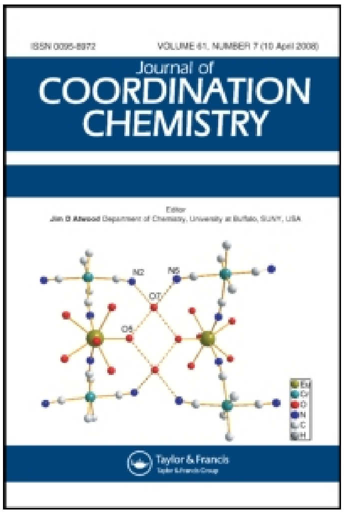

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Vinod P. Singh[a]; Parul Gupta[a]
[a] Chemistry Department, Institute of Engineering & Technology, Chhatrapati Shahu Ji Maharaj University, Kanpur-208024, India

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Synthesis, characterization and biocidal activities of some metal(II) complexes with diacetyl salicylaldehyde acyldihydrazones

VINOD P. SINGH* and PARUL GUPTA

Chemistry Department, Institute of Engineering & Technology, Chhatrapati Shahu Ji Maharaj University, Kanpur-208024, India

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Complexes of diacetyl salicylaldehyde oxalic acid dihydrazone, $CH_3COC(CH_3){=}NNHCOCONHN{=}CHC_6H_4(OH)$,(dsodh) and diacetyl salicylaldehyde malonic acid dihydrazone $CH_3COC(CH_3){=}NNHCOCH_2CONHN{=}CHC_6H_4(OH)$, (dsmdh) of general compositions [M(L)]Cl, [M′(L)Cl], [M(L′)]Cl and [M′(L′)Cl] (where M = Co(II), Cu(II), Zn(II), Cd(II) and M′ = Ni(II); HL = dsodh and HL′ = dsmdh) were prepared and characterized by elemental analyses, molar conductance, magnetic moments, electronic, ESR and infrared spectra and X-ray diffraction data. The magnetic moments and electronic spectra indicate six-coordinate octahedral geometry for Co(II) and square planar geometry for Ni(II) complexes. The ESR spectral data of Cu(II) complexes in DMF solution reveal a tetragonally distorted octahedral geometry. Both ligands bond through >C=O, >C=N and deprotonated phenolate groups in all octahedral complexes and through >C=N and deprotonated phenolate groups in Ni(II) square planar complexes. The lattice parameters for Cu(dsodh) and Co(dsmdh) correspond to an orthorhombic and Ni(dsodh) corresponds to a tetragonal crystal lattice.

The complexes show significant antifungal activity against a number of pathogenic fungi viz. *Stemphylium*, *Myrothecium* and *Alternaria*. The antibacterial activity was studied against *Pseudomonas fluorescence* (gram −ve) and *Clostridium thermocellum* (gram +ve).

Keywords: Diacetyl; Salicylaldehyde; Acyldihydrazones; Metal(II) complexes; Biocidal activity

1. Introduction

Schiff bases constitute an interesting class of chelating agents capable of coordination with one or more metal ions giving mononuclear as well as polynuclear metal complexes, which serve as model for metallo-protiens [1]. These complexes have a variety of applications such as corrosion inhibitors [2], photographic materials [3], antistatic additives for polyethylene, etc. [4]. A number of papers have been appeared [5–10] highlighting the flexible nature of Schiff base ligands, their analytical and biological properties.

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*Corresponding author. Email: singvp@yahoo.co.in

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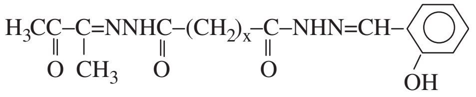
The Schiff base derived from acyldihydrazines $R(CONHNH_2)_2$ and two different >CO containing compounds, bond to the metal ions as monobasic or neutral ligands depending on the metal ion character and of the medium. Since such ligands contain three >C=O and two >C=N groups and can act as multidentate chelating agents, their complexes are likely to show different behaviour. We have synthesized Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes with the Schiff bases diacetyl salicylaldehyde oxalic acid dihydrazone and diacetyl salicylaldehyde malonic acid dihydrazone and characterized with the help of electronic spectra, magnetic moments, ESR spectra, infrared spectra and X-ray diffraction studies. The ligands and their complexes have also been screened for their antifungal and antibacterial activities.



(where $x = 0$ for dsodh and 1 for dsmdh).

