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Spectroscopic and structural study of some 2,5-hexanedione bis(salicyloylhydrazone) complexes: Crystal structures of its Ni(II) and Cu(II) complexes and N-(2,5-dimethyl-1H-pyrrol-1-yl)-2-hydroxybenzamide

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HIGHLIGHTS

- New transition metal complexes of 2,5-hexanedione bis(thiosemicarbazone).
- XRD structure of -1-(2,5-dimethyl-
- 1H-pyrrol-yl-2-hydroxynenzamide. • Octahedral and square-planar
- structures for [Ni(HDSH-2H)(EtOH)(H₂O)] and [Cu(HDSH-2H)].

G R A P H I C A L A B S T R A C T

The Cu(II) complex was found square-planar; the ligand coordinates through two nitrogens and two oxygens forming one seven and two five membered rings.



Crystal structure of [Cu(HDSH-2H)]

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ABSTRACT

The reaction between 2,5-hexanedione and salicylic acid hydrazide produced two compounds: 2,5-hexanedione bis(salicyloylhydrazone) [HDSH] (ethanol insoluble) and N-(2,5-dimethyl-1H-pyrrol-1-yl)-2hydroxybenzamide [DPH] (ethanol soluble). HDSH formed complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pd(II) which are characterized by elemental analyses, spectra (IR, ¹H NMR, ESR and MS), thermal and magnetic measurements. The crystals of [Ni(HDSH-2H)(EtOH)(H₂O)] and [Cu(HDSH-2H)] were solved having octahedral and square-planar geometries, respectively. The other complexes have the formulae [Co(HDSH-2H)(H₂O)₂], [Cu(HDSH-H)₂], [Zn(HDSH-2H)(H₂O)₄], [Cd₂(HDSH-2H)(H₂O)₄], [Cd₂(HDSH-2H)(H₂O)₄Cl₂]; [Hg(HDSH-2H)] and [Pd₂(HDSH-4H)(H₂O)₄]. The obtained complexes are stable in air and non-hygroscopic. The magnetic moments and electronic spectra of the complexes provide different geometries. The ESR spectra support the mononuclear geometry for [Cu(HDSH-2H)] and [Cu(HDSH-H)₂]. The thermal decomposition of the complexes revealed the coordinated waters as well as the end product which is in most cases the metal oxide. The crystal structure of N-(2,5-dimethyl-1H-pyrrol-1-yl)-2-hydroxybenzamide is solved by X-ray technique.

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Introduction

There is a continuous interest of the chemistry of hydrazones and their complexes because of their pharmacological, antitumour, fungicide, bactericide, anti-inflammatory and antiviral activities [1,2]. Great attention has been focused on the structural investigation of this class of compounds [3].

The complexes of salicylaldehydeisobutroyl hydrazone (SIBuH) and o-hydroxyacetophenoneisobutyroyl hydrazone (HAIBuH) were prepared and structurally characterized forming octahedral geometry: $[Ni(SIBuH)_2]$, $[Ni(HAIBuH)_2]$, $[Co(SIBuH)(OAc)-(H_2O)]$; low-spin octahedral: [Cu(SIBuH)₂]·H₂O, [Co(HAIBuH)₂] and square-planar: [Cu(AIBuH)–(H₂O)] [4]. Square-planar geometry for Cu^{2+} and octahedral for Ni^{2+} and Co^{2+} complexes $[M(HSS)_2]$ $(M = Cu^{2+}, Co^{2+}, Mn^{2+}, VO^{2+}, TiO^{2+}), [M'(SS)] (M' = Cu^{2+}, Ni^{2+}, Co^{2+})$ and [Cu(HSS)] were synthesized with salicylaldehydesalicyloyl hydrazone [5]. 2-Aceto-1-naphthol-N-salicoyl hydrazone was used for the microdetermination of metal ions in solution [6]. Salicaldehydefuronyl hydrazone behaved as a dibasic ONO forming [Ni(L) (H₂O)₂], [Co(L)(H₂O)₂], [CuL], [Zn(L)(H₂O)], [Zr(OH)₂(L)-(CH₃OH)₂], $[Zr(OH)_2(HL)_2]$, [MoO(L)Cl] and $[UO_2(L)(CH_3OH)]$. The Cu²⁺ and Mo(V)O complexes have subnormal magnetic moments with antiferromagnetic interaction [7]. Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} complexes of salicylidene-N-cyanoaceto hydrazone, H₂L¹ and 2-hydroxy-l-naphthylidene-N-cyanoaceto hydrazone. H₂L² were found having octahedral geometries, except for [Co(HL²)OAc] which has a tetrahedral structure [8].

