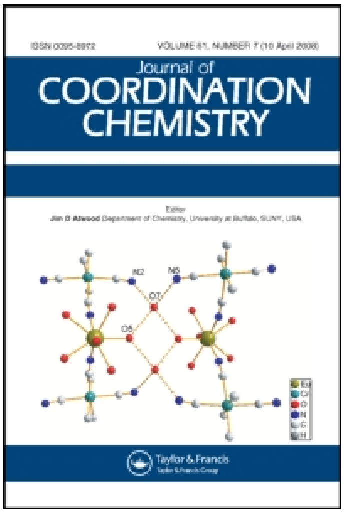

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, structural studies and bio-activity of some metal(II) complexes with glyoxal salicylaldehyde acyldihydrazones

Vinod P. Singh[a]; Parul Gupta[a]
[a] Chemistry Department, Banaras Hindu University, Varanasi, India

To cite this Article Singh, Vinod P. and Gupta, Parul(2008) 'Synthesis, structural studies and bio-activity of some metal(II) complexes with glyoxal salicylaldehyde acyldihydrazones', Journal of Coordination Chemistry, 61: 10, 1532 — 1544
To link to this Article: DOI: 10.1080/00958970701598944
URL: http://dx.doi.org/10.1080/00958970701598944

Journal of Coordination Chemistry
Vol. 61, No. 10, 20 May 2008, 1532–1544

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Synthesis, structural studies and bio-activity of some metal(II) complexes with glyoxal salicylaldehyde acyldihydrazones

VINOD P. SINGH* and PARUL GUPTA

Chemistry Department, Banaras Hindu University, Varanasi - 221005, India

(*Received 19 January 2007; revised 6 April 2007; in final form 20 May 2007*)

Complexes of the type [M(gssdh)]Cl and [M(gspdh)]Cl, where M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), Hgssdh = glyoxal salicylaldehyde succinic acid dihydrazone and Hgspdh = glyoxal salicylaldehyde phthalic acid dihydrazone, have been synthesized and characterized by elemental analyses, molar conductance, magnetic moments, electronic, ESR and IR spectra and X-ray powder diffraction studies. The metal complexes are insoluble in common organic solvents and are 1 : 1 electrolytes. The magnetic moment values and electronic spectra indicate a spin–free octahedral geometry for all Co(II), Ni(II) and Cu(II) complexes. ESR spectral parameters of Cu(II) complexes suggest an elongated tetragonally–distorted octahedral stereochemistry around copper. Both ligands are monobasic hexadentate ligands coordinating through three >C=O, two >C=N– and a deprotonated phenolate group to the metal. X-ray powder diffraction parameters for three of the complexes correspond to an orthorhombic crystal lattice. The complexes show appreciable activity against various fungi and bacteria.

Keywords: Synthesis; ESR and IR spectra; Glyoxal salicylaldehyde acyldihydrazones; Metal(III) complexes; Bioactivity

1. Introduction

Metal complexes of multidentate acylhydrazone Schiff bases have been extensively studied [1–3] because such ligands can bind with one, two or more metal centers involving various coordination modes giving homo and hetero-nuclear metal complexes with interesting stereochemistry [4–6]. Metal complexes of such acylhydrazones, particularly the copper(II) complexes of 2-pyridine carboxaldehyde-2′-pyridylhydrazone [7] and salicylaldehyde benzoylhydrazone [8], show antitumor activity. Similarly, metal complexes of 3- and 5-substituted salicylaldehyde *o*-hydroxy benzoylhydrazones [9], salicylaldehyde benzene sulphonyl hydrazone [10], furfurylidene and 5-nitrofurfurylidene benzoylhydrazones [10] have been found to be bioactive.

Since complexes of acylhydrazones involving bivalent transition metal ions have potential use in biological fields, we have synthesized and characterized a number of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes with glyoxal salicylaldehyde succinic acid dihydrazone (Hgssdh) and glyoxal salicylaldehyde phthalic acid

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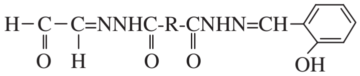
*Corresponding author. Email: singvp@yahoo.co.in

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970701598944

dihydrazone (Hgspdh) and studied their antifungal and antibacterial activity.



(R = $(CH_2)_2$ for gssdh, C_6H_4 for gspdh)

2. Experimental

2.1. *Materials*

All chemicals used were of BDH or equivalent grade. The precursor succinic acid dihydrazide (sdh) and phthalic acid dihydrazide (pdh) were prepared by reacting their corresponding diethyl esters with hydrazine hydrate in a 1 : 2 molar ratio [11].

