

# Chiral 1,2-ethanediyl-spaced quaterpyridines give a library of cyclic and double helicates with copper(I)

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A new enantiomeric pair of ligands in which a 2,2':6',2'':6'',2''':6'''-quaterpyridine has been split into two 2,2'-bipyridine binding domains by a CH<sub>2</sub>CH<sub>2</sub> spacer has been prepared: reaction with Ag(I) gives dinuclear double helicates whereas Cu(I) gives a library of {CuL}<sub>n</sub><sup>n+</sup> complexes (*n* = 2,3,4,5) of which the compounds with *n* = 2,3 have been structurally characterised as double helicates and cyclohelicates respectively.

It is established that oligopyridines can give helicates upon coordination to metal centres<sup>1,2</sup> and that structural development of the ligand allows subtle control to be exerted over the consequences of helication; for example, chiral ligands may be used to give a diastereomeric excess of left- or right-handed helicates<sup>3,4</sup> or spacers may be introduced which might lead to the formation of closed circular structures.<sup>4–8</sup> To date, only two examples of cyclohelicates with chiral ligands have been reported, and in each case the reactions were diastereoselective, giving trinuclear<sup>8</sup> or hexanuclear<sup>4</sup> solid state complexes. Here we report the formation of a library of {CuL}<sub>n</sub><sup>n+</sup> species from reactions of a new chiral helicand based upon a spaced 2,2':6',2'':6'',2''':6'''-quaterpyridine (qtpy).

The new chiral ligands all-(*S*)-**1** and all-(*R*)-**2** were obtained in 80–85% yield using standard methods and were fully characterised. The ligands exhibited equal and opposite optical rotations in chloroform (**1**: [α]<sub>D</sub><sup>23</sup> +82.2°; **2**: [α]<sub>D</sub><sup>23</sup> –82.3°) and circular dichroism (CD) spectra. The spectra exhibited two principal absorptions (**1**: Δε<sub>255</sub> +5.8, Δε<sub>307</sub> –1.7; **2**: Δε<sub>255</sub> –6.2, Δε<sub>301</sub> +2.4) which correspond to π–π\* transitions in the electronic spectra at 256 and 299 nm. The ligands are chiral analogues of **3** which has been shown to form dicopper(I) double helicates<sup>9–12</sup> and we were interested in comparing the diastereoselectivities obtained upon the formation of double helicates with **1** and **2** with the corresponding qtpy ligands **4** and **5**.<sup>13</sup>

Ultrasonication of a 1:1 stoichiometric mixture of AgO<sub>2</sub>CCH<sub>3</sub> or [Cu(MeCN)<sub>4</sub>][PF<sub>6</sub>]<sub>2</sub> and **1** or **2** in MeOH (Ag or Cu) or MeCN (Cu) gave solutions from which colourless or orange hexafluorophosphate salts of stoichiometry {[AgL]<sub>n</sub>}[PF<sub>6</sub>]<sub>n</sub> or {[CuL]<sub>n</sub>}[PF<sub>6</sub>]<sub>n</sub> were isolated in near

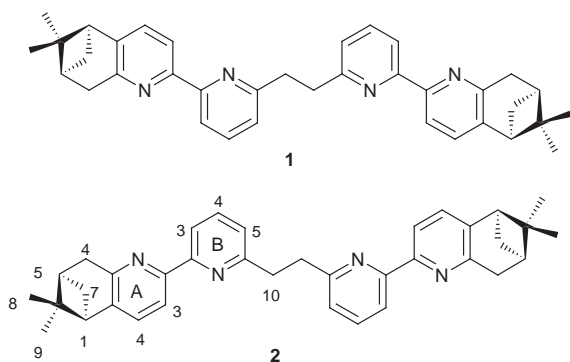
quantitative (≥97%) yield after recrystallisation of the initial precipitates by the diffusion of diethyl ether vapour into MeOH or MeCN solutions. In each case, the compounds only exhibited a single spot on tlc analysis (SiO<sub>2</sub>, MeCN, H<sub>2</sub>O, aqueous KNO<sub>3</sub>).