 $\begin{bmatrix} VO(H_2L) \end{bmatrix} \cdot 2H_2O, & [Ni(H_2L)] \cdot 3H_2O, & [Zn(H_2L)], & [Ni(H_4L)Cl_2] \cdot 2H_2O \\ and & [Cr_2(H_2L)(OAc)_2(OH)_2] \cdot 2H_2O, & [Cu(H_4L)(H_2L)(EtOH)_2] \cdot 2H_2O, \\ \begin{bmatrix} Co_2(H_2L)(OAc)_2 \end{bmatrix} \cdot H_2O, & [Mn_2(H_2L)(OH)_2] \cdot H_2O & [Cu_2(H_2L)(OAc)_2] \\ (H_2O)_6 \end{bmatrix}, and & [Co_2(H_2L)(H_2O)_4Cl_2] \cdot 2H_2O & were isolated with 2,5-hex-anedione bis(salicyloylhydrazone) & [H_4L] & and characterized by elemental analyses, spectral (IR, ¹H NMR, ESR and MS), thermal and magnetic measurements [9]. \\ \end{bmatrix}$

Extension to the work done on 2,5-hexanedione bis(salicyloylhydrazone) and its metal complexes [9], the present paper aims to synthesize enol-form complexes. Also, N-(2,5-dimethyl-1H-pyrrol-1-yl)-2-hydroxybenzamide was isolated and structurally investigated.

Experimental

2,5-Hexanedione, salicaldehyde, hydrazine hydrate, $CoCl_2 \cdot 6H_2O$, Ni $Cl_2 \cdot 6H_2O$, Cu $Cl_2 \cdot 2H_2O$, Cu $(OAc)_2 - H_2O$, Cd $Cl_2 \cdot 2H_2O$, Zn $Cl_2 \cdot 2H_2O$, Hg Cl_2 and K₂Pd Cl_4 were used as supplied. Ethanol, diethylether and dimethylsulphoxide were Merk products and directly used.

X-ray crystallography

The X-ray single-crystal diffraction data were collected on a Rigaku R-AXIS RAPID diffractometer using filtered Mo K α radiation. The structure was solved by the direct methods and expanded using Fourier techniques at Kuwait University. Crystallographic data and details of the data collection and structure refinements are listed in Table 1.

Synthesis of HDSH and DPH

The two ligands were prepared by adding 0.05 mol of 2,5-hexanedione to 0.1 mol of salicylic acid hydrazide, in 50 ml ethanol with continuous stirring. The reaction mixture was heated under reflux on a water bath for 2 h. The precipitate formed was separated by filtration, recrystallized from ethanol, dried and characterized as HDSH. On gathering the filtrate and concentrated by evaporation, a new compound with empirical formula $C_{13}H_{14}N_2O_2$ and name N-(2,5-dimethyl-1H-pyrrol-1-yl)-2-hydroxybenzamide is produced. This compound is isolated as crystals suitable for X-ray diffraction. The crystal of N-(2,5-dimethyl-1H-pyrrol-1-yl)-2hydroxybenzamide was formed with Pbca (#61) space group having orthorhombic crystal system as shown in Fig. 1 and Table 1. The N1– N2, O1–C2 and O2–C7 are 1.379, 1.362 and 1.230, respectively. Some selected bond lengths and bond angles are presented in Table 2.

Synthesis of the complexes

The complexes were prepared by adding a solution of the ligand (3 mmol), dissolved in 20 ml absolute ethanol to a solution of the metal salt (3 mmol) in 30 ml absolute ethanol and severely stirred on a hot plate under reflux for 2–4 h. The binuclear complexes were prepared by heating a mixture of the ligand (3 mmol) and the metal salts (6 mmol) in 30 ml aqueous–ethanol solution (v/v) on a water bath for 4–6 h. After completion of the reaction, the precipitate was filtered off, washed with ethanol, diethyl ether and finally dried. The single crystals of the Ni(II) and Cu(II) complexes were grown by slow evaporation technique in DMSO/ethanol solution. To isolate the Co(II) complex, water is added to help in the precipitation. No crystals are formed in the rest of the complexes and the trials are continued.

