Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Synthesis, Spectroscopy, Structures and Antimicrobial activity of Mixed-Ligand Zinc(II) Complexes with 5-Nitro-salicylaldehyde Thiosemicarbazones

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1. Ligands detail.

*5-NO_2-Salicylaldehyde-N^1H_2 thiosemicarbazone (**H_2L-NH_2**) **1***

To a solution of NH_2 thiosemicarbazide (1.0 g, 0.001 mol) in hot methanol (50 mL) and glacial acetic acid (5 mL), was added 5-NO_2 - salicyladehyde (1.83 g, 0.001 mol). The contents were refluxed for 6 h. The clear solution obtained was poured in a beaker and allowed to evaporate at room temperature. Slow evaporation of the solution gave pale yellow crystalline compound. (Yield 0.8 g, 80 %, M.p. 220–222 °C). IR (KBr, cm^{-1}, selected absorption bands) ν(N^1–H) 3435 br; ν(N^2–H) + ν(O−H) 3221s; ν(C–H) 3062w, 2985w, 2947 w, 2925m; ν(C=N) + ν(C=C)+ δ(N−H) 1603s, 1590 s,1603 s, 1591 s, 1544 s, 1516 s, ; δ(C−H) 1478s, 1428w, 1405m; 1345 s, 1373 s, 1344 m, 1309 s, 1241 s, 1193s, 1134 s, 1101s, 1085 s, ν(C–S)1035 s; 954 s, 845 s, 773 s, 726 s, 649m, 612m, 496 m, 459 s cm^{-1}. ^{1}H NMR (δ, ppm; $CDCl_3$): δ = 11.45 (1H, s, OH), 8.57 (1H, s, N^2H), 8.39 (1H, s, C^2H), , 8.10 (2H, d, C^4H + C^7H), 7.62 (2H, s, N^1H_2), 7.04 (1H, d, C^6H) ppm. Electronic absorption spectrum (10^{-4}) m in dmso, λmax /nm, ε /L·mol^{-1}·cm^{-1}): 448 (3.05x10^2), 358 (1.57x10^4).

*5-NO_2-Salicylaldehyde-N^1-methyl thiosemicarbazone (**H_2L-NHMe**)* **2**

(Yield 0.84 g, 83 %, M.P 267- 269°C). IR (KBr, cm^{-1}, selected absorption bands) ν(N^1–H) 3380 br; ν(N^2–H)+ ν(O–H), 3131 w, ν(C–H) 2990 m, 2943 s, 2853s ; ν(C=N) + ν(C=C)+ δ(N−H) 1622 s, 1600m, 1567 s, 1532 m, 1515 s; δ(C−H) 1483 s, 1440 m; 1386 sm, 1341 s, 1281s, 1256

s, 1204, 1180 s, 1097 s, ν(C–S) 1042 s; 965s,939 s, 892 s,841s, 749 s, 704 s, 658s, 637 s, 546m, 584s, 547m, 495m, 471 m cm^{-1}. ^1H NMR (δ, ppm; $CDCl_3$): δ = 11.10 (1H, s, OH), 8.50 (1H, s, N^2H), 8.31 (1H, s, C^2H), 8.12 (H, s, C^4H), 8.07(H, s, C^7H), 7.45 (1H, s, N^1H), 7.02 (1H, d, C^6H), 3.22 (3H, d, $CH_3(N^1)$) ppm. Electronic absorption spectrum (10^{-4}) m in dmso, λmax /nm, ε /L·mol^{-1}·cm^{-1}): 457 (3.05x10^2), 337 (2.97x10^4).

*5-NO_2-Salicylaldehyde-N^1-Ethyl thiosemicarbazone (**H_2L-NHEt**) **3***

(Yield 0.81 g, 82 %, M.p. 190–192°C). IR (KBr, cm^{-1}, selected absorption bands) ν(N^1–H) 3341 w, br, ν(O−H) 3304 br, ν(N^2–H) 3158 br, ν(C–H) 2974 w; 2974 s, 2933 m, 2873; ν(C=N) + ν(C=C)+ δ(N−H) 1658 m, 1552 s, 1514 s; δ(C−H) 1444 s; 1398 s, 1340 s, 1287 s, 1227 s, 1100 s, 1074 s, ν(C–S) 1012 s; 937 s, 848 s, 799 s, 705 s, 478 s cm^{-1}. ^1H NMR (δ, ppm; $CDCl_3$): δ = 11.50 (1H, s, OH), 8.80(1H, s, N^2H), 8.39(1H, s, C^2H), 8.10 (2H, d, C^4H + C^7H), 7.02 (1H, d, C^6H), 3.59 (2H, m, $N^1(CH_2)$, 1.28 (3H, m, CH^3) ppm. Electronic absorption spectrum (10^{-4}) m in dmso, λmax /nm, ε /L·mol^{-1}·cm^{-1}): 434 (3.33 x 10^2), 338 (2.65 x 10^4).

