

Supplementary Material

Insights into the Chemistry and Structural Features of the Copper(II) 2,2'-Bipyridyl-Thiosulfate System

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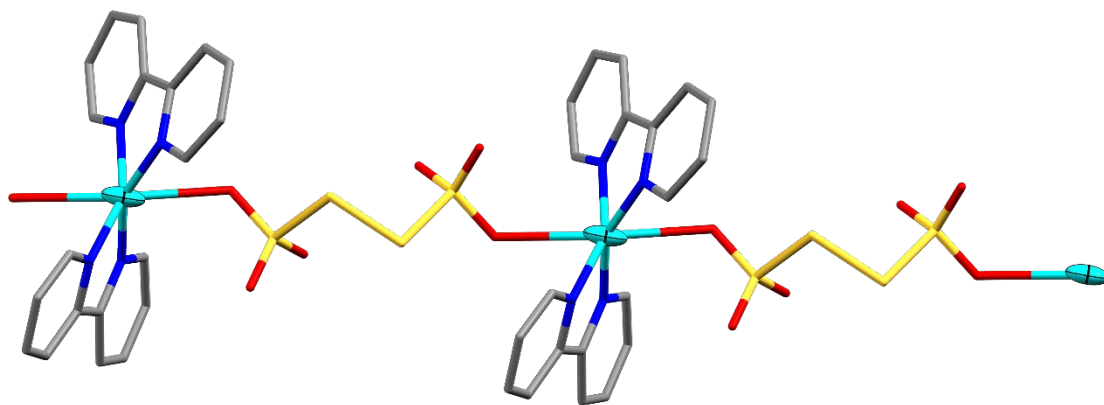


Figure S1: Crystal structure of the polymeric chain $[\{\text{Cu}(\text{bipy})_2(\text{S}_4\text{O}_6)\}]$, **C4**. Hydrogen atoms have been omitted for clarity. Colour code: Cu = light blue, N = dark blue, O = red, S = yellow, C = grey. Thermal ellipsoids at 50%.

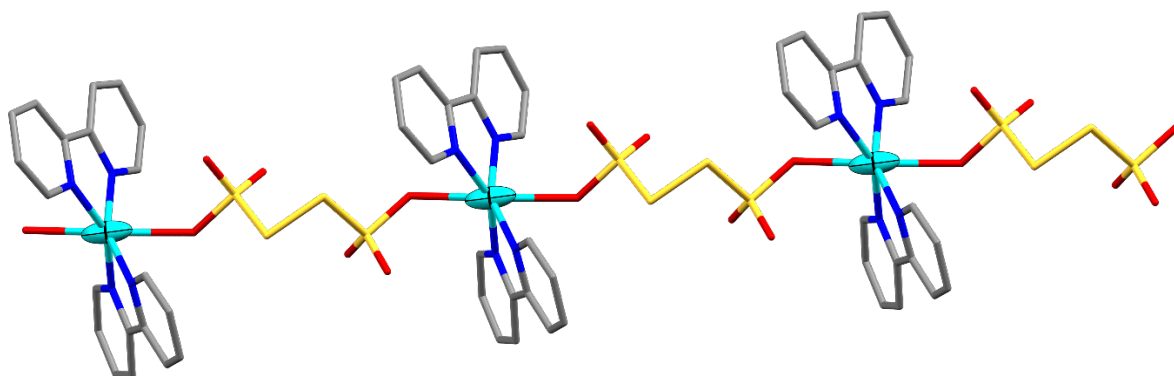


Figure S2: Crystal structure of the polymeric chain $[\{\text{Cu}(\text{bipy})_2(\text{S}_4\text{O}_6)\}]_2\text{S}_3\text{O}_6$, **C5**. This figure shows **C5a**, which is present 50% of the time. Hydrogen atoms have been omitted for clarity. Colour code: Cu = light blue, N = dark blue, O = red, S = yellow, C = grey. Thermal ellipsoids at 50%.

