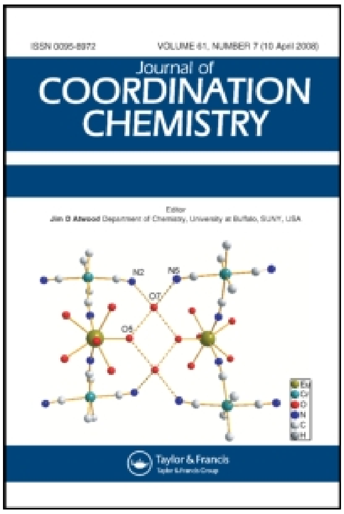

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Synthesis and physico-chemical studies of metal(II) complexes with diacetyl benzaldehyde acyldihydrazones and their bio-activity

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Synthesis and physico-chemical studies of metal(II) complexes with diacetyl benzaldehyde acyldihydrazones and their bio-activity

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Complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with diacetyl benzaldehyde oxalic acid dihydrazone (dbodh), $CH_3COC(CH_3){=}NNHCOCONHN{=}CHC_6H_5$ and diacetyl benzaldehyde malonic acid dihydrazone (dbmdh), $CH_3COC(CH_3){=}NNHCOCH_2CONHN{=}CHC_6H_5$ of general composition [M(dbodh)Cl]Cl and [M(dbmdh)Cl]Cl were synthesized and characterized by microanalyses, molar conductance, magnetic susceptibility, UV–Vis, ESR and IR spectra and X-ray diffraction studies. The complexes are 1 : 1 electrolytes in DMF and are insoluble in water and common organic solvents. The dbodh and dbmdh are neutral tridentate ligands in most complexes and coordinate via one >C=O and two >C=N– groups. In Cu(II) complexes the ligands are pentadentate coordinating through three >C=O and two >C=N– groups. The magnetic moment values and UV–Vis spectra suggest square-planar geometry for Co(II) and Ni(II) complexes and distorted octahedron for both Cu(II) complexes. The ESR spectra of Cu(II) complexes show well-defined copper hyperfine lines in DMSO solution at 120 K and exhibit $d_{x^2-y^2}$ as the ground state. The X-ray diffraction parameters for [Ni(dbodh)Cl]Cl and [Co(dbmdh)Cl]Cl correspond to a tetragonal crystal lattice. The complexes show significant antifungal activity against *Alternaria* sp., *Curvularia* sp. and *Colletotrichum* sp. and fair antibacterial activity against *Bacillus subtilis* and *Pseudomonas fluorescence*.

Keywords: Benzaldehyde acyldihydrazones; Metal(II) complexes; Antifungal; Antibacterial activity; Synthesis

1. Introduction

Metal ions play important roles in the synthesis and transport of organic molecules in living organisms and in catalyzing acid-base redox processes in biological systems [1]. Proteins are important binding sites for metal ions. Metals in proteins sometimes stabilize the ternary structure of metalloenzymes but more often have vital roles in catalytic processes.

Superoxide dismutase has normal Cu(II) enzyme active sites containing tetragonally coordinated Cu(II). The "blue" copper sites [2] are generally involved in electron transfer, with the copper cycling between +1 and +2 oxidation states [3]. There is spectroscopic evidence for nickel–methyl complexes in carbon monoxide

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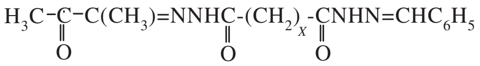
dehydrogenase (CODH) of anaerobic bacteria [4]. The interaction of Co(II) complexes in solution with O_2 has been the subject of intense study, some as reversible carriers of O_2, and have been used as models for natural oxygen transport systems [5]. Polydentate Co(II) complexes with ligands capable of intercalation into DNA strands are capable of inducing DNA cleavage under photo-chemical conditions [6]. A number of diseases and cogenital disorders have been traced due to zinc deficiency [7]. Cadmium is one of the five most toxic metals and accumulates in the kidneys, liver and blood vessels [8].

