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Synthesis, Antioxidant, and Antibacterial Studies of Zn(II), Cd(II), and Hg(II) Complexes with 3-Formylpyridinethiosemicarbazone and Its N^4-Methyl Analogue

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A**bstract**—Evaluation of stability constants of the complexes formed in solution by the biologically important ligands and metal ions can aid in understanding the application of metal complexes in chelation therapy. Hence, complexation equilibrium studies of the ligands (L), 3-formylpyridinethiosemicarbazone (H3FPT) and 3-formylpyridine-N^4-methylthiosemicarbazone (H3FP4MT) with Zn(II) and Cd(II) metal ions (M) are carried out in 70% v/v DMF–water medium at 0.1M KNO_3 ionic strength and the stability constants are determined pH-metrically at 303 K. The binary complexes are formed in 1 : 1 (M : L) ratio and are fairly stable. The binary complexes of H3FPT and H3FP4MT (L) with Zn(II), Cd(II) and Hg(II) ions are synthesized and characterized by various analytical and spectral techniques including elemental analysis, molar conductance, LC-MS, TGA, IR and ^{1}H NMR spectroscopy. According to the accumulated information, the complexes are polymeric $(ML)_n$ with n > 2, except that of Hg(II)–H3FP4MT, which is ML_2. The antioxidant activity of the ligands and their Zn(II) and Hg(II) complexes demonstrate higher activity than their corresponding ligands Cd(II) complexes. Antibacterial activity of the ligands and the complexes is tested against gram positive: *Staphylococcus aureus, Bacillus subtilis* and gram negative: *Escherichia coli* and *Klebsiella pneumonia* bacterial strains. Activity of complexes is determined to be higher than that of the corresponding free ligands.

Keywords: metal complexes, pH-metry, stability constant, characterization, antioxidant, antibacterial

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INTRODUCTION

2-Formylpyridinethiosemicarbazone demonstrates anticancer activity, while 3-aminopyridine-2-carboxaldehydethiosemicarbazone (Triapine) and 2-acetaminobenzaldehydethiosemicarbazone (thiacetazone) are known for their antitubercular activity [1,2]. Complexation of these organic compounds with metal ions may increase their activity and/or decrease their side effects [3]. 3-Formylpyridine thiosemicarbazone with isoniazid is used as antitubercular drug and its activity is influenced by the nature of the substituent on thiosemicarbazone moiety. Presence of an additional potential binding site along with bulky groups at the N^4 position of the thiosemicarbazone moiety can significantly enhance its biological activity [4, 5]. The present study is devoted to the formation and stability of binary complexes of 3-formylpyridinethiosemicarbazone (H3FPT) and 3-formylpyridine-N^4-methylthiosemicarbazone (H3FP4MT) (L) with Zn(II) and Cd(II) ions (M) in 70% v/v DMF-water medium at 303K and 0.1M KNO_3 ionic strength. Herein the synthesis, characterization, antioxidant and antibacterial activities of Zn(II), Cd(II) and Hg(II) complexes are also presented.

RESULTS AND DISCUSSION

pH-Metric equilibrium studies. *Determination of proton dissociation constants (*pK_a*) of the ligands.* The pH-metric titration curves are presented in Fig. 1. From the acid vs base and the acid+ligand vs base titration curves, the proton dissociation constant (pK_a) was determined [6-8]. On the basis of the linear plots of log $[(1 - \bar{n}_A)/\bar{n}_A]$ vs pH, the proton-ligand dissociation constants (pK_a) were found to be 12.70 for H3FPT and 12.91 for H3FP4MT. The higher value of pK_a for H3FP4MT could be due to presence of the