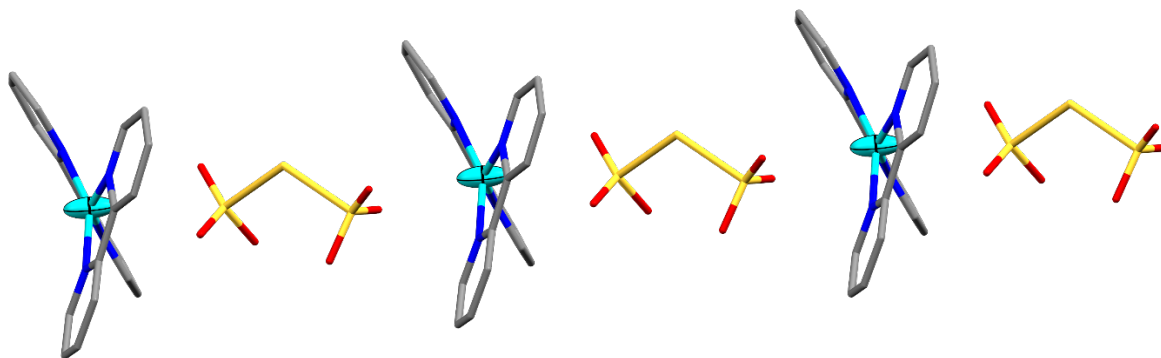


Figure S3: Crystal structure of the polymeric chain $[\{\text{Cu}(\text{bipy})_2(\text{S}_4\text{O}_6)\}]\text{S}_3\text{O}_6$, **C5**. This figure shows **C5b**, which is present 50% of the time. Hydrogen atoms have been omitted for clarity. Colour code: Cu = light blue, N = dark blue, O = red, S = yellow, C = grey. Thermal ellipsoids at 50%.

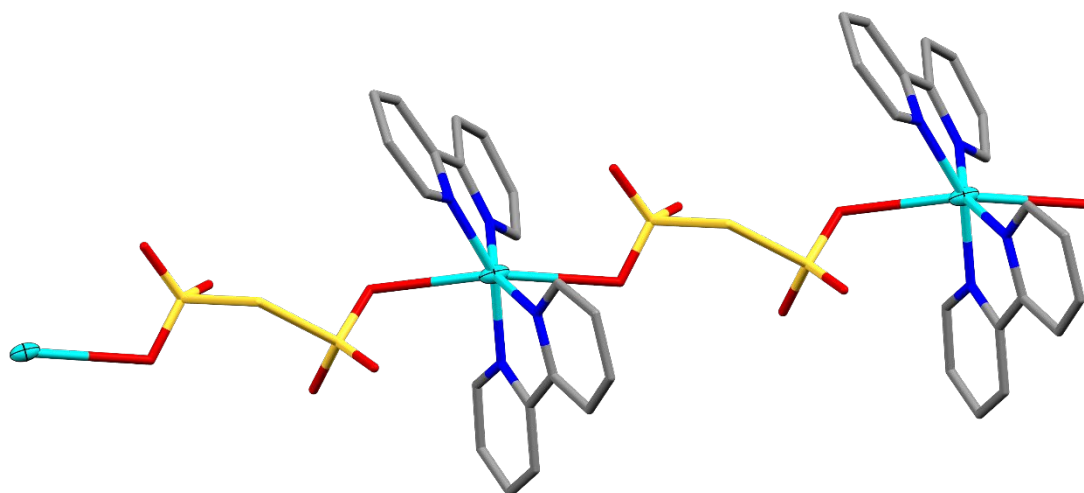


Figure S4: Crystal structure of the polymeric chain $[\{\text{Cu}(\text{bipy})_2(\text{S}_3\text{O}_6)\}]\text{S}_3\text{O}_6$, **C6**. Hydrogen atoms have been omitted for clarity. Colour code: Cu = light blue, N = dark blue, O = red, S = yellow, C = grey. Thermal ellipsoids at 50%.

Table S1: Selected bond lengths (Å) and angles (°) of the complex [Cu₂(bipy)₂(S₂O₃)]·2H₂O, **C2**

Cu1-N1	2.001(7)	Cu2-N4	2.018(8)	S2-O2	1.444(6)
Cu1-N2	2.067(8)	Cu2-S1	2.138(3)	S2-O3	1.440(6)
Cu1-S1	2.147(2)	S1-S2	2.111(3)	S2-S1-Cu2	108.23(11)
Cu2-N3	2.018(8)	S2-O1	1.442(6)	O1-S2-O2	111.9(4)
N1-Cu1-N2	81.8(3)	N3-Cu2-S1	140.5(2)	O1-S2-O3	112.5(4)
N1-Cu1-S1	144.6(2)	N4-Cu2-S1	138.1(2)	O2-S2-O3	114.6(5)
N2-Cu1-S1	132.9(2)	Cu1-S1-Cu2	85.79(9)		
N3-Cu2-N4	81.1(3)	S2-S1-Cu1	104.16(11)		

Table S2: Selected bond lengths (Å) and angles (°) of the complex [Cu(bipy)₃]S₄O₆·1.5H₂O, **C3**

