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Synthesis, Characterization, and Antimicrobial Activity of Complexes of Cu(II), Ni(II), Zn(II), Pb(II), Co(II), Mn(II), and U(VI) Containing Bidentate Schiff Base of [S-Methyl-3-(4-methoxybenzylidine)dithiocarbazate][1]

Md. Kudrat-E-Zahan and M. S. Islam

Inorganic Research Laboratory, Department of Chemistry, University of Rajshahi, Rajshahi-6205, Bangladesh
e-mail: kudrat.chem@ru.ac.bd

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Abstract—A novel bidentate Schiff base containing NS donor sequences was synthesized by condensing S-methyldithiocarbazate (SMDTC) with p-anisaldehyde. A series of complexes of the ligand with Cu(II), Ni(II), Zn(II), Pb(II), Co(II), Mn(II) and U(VI) were studied and characterized by various physico-chemical methods. Cu(II), Ni(II) and Zn(II), Pb(II) complexes were four-coordinate with square plannar and tetrahedral geometry respectively. Co(II), Mn(II), and U(VI) complexes were six-coordinate with octahedral geometry. Antimicrobial activity of the prepared complexes was tested as resistance to antimicrobial agents in a wide variety of nosocomial and community-acquired pathogens. The highest antimicrobial activity was detected for the complex Co(II) against *candida* species.

Keywords: transition metal complex, SMDTC, antimicrobial activity, Schiff base

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INTRODUCTION

The Schiff base ligands are produced by the condensation of a primary amine and an active carbonyl group and contain the azomethine group (−CH=N− or >C=N−:). Schiff bases can act as mono-, di-, tri-, or tetradentate ligands depending on the number of coordinating atoms present in the molecule and form generally five or six membered chelate rings with a metal ion. Among many Schiff bases dithiocarbazate (NH_2NHCS_2) and its substituted derivatives have been studied as ligands for long time [1–5]. The compounds have received considerable attention due to the following reasons: (1) They provide an interesting series of ligands whose properties can be significantly modified by introducing different organic substituents that impart a variety of donor properties. (2) Interaction of such donors with metal ions gives complexes of different geometries and features. (3) The complexes are potentially biologically active [6–9].

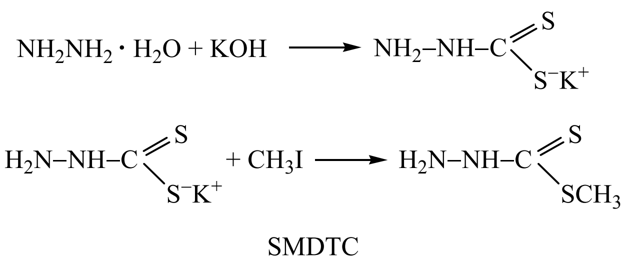
Previously, we have reported few complexes and their antimicrobial activity [10–14]. The major objective of the current study was synthesis of the new Schiff base ligand [*S*-methyl-3-(4-methoxybenzylidine)dithiocarbazate] by condensation of *p*-anisaldehyde with *S*-methyldithiocarbazate followed by testing antimicrobial activity of its metal complexes with Cu(II), Ni(II), Zn(II), Pb(II), Co(II), Mn(II), and U(VI).

EXPERIMENTAL

All reagents and chemicals were reagent grade and used as supplied.

Physical measurements. Melting points or decomposition temperature of all synthesized metal complexes were measured by an electro thermal melting

Scheme 1.



$$NH_2NH_2 \cdot H_2O + KOH \longrightarrow NH_2{-}NH{-}C(=S)S^-K^+$$

$$H_2N{-}NH{-}C(=S)S^-K^+ + CH_3I \longrightarrow H_2N{-}NH{-}C(=S)SCH_3$$

SMDTC

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[1] The text was submitted by the authors in English.