Physical measurements

Elemental analyses (C, H and N) of HDSH and its complexes were measured at the Microanalytical Unit on VarianMicro V1.5.8, CHNS Mode, 15073036 of Kuwait University. Metal contents were estimated using ICP-OES GBC Quantum Sequential. The FT-IR spectra were recorded as KBr disc on a FT/IR-6300 type A (400–4000 cm^{-1}). The electronic spectra of the complexes were recorded on Cary 5 UV-Vis Spectrophotometer, Varian (200-900 nm). The ¹H and ¹³C NMR spectra of the ligand and its diamagnetic complexes were recorded in DMSO-d6, on a Bruker WP 200 SY spectrometer (300 MHz) at room temperature using tetramethylsilane (TMS) as an internal standard. The magnetic measurements were carried out on a Johnson-Matthey magnetic balance, UK. Thermogravimetric analysis (TGA) was measured (10-850 °C) on a Shimadzu TGA-60; the nitrogen flow and heating rate were 50 ml/min and 10 °C min⁻¹, respectively. The ESR spectra were obtained on a Bruker EMX Spectrometer working in the X-band (9.66 GHz) with 100 kHz modulation frequency. The microwave power was set at 2.00e + 02 mW. A powder spectrum was obtained in a 2 mm quartz capillary at room temperature.

Results and discussion

Characterization of the complexes

General

In previous work [9], we reported $[VO(H_2L)] \cdot 2H_2O$, $[Ni(H_2L)] \cdot 3H_2O$, $[Zn(H_2L)]$, $[Ni(H_4L)Cl_2] \cdot 2H_2O$ and $[Cr_2(H_2L)(OAc)_2(OH)_2] \cdot 2H_2O$, $[Cu(H_4L)(H_2L)(EtOH)_2] - 2H_2O$, $[Co_2(H_2L)(OAc)_2] \cdot H_2O$, $[Mn_2(H_2L)(OH)_2] \cdot H_2O$ $[Cu_2(H_2L)(OAc)_2(H_2O)_6]$, and $[Co_2(H_2L)(H_2O)_4Cl_2] \cdot 2H_2O$ with the same ligand. Here, we aim to isolate different complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pd(II) ions and to prove their structures by X-ray crystallography. The formed complexes have the formulae: $[Co(HDSH-2H)(H_2O)_2]$, $[Ni(HDSH-2H)(EtOH)(H_2O)]$, [Cu(HDSH-2H)], $[Cu(HDSH-2H)(H_2O)_2]$, $[Ni(HDSH-2H)(EtOH)(H_2O)]$, [Cu(HDSH-2H)], $[Cd_2(HDSH-2H)(H_2O)_4$, $[Cl_2(HDSH-2H)(H_2O)_4]$, [

Table 1

Summary of the crystallographic data and structure analysis.

Parameters	N-(2,5-dimethyl-1H-pyrrol-1-yl)-2-hydroxy-benzamide	[Ni(HDSH-2H)(EtOH)(H ₂ O)]	[Cu(HDSH-2H)]
Empirical formula Formula weight	C ₁₃ H ₁₄ N ₂ O ₂ 230.27	C ₂₂ H ₂₈ N ₄ O ₆ Ni 503.19	C ₂₀ H ₂₀ CuN ₄ O ₄ 443.95
Crystal color, habit	Colorless, prism	Colorless, prism	Colorless, needle
Crystal dimensions	$0.20\times0.20\times0.20\ mm$	$0.20\times0.06\times0.03~mm$	$0.20\times0.04\times0.02~mm$
Crystal system	Orthorhombic	Triclinic	Monoclinic
Lattice type	Primitive	Primitive	Primitive
Lattice parameters	a = 13.4738(6)	a = 8.252(3) Å	a = 7.322(1) Å
	b = 15.3097(8)	b = 11.807(4) Å	b = 16.918(3) Å
	c = 24.903(2)	<i>c</i> = 27.583(9) Å	<i>c</i> = 15.631(2) Å
		$\alpha = 93.109(9)^{\circ}$	
		$\beta = 107.40(1)^{\circ}$	$\beta = 95.957(7)^{\circ}$
		$\gamma = 110.358(8)^{\circ}$	
	V = 5136.9(5)	$V = 2366(2) \text{ Å}^3$	$V = 1925.7(5) \text{ Å}^3$
Space group	Pbca (#61)	P-1 (#2)	P2 ₁ /n (#14)
Z value	16	4	4
Dcalc	1.191 g/cm ³	1.412 g/cm ³	1.531 g/cm ³
F000	1952.00	1056.00	916.00
μ(Μο Κα)	0.817 cm^{-1}	8.646 cm^{-1}	11.697 cm^{-1}



Fig. 1. N-(2,5-dimethyl-1H-pyrrol-1-yl)-2-hydroxybenzamide.

