

## Supplementary Material for A Concert of Weak Interactions Generates the Very Complex $\{\text{Cu}(\text{tmada})[\text{Au}(\text{CN})_4]_2\} \cdot \frac{1}{3}\text{H}_2\text{O}$ Structure

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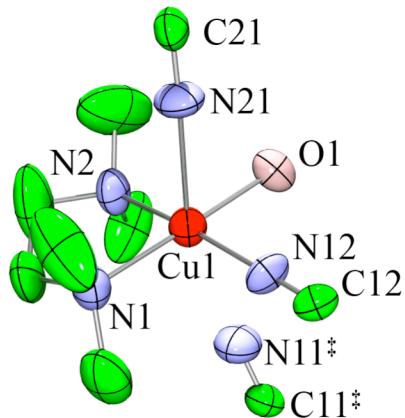
*Synthesis of 1:* To a 10 mL aqueous solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.029 g, 0.099 mmol) was added a 10 mL aqueous solution of tmada (0.075 M stock solution, 0.1 mmol). To the resulting pale green solution a 20 mL aqueous solution of  $\text{KAu}(\text{CN})_4$  (0.068 g, 0.200 mmol) was added dropwise. Slow evaporation of the solution for approximately 12 days yielded X-ray quality light blue crystals of  $\{\text{Ni}(\text{tmada})[\text{Au}(\text{CN})_4]_2\}$  (**1**) which were filtered and air dried. Yield: 0.045 g (58%). Anal. Calcd. for  $\text{C}_{14}\text{H}_{16}\text{N}_{10}\text{Au}_2\text{Ni}$ : C, 21.64; H 2.08; N 18.03. Found: C, 21.42; H, 2.11; N, 18.20. IR (KBr,  $\text{cm}^{-1}$ ): 3022 (m), 2990 (m), 2970 (m), 2946 (w), 2925 (m), 2907 (m, br), 2859 (m), 2820 (m), 2812 (m) 2253 (m  $\nu\text{CN}$ ), 2231 (m,  $\nu\text{CN}$ ), 2219 (m,  $\nu\text{CN}$ ), 2191 (w,  $\nu\text{CN}$ ), 2182 (w,  $\nu\text{CN}$ ), 1475 (s), 1286 (m,), 1242 (m), 1192 (m), 1168 (w), 1120 (m), 1101 (w), 1058 (s), 1044 (w), 1017 (s), 1004 (m), 951 (s), 930 (w), 805 (m), 768 (m), 591 (w), 501 (m), 483 (m).

*Synthesis of 2:* To a 3 mL aqueous solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.048 g, 0.199 mmol) was added a 2.6 mL aqueous solution of tmada (0.075 M stock solution, 0.2 mmol). To the resulting dark blue solution a 3 mL aqueous solution of  $\text{KAu}(\text{CN})_4$  (0.136 g, 0.400 mmol) was added dropwise. Allowing the solution to sit covered for 24 hours resulted in the formation of X-ray quality dark blue needle of  $\{\text{Cu}(\text{tmada})[\text{Au}(\text{CN})_4]_2\} \cdot \frac{1}{3}\text{H}_2\text{O}$  crystals (**2**), which were filtered and air dried. Yield: 0.040 g (26%). Anal. Calcd. for  $\text{C}_{14}\text{H}_{16.66}\text{N}_{10}\text{Au}_2\text{CuO}_{\frac{1}{3}}$ : C, 21.34; H 2.13; N 17.78. Found: C, 21.43; H, 2.11; N, 17.71. IR (KBr): 3390 (m, br), 3024 (w), 2998 (m), 2941 (m), 2927 (m), 2859 (w), 2250 (m,  $\nu\text{CN}$ ), 2243 (m,  $\nu\text{CN}$ ), 2220 (w,  $\nu\text{CN}$ ), 2209 (w,  $\nu\text{CN}$ ), 2201 (w,  $\nu\text{CN}$ ), 2192 (w,  $\nu\text{CN}$ ), 1630 (m), 1469 (s), 1280 (m), 1242 (m), 1195 (w), 1119 (m), 1101 (w), 1058 (w), 1046 (m), 1010 (m), 997 (m), 949 (m), 808 (m), 767 (m). Further evaporation of the remaining filtrate yielded crystals of  $\{[\text{Cu}(\text{tmada})(\text{OH})_2][\text{Au}(\text{CN})_4]_2\}$ .<sup>1</sup>