The metal complexes formed by the combination of a transition metal ion with a potent acyldihydrazone ligand should be more biologically active than the metal salts or the ligand individually. Therefore, we report here the synthesis and characterization of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes with diacetyl benzaldehyde oxalic acid dihydrazone and diacetyl benzaldehyde malonic acid dihydrazone ligands. The antifungal and antibacterial properties of the ligands and their complexes were also tested.



$$H_3C\text{-}\underset{\underset{O}{\parallel}}{C}\text{-}C(CH_3)\text{=}NNH\underset{\underset{O}{\parallel}}{C}\text{-}(CH_2)_x\text{-}\underset{\underset{O}{\parallel}}{C}NHN\text{=}CHC_6H_5$$

(where $x = 0$ for dbodh and 1 for dbmdh)

2. Experimental

2.1. *Materials*

All chemicals were of BDH or equivalent grade. Oxalic acid dihydrazide (odh), $(CONHNH_2)_2$, m.p. 232°C (lit. 232°C) and malonic acid dihydrazide (mdh), $CH_2(CONHNH_2)_2$, m.p. 150°C (lit. 152°C) were prepared by the literature method [9]. The metal salts $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $ZnCl_2 \cdot H_2O$, $CdCl_2 \cdot H_2O$, hydrazine hydrate, diacetyl, benzaldehyde, dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) were obtained from S.D. Fine-Chem Limited, Mumbai (India).

2.2. *Synthesis of the ligands*

For the synthesis of diacetyl benzaldehyde oxalic acid dihydrazone (dbodh), $CH_3COC(CH_3){=}NNHCOCONHN{=}CHC_6H_5$ and diacetyl benzaldehyde malonic acid dihydrazone (dbmdh), $CH_3COC(CH_3){=}NNHCOCH_2CONHN{=}CHC_6H_5$, a mixture of ethanolic solution (50 mL) of diacetyl (10 mmol, 0.86 mL, density 0.981 $g\,mL^{-1}$) and benzaldehyde (10 mmol, 1.06 mL, density 1.054 $g\,mL^{-1}$) was reacted with a hot aqueous solution (50 mL) of oxalic acid dihydrazide (10 mmol, 1.18 g) and malonic acid dihydrazide (10 mmol, 1.32 g) separately in a round bottom flask. The reaction mixtures were stirred continuously for ~1 h on a magnetic stirrer at room temperature with shaking at regular intervals. The products were filtered under suction, purified by washing several times with hot water and then with ethanol. The pure ligands thus obtained were dried in a desiccator over anhydrous $CaCl_2$.

The ligands were characterized by elemental analyses (C, H, N), melting points and infrared spectra.

2.3. *Synthesis of the complexes*

Metal complexes of dbodh and dbmdh were synthesized by reacting 50 mL aqueous solutions containing 5 mmol each of $CoCl_2 \cdot 6H_2O$ (1.19 g), $NiCl_2 \cdot 6H_2O$ (1.19 g), $CuCl_2 \cdot 2H_2O$ (0.86 g), $ZnCl_2$ (0.68 g) and $CdCl_2 \cdot 2.5H_2O$ (1.19 g) with suspended solutions of dbodh (5 mmol, 1.39 g) and dbmdh (5 mmol, 1.44 g) in 50 mL aqueous ethanol (v/v, 1 : 1) separately in 1 : 1 (M : L) molar ratio in a round bottom flask. The cobalt(II), nickel(II) and copper(II) complexes were obtained as colored precipitates after stirring the reaction mixture on a magnetic stirrer for 3–4 h, while zinc(II) and cadmium(II) complexes precipitated immediately. The products thus obtained were filtered, washed thoroughly with hot water and finally with ethanol and then dried in a desiccator over anhydrous $CaCl_2$ at room temperature.

2.4. *Analyses and instrumentation*

Metal content was determined gravimetrically by a literature procedure [10] after digesting the organic matter with aqua regia and evaporating the residue to dryness with concentrated sulfuric acid. The chloride content was analyzed gravimetrically as silver chloride [10]. C, H, N data were determined on an Elementar Vario EL model elemental analyzer.

The molar conductances of 10^{-3} M solutions of the complexes in DMF were measured at room temperature on a Systronic Conductivity meter model–306. Room temperature magnetic susceptibilities of the complexes were determined on a Faraday balance using $Hg[Co(SCN)_4]$ as calibrant and corrected for diamagnetism [11]. IR spectra of the ligands and their metal complexes were recorded in KBr in the 4000–500 cm^{-1} range on a Vertex 70 (Bruker) spectrophotometer; electronic spectra were recorded in DMF on a Cintra 10 spectrophotometer. The X-band ESR spectra of Cu(II) complexes were recorded on an EMX 1444 EPR spectrometer at liquid nitrogen temperature (LNT) in DMSO solution and at room temperature (300 K) in solid state. Powder X-ray diffraction patterns were recorded on Iso Debye Flex 2002 apparatus using Cu-Kα radiations.

