

# Novel cyano-bridged mixed-valent copper complexes formed by completely *in situ* synthetic method *via* the cleavage of C–C bond in acetonitrile†

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A series of novel cyano-bridged mixed-valent copper complexes with different nuclearities, where the cyanide group is obtained from the cleavage of a carbon–carbon (C–C) bond in acetonitrile under mild conditions, have been prepared and structurally characterized *via* a completely *in situ* synthetic method. The method is catalyzed by 2,2'-bipyridine and 1,10-phenanthroline-based Cu<sup>II</sup> complexes in the presence of certain reductants, such as aryl aldehydes or pyridyl amines. This work provides a facile *in situ* synthetic method to prepare mixed-valent cyano-bridged multinuclear complexes having novel Cu<sup>II</sup>(CN)Cu<sup>I</sup>(CN)Cu<sup>II</sup> and Cu<sup>II</sup>(CN)Cu<sup>I</sup>(CN)Cu<sup>I</sup>(CN)Cu<sup>II</sup> units and avoids using toxic cyanides. In addition, our preliminary studies demonstrate that the mixed-valent trinuclear copper complexes can effectively catalyze the oxidation of benzaldehyde by peroxide.

## Introduction

Recently, research on the C–C bond cleavage in nitriles, especially in acetonitrile, has attracted much attention. Since acetonitrile has stable chemical properties and lone pair electrons on the nitrogen atom, it is widely used as a solvent in organic synthesis and even as a ligand in coordination chemistry. Up till now, the cleavage of C–C bonds in acetonitrile by transition-metal complexes in homogeneous conditions remains a fundamental challenge. In most cases, the reactions of C–C bond cleavage of nitriles should be carried out under rigorous experimental conditions, wherein air-sensitive organometallic compounds are involved, probably because of their high affinity to the carbon atoms. For instance, low-valent group 10 transition-metal triads,<sup>1–9</sup> Fe, Rh and Ir complexes having different silyl ligands<sup>10–18</sup> as well as one Mo,<sup>19</sup> Co,<sup>20</sup> U<sup>21</sup> and Sm<sup>22</sup> and two Ag<sup>23–24</sup> complexes are mainly involved in the scission of the C–C bond.

To date, there have been only two examples on the investigation of copper catalyzed C–C bond cleavage under mild conditions. In one case, a dinuclear copper(II) cryptate was employed as a catalyst and the C–C bond scission was evidenced by the formation of a cyano-bridged dinuclear copper(II) cryptate.<sup>25</sup> While in the other case, a copper(II) compound, having ethylenediamine (en) and *N,N'*-dimethylpyridine-2,6-dicarboxamide dianionic ligands, was adopted to activate the C–C bond in acetonitrile, where the reduction process of Cu<sup>II</sup> to Cu<sup>I</sup> accompanied the reaction and a mixed-valent copper complex [Cu<sup>II</sup>(en)<sub>3</sub>][Cu<sup>I</sup>(CN)<sub>3</sub>] was yielded.<sup>26</sup>

With regard to the mixed-valent copper complexes, there have been four methods to obtain them, namely reduction, oxidation, replacement and electrochemical approaches. These mixed-valent

copper complexes are regarded as promising materials for applications in catalysis, magnetism, semiconductors and biological mimics. However, their possible applications are very limited mainly because of the synthetic difficulties. For example, it is very hard to exactly control the valence of the central copper ions and the ratio of the mixed-valent copper ions.

We have previously reported studies on C–S bond cleavage, catalyzed by tetranuclear Cu<sup>I</sup> clusters under mild conditions.<sup>27</sup> In this work, 2,2'-bipyridine and 1,10-phenanthroline-based copper(II) complexes are used to catalyze, *in situ*, the C–C bond cleavage of acetonitrile under mild conditions in the presence of certain reductants, such as aryl aldehydes or pyridyl amines and to capture the resulting cyanide group by forming a series of novel mixed-valent cyano-bridged copper complexes with different nuclearities (Scheme 1). These are four trinuclear and one tetranuclear complexes, formulated as [Cu<sup>II</sup>(bpy)<sub>2</sub>(NC)Cu<sup>I</sup>(bpy)(CN)Cu<sup>II</sup>(bpy)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**1**) and [Cu<sup>II</sup>(bpy)<sub>2</sub>(NC)Cu<sup>I</sup>(bpy)(CN)Cu<sup>II</sup>(bpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (**2**) in polymorphic forms, [Cu<sup>II</sup>(bpy)<sub>2</sub>(NC)Cu<sup>I</sup>(bpy)(CN)Cu<sup>II</sup>(bpy)<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**3**), [Cu<sup>II</sup>(phen)<sub>2</sub>(NC)Cu<sup>I</sup>(phen)(CN)Cu<sup>II</sup>(phen)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (**6**) and [Cu<sup>II</sup>(phen)<sub>2</sub>(NC)Cu<sup>I</sup>(phen)(CN)Cu<sup>I</sup>(phen)(CN)Cu<sup>II</sup>(phen)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> (**7**) (bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline, 4-ampy = 4-aminopyridine). Additionally, a cyano-bridged dinuclear copper(II) complex [Cu<sup>II</sup>(bpy)<sub>2</sub>(CN)Cu<sup>II</sup>(bpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>(CH<sub>3</sub>OH) (**4**) and a mononuclear copper(II) complex [Cu<sup>II</sup>(bpy)<sub>2</sub>(CN)](ClO<sub>4</sub>) (**5**) are also included.

