Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Synthesis and structures of 5-Nitro-salicylaldehyde thiosemicarb - azonates of Copper(II) : molecular spectroscopy, ESI-mass, antimicrobial activity and cytotoxicity

Tarlok S. Lobana,*[a] Shikha Indoria[a], Harpreet Kaur,[b] Daljit S. Arora,[b] Amanpreet K. Jassal,[a] Jerry P. Jasinski[c]

Tarlok S. Lobana,*[a] Shikha Indoria[a], Harpreet Kaur,[b] Daljit S. Arora,[b] Amanpreet Kaur,[a] Jerry P. Jasinski[c]

[a]*Department of Chemistry, Guru Nanak Dev University, Amritsar-143 005, India*

[b]*Department of Microbiology, Guru Nanak Dev University, Amritsar-143 005, India*

[c]*Department of Chemistry, Keene State College, Keene, NH 03435 USA*

USA

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1. Ligands detail.

*5-NO_2-Salicylaldehyde-N^1H_2 thiosemicarbazone (**H_2L^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 = 11.60 (1H, s, OH), 10.32 (1H, s, N^2H), 8.78 (1H, s, C^2H), 8.40 (2H, s, N^1H_2), 8.14 (2H, d, C^5H + C^8H), 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^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}. ^{1}H NMR (δ, ppm; $CDCl_3$): δ = 11.57 (1H, s, OH), 10.30 (1H, s, N^2H), 8.82 (1H, s, C^2H), 8.37 (1H, s, N^1H), 8.12 (2H, d, C^5H + C^8H), 7.06 (1H, d, C^6H), 3.79 3.01 (3H, d, CH_3(N1)) 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^3**)*

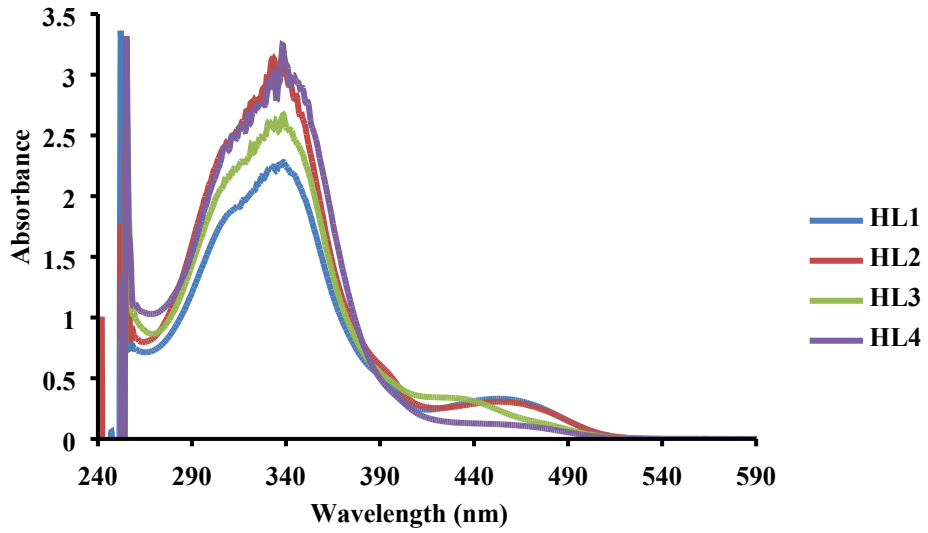
(Yield 0.81 g, 82 %, M.p. 190–192°C). IR (KBr, cm^{-1}, selected absorption bands) ν(N^1–H) 3341 w, br, ν(O−H) 3304 br, ν(N^2–H) 3158 br, ν(C–H) 2974 w; 2974 s, 2933 m, 2873; ν(C=N) + ν(C=C)+ δ(N−H) 1658 m, 1552 s, 1514 s; δ(C−H) 1444 s; 1398 s, 1340 s, 1287 s, 1227 s, 1100 s, 1074 s, ν(C–S) 1012 s; 937 s, 848 s, 799 s, 705 s, 478 s cm^{-1}. ^{1}H NMR (δ, ppm; $CDCl_3$): δ = 11.50 (1H, s, OH), 10.30 (1H, s, N^2H), 8.80 (1H, sb, N^1H), 8.00 (1H, s, C^2H), 8.80 (1H, s, C^2H), 8.37 (1H, s, N^1H), 8.12 (2H, d, C^5H + C^8H), 7.06 (1H, d, C^6H), 3.17 (2H, m, $N^1(CH_2)$, 1.17 (3H, t, 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^4**) **4***

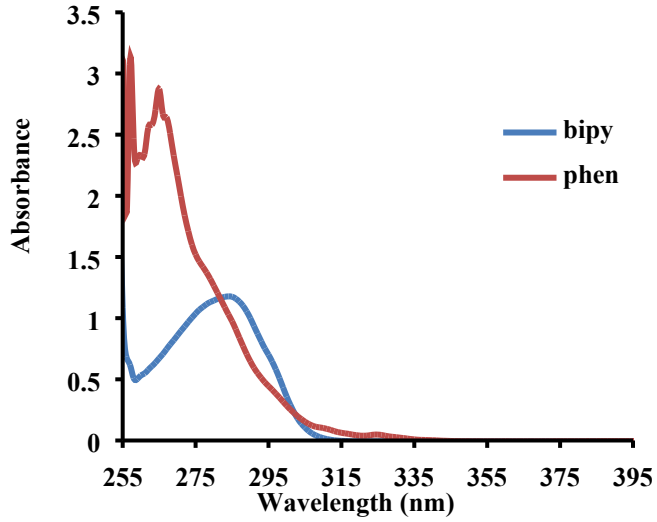
(Yield 0.79 g, 80 %, M.p. 204–206 °C). IR (KBr, cm^{-1}, selected absorption bands) ν(N^1–H) 3432 br; ν(O−H) 3302 br, ν(N^2–H) 3137 br, 2989 m; ν(C=N) + ν(C=C)+ δ(N-H) 1608 m, 1545 s, 1511 s; δ(C−H) 1489 s, 1446 w; 1399 s, 1345 s, 1293 s, 1262 s, 1197 s, 1134s, 1069 s, ν(C–S)

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}. ^{1}H NMR (δ, ppm; $CDCl_3$): δ = 11.80 (1H, s, OH), 10.32 (1H, s, N^2H), 8.97 (1H, sb, N^1H), 8.49 (1H, s, C^2H), 8.12 (2H, d, *o*-H_{ph}). 7.48 (3H, m, *m*-H_{ph} + *p*-H_{ph}), 7.37 (2H, m, C^5H + C^6H), 7.08 (2H, q, C^7H + C^8H) 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).

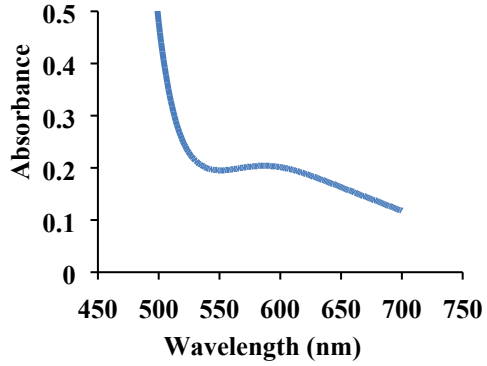
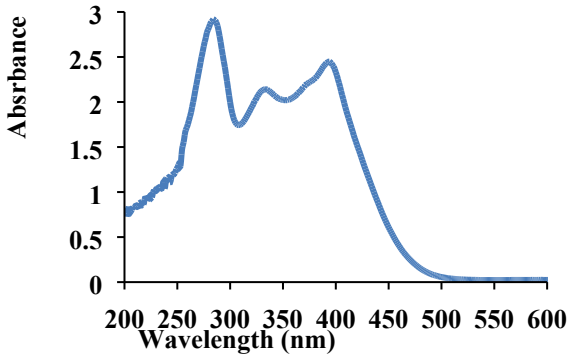
2. UV spectra of thio-ligands, 1-4.

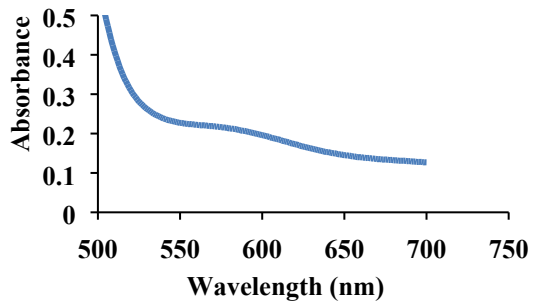


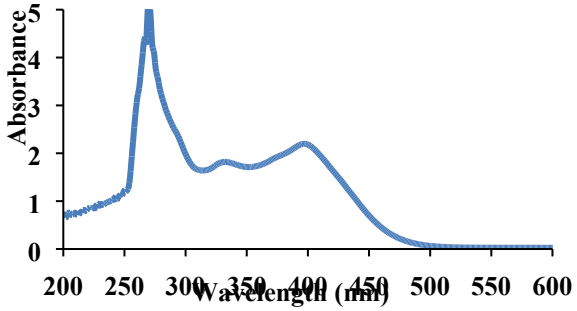
3. UV spectra of co-ligands.



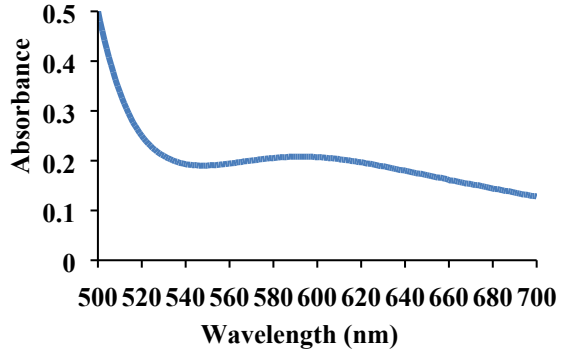
4. UV spectra of Cu(II) complexes, 1-8.

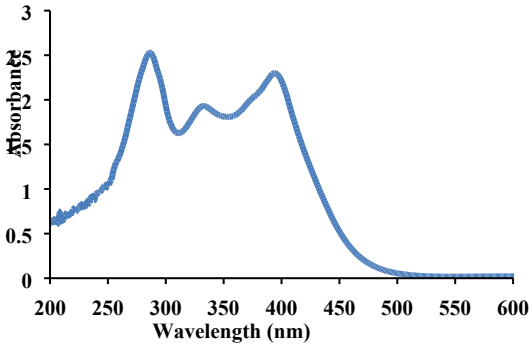
10^{-3} molar conc.	10^{-4} Molar conc.
[Cu(κ³-O,N,S-L¹)(κ²-N,N-bipy)]·CH₃OH (1) 	
[Cu(κ³-O,N,S-L¹)(κ²-N,N-phen)] (2)	



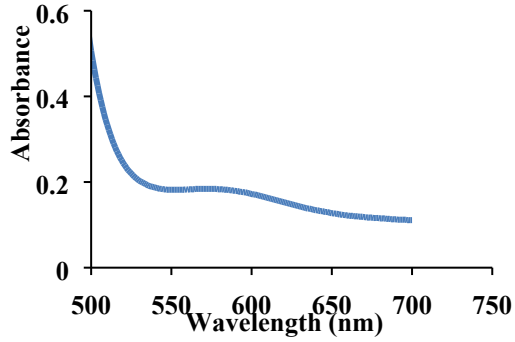


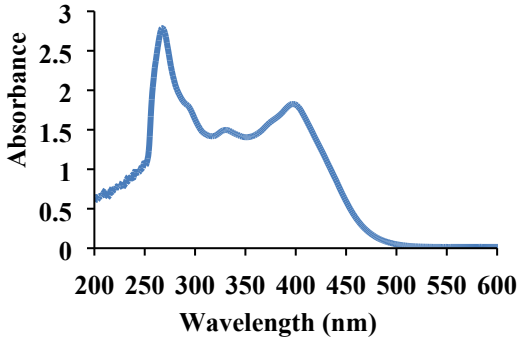
[Cu(κ³-O,N,S-L²)(κ²-N,N-bipy)] (3)



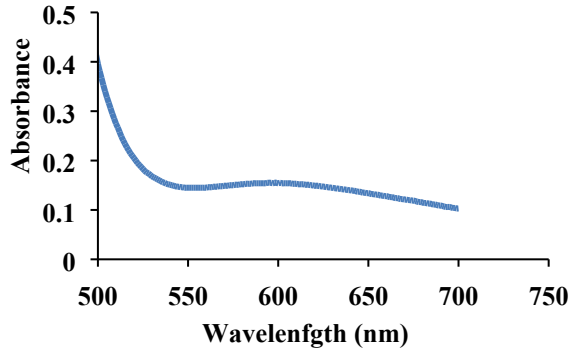


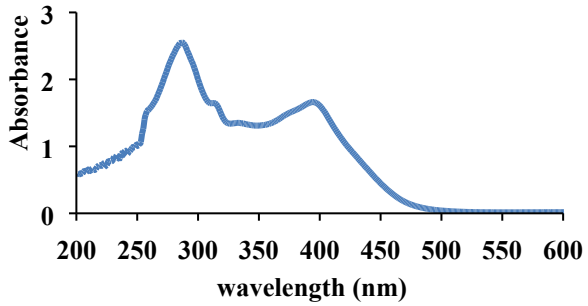
[Cu(κ³-O,N,S-L²)(κ²-N,N-phen)] (4)



