

Diastereoselective formation of *P* and *M* dicopper(i) double helicates with chiral 2,2':6',2''-terpyridines

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Chiral 2,2':6',2''-terpyridines bearing bornyl groups in the 6-position are prepared; these ligands preferentially form *P* or *M* dinuclear double helicates upon coordination to copper(i) which have been structurally characterised.

Oligopyridines and oligopyridine metal-binding domains are a recurrent feature in metallosupramolecular chemistry.¹ It is now well established that the higher oligopyridines can give multiple helical transition-metal complexes² and that 2,2':6',2''-terpyridine is a prototype ligand which forms dicopper(i) double helicates.³ We have recently addressed questions of directionality within helicates assembled from asymmetric ligand threads⁴ and now extend these studies to the diastereoselective formation of helicates from chiral ligands. Although pre-organised chiral ligands bearing multiple oligopyridine domains have been shown to lead to diastereomeric excesses of multiple helicates,^{5,6} this report provides the first fully characterised example of high diastereomeric discrimination in a multi-component self-assembly process.

A pair of enantiomeric 2,2':6',2''-terpyridines, L¹ and L², was obtained from the reaction of 6-bromo-6''-methyl-2,2':6',2''-terpyridine⁷ with the sodium salts of (1*S*)-(–) or (1*R*)-(+)-borneol (prepared *in situ* by reaction of the appropriate alcohols with sodium hydride) in *N,N*-dimethylformamide in 52 and 58% yield respectively. These reactions are stereoretentive and allow the facile and selective introduction of functionality from the chiral pool.

The coordination of 2,2':6',2''-terpyridines to copper(i) in the absence of other good ligands yields dinuclear double-helical [Cu₂L₂]²⁺ species.³ With the new chiral ligands there are a number of possible double helicates (Fig. 1). Firstly, head-to-head (HH) or head-to-tail (HT) isomers might be expected. Secondly, each double helix is itself chiral and might possess a

P or an *M* conformation. When chiral ligands are involved, the (S*)(S*)-(*M*) and (S*)(S*)-(*P*) forms are diastereomers. We hoped that the energy differences between the diastereomers might lead to partial or complete selectivity for the *P* or *M* forms.

The reaction of L¹ or L² with [Cu(MeCN)₄][PF₆]₂ in acetonitrile resulted in the formation of orange-red solutions from which orange solids were precipitated by the addition of [NH₄][PF₆]. Mass spectrometric analysis supported the formulation of these solids as [Cu₂L₂]²⁺[PF₆]₂ or [Cu₂L₂]²⁺[PF₆]₂ respectively. The ¹H NMR spectra of CD₃CN solutions of the two complexes were similar and indicated, in each case, the presence of two solution species present in a ratio of 6.5:1. Molecular modelling studies using parameters derived from structurally characterised [Cu₂L₂]²⁺ double helicates with 2,2':6',2''-terpyridines³ indicated that the enantiomeric (*S*)(*S*)-(*M*)-HT and (*R*)(*R*)-(*P*)-HT helicates should be stabilised with respect to the diastereomers (*R*)(*R*)-(*M*)-HT and (*S*)(*S*)-(*P*)-HT by about 10 kcal mol⁻¹ (1 cal = 4.184 J). Furthermore, the modelling studies indicated that the HH isomers would lie very much higher in energy.

Recrystallisation of the crude [Cu₂L₂]²⁺[PF₆]₂ or [Cu₂L₂]²⁺[PF₆]₂ complexes from acetonitrile by the diffusion of diethyl ether vapour into the solution yielded X-ray quality crystals of compounds shown by ¹H NMR spectroscopy to contain only the major isomer in each case. Each of the compounds crystallised as bis(acetonitrile) solvates in the non-centrosymmetric space group *P*2₁2₁2 and the molecular structures of [Cu₂L₂]²⁺[PF₆]₂·2MeCN and [Cu₂L₂]²⁺[PF₆]₂·2MeCN are presented in Fig. 2(a) and (b).§ The X-ray structural determination confirms the formation of the HT isomers in the solid state and furthermore shows the diastereoselective formation of the predicted (*S*)(*S*)-(*M*)-HT isomer of the [Cu₂L₂]²⁺ cation and the (*R*)(*R*)-(*P*)-HT isomer of the [Cu₂L₂]²⁺ cation. The solid-state structures of the two enantiomers are identical within experimental error and the gross structural features of the complex cations closely resemble those of previously characterised [Cu₂L₂]²⁺ double helicates with 2,2':6',2''-terpyridines³ although the pitch is dependent on the intermetallic separation; in this case, the copper–copper distance in each of the cations is 2.688(1) Å. The precise coordination geometry in copper(i) tpy double helicates is rather variable,³ but in this case the two copper centres are equivalent and best described as two-coordinate [Cu(1)–N(1) 1.947(3) Å, Cu(1)–N(3') 1.940(3) Å, N(1)–Cu(1)–N(3') 165.2(1)°]. Each copper exhibits longer contacts to N(2) and N(2') [2.431(2), 2.317(3) Å].