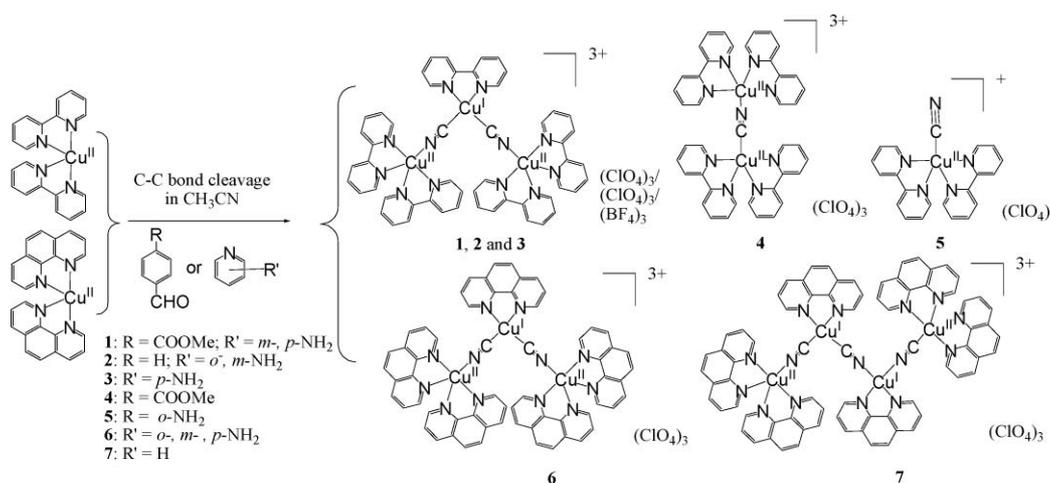
## Experimental

### Materials and physical measurements

Copper(II) compounds [Cu<sup>II</sup>(bpy)<sub>2</sub>(ClO<sub>4</sub>)](ClO<sub>4</sub>)·2H<sub>2</sub>O, [Cu<sup>II</sup>(bpy)<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub>](BF<sub>4</sub>)·2H<sub>2</sub>O and [Cu<sup>II</sup>(phen)<sub>2</sub>(ClO<sub>4</sub>)](ClO<sub>4</sub>)·H<sub>2</sub>O were synthesized by means of a literature method.<sup>28</sup> All other reagents were of analytical grade from commercial sources and were used without any further purification. Infrared spectra (IR, 4000–400 cm<sup>-1</sup>) were collected on a Nicolet FT-IR 170X spectrophotometer at 25 °C using KBr plates. Electrospray ionization mass spectra (ESI-MS) were recorded on a Finnigan

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† Electronic supplementary information (ESI) available: Intermolecular hydrogen bonding (Table ESI1) and π–π stacking interactions in 1–7 (Fig. ESI1–ESI7). CCDC reference numbers 694304, 752337, 773341, 694303 and 752338–75233840. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00345j



**Scheme 1** The C–C bond cleavage of acetonitrile catalyzed by copper complexes in the presence of certain reductants, forming mono-, di-, tri- and tetranuclear copper compounds.

MAT SSQ 710 mass spectrometer in a scan range 100–1200 amu. Ultraviolet-visible (UV-vis) spectra were recorded on a Shimadzu UV-3100 double-beam spectrophotometer using a Pyrex cell with a path length of 10 mm at room temperature. X-Ray Photoelectron Spectrometer (XPS) determination was carried out by a Thermo Scientific K-Alpha system, where a monochromatic Al K $\alpha$  X-ray source was used with a spot area of 400  $\mu\text{m}$ .

#### Preparation of mixed-valent copper complexes 1–7

**Synthesis of [Cu<sup>II</sup>(bpy)<sub>2</sub>(ClO<sub>4</sub>)(NC)Cu<sup>I</sup>(bpy)(CN)Cu<sup>II</sup>(bpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (1) and [Cu<sup>II</sup>(bpy)<sub>2</sub>(CN)Cu<sup>I</sup>(bpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>(CH<sub>3</sub>OH) (4).** A solution of [Cu<sup>II</sup>(bpy)<sub>2</sub>(ClO<sub>4</sub>)](ClO<sub>4</sub>) $\cdot$ 2H<sub>2</sub>O (0.0611 g, 0.1 mmol) in CH<sub>3</sub>CN (10 cm<sup>3</sup>) was added to a solution of 4-fbame (0.0164 g, 0.1 mmol) in CH<sub>3</sub>OH (10 cm<sup>3</sup>). The mixture was refluxed for 50 h and the colour of the solution gradually changed from blue to dark yellow. The solution was allowed to evaporate slowly at room temperature in air and dark yellow crystals of **1** (0.0310 g, 70% yield based on copper) suitable for single-crystal X-ray diffraction determination were collected after one week, together with a few blue crystals of **4** as a by-product (~5% yield). **1**: Main FT-IR absorptions (KBr pellets):  $\nu = 3116$  (w), 2966 (w), 2926 (w), 2872 (w), 2126 (m), 2109 (s), 1604 (m), 1510 (m), 1444 (m), 1085 (vs), 766 (s), and 622 (s). UV-vis (CH<sub>3</sub>OH):  $\lambda_{\text{max}} = 244$  and 298 nm. ESI-MS ( $m/z$ ): 278 ([Cu<sup>II</sup>(bpy)(CN)(CH<sub>3</sub>OH)]<sup>+</sup>), 375 ([Cu<sup>I</sup>(bpy)<sub>2</sub>]<sup>+</sup>), 434 ([Cu<sup>II</sup>(bpy)<sub>2</sub>(CN)(CH<sub>3</sub>OH)]<sup>+</sup>), 483 ([Cu<sub>2</sub>(bpy)<sub>2</sub>(CN)(H<sub>2</sub>O)]<sup>+</sup>), 563 ([Cu<sub>2</sub>Cu<sup>I</sup>(bpy)<sub>3</sub>(CN)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>]<sup>2+</sup>/2). **4**: Main FT-IR absorptions (KBr pellets):  $\nu = 3422$  (m), 3115 (w), 3083 (w), 3034 (w), 2924 (w), 2175 (w), 2109 (w), 1602 (m), 1445 (s), 1091 (vs), 770 (s), and 623 (s).

**Synthesis of [Cu<sup>II</sup>(bpy)<sub>2</sub>(NC)Cu<sup>I</sup>(bpy)(CN)Cu<sup>II</sup>(bpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> (2).** A solution of [Cu<sup>II</sup>(bpy)<sub>2</sub>(ClO<sub>4</sub>)](ClO<sub>4</sub>) $\cdot$ 2H<sub>2</sub>O (0.0611 g, 0.1 mmol) in CH<sub>3</sub>CN (10 cm<sup>3</sup>) was added to a solution of benzaldehyde in C<sub>2</sub>H<sub>5</sub>OH (10 cm<sup>3</sup>, 0.01 mmol cm<sup>-3</sup>). The mixture was refluxed for 50 h and the colour of the solution gradually changed from blue to dark yellow. The solution was allowed to evaporate slowly at room temperature in air and dark yellow crystals of **2** were obtained in a yield of 0.0310 g (70% based on copper) after 3 d. Main FT-IR absorptions (KBr pellets): 3113 (s), 3082 (m), 2126 (s),

2108 (s), 1690 (s), 1600 (s), 1567 (s), 1492 (m), 1443 (m), 1384 (s), 1316 (m), 1086 (vs), 1013 (s), 765 (m), 731 (s), and 623 (m). ESI-MS ( $m/z$ ): 278 ([Cu<sup>II</sup>(bpy)(CN)(CH<sub>3</sub>OH)]<sup>+</sup>), 375 ([Cu<sup>I</sup>(bpy)<sub>2</sub>]<sup>+</sup>), 401 ([Cu<sup>II</sup>(bpy)<sub>2</sub>(CN)]<sup>+</sup>), 474 ([Cu<sup>II</sup>(bpy)<sub>2</sub>(CN)(CH<sub>3</sub>CN)]<sup>+</sup>), 488 ([Cu<sup>II</sup>(bpy)<sub>2</sub>(CN)(CH<sub>3</sub>CN)(C<sub>2</sub>H<sub>5</sub>OH)]<sup>+</sup>).

