

Research Article

Synthesis, Characterization, and Biological Activity of Some Transition Metal Complexes of N-Benzoyl-N'-2-thiophenethiocarbohydrazide

Mahendra Yadav

Department of Applied Chemistry, Indian School of Mines, Dhanbad 826004, India

Correspondence should be addressed to Mahendra Yadav, yadav_drmahendra@yahoo.co.in

Received 5 September 2012; Accepted 24 October 2012

Academic Editor: Wolfgang Linert

Copyright © 2012 Mahendra Yadav. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

In the present study, Mn(II), Fe(II), Ni(II), and Cu(II) complexes of N-benzoyl-N'-2-thiophenethiocarbohydrazide (H_2 BTTH) have been synthesized and characterized by elemental analysis, magnetic susceptibility measurements, infrared, NMR, electronic, and ESR spectral studies. The complexes were found to have compositions $[Mn(H\ BTTH)_2]$, $[Ni(BTTH)(H_2O)_2]$, $[Cu(BTTH)]$, and $[Fe(H\ BTTH)_2EtOH]$. The antibacterial and antifungal properties of H_2 BTTH and its metal complexes have been screened against several bacteria and fungi.

1. Introduction

The expansion of research in the coordination chemistry of nitrogen-sulphur donor ligands such as substituted thiosemicarbazides [1], thiosemicarbazones [2–4], and dithiocarbazates [5], during the recent years has been due to their remarkable antineoplastic activity against a variety of tumors [6] in addition to their applicable antifungal [7] and antibacterial [8] activities. Sulphur and nitrogen containing ligands and their transition metal complexes were also used as corrosion inhibitors [9, 10] and extreme pressure lubricant additives [11]. Keeping in view the above biological activity of the sulfur and nitrogen containing ligands, we planned to undertake the synthesis, characterization, antibacterial, and antifungal activity of N-benzoyl-N'-2-thiophenethiocarbohydrazide (H_2 BTTH) (Figure 1) and its Mn(II), Fe(II), Ni(II), and Cu(II) complexes. This ligand is expected to form addition complexes without loss of protons, and deprotonated complexes by loss of one or both the hydrazinic protons.

2. Experimental

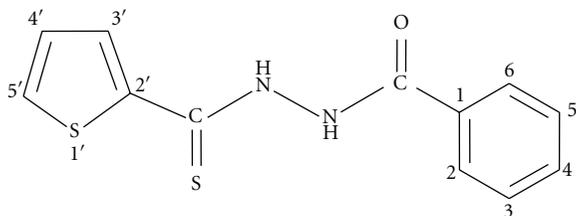
2.1. Starting Materials. All the chemicals used were of analytical grade. Ammonium polysulphide [12] and

carboxymethyl-2-thiophenedithioate [13] were prepared by literature methods.

2.2. Preparation of N-benzoyl-N'-2-thiophenethiocarbohydrazide (H_2 BTTH). N-benzoyl-N'-2-thiophenethiocarbohydrazide (H_2 BTTH) was prepared by mixing solutions of benzoic acid hydrazide (20 mmol) and carboxymethyl-2-thiophenedithioate (20 mmol) each dissolved separately in 50 mL of 0.5 N NaOH and allowing the mixture to stand at room temperature for 2 hrs. The product precipitated by adding dilute AcOH dropwise to the above ice-cold mixture, was filtered off, washed with H_2O , dried, and recrystallized from EtOH.

2.3. Synthesis of $[Mn(H\ BTTH)_2]$. The complex $[Mn(H\ BTTH)_2]$ was prepared by boiling together the methanolic solutions (25 mL) of $Mn(OAc)_2 \cdot nH_2O$ (1 mmol) and H_2BTTH (2 mmol) for 1 h under reflux. The precipitated complexes were filtered, washed with methanol, and dried *in vacuo*.

2.4. Synthesis of $[Ni\ (BTTH)(H_2O)_2]$ and $[Cu\ (BTTH)]$. The complexes $[Ni\ (BTTH)(H_2O)_2]$ and $[Cu\ (BTTH)]$ were synthesized by boiling together the methanolic solutions

FIGURE 1: Structure of H₂BTTH.

(25 mL) of the respective M(OAc)₂ · 2H₂O [M = Ni(II), Cu(II)] (1 mmol) and H₂BTTH (1 mmol) for about 1 h under reflux. The precipitated complexes were filtered, washed with methanol and dried *in vacuo*.

2.5. [Fe(HBTTH)₂(EtOH)]. [Fe(HBTTH)₂(EtOH)] was prepared by boiling together an aqueous-methanolic solution (25 mL) of (NH₄)₂SO₄ · FeSO₄ · 6H₂O (1 mmol) and H₂BTTH (2 mmol) in ethanol (25 mL) for about 1 h. The precipitated complex was filtered, washed with water, ethanol and dried *in vacuo*.

