

Synthesis and characterization of tri- and tetra-metallic complexes of N^1, N^4 -bis((*E*)-3,4-dihydroxybenzylidene)-succinohydrazide

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ABSTRACT

Single crystal of N^1, N^4 -bis((*E*)-3,4-dihydroxybenzylidene)succinohydrazide (SHBH) was grown by slow evaporation method. Its, Co(II), Ni(II), Cu(II), Zn(II), Co(II)/Zn(II), Ni(II)/Zn(II) and Cu(II)/Zn(II) complexes have been prepared and characterized by elemental analysis, UV-Vis, IR, NMR, MS spectra, thermal and magnetic measurements. The data confirm the formation of tri- and tetra-metallic complexes (homo- and hetero-nuclear). The ligand behaves as a tetranegative hexadentate in the Co(II)/Zn(II) complex; hexanegative hexadentate in the Co(II) complex and hexanegative octadentate in the tetrametallic complexes. A square-planar for $[Co_3(SHBH-6H)(H_2O)_6]$, $[Cu_4(SHBH-H)(H_2O)_4(OAc)_2] \cdot 3H_2O$, $[Ni_3Zn(SHBH-6H)(H_2O)_6Cl_2] \cdot H_2O$ and $[Cu_3Zn(SHBH-6H)(H_2O)_6Cl_2]$ and tetrahedral for $[Ni_4(SHBH-H)(H_2O)_4(OAc)_2] \cdot 6H_2O$, $[Zn_3(SHBH-4H)(H_2O)_4Cl_2] \cdot 2H_2O$ and $[Co_2Zn(SHBH-6H)(H_2O)_6Cl_2] \cdot 2H_2O$ were suggested based on the magnetic and spectral data. The TGA data confirm hydrated and coordinated water as well as the final product. The mass spectra depict their molecular ion peaks and the isotopic species of each complex. It is found that the homometallic complexes are highly stable than the heterometallic complexes. The calculated energies for $[Co_2Zn(SHBH-4H)(H_2O)_4Cl_2] \cdot 2H_2O$ are higher than $[Co_3(SHBH-6H)(H_2O)_6]$ indicating that the three Co stabilized the complex.

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1. Introduction

Hydrazones and their metal complexes have much interest due to their antimicrobial activities [1]. The complexes bind and cleave the DNA strands under different physiological conditions [2]. They have applications to hold therapeutic activity as well as pharmacological applications [3]. Aroyl hydrazone complexes act as enzyme inhibitors and are pharmacological useful. Isonicotinic acid hydrazide (INH) is used against a wide spectrum of bacterial ailments, e.g., tuberculosis. Hydrazones derived from condensation of INH and pyridine aldehydes showed better antitubercular activity than INH [4]. The antibacterial activity of acetophenone-4-aminobenzoylhydrazone and 4-hydroxy-acetophenone-4-aminobenzoylhydrazone complexes showed that the activity of Cu(II) complexes is more than Zn(II) complexes. 7-Chloro-4-benzylidene-hydrazoquinoline was proved to be biologically active. The chelation pushed the ligand to be potent bactericidal agent [5]. Binuclear complexes of oxalyl bis(di-acetylmonoximehydrazone) have octahedral geometry, tetrahedral for the Zn(II) and square-planar for the rest complexes [6]. Metal complexes of 2,5-hexanedione bis(isonicotinylhydrazone) released two protons from the two amide groups (NHCO) and behaves as a binate tetradentate (N_2O_2). The results provided a square-planar for $[Cu(L)] \cdot 2H_2O$,

square-pyramidal for $[VO(L)] \cdot H_2O$ and octahedral for the rest. The ESR spectra supported the mononuclear geometry for $[VO(L)] \cdot H_2O$ and $[Cu(L)(H_2O)_2] \cdot 2H_2O$ [7]. Single crystal of 3,4-dihydroxy-benzylidene isonicotinyl-hydrazone was grown and solved. The ligand acts as a neutral bidentate; dibasic tetradentate and tribasic tetradentate. A tetrahedral geometry was proposed for the Co(II), Cu(II) and Hg(II) complexes; square-pyramid for the VO(II) and octahedral for the Ni(II) and Cd(II). Some complexes have activities against *Bacillus sp.* M3010, *Candida albicans*, *Escherichia coli*, *Staphylococcus aureus* and *Salmonella sp.* PA393 [8]. In the three hetero-trinuclear complexes of substituted succinoyl dihydrazones, the metal centers have distorted octahedral stereochemistry. The IR spectra revealed the coordination through phenolate oxygen, enolate oxygen and azomethine nitrogen. NO_3^- is bonded as a monodentate ligand [9]. Bis(hydroxybenzylidene) substituted terphthalo and oxalo hydrazides were characterized. The complexes were evaluated for oxidation of hydrocarbons including cycloalkenes, cyclic alkanes and benzyl-alcohol using H_2O_2 as terminal oxidant. Of the studied aroyl hydrazone complexes, 4 showed the best selectivity and activity as catalyst [10].

On continuation to our earlier work [11-14] on bis(hydrazones) and up to date, no research was done on complexes containing Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)

ions (homo- or hetero-complexes) of *N*¹,*N*⁴-bis((*E*)-3,4-dihydroxybenzylidene)succinohydrazide. The complexes reported herein are investigated to the first time.

2. Experimental

2.1. Materials

Cobalt(II) chloride hexahydrate, nickel(II) chloride hexahydrate, nickel(II) acetate trihydrate, copper(II) chloride dihydrate, copper(II) acetate monohydrate, zinc(II) chloride dihydrate, diethyl succinate, hydrazine hydrate, 3,4-dihydroxy-benzaldehyde, ethanol, diethyl ether and DMSO were obtained from the BDH Chemicals.

2.2. Physical measurements

The IR spectra were recorded on a FT/IR-6300 type A (400-4000 cm⁻¹) as KBr discs. The ¹H NMR spectra of the ligand and its diamagnetic complexes were recorded in DMSO-*d*₆ on a Bruker WP 200 SY spectrometer (300 MHz) at room temperature using tetramethylsilane (TMS) as an external standard. Varian Micro V1.5.8, CHNS Mode 15073036 was used for elemental analysis of SHBH and its complexes at the Microanalytical Unit of Kuwait University, Kuwait. The metal content was determined using ICP-OES GBC Quantum Sequential at Kuwait University, Kuwait. Electronic spectra of the complexes were recorded on Cary 5 UV-Vis Spectrophotometer, Varian (200-900 nm). Mass spectra were recorded on a GC-MS Thermo-DFS (BG-FAB) mass spectrometer. Magnetic susceptibility was measured for powdered samples using a Johnson-Matthey magnetic balance, UK. Hg[Co(SCN)₄] was used as a calibrant and corrections for diamagnetism were calculated from Pascal's constants. Thermogravimetric analysis (TGA) was carried out (10-850 °C) using a Shimadzu TGA-60; the nitrogen flow and heating rate were 50 mL/min and 10 °C/min, respectively. The X-ray single crystal diffraction data were collected on a Rigaku R-Axis RAPID diffractometer using filtered MoK α radiation. The structure was solved by the direct methods and expanded using Fourier techniques at Kuwait University, Kuwait. The molecular geometry of the Co(II) and Ni(II) complexes are first optimized at molecular mechanics (MM+) level. Semi empirical method PM3 is then used for optimizing the full geometry of the system using Polak-Ribiere (conjugate gradient) algorithm and Unrestricted Hartree-Fock (UHF) is employed keeping RMS gradient of 0.01 kcal/Å.mol. Quantum chemical calculations for the ligand and some of its metal complexes were used to optimize the geometry and spectral calculation by Gaussian 03W suite program [15] using the Becke3-Lee-Yang-Parr (B3LYP) exchange-correlation functional with standard 6-311++G (d, p) basis set.