<sup>1</sup>

M. J. Katz, C. J. Shorrock, R. J. Batchelor, and D. B. Leznoff, *Inorg. Chem.*, 2006, **45**, 1757

Local geometry of each metal in **2**

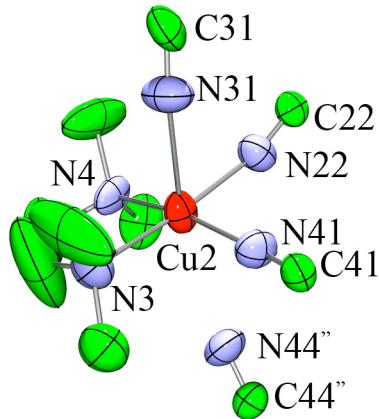


*Bond Lengths (Å):*

Cu(1) – N(1)	2.055(10)	Cu(1) – N(2)	2.045(11)
Cu(1) – O(1)	1.961(8)	Cu1 – N(12)	2.037(9)
Cu(1) – N(21)	2.456(11)	Cu1 … N(11‡)	2.636(12)

*Bond Angles (°):*

O(1) – Cu(1) – N(1)	92.2(4)	O(1) – Cu(1) – N(2)	178.8(4)
O(1) – Cu(1) – N(12)	89.5(4)	O(1) – Cu(1) – N(21)	81.3(4)
N(1) – Cu(1) – N(2)	86.7(5)	N(1) – Cu(1) – N(12)	175.8(5)
N(1) – Cu(1) – N(21)	95.4(5)	N(2) – Cu(1) – N(12)	91.7(4)
N(2) – Cu(1) – N(21)	98.4(4)	N(12) – Cu(1) – N(21)	88.7(4)
N(11‡) … Cu(1) – N(21)	163.7(4)	N(11‡) … Cu1 – N2	95.2(4)
N(11‡) … Cu(1) – N(12)	81.9(4)	N(11‡) … Cu(1) – N(1)	94.4(4)
N(11‡) … Cu(1) – O(1)	85.3(4)		




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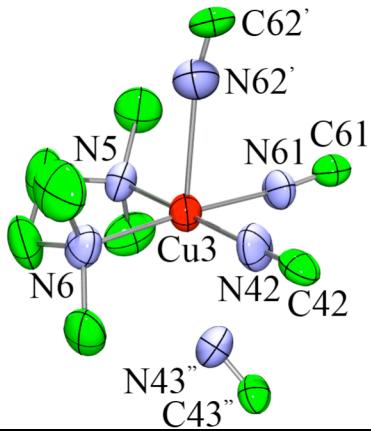
*Bond Lengths (Å):*

Cu(2) – N(3)	2.061(11)	Cu(2) – N(4)	2.021(10)
Cu(2) – N(41)	1.995(11)	Cu(2) – N(22)	2.032(11)
Cu(2) – N(31)	2.421(12)	Cu(2) ... N(44'')	2.878(12)

*Bond Angles (°):*

N(3) – Cu(2) – N(4)	86.7(5)	N(3) – Cu(2) – N(22)	175.2(5)
N(3) – Cu(2) – N(31)	94.9(5)	N(3) – Cu(2) – N(41)	90.8(5)
N(4) – Cu(2) – N(22)	90.3(5)	N(4) – Cu(2) – N(31)	101.9(5)
N(4) – Cu(2) – N(41)	169.9(5)	N(22) – Cu(2) – N(31)	82.0(4)
N(22) – Cu(2) – N(41)	92.8(4)	N(31) – Cu(2) – N(41)	88.1(4)
N(44'') ... Cu(2) – N(41)	78.6(4)	N(44'') ... Cu(2) – N(22)	95.1(4)
N(44'') ... Cu(2) – N(31)	166.3(4)	N(44'') ... Cu(2) – N(4)	91.5(4)
N(44'') ... Cu(2) – N(3)	88.8(4)		

