Synthesis, physico-chemical, and spectral studies of dimeric cobalt(II), nickel(II), copper(II), zinc(II), and cadmium(II) complexes with dibutanone acyldihydrazones

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Synthesis, physico-chemical, and spectral studies of dimeric cobalt(II), nickel(II), copper(II), zinc(II), and cadmium(II) complexes with dibutanone acyldihydrazones

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Dimeric metal complexes of two new ligands, dibutanone malonic acid dihydrazone (dbmdh), and dibutanone succinic acid dihydrazone (dbsdh) with monomer composition $[M(dbmdh)Cl_2]$ and $[M(dbsdh)(H_2O)_2]Cl_2$, $M = Co(II)$, Ni(II), Cu(II), Zn(II), Cd(II), were synthesized and characterized by elemental analyses, weight loss study, molecular weight determination, magnetic susceptibility measurements, electronic, ESR, infrared, ^1H, and ^{13}C NMR spectral studies. The metal complexes have octahedral geometry. Both ligands are neutral tetradentate, coordinating through two >C=N nitrogen atoms and two >C=O oxygen atoms to two metal ions in a dimer. The molecular weight determination indicates dimers for all the metal complexes. ESR spectral studies indicate a tetragonally distorted octahedral stereochemistry for both Cu(II) complexes. The $\Delta Ms = 2$ transition observed in these complexes suggest that the Cu(II) complexes are dimeric. ESR data indicate $d_{x^2-y^2}$ as the ground state and the bonding parameters, α^2, α'^2, and β_1^2 suggest appreciable covalency of the in-plane σ-bonding. The dbsdh complexes contain coordinated water as evinced by their weight loss.

Keywords: Dibutanone acyldihydrazones; Metal(II) complexes; Magnetic moments and electronic spectra; IR spectra; NMR spectra; ESR spectral studies

1. Introduction

Acylhydrazones of various aldehydes and ketones have occupied a special place among the biologically important organic ligands, since they contain a variety of donor groups and are able to change denticity depending on the reaction conditions [1, 2]. These ligands react with metal ions to give monometallic [3], homobimetallic [4], and heterobimetallic [5, 6] coordination compounds. Acylhydrazone derivatives are of interest for beneficial biological activities [7]. Such ligands create an environment similar to biological systems by coordinating through oxygen atoms and nitrogen atoms. Hydrazones find extensive applications in various fields [8, 9], widely applied as insecticides, medicines, and analytical reagents. Hydrazone derivatives possessing anti-inflammatory, analgesic [10], antipyretic [11], antibacterial [12], and antitumor [13] activities have been reported.

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Coordination chemistry of metal complexes of hydrazones is important due to biological activity and ability to act as potential inhibitors for enzymes [14, 15]. The biological activity has been related to the chelating of the acylhydrazones [16]. Metal complexes of hydrazones show potential application as catalysts [17], luminescent probes [18], and molecular sensors [19]. Pyridoxal isonicotinoyl hydrazone (PIH) analogs are effective iron chelators *in vivo* and *in vitro*, and may be valuable for the treatment of iron overload [20]. Although a few complexes of metal ions with dihydrazones of salicylaldehyde and 2-hydroxy-1-naphthaldehyde have been reported [21–23], work on dihydrazones derived from condensation of acyldihydrazines and butanone is virtually absent. The significant role played by metal complexes of acylhydrazones in biological systems and other fields led to our syntheses of dimeric cobalt(II), nickel(II), copper(II), zinc(II), and cadmium(II) complexes with dibutanone malonic acid dihydrazone and –succinic acid dihydrazone. The complexes were characterized by various physico-chemical and spectral techniques.

dbmdh

dbsdh
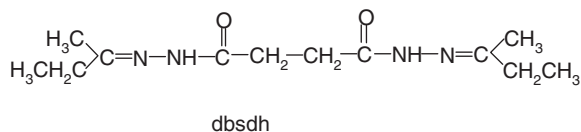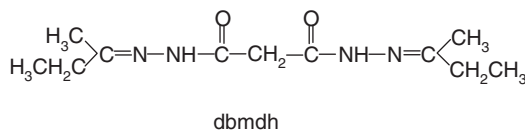
2. Experimental

2.1. *Materials and methods*

Commercial reagents have been used without purification and all experiments have been carried out in the atmosphere. The metal salts, butanone, and solvents were purchased from SD Fine Chemicals, India and were used as received. Diethyl malonate, diethylsuccinate and hydrazine hydrate (Merck Chemicals, India) were used in synthesis.