2.2. *Synthesis of the ligands*

The ligands glyoxal salicylaldehyde succinic acid dihydrazone (Hgssdh), $HCOCH{=}NNHCO(CH_2)_2CONHN{=}CHC_6H_4(OH)$ and glyoxal salicylaldehyde phthalic acid dihydrazone (Hgspdh), $HCOCH{=}NNHCOC_6H_4CONHN{=}CHC_6H_4(OH)$ were synthesized by reacting 50 mL aqueous solution of succinic acid dihydrazide (10 mmol, 1.44 g) or aqueous ethanolic solution (v/v, 1 : 1) of phthalic acid dihydrazide (10 mmol, 1.94 g) into 50 mL aqueous ethanolic solution of glyoxal (10 mmol, 0.58 mL) mixed with salicylaldehyde (10 mmol, 1.22 mL). The reactants were continuously stirred on a magnetic stirrer at room temperature for an hour to insure complete precipitation. The product was filtered by suction and purified by washing several times with aqueous ethanol (v/v, 1 : 1). The pure ligands were dried at room temperature in a desiccator over anhydrous $CaCl_2$.

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

2.3. *Synthesis of the complexes*

Metal complexes of Hgssdh and Hgspdh were synthesized by reacting 50 mL aqueous solutions of each metal salt (slightly more than 10 mmol) with a suspended solution of Hgssdh (10 mmol, 2.90 g) or Hgspdh (10 mmol, 3.38 g) in 50 mL aqueous ethanol (v/v, 1 : 1) in a round bottom flask. The complexes were formed by stirring the reaction solutions on a magnetic stirrer continuously for 2–3 h and then filtered in a glass crucible. Since the complexes are insoluble and non-crystallizable, they were purified by washing thoroughly first with water and then with ethanol to remove unreacted metal salts. The pure complexes were dried at room temperature in a desiccator containing anhydrous calcium chloride.

All the complexes were synthesized by the template method, reacting glyoxal, salicylaldehyde, metal salts and succinic acid dihydrazide/phthalic acid dihydrazide together. Complexes prepared by both methods were found to have similar chemical compositions, magnetic moments and spectral properties.

2.4. *Analyses and instrumentation*

Metal contents were determined gravimetrically by a literature procedure [12] after digesting the organic matter with aqua regia and evaporating the residue to dryness with conc. sulfuric acid. The chloride content was analyzed gravimetrically as silver chloride. 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 Conductivitymeter 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 [13]. 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 DMSO on a Cintra 10 spectrophotometer. 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 an Iso Debye Flex 2002 apparatus using CuK_α radiations.

Analytical and physico-chemical data are given in tables 1–5.

3. Bio-activity

3.1. *Antifungal activity*

The ligands as well as their complexes were screened for antifungal activity against several fungi viz. *Alternaria*, *Pseudocercospora* 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^{-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 $25 \pm 2^\circ C$ for 24 h. Each slide was observed under the microscope for spore germination and percent germination was finally calculated.

3.2. *Antibacterial activity*

The antibacterial activity of the ligands and their complexes was studied against *Escherichia coli* (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} concentration 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 petri dishes containing nutrient agar media (agar 15 g + beef extract 3 g + peptone 5 g) seeded with *Escherichia coli* and *Bacillus subtilis* 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 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:

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

4. Results and discussion

It appears from the analytical data table 1 that Hgssdh and Hgspdh deprotonate their phenolic protons during complexation with metal(II) chloride. The metal salts and ligands react in 1 : 1 (M : L) molar ratio to give complexes of general composition [M(gssdh)]Cl and [M(gspdh)]Cl. The reactions may be written as:

$$\begin{array}{ccc} \text{MCl}_2\cdot x\text{H}_2\text{O} + \text{Hgssdh} & \rightarrow & [\text{M(gssdh)}]\text{Cl} + \text{HCl} + x\text{H}_2\text{O} \\ \text{or} & & \text{or} \\ \text{Hgspdh} & & [\text{M(gspdh)}]\text{Cl} \end{array}$$

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

All the metal complexes are insoluble in water and common organic solvents such as ethanol, methanol, benzene, chloroform, carbon tetrachloride and diethyl ether but are soluble in polar solvents such as DMF and DMSO. Cobalt complexes are orange, nickel complexes are yellowish green and light green, copper complexes are dark green and brown, zinc and cadmium complexes are yellow. Most of the complexes are either high melting with decomposition or decompose above 300 °C. The molar conductance values of 10^{-3} M solution of the complexes at room temperatures lie between 66.4–76.2 $\Omega^{-1}\,\text{mol}^{-1}\,\text{cm}^2$, showing that they are 1 : 1 electrolytes [14].

