Resolution, X-ray structure and absolute configuration of a double-stranded helical diiron(II) bis(terpyridine) complex

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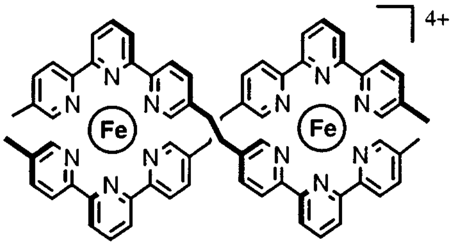
A dinuclear double helix constructed around two iron(II) bis(terpyridine) centres has been resolved by preparative column chromatography, several tens of milligrams of each enantiomer were obtained, with an excellent enantiomeric excess.

In the course of the last 30 years, coordination chemistry has afforded many examples of fascinating architectures based on metal–ligand interactions.[1] Of particular interest are double-stranded helical-type complexes, exemplified by transition-metal helical complexes[2] and molecular knots[3,4] (Fig. 1). Such compounds, with their helical topography and knotted topology, are reminiscent of more complex natural structures such as DNA[4] and proteins.[5] Interestingly, a major chemical difference between a molecular trefoil knot and a double helix is that the knot will retain its chirality even after demetallation.

Helical systems are intrinsically chiral and, in metallo-helical complexes, the coordination of the first metal centre determines the chirality of the neighboring centre.[6] If the ligand is achiral, synthesis will produce a racemic mixture containing the Δ- (right-handed) and the Λ- (left-handed) double helices. In the past few years, the challenge of isolation of the chiral forms of such systems has focussed on resolution[7] or enantioselective synthetic[8,9] techniques. Only a few examples of resolved transition-metal helical complexes[10–12] and one example of a resolved knot[13] have been reported in the literature.

In our search for new optically pure transition-metal based molecular knots, we explored the use of an iron(II) bis-(2,2′:6′,2″-terpyridine) {bis-terpy} fragment in the place of the original copper(I) bis(1,10-phenanthroline) motif. This fragment successfully yielded a racemic mixture of a diiron(II) molecular knot.[14] In order to find a more general resolution method than the diastereoselective crystallization used previously for the dicopper(I) trefoil knot,[13] for the case of the diiron(II) compound we attempted a chromatographic technique which had been recently applied to the resolution of a range of cationic mono-, di- and tri-nuclear transition metal complexes.[11,12,15] Here, we report the resolution of a dinuclear iron(II) double-stranded helix and its absolute configuration determined on the basis of an X-ray crystallographic study.

A racemic mixture of the previously described[13] dinuclear iron(II) double helix $\mathbf{1}^{4+}\cdot 2SO_4^{2-}$ (Scheme 1) was absorbed onto a column (100 × 2 cm) of SP Sephadex C-25 cation exchanger and eluted with aqueous 0.075 M sodium (−)-di-*O,O*′-4-toluoyl-L-tartrate. After an 'effective column length' of *ca.* 6 m (achieved by recycling using a peristaltic pump), two separate bands were collected. After isolation of the separated enantiomers as the PF_6^- salts by metathesis from the solutions of eluted bands, their molar rotations were measured in acetonitrile solution and observed to be equal in magnitude and opposite in sign.



$\mathbf{1}^{4+}$

Scheme 1

The circular dichroism (CD) spectra of the enantiomers are shown in Fig. 2. As expected, they are mirror images over the whole region of the spectrum. In the visible region, $\Delta\varepsilon$ reaches a highest absolute magnitude of *ca.* 23 dm^3 mol^{-1} cm^{-1}, which is associated with the absorption maximum of the metal-to-ligand charge transfer (MLCT) transition at 560 nm [d_π(Fe)–π^*(terpy)].†

After two months in acetonitrile solution at room temperature, no loss of any optical activity was observed, indicating high kinetic stability of the optically pure double helix. This can