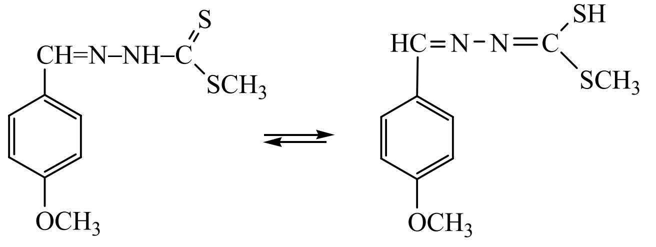
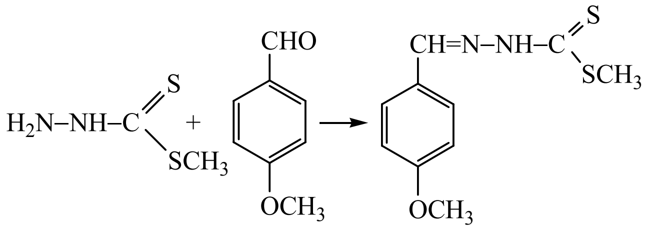


Fig. 1. Tautomeric forms of the Schiff base.

Scheme 2.



point apparatus model no. AZ6512. The SHERWOOD SCIENTIFIC Magnetic Susceptibility Balance was used for the present investigation. Infrared spectra as KBr disc were recorded by a SIMADZU FTIR-8400 (Japan) spectrophotometer in the range 4000–400 cm^{-1}. UV-Vis spectra were recorded on SHIMUDZU Spectrophotometer.

Synthesis. The ligand *S*-methyldithiocarbazate (SMDTC) was synthesized according to the previously reported method [2] (Scheme 1).

Synthesis of *p*-anisaldehyde Schiff base of SMDTC: [*S*-methyl-3-(4-methoxybenzylidine)dithiocarbazate] (NS). To a solution of SMDTC (0.2 mol) in hot absolute ethanol (35 mL) was added the equimolar amount of *p*-anisaldehyde in hot absolute ethanol (20 mL). The mixture was heated for 20 min and then cooled down to give white precipitate. It was separated and dried in *vacuo* over anhydrous $CaCl_2$. mp 165°C (Scheme 2).

General method for synthesis of metal complexes of the Schiff base. 1 mmol of one of metal salts, $[Cu(NO_3)_2{\cdot}3H_2O]$, $[Ni(NO_3)_2{\cdot}6H_2O]$, $[Zn(NO_3)_2{\cdot}6H_2O]$, $[CoCl_2{\cdot}6H_2O]$, $[MnSO_4{\cdot}7H_2O]$, or $[Pb(NO_3)_2{\cdot}6H_2O]$, was dissolved in absolute ethanol (15 mL) and added to the above synthesized Schiff base (2 mmol) solution in hot absolute ethanol (50 mL). The mixture was refluxed for 30 min and then cooled down. The precipitate was filtered off and washed with hot ethanol and dried in vacuo over anhydrous $CaCl_2$.

Metal salt of $UO_2(NO_3)_2{\cdot}7H_2O$ (1 mmol) was dissolved in ethanol (20 mL). The synthesized Schiff base (2 mmol) in hot absolute ethanol (40 mL) was added to the salt solution. The mixture was refluxed for 30 min and then cooled down. The corresponding product crystallized upon 30 days of storage at room temperature. The crystalline product was separated, washed with ethanol and dried in vacuo over anhydrous $CaCl_2$.

$$M(NO_3)_2{\cdot}nH_2O + NS \rightarrow [M(II)(NS)_2];\ M''Cl_2{\cdot}nH_2O + NS \rightarrow [M''(II)(NS)_2(H_2O)_2],$$

$$UO_2(NO_3)_2{\cdot}nH_2O + NS \rightarrow [U(VI)(NS)_3],$$

where M = Cu(II), Ni(II), Zn(II), Pb(II); M" = Co(II), Mn(II); NS = [*S*-methyl-3-(4-ethoxybenzylidine)dithiocarbazate].

