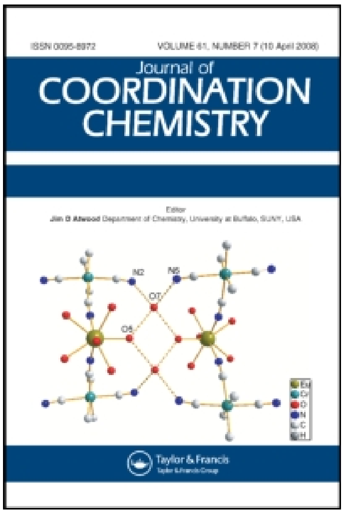

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Spectroscopic studies and biological evaluation of some transition metal complexes of Schiff-base ligands derived from 5-arylazo-salicylaldehyde and thiosemicarbazide

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Synthesis and spectroscopic characterization of Schiff-base complexes of Cu(II), Ni(II), and Mn(II) resulting from condensation of salicylaldehyde derivatives with thiosemicarbazide [PHBT = 1-(5-(2-phenyldiazenyl)-2-hydroxybenzylidene)thiosemicarbazide, CHBT = 1-(5-(2-(2-chlorophenyl)diazenyl)-2-hydroxybenzylidene)thiosemicarbazide, and MHBT = 1-(5-(2-p-tolyldiazenyl)-2-hydroxybenzylidene)thiosemicarbazide] are discussed. The solid complexes were confirmed by elemental analysis (CHN), molar conductance, and mass spectra. Important infrared (IR) spectral bands corresponding to the active groups in the three ligands, ^{1}H-NMR and UV-Vis spectra and thermogravimetric analysis were performed. The dehydration and decomposition of [Cu(PHBT)(H_2O)], [Ni(PHBT)(H_2O)] · 2H_2O, [Mn(PHBT)(H_2O)] · H_2O, [Cu(CHBT)(H_2O)], [Ni(CHBT)(H_2O)] · H_2O, [Mn(CHBT)(H_2O)] · H_2O, [Cu(MHBT)(H_2O)], [Ni(MHBT)(H_2O)] · 2H_2O, and [Mn(MHBT)(H_2O)] · 2H_2O complexes were studied. The ligands are tridentate forming chelates with 1 : 1 (metal : ligand) stoichiometry. The molar conductance measurements of the complexes in DMSO indicate non-electrolytes. The biological activities of the metal complexes have been studied against different gram positive and gram negative bacteria.

Keywords: Spectroscopic; Coordination; Thermal analysis

1. Introduction

Schiff-base ligands are easily prepared by condensation between aldehydes and imines. Stereogenic centers can be introduced in the synthetic design. Schiff-base ligands coordinate with many different metal ions [1–3] and stabilize various oxidation states. Schiff-base complexes have been used in catalytic reactions [4] and as models for biological systems [5, 6]. Schiff-base complexes containing Cu(II), Ni(II), Co(II), and Pd(II) have been studied for crystallographic features [7], enzymatic reactions [8],

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structure-redox relationships [9], mesogenic characteristics [10, 11], catalysis, magnetic properties [12, 13], and their roles in coordination chemistry of transition metal ions [14].

Schiff bases have numerous applications, e.g., anticancer [15], antibacterial [16, 17], antiviral [18, 19], antifungal [20, 21], and other biological properties [22]. Macrocyclic moieties have versatility as ligands [23] due to the presence of several potential donors, their flexibility, and ability to coordinate in either neutral or deprotonated form [24]. Those containing N=C–C=N form a strong chelate ring giving delocalization associated with extended conjugation. They can yield mono or polynuclear complexes [25, 26]. Thiosemicarbazide-based compounds have structural diversity due to the condensation of different carbonyls and alkylation of different parts of the thiosemicarbazide moiety.

While alkylation of nitrogen preserves its coordination through the sulfur and nitrogen [27, 28], alkylation of the sulfur changes to NN coordination, characteristic for isothiosemicarbazides [29, 30]. Although this combination of donors provides a different ligand field, the geometries of the analogous thiosemicarbazide and isothiosemicarbazide complexes are often similar [31, 32]. Transition metal complexes of bis(thiosemicarbazone) [33] attract attention for antitumor activity of thiosemicarbazone [34]. In particular, bis(thiosemicarbazone) complexes of copper(II) are antitumor agents [35, 36], showing a broad spectrum of biological activity [37–42]. Copper plays a crucial role in enzymes that catalyze oxidation/reduction reactions related to antioxidant systems [43] and is found in many metalloproteins [44–47].

Azo compounds have applications in dyes, pigments, and functional materials. For example, azo-containing photochromic organic compounds especially with liquid crystalline character and azo-conjugated metal complexes have possible applications in the area of photon-mode high-density information storage, photo-switching devices, and optical computing [48, 49]. Development of these materials requires discovery of compounds that exhibit two distinct chemical or physical forms that are interconverted and detected by light without their destruction [50, 51].