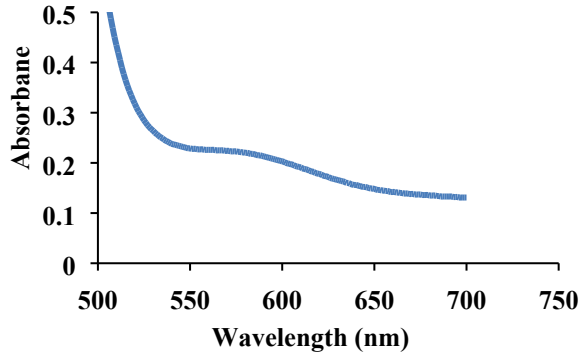


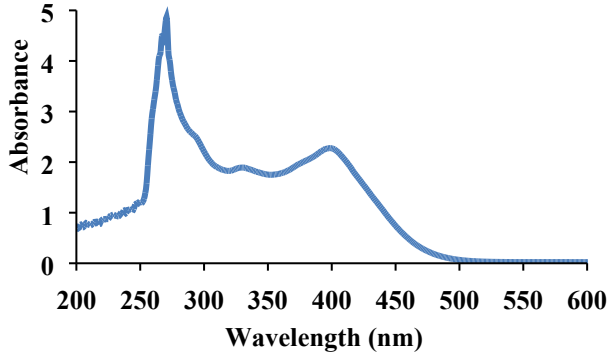
[Cu(κ³-O,N,S-L³)(κ²-N,N-bipy)] (5)



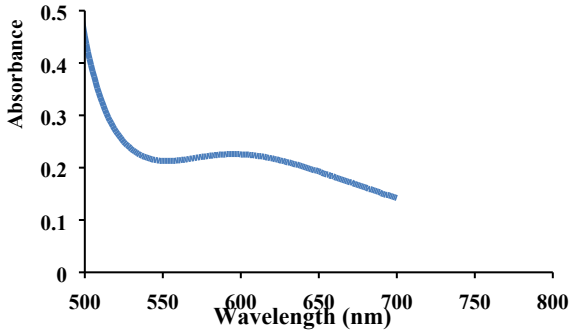


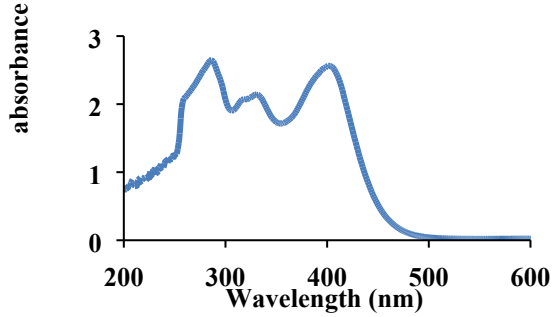
[Cu(κ³-O,N,S-L³)(κ²-N,N-phen)] (6)



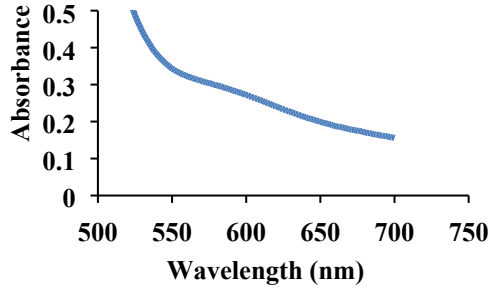


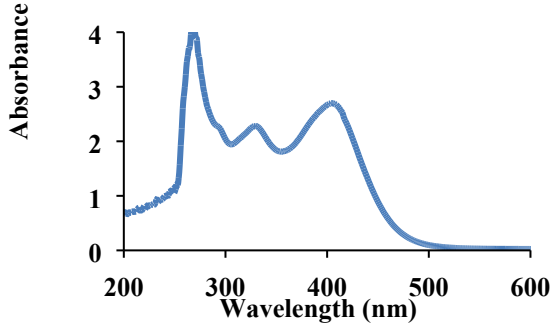
[Cu(κ³-O,N,S-L⁴(κ²-N,N-bipy)] (7)





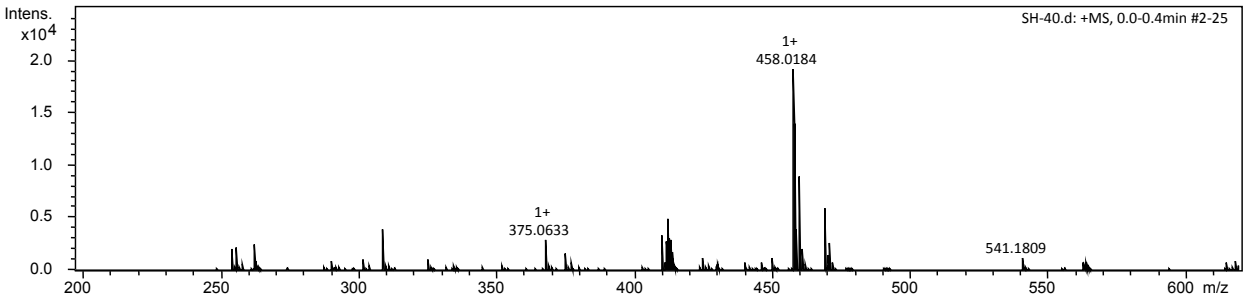
[Cu(κ³-O,N,S-L(κ²-N,N-phen)] (8)





5. Mass spectra of Cu(II) complexes, 1-8.

[Cu(κ³-O,N,S-L¹)(κ²-N,N-bipy)](1)



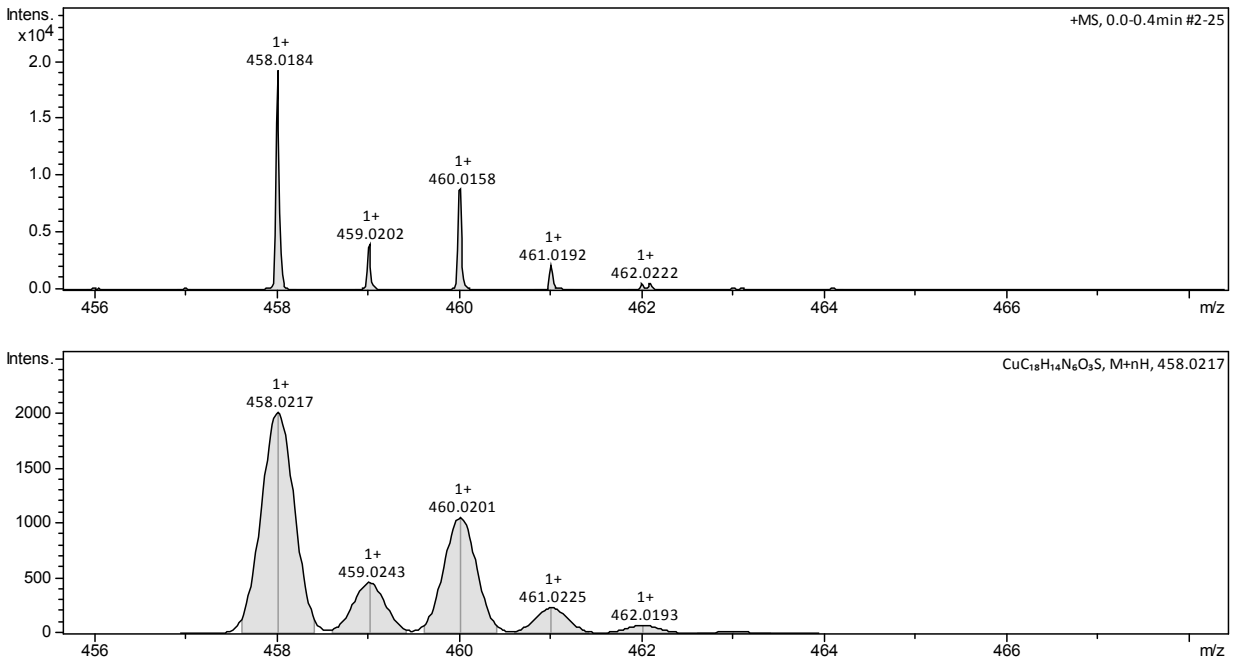


Figure. 1S ESI-mass spectrum due to molecular ion $[CuL^1(bipy)+ H]^+$ (m/z = calcd, 458.02, obsd. 458.01) with isotopic pattern (complex 1).

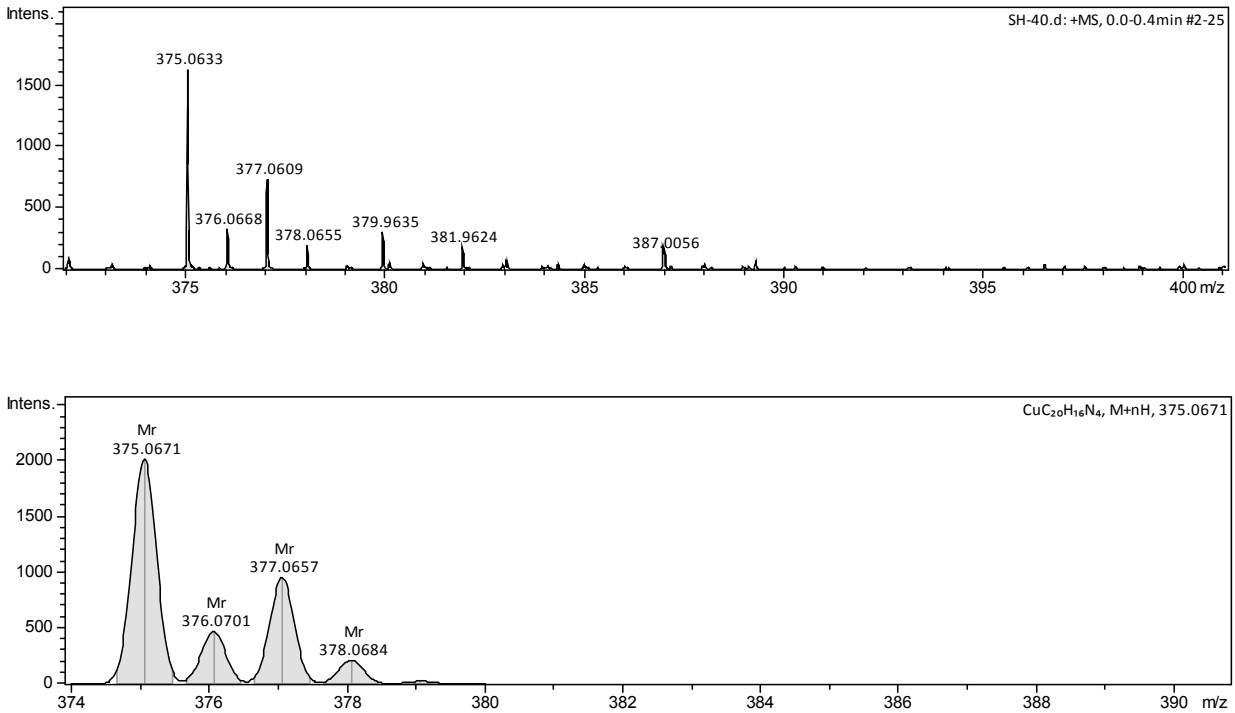
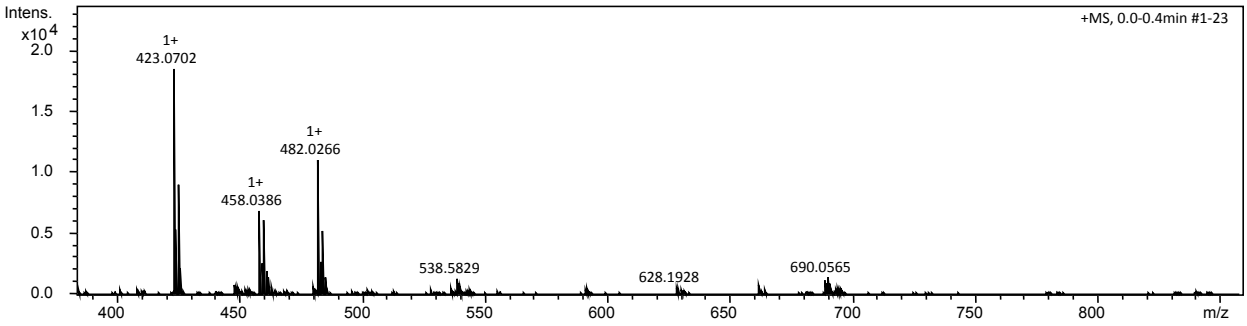


Figure. 2S ESI-mass peak due to $[Cu(bipy)_2 + H]^+$ (m/z = calcd, 376.06, obsd. 375.06) species with isotopic pattern (complex 1).

