Research Article

Synthesis, Characterization, and Biological Activity of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) Complexes of N-Thiophenoyl-N'-Phenylthiocarbohydrazide

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Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) complex of N-thiophenoyl-N'-phenylthiocarbohydrazide (H_2 TPTH) 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 $[Mn(H\ TPTH)_2]$, $[Co(TPTH)(H_2O)_2]$, $[Ni(TPTH)(H_2O)_2]$, $[Cu(TPTH)]$, $[Zn(H\ TPTH)]$, $[Cd(H\ TPTH)_2]$, and $[Fe(H\ TPTH)_2(EtOH)]$. The magnetic and electronic spectral studies suggest square planar geometry for $[Cu(TPTH)]$, tetrahedral geometry for $[Zn(TPTH)]$ and $[Cd(H\ TPTH)_2]$, 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. Thus, H_2 TPTH acts as a bidentate ligand. H_2 TPTH 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 are also used as corrosion inhibitors [9, 10] and extreme pressure lubricant additives [11]. Keeping in view the above biological activity of the ligands, we planned to undertake the synthesis, characterization, antibacterial, and antifungal activity of the 3d-metal complexes of N-thiophenoyl-N'-phenylthiocarbohydrazide (H_2 TPTH) (Figure 1), having oxygen and sulphur as donors. 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 carboxymethyldithiobenzoate [13] were prepared by literature methods.

2.2. Preparation of N-Thiophenoyl-N'-Phenylthiocarbohydrazide (H_2 TPTH). N-thiophenoyl-N'-phenylthiocarbohydrazide (H_2 TPTH) was prepared by mixing solutions of 2-thiophene carboxylic acid hydrazide (20 mmol) and carboxymethyldithiobenzoate (20 mmol) each dissolved separately in 50 mL of 0.5 N NaOH and allowing the mixture to

FIGURE 1: H₂ TPTH.

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 H₂O, dried, and recrystallized from EtOH.

2.3. Preparation of the Complexes

2.3.1. [M(H TPTH)₂]. The complexes of the type [M(H TPTH)₂] [M = Mn(II), Cd(II)] were prepared by boiling together the methanolic solutions (25 mL) of the respective M(OAc)₂·nH₂O (1 mmol) and H₂ TPTH (2 mmol) for 1 h under reflux. The precipitated complexes were filtered, washed with methanol and dried *in vacuo*.

2.3.2. [M(TPTH)(H₂O)₂] and [M(TPTH)]. The complexes of the type [M(TPTH)(H₂O)₂] [M = Co(II), Ni(II)] and [M(TPTH)] [M = Cu(II), Zn(II)] were prepared by boiling together the methanolic solutions (25 mL) of the respective M(OAc)₂·nH₂O (1 mmol) and H₂ TPTH (1 mmol) for about 1 h under reflux. The precipitated complexes were filtered, washed with methanol, and dried *in vacuo*.

2.3.3. [Fe(H TPTH)₂(EtOH)]. [Fe(H TPTH)₂(EtOH)] was prepared by boiling together an aqueous-methanolic solution (25 mL) of (NH₄)₂SO₄·FeSO₄·6H₂O (1 mmol) which was prepared in the presence of a small amount of ascorbic acid and H₂ TPTH (2 mmol) in ethanol (25 mL) for about 1 h. The precipitated complex was filtered, washed with water, ethanol, and dried *in vacuo*.

2.4. Instrumentation. Complexes were analysed for their metal content, following a standard procedure [14] by decomposing the complexes with a mixture of HNO₃ and HCl followed by H₂SO₄. Sulphur and chloride were determined as BaSO₄ and AgCl, respectively. Carbon, hydrogen, and nitrogen were estimated on a EA 1108 CHN Elemental Analyser. 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 JA SCO 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. A Keith ley 236 SMU was used to measure the resistance.

2.5. 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 upto 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. Cotrimoxazole 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.

2.6. Fungicidal Screening. The antifungal activity was evaluated by a drug dilution technique. The solution of the test compounds was 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. [Mn(H TPTH)₂] and [Co(TPTH)(H₂O)₂] are more soluble in DMSO than other complexes. The complexes having 1 : 1 metal-ligand stoichiometry (Table 1) are formed by loss of two protons from the legend, 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. Accordingly, the 1 : 1 complexes show high-melting points. The following equations represent the formation of the ligand and the complexes:

M = Mn(II), Cd(II); $n = 4, 2$

M = Co(II), Ni(II)