Because of the importance of azo-containing compounds [52–54] and our interest in syntheses of azo-based compounds [55], we report herein the syntheses, spectroscopic studies, thermal investigation, and biological activities of Schiff-base derivatives PHBT = 1-(5-(2-phenyldiazenyl)-2-hydroxybenzylidene)thiosemicarbazide, CHBT = 1-(5-(2-(2-chlorophenyl)diazenyl)-2-hydroxybenzylidene)thiosemicarbazide, and MHBT = 1-(5-(2-p-tolyldiazenyl)-2-hydroxybenzylidene)thiosemicarbazide and their Cu(II), Ni(II), and Mn(II) complexes.

2. Experimental

o-Chloroaniline, *p*-toluidine, salicylaldehyde, aniline, thiosemicarbazide, metal salts: $Cu(H_3CCOO)_2 \cdot 3H_2O$, $NiSO_4 \cdot 7H_2O$, $MnSO_4 \cdot 4H_2O$, and other chemicals were purchased from Fluka, Aldrich, and Merck Companies and used as received.

2.1. *Syntheses of the azo compounds*

Aniline (4.65 mL, 50 mmol), *o*-chloroaniline (6.40 mL, 50 mmol), or *p*-toluidine (5.35 g, 50 mmol) was mixed with hydrochloric acid (37%, 6.0 mL, 40 mmol) in distilled water (30 mL) and diazotized below 5°C with sodium nitrite (40.0 mmol, 2.8 g) in distilled water (30 mL). The diazotized aniline, *o*-chloroaniline, or *p*-toluidine compounds were coupled with salicylaldehyde in alkaline media below 5°C. The pH during the coupling was kept fixed between 7 and 9. Coupling to the salicylaldehyde occurred at the para position to the hydroxyl group [56]. All diazo compounds were recrystallized several times from ethyl alcohol (95%) with addition of hydrochloric acid to pH 3. All organic impurities were then extracted by washing with a small portion of diethyl ether. The precipitated compounds were dried under vacuum at 70°C and purity evaluated by thin layer chromatography.

2.2. *Synthesis of the Schiff-base ligand*

The Schiff bases were synthesized accordingly by condensation [57]. Methanol solution (50 mL) of thiosemicarbazide (4.55 g, 50 mmol) was mixed with a solution of 5-phenyl azo-salicylaldehyde (11.3 g, 50 mmol; PHBT), (13.02 g, 50 mmol; CHBT), or (12.0 g, 50 mmol; MHBT) in water (100 mL). The mixture was refluxed and stirred magnetically for 3 h at 70°C on a hot plate. After cooling, the solution was filtered and the solid was washed several times with methanol. All organic impurities were then extracted by washing with small portions of diethyl ether. The ligands were dried *in vacuo* over calcium chloride and were recrystallized several times from ethyl alcohol. The purity of the ligands was evaluated by thin layer chromatography. Elemental analysis CHN, IR, UV-Vis, mass, and ^{1}H NMR spectra confirm the composition of the ligands. The formulas of the azo-linked Schiff bases are given in figure 1.

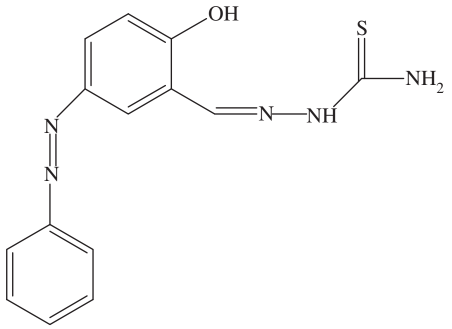
2.3. *Synthesis of metal complexes*

The PHBT, CHBT, and MHBT complexes were synthesized by adding appropriate metal salt, $Cu(H_3CCOO)_2 \cdot 3H_2O$, $NiSO_4 \cdot 7H_2O$, or $MnSO_4 \cdot 4H_2O$ [1.0 mmol, in 20 mL ethyl alcohol : water (1 : 1 v/v)] to a hot solution of the Schiff base [1.0 mmol, in 30 mL ethyl alcohol (95%)]. The mixtures were stirred and heated on a hot plate at 80°C for 30 min. The volume of the obtained solution was reduced to one half by evaporation. One day later, the colored complexes formed were filtered off, washed with ethanol and diethyl ether and finally dried under vacuum. All the isolated solid complexes are powders.