X-ray crystal structure of the Ni(II) and Cu(II) complexes

The structures of [Ni(HDSH-2H)(EtOH)(H₂O)] and [Cu(HDSH-2H)] are shown in Figs. 2 and 3. The parameters of the crystals are presented in Table 1 while the selected bond lengths and angles are summarized in Table 2. The Ni(II) and Cu(II) complexes have P1 (#2) and P21/n (#14) space groups, respectively. Ni(II) has six-coordination being bonded to two pairs of oxygen and nitrogen atoms from the ligand and completed its hexa-coordination with one water and one ethanol molecule. Its bond angles of 02-Ni-04; 02-Ni-05; 02-Ni-06; 02-Ni-N2; 04-Ni-05 and O4-Ni-O6 are 94.9; 89.1; 90.4; 78.7; 94.1 and 87.6, respectively. Those of O4-Ni-N2 and O5-Ni-O6 are 173.7; 173.4 and 178.3 corresponding to the octahedral geometry. On the other hand, the angles of Cu(II) complex are O2–Cu–O3 (91.65); O2-Cu-N2 (82.00) O2-Cu-O3 (91.65); O2-Cu-N3 (158.31); 03-Cu-N2 (169.53); 03-Cu-N3 (82.54) and N2-Cu-N3 (106.34). The values indicate a distortion for N2-Cu-N3 rather than O2–Cu–O3 in the square-planar geometry.

FT-IR and ¹H NMR spectra of the complexes

Examining the IR spectra of the complexes (Table 4) one may conclude the following observations:

- (i) The v(C=N) vibration observed at 1625 cm⁻¹ in the ligand spectrum shifted to lower wavenumbers (1581–1610 cm⁻¹) in all complexes with the appearance of a new band at 408–433 cm⁻¹ due to v(M-N) indicating the participation of this group in bonding [10].
- (ii) The v(OH) vibration not altered strongly in the spectra of complexes and appeared as medium or broad band more or less at the same position in HDSH (~3290 cm⁻¹) as well as the appearance of $\delta(OH)$ at 1357–1378 cm⁻¹ as observed in the ligand spectrum (1378 cm⁻¹).
- (iii) In the spectra of $[Pd_2(HDSH-4H)(H_2O)_4]$ and $[Cd_2(HDSH-4H)(H_2O)_4]$, the $\upsilon(OH)$ and $\delta(OH)$ bands disappear revealing the deprotonation of the phenolic OH and its participation in bonding.
- (iv) In most complexes, the (C=O) and (NH) bands appearing at 1644 and 3038 cm⁻¹ in the ligand spectrum disappear in the spectra of complexes indicating the enolization of amide group (CONH) and the participation of C–O group in coordination. Evidence for oxygen donor is the appearance of new bands at 1531–1577 and 1223–1258 cm⁻¹ due to $v(C=N^*)$ and v(C=O) vibrations [11].
- (v) The appearance of bands due to v(M-O) at 520–530 cm⁻¹ [12] in the spectra of all complexes is further support for oxygen coordination. The bands at ~3290, ~930 and ~600 cm⁻¹

Table 2

Some selected	bond	lengths	(Å)	and	bond	angles	of Ni	(II)) and Cu	(II) com	plexes.