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*Bond Lengths (Å):*

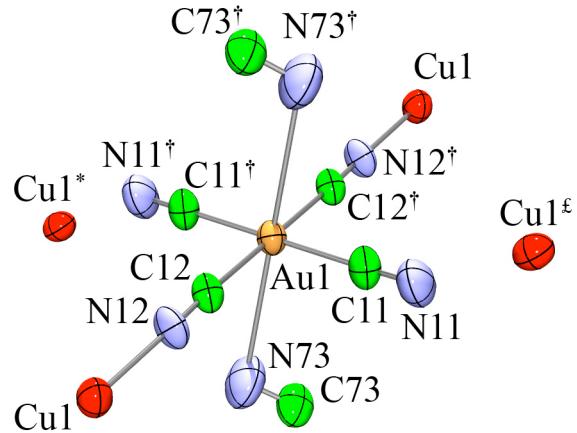
Cu(3) – N(5)	2.028(10)	Cu(3) – N(6)	2.044(10)
Cu(3) – N(42)	2.018(10)	Cu(3) – N(61)	1.976(10)
Cu(3) – N(62'')	2.453(13)	Cu(3) … N(43'')	2.603(12)

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*Bond Angles (°):*

N(5) – Cu(3) – N(6)	86.2(4)	N(5) – Cu(3) – N(42)	179.0(4)
N(5) – Cu(3) – N(61)	93.4(4)	N(6) – Cu(3) – N(61)	175.2(5)
N(6) – Cu(3) – N(42)	92.9(4)	N(42) – Cu(3) – N(61)	87.5(4)
N(62'') – Cu(3) – N(42)	85.5(4)	N(62'') – Cu(3) – N(5)	94.7(4)
N(62'') – Cu(3) – N(61)	86.5(4)	N(62'') – Cu(3) – N(6)	98.4(4)
N(43'') … Cu(3) – N(6)	93.2(4)	N(43'') … Cu(3) – N(61)	82.0(4)
N(43'') … Cu(3) – N(42)	83.1(4)	N(43'') … Cu(3) – N(5)	96.9(4)
N(62'') – Cu(3) … N(43'')	164.1(4)		

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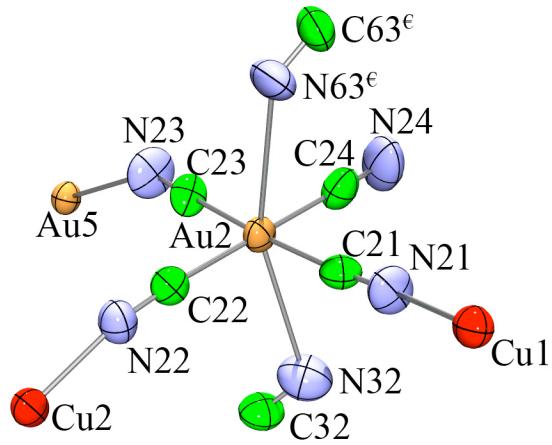
*Bond Lengths (Å):*

Au(1) – C(12 <sup>†</sup> )	2.025(12)	Au(1) – C(11 <sup>†</sup> )	2.003(13)
Au(1) – C(11)	2.003(13)	Au(1) – C(12)	2.025(12)
Au(1) – N(73)	3.107(7)	Au(1) – N(73 <sup>†</sup> )	3.107(7)

