

179. Helicity Induction in Helicate Self-Organisation from Chiral Tris(bipyridine) Ligand Strands¹⁾

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Dedicated to Vladimir Prelog on the occasion of his 85th birthday

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The chiral tris- and pentakis(bipyridine) ligand strands **3a** and **4** were synthesised, each in optically pure form with (*S,S*)-configuration. Ligand **3a** yielded substituted double-helical metal complexes, derived from the parent trihelicate structure **2**, with Cu^I and Ag^I ions. The spectral data, in particular the ¹H-NMR spectra and the large positive Cotton effect, indicate that helicate formation occurs with very high induction of helicity. Together with consideration of the steric effects in the two possible helical diastereoisomers (*P*)-**1** and (*M*)-**1** that may be formed, the data favour the preferential generation of the right-handed double helicate (*P*)-**1** from the tris(bipyridine) strand **3a** of (*S,S*)-configuration.

‘A helix is characterised by an axis, a screw sense (*i.e.* its chirality) and a pitch (*i.e.* the ratio of axially linear to angular properties). Thus, helicity is a special case of chirality...’ as wrote Cahn, Ingold, and Prelog [1]. It may be right-handed (plus, *P*) or left-handed (minus, *M*) and the same holds for a double helix (*Fig. 1*) [2].

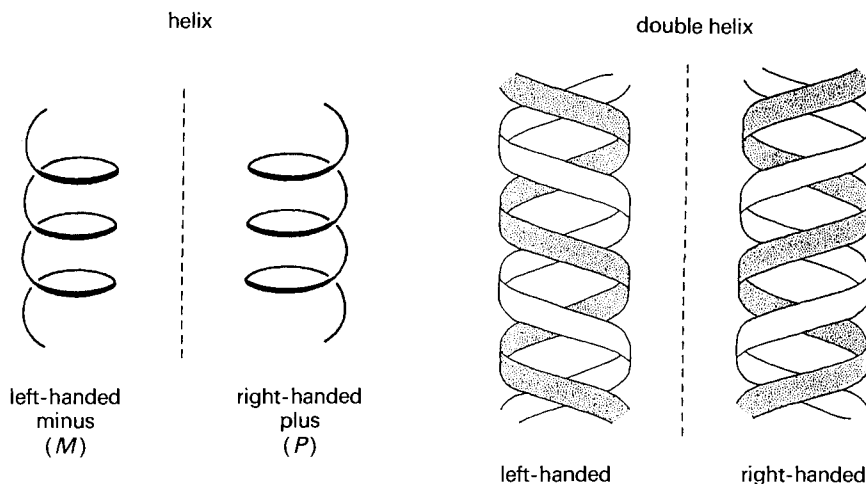


Fig. 1. Helicity of molecular helices and double helices

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The self-assembly [3] of double-stranded metal complexes, termed helicates \mathcal{H}_n , from achiral oligo(2,2'-bipyridine) ligands and copper(I) [4] [5] or silver(I) [6] ions yields a racemic mixture of double-helical species of opposite helicity, by a cooperative process [7] in which two ligand strands wrap around the metal ions. This is illustrated in Fig. 2 for the case of the formation of the (*P*)- and (*M*)-forms of the trihelicate \mathcal{H}_3 from a tris(bipyridine) ligand and three metal ions. These double helices are cylindrical (constant radius) and palindromic (constant pitch) [2].

