Supporting Information

Synthesis, structures and antimicrobial activity of copper derivatives of N-substituted imidazolidine-2-thiones : unusual bio-activity against *Staphylococcus epidermidis* and *Enterococcus faecalis*[†]

Tarlok S. Lobana^{a,*}, Jaspreet K. Aulakh^a, Heena Sood^b, Daljit S. Arora^b, Isabel Garcia-Santos^c, Manpreet Kaur^d, Courtney E. Duff^d and Jerry P. Jasinski^d

^aDepartment of Chemistry, Guru Nanak Dev University, Amritsar-143 005, India

^bDepartment of Microbiology, Guru Nanak Dev University, Amritsar-143 005, India

^cDepartamento de Quimica Inorganica, Facultad de Farmacia, Universidad de Santiago, 15782-Santiago, Spain

^dDepartment of Chemistry, Keene State College, Keene NH 03435–2001 USA

* Corresponding author: *E-mail address:* tarlokslobana@yahoo.co.in; Fax: +91-183-2258820

1S. ESI-mass data.



Fig. S1. ESI-mass spectrum due to $[Cu(L-NPr^n)(PPh_3)_2]^+$, species **A** $(CuC_{42}H_{42}N_2P_2S; m/z = calcd, 731.18, obsd 731.21)$ with isotopic pattern (complex **1**).



Fig. S2. ESI-mass spectrum due to $[Cu(L-NPr^n)(PPh_3)]^+$, species **B** $(CuC_{24}H_{27}N_2PS; m/z = calcd, 469.09, obsd 469.11)$ with isotopic pattern (complex **1**).



Fig. S3. ESI-mass spectrum due to $[Cu(L-NPr^n)_2]^+$, species **C** $(CuC_{12}H_{24}N_4S_2; m/z = calcd, 351.07, obsd 351.09)$ with isotopic pattern (complex **1**).



Fig. S4. ESI-mass spectrum due to $[Cu(PPh_3)_2]^+$, species **D** $(CuC_{36}H_{30}P_2; m/z = calcd, 587.11, obsd 587.13)$ with isotopic pattern (complex **1**).



Fig. S5. ESI-mass spectrum due to $[Cu(L-NPh)_2(PPh_3)]^+$, species **E**; m/z = calcd, 681.13, obsd 681.14) with isotopic pattern (complex **5**).



Fig. S6. ESI-mass spectrum due to $[Cu(L-NPr^n)(PPh_3)_2]^+$, species **A** $(CuC_{42}H_{42}N_2SP_2; m/z = calcd, 731.18, obsd 731.24)$ with isotopic pattern (complex **2**).



Fig. S7. ESI-mass spectrum due to $[Cu(L-NPr^n)(PPh_3)]^+$, species **B** $(CuC_{24}H_{27}N_2SP; m/z = calcd, 469.09, obsd 469.13)$ with isotopic pattern (complex **2**).



Fig. S8. ESI-mass spectrum due to $[Cu(L-NPr^n)_2]^+$, species **C** $(CuC_{12}H_{24}N_4S_2; m/z = calcd, 351.07, obsd 351.09)$ with isotopic pattern (complex **2**).



Fig. S9. ESI-mass spectrum due to $[Cu(PPh_3)_2]^+$, species **D** $(CuC_{36}H_{30}P_2; m/z = calcd, 587.11, obsd 587.15)$ with isotopic pattern (complex **2**).



Fig. S10. ESI-mass spectrum due to $[Cu(L-NBu^n)(PPh_3)]^+$, species **B** $(CuC_{25}H_{29}N_2SP; m/z = calcd, 483.10, obsd 483.11)$ with isotopic pattern (complex **3**).



Fig. S11. ESI-mass spectrum due to $[Cu(L-NBu^n)_2]^+$, species **C** $(CuC_{14}H_{28}N_4S_2; m/z = calcd, 379.10, obsd 379.11)$ with isotopic pattern (complex **3**).



Fig. S12. ESI-mass spectrum due to $[Cu(L-NBu^n)(PPh_3) + H]^+$, species (**B** + **H**⁺) (CuC₂₅H₂₉N₂SP; m/z = calcd, 484.11, obsd 484.74) with isotopic pattern (complex **4**).



Fig. S13. ESI-mass spectrum due to $[Cu(L-NBu^n)_2 + H]^+$, species (**C** + **H**⁺) (CuC₁₄H₂₉N₄S₂; m/z = calcd, 380.11, obsd 380.72) with isotopic pattern (complex **4**).



