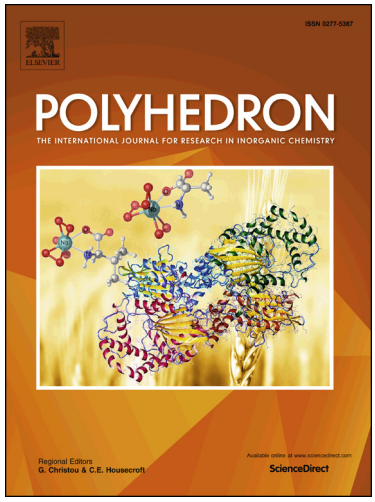


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# Synthesis, structures and antimicrobial activity of 5-nitro-salicylaldehyde-thiosemicarbazonates of zinc(II) coordinated to substituted bipyridines / phenanthrolines

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**A B S T R A C T**

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).

## 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].

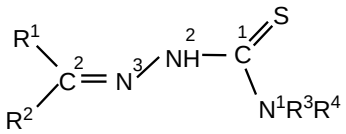



Chart **1**. General structure of thiosemicarbazone

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 investigations, while in literature co-ordination compounds reported were found to be inactive [20]. 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.

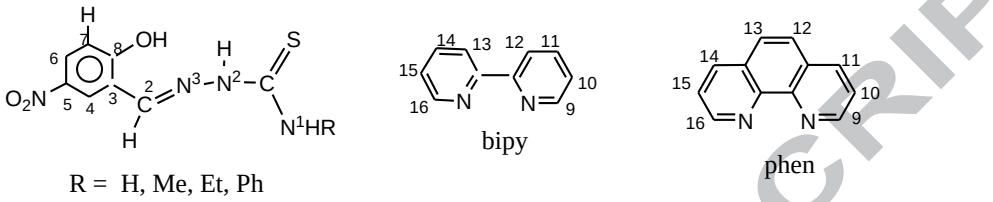



**Chart 2.** 5-nitro-salicyldehydethiosemicarbazones and co-ligands

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.

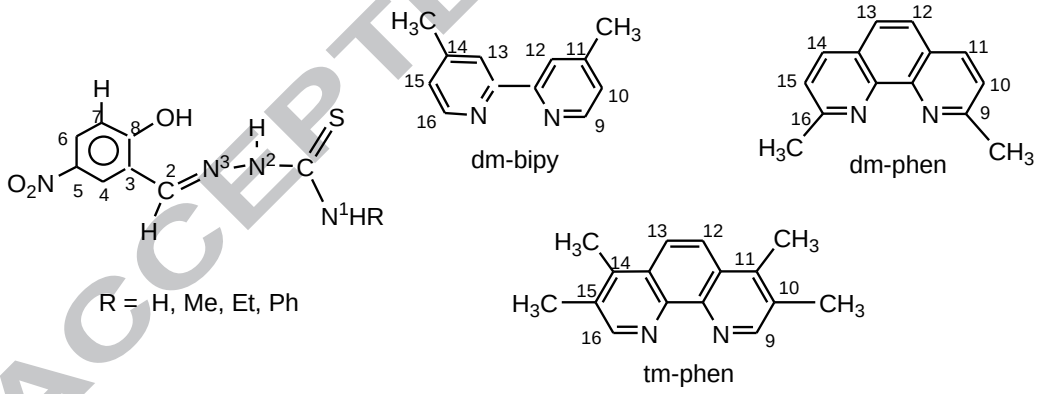



**Chart 3.** 5-Nitro-salicylaldehyde thiosemicarbazones with dm-bipy, dm-phen and tm-phen as co-ligands

## 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 [21-24]. 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-visible 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 $^{1}H$ 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 minutes which yielded white precipitate. To the white precipitate, solution of dm-bipy (0.021 g, 0.11 mmol) in dichloromethane (10mL) 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: 0.039g, 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 x $10^4$), 389 (1.74 x $10^4$), 284 (1.45 x $10^4$). Fluorescence spectrum: $\lambda_{max}^{em}$ = 434 nm; $\lambda_{max}^{ex}$ = 300 nm. $^{1}H$ 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: 0.044g, 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) : ν($N^1$–H) 3432 sb, 3384 s; ν(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; ν(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 x $10^4$), 380 (1.76 x $10^4$), 301 (1.55 x$10^4$), 271 (3.97 x $10^4$). Fluorescence spectrum: $\lambda_{max}^{em}$ = 435 nm; $\lambda_{max}^{ex}$ = 300 nm. $^1$H 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 $C_{24}H_{22}N_6O_3SZn$: 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) : ν($N^1$–H) 3477, 3328 m b; ν(C–H) 3156 w, 3062 w, 2930 w; 1609s; $\nu_{as}$(N-O) 1547s; 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; ν(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 x $10^4$); 387 (1.79 x $10^4$), 298 (1.58 x $10^4$), 271(3.22 x $10^4$). Fluorescence spectrum: $\lambda_{max}^{em}$ = 435 nm; $\lambda_{max}^{ex}$ = 300 nm. $^1$H 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 $C_{21}H_{20}N_6O_3SZn·CH_2Cl_2$: C 45.02; H 3.75; N 14.32; S 5.46; Found:C 44.89; H 3.51; N 14.65; S 5.29%. IR ($cm^{-1}$, KBr) : ν($N^1$–H) 3390s; ν(C–H) 3130 w, 3061 s, 2983 m, 2936 w, 2851w; 1609s; $\nu_{as}$(N-O) 1559 s; δ(C−H) 1515 s, 1491 s, 1436 m; 1335 m; $\nu_s$(N-O) 1302 s; 1257 s, 1171 s, 1093 s, 1019 m, 952 m; ν(C–S) 750 m; 710 w, 663 m, 553 m, 499 w, 452 w. Electronic absorption spectrum, DMSO, $\lambda_{max}$ /nm, ε / L $mol^{-1}$ $cm^{-1}$ : [$10^{-4}$ M] 425 (1.07 x $10^4$), 386 (1.74

x $10^4$), 283 (1.59 x $10^4$). Fluorescence spectrum: $\lambda_{max}^{em}$ = 437 nm; $\lambda_{max}^{ex}$ = 300 nm. $^1$H NMR (δ, ppm; $CDCl_3$: DMSO; 9:1): δ = 8.41 (2H, d, $C^9H_{dm\text{-}bipy}$ + $C^{16}H_{dm\text{-}bipy}$), 8.36 (2H, d, $C^{12}H_{dm\text{-}bipy}$+ $C^{13}H_{dm\text{-}bipy}$), 8.07 (3H, d, $C^2H$+ $C^4H$ + $C^7H$), 7.97(2H, s, $C^{10}H_{dm\text{-}bipy}$ + $C^{15}H_{dm\text{-}bipy}$), 7.75 (1H, d, $N^1H$), 6.40 (1H, s, $C^6H$), 2.98 (6H, $C^{11,14}H_3$), 3.12 (3H, m, $N^1(CH_3)$).

*2.1.5. [Zn($L^2$)(dm-phen)]·$CH_3CN$* ***(5)***.Yield: 0.046 g, 72%, m.p. 193-194°C. *Anal.* Calc. for $C_{23}H_{20}N_6O_3SZn{\cdot}CH_3CN$: C 52.97; H 4.06; N 17.30; S 5.65; Found: C 52.79; H 3.93; N 16.91; S 5.33 %. IR ($cm^{-1}$, KBr) : ν($N^1$–H) 3400 s; ν(C–H) 3070 w, 3000 w, 2930w; 1593s; $\nu_{as}$(N-O) 1548s; δ(C-H) 1485s, 1437s; 1398m, 1375m; $\nu_s$(N-O) 1305 s; 1250 s, 1194m, 1093s, 944w, 919 m, 883 s; ν(C–S) 760s; 646m, 602 m, 497m, 441m. Electronic absorption spectrum, DMSO, $\lambda_{max}$ /nm, ε / L $mol^{-1}$ $cm^{-1}$ : [$10^{-4}$ M] 430 (9.38 x $10^3$), 388 (1.46 x $10^4$), 294 (1.05 x $10^4$), 263(2.25 x $10^4$). Fluorescence spectrum: $\lambda_{max}^{em}$ = 436 nm; $\lambda_{max}^{ex}$ = 300 nm. $^1$H NMR (δ, ppm; $CDCl_3$: DMSO; 9:1): δ = 8.60 (1H, s, $C^2H$), 8.47 (2H, d, $C^{11}H_{dm\text{-}phen}$ + $C^{14}H_{dm\text{-}phen}$), 8.10 (1H, m, $N^1H$), 7.95 (2H, m, $C^4H$+$C^7H$), 7.95 (2H, m, $C^{12}H_{dm\text{-}phen}$ + $C^{13}H_{dm\text{-}phen}$), 7.79 (2H, d, $C^{10}H_{dm\text{-}phen}$+ $C^{15}H_{dm\text{-}phen}$), 6.36 (1H, s, $C^6H$), 3.11 (3H, d, $(CH_3)N^1$), 2.96 (6H, d, $C^{9,16}H_3$).

*2.1.6. [Zn($L^2$)(tm-phen)]* ***(6)***. Yield: 0.049 g, 78%, m.p. 205-207°C. *Anal.* Calc. for $C_{25}H_{24}N_6O_3SZn$: C 54.21; H 4.34; N 15.18; S 5.78 %; Found: C 54.18; H 4.12; N 15.30; S 5.53 %. IR ($cm^{-1}$, KBr) : ν($N^1$–H) 3390 m b; ν(C–H) 3078w, 2930 w, 2838 w; 1609 s; $\nu_{as}$(N-O) 1533 s; δ(C-H) 1485 s, 1430 s; 1398 m; $\nu_s$(N-O) 1305 s; 1250 s, 1094 s, 1023 w, 952 w, 890 w, 820 m; ν(C–S) 720 s; 687 s, 609 w, 531 w 492 w. Electronic absorption spectrum, DMSO, $\lambda_{max}$ /nm, ε / L $mol^{-1}$ $cm^{-1}$ : [$10^{-4}$ M] 427 (1.03 x $10^4$), 387 (1.93 x $10^4$), 303 (1.75 x $10^4$), 270 (2.89 x$10^4$). Fluorescence spectrum : $\lambda_{max}^{em}$ = 434 nm; $\lambda_{max}^{ex}$ = 300 nm. $^1$H NMR (δ, ppm; $CDCl_3$: DMSO; 9:1): δ = 8.97(2H, s, $C^9H_{tm\text{-}phen}$ + $C^{16}H_{tm\text{-}phen}$), 8.59 (2H, d, $C^{12}H_{tm\text{-}phen}$+ $C^{13}H_{tm\text{-}phen}$), 8.37 (1H, d, $C^2H$), 8.22 (2H, m, $C^4H$+$C^7H$), 8.10 (1H, m, $N^1H$), 6.70 (1H, s, $C^6H$), 2.98 (6H, d, $C^{11,14}H_3$), 2.79 (6H,d, $C^{10,15}H_3$), 3.17 (3H, s, $(CH_3)N^1$).