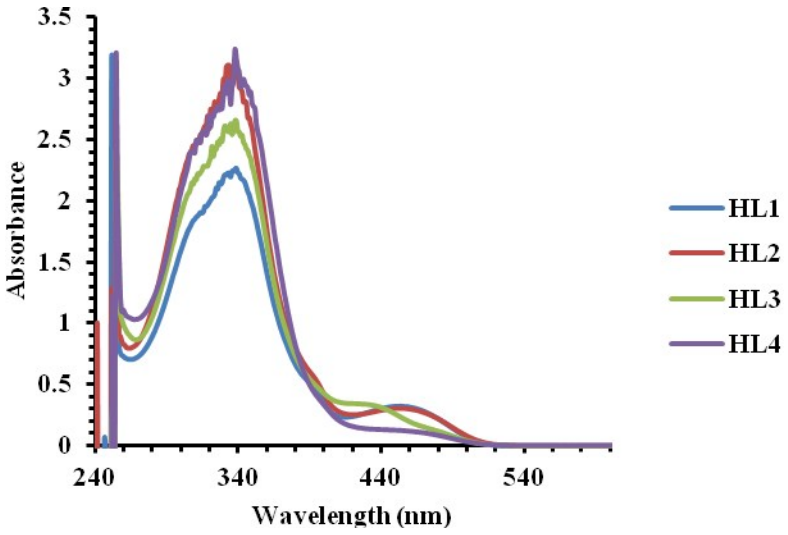
*5-NO_2-Salicylaldehyde-N^1Ph thiosemicarbazone (**H_2L-NHPh**) **4***

(Yield 0.79 g, 80 %, M.p. 204–206 °C). IR (KBr, cm^{-1}, selected absorption bands) ν(N^1–H) 3432 br; ν(O−H) 3302 br, ν(N^2–H) 3137 br, 2989 m; ν(C=N) + ν(C=C)+ δ(N-H) 1608 m, 1545 s, 1511 s; δ(C−H) 1489 s, 1446 w; 1399 s, 1345 s, 1293 s, 1262 s, 1197 s, 1134s, 1069 s, ν(C–S) 1027 s; 959 s, 850 s, 834 s, 784 s, 761 s, 726 s, 670 w, 635 s, 613 s, 593 br, 495 m cm^{-1}. ^1H NMR (δ, ppm; $CDCl_3$): δ = 11.89 (1H, s, OH), 10.32 (1H, s, N^2H), 9.00 (1H, s, C^2H), 8.49(1H, s, N^1 H), 8.10 (2H, d, C^4H + C^7H), 7.51 (2H, d, *m*-H_{ph}), 7.41(2H, m, *m*-$H_{ph)}$, 7.24 (1H, m, *p*-H_{ph}), 7.06 (1H, d, C^6H) ppm. Electronic absorption spectrum (10^{-4}) m in dmso, λmax /nm, ε /L·mol^{-1}·cm^{-1}): 455 (1.2x10^2), 338 (3.23 x 10^4).

^1H NMR of **bipyridine** (δ, ppm; $CDCl_3$): δ = 8.70 (2H, d, C^9H_{bipy} + $C^{16}H_{bipy}$); 8.42 (2H, d, $C^{11}H_{bipy}$ + $C^{14}H_{bipy}$), 7.87 (2H, m, $C^{12}H_{bipy}$ + $C^{13}H_{bipy}$), 7.32 (2H, m, $C^{10}H_{bipy}$ + $C^{15}H_{bipy}$).

^1H NMR of **phenanthroline** (δ, ppm; $CDCl_3$): δ = 9.20 (2H, d, C^9H_{phen} + $C^{16}H_{phen}$); 8.25 (2H, d, $C^{11}H_{phen}$ + $C^{14}H_{phen}$), 7.80 (2H, s, $C^{12}H_{phen}$ + $C^{13}H_{phen}$), 7.64 (2H, dd, $C^{11}H_{phen}$ + $C^{15}H_{phen}$).