2.6. Instrumentation. Complexes were analyzed for their metal content, following a standard procedure [14] by decomposing the complexes with a mixture of HNO₃ and HCl followed by H₂SO₄. Sulfur and chloride were determined as BaSO₄ and AgCl, respectively. Carbon, hydrogen, and nitrogen were estimated on EA 1108 CHN Elemental Analyzer. Magnetic susceptibility measurements were made at room temperature on a Cahn-Faraday balance using Hg [Co(NCS)₄] as calibrant. Electronic spectra were recorded on a CARY-2390 UV-Visible Spectrophotometer as Nujol mulls [15]. IR Spectra were recorded in the 4000–400 cm⁻¹ region (KBr disc) on a JASCO FT/FR-5300 spectrophotometer. The ¹H and ¹³C NMR spectra were obtained in DMSO-D₆ on a JEOL FX-300 Q FT/NMR spectrometer using TMS as internal reference. ESR spectra were recorded on a X-band spectrometer model EPR-112 using DPPH as a ⟨g⟩ marker. The electrical conductivity of the pressed pellets of the complexes was obtained by a conventional two-probe method in the 303–383 K range with contact made on the pellet surfaces using graphite paint.

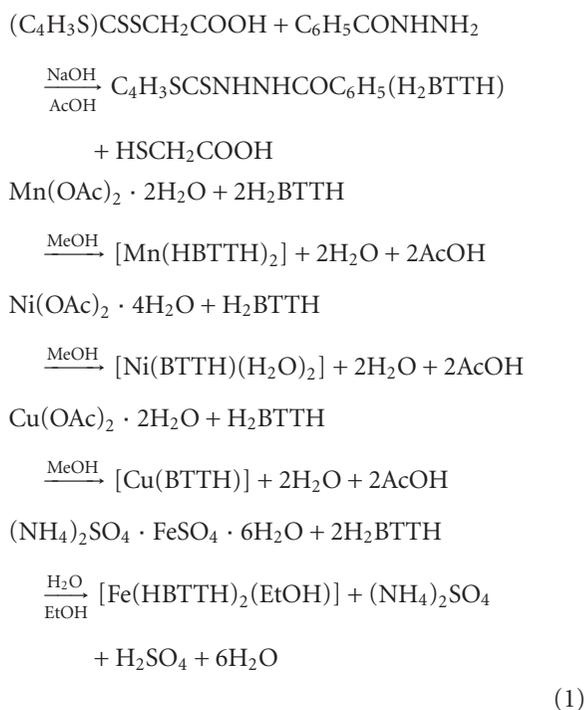
2.7. Bactericidal Screening. The antibacterial activity of the ligand and the complexes was evaluated using the disc diffusion technique [16]. A stock solution of 2000 μg cm⁻³ was made by dissolving 2 mg cm⁻³ of each compound in DMSO and it was serially doubled diluted up to five dilutions, giving the concentrations of 1000, 250, 125, and 62.5 μg cm⁻³. Filter paper (Whatman no.42) discs (6 mm dia) were soaked in these solutions of different concentrations and placed on nutrient agar plates. The plates were then incubated for 24 hrs at 37°C. The inhibition zones around the discs were measured after 24 hrs. Co-trimoxazole was used as a standard drug in the form of disc, containing trimethoprim = 1.25 μg and sulfamethoxazole = 23.75 μg per disc. The zones of

inhibition were found to be 20, 32, and 18 mm against *Staph aureus*, *Escherichia coli*, and *Pseudomonas aeruginosa*, respectively, in agreement with the sensitive zone reported in the literature.

2.8. Fungicidal Screening. The antifungal activity was evaluated by a drug dilution technique. The solution of the test compounds were prepared as described earlier to which sabouraud's dextrose broth and slightly turbid suspension of fungus in normal saline (10 μL) were added and placed in an incubator for 48–72 hrs. A turbidity in the solution indicated the growth of fungus, which is represented as – sign; however, a clear solution showed that there was no growth of fungus and is represented as + sign. The cases where compounds showed antifungal activity, no growth was observed in the solution. Amphotericin B was used as a standard drug.

3. Results and Discussion

All the complexes are insoluble in water, methanol, and ethanol but are soluble in polar organic solvents such as DMSO and DMF. It was determined by Job's method that the complexes having 1 : 1 metal-ligand stoichiometry (Table 1) are formed by loss of two protons from the ligand, generating a conjugated system. Because of steric considerations, all the four potential sites cannot be attached to a single metal and, therefore, the ligand binds in a polymeric fashion. The following equations represent the formation of the ligand and the complexes:



3.1. Magnetic Moments and Electronic Spectra. The magnetic moments and electronic spectral data of the complexes are given in Tables 1 and 2, respectively. [Mn(H BTTH)₂] shows a magnetic moment, 5.76 B.M. and exhibits a band

TABLE 1: Analytical data and physical properties of the complexes of N-benzoyl-N'-2-thiophenethiocarbohydrazide.

