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# Synthesis, structures and antimicrobial activity of 5-nitro-salicylaldehyde-thiosemicarbazonates of zinc(II) coordinated to substituted bipyridines/phenanthrolines

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ABSTRACT

Reactions of zinc(II) with 5-nitro-salicylaldehyde-$N^1$-substituted thiosemicarbazones {(5-$NO_2$-2-HO—$C_6H_4$)$C^2$(H)═$N^3$—$N^2$H—$C^1$(═S)—$N^1$H*R*; *R* = H, $H_2L^1$; Me, $H_2L^2$; Et, $H_2L^3$; Ph, $H_2L^4$} and 4,4′-dimethyl-2,2′-bipyridine (dm-bipy), 2,9-dimethyl-1,10-phenanthroline (dm-phen) and 3,4,7,8-tetramethyl-1,10-phenanthroline (tm-phen) as co-ligands, have yielded complexes of stoichiometry, [Zn($L^n$)(L)] {*n* = 1–4; L = dm-bipy, **1**, **4**, **7**, **10**; dm-phen, **2**, **5**, **8**, **11**; tm-phen, **3**, **6**, **9**, **12**) characterized by elemental analysis, infrared and electronic absorption spectroscopy and single crystal X-ray crystallography. Complexes **9** and **10** have distorted trigonal bipyramidal geometry ($\tau$ = 0.529–0.580), while complexes **5**, **8** and **11** have distorted square pyramidal geometry ($\tau$ = 0.004–0.250). They displayed fluorescence bands at $\lambda_{max}$ = 430–440 nm. In comparison to unsubstituted bipyridines/phenanthrolines, these zinc(II) complexes have shown higher antimicrobial activity with low minimum inhibitory concentration (MIC) against the clinical isolate methicillin resistant *Staphylococcus aureus* (MRSA), Gram positive bacteria, namely, *Staphylococcus aureus* (MTCC740), *Enterococcus faecalis* (MTCC439), Gram negative bacteria, namely, *Klebsiella pneumonia* 1 (MTCC109), *Escherichia coli* (MTCC119), *Salmonella typhimurium* 1 (MTCC98) and one yeast strain *Candida albicans* (MTCC227). These complexes tested were found to be cytotoxic to microorganisms (bactericidal/fungicidal).

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## 1. Introduction

The biochemistry of zinc(II) is very important due to the role of this metal in a number of enzymes such as zinc proteinases, carbonic anhydrous, histone deacetylase, alcohol hydrogenases, alkaline phosphates and amino peptidases which are involved in various metabolic processes of plants, animals, viruses and bacteria [1–5]. Among various N,S-donor thio-ligands, thiosemicarbazones (Chart 1) constitute an important category of ligands which have formed a variety of metal complexes and have also shown promising biochemical activity [6–10]. In the literature, the co-ordination compounds of thiosemicarbazones with zinc(II) have shown antimicrobial [11–14], anticancer [15–17] and antioxidant activities [18]. The antimicrobial activity has been studied when $R^1$ substituent at $C^2$ atom of thiosemicarbazone was 2-thiopheneyl [11], 2-acetylpyridine [12,13], furan [14], or 2-acetylbutyrolactone [14] and the substituent $R^2$ was hydrogen, methyl at $C^2$ carbon and finally $NR^3R^4$ was $NH_2$, NHR (R = Me, Et, Pr, Ph etc.) at $N^1$ nitrogen. It was noted from the literature that co-ordination compounds of zinc(II) investigated have shown poor antimicrobial activity at high minimum inhibitory concentration (MIC) [11–14].