[Cu(κ³-O,N,S-L¹)(κ²-N,N-phen)] (2)



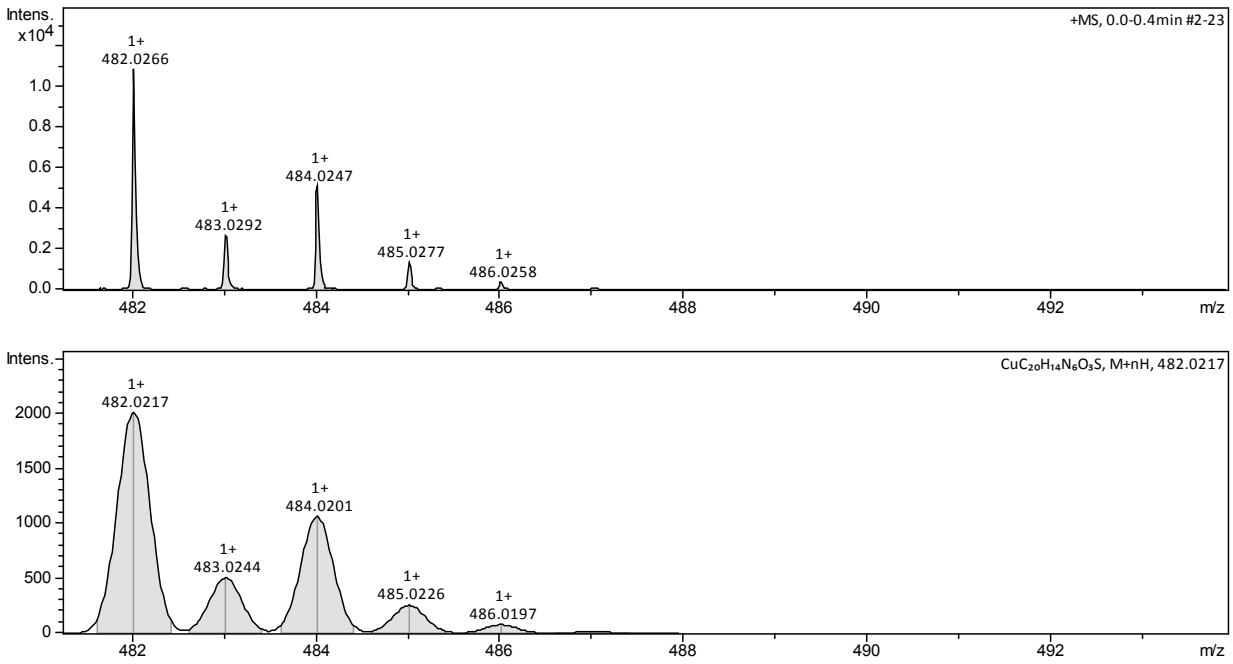


Figure. 3S ESI-mass spectrum due to molecular ion $[CuL^1(phen)+ H]^+$ (m/z = calcd, 482.02, obsd. 482.02) with isotopic pattern (complex 2).

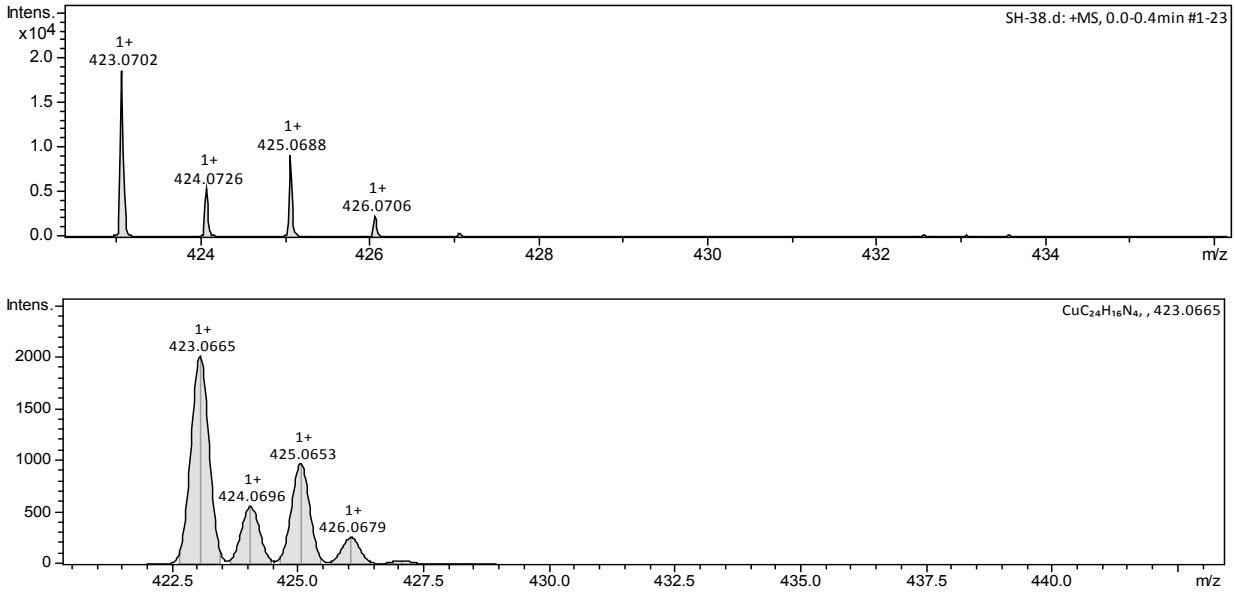


Figure.4S ESI-mass peak due to $[Cu(phen)_2+ H]^+$(m/z = calcd, 423.06, obsd. 423.06) species with isotopic pattern (complex **2**).

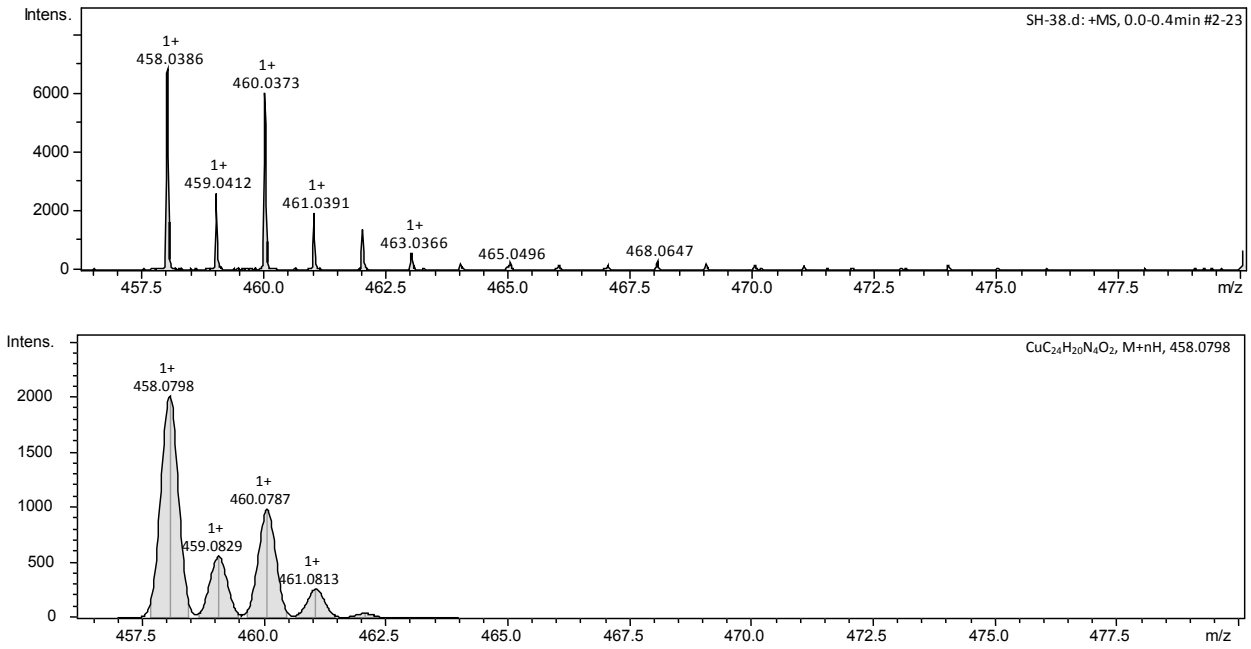


Figure.5S ESI-mass peak due to $[Cu(phen.H_2O)_2+ H]^+$(m/z = calcd, 458.03, obsd. 458.07) species with isotopic pattern (complex **2**).

[Cu(κ³-O,N,S-L²)(κ²-N,N-bipy)] (3)

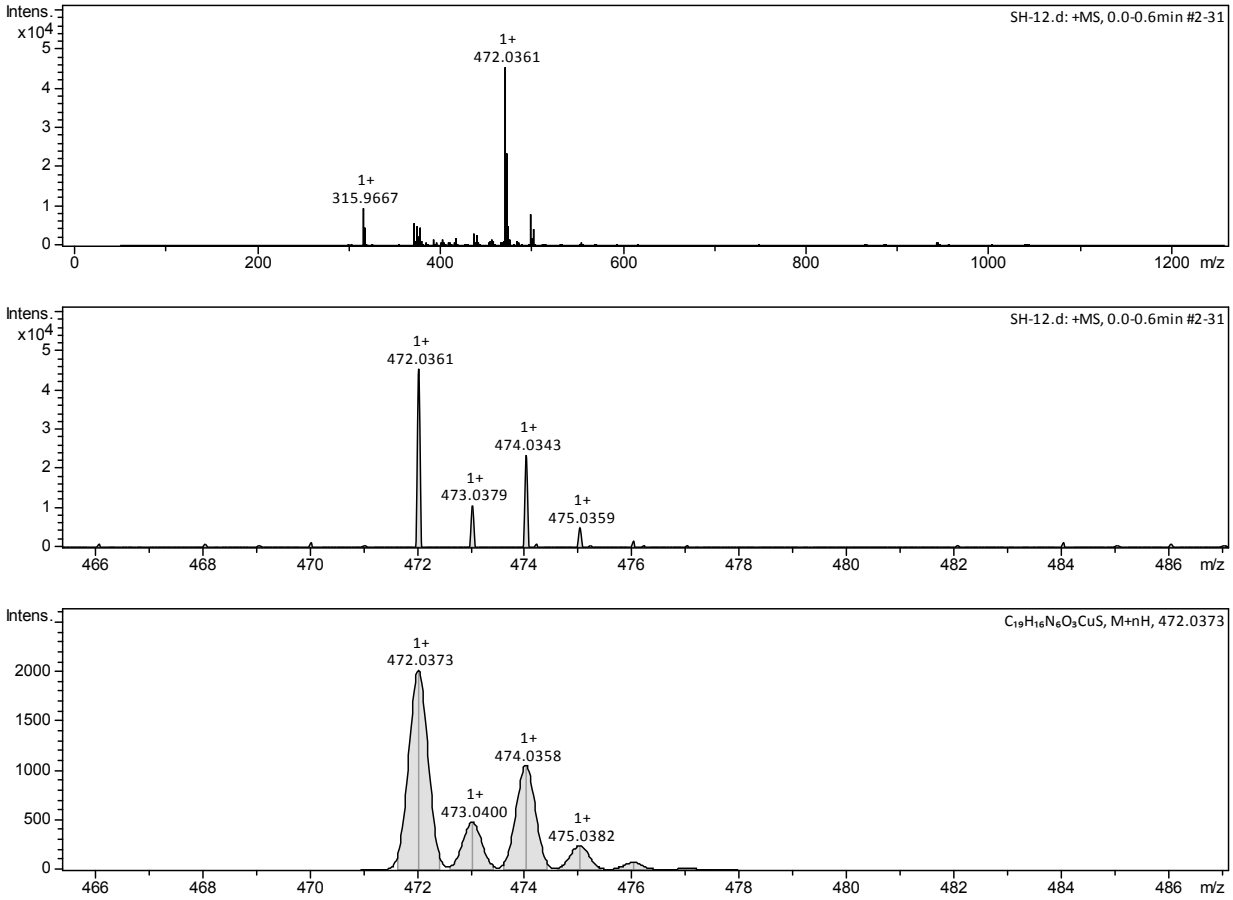
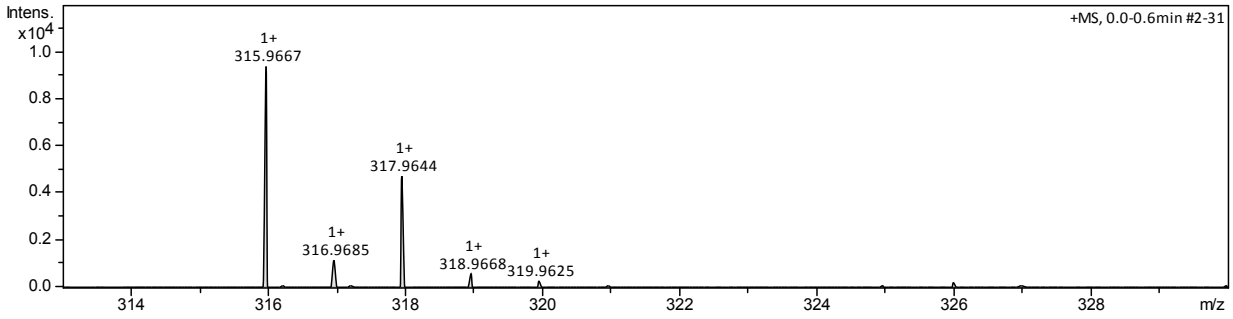


Figure. 6S ESI-mass spectrum due to molecular ion $[CuL^2(bipy)+ H]^+$ (m/z = calcd, 4782.03, obsd. 472.03) with isotopic pattern (complex 3).