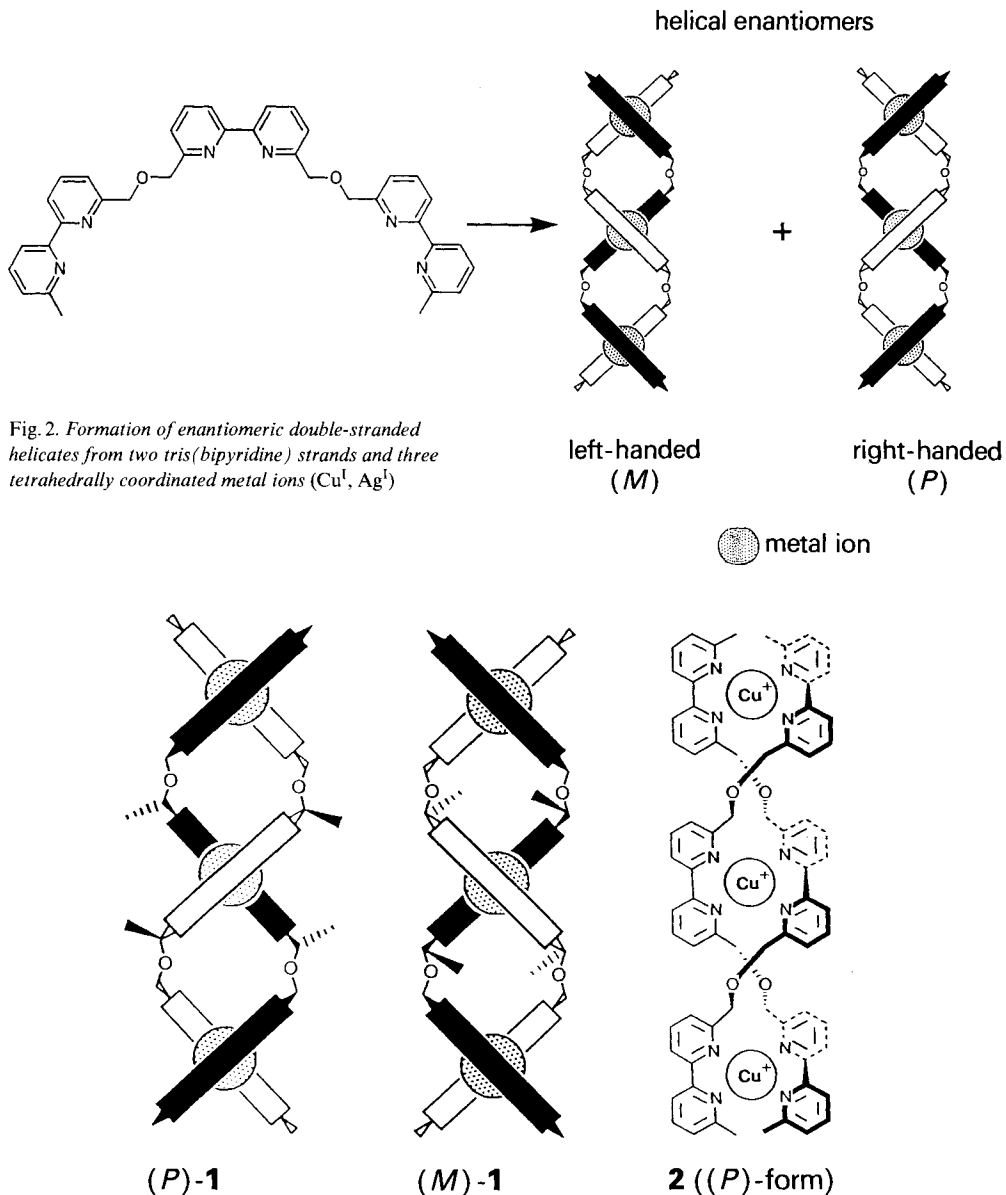


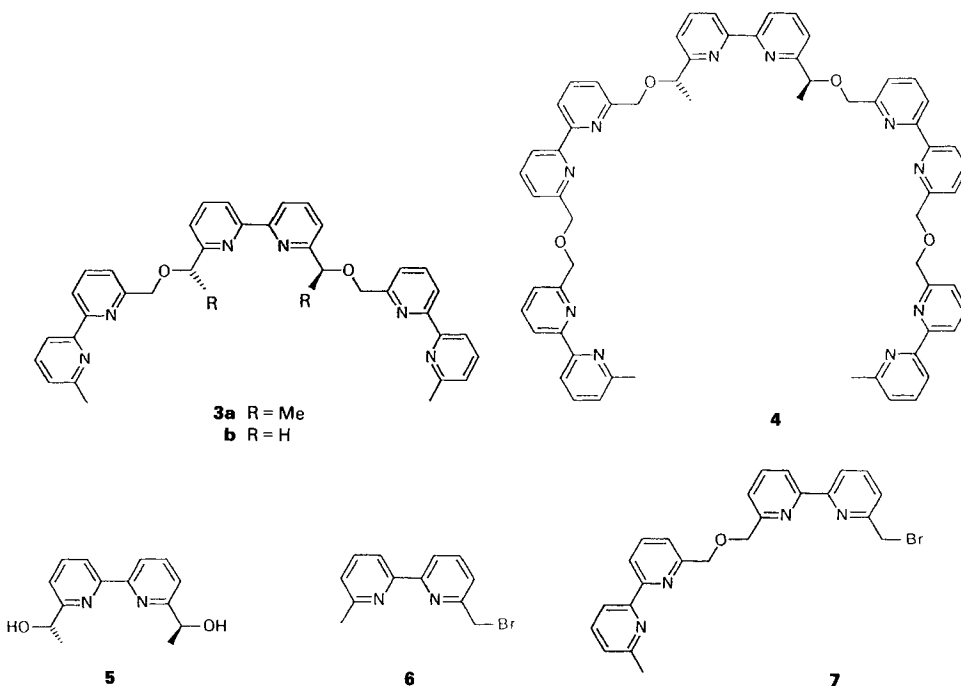
Fig. 2. Formation of enantiomeric double-stranded helicates from two tris(bipyridine) strands and three tetrahedrally coordinated metal ions (Cu^+ , Ag^+)

In view of the special structure of these double-helical complexes, it would be of much interest to be able to generate helicates of a given helicity by asymmetric induction. Three ways of helicity induction may be considered: 1) introduction of a chiral centre into the backbone of the ligand strand, 2) attachment of chiral groups to the bipyridine units of functionalized ligands⁴⁾ [9], and 3) chiral delivery of the metal ions by an optically active coordinating solvent.

We now wish to report the high induction of helical chirality in the substituted Cu^I trihelicate **1** (corresponding to the parent structure **2**), formed from two tris(bipyridine) strands **3a** that contain each two asymmetric C-atoms. The chiral pentakis(bipyridine) ligand **4** was also synthesised.

