

# Stable mixed phenanthroline copper(I) complexes. Key building blocks for supramolecular coordination chemistry†

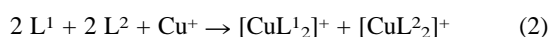
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A simple procedure is presented that is used to synthesise, for the first time, pure mixed phenanthroline copper(I) complexes that do not exchange ligands.

Our current interest in the coordination chemistry of phenanthroline ligands<sup>1–7</sup> stems from their fascinating potential to allow for the construction of the novel redox-active structures **A** as well as nanotubes **B** (Scheme 1) through the simple self-assembly of (i) Cu<sup>I</sup> as coordinating metal ion with a tetrahedral geometry, (ii) a macrocyclic bisphenanthroline with *exo*-coordination sites, and (iii) either a macrocyclic bisphenanthroline with *endo*-coordination sites (for **A**) or linear 3,8-linked oligophenanthrolines (for **B**).

As a prerequisite for the successful construction of such novel topologies a strategy is needed for the defined synthesis of mixed phenanthroline copper(I) complexes according to eqn. (1) while avoiding the formation of the two symmetrical complexes, eqn. (2).



Remarkably, there is no report so far on the clean formation of mixed-phenanthroline copper(I) species<sup>8</sup> except for oligomeric phenanthroline complexes<sup>9</sup> and in cases where the geometrical constraints of a phenanthroline with *endo*-coordination sites embedded in a cyclic ring system prevent formation of symmetrical complexes<sup>3,10</sup> according to eqn. (2).

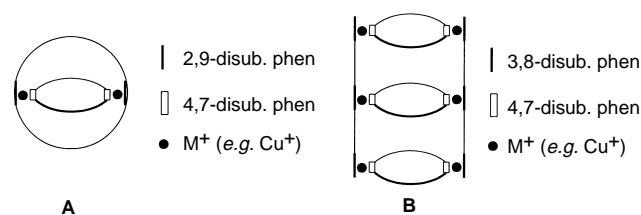
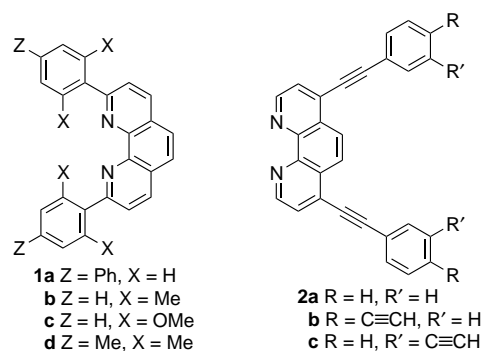
Herein, we report, for the first time, on a general strategy to synthesise mixed phenanthroline copper(I) complexes using acyclic ligands and its use for the preparation of a model complex of **A** demonstrating the feasibility of our approach.

The synthesis of phenanthrolines **1–4** is straightforward,<sup>11–14</sup> or is described elsewhere.<sup>15</sup> As expected, the symmetrical copper(I) complexes [Cu(**1a**)<sub>2</sub>]BF<sub>4</sub> and [Cu(**2a**)<sub>2</sub>]BF<sub>4</sub> formed quantitatively within seconds by mixing 2 equiv. of the ligands with [Cu(MeCN)<sub>4</sub>]BF<sub>4</sub> in MeCN.<sup>16</sup>

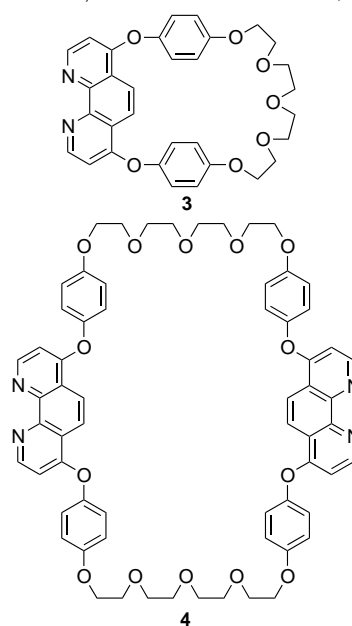
In order to synthesise mixed complexes of type [CuL<sup>1</sup>L<sup>2</sup>]<sup>+</sup> several mechanistic investigations using low-temperature NMR techniques on the influence of solvent, temperature and sequence of addition of the phenanthroline ligand were undertaken. The results proposed that the preparation of the mixed-ligand complex could possibly be achieved by adding 1 equiv. of the 4,7-disubstituted **2a** to [Cu(MeCN)<sub>4</sub>]<sup>+</sup> followed by addition of **1a** at low temperature in dichloromethane as solvent.