2.3. Synthesis

2.2.1. Synthesis of *N*¹,*N*⁴-bis((*E*)-3,4-dihydroxybenzylidene)succinohydrazide

The ligand was prepared by adding 7.3 g (0.05 mol) of succinic acid dihydrazide, dissolved in 30 mL ethanol, with 13.8 g (0.1 mol) of 3,4-dihydroxybenzaldehyde, in 30 mL ethanol, and heating the mixture on a water bath for 2 h. The off-white precipitate thus formed was filtered off, recrystallized from ethanol and allow to dry in a desiccator over silica gel. Single crystals were grown by slow evaporation and analyzed by X-ray spectroscopy. It was characterized by elemental analysis and spectral studies. Color: Off-white. Yield: 88%. M.p.: 206-208 °C. FT-IR (KBr, ν , cm⁻¹): 3282 (ν (OH)), 3163 (ν (NH)), 1644 (ν (C=O)), 1589 (ν (C=N)). ¹H NMR (300 MHz, DMSO-*d*₆, δ , ppm): 11.2 (s, 1H, NH), 11.0 (s, 1H, NH), 9.29 (s, 4H, OH), 7.97-7.82 (d, 2H, Ar-H), 7.17 (s, 2H, Ar-H), 6.90-6.86 (d, 4H, Ar-

H+CH=N), 2.92 (s, 2H, CH₂), 3.45 (s, 2H, CH₂). ¹³C NMR (300 MHz, DMSO-*d*₆, δ , ppm): 173.39, 167.92, 147.88, 146.42, 125.95, 29.03. MS (EI, *m/z* (%)): 386.12 (100), 387.13 (19.9), 388.13 (3.1), 387.12 (1.5). UV/Vis (Nujol, ν_{max} , cm⁻¹): 33330, 26040, 21830.

2.2.2. Synthesis of the complexes

In general, the solid complexes were prepared by reacting the calculated amounts for 4:1 ratio [M:L] of the metal salt and SHBH in EtOH and the mixture was heated under reflux on a water bath with continuous stirring for 3-6 h. In the preparation of the metal acetate complexes, the medium solution is H₂O:EtOH (1:1, v:v). The precipitate thus formed was filtered off, washed with hot water, hot ethanol and diethyl ether and finally dried.

The mixed Co/Zn complex was prepared by adding 0.387 g (0.01 mol) of the ligand, in 30 mL EtOH, to a mixture of 0.75 g (0.02 mol) CoCl₂·6H₂O and 0.33 g (0.02 mol) of ZnCl₂·2H₂O, in 30 mL EtOH, and heating the mixture on a water bath for 5 h. The color of the mixture was changed instantly followed by the formation of colored precipitate which is filtered, washed and allowed to dry. [Ni₃Zn(SHBH-6H)(H₂O)₆Cl₂]-H₂O was prepared by adding 0.387 g (0.01 mol) of SHBH, in 30 mL EtOH, to a mixture of 0.1 g (0.03 mol) NiCl₂·6H₂O and 0.17 g (0.01 mol) of ZnCl₂·2H₂O, in 30 mL EtOH, and heating the mixture on a water bath for 3 h. The formed precipitate is filtered, washed with water, ethanol and finally with ether and allowed to dry. Similar procedure was carried out for the preparation of [Cu₃Zn(SHBH-6H)(H₂O)₆Cl₂]. The purity of the compounds as formulated was established by microanalysis.

3. Results and discussion

3.1. General information

The CHN analysis of the ligand coincides with SHBH·3H₂O; its single crystal has 4H₂O. The color, melting points and elemental analyses of SHBH and its complexes are presented in Table 1. The data confirm: [Co₃(SHBH-6H)(H₂O)₆], [Co₂Zn(SHBH-4H)(H₂O)₄Cl₂]-2H₂O: [Ni₄(SHBH-6H)(H₂O)₄(OAc)₂]-6H₂O, [Cu₄(SHBH-6H)(H₂O)₄(OAc)₂]-3H₂O, [Zn₃(SHBH-4H)(H₂O)₄Cl₂]-2H₂O, [Ni₃Zn(SHBH-6H)(H₂O)₄Cl₂]-H₂O, and [Cu₃Zn(SHBH-6H)(H₂O)₆Cl₂]. The TGA data indicate a high stability for tetrametallic complexes. Unfortunately, the complexes are insoluble in all organic solvents, so, their molar conductance and NMR were not measured. Although single crystals are not grown, the suggested structures are consistent with all other evidence.

3.2. Analysis of SHBH single crystal

SHBH crystals (colorless, platelet) with the formula C₁₈H₂₆N₄O₁₆ have molecular weight of 458.42 g/mol. It belongs to monoclinic system with no centrosymmetric P2₁/c(#14) space group (Table 2) having four water molecules; its half molecule has two water molecules (Figure 1). The estimated cell parameters are *a* = 6.027(2) Å, *b* = 6.256(2) Å, *c* = 27.977(7) Å, β = 94.216 °. The distance of O1-C3 (1.378 Å) is more than that of O2-C4 (1.356 Å) because the O1-C3-C2 angle (123.7 °) is less than that of O2-C4-C5 (124.8 °). The O3-C8 (1.245 Å) is relevant to double bond character. The N1-C7 is less than N2-C8. The distance of N1-N2 is 1.415 Å. The higher distance is for C1-C7 due to the attraction of more electronegative N atom. The N1-C7 is shorter than N2-C8 related to its double bond nature confirming the condensation process (Table 3-6).

Table 1. Elemental analysis and some properties of SHBH and its complexes *.

Compound, Empirical formula	M.w; Calcd. (Found)	Color	M.p., °C	C	H	N	M
				Calcd. (Found)	Calcd. (Found)	Calcd. (Found)	Calcd. (Found)
SHBH·2H ₂ O C ₁₈ H ₂₂ N ₄ O ₈	440.422	Off-white	206-208	49.08 (49.18)	5.49 (5.26)	12.77 (13.06)	-
SHBH C ₁₈ H ₁₈ N ₄ O ₆	386.374 (387.50) ^a						
[Co ₃ (SHBH-6H)(H ₂ O) ₆] C ₁₈ H ₂₄ N ₄ O ₁₂ Co ₃	665.206 (577.00) ^b	Brown	> 325	32.50 (32.26)	3.64 (3.88)	8.42 (8.12)	26.58 (26.86)
[Ni ₄ (SHBH-6H)(H ₂ O) ₄ (OAc) ₂]-6H ₂ O C ₂₂ H ₃₈ N ₄ O ₂₀ Ni ₄	913.552 (603.50) ^c	Brown	>325	28.92 (28.67)	4.19 (3.96)	6.13 (6.25)	25.72 (26.17)
[Cu ₄ (SHBH-6H)(H ₂ O) ₄ (OAc) ₂]-3H ₂ O C ₂₂ H ₃₂ N ₄ O ₁₇ Cu ₄	878.704 (602.00) ^d	Light brown	>325	30.07 (29.86)	3.67 (3.53)	6.38 (6.67)	28.92 (28.61)
[Zn ₂ (SHBH-4H)(H ₂ O) ₄ Cl ₂]-2H ₂ O C ₁₈ H ₂₆ N ₄ O ₁₂ Zn ₃	757.416 (603.00) ^e	Orange	>325	28.54 (28.74)	3.46 (3.33)	7.40 (7.38)	25.88 (26.04)
[Co ₂ Zn(SHBH-4H)(H ₂ O) ₆ Cl ₂]-2H ₂ O C ₁₈ H ₃₀ N ₄ O ₁₄ Co ₂ ZnCl ₂	780.628 (781.90)	Brown	>325	27.69 (27.76)	3.87 (3.33)	7.17 (7.80)	Co=15.10 14.03) Zn=8.37 (9.50)
[Ni ₃ Zn(SHBH-6H)(H ₂ O) ₆ Cl ₂]-H ₂ O C ₁₈ H ₂₆ N ₄ O ₁₃ Ni ₃ ZnCl ₂	818.936 (693.00) ^f	Pale brown	>325	26.40 (26.69)	3.20 (3.17)	6.84 (6.71)	Ni=23.51 (23.78) Zn=7.98 (7.46)
[Cu ₃ Zn(SHBH-6H)(H ₂ O) ₆ Cl ₂] C ₁₈ H ₂₄ N ₄ O ₁₂ Cu ₃ Zn Cl ₂	815.272 (804.00)	Brown	>325	27.52 (27.66)	2.97 (2.40)	6.87 (7.07)	

* a Anhydrous ligand, b for [Co₃(SHBH-6H)], c for [Ni₃(SHBH-6H)]·3H₂O, d for [Cu₂(SHBH-6H)(OAc)(H₂O)₂], e for [Zn₃(SHBH-6H)], f [Ni₃Zn(SHBH-6H)(H₂O)₄].

Table 2. Crystal data and structure refinement for SHBH.