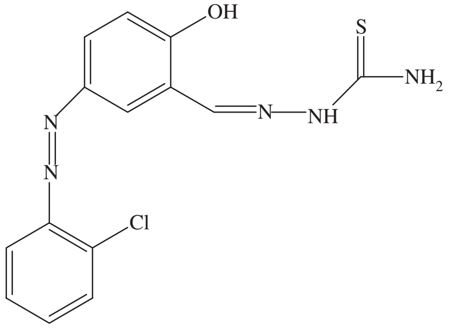
2.4. *Analysis*

Elemental analyses (C, H, and N) were performed using a Perkin–Elmer CHN 2400 elemental analyzer. The content of metal ions was calculated gravimetrically as metal oxides. Molar conductance measurements of PHBT, CHBT, and MHBT and their complexes with concentration $1.0 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ in DMSO were carried out using a Jenway 4010 conductivity meter. ^{1}H-NMR spectra are measured using a Varian 200 MHz spectrometer with DMSO as solvent; chemical shifts are given in parts per million (ppm) relative to tetramethylsilane. Electron impact mass spectra were recorded on a Jeol, JMS, DX-303 mass spectrometer. IR spectra (4000–400 cm^{-1}) were recorded as KBr pellets on a Bruker FT-IR spectrophotometer.

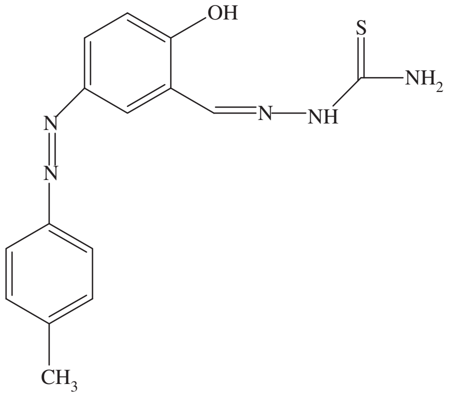
Thermogravimetric analyses (TG/DTG) were carried out from 25 to 800°C in a steam of nitrogen using a Shimadzu TGA 50H thermal analysis system. The experimental



1-(5-(2-Phenyldiazenyl)-2-hydroxybenzylidene)thiosemicarbazide(PHBT) ligand



1-(5-(2-(2-Chlorophenyl)diazenyl)-2-hydroxybenzylidene)thiosemicarbazide(CHBT) ligand



1-(5-(2-*p*-Tolyldiazenyl)-2-hydroxybenzylidene)thiosemicarbazide(MHBT) ligand

Figure 1. Structures of PHBT, CHBT, and MHBT.

conditions were platinum crucible, nitrogen atmosphere with a $30\,\mathrm{mL\,min^{-1}}$ flow rate and a heating rate $10^{\circ}\mathrm{C\,min^{-1}}$.

2.5. *Microbiological investigations*

The paper disc method was applied. Isolates of bacteria were seeded in tubes with nutrient broth (NB). The seeded NB (1 mL) was homogenized in the tubes with $9\,\mathrm{cm^3}$ of melted (45°C) nutrient agar (NA). The homogeneous suspensions were poured into Petri dishes. The discs of filter paper (diameter 4 mm) were ranged on the cool medium. After incubation for 24 h at 25–27°C, the inhibition (sterile) zone diameters (including disc) were measured in millimetre. An inhibition zone diameter over 7 mm indicates that the tested compound is active against the bacteria. Activities of the investigated compounds were tested against *Escherichia coli*, *Pseudomonas aeruginosa* as gram negative, *Bacillus subtilis* and *Staphylococcus aureus* as gram positive. The concentration of each solution was 1.0×10^{-3} mol dm. Commercial DMSO (control) was employed to dissolve the tested samples.

3. Results and discussion

Condensation of the 5-phenyl azo salicylaldehyde and its derivatives with thiosemicarbazide readily gives the corresponding imine (PHBT, CHBT, and MHBT) identified by IR, ^{1}H-NMR, and mass spectra. Four-coordinate complexes were obtained from 1 : 1 molar ratio of PHBT, CHBT, and MHBT with $Cu(CH_3COO)_2 \cdot 3H_2O$, $NiSO_4 \cdot 7H_2O$, and $MnSO_4 \cdot 4H_2O$, giving $[Cu(PHBT)(H_2O)]$ (**1**), $[Ni(PHBT)(H_2O)] \cdot 2H_2O$ (**2**), $[Mn(PHBT)(H_2O)] \cdot H_2O$ (**3**), $[Cu(CHBT)(H_2O)]$ (**4**), $[Ni(CHBT)(H_2O)] \cdot H_2O$ (**5**), $[Mn(CHBT)(H_2O)] \cdot H_2O$ (**6**), $[Cu(MHBT)(H_2O)]$ (**7**), $[Ni(MHBT)(H_2O)] \cdot 2H_2O$ (**8**), and $[Mn(MHBT)(H_2O)] \cdot 2H_2O$ (**9**). The Schiff-base ligands and their complexes are stable at room temperature in solid state. The ligands are insoluble in common organic solvents, but the ligands and metal complexes are generally soluble in DMF and DMSO. The colors, yield, melting/decomposition points, elemental analyses, and molar conductances of PHBT, CHBT, MHBT, and complexes **1**–**9** are presented in table 1. The analytical data are in agreement with the proposed stoichiometry of the complexes.