2. Experimental

2.1. *Materials*

All the chemicals used were of BDH or equivalent grade. The precursor acyldihydrazines, oxalic acid dihydrazide (odh) and malonic acid dihydrazide (mdh) were prepared as reported [7] and were characterized by their melting points. odh m.p. 232°C (lit 232°C); mdh m.p. 150°C (152°C).

2.2. *Synthesis of the ligands*

The ligands diacetyl salicylaldehyde oxalic acid dihydrazone (dsodh) and diacetyl salicylaldehyde malonic acid dihydrazone (dsmdh) were prepared by reacting ethanolic solutions (25 mL) of diacetyl (8.6 mL, 0.1 mole), salicylaldehyde (12.2 mL, 0.1 mole) and aqueous solution (50 mL) of oxalic acid dihydrazide (11.8 g, 0.1 mole)/malonic acid dihydrazide (13.2 g, 0.1 mole) in 1 : 1 : 1 molar ratio. The reaction mixture was stirred for ~1 h and the product was filtered by suction. Since the ligands were sparingly soluble in common organic solvents, they were purified by washing several times with distilled water and then with ethanol.

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

2.3. *Synthesis of the complexes*

Metal complexes of dsodh and dsmdh were synthesized by reacting 50 mL aqueous solutions containing 10 mmol each of $CoCl_2 \cdot 6H_2O$ (2.3 g), $NiCl_2 \cdot 6H_2O$ (2.38 g), $CuCl_2 \cdot 2H_2O$ (1.71 g), $ZnCl_2$ (1.37 g) and $CdCl_2 \cdot 2.5H_2O$ (2.28 g) with 50 mL aqueous ethanolic solutions (v/v 1 : 1) 10 mmol each of dsodh (2.9 g) and dsmdh (3.04 g) at room temperature (25°C). Cu(II), Zn(II) and Cd(II) complexes precipitated immediately while Co(II) and Ni(II) complexes were formed after stirring the reaction solution for

6–8 h at room temperature (25°C). The complexes were filtered in a glass crucible by suction, purified by washing several times with aqueous ethanol and then dried in a desiccator over anhydrous $CaCl_2$.

2.4. *Analysis and instrumentation*

The complexes were analysed for metal gravimetrically by literature procedures [11] after decomposing the organic matter with a mixture of conc. nitric acid and hydrochloric acid and evaporating the residue to dryness with conc. sulphuric acid. The chloride content in the complex was determined gravimetrically as AgCl. C, H, N data were determined on an Elementar Vario EL model elemental analyzer from the 'Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow'. The molar conductance of 10^{-3} M solutions of the complexes in DMF was measured at room temperature on a Systronic Conductivity meter model-306. Room temperature magnetic susceptibilities were determined on a Faraday balance using $Hg[Co(SCN)_4]$ as calibrant and corrected for diamagnetism [12]. IR spectra were recorded in KBr on a Vector-22 Spectrophotometer and electronic spectra were recorded in DMF on a Perkin Elmer Lambda-2 Spectrophotometer. The X-band ESR spectra of Cu(II) complexes were recorded on a EMX 1444 EPR Spectrometer at liquid nitrogen temperature (LNT) in DMF solution. Powder X-ray diffraction patterns were recorded on an Iso Debye Flex 2002 apparatus using Cu-Kα radiation from the Indian Institute of Technology, Kanpur.

The analytical and physicochemical data are given in tables 1–6.

2.5. *Biocidal screening*

2.5.1. Antifungal activity. The ligands as well as their complexes were screened for antifungal activity against several fungi *Stemphylium*, *Myrothecium* and *Alternaria*. These species were isolated from the infected organs of the 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.

The solutions in different concentrations (0.5, 1 and 2 mg mL^{-1}) of each compound in DMSO were prepared for testing against spore germination. A drop of the solution of each concentration was kept separately on glass slides. The conidia, fungal 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 set 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 activity of the ligands and their complexes were studied against *Pseudomonas fluorescence* (gram −ve) and *Clostridium thermocellum* (gram +ve) bacteria. Each of the compounds was dissolved in DMSO and solutions of concentration 2.0, and 1.0 mg mL^{-1} were prepared separately. Paper discs of Whatman filter paper (No. 42) of uniform diameter were

Table 1. Analytical data and other general characteristics of ligands and their metal complexes.