**Synthesis of [Cu<sup>II</sup>(bpy)<sub>2</sub>(NC)Cu<sup>I</sup>(bpy)(CN)Cu<sup>II</sup>(bpy)<sub>2</sub>](BF<sub>4</sub>)](BF<sub>4</sub>)<sub>2</sub> (3).** A solution of [Cu<sup>II</sup>(bpy)<sub>2</sub>(BF<sub>4</sub>)](BF<sub>4</sub>) $\cdot$ 2H<sub>2</sub>O (0.0586 g, 0.1 mmol) in CH<sub>3</sub>CN (10 cm<sup>3</sup>) was added to a solution of 4-ampy in C<sub>2</sub>H<sub>5</sub>OH (10 cm<sup>3</sup>, 0.01 mmol cm<sup>-3</sup>). The mixture was refluxed for 50 h and the colour of the solution gradually changed from blue to dark yellow. The solution was allowed to evaporate slowly at room temperature in air and dark yellow crystals of **3** were obtained in a yield of 0.0082 g (20% based on copper) after 10 d. Main FT-IR absorptions (KBr pellets): 3115 (w), 3022 (w), 2126 (m), 2108 (m), 1690 (s), 1600 (s), 1492 (m), 1444 (m), 1061 (s), 1013 (m), 766 (m), and 623 (m). ESI-MS ( $m/z$ ): 278 ([Cu<sup>II</sup>(bpy)(CN)(CH<sub>3</sub>OH)]<sup>+</sup>), 375 ([Cu<sup>I</sup>(bpy)<sub>2</sub>]<sup>+</sup>), 474 ([Cu<sup>II</sup>(bpy)<sub>2</sub>(CN)(CH<sub>3</sub>CN)]<sup>+</sup>).

**Synthesis of [Cu<sup>II</sup>(bpy)<sub>2</sub>(CN)](ClO<sub>4</sub>) (5).** A solution of [Cu<sup>II</sup>(bpy)<sub>2</sub>(ClO<sub>4</sub>)](ClO<sub>4</sub>) $\cdot$ 2H<sub>2</sub>O (0.0611 g, 0.1 mmol) in CH<sub>3</sub>CN (10 cm<sup>3</sup>) was added to a solution of 2-aminopyridine (0.0094 g, 0.1 mmol) in C<sub>2</sub>H<sub>5</sub>OH (10 cm<sup>3</sup>). The colour of the solution gradually changed from blue to yellow-green during 20 h reflux. The solution was allowed to evaporate slowly at room temperature in air and blue crystals appeared on the bottom of the beaker (0.0050 g, 10% yield based on copper) after 3 d. Main FT-IR absorptions (KBr pellets): 3110 (s), 3080 (s), 2018 (w), 1599 (s), 1473 (s), 1384 (s), 1089 (vs), 765 (s), and 623 (m). ESI-MS ( $m/z$ ): 225 ([Cu<sup>II</sup>(bpy)<sub>2</sub>(CH<sub>3</sub>CN)(CH<sub>3</sub>OH)]<sup>2+</sup>/2), 266 ([Cu<sup>II</sup>(bpy)<sub>3</sub>]<sup>2+</sup>/2), 375 ([Cu<sup>I</sup>(bpy)<sub>2</sub>]<sup>+</sup>).

**Synthesis of [Cu<sup>II</sup>(phen)<sub>2</sub>(NC)Cu<sup>I</sup>(phen)(CN)Cu<sup>II</sup>(phen)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>(C<sub>2</sub>H<sub>5</sub>OH)<sub>2</sub> (6).** A solution of [Cu<sup>II</sup>(phen)<sub>2</sub>(ClO<sub>4</sub>)](ClO<sub>4</sub>) $\cdot$ H<sub>2</sub>O (0.0641 g, 0.1 mmol) in CH<sub>3</sub>CN (10 cm<sup>3</sup>) was added to a solution of 2-aminopyridine (0.0094 g, 0.1 mmol) in C<sub>2</sub>H<sub>5</sub>OH (10 cm<sup>3</sup>). The colour of the solution gradually changed from blue to dark green during the 20 h reflux. The mixture was allowed to evaporate slowly at room temperature in air and dark green crystals appeared on the bottom of the

**Table 1** Experimental details for the studies of C–C bond cleavage in acetonitrile

| Entry | Reactants and solvents  | Time/h | FT-IR absorptions for CN <sup>-</sup> | Products and yields                  |
|-------|---|--------|---------------------------------------|--------------------------------------|
| 1     | [Cu <sup>II</sup> (bpy) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O], 4-fbame, C <sub>2</sub> H <sub>5</sub> OH, CH <sub>3</sub> CN    | 50     | 2108, 2126                            | <b>1</b> , 80%                       |
| 2     | [Cu <sup>II</sup> (bpy) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O], 4-fbame, CH <sub>3</sub> OH, CH <sub>3</sub> CN                  | 50     | 2108, 2126<br>2109 (w)                | <b>1</b> , 70%<br>and <b>4</b> , ~5% |
| 3     | [Cu <sup>II</sup> (bpy) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O], 2-ampy, C <sub>2</sub> H <sub>5</sub> OH, CH <sub>3</sub> CN     | 20     | 2108, 2126<br>2018 (w)                | <b>2</b> , 12%<br>and <b>5</b> , 10% |
| 4     | [Cu <sup>II</sup> (bpy) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O], 3-ampy, C <sub>2</sub> H <sub>5</sub> OH, CH <sub>3</sub> CN     | 20     | 2108, 2126<br>2108, 2126              | <b>1</b> , 10%,<br>or <b>2</b> , 12% |
| 5     | [Cu <sup>II</sup> (bpy) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O], 4-ampy, C <sub>2</sub> H <sub>5</sub> OH, CH <sub>3</sub> CN     | 20     | 2108, 2126                            | <b>1</b> , 10%,                      |
| 6     | [Cu <sup>II</sup> (bpy) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O], PhCHO, C <sub>2</sub> H <sub>5</sub> OH, CH <sub>3</sub> CN      | 50     | 2108, 2126                            | <b>2</b> , 70%                       |
| 7     | [Cu <sup>II</sup> (bpy) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O], 4-MeOPhCHO, C <sub>2</sub> H <sub>5</sub> OH, CH <sub>3</sub> CN | 50     | 2108, 2126                            | <b>2</b> , 20%                       |
| 8     | [Cu <sup>II</sup> (phen) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O], 2-ampy, C <sub>2</sub> H <sub>5</sub> OH, CH <sub>3</sub> CN     | 20     | 2110, 2129                            | <b>6</b> , 70%                       |
| 9     | [Cu <sup>II</sup> (phen) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O], 3-ampy, C <sub>2</sub> H <sub>5</sub> OH, CH <sub>3</sub> CN     | 20     | 2110, 2129                            | <b>6</b> , 15%                       |
| 10    | [Cu <sup>II</sup> (phen) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O], 4-ampy, C <sub>2</sub> H <sub>5</sub> OH, CH <sub>3</sub> CN     | 20     | 2110, 2129                            | <b>6</b> , 15%                       |
| 11    | [Cu <sup>II</sup> (phen) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O], 4-fbame, C <sub>2</sub> H <sub>5</sub> OH, CH <sub>3</sub> CN    | 50     | 2110, 2129                            | <b>6</b> , 40%                       |
| 12    | [Cu <sup>II</sup> (phen) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O], 4-MeOPhCHO, C <sub>2</sub> H <sub>5</sub> OH, CH <sub>3</sub> CN | 50     | 2110, 2129                            | <b>6</b> , 20%                       |
| 13    | [Cu <sup>II</sup> (phen) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O], PhCHO, C <sub>2</sub> H <sub>5</sub> OH, CH <sub>3</sub> CN      | 50     | 2109 (b)                              | <b>7</b> , 40%                       |
| 14    | [Cu <sup>II</sup> (bpy) <sub>2</sub> (BF <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O], 4-ampy, C <sub>2</sub> H <sub>5</sub> OH, CH <sub>3</sub> CN      | 50     | 2108, 2126                            | <b>3</b> , 20%                       |