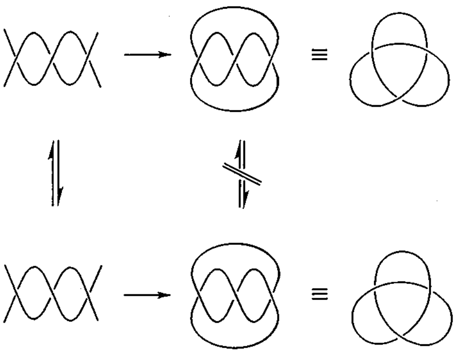


Fig. 1 From a double-stranded helix to a knot. The knotted topology makes the interconversion between both enantiomers impossible without breaking and reforming at least one chemical bond.

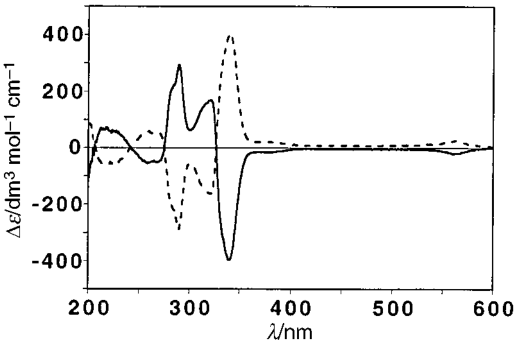


Fig. 2 Circular dichroism spectra of the enantiomers of the diiron(II) double helix in MeCN: (−)-$\mathbf{1}^{4+}\cdot 4PF_6^-$ (continuous line) and (+)-$\mathbf{1}^{4+}\cdot 4PF_6^-$ (dotted line).

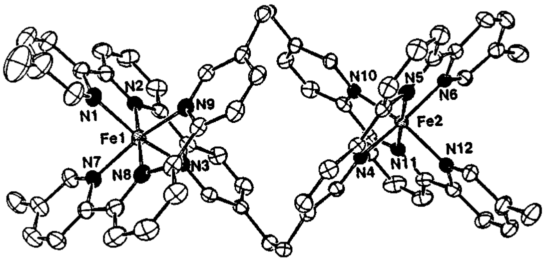


Fig. 3 Crystal structure‡ of the dextrorotatory diiron(II) double helix (+)-$\mathbf{1}^{4+}\cdot4\mathrm{PF}_6^-$. ORTEP representation showing the numbering scheme adopted for iron and nitrogen atoms. The solvent molecules, PF_6 anions and hydrogen atoms have been omitted and the nitrogen atoms are shown in black. Selected bond distances (Å) and angles (°) of the two pseudo-octahedral iron centres: Fe1–N1 1.990, Fe1–N2 1.899, Fe1–N3 1.992, Fe1–N7 2.008, Fe1–N8 1.869, Fe1–N9 1.981, Fe2–N4 1.963, Fe2–N5 1.872, Fe2–N6 1.976, Fe2–N10 1.981, Fe2–N11 1.902, Fe2–N12 1.966, N1–Fe1–N2 80.7, N1–Fe1–N8 99.7, N2–Fe1–N3 80.4, N2–Fe1–N7 97.4, N2–Fe1–N9 99.6, N3–Fe1–N8 99.3, N7–Fe1–N8 81.1, N8–Fe1–N9 81.9, N4–Fe2–N5 82.0, N4–Fe2–N11 99.8, N5–Fe2–N6 81.3, N5–Fe2–N10 99.7, N5–Fe2–N12 98.8, N6–Fe2–N11 97.0, N10–Fe2–N11 80.6, N11–Fe2–N12 80.9.

be compared to the mononuclear complex, $[\mathrm{Fe(terpy)}_2]^{2+}$, which readily racemizes in solution.[16] Crystals suitable for X-ray analysis were obtained by dissolution of 14 mg of the dextrorotatory double helix (+)-$\mathbf{1}^{4+}\cdot4\mathrm{PF}_6^-$ in one drop of acetonitrile diluted with methanol and slow liquid diffusion of benzene. The absolute configuration of the dextrorotatory enantiomer of the double helix was determined and the X-ray crystal structure is shown in Fig. 3.

