

# Synthesis, Characterization, and Biological Activity of the Schiff Base and Its Ni(II), Cu(II), and Zn(II) Complexes Derived from 4-(Dimethylamino)benzaldehyde and *S*-Benzyldithiocarbazate<sup>1</sup>

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**Abstract**—A Schiff base containing the nitrogen–sulfur donor chain  $[(\text{CH}_3)_2\text{N}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{NH}-\text{C}(\text{S})-\text{SCH}_2\text{C}_6\text{H}_5]$  was prepared by the condensation of 4-(dimethylamino)benzaldehyde and *S*-benzyldithiocarbazate and coordinated with Ni(II), Cu(II), and Zn(II). The Schiff base and its metal complexes were characterized by elemental analysis, IR, <sup>1</sup>H and <sup>13</sup>C NMR, electronic absorption spectroscopy and some of their physicochemical properties were determined. The Schiff bases behaved as a bidentate uninegative ligand in all the complexes, giving square-planar geometrical structures with Ni(II) and Cu(II) and a tetrahedral structure with Zn(II). The Schiff base and its complexes were screened for antibacterial activity. The biological activity testing results showed that the complexes were more potent antibiotics than the free ligand. The Cu(II) and Ni(II) complexes displayed high antibacterial potency and Zn(II) was moderately active against bacteria.

**Keywords:** metal complexes, SBDTC, Schiff base, biological activity

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## INTRODUCTION

Nitrogen–sulfur donor ligands, such as dithiocarbazate ( $\text{NH}_2\text{NHCS}_2$ ) and its substituted derivatives continue to attract great interest of researchers, because it has four potentially donor atoms, two of which are sterically available for metal chelation [1–3]. Researchers in this area have synthesized new nitrogen–sulfur donor ligands by the condensation of Schiff bases with aldehydes and ketones [4–6]. The properties of these ligands can be strongly modified by introducing organic substituents. The number of synthesized ligands continues to increase because of the intriguing observation that different ligands show different biological properties, even though they may only slightly differ in their molecular structure [7–10]. Transition metal complexes of these ligands are also widely studied due to their potential therapeutic use [11–14].

In this study, we synthesized a Schiff base and its metal complexes, starting from 4-(dimethylamino)-benzaldehyde. The ligand and its metal complexes were tested for biological activity against pathogenic and nonpathogenic bacteria.

## RESULTS AND DISCUSSION

The Schiff base, benzyl *N'*-(4-dimethylamino-benzylidene)hydrazinecarbodithioate (SB), was synthesized in high yield by the condensation of *S*-benzyldithiocarbazate (SBDTC) with 4-(dimethylamino)benzaldehyde in a neutral medium (Scheme 1).

The Ni(II), Cu(II), and Zn(II) complexes were obtained by reacting the synthesized Schiff base with the corresponding metal nitrates:

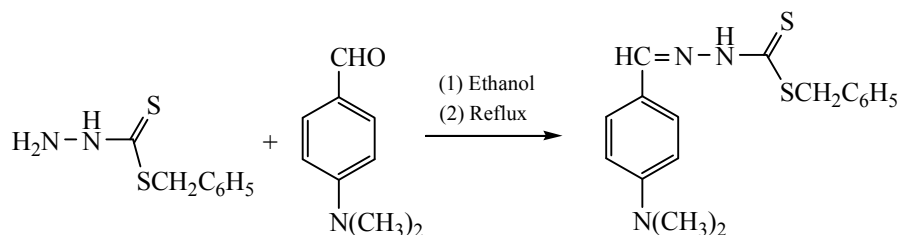


where M(II) = Ni(II), Cu(II), Zn(II) and SB = benzyl *N'*-(4-dimethylaminobenzylidene)hydrazinecarbodithioate.

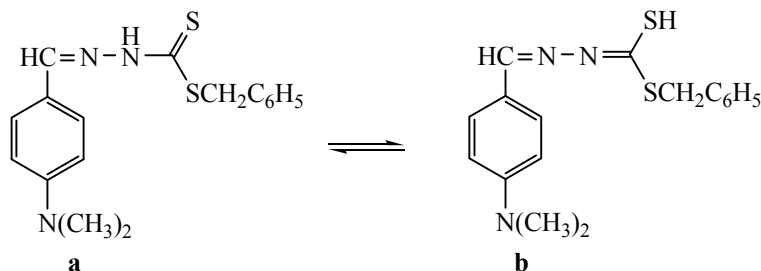
As known, hydrazinecarbodithioic acid exists in solutions as a mixture of the thione and thiol tautomers

<sup>1</sup> Supplementary materials are available for this article at <https://doi.org/10.1134/S107036321906015X> and are accessible for authorized users.

