



Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Hg²⁺ Complexes of Butanedione Hydrazones: Spectroscopic, Thermal and Biological Studies

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Authors' contributions

This work was carried out in collaboration between all authors. Author AAEA designed the study, wrote the protocol and wrote the first draft of the manuscript. Author OAAF helped in writing the protocol and help in writing the draft. Author AEES prepared the ligands and their complexes and managed the analyses of the study. All authors read and approved the final manuscript.

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ABSTRACT

Complexes of Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Hg²⁺ with malonyl- and succinoyl bis(2,3-butanedionehydrazone) [MBH, SBH] have been synthesized and characterized. Single crystal of SBH was found monoclinic with space group of P121/c14. The MBH complexes have the formulae: [Co(MBH)Cl₂].H₂O, [Ni(MBH-2H)(H₂O)₂].2H₂O, [Cu(MBH-2H)(H₂O)₂].2H₂O, [Cu(MBH-H)(OAc)].2H₂O while the SBH complexes have [Co(SBH-H)(H₂O)], [Ni(SBH-H)₂], [Ni(SBH)Cl₂], [Cu(SBH-H)Cl], [Cu(SBH-H)(OAc)].2H₂O, [Zn(SBH)₂Cl]Cl, [Cd(SBH-H)₂].-H₂O and [Hg₂(SBH)₂Cl₂]Cl₂. All complexes are nonelectrolytes except [Zn(SBH)₂Cl]Cl and [Hg₂(SBH)₂Cl₂]Cl₂.5H₂O. MBH and SBH ligate as neutral, mononegative and/or binegative bidentate. The carbonyl group (C=O)_{ketone} is not taking part in complexation. The magnetic moments and electronic spectra afford a tetrahedral geometry for the Zn²⁺ and Cd²⁺ complexes; square-planar for the Co²⁺ and [Ni(SBH)Cl₂] complexes and octahedral for the other complexes. The thermal decomposition of the complexes revealed the outer and inner solvents as well as the remaining part which is metal or metal oxide in some cases. The complexes have variable activities

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against some bacteria and fungi. $[\text{Hg}_2(\text{SBH})\text{Cl}_2] \cdot \text{Cl}_2 \cdot 5\text{H}_2\text{O}$ has the highest activity against all tested organisms. $[\text{Ni}(\text{SBH}-\text{H})_2]$ and $[\text{Zn}(\text{SBH})_2]\text{Cl}_2$ have activity against *Bacillus* and *E. coli*. On the other hand, MBH and $[\text{Co}(\text{MBH})\text{Cl}_2] \cdot \text{H}_2\text{O}$ have activity against *Penicillium* only.

Keywords: Dihydrazones; spectra; thermal; X-ray spectroscopy; antimicrobial activity.

1. INTRODUCTION

Much interest has been engrossed on the complexes of hydrazones due to their antiparasitic, fungicidal and bactericidal properties [1-3]. Complexes of some transition metal ions with 2-acetylpyridineisonicotinyl, pyrrolyl-2-carboxaldehyde isonicotinyl, 2,5-dihydroxyaceto-phenone isonicotinoyl, N-isonicotinamidofurfuraldimine, 2-thiophenecarbonyl and isonicotinoyl hydrazones of 3-(N-methyl)isatin were reported [4-6]. The Ni(II) and Cu(II) complexes of 2,3-butanedione bis(N(3)substituted thiosemicarbazones) were considered and some of these compounds were solved by X-ray crystallography [7,8]. The crystal structure of the Cu(II) complexes of 3,4-hexanedione bis(3-piperidylthiosemicarbazone), $[\text{Cu}(\text{HxPip}-2\text{H})]$ and 3,4-hexanedione bis(3-hexamethyleneiminylthiosemicarbazone), $[\text{Cu}(\text{HxHexim}-2\text{H})]$ was described [9]. Hydrazones resulting from the condensation of oxalic, malonic, succinic and/or phthalic acid dihydrazides and ketones have the ability to form homo- and heterometallic complexes stabilized by forming two six membered rings and one or more five rings.

On continuation to the work done on the dihydrazones of 3,4-hexanedione; 2,5-hexanedione, 2,3-butanedione and their complexes [9,10], the present work aims to synthesize and characterize novel complexes with malonyl- and succinoyl bis(2,3-butanedionehydrazone). Single crystal for succinoyl bis(2,3-butanedionehydrazone) is grown and analyzed.

2. EXPERIMENTAL

2.1 Materials

All chemicals used for the synthesis of ligands and their complexes were as supplied. The salts used are: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$; $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$; $\text{Ni}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$; $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$; $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$; $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$; $\text{HgCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Cu}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$.

2.2 Synthesis of Ligands

MBH and/or SBH were prepared similar to those previously reported [9,10] by mixing malonic- or

succinic acid dihydrazide (0.1 mol) and 2,3-butanedione (0.2 mol) in 50 ml ethanol and heating the mixture under reflux for 3 h. On evaporating the mother liquor to its half volume, the precipitate is formed, separated by filtration, recrystallized from ethanol and dried. The crystal structure of SBH was analyzed by X-ray crystallography.

2.3 Synthesis of MBH Complexes

2.3.1 Synthesis of $[\text{Co}(\text{MBH})\text{Cl}_2] \cdot \text{H}_2\text{O}$

A solution of MBH (0.804 g; 3 mmol) in 30 ml ethanol was added to 20 ml absolute ethanol of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.69 g; 3 mmol). The reaction mixture was heated under reflux on a water bath for 4 h. On evaporating the mother liquor, the reddish brown precipitate thus formed was filtered off, washed with ethanol and diethyl ether, and dried in a vacuum desiccator over anhydrous CaCl_2 .

2.3.2 Synthesis of $[\text{Ni}(\text{MBH}-2\text{H})(\text{H}_2\text{O})_2] \cdot 1.2\text{H}_2\text{O}$

On heating a mixture of MBH (0.804 g; 3 mmol), dissolved in 20 ml absolute ethanol and $\text{Ni}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.813 g; 3 mmol) in 30 ml absolute ethanol on a water bath for 3 h, a yellowish brown precipitate was formed. It was filtered off, washed with ethanol and diethyl ether and finally dried in a vacuum desiccator over anhydrous CaCl_2 .

2.3.3 Synthesis of $[\text{Cu}(\text{MBH})] \cdot 4\text{H}_2\text{O}$

The 1 : 1 (L : M) complex was prepared by reacting 0.804 g (3 mmol) of MBH dissolved in 50 ml absolute ethanol and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.511 g; 3 mmol) in 30 ml ethanol on a water bath for 5 h. The brown precipitate was filtered, washed with ethanol and diethyl ether and finally dried.

2.3.4 Synthesis of $[\text{Cu}(\text{MBH}-\text{H})(\text{OAc})] \cdot 2\text{H}_2\text{O}$

An ethanol solution (20 mL) of the ligand (0.536 g; 2 mmol) was mixed with 20 ml aqueous-ethanol (0.79 g; 2 mmol) of $\text{Cu}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$. The mixture was heated under reflux on a hot plate for 4 h. On evaporating the mother liquor, a

brown precipitate thus formed was filtered off, washed and dried.

2.3.5 Synthesis of [Cd(MBH-2H)].4H₂O

The complex was prepared by heating a mixture of MBH (0.268 g; 1 mmol) dissolved in 20 ml ethanol and CdCl₂.2H₂O (0.162 g; 1 mmol) in 30 ml ethanol on a water bath for 4 h. The brown precipitate was filtered off, washed with ethanol and diethyl ether and finally dried.

2.4 Synthesis of SBH Complexes

2.4.1 Synthesis of [Co(SBH-H)₂(H₂O)]

A solution of SBH (0.56 g; 2 mmol) in 50 ml ethanol was added to 30 ml ethanol of CoCl₂.6H₂O (0.23 g; 1 mmol). The reaction mixture was heated under reflux on a water bath for 4 h. On evaporating the mother liquor, the brown precipitate thus formed was filtered off, washed with ethanol and diethyl ether, and dried in a vacuum desiccator over anhydrous CaCl₂.

2.4.2 Synthesis of [Ni(SBH-H)₂]

On heating a mixture of SBH (0.56 g; 2 mmol), dissolved in 20 ml ethanol and Ni(OAc)₂.2H₂O (0.271 g; 1 mmol) in 30 ml ethanol on a water bath for 3 h, a brown precipitate was formed. It was filtered off, washed with ethanol and diethyl ether and finally dried in a vacuum desiccator over anhydrous CaCl₂.