The metal : ligand ratio in the complexes was found to be 1 : 1 and most have one or two molecules of water of crystallization. The molar conductivity values for all the complexes in DMSO at 10^{-3} M were in the range 6–15 $S\,cm^2\,mol^{-1}$, suggesting nonelectrolytes (table 1). The ligands decomposed at temperatures above 300°C, while all complexes decomposed at temperatures higher than 400°C. All new complexes and Schiff bases have high molar absorptivity. IR, UV-Vis, ^{1}H-NMR, and thermogravimetric data indicate the complexes of the tridentate ligands contain one coordinated water molecule.

3.1. *Molar conductivities of metal chelates*

Conductivity measurements in nonaqueous solutions provide a method of testing the degree of ionization of the complexes. The conductivity data reported for 10^{-3} M solution for these complexes are given in table 1. It is clear from the conductivity data that the complexes are nonelectrolytes. Thus, CH_3COO^- and SO_4^{2-} are absent, and a water molecule completes the coordination sphere.

3.2. *Mass spectra*

The purity of PHBT, CHBT, and MHBT ligands was checked using mass spectra, that the spectra showed clearly base peaks (*m*/*z*) at 299, 333, and 313 *m*/*z*, respectively.

Table 1. Elemental analyses and physical data of Schiff-base ligands (PHBT, CHBT, and MHBT) and their complexes.

							Elemental analyses			
							Calcd (found)			
Compounds	Empirical formula	Molecular weight	Λ Scm^{2}mol^{-1}	Color	m.p.	Yield	%C	% H	%N	%M
PHBT	$C_{14}H_{13}ON_5S$	299.35	8.5	Red	299	78	56.17(56.66)	4.38(4.82)	23.40(23.12)	–
[Cu(PHBT)(H_2O)]	$C_{14}H_{14}O_2N_5SCu$	379.9	12.4	Green	> 300	81	44.26(44.11)	3.71(3.96)	18.43(18.02)	16.73(17.45)
[Ni(PHBT)(H_2O)] · $2H_2O$	$C_{14}H_{18}O_4N_5SNi$	411.08	14.8	Brown	> 300	80	40.91(40.21)	4.41(4.20)	17.04(16.94)	14.28(15.13)
[Mn(PHBT)(H_2O)] · H_2O	$C_{14}H_{14}O_3N_5SMn$	387.02	10.6	Brown	> 300	79	43.42(44.0)	3.64(3.41)	18.08(18.58)	14.19(13.90)
CHBT	$C_{14}H_{12}ON_5SCl$	333.80	6.02	Red	270	79	50.38(50.09)	3.621(3.24)	20.98(20.13)	–
[Cu(CHBT)(H_2O)]	$C_{14}H_{13}O_2N_5SClCu$	414.35	12.3	Green	> 300	81	40.58(40.67)	3.16(3.26)	16.90(17.22)	15.43(14.45)
[Ni(CHBT)(H_2O)] · H_2O	$C_{14}H_{15}O_3N_5SClNi$	427.51	13.1	Brown	> 300	81	39.33(40.07)	3.54(3.79)	16.38(16.17)	13.73(14.32)
[Mn(CHBT)(H_2O)] · H_2O	$C_{14}H_{15}O_3N_5SClMn$	423	10.7	Brown	> 300	80	39.68(40.00)	3.57(3.81)	16.53(16.91)	12.96(11.22)
MHBT	$C_{15}H_{15}ON_5S$	313.38	8.2	Red	278	78	57.49(57.01)	4.82(4.98)	22.35(22.20)	–
[Cu(MHBT)(H_2O)]	$C_{15}H_{16}O_2N_5SCu$	393.93	14.6	Green	> 300	83	45.73(45.18)	4.09(4.36)	17.78(17.89)	16.13(17.01)
[Ni(MHBT)(H_2O)] · $2H_2O$	$C_{15}H_{20}O_4N_5SNi$	425.11	10.1	Brown	> 300	82	42.38(42.59)	4.74(4.49)	16.47(16.20)	13.81(14.66)
[Mn(MHBT)(H_2O)] · $2H_2O$	$C_{15}H_{20}O_4N_5SMn$	421.06	13.9	Brown	> 300	82	42.76(42.62)	4.78(4.58)	16.82(16.12)	13.04(11.97)

3.3. *Infrared spectra*

The most important bands in the IR spectra of the three salicylaldehyde thiosemicarbazone Schiff-base ligands and their metal complexes are summarized in supplementary material, along with their tentative assignment. The position of these bands indicate the bonding sites to Cu(II), Ni(II), and Mn(II). The ligand can exhibit thione–thiol tautomerism since it contains a thioamide NH–C=S group. The ν(S–H) band at $2556\,\mathrm{cm^{-1}}$ is absent from the IR spectra and ν(N–H) [58] at $3120\,\mathrm{cm^{-1}}$ is present, indicating that the ligands remain as the thione tautomer. Strong bands at 1625, 1620, and $1622\,\mathrm{cm^{-1}}$ may be assigned to asymmetric ν(C=N) [59] for PHBT, CHBT, and MHBT, respectively.