The analytical and physico-chemical data are given in tables 1–6.

2.5. *Bio-activity*

2.5.1. Antifungal activity. The ligands as well as their complexes were screened for antifungal activity against *Alternaria*, *Curvularia* and *Colletotrichum* species, isolated from infected organs of host plants on potato dextrose agar (potato 250 g + dextrose 20 g + agar 20 g) medium. The cultures of the fungi were purified by single spore isolation technique.

The solutions in different concentrations 0.5, 1.0 and 1.5 mg mL^{-1} of each compound in DMSO were prepared for testing against spore germination. A drop of the solution at each concentration was kept separately on glass slides. The conidia, fungal

Table 1. Analytical data of the ligands and their complexes.

Compound (Color)	Empirical formula (Formula weight)	M.P./D.P. (°C)	Analyses found (Calcd)%					Yield (%)	Λ_M in DMF ($\mathrm{Ohm^{-1}mol^{-1}cm^2}$)
			Metal	Cl	C	H	N		
dbodh (Creamy white)	$C_{13}H_{14}N_4O_3$ (274)	280			56.71 (56.93)	5.06 (5.11)	20.32 (20.44)	79	
dbmdh (White)	$C_{14}H_{16}N_4O_3$ (288)	210			58.10 (58.33)	5.47 (5.55)	19.25 (19.44)	86	
[Co(dbodh)Cl]Cl (Orange)	$C_{13}H_{14}N_4O_3Cl_2Co$ (404)	298	14.60 (14.60)	17.52 (17.57)	38.45 (38.61)	3.49 (3.47)	13.74 (13.86)	60	60.1
[Ni(dbodh)Cl]Cl (Pink)	$C_{13}H_{14}N_4O_3Cl_2Ni$ (404)	286	14.50 (14.60)	17.60 (17.57)	38.51 (38.61)	3.48 (3.47)	13.79 (13.86)	66	70.7
[Cu(dbodh)Cl]Cl (Yellow-green)	$C_{13}H_{14}N_4O_3Cl_2Cu$ (408.5)	294	15.50 (15.54)	17.25 (17.38)	38.25 (38.19)	3.46 (3.43)	13.62 (13.71)	74	65.0
[Zn(dbodh)Cl]Cl (Yellow)	$C_{13}H_{14}N_4O_3Cl_2Zn$ (410)	282	15.66 (15.85)	17.30 (17.32)	38.16 (38.05)	3.41 (3.41)	13.62 (13.66)	71	68.2
[Cd(dbodh)Cl]Cl (Yellow)	$C_{13}H_{14}N_4O_3Cl_2Cd$ (457.5)	290	24.52 (24.59)	15.50 (15.52)	33.92 (34.10)	3.09 (3.06)	12.16 (12.24)	68	71.3
[Co(dbmdh)Cl]Cl (Light orange)	$C_{14}H_{16}N_4O_3Cl_2Co$ (418)	226	14.10 (14.11)	16.87 (16.98)	40.36 (40.19)	3.85 (3.83)	13.33 (13.40)	71	67.1
[Ni(dbmdh)Cl]Cl (Light brown)	$C_{14}H_{16}N_4O_3Cl_2Ni$ (418)	228	14.00 (14.11)	16.90 (16.98)	40.28 (40.19)	3.79 (3.83)	13.45 (13.40)	62	72.4
[Cu(dbmdh)Cl]Cl (Greenish brown)	$C_{14}H_{16}N_4O_3Cl_2Cu$ (422.5)	222	15.15 (15.03)	16.90 (16.80)	39.71 (39.76)	3.64 (3.79)	13.18 (13.25)	79	66.8
[Zn(dbmdh)Cl]Cl (Light yellow)	$C_{14}H_{16}N_4O_3Cl_2Zn$ (424)	200	15.20 (15.33)	16.85 (16.75)	39.69 (39.62)	3.83 (3.77)	13.21 (13.21)	74	62.3
[Cd(dbmdh)Cl]Cl (Light yellow)	$C_{14}H_{16}N_4O_3Cl_2Cd$ (471.5)	220	23.70 (23.86)	15.00 (15.06)	35.51 (35.63)	3.44 (3.39)	11.78 (11.88)	69	69.2

Table 2. Magnetic moments and electronic spectral data of the complexes.