*2.1.7. [Zn($L^3$)(dm-bipy)]* ***(7)***. Yield: 0.044 g, 75%, m.p. 191-193°C. *Anal.* Calc. for $C_{22}H_{22}N_6O_3SZn$: C 51.22; H 4.30; N 16.29, S 6.22; Found: C 51.43; H 4.17; N 15.95, S 6.17 %. IR ($cm^{-1}$, KBr) : ν($N^1$–H) 3375 s, ν(C–H) 3075 w, 2992 w, 2922 w,2867 w; 1601 s; $\nu_{as}$(N-O) 1554 m; δ(C−H) 1485 s, 1430 m; $\nu_s$(N-O) 1305 s; 1235 m, 1196 w, 1164 w, 1101 m, 1030 w, 953 w, 820 s, ν(C–S) 757 w; 718 w, 680 m, 640 w, 547 w, 531 w, 421 w. Electronic absorption

spectrum, DMSO, $\lambda_{max}$ /nm, ε / L mol$^{-1}$ cm$^{-1}$ : [$10^{-4}$ M] 426 (1.02 x $10^4$), 387 (1.82 x $10^4$), 275 (1.29 x $10^4$). Fluorescence spectrum: $\lambda_{max}^{em}$ = 437 nm; $\lambda_{max}^{ex}$ = 300 nm. $^1$H NMR (δ, ppm; $CDCl_3$: DMSO; 9:1): δ = 8.41 (2H, m, $C^9H_{dm\text{-}bipy}$ + $C^{16}H_{dm\text{-}bipy}$), 8.36 (2H, m, $C^{12}H_{dm\text{-}bipy}$+ $C^{13}H_{dm\text{-}bipy}$), 8.16 ( 1H, s, $C^2$ H), 8.01 (2H, d, $C^4$H + $C^7$H), 7.75 (1H, d, $N^1$H), 7.69 (2H, d, $C^{10}H_{dm\text{-}bipy}$ + $C^{15}H_{dm\text{-}bipy}$), 6.32 (1H, s, $C^6$H), 3.41 (2H, m, $N^1(CH_2)$, 3.28(6H, m, $C^{11,14}H_3$), 1.03 (3H, m, $CH_3$).

*2.1.8. [Zn($L^3$)(dm-phen)]·$CH_3CN$* ***(8)***.Yield: 0.049 g, 74%, m.p. 196-198°C. *Anal.* Calc. for $C_{24}H_{22}N_6O_3SZn{\cdot}CH_3CN$: C 53.75; H 4.34; N 16.88; S 5.52 %.; Found: C 53.51; H 4.07; N 16.43; S 5.43 %. IR (cm$^{-1}$, KBr) : ν($N^1$–H) 3398 m b; ν(C–H) 3053 w, 2975 w, 2931 w, 2853 w; 1600 s; $\nu_{as}$(N-O) 1541m; δ(C-H) 1490 s, 1417 m; 1375 w, $\nu_s$(N-O) 1304 s; 1234 m, 1195 w, 1151 w, 1100 w, 958 w, 862 s; ν(C–S) 758 m; 683 s, 657 s, 535 w, 497 w, 439 w. Electronic absorption spectrum, DMSO, $\lambda_{max}$ /nm, ε / L mol$^{-1}$ cm$^{-1}$ : [$10^{-4}$ M] 429 (1.18 x $10^4$), 388 (2.10 x $10^4$), 308 (7.22 x $10^3$), 284 (1.58 x $10^4$). Fluorescence spectrum: $\lambda_{max}^{em}$ = 440 nm; $\lambda_{max}^{ex}$ = 300 nm. δ = 8.59 (2H, s, $C^{11}H_{dm\text{-}phen}$+ $C^{14}H_{dm\text{-}phen}$), 8.50 (3H, d, $C^2$H+ $C^{12}H_{dm\text{-}phen}$+ $C^{13}H_{dm\text{-}phen}$), 8.13 (2H, d, $C^4$H+$C^7$H), 7.99 (1H, s, $N^1$H), 7.79 (2H, m, $C^{10}H_{dm\text{-}phen}$+ $C^{15}H_{dm\text{-}phen}$), 6.35 (1H, d, $C^6$H), 3.47 (2H, m, $N^1(CH_2)$, 3.12 (6H, m, $C^{9,16}H_3$), 1.19 (3H, m, $CH^3$).

*2.1.9. [Zn($L^3$)(tm-phen)]* ***(9)***. Yield: 0.049 g, 71%, m.p. 204-206°C. *Anal.* Calc. for $C_{26}H_{26}N_6O_3SZn{\cdot}CH_3CN$: C 55.22; H 4.80; N 16.10; S 5.26 %; Found: C 55.31; H 4.58; N 16.24; S 5.23 %. IR (cm$^{-1}$, KBr) : ν($N^1$–H) 3375 m,b; ν(C–H) 3054 w, 2985 w, 2921 w; 1617 s; $\nu_{as}$(N-O) 1554 m; 1537 w; δ(C-H) 1476 s, 1422 m; $\nu_s$(N-O) 1327 s; 1250 m, 1127 w, 1093 m, 1023 w, 952 w, 882 w, 820 s; ν(C–S) 735 s; 671 s, 515 w, 429 w. Electronic absorption spectrum, DMSO, $\lambda_{max}$ /nm, ε / L mol$^{-1}$ cm$^{-1}$ : [$10^{-4}$ M] 430 (8.38 x $10^3$), 385 (1.20 x $10^4$), 305 (1.40 x $10^4$), 275 (2.49 x $10^4$). Fluorescence spectrum: $\lambda_{max}^{em}$ = 440 nm; $\lambda_{max}^{ex}$ = 300 nm. $^1$H NMR (δ, ppm; $CDCl_3$: DMSO; 9:1): δ = 8.64 (2H, s, $C^9H_{tm\text{-}phen}$+ $C^{16}H_{tm\text{-}phen}$), 8.57 (1H, d, $C^2$H), 8.47 (2H, d, $C^{12}H_{tm\text{-}phen}$+ $C^{13}H_{tm\text{-}phen}$), 8.21 (2H, s, $C^4$H+$C^7$H), 8.10 (1H, m, $N^1$H), 6.70 (1H, s, $C^6$H), 3.11 (6H, d, $C^{11,14}H_3$), 2.81 (6H,d, $C^{10,15}H_3$), 3.51 (2H, s, $CH_2N^1$), 1.21 (3H, m, $CH^3$).

*2.1.10. [Zn($L^4$)(dm-bipy)]* ***(10)***. Yield: 0.045 g, 70%, m.p. 221-223 °C. *Anal.* Calc. for $C_{26}H_{22}N_6O_3SZn$: C 55.37; H 3.93; N 14.90; S 5.69 %; Found: C 55.46; H 3.62; N 15.12; S 5.80 %. %. IR (cm$^{-1}$, KBr) : ν($N^1$–H) 3390 m b; ν(C–H) 3062 w, 2992 w, 2862 w; 1609 m; $\nu_{as}$(N-O)

1547s; δ(C-H) 1476 s, 1437 s; $\nu_s$(N-O) 1312 s; 1250 m, 1171 s, 1101s, 1015 w, 966 w, 836 w; ν(C–S) 757 m; 695 s, 648 m, 562 w, 515 w, 438 m. Electronic absorption spectrum, DMSO, $\lambda_{max}$ /nm, ε / L mol$^{-1}$ cm$^{-1}$ : [10$^{-4}$ M] 394 (1.37 x 10$^4$), 380 (1.26 x 10$^4$), 284 (1.79 x 10$^4$). Fluorescence spectrum: $\lambda_{max}^{em}$ = 438 nm; $\lambda_{max}^{ex}$ = 300 nm. $^1$H NMR (δ, ppm; $CDCl_3$): δ = 9.66 (2H, s, $C^9H_{dm\text{-}bipy}$ + $C^{16}H_{dm\text{-}bipy}$), 8.66 (2H, d ,$C^{12}H_{dm\text{-}bipy}$+ $C^{13}H_{dm\text{-}bipy}$), 8.41 (1H, s, $C^2H$), 8.14 (3H, m, $C^4H$ + $C^7H$ +$N^1$ H), 7.71 (2H, d, $C^{10}H_{dm\text{-}bipy}$+ $C^{15}H_{dm\text{-}bipy}$), 7.44 (2H, d, *m*-$H_{ph}$), 7.27(2H, m, *m*-$H_{ph)}$, 6.94 (1H, m, *p*-$H_{ph}$), 6.77 (1H, d, $C^6H$), 3.00 (6H, s, $C^{11,14}H_3$) .

*2.1.11. [Zn(L$^4$)(dm-phen)]·CH$_3$CN* ***(11)***.Yield: 0.052g, 73%, m.p. 216-218°C. *Anal.* Calc. for $C_{28}H_{22}N_6O_3SZn{\cdot}CH_3CN$: C 57.28; H 4.01; N 15.59; S 5.10 %; Found: C 57.33; H 4.07; N 15.61; S 5.29 %. IR (cm$^{-1}$, KBr) : ν($N^1$–H) 3360 br; ν(C–H) 3078 w, 3023 w, 2921 br, 2831 w; 1648 s, 1601 s; $\nu_{as}$(N-O) 1547 s; δ(C−H) 1492 s, 1414 s; 1312 s; $\nu_s$(N-O) 1312 s; 1257 m, 1164 m, 1101 m, 945 s, 870 s; ν(C–S) 749 m; 735 s, 694 m, 655 w, 554 w, 515 w, 414 w. Electronic absorption spectrum, DMSO, $\lambda_{max}$ /nm, ε / L mol$^{-1}$ cm$^{-1}$ : [10$^{-4}$ M] 425 (2.06 x 10$^4$), 376 (1.89 x 10$^4$), 298(1.07 x 10$^4$), 271(2.39 x 10$^4$). Fluorescence spectrum: $\lambda_{max}^{em}$ = 438 nm; $\lambda^{ex}$ = 300 nm. $^1$H NMR (δ, ppm; $CDCl_3$:DMSO, 9:1): δ = 9.93 (2H, s, $C^{11}H_{dm\text{-}phen}$ + $C^{14}H_{dm\text{-}phen}$), 8.75 3H, m, $C^2H$ +$C^{12}H_{dm\text{-}phen}$+ $C^{13}H_{dm\text{-}phen}$), 8.51 (2H, m, $C^{12}H_{dm\text{-}phen}$+ $C^{13}H_{dm\text{-}phen}$), 8.01 (2H, m, $C^4H$ + $C^7H$), 7.82 (1H, m, $N^1$ H), 7.68 (2H, m, $C^{10}H_{dm\text{-}phen}$+ $C^{15}H_{dm\text{-}phen}$), 7.41 (2H, d, *m*-$H_{ph}$), 7.24(2H, m, *m*-$H_{ph)}$, 6.91 (1H, m, *p*-$H_{ph}$), 6.34 (1H, d, $C^6H$), 3.05 (6H, s, $C^{9,16}H_3$).