Empirical formula	C ₁₈ H ₂₆ N ₄ O ₁₀
Formula weight	458.42
Temperature/K	293
Crystal system	Monoclinic
Space group	P2 ₁ /c
a/Å	6.0268(14)
b/Å	6.2560(14)
c/Å	27.977(7)
β/°	94.216(7)
Volume/Å ³	1052.0(5)
Z	2
ρ _{calc} /cm ³	1.447
μ/mm ⁻¹	0.119
F(000)	484.0
Crystal size/mm ³	0.200 × 0.080 × 0.030
Radiation	Mo Kα (λ = 0.71075)
Index ranges	-7 ≤ h ≤ 7, -7 ≤ k ≤ 6, -32 ≤ l ≤ 32
Reflections collected	7835
Independent reflections	1854 [R _{int} = 0.0758]
Data/restraints/parameters	1854/5/163
Goodness-of-fit on F ²	1.080
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0615
Final R indexes [all data]	wR ₂ = 0.2064
Largest diff. peak/hole / e Å ⁻³	0.42/-0.46

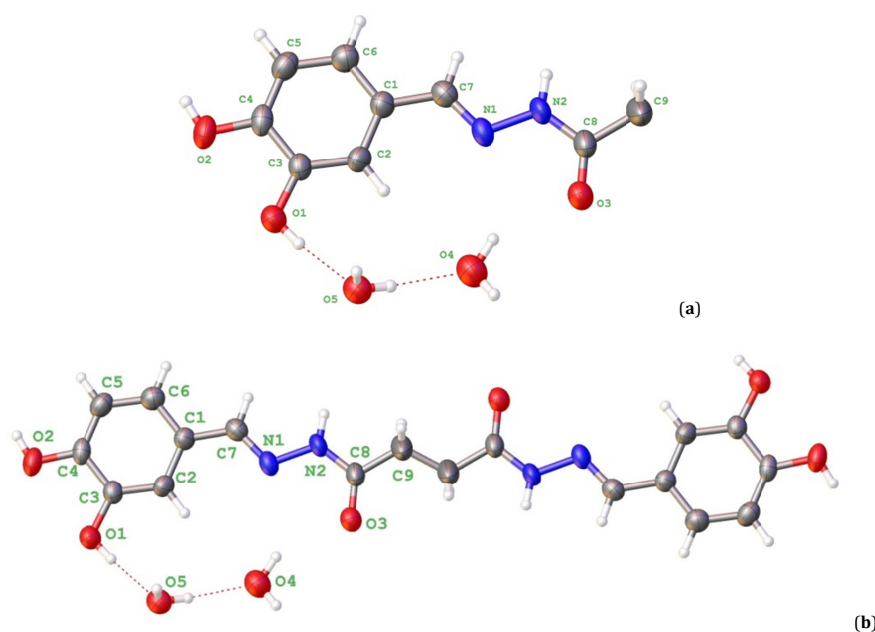
**Figure 1.** X-ray single crystal structure of a) half molecule and b) complete molecule.

Table 3. Bond lengths for SHBH.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C3	1.378(5)	C1	C7	1.439(6)
O2	C4	1.356(5)	C2	C3	1.375(5)
O3	C8	1.245(5)	C3	C4	1.409(6)
N1	N2	1.415(5)	C4	C5	1.377(6)
N1	C7	1.285(5)	C5	C6	1.389(6)
N2	C8	1.308(5)	C8	C9	1.451(7)
C1	C2	1.407(6)	C9	C9 ¹	1.415(8)
C1	C6	1.392(6)			

¹-1-x, 2-y, 1-z.**Table 4.** Bond angles for SHBH.

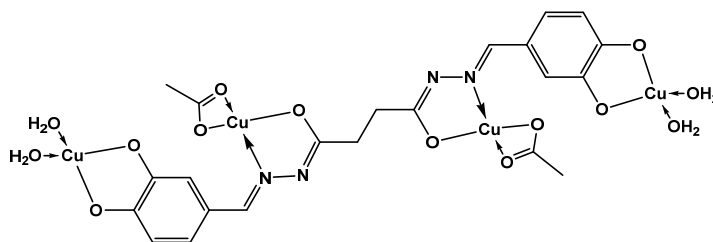
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	N1	C7	113.6(4)	O2	C4	C5	124.8(4)
N1	N2	C8	121.6(4)	C3	C4	C5	119.4(4)
C2	C1	C6	118.8(4)	C4	C5	C6	120.3(4)
C2	C1	C7	122.5(4)	C1	C6	C5	120.9(4)
C6	C1	C7	118.7(4)	N1	C7	C1	123.7(4)
C1	C2	C3	120.2(4)	O3	C8	N2	123.3(4)
O1	C3	C2	123.7(4)	O3	C8	C9	124.7(4)
O1	C3	C4	115.9(3)	N2	C8	C9	111.9(4)
C2	C3	C4	120.4(4)	C8	C9	C9 ¹	121.8(5)
O2	C4	C3	115.8(4)				

¹-1-x, 2-y, 1-z.**Table 5.** Hydrogen bonds for SHBH.

D	H	A	d(D-A)/Å	d(D-H)/Å	d(H-A)/Å	D-H-A/°
O1	H1	O5	2.800(5)	0.820	2.016	159.7
O2	H2	O1 ¹	2.858(4)	0.820	2.166	142.2
O4	H4A	O3 ²	2.903(5)	0.824	2.08(4)	177(5)
O5	H5A	O4	2.783(6)	0.821	1.966(19)	173(6)
O5	H5B	O3 ³	2.874(5)	0.820	2.07(6)	168(5)
N2	H2A	O5 ⁴	2.920(5)	0.860	2.064	173.1

¹2-x, 1/2+y, 3/2-z; ²2-x, 1-y, 1-z; ³1+x, +y, +z; ⁴-1+x, 1+y, +z.**Table 6.** Torsion angles for SHBH.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N2	N1	C7	C1	-176.8(3)	C1	C2	C3	C4	1.6(6)
C7	N1	N2	C8	-180.0(3)	O1	C3	C4	O2	-0.1(5)
N1	N2	C8	O3	3.8(6)	O1	C3	C4	C5	-179.3(3)
N1	N2	C8	C9	-177.0(3)	C2	C3	C4	O2	178.3(4)
C2	C1	C6	C5	-0.1(6)	C2	C3	C4	C5	-0.8(6)
C6	C1	C2	C3	-1.1(6)	O2	C4	C5	C6	-179.5(4)
C2	C1	C7	N1	-5.6(6)	C3	C4	C5	C6	-0.4(6)
C7	C1	C2	C3	178.5(4)	C4	C5	C6	C1	0.9(6)
C6	C1	C7	N1	173.9(4)	O3	C8	C9	C9 ¹	15.7(8)
C7	C1	C6	C5	-179.7(4)	N2	C8	C9	C9 ¹	-163.5(5)
C1	C2	C3	O1	179.9(4)	C8	C9	C9 ¹	C8 ¹	-180(4)

¹-1-x, 2-y, 1-z.**Figure 2.** Structure of $[\text{Cu}_4(\text{SHBH-6H})(\text{H}_2\text{O})_4(\text{OAc})_2] \cdot 3\text{H}_2\text{O}$.

3.3. IR and NMR spectra of SHBH and complexes

The positions of the important bands in the IR spectra of SHBH and its complexes are shown in Table 7. SHBH has good coordination ability for the studied metal ions. Its spectrum showed bands at 3282, 3163, 1644 and 1589 cm^{-1} due to $\nu(\text{OH})$, $\nu(\text{NH})$, $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$, respectively [16]. Its ^1H NMR spectrum has signals at δ 11.2 (s, 1H, NH), 11.0 (s, 1H, NH), 9.29 (s, 4H, OH), 7.97-7.82 (d, 2H, Ar-H), 7.17 (s, 2H, Ar-H), 6.90-6.86 (d, 4H, Ar-H+CH=N), 2.92 (s, 2H, CH_2), 3.45 (s, 2H, CH_2). ^{13}C NMR spectrum showed peaks at δ 173.39, 167.92 (C=O); δ 147.88, 146.42 (C=N); δ 125.95 (C-O) and 29.03 ppm (CH). The ligand has multi donor groups, so different modes of

chelation are proposed. Tentative assignments of the observed bands for the compounds were made by complete comparison of the spectra of complexes with that of SHBH.