Compound (Colour)	Empirical formula (Formula weight)	M.p./ Decomp. (°C)	Analysis found (Calcd)% Metal	Cl	C	H	N	Yield (%)	Molar conductance (Ω^{-1}mol^{-1}cm^2)
HL	$C_{13}H_{14}N_4O_4$	264			53.78	4.68	19.10	83	
(Light yellow)	(290)				(53.79)	(4.83)	(19.31)		
HL′	$C_{14}H_{16}N_4O_4$	206			55.04	5.16	18.13	82	
(Creamy white)	(304)				(55.26)	(5.26)	(18.42)		
[Co(L)]Cl	$C_{13}H_{13}N_4O_4$Cl.Co	272	15.33	9.08	40.48	3.18	14.38	57	76.6
(Orange)	(383.43)		(15.37)	(9.26)	(40.69)	(3.39)	(14.61)		
[Ni(L)Cl]	$C_{13}H_{13}N_4O_4$Cl.Ni	280	15.26	9.17	40.98	3.42	14.37	52	18.6
(Pinkish orange)	(383.19)		(15.32)	(9.26)	(40.71)	(3.39)	(14.61)		
[Cu(L)]Cl	$C_{13}H_{13}N_4O_4$Cl.Cu	290	16.45	9.03	40.09	3.18	14.39	57	74.5
(Yellow-green)	(388.05)		(16.38)	(9.15)	(40.20)	(3.35)	(14.43)		
[Zn(L)]Cl	$C_{13}H_{13}N_4O_4$Cl.Zn	276	16.57	8.89	40.17	3.21	14.28	56	72.2
(Yellow)	(389.87)		(16.57)	(9.10)	(40.01)	(3.33)	(14.36)		
[Cd(L)]Cl	$C_{13}H_{13}N_4O_4$Cl.Cd	220	25.48	8.02	35.98	2.83	12.74	51	70.1
(Light yellow)	(436.91)		(25.73)	(8.13)	(35.71)	(2.98)	(12.82)		
[Co(L′)]Cl	$C_{14}H_{15}N_4O_4$l.Co	210	14.56	8.73	42.08	3.58	13.94	54	80.2
(Light orange)	(399.43)		(14.75)	(8.89)	(42.06)	(3.76)	(14.02)		
[Ni(L′)Cl]	$C_{14}H_{15}N_4O_4$Cl.Ni	212	14.61	8.67	42.01	3.69	14.03	55	19.4
(Light orange)	(397.19)		(14.78)	(8.91)	(42.30)	(3.78)	(14.10)		
[Cu(L′)]Cl	$C_{14}H_{15}N_4O_4$Cl.Cu	216	15.58	8.64	41.59	3.54	13.92	61	77.8
(Green)	(402.05)		(15.81)	(8.83)	(41.78)	(3.73)	(13.92)		
[Zn(L′)]Cl	$C_{14}H_{15}N_4O_4$Cl.Zn	214	15.88	8.66	41.38	3.54	13.69	56	71.7
(Light yellow)	(403.87)		(16.19)	(8.79)	(41.60)	(3.71)	(13.87)		
[Cd(L′)]Cl	$C_{14}H_{15}N_4O_4$Cl.Cd	210	24.72	7.71	37.11	3.16	12.26	51	70.3
(Cream)	(450.91)		(24.93)	(7.87)	(37.26)	(3.33)	(12.42)		

where HL = dsodh and HL′ = dsmdh.

Table 2. Magnetic moments, electronic spectra and some ligand field parameters.

Compound	μ_{eff}	Band maxima (cm^{-1}) ν_1	ν_2	ν_3	10 Dq (cm^{-1})	B	β	β^0	LFSE
[Co(L)]Cl	4.76	10,100	16,660	20,580	10,050	695	0.71	29	22.90
[Ni(L)Cl]	0.15	13,510	18,250	–	13,510	–	–	–	–
[Cu(L)]Cl	1.75	15,385	–	–	15,385	–	–	–	26.29
[Co(L′)]Cl	4.68	9800	14,970	19,800	10,090	685	0.70	30	22.99
[Ni(L)′Cl]	0.18	14,860	17,330	–	14,860	–	–	–	–
[Cu(L′)]Cl	1.84	15,750	–	–	15,750	–	–	–	26.92

Table 3A. ESR parameters of Cu(II) complexes in solid state in room temperature.

Complex	$A_\parallel$	$A_\perp$	A_{av}	$g_\parallel$	$g_\perp$	g_{av}	G
[Cu(L)]Cl	–	–	$A_{\text{iso}} = 133$	–	–	$g_{\text{iso}} = 2.1161$	–
[Cu(L′)]Cl	140.74	100.00	113.58	2.3586	2.0597	2.1593	6.006

Table 3B. ESR and bonding parameters of Cu(II) complexes in DMF at LNT.

