Selectivity in the self-assembly of directional helicates

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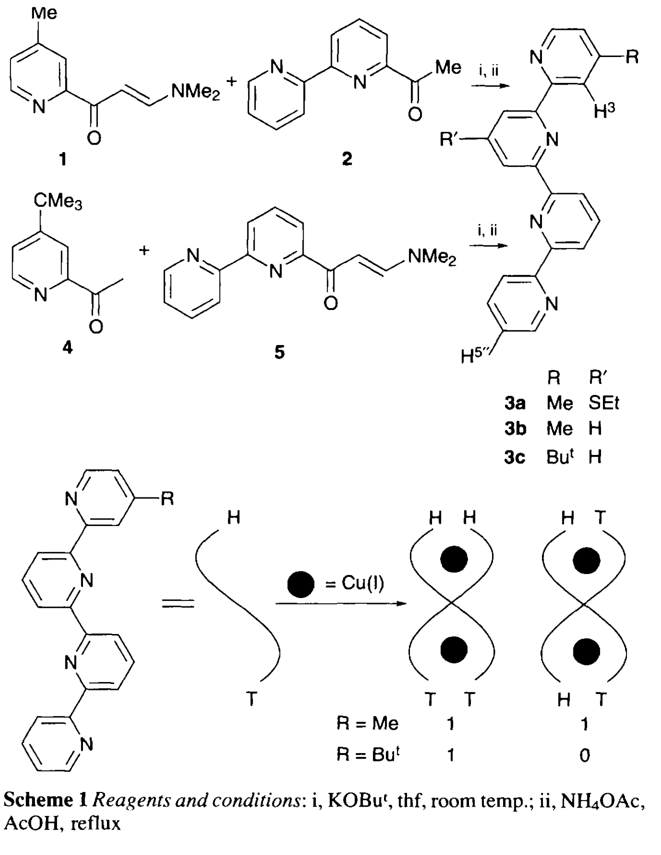
The reaction of the asymmetric 2,2′:6′,2″:6″,2‴-quaterpyridine 3c with $[Cu(MeCN)_4][PF_6]$ gives exclusively the head-to-head isomer of the double helical species $[Cu_2(3c)_2]^{2+}$.

Morphological variation within supramolecular arrays may be achieved through the transfer of structural information between the components.[1] In metallosupramolecular chemistry steric and electronic features of multidentate ligands may be exploited and transmitted through the metal centres to which they are bound. This methodology has recently been utilised in the preparation of diastereogenic mononuclear[2] and dinuclear[3] metal complexes of diimine ligands. We have developed this theme in the assembly of double-helical dicopper complexes of asymmetrically substituted 2,2′:6′,2″:6″,2‴-quaterpyridine (qtpy) ligands on the basis that interactions between the ligand strands might favour the specific formation of the head-to-head (HH) or head-to-tail (HT) conformational isomers.[4] Our preliminary studies with ligand **3a** were disappointing and only a modest excess of one of the conformational isomers was observed.[5] We now describe the preparation of two new ligands and show that one of them gives a single conformational isomer of the dinuclear double helix upon interaction with copper(I).

The asymmetric ligand strands **3b** and **3c** were prepared using extensions of standard methodology.[6] The reaction of the *N,N*-dimethyl enaminone **1** with 6-acetyl-2,2′-bipyridine **2** in the presence of base followed by cyclisation with NH_4OAc gave **3b** in 9.3% yield. The inverted strategy was adopted for the synthesis of **3c**, in which the acetylpyridine **4** was reacted with the enaminone **5** under similar conditions to give the desired compound in 18% yield. Inseparable mixtures of products were obtained in attempts to obtain **3b** from the reaction of **5** with 2-acetyl-4-methylpyridine under similar conditions. The ligand syntheses are presented in Scheme 1.



Scheme 1 *Reagents and conditions*: i, $KOBu^t$, thf, room temp.; ii, NH_4OAc, AcOH, reflux

The treatment of methanolic solutions of **3b** or **3c** with an excess of $[Cu(MeCN)_4][PF_6]$ under an atmosphere of argon resulted in the formation of dark brown solutions from which the brown complexes $[Cu_2L_2][PF_6]_2$ (L = **3b** or **3c**) could be obtained. These complexes were obtained pure as reasonable quality crystals by the diffusion of diethyl ether vapour into acetonitrile solutions. Analytic and mass spectrometric data were fully in accord with the sole formation of these dinuclear species.†

The ^1H NMR spectra of crude and recrystallised samples of these complexes were similar and part of the aromatic region of a CD_3CN solution of each is presented in Fig. 1. The most important feature to note is that in the spectrum of $[Cu_2(\mathbf{3b})_2]^{2+}$ *two* equal intensity doublet resonances (δ 7.69, 7.70) are observed for H^6 whilst for $[Cu_2(\mathbf{3c})_2]^{2+}$ a single doublet at δ 7.76 is observed. In each case the observed coupling constant of