Complex	μ_{eff} (B.M.)	Band maxima (cm^{-1})
[Co(dbodh)Cl]Cl	2.60	22935
[Ni(dbodh)Cl]Cl	Diamagnetic	14045, 18348
[Cu(dbodh)Cl]Cl	1.72	15500
[Co(dbmdh)Cl]Cl	2.45	22470
[Ni(dbmdh)Cl]Cl	Diamagnetic	13225, 18050
[Cu(dbmdh)Cl]Cl	1.86	15035

reproducing spores (approx. 200) lifted with the help of an inoculating needle, were mixed in every drop of each compound separately. Each treatment was replicated thrice and a parallel DMSO solvent control was run concurrently on separate glass slides. All the slides were incubated in humid chambers at 25 ± 2°C for 24 h. Each slide was observed under the microscope for spore germination and percent germination was finally calculated.

2.5.2. Antibacterial activity. The antibacterial activities of the ligands and their complexes were studied against *Pseudomonas fluorescence* (Gram –ve) and *Bacillus subtilis* (Gram + ve) bacteria. Each of the compounds was dissolved in DMSO and solutions of 1.0 and 2.0 mg mL^{-1} were prepared separately. Article discs of Whatman filter article (No. 42) of uniform diameter were cut and sterilized in an autoclave. The article disc soaked in the desired concentration of the complex solution was placed aseptically in the Petri dishes containing nutrient agar media (agar 15 g + beef extract 3 g + peptone 5 g) seeded with *Bacillus* and *Pseudomonas* sp. bacteria separately. The Petri dishes were incubated at 32°C and the inhibition zones were recorded after 24 h incubation. Each treatment was replicated nine times.

A common standard antibiotic Ampicillin was also screened for antibacterial activity in the same solvent and at the same concentration. The percent Activity Index data for the metal complexes were calculated as follows:

$$\%\ \text{Activity Index} = \frac{\text{Zone of inhibition by test compound (diameter)}}{\text{Zone of inhibition by standard (diameter)}} \times 100$$

3. Results and discussion

The analytical data (table 1) of the metal complexes show that dbodh and dbmdh react with metal(II) salts in 1 : 1 (M : L) molar ratio to form complexes of [M(dbodh)Cl]Cl and [M(dbmdh)Cl]Cl, expressed by the following equation:

$$\text{MCl}_2 \cdot x\text{H}_2\text{O} + \underset{\substack{\text{or}\\ \text{dbmdh}}}{\text{dbodh}} \longrightarrow \underset{\substack{\text{or}\\ \text{[M(dbmdh)Cl]Cl}}}{\text{[M(dbodh)Cl]Cl}} + \text{HCl} + x\text{H}_2\text{O}$$

where M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II); $x = 0$–6.

The complexes are colored powders, generally insoluble in water, ethanol, methanol, benzene, chloroform, carbon tetrachloride and diethyl ether, but are soluble in more

Table 3. ESR and bonding parameters of Cu(II) complexes.

Complex	Temp. (K)	Medium	$A_{\parallel}$ (G)	$A_{\perp}$ (G)	A_{av} (G)	$g_{\parallel}$	$g_{\perp}$	g_{av}	α^2	α'^2	β_1^2
[Cu(dbodh)Cl]Cl	300	Solid state	–	–	$A_{iso} = 165$	–	–	$g_{iso} = 2.0867$	–	–	–
	120	DMSO solution	172	84	113	2.3352	2.0445	2.1414	0.87	0.15	0.95
[Cu(dbmdh)Cl]Cl	300	Solid state	142	139	140	2.3586	2.0852	2.1763	–	–	–
	120	DMSO solution	156	102	120	2.3459	2.0491	2.1481	0.81	0.22	0.98

Table 4. IR spectral data (cm^{-1}) and assignment of important bands.

