C-C bond cleavage in acetonitrile by copper(II)-bipyridine complexes and *in situ* formation of cyano-bridged mixed-valent copper complexes

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Electronic Supporting Information

Table ESI1. Selected bond lengths (Å) and bond angles (°) for copper complexes **1-12**.

Complex **1**			
Cu1−N1	2.014(8)	Cu2−N7	2.064(8)
Cu1−N2	1.998(8)	Cu2−C16	1.894(8)
Cu1−N3	1.980(8)	Cu2−C29	1.892(9)
Cu1−N5	1.981(7)	N5−C16	1.152(11)
Cu1−N9	2.081(7)	N8−C28	1.158(16)
Cu2−N6	2.090(8)		
Cu1−N5−C16	174.7(8)	Cu2−C16−N5	167.5(8)
Cu1−N9−C29[a]	172.3(7)	Cu2−C29−N9[b]	174.6(8)
Complex **2**			
Cu1−N1	2.007(7)	Cu2−N7	2.074(7)
Cu1−N2	2.016(6)	Cu2−C16	1.862(8)
Cu1−N3	1.985(6)	Cu2−C27[c]	1.883(8)
Cu1−N5	1.991(6)	N5−C16	1.171(10)
Cu1−N8	2.046(7)	N9−C28	1.110(17)
Cu2−N6	2.049(7)		
Cu1−N5−C16	175.3(6)	Cu2−C16−N5	167.9(7)
Cu1−N8−C27	173.1(5)	Cu2[d]−C27−N8	174.8(6)

Complex **3**			
Cu1−N1	2.010(4)	Cu2−N7	2.090(5)
Cu1−N2	2.144(4)	Cu2−N8	1.999(4)
Cu1−N3	2.093(5)	Cu2−N9	2.103(5)
Cu1−N4	2.006(5)	Cu2−C42	1.966(6)
Cu1−C21	1.955(7)	N5−C21	1.137(10)
Cu2−N6	1.993(4)	N10−C42	1.136(9)
Cu1−C21−N5	174.5(7)	Cu2−C42−N10	175.4(6)
Complex **4**			
Cu1−N1	2.045(3)	Cu2−N6	1.999(4)
Cu1−N2	1.979(4)	Cu2−N7	2.142(3)
Cu1−N3	1.976(3)	Cu2−N8	2.033(3)
Cu1−N4	2.115(3)	Cu2−N9	1.982(3)
Cu1−C21	1.993(4)	N5−C21	1.138(5)
Cu2−N5	1.984(4)		
Cu1−C21−N5	175.8(3)	Cu2−N5−C21	177.6(4)
Complex **5**			
Cu1−N1	1.978(5)	Cu2−N6	2.123(5)
Cu1−N2	2.103(4)	Cu2−N7	2.065(5
Cu1−N3	2.076(5)	Cu2−N8	1.979(5)
Cu1−N4	1.971(5)	Cu2−C41	1.982(5)
Cu1−N9	1.983(5)	N9−C41	1.153(7)
Cu2−N5	1.976(5)		
Cu1−N9−C41	176.0(4)	Cu2−C41−N9	179.3(4)
Complex **6**			
Cu1−N1	2.085(4)	Cu1−N4	2.020(5)
Cu1−N2	2.012(5)	Cu1−C25	1.955(6)
Cu1−N3	2.135(5)	N5−C25	1.134(8)
Cu1−C25−N5	176.0(6)		
Complex **7**			
Cu1−N1	2.091(3)	Cu1−N4	1.995(3)
Cu1−N2	1.998(3)	Cu1−C25	1.972(4)
Cu1−N3	2.105(3)	N5−C25	1.145(6)
Cu1−C25−N5	176.7(4)		
Complex **8**			
Cu1−N1	2.054(5)	Cu1−N4	1.985(5)
Cu1−N2	1.988(5)	Cu1−N5	1.975(6)
Cu1−N3	2.102(7)	Cu1−C25	1.975(6)
Complex **9**			
Cu1−N1	2.053(4)	Cu2−N6	2.089(5)
Cu1−N2	1.984(4)	Cu2−N7	2.084(7)
Cu1−N3	2.174(4)	Cu2−C25	1.922(5)
Cu1−N4	1.978(5)	N5−C25	1.150(7)
Cu1−N5	1.954(5)		

Cu1−N5−C25	174.0(5)	Cu2−C25−N5	172.7(5)
Complex **10**			
Cu1−N1	1.985(2)	Cu1−N4	1.984(2)
Cu1−N2	2.097(2)	Cu1−N5	2.011(2)
Cu1−N3	2.109(3)		
N1−Cu1−N2	79.82(10)	N2−Cu1−N4	95.00(10)
N1−Cu1−N3	95.07(10)	N2−Cu1−N5	133.97(9)
N1−Cu1−N4	172.36(9)	N3−Cu1−N4	79.65(10)
N1−Cu1−N5	94.30(9)	N3−Cu1−N5	131.50(10)
N2−Cu1−N3	94.53(9)	N4−Cu1−N5	93.35(9)
Complex **11**			
Cu1−N1	2.054(3)	Cu1−N1^{h}	2.054(3)
Cu1−N2	2.055(3)	Cu1−N2^{h}	2.055(3)
Complex **12**			
Cu1−N1	2.047(5)	Cu1−N3	2.050(5)
Cu1−N2	2.018(4)	Cu1−N4	2.017(4)

