Electronic Supplementary Information (ESI)

Synthesis, Cu(II) complexation, $^{64}$Cu-labeling and biological evaluation of cross-bridged cyclam chelators with phosphonate pendant arms

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<td>³¹P{¹H} NMR</td>
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1. **Details of HPLC Purification of CB-TE1A1P (2)**

A batch of CB-TE1A1P that contained some impurities was purified by HPLC using a C\textsubscript{18} semipreparative column with a 3 mL/min flow rate and the following gradient:

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<td>24</td>
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<tr>
<td>30</td>
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The compound eluted with a broad peak starting at 8.0 minutes. The collection was stopped after minute 15.0. A UV chromatogram at 210 nm is shown in the figure below.

LC-MS was used to make sure that no impurity eluted in the 8.0-15.0 minute range. The only peaks visible in the MS chromatogram of the collected fractions are M*H\textsuperscript{+} (m/z = 379.3) and 2M*H\textsuperscript{+} (m/z = 757.4).
2. List of X-ray Crystallographic Software Employed

APEX2 Version 2.2 /SHELXTL (Bruker AXS Inc., 2007)
SAINT Version 7.34a (Bruker AXS Inc., 2007)
SADABS Version 2007/2 (Sheldrick, Bruker AXS Inc.)
XPREP Version 2005/2 (Sheldrick, Bruker AXS Inc.)

Bruker suite of programs APEX2/SHELXTL, SAINT, SADABS, XPREP may be obtained from Bruker AXS.Inx, 5467 East Cheryl Parkway, Madison WI 53711


X-ray crystal structure figures were prepared using CrystalMaker 8.5 for Mac (CrystalMaker Software Ltd., Centre for Innovation & Enterprise, Oxford University Begbroke Science Park, Sandy Lane, Yarnton, Oxfordshire, OX5 1PF, UK; http://www.crystalmaker.com)
3. Detailed Energetic Results for DFT Calculations

### Cu-CBTE2P

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<tr>
<th>Method</th>
<th>Conformer</th>
<th>E (kcal/mol)</th>
<th>ZPE (kcal/mol)</th>
<th>ZPE-corr E (kcal/mol)</th>
<th>H° (kcal/mol)</th>
<th>S° (cal/mol K)</th>
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| Cu-CBTE1A1P

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4. **UV/VIS Spectrum of Cu-CB-TE1A1P**

![UV/VIS Spectrum of Cu-CB-TE1A1P](image)

\[ \lambda_{\text{max}} \text{ (aq)/nm} = 613 \ (\varepsilon/dm^3 \text{ mol}^{-1} \text{ cm}^{-1} \) \]

5. **NMR spectra of ligand 2 and precursor 6**

### Table 1: NMR Spectral Parameters

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D$_2$O, 499.78 MHz, internal reference with MeCN set at $\delta$ 2.06
Region of interest: 1.70-1.89 ppm
Region of interest: 1.70-1.89 ppm

Exponential: -1.32
Gaussian: 0.70 GB
Region of interest: 1.70-1.89 ppm

Exponential: -1.32
Gaussian: 0.70 GB
Region of interest: 2.28 - 2.50 ppm
Region of interest: 2.28 - 2.50 ppm

Exponential: -1.32
Gaussian: 0.70 GB
Region of interest: 2.28 - 2.50 ppm

Exponential: -1.32
Gaussian: 0.70 GB
Region of interest: 2.52 - 2.61 ppm
Region of interest: 2.52 - 2.61 ppm

Exponential: -1.32
Gaussian: 0.60 GB
Region of interest: 2.52 - 2.61 ppm

Exponential: -1.32
Gaussian: 0.60 GB
Region of interest: 2.76 - 3.45 ppm
Region of interest: 2.76 - 3.45 ppm

Exponential: -1.32
Gaussian: 0.60 GB
Region of interest: 2.76 - 3.45 ppm

Exponential: -1.32
Gaussian: 0.60 GB
Region of interest: 3.49 - 3.78 ppm
Region of interest: 3.49 - 3.78 ppm

Exponential: -1.32
Gaussian: 0.60 GB
Region of interest: 3.49 - 3.78 ppm

Exponential: -1.32
Gaussian: 0.60 GB
Region of interest: 3.78 - 4.15 ppm
Region of interest: 3.78 - 4.15 ppm