2. UV spectra of thio-ligands, 1-4.



3. UV spectra of co-ligands.

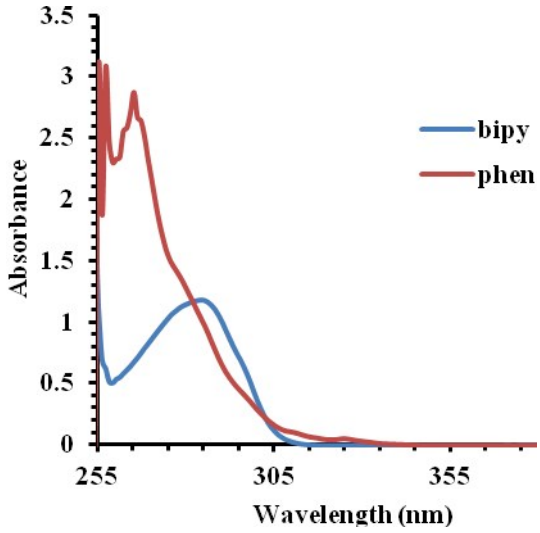


Table 1S. Bond distances (Å) and bond angles (°) in complexes **1–8.**

[Zn(κ³-O,N,S-L-NH₂)(κ²-N,N-bipy)] (1)			
Molecule **I**			
Zn(1) –O(3)	2.0181(18)	Zn(1)–N(4)	2.089(2)

Zn (1) –N(2)	2.107(2)	Zn(1)–S(1)	2.3504(10)
Zn(1)–N(1)	2.127(2)	S(1)–C(18)	1.736(2)
O(3)- Zn(1)-N(4)	88.37(8)	O(3)- Zn(1)-N(1)	90.16(8)
O(3)- Zn (1)-N(2)	96.66(8)	O(3)- Zn(1)-S(1)	152.77(6)
N(4)– Zn(1)–N(2)	114.89(8)	N(4)- Zn(1)-S(1)	82.64(6)
N(2)– Zn(1)–N(1)	78.33(8)	N(2)- Zn(1)-S(1)	110.45(6)
N(4)– Zn(1)–N(1)	166.79(9)	N(1)- Zn(1)-S(1)	92.81(6)
τ	0.233		
Molecule **II**			
Zn(2) –O(6)	1.9923(18)	Zn(2)–N(8)	2.185(2)
Zn (2) –N(7)	2.058(2)	Zn(2)–S(2)	2.3587(10)
Zn(2)–N(10)	2.107(2)	S(2)–C(36)	1.749(3)
O(6)- Zn(2)-N(10)	88.67(8)	O(6)- Zn(2)-N(8)	96.78(8)
O(6)- Zn (2)-N(7)	102.59(8)	O(6)- Zn(2)-S(2)	146.57(6)
N(7)– Zn(2)–N(10)	104.71(9)	N(10)- Zn(2)-S(2)	81.44(6)
N(7)– Zn(2)–N(8)	77.17(9)	N(7)- Zn(2)-S(2)	110.80(6)
N(10)– Zn(2)–N(8)	173.74(8)	N(8)- Zn(2)-S(2)	92.31(6)
τ	0.453		
*[Zn(κ^3-O,N,S-L-NHMe)(κ^2-N,N-phen)] (**4**)*			
Zn(1) –O(1)	1.9958(15)	Zn(1)–N(4)	2.0703(17)