4.1. *Magnetic moments*

Where spin–spin coupling between unpaired electrons belonging to different copper ions is absent, μ_{eff} varies between 1.75 and 2.20 B.M., depending on the geometries of the complexes due to difference in orbital contribution. The magnetic moments of the Cu(II) complexes, in the present study, correspond to μ_{eff} values for one unpaired electron (1.89 and 1.92 B.M.). Nickel(II) complexes show μ_{eff} values in the range 2.73–2.89 B.M. corresponding to two unpaired electrons, suggesting octahedral geometry for nickel complexes [15]. Cobalt(II) octahedral complexes generally show magnetic moments between 4.7–5.2 B.M. because of the orbital contribution [16]. In the present study μ_{eff} values are 4.96 and 5.12 B.M., close to those reported for three unpaired electrons in an octahedral environment.

4.2. *Electronic spectra*

Copper(II) complexes show a broad band centered at 14,640 cm^{-1} and 14,450 cm^{-1}, respectively, for [Cu(gssdh)]Cl and [Cu(gspdh)]Cl, which may be assigned to superimposed transitions $^2B_{1g} \rightarrow {}^2B_{2g}$ and $\rightarrow {}^2E_g$ suggesting a distorted octahedral

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

			Analyses found (Calcd)%						
Compound (Colour)	Empirical formula (Formula weight)	M.P./D.P. (°C)	Metal	Cl	C	H	N	Yield (%)	Λ_M ($ohm^{-1}\,mol^{-1}\,cm^2$) in DMF
Hgssdh (White)	$C_{13}H_{14}N_4O_4$ (290)	>300			53.63 (53.79)	4.79 (4.83)	19.22 (19.31)	80	
Hgspdh (Yellow)	$C_{17}H_{14}N_4O_4$ (338)	>300			60.24 (60.36)	4.16 (4.14)	16.48 (16.57)	78	
[Co(gssdh)]Cl (Light orange)	$C_{13}H_{13}N_4O_4ClCo$ (383.5)	297	15.30 (15.38)	9.27 (9.26)	40.47 (40.68)	3.34 (3.39)	14.52 (14.60)	62	67.2
[Ni(gssdh)]Cl (Light green)	$C_{13}H_{13}N_4O_4ClNi$ (383.5)	288	15.25 (15.38)	9.21 (9.26)	40.44 (40.68)	3.32 (3.39)	14.48 (14.60)	68	73.4
[Cu(gssdh)]Cl (Dark green)	$C_{13}H_{13}N_4O_4ClCu$ (388)	236	16.30 (16.37)	9.09 (9.15)	40.05 (40.21)	3.26 (3.35)	14.32 (14.43)	75	69.8
[Zn(gssdh)]Cl (Cream)	$C_{13}H_{13}N_4O_4ClZn$ (389.5)	290	16.60 (16.69)	9.08 (9.11)	40.02 (40.05)	3.31 (3.34)	14.26 (14.38)	72	76.2
[Cd(gssdh)]Cl (Light yellow)	$C_{13}H_{13}N_4O_4ClCd$ (437)	300	25.70 (25.74)	8.13 (8.12)	35.53 (35.70)	2.92 (2.97)	12.89 (12.81)	58	71.9
[Co(gspdh)]Cl (Orange)	$C_{17}H_{13}N_4O_4ClCo$ (431.5)	298	13.60 (13.67)	8.16 (8.23)	47.07 (47.28)	3.05 (3.01)	12.86 (12.98)	71	72.8
[Ni(gspdh)]Cl (Yellow green)	$C_{17}H_{13}N_4O_4ClNi$ (431.5)	298	13.50 (13.67)	8.15 (8.23)	47.35 (47.28)	3.03 (3.01)	12.88 (12.98)	64	69.3
[Cu(gspdh)]Cl (Brown)	$C_{17}H_{13}N_4O_4ClCu$ (436)	>300	14.50 (14.56)	8.10 (8.14)	46.63 (46.79)	2.95 (2.98)	12.74 (12.84)	76	66.4
[Zn(gspdh)]Cl (Yellow)	$C_{17}H_{13}N_4O_4ClZn$ (437.5)	296	14.70 (14.86)	8.15 (8.11)	46.46 (46.63)	2.99 (2.97)	12.72 (12.80)	67	71.7
[Cd(gspdh)]Cl (Dark yellow)	$C_{17}H_{13}N_4O_4Cl.Cd$ (485)	282	23.10 (23.20)	7.27 (7.32)	41.87 (42.06)	2.71 (2.68)	11.46 (11.55)	69	74.3

Table 2. Magnetic moments, electronic spectral data and ligand field parameters of the complexes.