Fig. S14. ESI-mass spectrum due to $[Cu(L-NPh)(PPh_3)]^+$, species (**B**) $(CuC_{27}H_{25}N_2SP; m/z = calcd, 503.07, obsd 503.08)$ with isotopic pattern (complex **5**).



Fig. S15. ESI-mass spectrum due to $[Cu(L-NPh)_2]^+$, species (**C**) $(CuC_{18}H_{20}N_4S_2; m/z = calcd, 419.04, obsd 419.05)$ with isotopic pattern (complex **5**).



Fig. S16. ESI-mass spectrum due to $[Cu(PPh_3)_2]^+$, species (**D**) $(CuC_{36}H_{30}P_2; m/z = calcd, 587.11, obsd 587.12)$ with isotopic pattern (complex **5**).



Fig. S17. ESI-mass spectrum due to $[Cu(L-NPh)(PPh_3)]^+$, species (**B**) $(CuC_{27}H_{25}N_2SP; m/z = calcd, 503.07, obsd 503.08)$ with isotopic pattern (complex **6**).



Fig. S18. ESI-mass spectrum due to $[Cu(PPh_3)_2]^+$, species (**D**) $(CuC_{36}H_{30}P_2; m/z = calcd, 587.11, obsd 587.11)$ with isotopic pattern (complex **6**).



Fig. S19. ESI-mass spectrum due to $[Cu(L-NEt)(PPh_3)_2]^+$, species (**A**) $(CuC_{41}H_{40}N_2SP_2; m/z = calcd, 717.16, obsd 717.62)$ with isotopic pattern (complex **7**).



Fig. S20. ESI-mass spectrum due to [Cu(L-NEt)(PPh₃)]⁺, species (**B**) (CuC₂₃H₂₅N₂SP; m/z = calcd, 455.07, obsd 455.43) with isotopic pattern (complex **7**).



Fig. S21. ESI-mass spectrum due to $[Cu(PPh_3)_2]^+$, species (**D**) $(CuC_{36}H_{30}P_2; m/z = calcd, 587.11, obsd 587.52)$ with isotopic pattern (complex **7**).



Fig. S22. ESI-mass spectrum due to [Cu(L-NPrⁿ)(PPh₃)₂]⁺, species (**A**) (CuC₄₂H₄₂N₂SP₂; m/z = calcd, 731.18, obsd 731.23) with isotopic pattern (complex **9**).



Fig. S23. ESI-mass spectrum due to [Cu(L-NPrⁿ)(PPh₃)]⁺, species (**B**) (CuC₂₄H₂₇N₂SP; m/z = calcd, 469.09, obsd 469.12) with isotopic pattern (complex **9**).



Fig. S24. ESI-mass spectrum due to $[Cu(L-NPr^n)_2]^+$, species (**C**) $(CuC_{12}H_{24}N_4S_2; m/z = calcd, 351.07, obsd 351.09)$ with isotopic pattern (complex **9**).



Fig. S25. ESI-mass spectrum due to $[Cu(PPh_3)_2]^+$, species (**D**) $(CuC_{36}H_{30}P_2; m/z = calcd, 587.11, obsd 587.15)$ with isotopic pattern (complex **9**).



Fig. S26. ESI-mass spectrum due to [Cu(L-NPrⁿ)(PPh₃)]⁺, species (**B**) (CuC₂₄H₂₇N₂SP; m/z = calcd, 469.09, obsd 469.12) with isotopic pattern (complex **10**).



Fig. S27. ESI-mass spectrum due to $[Cu(L-NPr^n)_2)]^+$, species (**C**) $(CuC_{12}H_{24}N_4S_2; m/z = calcd, 351.07, obsd 351.09)$ with isotopic pattern (complex **10**).



Fig. S28. ESI-mass spectrum due to $[Cu(PPh_3)_2)]^+$, species (**D**) $(CuC_{36}H_{30}P_2; m/z = calcd, 587.11, obsd 587.14)$ with isotopic pattern (complex **10**).



Fig. S29. ESI-mass spectrum due to [Cu(L-NPh)(PPh₃)]⁺, species (**B**) (CuC₂₇H₂₅N₂SP; m/z = calcd, 503.07, obsd 503.11) with isotopic pattern (complex **11**).



Fig. S30. ESI-mass spectrum due to $[Cu(L-NPh)_2]^+$, species (**C**) $(CuC_{18}H_{20}N_4S_2; m/z = calcd, 419.04, obsd 419.07)$ with isotopic pattern (complex **11**).



Fig. S31. ESI-mass spectrum due to $[Cu(PPh_3)_2]^+$, species (**D**) $(CuC_{36}H_{30}P_2; m/z = calcd, 587.11, obsd 587.15)$ with isotopic pattern (complex **11**).



