/54
$[Co^{II}(L)(A^2)(H_2O)]$	12/59	24/48	20/49
$[Ni^{II}(L)(A^2)(H_2O)]$	12/59	23/50	20/49
$[Cu^{II}(L)(A^2)(H_2O)]$	15/48	25/46	19/51
$[Zn^{II}(L)(A^2)(H_2O)]$	14/52	18/61	22/44
$[Cd^{II}(L)(A^2)(H_2O)]$	13/55	22/52	21/46

16.40 (16.44), 14.84 (14.82), 15.68 (15.63), 15.90 (15.93), and 23.06 (23.02), which correspond to metal oxides of the Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II), respectively.

Similarly, the first estimated mass losses for the $[M^{II}(L)(A^2)(H_2O)]$ complexes are (%): 3.88 (calcd. 3.86), 3.81 (3.83), 3.84 (3.83), 3.80 (3.79), 3.71 (3.78), and 3.47 (3.44) within a temperature range of 150–180°C and can be attributed to the loss of coordinated water molecules [30] of the Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) complexes, respectively. The second estimated mass losses for $[M^{II}(L)(A^2)(H_2O)]$ complexes are (%): 80.85 (calcd. 80.88), 78.42 (78.48), 80.23 (80.23), 79.46 (79.41), 79.18 (79.10), and 71.72 (71.78) within a temperature range of 180–800°C and can be attributed to the loss of ligand molecules of the Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) complexes, respectively. The masses of the remaining residue are (%): 15.25 (calcd. 15.24), 17.69 (17.67), 15.91 (15.92), 16.72 (16.78), 17.17 (17.11), and 24.54 (24.56), which correspond to metal oxides of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II), respectively.

Antifungal activity. The antifungal activity of the control (DMSO), fungicides (bavistin and emcarb), metal nitrates, ligands, and complexes were tested for their effect on the growth of microbial cultures and studied for their interaction with *A. niger, F. oxysporum*, and *A. flavus* using the plate poison technique [31]. A stock solution of 500 μg/ml was made by dissolving 50 mg of each compound in DMSO (100 ml). Sterilized medium with the added stock solution was poured into 90-mm sterile Petri plates, which were allowed to solidify. These were inoculated with a 5-mm actively growing mycelial disc and incubated at 27°C for 72 h. After inoculation and incubation, the percent reduction in radial growth and growth diameter over the control was calculated. All experiments were performed in triplicate. The complexes are soluble in DMSO. Therefore, the growth was compared with DMSO as the control. The control experiments were performed, where only equivalent volumes of solvents without added test compounds were added to the sterilized medium, and measured growth in a diameter (in mm) is expressed as growth diameter and percentage inhibition versus control.

The obtained data show that the complexes exhibit higher antifungal activity as compared to the control (blank), ligands, and metal salts. The complexes show moderate activity as compared to the standard fungicides (bavistin and emcarb). The results suggest that the changes in structure due to coordination in the complexes decrease the growth of microorganisms relative to the metal salt, ligands, and control. Hence, complexation increases antifungal activity due to the presence of azomethine(C=N) and/or sulfur groups [32]. The data are recorded in Table 4.

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