Bond length of N	i(II) complex Å	Bond angles of Ni(II) complex (°)	Bond length of Å	Bond length of Cu(II) complex Å		(II) complex (°)
Ni-O2 Ni-O5 Ni-N2 Ni-O8 Ni-O11 Ni-N6 O1-C3 O3-C16 O5-C21 O8-C23 O10-C36 N1-N2 N2-C8 N3-C12 N5-N6 N6-C30 N7-C34	2.074(5) 2.126(7) 2.030(10) 2.032(5) 2.151(6) 2.071(8) 1.372(16) 1.347(14) 1.406(18) 1.314(11) 1.285(10) 1.411(8) 1.306(16) 1.265(15) 1.399(10) 1.294(16) 1.294(16)	02-Ni-04 02-Ni-06 02-Ni-N3 04-Ni-06 04-Ni-N3 05-Ni-N2 06-Ni-N2 N2-Ni-N3 02-Ni-05 08-Ni-010 04-Ni-05 05-Ni-06	94.9(3) 90.4(2) 173.7(4) 87.6(3) 79.4(3) 84.4(3) 93.9(3) 107.0(4) 89.1(3) 95.5(3) 94.1(3) 178.3(3)	Cu02 CuN2 01C2 03C12 N1N2 N2C8 N3C11 C1C2 C1C7 C3C4 C5C6 C8C19 C10C11 C12C13 C13C18 C15C16 C17C18	$\begin{array}{c} 1.921(4)\\ 1.954(4)\\ 1.350(8)\\ 1.286(6)\\ 1.402(6)\\ 1.292(7)\\ 1.292(6)\\ 1.400(7)\\ 1.457(8)\\ 1.363(9)\\ 1.375(8)\\ 1.363(9)\\ 1.375(8)\\ 1.506(7)\\ 1.479(7)\\ 1.402(7)\\ 1.380(7)\\ 1.378(7)\end{array}$	02-Cu-O3 02-Cu-N3 03-Cu-N3 Cu-O2-C7 Cu-O3-C12 N2-N1-C7 Cu-N2-N1 Cu-N2-C8 N1-N2-C8 Cu-N3-N4 Cu-N3-C11	$\begin{array}{c} 91.65(14)\\ 158.31(16)\\ 82.54(14)\\ 111.3(3)\\ 110.8(3)\\ 110.3(4)\\ 112.4(3)\\ 129.4(4)\\ 118.1(4)\\ 109.9(3)\\ 133.8(4) \end{array}$
01 03 N1 N2 N3 N4 Some bond angle	C2 C15 N2 C8 N4 C21 es of N-(2,5-dimethyl	-1H-pyrrol-1-yl)-2-hydr	1.362(3) 1.357(3) 1.379(3) 1.380(3) 1.385(3) 1.367(3) roxybenzamide(°)	02 04 N1 N2 N3 N4		C7 C20 C7 C11 C20 C24	1.230(2) 1.226(2) 1.347(3) 1.373(3) 1.344(3) 1.377(3)
N2-N1-C7 N1-N2-C11 N4-N3-C20 N3-N4-C24 C2-C1-C6 C6-C1-C7 O1-C2-C3	<u></u>	120.18(14 124.08(18 121.29(14 123.42(18 117.72(18 116.30(15 120.86(15)	4) 3) 4) 3) 3) 5) 5)	N Ct Ct Ct O C C	1-N2-C8 3-N2-C11 3-N4-C21 21-N4-C24 20C1-C7 1-C2-C1 1-C2-C3		124.52(18) 111.40(18) 124.91(19) 111.42(19) 125.97(17) 119.21(17) 119.23(18)

Table 3

Elemental analysis of HDSH and its complexes.

Compound	M.F Calcd. (Found ^a)	Color	C Calcd. (Found)	H Calcd. (Found)	N Calcd. (Found)	M Calcd. (Found)
HDSH	384.44	Pale yellow	62.48	6.29	14.57	
	383		(62.10)	(5.94)	(14.32)	
$[Co(HDSH-2H)(H_2O)_2]$	477.40	Brown	50.31	5.49	11.74	12.35
			(50.64)	(5.32)	(11.56)	(12.00)
$[Cd_2(HDSH-4H)(H_2O)_4]$	677.29	Pale orange	35.47	4.17	8.26	
			(35.30)	(3.58)	(7.48)	
[Hg(HDSH-2H)]	583.23	Orange	41.18	3.80	9.61	
			(41.21)	(3.72)	(9.37)	
$[Zn(HDSH-2H)(H_2O)_2]$	485.82	Buff	49.44	5.39	11.53	13.45
	(485)		(48.95)	(4.72	(10.33)	(13.13)
[Ni(HDSH-2H)(EtOH)(H ₂ O)]	505.25	Pale brown	52.88	5.98	11.09	11.62
	(438)		(53.09)	(5.57)	(11.04)	(12.12)
$[Cd_2(HDSH-2H)Cl_2(H_2O)_4]$	748.20	Beige	32.10	4.04	7.49	30.04
	(665)		(31.52)	(3.69)	(7.41)	(30.31)
[Cu(HDSH-2H)]	445.97	Green	53.86	4.97	12.56	14.25
	(443)		(53.70)	(4.21)	(11.94)	(14.90)
[Cu(HDSH-H) ₂]	830.41	Brown	57.85	5.58	13.49	
			(57.82)	(4.98)	(12.82)	
$[Pd_2(HDSH-4H)(H_2O)_4]$	665.283	Dark brown	36.11	3.94	8.42	
			(36.17)	(3.91)	(8.82)	

