High-yield Synthesis of a Dicopper(I) Trefoil Knot Containing 1,3-Phenylene Groups as Bridges between the Chelate Units

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A dicopper(I) trefoil knot is synthesized in 30% yield by the use of 1,3-phenylene spacers, the double stranded helical precursor complex being formed quantitatively.

Molecular knots have been mentioned in the chemical literature as hypothetical objects several decades ago.[1] The synthesis of the first trefoil knot was described a few years ago,[2] but in very poor yield (3%). Some improvements were recently reported,[3] the best yields obtained still being modest (8%). We now would like to report that, by optimizing some structural parameters, gram scale preparation of knots is possible (yield of ≈30%). In addition, the dinuclear double-stranded helical complex utilized as precursor and the dicopper(I) knot obtained display unexpected properties originating from a very tight and rigid structure combined with a short Cu···Cu distance.

If numerous double-stranded helical complexes have been described in recent years,[4] very few contain chemical groups compatible with the harsh reaction conditions required in order to achieve the synthesis of knots. In fact, high yield formation of helical complexes from the metals and the strands is an essential requirement for an efficient preparation of knotted systems.

We thus explored various structures, especially by modifying the nature of the linker between the two 1,10-phenanthroline chelates. In view of the success recently reported by others when using 1,3-phenylene as spacer for constructing dinuclear helical complexes,[5,6] we investigated the potentialities of this linker. In addition, this spacer is very appealing owing to its expected chemical robustness and ease of introduction following our methodology.[7]

The organic precursors as well as the reactions leading to the dicopper(I) trefoil knot are represented in Scheme 1. **1a** was obtained in 55% yield by reacting 2-(*p*-anisyl)-1,10-phenanthroline[3] with 1,3-dilithiobenzene in THF, followed by hydrolysis and MnO_2 oxidation.

1b was prepared from **1a** in 84% yield (HCl–pyridine at 210 °C for 3 hours).†

The use of 1,3-phenylene as spacer group proved to be extremely beneficial. First, **1a** was used as a model and was treated with $[Cu(MeCN)_4]PF_6$ in CH_2Cl_2–MeCN (Scheme 1). Preparation of the double-stranded helix **2a**$^{2+}$ turned out to be quantitative. This complex salt could be crystallized from MeCN–toluene and its X-ray crystal structure was solved‡ (Fig. 1).

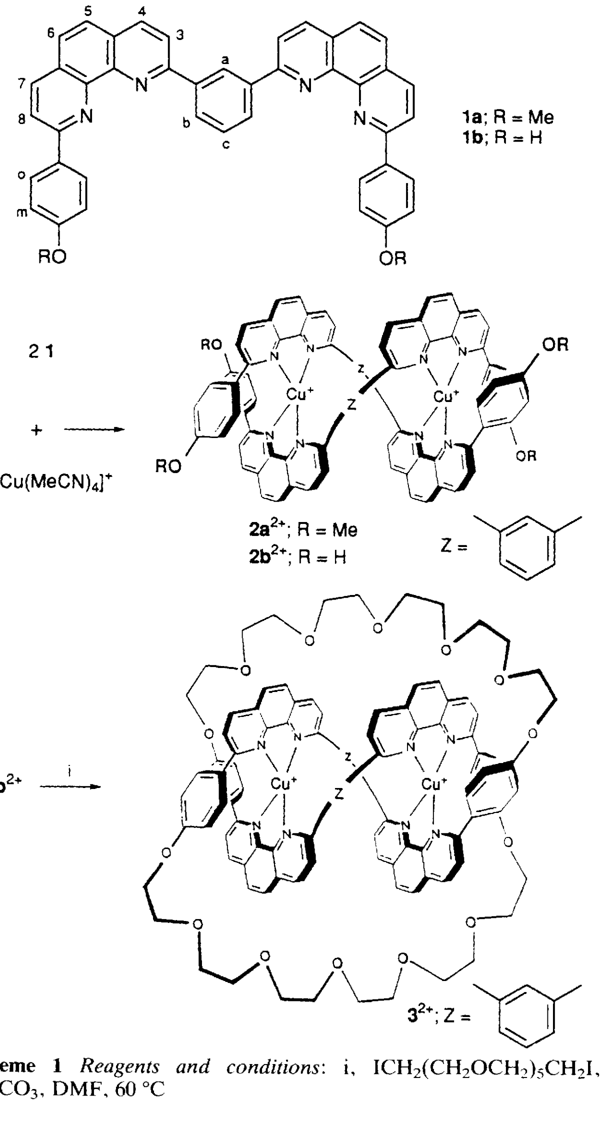
The structure of **2a**$^{2+}$ is nicely wound and is therefore well adapted to the formation of a knot by connecting the appropriate ends of the strands.