*Bond Angles (°):*

C(12 <sup>†</sup> ) – Au(1) – C(11 <sup>†</sup> )	89.1(5)	C(12 <sup>†</sup> ) – Au(1) – C(11)	90.9(5)
C(11 <sup>†</sup> ) – Au(1) – C(11)	179.994	C(12 <sup>†</sup> ) – Au(1) – C(12)	179.994
C(11 <sup>†</sup> ) – Au(1) – C(12)	90.9(5)	C(11) – Au(1) – C(12)	89.1(5)
C(12 <sup>†</sup> ) – Au(1) – N(73)	77.7(4)	C(11 <sup>†</sup> ) – Au(1) – N(73)	96.8(5)
C(11) – Au(1) – N(73)	83.2(5)	C(12) – Au(1) – N(73)	102.3(4)
C(12 <sup>†</sup> ) – Au(1) – N(73 <sup>†</sup> )	102.3(4)	C(11 <sup>†</sup> ) – Au(1) – N(73 <sup>†</sup> )	83.2(5)
C(11) – Au(1) – N(73 <sup>†</sup> )	96.8(5)	C(12) – Au(1) – N(73 <sup>†</sup> )	77.7(4)
N(73) – Au(1) – N(73 <sup>†</sup> )	179.996	C(73) – N(73) – Au(1)	112.6(3)

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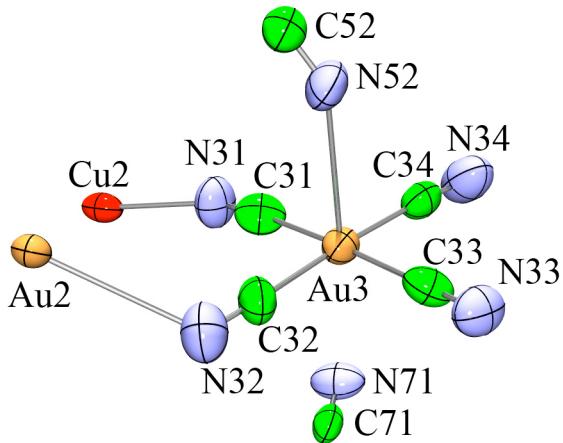
*Bond Lengths (Å):*

Au(2) – C(21)	2.002(13)	Au(2) – C(22)	2.011(13)
Au(2) – C(23)	2.000(13)	Au(2) – C(24)	1.979(15)
Au(2) – N(32)	3.070(14)	Au(2) – N(63 $\epsilon$ )	3.052(12)

*Bond Angles (°):*

C(21) – Au(2) – C(22)	92.4(5)	C(21) – Au(2) – C(23)	176.8(5)
C(22) – Au(2) – C(23)	90.4(5)	C(21) – Au(2) – C(24)	89.6(5)
C(22) – Au(2) – C(24)	177.4(6)	C(23) – Au(2) – C(24)	87.6(5)
C(21) – Au(2) – N(32)	81.8(4)	C(22) – Au(2) – N(32)	93.7(4)
C(23) – Au(2) – N(32)	99.7(4)	C(24) – Au(2) – N(32)	84.9(5)
C(21) – Au(2) – N(63 $\epsilon$ )	81.6(4)	C(22) – Au(2) – N(63 $\epsilon$ )	98.5(4)
C(23) – Au(2) – N(63 $\epsilon$ )	96.5(4)	C(24) – Au(2) – N(63 $\epsilon$ )	83.5(5)
N(32) – Au(2) – N(63 $\epsilon$ )	159.7(4)	C(63 $\epsilon$ ) – N(63 $\epsilon$ ) – Au(2)	133.1(12)
C(32) – N(32) – Au(2)	120.2(13)		