^a Values from MS.

in the spectra of $[Cd_2(HDSH-4H)(H_2O)_4]$, $[Zn(HDSH-2H)(H_2O)_2]$, $[Cd_2(HDSH-2H)(H_2O)_4Cl_2]$ and $[Pd_2(HDSH-4H)(H_2O)_4]$ are attributed to $\upsilon(OH)$, $\rho_r(H_2O)$ and $\rho_w(H_2O)$ of coordinated water [13].

(vi) The ¹H NMR spectra of [Zn(HDSH-2H)(H₂O)₂] and [Hg(HDSH-2H)] showed the signal of the OH protons at (13.825; 11.473) and 11.831 ppm. This signal is disappeared together with that of NH proton in the spectra of [Cd₂ (HDSH-4H)(H₂O)₄] and [Pd₂(HDSH-4H)·3H₂O] confirming the deprotonation and enolization of OH and CONH groups. On deuteration, the OH signal disappeared in all spectra (Table 5).

Spectral and magnetic studies

The electronic spectral bands, measured in DMSO, with the magnetic moments of the complexes are given in Table 6; DMSO has no effect on the color. The spectrum of HDSH showed the



Fig. 2. Crystal structure of [Ni(HDSH-2H)(EtOH)(H₂O)].





Table 4	
IR spectral data	of HDSH and its complexes.

Compound	ν(OH)	$\nu(NH)$	ν(C==0)	$\nu(C=N)$	$v(C=N^{b})$	δ(OH)	$\nu(N-N)$	v(M-N)
HDSH	3290	3038	1644	1625	-	1368	1069	-
$[Co(HDSH-2H)(H_2O)_2]$	3280	-	-	1610	-	1378	1055	433
$[Cd_2(HDSH-4H)(H_2O)_4]$	3554 ^a	-	1635	1608		-	1075	426
[Hg(HDSH-2H)]	3283	-	1641	1605	-	1362	1094	
$[Zn(HDSH-2H)(H_2O)_2]$	3450 ^a	3068	-	1581	-	-	1107	422
[Ni(HDSH-2H)(EtOH)(H ₂ O)]	3313br	-	-	1604	1536	1375	1088	416
$[Cd_2(HDSH-2H)Cl_2(H_2O)_4]$	3554ª, 3242		1644	1606	1578	1357	1066	408
[Cu(HDSH-2H)]	3326br	-	-	1603s	1540	1376s	1086	406
[Cu(HDSH-H) ₂]	-			1596		1376vs	1073	
$[Pd_2(HDSH-4H)(H_2O)_4]$	3500 ^a	-	-	1610	1591		1060	427

^a Coordinated water.
 ^b New azomethine group.

Table 5					
¹ H NMR s	pectra o	f HDSH	and its	comp	lexes.

I I				
OH	NH	CH_{ph}	CH_2	CH_3
12.490	11.249	7.968-7.020	-	3.184
-	-	7.945-7.041	1.990	3.362
11.831	-	7.952-7.453	1.360	2.046
13.825	-	7.954-7.012	1.078	2.139
11.473				
11.466	-	7.864-7.005	1.070	2.037
-	-	7.900-7.057	1.921	3.348
	OH 12.490 - 11.831 13.825 11.473 11.466 -	OH NH 12.490 11.249 - - 13.825 - 11.473 - 11.473 - 11.466 -	OH NH CH _{ph} 12.490 11.249 7.968-7.020 - - 7.945-7.041 11.831 - 7.952-7.453 13.825 - 7.954-7.012 11.473 - 7.952-7.453 11.474 - 7.952-7.453 11.475 - 7.964-7.015 - - 7.864-7.005 - - 7.900-7.057	OH NH CH _{ph} CH ₂ 12.490 11.249 7.968-7.020 - - - 7.945-7.041 1.990 11.831 - 7.952-7.453 1.360 13.825 - 7.954-7.012 1.078 11.473 - - 1.070 - - 7.864-7.005 1.070 - - 7.900-7.057 1.921

 $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands at 39,215 and 33,000 cm⁻¹ for the amide groups [14]. A small change is observed on the spectra of its complexes. The bands at 29,155–21,550 cm⁻¹ in the spectra of the complexes (Table 4) may be due to LMCT from N and O donors.