		Band maxima (cm^{-1})							
Complexes	μ_{eff} (B.M.)	ν_1	ν_2	ν_3	10 Dq (cm^{-1})	B (cm^{-1})	β	β^0 (%)	LFSE (Kcal mol^{-1})
[Co(gssdh)]Cl	4.96	9365	–	18940	10480	712	0.73	26.70	23.89
[Ni(gssdh)]Cl	2.73	10185	17065	26625	10185	875	0.85	15.00	34.82
[Cu(gssdh)]Cl	1.89	14640	–	–	–	–	–	–	–
[Co(gspdh)]Cl	5.12	10145	–	21785	11370	857	0.88	11.70	25.91
[Ni(gspdh)]Cl	2.89	11160	18250	25445	11160	681	0.66	33.90	38.15
[Cu(gspdh)]Cl	1.92	14450	–	–	–	–	–	–	–

configuration [17]. Nickel(II) complexes generally show three bands in octahedral environment corresponding to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), $\rightarrow {}^3T_{1g}(F)$ (ν_2) and $\rightarrow {}^3T_{1g}(P)$ (ν_3) [18]. Both Ni(II) complexes in this study show three transitions at 10,185 cm^{-1} (ν_1), 17,065 cm^{-1} (ν_2), and 26,625 cm^{-1} (ν_3) for [Ni(gssdh)]Cl and at 11,160 cm^{-1} (ν_1), 18,250 cm^{-1} (ν_2), and 25,445 cm^{-1} (ν_3) for [Ni(gspdh)]Cl, suggesting octahedral geometry for the nickel complexes [13]. [Co(gssdh)]Cl and [Co(gspdh)]Cl show two bands assigned as $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) and $\rightarrow {}^4T_{1g}(P)$ (ν_3) at 9365 cm^{-1} (ν_1) and 18,940 cm^{-1} (ν_3) for the former and at 10,145 cm^{-1} and 21,785 cm^{-1} for the latter complex. These transitions indicate octahedral geometry for both cobalt complexes [19]. The ν_2 transition is not observed due to very weak intensity [15]. Ligand field parameters (10 Dq, B, β, β^0 and LFSE) have also been calculated for both Ni(II) and Co(II) complexes by the procedure of Lever [15]. The low value of Racah parameter (B) for the complexes compared to the free ion value indicates significant covalent character of the metal–ligand bonds. The nephelauxetic ratio β and other parameters table 2 also support some covalent character in these complexes.

4.3. *ESR spectra*

ESR spectra of [Cu(gssdh)]Cl exhibit an axial signal figure 2 with separate $g_{\parallel}$ and $g_{\perp}$ values in the solid state at 300 K. The $g_{\parallel}$ and $g_{\perp}$ values are >2.04 table 3, indicating that Cu(II) is in axial symmetry with all the principal axes aligned parallel [20]. This would be consistent with an elongated tetragonally distorted octahedral geometry for the complexes. The solid state ESR spectra of [Cu(gspdh)]Cl show an intense broad signal with no hyperfine structure. The isotropic spectra give $A_{iso} = 211$ and $g_{iso} = 2.1238$, suggesting the presence of grossly misaligned tetragonal axes [21].

The frozen DMSO solution spectra of both the copper complexes exhibit an axial signal. The complexes show a well-defined hyperfine structure of four lines due to coupling of the electron with nuclear spin ($I = 3/2$) of the copper atom. The $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$ and $A_{\perp}$ values were accurately measured in the 120 K ESR spectra and their values suggest an elongated tetragonally distorted octahedral geometry for both complexes. The g_{av} and A_{av} values were calculated using the equations; $g_{av} = (g_{\parallel} + 2g_{\perp})/3$; $A_{av} = (A_{\parallel} + 2A_{\perp})/3$. Moreover, the observation that $g_{\parallel} > g_{\perp} > g_e$ (2.0023), shows that the unpaired electron is in the $d_{x^2-y^2}$ orbital of copper(II).