Compound empirical formula	(F.Wt.)	Colour/yield (%)	Found (Calcd.) %						M.P. (°C)	μ_{eff} (B.M.)
			M	C	H	N	S	N ₂ H ₄		
H ₂ BTTH	(262)	Cream	—	54.9	3.7	10.5	24.3	12.9	125	Diamag
C ₁₂ H ₁₀ N ₂ S ₂ O		(60)		(55.0)	(3.8)	(10.7)	(24.4)	(13.0)		
[Mn(HBTTH) ₂]	(560.93)	Yellow	9.7	51.2	3.1	9.9	17.0	11.6	276	5.76
C ₂₄ H ₁₈ N ₄ S ₃ O ₃ Mn		(55)	(9.8)	(51.3)	(3.2)	(10.0)	(17.1)	(11.7)		
[Fe(HBTTH) ₂ (EtOH)]	(607.86)	Dirty yellow	9.1	51.1	3.8	9.0	15.6	10.8	238	5.31
C ₂₆ H ₂₄ N ₄ S ₃ O ₄ Fe		(45)	(9.2)	(51.3)	(3.9)	(9.2)	(15.8)	(10.8)		
[Ni(BTTH)(H ₂ O) ₂]	(354.69)	Dark green	16.4	40.5	3.3	7.8	17.9	9.3	>364	3.06
C ₁₂ H ₁₂ N ₂ S ₂ O ₃ Ni		(55)	(16.5)	(40.6)	(3.4)	(7.9)	(18.0)	(9.4)		
[Cu(BTTH)]	(323.54)	Black	19.5	44.4	2.3	8.6	19.7	10.3	282	1.98
C ₁₂ H ₈ N ₂ S ₂ OCu		(60)	(19.6)	(44.5)	(2.5)	(8.7)	(19.8)	(10.4)		

TABLE 2: Electronic spectral bands and their assignments.

Compound	Band maxima (cm ⁻¹)	Assignments
H ₂ BTTH	30495, 35220	L
[Mn(HBTTH) ₂]	16140, 24620	⁶ A _{1g} → ⁴ T _{1g} , C.T.
[Fe(HBTTH) ₂ (EtOH)]	11770, 20840, 24380	⁵ T ₂ → ⁵ B ₁ , C.T.
[Ni(BTTH)(H ₂ O) ₂]	16140, 25000	³ A _{2g} (F) → ³ T _{1g} (F) (ν ₂), C.T.
[Cu(BTTH)]	15635, 21560, 27790	Envelope of ² B _{1g} → ² A _{1g} , ² B _{2g} , ² E _g , C.T.

C.T.: Charge-transfer; L: intraligand transition.

at 16140 cm⁻¹ assigned to the ⁶A_{1g} → ⁴T_{1g} transition (Figure 2) for the octahedral geometry [17]. The magnetic moment 5.31 B.M. and presence of bands at 11770 and 20840 cm⁻¹ owing to the ⁵T₂ → ⁵B₁ and charge-transfer transitions, respectively, suggests a high-spin square pyramidal geometry for [Fe(HBTTH)₂(EtOH)]. Ni(BTTH)(H₂O)₂ exhibits a magnetic moment of 3.06 B.M. and shows a band at 16140 cm⁻¹ (Figure 2) attributed to the ³A_{2g} (F) → ³T_{1g} (F)(ν₂) transition for a distorted octahedral geometry around Ni(II). [Cu(BTTH)] shows a magnetic moment of 1.98 B.M. indicating the presence of one unpaired electron. The complex shows a d-d band at 15635 cm⁻¹ due to the envelope of the ²B_{1g} → ²A_{1g}, ²B_{2g}, and ²E_g transitions, usually observed for square planar Cu(II) complexes [17].

3.2. IR Spectra. The important IR spectral bands and their assignments are given in Figure 3 and Table 3. The IR spectrum of H₂BTTH shows bands at 3125 and 3100 cm⁻¹ due to the presence of two NH groups. The bands at 1640, 1460, 1325, 1000, and 835 cm⁻¹ are assigned to ν(C=O), thioamide I [β(NH) + ν(CN)], thioamide II [ν(CN) + β(NH)], ν(N-N) and ν(C=S), respectively. The spectra of [Mn(HBTTH)₂] and [Fe(HBTTH)₂(EtOH)] show only one

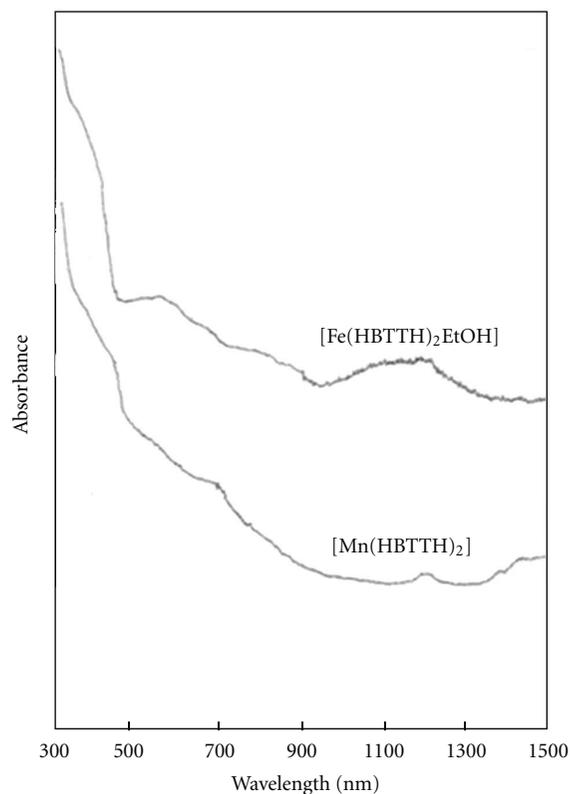


FIGURE 2: Electronic spectra.

peak at 3125 cm⁻¹ due to ν(NH), suggesting loss of one hydrazinic proton *via* enolisation/thioenolisation. A strong band at 1640 cm⁻¹ in the ligand due to ν(C=O) is found to be absent in these complexes, and in place of this a new band due to ν(N=C) of NCO appears, suggesting that enolic oxygen is involved in bonding. [Mn(HBTTH)₂] shows a negative shift of 15 cm⁻¹ in ν(C=S), suggesting an additional bonding through thione sulfur. Furthermore, the spectra of these complexes show a positive shift of 20 cm⁻¹ in ν(N-N)

TABLE 3: Important IR spectral bands (cm^{-1}) and their assignments.