Exponential: -1.32
Gaussian: 0.70 GB
Region of interest: 3.78 - 4.15 ppm

Exponential: -1.32
Gaussian: 0.70 GB
Electronic Supplementary Material (ESI) for Dalton Transactions
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RF-CB-TE1A1P

Varian

D2O

16

3.0000

2011-01-24T15:29:41

499.7707

7992.0

-1396.6

1H

23976

65536

D2O, 499.78 MHz, internal reference with MeCN set at δ 2.06
Parameters

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(See previous page for details of 1D proton spectrum.)
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D₂O, 125.68 MHz, internal reference with MeCN set at δ 1.47
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D$_2$O, 125.68 MHz, MeCN as internal interference, set at $\delta$ 1.47
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<table>
<thead>
<tr>
<th>Parameter</th>
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<td>2 Origin</td>
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<td>10 Nucleus</td>
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<td>12 Spectral Size</td>
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D$_2$O, 100.53 MHz,
MeCN as internal interference, set at $\delta$ 1.47
black - 125.7 MHz
blue - 100.5 MHz
125 MHz

100 MHz
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| 1  | Origin       | RF-CB-TE1A1P |
| 2  | Solvent      | D2O          |
| 3  | Temperature  | 25.0         |
| 4  | Number of Scans | 16       |
| 5  | Acquisition Time | 3.0000   |
| 6  | Acquisition Date | 2011-01-24T15:29:41 |
| 7  | Spectrometer Frequency | 499.77707 |
| 8  | Spectral Width | 7992.0      |
| 9  | Lowest Frequency | -1396.6     |
| 10 | Nucleus      | 1H           |
| 11 | Acquired Size | 23976        |
| 12 | Spectral Size | 65536        |

D$_2$O, 499.78 MHz, internal reference
with MeCN set at $\delta$ 2.06
Origin: RF-CB-TE1A1P
Solvent: D2O
Temperature: 25.0
Number of Scans: 38000
 Acquisition Time: 1.0000
 Acquisition Date: 2011-01-22T08:03:16
 Spectrometer Frequency: 125.68036
 Spectral Width: 31446.5
 Lowest Frequency: -3692.7
 Nucleus: 13C
 Acquired Size: 31447
 Spectral Size: 65536
(See previous two pages for corresponding
1D proton and carbon spectra)
RF-CB-TE1A1P_protected (CH2Cl2 extracts)

C6D6, 499.78 MHz, internal reference set to TMS at δ 0.00

Sample was dried over Na2SO4 prior to running NMR
Region of interest: 2.17 - 3.26 ppm
Region of interest: 2.44 - 3.00 ppm
Region of interest: 2.44 - 3.00 ppm
Region of interest: 2.44-3.00 ppm

Exponential: -1.32
Gaussian: 0.70 GB
Region of interest: 2.44-3.00 ppm

Exponential: -1.32
Gaussian: 0.70 GB
Region of interest: 2.99-3.50 ppm

Exponential: -1.32
Gaussian: -1.00 GB
Region of interest: 2.99-3.50 ppm

Exponential: -1.32
Gaussian: -1.00 GB
Region of interest: 3.45 - 4.30 ppm
Region of interest: 3.45 - 4.30 ppm
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(See previous page for corresponding 1D proton spectrum)
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RF-CB-TE1A1P_protected_PhMe extracts

$^{13}$C NMR, 125.68 MHz, $C_6D_6$ with reference peak set at $\delta$ 128.06 (central peak)
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![Chemical Structure]

**RF-CB-TE1A1P_protected_PhMe extracts**

$^{13}$C NMR, 125.68 MHz, C$_6$D$_6$ with reference peak set at 128.06 ppm (central peak)

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<td>13. Spectral Size</td>
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13C NMR, 100.52 MHz, C₆D₆ with reference peak set at 128.06 ppm (central peak)
apodisation for both = 3 Hz

black - 100.5 MHz
blue 125.7 MHz
125 MHz
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125 MHz
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C₆D₆, 499.78 MHz, internal reference set to TMS at δ 0.00
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<p>| | |</p>
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C₆D₆, 125.68 MHz, internal reference
set to TMS at δ 0.00
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(See previous two pages for corresponding 1D proton and carbon spectra)
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RF-CB-TE1A1P_protected_PhMe extracts

$^{31}$P NMR, 202.31 MHz, C$_6$D$_6$, external reference with 85% phosphoric acid set to $\delta$ 0.00