

## Synthesis, physico-chemical characterization and antimicrobial activity of cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) complexes with some acyldihydrazones

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### Abstract

Complexes of the type  $[M(\text{bssdh})]\text{Cl}$  and  $[M(\text{dspdh})]\text{Cl}$ , where  $M = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}$  and  $\text{Cd(II)}$ ;  $\text{Hbssdh} = \text{benzil salicylaldehyde succinic acid dihydrazone}$ ,  $\text{Hdspdh} = \text{diacetyl salicylaldehyde phthalic acid dihydrazone}$  have been synthesized and characterized with the help of elemental analyses, electrical conductance, magnetic susceptibility measurements, electronic, ESR and IR spectra and X-ray diffraction studies. Magnetic moment values and electronic spectral transitions indicate a spin free octahedral structure for  $\text{Co(II)}$ ,  $\text{Ni(II)}$  and  $\text{Cu(II)}$  complexes. IR spectral studies suggest that both the ligands behave as monobasic hexadentate ligands coordinating through three  $> \text{C}=\text{O}$ , two  $> \text{C}=\text{N}^-$  and a phenolate group to the metal. ESR spectra of  $\text{Cu(II)}$  complexes are axial type and suggest  $d_{x^2-y^2}$  as the ground state. X-ray powder diffraction parameters for  $[\text{Co}(\text{bssdh})]\text{Cl}$  and  $[\text{Co}(\text{dspdh})]\text{Cl}$  complexes correspond to an orthorhombic crystal lattice. The ligands as well as their metal complexes show a significant antifungal and antibacterial activity against various fungi and bacteria. The metal complexes are more active than the parent ligands.

**Keywords:** metal(II) complexes, acyldihydrazones, biocidal activity, characterization

### Introduction

A considerable interest is being shown in the phenomenon of metal chelation in biological systems. The role of several drugs in relation to their metal binding has been established. The discovery of antitumour activity of certain platinum coordination compounds [1] opened up a new class of antitumour agents, namely inorganic coordination complexes. It is accepted that the antitumour activity is due to inhibition of DNA synthesis in the cancer cells [2]. The antitumour activity of platinum(II) complexes with nucleosides and their bases have been investigated extensively [3]. Several bivalent [4–7] and trivalent [8–11] transition metal complexes of uracil, substituted uracils and its mixed ligand complexes have been reported to show appreciable antitumour activity.

Since acylhydrazones are strong biologically active compounds [12–14], their complexes may have

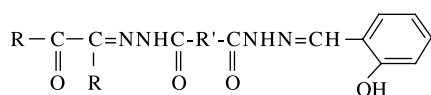
potential use as fungicides and bactericides. Expecting some new compounds of biological interest, we have synthesized and characterized a number of bivalent transition metal complexes with benzil salicylaldehyde succinic acid dihydrazone ( $\text{Hbssdh}$ ) and diacetyl salicylaldehyde phthalic acid dihydrazone ( $\text{Hdspdh}$ ) and studied their antifungal and antibacterial properties.

### Experimental

#### Materials

All the chemicals were of BDH (AnalaR) or equivalent grade. Succinic acid dihydrazide (sdh) and phthalic acid dihydrazide (pdh) were prepared by reacting hydrazine hydrate with the corresponding diethyl esters in 2:1 molar ratio [15].

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where, R = C<sub>6</sub>H<sub>5</sub>, R' = (CH<sub>2</sub>)<sub>2</sub> for Hbssdh  
or R = CH<sub>3</sub>, R' = C<sub>6</sub>H<sub>4</sub> for Hdspdh

Figure 1. Structure of the ligands.

### Synthesis of the ligands

For the synthesis of the ligand, benzil salicylaldehyde succinic acid dihydrazone (Hbssdh), C<sub>6</sub>H<sub>5</sub>COC(C<sub>6</sub>H<sub>5</sub>)=NNHCO(CH<sub>2</sub>)<sub>2</sub>CONHN=CHC<sub>6</sub>H<sub>4</sub>(OH), the solutions of benzil (10 mmol, 2.10 g) and salicylaldehyde (10 mmol, 1.22 mL) in 50 mL ethanol were mixed in a RB flask by stirring. To the above solution mixture, 50 mL of aqueous solution of succinic acid dihydrazide (10 mmol, 1.46 g) was added and stirred continuously for 2–3 h on a magnetic stirrer at room temperature. The product was filtered by suction and washed thoroughly with water and then with ethanol to ensure purity of the ligand. The pure ligand was dried in a desiccator over anhydrous CaCl<sub>2</sub>.