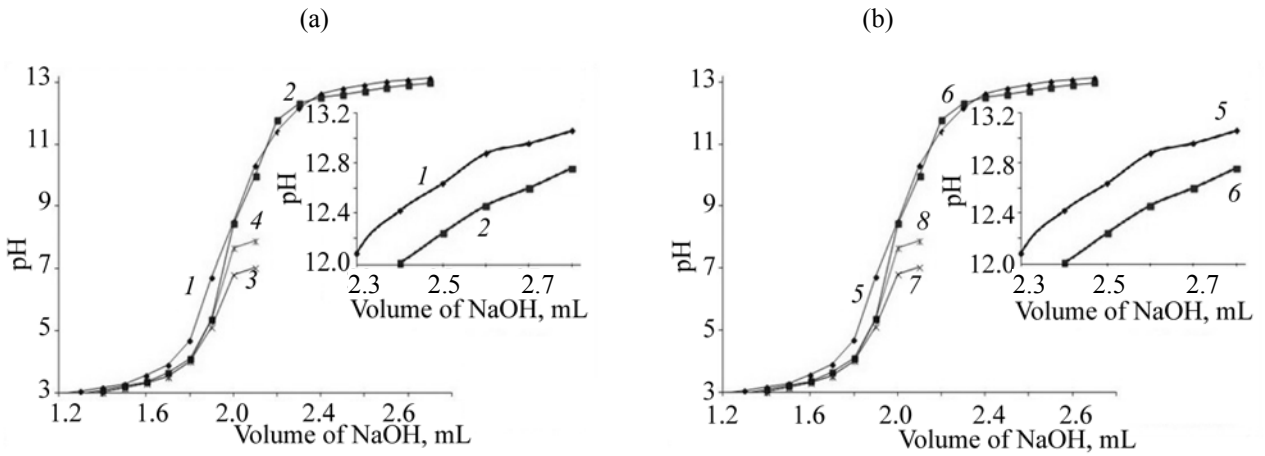


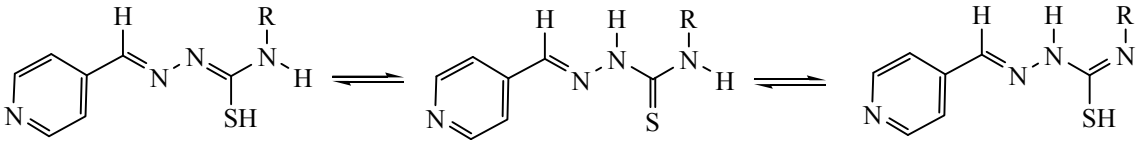
Fig. 1. pH-Metric titration curves of (a) H3FPT and (b) H3FP4MT (inset: expanded curves between pH 12.0 and 13.2): (*1*, *5*) free acid, (*2*) H3FPT, (*3*) Zn(II)-H3FPT, (*4*) Cd(II)-H3FPT, (*6*) H3FP4MT, (*7*) Zn-H3FP4MT, and (*8*) Cd-H3FP4MT.

methyl group on thioamide nitrogen which made the ligand more basic [9]. The pK_a value makes it evident that both ligands possess only one dissociable proton each via their thiol-1 form (Schemes 1and 2).

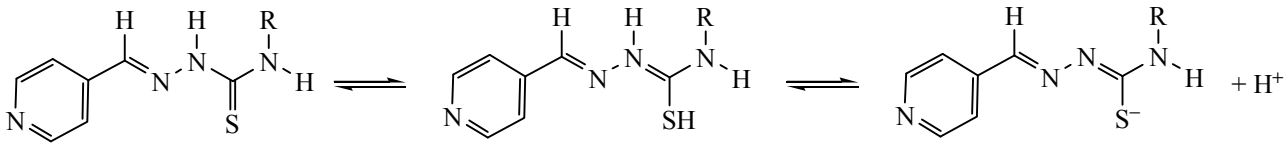
Determination of stability constants of metal complexes. According to the titration curves (Fig. 1), the metal-ligand curves run below the free acid and ligand curves indicating formation of the metal complexes in solutions. The values of $\bar{n}$ varied between 0.10 to 0.97, suggesting formation of 1 : 1 (M : L) complexes [10, 11]. The stability constants (log *K*) of the complexes derived from linear plots of log $[(1 - \bar{n})/\bar{n}]$ vs pL (Table 1) indicated that the Zn(II) complexes were more stable than Cd(II) complexes [12]. The complexes of H3FP4MT were more stable than H3FPT complexes, due to the greater basicity of the former one.

Characterization of the metal complexes. The solid complexes obtained were coloured, micro-crystalline, stable in the air and moisture, soluble in DMSO and DMF. Elemental analysis and mass spectra indicated that Cd(II)-H3FPT, Hg(II)-H3FPT, Zn(II)-H3FP4MT, and Cd(II)-H3FP4MT complexes were polymeric, $(ML)_n$, where $n > 2$, and composition of Hg(II)-H3FP4MT was ML_2. Molar conductivity of 10^{-3} M solutions of the complexes in DMSO at room temperature ranged between 0–8 Ω^{-1} cm^2 mol^{-1}, and indicated the non-electrolytic nature of Cd(II)-H3FPT, Hg(II)-H3FPT and Cd(II)-H3FP4MT complexes, while the values of 98 and 220 Ω^{-1} cm^2 mol^{-1} for Zn(II)-

Scheme 1. Thiol-thione tautomeric forms of the ligands H3FPT and H3FP4MT.



