Comparative Study of Donor Atom Effects on the Thermodynamic and Electron-Transfer Kinetic Properties of Copper(II/I) Complexes with Sexadentate Macrocyclic Ligands. $Cu^{II/I}([18]aneS_4N_2)$ and $Cu^{II/I}([18]aneS_4O_2)$

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SUPPLEMENTARY INFORMATION

TABULATION OF EXPERIMENTAL RATE CONSTANTS

Table S-1. Experimental Rate Constant Data for the Reduction of $Cu^{II}([18]aneS_4O_2)$ with $Ru^{II}(NH_3)_4bpy)$ under Second-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (PF_6^-).

Table S-2. Experimental Rate Constant Data for the Reduction of CuII($[18]aneS_4O_2$) with $Ru^{II}(NH_3)_4phen)$ under Second-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (ClO_4^-),

Table S-3. Experimental Rate Constant Data for the Reduction of $Cu^{II}([18]aneS_4O_2)$ with $Ru^{II}(NH_3)_5isn)$ under Second-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (ClO_4^-).

Table S-4. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4O_2)$ with $Ni^{III}([14]aneN_4)$ under Second-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (ClO_4^-).

Table S-5. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4O_2)$ with $Ni^{III}([9]aneN_3)_2$ under Pseudo-First-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (ClO_4^-).

Table S-6. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4O_2)$ with $Fe^{III}(bpy)_3$ under Second-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (ClO_4^-).

Table S-7. Experimental Rate Constant Data for the Reduction of $Cu^{II}([18]aneS_4N_2)$ with $Ni^{II}(cp)_2$ under Second-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (ClO_4^-).

Table S-8. Experimental Rate Constant Data for the Reduction of $Cu^{II}([18]aneS_4N_2)$ with $Co^{II}(sep)$ under Pseudo-First-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (ClO_4^-).

Table S-9. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4N_2)$ with $Co^{III}(phen)_3$ under Pseudo-First-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (ClO_4^-).

Table S-10. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4N_2)$ with $Co^{III}(bpy)_3$ under Pseudo-First-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (ClO_4^-).

Table S-11. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4N_2)$ with $Ru^{III}(NH_3)_5$isn under Second-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (ClO_4^-).

Table S-12. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4N_2)$ with $Ru^{III}(NH_3)_5$py under Second-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (ClO_4^-).

Table S-13. Experimental Rate Constant Data for the Reduction of $Cu^{II}([18]aneS_4N_2)$ with $Ru^{II}(NH_3)_6$ under Pseudo-First-Order Conditions in Water at 25 °C, μ = 0.10 M ($NaClO_4$), pH 5.0, $[Cu^{II}([18]aneS_4N_2)]$ = 8.75 μM.

Table S-14. Experimental Rate Constant Data for the Reduction of $Cu^{II}([18]aneS_4N_2)$ with $Ru^{II}(NH_3)_6$ under Pseudo-First-Order Conditions in Water at 25 °C, μ = 0.10 M ($NaClO_4$), pH 8.0, $[Cu^{II}([18]aneS_4N_2)]$ = 8.09 μM.

Table S-15. Experimental Rate Constant Data for the Reduction of $Cu^{II}([18]aneS_4N_2)$ with Co^{II}(sep) under Pseudo-First-Order Conditions in Water at 25 °C, μ = 0.10 M ($NaClO_4$), pH 5.0, $[Cu^{II}([18]aneS_4N_2)]$ = 3.88 μM.

Table S-16. Experimental Rate Constant Data for the Reduction of $Cu^{II}([18]aneS_4N_2)$ with Co^{II}(sep) under Pseudo-First-Order Conditions in Water at 25 °C, μ = 0.10 M ($NaClO_4$), pH 8.0, $[Cu^{II}([18]aneS_4N_2)]$ = 4.37 μM.

Table S-17. Experimental Rate Constant Data for the Reduction of $Cu^{II}([18]aneS_4N_2)$ with Co^{II}(sep) under Pseudo-First-Order Conditions in Water at 25 °C, μ = 0.10 M ($NaClO_4$), pH 10.0, $[Cu^{II}([18]aneS_4N_2)]$ = 3.97 μM.

Table S-18. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4N_2)$ with $Ru^{III}(NH_3)_5$isn under Pseudo-First-Order Conditions in Water at 25 °C, μ = 0.10 M ($NaClO_4$), pH 5.0, $[Cu^{II}([18]aneS_4N_2)]$ = 4.78 μM.

Table S-19. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4N_2)$ with $Ru^{III}(NH_3)_5$isn under Second-Order Conditions in Water at 25 °C, μ = 0.10 M ($NaClO_4$), pH 8.0, $[Cu^{II}([18]aneS_4N_2)]$ = 6.70 μM.