Diacetyl salicylaldehyde phthalic acid dihydrazone (Hdspdh), CH<sub>3</sub>COC(CH<sub>3</sub>)=NNHCOC<sub>6</sub>H<sub>4</sub>CONHN=CHC<sub>6</sub>H<sub>4</sub>(OH) was prepared by reacting 50 mL aqueous ethanol solution (v/v, 1:1) of phthalic acid dihydrazide (10 mmol, 1.94 g) with a mixed solution of diacetyl (10 mmol, 0.86 mL) and salicylaldehyde (10 mmol, 1.22 mL) in 50 mL ethanol. The reacting solution mixture was stirred for ~3 h at room temperature. The product was filtered, washed several times with water and aqueous ethanol (v/v, 1:1) and dried at room temperature in a desiccator.

The ligands were characterized by their melting points, elemental analyses (Table I), IR spectra (Table IV), <sup>1</sup>H and <sup>13</sup>C NMR spectra. Hbssdh, <sup>1</sup>H NMR (ppm): Two >CH<sub>2</sub> (2.5), two >NH (7.0 and 8.3), aromatic ring protons (7.4–8.1), =CH (9.0), –OH (11.3). Hbssdh, <sup>13</sup>C NMR (ppm): Two >CH<sub>2</sub> (28.316), aromatic ring carbons (116.131–146.476), two >C=N (156.375, 157.306), two >C=O (167.723 and 172.973). Hdspdh, <sup>1</sup>H NMR (ppm): Two –CH<sub>3</sub> (1.2 and 2.3), two >NH (6.8 and 7.1), aromatic ring protons (7.3–8.1), =CH (9.0), –OH (11.5). Hdspdh, <sup>13</sup>C NMR (ppm): Two –CH<sub>3</sub> (9.146 and 39.78), aromatic ring carbons (116.576–133.282), =CH (154.718), two >C=N (158.682), two >C=O (162.861 and 185.016).

### Synthesis of the metal complexes

The metal complexes were synthesized by reacting 50 mL aqueous solution of each metal(II) chloride (10 mmol) with 50 mL suspended ethanol solution of each ligands, Hbssdh (10 mmol, 4.42 g) and Hdspdh (10 mmol, 3.66 g) in 1:1 (M:L) molar ratio. Cu(II),

Zn(II) and Cd(II) complexes were formed by stirring the reaction mixture for 2–4 h on a magnetic stirrer at room temperature. However, Co(II) and Ni(II) complexes were obtained by refluxing the solution mixture for 4 h and 6 h, respectively. The resulting complexes were filtered in a glass crucible and washed several times with water and ethanol to remove unreacted metal chloride and ligand. The pure complexes were dried in a desiccator over anhydrous calcium chloride at room temperature.

### Analyses and instrumentation

Metal contents were determined gravimetrically by a literature procedure [16] after digesting the organic matter with aquaregia and evaporating the residue to dryness with conc. sulfuric acid. The chloride content was analysed gravimetrically as silver chloride. C, H, N data were determined on an Elementar Vario EL model elemental analyzer.

The molar conductance of 10<sup>–3</sup> 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)<sub>4</sub>] as calibrant and corrected for diamagnetism [17]. IR spectra of the ligands and their metal complexes were recorded in KBr medium in the 4000–500 cm<sup>–1</sup> range on a Vertex 70 (Bruker) Spectrophotometer and electronic spectra were recorded in DMF on a Cintra 10 Spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the ligands were recorded on a JEOL AL 300 FT NMR Spectrophotometer in DMSO-d<sub>6</sub> at 25°C. The X-band ESR spectra of Cu(II) complexes were recorded on a 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 CuK<sub>α</sub> radiations.

The analytical and physico-chemical data are given in Tables I–VI.

### Biocidal activity

**Antifungal activity.** The ligands as well as their complexes were screened for antifungal activity against several fungi viz. *Curvularia*, *Fusarium* and *Colletotrichum* species. 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 technique.

The solutions in different concentrations 0.5, 1.0 and 1.5 mg/mL 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