The shift toward lower wavenumber by *ca* $18\text{–}24\,\mathrm{cm^{-1}}$ of all metal complexes suggests coordination of nitrogen of the azomethine; metal–nitrogen bonds are indicated by frequencies [60, 61] in the region $\sim 500\,\mathrm{cm^{-1}}$. In spectra of ligands, the strong band observed at $817\text{–}838\,\mathrm{cm^{-1}}$ is shifted to lower wavenumber by *ca* $10\text{–}15\,\mathrm{cm^{-1}}$ in the complexes, indicating thione sulfur as a coordinating site. This is confirmed by a new band at $383\text{–}394\,\mathrm{cm^{-1}}$ assigned to ν(M–S) [62]. Bands from 1149 to $1186\,\mathrm{cm^{-1}}$ may be assigned to (C-OPh) stretching vibration shifted to higher wavenumber by *ca* $20\text{–}36\,\mathrm{cm^{-1}}$.

Broad bands at $\sim 3424\,\mathrm{cm^{-1}}$ are attributed to OH of crystal water molecules, while bands at $834\text{–}861\,\mathrm{cm^{-1}}$ are assigned to coordinated water [55]. IR data indicate that PHBT, CHBT, and MHBT function as tridentate ligands coordinating through thione sulfur, azomethine N, and oxygen of phenol.

3.4. *^{1}H-NMR spectra*

The ^{1}H-NMR spectra of the ligands were recorded using DMSO-d_6: ^{1}H-NMR of PHBT ligand (DMSO-d_6): δ 6.7(s, 2H, NH_2), 7.12–7.92(m, 8H, ArH), 8.36(s, 1H, CH=N), 10.89(s, 1H, NH), 11.90(s, 1H, OH) ppm. ^{1}H-NMR of CHBT ligand (DMSO-d_6): δ 6.69(s, 2H, NH_2), 7.13–7.96 (m, 7H, ArH), 8.34(s, 1H, CH=N), 10.20 (s, 1H, NH), 11.42 (s, 1H, OH) ppm. ^{1}H-NMR of MHBT ligand (DMSO-d_6): δ 2.31(s, 3H, CH_3), 6.29(s, 2H, NH_2), 7.13–7.92(m, 7H, ArH), 8.77 (s, 1H, CH=N), 10.36(s, 1H, NH), 11.32(s, 1H, OH) ppm.

3.5. *Thermogravimetric analysis (TGA)*

Thermal behavior of the complexes were investigated by thermogravimetric analysis (TGA) and differential thermogravimetric (DTG). TGA curves of nine complexes in nitrogen and data summary are in supplementary material. Decomposition of the complexes proceeds in three or four steps, crystal water was lost between 25° and 150°C, coordinated water molecules between 150° and 300°C. Metallic residues were formed above 800°C for all complexes except $[\mathrm{Mn(MHBT)(H_2O)}]\cdot 2\mathrm{H_2O}$, which gave MnO contaminated with residual carbon.

In general, the stages of thermal decomposition of the Schiff-base complexes can be written as shown in scheme 1.

$$[M(L)\mathrm{H_2O}].m\mathrm{H_2O} \xrightarrow[\text{dehydration}]{25\text{–}150^\circ\mathrm{C}} [M(L)\mathrm{H_2O}] + m\mathrm{H_2O}$$

$$[M(L)\mathrm{H_2O}] \xrightarrow{150\text{–}300^\circ\mathrm{C}} [M(L)] + \mathrm{H_2O}$$

$$[M(L)] \xrightarrow[\text{final decomposition}]{300\text{–}1000^\circ\mathrm{C}} \text{Metal/or/oxide} + L$$