The precursor malonic acid dihydrazide, $CH_2(CONHNH_2)_2$ and succinic acid dihydrazide, $CH_2CH_2(CONHNH_2)_2$ were prepared by the reported procedures [24, 25], reacting diethyl malonate and diethylsuccinate with hydrazine hydrate, respectively, in 1:2 molar ratio in a beaker containing 10 mL ethanol (95%).

2.2. *Synthesis of ligands*

Dibutanone malonic acid dihydrazone (dbmdh) and dibutanone succinic acid dihydrazone (dbsdh) were synthesized by reacting 20 mL butanone (50 mmol, 3.60 mL) solution in ethanol (95%) with 30 mL aqueous ethanolic solution each of malonic acid

dihydrazide (25 mmol, 3.30 g) and succinic acid dihydrazide (25 mmol, 3.65 g) in a round bottom flask. After refluxing the reaction solutions for 3–4 h, the ligands were obtained as cream yellow precipitates. The product was filtered by suction on a Buchner funnel and washed several times with aqueous ethanol (50%, v/v) to remove unreacted reactants. The pure product was dried in a desiccator over anhydrous calcium chloride.

The ligands were characterized by elemental analyses (C, H, N), melting points, NMR (^{1}H and ^{13}C), and infrared (IR) spectra. The ligands could not be crystallized because they are highly insoluble in common organic solvents.

2.3. *Synthesis of the metal complexes*

Metal(II) complexes of dbmdh and dbsdh were prepared by reacting 25 mL aqueous solution of Co(II), Ni(II), Cu(II), Zn(II), or Cd(II) chloride (10 mmol), separately with dbmdh (10 mmol, 2.40 g) or dbsdh (10 mmol, 2.54 g) suspended in 25 mL ethanol (95%), in 1 : 1 (M : L) molar ratio in a round bottom flask. The reactants were stirred on a magnetic stirrer at room temperature for 1 h to precipitate the complexes except the Cu(II) complexes, which precipitated immediately. The solid products thus obtained were filtered in a glass crucible, washed thoroughly with aqueous ethanol (50%, v/v) and finally with diethyl ether and dried in a desiccator at room temperature. The complexes could not be crystallized in DMF, DMSO, or in various mixtures of solvents.

2.4. *Physico-chemical measurements*

The metal and chloride contents were analyzed gravimetrically using standard literature procedures [26]. C, H, and N contents were determined on an Exeter Analytical Inc. CHN Analyser (Model CE-440). Molecular weights of the metal complexes were determined in spectroscopic grade DMF solution by freezing point depression. ^{1}H and ^{13}C NMR spectra of the ligands were recorded in DMSO-d_6 on a JEOL AL-300 FT-NMR multinuclear spectrometer. Chemical shifts are reported in parts per million (ppm) using tetramethylsilane (TMS) as an internal standard. All exchangeable protons were confirmed by the addition of D_2O. IR spectra were recorded in KBr on a Varian 3100 FT-IR spectrophotometer from 4000 to 400 cm^{-1}. Electronic spectra of the complexes were recorded on a Shimadzu spectrophotometer, model Pharmaspec UV-1700 in nujol. Magnetic susceptibility measurements were performed at room temperature on a Cahn-Faraday balance using Hg[Co(SCN)$_4$] as the calibrant. The X-band ESR spectra of Cu(II) complexes were recorded on a EMX 1444 EPR spectrometer at room temperature (300 K) in the solid state and in DMSO solution at 77 K using TCNE as *g* marker ($g = 2.00277$).
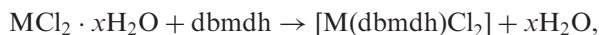
3. Results and discussion

From the analytical data (table 1) dbmdh and dbsdh react with metal(II) chloride in 1 : 1 (M : L) molar ratio to form the complexes of compositions [M(dbmdh)Cl$_2$] and