M = Cu(II), Zn(II); $n = 1, 2$

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. $[\text{Mn(H TPTH)}_2]$ shows a magnetic moment, 5.76 B.M. and exhibits a band at 16140 cm^{-1} assigned to the ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ transition 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 ${}^5\text{T}_2 \rightarrow {}^5\text{B}_1$ and charge-transfer transitions, respectively, suggests a high-spin square pyramidal geometry for $[\text{Fe(H TPTH)}_2(\text{EtOH})]$. $[\text{Co(TPTH)(H}_2\text{O)}_2]$ shows a magnetic moment of 4.92 B.M. and exhibits a $d-d$ band at 16675 cm^{-1} , assigned to the ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P}) (\nu_3)$ transition for a distorted octahedral geometry. $[\text{Ni(TPTH)(H}_2\text{O)}_2]$ exhibits a magnetic moment of 3.06 B.M. and shows a band at 16140 cm^{-1} attributed to the ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F}) (\nu_2)$ transition for a distorted octahedral geometry around Ni(II). $[\text{Cu(TPTH)}]$ 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 ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$, ${}^2\text{B}_{2g}$ and ${}^2\text{E}_g$ 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 Table 3. The IR spectrum of $\text{H}_2 \text{ TPTH}$ 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 $\nu(\text{C=O})$, thioamide I $[\beta(\text{NH}) + \nu(\text{CN})]$, thioamide II $[\nu(\text{CN}) + \beta(\text{NH})]$, $\nu(\text{N-N})$, and $\nu(\text{C=S})$, respectively. The spectra of $[\text{Mn(H TPTH)}_2]$ and $[\text{Fe(H TPTH)}_2(\text{EtOH})]$ show only one peak at 3125 cm^{-1} due to $\nu(\text{NH})$, suggesting loss of one hydrazinic proton via enolisation/thioenolisation. A strong band at 1640 cm^{-1} in the ligand due to $\nu(\text{C=O})$ is found to be absent in these complexes, and in place of this a new band due to $\nu(\text{N=C})$ of NCO appears, suggesting that enolic oxygen is involved in bonding. $[\text{Mn(H TPTH)}_2]$ shows a negative shift of 15 cm^{-1}

in $\nu(\text{C=S})$, suggesting an additional bonding through thione sulfur. Furthermore, the spectra of these complexes show a positive shift of 20 cm^{-1} in $\nu(\text{N-N})$ 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 $[\text{Cd(H TPTH)}_2]$ indicates loss of NH proton via thioenolisation. Further, the band 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 $[\text{M(TPTH)(H}_2\text{O)}_2]$ ($\text{M} = \text{Co(II), Ni(II)}$) and $[\text{M(TPTH)}]$ ($\text{M} = \text{Cu(II) and Zn(II)}$) 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, $\text{H}_2 \text{ TPTH}$ acts as a binegative tetradentate ligand in the $1:1$ complexes.

3.3. NMR Spectra. The ${}^1\text{H}$ NMR spectrum of $\text{H}_2 \text{ TPTH}$ (Table 4) in $\text{DMSO}-d_6$ shows a signal at δ 9.86 and 9.72 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 ${}^1\text{H}$ NMR spectrum of $[\text{Ni(TPTH)(H}_2\text{O)}_2]$, 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.

The ${}^1\text{H}$ NMR spectrum of $[\text{Mn(H TPTH)}_2]$ 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 9.66 and 4.16 ppm are due to the presence of $-\text{NH}-\text{C(O)}$ and $-\text{N=C(SH)}$ protons, respectively. 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 $\text{H}_2 \text{ TPTH}$, suggesting noninvolvement of the ring sulphur in bonding.

The ${}^{13}\text{C}$ NMR spectrum of $(\text{H}_2 \text{ TPTH})$ (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 $\text{H}_2 \text{ TPTH}$ are (δ , ppm) C' (2, 6) 151, 146, C' (4) 136, C' (3, 5) 126, 122, C (2) 150, C (3) 116, C (4) 112, and C (5) 144.

TABLE 1: Analytical data and physical properties of the complexes N-thiophenyl-N'-phenylthiocarbohydrazide (H₂ TPTH).

