

Self-Assembly of Tricuprous Double Helicates: Thermodynamics, Kinetics and Mechanism

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Supporting Information Available. Variation of the Pseudo-First Order Constants for the Formation of the Cuprous Complexes of **L'** as a Function of Copper(I) Concentrations^a

Table S1. ES-MS Data for **L** Cuprous Complexes as a Function of $[\text{Cu(I)}]_{\text{tot}}/[\text{L}]_{\text{tot}}$ Ratios.^a

Species	Observed Ion	Measured m/z						Calculated m/z
		$[\text{Cu(I)}]_{\text{tot}}/[\text{L}]_{\text{tot}}$ 0.1	0.2	0.5	1	5	20	
L	$[\text{L} + 2\text{Na}]^{2+}$	610.2	610.3					610.5
	$[\text{L} + \text{K} + \text{Na}]^{2+}$	618.3	618.3					618.5
	$[2\text{L} + 2\text{Na}]^{2+}$	1197.9	1198.0					1198.0
LCu⁺	$[\text{L} + \text{Cu}]^+$	1238.3	1238.5					1239.0
L₂Cu₂²⁺	$[2\text{L} + 2\text{Cu}]^{2+}$		1238.5	1238.5	1238.4			1239.0
L₂Cu₃³⁺	$[2\text{L} + 3\text{Cu}]^{3+}$	846.6	846.7	846.5	846.5	846.8	846.8	847.0
	$[2\text{L} + 3\text{Cu} + \text{BF}_4]^{2+}$		1313.6	1313.4	1313.6	1313.9	1313.8	1314.0
LCu₂²⁺	$[\text{L} + 2\text{Cu} + \text{BF}_4]^+$						1388.9	1389.0

^aSolvent: CH₃CN/H₂O/CH₂Cl₂, 80/15/5 v/v; $[\text{L}]_{\text{tot}} = 1.2 \times 10^{-4}$ M.

Table S2. Variation of the Pseudo-First Order Constants for the Formation of **L** Cuprous Complexes versus Copper(I) Concentrations.^a

$[\text{Cu(I)}]_{\text{tot}} \times 10^4$ (M)	$k_{2,\text{obs}} (\sigma) (\text{s}^{-1})$	$k_{3,\text{obs}} (\sigma) \times 10^2 (\text{s}^{-1})$	$k_{4,\text{obs}} (\sigma) \times 10^2 (\text{s}^{-1})$
2.42	56.7 (8)	13.0 (2)	2.12 (6)
3.15	56.3 (6)	12.0 (2)	1.95 (5)
4.36	54.7 (8)	11.8 (2)	1.78 (5)
6.78	55.4 (8)	11.5 (2)	1.90 (5)

9.70	52.4 (6)	10.6 (2)	1.78 (4)
12.10	52.5 (8)	10.1 (2)	1.68 (4)
14.50	52.6 (9)	9.3 (2)	1.59 (3)
15.7	53.0 (9)	9.3 (2)	1.52 (3)
16.90	55 (1)	8.9 (2)	1.45 (3)
18.10	53 (1)	9.2 (2)	1.53 (3)

^aSolvent: CH₃CN/H₂O/CH₂Cl₂, 80/15/5 v/v; *T* = 25.0 (2) °C; *I* = 0.1; [L]_{tot} = 2.5 × 10⁻⁵M.

Table S3. Variation of Absorbance at the End of Steps 1 and 2.^a

[Cu(I)] _{tot} × 10 ⁴ (M)	A _{1,∞}	A _{2,∞}
2.42	0.058 (3)	0.094 (9)
3.15	0.062 (3)	0.096 (9)
4.36	0.061 (3)	0.091 (9)
6.78	0.055 (3)	0.078 (8)
9.70	0.057 (3)	0.075 (6)
12.10	0.055 (3)	0.071 (5)
14.50	0.053 (3)	0.067 (5)
15.70	0.056 (3)	0.069 (4)
16.90	0.058 (3)	0.070 (4)
18.10	0.058 (3)	0.069 (4)

^aSolvent: CH₃CN/H₂O/CH₂Cl₂, 80/15/5 v/v; *T* = 25.0 (2) °C; *I* = 0.1; [L]_{tot} = 2.5 × 10⁻⁵M; λ = 465 nm; *l* = 1 cm. The errors are given as 3σ.

Fig. S1. Variation of the pseudo-first order rate constant for the formation of the L' cuprous complexes versus [L']_{tot}. Solvent: CH₃CN/CH₂Cl₂, 50/50 v/v; *T* = 25.0 (2) °C; *I* = 0.1; [Cu]_{tot} = 5.7 × 10⁻⁶ × M.