Scheme 1.



Scheme 2.



[5–7]. The thione form is relatively unstable in the monomeric form and tends to convert into a more stable thiol form by enethiolization (Scheme 2).

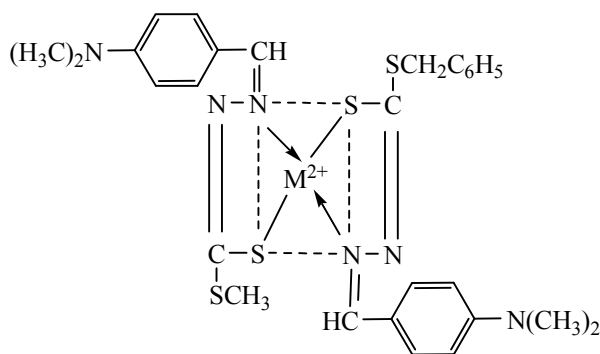
**IR spectra.** The important IR spectral bands of the ligand SB and its metal complexes were listed in Table 1. The absence of the  $\nu(\text{S-H})$  absorbance at about  $2565\text{ cm}^{-1}$  indicates that in the solid state the base exists primarily in the thione form. The disappearance of the  $\nu(\text{N-H})$  bands in the spectra of the metal complexes suggests deprotonation and subsequent coordination through the thiolate anion. The Schiff base also showed a strong band at  $1589\text{ cm}^{-1}$ , which was assigned to the  $\nu(\text{C=N})$  modes of the free ligand. In the IR spectra of the metal complexes, this stretching band was shifted to lower frequencies, because the  $\text{C=N}$  bond order decreases due to  $\text{M-N}$  bond formation. The  $\nu(\text{C=S})$  mode of the free ligand observed at  $1084\text{ cm}^{-1}$  disappears from the IR spectra of the complexes, thus supported the above suggestion of the thiolate bonding to metal ions. The  $\nu(\text{C-S})$

stretching frequency of the free Schiff base appeared as a sharp band at  $805\text{ cm}^{-1}$  was shifted to a lower frequency ( $750\text{ cm}^{-1}$ ) due to  $\text{M-N}$  bonding. This fact provides further evidence for thiolate coordination. The  $\nu(\text{C=N})$  stretching frequency of the free Schiff base observed at  $1589\text{ cm}^{-1}$  shifted towards the low-frequency region ( $1560\text{ cm}^{-1}$ ), supporting  $\text{M-N}$  bond. Thiolate coordination was also supported by the disappearance of the  $\nu(\text{M-S})$  band of the free Schiff base appears at  $1084\text{ cm}^{-1}$ . This band also disappeared from the IR spectra of the metal complexes, giving evidence for the coordination through the thiolate anion. Evidence for the coordination of the Schiff base through both the thiolate sulfur and  $\beta$ -nitrogen also comes from the observation in the IR spectra of the complexes of the  $\nu(\text{M-S})$  and  $\nu(\text{M-N})$  bands at  $460$  and  $503\text{ cm}^{-1}$ , respectively [15].

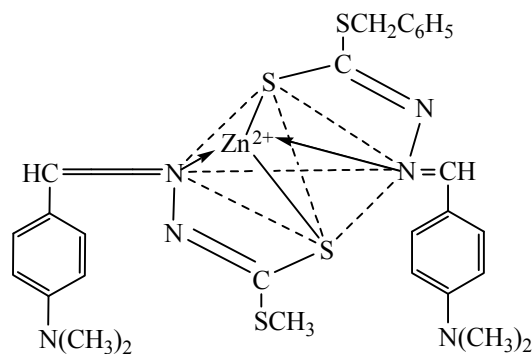
**Molar conductance, magnetic moments and electronic spectra.** The molar conductance and magnetic moments of the synthesized Schiff base and

**Table 1.** Important IR spectral bands of the ligand and metal complexes

Compound	$\nu, \text{cm}^{-1}$					
	N-H	C=S	C=N	C-S	M-S	M-N
SB	3125	1084	1589	805	–	–
$[\text{Ni(II)}(\text{SB})_2]$	–	–	1560	750	460	503
$[\text{Cu(II)}(\text{SB})_2]$	–	–	1557	750	465	501
$[\text{Zn(II)}(\text{SB})_2]$	–	–	1565	750	445	475