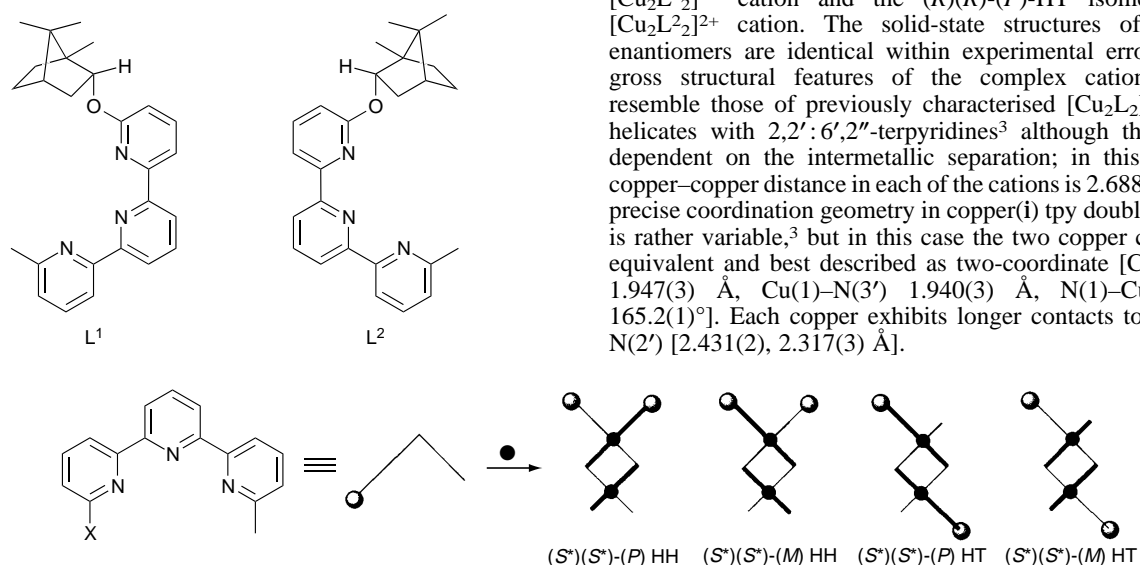


Fig. 1 The formation of a dinuclear double helicate from the reaction of a chiral 2,2':6',2''-terpyridine with copper(i) can yield a pair of diastereomeric HH and a pair of diastereomeric HT compounds. S* denotes homochiral compounds [*i.e.* either (*S,S*) or (*R,R*)]; ● = Cu^I.

The formation of the HT rather than HH isomers minimises steric interactions between the chiral substituents. The origin of the diastereoselectivity is not so easy to understand; no single interaction appears to be responsible, and, in contrast to previous studies⁶ there is no obvious steric destabilisation of the less-favoured helicate. We are currently further studying the origin of this selectivity.

In conclusion, we have unambiguously demonstrated the diastereoselective formation of *P* or *M* helicates upon the coordination of chiral helicands to copper(I). We are currently extending these studies to increase the diastereoselectivity and to observe similar effects with chiral derivatives of higher oligopyridines.

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Footnotes

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‡ Modelling studies were initially made using the previous structural determinations³ as a starting point. Once the structural determinations made in this paper had been made, the Cu–Cu distances were constrained to 2.70 Å. Calculations were made using the MM2 implementation in Chem 3D Pro version 3.5 or the Universal Force Field Implemented in Molecular Simulations Cerius²™ software.

§ *Crystal data:* [Cu₂L¹]₂[PF₆]₂·2MeCN: orange crystal, C₅₆H₆₄Cu₂F₁₂N₈P₂, *M* = 1298.18, orthorhombic, space group *P*2₁2₁2, *a* = 8.475(1), *b* = 28.268(2), *c* = 12.286(1) Å, *U* = 2943.5(3) Å³, *Z* = 2, *D*_c = 1.46 g cm⁻³, *F*(000) = 1336, λ = 1.54180 Å, μ(Cu-Kα) 2.14 mm⁻¹. Intensity data were collected by the ω–2θ scan method (4.2 < 2θ < 154°); for a crystal of dimensions 0.10 × 0.50 × 0.65 mm at room temp.; of 3250 (3238 independent) reflections measured, 2790 [*I* ≥ 3σ(*I*)] were used in the structure solution. The structure was solved by direct methods using SIR92 (A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435) and refined using CRYSTALS (D. J. Watkin, J. R. Carruthers and P. Betteridge, Chemical Crystallography Laboratory, Oxford, UK) to give final *R* and *R*_w values of 0.0513 and 0.0570 respectively (Chebychev polynomial weighting; J. R. Carruthers and D. J. Watkin, *Acta Crystallogr., Sect. A*, 1979, **35**, 698).