Notably, **2a**$^{2+}$ is a rigid and compact edifice, with a much shorter Cu···Cu distance than in previously synthesized knots (4.76 Å *cf.* 6.3 or 7 Å).[8,9] These factors are, of course, very favourable to the successful continuation of the synthesis. Indeed, reaction of **2b**$^{2+}$ (whose structure is certainly very similar to that of **2a**$^{2+}$ as shown by ^1H NMR) with $ICH_2(CH_2OCH_2)_5CH_2I$ and Cs_2CO_3 in DMF at 60 °C afforded a single isolable copper(I) complex (Scheme 1). The dicopper(I) knot **3**$^{2+}$ was isolated in 29% yield after chromatography (Silica gel, CH_2Cl_2–3–5% MeOH).† It forms sea urchin-shaped aggregates of crystals (BF_4^- salt).

Analogous to the previously synthesized dicopper(I) knots,[3] **3**$^{2+}$ shows characteristic ^1H NMR and FAB-MS spectroscopy data.† In particular, some of the aromatic protons of the bischelates are strongly shielded which indicates that **3**$^{2+}$ is compact and that its helical core is geometrically very similar to **2a**$^{2+}$.

An unexpected feature is the strong electronic interaction between both metal atoms, as demonstrated by electrochemical measurements. The cyclic voltammograms (CV) of both **2a**$^{2+}$ and **3**$^{2+}$ are very similar. Each complex shows two distinct waves for the Cu^{II}–Cu^{I} couples with $E^\circ(\mathbf{2a}^{3+}/\mathbf{2a}^{2+})$, $E^\circ(\mathbf{2a}^{4+}/\mathbf{2a}^{3+})$ = +0.69, +0.91 V and $E^\circ(\mathbf{3}^{3+}/\mathbf{3}^{2+})$, $E^\circ(\mathbf{3}^{4+}/\mathbf{3}^{3+})$ = +0.68, +0.92 V *vs.* SCE in MeCN.

The second oxidation process occurs at a surprisingly high potential, indicating the strong effect of the first copper(II) centre which renders oxidation of the second metal difficult. The difference between the redox potential values of the first and the second steps is large (ΔEp = 220 and 240 mV for **2a**$^{n+}$



Scheme 1 *Reagents and conditions*: i, $ICH_2(CH_2OCH_2)_5CH_2I$, Cs_2CO_3, DMF, 60 °C

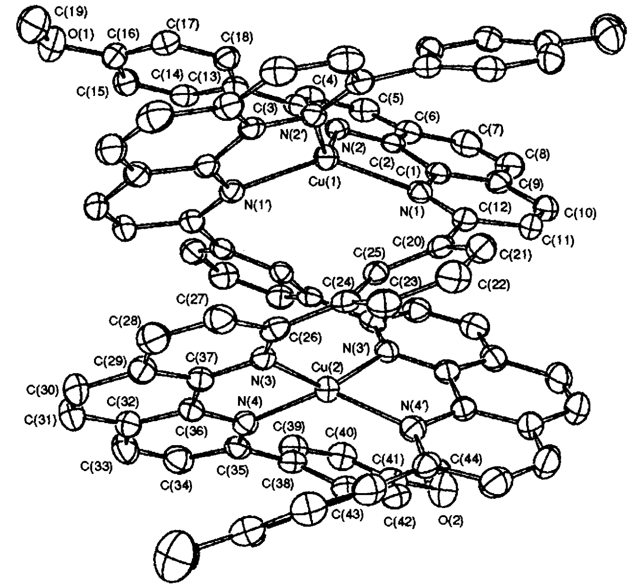


Fig. 1 The crystal structure of the dicopper(I) helical precursor analogue $\mathbf{2a}^{2+}$; ORTEP representation showing the numbering scheme adopted. Selected bond lengths (Å) and angles (°) Cu(1)–N(1) 2.104(4), Cu(1)–N(2) 2.036(4), Cu(2)–N(3) 2.079(4), Cu(2)–N(4) 2.020(4), N(1)–Cu(1)–N(1′) 140.8(2), N(1)–Cu(1)–N(2) 112.2(2), N(2)–Cu(1)–N(2′) 137.9(2), N(3)–Cu(2)–N(3′) 140.4(2), N(3)–Cu(2)–N(4) 112.5(2), N(4)–Cu(2)–N(4′) 136.3(3).

and $\mathbf{3}^{n+}$ respectively) which implies that a mixed-valence state should be isolable.[10,11]

Finally, preliminary demetalation experiments using CN^- as decomplexing agent show that both the acyclic double-stranded helical complex $\mathbf{2a}^{2+}$ and the knot $\mathbf{3}^{2+}$ are extremely inert to decomplexation, again pointing to the tightly packed structure of the core with its many aromatic nuclei, the two strands of the double helix fitting in together while wrapping the two copper(I) centres.