Table S-20. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4N_2)$ with $Co^{III}(bpy)_3$ under Pseudo-First-Order Conditions in Water at 25 °C, μ = 0.10 M ($NaClO_4$), pH 5.0, $[Cu^{II}([18]aneS_4N_2)]$ = 19.1 μM.

Table S-21. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4N_2)$ with $Co^{III}(bpy)_3$ under Pseudo-First-Order Conditions in Water at 25 °C, μ = 0.10 M ($NaClO_4$), pH 8.0, $[Cu^{II}([18]aneS_4N_2)]$ = 18.8 μM.

Table S-22. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4N_2)$ with $Co^{III}(bpy)_3$ under Pseudo-First-Order Conditions in Water at 25 °C, μ = 0.10 M ($NaClO_4$), pH 10.0, $[Cu^{II}([18]aneS_4N_2)]$ = 18.8 μM.

Table S-23. Experimental Rate Constant Data for the Oxidation of $Ni^{II}(cp)_2$ with $Co^{III}(dmg)_3(BC_5H_5)_2$ under Second-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M ($NaClO_4$, $[Co^{III}(dmg)_3(BC_5H_5)_2]$ = 15.0 μM.

Table S-24. Experimental Rate Constant Data for the Reduction of $Co^{III}(phen)_3$ with $Co^{II}(dmg)_3(BC_5H_5)_2$ under Pseudo-First-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M ($NaClO_4$), $[Co^{III}(dmg)_3(BC_5H_5)_2]$ = 49.4 μM.

Table S-1. Experimental Rate Constant Data for the Reduction of $Cu^{II}([18]aneS_4O_2)$ with $Ru^{II}(NH_3)_4bpy)$ under Second-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (PF_6^-).

$[Cu^{II}([18]aneS_4O_2)]$, μM	$[Ru^{II}]$, μM	Mean k_{12} x 10^{-6}, $M^{-1}s^{-1}$
5.55	14.6	3.3(3)
6.70	15.1	3.1(2)
6.70	18.8	2.8(2)
8.80	24.4	3.0(1)
8.80	34.1	3.1(2)

Table S-2. Experimental Rate Constant Data for the Reduction of $Cu^{II}([18]aneS_4O_2)$ with $Ru^{II}(NH_3)_4phen)$ under Second-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (ClO_4^-).

$[Cu^{II}([18]aneS_4O_2)]$, μM	$[Ru^{II}]$, μM	Mean k_{12} x 10^{-6}, $M^{-1}s^{-1}$
10.3	5.94	4.3(4)
14.5	5.94	3.5(3)
14.5	9.90	5.9(4)
20.7	5.94	2.5(3)
20.7	9.90	3.5(2)

Table S-3. Experimental Rate Constant Data for the Reduction of $Cu^{II}([18]aneS_4O_2)$ with $Ru^{II}(NH_3)_5isn$) under Second-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (ClO_4^-).

$[Cu^{II}([18]aneS_4O_2)]$, μM	$[Ru^{II}]$, μM	Mean k_{12} x 10^{-7}, $M^{-1}s^{-1}$
4.72	3.97	3.9(3)
7.36	5.95	3.6(3)
56.5	5.95	4.7(4)
56.5	7.95	5.2(5)
10.5	7.95	2.8(4)

Table S-4. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4O_2)$ with $Ni^{III}([14]aneN_4)$ under Second-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (ClO_4^-).

$[Cu^{I}([18]aneS_4O_2)]$, μM	$[Ni^{III}]$, μM	Mean k_{21} x 10^{-5}, $M^{-1}s^{-1}$
29.1	16.7	1.92(12)
29.1	25.0	2.93(6)
29.1	33.4	2.94(9)
29.1	50.1	1.82(4)
29.1	66.8	1.76(61)

Table S-5. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4O_2)$ with $Ni^{III}([9]aneN_3)_2$ under Pseudo-First-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (ClO_4^-) [$Cu^{I}([18]aneS_6)$] = 8.12 μM.

$[Ru^{II}]$, μM	Mean k_{obs}, s^{-1}
48.6	1.5
120	2.7
187	3.8
279	5.5
346	6.6

Table S-6. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4O_2)$ with $Fe^{III}(bpy)_3$ under Second-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (ClO_4^-).