Scheme 2. Dissociation of the ligands.



H3FP4MT and Hg(II)-H3FP4MT complexes respectively indicated their electrolytic nature.

LC-MS. All the complexes demonstrated single peak with retention time in the range of 0.539 to 0.622 min indicating their purity.

MS. **Cd(II)-H3FPT.** In the mass spectrum the peak at *m/z* 361 indicated monomeric unit [ML·Cl·$2H_2O$] of the complex. Peaks at *m/z* 327 and 291 were due to loss of two coordinated water molecules and chloride ion, respectively. Peak at *m/z* 726 represented the polymeric nature of the complex, $(ML)_n$ with $n > 2$.

Hg(II)-H3FPT. [ML·Cl·$2H_2O$]. MS: *m/z*: 450. The peaks at 415 and 379 were due to the loss of two coordinated water molecules and coordinated chloride ion, respectively.

Cd(II)-H3FP4MT. [ML·Cl·$2H_2O$]. MS: *m/z*: 377. Peaks at 341 and 306 indicated loss of two coordinated water molecules and one coordinated chloride ion, respectively. The peak at *m/z* 754 indicated polymeric nature of the complex, $(ML)_n$ with $n > 2$.

Hg(II)-H3FP4MT. MS: *m/z*: 696. Loss of two water molecules and two lattice chloride ions was confirmed by the peaks at *m/z* 625 and 589, respectively. A peak at *m/z* 388 indicated presence of two ligand moieties in the complex, ML_2.

Thermogravimetric analysis of the complexes demonstrated their decomposition in the range of 180–300°C due to loss of coordinated water molecules, followed by multistep decomposition of the complexes.

IR spectra. In the spectrum of Cd(II)-H3FPT complex ν(N–H) band of the hydrazine group and in Hg(II)-H3FPT complex ν(N–H) band of the thioamide group were replaced by new C=N stretching vibration bands due to thione-thiol tautomerism in the ligand. Shift of ν(C=N) band to lower frequency in Cd(II)-H3FPT and to higher frequency in Hg(II)-H3FPT indicated coordination of azomethine nitrogen with the metal ions. In both complexes the band of ν(C=S) was shifted to lower frequency, indicating sulphur atom as potential donor site [13]. A shift in ring deformation bands to higher frequency supported binding of pyridine nitrogen atom with the metal ions [14, 15]. Thus, H3FPT acted as a tridentate ligand with pyridine ring nitrogen, azomethine nitrogen and sulphur atom as coordination sites.

In IR spectra of Zn(II)-H3FP4MT and Cd(II)-H3FP4MT, hydrazine ν(N–H) band was replaced by a new C=N band at 1606–1602 cm^{-1} due to thione-thiol tautomerization in the ligand. The bands ν(C=N) and ν(C=S) shifted to lower frequencies in the spectra of complexes due to coordination of azomethine nitrogen and thiolate sulphur to metal ions. The spectra of complexes showed increase in pyridine ring deformation frequencies, indicating the coordination of pyridine nitrogen with the metal ions. Thus, the ligand was tridentate with its azomethine nitrogen, ring nitrogen and sulphur coordinated to metal ions forming five membered chelates [13–15].

Table 1. Stability constants (log *K*) of the complexes

Complex (ML)	log *K*
Zn(II)-H3FPT	9.166
Cd(II)-H3FPT	7.625
Zn(II)-H3FP4MT	9.777
Cd(II)-H3FP4MT	8.642

In the spectrum of Hg(II)-H3FP4MT shift of the band attributed to ν(C=N) to lower frequency and ν(C=S) to higher frequency was due to coordination of azomethine nitrogen and sulphur atom to the metal ions [15]. Thus H3FP4MT acted as a bidentate ligand forming five membered chelate.

In far IR region of the spectra of the complexes, the bands attributed to ν(M–N) (480–459 cm^{-1}), ν(M–S) (381–372 cm^{-1}), ν(M–Cl) (330–320 cm^{-1}), and ν(M–OH_2) (406–404 cm^{-1}) were observed.