Compound empirical formula	Colour/Yield (%)	M	C	H	N	S	N ₂ H ₄	M.P. (°C)	μ_{eff} (B.M.)
H ₂ TPTH C ₁₂ H ₁₀ N ₂ S ₂ O	Cream (60)	—	54.9 (55.0)	3.7 (3.8)	10.5 (10.7)	24.3 (24.4)	12.9 (13.0)	125	Diamag
[Mn(H TPTH) ₂] C ₂₄ H ₁₈ N ₄ S ₃ O ₃ Mn	Yellow (55)	9.7 (9.8)	51.2 (51.3)	3.1 (3.2)	9.9 (10.0)	17.0 (17.1)	11.6 (11.7)	276	5.76
[Fe(H TPTH) ₂ (Et)] C ₂₆ H ₂₄ N ₄ S ₃ O ₄ Fe	Dirty yellow (45)	9.1 (9.2)	51.1 (51.3)	3.8 (3.9)	9.0 (9.2)	15.6 (15.8)	10.8 (10.8)	238	5.31
[Co(TPTH) (H ₂ O)] C ₁₂ H ₁₂ N ₂ S ₂ O ₃ Co	Brick red (60)	16.4 (16.6)	40.4 (40.6)	3.3 (3.5)	7.7 (7.9)	17.8 (18.0)	9.3 (9.4)	>322	4.94
[Ni(TPTH) (H ₂ O) ₂] C ₁₂ H ₁₂ N ₂ S ₂ O ₃ Ni	Dark green 55)	16.4 (16.5)	40.5 (40.6)	3.3 (3.4)	7.8 (7.9)	17.9 (18.0)	9.3 (9.4)	>364	3.06
[Cu(TPTH)] C ₁₂ H ₈ N ₂ S ₂ OCu	Black (60)	19.5 (19.6)	44.4 (44.5)	2.3 (2.5)	8.6 (8.7)	19.7 (19.8)	10.3 (10.4)	282	1.98
[Zn(TPTH)] C ₁₂ H ₈ N ₂ S ₂ OZn	White (45)	19.9 (20.1)	44.2 (44.3)	2.4 (2.5)	8.4 (8.6)	19.5 (19.7)	10.2 (10.3)	>363	Diamag
[Cd(H TPTH) ₂] C ₂₄ H ₁₈ N ₄ S ₃ O ₃ Cd	White (50)	18.1 (18.2)	46.5 (46.6)	2.8 (2.9)	9.0 (9.1)	15.3 (15.5)	10.5 (10.6)	256	Diamag

TABLE 2: Electronic spectral bands and their assignments.

Compound	Band maxima (cm ⁻¹)	Assignments
H ₂ TPTH	30495, 35220	L
[Mn(H TPTH) ₂]	16140, 24620	⁶ A _{1g} → ⁴ T _{1g} , C.T.
[Fe(H TPTH) ₂ (Et(OH))]	11770, 20840, 24380	⁵ T ₂ → ⁵ B ₁ , C.T.
[Co(TPTH)(H ₂ O) ₂]	16675, 24080	⁴ T _{1g} (F) → ⁴ T _{1g} (P) (ν ₃), C.T.
[Ni(TPTH)(H ₂ O) ₂]	16140, 25000	³ A _{2g} (F) → ³ T _{1g} (F) (ν ₂), C.T.
[Cu(TPTH)]	15635, 21560, 27790	Envelope of ² B _{1g} → ² A _{1g} , ² B _{2g} , ² E _g , C.T.
[Zn(TPTH)]	25650	C.T.
[Cd(H TPTH) ₂]	27035	C.T.

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

TABLE 3: Important IR spectral bands (cm⁻¹) and their assignments.

Compound	ν(OH)	ν(N-H)	ν(C=O)/ ν(NCO)	Thioamide I [β(NH) + ν(CN)]	Thioamide II [ν(CN) + β(NH)]	Thioamide IV ν(C=S)/ν(C-S)	ν (N-N)
H ₂ TPTH	—	3125, 3100	1640	1460	1325	835	1000
[Mn(H TPTH) ₂]	—	3125	1605	1485	1340	820	1020
[Fe(H TPTH) ₂ (EtOH)]	—	3120	1605	1485	1340	835	1020
[Co(TPTH)(H ₂ O) ₂]	3425	—	1580	1490	1395	745	1070
[Ni(TPTH)(H ₂ O) ₂]	3420	—	1580	1490	1395	740	1070
[Cu(TPTH)]	—	—	1585	1490	1400	745	1070
[Zn(TPTH)]	—	—	1585	1490	1395	760	1070
[Cd(H TPTH) ₂]	—	3180	1625	1485	1340	740	1020

TABLE 4: ¹H-NMR data of H₂ TPTH and the complexes (δ, ppm).

Compound	Benzene ring	Thiophene ring	NH
H ₂ TPTH	6.64–6.92 (m, 5H)	7.12 (q, 1H), 7.32 (d, 1H), 7.56 (s, 1H)	9.86 (1H), 9.72 (1H)
[Ni(TPTH)(H ₂ O) ₂]	6.61–6.88 (m, 5H)	7.08 (s, 1H), 7.28 (d, 1H), 7.52 (s, 1H)	—
[Mn(H TPTH) ₂]	6.62–6.90 (m, 5H)	7.04 (s, 1H), 7.30 (d, 1H), 7.51 (s, 1H)	9.66

TABLE 5: ¹³C-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 ₂ TPTH	181	163	151, 146	136	126, 122	150	116	112	144
[Ni(TPTH)(H ₂ O) ₂]	188	171	150, 147	134	130, 122	150	116	112	144
[Mn(TPTH) ₂]	181	174	152, 148	135	128, 123	150	117	112	146

The ¹³C-NMR spectrum of [Ni(TPTH)(H₂O)₂] also shows eleven signals. 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 [Ni(TPTH)(H₂O)₂] shows 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 ¹³C-NMR spectrum of [Mn(H TPTH)₂] shows separate signals for all eleven carbons. 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 show 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 shows downfield shift of 11 ppm as compared to the ligand, suggesting the the involvement of C=S in bonding.