*2.1.12. [Zn(L$^4$)(tm-phen)]·CH$_3$CN* ***(12)***. Yield: 0.051 g, 69%, m.p. 224-226°C. *Anal.* Calc. for $C_{30}H_{26}N_6O_3SZn{\cdot}CH_3CN$: C 58.49; H 4.45; N 14.92; S 4.88 %; Found: C 58.67; H 4.58; N 15.03; S 5.02 %. IR (cm$^{-1}$, KBr) : ν($N^1$–H) 3382 m, b; ν(C–H) 3061 w, 2936 w, 2861 w; 1639 s, 1609 s; $\nu_{as}$(N-O) 1562 s; δ(C−H) 1494 s, 1429 s, 1406 s; $\nu_s$(N-O) 1328 s; 1242 m, 1171 s, 1101 s, 1093 s, 921 s; 865 s; ν(C–S) 757 m; 725 m, 631 m, 491 m, 452 w. Electronic absorption spectrum, DMSO, $\lambda_{max}$ /nm, ε / L mol$^{-1}$ cm$^{-1}$ : [10$^{-4}$ M] 421 (1.89 x 10$^4$), 371(1.66 x 10$^4$), 305 (1.12 x 10$^4$), 280(2.68 x 10$^4$). Fluorescence spectrum: $\lambda_{max}^{em}$ = 439 nm; $\lambda^{ex}$ = 300 nm. $^1$H NMR (δ, ppm; $CDCl_3$:DMSO, 9:1): δ = 9.52 (2H, s, $C^9H_{tm\text{-}phen}$ + $C^{16}H_{tm\text{-}phen}$), 8.82 (1H, s, $C^2H$), 8.68 (2H, s, $C^4H$ + $C^7H$), 8.60 (2H, m, $C^{12}H_{tm\text{-}phen}$+ $C^{13}H_{tm\text{-}phen}$), 8.31(1H, m, $N^1$ H), 8.11 (2H, d, *m*-$H_{ph}$), 7.71 (2H, m, o-$H_{ph)}$, 7.19 (1H, m, *p*-$H_{ph}$), 6.64 (1H, d, $C^6H$), 2.92 (6H, m, $C^{11,14}H_3$), 2.72 (6H, m, $C^{10,15}H_3$).

*2.2. X-ray crystallography*

X-ray data of complexes were collected on a Bruker's Apex-II CCD diffractometer (**5**, **8**, **9**; 296(2) K) using Mo Kα (λ = 0.71069 Å) and with an Agilent Eos (Gemini) diffractometer (**10**, **11**; 173(2) K) using Cu-Kα ($\lambda$ = 1.54178 for **10**, **11**) radiation. The data for **5**, **8** and **9** were processed by SAINT and that for **10** and **11** were processed with CrysAlisPro (data collection) and CrysAlisPro RED (cell refinement and data reduction). Lorentz and polarization effects and empirical absorption corrections were applied using SADABS. The structures of **5**, **8** and **9** were solved by direct methods, using SIR-92 [25] and refined by full-matrix least squares refinement methods based on $F^2$, using SHELX-2017 [26]. The hydrogen atoms of nitrogen were located from the difference Fourier synthesis and were refined isotropically with a distance of 0.84 Å with $U_{iso}$ values 1.2 times that of their carrier nitrogen atoms. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were fixed geometrically with their $U_{iso}$ values 1.2 times of phenyl carbons and in case of methyl carbons $U_{iso}$ values were fixed 1.5 times of methyl carbons. WE couldn't resolve disorder in some atoms of complexes **8** and **9** (acetonitrile molecule in complex **8**, and terminal methyl and nitro group groups in **9**). All calculations were performed using Wingx package [27]. The structures of **10** and **11** was solved by direct methods using Superflip (compound **10**) or SHELXS-97(compounds **11**), refined by full-matrix least-squares techniques against $F^2$ using SHELXL-97 and molecular graphics from SHELXTL. Atomic scattering factors were taken from the International Tables for Crystallography. All non-hydrogen atoms were refined anisotropically and the hydrogens were fixed geometrically [28-32].

*2.3. Antimicrobial studies*

*2.3.1. Test organisms and Inoculum preparation :* The reference strains of bacteria and yeasts were obtained from the Microbial Type Culture Collection (MTCC), Institute of Microbial Technology (IMTECH), Chandigarh, India and the clinical isolate methicillin resistant *Staphylococcus aureus* (MRSA) was obtained from the Post graduate Institute of Medical Education and Research, (PGIMER), Chandigarh, India. Reference strains included Gram

positive bacteria, *Staphylococcus aureus* (MTCC740), *Enterococcus faecalis* (MTCC439), Gram negative bacteria, *Klebsiella pneumonia* 1 (MTCC109), *Escherichia coli* (MTCC119), *Salmonella typhimurium* 1(MTCC98), and one yeast strain,*Candida albicans* (MTCC227). A loopful of isolated bacterial and yeast colonies were inoculated into 5 mL of their respective medium and incubated at 37 °C and 25 °C, respectively, for 4 h. This was used as inoculums after adjusting the turbidity as per the Mc Farland turbidity standard. This turbidity is equivalent to approximately 1 to 2 × $10^8$ colony forming units per ml (CFU/ml). The inoculums thus prepared was used further for further testing.

*2.2.2. Screening of Compounds for antimicrobial activity by agar well diffusion assay:* Sensitivity of different bacterial strains to different compounds was measured in terms of zone of inhibition using an agar well diffusion assay [33]. All the compounds were dissolved in dimethyl sulfoxide (dmso) to a final concentration of 0.1%. The plates containing Muller Hinton agar medium, yeast malt agar and Sabouraud agar were spread with 50 µL of the bacterial and yeast inoculums, respectively. Wells (6 mm diameter) were cut out from agar plates using a sterilized stainless steel cork borer and filled with 50 µL of the compound. The plates were incubated at 37˚C and 25˚C for 24 h and the diameter of the resultant zone of inhibition was measured. Experiments were run in duplicate for each combination of extract and microbial strains. The results were compared with a control in which compounds were replaced with dmso. In order to compare the effectiveness of the compounds, their activities were compared with a standard antibiotic, namely, Gentamicin (1 mg/ mL) for bacterial culture and Amphotericin (1 mg/ mL) for yeast culture. Gentamicin acts as a positive control against bacteria (MRSA, *S. aureus, K. pneumoniae , E. faecalis, E. coli, S. typhimurium)* and Amphotericin acts as a positive control against yeast (*Candida albicans*).

*2.2.3. Minimum inhibitory concenteration (MIC):* Minimum inhibitory concentration of the selected compounds was worked out by the agar dilution method [34]. A stock solution of (5 mg/mL) concentration was prepared and incorporated into a Muller Hinton agar medium for bacteria and yeast malt extract medium for yeast. The final concentrations of the compound in the medium containing plates ranged from (0.005-3 mg/mL). These plates were then inoculated with 0.1 mL of the activated bacterial and yeast strains by streaking with a sterile tooth pick. The plates were incubated at 37 °C for bacteria and 25 °C for yeast for 24 h. The minimum

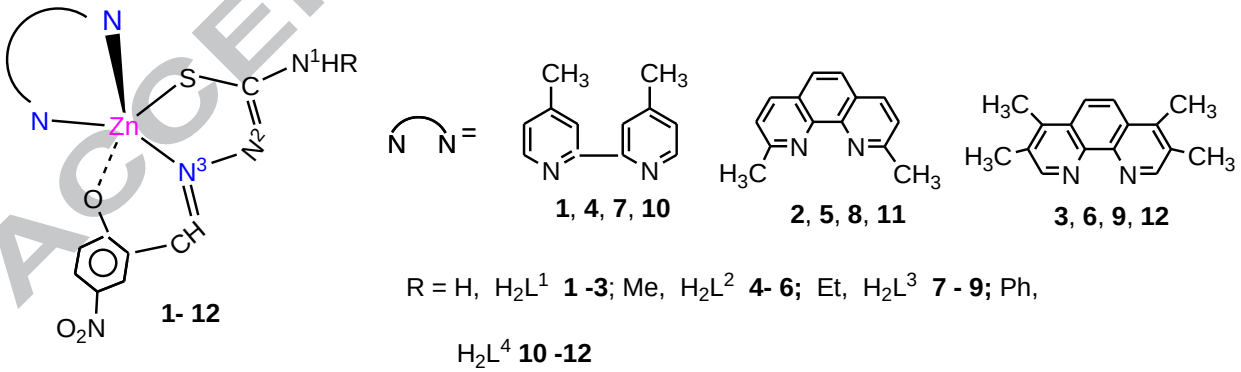
concentration of the extract causing complete inhibition of the microbial growth was taken as MIC. The results were compared with that of control in which the sample was replaced with DMSO.

*2.2.4.Cellular toxicity testing using MTT assay.*The calorimetric measurements of 3-[(4, 5-dimethylthiazol-2-yl)-2, 5-diphenyl] tetrazolium bromide (MTT) cytotoxicity assay is based on the capacity of mitochondrial succinate dehydrogenase enzymes in living cells (sheep blood used) to reduce the yellow water soluble substrate (MTT) into an insoluble purple colored formazan product that are dissolved in DMSO [19, 35].

## 3. Results and discussion

### *3.1. Synthesis, IR and $^1$H NMR spectroscopy*

Chart 4 shows coordination compounds of 5-nitro-salicylaldehyde-$N^1$-substituted thiosemicarbazonates of Zn(II) with dm-bipy, dm-phen or tm-phen as co-ligands. Here, the acetate anions of the zinc salt has removed OH and $N^2H$ protons of the thiosemicarbazones and thus the thio-ligands are coordinated to Zn(II) as O,N,S- terdentate dianions. Further, each of the co-ligands occupies two coordination sites leading to the formation of five coordinated compounds of general 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**). These compounds are soluble in dimethylsulfoxide and partially soluble in dichloromethane, methanol and acetonitrile.