In view of the above mentioned interests and observations, recently from our laboratory antimicrobial activity of co-ordination compounds of Zn(II) coordinated to 5-nitro-salicylaldehyde-N-substituted thiosemicarbazones and bipyridine (bipy)/1,10-phenanthroline (phen) co-ligands (Chart 2) has been reported [19]. It was found that these co-ordination compounds have significant antimicrobial activity against *Staphylococcus aureus* (MTCC740), methicillin resistant *Staphylococcus aureus* (MRSA), *Klebsiella pneumonia* 1 (MTCC109), *Shigella flexneri* (MTCC1457), *Salmonella typhimurium* 1 (MTCC98) and *Candida albicans* (MTCC227) [19]. Notably, the bio-activity against *K. pneumoniae* and *S. typhimurium* was an important outcome of the

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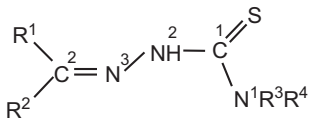

**Chart 1.** General structure of thiosemicarbazone.

investigations, while in literature co-ordination compounds reported were found to be inactive [14]. The in vitro cell viability studied using MTT assay {MTT stands for 3-[(4, 5-dimethylthiazol-2-yl)-2,5-diphenyl] tetrazolium bromide} was found to be low.

In this paper we report the antimicrobial activity of 5-nitro-salicyaldehyde-$N^1$-substituted thiosemicarbazonates of zinc(II) coordinated to chelating dm-bipy, dm-phen and tm-phen ligands against *Staphylococcus aureus* (MTCC740), methicillin resistant *Staphylococcus aureus* (MRSA), *Klebsiella pneumonia* 1 (MTCC109), *Enterococcus faecalis* (MTCC439), *Escherichia coli* (MTCC119), *Salmonella typhimurium* 1 (MTCC98) and *Candida albicans* (MTCC227) (Chart 3). The main focus of this study is to observe the effect of substituents (R) at $N^1$ atom of thiosemicarbazones as well as that of methyl substituents in the rings of bipyridine and 1,10-phenanthroline on the antimicrobial activity and cell viability of zinc(II) complexes.

## 2. Experimental

Zinc(II) acetate dihydrate, thiosemicarbazide, N-methyl-thiosemicarbazide, N-ethyl-thiosemicarbazide, N-phenyl-thiosemicarbazide, 5-nitro-salicylaldehyde, 4,4′-dimethyl-2,2′-bipyridine (dm-bipy), 2,9-dimethyl-1,10-phenanthroline (dm-phen) and 3,4,7,8-tetramethyl-1,10-phenanthroline (tm-phen) were procured from Aldrich Sigma Ltd. The thio-ligands (Chart 1) were prepared as reported earlier [20–23]. Elemental analysis for C, H and N were carried out with a thermoelectron FLASHEA1112 analyzer. Melting points were determined with a Gallenkamp electrically heated apparatus. IR spectra of the compounds were recorded in the 4000–450 $cm^{-1}$ region with a Perkin Elmer FT-IR Spectrometer by making their KBr pellets. UV–Vis spectra of the compounds ($10^{-3}$–$10^{-4}$ M) were recorded in dimethylsulfoxide (dmso) with the help of a UV-1601 PC Shimadzu spectrophotometer. Fluorescence spectra of the complexes ($10^{-4}$ M) were recorded with a Varian Cary Eclipse Fluorescence spectrophotometer. The $^1H$ NMR spectra were recorded on Bruker Avance 500 MHz NMR spectrometer in $CDCl_3$-DMSO mixture (9:1) with TMS as the internal reference.