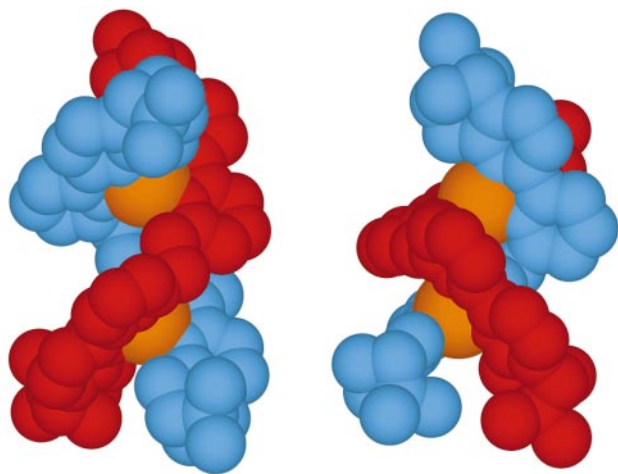
To simplify the discussion, only complexes with **1** will be explicitly discussed. Those with **2** parallel the behaviour exactly. In the case of the silver complex, both ES (MeCN or MeOH) and MALDI TOF (2,6-dihydroxybenzoic acid matrix) mass spectrometry showed an intense peak at *m/z* 1414 corresponding to {[Ag<sub>2</sub>(**1**)<sub>2</sub>][PF<sub>6</sub>]}<sup>+</sup> but no peaks corresponding to higher nuclearity species and suggesting a double-helical formulation. This is further supported by the observation of a single solution species in the <sup>1</sup>H NMR spectrum (CD<sub>3</sub>CN). The signals corresponding to H<sup>5B</sup>, H<sup>4A,4B</sup> and the ethylene bridge protons are broadened at ambient temperature but show no change over a temperature range –40 to +75 °C suggesting that a low energy intramolecular process is responsible for the broadening rather than a chemical exchange process. The complex is optically active and solutions in MeCN exhibit [α]<sub>D</sub><sup>23</sup>: +73.1° and CD spectra with Δε<sub>220</sub> +26, Δε<sub>298</sub> –31 and Δε<sub>322</sub> +64. The band at 322 nm with a large Δε is characteristic of a double helicate and the sign of Δε allows the unambiguous assignment of *P* helical chirality to the double helix obtained with **1** and *M* helical chirality to the complex with **2**.<sup>3,13,14</sup> To conclude, the reaction of **1** or **2** with AgO<sub>2</sub>Ac leads only to dinuclear double helicates.

The case of the copper(I) complexes was far more complicated. Solutions in CD<sub>3</sub>OD exhibited two subspectra in a ratio of 10:7 and comparison of chemical shifts with the double-helical copper(I) complexes of **3** strongly suggested the formation of a mixture of *P* and *M* dinuclear double helicates. Recrystallisation from MeOH yielded orange needles together with smaller amounts of fluffy solid consisting of small orange crystals. The <sup>1</sup>H NMR spectrum of the fluffy crystalline solid (in CD<sub>3</sub>OD) corresponded to the dominant species, but within 10 min the solution had equilibrated to give the 10:7 ratio of complexes, the most characteristic signals of which are doublets assigned to H<sup>5B</sup> at δ 7.16 and 7.03 for the major and minor species respectively. The ES MS of either type of crystal in MeOH revealed only peaks assigned to {[Cu<sub>2</sub>(**1**)<sub>2</sub>][PF<sub>6</sub>]}<sup>+</sup> and [Cu<sub>2</sub>(**1**)<sub>2</sub>]<sup>2+</sup>. The needles consisted of a 1:1 mixture of the two species and a solid state structural determination confirmed the formulation as a dinuclear double helicate.†