2.4.3 Synthesis of [Ni(SBH)]Cl₂

The complex was prepared by a reaction between solution of SBH (0.846 g; 3 mmol), dissolved in 20 ml ethanol and a solution of NiCl₂.6H₂O (0.7131 g; 3 mmol) in 30 ml ethanol. The reaction mixture was heated under reflux on a water bath for 3 h, a precipitate was formed. It was filtered off, washed with ethanol and diethyl ether and finally dried.

2.4.4 Synthesis of [Zn(SBH)₂Cl₂]

A solution of SBH (0.56 g; 2 mmol) in 50 ml ethanol was added to 30 ml ethanol of ZnCl₂.2H₂O (0.172 g; 1 mmol). The reaction mixture was heated on a water bath for 4 h. On evaporating the mother liquor, the yellow precipitate thus formed was filtered off, washed with ethanol and diethyl ether and dried in a vacuum desiccator over anhydrous CaCl₂.

2.4.5 Synthesis of [Cd(SBH-H)₂].H₂O

The complex was prepared by heating a mixture of SBH (0.56 g; 2 mmol), dissolved in 20 ml ethanol, and CdCl₂.2H₂O (0.162 g; 1 mmol) in 30 ml ethanol on a water bath for 4 h. The yellowish white precipitate was filtered off, washed with ethanol and diethyl ether and finally dried.

2.4.6 Synthesis of [Cu(SBH-H)Cl]

The 1 : 1 (L : M) complex was prepared by reacting (0.84 g; 3mmol) of SBH dissolved in 50 ml ethanol and CuCl₂.2H₂O (0.511 g; 3 mmol) in 30 ml ethanol on a water bath for 5 h. The brown precipitate was filtered, washed with ethanol and diethyl ether and finally dried.

2.4.7 Synthesis of [Cu(SBH-H)(OAc)].H₂O

An ethanol solution (20 mL) of the ligand (0.56 g; 2 mmol) was mixed with 20 ml aqueous- ethanol (0.79 g; 2 mmol) of Cu₂(OAc)₄.2H₂O. The mixture was heated under reflux for 4 h. On evaporating the mother liquor, a brown precipitate thus formed was filtered off, washed and dried.

2.4.8 Synthesis of [Hg₂(SBH)Cl₂].5H₂O

A keto and binuclear complex was prepared by mixing a solution of SBH (0.282 g; 1 mmol) in 20 ml ethanol and adding to 30 ml ethanol of HgCl₂.2H₂O (0.308 g; 1 mmol). The reaction mixture was heated on a water bath for 3 h. On evaporating the mother liquor, the precipitate thus formed was filtered off, washed with ethanol and diethyl ether, and dried.

The yield of the complexes is in the range 79-88%.

2.5 Antimicrobial Studies

The *in vitro* antibacterial activity of MBH and/or SBH and their complexes was evaluated against three bacteria (*Bacillus thuringiensis*, *E. coli* and *Aspergillus*) and two fungi (*Penicillium* and *Fusarium*). The hole plate diffusion method [11] was adopted for the activity measurements. The bacterial strains were grown in nutrient agar slants. A suspension of the studied compounds (0.2 ml of each (10 µg/ml) was incubated at 36°C for 36 h for the bacterial culture. After inoculation, the diameter (in mm) of the clear inhibition zone surrounding the sample is taken as a measure of the inhibition power against the particular organisms. The values recorded are

the mean average for experiments repeated three times.

2.6 Physical Measurements

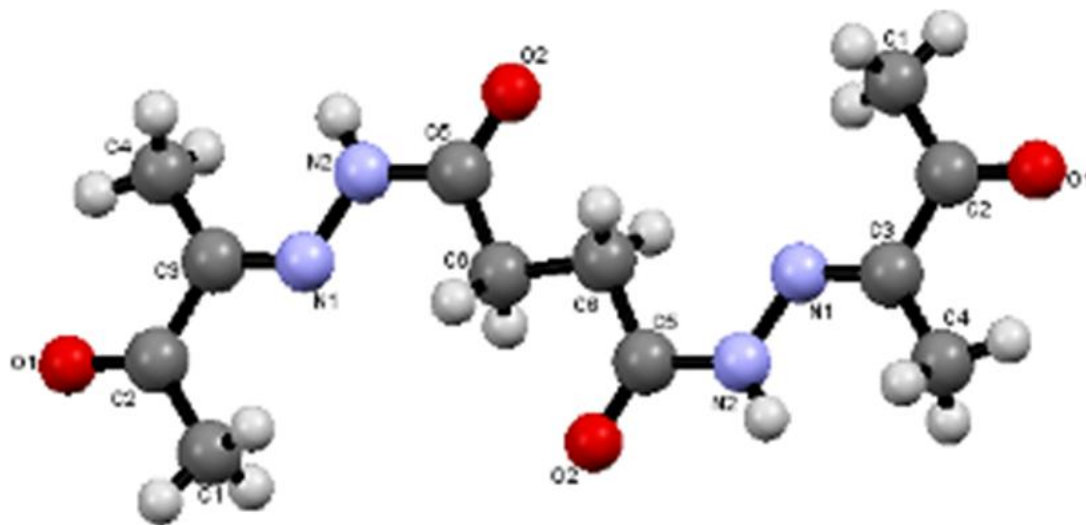
CHN content of MBH, SBH and their complexes was determined at the Microanalytical Unit (Varian Micro V1.5.8, CHNS Mode, 15073036) of Kuwait University. The molar conductivity (Λ_m) of the soluble chelates was recorded by dissolving the solid complex (1×10^{-3} M) in dimethylsulphoxide (DMSO) or dimethylformamide (DMF) and the measurements were carried out using an Orion 3 STAR conductivity bridge. The IR spectra were recorded as KBr discs on a FTIR-6300 type A ($400-4000 \text{ cm}^{-1}$). The ^1H NMR spectra of the ligand and its diamagnetic complexes were recorded in DMSO d_6 , on a Bruker WP 200 SY spectrometer (400 MHz) at room temperature (25°C) using tetramethylsilane (TMS) as external standard. The UV/V spectra of the ligand and its complexes were recorded on Cary 5 UV-Vis Spectrophotometer, Varian (200-900 nm). The magnetic measurements were carried out on a Johnson-Matthey magnetic balance, UK. Thermogravimetric Analysis (TGA) was measured ($10-850^\circ\text{C}$) on a Shimadzu TGA-60; the nitrogen flow and heating rate were 50 ml/min and $10^\circ\text{C min}^{-1}$, 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 $2.00e + 02 \text{ mW}$. A

powder spectrum was obtained in a 2 mm quartz capillary at room temperature. 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.

3. RESULTS AND DISCUSSION

3.1 Investigation of the Crystal Structure of SBH

The crystal structure of succinoyl bis(2,3-butanedionehydrazone) with the atomic numbering scheme is shown in Structure 1. The crystal data and structure refinement are summarized in Table 1 while the bond lengths and bond angles are in Table 2. SBH ($\text{C}_{12}\text{H}_{18}\text{N}_4\text{O}_4$) crystallized in a clear colorless flake with monoclinic crystal system and P 1 21/n 12 space group. Its volume is 737.65 \AA^3 and density of 1.271 g/cm^3 . The N_1-C_3 and O_1-C_2 are 1.286 and 1.209 \AA , respectively, indicating a true double bond. The N_2-C_5 is 1.351 \AA indicating a single bond. The N1-N2 length is 1.371 \AA more than the N2-C5 length. The amidic $\text{C}=\text{O}$ has more length than the ketonic $\text{C}=\text{O}$ due to the surrounding substituent atoms and the basicity of NH group. All bond angles are between $117.9-127.0$ and 109.5° meaning the tetrahedral and trigonal geometries with sp^3 and sp^2 hybridization.