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

Compound (Colour)	Empirical formula (Formula weight)	M.P./ D.P. (°C)	Analyses found (calc) %							Yield (%)	$\Lambda_M$ ( $\text{ohm}^{-1}\text{mol}^{-1}\text{cm}^{-2}$ ) in DMF
			Metal	Cl	C	H	N				
Hbssdh (Light yellow)	$\text{C}_{25}\text{H}_{22}\text{N}_4\text{O}_4$ (442)	206			67.65 (67.87)	4.92 (4.98)	12.60 (12.67)			82	
Hdspdh (Cream yellow)	$\text{C}_{19}\text{H}_{18}\text{N}_4\text{O}_4$ (366)	180			62.10 (62.29)	4.89 (4.92)	15.28 (15.30)			64	
[Co(bssdh)]Cl (Orange)	$\text{C}_{25}\text{H}_{21}\text{N}_4\text{O}_4\text{ClCo}$ (535.5)	278	10.90 (11.02)	6.60 (6.63)	55.75 (56.02)	3.84 (3.92)	10.31 (10.46)			76	71.9
[Ni(bssdh)]Cl (Green yellow)	$\text{C}_{25}\text{H}_{21}\text{N}_4\text{O}_4\text{ClNi}$ (535.5)	> 300	10.88 (11.02)	6.65 (6.63)	55.92 (56.02)	3.87 (3.92)	10.40 (10.46)			79	68.4
[Cu(bssdh)]Cl (Dark green)	$\text{C}_{25}\text{H}_{21}\text{N}_4\text{O}_4\text{ClCu}$ (540)	282	11.70 (11.76)	6.50 (6.57)	55.37 (55.55)	3.89 (3.89)	10.29 (10.37)			81	69.7
[Zn(bssdh)]Cl (Cream)	$\text{C}_{25}\text{H}_{21}\text{N}_4\text{O}_4\text{ClZn}$ (541.5)	268	12.00 (12.00)	6.50 (6.56)	55.23 (55.40)	3.86 (3.88)	10.25 (10.34)			74	72.3
[Cd(bssdh)]Cl (Cream)	$\text{C}_{25}\text{H}_{21}\text{N}_4\text{O}_4\text{ClCd}$ (589)	256	19.00 (19.10)	6.00 (6.03)	50.76 (50.93)	3.51 (3.57)	9.46 (9.50)			77	71.4
[Co(dspdh)]Cl (Orange)	$\text{C}_{19}\text{H}_{17}\text{N}_4\text{O}_4\text{ClCo}$ (459.5)	> 300	12.70 (12.84)	7.65 (7.73)	49.47 (49.61)	3.63 (3.70)	12.02 (12.19)			69	69.3
[Ni(dspdh)]Cl (Green yellow)	$\text{C}_{19}\text{H}_{17}\text{N}_4\text{O}_4\text{ClNi}$ (459.5)	> 300	12.70 (12.84)	7.67 (7.73)	49.49 (49.61)	3.65 (3.70)	12.26 (12.19)			72	67.1
[Cu(dspdh)]Cl (Green yellow)	$\text{C}_{19}\text{H}_{17}\text{N}_4\text{O}_4\text{ClCu}$ (464)	> 300	13.60 (13.69)	7.60 (7.65)	48.92 (49.13)	3.61 (3.66)	12.18 (12.07)			76	73.9
[Zn(dspdh)]Cl (Cream)	$\text{C}_{19}\text{H}_{17}\text{N}_4\text{O}_4\text{ClZn}$ (465.5)	> 300	13.90 (13.96)	7.60 (7.63)	49.01 (48.98)	3.68 (3.65)	12.12 (12.03)			68	65.8
[Cd(dspdh)]Cl (Light yellow)	$\text{C}_{19}\text{H}_{17}\text{N}_4\text{O}_4\text{ClCd}$ (513)	> 300	21.80 (21.93)	6.95 (6.92)	44.31 (44.44)	3.27 (3.31)	10.76 (10.92)			73	79.2

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  $25 \pm 2^\circ\text{C}$  for 24 h. Each slide was observed under the microscope for spore germination and percent germination was finally calculated. The results were also compared with a standard antifungal drug miconazole at the same concentrations.

**Antibacterial activity.** The antibacterial activity of the ligands and their complexes was studied against *Pseudomonas* (gram -ve) and *Bacillus* sp. (gram +ve) bacteria. Each of the compounds was dissolved in DMSO and solutions of the concentration 1.0 and 2.0 mg/mL were prepared separately. Paper discs of whatman filter paper (No. 42) of uniform diameter were cut and sterilized on an autoclave. The paper disc soaked in the desired concentration of the complex solution was placed aseptically in the petridishes containing nutrient agar media (agar 15 g + beef extract 3 g + peptone 5 g) seeded with *Bacillus* and *Pseudomonas* sp. bacteria separately. The Petridishes were incubated at  $32^\circ\text{C}$  and the inhibition zones were recorded after 24 h of incubation. Each treatment was replicated 9 times.

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

% Activity Index

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

**Determination of minimum inhibitory concentration (MIC) value.** The compounds showing antibacterial activity over 50 % were selected for the determination of minimum inhibition concentration (MIC). The MIC of the selected compounds against selected bacteria was estimated using the disc diffusion technique by preparing discs containing 0.1, 0.25, 0.5 and 1.0 mg/mL of the compounds and applying the protocol. The results of MIC values (mg/mL) are summarized below:

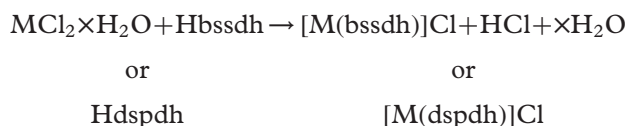
Compound	MIC value
[Ni(bssdh)]Cl	0.5 mg/mL against <i>Pseudomonas</i> sp.
[Cu(bssdh)]Cl	0.25 mg/mL against <i>Bacillus</i> sp.
[Cd(bssdh)]Cl	0.25 mg/mL against <i>Bacillus</i> sp.
[Cd(dspdh)]Cl	0.25 mg/mL against <i>Bacillus</i> sp.

