This facile interconversion of dinuclear double helicates and side-by-side species: a reprogrammable ligand with potential sensor applications†

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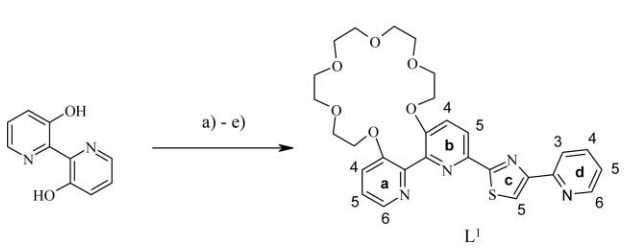
The ligand L^1 forms a dinuclear double helicate with Cu^+ but upon addition of Ba^{2+} to the system a side-by-side species is formed both in solution and in the solid state; in the presence of Na^+ both the helicate and the side-by-side species are formed in roughly equal amounts in solution.

The self-assembly of metallosupramolecular helicates from transition metal ions and multidentate N-donor ligands has gained considerable attention in recent years.[1] Recently we have demonstrated that the formation of helicate species can be controlled by a mixture of allosteric and electrostatic factors. For example, we have shown that the ditopic ligand L which contains a potentially tetradentate pyridyl-thiazole ligand chain and an additional "external" crown ether binding site connecting the two ligand halves can be reprogrammed by addition of s-block metal ions. Thus upon reaction with Hg^{2+} the helicate species $[Hg_2(L)_2]^{4+}$ is formed. However, upon addition of either Sr^{2+} or Ba^{2+} metal ions a mononuclear species results.[2] This change in the binding sites also changes the specificity towards different metal ions.[3] Furthermore, formation of a helicate from Cu^{2+} with a similar type of ligand but which contains a potentially hexadentate pyridyl-thiazole ligand chain results in a system where the pitch length can be tuned dependent upon the size and charge of the s-block metal ions present within the crown ether host.[4] In this paper we describe the first example of a ligand chain which forms a dinuclear double helicate with Cu^+ but upon addition of Ba^{2+} to the crown ether moiety forms a side-by-side species both in solution and in the solid state. In the presence of Na^+ both species are formed in roughly equal amounts in solution. The accompanying colour changes associated with the different species are striking, leading to possible colorimetric sensor applications.

The ditopic ligand L^1 was prepared from 2,2′-bipyridine-3,3′-diol as outlined in Scheme 1. This ligand has a potentially tetradentate pyridyl-thiazole/bipyridyl ligand chain with an "external" crown ether binding site bridging the bipyridyl moiety. Reaction of L^1 with $[Cu(NCMe)_4]PF_6$ in acetone afforded a dark red solution and ESI-MS suggested the formation of a dinuclear species with an ion at *m*/*z* 1372 corresponding to $[Cu_2(L^1)_2]PF_6^+$. Slow diffusion of CH_3CO_2Et into an acetone solution of the complex, in the presence of excess NH_4BPh_4, produced deep red crystals for which single crystal diffraction studies established the formation of a dinuclear double helicate structure $[Cu_2(L^1)_2]^{2+}$ **1** (Fig. 1).‡ In the crystal, the ligand partitions into two bis-bidentate binding domains, comprising pyridyl-thiazole and bipyridyl units, with both Cu^+ ions coordinated by two bridging ligands in a "head-to-tail" double stranded helicate arrangement. Both of the copper centres have a distorted tetrahedral geometry that arises from coordination of the pyridyl-thiazole "head" of the first ligand and the bipyridyl N-donor "tail" of the second ligand. A consequence of this binding mode is that it places the two crown ether moieties on the same side of the molecule, leading to the formation of a hydrophilic cavity or "molecular cup" which it was anticipated might act as an efficient cation receptor site.



Scheme 1 *Reagents*: yields: a) penta(ethylene glycol) di-*p*-toluenesulfonate, DMF, NaH: 69%; b) mCPBA (0.9 equiv.), CH_2Cl_2: 56%; c) TMSCN, PhCOCl, CH_2Cl_2: 80%; d) H_2S, Et_3N, EtOH: 87%; e) α-bromoacetylpyridine, EtOH: 81%.

Treatment of a dark red MeCN solution of $[Cu_2(L^1)_2]^{2+}$ with excess $Ba(ClO_4)_2$ afforded a pale yellow solution. The ESI-MS

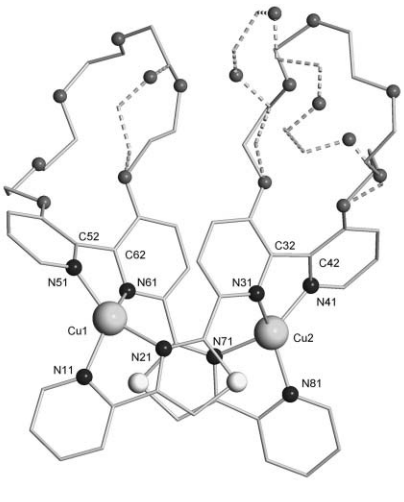


Fig. 1 Crystal structure of the helicate cation **1** $[Cu_2(L^1)_2]^{2+}$.