Structure 1. Crystal structure of SBH

Table 1. Crystal structural data of SBH

Property	SBH
Empirical Formula	C ₁₂ H ₁₈ N ₄ O ₄
Formula Weight	282.30
Crystal Color, habit	clear colorless Flake
Crystal Dimensions	0.030 x 0.180 x 0.340 mm
Crystal System	monoclinic
Lattice Parameters	a = 4.0805(5) Å b = 23.911(2) Å c = 7.7627(7) Å α = 90° β = 103.113(4)° γ = 90°
Volume	737.65(13) Å ³
Space Group	P 1 21/n 12
Z value	2
D _{calcd}	1.271 g/cm ³
Final R indices	848 data; I > 2σ(I) wR1 = 0.0604, wR2 = 0.1517

Table 2. Bond lengths (Å) and bond angles (°) of SBH

a- Bond lengths			
N2-C5	1.351(4)	N2-N1	1.371 (3)
N2-H2	0.86	O1-C2	1.209 (4)
C6-C5	1.501(4)	C6-C6#1	1.513 (5)
C6-H6A	0.97	C6-H6B	0.97
O2-C5	1.225 (3)	C1-C2	1.497 (5)
C1-H1A	0.96	C1-H1B	0.96
C1-H1C	0.96	C2-C3	1.494 (4)
C3-N1	1.286 (4)	C3-C4	1.486 (4)
b- Bond angles			
C5-N2-N1	119.4 (2)	C5-N2-H2	120.3
N1-N2-H2	120.3	C5-C6-C6#1	111.7 (3)
C5-C6-H6A	109.3	C6#1-C6-H6A	109.3
C5-C6-H6B	109.3	C6#1-C6-H6B	109.3
H6A-C6-H6B	107.9	C2-C1-H1A	109.5
C2-C1-H1B	109.5	H1A-C1-H1B	109.5
C2-C1-H1C	109.5	H1A-C1-H1C	109.5
H1B-C1-H1C	109.5	O1-C2-C3	118.8 (3)
O1-C2-C1	121.5 (3)	C3-C2-C1	119.7 (3)
N1-C3-C4	127.0 (3)	N1-C3-C2	113.7 (3)
C4-C3-C2	119.3 (3)	C3-N1-N2	118.8 (2)
O2-C5-N2	120.6 (3)	O2-C5-C6	121.6 (3)
N2-C5-C6	117.9 (3)	C3-C4-H4A	109.5

3.2 General

Novel transition metal complexes were formed on the reaction between MBH and the chloride salts of Co(II), Ni(II), Cu(II) and Cd(II); the acetate salt of Cu(II) or between the chloride salts of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) or Hg(II) or the metal acetate of Ni(II) and Cu(II) and

SBH. The elemental analysis together with the melting point, color and molar conductance values (Table 3) predicted the formation of [Co(SBH-H)₂(H₂O)], [Ni(SBH-H)₂], [Ni(SBH)Cl₂], [Zn(SBH)₂Cl]Cl, [Cd(SBH-H)₂].H₂O, [Cu(SBH-H)Cl], [Cu(SBH-H)(OAc)].2H₂O, [Hg₂(SBH)Cl₂].Cl₂.5H₂O for SBH and [Co(MBH)Cl₂].H₂O, [Ni(MBH-2H)-(H₂O)₂].2H₂O,

[Cu(MBH-2H)(H₂O)₂].2H₂O, [Cu(MBH-H)(OAc)].2H₂O and [Cd(MBH-H)-(OAc)].2H₂O. Most of these complexes are colored and some have high melting points (Table 3). They are insoluble in acetone, ethanol, benzene and chloroform but their considerable solubility has been noticed in DMF and DMSO. The complexes are fairly stable at room temperature (25°C). They are non-hygroscopic and could be stored for a pretty length of period without decomposition. Molar conductivity values of 10⁻³ M solutions of the metal complexes in DMF (Table 3) correspond to their non-electrolytic nature but the values measured for [Zn(SBH)Cl]Cl and [Hg₂(SBH)Cl₃].Cl.5H₂O are corresponding to 1:1 electrolytes [12]. The electrolytic behavior of these complexes is also supported by the formation of a white curdy precipitate by the addition of alcoholic AgNO₃ solution to the complex (DMF solution). The relatively high value recorded for [Co(MBH)Cl₂].H₂O (26.0 Ohm⁻¹ cm² mol⁻¹) may be due to solvolysis by DMF.

3.3 Characterization of MBH and SBH

The IR spectra displayed bands at 3187(m), 1680(vs) and 1612(s) for MBH and at 3186(m), 1686(vs) and 1615(s) for SBH (Fig. 1) assigned to $\nu(\text{NH})$, $\nu(\text{C}=\text{O})$ [ketonic and amidic] and $\nu(\text{C}=\text{N})$, respectively [13]. The two carbonyl groups have only one band which is strong. Their ¹H NMR spectra (Fig. 2) showed signals at [11.142; 10.945] (s, 2H), 2.324-2.351 (s, 2H) and 2.228-2.031 (s, 3H) due to the protons of NH, CH₂ and CH₃. The ¹⁴C NMR (Fig. 3) showed signals for the (C=O)_{ketonic}, (C=O)_{amidic} and C=N at 197, 170-174 and 147-150 ppm, respectively (Table 4).

The mass spectrum of SBH (Fig. 4) showed the molecular ion peak at $m/z = 283.3$ [Calcd. 282.03] confirming the empirical formula of the prepared compound. The second peak with loss of 44.1 corresponding to the removal of CH₃-C=O moiety. The third corresponding to the removal of CH₃-C=N-NH with loss of 56. The next evolved moiety is O=C-CH₂-CH₂-C=O. The final residue is NH-N=C-CH₃.

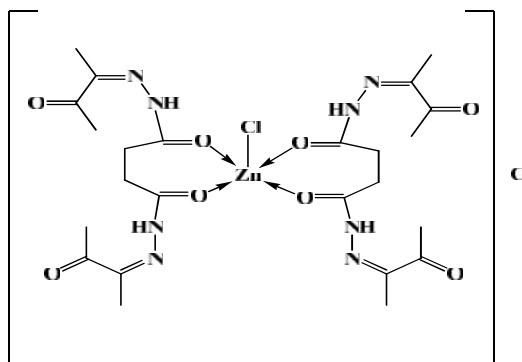
3.4 Characterization of MBH and SBH Complexes

3.4.1 IR spectra

Inspection of the IR spectral data of the complexes and comparing with the ligands,

Table 4, it may be concluded that MBH behaves in three modes while SBH in two only:

In the first mode, both of MBH and SBH act as neutral bidentate ligands in [Co(MBH)Cl₂].H₂O, [Ni(SBH)Cl₂] (Fig. 5) and [Zn(SBH)₂Cl]Cl (Fig. 6) coordinating through the two amidic carbonyl groups based on the following observations: The $\nu(\text{C}=\text{O})$ band observed at 1680 and/or 1688 cm⁻¹ in MBH or SBH, respectively, was shifted to 1636, 1650 or 1678 cm⁻¹, respectively in the complexes indicating that the two amidic carbonyl groups (C=O_{amidic}) participated in bonding while the other two carbonyl (C=O_{ketonic}) still at the same position. The new bands at 418 and 492 cm⁻¹ in the last two complexes are due to $\nu(\text{M}-\text{O})$ vibration [14]. The $\nu(\text{C}=\text{N})$ at 1612 and/or 1615 cm⁻¹ appeared weak. Structure 2 indicates the formula of [Zn(SBH)₂Cl]Cl in which the chlorides lie inside and outside the sphere. The Zn(II) ions prefer a trigonal bipyramid geometry than square-pyramid due to the d¹⁰-system.



Structure 2. [Zn(SBH)₂Cl]Cl

In the second mode, SBH acts as a mononegative bidentate in [Co(SBH-H)₂(H₂O)], [Ni(SBH-H)₂] and [Cd(SBH-H)₂].H₂O coordinating through the two amidic carbonyl (enolic form) from each ligand molecule. The shift of $\nu(\text{C}=\text{O})$ to lower wavenumbers with the appearance of $\nu(\text{C}=\text{N})^*$, $\nu(\text{C}-\text{O})$ [due to enolization of one amidic group] [15] and $\nu(\text{M}-\text{O})$ at [1563 - 1540]; [1160-1140] and [454-420] cm⁻¹ indicate the participation of the carbonyl group in bonding. In the Co²⁺ and Cd²⁺ complexes, the band observed at ≈ 3445 cm⁻¹ is attributed to the coordinated or the hydrated water [16]. The appearance of (C=N) [due to the conversion of NHC=O to N^{*}=C-O] and (C-O) bands confirm the enolization process [Structure 3].