beaker after one week (0.0471 g, 70% yield based on copper). Main FT-IR absorptions (KBr pellets): 3072 (s), 2129 (s), 2110 (s), 1637 (s), 1619 (s), 1518 (s), 1494 (m), 1384 (m), 1146 (s), 1083 (vs), 868 (s), 848 (s), 722 (s), 623 (m). ESI-MS (*m/z*): 212 ([Cu<sup>II</sup>(phen)<sub>2</sub>]<sup>2+</sup>/2), 232 ([Cu<sup>II</sup>(phen)<sub>2</sub>(CH<sub>3</sub>CN)]<sup>2+</sup>/2), 302 ([Cu<sup>II</sup>(phen)(CN)(CH<sub>3</sub>OH)]<sup>+</sup>), 423 ([Cu<sup>I</sup>(phen)<sub>2</sub>]<sup>+</sup>), 449 ([Cu<sup>II</sup>(phen)<sub>2</sub>(CN)]<sup>+</sup>), 512 ([Cu<sup>I</sup><sub>2</sub>(phen)<sub>2</sub>(CN)]<sup>+</sup>), 538 ([Cu<sup>II</sup>Cu<sup>I</sup>(phen)<sub>2</sub>(CN)<sub>2</sub>]<sup>+</sup>).

**Synthesis of [Cu<sup>II</sup>(phen)<sub>2</sub>(NC)Cu<sup>I</sup>(phen)(CN)Cu<sup>I</sup>(phen)(CN)Cu<sup>II</sup>(phen)](ClO<sub>4</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> (**7**).** A solution of [Cu<sup>II</sup>(phen)<sub>2</sub>(ClO<sub>4</sub>)](ClO<sub>4</sub>)·H<sub>2</sub>O (0.0641 g, 0.1 mmol) in CH<sub>3</sub>CN (10 cm<sup>3</sup>) was added to a solution of benzaldehyde in C<sub>2</sub>H<sub>5</sub>OH (10 cm<sup>3</sup>, 0.01 mmol cm<sup>-3</sup>). The mixture was refluxed for 50 h and the colour of the solution gradually changed from blue to dark yellow. The solution was allowed to evaporate slowly at room temperature and dark yellow crystals of **7** were collected (0.0175 g, 40% yield based on copper). Main FT-IR absorptions (KBr pellets): 3063 (s), 2109 (b, s), 1622 (s), 1606 (s), 1586 (s), 1427 (m), 1384 (m), 1146 (s), 1088 (vs), 849 (s), 777 (s), 723 (s), and 623 (m). ESI-MS (*m/z*): 212 ([Cu<sup>II</sup>(phen)<sub>2</sub>]<sup>2+</sup>/2), 232 ([Cu<sup>II</sup>(phen)<sub>2</sub>(CH<sub>3</sub>CN)]<sup>2+</sup>/2), 302 ([Cu<sup>II</sup>(phen)(CN)(CH<sub>3</sub>OH)]<sup>+</sup>), 423 ([Cu<sup>I</sup>(phen)<sub>2</sub>]<sup>+</sup>), 449 ([Cu<sup>II</sup>(phen)<sub>2</sub>(CN)]<sup>+</sup>), 512 ([Cu<sup>I</sup><sub>2</sub>(phen)<sub>2</sub>(CN)]<sup>+</sup>), 538 ([Cu<sup>II</sup>Cu<sup>I</sup>(phen)<sub>2</sub>(CN)<sub>2</sub>]<sup>+</sup>).

### X-Ray data collection and structural determination

Single-crystal samples of **1–7** were glue-covered and mounted on glass fibres and used for data collection. Crystallographic data of **1** and **4** were collected at 100(2) K, while the others were collected at 291(2) K on a Bruker SMART 1 K CCD diffractometer using graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The crystal systems were determined by laue symmetry and the space groups were assigned on the basis of systematic absences using XPREP. Absorption corrections were performed to all data and the structures were solved by direct methods and refined by full-matrix least-squares method on  $F^2_{\text{obs}}$  by using the SHELXTL-PC software package.<sup>29</sup> All non-H atoms were anisotropically refined and all hydrogen atoms were inserted in the calculated positions assigned fixed isotropic thermal parameters and allowed to ride

on their respective parent atoms. Some of the ClO<sub>4</sub><sup>-</sup> and BF<sub>4</sub><sup>-</sup> anions in **1**, **3**, **4** and **7** are refined as disordered with different site occupancy factors. The summary of the crystal data, experimental details and refinement results for **1–7** is listed in Table 2. Selected bond distances and bond angles related to the central copper ions are given in Table 3, while O–H $\cdots$ O and C–H $\cdots$ O types of hydrogen bonding interactions in **1–7** are listed in Table ESI1†.

## Results and discussion

### Synthetic, spectral and structural aspects

In our experiments, a Schiff-base ligand prepared from the condensation between 3-ampy and 4-fbame (4-fbame = 4-formylbenzoic acid methyl ester) was firstly used to react with [Cu<sup>II</sup>(bpy)<sub>2</sub>(ClO<sub>4</sub>)](ClO<sub>4</sub>)·2H<sub>2</sub>O in a mixture of acetonitrile and ethanol (1 : 1, v : v). After long-time at reflux, the colour of the solution changed from blue to dark yellow and yielded a novel cyano-bridged mixed-valent trinuclear copper complex **1** in a yield of 20%, indicative of the cleavage of the C–C bond in acetonitrile and the capture of the produced CN<sup>-</sup> groups from solution.