In $[\text{Cu}_4(\text{SHBH-6H})(\text{H}_2\text{O})_4(\text{OAc})_2] \cdot 3\text{H}_2\text{O}$ (Figure 2), $[\text{Ni}_4(\text{SHBH-6H})(\text{H}_2\text{O})_4(\text{OAc})_2] \cdot 6\text{H}_2\text{O}$, $[\text{Ni}_3\text{Zn}(\text{SHBH-6H})(\text{H}_2\text{O})_6\text{Cl}_2] \cdot \text{H}_2\text{O}$, $[\text{Cu}_3\text{Zn}(\text{SHBH-6H})(\text{H}_2\text{O})_6\text{Cl}_2] \cdot \text{H}_2\text{O}$, the ligand acts as a hexanegative octadentate with the four metal ions coordinating through the deprotonated OH's, the two enolic carbonyl and the two C=N groups. Complete disappearance of the OH band confirmed their involvement in coordination after deprotonation. New observed band at 3350-3550 cm^{-1} is due to the hydrated or coordinated water. The absence of $\nu(\text{NH})$ and $\nu(\text{C}=\text{O})$ bands indicates enolization of the amidic group.

Table 7. IR spectral data of SHBH and its metal complexes.

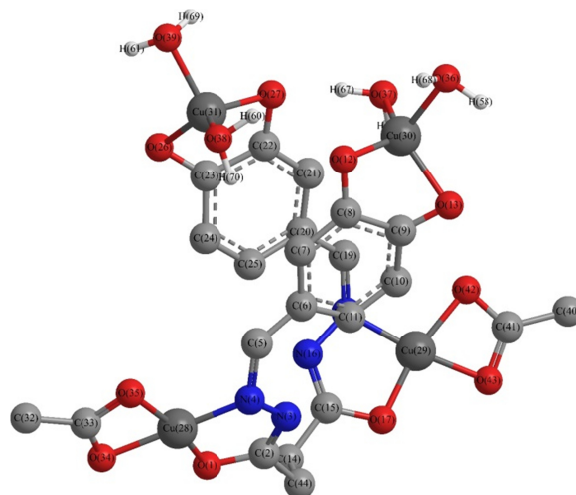
Compound	$\nu(\text{OH})$ (H_2O)	$\nu(\text{OH})$	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{C=N})^{**}$	$\nu(\text{C-O})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
SHBH	-	3282 (br)	3163 (w)	1644 (s)	1589 (s)	-	-	-	-
$[\text{Co}_3(\text{SHBH-6H})(\text{H}_2\text{O})_6]$	3423* (vbr)	-	-	-	1574 (m)	1490 (m)	1174 (m)	523 (w)	-
$[\text{Ni}_4(\text{SHBH-6H})(\text{H}_2\text{O})_4(\text{OAc})_2] \cdot 6\text{H}_2\text{O}$	3431* (vbr)	-	-	1642 (m)	1584 (m)	1488 (s)	1164 (w)	534 (vw)	434 (w)
$[\text{Cu}_4(\text{SHBH-6H})(\text{H}_2\text{O})_4(\text{OAc})_2] \cdot 3\text{H}_2\text{O}$	3425* (br)	-	-	-	1574 (m)	1487 (s)	-	520 (vw)	460 (vw)
$[\text{Zn}_3(\text{SHBH-6H})(\text{H}_2\text{O})_4\text{Cl}_2] \cdot 2\text{H}_2\text{O}$	3425* (br)	-	3246 (br)	1644 (vw)	1583 (m)	1491 (s)	1176 (w)	521 (br)	-
$[\text{Co}_2\text{Zn}(\text{SHBH-4H})(\text{H}_2\text{O})_4\text{Cl}_2] \cdot 2\text{H}_2\text{O}$	3398* (br)	-	-	1650 (w)	1578 (m)	1488 (s)	1170 (m)	510 (br)	-
$[\text{Ni}_3\text{Zn}(\text{SHBH-6H})(\text{H}_2\text{O})_6\text{Cl}_2] \cdot \text{H}_2\text{O}$	3418* (br)	3226 (br)	-	-	1583 (m)	1488 (s)	1163 (m)	530 (w)	425 (vw)
$[\text{Cu}_3\text{Zn}(\text{SHBH-6H})(\text{H}_2\text{O})_6\text{Cl}_2]$	3418* (vbr)	-	-	-	1551 (m)	1457 (s)	1199 (m)	543 (w)	458 (w)

* Hydrated or coordinated water.

** New azomethine group due to enolization of NHC=O.

Table 8. Molecular parameters of some complexes.

Parameters	$[\text{Co}_3(\text{SHBH-6H})(\text{H}_2\text{O})_6]$	$[\text{Cu}_4(\text{SHBH-6H})(\text{H}_2\text{O})_4(\text{OAc})_2] \cdot 3\text{H}_2\text{O}$	$[\text{Co}_2\text{Zn}(\text{SHBH-4H})(\text{H}_2\text{O})_4\text{Cl}_2] \cdot 2\text{H}_2\text{O}$
Total Energy (Kcal/mol)	265680.175	-288280.953	1290573.824
Total Energy (a.u)	423.388	-459.405	463.059
Binding Energy (Kcal/mol)	467492.521	-7224.877	475675.039
Isolated Atomic Energy (Kcal/mol)	-201812.346	-281056.076	-185101.215
Electronic Energy (Kcal/mol)	-1037819.785	-2480853.105	-893961.753
Core-Core Interaction (Kcal/mol)	1303499.961	2102572.152	1184535.577
Heat of Formation (Kcal/mol)	201812.346	-502.019	481238.843
Gradient (Kcal/mol)	1037819.785	66.394	2216.843
Dipole (Debyes)	46.889	11.269	24.987

**Figure 3.** Molecular modeling of $[\text{Cu}_4(\text{SHBH-6H})(\text{H}_2\text{O})_4(\text{OAc})_2] \cdot 3\text{H}_2\text{O}$.

The $\nu(\text{C=N})$ band is shifted to lower wavenumber indicating its coordination. The spectra of complexes showed new bands at 520-543 and 425-458 cm^{-1} due to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ [17]. The $\nu(\text{M-O})$ vibration is observed at higher wavenumber than $\nu(\text{M-N})$. Also, the new band at 1338 cm^{-1} is duo to $\delta(\text{OH})$ of the coordinated water [18]. In $[\text{Cu}_4(\text{SHBH-6H})(\text{H}_2\text{O})_4(\text{OAc})_2] \cdot 3\text{H}_2\text{O}$, two new bands at 1560 and 1410 cm^{-1} are attributed to ν_{as} and ν_{s} of the acetate ion; the difference (150 cm^{-1}) indicates a bidentate coordination.

Density functional theory (DFT) calculations were shown in Table 8 for $[\text{Cu}_4(\text{SHBH-6H})(\text{H}_2\text{O})_4(\text{OAc})_2] \cdot 3\text{H}_2\text{O}$ (Figure 3). The data of binding and total energy clearly out that the formation of metal complex process is endoergic. The lengths of Cu(31)-O(39), Cu(31)-O(38), O(27)-Cu(31) and O(26)-Cu(31) bonds are 1.953, 1.942, 1.930 and 1.965 Å, respectively, suggesting small distortion than the square-planar. The same observation was deduced for the coordination atoms around Cu(30). However, Cu(29) and Cu(28) in which the

Cu(II) is surrounded by acetate oxygen, azomethine nitrogen and enolic carbonyl oxygen have different bond lengths (Table 9). The N(18)-Cu(29) and N(4)-Cu(28) have the same length, 1.854 Å. The bond lengths of the acetate oxygens with copper are approximately similar. The bond angles (Table 9) are in the range 70-104 and 120-128 ° confirming sp^3 and sp^2 hybridization.

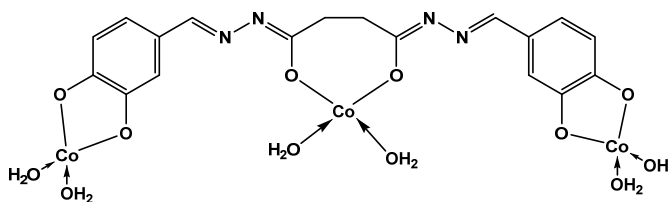
In $[\text{Co}_3(\text{SHBH-6H})(\text{H}_2\text{O})_6]$, the ligand acts as a hexanegative hexadentate with the three cobalt ions (Figure 4). The deprotonated OH's and the two enolic C-O groups are the donor groups according to disappearance of $\nu(\text{OH})$, $\nu(\text{NH})$ and $\nu(\text{C=O})$; appearance of new bands at 1490 and 1174 cm^{-1} , corresponding to $\nu(\text{C=N})^*$ and $\nu(\text{C-O})$ [19], and appearance of new band at 3423 cm^{-1} due to the coordinated water. Strong evidence for the OH coordination after deprotonation is the appearance of $\delta(\text{OH})$ at 1366 cm^{-1} which is due to the coordinated water. The spectrum showed a new band at 523 due to $\nu(\text{M-O})$ [17].