Table II. Magnetic moments, electronic spectral data and ligand field parameters of the complexes.

Complexes	$\mu_{\text{eff}}$ (B.M.)	Band maxima ( $\text{cm}^{-1}$ )			10 Dq ( $\text{cm}^{-1}$ )	B ( $\text{cm}^{-1}$ )	B	$\beta^a$ (%)	LFSE (Kcal/mol)
		$\nu_1$	$\nu_2$	$\nu_3$					
[Co(bssdh)]Cl	4.82	9025	—	18250	10300	700	0.72	28.00	23.48
[Ni(bssdh)]Cl	3.20	10255	18025	25305	10255	837	0.81	19.00	35.06
[Cu(bssdh)]Cl	1.93	15310	—	—	—	—	—	—	—
[Co(dspdh)]Cl	4.96	9060	—	18350	10370	707	0.73	27.30	23.64
[Ni(dspdh)]Cl	3.16	10460	16015	26250	10460	725	0.71	29.50	35.76
[Cu(dspdh)]Cl	1.87	14880	—	—	—	—	—	—	—

## Results and discussion

It appears from the analytical data (Table I) that both the ligands undergo deprotonation of their phenolic proton during the complex formation with metal(II) chloride. The ligands Hbssdh and Hdspdh react with metal salts in 1:1 (M:L) molar ratio to give complexes of the general compositions [M(bssdh)]Cl and [M(dspdh)]Cl. The reactions may have proceeded as follows:



The complexes are insoluble in water, methanol, ethanol, benzene, chloroform, carbon tetrachloride, diethyl ether and ethyl acetate but are fairly soluble in polar organic solvents such as DMF and DMSO. They are orange, green, green-yellow to light yellow in colour. Some of the complexes either melt or decompose above 300 °C while others between 250–300 °C. The molar conductance values of  $10^{-3}$  M solution of the complexes measured at room temperature fall in the range 65.8–79.2  $\Omega^{-1}\text{mol}^{-1}\text{cm}^2$  indicating that they are 1:1 electrolytes [18].

### Magnetic moments

Cobalt(II) tetrahedral complexes generally show magnetic moments between 4.0–4.6 B.M. while the octahedral complexes show between 4.7–5.2 B.M.

because of the orbital contribution [19]. The  $\mu_{\text{eff}}$  values 4.82 B.M. and 4.96 B.M. observed for Co(II) complexes with Hbssdh and Hdspdh, respectively, are fairly close to those reported for three unpaired electrons in an octahedral environment. The effective magnetic moments reported for high spin octahedral Ni(II) complexes are in the range 2.9–3.4 B.M., while for the tetrahedral nickel(II) complexes, the value ranges from 3.5–4.0 B.M. [17]. Both Ni(II) complexes in this study, show  $\mu_{\text{eff}}$  values 3.20 B.M. and 3.16 B.M. corresponding to two unpaired electrons in octahedral environment. The magnetic moments of two Cu(II) complexes (1.93 and 1.87 B.M.) correspond to  $\mu_{\text{eff}}$  values for one unpaired electron.

### Electronic spectra

Cobalt(II) complexes generally show three absorption bands in the visible range under the influence of the octahedral field by the excitation of the electron from ground state  ${}^4\text{T}_{1\text{g}}$  (F) to the excited states  ${}^4\text{T}_{2\text{g}}$  (F),  ${}^4\text{A}_{2\text{g}}$  (F) and  ${}^4\text{T}_{1\text{g}}$  (P). In case of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ , three transitions are observed at 8130, 17540 and 21980  $\text{cm}^{-1}$  [20]. [Co(bssdh)]Cl and [Co(dspdh)]Cl complexes show only two bands 9025 and 9060  $\text{cm}^{-1}$  ( $\nu_1$ ) and 18250 and 18350  $\text{cm}^{-1}$  ( $\nu_3$ ), respectively suggesting octahedral geometry for the complexes. The  $\nu_2$  transition was not observed due to very weak intensity [20]. Various ligand-field parameters (10 Dq, B,  $\beta$ ,  $\beta^0$  and LFSE) were also calculated for both Co(II) complexes (Table II) which indicate significant covalent bonding in metal–ligand bonds.