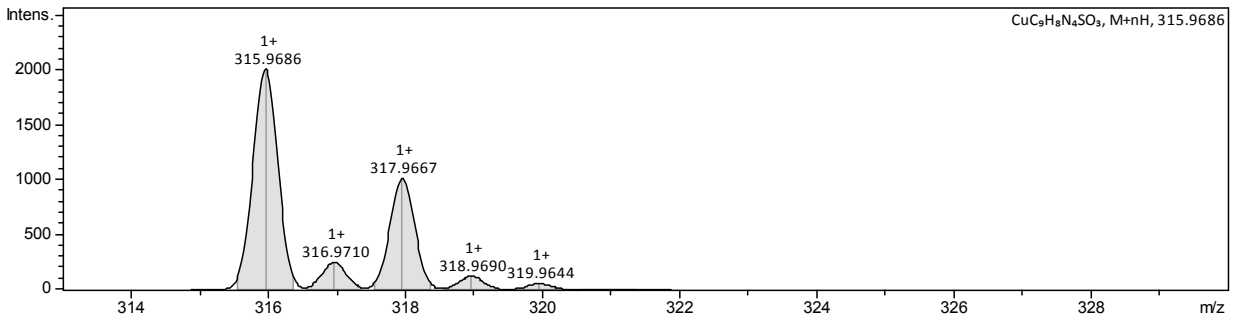


Figure. 7S ESI-mass peak due to [CuL+ H]$^{+}$, (m/z = calcd, 315. 97, obsd. 315.96) species with isotopic pattern (complex 3).

Cu(κ^{3}-O,N,S-L^{2})(κ^{2}-N,N-phen)] (4)

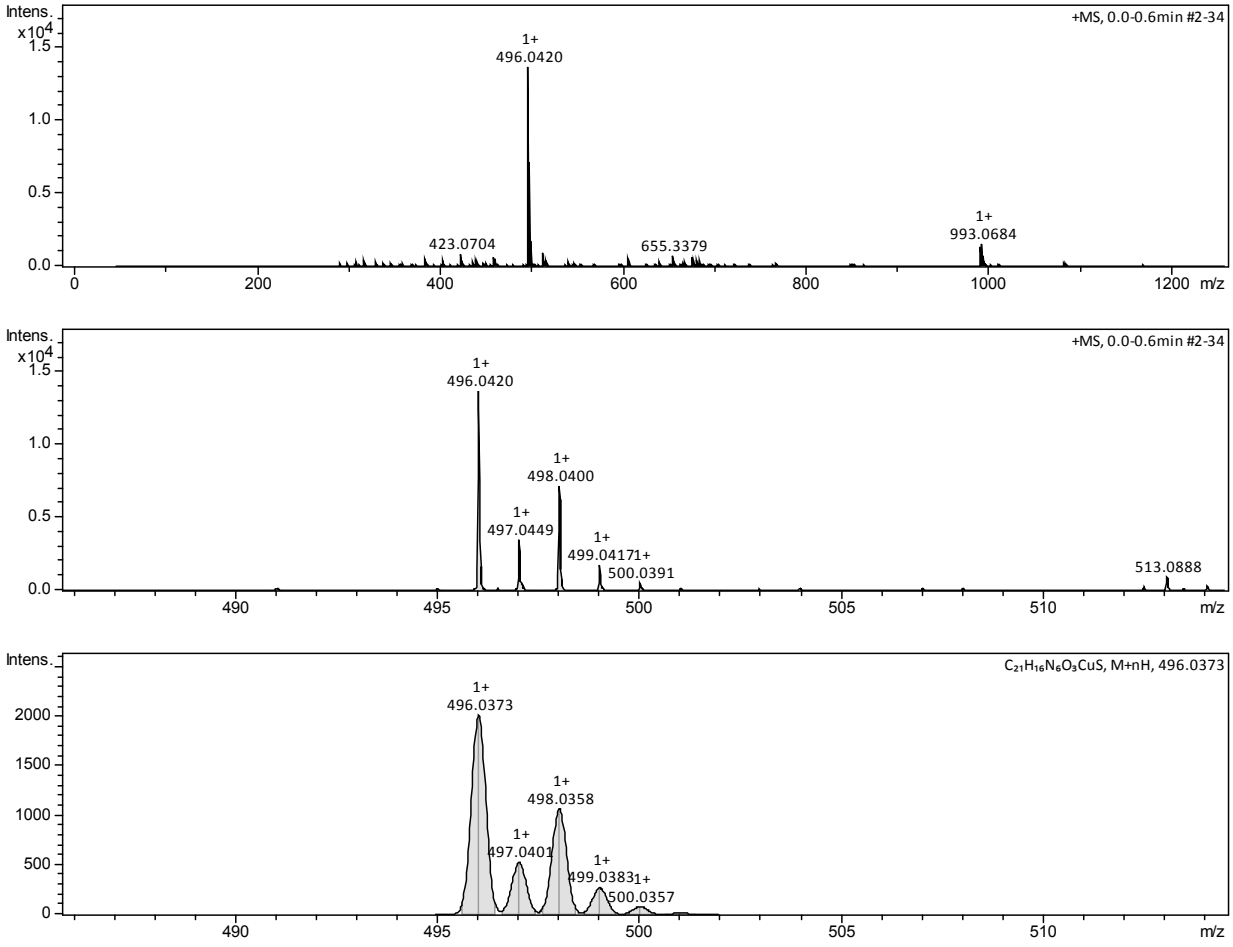


Figure. 8S ESI-mass spectrum due to molecular ion [CuL^{1}(phen)+ H]$^{+}$ (m/z = calcd, 496.04, obsd. 496.04) with isotopic pattern (complex 4).

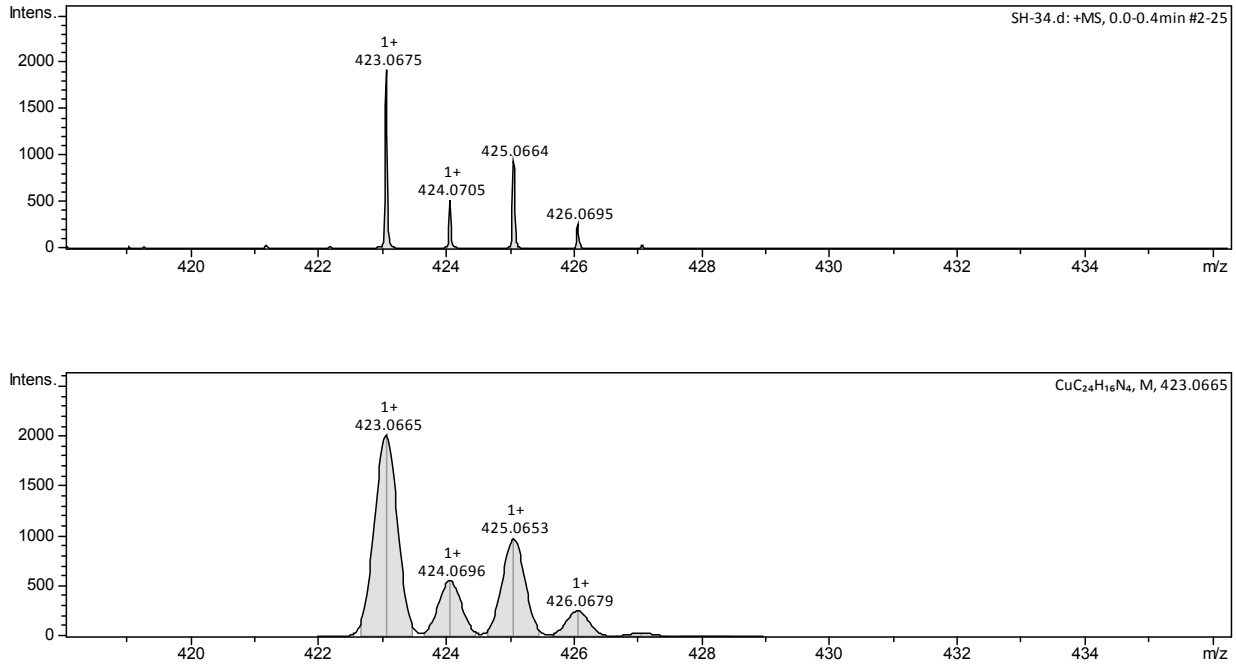
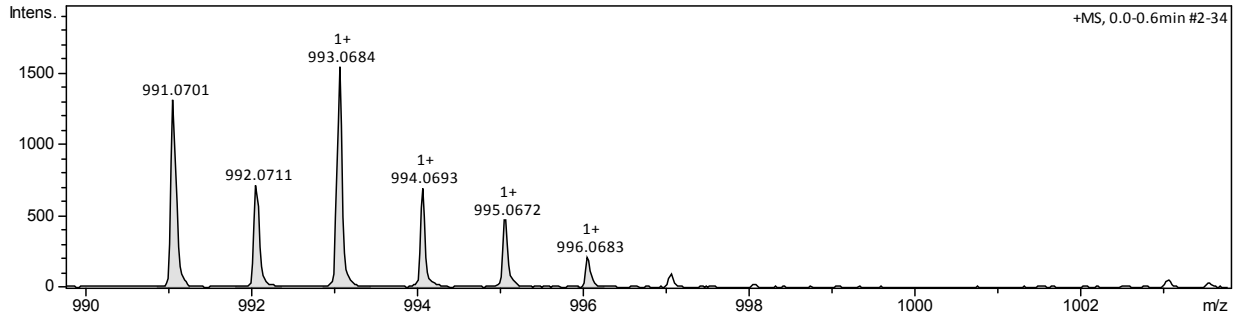


Figure.9S ESI-mass peak due to $[Cu(phen)_2 + H]^+$(m/z = calcd, 423.06, obsd. 423.06) species with isotopic pattern (complex **4**).



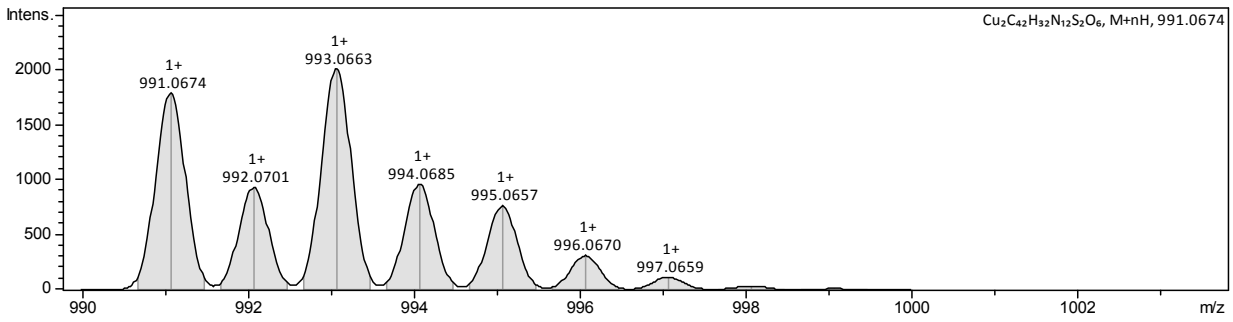


Figure. 10S ESI-mass peak of dimer $[Cu_2(L^2)_2(phen)_2+H]^+$ (m/z = calcd, 991.07, obsd. 991.06) with isotopic pattern (complex **4**).