Table 9. Bond length and bond angles of $[\text{Cu}_4(\text{SHBH-6H})(\text{H}_2\text{O})_4(\text{OAc})_2] \cdot 3\text{H}_2\text{O}$.

Atom-Atom	Length/Å	Atom-Atom-Atom	Length/Å
Cu(31)-O(39)	1.953	O(39)-Cu(31)-O(38)	102.963
Cu(31)-O(38)	1.942	O(39)-Cu(31)-O(27)	104.388
Cu(30)-O(37)	1.936	O(39)-Cu(31)-O(26)	101.106
Cu(30)-O(36)	1.954	O(38)-Cu(31)-O(27)	120.97
Cu(29)-O(43)	1.872	O(38)-Cu(31)-O(26)	128.653
Cu(29)-O(42)	1.87	O(27)-Cu(31)-O(26)	95.347
Cu(28)-O(35)	1.871	O(37)-Cu(30)-O(36)	101.571
Cu(28)-O(34)	1.873	O(37)-Cu(30)-O(13)	128.64
O(27)-Cu(31)	1.93	O(37)-Cu(30)-O(12)	124.103
O(26)-Cu(31)	1.965	O(36)-Cu(30)-O(13)	101.071
N(18)-Cu(29)	1.854	O(36)-Cu(30)-O(12)	102.83
O(17)-Cu(29)	1.82	O(13)-Cu(30)-O(12)	94.33
O(13)-Cu(30)	1.97	O(43)-Cu(29)-O(42)	70.514
O(12)-Cu(30)	1.93	O(43)-Cu(29)-N(18)	170.149
N(4)-Cu(28)	1.854	O(43)-Cu(29)-O(17)	97.062
O(1)-Cu(28)	1.821	O(42)-Cu(29)-N(18)	101.573
C(41)-O(43)-Cu(29)	89.677	O(42)-Cu(29)-O(17)	166.662
C(41)-O(42)-Cu(29)	89.518	N(18)-Cu(29)-O(17)	91.269
H(69)-O(39)-Cu(31)	95.891	O(35)-Cu(28)-O(34)	70.456
H(61)-O(39)-Cu(31)	96.387	O(35)-Cu(28)-N(4)	101.629
H(70)-O(38)-Cu(31)	99.53	O(35)-Cu(28)-O(1)	166.568
H(60)-O(38)-Cu(31)	96.948	O(34)-Cu(28)-N(4)	169.927
H(67)-O(37)-Cu(30)	100.547	O(34)-Cu(28)-O(1)	97.174
H(59)-O(37)-Cu(30)	98.975	N(4)-Cu(28)-O(1)	91.221
H(68)-O(36)-Cu(30)	95.91	Cu(31)-O(27)-C(22)	89.36
H(58)-O(36)-Cu(30)	96.702	Cu(31)-O(26)-C(23)	81.769
C(33)-O(35)-Cu(28)	89.544	Cu(29)-N(18)-C(19)	121.628
C(33)-O(34)-Cu(28)	89.643	Cu(29)-N(18)-N(16)	105.238
Cu(30)-O(13)-C(9)	81.681	Cu(28)-N(4)-N(3)	105.226
Cu(30)-O(12)-C(8)	88.907	Cu(28)-O(1)-C(2)	106.054
Cu(28)-N(4)-C(5)	121.623	C(15)-C(14)-C(44)-C(2)	86.748

Table 10. Bond length and bond angles of $[\text{Co}_3(\text{SHBH-6H})(\text{H}_2\text{O})_6]$.

Atom-Atom	Length/Å	Atom-Atom-Atom	Length/Å
Co(35)-O(37)	2.025	H(61)-O(32)-H(50)	107.729
Co(35)-O(36)	1.961	H(61)-O(32)-Co(29)	104.161
Co(29)-O(33)	2.021	H(50)-O(32)-Co(29)	106.879
Co(29)-O(32)	1.975	H(56)-O(31)-H(49)	107.77
Co(28)-O(31)	1.975	H(56)-O(31)-Co(28)	104.104
Co(28)-O(30)	2.021	H(49)-O(31)-Co(28)	106.855
O(27)-Co(29)	1.909	H(57)-O(30)-H(48)	108.279
O(26)-Co(29)	1.861	H(57)-O(30)-Co(28)	109.543
O(13)-Co(28)	1.913	H(48)-O(30)-Co(28)	105.901
O(12)-Co(28)	1.862	O(33)-Co(29)-O(32)	87.176
O(1)-Co(35)	1.9	O(33)-Co(29)-O(27)	96.637
H(59)-O(37)-Co(35)	105.558	O(33)-Co(29)-O(26)	92.96
H(55)-O(37)-Co(35)	104.434	O(32)-Co(29)-O(27)	89.072
H(58)-O(36)-Co(35)	107.937	O(32)-Co(29)-O(26)	178.956
H(54)-O(36)-Co(35)	102.559	O(27)-Co(29)-O(26)	89.884
O(37)-Co(35)-O(36)	90.429	O(31)-Co(28)-O(30)	87.221
O(37)-Co(35)-O(17)	90.677	O(31)-Co(28)-O(13)	89.427
O(37)-Co(35)-O(1)	88.106	O(31)-Co(28)-O(12)	178.878
O(36)-Co(35)-O(17)	178.044	O(30)-Co(28)-O(13)	97.948
O(36)-Co(35)-O(1)	71.645	O(30)-Co(28)-O(12)	92.726
O(17)-Co(35)-O(1)	106.781	O(13)-Co(28)-O(12)	89.47
H(60)-O(33)-Co(29)	108.862	O(1)-Co(35)-O(37)-H(55)	38.995
H(51)-O(33)-Co(29)	105.751	O(1)-Co(35)-O(37)-H(59)	152.668

**Figure 4.** Structure of $[\text{Co}_3(\text{SHBH-6H})(\text{H}_2\text{O})_6]$.

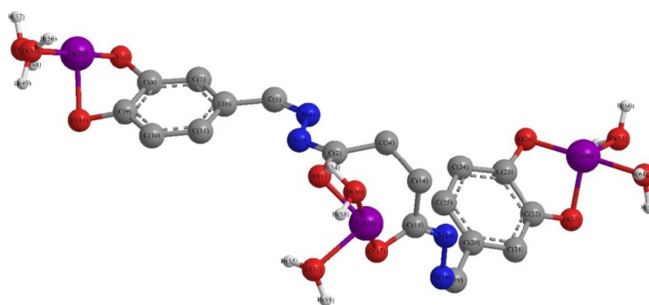
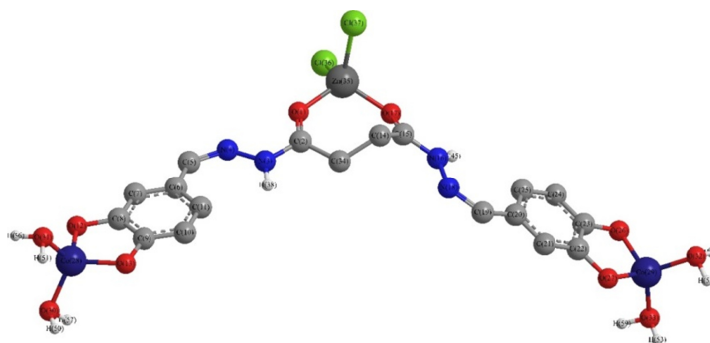
The calculated energetic parameters shown in Table 8 for $[\text{Co}_3(\text{SHBH-6H})(\text{H}_2\text{O})_6]$ (Figure 5) indicate exoergic process for the complex formation. Bond lengths and angles are shown in Table 10.