Synthesis of the Chiral Tris- and Pentakis(bipyridine) Strands 3a and 4. – The introduction of chiral centres directly into the backbone of the oligo(bipyridine) ligands could lead to marked chiral induction, by sterically hindering the formation of one of the diastereoisomeric helicates. However, a too strong hindrance should be avoided in order not to preclude helicate formation altogether.

A suitable unit appeared to be the chiral bipyridine component **5** [10] in which two asymmetric centres are created by introduction of a Me group into each of the CH₂OH residues in the 6,6' positions. Compound **5** was obtained by asymmetric reduction of 6-bromopyridin-2-yl methyl ketone with (–)-chlorodiisopinocampheylborane [11] to give



⁴⁾ Partial helicity induction was obtained in this way for the dihelicate formed from two Cu^I ions and two bis(bipyridine) strands bearing four (*S*)- or (*R*)-2-phenylethylamine groups in 4-position of the pyridine rings [8].

(–)-(S)-6-bromopyridine-2-ethanol (90% ee). The optical purity of the latter was further increased to > 99% ee by recrystallisation of its ester derived from (–)-(1S)-camphanoyl chloride. Finally, nickel-mediated coupling [12] of its acetate (> 99% ee) followed by saponification gave (+)-(S,S)-2,2'-bipyridine-6,6'-diethanol (**5**; > 99% ee, > 99% de). The experimental procedures will be described elsewhere [10].

Treatment of **5** with NaH in THF followed by reaction with the (bromomethyl)-bipyridine **6** [13] according to the published procedure [9] gave the tris(bipyridine) compound **3a** (76% yield). Condensation of **5** with the (bromomethyl)-bis(bipyridine) **7** [9] afforded the pentakis(bipyridine) strand **4** (56% yield). Both compounds **3a** and **4** are white, crystalline, optically active solids ($[\alpha]_D^{25} = -28$ for **3a** and -14 for **4**). Racemisation of the asymmetric centres is not expected in the reactions and under the conditions employed.

Formation and Properties of the Copper(I) and Silver(I) Complexes of the Chiral Ligand 3a. – In analogy to the formation of the parent trihelicates (see **2**) [4–6], treatment of 2 equiv. of ligand **3a** with 3 equiv. of CuClO_4 or $\text{Ag}(\text{CF}_3\text{SO}_3)$ in MeCN led to the formation of the corresponding Cu^I and Ag^I trinuclear complexes (see **1**). The Cu^I complex was isolated and fully characterised.

Spectrophotometric titration of an MeCN solution of **3a** with $[\text{Cu}(\text{MeCN})_4]\text{ClO}_4$ in MeCN gave clear isosbestic points indicating that a single species was formed (Fig. 3a). The titration plots (Fig. 3b) showed that this species had a composition of ca. 1.5 Cu-atoms for 1 equiv. of **3a**, in agreement with the stoichiometry expected for the trihelicate $[\text{Cu}_3(\text{3a})_2]^{3+5)}$.

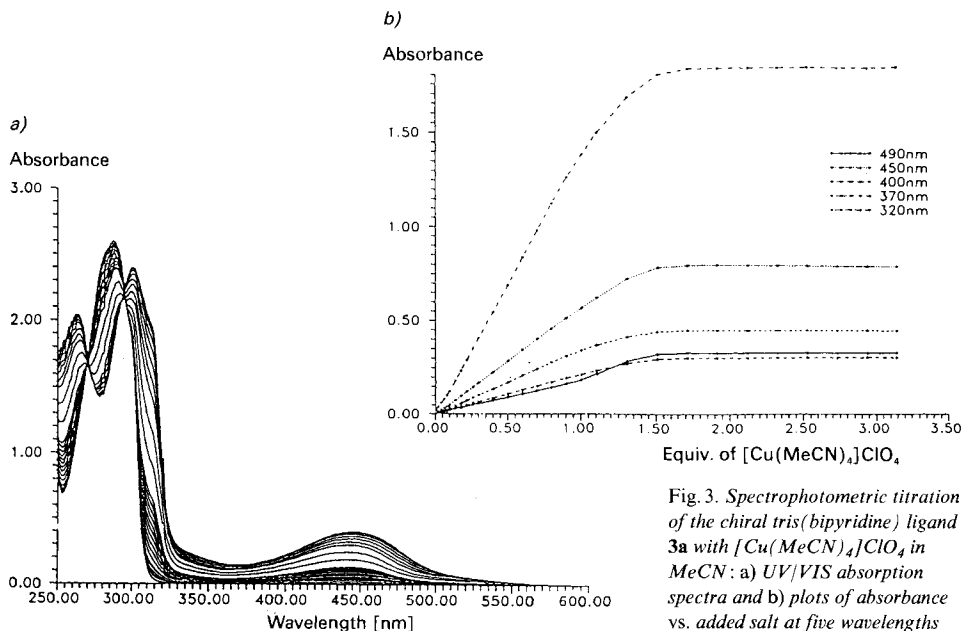


Fig. 3. Spectrophotometric titration of the chiral tris(bipyridine) ligand **3a** with $[\text{Cu}(\text{MeCN})_4]\text{ClO}_4$ in MeCN: a) UV/VIS absorption spectra and b) plots of absorbance vs. added salt at five wavelengths

⁵⁾ The behaviour of the titration curve at 490 nm could indicate the presence of another species at lower salt concentration.