The spin-Hamiltonian parameters obtained from the ESR spectra and the separation of d–orbitals from electronic spectra have been used to calculate the bonding parameters α^2, α'^2 and β_1^2 table 3. A significant degree of covalent character in the metal-ligand bonds is indicated by the values of in-plane σ–bonding parameter α^2 (0.83

Table 3. ESR and bonding parameters of the 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(gssdh)]Cl	300	Solid state	58	48	52	2.1879	2.0514	2.0969	–	–	–
	120	DMSO solution	168	56	93	2.3108	2.0411	2.1310	0.83	0.20	0.83
[Cu(gspdh)]Cl	300	Solid state	–	–	$A_{iso} = 211$	–	–	$g_{iso} = 2.1238$	–	–	–
	120	DMSO solution	188	67	107	2.2899	2.0419	2.1246	0.87	0.16	0.86

and 0.87), out of plane σ–bonding parameter α'^2 (0.20 and 0.16) and in-plane π-bonding parameter β_1^2 (0.83 and 0.86) in these complexes.

4.4. *IR spectra*

Hgssdh and Hgspdh show ν(OH) and ν(NH) bands at 3398, 3477 cm^{-1} and 3207, 3167 cm^{-1}, respectively. The absence of ν(OH) bands in all the metal complexes indicates deprotonation of the phenolic proton during complexation. This is further confirmed by the appearance of a new band between 1258–1272 cm^{-1} assigned as ν(C–O) in all the metal complexes. A negligible variation in the position of ν(NH) band in the metal complexes as compared to the ligands (table 4) suggests non-involvement of >NH in bonding.

A broad ν(C=O) band is observed at 1683 cm^{-1} in Hgssdh and at 1660 cm^{-1} in Hgspdh due to the presence of three >C=O groups in the ligands; these bands shift to lower frequency by 18–30 cm^{-1} in all the complexes indicating coordination of all three >C=O groups to the metal [22]. In the complexes, amide II bands appeared to have shifted considerably to lower frequency (17–25 cm^{-1}) compared to the ligands and a shift to higher frequency (10–15 cm^{-1}) in the amide III bands further support the coordination through >C=O groups [23].

The ν(C=N) band is at 1619 cm^{-1} and at 1617 cm^{-1} in the spectra of Hgssdh and Hgspdh, respectively, shifted to lower frequency by 15–20 cm^{-1} in the metal complexes suggesting bonding through the two azomethine groups [1]. ν(N–N) at 985 cm^{-1} in Hgssdh and 971 cm^{-1} in Hgspdh shifts to higher frequency by 18–34 cm^{-1} in the complexes, indicating coordination of one nitrogen of the N–N group with metal [24]. General structures are proposed for the metal complexes on the basis of the above discussion figure 1.

4.5. *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 three of the complexes were recorded and the prominent lines were indexed by Ito's method [25] table 5. The following lattice constants were calculated:

	a	b	c (Å)
[Cu(gssdh)]Cl	8.04	7.05	6.51
[Cd(gspdh)]Cl	8.18	7.22	6.65
[Zn(gspdh)]Cl	7.65	6.82	6.36

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

Compounds	ν(OH + NH)	ν(C=O)	ν(C=N)	Amide II	Amide III	ν(N–N)	ν(C–O)
Hgssdh	3398b, 3207s	1683b	1619s	1546s	1370s	985w	
Hgspdh	3477b, 3167s	1660b	1617s	1573s	1377m	971w	
[Co(gssdh)]Cl	3203s	1653b	1603s	1523s	1382m	1012w	1270s
[Ni(gssdh)]Cl	3209s	1658b	1601s	1521s	1380s	1018m	1269m
[Cu(gssdh)]Cl	3208s	1661b	1599s	1525s	1385m	1015w	1272m
[Zn(gssdh)]Cl	3206s	1659b	1605s	1529s	1382m	1009w	1263s
[Cd(gssdh)]Cl	3210s	1654b	1602s	1527s	1386s	1019m	1258m
[Co(gspdh)]Cl	3170s	1639b	1602s	1546s	1386m	1003w	1265w
[Ni(gspdh)]Cl	3168s	1636b	1597s	1549s	1386m	997w	1271s
[Cu(gspdh)]Cl	3166s	1632b	1604s	1553s	1390s	991m	1266m
[Zn(gspdh)]Cl	3170s	1640b	1603s	1551s	1389s	989w	1269m
[Cd(gspdh)]Cl	3168s	1642b	1598s	1555s	1387m	1005m	1262s