The last mode of chelation in which SHBH acts as a tetrabasic hexadentate through the four deprotonated OH and two C=O was depicted in $[\text{Zn}_3(\text{SHBH-4H})(\text{H}_2\text{O})_4\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ and

$[\text{Co}_2\text{Zn}(\text{SHBH-4H})(\text{H}_2\text{O})_4\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ (Figure 6). The $\nu(\text{C}=\text{O})$ appeared at 1650 (1644 cm^{-1}) indicating chelation through this group (keto form). Also, the disappearance of OH band confirmed its deprotonation through coordination. The complexes showed new band at 521 (510 cm^{-1}) due to $\nu(\text{M}-\text{O})$.

Table 11. Bond length and bond angles of $[\text{Co}_2\text{Zn}(\text{SHBH-6H})(\text{H}_2\text{O})_4\text{Cl}_2]\cdot 2\text{H}_2\text{O}$.

Atom-Atom-Atom	Length/Å	Atom-Atom-Atom	Length/Å
Cl(37)-Zn(35)-Cl(36)	108.871	O(30)-Co(28)-O(12)	112.312
Cl(37)-Zn(35)-O(17)	110.257	O(13)-Co(28)-O(12)	93.02
H(53)-O(33)-Co(29)	104.457	Zn(35)-O(17)-C(15)	122.112
H(58)-O(32)-H(52)	104.595	Co(28)-O(13)-C(9)	106.775
H(58)-O(32)-Co(29)	104.018	Co(28)-O(12)-C(8)	106.946
H(52)-O(32)-Co(29)	104.361	O(31)-Co(28)-O(12)	112.22
H(56)-O(31)-H(51)	104.605	O(30)-Co(28)-O(13)	112.337
H(56)-O(31)-Co(28)	104.023	O(30)-Co(28)-O(12)	112.312
H(51)-O(31)-Co(28)	104.363	O(13)-Co(28)-O(12)	93.02
H(57)-O(30)-H(50)	104.766	Zn(35)-O(17)-C(15)	122.112
H(57)-O(30)-Co(28)	104.362	Co(28)-O(13)-C(9)	106.775
H(50)-O(30)-Co(28)	104.435	Co(28)-O(12)-C(8)	106.946
O(33)-Co(29)-O(32)	113.033	Zn(35)-Cl(37)	2.24
O(33)-Co(29)-O(27)	112.354	Zn(35)-Cl(36)	2.239
O(33)-Co(29)-O(26)	112.292	Co(29)-O(33)	1.82
O(32)-Co(29)-O(27)	112.368	Co(29)-O(32)	1.82
O(32)-Co(29)-O(26)	112.245	Co(28)-O(31)	1.82
O(27)-Co(29)-O(26)	93.019	Co(28)-O(30)	1.82
O(31)-Co(28)-O(30)	113.028	O(27)-Co(29)	1.776
O(31)-Co(28)-O(13)	112.395	O(26)-Co(29)	1.776
O(31)-Co(28)-O(12)	112.22	O(17)-Zn(35)	1.87
O(30)-Co(28)-O(13)	112.337	O(1)-Zn(35)	1.871

**Figure 5.** Molecular modeling of $[\text{Co}_3(\text{SHBH-6H})(\text{H}_2\text{O})_6]$.**Figure 6.** Molecular modeling of $[\text{Co}_2\text{Zn}(\text{SHBH-4H})(\text{H}_2\text{O})_6\text{Cl}_2]\cdot 2\text{H}_2\text{O}$.

The broad band in the range 3398-3431 for $[\text{Co}_3(\text{SHBH-6H})(\text{H}_2\text{O})_6]$, $[\text{Co}_2\text{Zn}(\text{SHBH-4H})(\text{H}_2\text{O})_4\text{Cl}_2]\cdot 2\text{H}_2\text{O}$, $[\text{Ni}_4(\text{SHBH-6H})(\text{H}_2\text{O})_4(\text{OAc})_2]\cdot 6\text{H}_2\text{O}$, $[\text{Cu}_4(\text{SHBH-6H})(\text{H}_2\text{O})_4(\text{OAc})_2]\cdot 3\text{H}_2\text{O}$, $[\text{Zn}_3(\text{SHBH-4H})(\text{H}_2\text{O})_4\text{Cl}_2]\cdot 2\text{H}_2\text{O}$, $[\text{Ni}_3\text{Zn}(\text{SHBH-6H})(\text{H}_2\text{O})_6\text{Cl}_2]\cdot \text{H}_2\text{O}$ and $[\text{Cu}_3\text{Zn}(\text{SHBH-6H})(\text{H}_2\text{O})_6\text{Cl}_2]$ are attributed to $\nu(\text{OH})$ of the hydrated or coordinated water [20]. Other bands observed in $[\text{Co}_3(\text{SHBH-6H})(\text{H}_2\text{O})_6]$ and $[\text{Cu}_3\text{Zn}(\text{SHBH-6H})(\text{H}_2\text{O})_6\text{Cl}_2]$ at 1660 and 1317 cm^{-1} are due to bending $[\delta(\text{OH}_2)]$ and wagging $[\rho_w(\text{OH}_2)]$ vibrations of the coordinated water.

The calculated energies (Table 8) for $[\text{Co}_2\text{Zn}(\text{SHBH-4H})(\text{H}_2\text{O})_4\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ are higher than $[\text{Co}_3(\text{SHBH-6H})(\text{H}_2\text{O})_6]$ indicating that the three Co lowered the energy and stabilized the complex. Bond lengths and angles are presented in Table 11. The geometry around the Zn atom is purely tetrahedral (Figure 6).

3.4. Mass spectra

The data of FAB-MS of the ligand and its complexes are shown in Table 1. The MS of SHBH showed molecular ion peak at $m/z = 387.5$ corresponding to the anhydrous form of the ligand, $\text{C}_{18}\text{H}_{18}\text{N}_4\text{O}_6$ (386.374). The peak shown at 772.7 m/z with 5% intensity may be due to combination of two ligand molecules with hydrogen bond interaction. Also, the spectrum showed a peak at 235.3 with intensity of 88% corresponding to $\text{C}_{11}\text{H}_9\text{O}_4\text{N}_2$. Other peaks are observed at 110.9, 99.8 and 70.9 m/z due to $\text{C}_6\text{H}_5\text{O}_2$, $\text{C}_6\text{H}_3\text{O}$ and 6 C.

The spectrum of $[\text{Co}_3(\text{SHBH-6H})(\text{H}_2\text{O})_6]$ exhibit the molecular ion peak at 577.5 m/z (Calcd. 665.205) with intensity 6% may be due to $[\text{Co}_3(\text{SHBH-6H})(\text{H}_2\text{O})]$ followed by a peak at 551.4 m/z (intensity 13%) corresponding to $[\text{Co}_3(\text{SHBH-6H})]$. Numerous peaks are observed with the final one at 69.

Table 12. Magnetic moments and electronic spectral bands of the compounds.

Compound	μ_{eff} (BM)	Intra ligand and charge transfer (cm^{-1})	d-d transition (cm^{-1})	Probable Structure
SHBH		33330; 26040; 21830		
$[\text{Co}_3(\text{SHBH-6H})(\text{H}_2\text{O})_6]$	2.84*	27320; 23255	20830; 17670; 16080	Square-planar
$[\text{Ni}_4(\text{SHBH-6H})(\text{H}_2\text{O})_4(\text{OAc})_2] \cdot 6\text{H}_2\text{O}$	2.13*	33780; 30120; 25125; 21930	19610; 18315; 16720; 15625	Tetrahedral
$[\text{Cu}_4(\text{SHBH-H})(\text{H}_2\text{O})_4(\text{OAc})_2] \cdot 3\text{H}_2\text{O}$	1.19*	34010; 29410; 25125; 22730	20580; 17480; 15200	Square-planar
$[\text{Zn}_3(\text{SHBH-6H})(\text{H}_2\text{O})_4\text{Cl}_2] \cdot 2\text{H}_2\text{O}$		31850; 25125; 21275; 18315; 16600		Tetrahedral
$[\text{Co}_2\text{Zn}(\text{SHBH-4H})(\text{H}_2\text{O})_4\text{Cl}_2] \cdot 2\text{H}_2\text{O}$	3.66*	33780; 29240; 26880; 23360	20830; 20160; 18115; 16835; 15015	Tetrahedral
$[\text{Ni}_3\text{Zn}(\text{SHBH-6H})(\text{H}_2\text{O})_6\text{Cl}_2] \cdot \text{H}_2\text{O}$	0.00	27320; 238190; 22120	20160; 18380; 16835; 14580; 13620	Square-planar
$[\text{Cu}_3\text{Zn}(\text{SHBH-6H})(\text{H}_2\text{O})_6\text{Cl}_2]$	0.76*	33110; 28410; 23810	19920; 16555; 14750	Square-planar

* Value for each metal ion.