Compound	$\nu(\text{OH})$	$\nu(\text{N-H})$	$\nu(\text{C=O})/\nu(\text{NCO})$	Thioamide I [$\beta(\text{NH}) + \nu(\text{CN})$]	Thioamide II [$\nu(\text{CN}) + \beta(\text{NH})$]	Thioamide IV $\nu(\text{C=S})/\nu(\text{C-S})$	$\nu(\text{N-N})$
H_2BTTH	—	3125, 3100	1640	1460	1325	835	1000
$[\text{Mn}(\text{HBTTH})_2]$	—	3125	1605	1485	1340	820	1020
$[\text{Fe}(\text{HBTTH})_2(\text{EtOH})]$	—	3120	1605	1485	1340	835	1020
$[\text{Ni}(\text{BTTH})(\text{H}_2\text{O})_2]$	3420	—	1580	1490	1395	740	1070
$[\text{Cu}(\text{BTTH})]$	—	—	1585	1490	1400	745	1070

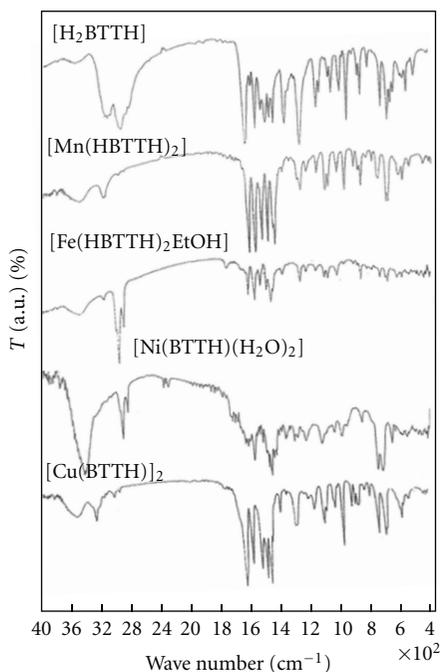
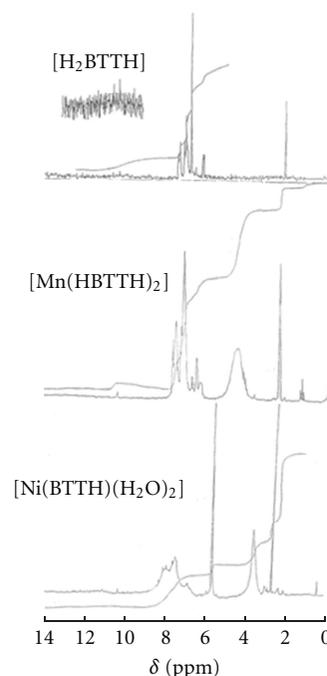


FIGURE 3: IR spectra.

FIGURE 4: ^1H NMR spectra.

indicating that one hydrazinic nitrogen is also involved in bonding. The presence of $\nu(\text{NH})$ at 3180 cm^{-1} and $\nu(\text{C=O})$ at 1625 cm^{-1} in $[\text{Cd}(\text{HBTTH})_2]$ indicates loss of NH proton *via* thioenolisation. Further, the bands at 1460 , 1325 , and 1000 cm^{-1} due to thioamide I, II and $\nu(\text{N-N})$ undergo positive shifts of 25 , 15 , and 20 cm^{-1} , respectively, showing the involvement of thiolato sulfur [18] and one hydrazinic nitrogen in bonding.

The IR spectra of $[\text{M}(\text{BTTH})(\text{H}_2\text{O})_2]$ ($\text{M} = \text{Co}(\text{II})$, $\text{Ni}(\text{II})$) and $[\text{M}(\text{BTTH})]$ ($\text{M} = \text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$) show the absence of both the $\nu(\text{NH})$, $\nu(\text{C=O})$, and $\nu(\text{C=S})$ bands and in place of these two new bands appear at 1580 and 745 cm^{-1} , due to $\nu(\text{N=C})$ of NCO and $\nu(\text{C-S})$ modes, respectively, suggesting that both $-\text{NH}-\text{NH}-$ protons are lost *via* enolisation and thioenolisation and bonding of the resulting enolic oxygen and thiolato sulfur takes place with the metal ion. Further, the thioamide I, II and $\nu(\text{N-N})$ bands at 1460 , 1325 , and 1000 in the free ligand undergo a positive shift of 33 , 65 , and 70 cm^{-1} , respectively, in the spectra of the

complexes [19] suggesting the involvement of these groups as bonding sites. These observations show the involvement of thiolato sulfur and both the hydrazinic nitrogens, in addition to the enolic oxygen in bonding. Thus, H_2BTTH acts as a binegative tetradentate ligand in the $1:1$ complexes.