R = H, $H_2L^1$ **1 -3**; Me, $H_2L^2$ **4- 6;** Et, $H_2L^3$ **7 - 9;** Ph, $H_2L^4$ **10 -12**

Chart **4**. Chem draw structral view of complexes.

The uncoordinated thiosemicarbazones have shown IR bands due to $\nu(N^1–H)$, $\nu(O–H)$ and $\nu(N^2–H)$ vibrational groups in the ranges, 3341-3435, 3302-338 and 3131-3221 $cm^{-1}$ respectively (see SI). In complexes only IR bands due to $\nu(N^1–H)$ were observed in the range, 3328 -3477 $cm^{-1}$ and it supported deprotonation of $N^2–H$ and O–H moieties and consequently the thio-ligands coordinated to the metal center as dianions, $(L^n)^{2-}$. The nitro group ($–NO_2$) of the aromatic ring at $C^2$ carbon of the coordinated thio-ligand showed medium to strong bands in the ranges, $\nu_{as}(N–O)$, 1533 -1562; $\nu_s(N–O)$, 1302 -1328 $cm^{-1}$ [36, 37]. Further, the diagnostic $\nu$(C-S) (intense bands) of the free ligands at 1042-1012 $cm^{-1}$shift to the low energy region, 773–720 $cm^{-1}$ (as medium to strong bands) in their coordination compounds supporting co-ordination by S-donor atoms [19].

The proton NMR spectra of the uncoordinated thio-ligands $H_2L^1$, $H_2L^2$, $H_2L^3$ and $H_2L^4$ showed the signals due to OH and $N^2H$ moieties in the ranges, 11.10 – 11.89, and 8.50 – 10.32 ppm, respectively and these signals disappeared in the complexes, **1-12.** It supports that the thio-ligands coordinate to zinc(II) metal center as dianions. The proton signals due to $C^2H$ and $N^1H$ moieties appeared in the ranges, 8.07 -8.82 and 7.33-8.31 ppm respectively in complexes, and were low / upfield relative to the free thio-ligands. The signals due to other protons of thio-ligands and co-ligands are listed in the experimental section (see SI).

*3.2. Crystal and molecular structures*

Coordination compounds **5**, **8-11** formed single crystals which have been studied using X-ray crystallography. Compounds **5, 8-10** crystallized in the triclinic crystal system with space groups $P\bar{1}$ in each case while compound **11** crystallized in the monoclinic crystal system with space group $P2_1/n$. Crystal data are given in Table 1 while bond parameters of the co-ordination polyhedron are given in Table 2. The crystal structure of compound, [Zn($L^4$)(dm-bipy)] **10,** showed the presence of two independent molecules, namely, molecule I and molecule II (Fig.1) with small differences in various bond parameters. In molecule I, zinc(II) is bonded to O(1A), N(1A) and S(1A) donor atoms of the thio-ligand at bond distances of 2.0134(13), 2.3441(6) and 2.0976(17) Å, respectively, and to $N(4A)_{ax}$ and $N(5A)_{eq}$ atoms of dm-bipy at bond distances of 2.1286(17) and 2.0895(15) Å, respectively (ax = axial; eq = equatorial). The angles around

zinc(II) vary in the range 77-175º (Table **2**). The chelating angle, $N(4A)_{ax}$-Zn(1A)-$N(5A)_{eq}$, made by the co-ligand dm-bipy is the shortest angle of 77.78(6)º. The distortion value of a five co-ordinated polyhedron is calculated by the two largest bond angles using the relationship, $\tau$ = (β-α)/60 (where α, β are the two largest bond angles). The value of $\tau$ = 1 supports an ideal trigonal bipyramid structure and the value of $\tau$ =0 supports a square pyramidal environment [38]. In molecule I, the trans bond angles, namely, N(1A)-Zn(1A)-$N(5A)_{eq}$, 175.55(6)º and O(1A)-Zn(1A)-S(1A), 140.74(5)º give a $\tau$ value of 0.580 which suggests that the geometry around zinc(II) is distorted from a square pyramid. Molecule II has similar bond parameters and a $\tau$ value of 0.529 suggests that this molecule has a similar distorted structure. In the literature, the analogous compound [Zn($L^4$)(bipy)] also showed a similar structure with a $\tau$ value of 0.567 [19]. Fig **2** shows a simplified structural view of molecules I and II and it can be seen that $N(5)_{eq}$-Zn-N(1) form the largest bond angles in both of the molecules. Two molecules are inversely positioned in the unit cell.

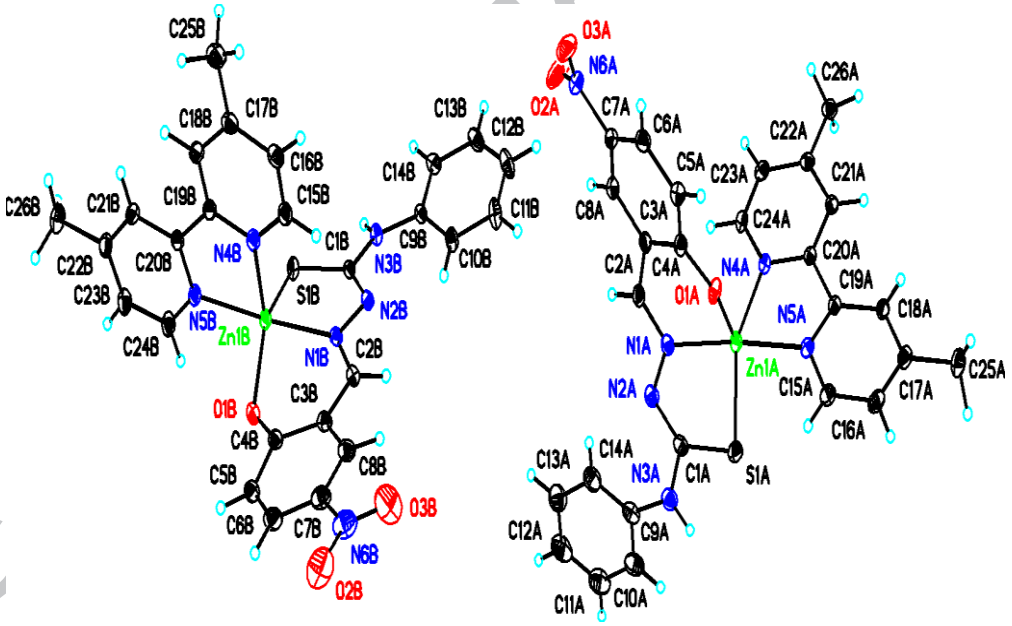



**Fig.1.** Molecular structure of compound, [Zn($L^4$)(dm-bipy)] **(10)**.

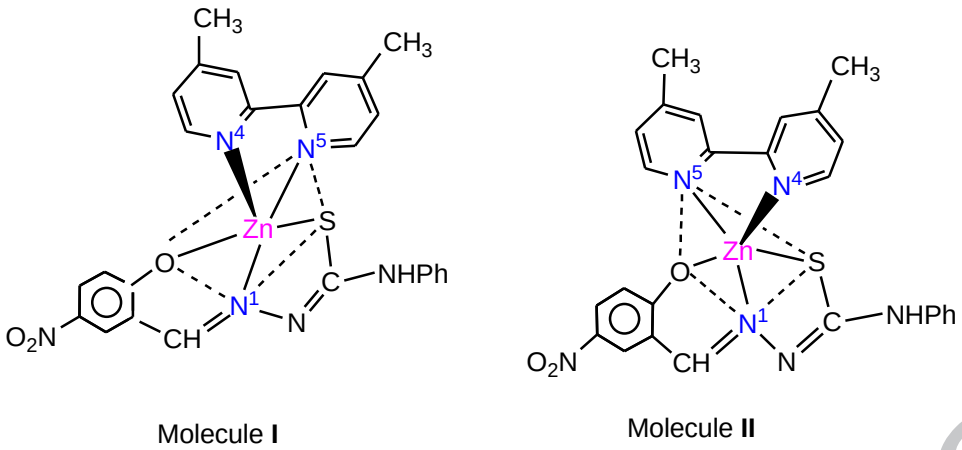



**Fig. 2.** A simple structural view of molecules **I** and **II** of compound **10**.

The crystal structure of co-ordination compound, $[Zn(L^2)(dm\text{-}phen)]\cdot CH_3CN$ **5** having dm-phen as the co-ligand also showed the presence of two independent molecules (Fig. 3). In molecule I, zinc(II) is coordinated to O(1A), N(4A) and S(1A) of the thio-ligand at bond distances of 1.992(2), 2.101(3) and 2.3870(10), respectively, and to $N(1A)_{ax}$ and $N(2A)_{eq}$ atoms of dm-phen at bond distances of 2.165(3) and 2.110(3), respectively. Atoms O(1A), N(4A), S(1A) and $N(2A)_{eq}$ occupy a square basal plane and $N(1A)_{ax}$ occupies an axial site. The trans bond angles in the square plane, namely, N(4)-Zn(1)-$N(2)_{eq}$, 164.00(10)$^o$ and O(1)-Zn(1)-S(1), 153.54(7)$^o$ give a $\tau$ value of 0.174 which suggests that the geometry around zinc(II) is close to a square pyramid. Molecule II has similar bond parametersand geometry with $\tau$ = 0.185. Compound **5** contains co-crystallized acetonitrile in the crystal. Fig. 4 shows a simplified structural view of molecules I and II.