Compound	ν(NH)	ν(C=O)	ν(C=N)	Amide II	Amide III	ν(N–N)
dbodh	3245m	1660b	1617s	1526s	1363s	966m
dbmdh	3214m	1656b	1619s	1562s	1372s	957w
[Co(dbodh)Cl]Cl	3246s	1659s, 1646m	1605s	1527s	1362s	979m
[Ni(dbodh)Cl]Cl	3245s	1660s, 1642m	1606s	1527s	1363s	986w
[Cu(dbodh)Cl]Cl	3245m	1645b	1607s	1511s	1372s	982w
[Zn(dbodh)Cl]Cl	3246b	1659m, 1639s	1606s	1525s	1362s	980m
[Cd(dbodh)Cl]Cl	3247m	1658b, 1647m	1600m	1520s	1365s	988m
[Co(dbmdh)Cl]Cl	3214s	1656s, 1638m	1609s	1563s	1371s	974w
[Ni(dbmdh)Cl]Cl	3216s	1657s, 1640m	1610s	1563s	1372s	979m
[Cu(dbmdh)Cl]Cl	3213m	1641b	1606s	1543s	1382s	978w
[Zn(dbmdh)Cl]Cl	3212s	1654s, 1637m	1608s	1561m	1371s	983w
[Cd(dbmdh)Cl]Cl	3214b	1656s, 1636m	1609s	1560s	1372s	978m

s = strong, w = weak, b = broad, m = medium.

Table 5. Observed and calculated Q and *hkl* values.

Powder patterns	Intensity	Angle°	d (Å)	Q_{obs} ($1/d^2$)	Q_{calc}	*hkl*
[Ni(dbodh)Cl]Cl						
1	36.40	10.95	8.073	0.0153	0.0153	100
2	32.57	13.25	6.677	0.0224	0.0224	001
3	38.31	16.85	5.257	0.0362	0.0377	101
4	100.00	24.09	3.691	0.0734	0.0767	120
5	60.92	25.75	3.457	0.0837	0.0838	021
6	81.23	26.55	3.355	0.0888	0.0897	002
7	47.89	30.55	2.924	0.1169	0.1204	112
8	33.33	35.65	2.516	0.1579	0.1534	130
9	28.74	40.45	2.228	0.2014	0.2018	003
10	25.29	54.20	1.691	0.3497	0.3589	004
[Co(dbmdh)Cl]Cl						
1	43.06	13.85	6.389	0.0245	0.0245	100
2	59.72	15.33	5.774	0.0299	0.0299	001
3	53.70	19.75	4.492	0.0495	0.0490	110
4	75.46	20.40	4.350	0.0528	0.0544	101
5	100.00	27.16	3.281	0.0929	0.0979	200
6	49.07	31.20	2.864	0.1219	0.1224	120
7	42.59	33.55	2.669	0.1404	0.1444	102
8	32.87	42.50	2.125	0.2214	0.2205	030
9	31.02	44.55	2.032	0.2422	0.2449	310
10	31.94	45.70	1.984	0.2540	0.2505	301

polar organic solvents DMF and DMSO. The complexes either melt or decompose between 200–298°C. All the complexes show molar conductance values between 60.1 to $72.4\,\Omega^{-1}\,\mathrm{mol}^{-1}\,\mathrm{cm}^2$ in 10^{-3} M DMF solution at room temperature, suggesting that they are 1 : 1 electrolytes [12].

3.1. *Magnetic moments*

The cobalt(II) complexes μ_{eff} values 2.60 and 2.45 B.M. are fairly close to those reported for one unpaired electron, suggesting square-planar geometry [13] (table 2). Both Ni(II) complexes are diamagnetic, suggesting square-planar geometry around Ni.

Table 6(a). Antifungal activity of the ligands and their complexes.

	% Inhibition of spore germination								
	Alternaria sp. (mg mL^{-1})			*Curvularia* sp. (mg mL^{-1})			*Colletotrichum* sp. (mg mL^{-1})		
Compound	0.5	1.0	1.5	0.5	1.0	1.5	0.5	1.0	1.5
dbodh	32	45	60	41	52	61	40	53	58
dbmdh	35	47	58	43	56	63	42	58	65
[Co(dbodh)Cl]Cl	54	75	87	52	75	84	55	63	82
[Ni(dbodh)Cl]Cl	56	77	89	55	78	83	52	76	88
[Cu(dbodh)Cl]Cl	60	80	93	59	82	94	63	70	97
[Zn(dbodh)Cl]Cl	58	82	90	62	84	96	65	72	95
[Cd(dbodh)Cl]Cl	60	86	96	61	80	97	65	78	100
[Co(dbmdh)Cl]Cl	55	72	90	53	72	89	52	60	91
[Ni(dbmdh)Cl]Cl	59	75	88	55	76	85	54	57	85
[Cu(dbmdh)Cl]Cl	56	82	97	63	77	95	62	79	98
[Zn(dbmdh)Cl]Cl	62	80	98	62	74	91	66	80	100
[Cd(dbmdh)Cl]Cl	65	84	100	66	80	96	70	86	100

Table 6(b). Antibacterial activity of the ligands, their complexes and standard drug.