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

Complex	Temp. (K)	Medium	$A_{\parallel}$ (G)	$A_{\perp}$ (G)	$A_{\text{av}}$ (G)	$g_{\parallel}$	$g_{\perp}$	$g_{\text{av}}$	$\alpha^2$	$\alpha'^2$	$B_1^2$
[Cu(bssdh)]Cl	300	Solid state	—	—	$A_{\text{iso}} = 101$	—	—	$g_{\text{iso}} = 2.1357$	—	—	—
	120	DMSO solution	168	74	105	2.3705	2.0459	2.1541	0.89	0.13	0.86
[Cu(dspdh)]Cl	300	Solid state	172	68	103	2.3573	2.0401	2.1458	—	—	—
	120	DMSO solution	181	70	107	2.3163	2.0408	2.1326	0.87	0.15	0.71

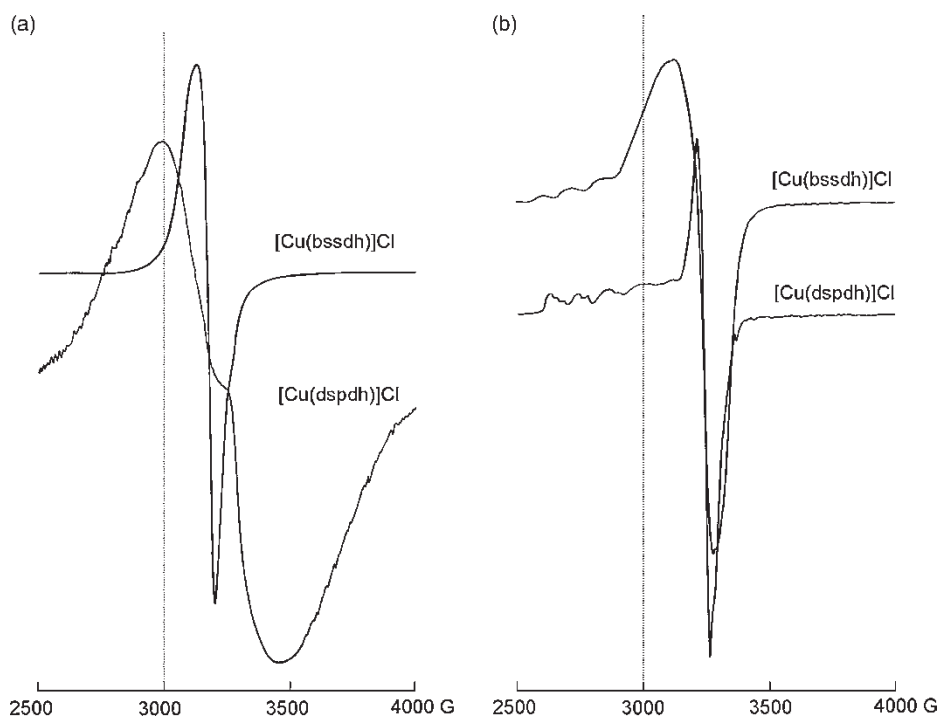


Figure 2. ESR spectra of copper (II) complexes (a) in solid state at 300 K (b) In DMSO solution at 120 K.

Nickel(II) complexes give rise to three bands in octahedral environment corresponding to transitions  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$  ( $\nu_1$ ),  $\rightarrow {}^3T_{1g}(F)$  ( $\nu_2$ ) and  $\rightarrow {}^3T_{1g}(P)$  ( $\nu_3$ ) [21]. In the spectra of  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ , these bands have been reported at 10700, 17540 and  $28170 \text{ cm}^{-1}$ , respectively [17]. Both the Ni(II) complexes also show above three transitions at 10255 and  $10460 \text{ cm}^{-1}$  ( $\nu_1$ ), 18025 and  $16015 \text{ cm}^{-1}$  ( $\nu_2$ ), 25305 and  $26250 \text{ cm}^{-1}$  ( $\nu_3$ ) for  $[\text{Ni}(\text{bssdh})]\text{Cl}$  and  $[\text{Ni}(\text{dspdh})]\text{Cl}$ , respectively suggesting an octahedral geometry for the complexes. The ligand-field parameters have also been calculated by the procedure given by Lever [20].

Both Cu(II) complexes show an intense broad band centered at  $15310 \text{ cm}^{-1}$  and  $14880 \text{ cm}^{-1}$  which may be due to envelope of the transitions  ${}^2B_1 \rightarrow {}^2B_{2g}$

and  $\rightarrow {}^2E_g$  suggesting a distorted octahedral geometry for the complexes [22].

#### ESR spectra

ESR spectra of  $[\text{Cu}(\text{bssdh})]\text{Cl}$  complex in solid state at 300 K exhibit isotropic spectra with a broad signal having no hyperfine structure. This may be due to dipolar exchange and unresolved hyperfine interactions [23]. The  $g_{\text{iso}} = 2.1357$  suggests a geometry involving grossly misaligned tetragonal axes.  $[\text{Cu}(\text{dspdh})]\text{Cl}$  shows an axial signal with two  $g$  values at 300 K (Figure 2). The  $g_{\parallel}$  and  $g_{\perp}$  values are  $> 2.04$  (Table III) indicating an elongated tetragonally distorted octahedral stereochemistry for the complex with all the principal axes aligned parallel.

Table IV. IR spectral data ( $\text{cm}^{-1}$ ) and assignment of important bands.