^1H NMR spectra. Absence of signals corresponding to hydrazine proton in the spectra of Cd(II)-H3FPT, Zn(II)-H3FP4MT and Cd(II)-H3FP4MT and one of the thioamide protons in the spectrum Hg(II)-H3FPT along with thiol signal at 4.0 ppm [3] indicated the

Table 2. Antioxidant activity of the ligands and their complexes

Ligand/Complex	IC_{50}, μM
H3FPT	7.82
Cd(II)-H3FPT	8.59
Hg(II)-H3FPT	5.33
H3FP4MT	21.87
Zn(II)-H3FP4MT	12.13
Cd(II)-H3FP4MT	23.93
Hg(II)-H3FP4MT	17.50

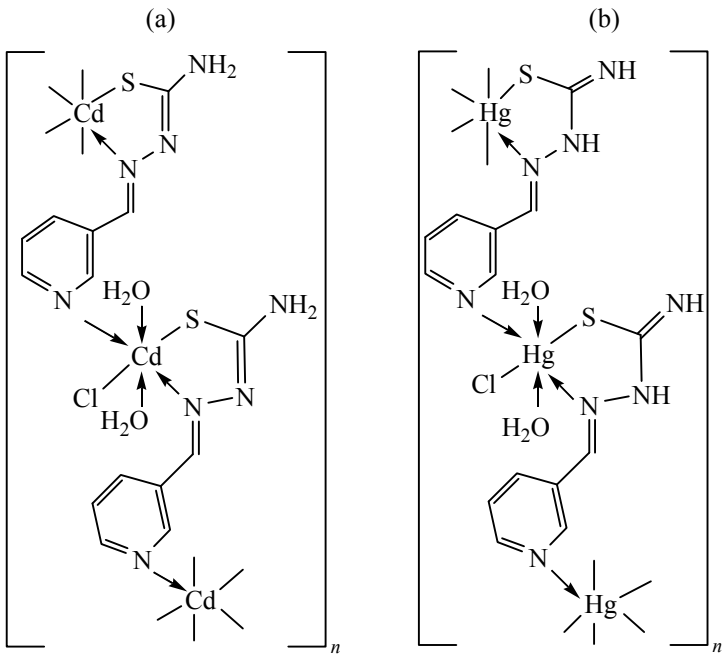


Fig. 2. Proposed structures of (a) Cd(II) and (b) Hg(II) complexes with H3FPT ($n > 2$).

ligands binding to metal ions in their thiolate form, and in Hg(II)-H3FP4MT thione sulphur binding with metal ions took place.

^{13}C NMR spectra. Complexation through pyridine nitrogen in Cd(II)-H3FPT and Hg(II)-H3FPT complexes was evidenced from downfield shifts of C^2 and C^6 carbons in the corresponding ^{13}C NMR spectra of the ligands in the complexes.

On the basis of the above data the structures of the complexes were assumed as presented in Figs. 2 and 3.

Antioxidant activity. The DPPH scavenging assay is one of the methods used to monitor antioxidant nature of a compound. The DPPH (1,1-diphenyl-2-picrylhydrazyl) free radical is very stable and is characterized by λ_{max} 517 nm. The purple DPPH turned yellow when it was reduced by the test compounds to DPPH-H. Depending upon the change in colour and decrease in absorbance of DPPH, the scavenging potential of the compounds could be estimated.

The IC_{50} values obtained from the plots of concentration of the sample vs SCV, % (Fig. 4), gave the concentration of the sample that led to its 50% reduction of the free radical [16] (Table 2). The accumulated data indicated that Zn(II) and Hg(II)

Table 3. Antibacterial activity of the ligands and their complexes

Ligand/Complex	Zone of inhibition, mm			
	gram positive		gram negative	
	S. aureus	*B. subtilis*	*K. pneumoniae*	*E.coli*
H3FPT	–	–	–	–
Cd(II)-H3FPT	15	16	15	10
Hg(II)-H3FPT	16	25	16	18
H3FP4MT	–	–	6	–
Zn(II)-H3FP4MT	6	12	–	–
Cd(II)-H3FP4MT	–	20	16	12
Hg(II)-H3FP4MT	25	30	20	18