	Diameter of inhibition zone (in mm)				% Activity index			
	Pseudomonas fluorescence (mg mL^{-1})		*Bacillus subtilis* (mg mL^{-1})		*Pseudomonas fluorescence* (mg mL^{-1})		*Bacillus subtilis* (mg mL^{-1})	
Compound	1.0	2.0	1.0	2.0	1.0	2.0	1.0	2.0
dbodh	3	4	3	4	23	29	27	31
dbmdh	4	5	3	5	31	36	27	38
[Co(dbodh)Cl]Cl	3	5	2	3	23	36	18	23
[Ni(dbodh)Cl]Cl	2	3	2	3	15	21	18	23
[Cu(dbodh)Cl]Cl	4	5	4	5	31	36	36	38
[Zn(dbodh)Cl]Cl	4	5	3	4	31	36	27	31
[Cd(dbodh)Cl]Cl	6	7	4	5	46	50	36	38
[Co(dbmdh)Cl]Cl	5	8	4	5	38	57	36	38
[Ni(dbmdh)Cl]Cl	6	7	3	4	46	50	27	31
[Cu(dbmdh)Cl]Cl	4	6	6	7	31	43	55	54
[Zn(dbmdh)Cl]Cl	5	7	6	7	38	50	55	54
[Cd(dbmdh)Cl]Cl	9	11	9	11	69	79	82	85
Ampicillin (standard drug)	13	14	11	13	100	100	100	100

The magnetic moments of the Cu(II) complexes correspond to μ_{eff} values for one unpaired electron (1.72 and 1.86 B.M.).

3.2. *Electronic spectra*

The square-planar Co(II) complexes generally exhibit a narrow band near 8500 cm^{-1} and a second stronger and broader band near 20,000 cm^{-1} due to $^2B_{2g} \rightarrow {}^2E_g$ (ν_1) and $\rightarrow {}^2A_{1g}$ (ν_2), respectively [14]. The bands observed at 22,935 cm^{-1} for [Co(dbodh)Cl]Cl and at 22,470 cm^{-1} for [Co(dbmdh)Cl]Cl indicate square-planar geometry for both complexes. The electronic spectra of Ni(II) complexes show two weak bands at 13225–14045 cm^{-1} and 18050–18348 cm^{-1} corresponding to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $\rightarrow {}^1B_{2g}$ transitions,