Compounds	$\nu(\text{OH} + \text{NH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	Amide II	Amide III	$\nu(\text{N}-\text{N})$	$\nu(\text{C}-\text{O})$
Hbssdh	3294b, 3207s	1672b	1619s	1587s	1379m	960w	
Hdspdh	3392b, 3162s	1686b	1635s	1572s	1361m	959m	
$[\text{Co}(\text{bssdh})]\text{Cl}$	3208s	1651b	1603s	1567s	1393s	992m	1282s
$[\text{Ni}(\text{bssdh})]\text{Cl}$	3206m	1649b	1605s	1571s	1397s	998w	1269s
$[\text{Cu}(\text{bssdh})]\text{Cl}$	3209m	1647b	1602s	1577s	1398m	996w	1289s
$[\text{Zn}(\text{bssdh})]\text{Cl}$	3205s	1646b	1609s	1564s	1391m	999m	1278s
$[\text{Cd}(\text{bssdh})]\text{Cl}$	3210m	1642b	1606s	1569s	1395s	1000m	1273s
$[\text{Co}(\text{dspdh})]\text{Cl}$	3163s	1661b	1618s	1557s	1376s	975w	1263s
$[\text{Ni}(\text{dspdh})]\text{Cl}$	3164m	1660b	1620s	1554s	1378m	980w	1296s
$[\text{Cu}(\text{dspdh})]\text{Cl}$	3161m	1656b	1616s	1559s	1371m	983m	1277s
$[\text{Zn}(\text{dspdh})]\text{Cl}$	3165s	1659b	1618s	1551s	1370m	979w	1281s
$[\text{Cd}(\text{dspdh})]\text{Cl}$	3166m	1658b	1615s	1549s	1375m	988w	1285s

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

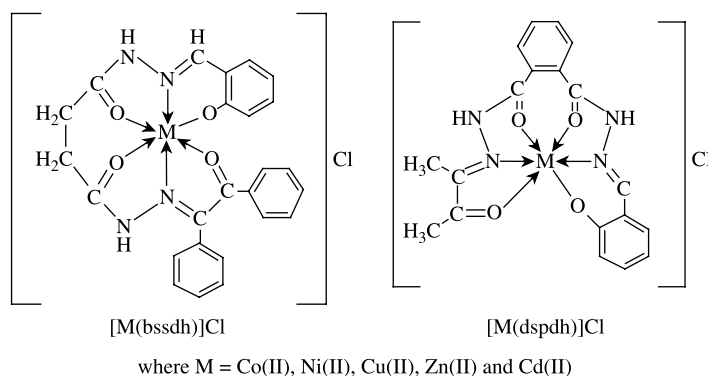


Figure 3. General structures of the metal complexes.

DMSO solution spectra at LNT give axial spectra with two anisotropic  $g$  values for both Cu(II) complexes. The  $g_{\parallel}$ ,  $g_{\perp}$ ,  $A_{\parallel}$  and  $A_{\perp}$  values were accurately measured from the spectra. The trend  $g_{\parallel} > g_{\perp} > g_e$  (2.0023) shows the presence of unpaired electron in  $d_{x^2-y^2}$  orbital of the copper(II) ion. Both the complexes show four well defined copper hyperfine lines due to coupling of the electron with nuclear spin ( $I = 3/2$ ) of the copper atom.

The  $g_{av}$  and  $A_{av}$  values were calculated using the equations;  $g_{av} = (g_{\parallel} + 2g_{\perp})/3$ ;  $A_{av} = (A_{\parallel} + 2A_{\perp})/3$ .

A significant degree of covalent character in the metal–ligand bonds is indicated by the values of the in-plane  $\sigma$ -bonding parameter  $\alpha^2$  (0.89, 0.87), out of plane  $\sigma$ -bonding parameter  $\alpha^{+2}$  (0.13, 0.15) and in-plane  $\pi$ -bonding parameter  $\beta_1^2$  (0.86, 0.71), respectively [24].

Table V. Observed and calculated Q and hkl values.