[Cu(κ³-O,N,S-L³)(κ²-N,N-bipy)] (5)

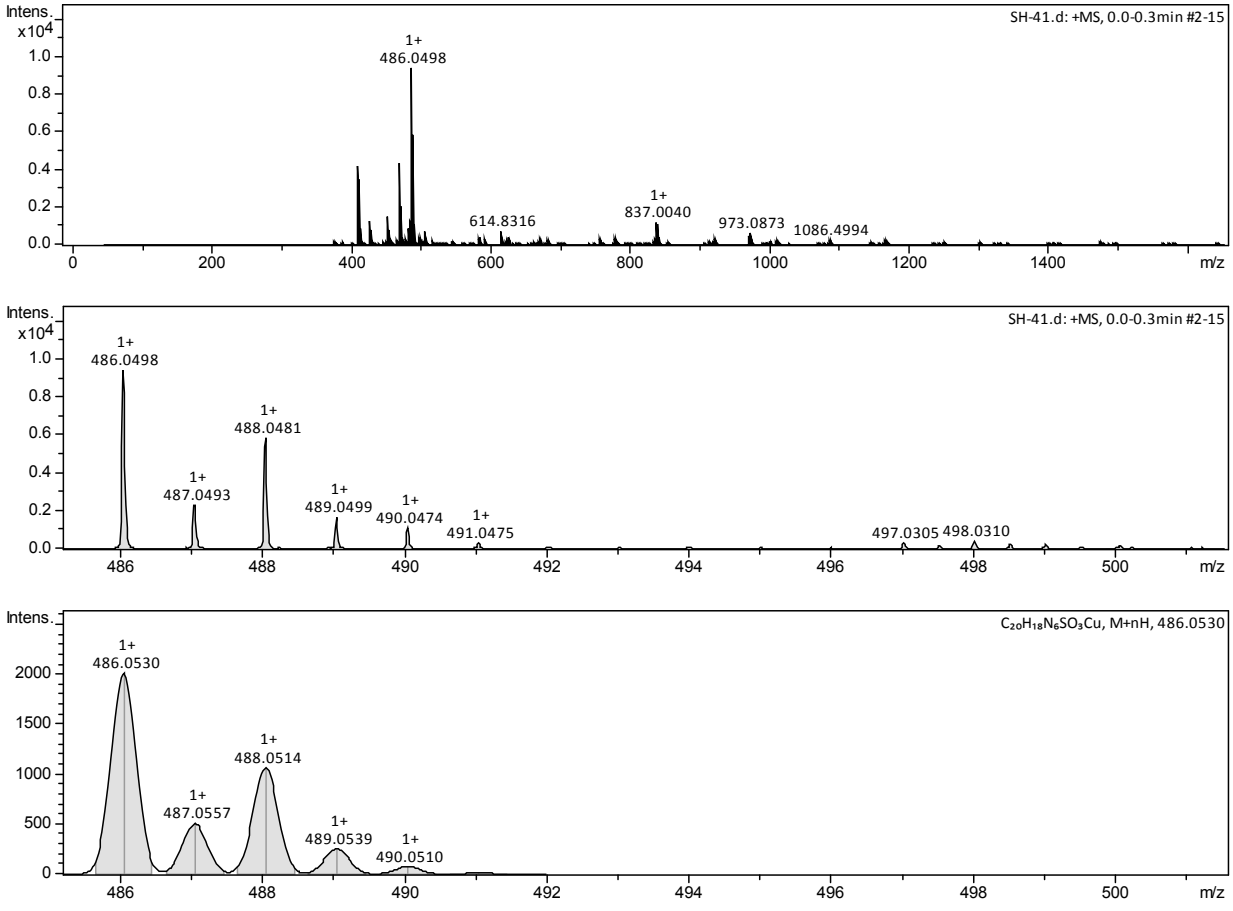


Figure. 11S ESI-mass spectrum due to molecular ion $[CuL^3(bipy)+ H]^+$ (m/z = calcd, 486.04, obsd. 486.05) with isotopic pattern (complex **5**).

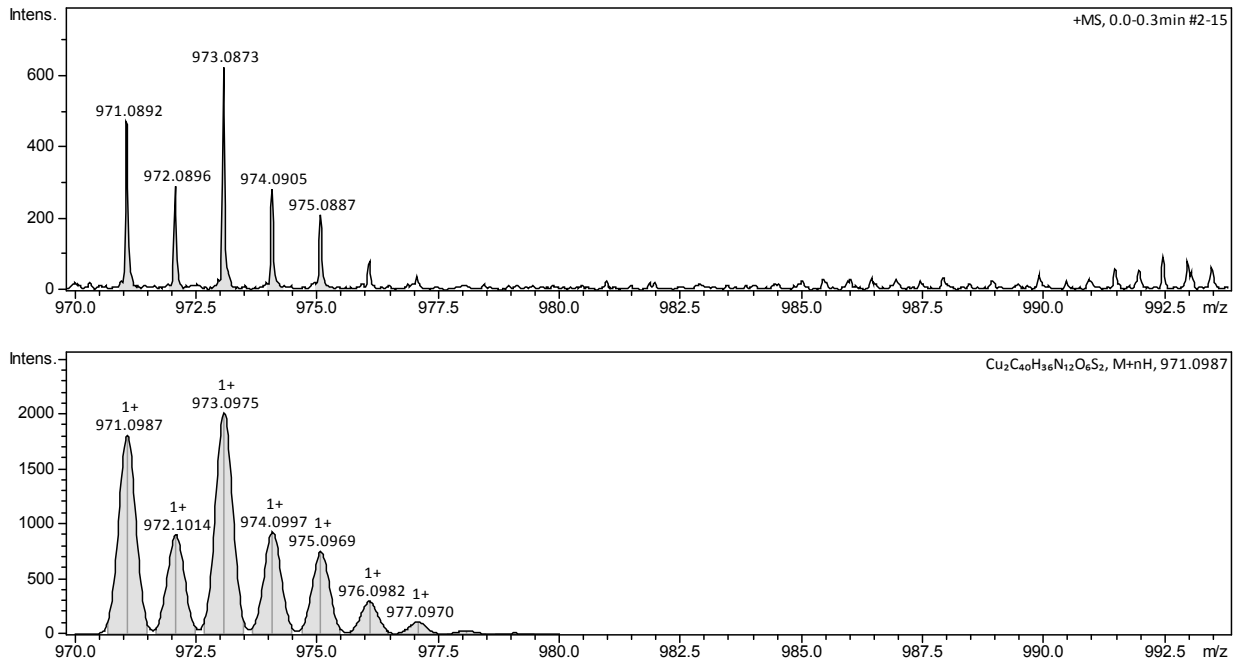
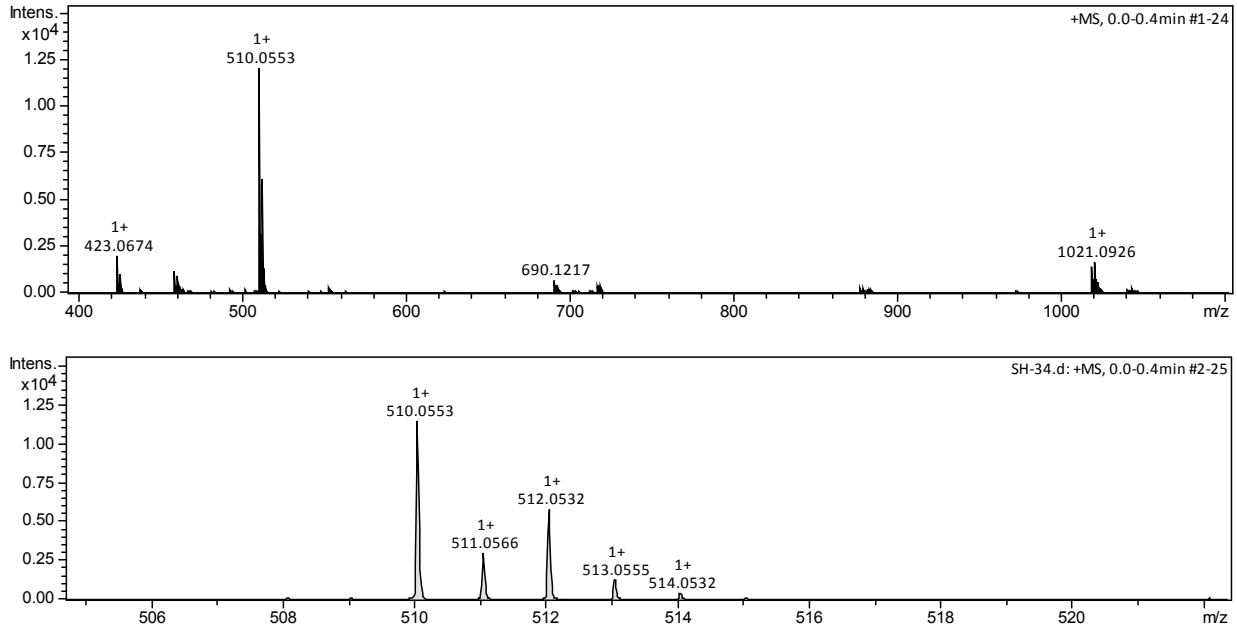


Figure. 12S ESI-mass peak of dimer $[Cu_2(L^3)_2(bipy)_2+H]^+$ (m/z = calcd, 971.08, obsd. 971.09) with isotopic pattern (complex **5**).

[Cu(κ³-O,N,S-L³)(κ²-N,N-phen)] (6)



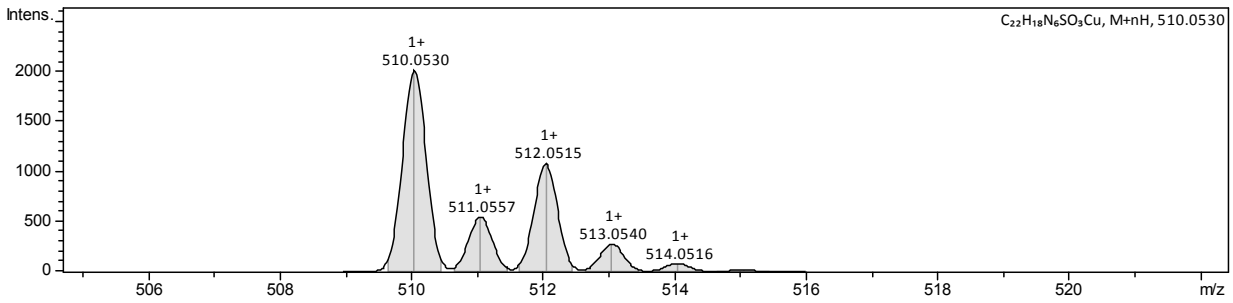


Figure. 13S ESI-mass spectrum due to molecular ion $[CuL^3(phen)+ H]^+$ (m/z = calcd, 510.05, obsd. 510.05) with isotopic pattern (complex **6**).

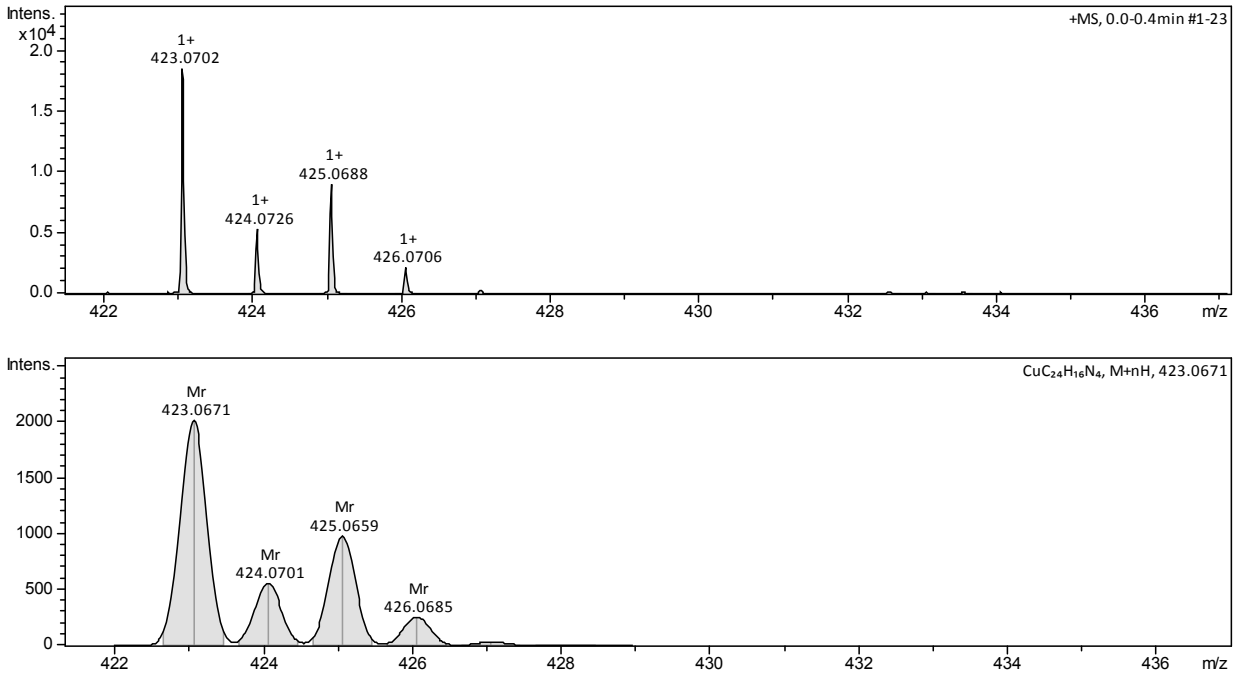
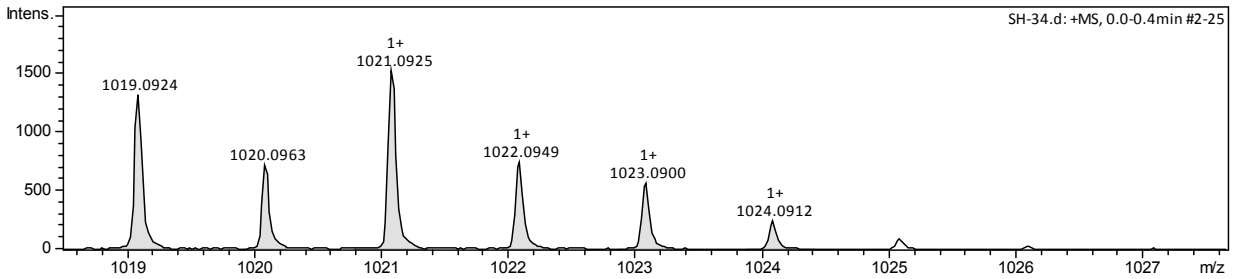


Figure.14S ESI-mass peak due to $[Cu(phen)_2+ H]^+$(m/z = calcd, 423.06, obsd. 423.06) species with isotopic pattern (complex **6**).