3.3. NMR Spectra. The ^1H NMR spectrum of H_2BTTH (Figure 4, Table 4) in DMSO-d_6 shows a signal at δ 9.88 and 9.24 ppm due to the presence of $-\text{NH}-\text{NH}-$ protons which are lost on D_2O exchange. The protons due to the thiophene ring appear at δ 7.12 (s,1H), 7.32 (d,1H), and 7.56 (s,1H) ppm and the benzene ring protons appear as a multiplet at δ 6.64–6.92 (m,5H) ppm [20].

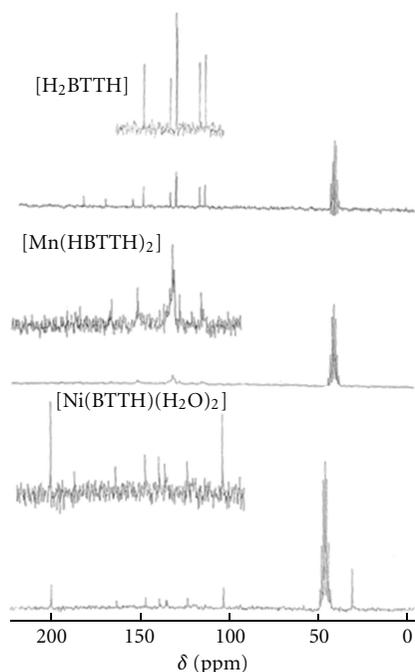
The NH signals are absent in the ^1H NMR spectrum of $[\text{Ni}(\text{BTTH})(\text{H}_2\text{O})_2]$, (Figure 4, Table 4) suggesting loss of both NH protons *via* enolization and thioenolization. The thiophene ring protons show three separate signals at δ 7.08 (q, 1H), 7.28 (d, 1H), and 7.52 (s, 1H) ppm and the benzene ring protons are observed at δ 6.61–6.88 (m,5H) ppm.

TABLE 4: ^1H NMR data of H_2BTTH and the complexes (δ , ppm).

Compound	Benzene ring	Thiophene ring	NH
H_2BTTH	6.64–6.92 (m, 5H)	7.12 (q, 1H), 7.32 (d, 1H), 7.56 (s, 1H)	11.06 (1H), 11.12 (1H)
$[\text{Ni}(\text{BTTH})(\text{H}_2\text{O})_2]$	6.61–6.88 (m, 5H)	7.08 (s, 1H), 7.28 (d, 1H), 7.52 (s, 1H)	—
$[\text{Mn}(\text{HBTTH})_2]$	6.62–6.90 (m, 5H)	7.04 (s, 1H), 7.30 (d, 1H), 7.51 (s, 1H)	11.16

TABLE 5: ^{13}C NMR data (δ , ppm).

Compound	>C=S	>C=O	C(2,6)	C(4)	C(3,5)	C'(2)	C'(3)	C'(4)	C'(5)
H_2BTTH	181	163	151, 146	136	126, 122	150	116	112	144
$[\text{Ni}(\text{BTTH})(\text{H}_2\text{O})_2]$	188	171	150, 147	134	130, 122	150	116	112	144
$[\text{Mn}(\text{BTTH})_2]$	181	174	152, 148	135	128, 123	150	117	112	146

FIGURE 5: ^{13}C NMR spectra.

The ^1H NMR spectrum of $[\text{Mn}(\text{HBTTH})_2]$ shows separate signals for the thiophene ring protons at δ 7.04 (s, 1H), 7.30 (d, 1H), and 7.51 (s, 1H) ppm and for benzene ring protons at δ 6.62–6.90 (m, 5H) ppm. The two signals appearing at δ 9.42 and 4.16 ppm are due to the presence of $-\text{NH}-\text{C}(\text{O})$ and $-\text{N}=\text{C}(\text{SH})$ protons, respectively (Figure 4, Table 4). The latter is formed due to the thioenolization of the ligand. All the thiophene and benzene ring protons are observed nearly at the same position in the complex as compared to those of the H_2BTTH , suggesting non-involvement of the ring sulphur in bonding.

The ^{13}C NMR spectrum of $[\text{H}_2\text{BTTH}]$ (Figure 5, Table 5) shows eleven signals, of which two signals at δ 181 and 163 ppm are due to the C=S and C=O carbons, respectively. The chemical shifts for the benzene and thiophene ring carbons in H_2BTTH are (δ , ppm) C(2, 6) 151, 146, C(4) 136,

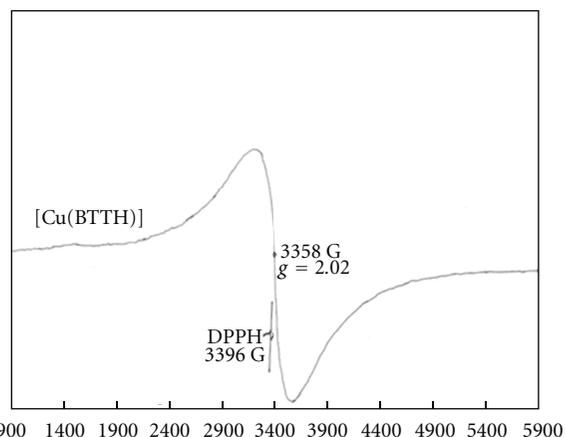


FIGURE 6: ESR spectra.