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*Bond Lengths (Å):*

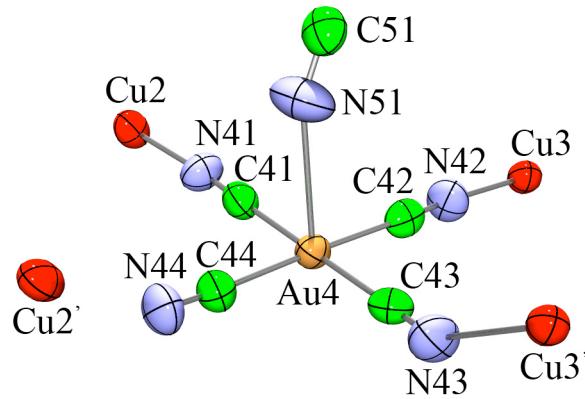
Au(3) – C(31)	1.994(16)	Au(3) – C(32)	2.003(14)
Au(3) – C(33)	2.012(15)	Au(3) – C(34)	1.967(15)
Au(3) – N(52)	3.039(12)		

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*Bond Angles (°):*

C(31) – Au(3) – C(32)	90.0(6)	C(31) – Au(3) – C(33)	176.9(6)
C(32) – Au(3) – C(33)	89.0(6)	C(31) – Au(3) – C(34)	92.5(6)
C(32) – Au(3) – C(34)	176.7(6)	C(33) – Au(3) – C(34)	88.4(6)
C(31) – Au(3) – N(52)	91.6(5)	C(32) – Au(3) – N(52)	92.7(5)
C(33) – Au(3) – N(52)	91.4(5)	C(34) – Au(3) – N(52)	89.5(5)
C(52) – N(52) – Au(3)	146.3(12)		

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*Bond Lengths (Å):*

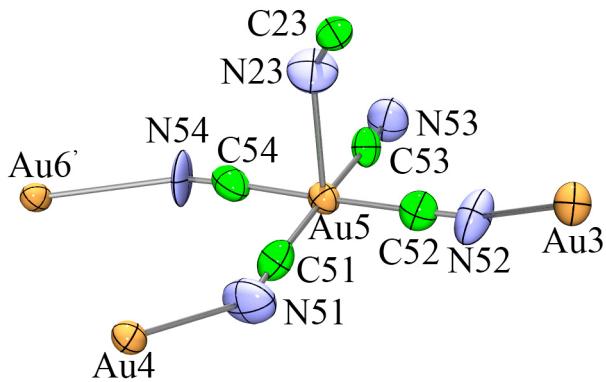
Au(4) – N(51)	2.764(13)	Au(4) – C(41)	1.984(13)
Au(4) – C(42)	2.037(14)	Au(4) – C(43)	2.000(13)
Au(4) – C(44)	2.022(13)		

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*Bond Angles (°):*

N(51) – Au(4) – C(41)	84.6(5)	N(51) – Au(4) – C(42)	95.3(5)
C(41) – Au(4) – C(42)	88.8(5)	N(51) – Au(4) – C(43)	94.1(5)
C(41) – Au(4) – C(43)	178.5(5)	C(42) – Au(4) – C(43)	92.1(5)
N(51) – Au(4) – C(44)	86.0(5)	C(41) – Au(4) – C(44)	92.6(5)
C(42) – Au(4) – C(44)	178.1(5)	C(43) – Au(4) – C(44)	86.5(5)
Au(4) – N(51) – C(51)	148.4(13)		

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*Bond Lengths (Å):*

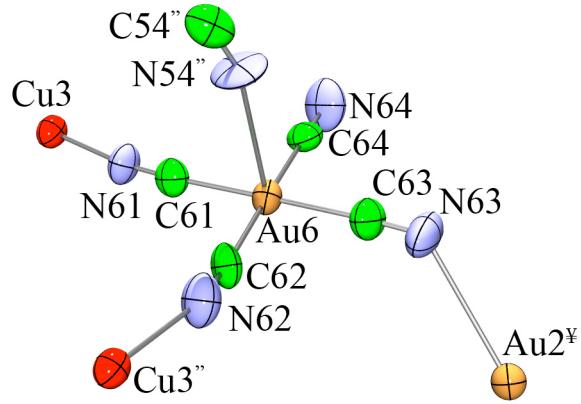
Au(5) – C(51)	2.012(15)	Au(5) – C(52)	1.995(14)
Au(5) – C(53)	1.965(13)	Au(5) – C(54)	2.056(15)
Au(5) – N(23)	2.874(11)		