The $^1\text{H-NMR}$ spectra of ligand **3a** and of its Cu^I and Ag^I complexes (Fig. 4) were compared with the published spectrum of the Cu^I helicate **2** of the unsubstituted tris(bipyridine) ligand **3b** [4]. The data confirm the assumption that only one of the diastereoisomeric helicites **1** was formed from **3a** and the Cu^I or Ag^I salt. Moreover, FAB-MS and UV/VIS spectra are in agreement with the proposed helicate structures $[\text{Cu}_3(\mathbf{3a})_2](\text{ClO}_4)_3$ and $[\text{Ag}_3(\mathbf{3a})_2](\text{CF}_3\text{SO}_3)_2$.

Three comments may be made on the $^1\text{H-NMR}$ spectra: 1) The spectra of the complexes obtained from **3a** and from the parent ligand **3b** display very similar features. 2) The spectral changes between the free ligand and the complexes are very similar to those observed earlier for the parent tris(bipyridine) ligand **3b** and its Cu^I [4] and Ag^I [6] complexes; the upfield shift and the splitting of the CH_2O signal into an *AB* pattern and the upfield shift of *2d* signals in the aromatic region are characteristic of helicate formation [4–6]; one also notes a pronounced upfield shift (*ca.* 0.9 and 0.6 ppm for the Cu^I and Ag^I complexes, resp.) of the *d* of the secondary Me group on the asymmetric C-centres; a smaller upfield shift is observed for the Me groups on the terminal pyridine rings (*ca.* 0.4 and 0.2 ppm, resp.). 3) The $^1\text{H-NMR}$ spectra of the Cu^I and Ag^I complexes of **3a** correspond to the presence of a single species in solution, admitting that it is very unlikely that all signals of the two diastereoisomeric species of opposite helicity would accidentally overlap.

The observation of only one set of $^1\text{H-NMR}$ signals could in principle also result from fast exchange between these two complexes. In such a case, however, one would expect a more or less pronounced

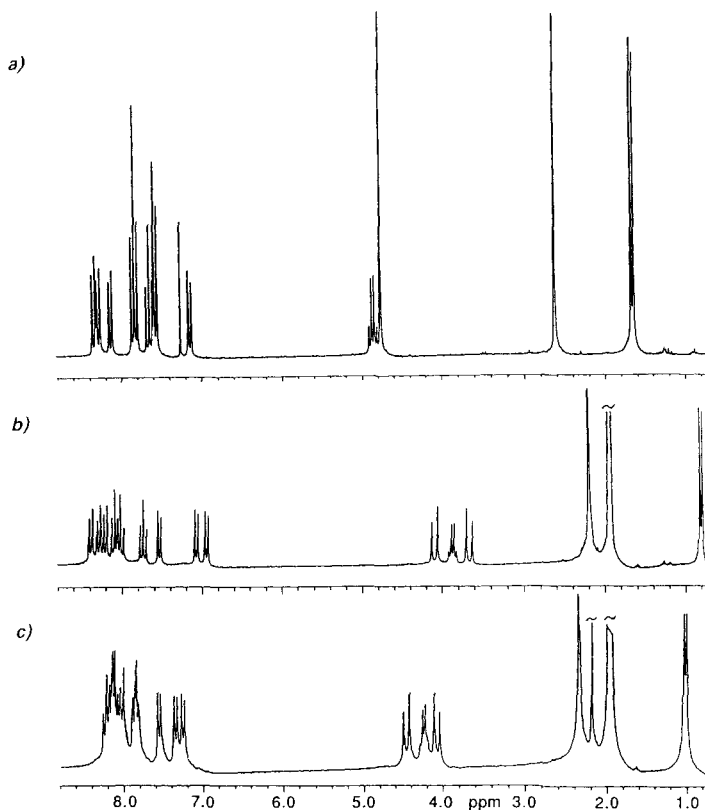


Fig. 4. 200-MHz $^1\text{H-NMR}$ spectra of a) ligand **3a** (in CDCl_3), b) trihelicate $[\text{Cu}_3(\mathbf{3a})_2](\text{ClO}_4)_3$ (in CD_3CN), and c) trihelicate $[\text{Ag}_3(\mathbf{3a})_2](\text{CF}_3\text{SO}_3)_2$ (in CD_3CN). For the spectrum of the trihelicate $[\text{Cu}_3(\mathbf{3b})_2](\text{ClO}_4)_3$ (= **2**(ClO_4)₃) of the parent unsubstituted tris(bipyridine) ligand, see [4].