The single-crystal X-ray analysis for **1** reveals that the three copper centres are alternately bridged by two cyanide anions and they are mixed-valent, with the middle one having a charge of +1 and the others having a charge of +2 (Fig. 1, **1**). The charge for the three copper centres is deduced from the coordination geometry and the charge equilibrium requirement for the whole molecule, because two CN<sup>-</sup> and three ClO<sub>4</sub><sup>-</sup> anions are found in the asymmetric unit. It is noted that the three copper ions adopt different coordination modes, *i.e.* a six-coordinate octahedron for Cu<sup>II</sup>1, a four-coordinate tetrahedron for Cu<sup>I</sup>2, and a five-coordinate trigonal bipyramid for Cu<sup>II</sup>3 ( $\tau = 0.875$ ).<sup>30</sup>

Further experiments illustrate that it is the reductants such as aryl aldehydes and pyridyl amines that contribute to the C–C bond cleavage in acetonitrile, rather than the Schiff-base ligand. With this idea in mind, [Cu<sup>II</sup>(bpy)<sub>2</sub>(ClO<sub>4</sub>)](ClO<sub>4</sub>)·2H<sub>2</sub>O is employed to react directly with certain reductants to simplify the reactions and improve the yields of the mixed-valent cyano-bridged copper complexes. In the reactions of [Cu<sup>II</sup>(bpy)<sub>2</sub>(ClO<sub>4</sub>)](ClO<sub>4</sub>)·2H<sub>2</sub>O with 4-fbame in mixed solvents of acetonitrile and ethanol or methanol

Table 2 Crystallographic data and structural refinements for complexes 1–7

| Compound                                    | 1   | 2   | 3  | 4  | 5   | 6   | 7   |
|---|---|---|--|--|---|---|---|
| Formula                                     | Cu <sub>3</sub> C <sub>32</sub> H <sub>40</sub> N <sub>12</sub> O <sub>12</sub> Cl <sub>3</sub> | Cu <sub>3</sub> C <sub>32</sub> H <sub>40</sub> N <sub>12</sub> O <sub>12</sub> Cl <sub>3</sub> | C <sub>52</sub> H <sub>40</sub> B <sub>3</sub> Cu <sub>3</sub> F <sub>12</sub> N <sub>12</sub> | Cu <sub>2</sub> C <sub>42</sub> H <sub>36</sub> N <sub>6</sub> O <sub>13</sub> Cl <sub>3</sub> | Cu <sub>21</sub> H <sub>16</sub> N <sub>5</sub> O <sub>4</sub> Cl | Cu <sub>3</sub> C <sub>66</sub> H <sub>52</sub> N <sub>12</sub> O <sub>14</sub> Cl <sub>3</sub> | Cu <sub>4</sub> C <sub>75</sub> H <sub>52</sub> N <sub>15</sub> O <sub>14</sub> Cl <sub>3</sub> |
| Formula weight                              | 1321.93   | 1321.96   | 1284.23  | 1108.23  | 501.38  | 1534.17   | 1747.87   |
| T/K   | 100(2)  | 291(2)  | 291(2)   | 100(2)   | 291(2)  | 291(2)  | 291(2)  |
| Crystal size/mm                             | 0.08 × 0.10 × 0.14  | 0.10 × 0.10 × 0.10  | 0.10 × 0.11 × 0.12   | 0.10 × 0.12 × 0.15   | 0.10 × 0.12 × 0.14  | 0.10 × 0.10 × 0.14  | 0.10 × 0.10 × 0.10  |
| Crystal system                              | Monoclinic  | Triclinic   | Monoclinic   | Triclinic  | Monoclinic  | Monoclinic  | Triclinic   |
| Space group                                 | C2/c  | P1  | C2/c   | P1   | P2 <sub>1</sub> /c  | P2 <sub>1</sub> /n  | P1  |
| a/Å   | 23.007(6)   | 9.658(2)  | 23.108(5)  | 9.3980(15)   | 13.304(3)   | 13.0200(12)   | 12.761(10)  |
| b/Å   | 21.202(5)   | 13.320(3)   | 21.442(5)  | 13.738(2)  | 11.451(2)   | 23.760(2)   | 13.021(11)  |
| c/Å   | 23.327(6)   | 22.255(5)   | 23.436(6)  | 19.206(3)  | 14.804(3)   | 21.3761(19)   | 13.671(12)  |
| α/°   | 90  | 74.632(3)   | 90   | 79.856(2)  | 90  | 90  | 96.256(13)  |
| β/°   | 110.605(3)  | 82.523(4)   | 110.934(3)   | 82.962(2)  | 110.524(3)  | 96.296(2)   | 99.056(13)  |
| γ/°   | 90  | 86.757(4)   | 90   | 72.719(2)  | 90  | 90  | 114.199(9)  |
| V/Å <sup>3</sup>                            | 10651(5)  | 2736.4(10)  | 10846(4)   | 2324.2(6)  | 2112.2(7)   | 6572.9(10)  | 2008(3)   |
| ρ <sub>c</sub> /g cm <sup>-3</sup> /Z       | 1.649/8   | 1.604/2   | 1.573/8  | 1.584/2  | 1.577/4   | 1.550/4   | 1.445/1   |
| F(000)                                      | 5360  | 1340  | 5169   | 1128   | 1020  | 3128  | 886   |
| μ/mm <sup>-1</sup>                          | 1.414   | 1.376   | 1.257  | 1.162  | 1.200   | 1.160   | 1.215   |
| Max./min. h, k, l                           | 27/−27, 25/−17, 26/−27  | 7/−11, 15/−15, 21/−26   | 25/−27, 25/−25, 25/−27   | 10/−11, 16/−16, 22/−19   | 13/−15, 13/−13, 17/−13  | 15/−12, 28/−28, 19/−25  | 10/−15, 15/−15, 15/−16  |
| Collected reflns                            | 25972   | 13854   | 27348  | 11802  | 10390   | 32911   | 9482  |
| Unique reflns                               | 9363  | 9488  | 9545   | 8065   | 3721  | 11566   | 6784  |
| Reflns with I > 2σ(I)                       | 4237  | 2949  | 5744   | 3911   | 2247  | 3928  | 2669  |
| Parameters                                  | 761   | 739   | 763  | 626  | 289   | 884   | 531   |
| R <sub>1</sub> /wR <sub>2</sub> [I > 2σ(I)] | 0.0607/0.1029   | 0.0631/0.1241   | 0.0464/0.1098  | 0.0597/0.1196  | 0.0637/0.1747   | 0.0603/0.0863   | 0.0797/0.1689   |
| R <sub>1</sub> /wR <sub>2</sub> (all data)  | 0.1544/0.1189   | 0.2125/0.1605   | 0.0815/0.1227  | 0.1232/0.1403  | 0.0973/0.1935   | 0.1728/0.0993   | 0.1919/0.1921   |
| GOF on F <sup>2</sup>                       | 0.89  | 0.74  | 0.89   | 0.83   | 0.94  | 0.88  | 0.99  |
| Max./min. Δρ/e Å <sup>-3</sup>              | 0.75/−0.72  | 0.55/−0.49  | 0.46/−0.55   | 1.04/−0.88   | 0.93/−0.48  | 0.59/−0.43  | 0.75/−0.59  |

$$R_1 = \sum |F_o| - |F_c| / \sum |F_o|, wR_2 = [\sum [w(F_o^2 - F_c^2)]^2 / \sum w(F_o^2)]^{1/2}$$