Fig. S32. ESI-mass spectrum due to [Cu(L-NPh)(PPh₃)₂]⁺, species (**A**) (CuC₄₅H₄₀N₂SP₂; m/z = calcd, 765.16, obsd 765.17) with isotopic pattern (complex **12**).



Fig. S33. ESI-mass spectrum due to [Cu(L-NPh)(PPh₃)]⁺, species (**B**) (CuC₂₇H₂₅N₂SP; m/z = calcd, 503.07, obsd 503.08) with isotopic pattern (complex **12**).



Fig. S34. ESI-mass spectrum due to $[Cu(L-NPh)_2]^+$, species (**C**) $(CuC_{18}H_{20}N_4S_2; m/z = calcd, 419.04, obsd 419.04)$ with isotopic pattern (complex **12**).



Fig. S35. ESI-mass spectrum due to $[Cu(PPh_3)_2]^+$, species (**D**) $(CuC_{36}H_{30}P_2; m/z = calcd, 587.11, obsd 587.11)$ with isotopic pattern (complex **12**).



Fig. S36. IR spectrum of complex [CuCl(L-NPrⁿ)(PPh₃)₂] (1).

IR (KBr, absorption bands): 3176 s, 3068 m, 3048 s, 3016 w, 3001 w, 2961 s, 2930 w, 2874 w, 1616 w, 1585 w, 1571 w, 1512 s, 1479 s, 1461 m, 1434 s, 1382 w, 1316 s, 1281 s, 1245 m, 1184 m, 1155 w, 1122 m, 1093 s, 1070 w, 1027 m, 997 w, 972 w, 859 w, 747 s, 722 w, 696 s, 619 w, 542 w, 515 s, 423 w cm⁻¹.





Fig. S37. IR spectrum of complex [CuBr(L-NPrⁿ)(PPh₃)₂] (2).

IR (KBr, absorption bands) : 3217 s, 3052 w, 2971 w, 2932 w, 2888 w, 1631 w, 1586 w, 1514 s, 1477 m, 1459 w, 1433 m, 1382 w, 1312 m,1283 m, 1246 m, 1183 w, 1124 m, 1093 s, 1029 w, 865 w, 799 w, 751 m, 723 m, 696 m, 628 w, 601 w, 542 w, 519 m, 504 m cm⁻¹.



Fig. S38. IR spectrum of complex [CuCl(L-NBuⁿ)(PPh₃)₂] (3).

IR (KBr, absorption bands): 3142 w, 3051 m, 2952 w, 2901 w, 2888 w, 1631 w, 1574 s, 1483 m, 1435 s, 1384 s, 1332 s, 1314 s, 1207 s, 1160 w, 1099 m, 1024 m, 999 m, 932 m, 855 m, 825 w, 780 m, 740 s, 722 m, 694 s, 649 m, 615 w, 588 m, 509 m, 476 w cm⁻¹.



Fig. S39. IR spectrum of complex [Cul(L-NBuⁿ)(PPh₃)₂](4).

IR (KBr, absorption bands): 3222 s, 2926 w, 1614 w, 1496 s, 1300 w, 1332 s, 1314 s, 1207 s, 1155 w, 1084 s, 1037 m, 884 w, 799 w, 771 w, 700 w, 651 w, 548 w, 534 w, 522 w cm⁻¹.

MACIG JP-8.spc

13/05/2016



Fig. S40. IR spectrum of complex [CuBr(L-NPh)₂(PPh₃)] (5).

IR (KBr, absorption bands): 3210 s, 3067 w, 3048 w, 3003 w, 2982 w, 2892 w, 1596 w, 1510 s, 1499 s, 1476 s, 1433 s, 1338 m, 1306 m, 1288 m, 1239 m, 1190 w, 1157 w, 1095 m, 1072 w, 1028 w, 999 w, 950 w, 923 w, 849 w, 750 s, 695 s, 615 w, 552 w, 518 w, 502 m, 437 w cm⁻¹.

MACIG JP-4.spc

13/05/2016



Fig. S41. IR spectrum of complex [Cul(L-NPh)(PPh₃)₂] (6).

IR (KBr, absorption bands): 3200 s, 3050 s, 3002 w, 2983 w, 2893 w, 1597 m, 1586 m, 1571 w, 1515 s, 1498 s, 1479 s, 1454 w, 1434 s, 1386 w, 1337 s, 1306 s, 1291 s, 1243 s, 1185 w, 1157 w, 1094 s, 1071 w, 1027 m, 998 w, 949 w, 850 w, 744 s, 694 s, 666 s, 617 w, 583 w, 553 m, 517 s, 506 s, 491 m, 442 w, 420 w cm⁻¹.