**Fig. 1.** Square-planar structure of the complexes  $M(II)(SB)_2$  [ $M = Ni(II), Cu(II)$ ].



**Fig. 2.** Tetrahedral structure of the complex  $[Zn(II)(SB)_2]$ .

its metal complexes are given in Table 2. As judged from the conductance values, the complexes were all nonelectrolytes in nature [16]. Magnetic susceptibility measurements (Table 2) showed that the complex  $[Ni(II)(SB)_2]$  was diamagnetic. The UV-Vis spectrum of the complex in DMSO were given evidence for a singlet ground state characteristic of square-planar  $Ni(II)$  complexes. The three bands observed in the spectrum were assigned to the  $^1A_{1g} \rightarrow ^1A_{2g}$  (280 nm),  $^1A_{1g} \rightarrow ^1B_{1g}$  (320 nm), and  $^1A_{1g} \rightarrow ^1A_{2g}$  transitions (360 nm), which were previously observed in the electronic absorption spectra of such square-planar  $Ni(II)$  complexes [17, 18]. Complex  $[Cu(II)(SB)_2]$  was paramagnetic (magnetic moment, 1.98 B.M) which corresponds to one unpaired electron. The UV-vis spectrum of the complex showed  $d-d$  bands at 342 and 292 nm (Table 3), arising from the  $^2B_{1g} \rightarrow ^2A_{1g}$  and  $^2B_{1g} \rightarrow ^2E_{1g}$  transitions, respectively, and characteristic of a square-planar stereochemistry [19, 20]. The strong band at 221 nm is presumably associated with a charge-transfer transition. The charge-transfer band of complex  $[Zn(II)(SB)_2]$  was observed at 295 nm which indicated that the complex diamagnetic in nature.

Together the above observations allowed us to suggest that the complexes  $[Ni(II)(SB)_2]$  and  $[Cu(II)(SB)_2]$  have a square-planar structure with the two ligands occupying four stereochemical sites, while the complex  $[Zn(II)(SB)_2]$  has a tetrahedral geometry (Figs. 1 and 2).

**Antibacterial activity.** The synthesized compounds were tested for antibacterial activity against three pathogenic bacteria, two gram-negative (*E. coli* and *S. sonnei*) and one gram-positive (*B. subtilis*). Disc diffusion method is a widely accepted procedure for in vitro investigation of the susceptibility of micro-organisms to the compounds, so this method was

adopted in this investigation [21–23]. The metal complexes yielded clear inhibition zones around the discs with all the three test bacteria (Table 4). As seen from the table, the complexes demonstrated moderate to strong activities against both gram-positive and gram-negative bacteria compared to the antibacterial standard Kanamycin.

## EXPERIMENTAL

All reagents were of chemical grade purity and solvents were purified by standard procedures. The IR spectra were recorded on a Shimadzu FTIR-8101 spectrophotometer in the range  $4000\text{--}225\text{ cm}^{-1}$  for KBr disks. The  $^1H$  NMR (400 MHz) and  $^{13}C$  NMR (100 MHz) spectra were recorded on a JEOL JNM-A400 spectrometer in  $CDCl_3$  with TMS as internal standard. The UV-Vis spectra were recorded on a Shimadzu UV-160 spectrophotometer in the range 200–900 nm. Conductivity measurements were carried out in  $10^{-3}$  M DMSO solutions at room temperature using a SCHOTT Geräte CG 857 digital conductivity meter. Magnetic measurements were performed using a Sherwood Scientific magnetic susceptibility balance. The metal contents were determined gravimetrically [24]. Microanalyses (C, H N) were executed by using a MLW-CHN micro analyser.

**Table 2.** Molar conductances and magnetic moments of the complexes

Complex	Molar conductance, $\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$	$\mu_{\text{eff}}$ , B.M.
SB	2.20	—
$[Ni(II)(SB)_2]$	1.90	Dia
$[Cu(II)(SB)_2]$	2.98	1.98
$[Zn(II)(SB)_2]$	3.15	Dia

**Table 3.** UV-Vis spectral data for the complexes

Complex	$\lambda_{\max}$ , nm		
	band I	band II	band III
[Ni(II)(SB) <sub>2</sub> ]	280	320	360
[Cu(II)(SB) <sub>2</sub> ]	221	292	342
[Zn(II)(SB) <sub>2</sub> ]	295	–	–

**Table 4.** Results of antibacterial activity testing

Compound	Diameter of the inhibition zone, mm		
	<i>E. coli</i>	<i>S. sonnei</i>	<i>B. subtilis</i>
SB	13	14	13
[Ni(SB) <sub>2</sub> ]	16	15	17
[Cu(SB) <sub>2</sub> ]	18	16	19
[Zn(SB) <sub>2</sub> ]	14	13	15
Kanamycin	20	20	22

*S*-benzylthiocarbamate (SBDTC) was prepared by the procedure described in [15].