**Table 3** Selected bond lengths (Å) and bond angles (°) for complexes 1–7

| Complex 1           |          |            |           |
|---------------------|----------|------------|-----------|
| Cu1–N1              | 1.984(5) | Cu2–C32    | 1.906(7)  |
| Cu1–N2              | 1.995(4) | Cu3–N8     | 1.991(4)  |
| Cu1–N3              | 2.240(6) | Cu3–N9     | 1.977(5)  |
| Cu1–N4              | 2.020(5) | Cu3–N10    | 2.073(4)  |
| Cu1–N5              | 1.962(4) | Cu3–N11    | 2.057(4)  |
| Cu1–O2              | 2.812(4) | Cu3–N12    | 1.982(5)  |
| Cu2–N6              | 2.078(7) | N5–C21     | 1.138(8)  |
| Cu2–N7              | 2.085(5) | N8–C32     | 1.134(8)  |
| Cu2–C21             | 1.914(6) |            |           |
| Cu1–N5–C21          | 176.3(5) | Cu2–C32–N8 | 177.1(6)  |
| Cu2–C21–N5          | 178.0(6) | Cu3–N8–C32 | 169.6(5)  |
| Complex 2           |          |            |           |
| Cu1–N1              | 2.007(9) | Cu2–C32    | 1.895(9)  |
| Cu1–N2              | 2.026(8) | Cu3–N8     | 1.970(6)  |
| Cu1–N3              | 2.160(9) | Cu3–N9     | 2.003(7)  |
| Cu1–N4              | 2.030(8) | Cu3–N10    | 2.139(7)  |
| Cu1–N5              | 1.962(7) | Cu3–N11    | 2.045(7)  |
| Cu2–N6              | 2.097(7) | Cu3–N12    | 1.969(7)  |
| Cu2–N7              | 2.104(7) | N5–C21     | 1.161(11) |
| Cu2–C21             | 1.896(9) | N8–C32     | 1.166(11) |
| Cu1–N5–C21          | 172.6(8) | Cu2–C32–N8 | 179.5(6)  |
| Cu2–C21–N5          | 167.0(8) | Cu3–N8–C32 | 175.0(7)  |
| Complex 3           |          |            |           |
| Cu1–N1              | 2.004(3) | Cu2–C32    | 1.908(4)  |
| Cu1–N2              | 1.994(4) | Cu3–N8     | 1.981(4)  |
| Cu1–N3              | 2.224(4) | Cu3–N9     | 1.997(4)  |
| Cu1–N4              | 2.025(4) | Cu3–N10    | 2.083(3)  |
| Cu1–N5              | 1.966(3) | Cu3–N11    | 1.997(3)  |
| Cu1–F6 <sup>a</sup> | 2.859(4) | Cu3–N12    | 2.070(3)  |
| Cu2–N6              | 2.112(4) | N5–C21     | 1.148(5)  |
| Cu2–N7              | 2.108(4) | N8–C32     | 1.145(5)  |
| Cu2–C21             | 1.909(4) |            |           |
| Cu1–N5–C21          | 178.2(3) | Cu2–C32–N8 | 176.2(4)  |
| Cu2–C21–N5          | 177.8(4) | Cu3–N8–C32 | 171.6(4)  |
| Complex 4           |          |            |           |
| Cu1–N1              | 1.987(4) | Cu2–N6     | 2.183(6)  |
| Cu1–N2              | 2.036(5) | Cu2–N7     | 2.007(4)  |
| Cu1–N3              | 2.154(5) | Cu2–N8     | 2.025(4)  |
| Cu1–N4              | 2.014(4) | Cu2–N9     | 1.978(4)  |
| Cu1–C21             | 1.942(5) | N5–C21     | 1.145(8)  |
| Cu2–N5              | 2.024(6) |            |           |
| Cu1–C21–N5          | 166.8(6) | Cu2–N5–C21 | 172.4(5)  |
| Complex 5           |          |            |           |
| Cu1–N1              | 2.103(4) | Cu1–N4     | 2.003(4)  |
| Cu1–N2              | 2.011(4) | Cu1–C21    | 1.960(7)  |
| Cu1–N3              | 2.132(4) | N5–C21     | 1.181(10) |
| Cu1–C21–N5          | 173.3(5) |            |           |
| Complex 6           |          |            |           |
| Cu1–N1              | 2.000(5) | Cu2–C38    | 1.906(6)  |
| Cu1–N2              | 2.121(5) | Cu3–N8     | 1.963(4)  |
| Cu1–N3              | 2.079(4) | Cu3–N9     | 2.009(5)  |
| Cu1–N4              | 1.985(5) | Cu3–N10    | 2.182(5)  |
| Cu1–N5              | 1.940(5) | Cu3–N11    | 2.038(4)  |
| Cu2–N6              | 2.087(7) | Cu3–N12    | 1.999(5)  |
| Cu2–N7              | 2.071(4) | N5–C25     | 1.156(9)  |
| Cu2–C25             | 1.909(7) | N8–C38     | 1.146(7)  |
| Cu1–N5–C25          | 173.6(4) | Cu2–C38–N8 | 172.9(6)  |
| Cu2–C25–N5          | 173.4(5) | Cu3–N8–C38 | 166.0(5)  |
| Complex 7           |          |            |           |
| Cu1–N1              | 1.961(8) | Cu2–N5     | 2.083(10) |
| Cu1–N2              | 2.051(7) | Cu2–N6     | 2.108(9)  |
| Cu1–N3              | 1.982(6) | Cu2–C25    | 1.887(9)  |
| Cu1–N4              | 2.176(9) | Cu2–C38    | 1.925(8)  |
| Cu1–N7              | 1.926(8) | N7–C25     | 1.131(12) |
| Cu1–N7–C25          | 174.4(7) |            |           |

<sup>a</sup> Symmetry operator:  $-1/2 + x, 1/2 - y, -1/2 + z$ .