However, the mass spectrum of $[\text{Ni}_4(\text{SHBH-6H})(\text{H}_2\text{O})_4(\text{OAc})_2] \cdot 6\text{H}_2\text{O}$ showed m/z value of 603.5 with 3% intensity. The value corresponds to $[\text{Ni}_3(\text{SHBH-6H})(\text{OAc})]$ without one acetate and eight water molecules. Multi-peaks were observed ending with a peak at 69.0 m/z (78% intensity) may correspond to 6 C.

The molecular ion peak of $[\text{Cu}_4(\text{SHBH-6H})(\text{H}_2\text{O})_4(\text{OAc})_2] \cdot 3\text{H}_2\text{O}$ is 602 m/z with intensity of 3% corresponding to $[\text{Cu}_2(\text{SHBH-6H})(\text{H}_2\text{O})_2(\text{OAc})]$ followed by one at 523.4 m/z due to the removal of $\text{OAc} + \text{H}_2\text{O}$. The base peak at 135 m/z (100% intensity) followed by peaks at 99, 73 and 69 m/z .

$[\text{Zn}_3(\text{SHBH-4H})(\text{H}_2\text{O})_4\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ has 603.5 m/z due to $[\text{Zn}_3(\text{SHBH-6H})]$ with intensity of 7%. It is noticed that the peak at 368.3 m/z is observed in all complexes with high intensity followed by peaks at 313.2, 236.2, 111.1, 97.1, 83 and 69 m/z which proved that the complexes degraded with the same mechanism after this step.

The m/z value 781.9 of $[\text{Co}_2\text{Zn}(\text{SHBH-4H})(\text{H}_2\text{O})_6\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ with intensity of 3% is due to its formula $\text{C}_{18}\text{H}_{30}\text{N}_4\text{O}_{14}\text{Co}_2\text{ZnCl}_2$. This peak has no isotopic species. Numerous peaks were observed containing the base peak at 133.0 m/z (100%) and final intense peak at 78.9 m/z having more isotopes.

The m/z value of $[\text{Cu}_3\text{Zn}(\text{SHBH-6H})(\text{H}_2\text{O})_6\text{Cl}_2]$ is 804.0 with no isotopic species and low intensity (2%). The suggested formula according to the elemental analysis is 815.336 m/z ; the difference is large. Another peak at 566.7 m/z is due to $[\text{Cu}_3(\text{SHBH-6H})]$. The base peak is observed at 176.3 and the final at 78.9 m/z .

Very small peak was observed at 693.0 m/z in $[\text{Ni}_3\text{Zn}(\text{SHBH-6H})(\text{H}_2\text{O})_6\text{Cl}_2] \cdot \text{H}_2\text{O}$ corresponding to $[\text{Ni}_3\text{Zn}(\text{SHBH-6H})(\text{H}_2\text{O})_4]$ followed by numerous small peaks. The high one was observed at 419.9 m/z with intensity of 16% and one isotope. The base peak at 115.0 m/z having multi isotopic peaks. The final peak at 57.0 m/z is due to the presence of 5C with three isotopes.

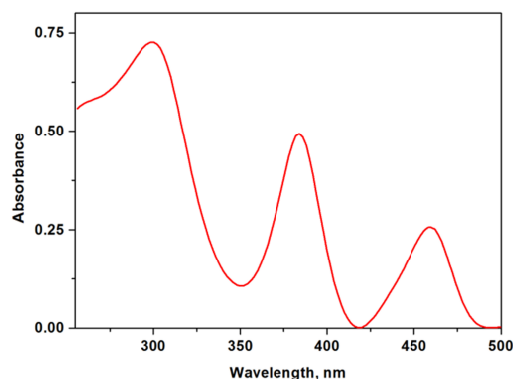
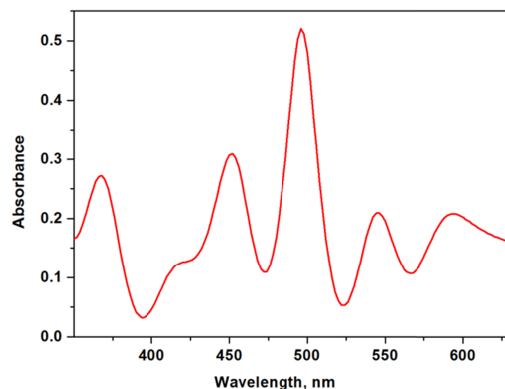
3.5. Electronic and magnetic studies

The magnetic moments and the electronic spectral bands of the complexes measured in Nujol (200-1000 nm) at room temperature are presented in Table 12.

The absorption spectrum of SHBH (Figure 7) showed the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands of C=C, C=O and C=N groups at 33330; 26040 and 21830 cm^{-1} . Different bands are observed in the spectra of its complexes at: 27320 and 23255 cm^{-1} for $[\text{Co}_3(\text{SHBH-6H})(\text{H}_2\text{O})_6]$; 33780, 29240, 26880 and 23360 cm^{-1} for $[\text{Co}_2\text{Zn}(\text{SHBH-6H})(\text{H}_2\text{O})_4\text{Cl}_2] \cdot 2\text{H}_2\text{O}$; 33780, 30120, 25125 and 21930 cm^{-1} for $[\text{Ni}_4(\text{SHBH-H})(\text{H}_2\text{O})_4(\text{OAc})_2] \cdot 6\text{H}_2\text{O}$, 27320, 238190 and 22120 cm^{-1} for $[\text{Ni}_3\text{Zn}(\text{SHBH-6H})(\text{H}_2\text{O})_6\text{Cl}_2] \cdot \text{H}_2\text{O}$; 31850, 25125, 21275, 18315 and 16600 cm^{-1} for $[\text{Zn}_3(\text{SHBH-6H})\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ and 34010, 29410, 25125 and 22730 cm^{-1} for $[\text{Cu}_4(\text{SHBH-H})(\text{H}_2\text{O})_4(\text{OAc})_2] \cdot 3\text{H}_2\text{O}$.

In the electronic spectrum of $[\text{Ni}_4(\text{SHBH-H})(\text{H}_2\text{O})_4(\text{OAc})_2] \cdot 6\text{H}_2\text{O}$, a strong band at 15625 cm^{-1} is assigned to ${}^3\text{T}_1 \rightarrow {}^3\text{A}_2$ of tetrahedral geometry. The distortion may be attributed to steric hindrance produced by the bulky ligand and the difference between size and space occupied by SHBH as compared to acetates. Additional bands centered at 19610;

18315 and 16720 cm^{-1} may be due to $\text{O} \rightarrow \text{MCT}$. The magnetic moment is 2.13 BM for each Ni atom which is less than the spin only value for the presence of two electrons (2.87 BM) and may be due to strong interaction between the four Ni atoms. On the other hand, the spectrum of $[\text{Ni}_3\text{Zn}(\text{SHBH-6H})(\text{H}_2\text{O})_4\text{Cl}_2] \cdot 3\text{H}_2\text{O}$ (Figure 8) showed bands at 20160, 18380, 16835, 14580 and 13620 cm^{-1} . The strong band at 20160 cm^{-1} is typical of a square-planar structure and is due to ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$ [21]. The diamagnetic nature supports the aforementioned structure.

**Figure 7.** Absorption spectrum of SHBH in Nujol.**Figure 8.** Electronic spectrum of $[\text{Ni}_3\text{Zn}(\text{SHBH-6H})(\text{H}_2\text{O})_6\text{Cl}_2] \cdot \text{H}_2\text{O}$ in Nujol.

$[\text{Co}_3(\text{SHBH-6H})(\text{H}_2\text{O})_6]$ showed bands at 20830, 17670 and 16080 (Figure 9a) in agreement with those reported for a tetrahedral geometry [22]. The band at 20830 cm^{-1} may be due to Co-SHBH CT. The magnetic moment (2.83 BM) supports the square-planar geometry. Its molecular modeling is consistent with a tetrahedral structure.