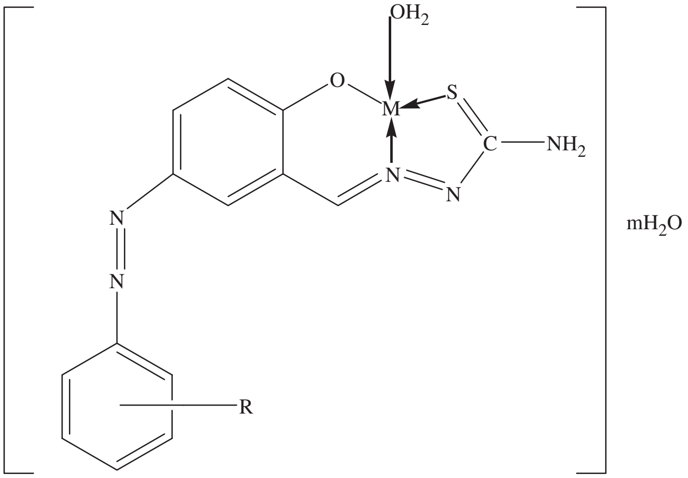
M=Cu; Ni, or Mn, L=PHBT; CHBT or MHBT; $m = 1$ or 2.

Scheme 1. Thermal degradation steps of Cu(II), Ni(II), and Mn(II) complees.

3.6. *Microbiological investigation*

The biological activity of the ligands and their complexes (table 2) was screened simultaneously with metal salts, and standards, against two gram-positive bacteria (*B. subtilis* and *S. aureus*) and two gram-negative bacteria (*E. coli* and *P. aereuginosa*) by the filter paper disc method. The concentration used for testing was 1 mg mL of DMSO. Norfloxacin was used as standard against respective bacteria. DMSO was used as the control. The antimicrobial activity was estimated on the basis of size of inhibition zone formed around the wells in the plates. In general, the Schiff bases represented in this study were less or equally active against the bacteria. In case of *B. subtilis* (G^+), the antibacterial activity of all Schiff bases and complexes show high activity, especially $[\mathrm{Ni(CHBT)(H_2O)}]\cdot\mathrm{H_2O}$. The ligands and their complexes have high activity toward *E. coli* in the order $[\mathrm{Ni(CHBT)(H_2O)}]\cdot\mathrm{H_2O} > \mathrm{CHBT} > [\mathrm{Ni(PHBT)(H_2O)}]\cdot 2\mathrm{H_2O} = [\mathrm{Cu(CHBT)(H_2O)}] = \mathrm{Mn(CHBT)(H_2O)}]\cdot\mathrm{H_2O} = \mathrm{MHBT} = [\mathrm{Ni(MHBT)(H_2O)}]\cdot 2\mathrm{H_2O}$. In case of *P. aereuginosa* (G^-), on comparison with CHBT, the complexes have increased activities attributed to the synergistic effect that increases the lipophilicity of the complex [63].

3.7. *Structure of the complexes*



[R = H, 2Cl, or 4CH$_3$; m = 0, 1 or 2; M = Cu(II), Ni(II), or Mn(II)]

Table 2. Antibacterial activity data of the PHBT, CHBT, and MHBT Schiff-base ligands and their metal complexes.

Compounds	*B. subtilis* (G^+)	*S. aureus* (G^+)	*E. coli* (G^-)	*P. aeruginosa* (G^-)
PHBT	16	15	17	14
[Cu(PHBT)(H_2O)]	17	15	17	16
[Ni(PHBT)(H_2O)] · $2H_2O$	18	16	18	16
[Mn(PHBT)(H_2O)] · H_2O	16	16	17	18
Norfloxacin	18	15	17	16
Control (DMSO)	0	0	0	0
CHBT	18	18	20	18
[Cu(CHBT)(H_2O)]	18	17	18	18
[Ni(CHBT)(H_2O)] · H_2O	20	18	22	18
[Mn(CHBT)(H_2O)] · H_2O	18	16	18	18
Norfloxacin	18	19	21	20
Control (DMSO)	0	0	0	0
MHBT	16	16	18	16
[Cu(MHBT)(H_2O)]	16	15	17	16
[Ni(MHBT)(H_2O)] · $2H_2O$	18	16	18	18
[Mn(MHBT)(H_2O)] · $2H_2O$	18	18	16	16
Norfloxacin	19	19	16	17
Control (DMSO)	0	0	0	0

4. Conclusion

Tetracoordinate complexes of Cu(II), Ni(II), and Mn(II) containing tridentate ONS chelating substituted of salicylaldehyde derivatives with thiosemicarbazide have been prepared and characterized by elemental analysis, molar conductance, and infrared, mass, ^{1}H-NMR and UV-Vis spectra, as well as thermogravimetric analysis. Under experimental conditions employed, only 1 : 1 (M : L) complexes have been found.