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

Compound (in monomer unit form) (Color)	Empirical monomer unit formula	M.P./ Dec. (°C)	Analyses found (Calcd) %					Yield (%)	Molecular weight Expt. (Calcd)
			Metal	Cl	C	H	N		
dbmdh (White)	$C_{11}H_{20}N_4O_2$	202			54.82 (55.00)	8.29 (8.33)	23.21 (23.33)	75	(240)
dbsdh (Cream)	$C_{12}H_{22}N_4O_2$	177			56.51 (56.69)	8.60 (8.66)	22.18 (22.05)	70	(254)
[Co(dbmdh)Cl₂] (Pink)	$C_{11}H_{20}N_4O_2CoCl_2$	272^d	16.00 (15.94)	19.10 (19.19)	35.59 (35.67)	5.41 (5.40)	15.07 (15.13)	67	735 ± 10 (370)
[Ni(dbmdh)Cl₂] (Bluish green)	$C_{11}H_{20}N_4O_2NiCl_2$	255^d	15.79 (15.88)	19.12 (19.20)	35.56 (35.70)	5.44 (5.41)	15.08 (15.15)	70	730 ± 15 (369.7)
[Cu(dbmdh)Cl₂] (Dark green)	$C_{11}H_{20}N_4O_2CuCl_2$	287^d	17.03 (16.95)	18.90 (18.96)	35.11 (35.25)	5.31 (5.34)	14.86 (14.95)	76	750 ± 10 (374.5)
[Zn(dbmdh)Cl₂] (Cream)	$C_{11}H_{20}N_4O_2ZnCl_2$	225^d	17.32 (17.37)	18.79 (18.86)	34.96 (35.07)	5.32 (5.31)	14.80 (14.88)	62	755 ± 20 (376.4)
[Cd(dbmdh)Cl₂] (White)	$C_{11}H_{20}N_4O_2CdCl_2$	268^d	26.45 (26.55)	16.69 (16.77)	31.06 (31.18)	4.75 (4.72)	13.19 (13.23)	68	840 ± 25 (423.4)
[Co(dbsdh)(H₂O)₂]Cl₂ (Pink)	$C_{12}H_{26}N_4O_4CoCl_2$	215^d	14.10 (14.05)	16.82 (16.90)	34.19 (34.28)	6.15 (6.19)	13.29 (13.33)	70	835 ± 10 (420)
[Ni(dbsdh)(H₂O)₂]Cl₂ (Light blue)	$C_{12}H_{26}N_4O_4NiCl_2$	248^d	14.00 (13.99)	16.81 (16.92)	34.40 (34.31)	6.17 (6.19)	13.24 (13.34)	72	830 ± 20 (419.7)
[Cu(dbsdh)(H₂O)₂]Cl₂ (Green)	$C_{12}H_{26}N_4O_4CuCl_2$	195^d	14.87 (14.96)	16.60 (16.72)	33.78 (33.92)	6.09 (6.12)	13.15 (13.19)	80	855 ± 15 (424.5)
[Zn(dbsdh)(H₂O)₂]Cl₂ (Cream)	$C_{12}H_{26}N_4O_4ZnCl_2$	212^d	15.30 (15.34)	16.56 (16.65)	33.65 (33.77)	6.12 (6.10)	13.05 (13.13)	66	850 ± 20 (426.4)
[Cd(dbsdh)(H₂O)₂]Cl₂ (White)	$C_{12}H_{26}N_4O_4CdCl_2$	250^d	23.63 (23.74)	14.96 (15.00)	30.31 (30.42)	5.46 (5.49)	11.78 (11.83)	70	940 ± 25 (473.4)

$[M(dbsdh)(H_2O)_2]Cl_2$. The reactions may be written as

$$MCl_2 \cdot xH_2O + dbmdh \rightarrow [M(dbmdh)Cl_2] + xH_2O,$$

$$MCl_2 \cdot xH_2O + dbsdh \rightarrow [M(dbsdh)(H_2O)_2]Cl_2 + (x-2)H_2O,$$

where $M = Co(II)$, $Ni(II)$, $Cu(II)$, $Zn(II)$, and $Cd(II)$. The ligand dbmdh has a fragment that is structurally similar to 1,3-diketones with some aromatic character in the six-membered chelate ring in the complexes. For complexes of 1,3-diketones, it happens because of the enolization of these ligands in basic media during complex formation. Similar possibility of diketonate-like chelation with dbmdh was eliminated because the reaction medium was not basic. We have found no evidence of enolization of dbmdh or dbsdh during complexation.

The cobalt(II) complexes are pink, nickel(II) complexes are bluish green and light blue, copper(II) complexes are green, zinc(II) complexes are cream, and cadmium(II) complexes are white. The ligands and their metal complexes are insoluble in water and common organic solvents like ethanol, methanol, chloroform, benzene, and diethyl ether. However, they are soluble in DMF and DMSO. All the complexes are stable, decomposing between 195 and 287°C.