Complex	$A_\parallel$	$A_\perp$	A_{av}	$g_\parallel$	$g_\perp$	g_{av}	G	α^2	α'^2	β_1^2
[Cu(L)]Cl	161.67	110.37	127.47	2.3336	2.0533	2.1467	6.2589	0.81	0.22	0.97
[Cu(L′)]Cl	157.00	103.33	121.22	2.3107	2.0630	2.1208	4.9317	0.79	0.24	0.96

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

Compound	ν(OH + NH)	Amide I ν(C=O)	ν(C=N)	Amide II	Amide III	ν(N–N)	ν(C–O)	ν(M–O) phenolic
HL	3545b 3250b	1665b	1625s	1571s	1354s	964s	–	–
HL′	3480b 3217b	1661b	1620s	1569s	1365s	960s	–	–
[Co(L)]Cl	3250b	1645s	1613s	1545m	1369s	985b	1268s	529b
[Ni(L)Cl]	3249b	1666b	1612s	1570m	1356s	979w	1267s	530b
[Cu(L)]Cl	3251b	1642m	1609m	1542s	1376m	981w	1266s	525s
[Zn(L)]Cl	3248b	1645s	1606s	1556w	1361s	982m	1264s	531s
[Cd(L)]Cl	3251b	1647m	1610m	1547w	1368s	978s	1273s	531s
[Co(L′)]Cl	3216b	1640s	1608s	1559b	1374s	978s	1270s	560w
[Ni(L′)Cl]	3218b	1660b	1611m	1568m	1366m	976w	1268s	545s
[Cu(L′)]Cl	3217b	1638s	1606s	1536s	1385b	981m	1272s	560w
[Zn(L′)]Cl	3218b	1642b	1605s	1545m	1379m	976b	1272s	551m
[Cd(L′)]Cl	3220b	1640m	1610m	1548m	1381s	980s	1269s	558m

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

cut and sterilized on an autoclave. The paper 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 *Clostridium* and *Pseudomonas* sp. bacteria separately.

The petri dishes were incubated at 32°C and the inhibition zones were recorded after 24 h of incubation. Each treatment was replicated 9 times.

Table 5. Observed and calculated Q and hkl values.

Powder pattern	Intensity	Angle	d (Å)	Q_{obs}	Q_{Calcd}	hkl
[Cu(L)]Cl						
1	52.66	15.22	5.698365	0.0308	0.0308	100
2	64.33	17.25	5.139943	0.0378	0.0378	010
3	61.13	18.05	4.913710	0.0414	0.0414	001
4	74.37	23.06	3.857218	0.0672	0.0686	110
5	86.94	24.06	3.698954	0.0731	0.0722	101
6	80.50	25.06	3.553427	0.0792	0.0792	011
7	68.45	29.61	3.016486	0.1099	0.1100	111
8	64.64	31.07	2.878783	0.1207	0.1232	200
9	59.02	34.47	2.601937	0.1477	0.1512	020
[Co(L′)]Cl						
1	41.24	17.44	5.085313	0.0386	0.0386	100
2	90.49	18.76	4.731084	0.0446	0.0446	010
3	47.20	20.80	4.269584	0.0548	0.0548	001
4	99.02	26.22	3.398863	0.0865	0.0833	110
5	45.87	27.78	3.211329	0.0969	0.0935	101
6	48.07	28.51	3.130560	0.1020	0.0995	011
7	27.34	33.15	2.702712	0.1368	0.1382	111
8	26.33	38.12	2.360629	0.1794	0.1787	020
[Ni(L)Cl]						
1	27.15	14.34	6.178224	0.0262	0.0262	100
2	26.48	14.79	5.989671	0.0279	0.0279	001
3	31.71	20.18	4.399308	0.0517	0.0524	110
4	46.40	21.70	4.095917	0.0596	0.0541	101
5	100.00	24.12	3.690101	0.0734	0.803	111
6	39.83	29.06	3.072903	0.1059	0.1048	200
7	37.49	29.56	3.021632	0.1095	0.1116	002
8	25.38	32.24	2.776986	0.1297	0.1310	210
9	26.42	32.99	2.715034	0.1356	0.1327	201
10	24.30	33.39	2.683158	0.1389	0.1378	102
11	21.29	36.07	2.490255	0.1612	0.1589	211
12	22.20	36.87	2.437606	0.1683	0.1640	112
13	22.85	41.46	2.177850	0.2108	0.2096	220
14	23.00	41.97	2.152843	0.2158	0.2164	202
15	22.19	42.92	2.106990	0.2252	0.2358	300
16	20.62	44.74	2.025635	0.2437	0.2426	212
17	19.42	45.39	1.997900	0.2505	0.2511	003
18	21.03	46.05	1.970978	0.2574	0.2620	310
19	21.56	48.07	1.892886	0.2791	0.2773	103