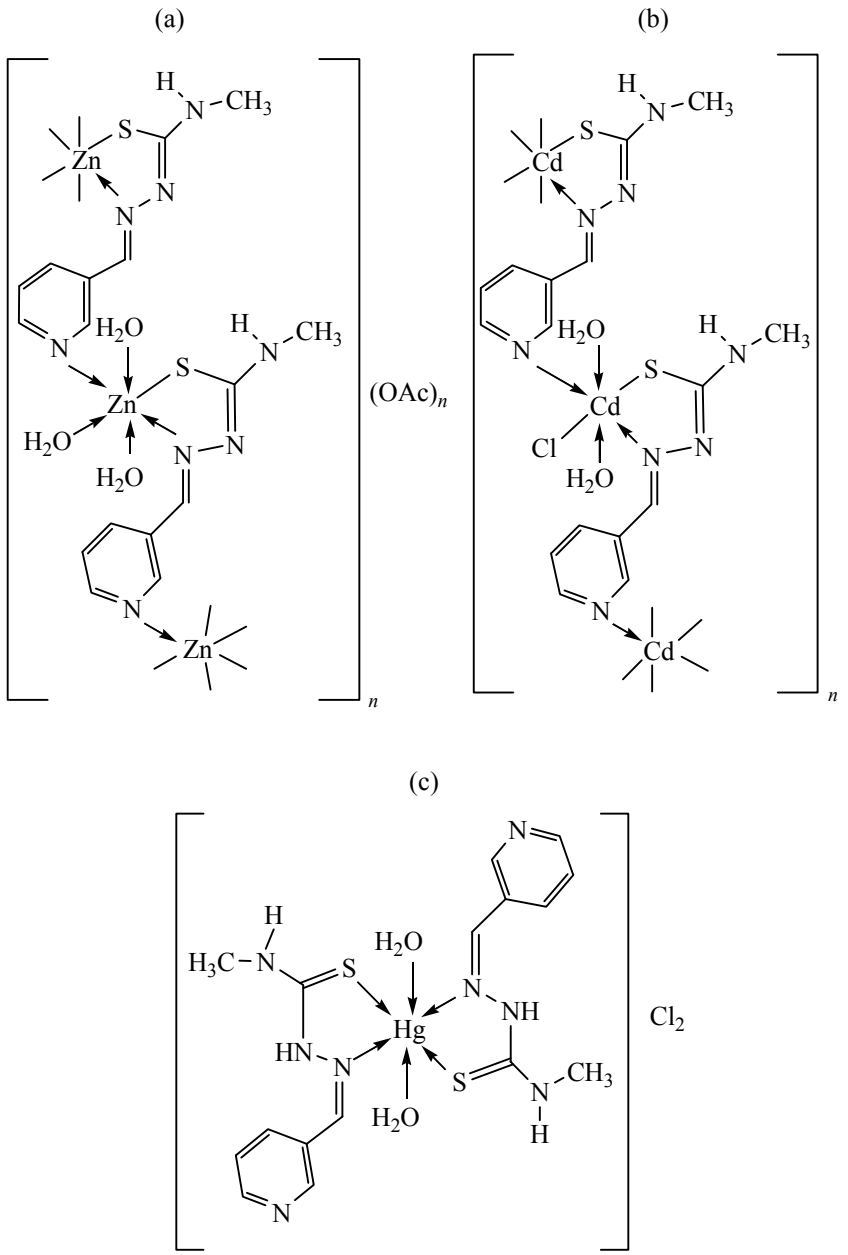


Fig. 3. Proposed structures of (a) Zn(II), (b) Cd(II), and (c) Hg(II) complexes with H3FP4MT.

complexes performed as better antioxidants than the corresponding ligands, while Cd(II) complexes were less active than the corresponding ligands.

Antibacterial activity. The ligands and complexes were tested for their bacterial growth inhibitory activity [3] against gram positive: *Staphylococcus aureus, Bacillus subtilis* and gram negative: *Escherichia coli* and *Klebsiella pneumonia* bacterial strains by the disc diffusion method using DMSO as a control and gentamicin as a standard (Table 3). The complexes of H3FP4MT were determined to be more active than H3FPT complexes, which could be assigned to more basic nature of H3FP4MT, which, in turn, increased lipophilicity of its complexes [3].