collapse of the *AB* system of the CH_2O protons depending on the amount of the minor diastereoisomer and on the chemical shifts for both species. In fact, one observes that $\Delta\delta(\text{AB})$ is larger in the Cu^{I} complex of **3a** (ca. 0.4 ppm) than in the parent trihelicate **2** (ca. 0.2 ppm) (Fig. 4). Furthermore, the latter is evidently in slow exchange, so that the same may be expected to hold also for the former. Definitive information was obtained from the complex formed with a sample of ligand **3a** that contained ca. 9% of its *meso*-diastereoisomer, synthesised from a preparation of **5** having a high ee (> 99%) but a lower de. The $^1\text{H-NMR}$ spectrum of the Cu^{I} complex showed, as expected, 4*d* for the Me groups at the asymmetric centres: a very large one for the $[\text{Cu}_3\{(\text{S,S})\text{-3a}\}_2]^{3+}$ form, as well as three small ones (at 0.46, 0.89, and 0.99 ppm, representing ca. 3, 5, and 3%, resp.) which can be assigned to the complexes containing the ((*S,S*)-**3**, *meso*-**3**) and eventually the (*meso*-**3**)₂ ligand strands⁶). In case of fast ligand exchange, one would expect only two averaged *d*, a large one and a small one for the (*S,S*)- and *meso*-ligand forms, respectively. One large (at 2.20 ppm) and two small (at 2.05 and 2.12 ppm) *s* are also observed for the Me-bpy groups; small signals are similarly found in the CH–O and aromatic regions of the spectrum. These data conclusively show that ligand exchange is slow on the NMR time scale, so that indeed only a single species (estimated > 95%) is present in solution.

The FAB-MS (positive mode) of the Cu^{I} complex also indicates the formation of the expected helicate $[\text{Cu}_3(\mathbf{3a})_2](\text{ClO}_4)_3$ (m/z 1607 ($[\text{Cu}_3(\mathbf{3a})_2](\text{ClO}_4)_2$)⁺). The same holds for the Ag^{I} trihelicate (m/z 1839.4).

The UV/VIS absorption spectrum of the Cu^{I} complex of **3a** (see also Fig. 3a) shows a band at 445.5 nm with an extinction coefficient $\epsilon = 13800 \text{ M}^{-1}\text{cm}^{-1}$ (in MeCN), slightly lower than for the parent unsubstituted trihelicate **2** ($\epsilon = 14600 \text{ M}^{-1}\text{cm}^{-1}$ in CHCl_3) [4].

The circular dichroism (CD) spectrum of the $[\text{Cu}_3(\mathbf{3a})_2]^{3+}$ complex is of particular interest (Fig. 5). Whereas the CD spectrum of the Cu^{I} complex $[\text{Cu}(\mathbf{5})]^+$ of the chiral subunit **5** shows a negative and a positive band (Fig. 5), that of the complex of **3a** displays a very strong positive Cotton effect, ca. 10 times larger than for the monomer. The $[\alpha]_{\text{D}}$ values for the Cu^{I} and Ag^{I} trihelicates are +361 and +153, respectively.

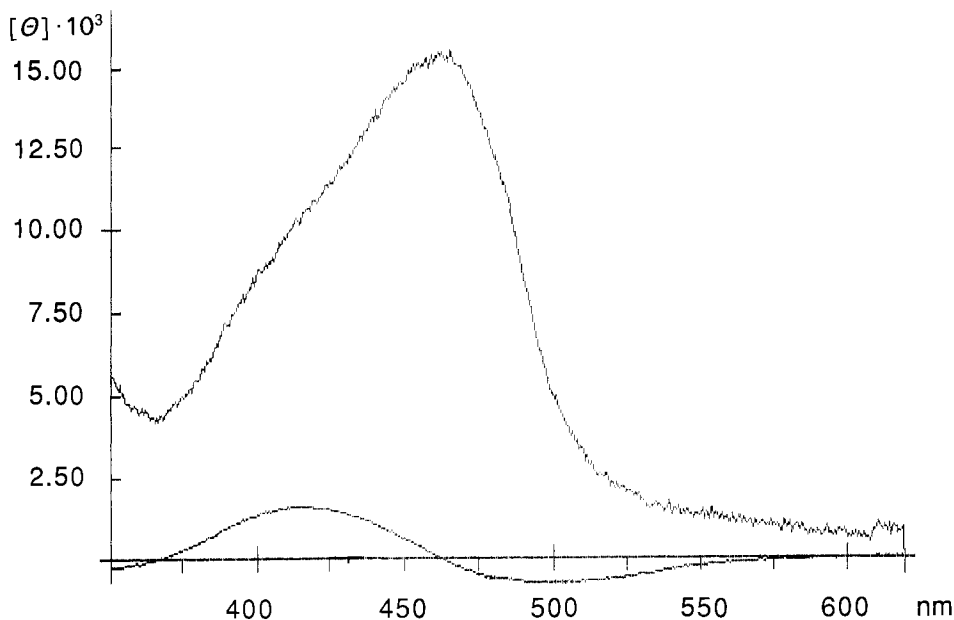


Fig. 5. Circular dichroism spectra of the trihelicate $[\text{Cu}_3(\mathbf{3a})_2](\text{ClO}_4)_3$ (top curve) and of complex $[\text{Cu}(\mathbf{5})_2]\text{ClO}_4$ (bottom curve) of the chiral unit **5** in MeCN

⁶) A precise assignment of the signals must await a more detailed study of these complexes.