Table 1. Analytical and physical data of the complexes

Compounds	Color	mp/decomp. temperature (± 5°C)	Molar conductance, Ω^{-1} cm^2 mol^{-1}	μ_{eff}, B.M.
SMDTC	White	81	10.80	–
[NS]	White	165	4.50	–
$[Cu(II)(NS)_2]$	Brown	265	3.25	1.94
$[Ni(II)(NS)_2]$	Golden brown	188	2.30	2.97
$[Zn(II)(NS)_2]$	Light yellow	205	5.72	Dia
$[Co(II)(NS)_2(H_2O)_2]$	Reddish black	220	3.54	3.94
$[Mn(II)(NS)_2(H_2O)_2]$	Chocolate	276	8.25	3.94
$[Pb(II))(NS)_2]$	Off white	223	5.05	2.79
$U(VI)(NS)_3]$	Golden brown	95	3.45	Dia

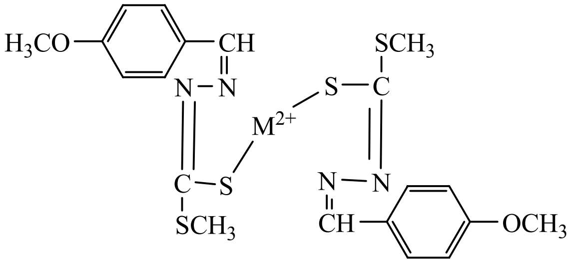


Fig. 2. Square planar geometry of the M^{2+}(II) complex, M^{2+} = Cu(II), Ni(II).

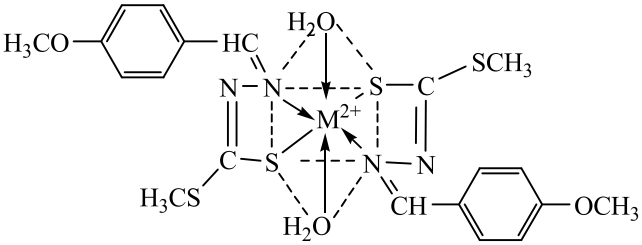


Fig. 3. Octahedral geometry of M^{2+}(II) complex, M^{2+} = Co(II), Mn(II).

RESULTS AND DISCUSSION

Physical properties of the complexes. Analytical data were in good agreement with the proposed empirical formula of the complexes (Table 1). According to conductance data the complexes were non electrolytes [15].

IR spectra. The (C=N) stretching vibrations of the free Schiff base (ca 1604 cm^{-1}) shifted to 1565 cm^{-1} upon complexation (Table 2). The Schiff base coordinated to the metal via the thiolate sulfur (Fig. 1) and β-nitrogen atoms which was evident from the IR spectrum demonstrating bands at ca 480 cm^{-1} and ca 531 cm^{-1} attributed to ν(M–S) and ν(M–N) stretching vibrations respectively. In case of complexes [Co(NS)$_2$·(H$_2$O)$_2$] and [Mn(II)(NS)$_2$(H$_2$O)$_2$] the bands in the region 3250–3467 cm^{-1} indicated presence of coordinated water molecules.

Table 2. IR data of the compounds

Compounds	ν, cm^{-1}							
	NH$_2$	N–H	C=S	C=N	C–S	M–S	M–N	OH
SMDTC	3309–3182	3415	1045	–	–	–	–	–
[NS]	–	3110	1043	1604	876	–	–	–
[Cu(II)(NS)$_2$]	–	–	–	1564	825	480	531	–
[Ni(II)(NS)$_2$]	–	–	–	1572	823	406	538	–
[Zn(II)(NS)$_2$]	–	–	–	1565	803	472	535	–
[Co(II)(NS)$_2$(H$_2$O)$_2$]	–	–	–	1580	829	465	530	3466–3250
[Pb(II)(NS)$_2$]	–	–	–	1567	828	445	524	–
[Mn(II)(NS)$_2$(H$_2$O)$_2$]	–	–	–	1598	834	472	518	3467–3280
U(VI)(NS)$_3$]	–	–	–	1571	838	486	694	–