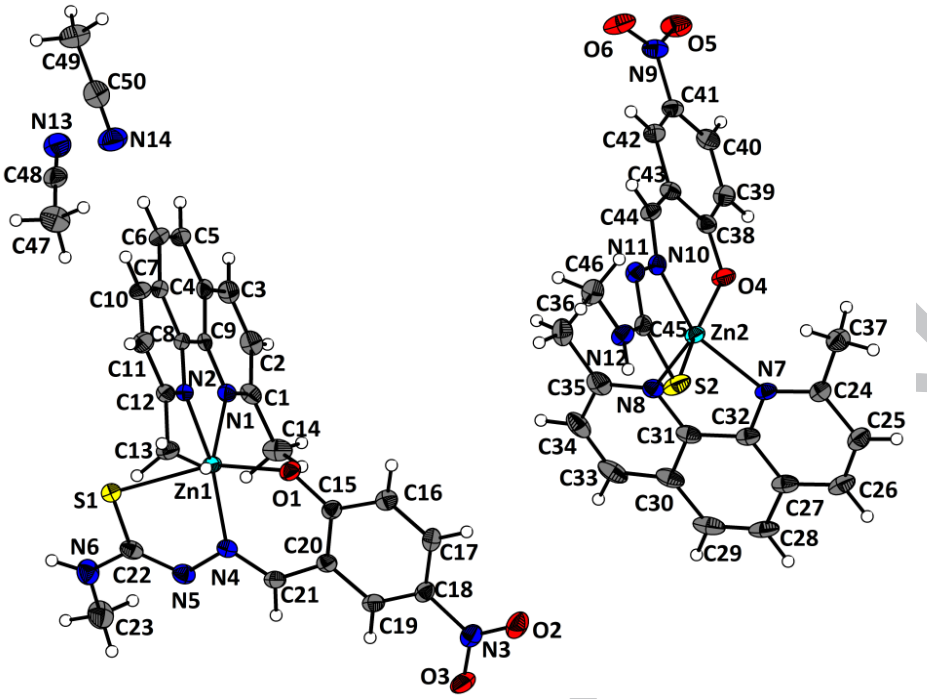



**Fig. 3.** Molecular structure of [Zn($L^2$)(dm-phen)]·$CH_3CN$(**5**).

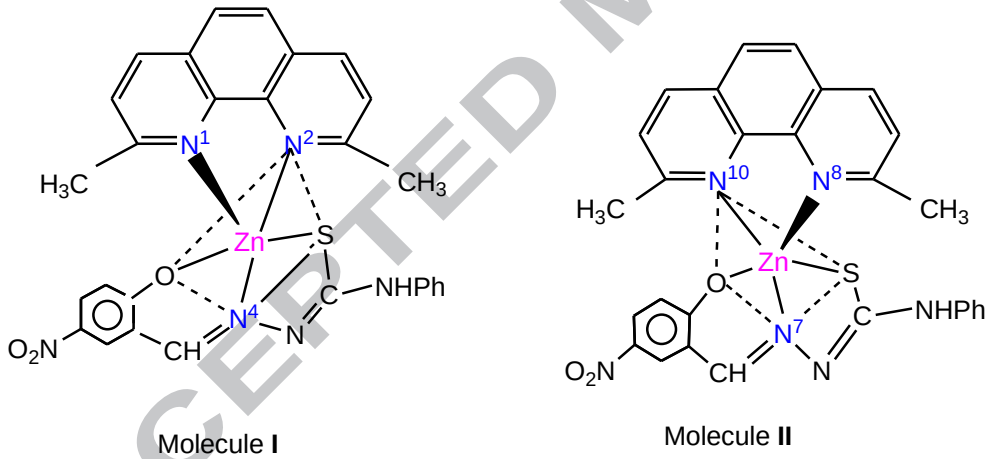



**Fig. 4.** A structural view of molecules **I** and **II** of complex **5**.

The molecular structures of compounds, [Zn($L^3$)(dm-phen)]·$CH_3CN$ **8** and [Zn($L^4$)(dm-phen)]·$CH_3CN$ **11** are given in Fig. 5 and Fig. 6 respectively.The co-ordination pattern of both these compounds is similar to that of compound **5.** The $\tau$ values of compounds **8** and **11** are 0.004 and 0.250, respectively, which suggests that the geometry of each compound is similar to that of compound **5**. Compound [Zn($L^3$)(tm-phen)] **9** with tm-phen as the co-ligand has a co-

ordination pattern similar to that of compound **8** (Fig. 7)**.** The $\tau$ value of 0.546 suggests that the geometry around zinc(II) is distorted from a square pyramid and the structure is similar to that of compound **10**. The donor atom $N^1$ occupies axial sites in compounds **8** and **9** while $N^4$ donor atom occupies the axial sites in compound **11.** Fig. 8 shows simplified the structural views of compounds **8, 9** and **11**.