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

Analytical data of the complexes indicate that the ligands diacetyl salicylaldehyde oxalic acid dihydrazone (dsodh) and diacetyl salicylaldehyde malonic acid dihydrazone (dsmdh) react with metal(II) chlorides in 1 : 1 molar ratio to give complexes of the

Table 6A. Antifungal activity of the complexes and their components.

	Inhibition of spore germination								
	Stemphylium sp. (mg mL^{-1})			*Myrothecium* sp. (mg mL^{-1})			*Alternaria* sp. (mg mL^{-1})		
Compound	0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0
HL	39.06	39.56	45.83	53.13	54.67	57.29	50.53	56.15	64.67
HL′	14.67	19.05	43.95	53.34	56.24	60.61	43.88	51.01	60.65
[Co(L)]Cl	40.75	46.67	48.29	64.99	69.2	71.79	54.22	55.79	61.32
[Ni(L)Cl]	37.99	50.34	62.87	43.45	52.28	75.76	50.54	66.99	73.34
[Cu(L)]Cl	48.32	56.68	64.18	63.99	64.78	71.4	50.85	55.03	70.08
[Zn(L)]Cl	49.46	63.34	68.46	56.89	59.16	60.61	59.46	61.46	73.02
[Cd(L)]Cl	51.68	61.22	77.89	54.99	65.00	69.93	58.78	59.54	63.47
[Co(L′)]Cl	40.75	49.73	67.15	65.82	67.44	69.34	40.42	42.19	62.17
[Ni(L′)Cl]	50.41	51.82	59.44	70.05	73.31	78.13	54.59	58.45	64.26
[Cu(L′)]Cl	49.37	59.37	61.22	62.97	68.27	72.73	59.6	62.64	71.68
[Zn(L′)]Cl	38.75	54.35	75.85	49.34	56.87	70.28	53.92	64.02	72.63
[Cd(L′)]Cl	47.99	59.04	71.08	62.98	64.15	74.87	43.04	50.54	62.54

Table 6B. Antibacterial activity of the complexes and their components.

	Diameter of inhibition zone				% Activity index			
	Pseudomonas fluorescence (mg mL^{-1})		*Clostridium thermocellum* (mg mL^{-1})		*Pseudomonas fluorescence* (mg mL^{-1})		*Clostridium thermocellum* (mg mL^{-1})	
Compound	1.0	2.0	1.0	2.0	1.0	2.0	1.0	2.0
HL	1.5	2.0	1.5	2.0	8.33	11.11	10.71	12.5
HL′	4.5	6.0	3.5	4.5	25.00	33.33	25.00	28.13
[Co(L)]Cl	4.0	5.0	4.0	5.0	22.22	27.77	28.57	31.25
[Ni(L)Cl]	2.0	5.2	6.0	8.0	11.11	28.88	42.85	50.00
[Cu(L)]Cl	3.0	5.0	4.0	5.0	16.66	27.77	28.57	31.25
[Zn(L)]Cl	4.0	5.0	4.5	6.0	22.22	27.77	32.14	37.5
[Cd(L)]Cl	7.5	9.5	8.5	9.5	41.66	52.77	57.14	58.12
[Co(L′)]Cl	8.0	9.0	6.0	7.0	44.44	50.0	42.85	43.75
[Ni(L′)Cl]	9.0	11.0	6.5	8.0	50.00	61.11	46.43	50.00
[Cu(L′)]Cl	8.5	10.0	5.5	7.0	47.22	55.55	39.29	44.37
[Zn(L′)]Cl	7.0	10.0	6.0	7.5	38.39	55.55	42.85	46.87
[Cd(L′)]Cl	8.0	12.0	10.5	9.0	44.44	66.67	53.57	56.25
Ampicillin	18.0	18.0	14.0	16.0	100.00	100.00	100.00	100.00

general compositions [M(L)]Cl, [M′(L)Cl], [M(L′)]Cl and [M′(L′)Cl] according to the following equations:

$$MCl_2 \cdot xH_2O + HL \text{ or } HL' \longrightarrow [M(L)]Cl \text{ or } [M(L')]Cl + HCl + xH_2O$$

$$M'Cl_2 \cdot xH_2O + HL \text{ or } HL' \longrightarrow [M'(L)]Cl \text{ or } [M'(L')Cl] + HCl + xH_2O$$

(where M = Co(II), Cu(II), Zn(II) and Cd(II), M′ = Ni(II); HL = dsodh and HL′ = dsmdh).