EXPERIMENTAL

All chemicals used were of reagent grade, obtained from Sigma-Aldrich. A digital Elico (L1-120) pH meter equipped with glass and calomel electrodes was used for equilibrium studies. LC-MS spectra were

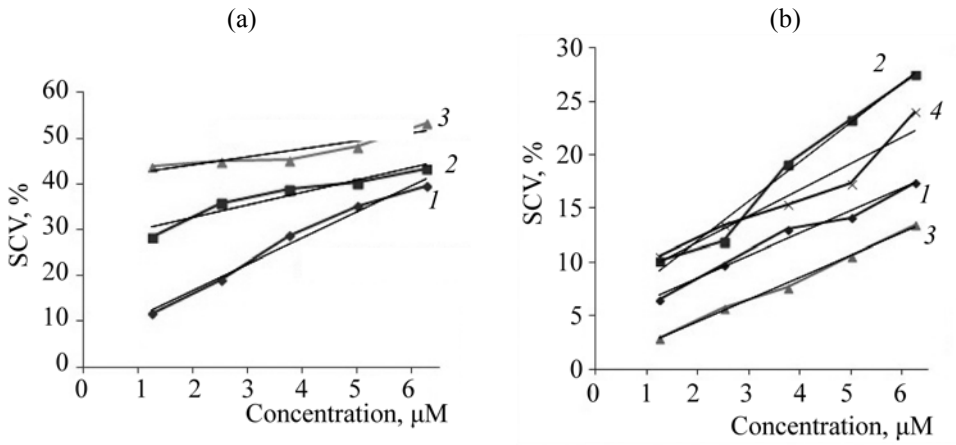


Fig. 4. Plots of concentration vs scavenging activity for (a) H3FPT [(*1*) H3FPT, $y = 5.7021x + 5.4255$; (*2*) Cd-H3FPT, $y = 2.7463x + 27.016$; (*3*) Hg-H3FPT, $y = 1.7708x + 40.553$] and (b) H3FP4MT [(*1*) H3FP4MT, $y = 2.087x + 4.3478$; (*2*) Zn-H3FP4MT, $y = 3.6886x + 4.6108$; (*3*) Cd-H3FP4MT, $y = 2.0769x + 0.2885$, (*4*) Hg-H3FP4MT, $y = 2.4615x + 6.92131$] , and their complexes.

measured on a Shimadzu LCMS 2010A spectrometer. Elemental analysis was carried out on a Thermo Finnigan 1112 elemental analyzer. Molar conductivity of the complexes was measured using a Digisun 909 digital conductivity meter. Thermo gravimetric analysis was carried out on a TG balance TA (Q/50) in the temperature range of 0 to 1000°C with a ramp of 20°C per min. IR spectra were recorded on a Schimadzu (Prestige-21) FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured on a Varian 400MHz NMR spectrometer. UV-Vis spectra in DMSO were recorded on a Schimadzu UV 2450 spectrophotometer. Antibacterial activity was studied following the disc diffusion method in sterile nutrient agar medium [3].

Synthesis of 3-formylpyridinethiosemicarbazone (H3FPT) and 3-formylpyridine N^4-methylthiosemicarbazone (H3FP4MT). Equimolar (2.5 mmol) solutions of thiosemicarbazide/N^4-methylthiosemicarbazide and 3-formyl pyridine were stirred for 2 h at room temperature. Solid precipitate formed was filtered off, washed with water and dried. The corresponding product was recrystallized from 1 : 1 ethanol – water mixture [8, 9].

(2*E*)-2-(Pyridin-3-ylmethylidene)hydrazinecarbothioamide (H3FPT). Yield 80%, mp 224–228°C. IR spectrum, ν, cm^{-1}: 416, 624 (δ_{Ar} ring), 827 (C=S), 987 (N–N), 1278 (N–CS–N), 1591 (C=N), 3130 (N–H hydrazine), 3340, 3263 (N–H thioamide). ^{1}H NMR spectrum, δ, ppm: 7.39–7.43 d.d (1H, Ar-H, J = 7.46, 4.4 Hz), 8.05 s (1H, H–C=N), 8.15 s (1H, N–CS–NH), 8.24–8.27 d.t (1H, Ar-H, J = 8.0, 2.0 Hz), 8.30 s (1H, N–CS–NH), 8.53–8.55 d (1H, Ar-H, J = 6.8 Hz), 8.91 s (1H, Ar-H), 11.59 s (1H, N–N–H). ^{13}C NMR spectrum, δ, ppm: 124.2, 130.6, 134.3, 139.8, 149.2, 150.4, 178.6. Found, %: C 46.58; H 4.36; N 31.26. $C_7H_8N_4S$. Calculated, %: C 46.66; H 4.44; N 31.11.