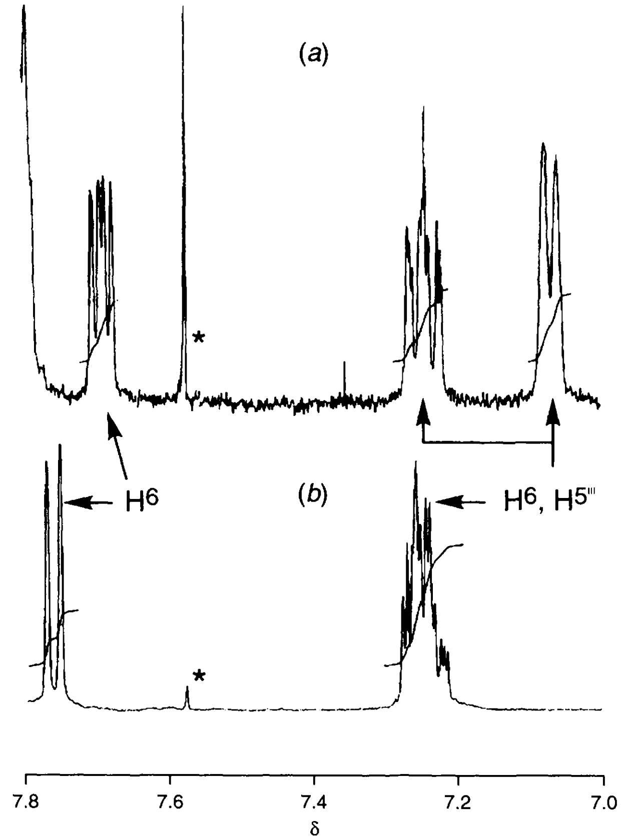


Fig. 1 Partial 300 MHz ^1H NMR spectra of CD_3CN solutions of (*a*) $[Cu_2(\mathbf{3b})_2][PF_6]_2$ and (*b*) $[Cu_2(\mathbf{3c})_2][PF_6]_2$ showing the presence of two conformational isomers in the first case and only one in the second

5.5 Hz allows unambiguous assignment of the doublet to an H^6. Full assignments were made on the basis of COSY and NOESY spectroscopy and by comparison with the parent qtpy complexes and those of **3a**. These data suggest that whilst a 1 : 1 mixture of HH and HT conformational isomers is present in $[Cu_2(\mathbf{3b})_2]^{2+}$, a single isomer is present in $[Cu_2(\mathbf{3c})_2]^{2+}$. Further support for this comes from the observation that *two* methyl resonances (in a 1 : 1 ratio) are observed for $[Cu_2(\mathbf{3b})_2]^{2+}$.

Molecular modelling provided no convincing evidence for the favouring of one of the two configurational isomers of $[Cu_2(\mathbf{3c})_2]^{2+}$ and we have made numerous attempts to obtain good quality crystals of the compound from a wide variety of solvents and solvent mixtures. The best crystals obtained allowed us to determine a partial structure ($R \approx 0.15$) but problems of crystal decomposition and lattice solvent loss and disorder prevented a full refinement. However, the gross structural features of the cation are apparent. As expected, the dinuclear double-helical cation is present in which the gross structural features very closely resemble those of $[Cu_2(qtpy)_2][BF_4]_2$.[7] The most important feature is that the cation uniquely exhibits the single HH configuration (Fig. 2).

Powder diffraction studies of powdered single crystalline material and the bulk microcrystalline sample revealed no differences in their scattering patterns. Thus, the bulk solid state material corresponds to the single conformer observed in the partial structural determination. Furthermore, the ^{1}H NMR spectra of solutions of the bulk material and of the single crystals were identical and showed only a single (presumably HH) isomer.

The directional specificity in these systems is clearly very subtle. Modelling studies reveal that the HH preference with the A-ring substituted compound **3c** arises from short contacts between the *tert*-butyl substituents in the HT isomer (H···H ≈ 2.4 Å). The introduction of alkylthio substituents on the B or C rings has been shown to increase the pitch of the helix.[8] As a result of this increase in pitch, the A-ring *tert*-butyl substituents in the HT isomer of our prototype complex $[Cu_2(\mathbf{3a})_2]^{2+}$ are relieved (closest contacts > 3.4 Å) accounting for the mixture of isomers in this case.

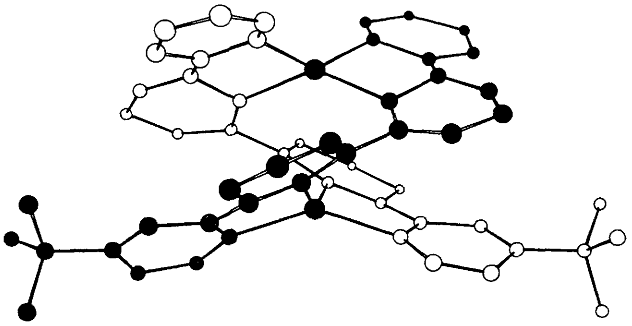


Fig. 2 A representation of the HH isomer of the $[Cu_2(\mathbf{3c})_2]^{2+}$ cation as found in the solid-state structure of $[Cu_2(\mathbf{3c})_2][PF_6]_2$. The ligand strands have been shaded differently to emphasise the helical structure.

In conclusion, we have shown that ligand **3c** gives a single conformational HH isomer of the double helicate $[Cu_2(\mathbf{3c})_2]^{2+}$ upon interaction with copper(I). No other asymmetric qtpy ligand studied to date shows a similar selectivity. We are currently extending the series of ligand strands in an attempt to further probe the origins of this selectivity.

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Footnote

† FAB-MS spectra (NBA matrix): $[Cu_2(\mathbf{3b})_2][PF_6]_2$: *m/z* 778, 776, 774 $\{Cu_2(\mathbf{3b})_2\}$, 389, 387 $\{Cu(\mathbf{3b})\}$; $[Cu_2(\mathbf{3c})_2][PF_6]_2$: *m/z* 1007, 1005, 1003 $\{Cu_2(\mathbf{3c})_2(PF_6)\}$, 862, 860, 858 $\{Cu_2(\mathbf{3c})_2\}$, 431, 429 $\{Cu(\mathbf{3c})\}$. Microanalytical results were obtained within acceptable limits for $[Cu_2(\mathbf{3b})_2][PF_6]_2$ and $[Cu_2(\mathbf{3c})_2][PF_6]_2$.

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