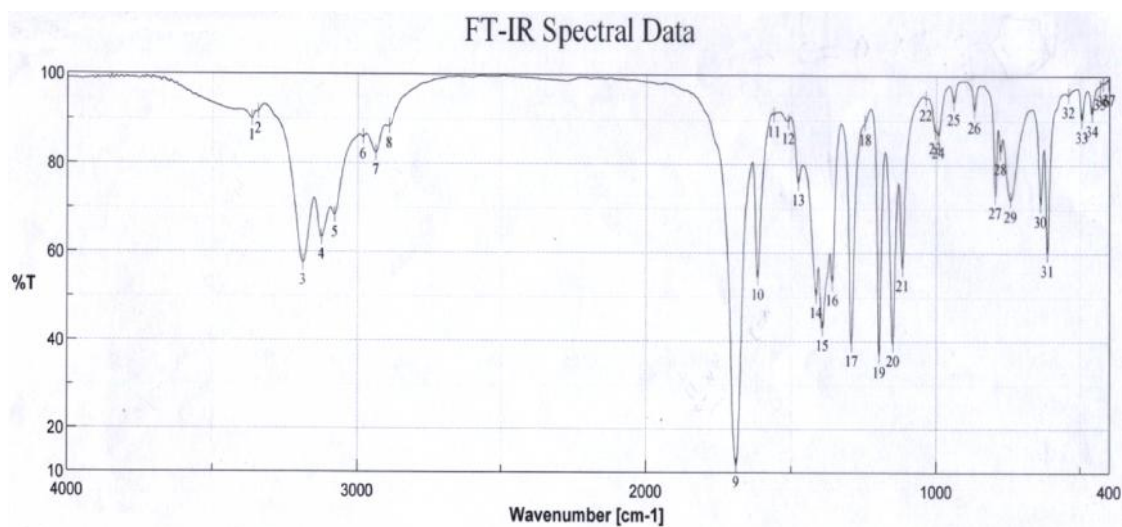
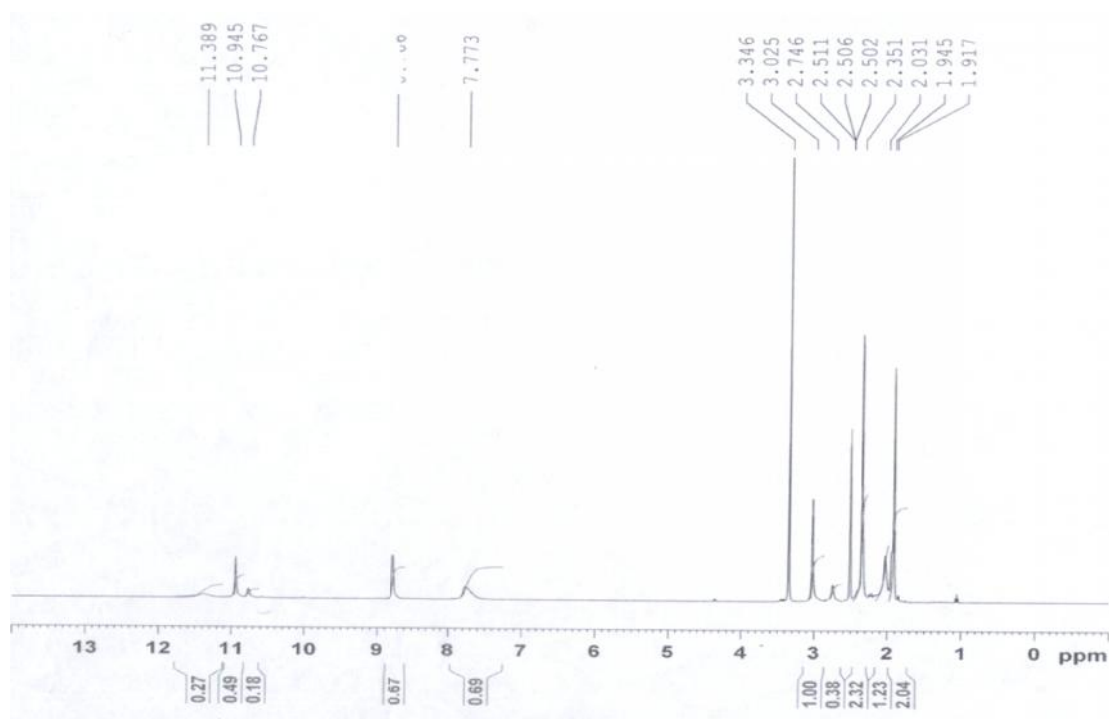


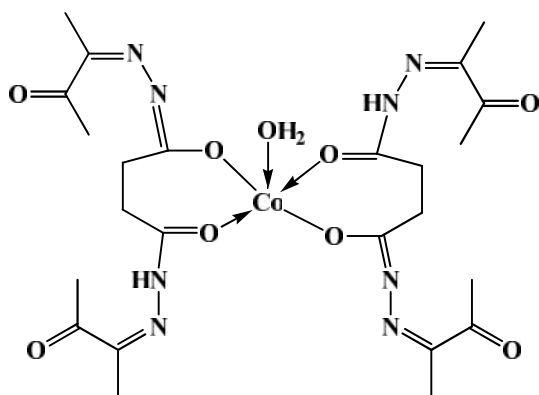
Fig. 1. IR spectrum of SBH as KBr disc

Fig. 2. ^1H NMR spectrum of SBH in $\text{d}_6\text{-DMSO}$

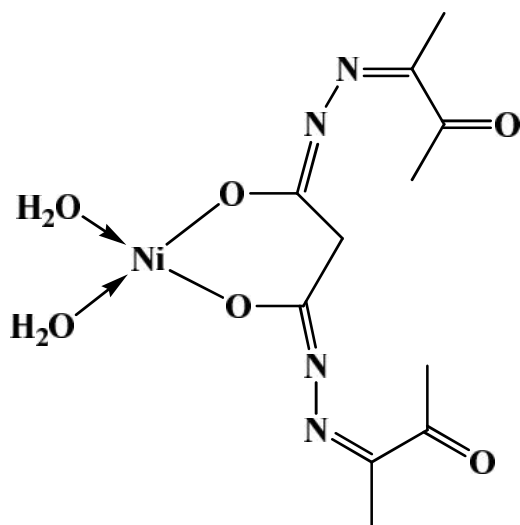
Extension to this mode of chelation, the ligands in the 1:1 complexes; $[\text{Cu}(\text{MBH-H})(\text{OAc})]\cdot 2\text{H}_2\text{O}$, $[\text{Cu}(\text{SBH-H})(\text{OAc})]\cdot \text{H}_2\text{O}$ and $[\text{Cu}(\text{MBH-H})\text{Cl}]\cdot \text{H}_2\text{O}$ have the same coordination sites. In addition, the first two complexes showed new bands at 1616 and 1545 cm^{-1} attributed to $\nu_{\text{as}}(\text{OAc})$ and $\nu_{\text{s}}(\text{OAc})$, respectively; the difference is 71 cm^{-1} indicating a bidentate nature of the acetate ion.

The third mode of coordination is depicted in $[\text{Ni}(\text{MBH-2H})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$, $[\text{Cu}(\text{MBH-2H})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ and $[\text{Cd}(\text{MBH-2H})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ in which the ligand, MBH, acts as a bidentate. The disappearance of $\nu(\text{C}=\text{O})_{\text{amidic}}$ together with the appearance of $\nu(\text{M}-\text{O})$ band at $\sim 465 \text{ cm}^{-1}$. Finally, the band at 3389, 3429 or 3432 cm^{-1} in the Ni(II),

Cu(II) or Cd(II) complex is due to the hydrated water.



Structure 3. Structure of $[\text{Co}(\text{SBH-H})_2(\text{H}_2\text{O})]$



Structure 4. Structure of $[\text{Ni}(\text{MBH-2H})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$

3.5 Magnetic Moments and Electronic Spectra

The electronic spectral bands of the complexes as well as the magnetic moment values are presented in Table 5. The DMSO solutions of the complexes have the same color as in the solid complexes.

The spectra of the ligands exhibit three absorption bands at 34100, 30670 and 24040 cm^{-1} for MBH, in Nujol, and 39840, 39525 and 36450 cm^{-1} for SBH (Fig. 7), in DMSO, due to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of $\text{C}=\text{N}$, $\text{C}=\text{O}_{\text{ketonic}}$ and

$\text{C}=\text{O}_{\text{amidic}}$ groups [17]. The broadness of the last band may be due to the existence of these groups in opposite sides.