### 2.1. Synthesis of complexes

#### 2.1.1. [Zn($L^1$)(dm-bipy)] (**1**)

To a pale yellow solution of thio-ligand, $H_2L^1$ (0.027 g, 0.11 mmol) in acetonitrile (10 mL) was added white solid $Zn(OAc)_2 \cdot 2H_2O$ (0.025 g, 0.11 mmol). The reaction mixture was stirred for 15 min which yielded white precipitate. To the white precipitate, solution of dm-bipy (0.021 g, 0.11 mmol) in dichloromethane (10 mL) was added and the contents were again stirred for 15 min. A clear orange solution formed was allowed to evaporate at room temperature which yielded an orange compound. Yield: 0.039 g, 71%, m.p. 210–212 °C. *Anal.* Calc. for $C_{20}H_{18}N_6O_3SZn$: C, 49.24; H, 3.69; N, 17.23; S, 6.57. Found: C, 50.14; H, 3.81; N, 17.46; S, 6.63%. IR ($cm^{-1}$, KBr): $\nu(N^1–H)$ 3421 s; $\nu$(C–H) 3109 w, 3062 w, 2921 w; 1648 s, 1601 s; $\nu_{as}$(N–O) 1547 s; 1492 s, 1437 w, 1414 w; $\nu_s$(N–O) 1320 s; 1234 m, 1189 w, 1093 s, 935 m, 831 m; $\nu$(C–S) 757 s; 726 s, 640 w, 492 w, 421 w. Electronic absorption spectrum, DMSO, $\lambda_{max}$/nm, ε/L $mol^{-1}$ $cm^{-1}$:[$10^{-4}$ M] 424 ($1.00 \times 10^4$), 389 ($1.74 \times 10^4$), 284 ($1.45 \times 10^4$). Fluorescence spectrum: $\lambda^{em}_{max}$ = 434 nm; $\lambda^{ex}_{max}$ = 300 nm. $^1H$ NMR (δ, ppm; $CDCl_3$: DMSO; 9:1): δ = 8.37 (2H, s, $C^9H_{dm\text{-}bipy}$ + $C^{16}H_{dm\text{-}bipy}$), 8.18(1H, m, $C^2H$), 8.01 (2H, m, $C^4H$ + $C^7H$), 7.80 (2H, s, $C^{12}H_{dm\text{-}bipy}$ + $C^{13}H_{dm\text{-}bipy}$), 7.72 (2H, s, $C^{10}H_{dm\text{-}bipy}$ + $C^{15}H_{dm\text{-}bipy}$), 7.33 (2H, d, $N^1H_2$), 6.40 (1H, s, $C^6H$), 2.98 (6H, $C^{11,\ 14}H_3$). Complexes **2**–**12** were prepared by a similar method.

#### 2.1.2. [Zn($L^1$)(dm-phen)] (**2**)

Yield: 0.044 g, 70%, m.p. 221–223 °C. *Anal.* Calc. for $C_{22}H_{18}N_6O_3$-SZn·$CH_3CN$: C, 52.13; H, 3.80; N, 17.74; S, 5.79. Found: C, 51.90; H, 4.01; N, 17.56; S, 6.08%. IR ($cm^{-1}$, KBr): $\nu(N^1–H)$ 3432 sb, 3384 s; $\nu$(C–H) 3156 w, 3098 w, 2926 w, 2858 w; 1691 s; $\nu_{as}$(N–O) 1547 m; δ(C–H) 1521 w, 1490 s, 1439 m; $\nu_s$(N–O) 1306 s; 1243 w, 1191 w, 1169 w, 1097 w, 1008 w, 951 w; 805 w; $\nu$(C–S) 750 m; 654 w, 621 w, 514 w, 440 w, 414 w. Electronic absorption spectrum, DMSO, $\lambda_{max}$/nm, ε/L $mol^{-1}$ $cm^{-1}$: [$10^{-4}$ M] 421 ($1.01 \times 10^4$), 380 ($1.76 \times 10^4$), 301 ($1.55 \times 10^4$), 271 ($3.97 \times 10^4$). Fluorescence spectrum: $\lambda^{em}_{max}$ = 435 nm; $\lambda^{ex}_{max}$ = 300 nm. $^1H$ NMR (δ, ppm; $CDCl_3$: DMSO; 9:1): δ = 8.95 (2H, s, $C^9H_{dm\text{-}phen}$ + $C^{16}H_2$ $C^9H_{dm\text{-}phen}$), 8.54 (1H, s, $C^2H$), 8.11(2H, d, $C^4H$ + $C^7H$), 7.83 (1H, s, $N^1H_2$), 7.73 (2H, s, $C^{12}H$ $C^9H_{dm\text{-}phen}$ + $C^{13}H_{dm\text{-}phen}$), 7.47 (2H, m, $C^{10}H_{dm\text{-}phen}$ + $C^{15}H_{dm\text{-}phen}$), 6.27 (1H, s, $C^6H$), 2.78 (6H, $C^{9,\ 16}H_3$).