$[Cu^{I}([18]aneS_4O_2)]$, μM	$[Fe^{III}]$, μM	Mean k_{21} x 10^{-7}, $M^{-1}s^{-1}$
3.25	1.32	2.6(4)
3.25	1.98	1.6(2)
3.25	2.64	1.4(1)
3.25	3.30	1.6(2)

Table S-7. Experimental Rate Constant Data for the Reduction of $Cu^{II}([18]aneS_4N_2)$ with $Ni^{II}(cp)_2$ under Second-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (ClO_4^-), $[Cu^{II}([18]aneS_4N_2)]$ = 13.1 μM.

$[Ni^{II}]$, μM	Mean k_{12} x 10^{-6}, $M^{-1}s^{-1}$
32.4	2.50(18)
48.6	2.62(17)
65.0	2.57(18)
81.0	2.50(14)
162	2.52(16)

Table S-8. Experimental Rate Constant Data for the Reduction of $Cu^{II}([18]aneS_4N_2)$ with Co^{II}(sep) under Pseudo-First-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (ClO_4^-), $[Cu^{II}([18]aneS_4N_2)]$ = 8.35 μM.

$[Co^{II}]$, μM	Mean k_{obs}, s^{-1}
49.5	15.5(16)
99.1	23.2(29)
149	32.4(15)
198	36.9(49)
248	49.8(56)

Table S-9. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4N_2)$ with $Co^{III}(phen)_3$ under Pseudo-First-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (ClO_4^-), $[Cu^{I}([18]aneS_4N_2)]$ = 7.80 μM.

$[Co^{II}]$, μM	Mean k_{obs}, s^{-1}
87.8	2.10(2)
186	4.79(5)
366	8.16(16)
607	12.2(34)
761	15.2(49)

Table S-10. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4N_2)$ with $Co^{III}(bpy)_3$ under Pseudo-First-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (ClO_4^-), $[Cu^{I}([18]aneS_4N_2)]$ = 23.4 μM.

$[Co^{III}]$, mM	Mean k_{obs}, s^{-1}
0.203	2.28(2)
0.406	4.68(6)
0.810	9.78(17)
1.22	14.5(4)
1.62	19.8(7)

Table S-11. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4N_2)$ with $Ru^{III}(NH_3)_5isn$ under Second-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (ClO_4^-), $[Cu^{I}([18]aneS_4N_2)]$ = 6.51 μM.

$[Ru^{III}]$, μM	Mean k_{21} x 10^{-7}, $M^{-1}s^{-1}$
3.76	5.3(4)
4.70	7.8(9)
8.47	5.4(3)
10.3	2.7(1)
14.1	1.2(1)

Table S-12. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4N_2)$ with $Ru^{III}(NH_3)_5py$ under Second-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M (ClO_4^-), $[Ru^{III}(NH_3)_5py]$ = 12.3 μM.

$[Cu^{I}]$, μM	Mean k_{21} x 10^{-6}, $M^{-1}s^{-1}$
58.3	2.84(28)
77.8	3.17(25)
87.5	3.28(25)
97.2	2.79(22)

Table S-13. Experimental Rate Constant Data for the Reduction of $Cu^{II}([18]aneS_4N_2)$ with $Ru^{II}(NH_3)_6$ under Pseudo-First-Order Conditions in Water at 25 °C, μ = 0.10 M ($NaClO_4$), pH 5.0, $[Cu^{II}([18]aneS_4N_2)]$ = 8.75 μM.

$[CRu^{II}]$, μM	Mean k_{obs}, s^{-1}
75.6	0.170(18)
151	0.423(25)
227	0.791(16)
302	0.971(79)
378	1.44(13)

Table S-14. Experimental Rate Constant Data for the Reduction of $Cu^{II}([18]aneS_4N_2)$ with $Ru^{II}(NH_3)_6$ under Pseudo-First-Order Conditions in Water at 25 °C, μ = 0.10 M ($NaClO_4$), pH 8.0, $[Cu^{II}([18]aneS_4N_2)]$ = 8.09 μM.

$[Ru^{II}]$, μM	Mean k_{obs}, s^{-1}
69.9	0.321(15)
140	0.577(17)
210	0.762(35)
280	0.981(72)
349	1.23(81)

Table S-15. Experimental Rate Constant Data for the Reduction of $Cu^{II}([18]aneS_4N_2)$ with Co^{II}(sep) under Pseudo-First-Order Conditions in Water at 25 °C, μ = 0.10 M ($NaClO_4$), pH 5.0, $[Cu^{II}([18]aneS_4N_2)]$ = 3.88 μM.

$[Co^{II}]$, μM	Mean k_{obs}, s^{-1}
45.6	7.86
91.2	16.6
182	34.2
274	41.1
365	50.5

Table S-16. Experimental Rate Constant Data for the Reduction of $Cu^{II}([18]aneS_4N_2)$ with Co^{II}(sep) under Pseudo-First-Order Conditions in Water at 25 °C, μ = 0.10 M ($NaClO_4$), pH 8.0, $[Cu^{II}([18]aneS_4N_2)]$ = 4.37 μM.

