New double-stranded helicate based on a chiral bis(bipyridine)-type chelator

Boris Quinodoz,[a] Helen Stoeckli-Evans[b] and Alex von Zelewsky*[a]

[a] *Department of Chemistry, University of Fribourg, CH-1700 Fribourg, Switzerland. Fax: +41 26 300 9738; e-mail: Alexander.vonzelewsky@unifr.ch*

[b] *Institute of Chemistry, University of Neuchâtel, CH-2007 Neuchâtel, Switzerland. E-mail: Helen.Stoeckli-Evans@unine.ch*

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A new ferrocene-bridged bis(bipyridine) ligand forms a configurationally predetermined 2:2 double helix with Cu^{I}.

The stereoselective synthesis of coordination compounds using chiral ligands has been developed during the past decade at an increasing rate.[1,2] This development was paralleled by a search for new chiral metal chelators. Here, we present the first chiral CHIRAGEN-type ligand **1**, which incorporates a metallocene, and its complex with Cu^{I} (Figure 1). Complex **2** is a configurationally predetermined double helix incorporating two copper(I) centres and two tetradentate ligands each comprising one ferrocene unit.

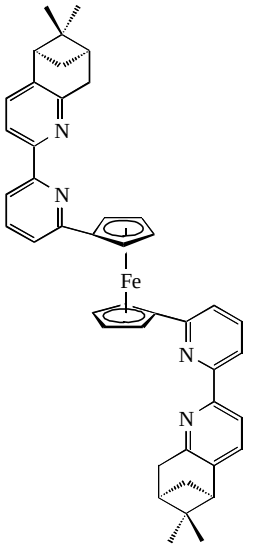
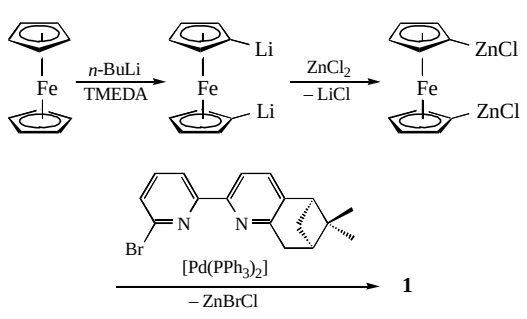


Figure 1 (*R*,*R*)-(–)-Bis([4,5]-pinene-bipyridyl-6′-[ferrocene]) **1**.

Compound **1** was synthesised according to Scheme 1 based on the Negishi coupling.[3] It was characterised by standard NMR techniques, high resolution ESI-MS, UV-VIS and CD spectra.

Addition of **1** to a solution of $Cu(MeCN)_4PF_6$ in acetonitrile leads to the spontaneous formation of the complex $Cu_2(\mathbf{1})_2(PF_6)_2$ **2**. This complex was characterised by NMR, ESI-MS, UV-VIS, CD, and X-ray structure analysis† (Figure 2).

The X-ray analysis shows a two-stranded helical structure, where the two copper centres lie on the axis of the helix, whereas the ferrocene units connect the 'upper' and 'lower' parts of the structure. The approximate symmetry of the supramolecular assembly is D_2. In the crystal, the packing of the molecules is stabilised by a number of C–H···F hydrogen bonds (Figure 3).



Scheme 1 Synthesis of ligand **1**.

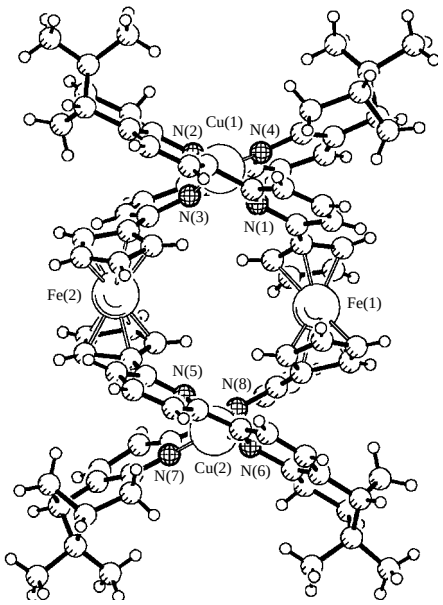


Figure 2 X-ray structure of the $Cu_2(\mathbf{1})_2(PF_6)_2$ **2** cation.

The ligand itself is CD-silent in the range 250–450 nm, whereas the complex with Cu^{I} shows a strong exciton couplet ($\Delta\varepsilon_{331} = +22$; $\Delta\varepsilon_{307} = -24$) indicating the same absolute configuration of the helical coordination (*M*) as that formed in the solid state. This, together with the NMR data hints to the same structure of the double helix in solution and in the solid state.

† $ZnCl_2$ was dried by refluxing in thionylchloride until no evolution of gas is observed. Crystals of **2** were obtained by slow evaporation of a solution of **2** in a mixture of chloroform and methanol. *Crystal data*: $[C_{88}H_{84}Cu_2Fe_2N_8](PF_6)_2 \cdot 3CHCl_3 \cdot 4.5MeOH$, $M = 2284.65$, monoclinic, space group $P2_1$, $a = 13.3902(7)$, $b = 31.172(2)$, $c = 14.3665(9)$ Å, $\beta = 109.671(7)°$, $V = 5646.61(6)$ Å^3, $Z = 2$, $d_{calc} = 1.344$ g cm^{-3}, $\lambda = 0.71073$ Å. A crystal with dimensions 0.50×0.50×0.15 mm was selected for indexing and intensity data collection at 153 K. The crystal did not diffract significantly beyond 35° in 2θ. The total numbers of measured, independent and observed reflections [$I > 2\sigma(I)$] are 44533, 21768 and 5001 ($R_{int} = 0.1651$), respectively. Only the Cl, Cu, F, Fe and P atoms were refined anisotropically. Three molecules of $CHCl_3$ per molecule of the complex were located from Fourier difference maps. The rest of the residual density was difficult to identify clearly and it was equated to 4.5 molecules of methanol per molecule of the complex using the SQUEEZE routine in PLATON;[4] potential solvent accessible area volume was 1416 Å^3, with an electron count of 162. Least-square refinement based on F^2 converged at $R_1 = 0.0748$, $wR_2 = 0.1468$ (observed data); $R_1 = 0.2015$, $wR_2 = 0.1894$ (all data).

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 175750. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2003.

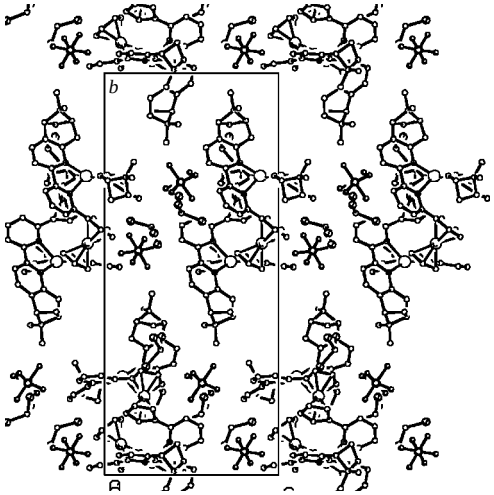


Figure 3 The crystal packing of **2** viewed down the *a* axis. The disordered solvent molecules of methanol normally fill the cavities shown. The hydrogen atoms have been omitted for clarity.

Analogous (*S*,*S*)-(–)-bis([4,5]-pinene-bipyridyl-6′-[ferrocene]) was also prepared. It seems to behave similarly in complexation reactions and will be reported later.

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