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

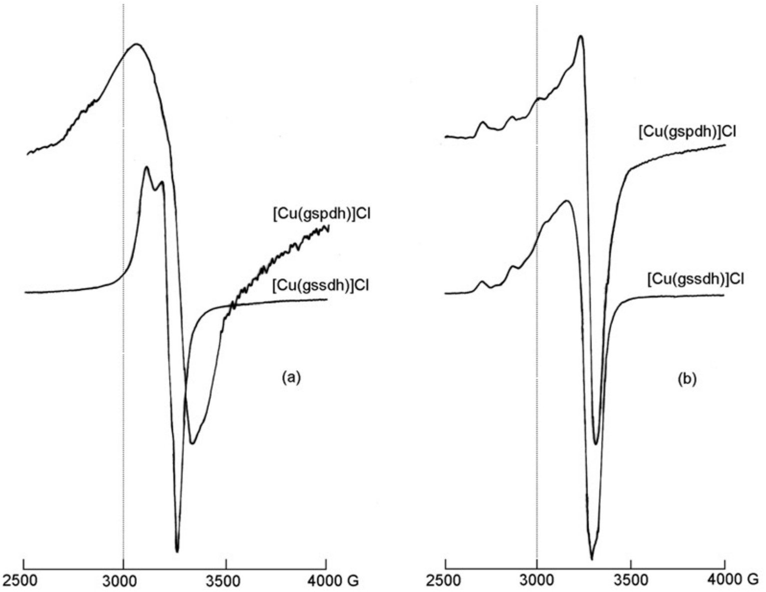


Figure 1. ESR spectra of copper(II) complexes (a) in solid state at 300 K (b) in DMSO solution at 120 K.

These values indicate an orthorhombic crystal lattice for all the above complexes. The X-ray spectrum of [Cd(gspdh)]Cl is shown in figure 3.

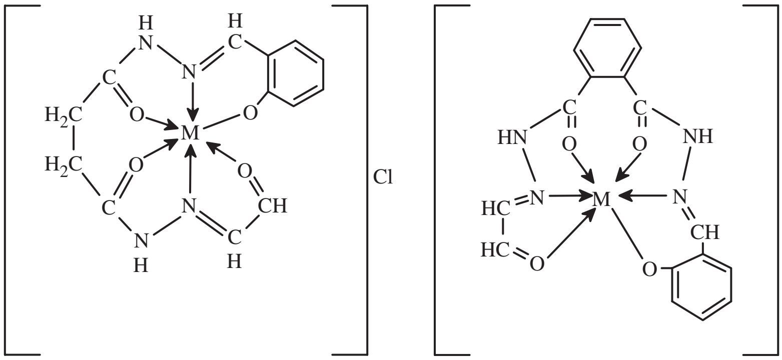
4.6. *Antifungal activity*

The antifungal experimental data (table 6A) indicate that the ligands and their complexes show appreciable activity against *Alternaria* sp., *Pseudocercospora* sp. and *Colletotrichum* sp. at 0.5, 1.0 and 1.5 mg mL^{-1} [26]. The effect is susceptible to the concentration of the compound used for inhibition, enhanced at higher concentration. DMSO control also has a little activity; the antifungal experimental results of the compounds were compared against DMSO as the control and are expressed as

Table 5. Observed and calculated Q and hkl values.