$[\text{Co}(\text{SBH-H})_2(\text{H}_2\text{O})]$ (brown color) has 2.04 BM magnetic moment. The value lies within the range (2.2-2.8 BM) stated for one unpaired electron of square-planar or square-pyramidal $\text{Co}(\text{II})$ complexes [18] having dsp^2 or dsp^3 hybridization. Its electronic spectrum displayed one band at 15015 cm^{-1} with molar extinction coefficient of 275 $\text{mol}^{-1} \text{L}$ which is resembled to the spectra of the five-coordinate $\text{Co}(\text{II})$ complexes [19]. So, a square-pyramidal is the suggested geometry. On the other hand, the magnetic moment of $[\text{Co}(\text{MBH})\text{Cl}_2] \cdot \text{H}_2\text{O}$ is 3.10 BM below the range reported for tetrahedral structures (4.4 - 4.8 BM) and higher than the square-planar geometry (2.2 - 2.8 BM). The value may be due to the presence of the complex in two different structures (tetrahedral + square-planar). The electronic spectrum in Nujol, showed bands at 20575, 19160, 17730, 16130 and 14840 cm^{-1} due to the presence of the two structures in the same unit cell.

The magnetic moment value of $[\text{Ni}(\text{MBH-2H})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ is 1.61 BM which is less than the normal values reported for tetrahedral or octahedral coordination containing two unpaired electrons. Its electronic spectrum showed bands at 19760 cm^{-1} typical of a square-planar structure with some distortion [20] may be of tetrahedral which supported by the presence of bands at 18250 and 16340 cm^{-1} ; the anomalous magnetic value is consistent with mixed stereochemistry (square-planar + tetrahedral) around the nickel ion [21]. Also, the spectrum of $[\text{Ni}(\text{SBH-H})_2]$ showed three bands in the visible region at 20240, 17790 and 16180 cm^{-1} attributed to mixed stereochemistry ((square-planar + tetrahedral) around the central nickel ion.

The electronic spectrum of $[\text{Cu}(\text{SBH-H})(\text{OAc})] \cdot \text{H}_2\text{O}$, in DMSO, exhibits one band with maximum at 14490 cm^{-1} while the spectrum of $[\text{Cu}(\text{MBH})] \cdot 4\text{H}_2\text{O}$, in Nujol, showed three bands at 19230, 17790 and 16340 cm^{-1} . The first band is assigned to the ${}^2E_{2g} \rightarrow {}^2T_{2g}$ transition in an octahedral geometry [22]. The band is broad due to the Jahn-Teller effect. The magnetic moment values (0.90 and 1.12 BM) for $[\text{Cu}(\text{SBH-H})(\text{OAc})] \cdot \text{H}_2\text{O}$ and $[\text{Cu}(\text{MBH})] \cdot 4\text{H}_2\text{O}$ are found lower than the values informed for the d^9 -system containing one unpaired electron (1.73 - 2.25 BM) suggesting interactions between the copper centers.

Table 3. Formula, molecular weight, color, melting point and elemental analysis of SBH, BBH and their complexes

Compound, empirical formula	Yield %	M.W. Calcd (found)	Color	M.P., °C	^a Λ Ohm ⁻¹ cm ² mol ⁻¹	C Calcd (found)	H Calcd (found)	N Calcd (found)
SBH C ₁₂ H ₁₈ N ₄ O ₄	85	282.03 (283.30)	Yellowish white	244-46		51.10 (50.96)	6.43 (6.51)	19.86 (19.78)
[Co(SBH-H) ₂ (H ₂ O)] C ₂₄ H ₃₆ N ₈ O ₉ Co	79	641.57	Brown	272-74		44.93 (45.19)	5.34 (5.39)	17.47 (18.05)
[Ni(SBH-H) ₂] C ₂₄ H ₃₄ N ₈ O ₈ Ni	82	623.41	Brown	>300	13.24	46.43 (46.65)	5.52 (5.32)	18.05 (17.66)
[Ni(SBH)Cl ₂] C ₁₂ H ₁₈ N ₄ O ₄ Cl ₂ Ni	79	411.68		>300		35.01 (34.89)	3.91 (4.18)	13.61 (13.30)
[Zn(SBH) ₂ Cl]Cl C ₂₄ H ₃₆ N ₈ O ₈ ZnCl ₂	70	698.31	Yellow	>300	58.3	41.29 (41.15)	5.19 (5.09)	16.05 (16.32)
[Cd(SBH-H) ₂].H ₂ O C ₂₄ H ₃₆ N ₈ O ₉ Cd	72	693.03	Yellowish white	>300		41.59 (41.66)	5.23 (4.97)	16.17 (15.95)
[Cu(SBH-H)Cl] C ₁₂ H ₁₇ N ₄ O ₄ ClCu	80	380.02	Brown	>300		37.92 (37.68)	4.51 (4.31)	14.74 (14.84)
[Cu(SBH-H)(OAc)].2H ₂ O C ₁₄ H ₂₂ N ₄ O ₇ Cu	86	421.62	Brown	>300	8.76	39.88 (39.56)	5.25 (4.89)	13.29 (13.04)
[Hg ₂ (SBH)Cl ₃].5H ₂ O	88	915.138	Yellow	>300	55.5	15.75 (15.41)	3.08 (3.38)	6.12 (5.97)
MBH C ₁₁ H ₁₆ N ₄ O ₄	90	268.281	Yellowish white		0.47	49.24 (49.17)	6.01 (6.12)	20.88 (21.37)
[Co(MBH)Cl ₂].H ₂ O C ₁₁ H ₁₈ N ₄ O ₅ CoCl ₂	83	416.151	Reddish brown	>300	26.27	31.75 (31.48)	4.36 (4.82)	13.46 (13.13)
[Ni(MBH-2H)(H ₂ O) ₂].2H ₂ O C ₁₁ H ₂₂ N ₄ O ₈ Ni	80	397.069	Yellowish brown	>300	9.20	33.27 (32.89)	5.58 (5.69)	14.11 (14.36)
[Cu(MBH-2H)(H ₂ O) ₂].2H ₂ O C ₁₁ H ₂₂ N ₄ O ₈ Cu	87	401.869	Brown	>300	15.40	32.88 (32.63)	5.52 (5.74)	13.94 (14.85)
[Cu(MBH-H)(OAc)].2H ₂ O	80	425.898	Brown	>300		36.66 (36.20)	5.20 (4.93)	13.15 (13.46)
[Cd(MBH-2H)(H ₂ O) ₂].2H ₂ O	84	450.739	Brown	>300		29.31 (28.96)	4.92 (4.74)	12.43 (12.94)

^aΛ is the molar conductivity in DMF

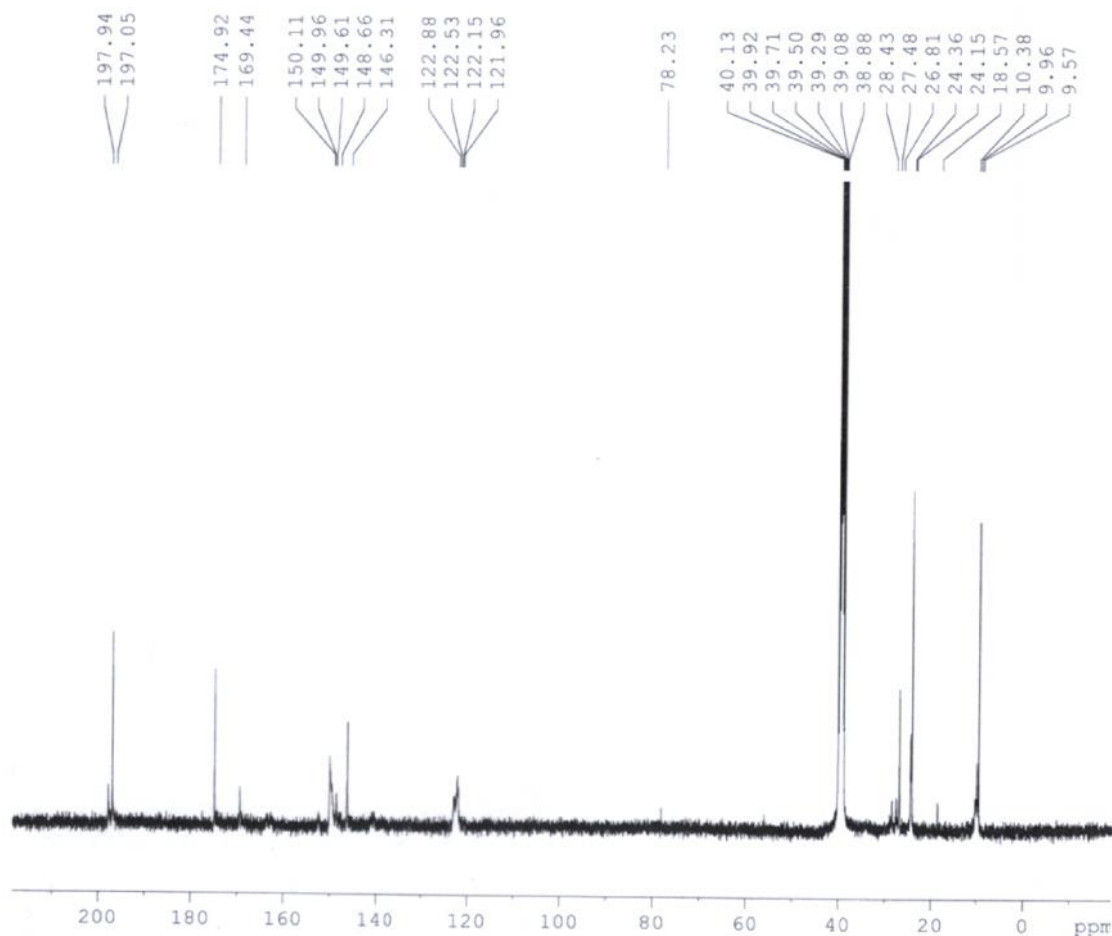
Table 4. IR spectral data of SBH, BBH and their metal complexes