The electronic spectrum of $[Co(HDSH-2H)(H_2O)_2]$ showed bands at 16,745 and 19,540 cm⁻¹ assigned to ${}^4T_{1g} \rightarrow {}^4A_{2g}$ (v₂) and ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ (v₃) characteristic for an octahedral geometry [15]. The μ_{eff} value is 4.83 BM which lies inside the range reported for complexes having the proposed geometry (4.7–5.2 BM). The previously reported Co(II) complexes with the same ligand [9] have a binuclear moiety containing Cl or acetate anion. The ligand field parameters (*B*, β , 10Dq) are calculated and their values are 869 cm⁻¹, 0.895 and 869 cm⁻¹. It is worthy to note that the value of 10Dq ordered the strength of the ligand, based on the crystal field splitting energy, in the series of moderate ligands. Considerable reduction in the *B* value from 971 in the free Co(II) to 869 cm⁻¹ in the complex and β from unity to 0.895 indicate more ionic character of L–M bonds.

The magnetic moment of [Ni(HDSH-2H)(EtOH)(H₂O)] is 3.23 BM expected for octahedral structure with ${}^{3}A_{2g}$ ground term [16]. Its electronic spectrum shows broad band at 13,245 cm⁻¹ assigned to the ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ (F) (ν_2) transition [17]. The value of *B* (656 cm⁻¹) and Dq (1054 cm⁻¹) are used to calculate β and ν_1 , ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$ (F), to be 0.62 and 10,540 cm⁻¹, respectively [18]. The previous complexes have tetrahedral and octahedral geometries; the octahedral one was formed in the keto-form [9].

The electronic spectra of [Cu(HDSH-2H)] and $[Cu(HDSH-H)_2]$ exhibit bands at 15,410 and 21,050 cm⁻¹, respectively, assigned to ${}^{2}T_{2g} \rightarrow {}^{2}E_{g}$. The band position with magnetic moments of 1.98 and 1.64 BM are consistent with a square-planar geometry [19,20]. The lower value in $[Cu(HDSH-H)_2]$ may be due to little effect of the diamagnetic ligands on the magnetic interaction due to the presence of two ligand molecules.

The spectrum of Pt(II) complex showed bands at 13,040 and 12,675 cm⁻¹ attributed to ${}^{1}A_{1g} \rightarrow {}^{1}Eg$ transition.

Thermal studies

The thermogravimetric data considering the decomposition temperature and the weight losses for most complexes are

Table 7	
Thermal decomposition stages of HDSH and its complexes.	

Compound	M.F.	Average temp., (°C)	Species removal (%)
HDSH	384.44	245	87.72 Residue 1.52%
[Cd ₂ (HDSH-4H)(H ₂ O) ₄]	678.16	302 641	11.33 63.67 Residue 10.75%
[Hg(HDSH-2H)]	583.23	275	65.17 Residue 34.83% (Hg)
$[Zn(HDSH-2H)(H_2O)_2]$	485.824	319	47.86 Residue 14.88% (Zn)
[Ni(HDSH- 2H)(EtOH)(H ₂ O)]	505.25	111 290	11.95 38.84 Residue 13.48% (NiO)
[Cd ₂ (HDSH- 2H)Cl ₂ (H ₂ O) ₄]	748.20	302 641	11.33 63.67 Residue 10.75%
[Cu(HDSH-2H)]	445.968	284	53.09 Residue 31.07%
[Pd ₂ (HDSH-4H)(H ₂ O) ₄]	665.283	235 288	23.00 14.88 Residue 45.35% (2PdO ₂)

presented in Table 7. [Ni(HDSH-2H)(EtOH)(H₂O)] is taken as an example.

The steady part of the thermogram of [Ni(HDSH-2H)(EtOH) (H₂O)] till 111 °C indicates the absence of any solvent outside the sphere. The 1st decomposition step at mid-point 111 °C is due to the removal of $C_2H_5OH + H_2O$ (% Found 11.95; Calcd. 12.67). The 2nd step indicates the decomposition of part of Ni(HDSH-2H) (% Found 38.84). NiO is the stable residue at 800 °C (% Found 13.48; Calcd. 14.85). The residual parts in the Zn(II) and Hg(II) complexes are the metal atoms (Table 6). In the Pd(II) complex, the residue is PdO₂.