Powder patterns [Cu(gssdh)]Cl	Intensity	Angle°	d (Å)	Q_{obs} $(1/d^2)$	Q_{Calcd}	Hkl
1	60.22	11.00	8.037	0.0155	0.0155	100
2	58.56	12.55	7.048	0.0201	0.0201	010
3	41.99	13.60	6.506	0.0236	0.0236	001
4	48.07	16.10	5.501	0.0330	0.0356	110
5	55.80	18.25	4.857	0.0424	0.0438	011
6	59.67	21.15	4.197	0.0568	0.0592	111
7	66.85	22.75	3.906	0.0655	0.0619	200
8	85.08	26.80	3.324	0.0905	0.0945	002
9	100.00	28.00	3.184	0.0986	0.0960	120
10	75.14	30.60	2.919	0.1174	0.1146	012
11	56.35	41.55	2.172	0.2120	0.2126	003
12	65.19	48.60	1.872	0.2854	0.2915	411
13	60.22	54.35	1.687	0.3514	0.3612	141
[Zn(gssdh)]Cl						
1	49.23	10.80	8.185	0.0149	0.0149	100
2	51.28	12.25	7.219	0.0192	0.0192	010
3	51.28	13.30	6.652	0.0226	0.0226	001
4	61.03	16.65	5.320	0.0353	0.0341	110
5	60.00	17.25	5.136	0.0379	0.0375	101
6	70.26	20.40	4.350	0.0528	0.0567	111
7	96.41	26.00	3.424	0.0853	0.0823	201
8	100.00	27.00	3.300	0.0918	0.0917	120
9	96.92	27.65	3.224	0.0962	0.0993	021
10	64.62	30.70	2.910	0.1181	0.1143	121
11	57.44	31.30	2.855	0.1227	0.1245	112
12	46.15	41.15	2.192	0.2081	0.2034	003
13	44.10	43.15	2.095	0.2278	0.2226	013
14	41.03	54.35	1.687	0.3514	0.3445	141
[Cd(gspdh)]Cl						
1	24.54	11.55	7.655	0.0171	0.0171	100
2	41.14	12.98	6.816	0.0215	0.0215	010
3	56.09	13.90	6.364	0.0247	0.0247	001
4	23.43	17.15	5.166	0.0375	0.0386	110
5	16.42	18.00	4.924	0.0412	0.0418	101
6	18.63	18.95	4.679	0.0457	0.0462	011
7	35.24	23.00	3.864	0.0670	0.0683	200
8	41.51	26.20	3.399	0.0866	0.0861	020
9	93.36	27.07	3.291	0.0923	0.0930	201
10	100.00	27.70	3.218	0.0966	0.0988	002
11	19.00	28.50	3.129	0.1021	0.1032	120
12	23.06	29.35	3.041	0.1081	0.1108	021
13	38.56	30.69	2.911	0.1180	0.1158	102
14	19.74	32.00	2.795	0.1280	0.1279	121
15	18.27	32.70	2.736	0.1336	0.1374	112
16	23.99	38.00	2.366	0.1786	0.1783	301
17	19.37	39.25	2.293	0.1902	0.1937	030
18	16.05	41.25	2.187	0.2091	0.2108	130
19	15.31	46.20	1.963	0.2595	0.2608	113
20	15.13	53.00	1.726	0.3357	0.3444	040

percentage inhibition versus control (table 6A). The ligand Hgspdh as well as its complexes shows better activity than Hgssdh and its complexes. The metal complexes are more active than the ligands. [Cd(gspdh)]Cl shows the highest (100%) activity against *Alternaria* sp. and *Pseudocercospora* sp. at the concentration of 1.5 mg mL^{-1}. However, [Cd(gssdh)]Cl shows 100% activity against *Colletotrichum*



[M(gssdh)]Cl M(gspdh)]Cl

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

Figure 2. General structures of the metal complexes.

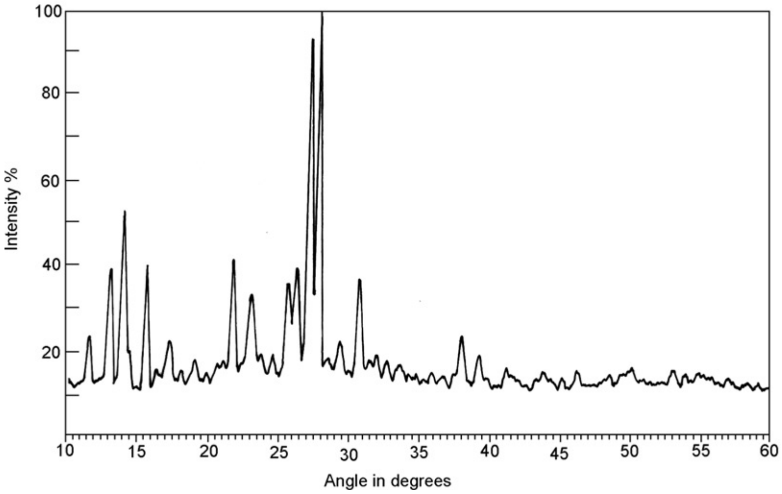


Figure 3. X-ray powder diffraction pattern of [Cd(gspdh)]Cl.

sp. at 1.5 mg mL^{-1}. The toxicity of Hgssdh complexes varies in the following order of the fungal species:

Colletotrichum sp. > *Alternaria* sp. > *Pseudocercospora* sp.