References

[1] A.H. Osman. *Transition Met. Chem.*, **31**, 35 (2006).
[2] S.A. Sallam. *Transition Met. Chem.*, **31**, 46 (2006).
[3] C. Sousa, C. Freire, B. de Castro. *Molecules*, **8**, 894 (2003).
[4] J. Costamagna, J. Vargas, R. Latorre, A. Alvarado, G. Mena. *Coord. Chem. Rev.*, **119**, 67 (1992).
[5] M. Cindric, N. Strukan, V. Vrdoljak, T. Kajfez, B. Kamenar. *Croatica Chim. Acta*, **76**, 157 (2003).
[6] D.E. Hamilton, R.S. Drago, A. Zombeck. *J. Am. Chem. Soc.*, **109**, 374 (1987).
[7] S.C. Bhatia, J.M. Bindlish, A.R. Saini, P.C. Jain. *J. Chem. Soc., Dalton Trans.*, 1773 (1981).
[8] J.M. Bindlish, S.C. Bhatia, P. Gautam, P.C. Jain. *Indian J. Chem., Sect. A*, **16**, 279 (1978).
[9] I. Bernal. *Stereochemical Control, Bonding and Steric Rearrangements*, Chap. 3, Elsevier, Amsterdam (1990).
[10] S.A. Hudson, P.M. Maitlis. *Chem. Rev.*, **93**, 861 (1993).
[11] J.L. Serrano. *Metallomesogens, Syntheses, Properties and Applications*, VCH, Weinheim (1996).
[12] K.K. Chaturvedl. *J. Inorg. Nucl. Chem.*, **39**, 901 (1993).
[13] R.D. Archer, B. Wang. *Inorg. Chem.*, **29**, 39 (1990).
[14] R.-G. Xiong, B.-L. Song, J.-Z. Zuo, X.-Z. You. *Polyhedron*, **15**, 903 (1996).
[15] M. Wang, L.-F. Wang, Q.-X. Li. *Transition Met. Chem.*, **26**, 307 (2001).
[16] S.D. Dhumwad, K.B. Gudasi, T.R. Goudar. *Ind. J. Chem.*, **33A**, 320 (1994).
[17] N.N. Gulerman, S. Rollas, H. Erdeniz, M. Kiraj. *J. Pharm. Sci.*, **26**, 11 (2001).
[18] K.H. Reddy, P.S. Reddy, P.R. Babu. *Transition Met. Chem.*, **25**, 154 (2000).
[19] P. Tarasconi, S. Capacchi, G. Pelosi, M. Cornia, R. Albertini, A. Bonati, P.P. Dall'Aglio, P. Lunghi, S. Pinelli. *Bioorganic Med. Chem.*, **8**, 154 (2000).