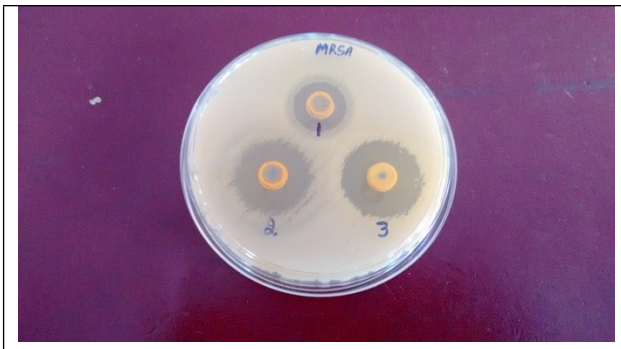
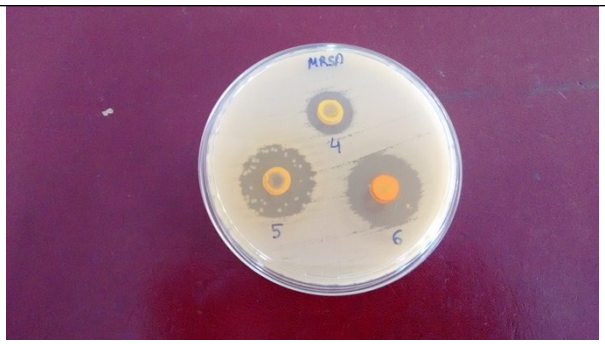
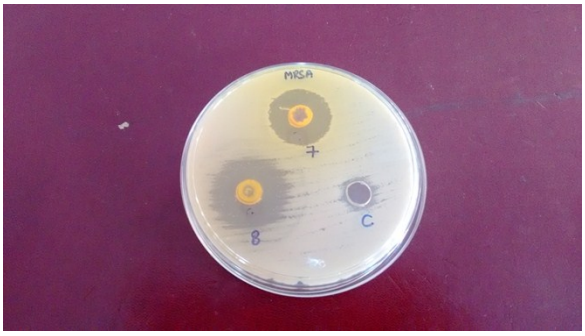
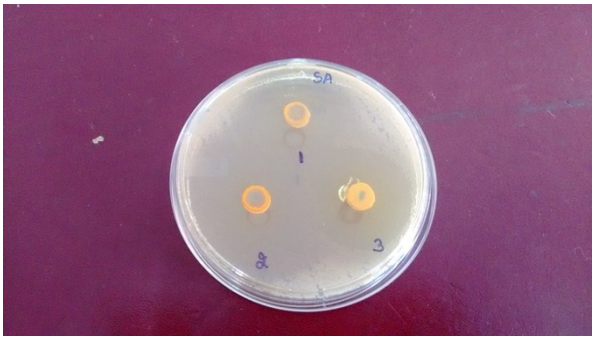
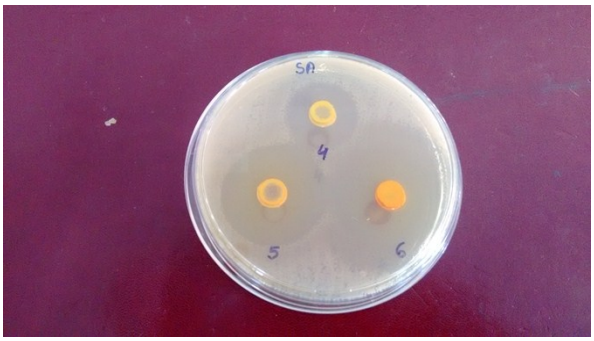
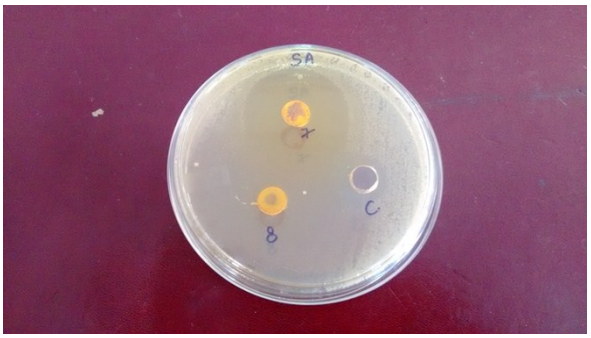
Zn (1) –N(2)	2.1267(18)	Zn(1)–S(1)	2.3385(7)
Zn(1)–N(1)	2.1606(17)	S(1)–C(20)	1.750(2)
O(1)- Zn(1)-N(4)	89.63(6)	O(1)- Zn(1)-N(1)	91.58(6)
O(1)- Zn (1)-N(2)	98.62(7)	O(1)- Zn(1)-S(1)	149.04(5)
N(4)– Zn(1)–N(2)	100.18(7)	N(4)- Zn(1)-S(1)	83.01(5)
N(2)– Zn(1)–N(1)	77.67(7)	N(2)- Zn(1)-S(1)	112.27(5)
N(4)– Zn(1)–N(1)	177.66(7)	N(1)- Zn(1)-S(1)	96.94(5)
τ	0.477		
*[Zn(κ³-O,N,S-L-NHEt)(κ²-N,N-bipy) (**5**)*			
Zn(1) –O(1)	1.9840(14)	Zn(1)–N(3)	2.0891(14)
Zn (1) –N(2)	2.1270(14)	Zn(1)–S(1)	2.3370(6)
Zn(1)–N(1)	2.1094(15)	S(1)–C(18)	1.750(2)
O(1)- Zn(1)-N(3)	87.81(5)	O(1)- Zn(1)-N(1)	90.87(6)
O(1)- Zn (1)-N(2)	110.75(6)	O(1)- Zn(1)-S(1)	133.79(5)
N(3)– Zn(1)–N(2)	96.80(6)	N(3)- Zn(1)-S(1)	81.75(4)
N(2)– Zn(1)–N(1)	77.19(6)	N(2)- Zn(1)-S(1)	115.12(4)
N(3)– Zn(1)–N(1)	172.94(6)	N(1)- Zn(1)-S(1)	104.06(4)
τ	0.653		
*[Zn(κ³-O,N,S-L-NHEt)(κ²-N,N-phen)] (**6**)*			
Zn(1) –O(1)	1.976(6)	Zn(1)–N(4)	2.111(7)
Zn (1) –N(2)	2.114(6)	Zn(1)–S(1)	2.356(2)