Cu1-N1	2.070(5)	Cu1-N6	2.298(6)	S1-O8	1.426(6)
Cu1-N2	2.005(6)	S1-S2	2.134(3)	S1-O9	1.432(5)
Cu1-N3	2.334(6)	S2-S3	2.031(3)	S4-O10	1.450(5)
Cu1-N4	2.104(6)	S3-S4	2.136(3)	S4-O11	1.436(5)
Cu1-N5	2.022(6)	S1-O7	1.420(6)	S4-O12	1.452(5)
N1-Cu1-N2	81.3(2)	N2-Cu1-N6	94.9(2)	S2-S3-S4	105.13(11)
N1-Cu1-N3	87.1(2)	N3-Cu1-N4	75.7(2)	O7-S1-O8	110.9(5)
N1-Cu1-N4	162.1(2)	N3-Cu1-N5	95.3(2)	O7-S1-O9	116.3(4)
N1-Cu1-N5	94.8(2)	N3-Cu1-N6	165.9(2)	O8-S1-O9	114.7(4)
N1-Cu1-N6	105.5(2)	N4-Cu1-N5	91.7(2)	O10-S4-O11	114.8(3)
N2-Cu1-N3	93.3(2)	N4-Cu1-N6	92.2(2)	O10-S4-O12	114.3(3)
N2-Cu1-N4	94.6(2)	N5-Cu1-N6	77.5(2)	O11-S4-O12	113.5(3)
N2-Cu1-N5	170.3(2)	S1-S2-S3	105.03(11)		

Table S3: Selected bond lengths (Å) and angles (°) of the complex [Cu(S₄O₆)(bipy)₂], **C4**

Cu1-N1	1.982(6)	N1-Cu1-O1	78.64(2)	N2-Cu1-O1	76.69(2)
Cu1-N2	1.987(6)	S1-O1	1.461(6)	Cu1-O1-S1	123.33(4)
Cu1-O1	2.587(7)	S1-O2	1.442(5)	S1-S2	2.092(3)
N1-Cu1-N2	82.1(2)	S1-O3	1.435(6)	O1-S1-O2	114.8(3)
N1-Cu1-N1 ¹	103.0(3)	N2-Cu1-N1 ¹	155.2(3)	O1-S1-O3	112.5(4)
N1-Cu1-N2 ¹	155.2(3)	N2-Cu1-N2 ¹	103.5(3)	O2-S1-O3	114.0(3)

1 = 1-X, +Y, ½-Z; 2 = 2-X, +Y, ½-Z

Table S4: Selected bond lengths (Å) and angles (°) of the complex [$\{\text{Cu}(\text{bipy})_2(\text{S}_4\text{O}_6)\}\}\text{S}_3\text{O}_6$, **C5**

Cu1-N1	1.984(5)	N2-Cu1-N1 ¹	155.4(3)	S1-S2b-S1 ²	113.9(3)
Cu1-N2	1.976(5)	S1-O1b	1.40(2)	S1-S2a-S2a ²	96.9(3)
Cu1-O1a	2.388(15)	S1-O2	1.430(5)	S1-S2b	2.213(4)
S1-O1a	1.57(2)	S1-O3	1.446(5)	S2a-S2a ²	1.848(11)
N1-Cu1-N2	82.4(2)	S1-S2a	1.978(5)	O1a-S1-O2	116.2(7)
N1-Cu1-N1 ¹	103.0(3)	N2-Cu1-N2 ¹	102.8(3)	O1b-S1-O2	108.1(7)
N1-Cu1-N2 ¹	155.4(3)	N2-Cu1-O1a	78.6(5)	O1a-S1-O3	101.6(5)
N1-Cu1-O1a	78.4(5)	N2-Cu1-O1a ¹	79.1(5)	O1b-S1-O3	125.2(6)
N1-Cu1-O1a ¹	125.9(5)	Cu1-O1a-S1	129.3(7)	O2-S1-O3	114.8(3)

1 = 1-X, +Y, ½-Z; 2 = -X, +Y, ½-Z

Table S5: Selected bond lengths (Å) and angles (°) of the complex [$\{\text{Cu}(\text{S}_3\text{O}_6)(\text{bipy})_2\}\}$, **C6**

Cu1-N1	1.9826(19)	S1-O1	1.4431(18)	S1-S2	2.1146(8)
Cu1-N2	1.9837(19)	S1-O2	1.4375(18)	S1-S2-S1 ²	106.64(5)
Cu1-O1	2.720(18)	S1-O3	1.4535(18)	O1-S1-O2	113.35(11)
N1-Cu1-N2	82.67(8)	N2-Cu1-N1 ¹	155.74(7)	O1-S1-O3	112.97(12)
N1-Cu1-N1 ¹	102.23(11)	N2-Cu1-N2 ¹	102.71(11)	O2-S1-O3	114.85(12)
N1-Cu1-N2 ¹	155.74(7)	N2-Cu1-O1	75.90(7)		
N1-Cu1-O1	77.12(6)	Cu1-O1-S1	113.54(10)		

1 = 1-X, +Y, ½-Z; 2 = -X, +Y, ½-Z