The molecule has effective D_2 symmetry, with three mutually perpendicular pseudo-twofold axes, one joining the two iron cations, another passing through the middle of the two bridges and the third being perpendicular to the others. Each ligand is twisted around the metal–metal axis in the same direction. The coordination polyhedra around each metal appeared as distorded octahedra, and it should be noted that the intramolecular Fe–Fe distance is 8.31 Å, which is larger than in the crystal obtained from a racemic mixture (7.93 Å).[14] Finally, the absolute configuration of (+)-$\mathbf{1}^{4+}\cdot4\mathrm{PF}_6^-$ could be determined. The two metal centres are homochiral as expected in a double-stranded helical compound where the first coordination centre induces the same chirality on the coordination of its neighbour. The *dextrorotatory* double helix corresponds to a Λ-*double helix* with the bis-terpy ligands wound in an anticlockwise fashion.

The present results demonstrate the power of the chromatographic resolution technique, although an important limitation is the requirement to have water soluble compounds. To the best of our knowledge, this is the first reported absolute configuration of an iron(II) double helix. Further developments of this work would be to achieve chromatographic resolution of the diiron(II) trefoil knot prepared recently.[14]

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Notes and references

† MS (HR-ES$^+$): *m*/*z* 1587.30 ($[\mathrm{M}-\mathrm{PF}_6^-]^+$, calc. 1587.23, uncalibrated region), 721.1362 ($[\mathrm{M}-2\mathrm{PF}_6^-]^{2+}$, calc. 721.1363), 432.4364 ($[\mathrm{M}-2\mathrm{PF}_6^-]^{3+}$, calc. 432.4360), 288.0863 ($[\mathrm{M}-3\mathrm{PF}_6^-]^{4+}$, calc. 288.0858). CD [$\lambda$/nm ($\Delta\varepsilon$/dm^3 mol^{-1} cm^{-1}), Band 1: (−)-$\mathbf{1}^{4+}\cdot4\mathrm{PF}_6^-$ (c = 2.80×10^{-5} M): 260 (−53), 268 (−51), 290 (292), 321 (169), 340 (−397), 560 (−21). Band 2: (+)-$\mathbf{1}^{4+}\cdot4\mathrm{PF}_6^-$ (c = 2.25×10^{-5}M): 260 (58), 268 (55), 290 (−289), 321 (−162), 340 (404), 560 (24). $[\alpha]_\mathrm{D}$ band 1 −2015°, band 2 +2070°.

‡ *Crystal data* for (+)-$\mathbf{1}^{4+}\cdot4\mathrm{PF}_6^-$: $\mathrm{C_{68}H_{56}N_{12}Fe_2\cdot4PF_6\cdot3C_6H_6\cdot CH_3OH}$, M = 1999.22, monoclinic, space group $P2_1$, a = 13.6870(2), b = 13.6560(3), c = 23.4480(5) Å, V = 4364.2 (3) Å^3, Z = 2, D_c = 1.52 g cm^{-3}, μ(Mo-Kα) = 0.512 mm^{-1}. Data were collected on a Nonius KappaCCD diffractometer using Mo-Kα graphite monochromated radiation (λ = 0.71073 Å) at 173 K. A dark red crystal of dimensions $0.20\times0.15\times0.10$ mm was used and a total of 32515 data was collected, $2.5<\theta<30.52°$. 8706 reflections having $I>3\sigma(I)$ were used for structure determination and refinement. The structure was solved using direct methods and refined against $|F|$. Hydrogen atoms were introduced as fixed contributors. No absorption corrections were applied. For all computations the Nonius OpenMoleN package[17] was used. The absolute structure was determined by refining Flack's x parameter: x = 0.03(0). Final results: $R(F)$ = 0.061, $Rw(F)$ = 0.077, GOF = 1.500, maximum residual electronic density = 0.707 e Å^{-3}.

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