(2*E*)-N-Methyl-2-(pyridin-3-ylmethylidene)hydrazinecarbothioamide (H3FP4MT). Yield 84%, mp 190–192°C. IR spectrum, ν, cm^{-1}: 410, 630, (δ_{Ar} ring), 804 (C=S), 1265 (N–CS–N), 1612 (C=N), 3143 (N–H hydrazine), 3358 (N–H thioamide). ^{1}H NMR spectrum, δ, ppm: 3.02 s (3H, N–CH_3), 7.41–7.45 d.d (1H, Ar-H, J = 7.48, 4.77 Hz), 8.06 s (1H, H–C=N), 8.23–8.25 d (1H, Ar-H, J = 7.78 Hz), 8.55–8.56 d (1H, Ar-H, J = 4.77 Hz), 8.64–8.65 d (1H, N–CS–NH, J = 4.52 Hz), 8.96 s (1H, Ar-H), 11.67 s (1H, N–N–H). ^{13}C NMR spectrum, δ, ppm: 31.3, 123.8, 130.1, 133.8, 138.9, 148.4, 150.0, 177.5. Found, %: C 49.5; H 5.21; N 28.72. $C_8H_{10}N_4S$. Calculated, %: C 49.48; H 5.15; N 28.86.

Synthesis of metal complexes. To hot methanolic solution of the corresponding ligand (2.6 mmol), aqueous solution of zinc(II) acetate/cadmium(II) chloride/ mercury(II) chloride (1.3 mmol) was added and refluxed for 12–18 h. pH of the solution was adjusted with methanolic ammonium hydroxide solution. The resultant solid complexes were filtered off, washed with hot methanol, water, petroleum ether, and dried in vacuum [8, 9].

Cd(II)-H3FPT. Pale yellow solid, yield 80%, mp >300°C. IR spectrum, ν, cm^{-1}: 428, 645 (δ_{Ar} ring), 813 (C=S), 1585, 1610 (C=N), 3442, 3315 (N–H thioamide). ^{1}H NMR spectrum, δ, ppm: 7.35–7.38 d.d (1H, Ar-H, J = 8.0, 5.2 Hz), 7.46 s (1H, N–CS–NH), 7.59 s (1H,

N–CS–NH), 8.12 s (1H, H–C=N), 8.13–8.15 d (1H, Ar-H, J = 8.0 Hz), 8.47–8.48 d (1H, Ar-H, J = 4.4 Hz), 8.77 s (1H, Ar-H). Found, %: C 24.46; H 3.31; N 15.51. $C_7H_{11}ClCdN_4O_2S$. Calculated, %: C 23.15; H 3.30; N 15.43

Hg(II)-H3FPT. White solid, yield 70%, mp >300°C. IR spectrum, ν, cm^{-1}: 426, 632 (δ_{Py} ring), 821 (C=S), 1594, 1605, (C=N), 3163 (N–H hydrazine), 3284 (N–H thioamide). ^{1}H NMR spectrum, δ, ppm: 7.44–7.47 d.d (1H, Ar-H, J = 7.6, 4.4 Hz), 8.18 s (1H, H–C=N), 8.30–8.32 d (1H, Ar-H, J = 9.2 Hz), 8.59–8.60 d (1H, Ar-H), 8.97 s (1H, Ar-H), 9.01 s (1H, N–CS–NH,), 12.35 s (1H, N–N–H). Found, %: C 18.15; H 2.46; N 12.85. $C_7H_{11}ClHgN_4O_2S$. Calculated, %: C 18.57; H 2.43; N 12.38

Zn(II)-H3FP4MT. Pale yellow solid, yield 40%, mp >300°C. IR spectrum, ν, cm^{-1}: 443, 638 (δ_{Py} ring), 798 (C=S), 1588, 1602, (C=N), 3215 (N–H thioamide). ^{1}H NMR spectrum, δ, ppm: 2.94 br.s (3H, N–CH_3), 7.43 s (1H, H–C=N), 7.52 br (1H, Ar-H), 7.77 br (1H, N–CS–NH), 8.56–8.60 m (1H, Ar-H), 8.86–8.87 d (1H, Ar-H, J = 7.53 Hz), 9.42 s (1H, Ar-H). Found, %: C 31.95; H 4.83; N 24.51. $C_{12}H_{18}ZnN_4O_5S$. Calculated, %: C 32.43; H 4.86; N 25.94

