

## SUPPORTING INFORMATION

"Influence of Coordination Geometry upon Copper(II/I) Redox Potentials. Physical Parameters for Twelve Copper Tripodal Ligand Complexes"

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**Table S1.** Formal Potential Values and Logarithmic Stability Constants for Copper(II/I) Complexes Included in Figure 4

Complexed Ligand	<i>E</i> <sup>f</sup> , V	$\log K_{\text{Cu}^{\text{II}}\text{L}}$	$\log K_{\text{Cu}^{\text{I}}\text{L}}$	ref
Macrocyclic S <sub>6</sub> [21]aneS <sub>6</sub>	0.89	1.09	14.9	a
Macrocyclic N <sub>x</sub> S <sub>5-x</sub> [15]aneS <sub>5</sub>	0.68	4.18	13.6	b, c
[15]aneNS <sub>4</sub>	0.46	9.80	15.6	b, c
[15]aneN <sub>2</sub> S <sub>3</sub>	0.10	16.02	15.7	b, c
Macrocyclic: N <sub>x</sub> S <sub>4-x</sub> [14]aneNS <sub>3</sub>	0.38	9.25	13.6	b, c
[14]aneN <sub>2</sub> S <sub>2</sub>	0.04	15.26	13.9	b, c
[14]aneNSSN	-0.01	15.72	13.5	b, c
[14]aneN <sub>3</sub> S	≈ -0.24	≈ 20	≈ 13.7	b, c
[14]aneN <sub>4</sub>	-0.66	27.2	13.8	b, c
Macrocyclic: S <sub>3</sub> [9]aneS <sub>3</sub>	0.72	4.42	14.4	d
Macrocyclic: S <sub>4</sub> , variable cavity [13]aneS <sub>4</sub>	0.52	3.44	10.0	e, f
[14]aneS <sub>4</sub>	0.58	4.34	12.0	c, e
[15]aneS <sub>4</sub>	0.64	3.17	11.8	e, f
[16]aneS <sub>4</sub>	0.71	2.20	12.0	e, f
Substituted Macrocyclic: S <sub>4</sub> , variable cavity oxathiane-[12]aneS <sub>4</sub>	0.72	3.02	13.0	g
[13]aneS <sub>4</sub> -ol	0.54	3.1	10.0	g
[14]aneS <sub>4</sub> -ol	0.49	5.59	10.7	g
[15]aneS <sub>4</sub> -ol	0.71	2.28	12.1	g
[16]aneS <sub>4</sub> -ol	0.73	1.51	11.6	g
Acyclic: S <sub>4</sub> Me <sub>2</sub> -2,3,2-S <sub>4</sub>	0.79	1.97	13.1	h
Me <sub>2</sub> -3,2,3-S <sub>4</sub>	0.83	1.18	13.0	h
cis-cyhx-Me <sub>2</sub> -3,2,3-S <sub>4</sub>	0.75	2.45	13.0	h
trans-cyhx-Me <sub>2</sub> -3,2,3-S <sub>4</sub>	0.77	2.94	13.8	h

Tripodal:  $\text{NS}_x\text{py}_{3-x}$ 

TMMEA	0.68	6.29	15.8	i
TEMEA	0.67	6.35	15.5	i
PMMEA	0.38	11.06	15.4	i
PMAS	0.40	10.48	15.0	i
PEMEA	0.60	7.89	15.8	i
PEAS	0.61	7.87	15.9	i
BPMMEA	0.06	16.10	15.0	i
BPMEAA	0.08	15.82	15.0	i
BPEMEA	0.46	9.10	14.6	i
BPEEA	0.47	9.20	15.0	i
TPMA	-0.15	17.6	12.9	i
TPEA	0.51	9.35	15.8	i

<sup>a</sup> Kulatileke, C. P.; Ochrymowycz, L. A.; Rorabacher, D. B., unpublished results. <sup>b</sup> Cu<sup>III</sup>L stability constants: Westerby, B. C.; Juntunen, K. L.; Leggett, G. H.; Pett, V. B.; Koenigbauer, M. J.; Purgett, M. D.; Taschner, M. J.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* 1991, 30, 2109-2120. <sup>c</sup> *E*<sup>f</sup> values: Bernardo, M. M.; Heeg, M. J.; Schroeder, R. R.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* 1992, 31, 191-198. <sup>d</sup> Krylova, K.; Kandegedara, A.; Ochrymowycz, L. A.; Rorabacher, D. B., unpublished results. <sup>e</sup> Cu<sup>II</sup>L stability constant: Sokol, L. S. W. L.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* 1981, 20, 3189-3195. <sup>f</sup> *E*<sup>f</sup> values: Bernardo, M. M.; Schroeder, R. R.; Rorabacher, D. B. *Inorg. Chem.* 1991, 30, 1241-1247. <sup>g</sup> Krylova, K.; Jackson, K. D.; Vroman, J. A.; Grall, A. J.; Snow, M. R.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* 1997, 36, 6216-6223. <sup>h</sup> Dunn, B. C.; Wijetunge, P.; Vyvyan, J. R.; Howard, T. A.; Grall, A. J.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* 1997, 36, 4484-4489. <sup>i</sup> This work.