The structural determination of the complex {[Cu<sub>2</sub>(**2**)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>•3Et<sub>2</sub>O} showed that the needles were a *quasi*-racemate containing equal amounts of the diastereomeric *P* and *M* double helicates in the crystal (Fig. 1). Each copper is in a distorted four coordinate environment and the bond angles and distances are typical with Cu–N distances of 1.995(4)–2.072(4) Å and bite angles of 81.2–82.2°. The Cu...Cu distances in the individual cations are 5.885 and 5.958 Å comparable to the complexes of **3**<sup>10</sup> but much longer than those with **4** and **5**.<sup>13</sup>

Dissolution of any of the crude solids, or the crystalline materials obtained from MeOH in CD<sub>3</sub>CN resulted in orange solutions whose <sup>1</sup>H NMR spectra contained between three and

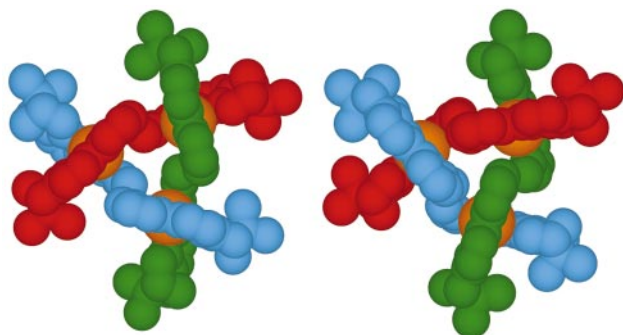




**Fig. 1** The solid state structures of the *M* and *P* cations in  $[\text{Cu}_2(\mathbf{2})_2][\text{PF}_6]_2 \cdot 3\text{Et}_2\text{O}$ ; hydrogen atoms have been omitted for clarity.

five species (as monitored by the upfield  $\text{H}^{\text{SB}}$  resonances) depending upon the concentration of the sample. Systematic and reversible changes in the spectra and speciation occurred upon varying the concentration, or upon titrating  $\text{CD}_3\text{OD}$  into  $\text{CD}_3\text{CN}$  solutions (or *vice versa*). ES MS studies of the MeCN or MeOH solutions revealed the presence of ions assigned to  $[\text{Cu}_2(\mathbf{1})_2]^{2+}$ ,  $\{[\text{Cu}_2(\mathbf{1})_2][\text{PF}_6]\}^+$ ,  $[\text{Cu}_3(\mathbf{1})_3]^{3+}$ ,  $\{[\text{Cu}_4(\mathbf{1})_4][\text{PF}_6]\}^{3+}$ ,  $\{[\text{Cu}_5(\mathbf{1})_5][\text{PF}_6]_2\}^{2+}$  and  $\{[\text{Cu}_5(\mathbf{1})_5][\text{PF}_6]_3\}^{3+}$  (all charges confirmed by partial mass isotopomer distribution) and allowed the assignment of the subspectrum containing a  $\delta$  5.94 resonance for  $\text{H}^{\text{SB}}$  to the trinuclear species. Higher concentrations favoured the formation of higher nuclearity species and at concentrations below  $10^{-4}$  M only the dinuclear species were present in MeCN according to both  $^1\text{H}$  NMR and ESMS measurements.

Diffusion of  $\text{Et}_2\text{O}$  vapour into MeCN solutions of the complexes at an initial concentration that the NMR studies indicated significant amounts of the trinuclear species should be present resulted in the formation of triangular orange crystals, fresh solutions of which only exhibited (in  $\text{CD}_3\text{OD}$ ) the subspectrum containing the  $\delta$  5.94  $^1\text{H}$  NMR resonance; upon standing the mixture of complexes was regenerated. A solid state structure determination<sup>†</sup> revealed a pair of diastereomeric *P* and *M* cyclic  $[\text{Cu}_3(\mathbf{1})_3]^{3+}$  cations (Fig. 2). The bond angles and distances are similar to those in  $[\text{Cu}_2(\mathbf{2})_2][\text{PF}_6]_2$  and the three Cu centres are in a distorted tetrahedral geometry (bite angles  $80.0$ – $82.4^\circ$ , Cu–N  $1.981$ – $2.048$  Å) and describe a triangle with Cu...Cu distances of  $6.905$ – $6.983$  Å. The pinene groups point outwards giving the cation an outer diameter of *ca.*  $20.5$  Å and a height of  $8$  Å. The shortest distance between the ligands is around  $3.7$  Å (C...C) or  $2.2$  Å (shortest H...H), making the cavity at the centre of the triangle too small to include any guests. By