Compound	$\nu(\text{NH})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{C=N}^{**})$	$\nu(\text{C-O})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	Additional bands
SBH	3186 (m)	1688 (vs)	1615 (s)	-	-	-	-	2937; 2890
[Co(SBH-H) ₂ (H ₂ O)]	3444 (br)* 3189 (w)	1682 (s)	1615 (w)	1522 (w)	-	420 (w)	-	
[Ni(SBH-H) ₂]	3415 (br)*	1644 (w)	1596 (w)	1563 (w)	-	5454 (w) 417 (w)	-	2922
[Ni(SBH)Cl ₂]	3380 (br)* 3185 (br)	1650 (m)	1616 (vw)	1539 (w)	-	418 (w)	-	2923
[Zn(SBH) ₂ Cl]Cl	3444 (br)* 3193 (m)	1678 (s)	1617 (vw)	-	-	492 (w)	-	
[Cd(SBH-H) ₂].H ₂ O	3444 (br)*	1683 (s)	1614 (m)	1572 (w)	1233 (w)	496 (w)	-	
[Cu(SBH-H)Cl]	3188 (m)	-	1608 (sh)	1574 (w)	1210 (w)	420 (w)	-	2922
[Cu(SBH-H)(OAc)].H ₂ O	3420 (br)*	-	1608 (sh)	1574 (w)	1210 (w)	420 (w)	-	2922
MBH	3187 (m)	1680 (vs)	1612 (s)	-	-	-	-	2937; 2890
[Co(MBH)Cl ₂].H ₂ O	3427 (br)* 3189 (w)	1636 (s)	1540 (w)	-	-	-	-	
[Ni(MBH-2H)(H ₂ O) ₂].2H ₂ O	3389 (br)*	-	1553 (w)	-	-	-	-	
[Cu(MBH)(H ₂ O) ₂].2H ₂ O	3429 (br)*	1619 (m)	1539 (vw)	-	-	-	-	
[Cu(MBH-H)(OAc)].2H ₂ O	3421 (br)* 3193 (m)	-	1564 (vw) 1551 (w)	-	-	492 (w)	-	
[Cd(MBH-2H)(H ₂ O) ₂].2H ₂ O	3432 (br)	-	1562 1544	-	-	-	-	

*hydrated or coordinated water; ** New C=N

Table 5. ^1H and ^{13}C NMR signals (ppm) of SBH and BBH

Compound	NH	CH ₂	CH ₃	^{13}C signals
SBH	10.945(s, 1H)	2.351 (s, 2H)	2.031 (s, 3H) 1.917 (s, 3H)	197.0 (C=O) _{ketonic} ; 174.92 (C=O) _{amidic} ; 150.11 (C=N) 122.88; 40.13; 28.43; 10.38
MBH	11.142(s, 2H)	2.324 (s, 2H)	2.228 (s, 6H)	197.38 (C=O) _{ketonic} ; 170.78 (C=O) _{amidic} ; 147.19 (C=N) 40.13; 24.54; 10.21

**Fig. 3.** ^{13}C NMR spectrum of SBH in d₆-DMSO KBr disc

The band at 28650 in $[\text{Cu}(\text{SBH-H})(\text{OAc})]\cdot\text{H}_2\text{O}$ and at 29760 cm^{-1} in $[\text{Co}(\text{SBH-H})_2]\cdot\text{H}_2\text{O}$ may be due to $\text{O} \rightarrow \text{MCT}$ [23,24].

3.6 Thermal Analysis

The decomposition steps, the DTG maximum temperature and the removing species are shown in Table 6.

The thermogram of $[\text{Ni}(\text{MBH-2H})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ showed three decomposition steps at mid-points of 75, 269 and 366°C consistent with the removal of the outside water (Found 11.07%; Calcd. 9.07%); $(2\text{H}_2\text{O} + \text{C}_4\text{H}_6\text{O}_2)$ (Found 26.66%; Calcd. 30.75%) and H_2N_4 (Found 28.34%; Calcd. 28.90%) leaving $[\text{C}_3\text{H}_2\text{O}_2\text{Ni}]$ moiety (Found 33.89%; Calcd. 32.43%).