C(3,5) 126, 122, C'(2) 150, C'(3) 116, C'(4) 112, and C'(5) 144.

The ^{13}C NMR spectrum of $[\text{Ni}(\text{BTTH})(\text{H}_2\text{O})_2]$ also shows eleven signals (Figure 5, Table 5). The chemical shifts for the ring carbons are: (δ , ppm) C(2,6) 150, 147, C(4) 134, C(3,5) 130, 122, C'(2) 150, C'(3) 116, C'(4) 112, and C'(5) 144. The signals at δ 188 and 171 ppm in $[\text{Ni}(\text{BTTH})(\text{H}_2\text{O})_2]$ show downfield shift of 7 and 8 ppm, respectively, as compared to the ligand, suggesting the formation of C–S and C–O groups from the ligand on thioenolization and enolization, respectively.

The ^{13}C NMR spectrum of $[\text{Mn}(\text{HBTTH})_2]$ shows separate signals for all eleven carbons (Figure 5, Table 5). The chemical shifts for the ring carbons are: (δ , ppm) C(2,6) 152, 148, C(4) 135, C(3,5) 128, 123, C'(2) 150, C'(3) 117, C'(4) 112, and C'(5) 146. The signal at 181 ppm due to C=S carbons shows nearly the same chemical shifts as for the ligand, suggesting that the double bond character is retained in the complex. The signals at δ 174 ppm in the complex show downfield shift of 11 ppm as compared to the ligand, suggesting the involvement of C=S in bonding.

3.4. ESR Spectra. The room temperature solid state ESR spectrum of $[\text{Cu}(\text{BTTH})]$ yields a broad signal with $\langle g \rangle$

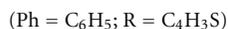
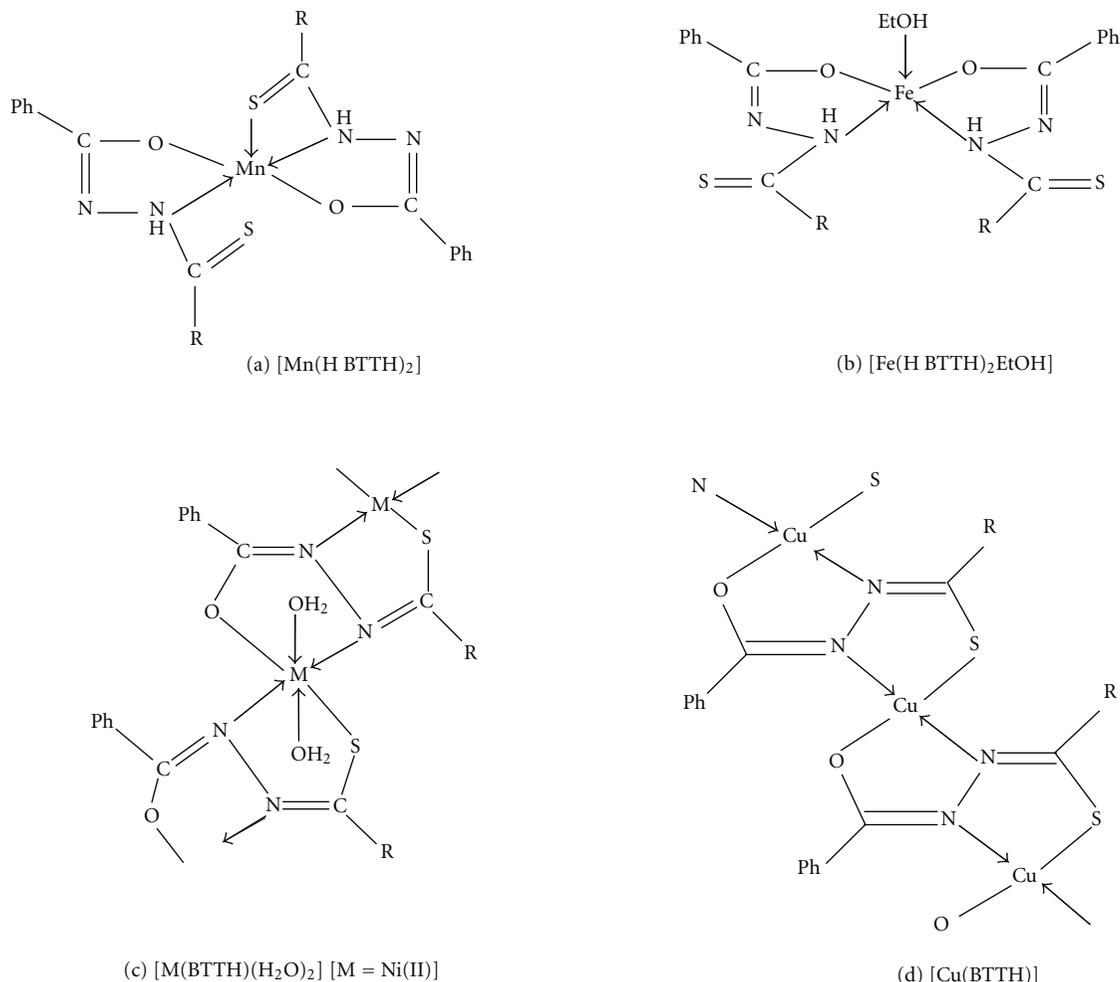


FIGURE 7: Proposed structure of the complexes.

value of 2.02 characteristic of square planar geometry around Cu(II) (Figure 6).