Symmetry operator: ^{a} = 1/2-x, -1/2+y, -1/2+z; ^{b} = 1/2-x, 1/2+y, 1/2+z; ^{c} = 1/2-x, 1/2+y, -1/2+z; ^{d} = 1/2-x, -1/2+y, 1/2+z; ^{e} = 1-y, -1+x-y, 1/3+z; ^{f} = 1-y, x-y, 1/3+z; ^{g} = 1-y, 1+x-y, 1/3+z; ^{h} = 2-x, y, 1/2-z.

Table ESI2. Intermolecular hydrogen bonding interactions (Å, °) in copper complexes **1-4** and **7-12**.

D−H···A	D−H	H−A	D···A	∠DHA	Sym. trans
1					
O1−H1A···N5	0.85	2.61	3.458(12)	180.0	1+x, y, z
O1−H1B···F1	0.85	2.24	3.043(13)	158.0	2-x, 1/2+y, 3/2-z
C1−H1···F4	0.93	2.31	3.199(9)	160.0	1-x, 1/2+y, 3/2-z
C8−H8···F5	0.93	2.31	3.105(10)	143.0	1+x, y, z
C12−H12···F6	0.93	2.45	3.281(10)	148.0	1-x, 1/2+y, 3/2-z
C23−H23···F7	0.93	2.45	3.132(11)	130.0	1+x, 3/2-y, -1/2+z
C25−H25···F4	0.93	2.52	3.438(9)	169.0	2-x, 1/2+y, 3/2-z
C39−H39···F8	0.93	2.46	3.274(12)	146.0	x, 3/2-y, -1/2+z
2					
O1−H1A···F11	0.85	2.01	2.831(18)	161.0	1-x, y, 1/2-z
C1−H1···F7	0.93	2.45	3.153(6)	133.0	x, -1+y, z
C4−H4···F4	0.93	2.54	3.334(8)	143.0	x, -y, -1/2+z
C9−H9···F3	0.93	2.54	3.306(8)	140.0	-x, y, 1/2-z
C11−H11···F13	0.93	2.30	3.163(17)	155.0	1-x, y, 1/2-z
C14−H14···F12	0.93	2.55	3.464(12)	169.0	1-x, -y, 1-z
C17−H17···F12	0.93	2.40	3.321(14)	173.0	1-x, -y, 1-z
C19−H19···F9	0.93	2.43	3.354(6)	173.0	x, -1+y, z

C23−H23···F2	0.93	2.24	3.153(9)	169.0	-x, y, 1/2-z
C25−H25···F3	0.93	2.49	3.362(7)	155.0	x, 1-y, -1/2+z
3					
N4−H4A···N8	0.86	2.37	3.088(13)	141.0	1/2-x, -1/2+y, 1/2+z
N4−H4B···O6	0.86	2.29	3.116(12)	160.0	-x, 1-y, -1/2+z
4					
N4−H4A···F3	0.86	2.23	3.058(10)	161.0	-1/2+x, 1/2-y, z
N4−H4B···N9	0.86	2.39	3.104(12)	141.0	1/2-x, -1/2+y, -1/2+z
7					
N8−H8A···N7	0.86	2.33	3.056(6)	142.0	x, 1/2-y, -1/2+z
N8−H8B···F4’	0.86	2.54	3.353(11)	158.0	1+x, y, z
C23−H23···F1’	0.93	2.33	3.229(9)	164.0	1-x, -y, 1-z
C30−H30···N6	0.93	2.48	2.804(5)	101.0	2-x, -y, 1-z
8					
C13−H13···O4	0.93	2.40	2.92(2)	115.0	1-x, 1-y, 1-z
9					
O10−H10D···O7	0.85	2.45	3.24(4)	155.0	1/2+x, y, 3/2-z
O12−H12A···O11’	0.86	2.43	3.22(8)	154.0	1-x, -y, -z
C16−H16A···O6	0.96	2.40	3.326(15)	162.0	1/2+x, y, 3/2-z
10					
N6−H6B···O5	0.86	2.56	3.289(6)	143.0	-x, -1/2+y, 1/2-z
C4−H4···O2	0.93	2.44	3.311(5)	155.0	1-x, -1/2+y, 1/2-z
C13−H13···O7	0.93	2.56	3.307(6)	138.0	-x, -3/2+y, 1/2-z
C21−H21···O5	0.93	2.53	3.314(7)	142.0	-x, -1/2+y, 1/2-z
11					
C9−H9···F4	0.93	2.48	3.250(5)	140.0	2-x, 1-y, 1-z
12					
C2−H2···O3	0.93	2.57	3.483(13)	169.0	1-x, 1-y, -z
C23−H23···O3’	0.93	2.52	3.405(13)	160.0	2-x, 1-y, -z
C28−H28···O4	0.93	2.53	3.457(14)	178.0	x, 1+y, z