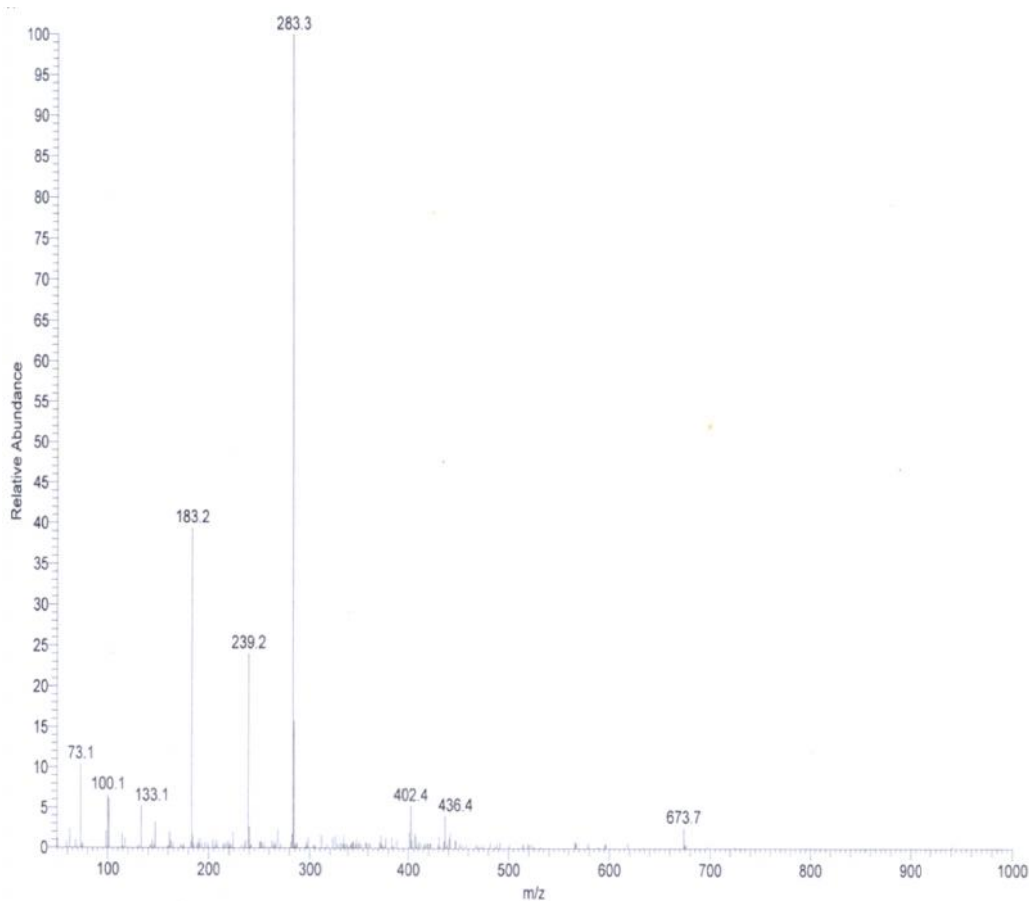


Fig. 4. Mass spectrum of SBH

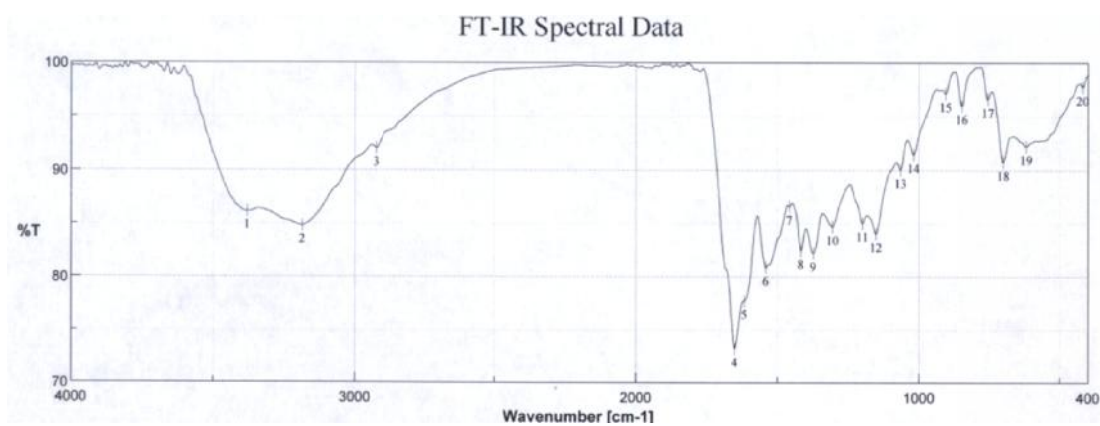


Fig. 5. IR spectrum of [Ni(SBH)Cl₂]

The TG curve of [Cu(SBH-H)(OAc)].2H₂O displayed three steps; the first (mid-point 67°C) represents the removal of the outside water molecules (Found 9.16%; Calcd 8.16%); the second (mid-point 252°C) represents the loss of acetate + C₄H₆O₂ (Found 35.02%; Calcd

33.01%) and the third for the repulsion of C₄H₆ (Found 14.68 (Calcd. 12.78%). The residue is C₄H₆N₄O₂Cu (Found 41.15; Calcd 46.78%).

[Zn(SBH)₂Cl]Cl thermogram revealed decomposition steps ending with C₈H₈O₄Zn at

Temp. > 800°C. The decomposition exhibited the removal of $\frac{1}{2}\text{Cl}_2$ in the first step at mid-point of 61°C. The other two steps were observed at 254 and 350-800°C corresponding to the exclusion of $\frac{1}{2}\text{Cl}_2 + 2\text{C}_4\text{H}_6\text{O}_2$ and $2\text{C}_4\text{H}_6\text{N}_4$, respectively (Table 7).

The TG curve of $[\text{Co}(\text{MBH})\text{Cl}_2]\cdot\text{H}_2\text{O}$ indicated four steps. The first at 80°C is due to the removal of the outside water and $\frac{1}{2}\text{Cl}_2$ (Found 10.64%; Calcd. 12.84%). The second step (289°C) represents the loss of $\frac{1}{2}\text{Cl}_2 + \text{C}_4\text{H}_{12}$ (Found 22.58%; Calcd 22.97%). The third step represents the repulsion of $2\text{C}_2\text{NO}$ (Found 26.73%; Calcd. 25.97%). The fourth step (Found 40.05%; Calcd. 38.21%)

corresponding to the residue which is $\text{C}_3\text{H}_4\text{N}_2\text{O}_2\text{Co}$.

The thermogram of $[\text{Cu}(\text{MBH}-2\text{H})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ has $\text{N}_2\text{O}_2\text{Cu}$ as remaining residue above 800°C with 34.77% (Calcd. 30.74%). The first four steps observed at mid. points of 67, 196, 295 and 400-800°C are corresponding to the elimination of $2\text{H}_2\text{O}$; $(2\text{H}_2\text{O} + \text{C}_4\text{H}_{12})$, C_4H_6 and $\text{C}_3\text{H}_4\text{N}_2$, respectively.

The thermogram of $[\text{Cu}(\text{MBH}-\text{H})(\text{OAc})]\cdot 2\text{H}_2\text{O}$ showed four main steps at 75, 249, 400 - 800 and >800°C due to the liberation of the outside water molecules, $(\text{OAc} + \text{C}_4\text{H}_6\text{O}_2)$, C_4H_6 and high residue ($\text{C}_3\text{H}_4\text{N}_4\text{O}_2\text{Cu}$) % was found over 800°C.

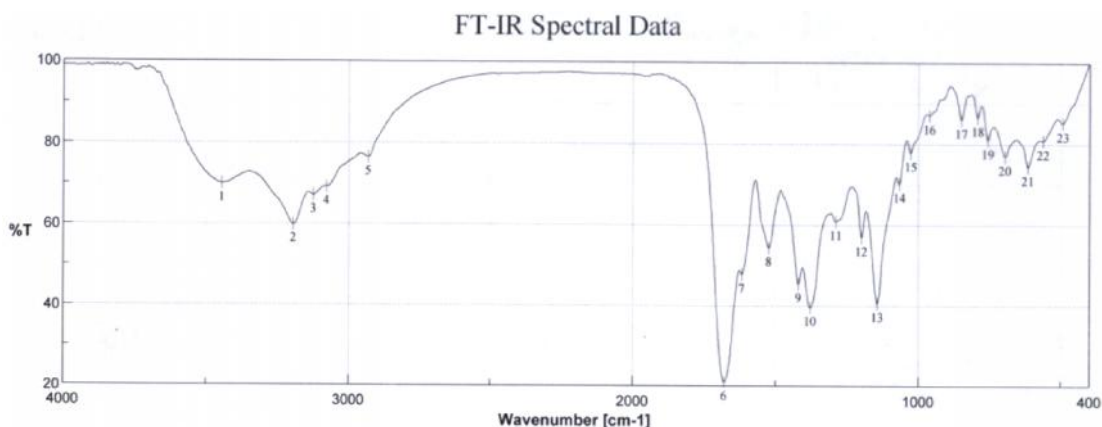


Fig. 6. IR spectrum of $[\text{Zn}(\text{SBH})_2\text{Cl}]\text{Cl}$

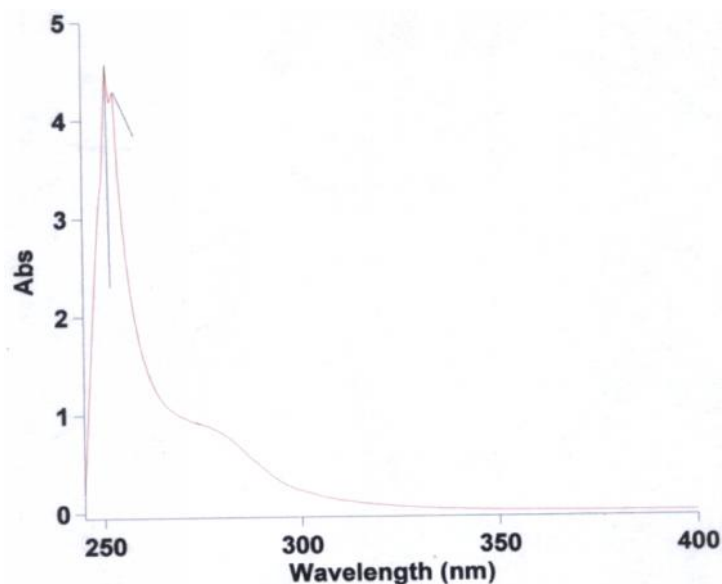


Fig. 7. Absorption spectrum of SBH in DMSO

3.7 Biological Activity

The antimicrobial activities of MBH, SBH and their complexes are given in Table 8. The data in

the table showed that $[\text{Cu}(\text{MBH})(\text{H}_2\text{O})_2].2\text{H}_2\text{O}$ has no activity against all the tested microorganisms (bacteria or fungi). The activity of $[\text{Hg}_2(\text{SBH})\text{Cl}_3]\text{Cl}.5\text{H}_2\text{O}$ (18 mm) is the highest