The complexation of the chiral penta(bipyridine) ligand **4** with Cu^{I} yields an orange-red solution showing λ_{max} 445 nm, with an extinction coefficient of $\epsilon = 17900 \text{ M}^{-1}\text{cm}^{-1}$ that is substantially lower than found for the pentahelicate complex of the parent unsubstituted ligand ($\epsilon \approx 22300 \text{ M}^{-1}\text{cm}^{-1}$ [5]). Also, the *Cotton* effect is only slightly larger than for the trihelicate of **3a**, and the $^1\text{H-NMR}$ spectrum shows only broad signals, even at low temperature (238 K). This may indicate that the pentahelicate structure is more difficult to form with **4** than with the unsubstituted parent ligand. The Ag^{I} complex displays a better resolved $^1\text{H-NMR}$ spectrum, and its FAB-MS spectrum shows the fragment $[\text{Ag}_5(\mathbf{4})_2(\text{CF}_3\text{SO}_3)_4]^+$ at m/z 3146.6 and $[\text{Ag}(\mathbf{4})]^+$ at 1113.8. Further studies are necessary for analyzing the nature of the complexes formed by **4**.

The Copper(I) Trihelicate of the Chiral Ligand 3a. Helicity Induction. – The chiral properties of double-stranded complexes resulting from tetrahedral coordination of several Cu^{I} ions by two oligo(bipyridine) ligands such as **3b** deserve some comments. Two types of complexes may be formed: double-helical species (see **C** and **D**, Fig. 6) and nonhelical ‘side-by-side’ complex (see **A** and **B**). Their chiral features depend on the number of [metal ion, (bipyridine)₂] centres, as schematically shown in Fig. 6⁷⁾.

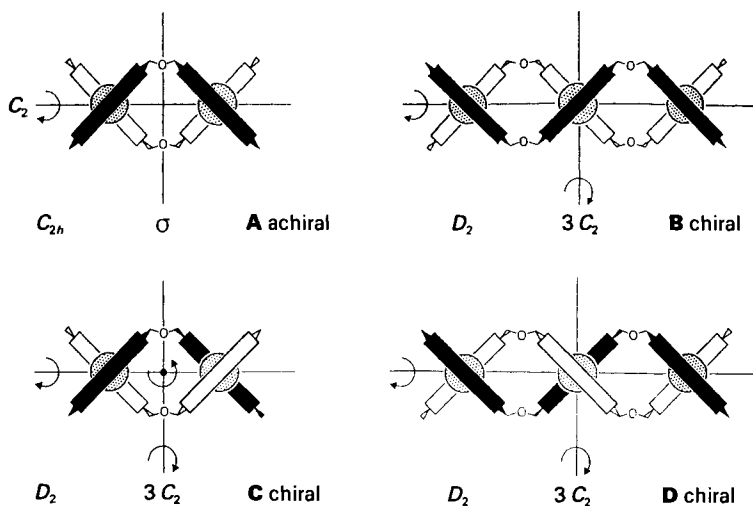


Fig. 6. Chiral properties of the two types of complexes formed by binding of tetrahedrally coordinated metal ions by two oligo(bipyridine) strands; **A** and **B**: nonhelical, ‘side-by-side’ complexes; **C** and **D**: double-helical complexes; left: complexes with an even number of sites, illustrated for two sites; right: complexes with an odd number of sites, shown for three sites; the representations **B** and **D** correspond to the tris(bipyridine) ligand **3b**.

With an *even* number of centres, the double-helical species is chiral and of D_2 symmetry, with all centres of the same screw sense, as illustrated in **C** for a two-centre (MM) left-handed (M) double helix; in contrast, the nonhelical species is an achiral, *meso*-form of C_{2h} symmetry, with an equal number of centres of opposite screw sense, *i.e.* (MP) for two centres (see **A**). With an *odd* number of centres both the double-helical and the

⁷⁾ In principle, mixed complexes containing double-helical and nonhelical domains could also form.

nonhelical species are chiral and of D_2 symmetry, but the double-helical forms have all centres of same helicity, whereas the nonhelical forms have one more centre of one type than of the other type, as illustrated for a three-centre (PPP) right-handed (P) double helix **D** and the corresponding nonhelical species ($PM P$) **B**. It is interesting to note that, whereas the chiral features of the double-helical species are independent of the parity of the number of centres, those of the nonhelical species alternate.

The strong similarity of the physicochemical data obtained for the Cu^I complex of ligand **3a** and of those of the parent trihelicate **2** indicate that a double-helical structure is indeed also formed in the present case. Such a structure had been confirmed for **2** by crystal-structure determination [4].