Table 3. Electronic spectra of the complexes

Complexes	λ$_{max}$, nm			
[Cu(II)(NS)$_2$]	280	320	470	–
[Ni(II)(NS)$_2$]	312	355	412	–
[Zn(II)(NS)$_2$]	320	–	–	–
[Mn(II)(NS)$_2$(H$_2$O)]$_2$]	235	380	505	–
[Co(II)(NS)$_2$(H$_2$O)]$_2$]	310	420	540	–
[Pb(II))(NS)$_2$]	384	–	–	–
U(VI)(NS)$_3$]	230	290	520	610

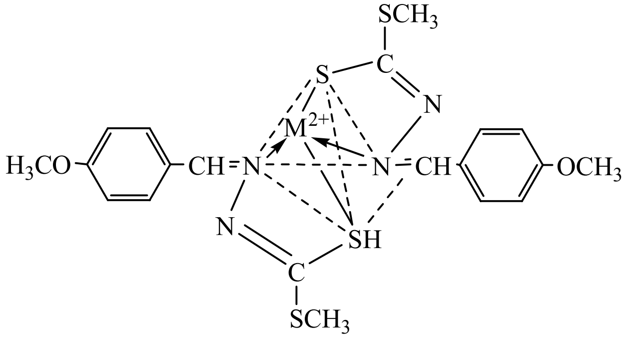


Fig. 4. Tetrahedral geometry of the M^{2+}(II) complex, M^{2+} = Zn(II), Pb(II).

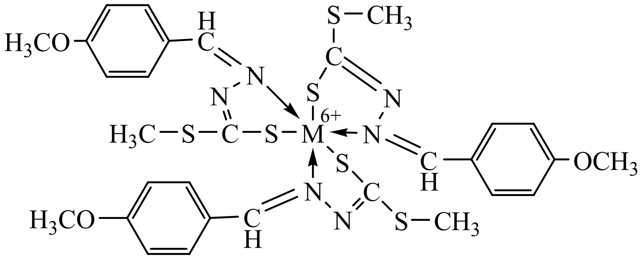


Fig. 5. Octahedral geometry of M^{6+}(VI) complex, M^{6+} = U(VI).

Magnetic moment and electronic spectra. Magnetic susceptibility measurement (Table 1) indicated that the complex [Cu(II)$(NS)_2$] was paramagnetic and its magnetic moment (1.94 B.M.) corresponded to one unpaired electron. UV-Vis spectrum of the complex demonstrated *d–d* bands at 470 and 320 nm (Table 3), arising from the $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_{1g}$ transitions, respectively, characteristic to a square planar structure [17] (Fig. 2). The intense band at 280 nm was presumably caused by charge transfer.

Magnetic susceptibility measurements (Table 1) and three bands corresponding to the transitions $^1A_{1g} \rightarrow {}^1A_{2g}$ (312 nm), $^1A_{1g} \rightarrow {}^1B_{1g}$ (355 nm) and $^1A_{1g} \rightarrow$

Table 4. In vitro antibacterial activities of the compounds and Kanamycine (K-30)

Bacteria	Gram staining	Diameter of inhibition zone (mm)				
		[Cu(II)$(NS)_2$] 100 mg/disc	[Ni(II)$(NS)_2$] 100 mg/disc	[U(VI)$(NS)_3$] 100 mg/disc	[Co(II)$(NS)_2(H_2O)_2$] 100 mg/disc	K-30 mg/disc
Bacillus subtilis	Positive	25	20	8	17	25
Staptococcus aureus	Positive	17	16	18	8	24
Bacillus megaterium	Positive	23	7	23	22	26
Streptococcus-β-haemolyticus	Positive	26	25	26	17	25
Escherichia coli	Negative	13	18	24	25	20
Shigella dysenteriae	Negative	22	26	8	24	21
Shigella sonnei	Negative	25	17	7	6	22
Shigella shiga	Negative	16	14	12	17	24

