

Supporting Information

Polynuclear and mixed-ligand mononuclear Cu^I complexes with *N*-thiophosphorylated thioureas and 1,10-phenanthroline or PPh₃

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Table S1 Selected bond lengths [Å] and bond angles [°] for [Cu₄L^I₄]

Bond lengths

Cu(1)···Cu(1C)	2.8682(13)	Cu(1A)···Cu(1C)	2.8956(13)
Cu(1)···Cu(1B)	2.9420(13)	Cu(1A)···Cu(1B)	2.9712(12)

Bond angles

S(1)–Cu(1)–S(2C)	132.72(8)	S(2B)–Cu(1B)–S(1)	130.71(8)
S(1)–Cu(1)–S(2)	113.67(8)	S(2B)–Cu(1B)–S(1B)	114.07(8)
S(2C)–Cu(1)–S(2)	111.17(8)	S(1)–Cu(1B)–S(1B)	113.32(8)
S(2A)–Cu(1A)–S(2B)	136.42(8)	S(2C)–Cu(1C)–S(2A)	135.37(8)
S(2A)–Cu(1A)–S(1A)	113.93(8)	S(2C)–Cu(1C)–S(1C)	114.35(8)
S(2B)–Cu(1A)–S(1A)	107.97(8)	S(2A)–Cu(1C)–S(1C)	108.63(8)

Table S2 Selected bond lengths [Å] and bond angles [°] for [Cu₈L^{II}₈]

Bond lengths

Cu(1)···Cu(2)	2.6914(8)	Cu(4)···Cu(5)	2.8147(8)
Cu(1)···Cu(8)	2.7496(8)	Cu(4)···Cu(6)	2.6889(8)
Cu(2)···Cu(3)	2.8112(8)	Cu(6)···Cu(7)	2.7449(8)
Cu(3)···Cu(5)	2.6684(8)	Cu(7)···Cu(8)	2.7447(7)

Bond angles

S(2)–Cu(1)–S(1)	110.72(4)	S(10)–Cu(5)–S(9)	110.41(4)
S(4)–Cu(2)–S(3)	110.55(4)	S(12)–Cu(6)–S(11)	110.54(4)
S(6)–Cu(3)–S(5)	109.99(4)	S(14)–Cu(7)–S(13)	111.04(4)
S(8)–Cu(4)–S(7)	110.88(4)	S(16)–Cu(8)–S(15)	110.93(4)

Table S3 Hydrogen bond lengths [Å] and angles [°] for [Cu₈L^{II}₈] and [Cu₃L^{III,IV}₃]

Complex	D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DH A)
[Cu ₈ L ^{II} ₈]	N(2)–H(2N)···S(6)	0.88	2.48	3.359(4)	172
	N(4)–H(4N)···S(16)	0.88	2.49	3.371(4)	174
	N(6)–H(6N)···S(8)	0.88	2.51	3.384(4)	175
	N(8)–H(8N)···S(14)	0.88	2.51	3.391(4)	174
	N(10)–H(10N)···S(4)	0.88	2.50	3.375(4)	176
	N(12)–H(12N)···S(10)	0.88	2.50	3.374(4)	173
	N(14)–H(14N)···S(2)	0.88	2.48	3.361(4)	174
	N(16)–H(16N)···S(12)	0.88	2.52	3.398(4)	175
[Cu ₃ L ^{III} ₃]	N(2)–H(2)···S(1)	0.86(3)	2.92(3)	3.747(2)	163(2)
[Cu ₃ L ^{IV} ₃]	N(4)–H(4)···S(3)	0.904(10)	2.72(2)	3.542(3)	152(2)
	N(5)–H(5)···S(1)	0.908(10)	2.99(2)	3.861(2)	161(3)
	N(6)–H(6)···S(2)	0.900(10)	2.86(2)	3.629(2)	144(3)

Table S4 Selected bond lengths [Å] and bond angles [°] for [Cu₃L^{III}₃]

Bond lengths

Cu(1)···Cu(1)a	3.8360(5)	Cu(1)···Cu(1)b	3.8360(4)
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Bond angles

S(1)–Cu(1)–S(2)	114.27(2)	Cu(1)–S(1)–P(1)	93.13(3)
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S(1)–Cu(1)–S(2)a	134.34(2)	Cu(1)–S(2)–C(1)	106.12(7)
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S(2)–Cu(1)–S(2)a	111.30(2)	Cu(1)–S(2)–Cu(1)b	120.27(3)
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Symmetry transformations used to generate equivalent atoms: 1 – y, 1 + x – y, z; –x + y, 1 – x, z.

Table S5 Selected bond lengths [Å] and bond angles [°] for [Cu₃L^{IV}₃]

Bond lengths

Cu(1)···Cu(2)	3.6392(5)	Cu(2)···Cu(3)	3.5374(5)
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Cu(1)···Cu(3)	3.7782(5)
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Bond angles

S(1)–Cu(1)–S(4)	134.09(3)	S(4)–Cu(2)–S(5)	117.22(3)
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S(1)–Cu(1)–S(6)	114.12(3)	S(3)–Cu(3)–S(5)	114.54(3)
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S(4)–Cu(1)–S(6)	111.73(3)	S(3)–Cu(3)–S(6)	129.94(3)
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S(2)–Cu(2)–S(4)	114.98(3)	S(5)–Cu(3)–S(6)	115.50(3)
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S(2)–Cu(2)–S(5)	127.62(3)
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