**Fig. 2** The solid state structures of the *M* and *P* cyclohelicate cations in  $[\text{Cu}_3(\mathbf{1})_3][\text{PF}_6]_2 \cdot 0.75\text{MeCN}$ , hydrogen atoms have been omitted for clarity.

analogy, we assume that the higher nuclearity species are also cyclohelicates.

In both of the complexes structurally characterised, the spacer reduces interactions between the chiral substituents and the other ligand strand such that the diastereoselectivity is reduced<sup>13</sup> and in the solid state, *quasi*-racemates are obtained. In contrast to previously reported cyclohelicates, which in the solid state exhibited diastereoselective formation of *P* or *M* helicates, our system shows no solid state diastereoselectivity. In contrast, modest diastereoselectivity is shown in solution; equilibrated MeOH solutions containing only the 10:7 mixture of diastereomers of the dinuclear double helicate have CD responses indicating an excess of the *P* helicate with **1** and the *M* helicate with **2**.

Detailed studies of the speciation and chiroptical properties of these systems are underway; however, we have established that in MeCN solution a library<sup>5</sup> of copper(I) helicates is formed. We should like to thank the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung and the University of Basel for support.

## Notes and references

<sup>†</sup> Crystal data for  $\text{C}_{144}\text{H}_{152}\text{Cu}_4\text{F}_{24}\text{N}_{16}\text{P}_4 \cdot 3(\text{C}_2\text{H}_5)_2\text{O}$ : *M* = 3163.22, triclinic, *a* = 12.576(3), *b* = 16.179(3), *c* = 21.058(4) Å,  $\alpha$  = 96.86(3),  $\beta$  = 95.34(3),  $\gamma$  = 111.00(3)°, *U* = 3928.5(14) Å<sup>3</sup>,  $\theta$  2.44–28.16°, *Z* = 1, *D<sub>c</sub>* = 1.337 Mg m<sup>-3</sup>, space group *P1* (no. 1), Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å),  $\mu(\text{Mo-K}\alpha)$  = 6.6 cm<sup>-1</sup>, *F*(000) = 1646, *T* = 200 K, 27400 independent reflections [*I* > 2.0 $\sigma$ (*I*)]. Refinement converged at a final *R* = 0.0565, *wR* = 0.1520. Minimum and maximum final residual electron density 0.66 and 0.91 e Å<sup>-3</sup>.

For  $4(\text{C}_{108}\text{H}_{114}\text{Cu}_3\text{N}_{12}\text{P}_3\text{F}_{18}) \cdot 3\text{CH}_3\text{CN}$ : *M* = 8 945.86, cubic, *a* = 36.533(5) Å, *U* = 48759(12) Å<sup>3</sup>,  $\theta$  1.6–23.3°, *Z* = 4, *D<sub>c</sub>* = 1.219 Mg m<sup>-3</sup>, space group *I213* (no. 199), Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å),  $\mu(\text{Mo-K}\alpha)$  = 6.33 cm<sup>-1</sup>, *F*(000) = 18 504, *T* = 200 K, 11702 independent reflections [*I* > 2.0 $\sigma$ (*I*)]. Refinement converged at a final *R* = 0.1098, *wR* = 0.2730. Minimum and maximum final residual electron density 0.57 and 1.41 e Å<sup>-3</sup>. In both structures the hexafluorophosphate anions were disordered and crystallographically imperfect models were adopted to allow subsequent refinement of the cations of interest.

Data collected were measured on a STOE IPDS Image Plate diffractometer; structure solution SHELXL-97, SHELXS-97. CCDC 182–1115. See <http://www.rsc.org/sappdata/cc/1999/195/> for crystallographic files in .cif format.

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