3.4. ESR Spectra. The room temperature solid state ESR spectrum of [Cu(TPTH)] yields a broad signal with ⟨g⟩ value of 2.072 characteristic of square planar geometry around Cu(II).

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

Compound	Bacteria*	Concentration ($\mu\text{g cm}^{-3}$)					
		62.5	125	250	500	1000	2000
H ₂ TPTH	a	(16) ⁺	(27) ⁺	(22) ⁺	(24) ⁺	(23) ⁺	(24) ⁺
	b	(9) ⁻	(11) ⁻	(14) ⁻	(16) ⁻	(17) ⁺	(18) ⁺
	c	—	—	—	—	—	—
[Mn(H TPTH) ₂]	a	(9) ⁻	(11) ⁻	(15) ⁻	(17) ⁺	(17) ⁺	(18) ⁺
	b	—	—	(9) ⁻	(14) ⁻	(16) ⁻	(18) ⁺
	c	—	—	—	—	—	—
[Zn(TPTH)]	a	—	—	—	—	—	—
	b	—	—	(10) ⁻	(13) ⁻	(16) ⁻	(17) ⁺
	c	—	—	—	—	—	—
[Cu(TPTH)]	a	—	(11) ⁻	(15) ⁻	(16) ⁻	(17) ⁺	(18) ⁺
	b	—	(10) ⁻	(12) ⁻	(15) ⁻	(17) ⁺	(17) ⁺
	c	(13) ⁻	(14) ⁻	(16) ⁻	(17) ⁺	(18) ⁺	(18) ⁺

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

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

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

* a: *Candida keftri*; b: *Candida albicans*. Control: amphotericin B. Growth and no growth of fungi are represented by — and + sign, respectively.

3.5. Bactericidal Screening. The antibacterial activity of H₂ TPTH (Table 6) and its complexes have been tested against *S. aureus*, *E. coli*, and *P. aeruginosa*. H₂ TPTH shows 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*. [Mn(H TPTH)₂], and [Cu(TPTH)] show the activity at higher concentration namely 500, 1000, and 2000 $\mu\text{g cm}^{-3}$ against *S. aureus*. [Mn(H TPTH)₂], [Zn(TPTH)], and [Cu(TPTH)] also show activity against *E. coli* at 2000 $\mu\text{g cm}^{-3}$. Only [Cu(TPTH)] has been found active against *P. aeruginosa* at 500 $\mu\text{g cm}^{-3}$. [Zn(TPTH)] shows activity against *E. coli* but is inactive against *S. aureus* and *P. aeruginosa* at 2000 $\mu\text{g cm}^{-1}$.

3.6. Fungicidal Screening. The antifungal screening results (Table 7) show that free H₂ TPTH is active from 125 to 2000 $\mu\text{g cm}^{-3}$ against *C. keftri*. However, [Mn(H TPTH)₂], [Cu(TPTH)], and [Zn(TPTH)] are found to be active even at a lower concentration of 62.5 $\mu\text{g cm}^{-3}$ against *C. keftri*. [Zn(TPTH)], [Mn(H TPTH)₂] and [Cu(TPTH)] does not show activity at any concentration against *C. albicans*.

On the basis of physicochemical studies and the foregoing discussion, the proposed structures of the complexes are shown in Figure 2.

4. Conclusion

The magnetic and electronic spectral studies suggest square planar geometry for [Cu(TPTH)], tetrahedral geometry for [Zn(TPTH)] and [Cd(H TPTH)₂], and octahedral geometry for the 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. The ESR spectrum of [Cu(TPTH)] shows that the unpaired electron is present in the $d_{x^2-y^2}$ orbital of Cu(II). The ligand H₂ TPTH shows antibacterial activity against *S. aureus*, *E. coli* and *P. aeruginosa* and antifungal activity against *C. keftri* and *C. albicans*. The complexes Mn(H TPTH)₂, [Cu(TPTH)] and [Zn(TPTH)] also show antibacterial activity against the bacteria *S. aureus*, *E. coli*, and *P. aeruginosa* and antifungal activity against the *C. keftri* and *C. albicans*.

FIGURE 2: Proposed structure of the complexes.

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