3.5. Bactericidal Screening. The antibacterial activity of H_2 BTTH (Table 6) and its complexes has been tested against *S. aureus*, *E. coli*, and *P. aeruginosa*. H_2 BTTH, $[\text{Mn}(\text{H NTTH})_2]$ and $[\text{Cu}(\text{BTTH})]$ show antibacterial activity starting from 62.5 to 2000 $\mu\text{g cm}^{-3}$ against *S. aureus* and the activity increases with an increase in the concentration. The ligand is found to be active at a concentration of 1000 $\mu\text{g cm}^{-3}$ against *E. coli*. $[\text{Mn}(\text{H NTTH})_2]$ and $[\text{Cu}(\text{BTTH})]$ also show activity against *E. coli* at 500 and 250 $\mu\text{g cm}^{-3}$, respectively. Only $[\text{Cu}(\text{BTTH})]$ has been found active against *P. aeruginosa* at 250 $\mu\text{g cm}^{-3}$.

3.6. Fungicidal Screening. The antifungal screening results (Table 7) show that free H_2 BTTH is active from 125

to 2000 $\mu\text{g cm}^{-3}$ against *C. kefri*. However, $[\text{Mn}(\text{HBTTH})_2]$ and $[\text{Cu}(\text{BTTH})]$ are found to be active even at a lower concentration of 62.5 $\mu\text{g cm}^{-3}$ against *C. kefri*. H_2 BTTH is active from 250 to 2000 $\mu\text{g cm}^{-3}$ against *C. albicans*. However, $[\text{Mn}(\text{HBTTH})_2]$ and $[\text{Cu}(\text{BTTH})]$ are found to be active even at a lower concentration of 62.5 $\mu\text{g cm}^{-3}$ against *C. albicans*.

On the basis of physicochemical studies and the foregoing discussion, the proposed structures of the complexes is shown in Figure 7.

4. Conclusion

The magnetic and electronic spectral studies suggest square planar geometry for $[\text{Cu}(\text{BTTH})]$ and octahedral geometry for rest of the complexes. The infrared spectral studies of the 1 : 1 deprotonated complexes suggest bonding through enolic oxygen, thiolato sulfur, and both the hydrazinic nitrogens.

TABLE 6: Antibacterial activity of H₂ BTTH and its complexes.

Compound	Bacteria*	Concentration ($\mu\text{g cm}^{-3}$)					
		62.5	125	250	500	1000	2000
H ₂ BTTH	a	(12) ⁺	(18) ⁺	(20) ⁺	(22) ⁺	(24) ⁺	(26) ⁺
	b	(14) ⁻	(19) ⁻	(17) ⁻	(18) ⁻	(16) ⁺	(18) ⁺
	c	—	—	—	—	—	—
[Mn(H BTTH) ₂]	a	(14) ⁺	(20) ⁺	(22) ⁺	(24) ⁺	(26) ⁺	(27) ⁺
	b	—	—	(9) ⁻	(15) ⁺	(17) ⁺	(19) ⁺
	c	—	—	—	—	—	—
[Cu(BTTH)]	a	(11) ⁺	(12) ⁺	(16) ⁺	(18) ⁺	(19) ⁺	(20) ⁺
	b	—	(10) ⁻	(12) ⁺	(17) ⁺	(19) ⁺	(21) ⁺
	c	(15) ⁻	(16) ⁻	(18) ⁺	(19) ⁺	(21) ⁺	(22) ⁺
DMSO	a	—	—	—	—	—	—
	b	—	—	—	—	—	—
	c	—	—	—	—	—	—

*a: *Staph aureus*; b: *Escherichia coli*; c: *Pseudomonas aeruginosa*. Control: Co-trimoxazole. + and -: over the parentheses indicate the zone of inhibition and no zone of inhibition, respectively.

TABLE 7: Antifungal activity of H₂ BTTH and its complexes.

Compound	Fungus*	Concentration ($\mu\text{g cm}^{-3}$)					
		62.5	125	250	500	1000	2000
H ₂ BTTH	a	—	+	+	+	+	+
	b	—	—	+	+	+	+
[Mn(HNTTH) ₂]	a	+	+	+	+	+	+
	b	+	+	+	+	+	+
[Cu(BTTH)]	a	+	+	+	+	+	+
	b	+	+	+	+	+	+
DMSO	a	—	—	—	—	—	—
	b	—	—	—	—	—	—

*a: *Candida kefir*; b: *Candida albicans*. Control: Amphotericin B. Growth and no growth of fungi are represented by + and - sign, respectively.

Thus, H₂BTTH acts as a binegative tetradentate ligand. The ESR spectrum of [Cu(BTTH)] shows that the unpaired electron is present in the d_{x²-y²} orbital of Cu(II).