MACIG JP-19.spc

08/07/2016



Fig. S42. IR spectrum of complex $[Cu_2(\mu-Br)_2(L-NEt)_2(PPh_3)_2]$ (7).

IR (KBr, absorption bands): 3226 s, 3050 w, 3015 w, 2973 w, 2930 w, 2886 w, 1633 w, 1585 w, 1568 w, 1515 s, 1478 s, 1460 w, 1433 m, 1381 w, 1359 w, 1322 m, 1283 m, 1259 m, 1219 w, 1183 w, 1126 w, 1093 m, 1028 w, 999 w, 944 w, 855 w, 788 w, 752 m, 696 s, 626 w, 593 w, 520 m, 505 m, 438 w cm⁻¹.

MACIG JP-9.spc



Fig. S43. IR spectrum of complex $[Cu_2(\mu-CI)_2(L-NPr^n)_2(PPh_3)_2]$ (8).

IR (KBr, absorption bands): 3194 s, 3052 w, 3012 w, 2965 w, 2933 w, 2880 w, 1631 w, v1585 s, 1514 s, 1478 s, 1460 w, 1433 s, 1383 w, 1313 m, 1282 m, 1246m, 1183 w, 1126m, 1094 s, 1029 w, 998 w, 897 w, 864 w, 801 w, 751 s, 723 w, 696 s, 630 w, 616 w, 542 w, 519 s, 505 s, 434 w cm⁻¹.



Fig. S44. IR spectrum of complex $[Cu_2(\mu-Br)_2(L-NPr^n)_2(PPh_3)_2]$ (9).

IR (KBr, absorption bands): 3218 s, 3052 w, 2968 w, 2931 w, 2876 w, 1633 w, v1585 w, 1513 s, 1477 m, 1460 w, 1434 m, 1382 w, 1313 m, 1283 m, 1245 w, 1185 w, 1124 m, 1093 m, other 1028 w, 997 w, 898 w, 863 w, 800 w, 751 m, 722 w, 696 s, 628 w, 600 w, 592 w, 519 m, 505 m, 432 w cm⁻¹.

MACIG JP-11.spc

08/07/2016



Fig. S45. IR spectrum of complex $[Cu_2(\mu-I)_2(L-NPr^n)_2(PPh_3)_2]$ (10).

IR (KBr, absorption bands): 3239 s, 3068 w, 3050 m, 3014 w, 3000 w, 2965 m, 2928 w, 2879 w, 1619 w, 1584 w, 1569 w, 1510 s, 1476 s, 1460 w, 1433 s, 1382 w, 1311 m, 1281 m, 1241 m, 1184 w, 1154 w, 1124 w, 1092 m, 1027 w, 998 w, 962 w, 863 w, 798 w, 747 s, 695 s, 624 w, 571 w, 517 s, 503 s, 430 w cm⁻¹.



Fig. S46. IR spectrum of complex [Cu₂(µ-Br)₂(L-NPh)₂(PPh₃)₂] (11).

IR (KBr, absorption bands): 3210 m, 3048 w, 2980 w, 2893 w, 1624 w, 1593 w, 1502 s, 1431 s, 1386 w, 1337 w, 1305 w, 1239 s, 1189 w, 1157 w, 1095 m, 1072 w, 1029 w, 999 w, 950 w, 850 w, 750 s, 696 s, 664 w, 613 w, 552 w, 518 s, 501 s, 436 w cm⁻¹.



Fig. S47. IR spectrum of complex $[Cu_2(\mu-I)_2(L-NPh)_2(PPh_3)_2]$ (12).

IR (KBr, absorption bands): 3241 s, 3066 w, 3046 w, 3002 w, 2980 w, 2893 w, 1595 w, 1506 s, 1476 s, 1452 s, 1431 s, 1337 w, 1305 w, 1269 w, 1095 s, 950 w, 797 w, 750 s, 695 s, 664 w, 640 w, 551 w, 517 w, 500 m, 472 m cm⁻¹.



Fig. S48. IR spectrum of ligand L-NEt.

IR (KBr, absorption bands): 3191 s, 3023 w, 2983 m, 2966 m, 2929 m, 2876 m, 1513 s, 1480 m, 1466 m, 1450 m, 1379 w, 1357 w, 1321 m, 1279 m, 1258 m, 1200 m, 1134 m, 1106 m, 1074 m; 1037 m, 945 w, 871 w, 792 m, 670 m, 631 m, 614 m, 516 m, 438 w cm⁻¹.



Fig. S49. IR spectrum of ligand L-NPrⁿ.