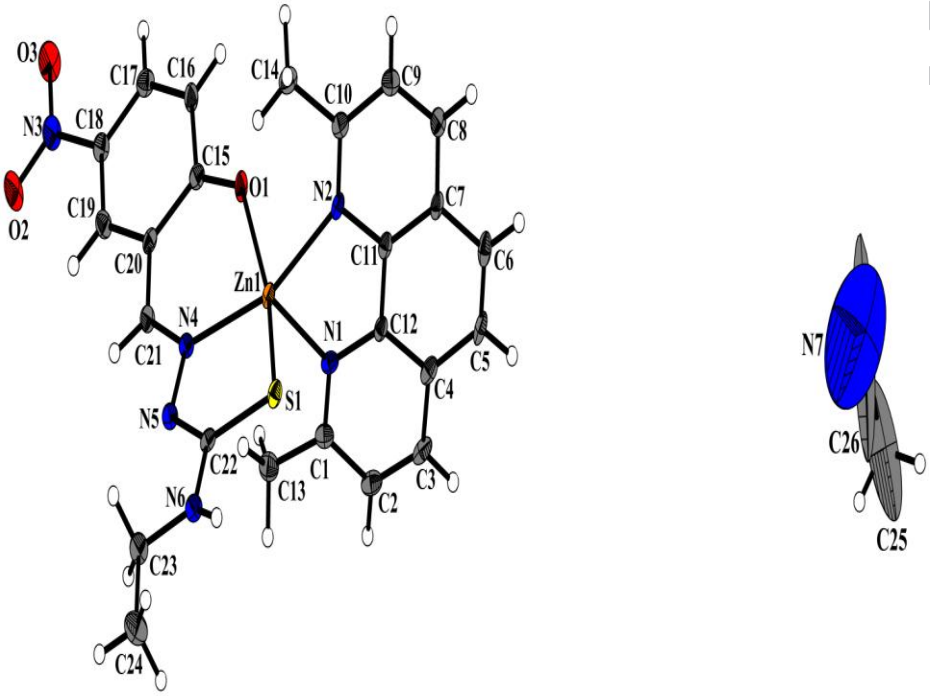



**Fig. 5.** Molecular structure of $[Zn(L^3)(\text{-dm-phen})]\cdot CH_3CN$ **(8)**

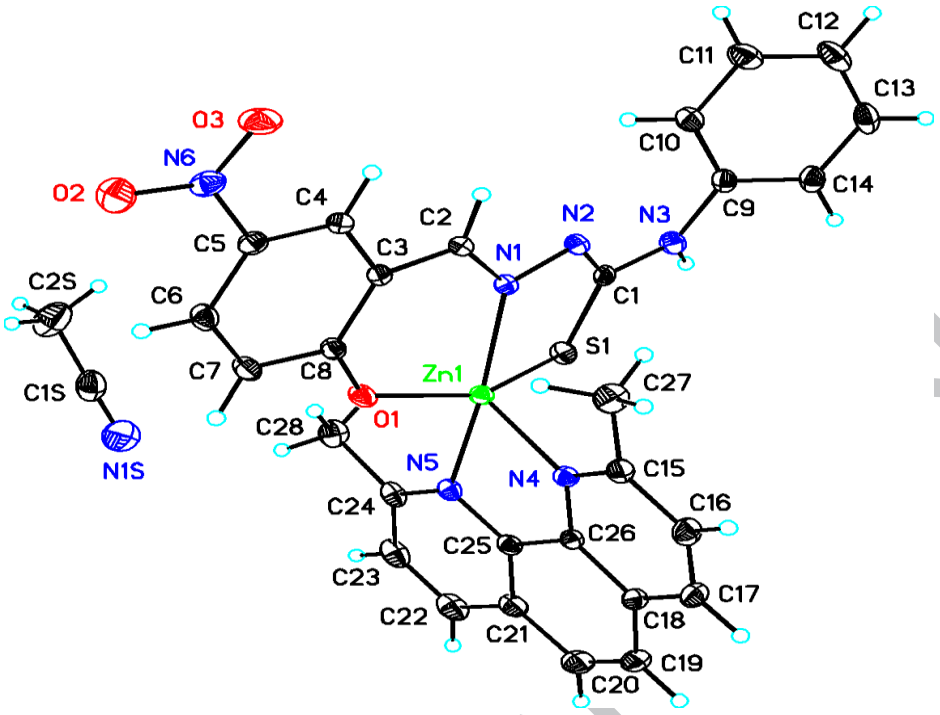



**Fig. 6.** Molecular structure of complex, [Zn($L^4$)(dm-phen)]·$CH_3CN$ (**11**).

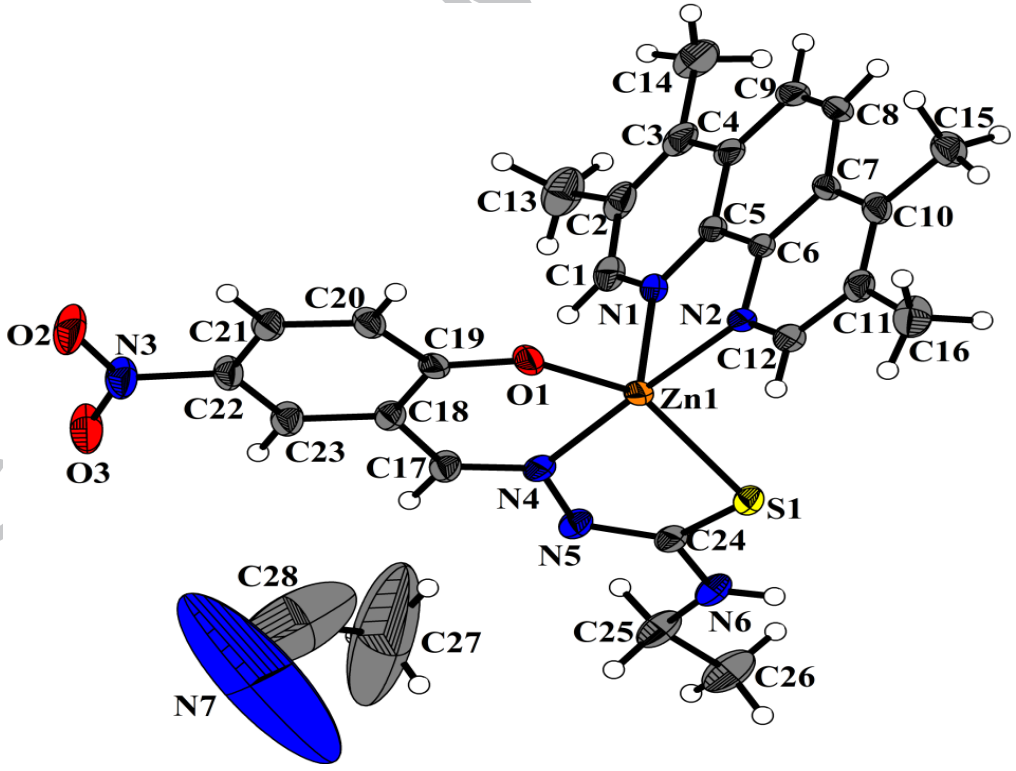



**Fig.7.** Molecular structure of [Zn($L^3$)(tm-phen)] **(9)**.

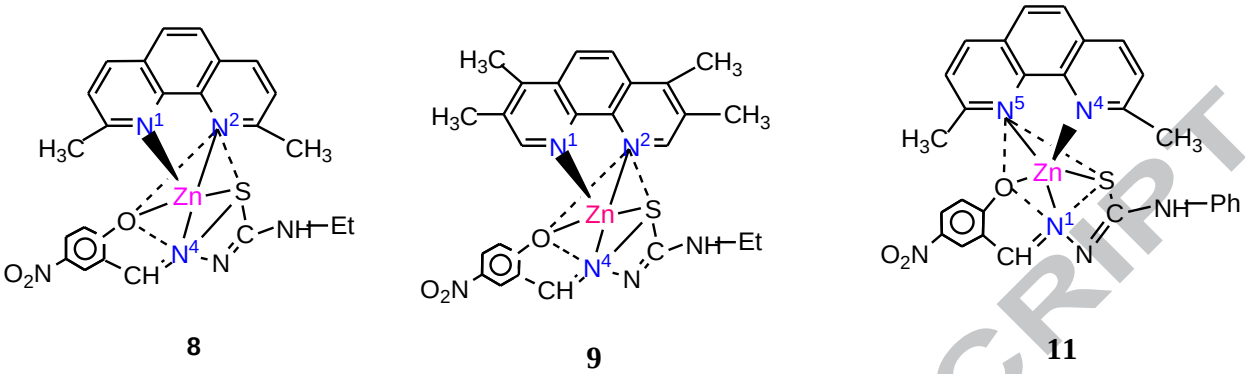



**Fig. 8.** A simplified structural view of molecules of complexes **8, 9** and **11**.

**Table 1**

Crystallographic data for compounds **5**, **8-11**.

| | **5** | **8** | **9** |
|---|---|---|---|
| Empirical formula | $C_{23}H_{20}N_6O_3SZn\cdot$ $C_2H_3N$ | $C_{24}H_{22}N_6O_3SZn\cdot$ $C_2H_3N$ | $C_{26}H_{26}N_6O_3SZn\cdot$ $C_2H_3N$ |
| M | 566.96 | 580.99 | 609.04 |
| T(K) | 296(2) | 296(2) | 296(2) |
| Crystal system | Triclinic | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| Unit cell dimensions | | | |
| a(Å) | 13.699(5) | 8.0073(12) | 8.5786(16) |
| b(Å) | 13.915(3) | 12.2681(19) | 12.192(3) |
| c(Å) | 15.304(3) | 14.628(2) | 15.426(3) |
| α(°) | 116.069(9) | 108.360(8) | 72.473(7) |
| β(°) | 94.562(10) | 104.303(8) | 84.978(7) |
| γ(°) | 107.541(10) | 97.679(8) | 82.119(7) |
| V(Å$^3$) | 2420.9(12) | 1286.2(3) | 1522.2(6) |
| Z | 4 | 2 | 2 |
| $D_{calcd}$(g cm$^{-3}$) | 1.556 | 1.500 | 1.329 |

| | | | |
|---|---|---|---|
| $\mu(mm^{-1})$ | 1.145 | 1.079 | 0.915 |
| F(000) | 1168 | 600 | 632 |
| Reflections collected | 80144 | 16145 | 26216 |
| Unique reflections | 10688, ($R_{int}$= 0.0843) | 4726, ($R_{int}$= 0.0470) | 7141, ($R_{int}$= 0.0366) |
| Data/restraints/ parameters | 10688 / 0/ 675 | 4726 /2/350 | 7141/3/ 370 |
| Reflens.with [I>2σ(I)] | 8695 | 3677 | 4643 |
| R Indices | | | |
| $R_1$ | 0.0509 | 0.0495 | 0.0626 |
| $WR_2$ | 0.1206 | 0.1238 | 0.1790 |
| R indices (all data) | | | |
| $R_1$ | 0.0675 | 0.0689 | 0.0974 |
| $WR_2$ | 0.1343 | 0.1330 | 0.2144 |
| Largest diff. Peak and hole | 0.570 and -0.463 e. Å-3 | 1.668 and -0.552 e.Å-3 | 0.875 and -0.513 e. Å-3 |

| | **10** | **11** |
|---|---|---|
| Empirical formula | $C_{26}H_{22}N_6O3SZn$ | $C_{28}H_{22}N_6O_3SZn\cdot C_2H_3N$ |
| M | 563.92 | 629.00 |
| T(K) | 173(2) | 173(2) |

| | | |
|---|---|---|
| Crystal system | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1/n$ |
| Unit cell dimensions | | |
| a(Å) | 10.4125(3) | 10.8178(2) |
| b(Å) | 12.7046(6) | 14.3720(3) |
| c(Å) | 18.9301(7) | 18.1175(4) |
| α(°) | 101.526(3) | 90 |
| β(°) | 91.235(3) | 98.325(2) |
| γ(°) | 91.318(3) | 90 |
| V(Å$^3$) | 2452.18(16) | 2787.12(10) |
| Z | 4 | 4 |
| $D_{calcd}$(g cm$^{-3}$) | 1.527 | 1.499 |
| μ(mm$^{-1}$) | 1.129 | 1.003 |
| F(000) | 1160 | 1296 |
| Reflections collected | 30382 | 37683 |
| Unique reflections | 16213, ($R_{int}$ = 0.0284) | 9595, ($R_{int}$ =0.0370) |
| Data/restraints/ parameters | 16213 / 0/ 671 | 9595/ 0/ 382 |
| Reflens.with [I>2σ(I)] | 12389 | 7524 |

| | | |
|---|---|---|
| R Indices | | |
| $R_1$ | 0.0437 | 0.0351 |
| $WR_2$ | 0.0947 | 0.0791 |
| R indices (all data) | | |
| $R_1$ | 0.0648 | 0.0539 |
| $WR_2$ | 0.1049 | 0.0893 |
| Largest diff. Peak and hole | 1.044 and -0.543e. Å-3 | 0.418 and -0.372 e. Å-3 |

**Table 2**

Important bond distances (Å) and bond angles (°) in complexes **5**, **8-11**.

| | **5** | **8** | **9** | **10** | **11** |
|---|---|---|---|---|---|
| Zn –O | 1.992(2)$^{I}$ | 1.994(3) | 1.986(3) | 2.0134(13)$^{I}$ | 1.9972(11) |
| | 2.022(2)$^{II}$ | | | 1.994(1)$^{II}$ | |
| Zn–N | 2.101(3)$^{I}$ | 2.123(3) | 2.085(3) | 2.0976(17)$^{I}$ | 2.0902(13) |
| | 2.081(3)$^{II}$ | | | 2.1038(16)$^{II}$ | |
| Zn–S | 2.387(1)$^{I}$ | 2.3874(10) | 2.3498(11) | 2.3441(6)$^{I}$ | 2.3817(4) |
| | 2.375(1)$^{II}$ | | | 2.3142(5)$^{II}$ | |
| Zn-$N_{eq}$ | 2.110(3)$^{I}$ | 2.138(3) | 2.142(3) | 2.1286(17)$^{I}$ | 2.1294(12) |
| | 2.107(3)$^{II}$ | | | 2.1207(17)$^{II}$ | |
| Zn–$N_{ax}$ | 2.165(3)$^{I}$ | 2.119(3) | 2.103(3) | 2.0895(15)$^{I}$ | 2.1141(13) |

| | | | | | |
|---|---|---|---|---|---|
| | 2.115(3)$^{II}$ | | | 2.0947(16)$^{II}$ | |
| O-Zn-N | 88.38(10)$^{I}$ | 86.95(11) | 88.47(11) | 86.53(6)$^{I}$ | 88.86(5) |
| | 88.77(10)$^{II}$ | | | 87.10(6)$^{II}$ | |
| N-Zn-S | 81.14(8)$^{I}$ | 81.00(8) | 81.91(8) | 81.79(5)$^{I}$ | 80.82(4) |
| | 82.59(8)$^{II}$ | | | 83.24(4)$^{II}$ | |
| O-Zn-S | 153.54(7)$^{I}$ | 156.48(9) | 144.91(10) | 140.74(5)$^{I}$ | 150.21(4) |
| | 163.92(8)$^{II}$ | | | 143.77(5)$^{II}$ | |
| O-Zn-$N_{eq}$ | 91.74(10) | 89.15(11) | 91.60(11) | 95.53(6)$^{I}$ | 95.61(5) |
| | 89.89(10) | | | 94.68(6)$^{II}$ | |
| $N_{eq}$-Zn-S | 91.88(7) | 93.99(8) | 96.74(8) | 94.16(4)$^{I}$ | 88.48(3) |
| | 91.64(8) | | | 97.63(5)$^{II}$ | |
| N-Zn-$N_{eq}$ | 164.00(10)$^{I}$ | 156.73(12) | 177.69(11) | 175.55(6)$^{I}$ | 165.25(5) |
| | 152.83(11)$^{II}$ | | | 175.51(6)$^{II}$ | |
| $N_{eq}$-Zn-$N_{ax}$ | 79.09(10)$^{I}$ | 79.15(12) | 78.45(12) | 77.78(6)$^{I}$ | 79.21(5) |
| | 79.87(11)$^{II}$ | | | 78.13(6)$^{II}$ | |
| τ value | 0.174$^{I}$ | 0.004 | 0.546 | 0.580$^{I}$ | 0.250 |
| | 0.185$^{II}$ | | | 0.529$^{II}$ | |

N = N(thio-ligand); $N_{eq}$ = Nitrogen atom of co-ligand forming the largest bond angle; $N_{ax}$ = second nitrogen atom of co-ligand; I = Molecule 1, II = Molecule 2.