The complexes are stable solids, insoluble in water and common organic solvents such as methanol, ethanol, chloroform, carbon tetrachloride, diethyl ether, ethyl acetate and benzene but soluble in DMF and DMSO. The Co(II) complexes are orange, Ni(II) complexes pinkish orange, Cu(II) complexes yellow-green to green, and, Zn(II) and Cd(II) complexes are cream yellow. All the complexes melt with decomposition in the range 198–290°C.

All the complexes except Ni(II) show molar conductance values between 70.1 to 80.2 $\Omega^{-1}\,\mathrm{mol}^{-1}\,\mathrm{cm}^2$ in 10^{-3} M DMF solution at room temperature. These values indicate that the complexes are 1 : 1 electrolytes [13]. Ni(II) complexes are non-electrolytes.

3.1. *Magnetic moments*

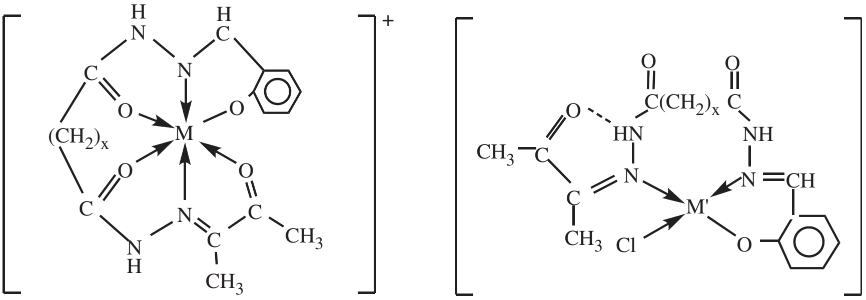
The μ_{eff} value observed for Co(dsodh) is reasonably close to that reported for three unpaired electrons in octahedral Co(II) [12]. Both Ni(II) complexes show extremely low magnetic moments (0.15 and 0.18 BM) indicating diamagnetic character. Square-planar stereochemistry is proposed for both the Ni(II) complexes similar to Ni(II) complexes of acetylacetone bis-acylhydrazones [14]. Where spin–spin coupling between unpaired electrons belonging to different copper ions is absent, μ_{eff} varies between 1.75 and 2.20. Cu(II) complexes with dsodh and dsmdh in this study show magnetic moments of 1.75 and 1.84 BM, respectively, indicating the presence of one unpaired electron [15].

3.2. *Electronic spectra*

The position of the bands observed at 10,100, 16,660 and 20,580 cm^{-1} in Co(dsodh) and at 9800, 14,970 and 19,800 in Co(dsmdh) suggest octahedral geometry for the Co(II) complexes where three transitions $^4T_{1g} \rightarrow {}^4T_{2g}$ $(\nu_1) \rightarrow {}^4A_{2g}$ (ν_2) and $\rightarrow {}^4T_{1g}(P)$ (ν_3) are possible [16]. The electronic spectra of Ni(II) complexes show two bands in the region 13,510–14,860 and 17,330–18,250 cm^{-1} corresponding to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $\rightarrow {}^1B_{2g}$ transitions. These transitions suggest a square-planar geometry similar to that reported for many Ni(II) complexes [14, 17]. The Cu(II) complexes show an intense broad absorption band centered at 15,385 and 15,750 cm^{-1}, respectively, for dsodh and dsmdh which may be assigned to superimposed transitions $^2B_{1g} \rightarrow {}^2B_{2g}$ and $\rightarrow {}^2E_g$ and suggest a distorted octahedral configuration [7]. The various ligand field parameters (10 Dq, β, β_0 and LFSE) are also calculated for Co(II) complexes which indicate a considerable covalent character of the M–L bonds [12].