**Synthesis of benzyl *N'*-(4-dimethylaminobenzylidene)hydrazinecarbodithioate (SB).** A solution of 1.98 g (10 mmol) of SBDTC in 50–60 mL of hot absolute ethanol was added to a solution of the equimolar amount of 4-(dimethylamino)benzaldehyde in 20 mL of the same solvent. The mixture was refluxed for 40 min. The yellow precipitate that formed was separated and dried in *vacuo* over anhydrous CaCl<sub>2</sub>. Yield 68%, orange powder, mp 178 °C. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 3.02 s [6H, N(CH<sub>3</sub>)<sub>2</sub>], 4.56 m (2H, SCH<sub>2</sub>), 6.64 d ( $J$  = 9.2 Hz, H<sup>12,14</sup>, C<sub>6</sub>H<sub>4</sub>), ( $J$  = 6.8 Hz, H<sup>11,15</sup>, C<sub>6</sub>H<sub>4</sub>), 7.55–7.30 m (5H, C<sub>6</sub>H<sub>5</sub>), 7.75 s (1H, CH=N), 10.22 s (1H, N–NH). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 38.39, 39.26, 40.06, 111.59, 120.07, 127.36, 127.89, 128.54, 128.71, 129.14, 129.42, 129.54, 135.69, 136.22, 146.80, 152.19, 164.0, 196.36. Calculated, %: C 61.97; H 5.81; S 19.46; N 12.75. C<sub>17</sub>H<sub>19</sub>S<sub>2</sub>N<sub>3</sub>. Found, %: C 61.99; H 5.81; S 19.40; N 12.74.

**Synthesis of metal complexes of the Schiff base (general procedure):** A solution of 0.329 g (1 mmol) of SB in 70 mL of hot absolute ethanol was added to a solution of the metal salt hydrate [Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O] (0.145 g, 0.5 mmol), [Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O] (0.121 g, 0.5 mmol), or [Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O] (0.148 g, 0.5 mmol) in 20 mL of absolute ethanol. The mixture was refluxed for 40 min and then cooled. The precipitate

that formed was filtered off, washed with hot ethanol, and dried in *vacuo* over anhydrous CaCl<sub>2</sub>.

**[Ni(SB)<sub>2</sub>].** Yield 70%, color greenish brown, mp 255 °C. Calculated, %: C 57.06; H 5.07; N 11.74; S 17.92; Ni 8.20. C<sub>34</sub>H<sub>36</sub>N<sub>6</sub>S<sub>4</sub>Ni Found, %: C 57.10; H 5.03; N 11.72; S 17.94; Ni 8.20.

**[Cu(SB)<sub>2</sub>].** Yield 65%, color reddish, mp 195 °C. Calculated, %: C 56.68; H 5.03; N 11.66; S 17.80; Cu 8.82. C<sub>34</sub>H<sub>36</sub>N<sub>6</sub>S<sub>4</sub>Cu. Found, %: C 56.70; H 5.05; N 11.69; S 17.76; Cu 8.85.

**[Ni(SB)<sub>2</sub>].** Yield 64%, color off white, mp 210 °C. Calculated, %: C 56.53; H 5.02; N 11.63; S 17.34; Zn 9.05. C<sub>34</sub>H<sub>36</sub>N<sub>6</sub>S<sub>4</sub>Zn. Found, %: C 56.57; H 5.05; N 11.59; S 17.38; Zn 9.10.

The standard test microorganisms for antibacterial studies were collected from the department of pharmacy, Rajshahi University, Rajshahi. The diameters of zones of inhibition produced by the compounds were compared with standard antibiotics (Kanamycin 30 µg/disc). The experiment was performed in duplicate to minimize errors.

## CONCLUSIONS

The Schiff base *N'*-(4-dimethylaminobenzylidene)hydrazinecarbodithioate was prepared by the condensation of *S*-benzylthiocarbamate and 4-(dimethyl-

amino)benzaldehyde. The present study revealed that the Schiff base acts as a uninegative bidentate ligand with its NS donor set and forms neutral bischelated Ni(II), Cu(II), and Zn(II) complexes. The Ni(II) and Cu(II) complexes have a square-planar geometry, while the Zn(II) complex is tetrahedral. The ligand and its metal complexes showed significant antimicrobial activity toward some bacterial strains.

#### FUNDING

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#### CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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