Cd(II)-H3FP4MT. Pale yellow solid, yield 80%, mp >300°C. IR spectrum, ν, cm^{-1}: 433, 644 (δ_{Ar} ring), 792 (C=S), 1593, 1606 (C=N), 3348 (N–H thioamide). ^{1}H NMR spectrum, δ, ppm: 3.02 s (3H, N-CH_3), 7.37–7.40 d.d (1H, Ar-H, J = 7.91, 4.89 Hz), 7.88 br (1H, N–CS–NH), 8.08 s (1H, H–C=N), 8.13–8.14 d (1H, Ar-H, J = 7.78 Hz), 8.47–8.49 d (1H, Ar-H, J = 4.77 Hz), 8.81 s (1H, Ar-H). Found, %: C 24.51; H 3.49; N 14.59. $C_8H_{13}ClCdN_4O_2S$. Calculated, %: C 24.57; H 3.44; N 14.85

Hg(II)-H3FP4MT. White solid, yield 70%, mp >300°C. IR spectrum, ν, cm^{-1}: 819 (C=S), 1589 (C=N), 3118 (N–H hydrazine), 3203 (N–H thioamide). ^{1}H NMR spectrum, δ, ppm: 3.14 s (3H, N–CH_3), 7.55–7.58 d.d (1H, Ar-H, J = 7.91, 4.89 Hz), 8.20 s (1H, H–C=N), 8.38–8.40 d (1H, Ar-H, J = 7.78 Hz), 8.66–8.67 d (1H, Ar-H, J = 3.51 Hz), 9.06 s (1H, Ar-H), 9.41 s (1H, N–CS–NH), 12.34 s (1H, N–N–H). Found, %: C 28.08; H 3.48; N 16.15. $C_{16}H_{24}Cl_2HgN_8O_2S_2$. Calculated, %: C 27.60; H 3.45; N 16.10

pH-Metric equilibrium studies. The Irving-Rossotti titration technique [6,8] was employed for the complexation equilibrium studies. Standard solutions of Zn(II) and Cd(II) metal ions were prepared in double distilled water using the corresponding metal nitrates. pH-Metric titrations were carried out in 70% v/v DMF–water medium at 303 K and 0.1 M KNO_3 ionic strength. Titration of 50 mL of the following sets of solutions against 0.1 M NaOH solution was carried out: (1) HNO_3 (4.0×10^{-3} M), (2) HNO_3 (4.0×10^{-3} M) + Ligand (1.0×10^{-3} M), (3) HNO_3 (4.0×10^{-3} M) + Ligand (1.0×10^{-3} M) + Metal ion (2.0×10^{-4} M).

The titration curves, V_{NaOH} vs pH (Fig. 1), linear plots of log $[(1-\bar{n}_A)/\bar{n}_A]$ vs pH and log $[(1-\bar{n})/\bar{n}]$ vs pL, ligand dissociation constant (pK_a), and stability constant of the complexes (log K) were obtained accordingly [6, 8, 9].

Antioxidant activity. Antioxidant nature of the ligands and the complexes was determined according to 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay [16, 17]. 50μM Sample solutions were prepared from their stock solutions. The test compounds of various concentrations (1.25, 2.5, 3.75, 5.0, 6.25 μM) were added to1.0 mL of 0.1 mM methanolic solution of DPPH and stirred vigorously. The antioxidant activity was measured as the decrease in absorbance of DPPH at 517 nm by UV-Vis spectrophotometer after 30 min of incubation at room temperature in darkness. Solution of DPPH was used as a control. Ascorbic acid was used as a reference [16, 17].

Antibacterial studies. Antibacterial activity of the ligands and complexes was tested by the disc diffusion method [3] against gram positive: Staphylococcus *aureus*, *Bacillus subtilis* and gram negative: *Escherichia coli*, and *Klebsiella pneumonia* bacterial strains. Bacterial inoculum (0.10 mL) was spread on sterile nutrient agar medium by spread plate technique. Sterile discs of 5 mm diameter (5 μL capacity) dipped in solution of test samples in DMSO were placed at equal distance to each other. Disc dipped in DMSO was used as a control. Gentamicin was used as a standard. Antibacterial activity was evaluated as zone of inhibition in mm after incubation for 24 h at 37°C.

CONCLUSIONS

The pH-metric equilibrium studies indicate the formation of 1 : 1 (M : L) binary complexes in solutions and their relative stability. Except Hg(II)-H3FP4MT, all other synthesized solid complexes are polymeric, $(ML)_n$. All the ligands and complexes demonstrate antioxidant activity and inhibit bacterial growth. The complexes of H3FP4MT exhibit higher activity than complexes of H3FPT.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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