IR (KBr, absorption bands): 3207 s, 2962 m, 2932 m, 2872 m, 1514 s, 1478 m, 1459 m, 1381 w, 1309 m, 1280 s, 1242 s, 1199 w, 1125 m, 1081 w, 1037 w, 964 w, 896 w, 866 w, 806 w, 744 w, 675 w, 619 m, 515 m cm⁻¹.



Fig. S50. IR spectrum of ligand L-NBuⁿ.

IR (KBr, absorption bands): 3196 s, 2958 m, 2923 m, 2895 m, 2873 m, 1514 s, 1462 m, 1438 m; 1367 w, 1324 m, 1284 s, 1234 s, 1122 m, 1041 w, 960 w, 941 w, 883 w, 803 w, 740 w, 677 w, 625 w, 608 w, 514 w, 464 w, 440 w, 421 w cm⁻¹.



Fig. S51. IR spectrum of ligand L-NPh.

IR (KBr, absorption bands): 3203 s, 3009 m, 2962 m, 2892 m, 1597 s, 1518 s, 1498 s, 1480 s, 1461 s, 1421 s, 1341 m, 1314 s, 1288 m, 1263 s, 1241 s, 1202 m, 1178 m, 1106 w, 1081 m, 1040 m, 956 m, 876 w, 757 s, 691 s, 665 m, 633 m, 614 m, 553 s, 506 m cm⁻¹.



Fig. S52. ¹H-NMR spectrum of complex [CuCl(L-NPrⁿ)(PPh₃)₂] (1).



Fig. S53. ¹H-NMR spectrum of complex [CuBr(L-NPrⁿ)(PPh₃)₂] (2).



Fig. S54. ¹H-NMR spectrum of complex [CuCl(L-NBuⁿ)(PPh₃)₂] (3).



Fig. S55. ¹H-NMR spectrum of complex [Cul(L-NBuⁿ)(PPh₃)₂] (4).



Fig. S56. ¹H-NMR spectrum of complex [CuBr(L-NPh)₂(PPh₃)] (5).



Fig. S57. ¹H-NMR spectrum of complex [Cul(L-NPh)(PPh₃)₂] (6).



Fig. S58. ¹H-NMR spectrum of complex $[Cu_2(\mu-Br)_2(L-NEt)_2(PPh_3)_2]$ (7).



Fig. S59. ¹H-NMR spectrum of complex $[Cu_2(\mu-CI)_2(L-NPr^n)_2(PPh_3)_2]$ (8).



Fig. S60. ¹H-NMR spectrum of complex $[Cu_2(\mu-Br)_2(L-NPr^n)_2(PPh_3)_2]$ (9).



Fig. S61. ¹H-NMR spectrum of complex $[Cu_2(\mu-I)_2(L-NPr^n)_2(PPh_3)_2]$ (10).



Fig. S62. ¹H-NMR spectrum of complex $[Cu_2(\mu-Br)_2(L-NPh)_2(PPh_3)_2]$ (11).



Fig. S63. ¹H-NMR spectrum of complex $[Cu_2(\mu-I)_2(L-NPh)_2(PPh_3)_2]$ (12).



Fig. S64. ¹H-NMR spectrum of ligand L-NEt.



Fig. S65. ¹H-NMR spectrum of ligand L-NPrⁿ.



Fig. S66. ¹H-NMR spectrum of ligand L-NBuⁿ.



Fig. S67. ¹H-NMR spectrum of ligand L-NPh.



Fig. S68. ¹³C-NMR spectrum of complex (1).



Fig. S69. ¹³C-NMR spectrum of complex (2).



Fig. S70. ¹³C-NMR spectrum of complex (3).



Fig. S71. ¹³C-NMR spectrum of complex (4).



Fig. S72. ¹³C-NMR spectrum of complex (**5**).



Fig. S73. ¹³C-NMR spectrum of complex (6).



Fig. S74. ¹³C-NMR spectrum of complex (7).



Fig. S75. ¹³C-NMR spectrum of complex (8).



Fig. S76. ¹³C-NMR spectrum of complex (9).



Fig. S77. ¹³C-NMR spectrum of complex (**10**).



Fig. S78. ¹³C-NMR spectrum of complex (**11**).



Fig. S79. ¹³C-NMR spectrum of complex (**12**).



Fig. S80. ¹³C-NMR spectrum of L-NEt.



Fig. S81. ¹³C-NMR spectrum of L-NPrⁿ.



Fig. S82. ¹³C-NMR spectrum of L-NBuⁿ.



Fig. S83. ¹³C-NMR spectrum of L-NPh.



Fig. S84. ¹³C-NMR spectrum of PPh₃.