Table 5. Antifungal activity of the complexes and standard Fluconazole

Fungal status	Diameter of inhibition zone (mm)				
	[Cu(II)$(NS)_2$] 100 mg/disc	[Ni(II)$(NS)_2$] 100 mg/disc	[U(VI)$(NS)_3$] 100 mg/disc	[Co(II)$(NS)_2(H_2O)_2$] 100 mg/disc	Fluconazole F-50 mg/disc
Aspergillus	11	13	12	9	17
Penicillium	15	15	8	14	20
Candida species	14	15	13	16	19
Aspergilius niger	14	7	11	9	20

^1E_g (412 nm) recorded in the electronic spectra (Table 3) indicated the square-planar structure of Ni(II) complex [17] (Fig. 2). Spectra of the complex [Zn(II)(NS)$_2$] demonstrated the absorption band at 320 nm assigned to charge transfer transitions (Table 3).

According to magnetic moment (Table 1) and electronic spectra bands, 310, 420 and 540 nm (Table 3), assigned to the transitions $^4T_{1g}\rightarrow{}^4T_{2g}(\nu_1)$, $^4T_{1g}\rightarrow{}^4A_{2g}(\nu_2)$, $^4T_{1g}\rightarrow{}^4T_{2g}(F)(\nu_3)$ respectively, the complex [Co(II)(NS)$_2$·(H$_2$O)$_2$] had octahedral structure [17] (Fig. 3). The octahedral complex [Mn(II)(NS)$_2$(H$_2$O)]$_2$] demonstrated similar characteristics (Tables 1 and 3). The absorption band at 384 nm of the complex [Pb(II)(NS)$_2$] was assigned to charge transfer transitions (Table 3). The magnetic susceptibility data indicated its distorted tetrahedral geometry (Fig. 4). The octahedral structure of U(VI) complex is shown in Fig. 5.

^{1}H NMR spectra. ^{1}H NMR spectrum of [Zn(II)(NS)$_2$] complex was typical for all synthesized complexes and demonstrated the following signals (ppm): 7.57–7.54 d (J = 8.4 Hz, 4H, Ar-H), 7.03–7.00 d (J = 8.4 Hz, 4H, Ar-H), 4.84 s (6H, –OCH$_3$), 3.86 s (2H, –CH), 2.73 s (6H, –SCH$_3$).

Antibacterial activity of the complexes. Complexes of Zn(II) and Cd(II) with tridentate ONS donor Schiff base ligands had been synthesized and their biological activity tested by Gunthkal et al [18]. Wang and co-authors [19] had synthesized and studied the biological activity of Cu(II), Co(II), and Ni(II) complexes with thiosemicarbazones. Complexes of Fe(II), Co(II), Ni(II), Cu(II,) and Zn(II) with 3-aminophenol-*N*-benzylidine Schiff base ligand had been synthesized and tested for antibacterial activity by Patil and co-workers [20].

Accumulated in the current study data revealed that the complexes had higher microbial toxicity than free metal ions or ligands. Co(II), Ni(II), Cu(II), and U(VI) Schiff bases complexes (Table 4) demonstrated moderate to strong activity against both Gram positive and Gram negative bacteria compared to standard Kanamycine.

Antifungal activity of the complexes. Antifungal activity of the complexes and standard fluconazole (F-50 mg/mL)) were determined in the concentration of 100 mg/mL against four pathogenic fungi (Table 5). The complexes of Co(II), Ni((II), Cu(II), and U(VI) demonstrated significant activity towards all fungi tested with the highest determined for the complex of Co(II) against *Candida* species.

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