Furthermore, the chiral ligand strand **3a** may yield the two diastereoisomeric species (P)- and (M)-**1** having identical tetrahedral C-center chirality and opposite helical chirality. The $^1\text{H-NMR}$ data as well as the large *Cotton* effect of the CD spectrum indicate the preferential formation of a single diastereoisomer, pointing to a *very high helicity induction* ($> 95\%$) by the asymmetric C-centres. One may also note that the strong optical activity observed agrees with the double-helical structure **D**, where all three $[\text{Cu}^I(\text{bipyridine})_2]$ centres have the same helicity, whereas in the nonhelical structure **B**, the screw sense of the central unit is opposite to that of the two lateral units (*Fig. 6*).

The remaining question is whether the induced helicity is right-handed or left-handed. Consideration of space-filling models and preliminary molecular-mechanics calculations [14] based on the crystal structure of the parent trihelicate **2** [4] give some insight into the effects caused by the introduction into the strands of **2** of the Me groups producing (S,S)-configuration in ligand **3a**. A more pronounced steric hindrance is indicated for the left-handed double helicate (M)-**1** than for the right-handed isomer (P)-**1**. The disposition of the Me groups in the representations (P)- and (M)-**1** is highly schematic but gives an idea of the steric crowding involved. In addition, the crystal structure of the Cu^I complex of an optically active α -diimine ligand was determined recently; it shows that the positive *Cotton* effect observed for this complex corresponds to a right-handed screw sense at the Cu^I centre [15].

These data are in favour of the conclusion that the presence of two Me groups creating (S,S)-configuration in the tris(bipyridine) strand **3a** leads to *high induction of right-handed helicity* into the double helicate $[\text{Cu}_3(\mathbf{3a})_2]^{3+}$. Confirmation could come from a crystal structure determination. A more detailed study of the optical activity of these and related helicates is also warranted.

Conclusion. – In addition to its interest as control feature in a self-organisation process, the induction of helicity in the double helicates derived from oligo(bipyridine) strands containing asymmetric centres, bears relation to the formation of the DNA double helix where the asymmetric unit is the deoxyribose group. Both aspects speak for further investigation of the structure-helicity relationship between ligand strands of diverse types and the helicates which they may form with various metal ions⁸). In the context of considering self-organising systems as programmed molecular systems [1], chirality induction in general and helicity induction in particular represent a further step

⁸) It would, *e.g.*, be of interest to study the pure and mixed double-stranded complexes of (S,S)-, (R,R)-, and *meso-3a*.

in the control of the spontaneous assembling of a defined supramolecular structure through storage of the correct structural information in the molecular components that undergo the process.

Experimental Part

General. All reactions were carried out under Ar in dry solvents: THF was distilled over Na/benzophenone and MeCN over CaH₂. Compounds **6** [13] and **7** [9] were obtained according to the literature procedures. M.p.: uncorrected, digital melting-point apparatus (*Electrothermal*). Optical rotation: *Perkin-Elmer-241-MC* polarimeter. UV-VIS: *Cary 13* spectrometer. CD Spectra: *DC-III-Jobin-Yvon-GB43* spectrometer. NMR Spectra: *Bruker AC-200*; chemical shifts in ppm rel. to TMS (= 0 ppm).

(*S,S*)-6,6'-{(2,2'-Bipyridine-6,6'-diyl)bis[*(ethane-1,1-diyl)oxymethylene*]}-6',6''-dimethylbis[2,2'-bipyridine] (**3a**). To a stirred suspension of NaH (60%; 26 mg, 0.66 mmol; washed with 2 × 2 ml of hexane before use) in THF (20 ml), **5** [10] (40 mg, 0.16 mmol) was added. After 1 h, solid **6** [13] (121 mg, 0.46 mmol) was added and after additional stirring at r.t. for 1 h, the mixture was heated at reflux for 12 h. Excess NaH was hydrolysed with some drops of H₂O, the solvent evaporated, the remaining solid suspended in 5 ml of CHCl₃, and insoluble material filtered off. Evaporation of the solvent gave crude **3a** which was purified by CC (alumina, hexane/Et₂O 1:2): 76 mg (76%) of **3a**. White solid. M.p. 147°. TLC (Al₂O₃, hexane/Et₂O 1:2): R_f 0.24. [α]_D²⁵ = -28 (*c* = 0.94 g/l, CHCl₃). ¹H-NMR (200 MHz, CDCl₃): 1.66 (*d*, *J* = 6.5, 2 Me); 2.63 (*s*, 2 Me); 4.76 (*s*, 4 H, CH₂); 4.85 (*q*, *J* = 6.5, 2 CH); 7.15 (*d*, 2 H); 7.57 (*d*, 4 H); 7.65 (*t*, 2 H); 7.83 (*t*, 4 H); 8.13 (*d*, 2 H); 8.29 (*d*, 2 H); 8.35 (*d*, 2 H); all arom. *J* = 7.7. FAB-MS: 609.2 ([*M* + H]⁺). Anal. calc. for C₃₈H₃₆N₆O₂ (608.72): C 74.79, H 5.96, N 13.81; found: C 74.93, H 5.87, N 13.66.