#### 2.1.3. [Zn($L^1$)(tm-phen)] (**3**)

Yield: 0.046 g, 75%, m.p. 214–216 °C. *Anal.* Calc. for $C_{24}H_{22}N_6O_3$-SZn: C, 53.39; H, 4.07; N, 15.57; S, 5.93.; Found: C, 53.51; H, 4.23; N, 15.69; S, 6.04%. IR ($cm^{-1}$, KBr): $\nu(N^1–H)$ 3477, 3328 m b; $\nu$(C–H) 3156 w, 3062 w, 2930 w; 1609 s; $\nu_{as}$(N–O) 1547 s; δ(C–H) 1500 s, 1422 m; 1383 m; $\nu_s$(N–O) 1305 s; 1250 w, 1188 w, 1156 m, 1094 w, 953 w, 896 w; $\nu$(C–S) 773 m; 726 w, 680 s, 664 s, 625 w, 547 w, 499 w, 460 w, 390 w. Electronic absorption spectrum, DMSO, $\lambda_{max}$/nm, ε/L $mol^{-1}$ $cm^{-1}$: [$10^{-4}$ M] 419 ($1.04 \times 10^4$); 387 ($1.79 \times 10^4$), 298 ($1.58 \times 10^4$), 271 ($3.22 \times 10^4$). Fluorescence spectrum: $\lambda^{em}_{max}$ = 435 nm; $\lambda^{ex}_{max}$ = 300 nm. $^1H$ NMR (δ, ppm; $CDCl_3$: DMSO; 9:1): δ = 8.50 (1H, s, $C^2H$), 8.43(2H, m, $C^9H_{dm\text{-}phen}$ + $C^{16}H_{dm\text{-}phen}$), 8.06(1H, s, $N^1H$), 7.93 (2H, m, $C^4H$ + $C^7H$), 7.78 (2H, s, $C^{12}H_{dm\text{-}phen}$ + $C_{13}H_{dm\text{-}phen}$), 6.28 (1H, s, $C^6H$), 2.90 (6H, s, $C^{10,\ 15}H_3$), 3.07 (6H, s, $C^{11,\ 14}H_3$).

#### 2.1.4. [Zn($L^2$)(dm-bipy)]·$CH_2Cl_2$ (**4**)

Yield: 0.047 g, 70%, m.p. 198–200 °C. *Anal.* Calc. for $C_{21}H_{20}N_6O_3$-SZn·$CH_2Cl_2$: C, 45.02; H, 3.75; N, 14.32; S, 5.46. Found: C, 44.89; H,

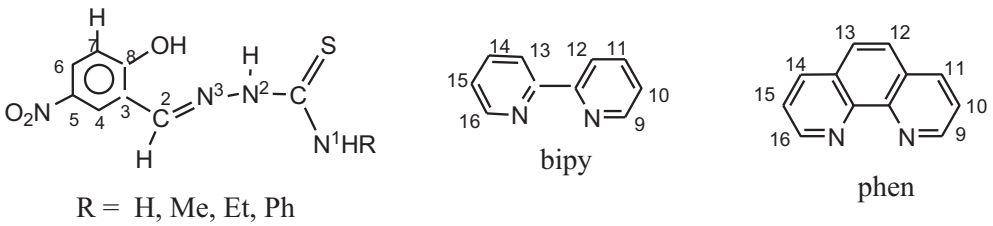


**Chart 2.** 5-nitro-nitro-salicyldehydethiosemicarbazones and co-ligands.

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