ESR spectra

The room temperature solid state ESR spectra of the copper complexes exhibit axially symmetric *g*-tensor parameters with $g_{||} > g_{\perp} > 2.0023$ indicating that the copper site has a $d_x^2 - y^2$ ground state [21]. The ESR spectra of [Cu(HDSH-2H)] and [Cu(HDSH-H)₂] are similar to the ESR spectra of the reported mononuclear Cu²⁺ complexes [22]. The spectra of the two complexes exhibit a single line centered at $g_{||} = 2.250$; 2.226 and $g_{\perp} = 2.070$; 2.059, respectively, attributable to dipolar broadening and enhanced spin lattice relaxation. This line is probably due to insufficient spin-exchange narrowing toward the coalescence of four copper hyperfine lines to a single line. Note that, the same kind of powder ESR line shapes have been observed for many tetrahedral or square-planar Cu²⁺

lable 6				
Magnetic moments and	electronic spectral	l bands of HDSH	and its metal	complexes

Compound	$\mu_{\rm eff}$ (BM)	Intraligand bands (nm)	d–d Bands, (nm)	Proposed structure
HDSH	-	39,215, 33,000	-	
[Co(HDSH-2H)(H ₂ O) ₂]	4.83	37,760, 33,365, 31,155	16,745, 19,540	Octahedral
$[Cd_2(HDSH-4H)(H_2O)_4]$	-	38,910, 33,000		Tetrahedral
[Hg(HDSH-2H)]	-	39,060, 33,110, 29,155		Tetrahedral
$[Zn(HDSH-2H)(H_2O)_2]$	-	36,495, 34,480, 32,050	-	Octahedral
[Ni(HDSH-2H)(EtOH)(H ₂ O)]	3.23	38,760, 35,970, 34,365, 32,155	17,300, 13,245	Octahedral
$[Cd_2(HDSH-2H)Cl_2(H_2O)_4]$	-	39,060, 33,000, 21,550	-	-
[Cu(HDSH-2H)]	1.98	27,400, 26,110	15,410	Square-planar
[Cu(HDSH-H) ₂]	1.64	39,215, 34,840, 32,785, 27,400	21,050	Square-planar
$[Pd_2(HDSH-4H)(H_2O)_4]$		38,760	13,040, 12,675	Square-planar

complexes with a strong intra-nuclear spin-exchange interaction. In axial symmetry, the g-values are related by the expression, $G=(g_{||}-2)/(g_{\perp}-2) = 4$. According to Hathaway [23], the calculated *G* values for [Cu(HDSH-2H)] and [Cu(HDSH-H)₂] are 3.57 and 3.83 suggesting copper–copper exchange interactions. The molecular orbital coefficients α^2 and β^2 for [Cu(HDSH-2H)] are calculated using the reported equations [24] and found to be 0.94 and 0.86, respectively. The low value of β^2 than α^2 indicates that the in-plane σ -bonding is less covalent [25].

Conclusion

Metal complexes of 2,5-hexanedione bis(salicyloylhydrazone) have been prepared and structurally investigated. The ligand has multi dentate donors with four ionizable protons. The complexes have tetrahedral: [Hg(HDSH-2H)] and $[Cd_2(HDSH-4H)(H_2O)_4]$; square-planar: [Cu(HDSH-2H)], $[Cu(HDSH-H)_2]$ and $[Pd_2(HDSH-4H)(H_2O)_4]$ and octahedral for $[Co(HDSH-2H)(H_2O)_2]$, $[Zn(HDSH-2H)(H_2O)_2]$ and $[Ni(HDSH-2H)(EtOH)(H_2O)]$. The stable metal or metal oxides remain as residues. The crystal of $[Ni(HDSH-2H)(EtOH)(H_2O)]$ was solved as octahedral while that of [Cu(HDSH-2H)] as square-planar. Another organic compound (ethanol soluble) was isolated during the preparation of HDSH and crystallographically analyzed.

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Appendix A. Supplementary material

CCDC reference numbers 842111 and 840137 contain the supplementary crystallographic data for this article. These data

can be obtained free of charge at www.ccdc.cam.ac.uk/conts/ retrieving.html.

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2014.02.195.

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