For Hgspdh complexes, the toxicity order is shown below:

Alternaria sp. > *Pseudocercospora* sp. > *Colletotrichum* sp.

The experimental data also indicate that the antifungal activity, in general, varies with the following order of metal ions:

Cd > Cu > Zn > Co > Ni

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

	% Inhibition of spore germination								
	Alternaria sp. (mg mL^{-1})			*Pseudocercospora* sp. (mg mL^{-1})			*Colletotrichum* sp. (mg mL^{-1})		
Compounds	0.5	1.0	1.5	0.5	1.0	1.5	0.5	1.0	1.5
Hgssdh	36	50	58	35	48	55	41	52	60
Hgspdh	42	55	66	40	54	62	38	52	60
[Co(gssdh)]Cl	50	76	90	48	65	86	56	80	92
[Ni(gssdh)]Cl	48	70	89	45	60	85	51	78	89
[Cu(gssdh)]Cl	52	72	92	46	69	94	60	82	96
[Zn(gssdh)]Cl	56	75	94	50	70	93	58	84	97
[Cd(gssdh)]Cl	60	78	98	52	76	97	62	85	100
[Co(gspdh)]Cl	60	82	96	56	80	92	54	79	90
[Ni(gspdh)]Cl	55	76	90	55	78	90	50	76	88
[Cu(gspdh)]Cl	65	84	100	62	81	97	58	82	95
[Zn(gspdh)]Cl	63	82	98	64	84	96	62	80	98
[Cd(gspdh)]Cl	67	86	100	65	85	100	60	83	99

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

	Diameter of inhibition zone (in mm)				% Activity Index			
	Escherichia coli (mg mL^{-1})		*Bacillus subtilis* (mg mL^{-1})		*Escherichia coli* (mg mL^{-1})		*Bacillus subtilis* (mg mL^{-1})	
Compounds	1.0	2.0	1.0	2.0	1.0	2.0	1.0	2.0
Hgssdh	4	5	4	6	40	45	36	46
Hgspdh	4	5	4	5	40	45	36	38
[Co(gssdh)]Cl	5	6	5	6	50	55	45	46
[Ni(gssdh)]Cl	4	6	4	6	40	55	36	46
[Cu(gssdh)]Cl	6	7	7	9	60	64	64	69
[Zn(gssdh)]Cl	4	5	5	7	40	45	45	54
[Cd(gssdh)]Cl	8	9	7	10	80	82	64	77
[Co(gspdh)]Cl	5	6	5	7	50	55	45	54
[Ni(gspdh)]Cl	4	6	5	6	40	55	45	46
[Cu(gspdh)]Cl	6	7	4	7	60	64	36	54
[Zn(gspdh)]Cl	5	6	5	6	50	55	45	46
[Cd(gspdh)]Cl	5	7	7	9	50	59	64	69
Ampicillin	10	11	11	13	100	100	100	100

The toxicity of the complexes can be related to the strength of the metal–ligand bond, and other factors such as size of the cation [27], receptor sites [28], diffusion [29] and a combined effect of the metal and the ligands [30] for inactivation of biomolecules.

4.7. *Antibacterial activity*

The metal complexes, ligands, standard drug Ampicillin and DMSO solvent control were screened separately for their antibacterial activity against *E. coli* and *B. subtilis*. The activity increases with increasing concentration of compounds. 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 results suggest that the ligands and their complexes (table 6B) show moderate activity against both the bacteria [31, 32] as compared to Ampicillin. The metal complexes show higher antibacterial activity than the ligands and DMSO control. The DMSO solvent showed insignificant activity. The % Activity Index data indicate that [Cd(gssdh)]Cl shows the highest activity (82%) against *E. coli* at 2.0 mg mL^{-1}. The ligands show poorer activity than the metal complexes. Hgssdh complexes show better activity than Hgspdh complexes. In general, the activity follows the following order of metal ions:

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

Acknowledgements

The authors thank the Director, Institute of Engineering & Technology, C.S.J.M. University, Kanpur, for providing laboratory facilities, Head, Department of Chemistry, Indian Institute of Technology, Kanpur, for recording UV-vis, IR, and ESR spectra, Dr Nand Lal, Department of Life Sciences, C.S.J.M. University, Kanpur, for the help in biological screening.

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