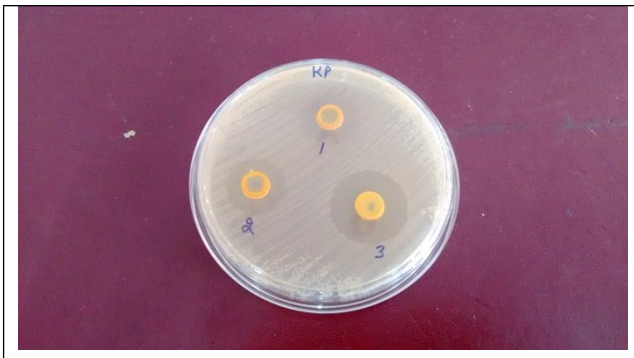
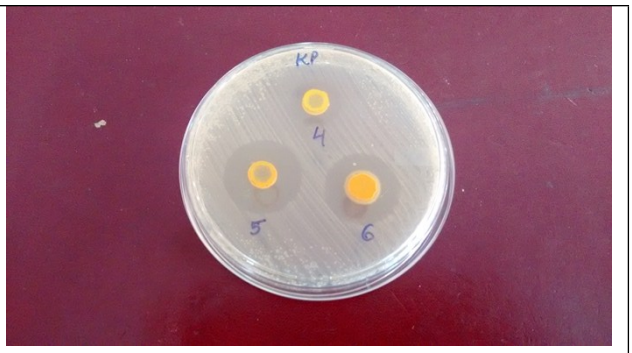
Zn(1)–N(1)	2.166(2)	S(1)–C(20)	1.760(8)
O(1)- Zn(1)-N(4)	87.3(2)	O(1)- Zn(1)-N(1)	88.0(2)
O(1)- Zn (1)-N(2)	103.0(2)	O(1)- Zn(1)-S(1)	149.04(5)
N(4)– Zn(1)–N(2)	121.8(3)	N(4)- Zn(1)-S(1)	81.82(19)
N(2)– Zn(1)–N(1)	79.1(2)	N(2)- Zn(1)-S(1)	103.01(18)
N(4)– Zn(1)–N(1)	159.1(2)	N(1)- Zn(1)-S(1)	93.67(19)
τ	0.089		
[Zn(κ³-O,N,S-L-NHPh)(κ²-N,N-bipy)] (7)			
Zn(1) –O(1)	1.9679(16)	Zn(1)–N(5)	2.0920(18)
Zn (1) –N(2)	2.1238(18)	Zn(1)–S(1)	2.3233(7)
Zn(1)–N(1)	2.1326(18)	S(1)–C(18)	1.756(2)
O(1)- Zn(1)-N(5)	89.18(7)	O(1)- Zn(1)-N(1)	107.31(7)
O(1)- Zn (1)-N(2)	95.16(7)	O(1)- Zn(1)-S(1)	138.57(5)
N(5)– Zn(1)–N(2)	172.56(7)	N(5)- Zn(1)-S(1)	81.77(5)
N(2)– Zn(1)–N(1)	77.19(6)	N(2)- Zn(1)-S(1)	113.81(5)
N(5)– Zn(1)–N(1)	96.17(7)	N(1)- Zn(1)-S(1)	98.79(5)
τ	0.567		
[Zn(κ³-O,N,S-L-NHPh)(κ²-N,N-phen)].0.5 CH_2Cl_2 (8)			
Molecule **I**			
Zn(1) –O(1)	1.994(9)	Zn(1)–N(4)	2.092(7)
Zn (1) –N(2)	2.147(6)	Zn(1)–S(1)	2.360(3)