The weight losses of the metal complexes were performed by heating them at 110°C and at 180°C and passing the vapors through a trap containing anhydrous copper sulfate to ensure the presence of different types of water molecules in the complexes. The dbmdh complexes show no weight loss at either temperature, confirming the absence of water in these complexes. However, the dbsdh complexes lose significant weight on heating at 180°C, corresponding to two coordinated water molecules per metal ion.

3.1. *Molecular weight determination*

Since all the metal complexes are soluble in DMF, the molecular weights of the complexes have been determined in DMF solution by freezing point depression. The experimental molecular weights for metal complexes of both the ligands are close to twice the theoretical formula weight calculated for monomer confirming their dimeric structure [23].

Although all the complexes are dimeric, calculations regarding weight loss studies and magnetic susceptibility measurements have been done by using monomer unit formula weight and the resulted values represent for single metal ion (half unit of the complex).

3.2. *Magnetic moments*

Monomeric cobalt(II) tetrahedral complexes generally show magnetic moments between 4.0 and 4.6 B.M. while the octahedral complexes show between 4.7 and 5.2 B.M. because of the orbital contribution [27]. The μ_{eff} values, 4.87 B.M. and 4.83 B.M. per metal ion observed for cobalt(II) complexes with dbmdh and dbsdh, respectively, are fairly close to those reported for an octahedral environment. The effective magnetic moments reported for high spin octahedral monomeric nickel(II) complexes are in the

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

Complexes (in monomer unit form)	μ_{eff} (B.M.)	Band maxima (cm^{-1})			10 Dq (cm^{-1})	B (cm^{-1})	β	β^0 (%)	LFSE (Kcal mol^{-1})
		ν_1	ν_2	ν_3					
[Co(dbmdh)Cl$_2$]	4.87	9175	15,875	19,800	10,276	782	0.805	19.50	23.42
[Ni(dbmdh)Cl$_2$]	2.90	10,100	16,420	26,660	10,100	852	0.818	18.20	34.53
[Cu(dbmdh)Cl$_2$]	1.78	13,605	23,200	24,690	13,605				23.26
[Co(dbsdh)(H$_2$O)$_2$]Cl$_2$	4.83	9225	16,000	20,240	10,332	808	0.832	16.80	23.55
[Ni(dbsdh)(H$_2$O)$_2$]Cl$_2$	2.86	10,060	15,600	27,025	10,060	830	0.797	20.30	34.39
[Cu(dbsdh)(H$_2$O)$_2$]Cl$_2$	1.81	14,085	21,740	25,000	14,085				24.08

range 2.8–3.2 B.M., while for the tetrahedral complexes, the value ranges from 3.5 to 4.0 B.M. [28]. Both the nickel(II) complexes in this study show μ_{eff} values 2.90 B.M. and 2.86 B.M. per metal ion corresponding to two unpaired electrons in octahedral environment. The magnetic moments of two copper(II) complexes (1.78 and 1.81 B.M. per metal ion) correspond to μ_{eff} values for one unpaired electron.

3.3. *Electronic spectra*

Cobalt(II) complexes generally show three transition bands in the visible range in an octahedral field by excitation from $^4T_{1g}(F)$ to the excited states $^4T_{2g}(F)$, $^4A_{2g}(F)$, and $^4T_{1g}(P)$. In the case of [Co(H$_2$O)$_6$]$^{2+}$, the transitions are observed at 8130, 17,540, and 21,980 cm^{-1} [29]. The dbmdh and dbsdh complexes of cobalt(II) show three bands at 9175, 15,875, and 19,800 cm^{-1}, respectively, suggesting octahedral geometry for the complexes. Nickel(II) complexes have 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) [24]. In spectra of [Ni(NH$_3$)$_6$]$^{2+}$, these bands have been observed at 10,700, 17,540, and 28,170 cm^{-1}, respectively [28]. Both nickel(II) complexes also show three transitions at 10,100, 16,420, 26,660 cm^{-1} for [Ni(dbmdh)Cl$_2$] and at 10,060, 15,600, 27,025 cm^{-1} for [Ni(dbsdh)(H$_2$O)$_2$]Cl$_2$ indicating octahedral complexes. Various ligand-field parameters (10 Dq, B, β, β^0, and LFSE) were calculated for the cobalt(II) and nickel(II) complexes (table 2), which indicate covalent metal–ligand bonds [29]. Both copper(II) complexes show three transitions, $^2B_{1g} \rightarrow {}^2A_{1g}$ (ν_1), $\rightarrow {}^2B_{2g}$ (ν_2), and $\rightarrow {}^2E_g$ (ν_3) at 13,605, 23,200, and 24,690 cm^{-1} and 14,085, 21,740, and 25,000 cm^{-1}, respectively, for dbmdh and dbsdh complexes, which indicate a distorted octahedral geometry [5].