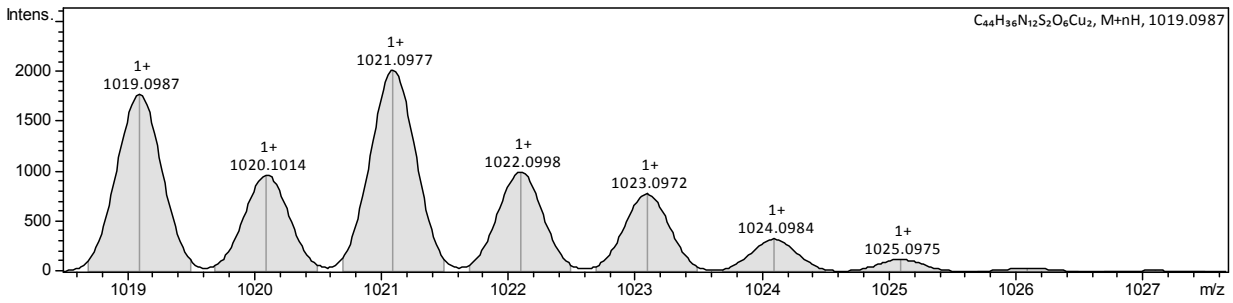


Figure. 15S ESI-mass peak of dimer $[Cu_2(L^3)_2(phen)_2+H]^+$ (m/z = calcd, 1019.09, obsd. 1019.09) with isotopic pattern (complex **6**).

[Cu(κ³-O,N,S-L⁴(κ²-N,N-bipy)] (7)

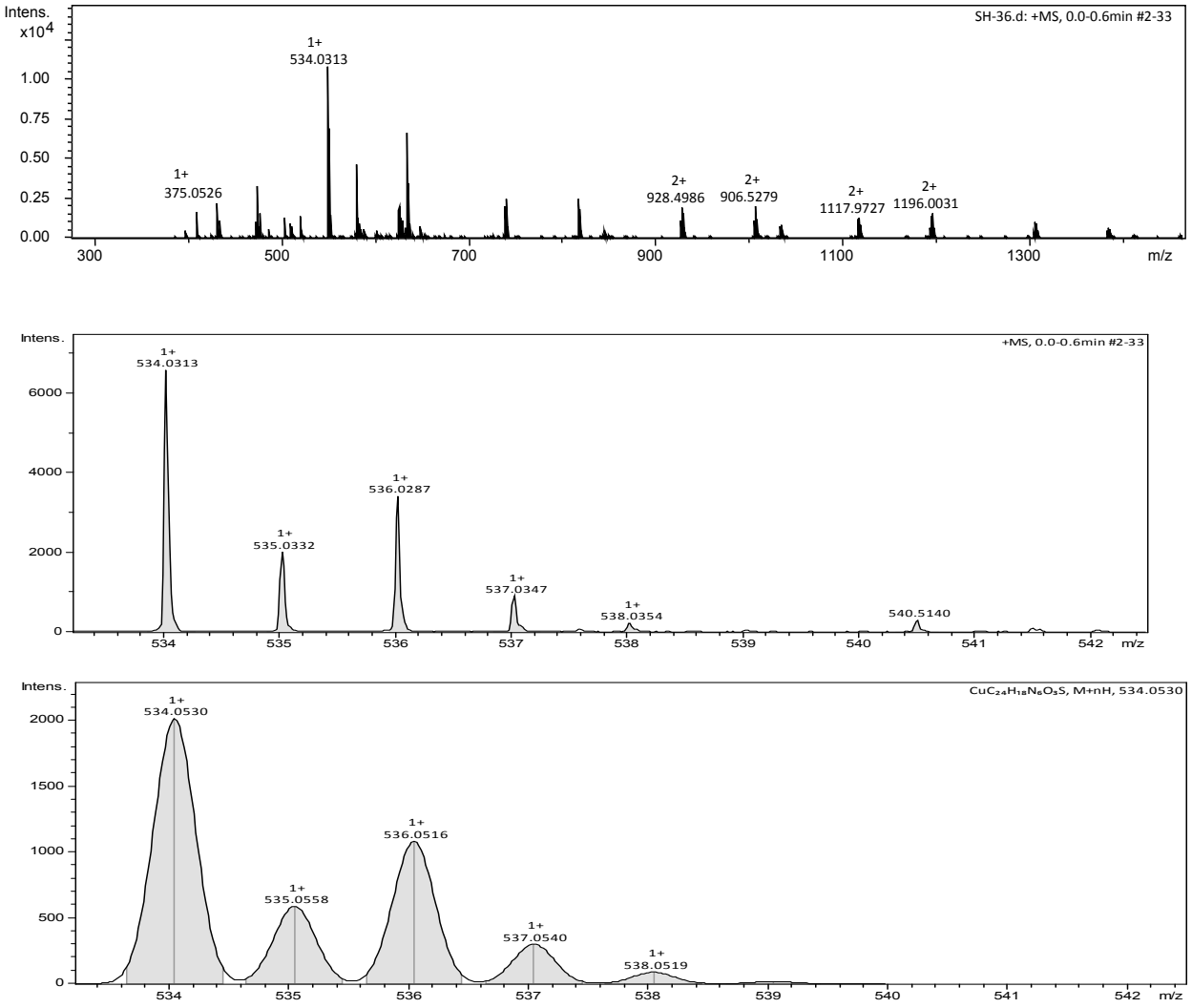


Figure. 16S ESI-mass spectrum due to molecular ion $[CuL^4(bipy)+ H]^+$ (m/z = calcd, 534.05, obsd. 534.05) with isotopic pattern (complex 7).

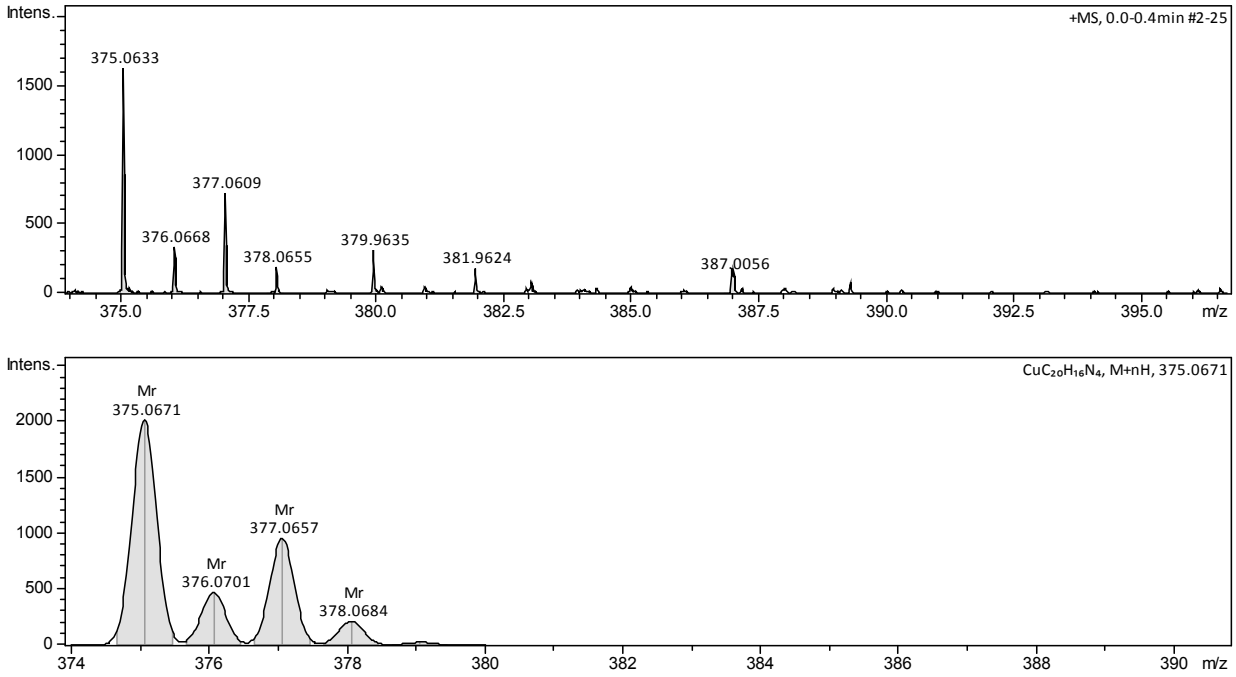
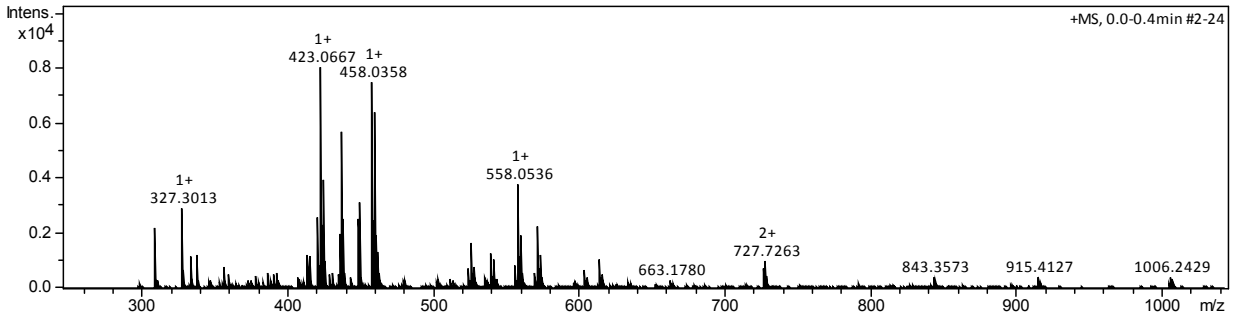


Figure. 17S ESI-mass peak due to $[Cu(bipy)_2 + H]^+$ (m/z = calcd, 375.06, obsd. 375.06) species with isotopic pattern (complex 1).

[Cu(κ³-O,N,S-L(κ²-N,N-phen)] (8)



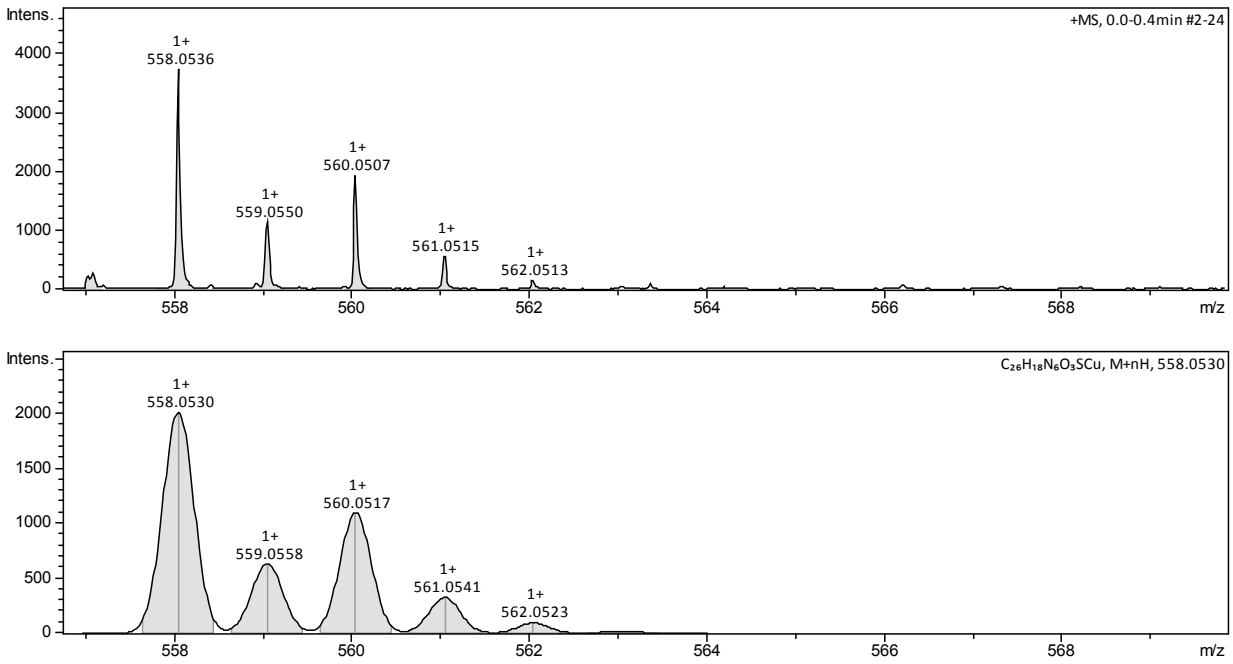


Figure. 18S ESI-mass spectrum due to molecular ion $[CuL^4(phen)+ H]^+$ (m/z = calcd, 558.05, obsd. 558.05) with isotopic pattern (complex 8).