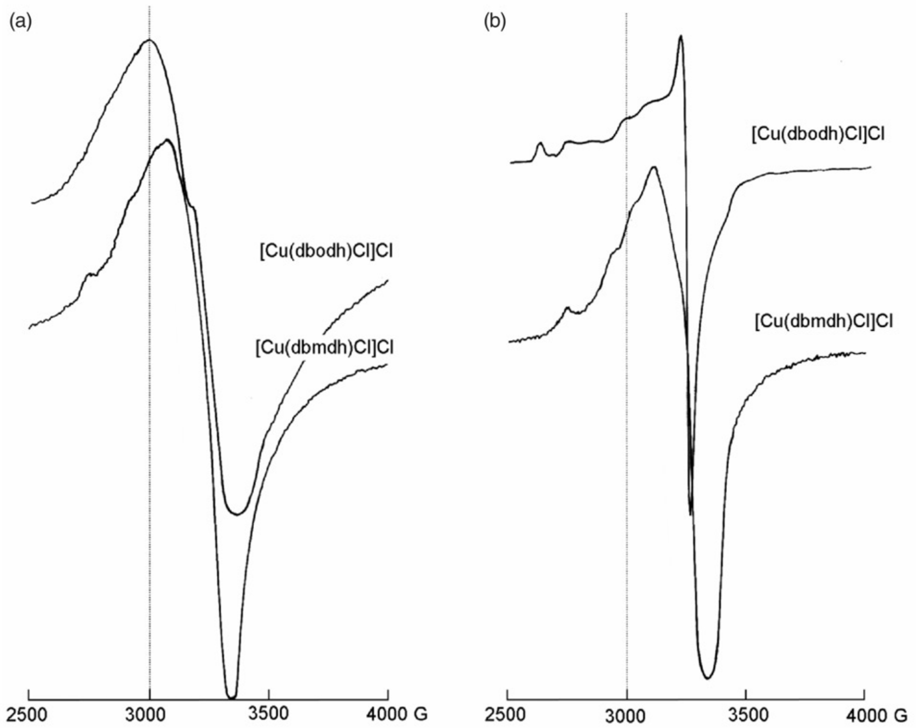


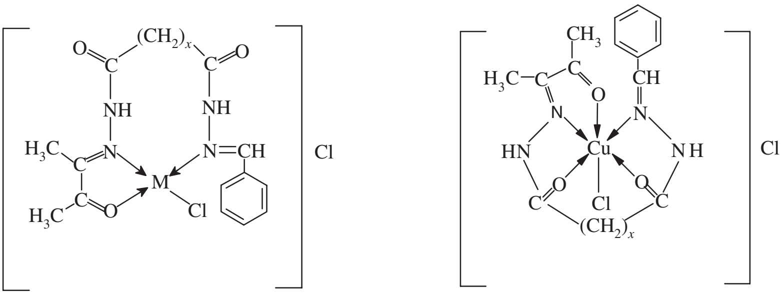
Figure 1. ESR spectra of copper(II) complexes (a) in solid state at 300 K, (b) in DMSO solution at 120 K.

comparable to those reported for Ni(II) square-planar complexes [15]. The Cu(II) complexes show an intense broad band in the region 15500 and 15035 cm^{-1}, respectively, for dbodh and dbmdh, which may be assigned to superimposed transitions $^2B_{1g} \rightarrow {}^2B_{2g}$ and $\rightarrow {}^2E_g$, suggesting a distorted octahedral geometry [16].

3.3. *ESR spectra*

ESR spectra of [Cu(dbodh)Cl]Cl in solid state at 300 K is isotropic with a broad signal having no hyperfine structure. The $g_{\mathrm{iso}} = 2.0867$ suggests a geometry involving grossly misaligned axes [17]. This may be due to dipolar exchange and unresolved hyperfine interactions in solid state [18]. [Cu(dbmdh)Cl]Cl shows an axial signal with two g values (figure 1) in solid state. Both g values ($g_{\|} = 2.3586$ and $g_{\perp} = 2.0852$) are >2.04 (table 3), indicating an elongated tetragonally distorted octahedral stereochemistry.

Both Cu(II) complexes in DMSO at 120 K show axial spectra with two anisotropic g values, $g_{\|} = 2.3352$, $g_{\perp} = 2.0445$ for dbodh complex and $g_{\|} = 2.3459$, $g_{\perp} = 2.0491$ for dbmdh complex, suggesting a tetragonally distorted octahedral geometry for both complexes. The spectra also show a set of four well-resolved copper hyperfine lines in the lower field region to allow accurate calculations of $g_{\|}$ and $A_{\|}$. The g_{av} and A_{av} values were calculated using the equations: $g_{\mathrm{av}} = (g_{\|} + 2g_{\perp})/3$; $A_{\mathrm{av}} = A_{\|} + 2A_{\perp})/3$. The trend $g_{\|} > g_{\perp} > g_e$ suggests the presence of the unpaired electron in a $\mathrm{d}_{x^2-y^2}$ orbital of copper [19, 20].



where M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II);
$x = 0$ for dbodh and 1 for dbmdh

Figure 2. General structures for the metal complexes.

Various bonding parameters α^2, α'^2 and β_1^2 calculated for the complexes (table 3) indicate increase in covalency after ligand coordination.