3.3. *ESR spectra*

ESR spectra of the powdered sample of Cu(dsmdh) complex exhibit an axial signal with two g values at 298 K (figure 2). The axial signals were analysed by using the procedure of Hathaway and Billing [18]. The g_2 and $g_\perp$ values are >2.04, indicating copper(II) in axial symmetry with all the principle axes aligned parallel. This would be consistent with an elongated tetragonally distorted octahedral stereochemistry [18]. The G factor [defined as $G = (g_2 - 2)/(g_\perp - 2)$] is >4.0, suggesting that the local tetragonal axes are slightly misaligned and exchange interactions between copper(II) centers in the solid state are negligible. The dsodh complex exhibits isotropic spectra with intense broad signals with no hyperfine structure, perhaps due to dipolar exchange and unresolved



Where M = Co(II), Cu(II), Zn(II) and Cd(II); M' = Ni(II)
x = 0 for dsodh and 1 for dsmdh.

Figure 1. General structure of the metal complexes.

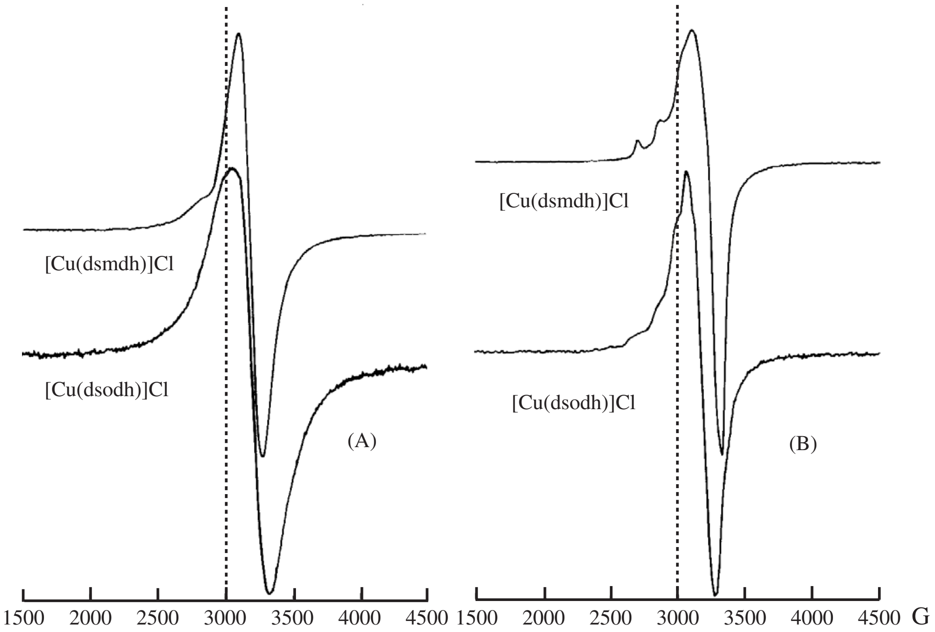


Figure 2. ESR spectra of Cu(II) complexes, (A) in solid state at 298 K, (B) in solution state at 120 K.

hyperfine interactions [19]. The g_{iso} value of 2.1161 suggests a geometry involving grossly misaligned axes.

The dsodh complex, which shows an isotropic spectrum at 298 K gives an axial signal at 120 K. The frozen DMF solution spectra of dsodh and dsmdh complexes show a well-defined hyperfine structure of four lines due to coupling of the electron with the nuclear spin ($I = 3/2$) of the copper atom (figure 1). The g_2, $g_\perp$ A_2 and $A_\perp$ values were accurately measured in the 120 K spectra. The g_{av} and A_{av} values were calculated using the equation; $g_{av} = (g_2 + 2g_\perp)/3$; $A_{av} = (A_2 + 2A_\perp)/3$. Moreover the observation that $g_2 > g_\perp > g_e$ (2.0023), shows that the unpaired electron is in the $d_{x^2-y^2}$ orbital of copper(II) and the spectral features are characteristic of axial symmetry [20].

No $\Delta Ms = 2$ transition at half field was observed for any of these complexes ruling out the possibility of dimerics [21].

Various bonding parameters [19] ($\alpha^2, \alpha'^2, \beta_1^2$) are calculated for both Cu(II) complexes. The α^2 values (0.81, 0.79) suggest appreciable covalency of the in-plane σ-bonding. The α'^2 values (0.22, 0.24) indicate the out of plane σ-bond strength increases with corresponding decrease in α^2 (table 3) suggesting that the axial σ-bonding decreases with corresponding increase in the in-plane σ-bonding. The β_1^2 values (0.97, 0.96) also indicate significant in-plane π bonding in these complexes.