[20] H. Singh, L.D.S. Yadav, S.B.S. Mishra. *J. Inorg. Nucl. Chem.*, **43**, 1701 (1981).
[21] D.X. West, S.L. Dietrich, I. Thientanavanich, C.A. Brown, A.E. Liberta. *Transition Met. Chem.*, **19**, 320 (1994).
[22] N.K. Singh, S.B. Singh. *Indian J. Chem.*, **40A**, 1070 (2001).
[23] P. Souza, M.A. Mendiola, A. Arquero, V. Fernandez, E.G. Puebla, C.R. Valero. *Z. Naturforsch.*, **49b**, 263 (1994).
[24] M.A. Ali, A.H. Mirza, A. Monsur, S. Hussain, M. Nizamuddin. *Polyhedron*, **20**, 1045 (2001).
[25] F.M. Belicchi, F. Bisceglie, G. Pelosi. *J. Inorg. Biochem.*, **83**, 169 (2001).
[26] V. Arion, K. Wieghardt, T. Weyhermueller, E. Bill, V. Leovac, A. Rufinska. *Inorg. Chem.*, **36**, 661 (1997).
[27] P.N. Yadav, M.A. Demertzis, D. Kovala-Demertzi, S. Skoulika, D.X. West. *Inorg. Chim. Acta*, **349**, 30 (2003).
[28] L. Papathanasis, M.A. Demertzis, P.N. Yadav, D. Kovala-Demertzi, C. Prentjas, A. Castineiras, S. Skoulika, D.X. West. *Inorg. Chim. Acta*, **357**, 4113 (2004).
[29] G.A. Bogdanoviic, V.M. Leovac, S.B. Novakovic, V.I. Cesljevic, A. Spasojevicde Bire. *Acta Cryst.*, **C57**, 1138 (2001).
[30] S. Blanchard, E. Bill, T. Weyhermueller, K. Wieghardt. *Inorg. Chem.*, **43**, 2324 (2004).
[31] T.M. Allen, A.D. Burrows, M.F. Mahon. *J. Chem. Soc., Dalton Trans.*, 215 (1999).
[32] S.B. Novakovic, G.A. Bogdanovic, V.M. Leovac. *Inorg. Chem. Commun.*, **8**, 9 (2005).
[33] S. Padhye, G.R. Kaufman. *Coord. Chem. Rev.*, **63**, 127 (1985).
[34] V.V. Zyelyentsov, I.G. Martgnova, N.A. Moskva. *J. Inorg. Chem. (Russ.)*, **30**, 3130 (1985).
[35] D.H. Petering. In *Metal Ions in Biological Systems*, H. Sigel (Ed.), p. 197, Marcel, Dekker, New York (1980).
[36] D.X. West, A.E. Liberta, S.B. Padhye, R.C. Chikate, P.B. Sonawane, A.S. Kumbhar, R.G. Yerande. *Coord. Chem. Rev.*, **123**, 49 (1993).
[37] D.X. West, I.H. Hall, K.G. Rajendran, A.E. Liberta. *Anticancer Drugs*, **4**, 231 (1993).
[38] K. Wada, Y. Fujibayahsi, A. Yokoyama. *Arch. Biochem. Biophys.*, **310**, 1 (1994).
[39] Y. Fujibayahsi, H. Taniuchi, Y. Yonekura, H. Ohtani, J. Konishi, A. Yokoyama. *J. Nucl. Med.*, **38**, 1155 (1997).
[40] J.L.J. Dearling, J.S. Lewis, D.W. McCarthy, M.J. Welch, P.J. Blower. *J. Chem. Soc., Chem. Commun.*, 2531 (1998).
[41] J.S. Lewis, T.L. Sharp, R. Laforest, Y. Fujibayahsi, M.J. Welch. *J. Nucl. Med.*, **42**, 655 (2001).
[42] J.S. Lewis, R. Laforest, T.L. Buettner, S.-K. Song, Y. Fujibayahsi, J.M. Connet, M.J. Welch. *Proc. Nat. Acad. Sci.*, **98**, 1206 (2001).
[43] M.C. Linder. *Biochemistry of Copper*, Plenum Press, New York (1991).
[44] I.A. Koval, K. van der Schilden, A.M. Schuitema, P. Gamez, C. Belle, J.-L. Pierre, M. Lueken, B. Krebs, O. Roubeau, J. Reedijk. *Inorg. Chem.*, **44**, 4372 (2006).
[45] T. Wang, Z. Guo. *Curr. Med. Chem.*, **13**, 525 (2006).
[46] D.X. West, S.B. Padhye, P.B. Sopawane. *Structure and Bonding*, Vol. 76, p. 1, Springer, Berlin (1991).
[47] S. Padhye, G.B. Kauffman. *Coord. Chem. Rev.*, **63**, 127 (1985).
[48] H.B. Nishihara. *Chem. Soc. Jpn.*, **77**, 407 (2004).
[49] M. Kurashina, M. Murata, T. Watanab, H. Nishihara. *J. Am. Chem. Soc.*, **125**, 12420 (2003).
[50] M.J. Lee, B.W. Yoo, S.T. Shin, S.R. Keum. *Dyes Pigm.*, **51**, 15 (2001).
[51] N. Tamai, H. Miasaka. *Chem. Rev.*, **100**, 1875 (2000).
[52] R. Egli, A.P. Peter, H.S. Freeman (Eds.). *Colour Chemistry*: *The Design and Synthesis of Organic Dyes and Pigments*, Chap. VII, Elsevier, London (1991).
[53] S.C. Catino, E. Farris. *Concise Encyclopedia of Chemical Technology*, John Wiley & Sons, New York (1985).
[54] Z. Rezvani, B. Divband, A.R. Abbasi, K. Nejati. *Polyhedron*, **25**, 1915 (2006).
[55] M.S. Refat, I.M. El-Deen, H.K. Ibrahim, S. El-Ghol. *Spectrochim. Acta, Part A*, **65**, 1208 (2006).
[56] A.A. Khandar, Z. Rezvani. *Polyhedron*, **18**, 129 (1999).
[57] R.J. Fessenden, J.S. Fessenden. *Inorganic Chemistry*, 4th Edn, Vol. 13, p. 587, Cole Publishing Company, California (1990).
[58] P.K. Singh, J.K. Koacher, J.P. Tondon. *J. Inorg. Nucl. Chem.*, **43**, 1755 (1981).
[59] H. Beraldo, D.X. West. *Transition Met. Chem.*, **22**, 249 (1997).
[60] N. Fahmi, R.V. Singh. *Transition Met. Chem.*, **19**, 12 (1994).
[61] A.K. El-Sawaf, D.X. West, F.A. El-Saied, R.M. El-Bahnasawy. *Trans. Met. Chem.*, **22**, 360 (1997).
[62] D.X. West, A.A. Nasser, F.A. El-Said, M.I. Ayad. *Transition Met. Chem.*, **24**, 617 (1999).
[63] S.S. Kukalenko, B.A. Borykin, S.I. Sheshtakova, A.M. Omelchenko. *Russ. Chem. Rev.*, **54**, 676 (1985).