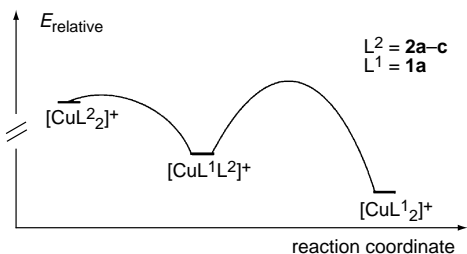
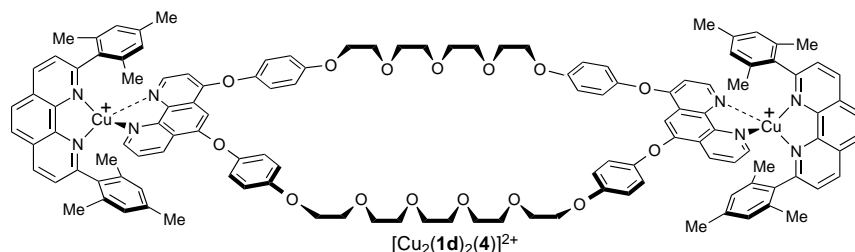
Indeed, after mixing 1 equiv. of **2a** with [Cu(MeCN)<sub>4</sub>]<sup>+</sup> at –80 °C in CD<sub>2</sub>Cl<sub>2</sub> and adding 1 equiv. of **1a** complex [Cu(**1a**)(**2a**)]<sup>+</sup> formed almost quantitatively. However, upon raising the temperature (*T* > –50 °C) increased formation of [Cu(**1a**)<sub>2</sub>]<sup>+</sup> was observed. Mixing [Cu(**2a**)<sub>2</sub>]<sup>+</sup> with 2 equiv. of ligand **1a** led to formation of the mixed complex [Cu(**1a**)(**2a**)]<sup>+</sup> besides the symmetrical complex [Cu(**1a**)<sub>2</sub>]<sup>+</sup> in a ratio of 1 : 2 remaining constant at –20 °C over several days. Apparently, the thermodynamics of the copper(I) complex equilibria follows qualitatively the course depicted in Fig. 1, but isolation of [Cu(**1a**)(**2a**)]<sup>+</sup> is precluded because of the rather low barrier for [Cu(**1a**)(**2a**)]<sup>+</sup> → [Cu(**1a**)<sub>2</sub>]<sup>+</sup>.

From the above results the use of 2,9-disubstituted phenanthrolines **1b–d** is proposed the steric congestion of which through larger groups (X = Me, OMe) precludes formation of symmetrical complexes [Cu(**1**)<sub>2</sub>]<sup>+</sup>. Indeed, when we reacted [Cu(MeCN)<sub>4</sub>]<sup>+</sup> with 2 equiv. of sterically encumbered 2,9-disubstituted phenanthrolines **1b–d**, formation of [Cu(**1b–d**)<sub>2</sub>]<sup>+</sup> was not observed! Now the reaction of [Cu(MeCN)<sub>4</sub>]<sup>+</sup> with 1 equiv. of each, **1b–d** and **2a–c**, resulted in the almost



**Scheme 1** Schematic representation of the ball-type structure **A** and nanotube **B** as examples of interesting topologies resulting from mixed phenanthroline copper(I) complexes with tetrahedral coordination





**Fig. 1** Energy diagram for the complexation equilibria of  $[\text{CuL}^1\text{L}^2]^+$  complexes in solution

**Table 1** Half-wave potentials  $E_{1/2}$  (V vs.  $\text{Fc}/\text{Fc}^+$ )<sup>†</sup> of mixed-ligand copper(I) complexes determined by cyclic voltammetry in dichloromethane at  $\nu = 100 \text{ mV s}^{-1}$  (electrolyte:  $\text{NBu}_4\text{PF}_6$ ) and yields after purification

