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Electron-Transfer Kinetics of Tris(2-(methylthioethyl))-aminecopper(II/I). A Tripodal Ligand Complex Exhibiting Virtual C_{3v} Symmetry

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SUPPORTING INFORMATION

TABULATIONS OF EXPERIMENTAL RATE CONSTANTS

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Table S-1. Cu^{II}(TMMEA) with $Ru^{II}(NH_3)_4$phen under Pseudo-First-Order Conditions in Aqueous Solution at 25 °C, μ = 0.10 M, pH 5.0

$[Cu^{II}L]$, μM	k_{obs}, s^{-1}	$[Cu^{II}L]$, μM	k_{obs}, s^{-1}
Series I: $[Ru^{II}(NH_3)_4phen]$ = 2.03 μM (monitored at λ = 471 nm)			
45.2	0.485 (16)	307	2.57 (10)
132	1.26 (3)	398	3.19 (21)
220	1.95 (4)		
k_{12} = Slope = (7.64 ± 0.25) x 10^3 M^{-1} s^{-1}; intercept = 0.21 ± 0.06; r^2 = 0.997			
Series II: $[Ru^{II}(NH_3)_4phen]$ = 3.73 μM (monitored at λ = 471 nm)			
78.8	0.597 (2)	426	3.25 (5)
182	1.49 (1)	553	4.16 (1)
311	2.40 (1)		
k_{12} = Slope = (7.45 ± 0.15) x 10^3 M^{-1} s^{-1}; intercept = 0.07 ± 0.05; r^2 = 0.999			

Table S-2. Kinetic Data for the Reduction of Cu^{II}(TMMEA) with $Ru^{II}(NH_3)_4$bpy under Pseudo-First-Order Conditions in Aqueous Solution at 25 °C, μ = 0.10 M, pH 5.0

$[Cu^{II}L]$, μM	k_{obs}, s^{-1}	$[Cu^{II}L]$, μM	k_{obs}, s^{-1}
Series I: $[Ru^{II}(NH_3)_4bpy$ = 2.11 μM (monitored at λ = 522 nm)			
45.2	0.459 (19)	307	2.26 (12)
132	0.973 (27)	398	2.78 (18)
220	1.64 (14)		
k_{12} = Slope = (6.74 ± 0.20) x 10^3 M^{-1} s^{-1}; intercept = 0.14 ± 0.05; r^2 = 0.998			
Series II: $[Ru^{II}(NH_3)_4bpy$ = 4.68 μM (monitored at λ = 522 nm)			
78.8	0.642 (52)	426	2.91 (8)
182	1.47 (3)	553	3.44 (8)
311	2.28 (7)		
k_{12} = Slope = (5.88 ± 0.40) x 10^3 M^{-1} s^{-1}; intercept = 0.32 ± 0.14; r^2 = 0.986			

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Table S-3. Kinetic Data for the Reduction of Cu^{II}(TMMEA) with $Ru^{II}(NH_3)_5$isn under Pseudo-First-Order Conditions in Aqueous Solution at 25 °C, μ = 0.10 M, pH 5.0

$[Cu^{II}L]$, μM	k_{obs}, s^{-1}	$[Cu^{II}L]$, μM	k_{obs}, s^{-1}
Series I: $[Ru^{II}(NH_3)_5isn]$ = 4.12 μM (monitored at λ = 478 nm)			
45.2	0.944 (23)	307	3.78 (17)
132	2.03 (3)	398	4.56 (32)
220	2.93 (13)		
k_{12} = Slope = (1.02 ± 0.04) x 10^4 M^{-1} s^{-1}; intercept = 0.60 ± 0.11; r^2 = 0.995			
Series II: $[Ru^{II}(NH_3)_5isn]$ = 2.86 μM (monitored at λ = 478 nm)			
78.8	1.10 (1)	426	4.59 (28)
182	2.21 (4)	553	6.05 (15)
311	3.54 (6)		
k_{12} = Slope = (1.03 ± 0.02) x 10^4 M^{-1} s^{-1}; intercept = 0.30 ± 0.07; r^2 = 0.999			

Table S-4. Kinetic Data for the Oxidation of Cu^{I}(TMMEA) with $Ni^{III}([14]aneN_4)(H_2O)_2$ under Pseudo-First-Order Conditions in Aqueous Solution at 25 °C, μ = 0.10 M, pH 1

$[Cu^{I}L]$, μM	k_{obs}, s^{-1}	$[Cu^{I}L]$, μM	k_{obs}, s^{-1}
$[Ni^{III}([14]aneN_4)(H_2O)_2]$ = 1.32 μM (monitored at λ = 308 nm)			
21.0	1.11 (4)	61.0	3.18 (7)
40.0	2.24 (11)		
k_{21} = Slope = (5.17 ± 0.44) x 10^4 M^{-1} s^{-1}; intercept = 0.08 ± 0.19; r^2 = 0.993			

Table S-5. Kinetic Data for the Oxidation of Cu^{I}(TMMEA) with $Ru^{III}(NH_3)_2(bpy)_2$ under Second-Order Conditions in Aqueous Solution at 25 °C, μ = 0.10 M, pH 1

$[Ru^{III}]$, μM	10^{-6} k_{21}, M^{-1} s^{-1}	$[Ru^{III}]$, μM	10^{-6} k_{21}, M^{-1} s^{-1}
Series I: $[Cu^{I}(TMMEA)]$ = 25.2 μM (monitored at λ = 488 nm)			
24.8	5.39 (21)	63.4	0.795 (44)
37.7	1.24 (2)	76.2	0.658 (67)
50.6	0.885 (62)		
Series II: $[Cu^{I}(TMMEA)]$ = 22.4 μM (monitored at λ = 488 nm)			
44.8	2.65 (13)	77.6	1.16 (9)
55.7	2.42 (12)	89.6	0.818 (61)
66.7	1.27 (6)		
Series III: $[Cu^{I}(TMMEA)]$ = 26.3 μM (monitored at λ = 488 nm))			
39.5	1.69 (12)	79.0	0.664 (64)
51.9	1.13 (6)	92.6	0.709 (68)
65.5	0.624 (48)	105	0.635 (117)

Table S-6. Kinetic Data for the Oxidation of Cu^{I}(TMMEA) with $Fe^{III}(4,7\text{-dmphen})_3$ under Second-Order Conditions in Aqueous Solution at 25 °C, μ = 0.10 M, pH 1

$[Fe^{III}]$, μM	10^{-6} k_{21}, M^{-1} s^{-1}	$[Fe^{III}]$, μM	10^{-6} k_{21}, M^{-1} s^{-1}
Series I: $[Cu^{I}(TMMEA)]$ = 5.05 μM (monitored at λ = 512 nm)			
7.80	4.83 (61)	13.0	3.53 (8)
10.4	4.12 (58)	15.6	2.81 (17)
Series II: $[Cu^{I}(TMMEA)]$ = 9.98 μM (monitored at λ = 512 nm)			
18.6	3.48 (13)	32.6	3.14 (9)
23.3	3.45 (9)	37.2	2.84 (7)
27.9	3.37 (6)		
Series III: $[Cu^{I}(TMMEA)]$ = 9.98 μM (monitored at λ = 512 nm)			
15.1	3.06 (69)	30.1	3.35 (16)
20.1	3.80(8)	35.2	3.35 (12)
25.1	3.45 (8)	40.2	3.09 (7)