$[Co^{II}]$, μM	Mean k_{obs}, s^{-1}
110	15.1
266	45.5
440	71.3
660	114.6
880	166.5

Table S-17. Experimental Rate Constant Data for the Reduction of $Cu^{II}([18]aneS_4N_2)$ with $Co^{II}(sep)$ under Pseudo-First-Order Conditions in Water at 25 °C, μ = 0.10 M ($NaClO_4$), pH 10.0, $[Cu^{II}([18]aneS_4N_2)]$ = 3.97 μM.

$[Co^{II}]$, μM	Mean k_{obs}, s^{-1}
66.4	6.66
102	10.2
284	28.3
580	58.0
887	88.7

Table S-18. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4N_2)$ with $Ru^{III}(NH_3)_5isn$ under Pseudo-First-Order Conditions in Water at 25 °C, μ = 0.10 M ($NaClO_4$), pH 5.0, $[Cu^{II}([18]aneS_4N_2)]$ = 4.78 μM.

$[Ru^{III}]$, μM	Mean k_{obs}, s^{-1}
39.2	1.11
65.3	1.96
91.4	2.89
131	4.16
196	6.07

Table S-19. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4N_2)$ with $Ru^{III}(NH_3)_5isn$ under Second-Order Conditions in Water at 25 °C, μ = 0.10 M ($NaClO_4$), pH 8.0, $[Cu^{II}([18]aneS_4N_2)]$ = 6.70 μM.

$[Ru^{III}]$, μM	Mean k_{21}, M^{-1} s^{-1}
14.5	7.34(1)
21.7	5.99(2)
29.0	6.09(1)
36.2	6.34(2)
50.5	5.88(1)

Table S-20. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4N_2)$ with $Co^{III}(bpy)_3$ under Pseudo-First-Order Conditions in Water at 25 °C, μ = 0.10 M ($NaClO_4$), pH 5.0, $[Cu^{II}([18]aneS_4N_2)]$ = 19.1 μM.

$[Co^{III}]$, mM	Mean k_{obs}, s^{-1}
0.209	0.144(3)
0.418	0.250(39)
0.627	0.368(59)
0.836	0.471(12)
1.04	0.594(12)

Table S-21. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4N_2)$ with $Co^{III}(bpy)_3$ under Pseudo-First-Order Conditions in Water at 25 °C, μ = 0.10 M ($NaClO_4$), pH 8.0, $[Cu^{II}([18]aneS_4N_2)]$ = 18.8 μM.

$[Co^{III}]$, mM	Mean k_{obs}, s^{-1}
0.104	0.650(9)
0.207	1.36(3)
0.414	2.66(6)
0.621	4.28(12)
0.828	6.42(12)

Table S-22. Experimental Rate Constant Data for the Oxidation of $Cu^{I}([18]aneS_4N_2)$ with $Co^{III}(bpy)_3$ under Pseudo-First-Order Conditions in Water at 25 °C, μ = 0.10 M ($NaClO_4$), pH 10.0, $[Cu^{II}([18]aneS_4N_2)]$ = 18.8 μM.

$[Co^{III}]$, mM	Mean k_{obs}, s^{-1}
0.107	0.738(4)
0.215	1.44(2))
0.430	2.72(3)
0.645	4.29(7)
0.860	5.52(17)

Table S-23. Experimental Rate Constant Data for the Oxidation of $Ni^{II}(cp)_2$ with $Co^{III}(dmg)_3(BC_5H_5)_2$ under Second-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M ($NaClO_4$), $[Co^{III}(dmg)_3(BC_5H_5)_2]$ = 15.0 μM.

$[Ni^{II}]$, μM	Mean k_{12} x 10^{-6}, M^{-1} s^{-1}
20.6	4.09(24)
30.9	3.20(14)
41.2	2.89(11)
51.5	2.45(12)
77.2	2.50(18)

Table S-24. Experimental Rate Constant Data for the Reduction of $Co^{III}(phen)_3$ with $Co^{II}(dmg)_3(BC_5H_5)_2$ under Pseudo-First-Order Conditions in Acetonitrile at 25 °C, μ = 0.10 M ($NaClO_4$), $[Co^{II}(dmg)_3(BC_5H_5)_2]$ = 49.4 μM.

$[Co^{III}]$, mM	Mean k_{obs}, s^{-1}
0.51	0.171(3)
1.02	0.339(7)
1.53	0.526(7)
2.04	0.721(9)
2.55	0.921(10)