3.4. *ESR spectra*

[Cu(dbmdh)Cl$_2$] exhibits isotropic spectra with intense broad signal with no hyperfine structure in the solid state at room temperature (figure 1a). The g_{iso} value of 2.1104 and $A_{iso} = 73$ suggest a geometry involving grossly misaligned tetragonal axes. [Cu(dbsdh)(H$_2$O)$_2$]Cl$_2$ gives an axial signal in solid state. The $g_{||}$ and $g_{\perp}$ values are >2.04, consistent with copper(II) in axial symmetry with all the principal axes aligned parallel. This would be consistent with an elongated tetragonally distorted octahedral stereochemistry. The G factor, defined as $G = (g_{||} - 2)/(g_{\perp} - 2)$, is 4.7642, indicating that

(a)

[Cu(dbmdh)Cl$_2$]

[Cu(dbsdh)(H$_2$O)$_2$]Cl$_2$

g marker

Magnetic Field(G) ⟶

(b)

[Cu(dbmdh)Cl$_2$]

g marker

[Cu(dbsdh)(H$_2$O)$_2$]Cl$_2$

Magnetic Field(G) ⟶

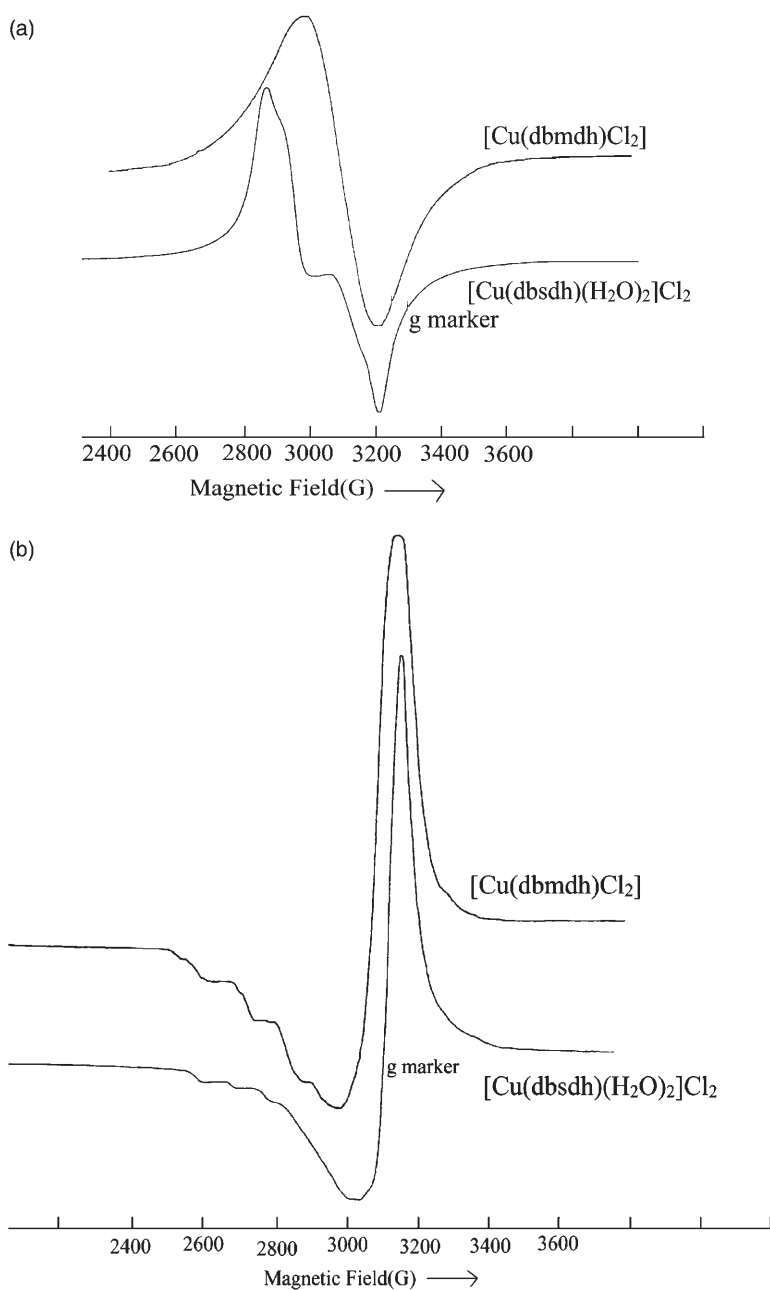Figure 1. ESR spectra of copper(II) complexes (a) in solid state and (b) in DMSO solution.

the local tetragonal axes are slightly misaligned and exchange interactions between copper(II) centers in the solid state are negligible [30].