Table 6. Magnetic moments and electronic spectral bands of the compounds

Compound	μ_{eff} (BM)	Intraligand and charge transfer (cm^{-1})	d-d transition (cm^{-1})	Proposed structure
SBH	-	39840; 39525; 36495		
$[\text{Co}(\text{SBH-H})_2(\text{H}_2\text{O})]$	2.04	40485; 36230; 29760	15015 (275)	Square-pyramid
$[\text{Ni}(\text{SBH-H})_2]$	2.86	35715; 30670; 28900; 22520; 21275	20240; 17790; 16180	Tetrahedral + square-planar
$[\text{Ni}(\text{SBH})\text{Cl}_2]$		34600		
$[\text{Cd}(\text{SBH-H})_2].\text{H}_2\text{O}$		40000; 36495		
$[\text{Cu}(\text{SBH-H})\text{Cl}]$		36230		
$[\text{Cu}(\text{SBH-H})(\text{OAc})].\text{H}_2\text{O}$	0.9	40485; 38460; 28650	14490	Square-planar
MBH		34100; 30670; 24040		
$[\text{Co}(\text{MBH})\text{Cl}_2].\text{H}_2\text{O}$	3.10	29585; 26740; 22730;	20575; 19160; 17730; 16130; 14840	Tetrahedral + square-planar
$[\text{Ni}(\text{MBH-2H})(\text{H}_2\text{O})_2].2\text{H}_2\text{O}$	1.61	34010; 28910; 25250; 22310	19760; 18250; 16340	Tetrahedral + square-planar
$[\text{Cu}(\text{MBH})(\text{H}_2\text{O})_2].2\text{H}_2\text{O}$	1.12	35710; 29585; 26040; 23695	19230; 17790; 16340	Octahedral

Table 7. Decomposition steps of the ligand and its complexes based on the TGA data

Complex	Middle temp. °C	Removed species	Weight loss % Calcd (found)
$[\text{Cu}(\text{SBH-H})(\text{OAc})].2\text{H}_2\text{O}$ $\text{C}_{14}\text{H}_{24}\text{N}_4\text{O}_8\text{Cu}$	67	- $2\text{H}_2\text{O}$	8.16 (9.16)
	252	- $\text{OAc} + \text{C}_4\text{H}_6\text{O}_2$	33.01 (35.02)
	400-800	- C_4H_6	12.30 (14.68)
	>800	$\text{C}_4\text{H}_6\text{N}_4\text{O}_2\text{Cu}$	46.78 (41.15),
$[\text{Zn}(\text{SBH})_2\text{Cl}]\text{Cl}$ $\text{C}_{24}\text{H}_{36}\text{N}_8\text{O}_8\text{ZnCl}_2$	61	- $\frac{1}{2}\text{Cl}_2$	5.07 (4.88)
	254	- $\frac{1}{2}\text{Cl}_2 + 2\text{C}_4\text{H}_6\text{O}_2$	29.73 (27.78)
	350-800	- $2\text{C}_4\text{H}_6\text{N}_4$	32.12 (36.33)
	>800	$\text{C}_8\text{H}_8\text{O}_4\text{Zn}$	33.44 (31.01)
$[\text{Ni}(\text{MBH-2H})(\text{H}_2\text{O})_2].2\text{H}_2\text{O}$	75	- $2\text{H}_2\text{O}$	9.07 (11.07)
	270	- $2\text{H}_2\text{O} + \text{C}_4\text{H}_6\text{O}_2$	30.75 (26.96)
	366	- H_2N_4	14.61 (18.18)
		$\text{C}_2\text{O}_2\text{Ni}$	28.90 (28.34)
$[\text{Co}(\text{MBH})\text{Cl}_2].\text{H}_2\text{O}$ $\text{C}_{11}\text{H}_{18}\text{N}_4\text{O}_5\text{CoCl}_2$	80	- $\text{H}_2\text{O} + \frac{1}{2}\text{Cl}_2$	12.84 (10.64)
	289	$\frac{1}{2}\text{Cl}_2 + \text{C}_4\text{H}_{12}$	22.97 (22.58)
	350-800	$2\text{C}_2\text{NO}$	25.97 (26.73)
	>800	$\text{C}_3\text{H}_4\text{N}_2\text{O}_2\text{Co}$	38.21 (40.05)
$[\text{Cu}(\text{MBH-2H})(\text{H}_2\text{O})_2].2\text{H}_2\text{O}$ $\text{C}_{11}\text{H}_{22}\text{N}_4\text{O}_8\text{Cu}$	67	- $2\text{H}_2\text{O}$	8.97 (8.79)
	196	- $2\text{H}_2\text{O} + \text{C}_4\text{H}_{12}$	23.93 (24.76)
	295	- C_4H_6	13.46 (12.65)
	400-800	$\text{C}_3\text{H}_4\text{N}_2$	16.94 (18.35)
	>800	$\text{N}_2\text{O}_2\text{Cu}$	30.74 (34.77)
$[\text{Cu}(\text{MBH-H})(\text{OAc})].2\text{H}_2\text{O}$	75	- $2\text{H}_2\text{O}$	8.45 (10.42)
	249	- $\text{OAc} + \text{C}_4\text{H}_6\text{O}_2$	34.08 (33.37)
	400-800	- C_4H_6	12.70 (11.31)
	>800	$\text{C}_3\text{H}_4\text{N}_4\text{O}_2\text{Cu}$	44.99 (45.10)

Table 8. Effect of SBH, MBH and their complexes on some bacteria and fungi

Compound	<i>Bacillus</i> (bacteria)	<i>E. coli</i> (gram negative bacteria)	<i>Aspergillus</i> (fungus)	<i>Penicillium</i> (fungus)	<i>Fusarium</i> (fungus)
DMF	Nil	Nil	Nil	Nil	Nil
[Ni(SBH-H) ₂]	5.0	10.0	Nil	5.0	Nil
[Zn(SBH) ₂ Cl]Cl	3.0	8.0	Nil	Nil	Nil
[Cu(SBH-H)(OAc)].H ₂ O	Nil	Nil	30	Nil	Nil
[Hg ₂ (SBH)Cl ₂] Cl ₂ .5H ₂ O	1.0	15.0	9.0	18.0	13.0
DMSO	Nil	Nil	Nil	Nil	Nil
MBH	Nil	Nil	Nil	9.0	Nil
[Co(MBH)Cl ₂].H ₂ O	Nil	Nil	Nil	6.0	Nil
[Ni(MBH-2H)(H ₂ O) ₂].2H ₂ O	Nil	5.0	Nil	Nil	Nil
[Cu(MBH)(H ₂ O) ₂].2H ₂ O	Nil	Nil	Nil	Nil	Nil

Reading in diameter (mm) after specific time

and more with *Penicillium* followed by *Fusarium* (15 mm) and *Aspergillus* (13 mm) as fungi. Its activity against *E. coli* (9.0 mm) as bacterium is higher than *Bacillus* (1.0 mm). The higher activity for fungi may be due the presence of ionizable chloride ions and to the less planarity of the complex making it more polar and more lipophilic. [Zn(SBH)₂Cl]Cl has a high activity against *E. coli* and followed by *Bacillus*. It has no activity against fungi.

The activity of this complex may be due to presence of ionizable chloride ions which is easily exchangeable with the microorganism cells as well as the effect of Zn(II) ions. [Ni(SBH-H)₂] has activity against bacteria and no against fungi. [Ni(MBH-2H)(H₂O)₂].2H₂O has activity (5 mm) only against *E. coli*. MBH and [Co(MBH)Cl₂].H₂O affected the *Penicillium* only with activity of 9.0 and 6.0 mm, respectively. The results are compared with complexes of different hydrazones [25].

4. CONCLUSION

Single crystal of SBH was found monoclinic with space group of P121/c14. Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Hg²⁺ complexes with MBH and/or SBH have: [Co(MBH)Cl₂].H₂O, [Ni(MBH-2H)(H₂O)₂].2H₂O, [Cu(MBH-2H)(H₂O)₂].2H₂O, [Cu(MBH-H)(OAc)].2H₂O, [Co(SBH-H)(H₂O)], [Ni(SBH-H)₂], [Ni(SBH)Cl₂], [Cu(SBH-H)Cl], [Cu(SBH-H)(OAc)].2H₂O, [Zn(SBH)₂Cl]Cl, [Cd(SBH-H)₂].H₂O and [Hg₂(SBH)₂Cl₂]Cl₂. The ligands act as neutral, mononegative and/or

binegative bidentate. A tetrahedral, square-planar and octahedral were proposed for the complexes. The remaining part is metal or metal oxide. Variable activities were found against some bacteria and fungi. [Hg₂(SBH)Cl₂] Cl₂.5H₂O has the highest activity.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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