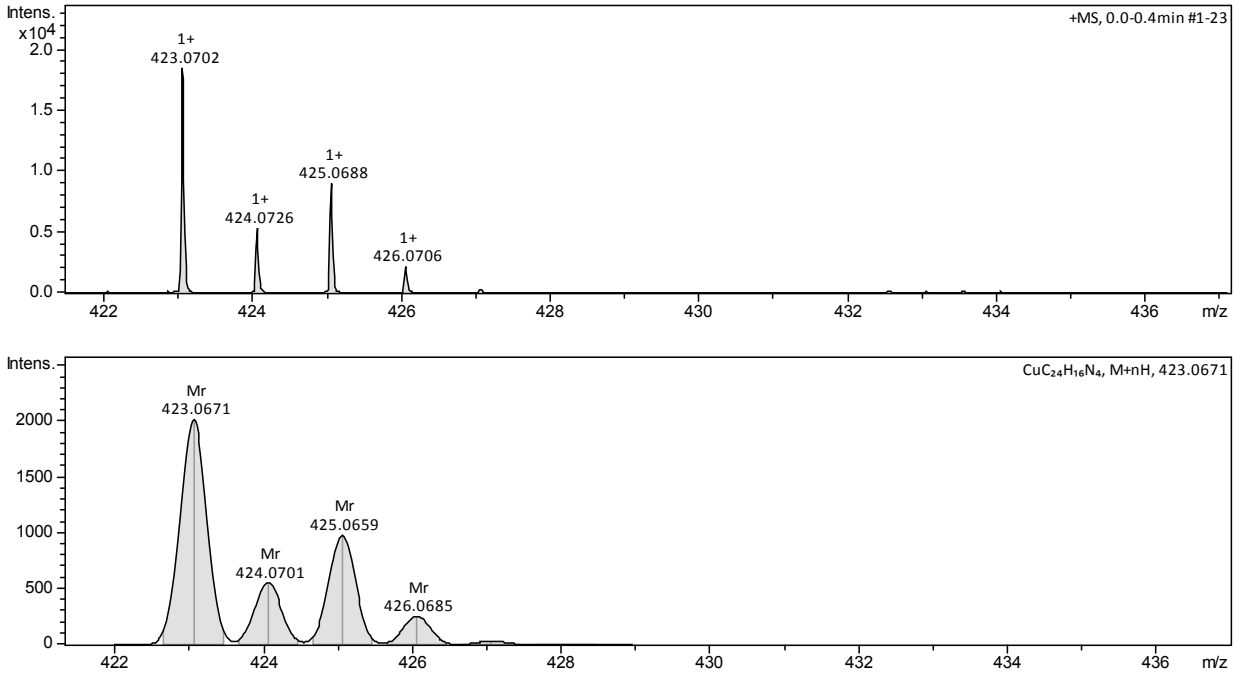


Figure. 19S ESI-mass peak due to $[Cu(phen)_2+ H]^+$(m/z = calcd, 423.06, obsd. 423.06) species with isotopic pattern (complex **8**).

6. Ortep diagrams of Cu(II) complexes, 1-8.

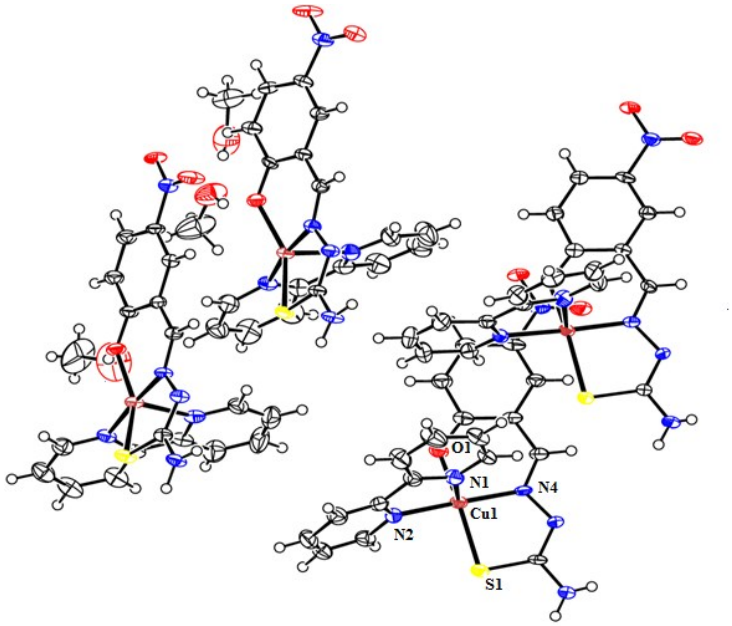


Figure. 20S Molecular structure of complex 4[Cu(κ^3-O,N,S-L^1)(κ^2-N,N-bipy)] .3CH_3OH (20 % probability)

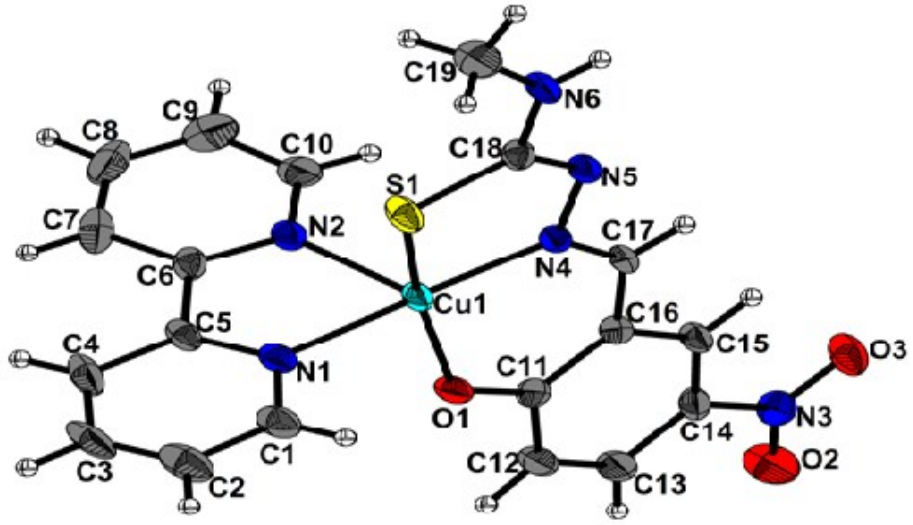


Figure 21S. Molecular structure of complex [Cu(κ^3-O,N,S-L^2)(κ^2-N,N-bipy)] (with 30 % probability) (**3**).

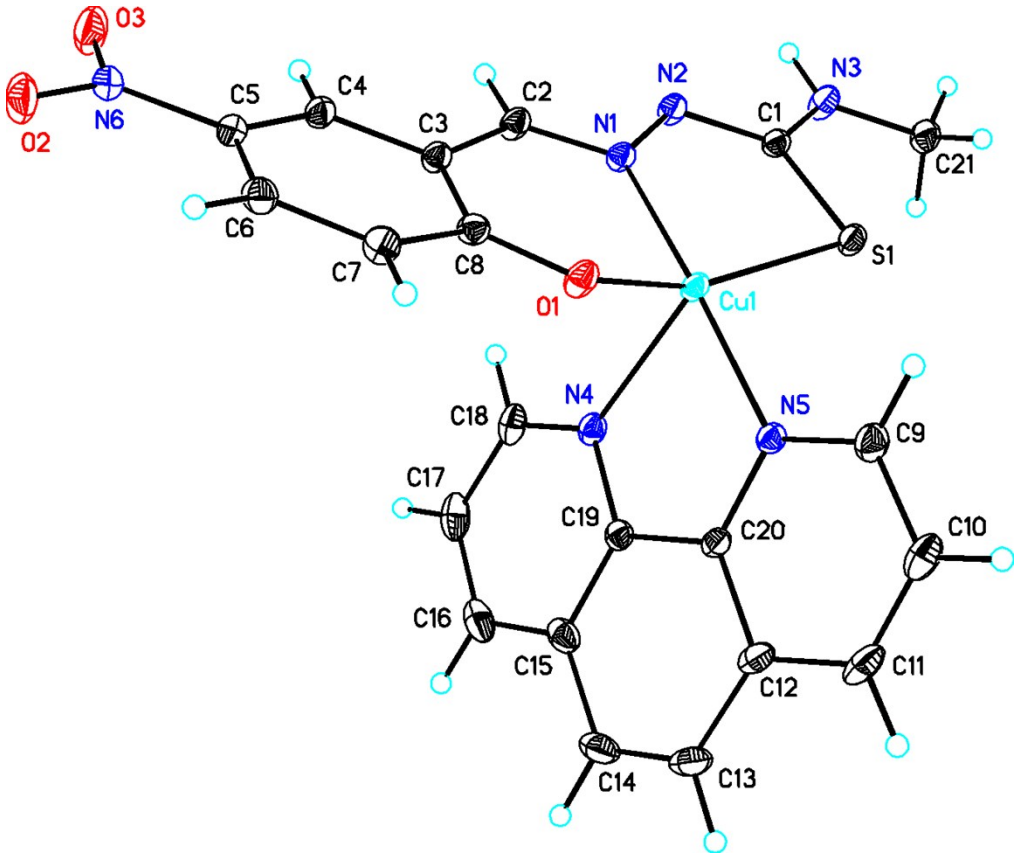


Figure22S. Molecular structure of complex [Cu(κ^3-O,N,S-L^2)(κ^2-N,N-phen)] (with 20 % probability) (**4**).

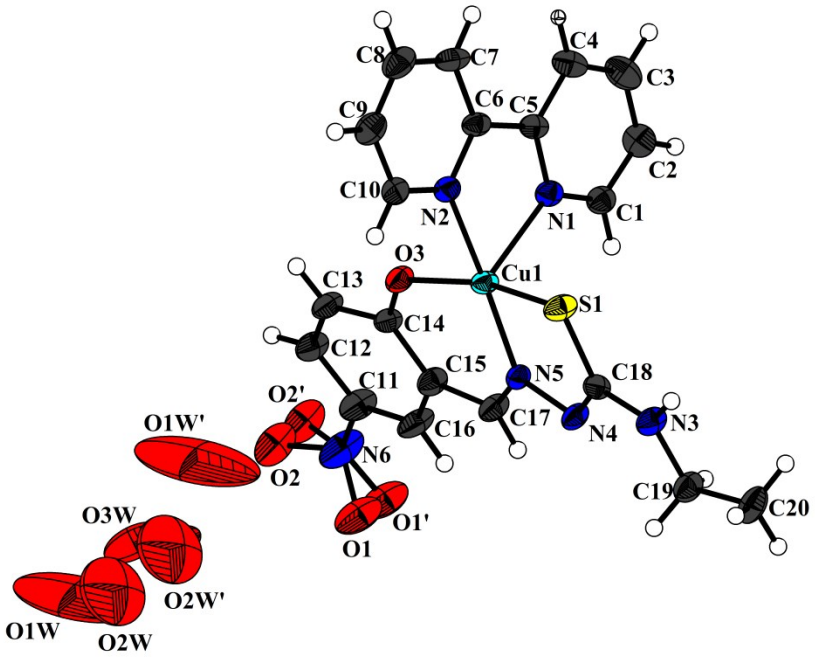


Figure 23S. Molecular structure of complex [Cu(κ^3-O,N,S-L^3)(κ^2-N,N-bipy)] .3H_2O (**5**) (with 30 % probability), disordered oxygen atoms of nitro group and lattice water molecules are shown in figure.

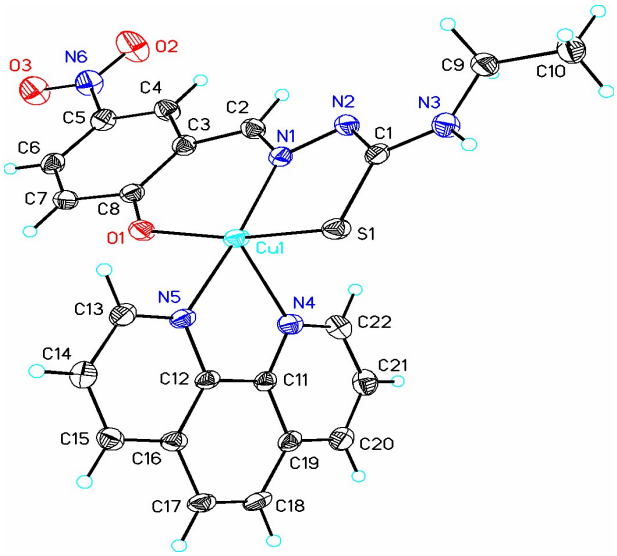


Figure 24S. Molecular structure of complex [Cu(κ^3-O,N,S-L^3)(κ^2-N,N-phen)] (with 20 % probability) (**6**).