DMSO solution spectra of both copper(II) complexes at 77 K give more intense axial signal and the Cu(II) hyperfine lines are well resolved (figure 1b). Both complexes show

a well-defined hyperfine structure of four lines due to copper(II) nuclei ($I = 3/2$) on the low field region (figure 1) to allow accurate calculation of $g_{\parallel}$ and $A_{\parallel}$ values. However, such splitting in the $g_{\perp}$ component is not observed in the higher field region, probably owing to poorly resolved ligand hyperfine interactions [31]. The g_{av} and A_{av} values were calculated using the equations $g_{av} = (g_{\parallel} + 2g_{\perp})/3$; $A_{av} = (A_{\parallel} + 2A_{\perp})/3$ and listed in table 3. These values predict an elongated tetragonally distorted octahedral geometry for both complexes in DMSO. The trend $g_{\parallel} > g_{\perp} > g_e$ (2.0023) suggests that the ground state of copper(II) is predominantly $d_{x^2-y^2}$ [32, 33]. In the spectra of both the complexes, an intense half-field signal appears at 1600 G, due to $\Delta Ms = 2$ transition, characteristic of dimers [4].

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). The coefficient which represents the in-plane σ-bond strength, α^2, indicates the axial σ-bonding decreases with a corresponding increase in the in-plane σ-bonding. The β_1^2 values also indicate significant in-plane π-bonding in these complexes [34].

3.5. ^1H and ^{13}C NMR

^{1}H NMR spectra of dbmdh exhibit signals due to four –CH$_3$ groups as triplet at δ 1.62 (6H) and singlet at 1.81 (6H), three >CH$_2$ protons as quartet at 3.05 (4H) and singlet at 3.20 (2H) and two –NH protons as singlet at 10.10 (2H) ppm [35]. In spectra of [Zn(dbmdh)Cl$_2$], both –NH protons show a slightly downfield shift compared to dbmdh, indicative of deshielding of >NH proton and in turn shows interaction of the two >C=N– groups with the metal. The signals for –CH$_3$ and >CH$_2$ protons show a minor shift in their position in the complexes (table 4). The dbsdh exhibits ^{1}H NMR signals for four –CH$_3$ protons as triplet at δ 1.01 (6H) and singlet at 1.72 (6H), four >CH$_2$ protons as quartet at 2.36 (4H) and triplet at 2.80 (4H) and two >NH protons as singlet at 9.50 (2H) ppm. The downfield shift of two >NH protons from 9.50 to 9.96 ppm in its Zn(II) complex indicates coordination of two >C=N– nitrogen atoms to the metal. There are minor shifts in the position of –CH$_3$ and >CH$_2$ signals. The disappearance of two >NH protons in both ligands in D$_2$O exchanged ^{1}H NMR spectra confirm their assignments.

The number of carbon signals in ^{13}C NMR spectra of the ligands and Zn(II) complexes correspond well to the number of carbons present. ^{13}C NMR spectra of dbmdh and dbsdh show peaks at 14.11, 18.04, 19.02, 21.55, and 10.56, 10.86, 15.62, 15.83 ppm, respectively, for four CH$_3$ carbons. Similarly three CH$_2$ peaks are observed at 35.60, 38.17, 54.07 ppm in dbmdh and four CH$_2$ peaks at 21.03, 28.43, 31.48, 31.55 ppm in dbsdh. The signals at 164.47, 165.10 and 157.92, 153.27 ppm in dbmdh and dbsdh, respectively, are assigned to two >C=O carbons, and signals at 170.44, 171.97, 170.72, and 173.89 ppm are assigned to two C=N carbons. In Zn(II) complexes of dbmdh and dbsdh, bonding through two >C=O and two >C=N– groups has been inferred from deshielding in these carbons as compared with the ligands. The –CH$_3$ and >CH$_2$ carbons show minor change in their positions compared with the ligands (table 5).

