Supporting information

μ-Hydroxyl Trinuclear Copper(II) Cluster: Reactivity and Unusual Formation in Three-Component Synthesis of 1,2,3-Triazoles in Aqueous Media

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Table of Contents

1. UV-vis spectra of Cu-1 and Cu-6 ..................................................2
2. Characterizations of μ-O(H) trinuclear copper(II) cluster (Cu-6): ESI-MS(negative) and FTIR spectra ...........................................................3
3. UV-vis spectra of trinuclear Cu(II) cluster Cu-7 ..................................5
4. GC detection of β-hydroxy benzyl azide ......................................6
5. Crystal data and structure refinement for Cu-1, Cu-5 and Cu-6 ........7
6. NMR spectra of catalysts and products .......................................10
7. ESI-MS spectra of catalysts and products ...................................25
1. UV-vis spectra of Cu-1 and Cu-6

![Graph](image)

**Figure S1.** UV-vis spectra of (a) μ-O(H) trinuclear copper(II) cluster (Cu-6) in aqueous solution with a concentration of 2.29×10^{-5} mol/L. Inset: A expanded spectra from 400 nm to 800, with a concentration of 2.29×10^{-4} mol/L. The λ_{max}/nm (ε/M^1•cm^{-1}) are 242 (91500), 270 (sh), 343 (10950), 564 (285); and (b) Cu-1 in aqueous solution. Inset: A expanded spectra from 400 nm to 800, with a concentration of 2.15×10^{-4} mol/L. The ε at 564 nm is 149 M^1•cm^{-1}. 
2. Characterizations of $\mu$-O(H) trinuclear copper(II) cluster (Cu-6): ESI-MS (negative) and FTIR spectra

$\mu$-O(H) trinuclear copper(II) cluster (Cu-6)

**Figure S2** ESI-MS (negative) spectra of $\mu$-O(H) trinuclear copper(II) cluster (Cu-6). Insert are the structure and simulated spectrum.
FTIR spectrum of μ-O(H) trinuclear copper(II) cluster (Cu-6)

Figure S3. FTIR spectrum of μ-O(H) trinuclear copper(II) cluster (Cu-6). (KBr)
3. UV-vis spectra of trinuclear copper(II) cluster Cu-7

Figure S4. UV-vis spectra of nuclear copper(II) cluster Cu-7 in methanol.
4. GC detection of $\beta$-hydroxy benzyl azide

Gas chromatography was performed on an Agilent 7890A gas chromatography with FID detector, using a 30 m×0.25 mm$^2$ Chiral G-TA capillary column.

Sample preparations: Cu-1 (0.03 mmol), NaN$_3$ (0.5 mmol), and styrene epoxide (0.5 mmol) was added to water (10 mL) and stirred at room temperature overnight. 1 mL of the suspension was extracted by ethyl acetate. Then 25 μL chlorobenzene was added as an internal standard. The solution was dried by anhydrous Na$_2$SO$_4$ and used for GC experiments.

GC conditions for measuring the enantiomers of $\beta$-hydroxy benzyl azide:
Inlet temperature: 250 °C
No split.
Step 1: 50 °C for 1 min.
Step 2: 70 °C for 10 min.
Step 3: 180 °C for 5 min.
Flow: 3.9 mL/min

![GC curve for $\beta$-hydroxy benzyl azide](image)

**Figure S5.** GC curve for $\beta$-hydroxy benzyl azide, the product of styrene epoxide and NaN$_3$ in aqueous solution in the presence of catalyst Cu-1. The integrated areas of two enantiomers are quite similar, which indicates that there is no enantiomeric excess for the products.
5. Crystal data and structure refinement for Cu-1.

<table>
<thead>
<tr>
<th>Identification code</th>
<th>Cu-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C20 H29 Cu N2 Na2 O14.50 S2</td>
</tr>
<tr>
<td>Formula weight</td>
<td>703.09</td>
</tr>
<tr>
<td>Temperature</td>
<td>296(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Triclinic, P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 7.8998(4) Å, alpha = 103.382(4) deg. b = 11.5756(7) Å, beta = 94.177(4) deg. c = 16.6900(9) Å, gamma = 103.844(4) deg.</td>
</tr>
<tr>
<td>Volume</td>
<td>1428.30(14) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>2, 1.635 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.013 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>724</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.10 x 0.06 x 0.04 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.52 to 27.75 deg.</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-10≤h≤10, -14≤k≤15, -21≤l≤21</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>12691 / 6590 [R(int) = 0.0460]</td>
</tr>
<tr>
<td>Completeness to theta = 27.75</td>
<td>97.7 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.8067 and 0.4012</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F^2</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>6590 / 0 / 436</td>
</tr>
<tr>
<td>Goodness-of-fit on F^2</td>
<td>1.121</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0762, wR2 = 0.2168</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0960, wR2 = 0.2273</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.500 and -0.758 e.Å⁻³</td>
</tr>
</tbody>
</table>
Crystal data and structure refinement for Cu-5.