3.4. *IR spectra*

The ligands dbodh and dbmdh show a medium intensity band at 3245 cm^{-1} and 3214 cm^{-1}, respectively, due to >NH groups. In all the metal complexes ν(NH) occurs either at the same wavenumber as in the parent ligands or slightly altered, indicating no participation of >NH groups in bonding. ν(C=O) in the ligands appears as a broad band at 1660 cm^{-1} and 1656 cm^{-1}, respectively, in dbodh and dbmdh due to presence of three >C=O groups in each ligand. In most of the metal complexes ν(C=O) appears at the two positions, one nearly at the same wavenumber as in the parent ligand and the other ν(C=O) at considerably lower wavenumber (15–20 cm^{-1}), indicating the coordination of diacetyl >C=O with metal ion. A negligible change in position of amide II and amide III bands in these complexes compared to corresponding ligands further supports coordination of only diacetyl >C=O. In Cu(II) complexes, however, only one broad ν(C=O) is observed at lower wavenumber (15 cm^{-1}) compared to the parent ligand (table 4), indicating coordination of all three >C=O groups to metal [21]. This is further supported by a decrease in amide II frequency (15–19 cm^{-1}) and an increase in amide III frequency (9–10 cm^{-1}) in both Cu(II) complexes.

The ν(C=N) frequency at 1617 cm^{-1} and 1619 cm^{-1} in the spectra of dbodh and dbmdh, respectively, shifted to lower frequency (10–17 cm^{-1}) in all metal complexes suggesting coordination through two azomethine groups [22]. ν(N–N) observed at 966 cm^{-1} in dbodh and at 957 cm^{-1} in dbmdh shifts to higher frequency by 15–25 cm^{-1} in their metal complexes, indicating the coordination of one nitrogen of the hydrazone (–NHN=C<) group [23].

General structures for the metal complexes are proposed (figure 2).

3.5. *X-ray diffraction studies*

Since the complexes are insoluble in common organic solvents suitable for single crystal growth for X-ray analysis, X-ray powder diffraction patterns for two of the complexes were recorded and the prominent lines were indexed by Ito's method [24] (table 5). The following lattice constants were calculated:

$$[\mathrm{Ni(dbodh)Cl]Cl} \quad a = 6.38 \quad b = 6.38 \quad c = 5.77\ (\mathrm{A}^0)$$
$$[\mathrm{Co(dbmdh)Cl]Cl} \quad a = 8.07 \quad b = 8.07 \quad c = 6.67(\mathrm{A}^0)$$

The above values of lattice constants indicate a tetragonal crystal lattice for both complexes.

3.6. Antifungal activity

The experimental antifungal activity data [table 6(a)] indicate that the ligands as well as their complexes exhibit significant activity against *Alternaria* sp., *Curvularia* sp. and *Colletotrichum* sp. at 0.5, 1.0 and 1.5 $\mathrm{mg\,mL^{-1}}$ concentration. The antifungal results of the compounds were compared against DMSO as the control and are expressed as percentage inhibition *versus* control. However, DMSO control has shown negligible activity compared to the metal complexes and ligands. The metal complexes are appreciably more active than the ligands [25]. Their activity generally increases with increasing concentration of the compounds. The metal complexes are more active than the parent ligands. [Cd(dbmdh)Cl]Cl shows 100% activity against *Alternaria* sp. and *Colletotrichum* sp. at 1.5 $\mathrm{mg\,mL^{-1}}$. [Cd(dbodh)Cl]Cl and [Zn(dbmdh)Cl]Cl also show 100% activity against *Colletotrichum* sp. at 1.5 $\mathrm{mg\,mL^{-1}}$. On comparing the antifungal data of different metal complexes with same ligand, the toxicity, in general, varies in the order:

$$\mathrm{Cd} > \mathrm{Zn} > \mathrm{Cu} > \mathrm{Ni} > \mathrm{Co}$$

and the following order of fungal species:

Colletotrichum sp. > *Alternaria* sp. > *Curvularia* sp.

3.7. *Antibacterial activity*

The metal complexes, ligands, standard drug Ampicillin and DMSO solvent control were screened separately for their antibacterial activity against *Bacillus* sp. and *Psuedomonas* sp. at concentration of 1.0 and 2.0 $\mathrm{mg\,mL^{-1}}$. The activity generally increases with increasing concentration of complex [26]. The antibacterial results suggest that the ligands and their complexes [table 6(b)] show moderate activity against both bacteria [27, 28] as compared to Ampicillin. The metal complexes show higher antibacterial activity than the ligands. The DMSO control showed no activity against any bacterial strain. The % Activity Index data indicate that [Cd(dbmdh)Cl]Cl shows the highest activity (85%) against *Bacillus* sp. and (79%) against *Pseudomonas* sp. at the dose of 2.0 $\mathrm{mg\,mL^{-1}}$. Activity is more pronounced against *Bacillus* sp.

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