Zn(1)–N(1)	2.085(8)	S(1)–C(20)	1.767(8)
O(1)- Zn(1)-N(4)	88.4(3)	O(1)- Zn(1)-N(1)	103.1(3)
O(1)- Zn (1)-N(2)	88.8(3)	O(1)- Zn(1)-S(1)	149.6(2)
N(4)– Zn(1)–N(2)	176.8(4)	N(4)- Zn(1)-S(1)	82.1(2)
N(2)– Zn(1)–N(1)	78.5(3)	N(2)- Zn(1)-S(1)	99.6(2)
N(4)– Zn(1)–N(1)	103.6(3)	N(1)- Zn(1)-S(1)	107.2(2)
τ	0.453		
Molecule **II**			
Zn(2) –O(4)	2.035(7)	Zn(2)–N(8)	2.115(7)
Zn (2) –N(7)	2.089(9)	Zn(2)–S(2)	2.384(2)
Zn(2)–N(10)	2.067(7)	S(2)–C(46)	1.759(9)
O(4)- Zn(2)-N(10)	87.2(3)	O(4)- Zn(2)-N(8)	91.1(3)
O(4)- Zn (2)-N(7)	96.7(3)	O(4)- Zn(2)-S(2)	152.1(2)
N(7)– Zn(2)–N(10)	109.8(3)	N(10)- Zn(2)-S(2)	82.07(19)
N(7)– Zn(2)–N(8)	78.1(3)	N(7)- Zn(2)-S(2)	111.2(3)
N(10)– Zn(2)–N(8)	172.0(3)	N(8)- Zn(2)-S(2)	95.9(2)
τ	0.331		