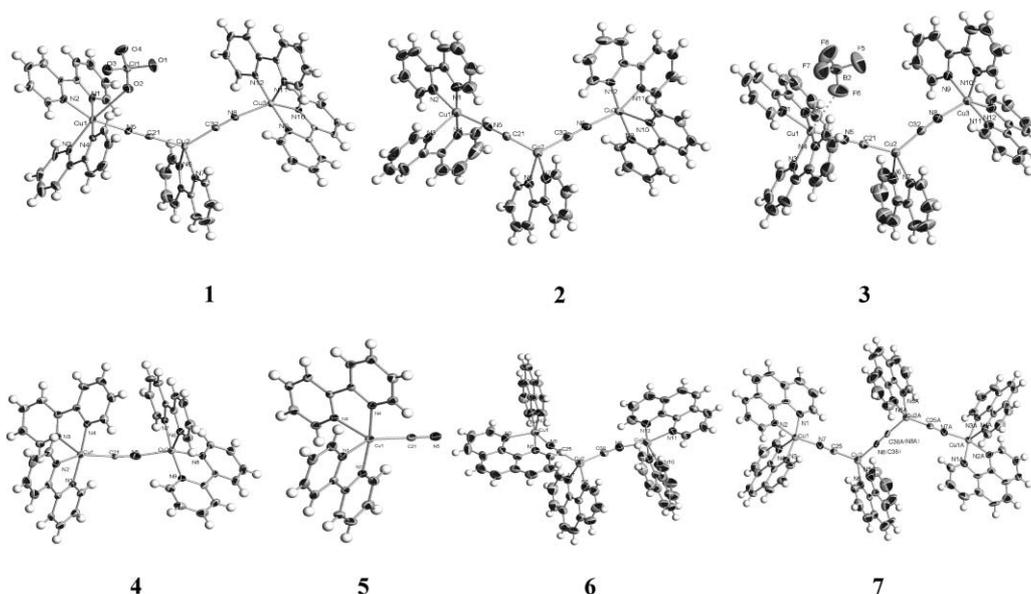
(Table 1, entries 1–2), high yields of **1** can be gained in both reaction, together with some white powder. ESI-MS spectra of the white powder show a large peak at  $m/z = 179.2$  corresponding to the 4-(methoxycarbonyl)benzoate anion, which is the oxidative product of 4-fbame. In the case of entry 2, a few blue crystals of **4** have been obtained as a by-product. A single-crystal X-ray study of **4** reveals that it consists of two  $[\text{Cu}^{\text{II}}(\text{bpy})_2]^{2+}$  cations bridged by one cyanide anion (Fig. 1, **4**), three free perchlorate counterions and one solvent ethanol molecule. Two five-coordinate  $\text{Cu}^{\text{II}}$  centres exhibit severely distorted trigonal bipyramidal and pyramidal geometry, respectively ( $\tau = 0.540$  for  $\text{Cu}^{\text{II}}1$  and  $0.433$  for  $\text{Cu}^{\text{II}}2$ ).

Inspired by the production of the above-mentioned novel cyano-bridged multinuclear copper complexes, and in order to further explore the possible mechanism of the C–C bond cleavage of acetonitrile, we extended our studies to a series of reactions with different reductants. In comparison with 4-fbame, the resulting products were somewhat complicated when different aminopyridines (2, 3, or 4-ampy) are used as the reductants to cleave the C–C bond in acetonitrile. Although the FT-IR spectra show that cyanide anions are much more easily and quickly produced, the isolated yields of the resulting products with cyanide anions are usually much lower. In addition, different products can be obtained by changing the molar ratios of the reactants or the experimental conditions (Table 1, entries 3–5). The possible reason is suggested to arise from the strong coordination ability of aminopyridines.<sup>31</sup>

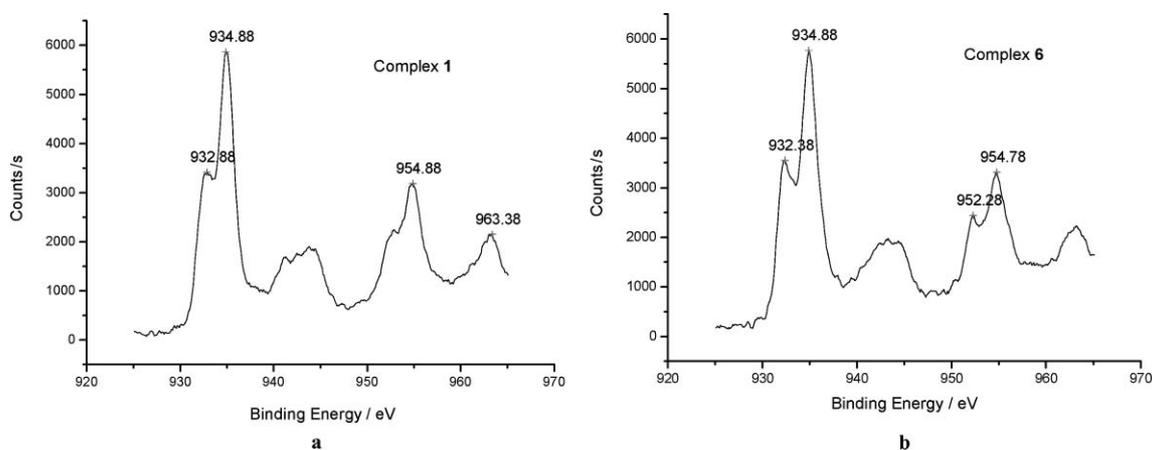
In the reactions between  $[\text{Cu}^{\text{II}}(\text{bpy})_2(\text{ClO}_4)](\text{ClO}_4) \cdot 2\text{H}_2\text{O}$  and 2-ampy or 3-ampy, dark yellow crystals of **2** and blue crystals of **5** (a mononuclear copper(II) complex) are isolated, respectively. A single crystal X-ray crystallographic study for **2** reveals that it is another polymorphous isomer of the trinuclear cyano-bridged mixed-valent copper complex **1**. **2** crystallizes in the triclinic  $P\bar{1}$  space group with the unit cell volume of  $2736.4(10) \text{ \AA}^3$ , while **1** crystallizes in the monoclinic  $C2/c$  space group with the unit cell volume of  $10651(5) \text{ \AA}^3$ . All of the three perchlorate anions in **2** are uncoordinated and both  $\text{Cu}^{\text{II}}1$  and  $\text{Cu}^{\text{II}}3$  ions adopt five-coordinate distorted pyramids ( $\tau = 0.187$  for  $\text{Cu}^{\text{II}}1$  and  $0.407$  for  $\text{Cu}^{\text{II}}3$ ) (Fig. 1, **2**), which are different from that of the  $\text{Cu}^{\text{II}}3$  in complex **1** ( $\tau = 0.875$ ). The  $\text{Cu}^{\text{II}}1$ – $\text{Cu}^{\text{II}}2$ – $\text{Cu}^{\text{II}}3$  angle in **2** is  $117.7(6)^\circ$ , which is also different from an angle of  $128.2(5)^\circ$  in **1**. The coordination geometry around the copper(II) centre in **5** is a severely distorted five-coordinate trigonal bipyramid with the  $\tau$  value of  $0.518$  (Fig. 1, **5**).

In contrast, a much higher yield of **2** has been achieved (Table 1, entry 6) when benzaldehyde is employed in the reaction, which is consistent with the use of 4-fbame as a reductant. 4-Methoxybenzaldehyde is also employed in this type of reaction giving a low yield of **2** (Table 1, entry 7).