Acknowledgments

Financial assistance from Indian School of Mines, Dhanbad under FRS to M. Yadav is gratefully acknowledged.

References

- [1] R. B. Rastogi, M. Yadav, and K. Singh, "Synthesis and spectroscopic studies of molybdenum and tungsten complexes of N-isonicotiny-N'-aryl-thiosemicarbazides," *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, vol. 33, no. 9, pp. 1585–1596, 2003.
- [2] D. X. West, G. A. Bain, R. J. Butcher et al., "Structural studies of three isomeric forms of heterocyclic N(4)-substituted thiosemicarbazones and two nickel(II) complexes," *Polyhedron*, vol. 15, no. 4, pp. 665–674, 1996.
- [3] H. Berlado, L. P. Boy, and D. X. West, "Copper(II) and nickel(II) complexes of glyoxaldehyde bisN(3)-substituted thiosemicarbazones," *Transition Metal Chemistry*, vol. 23, no. 1, pp. 67–71, 1997.
- [4] D. X. West, M. M. Salberg, G. A. Bain, and A. E. Liberta, "Nickel(II) and copper(II) complexes of 5-substituted-salicylaldehyde thiosemicarbazones," *Transition Metal Chemistry*, vol. 22, no. 2, pp. 180–184, 1997.
- [5] M. Akbar Ali and S. E. Livingstone, "Metal complexes of sulphur-nitrogen chelating agents," *Coordination Chemistry Reviews*, vol. 13, no. 2-3, pp. 101–132, 1974.
- [6] N. K. Singh, N. Singh, A. Sodhi, A. Shrivastava, and G. C. Prasad, "Synthesis, characterization and antitumour studies on N-salicyl-N'-thiobenzohydrazide and its copper(II) complex," *Transition Metal Chemistry*, vol. 21, no. 6, pp. 556–559, 1996.
- [7] H. Singh, L. D. S. Yadav, and S. B. S. Mishra, "Studies on some antifungal transition metal chelates of N-(5-phenyl-1, 3, 4-thiadiazol-2-yl) dithiocarbamic acid," *Journal of Inorganic and Nuclear Chemistry*, vol. 43, no. 7, pp. 1701–1704, 1981.
- [8] K. S. A. Melha, "In-vitro antibacterial, antifungal activity of some transition metal complexes of thiosemicarbazone Schiff

- base (HL) derived from N⁴-(7'-chloroquinolin-4'-ylamino)thiosemicarbazide," *Journal of Enzyme Inhibition and Medicinal Chemistry*, vol. 23, no. 4, pp. 493–503, 2008.
- [9] M. M. Singh, R. B. Rastogi, B. N. Upadhyay, and M. Yadav, "Thiosemicarbazide, phenyl isothiocyanate and their condensation product as corrosion inhibitors of copper in aqueous chloride solutions," *Materials Chemistry and Physics*, vol. 80, no. 1, pp. 283–293, 2003.
- [10] R. B. Rastogi, M. M. Singh, M. Yadav, and K. Singh, "Substituted thiobiurets and their molybdenum and tungsten complexes as corrosion inhibitors for mild steel in 1.0 N sulphuric acid," *Indian Journal of Engineering and Materials Sciences*, vol. 10, no. 2, pp. 155–160, 2003.
- [11] R. B. Rastogi, M. Yadav, and A. Bhattacharya, "Application of molybdenum complexes of 1-aryl-2,5-dithiohydrazodicarbonamides as extreme pressure lubricant additives," *Wear*, vol. 252, no. 9-10, pp. 686–692, 2002.
- [12] R. W. Bost and O. L. Shealy, " β -Dimethylaminoethyl esters of organic dithio acids. II. Esters of aromatic dithio acids," *Journal of the American Chemical Society*, vol. 73, no. 1, pp. 25–28, 1951.
- [13] K. A. Jensen and C. Pedersen, "Studies of thioacids and their derivatives. II. Carboxymethyl dithioesters," *Acta Chemica Scandinavica*, vol. 15, pp. 1087–1096, 1961.
- [14] A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, ELBS, Longman, London, UK, 3rd edition, 1969.
- [15] R. H. Lee, E. Griswold, and J. Kleinberg, "Studies on the stepwise controlled decomposition of 2,2'-bipyridine complexes of cobalt(II) and nickel(II) chlorides," *Inorganic Chemistry*, vol. 3, no. 9, pp. 1278–1283, 1964.
- [16] V. S. Shivankar, R. B. Vaidya, S. R. Dharwadkar, and N. V. Thakkar, "Synthesis, characterization, and biological activity of mixed ligand Co(II) complexes of 8-hydroxyquinoline and some amino acids," *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, vol. 33, no. 9, pp. 1597–1622, 2003.
- [17] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, The Netherlands, 2nd edition, 1984.
- [18] E. Sinn and C. M. Harris, "Schiff base metal complexes as ligands," *Coordination Chemistry Reviews*, vol. 4, no. 4, pp. 391–422, 1969.
- [19] R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, John Wiley & Sons, New York, NY, USA, 4th edition, 1991.
- [20] G. R. Burns, "Metal complexes of thiocarbohydrazide," *Inorganic Chemistry*, vol. 7, no. 2, pp. 277–283, 1968.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