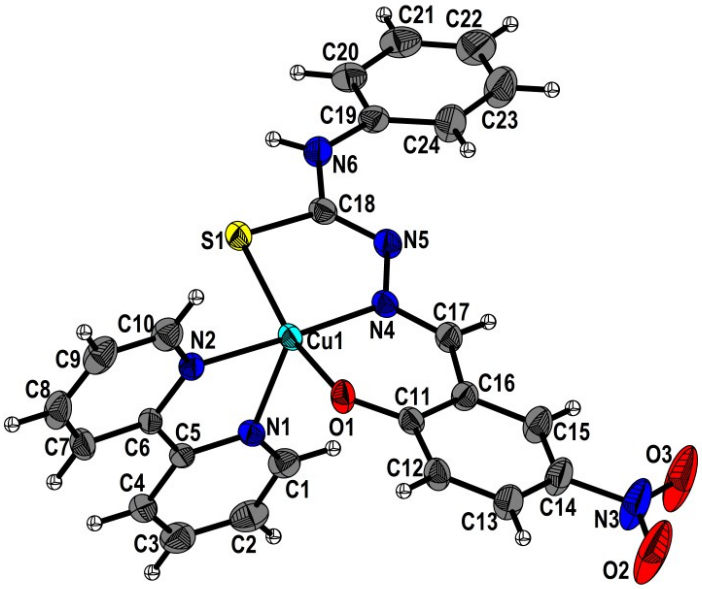


Figure 25S. Molecular structure of complex [Cu(κ^3-O,N,S-L^4)(κ^2-N,N-bipy)] **7** (with 50 % probability) (**7**).

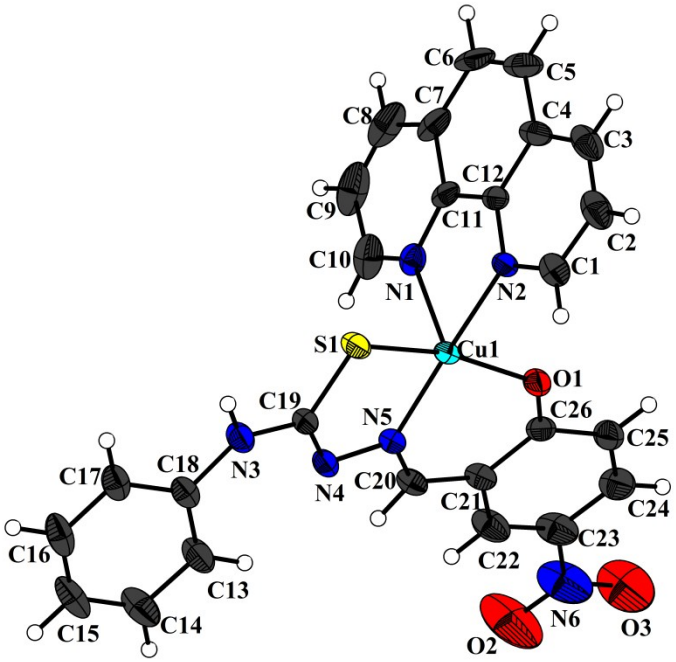


Figure 26S. Molecular structure of complex [Cu(κ^3-O,N,S-L^4)(κ^2-N,N-phen)] (with 30 % probability) (**8**).

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

Complex 1			
Molecule A			
Cu(1) –O(1)	1.974(4)	Cu(1)–N(4)	1.953(4)
Cu(1) –N(2)	2.012(4)	Cu(1)–S(1)	2.2510(14)
Cu(1)–N(1)	2.250(5)	S(1)–C(9)	1.7435(17)
O(1)-Cu(1)-N(2)	92.31(16)	O(1)-Cu(1)-N(5)	98.10(5)
O(1)-Cu(1)-N(4)	92.45(16)	O(1)-Cu(1)-S(1)	150.20(11)
N(4)–Cu(1)–N(2)	171.11(18)	N(4)-Cu(1)-S(1)	86.23(12)
N(2)–Cu(1)–N(1)	77.05(18)	N(2)-Cu(1)-S(1)	93.34(13)
N(1)–Cu(1)–N(1)	101.23(5)	N(1)-Cu(1)-S(1)	108.55(13)
τ	0.348		
Molecule B			
Cu(2) –O(4)	1.953(3)	Cu(2)–N(10)	1.952(4)
Cu(2) –N(7)	2.024(4)	Cu(2)–S(2)	2.2599(14)
Cu(2)–N(8)	2.245(4)	S(2)-C(36)	1.745(5)
O(4)-Cu(2)-N(10)	92.84(16)	O(4)-Cu(2)-N(7)	87.80(16)
O(4)-Cu(2)-N(7)	87.80(16)	O(4)-Cu(2)-S(2)	155.48(12)
N(10)–Cu(2)–N(7)	174.84(17)	N(10)-Cu(2)-S(2)	85.76(12)
N(8)–Cu(2)–N(7)	76.44(17)	N(7)-Cu(2)-S(2)	95.77(12)
N(10)–Cu(2)–N(8)	98.41(17)	N(8)-Cu(2)-S(2)	105.79(13)
τ	0.322		
MOLECULE C			
Cu(1) –O(7)	1.967(3)	Cu(3)–N(16)	1.958(4)
Cu(1) –N(14)	2.011(4)	Cu(3)–S(3)	2.2507(14)
Cu(3)–N(13)	2.251(5)	S(3)–C(54)	1.739(5)
O(7)-Cu(3)-N(16)	92.83(16)	N(14)–Cu(3)–N(13)	77.27(18)
O(7)-Cu(3)-N(14)	90.85(16)	O(7)-Cu(3)-S(3)	154.37(13)
N(16)–Cu(3)–N(14)	176.12(17)	N(4)-Cu(1)-S(1)	86.23(12)
O(7)-Cu(3)-N(13)	97.48(16)	N(14)-Cu(3)-S(3)	91.40(13)
N(16)–Cu(3)–N(14)	92.83(16)	N(13)-Cu(3)-S(1)	107.92(12)
τ	0.363		
MOLECULE 4			
Cu(4) –O(10)	1.950(4)	Cu(4)–N(22)	1.969(4)
Cu(4) –N(19)	2.030(4)	Cu(4)–S(4)	2.2653(14)
Cu(4)–N(20)	2.221(4)	S(4)–C(72)	1.735(5)
O(10)-Cu(4)-N(22)	92.44(16)	N(19)–Cu(4)–N(20)	76.90(17)
O(10)-Cu(4)-N(19)	90.60(16)	O(10)-Cu(4)-S(4)	156.89(12)
N(22)–Cu(4)–N(19)	175.66(18)	N(22)-Cu(4)-S(4)	85.88(12)
O(10)-Cu(4)-N(20)	95.90(16)	N(19)-Cu(4)-S(4)	92.53(13)
N(22)–Cu(4)–N(20)	99.69(17)	N(20)-Cu(4)-S(4)	107.11(12)

τ	0.312		
Complex-3			
Cu(1) –O(1)	1.942(5)	Cu(1)–N(4)	1.944(5)
Cu(1) –N(2)	2.031(6)	Cu(1)–S(1)	2.253(2)
Cu(1)–N(1)	2.253(6)	S(1)–C(18)	1.728(6)
O(1)-Cu(1)-N(4)	93.6(2)	O(1)-Cu(1)-N(1)	98. 0(2)
O(1)-Cu(1)-N(2)	88.3(2)	O(1)-Cu(1)-S(1)	162.04(19)
N(4)–Cu(1)–N(2)	175.3(2)	N(4)-Cu(1)-S(1)	85.46(17)
N(2)–Cu(1)–N(1)	76.1(2)	N(2)-Cu(1)-S(1)	91.37(18)
N(4)–Cu(1)–N(1)	107.81(19)	N(1)-Cu(1)-S(1)	99.39(16)
τ	0.221		
Complex-5			
Cu(1) –O(3)	1.961(3)	Cu(1)–N(5)	1.958(4)
Cu(1) –N(2)	2.031(4)	Cu(1)–S(1)	2.2828(14)
Cu(1)–N(1)	2.241(4)	S(1)–C(18)	1.745(5)
O(3)-Cu(1)-N(5)	93.04(15)	O(3)-Cu(1)-N(1)	96.88(16)
O(3)-Cu(1)-N(2)	88.55(15)	O(3)-Cu(1)-S(1)	162.80(13)
N(5)–Cu(1)–N(1)	175.05(16)	N(5)-Cu(1)-S(1)	84.96(12)
N(2)–Cu(1)–N(1)	76.62(15)	N(2)-Cu(1)-S(1)	92.11(12)
N(5)–Cu(1)–N(1)	107.92(16)	N(1)-Cu(1)-S(1)	99.99(11)
τ	0.204		
Complex 7			
Cu(1) –O(1)	1.9586(14)	Cu(1)–N(4)	1.9515(16)
Cu(1) –N(2)	2.0125(17)	Cu(1)–S(1)	2.2902(6)
Cu(1)–N(1)	2.2400(17	S(1)–C(18)	1.746(2)
O(1)-Cu(1)-N(4)	92.20(6)	O(1)-Cu(1)-N(2)	88.97(6)
O(1)-Cu(1)-N(1)	88.4(2)	O(1)-Cu(1)-S(1)	160.58(5)
N(4)–Cu(1)–N(2)	177.60(7)	N(4)-Cu(1)-S(1)	85.05(5)
N(2)–Cu(1)–N(1)	77.00(7)	N(2)-Cu(1)-S(1)	93.16(5)
N(4)–Cu(1)–N(1)	104.91(7)	N(1)-Cu(1)-S(1)	101.65(5)
τ	0.283		
Complex 4			
Cu(1) –O(1)	1.9699(14)	Cu(1)–N(1)	1.9492(15)
Cu(1) –N(5)	2.0161(15)	Cu(1)–S(1)	2.2694(5)
Cu(1)–N(4)	2.2714(17)	S(1)–C(1)	1.7401(18)
O(1)-Cu(1)-N(4)	92.75(6)	O(1)-Cu(1)-N(1)	92.96(6)
O(1)-Cu(1)-N(5)	89.79(6)	O(1)-Cu(1)-S(1)	156.03(5)
N(1)–Cu(1)–N(5)	174.46(7)	N(1)-Cu(1)-S(1)	85.34(5)
N(1)–Cu(1)–N(4)	97.38(6)	N(5)-Cu(1)-S(1)	94.09(5)
N(5)–Cu(1)–N(4)	77.67(6)	N(4)-Cu(1)-S(1)	111.19(4)
τ	0.307		
Complex 6			
Cu(1) –O(1)	1.940(2)	Cu(1)–N(1)	1.965(3)
Cu(1) –N(5)	2.024(3)	Cu(1)–S(1)	2.2737(8)

Cu(1)–N(4)	2.306(3)	S(1)–C(1)	1.757(3)
O(1)-Cu(1)-N(1)	92.62 (10)	O(1)-Cu(1)-N(5)	87.64(9)
O(1)-Cu(1)-N(4)	97.39(10)	O(1)-Cu(1)-S(1)	164.56(8)
N(4)–Cu(1)–N(5)	172.46(10)	N(1)-Cu(1)-S(1)	85.54(8)
N(5)–Cu(1)–N(4)	77.47(10)	N(4)-Cu(1)-S(1)	97.65(7)
N(4)–Cu(1)–N(1)	109.94(10)	N(5)-Cu(1)-S(1)	92.20(7)
τ	0.132		
Complex 8			
Cu(1) –O(1)	1.947(2)	Cu(1)–N(5)	1.951(2)
Cu(1) –N(2)	2.009(2)	Cu(1)–S(1)	2.29408(2)
Cu(1)–N(1)	2.276(2)	S(1)–C(19)	1.746(3)
O(1)-Cu(1)-N(5)	92.17(9)	O(1)-Cu(1)-N(1)	96.24(9)
O(1)-Cu(1)-N(2)	87.85(8)	O(1)-Cu(1)-S(1)	161.54(7)
N(5)–Cu(1)–N(2)	177.18(10)	N(5)-Cu(1)-S(1)	84.93(7)
N(2)–Cu(1)–N(1)	77.72(9)	N(1)-Cu(1)-S(1)	94.17(7)
N(5)–Cu(1)–N(1)	105.08(10)	N(1)-Cu(1)-S(1)	102.12(7)
τ	0.260		

τ is Addison parameter calculated by dividing difference of two largest core angles by sixty [A-B/60]