*3.3. Electronic absorption and fluorescence spectroscopy*

The electronic absorption spectra of $10^{-4}$ M solutions of **1-12** in dimethylsulfoxide display absorption bands in the UV−Visible region as shown in Figs. 6-9. The electronic spectral bands in the region, 270-308 nm are assigned to π→π* transitions, 371-389 nm are assigned to n→π* transitions and the bands in the region 421-430 nm are due to MLCT electronic absorption bands [39]. In order to check the change, if any, in the electronic absorption spectra of complexes, the

spectra were repeated after 24 h and it can be seem from the Figures S3.1-S3.4 that the spectra remain unchanged and it supports that complexes are stable in dmso. It supports the view that thio- and co-ligands are chelating strongly and are not replaced by dmso in its solutions. Complexes were found to be non-conducting in dmso (see supporting information).

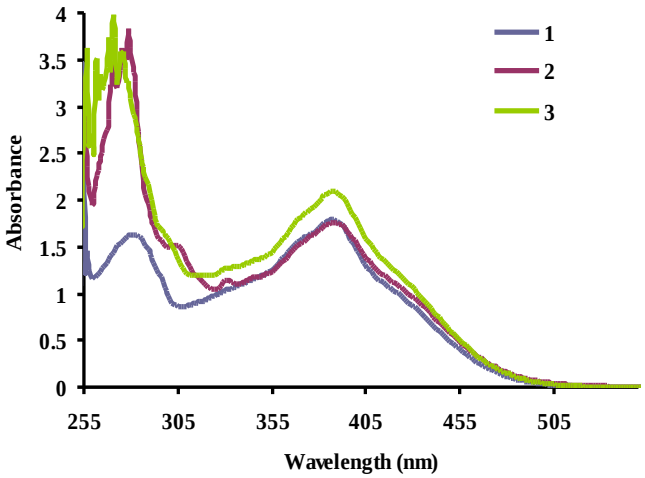



**Fig. 9.** UV-visible spectra of complexes **1-3**

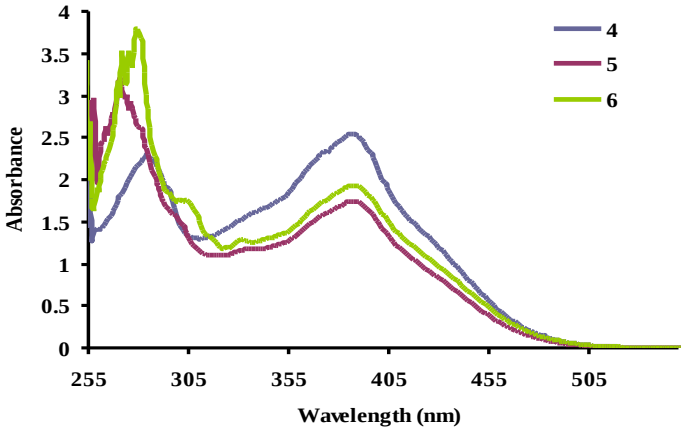



**Fig.10.** UV-visible spectra of complexes **4-6**

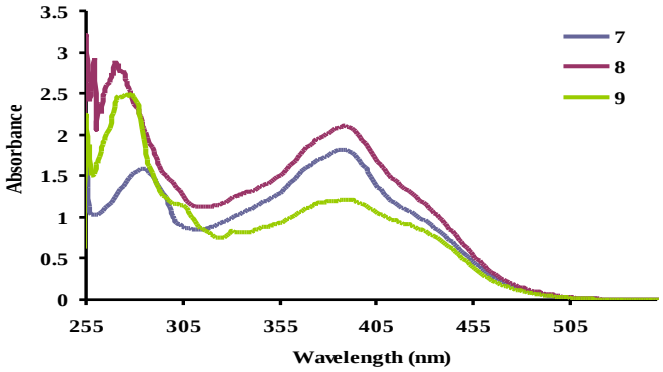



**Fig.11.** UV-visible spectra of complexes **7-9**

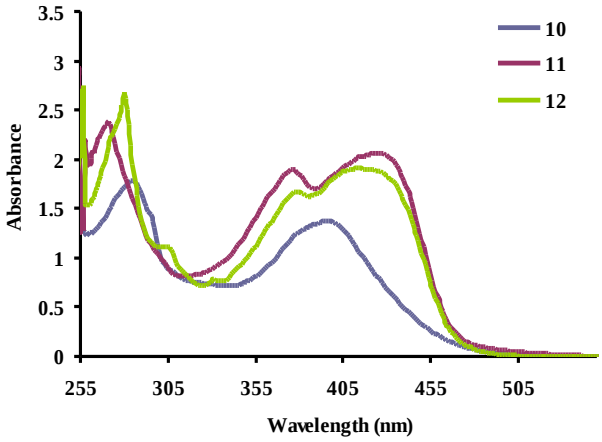



**Fig.12.** UV-visible spectra of complexes **10-12**

These complexes exhibit fluorescence in the range, 368-570 nm with $\lambda_{max}$ at 430-440 nm corresponding to the excitation wavelength, $\lambda$ = 300 nm (Fig. 13). The origin of fluorescence appears to be linked to the {Zn(N,N)}(N, N = substituted bipy/phen) moiety involving intraligand transitions [19]. It may be noted that compounds with dm-phen/tm-phen complexes display more intense fluorescent bands (Fluorescence Intensity, F.I. = 160-180 a.u.) in comparison to dm-bipy complexes (F.I. = 150 a.u.; Fig. 13). The difference in fluorescence intensity may be attributed to the fact that there occurs more conjugation in complexes with phen as co-ligand than that in complexes with bipy as co-ligand. In addition, zinc(II) complexes with methyl and phenyl substitution at $N^1$ nitrogen have shown less intense fluorescent bands.

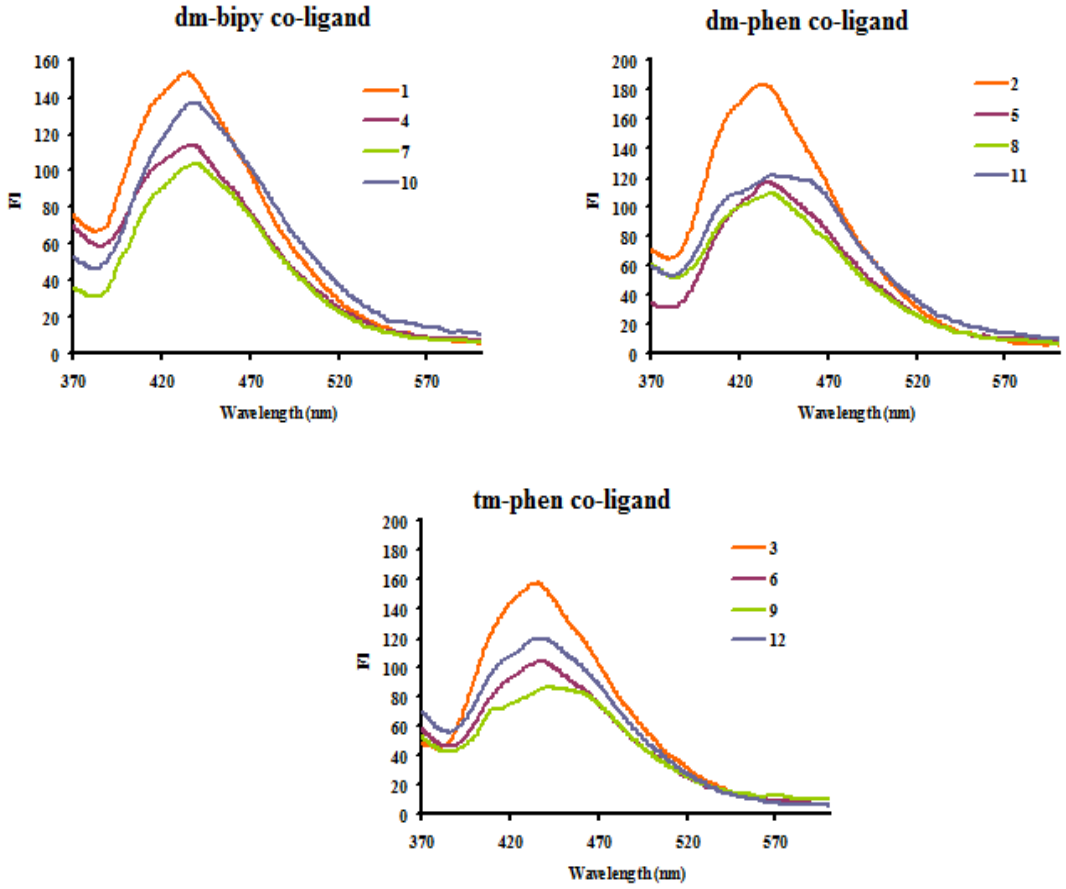



**Fig. 13.** Fluorescence spectra of zinc(II) complexes, **1-12** {$\lambda_{max}^{em}$ = 434 (**1**), 435 (**2**), 435 (**3**), 437 (**4**), 436 (**5**),434 (**6**), 437 (**7**),440 (**8**), 440 (**9**), 438 (**10**), 438 (**11**), 439 (**12**); $\lambda^{ex}$ = 300 nm}

*3.4. Antimicrobial activity*

*3.4.1. Discussion of antimicrobial activity and its comparison with literature*

Tables 3 and 4 contain data of zone of inhibition (zoi) and minimum inhibitory concentration (mic) and some important observations are delineated below. Complexes **2**, **4**, **7** and **8** have shown higher activity against *Methicillin resistant Staphylococcus aureus* (MRSA) with zoi in the range, 29-32 mm, which is comparable with that of the commercially available Gentamicin (zoi, 33 mm). Interestingly, the mic of complexes **2**, **4**, **7** and **8** (5-7 μg/mL, Table **4**) is less than that of Gentamicin (mic, 10 μg/mL). It was noted that the bio-activity of these complexes is higher at low mic values as compared with that of the analogous Zn(II) complexes

with bipy and phen as co-ligands [19]. The antimicrobial activity of complexes **2, 4, 10** and **11** against *Staphylococcus aureus*, with zoi in the range 25-27 mm, is comparable with that of commercially available Gentamicin (zoi, 26 mm, mic, 0.5 μg/mL), but complexes **2, 4** and **11** have mic of 7 μg/mL which is higher than that of Gentamicin. The bioactivity of these complexes against *Staphylococcus aureus* is low as compared with that of the analogous Zn(II) complexes with bipy and phen as co-ligands [19].