Table 3.   ESR spectral parameters for copper(II) complexes.

Complex (in monomer unit form)	Medium	Temp. (K)	$A_{\parallel}$ (G)	$A_{\perp}$ (G)	A_{av} (G)	$g_{\parallel}$	$g_{\perp}$	g_{av}	α^2	α'^2	β_1^2
[Cu(dbmdh)Cl$_2$]	Solid state	300									
	DMSO solution	77	150	70	$A_{iso} = 73$	2.3426	2.0406	$g_{iso} = 2.1104$	0.786	0.246	0.89
[Cu(dbsdh)(H$_2$O)$_2$]Cl$_2$	Solid state	300	87	60	69	2.2425	2.0509	2.1412			
	DMSO solution	77	166	80	108	2.3682	2.0535	2.1148	0.859	0.168	0.91

Table 4. ^{1}H NMR spectra of ligands and their complexes.

Compounds (in monomer unit form)	^{1}H NMR signals (ppm)		
	CH$_3$	CH$_2$	NH
dbmdh	1.62t (6H), 1.81s (6H)	3.05q (4H), 3.20s (2H)	10.10s (2H)
[Zn(dbmdh)Cl$_2$]	1.61t (6H), 1.80s (6H)	3.12q (4H), 3.21s (2H)	10.18s (2H)
dbsdh	1.01t (6H), 1.72s (6H)	2.36q (4H), 2.80t (4H)	9.50s (2H)
[Zn(dbsdh)(H$_2$O)$_2$]Cl$_2$	1.12t (6H), 1.75s (6H)	2.48q (4H), 2.88t (4H)	9.96s (2H)

s = singlet, t = triplet, q = quartet.

Table 5. ^{13}C NMR spectra of ligands and their complexes.

Compounds (in monomer unit form)	^{13}C NMR signals (ppm)			
	CH$_3$	CH$_2$	C=N	C=O
dbmdh	14.11 (2C), 18.04 (2C)	38.17 (2C), 54.07 (1C)	165.10 (2C)	171.97 (2C)
[Zn(dbmdh)Cl$_2$]	14.13 (2C), 18.08 (2C)	38.19 (2C), 54.11 (1C)	166.15 (2C)	173.07 (2C)
dbsdh	10.86 (2C), 15.83 (2C)	28.43 (2C), 31.51 (2C)	157.92 (2C),	173.89 (2C)
[Zn(dbsdh)(H$_2$O)$_2$]Cl$_2$	10.90 (2C), 15.87 (2C)	28.43 (2C), 31.55 (2C)	159.20 (2C)	175.11 (2C)

Table 6. Important IR spectral bands (cm^{-1}) and their assignments.

Compounds (in monomer unit form)	ν(OH) water	ν(NH)	ν(C=O)	ν(C=N)	ν(C–N)	ν(N–N)	ν(M–O)	ν(M–N)
dbmdh	–	3284b	1651s	1618s	1343s	960w	–	–
dbsdh	–	3237b	1657s	1620s	1347s	962w	–	–
[Co(dbmdh)Cl$_2$]	–	3282b	1632s	1601s	1352s	990w	541w	460w
[Ni(dbmdh)Cl$_2$]	–	3285b	1634s	1605s	1353s	995m	558w	454w
[Cu(dbmdh)Cl$_2$]	–	3282b	1635s	1607s	1353s	992w	531w	457w
[Zn(dbmdh)Cl$_2$]	–	3287b	1636s	1603s	1351m	996w	538w	462m
[Cd(dbmdh)Cl$_2$]	–	3284b	1632s	1602s	1352m	995w	532w	471w
[Co(dbsdh)(H$_2$O)$_2$]Cl$_2$	3435b	3238b	1639s	1606s	1357s	994m	535m	457w
[Ni(dbsdh)(H$_2$O)$_2$]Cl$_2$	3432b	3236m	1639s	1603m	1355s	991w	538w	469w
[Cu(dbsdh)(H$_2$O)$_2$]Cl$_2$	3448b	3233b	1636s	1605s	1355s	993w	542m	463w
[Zn(dbsdh)(H$_2$O)$_2$]Cl$_2$	3445b	3233m	1635s	1602s	1360m	991w	540w	456w
[Cd(dbsdh)(H$_2$O)$_2$]Cl$_2$	3455b	3237b	1640s	1606s	1358s	990m	530s	461w

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

3.6. *IR spectra*

Dbmdh and dbsdh show a broad ν(NH) centered at 3284 cm^{-1} and 3237 cm^{-1}, respectively, due to presence of two >NH groups in each ligand. In all the metal complexes ν(NH) occurs nearly at the same position as in the parent ligand (table 6), indicating non-involvement of >NH groups in bonding [36]. A broad band at 3432–3455 cm^{-1} assigned as ν(OH) is observed in all the dbsdh complexes, indicating the presence of water.