Copper(I) complex	Yield (%)	$E_{1/2}$	$\Delta E_p/\text{mV}$
$[\text{Cu}(\mathbf{1a})_2]\text{BF}_4$	95	+0.40	70
$[\text{Cu}(\mathbf{2a})_2]\text{BF}_4$	83	-0.05	150 <sup>a</sup>
$[\text{Cu}(\mathbf{1b})(\mathbf{2a})]\text{BF}_4$	86	+0.36	60
$[\text{Cu}(\mathbf{1c})(\mathbf{2a})]\text{BF}_4$	97	+0.04	70
$[\text{Cu}(\mathbf{1d})(\mathbf{2a})]\text{BF}_4$	86	+0.30	70
$[\text{Cu}(\mathbf{1d})(\mathbf{3})]\text{BF}_4$	81	+0.21	130 <sup>a</sup>
$[\text{Cu}_2(\mathbf{1d})_2(\mathbf{4})][\text{BF}_4]_2$	92	+0.20	220 <sup>a</sup>

<sup>a</sup> Large peak broadening because of slow heterogeneous electron transfer.

quantitative formation of the unsymmetrical complexes  $[\text{Cu}(\mathbf{1b-d})(\mathbf{2a-c})]^+$  that could easily be isolated at room temperature. All compounds were characterised by NMR, elemental analysis and/or ESI mass spectra.

Cyclic voltammetry investigations on the novel mixed complexes revealed fully or quasi-reversible waves for  $\text{Cu}^{\text{I}} \rightleftharpoons \text{Cu}^{\text{II}}$  indicating that the complexes remain intact despite the redox process.

The mixed-complex preparation technique was then used for the first time with macrocyclic phenanthroline ligands with *exo*-coordination sites in order to probe our concept for the preparation of precursors to the novel supramolecular systems **A** and **B**. Reaction of  $[\text{Cu}(\text{MeCN})_4]^+$  with 1 equiv. of **3** and **1c** or **1d** each provided  $[\text{Cu}(\mathbf{1c})(\mathbf{3})]^+$  and  $[\text{Cu}(\mathbf{1d})(\mathbf{3})]^+$ , whereas with 1 equiv. of **4** and 2 equiv. of **1d** the complex  $[\text{Cu}_2(\mathbf{1d})_2(\mathbf{4})]^{2+}$  was furnished.

Upon addition of phenanthroline **2a** to  $[\text{Cu}(\mathbf{1d})(\mathbf{3})]^+$  the immediate formation of a mixture of  $[\text{Cu}(\mathbf{1d})(\mathbf{2a})]^+$  and unreacted  $[\text{Cu}(\mathbf{1d})(\mathbf{3})]^+$  was observed (ratio: 1 : 1). At the same time the  $^1\text{H}$  NMR peaks were broadened indicating a dynamic process on the NMR timescale. Conversely, addition of phenanthroline **1d** to the complex  $[\text{Cu}(\mathbf{1c})(\mathbf{3})]^+$  also led to a mixture of  $[\text{Cu}(\mathbf{1d})(\mathbf{3})]^+$  and unreacted  $[\text{Cu}(\mathbf{1c})(\mathbf{3})]^+$  in a ratio of 1 : 3 that remained constant over several days at room temperature.

To accommodate this observation we have to assume that the mixed complexes  $[\text{Cu}(\mathbf{1})(\mathbf{3})]^+$  are always in a rapid dissociation-association equilibrium with a small amount of  $[\text{Cu}(\mathbf{1})]^+ + \mathbf{3}$  as well as  $[\text{Cu}(\mathbf{3})]^+ + \mathbf{1}$  present. Using sterically hindered

2,9-disubstituted phenanthrolines with  $\text{X} = \text{Me}$  or  $\text{OMe}$ , however, we have prevented the formation of  $[\text{Cu}(\mathbf{1b-d})_2]^+$  and forced the system to form the mixed-ligand complexes solely. As a consequence of such controlled ligand exchange processes the straightforward self-assembly of structures **A** and **B** should now be possible.

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## Footnotes

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<sup>†</sup> New building blocks for sensors and supramolecular arrays, Part 4; for Part 3 see ref. 7(a).

<sup>‡</sup> All potentials are referred to the ferrocene-ferrocenium redox couple. By addition of +0.39 V the values vs. SCE can be obtained.

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