(*S,S*)-6,6',6''-{(2,2'-Bipyridine-6,6'-diyl)bis[*(ethane-1,1-diyl)oxymethylene*]}bis(2,2'-bipyridine-6,6'-diyl)bis(methyleneoxymethylene)}-6',6''-dimethylbis[2,2'-bipyridine] (**4**). To a stirred suspension of NaH (60%; 26 mg, 0.66 mmol; washed with 2 × 2 ml of hexane before use), **5** [10] (40 mg, 0.16 mmol) was added. After 30 min at r.t., **7** [9] (197 mg, 0.43 mmol) was added and the mixture heated to reflux for 16 h. After hydrolysis of excess NaH, and evaporation, the residue was suspended in 10 ml of CHCl₃, insoluble material filtered off, the filtrate evaporated, and the remaining solid recrystallised from MeOH/CHCl₃ 2:1: 93 mg (56%) of **4**. White solid. M.p. 203°. [α]_D²⁵ = -14.1 (*c* = 5 g/l, CHCl₃). ¹H-NMR (200 MHz, CDCl₃): 1.65 (*d*, *J* = 6.5, 2 Me); 2.63 (*s*, 2 Me); 4.76 (*s*, 4 H, CH₂); 4.85 (*q*, *J* = 6.5, 2 CH); 4.90 (*s*, 8 H, CH₂); 7.18 (*d*, *J* = 7.6, 2 H); 7.5-7.9 (*m*, 18 H); 8.2 (*m*, 10 H). FAB-MS: 1005.1 (*M*⁺). Anal. calc. for C₆₂H₅₆N₁₀O₄ (1005.15): C 74.08, H 5.62, N 13.94; found: C 73.87, H 5.59, N 13.85.

Bis{ μ_3 -{(S,S)-6,6''-{(2,2'-bipyridine-6,6'-diyl)bis[*(ethane-1,1-diyl)oxymethylene*]}-6',6''-dimethylbis[2,2'-bipyridine]}}triccopper(I) Triperchlorate ([Cu₃(**3a**)₂](ClO₄)₃). A soln. of [Cu(MeCN)₄]ClO₄ (24 mg, 0.08 mmol) in MeCN (4 ml) was added to solid **3a** (30 mg, 0.05 mmol). Within a few min, all ligand was dissolved and the complex formed. [Cu₃(**3a**)₂](ClO₄)₃ was precipitated with Et₂O, separated by centrifugation, and dried. [α]_D²⁵ = +361 (*c* = 0.42 g/l, MeCN). ¹H-NMR (200 MHz, CD₃CN): 0.80 (*d*, *J* = 6.5, 4 Me); 2.20 (*s*, 4 Me); 3.66 (*d*, *J* = 14.6, 4 H, CH₂); 3.86 (*q*, *J* = 6.5, 4 CH); 4.08 (*d*, *J* = 14.6, 4 H, CH₂); 6.94 (*d*, 4 H); 7.07 (*d*, 4 H); 7.53 (*d*, 4 H); 7.74 (*t*, 4 H); 8.02 (*t*, 4 H); 8.09 (*t*, 4 H); 8.20 (*d*, 4 H); 8.28 (*t*, 4 H); 8.38 (*d*, 4 H); all arom. *J* = 7.5. UV/VIS (MeCN): 445.5 (13800) (*Fig. 3a*). FAB-MS: 1607 ([Cu₃(**3a**)₂(ClO₄)₃]⁺), 1506, 839, 671 ([Cu₃]⁺). Anal. calc. for C₇₆H₇₂Cl₃Cu₃N₁₂O₁₆ (1706.49): C 50.7, H 4.3, N 9.9; found: C 50.7, H 4.3, N 10.0.

Bis{ μ_3 -{(S,S)-6,6''-{(2,2'-bipyridine-6,6'-diyl)bis[*(ethane-1,1-diyl)oxymethylene*]}-6',6''-dimethylbis[2,2'-bipyridine]}}trisilver(I) Tris(trifluoromethanesulfonate) ([Ag₃(**3a**)₂](CF₃SO₃)₃). A soln. of Ag(CF₃SO₃) (13 mg, 0.05 mmol) in MeCN (3 ml) was added to a soln. of **3a** (20 mg, 0.03 mmol) in CHCl₃ (3 ml). After 30 min, the solvent was removed and the residue dried and then dissolved in CD₃CN for NMR spectroscopy. No crystalline form of the complex was obtained. [α]_D²⁵ = +153 (*c* = 0.55 g/l, MeCN). ¹H-NMR (200 MHz, CD₃CN): 0.99 (*d*, *J* = 6.5, 4 Me); 2.42 (*s*, 4 Me); 4.03 (*d*, *J* = 14.6, 4 H, CH₂); 4.20 (*q*, *J* = 6.5, 4 CH); 4.42 (*d*, *J* = 14.6, 4 H, CH₂); 7.20 (*d*, *J* = 7.5, 4 H); 7.25 (*d*, *J* = 7.5, 4 H); 7.52 (*d*, *J* = 7.5, 4 H); 7.74-8.20 (*m*, 24 H). FAB-MS: 1839.4 ([Ag₃(**3a**)₂(CF₃SO₃)₃]⁺).

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