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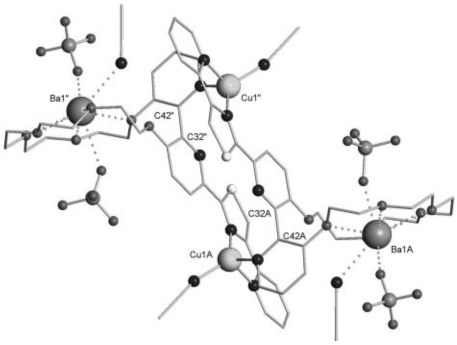

Fig. 2 Crystal structure of the side-by-side cation **2** $[Cu_2(L^1)_2Ba_2](ClO_4)_4(MeCN)_4{}^{2+}$.

showed an ion at *m*/*z* 949 corresponding to $[Cu_2(L^1)_2Ba_2](ClO_4)_4{}^{2+}$, thus confirming that a dinuclear metal structure is retained whilst providing evidence for the incorporation of Ba^{2+} ions in the crown ether cavities. Crystallisation of the solution by slow diffusion of CH_3CO_2Et gave pale yellow crystals, which X-ray analysis revealed had the dinuclear structure $[Cu_2(L^1)_2Ba_2]^{6+}$ **2** (Fig. 2).‡ The solid-state structure of **2** retains the head-to-tail arrangement of ligands found in the precursor **1** and the pyridyl-thiazole ends of the ligand chains still act as bidentate donors to the Cu centres. However, in marked contrast to **1**, the bipyridyl units in **2** are twisted about their backbones (C–N–N–C dihedral angle *ca.* 81°) such that only the terminal pyridyl units coordinate to the Cu centres. The Cu atoms in **2** retain a pseudo tetrahedral geometry by coordination of a molecule of MeCN and the resultant “opened out” geometry of **2** may be best described as a side-by-side complex. Both crown ether moieties incorporate Ba^{2+} ions that are bound by five of the six oxygen atoms of the crown and further stabilised by interaction with two perchlorate counteranions and a molecule of MeCN. The related reaction of $[Cu_2(L^1)_2]^{2+}$ with excess $Na(ClO_4)$, following crystallisation, afforded pale yellow crystals of $[Cu_2(L^1)_2Na_2]^{4+}$ **3**. The crystal structure of **3** (not shown) is effectively isostructural with the Ba^{2+} complex **2**, with Na^+ ions replacing Ba^{2+} ions in the crown ether cavities. Conversion of the helicate **1** to the side-by-side complexes **2** and **3** on addition of Ba^{2+} or Na^+, respectively, may be primarily ascribed to an allosteric effect. Coordination of the s-block cations in the crown ether moieties tends to impose a non-coplanar geometry on the bipyridyl ligands (C–N–N–C dihedral angle *ca.* 81°) making it energetically less favourable for them to act as bidentate donors. As a result the crown ether domain is allosterically reprogrammed by addition of s-block cations and a side-by-side geometry is observed for the complexes in the solid state.

The interconversion of helicate and side-by-side structures does not require ligand dissociation and could occur *via* an intra-molecular rearrangement involving an untwisting of the helicate structure with concomitant dissociation of two pyridyl donor ligands. As such, this is likely to be a low energy process and both ^1H NMR and UV/VIS spectroscopy provide evidence for facile interconversion of helicate and the side-by-side species in solution. Thus, addition of an excess of Ba^{2+} cations (3 equivalents) to a MeCN solution of **1** completely quenches the deep red colour associated with the helicate affording a pale yellow solution.[5] This suggests that both in solution and in the solid state, the pale yellow Ba^{2+} complex retains a side-by-side structure. In contrast, addition of excess Na^+ ions to a MeCN solution of **1** only partially quenches the deep red colour ascribed to the helicate, which indicates that in this case there may be an equilibrium in solution between red helicate and pale yellow side-by-side species. Consistent with these observations, a ^1H NMR spectrum (MeCN, 295 K) of the Ba^{2+} complex **2** shows 10 aromatic resonances as expected for a C_i symmetric side-by-side complex. The latter resonances are reasonably sharp at room temperature and there is no evidence for other species or exchange processes occurring in solution.

Interestingly, the ^1H NMR spectra in MeCN of the Na^+ complex **3** and of its precursor **1**, are both very broad at room temperature, which suggests that exchange between helicate and side-by-side species is taking place on the NMR timescale. At low temperature (MeCN, 243 K) the exchange is to some extent frozen out and the ^1H NMR spectra of **1** and **3** are sharper. The ^1H NMR spectrum of **3** reveals *two* sets of ten, partially overlapping, resonances in the aromatic region which are attributed to the presence of both helicate and side-by-side species in equal amounts. The sharper signals can be fully assigned by a combination of chemical shift and 2D NMR techniques. These signals correspond to the helicate species on the basis of their relatively high field shift, common to helicate moieties due to shielding by aromatic ring currents. The remaining set of 10 broader signals are attributed to the side-by-side structure. In contrast the ^1H NMR spectrum of **1** is still quite broad even at 243 K and the signals are correspondingly difficult to assign. However, careful comparison with the spectrum of **3** does indicate that *two* sets of 10 signals are present with one set of signals substantially less intense. Thus it is clear that the two species are in equilibrium. In the case of **1** the equilibrium favours the helicate (helicate : side-by-side 3 : 1) whilst excess Na^+ ions shift the equilibrium in favour of the side-by-side structure (helicate : side-by-side 1 : 1).