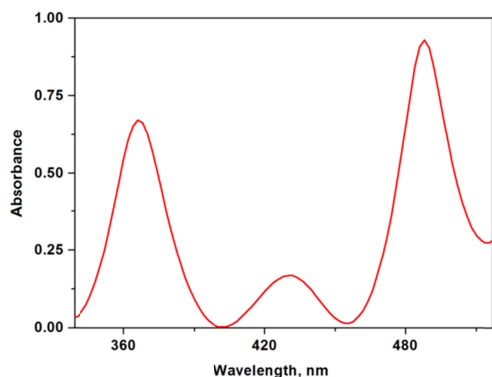
The room temperature magnetic moment of $[\text{Co}_2\text{Zn}(\text{SHBH-6H})(\text{H}_2\text{O})_4\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ (3.66 BM) is expected to be less than the spin-only value (3.87 BM). The electronic spectrum (Figure 9b) showed bands at 20160, 18115, 16835 and 15015 cm^{-1} .

Table 13. Decomposition steps of the compounds based on the thermogravimetric data.

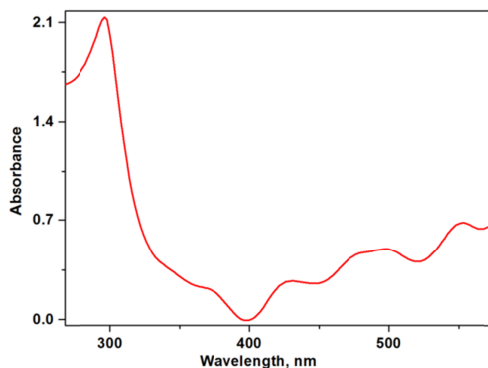
Complex	Mid-Point Temp. (°C)	Removed species	Weight loss %, Found (Calcd.)
SHBH.2H ₂ O	119	- 2H ₂ O	8.53 (9.32)
	226	- C ₆ H ₅ O ₂	25.55 (28.24)
	450	- C ₃ H ₅ N ₂	24.80 (21.76)
	>500	C ₉ H ₇ N ₂ O ₃	(50.35 (50.00))
[Co ₃ (SHBH-6H)(H ₂ O) ₆]	79	- 6H ₂ O	16.98 (16.25)
	352	- C ₉ H ₇ N ₂ O ₂	26.45 (26.33)
	522	- C ₉ H ₇ N ₂ O ₂	27.63 (26.33)
	>600	Co ₃ O ₂	30.67 (31.39)
[Ni ₄ (SHBH-6H)(H ₂ O) ₄ (OAc) ₂].6H ₂ O	77	- 6H ₂ O+2H ₂ O (coordinated)	15.44 (14.02)
	416	- 2H ₂ O + C ₁₈ H ₁₈ N ₄ O ₆	42.77 (42.29)
	600	- 2OAc	12.57 (12.92)
	>600	2NiO + 2Ni	29.22 (29.22)
[Cu ₄ (SHBH-6H)(H ₂ O) ₄ (OAc) ₂].3H ₂ O	75	- 3H ₂ O+2H ₂ O (coordinated)	11.44 (10.25)
	269	- 2H ₂ O+ C ₉ H ₇ N ₂ O ₃	23.68 (24.04)
	433	- C ₉ H ₇ N ₂ O ₃	19.59 (21.75)
	>500	4 CuO	37.96 (37.03)
[Zn ₃ (SHBH-4H)(H ₂ O) ₄ Cl ₂].2H ₂ O	71	- 6H ₂ O	11.20 (14.28)
	400	- ZnCl ₂ + O ₂	23.96 (22.21)
	575	- C ₆ H ₃ ZnO ₂	23.96 (22.76)
	>600	C ₁₂ H ₁₁ N ₄ O ₂ Zn	40.86 (40.74)
[Co ₂ Zn(SHBH-6H)(H ₂ O) ₄ Cl ₂].2H ₂ O	84	- 2H ₂ O	5.91 (4.92)
	234	- 4H ₂ O	9.82 (9.84)
[Ni ₃ Zn(SHBH-6H)(H ₂ O) ₆ Cl ₂].H ₂ O	79	-H ₂ O+4H ₂ O (coordinated)	11.18 (11.00)
	236	- 2H ₂ O + Cl ₂	13.44 (13.06)

The band at 16835 cm⁻¹ is due to ⁴A₂ → ⁴T₁ of tetrahedral structure [23].

Three bands observed in the spectra of [Cu₄(SHBH-H)(H₂O)₄(OAc)₂].3H₂O and [Cu₃Zn(SHBH-6H)(H₂O)₆Cl₂] at (20580, 17480 and 15200) and (19920, 16555 and 14750 cm⁻¹) are assigned to d_{xz} → d_{xy} in a square-planar geometry, respectively [24-26]. The subnormal magnetic moments, 1.19 and 0.76 BM, respectively, may be due to strong interaction between the four copper atoms in the first complex and three copper in the second complex.



(a)



(b)

Figure 9. Electronic spectra of a) [Co₃(SHBH-6H)(H₂O)₆] and b) [Co₂Zn(SHBH-6H)(H₂O)₄Cl₂].2H₂O.

3.6. Thermal analysis

The thermogravimetric curves (25-800 °C) of all complexes were recorded to give an insight into the thermal stability of the studied complexes. Investigation of the data in Table 13, the complexes were found stable than the ligand. They have stability temperature in the range 220-418 °C. The stable one is [Ni₄(SHBH-6H)(H₂O)₄(OAc)₂].6H₂O followed by [Zn₃(SHBH-6H)(H₂O)₄Cl₂].2H₂O. The stability of homo complex is found more than hetero complex. Some of the coordinated waters were evolved with the hydrated waters in the temperature below 100 °C indicating weak bonds.

The thermogram of the ligand showed three steps due to the removal of 2H₂O, C₆H₅O₂, C₃H₅N₂ leaving C₉H₇N₂O₃ as a residue at > 500 °C.

In [Cu₄(SHBH-6H)(H₂O)₄(OAc)₂].3H₂O, the decomposition steps at mid-points of 75, 269 and 433 °C are due to the loss of 5H₂O, (2H₂O + C₉H₇N₂O₃) and C₉H₇N₂O₃, respectively. The residue is 4 CuO with weight loss of calc. 37.96 (Found: 37.03).

The thermogram of [Zn₃(SHBH-4H)(H₂O)₄Cl₂].2H₂O showed three steps at 71, 400 and 575 °C, due to the evolution of 6H₂O, (ZnCl₂ + O₂) and C₆H₃ZnO₂, respectively. The residue is C₁₂H₁₁N₄O₂Zn.

The TGA thermogram of [Ni₄(SHBH-6H)(H₂O)₄(OAc)₂].6H₂O showed the evolution of 6H₂O and in the second step observed at 416 °C the loss of 4H₂O with C₁₈H₁₈N₄O₆. The third step at 600 °C is due to the evolution of 2 OAc.

The TG curve of [Co₃(SHBH-6H)(H₂O)₆] displayed three thermal steps after which it left Co₃O₂ at > 600 °C. The degradation steps were observed at 79, 352 and 522 due to the removal of 6H₂O with 16.98 (calcd. 16.25%), C₉H₇N₂O₂ [26.45 (calcd. 26.33)] and C₉H₇N₂O₂ [27.63 (26.33)]. The removal of the coordinated water at this mid-point may indicate the weak bond with the cobalt ions.

4. Conclusion

A new ligand was prepared and structurally characterized. It was introduced for chelation with individual metal ions: Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and combined metal ions: Co²⁺/Zn²⁺, Cu²⁺/Zn²⁺ or Ni²⁺/Zn²⁺. It chelated as a tetranegative hexadentate in the Co²⁺/Zn²⁺ complex; hexanegative hexadentate in the trimetallic Co(II) complex and hexanegative octadentate in the tetrametallic complexes. Square-planar geometry was proposed for [Co₃(SHBH-6H)(H₂O)₆],

[Cu₄(SHBH-H)(H₂O)₄(OAc)₂].3H₂O, [Ni₃Zn(SHBH-6H)(H₂O)₆Cl₂].H₂O and [Cu₃Zn(SHBH-6H)(H₂O)₆Cl₂] and tetrahedral for [Ni₄(SHBH-H)(H₂O)₄(OAc)₂].6H₂O, [Zn₃(SHBH-4H)-(H₂O)₄Cl₂].2H₂O and [Co₂Zn(SHBH-6H)(H₂O)₄Cl₂].2H₂O.

Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with Cambridge Crystallographic Data Center as supplementary publication CCDC-1053722. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/data_request/cif.

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