[Cu₂L²]₂[PF₆]₂·2MeCN: orange crystal, C₅₆H₆₄Cu₂F₁₂N₈P₂, *M* = 1298.18, orthorhombic, space group *P*2₁2₁2, *a* = 8.475(1), *b* = 28.231(2), *c* = 12.284(1) Å, *U* = 2932.7(4) Å³, *Z* = 2, *D*_c = 1.47 g cm⁻³, *F*(000) = 1336, λ = 1.54180 Å, μ(Cu-Kα) 2.15 mm⁻¹. Intensity data were collected by the ω–2θ scan method (4.2 < 2θ < 154°); for a crystal of dimensions 0.10 × 0.45 × 0.65 mm at room temp.; of 3188 (3174 independent) reflections measured, 2444 [*I* ≥ 3σ(*I*)] were used in the structure solution. The structure was solved by direct methods using SIR92 and refined using CRYSTALS to give final *R* and *R*_w values of 0.0679 and 0.0626 respectively (Chebychev polynomial weighting).

Atomic coordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/334.

References

- 1 J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995; E. C. Constable, in *Comprehensive Supramolecular Chemistry*, ed. J.-M. Lehn, Elsevier, 1996, vol. 9; E. C. Constable and D. R. Smith, *The Polymeric Materials Encyclopedia*, CRC Press, Boca Raton, FL, 1996, p. 4237.
- 2 E. C. Constable, *Tetrahedron*, 1992, **48**, 10 013; *Prog. Inorg. Chem.*, 1994, **42**, 67.
- 3 E. C. Constable, A. J. Edwards, M. J. Hannon and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1994, 1991; K. T. Potts, M. Keshavarz-K, F. S. Tham, H. D. Abruña and C. R. Arana, *Inorg. Chem.*, 1993, **32**, 4450.
- 4 E. C. Constable, M. Neuburger, D. R. Smith and M. Zehnder, *Chem. Commun.*, 1996, 1917; E. C. Constable, F. R. Heirtzler, M. Neuburger and M. Zehnder, *Supramol. Chem.*, 1995, **5**, 197; *Chem. Commun.*, 1996, 933; *J. Am. Chem. Soc.*, in the press.
- 5 C. R. Woods, M. Benaglia, F. Cozzi and J. S. Siegel, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1830.
- 6 W. Zarges, J. Hall and J.-M. Lehn, *Helv. Chim. Acta*, 1991, **74**, 1843.
- 7 This compound was prepared by an analogous route to that reported for 6-bromo-2,2':6',2''-terpyridine: R. Chotalia, E. C. Constable, M. J. Hannon and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1995, 3571.

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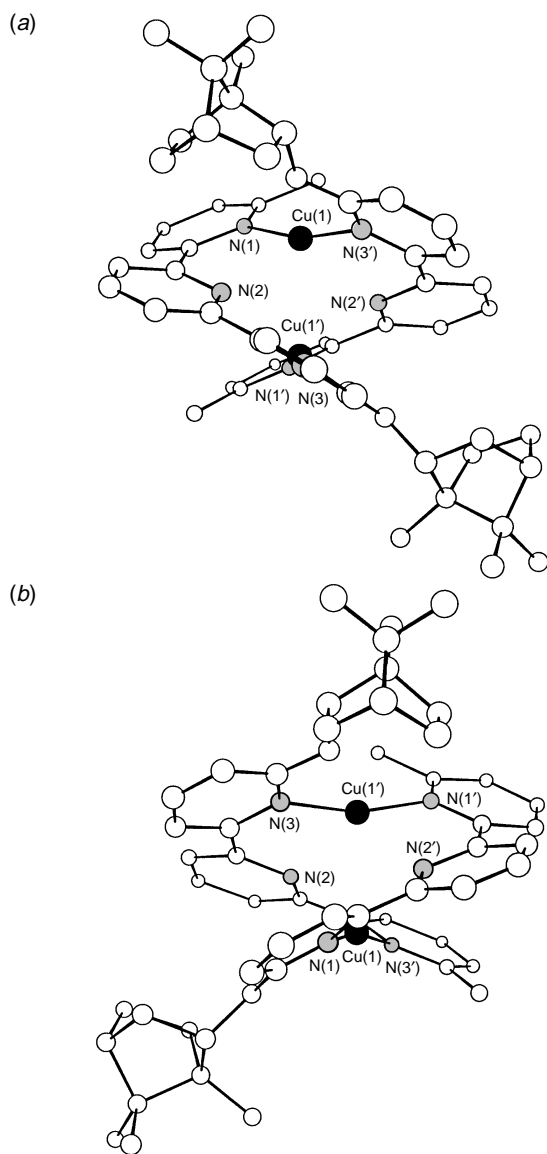


Fig. 2 Crystal and molecular structures of (a) the double-helical cation with *M* chirality in the lattice of [Cu₂L¹]₂[PF₆]₂·2MeCN and (b) the double-helical cation with *P* chirality in the lattice of [Cu₂L²]₂[PF₆]₂·2MeCN