Eight complexes (**2, 4-6, 8-11)** have shown antimicrobial activity (zoi, 30-34 mm) against *Klebsiella pneumoniae* 1 which is close to that of Gentamicin (zoi, 35 mm). Complexes **8** and **9** have mic of 1 μg/mL which is close to that of the reference compound (mic, 0.3 μg/mL), while other complexes **2, 4-6, 10** and **11** have higher mic of 5-7 μg/mL. The bio-activity of these compounds is found to be more than that of analogous Zn(II) complexes with bipy and phen as co-ligands reported in literature [19]. The activity of complexes against *Salmonella typhimurium* 1 and *Escherichia coli* is poor (zoi, 17-22 mm; mic high) as compared to that of the standard compounds (*Salmonella typhimurium* : zoi, 40 mm, mic 1μg/mL; *Escherichia coli* : zoi, 30.5 mm, mic 5μg/mL). Five complexes (**4**, **7**, **8**, **10** and **11**) have shown antimicrobial activity against *Enterococcus faecalis* in the range, 23-28 mm zoi, which is comparable to that shown by Gentamicin (zoi, 27 mm). Interestingly, complexes **4, 7, 8** and **11** have mic of 7 μg/mL which is much less than that of Gentamicin (mic, 30 μg/mL). In the case of *Candida albicans*, among complexes **1-12,** only complex **11** showed bio-activity **(**zoi, 31 mm; mic, 5 μg/mL) comparable to that of Amphotericin (zoi, 34 mm; mic, 0.1 μg/mL). Further, the bio-activity of these compounds against *Candida albicans* is more (zoi, 18 - 31 mm) than that of the previously reported analogous compounds [19].

In the literature only a few Zn(II) complexes of thiosemicarbazones have been studied for their antimicrobial activity, which are summarized as follows. 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]. For example, zinc complexes of 2-furanaldehyde and 2-acetyl-γ-butyrolactone thiosemicarbazone, namely, $[Zn(N, S\text{-}L)_2]$ and $[Zn(N, S\text{-}L)Cl_2]$, showed low antimicrobial activity against *Methicillin resistant Staphylococcus aureus* (MRSA), *Staphylococcus* aureus and *Candida albicans* and with high mic value of more

than 200 µg $mL^{-1}$. Further these complexes were inactive against *Klebsiella* pneumoniae 1 and *Salmonella* typhimurium [14]. The 2-acetylpyridine thiosemicarbazone complexes, [Zn(N,N, S-$HL)_2$], showed activity against *Staphylococcus aureus* with a mic of 125 µg $mL^{-1}$ and against *Candida albicans* with a mic of 65 µg $mL^{-1}$; other complexes of this ligand, namely, [$ZnCl_2$(N,N, S-HL)] and [$Zn(OSO_3)$(N,N, S-HL)($H_2O$)] were active against *Staphylococcus aureus* with a mic of 250 µg $mL^{-1}$ and showed no activity against *Candida albicans* [12, 13]. Finally, the thiophene-2-carbaldehyde thiosemicarbazone complex, namely, [Zn(S-$HL)_2Cl_2$], showed antimicrobial activity against *Candida albicans* with a zoi of 17 mm [11]. Higher antimicrobial bio-activity of complexes under present investigation may be attributed to the fact that the use of polypyridyl heterocyclic bases increases lipophilicity [40, 41], which enhances the cell membrane penetrating ability. The cause of inhibitory action of complexes can be due to their interaction with the enzyme prosthetic group in microbial cells, which inhibits the replication of DNA [42, 43]. In vitro cellular toxicity examined using MTT assay showed low cell viability .

Time kill studies was thought to be not necessary as we noted previously [19] that time needed to kill all bacteria by analogous complexes was maximum of 24 h. Similar time is expected for complexes under investigation.

**Table 3**

Antimicrobial activity[a,b,c] of complexes **1-12** (zone of inhibition)

| Complexes No.($R^3$) | *MRSA* | *S. Aureus* | *K. pneumonia* 1 | *S. typhimurium*1 | *E. Coli* | *E. Faecalis* | *C. Albicans* |
|---|---|---|---|---|---|---|---|
| [Zn($L^n$)(dm-bipy)] (n =1-4) | | | | | | | |
| **1** (H) | 20 | 16 | 23 | NA | 13 | 15 | 20 |
| **4** (Me) | 29 | 25 | 34 | 18 | 17 | 27 | 25 |
| **7** (Et) | 32 | 24 | 28 | 15 | 14 | 27 | 26 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **10**(Ph) | 27 | 25 | 34 | NA | NA | 28 | 27 |
| | | | [Zn($L^n$)(dm-phen)] (n =1-4) | | | | |
| **2** (H) | 30 | 27 | 30 | 21 | 22 | 21 | 20 |
| **5**(Me) | 27 | 23 | 30 | 15 | 13 | 21 | 25 |
| **8** (Et) | 29 | 23 | 33 | 15 | 15 | 25 | 25 |
| **11** (Ph) | 26 | 26 | 30 | 16 | 13 | 28 | 31 |
| | | | [Zn($L^n$)(tm-phen)] (n =1-4) | | | | |
| **3** (H) | 22 | 21 | 27 | NA | NA | 23 | 23 |
| **6** (Me) | 27 | 22 | 33 | 17 | 14 | 19 | 20 |
| **9** (Et) | 24 | 21 | 30 | NA | NA | 20 | 18 |
| **12** (Ph) | 25 | 22 | 25 | 14 | NA | 22 | 22 |
| Gentamicin[d] | 33 | 26 | 35 | 40 | 30.5 | 27 | |
| Amphotericin[e] | | | | | | | 34 |

[a)] All measurements are in mm diameter of the inhibition zone; [b)] The standard deviation varied in the range 0-1 based on three readings; [c)] Studies were made in DMSO; [d,e)] Commercially available anti-microbial agents. [d)] Gentamicin acts as positive control against bacteria (*MRSA, S. aureus, K. pneumonia* 1, *S. typhimurium* 1, E. *coli*, *E. Faecalis* ) and [e)] Amphotericin acts as positive control against yeast (*Candida albicans*); NA-not active

**Table 4**

Minimum Inhibitory concentration (MIC in μg/mL) of zinc(II) complexes, **1-12**

| Complex No. | *MRSA* | *S. aureus* | *K. pneumonia* 1 | *S. typhimurium*1 | *E. Coli* | *E. faecalis* | *C. albicans* |
|---|---|---|---|---|---|---|---|
| | | | [Zn($L^n$)(dm-bipy)] (n =1-4) | | | | |
| **1** (H) | 50 | 750 | 10 | NA | 1000 | 1000 | 50 |
| **4** (Me) | 7 | 7 | 5 | 500 | 500 | 7 | 7 |
| **7** (Et) | 5 | 10 | 7 | 1000 | 1000 | 7 | 7 |
| **10** (Ph) | 10 | 50 | 5 | N.A. | N.A. | 50 | 500 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| [Zn($L^n$)(dm-phen)] (n =1-4) | | | | | | | |
| **2**(H) | 5 | 7 | 5 | 50 | 50 | 50 | 50 |
| **5** (Me) | 7 | 10 | 7 | 1000 | 1000 | 50 | 7 |
| **8** (Et) | 7 | 10 | 1 | 1000 | 1000 | 7 | 7 |
| **11** (Ph) | 7 | 7 | 5 | 750 | 1000 | 7 | 5 |
| [Zn($L^n$)(tm-phen)] (n =1-4) | | | | | | | |
| **3** (H) | 50 | 50 | 7 | NA | NA | 10 | 10 |
| **6** (Me) | 7 | 50 | 5 | 500 | 1000 | 50 | 50 |
| **9** (Et) | 7 | 7 | 1 | NA | NA | 7 | 7 |
| **12** (Ph) | 7 | 50 | 7 | 1000 | NA | 50 | 50 |
| Gentamycin | 10 | 0.5 | 0.3 | 1 | 5 | 30 | |
| Amphotericin | | | | | | | 0.1 |

NA = Not active

## 4. Conclusion

Coordination compounds have shown either distorted trigonal bipyramidal (**10**) or distorted square pyramidal (**5**, **8**, **9**, **11)** geometry. These complexes have displayed intense fluorescence bands at $\lambda_{max}$ = 434-440 nm and it was noted that there was increased fluorescence with dm-phen and tm-phen as compared with that of dm-bipy co-ligands. In respect of *Methicillin resistant Staphylococcus aureus* (MRSA), the bio-activity of complexes **1-12** having dm-bipy, dm-phen and tm-phen as co-ligands is high at low mic values as compared with that of analogous Zn(II) complexes with bipy and phen [19]. These complexes are less active against *Staphylococcus aureus* as compared with analogous Zn(II) complexes with bipy and phen [19]. The bio-activity of compounds against *Klebsiella pneumonia* 1 and *Candida albicans* is found to be more than that of analogous Zn(II) complexes reported in literature [19]. Finally, against *Salmonella typhimurium* 1, the current compounds are less active and require high mic. Complexes have shown very good activity against *Enterococcus faecalis* with no similar study in literature to compare with and finally only a few complexes showed activity against *E. coli.* The variation in activity appears to be the cumulative effect of nature of the thio-ligand and the

type of co-ligand used. Complexes are found to be cytotoxic to microorganisms (bactericidal / fungicidal).

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**Appendix A. Supplementary data**

CCDC 1817863, 1817862, 1817861, 1810834 and 1810834 contain the supplementary crystallographic data for complexes **5, 8, 9**, **10** and **11** respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac. uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org.

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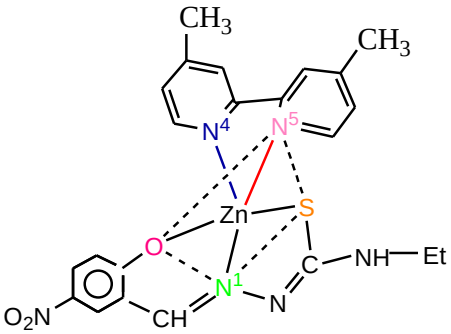
## Graphical abstract-Pictogram




**8**

High activity against **methicillin resistant** ***Staphylococcus aureus*** and ***Enterococcus faecalis*** with low minimum inhibitory concentartion as compared to the standard **Gentamicin**

## Graphical abstract-Synopsis

The 5-nitro-salicylaldehyde thiosemicarbazonates of zinc(II) coordinated to substituted bipyridines/phenanthrolines have slightly distorted trigonal bipyramidal or square pyramidal geometry and have shown intense fluorescence. They have shown high bactericidal/fungicidal bio-activity against methicillin resistant *Staphylococcus aureus* (MRSA), *Klebsiella pneumonia* 1, *Candida albicans and Enterococcus faecalis.* The activity was low against *Staphylococcus aureus, Salmonella typhimurium* 1 and *E. coli.*