3. Pictutres of Zone of inhibition of complexes 1-8

MRSA	*MRSA*

	
MRSA 	*S. aureus* 
S. aureus 	*S. aureus* 
K. Pneumoniae	*K. Pneumoniae*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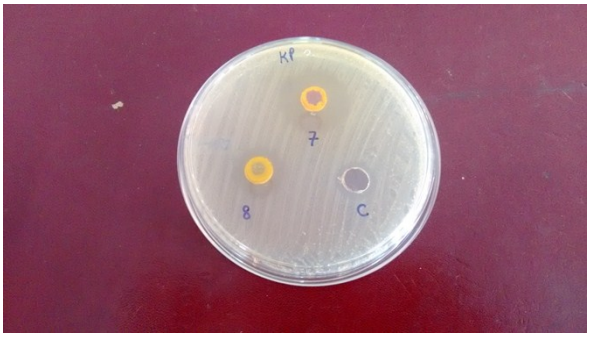	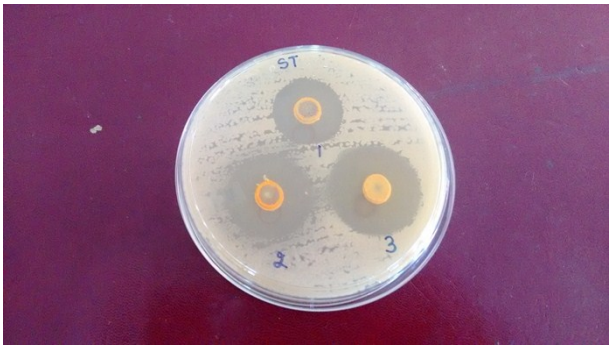
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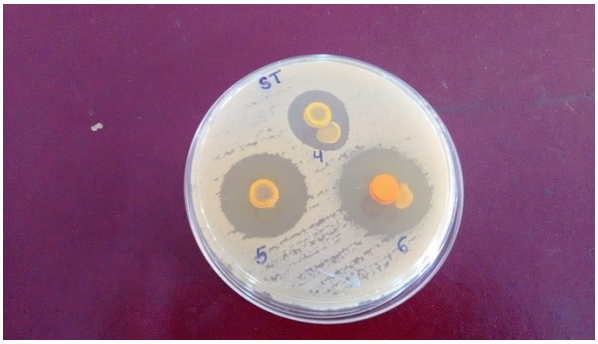
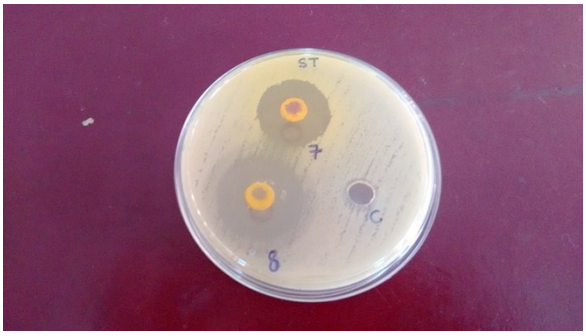
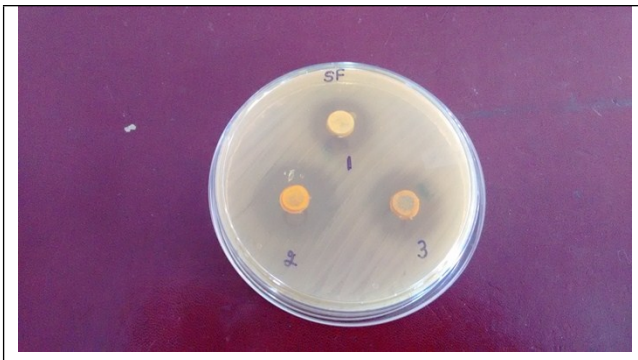
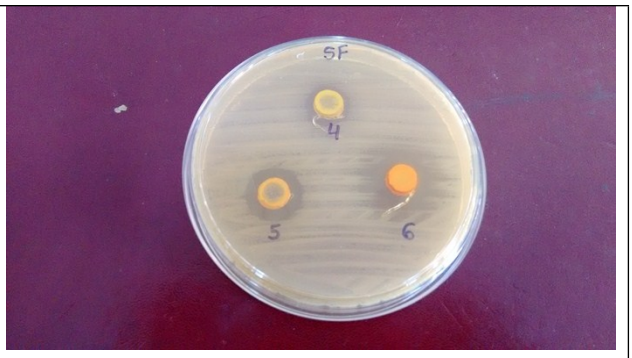
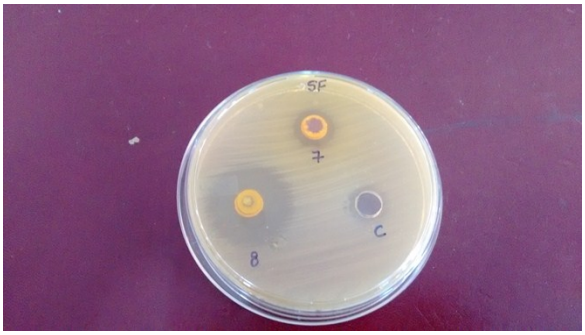
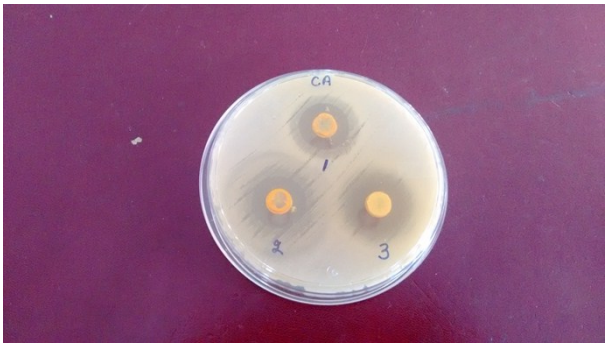
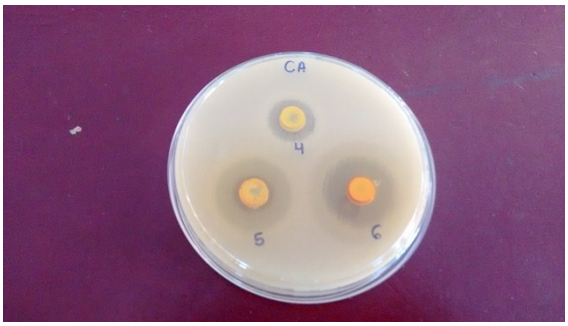
	
Sh. flexenri	*Sh. flexenri*

	
Sh. flexenri 	*C. albicans* 
C. albicans 	*C. albicans*