Powder patterns	Intensity	Angle $^{\circ}$	d (Å)	Q <sub>obs</sub> (1/d <sup>2</sup> )	Q <sub>calc</sub>	hkl
[Co(bssdh)]Cl						
1	58.38	12.30	7.190	0.0193	0.0193	100
2	53.51	13.95	6.343	0.0249	0.0249	010
3	52.43	15.45	5.731	0.0304	0.0304	001
4	48.65	18.85	4.704	0.0452	0.0442	110
5	68.11	21.45	4.139	0.0584	0.0553	011
6	100.00	24.63	3.611	0.0767	0.0774	200
7	68.65	28.95	3.082	0.1053	0.1078	201
8	54.59	30.60	2.919	0.1174	0.1188	120
9	62.16	33.35	2.685	0.1387	0.1327	211
10	42.16	35.15	2.551	0.1537	0.1492	121
11	44.86	39.40	2.285	0.1915	0.1989	310
12	41.08	42.20	2.140	0.2184	0.2237	030
13	43.24	47.05	1.930	0.2685	0.2735	131
14	35.14	51.00	1.789	0.3124	0.3095	400
[Co(dspdh)]Cl						
1	16.78	11.55	7.655	0.0171	0.0171	100
2	42.13	12.89	6.863	0.0212	0.0212	010
3	57.34	13.82	6.405	0.0244	0.0244	001
4	18.88	17.15	5.166	0.0375	0.0383	110
5	17.83	18.80	4.716	0.0450	0.0456	011
6	24.12	22.80	3.897	0.0658	0.0627	111
7	31.99	25.55	3.484	0.0824	0.0849	020
8	41.96	26.15	3.405	0.0863	0.0895	210
9	41.96	26.99	3.301	0.0918	0.0926	201
10	100.00	27.67	3.222	0.0963	0.0975	002
11	17.48	29.20	3.056	0.1071	0.1020	120
12	22.73	30.60	2.919	0.1174	0.1187	012
13	17.83	32.70	2.736	0.1336	0.1358	112
14	21.15	37.90	2.372	0.1777	0.1780	301
15	16.08	39.15	2.299	0.1892	0.1911	030
16	14.86	41.15	2.192	0.2081	0.2081	130

Table VIA. Antifungal activity of the ligands and their complexes.

Compounds	% Inhibition of spore germination								
	<i>Curvularia</i> sp. (mg mL <sup>-1</sup> )			<i>Fusarium</i> sp. (mg mL <sup>-1</sup> )			<i>Colletotrichum</i> sp. (mg mL <sup>-1</sup> )		
	0.5	1.0	1.5	0.5	1.0	1.5	0.5	1.0	1.5
Hbssdh	42	48	55	47	54	60	43	50	56
Hdspdh	38	43	52	40	52	58	39	46	55
[Co(bssdh)]Cl	55	76	94	58	75	96	55	72	95
[Ni(bssdh)]Cl	56	72	92	56	77	93	58	70	92
[Cu(bssdh)]Cl	62	80	98	65	82	100	62	80	100
[Zn(bssdh)]Cl	58	78	97	62	80	100	63	78	98
[Cd(bssdh)]Cl	60	85	100	68	86	100	65	84	100
[Co(dspdh)]Cl	58	74	94	55	76	93	54	72	92
[Ni(dspdh)]Cl	56	72	92	60	78	95	57	70	93
[Cu(dspdh)]Cl	62	81	98	65	83	98	61	80	97
[Zn(dspdh)]Cl	60	80	96	62	84	100	60	78	95
[Cd(dspdh)]Cl	65	83	100	67	85	100	62	81	100
Miconazole	70	78	95	71	80	100	72	80	98

IR spectra

The ligands Hbssdh and Hdspdh show  $\nu(\text{NH})$  at 3207 cm<sup>-1</sup> and 3162 cm<sup>-1</sup> respectively due to presence of two >NH groups in each ligand. In all the metal complexes  $\nu(\text{NH})$  occurs nearly at the same or slightly altered positions as in the ligands (Table IV) indicating non-involvement of >NH groups in bonding. Both the ligands also show a broad band due to phenolic OH group at 3294 cm<sup>-1</sup> and 3392 cm<sup>-1</sup> respectively in Hbssdh and Hdspdh.  $\nu(\text{OH})$  is not observed in metal complexes indicating deprotonation of phenolic proton during complexation. Appearance of a new band assigned as  $\nu(\text{C}-\text{O})$  in all complexes in the region 1263–1296 cm<sup>-1</sup> confirms deprotonation of the ligands.

$\nu(\text{C}=\text{O})$  in the ligands Hbssdh and Hdspdh appears as a broad band at 1672 cm<sup>-1</sup> and 1686 cm<sup>-1</sup>, respectively due to presence of three >C=O groups in each ligand.  $\nu(\text{C}=\text{O})$  shifts to lower frequency by 21–30 cm<sup>-1</sup> in the complexes as compare to the parent ligands suggesting coordination of all the three >C=O groups to the metal [25]. The amide II bands appear to have shifted to lower frequency by 10–23 cm<sup>-1</sup> upon complex formation. Compared to the ligand band, a shift to higher frequency (9–19 cm<sup>-1</sup>) is observed in amide III bands in all the metal complexes supporting coordination through the >C=O groups [26].

The  $\nu(\text{C}=\text{N})$  bands observed at 1619 cm<sup>-1</sup> in Hbssdh and at 1635 cm<sup>-1</sup> in Hdspdh ligands shifted considerably to lower frequency by 10–20 cm<sup>-1</sup> in the metal complexes suggesting coordination through two

Table VIB. Antibacterial activity of the ligands and their complexes.