In summary, these results demonstrate that even in the absence of s-block cations a MeCN solution of **1**, which has a helicate structure in the solid state, contains both helicate and side-by-side species, which interconvert on the NMR time scale at room temperature. In the presence of Na^+ ions this equilibrium is allosterically driven towards the side-by-side species, whilst addition of highly charged s-block cations such as Ba^{2+}, which bind very strongly to the crown ether ligands, further shifts the equilibrium so that only the side-by-side structure **2** is present in both the solid state and solution. The marked colour changes which occur on addition of s-block cations demonstrate the proof of principle that these and related systems have potential for cation sensing applications. Further investigations into their ability to act as sensors are ongoing.

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Notes and references

‡ X-Ray single-crystal diffraction data were collected on a Bruker PROTEUM-CCD area detector diffractometer under a stream of cold nitrogen. *Crystal data for* **1**$(BPh_4)_2$; M = 1866.74, Monoclinic, $P2_1/c$, a = 14.3802(3), b = 20.4058(4), c = 37.9889(7) Å, β = 94.8080(10)° V = 11108.2(4) Å^3, Z = 4, ρ_c = 1.116 Mg m^{-3}, $F(000)$ = 3904, $\mu(Cu_{K\alpha})$ = 1.275 mm^{-1}, T = 100 K. A total of 52309 reflections were measured in the range $2.33 \leqslant \theta \leqslant 70.40°$ (hkl range indices $-15 \leqslant h \leqslant 15$, $-23 \leqslant k \leqslant 24$,

$-44 \leqslant l \leqslant 38$), 18266 independent reflections ($R_{int} = 0.0599$). The structure was refined on F^2 to $R_w = 0.3838$ $R = 0.1439$ (9000 reflections with $I > 2\sigma(I)$) and GOF = 1.346 on F^2 for 741 refined parameters, largest difference peak and hole 1.630 and −1.519 eÅ^{-3}.The crystal suffered from rapid solvent loss on removal from the mother liquor, resulting in extensive structural disorder and subsequent weak high angle data. Accordingly, only the Cu, C, N and S atoms comprising the core of the complex moiety were assigned anisotropic displacement parameters and refined without positional restraints. The remaining fragments which were located in the electron density map (crown ethers and tetraphenyl borate anions) were very poorly resolved. Despite exhaustive attempts at modelling the disorder in the crown ethers and tetraphenyl borate anions, the poor quality of the data precluded complete parameterisation. Accordingly, the refinement converged to a rather unsatisfactory final *R*-value of *ca.* 14% and the resulting model does not merit detailed analysis beyond establishing the basic atomic connectivity of the complex cation. Solutions obtained from data collections on several different crystals were in agreement, but all suffered from similar problems. CCDC reference number 285237. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b600597g *Crystal data for* **2**$(ClO_4)_6 \cdot 2MeCN$; $M = 2380.07$, Triclinic, $P\bar{1}$, $a = 11.5874(7)$, $b = 12.9425(8)$, $c = 16.1980(10)$ Å, $\alpha = 86.496(2)$, $\beta = 88.891(2)$, $\gamma = 66.515(2)^\circ$ $V = 2223.8(2)$ Å^3, $Z = 1$, $\rho_c = 1.777$ Mg m^{-3}, $F(000) = 1196$, $\mu(Cu_{K\alpha}) = 10.266$ mm^{-1}, $T = 100$ K. A total of 17363 reflections were measured in the range $2.73 \leqslant \theta \leqslant 70.15^\circ$ (hkl range indices $-12 \leqslant h \leqslant 13$, $-15 \leqslant k \leqslant 15$, $-19 \leqslant l \leqslant 18$), 7570 independent reflections ($R_{int} = 0.0440$). The structure was refined on F^2 to $R_w = 0.108222$ $R = 0.0414$ (6354 reflections with $I > 2\sigma(I)$) and GOF = 0.916 on F^2 for 588 refined parameters, largest difference peak and hole 1.342 and −0.849 eÅ^{-3}. CCDC reference number 285238. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b600597g

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5 The absorbance occurs <350 nm, well within the ligand absorption region. Addition of either Na^+ or Ba^{2+} metal ions to **1** results in a decrease in the absorption intensity in this region with the effect greatest for Ba^{2+}. The dark red colour observed is presumably due to MLCT to the π* orbital of the planar bipyridine, which is usual for a Cu(I) system coordinated by bipyridine ligand. Upon reprogramming of the ligand strand the torsion angle of the bipyridine unit increases to 82°; with the bipyridine unit no longer planar and acting as a mono-dentate ligand the MLCT is quenched.