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Footnotes

† All new compounds were fully characterized by FAB–MS or IS–MS, ^{1}H NMR (400 HMz) and electronic spectroscopy. $\mathbf{2a}^{2+}$: $C_{88}H_{60}Cu_2F_{12}N_8O_4P_2$. IS–MS: *m/z* 1564.96 (Calc. for $\mathbf{2a}^{2+}\cdot PF_6^-$: 1565.53) and 710.26 (Calc. for $\mathbf{2a}^{2+}$: 710.28). ^{1}H NMR [$(CD_3)_2SO$] δ 9.55 (s, 2H^a), 8.58 (d, 4 H^7), 8.02 (AB, 8, H^{5,6}), 7.91 (d, 4, H^4), 7.80 (d, 4, H^8), 7.14 (t, 2, H^c), 7.09 (d, 8, H^0), 7.02 (d, 4, H^b), 6.57 (d, 4, H^3), 5.75 (d, 8, H^m), 3.20 (s, 12, OMe). UV–VIS [CH_2Cl_2, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})], 233 (128 700), 252 (118 800), 326 (76 300), 427 sh (3900), 518 (3300).

$\mathbf{3}^{2+}$: $C_{108}H_{96}B_2Cu_2F_8N_8O_{14}$. FAB–MS: *m/z* 1943.4 (Calc. for $\mathbf{3}^{2+}\cdot BF_4^-$: 1943.8) and 928.2 (Calc. for $\mathbf{3}^{2+}$: 928.5). ^{1}H NMR (CD_2Cl_2) δ 9.73 (s, 2, H^a), 8.40 (d, 4, H^7), 7.98 (AB, 8, H^{5,6}), 7.97 (d, 4, H^4), 7.67 (d, 4, H^8), 7.22 (t, 2, H^c), 7.08 (d, 8, H^0), 6.99 (dd, 4, H^b), 6.51 (d, 4, H^3), 5.70 (d, 8, H^m), 4.18–3.20 (m, 48H, polyoxyethylenic chains). UV–VIS [CH_2Cl_2, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})] 237 (118 100), 253 (115 000), 324 (69 200), 425 sh (3700), 519 (2960).

‡ *Crystal data*: $\mathbf{2a}^{2+}$ $C_{88}H_{60}Cu_2F_{12}N_8O_4P_2\cdot 4CH_3CN\cdot C_7H_8\cdot H_2O$, M = 1984.9, red crystals, monoclinic, space group *P*2/*n*, $a = 15.178(4)$, $b = 11.673(3)$, $c = 25.945(7)$ Å, $\beta = 102.63(2)°$, $V = 4485.5$ Å^3, $Z = 2$, $D_c = 1.470$ g cm^{-3}, $\mu = 16.515$ cm^{-1}. A suitable crystal (0.40 × 0.20 × 0.10 mm) was selected on a cool plate and mounted at the end of a glass fibre. 5484 reflections ($\pm h$, $+k$, $+1$) were collected on a Philips PW1100/16 instrument at −100 °C with Cu-graphite monochromated radiation ($\lambda = 1.5418$ Å), θ–2θ flying step-scans, scan speed = 0.020° s^{-1}, scan width = $1 + 0.14 \tan\theta°$, $3 < \theta < 52°$. Three standard reflections measured every hour during the data collection period showed no significant trend. The raw data were converted to intensities and corrected for Lorentz and polarization factors. 3750 reflections with $I > 3\sigma(I)$ were used to determine and refine the structure. The structure was solved by the heavy atom method. Hydrogen atoms were introduced as fixed contributors by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors such as $B_H = 1.3\ B_{eqv}$ (C) Å^2; C_7H_8 and water hydrogen atoms were omitted. Molen on a Vax computer was used for all calculations. Final $R(F) = 0.055$, $R_w(F) = 0.075$, $S = 1.299$ for 599 variables. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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