3.4. *Infrared spectra*

The ligands dsodh and dsmdh show two broad bands centered at 3545, 3250 cm^{-1}, respectively, due to –OH and >NH groups. In the complexes ν(NH) bands either occur at nearly the same or slightly higher wavenumber as for the ligands suggesting no participation of the –NH group in bonding. The ν(OH) band is not observed in the metal complexes indicating deprotonation of phenolic OH during complexation.

A broad ν(C=O) band observed at 1665 cm^{-1} in dsodh and at 1661 cm^{-1} in dsmdh may be due to the presence of three >C=O groups in the ligands. In most of the complexes ν(C=O) occurs at the lower wavenumber (20–30 cm^{-1}) suggesting participation of C=O groups in bonding [22]. The position of ν(C=O) in both Ni(II) complexes is unaffected indicating that C=O groups are not involved in coordination.

In the metal complexes (except Ni(II) complexes) amide II bands shift to lower frequency (15–25 cm^{-1}) compared to the ligand and a shift to higher frequency (5–20 cm^{-1}) is observed in the amide III bands, further supporting coordination through >C=O group.

The ν(C=N) band observed at 1625 cm^{-1} in dsodh and 1620 cm^{-1} in dsmdh shifted to lower frequency (10–20 cm^{-1}) in all the metal complexes suggesting coordination through the azomethine group [23]. ν(N–N) shifts to higher frequency by (15–20) cm^{-1} in the metal complexes indicating coordination of one nitrogen atom of the N–N group [24]. A new band assigned to ν(C–O) in the spectra of the metal complexes suggests that the ligands are coordinated through the deprotonated phenolate group [25]. In the complexes a band in the region (529–560 cm^{-1}) is assigned as ν(M–O).

Based on the above discussion, general structures for the metal complexes have been proposed.

3.5. *X-ray diffraction studies*

All complexes are very fine powdery solids. X-ray powder diffraction patterns for Cu(dsodh), Co(dsmdh) and Ni(dsodh) were recorded and d-spacings were calculated from the diffraction lines. The patterns observed for these complexes have been indexed by Ito's method and the lattice constants (*a*, *b*, *c*) were calculated as follows:

	a	*b*	*c* (Å)
[Cu(L)]Cl	5.69	5.1	4.91
[Co(L′)]Cl	5.09	4.73	4.27
[Ni(L)Cl]	6.18	6.18	5.99

where HL = dsodh and HL′ = dsmdh.

These constants indicate an orthorhombic crystal lattice for [Cu(L)]Cl and [Co(L′)]Cl and a tetragonal crystal lattice for [Ni(L)Cl] [7].

3.6. *Antifungal activity*

The ligands and their metal complexes show varying degrees of activity against fungi viz. *Stemphylium* sp., *Myrothecium* sp. and *Alternaria* sp. at 0.5, 1.0 and 2.0 mg mL^{-1} concentration. In all cases, the activity is greatly enhanced at higher concentration. The metal complexes show greater activity than the ligands [26]. The dsodh ligand shows better activity than dsmdh against *Stemphylium* and *Alternaria* sp., but lower activity against *Myrothecium* sp. Ni(dsodh) shows the highest activity at 2.0 mg mL^{-1} concentration against *Myrothecium* sp. (75.76%) and *Alternaria* sp. (73.34%) whereas Cd(dsodh) shows highest activity (77.89%) against *Stemphylium* sp. Zn(dsmdh) shows appreciable antifungal activity against *Stemphylium* (75.85%) and *Alternaria* sp. (72.63%) but Ni(dsmdh) shows the highest activity (78.13%) against *Myrothecium* at 2.0 mg mL^{-1} concentration.

3.7. *Antibacterial activity*

The antibacterial screening data of the ligands and their metal complexes indicate that dsmdh is more active than dsodh; both ligands show lower activity than the complexes. All the complexes show fair antibacterial activity against *P. fluorescence* and *C. thermocellum*. The activity increases at higher concentration [27]. Cd(II) complexes show highest activity against both the bacteria at 2.0 mg mL^{-1} concentration than other complexes. The percent activity index data also suggest a fair degree of antibacterial activity for the metal complexes as compared to the common standard antibiotic ampicillin.

The bacterial toxicities of the metal complexes, in general, vary with the metal ions in the following order:

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

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