Compounds	Diameter of inhibition zone (in mm)				% Activity Index			
	<i>Pseudomonas fluorescens</i> (mg mL <sup>-1</sup> )		<i>Bacillus subtilis</i> (mg mL <sup>-1</sup> )		<i>Pseudomonas fluorescens</i> (mg mL <sup>-1</sup> )		<i>Bacillus subtilis</i> (mg mL <sup>-1</sup> )	
	1.0	2.0	1.0	2.0	1.0	2.0	1.0	2.0
Hbssdh	3	4	4	5	23	29	36	38
Hdspdh	3	4	3	4	23	29	27	31
[Co(bssdh)]Cl	3	5	4	6	23	36	36	46
[Ni(bssdh)]Cl	5	7	4	6	38	50	36	46
[Cu(bssdh)]Cl	5	8	7	10	38	57	64	77
[Zn(bssdh)]Cl	4	5	5	7	31	36	45	54
[Cd(bssdh)]Cl	4	6	6	8	31	43	55	62
[Co(dspdh)]Cl	3	4	3	4	23	29	27	31
[Ni(dspdh)]Cl	3	4	4	5	23	29	36	38
[Cu(dspdh)]Cl	5	6	4	5	38	43	36	38
[Zn(dspdh)]Cl	4	5	5	6	31	36	45	46
[Cd(dspdh)]Cl	4	6	6	8	31	43	55	62
Ampicillin	13	14	11	13	100	100	100	100

azomethine groups [27]. The shift to higher wave numbers in  $\nu(\text{N}-\text{N})$  from the free ligands to their complexes by 20–40  $\text{cm}^{-1}$ , suggests involvement of only one nitrogen of the hydrazone ( $-\text{NHN}=\text{C}<$ ) group [28].

On the basis of above discussion, general structures for the metal complexes have been proposed in Figure 3.

#### X-ray diffraction studies

X-ray powder method provides a way of investigating within limits, the crystallography of a crystal in powder form. All the complexes in present study are stable microcrystalline powders. The diffraction patterns for  $[\text{Co}(\text{bssdh})]\text{Cl}$  and  $[\text{Co}(\text{dspdh})]\text{Cl}$  were recorded and successfully indexed by using Ito's method [29] and the lattice constants calculated (Table V) as follows:

	<i>a</i>	<i>b</i>	<i>c</i> (Å)
$[\text{Co}(\text{bssdh})]\text{Cl}$	7.19	6.34	5.73
$[\text{Co}(\text{dspdh})]\text{Cl}$	7.65	7.86	6.40

These constants indicate an orthorhombic crystal lattice for both complexes.

#### Antifungal activity

The antifungal experimental results of the compounds were compared against DMSO as the control and are expressed as percentage inhibition versus control (Table VIA). The experimental antifungal activity data show the following observations:

1. The complexes show a fair degree of activity against *Curvularia* sp., *Fusarium* sp. and *Colletotrichum* sp. at 0.5, 1.0 and 1.5 mg/mL concentration [30].
2. The metal complexes are appreciably more active than the ligands. Their activity is enhanced at higher concentration.
3. DMSO control showed negligible activity as compare to the metal complexes and ligands.
4. Hbssdh and its complexes are more effective than Hdspdh and its complexes.
5. All the metal complexes are more active against *Fusarium* sp. in comparison to other fungal species.
6. Cd(II) complexes with both ligands show 100% activity against all three fungal species at the concentration of 1.5 mg/mL.  $[\text{Cu}(\text{bssdh})]\text{Cl}$  complex also shows 100% activity against *Fusarium* sp. and *Colletotrichum* sp. at the dose of 1.5 mg/mL.
7. The antifungal activity of Hbssdh complexes varies in the following order of the fungal species: *Fusarium* sp. > *Colletotrichum* sp. > *Curvularia* sp.
8. For Hdspdh complexes antifungal activity varies as: *Fusarium* sp. > *Curvularia* sp. > *Colletotrichum* sp.
9. The activity varies in the following order of metal ions:  
Cd > Cu > Zn > Ni > Co

10. Cu(II), Zn(II) and Cd(II) complexes exhibited slightly better activity as compare to the standard drug miconazole against *Curvularia* and *Colletotrichum* sp.

#### Antibacterial activity

The metal complexes, ligands, standard drug Ampicillin and DMSO solvent control were screened separately for their antibacterial activity against *Pseudomonas* and *Bacillus* sp... The activity of the complexes has been compared with the activity of a common standard antibiotic ampicillin and % Activity Index has been calculated for the complexes. The antibacterial activity data (Table VIB) indicate the following observations:

1. All the complexes show a significant antifungal activity against both the bacteria [31,32] at the concentration of 1.0 and 2.0 mg/mL as compared to the standard drug (ampicillin).
2. The activity generally increases with increasing the concentration of the complexes.
3. The metal complexes are more effective than the ligands.
4. The DMSO control showed no activity against any bacterial strain.
5. The % Activity Index data indicate that  $[\text{Cu}(\text{bssdh})]\text{Cl}$  shows the highest activity (77%) against *Bacillus* sp. at the dose of 2.0 mg/mL.
6. Copper(II) complexes are highly effective against both the bacteria.

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