Reactions of  $[\text{Cu}^{\text{II}}(\text{phen})_2(\text{ClO}_4)](\text{ClO}_4) \cdot \text{H}_2\text{O}$  with 2, 3, 4-ampy and aryl aldehydes have also been carried out for comparison (Table 1, entries 8–13). In the cases of aminopyridines, 4-fbame and 4-methoxybenzaldehyde, similar dark green microcrystals of **6** have been obtained and a much higher yield is achieved in the reaction between  $[\text{Cu}^{\text{II}}(\text{phen})_2(\text{ClO}_4)](\text{ClO}_4) \cdot \text{H}_2\text{O}$  and 2-ampy. The structure of **6** is also a mixed-valent cyano-bridged trinuclear copper complex (Fig. 1, **6**) except that the bpy chelating ligands in **1** and **2** are replaced by the phen ligands. The coordination geometry for each five-coordinate copper(II) centre in **6** is slightly



**Fig. 1** ORTEP diagrams of the cationic structures of **1–7** (30% thermal probability ellipsoids, uncoordinated anions and solvent molecules excluded for clarity).



**Fig. 2** XPS spectra for the cyano-bridged mixed-valent trinuclear copper complexes **1** (a) and **6** (b).

different from that in complex **2**. The  $\tau$  values for the  $\text{Cu}^{\text{II}}$ 1 and  $\text{Cu}^{\text{II}}$ 3 centres are 0.528 and 0.168, showing distorted trigonal bipyramidal and pyramidal coordination geometry, respectively. Furthermore, XPS studies for the mixed-valent cyano-bridged trinuclear copper complexes **1** and **6** reveal two groups of double peaks at 955, 953 eV and 935, 933 eV in **1** and at 955, 952 eV and 935, 932 eV in **5**, respectively, corresponding to the  $\text{Cu}^{\text{II}}$  and  $\text{Cu}^{\text{I}}$  species in a peak area ratio of approximately 2:1 (Fig. 2).

With regard to benzaldehyde, another mixed-valent cyano-bridged tetranuclear copper complex **7** is yielded wherein two four-coordinate  $\text{Cu}^{\text{I}}$  ions lie in the middle and two five-coordinate  $\text{Cu}^{\text{II}}$  ions are positioned at both sides (Fig. 1, **7**) forming an  $[\text{Cu}^{\text{II}}(\text{NC})\text{Cu}^{\text{I}}(\text{CN})\text{Cu}^{\text{I}}(\text{CN})\text{Cu}^{\text{II}}]$  arrangement unprecedented in cyano copper complexes. The  $\tau$  value for the  $\text{Cu}^{\text{II}}$ 1 centre is 0.295, exhibiting distorted pyramidal coordination geometry. The angle between the three copper ions is  $117.3(7)^\circ$ , which is similar to those in **1** ( $128.2(5)^\circ$ ), **2** ( $117.7(6)^\circ$ ) and **6** ( $116.9(5)^\circ$ ).

Moreover, reactions between  $[\text{Cu}^{\text{II}}(\text{bpy})_2(\text{BF}_4)](\text{BF}_4) \cdot 2\text{H}_2\text{O}$  and reductants have been carried out for the comparison of anionic effects. It is found that the C–C bond cleavage in acetonitrile has been somewhat decreased in the presence of tetrafluoroborate anions. Up to now, only one mixed-valent cyano-bridged trinuclear copper complex **3** has been isolated with a relatively low yield of 20% from this experimental system (Table 1, entry 14). A single-crystal X-ray diffraction study on **3** exhibits that it is isostructural to **1** and the coordination modes for two  $\text{Cu}^{\text{II}}$  and one  $\text{Cu}^{\text{I}}$  centres are very similar to those in **1**, except for the existence of different anions (Fig. 1, **3**). The coordination environment for the  $\text{Cu}^{\text{II}}$ 3 ion in **3** is also a five-coordinate trigonal bipyramid with the  $\tau$  value of 0.841 and the angle between the three copper ions is  $129.8(4)^\circ$ . It is noted that the coordinative bond between the six-coordinate  $\text{Cu}^{\text{II}}$ 1 ion and the fluorine atom of tetrafluoroborate anion is very weak,  $2.859(4) \text{ \AA}$ , which is slightly longer than that in **1** between the  $\text{Cu}^{\text{II}}$ 1 ion and the oxygen atom of the perchlorate anion ( $2.812(4) \text{ \AA}$ ).

To get further insight into this reaction, some comparative experiments have been carried out by treating the copper(I) complex  $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4(\text{ClO}_4)]$  with bpy and phen, respectively, in acetonitrile. No FT-IR absorption can be observed in the triple-bond region, implying that these copper(I) complexes are not able to catalyze the C–C bond cleavage in acetonitrile. Similarly, the treatment of  $[\text{Cu}^{\text{II}}(\text{bpy})_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}]$  and acetonitrile gives no C≡N signal in the FT-IR spectrum. From these experimental results, we have learned that the presence of reductants is crucial for the heterolytic cleavage of acetonitrile, and the coexistence of mixed-valent copper centres is suggested to play an important role in the process of activating and cleaving the C–C bond in acetonitrile.

Our latest experiments demonstrate that mixed-valent trinuclear copper complexes can effectively catalyze the oxidation of benzaldehyde by peroxide. For instance, according to typical HPLC analyses, a 0.5% amount of the catalyst of complex **1** gives an 80.4% yield of benzoic acid after 0.5 h reaction, while only a 11.4% yield can be obtained in the absence of catalyst **1** under the same experimental conditions.

## Conclusions

In summary, a series of copper complexes (mono-, di-, tri-, and tetranuclear) containing cyanide anions have been isolated and structurally characterized in the reactions between 2,2'-bipyridine and 1,10-phenanthroline-based copper(II) complexes and certain reductants in mixed solvents including acetonitrile. It is suggested that the participation of certain reductants (aryl aldehydes or pyridyl amines) in the system is crucial for the scission of the C–C bond and for the formation of cyano-bridged mixed-valent copper complexes wherein the  $\text{Cu}^{\text{I}}$  and  $\text{Cu}^{\text{II}}$  centres are bridged by the  $\text{CN}^-$  group, alternately. Versatile hydrogen bonding and  $\pi$ - $\pi$  stacking interactions in the supramolecular level are found between adjacent molecules in all seven copper complexes (Table ES11 and Fig. ES11-ES17†). Although the detailed mechanism of the C–C bond cleavage in acetonitrile catalyzed by copper complexes is still not clearly understood, we have provided a simple method for the scission of the C–C bond in acetonitrile under mild condition at low cost.

This work also provides a facile completely *in situ* synthetic method to prepare mixed-valent cyano-bridged multinuclear complexes having novel  $\text{Cu}^{\text{II}}(\text{CN})\text{Cu}^{\text{I}}(\text{CN})\text{Cu}^{\text{II}}$  and  $\text{Cu}^{\text{II}}(\text{CN})\text{Cu}^{\text{I}}(\text{CN})\text{Cu}^{\text{I}}(\text{CN})\text{Cu}^{\text{II}}$  units and avoids using toxic cyanides. In addition, our preliminary studies reveal that the mixed-valent trinuclear copper complexes can effectively catalyze the oxidation of benzaldehyde by peroxide. Further investigation is being undertaken on the possible applications of our synthetic method and mixed-valent cyano-bridged copper complexes.

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