[M(dbmdh)Cl₂]

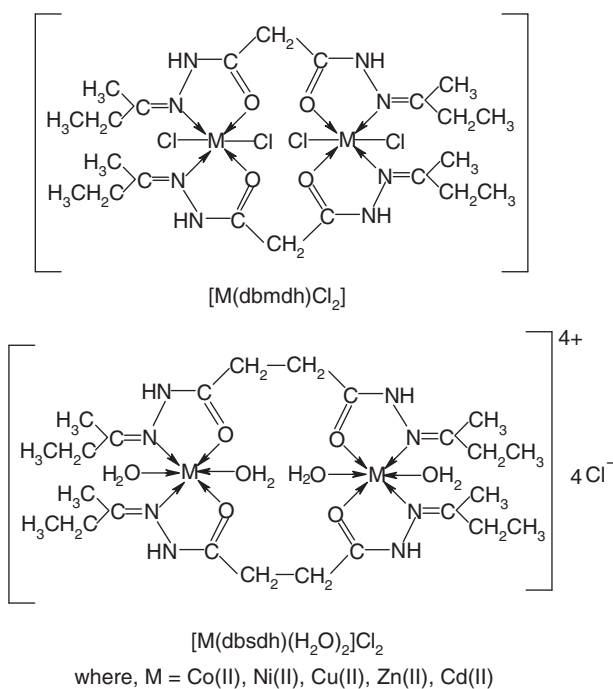[M(dbsdh)(H₂O)₂]Cl₂

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

Figure 2.   Representative structures of the metal complexes.

ν(C=O) bands appear at $1651\,cm^{-1}$ and $1657\,cm^{-1}$ in dbmdh and dbsdh, respectively, due to the presence of two >C=O groups in each ligand; ν(C=O) shifts to lower frequency by 15–$19\,cm^{-1}$ in dbmdh complexes and 17–$22\,cm^{-1}$ in dbsdh complexes suggesting coordination of both >C=O groups to the metal [12]. Compared to the ligands, a shift to higher frequency (8–$10\,cm^{-1}$ and 8–$13\,cm^{-1}$) is observed in ν(C–N) in dbmdh and dbsdh complexes, respectively, supporting coordination through >C=O. The ν(C=N) bands observed at $1618\,cm^{-1}$ in dbmdh and at $1620\,cm^{-1}$ in dbsdh due to >C=N– shifts considerably to lower frequency by 11–$17\,cm^{-1}$ and 14–$18\,cm^{-1}$ in their metal complexes, respectively, indicating coordination through the two >C=N⁻ groups [3].

A weak band due to ν(N–N) observed at $960\,cm^{-1}$ in dbmdh and $962\,cm^{-1}$ in dbsdh shifts to higher frequency by 30–$36\,cm^{-1}$ and 28–$32\,cm^{-1}$, respectively, in their metal complexes, suggesting involvement of only one nitrogen atom of the hydrazone (–NHN=C<) in bonding. All the metal complexes show weak bands at 530–$558\,cm^{-1}$ and 454–$471\,cm^{-1}$, which may be tentatively assigned to ν(M–O) and ν(M–N), respectively. All dbsdh complexes also show weak bands at 936–$961\,cm^{-1}$, 733–$767\,cm^{-1}$, and 641–$667\,cm^{-1}$ due to coordinated water. On the basis of above discussion, general structures for the metal complexes are proposed (figure 2).

4. Conclusion

This article includes synthesis of two symmetrical Schiff bases, dibutanone malonic acid dihydrazone, and succinic acid dihydrazone. The Co(II), Ni(II), Cu(II), Zn(II), and

Cd(II) complexes of these ligands have been synthesized and characterized. The complexes are stable and soluble only in DMF and DMSO. The IR and NMR spectra show both ligands coordinate through two >C=O and two >C=N groups. Magnetic moment, electronic, and ESR spectral studies indicate a six-coordinate octahedral geometry for all the complexes.

Acknowledgments

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