Identification code                  Cu-5
Empirical formula                 C13 H22 Cu N2 O7 S
Formula weight                     413.93
Temperature                       296(2) K
Wavelength                        0.71073 Å
Crystal system, space group       Triclinic,   P-1
Unit cell dimensions              a = 9.4021(13) Å  alpha = 65.210(2) deg.  b = 9.6265(13) Å  beta = 76.389(2) deg.  c = 10.5993(14) Å gamma = 73.383(2) deg.
Volume                             827.18(19) Å³
Z, Calculated density             2,   1.662 Mg/m³
Absorption coefficient            1.485 mm⁻¹
F(000)                             430
Crystal size                      0.20 x 0.18 x 0.10 mm
Theta range for data collection   2.28 to 27.58 deg.
Limiting indices                  -12 <= h <= 11, -12 <= k <= 11, -13 <= l <= 13
Reflections collected / unique    4890 / 3650 [R(int) = 0.0138]
Completeness to theta = 27.58     95.3 %
Absorption correction             Semi-empirical from equivalents
Max. and min. transmission        0.8657 and 0.7555
Refinement method                 Full-matrix least-squares on F²
Data / restraints / parameters    3650 / 6 / 286
Goodness-of-fit on F²             1.035
Final R indices [I>2sigma(I)]     R1 = 0.0328, wR2 = 0.0837
R indices (all data)              R1 = 0.0391, wR2 = 0.0872
Largest diff. peak and hole       0.502 and -0.368 e.Å⁻³
# Crystal data and structure refinement for Cu-6.

<table>
<thead>
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<th>Property</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>Cu-6</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C41 H66 Cu3 N6 O19 S3</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1233.80</td>
</tr>
<tr>
<td>Temperature</td>
<td>293(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Trigonal, P3(1)</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 14.083(2) Å, b = 14.083(2) Å, c = 23.118(5) Å</td>
</tr>
<tr>
<td>Volume</td>
<td>3970.4(11) Å</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>3, 1.548 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.389 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>1923</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.15 x 0.13 x 0.10 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.89 to 27.62 deg.</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-13&lt;=h&lt;=18, -18&lt;=k&lt;=13, -26&lt;=l&lt;=29</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>23778 / 11017 [R(int) = 0.0286]</td>
</tr>
<tr>
<td>Completeness to theta</td>
<td>99.4 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>None</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.8187 and 0.7996</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<tr>
<td>Data / restraints / parameters</td>
<td>11017 / 2 / 654</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>0.969</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0387, wR2 = 0.0970</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0525, wR2 = 0.1046</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
<td>0.032(10)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.746 and -0.579 e Å⁻³</td>
</tr>
</tbody>
</table>
6. NMR spectra of catalysts and products
The above spectra is $^1$H NMR, and the below spectra is $^{13}$C NMR.
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The above spectra is $^1$H NMR, and the below spectra is $^{13}$C NMR
7. ESI-MS spectra of catalysts and products

![Chemical structure and ESI-MS spectrum diagram]
Cu-7

Peking University Mass Spectrometry Analysis Report

Analysis Info
Analysis Name: 11120546_20111202_00001.d  Acquisition Date: 12/2/2011 4:36:34 PM
Sample: PbII(Cu)  Instrument: Bruker Apex IV FTMS
Comment: ESI Positive  Operator: Peking University

Electronic Supplementary Material (ESI) for Dalton Transactions
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Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
Analysis Name: 10990270_20100820_000001.d
Sample: Quin-ethyl
Comment: ESI Positive

Acquisition Data: 2010/08/20 16:32:31 PM
Instrument: Thermo Finnigan FTMS
Operator: Peking University

Mass, mg / Formula / Score / Error (ppm) / Error (ppm) / Confidence / M Value
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354.13224 / C20 H18 N4 O2a / 100.00 / 0.0 / 0.0 / 15.0 / 13.5 / awen
Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
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Sample: Chloro-Mes-White
Comment: ESI Positive
Acquisition Date: 02/06/2013 10:35:55 AM
Instrument: Bruker Apex II FTMS
Operator: Peking University

Bruker Compass DataAnalysis 4.0
Printed: 12/06/2013 5:26:23 PM
16
Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
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Sample: Click-Oxide
Comment: ESI-Positive

Acquisition Date: 9/10/2012 2:51:12 PM
Instrument: Bruker Apex IV FTMS
Operator: Peking University

Chemical structure:

![Chemical structure image]

17

10090418_50_100_05_000001.d - rel5

Mass, eqz, # Formula, Score, arr [m/z], arr [ppm], m/z, rel. a ' Conf. N.Ratio
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595.2275 1 C 21 H 27 N 4 O 3 100.00 377.0654 0.2 0.4 Total 13.5 even 66

Bruker Compass Cell/Analyser 4.5
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Page 1 of 1