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*Bond Angles (°):*

C(51) – Au(5) – C(52)	90.6(6)	C(51) – Au(5) – C(53)	175.9(6)
C(52) – Au(5) – C(53)	90.7(5)	C(51) – Au(5) – C(54)	89.3(6)
C(52) – Au(5) – C(54)	178.3(6)	C(53) – Au(5) – C(54)	89.5(5)
C(51) – Au(5) – N(23)	91.8(5)	C(52) – Au(5) – N(23)	84.3(5)
C(53) – Au(5) – N(23)	92.1(5)	C(54) – Au(5) – N(23)	94.0(5)
C(23) – N(23) – Au(5)	148.8(12)		

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*Bond Lengths (Å):*

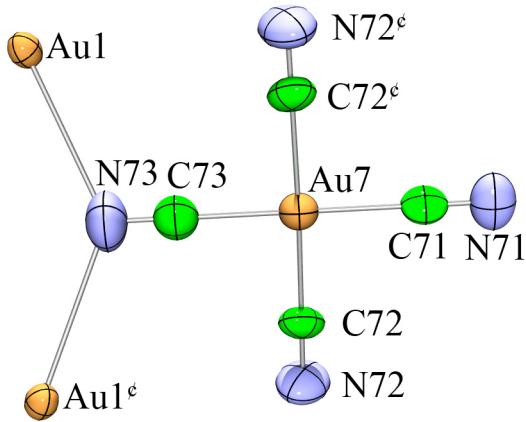
Au(6) – C(61)	2.013(13)	Au(6) – C(62)	2.036(14)
Au(6) – C(63)	2.004(13)	Au(6) – C(64)	2.019(14)
Au(6) – N(54'')	3.068(10)		

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*Bond Angles (°):*

C(61) – Au(6) – C(62)	93.9(5)	C(61) – Au(6) – C(63 )	176.8(5)
C(62) – Au(6) – C(63)	88.1(6)	C(61) – Au(6) – C(64)	86.4(5)
C(62) – Au(6) – C(64)	178.5(5)	C(63) – Au(6) – C(64)	91.5(6)
C(61) – Au(6) – N(54'')	88.7(5)	C(62) – Au(6) – N(54'')	84.8(5)
C(63) – Au(6) – N(54'')	94.0(5)	C(64) – Au(6) – N(54'')	96.6(4)
C(54'') – N(54'') – Au(6)	162.1(14)		

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*Bond Lengths (Å):*

Au(7) – C(72 <sup>¢</sup> )	2.022(14)	Au(7) – C(71)	2.04(2)
Au(7) – C(72)	2.022(14)	Au(7) – C(73)	2.00(2)

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*Bond Angles (°):*

C(72 <sup>¢</sup> ) – Au(7) – C(71)	90.9(4)	C(72 <sup>¢</sup> ) – Au(7) – C(72)	178.3(8)
C(71) – Au(7) – C(72)	90.9(4)	C(72 <sup>¢</sup> ) – Au(7) – C(73)	89.1(4)
C(71) – Au(7) – C(73)	180	C(72) – Au(7) – C(73)	89.1(4)
Au(1) – N(73) – Au(1 <sup>¢</sup> )	134.8(6)		

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: x, -y,  $\frac{1}{2} + z$

": x, -y,  $-\frac{1}{2} + z$

\*: 1-x, y,  $3/2 - z$

†: 1-x, -1-y, 2-z

‡: x, -1-y,  $-\frac{1}{2} + z$

§:  $\frac{1}{2} - x, -\frac{1}{2} - y, 2 - z$

€:  $\frac{1}{2} - x, -\frac{1}{2} + y, 3/2 - z$

£: x, -1-y,  $\frac{1}{2} + z$

¥:  $\frac{1}{2} - x, \frac{1}{2} + y, 3/2 - z'$

¢: 1-x, y,  $5/2 - z$